Magnetic, structural, and dielectric properties of CuB_2O_4

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We have studied the magnetic, structural, and dielectric properties of a single crystal of CuB_2O_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_2O_4 received much attention due to a rich magnetic phase diagram.[1–6] 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[7] lead to the formation of a magnetic soliton lattice in this material.[1] 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.[4] This suggestion is supported by the reported polar magnetic phase proposed from a study of CuB_2O_4 by second harmonic generation.[3] The crystallographic and magnetic structure of CuB_2O_4 was already investigated by x-ray and neutron diffractions and by specific-heat, magnetic-susceptibility, magnetization, and muon-spin-rotation experiments.[2,5,6]

CuB_2O_4 crystallizes in a piezoelectric tetragonal $I\bar{4}2d$ (n°122) space group (point symmetry $\bar{4}2m$). 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 4*b* Wyckoff site are at the center of a square unit formed by four oxygen ions, while the ions at the 8*d* 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.[2,5]

In this paper, we investigate the magnetic, structural, and dielectric properties of a CuB_2O_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.*[4] and the reported polar magnetoelectric magnetic group by Pisarev *et al.*,[3] CuB_2O_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 $\underline{2}$ reported in Ref. 3.

II. EXPERIMENTAL DETAILS

CuB_2O_4 single crystals in weight up to 70 g have been grown by the Kiropulos method from the melt of B_2O_3-CuO-Li_2O-MoO_3.[8] The crystals have bright blue-violet color and a maximum size of $2\times1\times1$ cm^3. We oriented and cut several single crystals from the grown boule along the different crystallographic directions. CuB_2O_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 $K\alpha_1$. The low-temperature setup was a Helix Technology Corporation Cryodyne refrigerator 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_2O_4. Thus, we could investigate the structural features only around the Néel temperature $T_{N2}=21$ K.

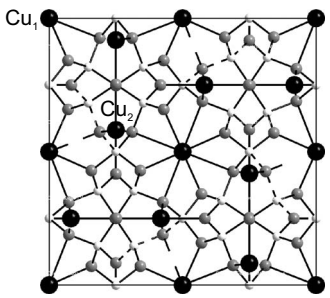

FIG. 1. Crystal structure of the copper metaborate CuB_2O_4. Copper atoms are represented in black (Cu_1 in Wyckoff position 4*b* and Cu_2 in Wyckoff position 8*d*), oxygen atoms are in grey, and boron atoms are in white.

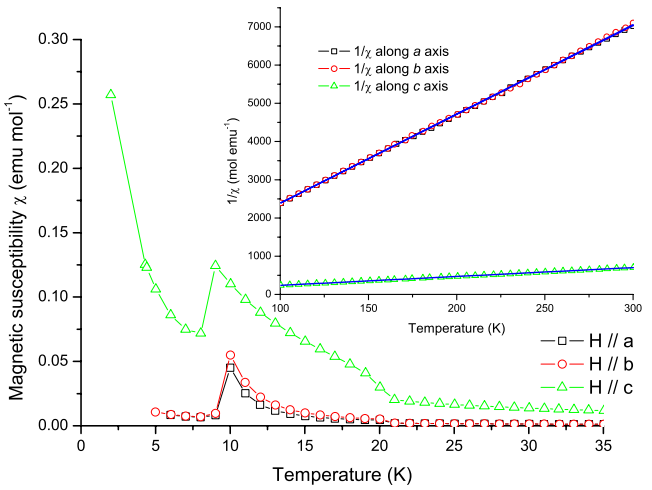

FIG. 2. (Color online) Magnetic susceptibility measured on a single crystal of CuB_2O_4 along the three crystallographic directions: (100) (with squares), (010) (with circles), and (001) (with triangles) (zero field cooled mode $H=1000$ Oe). The inset shows the inverse susceptibility measured along the 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 ≃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.[2,5] These results are compatible with the reported magnetic point group $\underline{2}$.[3] On further cooling, we observe a sharp increase of the magnetic susceptibilities at $T_{N1}=9$ K. This transition has been shown to arise from an incommensurate spin structure.[5] As reported earlier, we observe a strong anisotropy between measurement along the c tetragonal axis and the basal (a,b) plane.[2] This anisotropy is about 1 order of magnitude. However, contrary to Petrakovskii *et al.*,[2] the different anomalies revealing the various magnetic phase transitions are also noticeable along the a and b axes. This is in agreement with the reported magnetic structure from neutron diffraction.[5] Surprisingly, Petrakovskii *et al.* 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).

TABLE I. Curie-Weiss temperature and associated effective magnetic moment (μ_{eff}) determined for the different crystallographic directions.

Direction	H parallel to a	H parallel to b	H parallel to c
θ (in K)	−2.7	−2.2	−1.9
μ_{eff} (in μ_B)	0.59	0.59	1.85

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 (μ_{eff}) extracted from the fits of inverse susceptibilities (see the inset of Fig. 2). The anisotropy in CuB_2O_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 $\mu_{eff}=1.77\mu_B$ and $\theta=-9.5$ K. Our value is higher than the free ion picture. Covalency effects may be responsible for such discrepancy.

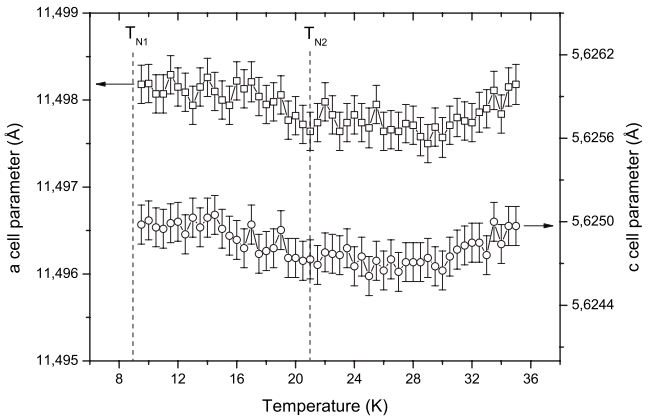

FIG. 3. Cell parameters of CuB_2O_4 determined from Rietvelt refinements of a crushed single crystal.

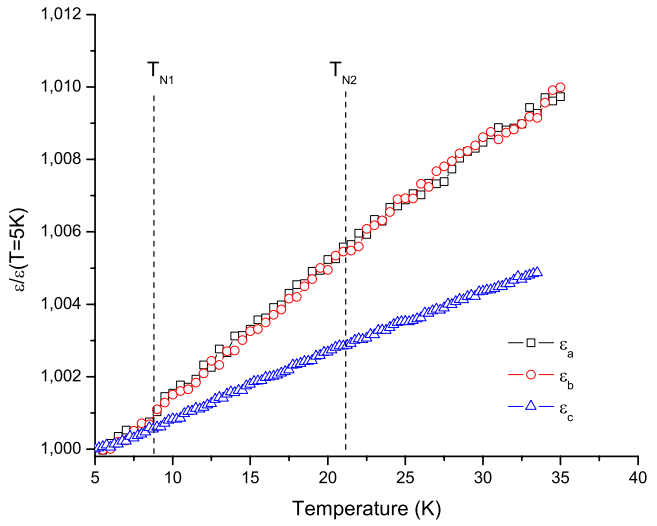

FIG. 4. (Color online) Dielectric constant (ε) of CuB_2O_4 measured versus temperature normalized at its value at 5 K. With squares, we show ε measured along the a axis, with circles along the b axis, and with triangles along the c axis ($f=1$ kHz). The associated loss [$\tan(\delta)$] was $\leqslant 1\times 10^{-3}$.

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.[4] The structural properties of magnetically induced ferroelectrics have been studied in detail.[10] Most of the recent magnetically induced ferroelectrics present magnetoelastic 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_2O_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 ε 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.[11] 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.*[4] This observation confirms the magnetic structure reported by Boehm *et al.*[5] who reported a transverse spin-density wave below T_{N1}. Indeed, in light of the recent work of Mostovoy[9] on spiral magnets, the ferroelectricity can arise only if the rotation axis of the spins is perpendicular to the propagation wave vector $\mathbf{k}$. In CuB_2O_4, we have $\mathbf{k}=(0,0,k_z)$ with the rotation axis of the spins being the c axis.[5] 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 $\underline{2}$ and thus allows a linear magnetoelectric effect.[11] $BaMnF_4$ presents the same magnetic symmetry, and its dielectric properties have been studied in detail.[12,13] 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.[12–16] 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 $p_x m_z l_y$ and $p_x^2 m_z l_y$.[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_2O_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 ε along this direction in our material. It was suggested that the spin canting in $BaMnF_4$ was partially induced by the magnetoelectric effect.[12] Often, Dzyaloshinskii-Moriya-type interactions contribute to the magnetoelectric effect.[17,18] The direction of the Dzyaloshinskii-Moriya vector is determined by the bond symmetry and its scalar by the strength of the spin-orbit coupling.[7] In $BaMnF_4$, spin-orbit coupling is likely to not contribute to the magnetoelectric effect since $L=0$ for Mn^{2+} ions ($3d^5$). On the contrary, Dzyaloshinskii-Moriya-type interactions are present and non-negligible in CuB_2O_4.[1,18] Consequently, we think that if any magnetoelec-

tric effect exists, this should be observable in CuB_2O_4. We stress that an anomaly in the temperature dependence of ε 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_2O_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_2O_4 down to low temperatures. This work suggests two possibilities. The first one is that the reported magnetic symmetry of CuB_2O_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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