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MAGNETISM AND FERROELECTRICITY

Magnetic Structure and Magnetic Excitations in the Two-Dimensional Spin System of the $Cu_3B_2O_6$ Compound

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Abstract—This paper reports on the results of measurements of the magnetic susceptibility, heat capacity, neutron scattering, muon spin relaxation, and electron paramagnetic resonance in $Cu_3B_2O_6$ for the study of the ground state of the spin system of this compound. The results obtained suggest that, at a temperature of 10 K, the spin subsystem of the crystal, which consists of single spins and clusters of pairs and fours of spins interacting with one another, undergoes a transition to a state representing a superposition of the singlet (for clusters) and magnetically ordered (for single spins) states.

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1. INTRODUCTION

Low-dimensional compounds with integer and half-integer spins continue to attract unwaning interest of researchers owing to the diversity of their magnetic states and types of magnetic excitations. Among them, the Holdane $PbNi_2V_2O_8$ [1], spin-Peierls $CuGeO_3$ [2], and spin ladder $SrCu_2O_3$ [3] compounds have singlet ground states, which becomes manifest in the existence of an energy gap in their spin dynamics. The spin systems of all these compounds are classified as one-dimensional spin systems. On the other hand, two-dimensional spin systems with a singlet ground state are met very infrequently. We are aware of only a few such compounds, for instance, the plaquette system CaV_4O_9 [4, 5] and the orthogonal dimer system $SrCu_2B_2O_6$ [6–8]. The tetrahedral compound CaV_4O_9 consists of two-dimensional layers of VO_5 pyramids with Ca ions embedded between them. The spin of the paramagnetic V^{4+} ions is $S = 1/2$. The ground state of the system is the singlet with an energy gap of 107 K. The $SrCu_2B_2O_6$ compound also has a tetragonal unit cell. All Cu^{2+} ions with spin $S = 1/2$ occupy crystallographically equivalent positions. The structure of this compound consists of layers of tetragonal CuO_4 planar groups bound to triangular BO_3 planar groups. High-field magnetic susceptibility and magnetization measurements and neutron scattering studies [7] revealed that the magnetic system of this compound is characterized by a singlet ground state with an energy gap of 30 K. The properties of this system can be described by the two-dimensional Heisenberg model [9] with two exchange interaction parameters, whose magnetic excitation dispersion is modified by the Dzyaloshinski–Moriya interaction [10].

The $Cu_3B_2O_6$ crystal belongs to copper oxide compounds with a quasi-two-dimensional crystal structure. This compound exhibits an extremely high chemical and thermal stability; indeed, due to its stability and intense green color it can be used as a pigment. The temperature dependence of the magnetic susceptibility of this compound resembles the corresponding dependence of $SrCu_2B_2O_6$ in that it passes through a broad maximum near 40 K followed by a sharp decrease below 10 K [11]. The feature in the susceptibility near 10 K was assigned [11] to a possible paramagnetic phase transition to the singlet ground state. Incidentally, the possibility of such a transition in two-dimensional spin models was demonstrated theoretically [12] for the case of magnetoelastic coupling present, a mechanism similar to that of the spin-Peierls transition in one-dimensional spin systems [13]. Subsequent studies [14–16] revealed that $Cu_3B_2O_6$ has a more complex magnetic structure which could be conceived of as a mixture of magnetic ordering with the singlet state. NMR measurements suggest [16] that part of the magnetic system forms a modulated spin density wave. These measurements and μSR spectroscopic data gave the authors of [16] grounds to believe that below 10 K $Cu_3B_2O_6$ supports coexistence of antiferromagnetically ordered pairs with singlet spins. In our opinion, the

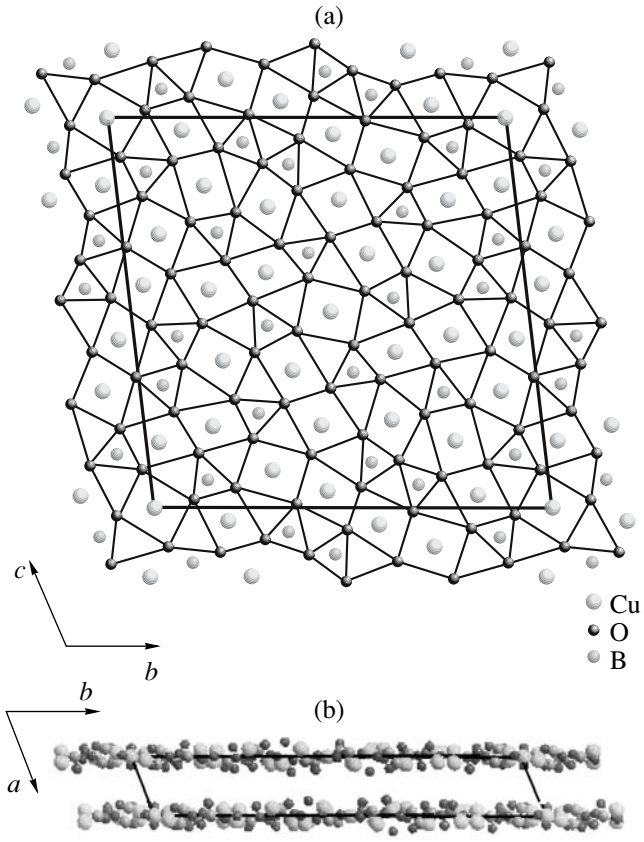

Fig. 1. Crystal structure of the $Cu_3B_2O_6$ compound in projections onto (a) the *bc* plane and (b) the *ab* plane. Solid straight lines indicate clusters into which the crystal structure is divided within the model under consideration.

available experimental data are clearly insufficient for reliable establishment of the magnetic structure of $Cu_3B_2O_6$. The neutron scattering technique appeared to be most promising in this respect.

This paper reports on the results of our measurements of the magnetic susceptibility, heat capacity, neutron scattering, muon spin relaxation (MSR), and electron paramagnetic resonance (EPR) in $Cu_3B_2O_6$ for the study of the ground state of the spin system of this compound.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

2.1. Sample Preparation

A $Cu_3B_2O_6$ single crystal with the ^{11}B isotope used to reduce neutron absorption was grown by spontaneous crystallization to a volume of approximately 1 cm^3. The $Cu_3B_2O_6$ powder was prepared by standard ceramic technology. X-ray and neutron diffraction measurements showed $Cu_3B_2O_6$ to crystallize in the triclinic $P\bar{1}$ space group. The lattice parameters were found to be close to those reported in [11, 17]. The

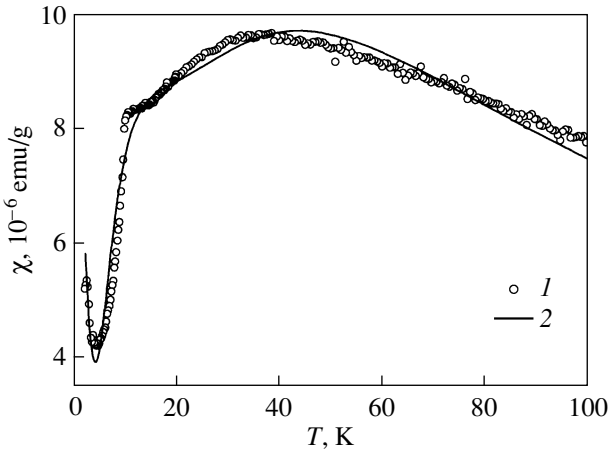

Fig. 2. Temperature dependence of the magnetic susceptibility of the $Cu_3B_2O_6$ single crystal in the *bc* plane according to the (*1*) experimental data and (*2*) calculation.

structure of this crystal (Fig. 1) consists of two-dimensional layers arranged in the *bc* plane. The copper atom in a layer is coordinated by four oxygen atoms. The average Cu–O bond length in the *bc* plane is 1.95 Å, whereas between adjacent layers it is 2.90 Å. This gives grounds to expect the spin system of this compound to be two-dimensional [11].

2.2. Magnetic Measurements

Measurements of the magnetic susceptibility of the powder and of the single crystal were performed with a PPMS instrument (Quantum Design). Figure 2 plots the results of the measurements for the single crystal in a magnetic field lying in the *bc* plane. In full agreement with earlier studies [11, 16], the temperature dependence of the magnetic susceptibility was found to pass through a broad maximum at approximately 39 K, followed by a sharp decrease at temperatures below 10 K and a rise below 5 K. Incidentally, the magnetization is only ~$0.05\mu_B$/Cu in a magnetic field of 30 T at 1.5 K [18]. The temperature dependence of the magnetic susceptibility of the powder sample exhibits the same features. A broad maximum in the temperature dependence of the magnetic susceptibility is characteristic of two-dimensional spin systems [19].

2.3. Heat Capacity Measurements

Measurements of the heat capacity were performed with PPMS in the temperature range 1.8–27.0 K. The single crystals had a small weight approximately equal to 4.5 mg. Figure 3 plots the temperature dependence of the heat capacity. At T_c = 9.8 K, an anomaly with a shape suggesting a second-order phase transition is present. The same anomaly, with a strong dependence of T_c on external magnetic field, in $Cu_3B_2O_6$ was reported also in [14]. In both cases, the values of T_c and

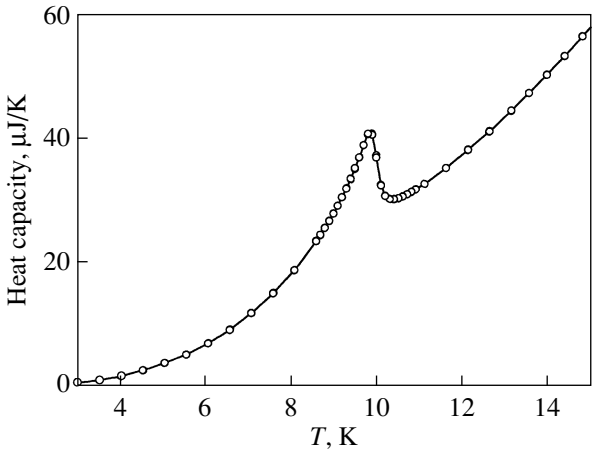

Fig. 3. Temperature dependence of the heat capacity of the $Cu_3B_2O_6$ single crystal.

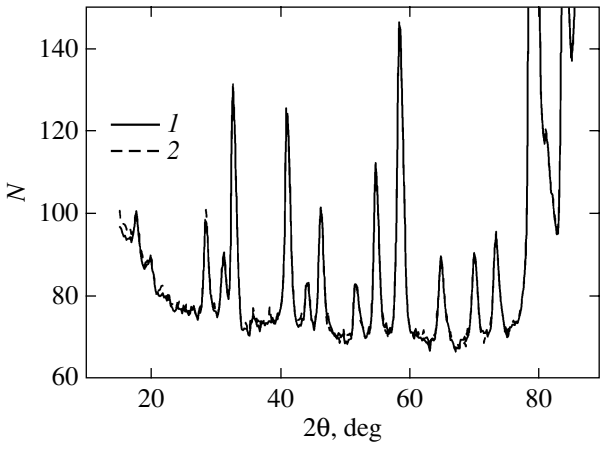

Fig. 4. Powder diffraction pattern of neutron elastic scattering from $Cu_3B_2O_6$ (λ = 4.2 Å) at temperatures T = (*1*) 1.5 and (*2*) 15 K. N is the number of detected neutrons divided by 10^4.

of the heat capacity C at T_c are in a good agreement. Because this compound does not reveal structural anomalies, it appears only natural to assume that at 9.8 K the spin system changes its state. A similar temperature anomaly of the heat capacity was observed for the spin-Peierls compound $CuGeO_3$ [20]. The change in T_c by approximately –1 K in a magnetic field of 6 T is also the same in both cases. The value of T_c was found to depend on magnetic field; indeed, it scaled approximately as H^2. The strong dependence of T_c on magnetic field argues itself for the existence of a magnetic phase transition [20]. The temperature dependence of the heat capacity in the temperature range 3–9 K can be fitted with the relationship $\mathbf{C} = \beta T^3 + \gamma\exp(-\Delta E/T)$. The exponential temperature dependence of the magnetic contribution is typical of a magnetic system with the singlet ground state separated by a gap ΔE from the excited states. The best-fit value of the gap was found to be approximately 38 K, a figure close to the value derived from inelastic neutron scattering measurements (39 K) and concordant with the broad maximum in the temperature dependence of the magnetic susceptibility (33 K) found in [11].

2.4. Neutron Scattering

The elastic and inelastic neutron scattering experiments were conducted on a TriCS single-crystal diffractometer, a DMC powder diffractometer, and a single-crystal inelastic neutron scattering spectrometer. Figure 4 displays the results of the elastic scattering study obtained at $\lambda = 4.2$ Å on $Cu_3B_2O_6$ at temperatures of 1.5 and 15 K. We readily see that the results obtained at these two temperatures do not differ from one another. The same conclusion was drawn from studies of elastic scattering by the single crystal. One may therefore conclude that this method did not reveal the onset of long-range magnetic order in this compound down to a temperature of 1.5 K.

The inelastic scattering measurements were performed at λ = 1.97 Å with a horizontal focusing analyzer and without collimation. To eliminate longer-wavelength neutrons, a graphite filter was inserted into the incident neutron beam. The measurement at 1.5 K added a peak to the diffractogram obtained at 100 K, with an energy gap of approximately 3.4 meV.

2.5. MSR Measurements

Figure 5 presents the results of MSR measurements conducted in a magnetic field of 100 G in the direction perpendicular to the muon spin direction. Above 10 K, the spin precesses with the Larmor frequency corre-

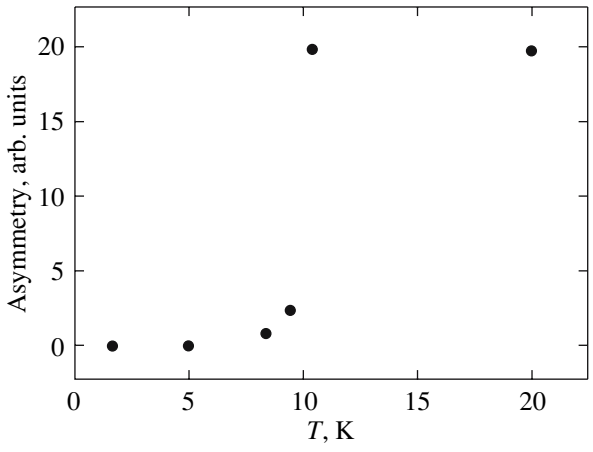

Fig. 5. Temperature dependence of the temporal MSR spectrum of the $Cu_3B_2O_6$ single crystal in a magnetic field of 100 G in the direction perpendicular to the muon spin direction.

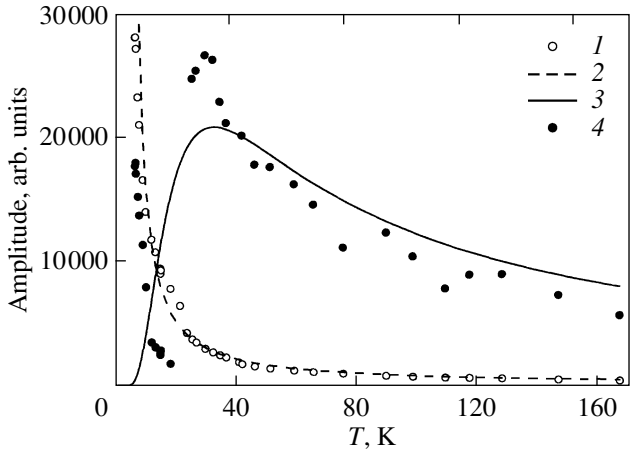

Fig. 6. Temperature dependences of the EPR line intensity of the $Cu_3B_2O_6$ single crystal at a frequency of 9.241 GHz according to (*1*, *4*) experimental data and (*2*, *3*) calculations. The external constant magnetic field is perpendicular to the *bc* plane.

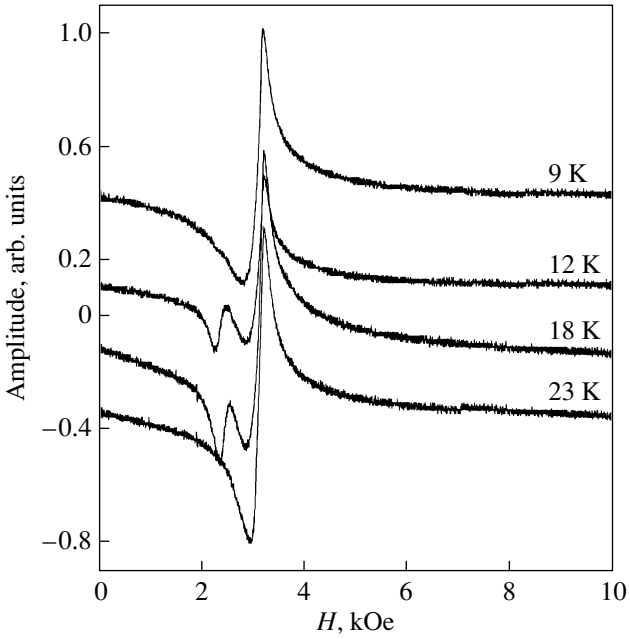

Fig. 7. EPR spectra of the $Cu_3B_2O_6$ single crystal at different temperatures. The experimental conditions are same as in Fig. 6.

sponding to the external field and without pronounced dephasing. At low temperatures, the effective field and the muon spin precession frequency vary, thus reducing the measured spectral asymmetry.

The temporal spectra measured above and below 10 K differ substantially. The spectrum obtained in the paramagnetic phase exhibits a slow Gaussian falloff because of the nuclear magnetic moments being static. By contrast, the low-temperature spectrum contains both a very fast decay of a part of the muon polarization in the early times and rotation with a Gaussian damping of the remainder of the polarization around the direction of the effective field. The results of these measurements resemble very much the data reported in [15], but because of the pulsed beam temporal structure used the fast decay obtained in [15] was not resolved, although the initial asymmetry was shown to decrease.

2.6. EPR Measurements

The measurements were performed on an *X*-band spectrometer in the temperature range 5–300 K at a frequency of 9.241 GHz, with the external magnetic field oriented perpendicular to the *bc* plane. Shown in Fig. 6 is the temperature dependence of the intensity of the two observed EPR lines. This graph was obtained by least-squares fitting of two Lorentzian lines with fixed resonance frequencies. The open circles *1* refer to the line with a *g* factor of 2.16 seen at all temperatures. The filled circles *4* correspond to the line with a *g* factor of 2.76, which was pronounced in the temperature range 9.5–22.0 K. Figure 7 displays for comparison EPR spectra measured at temperatures of 9, 12, 18, and 23 K. The implicit presence of the $g = 2.76$ line at temperatures of 9 and 23 K manifests itself in the asymmetry of the spectra.

3. DISCUSSION

The unit cell of $Cu_3B_2O_6$ contains 30 Cu^{2+} cations, 6 of which are inside the squares, 4, inside the distorted pyramids, and 20, inside the distorted oxygen octahedra. There are 16 inequivalent positions for the Cu^{2+} ions in the cell. As already mentioned, the crystal structure of $Cu_3B_2O_6$ can be conceived of as made up of fairly well spaced layers parallel to the *bc* plane. Therefore, in a first approximation one may take into account exchange interaction in this plane only. In this case, one can isolate six Cu^{2+} ions linked to the neighbors through 135° exchange interaction; eight pairs of Cu^{2+} ions coupled inside with one another by 90° exchange interaction, and with the neighboring Cu^{2+} ions through one of the two 135° exchange interactions; and two fours of Cu^{2+} ions linked inside by 90° exchange interaction, with the two inner ions coupled with the outer neighboring Cu^{2+} ion through 135° exchange interaction. Using a simple exchange interaction model [21], we arrived at the following exchange parameters: $J_{135°} = 42$ K, $J_{90°} = -18$ K for the standard situation in which all the holes on the Cu^{2+} ions are in the $d_{x^2-y^2}$ orbitals; for the case of orbital ordering we obtained $J_{135°} = 42$ K, $J'_{135°} = 14$ K, $J''_{135°} = 8$ K, and $J_{90°} = 72$ K. We used here an exchange spin Hamiltonian in the form $J\mathbf{S}_1\mathbf{S}_2$. In the case of orbital ordering, the ground state for both the pairs and fours of spins is the zero total-spin singlet, and this is what accounts for the decay of the magnetic susceptibility at temperatures substantially lower than the exchange integrals. These antifer-

romagnetically coupled pairs and fours form a two-dimensional lattice. Part of the exchange interactions is frustrated. Single spins are ordered at low temperatures, but the smallness of their exchange coupling and the anisotropy give rise to a strong reduction of the spins of individual ions. Therefore, the spontaneous moment of the spin subsystem is also small (it is by approximately an order of magnitude smaller than its nominal value), which accounts for the difficulties encountered in detecting magnetic ordering by elastic neutron scattering. The exchange interaction of individual Cu^{2+} ions with their neighbors is relatively weak, which gives grounds to consider such an ion as paramagnetic down to fairly low temperatures. Below 5 K, the magnetic susceptibility obeys the Curie law due to the presence of magnetic impurities.

The experimental data suggest the following pattern of the ground state for the $Cu_3B_2O_6$ spin subsystem. Ignoring the comparatively weak interaction among the above clusters of the magnetic system of the crystal, i.e., in the cluster approximation, its spin Hamiltonian can be written as $H = N_1H_1 + N_2H_2 + N_4H_4$, where H_n and N_n are, respectively, the Hamiltonian of a cluster of n spins and their number in the crystal. Whereas inside the pairs and fours the spins are strongly coupled and the ratio $c_{24} = N_2/N_4 = 4$ valid for a unit cell should be met, description of single spins in terms of purely Zeeman interaction H_1 is nothing more than a convention, and the ratio $c_{14} \equiv N_1/N_4$ may be not equal to three at all. Because all the measurements were conducted on different samples, the value of c_{14} used in the fitting of theoretical curves to the results of different measurements varied, and in actual fact was smaller than unity.

Fitting of the magnetic measurements (solid line in Fig. 2) yielded $J_2 = 136$ K and $J_4 = 33$ K. The cluster approximation considers the whole temperature range as paramagnetic, and this is what accounts for the disagreement between the calculated J_2 and J_4 and the values derived from heat capacity and inelastic neutron scattering measurements. On the other hand, in estimating the exchange integrals, one should take into account also the approximate character of the model [21].

The lines in Fig. 6 are fits to the temperature dependence of the EPR line intensities. The best agreement with experimental data for the resonance line with $g = 2.16$ (*1*) is reached by using for the fitting the Curie–Weiss relationship with a Curie paramagnetic temperature of 5.3 K (*2*). The values of the exchange integrals obtained suggest that it is the four-spin clusters (*3*) that account for the EPR line with $g = 2.76$ (*4*). This value of the g factor is anomalously large for the Cu^{2+} ion, but the suggestion of spin interaction anisotropy being responsible for the line displacement comes in conflict with the absence of a line with a displacement anisotropy of the opposite sign and of a comparable intensity. Therefore, a noticeable anisotropy in spin interaction can be accepted only for spin pair clusters which were not detected by EPR. Fitting of magnetic measurements yields $\Delta J_2 = -93$ K for the uniaxial anisotropy in the pair interaction $\Delta J_2 S_1^z S_2^z$, which argues for the easy plane anisotropy.

The distinct manifestation of this resonance line in the temperature range 9–22 K should be assigned to its becoming increasingly more narrow as one approaches the temperature $T_c \approx 9.8$ K. At this temperature, a feature is seen in the experimental plot of the magnetic susceptibility (Fig. 2). The coincidence with the position of the heat capacity anomaly on the temperature axis (Fig. 3) suggests a transition of a part of the spin subsystem to the magnetically ordered phase. This specific structure of the spin subsystem of the crystal conforms well both with the rearrangement of the magnetic excitation spectrum revealed in inelastic scattering and with the variation of the MSR temporal spectrum with temperature.

4. CONCLUSIONS

Thus, the experimental data presented above suggest that, at a temperature of 10 K, the spin subsystem of the $Cu_3B_2O_6$ compound, which consists of single spins and clusters of pairs and fours of spins interacting with one another, undergoes a transition to a state representing a superposition of the singlet (for clusters) and magnetically ordered (for single spins) states.

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