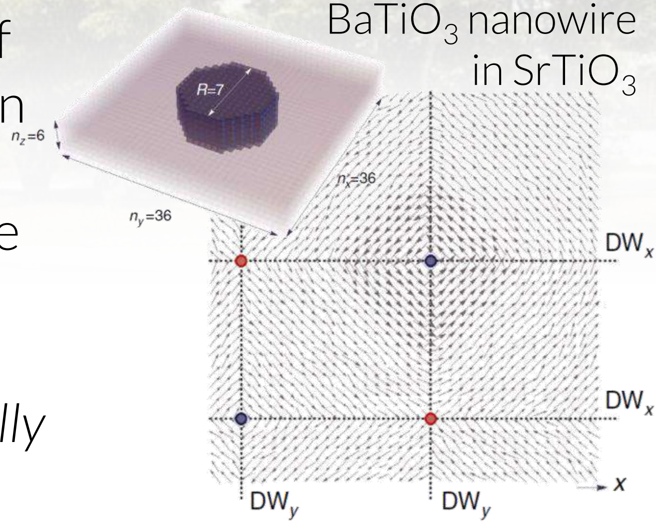
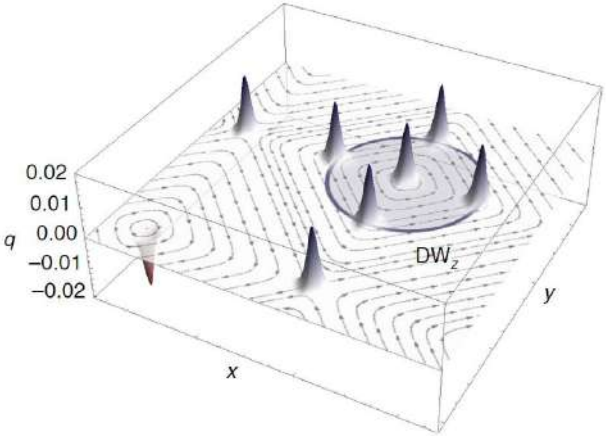
Skyrmions in Ferroelectrics

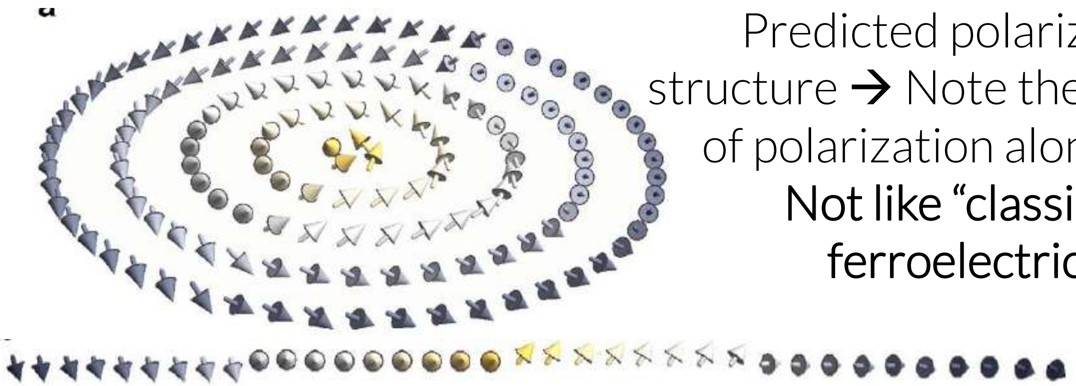
- Skyrmions not expected in FEs →In magnets nature of magnetic order (constant moment across T_C, at domain walls, etc.), presence of chiral interactions are key
- Magnets → Skyrmions are *topological objects* which are *intrinsically* stabilized
- FEs → No such chiral interactions = no Skyrmions
- First-principles → Skyrmions of polarization *extrinsically stabilized* in ferroelectric nanocomposites
- Key → Interplay btw *confined geometry, dipolar interaction*
- Predicted → *Electrical skyrmion* which can be mapped onto the topology of domain-wall junctions; small sizes - few nm (vs. 100s nm in magnets)

$BaTiO_3$ nanowire in $SrTiO_3$





Topological charge density → Mathematical "proof" of Skyrmion formation; Pontryagin density



Predicted polarization structure → Note the evolution of polarization along a line

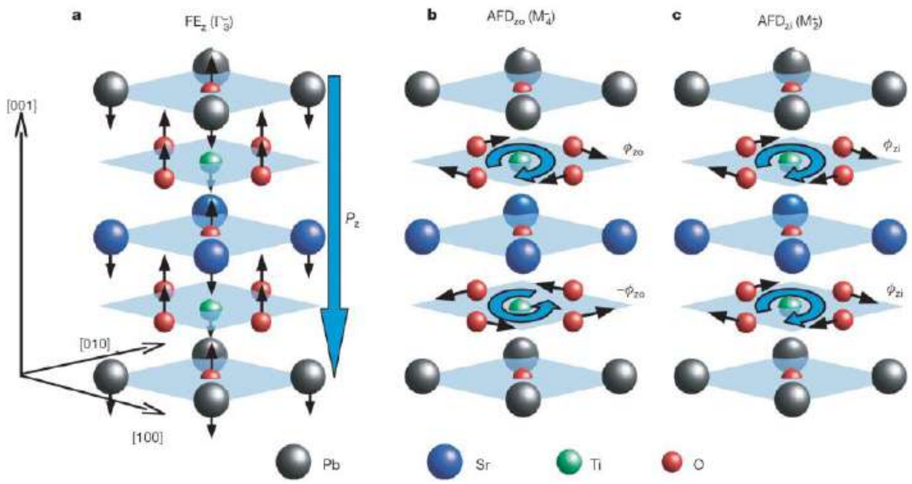
Not like "classical" ferroelectrics

Nahas *et al.*, *Nature Commun.* **6**, 8542 (2015)

Why Superlattices?

Example: $(PbTiO_3)_n/(SrTiO_3)_m$

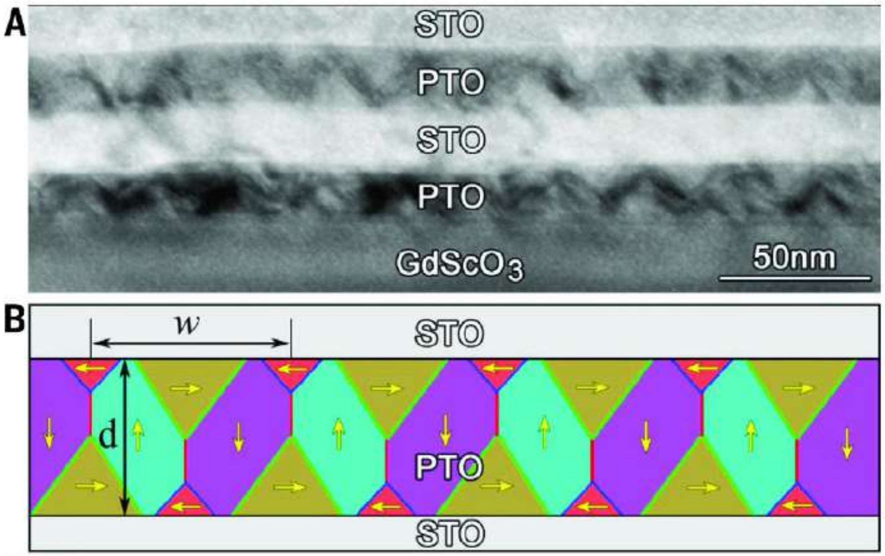
Short Period Superlattices
(n < 9, m < 5)



M. Dawber *et al. Phys. Rev. Lett.* **95**, 177601 (2005)
E. Bousquet *et al. Nature* **452**, 732 (2008)

- New ferroelectric order → "Improper" ferroelectricity
- Dominated by interfacial, strain effects

Long Period Superlattices
(n > 50, m > 50)



Y. L. Tang *et al. Science* **348**, 547 (2015)

- "Classic" ferroelectric domain structures → flux closure
- Dominated by electrostatic, strain effects

What happens in the middle?
What happens when no one energy dominates?

Emergent Polarization Structures

Core Team

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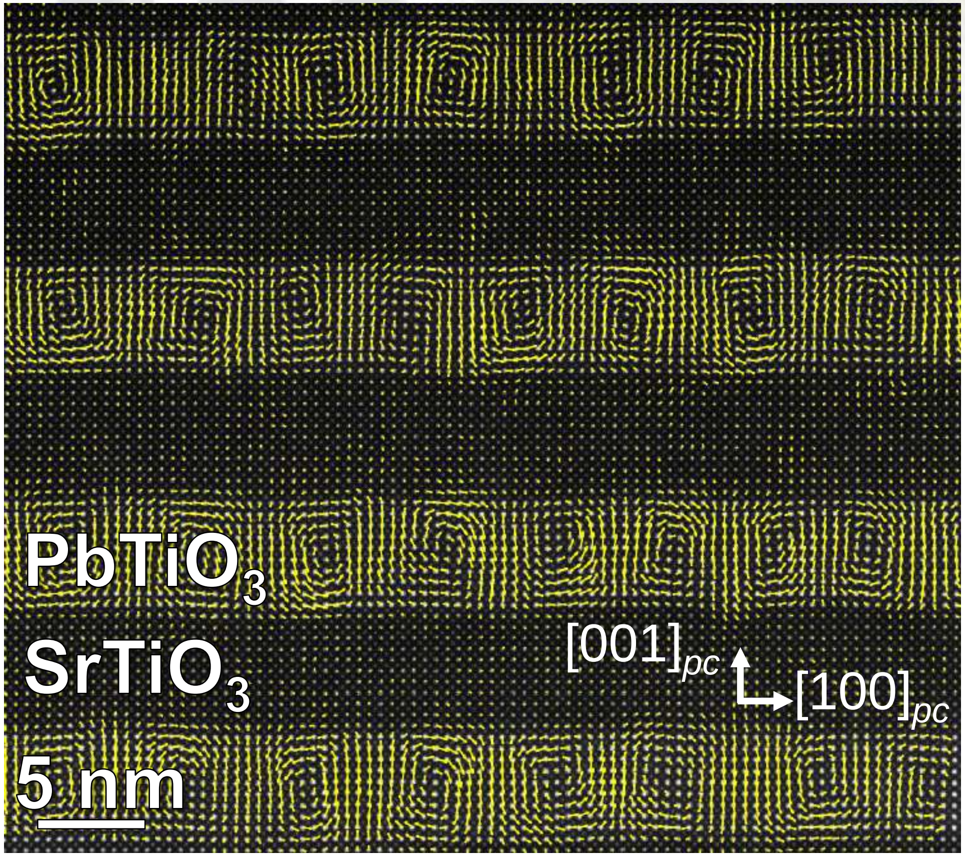
Phenomenological Modeling

Z. Hong, L.-Q. Chen (Penn State)

Ab initio Modeling

J. Junquera (U. Cantabria)



Resonant X-ray Scattering

P. Shafer, E. Arenholz (ALS/LBNL)

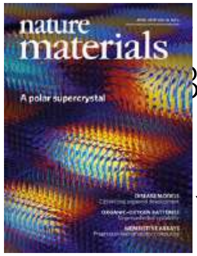
Synchrotron X-ray Scattering

V. Stoica, V. Gopalan (Penn State); L. Huajun, Z. Hong, D. Fong, E. Dufresne (APS/ANL)

PEEM

A. Farhan, A. Scholl (ALS/LBNL)

STEM Imaging



lson (ORNL), A.
erkeley); D. Muller
(Cornell)

Ultrafast Studies

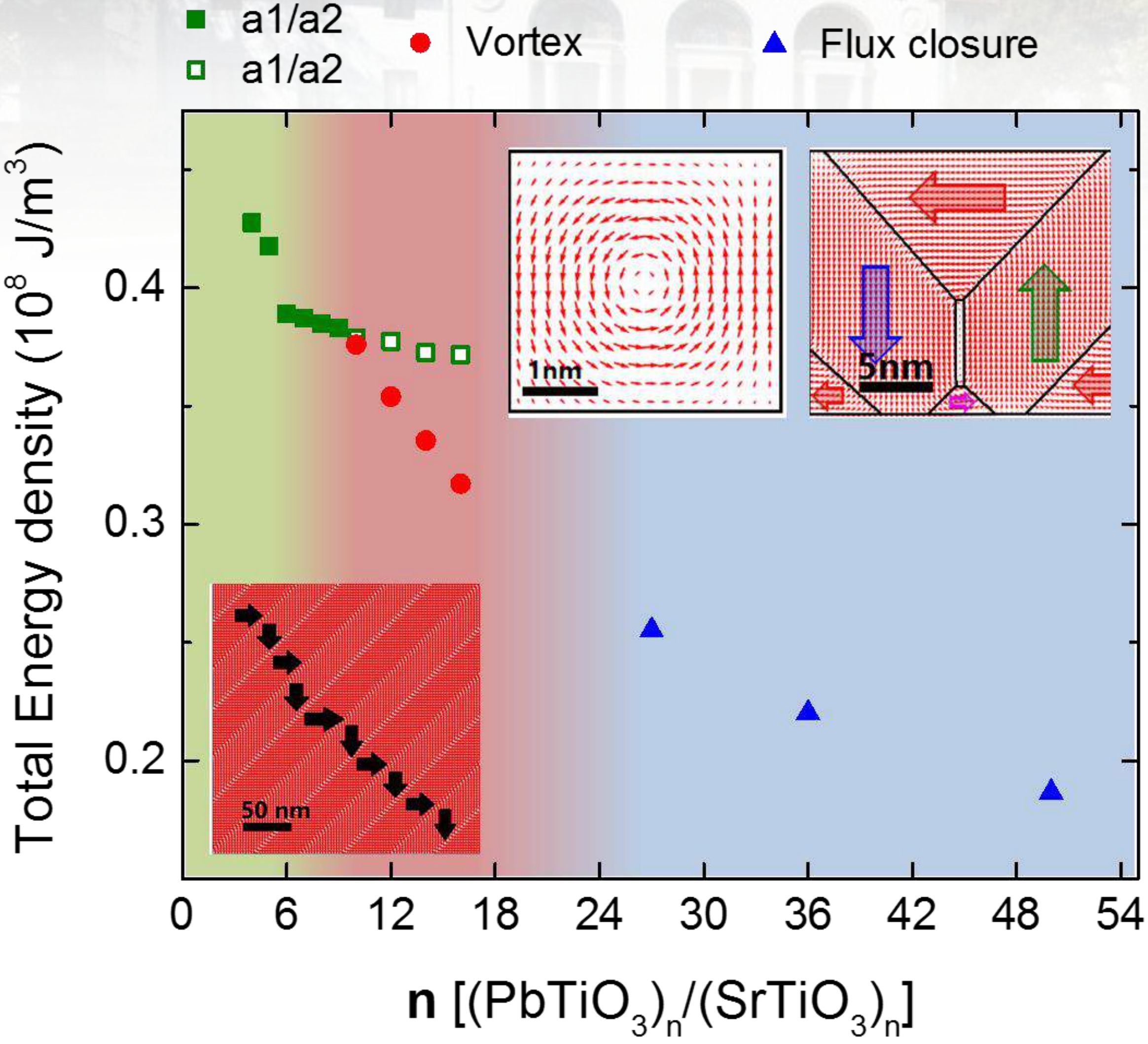
H. Wen, J. Freeland (APS/ANL); V. Stoica, V. Gopalan (Penn State); D. Basov (Columbia)

Near-Field Optical

K.-D. Park, V. Kravstov, M. Raschke (UC Boulder)

Yadav *et al. Nature* **530**, 198 (2016); Hong *et al. Nano Lett.* **17**, 2246 (2017); Damodaran *et al. Nature Mater.* **16**, 1003 (2017); Shafer *et al. PNAS* **115**, 915 (2018); V. Stoica *et al. Nature Mater.* **18**, 377 (2019); Das *et al. Nature* **568**, 368 (2019); Ghosh *et al.* in preparation (2019)

Evolution with Periodicity

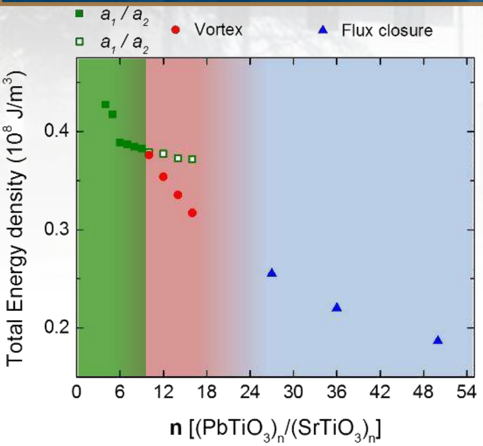


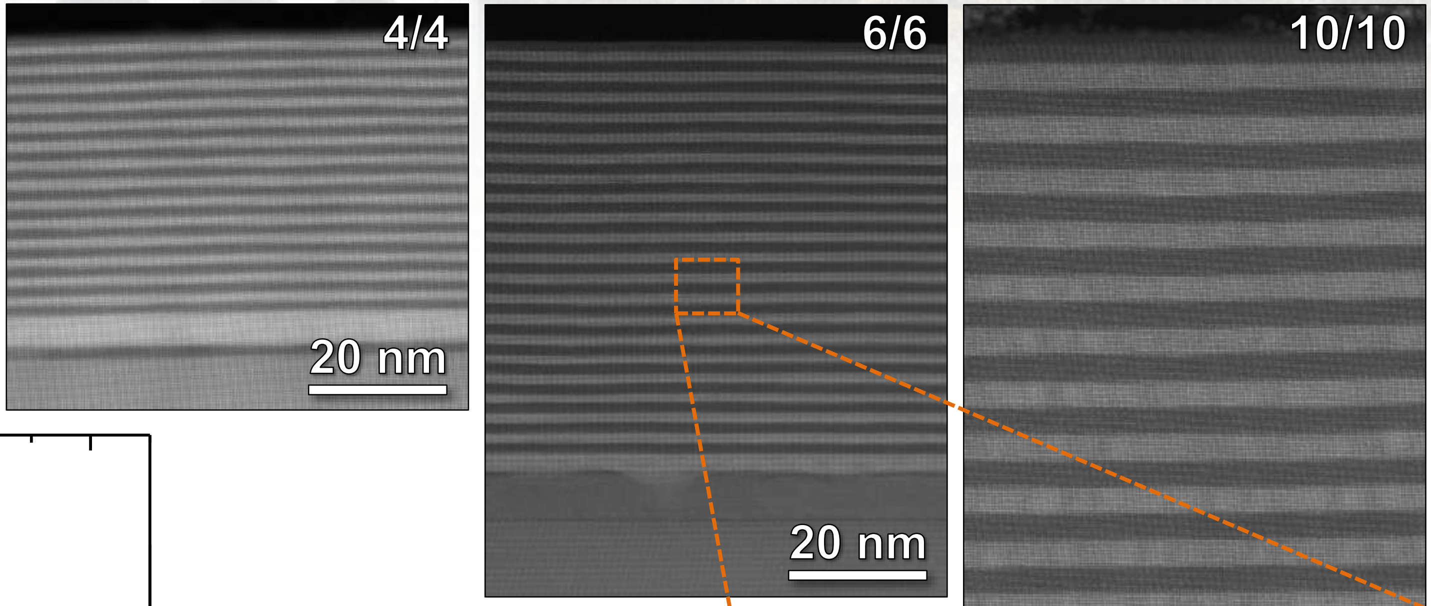
- **Short Period →** Strong depolarization effects (n < 10) drive in-plane polarized ferroelectric a_1/a_2 states
- **Large Period →** Strain effects dominate (n > 20) drive formation of flux closure domains
- **Intermediate Period →** strain, depolarization, and gradient effects compete, drive novel inhomogeneous polarization modes

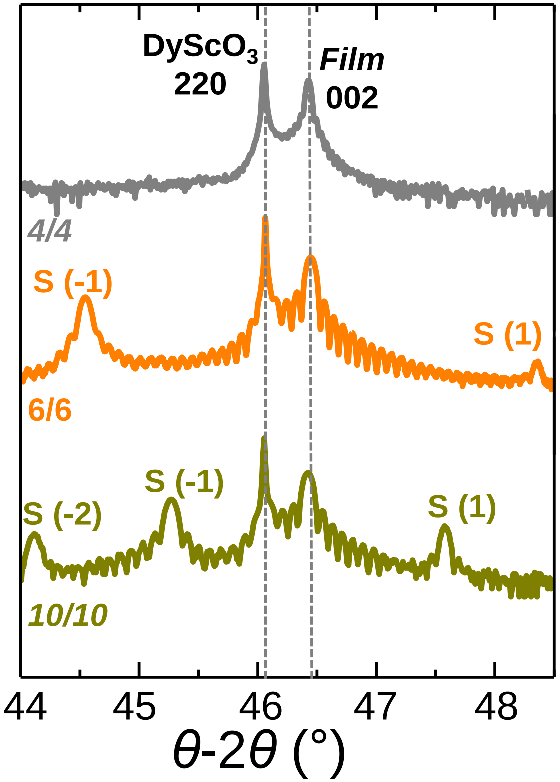
Complex phase evolution with ferroelectric and vortex (toroidal) order is predicted…

Yadav *et al.* *Nature* **530**, 198 (2016)

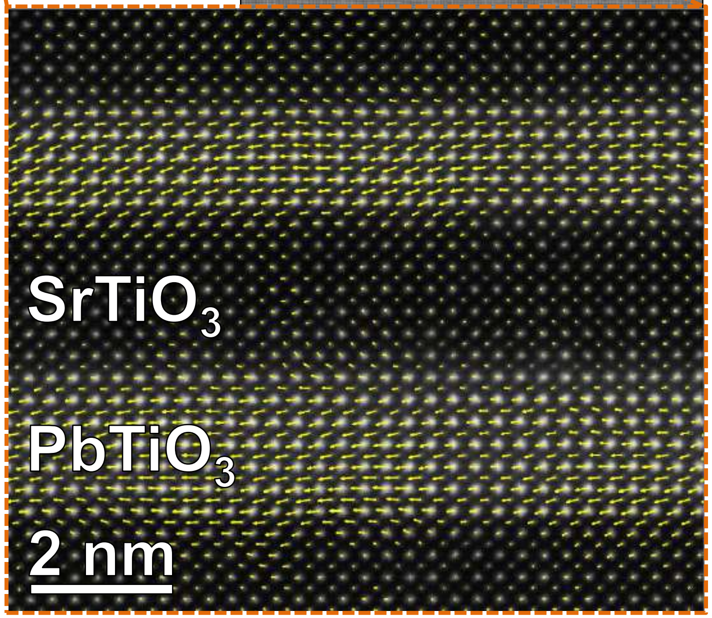
Short-Period Superlattices







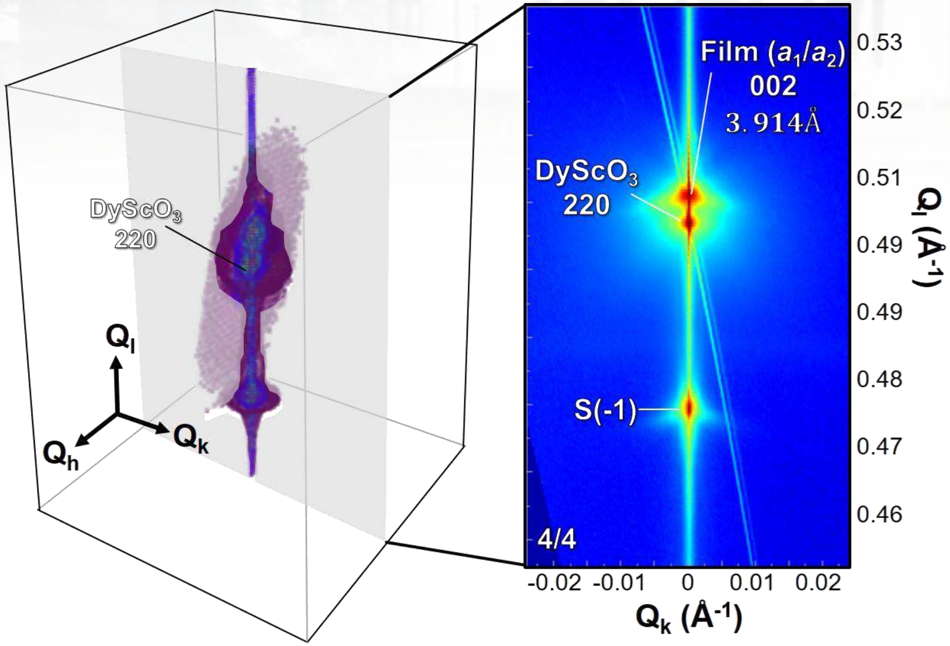
- ϑ-2ϑ scans → Single film (alloy) peak + superlattice peaks (S)
- High-quality heterostructures
- Atomic-resolution imaging reveals in-plane aligned polarization in $PbTiO_3$



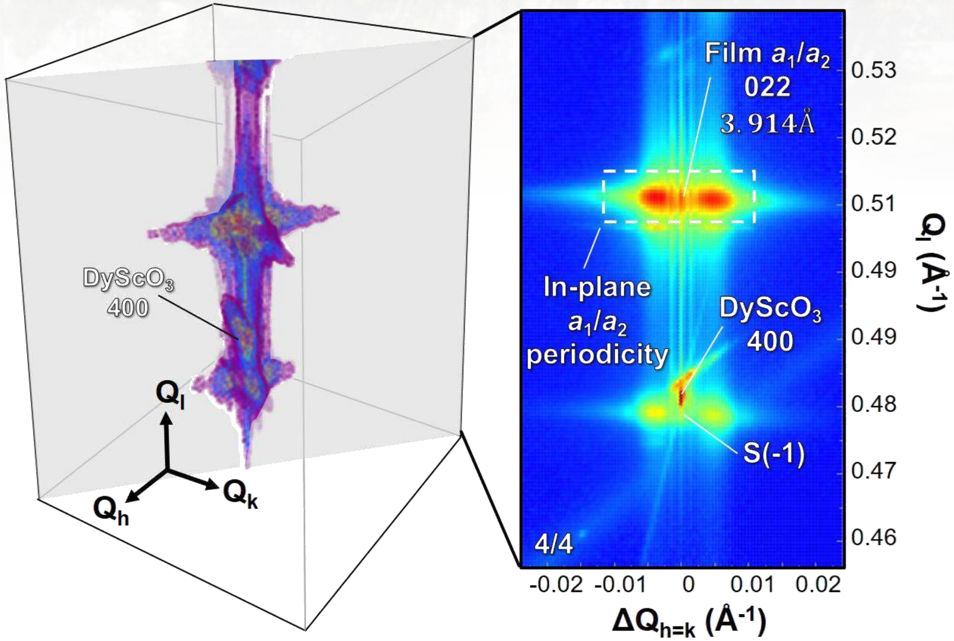
Damodaran *et al*. *Nature Mater*. **16**, 1003 (2017)

Short-Period Superlattices – 3D RSMs

220-Diffraction Condition



400-Diffraction Condition

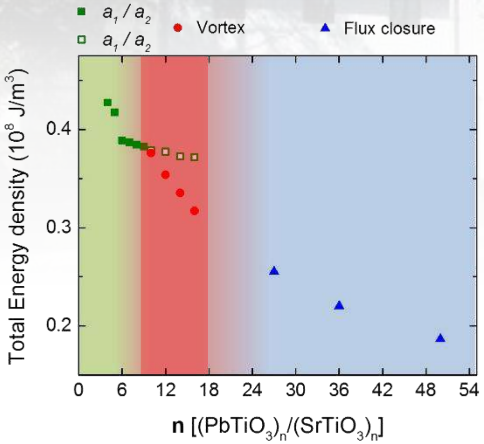


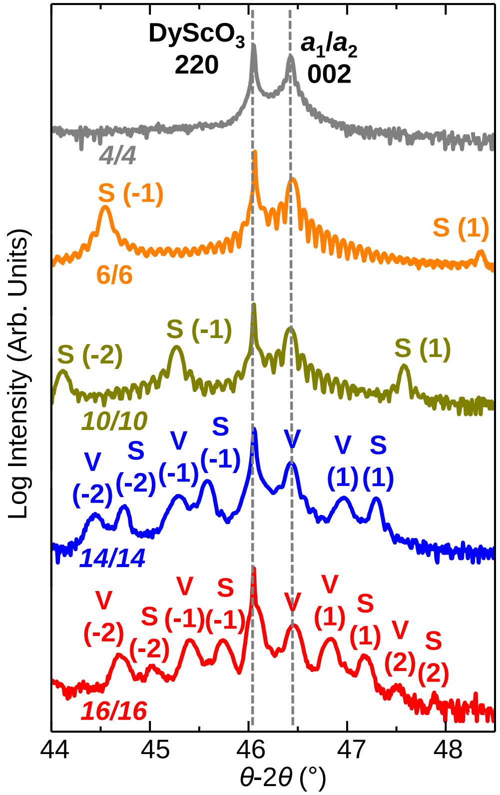
- No periodicity related satellites about 220-diffraction condition → absence of out-of-plane modulation of polarization, consistent with in-plane polarized a_1/a_2 domains
- Satellites along $h = k$ directions about the 400-diffraction condition → consistent with a_1/a_2 domains

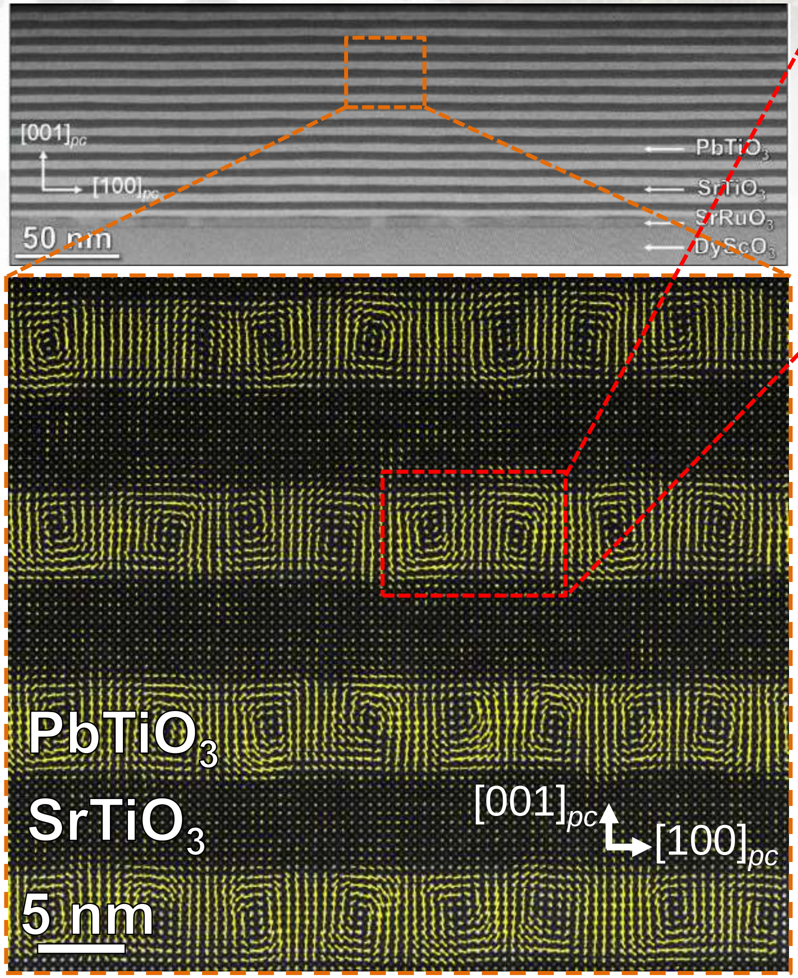
Short-period superlattices → conventional a_1/a_2 domains

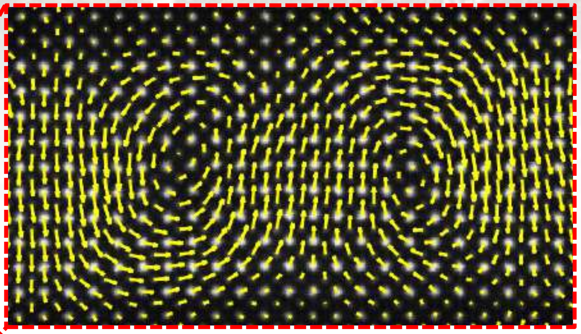
Damodaran *et al*. *Nature Mater.* **16**, 1003 (2017)

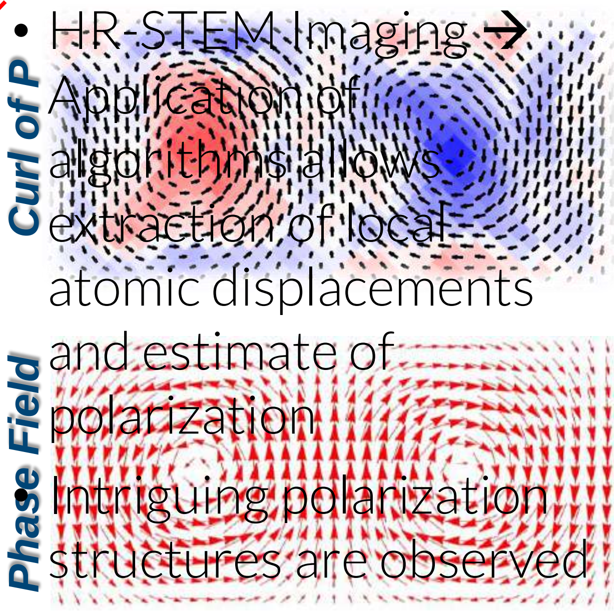
Intermediate-Period Superlattices











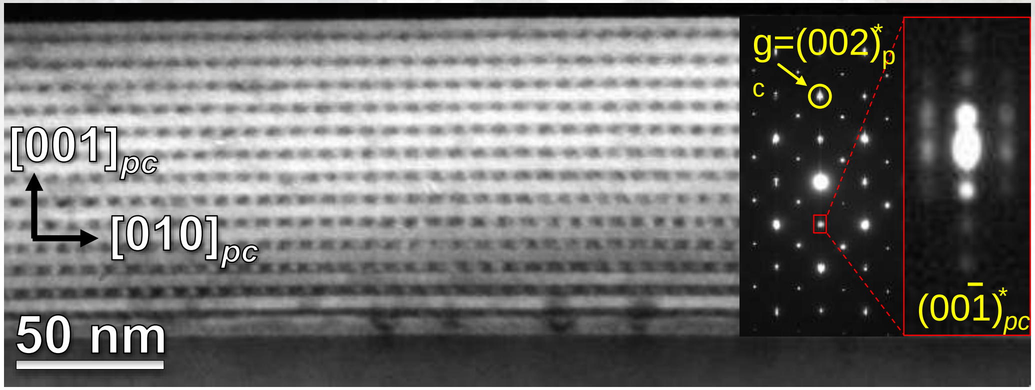
- HR-STEM Imaging → Application of algorithms allows extraction of local atomic displacements and estimate of polarization
- Intriguing polarization structures are observed
- Continuously rotating polarization profile → Polar Vortices

Realization and direct imaging of polarization vortex structures → Smoothly rotating polarization, novel structures

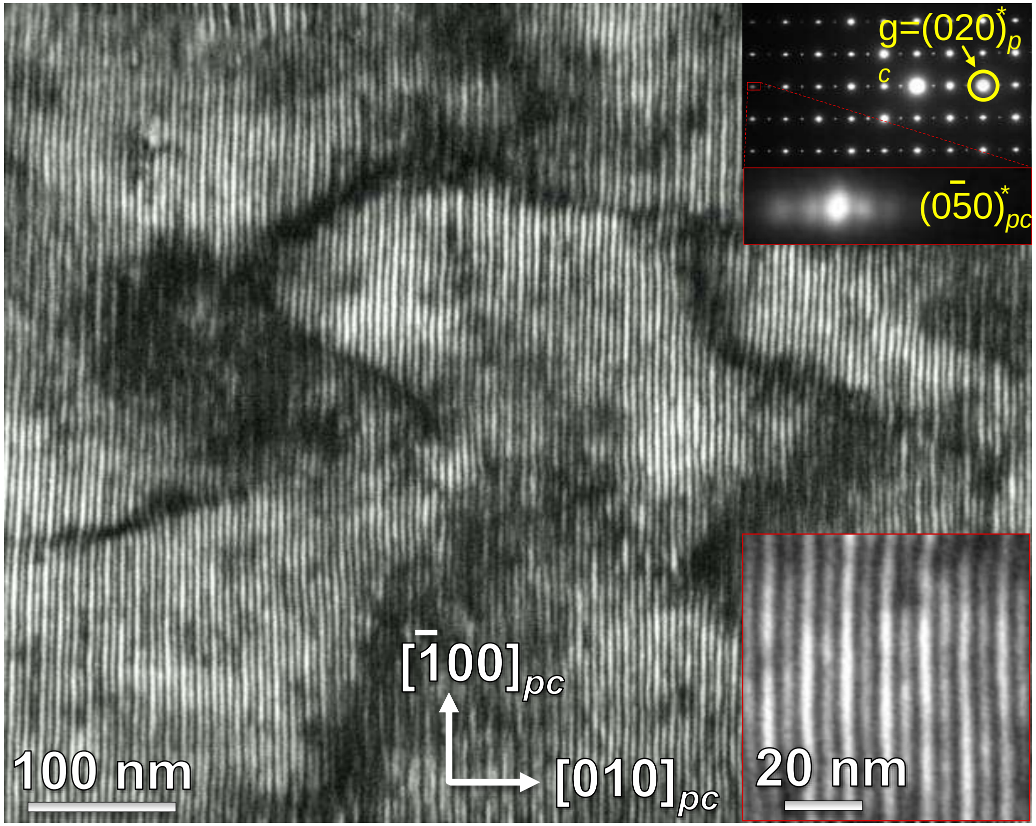
Yadav *et al. Nature* **530**, 198 (2016)

Long-Range Order of Polar Vortices

Cross-Section



Plan-View



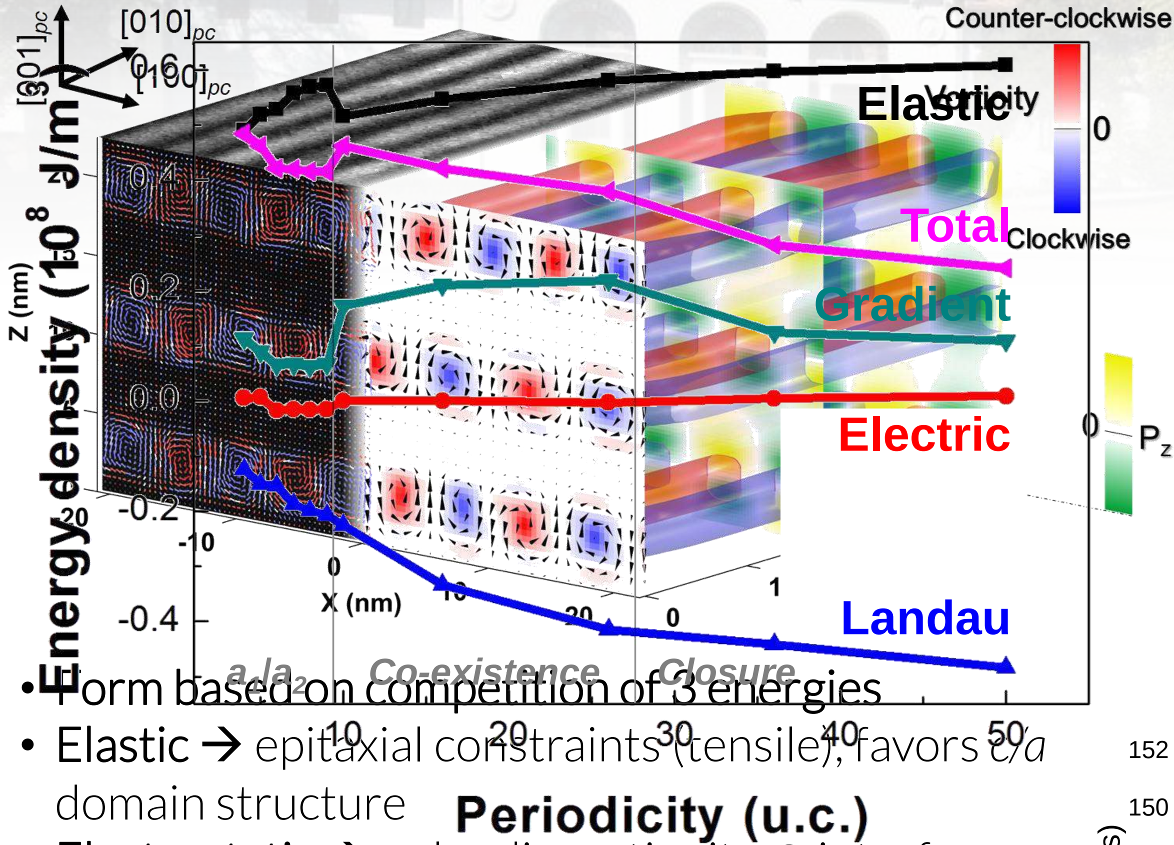
Diffraction Contrast Imaging

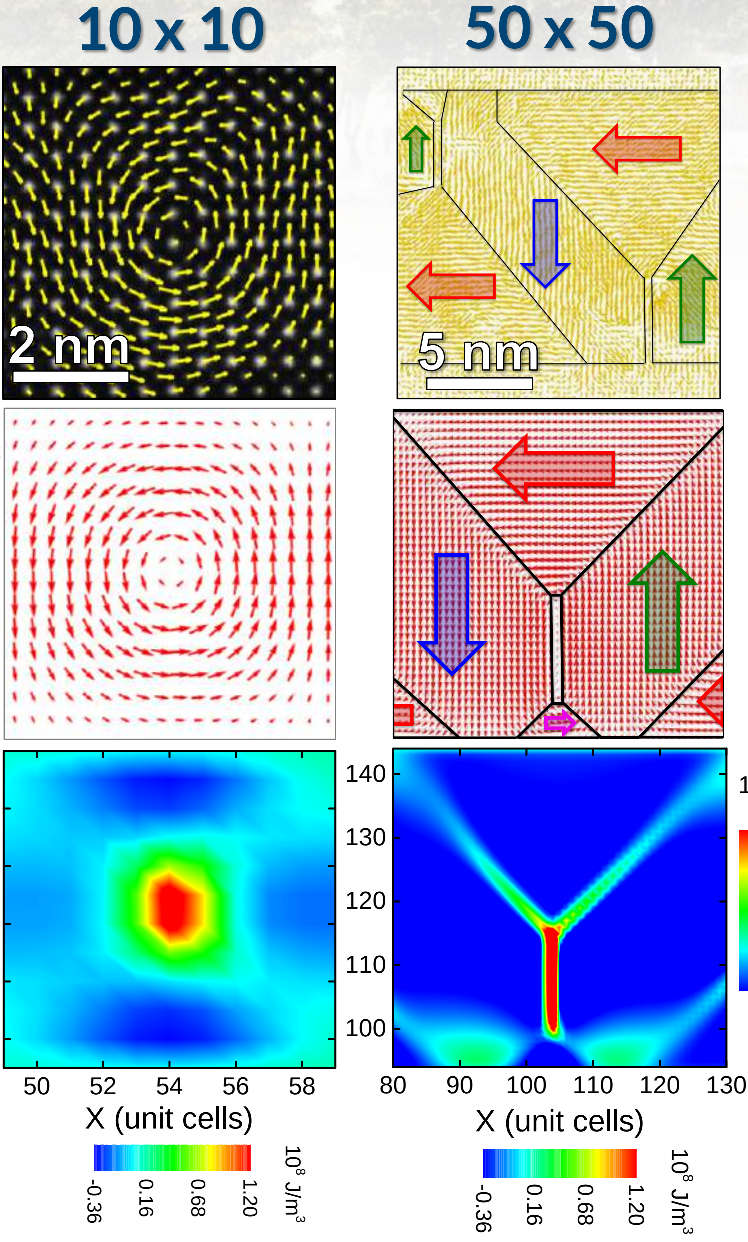
- Consistent with HR-STEM imaging → ordered vortex structures exist over large length-scales
- Cross-section
  - In-plane order → periodicity of ~10 nm
  - Out-of-plane → ordered arrays from layer to layer
- Planar-view
  - Local order → ~10 nm periodicity
  - Vortex “tubes” extend >1 micron

Novel state of matter → polar vortex tubes

Yadav *et al. Nature* **530**, 198 (2016)

Origin of the Polar Vortices





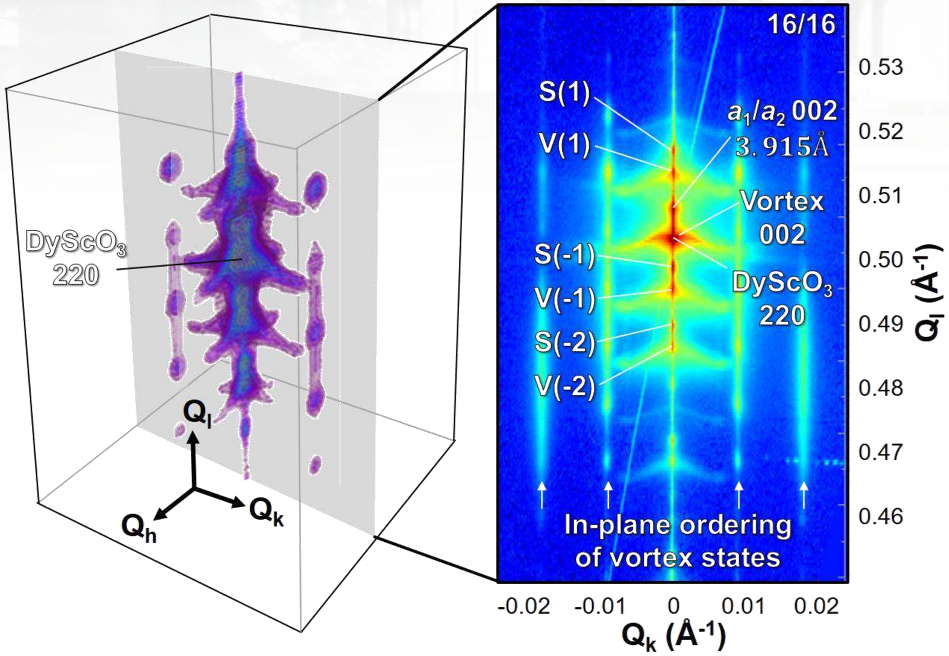
- Form based on competition of 3 energies
- Elastic → epitaxial constraints (tensile), favors c/a domain structure
- Electrostatic → polar discontinuity @ interface; driving force for bound charges, $\nabla \cdot \boldsymbol{P} \neq 0$
- Gradient → energy required to rotate/change the direction/magnitude of the polarization
- Result → localized in-plane *P* components at the interfaces and alternating out-of-plane *P* components mid layer → rotating polarization

- Landau → diminishing values of *P* as you move from flux-closure to vortex to a_1/a_2
- a_1/a_2 to Vortex → Discontinuous changes in elastic (down), gradient (up), and electric (up) energies

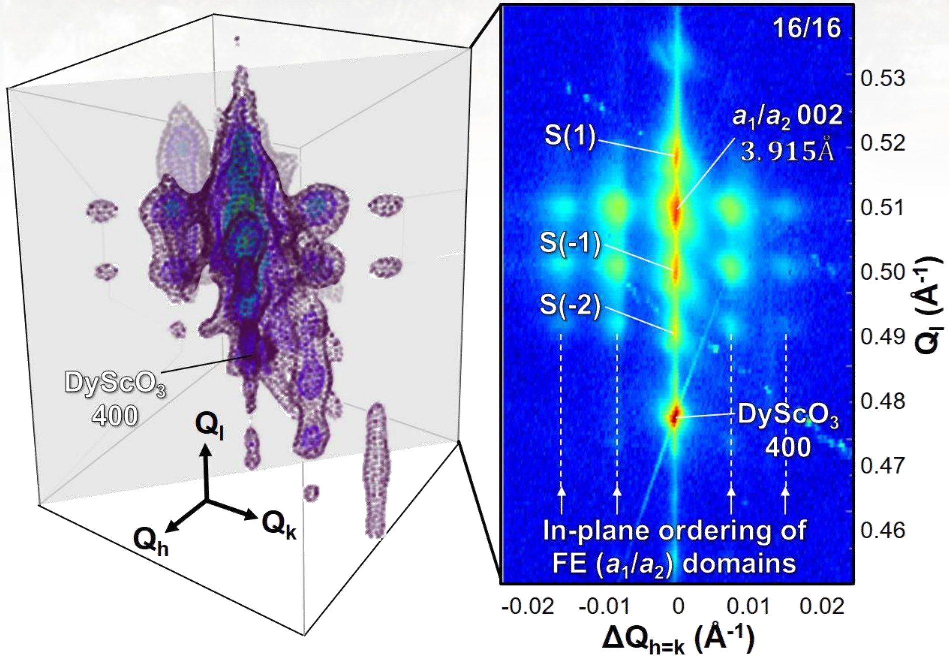
Yadav *et al.* *Nature* **530**, 198 (2016)

Inter.-Period Superlattices – 3D RSMs

220-Diffraction Condition



400-Diffraction Condition

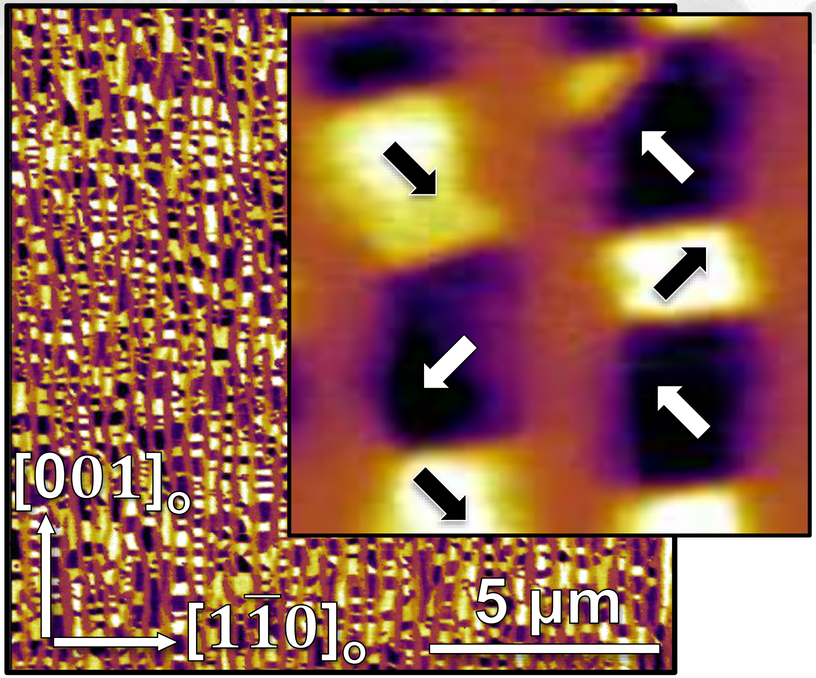


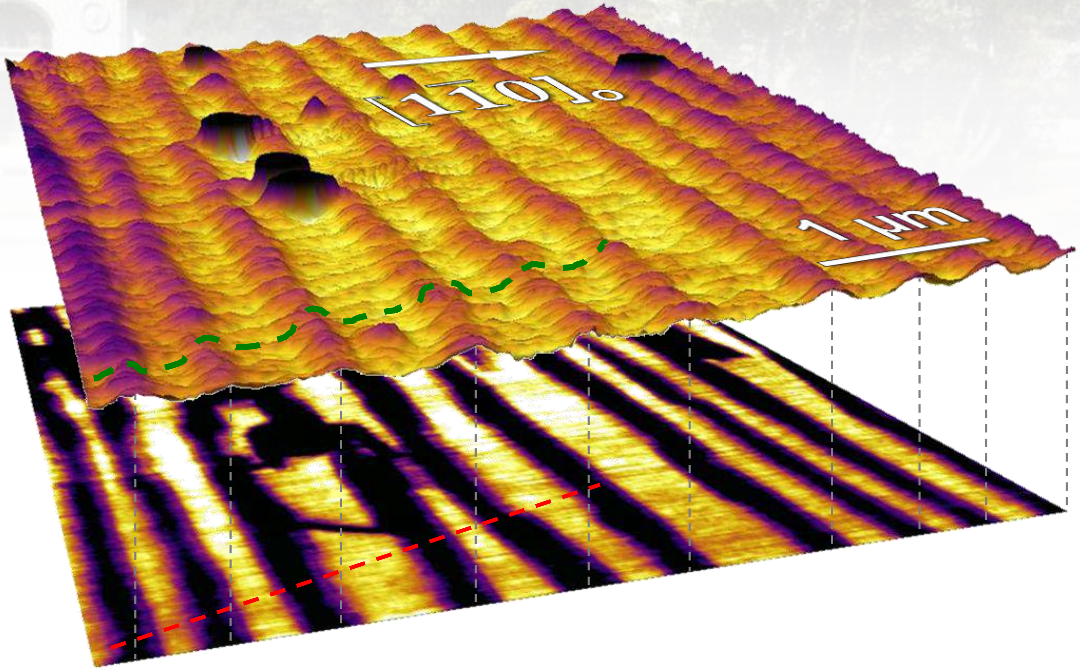
- Emergence of satellites indicating P_z modulation with periodicity of ~10 nm in the $[100]_{pc}$ – signature of the *vortex phase*
- a_1/a_2 domains give rise to satellites (~13 nm periodicity) along $h = k$ directions about the 400-diffraction condition → coexistence with vortex states

XRD → Co-existence of ferroelectric & vortex phases

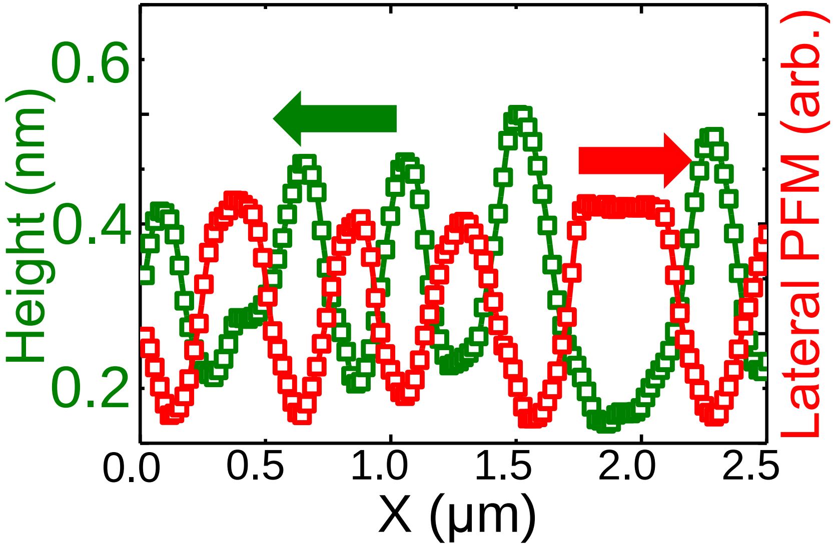
Damodaran *et al. Nature Mater.* **16**, 1003 (2017)

Nanoscale Distribution of Phases





- Complex patterns → stripes of low (0) response (*vortex*) separated by regions of large response (*a domains*)
- Elevated regions (larger lattice parameter) have near 0 piezoresponse → *Vortex*
- Recessed regions (smaller lattice parameter) have strong in-plane piezoresponse along <110> → a_1/a_2



Damodaran *et al. Nature Mater.* **16**, 1003 (2017)