Synthesis and properties of NaZn$_{13}$-type interstitial compounds

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Abstract

The effect of interstitial nitrogen and hydrogen atoms on the structural and magnetic properties of LaCo$_{11}$Al$_2$ and CeNi$_8$Si$_4$ was studied. Synthesis of LaCo$_{11}$Al$_2$H$_3$ and LaCo$_{11}$Al$_2$N$_2$ was performed under a pressure of 30 bar hydrogen and nitrogen and at the temperatures 623 and 773 K. Synthesis of CeNi$_8$Si$_4$H$_{0.9}$ and CeNi$_8$Si$_4$N$_{0.5}$ was realized under a pressure of 30 bar hydrogen and nitrogen at the temperatures 723 and 923 K. Magnetic measurements were made for randomly oriented and aligned samples in the temperature range 4.2–750 K and at magnetic fields up to 140 kOe. The saturation magnetization of LaCo$_{13}$ is decreased by a partial substitution of the transition metal in the 3d sublattice by Al and further reduced by hydrogenation of LaCo$_{11}$Al$_2$.

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1. Introduction

The NaZn$_{13}$-type structure LaCo$_{13}$ intermetallic compound (IMC) has the largest 3d-metal content among the known rare earth (R)–transition metal (T) alloys, resulting in a very large magnetization, $4\pi M_s = 13$ kG, and a high Curie temperature, $T_C = 1318$ K [1]. However, its use as a permanent magnetic material is impossible, since the cubic NaZn$_{13}$-type structure of the LaCo$_{13}$ compound is highly symmetric and so its magnetocrystalline anisotropy is small. Moreover, the NaZn$_{13}$-type structure is not stable for other R–T binary compounds. By substituting part of the transition metal by Al or Si, the NaZn$_{13}$-type structure can be stabilized in other binary rare earth–transition metal systems [2]. In this case, there exists the possibility that the substituting atoms occupy some specific positions in the structure, in other words, ordered substitution may occur and the symmetry of the crystal structure can decrease from cubic symmetry to a lower (tetragonal or orthorhombic) symmetry [3,4]. A much larger magnetic anisotropy is expected in materials with a strongly anisotropic crystal structure.

Recently, some attempts to lower the symmetry of NaZn$_{13}$-type compounds by nitrogenation, for example [5,6], failed, but there is an ongoing motivation for many works [4,7,8] to study the possibility and ways of NaZn$_{13}$-type symmetry reduction.

In this study, our earlier investigations [5] have been extended to the LaCo$_{11}$Al$_2$ compound with initial cubic NaZn$_{13}$-type structure and to the CeNi$_8$Si$_4$-type compound, where such a symmetry reduction to the tetragonal derivative Ce$_2$Ni$_{17}$Si$_9$-type structure is observed [9]. The aim was to study the influence of light interstitial elements (hydrogen, nitrogen) on the crystallochemical and physical properties of these compounds.

2. Experimental details

The compounds were prepared by induction melting of appropriate amounts of the constituent components under a pure argon atmosphere and then vacuum-annealed at 900 °C for 2 weeks. The samples were single phase with a cubic NaZn$_{13}$-type structure for the LaCo$_{11}$Al$_2$ compound and a tetragonal NaZn$_{13}$-derivative structure for the CeNi$_8$Si$_4$-type compound. The symmetry and atom sites of the latter were consistent with the Ce$_2$Ni$_{17}$Si$_9$-type structure [9].

The synthesis of LaCo$_{11}$Al$_2$H$_3$ and LaCo$_{11}$Al$_2$N$_2$ was realized under hydrogen and nitrogen pressures of 30 bar at the temperatures 350 and 500 °C. The synthesis of CeNi$_8$Si$_4$H$_3$ and CeNi$_8$Si$_4$N$_{0.5}$ was carried out under a pressure of 30 bar at the temperatures 500 and 700 °C.
Hydrogen with an impurity content of $10^{-3} - 10^{-6}$ g, obtained by the decomposition of LaNi$_5$H$_6$, was employed for the hydrogenation. The X-ray diffraction patterns of the hydrides and nitrides showed that the samples consisted of a single phase, without any traces of disproportionation. The obtained hydrides and nitrides are isostructural to the initial compounds. The lattice constants and volume effects resulting from the hydrogenation and nitrogenation processes were measured.

Magnetic measurements were made for randomly oriented and aligned samples in the temperature range 4.2–750 K and magnetic fields up to 140 kOe, using a pendulum magnetometer.

### 3. Results and discussion

The experimental data obtained under the conditions described above are presented in Table 1, where the lattice constants of the investigated intermetallic compound and their hydrides and nitrides are displayed together with the volume effects due to the hydrogenation and nitrogenation processes. X-ray powder diffraction analysis of the as cast and annealed alloys proved the existence of the incongruently"1 processes. X-ray powder and nitrogenation pro- hydrides and nitrides are displayed together with the vol- umetics of the investigated intermetallic compound and their

Table 1. A comparison with the data for the LaCo$_{13}$ hydro- nitrides have, however, not been reported previously and genation and nitrogenation processes, displayed in the same table, shows much lower hydrogen and nitrogen contents in the hydride and nitride of CeNi$_8$Si$_4$. These results agree well with results for the LaFe$_{13-x}$Al$_x$ system investigated in [10], where the possibility of synthesizing nitrides with increasing Al concentration was studied. The introduction of nitrogen becomes more difficult with increasing Al concentration, and for $x = 4.5$ no nitrogen can be introduced. A similar dependence of the quantitative composition of the hydrides and nitrides on the Si content is probably observed in CeNi$_{13-x}$Si$_x$, which explains the low quantities of hydro- gen and nitrogen present in the Si-rich compounds obtained here (Table 1).

It has recently been established [10] that the magnetic properties of LaFe$_{13}$, Al$_{13}$, compounds are strongly influ- enced by the introduction of nitrogen into the lattice. The increase of the Curie temperature is about 600 K for the LaFe$_{13}$Al$_2$N$_{15}$ compound, i.e. even larger than for R$_2$Fe$_{17}$N$_5$ compounds.

We have investigated the effect of interstitial nitrogen and hydrogen atoms on the magnetic properties of LaCo$_{13}$ [5] and LaCo$_{13}$Al$_2$ compounds. Magnetic measurements were made on randomly oriented and aligned samples in the tem- perature range 4.2–750 K and magnetic fields up to 140 kOe. The saturation magnetizations of the LaCo$_{13}$ hydride and nitride were measured on fine powder samples at 300 and 78 K. The obtained data are summarized in Table 2 and indi- cate an insignificant change of the saturation magnetization of the hydride in comparison with the initial samples, while the saturation magnetization of the nitride has decreased by 25%. The explanation of the variation of the magnetic moment upon interstitial insertion is a complicated subject and demands a band structure calculation. The anisotropy field $H_T$ was determined as the field for which the magnetization curves measured along and perpendicular to the alignment direction cross each other.

The magnetization curves of LaCo$_{13}$, LaCo$_{13}$H$_{1.5}$ and LaCo$_{13}$N$_3$ at 300, 78 and 4.2 K are plotted in Figs. 1–3. The analysis of the data shows (Table 2) that the anisotropy field values for these compounds, as well as their saturation magnetization values, are similar at room temperature and at 78 K, as is characteristic for compounds with high Curie temperatures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure type</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\Delta V$ (%)</th>
</tr>
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<tr>
<td>LaCo$_{13}$</td>
<td>NaZn$_{13}$</td>
<td>Fm-3c</td>
<td>11.324</td>
<td>11.486</td>
<td>3.8 [5]</td>
</tr>
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<td>LaCo$<em>{13}$H$</em>{1.5}$</td>
<td>NaZn$_{13}$</td>
<td>Fm-3c</td>
<td>11.699</td>
<td>11.468</td>
<td>10 [5]</td>
</tr>
<tr>
<td>LaCo$_{13}$N$_3$</td>
<td>NaZn$_{13}$</td>
<td>Fm-3c</td>
<td>11.324</td>
<td>11.486</td>
<td>3.8 [5]</td>
</tr>
<tr>
<td>CeNi$_8$Si$_4$</td>
<td>Ce$_2$Ni$_7$Si$_9$</td>
<td>$I4_1/amc$</td>
<td>7.832</td>
<td>11.473</td>
<td>5.8</td>
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<td>CeNi$_8$Si$<em>4$H$</em>{1.5}$</td>
<td>Ce$_2$Ni$_7$Si$_9$</td>
<td>$I4_1/amc$</td>
<td>7.848</td>
<td>11.493</td>
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<td>CeNi$_8$Si$_4$N$_3$</td>
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<td>$I4_1/amc$</td>
<td>7.852</td>
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<td>2.0</td>
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<td>Fm-3c</td>
<td>11.630</td>
<td>11.324</td>
<td>3.5</td>
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<td>LaCo$_{13}$Al$<em>2$H$</em>{1.5}$</td>
<td>NaZn$_{13}$</td>
<td>Fm-3c</td>
<td>11.560</td>
<td>11.495</td>
<td>8.0</td>
</tr>
</tbody>
</table>

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Table 2
Magnetic properties of LaCo$_{13}$ and hydrogenation and nitrogenation products

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_s$, $T = 4.2$ K (emu/g)</th>
<th>$\sigma_s$, $T = 300$ K (emu/g)</th>
<th>$H_a$, $T = 78$ K (kOe)</th>
<th>$H_a$, $T = 300$ K (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCo$_{13}$</td>
<td>137</td>
<td>132</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>LaCo$<em>{13}$H$</em>{3.5}$</td>
<td>128</td>
<td>126</td>
<td>14</td>
<td>12.5</td>
</tr>
<tr>
<td>LaCo$_{13}$N$_3$</td>
<td>110</td>
<td>97</td>
<td>11.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Fig. 1. Magnetization curves of LaCo$_{13}$ (1), LaCo$_{13}$H$_{3.5}$ (2), LaCo$_{13}$N$_3$ (3) at 300 K along (filled symbols) and perpendicular (open symbols) to the alignment direction.

Fig. 2. Magnetization curves of LaCo$_{13}$N$_3$ at 78 K (1) and 300 K (2) along (filled symbols) and perpendicular (open symbols) to the alignment direction.

Fig. 3. Magnetization curves of LaCo$_{13}$ (1), LaCo$_{13}$H$_{3.5}$ (2), LaCo$_{13}$N$_3$ (3) at 4.2 K along the alignment direction.

Fig. 4. Magnetization curves of LaCo$_{11}$Al$_2$ (1) and LaCo$_{11}$Al$_2$H$_3$ (2) at 4.2 K along the alignment direction.

Magnetization curves of LaCo$_{11}$Al$_2$ and LaCo$_{11}$Al$_2$H$_3$ at 4.2 K are plotted in Fig. 4. These curves show that the substitution of part of the Co atoms by Al atoms leads to a decrease of the saturation magnetization in comparison with the initial LaCo$_{13}$. This tendency is preserved upon hydrogenation of LaCo$_{11}$Al$_2$. Hence, good magnetic properties cannot be achieved by substitution of the transition metal in the 3d sublattice of LaCo$_{13}$ and hydrogenation.

4. Conclusion

The essential feature of Co-containing compounds compared with Fe-containing ones is a more significant delocalization of the 3d electrons and a significant redistribution of the electron density due to the influence of the interstitial elements (H, N). The decrease of the saturation magnetization of LaCo$_{11}$Al$_2$ in comparison with the initial LaCo$_{13}$, and the preservation of this tendency after hydrogenation, can be associated with opposite directions of the processes of charge transfer between hydrogen and 3d atoms with respect to R–Fe-based hydrides (from hydrogen to Co atoms in R–Co compounds and from Fe to hydrogen atoms in R–Fe compounds). A more detailed conclusion can only be given after more complete investigations of compounds with NaZn$_{13}$-type structures.

Acknowledgements

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References