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Experimental studies of spin reorientations in $Er_{2-x}Pr_xFe_{14}B$

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Abstract

^{57}Fe Mössbauer spectroscopy, x-ray diffraction and magnetic measurements have been used to study the polycrystalline $Er_{2-x}Pr_xFe_{14}B$ ($x = 0.25, 0.5, 0.75, 1.0, 1.5$) compounds. Special emphasis was put on the spin reorientation phenomena (change of spin orientation from planar to axial arrangement) occurring in this series. The spin reorientation in each compound has been investigated mainly by means of narrow step temperature scanning in the neighbourhood of the spin reorientation temperature, T_{SR}.

Initial magnetization versus temperature measurements allowed us to establish the temperature regions of reorientations and also the Curie temperatures of the compounds.

Mössbauer temperature scanning was performed with a step of 2 K in the vicinity of T_{SR}. The spectra obtained were analysed by using a procedure of simultaneous fitting and the transmission integral approach. Consistent fits were obtained; T_{SR} and the composition dependences of hyperfine interaction parameters were derived from fits for all compounds studied.

The T_{SR} values obtained with both methods were compared and the spin phase diagram for the series was constructed.

1. Introduction

The intermetallic compounds based on $Er_2Fe_{14}B$ have a tetragonal crystal lattice with the $P4_2/mnm$ space group and belong to the $Nd_2Fe_{14}B$ structure type, in which there are two non-equivalent positions of Nd ions (4f and 4g), six positions of Fe ions ($16k_1$, $16k_2$, $8j_1$, $8j_2$, 4e, 4c) whereas the boron atom is located at one type of site (4g) [1].

From the point of view of fundamental studies, one of the most interesting properties of the Er-based 2:14:1 intermetallic compounds is the spin reorientation occurring in these

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compounds. In this process the direction of easy magnetization vector is changing at the reorientation temperature, T_{SR}, from planar (in basal plane) to axial (along the c axis) with increasing temperature. This is the result of a competition between axial and planar tendencies in Fe and Er [2, 3] sublattice. This phenomenon was studied previously by different groups for Gd, Th, Ce, Nd, Ho, Er, Tm [4–11]. The study via single crystal neutron diffraction of $Er_2Fe_{14}B$ revealed that there is a change of crystal structure to orthorhombic below the spin reorientation transition [12].

The main goal of this work was to study the effect of competing anisotropies of the two rare earth ions (Er and Pr ions have opposite signs of the Stevens factor) on the spin reorientation phenomena in $Er_{2-x}Pr_xFe_{14}B$ using ^{57}Fe Mössbauer spectroscopy and magnetic measurements. An additional goal was to propose a consistent description of complex Mössbauer spectra over the whole range of temperatures.

2. Experimental details

The samples of $Er_{2-x}Pr_xFe_{14}B$ ($x = 0.25, 0.5, 0.75, 1.0, 1.5$) were prepared by means of induction melting stoichiometric proportions of the starting materials in a high purity argon atmosphere followed by annealing them at 900 °C for two weeks and then rapidly cooling them to room temperature.

X-ray, thermomagnetic analysis (TMA) and metallographical microscopy indicated the single phase character of the materials. X-ray diffraction analysis was performed at room temperature on randomly oriented powdered samples with the use of Cr radiation. Lattice parameter refinement was conducted by a computer procedure based on Cohen's method. TMA was performed by recording magnetization versus temperature, M versus T, curves at low external magnetic field with the use of a Faraday-type magnetic balance. The Curie temperatures, T_C, were also determined from those measurements.

Mössbauer spectra of $Er_{2-x}Pr_xFe_{14}B$ were recorded in the temperature range 18–340 K (with a 2 K step in the vicinity of T_{SR}) using a ^{57}Co (Rh) source and a computer driven constant acceleration mode spectrometer. The velocity scale was calibrated by a high purity iron foil. Isomer shifts were established with respect to the centre of gravity of the room temperature iron Mössbauer spectrum.

3. Results and discussion

The lattice constants of the $Er_{2-x}Pr_xFe_{14}B$ series are given in table 1. A continuous increase of lattice parameters a and c is evidenced while the larger Pr ion is gradually replacing the Er ion in the crystal lattice.

The magnetization curves obtained at low external magnetic field for coarse grained materials exhibited some anomalies in the vicinity of reorientations (see figure 1). The significant decrease in the $M(T)$ curves in the vicinity of T_{SR} is due to imperfect alignment of polycrystalline coarse grains. In addition, in T_{SR} there is a change of magnetization direction causing a 'step' or a 'spike' on the $M(T)$ curve (depending on the relation between the K_1 and K_2 anisotropy constants) [13]. The 'step' in the $M(T)$ curve enabled the estimation of temperature ranges of the transitions and the approximate determination of the spin reorientation temperatures, T_{SRH}. They were taken as inflection points of the descending portion of the curve, following the procedure described in [13].

The values of T_{SRH} are listed in table 1, showing a gradual decrease with increasing Pr content. The Curie temperatures obtained from M versus T curves for the series are also listed in table 1. They differ by 12 K between the end members of the series.

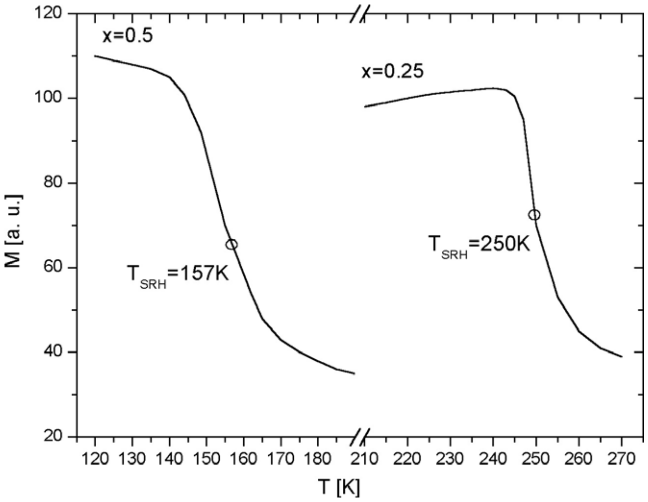

Figure 1. Examples of irregularities in magnetization versus temperature curves evidenced in the vicinity of spin reorientations for $Er_{2-x}Pr_xFe_{14}B$ ($x = 0.5, 0.25$).

Table 1. Lattice parameters for $Er_{2-x}Pr_xFe_{14}B$ (room temperature) and values of the spin reorientation temperatures: T_{SRH}—from magnetic measurements, T_{SRM}—from Mössbauer studies, T_C—Curie temperature. The T_{SRH} error is ±2 K, T_{SRM} error is ±1 K, T_C error is ±2 K, a and c error is ±0.001 Å.

x	a (Å)	c (Å)	T_{SRH} (K)	T_{SRM} (K)	T_C (K)
0.0 [14]	8.741	11.949	325	324	554
0.25	8.759	11.987	250	269	557
0.5	8.780	12.005	157	167	559
0.75	8.791	12.030	37	36	561
1.0	8.799	12.076	—	—	563
1.5	8.812	12.165	—	—	564
2.0 [15]	8.814	12.253	—	—	566

A large number of ^{57}Fe Mössbauer effect spectra for $Er_{2-x}Pr_xFe_{14}B$ were measured in regions below, above and during the transitions. The Mössbauer spectra were analysed with a transmission integral approach [16]. Each subspectrum was characterized by the three hyperfine interaction parameters: isomer shift—IS, hyperfine magnetic field—B, and quadrupole splitting—QS (defined as $[(V_6 - V_5) - (V_2 - V_1)]2^{-1}$, where V_i are velocities corresponding to Mössbauer line positions). One common set of three linewidths 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, similarly to in our previous studies [11, 14]. Exemplary spectra are presented in figure 2. The spectrum at the top of figure was recorded at a temperature below the spin reorientation, whereas the bottom one was obtained far above the transition process; the three intermediate spectra were measured at temperatures inside the spin reorientation region. The spectra below and above the temperature region of spin reorientation were described using six Zeeman subspectra, called, 'low temperature' and 'high temperature' Zeeman subspectra, respectively, with relative intensities according to the iron occupation of the crystallographic

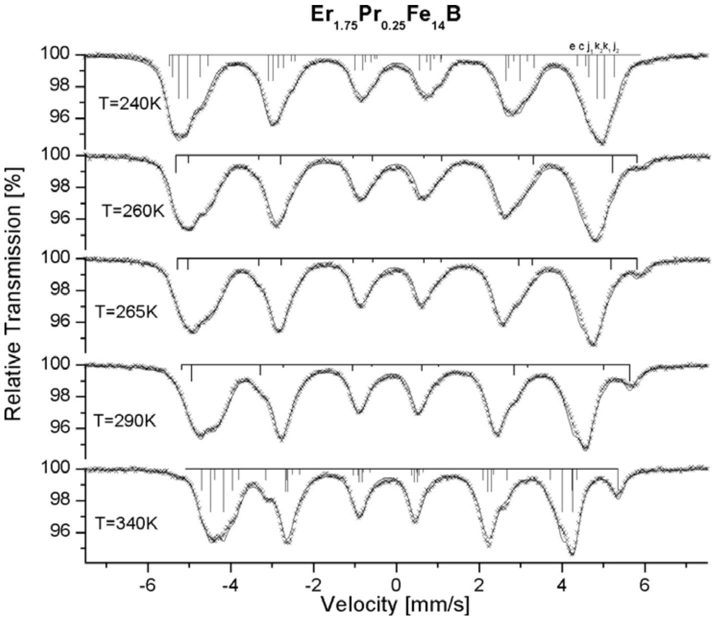

Figure 2. Selected experimental ^{57}Fe Mössbauer spectra of $Er_{2-x}Pr_xFe_{14}B$, $x = 0.25$ intermetallic compound. The solid lines are fits to the data. The stick diagrams show the line positions and their relative intensities. Inside the region of spin reorientation, for clarity of presentation, only the positions of lines of the $8j_2$ sublattice are marked.

sublattices (4:4:2:2:1:1). Inside the temperature region of spin transition a coexistence of the 'low temperature' and the 'high temperature' Zeeman subspectra was assumed, which, in consequence, gave twelve Zeeman sextets in the spectrum. This assumption was chosen as giving the best results out of many attempts at fitting the spectra using different configurations of Zeeman subspectra and is supported by the analysis of fitting procedure for similar (Gd-substituted) compounds [11]. In figure 2 for clarity of presentation, inside the transition region, only the positions of $8j_2$ sublattice lines were marked. In the course of transition, the 'low temperature' 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 clear separation of the sixth line of the sublattice $8j_2$ in the spectra (see figure 2) makes it easier to estimate those contributions and to determine the spin reorientation temperature from Mössbauer studies, T_{SRM}, taken as intersection points of C_l and C_h curves (see figure 3). It was found that the substitution of Pr for Er causes a decrease of the spin reorientation temperature and a reduction of the planar anisotropy range.

A common linear temperature dependence of IS caused by the second order Doppler shift effect was assumed for 'low temperature' and 'high temperature' Zeeman sextets (see figure 4). The systematic changes with temperature of QS (linear) and B (square polynomial) were taken into account. Also the possibility of a shift of these dependences between 'low temperature' and 'high temperature' Zeeman sextets was assumed. Figure 5 shows the temperature dependences of the hyperfine fields for the $8j_2$ sublattice of the $Er_{2-x}Pr_xFe_{14}B$ system. In order to present clearly the behaviour of B in the reorientation region, the values are shown for one only sublattice. The value of B for subspectrum $8j_2$ is the largest because this sublattice has the largest number of Fe ions in its nearest vicinity [17]. For all sublattices the hyperfine field

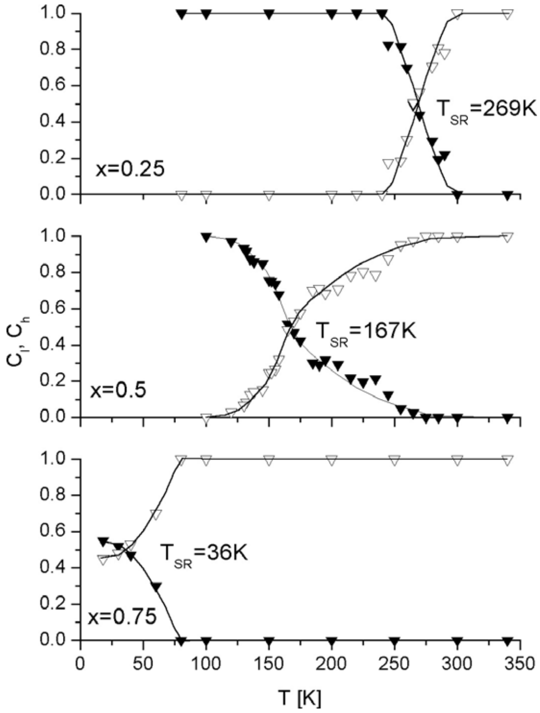

Figure 3. The temperature dependences of subspectrum contributions for C_l—'low temperature' (solid triangle) and C_h—'high temperature' (open triangle) Zeeman sextets for $Er_{2-x}Pr_xFe_{14}B$.

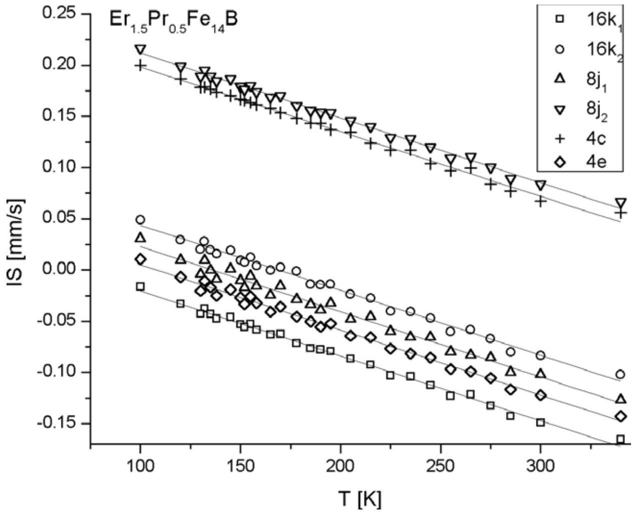

Figure 4. The temperature dependence of IS for different crystal sites of $Er_{1.5}Pr_{0.5}Fe_{14}B$. The average error is 0.01 mm s^{-1}.

decreases with the increase in temperature. A splitting of each Zeeman subspectrum into two components in the region of the transition is visible.

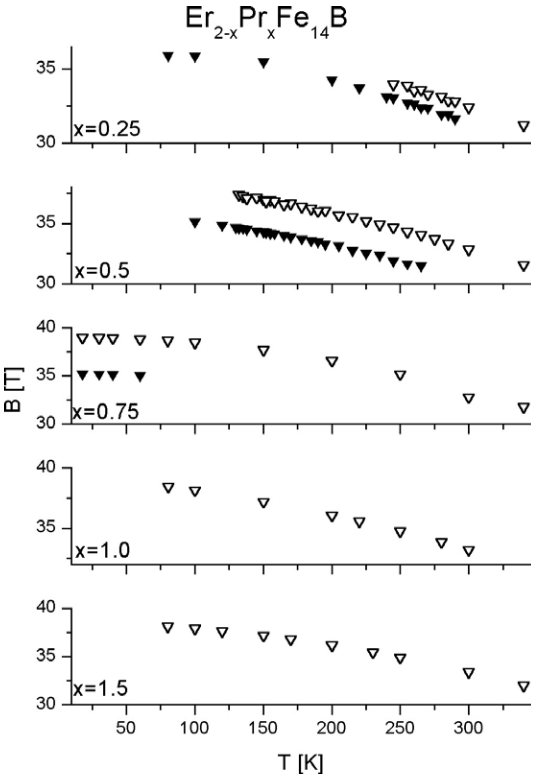

Figure 5. The temperature dependences of the hyperfine field, B, for $8j_2$ crystal sites of $Er_{2-x}Pr_xFe_{14}B$ ('low temperature'—solid triangle, 'high temperature'—open triangle). The average error is 0.1 T.

The behaviour of QS is connected with the change of angle between the easy axis of magnetization and the electric field gradient [18]. In the process of reorientation the magnetization vector changes its orientation from planar to an axial (c axis) direction (90°), but the change of angle between the magnetization vector and the V_{zz} axis of the electric field gradient (EFG) may be quite different. It depends on the orientation of V_{zz} with respect to the crystallographic axes which is different for each sublattice [19]. The experimental temperature behaviour of QS for the $8j_2$ sublattice is shown in figure 6. For the quadrupole splitting the temperature dependence is very weak, but the values of QS change visibly in the reorientation process; they are different for 'high temperature' and 'low temperature' sextets. Analogous changes of QS values for other sublattices are also observed.

Figure 7 shows the magnetic phase diagram for the system studied. It is visible that the increasing content of Pr results in a decrease of the value of the spin reorientation temperature and—as a consequence—the range of axial anisotropy becomes larger. For each composition, the axial spin arrangement dominates at high temperatures while a planar arrangement is present at lower temperature. The values of spin reorientation temperatures obtained with different methods (Mössbauer spectroscopy and magnetic measurements) show a reasonably good agreement for all compounds studied. The region of coexistence of axial and planar arrangements, which results from Mössbauer measurements, is marked by a shaded area in figure 7. The concept of conical arrangements of spins in the shaded region [20] was not confirmed by Mössbauer results. One can note that Pr substitution has a much stronger

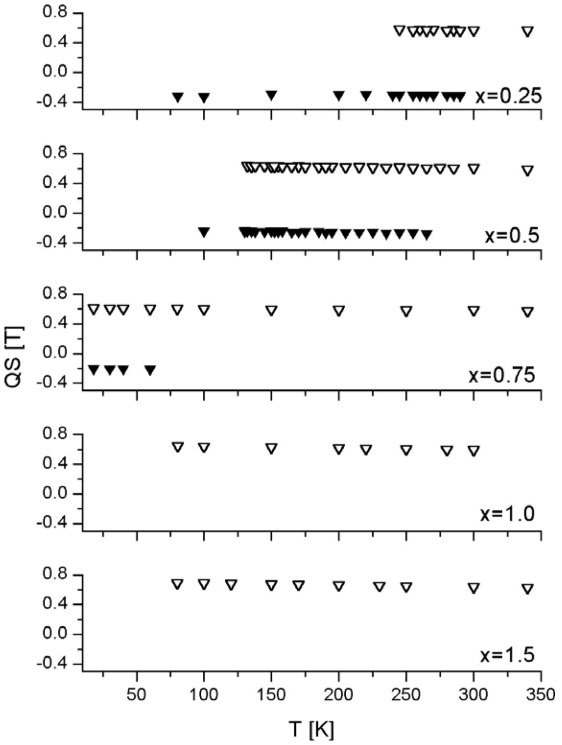

Figure 6. The temperature dependences of the quadrupole splitting, QS, for $8j_2$ crystal sites of $Er_{2-x}Pr_xFe_{14}B$ ('low temperature'—solid triangle, 'high temperature'—open triangle). The average error is 0.01 mm s^{-1}.

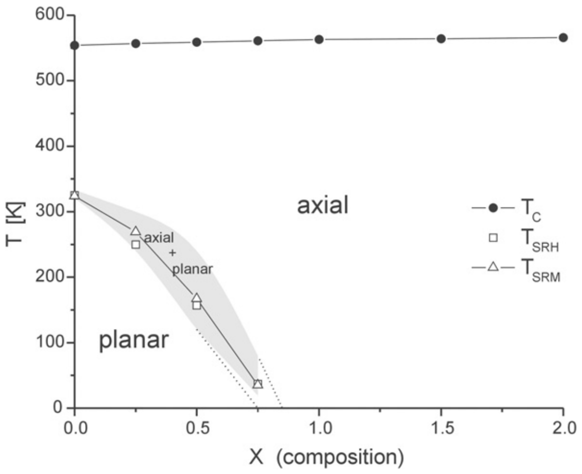

Figure 7. Spin structure phase diagram for the $Er_{2-x}Pr_xFe_{14}B$ compounds. T_C—Curie temperature, T_{SRH}, T_{SRM}—spin reorientation temperatures determined from magnetic and Mössbauer measurements, respectively. The shaded area marks the coexistence of axial and planar arrangements. Dotted lines mark the probable area of coexistence of planar and axial spin arrangements.

influence on T_{SR} in the $Er_{2-x}R_xFe_{14}B$ system than other R ions (e.g. Gd, Y, Ce [11, 20]) which is understandable due to the strong negative value of the Stevens factor for the Pr ion.

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