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Spin reorientations in $RFe_{11-x}Co_xTi$ compounds (R=Tb, Er, Y)

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Abstract

We have studied the magnetic properties of several series of $RFe_{11-x}Co_xTi$ compounds (R=Tb, Er and Y) by means of magnetic measurements and X-ray diffraction of magnetically aligned powder samples. The spin reorientations observed in several of these compounds were attributed to three different mechanisms. Spin-reorientation transitions observed at fairly low temperatures originate mainly from a competition between the various crystal-field terms associated with the crystal-field-induced R-sublattice anisotropy. At fairly high temperatures, spin reorientation transitions can arise as a consequence of a sign change of the 3d-sublattice anisotropy as a function of temperature. In the intermediate temperature range, spin-reorientation transitions were interpreted as resulting from a competition between the R-sublattice anisotropy and 3d-sublattice anisotropy.

Keywords: Rare earth compounds; Transition metal compounds; Anisotropy; Magnetic measurements

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1. Introduction

An interesting class of magnetic materials is formed by the rare earth (R) compounds of 1:12 stoichiometry (tetragonal $ThMn_{12}$ structure). From results of previous investigations it is known that, for a given R-component, a sign change of the R sublattice anisotropy can be induced in $RT_{11}Ti$ when changing the nature of the 3d-element T [1,2]. Apparently, the 3d sublattice anisotropy does not change its uniaxial character, being the same in $YFe_{11}Ti$ and $YCo_{11}Ti$. We have studied the effect of the sign change of the R-sublattice anisotropy on the spin reorientation transitions in the series $ErFe_{11-x}Co_xTi$ and $TbFe_{11-x}Co_xTi$. By means of results obtained on the $YFe_{11-x}Co_xTi$ series we will show that not only the sign of the anisotropy of the R sublattice is concentration dependent, but also that of the 3d sublattice.

2. Experimental procedures and sample characterization

$RFe_{11-x}Co_xTi$ samples with R=Tb, Er and Y and various Co concentrations were prepared by arc melting starting materials of at least 99.9% purity. After arc melting, the samples were wrapped into Ta foil, sealed into an evacuated quartz tube and annealed for 3 weeks at 1050°C. The X-ray diffraction diagrams showed that the annealed samples were approximately single phase, belonging to the tetragonal $ThMn_{12}$ structure type. The amount of impurity phases was below about 5%. Because all compounds have Curie temperatures above room temperature, X-ray diffraction data could also be taken on finely ground powder samples of which the particles were magnetically aligned at room temperature and fixed in the alignment direction with glue. In this way, information about the easy magnetization directions was obtained.

The magnetic measurements were made in a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 5 T. For the measurements above 300 K, we used a home-built magnetometer based on the Faraday principle. In the latter case, the measurements were made on pieces of polycrystalline bulk material

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sealed into an evacuated silica tube in order to avoid oxidation at elevated temperatures as far as possible.

3. Experimental results

3.1. $ErFe_{11-x}Co_xTi$

Results of the X-ray diffraction measurements made on magnetically aligned powder samples are displayed in Fig. 1. It follows from these data that the easy magnetization direction is parallel to the *c* direction in the Fe-rich samples ($x=0$ and 2) of the series and the Co-rich samples ($x=11$). By contrast, the easy magnetization is perpendicular to the *c* direction in the intermediate concentration range ($x=5$ and 8). The magnetic alignment in the sample with $x=5$ is apparently less perfect. As will be further discussed below, the reason for the less perfect alignment is the occurrence of a spin-reorientation transition close to room temperature. In fact, most of the $ErFe_{11-x}Co_xTi$ compounds give rise to a spin reorientation transition. These transitions show up in the form of a maximum in the temperature dependence of the magnetization. They occur below room temperature for the samples with $x=0$, 2 and 11, as can be seen in Fig. 2. In the sample with $x=8$, the spin reorientation transition occurs at a much higher temperature ($T_{SR}=663$) as can be seen in Fig. 3. The spin reorientation temperatures and the corresponding Curie temperatures for the $ErFe_{11-x}Co_xTi$ compounds have been listed in Table 1. For the parent compounds, our data are in satisfactory agreement with literature data [3–5]. The magnetic isotherms of the $ErFe_{11-x}Co_xTi$ compounds have been measured at 5 K on powder particles that were free to rotate within the sample holder. The results are shown in Fig. 4. The spontaneous moments, M_0, were derived from the magnetic isotherms by extrapolation to zero field strength. The corresponding values have been listed in Table 1.

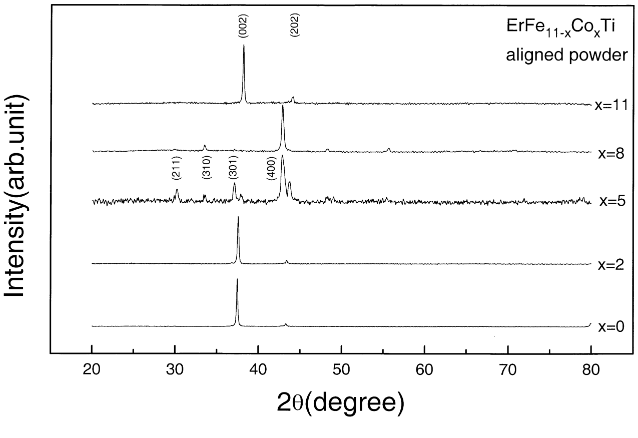

Fig. 1. Examples of X-ray diagrams obtained on magnetically aligned powder samples of $ErFe_{11-x}Co_xTi$ compounds.

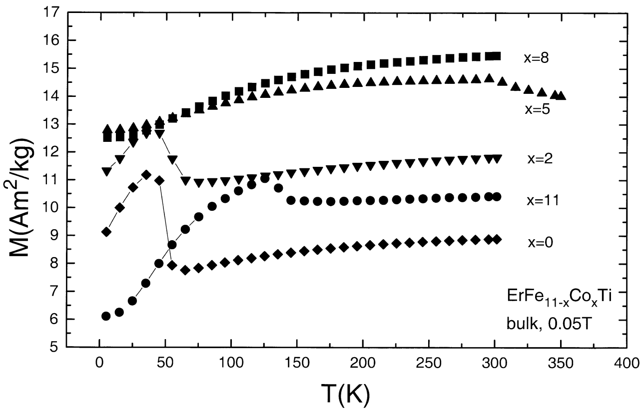

Fig. 2. Temperature dependence of the magnetisation of $ErFe_{11-x}Co_xTi$ compounds, measured below room temperature in a field of 0.05 T.

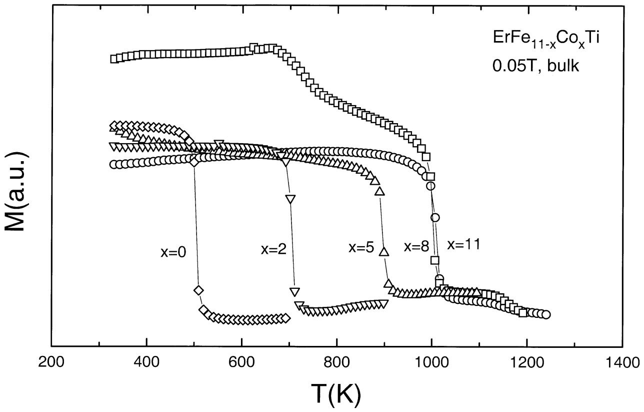

Fig. 3. Temperature dependence of the magnetisation of $ErFe_{11-x}Co_xTi$ compounds, measured above room temperature in a field of 0.05 T.

3.2. $TbFe_{11-x}Co_xTi$

At room temperature, the compounds with $x=0$ and 11 have been reported to have their easy magnetization direction perpendicular and parallel to the *c* direction, respectively [3,4]. From our X-ray data we derive that the compounds in the intermediate concentration range have their easy magnetization direction parallel to the *c* direction, see Fig. 5. The temperature dependence of the

Table 1
The spontaneous moment M_0 (5 K), the T-sublattice moment M_T (5 K), the Curie temperature T_C, the spin-reorientation temperature T_{SR} and the easy magnetization direction (EMD) of the $ErFe_{11-x}Co_xTi$ compounds

$ErFe_{11-x}Co_xTi$ (x)	M_0 (5 K) μ_B/f.u.	M_T (5 K) μ_B/f.u.	T_C (K)	T_{SR} (K)	EMD at 295 K
0	10.94	19.94	505	35	Easy-axis
2	12.47	21.47	704	45	Easy-axis
5	11.37	20.37	895	295	(Easy-plane)
8	9.31	18.31	999	663	Easy-plane
11	6.69	15.69	1008	125	Easy-axis

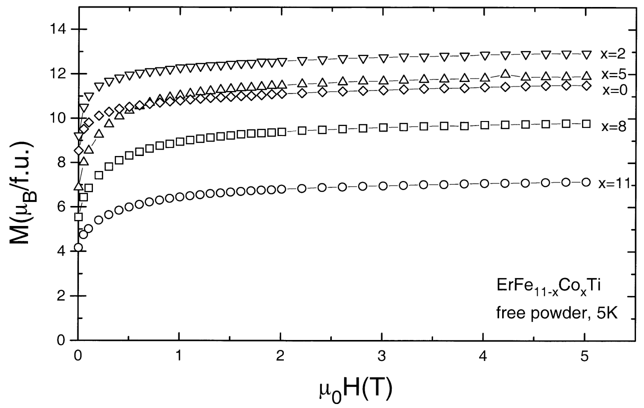

Fig. 4. Field dependence of the magnetic moment of $ErFe_{11-x}Co_xTi$ compounds, measured at 4.2 K on free powder particles with decreasing field.

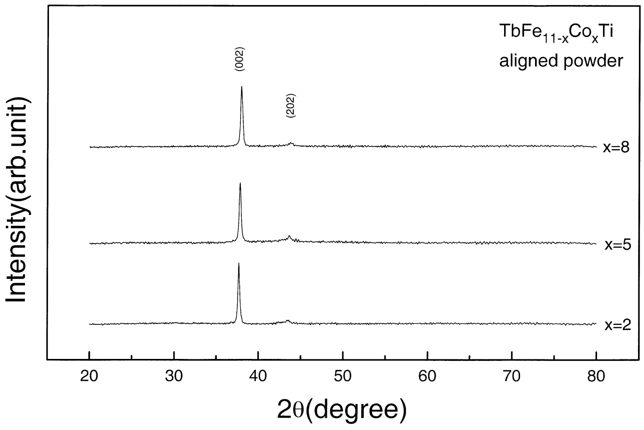

Fig. 5. Examples of X-ray diagrams obtained on magnetically aligned powder samples of $TbFe_{11-x}Co_xTi$ compounds.

magnetization of the latter compounds is shown in Figs. 6 and 7. From these data we derive that only the compound with $x=2$ has a spin-reorientation transition, albeit at a much lower temperature ($T_{SR}=195$ K) than the transition reported for the compound with $x=0$ ($T_{SR}=339$ K [5]).

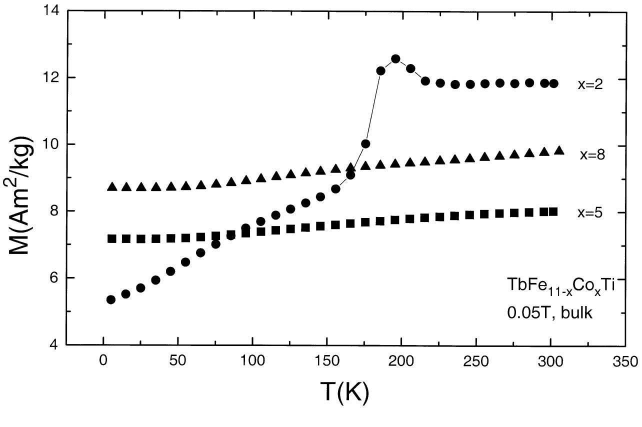

Fig. 6. Temperature dependence of the magnetisation of $TbFe_{11-x}Co_xTi$ compounds, measured below room temperature in a field of 0.05 T.

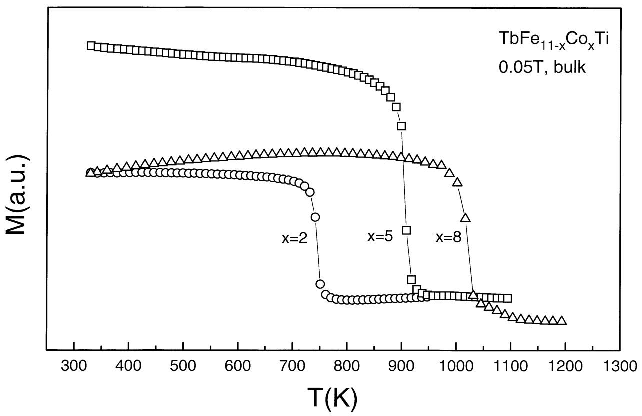

Fig. 7. Temperature dependence of the magnetisation of $TbFe_{11-x}Co_xTi$ compounds, measured above room temperature in a field of 0.05 T.

The values of the Curie temperatures and spontaneous moments derived from our data for the $TbFe_{11-x}Co_xTi$ compounds are listed in Table 2.

3.3. $YFe_{11-x}Co_xTi$

In order to determine the magnetic behaviour of the 3d sublattice in the various $TbFe_{11-x}Co_xTi$ compounds we have also studied the magnetic properties of several $YFe_{11-x}Co_xTi$ compounds. Both $YFe_{11}Ti$ and $YCo_{11}Ti$ have been reported to have the easy magnetization direction parallel to the *c* direction at room temperature [2]. As can be seen in Fig. 8, this is also the case for the compounds with $x=2$ and 5. However, the compound with $x=8$ has its easy direction perpendicular to *c*. From the temperature dependence of the magnetization shown in Fig. 9, it can be derived that the latter compound exhibits a spin reorientation transition ($T_{SR}=602$ K), suggesting that also the compound with $x=8$ has an easy magnetization direction parallel to the *c* direction at higher temperatures. The values of the Curie temperatures and spontaneous moments derived from our data for the $YFe_{11-x}Co_xTi$ compounds are listed in Table 3. As in the two previous series one may notice that the concentration dependence of the 3d sublattice moment shows a shallow maximum, reminiscent of the maximum found in the Pauling–Slater curve. Such maxima were also observed in the concentration dependence of the Fe hyperfine fields determined by Mössbauer spectroscopy [6].

4. Discussion

Before discussing the competition between the R and 3d sublattice anisotropies we first wish to discuss some peculiarities associated with the former anisotropy at sufficiently low temperatures.

Crystal-field theory gives the following expression for

Table 2
The spontaneous moment M_0 (5 K), the T-sublattice moment M_T (5 K), the Curie temperature T_C, the spin reorientation temperature T_{SR} and the easy magnetization direction (EMD) of the $TbFe_{11-x}Co_xTi$ compounds

$TbFe_{11-x}Co_xTi$ (x)	M_0 (5 K) μ_B/f.u.	M_T (5 K) μ_B/f.u.	T_C (K)	T_{SR} (K)	EMD at 295 K
0	11.20[a]	20.20[a]	554[a]	339[a]	Easy-plane
2	12.04	21.04	743	195	Easy-axis
5	11.56	20.56	903	–	Easy-axis
8	8.91	17.91	1018	–	Easy-axis
11	6.16[b]	15.16[b]	–	–	Easy-axis

[a] Taken from Ref. [5].

[b] Taken from Ref. [3].

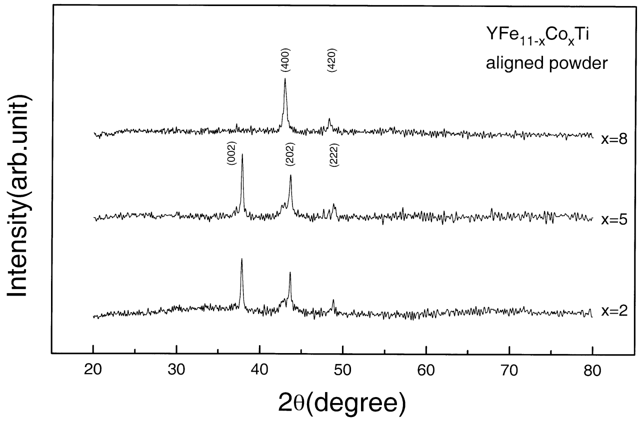

Fig. 8. Examples of X-ray diagrams obtained on magnetically aligned powder samples of $YFe_{11-x}Co_xTi$ compounds.

the first- and second-order anisotropy constant of the R sublattice:

$$K_1^R = -2/3\alpha_J\langle r^2\rangle A_2^o\langle O_2^o\rangle - 5\beta_J\langle r^4\rangle A_4^o\langle O_4^o\rangle - 21/2\,\gamma_J\langle r^6\rangle A_6^o\langle O_6^o\rangle \quad (1)$$

$$K_2^R = 7/8\,[5\,\beta_J\langle r^4\rangle A_4^o\langle O_4^o\rangle + 27\gamma_J\langle r^6\rangle A_6^o\langle O_6^o\rangle] \quad (2)$$

Roughly speaking, the crystal-field terms of order 2, 4 and 6 decay with temperature as the 3rd, 10th and 21st power of the reduced R-sublattice magnetization, respectively. Therefore, the crystal-field terms of order 4 and 6 need generally not be considered at higher temperatures, above 50 K say. In $ErFe_{11}Ti$, the Fe sublattice, as well as the second- and fourth-order crystal field term, favour an easy c axis. However, the sixth-order term is exceptionally large for Er due to its large (positive) γ_J value. This leads to a situation that an easy c axis is only observed at sufficiently high temperatures. Upon lowering of the temperature, the sixth-order term gains more importance, leading to a negative value of K_1^R and consequently to easy-cone anisotropy ($0 < -K_1 < 2K_2$). This means that the spin reorientation in this compound is driven by the strong difference in temperature variation of the Er crystal-field terms and not by a competition between R- and 3d-sublattice anisotropies [4]. We attribute the spin reorientation observed for $ErFe_9Co_2Ti$ in the same temperature interval (Fig. 2) to a similar competition between the various Er crystal field contributions.

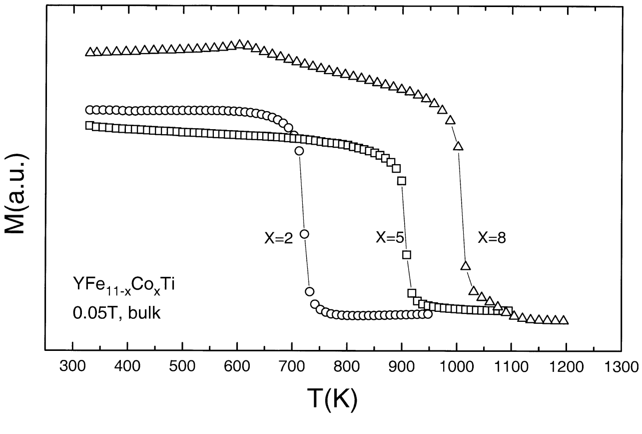

Fig. 9. Temperature dependence of the magnetisation of $YFe_{11-x}Co_xTi$ compounds, measured above room temperature in a field of 0.05 T.

Concentrating on the temperature range (above 50 K) where only the second-order crystal-field term needs to be considered, we can use the values $A_2^o\langle r^2\rangle = -25$ K for $RFe_{11}Ti$ and $A_2^o\langle r^2\rangle = 130$ K for $RCo_{11}Ti$ [2] to construct a bar diagram for the preferred Er-sublattice-moment direction as shown in the bottom part of Fig. 10. For simplicity we have assumed here that $A_2^o\langle r^2\rangle$ varies linearly with x between the two mentioned values, implying a sign reversal of K_1^R around $x = 2$. We have represented the easy-moment direction of the 3d sublattice in $RFe_{11-x}Co_xTi$ by means of the bar diagram in the middle

Table 3
The spontaneous moment M_0 (5 K), the T-sublattice moment M_T (5 K), the Curie temperature T_C, the spin-reorientation temperature T_{SR} and the easy magnetization direction (EMD) of the $YFe_{11-x}Co_xTi$ compounds

$YFe_{11-x}Co_xTi$ (x)	M_0 (5 K) μ_B/f.u.	T_C (K)	T_{SR} (K)	EMD at 295 K
0	19.0[a]	524[a]	–	Easy-axis
2	20.37	722	–	Easy-axis
5	20.35	905	–	Easy-axis
8	18.09	1008	602	Easy-plane
11	15.16[b]	–	–	Easy-axis

[a] Taken from Ref. [4].

[b] Taken from Ref. [3].

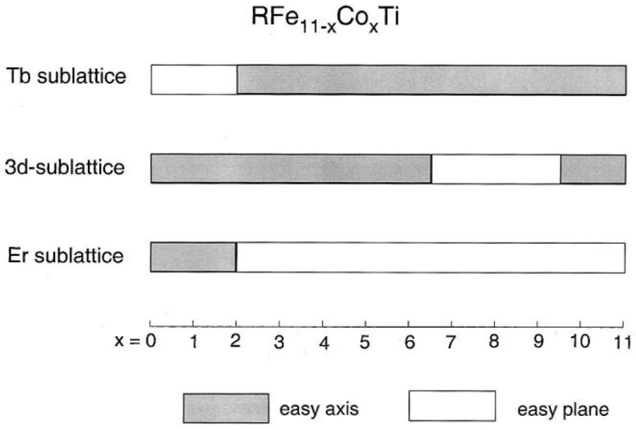

Fig. 10. Bar diagrams showing the concentration dependence of the easy magnetization direction of $RFe_{11-x}Co_xTi$ compounds expected for the R=Tb (top) and R=Er (bottom).

part of Fig. 10, using the X-ray data obtained at room temperature for several $YFe_{11-x}Co_xTi$ compounds and using the well established fact that the easy moment direction in $YCo_{11}Ti$ is parallel to the *c* axis [7]. Because we found that the compound with $x=8$ has an easy moment direction perpendicular to the *c* axis at room temperature, we have indicated this in the bar diagram by an easy plane range around this concentration, with the boundaries of this range fixed somewhat arbitrarily at $x=6.5$ and 9.5.

Comparing the two lower bar diagrams in Fig. 10, we are now able to discuss the possibility of spin reorientation transitions associated with the competition between the Er- and 3d-sublattice anisotropies. With increasing temperature, we expect the occurrence of such transitions when there is a difference in easy direction between the lower bar diagram (representing the dominance of the Er-sublattice anisotropy at low temperatures) and the middle bar diagram (representing the dominance of the 3d sublattice anisotropy at higher temperatures). With increasing temperature, transitions from easy plane (EP) to easy axis (EA) are then expected in the concentration ranges $2 \leq x \leq 6.5$ and $x \geq 9.5$. The spin reorientations observed for the compounds with $x=5$ ($T_{SR}=295$ K) and $x=11$ ($T_{SR}=125$ K) fall into this category. According to the bar diagrams in Fig. 10, the competition between the Er- and 3d-sublattice anisotropies is not expected to lead to an EP-to-EA transition in the compound with $x=8$. The transition observed for this compound at $T_{SR}=663$ K has therefore to be of a different origin. In fact, the data listed in Table 3 show that the 3d sublattice itself gives rise to an EP-to-EA transition in this temperature range ($T_{SR}=602$ K). It can be seen in the lower bar diagram in Fig. 10 that the Er sublattice favours an easy plane in this concentration range. This means that the replacement of Y by Er in YFe_3Co_8Ti stabilizes the EP configuration and destabilizes the EA configuration. As a consequence the EP-to-EA transition in $ErFe_3Co_8Ti$ ($T_{SR}=663$ K) occurs at a higher temperature than in YFe_3Co_8Ti ($T_{SR}=602$ K).

Because the second order Stevens factor of Tb is of a different sign than that of Er, the Tb sublattice anisotropy behaves opposite to that of Er. This has been expressed in the bar diagram shown in the top part of Fig. 10. With increasing temperature, we expect the occurrence of spin-reorientation transitions when there is a difference in easy direction between the upper bar diagram (representing the dominance of the Tb-sublattice anisotropy at low temperatures) and the middle bar diagram (representing the dominance of the 3d-sublattice anisotropy at higher temperatures). There are two concentration ranges that qualify in this respect. In the range below $x=2$, we expect EP-to-EA transitions, whereas in the range around $x=8$ we expect EA-to-EP transitions. The spin reorientations observed for the compounds with $x=0$ ($T_{SR}=339$ K) and $x=2$ ($T_{SR}=195$ K) agree with the predictions made for the former range. Surprisingly, no transition is observed for the compound with $x=8$ belonging to the latter range. However, we have to bear in mind that the bar diagram in the middle part of Fig. 10 represents the 3d-sublattice behaviour at room temperature (EP) while above 602 K (see Table 3) the easy direction is of the same type as favoured by the Tb-sublattice (EA). This means that the presence of Tb stabilizes the EA range and destabilizes the EP range and hence shifts the transition at 602 K towards lower temperatures. The fact that no transition is observed at any temperature below 602 K means that the Tb-sublattice anisotropy dominates the 3d-sublattice anisotropy in the whole temperature range. This is in agreement with the observation made by X-ray diffraction that at room temperature one has an easy magnetization direction corresponding to EA for $TbFe_3Co_8Ti$, compared to EP for YFe_3Co_8Ti.

5. Concluding remarks

We have investigated the occurrence of spin reorientations in several series of $RFe_{11-x}Co_xTi$ compounds and we have shown that these fall into three different categories. Spin-reorientation transitions observed at temperatures far below room temperature can originate mainly from a competition between the various crystal-field terms associated with the crystal-field-induced R sublattice anisotropy. At temperatures far above room temperature, spin-reorientation transitions may arise as a consequence of a sign change of the 3d-sublattice anisotropy as a function of temperature. In the intermediate temperature range, spin-reorientation transitions are generally the result of a competition between the R-sublattice anisotropy and 3d-sublattice anisotropy.

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