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Magnetic properties of $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ quasi-binary compounds

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Abstract. In this paper the results of magnetic properties study for a series samples of $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ type intermetallic compounds with a heavy rare-earth elements ($R = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$) are presented. Such materials having a plateau-like temperature dependences of magnetic entropy change in the temperature range lower Curie point are considered as a promising functional materials for magnetic refrigerators. Their phase composition was controlled by X-ray diffraction analysis with a help of Bruker D8 Advance diffractometer. Magnetic field magnetization dependences – $M(H)$ were measured using a SQUID magnetometer (MPMS-XL-7, Quantum Design) within the temperature range of 5 – 600 K in magnetic fields up to 5600 kA/m. The crystal lattice parameter – a , Curie temperature – T_C , coercivity – H_c and residual magnetization – M_r values are analyzed as a functions of R-element atomic number. For compounds with Tb, Dy, Ho and Er the second peaks on the high field susceptibility temperature dependences – $\chi_{hf}(T)$ were found in the temperature range lower their T_C .

1. Introduction

Cubic RT_2 type Laves phases, where R – Rare Earth element, T – 3d transition metal (Fe, Co, Ni) are actively studied from the middle of the XX century because a some of them on the Fe-base possess a great anisotropic magnetostriction values [1].

Binary compounds on the Co-base have an interest due to the large magnetocaloric effect – MCE in the vicinity of their Curie point – T_C [2]. However, they are not appropriate for magnetic refrigerators working at room temperature – RT due to a low their T_C values. Its increase up to the RT can be realized via a partial Co substitution by Fe [3], which drastically influences the exchange energy in 3d-sublattice and changes the kind of magnetic phase transition in the T_C - point (from the first to the second order). The former takes place particularly for RCO_2 compounds where the spin quantum number of the 4f-electronic shell has a not so large value (DyCo_2 , HoCo_2 , ErCo_2) [4,5].

The MCE studies in the quasi-binary $R(\text{Co}_{1-x}\text{Fe}_x)_2$ compounds with a heavy R have shown that a partial Co substitution with Fe leads to the emergence of significant MCE in a wide temperature range below its T_C [5]. Later the authors [6] were found that the difference between the maximum and minimum temperatures at the half of maximum height of magnetic entropy change – ΔT_{FWHM} depends not only on the Fe- content but also on the R-element type (atomic number). This phenomenon they explained by the difference in R-3d intersublattice exchange energy values in such compounds basing on the paper [7] data, where the properties of only binary compounds have been investigated.



In this paper we present the results of magnetic properties study of quasi-binary $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ compounds, where $R = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ with the fixed Co/Fe ratio – 0.88/0.12.

2. Experimental details

$R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ type alloys were melted in an electric arc or induction furnaces under a pure helium or argon protection atmospheres. An excess of Rare Earths metal (5 wt. %) was added to the starting compositions for preventing of 3d-metal rich phases formation. A homogenizing annealing of alloys was made in a vacuum furnace at 800 – 950 °C during 24 – 36 hours. The samples phase structure was checked by X-ray diffraction technique (D8 Advance, Bruker) with Cu K_α radiation source. Diffraction patterns were analyzed by Rietveld method using the Fullprof software. Magnetic field magnetization dependences – $M(H)$ were measured using a SQUID magnetometer (MPMS-XL-7, Quantum Design) within the temperature range of 5 – 600 K in magnetic fields up to 5600 kA/m.

3. Results

Analysis of the X-ray diffraction data at room temperatures showed (figures 1 and 2) that all samples contain mainly the 1:2 type Laves phase. Their crystal lattices belong to the $Fd-3m$ space group. The content of a secondary R_2O_3 phase was mainly lower of 1 %, excepting $\text{Gd}(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ samples where its volume was about 2-3 %. The calculated crystal lattice parameter – a presented in table 1. Its lowering in the row $\text{Gd} \rightarrow \text{Er}$ compounds is obviously explained by the so called “lanthanoid contraction” effect.

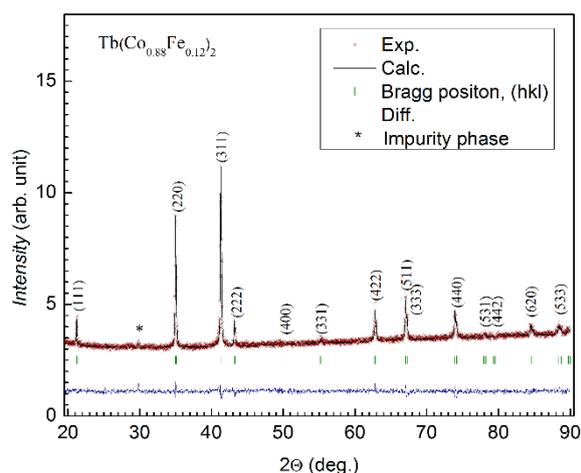


Figure 1. X-rays diffraction pattern of $\text{Tb}(\text{Co}_{0.88}\text{Fe}_{0.12})_2$.

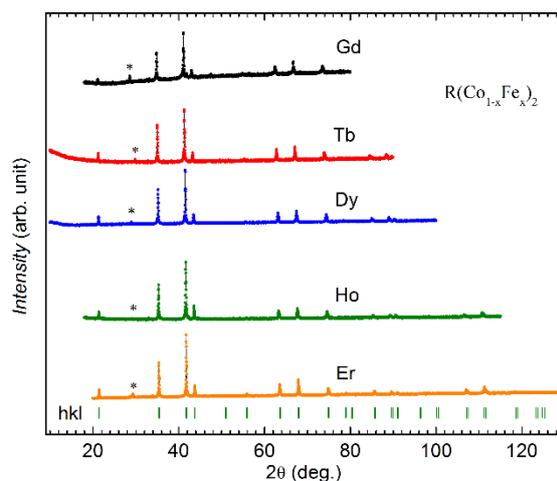


Figure 2. X-rays diffraction patterns of all $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$.

3.1. Magnetic field and temperature dependences of magnetization

Figure 3 shows the magnetization temperature dependences of the studied materials samples measured in the external magnetic field of 400 kA/m – $M_{400}(T)$. They confirm the absence of the secondary magnetic phases in the given temperature range. Initial $M_{400}(T)$ rise with temperature increase from 5 K up to 50 K for the samples with Tb, Dy and Er is caused by the sharp magnetocrystalline anisotropy – MA energy lowering in these compounds for that temperature range [8]. The high MA existence at $T = 5$ K is confirmed by the magnetization saturation absence on $M(H)$ curves up to the maximal magnetic field of 5.6 MA/m (as it follows from the figure 4). It should be mention for example that in binary compounds the magnetic anisotropy field – H_a at $T = 4.2$ K is equal to 6.72 MA/m for HoFe_2 , 54.4 MA/m for ErCo_2 and 52.0 MA/m for ErFe_2 [9].

Taking the M (at 5600 kA/m) magnetization values at $T = 5$ K for all compound samples we have calculated the formulae unit magnetic moments in Bohr magnetons μ_B (presented in table 1).

Curie temperature data for the studied $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ compounds have been determined from the extremum $dM(T)/dT$ position at the T -axis under $M(T)$ measurements in the external magnetic field of 8 kA/m. These values are presented also in table 1. As it seen the T_C values are lowered with the R -element atomic number increase and reaches the minimal value for $\text{Er}(\text{Co}_{0.88}\text{Fe}_{0.12})_2$.

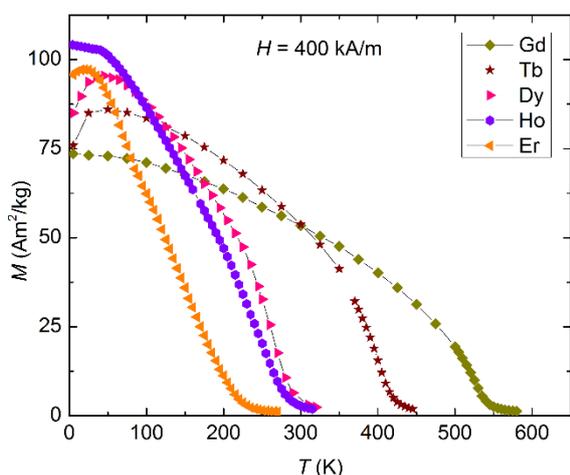


Figure 3. Specific magnetization temperature dependences of $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ compounds samples in the external magnetic field of 400 kA/m.

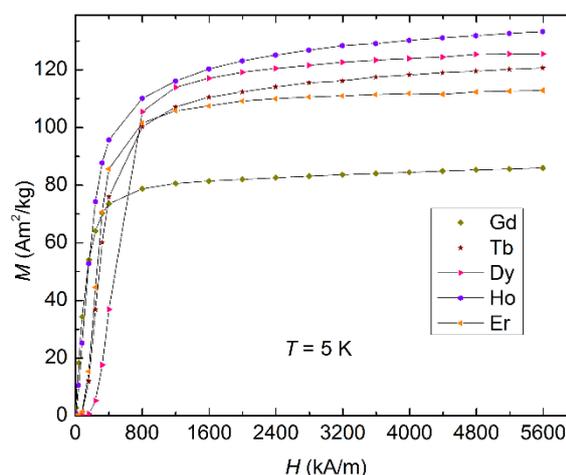


Figure 4. Magnetization curves of $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ samples at the temperature of 5 K.

It is well known that the Curie temperature of Fe-containing $R(\text{Co}_{1-x}\text{Fe}_x)_2$ compounds are determined strongly by the d-d exchange interaction basically between Fe-atoms. [10]. As far as in the studied compounds the Co/Fe ratio is fixed, and so this interaction can be more or less identical in all compound's series, the observed T_C value change obviously originates from the intersublattice R-3d exchange energy lowering (which also gives some additional contribution to the total compound exchange energy). R-atoms number increase from Gd to Er is accompanied by the 4f-electronic shell spin number steady reduction giving a drop of R-3d exchange interaction energy [7, 11].

Table 1. Crystal lattice parameter – a and Curie temperature – T_C data and formulae unit magnetization (in Bohr magnetons) in the field of 5600 kA/m – M_B , residual magnetization – M_r and coercivity – H_c values of the studied $R(\text{Co}_{1-x}\text{Fe}_x)_2$ compounds samples at $T = 5$ K.

	$R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$				
	Gd	Tb	Dy	Ho	Er
a , Å	7.2793(2)	7.2444(6)	7.2087(2)	7.1830(2)	7.1668(2)
T_C , K	535	404	265	256	195
M_B , μ_B at 5 K	4.22	5.96	6.58	6.99	5.86
M_r , Am^2/kg at 5 K	0	40	81	3	47
H_c , kA/m at 5 K	0	112	268	9	110

Figure 5 shows the magnetization curve and hysteresis loop for $\text{Dy}(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ compound sample measured at $T = 5$ K. Its central part in the increased scale is placed as insertion. This sample has the residual magnetization value of 81 Am^2/kg and intrinsic coercivity – 268 kA/m. Looking on the shape of a low field part of $M(H)$ -curve it is possible to infer that its coercivity originates from the domain's

walls pinning mechanism. Identical magnetization curves and hysteresis loops are observed for the compound's samples with Tb, Ho and Er. Such sample with Gd has a practically zero coercivity, that can be explained by the very low magnetic anisotropy energy of Gd-sublattice due to an orbital moment absence for 4f-electronic shell in Gd^{3+} ions (crystal field magnetocrystalline anisotropy – MCA mechanism). Obtained magnetic hysteresis parameters for all samples are presented also in table 1.

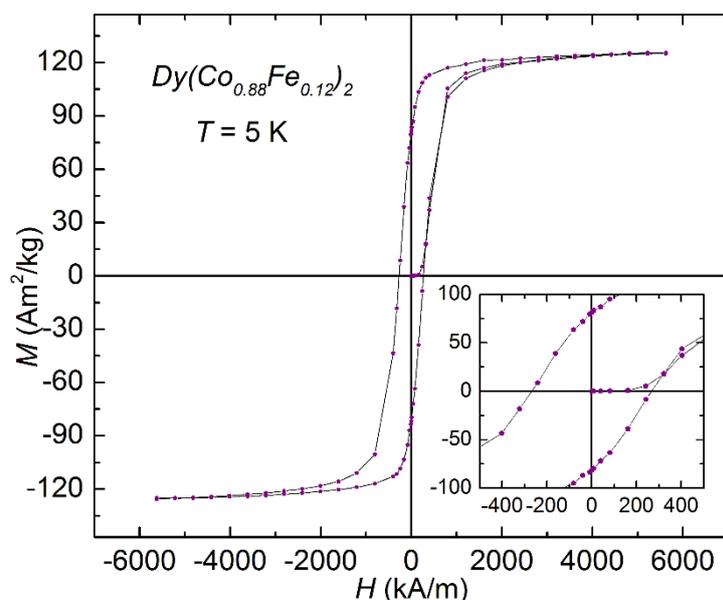


Figure 5. Magnetic hysteresis loop and specific magnetization curve of the sample of $Dy(Co_{0.88}Fe_{0.12})_2$ compound measured at $T = 5$ K. Their low field parts are shown in the insertion.

It should be mentioned here that the coercivity value of $Ho(Co_{0.88}Fe_{0.12})_2$ sample is relatively low also than those for compounds with Tb, Dy and Er, though the Ho^{3+} -ions have non zero orbital moment of the 4f-electronic shell. It can be explained by the low value of its total MCA energy due to the different signs of K_1 and K_2 MCA constants [9].

3.2. The high-field susceptibility

Temperature dependences of a high-field susceptibility $\chi(T)$ of the studied compounds are presented in figure 6. The χ -values were calculated from the linear part of $M(H)$ curves in the field range 1600 – 5600 kA/m ($\chi = dM/dH$). Taking into consideration a huge MCA energy of the studied compounds at low and medium temperatures, only the χ -data at the temperatures near T_C are adequate to the paraprocess susceptibility. For all samples near the Curie point, the susceptibility has a characteristic maximum, which is typical for the classical ferro- and ferrimagnets. Excepting the Gd-compound the specific feature of $\chi(T)$ dependences of all other ones is the presence of the second high-field susceptibility maximum or $\chi(T)$ bend at medium temperatures below T_C . In the $\chi(T)$ dependence for $Er(Co_{0.88}Fe_{0.12})_2$ both maxima are overlapped and the one corresponding to the T_C point cannot be distinguished clearly from the low-temperature one (further “low T-point”). A similar maximum was observed in paraprocess susceptibilities studies for the case of $HoFe_3$ [12]. Such phenomena usually are interpreted using the model of a “weak magnetic sublattice” [12]. Due to a relatively low energy of R-3d exchange interaction the magnetic order in R-sublattice at the intermediate temperatures can be partially destroyed by the thermal energy. But such sublattice can very strongly react on the external magnetic field giving magnetization or $\chi(T)$ rise. It was experimentally confirmed for $ErFe_2$ [13].

Analyzing the $\chi(T)$ - dependences it is possible to define the different studied compound groups. For those with Dy and Ho the low T-points are distinctly observed but they are expressed worse in Tb- and Er-containing materials. Obviously that all such effects are determined by the strength of intersublattice exchange interaction, which is highest in Gd-containing compound and lowest in Er

one. Thus, the Er-sublattice has in the low T-point the maximal “reply” on the magnetic field action and owe the maximal magnetic contribution to the entropy in these temperature range [5].

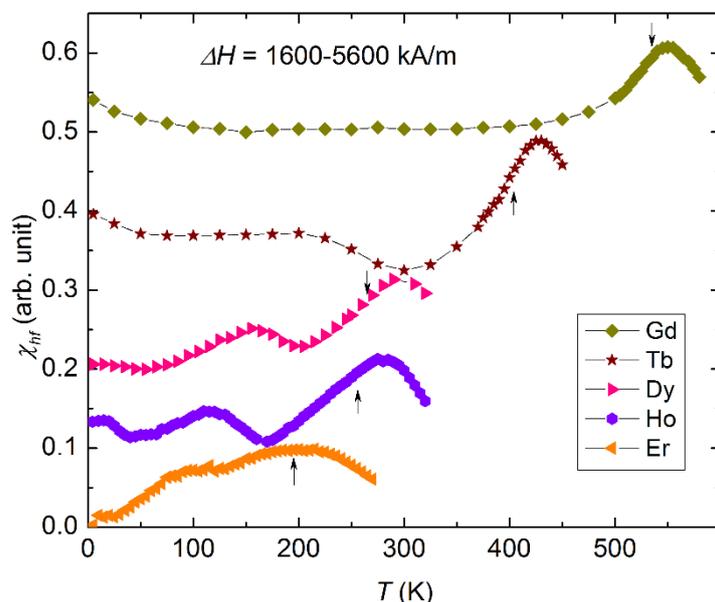


Figure 6. High magnetic field susceptibility temperature dependences - $\chi_{hf}(T)$ of $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ intermetallics.

4. Conclusions

Magnetic properties study of $R(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ type intermetallic compounds samples ($R = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$) has shown the following:

1. The Rare Earth element atomic number rise in them from Gd to Er gives the steady crystal lattice contraction and Curie temperature lowering.
2. A large magnetocrystalline anisotropy existence at the low temperature (5 K) in the compounds with Tb, Dy, Ho and Er. Anisotropy field value is much higher than the measuring maximal magnetic field strength of 5600 kA/m.
3. A large MCA in these compounds at low temperature courses an evident hysteresis phenomena and coercivity due to the domain walls pinning.
4. The presence at the temperature dependences of high magnetic field susceptibility $\chi(T)$ a “low T-point” corresponding to the second $\chi(T)$ maximum. Such phenomenon was interpreted using a “weak magnetic sublattice” model.
5. Intersublattice exchange interaction strength has an important role for the formation of a high magnetic field susceptibility temperature behavior. Its value is maximal for Gd containing compound and minimal for Er-containing one.

Acknowledgments

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