

Role of Fe magnetic subsystems to form a magnetic spin glass state in $RFeTi_2O_7$



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ABSTRACT

The experimental studies on $R^{3+}Fe^{3+}Ti_2O_7$ (R=Sm, Gd, Tb, Tm, Dy) magnetic properties evidence the low temperature spin glass state in all compounds. The possibility of rare-earth cation substitution allows the investigation of the role of magnetic iron Fe^{3+} ions and rare earth R^{3+} ions subsystems in a ground state formation in these oxide compounds.

1. Introduction

The physical properties and possible applications of the new compounds that exhibit spin-glass behavior have been studied during last decades. The magnetic behavior of the rare-earth oxides with the spin-glass ground state has been studied in the past years, among them titanates with the general formula $R^{3+}Fe^{3+}Ti_2O_7$ (R=rare earth element) [1–5]. One of the open questions for the $RFeTi_2O_7$ system is the role of the transition metal Fe and magnetic rare earth ions sublattices in the formation of a ground magnetic state. Since Lu is not magnetic, it has been used as non-magnetic reference in rare earth element substitution in $R^{3+}Fe^{3+}Ti_2O_7$ system allowing the investigation of the Fe subsystem role in the magnetic state formation. In this paper we report the properties of new magnetic compound $LuFeTi_2O_7$. These studies are focused on the magnetic sublattices role determination in the formation of a ground magnetic state in $RFeTi_2O_7$.

2. Experimental

Samples of $LuFeTi_2O_7$ were prepared by solid-phase reaction at temperature of 1250 °C.

The X-ray diffraction patterns for Rietveld analysis were collected on a Bruker D8-ADVANCE diffractometer (Cu-K α radiation) with linear VANTEC detector at room temperature. All refinements of the patterns were performed with TOPAS 4.2 (Bruker).

The Mössbauer measurements were performed using an MS-1104Em spectrometer at room temperature with $^{57}Co(Cr)$ source for

powders 5–10 mg/cm² thick by natural iron content.

Magnetization measurements were carried out by a SQUID magnetometer in the temperature range of 2–300 K and external magnetic field of 500 Oe.

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 was measured using a Quantum Design PPMS in the temperature range 1.9–300 K.

3. Results and discussion

According to the results of the X-ray investigation the $LuFeTi_2O_7$ crystallizes in the orthorhombic crystal structure, with space group $Pcnb$ and parameters $a=9.8093(1)$ Å, $b=13.5069(1)$ Å, $c=7.30302(7)$ Å, $V=967.61(2)$ Å³ (cation coordinates and population of the crystal sites, p are presented in Table 1). The X-ray structural data of the $LuFeTi_2O_7$ is comparable to the $RFeTi_2O_7$ (R=Sm, Gd, Tb, Tm, Dy); they have orthorhombic crystal structure $Pcnb$ [1–5]. The main structural feature is the presence of five non-equivalent crystallographic positions of the iron ions.

Additionally, to evaluate the state of the iron ions in $LuFeTi_2O_7$, Mössbauer measurements were performed. In Fig. 1a the Mössbauer spectrum is shown as consisting of a sum of overlapping quadrupole doublets. To determine the composition of the model spectrum the probability distribution of quadrupole splittings $P(QS)$ in the experimental spectrum was calculated. Two groups of doublets with various

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Table 1Cation coordinates, occupation of the structural sites p , and isotropic thermal parameter B_{iso} .

Atom	Site multiplicity	x	y	z	p	$B_{\text{iso}}, \text{\AA}^2$
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(3)	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
Fet	4	0	0.25	0.338(2)	0.78	2.5(3)
Fef	8	0.027(6)	0.285(4)	0.190(7)	0.11	2.5(3)

chemical shifts were used as starting ones.

The maxima and features in $P(QS)$ distribution (Fig. 1b) indicate the possible nonequivalent iron sites. The information extracted from distribution $P(QS)$ was used to construct the model spectrum, which was then adjusted to the experimental spectrum upon varying the entire set of hyperfine parameters of doublets. The Mössbauer parameters are collected in Table 2. The magnitudes of isomer chemical shifts correspond to cations of iron Fe^{3+} . In order to assign the iron atoms, which were revealed using the Mössbauer procedure, to crystallographic sites, we used the results of X-ray diffractometry, notably the population of sites with iron and the degree of distortion of coordination oxygen polyhedral [2]. Emergence of several Fe3, Fet and Fef positions is caused by various number of diverse cations in the immediate environment of the central cation at their chaotic distribution in a crystal.

Note: IS is isomer chemical shift relative to $\alpha\text{-Fe}$, QS is the quadrupole splitting, W is the line width, A is the partial site population with iron, A^R is the site population with iron evaluated using the X-ray procedure, V_{ZZ}^R is the gradient of the electric field induced by the coordination oxygen polyhedron. Only the positions having population more than 2% are given in the table.

Measurements of the temperature variation of the magnetic moment $M(T)$ of $\text{LuFeTi}_2\text{O}_7$ at 500 Oe, displayed in Fig. 2 (left), show differences typical of a spin-glass state between field-cooled (FC) and

zero field-cooled (ZFC) data. The analysis of magnetic susceptibility in the range 120–300 K according to Curie-Weiss formula shows negative Neel asymptotic temperature $\theta_N = -97$ K indicating predominance of antiferromagnetic exchange interactions.

Fig. 2 (left, inset) includes the information obtained by the temperature dependences of specific heat C_p measurements on $\text{LuFeTi}_2\text{O}_7$. C_p vs T curve shows a smooth increase of heat capacity with temperature; there is no singularity indicating a long range magnetic transition.

The χ' component of AC susceptibility as a function of temperature, exhibits a cusp-like anomaly (Fig. 2 (right)). The cusp position shifts to lower temperatures at lower driving frequency (Fig. 2 (right, inset)). We have used Dynamical scaling theory near a phase transition at T_c to obtain a fit of the maximum frequency dependence. The relaxation time close to the transition follows the critical slowing down law: $f = f_0(T_f(\omega)/T_c - 1)^{z\nu}$, 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 analysis of the data for the critical slowing down gives the results: $T_c = 5.0 \pm 0.5$ K, $f_0 = 6 \pm 4 \times 10^{11}$ Hz, $z\nu = 9 \pm 1$. Moreover, we obtain a value of the empirical parameter p_f of 0.013 ± 0.002 , which is used to express the maximum peak temperature T_f vs. frequency f dependence, as following [6] $p_f = (\Delta T_f/T_f)\Delta(\log f)$. The observed dynamic characteristics are comparable to those found in canonical spin-glasses [6].

4. Conclusions

Combining the results of X-ray diffraction, Mössbauer spectroscopy, DC magnetization, AC susceptibility and calorimetric measurements the strong indication for a frozen spin-glass magnetic state with freezing temperature of $T_{SG} \approx 4.5$ K is found in $\text{LuFeTi}_2\text{O}_7$: i) the presence of atomic disorder in the distribution of the iron ions in the crystal structure; ii) a field-cooled, zero-field-cooled divergence below freezing temperature T_{SG} in the temperature dependence of magnetic moment; iii) a frequency dependence in the magnetic susceptibility of χ' below the freezing temperature and values of the empirical parameter p_f and the critical dynamical exponent $z\nu$ are similar to those

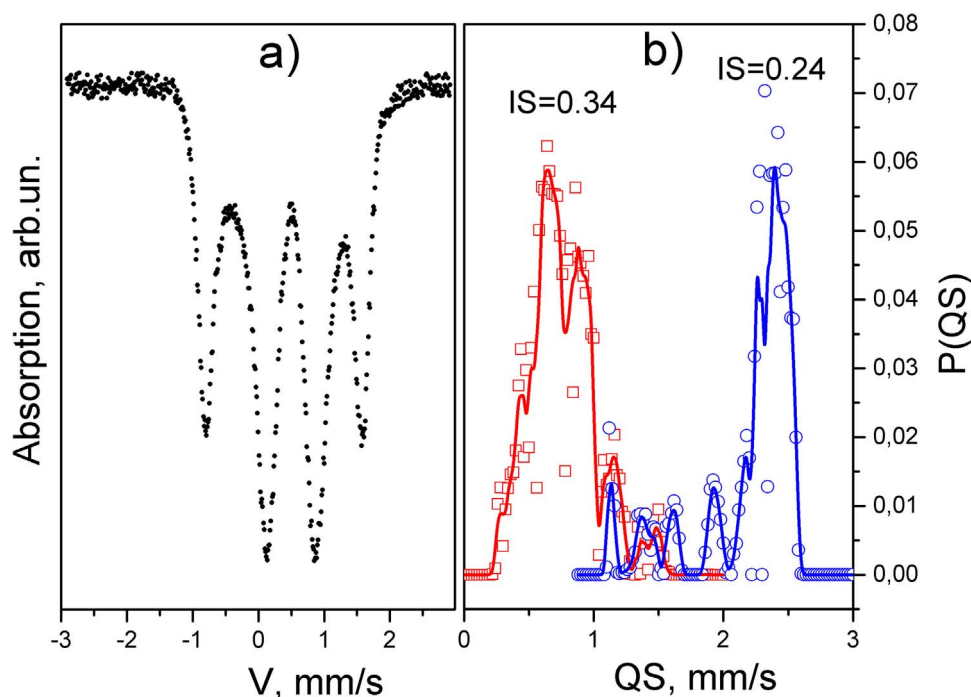


Fig. 1. The Mössbauer spectrum (a) and the probability distribution of quadrupole splitting in the experimental spectrum (b) of the $\text{LuFeTi}_2\text{O}_7$ at $T=300$ K.

Table 2The Mössbauer parameters of the LuFeTi₂O₇ at 300 K.

IS, mm/s ± 0.005	QS, mm/s ± 0.01	W, mm/s ± 0.01	A, fr.% ± 0.03	Sates	A ^R	V _{ZZ} ² , e/Å ³
0.344	0.48	0.22	0.14	Fe3	0.559	+0.043
0.344	0.70	0.21	0.19			
0.354	0.94	0.25	0.20			
0.355	1.32	0.31	0.09	Fe2	0.056	-0.089
0.107	1.29	0.29	0.05	Fef	0.076	+0.421
0.259	2.01	0.21	0.05			
0.238	2.30	0.19	0.16	Fet	0.271	+0.211
0.235	2.49	0.18	0.13			

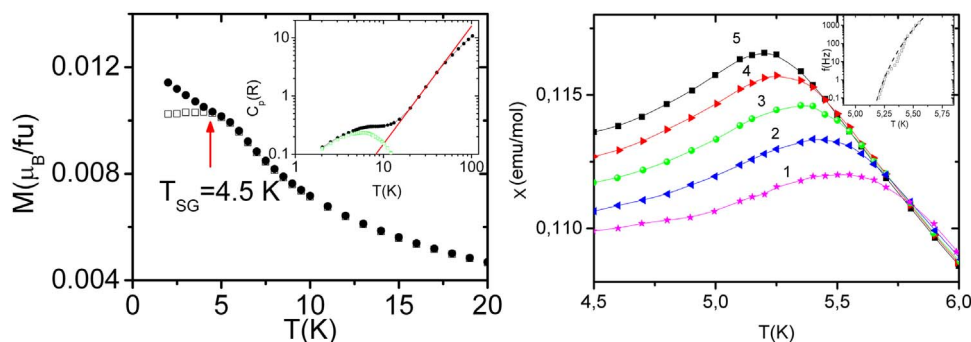


Fig. 2. Temperature dependence of the magnetization (ZFC (open squares) and FC (solid circles) curves at $H=0.5$ k Oe) (left) and the in-phase component χ' of AC magnetic susceptibilities using an AC magnetic field of 4 Oe at different frequencies: 997 Hz (1), 100 Hz (2), 10 Hz (3), 1 Hz (4) and 0.1 Hz (5) (right) for LuFeTi₂O₇. Inset (left): Temperature dependence of the heat capacity (solid circles). Lattice contribution (red line) has been removed to obtain the magnetic contribution attributed to the spin glass transition (green squares). Inset (right): Variation of the spin-glass transition temperature as a function of frequency. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

obtained in canonical spin-glasses; iii) no peak in the temperature dependence of specific heat.

The comparison of LuFeTi₂O₇ and R³⁺Fe³⁺Ti₂O₇ (R=Sm, Gd, Tb, Tm, Dy) showed that the magnetic state does not depend on the nature of the rare-earth ion. The disordered magnetism is connected with the crystal structure features. The different positions of the iron ions; a random occupation of the mixed positions (Fe-Ti) by Fe ions lead to a competing magnetic interactions between Fe³⁺ ions, the frustration and the “frozen” spatial distribution of the magnetization.

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