Hydrogenation Induced Metal Atom Exchange near Room Temperature in the C14-Type Metal 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 H atoms per formula unit near ambient conditions, thereby undergoing a volume expansion ($\Delta V/V$=42.5%) that is the largest known among metal hydrides. While the Mn/Al distribution in the C14 type alloy is partially ordered (preference of Al for site 2*a*), it is disordered in the hydride (equal Mn/Al occupancies for sites 2*a* and 6*h*). Only very slow hydrogenation while cooling the sample to low temperature (-70°C) is capable of maintaining a partial Mn/Al order

Deuterium in $CeMn_{1.8}Al_{0.2}D_{4.36(7)}$ occupies exclusively tetrahedral $Ce_2(Mn,Al)_2$ type interstices. The more Al rich site 2*a* is surrounded by less deuterium atoms, on the average, than the less Al rich site 6*h*. Magnetic measurements confirm that the very large volume expansion during hydrogenation is partly due to a valence change of cerium (Ce^{IV} to Ce^{III}).

Samples preparation

Look at the table →

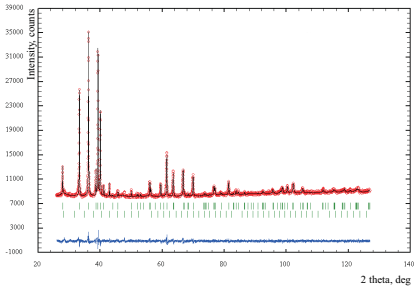
Alloy samples $CeMn_{1.8}Al_{0.2}$ (~3 gram) were prepared from high purity elements at a slight excess of cerium (~3 at.%) by arc-melting and annealing at 700C. All operations were performed in an argon filled glove box. Before the X-ray measurements or hydrogen treatments the samples were ground and sieved to a particle size of less than 25 micron .

The samples were hydrided (deuterated) in a stainless autoclave. Various measures were taken to avoid the formation of binary $CeH_{\sim 2}$ 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 hours under 3 bars of H_2 pressure at slightly elevated temperatures (~ 175°C)

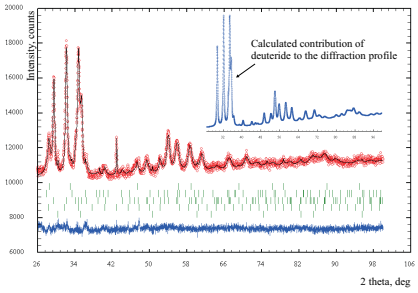
Sample compositions, preparation conditions and refined aluminium occupancies

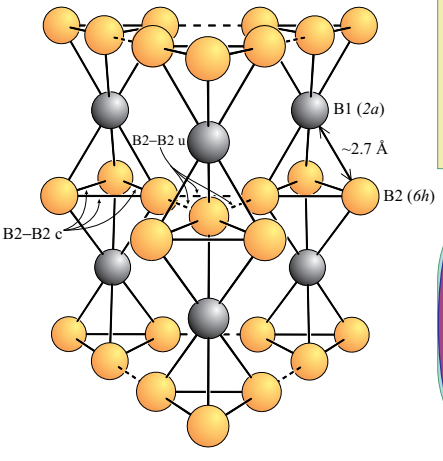
Sample	preparation conditions	method	Al(B1)	Al(B2)
1 Alloy $CeMn_{1.8}Al_{0.2}$	arc melting, annealed at 700°C for 1 week; single crystal isolated on surface of ingot	single crystal, X-ray	0.18(2)	0.10(1)
2 Alloy $CeMn_{1.8}Al_{0.2}$	as **1**, ingot ground to a powder of 25 µm grain size	powder X-ray	0.284(9)	0.039(3)
3 Hydride $CeMn_{1.8}Al_{0.2}H_x$	as **2**, hydrogenated at ~ –70°C by increasing H_2 pressure up to 3 bar stepwise during 4 hours and leaving at 3 bar for 15 hours.	powder X-ray	0.12(2)	0.093(7)
4 Deuteride $CeMn_{1.8}Al_{0.2}D_{4.37}$	arc melted alloy annealed at 700°C for 2 months, ground and deuterated at -70°C by mixing D_2 with 1 bar Ar and increasing D_2 pressure stepwise during 8 hours to 2 bar and leaving for 15 hours.	powder neutrons	0.296(12)	0.035(4)
5 / **5a** Annealed deuteride $CeMn_{1.8}Al_{0.2}D_{3.52}$	identical to **4**, with subsequent annealing at 175°C for 8 hours	powder neutrons / synchrotron	0.033(12) / 0.115(5)	0.123(4) / 0.095(2)

$CeMn_{1.8}Al_{0.2}$, annealed at 700C, X-ray

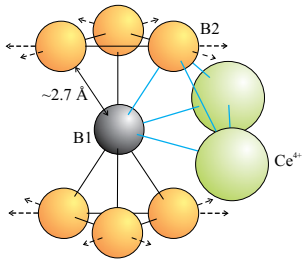


$CeMn_{1.8}Al_{0.2}H_{\sim 4.7}$, obtained at -70C, not annealed, X-ray

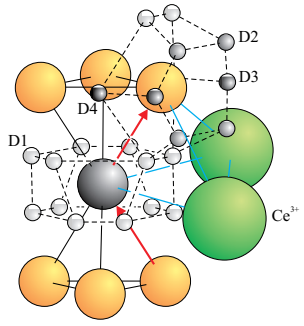




Mn/Al metal substructure in the hexagonal Laves phase derivative structure of $CeMn_{1.8}Al_{0.2}D_{4.4}$



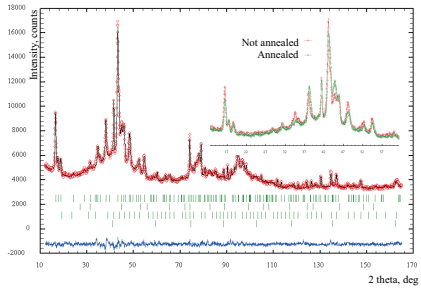
a) $CeMn_{1.8}Al_{0.2}$



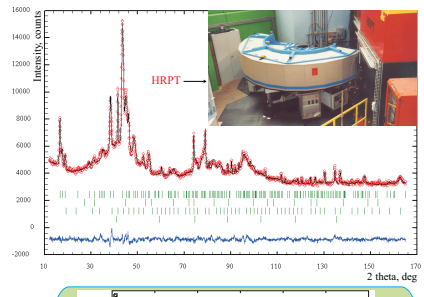
b) $CeMn_{1.8}Al_{0.2}D_{4.4}$

During hydrogenation Ce atoms expand, Al atoms migrate from B1 to B2 (see red arrows in **b**).

$CeMn_{1.8}Al_{0.2}D_{4.4}$, obtained at -70C, not annealed, Neutrons



$CeMn_{1.8}Al_{0.2}D_{3.7}$, obtained at -70C, annealed at 175C, Neutrons



Structure investigations

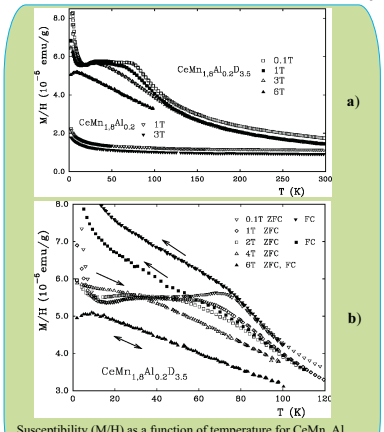
Single crystal

1: Stoe IPDS image plate diffractometer, MoK_{alpha} radiation
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; individual anisotropic *U*'s.

Rietveld refinement

Powders **2** and **3**: Bruker D8 Advance diffractometer, $CuK_{alpha\ 1}$ radiation;
Powders **4** and **5**: HRPT, spallation neutron source SINQ of PSI (Villigen), 1.494 Å;
Powder **5a**: Swiss Norwegian Beamline (BM1) at ESRF (Grenoble), 0.48562 Å
the occupancies of the metal sites were constrained to 100% and their overall ratio as given by the nominal composition. Isotropic *U*'s were constrained to be equal.

Magnetic measurements on the alloy **2** and the deuteride **5** in a quartz capillaries were performed by using a SQUID magnetometer.



Susceptibility (M/H) as a function of temperature for $CeMn_{1.8}Al_{0.2}$ and $CeMn_{1.8}Al_{0.2}D_{3.5}$ (**a**) and zero field cooled (ZFC) and field cooled (FC) susceptibility (M/H) for $CeMn_{1.8}Al_{0.2}D_{3.5}$ (**b**) as a function of temperature and various fields.

Conclusions

- $CeMn_{1.8}Al_{0.2}$, if carefully hydrided, absorbs more than 4.4 H atoms/f.u;
- the very large volume expansion (43%) - the highest for metal hydrides;
- metal atom site exchange occurs over a distance of 2.7 Å at room temperature - the first reported for Laves phase structures;
- the exceptionally high mobility of the metal atom substructure during hydrogenation is presumably related to a valence transition and the tendency of segregation into binary cerium hydride;
- both the volume expansion and the change from Pauli paramagnetism to local moment - Curie Weiss behaviour with an effective moment of 3.5 μ_B provide evidence for a hydrogen induced valence transition Ce^{IV} to Ce^{III}.

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