

Metal hydrides are of importance for hydrogen storage applications. Hydrogenation of intermetallic compounds is generally considered to leave their metal atom substructures intact except for a volume increase and possible lattice distortions. The present study on the pseudo-ternary compound $\text{CeMn}_{1.8}\text{Al}_{0.2}$ shows that this is not necessarily true. The compound crystallizes with the hexagonal MgNi_2 (C14) type structure and contains two transition metal sites ($2a$, $6h$ in space group $P6_3/mmc$) on which aluminium partially substitutes manganese. The sites are some 2.7 Å apart from each other and one ($2a$) shows a slight preference for aluminium. It will be shown that hydrogenation of $\text{CeMn}_{1.8}\text{Al}_{0.2}$ leads to a metal atom exchange between these sites in the sense that aluminium in the hydride shows a clear preference for site $6h$. These findings are of importance from a practical point of view because they could lead to a better understanding of hitherto unexplained effects observed during the first hydrogenation cycles in this and related metal hydrides.

Sample preparation

Alloy samples of nominal composition $\text{CeMn}_{1.8}\text{Al}_{0.2}$ (~3 gram) were prepared from high purity elements at a slight excess of cerium (~3 at.%) by arc-melting and annealing at 700°C for 3 months. All operations were performed in an argon filled glove box to reduce oxygen contamination. Before the X-ray measurements and/or hydrogen treatments the samples were ground and sieved to a particle size of less than 25µm.

The samples were hydrided (deuterated) in a stainless autoclave. Various measures were taken to avoid the formation of binary CeH_2 and to improve the crystallinity of the ternary hydride, such as mixing initially hydrogen with argon, slowly increasing the hydrogen pressure, cooling the sample to ~-70°C during hydrogenation by using a mixtures of solid carbon dioxide and acetone, and annealing the hydride (deuteride) sample for 8-10 hours under 3 bars of H_2 pressure at slightly elevated temperatures (~175°C).

Structure investigations

The alloys and hydrides (deuterides) were investigated by X-ray and neutron powder diffraction. For the X-ray measurements a Bruker D8 Advance diffractometer was used (Bragg-Brentano geometry, PSD, sample holder for air-sensitive substances, $\text{CuK}\alpha_1$ radiation, 2θ range 25-127° for the alloy and 25-100° for the hydrides; 2θ step 0.0144°; $T = 293$ K, scan time up to 25 s per step). Structure refinements by the Rietveld method were performed with Fullprof by taking starting parameters for the atomic coordinates from [1]. The Al/Mn occupancies were constrained such as to yield to overall nominal composition of 10 at.% Al, i.e. only one parameter was refined to describe the Al/Mn distribution over sites $2a$ and $6h$. The refinement results and X-ray diffraction patterns of one alloy sample and hydride obtained at low temperature are summarised in (1) and (2) respectively.

Neutron diffraction data were collected on two (low-temperature) deuteride samples by using HRPT at the spallation neutron source SINQ of PSI (Villigen, $\lambda = 1.494$ Å; cylindrical vanadium holders, 2θ range 4.95-164.9°; 2θ step 0.05°; $T = 293$ K, 8 hours per sample, high intensity mode). One sample (3) was measured immediately after deuteration while the other (4) was annealed at 175°C for 8 hours under 3 bars of deuterium pressure. During structure refinement the Al/Mn occupancies were refined under the same constraints as those used for the X-ray refinement. Isotropic temperature factors for Al/Mn positions were constrained to be equal.

Results

Summary of occupancy factors for sites $2a$ and $6h$ for $\text{CeMn}_{1.8}\text{Al}_{0.2}$ and its hydride (deuteride):

(1) Alloy (2) Hydride (3) Deuteride (4) Annealed deuteride

Al($2a$)	0.29(1)	0.12(2)	0.306(15)	0.091(18)
Mn($2a$)	0.71(1)	0.88(2)	0.694(15)	0.909(18)
Al($6h$)	0.035(3)	0.093(7)	0.035(9)	0.099(11)
Mn($6h$)	0.965(3)	0.907(7)	0.965(9)	0.901(11)

- > alloy: the aluminium distribution over sites $2a$ and $6h$ is not random; aluminium clearly prefers site $2a$. The sample is nearly single phase;
- > hydride: no site preference is apparent within experimental error. The sample has partially segregated into CeH_x (8%). The cell volume has expanded by 42.5%;
- > deuteride: aluminium prefers site $2a$ as in the alloy sample. The sample has partially segregated into CeH_x (6%) and Mn (22%);
- > deuteride annealed: after annealing at 175°C no site preference is apparent within experimental error.

[1] K.J. Gross, D. Chartuni, F. Fauth, J. Alloys Comp., 2000, 306, 203-218.

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(1) Refinement results on X-ray data of the alloy

Atom (site)	x	y	z	B_{iso}	Occup.
Ce ($4f$)	1/2	2/3	0.06277(12)	0.958(28)	
Mn1 ($2a$)	0	0	0	1.364(53)	0.71(1)
Al1 ($2a$)					0.29(1)
Mn2 ($6h$)	0.8305(6)	2x	1/4	1.364(53)	0.965(3)
Al2 ($6h$)					0.035(3)

$$a = 5.37446(9), c = 8.76403(16) \text{ \AA}, V = 219.232(6) \text{ \AA}^3$$

$$R_B = 2.94\%, R_p = 31.0\%, R_{wp} = 14.1\%, S = 1.86. \text{ Mn (1.33\%)}$$

(2) Refinement results on X-ray data of hydrogenated at -70°C alloy

Atom (site)	x	y	z	B_{iso}	Occup.
Ce ($4f$)	1/2	2/3	0.0641(2)	0.20(7)	
Mn1 ($2a$)	0	0	0	0.66(7)	0.88(2)
Al1 ($2a$)					0.12(2)
Mn2 ($6h$)	0.8382(13)	2x	1/4	0.66(7)	0.907(7)
Al2 ($6h$)					0.093(7)

$$a = 6.0559(6), c = 9.8442(11) \text{ \AA}, V = 312.66(6) \text{ \AA}^3 \text{ - for the hydride}$$

$$a = 5.37473(13), c = 8.7663(3) \text{ \AA}, V = 219.31(1) \text{ \AA}^3 \text{ - for the alloy}$$

$$R_B = 5.13\%, R_p = 18.5\%, R_{wp} = 13.6\%, S = 1.47.$$

$$\text{CeH}_x (8.3\%), \text{unreacted alloy (1.5\%), } \alpha\text{-Mn (2.5\%) and CeO}_{1-x} (1.2\%).$$

(3) Refinement results on neutron diffraction data of non-annealed deuteride

Atom (site)	x	y	z	B_{iso}	Occup.
Ce ($4f$)	1/2	2/3	0.0643(5)	0.30(6)	
Mn1 ($2a$)	0	0	0	1.41(10)	0.694(15)
Al1 ($2a$)					0.306(15)
Mn2 ($6h$)	0.8390(10)	2x	1/4	1.41(10)	0.965(9)
Al2 ($6h$)					0.035(9)
D1 ($24f$)	0.0582(7)	0.3123(9)	0.5730(6)	2.33(6)	0.313(5)
D2 ($12k$)	0.4539(11)	2x	0.6422(6)	2.33(6)	0.413(8)
D3 ($6h$)	0.487(3)	2x	1/4	2.33(6)	0.273(7)
D4 ($6h$)	0.1883(12)	2x	1/4	2.33(6)	0.584(9)

$$a = 5.9789(6), c = 9.7601(13) \text{ \AA}, V = 302.15(6) \text{ \AA}^3$$

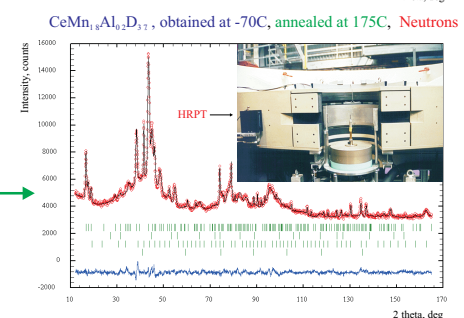
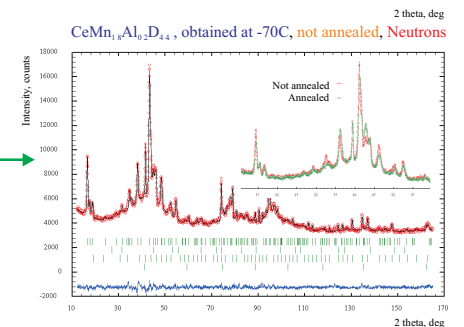
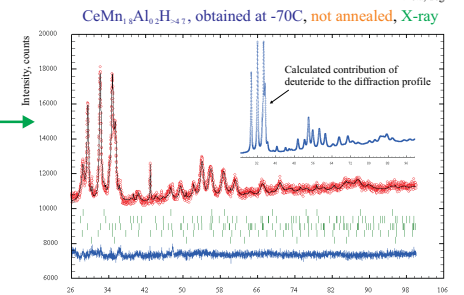
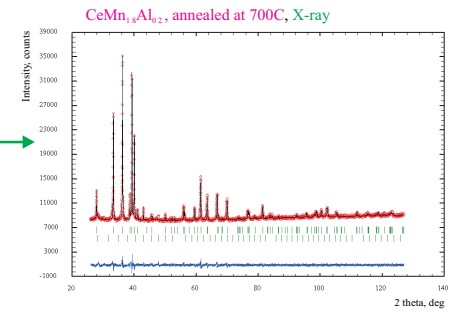
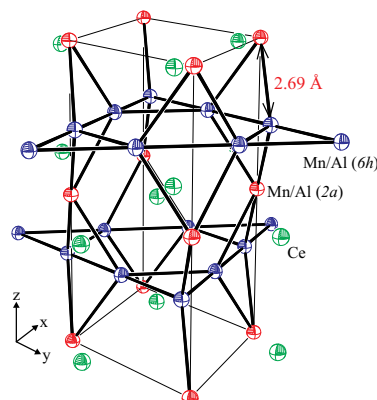
$$R_B = 4.29\%, R_p = 15.6\%, R_{wp} = 15.8\%, S = 3.14. \text{ CeH}_x (5.6\%) \text{ and } \beta\text{-Mn (21.5\%).}$$

(4) Refinement results on neutron diffraction data on annealed deuteride (175°C)

Atom (site)	x	y	z	B_{iso}	Occup.
Ce ($4f$)	1/2	2/3	0.0657(6)	1.28(10)	
Mn1 ($2a$)	0	0	0	3.26(15)	0.909(18)
Al1 ($2a$)					0.091(18)
Mn2 ($6h$)	0.8384(18)	2x	1/4	3.26(15)	0.901(11)
Al2 ($6h$)					0.099(11)
D1 ($24f$)	0.0585(7)	0.3049(9)	0.5735(6)	1.80(7)	0.317(6)
D2 ($12k$)	0.4499(16)	2x	0.6426(9)	1.80(7)	0.251(7)
D3 ($6h$)	0.496(2)	2x	1/4	1.80(7)	0.307(8)
D4 ($6h$)	0.1853(18)	2x	1/4	1.80(7)	0.426(9)

$$a = 5.9363(8), c = 9.7629(17) \text{ \AA}, V = 297.94(8) \text{ \AA}^3$$

$$R_B = 6.06\%, R_p = 18.7\%, R_{wp} = 16.0\%, S = 2.70. \text{ CeH}_x (8.5\%), \beta\text{-Mn (19.2\%).}$$



Conclusions

- The metal atom distribution in the C14 structure of $\text{CeMn}_{1.8}\text{Al}_{0.2}$ changes during hydrogenation (deuteration) near ambient conditions. While the alloy shows a preference of aluminium for site $2a$, the hydride and the annealed deuteride show nearly random occupancies of sites $2a$ and $6h$ by aluminium and manganese.
- The metal atom exchange during hydrogenation (deuteration) presumably occurs between nearest neighbors that are distant by ~2.7 Å. The reasons for this exchange are unknown. During the rearrangement of the metal atom substructure repulsive H-Al interactions could play a role.
- The effect presumably depends on the speed of hydrogenation (deuteration) and the local temperature increase of the metal grains during the (strongly exothermic) reaction.
- The volume expansion between the alloy and the hydride (42.5%) is the biggest known so far among reversible metal hydrides.
- The reasons for the exceptionally high mobility of the metal atom substructure of $\text{CeMn}_{1.8}\text{Al}_{0.2}$ during hydrogenation near ambient conditions, and for the exceedingly big hydrogen induced volume expansion are not yet clear. A valence change of Ce (from +4 to +3) could be the reason of this.