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**Author:** A.T. Pędziwiatr, K. Krawiec, B.F. Bogacz, Cz. Kapusta, J. Przewoźnik, D. Kaczorowski, Ewa Talik

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# Influence of Carbon on Spin Reorientation Processes in $\text{Er}_{2-x}\text{R}_x\text{Fe}_{14}\text{C}$ ( $\text{R} = \text{Gd}, \text{Pr}$ ) — Mössbauer and Magnetometric Studies

A.T. PĘDZIWIATR<sup>a</sup>, K. KRAWIEC<sup>a</sup>, B.F. BOGACZ<sup>a</sup>, CZ. KAPUSTA<sup>b</sup>, J. PRZEWOŹNIK<sup>b</sup>,  
D. KACZOROWSKI<sup>c</sup> AND E. TALIK<sup>d</sup>

<sup>a</sup>M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland

<sup>b</sup>AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

<sup>c</sup>W. Trzebiatowski Institute for Low Temperature and Structure Research, Polish Academy of Sciences  
Okólna 2, 50-950 Wrocław, Poland

<sup>d</sup>A. Chełkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

The  $\text{Er}_{2-x}\text{R}_x\text{Fe}_{14}\text{C}$  ( $\text{R}=\text{Gd}, \text{Pr}$ ) polycrystalline compounds have been synthesized and investigated with <sup>57</sup>Fe Mössbauer spectroscopy and magnetic measurements. The spin reorientation phenomena were studied extensively by 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 and composition dependencies of hyperfine interaction parameters and subspectra contributions were derived from fits and the transition temperatures were determined for all the compounds studied. Initial magnetization versus temperature measurements (in zero and non-zero external field) for  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  compounds allowed to establish the temperature regions of reorientation, change of magnetization value during the transition process. The results obtained with different methods were analyzed and the spin arrangement diagrams were constructed. Data obtained for  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  were compared with those for  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{B}$  series.

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## 1. Introduction.

Since the discovery of unique magnetic properties of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  permanent magnets, a great number of studies were devoted to  $\text{R}_2\text{Fe}_{14}\text{B}$  compounds, where R is a rare-earth [1–7]. Less attention was put on carbides  $\text{R}_2\text{Fe}_{14}\text{C}$ , which are known to be less stable than borides. However, higher anisotropy field of carbides as well as fact that carbon doesn't have negative influence on health and environment during processing, made  $\text{R}_2\text{Fe}_{14}\text{C}$  compounds worthy of investigations.

Similar to  $\text{Er}_2\text{Fe}_{14}\text{C}$  compound [8],  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  and  $\text{Er}_{2-x}\text{Pr}_x\text{Fe}_{14}\text{C}$  have 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<sub>1</sub>, 16k<sub>2</sub>, 8j<sub>1</sub>, 8j<sub>2</sub>, 4e, 4c; rare earth atoms locate themselves at 4f and 4g positions; and carbon atom at 4g position. Planar anisotropy of rare earth sublattices has stronger temperature dependences than axial anisotropy of iron sublattice. Gadolinium or praseodymium atoms replace Er atoms on 4f and 4g sites and weaken rare earth anisotropy. 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, the direction of

easy magnetization changes from planar (in basal plane) to axial (along the *c*-axis) with increasing temperature.

The spin reorientation temperature,  $T_{SR}$ , determines the onset of axial anisotropy region, and it is sensitive to the R-content ( $\text{R}=\text{Gd}, \text{Pr}$ ) in the sample.

The spin reorientation phenomenon in  $\text{R}_2\text{Fe}_{14}\text{B}$  compounds was confirmed by neutron diffraction investigations on single crystals [9]. It was studied previously for different rare earth ions [1–2] in borides and for few carbide compounds  $\text{R}=\text{Nd}, \text{Er}, \text{Gd}$ . Also, change of magnetic structure with increasing temperature (axis/plane) takes place in  $\text{Er}_{2-x}\text{Fe}_{14+2x}\text{Si}_3$  compound [10] with  $P6_3/mmc$  structure type.

The main goal of this work was to synthesize the carbides and study the influence of carbon on the spin reorientation phenomena in substitutions  $\text{R}=\text{Gd}, \text{Pr}$  — using <sup>57</sup>Fe Mössbauer spectroscopy and magnetic measurements. Additional tasks were: to get a consistent description of Mössbauer spectra in the whole range of temperatures and to establish spin structure phase diagram for the  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  compounds.

We also investigated the influence of spin reorientation process on hyperfine interaction parameters and compared this process in  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  and  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{B}$  compounds.

## 2. Experimental methods

The samples  $Er_{2-x}R_xFe_{14}C$  ( $R=Gd, Pr$ ) were prepared by means of induction or arc melting stoichiometric proportions of the starting materials in a high purity argon atmosphere followed by annealing in quartz ampoules at 900 °C for two weeks and then rapid cooling in water to room temperature.

X-ray diffraction analysis performed at room temperature on randomly oriented powdered samples with the use of Cu-radiation exhibit a small amount of natural iron impurity in the samples (the worst case was 10%). The amount of iron impurity has a tendency to increase with increasing Gd amount in the sample. These impurity patterns were subtracted from the experimental spectra by the numerical procedure.

The absorbers for Mössbauer investigations, were prepared in the form of thin layer of powdered material. As for the polycrystalline material the distribution of orientation of magnetic moments is random, so there is no preferential orientation of powder sample, and it would give 3:2:1 ratio for line intensities in a single Zeeman pattern for a thin absorber.

The Mössbauer spectra of  $Er_{2-x}Gd_xFe_{14}C$  were recorded in the temperature range 80–330 K, with 2 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.

Magnetic measurements were performed on Physical Property Measurement System (PPMS) device on  $Er_{2-x}Gd_xFe_{14}C$  compounds by recording magnetization versus temperature,  $M$  versus  $T$ , curves in zero and non-zero external magnetic field. Reorientation temperatures  $T_{SR}$ , change of magnetization value during the transition process in the sample were determined from these measurements.

## 3. Results and discussion

For the  $Er_{2-x}Gd_xFe_{14}C$  ( $x = 0.25, 0.5, 1.5, 2$ ) and  $Er_{2-x}Pr_xFe_{14}C$  ( $x = 0.25$ ) a large number of spectra was obtained by  $^{57}Fe$  Mössbauer spectroscopy method in regions below, above and during the transitions. All spectra were analysed by fitting six Zeeman subspectra according to six iron occupations of the crystallographic sublattices, using “exponential” approximation [11] of the transmission integral, which takes into account the influence of sample thickness on the ratio of line intensities in Mössbauer spectrum.

Each subspectrum was characterized by the three hyperfine interaction parameters: isomer shift ( $IS$ ), quadrupole splitting ( $QS$ ), define as  $[(v_6 - v_5) - (v_2 - v_1)]/2$ , 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, similar to previous studies [8, 12], was applied in order to get a consistent description of spectra throughout the series.

Exemplary spectra are presented in Fig. 1. The spectra at the top and the bottom of the figure are related to the planar and axial spin arrangements, respectively. The spectra below and above the transition process were described with six Zeeman sextets called “low” and “high temperature”, respectively with relative intensities according to iron occupations of the crystallographic sublattices (4:4:2:2:1:1).

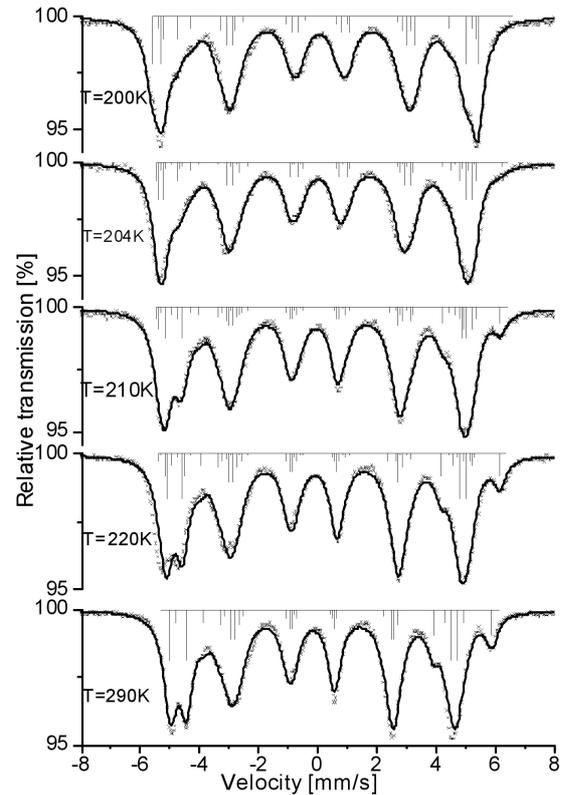


Fig. 1. The selected experimental  $^{57}Fe$  Mössbauer spectra of  $Er_{2-x}Gd_xFe_{14}C$ ,  $x = 1.5$  intermetallic compound. The solid lines are fits to the data. The stick diagrams show the line positions and their relative intensities.

The intermediate spectra were measured inside the spin reorientation region, where a coexistence of the “low” and the “high temperature” Zeeman subspectra was assumed, and described with twelve Zeeman sextets in the spectrum. During the transition, these “low” and “high temperature” Zeeman sextets exchange gradually (between themselves) their contributions  $C_l$ ,  $C_h$  to the total spectrum, ( $C_l + C_h = 1$ ). The separation of the sixth line of  $8j_2$  sublattice from other lines in “high temperature” spectra allow us to establish precisely those contributions to the spectrum and to determine the spin reorientation temperature from Mössbauer studies,  $T_{SRM}$ , taken as intersection points of  $C_l$  and  $C_h$  curves (Fig. 2).

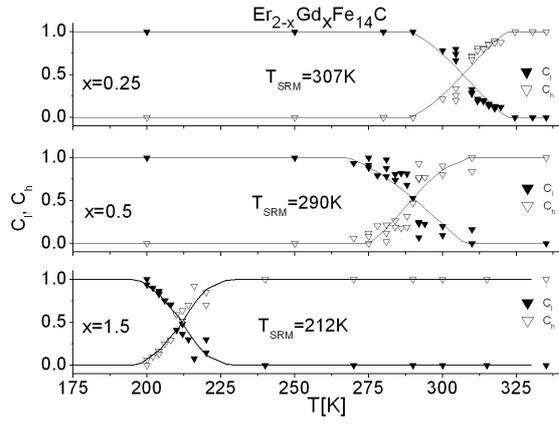


Fig. 2. The temperature dependencies of subspectra contributions for  $C_l$  — low temperature (solid triangle) and  $C_h$  — high temperature (open triangle) Zeeman sextets for  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$ .

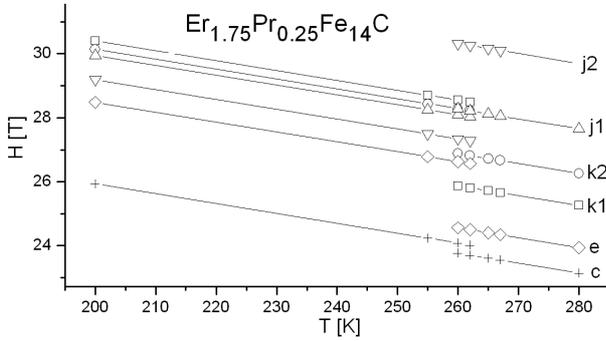


Fig. 3. The temperature dependencies of the hyperfine fields,  $B$ , for different crystal sites of  $\text{Er}_{1.75}\text{Pr}_{0.25}\text{Fe}_{14}\text{C}$ . The average error is 0.1 T.

A common linear temperature dependence of  $IS$  caused by second order Doppler shift effect was assumed for “low” and “high temperature” Zeeman sextets. The systematic changes with temperature of  $QS$  (linear) and  $B$  (square polynomial) were taken into account. Figure 3 shows the temperature dependencies of the hyperfine fields for the  $\text{Er}_{1.75}\text{Pr}_{0.25}\text{Fe}_{14}\text{C}$  system. The value of  $B$  for subspectrum  $8j_2$  is the largest because this sublattice has the largest number of Fe ions in its nearest neighbourhood. For all sublattices the hyperfine field decreases with the increase in temperature.

Quadrupole splitting is related to the angle between the easy axis of magnetization and the electric field gradient direction [13]. The  $QS$  values are different for “high” and “low temperature” sextets and almost independent of temperature.

Magnetization curves obtained at low external magnetic field for solid polycrystalline  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  pieces exhibited some anomalies in the vicinity of reorientations. This enabled the estimation of the spin reorientation temperature,  $T_{SRH}$ , which was taken as an inflection point

of the descending portion of curve [12]. Changes of magnetization value during the transition process in the samples were determined from magnetization measurements at high external magnetic field (see Table).

TABLE

Values of the spin reorientation temperatures for  $\text{Er}_{2-x}\text{R}_x\text{Fe}_{14}\text{C}$  ( $\text{R}=\text{Gd}, \text{Pr}$ ) compounds:  $T_{SRH}$  — from magnetic measurements,  $T_{SRM}$  — from Mössbauer studies,  $\Delta M$  — change of magnetization value.

$x$ , Gd	$T_{SRH}$ [K]	$T_{SRM}$ [K]	$\Delta M$ [ $\text{emu}/\text{cm}^3$ ]	$T_{SRM}$ [K], boron compounds
0	—	316	—	325
0.25	306	307	144	—
0.5	299	290	183	306
1.5	211	212	23	220
$x$ , Pr				
0.25	—	267	—	269

$T_{SRH}$  error is  $\pm 2$  K,  $T_{SRM}$  and  $T_{SRM}$  error is  $\pm 2$  K,  $\Delta M$  error is  $\pm 5$   $\text{emu}/\text{cm}^3$ .

The reorientation temperatures obtained for the series are listed in Table. The values of reorientation temperature obtained with different methods for the carbide series are approximately 10 K lower than those for corresponding borides.

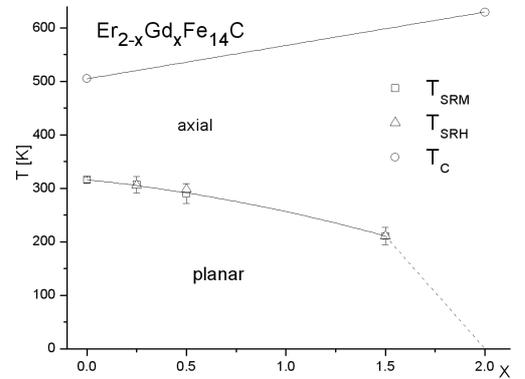


Fig. 4. Spin structure phase diagram for the  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$  compounds.  $T_{SRM}$  — spin reorientation temperature determined from Mössbauer measurements,  $T_{SRH}$  — spin reorientation temperature determined from magnetic measurements.  $T_C$  — Curie temperature [1]. Dotted line — hypothetical line to guide the eye. Vertical solid lines refer to the temperature range of reorientation process.

Figure 4 shows the magnetic phase diagram for the  $\text{Er}_{2-x}\text{Gd}_x\text{Fe}_{14}\text{C}$ . The values of spin reorientation temperatures obtained with different methods show a good agreement for all compounds studied. The increasing content of gadolinium results in a decrease of the value

of  $T_{SR}$  temperature as well as Curie temperature. Substitution of boron by carbon in the compounds mentioned above, retains the region of axial spin arrangement approximately the same, but moves it to lower temperatures. Significant difficulty is the preparation of single-phase carbide samples.

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