



Spin reorientation process in $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ – analysis of conical arrangement based on Mössbauer spectra

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Abstract. The spin reorientation process in the $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ series of compounds was studied using ^{57}Fe Mössbauer spectroscopy over the temperature range 5.2–320 K with a focus on the analysis of conical spin arrangement. Each compound was studied by precise Mössbauer scanning in the vicinity of the transition and during the transition. By applying computer simulations based on the simplified Yamada-Kato model, as well as on some literature data for $\text{R}_2\text{Fe}_{14}\text{B}$ ($\text{R} = \text{Tm}, \text{Ho}$) compounds, the above series was selected for studies as it contains compounds with different spin arrangements (axial, planar, conical). It was a crucial requirement for obtaining unambiguous angular dependences when applying a simultaneous fitting procedure of Mössbauer spectra. Such an extended procedure was applied which allowed the temperature dependence of the angle describing the position of the magnetization vector to be obtained. The results were compared with those from theoretical simulations. The spin arrangement diagram was constructed. A conical spin arrangement was confirmed over a wide temperature range.

Keywords: permanent magnetic materials • Mössbauer effect • spin reorientation • spin diagrams

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Introduction

Many compounds based on the general formula $\text{R}_2\text{Fe}_{14}\text{B}$ (R – rare earth element) have been studied so far, including the most common $\text{Nd}_2\text{Fe}_{14}\text{B}$ which composes the strongest permanent magnets [1–5]. $\text{Tm}_2\text{Fe}_{14}\text{B}$ and $\text{Ho}_2\text{Fe}_{14}\text{B}$ also belong to this group. Although their basic properties are known [5–9], the series of $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ is worth paying attention to as it provides the opportunity to observe possible different types of spin arrangements which are likely to appear when R , a sublattice, is composed of elements with competing anisotropies. These R ions have different Stevens coefficients α_j : positive for Tm and negative for Ho [1].

All these compounds belong to $P4_2/mnm$ space group symmetry. In a tetragonal crystal lattice, iron atoms occupy six inequivalent positions ($16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$, $4e$), rare earth atoms are located in $4f$ and $4g$ positions and boron is in the $4g$ position.

The aim of this study was to determine the changes in magnetic spin direction during the spin reorientation process. At the beginning, computer simulations were performed in order to check for a possible course of the transition process. It was expected that simulation results can yield some indications with regard to the selection of the most interesting compositions for experimental studies. Subsequently, the compounds of interesting Tm and

Table 1. Crystal field parameters [12], Curie temperatures, exchange parameters, $C_{ex} \approx 2(g_s - 1)B_{ex}$ used in our calculations. Values of crystal field parameters were calculated using the relation A_n^m/B_n^m [13]

	B_2^0	B_2^{-2}	B_4^0	B_6^0	B_6^4	T_C /K	C_{ex}
$Tm_2Fe_{14}B$	2.09	-3.25	$-2.5 \cdot 10^{-5}$	$2.39 \cdot 10^{-5}$	$1.30 \cdot 10^{-4}$	541	40.8
$Ho_2Fe_{14}B$	-5.13	7.24	$5.8 \cdot 10^{-5}$	0	$6.79 \cdot 10^{-5}$	573	41.0

Ho content were prepared and Mössbauer measurements were performed. It was also important to verify if the reorientation process can be described using similar methods as those utilized for the $Er_{2-x}Ho_xFe_{14}B$ series [10] (Er and Tm ions have similar values of α_f [1]).

Experimental methods

Samples of $Tm_{2-x}Ho_xFe_{14}B$ ($x = 0, 0.3, 1.0, 1.5, 2.0$) compounds were prepared for further studies by alloying in an electric arc furnace and annealing at 900°C, similar to a previous experiment [10].

All samples were tested using XRD analysis at room temperature. A Siemens D5000 X-ray diffractometer was used. All samples were qualified for further analysis, although the presence of small amounts of Fe impurities (the compounds are very difficult to be synthesized in a pure single phase form [2]) was taken into account for the numerical analysis of the final spectra.

The samples were studied using Mössbauer spectroscopy with a $^{57}Co(Rh)$ source and a computer-driven spectrometer in constant acceleration mode. Spectra were recorded within the temperature range of 5.2–320.0 K. The Mössbauer scanning in the vicinity of the spin reorientation temperature, T_{SR} , was performed with a higher degree of precision – up to 1 K.

Data analysis

Computer simulations – theoretical model

The simplified Yamada-Kato model [11] was used to conduct the computer simulation of possible spin arrangements. The program is based on crystal field and exchange parameters, quantum numbers, Curie temperatures, and the anisotropy constant. The entry parameters (see Table 1) were taken from the literature [12, 13] as well as calculated using our earlier work [14]. The utilized procedure allows us to determine the position angle of vector \vec{M} by minimizing the free energy function $F(T)$ of two coupled sublattices – associated with R atoms and Fe atoms. The procedure was analogous to that used for $Er_{2-x}Ho_xFe_{14}B$ and its extended description can be found in [10]. The final formula, presenting the dependence of the total free energy as a function of temperature T and angle ψ , can be written in the following way:

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

where $Z(i)$ is the partition function:

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

ψ is the angle between the magnetization direction and the plane that is perpendicular to the crystal c axis (Fig. 1) and $E_j(i)$ are the energy levels of ion R in $i = 4f, 4g$ lattice sites. The equivalence between $4f$ and $4g$ sites was assumed.

The simulation procedure assumed a collective behaviour of all spins. The simulation results yielded the temperature dependences of spin arrangement angles in the whole series. It was also helpful in selecting the compositions for detailed measurements.

Mössbauer spectra analysis

A spectra of impurities deriving from the unreacted Fe phase as observed during XRD measurements were numerically subtracted from every spectrum. This procedure, although debatable, was necessary to technically enable the procedure of further fitting.

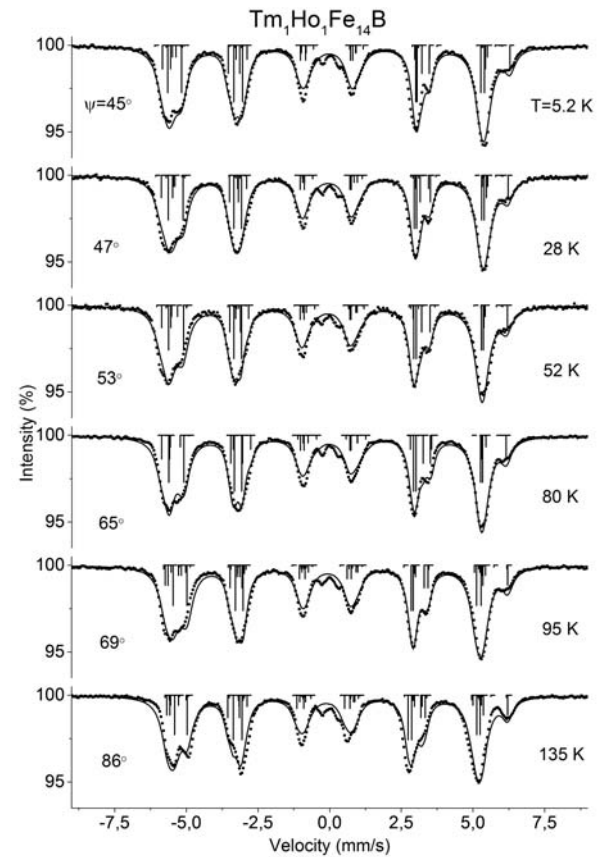


Fig. 1. The ^{57}Fe Mössbauer transmission spectra for $Tm_1Ho_1Fe_{14}B$ (crosses – experimental data) and fits from the model (solid lines) illustrating the evolution of line positions and amplitudes. The change in lines of the $8j_2$ sextet is visible. The angle ψ describing the rotation of magnetic moment and the temperature are indicated.

It was expected that the series of $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ ($x = 0, 0.3, 1.0, 1.5, 2.0$) constitutes a series of compounds that are similar to $\text{Er}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ (Tm and Er are similar ions), especially in terms of the Stevens coefficient α_j , the spin reorientation temperature T_{SR} , and the Curie temperature T_{C} . Also the obtained Mössbauer spectra compared with data from simulations confirmed this similarity, and hence the suspicion of the existence of the conical spin arrangement in the studied series. It was a premise to use the same analysing procedure, developed and used for $\text{Er}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ compounds, where a conical spin arrangement was observed and described [10].

All spectra were processed by the simultaneous extended fitting procedure to determine the consistent description of the spin reorientation process and to obtain coherent values of hyperfine interaction parameters throughout the whole series. It was important to obtain the temperature dependence of the angle between the magnetic moment \vec{M} and the principal axis of the EFG (electric field gradient) tensor (V_{xx} , V_{yy} , V_{zz}). In this procedure the shapes of the spectra are described by the convolution of six Zeeman subspectra. Their intensities reflect the iron occupation in the crystallographic lattice, i.e. 4:4:2:2:1:1. In every subspectrum, the following hyperfine interaction parameters were used: magnetic field – B , isomer shift – IS, and quadrupole splitting – QS. A transmission integral was used in the fitting procedure. The analysis led to the description of the spin reorientation process from the proper fitting of results.

The fitting procedure allows us to describe the spin reorientation process by finding the position angle ψ (Fig. 1) of total magnetization of vector \vec{M} at a specific temperature [10]. This position can change from planar (within the a - b crystallographic plane, ($\psi = 0^\circ$)), via tilted (within the plane perpendicular to the a - b plane ($0^\circ < \psi < 90^\circ$)), to final axial (parallel to the crystallographic axis c ($\psi = 90^\circ$)) [10, 15]. It is possible to describe the reorientation process in a featured way, where the total magnetization \vec{M} not only flips but also rotates from a planar to axial position. The plane in which the rotation takes place is called the rotation plane. It was assumed that the rotation plane was fixed during the whole reorientation process.

The spectra from temperatures below the transition region are described by low-temperature Zeeman sextets, those from temperatures above the transition region are described by high-temperature Zeeman sextets. Within the temperature range of the transition region, the low- and high-temperature Zeeman sextets can coexist.

The change in the position of vector \vec{M} (described by angle ψ) causes the change of angle Θ between vector \vec{M} and the principal axis of EFG which is reflected in terms of changes to the QS value (here the anisotropy term is neglected) [10]:

$$(3) \quad \text{QS} = \text{QS}_0 \left[\frac{3 \cos^2 \Theta(\psi) - 1}{2} \right]$$

The fitting procedure was applied to selected compositions where a conical arrangement was

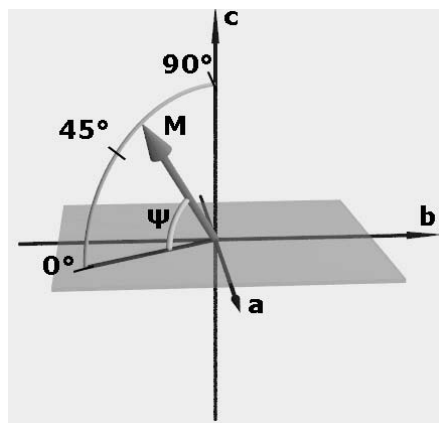


Fig. 2. The position of vector \vec{M} in the rotation plane described by angle ψ .

observed ($x = 0.3, 1.0, 1.5, 2.0$). An exemplary set of Mössbauer spectra with fits generated by the simultaneous fitting procedure is presented in Fig. 2, where the effects corresponding to the transition process for the compound where $x = 1.0$ are visible. This is the compound where the widest temperature region of conical arrangement for the transition process was found. The fits describe the shape of the spectra in an appropriate way. Also the sixth line of the $8j_2$ Zeeman sextet is described correctly. The same is true for the first set of lines. The most significant is that the drift of the sixth line of the $8j_2$ Zeeman sextet on the velocity scale is reflected in the fits. This is one of the most characteristic manifestations of existing conical spin arrangements for the measured sample. Similar behaviour was also observed for compounds containing Ho where $x = 0.3, 1.5$ and 2.0 , however, the temperature transition range was smaller.

The transition process was tested in order to investigate its consistency, i.e. if all the spins rotate coherently. This was realized by checking the contribution of the initial and rotating phases – low and high Zeeman sextets – to the fitting procedure. The results reveal that in all samples only small amounts of initial phases, namely less than 9%, exist over the whole transition process.

Results and discussion

The computer simulation based on a theoretical model enabled us to identify the composition of compounds, where conical spin arrangements exist over a wide temperature range. The simultaneous fitting procedure yielded good and coherent descriptions of recorded Mössbauer spectra. The values of angle ψ that determine the \vec{M} arrangement in the rotation plane, and thus the reorientation angle, were measured by the spectra analysis procedure and compared with those from theoretical simulations.

Figure 3 shows a very good agreement between the model and data analysis of Ho content when $x = 0.3$ and even strong agreement when $x = 1.0$. For this compound, the only disagreement occurs at the end of the rotation process which is probably caused by an oversimplified assumption applied to

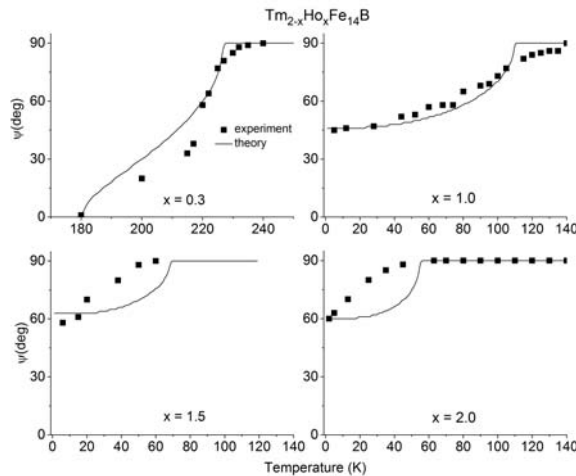


Fig. 3. The temperature dependence of spin reorientation angle ψ for the $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ series. Black squares illustrate values determined by the fitting program while solid lines are data from simulations of the Yamada-Kato model.

the theoretical considerations. For other compounds where conical arrangements exist, i.e. when $x = 1.5$ and 2.0 , a stronger disagreement is observed. However, the experimentally found temperature transition range was correctly simulated along with the initial values of the spin arrangement angle ψ .

The temperature transition range measured for $\text{Ho}_2\text{Fe}_{14}\text{B}$ is exactly equal to that from the literature [6]. For $\text{Tm}_2\text{Fe}_{14}\text{B}$ the two-state model was applied. This model is a simplified version of the fitting procedure that assumes only abrupt flips of spins during the reorientation process (without any conical arrangements). This procedure yielded a value of T_{SR} equal to 313 K, which is exactly equal to data from the literature [1, 7].

All data were used to construct a spin arrangement diagram (Fig. 4). The theoretical data are presented together with those from the experiment. The areas of planar, conical and axial spin arrangements are visible. The vector \mathbf{M} remains in tilted positions for compounds containing Ho where $x \geq 0.5$. For com-

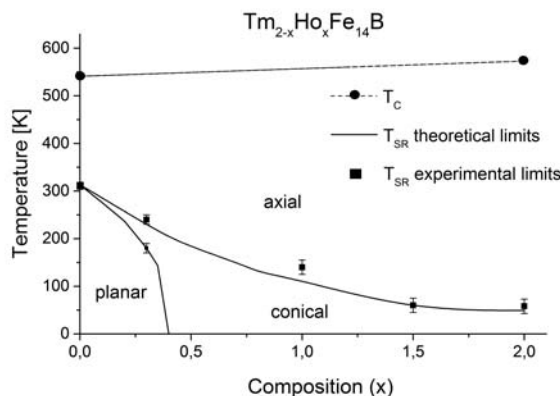


Fig. 4. Spin arrangement diagram for the $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ series. T_{C} – Curie temperature, T_{SR} (black squares) – temperature limits of spin reorientation from Mössbauer measurements and the fitting procedure, T_{SR} (solid lines) – temperature limits of spin reorientation determined by the simulations of the Yamada-Kato model, area between the lines – area of conical spin arrangement.

pounds containing Ho where $x < 0.5$ the conical region shrinks suddenly as Tm content increases.

Conclusion

The applied processes as well as the simulations and the fitting results confirm the existence of conical spin arrangements over a wide range of compositions in the $\text{Tm}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ series. Theoretical and experimental techniques applied as part of the analysis yield a coherent description of the reorientation processes. The extended procedure of simultaneous fitting developed earlier for other compounds could be used successfully for this series in describing most phenomena connected with the reorientation process. Data from the literature confirm the obtained results, especially the values of T_{SR} for the compounds $\text{Tm}_2\text{Fe}_{14}\text{B}$ and $\text{Ho}_2\text{Fe}_{14}\text{B}$.

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References

- Herbst, I. F. (1991). $\text{R}_2\text{Fe}_{14}\text{B}$ materials: Intrinsic properties and technological aspects. *Rev. Mod. Phys.*, 63(4), 819.
- O'Handley, R. C. (2000). *Modern magnetic materials: Principles and applications*. New York: Wiley.
- Lim, J. T., Kim, H. K., Kim, C. S., An, S. Y., & Choi, K. R. (2015). Investigation of the magnetic properties of Dy doped Nd-Fe-B permanent magnet by using Mössbauer spectroscopy. *J. Korean Phys. Soc.*, 66, 1913–1917. DOI: 10.3938/jkps.66.1913.
- Pankratov, N. Yu., Nikitin, A. A., Iwasieczko, W., Drulis, H., Skokov, K. P., Pastushenkov, Yu. G., Harutjunjan, N., Lyubina, J., Gutfleisch, O., Handstein, A., & Müller, K. -H. (2006). Spin-reorientation transition in $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ compounds and their hydrides. *J. Magn. Magn. Mater.*, 300, e465–e468. DOI: 10.1016/j.jmmm.2005.10.195.
- Hirosawa, S., Yutaka, M., Hitoshi, Y., Setsuo, F., Masato, S., & Hiroshi, Y. (1986). Magnetization and magnetic anisotropy of $\text{R}_2\text{Fe}_{14}\text{B}$ measured on single crystals. *J. Appl. Phys.*, 59, 873. DOI: 10.1063/1.336611.
- Ibarra, M. R., Pareti, L., Algarabel, P. A., Morellon, L., Marquina, C., & Solzi, M. (1993). Magnetic anisotropy in $(\text{Er}_x\text{Ho}_{1-x})_2\text{Fe}_{14}\text{B}$ pseudoternary intermetallic compounds. *J. Phys.-Condens. Matter*, 5(31), 5637. DOI: 10.1088/0953-8984/5/31/025.
- Piqué, C., Burriel, R., & Bartolomé, J. (1996). Spin reorientation phase transitions in $\text{R}_2\text{Fe}_{14}\text{B}$ ($\text{R} = \text{Y}, \text{Nd}, \text{Ho}, \text{Er}, \text{Tm}$) investigated by heat capacity measurements. *J. Magn. Magn. Mater.*, 154, 71–82. DOI: 10.1016/0304-8853(95)00571-4.
- Wolfers, P., Bacmann, M., & Fruchart, D. (2001). Single crystal neutron diffraction investigations of the crystal and magnetic structures of $\text{R}_2\text{Fe}_{14}\text{B}$ ($\text{R} = \text{Y}$,

- Nd, Ho, Er). *J. Alloy. Compd.*, 317/318, 39–43. DOI: 10.1016/S0925-8388(00)01353-0.
9. Rillo, C., Chaboy, J., Navarro, R., Bartolome, J., Fruchart, D., Chenevier, B., Yaouanc, A., Sagawa, M., & Hirosawa, S. (1988). Dynamical susceptibility of $\text{Ho}_2\text{Fe}_{14}\text{B}$ single crystal: Spin rotation and domain wall motions. *J. Appl. Phys.*, 64, 5534–5536. DOI: 10.1063/1.342327.
 10. Kurzydło, P. M., Pędziwiatr, A. T., Bogacz, B. F., Przewoźnik, J., & Oleszak, D. (2016). Conical spin arrangement and spin reorientation process in $\text{Er}_{2-x}\text{Ho}_x\text{Fe}_{14}\text{B}$ observed with Mössbauer spectroscopy. *J. Alloy. Compd.*, 684, 587–593. DOI: 10.1016/j.jalcom.2016.05.140.
 11. Yamada, M., Kato, H., Yamamoto, H., & Nakagawa, Y. (1988). Crystal-field analysis of the magnetization process in a series of $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type compounds. *Phys. Rev. B*, 38, 620–633. DOI: 10.1103/PhysRevB.38.620.
 12. Burzo, E. (1998). Permanent magnets based on R–Fe–B and R–Fe–C alloys. *Rep. Prog. Phys.*, 60, 1099–1266. DOI: 10.1088/0034-4885/61/9/001.
 13. Coey, J. M. D. (1996). *Rare-earth iron permanent magnet*. Oxford: Clarendon Press.
 14. Bogacz, B. F., & Pędziwiatr, A. T. (2013). Crystal electric field parameters determination for $\text{R}_2\text{Fe}_{14}\text{B}$ compounds based on Yamada-Kato model. *Nukleonika*, 58(1), 31–33.
 15. Susilo, R. A., Munoz Perez, S., Cobas, R., Cadogan, J. M., & Avdeev, M. (2012). Magnetic order and spin-reorientation in HoGa. *J. Phys.-Conf. Series*, 340, 012071. DOI: 10.1088/1742-6596/340/1/012071.