Electric-field-induced switching dynamics of cycloidal spins in multiferroic BiFeO₃: phase-field simulations

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A phase-field model is developed to describe polarization and cycloidal antiferromagnetic orders in BiFeO₃. From symmetry argument and phase-field simulations, we identify and calculate 12 types of transitional spin structures between two cycloids, and 7 paths of electric-field-induced spin switching. Due to the magnetoelectric coupling, electric fields can rotate the wave vector of cycloidal spins by 0°, 60°, or 90°. The cycloidal spins demonstrate two types of switching dynamics: fast local flipping while maintaining its wave vector and slow growth of the region with a new wave vector.
In ferroelectrics and ferromagnets, electric and magnetic fields control electric-polarization and magnetization, respectively, and yet the cross-control, namely the magnetoelectric effect, is highly nontrivial and may provide foundation for next generation electronic devices [1,2]. Multiferroics, with more than one ferroic orders, may possess strong magnetoelectric effect, if its ferroelectric and magnetic orders are directly coupled to each other. In certain multiferroics, ferroelectric polarization coexists with spin density waves, where the spin helicity is coupled to the polarization direction [3,4]. In these materials, the polarization can be switched by magnetic fields [5], and the spin helicity is controlled by the direction of polarization [6].

BiFeO$_3$ crystals are room-temperature multiferroics with spontaneous polarization and cycloidal antiferromagnetic (AFM) order [7]. BiFeO$_3$ exists in $R\bar{3}c$ perovskite structure, and its polarization, with magnitude as large as $\sim$100 $\mu$C/cm$^2$, is along one of its eight $[111]_{\text{pseudocubic}}$ directions [8]. Below the Neel temperature 370 $^\circ$C, the short-range magnetic ordering of BiFeO$_3$ is G-type antiferromagnet, i.e., each Fe$^{3+}$ spin is surrounded by six antiparallel spins on the nearest Fe neighbors. The spins on the nearest Fe neighbors are not exactly antiparallel to each other due to a weak canting moment caused by the local magnetoelectric coupling [9], and a net magnetization exists locally [10]. A long-range superstructure, with period of 62-64 nm, is superimposed on this canting, resulting in an incommensurate spin cycloid of the AFM ordered sublattices [11]. The AFM easy plane, within which the spins rotate, is spanned by the polarization vector and a wave vector. The wave vector is perpendicular to polarization and along one of the twelve $[110]_{\text{pseudocubic}}$ directions (Fig. 1b). The cycloidal spin order is known to exist in BiFeO$_3$ bulks [11,12], and was thought to be suppressed by epitaxial strains in BiFeO$_3$ films [13,14]. Recently, the spin cycloid is also observed in BiFeO$_3$ films [10,15-17], and the cycloidal spins can be controlled by applied electric fields [10,16]. However, a systematic study on the cycloidal spin structures and electric-field-induced spin switching dynamics has not been achieved.

In this Letter, we employ Landau theory and phase-field simulations to investigate the spin configurations and magnetoelectric switching dynamics of the cycloidal spin orders in BiFeO$_3$. The region with uniform polarization and spin wave vectors is regarded as one AFM domain. 24 AFM domains and 12 types of domain walls are identified, and the corresponding domain wall energies are calculated. After the polarization is switched by electric fields, the cycloidal spin demonstrates 7 types of switching paths, where the wave vector is rotated by 0°, 60°, or 90°. When
the wave vector maintains its direction during the whole process, the switching is fast and only involve with the local flop of spins. For the other cases, the switching is characterized by two steps: local spin flipping while maintaining the wave vector, and growth of the domains with a new wave vector.

Three sets of order parameters are included in the free energy expression, i.e., polarization \( P_i(i = 1 – 3) \), oxygen octahedral tilt \( \theta_i(i = 1 – 3) \) [18], and AFM order parameter \( L_i(i = 1 – 3) \).

\( L_i = \frac{1}{2}(M_{ai} - M_{bi}) \) is the Neel vector describing the staggered sublattice magnetization (Fig. 1a). The total free energy is written as [15,18,19]

\[
F = \int dV \left[ \alpha_{ij} P_i P_j + \alpha_{ijkl} P_i P_j P_k P_l + \beta_{ij} \theta_i \theta_j + \beta_{ijkl} \theta_i \theta_j \theta_k \theta_i + t_{ijkl} P_i P_j \theta_k \theta_i + K_1 (L_1^2 L_2^2 + L_1^2 L_3^2 + L_2^2 L_3^2) + K_2 L_1^2 L_2^2 L_3^2 + h(L \cdot P)^2 + \frac{1}{2} g_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l} + A \sum_{i=1,2,3} (\nabla L_i)^2 + \gamma P \cdot [L(L \cdot L) - (L \cdot \nabla) L] \right]
\]

where \( \alpha_{ij}, \alpha_{ijkl}, \beta_{ij}, \beta_{ijkl}, \) and \( t_{ijkl} \) are the coefficients of Landau polynomial for \( P \) and \( \theta \); \( K_1 \) and \( K_2 \) are the anisotropy constants for \( L \); \( h \) is the biquadratic coupling coefficient between \( L \) and \( P \); \( g_{ijkl} \) and \( \kappa_{ijkl} \) are the gradient energy coefficients for \( P \) and \( \theta \); \( A \) is the antiferromagnetic exchange constant; \( \gamma \) is the coefficient for the inhomogeneous magnetoelectric interaction [15]. The last term is called the Lifshitz invariant, which is responsible for the incommensurate spin cycloid [3,20]. Note that \( L \) is assumed to be only coupled to \( P \), and independent of \( \theta \). The reason that \( \theta \) is incorporated in Eq. (1) is to stabilize the Ising-like 180° ferroelectric domain walls [18,21]. The coefficients related to \( P \) and \( \theta \) are taken from Ref. [18], and the values of \( h, A, \) and \( \gamma \) are from Ref. [15]. The anisotropy constants are approximated to be \( K_1 = -1.0 \times 10^4 J/m^3 \), and \( K_2 = 3.1 \times 10^4 J/m^3 \), which produces an easy direction of \( L \) along \([110]_{\text{pseudocubic}} \) [22]. All the coefficients are listed in Table SI. The coordinate system is rotated when needed [18].

The evolution of \( P \) and \( \theta \) is described by the time-dependent Ginzburg-Landau (TDGL) equations
\begin{align}
\frac{\delta P_i}{\delta t} &= -K_p \frac{\delta F}{\delta P_i}, \quad \frac{\delta \theta_i}{\delta t} = -K_\theta \frac{\delta F}{\delta \theta_i},
\end{align}

where $K_p$ and $K_\theta$ are the kinetic coefficients related to the domain wall mobility. The TDGL equations are solved based on a semi-implicit spectral method [23-25], and it is assumed that $K_p = K_\theta = 0.01\text{ arb.units}$ in the simulations.

$L$ is evolved by solving the Landau-Lifshitz-Gilbert (LLG) equation

\begin{align}
\frac{\delta L}{\delta t} &= -\mu L \times H_{\text{eff}} + \nu L \times \frac{\delta L}{\delta t},
\end{align}

where $\mu$ is the electron gyromagnetic ratio ($\mu = 2.21 \times 10^8 \text{ m/(A \cdot s)}$) and $\nu$ the Gilbert damping constant ($\nu = 0.5$). $H_{\text{eff}}$ is the effective field acting on $L$, calculated as $H_{\text{eff}} = -\frac{1}{\mu_0 L_s} \frac{\delta F}{\delta L}$, where $\mu_0$ is the vacuum permeability and $L_s$ is the saturation AFE magnetization ($L_s \approx 5.6 \times 10^5 \text{ A/m}$ following [26]). The details on the numerical solution of the LLG equation can be found in Ref. [27].

We first consider the ground state of $L$, which is a spin density wave, as illustrated in Fig. 1(b). Given polarization $P$ and wave vector $k$, the cycloidal distribution of $L$ is expressed by (see supplementary materials for the derivation details)

\begin{align}
L = -\frac{\gamma P}{|\gamma P|} \cos(\mathbf{k} \cdot \mathbf{x}) + \frac{k}{|k|} \sin(\mathbf{k} \cdot \mathbf{x}),
\end{align}

where $\mathbf{x}$ is a spatial vector. In the description by Eq. (4), the helicity of a cycloid is determined by the sign of $\gamma P$, and independent of the sign of $\mathbf{k}$, i.e., $\mathbf{k}$ and $-\mathbf{k}$ correspond to the same spin cycloid. This is illustrated in Fig. 1(b), where the spin cycloid possesses 2-fold rotation symmetry and can be interpreted with two antiparallel $\mathbf{k}$.

The Lifshitz invariant guarantees that the system obtains its energy minima when $\mathbf{k}$ is perpendicular to $P$ [3]. With $\mathbf{k}$ rotating within the plane perpendicular to $P$, the free energy versus the direction of $\mathbf{k}$ is plotted in Fig. 1(c), which shows six energy minima. Since antiparallel $\mathbf{k}$ correspond to the same spin cycloid, the six energy minima degenerate to three distinct
distributions of $\mathbf{L}$. The orientation anisotropy in Fig. 1(c) is caused by the anisotropy term (see Fig. S2b for the isotropic energy surface with $K_1 = K_2 = 0.0 \text{J/m}^3$). The free energy also depends on the wavelength of the spin cycloid, and the corresponding profile is plotted in Fig. S1(b), which shows an equilibrium wavelength of $\sim 62 \text{ nm}$ [12].

![Diagram](image)

**FIG. 1.** Illustration of cycloidal AFM orders. (a) Schematic of AFM sublattice. (b) Spin cycloid with green arrows indicating the $\mathbf{L}$ vectors. The red arrows specify 2-fold rotation axes. (c) Polar plot of free energy versus the direction of $\mathbf{k}$.

A spin cycloid can be specified by the directions of $\mathbf{P}$ and $\mathbf{k}$, assuming that its wavelength maintains the equilibrium value. $\mathbf{P}$ has 8 [111]pseudocubic directions, and each $\mathbf{P}$ direction possesses 3 options of $\mathbf{k}$ as in Fig. 1(c). Therefore, there exist a total of $8 \times 3 = 24$ types of cycloidal spin patterns (domains), which are symmetry-related and energy-degenerate. Alternatively, we may start from the $\mathbf{k}$ vectors. Since antiparallel $\mathbf{k}$ produces the same distribution of $\mathbf{L}$, 12 [110]pseudocubic directions correspond to 6 $\mathbf{k}$ vectors. 4 $\mathbf{P}$ directions are perpendicular to each $\mathbf{k}$, e.g., $\mathbf{P} = [1\bar{1}\bar{1}],[1\bar{1}1],[\bar{1}11]$, and $[\bar{1}1\bar{1}]$ are perpendicular to $\mathbf{k}=[110]$. Again, the number of spin cycloid variants is $6 \times 4 = 24$. 
Next we consider magnetic domain walls, which are the transition regions between 2 spin cycloids. Similar to the classification of traditional ferroelectric domain walls [28], symmetry-related magnetic domain walls will be considered as one type. A domain wall is characterized by three factors: angle change of $\mathbf{P}$ across the wall $\Delta \mathbf{P}$, angle change of $\mathbf{k} \Delta \mathbf{k}$, and domain wall orientation. We label a domain wall by $\Delta \mathbf{P} \cdot \Delta \mathbf{k}$, and add more description when a specific $\Delta \mathbf{P} \cdot \Delta \mathbf{k}$ corresponds to more than one wall orientations. $\Delta \mathbf{P}$ has four options, i.e., 0°, 71°, 109°, and 180°. $\Delta \mathbf{k}$ has three options, i.e., 0°, 60°, and 90°.

In the domain wall calculation, the system is $600 \Delta x \times 600 \Delta x \times 1 \Delta x$ with $\Delta x = 1.0 \text{nm}$ for BiFeO$_3$, and buffer layers with the thickness $202 \Delta x$ are added to the boundaries of BiFeO$_3$ to eliminate the effect of periodic boundary conditions (see Fig. S4). Within the buffer layer, $\mathbf{L}$ is maintained as $\mathbf{0}$. We run phase-field simulations with two preset domains, and show the distribution of $\mathbf{L}$ after the system is fully relaxed. Since 71° and 180° polarization switching is observed in BiFeO$_3$ films and bulks [11,29,30], the main text shows the domain walls with $\Delta \mathbf{P} = 180°$ and $\Delta \mathbf{P} = 71°$, with the other cases listed in the supplemental materials.

With $\Delta \mathbf{P} = 180°$, the $\mathbf{P}$ vectors in the two domains are antiparallel, and thus share the same set of permissible $\mathbf{k}$ vectors. As shown in Fig. 1(c), $\Delta \mathbf{k}$ has two options: 0° and 60°. To reduce the electrostatic energy, the domain wall normal $\mathbf{n}$ is confined within the plane perpendicular to $\mathbf{P}$ [28]. If we only consider domain walls with low Miller indices, $\mathbf{n}$ has three options, the same set of directions as $\mathbf{k}$. For example, for $\mathbf{P} = [111]$ and $\mathbf{P}' = [\overline{1} \overline{1} \overline{1}]$, the possible directions of $\mathbf{n}$ and $\mathbf{k}$ are $[1 \overline{1} 0]$, $[10 \overline{1}]$, and $[01 \overline{1}]$. A spin cycloid can be labelled by $\mathbf{P} \cdot \mathbf{k}$. With $\Delta \mathbf{k} = 0°$, the 180°-0° domain walls include two types of domain walls considering different orientations of $\mathbf{n}$. For example, if the two domains are $[111] - [\overline{1} \overline{1} 0]$ and $[\overline{1} \overline{1} \overline{1}] - [1 \overline{1} 0]$, and $\mathbf{n}$ is along $[1 \overline{1} 0]$, the two $\mathbf{k}$ vectors are symmetric with respect to the domain wall plane (Fig. 2a), which is thus labelled as 180°-0° symmetric walls. On the other hand, when $\mathbf{n}$ is changed to along $[10 \overline{1}]$ or $[01 \overline{1}]$, the two $\mathbf{k}$ vectors are asymmetric relative to the domain wall as shown in Fig. 2(b), labelled as a 180°-0° asymmetric wall. Similarly, 180°-60° walls can be symmetric or asymmetric, as in Figs. 2(c) and S3(c).
With $\Delta P=0^\circ$, $\Delta k$ can only take the value of $60^\circ$ ($0^\circ-0^\circ$ corresponds to a single domain). Similar to the cases with $\Delta P=180^\circ$, $k$ across $0^\circ-60^\circ$ walls can be symmetric or asymmetric with respect to the domain walls, as shown in Figs. S3(a) and S3(b).

The domain wall orientations with $\Delta P=71^\circ$ and $\Delta P=109^\circ$ are fixed by the mechanical compatibility condition and electrical neutrality condition [28], and thus the corresponding domain walls are fully specified by $\Delta P$ and $\Delta k$. For both the cases, $\Delta k$ has three options: $0^\circ$, $60^\circ$, and $90^\circ$. The spin structures across the $71^\circ-0^\circ$, $71^\circ-60^\circ$, and $71^\circ-90^\circ$ walls are illustrated in Figs. 2(d)-2(f), among which the $71^\circ-90^\circ$ walls are experimentally observed with a single-spin magnetometer [10]. Three domain walls with $\Delta P=109^\circ$ are shown in Figs. S3(d)-S3(f). Therefore, there are totally 12 types of domain walls for the cycloidal AFM order in BiFeO$_3$.

The domain wall energies are further calculated. We compute the system energies for three cases: single domain 1, single domain 2, and two domains with a wall in the middle, whose system energies are labelled by $F_1$, $F_2$, and $F_{12}$, respectively. Then the domain wall energy is obtained by $\Delta F = F_{12} - (F_1 + F_2) / 2$. Note that only the energy terms dependent on $L$ are included in the energy calculation, since the energy penalty from the magnetic part is much smaller than that from the structural part as will be discussed later.

The obtained domain wall energies for the 12 types of domain walls are listed in Table I. The domain wall energies are on the order of $1$-$200$ $\mu$J/m$^2$, much smaller than the domain wall energies from the structural part (50-300 mJ/m$^2$) [18]. Therefore, the energy penalty from the magnetic part makes small contribution to the total domain wall energy. Note that the $180^\circ-0^\circ$ symmetric wall has the smallest energy in Table I. From Eq. (4), $L$ rotates in the opposite senses across a $180^\circ-0^\circ$ domain wall. As shown in Fig. 2(a), the $180^\circ-0^\circ$ symmetric wall serves as a mirror, resulting in small energy penalty. On the other hand, the $180^\circ-0^\circ$ asymmetric wall has the largest domain wall energy due to the large variation of $L$, as shown in Fig. 2(b). The energy sequence for $\Delta P=71^\circ$ is $71^\circ-90^\circ$-$71^\circ-0^\circ$-$71^\circ-60^\circ$ walls. However, it is reasonable to observe the $71^\circ-90^\circ$ walls in (001) BiFeO$_3$ thin films [10], since the $k$ vectors are constrained within the plane of the film. Similarly, in the (001) films with walls $\Delta P=109^\circ$ [31], $109^\circ-90^\circ$ walls are expected.
FIG. 2. AFM domain walls from phase-field simulations. Distribution of \( \mathbf{L} \) in a 180°-0° symmetric wall (a), 180°-0° asymmetric wall (b), 180°-60° symmetric wall (c), 71°-0° wall (d), 71°-60° wall (e), and 71°-90° wall (f). The colors of the arrows indicate the components along out of the plane (OOP) of the page. On the bottom of each panel, we label the directions of \( \mathbf{P} \) and \( \mathbf{n} \). The red dashed arrows specify the \( \mathbf{k} \) direction.

TABLE I. Domain wall energies of 12 types of AFM walls in BiFeO\(_3\). Only the energy terms related to \( \mathbf{L} \) are included.

| Domain wall types (\( \Delta \mathbf{P} - \Delta \mathbf{k} \)) | Wall energy (\( \mu \)J/m\(^2\)) |
|----------------------------------------------------------|-------------------------------------|
| 0°-60° (symmetric)                                       | 28.0                                |
| 0°-60° (asymmetric)                                      | 89.8                                |
| 180°-0° (symmetric)                                      | 1.40                                |
The above spin structures across a domain wall suggest how $L$ may be redistributed when $P$ rotates. Next we analyze how $L$ evolves after $P$ is switched by electric fields. In a domain with pre-equilibrium distribution of $P$ and $L$, $P$ is artificially switched at step 0, and the temporal evolution of $L$ is simulated. As discussed above, 4 $P$ orientations share one $k$ vector, and thus it is possible that $k$ maintains unchanged after $P$ is switched. Although three types of 71° switching of $P$ are possible, they are symmetrically inequivalent considering the existence of $L$. For example, for the $[111] - [1\overline{1}0]$ domain, if $P$ is switched to $P'=[1\overline{1}1]$, the initial $k$ is still perpendicular to $P'$, whereas it is not true if $P'=[1\overline{1}1]$ or $[\overline{1}11]$. For the former case, phase-field simulations show that $k$ maintains its direction during the switching. Adopting the same notation as domain walls, the process is labeled as 71°-0° switching. Similarly, we have 109°-0° and 180°-0° switching. Note that for $\Delta P=180^\circ$, the initial $k$ is always perpendicular to $P'$, resulting in 180°-0° switching. However, for $\Delta P=71^\circ$ and $\Delta P=109^\circ$, it is possible that the initial $k$ is not perpendicular to $P'$. In this case, the $k$ vector will rotate by 60° or 90° to reach the low energy state. From the domain wall types in Table I, four types of switching processes are possible with $\Delta k \neq 0$, i.e., 71°-60°, 71°-90°, 109°-60°, and 109°-90° switching. Overall, 7 types of switching dynamics are identified: 3 types with $\Delta k = 0$ and 4 types with $\Delta k \neq 0$. 

| Switching Type | Angle |
|----------------|-------|
| 180°-0° (asymmetric) | 204 |
| 180°-60° (symmetric) | 184 |
| 180°-60° (asymmetric) | 104 |
| 71°-0° | 73.3 |
| 71°-60° | 28.7 |
| 71°-90° | 113 |
| 109°-0° | 158 |
| 109°-60° | 139 |
| 109°-90° | 114 |
By solving the LLG equation of a one-dimension (1D) system \(1024 \Delta x \times 1 \Delta x \times 1 \Delta x\), we obtain the temporal evolution of \(L\) for the 71°-0° switching as shown in Movie I, and four snapshots are listed in Fig. 3(a). In the initial configuration, the spin with \(L\) parallel to \(P\) is labelled by \(L_P\), and the spin with \(L\) parallel to \(k\) by \(L_k\). As demonstrated in Fig. 3(a), \(L_k\) is almost unchanged, and \(L_P\) rotates to the \(P'\) direction finally. Using the spherical coordinates with the polar axis aligned to \(k\) and the azimuthal axis along \(P\), the change of \(L_P\) is plotted in Fig. 3(b). The precession of \(L_P\) is observed similar to the classical magnetizations [22]. Although the initial and final \(L_P\) is perpendicular to \(k\), \(L_P\) rotates out of the plane perpendicular to \(k\) in the transient state. In the this case, the distribution of \(L\) deviates from the sinusoidal function as described in Eq. (4), and the spin on the left side of \(L_P\) rotates to the \(P'\) direction the earliest, as indicated by red circles in Fig. 3(a).

The evolution of \(L\) for the 180°-0° switching is demonstrated in Movie II and in Figs. 3(c) and 3(d). Similar to the 71°-0° switching, \(L_k\) maintains unchanged, and \(L_P\) rotates from the direction of initial \(P\), tilts towards \(k\), and finally stops at the direction of \(P'\). The results for the 109°-0° switching are shown in Movie III, and Fig. S5. Note that the switching processes with \(\Delta k=0°\) only involve with the local flop of \(L\). The 71°-0° and 180°-0° switchings are experimentally observed in BiFeO3 crystals and (111) films, respectively, by analyzing the wave vectors of spins before and after polarization switching [11,32].
FIG. 3. Spin switching dynamics with $\Delta k = 0$. (a) Four snapshots during $71^\circ$-$0^\circ$ switching. $L_P$ is the spin with the initial $L$ parallel to $P$. (b) Evolution of $L_P$ during $71^\circ$-$0^\circ$ switching using spherical coordinates. (c) Four snapshots during $180^\circ$-$0^\circ$ switching. (d) Evolution of $L_P$ during $180^\circ$-$0^\circ$ switching. In (a) and (c), the colors of the arrows indicate the component along OOP of the page.

To study the switching dynamics with $\Delta k \neq 0$, 2D simulations are employed. We use the same system setting as the domain wall energy calculation with buffer layers added (Fig. S4). $71^\circ$-$60^\circ$ switching is analyzed first, which is found to be characterized by two steps. In step-I, $k$ maintains unchanged, and $L$ rotates locally similar to the $71^\circ$-$0^\circ$ switching, as demonstrated in Figs. 4(b) and 4(c). However, at the end of step-I, $L_P$ does not align along the $P'$ direction. Instead, $L_P$ is parallel to the projection of $P'$ on the plane perpendicular to $k$. We also run a 1D simulation to confirm this, as shown in Fig. 4(a). Step-II mainly involves the rotation of $k$. As shown in Figs. 4(d) and 4(e), step-II is “first-order” like, and the region with a new $k$ vector nucleates and grows at the cost of the region with the initial $k$ vector. In the 2D simulation, the boundaries between BiFeO$_3$ and buffer layers serve as the nucleation sites as illustrated by Movie IV. The domain wall
motion in step-II is slow compared to the local spin flipping in step-I, e.g., for the 71°-60° switching, step-I is completed before 3,000 simulation steps, while step-II requires more than 70,000 simulation steps.

The simulation results for the 71°-90°, 109°-60°, and 109°-90° switching are shown in Movies V-VII and Figs. S6-S8. All the three processes exhibit two-step dynamics similar to that of 71°-60°. Note that with $\Delta P = 71^\circ$ and the initial $k$ not perpendicular to $P'$, both 71°-60° and 71°-90° switchings are permissible. We run a 3D simulation with grids $256\Delta x \times 256\Delta x \times 256\Delta x$, which shows that the 71°-60° switching is kinetically favored over the 71°-90° switching. Similarly, the 109°-60° switching is observed in 3D simulations. Therefore, the $k$ vector tends to rotate by smaller angles in BiFeO$_3$ bulks. However, in (001) BiFeO$_3$ films with $k$ constrained in the film plane, the 109°-90° switching is expected and observed in experiments [10].
FIG. 4. Spin evolution during 71°-60° switching. (a) Evolution of L based on a 1D simulation. (b)-(e) Zoomed snapshots from a 2D simulation, which are the results at (b) 0, (c) 2,000, (d) 7,000, and (e) 123,500 steps. The colors of the solid arrows indicate the component along OOP of the page. The red dashed arrows specify the k direction.

In summary, we systematically analyze the magnetic domain walls and electrically controlled spin switching dynamics in the cycloidal antiferromagnetic state of BiFeO$_3$. We identify 12 types of domain walls, and calculate the domain wall energies based on the phase-field method. After polarization is switched by electric fields, 7 paths of spin switching are found, among which 3 types maintain the k vector and 4 types rotate k by either 60° or 90°. Interestingly, the switching process with the k rotation is divided into two distinct steps: step-I, fast local flipping, and step-II, slow rotation of wave vectors. Since cycloidal spin orders are common in multiferroics, and
BiFeO$_3$ is an important ingredient in the multiferroic/ferromagnet heterostructures [33,34], our work paves a new way to understand and design the mutual control of polarization and magnetic orders.

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Supplementary Materials: Electric-field-induced switching dynamics of cycloidal spins in multiferroic BiFeO₃: phase-field simulations

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Supplementary movies

Supplementary Movie I: Evolution of the antiferromagnetic order parameter L during the 71°-0° switching. The dimensionless time step \( \tau = 0.01 \) (real time \( t \) is related to \( \tau \) through \( t = \frac{1 + v^2}{\mu L_s} \tau \) [1]).

Supplementary Movie II: Evolution of the antiferromagnetic order parameter L during the 180°-0° switching. The dimensionless time step \( \tau = 0.01 \).

Supplementary Movie III: Evolution of the antiferromagnetic order parameter L during the 109°-0° switching. The dimensionless time step \( \tau = 0.01 \).

Supplementary Movie IV: Evolution of the antiferromagnetic order parameter L during the 71°-60° switching. The switching process is slow, and the dimensionless time step is set to \( \tau = 0.05 \). To reduce the file size, we choose different simulation steps between neighboring frames since the evolution becomes slower with larger simulation steps. 0-5,000 steps, we choose one frame after each 500 steps; 5,000-20,000 steps, we choose one frame after each 3,000 steps; 20,000-120,000 steps, we choose one frame after each 20,000 steps.

Supplementary Movie V: Evolution of the antiferromagnetic order parameter L during the 71°-90° switching. The process is slow, and the dimensionless time step is set to \( \tau = 0.05 \). To reduce the file size, we choose different simulation steps between neighboring frames. 0-5,000 steps, we choose one frame after each 500 steps; 5,000-20,000 steps, we choose one frame after each 3,000 steps; 20,000-120,000 steps, we choose one frame after each 20,000 steps.

Supplementary Movie VI: Evolution of the antiferromagnetic order parameter L during the 109°-60° switching. The process is slow, and the dimensionless time step is set to \( \tau = 0.05 \). To reduce
the file size, we choose different simulation steps between neighboring frames. 0-5, 000 steps, we choose one frame after each 500 steps; 5,000-20,000 steps, we choose one frame after each 3,000 steps; 20,000-120,000 steps, we choose one frame after each 20,000 steps.

Supplementary Movie VII: Evolution of the antiferromagnetic order parameter $L$ during the $109^\circ$-$90^\circ$ switching. The process is slow, and the dimensionless time step is set to $\tau = 0.05$. To reduce the file size, we choose different simulation steps between neighboring frames. 0-5, 000 steps, we choose one frame after each 500 steps; 5,000-20,000 steps, we choose one frame after each 3,000 steps; 20,000-120,000 steps, we choose one frame after each 20,000 steps.

I. Derivation of cycloidal distribution Eq. (4)

A spin cycloid rotates $L$ within a two-dimensional (2D) plane, and we assume the plane is spanned by the unit vectors $e_1$, $e_2$. Since $P$ is within the 2D plane, we can choose $e_1$ along the $P$ direction, i.e., $e_1 = \frac{P}{|P|}$. Note that in 3D spaces, the distribution of $L$ is uniform along the third direction, and the component along the third direction maintains as zero. Assuming that the wave vector is $k$, the distribution of $L$ is given by

$$L = e_1 \cos(k \cdot x) + e_2 \sin(k \cdot x), \quad (S1)$$

where $x$ is a spatial vector. Since $P$ is perpendicular to $k$, and $k$ is also within the 2D plane, we have either $k = |k| e_2$, or $k = -|k| e_2$, which correspond to opposite rotation senses with the fixed $e_2$. The two rotation senses produce different energies in the term $\gamma P \cdot [L(\nabla \cdot L) - (L \cdot \nabla)L]$, which is linearly proportional to the gradient of $L$. Therefore, based on the sign of $\gamma$, either $k = |k| e_2$ or $k = -|k| e_2$ has the lower energy. Considering only the low energy state, we have the relation $e_2 = -\frac{\gamma k}{|\gamma k|}$. Then Eq. (S1) becomes

$$L = \frac{P}{|P|} \cos(k \cdot x) - \frac{\gamma k}{|\gamma k|} \sin(k \cdot x), \quad (S2)$$
Eq. (S2) can be further modified to
\[ \mathbf{L} = -\frac{\gamma \mathbf{P}}{||\mathbf{P}||} \cos(\mathbf{k} \cdot \mathbf{x}) + \frac{\mathbf{k}}{||\mathbf{k}||} \sin(\mathbf{k} \cdot \mathbf{x}), \tag{S3} \]

When \( \gamma > 0 \), Eqs. (S2) and (S3) are differentiated by a phase shift, i.e., \( x \rightarrow x + \pi \). When \( \gamma < 0 \), Eqs. (S2) and (S3) are equivalent. Eq. (S3) is Eq. (4) in the main text. Eqs. (S2) and (S3) indicate \( \mathbf{L}(\mathbf{k}) = \mathbf{L}(-\mathbf{k}) \). The physical meaning is that if \( \mathbf{P} \) is fixed, and \( \mathbf{k} \) rotates its direction within the plane perpendicular to \( \mathbf{P} \), then the spins returns to the original configuration after a 180° rotation, i.e., the spin cycloid possesses 2-fold rotation symmetry as shown in Fig. 1(b).

II. Coefficients of BiFeO\(_3\) used in the phase-field simulation

| Table SI. Coefficients of BiFeO\(_3\) used in the simulation (SI units) |
|---------------------------------------------------------------|
| \( \alpha_{11} \)   | \( -3.580 \times 10^8 \) | \( g_{1122} \)   | \( -3.400 \times 10^{-12} \) |
| \( \alpha_{1111} \) | \( 3.000 \times 10^8 \)  | \( g_{1212} \)   | \( 3.400 \times 10^{-12} \) |
| \( \alpha_{1122} \) | \( 1.188 \times 10^8 \)  | \( \kappa_{1111} \) | \( 7.840 \times 10^{-11} \) |
| \( \beta_{11} \)   | \( -5.400 \times 10^9 \) | \( \kappa_{1122} \) | \( -5.138 \times 10^{-9} \) |
| \( \beta_{1111} \) | \( 3.440 \times 10^{10} \) | \( \kappa_{1212} \) | \( 4.977 \times 10^{-9} \) |
| \( \beta_{1122} \) | \( 6.799 \times 10^{10} \) | \( h \)             | \( -3.2 \times 10^4 \) |
| \( t_{11} \)      | \( 4.532 \times 10^9 \)  | \( A \)             | \( 4.0 \times 10^{-12} \) |
| \( t_{1111} \)    | \( 2.266 \times 10^9 \)  | \( \gamma \)        | \( 8.1 \times 10^{-4} \) |
| \( t_{1122} \)    | \( -4.840 \times 10^9 \) | \( K_1 \)           | \( -1.0 \times 10^4 \) |
| \( g_{1111} \)    | \( 4.335 \times 10^{-11} \) | \( K_2 \)           | \( 3.1 \times 10^4 \) |

III. Free energy as a function of the wavelength of the spin cycloid
First, we study the free energy as a function of wavelength based on analytical derivation. To simplify the problem, we only consider the exchange energy and inhomogeneous magnetoelectric interaction. The total free energy density is given by

\[ f = A \sum_{i=x,y,z} (\nabla L_i)^2 + \gamma \mathbf{P} \cdot [\mathbf{L} \cdot (\nabla \cdot \mathbf{L}) - (\mathbf{L} \cdot \nabla \mathbf{L})] , \quad (S4) \]

\[ \mathbf{L} \text{ can be written as } \mathbf{L} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \text{ in the spherical coordinate system as established in Fig. S1(a). If the polarization is set along the polar axis direction, Eq. (S4) can be rewritten as } [2] \]

\[ f = A((\nabla \theta)^2 + \sin^2 \theta (\nabla \phi)^2) \]
\[ + \gamma (\nabla_x \theta \cos \phi + \nabla_y \theta \sin \phi - \cos \theta \sin \theta (\sin \phi \nabla_x \phi - \cos \phi \nabla_y \phi))' , \quad (S5) \]

Since the modulation direction is perpendicular to the polarization, we assume the modulation direction is along \([1\bar{1}0]_{\text{pseudocubic}}\), which is defined as the y axis. Since \(\mathbf{L}\) is rotated within the plane spanned by \([111]_{\text{pseudocubic}}\) and \([1\bar{1}0]_{\text{pseudocubic}}\), we have \(\phi = \frac{\pi}{2}, \theta[x, y, z] = \theta[y]\), i.e., \(\phi\) is a constant, and \(\theta\) is a function of \(y\). Eq. (S5) is simplified to

\[ f = A(\frac{\partial \theta}{\partial y})^2 + \gamma \frac{\partial \theta}{\partial y} , \quad (S6) \]

The Euler-Lagrange equation gives

\[ \frac{\delta f}{\delta \theta} = -A \frac{\partial^2 \theta}{\partial y^2} = 0 , \quad (S7) \]

Therefore, \(\theta[y] = \frac{2\pi}{\lambda} y + y_0\), where \(\lambda\) is the wavelength, and \(y_0\) is the integration constant. If we set \(y_0\) as 0, and substitute the solution into Eq. (S6), we have

\[ f = A(\frac{2\pi}{\lambda})^2 - \gamma \frac{2\pi}{\lambda} , \quad (S8) \]

Eq. (S8) is plotted as a red line in Fig. S1(b), in comparison with the numerical results from phase-field simulations. The analytical and numerical results show good agreement, which
both give an energy minimum at equilibrium wavelength $\lambda_0 = \frac{4\pi A}{\gamma} \approx 62 \text{ nm}$. The value of the wavelength is in good agreement with experimental measurements [3].

FIG. S1. (a) Schematic of a spherical coordinate system with the polar axis aligned with the $[111]_{\text{pseudocubic}}$ direction and the azimuthal axis along $[\overline{1}12]$. (b) Free energy as a function of the wavelength of the spin cycloid. The red line represents the analytical solution, while the blue dots are from phase-field methods.

IV. Free energy as a function of modulation direction of the spin cycloid
FIG. S2. Polar plot of free energy versus the direction of \( \mathbf{k} \) for (a) \( K_1 = -1.0 \times 10^4 \text{J/m}^3 \), \( K_2 = 3.1 \times 10^4 \text{J/m}^3 \), and (b) \( K_1 = K_2 = 0.0 \text{J/m}^3 \). The polarization points along the direction of into-the-plane of the page.

V. Distribution of \( L \) in six magnetic domain walls

FIG. S3. Six magnetic domain walls from phase-field simulations. Distribution of \( L \) in (a) 0°-60° symmetric walls, (b) 0°-60° asymmetric walls, (c) 180°-60° asymmetric wall, (d) 109°-0° walls, (e) 109°-60° walls, and (f) 109°-90° walls. The colors of the arrows indicate the components along out-of-the-plane (OOP) of the page. On the bottom of each panel, we labelled the direction of polarization and \( n \) vectors. The red dashed arrows specify the \( k \) vectors.
VI. System setting to remove the effect of periodic boundary conditions

To remove the effect of periodic boundary conditions, BiFeO$_3$ is surrounded by buffer layers where L is maintained as 0, as shown in Fig. S4.

![Diagram](image)

FIG. S4. Schematic for system setting to remove the influence of periodic boundary conditions. Within the green box is BiFeO$_3$, and the surrounding pink regions are buffer layers with L maintained as 0. The blue box indicates the region within which the spins are plotted in Figs. 2 and S3.

VII. Spin evolution during 109°-0° switching
FIG. S5. (a) Four snapshots during $109^\circ-0^\circ$ switching. The colors of the arrows indicate the component along out-of-the-plane of the page. $L_P$ is the spins with the initial $L$ parallel to $P$. (b) Evolution of $L_P$ during the $109^\circ-0^\circ$ switching using a spherical coordinate. In the spherical coordinate system setting, the direction of the $k$ vector is chosen as the polar axis, and the initial polarization direction is chosen as the reference direction of the azimuth angle $\varphi$. 
VIII. Spin evolution during 71°-90° switching

FIG. S6. Spin evolution during 71°-90° switching. Four zoomed snapshots from a 2D simulation, which are the results at (a) 0, (b) 1,500, (c) 6,000, and (d) 122,500 steps. The colors of the solid arrows indicate the component along out of the plane of the page. The red dashed arrows specify the k direction.

IX. Spin evolution during 109°-60° switching
FIG. S7. Spin evolution during 109°-60° switching. Four zoomed snapshots from a 2D simulation, which are the results at (a) 0, (b) 1,000, (c) 3,000, and (d) 122,500 steps. The colors of the solid arrows indicate the component along out of the plane of the page. The red dashed arrows specify the k direction.

\[ P_{OOP} \ (C/m^2) \quad -1 \quad \text{red} \quad 1 \quad -1 \quad \text{red} \quad 1 \quad L_{OOP} \ (a.u.) \]

X. Spin evolution during 109°-90° switching
FIG. S8. Spin evolution during 109°-90° switching. Four zoomed snapshots from a 2D simulation, which are the results at (a) 0, (b) 1,500, (c) 6,000, and (d) 122,500 steps. The colors of the solid arrows indicate the component along out of the plane of the page. The red dashed arrows specify the \( \mathbf{k} \) direction.

\[
P_{OOP} \ (C/m^2) \quad -1 \quad \text{---} \quad 1 \quad -1 \quad \text{---} \quad 1 \\
L_{OOP} \ (\text{a.u.})
\]

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