Effect of hydrogenation and nitrogenation on the magnetostriction of LaCo$_{13}$compound

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Abstract

The magnetostrictions of polycrystalline LaCo$_{13}$, LaCo$_{13}$H$_{3.5}$ and LaCo$_{13}$N$_3$ compounds were measured in temperature range from 78 to 350 K in magnetic fields up to 13 kOe. It was shown that hydrogenation and nitrogenation are methods of regulation of the magnetostriction in LaCo$_{13}$ compounds. © 1999 Elsevier Science S.A. All rights reserved.

The LaCo$_{13}$ compound has the highest 3d metal content of any known rare-earth–transition-metal intermetallic and is of potential application interest due to a large magnetization and high Curie temperature [1–3]. It crystallizes in the cubic NaZn$_{13}$-type structure (space group *Fm3c*). This structure is highly symmetric and therefore the magnetocrystalline anisotropy of LaCo$_{13}$ is small. Much larger magnetic anisotropy is expected in materials with a strongly anisotropic crystal structure (for example, tetragonal or hexagonal symmetry). Unfortunately, the NaZn$_{13}$-type structure is not stable for other rare-earth elements except for La. However, it is known that the structure can be stabilized in other La–Co systems by substituting Fe, Al or Si for part of the Co atoms.

It has recently been established by Liu et al. [4] that the magnetic properties of the La(Fe,Al)$_{13}$ compounds are strongly influenced by the introduction of nitrogen into the lattice. The increase in the Curie temperature is about 600 K for LaFe$_{10.5}$Al$_{2.5}$N$_{2.6}$ compound and is even larger than in R$_2$Fe$_{17}$N$_x$ compounds. We investigated the effect of the interstitial nitrogen and hydrogen atoms on the magnetic properties of the LaCo$_{13}$ compound [5]. Marked changes of the magnetization and magnetic anisotropy of the LaCo$_{13}$ compound are induced by hydrogen and nitrogen insertions. This compounds displays complex magnetic behavior. The purpose of this study is to determine the effect of hydrogenation and nitrogenation on the magnetostrictive properties.

The alloy is prepared by arc melting the appropriate amounts of the starting materials (La-99.979%; Co-99.99%) under pure argon atmosphere. Synthesis of LaCo$_{13}$H$_x$ was realized under a 10 bar pressure of hydrogen and at a temperature of 600 K. Hydrogen with an impurity content of 10^{-3}–10^{-4}% was obtained by decomposition of LaNi$_5$H$_6$. Nitriding was carried out in the nitrogen under a pressure of 30 bar and at a temperature of 700 K. A period of 24 h is needed for the synthesis of LaCo$_{13}$N$_x$. The concentration of absorbed hydrogen and nitrogen in the samples was calculated using the Van-der-Waals equation. The X-ray diffraction experiments were made for the phase identification both of the parent compound and its hydride and nitride and to determine the unit cell parameter. Disks of ≈5-mm diameter and 1.5-mm thickness were cut from the ingots for LaCo$_{13}$ and LaCo$_{13}$H$_{3.5}$. The anisotropic magnetostrictions $\lambda_t = \lambda_\parallel - \lambda_\perp$ were measured using standard strain gauge techniques in magnetic field up to 12 kOe. Here $\lambda_\parallel$ and $\lambda_\perp$ denote the fractional changes in length for fields applied parallel and perpendicular to the measurement direction. Since the nitride was available only in powder form, the measurements were made also with powder pressed samples for all investigated compounds. For this reason the fine powder of the compounds were compacted under pressure near 3 GPa into disks. The densities of the samples produced in this way were near 80% of the powder X-ray densities. We

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took the values measured on the pressed sample multiplied by the ration of the X-ray density to the pressed sample density as the values of the magnetostriction for the investigated compounds. It was found that these values are rather insensitive to small variations of the pressed sample densities.

The crystal structure of $LaCo_{13}$ compounds was confirmed to be of the cubic $NaZn_{13}$-type structure. The unit cell holds eight formula units. The Co atoms occupy two different positions. The room-temperature lattice constant, a, and unit cell volume, V, for $LaCo_{13}$ are 11.324 Å and 1452.105 Å^3, respectively. The determination of the H and N concentrations indicated that the H and N concentrations are close to 3.5 and 3 atoms per formula unit, respectively. The hydrogenation and nitrogenation lead to a lattice expansion of the compounds without change of the cubic $NaZn_{13}$-type structure. The relative cell volume increases $\Delta V/V$ show a consistent ~3.8% volume expansion over the hydrogen-free unit cell and ~10% volume expansion over the nitrogen-free unit cell.

We investigated the temperature and field dependence of magnetostriction of both the parent and H and N modified compounds. The magnetostriction $(\lambda_\parallel - \lambda_\perp)$ vs. magnetic fields are shown in Fig. 1. It was found that the magnetostriction of the $LaCo_{13}$ compounds is positive, saturating with a magnitude of 60×10^{-6} at $T=80$ K and 40×10^{-6} at $T=290$ K (curves 1–5). The curves for $LaCo_{13}H_{3.5}$ (6–8, Fig. 1) show that the magnetostriction has changed upon hydrogenation. It has become smaller in magnitude than that for $LaCo_{13}$ namely $\lambda_t = 25 \times 10^{-6}$ at $T=290$ K and $\lambda_t = 13 \times 10^{-6}$ at $T=80$ K. Following nitrogenation, the magnetostriction also decreases in value, becoming almost temperature-independent and $\lambda_t = 10 \times 10^{-6}$. Saturation is achieved at all temperatures.

In Fig. 2 anisotropic magnetostriction $(\lambda_\parallel - \lambda_\perp)$ vs. temperatures in different fields are plotted for the $LaCo_{13}$
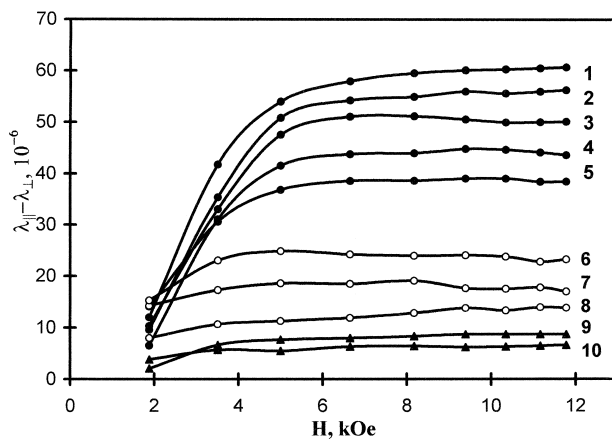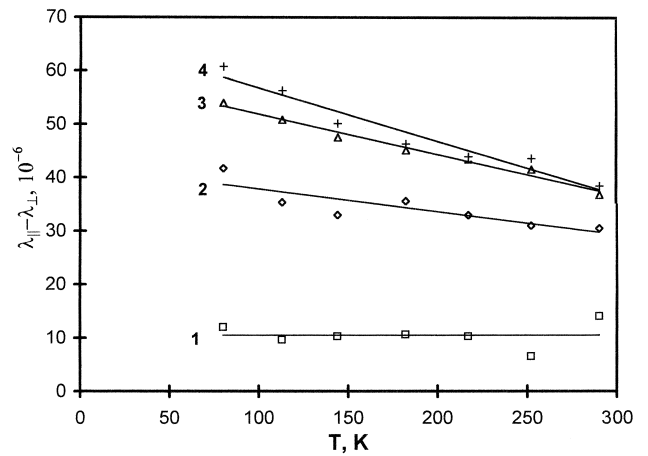
Fig. 2. Magnetostriction as a function of temperatures at various fields for $LaCo_{13}$ compounds (1, H=2 kOe; 2, H=4 kOe; 3, H=5 kOe; 4, H=12 kOe).

compound. It is clearly seen that λ_t decreases monotonically with increasing temperature in high magnetic fields. Interestingly, the $LaCo_{13}H_{3.5}$ and $LaCo_{13}N_3$ compounds have magnetostrictions with different temperature dependence (see Fig. 3). The anisotropic magnetostriction $(\lambda_\parallel - \lambda_\perp)$ increases with increasing temperature for the $LaCo_{13}H_{3.5}$ compound and are temperature-independent for the $LaCo_{13}N_3$ compound in the whole investigated temperature range.

Since La is a nonmagnetic ion, and the rare-earth sublattice can be assumed to contribute negligibly to the magnetostriction, it was possible to determine the influence of H and N on the magnetostriction of the Co sublattice. The expansion of the unit-cell volume in $LaCo_{13}$ upon hydrogenation and nitrogenation is quite large. The large expansion results in a very strong increase of the Co–Co interatomic distance in $LaCo_{13}$. It was shown [5] that the saturation magnetization insignificantly changes in the hydride in comparison with the initial sample ($\sigma_S = 136$
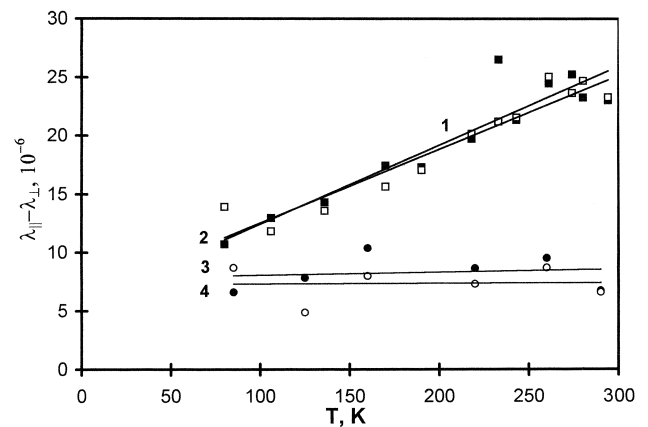
Fig. 1. Magnetostriction as a function of applied field at various temperatures: $LaCo_{13}$ (●, curves 1–5, 1, $T=80$ K; 2, $T=113$ K; 3, 144 K; 4, 252 K; 5, 290 K), $LaCo_{13}H_{3.5}$ (○, curves 6–8, 6, $T=290$ K; 7, $T=190$ K; 8, $T=80$ K) and $LaCo_{13}N_3$ (▲, curves 9–10, 9, $T=80$ K, 10, $T=290$ K).

Fig. 3. Temperature dependencies of magnetostriction at various magnetic fields for $LaCo_{13}H_{3.5}$ (1, H=12 kOe; 2, H=4 kOe) and $LaCo_{13}N_3$ (3, H=12 kOe; 4, H=4 kOe).

emu/g for $LaCo_{13}$ and $\sigma_S = 129$ emu/g for $LaCo_{13}H_{3.5}$ at $T = 78$ K) while the saturation magnetization of the nitride decreases by 26.5%. The value of magnetic moment per Co atom changes from 1.69 μ_B in the host alloys to 1.58 and 1.27 μ_B at $T = 78$ K in the hydride and nitride, respectively. Values of the anisotropy fields of these compounds show an insignificant increase in hydride ($H_a = 13$ kOe for $LaCo_{13}$ and $H_a = 14$ kOe for $LaCo_{13}H_{3.5}$ at $T = 78$ K) and a decrease in the nitride ($H_a = 11.5$ kOe for $LaCo_{13}N_3$). However, there is marked change in the magnetostriction of the hydrogenated and nitrogenated samples. In fact, on hydrogenation the magnetostriction decreases (λ_t of parent compound is about twice that of its hydride), while the nitrogenation leads to a suppression of the magnetostriction. The temperature dependence of the magnetostriction of $LaCo_{13}N_3$, on the other hand, changes very little. According to the present data one can assume that the insertion of the light interstitial elements (hydrogen, nitrogen) into the crystalline lattice is a method of regulation of the magnetostriction in $LaCo_{13}$ intermetallic compounds. However, a more specific conclusion can only be drawn after the location of the interstitial hydrogen and nitrogen atoms in the complex cubic structure has been established.

Acknowledgements

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