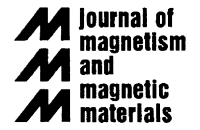




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Multiferroics—toward strong coupling between magnetization and polarization in a solid

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Abstract

Multiferroics, in which magnetization and polarization can coexist, are potential candidates of the new spintronic materials which may enable the electrical control of magnetic state. The materials design of the multiferroics and the strategy to enhance the DC and optical magnetoelectric effect are argued in terms of the toroidal moment, helical spin structure, and critical-state phase control.

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1. Introduction

Highly efficient control of magnetism in terms of electric field or current in a solid may widen the bottle-neck of the state-of-art spin-electronics technology. Since the magnetoelectric (ME) effect, meaning magnetic (electric) induction of polarization P (magnetization M), was first confirmed in 1959–1960 theoretically by Dzyaloshinsky [1] and experimentally by Astrov [2], many magnetic materials have been demonstrated to show this effect [3]. Nevertheless, the magnitude of the observed ME effect has been too small to apply to any practical devices.

Multiferroics, the materials in which both ferromagnetism and ferroelectricity can coexist (Fig. 1), are the prospective candidates which can potentially host the gigantic ME effect. Strategy for exploring such multiferroics as showing strong M – P coupling and novel optical functions is argued in terms of the designed spin superstructure and tailor-made materials.

2. Toroidal moment as the source of ME effect

To describe the genuinely electronic coupling between P and M in a solid, the toroidal moment, as defined by

$$T = \frac{1}{2} \sum r_i \times S_i \sim P \times M, \quad (1)$$

is the most fundamental quantity or order parameter [3–5]. The spin–orbit coupling term (λLS) in Hamiltonian as the quantum-mechanical source for the ME coupling can be converted to $-\lambda Tp$, where p is the electron momentum, and thereby the toroidal moment can be considered as built-in DC vector potential acting on the electrons. The macroscopic toroidal moment is expected not only to behave as the order parameter for the multiferroics, but also to cause various DC/optical ME phenomena.

Optical ME effects are exemplified in Figs. 2(b) and (d) as compared with the conventional magneto- and electro-optical (nonlinear optical) effects. The Farady (or Kerr) rotation shown in Fig. 2(a) stems from the dichroism or birefringence with respect to the right-hand or left-hand circularly polarized light. By contrast, the optical ME effect means the dichroism/birefringence with respect to the light propagation vector, irrespective of the light polarization [6]. This originates from the polarization component

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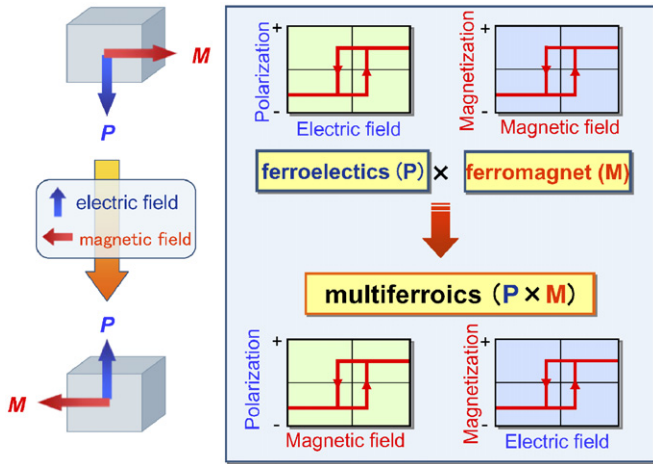


Fig. 1. Multiferroics and magneto-electric control.

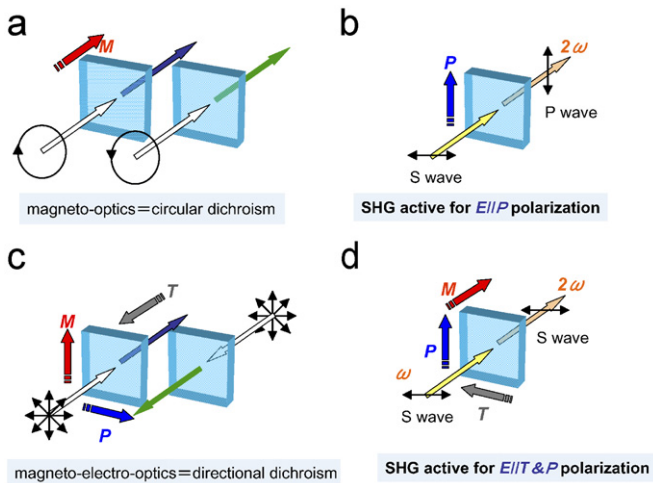


Fig. 2. Optical magneto-electric effect: (a) conventional magneto-optical effect with dichroism for circular polarized light; (b) optical magneto-electric effect with directional dichroism irrespective of polarization, where light k -vector is parallel or antiparallel to the toroidal moment $T = P \times M$; (c) conventional second-order nonlinear optical effect, representing the second-harmonic generation (SHG) for the light polarization parallel to the polarization P ; and (d) toroidal moment induced SHG (or so-called MSHG) for the light polarization parallel to the toroidal moment.

induced by the light magnetic field as the optical frequency analog of the ME effect.

Another important feature of the optical-frequency ME effect is the second-order nonlinear optical activity [3]. Due to the presence of the toroidal moment T (built-in vector potential) in the multiferroics, the second-harmonic (SH) light with the light polarization along T can be generated (Fig. 2(d)), in addition to the ordinary SH light polarized along the P direction (Fig. 2(c)). Then, the incident light polarized along the T direction can generate the SH components polarized along both the P and T directions. The phase of the T -induced component can be reversed by the reversal of the magnetization. Therefore, the SH light shows the polarization rotation depending on the magne-

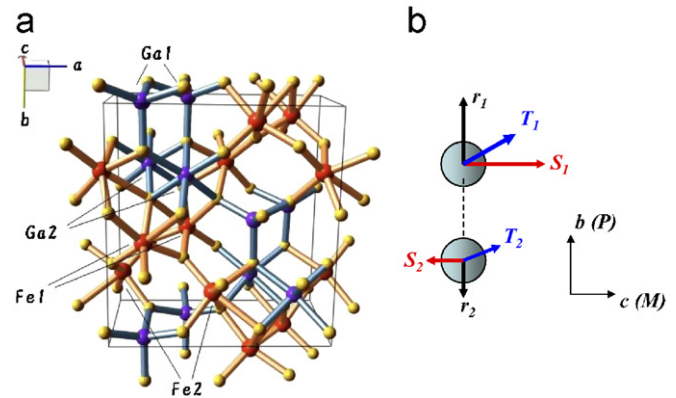


Fig. 3. (a) Crystal structure of magneto-electric GaFeO₃ (Remeikite) crystal. (b) Schematics for the patterns of ordered moments, spin (S), electric (r), and toroidal (T) moments, on the Fe1 and Fe2 sites.

tization direction or equivalently the toroidal moment direction. This has been called nonlinear Kerr rotation, and can be used as a sensitive probe of the toroidal moment or the magnetization at the point where the inversion symmetry is broken such as an interface of the magnetic layer.

The importance of the toroidal moment in the ME process is clear in a prototypical ME material, GaFeO₃ (Fig. 3), as pointed out by Popov et al. [5]. The GaFeO₃ is pyroelectric in nature, i.e. endowed with the built-in electric polarity along the b -axis in the orthorhombic cell. The spontaneous magnetization stems from the *ferrimagnetic* arrangement of Fe spins, as shown in Fig. 3(b), whose easy axis is the c -axis. Thus, the macroscopic toroidal moment is present in this crystal, but its magnitude should be more than the simple formula, $P \times M$. As indicated schematically in Fig. 3(b), the displacement of two Fe-ion sites is opposite, as if it were *ferrielectric*, like the case of the ferrimagnetic spin arrangement. Therefore, the microscopic toroidal moments as defined by Eq. (1) are *ferritic* in spite of almost *antiferroic* arrangements of the spins and electric moments. Such an idea of *ferrotroidicity* will be applied to the future materials design for gigantic ME effect, since it does not necessarily require the macroscopic coexistence of P and M .

In addition to the hitherto known DC-ME activity [5,7], a GaFeO₃ crystal shows the aforementioned optical ME effects; the directional dichroism [8–10] and the nonlinear Kerr rotation [11]. Below the ferrimagnetic transition temperature around 200 K, the GaFeO₃ shows the light k -vector direction dependent response both in the visible light region [9,10] and in the X-ray region near the K-edge absorption of Fe ions [8]. On the other hand, the toroidal moment produces the large SH component, even larger than the crystal (P) component, thereby leading to the gigantic nonlinear Kerr rotation, e.g. $>70^\circ$ at 100 K [11]. In fact, the mapping of the toroidal moment distribution (equivalently the magnetization distribution for a fixed electric polarity) was demonstrated by making use of such

a large nonlinear Kerr rotation [11]. A similar toroidal-moment-induced SHG has recently been extensively utilized to probe the multiferroic interface state of the transition-metal oxide junctions/superlattices (see Section 4).

3. Bicritical-state phase control to enhance the ME effect

The multiferroic state or more generally the ferrotoroidic state is sure to show the linear ME effect, that is the linearly magnetic (electric) field induced polarization (magnetization). The ferrotoroidic GaFeO_3 is one such example, in which the spin–orbit interaction converting the toroidal moment to the vector potential plays an essential role [5]. Therefore, the enhancement of the linear ME effect can be brought about by enlarging the spin–orbit interaction of the electrons which are responsible for both of the magnetization and polarization. Of course, the proper magnetoelastic coupling is another important source of the ME coupling, but is not discussed in this article which focuses on the genuine electronic coupling between M and P .

As another strategy to enhance the ME effect, we propose here the bicritical-state phase control based on the multiferroics, in analogy to the case of colossal magnetoresistive (CMR) effect. In the case of CMR (Fig. 4(a)), it is known [12] that the charge-ordered (CO) state competes with the double-exchange ferromagnetic (FM) metallic state. An external magnetic field induces the phase change from $M = 0$ (antiferromagnetic or paramagnetic or spin-glass state) to $M > 0$ (FM state), thereby simultaneously switching the resistive state from the insulating to metallic state. Near the bicritical point as indicated by vertical arrows in Fig. 4, the system responds to the external field

quite sensitively, not only between the ordered phases but also between one ordered phase and disordered phase above the critical temperature. In the case of CMR, the former is the magnetic field induced insulator–metal transition associated with the melting of the long-range CO and orbital-ordered state, while in the latter the CMR phenomenon observed around the FM transition temperature.

An analogous feature is anticipated for the bicriticality based on the multiferroics, as schematized in Fig. 4(b). Near the bicritical point, an external magnetic (electric) field may drive the phase to the multiferroic state, leading to the simultaneous switching to the magnetic ($M > 0$) and electric ($P > 0$) state. This can provide exotic and enormous control of the electric (magnetic) state in terms of external magnetic (electric) field. An alternative case will be the bicritical competition between the FM ($M > 0$) and paraelectric ($P = 0$) phase and the antiferromagnetic or paramagnetic ($M = 0$) and ferroelectric ($P > 0$) one. In this case, magnetic (electric) field destruction of P (M) should be observed. Both the features can be viewed as the colossal magnetoelectric (CME) effect.

In fact, the huge or switching type ME effects, which have recently been observed in magnetic ferroelectrics such as RMnO_3 [13,14] and RMn_2O_5 [15,16] with R being Tb, Dy, etc., are all derived from the above bicritical-state phase control. Near the multiferroic (or magnetic ferroelectric) phase of the actual compound, the competing nonmultiferroic phase can be almost always found. This means that the bicritical-state CME phenomena based on the scheme shown in Fig. 4(b) are quite ubiquitous as far as the ferroelectricity of magnetic origin is realized. Then, the problem is how to design the multiferroic material with possibly strong M – P coupling.

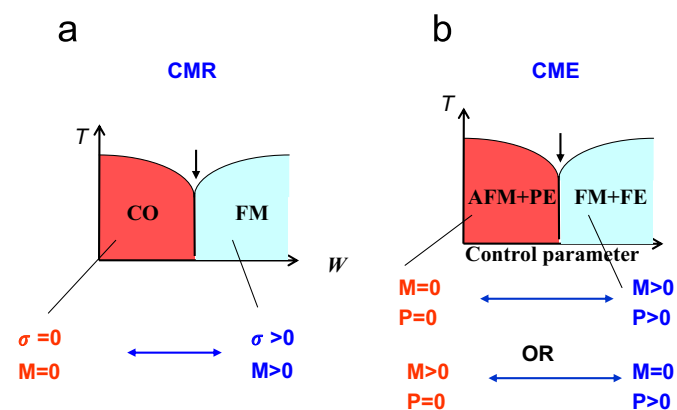


Fig. 4. Bicritical-state phase control. (a) Colossal magnetoresistive (CMR) effect. The insulating charge-ordered (CO) state with small conductivity σ and no magnetization bicritically competes with the metallic and ferromagnetic ($M > 0$) state with the one-electron bandwidth (W) as the control parameter. (b) Colossal magnetoelectric (CME) effect. In case the bicritical competition is present between the multiferroic (FM + FE) and nonmultiferroic (e.g., antiferromagnetic AFE + paraelectric PE) states with respect to some control parameter, the CME effect is caused via the electric-field or magnetic-field induced phase change.

4. How to make magnetic ferroelectrics

To produce a ferroelectric state in a magnetically ordered state, the following cases may be considered:

- (1) Bi^{3+} or Pb^{2+} (on the A-site) based perovskites with magnetic transition-metal ions on the B-site;
- (2) FM tricolor superlattices;
- (3) Charge ordering on a specific chemical lattice; and
- (4) transverse-spiral (cycloidal) spin order.

As for (1), in literature it has been known that some polar (with build-in P) crystals can also show spontaneous M (FM), in particular, the perovskite structure involving the Bi^{3+} or Pb^{2+} ions (on the A-site) as well as the magnetic B-site ions [17]. These polar ferromagnets can generally show very interesting linear and nonlinear optical properties arising from the ME response in the optical frequency region, yet the coupling between M and P at the electronic ground state appears to remain very small [18].

The tricolor superlattices (2) can be viewed as tailor-made multiferroics. Those are sequentially composed of

three layers, say A–C, among which at least one layer or one interface should be FM (Fig. 5). The interface of the ferromagnet is always polar, namely multiferroic or ferrotoroidic. To obtain macroscopic response, the fabrication of superlattice is conventional, but the accumulation of two kinds of layers, termed *bicolor* superlattice, leads to cancellation of the polarization or of the toroidal moments. In the tricolor superlattice, by contrast, the toroidal moments are not cancelled but rather accumulated, giving rise to the ferrotoroidic tailor-made compound.

In the actual tricolor superlattice, the respective layers, typically perovskite oxides, are of several unit-cell (u.c.) thicknesses (0.8–4 nm). The first example as designed is the combination of LaAlO_3 (LAO)– $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (LSMO)– SrTiO_3 (STO) [19]. The respective interfaces of the FM LSMO with STO and LAO should show different polarizations (and perhaps different magnetizations), which gives rise to the uncanceled toroidal moment. The nonlinear Kerr rotation experiment could clearly indicate the response of the toroidal moments at the interface and also the distinct variation of the interface ferromagnetism from that of the whole LSMO film [19].

More lately, the combination of non-ferromagnetic three kinds of layers, namely LaMnO_3 (LMO), SrMnO_3 (SMO), and LAO, has been tested [20]. Here, the interface between SMO (4 u.c. thick) and LMO (6 u.c. thick) is turned into FM due to the charge transfer via the interface, where the strong polarization generation is anticipated. In this case, the temperature variation of the interface magnetization as probed by the nonlinear Kerr rotation shows excellent agreement with that measured by a SQUID magnetometer. This kind of tailor-made multiferroic superlattices or

junctions may produce a unique arena to test the electric control of the magnetic structure in the future.

The case (3) is relevant to the charge ordering in the layered transition-metal oxides. The well-known example is RFe_2O_4 ($R = \text{Y, Lu, Eu, etc.}$), a bilayered-structure oxide with triangular Fe lattice, as pioneered by Kohn's group [21]. The charge ordering on this geometrically frustrated lattice appears to give rise to the charge-polarized state [22]. Another example is the bilayered manganites, $\text{PrCa}_2\text{Mn}_2\text{O}_7$ and its analogs [23]. The checker-board type charge ordering on the orthorhombically distorted bilayered lattice can give rise to the charge-polarized state as well, which further undergoes the antiferromagnetic transition. Such bilayered-structure transition-metal oxides with commensurate hole (electron)-doping levels may be a rich mine of magnetic ferroelectrics.

The case (4) represents the situation where some spin superstructure may intrinsically generate the ferroelectricity by itself. With respect to this, a useful hint to the designing of the strong M – P coupling has recently been gained by the discovery of the ferroelectricity in the spiral-spin magnets [13,24–26], as schematically shown in Fig. 6. When the spins on the adjacent atomic sites are canted from each other (Fig. 6(a)), the horizontal mirror-plane symmetry is lost, meaning the possible generation of polarization along the vertical direction. Recently, it has been theoretically shown [27,28] that the overlap of the electronic wave function between the two atomic sites with canted spins generates genuine electronic polarization via spin–orbit interaction. When the spins form the cycloidal modulation along the specific crystallographic direction (Fig. 6(b)), then every nearest-neighbor pair produces local unidirectional polarization and hence the macroscopic P of electronic (spin) origin should be generated. The direction of the polarization can be totally determined by the clockwise or counter-clockwise rotation of the spin in proceeding along the spiral propagation axis, that is called the spin helicity.

The spiral spin states are widely seen in complex transition-metal compounds like spinels and perovskites, where competing exchange interactions of the neighboring

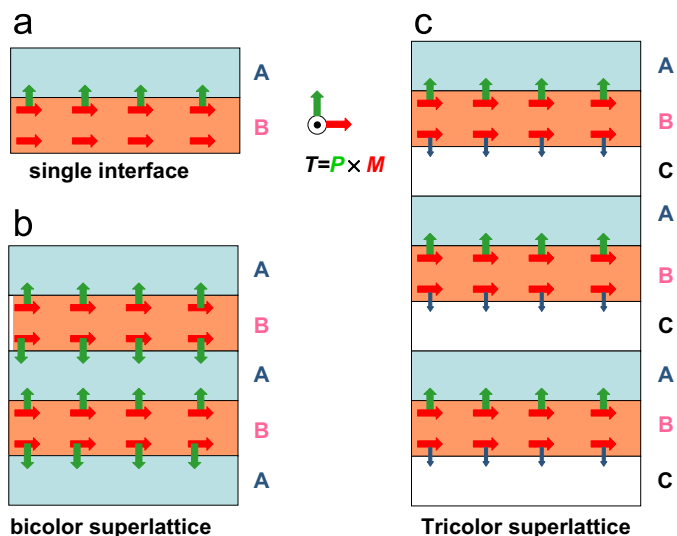


Fig. 5. The superlattices as tailor-made multiferroics; (a) single interface, (b) bicolor superlattice, and (c) tricolor superlattice. Solid thick arrows and gray arrows represent the spontaneous magnetization and the interface-related electric polarization, respectively. The toroidal moment is cancelled in bicolor superlattice (b), while uncanceled in the tricolor superlattice (c).

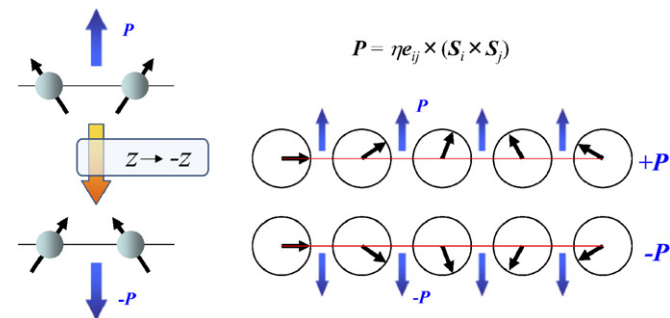


Fig. 6. (a) Interacting canted spins can generate electric polarization under the presence of spin–orbit interaction. (b) When the spins show the transverse-spiral or toroidal configurations, each neighboring spin pair shows local polarization, and the sum leads to the macroscopic polarization. The polarity depends on the helicity of the spiral mode, either clockwise or counter-clockwise.

spins can produce such a periodically modulated spin structure. In those compounds, the spin structure responsible for the spontaneous polarization can often be controlled by an external magnetic field of specific direction. Such a ferroelectric state of magnetic origin may in most cases compete with another ME phase, say a paraelectric–antiferromagnetic phase. As already argued in Section 3, the application of magnetic (or electric) field may induce first-order phase transition between those ME phases, resulting in the magnetic (or electric) control of the ME phases and hence the P (or M). In fact, this is the microscopic origin of the magnetic P -control as observed for the spiral-spin ferroelectrics [13,14]. The critical tuning of the ME phase competition may realize the CME phenomena, such as the electric-field induction of the FM phase, i.e. the function of *quantum electromagnet*.

5. Toward electric control of magnetism

To realize the real multiferroics, namely the concurrent FM and ferroelectric state, with use of spiral (cycloidal) spin configuration, one may consider the conical spin state (Fig. 7(a)), that can be viewed as the sum of the FM component and transverse-spiral one. A remarkable characteristic expected for this kind of multiferroics is the electric (magnetic) reversal of the M (P) vector, as schematically shown in Fig. 1. Namely, the multiferroics of all spin origin may show the clamping of the FM and ferroelectric domain walls. The directions of M and spin helicity (or equivalently P) are orthogonal, and hence the toroidal moment defined as $T = P \times M$ may behave as the most robust order parameter. Note that the toroidal moment T shows no domain wall in Fig. 7(b), albeit the clamped M and P domain walls.

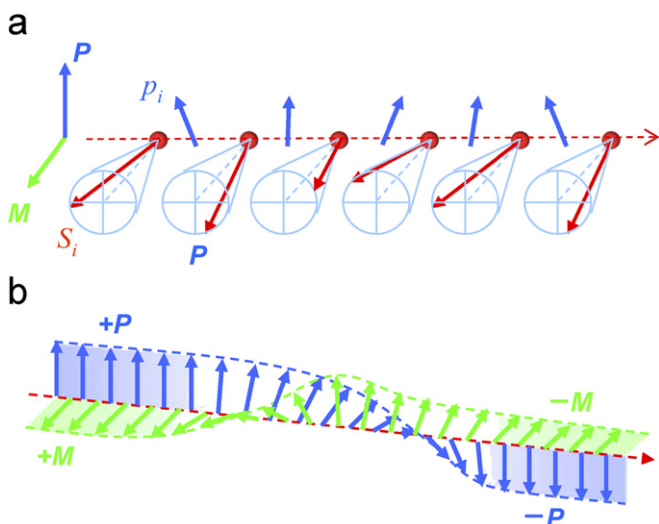


Fig. 7. (a) Spin conical structure as a candidate of multiferroics of all magnetic origin. p_i represents the local polarizations, the sum of which generates the macroscopic polarization P . Thus, the magnetization M of the conical spin is always orthogonal to P , directing its toroidal moment along the propagation vector. (b) Possible domain wall clamping of the multiferroics of the magnetic origin.

Recently, such a multiferroic state has been observed for the spinel oxide, CoCr_2O_4 . It has long been known that the Cr-oxide spinels MCr_2O_4 ($M = \text{Mn, Fe, and Co}$) show the conical spin structure due to the combined effect of the geometrical spin frustration on the Cr sites and the exchange interaction between the Cr and M spins [29]. According to the scenario shown in Figs. 6 and 7, these should be ferroelectrics, which was in fact confirmed experimentally [30].

Fig. 8 as reproduced from Ref. [30] shows the magnetic field induced reversal of the ferroelectric polarization in CoCr_2O_4 . As shown in Fig. 8(a), the crystal which was once cooled under low electric ($E_c = 400 \text{ kV/m}$) and magnetic ($H_c = 0.5 \text{ T}$) fields to prepare a single multiferroic domain, shows reversal of the polarization with reversal of the magnetization, irrespective of starting from $+H_c$ or $-H_c$ side. When the magnetic field scan enabling the reversal of the magnetization is repeated, the polarization is also reversed in a synchronized manner, as shown in Fig. 8(b). These experimental observations clearly indicate the multiferroic domain wall clamping, as shown in Fig. 7(b). In other words, once the toroidal moment $T = P \times M$ is fixed

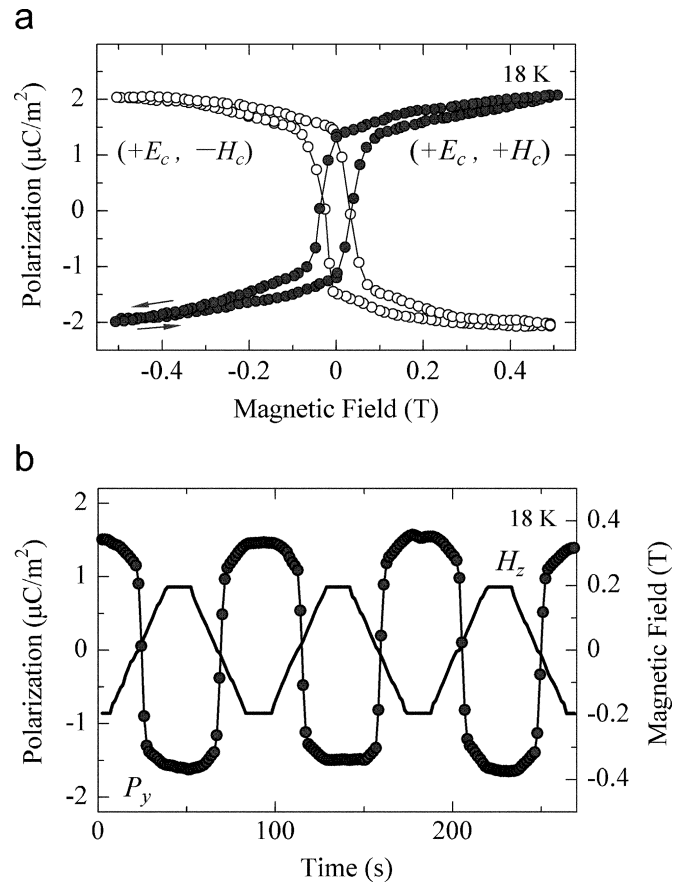


Fig. 8. (a) Magnetic field dependence of electric polarization at the multiferroic state (18 K) in CoCr_2O_4 with conical spin structure for the respective cases of electric (E_c) and magnetic (H_c) cooling procedures. ($E_c = 400 \text{ kV/m}$ and $H_c = 0.5 \text{ T}$) (b) The synchronized reversal of the polarization P_y , with reversal of the external magnetic field H_z . The reversal of H means that of the magnetization, which is orthogonal ($\parallel z$) to the direction of polarization ($\parallel y$). Reproduced from Ref. [30].

in a single-domain manner, it remains as a robust order parameter even when the M (and perhaps also P) is reversed. Specifically to the multiferroics with conical spin structure, the spin helicity (say, counter-clockwise) is expected to be simply reversed (say, to clockwise) by the reversal of the magnetization along the cone axis (see Fig. 7). This is quite reasonable in case the spin spiral habit is not violated across the magnetic domain wall.

Such a synchronized reversal of the ferroelectric domain with that of the FM domain strongly indicates the possibility of electric-field reversal of the magnetic domain. (In CoCr_2O_4 , unfortunately, the spontaneous polarization is too small to reverse the ferroelectric domain by a manageable electric field, in spite of the easy and unusual reversal in terms of an external magnetic field.) The clamping of the ferroelectric and FM domain walls should be possible as far as the toroidal moment as derived from spin–orbit coupling is a robust order parameter. Therefore the synchronized reversal of the FM and ferroelectric domains may not be a feature specific to the conical-spin multiferroics. The electric control of the magnetic domains or the magnetic structure, which bears the important implication for application to spintronics, will be realized in the field of the multiferroics.

Acknowledgments

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