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Spin–glass magnetism in $RFeTi_2O_7$ (R=Lu and Tb) compounds

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Abstract
The compounds $RFeTi_2O_7$ (R=Lu and Tb) crystallize at room temperature in centrosymmetric orthorhombic space group *Pcnb*. There are five non-equivalent positions of the iron ions: the two positions, Fe' and Fe", in the octahedron consisting of the Fe' tetrahedron and Fe" five-vertex polyhedron and the three positions, Fe1, Fe2 and Fe3 in the mixed Fe-Ti octahedra [1]. The populations of the mixed Fe-Ti sites are different. The crystal structure features lead to atomic disorder in the distribution of the magnetic ions in this compound. From low temperature heat capacity, magnetization and frequency dependent ac susceptibility we conclude that both compounds undergo a spin glass transition at T_{SG}=4.5 and 6 K for R =Lu and Tb, respectively. Since Lu is not magnetic, in $RFeTi_2O_7$ the spin glass behavior is caused by the disordered distribution of the magnetic Fe^{3+} ions in the different crystallographic positions. The substitution of the magnetic and highly anisotropic Tb ion instead of Lu increases T_{SG} because of the additional Tb-Fe exchange interaction, while the critical exponent of the frequency dependence on temperature hardly varies. The spin glass behavior in these crystalline compounds is caused by the presence of competitive interactions that lead to frustration.

Keywords: spin-glass, magnetic oxides

1 Introduction

The compounds with geometrically frustrated magnetism are known to display very interesting magnetic properties. Pyrochlore structure compounds, $R_2Ti_2O_7$ (R= Tb, Dy, Ho) are regarded as the classical example of what is called spin-ice materials [2]. The study of spin liquids and frustrated magnetism in general has become recently a hot topic as many exotic phenomena are predicted. When the rare earth element is substituted by a 3d metal, a different structure and behavior emerge; magnetic disorder induces the formation of spin-glass ground state at low temperatures. Therefore, as regards

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disordered magnetism and spin-glass phase transition, of particular interest is the study of compounds with the general formula $R^{3+}Fe^{3+}Ti_2O_7$ (R-rare earth element) [1][3][4]. The compounds $RFeTi_2O_7$ (R=Sm, Gd and Tm) crystallize at room temperature in centrosymmetric orthorhombic space group *Pcnb*. One characteristic of these materials crystal structure is that there are four nonequivalent positions of the iron ions in the independent part of unit cell; one of these sites is disordered between two different positions. As a result one can find five nonequivalent positions of iron in the crystal structure.

The magnetism of these oxides is determined by the magnetic moment of the Fe^{3+} and R^{3+} (Sm, Gd and Tm) ions. The coexistence of two different magnetic ions iron Fe^{3+} and rare earth R^{3+} and the disorder in position of iron ions lead to competition between magnetic interactions and formation of a spin-glass ground state.

The special interest to these systems comes from the determination of the roles of iron and rare earth ions on magnetic properties of compounds $RFeTi_2O_7$ and in the effect of introducing a magnetic or a nonmagnetic rare earth ion.

In this work, in order to characterize the prepared compounds $TbFeTi_2O_7$ and $LuFeTi_2O_7$ we present results from X-ray powder diffraction, as well as magnetization, frequency dependent AC susceptibility and calorimetric measurements. The crystal structure, the thermal properties, the static and dynamic magnetic properties are reported herein.

2 Experimental

Polycrystalline samples of $RFeTi_2O_7$ (R=Lu and Tb) were prepared by the solid-phase reaction from a stoichiometric mixture of oxides Fe_2O_3, TiO_2 and Lu_2O_3 or Tb_2O_3. The samples formed in pellets were subjected to a high-temperature treatment at a maximum temperature of 1250º C. The chemical and phase compositions of the samples were controlled by the X-ray diffraction method.

The X-ray powder diffraction patterns of the samples $RFeTi_2O_7$ (R=Lu and Tb) for Rietveld analysis were collected on a Bruker D8-ADVANCE diffractometer (Cu-Kα radiation) with linear VANTEC detector at room temperature. All refinements of the powder patterns were performed with TOPAS 4.2 (Bruker).

Dc magnetic measurements were performed in a superconducting quantum interference device (SQUID) magnetometer in the 2.0-300 K temperature range. The magnetization was measured both in zero-field-cooled (ZFC) and field-cooled (FC) regimes. Ac susceptibility measurements were performed in a SQUID magnetometer with AC option, in the frequency range $0.01 < f < 1400$ Hz, with an exciting field of 4 Oe.

Heat capacity as a function of temperature and magnetic field was measured on pellets using a Quantum Design PPMS (Physical Properties Measurement System). The samples were glued to the sample holder with Apiezon grease.

3 Results and Discussion

3.1 Crystal Structure

The previously studied isostructural compound $GdGaTi_2O_7$ [5] was taken as the initial model for the determination of the $RFeTi_2O_7$ (R=Lu and Tb) crystal structures.

According to the results of the X-ray investigation the $TbFeTi_2O_7$ and $LuFeTi_2O_7$ compounds crystallize in the orthorhombic crystal structure, with space group *Pcnb*, at room temperature. A small amount (3.05 % and 5.95 %) of the impurity Fe_2TiO_5 was found in the substances, respectively. In table 1 the key crystallographic data of $TbFeTi_2O_7$ and X-ray experimental details are given. Atomic coordinates, population of the sites, *p*, and thermal parameters are presented in Table 2. The features of the crystal structure allow the existence of competing magnetic exchange interactions in $TbFeTi_2O_7$ and $LuFeTi_2O_7$. Analysis of $RFeTi_2O_7$ (R=Lu and Tb) crystal structure shows that there are five non-equivalent positions of the iron ions: the two positions, Fe' and Fe", in the octahedron consisting of the Fe' tetrahedron and Fe" five-vertex polyhedron (Fig. 1) and the three positions, Fe1, Fe2 and Fe3 in the mixed Fe-Ti octahedra. The populations of the mixed Fe-Ti sites are different (Table 2). The crystal structure features lead to atomic disorder in the distribution of the magnetic ions in these compounds.

Sample	$TbFeTi_2O_7$	$LuFeTi_2O_7$
Space group	*Pcnb*	*Pcnb*
a , Å	9.8568(1)	9.8093(1)
b, Å	13.5942(2)	13.5069(1)
c, Å	7.3788(1)	7.30302(7)
V, $Å^3$	988.73(2)	967.61(2)
Z	8	8
D_x, g/cm^3	5.668	6.069
μ, mm^{-1}	117.798	92.808
2θ-range, deg.	5–140	5–140
Number of reflections	944	927
Number of refined parameters	84	74
R_{wp}, %	1.153	2.011
R_{exp}, %	0.707	0.642
R_{p}, %	1.068	1.862
GOF (χ^2)	1.631	3.134
R_{Bragg}, %	0.52	1.49

Table 1. Crystallographic parameters of the $TbFeTi_2O_7$ and $LuFeTi_2O_7$ samples.

Note: V is the unit cell volume, Z is the number of formula units in the cell, D_x is the calculated density, μ is the absorption coefficient, R_{wp} is the weight profile uncertainly factor, R_{exp} is the expected uncertainly factor, R_p is the profile uncertainly factor, *GOF* (χ^2) is the adjustment quality, and R_{Bragg} is the Bragg integral discrepancy factor.

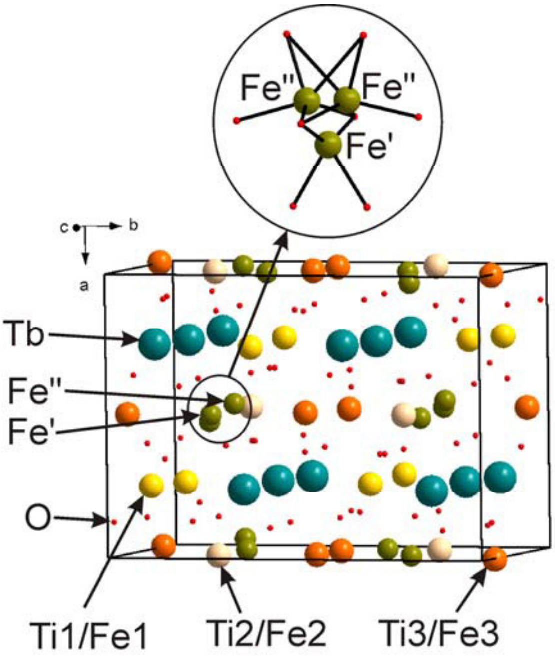

Fig. 1. Schematic structure of $TbFeTi_2O_7$ showing the different non-equivalent positions for the Fe ions.

Table 2. Atomic coordinates, population of the structural sites *p*, and isotropic thermal parameter in TbFeTi$_2$O$_7$ (a) and LuFeTi$_2$O$_7$ (b).

a)

Atom	Site multiplicity	*x/a*	*y/b*	*z/c*	*p*	B_{iso}, Å^2
Tb	8	0.2460 (5)	0.1328 (2)	0.0062 (5)	1	1.24 (8)
Ti1	8	0.245 (1)	0.3845 (5)	0.483 (1)	0.87 (2)	1.5
Fe1	8	0.245 (1)	0.3845 (5)	0.483 (1)	0.18 (2)	1.5
Ti2	4	0.5	0.25	0.250 (3)	0.57 (1)	1.5
Fe2	4	0.5	0.25	0.250 (3)	0.51 (6)	1.5
Ti3	8	0.005 (1)	0.4880 (5)	0.255 (2)	0.93 (8)	1.5
Fe3	8	0.005 (1)	0.4880 (5)	0.255 (2)	0.13 (3)	1.5
Fe'	4	0	0.25	0.337 (2)	0.78	2.3 (3)
Fe"	8	0.031 (7)	0.283 (5)	0.175 (1)	0.11	2.3 (3)
O1	8	0.161 (1)	0.392 (1)	0.242 (5)	1	1
O2	8	0.402 (2)	0.110 (2)	0.242 (5)	1	1
O3	8	0.094 (3)	0.149 (1)	0.247 (6)	1	1
O4	8	0.372 (4)	0.285 (3)	0.432 (5)	1	1
O5	8	0.372 (4)	0.282 (3)	0.068 (5)	1	1
O6	8	0.377 (3)	0.495 (2)	0.432 (4)	1	1
O7	8	0.389 (3)	0.477 (2)	0.044 (4)	1	1

b)

Atom	Site multiplicity	*x/a*	*y/b*	*z/c*	*p*	B_{iso}, Å^2
Lu	8	0.2483(7)	0.1319(1)	0.0046(4)	1	1.40(3)
Ti1	8	0.255(2)	0.3863(4)	0.489(1)	1.00(31)	1.5
Fe1	8	0.255(2)	0.3863(4)	0.489(1)	0.00(3)	1.5
Ti2	4	0.5	0.25	0.261(2)	0.84(12)	1.5
Fe2	4	0.5	0.25	0.261(2)	0.16(12)	1.5
Ti3	8	0.0060(8)	0.4871(4)	0.259(2)	0.14(7)	1.5
Fe3	8	0.0060(8)	0.4871(4)	0.259(2)	0.86(7)	1.5
Fe'	4	0	0.25	0.338(2)	0.78	2.5(3)
Fe"	8	0.027(6)	0.285(4)	0.190(7)	0.11	2.5(3)
O1	8	0.1639(9)	0.392(1)	0.234(3)	1	0.97(14)
O2	8	0.403(2)	0.113(3)	0.256(5)	1	0.97(14)
O3	8	0.110(2)	0.149(1)	0.235(4)	1	0.97(14)
O4	8	0.364(2)	0.292(2)	0.443(3)	1	0.97(14)
O5	8	0.388(3)	0.267(2)	0.053(3)	1	0.97(14)
O6	8	0.376(3)	0.490(2)	0.406(3)	1	0.97(14)
O7	8	0.372(2)	0.486(2)	0.042(3)	1	0.97(14)

3.2 Magnetic Properties

The temperature dependence of dc magnetic susceptibility shows a paramagnetic behaviour at high temperatures; T>75K for $TbFeTi_2O_7$ and T>125K for $LuFeTi_2O_7$. The observed linear variation of inverse susceptibility with temperature has been fitted to a Curie-Weiss law. Fit parameters are given in Table 3. The obtained negative asymptotic Néel temperatures, θ_N = - 27 K for $TbFeTi_2O_7$ and θ_N = - 97 K for $LuFeTi_2O_7$ indicates the prevailing presence of antiferromagnetic exchange interaction within the magnetic ions system. Additionally, the obtained effective magnetic moments are close to the expected values; μ_{eff} = 10.8 μ_B and μ_{eff}= 5.08 μ_B for $TbFeTi_2O_7$ and $LuFeTi_2O_7$ respectively.

Compound	Θ_N (K)	μ_{eff},(μ_B)		T_{SG}(K)
		μ_{calc}	μ_{exp}	
$LuFeTi_2O_7$	- 97	5.91	5.08	4.5
$TbFeTi_2O_7$	- 27	11.4	10.8	6

Table 3. Magnetic parameters for the $LuFeTi_2O_7$ and $TbFeTi_2O_7$ compounds.
Note: μ_{exp} is the experimental effective magnetic moment, μ_{calc} is the calculated effective magnetic moment, $\mu_{calc} = (\mu_{Fe}^2+\mu_{Tb}^2)^{1/2}$.

At low temperatures a cusp-like maximum in the zero field cooled (ZFC) curve points to the presence of a spin-glass transition for both compounds, T_{SG} = 6K for $TbFeTi_2O_7$ and T_{SG} = 4.5K for $LuFeTi_2O_7$ for a magnetic field of H = 0.5 kOe (see Fig. 2). At $T<T_{SG}$ there is magnetization dependence not only on the temperature but also on the sample cooling conditions.

The degree of frustration can be estimated as the ratio $|\theta_N|/ T_{SG}$ [6] which is of 21.5 for $LuFeTi_2O_7$ and 4.5 for $TbFeTi_2O_7$, indicating a much larger frustration in $LuFeTi_2O_7$ compound.

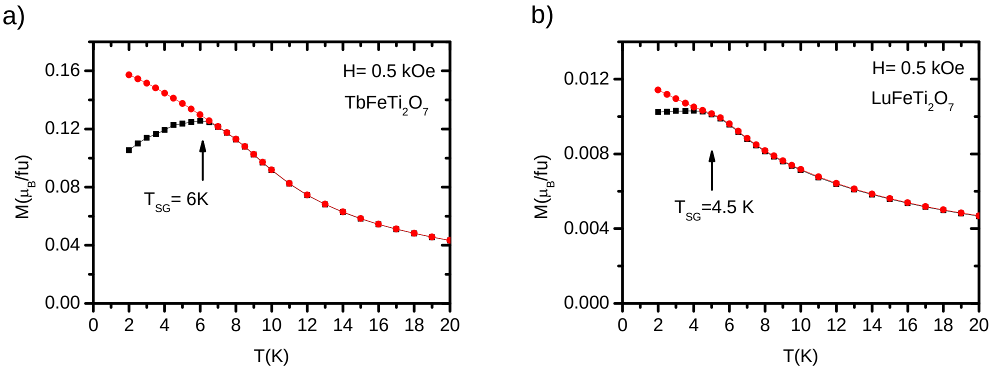

Fig. 2. Temperature dependence of the magnetization in the $TbFeTi_2O_7$ (a) and $LuFeTi_2O_7$ (b). ZFC (black squares) and FC (red circles) curves at H = 0.5 kOe.

Dc magnetization measurements have shown typical characteristics of spin-glass magnetic state. Note, since Lu is not magnetic, in $LuFeTi_2O_7$ the spin-glass behavior is caused by the disordered distribution of the magnetic Fe^{3+} ions in the different crystallographic positions.

To further illustrate the magnetic behavior of $RFeTi_2O_7$ (R=Lu and Tb) compounds the dynamic magnetic properties have been studied. Ac magnetic susceptibility as a function of frequency was measured in $TbFeTi_2O_7$ and $LuFeTi_2O_7$. Figs. 3a and 3b display the in-phase and out-of-phase components $\chi'(T)$ and $\chi''(T)$ of the ac magnetic susceptibility at several fixed frequencies as a function of temperature for $TbFeTi_2O_7$ and $LuFeTi_2O_7$ respectively. As can be observed, the maximum of $\chi'(T)$

is frequency dependent and shifts to high temperature with increasing frequency, decreasing in magnitude. Similar shift is observed in the out of phase susceptibility component, $\chi''(T)$ (see Fig.3 inset), with increasing amplitude as frequency increases.

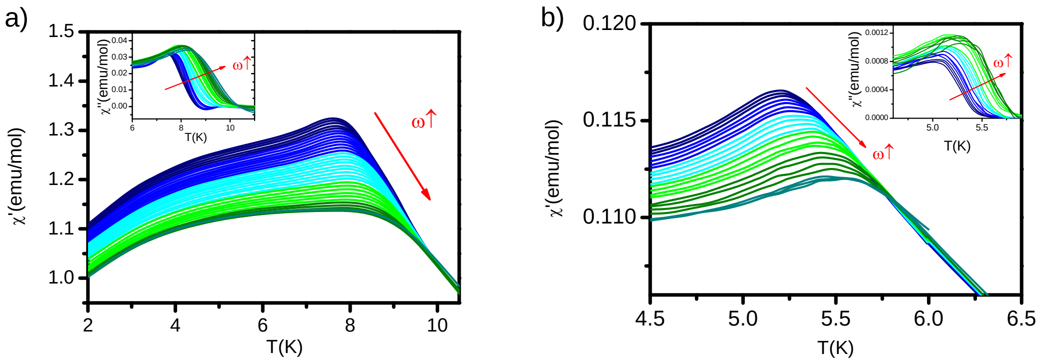

Fig. 3. Temperature dependence of χ' and χ'' (inset) as a function of frequency. a) $TbFeTi_2O_7$, b) $LuFeTi_2O_7$.

The frequency dependence of the $\chi'(T)$ maximum temperature has a clear spin-glass tendency signature. A way to evaluate the frequency sensibility of freezing temperature, T_f, is to calculate the p_f factor, defined as $p_f = \Delta T_f / [T_f \Delta(\log f)]$. We obtain a value of 0.016±0.002 for $TbFeTi_2O_7$ and ~~1-#~~ 0.013±0.002 for $LuFeTi_2O_7$, which are similar to those obtained in canonical spin-glasses: 0.005-0.018 [7].

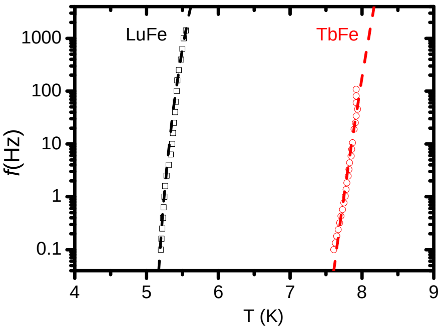

Table 4. Best fit parameters for the frequency dependence of the spin-glass transition

	$T_{SG}(K)$	$T_c(K)$	f_o (Hz)	$z\nu$
LuFe	4.5	5.0±0.5	$6\pm4\cdot10^{11}$	9±1
TbFe	6	7.3±0.5	$1\pm0.5\ 10^{11}$	9±1

Fig. 4. Variation of the spin-glass transition temperature as a function of frequency. Results for $TbFeTi_2O_7$ (red circles) and $LuFeTi_2O_7$ (black squares). Dashed lines show the fit to a critical slowing down law.

To analyze the frequency dependence of the spin-glass transition temperature (see Fig.4) we have made use of the Dynamical scaling theory near a phase transition at T_c. According to this theory, the relaxation time close to the transition follows the critical slowing down law, which in terms of frequency stays:

$$f = fo\,(T_f(\omega)/T_c - 1)^{z\nu} \qquad (1)$$

where $T_f(\omega)$ is the frequency dependent freezing temperature, determined by the maximum in $\chi'(T)$ and T_c is the phase transition temperature in the limit of zero frequency, ν is the critical exponent for correlation length ξ and z is the dynamical exponent.

The best fit parameters are given in Table 4. The spin-glass transition temperature obtained from the FC/ZFC experiments is given for the sake of comparison. The dynamics of the spin-glass transition is very similar for both compounds.

The observed spin-glass characteristics are comparable to those found in canonical spin-glasses, which typically are magnetic alloys with a few percentages of magnetic impurities [7]. In the present case, we are dealing with a magnetic insulator and therefore, the interactions are short range and dominantly of antiferromagnetic nature. Spin-glass state is our case is caused by site disorder and a distribution of magnetic impurity distances which leads to exchange interaction randomness and frustration.

3.3 Heat Capacity

Heat capacity of $TbFeTi_2O_7$ and $LuFeTi_2O_7$ compounds shows a broad magnetic contribution at low temperatures (Fig. 5a inset). The lattice phonon contribution has been removed to obtain the magnetic contribution which is shown in Fig. 5a. In the case of $TbFeTi_2O_7$, it has been estimated the magnetic heat capacity assigned to Tb^{3+} by removing the contribution of $LuFeTi_2O_7$. The rounded shape indicates that no long-range magnetic order transition takes place fully compatible with spin-glass state. Additionally, we can assert that there is no evidence for a change in symmetry between 1.9 and 300 K.

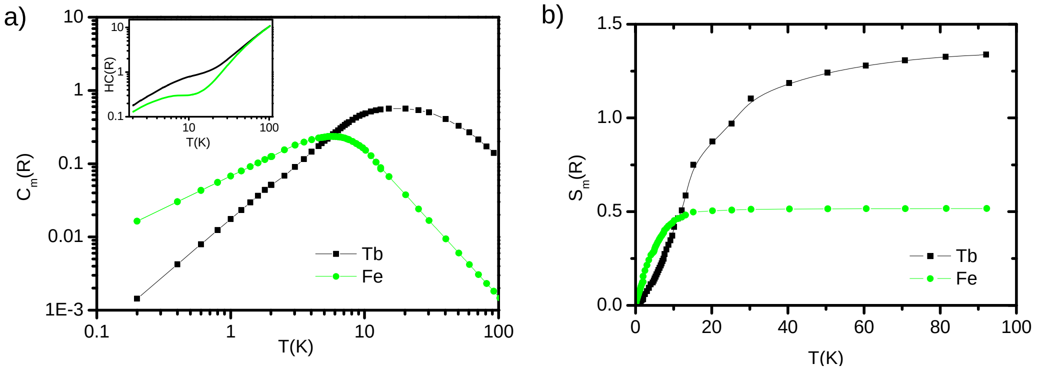

Fig. 5. a) Temperature dependences of the magnetic contribution to the heat capacity, C_m, of Tb^{3+} in $TbFeTi_2O_7$ (black squares) and Fe^{3+} in $LuFeTi_2O_7$ (green circles); inset: HC of both compounds before removing lattice contribution. b) Magnetic entropy as a function of temperature.

The magnetic entropy for $LuFeTi_2O_7$ increases up to a value of about 0.5R at 20K. This contribution is due uniquely to Fe^{3+} ions, being much less than the otherwise expected value for a S=5/2 system, namely 1.79R, clear indication of the multiplicity of the ground state typical of spin-glasses. On the other hand, the calculated entropy of Tb^{3+} in $TbFeTi_2O_7$ system shows an increase up to much higher temperatures, reaching 1.3R, neatly lower than $R\ln(2J_{Tb}+1)=2.56R$, evidencing as well a lack of entropy, characteristic of spin-glass behavior (Fig. 5b).

4 Summary

Polycrystalline samples of $TbFeTi_2O_7$ and $LuFeTi_2O_7$ are synthesized by the solid-phase reaction. As determined from X-ray measurements at room temperature, the compounds crystallize in orthorhombic space group *Pcnb*. There are five nonequivalent crystallographic positions for magnetic iron ions Fe^{3+} and one position of the R^{3+} ion in $RFeTi_2O_7$. Therefore, the atomic disorder in the distribution of the Fe^{3+} ions over several nonequivalent structural sites is confirmed.

Static and dynamic magnetic measurements demonstrate that $RFeTi_2O_7$ (R=Lu and Tb) exhibit spin glass behavior at low temperatures. Spin-glass transition is observed at T_{SG} = 4.5K for $LuFeTi_2O_7$ and T_{SG}=6K for $TbFeTi_2O_7$.

The heat capacity behavior indicates that no structural or magnetic order transition has been observed in $TbFeTi_2O_7$ and $LuFeTi_2O_7$ compounds in temperature range 2-300 K. Magnetic contribution to heat capacity is fully compatible with spin-glass state, with a broad maximum at temperatures higher than T_{SG}. The subtended entropy indicates that an important contribution is due to the ground state entropy, characteristic of frustrated systems.

The study of the $RFeTi_2O_7$ (R=Lu and Tb) compounds allow to understand the main role of Fe^{3+} ions in the magnetic properties formation. In the $LuFeTi_2O_7$ compound lutetium is nonmagnetic and only Fe-moments take a part in the ground magnetic state formation. The substitution of the magnetic and highly anisotropic Tb ion instead of Lu increases spin-glass temperature T_{SG} because of the additional Tb-Fe exchange magnetic interaction, while the critical exponent of the frequency dependence on temperature hardly varies. Additionally, a lower degree of frustration is found for the TbFe compound, indicating that the presence of magnetic Tb^{3+} in fixed positions in the structure, increases magnetic interaction and reduces frustration in these compounds.

As a final conclusion, the nature of the “frozen” spatial distribution of the spin magnetic moments orientations in the $RFeTi_2O_7$ (R=Lu and Tb) is most likely associated with the competitive magnetic interactions between the nearest neighbors of Fe^{3+} ions in different crystallographic sites, and by the frustration of the magnetic moments caused by them.

Acknowledgements

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