Weak ferromagnetism in copper metaborate CuB_2O_4

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CuB_2O_4 single crystals have been grown and their magnetic and resonance properties have been investigated for the first time. The temperature dependence of the susceptibility was found to contain features at $T=21$ and 10 K. The CuB_2O_4 single crystal transformed at $T=21$ K to a weakly ferromagnetic state. The sharp drop in susceptibility at $T<10$ K is caused by a transition of the magnetic system of CuB_2O_4 to an antiferromagnetic state. The effective magnetic moment of the Cu^{2+} ion, determined from the high-temperature part of the magnetic susceptibility, is $1.77\mu_B$. The room-temperature g factors are, respectively, 2.170 and 2.133 for magnetic field parallel and perpendicular to the c axis of the crystal. The antiferromagnetic resonance parameters in the weakly ferromagnetic and antiferromagnetic phases were measured.
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Copper oxide compounds are attracting attention due to their unusual low-temperature magnetic properties. Chain, planar, and ladder magnetic structures with nonmagnetic singlet and antiferromagnetic ground states are found in these compounds.[1–3] Since divalent copper ions possess spin $S=1/2$, quantum effects play a large role in these compounds at low temperatures.

This paper reports the results of the first investigation of the temperature dependence of the magnetization and electronic magnetic resonance of CuB_2O_4 single crystals.

1. SYNTHESIS OF THE CRYSTALS

The binary system $CuO–B_2O_3$ was first studied in Ref. 4. It was established that this system contains two congruently melting compounds: CuB_2O_4 and $Cu_3B_2O_6$. In Ref. 5 these same compounds were observed in an investigation of the phase diagram of melting of the ternary system $Li_2O–CuO–B_2O_3$. Later,[6,7] phase formation was studied and the regions of glass formation in the ternary systems $CuO–PbO–B_2O_3$ and $CuO–Bi_2O_3–B_2O_3$, where the compositions CuB_2O_4 and $Cu_3B_2O_6$ were also found, were determined. The crystal structure of CuB_2O_4 was investigated in Ref. 8. Based on these studies, we searched for a technology for growing CuB_2O_4 single crystals. The system $Li_2O–CuO–B_2O_3$ was chosen as the basis.

The components CuO, B_2O_3, and Li_2CO_3 in the ratios 25, 60, and 15 mole%, respectively, which were pulverized in a ball mill, were placed after mixing into a 50 cm^3 platinum crucible without premelting. The temperature was raised slowly to 800 °C and then rapidly to 1020 °C where it was held for 2 h. Then the melt was cooled to 800 °C at a rate of 1 deg/h.

The crystals were extracted by washing off the contents of the crucible in a 20% boiling-water solution of nitric acid. The crystals were well-faceted prisms, transparent, and violet-blue in color, and their maximum dimensions were $2\times1\times1$ cm^3. X-ray analysis of a powder obtained by grinding the crystals confirmed that the parameters of the crystals obtained were close to those found in Ref. 8 for CuB_2O_4.

2. CRYSTAL STRUCTURE

Copper metaborate, CuB_2O_4, crystallizes in the tetragonal system with space group $I\bar{4}2d$. The unit cell contains 12 formula units. The cell parameters are $a=11.484$ Å and $c=5.620$ Å . The computed density of the crystal is 4.022 g/cm^3. The resistivity at 300 K is 10^9 $\Omega\cdot$cm.[6] It is noted in Ref. 5 that CuB_2O_4 undergoes a structural phase transition at 1000 °C.

The unit cell contains two nonequivalent copper ion positions: four copper ions Cu(1) are located in a planar square environment of oxygen ions; eight copper ions Cu(2) are located in a distorted octahedron of oxygen ions (Fig. 1).

The characteristic $O^2–Cu^{2+}$ distances for two nonequivalent positions of the copper ions are[8]

$$Cu^{2+}(1)-O^{2-}(1)=1.998\ \text{Å},$$

$$Cu^{2+}(2)-O^{2-}(2)=1.902\ \text{Å},$$

$$Cu^{2+}(2)-O^{2-}(3)=1.886\ \text{Å},$$

$$Cu^{2+}(2)-O^{2-}(4)=1.980\ \text{Å},$$

$$Cu^{2+}(2)-O^{2-}(4')=1.980\ \text{Å},$$

$$Cu^{2+}(2)-O^{2-}(1)=3.069\ \text{Å}.$$

The Cu^{2+} (2) positions are characterized by the following angles:

$$O^{2-}(2)-Cu^{2+}(2)-O^{2-}(4)=92.3°,$$

$$O^{2-}(4)-Cu^{2+}(2)-O^{2-}(3)=87.7°,$$

$$O^{2-}(3)-Cu^{2+}(2)-O^{2-}(4')=87.7°,$$

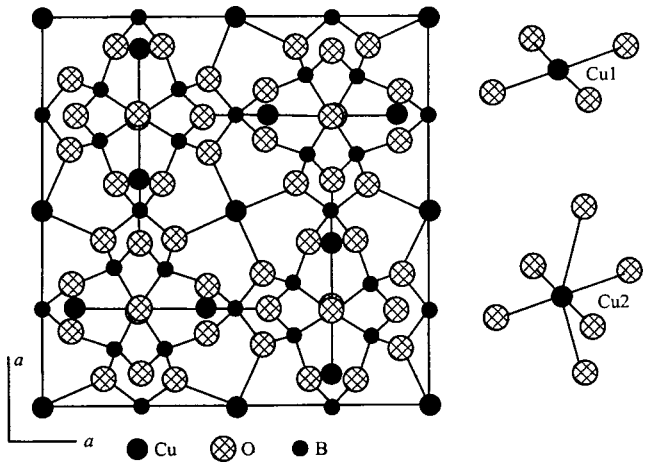

FIG. 1. Crystal structure of CuB_2O_4.

$$O^{2-}(4')-Cu^{2+}(2)-O^{2-}(2)=92.3°,$$

$$O^{2-}(1)-Cu^{2+}(2)-O^{2-}(2)=73.1°,$$

$$O^{2-}(1)-Cu^{2+}(2)-O^{2-}(4')=67.0°.$$

3. MAGNETIC SUSCEPTIBILITY

The magnetization of CuB_2O_4 single crystals was measured with a SQUID magnetometer in the temperature 4.2–200 K in magnetic fields of 50 and 330 Oe. The temperature dependence of the magnetic susceptibility for a 50 Oe magnetic field is shown in Fig. 2. The susceptibility is sharply anisotropic: in a magnetic field along the tetragonal *c* axis of the crystal it increases monotonically with decreasing temperature, while for a field oriented perpendicular to this axis the susceptibility is higher and depends on the temperature nonmonotonically. The paramagnetic Curie temperature and the effective magnetic moment, which are determined from the high-temperature part of the temperature dependence of the reciprocal of the susceptibility, are $\theta=-9.5$ K and 1.77 μ_B for the magnetic field directed along the *c* axis of the crystal.

At temperatures 21 and 10 K sharp anomalies are observed in the temperature dependence of the susceptibility with the field oriented perpendicular to the *c* axis. At $T=21$ K a jump is observed in the temperature dependence of the susceptibility, and as temperature decreases further, the susceptibility increases rapidly. At 10 K the susceptibility decreases abruptly by approximately an order of magnitude. Measurements in a 300 Oe field show qualitatively similar results.

4. ELECTRONIC MAGNETIC RESONANCE

The results of electronic magnetic resonance measurements in the temperature range 80–300 K are displayed in Figs. 3 and 4. The magnetic resonance spectrum is a single Lorentzian line. The angular dependences of the line width and *g* factor are characteristic for a Cu^{2+} ion in a tetragonal crystal. The linewidth and *g* factor for magnetic field parallel and perpendicular to the tetragonal axis of the crystal are,

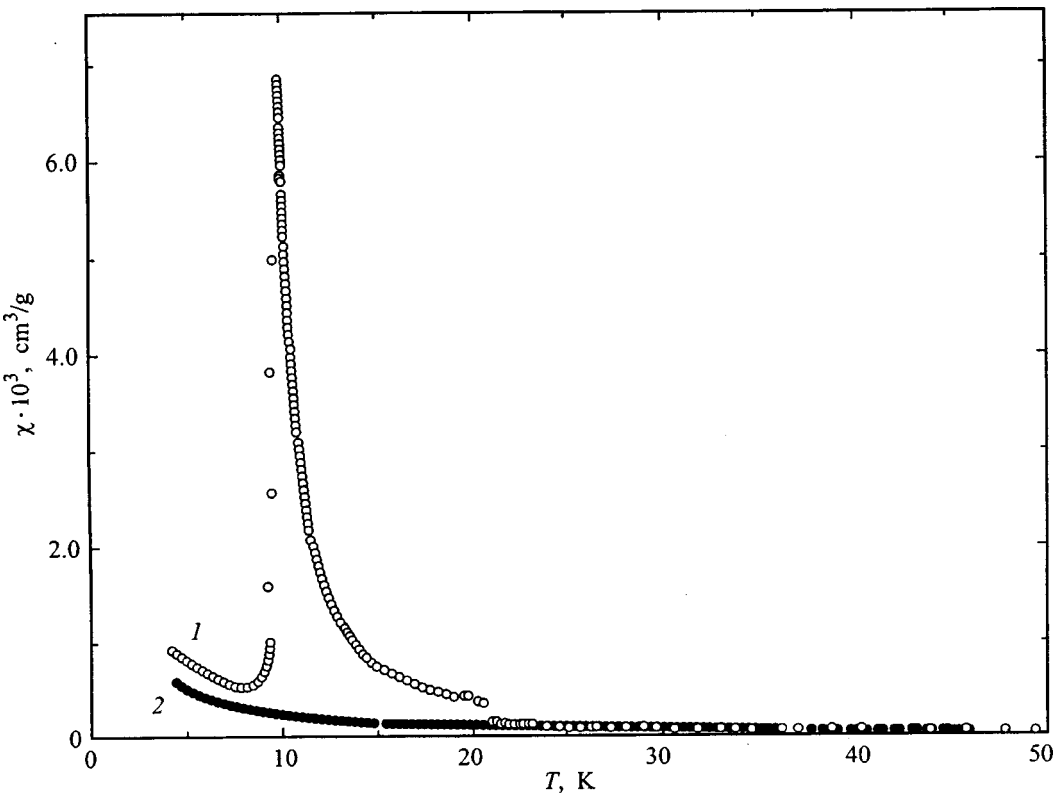

FIG. 2. Temperature dependence of the magnetic susceptibility of a CuB_2O_4 crystal. *1, 2* — Magnetic field *H* perpendicular and parallel to the *c* axis of the crystal, respectively.

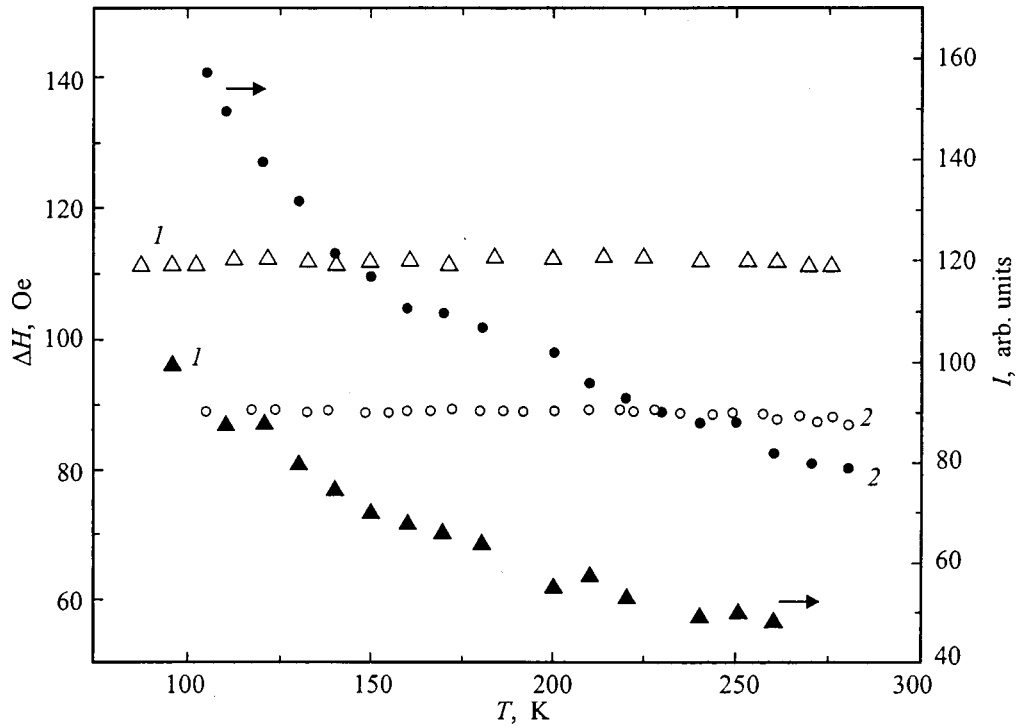

FIG. 3. Temperature dependences of the linewidth and electronic magnetic resonance intensity at frequency $\nu = 9.4$ GHz. *1, 2* — H parallel and perpendicular to the c axis of the crystal, respectively.

respectively, $\Delta H_{\parallel} = 112$ Oe, $\Delta H_{\perp} = 87$ Oe, $g_{\parallel} = 2.17$, and $g_{\perp} = 2.133$. The single Lorentzian line attests to the existence of an exchange interaction between all copper ions in the crystal.

Anomalies are observed in the magnetic resonance parameters as temperature decreases further. The temperatures of these anomalies correlate with the anomalies in the temperature dependence of the susceptibility (Figs. 5 and 6). The

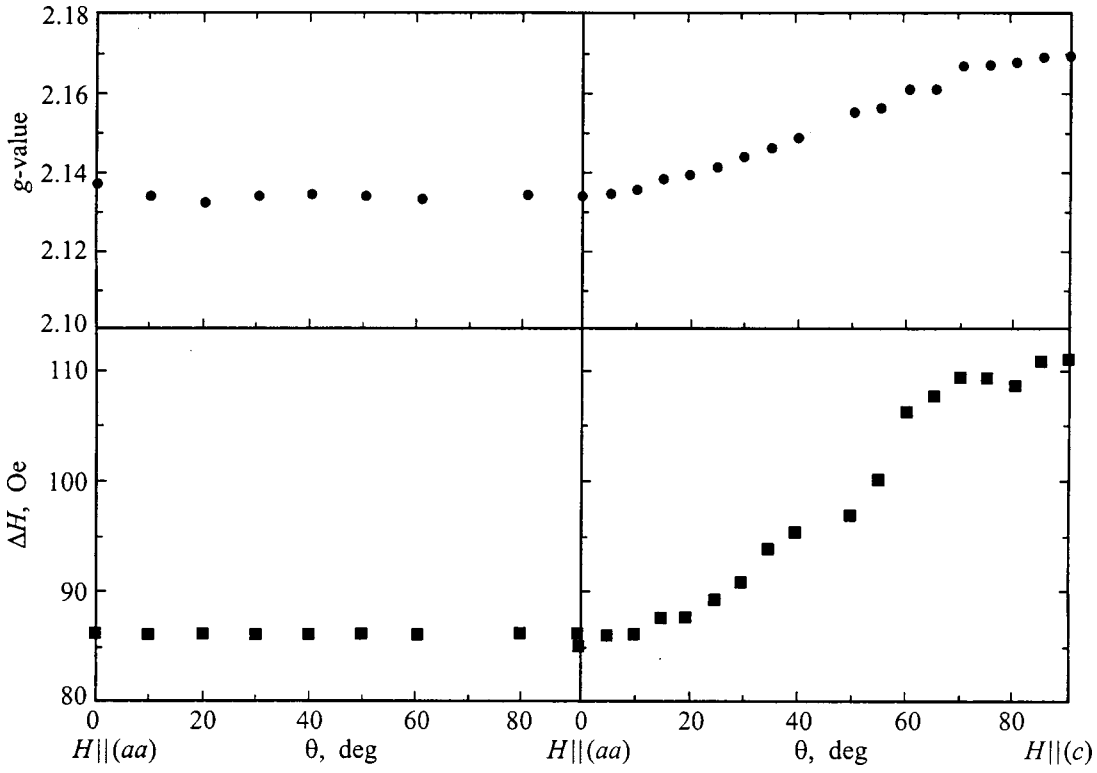

FIG. 4. Angular dependences of the linewidth and g factor of the electronic magnetic resonance of a CuB_2O_4 single crystal at room temperature ($\nu = 9.4$ GHz).

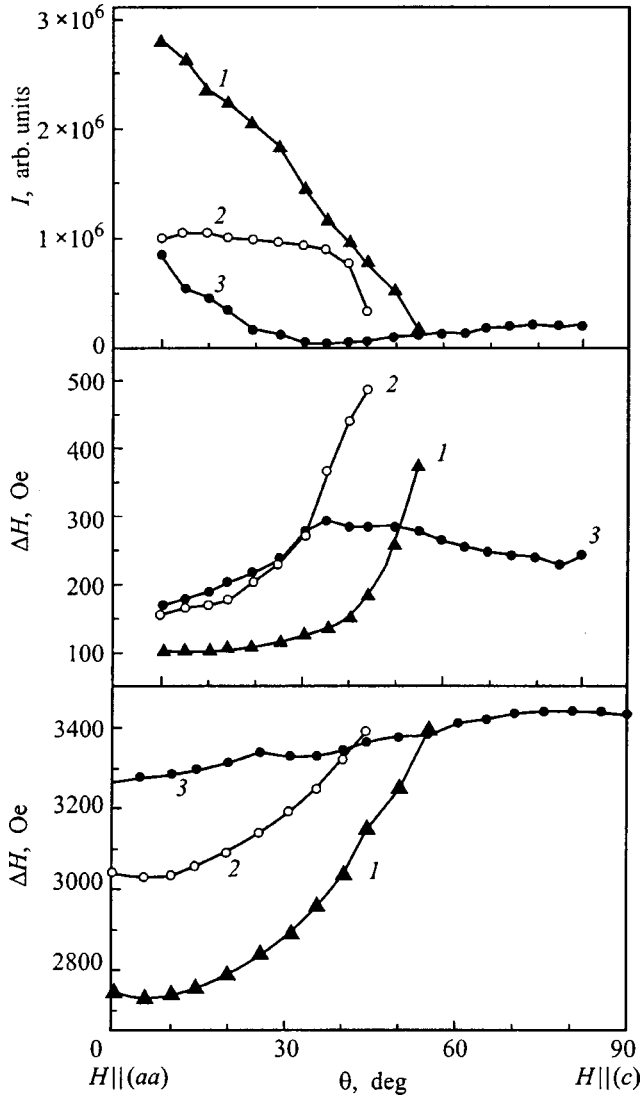

FIG. 5. Angular dependences of the intensity, linewidth, and resonance field of the electronic magnetic resonance signal ($\nu = 10$ GHz) in a CuB_2O_4 single crystal at liquid-helium temperatures T, K: *1* — 10, *2* — 7.5. *3* — 6.

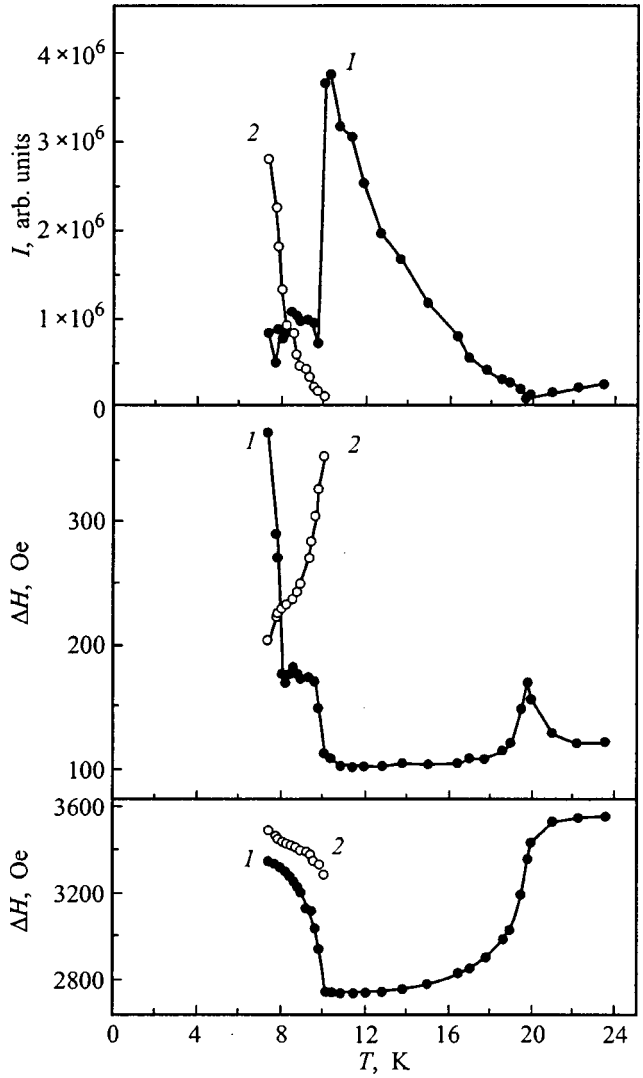

FIG. 6. Temperature dependences of the intensity, linewidth, and resonance field of the electronic magnetic resonance signal ($\nu = 10$ GHz) in a CuB_2O_4 single crystal at liquid-helium temperatures: *1, 2* — H perpendicular and parallel to the c axis, respectively.

resonance field in the tetragonal plane of the crystal decreases gradually from 3560 Oe at $T = 21$ K to 2740 Oe at $T = 10$ K. At temperatures below 10 K, the magnetic resonance signal is observed for any orientation of the magnetic field relative to the crystallographic axes, the resonance field in the plane of the crystal being higher than along the principal axis: $H_r^{\parallel} > H_r^{\perp}$.

5. DISCUSSION

Analysis of the geometry of the arrangement of the Cu^{2+} ions in the CuB_2O_4 crystal lattice shows that an exchange interaction between the nearest neighbors occurs only via the oxgyen and boron ions according to the scheme Cu–O–B–O–Cu. The Cu^{2+} (1) and Cu^{2+} (2) ions have a different number of exchange bonds, so that the parameters of their effective exchange bonds are different. Symmetry analysis of the crystal structure of CuB_2O_4[9] has shown that antiferromagnetic structures admitting the existence of a spontaneous weak ferromagnetic moment in the basal plane can form in this crystal. The magnetic moments of the Cu^{2+} ions also lie in the basal plane of the crystal. Analysis of the local environment of copper ions based on the Moriya rules[10] suggests the existence of a Dzyaloshinskiĭ–Moriya interaction between the Cu^{2+} ions, which causes canting of the magnetic moments of the sublattices.

In our opinion, at $T = 21$ K a CuB_2O_4 single crystal transforms into a weakly ferromagnetic state. This leads to a strong increase in the magnetization as temperature decreases further.

The magnetic resonance signal in the temperature interval 21–10 K can also be explained by the presence of a weakly ferromagnetic state. The decrease of the resonance field as temperature decreases from 21 to 10 K is apparently caused in this case by an increase in the Dzyaloshinskiĭ field. The angular dependence of the resonance field in a plane containing the tetragonal axis also agrees with this assumption. The Dzyaloshinskiĭ field can be estimated from the temperature dependence of the resonance field as $H_D = 1900$ Oe

at $T=10$ K. Here the possible existence of a gap in the spectrum of collective excitations and the influence of anisotropy were neglected.

Our data on the magnetization and magnetic resonance allow us to conclude that at a CuB_2O_4 single crystal transforms $T_N=21$ K from the paramagnetic into a weakly ferromagnetic state. The latter remains as temperature decreases to $T=10$ K. The sharp drop in the susceptibility at temperature $T_M=10$ K is due to the transition of the system to an antiferromagnetic state — Morin's transition.

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