Hydrogenation induced valence change and metal atom site exchange at room temperature in the C14-type sub-structure of CeMn$_{1.8}$Al$_{0.2}$H$_{4.4}$

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Abstract

CeMn$_{1.8}$Al$_{0.2}$ absorbs more than 4.4 hydrogen atoms near ambient conditions, thereby undergoing a volume expansion ($\Delta V/V$~43%) that is the largest known among metal hydrides. While the Mn/Al distribution in the C14-type alloy [P6$_3$/mmc, $a=5.37393(6)$, $c=8.76321(12)$ Å] is partially ordered (preference of Al for site 2$a$), it tends to become disordered in the hydride (equal Mn/Al occupancies for sites 2$a$ and 6$h$). Only very slow hydrogenation while cooling the sample to $\sim 70$ °C is capable of maintaining a partial Mn/Al order. Deuterium in CeMn$_{1.8}$Al$_{0.2}$D$_{4.4}(7)$ [$a=5.9788(6)$, $c=9.7600(13)$ Å] occupies exclusively tetrahedral Ce(Mn,Al)$_2$ type interstices. Magnetic susceptibility data suggest that the volume expansion during hydrogenation is enhanced by a valence change of cerium (Ce$^{IV}$→Ce$^{III}$).

Keywords: Hydrogen storage materials; Magnetic measurements; Valence change; Crystal structure; Neutron diffraction

1. Introduction

The solid solution series Ce(Mn$_{1-x}$Al$_x$)$_2$ crystallises with a hexagonal C14-type structure in the range 0.15 $\leq x \leq 0.35$ and a cubic C15-type structure for $x>0.35$ and $x<0.1$ [1]. Binary CeMn$_2$ ($x=0$) does not seem to exist. A recent in-situ neutron diffraction study of hexagonal CeMn$_{1.8}$Al$_{0.2}$ ($x=0.25$) as a function of deuterium pressure has shown [2] that the compound absorbs up to ~four deuterium atoms per formula unit (f.u.) at room temperature and 25 bar pressure, thereby undergoing a lattice expansion of ~34%. The authors concluded that the Mn and Al atoms on the two available sites in the structure (2$a$ and 6$h$ in the space group P6$_3$/mmc) were distributed at random in both the alloy and the deuteride. In this paper we report on the synthesis, structure and hydrogenation properties of a more Mn rich alloy of composition CeMn$_{1.8}$Al$_{0.2}$ ($x=0.1$). It will be shown that this compound absorbs ~10% more hydrogen (~4.4 H/f.u.) than the previously investigated one, and undergoes a volume expansion of ~43% that is the biggest known among reversible metal hydrides. Diffraction data reveal a partially ordered Mn/Al atom distribution that tends to become disordered during hydrogenation. Magnetic measurements show a hydrogenation induced valence change of cerium (Ce$^{IV}$→Ce$^{III}$).

2. Experimental

2.1. Synthesis of alloys

Samples of nominal composition CeMn$_{1.8}$Al$_{0.2}$ were prepared by arc-melting mixtures of high purity elements (Ce: Ames Lab., ingot, 99.93%; Mn: Koklite, pieces, 99.99%; Al: JMC, wire, 99.999%) at a small excess of cerium (3 wt.%). The ingots (~3 g) were sealed into quartz tubes under 0.3 bar argon pressure and annealed at 700 °C for up to 8 weeks. They were essentially single phase and crystallised with a hexagonal C14-type structure. Those annealed for a week (samples 1–3) contained traces of α-Mn while those annealed for 2 months (samples 4 and 5) contained some β-Mn.
2.2. Hydrogenation (deuteration)

The alloys 3–5 were hydrogenated (deuterated) under a pressure of 0.2–3 bar in a stainless autoclave (D₂, purity 99.4%). Considerable difficulties were encountered to obtain reproducible results because the hydrogenation properties depended not only on obvious parameters such as temperature, pressure and time, but also on less obvious parameters such as hydrogenation speed, grain size and total sample mass. Generally, rapid hydrogenation at room temperature of coarse powders having a large mass lead to substantial diffraction peak broadening and/or disproportionation of the alloy into binary Ce hydride and manganese. To reduce these undesirable effects, hydrogenation was carried out at low temperature on finely ground and sieved powders of small mass. The best results (i.e. large hydrogen contents, little disproportionation, good sample crystallinity) were obtained on powders not exceeding 25 μm in grain size and 3 g in total mass that were hydrogenated (deuterated) at −70 °C by using a cooling mixture of solid carbon dioxide and acetone. For sample 3, the hydrogen pressure was increased stepwise during 4 h up to 3 bar and left at that level for 15 h. For samples 4 and 5, deuterium/argon/manganese were used, the pressure of which was increased stepwise during 8 h to 2 bar and left at that level for 15 h. In order to reduce lattice strain and favour a possible Mn/Al rearrangement in the structure, Al(B1) and Al(B2) sites of space group P6₃/mmc; D in four tetrahedral (A₂B₂) type interstices. For sample 1 single crystals were isolated from the surface of the annealed ingot and investigated on a Stoe IPDS image plate diffractometer (Mo Kα radiation). During structure refinement the total occupancy (Al + Mn) of each metal site (B1, B2) was constrained to 100% but left unconstrained with respect to the Mn/Al ratio, and individual anisotropic displacement parameters were used. Samples 2–5 were investigated by powder X-ray (2, 3: Bruker D8 Advance diffractometer, Cu Kα₁ radiation) and neutron diffraction (4, 5: HRPT [3] at SINQ, PSI, Villigen, λ = 1.494 Å). All samples contained a C14-type majority phase. While the alloy 2 was practically single-phase, the hydride 3 and the deuterides 4 and 5 contained considerable amounts of secondary phases due to disproportionation (mainly manganese and cerium based impurities). During structure refinement the occupancies of the metal sites of the C14-type phase were constrained with respect to both their sums (Mn + Al = 100% for B1 and B2 each) and nominal composition (Mn/Al = 9). Isotropic displacement parameters were used and constrained to be equal. Refined cell parameters and occupancy factors for the metal sites for the various samples are summarized in Table 1. Detailed structure results are given only for the deuterides 4 and 5 as shown in Table 2. Structure data for the other samples will be presented elsewhere. The neutron patterns of sample 4 are shown in Fig. 1 and a partial view of the CeMn₁₈Al₀₂D₄₋₄₋ structure is given in Fig. 2.

2.4. Magnetic susceptibility

Magnetic measurements on the alloy 2, the hydride 3 and the deuterides 4 and 5 were performed by using a SQUID magnetometer. The comparison of the d.c. susceptibilities (M/H) of CeMn₁₈Al₀₂ and CeMn₁₈Al₀₂D₅ in Fig. 3 demonstrates the significant influence of deuterium (hydrogen) uptake on the magnetic properties in these compounds.

3. Results and discussion

3.1. Hydrogenation induced volume increase

The volume increase during hydrogenation (deuteration) of the presently studied compounds (3 CeMn₁₈Al₀₂H₄; ΔV/V = 42.5%; 4 CeMn₁₈Al₀₂D₄₋₄₋: ΔV/V = 37.9%) is

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Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cell parameters</th>
<th>Method</th>
<th>Al(B1)</th>
<th>Al(B2)</th>
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<tr>
<td>1 Alloy CeMn₁₈Al₀₂</td>
<td>a = 5.3980(10), c = 8.806(2) Å, V = 222.21(8) Å³</td>
<td>Single crystal X-ray</td>
<td>0.18(2)</td>
<td>0.10(1)</td>
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<tr>
<td>2 Alloy CeMn₁₈Al₀₂</td>
<td>a = 5.3739(6), c = 8.76321(12) Å, V = 219.169(5) Å³</td>
<td>Powder X-ray</td>
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<td>0.093(7)</td>
</tr>
<tr>
<td>3 Hydride CeMn₁₈Al₀₂H₄</td>
<td>a = 6.055(9), c = 9.844(9) Å, V = 312.66(6) Å³</td>
<td>Powder X-ray</td>
<td>0.12(2)</td>
<td>0.093(7)</td>
</tr>
<tr>
<td>4 Deuteride CeMn₁₈Al₀₂D₄₋₄₋</td>
<td>a = 5.9788(6), c = 9.7600(13) Å, V = 302.14(6) Å³</td>
<td>Powder neutrons</td>
<td>0.296(12)</td>
<td>0.035(4)</td>
</tr>
<tr>
<td>5 Annealed deuteride CeMn₁₈Al₀₂D₅₋₅₋</td>
<td>a = 5.9353(8), c = 9.7641(17) Å, V = 297.88(8) Å³</td>
<td>Powder neutrons</td>
<td>0.033(12)</td>
<td>0.123(4)</td>
</tr>
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</table>

E.S.D.s in parentheses.
Table 2
Neutron powder diffraction refinement results on deuteride samples 4 (first lines) and 5 (second lines, in italics)

<table>
<thead>
<tr>
<th>Atom (site)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B</th>
<th>Occupancy</th>
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<td>D1 (24l)</td>
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4: Refined composition CeMn<sub>1.5</sub>Al<sub>0.5</sub>D<sub>4.5</sub>, agreement indices: \( R_a = 4.16\% \), \( R_p = 15.7\% \), \( R_{wp} = 15.8\% \), \( S = 3.10 \); secondary phases CeD<sub>3</sub> (5.6\%) and \( \beta \)-Mn (21.3\%).

5: Refined composition CeMn<sub>1.5</sub>Al<sub>0.5</sub>D<sub>4.5</sub>, agreement indices: \( R_a = 4.59\% \), \( R_p = 16.8\% \), \( R_{wp} = 15.0\% \), \( S = 2.68 \); secondary phases CeD<sub>3</sub> (8.6\%) and \( \beta \)-Mn (18.2\%).

much bigger than that of previously investigated more Al rich compositions (CeMn<sub>1.5</sub>Al<sub>0.5</sub>D<sub>3.6</sub> obtained at 2.7 bar \( H_2 \) pressure; \( \Delta V/V = 30.1\% \) [2]). It is the largest known so far for reversible metal hydrides. Given the usually observed volume increments in Laves phase hydrides (~2.5–3 \( \AA^3/D \) atom), those in the present compounds (4: ~4.75 \( \AA^3/D \) atom) cannot be exclusively due to the space requirement of hydrogen and suggest the onset of a valence transition of cerium (Ce\(^{IV} \rightarrow Ce^{III}\)). Large hydro-
gen induced volume expansions are not uncommon in cerium based intermetallics as shown by CeCo<sub>3</sub>H<sub>4</sub> for which the rhombohedral c axis increases by more than 30\% [4], and CeRu<sub>2</sub>H<sub>4</sub> for which the cell volume increases by ~37\% [5]. For the latter, neutron diffraction experiments [6] and X-ray photoemission spectroscopy data [7] have provided evidence for hydrogen induced magnetic ordering. A hydrogen induced valence transition was also found in the nickel analogue CeNiAlH<sub>4</sub> as shown by

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Fig. 1. Observed (circles) calculated (line) and difference (bottom) neutron powder diffraction patterns of the deuteride CeMn<sub>1.5</sub>Al<sub>0.5</sub>D<sub>4.5</sub> (sample 4, \( \lambda = 1.494 \AA \)). Vertical bars indicate Bragg positions of main phase, CeD<sub>3</sub> and Mn (from top to bottom). Broad maxima correspond to diffraction orders \( n = 1, 2 \) for short-range ordered D–D distances of 2.1 \( \AA \).
3.2. Metal atom site preference

The two B metal sites in the structure are not occupied at random, at least not in the alloys 1 and 2 for which aluminium clearly prefers B1 over B2 (see Table 1). A deviation from random occupancy of these sites is not surprising because they are crystallographic non-equivalent. While B1 (site 2a, \( \bar{3}m \) symmetry) joins double-tetrahedrons of B-atoms via corners to chains running along the hexagonal axis, B2 (site 6h, \( m \bar{m}2 \) symmetry) forms the triangular base of the double-tetrahedrons (see Fig. 2). Surprisingly, however, this site preference is attenuated in the hydrides (deuterides). In 3, for example, the B sites show nearly random occupancy [12(2)% Al for B1 and 9(1)% Al for B2, compared to 10% Al for random occupancy]. In other words, a significant fraction of aluminium (\( \sim 40\% \)) has migrated during hydrogenation from B1 to B2 (and manganese from B2 to B1) thus increasing the structural disorder. This is the first time that such a hydrogenation induced rearrangement of metal atoms is detected in Laves phase compounds. Interestingly, the \( \text{CeMnAlH}_2 \) for which the volume expansion is \(<7\% \) [9]. This behaviour is consistent with earlier suggestions [10] concerning the valence state of cerium in \( \text{Ce(Mn}_{1-x}\text{Al})_2 \) alloys that is Ce\(^{III}\)-like in Al rich (cubic) and Ce\(^{IV}\)-like in Al poor (hexagonal) compositions.

Fig. 2. Partial view of the hexagonal Laves phase derivative structure of \( \text{CeMn}_{1.3}\text{Al}_{0.2}\text{D}_{3.5} \). Large spheres Ce, medium spheres Mn(Al), small spheres deuterium (sites numbered). During hydrogenation aluminum atoms migrate from B1 (dark spheres) to B2 (light spheres), and manganese from B2 to B1 (see arrows).

Fig. 3. Susceptibility (M/H) after zero-field cooling as a function of temperature for \( \text{CeMn}_{1.8}\text{Al}_{0.2} \) and \( \text{CeMn}_{1.8}\text{Al}_{0.2}\text{D}_{3.5} \).
of the sample environment during the reaction was kept rather low (−70 °C) it did presumably not prevent individual metal grains from heating up and inducing an atom exchange between nearest neighbour sites (see B1 and B2 in Fig. 2). Such a picture is consistent with the observed dependence of hydrogenation on experimental conditions such as speed of hydrogenation, grain size and sample mass.

3.3. Influence of aluminum content on hydrogenation properties

Similar to the cubic series Ce(Mn_{1−x}Al)_{2} (0.5<x<1) [11] the relatively Al rich composition CeMn_{1.5}Al_{0.5} [2] of the hexagonal series absorbs less hydrogen than the Al poorer composition CeMn_{1.8}Al_{0.2}. For the cubic series the decrease of hydrogen capacity as a function of Al content has been modeled by a statistical analysis [11] and attributed to a preferential hydrogen occupancy of Al free metal tetrahedra [Ce_{2}Mn_{2}] at the expense of Al containing tetrahedra [Ce_{2}AlMn] and [Ce_{2}Al]. A similar model also appears to be applicable for the present hexagonal series because the average number of metal–deuterium contacts per B atom site, N_{D}, in 4 CeMn_{1.8}Al_{0.2}D_{4.4} is smaller for the more Al rich site B1 (N_{D}=3.74; ~30% Al) than for the less Al rich site B2 (N_{D}=4.57; ~4% Al). However, the data for 5 CeMn_{1.8}Al_{0.2}D_{4.4} (B1: N_{D}=3.12, ~3% Al; B2: N_{D}=3.36, ~12% Al) show the opposite trend, thus suggesting a more complex behaviour. Finally, an estimation of the maximum hydrogen site occupancies and hydrogen contents based on purely geometric grounds [12], i.e. without considering the influence of preferential occupancy of Al free metal tetrahedrons, yields values (24l: 1/2−1/3, 12k_{1}: 1/3−2/3, 6h_{1}: 0, 6h_{1}: 1; H_{max}=5.5 H/f.u.) that differ significantly from those estimated previously for CeMn_{1.5}Al_{0.2}D_{4.0} (24l: 1/4, 12k_{2}: 1/2, 6h_{2}: 0; 6h_{1}: 1; H_{max}=4.5 H/f.u. [2]).

3.4. Magnetic properties

As shown in Fig. 3 the susceptibilities of the alloy 2 CeMn_{1.8}Al_{0.2} and the deuteride 5 CeMn_{1.8}Al_{0.2}D_{4.52} can be properly described with a modified Curie Weiss law \( \chi = \chi_0 + C/(T−\Theta) \) (\( \chi_0 \) Pauli susceptibility, C Curie constant, \( \Theta \) paramagnetic Curie temperature). The susceptibility of the alloy is dominated by an essentially temperature independent susceptibility \( \chi_0 \) of ~2.6(2)·10^{-3} emu/mol above 50 K. The low temperature upturn can be attributed to a Curie Weiss contribution of impurity phases (β-Mn and CeO_{2−}), see Section 2.1) corresponding to a rather low effective moment of about \( \mu_{eff}=0.55(4) \mu_B \) and to a paramagnetic Curie temperature of 16 K. The latter is indicative for ferromagnetic correlations, but no long range order occurs down to 2 K. For the deuterides 4 and 5 the analysis of the susceptibility data above 110 K yields a significantly smaller \( \chi_0 \) of about 6(2)·10^{-4} emu/mol than for the parent compound but gives an effective moment of \( \mu_{eff}=3.5(2) \mu_B \) and 3.2(2) \( \mu_B \), respectively, which is close to that of trivalent Ce^{3+} (\( \mu_{eff}=3.6 \mu_B \)). The effective moment of the hydride 3 [3.2(2) \( \mu_B \)] coincides with those of the deuterides. The remarkably large increase in effective moment by 3 \( \mu_B \) under hydrogenation together with the big volume expansion provides strong evidence for a valence change Ce^{IV}→Ce^{III}. The anomalous flattening of the susceptibility of the deuteride below 75 K together with the appearance of an irreversibility between field cooling (not shown for clarity) and zero field cooling is reminiscent to freezing of magnetic clusters over a rather broad range of temperatures. Freezing phenomena may arise from the fine granularity of the powder specimens. The transition at 75 K and the irreversibility exhibits a remarkable field dependence: The former is washed out and shifted to lower temperatures as external fields are increased and freezing diminishes at about 3 T. Although the fairly complex field and temperature dependence of the susceptibility for \( T<80 \) K does not allow a straightforward interpretation to be made, we suggest that the broad peak at 75 K in the zero-field cooling susceptibilities of the deuterides and the cusp at 70 K in the hydride arises from antiferromagnetic order within the grains of the fine powder.

4. Conclusion

CeMn_{1.8}Al_{0.2}, if carefully hydrided, absorbs more than 4.4 H atoms/f.u., thereby undergoing a very large volume expansion and a metal atom site exchange that is the first of that type reported in Laves phase structures. While the exchange as such is not surprising, the fact that it occurs over a distance of 2.7 Å at room temperature is remarkable. The exceptional mobility of the metal atom substructure during hydrogenation is enhanced by a valence transition of cerium and a structural segregation into manganese (aluminium) and binary cerium hydride. Both the volume expansion and the change from Pauli paramagnetism to local moment, i.e. Curie Weiss behaviour with an effective moment of 3.5 \( \mu_B \), provide evidence for a hydrogen induced valence transition Ce^{IV}→Ce^{III}. The anomalous temperature and field dependence of the susceptibility of the deuterides and the hydride at low temperatures presumably arises from antiferromagnetic order within the grains at about 75 and 70 K, respectively, and seems to be complicated by freezing phenomena due to the fine granularity of the deuterided or hydrided powder.

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