Mössbauer and calorimetric studies of spin reorientation processes in $Er_{2-x}Pr_xFe_{14}C$.

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Abstract. The $Er_{2-x}Pr_xFe_{14}C$ (x = 0.25, 0.5) polycrystalline compounds have been synthesized and investigated by means of X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and Differential Scanning Calorimetry (DSC). The influence of carbon on the spin reorientation phenomena with increasing praseodymium content was of special interest in these compounds. Investigations of spin reorientation phenomena were performed by means of ^{57}Fe Mössbauer spectroscopy with a narrow step temperature scanning in the neighborhood of the spin reorientation temperature. Obtained Mössbauer spectra were analyzed using a procedure of simultaneous fitting and the transmission integral approach. Consistent description of Mössbauer spectra were obtained. 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 revealed weak thermal effect (heat absorption) during the transition process. Heat absorption was detected only for the compound with the lowest content of Pr (x = 0.25). The results obtained with different methods were analyzed and data were compared with those for $Er_{2-x}Pr_xFe_{14}B$ series. The spin arrangement diagram was constructed.

1. Introduction

Compared with $R_2Fe_{14}B$ – where R stands for rare-earth, carbides $R_2Fe_{14}C$ are known to be less stable and having somewhat lower Curie temperature. However, higher anisotropy field of carbides as well as fact that carbon doesn't have negative influence on health and environment during processing, made $R_2Fe_{14}C$ compounds worthy of investigations. We have made an attempt to synthesize 2-14-1 phase, substituting heavy rare earth Er with light one – Pr.

$Er_{2-x}Pr_xFe_{14}C$ (x = 0.25, 0.5) compound belongs to $Nd_2Fe_{14}B$ structure type, with a tetragonal crystal lattice of the $P4_2/mmm$ space group with 68 atoms in elementary cell, where Fe atoms occupy six different positions denoted: $16k_1$, $16k_2$, $8j_1$, $8j_2$, 4e, 4c; rare earth atoms locate themselves at 4f and 4g positions; and carbon atom at 4g position [1]. Planar anisotropy of rare earth sublattices has stronger temperature dependences than axial anisotropy of iron sublattice. Due to the weak coupling between sublattices in comparison with coupling within the particular sublattice and a competition between planar and axial tendency in rare earth and Fe sublattice [2, 3], the direction of easy magnetization changes from planar (in basal plane) to axial (along the *c*-axis) with increasing temperature. This phenomenon, called spin reorientation phenomenon, was studied previously for different borides and for few carbide compounds prepared by different techniques [4-11]. For $R_2Fe_{14}B$ compound spin reorientation phenomenon was confirmed by neutron diffraction investigations on single crystals [12]. Similar change of magnetic structure with increasing temperature (axis/plane)

takes place also in $Er_{2-x}Fe_{14+2x}Si_3$ compounds [13] with $P6_3/mmc$ structure type due to different exchange interactions in various sublattices.

The spin reorientation temperature, T_{SR}, determines the onset of axial anisotropy region and it is sensitive to the Pr content in the sample.

The main goal of this work was to synthesize $Er_{2-x}Pr_xFe_{14}C$ carbides and study the influence of carbon on the spin reorientation phenomena in substitutions R = Pr – using [57]Fe Mössbauer spectroscopy and Differential Scanning Calorimetry methods. Additional tasks were: to establish spin structure phase diagram, to investigate influence of spin reorientation process on hyperfine interaction parameters and to compare this process with the reorientation process in borides of the same composition.

2. Experimental methods

The $Er_{2-x}Pr_xFe_{14}C$ alloys were prepared by arc melting stoichiometric proportions of the pure starting materials under protective argon atmosphere followed by annealing at 900 °C for two weeks and then rapid cooling in water to room temperature.

X-ray diffraction analysis was performed at room temperature on randomly oriented powdered samples with the use of Cu-radiation. Data were analyzed by using Rietveld method implemented within the Fullprof program. Apart from the main phase ($R_2Fe_{14}C$), X-ray data exhibited a small amount of natural iron impurity in the samples (up to 5%). Additionally, small amount (up to 2%) of other rare earth containing phase was detected. Iron impurity patterns were consequently subtracted from the experimental spectra by the numerical procedure.

For Mössbauer investigations, samples were prepared in the form of thin layer of powdered material. There is a random distribution of orientations of magnetic moments for polycrystalline material, so – in a thin absorber approximation – it would give 3:2:1 ratio for line intensities in a single Zeeman pattern.

The Mössbauer spectra were recorded in the temperature range 80–330 K, with 5 K step in the vicinity of reorientation temperature T_{SR}, using a [57]Co (Rh) source and a computer driven constant acceleration mode spectrometer. The velocity scale was calibrated with a high purity iron foil. Isomer shift was established with respect to the center of the room temperature iron Mössbauer spectrum.

DSC (Differential Scanning Calorimetry) measurements were performed on the calorimeter Pyris 1. Measurement procedure for all compounds was repeated several times in the temperature range 100-373 K, with different scanning rates (100 K/min – 10 K/min) for heating and cooling cycles.

3. Results and discussion

3.1. Mössbauer spectroscopy method.

Elementary cell for the $R_2Fe_{14}C$ compounds is smaller than in the case of borides of the same composition, due to smaller size of carbon atoms. In case of larger Pr ion replacing Er ion on its crystallographic position, lattice parameters increase in both carbides and borides (Fig. 1, Table 1).

A large number of spectra in the temperature region 80-340 K was obtained by performing [57]Fe Mössbauer measurements with a narrow step temperature scanning in the neighborhood of the spin reorientation temperature. Similar like in our previous studies [14,15], obtained spectra were analysed by fitting six Zeeman subspectra according to six iron occupations of the crystallographic sublattices, using "exponential" approximation [16] of the transmission integral, which takes into account the influence of sample thickness on the ratio of line intensities in Mössbauer spectrum. According to the assumption that inside the temperature region of reorientation some part of magnetic moments already switch to axial arrangement, and some part still remains in (a-b) plane, each Zeeman sextet splits into two subspectra in the transition region, which gives twelve Zeeman sextets in the whole spectrum. These sextets, called "low" and the "high temperature" subspectra, are related to planar and axial magnetic arrangements, respectively.

Each subspectrum was characterized by the three hyperfine interaction parameters: isomer shift – IS, quadrupole splitting – QS, define as $[(v_6 - v_5) - (v_2 - v_1)]/4$, where v_i are velocities corresponding to Mössbauer line positions, and hyperfine magnetic field – B. One common set of three line widths was used for all Zeeman subspectra. A procedure of simultaneous fitting of several spectra with interconnected parameters was applied in order to get a consistent description of spectra throughout the series.

Exemplary spectra are presented in Fig. 2. The spectra at the top and the bottom of the figure are related to the planar and axial spin arrangements, respectively. They were described with six Zeeman sextets with relative intensities taken as 4:4:2:2:1:1, according to iron occupations of the crystallographic sublattices. The intermediate spectra described with twelve Zeeman sextets, including "low" and "high temperature" components, are related to the region of changing magnetic structure. The separation of the sixth line of $8j_2$ "high temperature" sextet from other lines in a spectrum allows to establish precisely its contributions to the spectrum and to estimate the stage of reorientation process. During the transition, "low" and "high temperature" Zeeman sextets exchange gradually (between themselves) their contributions C_l, C_h to the total spectrum, $(C_l + C_h = 1)$. Spin reorientation temperature, T_{SR}, is taken as intersection points of C_l and C_h curves (Fig. 3).

A common linear temperature dependence of IS caused by second order Doppler shift effect was assumed for all sextets (Fig.4), whereas for quadrupole splitting QS and hyperfine magnetic field B there is a shift in the values of temperature dependencies between "low" and "high temperature" Zeeman sextets (Fig.5-6). As quadrupole splitting QS is related to the angle between the easy axis of magnetization and the electric field gradient direction [17], its temperature dependence is very weak (Fig.5). For all iron sites the values of QS parameters increase during the transition process (plane-axis) and the largest values of QS before and after reorientation belong to $8j_2$ sublattice. The values of hyperfine field B have temperature dependences of square polynomial character, and they decrease with the increase in temperature (Fig.6). During the transition process parameters B increase their values only for the $8j_2$ and 4e iron sites. The largest value of B after reorientation belongs to $8j_2$ sublattice.

3.2. Differential Scanning Calorimetry (DSC) method.

Considering thermal effects, which may accompany the process of change in magnetic structure [14], a number of DSC measurements were performed in the temperature range 100-373 K, with different scanning rates (100 K/min – 10 K/min) for heating and cooling cycles of measurements. With increasing scanning rate up to 100K/min for the sample with the lowest content of Pr x=0.25, we observed a peak on the endothermic curve, corresponding to the heat absorption during the reorientation process (Fig.7). Hence, reorientation temperature for this compound was estimated as 283 K, which is 20 degrees higher than the result obtained from Mössbauer measurements, however there is a relatively large error in determining ($\Delta T = \pm 10$ K) arising from broad peak shape. The area under the DSC peak, defined as the transformation enthalpy $\Delta H = 0.302 \pm 0.05$ J/g, is close to the value, obtained for the $Er_2Fe_{14}C$ compound [14]. Measurements performed on other compounds with different scanning rates didn't give any significant results, similar as in the case of boron compounds [15]. Apparently, substitution Er with even small amount of Pr change the character of reorientation process reducing strongly calorimetric effects, making them undetectable.

3.3. Conclusions.

The reorientation temperatures obtained for the series with different methods are listed in Table 1. Fig.8 shows the partial magnetic phase diagram for the studied $Er_{2-x}Pr_xFe_{14}C$ series. Spin reorientation temperature separates axial magnetic arrangement area, dominating in high temperatures, from planar arrangement, taking place in low temperature. Pr substitution influences strongly the reorientation temperature, shifting it to the lower values and making the reorientation region broader.

In the case of sample $Er_{2-x}Pr_xFe_{14}C$ with x = 0.5, the obtained value of T_{SR} is higher than in the case of boride of the same composition, contrary to expectations.

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Tables and figures.

x, Pr	$a,(\text{Å})$	$c,(\text{Å})$	T_{SRM} (K)	T_{SRC} (K)	T_{SRM} (K), boron compounds
0	8,740	11,788	316	313	324
0.25	8,749	11,813	263	283	269
0.5	8,755	11,838	224	-	167

Table 1.

Values of the lattice parameters and spin reorientation temperatures for $Er_{2-x}Pr_xFe_{14}C$ compounds: T_{SRM} – determined from Mössbauer measurements, T_{SRM} – from calorimetric studies. Values for compound with x = 0 are taken from [8], values for boron compounds are taken from [11]. T_{SRM} error is ± 2 K.
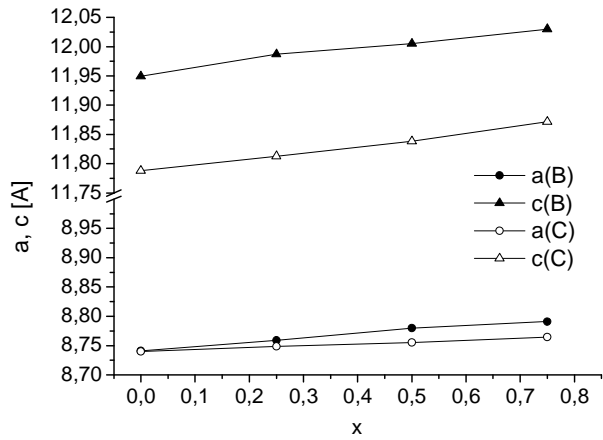
Fig. 1. The composition dependencies of lattice parameters for $Er_{2-x}Pr_xFe_{14}C$ and $Er_{2-x}Pr_xFe_{14}B$ compounds. a(C) and c(C) are lattice parameters for the carbides and a(B) and c(B) – for borides, taken from [11].
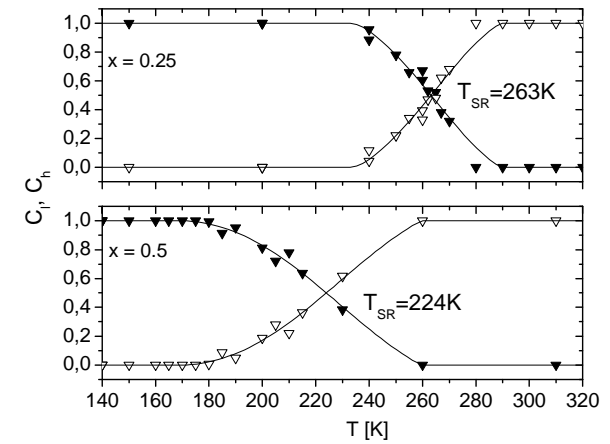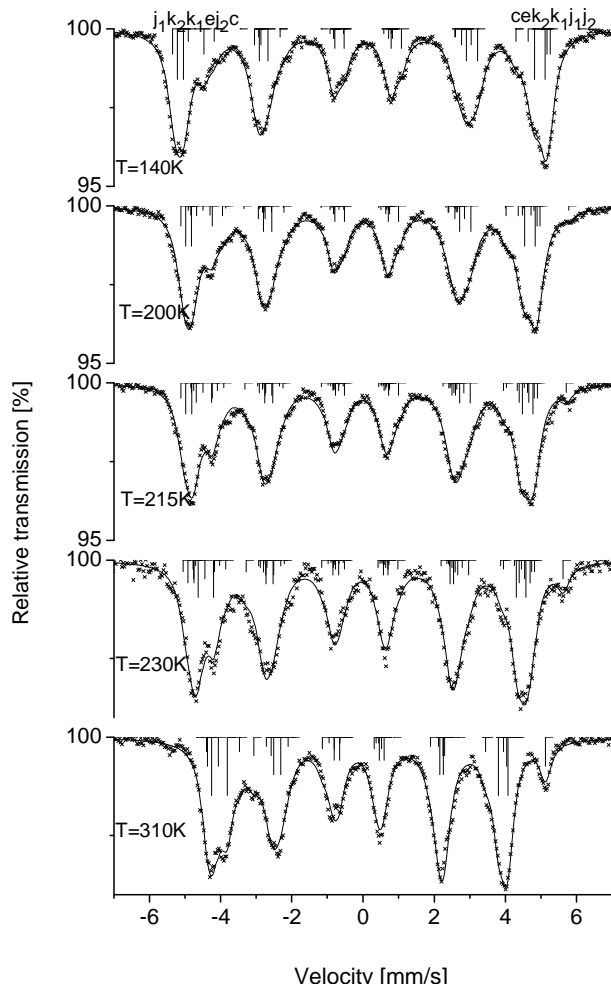

Fig. 3. The temperature dependences of subspectra contributions for C_l – "low temperature" (solid triangle) and C_h – "high temperature" (open triangle) Zeeman sextets for the samples x = 0.25, 0.5.

Fig.2. The selected experimental ^{57}Fe Mossbauer spectra of $Er_{2-x}Pr_xFe_{14}C$, x = 0.5 compound. The solid lines are fits to the data. The stick diagrams show the line positions and their relative intensities.
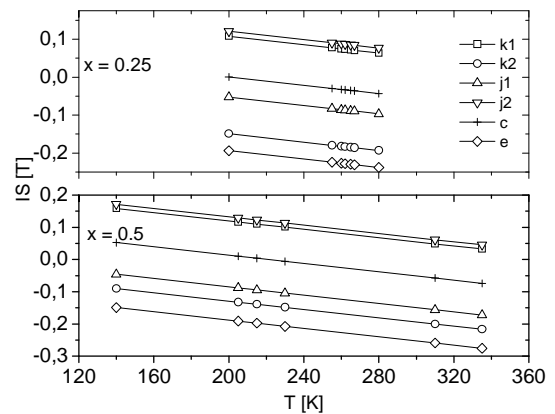
Fig. 4. The temperature dependences of the isomer shift IS for different crystal sites of $Er_{2-x}Pr_xFe_{14}C$.
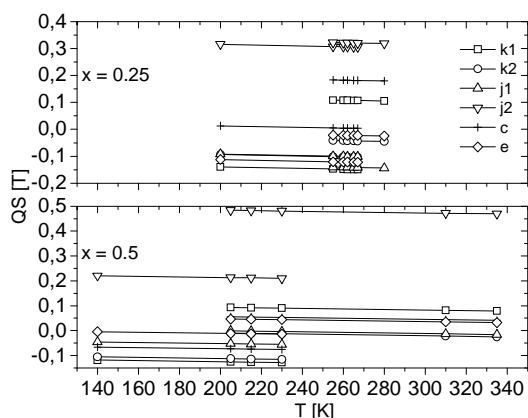
Fig.5. The temperature dependences of the quadrupole splitting QS for different crystal sites of $Er_{2-x}Pr_xFe_{14}C$.

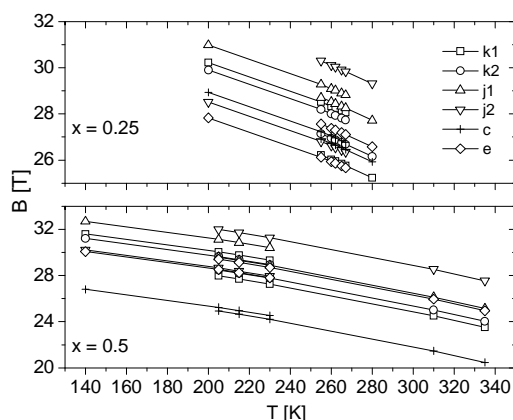Fig.6. The temperature dependences of the hyperfine field B for different crystal sites of $Er_{2-x}Pr_xFe_{14}C$
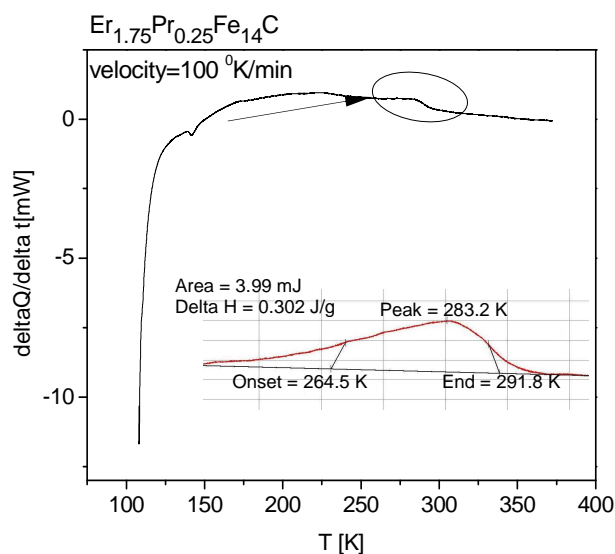

Fig. 7. Endothermic curve for the $Er_{1.17}Pr_{0.25}Fe_{14}C$ compound. Peak corresponds to the heat absorption of sample during the transition process. Measurements performed on heating with the rate of 100 K/min.
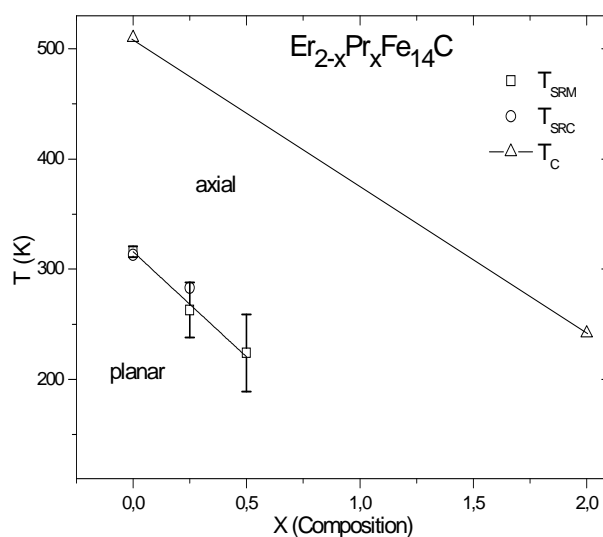

Fig. 8. Partial spin structure phase diagram for the $Er_{2-x}Pr_x Fe_{14}C$ compounds. T_C — Curie temperature, T_{SRM}, T_{SRC} —spin reorientation temperatures determined from Mössbauer and calorimetric measurements, respectively. Solid vertical lines (not error bars) mark area of the coexistence of axial and planar arrangements. The value of Curie temperature for $Pr_2Fe_{14}C$ compound is taken from [11].