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The synthesis and magnetic properties of $LaCo_{13}$ hydrides and nitrides

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Abstract

Synthesis of $LaCo_{13}H_{3.5}$ was performed under a 10-bar pressure of hydrogen and at the temperature of 600 K. Nitriding was carried out in a nitrogen atmosphere of 30 bar pressure and at temperature 700 K. The structure of $LaCo_{13}N_3$ was refined by the full-profile analysis using the GSAS program. Magnetic measurements were made on free and aligned samples in the temperature range 78–750 K and magnetic fields up to 13 kOe with a pendulum magnetometer. The saturation magnetisations σ_s of $LaCo_{13}$ hydride and nitride were measured on fine powder samples at temperatures of 300 and 78 K. The data obtained indicate insignificant change of the hydride saturation magnetisation in comparison with initial sample, while the saturation magnetization of nitride decreases by 26.5%. Values of the anisotropy fields of these compounds, as well as their saturation magnetisation values, show insignificant changes at the room temperature and 78 K, which are the characteristics of compounds with high Curie temperatures. However, hydriding and nitriding lead to a rise in the peculiarities in the behaviour of $\sigma(T)$ at temperature $T=480$ K, namely, an increase of magnetization in the hydride $LaCo_{13}H_{3.5}$ and a decrease in the nitride $LaCo_{13}N_{3.}$

Keywords: Hydride; Nitride; Saturation magnetization; Electron-density distribution

Introduction

The intermetallic compounds (IMC) that consist of a rare earth and a significant quantity of a transitional metals are the most interesting objects for study of the influence of the interstitial elements (hydrogen, nitrogen, carbon) on crystallochemical and physical properties. The numerous researches devoted to study RT_{12} [1] and R_2T_{17} [2,3] type IMC hydrides and nitrides testify that the insertion of the interstitial elements induces drastic changes in the magnetic properties of these compounds. However, similar researches for compounds of a RT_{13} type are not available, and the successful attempts at the synthesis of these compounds hydrides are not known to us.

Experimental details

IMC $LaCo_{13}$ with a crystalline structure of the $NaZn_{13}$ type is prepared by arc melting of the initial components (La 99.979%, Co 99.99% purity) in an argon atmosphere. Synthesis of $LaCo_{13}H_{3.5}$ was performed under the 10-bar pressure of hydrogen and at the temperature of 600 K. Hydrogen with a impurities content of 10^{-3}–10^{-4}% was obtained by decomposition of $LaNi_5H_6$. Nitriding was carried out in nitrogen under pressure of 30 bar and temperature 700 K. Twenty-four hours are needed for the synthesis of the nitride of $LaCo_{13}N_3$ composition. The X-ray diffraction patterns showed that the samples consisted of a single phase without any disproportionation products.

The structures of $LaCo_{13}N_3$ have been refined by the Rietveld [4] method (space group $Fm\bar{3}c$). Powder diffraction data for determining and refining structures were obtained using a Siemens D500 powder diffractometer equipped with a primary SiO_2 monochromator (Cu $K\alpha_1$ radiation, $l=1.5406$ Å) with a position-sensitive detector and a primary beam focusing. The data were collected from 10° to 80° in 2θ°. The structures were refined by the full-profile analysis using the GSAS program [5]. Magnetic measurements were made on free and aligned samples in the temperature range 78–750 K and magnetic fields up to 13 kOe using a pendulum magnetometer.

Results and discussion

The structural study of the synthesised nitride was based on the experimental data obtained in conditions described

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Table 1
Lattice constants and volume effects at the hydrogenation and nitrogenation process

Compounds	a (Å)	V	ΔV (%)
$LaCo_{13}$	11.324	1452.105	
$LaCo_{13}N_3$	11.699	1601.365	10
$LaCo_{13}H_{3.5}$	11.466	1507.400	3.8

above and presented in Table 1. We used, as the initial data for the determination of the crystal structure of $LaCo_{13}N_3$ the atomic coordinates of the $LaCo_{13}$ structure (space group $Fm\bar{3}c$, $Z=8$).

At the first stage of refinement, the GSAS program was used. Upon refinement the profile, thermal and positional parameters of La and Co atoms, it was established that the model chosen provides satisfactory agreement between the experimentally observed and calculated X-ray diffraction patterns; R factors are $R_{wp}=2.27$; $R_p=1.67$. These low values of R factors signify the correct change of model. On the Fourier map electron-density distribution $\rho(xyz)$ and $\Delta\rho(xyz)$ the peak of electron density is observed (7 $Å^{-3}$) with coordinates of 0.25, 0.11, 0.25 (Fig. 1). The form and value of the electron density peak can be indicative as location of N atoms in the structure. Maxima of electron density (Fig. 1) are disposed inside the tetrahedras which are formed by three atoms Co in position Co(2) and La atom. But the attempt to set nitrogen atoms in space group

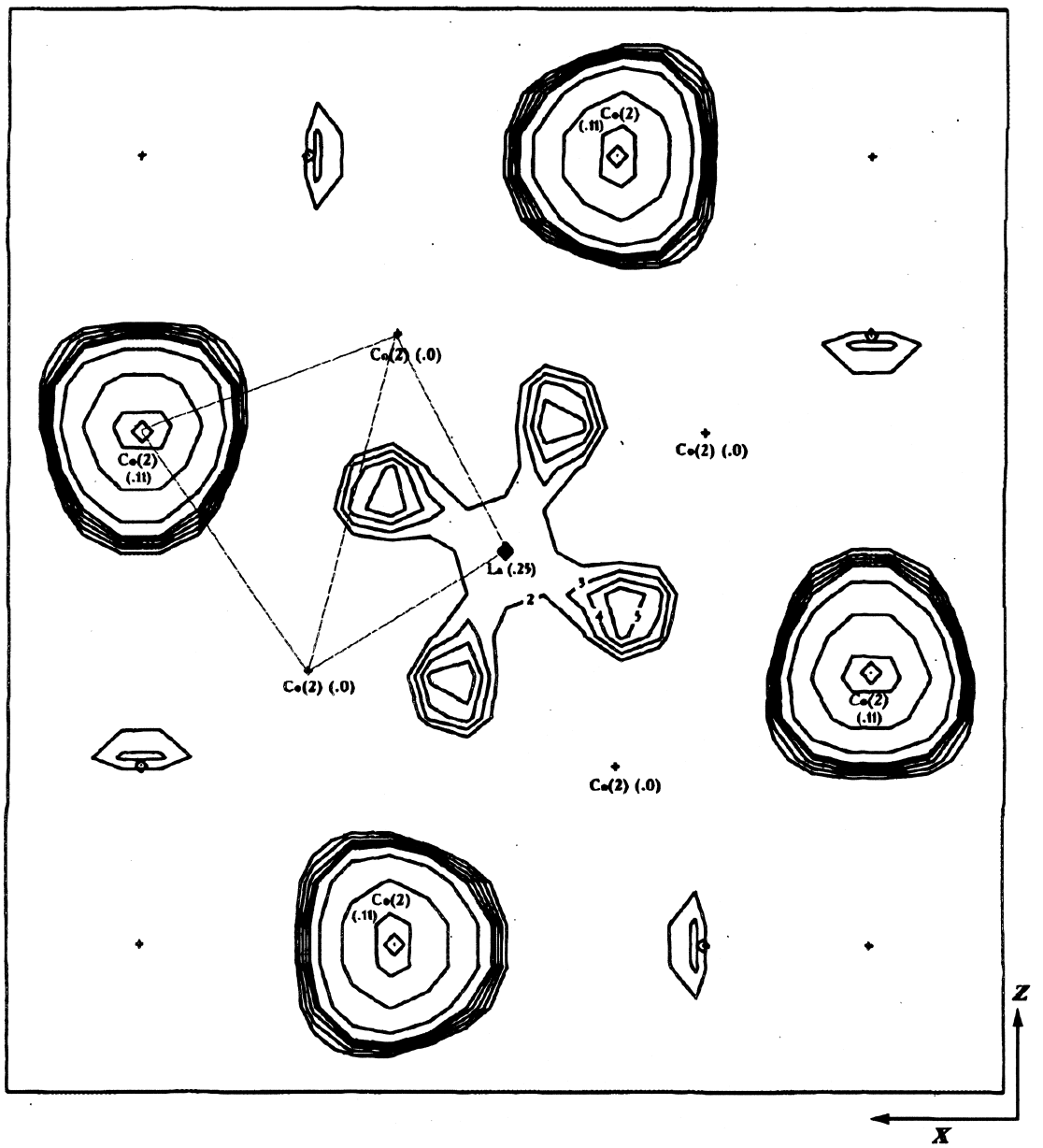

Fig. 1. Fourier map of electron density distribution ρ_{obs} (xyz) in the (101) plane of $LaCo_{13}N_3$. The 8×8 Å fragment is shown (the coordinate of the centre of the square is 0.25, 0.11, 0.25).

Table 2
The magnetic properties of the studied compounds

Compounds	σ_s (emu/g) $T=78$ K	σ_s (emu/g) $T=300$ K	H_a (kOe) $T=78$ K	H_a (kOe) $T=300$ K
$LaCo_{13}$	136	132	13	12
$LaCo_{13}H_{3.5}$	129	126	14	12.5
$LaCo_{13}N_3$	101	97	11.5	10.5

$Fm\bar{3}c$ was unsuccessful. Apparently, insertion of nitrogen atoms in $LaCo_{13}$ leads to distortion of initial structure and as a consequence, a lowering of the crystallographic lattice symmetry takes place. However, further investigations are necessary for localisation of nitrogen atoms.

Magnetic measurements were made on free and aligned samples in the temperature range 78–750 K and magnetic fields up to 13 kOe using a pendulum magnetometer. The saturation magnetisations σ_s of $LaCo_{13}$ hydride and nitride were measured on fine powder samples at temperature 300 and 78 K. The data obtained are summarised in Table 2 and show only just significant change of the hydride saturation magnetisation in comparison with initial sample while the saturation magnetisation of nitride decreases by 26.5%. The value of magnetic moment per Co atom changes from 1.69 in the host alloy to 1.58 and 1.27 at 78 K in the hydride and nitride, respectively. The explanation

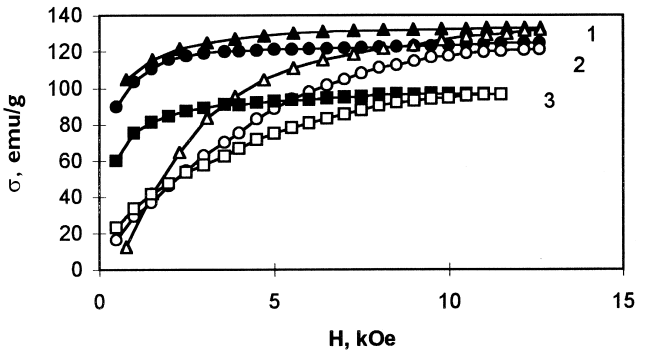

Fig. 2. Magnetisation curves of $LaCo_{13}$ (triangles), its hydride (circles) and nitride (squares) at $T=300$ K along (dark) and perpendicular (light) to the alignment direction.

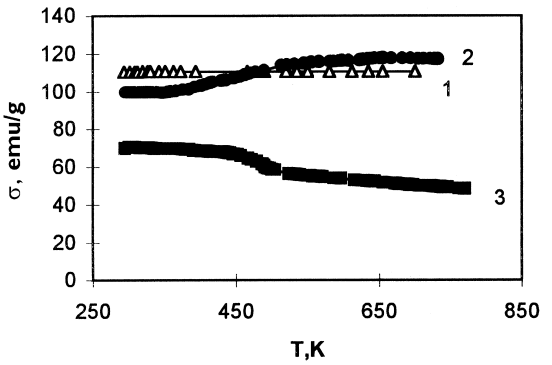

Fig. 4. Magnetisation versus temperature plot. Curves 1,2,3, host alloy, hydride and nitride, respectively ($H=1.5$ kOe).

of the magnetic moment variation upon interstitial insertion is a complicated subject and demands a band structure calculation. The anisotropy field H_a was determined as one where magnetisation curves measuring along and perpendicular to the alignment direction are crossed. The magnetisation curves of $LaCo_{13}$, $LaCo_{13}H_{3.5}$, $LaCo_{13}N_3$ at temperature of 300 K are plotted in Fig. 2 and the magnetisation curves of $LaCo_{13}N_3$ at temperature 78 and 300 K are plotted in Fig. 3. The analysis of the data obtained shows (Table 2) that the anisotropy fields values of these compounds as well as their saturation magnetisation values show insignificant differences at the room temperature and 78 K as is characteristic for compounds with high Curie temperatures.

The temperature dependencies of magnetisation measured in field of 1.5 kOe are plotted in Fig. 4. Curve 1 corresponds to initial alloy $LaCo_{13}$ ($T_c=1290$ K) and has no peculiarities in the studied temperature range. However, hydriding and nitriding lead to peculiarities in the behaviour of $\sigma(T)$ at temperature $T=480$ K, namely an increase of magnetisation in hydride $LaCo_{13}H_{3.5}$ and a decrease in nitride $LaCo_{13}N_{3.}$ This effect cannot be connected with desorption of hydrogen and nitrogen in the course of the high temperature measurements because the results are reproducible with high accuracy. Furthermore, the field magnetisation dependencies at the high temperatures were measured. These field dependencies for the

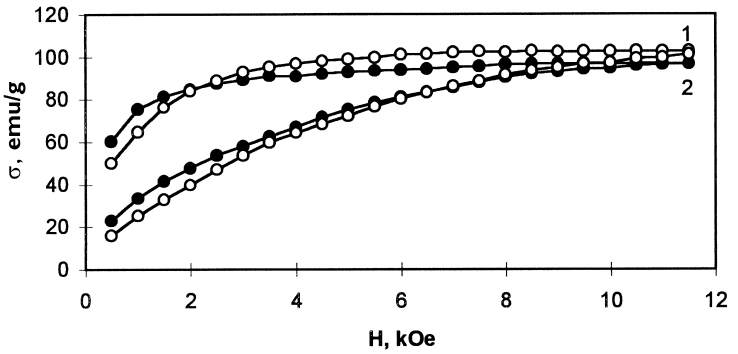

Fig. 3. Magnetisation curves of $LaCo_{13}N_3$ at $T=78$ K (1) and 300 K (2) along (dark) and perpendicular (light) to the alignment direction.

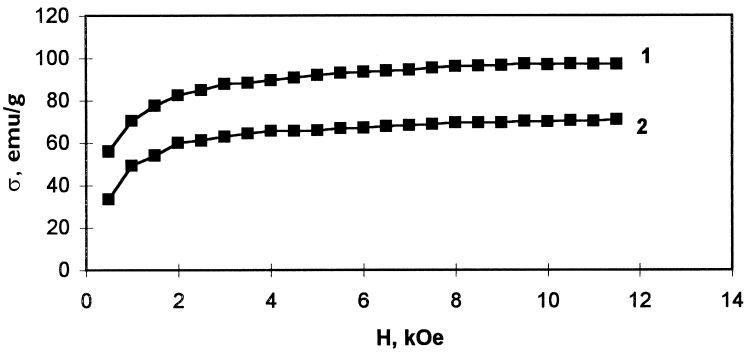

Fig. 5. Field dependencies of the magnetisation of $LaCo_{13}N_3$ compound along the alignment direction at $T=300$ K (1) and 600 K (2).

$LaCo_{13}N_3$ sample measured along the alignment direction at two different temperatures are plotted in Fig. 5. It is seen that magnetisation decreases with increasing temperature ($\sigma_s=97$emu/g at $T=300$ K, $\sigma_s=70$ emu/g at 600 K); however, the characteristic shape of the curves is not changed. Apparently, this is connected with the fact that hydrogen and nitrogen have different radii and are disposed in different crystallographic positions in the complex cubic structure. The magnetocrystalline anisotropy is very sensitive to local surrounding and different temperature dependence anisotropy constants for hydride and nitride can lead to different effects of its influence (Fig. 4). On the other hand, the different volume effects (Table 1) at the process of hydriding and nitriding can be cause of magnetisation-temperature dependency behaviour (Fig. 4). At any rate, explanation of this behaviour will be possible after making more precise measurement of the crystal structure.

Acknowledgements

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