STUDIA UBB PHYSICA, Vol. 66 (LXVI), 1-2, 2021, pp. 9-17
(RECOMMENDED CITATION)
doi:10.24193/subbphys.2021.01

# MAGNETIC PROPERTIES OF $PrFe_{11}Ti$ ALLOYS BY Co AND Zr DOPING

**D. BENEA**[1]

**ABSTRACT.** Theoretical investigations on the electronic and magnetic properties (magnetic moments, magneto-crystalline anisotropy, exchange-coupling parameters) of the $PrFe_{11-x}Co_xTi$ (x = 0 – 3) and $Pr_{0.8}Zr_{0.2}Fe_{11}Ti$ alloys are presented. Our calculations show that Co for Fe doping in $PrFe_{11-x}Co_xTi$ maximize the calculated total magnetic moment and magnetocrystalline anisotropy energy (MAE) for x = 1. The calculated exchange-coupling parameters for the first neighbours of each Fe site (*8i*, *8j* and *8f*) show an increase by increasing the Co content suggesting higher Curie temperatures for Co doped $PrFe_{11}Ti$-based alloys. On the other hand, the Zr for Y substitution in $Pr_{1-y}Zr_yFe_{11}Ti$ (y = 0 - 0.2) decreases MAE without a noticeable decrease of the calculated total magnetic moment. Zr doping has opposite effects on the exchange coupling parameters $J_{ij}$ for different spin pairs. As consequence, any significant changes of the Curie temperatures are predicted for Zr doped $PrFe_{11}Ti$ based alloys in the investigated doping range.

***Keywords:*** *A. ab-initio calculations; B. magneto-crystalline anisotropy; C. magnetization; D. rare earth magnets.*

## INTRODUCTION

Between the R-T (R- rare earth, T- 3d transition metals) intermetallic compounds, the 1:12 compounds with $ThMn_{12}$ structure type (space group I4/mmm) have been intensely studied due to their low ratio of rare earth and high content of low-cost iron. The partial substitution of Fe with M (Ti, V, Cr, Mo, W or Al) it is necessary to stabilize the phase, as binary R - Fe intermetallic phase is not formed for each rare earth element R. All the $RFe_{12-x}M_x$ compounds are characterized by high values of saturation magnetization and Curie temperatures, respectively. The relatively high values of magnetocrystalline anisotropy allow them to be considered as candidates for permanent magnets applications [1].

---

[1] *Faculty of Physics, Babeș-Bolyai University Cluj-Napoca, Kogălniceanu str. 1, 400084 Cluj-Napoca, Romania*

The recent research directions are oriented to reduction of critical rare earth content in order to obtain low-cost permanent magnets [2]. In this sense, several substitutions were employed to decrease the critical rare-earth content, either by non-critical rare earth elements (Ce) or by other elements (Y, Zr) with similar atomic radius with the rare earth elements [3]. Moreover, partial Co for Fe substitution increase the magnetization and the Curie temperature of the $RFe_{11-x}Co_xTi$ alloys [3-5]. Other method used to enhance coercivity and magnetization of the $R(Fe,M)_{12}$ compounds is the light elements (H, B, C) interstitial addition [4]. Some substitutions have adverse effects, as for $CeFe_9Co_2Ti$, where the low value of coercivity has been reported [6].

In the present paper we present our investigations on the magnetic properties of Co and Zr doped $PrFe_{11}Ti$-based alloys. The calculated total magnetic moments, MAE and the exchange coupling parameters are analysed and compared with the corresponding values obtained for Zr and Co doped $YFe_{11}Ti$ -alloys [4]. Our investigations results may give insight on the possible routes of enhancement for main magnetic properties (magnetization, MAE and Curie temperature) which are important for permanent magnet applications.

## CALCULATIONS DETAILS

Electronic band structure calculations have been done 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 k-space integration was performed using the special points method [9]. 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 $\overrightarrow{\mathrm{m_i}}$ of the atomic site *i,* oriented along the magnetization direction $\vec{M}$ [11,12]. As the component of the magnetic torque with respect to axis $\hat{u}$ is defined by $T_{\hat{u}}(\theta,\varphi) = -\partial E(\overrightarrow{M(\theta,\varphi)})/\partial\theta$, where $\theta$ and $\varphi$ are the polar angles, a special geometry can be used to relate the magnetic torque and the energy difference between the in-plane and out-of-plane magnetization directions. For a uniaxial anisotropy, by setting the angles to $\theta = \pi/4$ and $\varphi = 0$, the calculated magnetic torque is $T_{\hat{u}}(\pi/4,0) = E_{[100]} - E_{[001]}$ [12].

A complementary approach to investigate the magnetic behaviour of solids is to consider particular microscopic models making use of magnetic interaction. One of the approaches widely used is based on the classical Heisenberg Hamiltonian described by the expression:

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

where the summation is performed on all lattice sites *i* and *j* and $\hat{e}_i / \hat{e}_j$ are the unit vectors of magnetic moments on sites *i* and *j,* respectively. The $J_{ij}$ exchange coupling parameters for the Fe and Co magnetic moments have been calculated as a function of distance using the expression derived by Liechtenstein [13] based on the magnetic force theorem.

## RESULTS AND DISCUSSIONS

- ***Crystal structure***

The $R(Fe,M)_{12}$ compounds crystallize in the $ThMn_{12}$ structure (space group *I4/mmm*) having Fe atoms on 3 inequivalent crystal sites (*8i*, *8j* and *8f*) and the R atoms on *2a* sites (Figure 1). By Ti for Fe substitution, as determined by neutron diffraction experiments [6], the Ti atoms occupy preferentially the *8i* sites. On the other hand, by experimental investigations if was found that Co atoms occupy preferentially sites in the sequence *8j* > *8f* > *8i* in $PrFe_{11-x}Co_xTi$ alloys [4]. For interstitial dopants (H, C and B), the *2b* sites within the structure are occupied [4, 6].

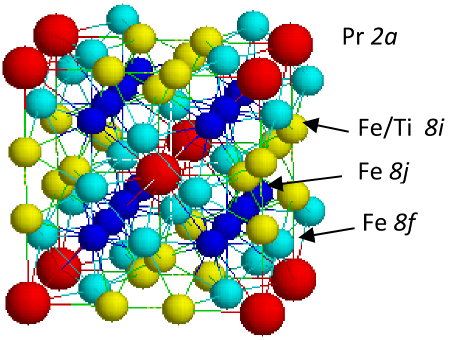

**Figure 1.** The $ThMn_{12}$ structure (space group *I4/mmm*) of $PrFe_{11}Ti$. The Pr atoms on *2a* sites are red spheres, whilst Fe atoms are represented as green (*8i)*, blue (*8j)* and grey (*8f*) spheres, respectively.

- ***Magnetic moments***

Band structure calculations have been performed using the SPR-KKR method for the $PrFe_{11-x}Co_xTi$ using the experimental lattice constants [14, 15]. Calculated magnetic moments (in Bohr magnetons $\mu_B$) for the $PrFe_{11-x}Co_xTi$ and $Pr_{0.8}Zr_{0.2}Fe_{11}Ti$ are shown in Table 1. Our theoretical calculations show monotonic increase of Fe magnetic moment on each crystal site by increasing Co content. The Fe spin magnetic moments are in following the sequence $m_s^{Fe}$(*8j*) > $m_s^{Fe}$ (*8i*) > $m_s^{Fe}$ (*8f*), which is consistent with the sequence determined experimentally for other 1:12 phases [16].

**Table 1.** Calculated magnetic moments (in Bohr magnetons $\mu_B$) for the $PrFe_{11-x}Co_xTi$ and $Pr_{0.8}Zr_{0.2}Fe_{11}Ti$. Preferential occupation of Co for *8j* and *8f* sites has been considered. Lattice constants for $PrFe_{11-x}Co_xTi$ from [15] are considered.

| | **$PrFe_{11}Ti$** | | **$PrFe_{10}CoTi$** | | **$PrFe_9Co_2Ti$** | | **$PrFe_8Co_3Ti$** | | **$Pr_{0.8}Zr_{0.2}Fe_{11}Ti$** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $m_s(\mu_B)$ | $m_l(\mu_B)$ | $m_s(\mu_B)$ | $m_l(\mu_B)$ | $m_s(\mu_B)$ | $m_l(\mu_B)$ | $m_s(\mu_B)$ | $m_l(\mu_B)$ | $m_s(\mu_B)$ | $m_l(\mu_B)$ |
| Pr | 1.04 | -0.01 | 0.97 | -0.01 | 0.90 | -0.01 | 0.86 | -0.01 | 1.05 | -0.02 |
| Zr | | | | | | | | | 1.05 | -0.02 |
| Fe *8i* | 2.34 | 0.06 | 2.37 | 0.07 | 2.41 | 0.08 | 2.42 | 0.08 | 2.35 | 0.06 |
| Ti *8i* | -0.93 | 0.01 | -0.91 | 0.02 | -0.88 | 0.02 | -0.86 | 0.02 | -0.95 | 0.01 |
| Fe *8j* | 2.40 | 0.06 | 2.45 | 0.07 | 2.49 | 0.07 | 2.50 | 0.08 | 2.40 | 0.06 |
| Co *8j* | | | 1.60 | 0.11 | 1.60 | 0.12 | 1.60 | 0.12 | | |
| Fe *8f* | 2.06 | 0.05 | 2.17 | 0.06 | 2.24 | 0.06 | 2.27 | 0.06 | 2.07 | 0.05 |
| Co *8f* | | | 1.56 | 0.09 | 1.56 | 0.10 | 1.56 | 0.10 | | |
| Total | 24.97 | 0.64 | 24.96 | 0.75 | 24.60 | 0.86 | 23.90 | 0.93 | 25.03 | 0.62 |

The calculated spin magnetic moments of Fe for undoped $PrFe_{11}Ti$ alloy values range between 2.06 $\mu_B$ for Fe *8f* and 2.40 $\mu_B$ for Fe *8j*. The lowest value of the $m_s^{Fe}$ (*8f*) could be related with the interatomic Fe-Fe distances, as those of *8f* site are the smallest and those of *8i* sites are the longest.

By Co doping, each Fe spin moment is increased, the highest rate of increase (10%) being obtained for Fe *8f* atoms (from 2.06 to 2.27 $\mu_B$). The orbital moments ($m_l$) of Fe atoms on *8i* and *8j* sites are also showing small increase (from 0.06 to 0.08 $\mu_B$) whilst the $m_l$ values for Fe *8f* sites do not change by changing the Fe/Co ratio in the alloys. The spin magnetic moment of substitutional Co is 1.60 $\mu_B$ on *8j* sites and 1.56 on *8f* sites, independent on Co content within the considered doping range. In the same time, Co substituting atoms have increased orbital moments, which contribute also at the total orbital magnetic moment enhancement, which is increasing from

0.64 $\mu_B$/f.u. (x = 0) to 0.93 $\mu_B$/f.u. (x = 3). The calculated maximum value of the total magnetic moment is obtained for x = 1, with values of $m_s = 24.96\ \mu_B$ and $m_l = 0.75\ \mu_B$ for $PrFe_{10}CoTi$. The total magnetic moment is in agreement with other reported experimental and theoretical investigations (22.72 $\mu_B$ and 23.02 $\mu_B$, respectively) [14]. We note that Co distribution on crystallographic sites has important influence on calculated magnetic moments. Also, as the electronic correlations are not accounted in the present study, the Pr magnetic moment is expected to be underestimated. However, Pr calculated moment shows agreement with the corresponding calculated value for $PrFe_{11}Ti$ (1.31 $\mu_B$) of Bouhbou et al. [14].

- ***Magnetocrystalline anisotropy***

The magnetocrystalline anisotropy for Co doped alloys is shown in Figure 2, together with similar calculations for $YFe_{11-x}Co_xTi$ alloys [17]. As can be seen in Figure 2, MAE reaches a maximum value for x = 1. The site-dependence of the MAE shown in Figure 2 reveals the origin of this change. As can be seen, the transition metals on *8j* sites, followed by those from *8i* sites have the largest main MAE contributions. A small MAE contribution comes from *8f* site, which is negative for undoped $PrFe_{11}Ti$, changing to positive sign for x = 1, 2 and again negative for x = 3. The *2a* site contribution, occupied by Pr is underestimated, as the electronic correlations are not accounted. Pr is expected to add a negative contribution at MAE [18, 19], higher in modulus than current calculated values (~ -0.07 meV for x = 1). Due to this known deficiency, only the MAE behavior in Fe sublattices is discussed. The overall MAE contribution of transition metal atoms increases with Co content, reaching the maximum value for x = 1. This dependence is explained also by the interplay between the Fe axial local anisotropy and that of Co which is planar [16]. The evolution of transition metals MAE with Co content x is very similar with the experimental determined anisotropy constant $K_1$ for by Tereshina et al. [16] for $YFe_{12-x}Co_xTi$ alloys where a maximum at x = 1 is also reached, with a $K_1$ value of 0.98 $MJ/m^3$ deduced from measurements at 300 K. Our calculations show a value for magnetic anisotropy energy of $YFe_{10}CoTi$ alloy of 1.57 $MJ/m^3$ [17], whilst for $PrFe_{10}CoTi$ alloy a higher value is obtained (2.24 $MJ/m^3$). The calculated value is in the relative agreement with other calculations for $PrFe_{11}Ti$ [14].

By Zr for Y substitution in $Pr_{0.8}Zr_{0.2}Fe_{11}Ti$, the main MAE contribution of transition metals comes from *8j* site (0.35 meV), the *8i* site contribution being reduced compared with undoped alloy (0.06 meV), whilst 8f site has negative contribution (-0.11 meV). As consequence, total MAE is reduced by Zr doping compared to $PrFe_{11}Ti$ alloy.

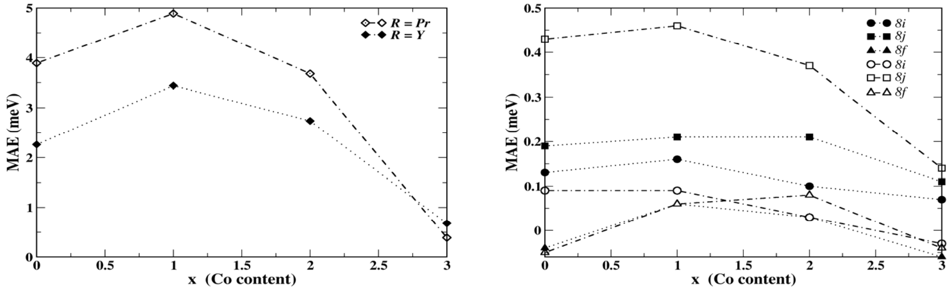

**Figure 2.** Site-dependent average magnetocrystalline anisotropy (in meV) calculated using the torque method [8] for RFe$_{11-x}$Co$_x$Ti (R = Y, Pr). Filled symbols (● – *8i*; ■ - *8j* and ▲ - *8f*) have been used for R = Y and open symbols (○ - *8i*, □ - *8j* and Δ - *8f*) for R = Pr.

- ***Exchange-coupling parameters***

The exchange coupling parameters $J_{ij}$ between Fe spins from *8i*, *8j* and *8f* sites calculated using the magnetic force theorem [13] for the PrFe$_{11-x}$Co$_x$Ti alloy and Pr$_{0.8}$Zr$_{0.2}$Fe$_{11}$Ti alloys are shown on Figure 3. The highest strength of the exchange interaction is obtained between Fe *8i* spins, followed by Fe *8f* – Fe *8f* exchange interaction; other exchange interactions between pair of Fe spins are lower than half in magnitude compared with Fe *8i* - Fe *8i* exchange interaction. The highest $J_{ij}$ values obtained for nearest neighbours are increasing by Co substitution for almost all pairs of spins.

The exchange coupling parameters $J_{ij}$ between Co spins from *8i* sites and the spins of Fe and Co neighbours have been also checked. Analysing their behaviour with Co content x we concluded that that these exchange interactions are almost independent on the Co content and for simplicity are not shown here. We note that the highest values of $J_{ij}$ appear for Co – Fe *8f* next neighbour interaction. Based on discussed dependencies of the exchange coupling parameters of Co and Fe spins by Co doping, it is expected that the Curie temperatures for PrFe$_{11-x}$Co$_x$Ti alloys to increase by increasing the Co content x, in agreement with experimental measurements [15].

By Zr for Pr doping, the calculated exchange-coupling parameters between pairs of Fe spins, considering by turn Fe *8i, 8j* and *8f* spins at the origin, are also shown in Fig. 1. For the Fe 8*i* -Fe *8i,* the Fe 8*i* -Fe *8i* and Fe *8j* -Fe *8f* pairs, the exchange coupling parameters $J_{ij}$ with first neighbours decrease by Zr doping, in contrast to $J_{ij}$s of the other Fe spin pairs which show opposite trend. Accounting the number of such pairs showing enhancement/decrease of next neighbours $J_{ij}$, the Curie temperature of Pr$_{0.8}$Zr$_{0.2}$Fe$_{11}$Ti is not expected to be strongly influenced by Zr substitution.

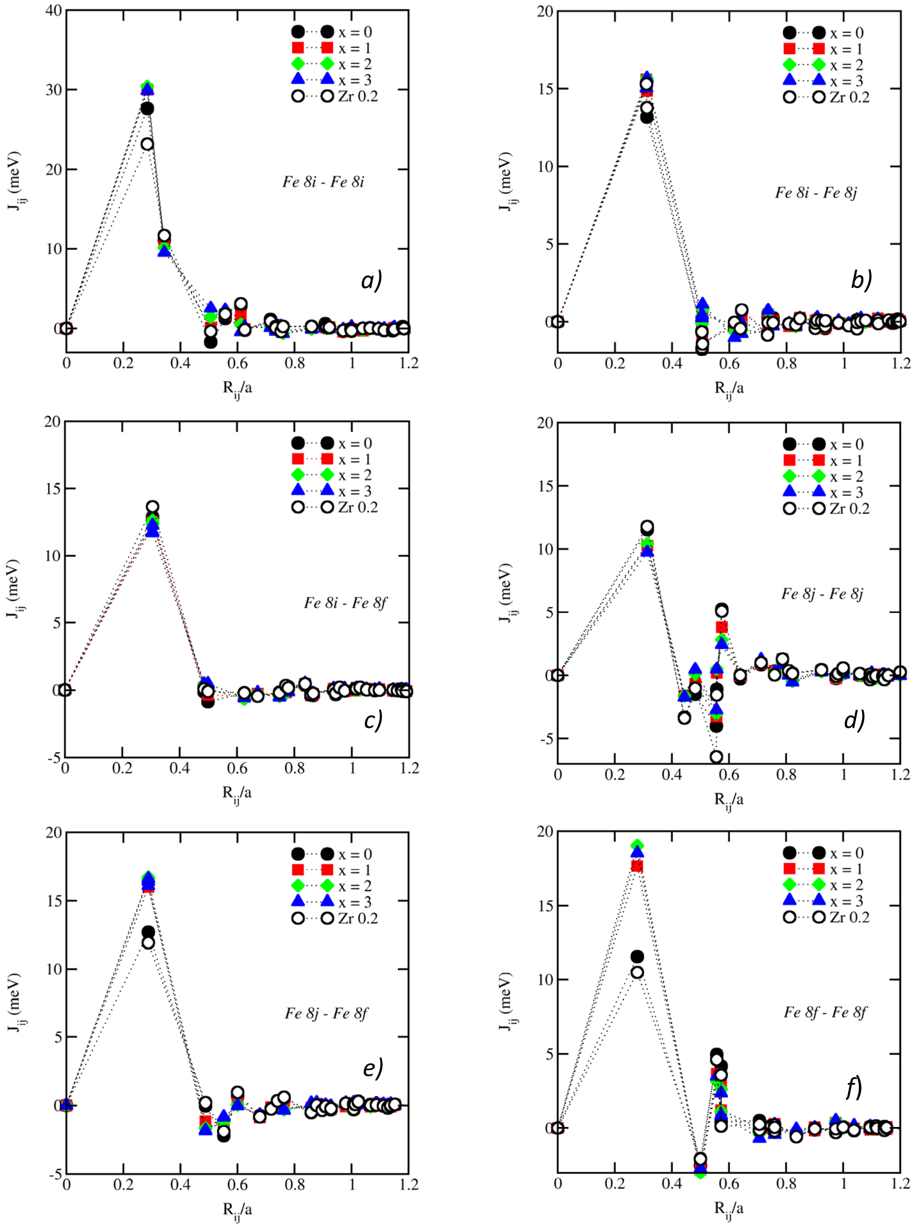

**Figure 3.** The exchange coupling parameters $J_{ij}$ between Fe spins from *8i*, *8j* and *8f* sites for $PrFe_{11-x}Co_xTi$ and $Pr_{0.8}Zr_{0.2}Fe_{11}Ti$ (y = 0.2) alloys, with Fe *8i* (*a, b* and *c*), Fe *8j* (*d* and *e*) and Fe *8f* (*f*) at the origin.

## CONCLUSIONS

Theoretical studies presented here show that Co for Fe substitutions in $PrFe_{11}Ti$ alloys increase Fe magnetic moments, transition metals contribution at MAE for $x \leq 1$ and the exchange-coupling parameters ($J_{ij}$) between nearest neighbours. Also, Zr for Pr substitution preserve the magnetic moments magnitude, but reduces slightly the transition metals contribution at MAE. In addition, Zr doping in $PrFe_{11}Ti$ alloys do not cause overall diminishment of the exchange coupling between Fe pairs from different crystal sites. As consequence, Zr doping could be used in $PrFe_{11}Ti$- alloys in order to stabilize the phase and to reduce the Pr content, without significant weakening of the magnetic properties important for applications as permanent magnets.

### ACKNOWLEDGEMENTS

The author acknowledges the long and fruitful collaboration with Prof. Dr. Viorel Pop, counting over 20 common ISI papers, other 3 BDI indexed papers and the partnership in 12 scientific projects. Also, Diana Benea thanks for all encouragement, guidance and support during over 15 years of scientific collaboration.

The financial support from the Romanian Ministry of Education and Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI grant PN-III-P2-2.1-PED-2019-3484 is acknowledged.

## References

[1] K. H. J. Buschow, *J. Magn. Magn. Mater.,* 100 79 (1991).
[2] A.M. Gabay and C. C. Hadjipanayis, *Scripta Materialia,* 154 284 (2018).
[3] P. Tozman, H. Sepehri-Amin, Y. K. Takahashi, S. Hirosawa and K. Hono, *Acta Materialia,* 153 354 (2018).
[4] L. Ke and D. D. Johnson, *Phys. Rev. B,* 94 024423 (2016).
[5] A. M. Gabay, A. Martin-Cid, J. M. Barandiaran, D. Salazar and G. C. Hadjipanayis, *AIP Advances,* 6, 056015 (2016).
[6] J. M. D. Coey, *Engineering,* 6 119 (2020).
[6] Von Barth U. and Hedin L., *J. Phys*., C5 1629 (1972).
[7] Ebert H., Ködderitzsch D. and Minar J., *Rep. Prog. Phys.,* 74 096501 (2011).
[8] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.,* 77 3865 (1996).
[9] Monkhorst H. and Pack J., *Phys. Rev. B*, 13, 5188 (1976).
[10] Faulkner J.S., *Prog. Mater. Sci.,* 27 1 (1982); Faulkner J. S. and Stocks G.M., *Phys. Rev. B*, 21 3222 (1980).

[11] J.B. Staunton, L. Szunyogh, A. Buruzs, B.L. Gyorffy, S. Ostanin, and L. Udvardi, *Phys. Rev. B,* 74 144411 (2006).

[12] S. Mankovsky, S. Polesya, J. Minar, F. Hoffmann, D.H. Back and H. Ebert, *Phys. Rev. B,* 84 201201 (2011).

[13] Liechtenstein A.I., Katsnelson M.I., Antropov V.P. and Gubanov V.A., *J. Magn. Magn. Mater.,* 67 65 (1987).

[14] M. Bouhbou, R. Moubah, E.K. Hlil, H. Lassri and L. Bessais, *J. Magn. Magn. Mater.,* 518 167362 (2021).

[15] L. Bessais, S. Sab and C. Djega-Mariadassou, *Phys. Rev. B*, 66 054430 (2002).

[16] I.S. Tereshina, P. Gaczynski, V.S. Rusakov, H. Drulis, S.A. Nikitin, W. Suski, N.V. Tristan and T. Palewski, *Phys. Condens. Matter.,* 13 8161 (2001); I.S. Tereshina, S.A. Nikitin, T.I. Ivanova, K.P. Skokov, *J. Alloys Compd.*, 275-277 625 (1990).

[17] D. Benea et al., Co, Zr and C doping on $RFe_{11}Ti$-based alloys (R = Y, Gd), in press (2022).

[18]. R. Skomski and D.J. Sellmyer, *J. of Rare Earth*, 27 675 (2009).

[19] X. C. Kou, T.S. Zhao, R. Grossinger, H.R. Kirchmayr, X. Li and F.R. de Boer, *Phys. Rev. B,* 47 3231 (1993).