Hydrogen-induced structure transition in LaNi$_3$B

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**Synthesis**

A structure transition has been monitored by X-ray diffraction on a single-crystal measured before and after hydrogen treatment.

**For the first time**

The symmetry of the structure lowers from Imma to Cmcm ($a' = 2a$, $b' = 2b$) upon hydrogenation!!!

Deuteride: autoclave hydrogenation

LaNi$_3$BD$_{3.73}$ - room temperature, 5-100 bar D$_2$

Single crystal data for LaNi$_3$B and LaNi$_3$BH$_{2.7}$

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>LaNi$_3$B</th>
<th>LaNi$<em>3$BH$</em>{2.7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>325.85</td>
<td>325.85 (no H atoms)</td>
</tr>
<tr>
<td>Space group</td>
<td>Imma Cmcm</td>
<td>Imma Cmcm</td>
</tr>
<tr>
<td>c/a</td>
<td>4.78(3)</td>
<td>4.78(3)</td>
</tr>
<tr>
<td>b/a</td>
<td>10.76(2)</td>
<td>10.76(2)</td>
</tr>
<tr>
<td>Z, D$_2$ (H atoms) $^1$</td>
<td>4, 7.353</td>
<td>4, 7.353</td>
</tr>
<tr>
<td>$\delta_{Ga}$ / $\delta_{Ga}$ $^2$</td>
<td>0.65 / 85.4</td>
<td>0.65 / 85.4</td>
</tr>
<tr>
<td>R$<em>{int}$/R$</em>{sigma}$</td>
<td>0.0304 / 0.0127</td>
<td>0.0304 / 0.0127</td>
</tr>
<tr>
<td>R$_1$/$wR$_1$</td>
<td>0.0543 / 0.0684</td>
<td>0.0543 / 0.0684</td>
</tr>
<tr>
<td>Goodness of fit on $R^2$</td>
<td>1.853</td>
<td>1.853</td>
</tr>
<tr>
<td>Largest diff. peak and hole in $\AA^3$</td>
<td>-3.501 and -1.748</td>
<td>-3.501 and -1.748</td>
</tr>
</tbody>
</table>

**Thermal displacements for the Ni2 and La atoms in the alloy structure**

- Foresee site symmetry degeneration observed in the structure of the hydride.
- 95% and 50% probability anisotropic thermal ellipsoids are shown for LaNi$_3$B and LaNi$_3$BH$_{2.7}$ structures (single crystal XRD).

**Symmetry:** changes upon hydrogenation according to a group-subgroup sequence: Imma $\rightarrow$ [2] Pmnb $\rightarrow$ [2] Bnmb ($a' = 2a$, $c' = 2c$), $b'$ and $c'$ interchanged to use the standard setting Cmcm

**Synchrotron powder diffraction** on the alloy and hydride samples confirmed our observations of the structure transition, resulting in a single-crystal-like quality of the structural parameters derived by Rietveld refinement.

The same thermal ellipsoid for Ni2 atom as from single-crystal data

**Cell expansion:**

- Apart from a unit cell doubling along $a$ and $b$ the structure expands in the $a$-$b$ plane (by up to $\sim 8\%$) and contracts along $c$ (by $\sim 3\%$).

**D atom sites:**

- Four deuterium positions tend to be fully occupied in stoichiometric LaNi$_3$BD$_3$;
  - D1, D2 – La$_3$Ni$_7$ tetrahedron, D3 – La$_3$Ni$_3$ prism, D4 – La$_3$Ni$_3$ TBP;
  - La-B planes do not accommodate hydrogen.

**Neutron powder diffraction**

**HRPT at PSI**

**D1, D2**

**D4**

**Ni atoms environment:**

- Ni1 - cis-square B,D$_2$;
  - Ni2 - strongly distorted B,D$_2$ tetrahedron;
  - Ni3, Ni4 - TBP with 3D plus 2B in apices

**Two dimensional Ni-D framework** in the LaNi$_3$BD$_{3.73}$ unique in metal hydride structures

**Neutron powder diffraction** in a double-walled V-cylinder

**HRPT instrument at PSI, 1.494 Å**

**Alcohols hydrogenation at near ambient conditions**

- Pressure-composition isotherm of LaNi$_3$BH$_3$ at 28°C; max. H-content 2.4 H/f.u. (1st cycle)

**Weight increase, %**

- Ni$_2$B$_x$ - strongly distorted B,D$_2$ tetrahedron;
  - Ni$_3$, Ni$_4$ - TBP with 3D plus 2B in apices

**Two dimensional Ni-D framework** in the LaNi$_3$BD$_{3.73}$ unique in metal hydride structures

**Synthesis**

- arc-melting, the phase appears only after annealing at 800°C

- autoclave hydrogenation

- room temperature, 5-100 bar D$_2$