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Interrelation of Anisotropy of Magnetic Properties and Magnetodielectric Effect in a $Cu_3B_2O_6$ Single Crystal

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Abstract—The effect of an external magnetic field on permittivity has been studied in a $Cu_3B_2O_6$ single crystal with a layered structure in the direction perpendicular to layers (*bc*-planes). It has been found that the appreciable magnetodielectric effect in the temperature range below the Néel temperature (≈10 K) takes place only at one magnetic field orientation **H** and one crystallographic direction, i.e., **H** ∥ **b**. Such "selectivity" of the magnetodielectric effect correlates with the anisotropic behavior of magnetic properties of the crystal.

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1. INTRODUCTION

Interest in magnetic dielectrics exhibiting the interrelation of magnetic and charge subsystems appeared in the early 21st century [1], has not weakened, and has only strengthened at the present time; see, e.g., [2–10]. This is caused by possible practical applications of some observed effects such as the magnetoelectric ME_H (the dependence of the electric polarization on the external magnetic field) [2–5], the inverse to it ME_E (the effect of the electric field on the magnetization) [6, 7] effects, and the magnetodielectric (the dependence of the permittivity ε on the external magnetic field) [8–10] effect. Fundamental interest is caused by the variety of possible mechanisms of the interrelation of magnetic and charge subsystems.

Therefore, it is urgent to search for and study new materials exhibiting such interrelation. In this paper, we present the results of the study of the magnetodielectric (MD) effect in the $Cu_3B_2O_6$ single crystal. This compound in the form of single crystals was first obtained in [11]. Studies of physical properties of this crystal showed [11–14] that it exhibits antiferromagnetic (AF) ordering, and the contribution of the singlet state probably takes place in the low-temperature region [11, 12]. The crystal has a layered structure; of particular interest is anisotropy of magnetic properties in the *bc* plane with magnetic moments of copper atoms. In this study, the correlation of anisotropy of magnetic properties with the anisotropic behavior of the MD effect was detected.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

$Cu_3B_2O_6$ single crystals were grown by the spontaneous solution–melt crystallization method; the synthesis conditions and characterization are described in [11]. According to an X-ray diffraction analysis, $Cu_3B_2O_6$ belongs to the triclinic crystal system; the space group is $P1$, the unit cell parameters are a = 3.344 Å, b = 19.757 Å, c = 19.587 Å, α = 88.91°, β = 70.05°, γ = 69.93°. The crystal has a layered structure in which layers correspond to *bc*-planes spaced by 2.90 Å, and the average Cu–O distance in the *bc* plane is 1.95 Å [11], see Fig. 1. The crystal studied was shaped as an oblique prism with pentagons in the base and base side sizes of ~1–3 mm. An analysis of X-ray diffraction reflections from the crystal bases and side surfaces confirmed the correspondence of bases to *bc*-planes, and allowed the determination of the crystallographic direction corresponding to one of the base sides.

To measure the permittivity, conductive plates were applied to crystal bases; the distance between bases was ~0.6 mm. The capacitance of such a capacitor was measured at a frequency of 10 kHz at a voltage of 1 V. The data on the temperature dependence $\varepsilon(T)$ are given in the units of the capacitor capacitance (in view of close thickness and linear sizes of plates).

The magnetic field **H** (a superconducting solenoid was used) was applied perpendicular to the *bc* plane (**H** ⊥ *bc*) and in the *bc* plane. In the latter case, measurements were performed at various orientations of **H** and one of the base sides, which appeared close to the crystallographic *b* direction. The data on the depen-

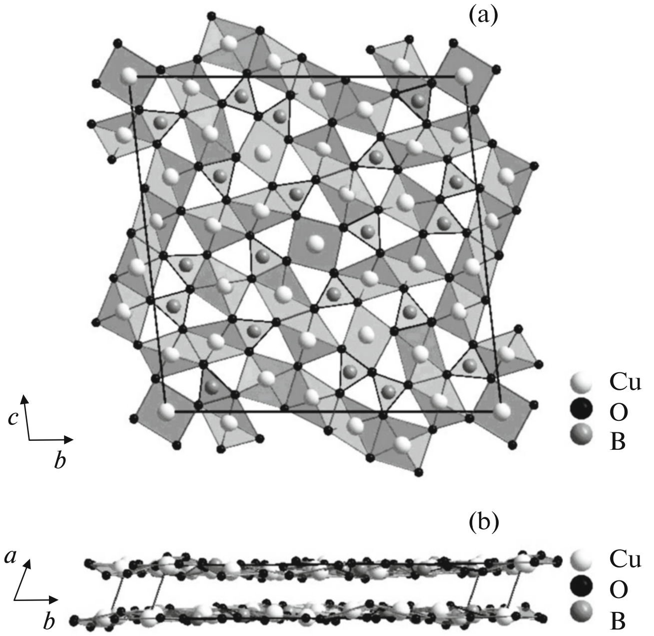

Fig. 1. $Cu_3B_2O_6$ crystal structure: (a, b) structure projections onto *bc*- and *ab*-planes, respectively.

dence $\varepsilon(H)$ are given in the relative units of

$$\Delta\varepsilon_H(H) = \frac{\varepsilon(H) - \varepsilon(H = 0)}{\varepsilon(H = 0)} \times 100\%.$$

Magnetic measurements were performed on a vibrating magnetometer [15]. The same sample orientations with respect to the external field as for magnetodielectric measurements were used.

3. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependences of the magnetic moment $M(T)$ (the M axis is the left scale) of the sample in the field $H = 5$ kOe at various **H** orientations. The broad maximum in the vicinity of ~35 K, observed previously as well [11–14], is characteristic of two-dimensional spin systems [11]. The rather sharp decrease in the magnetic moment for orientations $\mathbf{H} \parallel \mathbf{bc}$ at temperatures below 10 K is associated with establishing the AF order. The absence of such a “jump” for the $\mathbf{H} \perp \mathbf{bc}$ direction suggests that magnetic moments of copper atoms are in the *bc*-plane.

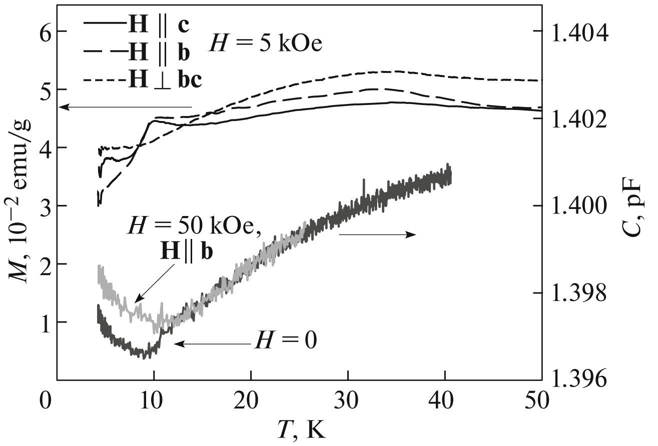

Fig. 2. Temperature dependences of the magnetic moment $M(T)$ (the M axis is the left scale) in the field $H = 5$ kOe in various orientations of the magnetic field **H** and $Cu_3B_2O_6$ crystallographic axes and of the permittivity (in the units of the capacitance, the C axis is the right scale) in zero field and $H = 50$ kOe, $\mathbf{H} \parallel \mathbf{b}$.

In the vicinity of the Néel temperatures (≈10 K) in zero external field, an anomaly is also observed in the temperature dependence of the permittivity, see Fig. 2. The MD effect was measured for various angles between the external field and the b axis of the crystal with a step of $\pi/8$ and in the $\mathbf{H} \perp \mathbf{bc}$ direction (in the latter case, the external field is perpendicular to the plane of “capacitor” plates). It turned out that the appreciable MD effect is observed only in the $\mathbf{H} \parallel \mathbf{b}$ direction. Figure 2 also illustrates the temperature behavior of the permittivity (capacitance) in the magnetic field $H = 50$ kOe parallel to the crystallographic b axis. We can see that this effect occurs in the temperature region below the Néel temperature.

The dependence of $\Delta\varepsilon_H(H)$ at $T = 4.2$ K in the $\mathbf{H} \parallel \mathbf{b}$ direction is shown in Fig. 3. The value of $\Delta\varepsilon_H$ at $H = 60$ kOe is about 0.1%; although this value is small, it is of interest to relate the detected “selectivity” of the MD effect to the anisotropy of magnetic properties.

Figure 3 shows also the field dependences of the magnetic moment $M(H)$ at various external field directions with respect to crystallographic directions of the studied $Cu_3B_2O_6$ crystal. For the $\mathbf{H} \perp \mathbf{bc}$ orientation, the dependence $M(H)$ is linear, since magnetic moments of copper atoms are in the *bc*-plane. How-

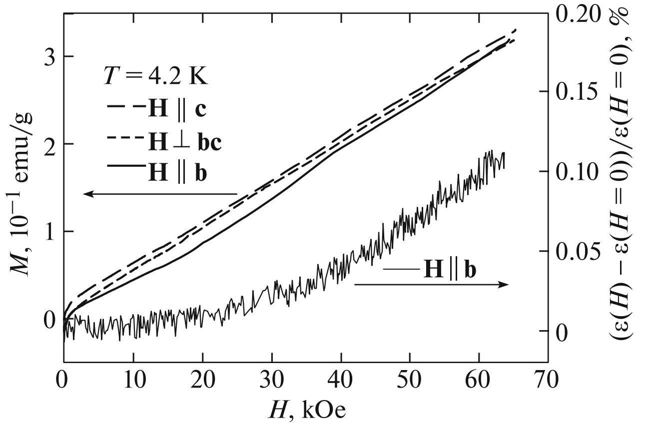

Fig. 3. Field dependences of the magnetic moment $M(H)$ at $T = 4.2$ K (the M axis is the left scale) in various orientations of the magnetic field **H** and $Cu_3B_2O_6$ crystallographic axes and of the relative permittivity $\Delta\varepsilon_H(H)$ (the $\Delta\varepsilon_H(H)$ axis is the right scale).

ever, for the *bc*-plane, the magnetic susceptibility anisotropy is observed [11–13]. In [13], it was shown that spin-flop transitions in $Cu_3B_2O_6$ are observed at **H** ‖ **bc** in fields ~100 kOe. Therewith, there is the direction in which the dependence *M*(*H*) is linear until the spin-flop transition field, and there is the direction in which the dependence *M*(*H*) has positive curvature ("knee") in a wide field range [11], and the spin-flop transition is observed in the vicinity of *H* ~ 100 kOe [13]. Our data (Fig. 3) are in good agreement with the described behavior. The dependence *M*(*H*) for the **H** ‖ **c** direction is linear in fields to 65 kOe; for **H** ‖ **b**, the characteristic feature of the dependence *M*(*H*) is its positive curvature. And exactly for the **H** ‖ **b** direction, the MD effect is observed. According to [13], the dependence *M*(*H*) portion with positive curvature reflects "sequential spin-flop transitions" between various magnetic structures. Therefore, it is quite possible that such transitions appear in be observed MD effect.

The microscopic mechanism of the detected MD effect requires independent consideration. We note that the dependence $\Delta\varepsilon_H(H)$ (Fig. 3) is close to the quadratic function $\Delta\varepsilon_H(H) \sim H^2$. It is known that the quadratic dependence of the linear sample size ΔL on the magnetic field is characteristic of magnetostrictive effects. However, it is of low probability that the observed change in the capacitance is caused by a decrease in the sample size, hence, the capacitor plate spacings L^1 since the obtained value $\Delta L/L \sim 10^{-3}$ is sufficiently large for magnetostrictive effects and it is difficult to explain such a strong magnetostriction anisotropy (only along the *b* axis). Nevertheless, the quadratic shape of the dependence can point to the indirect relation of the MD effect to magnetostriction.

The set of the experimental data obtained in this study unambiguously shows that the appreciable MD effect is observed is observed in the case of the relative **H** direction in the sample crystallographic orientation in which the external field induces spin-flop-type magnetic transitions. Here the interrelation of such magnetic transitions and the MD effect can be discussed with certainty.

4. CONCLUSIONS

In this study, the MD effect in a $Cu_3B_2O_6$ single crystal exhibiting AF ordering was studied for the first time. The MD effect exists in the temperature region below the Néel temperature (≈10 K) at which the dependence ε(*T*) exhibits an anomaly in the absence of external field. When applying an electric field between crystal *bc*-planes, the MD effect "selectivity" with respect to the external field direction and sample crystallographic axes was detected. In the **H** ‖ **b** direction at *T* = 4.2 K, $\Delta\varepsilon_H(H)$ is ≈0.1% in the magnetic field *H* = 60 kOe, whereas the MD effect for other directions is weaker by at least an order of magnitude. The existence of the MD effect correlates with the anisotropic behavior of magnetic properties: for the direction **H** ‖ **b**, the dependence *M*(*H*) exhibits the characteristic positive curvature, which can be caused by sequential transitions between various spin-flop-type magnetic structures.

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[1] To a first approximation, at $C \sim 1/L$ and $\Delta L/L \sim H^2$, it can be shown that $\Delta\varepsilon_H(H) \sim H^2$.