

Goldstone-Mediated Polar Instability in Hexagonal Barium Titanate

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We discover a rare structural manifestation of the Goldstone paradigm in a hexagonal polytype of the prototypical ferroelectric BaTiO₃. First-principles calculations confirm the Goldstone character of the order parameter, while our high-resolution diffraction measurements unveil an unusual reentrant Goldstone regime manifesting as a quasicontinuous domain texture in the vicinity of the ferroelectric transition. We develop a minimal Landau model that encapsulates these observations, illustrating how U(1) symmetry can be restored at the ferroelectric transition. Our findings demonstrate how exotic Goldstone physics can be unlocked in systems dominated by highly anharmonic interactions, presenting a promising pathway to stabilize emergent polar topologies in bulk materials.

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Recent years have seen an influx of interest in ferroelectric (FE) materials due to the discovery of rich topological defects such as charged domain walls [1–3], polar skyrmions [4,5], and intricate vortex patterns [6–8]. Coupling between the polarization and the crystal lattice, in conjunction with large anisotropy energies, was thought to prohibit the formation of nontrivial dipole topologies in FE materials. However, recent advancements in epitaxial thin-film growth and real-space imaging techniques have since facilitated their observation [9,10]. This has precipitated a wider reconsideration of the capacity of FE materials to exhibit unusual topological structures with prospects in next-generation device applications.

In general, nontrivial topologies may form when the local order parameter can possess a continuous rotational symmetry. This possibility is well established in FE nanostructures, where surface-depolarizing fields promote a continuous rotation of the polarization direction at the surfaces to stabilize topological structures over conventional long-range ordered domains [11,12]. However, this mechanism is infeasible in bulk FEs, precluding the

possibility of polar topologies at this length scale. Extrinsic compositional disorder in relaxor FEs can yield polar nanodomains described by a continuous rotational symmetry [13], but compositional disorder inevitably introduces experimental and theoretical challenges that preclude deeper fundamental insight. Alternative sources of continuous symmetry must be investigated to assist in exploring the fundamental physics of topological structures at the bulk scale.

Here, we show how simple modifications in structural topology can confer continuous rotational symmetry to the archetypal FE perovskite BaTiO₃ [Fig. 1(a)]. Using group-theoretical methods, high-resolution diffraction measurements, and first-principles calculations, we show how the six-layer hexagonal polytype (6H-BaTiO₃) [Fig. 1(b)] exhibits quasicontinuous symmetry breaking driven by a rare structural manifestation of the Goldstone paradigm. The change in structure from the 3C polytype confines the salient dipole interactions to 2D planes [Fig. 1(c)], enabling the order parameter to possess continuous rotational symmetry without the need for extrinsic compositional disorder. We also demonstrate the generality of our findings with respect to several other polytype structures, ultimately demonstrating how continuous rotational symmetries may be realized in highly anharmonic FE systems which are otherwise characterized by discrete symmetries.

Pristine polycrystalline samples of 6H-BaTiO₃ were prepared based on a high-temperature treatment of the 3C phase [14]. Laboratory x-ray diffraction (XRD) measurements confirmed the samples typically contained only

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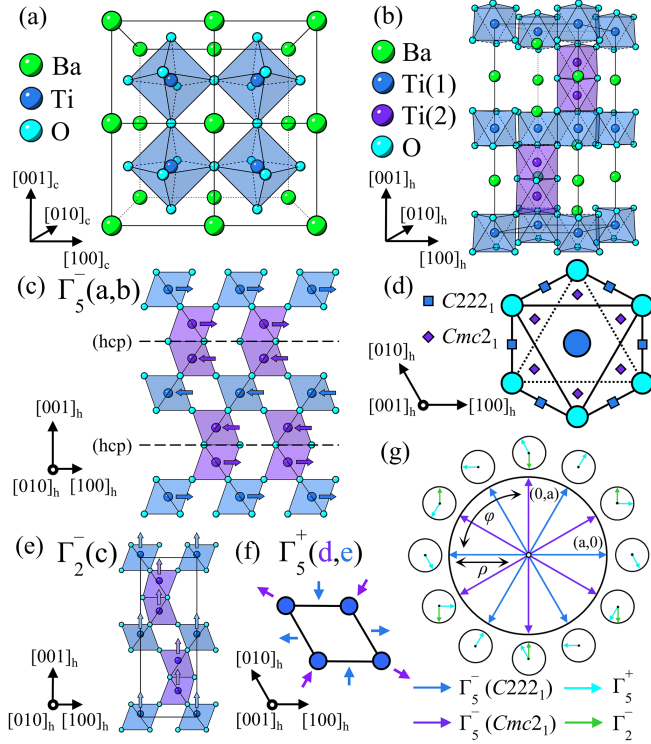


FIG. 1. (a),(b) The aristotype structures of the cubic (3C) and hexagonal (6H) polytypes, respectively. (c) The Goldstone-like mode in 6H-BaTiO₃. Dashed lines denote hexagonal close-packed (hcp) BaO₃ layers, across which the orientation of the antipolar Γ_5^- displacements switches by 180°; the Ba atoms have been omitted for visual clarity. (d) Projection of the high-symmetry Γ_5^- OPDs onto an individual TiO₆ octahedron viewed down [001]. Blue squares and purple diamonds have been mapped onto the octahedral edges and faces to illustrate the difference between $C222_1$ and $Cmc2_1$ domains, respectively. (e),(f) Eigenvectors of the polar mode (Γ_2^-) and ferroelastic strain (Γ_5^+), respectively. (g) Relationships between the Γ_5^- , Γ_5^+ , and Γ_2^- order parameter spaces. The large circle depicts the Γ_5^- space, while the outer circles show how the Γ_5^- OPD propagates to the Γ_5^+ and Γ_2^- spaces. Variations of the amplitude (ρ) and phase (ϕ) of the Γ_5^- order parameter have been illustrated for reference.

trace quantities (< 0.6 wt%) of the 3C polytype. High-resolution synchrotron XRD (S-XRD) experiments were performed at the ID22 beamline (ESRF, France), while high-resolution neutron powder diffraction (NPD) measurements were performed on the D2B beamline (ILL, France). Symmetry-adapted Rietveld fits were performed using TOPAS [15,16], while additional group-theoretical analysis was performed using a combination of ISODISTORT [17,18] and INVARIANTS [19,20]. 3D-XRD data were collected at the ID11 beamline at the ESRF [21] using a ~ 120 nm x-ray beam with an energy of 43.5 keV. Measurements were performed at 150 K on an individual grain from our polycrystalline sample with approximate dimensions $\sim 12 \times 20 \times 3$ μm . Sinogram scans of 2D image data were collected while rotating the crystal by

180° with a 0.05° step size and translating with a step size of 50 nm over a 34 μm range. First-principles calculations were carried out within the framework of density functional theory (DFT) as implemented in the VASP code, version 6.3.2 [22,23]. Further details of the synthesis, diffraction experiments, and DFT calculations are given in Supplemental Material [24].

We begin by revisiting the sequence of phase transitions in 6H-BaTiO₃. The aristotype structure [Fig. 1(b)] is described by $P6_3/mmc$ symmetry [40], but two dielectric features on cooling [41] were concluded to reflect phase transitions to a nonpolar $C222_1$ structure at $T_o \approx 220$ K and a polar $P2_1$ structure at $T_c \approx 70$ K [42,43]. Group-theoretical methods have previously shown the order parameter transforms as the Γ_5^- irreducible representation (irrep) with respect to the $P6_3/mmc$ aristotype structure [44]. This corresponds to a series of antipolar Ti displacements within the hexagonal basal plane [Fig. 1(c)]. The Ti displacements contribute $\sim 90\%$ of the total Γ_5^- amplitude (Table S2 [24]), so for brevity we restrict our discussion to these. Three discrete subgroup symmetries can result from condensing Γ_5^- : $C222_1$, $Cmc2_1$, and $P2_1$. These correspond to order parameter directions (OPDs) of $(a, 0)$, $[a, (\sqrt{3}/3)a]$, and (a, b) , respectively. The $(a, 0)$ and $(0, a)$ branches of the Γ_5^- OPD map to displacements along the $\langle 100 \rangle$ and $\langle 120 \rangle$ directions, respectively, of the parent hexagonal cell [Fig. 1(d)]; the general (a, b) OPD maps to intermediate directions. For certain Γ_5^- OPDs, there can also be a polar displacement along [001] transforming as Γ_2^- (c) [Fig. 1(e)]. This polar component is stabilized by a fourth-order invariant term in a Landau-style free energy expansion of the form $F \sim 3a^2bc - b^3c$ (see Supplemental Material, Note 6 for the full Landau free energy expansion [24]). For $b = 0$ or $\pm\sqrt{3}a$, the stabilization from the Γ_2^- mode is negated, hence the polar component only emerges in the $Cmc2_1$ and $P2_1$ phases. There is also an improper ferroelastic strain transforming as the two-dimensional irrep Γ_5^+ (d, e) [Fig. 1(f)]. The relationship between the 3 order parameter spaces is depicted in Fig. 1(g).

Our high-resolution S-XRD and NPD data [Figs. 2(a) and 2(b)] capture the same phase transitions reported previously [42,43]. However, we find that the low-temperature monoclinic distortion is suppressed below 40 K so that the system tends toward a reentrant orthorhombic symmetry in the ground state [Fig. 2(c)]. It is not possible to differentiate between the Γ_5^- OPDs by conventional Rietveld refinement (Table S1, Figs. S1 and S2 [24]), so to circumvent this we exploit the greater sensitivity of powder diffraction to precise peak positions and treat the improper Γ_5^+ strain as a proxy for the orientation of the Γ_5^- OPD. The $C222_1$ and $Cmc2_1$ models are associated with discrete Γ_5^+ OPDs [Fig. 1(g)], hence there is a trivial mapping between the bases of the Γ_5^- and Γ_5^+ OPDs. Treating the strain as a two-dimensional order parameter

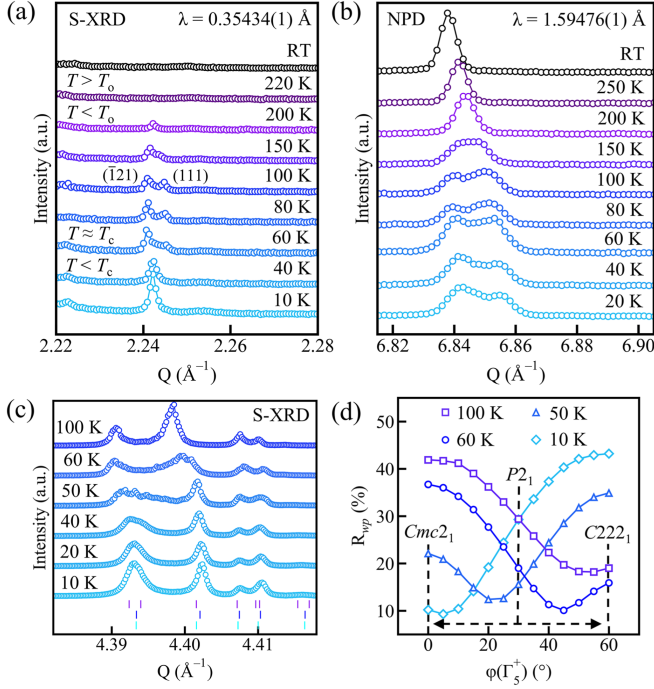


FIG. 2. Excerpts of the low-temperature *S*-XRD (a) and NPD (b) patterns, tracking the evolution of the $C222_1$ ($T < T_0$), $P2_1$ ($T \approx T_c$), and $Cmc2_1$ ($T < T_c$) phases. (c) Suppression of monoclinic peak splitting in the *S*-XRD patterns near and below T_c . Expected Bragg reflections for the $C222_1$ (cyan ticks), $Cmc2_1$ (blue ticks), and $P2_1$ (purple ticks) phases at 50 K are shown below the diffraction patterns for reference. (d) Fitting statistics from strain-mode refinements against *S*-XRD data based on fixed variations in $\phi(\Gamma_5^+)$.

of the form (ρ, ϕ) , where $\rho = (d^2 + e^2)^{1/2}$ and $\phi = \tan^{-1}(e/d)$, we find that the system exhibits a clear crossover between $C222_1$ and $Cmc2_1$ symmetries via the intermediate $P2_1$ phase in the 10–100 K temperature range (Fig. 2). Any monoclinic distortion at 10 K is negligible within the very high resolution of our *S*-XRD experiments ($\Delta d/d \sim 10^{-4}$), so the system clearly tends toward $Cmc2_1$ symmetry in the ground state. Our first-principles calculations corroborate this picture—a geometry-relaxed $P2_1$ structure closely resembles the relaxed $Cmc2_1$ structure, showing the $Cmc2_1$ OPDs represent well-defined energy minima (Supplemental Material, Table S4 [24]).

The sequence of phase transitions we identify arises due to a progressive rotation of the Γ_5^- displacements away from the $Cmc2_1$ ground state configuration. In the 6H polytype, the $\langle 120 \rangle_h$ -oriented octahedral faces are tilted by $\sim 9^\circ$ out of the hexagonal basal plane [Fig. 3(a)]. This means that enacting the second-order Jahn-Teller (SOJT) distortion in an equivalent fashion to the 3C polytype—where the local dipoles orient toward the centers of the octahedral faces perpendicular to $\langle 111 \rangle_c$ [45]—requires an additional out-of-plane Γ_2^- displacive component. Our NPD data show that the Ti environments in the 3C and 6H

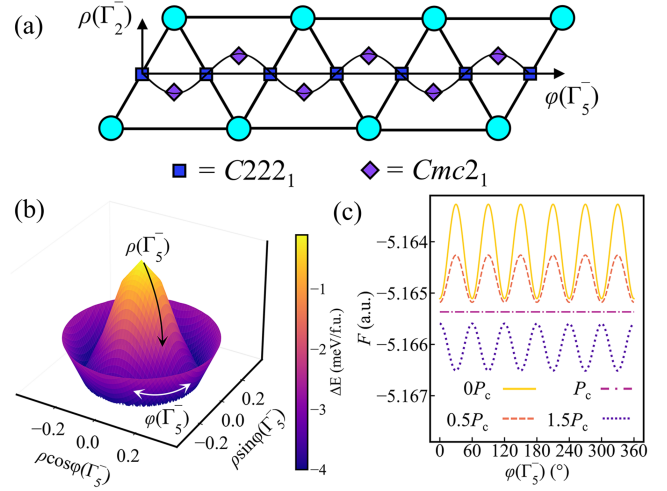


FIG. 3. (a) Schematic of a TiO_6 octahedron “unfolded” with respect to the hexagonal basal plane, mapping the continuous rotation pathway in terms of the phase of the Γ_5^- mode $[\phi(\Gamma_5^-)]$ and the amplitude of the Γ_2^- mode $[\rho(\Gamma_2^-)]$. The high-symmetry OPDs have been highlighted with blue squares ($C222_1$) and purple diamonds ($Cmc2_1$), respectively. (b) PES of 6H-BaTiO₃ with respect to Γ_5^- , with variations in $\phi(\Gamma_5^-)$ and $\rho(\Gamma_5^-)$ depicted for reference. (c) Variation in free energy (F) based on a minimal Landau model [Eq. (1)], showing how scaling $\rho(\Gamma_2^-)$ to a critical value (P_c) can produce a reentrant Goldstone regime.

polytypes are very similar despite their contrasting structural topologies (Table S3 [24]), so the SOJT instability remains the dominant structure-determining force in the 6H polytype. However, it is precisely the mismatch in the orientation of the octahedral faces with the hexagonal crystal axes that orthogonalizes the SOJT instability into two modes with in-plane Γ_5^- and out-of-plane Γ_2^- displacive components. The Γ_5^- OPD ultimately dictates the global symmetry, so the salient dipole interactions are effectively confined to 2D planes allowing a continuous rotational symmetry to emerge [46]. This is in contrast to 3C-BaTiO₃, where the $\langle 111 \rangle_c$ -oriented dipoles are thought to remain discrete across the entire phase diagram [45].

To establish the continuous symmetry of the order parameter in 6H-BaTiO₃, we performed a series of single-point energy calculations by DFT and mapped out the $T = 0$ K potential energy surface (PES) around the $P6_3/mmc$ aristotype structure with respect to the $\Gamma_5^-(a, b)$ components [Fig. 3(b)]. We obtain a characteristic Mexican hat potential with very small energy barriers (< 0.02 meV/f.u.) in the brim of the hat, which are negligible within the energy resolution of our DFT calculations (~ 0.06 meV/f.u.). This unambiguously demonstrates the Goldstone character of the Γ_5^- mode. Analogous Goldstone-like modes are not thought to arise in the 3C polytype as the PES is distinguished by discrete minima [47], hence the continuous character of the Γ_5^- mode in 6H-BaTiO₃ can be directly attributed to the change in structural topology. Nevertheless, our ability to

resolve long-range domains below T_o by diffraction shows that couplings must induce some minima in the PES to determine the global crystallographic symmetry. By comparing the mode amplitudes and energy lowering from our fully relaxed and fixed-cell (zero strain) calculations, we conclude that the Γ_5^+ strain plays only a tertiary role so that the anharmonic coupling between the Γ_5^- and Γ_2^- modes is responsible for inducing discrete minima into the PES. Our analysis of the Landau free energy expansion corroborates this (see Supplemental Material, Note 6 [24]).

The Goldstone character of the Γ_5^- mode provides the necessary continuous rotational symmetry to enable topological structures to emerge. Similar Goldstone-like modes underpin the intricate vortex patterns which have been stabilized in improper FE hexagonal manganites of the form RMnO_3 [48,49], and they likely drive similar behavior in CsNbW_2O_9 [50]. We have been unable to observe any long-range domain structure in 6H-BaTiO_3 by electron diffraction and transmission electron microscopy (TEM) (Fig. S7 [24]), but our ability to distinguish sharp Bragg reflections in our high-resolution S -XRD measurements shows that domains must arise across length scales which we are insensitive to in our TEM experiments. To resolve the domain texture, we collected 3D-XRD data on an individual grain of our polycrystalline sample at 150 K. The reconstructed strain map [Fig. 4(a)] shows that a complex microstructure emerges characterized by a mixture of coexisting structural symmetries. Further details of the strain reconstruction procedure have been provided in Supplemental Material [24].

The sample is predominantly described by $C222_1$ symmetry at 150 K, but we find that sizable $Cmc2_1$ and $P2_1$ inclusions on the order of $\sim 1 \mu\text{m}$ in width prevail well above T_c . Curved boundaries between long-range $Cmc2_1$ and $C222_1$ domains indicate the low-energy nature of the domain walls, while the persistence of spatially extended $P2_1$ inclusions above T_c indicates extensive local fluctuations of the Γ_5^- OPD. The current temperature limitations of the 3D-XRD technique prevent us from probing the domain texture at lower temperatures, but our high-resolution S -XRD data corroborate this picture: multiple diffuse scattering contributions, akin to domain-wall scattering, arise between split diffraction peaks below T_o [Fig. S12(a) [24]]. These scattering contributions persist down to 10 K, and they become particularly prominent in the vicinity of T_c [see Fig. 2(c)] suggesting a continuous distribution of Γ_5^- OPDs emerges.

To interrogate the domain-wall-like scattering contributions, we performed a series of strain models based on a linear interpolation between $\varphi(\Gamma_5^+)$ in the $C222_1$ and $Cmc2_1$ structures [Fig. S12(c) [24]]. Further details of the interpolation procedure are provided in the Supplemental Material [24]. Histograms of the phase distributions obtained from our strain-interpolated models are shown in Fig. 4(b). As these histograms are obtained from powder

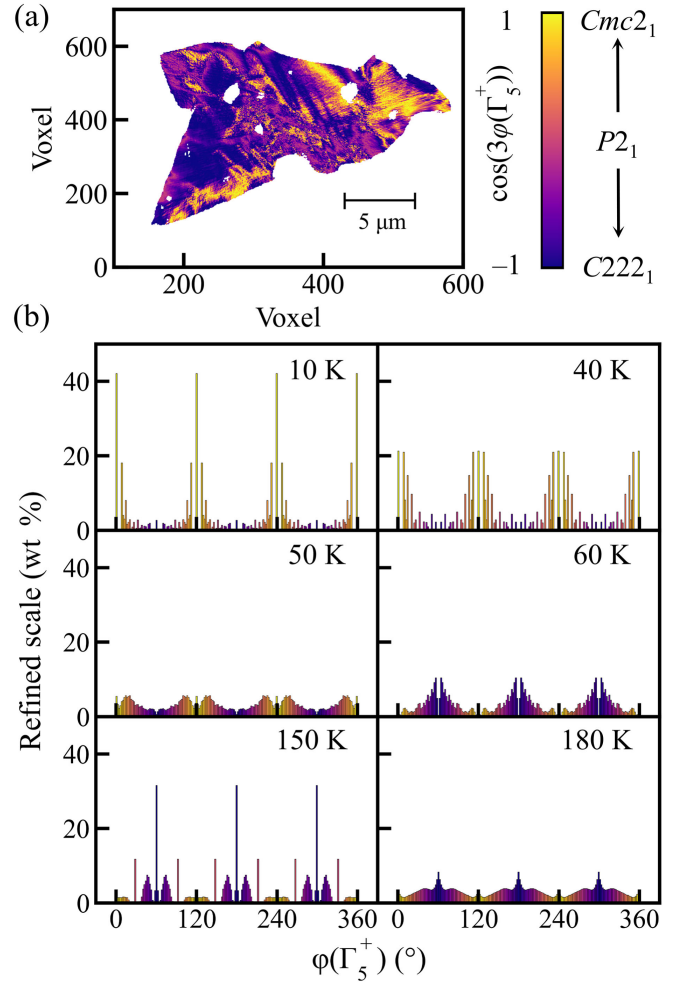


FIG. 4. (a) 3D-XRD strain map based on a least-squares refinement of the local cell parameters of an individual 6H-BaTiO_3 crystallite measured at 150 K. (b) Histograms depicting the powder-averaged domain distributions obtained at select temperatures based on a strain-interpolated model between the limiting $C222_1$ (purple) and $Cmc2_1$ (yellow) strain states.

diffraction models, we cannot resolve the absolute orientations of the different domains so instead we show the powder-averaged distribution at each temperature. The distribution we model at 150 K qualitatively matches the equivalent distribution obtained from our 3D-XRD strain map (Fig. S16 [24]), corroborating the validity of our approach. At 10 K, the mean strain distribution is largely concentrated on the high-symmetry $Cmc2_1$ directions [$\varphi(\Gamma_5^+) = 0^\circ, 120^\circ, 240^\circ$]. However, the distribution becomes increasingly broad upon approach to T_c with estimated full-widths at half-maxima of $\sim 10^\circ$ and $\sim 25^\circ$ at 10 K and 40 K, respectively (Table S6 and Fig. S15 [24]). Near T_c , the distribution collapses away from the high-symmetry directions so that a structural continuum emerges between the limiting $Cmc2_1$ and $C222_1$ [$\varphi(\Gamma_5^+) = 60^\circ, 180^\circ, 300^\circ$] symmetries. $\rho(\Gamma_5^+)$ is comparable for each

phase component in this regime (Table S6 [24]), hence our diffraction data effectively sample a horizontal cut through the brim of the PES that corroborates the Goldstone character of the Γ_5^- mode. Considering the continuous $\varphi(\Gamma_5^-)$ distribution near T_c , it is highly likely that polar topological defects emerge in this regime; further experiments would be beneficial to confirm this.

Above T_c , the strain distribution recondenses around the $C222_1$ directions, and we find that $U(1)$ symmetry is restored for small $\rho(\Gamma_5^-)$ in the vicinity of T_o . Although this is the expected behavior of a two-dimensional order parameter, our observation of a reentrant $U(1)$ symmetry near T_c distinguishes 6H-BaTiO₃ from previous examples of Goldstone-like modes in other ferroelectrics [49,51]. We rationalize these observations using a minimal Landau model:

$$F = \alpha_1 \rho^2 + \alpha_2 \rho^4 + \alpha_3 \rho^6 (10 + \cos 6\varphi) + \alpha_4 \rho^8 + \beta P \rho^3 \sin 3\varphi + \gamma_1 P^2 + \gamma_2 P^4, \quad (1)$$

where (ρ, φ) refer to $\rho(\Gamma_5^-)$ and $\varphi(\Gamma_5^-)$ and P refers to $\Gamma_2^-(c)$. We use this model to illustrate a set of conditions which can yield the reentrant Goldstone regime observed in our diffraction experiments (see Supplemental Material, Note 6 for further details, including the derivation of this model [24]). The relative stability of the $C222_1$ and $Cmc2_1$ phases in this scenario is governed by the α_3 and β anisotropy terms, highlighting the importance of the anharmonicity of the Γ_5^- and Γ_2^- modes. From fits against our DFT data (Supplemental Material, Note 6 [24]), we obtained $\alpha_3 < 0$ so that the $C222_1$ phase is initially favored in the absence of P . However, the relative stability of the $C222_1$ and $Cmc2_1$ phases can be flipped by scaling the magnitude of P ($\langle P \rangle$) [Fig. 3(c)]. This can be rationalized by considering the temperature dependence of P , where, for $T \gg T_c$:

$$\langle P \rangle = \frac{\beta \rho^3 \sin 3\varphi}{2\gamma_1 \left(\frac{T-T_c}{T_c} \right)}. \quad (2)$$

Upon decreasing T , P softens and attains a critical value (P_c) that will induce an exact cancellation of the α_3 and β anisotropy terms, meaning all points within the brim of the hat are made degenerate to establish the reentrant Goldstone regime near T_c . This is opposed to the initial Goldstone regime near T_o , where the degeneracy is contingent on temperature-based fluctuations. Below T_c , the free energy stabilization imparted by the β anisotropy term outweighs the α_3 term, yielding a new set of minima corresponding to the $Cmc2_1$ phase. This minimal model thus encapsulates both the phase crossover and reentrant Goldstone regime we observe in our diffraction experiments, emphasizing the importance of P in driving this behavior.

Our discovery of a reentrant Goldstone-like mode in 6H-BaTiO₃ suggests similar polytype transformations could be leveraged to unlock continuous rotational symmetries in other anharmonic FEs which are otherwise dominated by discrete symmetries. The recent prediction of a Goldstone mode in 2H-BaMnO₃ [51] supports this idea, but this possibility has yet to be established as a generalizable mechanism. From our preliminary DFT calculations, we have found that several simulated polytypes of BaTiO₃ exhibit analogous low-symmetry phases to the 6H polytype (Fig. S17 and Tables S7–S10 [24]). Our phonon calculations show that the Γ_5^- mode is unstable for the 4H, 8H, and 10H polytypes, with the $C222_1$, $Cmc2_1$, and $P2_1$ structures being very similar in energy. Although we have not explicitly computed the full PES for each polytype, the energetic similarity of their low-symmetry phases strongly implies that the SOJT instability retains Goldstone character, despite each polytype representing distinct transformations of the fundamental 3C topology. Such transformations thus appear to represent a generalizable strategy by which to realize continuous rotational symmetries, so we consider perovskite polytypes to be a highly promising compositional space in which to explore emergent topological structures in bulk materials.

Our symmetry-adapted parametrization of the order parameter manifold in 6H-BaTiO₃ has allowed us to demonstrate how changes in structural topology can confer order parameters with continuous rotational symmetry and yield reentrant Goldstone physics. 6H-BaTiO₃ represents a model system in which to unravel the influence of crystal anisotropy in stabilizing unusual topological structures in bulk FE perovskites, and our preliminary DFT calculations indicate that similar physics may be encountered in other polytypes as well. Strain coupling also presents opportunities to acquire deeper insight regarding the stability of topological structures beyond the canonical thin-film limit. Similar structural transformations of other perovskite compositions offer the possibility to study a much richer array of couplings to magnetic or ferroaxial orders, prompting deeper consideration of the emergent microscopic phenomena which have yet to be discovered in polytypes of perovskite materials.

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Data availability—The data that support the findings of this article are openly available [52–54], embargo periods may apply.

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