Thermally or Magnetically Induced Polarization Reversal in the Multiferroic $CoCr_2O_4$

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We report the unexpected evolution, with thermal and magnetic-field (H) variations, of the interrelation between the polarization $\mathbf{P}$, magnetization $\mathbf{M}$, and spiral wave vector $\mathbf{Q}$ in $CoCr_2O_4$, which has a ferrimagnetic conical-spiral magnetic order. For example, $\mathbf{P}$ suddenly jumps and changes its sign at the magnetic lock-in transition (T_L) with thermal variation, or with isothermal variation of H (without changing its direction) at T_L, which surprisingly occurs without change in spiral handedness (i.e., the sign of $\mathbf{Q}$). The presence of multiple spiral sublattices may be behind this unusual behavior.

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Magnetically driven ferroelectrics where magnetic order with broken inversion symmetry accompanies the occurrence of ferroelectric polarization have been of great recent interest [1,2], the first example of which was reported by Newnham *et al.* [3]. Recently, the high tunability of dielectric properties by applied magnetic fields (H), such as reversibly flipping ferroelectric polarization or a drastic change of dielectric constant, has been found in such materials [4]. Spinel $CoCr_2O_4$, which shows a complex conical-spiral ferrimagnetic spin order [5], is unique among such materials [3,6–10] in that it has a spontaneous magnetization $\mathbf{M}$; the spiral component induces the observed electric polarization $\mathbf{P}$ [8] in common with the others. In addition to $\mathbf{M}$ and $\mathbf{P}$, a multiferroic domain is characterized by the spiral wave vector $\mathbf{Q}$, and single such domains can be produced by poling. Here we report the first comprehensive study of the switching behavior of these domains under a variation of applied H, and temperature (T). We find that $\mathbf{Q}$ dependence of $\mathbf{P}$ differs from that expected from previous simpler spiral orderings, where a change in sgn($\mathbf{P}$) accompanies a change in sgn($\mathbf{Q}$).

$CoCr_2O_4$ crystallizes in a cubic spinel structure, magnetic Co^{2+} and Cr^{3+} ions occupying the tetrahedral (A) and octahedral (B) sites, respectively [Fig. 1(a)]. For nearest-neighbor and isotropic antiferromagnetic A-B and B-B exchange interactions (J_{AB} and J_{BB}), with $J_{BB}/J_{AB} > 2/3$, an approximate, variational solution for the ground state was found, a "ferrimagnetic spiral," where the spins lie on conical surfaces [11–13]: The spins on the 6 fcc sublattices containing the magnetic sites are given by

$$\mathbf{S}_{n\nu} = \sin\theta_\nu[\hat{x}\cos(\mathbf{Q}\cdot\mathbf{r}_{n\nu} + \gamma_\nu) + \hat{y}\sin(\mathbf{Q}\cdot\mathbf{r}_{n\nu} + \gamma_\nu)] + \hat{z}\cos\theta_\nu, \qquad 0 \le \theta_\nu \le \pi,\ \nu = 1, \cdots, 6. \tag{1}$$

For fixed ν, $\mathbf{r}_{n\nu}$ goes over the sites of sublattice ν, the values of the cone $\frac{1}{2}$-angle θ_ν and phase γ_ν depend on ν, and the wave vector $\mathbf{Q} \cong 0.6\,[110]$, in units of 2π/lattice constant, is along the crystallographic [110]; $\hat{x}$, $\hat{y}$, $\hat{z}$ are orthonormal vectors [11–13] [see Fig. 1(a)].

A state approximately of this form was found from neutron diffraction in $CoCr_2O_4$ [5,14], with $\hat{z}$ the [001] crystal direction when $\mathbf{Q}$ is in the + or − [110] direction, "[110] $\mathbf{Q}$ domains" (with the same relative orientation for the cubically equivalent $\mathbf{Q}$'s). In [110] domains, the z components produce the magnetization $\mathbf{M}$ (along ± [001]). According to Yamasaki *et al.* [8], the spiral components give rise to ferroelectricity, where $\mathbf{P} \propto \mathbf{e}_{12} \times (\mathbf{S}_1 \times \mathbf{S}_2)$ for a pair of spins $\mathbf{S}_1$ and $\mathbf{S}_2$ with relative displacement $\mathbf{e}_{12}$ [15–17]. For the spiraling components of the Cr spins lying along the [110] chains, shown in Fig. 1(a), this gives the same contribution for every nearest-neighbor pair, namely $\mathbf{P} \propto \mathbf{Q} \times [001] \propto [\bar{1}10]$, as seen in Fig. 1(a) and as observed [8].

Magnetic measurement was performed in a SQUID magnetometer, specific heat was measured using a Quantum Design PPMS, and the dielectric constant, ε, was measured using an LCR meter at $f = 44$ kHz. The T (H) dependence of electric polarization, $\mathbf{P}$, was obtained by the integration of a pyroelectric (magnetoelectric) current measured using an electrometer with the T (H) variation of 4 K/min (0.01–0.02 T/s). While poling in $E \approx 10$ kV/cm, a small static H ($H = 0.5$ T for Fig. 2)

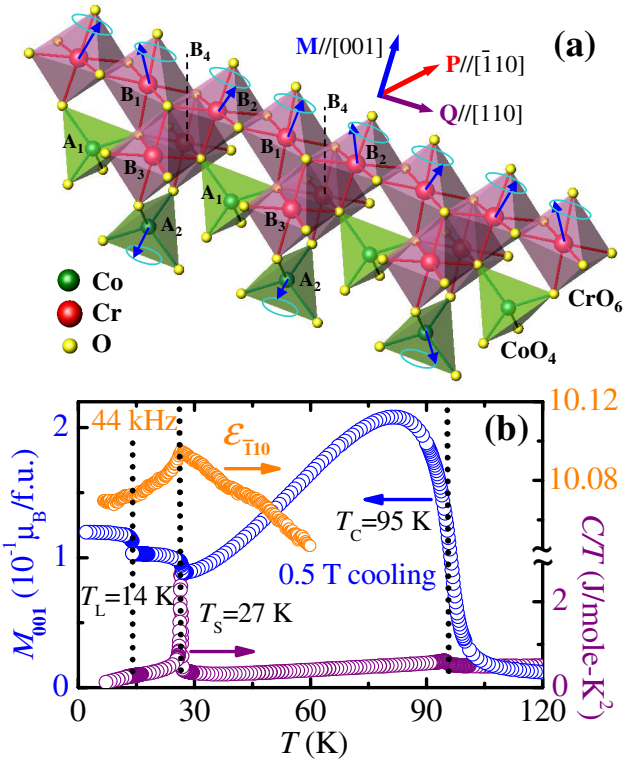

FIG. 1 (color online). (a) Crystallographic and low-T magnetic structure of spinel $CoCr_2O_4$. Co^{2+} and Cr^{3+} ions are located at the center of tetrahedral and octahedral O^{2-} cages, respectively. Conical-spiral spins of Co^{2+} and Cr^{3+} ions for only 3 of the 6 sublattices (A_2, B_1, and B_2) are shown for clarity. Cone angles shown are from [12], which, with [13], should be consulted for more details. Also shown are the directions of **M**, **P**, and **Q**. (b) T dependence of magnetization, **M**, along the [001] direction in $H = 0.5$ T upon cooling, specific heat divided by temperature in $H = 0$ T upon cooling, and dielectric constant in $H = 0$ T at 44 kHz upon warming. The existence of three phase transitions is evident, and T_C, T_S, and T_L denote temperatures for ferrimagnetic transition, conical spin ordering, and lock-in transition, respectively.

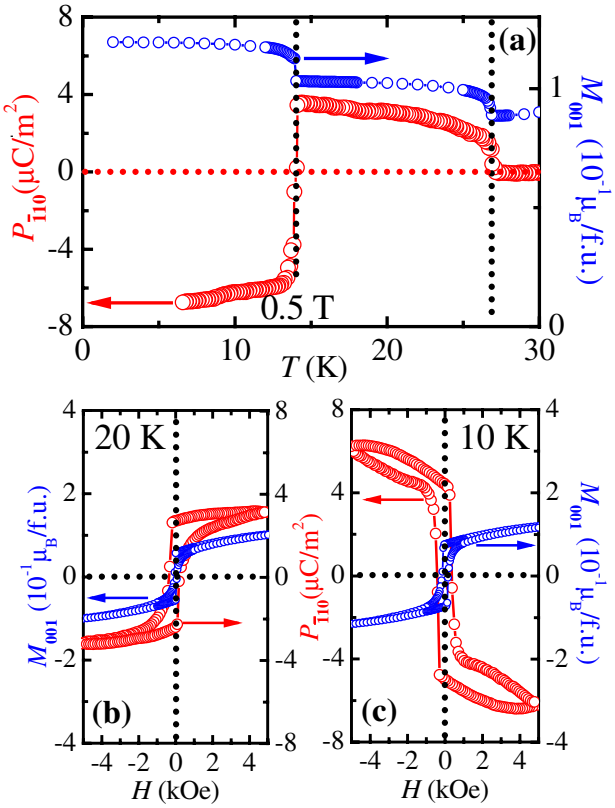

FIG. 2 (color online). (a) T dependence of electric polarization, **P**, along the [1̄10] direction, and **M** along the [001] direction below 30 K. **P** suddenly switches sign when cooling across 14 K without changing the signs of **M** and **Q**. (b) and (c) H dependence of **M** and **P** at 20 K and 10 K, respectively. The reversal of all of **M**, **P**, and **Q** is achieved by H reversal.

was also applied along the magnetic easy axis, along [001], so this magnetoelectric cooling procedure with E and H fixes the directions of the possible **M**, **P**, and **Q**; i.e., the procedure chooses a single (**M**, **P**, **Q**) domain.

The T dependence of physical properties of our single-crystalline $CoCr_2O_4$, grown with a vapor-transport method [18], exhibits sharp features, indicative of three phase transitions, as displayed in Fig. 1(b). The long-range ferrimagnetic collinear spin order appears below $T_C = 95$ K. A sharp but continuous increase of $M(T)$ at $T_S = 27$ K is ascribed to the conical-spiral order of spins, going along with a sharp peak in the specific heat, $C(T)$, and a peaky anomaly in $\varepsilon(T)$ along the [1̄10] direction where the electric polarization emerges. A steplike jump of $M(T)$ at $T_L = 14$ K [see also Fig. 2(a)], accompanied by a small feature in $C(T)$ and $\varepsilon(T)$, is associated with a small but clear thermal hysteresis (not shown), indicating the 1st order nature of this transition.

The onset of ferroelectricity along the [1̄10] direction, matches the spiral magnetic ordering transition at $T_S = 27$ K [Fig. 2(a)]. At the 14 K transition, when **M** is kept in one direction with H, **P** suddenly flips its direction, in contrast to the previous finding [8]. But in agreement with [8], when H, and therefore **M**, is reversed at fixed T, we find **P** to be reversed, as seen in Figs. 2(b) and 2(c). This correlation between **M** and **P** was attributed [8] to Bloch domain wall motion involved in reversing **M**. Such an essentially uniform rotation of the spin state characterizing the wall, taking **M** to $-$**M**, can be seen to take a **Q** domain to a $-$**Q** domain [19]. We have observed directly this sign change of **Q** upon H reversal by our circularly polarized resonant magnetic x-ray scattering experiment. Thus, **M**, **P**, and **Q** change to $-$**M**, $-$**P**, $-$**Q** in $-H$, respectively [Fig. 2(b)]. Furthermore, at 10 K (below T_L), H reversal also induces the 180° flipping of **M**, $-$**P**, and **Q** [Fig. 2(c)].

In contrast to this behavior, we find that the sign flip of **P** across the 14 K transition is not accompanied by a change of sgn(**Q**); rather our results indicate that the sign of **Q** (or spiral handedness) is invariant at the 14 K transition (discussed further below). The low-temperature state is asso-

ciated with a slight increase of the magnitude of **M** as well as **P**, as shown in Fig. 2(a). Note that in a multiferroic with a spiral magnetic order with only one magnetic sublattice, switching of **P** results from a sign change of **Q** [20]. (This is the usual behavior found in other multiferroics with spiral magnetism.)

Our resonant magnetic soft x-ray scattering experiment was performed with the elliptically polarized-undulator beam line at the National Synchrotron Radiation Research Center in Taiwan. With photon energy tuned at the Co L_3 edge, the scattering results reveal that there is an abrupt change in magnetic modulations at ~14 K. Unlike earlier neutron results [5,14,21], we found two incommensurate magnetic modulations $\mathbf{Q}_+$ and $\mathbf{Q}_-$ at 15 K, a temperature above T_L, while, for T below T_L, there are one commensurate modulation $\mathbf{Q}_C = 2/3[110]$ and two incommensurate ones, $\mathbf{Q}'_+$ and $\mathbf{Q}'_-$, with a separation along $[1\bar{1}0]$ much larger than that between $\mathbf{Q}_+$ and $\mathbf{Q}_-$, as illustrated in the contour plots [Fig. 3(a)]. The intensities of the $\mathbf{Q}'$ peaks are 1 to 2 orders of magnitude smaller than the $\mathbf{Q}_C$ peak, and the three vectors are approximately equal in direction as well as magnitude; similarly, the vectors $\mathbf{Q}_+$, $\mathbf{Q}_-$ are approximately equal [Fig. 3(a)]. The x-ray scattering intensity can distinguish between spirals with wave vector **Q** and $-\mathbf{Q}$, if the incident beam is circularly polarized [22]. This is similar to the scattering of polarized neutrons [20,23]. Figures 3(b), 3(d), and 3(e) show that the measured scattering intensities with circularly polarized light indeed change upon the reversal of magnetization along [001], disclosing the expected flip of **Q** with H reversal. Figure 3(c) also illustrates conical-spiral spins above and below the 14 K transition where $\pm\mathbf{M}$ correspond to $\pm\mathbf{Q}$, respectively. Strikingly, the scattering results also reveal that the sign of the **Q** of the largest peak at each T ($\mathbf{Q}_C$ and $\mathbf{Q}_-$) remains unchanged as T changes across T_L: The H dependences of the intensities of these peaks do not reverse. Thus, to the extent that we can consider a single-wave-vector spiral as a good approximation to the observed state, this is solid evidence of sgn (**Q**) invariance across T_L. In addition, the only one of the smaller peaks ($\mathbf{Q}'_+$) that has an observable intensity change on H reversal also shows this invariance, and further, the wave vectors of all the peaks are approximately equal. Therefore, even considering the complexity of having multiple Fourier components in the spin configuration, the data strongly suggest that the sign of **Q** (for each Fourier component) does not change across the 1st order transition.

A plausible interpretation for the switch in the sign of **P** across 14 K without sign change of **Q** and **M** (despite its impossibility for a single sublattice conical spiral, as noted above) is found in a "ferrielectric"-type scenario. Now, Co^{2+} has a more-than-half-filled d shell, while Cr^{3+} has a less-than-half-filled shell, suggesting that Co-Cr and Cr-Cr bonds have the opposite sign of spin-orbit interaction, resulting in the opposite directions of electric dipole moments, $\mathbf{P}_{\mathrm{Co-Cr}}$ and $\mathbf{P}_{\mathrm{Cr-Cr}}$ from the different bonds of form Eq. (1) [24]. Furthermore, the bond charges that give rise to the dipole moments are interionic overlap charge densities [15,16], and are therefore very sensitive to small changes in interionic distances expected to occur through the 1st order phase transition at T_L. Then, it is conceivable that the delicately balanced net polarization can change its sign at T_L without a change in sgn(**Q**) (the directions of each contribution $\mathbf{P}_{\mathrm{Co-Cr}}$ and $\mathbf{P}_{\mathrm{Cr-Cr}}$ do not change, but their magnitudes do).

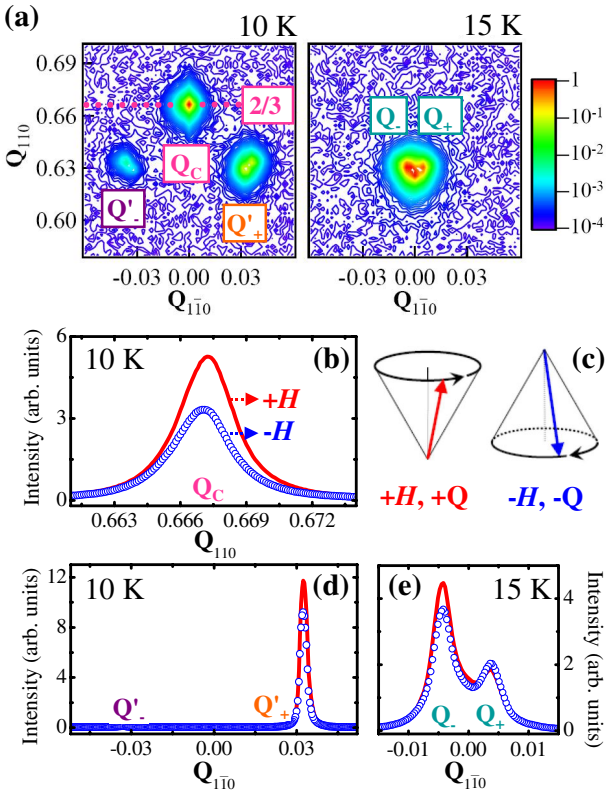

FIG. 3 (color online). (a) Contour plots of the Co L_3 edge magnetic soft x-ray scattering intensity in the plane defined by $\mathbf{Q}_{110}$ and $\mathbf{Q}_{1\bar{1}0}$ recorded at temperatures above and below T_L (14 K) with photon energy of 778.4 eV. The **E** vector of incident x-rays was parallel to the [001] axis. The contour plots are shown in a logarithmic scale with its order of magnitude expressed by means of color. (b), (d), and (e) Scattering intensity of **Q** scans along [110] and $[1\bar{1}0]$ under $+\mathbf{M}$ (solid curves) and $-\mathbf{M}$ (open circles) with circularly polarized x-rays. (c) Depiction of conical-spiral spins where $\pm\mathbf{M}$ go with $\pm\mathbf{Q}$ above and below T_L, respectively.

Repeated switching of electric polarization direction is achieved by varying temperature step-linearly with time between 8 K and 20 K as shown in Fig. 4(a). The measurement of the pyroelectric current began at 8 K in the (+, −, +) state defined as [sgn(**M**), sgn(**P**), sgn(**Q**)] after poling in $H = 0.1$ T and $E \approx 10$ kV/cm. Upon warming, this state switches to the (+, +, +) state, but the initial state is recovered by cooling back to 8 K. Because of the 1st order nature of the T_L transition, the temperatures at which **P** flips differ by ~1.6 K between warming and cooling. Figure 4(b) displays how $\mathbf{P}(T)$ depends on large

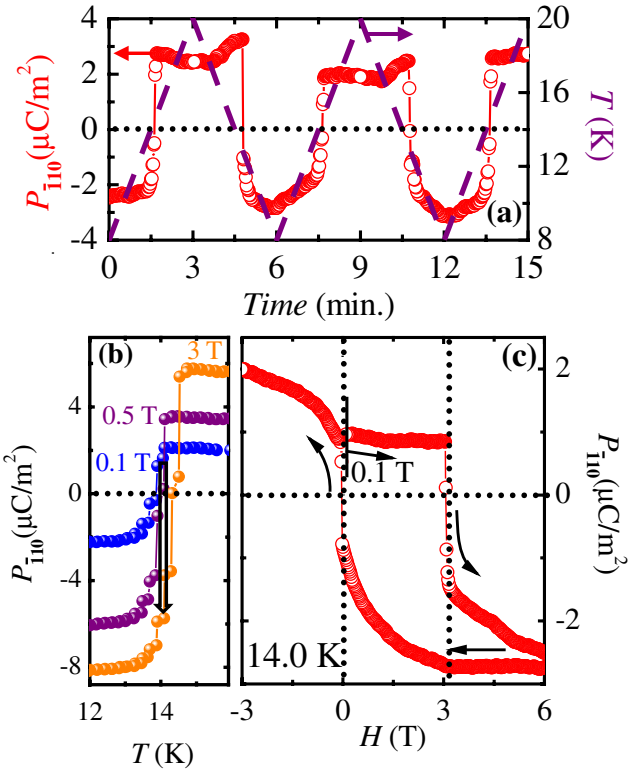

FIG. 4 (color online). (a) Repeatable polarization switching with T varied linearly with time between 8 K and 20 K. (b) T dependence of polarization around the T_L transition in different applied H (0.1, 0.5, and 3 T), indicating that T_L increases slightly with increasing H. (c) **P** at 14.0 K vs H after poling the specimen in $H = 0.1$ T and $E \approx 10$ kV/cm. The initial $(+, +, +)$ state which is defined as [sgn(**M**), sgn(**P**), sgn(**Q**)] changes to the $(+, -, +)$ state in $H \approx 3$ T. Negative H scan, reversing **M**, induces switching of **P** and **Q**, i.e., resulting in the $(-, +, -)$ state.

cooling H, showing a slight increasing tendency of T_L with increasing H. At exactly 14.0 K, the phase cooled in 0.1 T is in the $(+, +, +)$ state, whereas cooling in 3 T puts the phase in the $(+, -, +)$ state. The black downward arrow denotes the possible switching of the physical state with increasing H at 14.0 K. As demonstrated in Fig. 4(c), the isothermal polarization reversal is, indeed, achieved by varying H at 14.0 K. After cooling down to 14.0 K in 0.1 T, the phase is initially in the $(+, +, +)$ state. The isothermal increase of H results in changing the state to $(+, -, +)$ by reversing **P**, but keeping the direction of **M** and **Q** fixed. Because of the 1st order nature of the T_L transition, the $(+, -, +)$ state does not go back to the initial state of $(+, +, +)$ when H is reduced to zero (or the original 0.1 T). When the H direction is reversed, **M** flips, so do **P** and **Q**, and thus the $(+, -, +)$ state becomes the $(-, +, -)$ state.

In summary, the conical-spiral ferroelectricity in $CoCr_2O_4$ can be described by the interrelationship among ferroelectric polarization (**P**), magnetization (**M**), and spiral wave vector (**Q**). Our results demonstrate that spontaneous electric polarization induced by the noncollinear spin order shows a discontinuous jump with a change in sign across the magnetic lock-in transition temperature ($T_L = 14$ K); furthermore the sign change occurs while keeping fixed the spin rotation direction, i.e., spiral handedness or sgn(**Q**). This differs from the usual behavior wherein for a simple spiral, change in sgn(**P**) requires the handedness to change sign, and we give a possible mechanism for such unusual behavior. We also recover the previous finding wherein $\mathbf{P} \rightarrow -\mathbf{P}$ when $\mathbf{M} \rightarrow -\mathbf{M}$ [8], but further show experimentally that this is accompanied by $\mathbf{Q} \rightarrow -\mathbf{Q}$, consistent with the Bloch wall mechanism [8] for switching **M**. We further show that **P** reverses its direction in ~3 T at exactly 14.0 K, due to a slight increasing trend of T_L with increasing H.

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