

Synthesis and properties of NaZn₁₃-type interstitial compounds

S.A. Nikitin^a, I.S. Tereshina^a, V.N. Verbetsky^b, A.A. Salamova^{b,*}, E.V. Anosova^b

^a Faculty of Physics, Moscow State University, 119899 Moscow, Russia

^b Faculty of Chemistry, Moscow State University, Vorobiev Gory, 119899 Moscow, Russia

Abstract

The effect of interstitial nitrogen and hydrogen atoms on the structural and magnetic properties of LaCo₁₁Al₂ and CeNi_{8.5}Si_{4.5} was studied. Synthesis of LaCo₁₁Al₂H₃ and LaCo₁₁Al₂N_{2.5} was performed under a pressure of 30 bar hydrogen and nitrogen and at the temperatures 623 and 773 K. Synthesis of CeNi_{8.5}Si_{4.5}H_{0.9} and CeNi_{8.5}Si_{4.5}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 LaCo₁₃ is decreased by a partial substitution of the transition metal in the 3d sublattice by Al and further reduced by hydrogenation of LaCo₁₁Al₂.

© 2003 Published by Elsevier B.V.

Keywords: Hydride; Nitride; Interstitial elements; Saturation magnetization; Electron density distribution

1. Introduction

The NaZn₁₃-type structure LaCo₁₃ 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 NaZn₁₃-type structure of the LaCo₁₃ compound is highly symmetric and so its magnetocrystalline anisotropy is small. Moreover, the NaZn₁₃-type structure is not stable for other R–T binary compounds. By substituting part of the transition metal by Al or Si, the NaZn₁₃-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 NaZn₁₃-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 NaZn₁₃-type symmetry reduction.

In this study, our earlier investigations [5] have been extended to the LaCo₁₁Al₂ compound with initial cubic NaZn₁₃-type structure and to the CeNi_{8.5}Si_{4.5} compound, where such a symmetry reduction to the tetragonal derivative Ce₂Ni₁₇Si₉-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 NaZn₁₃-type structure for the LaCo₁₁Al₂ compound and a tetragonal NaZn₁₃-derivative structure for the CeNi_{8.5}Si_{4.5} compound. The symmetry and atom sites of the latter were consistent with the Ce₂Ni₁₇Si₉-type structure [9].

The synthesis of LaCo₁₁Al₂H₃ and LaCo₁₁Al₂N₃ was realized under hydrogen and nitrogen pressures of 30 bar at the temperatures 350 and 500 °C. The synthesis of CeNi_{8.5}Si_{4.5}H and CeNi_{8.5}Si_{4.5}N_{0.5} was carried out under a pressure of 30 bar at the temperatures 500 and 700 °C.

* Corresponding author.

E-mail address: salamova@hydride.chem.msu.ru (A.A. Salamova).

Hydrogen with an impurity content of 10^{-3} – $10^{-4}\%$, obtained by the decomposition of LaNi_5H_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 melting homogeneous phases $\text{CeNi}_{8.5}\text{Si}_{4.5}$ and $\text{LaCo}_{11}\text{Al}_2$. Both samples were single phase, with a cubic NaZn_{13} -type structure for the $\text{LaCo}_{11}\text{Al}_2$ compound. Indexing of the X-ray powder pattern of $\text{CeNi}_{8.5}\text{Si}_{4.5}$ was performed on the basis of a body-centered tetragonal unit cell. The composition, unit cell dimensions, extinctions (hkl) observed for $h+k+l=2n+1$ and $(0kl)$ for $k, l=2n+1$, and X-ray intensities were all consistent with the NaZn_{13} -distortion derivative structure $\text{Ce}_2\text{Ni}_{17}\text{Si}_9$ with the space group $I4/mcm$ [9].

The investigations that were mainly focused on the study of the influence of interstitial elements (H, N) indicate a complete change of the fundamental magnetic behavior induced by these elements in NaZn_{13} -type IMC [3,4,6–8]. Successful attempts to synthesize $\text{RT}_{13-x}\text{Si}_x$ hydrides and nitrides have, however, not been reported previously and the lattice constants and volume effects of the compounds that were synthesized here for the first time are displayed in Table 1. A comparison with the data for the LaCo_{13} hydro-

genation and nitrogenation processes, displayed in the same table, shows much lower hydrogen and nitrogen contents in the hydride and nitride of $\text{CeNi}_{8.5}\text{Si}_{4.5}$. These results agree well with results for the $\text{LaFe}_{13-x}\text{Al}_x$ 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 $\text{CeNi}_{13-x}\text{Si}_x$, which explains the low quantities of hydrogen and nitrogen present in the Si-rich compounds obtained here (Table 1).

It has recently been established [10] that the magnetic properties of $\text{La}(\text{Fe}, \text{Al})_{13}$ compounds are strongly influenced by the introduction of nitrogen into the lattice. The increase of the Curie temperature is about 600 K for the $\text{LaFe}_{10.5}\text{Al}_{2.5}\text{N}_{2.6}$ compound, i.e. even larger than for $\text{R}_2\text{Fe}_{17}\text{N}_x$ compounds.

We have investigated the effect of interstitial nitrogen and hydrogen atoms on the magnetic properties of LaCo_{13} [5] and $\text{LaCo}_{11}\text{Al}_2$ compounds. Magnetic measurements were made on randomly oriented and aligned samples in the temperature 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 indicate 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_a 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} , $\text{LaCo}_{13}\text{H}_{3.5}$ and $\text{LaCo}_{13}\text{N}_3$ 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 1
Lattice constants and volume effects due to the hydrogenation and nitrogenation processes

Compound	Structure type, space group		a (Å)	c (Å)	ΔV (%)
LaCo_{13}	NaZn_{13}	$Fm-3c$	11.324		
$\text{LaCo}_{13}\text{H}_{3.5}$	NaZn_{13}	$Fm-3c$	11.466		3.8 [5]
$\text{LaCo}_{13}\text{N}_3$	NaZn_{13}	$Fm-3c$	11.699		10 [5]
$\text{CeNi}_{8.5}\text{Si}_{4.5}$	$\text{Ce}_2\text{Ni}_{17}\text{Si}_9$	$I4/mcm$	7.832	11.473	
$\text{CeNi}_{8.5}\text{Si}_{4.5}\text{H}_{0.9}$	$\text{Ce}_2\text{Ni}_{17}\text{Si}_9$	$I4/mcm$	7.848	11.493	1.0
$\text{CeNi}_{8.5}\text{Si}_{4.5}\text{N}_{0.5}$	$\text{Ce}_2\text{Ni}_{17}\text{Si}_9$	$I4/mcm$	7.852	11.507	2.0
$\text{LaCo}_{11}\text{Al}_2$	NaZn_{13}	$Fm-3c$	11.630		
$\text{LaCo}_{11}\text{Al}_2\text{H}_3$	NaZn_{13}	$Fm-3c$	11.569		3.5
$\text{LaCo}_{11}\text{Al}_2\text{N}_{2.5}$	NaZn_{13}	$Fm-3c$	11.949		8.0

Table 2
Magnetic properties of LaCo_{13} and hydrogenation and nitrogenation products

Compound	$\sigma_s, T = 4.2 \text{ K}$ (emu/g)	$\sigma_s, T = 300 \text{ K}$ (emu/g)	$H_a, T = 78 \text{ K}$ (kOe)	$H_a, T = 300 \text{ K}$ (kOe)
LaCo_{13}	137	132	13	12
$\text{LaCo}_{13}\text{H}_{3.5}$	128	126	14	12.5
$\text{LaCo}_{13}\text{N}_3$	110	97	11.5	10.5

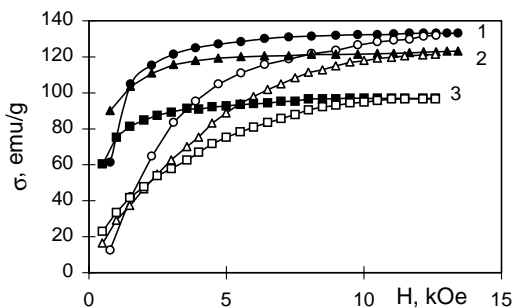


Fig. 1. Magnetization curves of LaCo_{13} (1), $\text{LaCo}_{13}\text{H}_{3.5}$ (2), $\text{LaCo}_{13}\text{N}_3$ (3) at 300 K along (filled symbols) and perpendicular (open symbols) to the alignment direction.

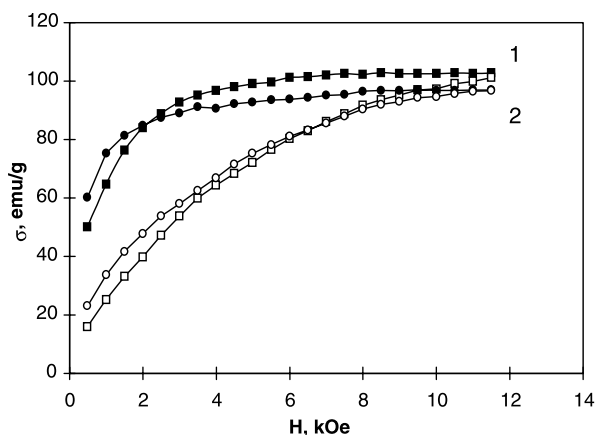


Fig. 2. Magnetization curves of $\text{LaCo}_{13}\text{N}_3$ at 78 K (1) and 300 K (2) along (filled symbols) and perpendicular (open symbols) to the alignment direction.

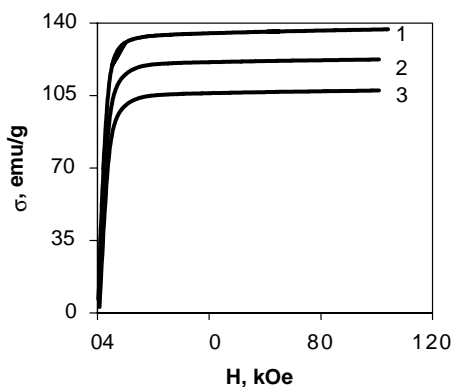


Fig. 3. Magnetization curves of LaCo_{13} (1), $\text{LaCo}_{13}\text{H}_{3.5}$ (2), $\text{LaCo}_{13}\text{N}_3$ (3) at 4.2 K along the alignment direction.

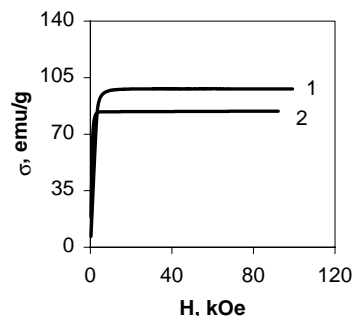


Fig. 4. Magnetization curves of $\text{LaCo}_{11}\text{Al}_2$ (1) and $\text{LaCo}_{11}\text{Al}_2\text{H}_3$ (2) at 4.2 K along the alignment direction.

Magnetization curves of $\text{LaCo}_{11}\text{Al}_2$ and $\text{LaCo}_{11}\text{Al}_2\text{H}_3$ 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 $\text{LaCo}_{11}\text{Al}_2$. 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 $\text{LaCo}_{11}\text{Al}_2$ 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

This work was supported by the Russian Foundation for Fundamental Science (00-03-02001 and 02-02-16523).

References

- [1] W.A.J.J. Velge, K.H.J. Buschow, *J. Appl. Phys.* 39 (1968) 1717.
- [2] P.I. Kripyakevich, O.S. Zarechnyuk, E.I. Gladyshevsky, O.I. Bodak, *Z. Anorg. Chem.* 358 (1968) 90.
- [3] T.T.M. Palstra, G.J. Nieuwenhuys, J.A. Mydosh, K.H.J. Buschow, *Phys. Rev. B* 31 (1985) 4622.
- [4] G.H. Rao, J.K. Liang, Y.L. Zhang, X.R. Cheng, W.H. Tang, C. Dong, *Phys. Rev. B* 51 (1995) 60.
- [5] S.A. Nikitin, I.S. Tereshina, V.N. Verbetsky, A.A. Salamova, B.I. Lazoryak, V.A. Morozov, *J. Alloys Compd.* 293–295 (1999) 247.
- [6] M.Q. Huang, Y. Zheng, K. Miller, J. Elbicki, W.E. Wallace, S.G. Sankar, *IEEE Trans. Magn.* 28 (1992) 2859.
- [7] W.H. Tang, J.K. Liang, X.H. Yan, G.H. Rao, S.S. Xie, *Phys. Rev. B* 49 (1994) 3864.
- [8] G.H. Rao, J.K. Liang, Y.L. Zhang, X.R. Cheng, W.H. Tang, *Appl. Phys. Lett.* 64 (1994) 1650.
- [9] O.I. Bodak, *Sov. Phys. Crystallogr.* 24 (1979) 1280.
- [10] J.P. Liu, N. Tang, E.R. de Boer, P.F. de Chatel, K.H.J. Buschow, *J. Magn. Mater.* 140–144 (1995) 1035.