Ferroelectric domain walls (DWs) are nanoscale topological defects that can be easily tailored to create nanoscale devices. Their excitations, recently discovered to be responsible for GHz DW conductivity, hold promise for faster signal transmission and processing compared to the existing technology. Here we find that DW phonons have unprecedented dispersion going from GHz all the way to THz frequencies, and resulting in a surprisingly broad GHz signature in DW conductivity. Puzzling activation of nominally forbidden DW sliding modes in BiFeO₃ is traced back to DW tilting and resulting asymmetry in wall-localized phonons. The obtained phonon spectra and selection rules are used to simulate scanning impedance microscopy, emerging as a powerful probe in nanophononics. The results will guide the experimental discovery of the predicted phonon branches and design of DW-based nanodevices operating in the technologically important frequency range.
invariance and therefore the modes are not characterized by a well-defined quasimomentum. The traditional phonon band structure is then replaced by a spectral function, as seen in Fig. 3a, where the intensity at frequency $\omega$ and wavevector $\mathbf{k}$ indicates the content of plane waves with that wavevector in the eigenmodes at that frequency. For a translationally invariant system, sharp peaks would then appear in the spectral function $A_j(\omega, \mathbf{k}) = \sum_v \delta(\omega \pm \omega_v) \left| \langle \delta P_j(r) \exp\left( i \mathbf{k} \cdot \mathbf{r} \right) \rangle \right|^2$ at frequencies $\omega_v$ of phonon modes $v$, where $\delta P_j(r)$ is the polarization profile due to the mode $v$ of unit amplitude. The long-ranged strain texture of the wall, shown in Fig. 2, is responsible for strong mixing between the DW sliding modes and acoustic phonons, whose frequency ranges overlap. This mixing is evident from the rays in the phonon polarization profile $\delta P_j$, Fig. 3c (lower), repeating the shape of the strain texture, Fig. 2.

Figure 3a, b shows for every frequency $\omega$ the content of plane waves with $P_2 \sim e^{i \mathbf{k} \cdot \mathbf{r}}$ in modes of that frequency, while Fig. 3d shows the phonon dispersion along the wall. At low frequencies acoustic phonons are observed (their intensity is divided by 10 in Fig. 3d to make the DW branch visible). They correspond to strain modulations and mix with $P_2$ modes due to electrostriction, $f_g = -\frac{1}{2} \epsilon_{ijk} q_{\beta\alpha m} P_{\alpha m}$. The V-shaped low frequency branch, marked with (1–3) in Fig. 3a, extends from around 10 GHz at $\Gamma$-point all the
way to the bulk polar phonons, and corresponds to the DW sliding and wobbling modes, illustrated in Fig. 3e–g. The phonons in this branch disperse along the wall (along $k_{||}$), but are localized in the perpendicular direction, and therefore their Fourier components extend to $k_{\perp} \sim \pm \pi/\lambda$, where $\lambda$ stands for the DW width. The intensity of the DW-localized branch is lower than that of the bulk phonons due to the low volume fraction occupied by DWs. The higher frequency modes are the bulk polar phonons.

Figure 3e–i shows $\partial P_{2}$ profiles corresponding to some of the lowest frequency DW sliding modes (e–g) and breathing modes (h, i). The nodeless mode shown in the upper panel of Fig. 3e corresponds to the $P_{2}$ increase at the wall during half-period of the oscillation, therefore adding the DW area to the positive domain. During another half-period the negative domain grows. Therefore this mode can be thought of as DW sliding, depicted schematically in the lower panels of Fig. 3e. A higher energy mode with a node in that branch, shown in the upper panel of Fig. 3f, corresponds to DW wobbling. The DW breathing modes, schematically shown in Fig. 3h, i, are found below the band of bulk polar modes, and are indicated with markers (4 and 5) in Fig. 3a.

SMIM signal simulations

Now we move to the origin of the SMIM signal. In the experiments, an AC electric field is applied between the tip and the back electrode, as shown in Fig. 1, and the current is measured. The phonons that have a non-zero energy in the oscillating field of the tip, $-i \omega \delta P(r) \cdot E(r)e^{i\omega t}$, are excited and give rise to a displacement current component in phase with the field. The corresponding loss, $\text{Re} \int \delta P(r) \cdot E(r)e^{i\omega t}$, is measured in addition to the Ohmic losses due to itinerant electrons. The amplitude $x_j$ of a phonon mode $j$ with an eigenfrequency $\omega_j$ is governed by the equation of motion

$$m_j \ddot{x}_j + \gamma_j x_j + m_j \omega_j^2 x_j = \int dr \delta P(r) \cdot E(r)e^{i\omega t},$$

where the mode is characterized by its effective mass $m_j$, damping $\gamma_j$, and the spatial polarization profile $\delta P(r)$. The oscillating driving force on the right-hand side is due to the electric field $E(r)e^{i\omega t}$ of the SMIM tip. The tip function $E(r)$ mimics the electrostatic potential arising due to a voltage applied between the tip and the back electrode. It is a sum of the potential of a point charge, placed 20 nm above the surface, and an opposite image charge due to the back electrode. Damping of $\gamma = 0.1 \text{THz}$ was used throughout the manuscript for illustration purposes, as we leave phonon–phonon interactions and phonon damping outside the scope of the present study. Looking for the solution in the form $x_j = x_j^{\text{in}} e^{i\omega t}$, we obtain the loss power at the tip position $r$,

$$l(r, \omega) = \omega^2 \sum_j \left[ \frac{\int dr' \delta P(r') \cdot E(r')e^{i\omega t}}{m_j (\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2} \right].$$

The frequency dependence is characterized by a Lorentzian. The integral in the numerator is negligible for phonons whose spatial oscillation period is much smaller than the length scale of the electric field inhomogeneity, roughly determined by the tip radius $R$, therefore the phonons with wavevectors $k \ll R^{-1}$ are excited. Figure 3c shows the simulated signal for a BFO sample containing a R71 DW. An asymmetric peak at the DW and a weak signature due to the long-range strain features are visible. We note that Eq. (2) only describes the phonon contributions to SMIM signal, i.e., the contribution of bound charges. It does not capture contributions of itinerant carriers, mobile defects, and artefacts seen in SMIM due to surface topography and Schottky barriers.

DISCUSSION

Figure 3c shows that SMIM conductivity is much higher at DW than in the bulk due to low-frequency DW sliding and wobbling modes. Their dispersion spans the whole GHz range and extends
to the bulk polar phonon band, usually positioned at THz frequency. This explains why the GHZ microwave conductivity at DWs in hexagonal manganites does not show a narrow peak in the frequency domain, but rather rises monotonically towards higher frequencies. The proximity of DW phonons to acoustic branches also leads to phonon scattering and affects thermal conductivity\textsuperscript{27}. The low frequency of sliding modes is also behind their populations in the sample can then be inferred from the orientation and intensity of low-energy branches, as discussed in Supplementary Note 2 and Supplementary Fig. 2.

The recent observation of nominally silent DW modes in BFO\textsuperscript{18} being activated is a surprising evidence that DW type and intensity of low-energy branches, as discussed in Supplementary Note 2 and Supplementary Fig. 2.

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observation in inelastic neutron scattering experiments and other bulk spectroscopies.

In summary, the simulated phonon spectra reveal the DW-localized phonon branches starting from GHz and extending all the way to THz frequencies. This explains a wide frequency range of the conductivity anomaly observed in hexagonal manganites and other materials. The surprising activation of the nominally silent DW mode at R71° DWs in BFO is interpreted in terms of phonon polarization asymmetry due to the interplay of electrostriction and elastic compatibility at a tilted DW. The proposed way to simulate SMIM experiments may be used in emerging second-principles methodologies. Since the low-energy theory used here is rather general, similar phonon spectra must be expected for all ferroic materials, where the order parameter couples strongly to the lattice. We hope this work will motivate the experimental search for DW-localized phonon branches, guide the interpretation of SMIM studies and eventually inspire the development of high-speed DW-based phononic devices, extending surface acoustic wave-based technology to THz DW-based circuits.

METHODS
Computational
In order to elucidate the essential physics that is responsible for the activation of the tilted R71 walls, we use a simplified GLD model. To this end, we focus on the polar mode that connects the parent centrosymmetric phase with the ferroelectric one and consider its interactions with strains (through electrostriction), while neglecting octahedral rotations.

The free energy density, expanded near the centrosymmetric paramagnetic parent structure is written as:

\[ f = f_L + f_g + f_c + f_q + f_f, \]

\[ f_L = \alpha P^2 + \frac{1}{2} \epsilon_{ijk} \partial_i P_j \partial_j P_k + \frac{1}{2} \epsilon_{ijk} \partial_i P_j \partial_j P_k, \]

\[ f_g = \frac{1}{2} C_{iklm} \partial_i P_j \partial_l P_m, \]

\[ f_c = \frac{1}{2} \varepsilon_{ijk} C_{iklm} \epsilon_{lm}. \]

\[ f_q = \frac{1}{2} \epsilon_{ijk} q_{iklm} P_j \partial_l P_m. \]

\[ f_f = \frac{1}{2} \delta_{iklm} \varepsilon_{iklm} P_j - \partial_P \left( \delta_{iklm} P_j \right), \]

where \( P \) stands for the components of the ferroelectric polarization; the strain tensor \( \varepsilon_{ik} \) is related to symmetrized gradients of deformations \( u \) as \( \varepsilon_{ik} = \partial_2 u_\alpha + \partial_\alpha u_2 / 2 \), where the deformation vector \( \delta \) relates points \( r \) in the reference structure to \( r + \delta(r) \), in the deformed structure; summation over repeated indices is implied. \( f_L \) represents the distorted Mexican hat-shaped potential that determines the amplitude and anisotropy of the polarization. \( f_g \) describes strain energy penalty due to spatial variations of the polarization. \( f_c \) describes elastic energy, while \( f_q \) is the electrostriction term that refers to the interaction between polarization and strain. The flexoelectric coupling \( f_q \) that describes interactions of strain gradient with the polarization, was also included as in ref. \(^{43}\), but does not change the qualitative results reported here. The parameters of the model were adopted from ref. \(^{44}\). To obtain the equilibrium configuration, we minimize the free energy \( f(r) \) in Eq. (3) with respect to \( u_\alpha \) by solving Euler–Lagrange equations with the Lagrangian density given by \( -f \), namely \( \delta f/\delta u_\alpha = 0 \), \( \delta f/\delta u_\alpha = 0 \) with \( \delta \) being variational derivatives, using the finite element method as implemented in Fenics software. \(^{45,46}\) The real space was discretized with element dimensions 0.4 nm. The simulated thin film was 60 nm thick and 180 nm wide, and a single DW was placed in the middle. Test calculations were performed for the 360 nm wide film to validate the long-range strain profile. Zero external stress boundary conditions were applied on the top surface while \( u_\alpha = 0 \) was used at the bottom one. At the two ends in the \( x_1 \) direction, both open and twisted boundary conditions were tested to ensure the absence of boundary effects within the domain wall area. Periodic boundary conditions were applied in the translational direction \( x_2 \) to mimic an infinite system.

Phonons are computed using a 20 x 1 x 20 square finite difference mesh with 0.4 nm elements and a single domain wall in the middle. The finite element size gives rise to a periodic lattice potential acting on the DW and gapping the sliding mode at 8 GHz. \(^{20}\) It is analogous to a Pierls–Nabarro washboard potential in a realistic lattice. The resulting oscillation frequency is an order of magnitude higher than characteristic frequencies of DW vibrations due to electrostatic effects. \(^{47}\)

The energy was minimized numerically and the equations of motion (Euler–Lagrange equations \( \delta L/\delta u_\alpha = 0 \), \( \delta L/\delta \dot{u}_\alpha = 0 \) for the Lagrangian density \( L = \frac{1}{2} \left( M_{uu} (\dot{u}_i \dot{u}_j P_{jk} - P_{ij} \dot{P}_k) \right) - \left( P \cdot u \right) \) were expanded to a linear order in small deviations \( \delta u(r) = \delta u(r) e^{-i \omega} \), \( \delta P(r) = \delta P(r) e^{-i \omega} \) around the equilibrium state. That leads to a standard generalized eigenvalue problem \( F^P \delta u = \omega^2 M^P \delta u \) for phonon polarization vectors \( \delta u \) containing all displacement and polarization variations \( \delta u(r), \delta P(r) \); force constants \( F^P \) were computed as second derivatives of \( L \) and the mass of the polarization mode was chosen to fit the gap between acoustic and optical bands of the spectrum to DFT calculations \(^{48} \), \( M^P = 3m e V \) and \( M^P = (m Bi + m Fe + 3mO) V / V \), where \( V \) is the unit cell volume. Phonon polarization vectors were then projected on the plane waves to obtain the phonon spectral functions, shown in Fig. 3a, b, d.

In order to reproduce the realistic 45° tilt of the wall, necessary to simulate the SMIM signal, shown in Fig. 3c, we used a larger grid of 360 x 1 x 120 with 4 nm elements.

DATA AVAILABILITY
The main data supporting the findings of this study are available within the article and its Supplementary Information. Extra data are available from the corresponding author upon reasonable request.

CODE AVAILABILITY
The codes that were used in this study are available at https://github.com/PaulChern/L-INVARINTS/tree/master/Example.

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