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Spin reorientation phenomena in $Er_{2-x}R_xFe_{14}B$ (R = Gd, Th) – Mössbauer and calorimetric study

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Abstract. The $Er_{2-x}Gd_xFe_{14}B$ (x = 0.5, 1.0, 1.5) and $Er_{2-x}Th_xFe_{14}B$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) polycrystalline compounds have been investigated with ^{57}Fe Mössbauer spectroscopy and differential scanning calorimetry (DSC). A comparison of results related to spin reorientation phenomena obtained for Gd- and Th-substituted compounds is presented in this paper. Spin reorientation phenomena (changes from planar to axial spin arrangements) have been studied extensively by a narrow step temperature scanning in the neighbourhood of the spin reorientation temperature, T_{SR}. From the analysis of Mössbauer spectra, it was deduced that in the region of transition each subspectrum was split into two Zeeman sextets, which were characterised by different hyperfine magnetic fields and quadrupole splittings. A consistent way of fitting the spectra in the wide range of temperatures was proposed. The composition and temperature dependencies of hyperfine interaction parameters and subspectra contributions were derived from fits and the transition temperatures were determined for all the compounds studied. DSC studies proved that the spin reorientations were accompanied by thermal effects for all compositions of the Gd- and for x = 0.5 of the Th-series. Transformation enthalpy and T_{SR} were determined from these studies and the two-stage character of transition was confirmed. Magnetic spin arrangement diagrams for R = Th and Gd series were constructed and compared using combined data obtained with both methods.

Key words: Mössbauer effect • spin reorientation

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Introduction

In Er-based $R_2Fe_{14}B$ (R = rare earth) compounds, the magnetocrystalline anisotropy changes from planar (basal plane) to axial (along the c-axis) with increasing temperature. The easy magnetisation direction of $Er_{2-x}R_xFe_{14}B$ depends on the temperature induced competition between the uniaxial Fe sublattice anisotropy [3] and the basal plane (Er,R) sublattice anisotropy [5].

The $Er_{2-x}R_xFe_{14}B$ crystallize in a tetragonal structure with the $P4_2/mnm$ space group. Iron atoms occupy six non-equivalent crystal sites ($16k_1$, $16k_2$, $8j_1$, $8j_2$, $4e$, $4c$), the rare earth ions occupy $4f$ and $4g$ crystallographic sites and boron is located at $4g$ site [4]. Thorium is not a lanthanide, yet it was possible to incorporate it into Er sites of the crystal lattice of the $Nd_2Fe_{14}B$ type [2] which made studies of this material more interesting.

The main goal of this work was to compare the effects of competing anisotropies of the two rare earth ions (Er vs. Gd and Er vs. Th, respectively) on the spin reorientation phenomena in $Er_{2-x}R_xFe_{14}B$ (R = Gd, Th).

Experimental

Materials preparation and experimental details are described in [7]. The ^{57}Fe Mössbauer transmission

spectra were recorded in the temperature range 80–330 K for R = Gd and 50–340 K for R = Th. In case of DSC method, the Gd-compounds have been studied in the temperature range 170–370 K and the Th-compounds in 100–370 K range. The scanning rates were selected from 10 to 100 K/min for heating and cooling cycles of measurements.

Results and discussion

The "exponential" approximation [1] of the transmission integral and a simultaneous fitting of several spectra was applied (as in [7]) to describe the investigated Mössbauer spectra and obtain consistent fits. For temperatures outside the transition region, the Mössbauer spectra were analysed using six Zeeman subspectra with relative intensities in agreement with iron occupation of crystallographic sublattices (4:4:2:2:1:1). For temperatures inside the region of reorientation, each subspectrum splits into two parts.

All subspectra were characterised by the following hyperfine interaction parameters: magnetic field, B; isomer shift, IS; quadrupole splitting, QS (defined as $[(V_5 - V_6) - (V_2 - V_1)]/2$ where V_i are the velocities corresponding to Mössbauer line positions). It is significant that spectra below spin reorientation region (described by "low temperature" Zeeman sextets) and above (described by "high temperature" Zeeman sextets) have different values of B and QS. There is a coexistence of the "low" and "high temperature" Zeeman sextets in the region of reorientation. Both kinds of Zeeman sextets exchange gradually (between themselves) their contributions C_l, C_h to the total spectrum. From the temperature dependence of the contributions of both "low" and "high temperature" Zeeman sextets (C_l, C_h), the T_{SR} (corresponding to reorientation of half the number of spins) was derived for $Er_{2-x}Gd_xFe_{14}B$ and $Er_{2-x}Th_xFe_{14}B$ (x = 0.5). For $Er_{2-x}Th_xFe_{14}B$ (x = 1.0, 1.5) compounds a two-stage character of the transitions was evidenced and the $T_{SR1,2}$ were taken as the temperature corresponding to reorientation of half the number of spins on a given stage of reorientation. Figure 1 shows the temperature dependencies of subspectra contributions for C_l – "low temperature" (solid triangle) and C_h – "high temperature" (open triangle) Zeeman sextets for $Er_{1.0}R_{1.0}Fe_{14}B$ (R = Gd, Th). The spin reorientation temperatures obtained with this method are given in Table 1. It was found that the substitution of Gd and Th for Er causes the decrease of the spin reorientation temperature and the reduction of planar anisotropy range.

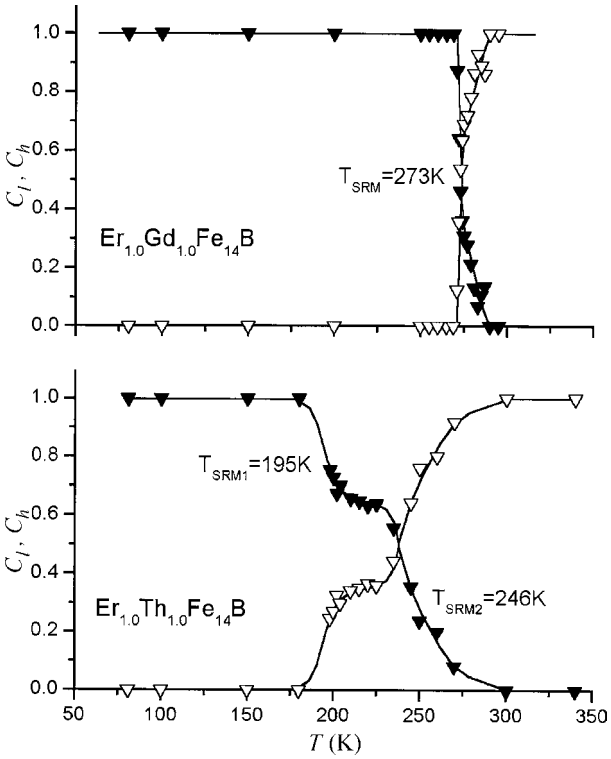

Fig. 1. The temperature dependencies of subspectra contributions for C_l – "low temperature" (solid triangle) and C_h – "high temperature" (open triangle) Zeeman sextets for $Er_{1.0}R_{1.0}Fe_{14}B$ (R = Gd, Th).

In the DSC studies, the endo- and exothermic curves were observed only for the compounds with Gd and for $Er_{1.5}Th_{0.5}Fe_{14}B$. For other compositions, no conclusive results were obtained (the signal was too weak, the maxima were spread out). The spin reorientation temperatures derived from this methods T_{SRC}, were taken as the arithmetic average of temperatures obtained for heating and cooling cycles. The values of T_{SR} determined from DSC measurements are given in Table 1. This method also confirmed that spin reorientation phenomena is a two-stage process for

Table 1. Values of the spin reorientation temperatures for $Er_{2-x}Th_xFe_{14}B$ and $Er_{2-x}Gd_xFe_{14}B$: $T_{SRM1,2}$ – from Mössbauer studies, $T_{SRC1,2}$ – from DSC, ΔH – transformation enthalpy, T_C – Curie temperature, T_{SRM} and T_{SRC} error is ±1 K, ΔH error is ± 0.03 J·g^{-1}, ΔT_C error is ±1 K

Series	x	T_{SRM1} (K)	T_{SRM2} (K)	T_{SRC1} (K)	T_{SRC2} (K)	ΔH (J·g^{-1})	T_C [6, 7] (K)
$Er_{2-x}Gd_xFe14B$	0.5	306	–	302	–	0.22	582
	1.0	273	–	270	–	0.14	603
	1.5	220	–	211	–	0.08	634
$Er_{2-x}Th_xFe14B$	0.0 [8]	324	–	–	–	0.32	559
	0.5	281	281	290	300	0.14	540
	1.0	195	246	–	–	–	526
	1.5	86	145	–	–	–	510
	2.0	–	–	–	–	–	481

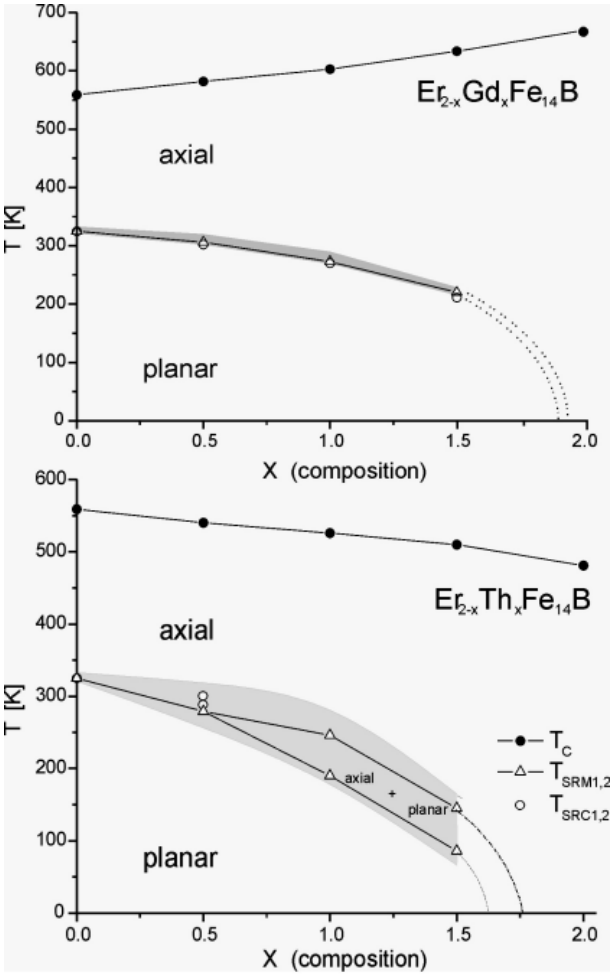

Fig. 2. Spin structure phase diagrams for the $Er_{2-x}Gd_xFe_{14}B$ and $Er_{2-x}Th_xFe_{14}B$ compounds. T_C – Curie temperature, T_{SRM}, T_{SRC} – spin reorientation temperatures determined from Mössbauer and DSC, respectively. The shaded area marks the coexistence of axial and planar arrangements. Dotted lines mark the probable area of coexistence of planar and axial spin arrangements.

Th-based compounds. The area under the DSC peak is defined as the transformation enthalpy, ΔH. It was obtained as the arithmetic average of enthalpies for the cooling and heating cycles (Table 1).

Figure 2 shows the magnetic phase diagrams for the $Er_{2-x}Gd_xFe_{14}B$ and $Er_{2-x}Th_xFe_{14}B$ systems. The Th-substituted systems show a much wider temperature range of spin reorientation process as compared to Gd-substituted system, which may be connected with the two-stage character of this process. Such character of this process is now under study.

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