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Spin-glass magnetic ordering in $CoMgGaO_2BO_3$ ludwigite

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Single crystal, needle shaped samples of diamagnetically diluted cobalt ludwigite $CoMgGaO_2BO_3$ have been grown by the flux method. X-ray diffraction and both dc and ac magnetic measurements are described. The unit cell volume changes significantly with dilution, from 328.31 $Å^3$ for the parent compound $Co_3O_2BO_3$ to 345.46 $Å^3$ for $CoMgGaO_2BO_3$. The magnetic transition temperature is considerably lower for the latter compound (25 K against 43 K for $Co_2O_2BO_3$). The dc magnetization temperature dependences are split between the field cooled and zero-field cooled regimes and the ac magnetic susceptibility temperature curves are frequency dependent, which indicates possible spin-glass freezing in the magnetic system.

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I. INTRODUCTION

The transition metal oxyborate compounds with ludwigite structures have received a great deal of attention in the past few years.[1–4] This is because of a complex hierarchy of exchange interactions owing to the presence of low-dimensional subunits in the crystallographic structure and magnetic ions in different valence states. The most interesting of these compounds appear to be $Fe_3O_2BO_3$, $Co_3O_2BO_3$ and their solid solutions $Co_{3\text{-}x}Fe_xO_2BO_3$, where nontrivial magnetic behavior has been detected through magnetization measurements,[5] Mössbauer spectroscopy,[6] and neutron diffraction.[7]

When cooled, all the members of the series $Co_{3-x}Fe_xO_2BO_3$ manifest long-range magnetic ordering with a highly pronounced anisotropy and a very complex magnetic ordering configuration. A first attempt to estimate the strength of the superexchange interactions in these systems was made in Ref. 8, where frustration of superexchange interactions was demonstrated.

In order to extend our understanding of the magnetic interactions in the transition metal ludwigites, it is necessary to investigate materials where one transition ion is replaced by another transition ion (in this case the picture is very complex), as well as materials with nonmagnetic dilution. The first step in this direction has been taken[9] for $Co_5Ti(O_2BO_3)_2$, for which it was shown that the presence of Ti^{4+} nonmagnetic ions destroys long-range magnetic order and leads to spin-glass freezing. This paper continues that earlier study,[9] but here we focus more intently on the valence state of the nonmagnetic ions. In fact, there are four distinct crystallographic positions of the transition metal in a ludwigite structure occupied by ions in different valence states with distinct preferences. It has been shown[8] that three positions belong mostly to divalent transition ions, while the last position is filled by trivalent ions. For this reason we decided to add simultaneously the di- and trivalent nonmagnetic ions Mg^{2+} and Ga^{3+} to the cobalt ludwigite $Co_3O_2BO_3$ and investigate their effect on magnetic ordering.

II. SYNTHESIS, X-RAY DIFFRACTION AND EXPERIMENTAL TECHNIQUE

Single crystals of $Co_3O_2BO_3$ were prepared by the flux method. The components $Bi_3Mo_3O_{12}$, B_2O_3, Li_2CO_3, Co_2O_3, Ga_2O_3, and MgO were taken in molar proportions corresponding to almost equal concentrations of Co, Mg and Ga ions. Thus, we propose the chemical formula $CoMgGaO_2BO_3$ for the prepared compound. The total mass of the components was 50 g. The mixture was melted at temperature $T = 1100\,^{\circ}$C. Then spontaneous crystallization occurred in the temperature interval 980–990 °C. This produced small, needle shaped single crystals. The needles were up to several millimeters in length, but their thickness was too small for precise weighing and single-crystal magnetic measurements. For this reason, the magnetic and x-ray diffraction studies were made on a powder, prepared by grinding single crystals. The x-ray measurements have been done at room temperature using a D8 ADVANCE diffractometer with a Vantec detector (CuK_α radiation, $\lambda = 1.5406$ Å, scanning angle $2\theta = 6$–70°).

The x-ray diffraction data revealed the ludwigite structure of the samples, as in the case of $Co_3O_2BO_3$. The lattice parameters of the diluted ludwigite $CoMgGaO_2BO_3$ are compared with those of the parent compound $Co_2O_2BO_2$ in Table I. The unit cell volume of the former compound is about 5% greater than that of the latter. Given the similarity of di- and trivalent ionic radii ($r_{Co^{2+}} = 0.745$, $r_{Mg^{2+}} = 0.72$, $r_{Co^{3+}} = 0.61$, $r_{Ga^{3+}} = 0.62$ Å), it appears that the increase of the unit cell volume is a result of the high level of disorder in the substituted system.

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

III. MAGNETIC DATA

The static magnetization vs. temperature curves shown in Fig. 1 manifest (i) a peak near 20 K and (ii) strongly pronounced splitting of the curves corresponding to field cooled (FC) and zero-field cooled (ZFC) regimes. The inverse temperature dependence of the dc magnetic susceptibility above $T = 150$ K appears to be close to linear as the Curie-Weiss law predicts (not shown here). Assuming that the Curie-Weiss law holds, the paramagnetic Curie temperature $\Theta = -260$ K is high negative, indicating a strong predominance of antiferromagnetic interactions. This is typical for the oxiborates.[10] Nevertheless the effective magnetic moment per formula unit, $\mu_{\text{eff}} = 12\,\mu B$, seems unexpectedly high. The typical value for the parent compound Co_3BO_5 with only cobalt magnetic ions is only about $7\,\mu B$ per formula unit,[11] and we expected a much lower value for our diluted material. Thus, we have to admit that, even far above the magnetic transition, the magnetic behavior of $CoMgGaO_2BO_2$ is not simply paramagnetic and cannot be described in terms of the Curie-Weiss mechanism.

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

TABLE I. 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)

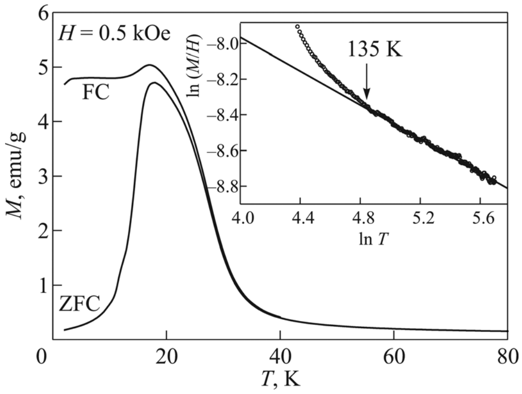

FIG. 1. Static magnetization temperature curves in the field cooled (FC) and zero-field cooled (ZFC) regimes. Inset: magnetic susceptibility as a function of temperature on a log-log scale. A power law approximation is shown as a solid curve.

The behavior of χ', the real part of the ac magnetic susceptibility, as a function of temperature at different frequencies is shown in the inset of Fig. 2. The first noteworthy feature is a high peak near $T = 25$ K. The maximum of $\chi'(T)$ clearly has a frequency dependence. The temperature corresponding to the peak susceptibility increases slightly with frequency. The magnetic ordering transition temperature in $CoMgGaO_2BO_2$ is considerably lower than that in the parent $Co_3O_2BO_3$ with $T_N = 43$ K.

IV. DISCUSSION

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

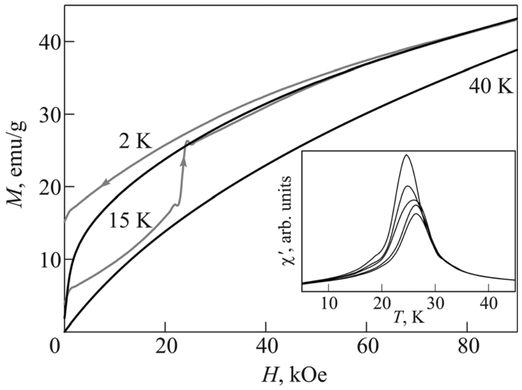

FIG. 2. Magnetization isotherms of $CoMgGaO_2BO_3$ below and above the magnetic transition. Inset: ac magnetic susceptibility (real component) as a function of temperature for frequencies of 0.1, 0.5, 1, 5, and 10 kHz (top-to-bottom).

temperature, it appears that in our case, this superexchange has an antiferromagnetic character.

Our diluted $CoMgGaO_2BO_3$ ludwigite exhibits a strongly pronounced bifurcation between FC and ZFC magnetization temperature dependences, as well as a frequency dependent dynamic susceptibility and a step-like magnetization isotherm. These peculiarities are not typical of long-range magnetically-ordered systems, but, rather, are the characteristics of metastable magnetic phases such as spin-glass systems. Similar behavior was been observed in the related diluted compound $Co_5Ti(O_2BO_3)_2$,[9] and also in the member of manganite family, the highly disordered $La_{1.1}Sr_{1.9}Mn_2O_7$.[12] In the first, ludwigite material, the heat capacity as a function of temperature did not have a peak, which indicates the absence of first-order phase transition. In the latter, manganite, material the steps in the $M(H)$ curve are followed by a distinct memory effect, which is a well known property of spin glasses. In all cases, steps in the magnetization isotherm could be seen below the magnetic transition, where the energy of the exchange interactions is substantially higher than the thermal energy. Comparing our results with the previously obtained data[9,12] one can see that the picture is quite similar in all cases. Presumably the magnetic moments freeze at 25 K in our compound, but long-range magnetic ordering does not occur.

The behavior of our $CoMgGaO_2BO_3$ in the paramagnetic phase is still not entirely clear. On one hand, the inverse susceptibility curve seems nearly linear at high temperatures as predicted by the Curie-Weiss law, and the paramagnetic Curie temperature is negative, as is typical for the oxyborates. On the other hand, the Curie-Weiss estimate for the effective magnetic moment is unexpectedly high. It has been pointed out[10] that the magnetic susceptibility can be higher than implied by Curie-Weiss law in the case where random magnetic chains form. In our material with its low-dimensional structural subunits and nonmagnetic dilution, this situation is quite probable. In the case of ludwigites the number of steps forming the ladder is odd (3) and antiferromagnetic interactions predominate, so are dealing with $S = 3/2$ random antiferromagnetic Heisenberg chains. In this case the magnetic susceptibility follows a power law $\chi \sim T^{-\alpha}$, where α is a weakly temperature dependent exponent. This power law for the susceptibility has been observed previously in different oxyborates with warwickite structure and $MnMgO_2BO_3$ ludwigite,[10] with $\alpha = 0.50$–0.83. For our $CoMgGaO_2BO_3$ the susceptibility is plotted as a function of temperature on a log-log scale in the inset of Fig. 1; here it can be seen that the power-law dependence with $\alpha = 0.48$ gives good fit to the experimental data at temperatures above 135 K. The temperature interval where the power law holds is wider than that for Curie-Weiss behavior, so we propose that the Heisenberg model is better in our case. The value of α is close to that for the other random oxyborates. For the temperatures between the magnetic transition point and 135 K, neither the Curie-Weiss law nor the power law are consistent with the observed magnetic susceptibility. This indicates a large contribution from short-range order correlations (SRO) of the sort observed in the nonmagnetically diluted iron ludwigite $FeMg_2BO_5$ with spin-glass freezing.[13]

V. CONCLUSION

We have shown that diamagnetic dilution destroys the net magnetic ordering in cobalt ludwigite. At temperature $T = 25$ K the system undergoes spin-glass freezing with predominant antiferromagnetic interactions. Above the spin-glass transition, the magnetic behavior of the system is rather complex. Below $T = 135$ K the material manifests distinct short-range magnetic order correlations. Up to room temperature it is not possible to distinguish clearly between random Heisenberg $S = 3/2$ antiferromagnetic chains and simple Curie-Weiss paramagnetic behavior. This question requires further study.

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