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Magnetic Susceptibility and Magnetic-Field Behavior of CuB_2O_4 Copper Metaborate

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Abstract—An experimental study is reported regarding the temperature dependence of the magnetic susceptibility of a CuB_2O_4 tetragonal single crystal within the 4.2–200-K range. It has been established that the magnetic susceptibility exhibits anomalies at 21 and 10 K and depends strongly on crystal orientation in the magnetic field. A study has been carried out of the field dependences of the magnetization of CuB_2O_4 at various temperatures and crystal orientations. It is shown that for $T > 21$ K, the crystal is in a paramagnetic state determined by Cu^{2+} copper ions with an effective magnetic moment of 1.77 μ_B. Within the 10–21 K interval, the field dependence of the magnetization is typical of a weak ferromagnet with magnetic moments of the two antiferromagnetically coupled sublattices lying in the tetragonal plane of the crystal. The spontaneous weakly-ferromagnetic moment is 0.56 emu/g at 10 K. The canting angle of the sublattice magnetic moments, determined by the Dzyaloshinski–Moriya interaction, is 0.49°. It is believed that below 10 K, the CuB_2O_4 crystal retains its easy-plane magnetic structure, but with a zero spontaneous magnetic moment. *© 2000 MAIK "Nauka/Interperiodica".*

Copper oxide compounds exhibit a rich variety of electrical and magnetic properties. It is in these compounds that high-temperature superconductivity was discovered and studied extensively. The diversity of the magnetic properties of the cuprates is accounted for by the specific features of the electronic configuration ($3d^0$) of the Cu^{2+} ion, in which it is mainly present in these compounds. The spin of the Cu^{2+} ion is 1/2. From the theoretical viewpoint, this makes the investigation of the properties of such magnets easier. At the same time, the small spin and the possibility of formation of quasi-low-dimensional magnets makes such effects as quantum spin reduction and quantum fluctuations important. One of the interesting quantum effects is the Peierls spin transition in antiferromagnetic chains with an $S = 1/2$ spin. This transition was found to occur in $CuGeO_3$ [1]. The transition is associated with the instability of a uniform antiferromagnetic chain in a three-dimensional phonon system with respect to dimerization and transition to the singlet state of the spin system. The transition of low-dimensional systems to a singlet ground state accompanied by the formation of an energy gap in the spectrum of elementary magnetic excitations is also characteristic of the Holdane systems [2] and systems exhibiting competition among the exchange interactions [3].

In order to understand the nature of the specific properties of the cuprates, one has to comprehensively study their magnetic properties at the level of the electronic structure. This paper presents the results of a measurement of the magnetic characteristics of a single crystal copper metaborate of CuB_2O_4.

EXPERIMENTAL RESULTS

The magnetic properties of a single-crystal of CuB_2O_4 were measured on samples grown from a melt solution by the technology described by us elsewhere [4]. The temperature and field dependences of the magnetic moments were determined with a vibrating-sample magnetometer within the 4.2–200-K temperature range and in magnetic fields of up to 70 kOe.

The temperature dependences of the crystal susceptibility in fields of 350 and 500 Oe obtained for magnetic-field orientations along and perpendicular to the tetragonal axis are shown graphically in Fig. 1. Note the strong anisotropy of the susceptibility. In a magnetic field applied in the basal plane of the crystal, one observes a jump in the susceptibility at 21 K and its fast growth with a further decrease of temperature. At 10 K, the susceptibility decreases in a jump by about an order of magnitude and then increases monotonically as the temperature continues to fall. It should be pointed out that the temperature dependence of the susceptibility measured at 20 kOe does not exhibit any anomalies within the temperature interval specified (Fig. 2). When measured in a magnetic field applied along the tetragonal axis of the crystal, the temperature dependence of the susceptibility is monotonic throughout the temperature and field ranges studied (Fig. 1). The paramagnetic Néel temperature and the effective magnetic

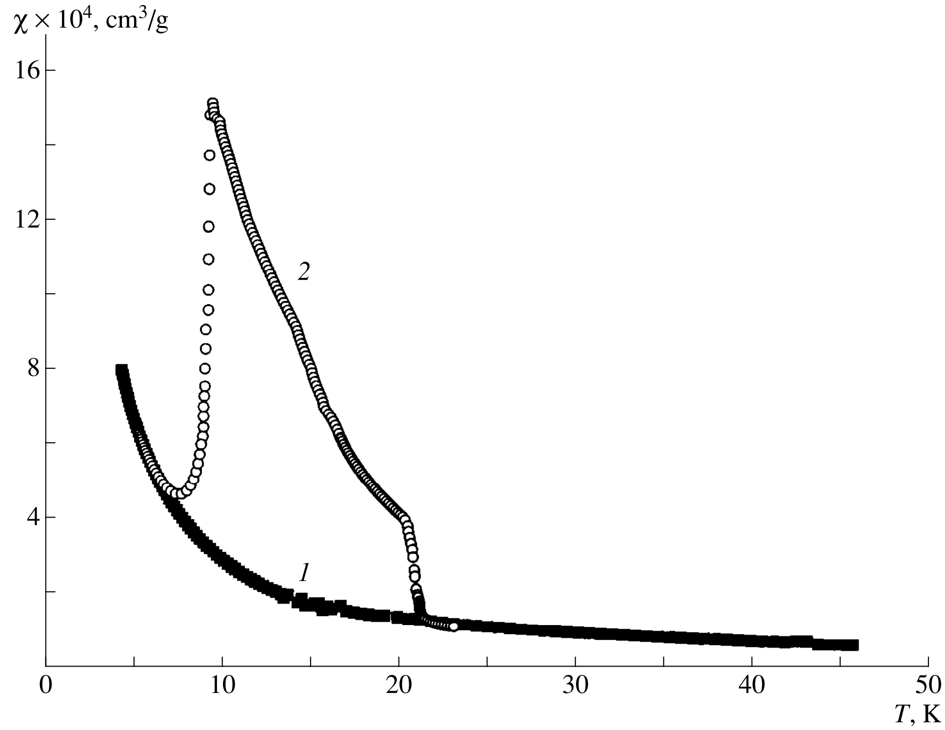

Fig. 1. Temperature dependence of the magnetic susceptibility of single-crystal CuB_2O_4: (*1*) the field is parallel to the tetragonal axis of the crystal (H = 350 Oe), (*2*) the field is parallel to the crystal basal plane (H = 500 Oe).

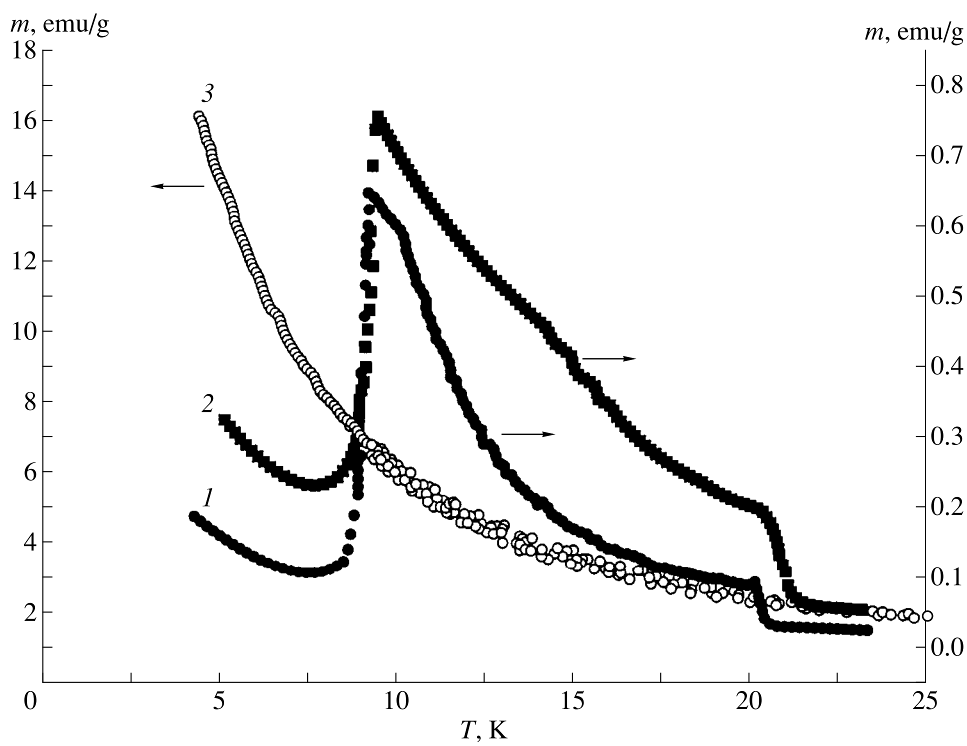

Fig. 2. Temperature dependence of the magnetization of single-crystal CuB_2O_4 plotted for different external magnetic fields H (kOe) applied in the basal plane of the crystal: (*1*) 0.2, (*2*) 0.5, (***3***) 20.

moment of the copper ion derived from the high-temperature part of the magnetic susceptibility are Θ_N = –9.5 K and μ_{eff} = 1.77 μ_B, respectively.

To establish the nature of the anomalies in the temperature dependence of the susceptibility, one measured the field dependences of magnetization at various temperatures and for different magnetic-field orientations relative to the crystal axes. The results obtained are shown in Figs. 3 and 4. The field dependences of magnetization obtained with a magnetic field oriented along the tetragonal axis of the crystal are mostly monotonic throughout the temperature interval studied. However, when the magnetic field is oriented in the tetragonal plane, the magnetization exhibits characteristic features. Within the 10–18-K region, the magnetization curves give evidence for the existence of a weak spontaneous magnetic moment in the basal plane of the crystal, which is characteristic of weak ferromagnets. The spontaneous moment is m_0 = 0.56 emu/g at T = 10 K. As the temperature is brought below 10 K, the spontaneous magnetization vanishes, and a feature typical of a magnetic spin-reorientational transition appears in the magnetization curve. Linear extrapolation of the high-field rectilinear portions (directly above the anomalies characteristic of spin-reorientational transitions) of magnetization curves made within the 10–4.2-K interval again reveals the appearance of a spontaneous magnetic moment above these fields.

The temperature dependences of the spontaneous magnetic moment and of the spin-reorientational transition field obtained in this way are shown graphically in Fig. 5.

DISCUSSION

The CuB_2O_4 metaborate crystallizes in tetragonal symmetry, space group $I42d$ [4]. The unit cell contains 12 formula units, and the cell parameters are a = 11.484 Å and c = 5.620 Å. A symmetry analysis [5] of the crystal structure of CuB_2O_4 showed the possibility of formation of several antiferromagnetic structures, which allow the existence of a small spontaneous magnetic moment in the basal plane of the crystal.

The crystal has two inequivalent copper-ion positions: Cu(1), at the 4a site (0, 0, 1/2), and Cu(2), in the 8d position (0.08, 1/4, 1/8). As the symmetry-forming elements, one can take, besides the elementary translations, the fourfold inversion axis $(\bar{4})$ and the vertical diagonal plane with a glide along the body diagonal by 1/4(σ_d). The symmetry-forming elements for the 4a position can produce only one parity combination $(\bar{4})^+(\sigma_d)^-$ compatible with the existence of antiferromagnetism. The possible combinations for the 8d position are $(\bar{4})^+(\sigma_d)^-$, $(\bar{4})(\sigma_d)^+$, and $(\bar{4})(\sigma_d)^-$. Thus, in this crystal there can exist three antiferromagnetic structures allowing weak ferromagnetism (Fig. 6). The

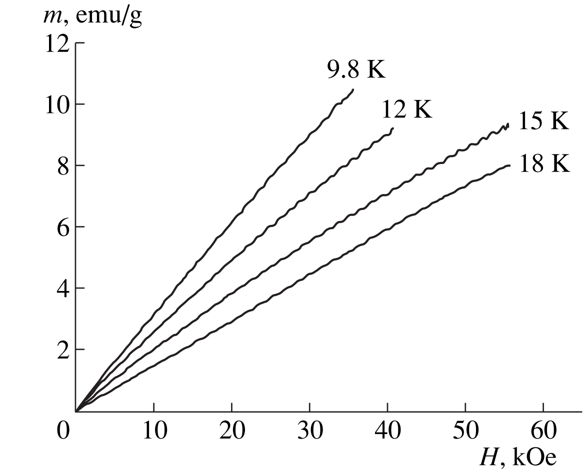

Fig. 3. Field dependence of the magnetization of single-crystal CuB_2O_4. The magnetic field is parallel to the tetragonal axis of the crystal.

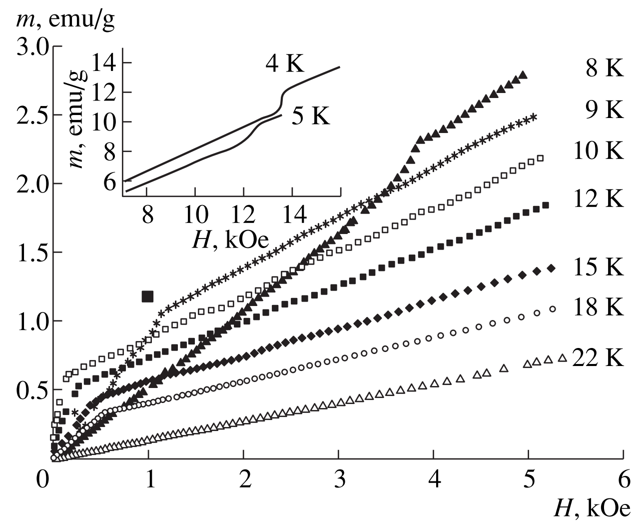

Fig. 4. Field dependence of the magnetization of single-crystal CuB_2O_4. The magnetic field is parallel to the basal plane of the crystal.

copper-ion magnetic moments lie in the basal plane of the crystal. The second-order invariant in the expression for the free-energy density, which is responsible for the formation of the weak ferromagnetism, in this case, has the form $[\mathbf{ml}]_z$, where **m** and **l** are the ferromagnetism and antiferromagnetism vectors, respectively [5].

The copper ions in the CuB_2O_4 crystal are exchange-coupled through the oxygen and boron ions in the Cu–O–B–O–Cu chain. Note that there is no inversion center on the straight line connecting the nearest copper ions. According to the symmetry rules for determination of the direction of the Dzyaloshinski vector [6], the Cu^{2+} ions can in this case be coupled through the Dzyaloshinski–Moriya interaction, which

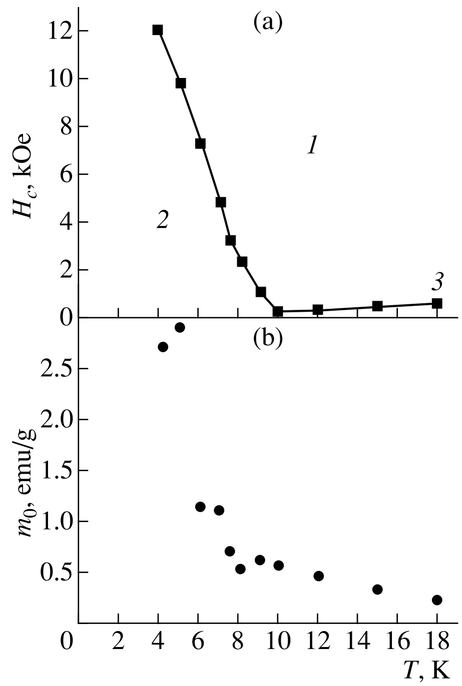

Fig. 5. (a) Temperature dependence of the spin-reorientational transition field H_c: (*1*) region of existence of a weakly ferromagnetic state, (***2***) compensated antiferromagnet; and (b) temperature dependence of the weak magnetic moment m_0 in the basal plane of single-crystal CuB_2O_4. The magnetic field is everywhere parallel to the basal plane of the crystal.

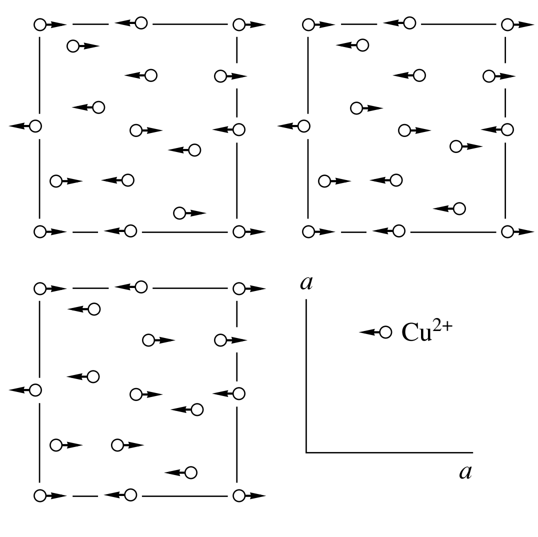

Fig. 6. Three possible antiferromagnetic structures allowing the existence of a weak ferromagnetism in single-crystal CuB_2O_4. The structures are projected onto the tetragonal plane of the crystal.

gives rise to the appearance of a small spontaneous moment due to the weak noncollinearity between the magnetizations of the antiferromagnet sublattices. In view of the fact that a twofold axis passes through the midpoint of the segment that connects the Cu(1) ions, and this axis is perpendicular to the segment and parallel to the tetragonal plane of the crystal, one may conclude that the Dzyaloshinski vector is perpendicular to this axis [6]; it can be directed, for instance, along the *c* axis of the crystal.

With this in mind, and taking into account the available experimental data on magnetization, it appears reasonable to assume that, within the 10–21-K interval, the CuB_2O_4 crystal has an easy-plane magnetic structure with a small spontaneous magnetic moment m_0 = 0.56 emu/g at T = 10 K lying in the basal plane. The canting angle of the sublattice magnetizations is 0.49°. A similar structure is found, for example, in the α-Fe_2O_3 hematite at temperatures above the Morin point [7]. The behavior of such a magnetic structure in magnetic fields can be analyzed using the expression for free energy in the form [7]

$$F = J\mathbf{M}_1\mathbf{M}_2 - D[\mathbf{M}_1 \times \mathbf{M}_2]_2 - \mathbf{H}(\mathbf{M}_1 + \mathbf{M}_2)$$
$$- K_1(\cos^2\beta_1 + \cos^2\beta_2)/2 - K_2(\cos^4\beta_1 + \cos^4\beta_2)/2, \quad (1)$$

where J is the parameter of the intersublattice exchange interaction, $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetizations of the first and second sublattices, $\mathbf{H}$ is the external magnetic field, K_1 and K_2 are the constants of uniaxial magnetocrystalline anisotropy of the second and fourth orders, respectively, and β_1 and β_2 are the angles that the sublattice magnetizations $\mathbf{M}_1$ and $\mathbf{M}_2$, respectively, make with the crystal tetragonal axis. Obviously enough, the easy-plane state occurs in zero external magnetic field for $K_1 < 0$. The presence of the Dzyaloshinski–Moriya interaction gives rise in this case to a weakly ferromagnetic moment m_0 because of the sublattice magnetizations being not collinear. For an external magnetic field $\mathbf{H}$ oriented in the basal plane, the field dependence of the magnetization can be written as

$$m = m_0 + \chi_{\perp}H, \quad (2)$$

where $\chi_{\perp} = 1/J$, $m_0 = DM_0/J$, and M_0 is the sublattice magnetization at T = 0 K. The saturation magnetization of single-crystal CuB_2O_4 is $2M_0$ = 160 G. Using (2) and the experimental data of Fig. 4, one can construct the temperature dependence of the Dzyaloshinski field $H_D = DM_0$. The results are shown in Fig. 7. Note the satisfactory agreement of the Dzyaloshinski field thus obtained with its value derived from magnetic resonance data [8]. The effective exchange field $H_E = JM_0$ is estimated as 29 kOe at T = 4.2 K.

An analysis of the field dependences of magnetization in the basal plane obtained at temperatures below 10 K (Fig. 4) indicates the absence of a spontaneous magnetic moment in weak magnetic fields and its formation as the magnetic field increases above a certain critical level. Note that the lower the temperature, the higher the critical field is. The phase boundary constructed in this way, and separating the states with a weak spontaneous magnetic moment and a weak field-induced magnetic moment, is indicated in Fig. 5a. The vanishing of the spontaneous magnetic moment can be caused, in our opinion, by antiferromagnetic ordering of weak ferromagnetic moments below 10 K. A similar situation was reported by some authors [9, 10]. Besides, the disappearance of the spontaneous magnetic moment can be associated with distortions of the CuB_2O_4 structure, which impose symmetry-induced restrictions on its existence.

As follows from studies of antiferromagnetic resonance in CuB_2O_4 [8], at temperatures below 10 K the magnetic structure of the crystal is also easy plane. This conclusion is also argued for by the observation that the magnetic susceptibility grows monotonically with decreasing temperature, irrespective of the magnetic field orientation relative to the crystallographic axes. In this case, the susceptibility of a sample is determined, for any orientation of the external magnetic field, by the perpendicular susceptibility $\chi_\perp$. Now, if an easy-axis magnetic structure with magnetic moments parallel to the tetragonal axis formed below 10 K, the susceptibility would be strongly anisotropic, and its temperature dependence would be governed by the perpendicular ($\chi_\perp$) and parallel ($\chi_\parallel$) susceptibilities; this is not supported by experimental data.

Note the parts of the magnetization curves for the basal plane of the crystal at temperatures from 18 to 10 K, which lie within the field range of 0 to 600 Oe in Fig. 4. Significantly, these parts of the curves are linear functions of the field, and the field at which the curve slope changes (identified by an arrow) increases with increasing temperature. Fig. 5a also shows the strengths of these fields, which permit one to isolate a certain region (3) in the phase diagram. Assuming this behavior of the magnetization in these temperature and field regions not to be due to the sample becoming a single domain, one could suggest the existence within the 21–10-K interval of one more magnetic phase, the nature of which remains unclear.

Summing up, we can conclude that, for temperatures $T_N > 21$ K, the CuB_2O_4 tetragonal crystal is a paramagnet with an effective magnetic moment $\mu_{eff} = 1.77\mu_B$. The magnetic susceptibility obeys the Curie–Weiss law with a Néel paramagnetic temperature $\Theta = -9.5$ K, which shows antiferromagnetic exchange interactions to be dominant. Below the Néel temperature $T_N = 21$ K, the crystal is in a magnetically ordered state. Within the 10–21-K temperature interval it is a weak ferromagnet with the sublattice magnetic moments lying in the basal plane of the crystal and being slightly noncollinear. At $T = 10$ K, a magnetic phase transition occurs, which results in a disappearance of the weak spontaneous magnetic moment. To reveal the nature of this transition and to better identify the magnetic state of the crystal for $T < 10$ K, antiferromagnetic resonance studies are presently under way, and neutron diffraction measurements on a crystal with the ^{11}B isotope are being planned for the future.

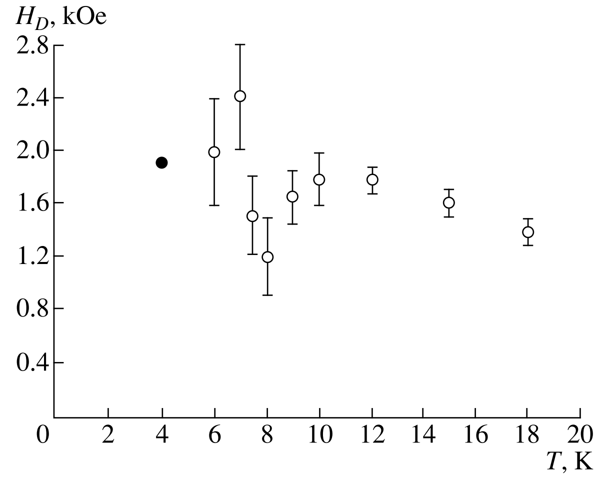

Fig. 7. Temperature dependence of the Dzyaloshinski field H_D in single-crystal CuB_2O_4: the filled circle is antiferromagnetic-resonance data.

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