Magnetic Reversal of the Ferroelectric Polarization in a Multiferroic Spinel Oxide

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Ferroelectric transition has been detected in a ferrimagnetic spinel oxide of $CoCr_2O_4$ upon the transition to the conical spin order below 25 K. The direction $[\bar{1}10]$ of the spontaneous polarization is normal to both the magnetization easy axis $[001]$ and to the propagation axis $[110]$ of the transverse spiral component, in accord with the prediction based on the spin-current model. The reversal of the spontaneous magnetization by a small magnetic field (~ 0.1 T) induces the reversal of the spontaneous polarization, indicating the clamping of the ferromagnetic and ferroelectric domain walls.

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Multiferroics, i.e., materials in which ferroelectricity and ferromagnetism can coexist, have recently been of increasing interest since they are anticipated to potentially bring about a very large magnetoelectric (ME) effect [1–3]. The ME effect, that is, the induction of electric polarization (magnetization) by a magnetic (electric) field, may widen a bottleneck channel (e.g., use of external magnetic field) of spintronics by enabling the electric control of the spin state, when it can be made gigantic. If the multiferroic phase is realized and both orders can be effectively tied with each other, then the colossal ME phenomenon is expected to emerge through the magnetic or electric field induced phase transformation [4] or otherwise in terms of the control of the multiferroic domain walls [5]. The problem is how to realize such multiferroics as can host ferroelectricity of magnetic origin while keeping the macroscopic magnetization. Here we report the first example of the multiferroic compounds with both spontaneous magnetization and polarization of spin origin, in which the electric polarization can be reversed by the reversal of the magnetization.

A useful hint to the material design of multiferroics has recently been obtained by the studies on the new magnetic ferroelectrics. $TbMnO_3$ [4] and $DyMnO_3$ [6,7] with distorted perovskite ($GdFeO_3$-type) structure undergo the successive transitions to the incommensurate spin order with lowering temperature below about 40 K, at first to the collinear sinusoidal spin modulation state at T_N and then to the transverse spiral (elliptical) state at T_C. Upon the latter collinear to spiral spin transition at T_C, the ferroelectric state is observed to emerge, irrespective of the spiral propagation vector being commensurate or incommensurate [8,9]. The direction of the spontaneous polarization is perpendicular to the spin-spiral plane as well as to the propagation vector. The feature is in accord with the spin-current model for the magnetic ferroelectricity proposed by Katsura *et al.* [10]. The model describes the relation between the polarization ($\boldsymbol{P}$) and the spin canting ($\boldsymbol{S}_i$ and $\boldsymbol{S}_j$) on the neighboring two sites (i and j),

$$\boldsymbol{P} = a\boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j). \tag{1}$$

Here, $\boldsymbol{e}_{ij}$ denotes the vector connecting the two sites, being parallel to the spontaneous spin-current flow, as depicted in Fig. 1(c), and a is the proportional constant as determined by the spin exchange interaction and the spin-orbit inter-

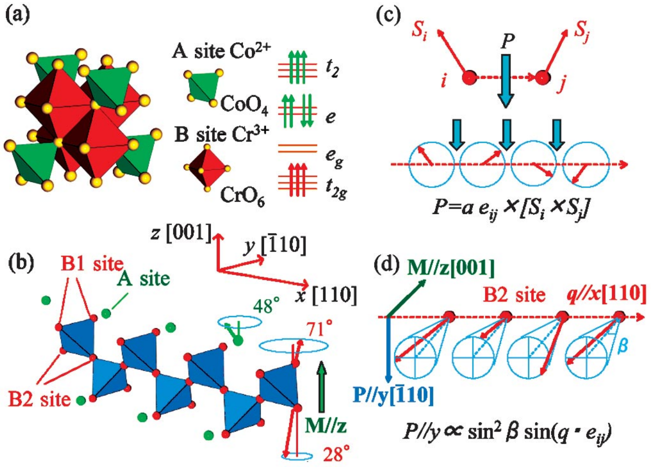

FIG. 1 (color). (a) Schematic structure of spinel $CoCr_2O_4$ and the electronic configurations of constituent Co^{2+} and Cr^{3+} ions. (b) The structure viewed along the conical spin modulation direction $[110]$ (denoted as the x axis). The circles with slanted arrows indicate the spiral plane of the respective spins with conical structure [22]. (c) The spin ($\boldsymbol{S}_i$ and $\boldsymbol{S}_j$) canting between the two sites (i and j) and the direction of induced polarization $\boldsymbol{P}$. The spiral spin modulation as shown in the lower panel produces the homogeneous (macroscopic) polarization. (d) The relation among the net magnetization $\boldsymbol{M}$, the spiral spin modulation vector $\boldsymbol{q}$, and the induced polarization $\boldsymbol{P}$, as represented for the case of the B2-site chain in $CoCr_2O_4$.

action [10,11]. An alternative view of the generation mechanism of electric polarization is the inverse Dzyaloshinskii-Moriya interaction [12,13] as argued by Sergienko and Dagotto [14], where the canted spin configuration may polarize the oxygen (ligand) atom through the electron-lattice interaction. When the transverse spiral spin order is realized as shown in Fig. 1(c), the spontaneous (uniform) polarization is expected to be present in the direction perpendicular to the spiral propagation vector $\boldsymbol{q}$ and spin rotation axis. This is the origin of the magnetic ferroelectricity observed not only for RMnO$_3$ (R = Tb and Dy) but also for other magnetic ferroelectrics, such as $Ni_3V_2O_8$ [15] and $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ [16]. In the ferroelectrics of magnetic origin, various magnetic control of the $\boldsymbol{P}$, such as flopping [4,7], apparent reversal or generation [15,17,18], and rotation [16], have recently been demonstrated.

All the above cases present the ferroelectricity of the magnetic origin but with no spontaneous magnetization. Nevertheless, this scenario can be extended to the conical spin state [Fig. 1(d)] [10] in which the spontaneous (homogeneous) and spiral components of the magnetization can coexist. It is novel to see multiferroic behavior on a material that exhibits spontaneous magnetization. A family of chromite spinels, MCr$_2$O$_4$ with M = Mn, Fe, and Co, can show the conical spin structures [19–23]. The purpose of this study is to confirm the ferroelectric and ferromagnetic state of MCr$_2$O$_4$, and to investigate its electric response to external magnetic field. Here we focus on the case of $CoCr_2O_4$ crystal as the typical example, but quite a similar multiferroic feature could be observed for other MCr$_2$O$_4$.

Crystal and magnetic structures of $CoCr_2O_4$ are depicted in Figs. 1(a) and 1(b). The structure is a cubic normal spinel, in which magnetic Co^{2+} ions occupy the A (8a) sites and Cr^{3+} ions the B (16d) sites [19,20]. The ferrimagnetic transition occurs at $T_C = 93$ K, and with further lowering temperature the compound undergoes the transition to conical spin states, i.e., uniform plus transverse spiral spin state, with the incommensurate propagation vector of $[qq0]$ ($q \sim 0.63$) at 26 K [22]. The lock-in transition occurs around 15 K with minimal change of the q value [24]. As shown in Fig. 1(b), the rotating spin components lie in the (001) plane, while the spontaneous magnetization directs along the [001] or equivalent directions. Then, according to the above spin-current model, the spontaneous polarization vector is expected to be along the $[\bar{1}10]$ axis and perpendicular to the [001] spontaneous magnetization direction. With this in mind, we have explored the spontaneous polarization induced by conical spin order in $CoCr_2O_4$.

A large-size (3 mm in diameter and 20 mm in length) single crystal of $CoCr_2O_4$ was successfully grown for the first time by a floating zone method. First, a stoichiometric mixture of CoO and Cr_2O_3 powder was fired at 1200 °C for 12 h, and then pressed into a rod and fired again at 1300 °C for 12 h in flowing argon gas. The crystal was grown at a rate of 40 mm/h in argon gas of 10 atm with use of a Xe-lamp image furnace equipped with a hemielliptic focusing mirror. A plate with the large $(\bar{1}10)$ plane of 2×2 mm^2 was sliced out from the crystal rod, and both the end $(\bar{1}10)$ surfaces were painted with silver paste as the electrodes. To fix the direction of the magnetic domain, the spin $\boldsymbol{q}$-vector propagation axis, and the possible electric polarization, the specimen was cooled down to 5 K while applying an external magnetic field of 0.01 T along [001] as well as an electric field of 400 kV/m along $[\bar{1}10]$. This procedure will be referred to hereafter as the ME cooling. Then, the pyroelectric current was measured with an electrometer while warming the specimen at a rate of 20 K/min. To measure the magnetic-field dependence of the electric polarization, the specimen was once ME cooled as above to a fixed temperature, and then the displacement current was measured while scanning the magnetic field, mostly at a rate of 0.01 T/s.

Figure 2 shows the temperature dependence of (a) magnetization ($\boldsymbol{M}$), and (b) polarization ($\boldsymbol{P}$) and dielectric constant (ϵ) for a single crystal of $CoCr_2O_4$. The magnetization was measured in the field (0.01 T) cooling run in the [001] direction (z direction). The onset of the magnetization at $T_C = 93$ K is due to the ferrimagnetic

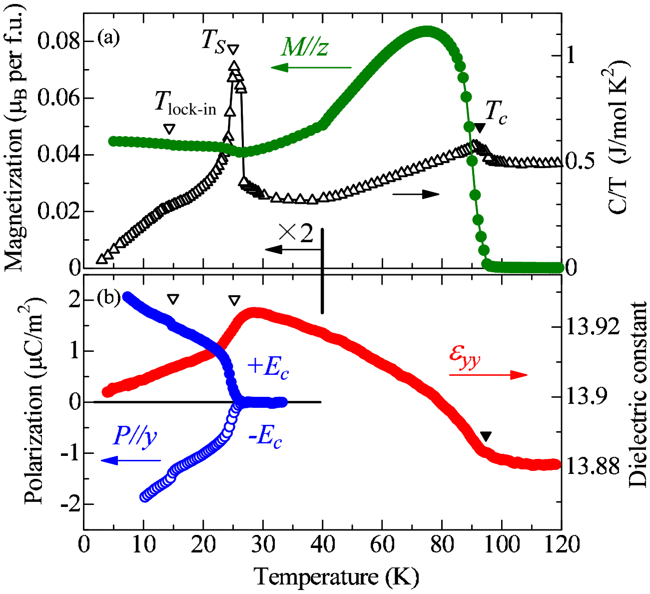

FIG. 2 (color online). The temperature dependence of (a) magnetization $\boldsymbol{M}$ and specific heat divided by temperature (C/T), and (b) dielectric constant ϵ measured in the y direction at 10 kHz and the induced polarization along the y axis ($\parallel [\bar{1}10]$). T_C, T_S, and $T_{\text{lock-in}}$ in (a) stand for the critical temperatures of ferrimagnetic transition, incommensurate conical spin transition, and its lock-in transition, respectively. The electric polarization $\boldsymbol{P}$ in (b) was measured after the ME field cooling procedure, with the cooling magnetic field $H_c \parallel z (= 0.01$ T) and electric field $E_c \parallel y (= 400$ kV/m).

transition. The tiny anomalies are discerned at $T_S = 26$ K and $T_{\text{lock-in}} = 15$ K, which correspond to the conical spin transitions with slightly different propagation vectors of $[qq0]$ ($q \sim 0.63$). The electric polarization $\boldsymbol{P}$, which was deduced from the pyroelectric current in the zero-electric- and zero-magnetic-field warming after the above-mentioned ME cooling procedure, shows the onset at T_S and subsequently a tiny anomaly at $T_{\text{lock-in}}$. The direction of the $\boldsymbol{P}$ was confirmed to coincide with that of the electric field E_c applied in the ME cooling procedure, as shown in Fig. 2(b). These features ensure that the observed $\boldsymbol{P}$ is the spontaneous polarization in the ferroelectric phase below T_S, irrespective of the conical spin phases with slightly different q values. The observed magnitude of polarization ($\sim 2\mu C/m^2$) in this compound is by 5 orders of magnitude smaller than that of the prototypical ferroelectrics $BaTiO_3$ and even smaller by 2–3 orders of magnitude than those of the manganite ferroelectrics, RMnO$_3$ [7] and RMn$_2$O$_5$ [17], of similar magnetic origin. Such a small magnitude as well as the first-order nature of the phase transition at T_S may explain a merely tiny anomaly of the dielectric constant around T_S.

The observed features of the $\boldsymbol{P}$, i.e., its presence only in the conical spin structure below T_S and its direction perpendicular to $\boldsymbol{q}$ ($\parallel [110]$) and $\boldsymbol{M}$ ($\parallel [001]$), are consistent with the aforementioned spin-current model as expressed by Eq. (1) and Fig. 1(d). The magnitude of the $\boldsymbol{P}$ or the coefficient a in Eq. (1) is anticipated to be in proportion to the magnitude of spin-orbit interaction and also to the spin exchange interaction. Obviously, the much smaller $\boldsymbol{P}$ value than the RMnO$_3$ case with comparable transition temperatures is due to the very weak spin-orbit coupling strength of Cr^{3+} ions, whose electronic configurations is t_{2g}^3 with no apparent orbital moment in the spinel octahedral ligand field. Despite its smallness, the $\boldsymbol{P}$ in this multiferroic state was proven to show the following remarkable feature responding to the reversal of the magnetization.

We show in Fig. 3(b) the magnetic-field dependence of the $\boldsymbol{P}$ at selected temperatures (18 and 27 K) in comparison with the magnetization curve [Fig. 3(a)]. Prior to the magnetic-field scan, the $\boldsymbol{P}$ direction could be thoroughly determined by the direction of the cooling electric field ($E_c = 400$ kV/m) in the aforementioned ME cooling procedure, as shown in Fig. 2(b). Then the magnetic field was scanned between $+H_c$ and $-H_c$ ($H_c = 0.5$ T) at a rate of 0.01 T/s while measuring the displacement current. As is clearly seen in Fig. 3(b), whichever direction of $\boldsymbol{M}$ is taken as the starting point, $\boldsymbol{P}$ is always reversed upon the reversal of the $\boldsymbol{M}$ direction [Fig. 3(a)]. After the $\boldsymbol{P}$ direction is reversed once and twice by the magnetic field, namely, at states (2) and (3) in Fig. 3(b), respectively, the temperature dependence of the polarization obeys the almost identical behavior with the original oppositely ME cooled states [see Fig. 2(b)], as shown in the inset of Fig. 3. This ensures the full reversal of the whole polarization domain by the magnetic field.

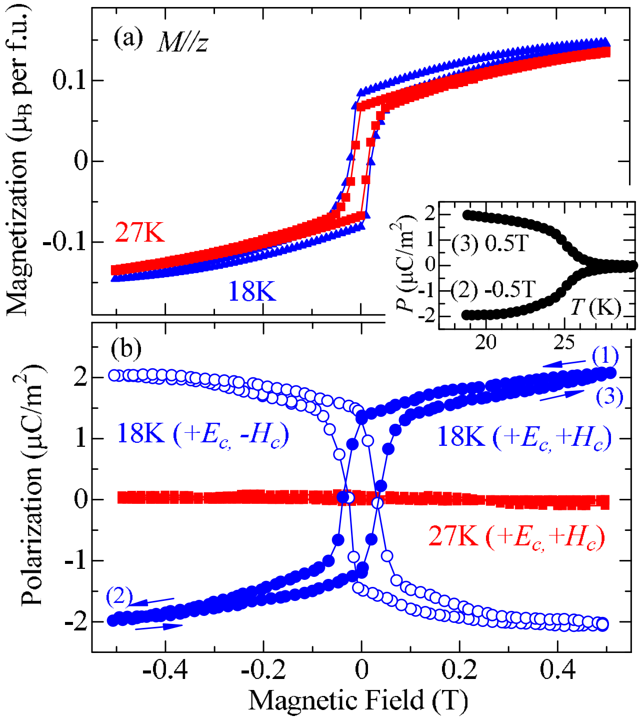

FIG. 3 (color online). Magnetic-field dependence of (a) magnetization and (b) electric polarization at temperatures above (27 K) and below (18 K) the ferroelectric transition temperature ($T_S = 25$ K). For measurements of the polarization (b), the magnetic field was scanned between $+H_c$ and $-H_c$, for each ME cooled state prepared with ($+E_c$, $+H_c$) and ($+E_c$, $-H_c$), as represented by solid and open circles. Here, E_c($= 400$ kV/m) and H_c($= 0.5$ T) stand for the cooling electric and magnetic fields, respectively. The inset shows the temperature dependence of the polarization ($\boldsymbol{P}$) in the warming runs starting from the magnetic-field scan points (2) and (3) shown in (b).

The synchronized reversal of the spontaneous $\boldsymbol{M}$ and $\boldsymbol{P}$ can be more directly confirmed by the sequential scan of the magnetic field between $+0.2$ and -0.2 T at 18 K, as shown in Fig. 4. The magnitude of flopped $\boldsymbol{P}$ is almost constant and reaches the full value as observed by the quasistatic measurement [Fig. 2(b)], indicating that there is no complexity such as multiple ferroelectric domains. Namely, the ferroelectric and ferromagnetic single-domain feature, which had been achieved by the ME cooling procedure, was almost perfectly maintained during the magnetic-field induced reversal of $\boldsymbol{M}$ and $\boldsymbol{P}$. This indicates that the relative directional relation between $\boldsymbol{P}$ and $\boldsymbol{M}$ is kept intact even upon the reversal of $\boldsymbol{M}$ once the ME cooled multiferroic state is established.

Among the order parameters characterizing the multiferroic state, the toroidal moment, $\boldsymbol{T} \equiv \sum_i \boldsymbol{r}_i \times \boldsymbol{S}_i \propto \boldsymbol{P} \times \boldsymbol{M}$, where $\boldsymbol{r}_i$ is the displacement of the center position from atoms at ith site, is the most basic one and can be viewed as the built-in vector potential in the presence of spin-orbit interaction [2,25]. The presently observed $\boldsymbol{P}$ reversal upon

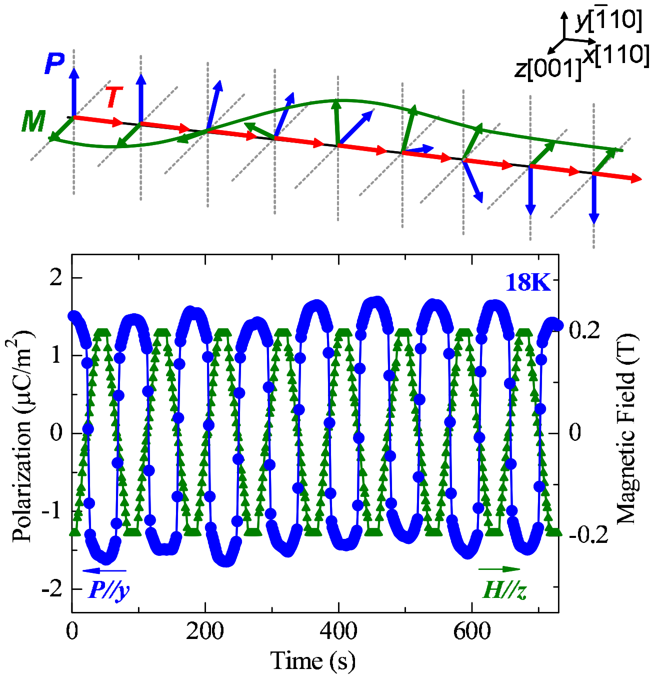

FIG. 4 (color online). The synchronized reversal of the polarization (***P*** ∥ y, solid circles) at 18 K with change of the external magnetic field (***H*** ∥ z) which periodically reverses the magnetization direction (***M*** ∥ z). Upper panel depicts the plausible clamping process of the ferromagnetic and polarization domain walls. Note that every toroidal moment, defined as $\boldsymbol{T} \propto \boldsymbol{P} \times \boldsymbol{M}$, is kept intact across the domain wall.

the ***M*** reversal clearly indicates that ***T*** is invariant in this process and well characterizes the present multiferroic state. In other words, the ferromagnetic and ferroelectric domain walls are anticipated to be always clamped: The magnetic domain wall, e.g., of the Bloch type, may sustain the similar spin-spiral habit and hence the direction of ***P*** may also rotate, while keeping the orthogonal relation with the cone axis or ***M***, as schematically depicted in the upper panel of Fig. 4. In other words, the ***T*** direction is not changed across the domain wall. This situation for the Bloch-type domain wall is expected to occur for the relatively week magnetic anisotropy as in the present case of the spinel chromite. The only exception to this rule is that the spin helicity, or equivalently the polarization ***P***, crosses zero to change the sign at the middle of the magnetic domain wall. But this is not the case for the present materials, perhaps due to the energy cost of the spin exchange interaction on the frustrated lattice.

In conclusion, we have demonstrated the presence of ferroelectricity based on the conical spin modulation for $CoCr_2O_4$. Being distinct from the hitherto known magnetic ferroelectrics, this and related spinel chromites can show the spontaneous magnetization originating from the conical spin state. This leads to the multiferroic behavior with a spontaneous magnetization, in which we verified the strong clamping between the ferromagnetic and ferroelectric domains, namely, the magnetic reversal of the ferroelectric polarization. The present observation also suggests the possible presence of the inverse effect in multiferroics [26], that is, the electric field reversal of the ferromagnetic domain, which may have an important implication for application of the multiferroics to the spin technology.

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