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The superexchange interactions in mixed Co–Fe ludwigite

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ABSTRACT

The crystal structure, cation distribution and exchange interactions in the $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ ludwigite have been explored through X-ray diffraction, electrical resistivity, *ac*-susceptibility and Mossbauer effect measurements. The crystal data have shown that iron atoms occupy the most symmetric crystallographic sites Fe4 and Fe2. The complex magnetic behavior with two magnetic transitions near 70 and 115 K at low temperatures was found. The Mossbauer data have displayed the trivalent iron states only. The values of superexchange energies have been estimated for $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ yielding a significant role of frustrations in the ludwigite magnetic system. Variable range Mott hopping conductivity law was proved to be valid in the wide temperature region, pointing out a localized character of charge carriers rather than collective.

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1. Introduction

Cobalt oxides are attracting a great interest during some last decades mostly due to possibility of different valence, spin and orbital states of cobalt ion. Some classes of cobalt containing oxides, for example, rare-earth perovskites with the parent compound LaCoO_3 , are investigated in detail [1]. But for some other groups of cobalt oxides, only the first steps of their study have been done. The reason often is the technological difficulties of high quality single crystal synthesis. Now this problem is partially solved for cobalt oxyborates, which can crystallize in the forms of pyroborates, kotoites, warwickites, ludwigites and others. Most of these materials show a variety of interesting structural, magnetic, electric and optic properties. In the present work we focus on the ludwigite family of cobalt oxyborates.

The oxyborates $\text{M}_2\text{M}'\text{O}_2(\text{BO}_3)$ are of a ludwigite crystal structure (space group P_{bam}), where M acts as a divalent ion and M' is trivalent. In the heterometallic ludwigite, M and M' are different type ions while in the homometallic one $\text{M}=\text{M}'$. Both the types of ions occupy four nonequivalent crystallographic positions 1–2–3–4. The ludwigite crystal structure consists of low dimensional subunits, the so-called three-leg ladders (3LL). The columns of edge-sharing octahedra in these ladders form zigzag walls. The transition ions in the positions 4–2–4 form the so-named triads with an inter-ion

distance smaller than 3 Å. These triads play an important role in the magnetic ordering, because the direct overlap of transition ions electron clouds is possible inside them. As is known for $\text{Fe}_3\text{O}_2\text{BO}_3$, the triads consist of two trivalent and one divalent ion. In another words there is one extra electron per every triad. This allows double exchange inside the triad additionally to the direct one. The importance role of low dimensionality in magnetic and transport properties of oxyborates was underlined in Ref. [2].

At present there are only two homometallic ludwigites known: $\text{Fe}_3\text{O}_2\text{BO}_3$ and $\text{Co}_3\text{O}_2\text{BO}_3$. The physical properties of these two compounds are extremely different (structural transition and many-step magnetic ordering for the first and no structural transition and one-step magnetic ordering for the second). This striking difference attracts the attention to the mixed materials $\text{Co}_{3-x}\text{Fe}_x\text{O}_2\text{BO}_3$ [3–5].

The magnetic structure is not defined either for $\text{Fe}_3\text{O}_2\text{BO}_3$, or for $\text{Co}_3\text{O}_2\text{BO}_3$. However, it is clear that the magnetic ordering scenario and phase diagram are very complex, especially for the first compound. According to the Mössbauer data obtained in Refs. [6,7], the antiferromagnetic (AF) magnetic ordering in $\text{Fe}_3\text{O}_2\text{BO}_3$ begins near $T_1=114$ K and concerns the iron ions in the triads 4–2–4 and probably the ions in the position 3. The whole ensemble of di- and tri-valent ions in $\text{Fe}_3\text{O}_2\text{BO}_3$ orders below $T_2=70$ K, forming a weak ferromagnetic or ferrimagnetic (F) state, which probably transforms below 50 K to antiferromagnetic (AF) state. In the F-phase canted spin configuration is possible in accordance with the theoretical work [8]. But the neutron scattering study of $\text{Fe}_3\text{O}_2\text{BO}_3$ has shown no magnetic transition

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at 50 K and no canted spins but perpendicular magnetic ordering in different structural subunits [9]. So, it has been admitted that the picture of magnetic ordering in $\text{Fe}_3\text{O}_2\text{BO}_3$ remains unclear.

The other homometallic ludwigite $\text{Co}_3\text{O}_2\text{BO}_3$ demonstrates the predominance of ferromagnetic interactions and ferrimagnetic or weak ferromagnetic ordering below $T_N=43$ K [3,10]. Magnetic properties of the both parent materials $\text{Fe}_3\text{O}_2\text{BO}_3$ and $\text{Co}_3\text{O}_2\text{BO}_3$ are highly anisotropic.

The complexity of the transition metal ludwigites magnetic behavior opens the question about the relative strength of the different type exchange interactions: (1) the direct exchange between the transition ions inside the triads; (2) the double exchange (DE) by the extra electron inside the triads; (3) the superexchange (SE) through the oxygen ions. In this paper we will concentrate on the last type of exchange interactions for the mixed compound $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$. To understand the sign and the strength of SE we have to establish, which positions in cobalt ludwigite are occupied by iron ions; and then estimate the strength of superexchange interactions between all the magnetic ions in the lattice.

2. Experimental technique

The single crystals $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ were grown by the flux method in the system $\text{Co}_3\text{O}_4\text{--Fe}_2\text{O}_3\text{--B}_2\text{O}_3\text{--PbO--PbF}_2$. The relative content of Co and Fe in the prepared compounds was calculated from the mass ratio of initial components $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3+\text{Co}_3\text{O}_4)$. All the samples were of needle shape with different cross-section and up to 4 mm long.

The *ac* magnetic susceptibility temperature dependence was measured by commercial PPMS platform Quantum Design. The measurements have been done at the magnetic field perpendicular to the needle and lying in crystallographic *ab* plane. For these measurements the small sample quantity was not enough to give a good signal to noise ratio, so we had to measure the collective signal for the several samples.

The electric resistance *R* for the single crystal was measured by a dc two-terminal method in the temperature interval 190–400 K parallel to the needle (crystallographic *c* axis). The sample resistance was too high to use four-terminal technique.

The X-ray diffraction measurements were carried out for the single crystal of $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ ($0.38 \times 0.09 \times 0.12$ mm) and its structure was solved in detail. SMART APEX II diffractometer was used (Mo K_α radiation, CCD detector). The scanning angle $2\theta=5.4\text{--}58^\circ$ ($R1=1.40\%$, $wR2=3.31\%$).

The Mössbauer effect study was carried out for the powder made from single crystals of $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ using the source of $\text{Co}^{57}(\text{Cr})$. The sample's mass was about 5–10 mg/cm² according to the natural iron content, at which the intensity of the spectral lines is linearly dependent on it. The measurements have been done in the regime of constant accelerations at room temperature (RT). The isomer shift value was determined according to the metallic $\alpha\text{-Fe}$.

3. The magnetic susceptibility

The temperature dependencies of real and imaginary parts of *ac*-susceptibility for $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ are shown in Fig. 1. In spite of the fact that Co:Fe ratio equals 3:1, the susceptibility behavior is much closer to $\text{Fe}_3\text{O}_2\text{BO}_3$ but not to $\text{Co}_3\text{O}_2\text{BO}_3$. There is no sign of phase transition near 43 K as it is typical for $\text{Co}_3\text{O}_2\text{BO}_3$, but the sharp peak near 70 K and small anomaly at 115 K are visible. These two magnetic transitions near 70 and 115 K point out the magnetic ordering in iron subsystem as confirmed in Ref. [10] by specific heat measurements for $\text{Fe}_3\text{O}_2\text{BO}_3$.

The sharp susceptibility peak is frequency dependent, pointing to domain wall motion process. This peak is slightly shifted to higher temperature as the frequency increases.

4. The electric resistance

Measuring the electric conductivity allows making the indirect proposals about the role of double exchange, because it is usually accompanied by metallic type of conductivity.

Earlier we have measured the electric resistance *R* of $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_3\text{O}_2\text{BO}_3\text{:Fe}$ single crystals [3,4]. It was found to be rather high and of semiconducting character even in the stoichiometric sample with no disorder. The specific resistance was of the order $10^4 \Omega \text{ m}$ at room temperature and rapidly grew under cooling. No metallic-like behavior or magnetoresistance was observable. Because of high resistivity values at low temperatures in our previous work we

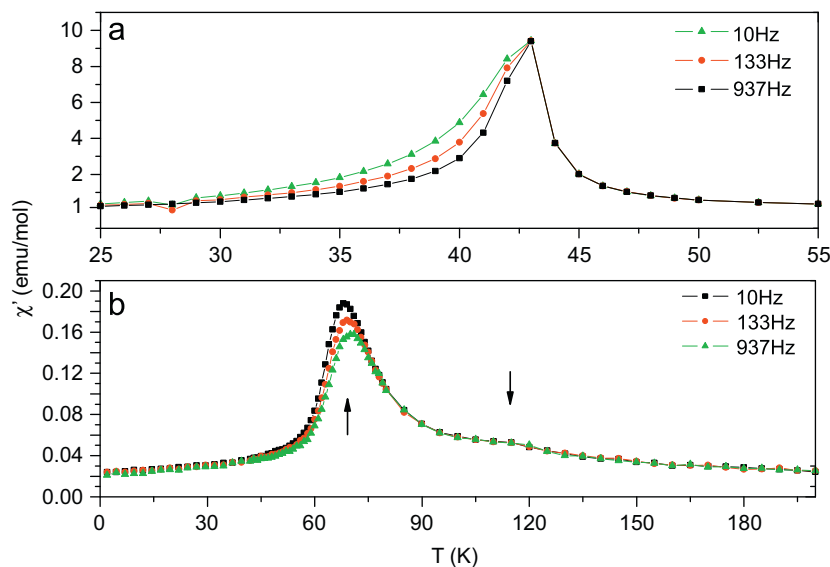


Fig. 1. *ac*-susceptibility temperature dependences for (a) $\text{Co}_3\text{O}_2\text{BO}_3$ and (b) $\text{Co}_{2.25}\text{Fe}_{0.75}\text{O}_2\text{BO}_3$ at different frequencies. Two magnetic transitions are pointed out—high peak at 70 K and small anomaly at 115 K.

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