Magnetic properties of $\text{Cu}_2\text{MnBO}_5$ ludwigite in weak magnetic fields

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Abstract. The results of magnetization measurements in low and ultralow ($0<|H|<10$ Oe) magnetic fields are presented for single-crystal $\text{Cu}_2\text{MnBO}_5$ ludwigite. An own SQUID magnetometer and AC measurement system and vibrating sample magnetometer options of PPMS were used. Magnetic properties have been investigated at different cooling modes of the sample. The features of the magnetic moment behaviour are revealed. The dissimilarity of magnetic measurement data obtained using various types of magnetometers is observed. The reasons for this are discussed.

1. Introduction

$\text{Cu}_2\text{MnBO}_5$ ludwigite is one of the most prominent heterometalic representative of the oxyborate family with a ludwigite structure. Nowadays, this compound is the only heterometalic ludwigite whose magnetic structure has been investigated experimentally using the neutron diffraction [1]. Compared to other isostructural analogues [2, 3], $\text{Cu}_2\text{MnBO}_5$ has a relatively high magnetic ordering temperature $T_c=92$ K and a sufficiently high magnetic moment, indicating a ferrimagnetic type of ordering. The quasi-low-dimensional ludwigite structure contains such structural elements as zig-zag walls and three-legged ladders constructed by metal-oxygen octahedra [4]. The unit cell of ludwigites contains $Z=4$ formula units and thus has 12 magnetic ions in the case of $\text{Cu}_2\text{MnBO}_5$. There are 4 nonequivalent positions for metal cations. According to neutron diffraction data the compound under investigation has a complex magnetic structure which contains 4 pairwise almost anticoillinear magnetic sublattices (see figure 1). The directions of magnetic moments do not coincide with the directions of the main crystallographic axes. The sublattices oriented at an angle of approximately 60 degrees to each other [1].

2. AC magnetic susceptibility

Figure 2 shows the temperature dependence of alternating current (AC) magnetic susceptibility measured with Physical property measurement system (PPMS) manufactured by Quantum Design [5]. The sharp peak at $T=88$ K indicates a magnetic phase transition. No other anomalies in the temperature dependence were observed, which indicates the absence of any other changes in the magnetic state. Measurements were performed for different frequencies in the range from 10 Hz to 10 kHz with the amplitude of the alternating magnetic field of 10 Oe. The curves of the real and imaginary parts of the
susceptibility do not show a frequency dependence in the entire temperature range of 4.2÷250 K. This indicates the absence of a spin-glass state in Cu$_2$MnBO$_5$ ludwigite.

**Figure 1.** Orientations of Cu$_2$MnBO$_5$ magnetic moments [1]

**Figure 2.** Temperature dependences of Cu$_2$MnBO$_5$ AC magnetic susceptibility.

### 3. Static magnetic properties

Initially, the study of Cu$_2$MnBO$_5$ static magnetic properties was carried out using vibrating sample magnetometer (VSM) option of PPMS [6]. The magnetization of a single-crystal sample was measured in a magnetic field applied both along the $a$ axis of the crystal and in the plane perpendicular to one. The range of the magnetizing field was up to $H = 1$ kOe. Magnetic measurements were carried out in various modes of sample cooling: 1) cooling in zero magnetic field (ZFC), 2) cooling in nonzero magnetic field (FC), and 3) heating of the sample in nonzero magnetic field after cooling in the same nonzero field (FH). During the measurements, it was revealed in the ZFC mode the region of negative magnetization fixed in a quite wide temperature range in the ordered phase (see figure 3 $a$, $b$, $c$). When measuring a magnetic hysteresis loop, the initial irreversible part of the magnetization curve also starts from negative values (see figure 3 $d$). This observation was an artifact of the experiment. Thus, it was not allowed to obtain the real dependences of magnetization in the ZFC mode using the PPMS device.

Since there was not enough confidence in the reliability of the obtained results, precise measurements of Cu$_2$MnBO$_5$ single-crystal magnetization were performed with a highly sensitive SQUID magnetometer [7] designed and made in Kirensky Institute of Physics. The crystallographic $a$ axis of Cu$_2$MnBO$_5$ single crystal of 14.4 mg weigh was oriented parallel to the magnetizing field. Measurements of the magnetic moment of the sample were performed in low and ultralow magnetic fields ($0 < H < 10$ Oe), and the field sign was both positive and negative. It was found that the behavior of the magnetic moment during the inversion of the magnetizing field of 1÷10 Oe is absolutely symmetric (see figure 4 $a$, $b$). Slight asymmetry is observed in a weaker field $H = 0.1$ Oe (see figure 4 $c$). This is most likely caused by the presence of a slight bias of the magnetizing field. Figure 4 $d$ shows the results of magnetic measurements in a quasi-zero field. The feature observed here in the temperature range 80 ÷ 92 K is probably related to the compensation point that is typical for ferrimagnets. Taking into account the linear magnetic field dependence of the magnetization in low fields, the estimation of the residual field is about ~0.005 Oe. In particular, it could be caused by the incomplete shielding of the geomagnetic field.
Figure 3. Temperature dependences of $\text{Cu}_2\text{MnBO}_5$ magnetization measured in a magnetic field of 1 kOe ($a$); 200 Oe ($b$); in ZFC mode ($c$). Magnetic hysteresis loop ($d$).

Figure 4. Temperature dependences of $\text{Cu}_2\text{MnBO}_5$ magnetic moment measured in a magnetic field of ±10 Oe ($a$); ±1 Oe ($b$); ±0.1 Oe ($c$); ~0.005 Oe ($d$), directed along the crystallographic $a$ axis. Sample weight is 14.4 mg.
4. Discussion

Negative magnetization in a supposedly zero magnetic field was observed on different compounds. Mainly some researchers explain such experimental results by the presence of superconductivity in the materials under study [8, 9, 10].

In particular, this applies to some weakly ferromagnetic compounds. Thus, the authors of [10] reported the observation of the “anomalous diamagnetic transitions” in copper oxychlorides, and explained it by the occurrence of superconductivity at temperatures up to 386 K. Magnetic measurements were carried out in weak and quasi-zero magnetic fields using PPMS. At the same time, those authors did not take into account that high-temperature superconductors (HTSC) have magnetic field dependences of magnetization, which have an exclusive form inherent only to HTSC [11, 12]. Moreover, those authors did not investigate magnetic field dependences at all. Later, a carefully performed recheck of these questionable results proved that there is no superconductivity in the copper oxychlorides even at liquid helium temperatures [13].

What can cause the negative magnetization or “false diamagnetism” observed betweenwhiles in weak magnetic fields, which some researchers tend to misinterpret as a demonstration of high-temperature superconductivity?

One reason is obvious enough. This is the presence of the residual magnetic moment oriented counter to the direction of the magnetizing field, which the authors overlooked because of lack of a deep and comprehensive study of the magnetic properties of the investigated samples.

The other reason is not so apparent and therefore more treacherous. It is associated with the instrumental error of determining the value of magnetizing field strength in the magnetometric installations. It is known that in superconducting solenoids there is a residual field phenomenon [14]. In many magnetometers, including widespread PPMS (VSM) [6] and MPMS (SQUID) [15] produced by Quantum Design, a superconducting solenoid is used as a magnetic field source. Usually magnetic measuring sensor is absent inside magnetometers with a superconducting solenoid. So the magnetic field strength $H$ is calculated by the direct electric current $I$ flowing through the coil of the superconducting solenoid as

$$H = \text{const} \cdot I.$$  \hspace{1cm} (1)

This expression does not account for the residual field $H_R$, which appears in a magnetic field scanning cycle and usually has the opposite sign (see figure 5). For example, in a magnetometer MPMS XL-7, with a sweep of the field to the value $H_{\text{max}} = +70$ kOe, the residual field is $H_R \sim -20$ Oe [16]. In this case, even the phenomenon of “reverse magnetic hysteresis” is observed [16]. The residual field $H_R$ is induced by the magnetic vortices, which arise in high fields and persist due to the pinning even when the electric current $I$ is actually equal to zero. Expression (1) becomes incorrect. In order for the magnetic field to become zero, it is necessary to pass an electric current $I_0$ through the coil.

Figure 5. The dependence of the magnetic field of a superconducting solenoid from the electric current flowing through the coil.

Another implicit reason may be a slight zero current offset in the coil of a superconducting solenoid due to insufficiently fine tuning of the electrical circuit responsible for the sweep of the magnetic field. Since the maximum magnitude of the magnetic field in PPMS reaches the value of 90 kOe, then for the...
appearance of a bias, for example, of –10 Oe, it is enough to have the control electronics detuning of only about 0.01%.

Note that all of the above factors can occur simultaneously, leading to further aggravating the situation. Therefore, magnetic measurements in weak magnetizing fields have to be carried out extremely scrupulously.

5. Conclusions
Thus, a carefully performed study of Cu2MnBO5 ludwigite magnetization in weak magnetic fields using SQUID magnetometer [7] definitely proves the absence of negative magnetic moment in a zero magnetic field in the ZFC mode. Incorrect data was obtained with the PPMS due to the presence of an uncontrolled significant residual magnetic field in a superconducting solenoid. The appearance of the residual field is evidenced by both our own observations and by the observations of the others authors [14, 16].

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