Synthesis and magnetic properties of $Cu_3B_2O_6$ single crystals

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The temperature dependence of the magnetic susceptibility of $Cu_3B_2O_6$ single crystals grown by spontaneous crystallization from a melt consisting of a mixture of CuO and B_2O_3 and the behavior of their magnetization are investigated in magnetic fields up to 55 kOe. A broad susceptibility maximum is observed near 39 K, and a sharp drop in susceptibility is observed at $T<10$ K. The paramagnetic Néel temperatures for all orientations of the magnetic field in the crystal investigated are negative, attesting to the predominantly antiferromagnetic character of the exchange interactions. The effective magnetic moment of the Cu^{2+} ion is anisotropic and lies in the range from $1.054\mu_B$ to $1.545\mu_B$. The magnetization depends linearly on magnetic field at $T>10$ K, whereas at temperatures below 10 K a discontinuity is observed at fields of the order of 40 kOe. At room temperature, electron magnetic resonance characterized by an almost isotropic g factor ($g=2.165$) is detected at 36.22 GHz. The exchange interactions in $Cu_3B_2O_6$ are analyzed on the basis of the Goodenough–Kanamori rules. The possibility of the establishment of a singlet magnetic state in the crystal is analyzed. [S1063-7834(99)02404-1]

The main reason for the great interest of researchers in oxide compounds of copper is the high-temperature superconductivity observed in some of them. In particular, it is important to understand the mechanisms which shape the magnetic state, especially the singlet ground state, in such compounds.[1–3] For example, in crystalline $CuGeO_3$ the mechanism which shapes the singlet state is probably associated with a spin-lattice interaction and competition between exchange interactions, while in ladder systems it is a purely quantum fluctuation effect.

This paper is the first to present the results of an experimental investigation of the magnetic susceptibility, magnetization, and electron magnetic resonance of $Cu_3B_2O_6$ single crystals.

1. SYNTHESIS AND CRYSTAL STRUCTURE OF $Cu_3B_2O_6$

Single crystals of $Cu_3B_2O_6$ were grown by spontaneous crystallization from a solution in a melt on the basis of the results of the physicochemical investigation of the ternary Li_2O–CuO–B_2O_3 system in Ref. 4. The mixture of the starting materials CuO and B_2O_3 containing 70 mol % CuO and 30 mol % B_2O_3 was placed in a platinum crucible and heated to 1200°C. Crystallization took place as the temperature was lowered at the rate of 2 deg/h to 900°C. The crystals were extracted by mechanical means and had the form of oblique prisms of dark green color with dimensions up to $3\times3\times3$ mm^3.

X-ray fluorescence analysis confirmed the chemical formula $Cu_3B_2O_6$ and the absence of foreign phases. X-ray diffraction analysis of the crystals obtained showed that they belong to the triclinic system with space group $P1$ and the unit cell parameters $a=3.344$ Å, $b=19.757$ Å, $c=19.587$ Å, $\alpha=88.91°$, $\beta=70.05°$, and $\gamma=69.93°$, in agreement with the data in Ref. 5. It can be seen from the crystal structure shown in Fig. 1 that the magnetic Cu^{2+} ions are coordinated in octahedral, square, and pyramidal environments of oxygen ions. The mean Cu–O distances within a layer in the bc plane and between layers are equal to 1.95 and 2.90 Å, respectively, clearly suggesting a quasi-two-dimensional magnetic state. An analysis of the exchange interactions on the basis of the Goodenough–Kanamori rules[6] shows that there are two types of exchange interactions in the system: 135° antiferromagnetic Cu–O–Cu interactions with an energy of the order of 100 K and 90° ferromagnetic interactions with an energy of the order of 10 K. The dominant type of exchange is antiferromagnetic according to the results of the magnetic-susceptibility measurements. The following fragments of Cu^{2+} ions can be identified in the structure of $Cu_3B_2O_6$: chains of four copper ions in an octahedral oxygen environment; chains of four copper ions, two of which have an octahedral environment while the other two have a square environment; pairs of copper ions, one of which has an octahedral environment while the other has a pyramidal environment; groups of copper ions in an octahedral environment; and, finally, copper ions in a square environment. All of these groups of copper ions are coupled predominantly by

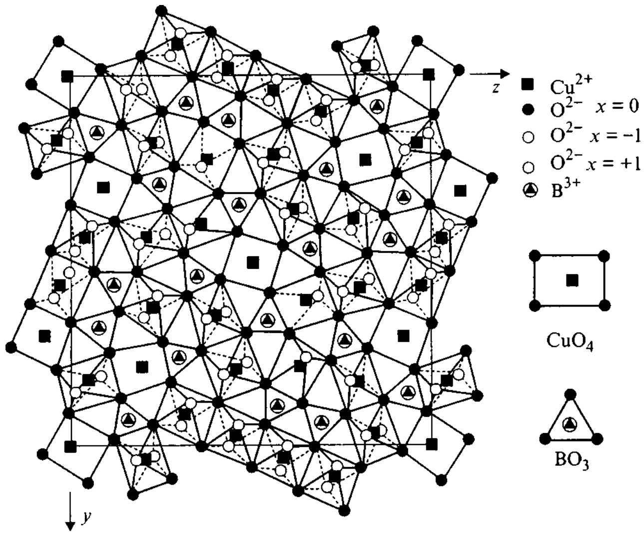

FIG. 1. Crystal structure of $Cu_3B_2O_6$.

negative exchange interactions to form two-dimensional layers in the bc plane.

2. MAGNETIC PROPERTIES

The static magnetic properties of the crystals were investigated on SQUID and vibrating sample magnetometers in fields up to 50 kOe at temperatures between 2 and 300 K. The results of the SQUID measurements of the temperature dependence of the magnetic susceptibility determined in an arbitrary direction in the bc plane of the crystal in 6- and 20-kOe fields are shown in Fig. 2. The presence of a broad susceptibility maximum at a temperature of about 39 K, the sharp drop in susceptibility at temperatures below 10 K, and the identity of the results of the measurements in 6- and 20-kOe fields are noteworthy. The high-temperature behavior of the susceptibility is described by the Curie–Weiss law with the parameters $\Theta=-422$ K and $\mu_{\text{eff}}=1/06\mu_B$. Deviations from the Curie–Weiss law are observed at temperatures below 150 K. The results of the magnetic-susceptibility measurements performed on the vibrating sample magnetometer for two mutually perpendicular directions of the external magnetic field in the bc plane and in a direction perpendicular to that plane are shown in Fig. 3. The measurements were performed in a 14.14-kOe magnetic field. The asymptotic

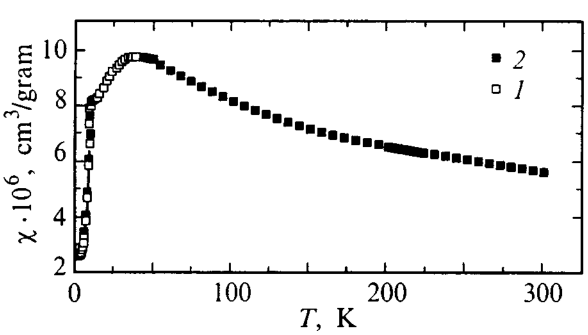

FIG. 2. Temperature dependence of the magnetic susceptibility of a $Cu_3B_2O_6$ single crystal measured in a SQUID magnetometer for $H\|(bc)$: *1* — $H=6$ kOe, *2* — $H=20$ kOe, solid curve — Eq. (1)

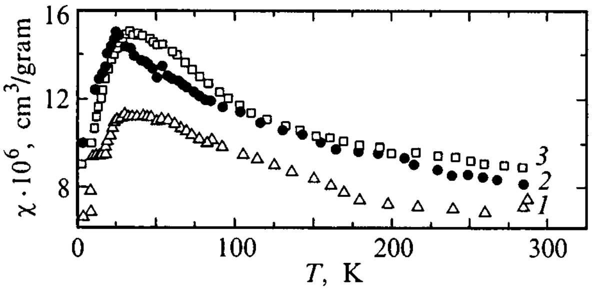

FIG. 3. Temperature dependence of the magnetic susceptibility of a $Cu_3B_2O_6$ single crystal measured in a vibrating sample magnetometer: *1*, *2* — magnetic field in two mutually perpendicular directions in the bc plane, *3* — $H\perp(bc)$.

Néel temperatures and effective magnetic moments corresponding to these three orientations of the magnetic field have the following values: $\Theta_1=-335$, $\Theta_2=-400$, $\Theta_3=-691$, $\mu_{\text{ef1}}=1.054$, $\mu_{\text{ef2}}=1.247$, and $\mu_{\text{ef3}}=1.545\mu_B$. As can be seen from Fig. 3, a low-temperature drop in the magnetic susceptibility is observed for all three orientations of the magnetic field. We note that fairly strong anisotropy of the susceptibility is observed in the (bc) plane of the crystal. Just this anisotropy may be responsible for the difference between the results of the magnetic-susceptibility measurements in Figs. 2 and 3. The sharp drop in the susceptibility χ (Fig. 2) observed when the temperature was lowered below 10 K is described by the dependence

$$\chi=A+B\exp(-\Delta/T) \tag{1}$$

with the parameters $A=2.66\times10^{-6}\text{cm}^3/\text{g}$, $B=1.4\times10^{-4}\text{cm}^3/\text{g}$, and $\Delta=33.3$ K. Such a dependence is characteristic of systems having a singlet ground state separated from the excited states by an energy gap Δ. Estimates show that the residual low-temperature susceptibility A can be attributed to the Van Vleck paramagnetic contribution. The singlet ground magnetic state can be either a result of a collective phase transition (such as a spin-Peierls state) or a state of cluster formations.[7,8]

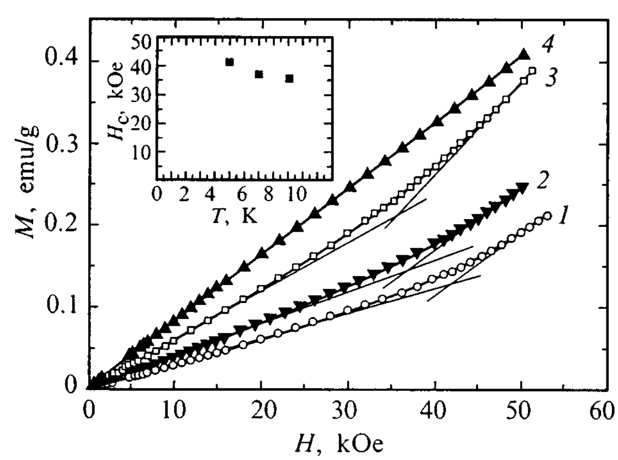

FIG. 4. Field dependences of the magnetization of a $Cu_3B_2O_6$ single crystal (orientation of the field as in Fig. 2) at various temperatures: *1*, *2*, *3*, *4*: — 5, 7, 9, and 12 K respectively. Inset — temperature dependence of the field corresponding to the discontinuity (see text).

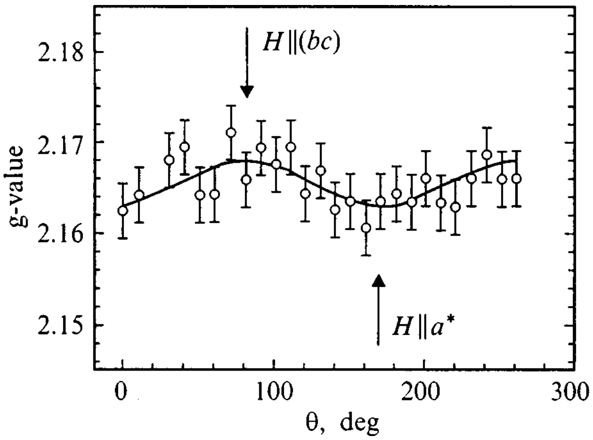

FIG. 5. Angular dependence of the g factor of the magnetic resonance line at room temperature for $Cu_3B_2O_6$, $\nu = 36.22$ GHz; a^* — magnetic field perpendicular to the bc plane of the crystal.

The field dependences of the magnetization of $Cu_3B_2O_6$ for the same orientation of the magnetic field as in Fig. 2 and various temperatures are shown in Fig. 4. At temperatures below 12 K the field dependence of the magnetization becomes nonlinear. The characteristic field corresponding to the magnetization discontinuity depends on temperature. This dependence is shown in the inset in Fig. 4; the field corresponding to the discontinuity was obtained by extrapolating the linear segments on the magnetization curves to the point where they intersect.

We also performed preliminary measurements of the electron magnetic resonance of a $Cu_3B_2O_6$ single crystal at a frequency of 36.22 GHz and a temperature of 300 K. Measurements performed for different orientations of the magnetic field showed that there is resonant absorption line, whose position depends weakly on orientation and is determined by an almost isotropic g factor roughly equal to 2.165 (Fig. 5).

Thus, the principal results of our investigation are the discovery of a low-temperature drop in magnetic susceptibility, a nonlinear dependence of the magnetization at temperatures below 10 K, and electron magnetic resonance. The exchange interactions of the Cu^{+2} ions in crystalline $Cu_3B_2O_6$ are predominantly antiferromagnetic. The crystal structure suggests an in-plane magnetic state with a probable ground-state singlet separated from the excited states by an energy gap. Additional experimental studies are needed to establish a more detailed picture of the magnetic state of the crystal investigated.

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