



Influence of Co substitution on magnetoelastic properties of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x = 1, 3$ and 5) intermetallic compounds

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ABSTRACT

The magnetostriction and thermal expansion of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x = 1, 3$ and 5) intermetallic compounds were measured, using the strain gauge method in the temperature range 75–450 K under applied magnetic fields up to 1.5 T. For all samples the longitudinal magnetostriction (λ_l) undergoes an anomaly around the spin reorientation temperature (T_{SR}). It is also observed that λ_l decreases with increasing the Co content. All compounds show saturation type behaviour in their anisotropic magnetostriction curves at different temperatures and applied fields. The saturation behaviour of the compound with $x = 3$ occurs at higher temperatures than with $x = 1$ and 5 . The volume magnetostriction strongly increases below $\mu_0 H = 0.3$ T, then monotonically rises with applied field up to the spin reorientation temperature. An invar type behaviour is observed above 200 K in the compound with $x = 1$. The results are discussed based on the temperature dependence of magnetocrystalline anisotropy of compounds below and above their T_{SR} .

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1. Introduction

The intermetallic $\text{RE}_2\text{Fe}_{14}\text{B}$ compounds (RE = rare-earth elements) have been extensively investigated during the past two decades because of their application as permanent magnets [1,2]. These compounds crystallize in tetragonal structure with $P4_2/mnm$ space group, where the RE ions are located on two different crystallographic sites and Fe (or Co) atoms occupy six nonequivalent crystallographic sites. Some of these studies have been carried out in order to improve magnetic properties (increase of Curie temperature (T_C), anisotropy field (H_A) and saturation magnetisation (M_S)) by partial substitution of cobalt for iron atoms [3–6]. Drastic modifications of their fundamental properties have been achieved, especially those related to the magnetocrystalline anisotropy [7].

$\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds have ferrimagnetic structure and Fe can be successfully replaced by Co up to $x = 5$ [5]. Previous results for the compounds with $x = 0, 2, 4$ and 5 revealed that both lattice parameters decrease and Curie temperature increases when the cobalt content is increased. The maximum value of M_S at room temperature is observed for $x = 2$ [5,6]. In addition, by increasing

temperature above room temperature, these compounds exhibit a spin reorientation transition at T_{SR} from planar ($T < T_{\text{SR}}$) to axial ($T > T_{\text{SR}}$) magnetic anisotropy. The spin reorientation temperature (T_{SR}) increases from 323 K for $x = 0$ to 390 K for $x = 5$ [5,8].

Although some reports are available on the magnetoelastic properties of the $\text{RE}_2\text{Fe}_{14}\text{B}$ compounds [9–11], there is no real information on the magnetostriction of the $\text{RE}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds. In this work, we study the magnetoelastic properties of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds, from 77 K up to above their spin reorientation temperatures.

2. Experimental methods

$\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds with $x = 1, 3$ and 5 were synthesized from the constituent elements under argon atmosphere (purity 5N) by high-frequency melting in a cold crucible. The purity of the starting elements was at least 3N. To homogenize the samples, the melted ingots were subsequently wrapped into Ta foil and annealed in evacuated quartz ampoules at 950 °C for a week then quenched in air to room temperature. X-ray diffraction (Cu-K α radiation) patterns showed that the annealed samples were exactly single phases.

Thermomagnetic analyses were performed by recording magnetisation versus temperature in the range of 300–1150 K under a constant magnetic field of 0.2 T, by using a homemade Faraday balance, with the accuracy of the temperature and magnetisation measurements of $\pm 0.1^\circ$ and 0.001 a.u., respectively. The magnetic ordering temperatures and spin reorientation temperatures of the compounds were determined from these measurements. Magnetisation measurements of powders pressed and blocked in sample holders to avoid free rotation of particles, were

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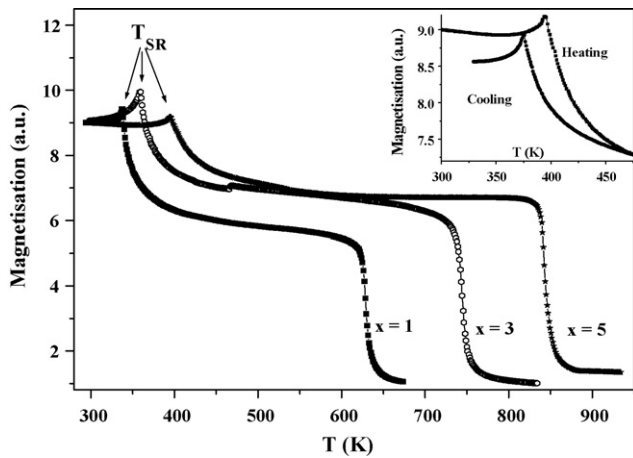


Fig. 1. Magnetisation versus temperature for $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x=1, 3$ and 5) compounds. The inset shows in more details the M versus T variation around the spin reorientation transition for $x=5$ and for heating and cooling cycles.

performed at 5, 50, 100, 150, 200 and 300 K by using an extraction type magnetometer under magnetic fields up to 7.0 T.

Magnetostriction and thermal expansion measurements were performed by using a strain gauge method on disk-shaped samples (10 mm diameter, 3 mm thick), which were cut from the annealed bulk ingots, under magnetic fields up to 1.5 T, the temperature ranging from 75 to 450 K. The magnetostriction coefficients were measured parallel (longitudinal magnetostriction, λ_l) and perpendicular (transverse magnetostriction, λ_t) to the field direction, thus allowing to deduce the anisotropic ($\Delta\lambda = \lambda_l - \lambda_t$) and the volume ($\Delta V/V = \lambda_l + 2\lambda_t$) magnetostriction. The thermal expansions $\Delta l/l = [l(T) - l(77\text{K})]/l(77\text{K})$ were deduced by measuring the relative change of length of the samples versus temperature. The accuracy of these measurements was better than 2×10^{-6} .

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetisation of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x=1, 3$ and 5) compounds. The cusp-like peak in M - T curves below 400 K show clearly the first order spin reorientation transition in these compounds [12]. Such anomaly is taken as evidence of a change in the easy-magnetisation direction which may be attributed to the fact that both Er and Co moments prefer planar anisotropy whereas Fe seeks axial anisotropy. Therefore, an increase in T_{SR} is observed with increasing Co content. This phenomenon was also found in other related heavy-rare-earth transition metal compounds [13] whereas in $\text{Nd}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds T_{SR} decreases when the Co content is increased [14]. Moreover, in each M - T curve of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds two cusps at different temperatures appear for heating and cooling cycle as shown for the compound with $x=5$ in the inset of Fig. 1. This behaviour can be attributed to the thermal hysteresis of the compounds. The Curie temperatures of the compounds were determined from the second derivative of M versus T curves. As expected T_{C} increases with the Co content that may be attributed to the increase of 3d-3d exchange interaction resulting from the decrease

Table 1

Magnetic properties of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds: spin reorientation temperature T_{SR} , Curie temperature T_{C} , saturation magnetisation M_{S} at 5 and 300 K and average moment of the 3d atoms (m_{3d}) at 5 K.

x	T_{SR} (K) (Heating)	T_{C} (K)	M_{S} (μ_{B} /f.u.) 5 K	M_{S} (μ_{B} /f.u.) 300 K	$\langle m_{3d} \rangle$ (μ_{B}) 5 K
0	330 ^a	554 ^a	14.1 ^b	19.6 ^b	2.26
1	337	623	14.6	21.8	2.29
3	358	735	13.8	22.2	2.24
5	395	838	13.0	21.9	2.18

^a [5].

^b [15].

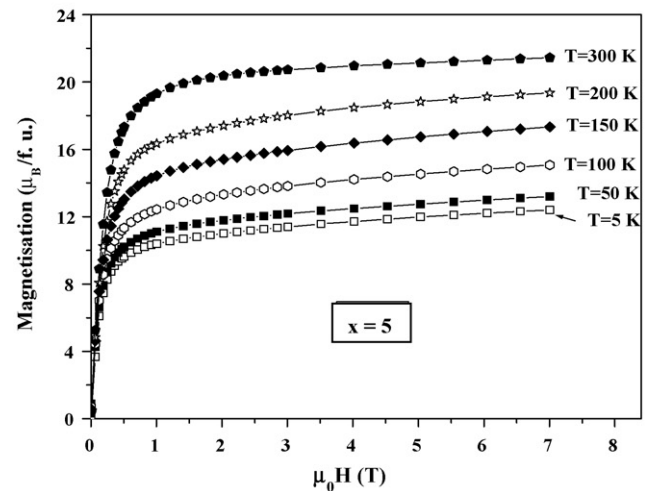
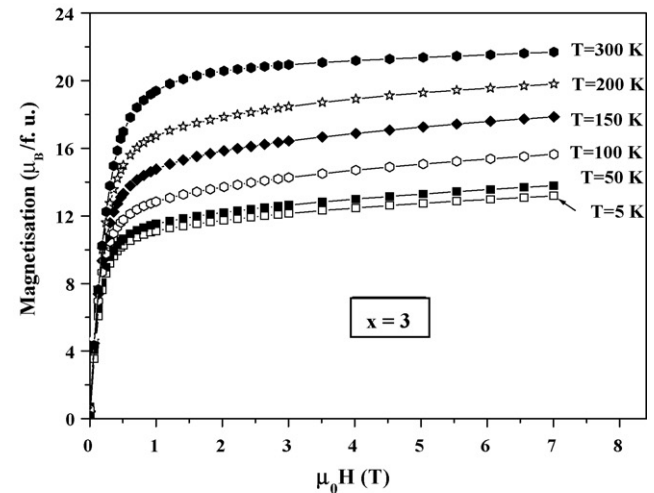
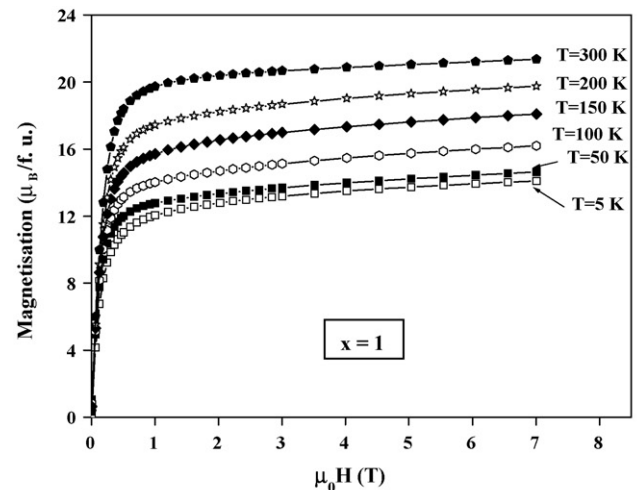


Fig. 2. Field dependence of magnetisation of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x=1, 3$ and 5) compounds, measured at 5, 50, 100, 150, 200 and 300 K.

of the lattice parameters. These results are presented in Table 1 and are consistent with previous reports for $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds with $x=0, 2, 4$, and 5 [5,6].

The field dependences of magnetisation of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds, with $x=1, 3$, and 5 , at temperatures ranging from 5 to 300 K are shown in Fig. 2. Saturation magnetisations were obtained by using M versus $1/H^2$ plots and are presented in Table 1 for 5

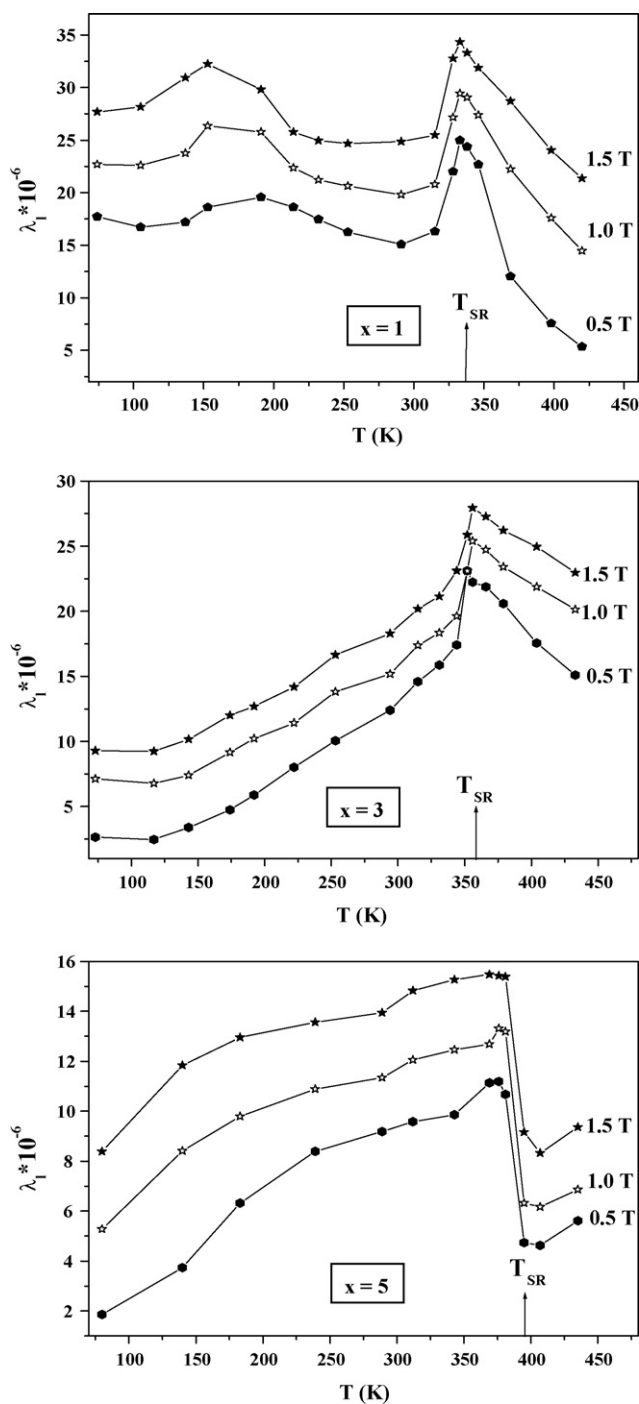


Fig. 3. Temperature dependence of the longitudinal magnetostriction of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x=1, 3$ and 5) compounds at selected magnetic fields. The accuracy of measurements was better than 2×10^{-6} .

and 300 K. The maximum values of M_S were observed for $x=3$ at room temperature. It is known that there is an antiparallel coupling between the RE and 3d moments which leads to ferrimagnetic structures for compounds with heavy RE elements. By using the magnitude of the magnetic moment of Er determined at 4 K in $\text{Er}_2\text{Fe}_{14}\text{B}$ [15], then from our results we deduced the average 3d moments at 5 K in the studied $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds, which are also presented in Table 1. As is clear from the data in this table the maximum value of M_S at room temperature is for the compound with $x=3$, but the maximum value of (m_{3d}) at 5 K is for $x=1$.

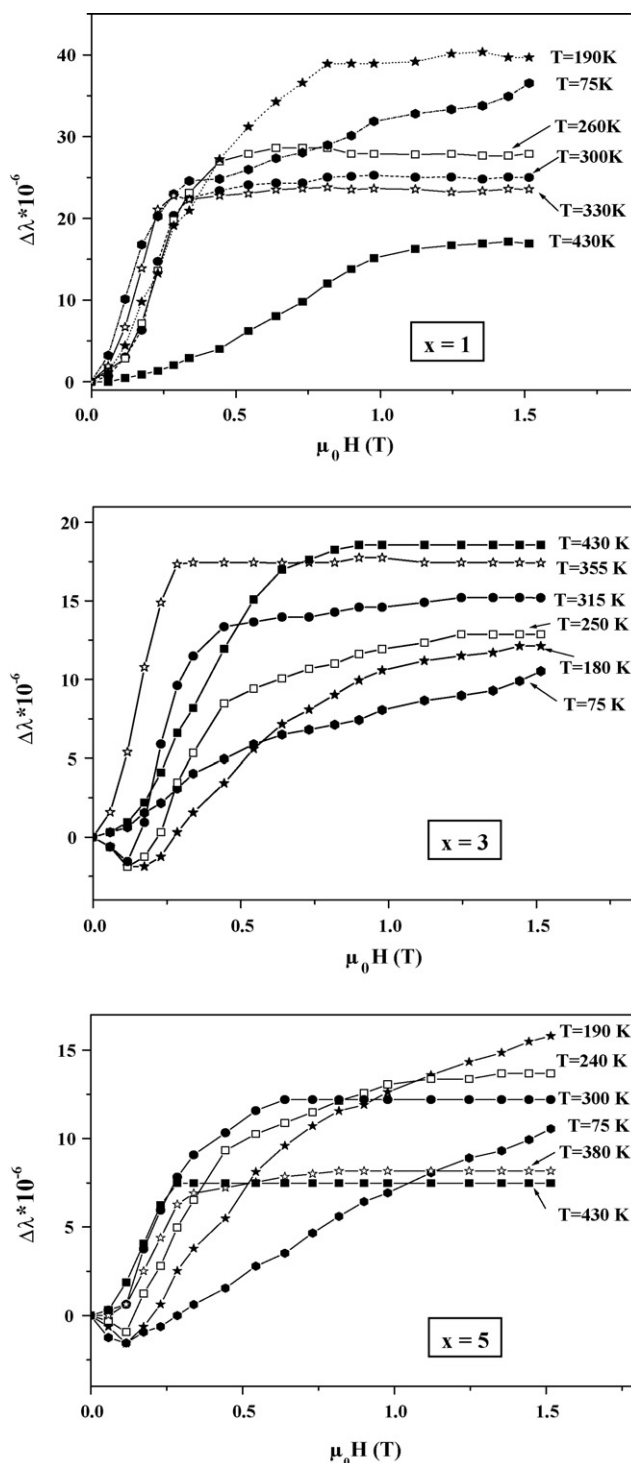


Fig. 4. Field dependences of the anisotropic magnetostriction of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x=1, 3$ and 5) compounds at different temperatures.

The temperature dependence of the longitudinal magnetostrictions (λ_1) of the $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds at typical applied fields is shown in Fig. 3. All samples exhibit an anomaly around their spin reorientation transitions. In $\text{Er}_2\text{Fe}_{14}\text{B}$ [9], λ_1 changes its sign at T_{SR} from negative value below this temperature to positive above. This was not observed in the compounds with cobalt content. As shown in Fig. 3, below T_{SR} , λ_1 decreases when the Co content increases. This behaviour is consistent with the decrease of magnetisation with the Co content at applied magnetic field of 1.5 T. The anomalies in the λ_1 curves for compound with $x=1$ in the temperature range from 100

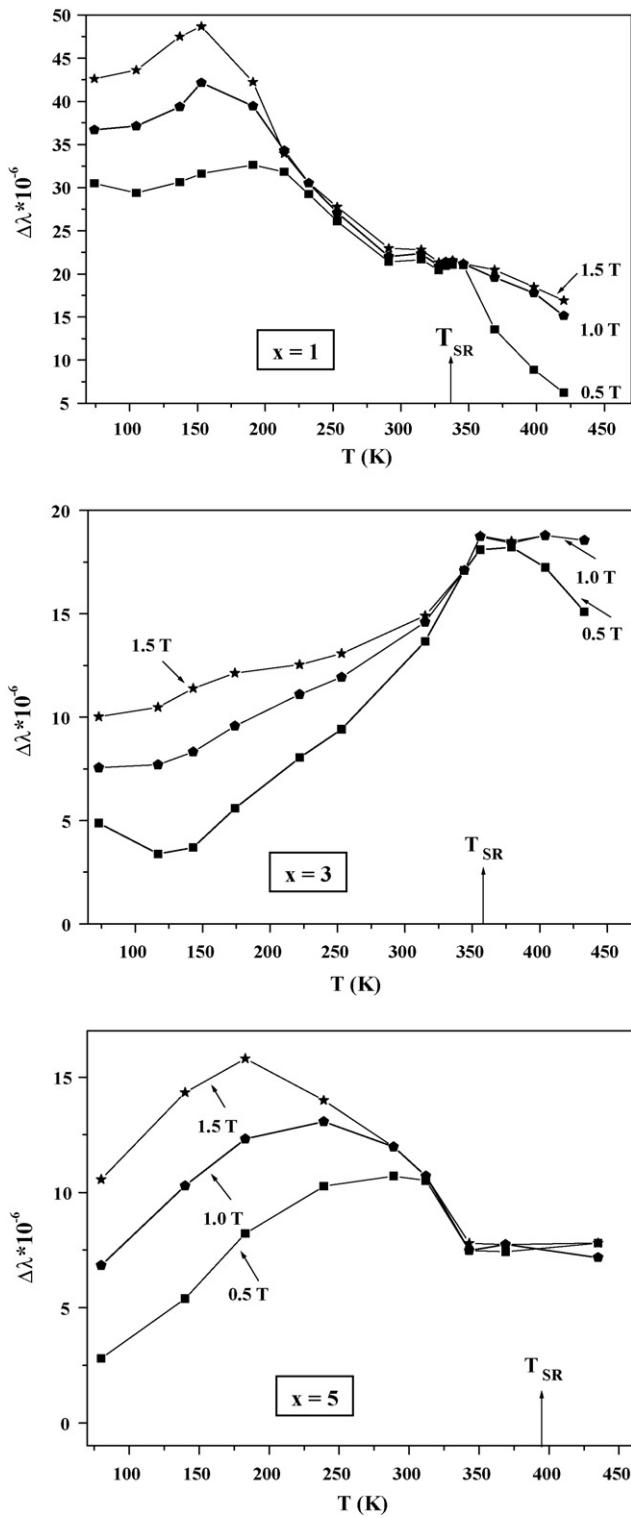


Fig. 5. Temperature dependence of the anisotropic magnetostriction of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x = 1, 3$ and 5) compounds at the selected magnetic fields.

to about 200 K are difficult to understand. But, as a possibility, this behaviour may be attributed to the competition between different magnetostriction modes in this temperature range.

Fig. 4 shows the anisotropic magnetostriction of the studied compounds as a function of applied field at selected temperatures. It is clear that saturation behaviour starts at different temperature and applied field for each compound. A clear change occurs around T_{SR} . Below T_{SR} , the saturation begins at lower field than above this

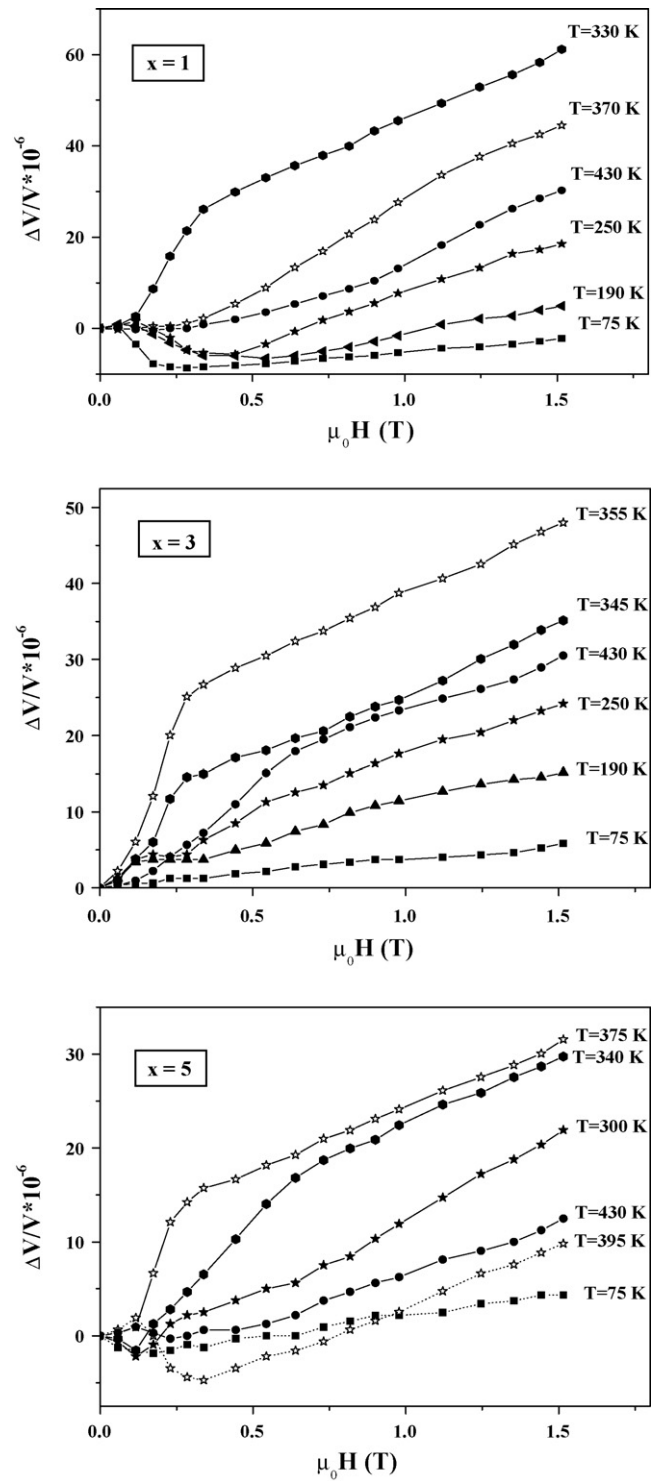


Fig. 6. Field dependences of the volume magnetostriction of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x = 1, 3$ and 5) compounds at typical temperatures.

temperature for all samples. For instance for $x = 1$, these fields are around 0.3 T and 1 T, respectively. This effect can be ascribed to the fact that materials pass from a planar anisotropy below T_{SR} to an axial anisotropy field above T_{SR} . With reference to the magnitude of anisotropy field in $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds ($H_A > 10$ T) for $x = 0$ and 5 [8,16], our available applied fields are much smaller than H_A . Thus, we can assume that $\Delta\lambda$ depends on rotation of magnetic moments in tetragonal basal planes by applied field up to 1.5 T in low temperatures so that the values of $\Delta\lambda$ reflect mainly

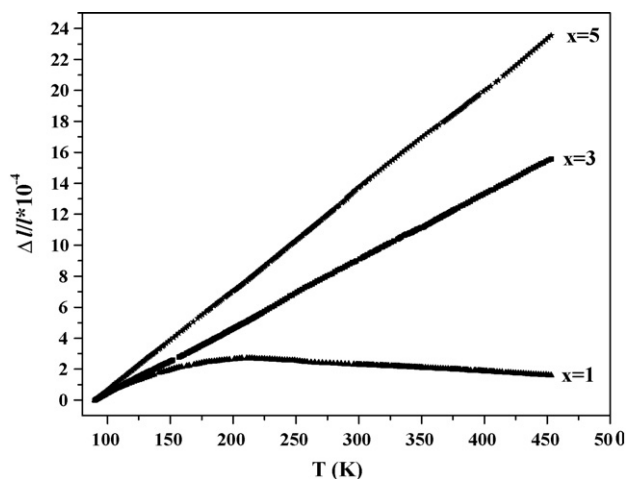


Fig. 7. Temperature dependence of the thermal expansion of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds.

the λ^γ mode [17]; the λ^γ mode dominates the value of other magnetostriction modes in single crystal compounds with strong planar anisotropy at low temperatures and in applied fields which are about one order of magnitude smaller than anisotropy fields of these compounds [17,18]. However, with increasing temperature and the associated decrease of planar anisotropy field, all magnetostriction modes contribute to the magnetostriction of these compounds. In addition the occurrence of saturation of $\Delta\lambda$ confirms that Co substitution does not have strong effect on the overall magnetostriction modes.

Fig. 5 shows the temperature dependence of the anisotropic magnetostrictions for the compounds at typical applied fields. It is clear that the saturation behaviour for $x=3$ occurs at higher temperatures than for $x=1$ and 5. The temperature dependence of $\Delta\lambda$ for compound with $x=3$ behaves differently with respect to other samples. For compounds with $x=1$ and 5, $\Delta\lambda$ increases with temperature up to around $T=150$ K and then starts to decrease at highest applied field (1.5 T), whereas in sample with $x=3$, $\Delta\lambda$ increases with temperature up to T_{SR} . Also, the sign of curvature of the $\Delta\lambda$ curves in the compound with $x=3$ is reversed with respect to other ones. This indicates that the effect of Co substitution on the anisotropy constants of these systems does not follow the same trend [19].

Fig. 6 shows the volume magnetostriction ($\Delta V/V$) of $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ compounds as a function of applied fields at the selected temperatures. All compounds show similar behaviour close to their T_{SR} (the highest curves in each set), so that the volume magnetostrictions strongly increase up to $\mu_0 H = 0.3$ T, then monotonically rise with applied field. The maximum value of $\Delta V/V$ (60×10^{-6}) occurs in compound with $x=1$ at its T_{SR} . As well, the values of $\Delta V/V$ in all compounds are approximately constant versus applied field below 160 K, and then increase with increasing magnetic field up to their T_{SR} . After passing T_{SR} , $\Delta V/V$ decreases when temperature increases. All maxima appearing close to T_{SR} can be ascribed to the decrease of the magnetic anisotropy. The sudden fall of volume striction beyond T_{SR} is the direct consequence of rotation of magnetic moments toward the tetragonal c -axis and the increase of uniaxial anisotropy field. However, it is worth noticing that $\Delta V/V$ in the compound with $x=5$ increases

again with temperature above 395 K. This indicates that uniaxial anisotropy field in this compound is smaller than that for $x=1$ and 3 at $T > T_{\text{SR}}$.

The linear thermal expansions ($\Delta l/l$) of the studied compounds are shown in Fig. 7. It is clear that the thermal expansion increases with the Co content. An invar type behaviour is observed only in the compound with $x=1$ above 200 K. Such behaviour was previously reported in $\text{Er}_2\text{Fe}_{14}\text{B}$ compound [9]. Since the temperature dependence of the thermal expansion is the consequence of a superposition of contributions of phonons and magnons, therefore results of ($\Delta l/l$) in compounds with $x=3$ and 5 show that contribution of phonons is dominant.

4. Conclusion

The magnetic and magnetoelastic properties of the $\text{Er}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ ($x=1, 3$ and 5) intermetallic compounds were investigated via magnetisation, magnetostriction and thermal expansion measurements. From magnetisation measurements, spin reorientation temperature, Curie temperature and saturation magnetisation of all samples were obtained. The longitudinal and volume magnetostrictions exhibit an anomaly around T_{SR} that can be ascribed to the weakness of magnetocrystalline anisotropy around the spin reorientation temperature. The maximum value of $\Delta V/V$ occurs in compound with $x=1$ at its T_{SR} . Results of anisotropic magnetostriction show that saturation takes place at smaller applied fields when temperature is close to T_{SR} . Thus we conclude that the values of $\Delta\lambda$ reflect mainly the λ^γ mode in low temperatures. An invar type behaviour is also observed only in the compound with $x=1$ above 200 K that can be attributed to the compensation of phonon and magnetic contributions.

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