Magnetocaloric and magnetoelastic effects in 
(Tb$_{0.45}$Dy$_{0.55}$)$_{1-x}$Er$_x$Co$_2$ multicomponent compounds

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Abstract. The magnetocaloric effect (MCE) and magnetoelastic (ME) anomalies at the magnetic phase transitions in (Tb$_{0.45}$Dy$_{0.55}$)$_{1-x}$Er$_x$Co$_2$ compounds ($0.1 \leq x \leq 0.3$) are studied. For the compounds synthesized with the use of high-pure rare-earth metals, the measurements of MCE performed by a direct method and the study of magnetostriction and thermal expansion by a strain-gauge technique are carried out. Large MCE and a maximum of magnetostriction are observed in the vicinity of phase transitions in the studied compounds, which can be considered as potential materials for magnetic refrigeration. It is shown that the magnetoelastic energy contribution to the MCE for (Tb$_{0.45}$Dy$_{0.55}$)$_{1-x}$Er$_x$Co$_2$ cannot be neglected.

1. Introduction

The large variety of magnetic phenomena was previously observed in the RCo$_2$ (R is a rare earth metal) cubic Laves phase compounds [1]. The magnetocaloric effect (MCE) was widely investigated for RCo$_2$ with magnetic R [2-4]. These compounds were found to experience large changes of magnetic entropy attributed mainly to the abrupt changes of magnetization in the vicinity of magnetic phase transition, i.e. near the Curie temperature. RCo$_2$ compounds are also well known due to observed giant magnetostriction effects [5] (for example in TbCo$_2$ at $T = 4.2$ K, the spontaneous anisotropic magnetostriction constant $\lambda_{111}$ and the volume magnetostriction $\omega_s$ reach the values of $4.5 \times 10^{-3}$ and $6.8 \times 10^{-3}$, respectively [6]).

During the past decade numerous investigations of magnetocaloric effect performed on RCo$_2$ compounds with different substitutions either in the rare-earth (R$_1$,R$_2$,Co$_2$ [7-10]) or in the Co sublattices (RCo$_{2-x}$T$_x$, where T = Si, Ga, Ge, Al, Fe, Ni, Mn [11-14]) were carried out. Nevertheless, no information on combined investigation of magnetothermal and magnetoelastic properties is available up to date. Moreover, the data on magnetothermal properties of multicomponent compounds (R$_1$,R$_2$,R$_3$,Co$_2$ with $x + y + z = 1$ is rather scant.

In the present work the following goals were aimed. The synthesis of high-purity multicomponent compounds (Tb$_{0.45}$Dy$_{0.55}$)$_{1-x}$Er$_x$Co$_2$ including purification of the rare-earth metals with the use of special regimes of melting and heat-treatment, and the complex study of properties (magnetic,
magnetothermal and magnetoelastic) of synthesized compounds that allowed us to reliably determine the principal magnetic parameters of the alloys and to reveal the peculiarities of magnetic behavior.

2. Experimental details
The purified rare-earth metals (of 99.956-99.983 wt % purity) characterized by low contents of metallic and interstitial elements, in particular oxygen with concentration decreased by two orders of magnitude after the purification process, were used as starting materials. An original furnace was designed and purification regimes (double vacuum distillation (Tb) and sublimation (Dy, Er)) were developed at the Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences. 

\[(\text{Tb}_{0.45}\text{Dy}_{0.55})_{1-x}\text{Er}_x\text{Co}_2 \ (0.1 \leq x \leq 0.3)\] compounds were prepared by arc melting in a high-purity helium atmosphere using a water-cooled copper bottom and non-consumable tungsten electrode. Ingots after melting were wrapped in a tantalum foil, sealed in quartz tube and annealed at 900°C for 100 h. The phase composition of the samples was determined by X-ray diffraction analysis using the DRON-3M diffractometer. The elemental composition was confirmed by EDAX that allowed also simultaneous study of the alloys microstructure (Institute of Low Temperatures and Structural Researches, Wroclaw, Poland).

The MCE measurements were performed by a direct method, namely, by a measurement of the electromotive difference of the thermocouple placed inside the sample of the spherical shape under adiabatic conditions when the external magnetic field is turned on. The magnetostriction and thermal expansion were measured by the strain-gauge technique. The magnetization was measured using a standard SQUID magnetometer.

3. Results and discussion
The X-ray diffraction analysis confirmed that \[(\text{Tb}_{0.45}\text{Dy}_{0.55})_{1-x}\text{Er}_x\text{Co}_2 \ (0.1 \leq x \leq 0.3)\] alloys are single-phase with the C15 cubic Laves phase crystal structure (MgCu2-type). No impurity peaks were found within the experimental accuracy. The lattice parameters deduced by the least-square method from the powder XRD data are shown in Table 1.

| Compound | \(a, \text{Å}\) | \(V, \text{Å}^3\) | \(T_C, \text{K}\) | Type of transition |
|----------|----------------|----------------|-----------------|-------------------|
| \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{0.9}\text{Er}_0.1\text{Co}_2\) | 7.1917 | 371.96 | 168 | First-order |
| \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{0.8}\text{Er}_0.2\text{Co}_2\) | 7.1878 | 371.36 | 162 | First-order |
| \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{0.7}\text{Er}_0.3\text{Co}_2\) | 7.1776 | 369.77 | 146 | Second-order |

Since the alloys under study are multicomponent, the prepared samples were examined by the X-ray fluorescent microanalysis in order to determine the exact composition. We estimated not only the integrated content of the components, but also considered the local distribution of the composition over the individual regions. Such procedure allowed the unambiguous conclusion that selected samples possessed the required stoichiometry and had a uniform structure.

The temperature dependence of magnetization for \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{0.8}\text{Er}_0.2\text{Co}_2\) compound measured in magnetic field of 1 kOe is shown in Fig. 1. The Curie temperature was determined from the peak at the \(d\sigma/dT\) curve. The Er-concentration dependence of the Curie temperature \(T_C\) is given in Table 1. It is seen that the Curie temperature decreases from 168 down to 146 K as the Er content increases from 0.1 to 0.3. The \(T_C\) values and the order of transition in \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{1-x}\text{Er}_x\text{Co}_2\) compounds were determined according to Landau theory by analyzing the temperature dependence of Landau coefficients \(a(T)\) and \(b(T)\). The obtained values of \(b(T_C)\) were found to be negative for \(x = 0.1\) and 0.2, confirming an occurrence of the first order magnetic phase transition at \(T_C\). On the other hand the absolute value \(b(T_C)\) for \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{0.3}\text{Er}_0.7\text{Co}_2\) is close to zero and \(b(T)\) for \((\text{Tb}_{0.45}\text{Dy}_{0.55})_{0.2}\text{Er}_0.8\text{Co}_2\) becomes positive at \(T_C\), so that indicating the magnetic phase transition of the second order. The Curie...
temperatures obtained from the a(T) dependencies are in a good agreement with those obtained from the magnetization measurements. These results were also confirmed from the visual analysis of the linear thermal expansion of (Tb_{0.45}Dy_{0.55})_{1-x}\text{Er}_x\text{Co}_2 compounds (see Fig. 2).

Figure 2 demonstrates the temperature evolution of thermal expansion of (Tb_{0.45}Dy_{0.55})_{1.0-0.3}\text{Er}_x\text{Co}_2 (x = 0.1 and x = 0.3) compounds (ferrimagnetic) in comparison with that of YCo_2 (paramagnetic). One can see that the thermal expansion $\Delta l/l$ of YCo_2 shows a linear dependence on temperature within the indicated temperature range, whereas in (Tb_{0.45}Dy_{0.55})_{0.9}\text{Er}_0.1\text{Co}_2 and (Tb_{0.45}Dy_{0.55})_{0.7}\text{Er}_0.3\text{Co}_2, the linear behavior is observed only at $T > T_C$. At temperatures lower than $T_C$, the thermal expansion curves of (Tb_{0.45}Dy_{0.55})_{0.9}\text{Er}_0.1\text{Co}_2 and (Tb_{0.45}Dy_{0.55})_{0.7}\text{Er}_0.3\text{Co}_2 differ considerably from that of paramagnetic YCo_2.

Figure 3 shows the temperature dependence of MCE of (Tb_{0.45}Dy_{0.55})_{0.9}\text{Er}_0.1\text{Co}_2 and (Tb_{0.45}Dy_{0.55})_{0.8}\text{Er}_0.2\text{Co}_2 compounds in magnetic field of 12 kOe. For these compounds a large magnetocaloric effect (adiabatic temperature change $\Delta T_{ad} \approx 1.45$ K at $H = 12$ kOe) is observed in the vicinity of the magnetic phase transition. The temperature dependencies of the volume magnetostriction of (Tb_{0.45}Dy_{0.55})_{0.9}\text{Er}_0.1\text{Co}_2 and (Tb_{0.45}Dy_{0.55})_{0.7}\text{Er}_0.3\text{Co}_2 (x = 0.1 and 0.2) compounds measured in magnetic field of 12 kOe are presented in Fig. 4. Both curves also show a maximum at the magnetic phase transition with $\lambda_{str} = 770$ and $670 \times 10^{-6}$, respectively.

The estimation of the contribution of magnetoelastic energy to the change of magnetic entropy ($\Delta S_{me} = C_p \Delta T_{me}/T$) was performed using following formula

$$\Delta T_{me} = \frac{T}{C_p} \frac{E}{2} \left( \frac{\partial^2 \lambda_{str}/\partial T^2}{\partial T} - \frac{\partial^2 \lambda_{str}/\partial H^2}{\partial H} \right)$$

where E is Young’ modulus, $C_p$ is specific heat at constant pressure [15]. In order to define $\lambda_{str}$ and $\lambda_{E}$ values, experimental data on thermal expansion (Fig. 2) and volume magnetostriction (Fig. 4) were used. The temperature change $\Delta T_{me}$ calculated was found as 0.5K at $H=12$ kOe. Our calculations conducted for the polycrystalline (Tb_{0.45}Dy_{0.55})_{1.0-0.2}\text{Er}_x\text{Co}_2 multicomponent compounds have shown that the change of magnetoelastic energy provides significant contribution to the change of magnetic entropy (of up to 35%). More precise calculations of both magnetoelastic and other (the exchange, anisotropic and magnetic) energy contributions to the MCE [15, 16] can be performed during the study of single-crystalline samples.
Figure 3. Temperature dependence of MKE of (Tb_{0.45}Dy_{0.55})_{1-x}Er_{x}Co_{2} (1 - x =0.1 and 2 – x = 0.2) compounds in a field change of 12 kOe.

Figure 4. Temperature dependence of volume magnetostriction of (Tb_{0.45}Dy_{0.55})_{1-x}Er_{x}Co_{2} (1 - x =0.1 and 2 – x = 0.2) compounds measured in magnetic field of 12 kOe.

As a conclusion, we suggest that the multicomponent (R_{x}R'_{y}R''_{z})Co_{2} (x+y+z=1) compounds with high values of volume magnetostriction can be considered as potential materials for magnetic refrigeration (the value of ΔT/ΔH for alloys (Tb_{0.45}Dy_{0.55})_{1-x}Er_{x}Co_{2} (x=0.1 and 0.2) is 1.2 K/T, which is reasonably high as compared with other known materials [17]).

References
[1] Duc N C, Brommer P E, in: K.H.J. Buschow (Ed.) 1999 Handbook of Magnetic Materials, vol. 12 (Amsterdam, Elsevier Science).
[2] Nikitin S A and Tishin A M 1991 Cryogenics 31 166.
[3] Gschneider Jr. K A and Pecharsky V K 2000 Ann. Rev. Mater. Sci. 30 378.
[4] Dunhui W, Shaolong T, Songling H, Zhenghua S, Zhida H and Youwei D 2003 J. Alloys Compd. 360 11.
[5] Levitin R Z and Markosyan AS. 1988 Usp. Fiz. Nauk 155 623. Engl. Transl. Sov. Phys.-Usp. 31 730.
[6] Andreev A V, in: K.H.J. Buschow (ed.) 1995 Handbook of Magnetic Materials, vol. 8 (Amsterdam, North-Holland) p 68.
[7] Gomes A M, Reis M S, Oliveira I S, Guimaraes A P and Takeuchi A Y 2002 J. Magn. Magn. Matter., 242-45 870.
[8] Ouyang Z W, Rao G H, Yang H F, Liu W F, Liu G Y, Feng X M and Liang J K 2004 J. Alloys Compd. 372 76.
[9] Liu X B and Altounian Z. 2005 J. Magn. Magn. Matter. 292 83.
[10] Balli M, Fruchart D and Gignoux D 2007 J. Magn. Magn. Matter. 314 16.
[11] Wada H, Tanabe Y, Shiga M, Sugawara H and Sato H 2001 J. Alloys Compd. 316 245.
[12] Liu H, Wang D, Tang S, Cao Q, Tang T, Gu B and Du Y 2002 J. Alloys Compd. 346 314.
[13] Prokleska J, Vejpravova J, Vasilyev D, Danis S and Sechovsky V 2005 J. Magn. Magn. Matter. 290-291 676.
[14] Singh N K, Suresh K G and Nigam A K 2003 Solid State Commun. 127 373.
[15] Nikitin S A 1984, Sov. Phys. JETP 59 (5) 1010
[16] Spichkin Y I and Tishin A M 2005 JMMM 290-291 700
[17] Tishin A M, in: K.H.J. Buschow (Ed.) 1999 Handbook of Magnetic Materials, vol. 12 pp 395-524.