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High-temperature features in the EPR spectra of Cu_2MnBO_5

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Abstract

Single crystals of the $\text{Cu}_{3-x}\text{Mn}_x\text{BO}_5$ ludwigite phase were synthesized by the flux-growth method. The crystal had a needle-like shape, and for the measurements the crystals were ground into a powder. Electron paramagnetic resonance (EPR) spectra have been measured above 300 K. In the magnetic resonance spectrum, three lines are observed, two lines with an effective g-factor close to two are observed, one broad and the other narrow. A third EPR line associated with the formation of a magnetic polaron was observed between 425 and 520 K. It is shown that the temperature dependence of the inverse magnetic susceptibility depends on the magnitude of the magnetic field at which the measurements were performed.

Keywords: EPR, ludwigite, magnetic polaron, magnetization

1 Introduction

The ludwigites refers to oxyborates having the stoichiometry $M_2M'\text{BO}_5$, in which M and M' represent divalent and trivalent metal ions, respectively. The metal ions in these compounds occupy four inequivalent crystallographic positions per unit cell, in octahedral coordination by oxygen ions, leading to a random occupancy of magnetic cations, mixed valency, strong electron-electron interactions, and peculiar charge ordering patterns. Due to the different valences of the transition metal ions and the diverse spin states, ludwigites exhibit a rich phase diagram. As a result, these materials possess extraordinary magnetic characteristics [1].

These compounds have a complex crystal structure and are dielectrics at low temperatures. When heated above room temperature, these compounds exhibit semi-conducting properties. The resonant phonon contribution is expected to occur near temperatures comparable to the Einstein temperatures derived from fitting the temperature dependence of the specific heat capacity. Analyzing the temperature dependence of the specific heat, the Debye and Einstein temperatures for acoustic and optical phonons were empirically determined. Thus, for ludwigites, the temperature dependence of the specific heat has been repeatedly analyzed using the Debye and Einstein models. For $\text{Cu}_2\text{MnBO}_5\text{:Cr}$ Debye temperature is $\Theta_D = 165 \pm 5$ K with $\alpha = 1$, Einstein temperatures are $\Theta_E = 252 \pm 2$ K at zero magnetic field and $\Theta_E = 263 \pm 5$ K at 9 T magnetic field; $\Theta_E = 465 \pm 5$ K at zero magnetic field, $\Theta_E = 450 \pm 5$ K at 9 T magnetic field [2]. Early, the lattice specific heat in Cu_2MnBO_5 was determined using linear combinations of the Debye-Einstein functions with the characteristic temperatures found to be $\Theta_D = 331$ K and $\Theta_E = 780$ K [3].

This article will present the high-temperature magnetic properties of ludwigite with the composition Cu_2MnBO_5 . For this compound, the temperature dependencies of magnetization, magnetostriction, and EPR spectra, and neutron scattering were studied at room and low temperatures [4]. It was shown that the inverse temperature dependence at temperatures above the phase transition temperature, which is observed around 90 K, does not obey the Curie-Weiss law. The observation of a loop near the phase transition between the magnetization data measured upon cooling in a nonzero magnetic field and a sample heating in a field of $H = 200$ Oe after precooling at $H = 200$ Oe raises questions [3]. In Sofronova's article [1], an analysis of neutron scattering data at room temperature was carried out. The distribution of manganese and copper ions over crystallographic positions was established. It was shown that in the position for the trivalent ion, 90 percent is occupied by manganese ions, and 10 percent by copper ions. The most probable valence of the copper ions is Cu^{2+} . Consequently, for electrical neutrality, the valence of the manganese ions must change from Mn^{3+} to Mn^{4+} . It is known that in the $\text{Mn}^{3+}\text{--Mn}^{4+}$ pair, charge transfer occurs and double exchange is realized [5]. The mixed valence of manganese ions 3+ and 4+ has been actively studied in manganites, where the presence of mixed valence and

hole localization leads to the formation of magnetic polarons [6]. Magnetic polarons in manganites are observed by the magnetic resonance method. It is expected that in ludwigite Cu_2MnBO_5 , in the presence of copper ions at the position of the trivalent ion, magnetic polarons are formed, which should be detected in the magnetic resonance spectra. The aim of this work is to study the manifestation of the magnetic polaron in the magnetic resonance spectra and magnetization in ludwigite Cu_2MnBO_5 .

2 Sample Growth

Single crystals of the $\text{Cu}_{3-x}\text{Mn}_x\text{BO}_5$ ludwigite phase were synthesized by the flux-growth method. The crystallization process was investigated using the $\text{Bi}_2\text{Mo}_3\text{O}_{12}$: $0.93\text{B}_2\text{O}_3$: $0.7\text{Na}_2\text{O}$: $0.16\text{Mn}_2\text{O}_3$: 2CuO flux system. The flux was prepared by sequential melting of the powder components at $T = 1100^\circ\text{C}$. The melt was then homogenized at 1100°C for approximately 3 hours to ensure uniform dissolution and mixing of the starting components. For the growth stage, the temperature was first rapidly decreased at a rate of 200°C/h to $T_{\text{start}} = 850^\circ\text{C}$ and then slowly at a rate of 4°C/day to provide controlled supersaturation and crystal growth. The use of slow cooling is consistent with the general principles of flux growth, in which crystal growth is driven by supersaturation generated by a controlled decrease in temperature. [1, 7, 8]

After 6 days, the flux was poured off, and the grown single crystals were removed from the crucible and etched in a 20% aqueous nitric acid solution to remove residual flux. The chemical composition of the synthesized compound was determined by X-ray fluorescence analysis and is presented in the Discussion section.

3 Experiment

The X-ray fluorescence (XRF) analysis was performed using a Bruker S2 Ranger X-ray fluorescence spectrometer.

The phase composition and structure of the grown samples were studied by powder X-ray diffraction. The diffractogram pattern was recorded using the Haoyuan DX-2700BH powder diffractometer of the Krasnoyarsk Scientific Center with Cu-K_α radiation and a linear detector. The step size of 2θ was 0.01° , and the counting time was 0.2 s per step.

DC magnetization was measured in the temperature range of 295-600 K and the external magnetic field values $H = 0.1$ and 10 kOe using a PPMS-9 Quantum Design device.

ESR measurements were performed using a Varian E12 spectrometer equipped with a Bruker EP 4114 XT high-temperature resonator with a TE_{011} resonant mode. Temperature dependence measurements in range of 295-650 K were performed in the X-band with a frequency of 9.4 GHz and a magnetic-field range of 0-1 T.

4 Discussion

4.1 X-ray diffraction

X-ray fluorescence analysis of the sample showed that the ions are evenly distributed in the crystals. XRF revealed that Cu ions occupy fewer positions than expected – 1.923 per unit cell, Mn ions have a concentration of 1.077 per unit cell. Below, the composition of the compound under study is denoted as Cu_2MnBO_5 .

The experimental powder diffraction patterns of the studied samples are shown in Fig. 1.

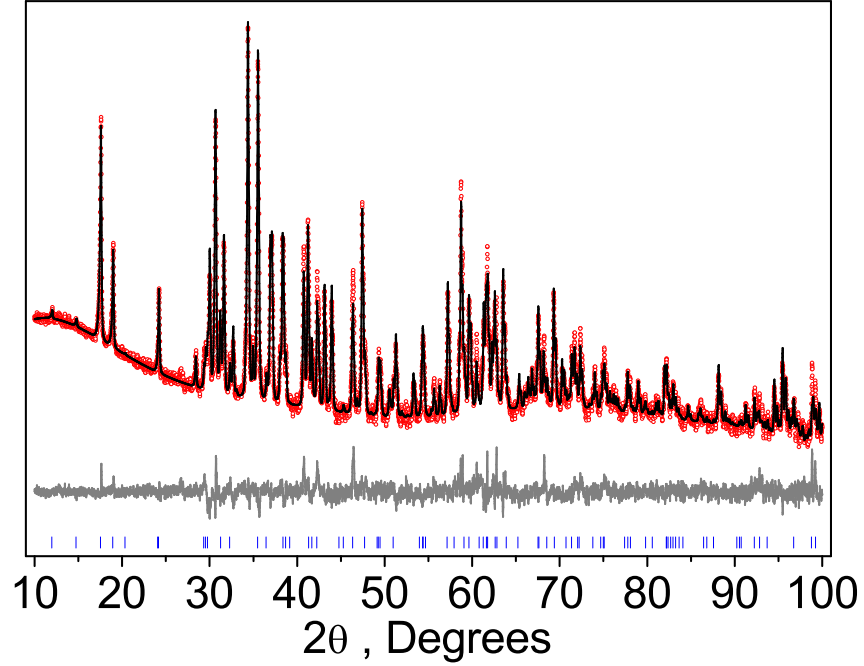


Fig. 1 Rietveld refinement patterns for the obtained sample Cu_2MnBO_5 . Red symbols denote the experimental values, the black solid line is the Rietveld fit, and the blue ticks indicate the Bragg peaks

Almost all peaks were indexed by Cu_2MnBO_5 ludwigite and these structures were refined using the Rietveld method with TOPAS 4.2 software [9]. Refinements were stable and gave reasonable R-factors (Table 1). The lattice parameters of the synthesized ludwigite have a well agreement with the same of earlier obtained $\text{Cu}_{1.94}\text{Mn}_{1.06}\text{BO}_5$ [1, 3] where the concentration of the copper is less than 2. The structure of Cu_2MnBO_5 is presented in Fig. 2. Metal ions are surrounded by an octahedral environment highlighted in different colors for M1-M4 positions.

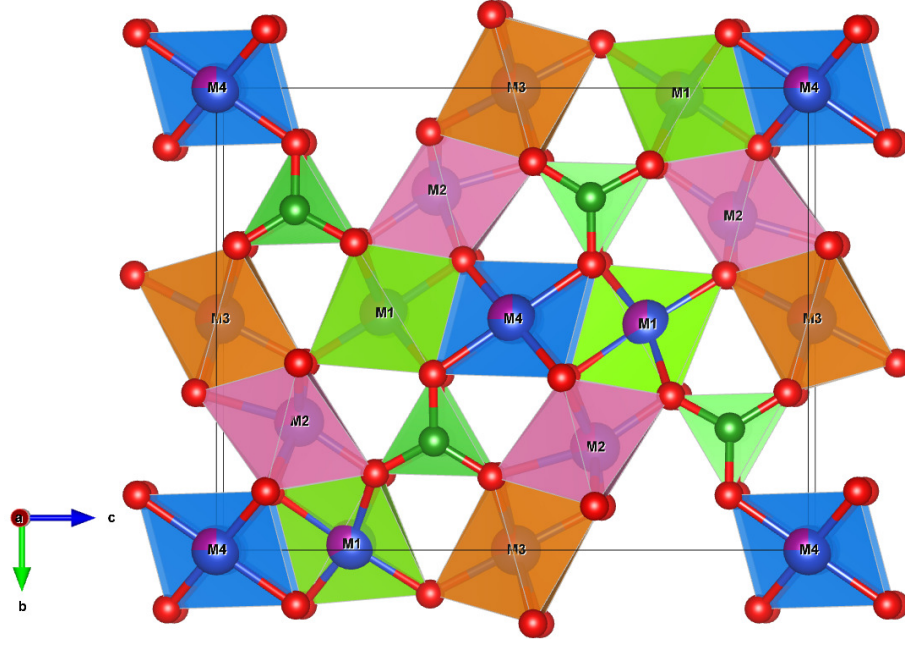


Fig. 2 The structure of Cu_2MnBO_5 . Metal ions are surrounded by an octahedral environment highlighted in different colors for M1-M4 positions. Green orbs are boron ions, red orbs are oxygen ions. The figure was created using VESTA free software [10]

Table 1 Crystallographic parameters and refinement statistics. The data for $\text{Cu}_{1.94}\text{Mn}_{1.06}\text{BO}_5$ was taken from [1, 3].

Sample	Space group	Cell parameters (Å)	Cell volume V (Å ³)	R_{wp} , R_p , χ^2
Cu_2MnBO_5	$P2_1/c$	$a = 3.14652(6)$ $b = 9.3760(2)$ $c = 12.0232(3)$ $\beta = 92.2686(11)$	354.435(13)	9.84; 7.07; 4.53
$\text{Cu}_{1.94}\text{Mn}_{1.06}\text{BO}_5$ [1, 3]	$P2_1/c$	$a = 3.14003(7)$ $b = 9.3973(2)$ $c = 12.0242(3)$ $\beta = 92.261(2)$	354.531(15)	—

4.2 Magnetic susceptibility

The temperature curves of the inverse magnetic susceptibility in magnetic fields were measured at 0.1 kOe and 10 kOe and are presented in Fig. 3. The measurement procedure was as follows: at room temperature, the target magnetic field was set, measurements were taken during heating, and at 800 K the magnetic field was linearly reduced to zero; then the sample was cooled to room temperature, followed by the next field and the same process. Initially, a measurement was conducted in a 0.1 kOe

magnetic field, then in a 10 kOe magnetic field, and then again in a 0.1 kOe magnetic field.

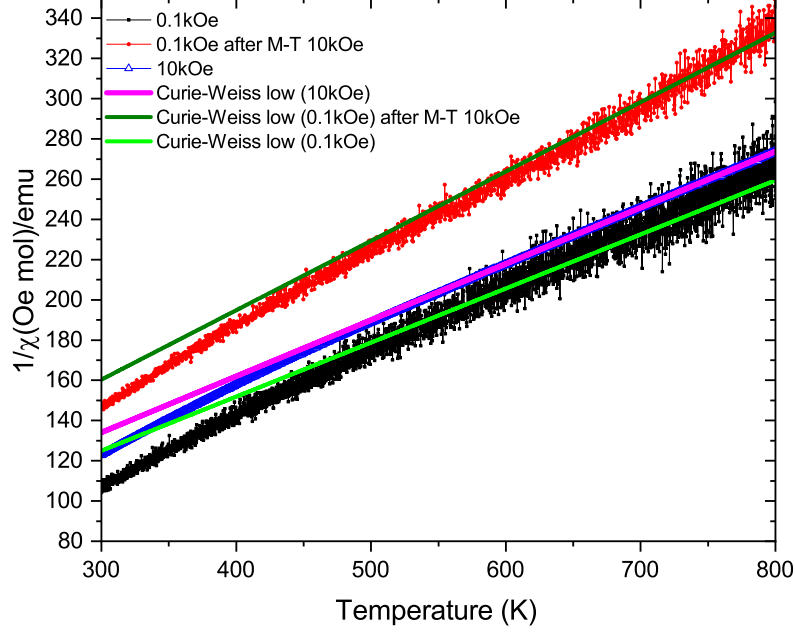


Fig. 3 The temperature dependence of inverse magnetic susceptibility in Cu_2MnBO_5 . Solid lines are drawn according to the Curie-Weiss law

The data for the smaller field of 0.1 kOe were quite noisy, so after completing the measurement program, the curve was remeasured with a longer averaging time (5 seconds instead of the default 1 second), but the data were significantly different from the first set. The slope of the inverse magnetic susceptibility curve is shifted with a change in the external magnetic field applied to the sample (Fig. 3), probably indicating the presence of a magnetic polaron in the compound.

The paramagnetic part of the inverse magnetic susceptibility was approximated by using the Curie-Weiss law:

$$\chi = \frac{C}{T - \Theta_{\text{CW}}} + \chi_0, \quad (1)$$

where χ is the magnetic susceptibility, C is the Curie constant, and Θ_{CW} is the Curie-Weiss temperature [11], χ_0 is fitting constant. For data approximation we used $\chi_0 = 0$. The approximation parameters are shown in Table 2. As can be seen from Table 2, the

Curie-Weiss temperature is negative for measurement results in all magnetic fields. A negative Curie-Weiss temperature indicates the presence of antiferromagnetic interactions between spins in the sample. However, the value of the Curie-Weiss temperature and the Curie constant depend on the history of magnetic measurements. Note that the experimental values deviate from the linear dependence below 480 K that is not typical in paramagnetic region. The experimental effective magnetic moments were calculated using the equation:

$$\mu_{\text{eff}} = \sqrt{\frac{3k \cdot C}{N_A}}. \quad (2)$$

From the initial measurements of the temperature dependence of the magnetic susceptibility, the experimental effective magnetic moment is found to be $5.352 \div 5.455 \mu_B$. After applying an external magnetic field of 10 kOe and increasing the recording and measurement time in a magnetic field of 0.1 kOe, the effective magnetic moment decreased and amounted to $4.817 \mu_B$. The obtained values are slightly bigger than the one obtained earlier for the Cu_2MnBO_5 sample, with $\mu_{\text{eff}} = 4.5 \mu_B$ for the same external magnetic field values [1], which were measured in the temperature range from 4 to 300 K.

Table 2 Parameters of magnetization approximation in Cu_2MnBO_5 compound

H (kOe)	Θ_{CW} (K)	C (K · emu/mol)	$\mu_{\text{eff}} (\mu_B)$
0.1 (before M-T 1 T)	-165	3.72	5.455
10	-180	3.58	5.352
0.1 (after M-T 10 kOe)	-165	2.9	4.817

Let us compare the experimental values and the theoretical estimate of the effective magnetic moment. For simplicity, we assume that the g -factors of the manganese and copper ions are the same and equal to 2; $S = 1/2$ for Cu^{2+} , $S = 2$ for Mn^{3+} , $S = 5/2$ for Mn^{2+} . The theoretical effective magnetic moment was calculated using the following equation:

$$\mu_{\text{Theory}} = \sqrt{\sum [N_i \cdot g_i \cdot S_i(S_i + 1)]}, \quad (3)$$

where g is the g -factor of ion and N is the number of ions [12] of one type. If $g = 2$ for all ions than μ_{Theory} is equal $5.69 \mu_B$.

The low value of the experimental effective magnetic moment can be attributed to several reasons. Manganese ions in the compound can be either divalent, trivalent or tetravalent. Another possible reason is the presence of a magnetic polaron formed by charge transfer between manganese ions via double exchange. It should be noted that the experimental values deviate from the linear dependence, suggesting the existence of a polaron below 520 K.

4.3 EPR

Lines in the EPR spectrum are recorded in temperature range above 295 K in the X-band for Cu_2MnBO_5 .

The obtained EPR lines are shown on Fig. 4. Three lines were recorded in the magnetic resonance spectrum. The line shape of each was approximated via the equation;

$$\frac{dP}{dH} = \frac{d}{dH} \left(\frac{\Delta H + \alpha(H - H_{\text{res}})}{(H - H_{\text{res}})^2 + \Delta H^2} + \frac{\Delta H - \alpha(H + H_{\text{res}})}{(H + H_{\text{res}})^2 + \Delta H^2} \right), \quad (4)$$

where H_{res} is the resonance magnetic field, ΔH is the linewidth, and α is the asymmetry parameter [2, 13]. The temperature dependencies of g -factors, linewidths, and intensities are shown on Fig. 5. For fitting of the shape EPR lines we used $\alpha = 0$.

During the fitting process, the g -factor of the first line was constrained to $g < 2.2$, corresponding to the typical g -factor values for Cu^{2+} . At high temperatures, the intensity of line 1 becomes too low for its fitting parameters to be determined reliably because of the noise level; therefore, the parameters of the first line are not shown above 580 K. Additionally, the relatively large uncertainty of the fitted parameters is due to the significant linewidth (approximately 5 kOe), which is comparable to the magnetic-field scan range (10 kOe).

The second line is narrower, and as the temperature increases from 296 K to 650 K, the line narrows from 500 Oe to 200 Oe, and its effective g -factor decreases from 2.1 to 2. It should be noted that the magnetic resonance spectrum does not show the fine-structure lines of manganese and the hyperfine-structure lines of copper ions. Therefore, the spectrum in Cu_2MnBO_5 shows two exchange-narrowed lines from two regions with different magnetic properties.

Since the linewidth of the exchange-narrowed line is determined by the ratio of the second moment of line to the magnitude of the isotropic exchange interaction, we can assume that the magnitude of the isotropic symmetric exchange interaction for ions from the second region is much greater than for ions from the first region.

The third line is observed in a narrow temperature interval between 425 K and 520 K. At first, the line is recorded at zero values of the resonant magnetic field. As the temperature increases, the line shifts towards higher magnetic fields. It can be assumed that the nature of this line is related to the formation of a magnetic polaron. The temperature range in which this line appears is much above 90 K (the sample's ordering temperature), so it is unlikely to correspond to ferromagnetic or antiferromagnetic regions.

Let's take a closer look at the nature of polaron formation. Polaron hallmarks have been measured in transition-metal oxides, amorphous compounds, organic semiconductors, conducting polymers, diluted magnetic semiconductors, manganites, cuprates, hybrid perovskites, and 2D materials. Polaron-mediated effects have been identified as the key factor in physical phenomena such as charge transport, surface reactivity, colossal magnetoresistance, thermoelectricity, photoemission and multiferoism, to name just the most relevant ones [14]. The models describing polarons are usually divided into two classes, based on the original theories of Fröhlich (continuum large polarons) and Holstein (lattice small polarons). The Fröhlich approach follows

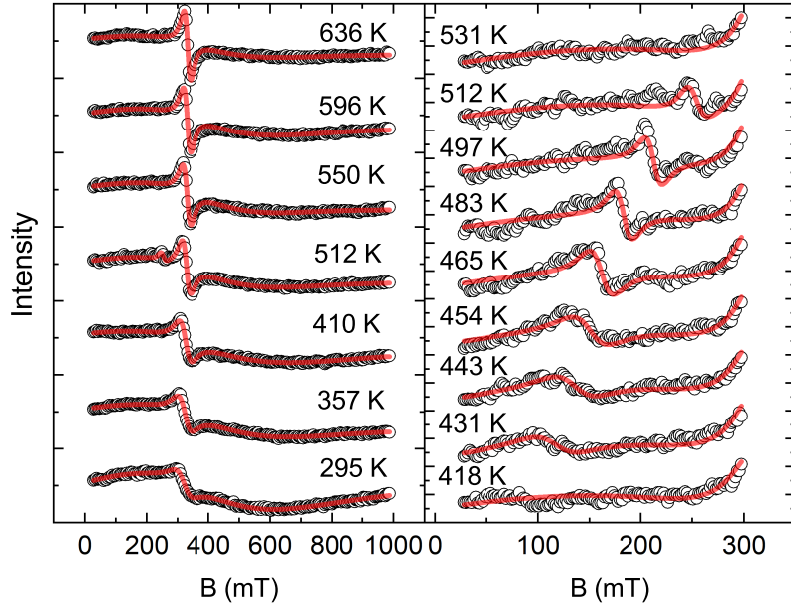


Fig. 4 The temperature dependence of EPR spectra in Cu_2MnBO_5

the continuum approximation and neglects the discreteness of the crystal lattice. It allows the description of large polarons in ionic, polar and ferroelectric materials, caused by the long-range component of the electron-phonon interaction. By contrast, the Holstein theory considers short-range electron-phonon interactions resulting from the coupling between a carrier and the strain where it resides. This model explicitly takes into account the discreteness of the lattice. Types of polarons in materials are presented in Table 3 in review [14]. As suggested by David Emin [15], the enhancement of the Seebeck coefficient via softening of vibrations induced by charge carriers is determined by the polaron radius. A polaron forms when an electronic carrier is bound within the potential well produced by the equilibrium positions of the atoms surrounding the carrier being displaced from their carrier-free equilibrium positions to equilibrium positions consistent with the presence of the bound electronic carrier. In particular, the binding energy of the self-trapped carrier must exceed the characteristic phonon energy $E_{\text{self-trapped}} > h\nu$. The authors showed that with rising temperature vibration contribution rises monotonically from zero toward a near constant value at sufficiently high temperatures and transport polaron contribution is a peaked function of temperature that vanishes at both the low- and high-temperature limits. It can be assumed that the visualization in the EPR spectrum of the polaron signal at a temperature of 425 K can be associated with vibrations of the triangular BO_3 structure

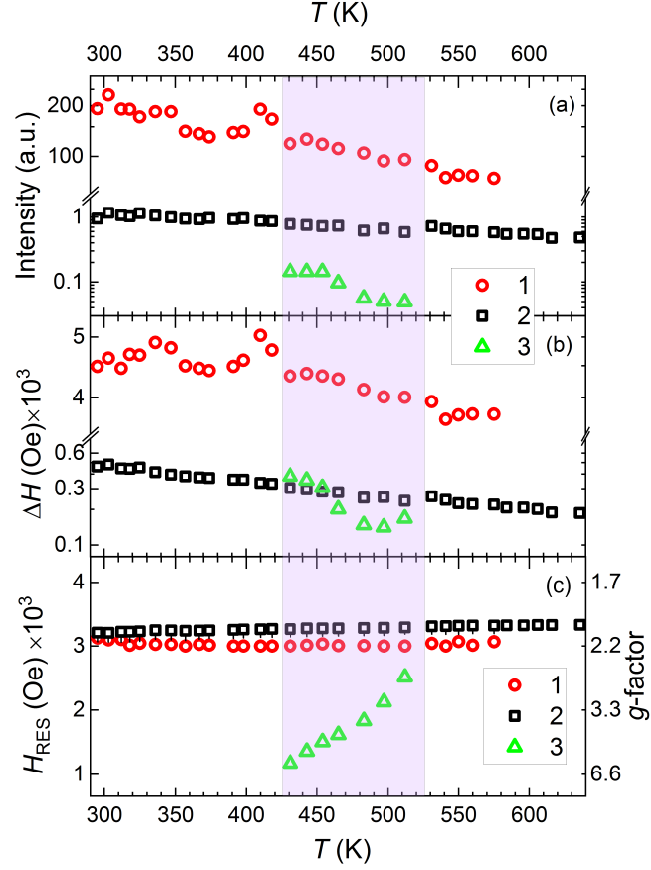


Fig. 5 The EPR lines approximation of Cu_2MnBO_5 , temperature dependencies a) intensity; b) linewidth; c) g -factor

in ludwigite, for which the Einstein temperature presumably corresponds to 450 K in magnetic field [2].

The formation of magnetic polarons by the spins of manganese ions and charge carriers was reported in [16] a study on a compound $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. It is assumed that in quasi-two-dimensional manganites the polarons are preserved in the magnetically ordered state as well, and that small magnetic polarons become big polaron at low temperatures in [16]. At temperatures below $T < 300$ K a paramagnetic matrix consists of small (1 nm sized) and large (up to 1 μm) magnetic clusters in the magnetically ordered state.

Since the model of small polaron hopping conduction is used to describe the conducting properties of manganites [17], we assume that a small magnetic polaron of the Holstein type is formed in the ludwigite.

5 Conclusion

Cu_2MnBO_5 compounds were grown by the flux technique. According X-ray complex ludwigite Cu_2MnBO_5 has $P2_1/c$ space group with $a = 3.146(5) \text{ \AA}$, $b = 9.376(2) \text{ \AA}$, $c = 12.02(3) \text{ \AA}$, and $\beta = 92.238(6)^\circ$ at room temperature. The EPR line from magnetic polarons was observed in magnetic resonance spectra in the temperature range between 425 to 520 K. The compound demonstrates shift of the effective magnetic moment value with change of the external magnetic field, applied to the sample, most likely due to influences of the magnetic polaron.

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- **Materials availability:** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request
- **Code availability:** Not applicable.
- **Author contribution:**
 - Conceptualization and Methodology: [Eremina R.M.]
 - Validation and Formal analysis, Writing - Review & Editing: [Yatsyk I.V., Shestakov A.V., Eremina R.M.]
 - Investigation and Resources: [Shestakov A.V., Fazlizhanov I.I., Batulin R.G., Cherosov M.A., Yatsyk I.V., Eremina R.M.]
 - Data Curation: [Shestakov A.V., Yatsyk I.V., Molokeev M.S., Eremina R.M.]
 - Writing - Original Draft: [Yatsyk I.V., Moshkina E.M., Eremina R.M.]
- Fazlizhanov I.I., Batulin R.G. and Cherosov M.A. - Investigation, Resources;
- Shestakov A.V. - Validation, Formal analysis, Investigation, Data Curation, Resources, Writing - Review and Editing;
- Yatsyk I.V. - Validation, Formal analysis, Investigation, Data Curation, Resources, Writing - Original Draft, Writing - Review and Editing;
- Moshkina E.M. - Synthesis of samples, Writing - Original Draft;
- Molokeev M.S. - Data Curation;
- Eremina R.M. - Conceptualization, Methodology, Investigation, Data Curation, Validation and Formal analysis, Resources, Writing - Original Draft.

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