Hydrogenation Induced Metal Atom Exchange near Room Temperature in the C14-Type Metal Sub-Structure of CeMn$_{1.8}$Al$_{0.2}$H$_{4.4}$

**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 ($\Delta V/V=42.5\%$) which 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 2a), it is disordered in the hydrate (equal Mn/Al occupancies for sites 2a and 6b). Only very slow hydrogenation while cooling the sample to low temperature ($-70^\circ$C) is capable of maintaining a partial Mn/Al order.

Deuterium in CeMn$_{1.8}$Al$_{0.2}$D$_{3.52}$ was exclusively tetrahedral Ce(Ce,Al) type interstices. The more Al rich site 2a is surrounded by less deuterium atoms, on the average, than the less Al rich site 6b. Magnetic measurements confirm that the very large volume expansion during hydrogenation is partly due to a valence change of cerium (Ce$^{4+}$ to Ce$^{3+}$).

**Structure investigations**

*Y. Filinchuk*, D. Sheptyakov, G. Hilscher, K. Yvon

1 Laboratoire de Cristallographie, Université de Genève, Switzerland
2 Laboratory for Neutron Scattering, ETHZ & PSI, Villigen PSI, Switzerland
3 Institut für Experimentalphysik, Technical University, Vienna, Austria

**Sample compositions, preparation conditions and refined aluminium occupancies**

<table>
<thead>
<tr>
<th>Sample</th>
<th>preparation conditions</th>
<th>method</th>
<th>Al(B1)</th>
<th>Al(B2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Alloy CeMn$<em>{1.8}$Al$</em>{0.2}$</td>
<td>arc melting, annealed at 700°C for 1 week; single crystal isolated on surface of ingot</td>
<td>single crystal, X-ray</td>
<td>0.18(2)</td>
<td>0.10(1)</td>
</tr>
<tr>
<td>2 Alloy CeMn$<em>{1.8}$Al$</em>{0.2}$</td>
<td>as 1, ingot ground to a powder of 25 µm grain size</td>
<td>powder X-ray</td>
<td>0.284(9)</td>
<td>0.039(3)</td>
</tr>
<tr>
<td>3 Hydride</td>
<td>as 2, hydrogenated at $-70^\circ$C by increasing H$_2$ pressure up to 3 bar stepwise during 8 hours and leaving at 3 bar for 15 hours.</td>
<td>powder X-ray</td>
<td>0.12(2)</td>
<td>0.093(7)</td>
</tr>
<tr>
<td>4 Deuteride</td>
<td>as 2, hydrogenated at $-70^\circ$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.</td>
<td>powder neutrons</td>
<td>0.296(12)</td>
<td>0.035(4)</td>
</tr>
<tr>
<td>5 5a Annealed deuteride</td>
<td>CeMn$<em>{1.8}$Al$</em>{0.2}$D$_{3.52}$</td>
<td>identical to 4, with subsequent annealing at 175°C for 8 hours</td>
<td>powder neutrons / synchrotron</td>
<td>0.033(12)</td>
</tr>
</tbody>
</table>

**Conclusions**

- CeMn$_{1.8}$Al$_{0.2}$, if carefully hydried, absorbs more than 4.4 H atoms/Fa;
- 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$^{4+}$ to Ce$^{3+}$.