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Direct visualization of magnetoelectric domains

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The coupling between the magnetic and electric dipoles in multiferroic and magnetoelectric materials holds promise for conceptually novel electronic devices¹–³. This calls for the development of local probes of the magnetoelectric response, which is strongly affected by defects in magnetic and ferroelectric ground states. For example, multiferroic hexagonal rare earth manganites exhibit a dense network of boundaries between six degenerate states of their crystal lattice, which are locked to both ferroelectric and magnetic domain walls. Here we present the application of a magnetoelectric force microscopy technique that combines magnetic force microscopy with in situ modulating high electric fields. This method allows us to image the magnetoelectric response of the domain patterns in hexagonal manganites directly. We find that this response changes sign at each structural domain wall, a result that is corroborated by symmetry analysis and phenomenological modelling⁴, and provides compelling evidence for a lattice-mediated magnetoelectric coupling. The direct visualization of magnetoelectric domains at mesoscopic scales opens up explorations of emergent phenomena in multifunctional materials with multiple coupled orders.

The magnetoelectric effect, first discussed by Landau and Lifshitz, has an outstanding history in condensed matter physics beginning with Dzyaloshinchi’s seminal prediction of the effect in Cr₂O₃ that was quickly confirmed by experiments⁵–⁷. The potential applications in data storage and sensors had generated an intensive research interest in magnetoelectric materials throughout the 1970s (refs 8,9). The revival of magnetoelectricity in the past decade has been fuelled by the discoveries of new multiferroic materials exhibiting giant magnetoelectric effects due to the cross-coupling between the coexisting ferroelectric and magnetic orders⁸–¹¹. Recently, the quantized magnetoelectric polarizability has been proposed to classify three-dimensional topological insulators in the presence of strong correlations¹²–¹³. Therefore, the magnetoelectric effect has a profound and broad impact on diverse areas of materials science.

Although sensitive techniques have been developed for macroscopic measurements of magnetoelectric effects, little has been done on mesoscopic detection of such an effect within a single domain or at domain walls¹⁴. Macroscopic magnetoelectric measurements also require preparations of a single-domain state, which could be problematic for many materials¹⁵–¹⁷. On the other hand, the coupled ferroelectric and magnetic domains or walls are the key to understand the mechanisms of the giant responses in many multiferroics¹⁷–²⁰. Furthermore, understanding and controlling domains and domain walls is critical for using any ferroic material in technological applications. Therefore, it is of both fundamental and practical interest to directly visualize magnetoelectric domains or domain walls. Some efforts on visualizing electric-field-induced changes of local magnetic configuration have been reported²¹, yet the direct detection of magnetoelectric coupling within a domain or at the domain wall is still lacking. Here, we demonstrate a microscopy technique we call magnetoelectric force microscopy (MeFM), which is a combination of magnetic force microscopy (MFM) and in situ modulated electric fields (E), and can be employed to detect the E-induced magnetization (Mₑ), as illustrated in Fig. 1. Using MeFM, we directly observed the local, intrinsic bulk magnetoelectric response of each multiferroic domain in hexagonal (h-) ErMnO₃, in excellent agreement with a symmetry analysis, a microscopic model and first-principles calculations⁶. Furthermore, a giant enhancement of the magnetoelectric response was observed in the proximity of a critical point below 2 K, suggesting that critical fluctuations of competing orders may be harnessed for colossal E-induced magnetic responses.

Figure 1 shows the basic principle of the MeFM, which can be summarized as a lock-in detection of Mₑ. The top electrode (a thin metal film deposited on the sample surface) was grounded to screen all E-fields. A modulated voltage V(ω) is applied to the bottom electrode to generate a modulated E-field across the sample. If the linear magnetoelectric tensor (α) is non-zero, this results in a magnetic stray field B(ω) proportional to Mₑ(ω). B(ω) is sensed by a MFM tip lifted from the surface, producing a modulated MFM signal δf(ω) (the change of the resonant frequency of the cantilever) that is extracted by a phase-locked loop²⁵. The δf(ω) signal is then fed to a lock-in amplifier to extract δfₑ, which we refer to as the MeFM signal. A MeFM image is generated by recording the MeFM signal at every pixel. As MFM is sensitive only to the out-of-plane component of the magnetic stray field, the MeFM signal corresponds to the diagonal component of α. Our MeFM technique is demonstrated by imaging the magnetoelectric response of multiferroic domains in h-ErMnO₃ single crystals. In addition, we have performed several control experiments to exclude possible extrinsic origins of MeFM signals (Supplementary Discussion 1 and Figs 1–3).

The h-REMnO₃ (RE—rare earths) compounds²²–²³ are improper ferroelectrics²⁴–²⁵, in which the polarization (P) is induced by a structural instability called the trimerization mode (Qₕ) that condenses at Tₑ ~ 1,300–1,500 K. The Mn⁺⁺⁻⁻ spins form a 120° non-collinear antiferromagnetic order (L) in the crystallographic xy-plane below the Néel temperature (Tₙ ≈ 70–90 K; ref. 26). The nonlinear coupling between P and Qₕ modes results in six-state topological vortexes with interlocked ferroelectric and structural anti-phase domain walls²⁶–²⁸, where a net magnetization was discovered in h-ErMnO₃ (ref. 20). Although the magnetization is only non-zero at the domain wall, its appearance is a direct manifestation of a strong and non-trivial bulk coupling of L, P

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within each domain. We, indeed, observed a sharp h-ErMnO$_3$ phase, the MeFM results of h-ErMnO$_3$. a-c. Room-temperature PFM image (a), and low-temperature (4 K) MeFM images at zero magnetic field (b) and 8.0 T (c), were taken at the same location on the (001) surface of a h-ErMnO$_3$ single crystal. The white (dark) colour in the PFM image represents an up (down) ferroelectric domain. d. A cartoon of the magnetoelectric coefficient ($\alpha_{zz}$) of the A$_2$ phase in different ferroelectric domains in h-ErMnO$_3$. e. A cartoon of the effective magnetoelectric coupling through structural instability trimerization. f. Cartoons of the changes of the buckling of MnO$_5$ polyhedra (trimer mode Q$_{32}$) induced by E-fields through P resulting in the changes of the canting moment M of Mn$^{3+}$ spins.

and Q$_{32}$ within each domain$^{4,20,25,28}$. The same coupling can give rise to a bulk linear magnetoelectric effect if the magnetic structure of the domain wall could be realized throughout the domain. This is, in fact, possible to do by applying a strong magnetic field (H), which induces a transition from the B$_1$ (P$_6$cm) phase to the A$_2$ (P$_6$cm) phase that emerges at the domain walls in the B$_2$ phase$^{25}$. Our MeFM technique allows for the first time a direct visualization of the resulting magnetoelectric domains, which we now discuss.

The ferroelectric domain pattern on the (001) surface of h-ErMnO$_3$ was visualized with piezo-response force microscopy (PFM) at room temperature. The resulting image (Fig. 2a) shows the network of ferroelectric domains coinciding with structural domains, which explains the origin of the clearly visible six-fold vortex structures. Using topographic features as alignment marks, MeFM images were taken at the same location$^{20}$. In zero magnetic field, the Mn$^{3+}$ spins order in a 120° pattern with magnetic symmetry P$_6$cm (B$_1$), which forbids any linear magnetoelectric effect$^{4}$. Consistently, no MeFM contrast was observed in zero magnetic field at 4 K (Fig. 2b) with $E = 10$ kV cm$^{-1}$. The spin configuration of the h-ErMnO$_3$ can be controlled with the application of a magnetic field along the z axis$^{26}$. In a large field, an A$_2$ (P$_6$cm) phase, which allows diagonal components of $\alpha$$_{zz}$ emerges from the B$_2$ ground state$^{4,29}$. In the A$_2$ phase, the in-plane Mn$^{3+}$ spins rotate through 90° from that of the B$_2$ phase, resulting in a net magnetic moment (M$_z$) along the z axis due to canting of spins of Mn$^{3+}$ ions. We, indeed, observed a sharp MeFM contrast in 8 T at 4 K (Fig. 2c) with $E = 10$ kV cm$^{-1}$. The sign of the MeFM signal changes at ferroelectric domain walls, that is, the magnetoelectric domain pattern is identical to the...
Figure 3 | MeFM images and the H-dependence of the MeFM signal. a–f. The representative MeFM images taken at 2.8 K in various magnetic fields. All of the images are in the same colour scale. g, H-dependence of the MeFM signal at 2.8, 4.0, 5.2 and 10 K, respectively. The solid curve (magenta) is the polynomial fitting $MeFM(H) = a + c \cdot (\mu_0H)^2$ of the high-field $A_2$ phase with extrapolation to zero field. The intercept ($a$) of the fitting curve corresponds to the linear magnetoelectric effect in the $A_2$ phase.

In the $A_2$ phase, $M_z$ originates from anisotropic Dzyaloshinskii–Moriya interactions between neighbouring $\text{Mn}^{3+}$ spins. A symmetry analysis shows that $M_z \propto L_{A_2} \cdot Q_{K^3}$, where $L_{A_2}$ is the magnetic order parameter describing the symmetry of the $A_2$ phase (Supplementary Fig. 5). As $P_z \propto Q_{K^3} \cos3\Phi$ at $T \ll T_c$ (ref. 24), the trimer mode ($Q_{K^3}$) mediates an effective cross-coupling between $P_z$ and $M_z(L_{A_2})$, that is, a linear magnetoelectric effect (Fig. 2e). This effect can also be understood in terms of a simple phenomenological free-energy expansion $f^{\text{ME}} \propto \cos(3\Phi)L_{A_2}E_zH_z$ derived from a symmetry analysis (Supplementary Fig. 5 and Discussion 2), giving $\alpha_{zz} \propto \cos(3\Phi)L_{A_2} \propto M_zP_z$, which is in excellent agreement with our experimental observation and the recent microscopic model4.

In addition, our systematic MeFM studies at various temperatures (2.8–10 K) and magnetic fields (0–8 T) reveal a giant enhancement of the magnetoelectric effect. Figure 3a–f shows representative MeFM images taken at 2.8 K in various magnetic fields (complete data in Supplementary Fig. 7). Overall, the MeFM contrast increases with increasing magnetic field. Surprisingly, the contrast is strongest at $\sim$1.4 T, indicating a non-monotonic field dependence.
of the magnetoelectric effect. More quantitative information can be obtained by plotting the MeFM contrast (the difference between neighbouring domains) as a function of magnetic field ($\mu_0 H$) measured at various temperatures (2.8, 4.0, 5.2 and 10.0 K), as shown in Fig. 3g. The $H$-dependence of MeFM data can be approximately divided into three different intervals: the high-field ($\mu_0 H > 2–3$ T) $A_2$ region, the low-field ($0 < \mu_0 H < 1$ T) $B_2$ region and the intermediate-field ($1 < \mu_0 H < 2–3$ T) $A_2'$ region.

In the $A_2$ region, the MeFM signal is approximately $T$-independent below 10 K, that is, all of the high-field data points collapse to a single curve described by MeFM($H$) = $a + c \cdot (\mu_0 H)^2$ (solid line in Fig. 3g), which is consistent with the $A_2$ magnetic symmetry and the saturation of both Mn$^{3+}$ and Er$^{3+}$ ordered moments at $T \ll T_0$ ($\sim 80$ K). Here $a$ and $c$ are the fitting parameters. The intercept ($a$) is proportional to $\alpha_{sp}$ originating from the $L_{\alpha E} H_z$ term in the free-energy expansion, and the second part is the nonlinear magnetoelectric coefficient due to the $L_{\alpha E} H_z^2$ term in free energy (Supplementary Discussion 5). This behaviour is more apparent when plotting the MeFM signal versus $H^2$ (Supplementary Fig. 8). This suggests that the linear magnetoelectric effect dominates at low fields, whereas the nonlinear one prevails at high magnetic fields. By calibrating the MFM tip using known magnetic materials, we obtained an estimate of the measured linear magnetoelectric coefficient $\alpha_{sp}$ $\sim 13$ pm T$^{-1}$ on $\sim 0.7$ pm T$^{-1}$, where only the contribution of Mn$^{3+}$ spins is taken into account (Supplementary Discussion 2 and 3 and Figs 6 and 9). This indicates that the strong spin–orbital coupling from rare-earth elements may enhance $\alpha_{sp}$ in the $A_2$ phase. Our results are also consistent with the previous macroscopic magnetoelectric measurements ($\alpha_{sp} \sim 3$ pm T$^{-1}$) on (partially) poled $h$-ErMnO$_3$ single crystals$^{31}$. In the $B_2$ region, MeFM($H$) = $b \cdot (\mu_0 H)$, corresponding to the $E_z H_z^2$ term in the free energy. Here $b$ is the fitting parameter. Interestingly, the low-field MeFM data collapse to a single curve with the $H/T$ scaling, indicating that it may originate from the paramagnetic moments of, for example, Er$^{3+}$ spins on the 2a sites (Supplementary Discussion 4 and Fig. 10). This behaviour is consistent with the $P_6\text{cm}$ ($B_2$) magnetic symmetry, which forbids any linear magnetoelectric effect, but does allow nonlinear ones$^{8}$.

The most prominent feature in Fig. 3g is the pronounced divergence of the MeFM signal observed as the temperature is lowered in the intermediate-field $A_2'$ ($P3c$) phase confined between 2 magnetoelectric anomalies: a kink and an asymmetric peak. These two anomalies are consistent with the two ‘steps’ in magnetization.

Here we provide a route for exploring emergent phenomena at the mesoscopic scale such as magnetoelectric coupling in multiferroic domains and domain walls$^{15–18,28–31}$, in multiferroic skyrmions$^{32}$, or in magnetic

Figure 4 | $T$–$H$ phase diagram and a cartoon of critical fluctuation in the $A_2'$ phase. a, The $T$–$H$ phase diagram of $h$-ErMnO$_3$ constructed from the anomalies in MeFM (red spheres) and in $dM/dH$ data (blue triangles) at various temperatures. The two crossovers converge into a possibly critical point (the black star) of a first-order phase transition of $B_2$ $\rightarrow$ $A_2$ (the red dashed line) below 2 K. b, A simulated $T$–$H$ phase diagram using a phenomenological Landau theory (see Supplementary Discussion 5). The colour contrast represents the order parameter (the angle of Mn$^{3+}$ spin) $\psi$ ranging from 0 (B$_2$) to $\pi/2$ (A$_2$). The continuous (second order) spin reorientation transition in the $A_2'$ region becomes an abrupt jump (that is, first order) below the tri-critical point. c, A cartoon illustration of giant responses due to critical fluctuations of Mn$^{3+}$ spins in the intermediate $A_2'$ phase near the critical point of the transition from the $B_2$ phase ($M_z = 0$) to the $A_2$ phase ($M_z \neq 0$). The canting angle of Mn$^{3+}$ spins is exaggerated for illustration.

The first term describes the conventional response in the $B_2$ or $A_2$ phase, and the second term is the anomalous response resulting from the dependence of the magnetic order parameter $L_{\alpha}$ on applied $H$ and $E$ fields (see Supplementary Discussion 5 for details). The anomalous response is large in the continuous reorientation region (the $A_2$ phase), in which the magnetic state is extremely sensitive to external perturbations. It blows up near the tri-critical point where the system loses stiffness, $\partial^2 f / \partial L_{\alpha}^2$, with respect to spin rotations (Supplementary Fig. 12). In other words, the diminishing energy barrier between $B_2$ and $A_2$ phases allows small perturbations such as $H$ or $E$ fields to swing the Mn$^{3+}$ spins towards the $A_2$ phase by gaining either the Zeeman or the magnetoelectric free energy (Fig. 4c), resulting in an additional increase of the canting moment ($M_z$). This scenario is corroborated by the fact that in the vicinity of the tri-critical point not only the magnetoelectric, but also the magnetic susceptibility tends to diverge (Supplementary Fig. 11). The peak in the magnetoelectric response is remarkably well reproduced within our phenomenological theory (Fig. 3h and Supplementary Fig. 12).

In summary, we have demonstrated a direct visualization of magnetoelectric domains in multiferroic $h$-ErMnO$_3$ using newly developed MeFM. This technique provides a route for exploring emergent phenomena at the mesoscopic scale such as magnetoelectric coupling in multiferroic domains and domain walls$^{15–18,28–31}$, in multiferroic skyrmions$^{32}$, or in magnetic
topological insulators. Our results are in agreement with a microscopic model derived from first-principles calculations, providing compelling evidence of the new mechanism of magnetoelectric couplings mediated by lattice instability. Furthermore, our MeFM results reveal a divergent magnetoelectric effect near the tricritical point, suggesting a possibility to enhance magnetoelectric effects by harnessing critical fluctuations.

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Author contributions
W.W. conceived and designed the project. S.W.C. and X.W. grew and annealed b-ErMnO$_3$ crystals and characterized the magnetic properties. Y.G. carried out PFM and MeFM measurements and analysed the data. A.L.W., H.D. and C.J.F. performed first-principles calculations and developed a phenomenological theory of the linear magnetoelectric effect. M.M. performed the phenomenological Landau theory symmetry analysis of the linear magnetoelectric and the anomalous magnetoelectric response. Y.G., C.J.F., M.M. and W.W. wrote the manuscript with input from all authors. Y.G., A.L.W., M.M. and W.W. wrote the Supplementary Information. All authors participated in discussions.

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Competing financial interests
The authors declare no competing financial interests.