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Magnetostriction of $LaCo_{13}$-based alloys

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Abstract

The magnetostriction, Curie temperature, phase composition and crystal lattice parameters in $La_{1-x}R_xCo_{13}$ (R≡Pr, Sm, Tb) and $LaCo_{11}M_2$ (M≡Fe, Ni, Al, Si) were measured. The introduction of a lanthanum excess relative to the $LaCo_{13}$ stoichiometry was found to cause an increase in the Curie temperature by more than 50 K, which indicates the presence of a homogeneity region in $LaCo_{13}$ alloy. The room temperature saturation magnetostriction is $(\lambda_{\parallel}-\lambda_{\perp})_s=100\times10^{-6}$ and weakly changes in the homogeneity region. Substitution of lanthanum by praseodymium and terbium allows one to increase the magnetostriction slightly, but this is accompanied by a decrease in magnetostriction susceptibility $d\lambda/dH$. Introduction of samarium, iron, nickel, silicon and aluminium leads to a decrease in magnetostriction.

1. Introduction

The magnetic materials which combine a large magnetostriction with a small magnetocrystalline anisotropy are widely used in different electronic device components such as magnetoacoustic transducers, acoustic delay lines and micropositioning devices [1]. Traditional materials based on nickel, cobalt and iron possess relatively small values of saturation magnetostriction on $\lambda_s\approx(40–90)\times10^{-6}$. The RFe_2 compounds (R≡rare earth) have a huge room temperature magnetostriction but, as a rule, these compounds display small values of magnetostriction susceptibility $d\lambda/dH$ even in the case of pseudo-binary compounds when the magnetocrystalline anisotropy of the R sublattice is suppressed. This reason, together with the brittleness and high cost, reduces wide practical application of these materials. Hence it is of interest to find

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new magnetostriction materials which will combine the high values of λ and $d\lambda/dH$ with minimal possible rare earth metal content.

The present paper reports the magnetostriction measurement of $LaCo_{13}$-based $NaZn_{13}$-type cubic compounds [2]. It is known that $LaCo_{13}$ possesses a high $T_C = 1290$ K [3] and a high saturation magnetization $\sigma_s = 130$ emu g^{-1}. Since the lanthanum ion is non-magnetic, the magnetostriction of this compound is due to the cobalt sublattice. In order to increase the magnetostriction we have also investigated the pseudo-binary $La_{1-x}R_xCo_{13}$ ($R \equiv$ Pr, Sm, Tb) and $LaCo_{11}M_2$ ($M \equiv$ Fe, Ni, Si, Al) compounds.

2. Experimental details

The investigated samples were prepared by induction melting in a levitation crucible without contact of the melt with the crucible. The ingots were annealed at $T = 1220$ K for 75 h.

The measurements of longitudinal magnetostriction $\lambda_{\parallel}$ and transverse magnetostriction $\lambda_{\perp}$ were carried out at room temperature on disc-shaped samples 4 mm in diameter and 1 mm thick in a magnetic field of up to 18 kOe using strain gauges attached directly to the surface of the specimen. The Curie temperature was determined from the temperature dependences of the initial susceptibility.

Phase analysis was carried out on a X-ray diffractometer using Cr $K\alpha$ radiation.

3. Results and discussion

3.1. *The homogeneity region of the $LaCo_{13}$ intermetallic compound*

Just after induction melting the samples are multiphase. In addition to $LaCo_{13}$ they contain free cobalt and $LaCo_5$. The stoichiometric composition contains a small amount of cobalt even after prolonged annealing. In order to obtain single-phase alloy, $La_{1+\delta}Co_{13}$ samples with different δ values were prepared. Single-phase samples were found to be obtained when $0.04 \leqslant \delta \leqslant 0.08$. A further increase in lanthanum content leads to the appearance of the $LaCo_5$ phase in alloy.

Figure 1 shows the magnetostriction of $LaCo_{13}$ alloys with different lanthanum excesses. The values of magnetostriction display a small decrease with increase in lanthanum content. $(\lambda_{\parallel} - \lambda_{\perp})_s$ values for all alloys are in the range $(85\text{–}101) \times 10^{-6}$. It can be seen from Fig. 2 that the samples are isotropic and the saturation of magnetostriction takes place in the external magnetic field of the order of 2 kOe. The maximum value of $d\lambda/dH$ taking into account the demagnetizing factor is 1.4×10^{-7} Oe^{-1}. Hence, $LaCo_{13}$ can be considered as a magnetostriction material with properties of the same order as Fe–Co alloys.

The Curie temperature dependence on the additional lanthanum content is shown Fig. 3. It can be seen that the increase in lanthanum concentration

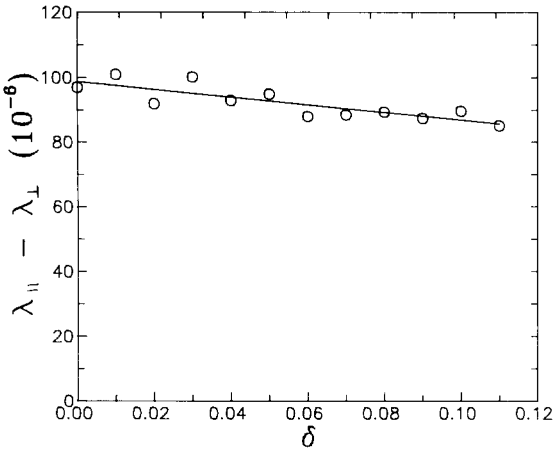

Fig. 1. Magnetostriction $(\lambda_{\parallel} - \lambda_{\perp})_s$ dependence of $La_{1+\delta}Co_{13}$ on the concentration of lanthanum excess in a magnetic field of 10 kOe at room temperature.

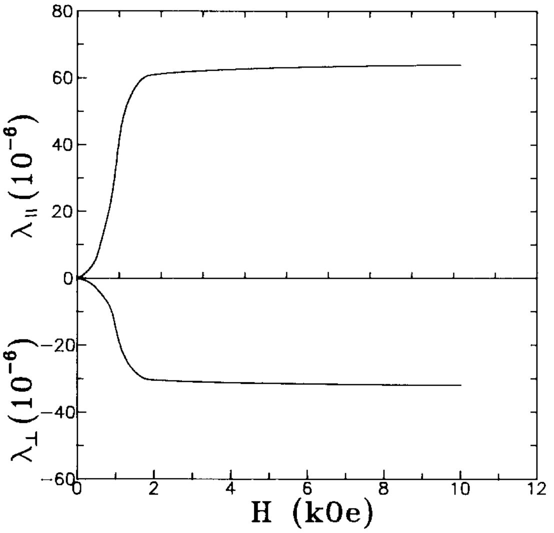

Fig. 2. Field dependence of the magnetostriction of an $La_{1.04}Co_{13}$ sample.

causes the increase in T_C. This dependence is opposite to the general tendency in the La–Co intermetallics, where T_C decreases with increase in lanthanum content. The possible reason for the T_C rise is the change in Co–Co interatomic distances caused by either the internal stresses or the changes in the coordination number of cobalt atoms. It is easy to show that the increase in T_C from 1253 to 1308 K (Fig. 3) cannot be explained by the stresses only. As is typical for intermetallic compounds, the dT_C/dP values are 1–2 K $Kbar^{-1}$ [4]; the internal stresses in this case should exceed the limit of strength of the alloy.

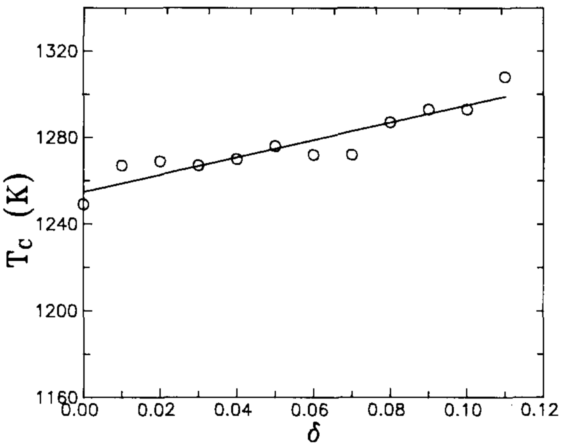

Fig. 3. Curie temperature dependence of $La_{1+\delta}Co_{13}$ on the concentration δ.

If the change in T_C is due to the interatomic distance changes, it can be expected that Co–Co distances decrease with increasing lanthanum concentration. Indeed, in R_2Co_{17} compounds, T_C increases under an external pressure [4], *i.e.* when the Co–Co distances became shorter. The dependence of the exchange integral on the interatomic distance [5] also indicates an increase in T_C when Co–Co distances decrease in free cobalt. In our case, both the decrease in interatomic distances and the changes in the cobalt local environment in the single-phase samples show that $LaCo_{13}$ probably has a homogeneity region.

Let us estimate the lattice parameter change in the homogeneity region in order to provide a 50 K change in T_C. From ref. 4 for R_2Co_{17} we have $d(\ln T_C)/d(\ln V) = -1.5$. Since the T_C values of the 2:17 and the 1:13 phases are nearly the same, it can be supposed that $LaCo_{13}$ have the same order of magnitude for $d(\ln T_C)/d(\ln V)$. Then it is easy to show that for a lattice parameter $a = 11.35$ Å the change in parameter should be of the order of 0.1 Å.

Figure 4 shows the lattice parameter dependence on the additional lanthanum content, measured both on powdered samples of different dispersities and on the bulk samples. The observed difference in parameters is probably connected either with internal stresses or with the cobalt nearest-neighbour change in the type of "order–disorder" in the process of crushing the alloy. In any case, the lattice parameter change seems to be an order of magnitude smaller than is expected from above-mentioned estimations.

The crystal structure of $LaCo_{13}$ to a first approximation can be considered as a CsCl-type lattice, where the lanthanum atom (8a site in the $NaZn_{13}$ structure) corresponds to the caesium position, and the cobalt atom (8b site) to the chlorine position surrounded by an icosahedron formed from 12 cobalt atoms (96i site) [6]. The interatomic Co(8b)–Co(96i) distance is 2.45 Å, *i.e.* essentially smaller than the sum of the atomic radii of cobalt and lanthanum (3.12 Å). Hence replacement of cobalt by lanthanum atoms is

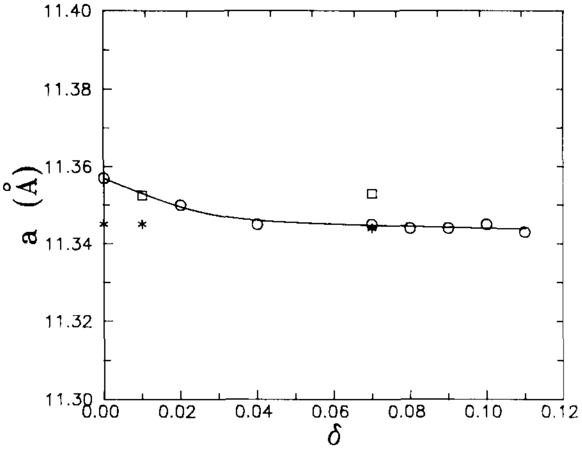

Fig. 4. Lattice parameter dependence of $La_{1+\delta}Co_{13}$ on the content of additional lanthanum, measured on bulk samples (□), powders with a mean particle size of 200–300 μm (○) and powders with a mean particle size of 60–40 μm (*).

TABLE 1

Calculated and experimental values of the intensities of some X-ray diffraction lines

$(h\ k\ l)$	I_{calc} (1:13 phase)	I_{exp}	I_{calc} (1:12 phase)
(0 0 4)	8	7	2.7
(0 2 4)	57.6	52.2	100
(2 2 4)	100	100	72.3
(0 2 6)	21.5	20.8	12.9
(4 4 4)	13.5	15	10.2
(0 4 6)	15.5	20	26
(2 4 6)	16.7	20.1	8
(0 0 8)	13.2	14.2	10.7
(0 2 8)	25.3	24.6	43.3

hardly probable, because this should lead to an appreciable increase in the lattice parameter. When the alloy contains additional lanthanum, the compound probably becomes cobalt deficient.

Let us suppose first that the vacancy appeared in the 8b site. The boundary of such a solution is the composition $LaCo_{12}$, for which all the 8b sites are vacant. This composition corresponds to the excess of lanthanum $\delta = 0.083$, close to the experimental boundary of the single-phase region (0.08). A detailed X-ray diffraction study of the samples with $\delta = 0$ and $\delta = 0.08$ was carried out in order to verify this supposition. It was found that the intensities of the X-ray diffraction lines of both samples are the same. These intensities together with the calculated values for $LaCo_{13}$ and $LaCo_{12}$ (the latter was considered as an $NaZn_{13}$ structure with a vacant 8b site) are listed in Table 1. It can be seen that the experimental values of intensities are close to the calculated values for $LaCo_{13}$ and essentially differ from $LaCo_{12}$. Hence, the addition of lanthanum to $LaCo_{13}$ leads to the substitution of vacancies for cobalt either in the 96i sites or in both types of cobalt site. In this case, the increase in T_C (Fig. 3) is connected to the change in coordination number of the cobalt atoms.

Another possible explanation can be given for why the change in T_C is not accompanied by a change in the lattice parameter. In $LaCo_{13}$ the homogeneity region possibly exists only at high temperatures, of the order of T_C. When the sample is cooled, a phase transformation takes place, but our efforts to quench the sample from 1300 K did not lead to a noticeable change in the 1:13 phase lattice parameter.

3.2. *Magnetostriction of pseudo-binary alloys based on $LaCo_{13}$*

The magnetostriction of $LaCo_{13}$ is due to the cobalt sublattice, because the lanthanum atom does not possess a magnetic moment. On the contrary, the huge magnetostriction of RFe_2 and other R-containing intermetallics is caused by the R sublattice. Hence, it is interesting to investigate the magnetostriction of the RCo_{13} compounds, where some of the lanthanum atoms are replaced by R atoms having a large orbital moment.

The magnetostriction caused by the R sublattice is known to have a single-ion origin [7]. In this case, $\lambda \approx \alpha J(J-\frac{1}{2})\langle r_f^2 \rangle$, where α is the Stevens factor [8], J is the quantum number of the total magnetic moment and $\langle r_f \rangle$ is the mean radius of the 4f shell [9]. The largest contribution to the magnetostriction should be given by such R elements as praseodymium, samarium and terbium (the α factors are -2.101×10^{-2}, $+4.127\times10^{-2}$ and -1.010×10^{-2} respectively).

Figure 5 shows the field dependences of the magnetostrictions of $La_{1-x}Pr_xCo_{13}$ compounds with $x\leqslant0.4$, which were obtained as almost a single phase. It can be seen from Fig. 5 that the values of saturation magnetostriction increase with increasing x, but simultaneously the fields of saturation also increased. Obviously, the introduction of praseodymium leads

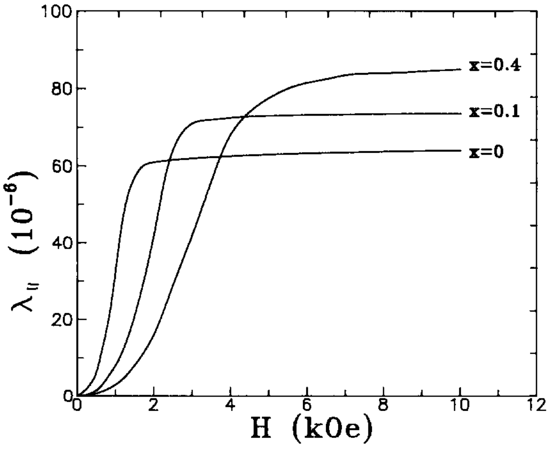

Fig. 5. Field dependences of the magnetostriction of $La_{1-x}Pr_xCo_{13}$ compounds.

to an increase in the constant of magnetocrystalline anisotropy. As a result, the values of $d\lambda/dH$ became smaller compared with that for $LaCo_{13}$, which makes the practical application of these alloys more difficult.

If the praseodymium concentration increases at $x>0.4$, $(\lambda_{\parallel}-\lambda_{\perp})_s$ rises to 210×10^{-6} for $x=0.8$, but the last composition contains mainly the 2:17 phase and α-Co and only a small amount of the 1:13 phase. Hence, the increase in λ_s at $x>0.4$ is due to the magnetostriction of the 2:17 phase, the value of which is of the order of 400×10^{-6} at room temperature [10].

In the case of replacement of lanthanum by terbium and samarium we cannot obtain single-phase alloys even at $x>0.1$. In the multiphase alloys $La_{1-x}Tb_xCo_{13}$, λ increases with increasing x. This is probably linked to a positive contribution of the 2:17 phase to the alloy magnetostriction. Contrary to this, the addition of samarium causes a decrease in the magnetostriction to 15×10^{-6} for $x=0.8$, in agreement with the difference in the signs of the Stevens factor for samarium and terbium.

It is known that the replacement of iron by silicon and aluminium stabilizes $R(Fe_{1-x}M_x)_{13}$ phases [11, 12]. We have investigated the effect of replacement of cobalt in $LaCo_{13}$ by iron, nickel, silicon and aluminium on the magnetostriction of the alloy. It was found that $LaCo_{11}Al_2$ and $LaCo_{11}Si_2$ are single phases after annealing. These alloys have much smaller values of T_C (881 K and 827 K respectively) than $LaCo_{13}$, and values of $(\lambda_{\parallel}-\lambda_{\perp})_s$ of the order of 30×10^{-6}. The lattice parameters are 11.438 Å for $LaCo_{11}Al_2$ and 11.282 Å for $LaCo_{11}Si_2$. The compounds $LaCo_{11}Fe_2$ and $LaCo_{11}Ni_2$ have $(\lambda_{\parallel}-\lambda_{\perp})_s$ values of 42×10^{-6} and 61×10^{-6} respectively; the T_C values are 1300 K and 1290 K respectively. Even after prolonged annealing, these samples contained a small amount of free 3d elements.

4. Conclusion

We have found that the $LaCo_{13}$ compound displays properties which have a discrepancy from the viewpoint of stability. On the one hand, the difference between the T_C of the alloys containing different additions of lanthanum indicate the presence of rather wide homogeneity region. On the other hand, the single-phase regions of pseudo-binary $La_{1-x}R_xCo_{13}$ and $La(Co_{1-x}M_x)_{13}$ (M ≡ Ni, Fe) are very narrow. The only exception is R ≡ Pr, for which the 1:13 phase was found up to $x=0.4$.

The presence of the homogeneity region allows one to explain why the T_C values of $LaCo_{13}$ obtained by different groups are essentially different, ranging from 1290 K [3] to 1318 K [13].

The saturation magnetostriction value $(\lambda_{\parallel}-\lambda_{\perp})_s$ of $LaCo_{13}$ reaches 100×10^{-6}. This value can be increased by partial replacement of lanthanum by praseodymium, but this leads to a decrease in the magnetostriction susceptibility $d\lambda/dH$.

The substitution of some of the cobalt atoms by aluminium and silicon leads to the appearance of single-phase alloys having much smaller values of magnetostriction and Curie temperature.

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