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Abstract:

We present theoretical investigations on the electronic and magnetic properties of the $RFe_{11-x}Co_xTi$ and $R_yZr_{1-y}Fe_{11}Ti$ ($R = Y$ and Pr ; $y = 0 - 0.2$; $x = 0 - 3$; $z = 1$) alloys describing the dependence of the magnetic properties (magnetic moments, magneto-crystalline anisotropy, exchange-coupling parameters) on the R/Zr and Fe/Co ratios. The Co for Fe doping in $YFe_{11-x}Co_xTi$ maximize the calculated total magnetic moment and magneto-crystalline anisotropy energy (MAE) for $x = 1$. Also, for the $YFe_{11}Ti$ alloy an improvement of the magnetic properties (total magnetic moment, MAE) important for permanent magnets applications was found, in agreement with the experimental findings. The calculated exchange-coupling parameters for the first neighbours of each Fe site ($\delta i, \delta j$ and δf) show an increase by increasing the Co content or by adding C in the interstitial 2b sites, suggesting higher Curie temperatures for Co and C doped $YFe_{11}Ti$ -based alloys. On the other hand, the Zr for Y substitution in $Y_zZr_{1-z}Fe_{11}Ti$ ($y = 0 - 0.2$) increases MAE without a noticeable decrease of the calculated total magnetic moment. Also, the Fe δi -Fe δj and Fe δi -Fe δf exchange coupling parameters J_{ij} with first neighbours decrease by Zr doping, in contrast to J_{ij} of the other Fe spin pairs which show opposite trend. The experimental measurements are in progress to test the theoretical findings.

Introduction:

The R-T intermetallic compounds (R-rare earth, T- transition metal) have been studied last decades due to their magnetic properties compatible with the permanent magnet requirements. Their sublattices are responsible for magnetic properties, the enhanced anisotropy being associated with the R-sublattice, whilst the T-sublattice is usually associated with high magnetization.

Between the R-T intermetallic compounds, the 1:12 compounds with general formula $R(Fe,M)_2$ have been intensely studied. The partial substitution of Fe with M (Ti, V, Cr, Mo, W or Al) has been used to stabilize the phase. The recent research has been directed to obtain low-cost magnetic materials by reducing the critical rare earth content [1]. In this direction, Y and Zr for R substitutions were employed in order to decrease the rare-earth content and in several cases the initial magnetic properties were preserved.

Moreover, the partial Co for Fe substitution has been employed in $Sm(Fe,Ti)_{12}$ [2] in order to increase the magnetization of the samples and to enhance their Curie temperatures. By simultaneous Zr for Sm and Co for Fe substitutions, the phase with $(Sm_{0.8}Zr_{0.2})(Fe_{0.75}Co_{0.25})_{11.5}Ti_{0.5}$ composition showed superior magnetic properties at high temperatures to those of $Nd_2Fe_{14}B$ [3].

Adverse effects have been reported too, as for $CeFe_3Co_2Ti$, where the low value of coercivity do not recommend these compounds for permanent magnet applications [4]. Other possible method to enhance coercivity and magnetization of $R(Fe,M)_2$ is the light elements (H, B, C) interstitial addition [4].

Another route to build lower costs permanent magnets is by the replacement of expensive rare earth elements (as Sm and Nd) with less expensive Ce. For example, in $(Sm, Zr)Fe_{12-x}M_x$ ($M = Zr, Ti, Co$) compounds, electron doping due to Zr and Ce for Sm substitution can be exploited to gain both structure stability and magnetization [5]. Both of these happens because of the particular electronic structure with the hybridization between the 3d-electron band from the Fe sublattices and the 5d-electron band from the rare-earth sublattice [5].

In the present paper we present our investigations on the magnetic properties by Co, Zr and C doping in $RFe_{11}Ti$ -based alloys ($R = Y, Pr$). The calculated total magnetic moments, MAE and the exchange coupling parameters are analysed in order to propose for subsequent experimental investigations those substitutions which would enhance the magnetization, MAE and Curie temperature, respectively.

Theoretical details:

Electronic band structure calculations have been done in the framework of the Density Functional Theory [6] using the SPRKKR band structure method. The method is based on the KKR-Green's function formalism that makes use of multiple scattering theory [7].

- The fully relativistic approach has been employed, i.e., all relativistic effects have been taken into account, including the spin-orbit coupling, for ferromagnetic and antiferromagnetic spin configurations.
- The angular momentum expansion of the basis functions was taken up to $l = 3$ for rare earth elements and $l = 2$ for Fe, Co, Zr and Ti.
- The exchange and correlation effects have been accounted for by means of the generalized gradient approximation with the parametrization of Perdew et al. (GGA-PBE) [8].
- The substitutional disorder in the system has been treated within the Coherent Potential Approximation (CPA) theory [10].
- Full potential approach has been used for self-consistent band structure calculations.

Additionally, the study of the magnetic anisotropy has been performed by calculating the magnetic torque acting on the magnetic moment \vec{m}_i of the atomic site i , with a unit vector $\vec{e}_i = \vec{m}_i/|\vec{m}_i|$ oriented along the magnetization direction \vec{M} [11,12]. As the component of the magnetic torque with respect to axis \hat{u} defined by the polar angles θ and φ is $T_{\hat{u}}(\theta, \varphi) = -\partial E(\vec{M}(\theta, \varphi))/\partial \theta$, the calculated magnetic torque is $T_{\hat{u}}(\pi/4, 0) = E_{[100]} - E_{[001]}$ [12].

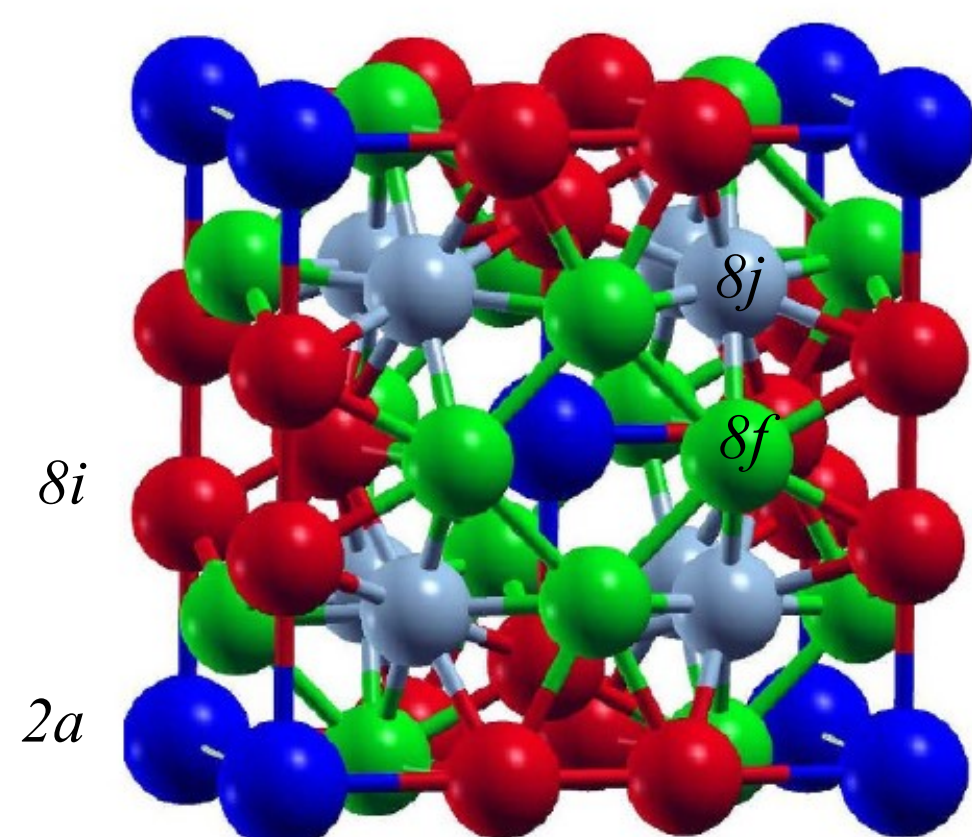
By classical Heisenberg Hamiltonian described by the expression:

$$H_{ex} = - \sum_{i,j} J_{ij} \vec{e}_i \cdot \vec{e}_j$$

with the summation performed on all lattice sites i and j and \vec{e}_i, \vec{e}_j - the unit vectors of magnetic moments on sites i and j , respectively. The J_{ij} is the exchange coupling parameter for the corresponding magnetic moments calculated using the expression of Liechtenstein [13] based on the magnetic force theorem.

Crystal structure

- Fe atoms sit on 3 inequivalent crystal sites ($\delta i, \delta j$ and δf) whilst the R atoms sit on 2a sites.
- By Ti for Fe substitution, the Ti atoms occupy preferentially the δi sites [14].
- The Co atoms occupy preferentially sites in the sequence $\delta j > \delta f > \delta i$ [4].
- The interstitial dopants (H, C and B) sit on the 2b sites [4, 14].



ThMn₁₂ structure (space group $I4/mmm$)

Magnetic moments

	$YFe_{11}Ti$		$YFe_{10}CoTi$		YFe_9Co_2Ti		YFe_8Co_4Ti		$YFe_{11}TiC$		$Y_{0.9}Zr_{0.1}Fe_{11}Ti$		$Y_{0.8}Zr_{0.2}Fe_{11}Ti$		
	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	
Y	-0.36	-	-0.35	-	-0.34	-	-0.34	-	-0.28	0.00	Y	-0.36	-	-0.36	0.00
Fe δi	2.24	0.06	2.53	0.06	2.55	0.06	2.57	0.06	2.54	0.06	Zr	-0.70	0.01	-0.70	0.01
Ti δi	-0.96	0.01	-1.0	0.01	-0.99	0.01	-0.98	0.01	-0.97	0.01	Fe δi	2.24	0.06	2.24	0.06
Fe δj	2.17	0.06	2.21	0.06	2.22	0.06	2.22	0.06	1.92	0.04	Ti δi	-0.95	0.01	-0.94	0.01
Co δj			1.43	0.09	1.43	0.09	1.43	0.09			Fe δj	2.17	0.06	2.17	0.06
Fe δf	1.85	0.04	1.97	0.05	2.07	0.05	2.12	0.05	2.21	0.05	Fe δf	1.87	0.04	1.88	0.04
C 2b									-0.18	-	C	-0.21	-	-	-
Total	21.49	0.58	22.13	0.66	21.87	0.72	21.34	0.81	22.75	0.57	Total	21.52	0.59	21.52	0.59

Table 1. Calculated magnetic moments (in Bohr magnetons μ_B) for the $YFe_{11-x}Co_xTi$, $YFe_{11}TiC$ and $Y_{1-z}Zr_zFe_{11}Ti$ ($z = 0.1, 0.2$) alloys.

	$GdFe_{11}Ti$		$GdFe_{10}CoTi$		$GdFe_9Co_2Ti$		$GdFe_8Co_4Ti$		$GdFe_{11}TiC$		$Gd_{0.9}Zr_{0.1}Fe_{11}Ti$		$Gd_{0.8}Zr_{0.2}Fe_{11}Ti$		
	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	
Gd	-7.66	0.02	-7.66	0.02	-7.64	0.01	-7.64	0.01	Gd	-7.44	0.01	-7.66	0.02	-7.67	0.02
Fe δi	2.35	0.05	2.37	0.06	2.38	0.07	2.40	0.07	Zr			-1.03	0	-1.03	0
Ti δi	-0.98	0	-0.98	0.01	-0.97	0.01	-0.96	0.02	Fe δi	2.64	0.05	2.34	0.05	2.34	0.05
Fe δj	2.37	0.05	2.40	0.06	2.43	0.06	2.45	0.06	Ti δi	-0.95	0.01	-0.98	0.01	-0.97	0.01
Co δj			1.56	0.10	1.58	0.10	1.58	0.10	Fe δj	1.72	0.03	2.37	0.06	2.37	0.06
Fe δf	1.95	0.04	2.04	0.04	2.12	0.05	2.19	0.05	Fe δf	2.46	0.05	1.96	0.03	1.96	0.04
Co δf			1.48	0.08	1.50	0.08	1.52	0.09	C	-0.21	-	-	-	-	-
Total	15.69	0.51	15.50	0.60	15.28	0.72	14.86	0.82	Total	16.01	0.53	16.55	0.51	17.04	0.50

Table 2. Calculated magnetic moments (in Bohr magnetons μ_B) for the $GdFe_{11-x}Co_xTi$, $GdFe_{11}TiC$ and $Gd_{1-z}Zr_zFe_{11}Ti$ ($z = 0.1, 0.2$) alloys.

	$PrFe_{11}Ti$		$PrFe_{10}CoTi$		$PrFe_9Co_2Ti$		$PrFe_8Co_4Ti$		$Pr_{0.9}Zr_{0.1}Fe_{11}Ti$		$Pr_{0.8}Zr_{0.2}Fe_{11}Ti$		
	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	$m_i(\mu_B)$	$m_j(\mu_B)$	
Pr	1.04	-0.01	0.97	-0.01	0.90	-0.01	0.86	-0.01	Pr	1.04	-0.02	1.05	-0.02
Fe δi	2.34	0.06	2.37	0.07	2.41	0.08	2.42	0.08	Zr	1.04	-	1.05	-0.02
Ti δi	-0.93	0.01	-0.91	0.02	-0.88	0.02	-0.86	0.02	Fe δi	2.34	0.06	2.35	0.06
Fe δj	2.40	0.06	2.45	0.07	2.49	0.07	2.50	0.08	Ti δi	-0.93	0.01	-0.95	0.01
Co δj			1.60	0.11	1.60	0.12	1.60	0.12	Fe δj	2.40	0.06	2.40	0.06
Fe δf	2.06	0.05	2.17	0.06	2.24	0.06	2.27	0.06	Fe δf	2.07	0.05	2.07	0.05
Co δf			1.56	0.09	1.57	0.10	1.56	0.10	Total	25.00	0.63	25.03	0.62
Total	24.97	0.64	24.96	0.75	24.60	0.86	23.90	0.93	MAE (meV)	1.703		1.461	
MAE (meV)	1.956		2.461		1.817		0.181						

Table 3. Calculated magnetic moments (in Bohr magnetons μ_B) and MAE for the $PrFe_{11-x}Co_xTi$ and $Pr_{1-z}Zr_zFe_{11}Ti$ ($z = 0.1, 0.2$) alloys.

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Exchange-coupling parameters J_{ij}

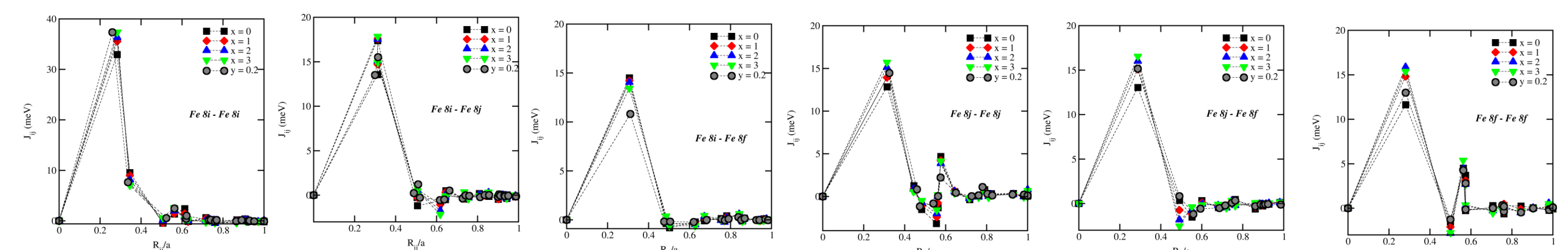


Figure 1. The exchange coupling parameters J_{ij} between Fe spins from $\delta i, \delta j$ and δf sites for $YFe_{11-x}Co_xTi$ and $Y_zZr_{1-z}Fe_{11}Ti$ ($y = 0.2$) alloys, with Fe δi (a, b and c), Γ (d, e and f) sites of the first neighbours.

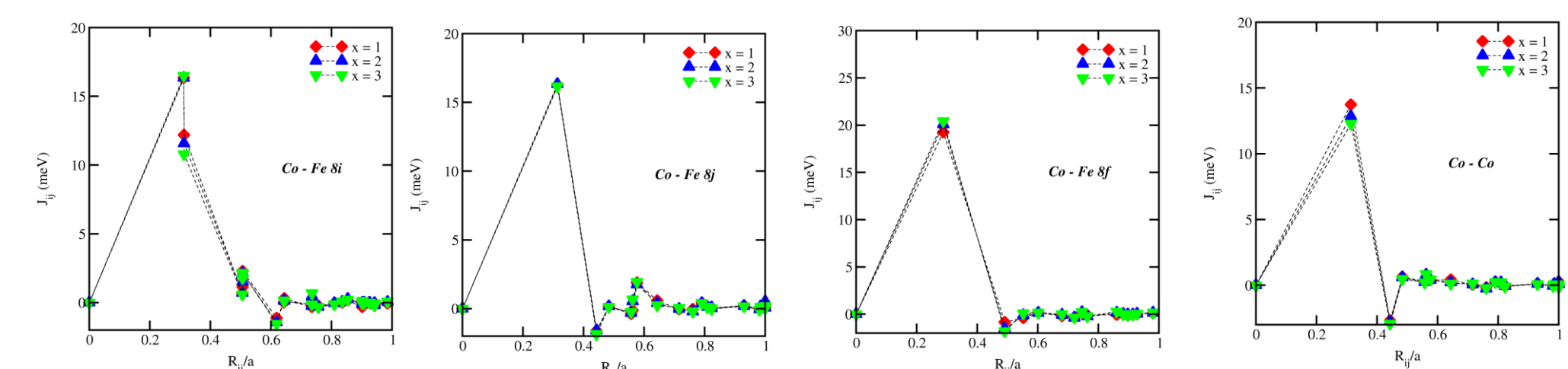


Figure 2. The exchange coupling parameters J_{ij} between Co spins (at the origin) from δj sites and Fe and Co spins of neighbouring atoms, for $YFe_{11-x}Co_xTi$ ($x = 0 - 3$).

Magneto-crystalline anisotropy energy

site	$YFe_{11}Ti$	$YFe_{10}CoTi$	YFe_9Co_2Ti	YFe_8Co_4Ti	$YFe_{11}TiC$	$Y_{0.9}Zr_{0.1}Fe_{11}Ti$
2a	0.0104	0.0028	-0.0063	-0.0157	-0.0082	-0.0067
δi	0.1231	0.1364	0.0495	0.0416	-0.0263	0.0699
	0.1309	0.1879	0.1584	0.0955	-0.0117	0.1149
δj	0.1955	0.1842	0.1536	0.0528	0.0015	0.2337
	0.1791	0.2293	0.2554	0.1842	0.2226	0.2740
δf	-1.5490	-1.1808	-0.6888	-0.4444	-0.2954	-1.4126
	1.4679	1.2963	0.7486	0.3318	0.7703	1.4752
2b					-0.0096	
MAE (meV)	1.106	1.710	1.345	0.341	1.304	1.503

Table 2 Site-dependent magneto-crystalline anisotropy (in meV) calculated using the torque method [8] for $YFe_{11-x}Co_xTi$ and $YFe_{11}TiC$ alloys.

Conclusions

This study may give an insight on the influence of the Zr, Co and C doping on the magnetic properties of the $RFe_{11}Ti$ -based alloys ($R = Y, Gd, Pr$) alloys, aiming to obtain rare-earth free permanent magnets with enhanced magneto-crystalline anisotropy (MAE) and higher magnetization. According to this study:

- The Co for Fe doping in $YFe_{11-x}Co_xTi$ maximize the calculated total magnetic moment and magneto-crystalline anisotropy energy (MAE) for $x = 1$
- The calculated exchange-coupling parameters for the first neighbours of each Fe site ($\delta i, \delta j$ and δf) show an increase by increasing the Co content or by adding C in the interstitial 2b sites, suggesting higher Curie temperatures for Co and C doped $YFe_{11}Ti$ -based alloys
- The Zr for Y substitution in $Y_zZr_{1-z}Fe_{11}Ti$ ($y = 0 - 0.2$) increases MAE without a noticeable decrease of the calculated total magnetic moment
- The Fe δi -Fe δj and Fe δi -Fe δf exchange coupling parameters J_{ij} with first neighbours decrease by Zr doping, in contrast to J_{ij} of the other Fe spin pairs which show opposite trend
- One has to notice a change in the magnetic moments sequence due to C addition for both $R=Y, Gd$, which become $m_i^{Fe}(\delta i) > m_i^{Fe}(\delta f) > m_i^{Fe}(\delta j)$
- The Zr for Y substitution in $Pr_zZr_{1-z}Fe_{11}Ti$ ($y = 0 - 0.2$) preserve the total magnetic moment but produces a slight decrease of MAE.

Acknowledgments

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