



# Search for canted spin arrangement in $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$ with Mössbauer spectroscopy

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**Abstract.** The materials studied were polycrystalline compounds  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$  ( $x = 0.1, 0.2, 0.3, 0.4$ ) which crystallize in a tetragonal lattice and display a variety of spin arrangements. The compounds have been measured with  $^{57}\text{Fe}$  Mössbauer spectroscopy over the temperature range 80–320 K in order to investigate the spin reorientation processes. Each compound was studied in a wide temperature range, with precise Mössbauer scanning in the vicinity of the transition. The set of spectra obtained for a given compound was analyzed using simultaneous fitting procedure to investigate the influence of the transition on the shape of the spectra. The fitting program was specified to analyze the transition according to the ‘two state model’: spins flip abruptly from initial angle to final arrangement ( $90^\circ$  angle). Obtained results suggest that spin reorientation process cannot be described using only the mentioned above model. Additional computer simulations based on the Yamada–Kato model were conducted to determine temperature range and the type of spin alignments in the vicinity of the transition. These theoretical results supported by spectra analysis suggest the existence of intermediate (canted) spin arrangements in the studied compounds. The spin arrangement diagram was constructed.

**Key words:** Mössbauer effect • permanent magnet materials • spin diagrams • spin reorientation

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## Introduction

$\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$  belong to the intermetallic compounds of general formula  $\text{R}_2\text{Fe}_{14}\text{B}$  (R – rare earth). These compounds form a series of magnetic materials, where high-performance permanent magnets can be found. For instance, consider  $\text{Nd}_2\text{Fe}_{14}\text{B}$  – material for the so far strongest permanent magnet. The compounds’ crystal structure is tetragonal and belongs to space group  $P4_2/mnm$ . Recently the series of  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$  with  $x = 0.1, 0.2, 0.3, 0.4$  has been studied using magnetization and magnetostriction measurements [1–3] in order to observe phenomena connected with crystalline electric field (CEF) and R-Fe exchange interaction, such as spin reorientation process and other magnetic properties like the first-order magnetization process. It seems to be interesting to observe these effects also using Mössbauer spectroscopy. The theoretical model, describing the mentioned above processes, was constructed in 1988 by M. Yamada, H. Kato, and Y. Nakagawa [4]. Recently the model was expanded from simple  $\text{R}_2\text{Fe}_{14}\text{B}$  to mixed  $\text{R}_{2-x}\text{R}'_x\text{Fe}_{14}\text{B}$  which allows describing compounds like  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$ . The free energy is obtained by numerical diagonalization of the  $(2J + 1) \times (2J + 1)$  matrix in  $|J, M\rangle$  representation, J, M being quantum numbers, for R sublattice, with the

limit of taking only the lowest  $J$  multiplet, whereas for the Fe sublattices the phenomenological data are used [5, 6]. In the mixed compounds with R and R' atoms, the total free energy is taken as a superposition of the R, R', and Fe sublattices.

### Experimental method

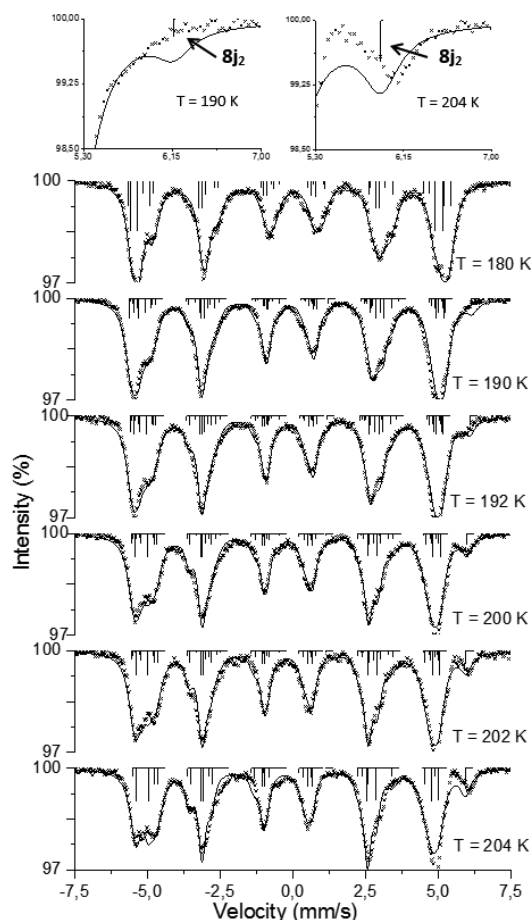
The experimental procedure was divided into three steps. First, the samples of  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$  with  $x = 0.1, 0.2, 0.3, 0.4$  were prepared by melting the pure elements in an electric arc furnace under argon atmosphere. Then the ingots were annealed at  $900^\circ\text{C}$  for three weeks in argon atmosphere. The ingots were crushed into 'coarse powder' and the first step XRD measurements were taken (step 1). When the X-ray analysis confirmed existence of the main phase in the samples, 'coarse powder' was directed to the next step measurements. The samples were triturated into fine powder, of which absorbers for Mössbauer spectroscopy were prepared (step 2). Simultaneously the second step XRD, high precision (Philips PANalytical Empyrean apparatus) measurements were taken (step 3). For Mössbauer measurements a  $^{57}\text{Co}(\text{Rh})$  source and computer controlled spectrometer with constant acceleration mode drive, in transmission geometry, were used. Velocity scale was calibrated using high purity natural iron foil. Isomer shifts were established with respect to the center of gravity of the room temperature iron Mössbauer spectrum. The iron foil was measured in the temperature range of 80–300 K in order to enable the identification of iron impurity in every spectrum because the precise X-ray analysis indicated existence of natural iron impurity (up to 9%) and marginal amount of other phases in the samples. All samples were measured in a wide temperature range of 80–330 K with careful scanning (2 K step) in the vicinity of the transition.

### Results and discussion

$\text{R}_2\text{Fe}_{14}\text{B}$  materials are very difficult to be synthesized in a pure single phase form [7]. Due to impurities evidenced in our materials, all Mössbauer spectra were first analyzed in order to eliminate contamination discovered in precise XRD measurements. Subspectra derived from the impurities were numerically subtracted from every spectrum. After that the main analysis was conducted. The transmission integral method was used to describe the shape of investigated Mössbauer spectra. The procedure of simultaneous fitting of several spectra was used to obtain the consistent description of hyperfine interaction parameters. Each subspectrum was characterized by the following hyperfine interaction parameters: magnetic field ( $B$ ), isomer shift (IS), quadrupole splitting (QS). For temperatures outside the phase transition region, the Mössbauer spectra were analyzed using six Zeeman subspectra with relative intensities according to iron occupation of crystallographic sublattices (4:4:2:2:1:1). Spectra

below and above the transition region differ in  $B$  and QS values and are described by 'low temperature' and 'high temperature' Zeeman sextets, respectively. The fitting program was specified to analyze the transition according to the 'two state model', where spins flip abruptly from initial to final arrangement, successively with temperature increase. For the temperatures inside the transition region, 'low' and 'high temperature' Zeeman sextets coexist expressing the contribution of spins before ( $C_i$ ) and after ( $C_h$ ) the transition. Within two state flip model, both kinds of Zeeman sextets exchange intensities between themselves following a gradual spin flip from initial to the final state during the transition. It is assumed that not all spins flip exactly in the same temperature and this effect causes the range of the transition, not just one, well defined temperature.

The spectra shapes were described by fits according to the discussed model. An exemplary set of experimental Mössbauer spectra of  $\text{Er}_{1.8}\text{Tb}_{0.2}\text{Fe}_{14}\text{B}$  at selected temperatures for the transition process is shown in Fig. 1. This model was applied earlier for the series of compounds e.g.  $\text{Er}_{2-x}\text{Y}_x\text{Fe}_{14}\text{B}$  [8] and gave very good description of experimentally obtained Mössbauer spectra before, after the transition as well as inside the transition temperature range.



**Fig. 1.** The  $^{57}\text{Fe}$  Mössbauer transmission spectra for the  $\text{Er}_{1.8}\text{Tb}_{0.2}\text{Fe}_{14}\text{B}$  compound in selected temperatures. The solid lines are fits to the experimental data. The set of diagrams shows line position in 'two state model'. The misfit of  $8j_2$  line in  $T = 190\text{ K}$  and  $T = 204\text{ K}$  is shown additionally on top of the figure.

**Table 1.** Crystal and exchange field parameters (in Kelvins) for  $\text{Re}_2\text{Fe}_{14}\text{B}$  ( $\text{R} = \text{Er}, \text{Tb}$ ) compounds taken from literature [5, 6]. Parameters for  $\text{R} = \text{Tb}$  were taken as appropriate  $A_n^m$  and calculated using the relations  $B_n^m/A_n^m$  [10]

R	$B_2^0$	$B_2^2$	$B_4^0$	$B_6^0$	$2(g_s - 1)B_{\text{ex}}$
Er	0.562	-0.417	$-1.38 \times 10^{-3}$	$-0.79 \times 10^{-5}$	56.74
Tb	-2.49	3.89	-0.0026	$-7.40 \times 10^{-6}$	140

However, in case of Tb substitution, in the transition temperature range we encountered difficulty: it was impossible to obtain good fits by adjusting fitting parameters. During the transition, a significant change of  $8j_2$  sublattice line is observed. The line position drifts on the velocity scale and its amplitude changes. This fact has no explanation in this simple model, which assumes a gradual increase of  $8j_2$  sublattice line in an approximately fixed position (weak drift connected with the temperature effect is taken into account in the model). At this point, it is almost certain that the process of spin reorientation in this case cannot be described by the model with only the above mentioned assumptions. The fundamental idea of the mechanism gives satisfactory results but additional parameters and assumptions are needed to describe the transition process accurately.

Disagreement between theoretical description and experimental data can be removed assuming the intermediate conical spin arrangement for the transition. Magnetostriction and magnetometric measurements [1, 2] report that total magnetization in this series can be as well parallel to the [001] axis and parallel to the [100] axis as tilted, that is, within the (010) plane. These studies show also the increasing temperature range for conical arrangement with increasing composition of Tb.

Following these reports, further computer simulations of angle alignments and the temperature dependence of spin reorientation in the system were conducted in order to check the possibility of existence of the conical spin arrangements in the studied temperature range. A program based on simplified Yamada–Kato model [4] was applied to simulate spin reorientation phenomenon. The procedure was similar to that described in [6, 8]. The simulation procedure is based on the minimization of free energy, scanning the angles of magnetic moment, and finding the alignment for which the free energy is the lowest [9]. Magnetic atoms in the unit cell are divided into two coupled sublattices ( $\text{R}$  – rare earth sublattice and  $\text{Fe}$  – sublattice). During calculations, each sublattice is taken into account in a different way. The total free energy dependence on temperature,  $F(T)$ , for the system is taken as the sum of contributions from the  $\text{R}$  and  $\text{Fe}$  sublattices:  $F(T) = F_{\text{R}}(T) + F_{\text{Fe}}(T)$ . The  $\text{R}$  sublattice is treated as an assembly of isolated atoms ( $\text{R}$ - $\text{R}$  interaction is neglected) in the crystal electric field (CEF) and exchange field which describe the  $\text{R}$ - $\text{Fe}$  interaction. Contribution to the free energy is calculated from a single ion Hamiltonian. The contributions from different  $\text{R}$  ions are assumed to be linear.

The  $\text{Fe}$ -sublattice was introduced into the model based on experimental data. The free energy of  $3d$  sublattice is taken as  $E = K_1(T)\sin^2\theta$  [9], where  $K_1(T)$  is the anisotropy constant obtained experimentally and scaled with the temperature up to

the Curie temperature and  $\theta$  is the angle between the magnetization direction and the crystal  $c$ -axis. The entropy term can be neglected in this case.

The magnetization of the  $3d$  sublattice acts on the magnetization of the rare earth sublattice, coupling these two sites with an exchange energy of the molecular magnetic field. Parameters such as quantum numbers, crystal field parameter, exchange energy parameter, are taken from literature and presented in Table 1. They constitute input for the program.

According to the Yamada–Kato model, the total free energy is given by the formula:

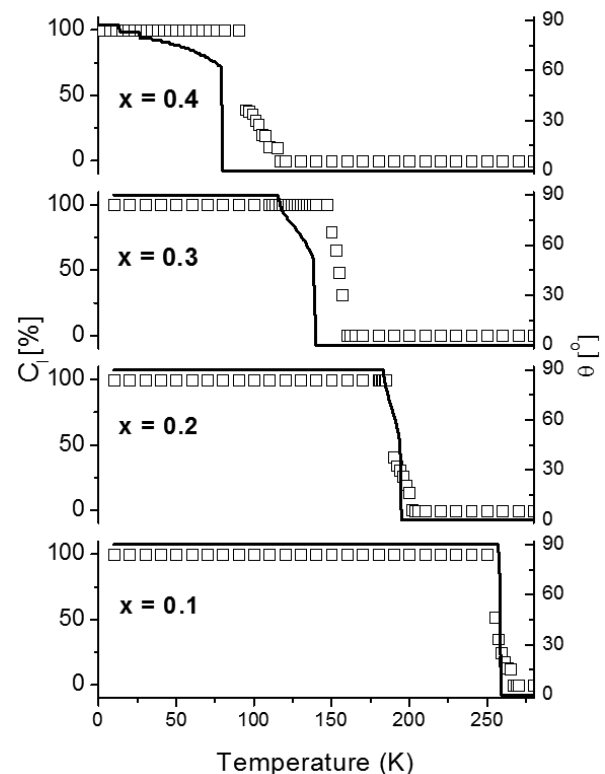
$$F(T, \theta) = -kT \sum_{i=1}^4 \ln Z(i) + 28K_1(T) \sin^2(\theta),$$

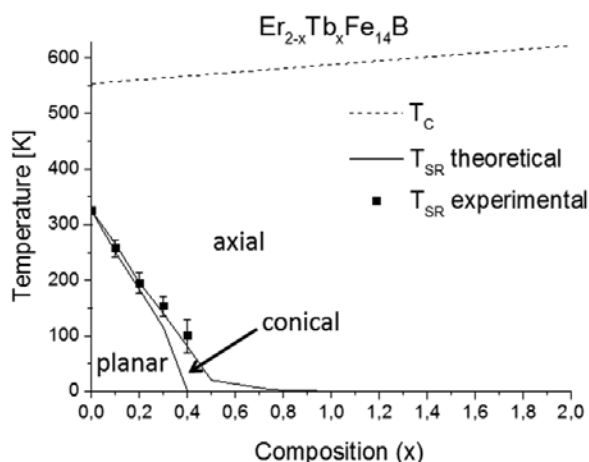
where  $Z(i)$  is the partition function

$$Z(i) = \sum_{j=1}^{2J+1} e^{-\frac{E_j(i)}{kT}}$$

and  $E_j(i)$  are the energy levels of  $\text{R}$ -ion in  $i = 4f, 4g$  lattice sites. In our calculations we assume that parameters for  $f$  and  $g$  sites have the same values.

The model was applied to simulate a character of spin reorientation phenomenon in a series of  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$ . Obtained results (Fig. 2) show a surprising agreement with experimentally determined

**Fig. 2.** Temperature dependence of the ‘low temperature’ Zeeman sextet contributions –  $C_i$  for  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$  series (open squares) and the angle  $\theta$  of spin orientation obtained from the model (solid lines).



**Fig. 3.** Spin arrangement diagram for  $\text{Er}_{2-x}\text{Tb}_x\text{Fe}_{14}\text{B}$  compounds.  $T_C$  – Curie temperature [11],  $T_{\text{SR}}$  (black squares) – spin reorientation temperatures from Mössbauer measurement and ‘two state model’,  $T_{\text{SR}}$  (solid lines) – limits of spin reorientation temperature determined by a model; between the lines the conical spin arrangements are expected.

spin reorientation temperatures for compounds with Tb content  $x = 0.1$  and  $x = 0.2$ . For higher Tb content the agreement is not so good.

Results of the model correspond to experimental data for all compositions. In some cases the obtained results give almost ideal compatibility with phenomenologically determined spin reorientation temperatures. The ‘two state model’ simply cannot cope with significant change in line position. Additionally, modeling data propose the description where spins start flipping slowly and just during the process flipping becomes more rapid. However, it requires more detailed studies and may explain the description obtained from two-state model. Data from the model also confirm the existence of conical spin arrangements from 0 K for compound with Tb composition  $x = 0.4$ .

In the spin arrangement diagram (Fig. 3), it is clearly visible that all  $T_{\text{SR}}$  determined experimentally agree with those calculated from the model within the limit of measurement uncertainty. The overlap between  $T_{\text{SR}}$  obtained from the ‘two-state model’ and those from simulations confirm that the process of spin reorientation occurs in presented temperature range for all compounds (Tb composition  $x = 0.1, 0.2, 0.3, 0.4$ ). Results obtained from two-state model and the clear declaration of the existence of the conical arrangement in this type of compounds in literature [1–3] as well as data obtained from theoretical model make it almost certain that spins flip from planar to axial arrangement with intermediate

canted arrangement. The process of determining the angle of spins in intermediate position constitutes a point of interest, which is being studied further in our group.

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