

Magnetic State of the $\text{GdFeTi}_2\text{O}_7$ Compound

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Abstract—The X-ray diffraction, Mössbauer, calorimetric, and magnetic characteristics of zirconolite $\text{GdFeTi}_2\text{O}_7$ have been measured to determine the ground magnetic state. A kink dependent on the magnetic prehistory of the sample has been revealed in the temperature dependence of the magnetic moment at $T = 3$ K. Mössbauer spectroscopy has confirmed the nonequivalence of the iron ion positions in $\text{GdFeTi}_2\text{O}_7$. The experimental data obtained allow the conclusion on the formation of a spin glass state with the freezing temperature $T_f = 3$ K in the $\text{GdFeTi}_2\text{O}_7$ compound.

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1. INTRODUCTION

Investigation of compounds containing $3d$ and $4f$ elements is associated with both the synthesis of new materials and the specific features of their magnetic properties. Of particular interest is the study of frustrated magnetic systems, in particular, systems with a spin glass magnetic state. In spin glasses, below a certain temperature T_f (freezing temperature), a thermodynamically nonequilibrium metastable magnetic state with a frozen spatial random distribution of the orientations of the spin magnetic moments arises [1]. A spin glass state provided by competing interactions in the magnetic subsystem of a sample is mainly manifested as the absence of anomalies in the temperature dependence of the heat capacity, the existence of a kink in the temperature dependence of the magnetic susceptibility at $T = T_f$, and also the dependence of the magnetization on the magnetic prehistory of a sample [1, 2].

There is a wide series of materials with the spin glass magnetic state, among them are oxide compounds [1–8]. Among spin glass materials are compounds with the cubic spinel structure, e.g., CuGa_2O_4 (space group $Fd\bar{3}m$) with the freezing temperature $T_f = 2.5$ K [3]. The compounds with the rutile structure, e.g., CrNbO_4 (space group $P4_2/mnm$) and FeTaO_4 manifest the spin glass properties below temperatures of 9.3 and 25.0 K, respectively [4]. The compounds with the pyrochlore-type structure crystallizing in space group $Fd\bar{3}m$, e.g., $(\text{Y,Sm, Gd})_2\text{Mo}_2\text{O}_7$ ($T_f = 18, 68, 55$ K, respectively) [5] and $(\text{Gd,Sm,Y})_2\text{Mn}_{2/3}\text{Mo}_{4/3}\text{O}_7$ ($T_f < 10–12$ K) [6] are also characterized by the spin-glass behavior. The $\text{Ba}_2\text{Fe}_2\text{GeO}_7$ com-

ound with the melilite $\text{Ga}_2\text{Al}_2\text{SiO}_7$ structure (space group $P\bar{4}2_1m$) exhibits spin-glass properties at temperatures below $T_f = 8$ K [7]. The spin glass state with $T_f = 7$ K also exists in zirconolite $\text{SmFeTi}_2\text{O}_7$ crystallizing in space group $Pbcn$.

The above-mentioned compounds are characterized by the existence of different positions of magnetic ions, which introduces a disorder in their magnetic subsystem and, as a result, leads to the frustration of magnetic interactions during formation of a disordered magnetic structure.

Of interest is further studying Ti-containing oxide compounds. In this work, we perform the X-ray diffraction, Mössbauer, calorimetric, and magnetic studies to determine the magnetic state of the $\text{GdFeTi}_2\text{O}_7$ compound.

The $\text{GdFeTi}_2\text{O}_7$ crystal is known to be isostructural to the $\text{SmFeTi}_2\text{O}_7$ $\text{GdGaTi}_2\text{O}_7$ compounds [9]. According to the X-ray diffraction data, zirconolite $\text{GdGaTi}_2\text{O}_7$ crystallizes at room temperature in centrosymmetric orthorhombic space group $Pcnb$ with the unit cell parameters $a = 9.7804(3)$ Å, $b = 13.605(4)$ Å, $c = 7.4186(2)$ Å, and the unit cell volume $V = 987.16(1)$ Å³ [9]. It is built from four-, five-, six-, and eight-vertex polyhedra. The eight-vertex polyhedron contains a rare-earth ion Gd. Gallium (iron) can be located in three closely spaced but nonequivalent crystallographic positions. The Ga(Fe) environment is an octahedron consisting of a Ga(Fe) tetrahedron and Ga'(Fe'), Ga''(Fe'') five-vertex polyhedron (Fig. 1). The Ga'(Fe') and Ga''(Fe'') atoms are arranged along the long space diagonal of this octahedron with the Ga–Ga'(Ga'') distance of 0.554(8) Å and the Ga'–

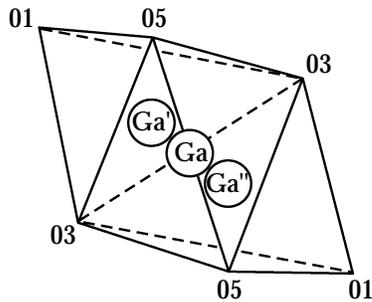


Fig. 1. An octahedron formed by the Ga(Fe) tetrahedron and Ga'(Fe'), Ga''(Fe'') five-vertex polyhedra [9].

Ga'' distance of 1.011(11) Å. The structure of the compound also contains the mixed Ti–Fe positions, polyhedra around which are octahedra. Thus, iron is disordered over different crystallographic positions.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The GdFeTi₂O₇ compound was prepared by the solid-phase reaction method from a mixture of oxides Fe₂O₃, Gd₂O₃, and TiO₂. The samples being 1.5–2.0-mm-thick pellets 10 mm in diameter was subjected to a high-temperature treatment at a temperature of 1250°C and normal pressure. The synthesis was carried out for three stages with intermediate grinding and repeated pressing. The chemical and phase compositions of the sample was controlled using X-ray diffraction and nuclear γ resonance, and also an optical microscope.

The X-ray diffraction study of the polycrystalline samples was performed on a D8-ADVANCE diffractometer (CuK α radiation, θ – 2θ scan mode) using a VANTEC linear detector and a TTK 450 Anton Paar temperature chamber at $T = 130$ and 300 K. The scan step in the angle 2θ was 0.016°. The unit cell parameters were found and refined during fitting of the profiles using the WTROR and DDM programs [10, 11].

The Mössbauer studies were performed at room temperature on powders (5–10 mg/cm²) in natural iron content on an MC-1104Em spectrometer (Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences) using a ⁵⁷Co(Cr)

Table 1. Parameters of the crystal unit cell of GdFeTi₂O₇

Parameter	Value
a , Å	7.4248(2)
b , Å	13.6466(4)
c , Å	9.8455(3)
V , Å ³	997.32(5)

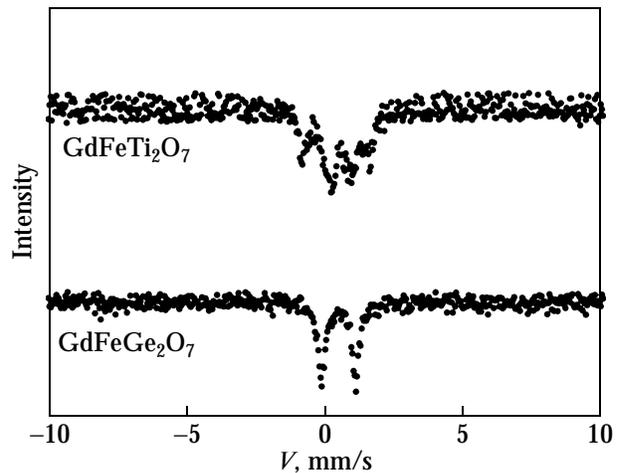


Fig. 2. Mössbauer spectra of GdFe(Ge,Ti)₂O₇ compounds at $T = 300$ K.

source. The isomer chemical shifts were measured with respect to metallic α -Fe.

The magnetic measurements were carried out on an MPMS-XL magnetometer (Siberian Federal University) in the temperature range 2–300 K in a magnetic field of 500 Oe.

The calorimetric measurements were performed on a Quantum Design PPMS 6000 setup (Center of Collective Usage of the Krasnoyarsk Scientific Center) in the temperature range 2–300 K.

3. EXPERIMENTAL RESULTS

The X-ray diffraction studies of the polycrystalline samples at room temperature showed that the material synthesized does not contain impurity, it has the orthorhombic crystal structure, space group $Pbcn$; in addition, the studies allowed the refinement of the unit cell parameters (Table 1). No changes in the structure were observed with decreasing temperature to 130 K.

To confirm the nonequivalence of the crystallographic positions of the Fe³⁺ ions in the GdFeTi₂O₇ compound, we studied the samples by the nuclear γ resonance method. Figure 2 depicts the Mössbauer spectrum of GdFeTi₂O₇. For comparison, the spectrum of GdFeGe₂O₇ is shown in this figure. Unlike GdFeTi₂O₇, the quadrupole doublet observed in GdFeGe₂O₇ is due to the only crystallographic position of Fe³⁺. Table 2 gives the Mössbauer spectrum parameters of the GdFe(Ge,Ti)₂O₇ compounds: the isomer shift IS, quadrupole splitting QS, line width W , and occupancy A . In contrast to germanium oxides, titanium oxides have at least two nonequivalent iron positions (1 and 2) with different occupancies.

A relatively small chemical shift (IS = 0.22 mm/s) and high value of the quadrupole splitting (QS = 2.42)

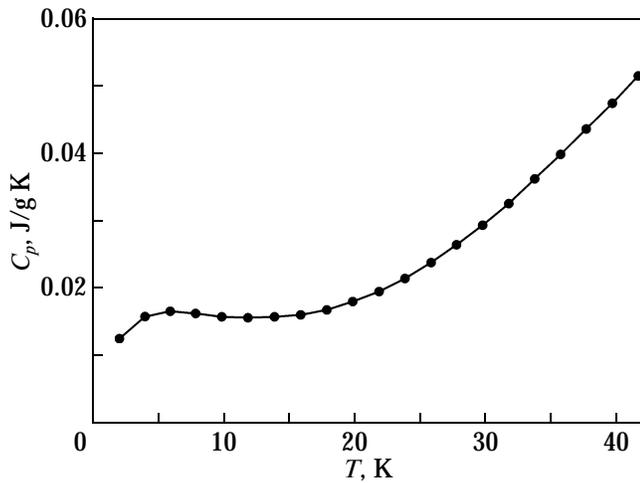


Fig. 3. Temperature dependence of the heat capacity of the GdFeTi₂O₇ compound.

demonstrate that the coordination of surrounding anions and strong distortion of the local symmetry in position 1 of iron are lower as compared to the octahedron. The parameters of position 2 are characteristic of the iron that is in the octahedron.

The study of the thermal properties of the GdFeTi₂O₇ compound shows that the temperature dependence of the heat capacity shown in Fig. 3 has no anomalies characteristic of a magnetic phase transition. Thus, it may be suggested that there is no long-range magnetic order in GdFeTi₂O₇ in the temperature range 2–300 K.

We studied the magnetic properties of the GdFeTi₂O₇ compound. The temperature dependence of the magnetic moment measured in a field of 0.05 T is shown in Fig. 4. There is a kink in the curve of the magnetic moment measured during cooling in a zero magnetic field (ZFC). The specific feature of the magnetic properties is also the dependence of the magnetic moment on the thermal prehistory (cooling the sample in the magnetic field $H = 0.05$ T (FC) and in a zero magnetic field $H = 0$ (ZFC)) observed below the temperature $T = 3$ K.

The results of the magnetic measurements become understood by assuming that the spin glass state char-

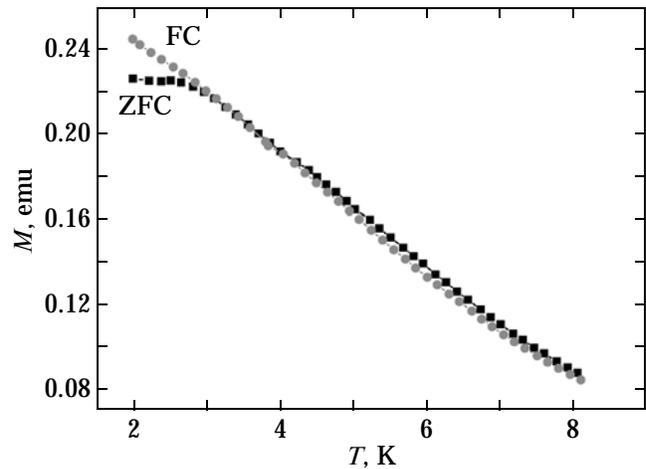


Fig. 4. Temperature dependence of the magnetic moment of GdFeTi₂O₇ measured in a field of 0.05 T. The sample was cooled in a zero magnetic field (ZFC) and in a magnetic field (FC).

acterized by an ensemble of randomly arranged and frozen magnetic moments exists in the GdFeTi₂O₇ at temperatures below 3 K. The both peculiarities of the temperature dependence of the magnetic moment of the GdFeTi₂O₇ compound are characteristic of systems in which the ground magnetic state is characterized as the spin glass state. This fact is also confirmed by the calorimetric measurements (the absence of a phase transition in the temperature dependence of the heat capacity). The formation of the spin-glass state is favored by a random distribution of the magnetic Fe³⁺ ions along different crystallographic positions as demonstrated by the X-ray diffraction and Mössbauer studies.

Thus, the experimental facts characterizing the properties of GdFeTi₂O₇ indicate on the magnetic transition from the paramagnetic state to the spin-glass state at the freezing temperature $T_f = 3$ K.

4. CONCLUSIONS

The GdFeTi₂O₇ compound was synthesized by the solid-phase reaction method. We performed the X-ray diffraction, Mössbauer, calorimetric, and magnetic studies of zirconolite GdFeTi₂O₇. Based on the experimental data, it was found that the spin-glass magnetic state is formed in the GdFeTi₂O₇ compound at temperatures below $T_f = 3$ K.

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Table 2. Mössbauer parameters of the GdFe(Ge, Ti)₂O₇ samples

Sample (iron position)	IS, mm/s	QS, mm/s	W , mm/s	A
GdFeGe ₂ O ₇	0.31	1.22	0.3	1
GdFeTi ₂ O ₇ (1)	0.22	2.42	0.28	0.25
GdFeTi ₂ O ₇ (2)	0.38	0.78	0.60	0.75

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