

## Switching the curl of polarization vectors by an irrotational electric field

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Ferroelectric vortex domains are of significant interest due to their rich physics and potential applications. Here, we propose the crystallographic, strain, and electric conditions for spontaneous vortex domains and study the influence of oxygen octahedral tilt on vortex wall orientations. Using  $109^\circ$  domain walls in  $\text{BiFeO}_3$  films as an example, it is demonstrated that vortex domains result from bound charge-density waves, i.e., from alternating positive and negative bound charges. The vortex domains lead to a net curl of the polarization vectors that can be switched by an irrotational electric field.

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In ferroic materials, polarization and magnetization vectors may rotate around a point and form flux-closure domains, i.e., vortex domains. Although magnetic vortex domains are well known [1], polar vortex domains have only recently been observed and investigated [2–6]. Polar vortex domains are typically caused by either reduced size in three dimensions, such as in ferroelectric nanodots or nanoislands without charge compensation on the surfaces [7–9], or induced by local external electric fields, e.g., from a piezoresponse force microscope [10,11]. Although spontaneous vortex domains in ferroelectric thin films have been experimentally observed in  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  and  $\text{BiFeO}_3$  (BFO) [12–14], the necessary conditions for forming vortex domains in a heterostructure, e.g., a ferroelectric film on a substrate or one-dimensional superlattice (finite size in one dimension) are not known. Furthermore, the usefulness of these observed domains has been questionable due to the inability to reverse the chirality of the static vertices under experimental conditions.

BFO is a room-temperature antiferromagnet and ferroelectric with spontaneous electric polarization along the pseudocubic body diagonal directions as sketched in Fig. 1(a) [15]. The ferroelectric domains form  $71^\circ$ ,  $109^\circ$ , and  $180^\circ$  walls with the angles denoting the change in polarization directions across the domain walls. Vortex domains resulting from  $180^\circ$  polarization rotations within triangular-shaped domains have been observed near the intersection between the vertical  $109^\circ$  domain walls and the film/substrate interface in  $(001)_p$ -orientated BFO films (where the subscript  $p$  indicates pseudocubic indices) as illustrated in Fig. 1(c) [13,16]. We will refer to this vortex domain configuration as  $109/180$  vortex domains.

Besides having ferroelectric and antiferromagnetic orders, BFO also shows an out-of-phase oxygen octahedral tilt pattern, which is described by an axial vector. As shown in Figs. 1(e) and 1(f), the direction of the axial vector is chosen to be along the rotation axis of one octahedron, and the two situations with the axial vector parallel and antiparallel to the polarization direction are energetically degenerate [17]. Furthermore, the corner-sharing network of oxygen octahedra serves as the “skeleton” of the crystal, and the distortion

of the tilt vectors costs substantial energy [18]. Due to the possibility of the polarization and tilt vectors being antiparallel and the substantial energy cost related to the tilt vectors, the domain-wall energy hierarchy in BFO becomes  $109^\circ < 180^\circ < 71^\circ$  rather than the expected  $71^\circ < 109^\circ < 180^\circ$  [17–20].

In this Rapid Communication we propose the basic crystallographic, electric, and strain conditions for the formation of vortex domain structures in ferroelectric thin films and demonstrate that the handedness of these structures can be switched with experimentally accessible electric fields. The conditions are illustrated using the  $109^\circ$  domain walls in BFO as an example based on the Ginzburg-Landau-Devonshire theory with the equilibrium equations solved by the phase-field method [21,22]. From the phase-field simulations, we not only reveal the underlying origins of the vortex domains, but also show the significant contribution of the oxygen octahedral tilt to the vortex domain stability ignored in prior theoretical analyses.

We show that two conditions are required for the spontaneous generation of vortex domains in ferroelectric films or superlattices. The first is an interface separating a ferroelectric film from a nonpolar insulator. This can be easily realized by well-developed film growth techniques [23]. The interface locally reduces the polarization components perpendicular to the interface to minimize the depolarization field. The second is a driving force maintaining the overall polarization component perpendicular to the interface. The driving force can be a compressive strain due to the mismatch between the film and the substrate, or a crystallographic constraint as in the case of the  $(001)_p$  BFO films. Note that the first condition is short range with an influence local to the interface, whereas the second condition is global to the whole system.

To demonstrate the formation of vortex domains under the above conditions, the  $109^\circ$  domain walls in the  $(001)_p$  BFO films under a small epitaxial strain are studied as a model system. We choose the  $109^\circ$  domain walls since they have the lowest wall energy in BFO [18–20].

In the phase-field simulations, both polarization  $P_i$  ( $i = 1-3$ ) and oxygen octahedral tilt order parameters  $\theta_i$  ( $i = 1-3$ ) are incorporated [21,24,25]. The total free energy includes the contributions from the Landau bulk free energy, gradient

energy, elastic energy, and electrostatic energy [18,26],

$$F = \int_V \left[ \alpha_{ij} P_i P_j + \alpha_{ijkl} P_i P_j P_k P_l + \beta_{ij} \theta_i \theta_j + \beta_{ijkl} \theta_i \theta_j \theta_k \theta_l + t_{ijkl} P_i P_j \theta_k \theta_l + \frac{1}{2} g_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l} + \frac{1}{2} \kappa_{ijkl} \frac{\partial \theta_i}{\partial x_j} \frac{\partial \theta_k}{\partial x_l} + \frac{1}{2} c_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl} - \varepsilon_{kl}^0) - E_i P_i - \frac{1}{2} \varepsilon_0 \kappa_b E_i E_i \right] dV, \quad (1)$$

where  $\alpha_{ij}, \alpha_{ijkl}, \beta_{ij}, \beta_{ijkl}$ , and  $t_{ijkl}$  are coefficients of the Landau polynomial under stress-free boundary conditions,  $g_{ijkl}$  and  $\kappa_{ijkl}$  are the gradient energy coefficients,  $x_i$  is the spatial coordinate,  $c_{ijkl}$  is the elastic stiffness tensor,  $\varepsilon_{ij}$  and  $\varepsilon_{kl}^0$  are the total strain and eigenstrain, respectively,  $E_i$  is the electric field,  $\varepsilon_0$  is the permittivity of free space, and  $\kappa_b$  is the background dielectric constant [27].

Since the coupling term  $t_{ijkl} P_i P_j \theta_k \theta_l$  is biquadratic, the parallel and antiparallel orientations of  $[P_1 P_2 P_3]$  and  $[\theta_1 \theta_2 \theta_3]$  are energetically degenerate as shown in Figs. 1(e) and 1(f). The eigenstrain is related to the order parameters through  $\varepsilon_{ij}^0 = \lambda_{ijkl} \theta_k \theta_l + h_{ijkl} P_k P_l$ , where  $\lambda_{ijkl}$  and  $h_{ijkl}$  are coupling coefficients [28]. The electric field is calculated by  $E_i = -\frac{\partial \varphi}{\partial x_i}$  with  $\varphi$  denoting the electrostatic potential.

As shown in Fig. 1(b), the electrical boundary conditions of the top surface and bottom interface are set as a short circuit with  $\varphi = 0$  and an open circuit with  $D_3 = P_3 - \varepsilon_0 \kappa_b \frac{\partial \varphi}{\partial x_3} = 0$ , respectively [25]. The boundary conditions simulate the situation that the bottom interface has uncompensated bound charges due to a nonpolar insulator substrate, whereas the top surface is compensated by unavoidable screening charges adsorbed from the air [13,29].

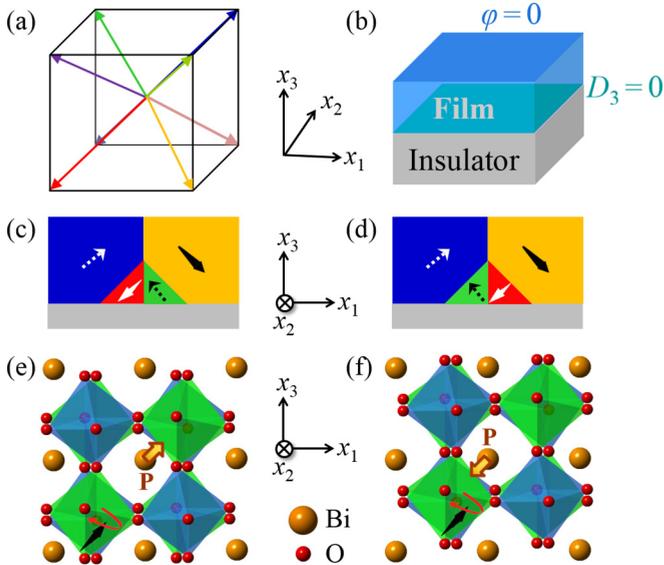


FIG. 1. (a) Symmetry-allowed polarization directions in BFO. (b) A schematic of the electrical boundary conditions of the BFO films. (c) A schematic of the vortex domains with the combination of 109° and 180° walls (109/180 vortex domains). (d) A schematic of the vortex domains with the combination of 109° and 71° walls (109/71 vortex domains). (e) and (f) Crystal structures of BFO with the same rotation axis (tilt vectors) and antiparallel polarization vectors as labeled by the black and orange arrows, respectively.

The mechanical and electrostatic equilibrium equations are solved using the methods described in Refs. [24,25]. All of the coefficients are listed in the Supplemental Material of Ref. [18]. The phase-field equations are solved with periodic boundary conditions along the in-plane  $x_1$  and  $x_2$  directions, and a superposition method is used along the  $x_3$  direction [22,24]. The system size is  $128\Delta x \times 128\Delta x \times 20\Delta x$  with a grid spacing of  $\Delta x = 0.38$  nm.

First, the 109° domain walls in Fig. 2(a) are analyzed to determine the driving force for the formation of vortex domains. The 109° walls separate two domains, which are denoted by  $[111, 111]$  and  $[\bar{1}\bar{1}\bar{1}, \bar{1}\bar{1}\bar{1}]$  with the notation  $[P_1 P_2 P_3, \theta_1 \theta_2 \theta_3]$  labeling the order parameters in a domain [18]. The two domains are modulated along the  $[100]_p$  direction, and the depolarization field is reduced by the alternating upward and downward polarization components [30,31]. Due to the presence of the electrically insulating substrate, the depolarization field tends to reduce the polarization component  $P_3$  near the bottom interface, and the polarization gradient gives rise to a bound charge density expressed by  $\rho_b = \frac{\partial P_3}{\partial x_3}$ .

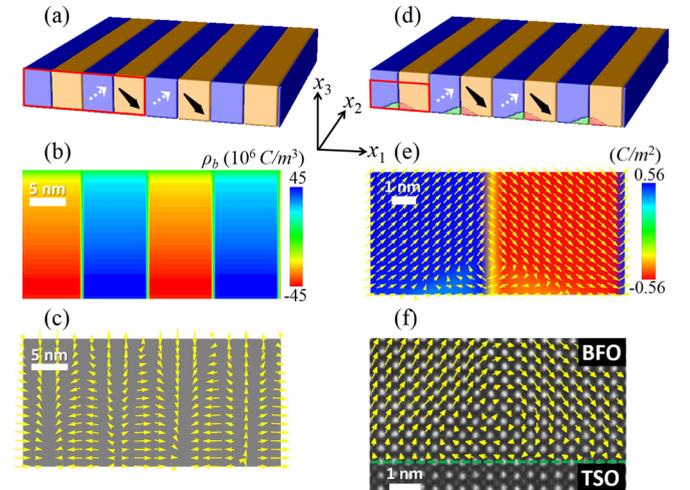


FIG. 2. The origin of vortex domains in BFO films. (a) The 109° domain walls without vortex domains. (b) The distribution of bound charges within the rectangular region in (a). (c) The distribution of electric fields induced by the bound charges in (b). (d) The 109/71 vortex domains from a phase-field simulation. (e) Polarization vectors within the region noted by the rectangle in (d). The color in (e) represents the polarization component out of the plane of the page. (f) Experimental HAADF STEM image of a 5-nm-thick BFO film grown on a (110) TbScO<sub>3</sub> substrate. The overlaid yellow vectors show the polarization distributions calculated from the atomic displacements between the Fe and the Bi atoms. (a)–(c) represent unstable structures and are plotted to explain the origin of the vortex domains in (d) and (e).

The upward and downward polarization components result in alternating positive and negative bound charges as plotted in Fig. 2(b). The modulation of the bound charges further induces an in-plane electric field alternating between  $+x_1$  and  $-x_1$  as shown in Fig. 2(c). The electric field pointing to  $+x_1$  lies along the same direction as the original  $P_1$ , which increases the magnitude of  $P_1$ . The electric field along  $-x_1$ , however, acts against the original  $P_1$ . Consequently, small triangular-shaped domains with switched  $P_1$  are nucleated at one half of the domain walls as shown in Fig. 2(d). The polarization vectors show continuous rotations and form flux-closure vortex domains as shown in Fig. 2(e). The vortex domains consist of two  $109^\circ$  walls and two  $71^\circ$  walls, which we call the 109/71 vortex domains as illustrated in Fig. 1(d). These are different from the previously discussed 109/180 vortex domains [13].

Similar vortex domains are observed in BFO films by atomic-scale high-angle annular-dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging as shown in Fig. 2(f) and Supplemental Material Fig. S6 [32]. Following the previous work [13,33], the HAADF STEM image was processed to generate a unit-cell-by-unit-cell map of the polarization vectors. In both Figs. 2(e) and 2(f),  $P_3$  is reduced near the bottom interface. Although the experimentally observed continuous rotation of the polarization vectors generally follows the calculated domain patterns shown in Fig. 2(e), there are subtle differences in the polarization directions and magnitudes near the vortex cores. It should be pointed out that the polarization vector distribution in the experiment is subject to measurement errors and can be affected by the presence of unavoidable defects in the sample, such as oxygen vacancies. Therefore, the agreement between the simulation and the experimental mappings is only considered to be qualitative.

The vortex domains in a ferroelectric film or superlattice are caused by the competition between the Landau bulk free energy (or elastic energy) and the electrostatic energy. Under large compressive strains or due to crystallographic constraint, e.g., rhombohedral phases in  $(001)_p$  films, the out-of-plane polarization component is unavoidable. Subjected to open-circuit boundary conditions, on either one or two interfaces, the ferroelectric domains tend to exist with alternating upward and downward polarization components to reduce the overall depolarization fields, leading to alternating positive and negative bound charges near the uncompensated interface. The bound charges yield an internal in-plane electric field, which gives rise to vortex domains near the domain walls. Here, in the main text, we show that vortex domains can be caused by the competition between the Landau bulk free energy and the electrostatic energy, whereas in the Supplemental Material [32] we show an example of vortex domains resulting from a large compressive strain in a tetragonal system.

If only one interface is in contact with an insulating nonpolar substrate as shown in Fig. 1(b), vortex domains are induced near the uncompensated interface. When both interfaces to the ferroelectric are subjected to insulating materials as in the case of superlattices or multilayers [14], vortex domains are formed near both interfaces, and the vortex domains near the  $109^\circ$  domain walls in BFO films with open-circuit boundary conditions on both interfaces are demonstrated in the Supplemental Material [32].

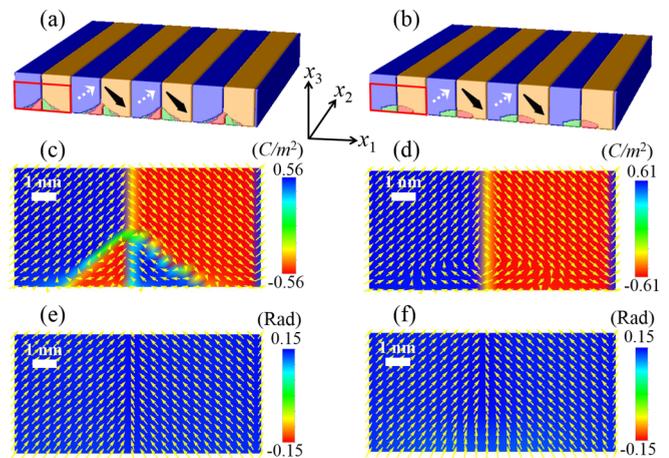


FIG. 3. Vortex domains in rhombohedral systems with and without oxygen octahedral tilt. (a) and (b) Domain structures in  $109^\circ$  domain walls with and without oxygen octahedral tilt, respectively. (c) and (d) Polarization vector distributions within the regions denoted by the rectangles in (a) and (b), respectively. (e) and (f) Distribution of the tilt vectors in the 109/180 and 109/71 vortex domains, respectively. The colors in (c)–(f) represent the vector components out of the plane of the page. The color bars for the tilt vectors in (e) and (f) are in full scale to emphasize the small variation of the out-of-plane tilt component.

When set as initial configurations in the phase-field simulations, the 109/180 vortex domains are found to be stable. Within the triangular-shaped regions, the polarization vectors in Fig. 3(c) are rotated by  $180^\circ$ , whereas the oxygen octahedral tilt vectors in Fig. 3(e) exhibit almost no change since the polarization can be parallel or antiparallel to the tilt vectors. On the other hand, in the 109/71 vortex domains, although the polarization is rotated by  $71^\circ$  in the triangular-shaped regions, the tilt vectors do not change significantly due to the substantial energy cost related to the variation of the tilt vectors as shown in Fig. 3(f). With the polarization and tilt vectors not parallel or antiparallel, the magnitude of the polarization vectors in the triangular-shaped regions is reduced as shown in Figs. 2(e) and 2(f).

The stabilities of the two types of vortex domains are determined by the competition between the differences of bulk energy and interfacial energy, i.e., dependent on the length scale. Since the angles between the polarization and the tilt vectors in the triangular-shaped regions of the 109/71 vortex domains are quite different from the equilibrium values, leading to larger bulk energy, the 109/180 vortex domains are more energetically favorable when the triangular-shaped regions are sufficiently large, and experimentally the 109/180 vortex domains are observed in BFO films thicker than 20 nm [13]. When the film thickness becomes 5 nm with the domain width reduced and the triangular-shaped regions shrinking correspondingly, the interfacial energy dominates, and the 109/71 vortex domains with smaller polarization variation are more energetically favorable. Therefore, both types of vortex domains are stabilized in the phase-field simulations and observed experimentally in BFO films; the appearance of each structure depends on film thickness.

Based on phase-field simulations, we also investigated the effect of the oxygen octahedral tilt on the formation of the vortex domains. The tilt order parameter is maintained at zero in the simulations, i.e.,  $\theta_i = 0 (i = 1-3)$ , which is the case for the rhombohedral phase in the classic ferroelectrics, e.g., rhombohedral  $\text{BaTiO}_3$ . Again the  $109^\circ$  domain walls are analyzed for comparison (for vortex domains near  $71^\circ$  and  $180^\circ$  walls, see the Supplemental Material [32]). In the  $109^\circ$  domain walls, separating the domains  $[111,000]$  and  $[1\bar{1}\bar{1},000]$ , the vortex domains in Figs. 3(b) and 3(d) are similar to  $109/71$  vortex domains with oxygen octahedral tilt as shown in Fig. 2(e). With polarization as the only order parameter, however, the  $109/180$  vortex domains are unstable when set as the initial conditions in the simulations, and the  $180^\circ$  walls change to  $71^\circ$  walls (the instability of the  $109/180$  vortex domains is independent of film thickness). This is because the domain-wall energy of the  $180^\circ$  walls is much larger than that of the  $71^\circ$  walls with polarization as the only order parameter [34] and the electric field induced by the bound charges only has in-plane components as shown in Fig. 2(c). Therefore, the oxygen octahedral tilt plays a significant role in stabilizing the  $109/180$  vortex domains.

Next the switching process of the vortex domains under external electric fields will be demonstrated. One unique property of rhombohedral domains is the net curl of the polarization vectors. As shown in Fig. 2(c), the induced electric field is symmetric along the  $x_1$  direction. The resulting vortex domains are, however, asymmetric and only appear on one side of the original domains since the original domain structures are asymmetric with a positive  $P_1$ , which suppresses one half of the possible vortex domains as shown in Figs. 2(e), 3(c), and 3(d). If we name clockwise vortex domains as vortices and counterclockwise vortex domains as antivortices, Figs. 2(e), 3(c), and 3(d) only show vortices; antivortices are suppressed, which results in a net curl. This is different from the situations of thin films and superlattices in a tetragonal structure where the vortices and antivortices are paired and the net curl is zero [12,14].

As discussed above, it is determined by the sign of  $P_1$  whether the vortices or antivortices survive, and thus the vortices can be switched to antivortices if  $P_1$  can be flipped by adding an in-plane electric field. In the phase-field simulations, an in-plane electric field with an increment of  $\Delta E_1 = 6.0 \times 10^6 \text{ V/m}$  is applied to the system, and 2000 simulation steps are given for the relaxation at a specific electric field (for the details about how to apply in-plane electric fields, see the Supplemental Material [32] and Ref. [35]). The domain structures in Fig. 2(c) are set as the initial domain structures with the nonzero curl component  $C_2 = (\nabla \times \vec{P})_2$ .

The phase-field simulation results for the switching process are given in Fig. 4. As shown in Fig. 4(a), the change in  $P_1$  produces a classical  $P$ - $E$  hysteresis loop, and the net curl  $C_2$  also forms a hysteresis loop. At point B, the vortices give rise to a positive  $C_2$  as shown in Fig. 4(b). When the electric field changes from point B to point C,  $P_1$  decreases, whereas  $C_2$  increases. This is because the net curl comes from the polarization vectors in the triangular-shaped regions with the local  $P_1$  opposite the overall  $P_1$ . Compared with Fig. 4(b), Fig. 4(c) shows larger triangular-shaped regions and, consequently, smaller  $P_1$  and larger  $C_2$ . For the same

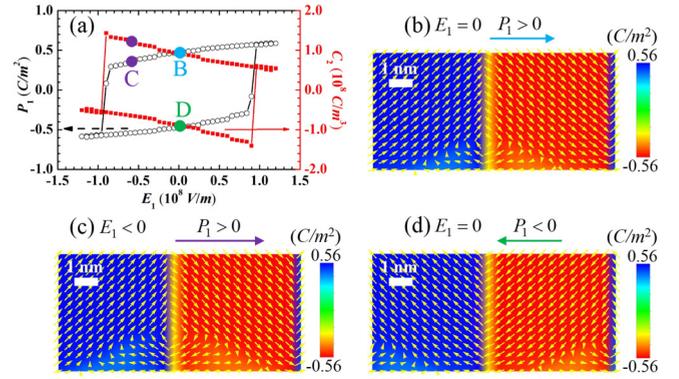


FIG. 4. Switching the curl of the polarization vectors. (a) Hysteresis loops of the polarization and curl components. (b)–(d) Polarization vector distributions corresponding to the points B–D in (a), respectively. The plotted region corresponds to the red rectangular in Fig. 2(d), and the colors in (b)–(d) represent the polarization components out of the plane of the page. The arrows on top of (b)–(d) indicate the overall magnitude of  $P_1$ .

reason,  $C_2$  reaches its maximum before switching. In addition, when the electric field increases from negative to zero, i.e., at point D, the polarization vectors only show antivortices as demonstrated in Fig. 4(d). Therefore, when  $P_1$  flips its sign under the applied electric field, the vortex domains can be switched between vortices and antivortices with the locations shifted, which results in the switching of  $C_2$ . Note that the vortex domains in Figs. 4(b) and 4(d) are both stable after the removal of the external electric fields and can potentially serve as the units of information memory storage.

Intuitively, the vortex domains should be switched by a vortex electric field [36,37]. It may be challenging, however, to generate a large vortex electric field on the nanoscale. Here, based on the fact that the survived vortex domains are determined by the overall in-plane polarization component, it is proposed that the curl can be switched by applying an irrotational in-plane electric field. Note that the coercive fields in the phase-field simulations are larger than that of the experimental measured value ( $75 \text{ kV/cm}$  using planar electrodes on constrained BFO films [35]). This is reasonable since defects and thermal fluctuations are neglected in the model.

To summarize, we propose conditions to produce vortex domains in ferroelectric films and superlattices. Using the  $\text{BiFeO}_3$  film as an example, the underlying mechanism of the vortex domains is revealed, and two types of vortex domains are predicted for  $109^\circ$  domain walls, both of which are experimentally observed. Oxygen octahedral tilt may alter the relative stability of the vortex domains. Also, it is shown that the net curl of the polarization vectors can be switched by applying a homogenous in-plane electric field. With well-developed film growth techniques, the proposed conditions may open a new route for engineering vortex domain structures in ferroelectric thin films and superlattices.

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