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New Magnetic States in Copper Metaborate CuB_2O_4

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The static and resonance properties of copper metaborate CuB_2O_4 were experimentally studied in a magnetic field applied in the crystal tetragonal plane. The field-induced second-order phase transition to a weakly ferromagnetic state was observed in the temperature range 10–20 K. The low-field state is characterized by the absence of spontaneous moment, and it represents, presumably, a long-period helicoid. At temperatures below 2 K, two sequential first-order phase transitions were observed. They were accompanied by jumps in resonance absorption with a hysteresis upon changing field-scan direction. These transitions can be caused by the transformation of the incommensurate spin structure into the helicoidal states with periods commensurate with the lattice translation period. © *2003 MAIK "Nauka/Interperiodica".*

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1. INTRODUCTION

The tetragonal copper metaborate crystal CuB_2O_4 belongs to the family of copper oxides whose intense research was stimulated by the discovery of high-temperature superconductivity. In the early works devoted to the magnetic properties of a CuB_2O_4 single crystal [1], it was found that, in the temperature range from 10 K to the Néel temperature $T_N = 20$ K, this compound is a weak ferromagnet, in which the magnetic moments of sublattices and the spontaneous magnetic moment lie in the tetragonal crystal plane. Upon a decrease in temperature, an abrupt decrease in magnetization was observed near $T = 10$ K, indicating the transition to a new magnetic phase. The resonance studies [2] showed that, although the magnetic moments of copper ions remain in the basal crystal plane, the spontaneous moment disappears. It was conjectured in the cited work that the low-temperature magnetic state of CuB_2O_4 can be helicoidal. Neutron inelastic scattering studies [3] showed that, in the absence of a magnetic field, an incommensurate magnetic state of the type of magnetic soliton lattice with the structure wave vector oriented along the tetragonal axis is established below 10 K. The magnetic resonance [2] and magnetostatic [4] studies in a magnetic field applied in the crystal tetragonal plane showed that, in the temperature range $T < 10$ K, the modulated magnetic structure transforms into a weakly ferromagnetic state with a magnetic moment lying in the same plane. The temperature dependence of the interface separating these two states was obtained and subsequently confirmed by neutron diffraction measurements [5]. Analysis of the field dependences of magnetization [4] allowed the assumption to be made [6] that the weakly ferromagnetic state is induced in the temperature range 10–20 K by the magnetic field and transforms into a new magnetic state with zero spontaneous magnetic moment upon lowering the field. The purpose of this work was to study the assumed phase transition by the magnetic resonance method, which is one of the most sensitive to the magnetic state of a substance, and by the magnetostatic measurements. It was also of interest to carry out magnetic resonance studies at temperatures $T < 2$ K, where the anomalies were observed in the neutron elastic scattering and μSR data [7].

2. SAMPLES AND EXPERIMENTAL METHOD

Single-crystal samples of copper metaborate CuB_2O_4 were grown by the spontaneous crystallization method [8]. Since the critical magnetic fields of the assumed phase transition are rather low (less than 800 Oe), the resonance measurements should be performed in the frequency range 3–6 GHz. For this purpose, a spectrometer of the transmission type with a quasi-toroidal cavity was used (for details, see [9]). The cavity operating frequency was tuned using accessory quartz plates of different size, which were placed in a node of electric field. The static magnetic field was created by a superconducting solenoid. Single crystal CuB_2O_4 of size $1.2 \times 1.8 \times 2.8$ mm was placed in a node of magnetic field so that the static field was oriented in the [110] direction of the basal plane, while the perpen-

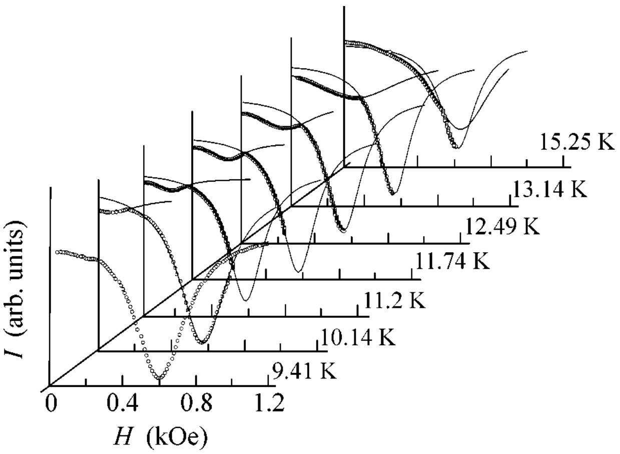

Fig. 1. Resonance absorption spectra of CuB_2O_4 at $T >$ 10 K and a frequency of 3.48 GHz. Dots are the experimental data and solid lines are the Lorentzian fits.

dicular microwave magnetic field was directed along the tetragonal axis C_4. Magnetostatic measurements were performed on an MPMS-5 SQUID magnetometer.

3. EXPERIMENTAL RESULTS

The examples of resonance absorption spectra recorded with a magnetic field scan at frequency ν = 3.48 GHz are presented in Fig. 1 for various temperatures above 9 K. At T = 9.4 K, a single high-intensity resonance line with a width of about 300 Oe is observed at a resonance field of 600 Oe. As the temperature increases, an additional low-intensity line appears at low fields starting with $T \simeq$ 9.5 K. With an increase in temperature, this line rapidly shifts to higher fields, and its amplitude and width increase. The solid lines in the figure are fits of the Lorentzian curves to the experimental points. Similar transformation of the resonance spectrum is observed at frequency ν = 5.15 GHz, but the additional line now appears at temperatures above 12.6 K. In all spectra, kink points can be set off in the field $H = H_{c_\perp}$, where one absorption line changes to the other. Magnetic hysteresis upon changing the scan direction was not observed.

The curves for the field dependence of magnetization at temperatures 10, 11, and 14 K in a magnetic field applied in the [110] direction of the tetragonal plane are shown in Fig. 2. These curves were recorded in the interval from 0 to ±1000 Oe with the back and forth field scans. They are symmetric about the origin of coordinates and do not show magnetic hysteresis. At all temperatures, the curves for magnetization field dependence have a kink point coinciding with the kink points in the resonance absorption spectra. The kink points $H_{c_\perp}$ separate these curves into two parts. The initial portions of the curves emanate from the origin of coordinates and are nonlinear, with the degree of nonlinearity decreasing upon elevation of temperature. At $H > H_{c_\perp}$, the dependences become nonlinear and can be represented as $m(H) = m_0 + \chi H$, where m_0 is the spontaneous magnetic moment and χ is magnetic susceptibility. The curves measured in a field directed along [100] is qualitatively analogous to the curves measured for a [110]-directed field.

Magnetic resonance at temperatures below 4.2 K was studied at a frequency of 5.15 GHz. As the temperature decreased down to $T \simeq$ 2 K, a single smooth absorption line with a width of about 900 Oe was observed. Upon further decrease in temperature, weak

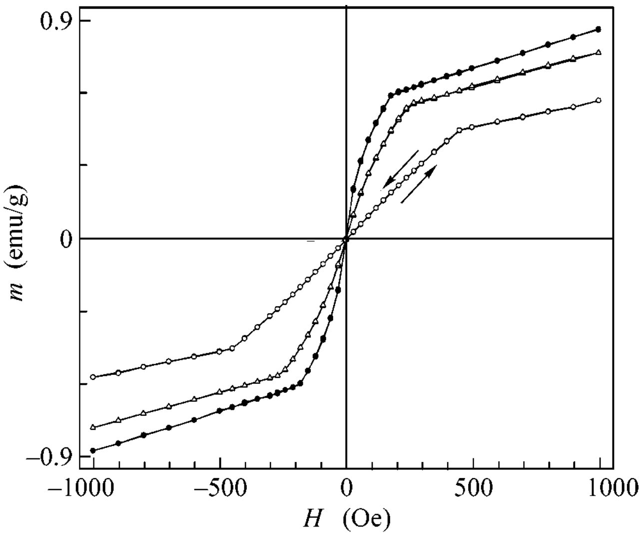

Fig. 2. Magnetization as a function of magnetic field applied in the [110] direction at temperatures of 10, 11, and 14 K.

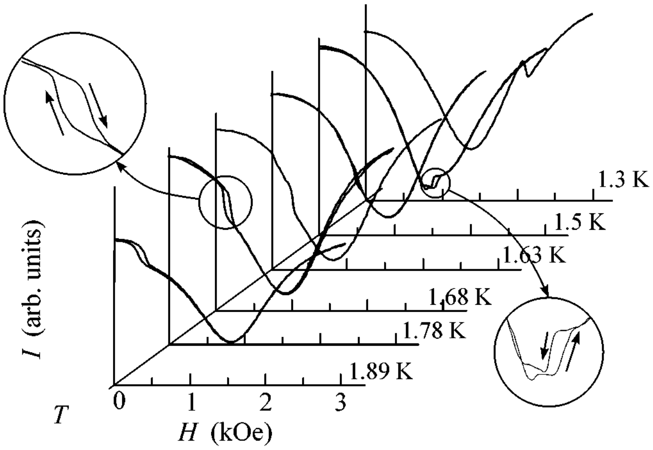

Fig. 3. Resonance absorption spectra of CuB_2O_4 in a low-temperature range at a frequency of 5.15 GHz.

features appeared in the absorption spectrum (Fig. 3). At T = 1.89 K, a step appears at the left wing of resonance line in the field H_{c_1}, and it demonstrates a hysteresis upon the back and forth field scans. With lowering the temperature of the sample, this step shifts to higher fields, while another step of the same form appears at low fields at H_{c_2}. As the temperature further decreases, both steps undergo upfield shift with a decrease in the distance between them, and they virtually merge into a single continuous transition at T = 1.3 K.

4. DISCUSSION

An analysis of the experimental data presented in Fig. 1 and a comparison with the results of Lorentzian curve fitting allow one to assert that the absorption spectrum in the temperature range 10–20 K is not a sum of two lines but consists of two single lines that change each other in the field $H = H_{c_\perp}$. Therefore, $H_{c_\perp}$ is the phase-transition field, and the fragments of resonance lines observed at $H < H_{c_\perp}$ and $H > H_{c_\perp}$ belong to the different states. The conclusion about the phase transition is confirmed by the analysis of the magnetization field dependences measured in the [100] and [110] directions. The magnetostatic properties will be discussed in detail elsewhere; in this work, we will focus only on the results concerning the phase diagram. As was pointed out above, for all temperature in the range 10–20 K, the field $H_{c_\perp}$ separates the curve for the magnetization field dependence into two parts, with its initial portion emanating from the origin of coordinates. Consequently, this field corresponds to the phase transition from the state with zero spontaneous moment to a weakly ferromagnetic state. The temperature dependence of the critical field was reproduced from the data of resonance and static experiments (boundary between states *2* and *3* in the phase diagram in Fig. 4). With an increase in temperature, $H_{c_\perp}$ first increases and then decreases as T_N is approached. The resonance and static data for the [110] direction well correlate with each other. The $H_{c_\perp}(T)$ curve for the [100] direction goes slightly lower, but the anisotropy in the tetragonal plane is small. The absence of magnetic hysteresis in the transition region for both static and resonance data and the continuous (without jumps in absorption) transformation of one resonance line to the other are evidence of the second-order phase transition.

To elucidate the nature of low-field state, it is necessary to analyze the field-and-frequency dependence of magnetic resonance in both phases at $T \simeq 13.1$ K (Fig. 5). The curve for the high-field phase was constructed using our data and the data of [2], which are well described by the corresponding dependence for a weak ferromagnet:

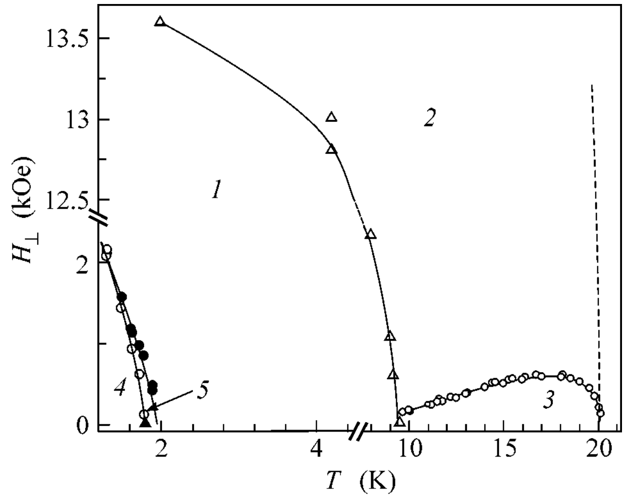

Fig. 4. Phase diagram of CuB_2O_4 in a magnetic field perpendicular to the tetragonal axis; circles are for the results of resonance and magnetostatic measurements, △ are the data from [2, 4], ▲ are the neutron diffraction results [7], solid lines are drawn for clarity, and the dotted line is the line of transition to the paramagnetic state.

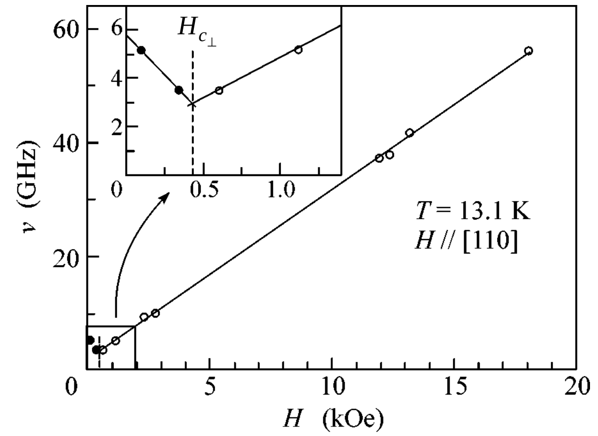

Fig. 5. Field-and-frequency dependences for the high- and low-field states at $T \simeq 13.1$ K; solid line is drawn according to Eq. (1).

$$\nu^2 = \gamma^2 H(H + H_D) + \Delta^2, \qquad (1)$$

where H_D and Δ are the Dzyaloshinski field and the energy gap, respectively. The solid line in Fig. 5 corresponds to dependence (1) with the parameters H_D = (1.6 ± 0.4) kOe and Δ = (1.5 ± 1) GHz. The relatively low accuracy of determining these parameters is caused by the poor temperature stability in these measurements. At $H < H_{c_\perp}$, this dependence can be analyzed only qualitatively, because measurements were made only for two frequencies. Nevertheless, one can firmly state that the resonance frequency in this phase decreases with an increasing magnetic field. An analogous dependence can occur in the presence of tetragonal anisotropy in an easy plane or if C_4 is the easy magnetic axis. In the first case, the critical field $H_{c_\perp}$ can be interpreted as a turnover field in the basal plane and, in the second, as a field at which the smooth reorientation of antiferromagnetic vector from the $\mathbf{L} \parallel C_4$ to the $\mathbf{L} \perp C_4$ position is completed, as a result of which a weak ferromagnetic moment increases linearly with field. However, these variants are inconsistent with the magnetostatic measurements of this work and of [4], and, hence, the observed phase transition is caused by different reasons. It is conceivable that the observed magnetic resonance spectrum is caused by the existence of a modulated (commensurate or incommensurate) state in the low-field phase. With an increase in magnetic field, the translation period λ of this structure increases [10] and the dispersion curve $\omega(k)$ splits into the phason and acoustic branches at the boundary $q_0 = \pi/\lambda$ of the "first Brillouin zone" [11]. Inasmuch as a uniform microwave field can excite magnons with $k = 2q_0$ corresponding to zero-quasimomentum transfer in a spin structure with long-wave modulation, the magnetic resonance spectrum should display a branch which has zero-field gap $\omega(2q_0)/(2\pi)$ and smoothly changes to the corresponding branch of the commensurate phase in the vicinity of critical field $H_{c_\perp}$.

This assumption also enables one to explain why the spontaneous magnetic moment is zero and the field-dependence curve for magnetization has a kink at $H = H_{c_\perp}$. The helicoidal spatial distribution averages out the local weak ferromagnetic moments at $H = 0$. Due to the distortion of ideal helicoid by a magnetic field, the moments are reoriented along the field and, simultaneously, the antiferromagnetic susceptibility increases, and both processes are completed upon the transition to the commensurate weakly ferromagnetic state. The absence of zero-field splitting (typical of modulated structures) of magnetic peaks in the neutron diffraction patterns at $T > 10$ K [3] may be caused by the fact that the modulation has a long period and its wave vector is, likely, much smaller than the experimental resolution.

Let us now consider the resonance properties in the low-temperature region. The absorption step observed in the resonance spectrum at 1.89 K correlates with the jump in intensity of magnetic satellites in the neutron diffraction pattern at $T \simeq 1.8$ K [7] and allows one to assume that it is caused by the magnetic phase transition. At even lower temperatures, one more jump in absorption appears in the resonance lines at $H_{c_1} < H_{c_2}$. The presence of hysteresis for both jumps upon the back and forth field scans allows the conclusion to be drawn that the phase transitions at H_{c_1} and H_{c_2} are first-order transitions. The temperature dependences for both critical fields are shown in the phase diagram (Fig. 4). As compared to the published phase diagrams [2, 4, 5] containing incommensurate 1 and weakly ferromagnetic 2 states, new states 3, 4, and 5 are added in the diagram in Fig. 4. State 3 appears in the temperature range 10–20 K and, most probably, is a long-period modulated state [12]. When analyzing states 4 and 5, one should take into account that, according to the neutron diffraction data [7, 13], the magnetic structure remains modulated down to a temperature of 200 mK. One can assume that the transition observed in the neutron diffraction experiment at $T \simeq 1.8$ K is a lock-in transition from the incommensurate phase to the modulated state with a wave vector commensurate with the lattice translation period [14]. In the phase diagram, this corresponds to the transition from state 1 to state 5. In this case, the wave vector in the commensurate state can take values $k_{mn} = (2\pi/c)(m/n)$, where c is the lattice constant and m and n are mutually prime numbers. Since the resonance lines for states 4 and 5 differ only slightly, one can assume that they (as well as the new states observed upon further decrease in temperature in the range $T \simeq 1$ K [13]) differ only in the numbers m and n. This signifies that the cascade of transitions at $T < 2$ K represents a so-called "devil staircase" of transitions between the commensurate states.

5. CONCLUSIONS

The magnetic phase diagram of copper metaborate CuB_2O_4 in a magnetic field lying in the tetragonal crystal plane has been studied in detail in this work. Analysis of the obtained static and resonance data enables one to assume that the magnetic state in the temperature range 10–20 K forms a helicoidal long-period structure. It has been established that, in magnetic fields below 1 kOe, this state transforms into a weakly ferromagnetic state that is not spontaneous at all temperatures below T_N, but is induced by a magnetic field. At low temperatures $T < 2$ K, two sequential close-spaced first-order phase transitions have been observed. These are presumably transitions to the modulated states with different magnetic wave vectors that are commensurate with the lattice translation period.

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