All-physics multi-scale approach to improve and invent advanced functional materials

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(Thanks to the FNR for funding almost all our work)

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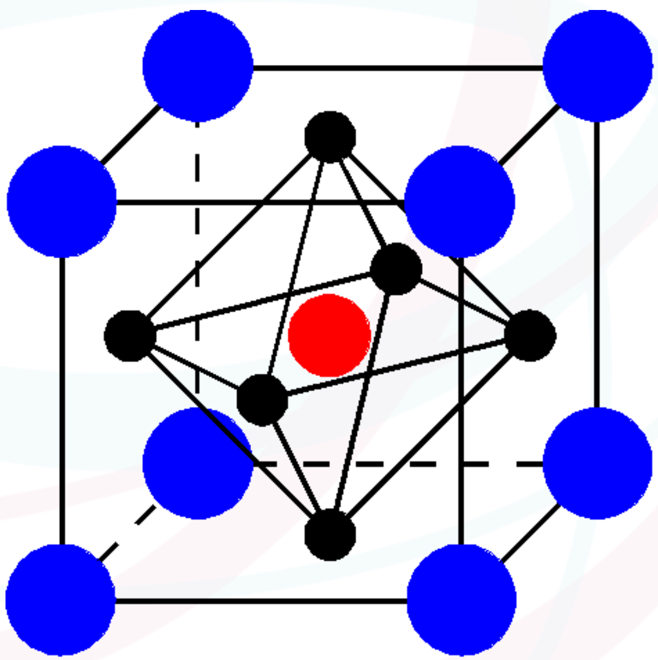
The Materials
& the Effects

(Ferroelectric) perovskite oxides

• Perovskite oxides: large family of “very similar” materials, which present very different behaviors (structural, electric, magnetic, optical) depending on their composition & the polymorph they adopt



ABO_3

A = K, Ba, Pb, Ca, Bi ...

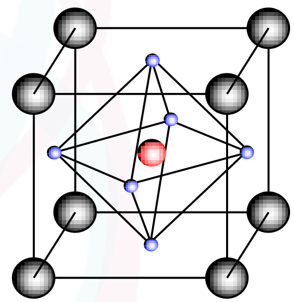
B = Ti, Zr, Nb, Sc, Fe, Ni ...

Crystals: $BaTiO_3$, $PbTiO_3$, $KNbO_3$, $SrTiO_3$, $BiFeO_3$, $BiCoO_3$, ...

Solid solutions: $PbZr_{1-x}Ti_xO_3$ (PZT), $PbMn_{1/3}Nb_{2/3}O_3$ (PMN), $Ba_{1-x}Sr_xTiO_3$ (BST), $Bi_{1-x}La_xFeO_3$, ...

Our Advanced Functional Materials…

… transform cause into effect

Cause		Effect
electric field		polarization
magnetic field		magnetic order
mechanical pressure		volume & shape
heat		temperature
light		electric conductivity
chem. environment	transducer	dielectric permittivity
various gradients		electric voltage

Small cause → big temporary effect : sensors, harvesters, etc.

Bigger cause → permanent effect : switches, memories, etc.

Our Advanced Functional Materials…

… transform cause into effect

Cause		**Effect**
electric field		polarization
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mechanical pressure		volume & shape
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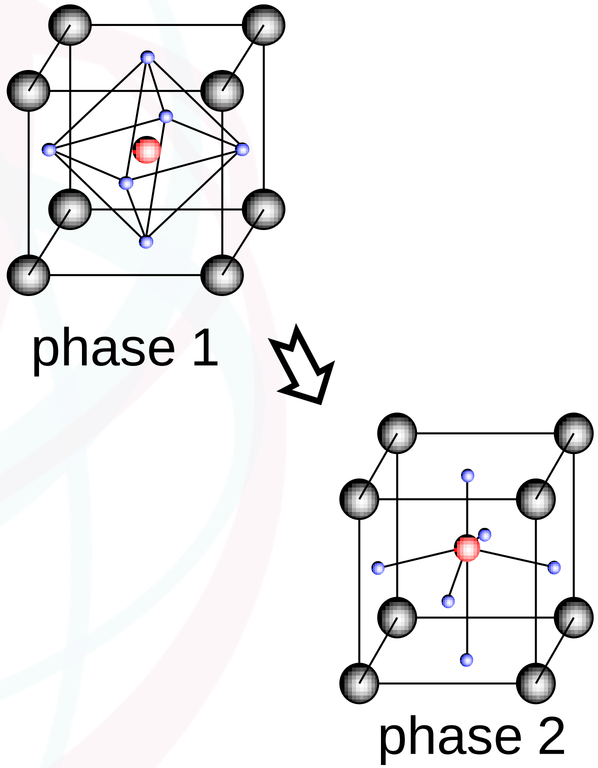
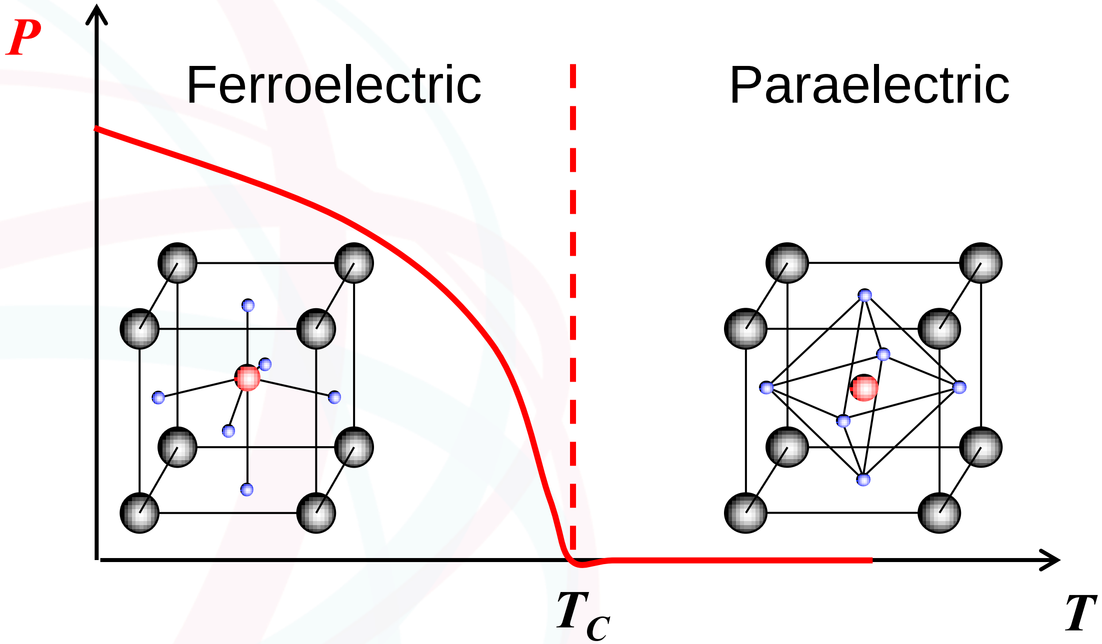
light		electric conductivity
chem. environment		dielectric permittivity
various gradients		electric voltage



stimulus → structural phase transition → effect

Structural phase transitions

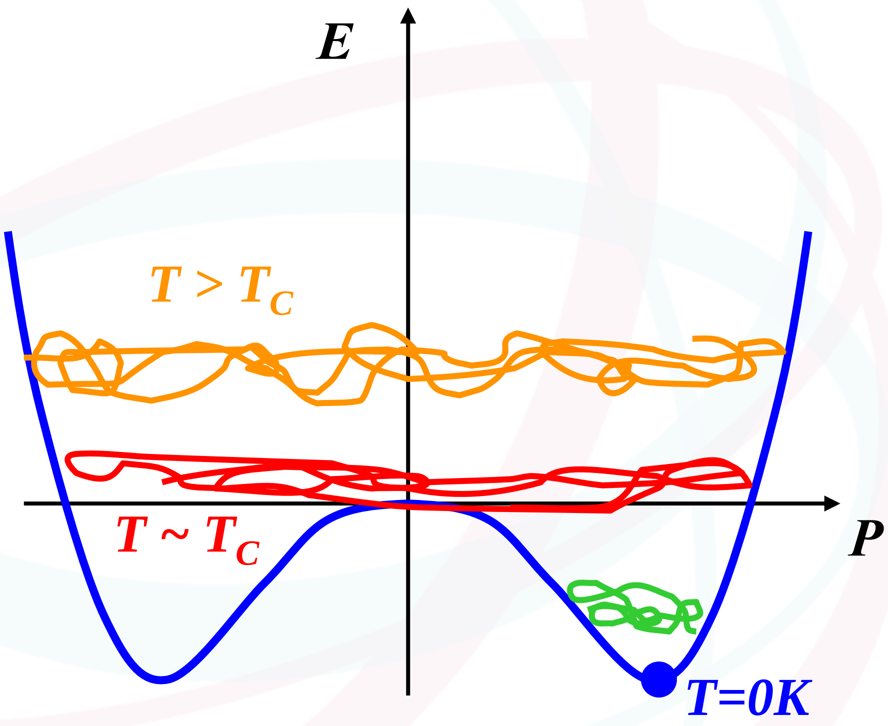


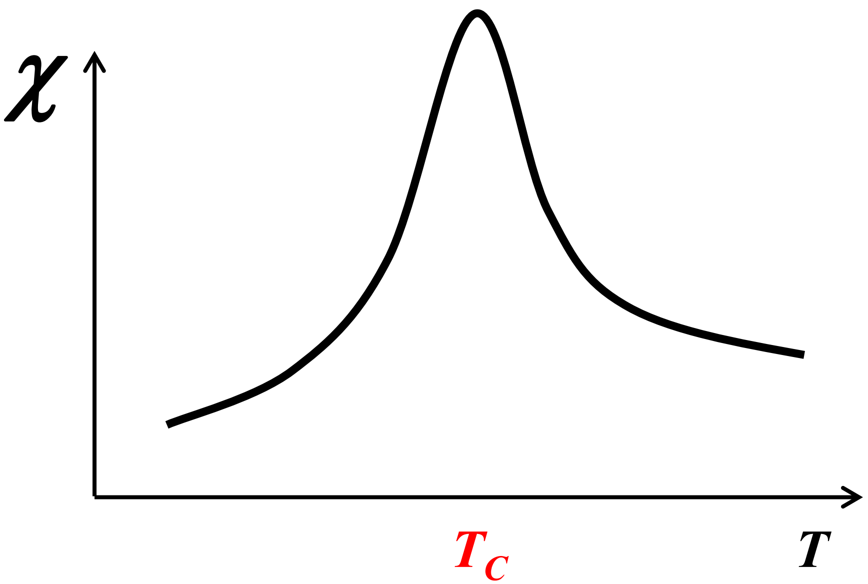
• Many materials change their average atomic structure at a given temperature T_C (critical, Curie temperature)

• Structural phase transitions usually involve changes in the physical properties of the materials (example above: material becomes piezoelectric below T_C)

Displacive transitions, large responses

• High temperature causes disorder → Material orders upon cooling



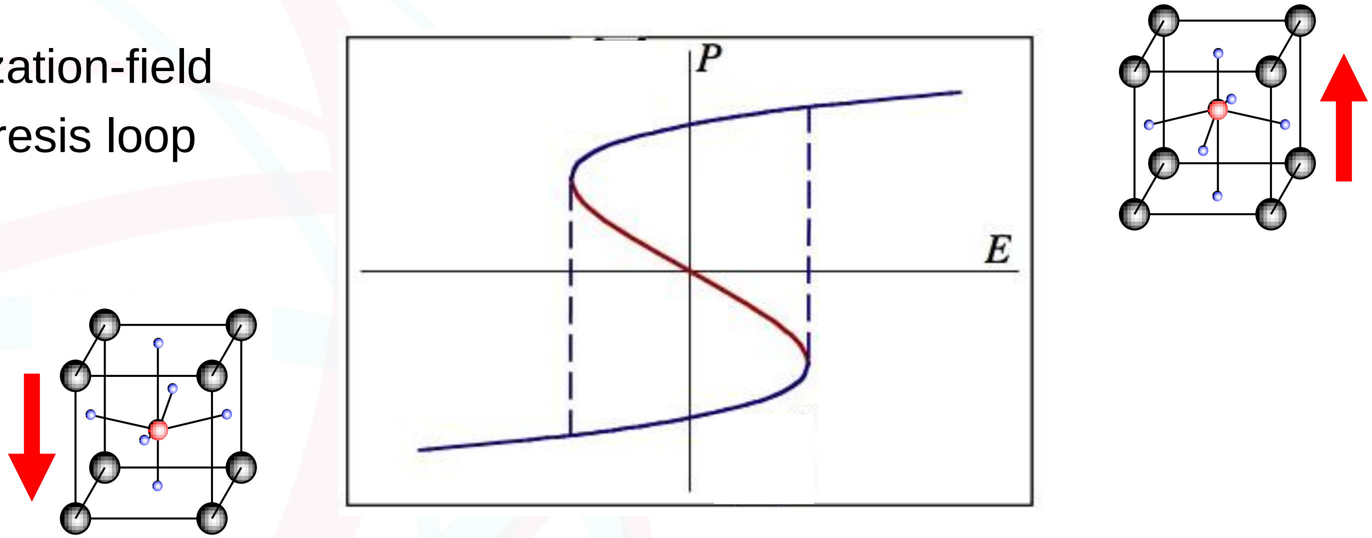


Very large (even divergent!) properties at transition region

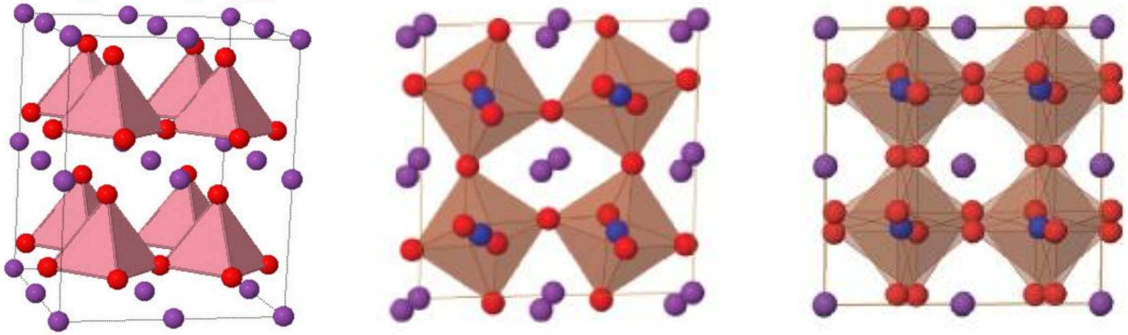
• Application: sensors, actuators, energy harvesters, field-effects, etc.

Static and reversible structural changes

Polarization-field hysteresis loop



Different polymorphs, different properties



• Application: switches, memories, etc.

Our Goals

1. Identify (discover) new materials or states with optimized or novel properties

2. Identify efficient and robust ways to induce structural transitions…

   … by means of:

   - Electric fields (low cost)
   - Strain (e.g., via substrates)
   - Light (remote actuation, etc.)

   … to control functional properties (electromechanical responses, magnetism, electric & thermal conductivity, etc.)

Example I:

Room-Temperature Magnetoelectric Switching

Heron, Íñiguez, Ramesh *et al.*, Nature 516, 370 (2104)

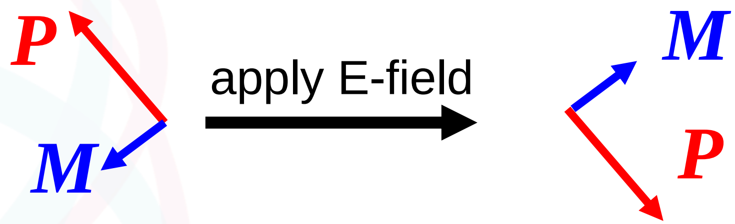
MESO device → Manipatruni *et al.*, Nature 565, 35 (2019)

On-going project funded by intel

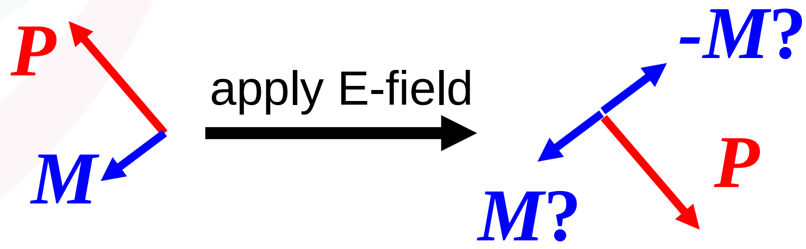
Low-power magnetization-reversal

• Applying an electric voltage is much easier and cheaper than applying a magnetic field

Wanted:

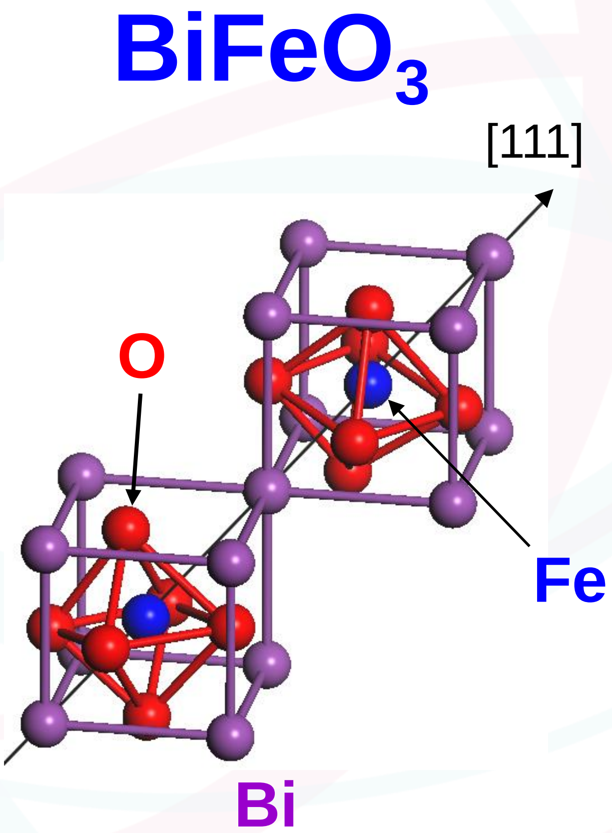


Reality:

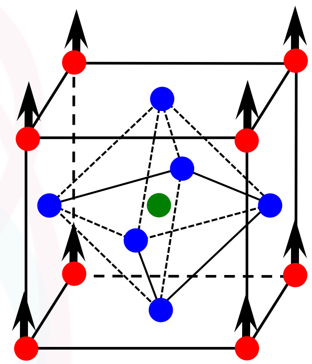


Room temperature multiferroic $BiFeO_3$

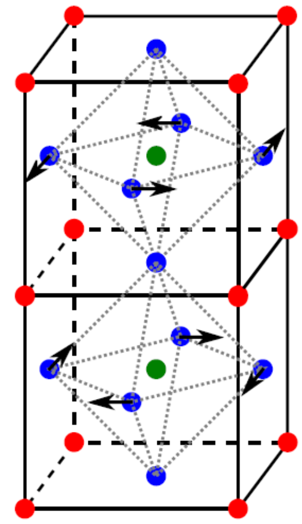
- One of the very few materials that are magnetoelectric multiferroic at T_{room}



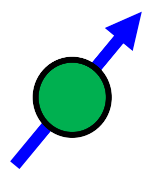
Three main ingredients:



Ferroelectric polarization (**P**)



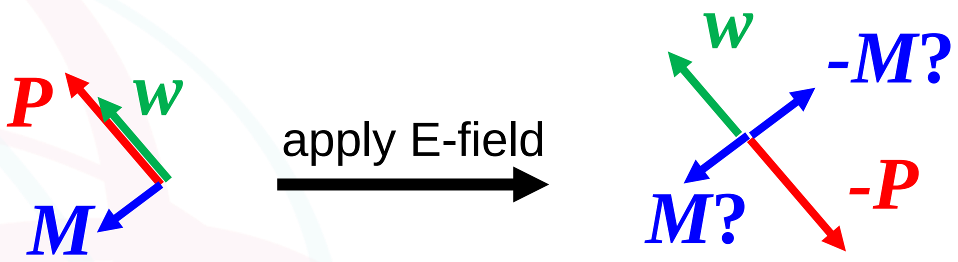
Rotations of the O_6 groups (**w**)



Fe's spin & resulting magnetization (**M**)

Magnetoelectric switching in $BiFeO_3$

Expected:

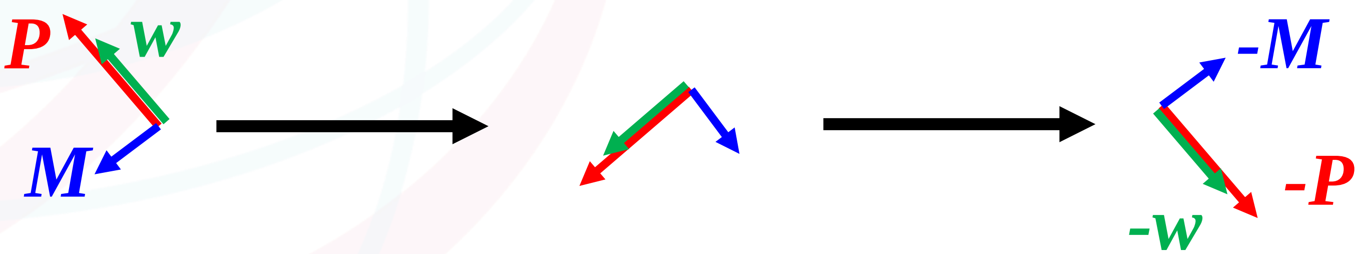


- P switches but M does not… because M is not coupled to P

→ P and w are coupled: they want to be parallel or anti-parallel

→ w and M are coupled

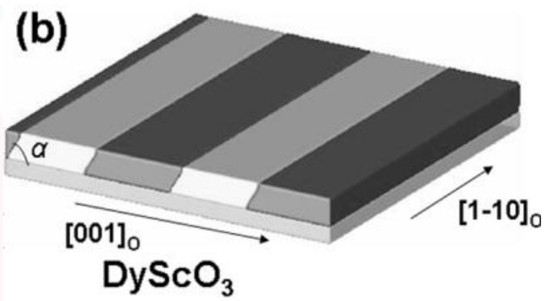
Solution: Switch in several steps !!

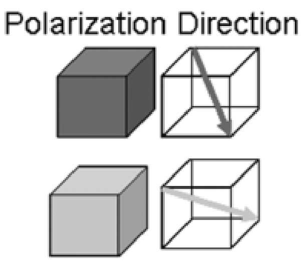


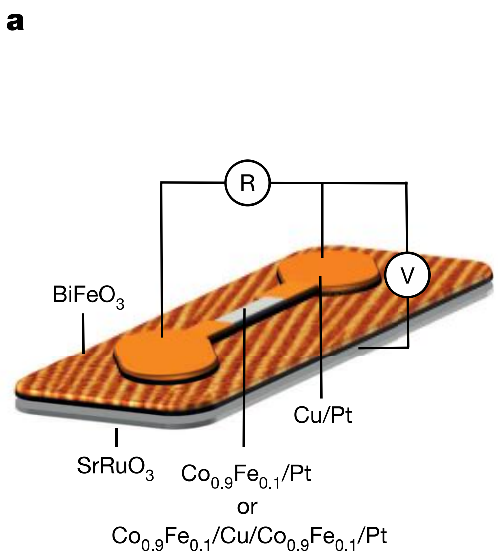
Switch by rotating P → w follows → M follows !!!

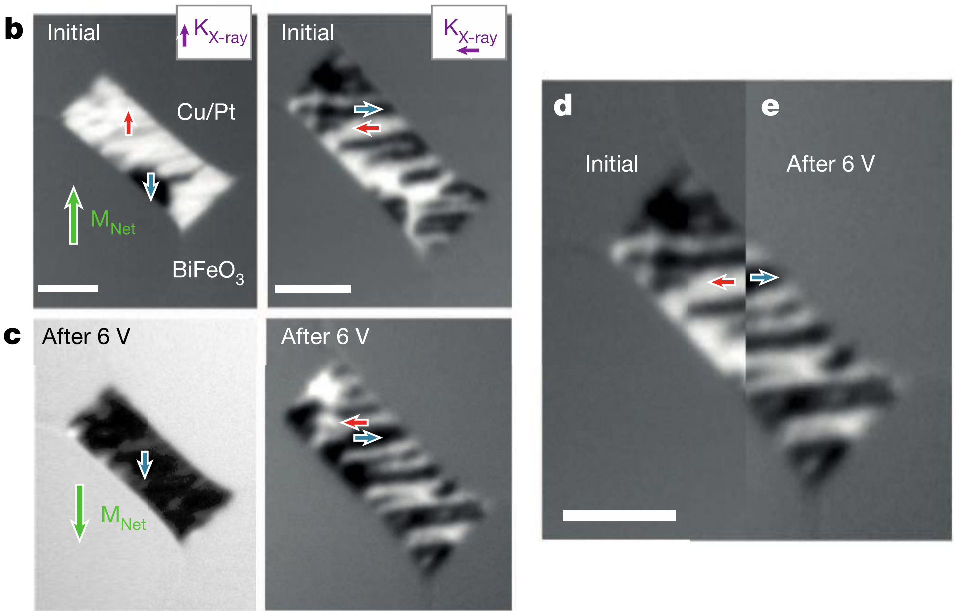
M-reversal at room temperature in $BiFeO_3$

$BiFeO_3$ on $DyScO_3$



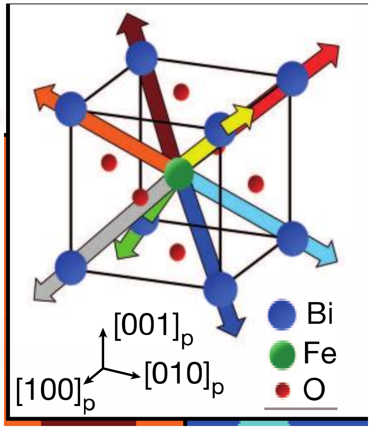


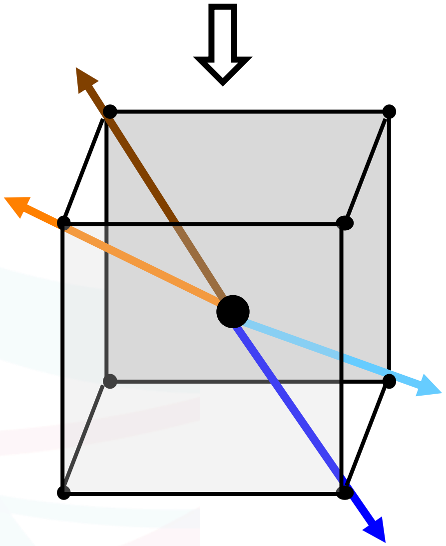


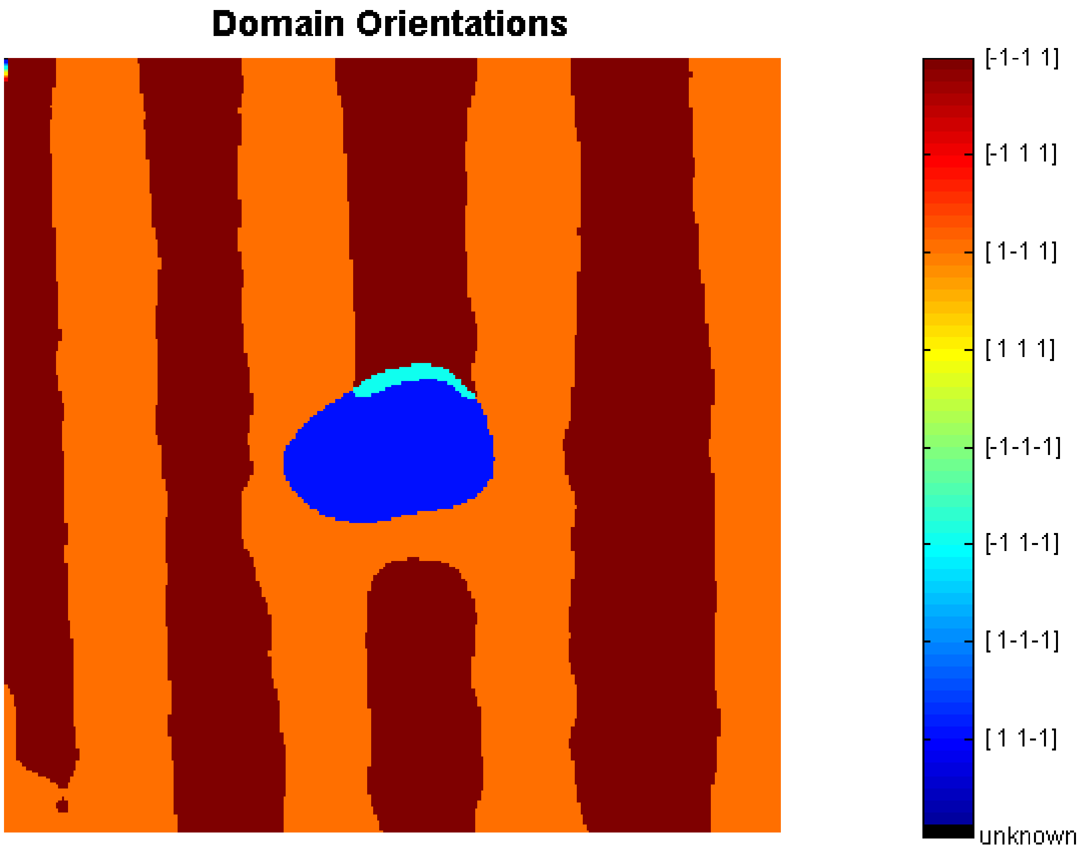


XMCD–PEEM images

Polarization switching path



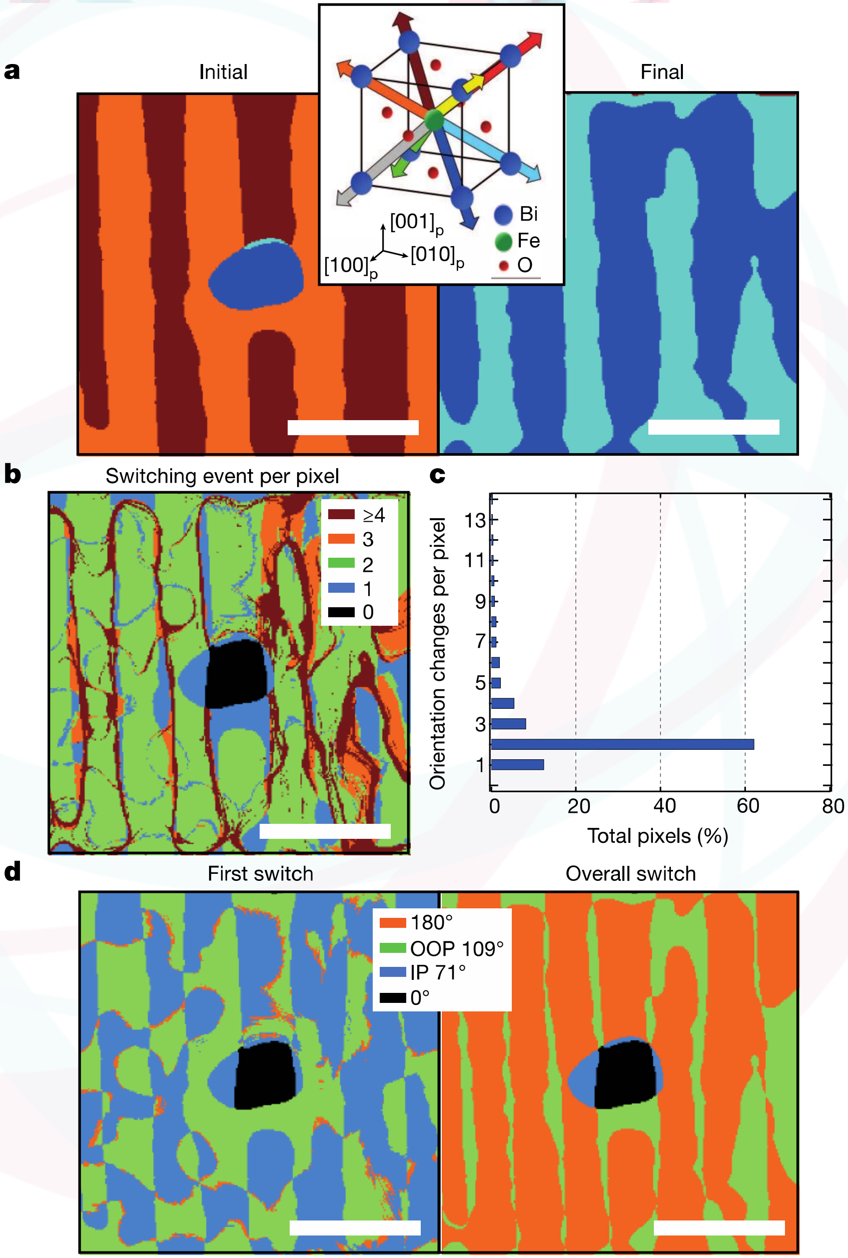




Time-dependent, dual-frequency PFM (~ 40 μs/frame)

- Courtesy of J. L. Bosse, L. Ye and B. D. Huey, University of Connecticut

Polarization switching path



Two-step polarization switch

Why does it happen?

- Domain wall (DW) planes preserved throughout the switching (**elastic**)
- **Electrostatics** (neutral DWs)

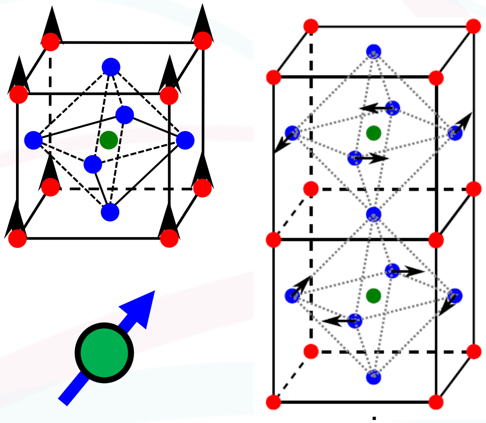
→ selects polarization variants

→ forbids direct out-of-plane switch

- Multi-step switch occurs

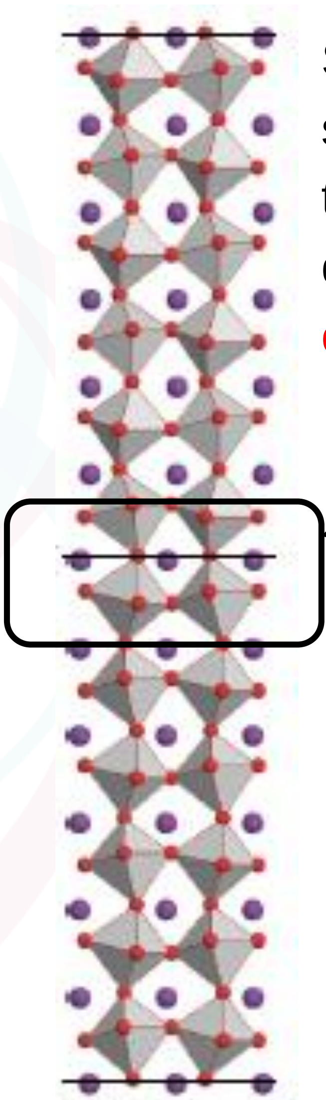
P switches in steps → w follows → M follows !!

Simulating switching: needed ingredients

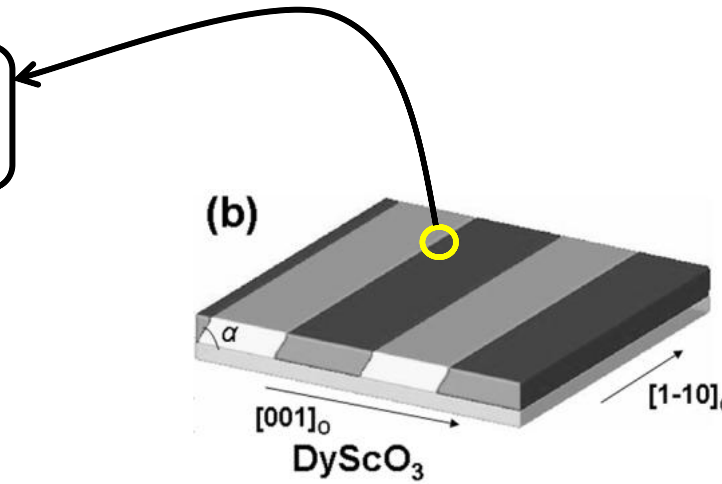


Atomistic description of structural and magnetic degrees of freedom, and their mutual couplings.
Energy scale ~ 1 - 50 meV/atom
(Quantum Mechanics)

Thermal effects not trivial, simple approximations do not work
(Statistical Mechanics)



Switching path determined by states that can or cannot for at the boundaries between domains **(QM accuracy and detail for ~ 10^3-10^4 atoms)**



Switching kinetics, under elastic and electric constraints, of mesoscopic domain patterns (FEMs)

Example II:

Domain-wall devices

Farokhipoor, Magen, Íñiguez, Noheda *et al.*, Nature 515, 379 (2014)

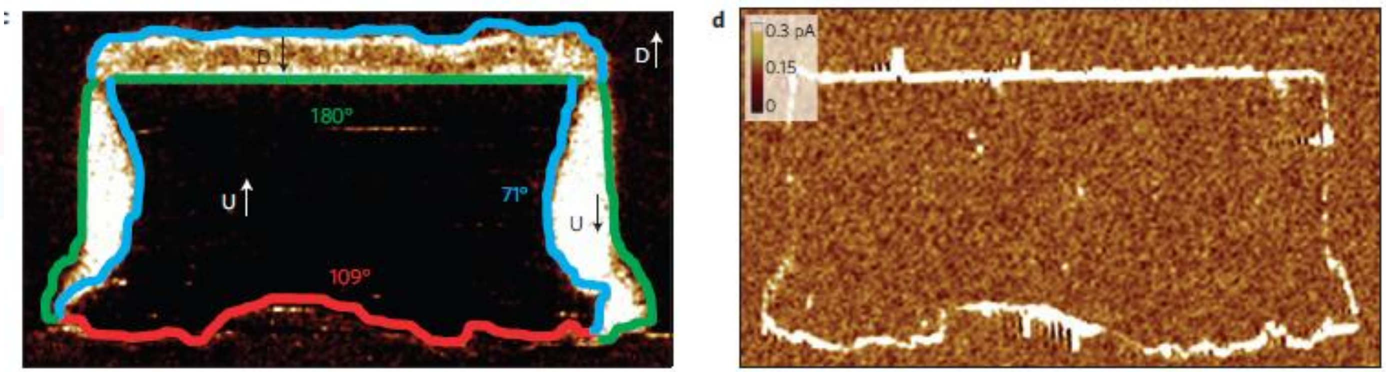
Zhao & Íñiguez, NPJ Comp. Mats. (in press)

FNR-funded CORE project “NEWALLS”

“The wall is the device”

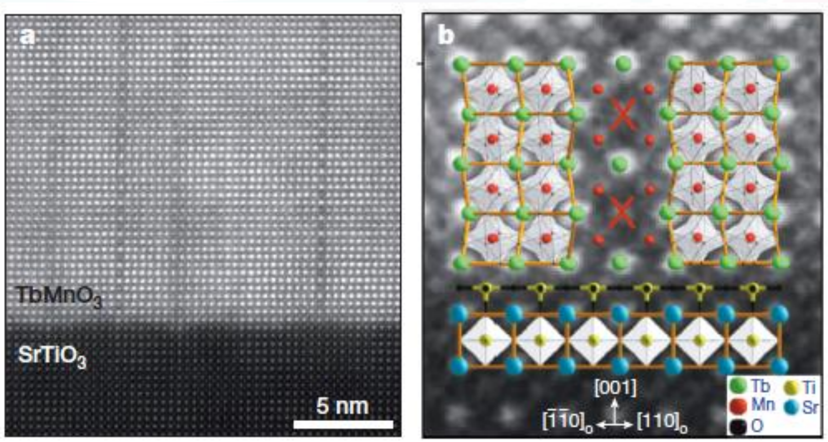
- Enhanced conductivity at domain walls of $BiFeO_3$

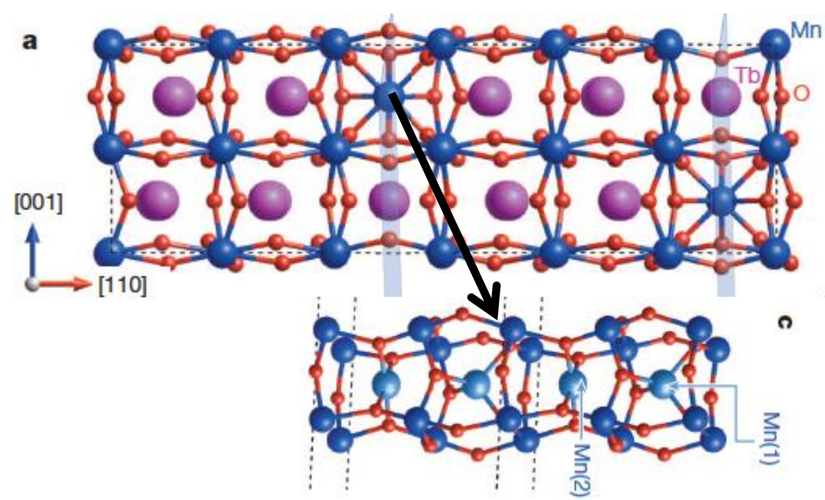
  Seidel *et al*., Nat. Mats. 8, 229 (2009); Farokhipoor and Noheda, PRL 107, 127601 (2011)



- Novel never-seen-in-bulk-form 2D structures at structural domain walls

  Farokhipoor, Magen, Íñiguez, Noheda *et al*., Nature 515, 379 (2014)





New 2D materials at domain walls

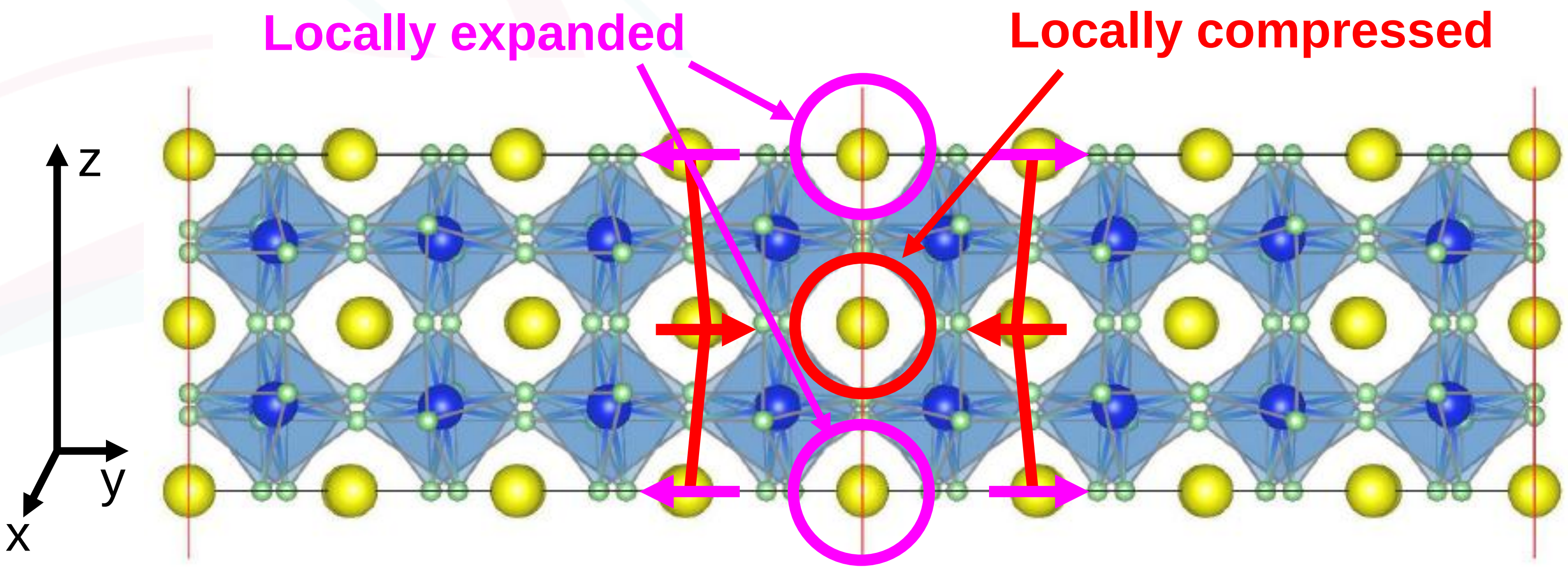
Using <u>heavy</u> first-principles simulation methods

(based on Quantum Mechanics)

- Materials: **$LaGaO_3$**, $CaTiO_3$, $TbMnO_3$
- Dopants: representative 3d, 4d and 5d transition metals
- Predict at which site substitution will take place
  - A vs. B site
  - Domain wall vs. domain
  - Specific site within domain wall
- Study induced electronic, magnetic, ferroelectric properties

Zhao & Íñiguez, NPJ Comp. Mats. (in press)

Our favorite domain wall in orthorhombic perovskites



antiphase tilts about [110]

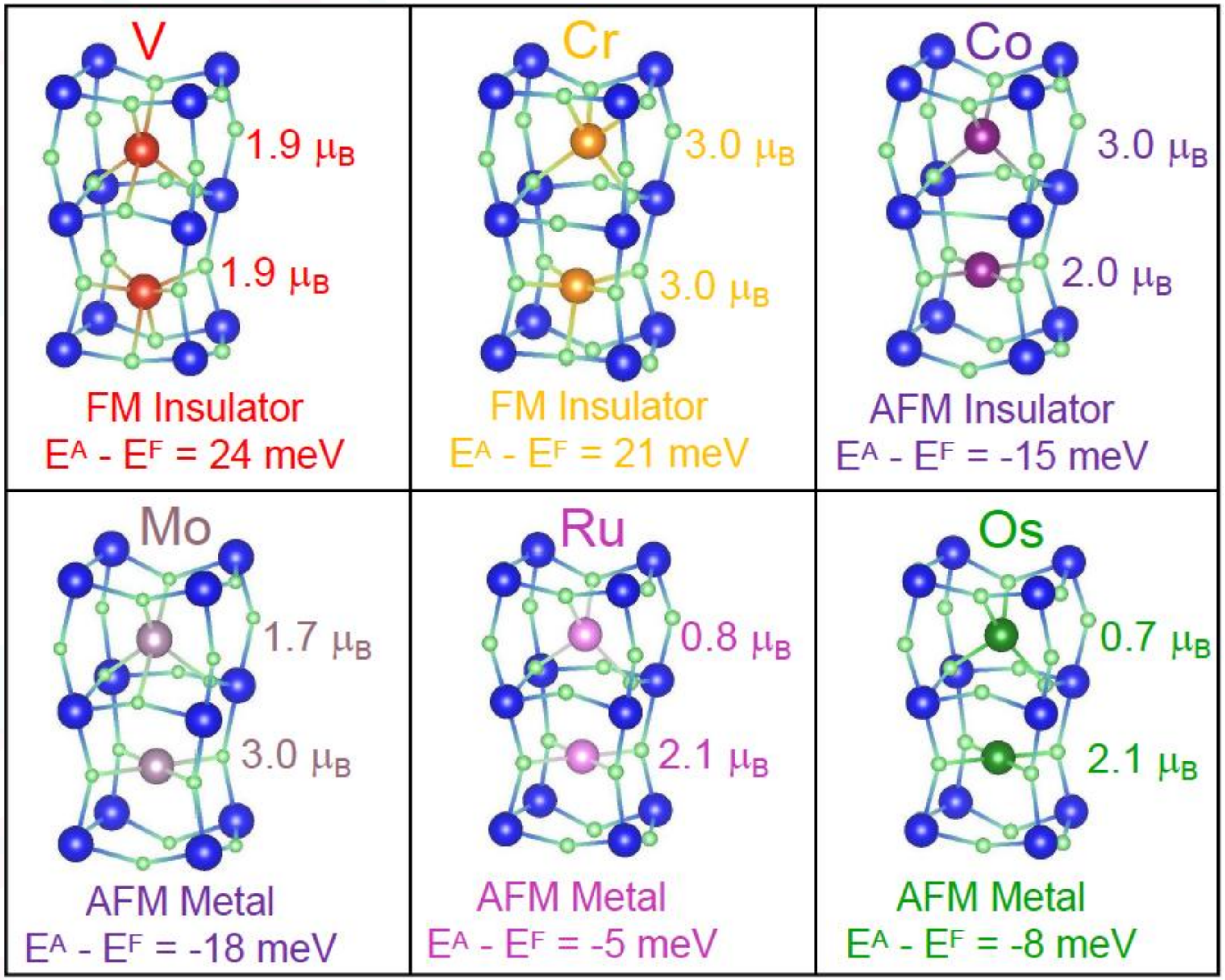
in-phase tilts about [001]

antiphase tilts about [1-10]

in-phase tilts about [001]

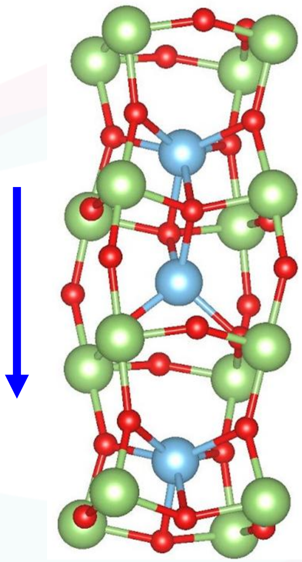
- Confirmed: Smaller dopants replace cations at compressed DW sites (e.g., V → La)

A catalogue of substitutions in $LaGaO_3$



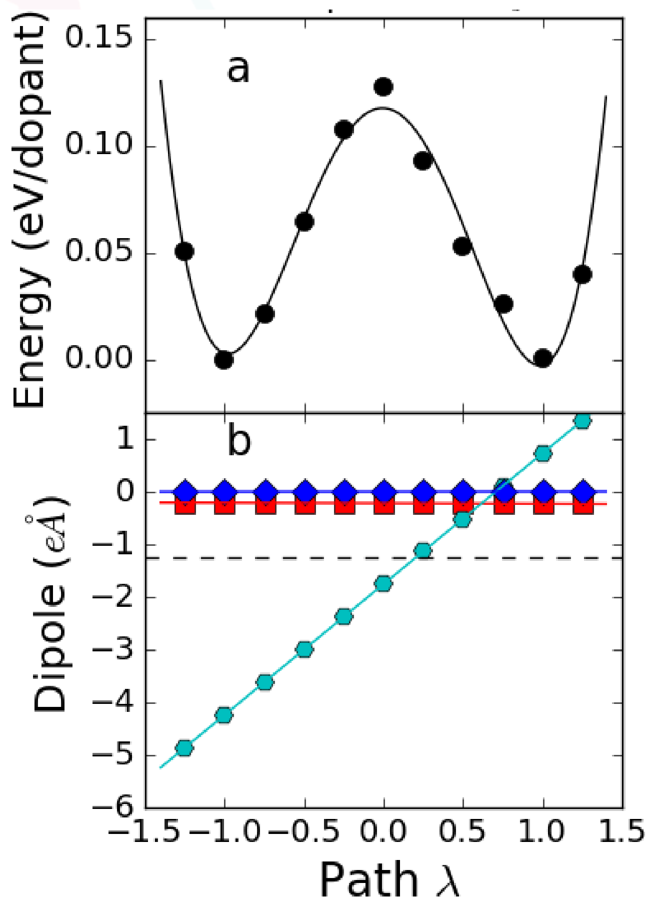
Switchable ferroelectric polarization !

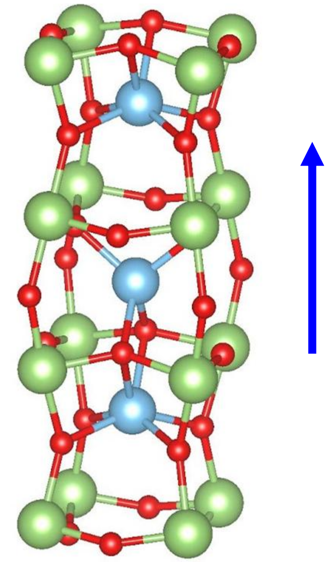
Ti @ $LaGaO_3$



P down

(λ = -1)





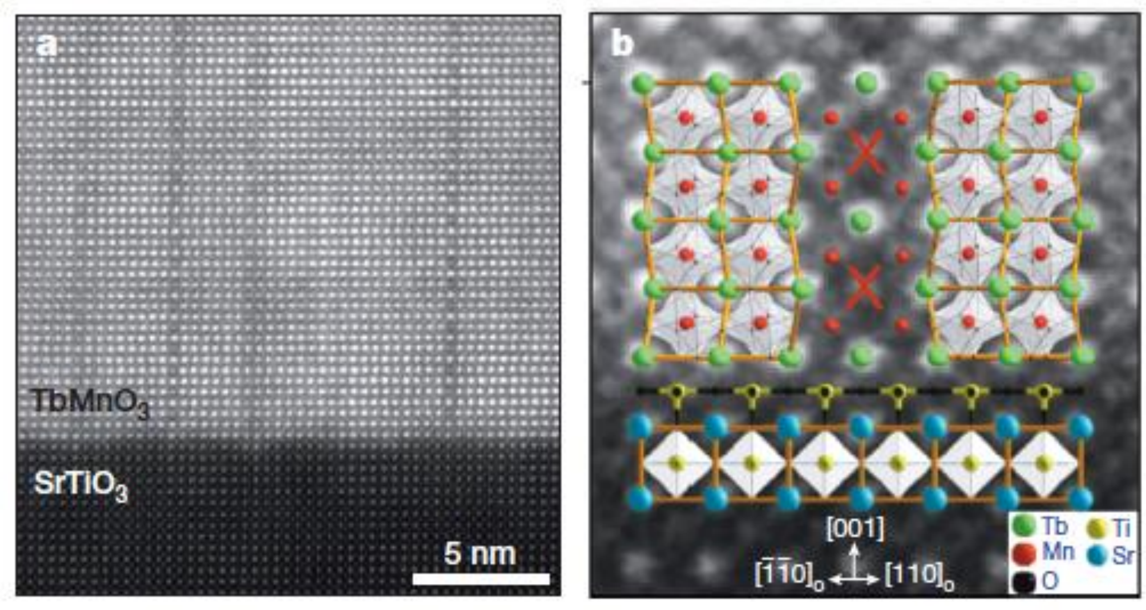
P up

(λ = 1)

New 2D materials at DWs

We have identified candidates to obtain:

- ✓ Insulating DWs with a net magnetization
- ✓ Metallic and half-metallic DWs with a net magnetization
- ✓ Some of these also present switchable ferroelectric polarization



All those properties confined in a region less than 1 nm thick !

Zhao & Íñiguez, NPJ Comp. Mats. (in press)

Example III:

Control by Light

Li, Íñiguez, Gruverman *et al*., Nature Communications 9, 3344 (2018)

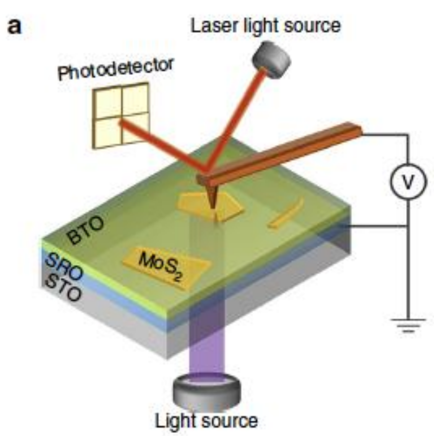
Paillard, Íñiguez, Bellaiche *et al*., Physical Review Letters 123, 087601 (2019)

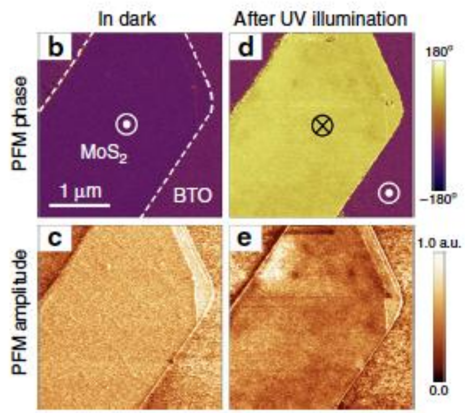
FNR-funded via CORE and inter-mobility projects

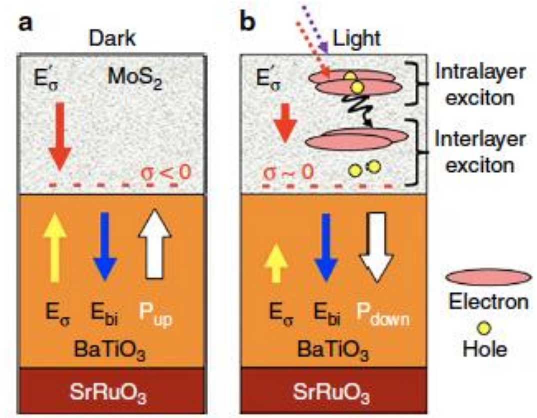
Controlling ferroic phases with light

- Switching ferroelectric polarization in $SrRuO_3/BaTiO_3/MoS_2$ trilayers

  Li, Íñiguez, Gruverman *et al*., Nat. Comms. 9, 3344 (2018)

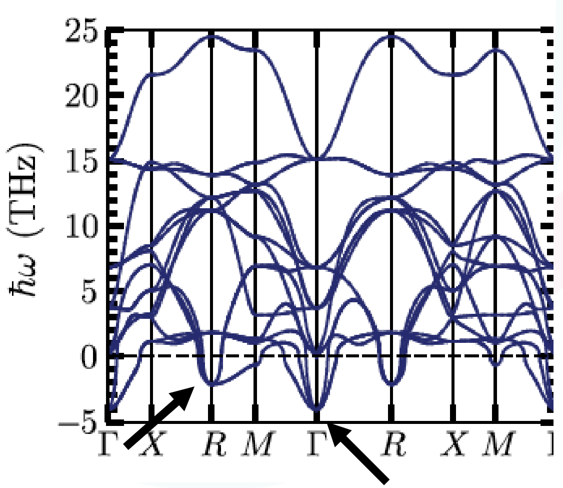






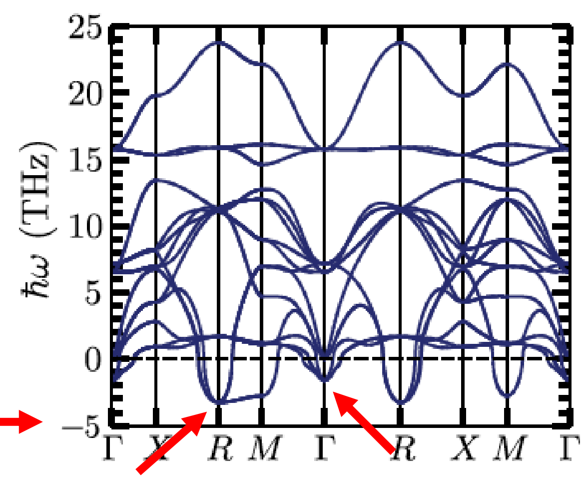
- Switching between two ferroic states in $PbTiO_3$

  Paillard, Torun, Wirtz, Íñiguez & Bellaiche, Phys. Rev. Lett. 123, 087601 (2019)

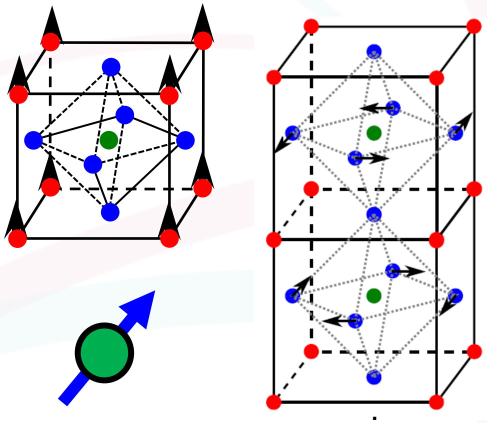


dark

under light



“All-physics” & multi-scale



Atoms, electrons, spins, and their mutual interactions

Regions (domain walls, interfaces) where behavior may be “odd”

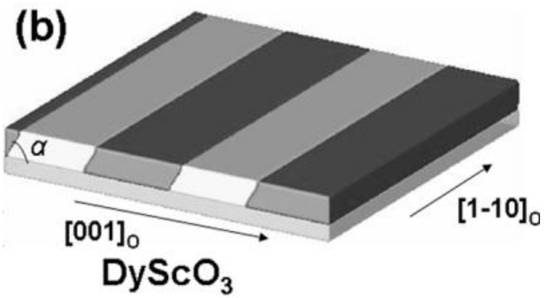
Rigorous statistical treatment

Kinetics of mesoscopic objects

Electric currents

Optical excitations

Chemical inhomogeneities, nano-structures

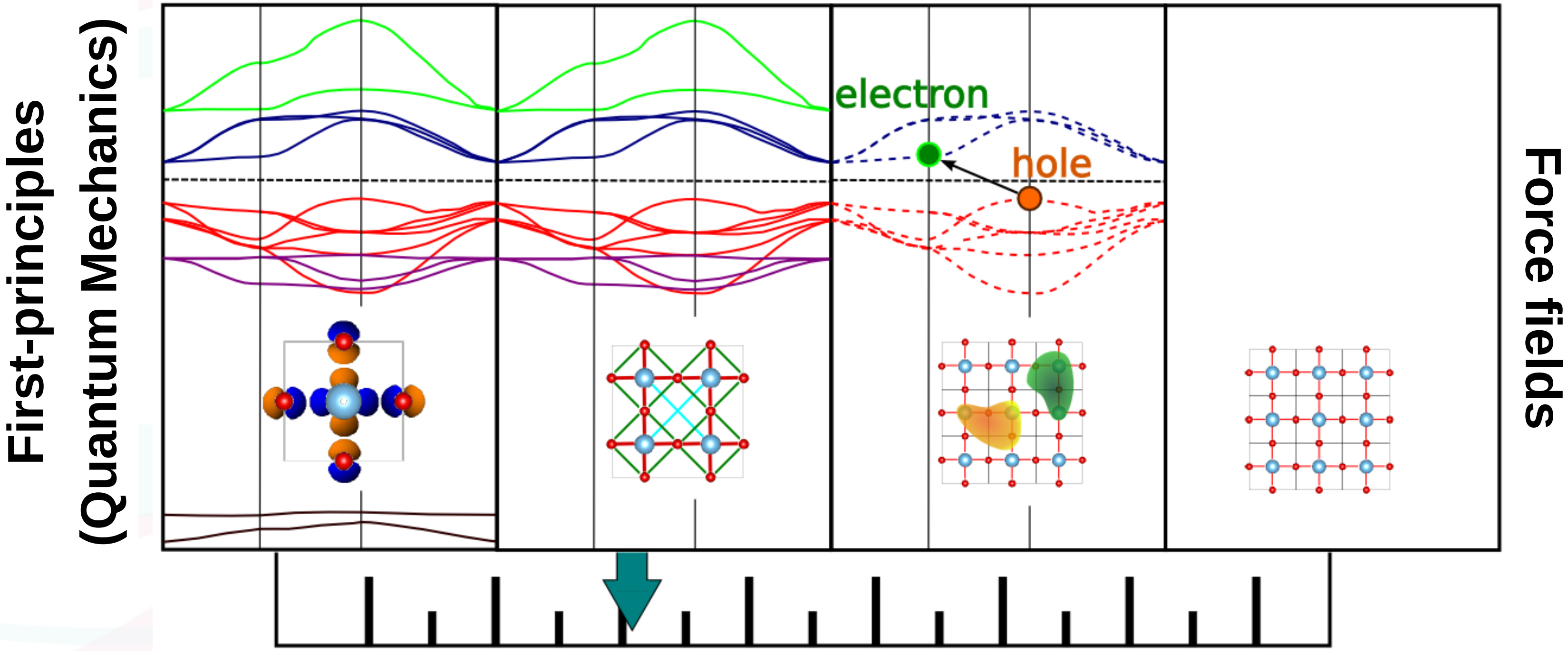


Our Digital Twin:

“Second-Principles” Methods

Second-Principles Density Functional Theory

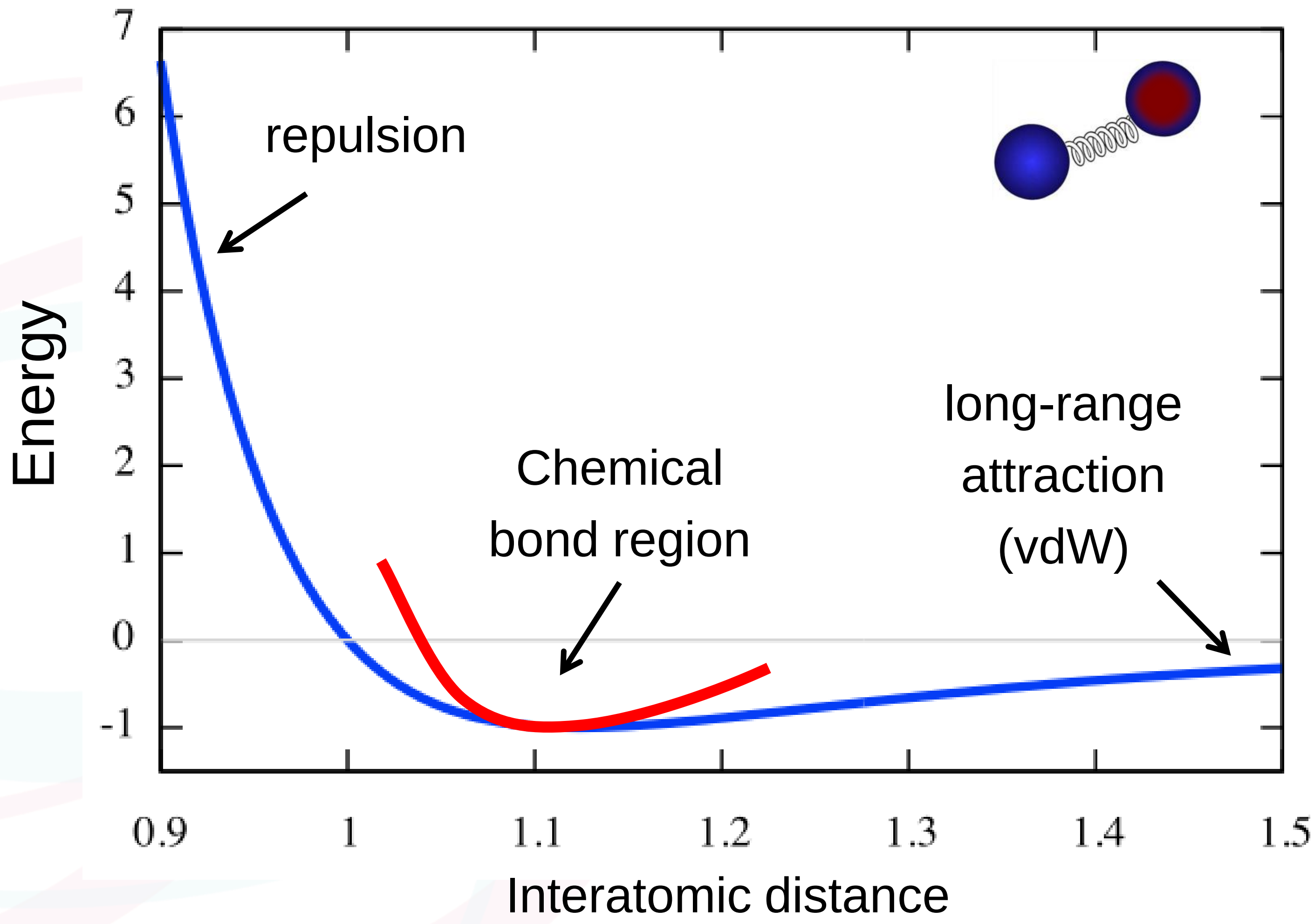
SPDFT & SCALE-UP: A flexible tool that allows us to simulate materials with an optimum compromise between level of detail, accuracy and computational efficiency.



PRB 93, 195137 (2016) ; JPCM 25, 305401 (2013) ; PRB 95, 094115 (2017)

Collaboration of LIST and U. Cantabria (Spain) – www.secondprinciples.unican.es

Lattice model potentials

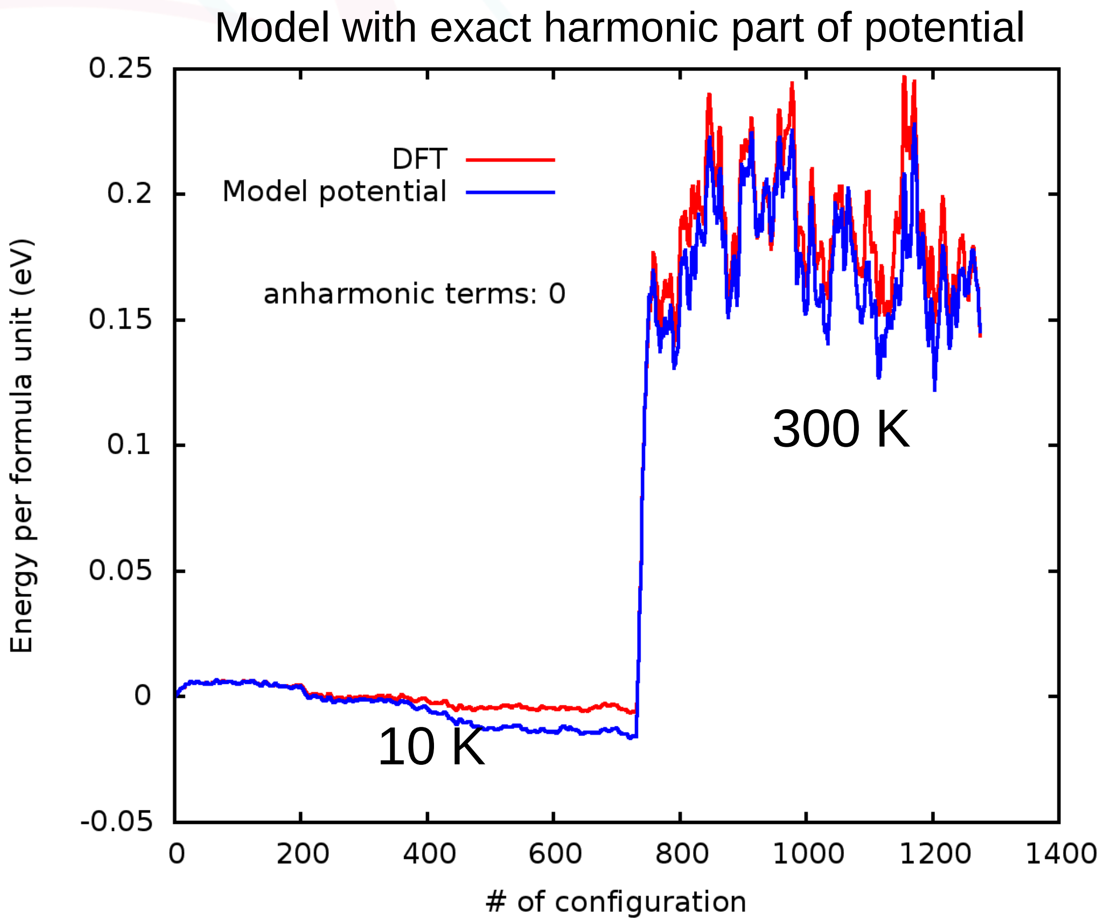


90's: Zhong, Vanderbilt & Rabe, PRL 73, 1861 (1994); PRB 52, 6301 (1995)

Today: Wojdeł, Hermet, Ljungberg, Ghosez & Íñiguez, JPCM 25, 305401 (2013)

Systematic improvement, first-principles accuracy

$SrTiO_3$ simulated in a 2x2x2 (40 atom) box



ΔE

@ 10 K

0.1 meV/atom

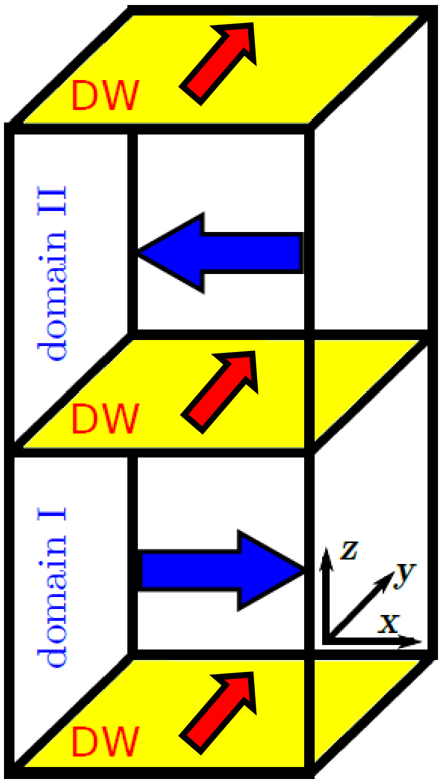
@ 300 K

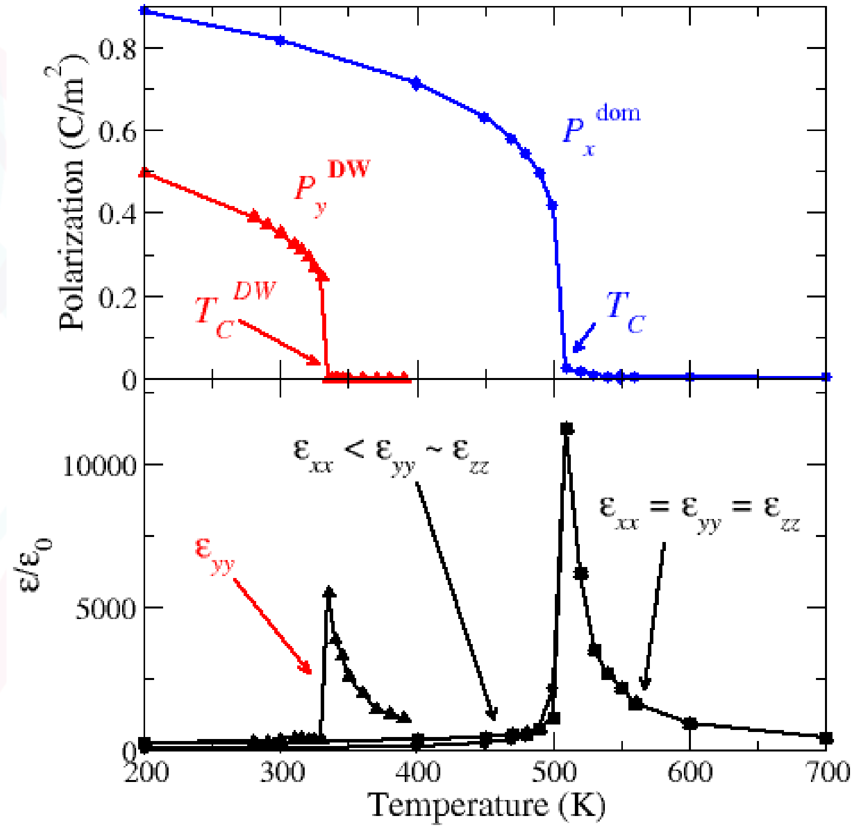
0.3 meV/atom

C. Escorihuela-Sayalero, J.C. Wojdel & J. Íñiguez, PRB 95, 094115 (2017)

Ferroelectricity at ferroelectric domain walls

Simulating the multi-domain state of ferroelectric $PbTiO_3$



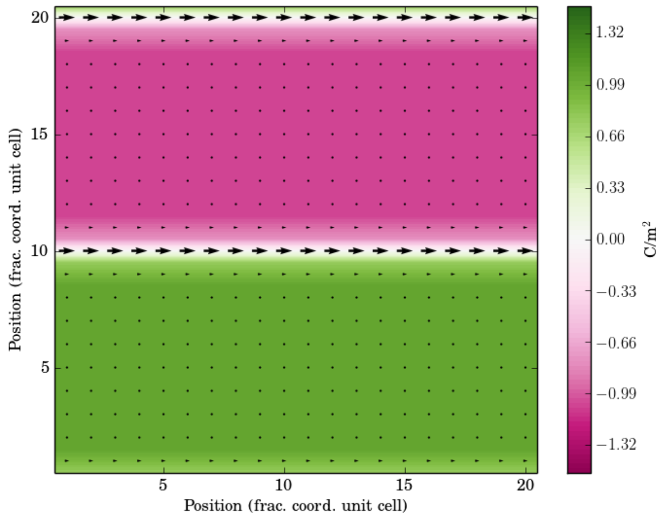


Wojdeł & Íñiguez, Phys. Rev. Lett. 112, 247603 (2014)

Topology games

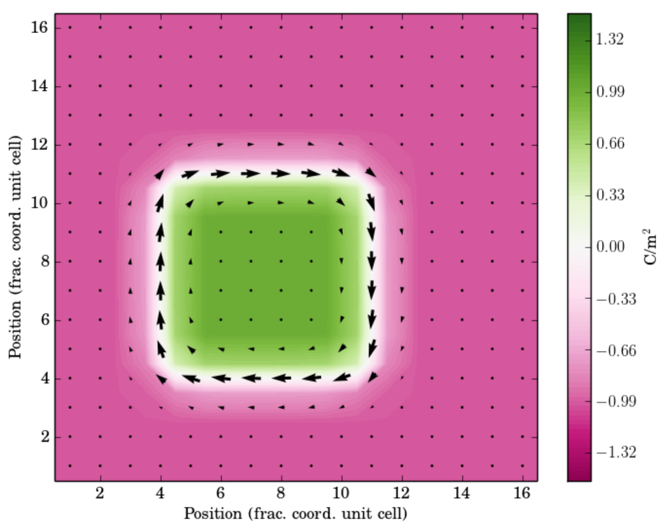
Ideal planar 180º DW in $PbTiO_3$

PRL (2014)

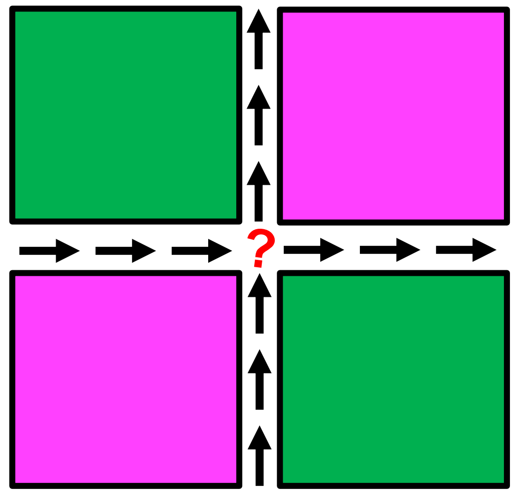


closed DW → skyrmion!

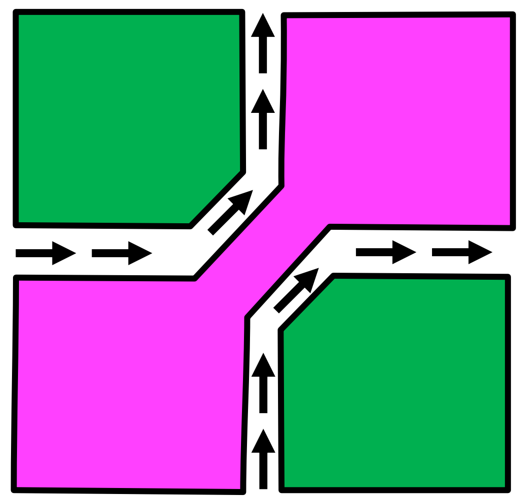
Sci. Adv. (2019)



What happens in this case?

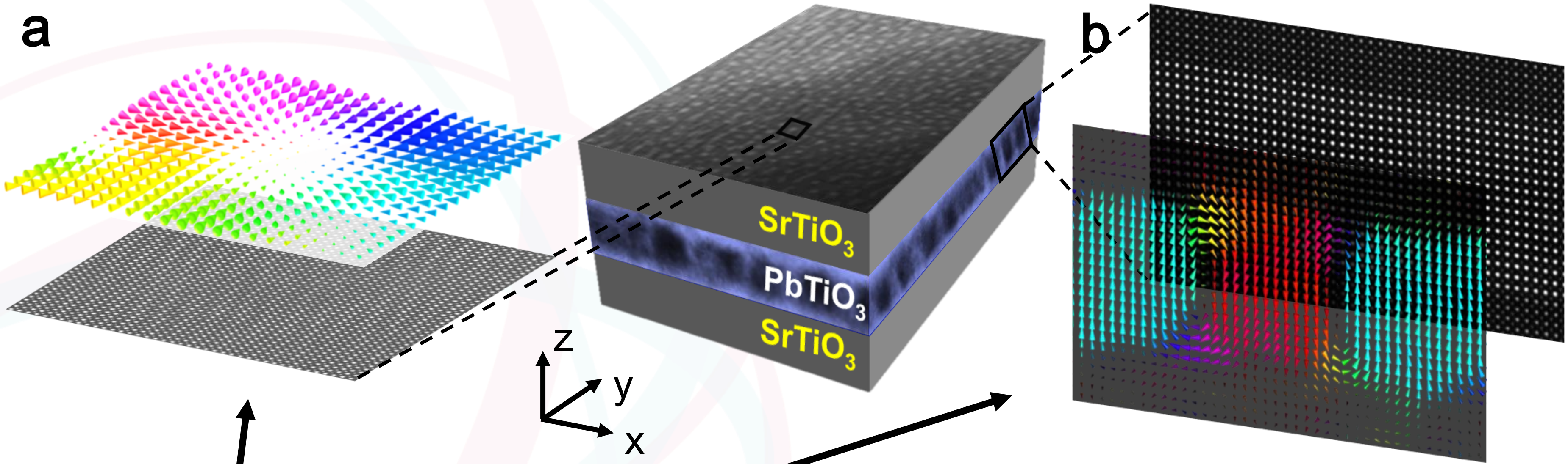


relaxes to…



$PbTiO_3/SrTiO_3$ superlattices

Das *et al*., Nature 568, 368 (2019)

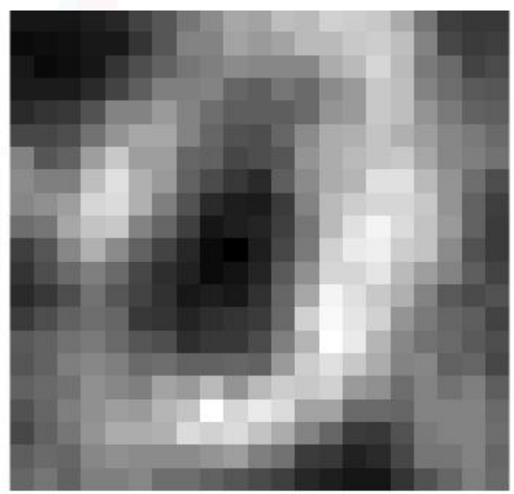


HAADF-STEM (@ Berkeley)

beam convergence angle: 17 mrad

4D-STEM (@ Cornell, Nguyen, Muller's group)

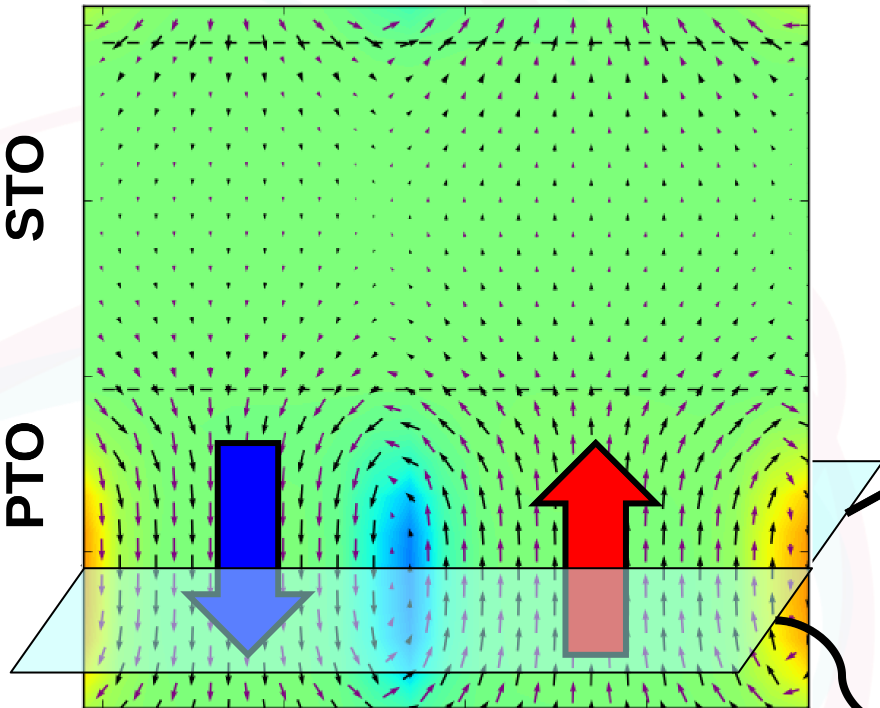
beam convergence angle: 1.7 mrad

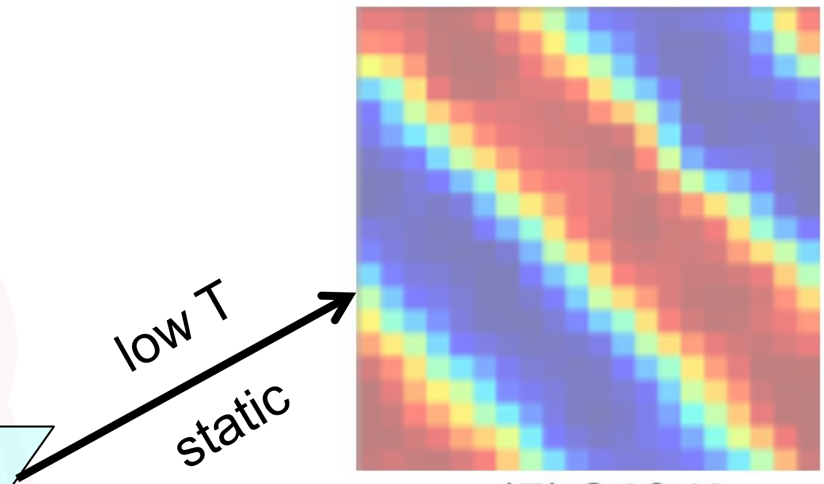


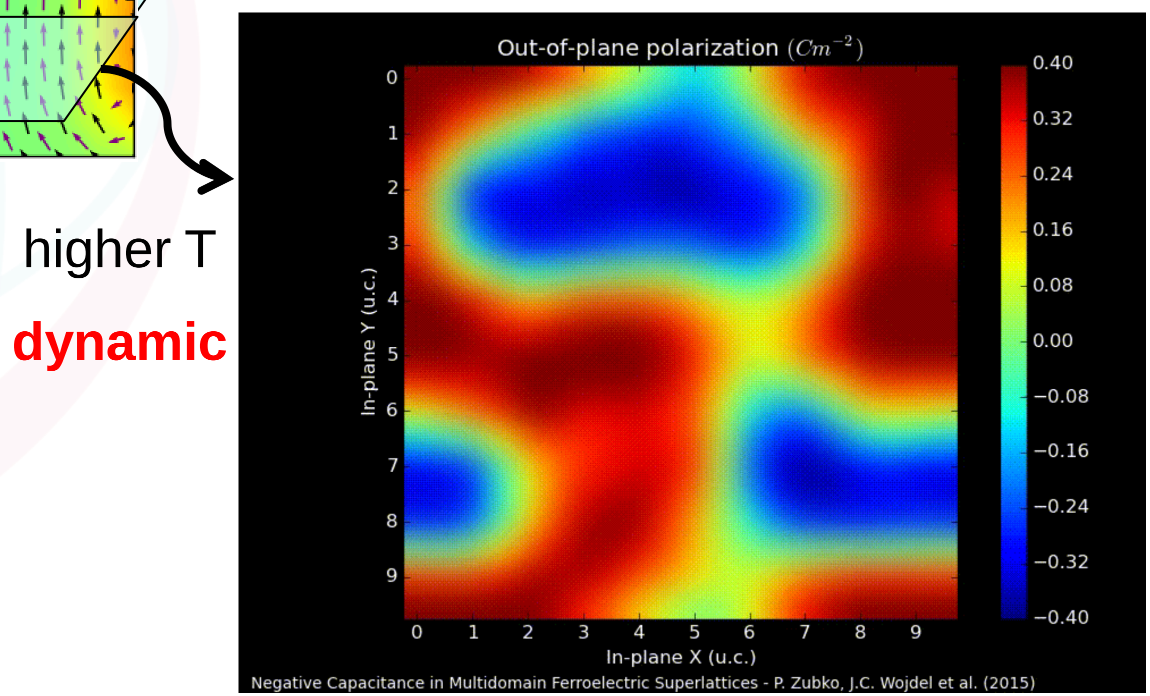
ADF image

in-plane dipoles

Dynamic equilibrium in $PbTiO_3/SrTiO_3$







Highly reactive "domain liquid"!!

Zubko, Íñiguez *et al*.,

Nature 534, 524 (2016)

To take home

• LIST works on “digital twins” for pretty rich and complex materials

• Our “twins” retain a full atomistic description (atoms, electrons) with quantum-mechanical accuracy (~ 1-10 meV/atom), while allowing for medium-size simulations of 10^4—10^6 atoms

• To construct the “twins”: so far “home-made machine-learning tools”, but we suspect much more (and better) can be done

• <u>Methods are general</u>, not limited to perovskite oxides

• Models ideal to combine with other simulation methods (multi-scale)

• Can be used to feed parameters to finite-element methods (e.g., to have <u>predictive</u> T-dependent <u>FEM simulations</u> w/o exp. information)