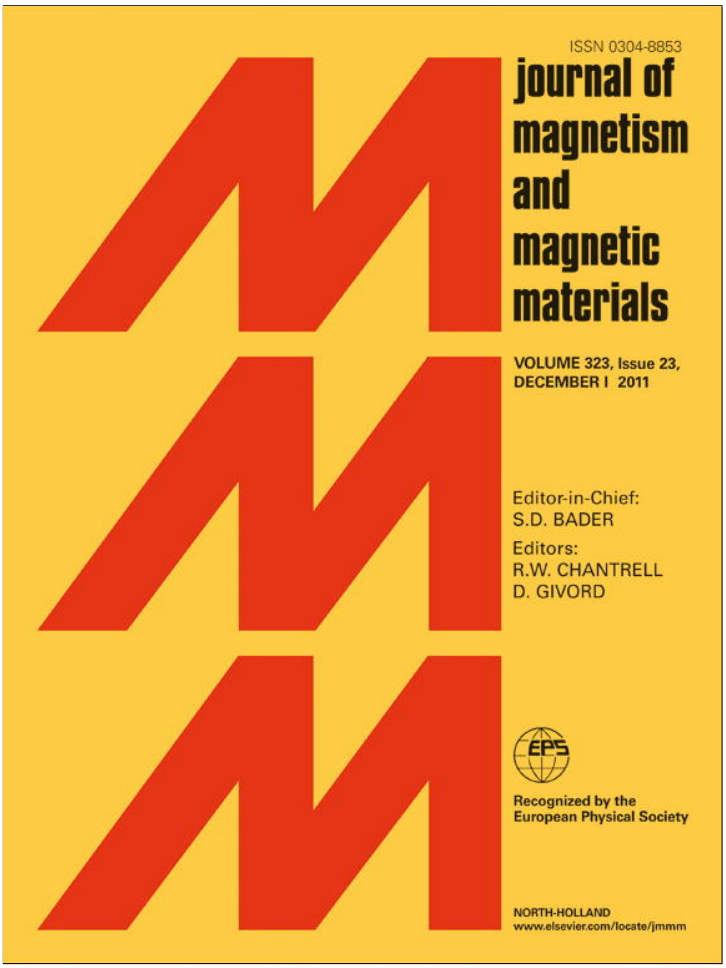

Journal of Magnetism and Magnetic Materials 323 (2011) 2968–2972

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetic structure studies of ternary borides $Er_{2-x}Ce_xFe_{14}B$

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ARTICLE INFO

Article history:
Received 25 February 2011
Received in revised form
1 June 2011
Available online 24 June 2011

Keywords:
Spin reorientation
Mössbauer spectroscopy
Magnetometry

ABSTRACT

The ternary borides $Er_{2-x}Ce_xFe_{14}B$ (x=0.25, 1, 1.5and 1.7) have been studied by means of X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and magnetic measurements in order to verify the postulated occurrence of conical arrangement of magnetic moments in the region of high Ce-composition. Character of spin reorientation phenomena was investigated by means of ^{57}Fe Mössbauer spectroscopy in the spin reorientation temperature region for polycrystalline and pseudo-single crystal samples. Obtained Mössbauer spectra were analyzed using a procedure of transmission integral. Consistent description of Mössbauer spectra was obtained. Initial magnetization versus temperature measurements (field cooled and zero-field cooled) allowed to estimate the character and temperature regions of reorientation process. The results that are obtained with different methods were compared. The obtained experimental data do not support the hypothesis of conical arrangement of magnetic moments at low temperatures for the compounds with high Ce-composition. Our results are consistent with the current model of spin reorientation in these compounds as a process where magnetic moments rapidly change their orientation from planar to axial arrangement without intermediate conical states.

1. Introduction

The $Er_{2-x}Ce_xFe_{14}B$ compounds belong to $Nd_2Fe_{14}B$ structure type and have a tetragonal crystal lattice of the $P4_2/mnm$ space group with 68 atoms in elementary cell [1]. Fe atoms occupy six positions denoted by $16k_1$, $16k_2$, $8j_1$, $8j_2$, 4eand 4c; rare earth atoms are located at 4f and 4g and boron atom at 4g position. There is a ferrimagnetic coupling between rare earth and transition metal sublattices.

Due to the competition between planar and axial tendency in rare earth and Fe sublattices [2–4], the direction of easy magnetization changes from planar (in basal plane) to axial (along the c-axis) with increasing temperature. This so-called spin reorientation phenomenon was studied previously for 2:14:1 borides and carbides [5–12]. The spin reorientation temperature, T_{SR}, determines the onset of axial anisotropy region.

In the $Er_{2-x}Ce_xFe_{14}B$ series, light Ce atoms substitute heavy Er atoms, weakening planar anisotropy of rare earth sublattices. These borides were studied before [13–16] for the wide range of Ce-content x=0–1.5.

Theoretical model of Yamada et al. [15] and Pędziwiatr et al. [17] shows a good agreement with experimental data for low Ce-content compounds, however, in the case of higher Ce-content compounds there is a divergence between the experimental data for T_{SR} and the theoretically predicted data. The model also predicts the existence of conical spin arrangement region for some of the compounds at low temperatures [17].

In the present work $Er_{2-x}Ce_xFe_{14}B$ compounds (x=0.25, 1, 1.5 and 1.7) were studied using X-ray diffraction, ^{57}Fe Mössbauer spectroscopy method and magnetic measurements. Obtained data allowed to analyze the character and stage of reorientation process in order to verify the existence of conical spin arrangement region and establish the reorientation temperature values for x=1.5, 1.7.

2. Experimental methods

The $Er_{2-x}Ce_xFe_{14}B$ alloys were prepared from stoichiometric proportions of high purity (99.9% or better) starting materials by means of induction heating in a purified argon protective atmosphere, annealing at 900 °C for 2 weeks and then rapid cooling in water to room temperature.

X-ray diffraction analysis was performed at 300 K with a D5000 Siemens diffractometer (using CuK_α radiation and a graphite secondary monochromator) on randomly oriented powdered samples. Datas were analyzed using the Rietveld method implemented within the Full proof program [18]. Apart from the main phase, ($R_2Fe_{14}B$), X-ray data exhibited a small amount of impurity phases in the samples (up to 5%).

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doi:10.1016/j.jmmm.2011.06.010

Magnetic measurements were performed for polycrystalline bulk material. The field cooled–zero-field cooled (FC–ZFC) dc magnetization values at the fields 100 Oe, as well as hysteresis loops up to 89 kOe and dc magnetization values at the field 80 kOe were measured in the temperature range 4–400 K using the vibrating sample magnetometer (VSM) option of the Quantum design physical property measurement system (PPMS).

For Mössbauer investigations, polycrystalline 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, and it would give 3:2:1 ratio for line intensities in a thin absorber approximation for a single Zeeman pattern.

A pseudo-single crystal for Mössbauer investigations was prepared for $Er_1Ce_1Fe_{14}B$ compound as a composite of paraffin and powder material, in 0.25 T external magnetic field at 313 K. There is an axial spin arrangement (along the *c*-axis) in the compound at this temperature, and individual crystallites were subjected to magnetic alignment in ordering external field, oriented perpendicular to the surface of thin layer sample. Thereafter paraffin was cooled to maintain this orientation.

The Mössbauer spectra were recorded in the temperature range 4–300 K, 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.

3. Results and discussion

3.1. Magnetic measurements

Initial magnetization versus temperature measurements (in zero and non-zero external field) were performed for the following compounds: $x=0.25$, 1, 1.5, 1.7 (Figs. 1 and 2), as well as for hysteresis loops in different temperatures before, during and after reorientation process. In the case of magnetization versus temperature measurements the shape of curves not only allowed to estimate the reorientation temperature, but also suggests that the transition in the case of high Ce-content could have plane-to-cone-to-axis character, contrary to the commonly used plane-to-axis model. The assumption is based on the curve shapes obtained for simulated transitions in [19].

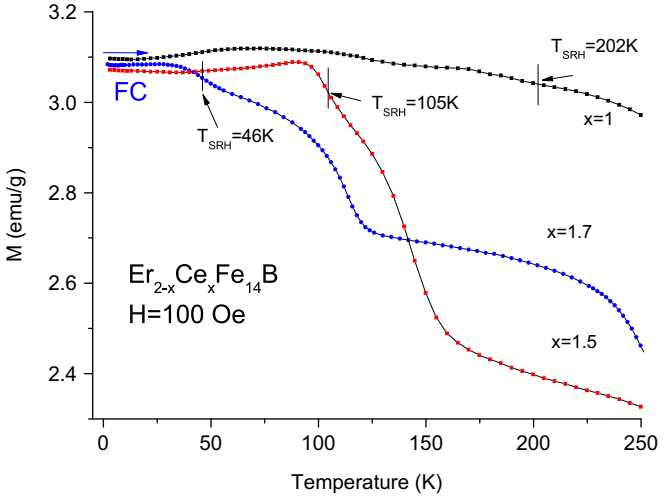

Fig. 1. Magnetization versus temperature curves with irregularities in the vicinity of spin reorientations. Plot represents data that are obtained by field cooled (FC) method for $Er_{2-x}Ce_xFe_{14}B$, $x=1$, 1.5, 1.7.

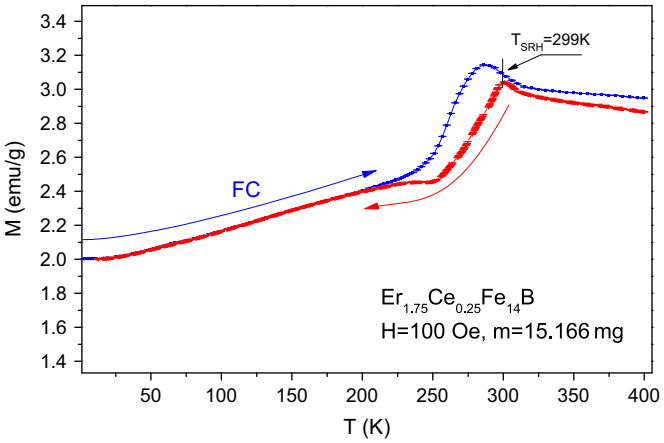

Fig. 2. Magnetization versus temperature curves with irregularities in the vicinity of spin reorientations. Plot represents data that are obtained by field cooled (FC) method for $Er_{2-x}Ce_xFe_{14}B$, $x=0.25$.

Table 1

x- Ce	a,(Å)	c,(Å)	T_{SRH} (K)	T_{SRM} (K)	T_{SRM}[a] (K)
0	8.741	11.949	–	–	324
0.25	8.7414(4)	11.9750(7)	299	–	297
1	8.7508(4)	12.0329(7)	202	201	201
1.5	8.7543(3)	12.0720(5)	105	113	–
1.7	8.7558(4)	12.0872(6)	46	<4	–

Values of the lattice parameters at 300 K and spin reorientation temperatures for $Er_{2-x}Ce_xFe_{14}B$ compounds: T_{SRH}— determined from magnetic measurements, T_{SRM}— from Mössbauer measurements. T_{SRH} error is ± 5 K.

[a] Data for the T_{SRM} are taken from [16], for the $x=0$ compound are taken from [21].

Reorientation temperatures T_{SR} were taken as a first inflection points of decreasing part of the curves. They are shown in Table 1, where one can see a good agreement with the data obtained from Mössbauer spectroscopy method.

Comparing magnetization curves for all the four compounds, one can notice that most clear and strong effect on magnetization under reorientation process reveals $x=0.25$ Ce-content sample, whereas $x=1$ one shows the lowest effect. In the case of four samples, studied magnetization is decreasing with increasing the Ce-content in low external field and has a tendency to increase in high field (Fig. 3). It could be explained by the fact that non-magnetic cerium substitute erbium atoms on their positions weaken anisotropy of rare earth sublattices. As rare earth sublattice couples ferrimagnetically with iron sublattices, resulting magnetic moment of particular crystallites increases. Thus, in high field, when the majority of magnetic moments is subjected to magnetic alignment, total magnetization increases with the Ce-content. However, in low field, due to the random orientation of crystallites in a polycrystalline material, total magnetic moment of a bulk material decreases.

The appearance of few inflection points on each of the magnetization curve, which vanish for lower content of cerium, could be explained by two-stage character of reorientation process: it could be two phase plane-to-axis-to-axis or plane-to-cone-to-axis transition with well defined intermediate "cone" state and switching of magnetic arrangement from one to another. Data obtained from Mössbauer spectroscopy measurements for the $x=1$, 1.1, 1.2, 1.3 compounds [16] do not support any of these models. Therefore, we made an attempt to verify the character of reorientation process with additional measurements by means of Mössbauer spectroscopy.

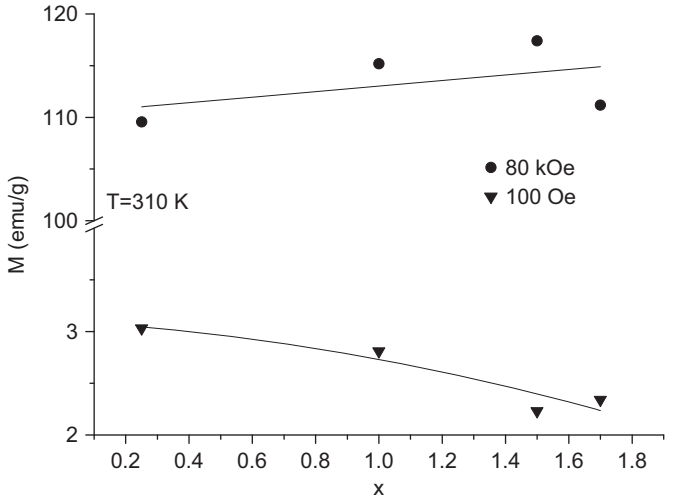

Fig. 3. Magnetization versus Ce-content curves in 100 and 80 kOe external field at 310 K for $Er_{2-x}Ce_xFe_{14}B$.

3.2. Mössbauer spectroscopy method

3.2.1. Mössbauer measurements of pseudo-single crystal

The pseudo-single crystal sample was prepared for Er_1Ce_1-$Fe_{14}B$ compound as a composite of paraffin and fine powder material and measured at 80, 180, 240 and 300 K (Fig. 4). These are temperatures below, inside and above the reorientation regions, respectively [14].

In the case of polycrystalline samples, we used to study the reorientation process by means of analyzing changes of quadrupole splitting values, specifically for sixth line of $8j_2$ sextet, which stands separately from the rest of the spectrum [14]. Pseudo-single crystal sample gives us the additional opportunity to study the reorientation process by observing changes of lines relative intensities in a sextet, which in case of single crystal are $3{:}4\sin^2\Theta/(1+\cos^2\Theta){:}1$where Θ-angle is the angle between the direction of effective field in a crystal and radiation beam—Fig. 5.

Obtained data were analyzed with the computer program, which allows to set different Θ-angles for different sextets, and as a consequence to change relative intensities of lines in a sextet. This feature will be used while analyzing complicated spectra (180 and 240 K), obtained during the transition process.

Data obtained for hyperfine parameters for all the fitted spectra are consistent (within the limit of experimental error) with those previously reported [14]. For the 300 K spectrum with the axial arrangement of magnetic moments in elementary cell, the Θ-angle is equal to zero as far as sample has easy-magnetization axis oriented along the radiation beam. Therefore, second and fifth lines of the Zeeman sextet should vanish to zero. However, it appears that there is still some non-zero intensities of these lines in the sextets and the average Θ-angle derived from the fit is equal to 29° This suggests that probably the powder grains are not small enough and some of them contain few single crystals, so grain as a whole is oriented in the direction, which is a composition of easy magnetization directions of single crystal components. Assuming that easy magnetization direction of the sample is tilted from $\Theta=29°$ from the direction of radiation beam, which is also true for the magnetic moments of all Fe atoms in the particular positions; thus, we have a model of six sextets with the same relative lines intensities inside each sextet. This model gave a good fit to the data, therefore, we accepted it for further studies.

At 80 K there is a planar arrangement of magnetic moments in elementary cell [14] and the Θ-angle between the direction of radiation beam and effective field turns to be equal to 90°.

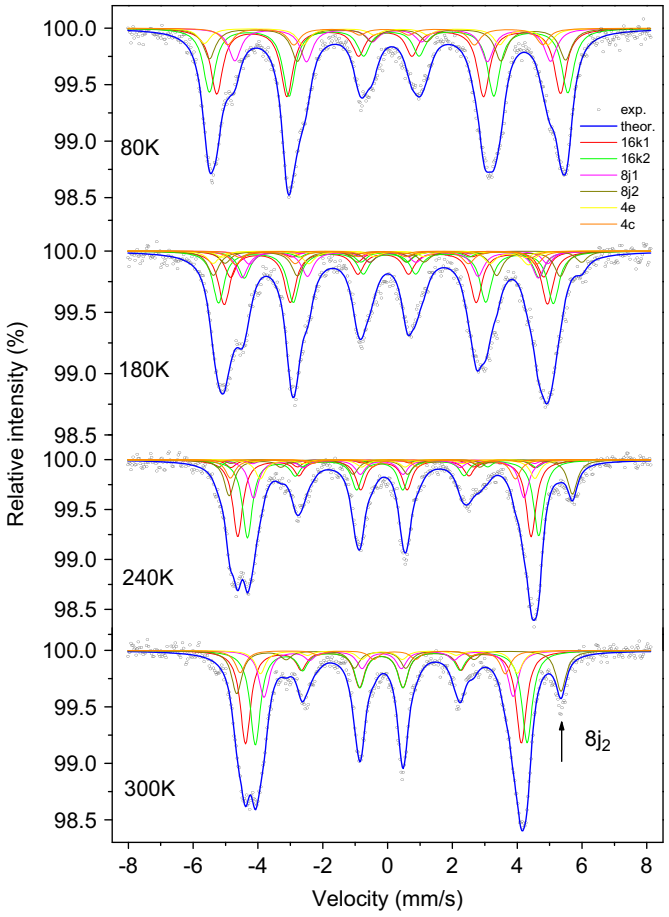

Fig. 4. The experimental ^{57}Fe Mossbauer spectra of pseudo single-crystal Er_1Ce_1-$Fe_{14}B$. Solid lines are fits to the experimental data. The sixth line of $8j_2$ "high temperature" Zeeman sextet, which stands separately from the rest of spectrum, is marked on the 300 K-spectrum.

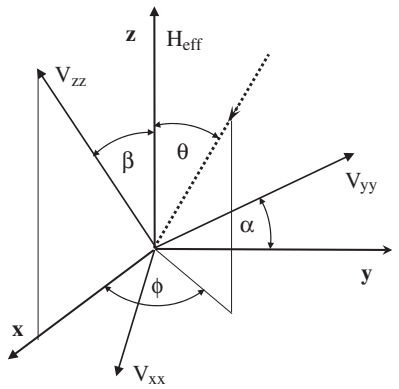

Fig. 5. Relative directions of effective field, components of electric field gradient (V_{xx}, V_{yy}, V_{zz},) and radiation beam (dotted line).The Z-axis is a quantization axis, xyz-coordinate system related to the geometry of elementary cell.

Analyzing 80 K spectrum with six sextets with the same relative intensities, it appears that the best fit was achieved for the average Θ-angle value about 119°, which refers to the cone of $\Theta=29°$ (in case of axial arrangement) rotated by 90° (Fig. 6). As it fits to our model with tilted effective field in the sample from easy magnetization direction in the case of ideal single crystal, we decided to use it in further investigations.

Two other spectra —180 and 240 K were recorded inside the reorientation temperature region, and here situation is more

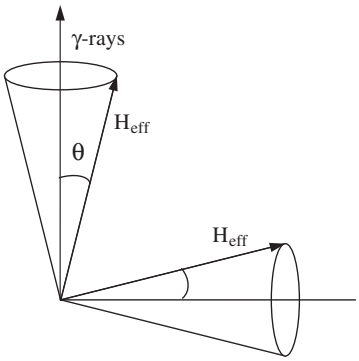

Fig. 6. Change of relative position of effective magnetic field in nucleus (located on the lateral surface of the cone) by 90° during spin reorientation.

complicated. According to the conventional assumption, that particular spins "switch" their orientation rapidly from planar to axial with increasing temperature, two groups of spins are present inside the reorientation region of the so-called "low" and "high" temperatures, related to planar and axial arrangement. Each group contributes to the resulting spectrum according to the stage of reorientation process and each could be described by six Zeeman subspectra related to six iron occupations of the crystallographic sublattices. Also each group is related to different Θ-angle and consequently, has different relative lines intensities in sextets. It gives us 12 components in the resulting spectrum—six "low temperature" and six "high temperature" sextets shown in Fig. 4 as subspectra for 80 and 300 K spectra, respectively.

The hyperfine parameters for the particular sextets taken from [14], Θ-angle was set at 29 and 119° for the "high" and "low" temperature subspectra, respectively. Transmission integral, which takes into account the influence of sample thickness on the ratio of line intensities in Mössbauer spectrum, was used for fitting. This model gives a good fit to the experimental data, and subspectra contributions C_l for "low temperature" (C_h for "high temperature") Zeeman sextets were determined: for 180 K-spectrum—$C_l=0.75$ ($C_h=0.25$); for 240 K-spectrum—$C_l=0.12$ ($C_h=0.88$), which are consistent in the error bounds with the values, reported earlier [14], and confirm the applied model.

Additional model with all the spins tilted by some angle with respect to the c-axis, and Θ-angle having an intermediate value between 29 and 119°, was applied to all the spectra with the intent ion to verify the character of reorientation process. The model gave worse fits to data compared with the conventional one.

Thus, the results that are obtained support the conventional model that the spins "switch" their orientation rapidly from planar to axial arrangement during the reorientation process, without intermediate states.

3.2.2. Low temperature Mössbauer measurements

The Mössbauer measurements were performed on polycrystalline samples for $x=1.5$,and 1.7 compounds from $Er_{2-x}Ce_xFe_{14}B$ series in the temperature region 4–200 K. These compounds have low reorientation temperature and wide reorientation region and according to the theoretical calculations [17], there is a possibility of conical spin arrangement taking place during reorientation.

Obtained spectra were analyzed using transmission integral and a procedure of simultaneous fitting of several spectra with interconnected parameters.

For both samples, the rapid separation character of sixth line of $8j_2$ sextet apart from the rest of the spectrum with a growing amplitude, proved that spins "switching" taking place also in low temperature with the same character of "switching"; no intermediate (conical) position, which would lead to the smearing of the line, was found.

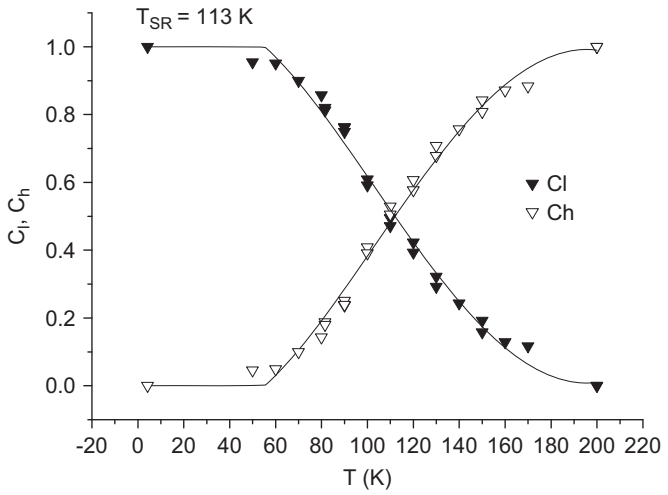

Fig. 7. The temperature dependence of subspectra contributions for C_l —"low temperature" (solid triangle) and C_h—"high temperature" (open triangle) Zeeman sextets for the samples $x=1.5$, $Er_{2-x}Ce_xFe_{14}B$.

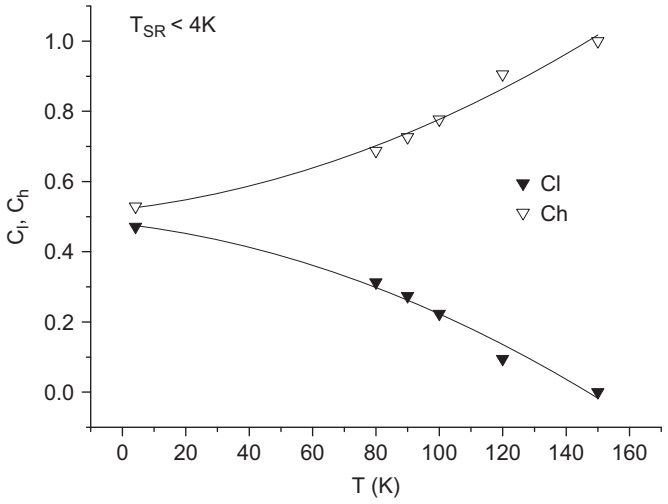

Fig. 8. The temperature dependence of subspectra contributions for C_l—"low temperature" (solid triangle) and C_h—"high temperature" (open triangle) Zeeman sextets for the sample $x=1.7$, $Er_{2-x}Ce_xFe_{14}B$.

Thus, the hypothesis of conical spin arrangement was not supported by the obtained results.

For the $x=1.5$ compound reorientation temperature was estimated as 113 K (Fig. 7, Table 1), for the $x=1.7$ reorientation temperature value is lower than 4 K (Fig. 8).

As coupling between sublattices become weaker [20] in the low temperature non-magnetic Ce atoms replace Er atoms weakening rare earth anisotropy, and exchange interaction between sublattices could become too weak to keep magnetic moments coupled.

3.3. Conclusions

The reorientation temperatures of $Er_{2-x}Ce_xFe_{14}B$ series are strongly influenced by Ce substitution, which is weakening planar anisotropy of rare earth sublattices.

Pseudo-single crystal Mössbauer measurements allow to study reorientation process by observing changes in line intensities.

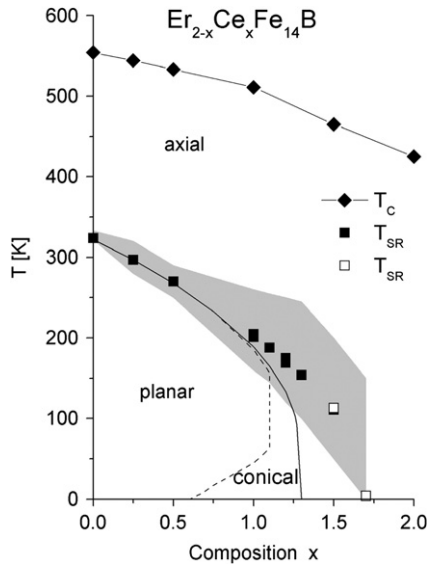

Fig. 9. Magnetic spin arrangement diagram for $Er_{2-x}Ce_xFe_{14}B$. T_C=Curie temperature, T_{SR}—spin reorientation temperatures. The solid and dashed lines represent the theoretically obtained limits of the conical spin arrangement region. The shaded area marks the experimentally estimated temperature region of transition process with the coexistence of axial and planar arrangements.

Data obtained from Mössbauer measurements prove that for the compounds studied, we can apply plane-to-axis model of spin reorientation with gradual exchange of contributions between "axial" and "planar" spins. They also do not support hypothesis of conical spin arrangement at low temperatures for high Ce-content compounds. All the results are consistent with conventional model of spin reorientation and with data obtained from previous works [16].

In case of $x=1.7$ compound with highest content of Ce, T_{SR}, if any, is lower than 4 K. Even at the lowest measurable by our equipment temperature partial axial spin arrangement is still present.

Complete spin magnetic arrangement diagram is shown in Fig. 9. Shaded area is related to the temperature region of transition process.

Acknowledgments

Support from the Polish Ministry of Science and Higher Education and the Structural Funds of the European Commission, Project no. SPO WKP 1.4.3 and program ATOMIN (project POIG.02.01.00-12-023/08) is gratefully acknowledged.

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