Magnetic, structural, and dielectric properties of CuB$_2$O$_4$

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We have studied the magnetic, structural, and dielectric properties of a single crystal of CuB$_2$O$_4$. We show that both reported magnetic transitions are observable in the magnetization, irrespective of the measured direction of the crystal. This is in agreement with recent neutron data. More importantly, our study demonstrates the absence of dielectric anomalies at the various magnetic transitions despite the reported magnetoelectric symmetry. This demonstrates that the polarization remains zero at any temperature. Consequently, we interpret our data as the evidence for a very weak or the absence of linear magnetoelectric coupling in this material.

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I. INTRODUCTION

Recently, the copper metaborate CuB$_2$O$_4$ received much attention due to a rich magnetic phase diagram. Commensurate and incommensurate magnetic structures as well as frustration have been observed in this compound. Moreover, it has been reported that the Dzyaloshinskii–Moriya interactions lead to the formation of a magnetic soliton lattice in this material. Modulated magnetic systems of relativistic origin are rare, and thus their study is of considerable interest. In addition, recent high field electron spin resonance (ESR) experiment suggested the possible presence of ferroelectricity below the incommensurate magnetic transition temperature. This suggestion is supported by the reported polar magnetic phase proposed from a study of CuB$_2$O$_4$ by second harmonic generation. The crystallographic and magnetic structure of CuB$_2$O$_4$ was already investigated by x-ray and neutron diffractions and by specific-heat, magnetic susceptibility, magnetization, and muon-spin-rotation experiments.

CuB$_2$O$_4$ crystallizes in a piezoelectric tetragonal $I4_2d$ (n°122) space group (point symmetry 42m). The unit cell contains 12 f.u. and is shown in Fig. 1. The Cu$^{2+}$ ions occupy two unequal positions. The ions at the 4b Wyckoff site are at the center of a square unit formed by four oxygen ions, while the ions at the 8d Wyckoff site are located near the center of a distorted oxygen octahedron. Below, $T_{N2}$ = 21 K, a commensurate canted antiferromagnetic ordering appears, which is followed by an incommensurate and purely antiferromagnetic ordering below $T_{N1}$ = 9 K.

In this paper, we investigate the magnetic, structural, and dielectric properties of a CuB$_2$O$_4$ single crystal. We measured the various properties along the main crystallographic axes ($a$, $b$, and $c$ axes of the tetragonal symmetry). We show that, in contrary to the suggestion of Fujita et al. and the reported polar magnetoelectric magnetic group by Pisarev et al., CuB$_2$O$_4$ does not exhibit any dielectric anomaly at the different Néel temperatures. These results suggest that the linear magnetoelectric coupling remains small to very low temperatures or even absent. This seems incompatible with the magnetic point group $\overline{2}$ reported in Ref. 3.

II. EXPERIMENTAL DETAILS

CuB$_2$O$_4$ single crystals in weight up to 70 g have been grown by the Kirooulos method from the melt of B$_2$O$_3$-CuO-Li$_2$O-MoO$_3$. The crystals have bright blue-violet color and a maximum size of $2 \times 1 \times 1$ cm$^3$. We oriented and cut several single crystals from the grown boule along the different crystallographic directions. CuB$_2$O$_4$ single crystal magnetization measurements were carried out by a superconducting quantum interference device magnetometer in the temperature range of 2–300 K and external magnetic fields between 0.1 and 7 T. The structural characterization was made using a Huber imaging plate camera G670 using the wavelength of Mo K$_\alpha$. The low-temperature setup was a Helix Technology Corporation Cryodyne refrigeration driven by a Helix Technology Corporation 8200 compressor. Each scan lasted 30 min with a temperature step of 0.5 K. The lowest stable temperature that we could reach was 9 K, which is just the temperature at which the incommensurate magnetic transition appears in CuB$_2$O$_4$. Thus, we could investigate the structural features only around the Néel temperature $T_{N2}$ = 21 K.

![FIG. 1. Crystal structure of the copper metaborate CuB$_2$O$_4$. Copper atoms are represented in black (Cu$_1$ in Wyckoff position 4b and Cu$_2$ in Wyckoff position 8d), oxygen atoms are in grey, and boron atoms are in white.](image)
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FIG. 2. (Color online) Magnetic susceptibility measured on a single crystal of CuB$_2$O$_4$ along the three crystallographic directions: (100) (with squares), (010) (with circles), and (001) (with triangles) (zero field cooled mode $H=1000$ Oe). The inset shows the inverse susceptibility measured along the three different directions. The line represents a Curie-Weiss temperature dependence fit defined by $\frac{1}{\chi} = \frac{T - \theta}{C}$.

Complex impedance measurements were performed using an Agilent AG4284A LCR meter. The measurement of the dielectric constant was carried out by using a homemade sample holder with four coaxial cables. The sample holder fits inside a commercial Quantum Design physical property measurement system apparatus, allowing measurements of the dielectric constant at different temperatures. An ac voltage of 1 V was applied to the sample. The dielectric constant was extracted from the value of capacitance using the sample dimensions. No correction for edge effects was applied.

III. RESULTS AND DISCUSSION

A. Magnetic properties

The measured temperature dependencies of the magnetic susceptibility along the different crystallographic axes in an external magnetic field of 1 kOe are shown in Fig. 2. We notice that this external magnetic field is larger than the coercive field of $\approx 300$ Oe reported by Petrakovskii et al.$^2$ Two anomalies are clearly noticeable in the magnetic susceptibilities: one about 21 K and the other one at 9 K. The transition at $T_{N2}=21$ K is noticeable by a small anomaly. This change in the magnetic susceptibility has been shown to arise from a canted antiferromagnetic ordering.$^3\,$4 These results are compatible with the reported magnetic point group $2\,^3$. On further cooling, we observe a sharp increase of the magnetic susceptibility along the $a$ and $b$ axes. This is in agreement with the reported magnetic structure from neutron diffraction.$^5$ Surprisingly, Petrakovskii et al.$^2$ observed a paramagnetic behavior for the magnetic susceptibility measured perpendicular to the $c$ axis.$^2$ Below $T_{N1}$, the spins are mostly confined in the ($a,b$) plane. Thus, one expects that the magnetic susceptibility is larger along the $c$ axis and is identical along the $a$ and $b$ axes. This is in agreement with our experimental observations (see Fig. 2).

We present in the inset of Fig. 2 the inverse magnetic susceptibilities along the different directions. As in the magnetic susceptibility, the anisotropy between the measurements made along the $c$ axis and the ($a,b$) plane is clearly noticeable. This anisotropy is reflected in the high-temperature regime. In the inset of Fig. 2, the different straight lines represent the fit using a Curie-Weiss temperature dependence defined by $\frac{1}{\chi} = \frac{T - \theta}{C}$.

We report in Table I the various Curie-Weiss temperatures and associated effective magnetic moments ($\mu_{\text{eff}}$) extracted from the fits of inverse susceptibilities (see the inset of Fig. 2). The anisotropy in CuB$_2$O$_4$ is further evidenced in the effective magnetic moments for the different directions. The effective moment along the $c$ axis is 1.85$\mu_B$/Cu, which can be compared to the theoretical value of 1.77$\mu_B$/Cu. Petrakovskii et al.$^2$ reported experimentally $\mu_{\text{eff}}=1.77\mu_B$ and $\theta =-9.5$ K. Our value is higher than the free ion picture. Covalency effects may be responsible for such discrepancy.

![TABLE I. Curie-Weiss temperature and associated effective magnetic moment ($\mu_{\text{eff}}$) determined for the different crystallographic directions.](image)

<table>
<thead>
<tr>
<th>Direction</th>
<th>$H$ parallel to $a$</th>
<th>$H$ parallel to $b$</th>
<th>$H$ parallel to $c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$ (in K)</td>
<td>$-2.7$</td>
<td>$-2.2$</td>
<td>$-1.9$</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$ (in $\mu_B$)</td>
<td>0.59</td>
<td>0.59</td>
<td>1.85</td>
</tr>
</tbody>
</table>

FIG. 3. Cell parameters of CuB$_2$O$_4$ determined from Rietveld refinements of a crushed single crystal.
CuB$_2$O$_4$ does not present strong structural distortions around $\delta$ of the order of the expected anomaly. We can only say that low $\delta$ to detect such small anomalies since our error bar is ferroelectric phase. Consequently, our resolution does not allow us to detect such small anomalies since our error bar is $\approx 1 \times 10^{-3}$.

### B. Structural investigation

We present in Fig. 3 the results of the refinements carried out using the Huber imaging plate camera. In the resolution of our measurement ($10^{-4}$ Å), we do not observe structural anomalies in the cell parameters which could be the signature of a structural phase transition.

However, Fujita et al. suggested the possibility of magnetically induced structural phase transition resulting in a ferroelectric phase. The structural properties of magnetically induced ferroelectrics have been studied in detail. Most of the recent magnetically induced ferroelectrics present magnetoelectric anomalies of the order of $10^{-4}$ at the onset of the ferroelectric phase. Consequently, our resolution does not allow us to detect such small anomalies since our error bar is of the order of the expected anomaly. We can only say that CuB$_2$O$_4$ does not present strong structural distortions around $T_{N1}$. Our dielectric measurement will demonstrate that actually no anomalies are noticeable both at $T_{N1}$ and $T_{N2}$, excluding the possibility for a magnetically induced phase transition (see Sec. III C).

### C. Dielectric measurement

We have performed dielectric measurement on several single crystals oriented along the different crystallographic directions. We present in Fig. 4 the variation of the dielectric constant $\varepsilon$ along the $a$, $b$, and $c$ crystallographic axes as a function of temperature. The first feature to be noticed is the identical temperature behavior of $\Delta\varepsilon_a$ and $\Delta\varepsilon_b$. This suggests that the dielectric constants along the $a$ and $b$ axes are identical. The temperature dependence of these two components of the dielectric tensor is different from the one along the $c$ axis. These observations suggest that the dielectric tensor is characterized by $\varepsilon_a=\varepsilon_b \neq \varepsilon_c$ and thus has the following expression:

\[\varepsilon_{ij} = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}.\]

The tensor described above is compatible with trigonal, hexagonal, and tetragonal symmetries. Hexagonal and trigonal symmetries are incompatible with the space group $I\bar{4}2d$. Consequently, we interpret this result as the signature of the invariance of the tetragonal symmetry of the system through the two magnetic transitions ($T_{N1}=9$ K and $T_{N2}=21$ K).

We do not notice any anomalies in $\varepsilon(T)$ along any of the measured crystallographic directions. Especially, we do not observe any divergence of the dielectric constant. Consequently, we conclude that there is no ferroelectric transition below $T_{N1}$ contrary to the suggestion of Fujita et al. This observation confirms the magnetic structure reported by Boehm et al. who reported a transverse spin-density wave below $T_{N1}$. Indeed, in light of the recent work of Mostovoy on spiral magnets, the ferroelectricity can arise only if the rotation axis of the spins is perpendicular to the propagation wave vector $k$. In CuB$_2$O$_4$, we have $k=(0,0,k_z)$ with the rotation axis of the spins being the $c$ axis. Consequently, we should not observe any ferroelectricity induced by symmetry breaking. This is in agreement with the neutron data, our structural investigation and dielectric measurements.

As stated earlier, we do not observe anomalies in the dielectric constant irrespective of the direction along which the measurement has been made. This is a surprising feature. The magnetic point group reported is 2 and thus allows a linear magnetoelectric effect. BaMnF$_4$ presents the same magnetic symmetry, and its dielectric properties have been studied in detail. It has been shown that BaMnF$_4$ exhibits an anomaly in the dielectric constant at the onset of the weak ferromagnetic order.

It is well known from literature that below $T_N$, a renormalization of the dielectric constant occurs due to magnetoelectric effects. This has been observed for various magnetoelectric systems. In BaMnF$_4$, an anomaly of the dielectric constant is observed for the direction parallel to the twofold axis along the $a$ axis remaining below $T_N$. Scott and co-workers have demonstrated that the renormalization $\Delta\varepsilon(T)$ in BaMnF$_4$ was the result of the coupling terms $p_mJ_x$ and $p^2mJ_y,12,13$ Due to these terms, only along the $a$ axis, an anomaly in the dielectric constant could be observed at $T_N$. In CuB$_2$O$_4$, the magnetic symmetry is identical to the one of BaMnF$_4$ with the difference that the twofold axis is along the $c$ axis. Consequently, we would expect a renormalization of $\varepsilon$ along this direction in our material. It was suggested that the spin canting in BaMnF$_4$ was partially induced by the magnetoelectric effect. Often, Dzyaloshinskii-Moriya-type interactions contribute to the magnetoelectric effect. The direction of the Dzyaloshinskii-Moriya vector is determined by the bond symmetry and its scalar by the strength of the spin-orbit coupling. In BaMnF$_4$, spin-orbit coupling is likely to not contribute to the magnetoelectric effect since $L=0$ for Mn$^{2+}$ ions (3$d^5$). On the contrary, Dzyaloshinskii-Moriya-type interactions are present and non-negligible in CuB$_2$O$_4$. Consequently, we think that if any magnetoelec-
tric effect exists, this should be observable in CuB$_2$O$_4$. We stress that an anomaly in the temperature dependence of $e$ is expected in magnetoelectric materials, since it is one of the signatures of the coupling between the dielectric and magnetic properties. Our results suggest that if there is a magnetoelectric coupling, this remains very small down to low temperatures or even absent. In the latter case, possible explanation would be that the magnetic symmetry determination is incorrect and that a redetermination of its magnetic symmetry is necessary.

IV. CONCLUSION

We have investigated the magnetic, dielectric, and structural properties of a single crystal of CuB$_2$O$_4$. We show that our magnetic susceptibility results are in agreement with recent neutron data with noticeable magnetic transitions along the three main crystallographic axes. We demonstrate, using dielectric measurements, the absence of magnetically induced structural phase transitions, contradicting the suggestion based on ESR data. More importantly, despite the reported magnetoelectric symmetry, we demonstrate the absence of a linear coupling between the dielectric and magnetic properties in CuB$_2$O$_4$ down to low temperatures. This work suggests two possibilities. The first one is that the reported magnetic symmetry of CuB$_2$O$_4$ is incorrect and it does not belong to the family of magnetoelectric materials. The second possibility would be the report for the unexpected absence of macroscopic coupling between dielectric and magnetic properties in a magnetoelectric system. In both cases, this work suggests further investigation of the magnetic and dielectric properties of this compound.

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