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Direct visualization of magnetoelectric domains

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Methods

Plate-like h -ErMnO₃ single crystals with flat surfaces perpendicular to the c axis were grown by a conventional flux method with Bi₂O₃ flux. A mixture of 80 mol % of Bi₂O₃ and 20 mol % of h -ErMnO₃ powders was heated up to 1260 °C in a platinum crucible, and cooled slowly with 2.5 °C/h rate. Two pieces from the same batch were heated again up to 1200 °C, and slowly cooled to 1130 °C with 15 °C/h. One piece is used in SQUID measurement, the other is used in PFM and MeFM experiments. The specimen (thickness ~200 μm) was glued to a sapphire substrate by Ag epoxy, which also serves as the bottom electrode.

Ambient PFM images were taken on the bare (001) surface with a Multimode atomic force microscope (Bruker) interfaced with homemade circuits. After PFM measurements, a thin gold film (~50 nm) was deposited onto the top (001) surface using magnetron sputtering before MeFM experiments. The MeFM setup is based on a home-made cryogenic MFM¹⁻³, which is interfaced with a Nanoscope IIIa controller and a Nanonis phase-locked loop (SPECS). Using a Nanonis high voltage amplifier, AC high voltages (10 – 300 Hz, $V_{pp} \sim 600$ V) was applied to the bottom electrode. The MeFM signal was taken in a constant height (~100 nm) mode after topography measurements. The demodulated MFM signal is fed to the

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input of a lock-in amplifier (SR830) and the in-phase signal (from the x-channel) is recorded as the MeFM image. During MeFM experiments, the sample space was kept in cryogenic high vacuum ($<10^{-6}$ mbar) for high sensitivity detection. The alignment between PFM and MeFM images was achieved by correlating topographic features.

The first principles calculations were performed using the DFT+U method⁴ with the PBE form of the exchange-correlation functional⁵. For Mn 3d states we used $U = 4.5$ eV and $J_H = 0.95$ eV. The partially filled Er 4f states were put in the core. The Kohn-Sham equations were solved using the projector augmented wave method as implemented in the VASP code^{6,7}. We used a $4 \times 4 \times 2$ k-point mesh and a kinetic energy cut-off of 500 eV. Structural relaxations and electric polarization calculations were performed without the spin-orbit coupling (SOC) while the magnetization was calculated in the presence of SOC.

Discussion 1 Control experiments of MeFM measurement

We have performed several control experiments to confirm that our MeFM signal is purely from the **E**-induced magnetization ($\mathbf{M}_E$).

First, our MFM does not detect any electric field from ferroelectric domains, as the latter is screened by the top electrode (Au film). The lack of MeFM signal at zero field and the significant **H**-dependence of MeFM contrast also excludes the electrostatic origin.

Second, piezoelectric response induced tip-surface distance modulation can be excluded because of the weakness of d_{33} (<1 pm/V) of hexagonal manganites and the cancellation of d_{33} due to the random stacking of ferroelectric domains along the *c*-axis.

Third, the MeFM contrast is linearly proportional to the amplitude of applied **E** field, as shown in Fig. S1.

Fourth, the magnitude and the phase of MeFM signal are independent of the modulation frequency, excluding the possibility of the contamination from static magnetic signal.

Furthermore, we observed the *expected* giant magnetoelectric response in magnetoelectric orthoferrite DyFeO₃ using our MeFM. The *T*-dependence of the MeFM signals shown in Fig. S2, were measured on (001) surface of a single crystal DyFeO₃ after preparing bulk single domain states with different ME annealing conditions.

Finally, we observed similar domain contrast and **H**-dependence in *h*-ErMnO₃ single crystals with a stripe domain pattern⁸. PFM image and typical MeFM images at the same location are shown in Fig. S3. This demonstrates that the magnetoelectric effect and the clamping of ferroelectric, structural anti-phase and antiferromagnetic orders in *h*-ErMnO₃ are independent of domain structure.

Figure S1 | Linear electric field dependence of the MeFM signal. E-field dependence of the MeFM contrast at various representative magnetic field and temperature points.

Figure S2 | T -dependence of the linear magnetoelectric effect of DyFeO_3 after ME annealing. A single magnetoelectric domain state can be prepared after the magnetoelectric annealing i.e., cooling the sample with different $\mathbf{E}$ and $\mathbf{H}$ fields through the ordering temperature. The combination of the annealing $\mathbf{E}$ and $\mathbf{H}$ fields determines the sign of the magnetoelectric coupling coefficient, and the amplitude scales with the antiferromagnetic order parameter below T_N . In this control experiment, the T -dependences of the magnetoelectric effects in DyFeO_3 ($T_N^{\text{Dy}} \sim 3.5$ K) were measured with MeFM after different magnetoelectric annealing conditions ($E = \pm 10$ kV/cm, $\mu_0 H = 1.0$ T). Our results are consistent with the previous studies⁹.

Figure S3 | PFM and MeFM results of *h*-ErMnO₃ with stripe domain pattern. **a**, room temperature PFM image of the (001) surface of a *h*-ErMnO₃ single crystal with stripe domain pattern. The white (dark) color in PFM image represents up (down) ferroelectric domain. **b-d**, low temperature (5 K) MeFM images were taken at the same location at 0.1, 4.0, and 6.0 T, respectively.

Figure S4 | MeFM images in opposite magnetic fields. The canted moment M_z is reversed in opposite magnetic fields, resulting in opposite magnetoelectric coefficient between **a** and **b**. At the same time, the direction of the MFM tip moment M_{tip} follows that of applied magnetic field. Hence, the image contrasts are identical for opposite magnetic fields, as shown in the +4 T and -4 T MeFM images.

	S_a	3_c	$\tilde{2}_c$	m_{a+b}	I	T
$E_z H_z$	+	+	+	−	−	−
$P_z _{E_z=0} \propto Q_{K_3} \cos 3\Phi$	+	+	+	+	−	+
$\chi_1 = \psi_1 - \Phi$	χ_1	χ_1	$\pi - \chi_2$	$-\chi_1$	$-\chi_2 - \pi$	$\chi_1 + \pi$
$\chi_2 = \psi_2 - \Phi$	χ_2	χ_2	$\pi - \chi_1$	$-\chi_2$	$-\chi_1 - \pi$	$\chi_2 + \pi$
$M_z \propto \mathbf{L}_{A_2} \cdot \mathbf{Q}_{K_3}$ $\propto (\sin \chi_1 + \sin \chi_2)$	+	+	+	−	+	−
$\cos(3\Phi) L_{A_2} H_z E_z$	+	+	+	+	+	+

Figure S5 | Symmetry analysis of phenomenological Landau free energy of the A_2 phase.

The table shows symmetry transformations of the allowed linear magnetoelectric term $f^{\text{ME}} = \cos(3\Phi) L_{A_2} H_z E_z$ in the Landau free energy expansion of the A_2 ($P6_3\text{cm}$) phase under the generators of the $P6_3/mmc1'$ space group of hexagonal manganites. Here we follow the notations of Artyukhin *et al* for the definitions of Mn^{3+} spin angle $\psi_{1,2}$ (of even and odd layers of Mn trimmers) and the structural trimerization phase Φ ¹⁰. The four magnetic states (A_1 , A_2 , B_1 and B_2) of hexagonal manganites with spin directions are indicated by red arrows.

L_{A_2} is the magnetic order parameter describing the symmetry of the A_2 phase. It can be

formally defined as $L_{A_2} \equiv \frac{1}{N} \sum_i \mathbf{S}_i \cdot \mathbf{n}_i$, where $\mathbf{n}_i$ is the unit vector in the spin direction on the

Mn site i in the A_2 phase (indicated by red arrows), $\mathbf{S}_i$ is the average spin on the site i and N

is the total number of Mn sites. For $T \ll T_N$, the magnetic order parameter of the A_2 phase is

reduced to $L_{A_2} = \frac{1}{2} L (\sin \chi_1 + \sin \chi_2)$, where L is the magnitude of the 120° spin ordering in

Mn layers. Similarly, the magnetic order parameter of B₂ phase is $L_{B_2} = \frac{1}{2}L(\cos \chi_1 + \cos \chi_2)$ at $T \ll T_N$. See Artyukhin *et al* for detailed discussion of various magnetic states in hexagonal manganites¹⁰.

As shown in the table, the free energy term $\cos(3\Phi)L_{A_2}H_zE_z$ is invariant under all generators of the $P6_3/mmc1'$ space group, so the linear magnetoelectric coupling is allowed.

$$\alpha_{zz} = -\frac{\partial^2 f^{\text{ME}}}{\partial E_z \partial H_z} \propto \cos(3\Phi)L_{A_2} \propto P_z M_z \quad (\text{S1})$$

Therefore, the coefficient α_{zz} of the A₂ phase is proportional to the product of the canted moment $\mathbf{M}_z$ and the polarization $\mathbf{P}$. This is consistent with our MeFM observation.

Discussion 2 Linear magnetoelectric effect in the A_2 phase

To clarify the origin of the diagonal linear magnetoelectric susceptibility (α_{zz}) in h -ErMnO₃, we consider the phenomenological Landau expansion of the free energy with respect to the $P6_3/mmc1'$ reference structure:

$$f_0 = \frac{1}{2}a_Q Q_{K_3}^2 + \frac{1}{4}b_Q Q_{K_3}^4 + \frac{1}{2}a_P P_z^2 + d_{13}P_z Q_{K_3}^3 \cos 3\Phi + \frac{1}{2}d_{22}P_z^2 Q_{K_3}^2 \quad (S2)$$

to which we add the invariant coupling between the antiferromagnetic order parameter $L_{A_2} = \frac{1}{2}L(\sin \chi_1 + \sin \chi_2)$ of the A_2 phase and the magnetic field (see Fig. S5),

$$f_H = -cL_{A_2} Q_{K_3} H_z \quad (S3)$$

and the interaction with the applied electric field, $f_E = -P_z E_z$. Here we follow the notation of Artyukhin *et al.* for the definitions of the trimerization phase Φ and the spin angles $\psi_{1,2}$ (see Fig. S5). Furthermore, $\chi_{1,2} = \psi_{1,2} - \Phi$, while Q_{K_3} and L are the amplitudes of the trimerization and the 120° antiferromagnetic spin order, respectively¹⁰. The equilibrium magnetization is then given by

$$M_z \equiv -\frac{\partial f}{\partial H_z} = cL_{A_2} Q_{K_3} \quad (S4)$$

In the A_2 phase (in high magnetic fields $H > H_c$) the in-plane components of spins are rigid ($\chi_1 = \chi_2 = \frac{\pi}{2}$) so that $L_{A_2} = L$ and $M_z = cL Q_{K_3}$ for weak electric field. The linear magnetoelectric susceptibility is then,

$$\alpha_{zz} \equiv \left. \frac{\partial M_z}{\partial E_z} \right|_{E_z=0} = cL_{A_2} \left. \frac{\partial Q_{K_3}}{\partial E_z} \right|_{E_z=0} \quad (S5)$$

We note that the electric field dependence of magnetic ordering cannot be neglected in the spin reorientation region (the A_2' phase), where it results in large anomalous magnetoelectric response (see Discussion 5). This anomalous contribution vanishes in the A_2 phase.

To find the electric field dependence of Q_{K_3} , we minimize $f_0 + f_E$ with respect to Q_{K_3} and P_z , and differentiate the coupled equations for these two order parameters with respect to E_z at $E_z=0$, which gives

$$\left. \frac{\partial Q_{K_3}}{\partial E_z} \right|_{E_z=0} = \frac{d_{13} \cos 3\Phi}{d_{22}} \cdot \frac{1}{2a} \quad (S6)$$

where $a = a_Q - \frac{d_{13}^2}{2d_{22}^2}a_P \approx a_Q$. In this derivation we used approximation $d_{22}Q_{K_3}^2 \gg a_P$.¹¹

Therefore,

$$\alpha_{zz} = cL \cdot \frac{d_{13} \cos 3\Phi}{d_{22}} \cdot \frac{1}{2a_Q} \quad (\text{S7})$$

Here $\cos 3\Phi$ determine the *sign* of α_{zz} in structural anti-phase domains. It follows that of P_z because $P_z \approx -\frac{d_{13}}{d_{22}}Q_{K_3} \cos 3\Phi$ ¹¹. This result can also be obtained by integrating out Q_{K_3} and P_z to derive an explicit expression of free energy $f(E_z, H_z)$, which would naturally contain the corresponding free energy term $-\alpha_{zz} E_z H_z$ with α_{zz} given by Eq. (S7).

For quantitative estimation of the magnitude of α_{zz} in *h*-REMnO₃, one needs know the numerical values of the parameters in Eq.(S7). Note that $cL = \frac{\partial M_z}{\partial Q_{K_3}}$ and $\frac{d_{13}}{d_{22}} = \frac{\partial P_z}{\partial Q_{K_3}}$ lead to

$$|\alpha_{zz}| = \left| \frac{1}{2a_Q} \cdot \frac{\partial M_z}{\partial Q_{K_3}} \cdot \frac{\partial P_z}{\partial Q_{K_3}} \right|. \text{ The parameter } a_Q \text{ as well as the slopes } \frac{\partial M_z}{\partial Q_{K_3}} \text{ and } \frac{\partial P_z}{\partial Q_{K_3}} \text{ were}$$

extracted from first principles calculations. Here we considered the high-temperature *P6₃/mmc* structure with the A₂ magnetic ordering and freezing-in the zone boundary *K₃* mode (the trimerization distortion). The total energy per unit cell[†] (E), polarization (P) and canting magnetization (M_z) were computed as a function of the amplitude of the *K₃* mode. The results are shown in Fig S6. The $E(Q_{K_3})$ curve was well fitted with the phenomenological Landau

free energy expansion $f_0 = \frac{1}{2}a_Q Q_{K_3}^2 + \frac{1}{4}b_Q Q_{K_3}^4$, resulting in $a_Q = -3.50 \text{ eV/\AA}^2/(\text{u.c.})$ and $b_Q = 5.78 \text{ eV/\AA}^4/(\text{u.c.})$, with energy minimum at $Q_{K_3}^{\min} \approx 0.778 \text{ \AA}$. Therefore, we obtained

$$\text{values of the slopes } \left. \frac{\partial P_z}{\partial Q_{K_3}} \right|_{Q_{K_3}^{\min}} \approx -18.3 \text{ } \mu\text{C/cm}^2/\text{\AA} \text{ and } \left. \frac{\partial M_z}{\partial Q_{K_3}} \right|_{Q_{K_3}^{\min}} \approx -0.062 \text{ } \mu_B/\text{f.u.}/\text{\AA} \text{ from}$$

the linear part of the $P_z(Q_{K_3})$ and $M_z(Q_{K_3})$ curves, respectively. We thus obtain the theoretical estimation of the $|\alpha_{zz}^{\text{th}}| \approx 0.7 \text{ ps/m}$.

[†] Note that there are 6 formula units of ErMnO₃ (i.e. 6 Mn ions) in one unit cell.

Figure S6 | First principle calculations of the A2 phase of $h\text{-ErMnO}_3$. First principles results: calculated **a**, Energy (per unit cell), **b**, polarization (P) and **c**, canting magnetic moment per formula unit (M_z) as a function of the amplitude of trimer distortion Q_{K_3} .

Figure S7a | Complete data set of MeFM measurements at 2.8 K in various H -fields. **a**, topography of the scanned area. **b**, PFM image of the same location. **c-q**, MeFM images of the same location in various magnetic fields (0.3 – 4.0 T). Same color scale for all MeFM images.

Figure S7b | Complete data set of MeFM measurements at 4.0 K in various H -fields. **a**, topography of the scanned area. **b**, PFM image of the same location. **c-q**, MeFM images of the same location in various magnetic fields (0 – 8.0 T).

Figure S8 | H^2 dependence of the magnetoelectric effect in the high field A_2 phase. a, H -dependences of MeFM signals at various T 's (the same as Fig. 3g). The MeFM signal in the high field A_2 phase ($\mu_0 H > 2$ -3 T) is well fitted with $\text{MeFM}(H) = a + c \cdot (\mu_0 H)^2$ (the solid magenta line) where $a = 3.83$ mHz, and $c = 0.32$ mHz/T². b, MeFM vs. H^2 of the MeFM(H) data in the high field A_2 phase to demonstrate the H^2 dependence is independent of temperature below 10 K.

Discussion 3 Estimation of the measured α_{zz}

The **E**-field induced magnetization ($\mathbf{M}_E$) was estimated by comparing the MeFM signal (δf_{MeFM}) with the MFM signal measured on a ferromagnet. Since the MFM signal (δf_{MFM}) originates from the dipolar interaction between the MFM tip and the local magnetic domain, the δf_{MFM} signal is approximately proportional to the product of the moment of the MFM tip (m_{tip}) and the magnetization of the local domain (M_{domain}), i.e.

$$\delta f_{\text{MFM}} \propto m_{\text{tip}} \cdot M_{\text{domain}} \quad (\text{S8})$$

The same is true for the MeFM signal (δf_{MeFM}), i.e.,

$$\delta f_{\text{MeFM}} \propto m_{\text{tip}} \cdot \mathbf{M}_E \quad (\text{S9})$$

By comparing the image contrast of the MeFM images of *h*-ErMnO₃ and that of the MFM images of a known ferromagnet, the $\mathbf{M}_E$ signal can be estimated as following:

$$\mathbf{M}_E = \frac{\delta f_{\text{MeFM}}}{\delta f_{\text{MFM}}} \frac{m_{\text{tip(MFM)}}}{m_{\text{tip(MeFM)}}} M_{\text{domain(MFM)}} \quad (\text{S10})$$

Here we used MFM images on a ferromagnetic Fe_{1/4}TaS₂ ($T_C \sim 160$ K) with strong uniaxial anisotropy¹². Out-of-plane ferromagnetic domain patterns were observed on single crystals of Fe_{1/4}TaS₂ after zero field cooling (ZFC) using our homemade cryogenic MFM². A representative MFM image measured at 60 K is shown in Fig. S9. The ratio of the MFM tips' moments was estimated from MFM measurements on the *same* reference sample (a magnetic tape) at room temperature. From Eq. (S8), we can obtain the ratio between different tips:

$$\frac{m_{\text{tip(MFM)}}}{m_{\text{tip(MeFM)}}} = \frac{\delta f_{\text{tip(MeFM)}^{\text{tape}}}}{\delta f_{\text{tip(MFM)}^{\text{tape}}}} \quad (\text{S11})$$

The tip moment ratio is ~ 0.275 . Using the saturated magnetization of Fe_{1/4}TaS₂ (1 μ_B /f.u.) for M_{domain} , the MFM image contrast of Fig. S9a ($\delta f_{\text{MFM}} \sim 16.5$ Hz), the intercept value fitting curve in Fig. 3 ($\delta f_{\text{MeFM}} = 3.83$ mHz), the **E** ($\sim 10^6$ V/m) induced magnetization $\mathbf{M}_E$ of *h*-ErMnO₃ is estimated to be 6.8×10^{-5} (μ_B /f.u.).[‡] Therefore, the linear magnetoelectric

[‡] Note that one needs to take in account the unit cell volume difference between Fe_{1/4}TaS₂ ($v \sim 57.6$ Å³/f.u.) and *h*-ErMnO₃ ($v \sim 61.6$ Å³/f.u.).

coefficient α of the A_2 phase can be estimated using the definition $\alpha = \mathbf{M}_E / E \approx 13 \text{ ps/m}$. Similar results (within a factor of 2) were obtained using the same calibration procedure on different $\text{Fe}_{1/4}\text{TaS}_2$ single crystals and other ferromagnetic samples.

Therefore, the order of magnitude of the experimental value of the linear magnetoelectric coefficient is $\alpha_{zz}^{\text{exp}} \approx 13 \text{ ps/m}$ for the A_2 phase of $h\text{-ErMnO}_3$.

Figure S9 | MFM image of $\text{Fe}_{1/4}\text{TaS}_2$ and the line profile. **a**, the out-of-plane magnetic domain patterns on the (001) surface of a $\text{Fe}_{1/4}\text{TaS}_2$ single crystal were observed in MFM at 60 K after ZFC. **b**, a representative line cut of the blue line in **a** shows the profile of the ferromagnetic domains.

Discussion 4 Exchange interactions between Mn^{3+} and Er^{3+} spins

In $h\text{-ErMnO}_3$, the anisotropic exchange interactions, e.g. the Dzyaloshinskii-Moriya (DM) interactions^{13,14}, between the Mn^{3+} and Er^{3+} spins provide an effective exchange field to polarize the Er^{3+} spins. For B_2 ($P\bar{6}_3cm$) phase, Er^{3+} at 4b sites are polarized antiferromagnetically, while the Er^{3+} spin at 2a sites remain disordered due to the zero net DM exchange fields (see Fig. S10a)¹. Therefore, the Er^{3+} spins at 2a sites are expected to show paramagnetic behavior, i.e. the H/T scaling. The non-linear magnetoelectric effect ($E_z H_z^2$) at low field likely comes from the $\mathbf{H}$ -induced Er^{3+} moments at the 2a site.

Figure S10 | Cartoon of anisotropic exchange field induced Er³⁺ “order” moment and the H/T scaling of the MeFM signal at low magnetic fields. **a**, a 3D cartoon of the h -ErMnO₃ ($P6_3cm$) crystal structure, where yellow, brown, light blue spheres represent Er, Mn, O atoms, respectively. The black arrows at the 4b sites denote the Er³⁺ moments polarized by Mn³⁺ through DM interactions. The red hollow arrow at 2a site describes the paramagnetic spins induced by applied magnetic field. **b**, the MeFM signal is plotted against H/T at various T and H . Clearly, it scales linearly with $\mu_0 H / T$ in the low field/high temperature region ($\mu_0 H / T < 0.2$), suggesting it may originate from the paramagnetic Er³⁺ spins at 2a site.

Figure S11 | the $M(H)$ and the derivative dM/dH data. **a**, $M(H)$ data of h -ErMnO₃ at various temperatures. **b**, derivative dM/dH of the $M(H)$ data in **a**. A two-peak feature was observed in the dM/dH data at various temperatures. As T decreases, the two peaks get closer and tend to merge to a single peak, i.e. a critical endpoint below 2 K.

Discussion 5 Anomalous magnetoelectric response

The low-temperature magnetic states of h -ErMnO₃ can be described by a single angle $\psi = \psi_1 = \psi_2$ (see Fig. S5 for definitions) with $\psi = 0$ and $\psi = \pi/2$ corresponding to the B₂ and A₂ phase, respectively. The observed B₂ → A₂ transition under an applied magnetic field is the spin re-orientation transition, at which ψ varies between 0 and $\pi/2$. The expansion of free energy in powers of $L_{A_2} = L \sin \psi$ compatible with $P6_3cm$ symmetry of the paramagnetic ferroelectric state is

$$f = C_{20}L_{A_2}^2 + C_{11}L_{A_2}H_z + C_{02}H_z^2 + C_{40}L_{A_2}^4 + C_{31}L_{A_2}^3H_z + C_{22}L_{A_2}^2H_z^2 + C_{13}L_{A_2}H_z^3 + C_{04}H_z^4 + E_z(D_{20}L_{A_2}^2 + D_{11}L_{A_2}H_z + D_{02}H_z^2 + D_{13}L_{A_2}H_z^3) + \dots, \quad (\text{S12})$$

where the terms proportional to C_{20} and C_{40} describe the 2nd and 4th-order magnetic anisotropies, the term $\propto C_{11}$ describes the weak ferromagnetism in the A₂ phase, D_{11} is the linear magnetoelectric coupling, etc. The P_z -dependence is not explicitly shown, since P_z is invariant under symmetry transformations of the ferroelectric phase ($P6_3cm$).

Due to the weak ferromagnetism of the A₂ phase, the angle ψ is nonzero as soon as $H_z \neq 0$. However, the re-orientation largely occurs near $C_{20} + C_{22}H_z^2 = 0$ and the character of the spin rotation depends on the sign of the 4th-order anisotropy C_{40} . For $C_{40} > 0$, the spin re-orientation goes continuously in an extended interval of H_z , while for $C_{40} < 0$, the angle ψ abruptly jumps from a small value to $\pi/2$. Assuming that C_{40} changes sign at ~ 2 K, we can reproduce the experimentally observed phase diagram using the Landau expansion Eq.(S12), as shown in Fig. S12a where the color represents the value of ψ .

Figure S12 | the simulated T - H phase diagrams of the spin re-orientation transition of h -ErMnO₃ based on phenomenological Landau theory. a, T - H phase diagram of the order parameter (the Mn³⁺ spin angle ψ). b, T - H phase diagram of the magnetoelectric response $(\partial M_z / \partial E_z)_{E_z=0}$.

In the continuous re-orientation region the angle ψ is very sensitive to applied magnetic and electric fields, which gives rise to the anomaly in the magnetoelectric coefficient,

$$\left(\frac{\partial M_z}{\partial E_z} \right)_{E_z=0} = - \frac{\partial^2 f}{\partial E_z \partial H_z} + \frac{\frac{\partial^2 f}{\partial L_{A_2} \partial H_z} \frac{\partial^2 f}{\partial L_{A_2} \partial E_z}}{\frac{\partial^2 f}{\partial L_{A_2}^2}}. \quad (\text{S13})$$

Here, the first term is proportional to the linear magnetoelectric coupling D_{11} , while the second term describes the anomalous response, which is large only in the re-orientation region. As this region shrinks to a point (also the end-point of the first-order transition line) the stiffness $\frac{\partial^2 f}{\partial L_{A_2}^2}$ becomes small, resulting in a sharp peak in the magnetoelectric

susceptibility. The calculated H_z -dependence of $\left(\frac{\partial M_z}{\partial E_z} \right)_{E_z=0}$ (see Fig. S12b and Fig. 3h in main text) reproduces well the observed field and temperature dependence of the magnetoelectric response.

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