From Flip to Slow Rotation–Spin Reorientation Process in $Tm_{2-x}Tb_xFe_{14}B$ Observed by Mössbauer Spectroscopy

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The series of $Tm_{2-x}Tb_xFe_{14}B$ compounds with tetragonal crystal structure was selected for studies as it contains a mix of competing rare-earth ions which are characterized by exactly opposite values of the Stevens coefficient, α_J, a parameter which corresponds, however indirectly, to macroscopic magnetic anisotropy of the whole compound in which this ion is built in. Thulium ($\alpha_J > 0$) exhibits strong planar magnetic anisotropy while terbium ($\alpha_J < 0$) exhibits strong axial magnetic anisotropy. Following earlier studies for Er-based compounds, a series of Tm-based compounds with $x = 0, 0.1, 0.3$ was synthesized as they were likely to show spin reorientation process, allowing to study a path of the transition, angle of conical arrangement, and an influence of α_J on the spin reorientation process. All compounds were studied with ^{57}Fe Mössbauer spectroscopy in the temperature range 80–330 K with precision scanning in the vicinity of the spin transition. Experimental data were processed using simultaneous fitting procedure which includes a flipping and rotation of spins during the reorientation process. A computer simulation of spin reorientation process based on the Yamada–Kato model was conducted. As a summary, a spin arrangement diagram was constructed.

1. Introduction

The series of $Tm_{2-x}Tb_xFe_{14}B$ belongs to a larger group of compounds $R_2Fe_{14}B$ (R = rare earth), known mainly because of the $Nd_2Fe_{14}B$ compound which is a material used to manufacture the strongest permanent magnets known so far. Many extensive studies of compounds from this group have been performed so far [1–5], including our recent studies of $Er_{2-x}Tb_xFe_{14}B$ and $Er_{2-x}Ho_xFe_{14}B$ [6, 7]. These compounds crystallize in a tetragonal crystal structure with $P4_2/mnm$ space group symmetry. The occurrence of a spin reorientation process is a characteristic feature for this group of compounds. According to earlier studies, spin reorientation process can occur generally in two ways: spins can abruptly change orientation from initial planar to final axial with changing temperature or rotate smoothly through conical arrangements. This process appears as a result of competition between magnetic anisotropies of $4f$ (two rare-earth) and $3d$ atoms being components of the compound. The selected for studies series of $Tm_{2-x}Tb_xFe_{14}B$ constitutes a mix of competing rare-earth ions which are characterized by exactly opposite values of the Stevens coefficient, α_J [3]. This coefficient corresponds to a distribution of electron cloud in a free ion and thus, however indirectly, to macroscopic magnetic anisotropy of the whole compound.

Observation of spin reorientation process in this series was considered interesting because in $Tm_2Fe_{14}B$ spins flip abruptly in temperature of 315 K but in $Tb_2Fe_{14}B$ no spin reorientation process is observed — an axial spin arrangement is observed in the whole temperature range [3, 8–10] so the result of competition in R-sublattice was worth studying. Based on the results achieved for $Er_{2-x}Tb_xFe_{14}B$ series (erbium ion has very similar magnetocrystalline properties to those for thulium ion but its α_J is four times bigger), compounds of $x = 0, 0.1, 0.3$ composition were synthesized and chosen for further studies as they were likely to show a spin reorientation process allowing to study an influence of Stevens coefficient on the local spin arrangement.

Our goal was to describe a path from planar to axial spin arrangements during spin reorientation process and to determine angles of conical arrangement by applying a procedure which was successfully used before for $Er_{2-x}Ho_xFe_{14}B$ and $Tm_{2-x}Ho_xFe_{14}B$ [7, 11]. Additionally, a qualitative influence of α_J on the process was of interest.

2. Experimental methods

Procedure of preparing materials for further studies was similar to that used before for $Er_{2-x}Ho_xFe_{14}B$ series [7]. Samples of $Tm_{2-x}Tb_xFe_{14}B$ ($x = 0.0, 0.1, 0.3$) were prepared by alloying high purity elements in an electric arc furnace and annealing in 900 °C for two weeks.

X-ray diffraction (XRD) analysis at room temperature (Siemens D5000 diffractometer) was performed for all samples in order to qualify them for further analysis. Existence of the expected phase was confirmed, however,

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a small amount of Fe impurity was also evidenced. These compounds are very difficult to be synthesized in a pure single phase form [12]. Final ^{57}Fe spectra analysis took into consideration the presence of the Fe impurity.

The measurements were conducted using the Mössbauer spectroscopy with a ^{57}Co(Rh) source and a computer driven constant acceleration mode spectrometer. All samples were scanned in temperature range 80–330 K with high precision of 1 K in the vicinity of the spin reorientation temperature, T_{SR}. As a result, over 40 spectra were collected for each compound.

3. Data analysis

3.1. Mössbauer spectra analysis

Obtained Mössbauer spectra (Fig. 1) were similar to those recorded for $Er_{2-x}Tb_xFe_{14}B$ and $Er_{2x}Ho_xFe_{14}B$ compounds [6, 7, 13]. In these series, too, abrupt flips and slow rotation of spins during a spin reorientation process were discovered. Taking this fact as indication for further spectra analysis, a procedure of simultaneous spectra fitting regarding conical spin arrangements and abrupt spin flipping were used. The procedure including conical spin arrangement was developed for $Er_{2x}Ho_xFe_{14}B$ compounds [7]. By implementing a simultaneous fitting in analysing procedure it is possible to determine the temperature dependence of orientation angle ψ between magnetic moment $\boldsymbol{M}$ and principal axis of electric field gradient (EFG) tensor (Vxx, Vyy, Vzz) — and also the amount (fraction) of spins remaining in planar arrangement and a fraction of spins which passed to axial arrangements in a given temperature range during the spin reorientation process.

The spectra shapes were described by a convolution of six Zeeman subspectra with intensities corresponding to iron occupation in crystallographic lattice i.e. 4:4:2:2:1:1. Each subspectrum was described by specific hyperfine interaction parameters: magnetic field — B, isomer shift — IS, quadruple splitting — QS. In the fitting procedure a transmission integral was used.

In the temperature range of the spin reorientation process, each spectrum was described by two sets of six Zeeman sextets. One set corresponds to the situation below the reorientation (low temperature Zeeman sextets), while another set corresponds to the situation after the reorientation (high temperature Zeeman sextets). The rotation of spins is described by the high temperature Zeeman sextets, while low temperature Zeeman sextets describes fraction of spins which remain in initial position. During the spin reorientation process, the position of total magnetization vector, $\boldsymbol{M}$ can change smoothly from initial, within a–b plane, to final, parallel to c axis. Its position is described by an orientation angle ψ (ψ changes from 0° to 90° during the reorientation process) and the rotation takes place within so-called "rotation plane", which is perpendicular to a–b plane. It was assumed that the rotation plane is fixed during the whole reorientation process. The position of $\boldsymbol{M}$ vector can be
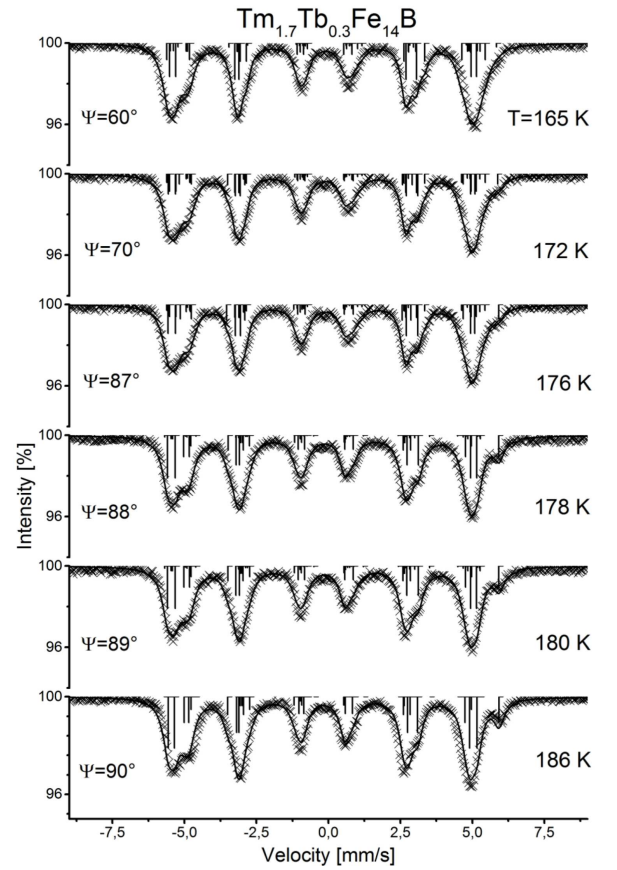

Fig. 1. The set of Mössbauer spectra for $Tm_{1.7}Tb_{0.3}Fe_{14}B$ at selected temperatures. Experimental data (crosses) and data from theoretical model (solid lines) presenting evolution of line positions and amplitudes. For each spectrum a value of the orientation angle ψ was indicated.

determined by analysing the changes in QS value, which is given by the following formula (the anisotropy term is neglected):

$$QS = QS_0 \left(\frac{3\cos^2\theta(\psi) - 1}{2} \right), \qquad (1)$$

where θ is an angle between $\boldsymbol{M}$ vector and principal axis of EFG. Changes of θ angle have their reflections in changes of ψ angle. The smooth rotation of $\boldsymbol{M}$ vector is visible on the spectra as a shift of $8j_2$ sixth line on the velocity scale, while increasing amount of spins starting to rotate or passing to final (axial) position as an increasing intensity of this line.

3.2. Computer simulations — theoretical model

The computer simulation program, based on a simplified Yamada–Kato model [14], was used to compare experimental results with this theoretical model. The program takes as input values the parameters of crystal field and exchange parameters, quantum numbers, the Curie temperature and anisotropy constants (Table I). The procedure was identical with that performed for $Er_{2-x}Tb_xFe_{14}B$ series [6].

Crystal field parameters, Curie temperatures and exchange parameters (in K), $C_{ex} \approx 2(g_s - 1)B_{ex}$, used in our calculations. Values of crystal field parameters were taken from [15] and calculated using relations A_n^m/B_n^m [16].

	B_2^0	B_2^{-2}	B_4^0	B_6^0	B_6^4	T_C	C_{ex}
$Tm_2Fe_{14}B$	2.09	-3.25	-2.5×10^{-3}	2.39×10^{-5}	1.3×10^{-4}	541	40.8
$Tb_2Fe_{14}B$	-2.49	3.89	-0.0026	-7.4×10^{-6}	0	620	120

The position of M vector, described as an angle ψ of deviation from a–b plane, is obtained by minimizing the free energy function $F(T)$ of two coupled sublattices — associated with R atoms and Fe atoms. The formula, presenting the dependence of the total free energy as a function of temperature T and angle ψ, can be written in a following way:

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

where Z(i) is the partition function

$$Z(i) = \sum_{j=1}^{2J+1} \exp\left(-\frac{E_j(i)}{kT}\right), \quad (3)$$

$E_j(i)$ are the energy levels of R-ion in i =4f, 4g lattice sites. The equivalence between 4f and 4g sites was assumed. A collective behavior of all spins was assumed.

4. Results and discussion

The analysis indicates very strong dependence of local spin arrangements on terbium content in the compound. In the spectra obtained for compound with $x = 0.3$ (Fig. 1) a shift of $8j_2$ line on the velocity scale is clearly visible, however changes in spectra shape, caused by changes of the angle between M vector and principal axis of EFG, appear for every subspectrum. For this compound also, the widest temperature region of the spin reorientation process was recorded.

With decreasing amount of terbium content in the compounds the character of the spin reorientation process changes. Smooth rotation converses to abrupt flips, temperature region of spin reorientation process reduces and spin reorientation temperature increases.

The procedure of simultaneous fitting brings a good description of spectra with no significant misfits which allows to describe the local spin arrangements in quite exact way. The temperature limits of spin reorientation, values of the reorientation angle ψ and amount of rotating and non-rotating phase (high and low Zeeman sextets) during the spin reorientation process were determined (Fig. 2). For the compound $Tm_2Fe_{14}B$ only abrupt flips of spins during the spin reorientation process were recorded.

The computer simulation results based on theoretical model show very good agreement with experimental data. For $Tm_2Fe_{14}B$ values of spin reorientation temperature obtained from the simulations and those achieved from spectra analysis are equal and confirm the literature data [8–10]. In this case all sources confirm only abrupt flips of spin during the reorientation process. For com-
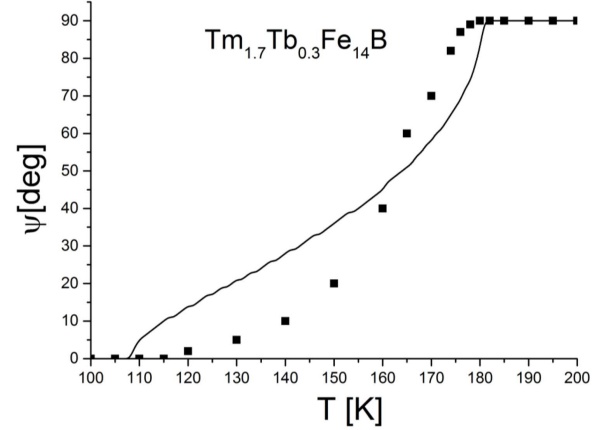

Fig. 2. The temperature dependence of the orientation angle ψ for $Tm_{1.7}Tb_{0.3}Fe_{14}B$. The Mössbauer experimental data (black squares) are presented together with computer simulation data (solid lines).
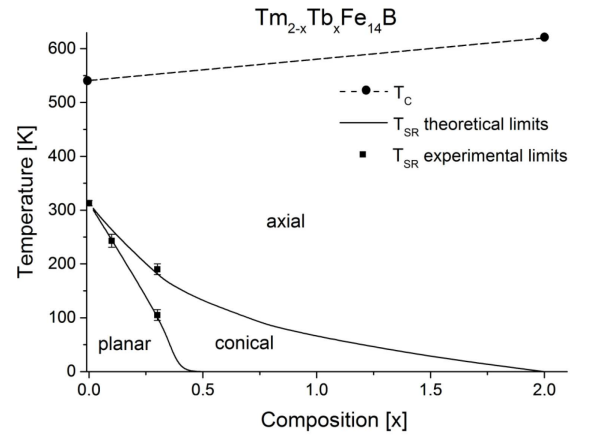

Fig. 3. Spin arrangement diagram for $Tm_{2-x}Tb_xFe_{14}B$ compounds. T_{SR} (black squares) — spin reorientation temperature limits from Mössbauer measurement and fitting procedure, T_{SR} (solid lines) — limits of spin reorientation temperature determined by the computer simulations.

pound of $x = 0.1$ the temperature region of the spin reorientation process achieved from the simulation is in good coherence with those obtained from spectra analysis. For compound of $x = 0.3$ also there is quite good coherence between simulation and experiment data (Fig. 2). Computer simulations indicate a lower temperature in which the spin reorientation process begins. It is expected that the reason is in the assumption that in model data all spins rotate coherently. The temperature value of the

end of the spin reorientation process and general way of the ψ angle changes are in agreement between model and experiments.

Obtained model and experimental data were used to construct spin arrangement diagram (Fig. 3). Clearly visible are the areas of the planar, conical, and axial spin arrangement, as well as a coherence between model and experimental data. Smooth rotation of the $\boldsymbol{M}$ vector does not appear only for $Tm_2Fe_{14}B$. Spin reorientation process begins at lower temperatures and the region of conical spin arrangement mightily increases with increasing terbium content in a compound, up to terbium content $x \leq 0.5$. For higher terbium content a conical arrangement exists from the lowest temperature.

5. Conclusion

The applied procedure of simultaneous fitting brought a good spectra description. The temperature region and values of the angle of the local spin arrangement were determined. Experimental data were compared with results of computer simulations. The series of $Tm_{2-x}Tb_xFe_{14}B$ turned out to be very similar to the series $Er_{2-x}Tb_xFe_{14}B$. The temperature limits of the end of the spin reorientation process are the same for each series. For the series containing thulium obtained wider temperature regions of the spin reorientations process, and the reorientation starts at lower temperatures. As expected, erbium content decides especially on the temperature in which spins pass to axial positions, and thulium or erbium content decide in which temperature the spin reorientation process begins. For $Tm_{2-x}Tb_xFe_{14}B$, where value of the Stevens coefficient of thulium ion is four times greater than for erbium ion, the obtained temperature region of spin reorientation process is four times wider. This observation may indicate some form of correlation of the Stevens factor and the temperature span of the spin reorientation process in case of competition in R-sublattice.

Acknowledgments

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