

Magnetoelectric initialization of multiferroic Mn_2GeO_4

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Magnetoelectric multiferroics promise direct cross control between coexisting ferroelectric and ferromagnetic orders, which is of interest for applications in magnetism and spintronics. A particularly interesting type of cross control is found in spin-spiral multiferroic Mn_2GeO_4 , in which a ferroelectric multidomain distribution can be globally inverted by a single magnetic field sweep. In this work we show that this repeatable response is not obtained immediately after entering the multiferroic phase via zero-field cooling. Instead, an initial metastable multidomain state forms in which polarization, magnetization, and antiferromagnetic order do not yet minimize the trilinear magnetoelectric coupling. Using optical second-harmonic generation for ferroelectric domain imaging, we demonstrate that a single field cycle deterministically drives the system from the initial metastable state into an equilibrium domain configuration that shows repeatable domain interconversion. This initialization behavior originates from a deterministic pathway from metastable to equilibrium domain patterns, in contrast to the more common—and less reliable—stochastic domain “training” procedures that require repeated field cycles. Understanding the initial domain evolution thus enables reliable cross control in magnetoelectric devices with highly interlinked order parameters.

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I. INTRODUCTION

Magnetoelectric engineering, such as electric-field-induced switching of a magnetic order, underlies much of the recent research on multiferroics, that is, on materials with coexisting magnetic and ferroelectric orders within the same phase [1–5]. Coexisting multiple-order parameters can facilitate pronounced magnetoelectric cross-coupling, and in particular, rigid one-to-one coupling between macroscopic magnetization and electric polarization is highly desirable for functional devices [6,7]. A complication in field-driven domain control, however, is that the first field cycles after cooling often produce irreversible changes in the domain pattern. This behavior is known as “training” or “annealing” procedures [8–11] and is little studied in multiferroics, limiting the practical value of the magnetoelectric coupling.

Especially strong magnetoelectric effects are observed in antiferromagnetic spin-spiral multiferroics, in which the

inversion-symmetry-breaking compensated spin order is directly responsible for the emergence of a spontaneous electric polarization [12–14]. A particular case of such magnetoelectric domain cross control was demonstrated in conical-spiral multiferroic Mn_2GeO_4 [15–18]. As we showed in a previous work [19], a trilinear magnetoelectric coupling term, favoring specific relative orientations of magnetization, polarization, and antiferromagnetic order, enables the complete inversion of a ferroelectric multidomain pattern by a homogeneous magnetic field, where the spontaneous polarization is reversed in every position on the sample, while the domain pattern as such remains unchanged. This reliable interconversion is, however, observed only for an equilibrium domain configuration.

In this work, we investigate the initial field-driven domain evolution in Mn_2GeO_4 after zero-field cooling, using optical second-harmonic generation (SHG) as a spatially resolving domain-imaging technique. We find that the initial ferroelectric and ferromagnetic domains form independently and that a single magnetic-field cycle enables a deterministic pathway towards a global equilibrium domain state in which the magnetization and polarization are rigidly coupled to allow for repeatable magnetoelectric domain inversion. The initialization procedure described here differs markedly from that of other training procedures and is driven by a stepwise minimization of the global free energy, which we discuss on a phenomenological level and for which we propose a

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microscopic mechanism. Our findings emphasize the importance of a comprehensive understanding of the domain evolution away from equilibrium for obtaining fully reproducible magnetoelectric control, a prerequisite for reliable multiferroic devices.

This paper is structured as follows: We first summarize the relevant properties of Mn_2GeO_4 (Sec. II), the experimental methods (Sec. III), and the optical properties relevant to the domain imaging via SHG (Sec. IV). In Sec. V we show experimental domain observations after zero-field cooling and with applied fields, and in Secs. VI and VII we discuss the initialization procedure, its distinction from more common training cycles, and possible consequences for multiferroic domain engineering.

II. FERROIC PROPERTIES OF Mn_2GeO_4

The olivine compound Mn_2GeO_4 crystallizes in the orthorhombic space group $Pnma$ with principal axes $a > b > c$ [20]. Its optical and magnetic properties are closely linked to the electronic configuration of the Mn^{2+} ions [21], which occupy two crystallographic sites with octahedral coordination. The Mn1 ions occupy centrosymmetric $4a$ positions, while the Mn2 ions are situated in acentric $4c$ positions, but with local mirror symmetry [20].

Mn_2GeO_4 exhibits a series of magnetic phase transitions [15–18]. In the current work, we focus on the conical spin-spiral phase, which is entered through a first-order phase transition at about $T_N = 5.5$ K [15,16,22]. The conical spin-spiral order in this low-temperature multiferroic phase is characterized by the coexistence of a multitude of order parameters associated with the commensurate wave vector $\mathbf{Q}_c = 0$ and the incommensurate wave vectors $\mathbf{Q}_A = (0.136, 0.211, 0)$ and $\mathbf{Q}_B = (0.136, -0.211, 0)$ [15,16]. Associated with the commensurate order parameterized by $\mathbf{Q}_c$ are the antiferromagnetic order parameters X_1 and X_3 . Here, $X_1 \propto \mathcal{C}$ is purely antiferromagnetic, while X_3 is related to a small canted magnetization $M \parallel c$ with magnitude $M = 7 \times 10^{-3} \mu_B/\text{Mn}^{2+}$. The incommensurate modulation associated with $\mathbf{Q}_{A,B}$ describes a cycloidally modulated spin structure and induces a spontaneous “improper” electric polarization $P \parallel M \parallel c$ with magnitude $P = 16 \mu\text{C}/\text{m}^2$. The macroscopic magnetization M and polarization P can be completely switched to a ferromagnetic or ferroelectric single-domain state by magnetic fields ($H_{\text{coerc}} \approx 100$ mT $\parallel c$) or electric fields ($E_{\text{coerc}} \approx 5$ MV/m $\parallel c$), respectively [15,18].

In the multiferroic phase below T_N , the spontaneous magnetization and polarization are strongly coupled. This fact has been demonstrated by the synchronous reversal of both magnetization and polarization in a magnetic field for a single- P -single- M domain configuration [15,18] as well as by the magnetic-field-driven inversion of a multi- P -single- M domain pattern. In the latter case, the spatial distribution of the ferroelectric domains is retained while the local polarization is flipped [19]. Macroscopically, the domain inversion has been attributed to a trilinear magnetoelectric coupling term [19,23]. Microscopically, the simultaneous switching of polarization and magnetization in Mn_2GeO_4 originates from a magnetic-field-induced directional flop of the Mn spin-spiral cone axis, which reverses both the net magnetization

and the projected spiral helicity and thus the spin-induced polarization [18].

III. METHODS

Single crystals of Mn_2GeO_4 were grown by the floating-zone method [15,16], oriented by Laue diffraction, and cut into platelets with faces perpendicular to the crystallographic a or c axis. The samples were lapped and polished from both sides with silica slurry (Eminess Ultrasol 555). The final thicknesses were approximately $70 \mu\text{m}$ (a cut) and $60 \mu\text{m}$ (c cut).

Linear optical absorption spectra were measured at room temperature, using a microspectrometer (JASCO MSV-370). SHG experiments were performed with amplified 120 fs laser pulses of variable photon energy in a transmission geometry using a setup described elsewhere [25]. The spatial distribution of the ferroelectric domains was imaged with a telephotography lens (Soligor 135 mm, 1:3.5) using a liquid-nitrogen-cooled charged-coupled device camera as the detector (Photometrics CH270). All imaging experiments were performed in the multiferroic phase at $T \approx 4.5$ K, with the low-temperature sample environment provided by a liquid-helium-operated magnetic-field cryostat (Oxford Spectromag 4000).

To switch the spontaneous magnetization M of Mn_2GeO_4 , magnetic fields H were applied along the crystallographic c direction. To be able to observe the SHG signal of the c -cut platelet, the sample had to be rotated by approximately 20° around the b direction [see Fig. 1(f)]. This rotation leads to a perspective distortion of the SHG images. It is corrected by stretching the images in Figs. 2 and 5 below along their horizontal direction.

To obtain electric-field poling within the multiferroic phase in the c -cut sample, transparent indium tin oxide (ITO) electrodes were sputtered onto both sides of the polished crystal, which allows application of electric fields of up to 15 MV/m before electrical breakthroughs occur. The ITO layer does not completely extend over each sample surface; hence, the electric field $e \parallel c$ is applied only in the overlap region (highlighted blue in Fig. 5).

IV. OPTICAL CHARACTERIZATION

The $3d^5$ electronic configuration of the Mn^{2+} ions dominates the optical response in Mn_2GeO_4 for which d - d transitions are parity forbidden [26]. Mn_2GeO_4 crystals appear reddish brown, however, due to the low-energy tail of the lowest-lying $\text{Mn} \rightarrow \text{O}$ charge-transfer excitation peaking around 3.7 eV. The polarization-dependent linear spectra in Fig. 1(a) show the strongest absorption for light polarized along the crystallographic c direction, leading to a pronounced dichroism. Each spectrum was fitted with a multi-Gauss function to extract the central energies E_c and the full width at half maximum peak widths w of crystal-field transitions No. 1 to No. 4. The transitions are indicated in Fig. 1(a) and are listed in Table I [21,26,27]. The peak labeled No. 0 at 1.76 eV was found only in the c -polarized spectrum and thus is not related to a crystal-field transition.

TABLE I. Optical transitions, as observed in Fig. 1(a). The metal-oxygen charge-transfer edge (CT), the low-energy excitation No. 0, and crystal-field transitions No. 1 to No. 4 were fitted with Gaussian functions centered at E_c with amplitude A and full width at half maximum w . A constant background with amplitude A'_0 was also assumed.

Spectral feature	Symbol	Units	$E \parallel a$	$E \parallel b$	$E \parallel c$	Transition
	A'_0	m^{-1}	1393	1146	2310	
No. 0	E_c	eV			1.760	
	w	eV			0.205	
	A	m^{-1}			271	
No. 1	E_c	eV	2.172	2.177	2.103	${}^6A_{1g} \rightarrow {}^4T_{1g}$
	w	eV	0.398	0.474	0.339	
	A	m^{-1}	1090	1017	2025	
No. 2	E_c	eV	2.784	2.672	2.755	${}^6A_{1g} \rightarrow {}^4T_{2g}$
	w	eV	0.690	0.576	0.815	
	A	m^{-1}	4360	2406	7955	
No. 3	E_c	eV	2.990	3.000	2.990	${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$
	w	eV	0.116	0.122	0.118	
	A	m^{-1}	681	621	948	
No. 3'	E_c	eV	3.090		3.106	$({}^6A_{1g} \rightarrow {}^4E_g)$
	w	eV	0.163		0.129	
	A	m^{-1}	264		201	
No. 4'	E_c	eV		3.262		
	w	eV		(0.850)		
	A	m^{-1}		(6160)		
No. 4	E_c	eV	3.375	3.387	3.419	${}^6A_{1g} \rightarrow {}^4T_{2g}$
	w	eV	0.357	(0.080)	0.380	
	A	m^{-1}	1843	(101)	2159	
CT	E_c	eV	3.716	3.638	3.861	charge transfer
	w	eV	0.482	0.432	0.626	
	A	m^{-1}	77364	49271	102906	
	A_0	m^{-1}	8821	10623	11069	

To spatially resolve domains and to image the effect of field-driven ferroic switching and magnetoelectric coupling in Mn_2GeO_4 , we employ optical SHG, which describes the emission of light at frequency 2ω from a material irradiated with laser light at frequency ω , as described by the equation

$$\mathbf{S}(2\omega) \propto \hat{\chi}^{(2)} \mathbf{E}(\omega) \mathbf{E}(\omega). \quad (1)$$

Here, the electric-field components of the incident light field $\mathbf{E}(\omega)$ induce a source term $\mathbf{S}(2\omega)$ for the emitted frequency-doubled light wave. The tensor components of the nonlinear susceptibility $\chi_{ijk}^{(2)}(2\omega)$ depend on the point-group symmetry of the host material and vanish in the leading electric dipole order for materials with inversion symmetry [28,29]. Therefore, SHG is especially suitable for investigating ferroelectrics and spin-spiral multiferroics [30,31], where spontaneous polarization arises as an inversion-symmetry-breaking order parameter.

In agreement with symmetry selection rules [29], in a -cut Mn_2GeO_4 samples we observe SHG signals arising from the components χ_{bbc} [Fig. 1(e)] and χ_{cbb} [Fig. 1(g)]. These signals appear with a jump below T_N , shown for χ_{cbb} in Fig. 1(b), showing a temperature dependence similar to the spontaneous polarization P [15]. In addition, we find an electric-field-induced second-harmonic (EFISH) contribution

with an amplitude proportional to the strength of the applied external field $E \parallel c$ and independent of the sample temperature.

The spontaneous SHG signal [blue peak in Fig. 1(a)] and the EFISH contribution with $E \parallel c$ exhibit the same spectral dependence, peaking for photon energies $2\hbar\omega$ around 1.90 eV.

Interestingly, for both observed SHG components, the polarization of the incoming light field $\mathbf{E}(\omega)$ is parallel to the Mn2-O-Mn2 bonds promoting strong antiferromagnetic exchange and linking neighboring zigzag chains [red in Fig. 1(c)] [15,16,22,32]. Because of the particular polarization dependence and the spectral vicinity of the SHG peak to the absorption peak No. 0 (which is unrelated to crystal-field splitting; see above) we assume that both linear and nonlinear responses are related to pairwise spin-flip transitions enhanced by exchange interactions between neighboring Mn^{2+} ions [33]. To corroborate this relation, however, more detailed spectroscopy or optical simulations are required, which is beyond the scope of this work.

The SHG signals present in the multiferroic phase of Mn_2GeO_4 , which are sensitive to the spontaneous polarization, can be used for the background-free observation of the ferroelectric multidomain pattern with a spatial resolution down to about 1 μm . Neighboring $\pm P$ domains typically appear in SHG images with constant brightness $I_{\text{SHG}} \propto |\chi_{\text{SHG}}|^2 \propto |\pm P|^2$, separated by dark lines that mark the

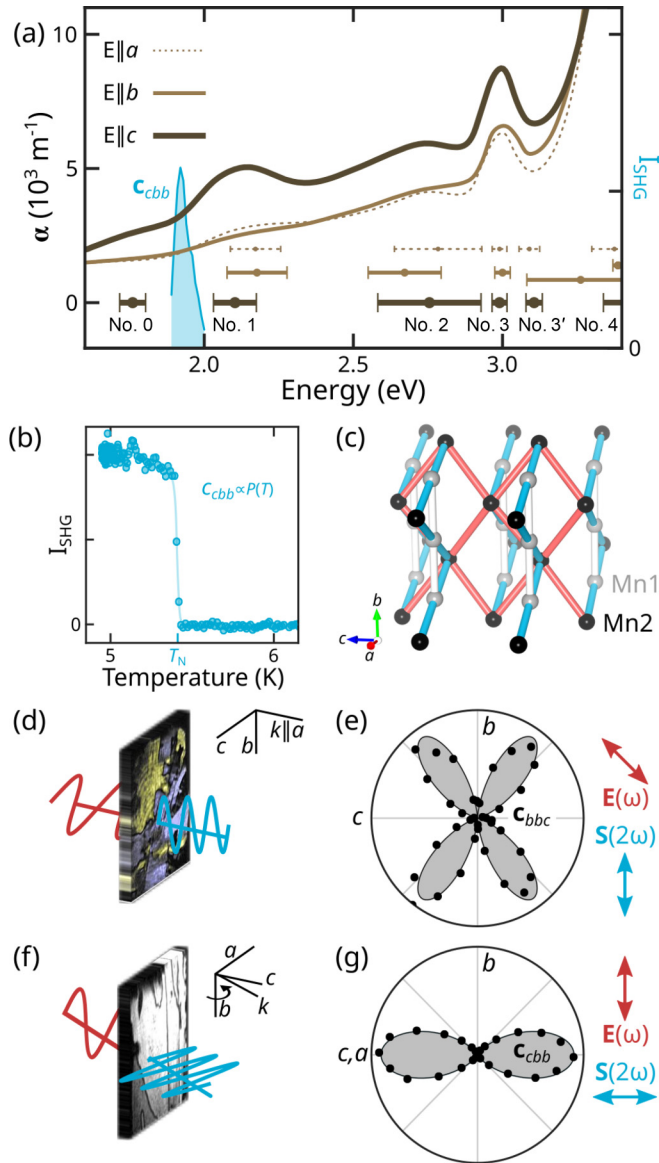


FIG. 1. Optical properties of Mn_2GeO_4 . (a) Linear optical absorption coefficient $\alpha(\hbar\omega)$ with light polarized along the a , b , and c axes of orthorhombic Mn_2GeO_4 (linear scale on left). The central energies and width of the optical excitations are indicated by bars at the bottom (Table I). The blue peak indicates the spectral dependence of the SHG response of χ_{cbb} at $2\hbar\omega$ (linear scale on right). (b) Temperature dependence of the SHG signal $\chi_{cbb} \propto P$ at 1.85 eV. The signal is present only in the multiferroic phase below T_N and couples to the ferroelectric polarization P . (c) Crystal structure of Mn_2GeO_4 , with centric Mn1 and acentric Mn2 sites in gray and black, respectively. (d) and (f) SHG transmission setup for domain imaging of a -cut and c -cut samples, respectively. To observe the SHG response of the c -cut sample, it needs to be rotated around the b axis so that c -polarized contributions to the light waves can be excited. (e) and (g) Rotational SHG anisotropies, measured between crossed polarizers, of the a -cut and c -cut samples, respectively. For SHG components χ_{cbb} and χ_{bbc} the incident light field $\mathbf{E}(\omega)$ is polarized parallel to the Mn2-O-Mn2 bonds (red) that promote strong antiferromagnetic exchange.

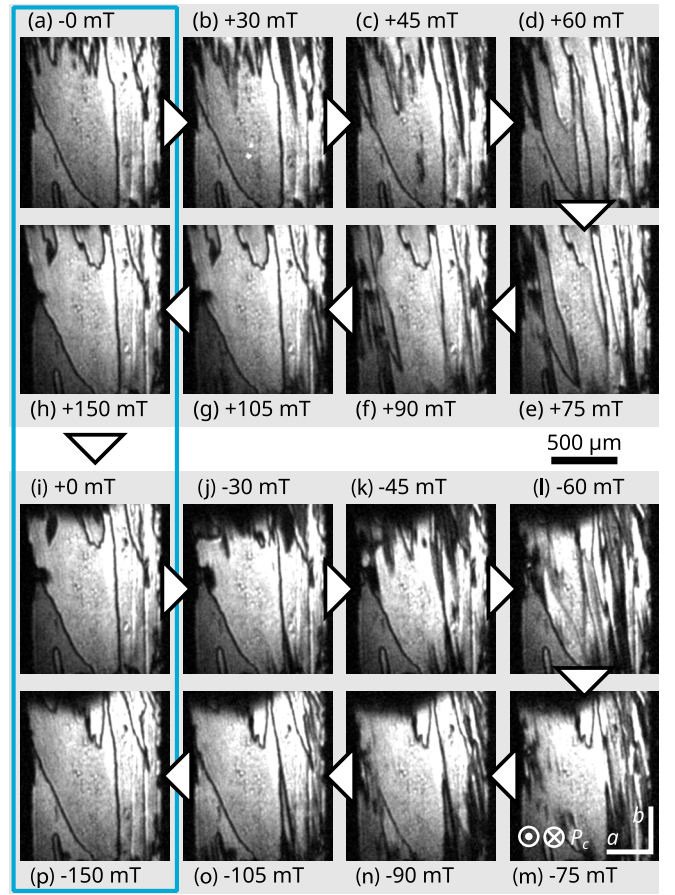


FIG. 2. Polarization domains upon magnetization reversal. Evolution of a multi- P -single- M domain pattern obtained after an initial field cycling with (a)–(h) rising and (i)–(p) falling applied magnetic field H_c . Neighboring $\pm P$ domains appear with equal brightness separated by black lines. Intermediate magnetic fields lead to multi- P -multi- M domain patterns that differ in subsequent field cycles, as demonstrated by the transient ferroelectric domains. After a complete magnetization reversal, that is, comparing (a) to (h) and (i) to (p), the domain pattern is largely recovered (first column), but with the polarity of each local domain inverted, i.e., $\pm P \rightarrow \mp P$.

position of the ferroelectric domain walls. These lines are caused by local destructive interference between SHG contributions from neighboring domains due to the 180° phase shift ($\leftrightarrow \pm P$) associated with them. For the a -cut sample, interference with a reference EFISH signal was used to generate a domain contrast (to distinguish the ferroelectric signal from crystallographic defects), with $\pm P$ domains highlighted in yellow and blue, respectively.

V. MAGNETOELECTRIC DOMAIN INTERCONVERSION

Imaging the ferroelectric domains via SHG allows us to track the field-driven evolution of coupled domain states. To discuss the underlying cross-coupling effects, two switching mechanisms need to be distinguished in Mn_2GeO_4 . They are represented by bilinear and trilinear coupling terms as

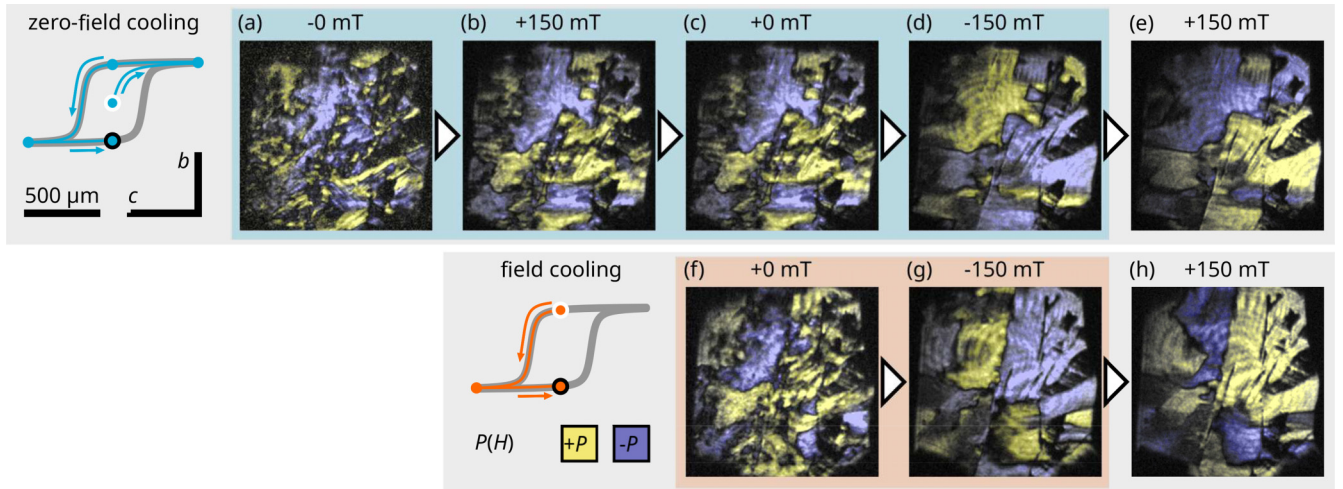


FIG. 3. Initial domain evolution. Ferroelectric domains in a -cut Mn_2GeO_4 after (a)–(e) zero-field cooling and (f)–(h) E_c - H_c -field cooling at 0.6 MV/m and 500 mT. Blue and yellow areas denote domains of opposite polarity $\pm P$. Both morphology and the size of the domains change after the first field-poling steps, before repeatable magnetoelectric domain inversion is achieved. This indicates an initial nonequilibrium distribution of P , M , and antiferromagnetic C domains. (a)–(e) After zero-field cooling (state with white outline), intermittent domain patterns changing in morphology and typical length scales are observed. They indicate an initial nonequilibrium distribution of the P , M , and antiferromagnetic C domains. After a full field cycle (blue path), a remanent domain state that shows fully reversible magnetoelectric interconversion is reached (state with black outline). (f)–(h) After field cooling, an initial magnetic field induces domain changes similar to those in (c)–(e) before stabilization of the magnetoelectric interconversion; in this case, only half a magnetic field cycle is required (orange path). Minor variations in (g) and (h) can be attributed to temperature fluctuations close to T_N , possibly in combination with strain.

contributions to the free energy, which must be minimized in equilibrium. First, the bilinear coupling terms describe how the applied fields act directly on the conjugated order parameter, that is, magnetization $M(H)$ and polarization $P(E)$, via

$$F_M \propto -M(H)H < 0, \quad F_E \propto -P(E)E < 0. \quad (2)$$

Second, the magnetoelectric trilinear coupling term is associated with the response of nonconjugated macroscopic order parameters according to [18,19,23]

$$F_{ME} \propto -CM(H)P(E) < 0. \quad (3)$$

Due to the compensated spin order, the antiferromagnetic domains associated with the parameter C (a combination of commensurate and incommensurate order parameters; see [18,19]) are robust against moderate electric and magnetic fields. As a consequence of this stability of C , when M is switched through H via the bilinear contribution F_M in Eq. (2), P needs to reverse simultaneously in order to satisfy minimization of the trilinear free-energy contribution F_{ME} in Eq. (3). Conversely, if P is switched by an electric field E , the magnetization M must reverse at the same time.

In the following we will distinguish the effects of *domain poling*, that is, the transformation of the virgin multidomain pattern obtained after zero-field cooling into a single-domain configuration, and *domain switching*, describing the inversion of a single-domain pattern via an intermittent multidomain state as described in Fig. 2. In other words, poling affects only a subset of domains, whereas switching inverts an order parameter in *all* domains.

A. Zero-field-cooled nonequilibrium domains and initialization of the equilibrium configuration

In contrast to the highly repeatable domain interconversion, the initial evolution of a multi- P –multi- M domain pattern after zero-field cooling is strikingly different. Specifically, we find that upon zero-field cooling to the multiferroic phase ($H = E = 0$), polarization (P) and magnetization (M) domains form independently.

As shown in Fig. 3(a), the initial multi- P –multi- M domain pattern features small $\pm P$ domains with predominantly diagonally oriented boundaries. An applied magnetic field converts the initial state to a multi- P –single- M domain pattern. Due to the magnetoelectric coupling parameterized by Eq. (3), the ferroelectric domain pattern is expected to change in the regions where the magnetization has been switched. Indeed, as shown in Figs. 3(b) and 3(c), after H -field poling, the $\pm P$ domains appear larger, with boundaries preferably aligned with the horizontal (polar) c axis and slightly inclined in the vertical b direction. The magnetic-field-driven change in the morphology and size of the P domain pattern hence confirms the independent formation of ferroelectric and ferromagnetic multidomain states on zero-field cooling into the multiferroic phase.

To obtain the repeatable global magnetoelectric domain interconversion discussed above a deterministic multistep magnetic-field initialization procedure is required. The image sequence shown in Figs. 3(a)–3(c) represents the initial poling toward a single- M domain configuration. Upon the first global switching of the magnetization $+M \rightarrow -M$ [Figs. 3(c) and 3(d)], the majority of $\pm P$ domains invert to $\mp P$; however, this step is still distinct from the rigid and repeatable interconversion discussed above. In particular, some domains

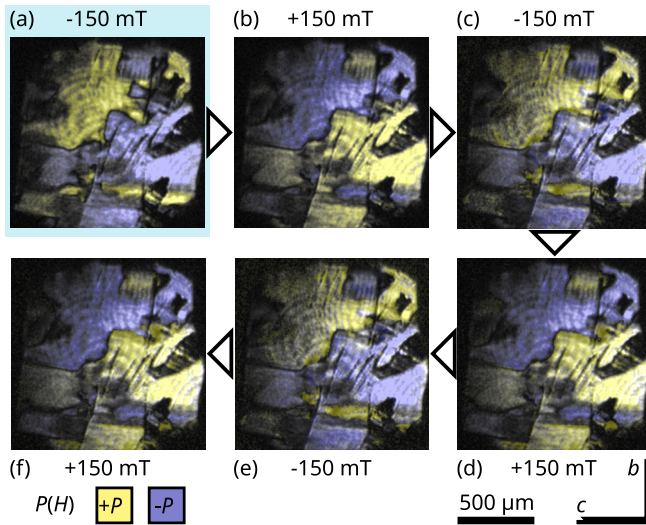


FIG. 4. Repeatability of magnetoelectric domain inversion. Five subsequent reversals of the ferroelectric domain pattern, indicated by the interchange of blue and yellow contrasts that indicate domains of opposite polarity $\pm P \parallel c$, are shown for switched magnetization $M(H_c)$. The initial domain configuration, highlighted in light blue, corresponds to the one shown in Fig. 3(d), obtained after a magnetoelectric initialization procedure from a zero-field-cooled domain configuration.

(especially smaller ones) disappear, and the domain walls straighten considerably. Consequently, the resulting multi- $(\mp P)$ -single- $(-M)$ domain pattern is different from the previous multi- $(\pm P)$ -single- $(+M)$ domain pattern, in contrast to what would naively be expected from the magnetoelectric coupling term in Eq. (3).

A similar initialization behavior is observed even if the sample is initially cooled in a moderate magnetic field of $H = 500$ mT, as shown in Figs. 3(f) and 3(g). Only subsequent reversals reveal the magnetic-field-driven equilibrium inversion of the ferroelectric domain pattern [Figs. 3(d), 3(e), 3(g), and 3(h)].

The observed changes indicate that the relationship between the P , M , and C domain populations is not yet in equilibrium after cooling in zero field or with a moderate bias field applied, as illustrated by the blue and orange paths on the hysteresis loops in Fig. 3. Instead, obtaining the equilibrium state of field-induced domain inversion requires one full or one half magnetic-field initialization cycle, respectively. After these initial steps, the system globally minimizes the magnetoelectric coupling term in Eq. (3) and allows for repeated domain inversion in successive switching cycles, as illustrated in Fig. 4.

B. Repeated magnetoelectric domain inversion

Once the system has reached an equilibrium configuration, as shown in previous work [15,18], repeated application of a magnetic field along c not only switches the magnetization of Mn_2GeO_4 but simultaneously reverses the improper polarization. This effect leads to inversion of the ferroelectric domain pattern with one integral magnetic field sweep. Locally, each polarization state is inverted, $\pm P \rightarrow \mp P$, while the position of the ferroelectric domain walls as such is left unchanged [19].

The associated magnetoelectric domain interconversion, which results in the transition of a multi- $(\mp P)$ -single- $(-M)$ domain pattern to its inverted multi- $(\pm P)$ -single- $(+M)$ state, is demonstrated for a c -cut Mn_2GeO_4 sample in Figs. 2(a), 2(h), 2(i), and 2(p). Note how the final domain pattern in Fig. 2(p) still resembles that of the initial pattern in Fig. 2(a). Minor deviations occur only towards the edges of the image where the sample is mounted, which points to the disruptive influence of sample strain.

Regardless of the repeatable interconversion, in intermediate fields [Figs. 2(b)–2(g) and 2(j)–2(o)], additional needlelike domains appear at the top of the sample and grow downwards. These domains appear at different positions in subsequent field cycles, indicating that pinning at structural or magnetic defects is not relevant for this process. As the spatial distribution and temporal evolution of domains in this transient multi- P -multi- M configuration is different in each poling cycle, the recovery of the initial domain state cannot be attributed to local pinning centers or other memory effects and instead is governed by the intrinsic global magnetoelectric coupling.

The magnetoelectric inversion of the domain pattern is highly repeatable, as shown for five subsequent magnetic field reversals in Fig. 4.

C. Electric-field control of multiferroic domains

The ferroelectric domains of Mn_2GeO_4 can also be directly controlled via a conjugated applied electric field [see F_E in Eq. (2)]. After zero-field cooling, the c -cut sample obtains a multi- M -multi- P domain pattern [Figs. 5(a) and 5(b)]. Here, domains with opposite polarity $\pm P$ show up as white stripes with a typical width of 20 to 50 μm preferably aligned along the crystallographic b direction and separated by black domain walls, as explained in Sec. IV.

Application of a sufficiently large electric field leads to the growth of a region with uniform brightness associated with a single polarization domain, as shown in Fig. 5(a). Approximately 5 MV/m are required to initiate domain growth, giving a lower bound for the coercive field to orient the ferroelectric domains. The domain evolution is limited to the area in which the front and back ITO overlap (blue outline), whereas the material surrounding it remains unaffected.

Saturation is achieved for fields of about 14 MV/m, and the resulting single- P domain configuration is retained after the applied electric field is removed [see Fig. 5(c)]. Thus, application of an electric field converts a multi- P -multi- M domain pattern, as shown in Fig. 5(b), to a single- P -multi- M domain pattern, as shown in Fig. 5(c).

In addition to acting on the polarization P , due to the magnetoelectric cross-coupling term in Eq. (3), the electric field also acts on the magnetization domains of Mn_2GeO_4 . This is revealed by the image sequence shown in Figs. 5(c)–5(e): Starting from the electric-field-poled single- P -multiple- M state, subsequent magnetic-field poling and magnetization reversal lead to a multi- P -single- M domain pattern, resulting in the reappearance of domains indicated by black domain walls.

Assuming the magnetoelectric coupling term in Eq. (3) has been globally minimized after zero-field cooling, the final ferroelectric domain pattern after electric- and magnetic-field

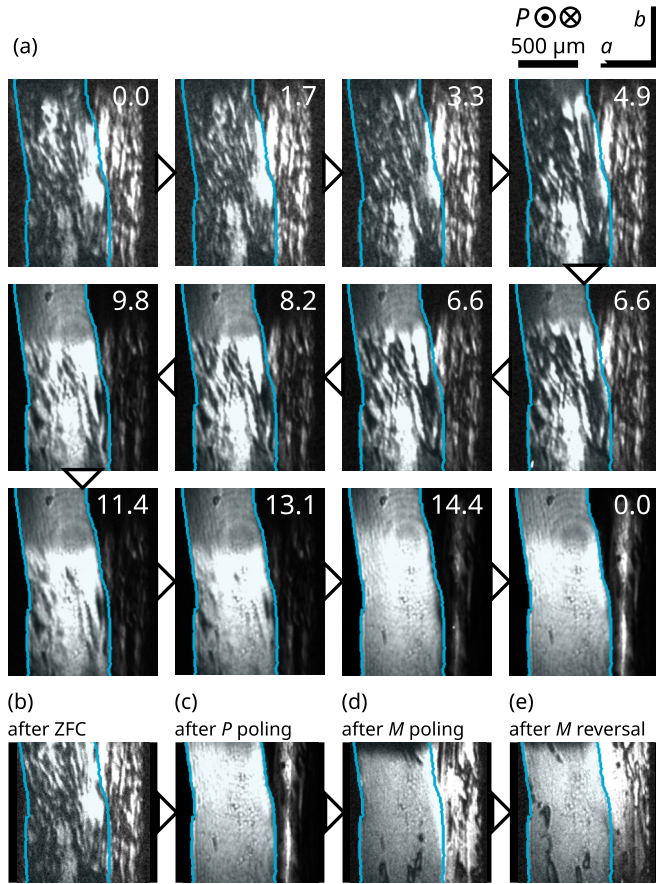


FIG. 5. Electric-field-induced ferroelectric domain evolution. (a)–(c) Sequential images show the ferroelectric domain poling, starting from a multi- P -multi- M domain pattern obtained after zero-field cooling with increasing electric field (top right corner, in MV/m). In the region of overlap between the front and back ITO electrodes (blue outline), a single- P -multi- M domain pattern, indicated by its uniform brightness, is obtained after application of $E > 14$ MV/m and is retained when the field is removed (last panel). (c)–(e) The single- P -multi- M domain pattern in (c), obtained after electric-field poling, can be converted to a multi- P -single- M domain pattern via the trilinear magnetoelectric effect in Eq. (3), as demonstrated by the reappearance of ferroelectric domains upon application of a magnetic field H_c in (d) and (e).

poling should correspond to the product of the initially largely independent P and M domain distributions. In this case, the observed domain size should be similar to the smaller size of the initial P or M domains. The prediction of smaller domains contradicts our experimental observations, however, because after the initializing magnetic-field cycle [Figs. 5(d) and 5(e)], the ferroelectric domains are larger than after zero-field cooling [Fig. 5(b)].

The observation of apparent domain-size evolution further corroborates our earlier conclusion that zero-field cooling into the multiferroic state of Mn_2GeO_4 results in a metastable domain configuration. In this initial state, the order parameters P , M , and C do not yet conform globally to the energy minimization dictated by the trilinear magnetoelectric coupling term in Eq. (3). The first field cycle then leads to a minimization of the trilinear coupling term F_{ME} according

to Eq. (3), accompanied by the formation of larger domains. In addition, the appearance of predominantly straight domain walls reveals a tendency to minimize the total length of the costly (energywise) domain boundaries.

VI. DISCUSSION

Experiments show that Mn_2GeO_4 reaches reproducible magnetoelectric interconversion only after an irreversible but deterministic initialization cycle. At the heart of this behavior are two key observations: First, the ferroelectric polarization P and the ferromagnetic magnetization M form distinct multidomain patterns upon entering the multiferroic phase. Second, upon zero-field cooling or after cooling with only moderate fields applied, the system adopts a metastable configuration where the trilinear magnetoelectric coupling term F_{ME} in Eq. (3) is not yet globally minimized. The initial formation of largely independent domains in P , M , and C is facilitated by the first-order multiferroic transition in Mn_2GeO_4 , which leads to the discontinuous, spontaneous emergence of the ordered state and its domains below T_N . Consequently, higher-order terms in the free energy, such as F_{ME} in Eq. (3), are unlikely to be minimized on a global scale when cooling in zero (or moderate) field.

In the following, we derive a phenomenological two-step model to explain the irreversible, but deterministic, changes following the magnetoelectric initialization procedure. We furthermore explain key differences from domain annealing or training procedures commonly discussed in the literature. Finally, we also propose a specific microscopic model for the domain initialization in conical spin-spiral multiferroic Mn_2GeO_4 .

A. Generalized initialization procedure

On a phenomenological level, the effects of the magnetoelectric initialization procedure on the mesoscale domain distributions are illustrated in Fig. 6. Here, pictograms show the domain distributions of polarization P (yellow and blue), magnetization M (pink and green), and antiferromagnetic order C (white and gray), as well as the local sign of the trilinear magnetoelectric coupling term $\sigma(F_{\text{ME}}) = \sigma(PMC)$ (gray and black). In regions where $\sigma(F_{\text{ME}}) > 0$ (highlighted in gray), the system is *not* in local equilibrium with respect to the magnetoelectric coupling term.

In the first step of the initialization protocol [Fig. 6(b)], poling with a magnetic field transforms the multi- P -multi- M domain pattern to a multi- P -single- M state. At the same time, the system strives to minimize F_{ME} , which can happen in two ways: First, if $\sigma(F_{\text{ME}}) < 0$ is already in place, both M and P will switch simultaneously. Second, if $\sigma(F_{\text{ME}}) > 0$, only the magnetic-field-driven order parameter M will switch, so that $\sigma(F_{\text{ME}}) < 0$. As a result, the pattern of the P domain observed after poling is *not* a simple product between the initial M and P domains, and the change in domain morphology (that is, shape and size) is apparent, as also observed experimentally.

In the second step of the initialization protocol [Fig. 6(c)], the magnetizations of all the regions that did not reorient under the first magnetic poling field are reversed. This gives the associated P domains the opportunity to reverse—or

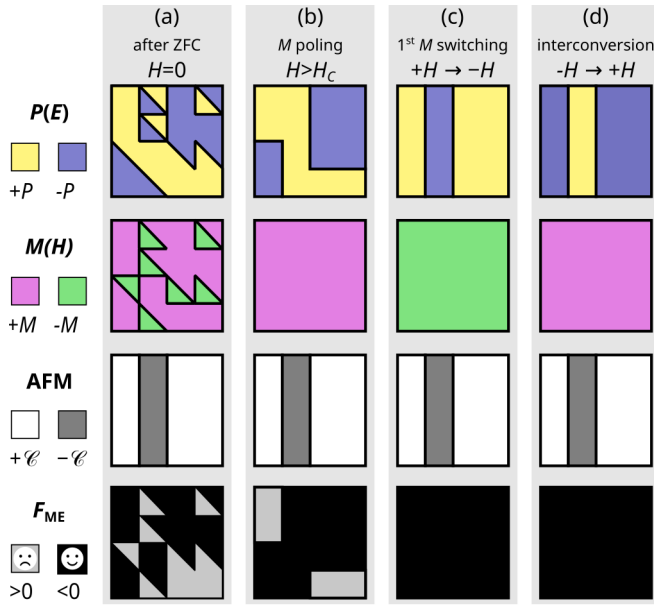


FIG. 6. Phenomenological model for magnetoelectric initialization. Pictograms show the spatial distribution of the observed polarization P (top row, yellow and blue), of the accompanying magnetization M (second row, pink and green), of the “hidden” antiferromagnetic domains characterized by C (third row, white and gray), and of the sign of the magnetoelectric coupling term F_{ME} in Eq. (3) (bottom row, gray and black). (a) After zero-field cooling a metastable multi- P –multi- M domain pattern is obtained, which does not yet minimize the trilinear magnetoelectric coupling term F_{ME} . (b)–(d) A magnetoelectric initialization procedure, combining poling of the initial multi- M domain pattern and subsequent switching of the single- M domain pattern, leads to a stepwise minimization of F_{ME} until an equilibrium domain configuration with global $F_{ME} < 0$ is obtained. (a)–(d) [(b)–(d)] correspond, respectively, to the zero-field-cooling results shown in Figs. 3(a)–3(d) [field-cooled results in Figs. 3(f)–3(h)].

not—towards the state of minimum energy, just as in the first step. Hence, by globally switching the magnetization from a single-($+M$) to a single-($-M$) state, the system can adopt a configuration that globally minimizes F_{ME} , imprinting the domain pattern of antiferromagnetic C order onto the P order.

If all possible domain states characterized by the combination of P , M , and C form with equal probability upon zero-field cooling into the multiferroic phase, a specific sequence of the switched P domain fraction can be predicted: The first poling reverses 50% of the $\pm M$ domains, and for 50% of these, $\pm \rightarrow \mp P$ follows, which implies switching of only 25% of the P domains. The subsequent field switch $+H \rightarrow -H$ reverses all P domains from the first poling and half of the remaining $\pm P$ domains, leading to a switched domain fraction of 75%. This step completes the initialization procedure, and henceforth, all P domains (100%) switch repeatedly with every magnetic-field reversal, as shown in Fig. 4. Although Figs. 3(a)–3(d) imply such a trend, a quantitative analysis is prohibited by the small sample size in relation to the extension of the domains and the high density of crystal defects.

After this initialization spanning exactly a full field cycle, the system has adopted a remanent domain configuration that leads to a global minimization of F_{ME} (highlighted in black). Subsequent switching of the magnetization [Fig. 6(d)] then leads to repeatable magnetoelectric inversion of the ferroelectric multidomain pattern, in agreement with previously published results [16,18,19].

B. Differences to domain training cycles

The fully deterministic stepwise initialization procedure described in this work differs fundamentally from so-called domain training procedures commonly associated with improving the hysteretic response in ferroelectric materials [8–11]: For these, field or temperature cycling redistributes domain walls to energetically favorable positions and removes trapped charges at the electrodes. These stochastic processes gradually change the electrochemical sample properties dependent on local energy contributions and require repeated poling cycles to approach a stable response.

In contrast, the procedure shown here for Mn_2GeO_4 is a fully deterministic process that requires a single full (half) field cycle to a fully reversible remanent domain state when starting from a zero-field-cooled (single-field-cooled) initial domain state: The irreversible changes in the domain distribution are driven by the stepwise field-driven global minimization of the trilinear magnetoelectric coupling term. The irreversible switching processes involved explain the change in the observed domain morphology, i.e., preferred domain boundary orientations and apparent domain sizes, and the expected switching fractions of 25% $\rightarrow$ 75% $\rightarrow$ 100% in the first consecutive field steps.

The magnetoelectric initialization procedure demonstrated here for the example of Mn_2GeO_4 is key to obtain a domain configuration that shows the repeated domain interconversion mediated by the trilinear coupling term in Eq. (3). Such strong and reversible coupling between spontaneous order parameters allows for deterministic magnetoelectric cross control and is robust against disruptive effects such as strain and magnetic stray fields.

We expect that similar initialization procedures are relevant in other materials featuring a complex configuration of order parameters and where a first-order phase transition or rapid quenching through a second-order phase transition promotes nonequilibrium domain configurations. Similar effects could, for example, occur in bulk multiferroics such as spinel $CoCr_2O_4$ [34], orthoferrites [35,36], or hexaferrites [24,37–39], as well as artificial multiferroic heterostructures and interfaces with engineered trilinear coupling terms [9,40]. The presented understanding of the initialization field protocol and switching processes to achieve reliable magnetoelectric cross control is thus key to harnessing these materials for future applications.

C. Microscopic magnetoelectric effect in Mn_2GeO_4

The effects underlying the evolution of multiferroic domains in Mn_2GeO_4 were not studied earlier because integrated pyroelectric current and neutron scattering experiments require single- P –single- M domain patterns to lead to meaningful results [15,16,18]. Note that the combined cooling fields

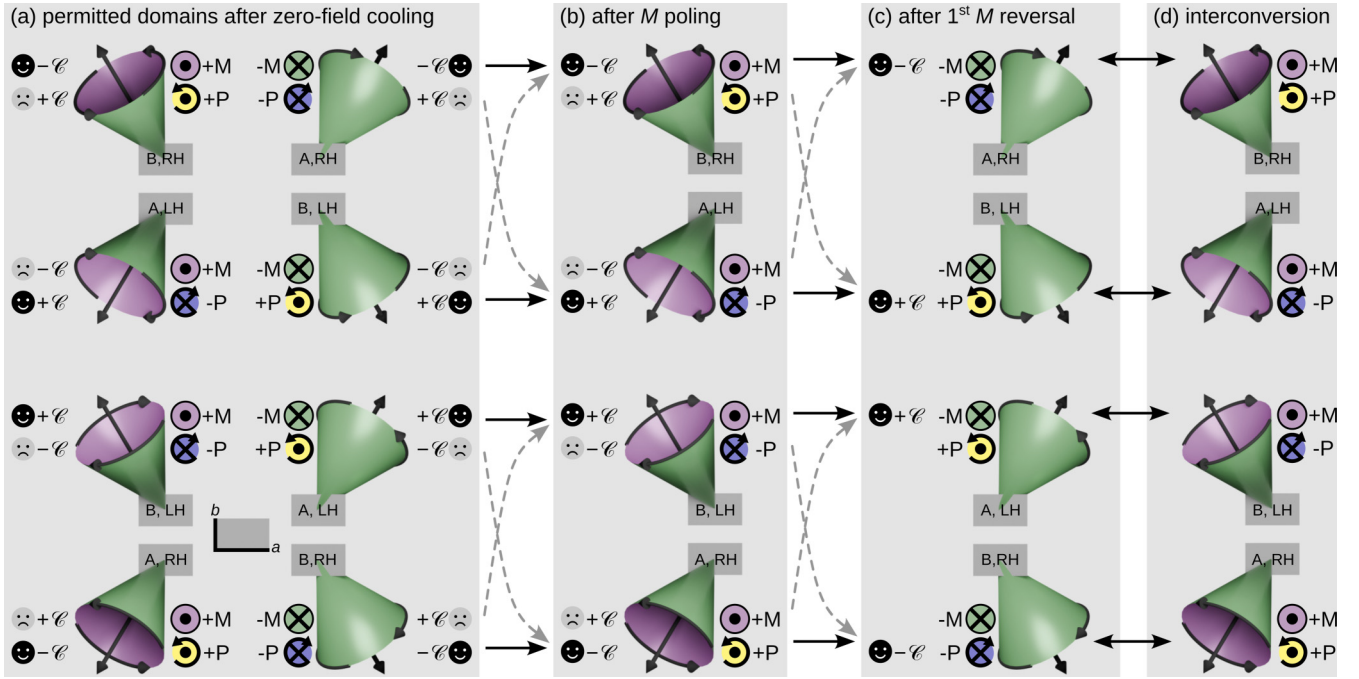


FIG. 7. Microscopic model for deterministic domain initialization in Mn_2GeO_4 . Here, the spin-spiral state is represented by a single cone denoting the spiral component of one of the several conical spin spirals within the unit cell, adapted from [18]. The cone-axis orientation (central straight black arrow) determines the sign of the spontaneous magnetization M (green and pink). The circulation around the cone with clockwise or counterclockwise projections onto the c plane determines the sign of the spontaneous polarization P (black arrows, green and blue). A and B denote the translation domains associated with $\mathbf{Q}_A$ and $\mathbf{Q}_B$, respectively, and the sign of C determines the spiral chirality (left-handed: LH, right-handed: RH). (a) After zero-field cooling, 16 possible domain states characterized by a combination of P , M , and C can arise, although only half of these minimize the trilinear magnetoelectric coupling term F_{ME} in Eq. (3). (b) and (c) A magnetoelectric two-step initialization procedure leads to a stepwise elimination of energetically unfavorable domain states (with $F_{\text{ME}} > 0$, $\odot$) from the sample via irreversible transformations (dashed gray arrows). (d) Afterwards, an equilibrium single- M -multi- P domain configuration with global $F_{\text{ME}} < 0$ ($\oplus$) is obtained, and the ferroelectric domain pattern can be repeatedly inverted upon magnetic-field reversal.

applied in experiments of this type [18], that is, $H = 1.5$ T and $E = 3$ MV/m (and therefore $EH = 4.5 \times 10^6$ V T/m), are at least 1 order of magnitude larger than the moderate fields used for the SHG domain imaging experiments in this work, that is, $H^{\text{max}} = 0.5$ T and $E^{\text{max}} = 0.6$ MV/m [$EH = 0.3 \times 10^6$ V T/m].

An interesting observation that might point to the influence of the nonequilibrium domain configuration on macroscopic measurements even after field cooling was presented in [41], where the authors reported an irreversible polarization increase by 15% upon the first application of a field.

On a microscopic level, the initialization procedure is related to the magnetic-field-driven response of the complex conical spin-spiral structure of Mn_2GeO_4 . The corresponding steps are schematically depicted in Fig. 7. Here, a representative cone of the conical Mn spin spiral is shown. The orientation of the axis determines the sign of the magnetization M (green and pink), and the projected circulation around the cone determines the sign of the polarization P (black arrows, green and blue). In ground-state equilibrium, each incommensurate domain state characterized by $\mathbf{Q}_A$ or $\mathbf{Q}_B$ (labeled just A and B in Fig. 7) can exist in a left- or right-handed chirality, determined by the sign of C [18] [Figs. 7(c) and 7(d)].

After zero-field cooling across the first-order transition, domains of any of the combinations of M , P , and incommensurate translation vectors (A or B) can form. Furthermore, there are two possible cone chiralities C for each of these sign combinations, resulting in a total of 16 possible initial domain states. Eight of them are schematically represented in Fig. 7(a). The choice of $+C$ or $-C$ for each of these is indicated by icons to the left or right.

If the relative sign of MP is the opposite of the sign of C (indicated by $\odot$), we have a ground-state configuration, where Eq. (3) is minimized. A switching field then leads to a reversible rotation of the cone axis, inverting both P and M simultaneously, as well as interchanging the $\mathbf{Q}_A$ and $\mathbf{Q}_B$ domains, while leaving the chirality (and therefore C) unchanged (solid black arrows).

In contrast, if $\sigma(PM) = \sigma(C)$, the domain state is energetically unfavorable (indicated by $\oplus$), and a likely irreversible transformation under applied fields is a reorientation of the cone axis via a “cone flop” (similar to an umbrella flipping over). This reverses M but leaves the translation vector, $\mathbf{Q}_A$ or $\mathbf{Q}_B$, and the polarity (i.e., projected circulation) unchanged. As this operation changes only the sign of M , the trilinear energy term is then minimized.

VII. CONCLUSIONS

In this work we showed that repeatable magnetoelectric domain interconversion in Mn_2GeO_4 can be achieved only by performing a deterministic initialization procedure, which transforms a zero-field-cooled metastable configuration of magnetization, polarization, and antiferromagnetic domains into a fully coupled global equilibrium state. This fully deterministic behavior in Mn_2GeO_4 is in marked contrast to often-discussed ferroelectric training, which relies on the stochastic motion of domains under repeated field or temperature cycles. The understanding of the domain initialization protocol is key to future reliable magnetoelectric functionalities based on multiferroic bulk and composite materials with trilinear coupling terms.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [42].

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