Tuning Ferroelectric Polarization Reversal by Electric and Magnetic Fields in $CuCrO_2$

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The effects of electric and magnetic fields on magnetic and electric properties have been investigated for a triangular lattice antiferromagnet $CuCrO_2$ showing magnetically induced ferroelectric order. We demonstrate that ferroelectric polarization reversal can be finely tuned by using both magnetic and electric fields in the triangular lattice antiferromagnet. The observed magnetoelectric tunability can be attributed to small in-plane spin anisotropy and a resultant high degree of freedom for the direction of ferroelectric polarization, which is characteristic of a multiferroic triangular lattice antiferromagnet with out-of-plane 120° spin structure.

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Manipulation of an electron's spin (charge) using electric fields (magnetic fields), such as electric-current control of the ferromagnetic domain and magnetic control of ferroelectricity, has received great interests in recent years, because it is crucial for the realization of future devices [1–3]. The magnetoelectric (ME) multiferroic system [4] where magnetic and ferroelectric orders coexist and often couple with each other is one of the promising candidates to achieve such ME control. Among several classes of multiferrioics [5,6], control of magnetic behavior using electric fields has been realized in composite multiferroic thin films and heterostructures [7]. In contrast, magnetic-field control of ferroelectric property has been achieved in magnetically induced ferroelectrics (e.g., $TbMnO_3$, $Ni_3V_2O_8$, $CoCr_2O_4$, and $Ca_3Co_{2-x}Mn_xO_6$) where ferroelectricity is induced by magnetic structures breaking inversion symmetry [8–11]. However, we rarely encounter systems which respond to both magnetic and electric fields sensitively though such responsibility provides a wide variety of ME control. In this Letter, we report on both electric and magnetic-field effects on the ferroelectric polarization reversal in one of the most typical frustrated spin systems, a triangular lattice antiferromagnet $CuCrO_2$. We found that coercive electric and magnetic fields for ferroelectric polarization reversal can be finely tuned by both external magnetic and electric fields in $CuCrO_2$. We will discuss a possible relationship between the observed ME tunability and unique spin-chiral ferroelectric properties in the frustrated spin system.

$CuCrO_2$ with the delafossite structure (space group $R\bar{3}m$) belongs to triangular lattice antiferromagnets in which triangular lattice planes (TLPs) formed by Cr^{3+} ($S = 3/2$) are stacking along the [001] axis rhombohedrally [12,13]. (The hexagonal basis is used in this Letter.) Former powder neutron diffraction studies [13] proposed that the ground state of $CuCrO_2$ exhibits a spin-chiral out-of-plane 120° spin structure in which three spins on a triangle form a 120° angle to each other and the spiral plane is normal to the TLP. Thus, the spin system can be described as a highly isotropic one (namely, Heisenberg type) with a weak easy axis type of single ion anisotropy. Recently, Seki and coworkers found ferroelectricity driven by the magnetic order in polycrystalline samples [14]. More lately, detailed measurements for single-crystal samples revealed that $CuCrO_2$ undergoes two successive magnetic transitions at $T_{N1} \sim 23.6$ K and $T_{N2} \sim 24.2$ K, and that the ferroelectric polarization along the TLP appears below T_{N1} [15]. These results show the onset of the out-of-plane 120° spin-chiral structure breaking inversion symmetry below T_{N1}.

Single crystals of $CuCrO_2$ were grown by the flux method as reported previously [15]. Magnetization (M) curves were measured by a commercial SQUID (superconducting quantum interference device) magnetometer (Quantum Design, MPMS). For measurements of dielectric constant (ε) and electric polarization (P), the crystals were cut into thin plates with the widest plane parallel to the (110) and $(1\bar{1}0)$ plane, and then silver electrodes were vacuum deposited onto the opposite faces of the crystals. We measured ε at 100 kHz by an LCR meter. The ME current was measured after applying a poling electric field (E) of $\sim$0.54 MV/m from 35 to 5 K, without removal of the poling E to keep ferroelectric domains. The magnetic field (H) dependence of P was obtained by integration of the ME current as a function of time. P-E curves in various H were obtained by measurements of electric-current which is induced by sweeping E at a constant rate of 7.1×10^{-3} MV/m sec.

Figure 1(a) shows the H dependence of M along the [110] axis ($M_{[110]}$) and $[1\bar{1}0]$ axis ($M_{[1\bar{1}0]}$) at 5 K. Both $M_{[110]}$ and $M_{[1\bar{1}0]}$ increase almost linearly with increasing H, and no significant difference is seen between them. As displayed in Fig. 1(b), however, the derivative of M with respect to H along the [110] axis $[(dM/dH)_{[110]}]$ and $[1\bar{1}0]$

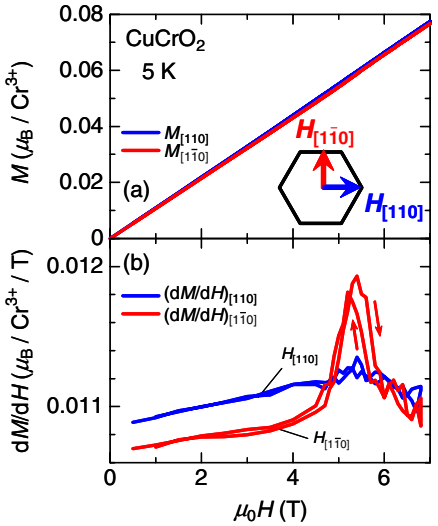

FIG. 1 (color online). (a) H dependence of $M_{[110]}$ (blue line) and $M_{[1\bar{1}0]}$ (red line) at 5 K. (b) H dependence of $(dM/dH)_{[110]}$ (blue line) and $(dM/dH)_{[1\bar{1}0]}$ (red line).

axis $[(dM/dH)_{[1\bar{1}0]}]$ shows a clear anisotropic behavior. Whereas no clear anomaly is observed in $(dM/dH)_{[110]}$, a distinct peak structure with hysteresis is observed in $(dM/dH)_{[1\bar{1}0]}$ at $H_{\mathrm{flop}} \sim 5.3$ T. These results suggest that a magnetic transition occurs at $H_{[1\bar{1}0]}$ of H_{flop}. We also measured $M_{[110]}$, $M_{[1\bar{1}0]}$, and $M_{[001]}$ up to 53 T by using a 60 T pulsed magnet. However, no distinct feature was observed (not shown), except for the above-mentioned anomaly in $M_{[1\bar{1}0]}$ at H_{flop}.

Figures 2(a)–2(d) show the $H_{[110]}$ (blue line) and $H_{[1\bar{1}0]}$ (red line) profiles of $\varepsilon_{[110]}$, $P_{[110]}$, $\varepsilon_{[1\bar{1}0]}$, and $P_{[1\bar{1}0]}$ at 5 K, respectively. When $H_{[1\bar{1}0]}$ is applied, a distinct peak in $\varepsilon_{[110]}$ [Fig. 2(a)] and a small hump in $\varepsilon_{[1\bar{1}0]}$ [Fig. 2(c)] are detected around H_{flop} where remarkable hystereses are observed between the increasing- and decreasing-H run. Accompanied by these dielectric anomalies, sudden changes of P were also observed. With increasing $H_{[1\bar{1}0]}$, $P_{[110]}$ ($P_{[1\bar{1}0]}$) first gradually decreases (increases), and then drastically decreases down to almost zero (increases slightly but discontinuously) around H_{flop}. [See red curves in Figs. 2(b) and 2(d).] Thus, the application of $H_{[1\bar{1}0]}$ of H_{flop} causes a first-order ME transition triggered by a magnetic transition. For $H_{[110]}$, on the other hand, no abrupt change of $\varepsilon_{[110]}$ and $\varepsilon_{[1\bar{1}0]}$ is found around H_{flop} though $P_{[110]}$ ($P_{[1\bar{1}0]}$) gradually increase (decrease) with increasing $H_{[110]}$. It should be also noted that no detectable change has been observed for $H_{[110]}$ and $H_{[1\bar{1}0]}$ dependence of $P_{[001]}$.

To discuss the nature of the magnetic (and ME) transition, we revisit the magnetic ground state of $CuCrO_2$. From the previous experimental results and symmetry analysis [13–16], there are two possible spin configurations for the out-of-plane 120° spin structure in terms of the direction of the spiral plane [spiral plane ∥ (110) or $(1\bar{1}0)$ plane]. In either case, there are three spiral plane domains which are at 120° angle with one another owing to the hexagonal symmetry in a TLP. In addition, each spiral plane domain consists of two different spin-chiral ferroelectric domains with P normal to the spiral plane. Thus, $CuCrO_2$ can contain six different spin-chiral ferroelectric domains. The respective domains form a $60 \times n$ degrees angle with one another ($n = 1$, 2, and 3), which implies the presence of 60°, 120°, and 180° domain walls ($60 \times n$° domain wall structures).

Assuming the out-of-plane 120° spin structure with spiral plane parallel to (110) [(110) spiral plane structure] as the magnetic ground state [17], we can explain the appearance of the first-order phase transition by applying $H_{[1\bar{1}0]}$. In Fig. 3, we illustrate a possible evolution of magnetic structures by applying $H_{[1\bar{1}0]}$ and $H_{[110]}$. In the (110) spiral plane structure, three types of domains labeled A, B, and C are stabilized by applying E along [110]. In these three domains, magnetic symmetry allows sponta-

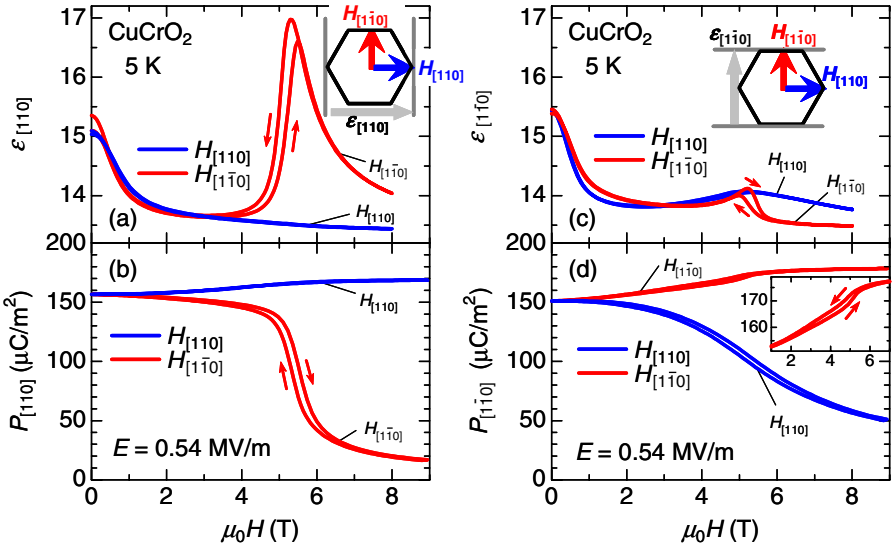

FIG. 2 (color online). $\varepsilon_{[110]}$ (a), $P_{[110]}$ (b), $\varepsilon_{[1\bar{1}0]}$ (c), and $P_{[1\bar{1}0]}$ (d) as a function of $H_{[110]}$ (blue line) and $H_{[1\bar{1}0]}$ (red line). Insets of (a) and (c): schematic experimental configurations. Inset of (d): enlargement of $P_{[1\bar{1}0]}$ as a function of $H_{[1\bar{1}0]}$. Measurements of $P_{[110]}$ and $P_{[1\bar{1}0]}$ were done with the poling E of ~0.54 MV/m.

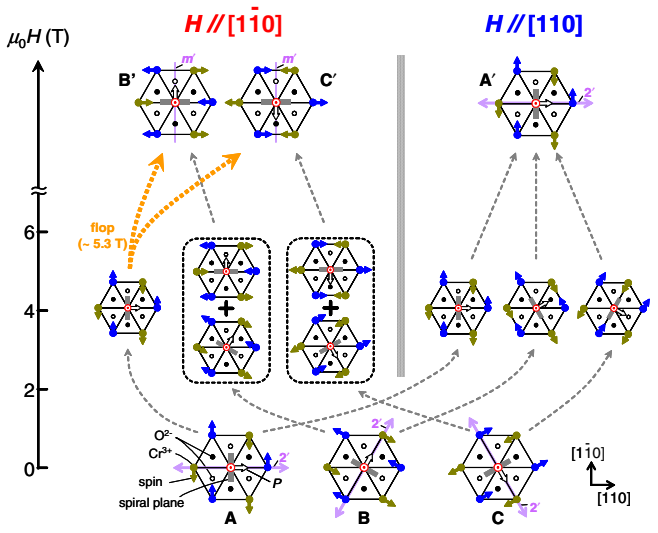

FIG. 3 (color online). Schematic illustrations of a proposed evolution of magnetic structures by applying $H_{[1\bar{1}0]}$ (left) and $H_{[110]}$ (right) in the case of the $P_{[110]}$ measurement. Each hexagon denotes the (001) projection of a spin configuration on a TLP of Cr^{3+} ions (red, blue, and green circles). Red, blue, and green colored arrows denote spin components of 120° spin structures. Two TLP's of O^{2-} ions (open and closed black circles) located adjacently above or below the Cr^{3+} TLP are also shown. Gray rectangles denote the spiral planes. Purple arrows and lines represent the $2'$ axes and the projections of the m' planes, respectively. Open arrows describe the expected direction of P. In this figure, the initial magnetic structure is assumed to be the (110) spiral plane. By applying $E_{[110]}$, the (110) spiral plane has three kinds of domains labeled A, B, and C. The bottom, middle, and top panels denote possible domains in zero, intermediate (~4 T), and sufficiently high (≫9 T) magnetic fields, respectively.

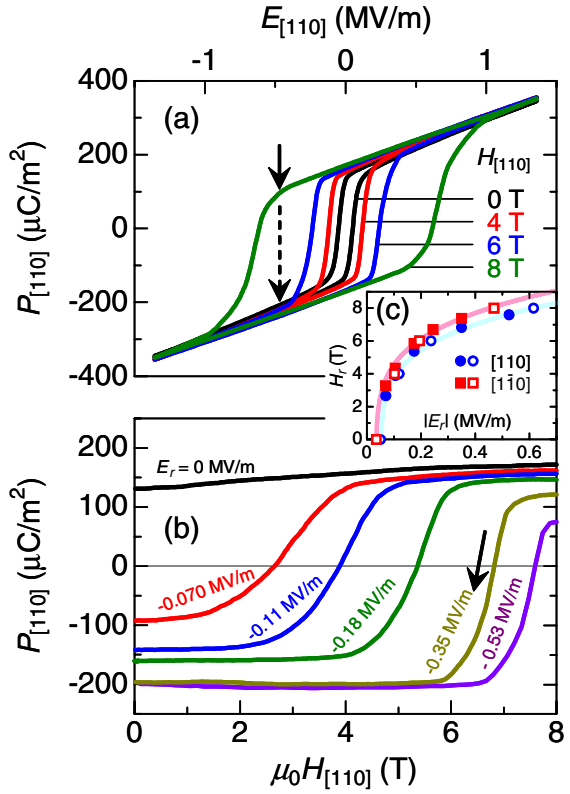

FIG. 4 (color online). (a) P-E hysteresis loops in various H at 5 K for $P\|H\|$ [110]. A sweep rate of E is 7.1×10^{-3} MV/m sec. (b) H profiles of P in various E at 5 K. All data were obtained in the H-decreasing run, and more detailed experimental procedures are shown in the text. (c) H_r vs E_r diagram for the P reversal. Closed (open) blue circles correspond to the P reversal by $E(H)$ sweeping in various $H(E)$ for $P\|H\|$ [110]. Closed (open) red squares are used for $P\|H\|$ [1$\bar{1}$0]. E_r increases approximately as a function of H_r^4 both for the [110] and [1$\bar{1}$0] axes.

neous polarization only along the $2'$ axis (purple arrows in Fig. 3) which is normal to the spiral plane. Attributed to the small but finite anisotropy of the magnetic susceptibility parallel and perpendicular to the spiral plane [15], the domains whose spiral plane is normal to H become more stable than the others at high H for both $H_{[1\bar{1}0]}$ and $H_{[110]}$ configurations. Thus, by applying sufficiently high H (≫9 T), all three domains (A, B, and C) may transform into domains B′ and C′ with the (1$\bar{1}$0) spiral plane for $H_{[1\bar{1}0]}$ and into domain A′ for $H_{[110]}$, as illustrated in the top panels of Fig. 3. In the $H_{[110]}$ configuration, the gradual changes of $P_{[110]}$ and $P_{[1\bar{1}0]}$ without the first-order ME transition are observed, which can be explained by gradual domain rearrangement from the three domain states (A, B, C) toward a single domain state (A′). By contrast, in the $H_{[1\bar{1}0]}$ configuration, domain A has the spiral plane parallel to applied H. In such a parallel configuration, it is possible that the application of $H_{[1\bar{1}0]}$ causes a sudden spiral plane flop from the domain state A to B′ or C′ (orange thick dotted arrows in Fig. 3). In the domains B′ and C′, m' depicted as purple lines in Fig. 3 can be only a symmetry operation, meaning that spontaneous polarization is allowed only within the m' plane. Thus, the sudden spiral plane flop can well explain the first-order ME transition at $H_{[1\bar{1}0]} = H_{\text{flop}}$ where both ε and P show discontinuous changes. We emphasize that the application of high H along both [1$\bar{1}$0] and [110] can reduce the number of domains and stabilize the 180° domain wall structure.

Figure 4(a) shows P-E hysteresis loops in various H for $P\|H\|$ [110]. The measurements have been done at 5 K far below the ferroelectric transition temperature T_C ($=T_{N1}$). In the absence of H, the electric coercive field for the P reversal (E_r) is 5.1×10^{-2} MV/m. This value is much smaller than that of typical magnetically induced ferroelectrics (e.g., 4.0 MV/m at 15.8 K for $DyMnO_3$ with $T_C = 20$ K [18]). Therefore, $CuCrO_2$ is a rare magnetically induced ferroelectric compound in terms of the smallness of E_r. The origin of such a small E_r will be discussed later. Another distinct feature in Fig. 4(a) is that E_r increases drastically with increasing H and reaches 0.62 MV/m at 8 T, which is more than 10 times larger

than that at 0 T. Note that similar results were observed for the case of $P\|H\|[1\bar{1}0]$, but no effect on the P-E hysteresis loop was observed by applying $H_{[001]}$ (not shown). Thus, we can finely tune E_r by applying H parallel to the TLP in $CuCrO_2$.

Here, let us discuss the origin of the H dependence of E_r. Since the P reversal process includes the rotation of polarization via the hard axis, anisotropy of P should be an important factor of E_r, and it is natural to consider that a higher degree of freedom for the direction of P makes E_r smaller. Considering the close relationship between P and spin system as mentioned above, small P anisotropy is expected at 0 T in the triangular lattice antiferromagnet possessing small in-plane spin anisotropy. Combined with the existence of the 60° ferroelectric domain wall structure (bottom drawings in Fig. 3), this allows a high degree of freedom for the direction of P. This scenario can well describe such a small E_r at 0 T. The enhancement of E_r by applying H within the TLP can be also explained by this scenario. As illustrated in Fig. 3, the application of H within the TLP induces the domain rearrangement, reduces the number of domains, and stabilizes the 180° domain wall structure. In other words, the degree of the anisotropy within the TLP is enhanced by applying H, resulting in the enhancement of E_r. Recently, Ishibashi and coworkers performed computer simulations to investigate polarization reversal of conventional ferroelectrics in the presence of 90° domain walls [19]. Their results suggested that E_r is strongly enhanced as the anisotropy of P increases, supporting our scenario.

Such a good tunability of E_r by H gives us a chance of the P reversal by H. Let us position the system at a point denoted by an arrow with a solid line in Fig. 4(a) and then sweep off H. Because E_r becomes weak with lowering H, P should be reversed at a critical H (magnetic coercive field for the P reversal H_r), as schematically depicted by an arrow with a dotted line in Fig. 4(a). Then, we measured the E dependence of H_r for the P reversal. The procedure was as follows: First, the sample was cooled from 35 to 5 K without any field. Second, H of 8 T parallel to E was applied, and then positive E of $+1.4$ MV/m was applied. Finally, E was swept to negative value, and then the H dependence of P was obtained from ME current measurements in the H-decreasing run. The results for $P\|H\|$ [110] are shown in Fig. 4(b). By applying appropriate negative E, the P reversal is clearly induced by H. The change of P from 8 to 0 T in Fig. 4(b) corresponds to the change from an upper curve of 8 to that of 0 T in Fig. 4(a). As seen in Fig. 4(b), H_r increases monotonically by increasing the absolute value of negative E applied. Similar results were also observed for $P\|H\|[1\bar{1}0]$ (not shown). These results clearly show that H_r for the P reversal can be tuned by changing E. The relation of the electric and magnetic coercive fields (E_r and H_r) for both $P\|H\|$ [110] and $P\|H\|[1\bar{1}0]$ is summarized in Fig. 4(c). Thus, the P reversal process can be tuned by the combination of electric and magnetic fields in $CuCrO_2$.

In summary, we investigated magnetic, ferroelectric, and magnetoelectric properties of a triangular lattice antiferromagnet, $CuCrO_2$, with the out-of-plane 120° spin structure. We found a first-order magnetoelectric phase transition induced by magnetic fields applied along the $[1\bar{1}0]$ direction. $CuCrO_2$ shows an extremely low electric coercive field for the ferroelectric polarization reversal in the absence of magnetic fields among magnetically induced ferroelectrics. The electric coercive field is highly sensitive to the external magnetic field, which enables the polarization reversal by magnetic fields. Importantly, we demonstrate that the coercive magnetic field for the polarization reversal can be tuned by the electric field, meaning that the electric field can change the magnetic property in $CuCrO_2$. Although not a few magnetically induced ferroelectrics have been reported in recent years, we have never seen such tunability of electric property by both magnetic and electric fields. Thus, the present compound, $CuCrO_2$, is a rare example in terms of its magnetoelectric tunablity by using "both magnetic and electric fields."

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