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Spin reorientation studies in $Er_{2-x}Gd_xFe_{14}B$

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Abstract

^{57}Fe Mössbauer spectroscopy, differential scanning calorimetry (DSC), magnetic measurements and X-ray diffraction have been used to study the polycrystalline $Er_{2-x}Gd_xFe_{14}B$ ($x = 0.0$, 0.5, 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 narrow step temperature scanning in the neighborhood of the spin reorientation temperature, T_{SR}.

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

Mössbauer temperature scanning was performed with a step of 1 K in the vicinity of T_{SR}. The obtained spectra were analyzed by using a procedure of simultaneous fitting, and the transmission integral approach. Consistent fits were obtained, T_{SR} and the composition dependencies of hyperfine interaction parameters were derived from fits for all studied compounds.

DSC studies proved that the spin reorientations were accompanied by thermal effects. Transformation enthalpy and T_{SR} were determined from these studies.

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

Keywords: Spin reorientation; Spin phase diagrams; Mössbauer spectroscopy; Simultaneous fitting; DSC

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1. Introduction

The crystal structure of all $Er_{2-x}Gd_xFe_{14}B$ compounds is tetragonal, belonging to space group $P4_2/mnm$ [1]. The rare earth ions occupy two positions 4f and 4g, the iron atoms are spaced in six positions: $16k_1$, $16k_2$, $8j_1$, $8j_2$, 4e, 4c, whereas the boron atom is located at one type of site (4g).

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 compounds. In this process the direction of easy magnetisation vector is changing at the reorientation temperature, T_{SR}, from planar (in basal plane) to axial (along the *c*-axis) with increasing temperature. It is the result of a competition between axial and planar tendency in Fe and Er [2,3] sublattice. This phenomenon was studied previously by different groups for Y, Ce, Nd, Ho, Er, Tm [4–12]. The study by single crystal neutron diffraction on $Er_2Fe_{14}B$ revealed that there is a change of crystal structure to orthorhombic below the spin reorientation transition [13].

The main goal of this work was to study the influence of Gd substitution on the spin reorientation phenomena using ^{57}Fe Mössbauer spectroscopy, DSC and magnetic measurements and to propose a consistent description of the Mössbauer spectra in the whole range of temperatures. In addition, the thermal effects accompanying the transitions were studied quantitatively.

2. Experimental

The samples of $Er_{2-x}Gd_xFe_{14}B$ ($x = 0.0$, 0.5, 1.0, 1.5) were prepared by a standard procedure of induction melting in a high purity argon atmosphere followed by annealing at 900 °C for 2 weeks. X-ray, thermomagnetic analysis (TMA)

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Table 1
Lattice parameters for $Er_{2-x}Gd_xFe_{14}B$

x	a (Å)	c (Å)
0.0	8.748	11.969
0.5	8.770	11.990
1.0	8.782	12.031
1.5	8.785	12.069
2.0	8.790	12.075

and metallographical microscopy confirmed 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 $Er_{2-x}Gd_xFe_{14}B$ were recorded in the temperature range 80–320 K 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.

In case of DSC method, the $Er_{2-x}Gd_xFe_{14}B$ compounds have been investigated in the temperature range 170–370 K by differential scanning calorimetry Pyris 1. The scanning rates were selected from 10 to 60 K/min for heating and cooling cycles of measurements.

3. Results and discussion

The crystallographic data for $Er_{2-x}Gd_xFe_{14}B$ series are given in Table 1. A continuous increase of lattice parameters a and c is evidenced when the larger Gd ion is gradually replacing the Er ion in the crystal lattice.

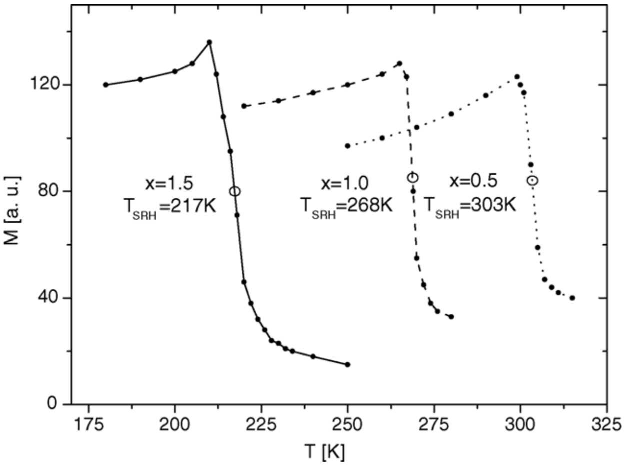

Fig. 1. Irregularities on magnetization vs. temperature curves evidenced in the vicinity of spin reorientations for $Er_{2-x}Gd_xFe_{14}B$.

Table 2
Values of the spin reorientation temperatures for $Er_{2-x}Gd_xFe_{14}B$: T_{SRH}—from magnetic measurements, T_{SRM}—from Mössbauer studies, T_{SRC}—from DSC, T_C—Curie temperature, ΔH—transformation enthalpy

x	T_{SRH} (K)	T_{SRM} (K)	T_{SRC} (K)	T_C (K)	ΔH (J/g)
0.0	325	325	326	559	0.32
0.5	303	306	302	582	0.22
1.0	268	273	270	603	0.14
1.5	217	220	211	634	0.08
2.0	–	–	–	669	–

T_{SRH} error is ±2 K, T_{SRM} and T_{SRC} error is ±1 K, ΔH error is ±0.03 J/g.

Magnetization curves obtained at low external magnetic field for rough chunks of materials exhibited some anomalies in the vicinity of reorientations (see Fig. 1) which enabled the estimation of temperature ranges of the transitions and the approximate determination of the spin reorientation temperature, T_{SRH}, which was taken as an inflection point of the descending portion of curve, following the procedure described in [14]. The values of T_{SRH} are listed in Table 2, showing a gradual decrease with increasing Gd content. The Curie temperatures obtained for the series are also listed in Table 2. They differ by 110 K between the end members of the series.

A large number of ^{57}Fe Mössbauer effect spectra for the $Er_{2-x}Gd_xFe_{14}B$ was measured in the regions: below, above and during the transitions. The Mössbauer spectra were analyzed with a transmission integral approach [15]. Each subspectrum was characterised by the three hyperfine interaction parameters: isomer shift—IS, hyperfine magnetic field—B, and quadrupole splitting—QS (defined as $[(V_6-V_7)-(V_2-V_1)]/2$, where V_i are velocities corresponding to Mössbauer line positions). One common set of three line widths was used for all Zeeman subspectra. A procedure of simultaneous fitting of several spectra with

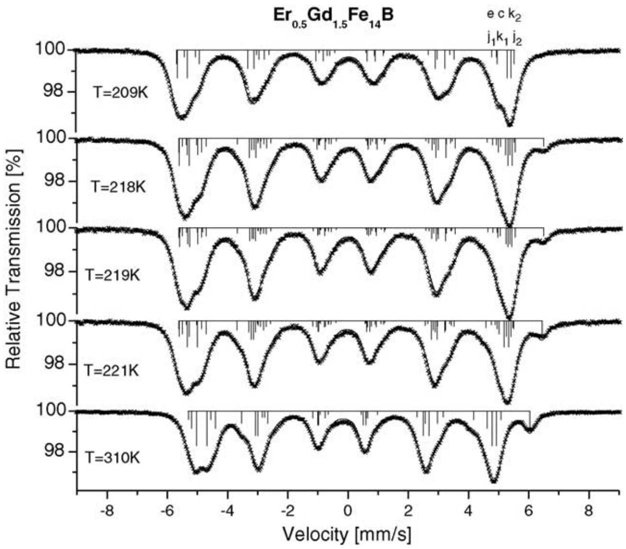

Fig. 2. The selected experimental ^{57}Fe Mössbauer spectra of $Er_{2-x}Gd_xFe_{14}B$, $x = 1.5$ intermetallic compound. The solid lines fit to the data. The stick diagrams show the line positions and their relative intensities.

interconnected parameters was applied in order to get a consistent description of spectra throughout the series, similarly as in our previous studies [12,16,17]. Exemplary spectra are presented in Fig. 2. The spectrum on the top of figure was recorded in the temperature far below the spin reorientation, whereas the bottom one was obtained far above the transition process, the three intermediate spectra were measured inside the spin reorientation region. The spectra below and above the temperature region of spin reorientation were described using six Zeeman subspectra, called "low" and "high temperature" Zeeman subspectra, respectively, with relative intensities according to iron occupation of the crystallographics sublattices (4:4:2:2:1:1). Inside the temperature region of spin transition a coexistence of the "low" and the "high temperature" Zeeman subspectra was assumed, which in consequence, gave 12 Zeeman sextets in the spectrum. This assumption was chosen as giving best results out of many attempts of fitting the spectra using different configurations of Zeeman subspectra and is supported by the analysis of fitting procedure for similar (Y- and Ce-substituted) compounds [12,17]. In the course of 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 clear separation of the sixth line of sublattice $8j_2$ in the spectra (see Fig. 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 Fig. 3). 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. Also the possibility of a shift of these dependencies between "low" and "high temperature" Zeeman sextets was assumed. Fig. 4 shows the temperature dependencies of the hyperfine fields for the $Er_{2-x}Gd_xFe_{14}B$ 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 [18]. For all sublattices the hyperfine field decreases with the increase in temperature. A splitting of each Zeeman subspectrum into two components in the region of transition is indicated. The behaviour of QS is connected with the change of angle between the easy axis of magnetisation and the electric field gradient [19]. The temperature behaviour of QS is shown in Fig. 5. The QS are almost independent of temperature, but the values of QS are different for "high" and "low temperature" sextets.

In the DS calorimetry studies the endo- and exothermic curves were obtained (Fig. 6). For all studied compounds the endothermic peaks correspond to the transition from basal to axial easy magnetization direction on increasing temperature.

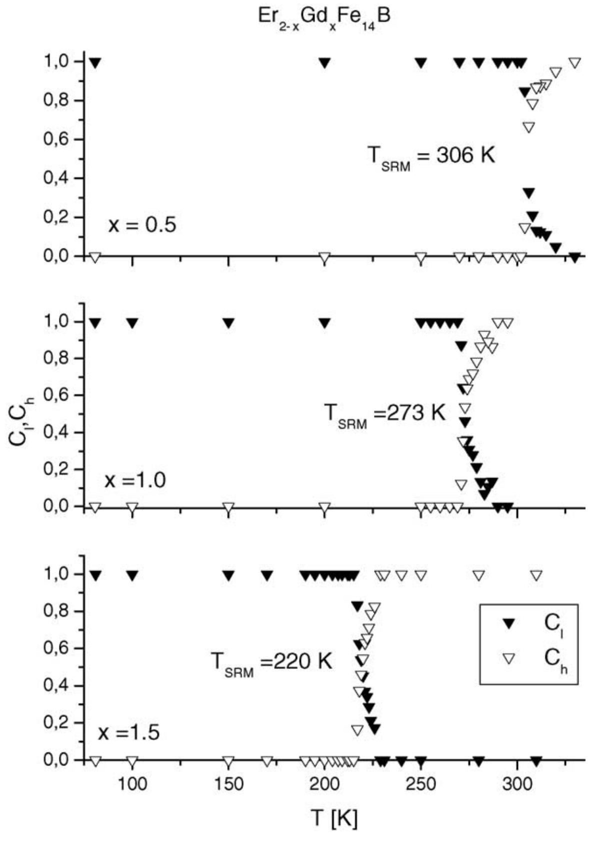

Fig. 3. The temperature dependencies of subspectra contributions for C_l—low temperature (solid triangle) and C_h—high temperature (open triangle) Zeeman sextets for $Er_{2-x}Gd_xFe_{14}B$. T_{SRM} was taken as an intersection of C_l and C_h curves.

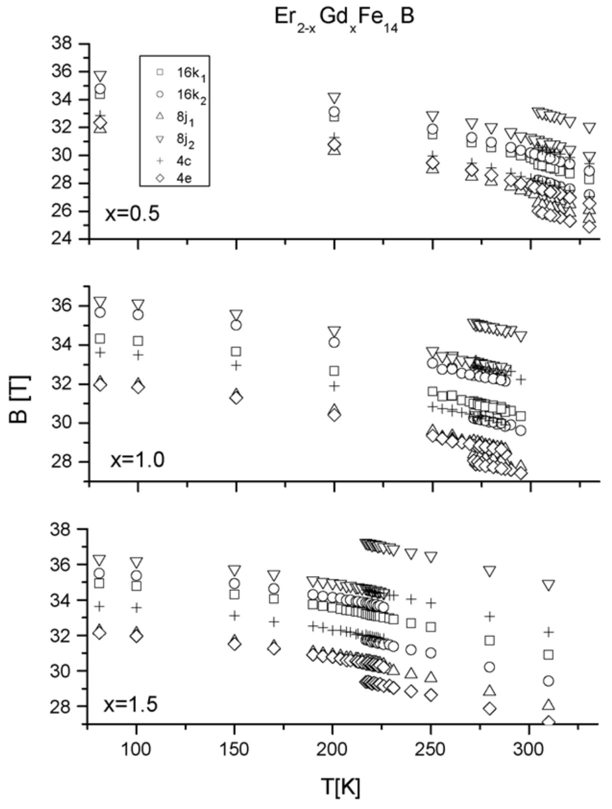

Fig. 4. The temperature dependencies of the hyperfine fields, B, for different crystal sites of $Er_{2-x}Gd_xFe_{14}B$. The average error is 0.1 T.

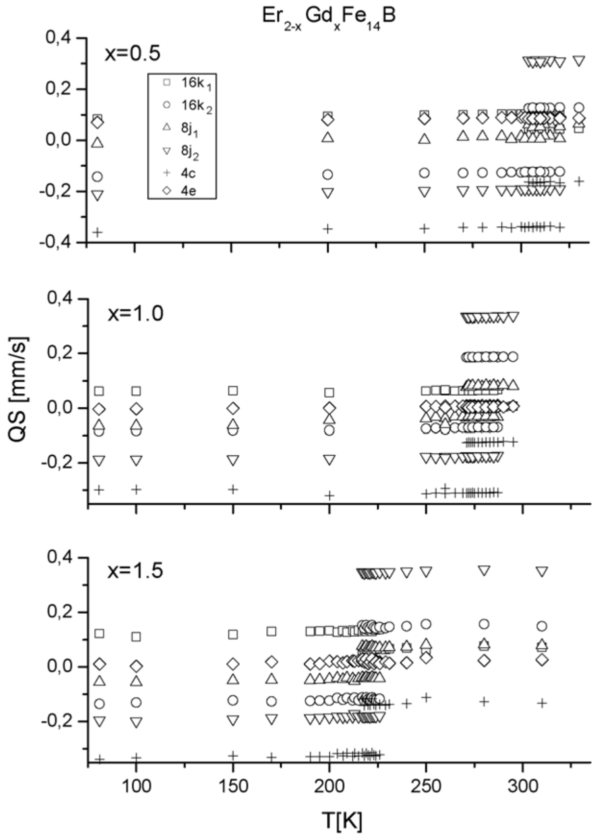

Fig. 5. The temperature dependencies of the quadrupole splitting, QS, for different crystal sites of the $Er_{2-x}Gd_xFe_{14}B$. The average error is 0.01 mm/s.

The spin reorientation temperature derived from this methods, T_{SRC}, was taken as the arithmetic average of temperatures obtained for heating and cooling cycles. The values of the spin reorientation temperatures determined from DSC measurements for all compounds studied are given in Table 2. The area under the DSC peak is defined as the transformation enthalpy, ΔH. It was obtained as the arithmetic average of entalpies for the cooling and heating cycles (Table 2). The values of the transformation enthalpy are decreasing with increasing amount of gadolinium; thermal effects become smaller.

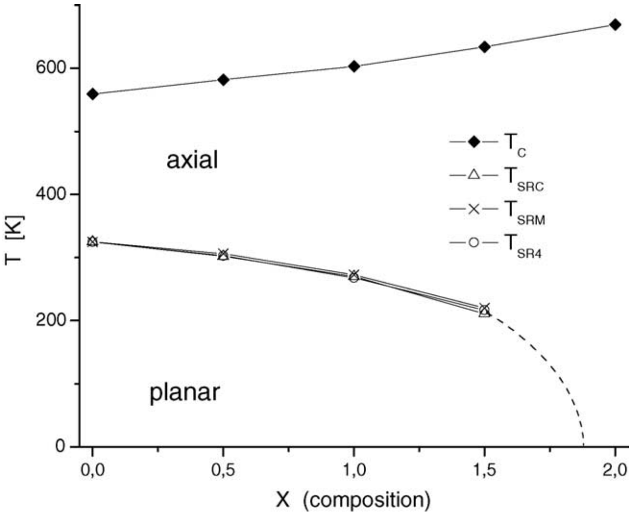

Fig. 7. Spin structure phase diagram for the $Er_{2-x}Gd_xFe_{14}B$ compounds. T_C—Curie temperature, T_{SRC}—spin reorientation temperature determined from DSC, T_{SRM}—spin reorientation temperature determined from Mössbauer measurements, T_{SRH}—spin reorientation temperature determined from magnetic measurements. Dotted line—hypothetical line to guide the eye.

Fig. 7 shows the magnetic phase diagram for the studied system. It is visible that the increasing content of gadolinium results in a decrease of the value of the spin reorientation temperature and—as a consequence—the range of axial

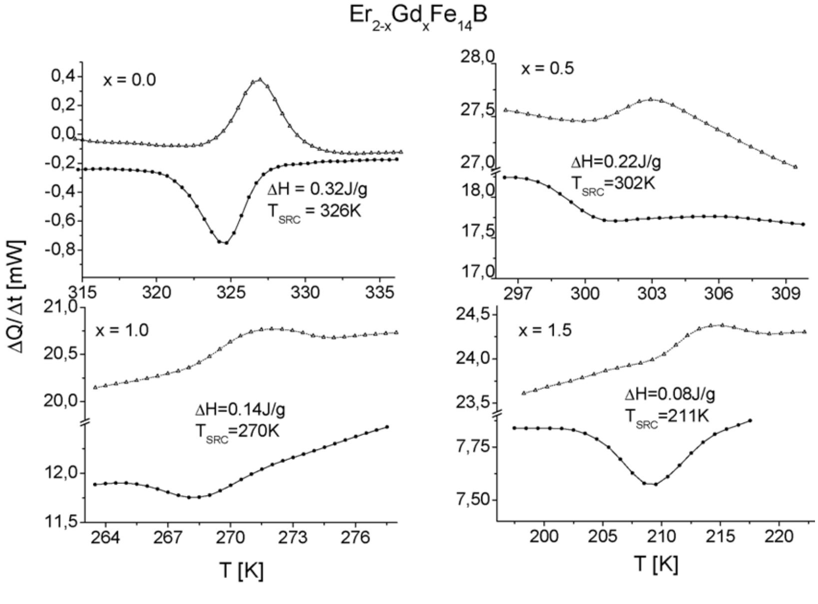

Fig. 6. Endo- and exothermic transitions due to the spin reorientations measured with DSC for the $Er_{2-x}Gd_xFe_{14}B$ system. T_{SRC} was taken as an arithmetic average of peak positions for heating (upper curves) and cooling (lower curves) cycles.

anisotropy becomes larger. For each composition, the axial spin arrangement dominates at high temperatures while planar arrangement is present at lower temperature. The values of spin reorientation temperatures obtained with different methods (Mössbauer spectroscopy, differential scanning calorimetry and magnetic measurements) show a good agreement for all compounds studied.

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