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Hyperfine interactions and crystal site occupancies in $\text{RTiFe}_{11-x}\text{Co}_x$ (R=Y, Dy and Er) as seen by Mössbauer spectroscopy

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Abstract

$\text{RTiFe}_{11-x}\text{Co}_x$ (R=Y, Dy, Er) systems have been studied by ^{57}Fe Mössbauer spectroscopy at 295 and 78 K. The composition dependencies of hyperfine interaction parameters and the relative occupancies of Fe crystal sites by Co atoms were derived from the spectra. It was found that Co atoms strongly avoid the 8i sublattice and strongly prefer the 8f and 8j sites for the three studied systems. Some anomalies in behaviour of the quadrupole interaction were observed for $\text{ErTiFe}_{11-x}\text{Co}_x$ system which can be attributed to spin reorientation transition. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

After the development of permanent magnets based on the ternary compound $\text{Nd}_2\text{Fe}_{14}\text{B}$, the next step in the search for new magnetic materials was the ternary system of the ThMn_{12} -type. Although pure RFe_{12} does not exist for any rare earth, this phase can be stabilised when Ti, V, Cr, Mo, W or Al are substituted for Fe [1,2].

It has been reported that Ti is the element that requires the lowest concentration to stabilise the ThMn_{12} structure [3], thus making $\text{R}(\text{Ti}, \text{Fe})_{12}$ compounds attractive due to the possibility of obtaining large magnetisation, large uniaxial anisotropy and high Curie temperature. The RTiFe_{11} compounds crystallise in the tetragonal structure with space group of $I4/mmm$ [4]. In this structure, the rare earth ion occupies the 2a crystallographic site and Fe atoms occupy the 8i (5, 4, 4), 8j (4, 2, 4) and 8f (4, 4, 2) sites while the Ti atoms reside only in the 8i site [5,6]. The number of 8i, 8j and 8f nearest neighbours of each Fe site are given in parentheses. In order to improve the understanding of the behaviour of Co and Fe in RTiFe_{11} -substituted alloys, several groups have studied the replacement of Fe by Co in this system synthesised with various rare earths [7–17]. In $\text{YTi}(\text{Fe}_{0.5}\text{Co}_{0.5})_{11}$ the Co atoms are

observed to have a preferential occupation of the 8f and 8j sites [5].

The magnetic phase diagrams for $\text{RTiFe}_{11-x}\text{Co}_x$ compounds [9] show complex structures as a consequence of the competition between magnetic anisotropies of Fe and Co, which gives rise to spin reorientation transitions.

^{57}Fe Mössbauer spectroscopy can give valuable microscopic information about Co site occupancies so we have studied the Mössbauer spectra of $\text{RTiFe}_{11-x}\text{Co}_x$ (R=Y, Dy, Er) compounds, trying to establish the site preference of the Co atoms in systems synthesised with rare earths which have different signs of the Stevens coefficient, α_j (for Y $\alpha_j=0$, for Dy $\alpha_j<0$ and for Er $\alpha_j>0$).

2. Experimental details

The $\text{RTiFe}_{11-x}\text{Co}_x$ (R=Y, Dy, Er) were prepared by melting constituent elements of purity 99.9 wt.% or better in a 450 kHz induction furnace. To ensure homogeneity the alloys were melted several times in a high purity argon atmosphere. After melting, the samples were wrapped in Ta foil, sealed in an evacuated quartz tube and heat-treated at temperatures ranging from 1000 to 1200°C for several days to 2 weeks. They were then water quenched to room temperature. The X-ray and thermomagnetic analysis proved the single-phase integrity of all the materials. However, the Mössbauer spectra indicate a small amount

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of iron impurity (about 3%) in the sample YTiFe_{11} . This impurity was subtracted from the spectra by the numerical procedure. The ^{57}Fe Mössbauer absorption spectra were recorded at 295 and 78 K using a $^{57}\text{Co}(\text{Cr})$ source and a computer driven constant acceleration spectrometer. A high purity metallic iron foil was used to calibrate the velocity scale. Isomer shifts were established with respect to the centre of gravity of the room temperature iron Mössbauer spectrum.

3. Data analysis

The Mössbauer spectra of $\text{RTiFe}_{11-x}\text{Co}_x$ ($\text{R}=\text{Y}, \text{Dy}, \text{Er}$) intermetallic compounds were analysed using three Zeeman subspectra corresponding to three non-equivalent crystal sites occupied by Fe. Each subspectrum was characterised by the following parameters: hyperfine field – H , isomer shift – IS , quadrupole interaction – QS and a subspectrum contribution – c . Additionally, there were (common to all the subspectra) three line widths and one relative intensity ratio of lines in the Zeeman subspectrum.

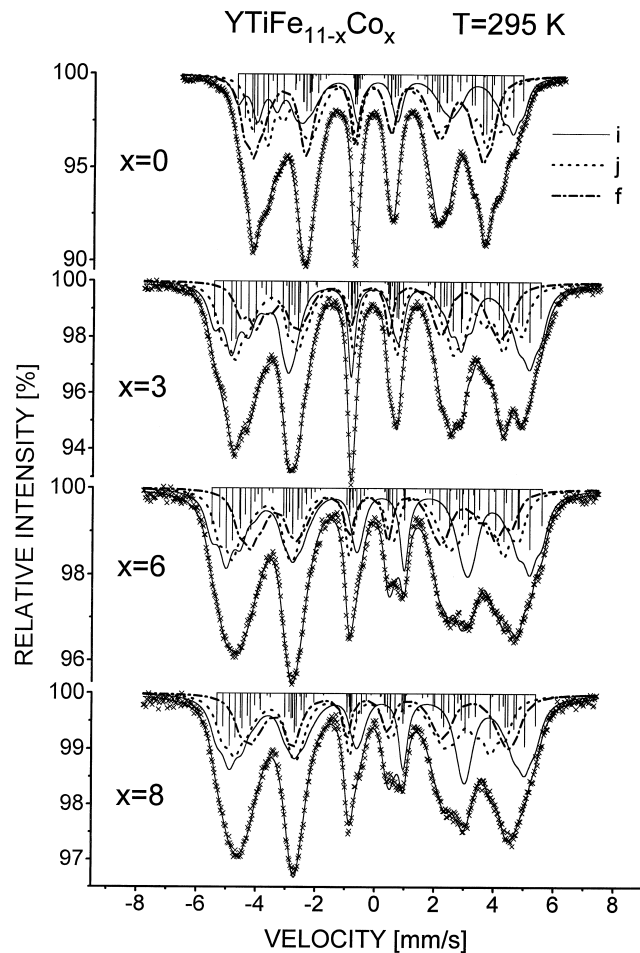


Fig. 1. The typical ^{57}Fe Mössbauer absorption spectra recorded at 295 K for the $\text{YTiFe}_{11-x}\text{Co}_x$ intermetallic compounds.

For RTiFe_{11} ($\text{R}=\text{Y}, \text{Dy}, \text{Er}$) intermetallic compounds Ti and Fe randomly share the 8i sites and therefore the Fe atoms in the three types of sites are subject to different atomic and magnetic environments due to the various numbers of Ti atoms in the Fe neighbourhood. As a consequence, the Zeeman sextets of the 8i, 8j and 8f sites are split into three sets of subspectra whose intensities are related to the probability, $P_n(k)$, of finding k nearest neighbour Ti atoms in a set of n 8i nearest neighbour atoms of a considered ($m=i, j, f$) Fe crystal site. The probabilities $P_n(k)$ are calculated from a binomial distribution law [18,19]:

$$P_n(k) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k},$$

where p is the relative fraction of Ti atoms in the 8i site and k varies in steps of one from 0 to n . The fraction p was

Table 1

Hyperfine interaction parameters and site occupancies by Co atoms derived from Mössbauer spectra recorded at 78 and 295 K for $\text{YTiFe}_{11-x}\text{Co}_x$ ^a

x	Parameter	T [K]	Crystal site		
			8i	8j	8f
0	H	78	33.5	31.0	28.1
		295	29.5	26.6	24.2
	IS	78	0.128	0.049	0.099
		295	0.014	0.131	0.186
	QS	78	0.108	0.134	0.142
		295	0.09	4.124	0.162
P	78	0	0	0	
	295	0	0	0	
3	H	78	35.5	33.2	30.6
		295	34.1	31.2	28.3
	IS	78	0.067	0.049	0.092
		295	0.016	0.105	0.167
	QS	78	0.038	0.080	0.122
		295	0.006	0.126	0.216
P	78	6.3	29.8	38.9	
	295	1.0	25.0	49.0	
6	H	78	35.3	32.0	29.2
		295	34.3	31.2	28.4
	IS	78	0.128	0.081	0.056
		295	0.059	0.167	0.139
	QS	78	0.100	0.160	0.344
		295	0.076	0.120	0.252
P	78	27.1	48.7	74.2	
	295	24.1	58.7	67.2	
8	H	78	34.0	30.3	29.6
		295	33.1	29.5	28.7
	IS	78	0.129	0.085	0.059
		295	0.048	0.213	0.052
	QS	78	0.056	0.260	0.316
		295	0.028	0.280	0.314
P	78	43.3	69.2	87.5	
	295	43.4	75.2	81.3	

^a H [T] is the hyperfine magnetic field, IS [mm s^{-1}] is the isomer shift with respect to metallic iron at room temperature, QS [mm s^{-1}] is the quadrupole shift of the spectra lines: $[(V_0 - V_2) - (V_2 - V_4)]/2$, P (%) is the relative occupancy of the crystal sites by Co atoms. Errors: H (0.1 T), IS (0.008 mm s^{-1}), QS (0.008 mm s^{-1}), P (7%).

taken as $p=0.25$ since Ti atoms occupy the 8i site exclusively.

Taking into account five 8i nearest neighbours for the 8i site, four for the 8j site and four for the 8f site we have 16 subspectra out of which three subspectra have negligible intensity. Thus, we consider 13 subspectra in the full Mössbauer spectrum. We used this repartition to analyse the Mössbauer spectra. In the fitting procedure, the relative intensities of the different subspectra were set proportional to $P_n(k)$ for a given iron crystal site. The hyperfine field, the isomer shift and quadrupole interaction were assumed to change linearly with the number of Ti neighbours of the 8i, 8f and 8j crystal sites, according to [20]. We also studied the effect of the substitution of Co for Fe on the Mössbauer spectra. It was assumed that Co produces much smaller changes in the magnetic environments of the Fe nuclei than Ti, since Ti is non-magnetic, while Co is magnetically similar to Fe. Therefore, Co substitution should not give rise to further splitting of spectra. However, Co modifies the values of hyperfine field. Typical plots of the Mössbauer spectra are shown in Fig. 1 for four compositions ($x=0, 3, 6, 8$) of the $\text{YTiFe}_{11-x}\text{Co}_x$ com-

Table 2

Hyperfine interaction parameters and site occupancies by Co atoms derived from Mössbauer spectra recorded at 78 and 295 K for $\text{DyTiFe}_{11-x}\text{Co}_x$ ^a

x	Parameter	T [K]	Crystal site			
			8i	8j	8f	
1	H	78	35.6	31.4	29.8	
		295	31.5	29.1	26.7	
	IS	78	0.150	0.038	0.039	
		295	0.005	0.122	0.190	
	QS	78	0.002	0.066	0.066	
		295	0.082	0.100	0.148	
	P	78	3.0	7.6	14.4	
		295	0.9	12.2	12.0	
	3	H	78	36.0	32.1	30.2
			295	33.6	31.1	28.3
		IS	78	0.144	0.083	0.039
			295	0.006	0.120	0.171
QS		78	0.042	0.082	0.146	
		295	0.048	0.098	0.190	
P		78	2.86	30.1	42.1	
		295	0.2	24.1	50.7	
6		H	78	33.6	30.2	28.8
			295	32.3	29.7	27.5
		IS	78	0.112	0.086	0.015
			295	0.006	0.130	0.192
	QS	78	0.122	0.090	0.088	
		295	0.086	0.024	0.258	
	P	78	23.2	60.1	66.7	
		295	20.7	60.9	68.4	

^a H [T] is the hyperfine magnetic field, IS [mm s^{-1}] is the isomer shift with respect to metallic iron at room temperature, QS [mm s^{-1}] is the quadrupole shift of the spectra lines: $[(V_6 - V_3) - (V_2 - V_1)]/2$, P (%) is the relative occupancy of the crystal sites by Co atoms. Errors: H (0.1 T), IS (0.008 mm s^{-1}), QS (0.008 mm s^{-1}), P (7%).

Table 3

Hyperfine interaction parameters and site occupancies by Co atoms derived from Mössbauer spectra recorded at 78 and 295 K for $\text{ErTiFe}_{11-x}\text{Co}_x$ ^a

x	Parameter	T [K]	Crystal site			
			8i	8j	8f	
0	H	78	32.5	29.2	27.7	
		295	28.1	25.2	23.8	
	IS	78	0.081	0.009	0.111	
		295	0.010	0.106	0.236	
	QS	78	0.132	0.052	0.094	
		295	0.120	0.002	0.052	
	P	78	0	0	0	
		295	0	0	0	
	5	H	78	34.9	33.3	30.5
			295	33.1	30.2	27.7
		IS	78	0.190	0.050	0.104
			295	0.005	0.078	0.239
QS		78	0.060	0.766	0.150	
		295	0.100	0.248	0.004	
P		78	1.0	55.6	68.3	
		295	1.6	57.4	75.4	
7		H	78	33.9	31.5	29.6
			295	32.6	31.1	28.4
		IS	78	0.216	0.069	0.104
			295	0.146	0.009	0.200
	QS	78	0.010	0.896	0.174	
		295	0.006	0.666	0.228	
	P	78	24.5	75.5	77.0	
		295	20.0	76.6	78.5	
	9	H	78	33.2	31.6	28.4
			295	31.8	30.9	28.5
		IS	78	0.170	0.104	0.094
			295	0.102	0.067	0.216
QS		78	0.140	0.582	0.324	
		295	0.070	0.460	0.180	
P		78	54.4	82.7	87.9	
		295	56.2	83.7	85.1	

^a H [T] is the hyperfine magnetic field, IS [mm s^{-1}] is the isomer shift with respect to metallic iron at room temperature, QS [mm s^{-1}] is the quadrupole shift of the spectra lines: $[(V_6 - V_3) - (V_2 - V_1)]/2$, P (%) is the relative occupancy of the crystal sites by Co atoms. Errors: H (0.1 T), IS (0.008 mm s^{-1}), QS (0.008 mm s^{-1}), P (7%).

pounds, while the fitted parameters are collected in Tables 1–3 for all series investigated.

Our main goal was to establish the mode of occupation of the Fe crystal sublattices by Co atoms. This was done by observing the influence of the replacement of Fe by Co atoms on the ^{57}Fe Mössbauer spectra. The relative occupancies,

$$p_m = 0.25\{a_m - (11 - x)c_m\},$$

of $m=i, j, f$ crystal sites by Co atoms were determined from the relative contributions c_m of each sublattice to the total area of the Mössbauer spectrum. x is the sample composition parameter, while the total occupancies a_m of the iron sites are three for $m=i$ and four for $m=j$ and f .

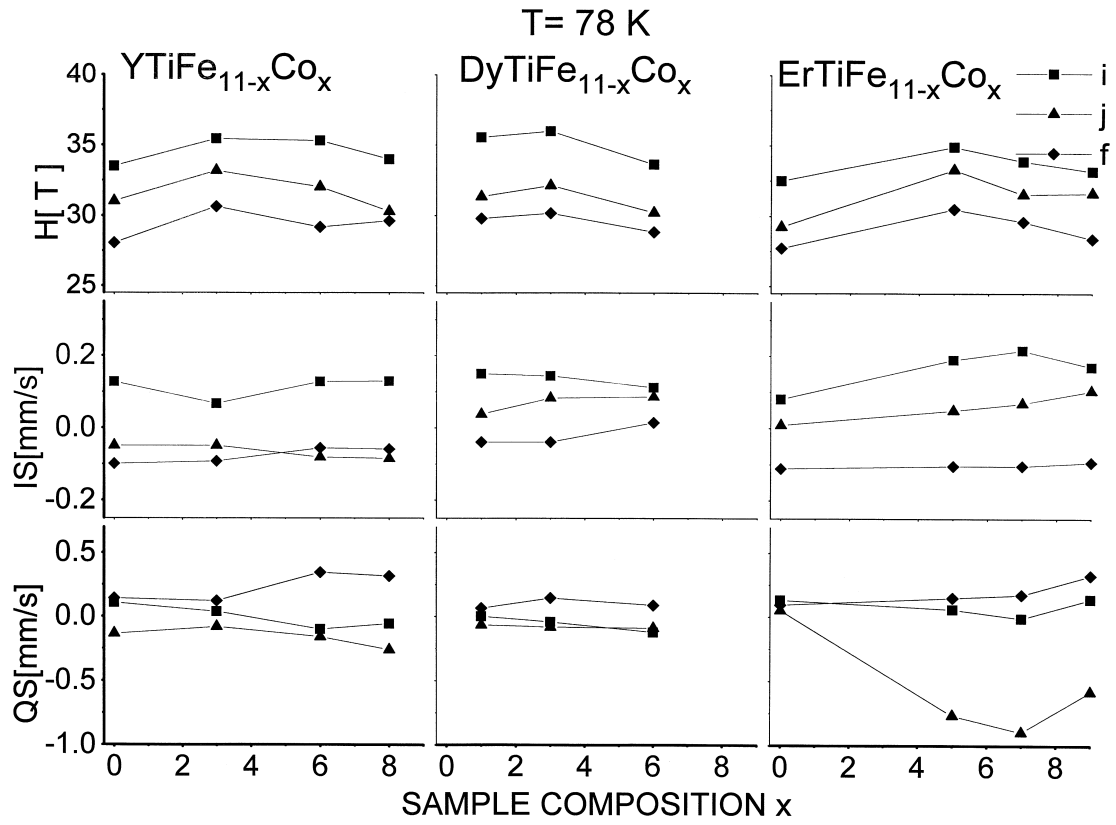


Fig. 2. Composition dependencies of the hyperfine magnetic field, the isomer shift and the quadrupole interaction for $RTiFe_{11-x}Co_x$ ($R=Y, Dy, Er$) at 78 K.

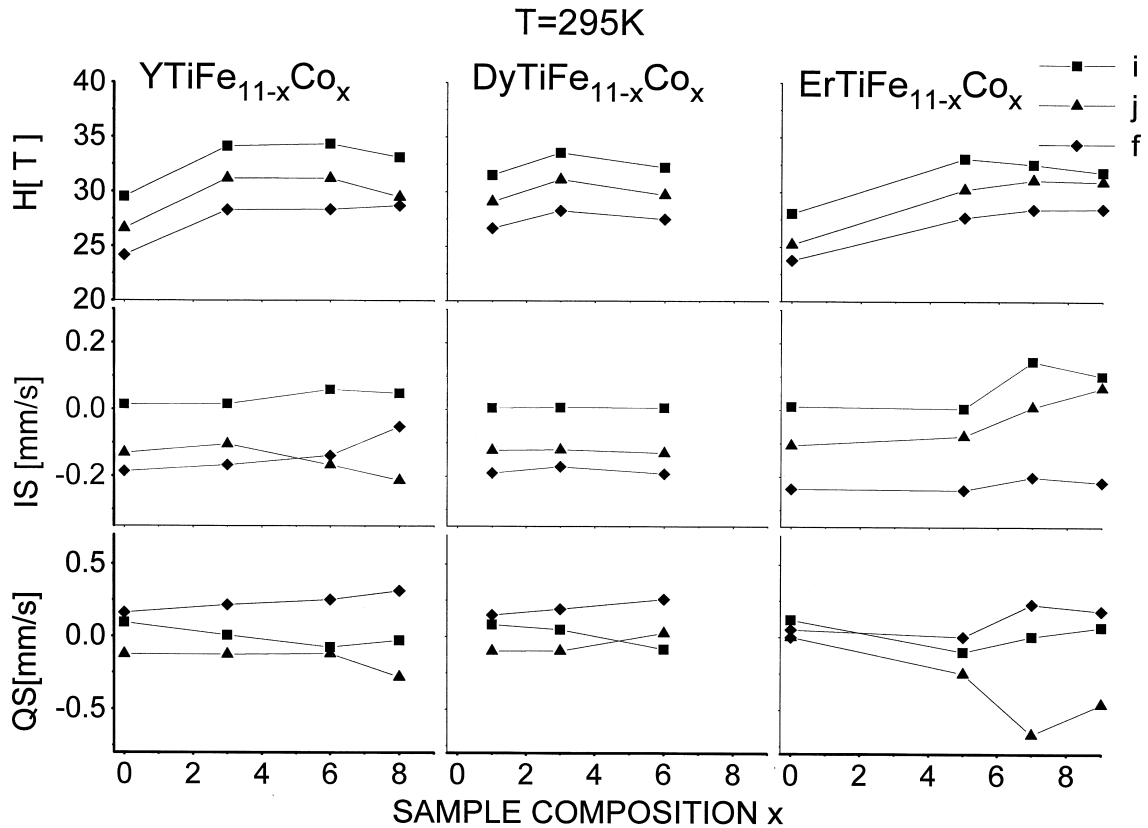


Fig. 3. Composition dependencies of the hyperfine magnetic field, the isomer shift and the quadrupole interaction for $RTiFe_{11-x}Co_x$ ($R=Y, Dy, Er$) at 295 K.

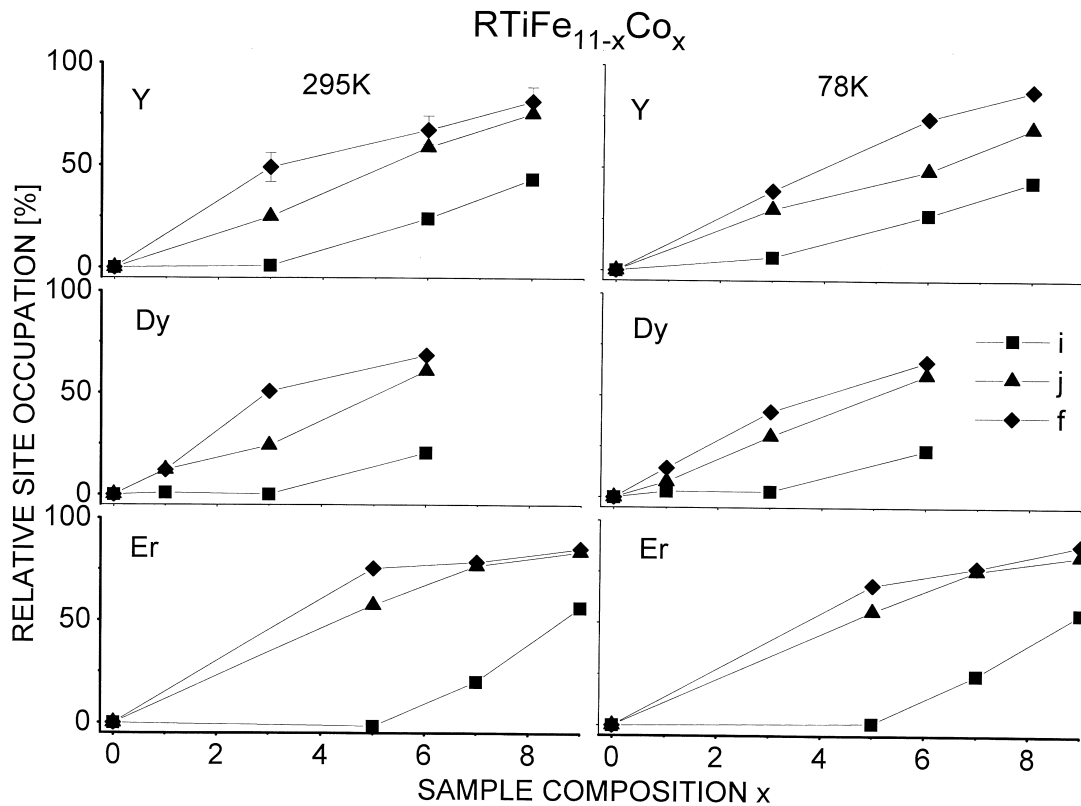


Fig. 4. The relative occupancies of the crystal sublattices by Co atoms for $\text{RTiFe}_{11-x}\text{Co}_x$ ($R=\text{Y, Dy, Er}$) at 295 and 78 K.

4. Results and discussion

Typical Mössbauer spectra are shown in Fig. 1 for the $\text{YTiFe}_{11-x}\text{Co}_x$ series. The composition dependencies of the hyperfine interaction parameters derived from the spectra recorded for all three series investigated at 78 and 295 K are shown in Figs. 2 and 3, respectively. The attribution of hyperfine fields to the crystal sublattices was based on the nearest neighbours argumentation: the largest field is attributed to the 8i crystal site which has the largest number of the Fe nearest neighbours (nine). The 8j and 8f sites have the same number of the Fe nearest neighbours (eight). The average Fe–Fe distances in the RTiFe_{11} are 2.49, 2.69 and 2.57 Å for 8f, 8i, 8j sites, respectively [21]. Therefore, we may expect a larger hyperfine field in the 8f sites than in the 8j sites.

We fitted the Mössbauer spectra under the following assumptions: for the hyperfine field of the three different Fe sites we took $H(8i) > H(8f) > H(8j)$, in agreement with the sequence of the magnetic moments determined by neutron diffraction data on $\text{YTi}(\text{Fe}_{0.5}\text{Co}_{0.5})_{11}$: 8i ($2.56 \mu_B$), 8f ($2.02 \mu_B$) and 8j ($1.84 \mu_B$) [5]. We chose this assignment for the whole $\text{RTiFe}_{11-x}\text{Co}_x$ ($R=\text{Y, Dy, Er}$) series, in accordance with Refs. [10,18]. As shown in Figs. 2 and 3, the introduction of Co into the Fe sublattice causes an increase in the values of hyperfine field for all crystal sites. Such behaviour was observed in both temperatures (78 and 295 K), for all studied $\text{RTiFe}_{11-x}\text{Co}_x$ ($R=\text{Y, Dy, Er}$) compounds. The substitution of Co for Fe

has a minute influence on IS and QS in three investigated series as shown in Figs. 2 and 3. Only some anomaly in behaviour of quadrupole interaction for the 8j site in the $\text{ErTiFe}_{11-x}\text{Co}_x$ system is observed. It can be attributed to spin reorientation transition, according to the spin phase diagram [9].

The relative occupancies of $m=i, j$ and f crystal sublattices by Co atoms, determined from contributions of each sublattice to the area of the Mössbauer spectra recorded at 78 and 295 K are plotted in Fig. 4. It is clearly seen that in all three studied systems, independent of the type of R element, the Co atoms strongly avoid the 8i sublattice and strongly prefer the 8f and 8j sites. The results from both temperatures are in agreement within the limits of the experimental error.

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