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Spin-glass magnetic ordering in $CoMgGaO_2BO_3$ ludwigite

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The single crystal needle shape samples of diamagnetically diluted cobalt ludwigite $CoMgGaO_2BO_3$ have been grown by the flux method. The results of x-ray diffraction and both dc and ac magnetic measurements are presented. The unit cell volume undergoes a noticable growth under dilution from 328.31 Å^3 for the parent compound $Co_3O_2BO_3$ to 345.46 Å^3 for $CoMgGaO_2BO_3$. The temperature of magnetic transition is considerably lower for the latter compound (25 K against 43 K for $Co_3O_2BO_3$). The dc magnetization temperature dependencies undergo the splitting of field cooled and zero-field cooled regimes and the ac magnetic susceptibility temperature dependencies are frequency dependent pointing out a possible spin-glass freezing in the magnetic system.

PACS: 74.62.Bf Effects of material synthesis, crystal structure, and chemical composition;
75.50.Lk Spin glasses and other random magnets.

Keywords: transition metal ludwigites, spin-glass freezing.

1. Introduction

The transition metal oxyborate compounds with the ludwigite structure are under grate attentively consideration during last few years [1–4]. The reason is the complex hierarchy of exchange interactions coming from the presence of low-dimensional subunits in the crystallographic structure and the magnetic ions in different valence states. The most interesting among these compounds seem being the materials $Fe_3O_2BO_3$, $Co_3O_2BO_3$ and their solid solutions $Co_{3-x}Fe_xO_2BO_3$, where nontrivial magnetic behavior was found out by the means of magnetization measurements [5], Mössbauer spectroscopy [6] and neutron diffraction [7].

All the materials in the row $Co_{3-x}Fe_xO_2BO_3$ under cooling demonstrate long magnetic ordering with brightly pronounced anisotropy, the scenario of the magnetic ordering being very complex. The first attempt to estimate the strength of superexchange interactions in these systems have been made in [8], where the frustrated character of the superexchange interactions has been proved.

In order to extend the understanding of the magnetic interactions nature in the transition metal ludwigites it is necessary to investigate not only the materials where one transition ion is substituted by the other transition ion (in this case the picture is very complex), but also the materials with nonmagnetic dilution. The first step in this direction have been made in [9] for $Co_5Ti(O_2BO_3)_2$, where it was shown that the presence of Ti^{4+} nonmagnetic ions destroys long magnetic order and leads to the spin-glass freezing. The present work continues the investigations made in [9], but in our case we more intently focus on the valence state of nonmagnetic ions. The matter is in the fact that there are four distinct crystallographic positions of the transition metal in the ludwigite structure occupying by the ions in the different valence state with brightly pronounced preference. As it is shown in [8], the three positions belong mostly to divalent transition ions, and the last position is filled by trivalent ions. By this reason we decided entering both di- and trivalent nonmagnetic ions Mg^{2+} and Ga^{3+} to the cobalt ludwigite $Co_3O_2BO_3$ and investigating their influence to the magnetic ordering scenario.

2. Synthesis, x-ray diffraction and experimental technique

The single crystals $Co_3O_2BO_3$ were prepared by the flux method. The components $Bi_2Mo_3O_{12}$, B_2O_3, Li_2CO_3, Co_2O_3, Ga_2O_3, MgO were taken in molar relation corresponding to almost equal concentration of Co, Mg and Ga ions. So, we propose the chemical formula of the prepared compound being $CoMgGaO_2BO_3$. The total mass of the components was 50 g. The mixture was melted under the temperature $T = 1100$ °C. Then the spontaneous crystallization occurred in the temperature interval 980–990 °C. As the result small needle shape single crystals were obtained. The needles were up to some millimeters long but their thickness was too small carrying out the precise weighting and one single crystal magnetic measurements. By this reason the magnetic and x-ray diffraction investigations have been made for the powder, prepared by means of single crystals grinding. The x-ray measurements have been done at room temperature using the diffractometer D8 ADVANCE with Vantec detector (CuK_α radiation, $\lambda = 1.5406$ Å, scanning angle $2\theta = 6–70°$).

The x-ray diffraction data pointed out the ludwigite structure of the samples, the same as for $Co_3O_2BO_3$. The lattice parameters of the diluted ludwigite $CoMgGaO_2BO_3$ in the comparison with the same for the parent compound $Co_3O_2BO_3$ are shown in the Table 1. The unit cell volume for the former compound about 5% exceeds the same for the latter. Taking into account the closeness of di- and trivalent the ionic radii ($r_{Co^{2+}} = 0.745$, $r_{Mg^{2+}} = 0.72$, $r_{Co^{3+}} = 0.61$, $r_{Ga^{3+}} = 0.62$ Å), one can assume that the increase of the unit cell volume is called by the high value of disorder in the substituted system.

Table 1. The lattice parameters of $Co_3O_2BO_3$ and $CoMgGaO_2BO_3$

Compound	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
$Co_3O_2BO_3$	9.2800(9)	11.9278(11)	2.9660(3)	328.31(6)
$CoMgGaO_2BO_3$	9.288(3)	12.263(4)	3.033(1)	345.46(6)

The magnetic properties were investigated using a commercial PPMS 6000 platform (Quantum Design). The temperature dependences of the dc magnetization were measured at an applied field $H = 500$ Oe in the temperature interval 2–300 K. The magnetization isotherms were obtained in the field up to 90 kOe at 2–40 K. The ac magnetic susceptibility temperature dependencies (phase component) were measured for the frequencies 10^2–10^4 Hz.

3. Magnetic data

The static magnetization temperature dependencies presented at Fig. 1 demonstrate i) the peak near 20 K, ii) brightly pronounced splitting of the curves corresponding to field cooled (FC) and zero-field cooled (ZFC) regimes. The inverse dc magnetic susceptibility temperature dependence at the temperatures above $T = 150$ K by the eye seems being close to linear as Curie–Weiss law predicts (not shown). Under the proposal that Curie–Weiss law obeys, the paramagnetic Curie temperature $\Theta = -260$ K is high negative pointing out the pronounced predominance of antiferromagnetic interactions. This is typical for the oxiborates [10]. Nevertheless the formula unit effective magnetic moment $\mu_{\text{eff}} = 12\ \mu_B$ appears to be unexpectedly high. The typical value for the parent compound Co_3BO_5 with only cobalt magnetic ions is only near 7 μ_B per formula unit [11], and we have expected a much lower value in our diluted material. So we have to admit that the magnetic behavior of $CoMgGaO_2BO_3$ even far above the magnetic transition isn't simple paramagnetic and can't be described in the frame of Curie–Weiss mechanism.

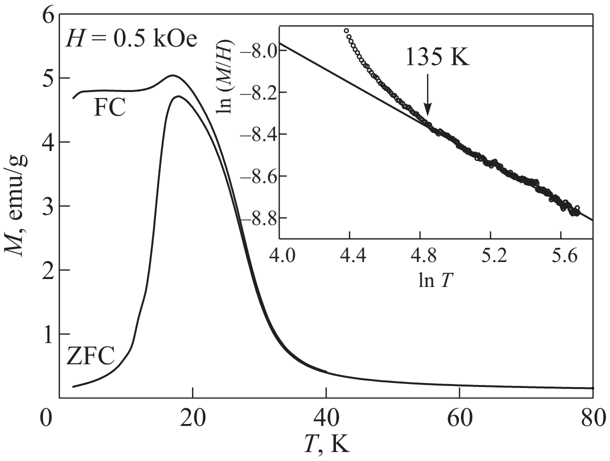

Fig. 1. Static magnetization temperature dependencies in the field cooled (FC) and zero-field cooled (ZFC) regimes. In the inset: the magnetic susceptibility temperature dependence in the logarithmic scale. Power law approximation is shown as a solid line.

The magnetization isotherms (Fig. 2) aren't linear as below the magnetic transition, as not far above it. At all the temperatures the magnetization is far from the saturation even in the field 90 kOe. The *M*(*H*) curve at $T = 2$ K is irreversible and present the jump of magnetization.

The behavior of χ' — the real part of ac magnetic susceptibility — as a function of the temperature at different frequencies is shown in the inset of Fig. 2. The first that catch an eye is a high peak near $T = 25$ K. A frequency dependence of $\chi'(T)$ maxima position can be noticed. The temperature corresponding to the peak susceptibility value slightly grows with the frequency. The temperature of

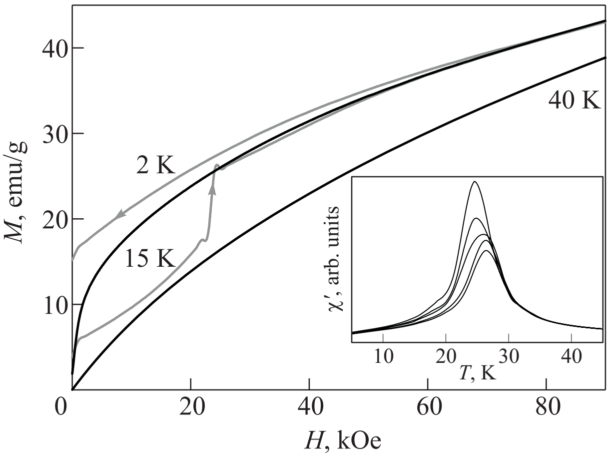

Fig. 2. The magnetization isotherms of $CoMgGaO_2BO_3$ below and above the magnetic transition. In the inset: ac magnetic susceptibility (real component) temperature dependences at the frequencies 0.1, 0.5, 1, 5 and 10 kHz (up – bottom).

magnetic ordering in $CoMgGaO_2BO_3$ is considerably lower than that in the parent $Co_3O_2BO_3$ with $T_N = 43$ K.

4. Discussion

In ludwigites the ratio of divalent metal ions to trivalent metal ions is 2:1. According to charge equilibrium we need to assume that in $CoMgGaO_2BO_3$ divalent Mg^{2+} substitutes divalent Co^{2+} and trivalent Ga^{3+} substitutes trivalent Co^{3+}. Looking at the chemical formula of our compound $CoMgGaO_2BO_3$ one can see that at the equal concentrations of Co, Mg and Ga cobalt ions in the trivalent state have to be totally substituted by Ga. The last cobalt ions are mostly in divalent state with d^7 configuration and $S =$ $= 3/2$. In the insulating oxyborates the predominant type of the exchange interactions is the superexchange through the oxygen cations. According to the high negative value of the paramagnetic Curie temperature one may admit that in our case this superexchange is of antiferromagnetic character.

Our diluted $CoMgGaO_2BO_3$ ludwigite demonstrates brightly pronounced bifurcation between FC and ZFC magnetization temperature dependences together with frequency dependent dynamic susceptibility and step-like magnetization isotherm. These peculiarities aren't typical for long-magnetic-ordered system but contrary are the characteristics of metastable magnetic phases such as spin-glass systems. The similar behavior was previously observed for the related diluted compound $Co_5Ti(O_2BO_3)_2$ [9], and also for the member of manganite family — highly disordered $La_{1.1}Sr_{1.9}Mn_2O_7$ [12]. In the former ludwigite material the heat capacity temperature dependence wasn't a peak-like showing the absence of first-order phase transition. In the latter manganite the steps on $M(H)$ curve were followed by the pronounced memory effect — well known property of the spin glasses. In all the cases the steps in the magnetization isotherm were visible below the magnetic transition were the energy of exchange interactions noticeably exceeds the heat energy. Comparing our results with the previously obtained data [9,12] one can see that in all the cases the picture is quite similar. Probably in our compound we also deal with magnetic moments freezing at 25 K but not long-range magnetic ordering.

The behavior of our $CoMgGaO_2BO_3$ in the paramagnetic phase now isn't totally cleared up. From the one hand, the inverse susceptibility trace seems being close to linear at high temperatures as Curie–Weiss law predicts and paramagnetic Curie temperature accepts negative value typical for the oxyborates. From the other hand, the estimated in the frame of Curie–Weiss behavior effective magnetic moment value is unexpectedly high. As it is noted in [10], the magnetic susceptibility can be higher than it follows from Curie–Weiss law in the case of random magnetic chains forming. In our material with low-dimensional structural subunits and nonmagnetic dilution this situation is quite probable. In the case of ludwigites the number of legs forming the ladder is odd (3) and antiferromagnetic interactions predominate, so we can deal with $S = 3/2$ random antiferromagnetic Heizenberg chains. In this case the magnetic susceptibility obeys power law $\chi \sim T^{-\alpha}$, where α is weakly temperature dependent exponent. This power law of susceptibility behavior was early registrated in different oxyborates with warwickite structure and $MnMgO_2BO_3$ ludwigite [10], α lying in the interval 0.50–0.83. For our $CoMgGaO_2BO_3$ the susceptibility versus temperature in the logarithmic scale is presented in the inset of Fig. 1, where one can see that the power dependence with $\alpha = 0.48$ well describes the experimental data at the temperatures higher than 135 K. The temperature interval where the power law obeys is wider than that for Curie–Weiss behavior so we can propose that in our case the Heisenberg model is more adequate. The α value is close to the same known for the other random oxyborates. For the temperatures between magnetic transition point and 135 K nor Curie–Weiss nor power law aren't consisting with the magnetic susceptibility behavior pointing the large contribution of short range order correlations (SRO) previously observed for nonmagnetically diluted iron ludwigite $FeMg_2BO_5$ with spin-glass freezing [13].

Conclusion

As a result of present investigation we can conclude that the diamagnetic dilution destroys the net magnetic ordering in cobalt ludwigite. At the temperature $T = 25$ K the system undergoes a spin-glass freezing with predominating antiferromagnetic interactions. Above the spin-glass transition the magnetic behavior of the system is rather complex. Below $T = 135$ K the material demonstrates brightly pronounced short range order magnetic correlations. Up to room temperature it isn't possible clearly distinguish between random Heisenberg $S = 3/2$ antiferromagnetic chains and simple Curie–Weiss paramagnetic behavior. This question needs the additional investigation.

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