THE UNIVERSITY of TENNESSEE KNOXVILLE

Day 2: Physics and Chemistry from the STEM Imaging Data

Sergei V. Kalinin

Learning Physics from STEM Data

1. **Quantitative data in STEM**

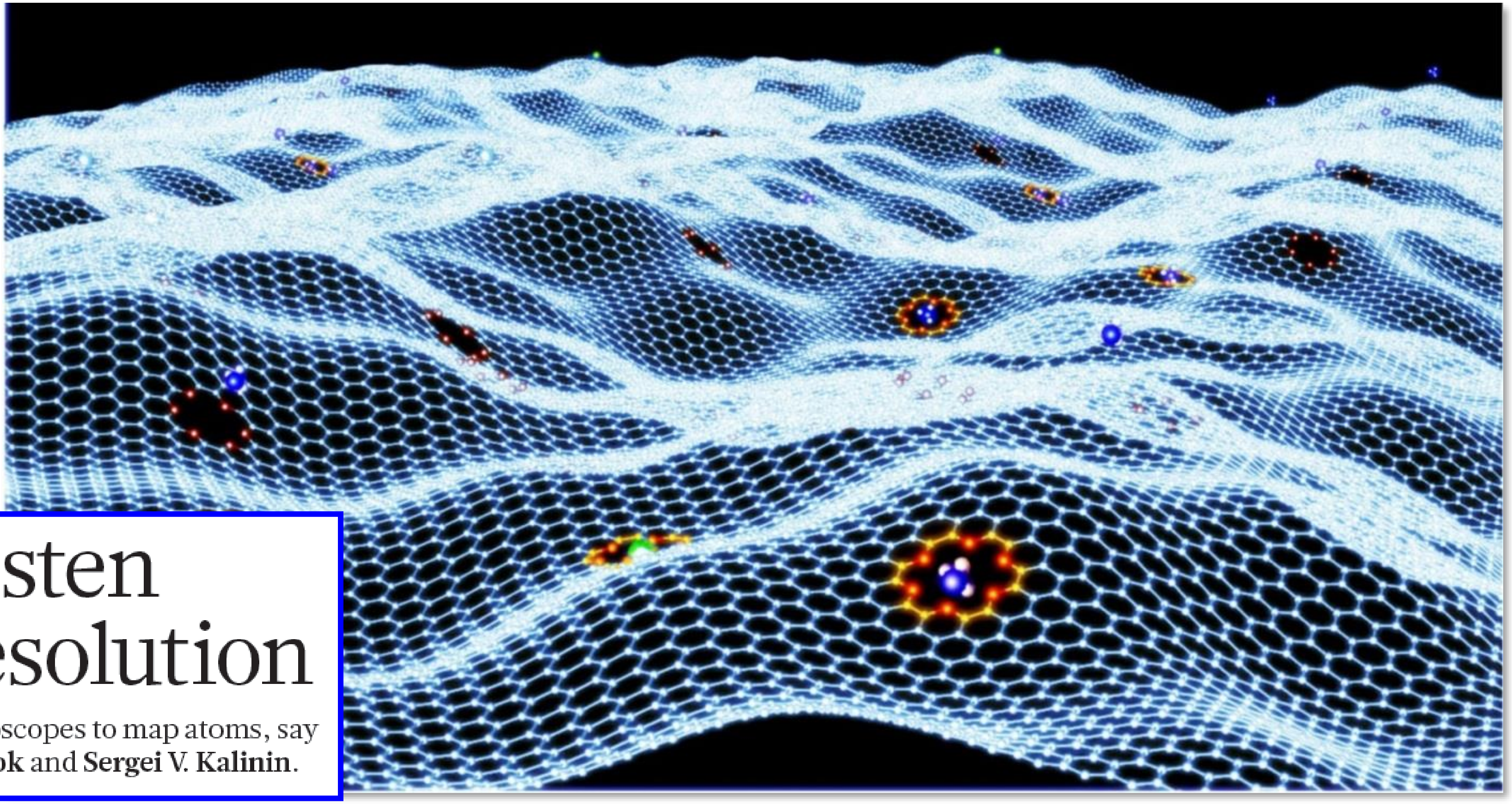
2. **Physics-based descriptors**
   - Polarization
   - Strain
   - Octahedra tilts

3. **Matching to mesoscopic model**

4. **Dynamic mesoscopic model**

5. **Stochastic models**

More then Atoms



Hasten
high resolution

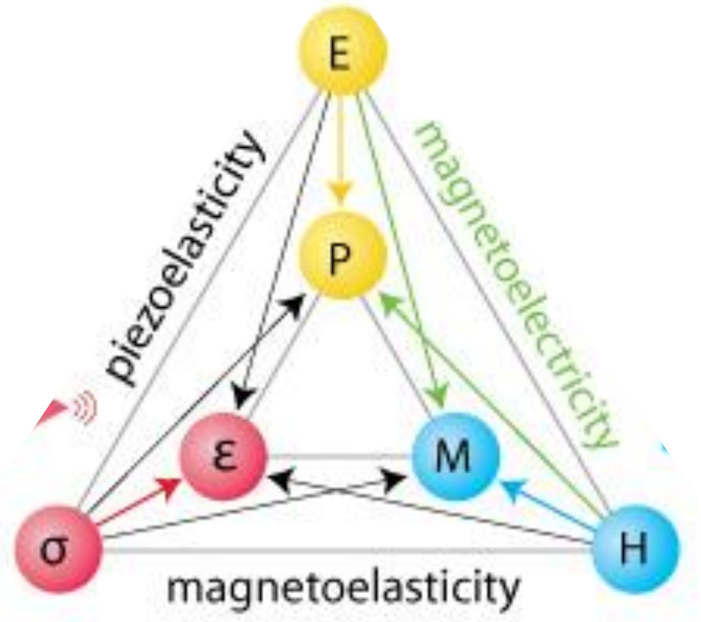
Build precision microscopes to map atoms, say
Stephen J. Pennycook and **Sergei V. Kalinin**.

Nature 515, 487 (2014)

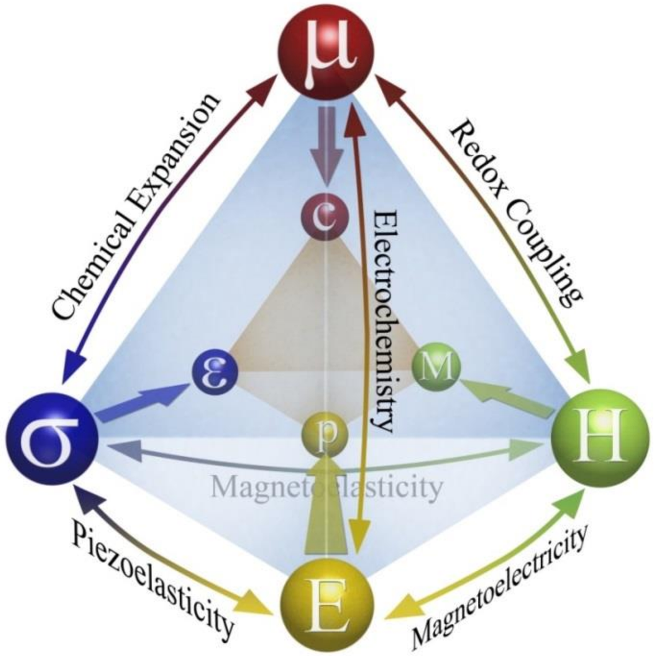
J.J. Guo et al.,
Nat. Comm. 5, 5389 (2014)

Atomic positions can be determined to <1-pm precision	Bond length: Chemical reactivity, catalytic activity	Bond angles: Magnetism and transport	Configurations and repeating elements?

Multiferroic phenomena



Spaldin & Fiebig, *Science* **309**, 391 (2005).



Jesse et al, *MRS Bull*. 2012
Kalinin and Spaldin, *Science* 2013

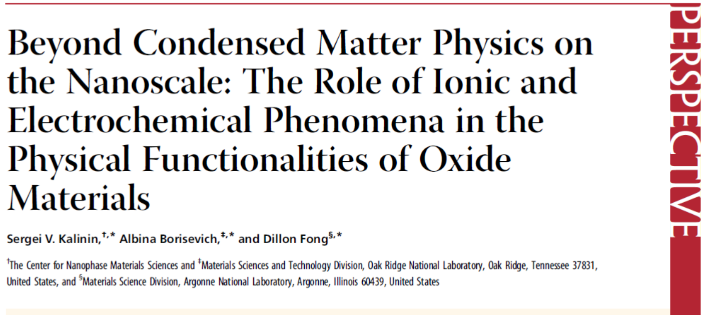
PERSPECTIVES SCIENCE GALLEY

MATERIALS SCIENCE

Functional ionicity in Transition Metal Oxides

Dynamically tuning the concentration and profile of ions and vacancies in transition metal oxides provides a route to control of new functionalities.

Sergei V. Kalinin[1] and Nicola A. Spaldin[2]



Beyond Condensed Matter Physics on the Nanoscale: The Role of Ionic and Electrochemical Phenomena in the Physical Functionalities of Oxide Materials

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PERSPECTIVE

Oxides: mobile oxygen vacancies and surface electrochemistry

1. **Oxidation states:** induce metal insulator transition, control charge compensation
2. **Molar volume:** effect similar to chemical pressure in bulk phase diagram
3. **Molar volume:** strain compensation at defects
4. **Crystal field effects:** changing environment of cation

Physics and Chemistry from STEM Data

- **Can we get materials specific information** (e.g. atomic coordinates from STEM, scattering potentials from 4D STEM, etc.) **from microscopy data**, at which level of confidence, and how this knowledge is affected and can be improved from knowledge of imaging system (e.g. classical beam parameters, resolution function, all the way to full imaging system modelling), and knowledge of material.

- **Can we use the materials-specific information** with uncertainties determined by incomplete knowledge of imaging system or intrinsic limitations **to infer physics and chemistry, either via correlative models or recovery of generative physics** (force fields, exchange integrals, etc.)

- **Can we use thus determined materials information**, either correlative or causative, **to reconstruct materials behaviors** (phase diagrams, etc) in the broader parameter space (e.g. for temperatures and concentrations different for specific sample studied), and determine how reliability of such prediction depends on position in parameter space.

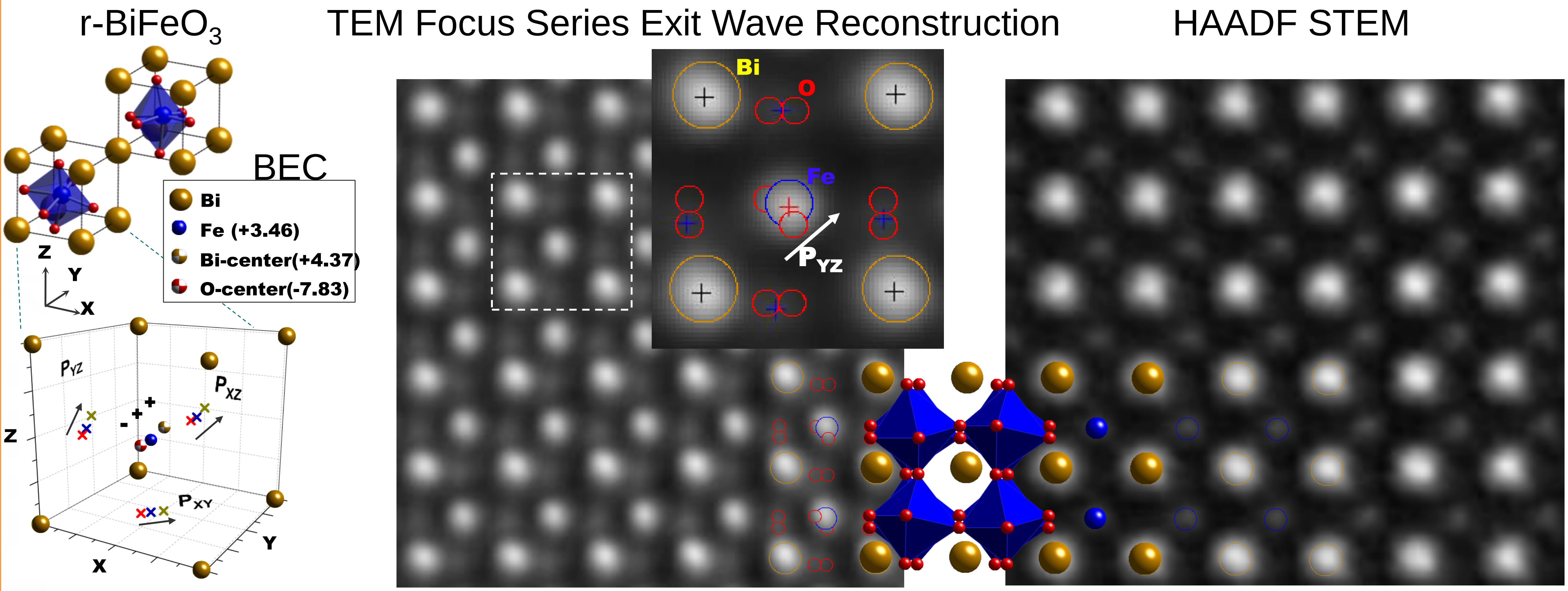
- Can we harness the data stream from the microscope to engender real time feedback, e.g. for autonomous experimentation and atomic manipulation

Natural Physics Descriptors

- Polarization
- Octahedra tilts
- Strains (physics and Vegard/chemical)

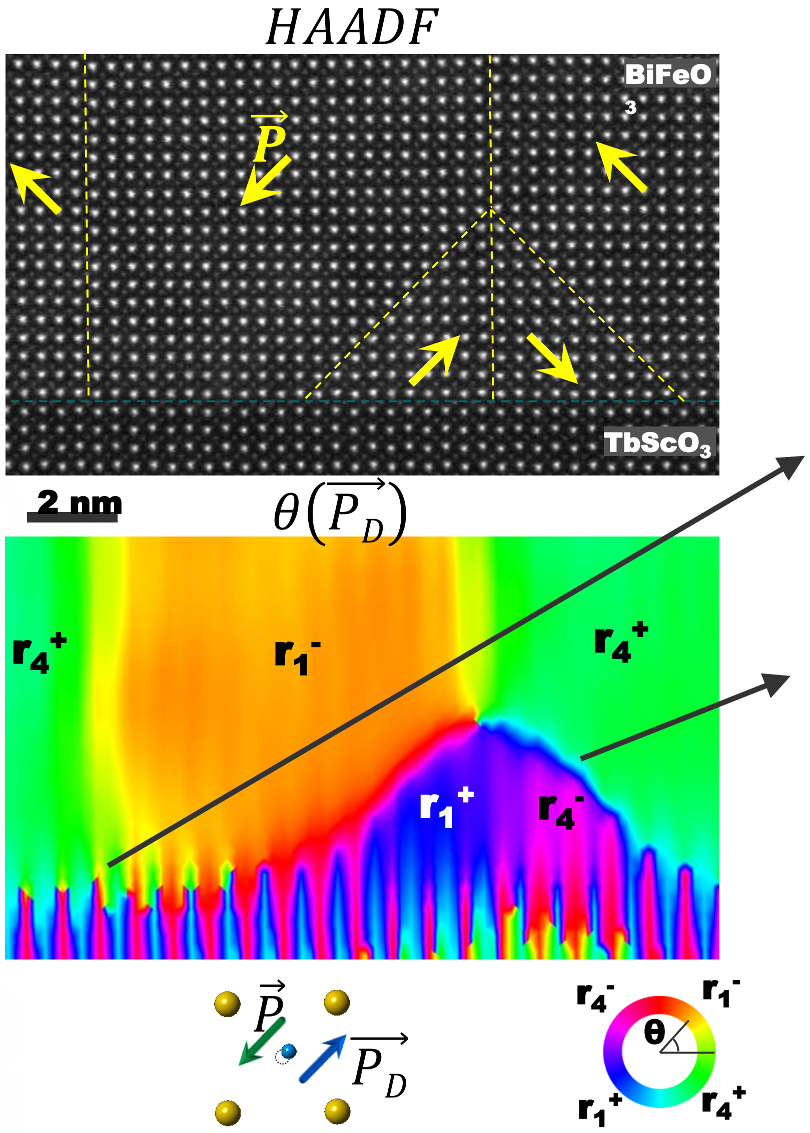
Caveat: STEM image is a projection. We have to treat image plane and beam direction differently

Polarization Imaging by STEM

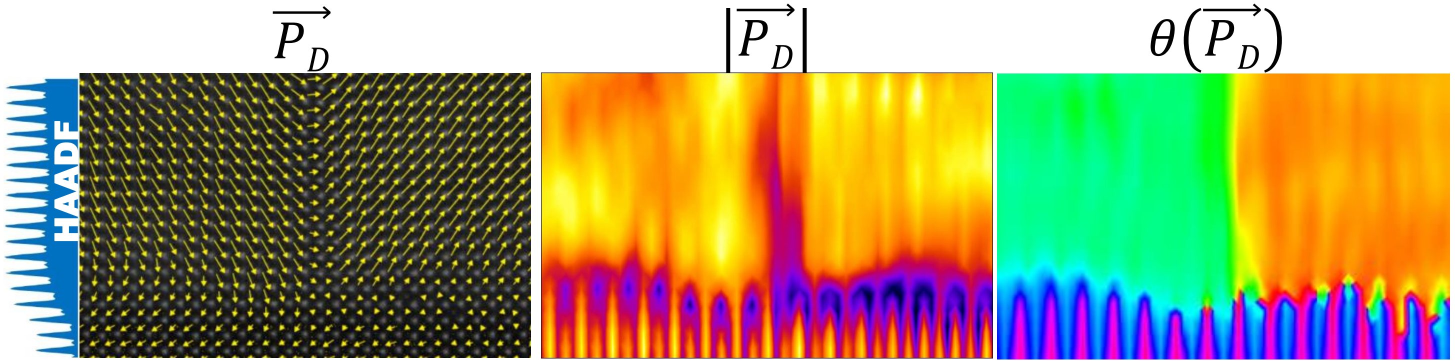


C.T. Nelson, B. Winchester, Y. Zhang, S.J. Kim, A. Melville, C. Adamo, C.M. Folkman, S.H. Baek, C.B. Eom, D.G. Schlom, L.Q. Chen, X.Q. Pan, *Spontaneous vortex nanodomain arrays at ferroelectric heterointerfaces*, Nano Letters, 11 (2011) 828-834.

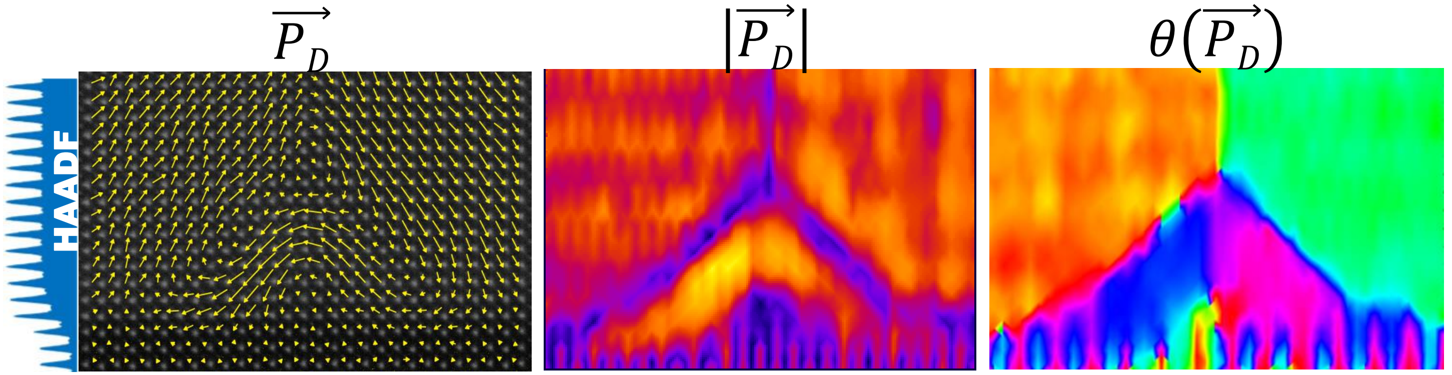
Polarization Imaging by STEM



Direct Domain Wall Termination



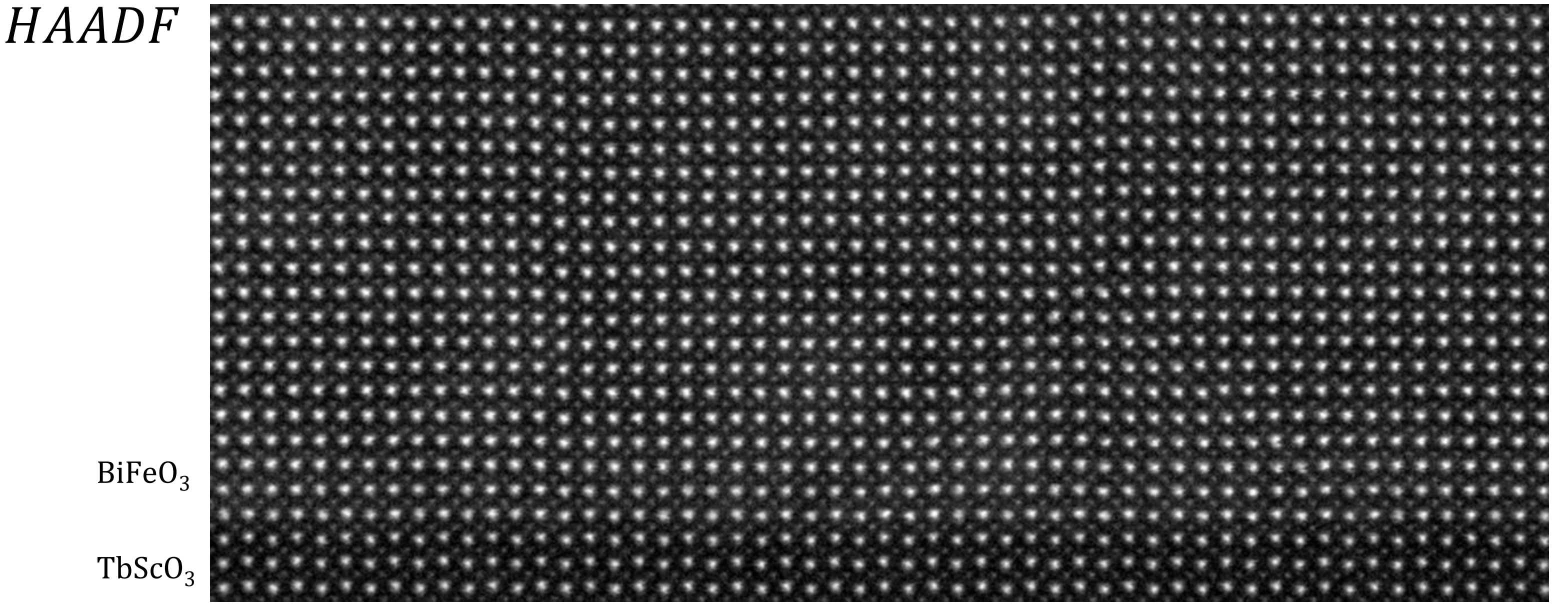
Flux-Closure at Domain Wall Termination

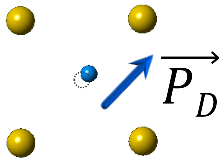


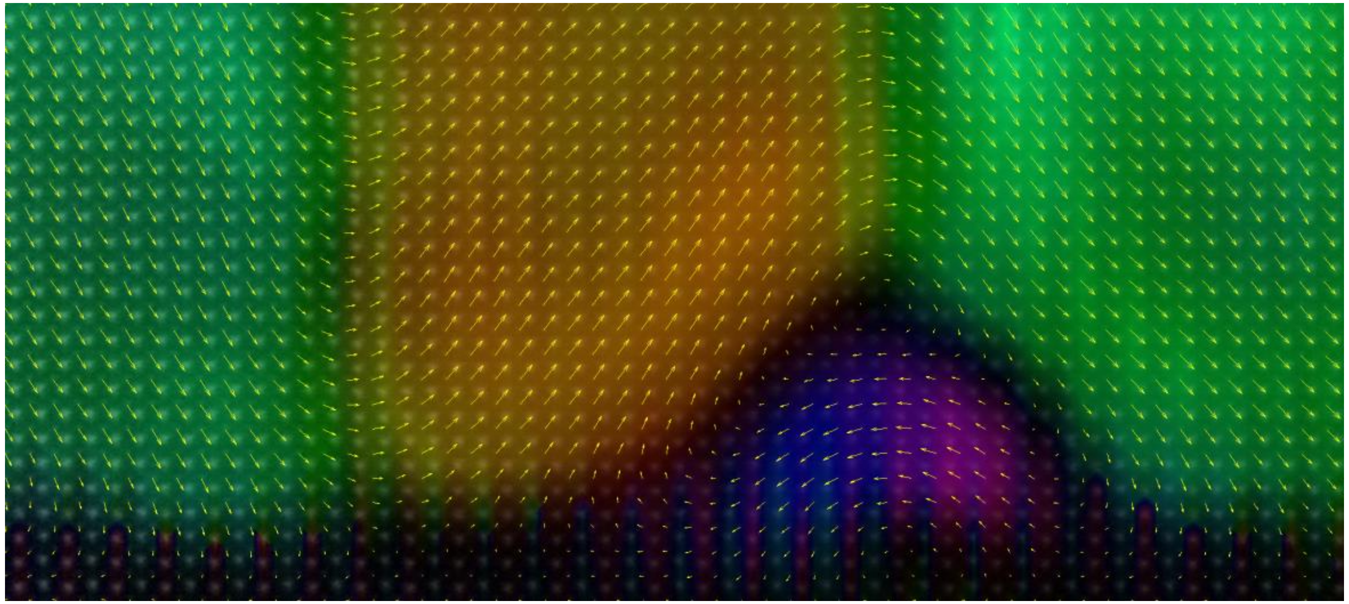
C.T. Nelson et al, Nano Letters, 11 (2011) 828-834.

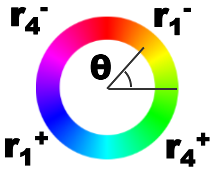
Polarization Imaging by STEM

Image by C. Nelson

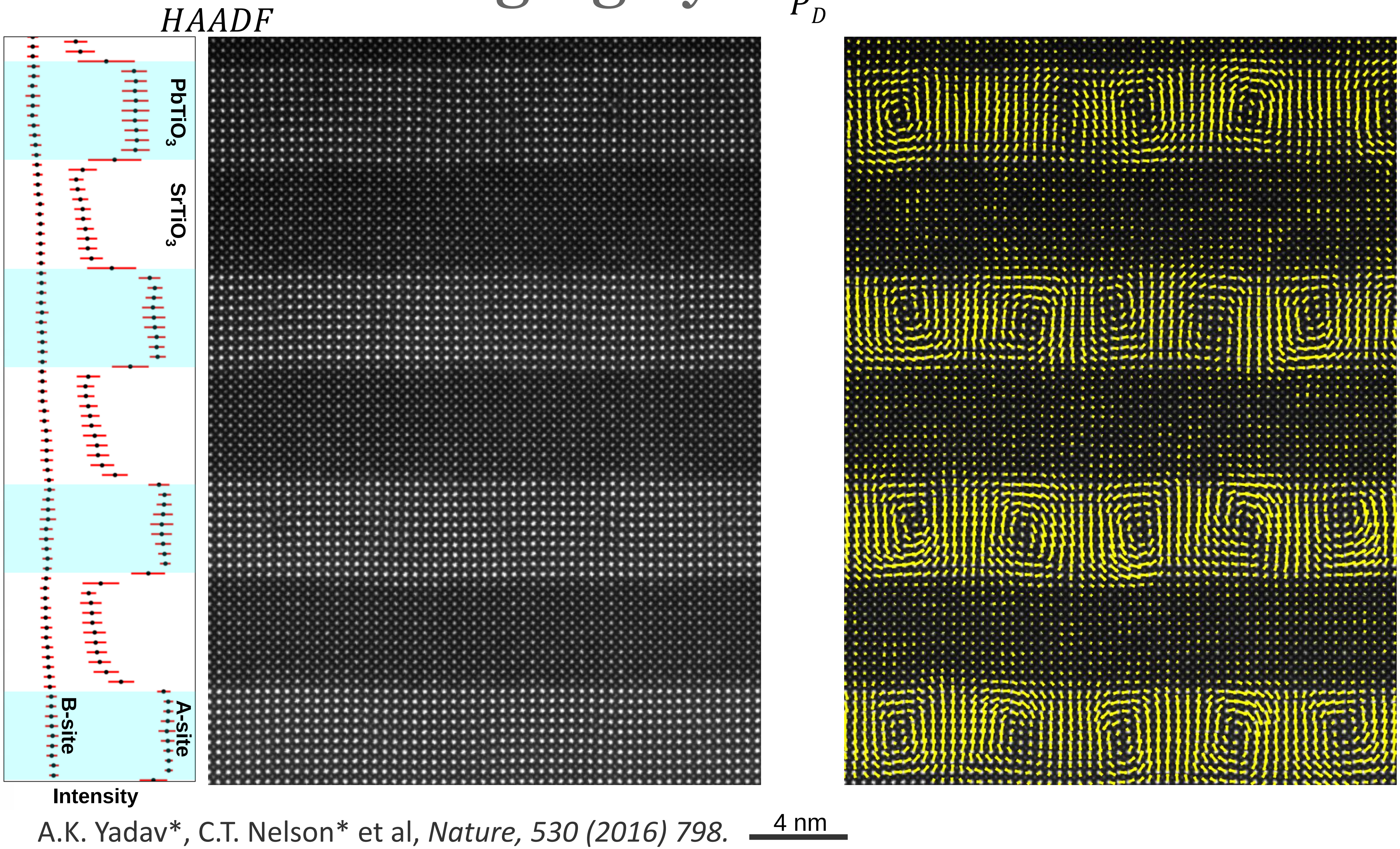








Polarization Imaging by STEM



A.K. Yadav*, C.T. Nelson* et al, *Nature, 530 (2016) 798.*

Octahedra Tilt Imaging by STEM and TEM

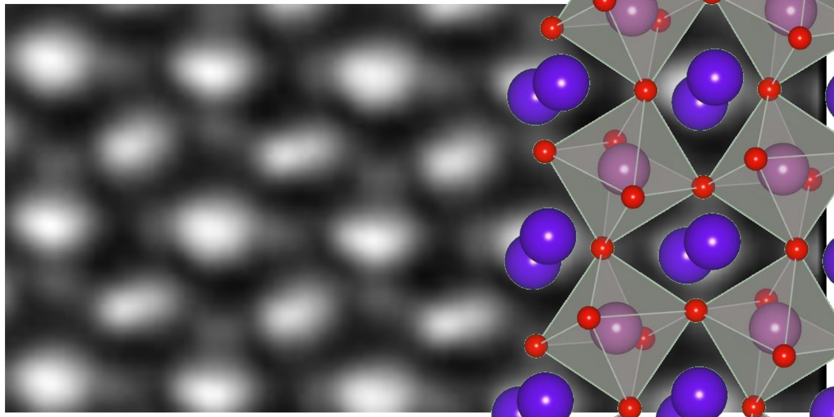
TEM Exit Wave Reconstruction

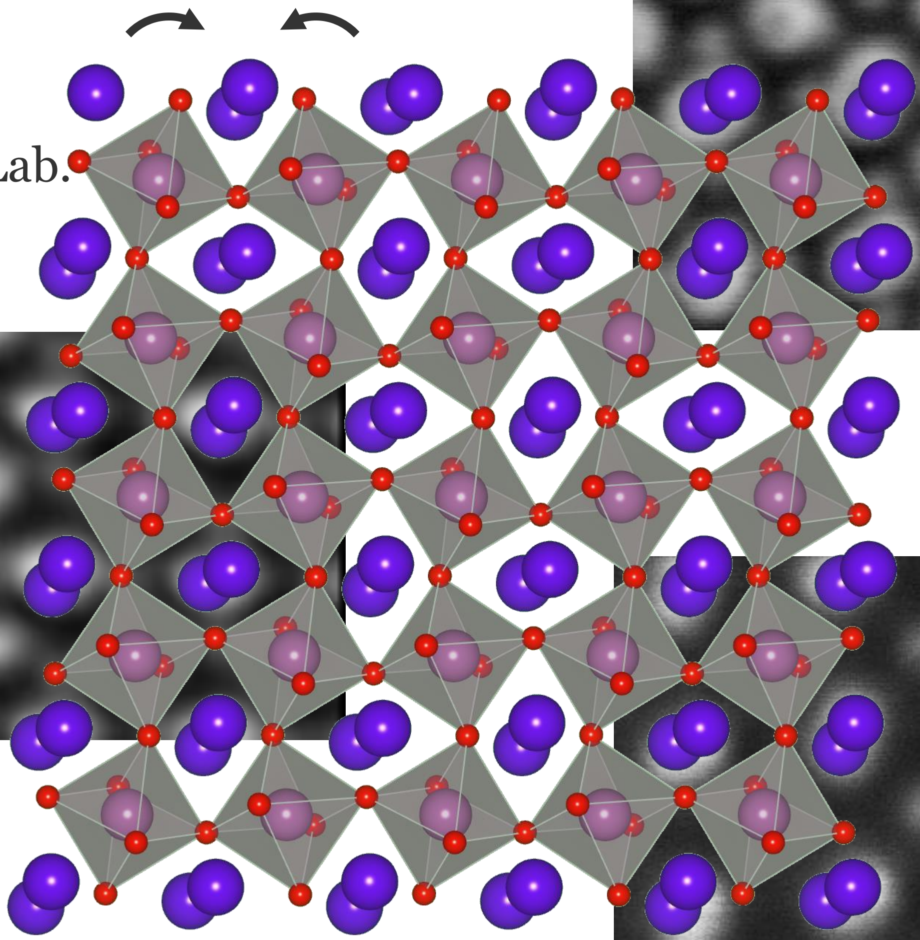
Unpublished.

Data from C. Nelson taken at NCEM, Molecular Foundry, Lawrence Berkeley National Lab.

$TbScO_3$

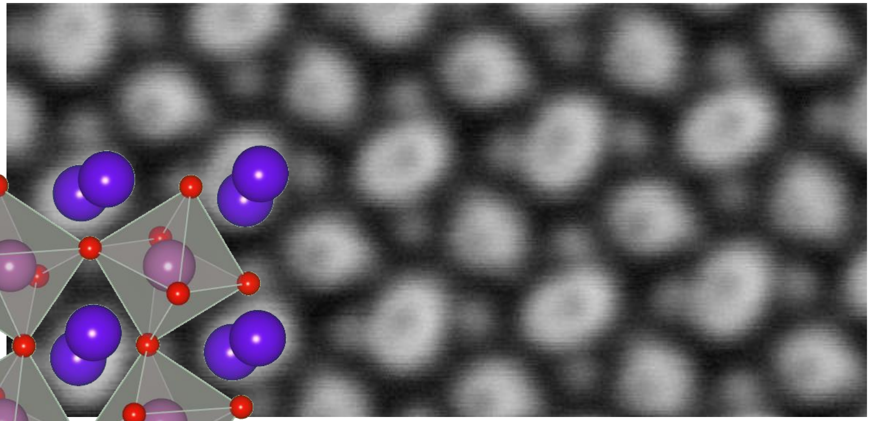
pnma a^-, a^-, c^+



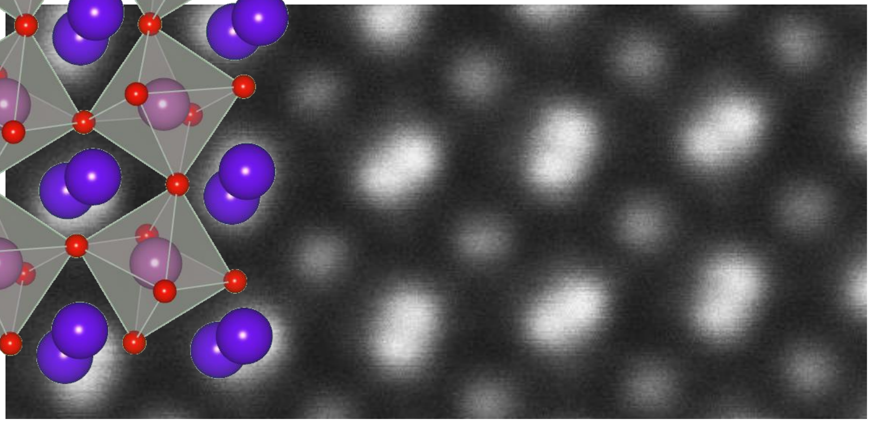


STEM

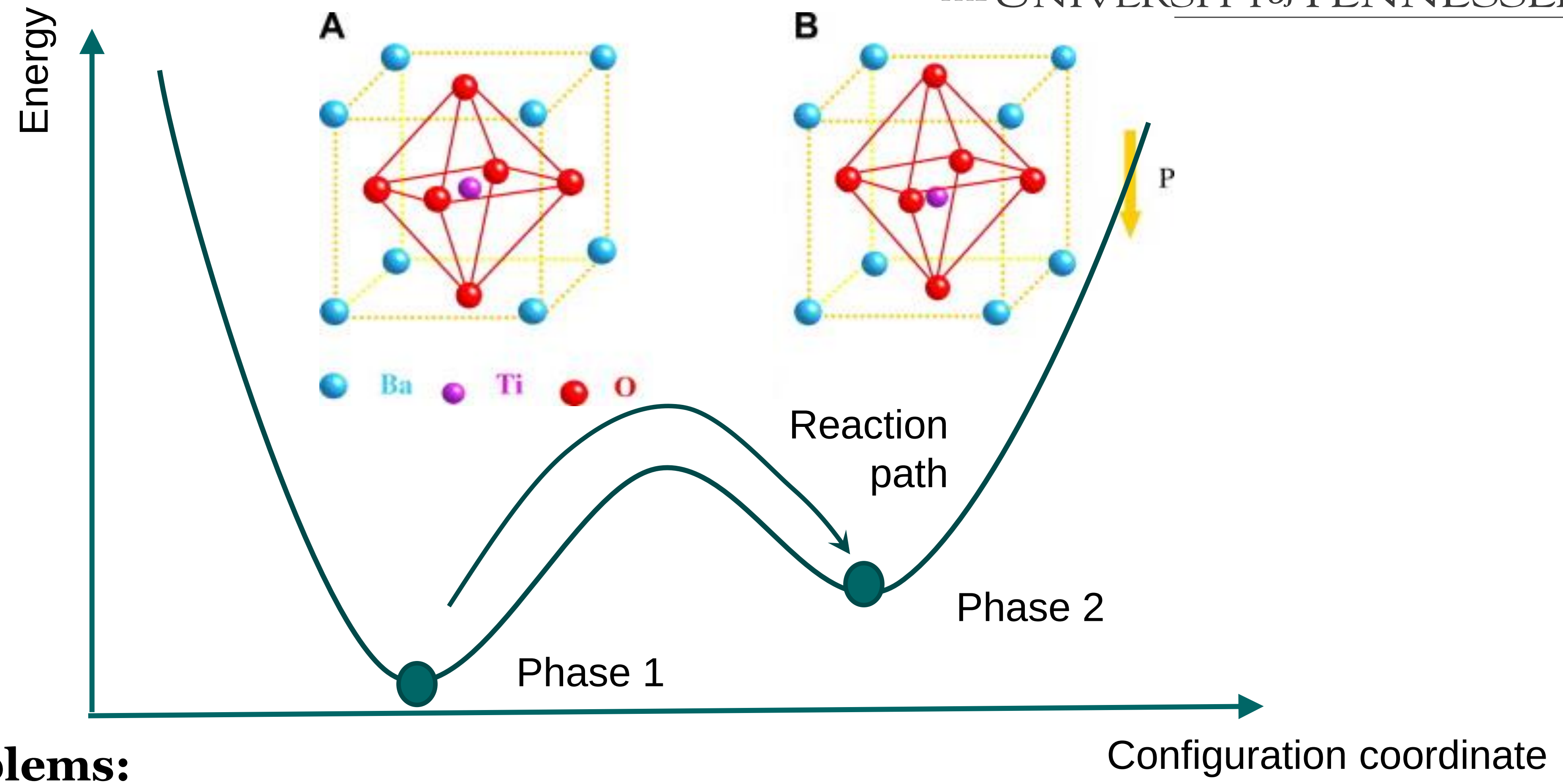
Bright Field (Inverted)



HAADF



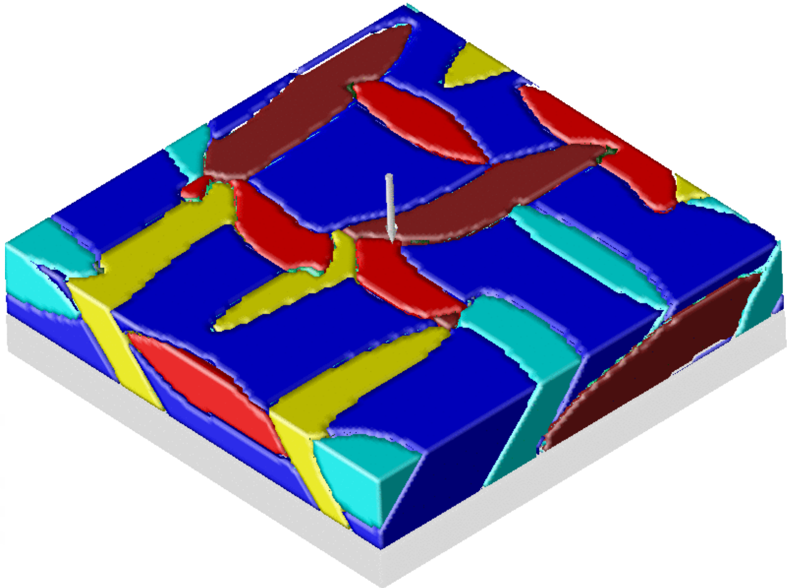
We can map (partially) physical order parameter fields. So what?



Problems:

- There are $10^{(10 - 23)}$ degrees of freedom
- Which (in most materials) correspond to small number of collective variables (order parameters)
- Naturally, materials where this is likely not the case are really interesting
- As well as are phenomena at surfaces, topological defects, structural defects
- Only small part of these degrees of freedom is accessible (imaging volume)
- And often with loss of information (z-averaging)

Phase Field Models



LGD equation:

$$\boxed{F = \int_V \left[f_{bulk}(P_i) + f_{grad}(P_{i,j}) + f_{elas}(P_i, \varepsilon_{kl}) + f_{elec}(P_i, E_i) \right] dV}$$

LGD equation:

$$\boxed{\frac{dP_i}{dt} = -L \frac{\delta F}{\delta P_i}}$$

Conventional fixed ϕ b.c.

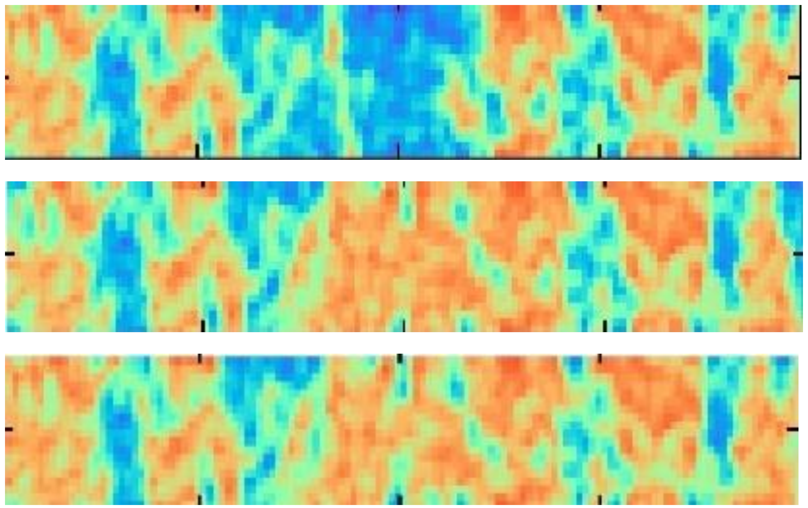
$$\phi\big|_{z=L+\lambda} = V_{\text{planar}}$$

$$\left.\frac{\partial P_z}{\partial z}\right|_{z=0,L+\lambda} = 0$$

On mesoscale, materials functionalities can often be described via order parameter fields:

- Mesoscopic order parameter is often known from macroscopic measurements
- What are the boundary conditions at surfaces and interfaces
- What are the roles of defects?
- Can we describe spatially inhomogeneous states (relaxors, charge ordered materials, MPB systems)?

Disordered states



Levels of Physical Models

Experiment:

- Observe real material
- Partial information on spatial degrees of freedom
- No information on energies/forces
- Instrumental corrections

Theory:

- different levels of approximation,
- “known knowns”

Theory-experiment comparison:

- Qualitative observation
- Comparison with simulation
- Elucidation of new mechanisms
- Direct analysis for theoretical parameters

… there are known knowns; there are things we know we know. We also know there are known unknowns; that is to say we know there are some things we do not know. But there are also unknown unknowns – the ones we don't know we don't know. …. it is the latter category that tend to be the difficult ones.

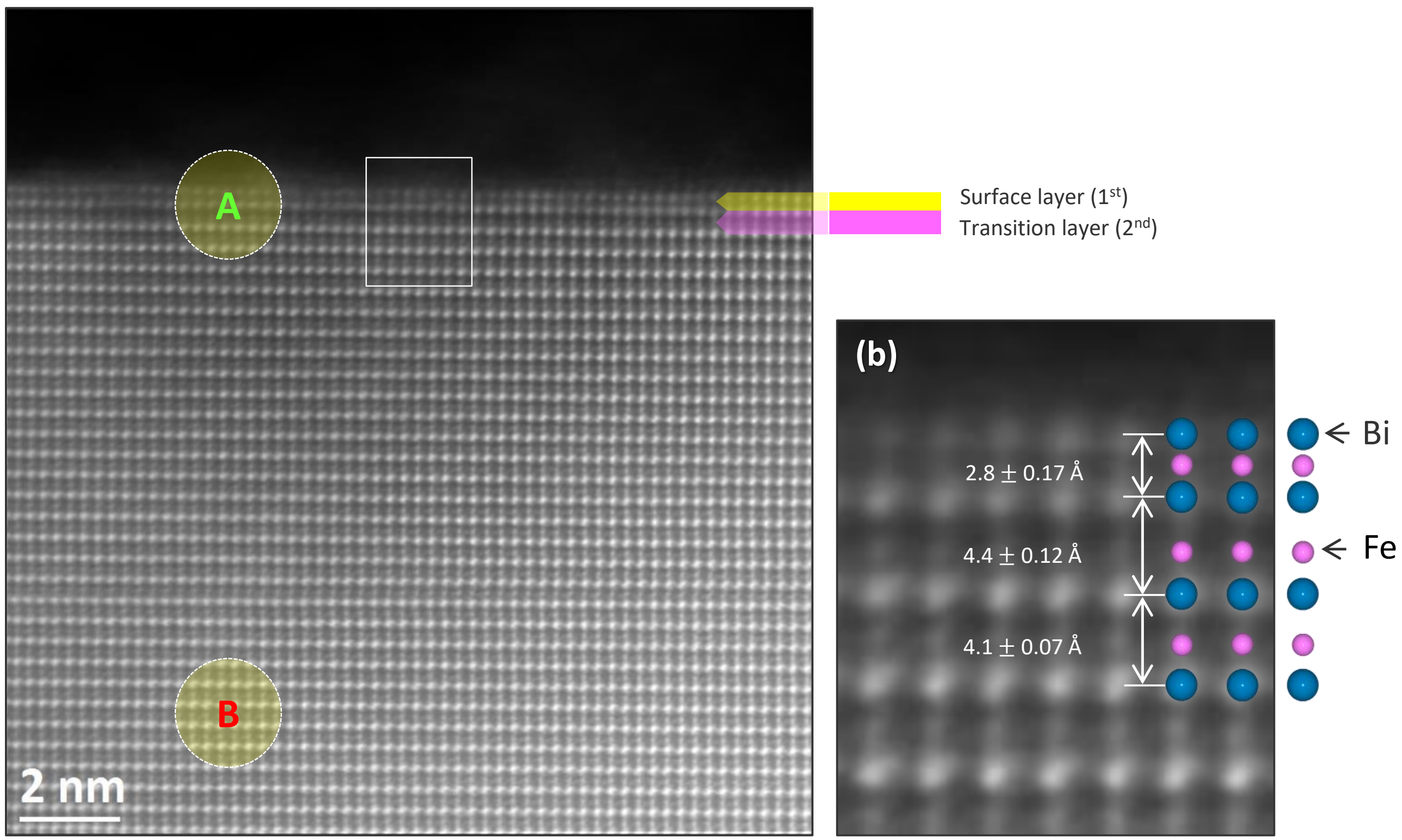
Donald Rumsfeld

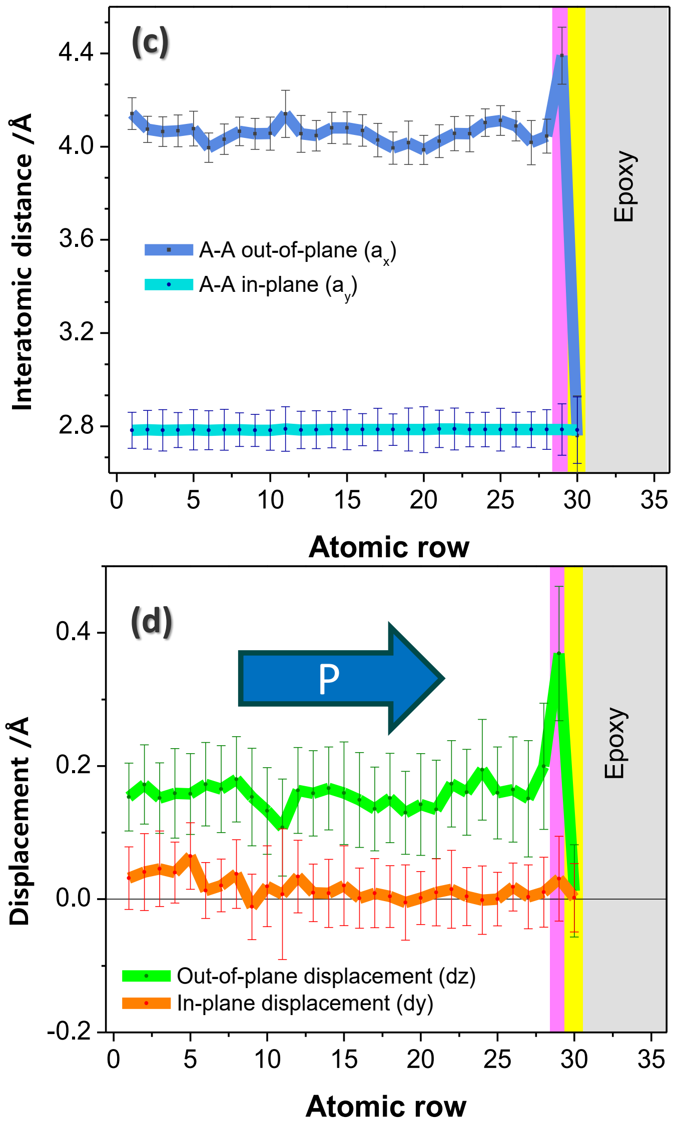
Har kas ke bedanad va bedanad ke bedanad
Asb-e kherad az gombad-e gardun bejahanad
Har kas ke nadanad va bedanad ke nadanad
Langan kharak-e khish be manzel beresanad
Har kas ke nadanad va nadanad ke nadanad
Dar jahl-e morakkab'abad od-dar bemanad

Anyone who knows, and knows that he knows
Makes the steed of intelligence leap over the vault of heaven
Anyone who does not know, but knows that he does not know
Can bring his lame little donkey to the destination nonetheless
Anyone who does not know, and does not know that he does not know
Is stuck forever in the double ignorance

Naser od-Din Tusi (1201-1274)

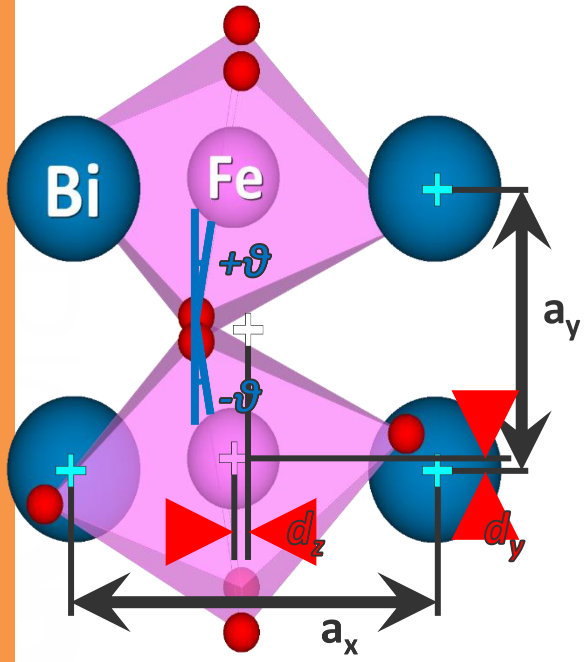
Surface Layers on BFO Surface

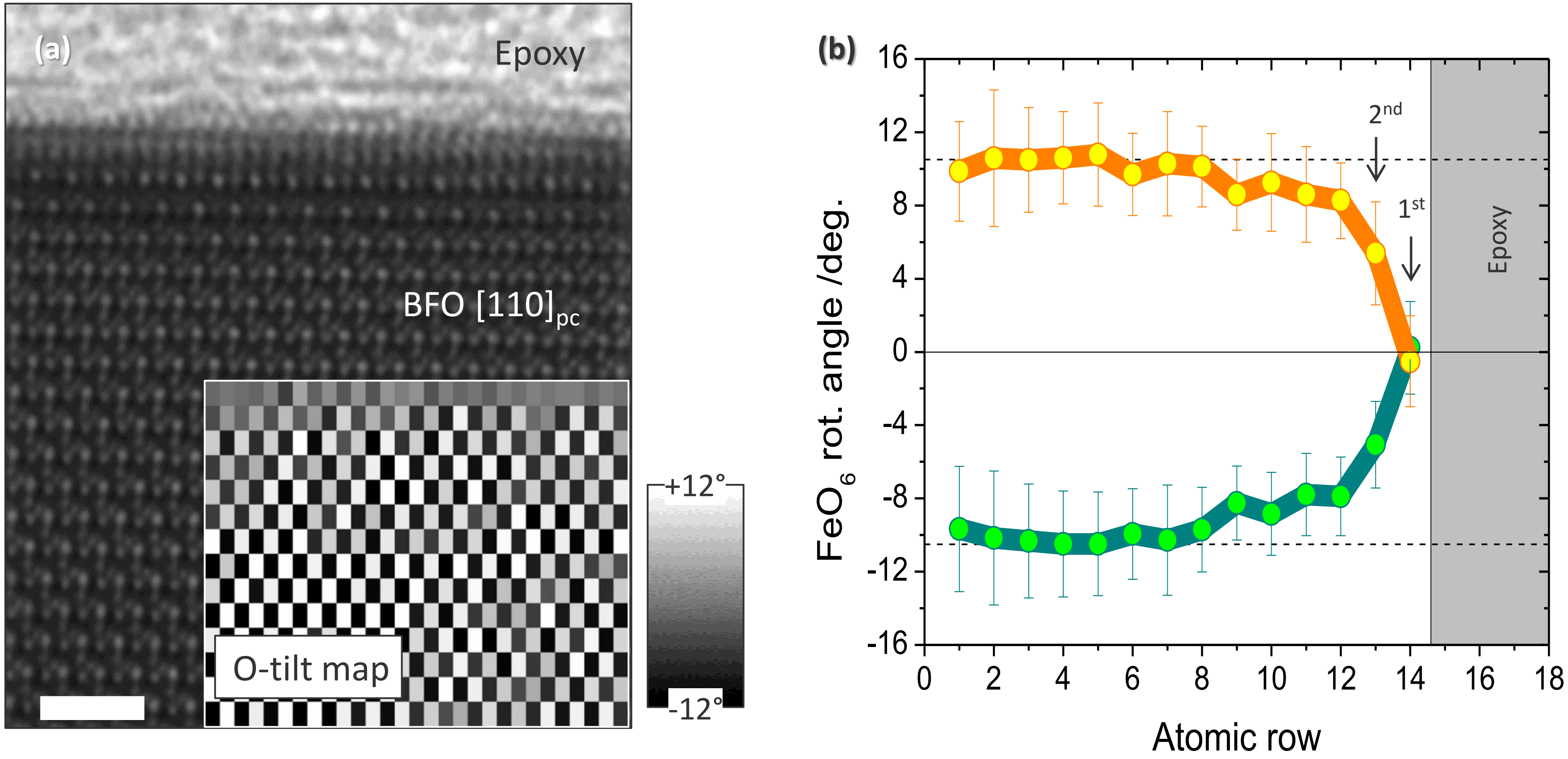




Y.M. Kim, A. Kumar, A. Hatt, Anna Morozovska, A. Tselev, M. Biegalski, I. Ivanov, E. Eliseev, S.J. Pennycook, J.M. Rondinelli, S.V. Kalinin, and A.Y. Borisevich, *Interplay of octahedral tilts and polar order in* $BiFeO_3$ *films*, Adv. Mat. **25**, 2497 (2013).

Oxygen Rotation Maps





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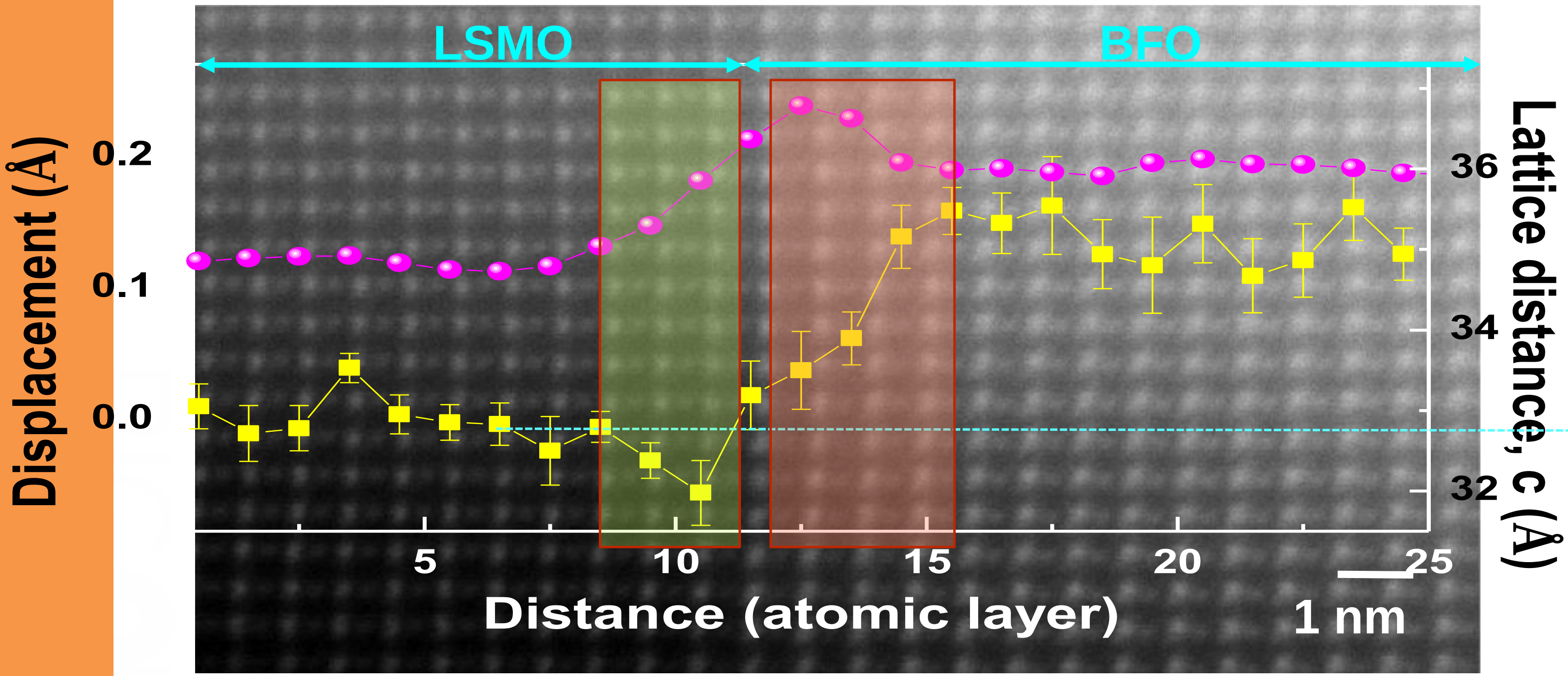
BFO-LSMO Interface



H.J. Chang, S.V. Kalinin, A.N. Morozovska, M. Huijben, Y.H. Chu, P. Yu, R. Ramesh, E.A. Eliseev, G.S. Svechnikov, S.J. Pennycook and A. Borisevich, *Atomically-resolved mapping of polarization and electric fields across ferroelectric-oxide interfaces by Z-contrast imaging*, Adv. Mat. **23**, 2474 (2011).

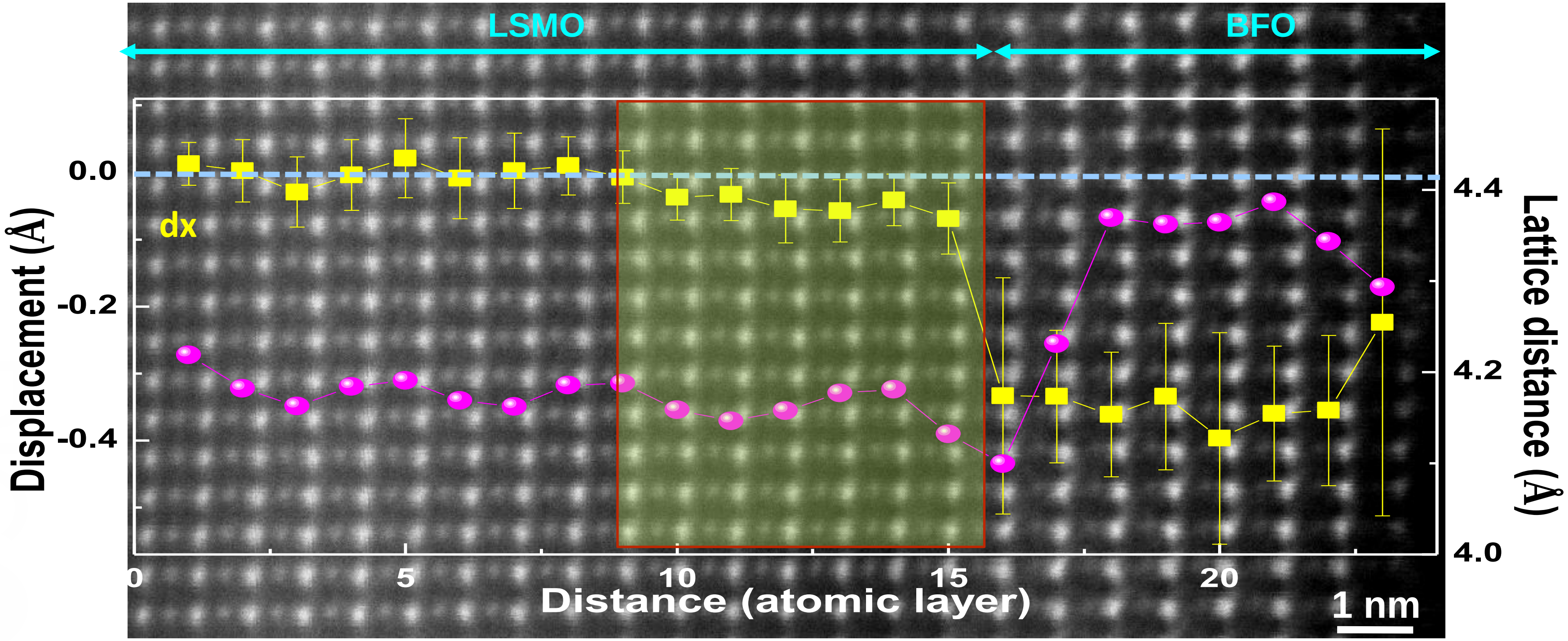
BFO:

- Positive displacement of Fe (towards the interface)
- Gradual decrease of polarization
- First few atomic layers show out-of-plane lattice expansion

LSMO:

- Small negative displacement of Mn in LSMO at the interface

BFO-LSMO Interface



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BFO:

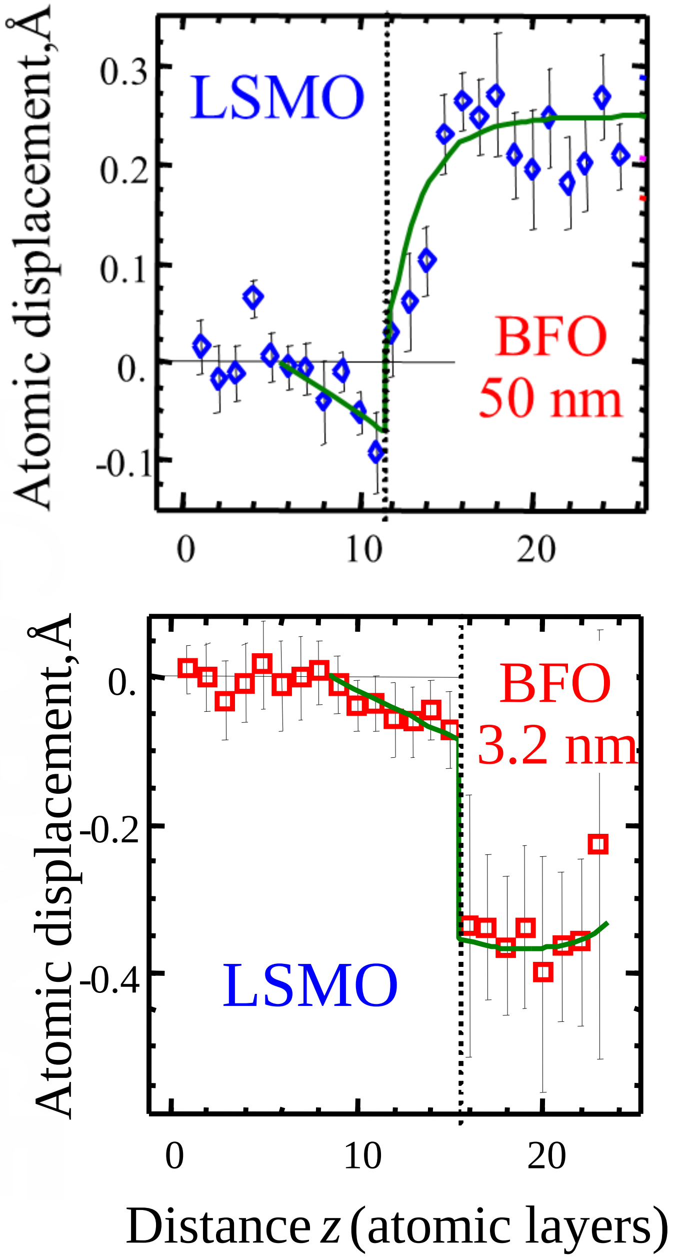
- Opposite polarization direction (negative displacement of Fe)
- Most polarization falls off at the interface.
- Same value of out-of-plane lattice parameter close to interface

LSMO:

- Small negative displacement in LSMO

Same induced polarization in LSMO for both positive and negative BFO polarization

Analysis via Simple Electrostatics



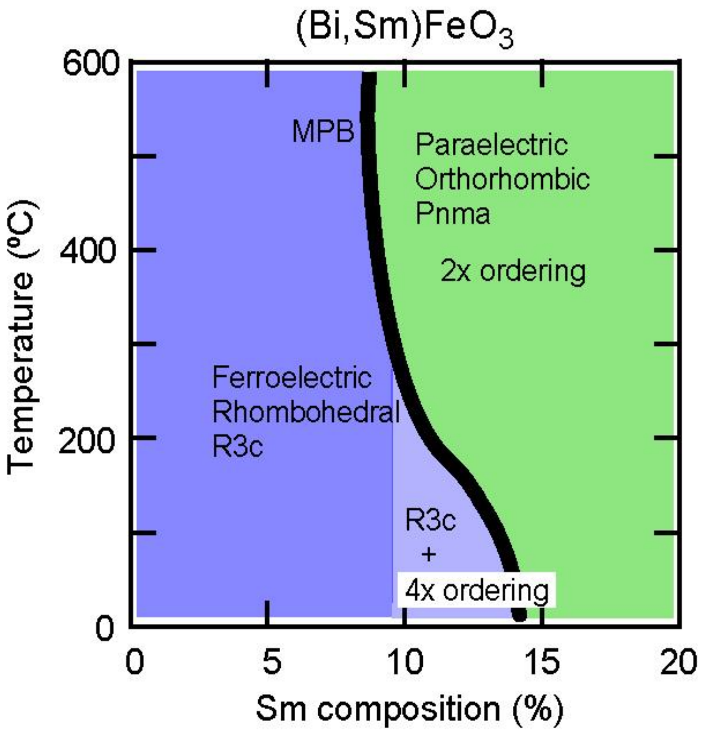
- Based on Ginzburg-Landau equation
- Interface parameters from fit of experimental data
- Two contributions to interface behavior:
  - Polarization charge
  - Built-in charge of the polar interface

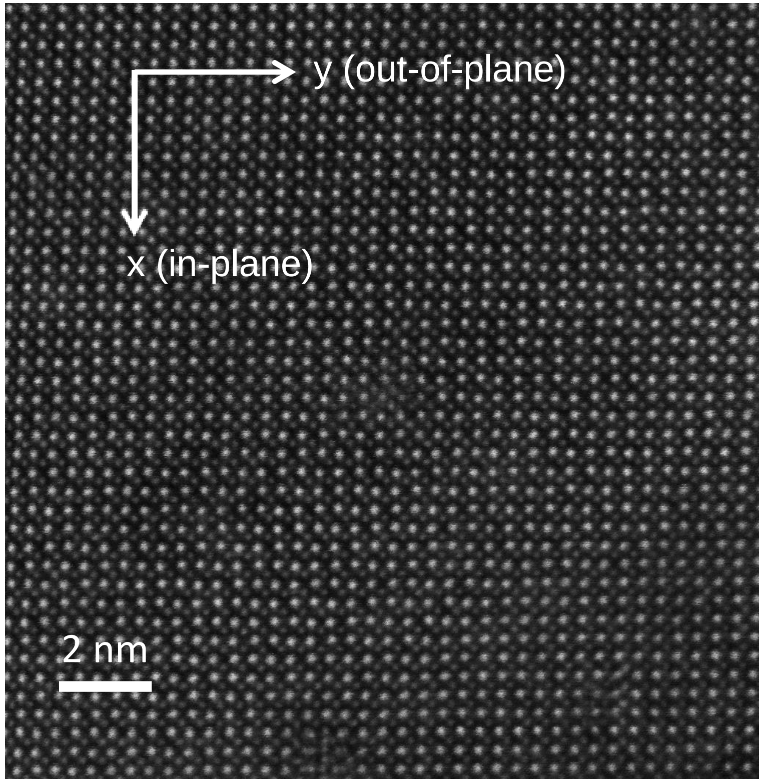
(LSMO) $$P_3(z) = \frac{2\varepsilon_0\varepsilon_{33}^b\beta\langle P_3\rangle^3 + \rho W + \sigma_S}{\varepsilon_0\varepsilon_{33}^b\left(\alpha + 3\beta\langle P_3\rangle^2\right) + 1} \cdot f(z, L), \quad 0 < z \le L$$

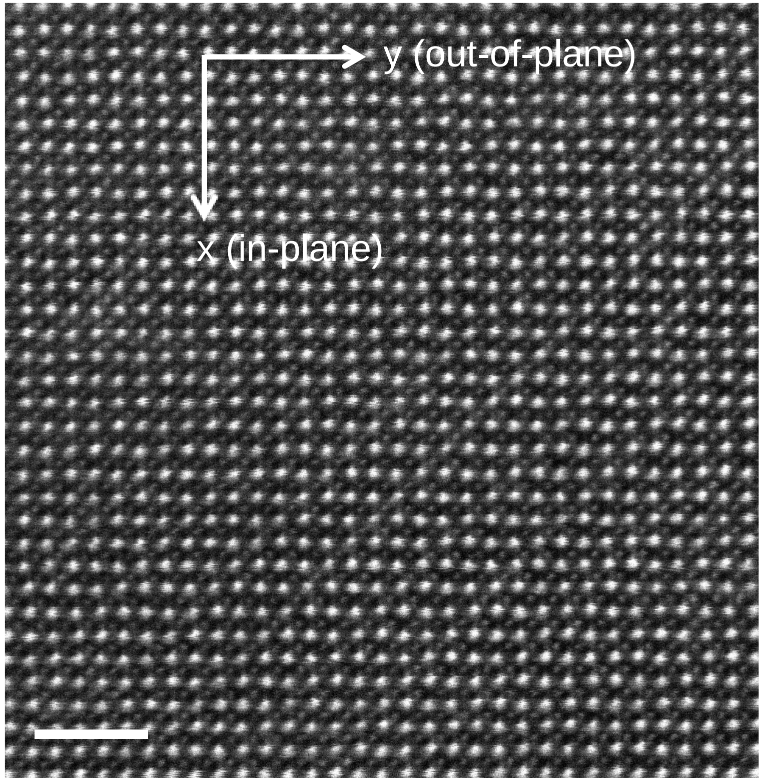
(BFO) $$P_3(z) = \frac{\varepsilon_S - 1}{\varepsilon_S}\rho(z - W)\theta(W - z), \quad z \le 0,$$

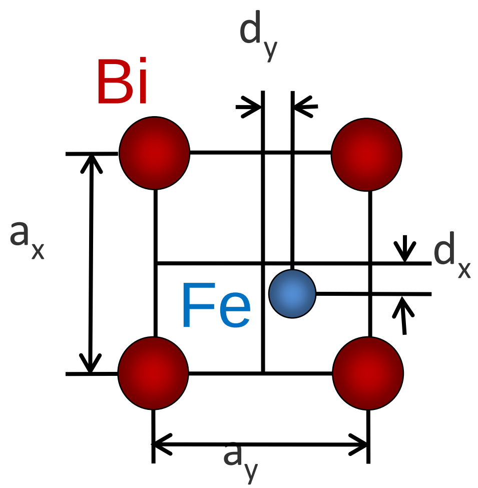
- Both thick (positive polarization) and thin (negative polarization) films can be fitted within the same model
- Behavior in LSMO determined mostly by built-in charge
- Magnitude of polarization in BFO depends on polarization direction due to non-symmetric effect of built-in charge

Patterns in Doped BFO



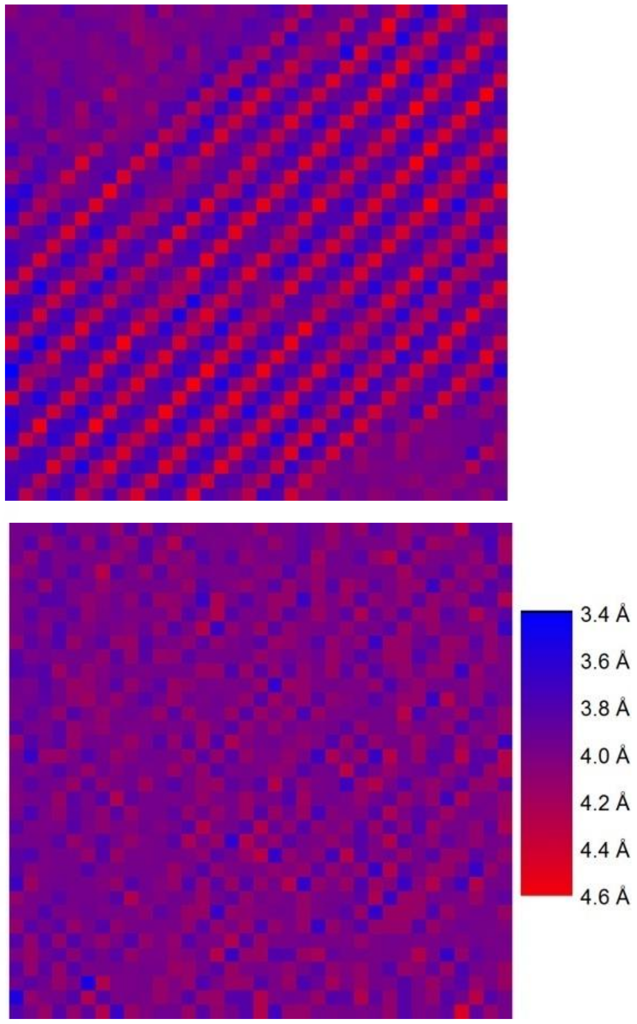


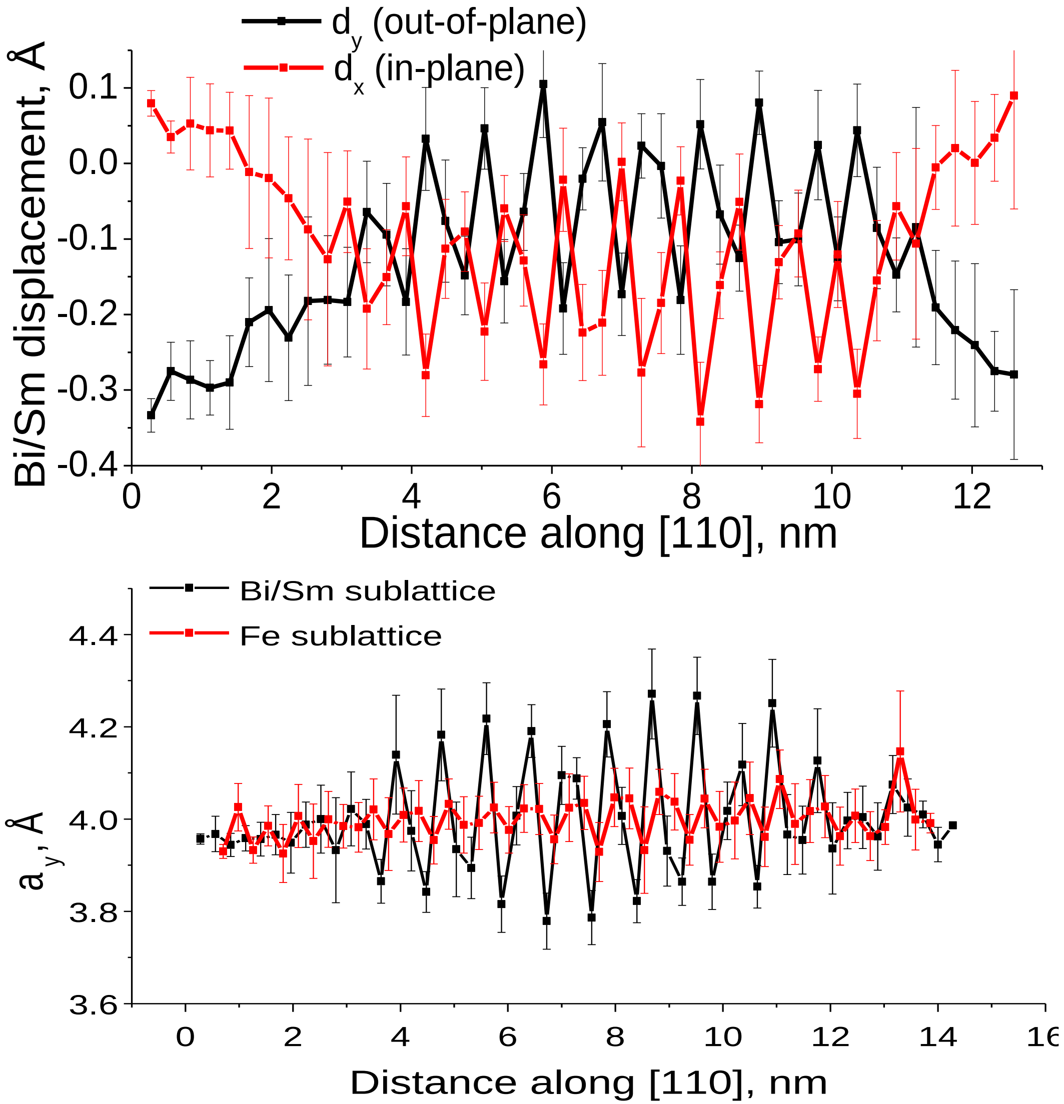




A.Y. BORISEVICH, E.A. ELISEEV, A.N. MOROZOVSKA, C.J. CHENG, J.Y. LIN, Y.H. CHU, D. KAN, I. TAKEUCHI, V. NAGARAJAN, and S.V. KALININ, *Atomic-scale evolution of modulated phases at the ferroelectric-antiferroelectric morphotropic phase boundary controlled by flexoelectric interaction*, Nature Communications **3**, 775 (2012)

Patterns in Doped BFO

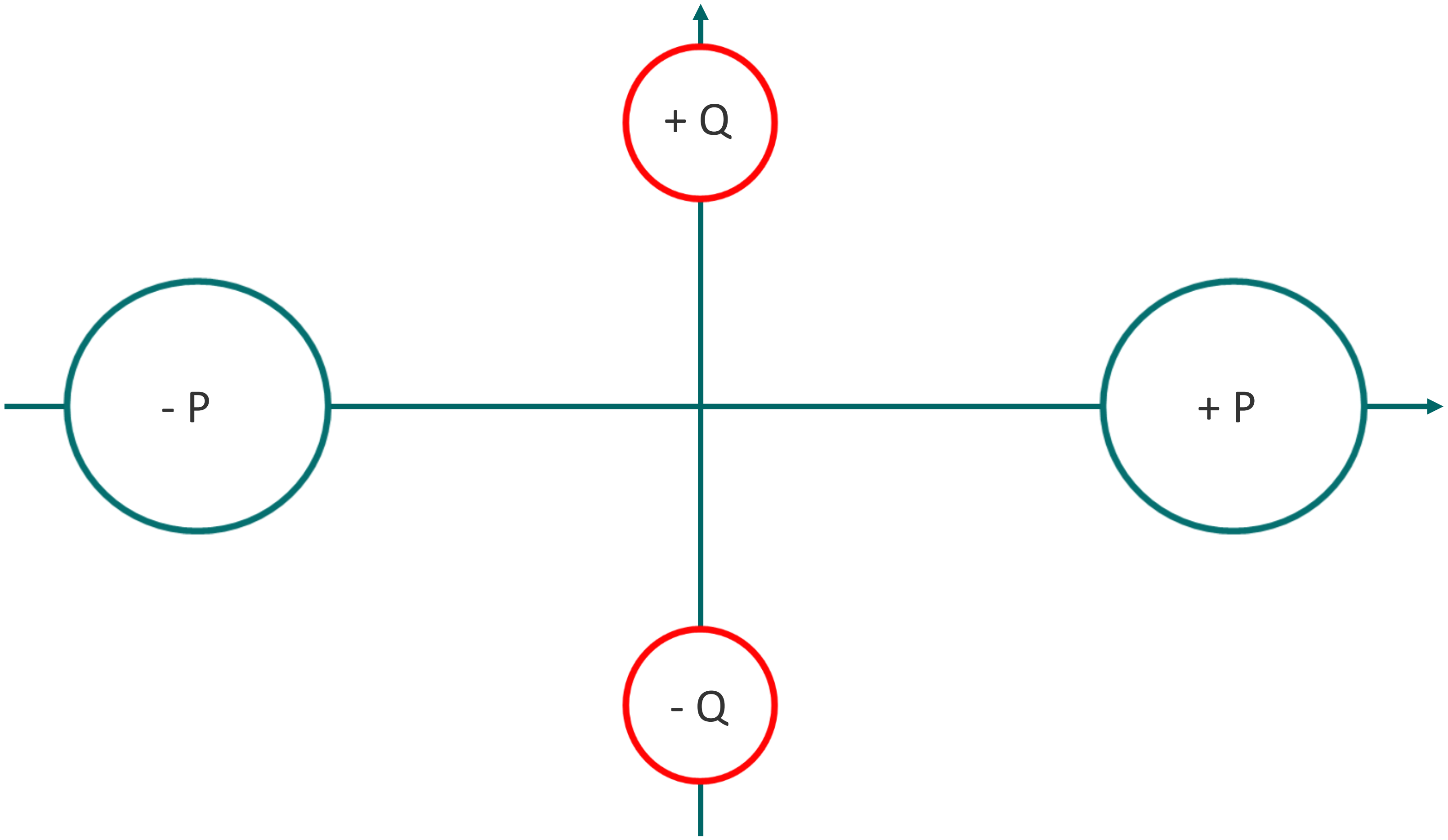




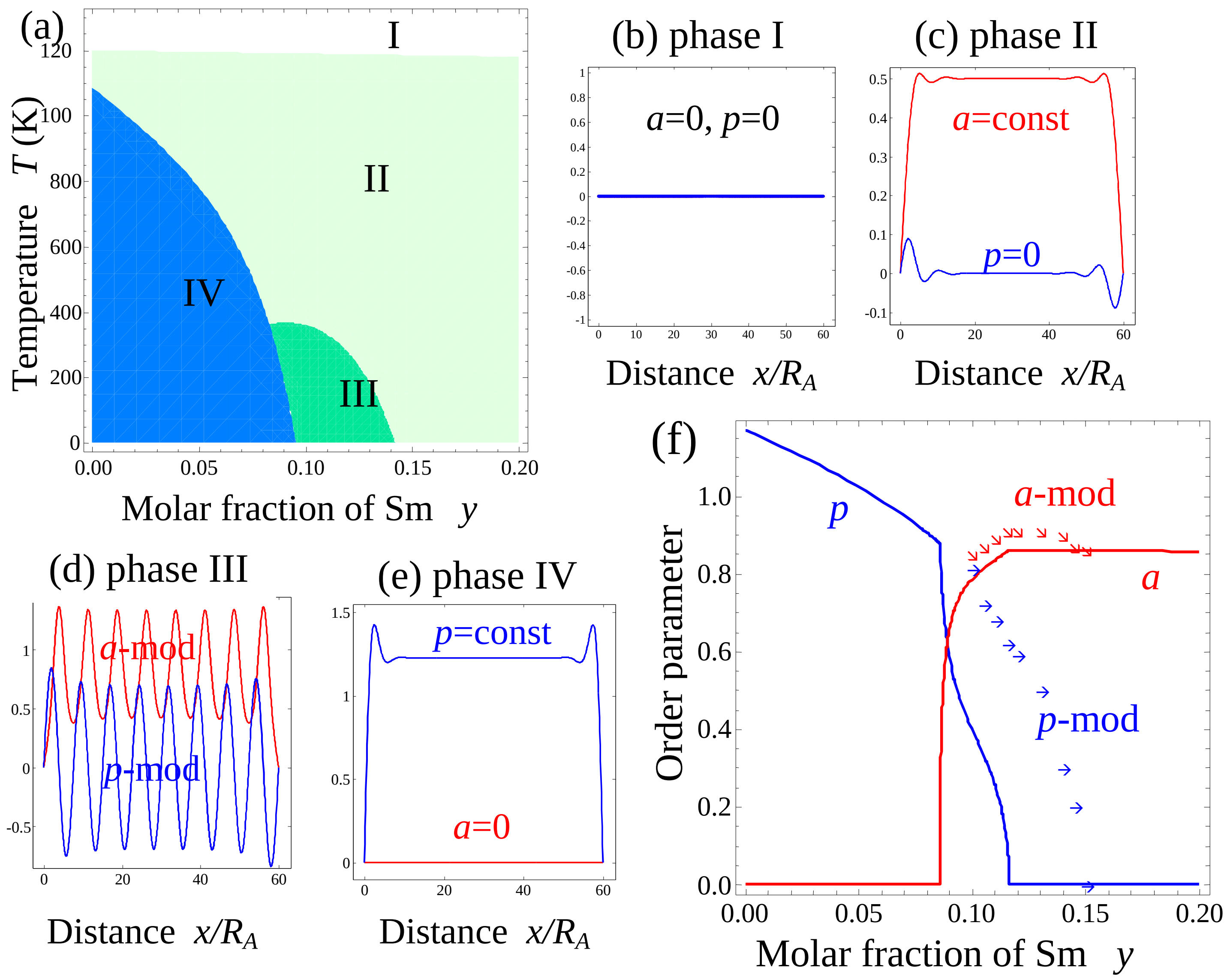
A.Y. BORISEVICH, ET AL

Nature Communications **3**, 775 (2012)

Model: Instability at the Domain



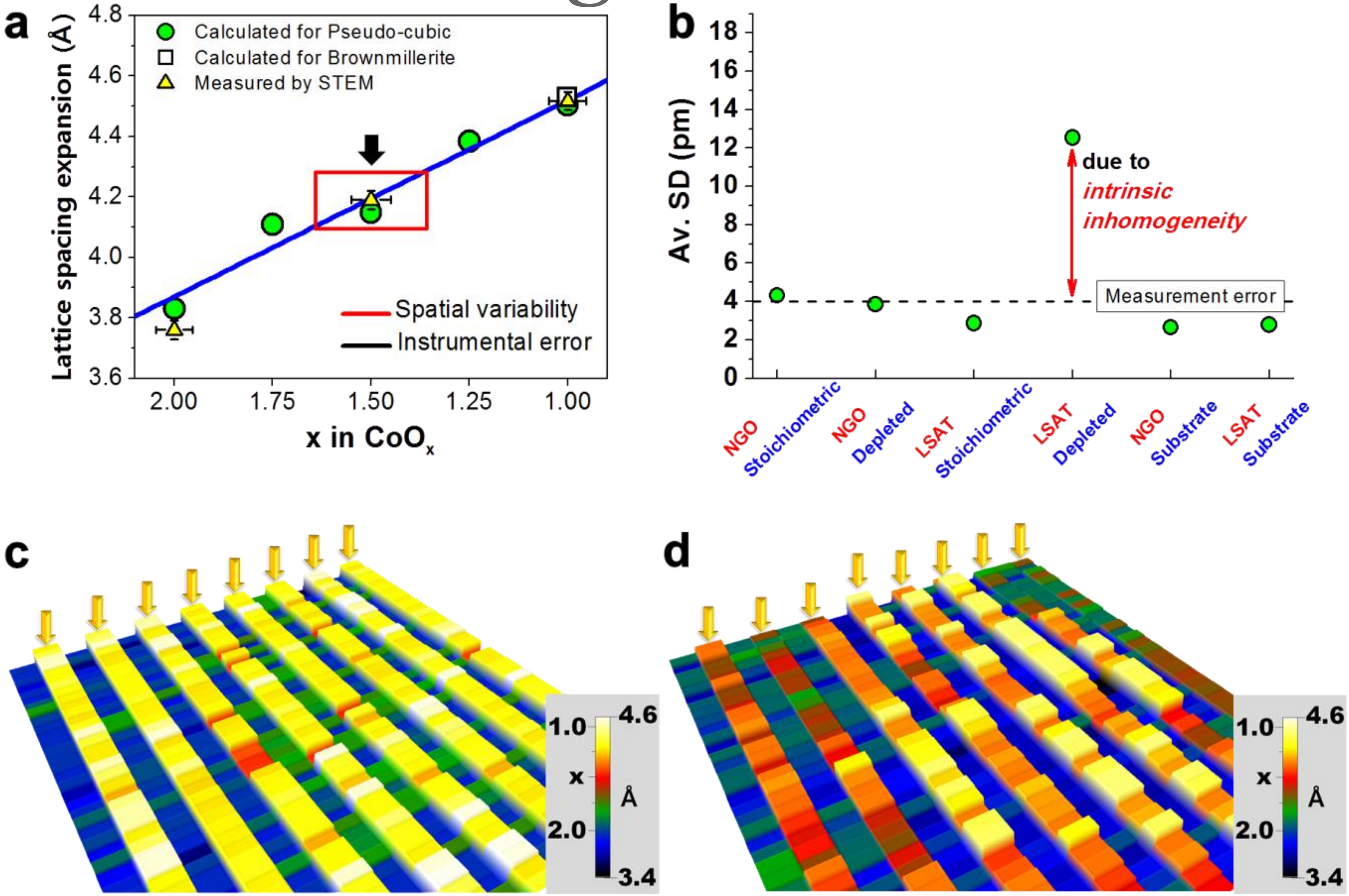
Flexoelectric Instability



- Flexoelectric coupling at domain walls causes the wall to loose stability: rippling
- Ripple can propagate in material, forming a new phase

A.Y. Borisevich, et al, Nature Communications **3**, 775 (2012)

Chemical Effects: Vegard Strains

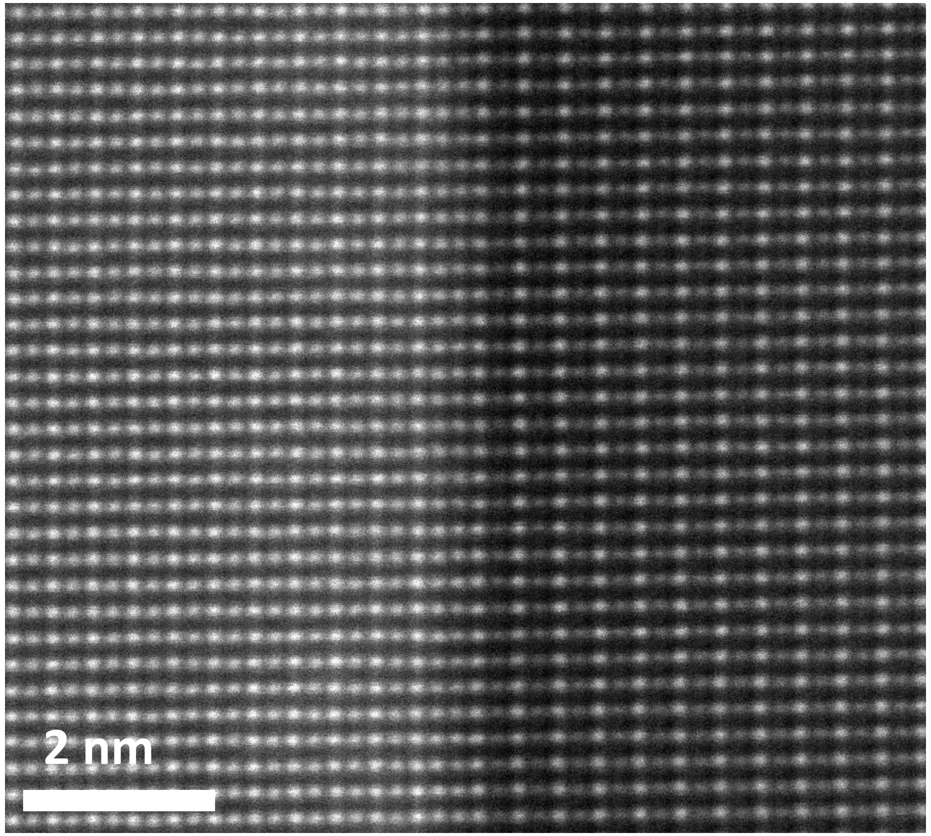


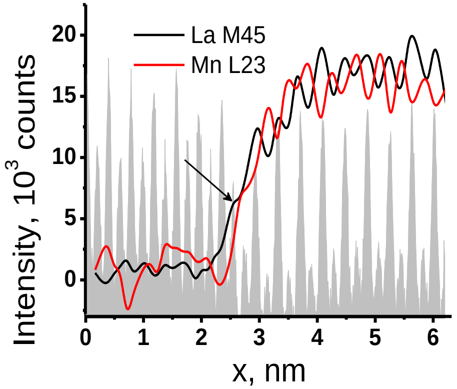
Y.M. Kim, J. He, M.D. Biegalski, H. Ambaye, V. Lauter, H.M. Christen, S.T. Pantelides, S.J. Pennycook, S.V. Kalinin, and A.Y. Borisevich, *Probing Oxygen Vacancy Concentration and Homogeneity in Solid Oxide Fuel Cell Cathode Materials on the (sub) Unit Cell Level*, Nature Materials **11**, 888 (2012)

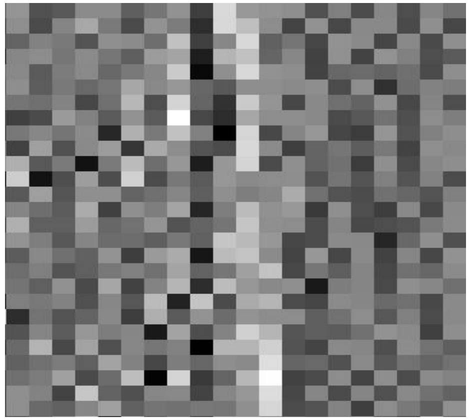
Chemical Effects on Oxide-Oxide Interfaces

Descriptive analysis:

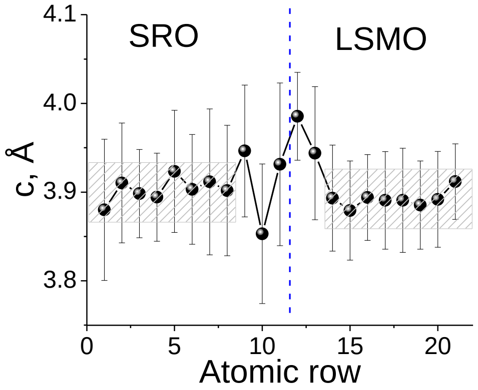
- *c* lattice parameter
- *a* lattice parameter
- Tilts
- Polarization
- EELS descriptors

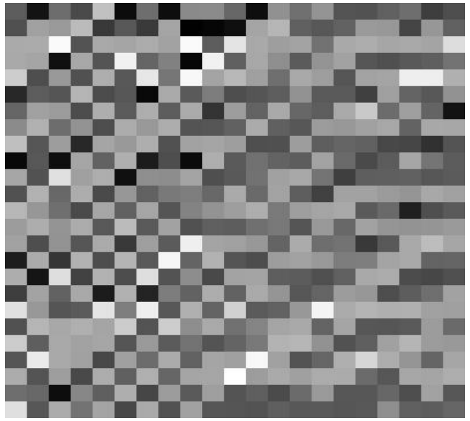


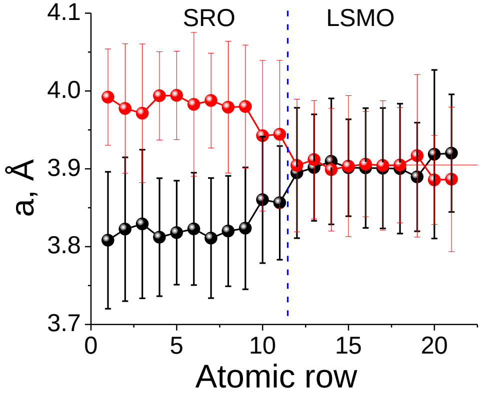




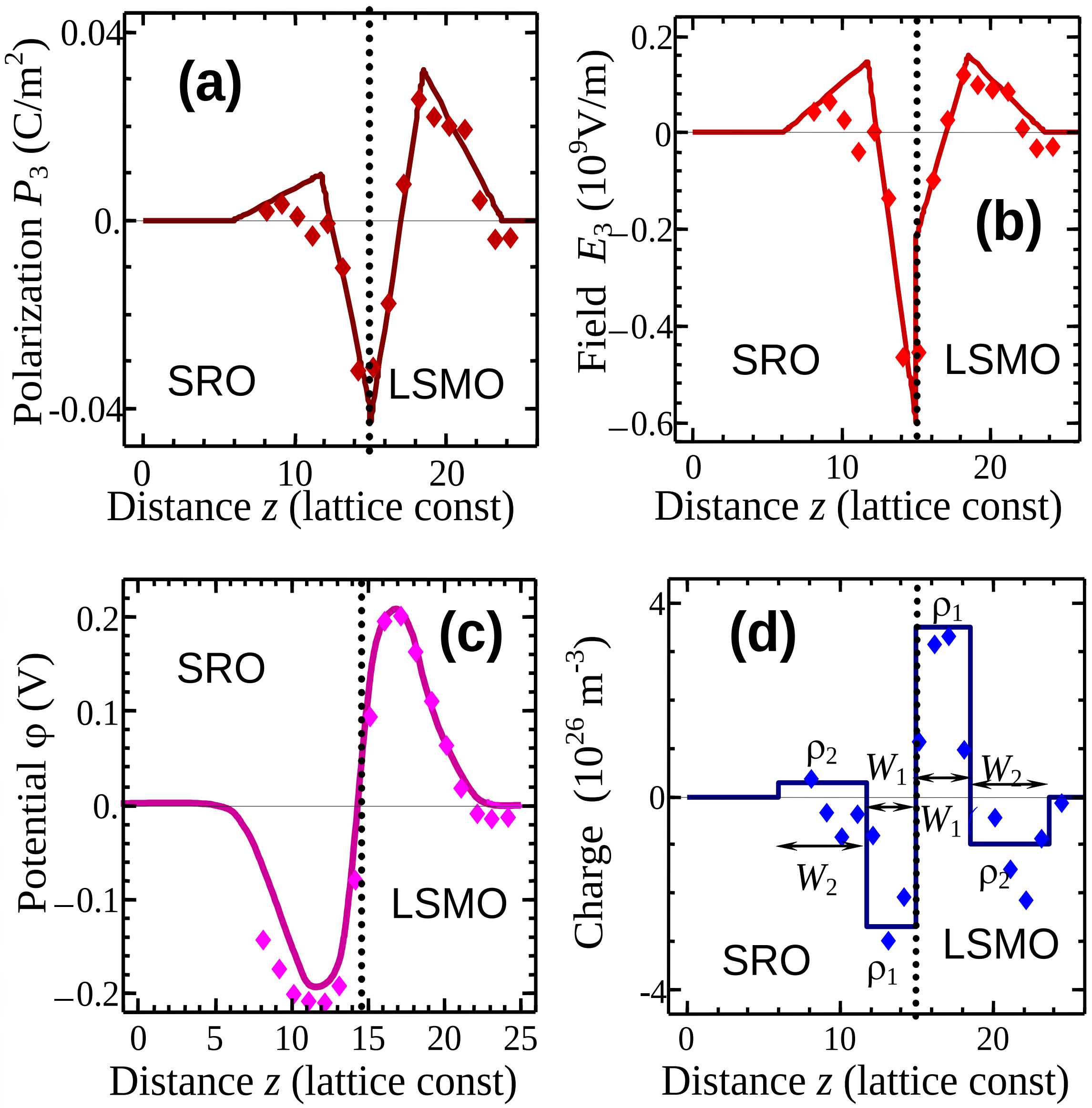
A.Y. Borisevich, et al Phys. Rev. **B 86**, 140102 (2012).







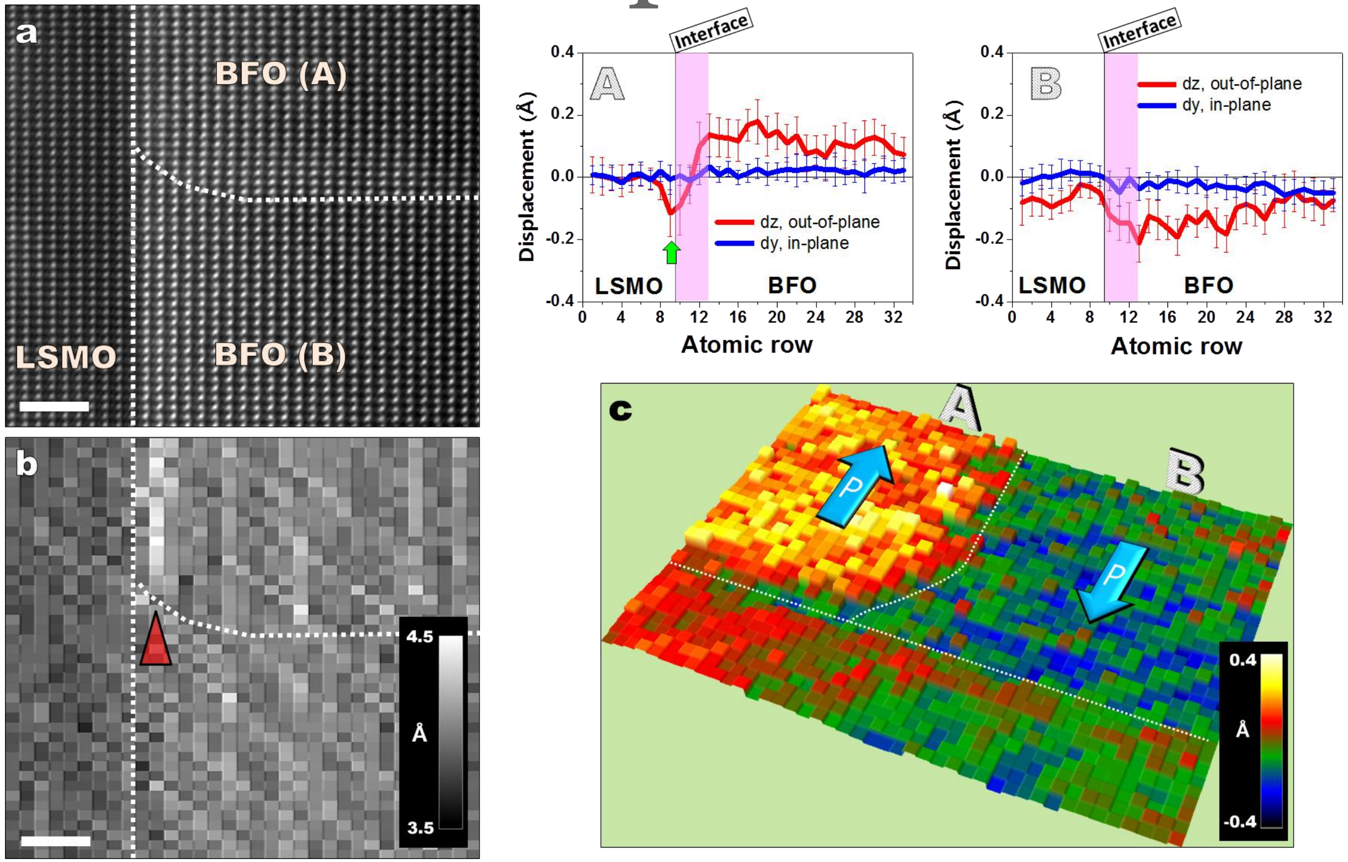
Analysis

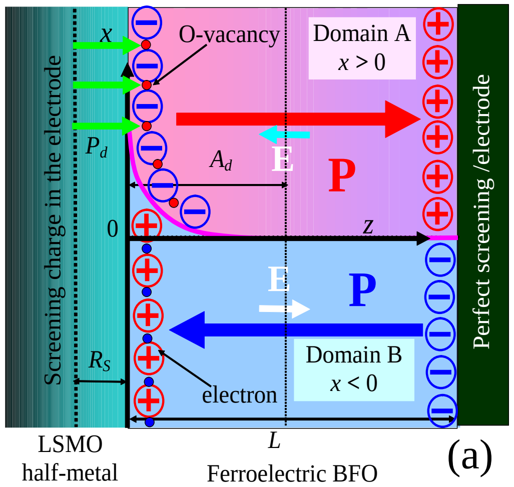


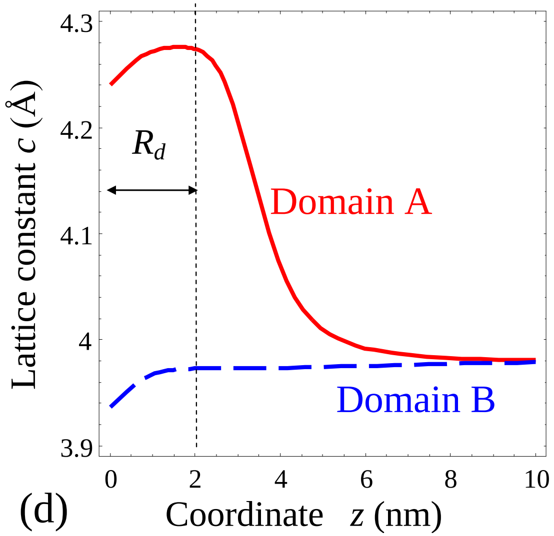
- Based on Ginzburg-Landau equation
- Interface parameters from fit of experimental data
- Two contributions to interface behavior:
  - Polarization charge
  - Built-in charge of the polar interface

A.Y. Borisevich, A.R. Lupini, J. He, E.A. Eliseev, A.N. Morozovska, G.S. Svechnikov, P. Yu, Y.H. Chu, R. Ramesh, S.T. Pantelides, S.V. Kalinin, and S.J. Pennycook, *Interface dipole between two metallic oxides caused by localized oxygen vacancies*, Phys. Rev. **B 86**, 140102 (2012).

Polarization Dependent Screening



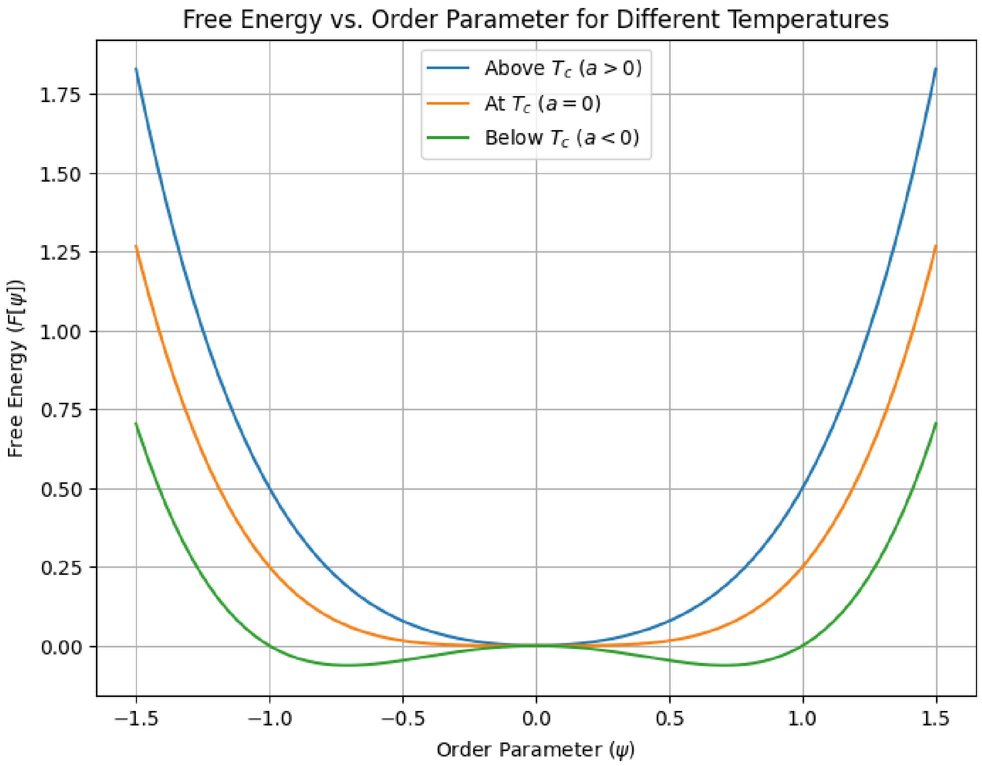


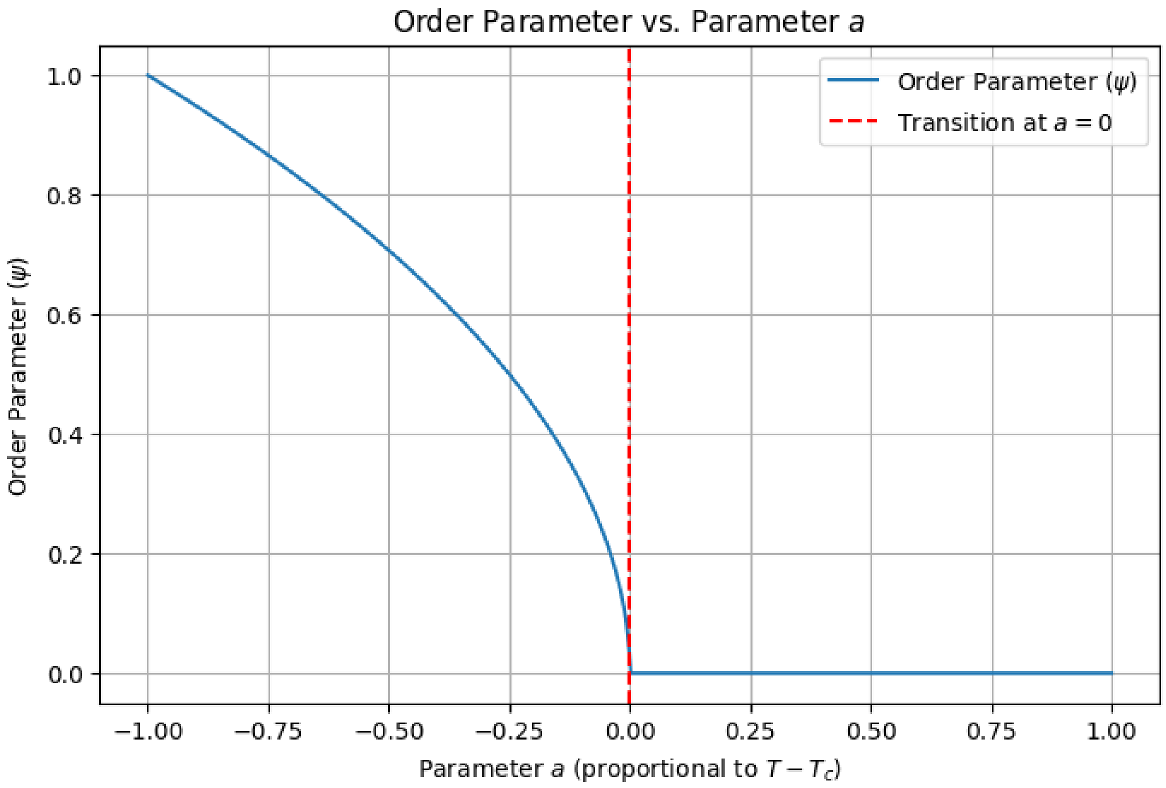


- For positive polarization, screening by electrons
- For negative polarization, screening by oxygen vacancies (not holes!)

Y.M. Kim, A. Morozovska, E. Eliseev, M.P. Oxley, R. Mishra, S.T. Pantelides, S.M. Selbach, T. Grande, S.V. Kalinin, and A.Y. Borisevich, *Direct observation of ferroelectric field effect and vacancy-controlled screening at the* $BiFeO_3$-$La_xSr_{1-x}MnO_3$ *interface*, Nature Materials **13**, 1019 (2014).

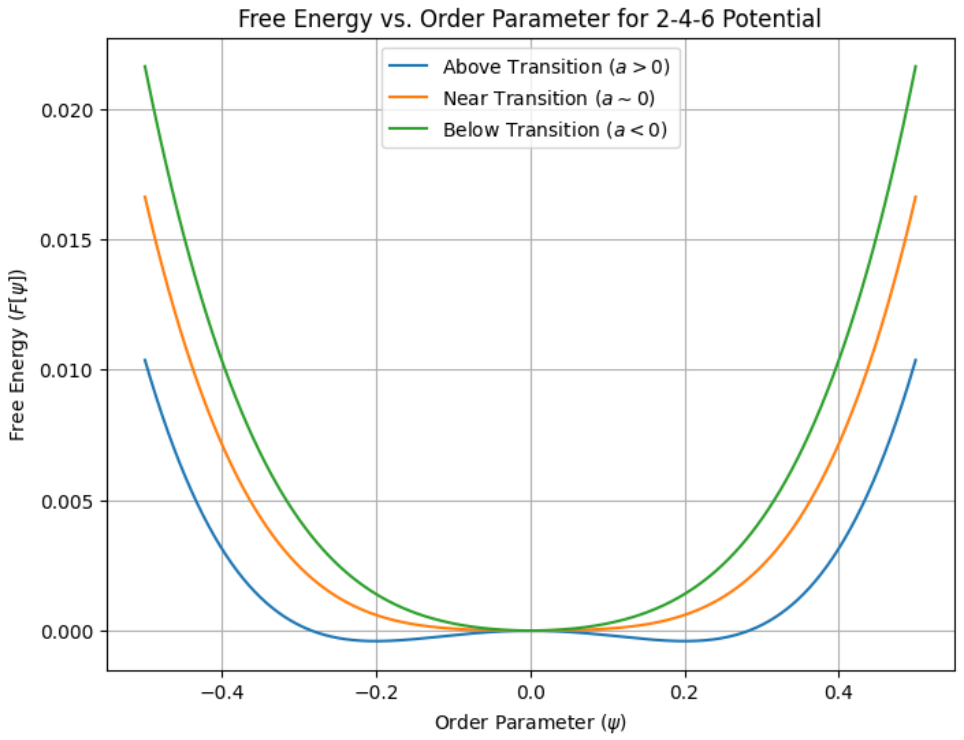
Ginzburg-Landau Theory

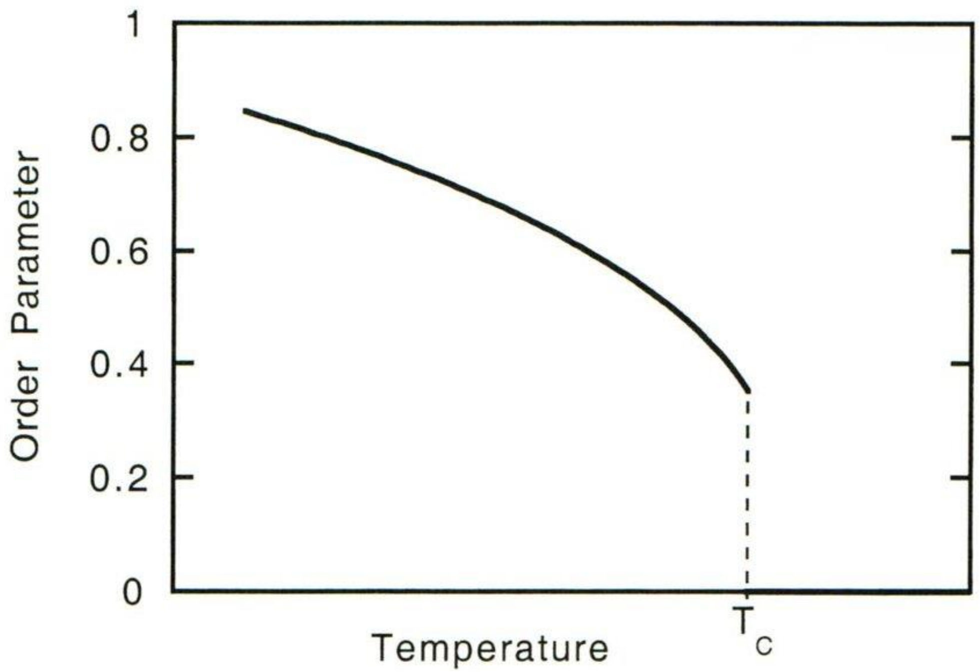




$$F = a(T\text{-}Tc)\, x^2 + b\, x^4$$

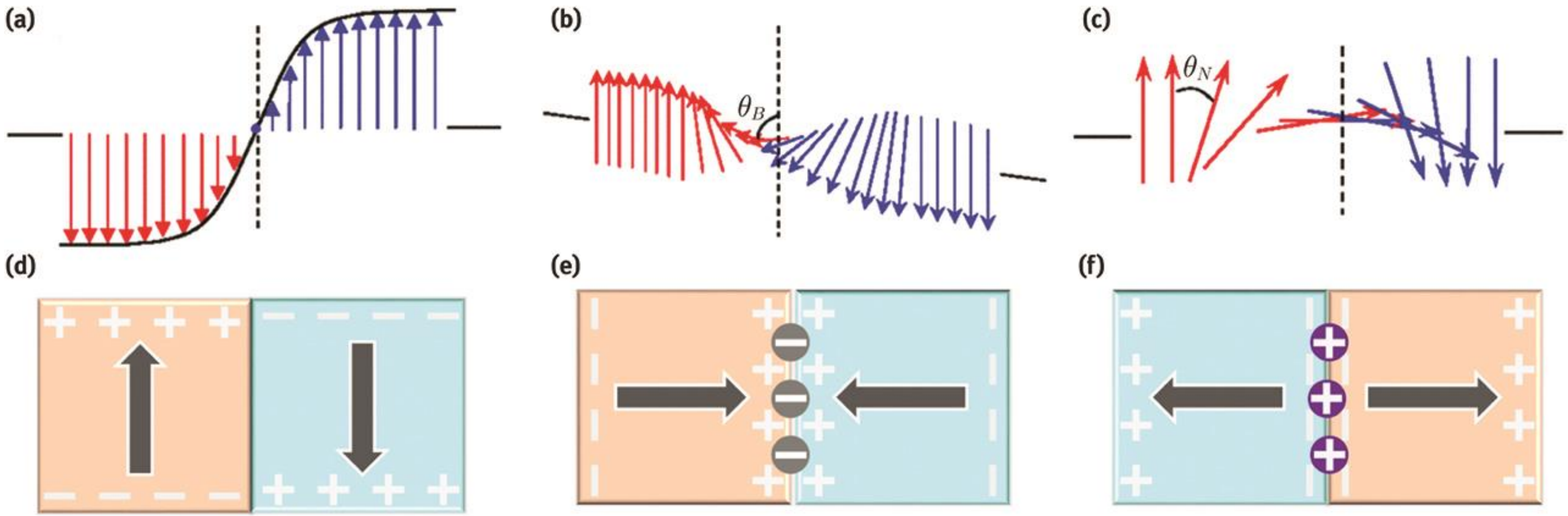
Ginzburg-Landau Theory





$$F = a(T-Tc)\, x^2 + b\, x^4 + c\, x^6$$

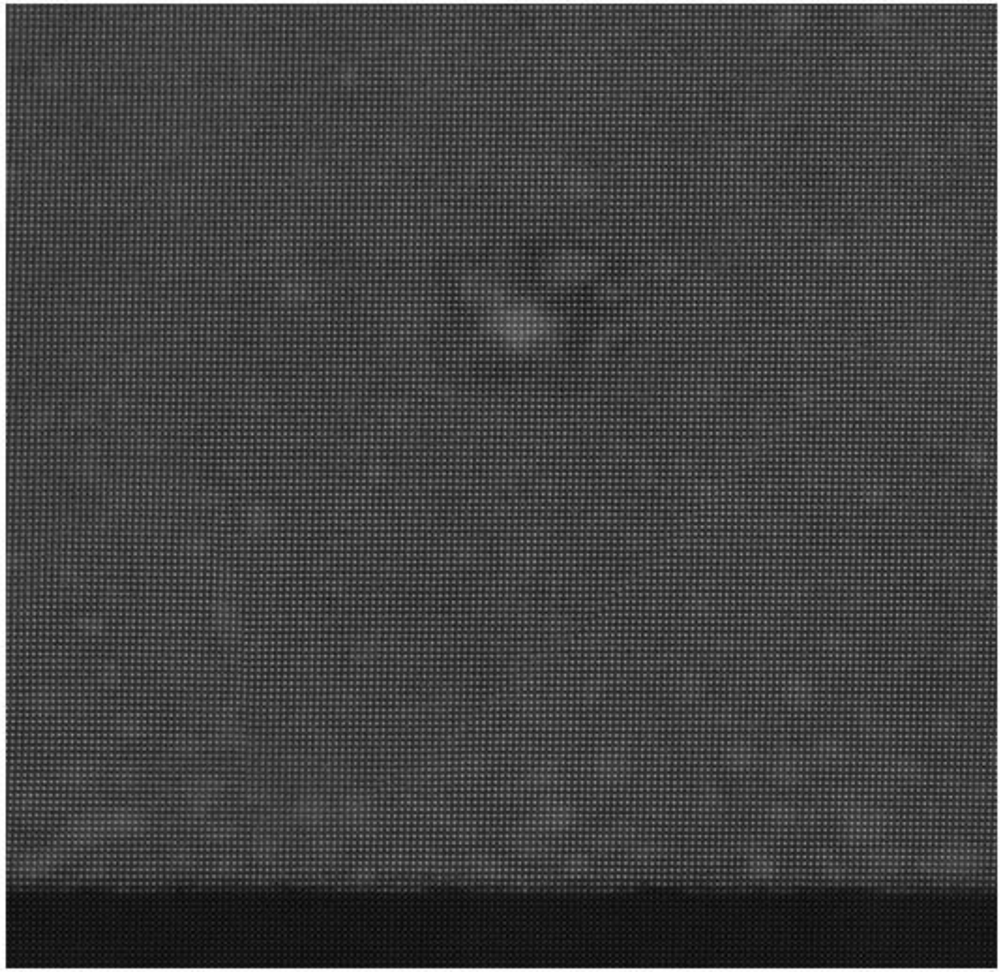
Topological defects and gradient terms

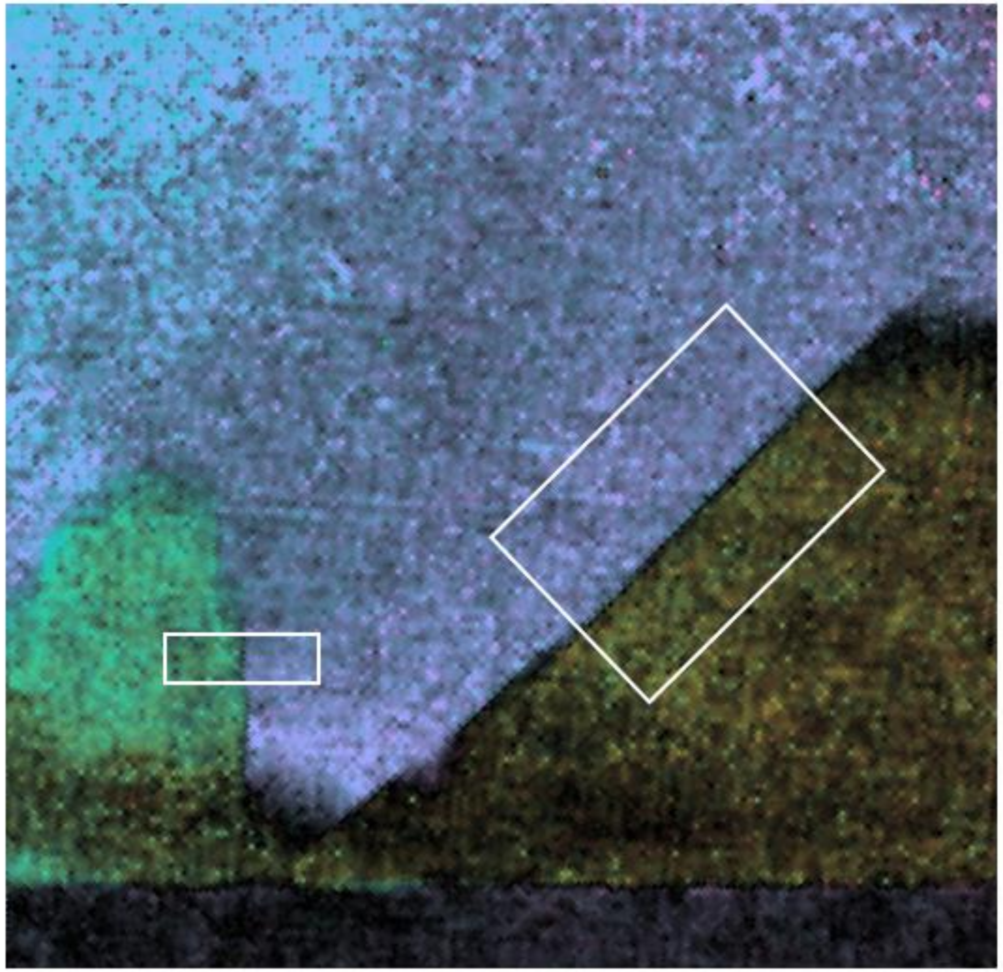


Energy ~ gradient of order parameter

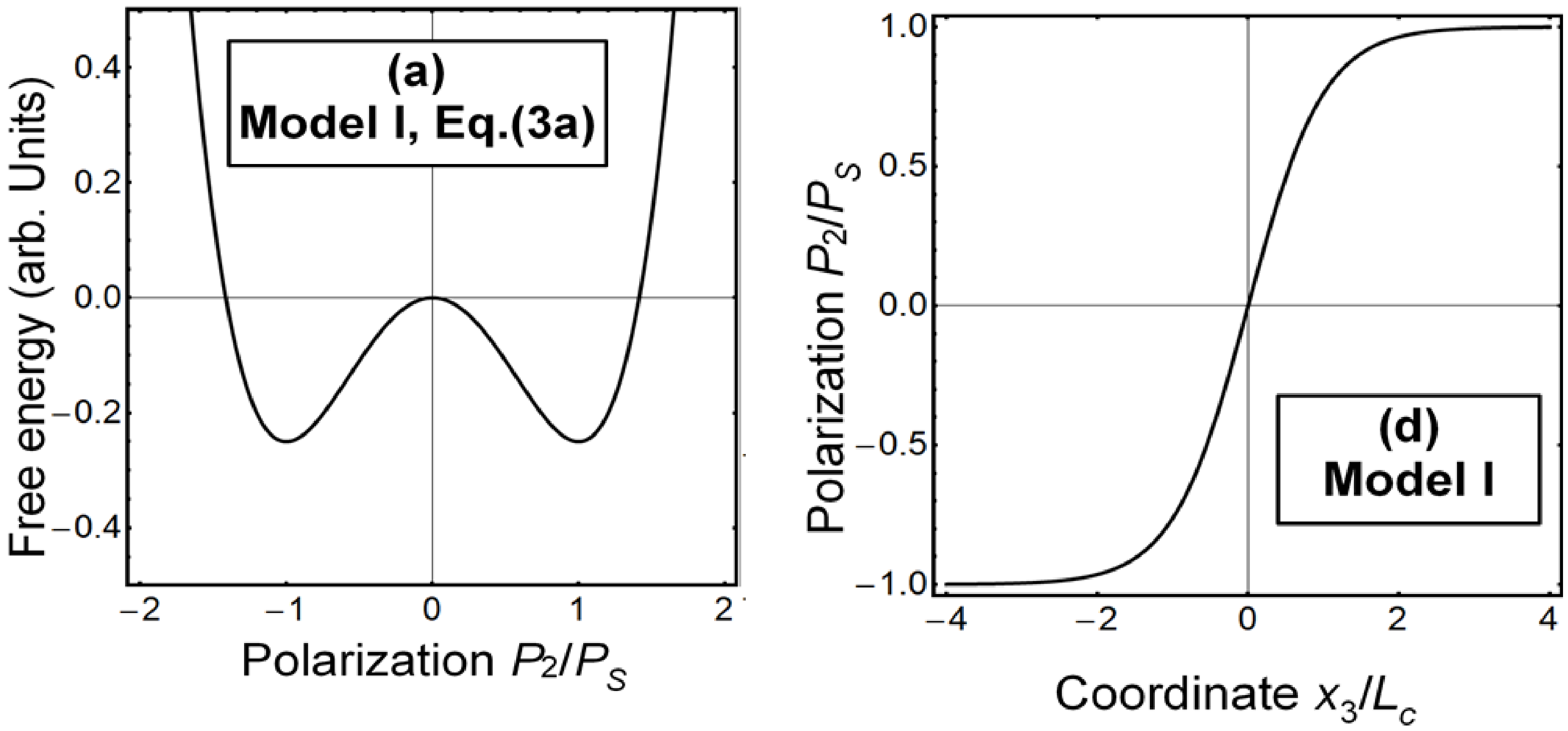
https://www.degruyter.com/document/doi/10.1515/psr-2019-0067/html

Experiment: Electron Microscopy





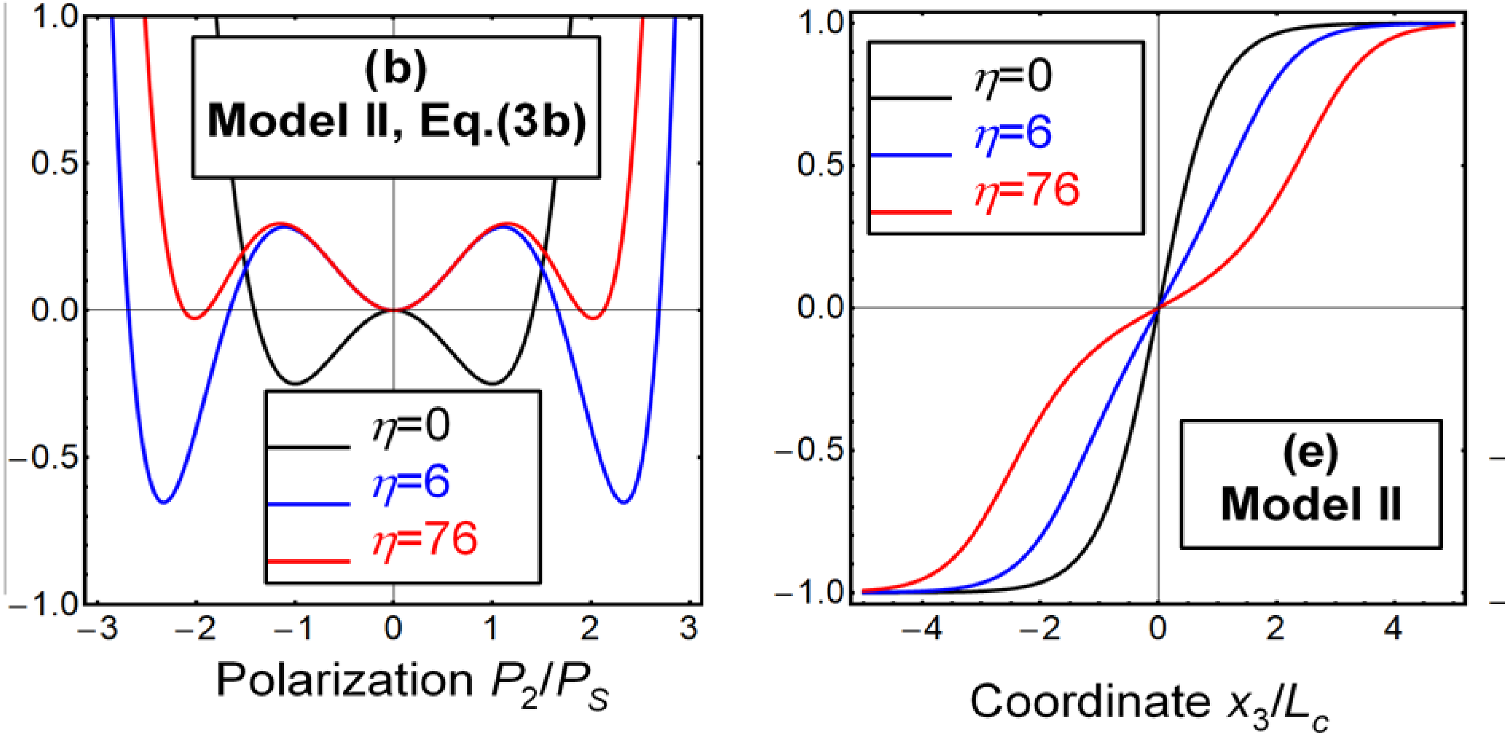
Model: Ferroelectric order parameter



Model 1. For the ferroelectrics with the second order phase transition the order parameter **P** across the uncharged domain wall can be found in the one component and one-dimensional approximations. Namely:

$$P_2\left(x_3\right) = P_S \cdot \tanh\left[\frac{x_3 - x_0}{L_c}\right], P_1\left(x_3\right) = 0, \tag{3a}$$

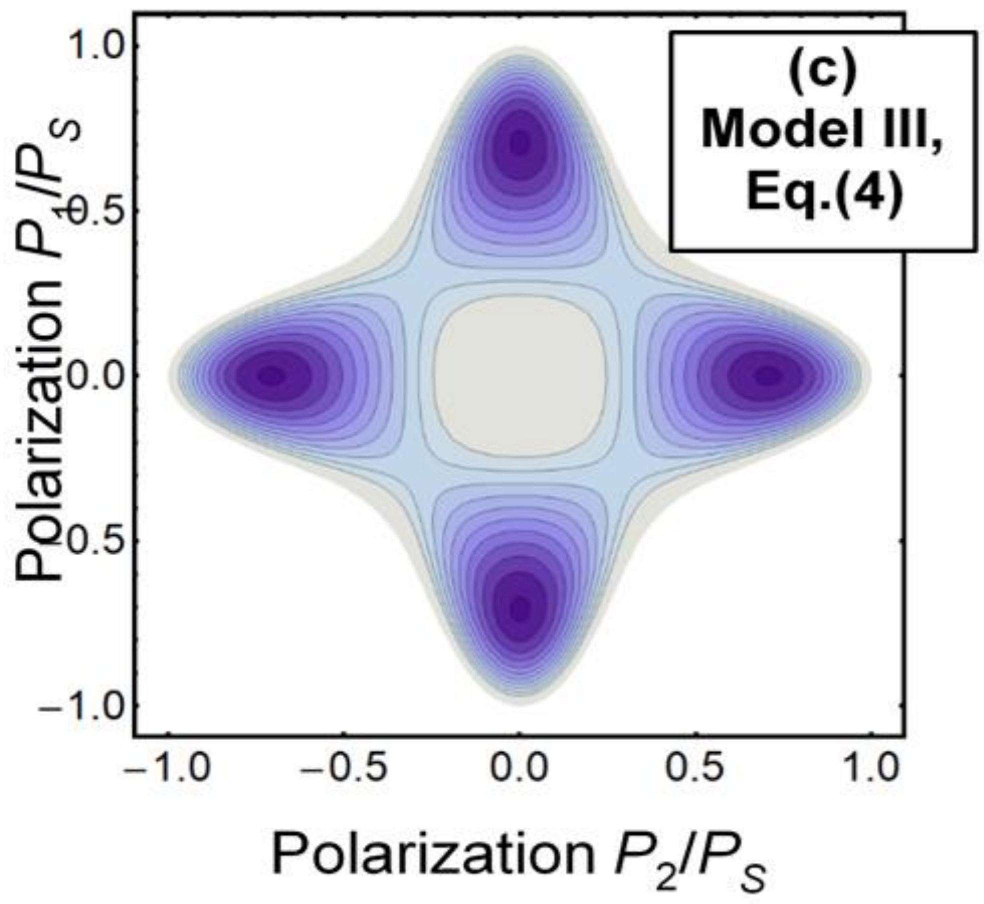
Model: Ferroelectric order parameter

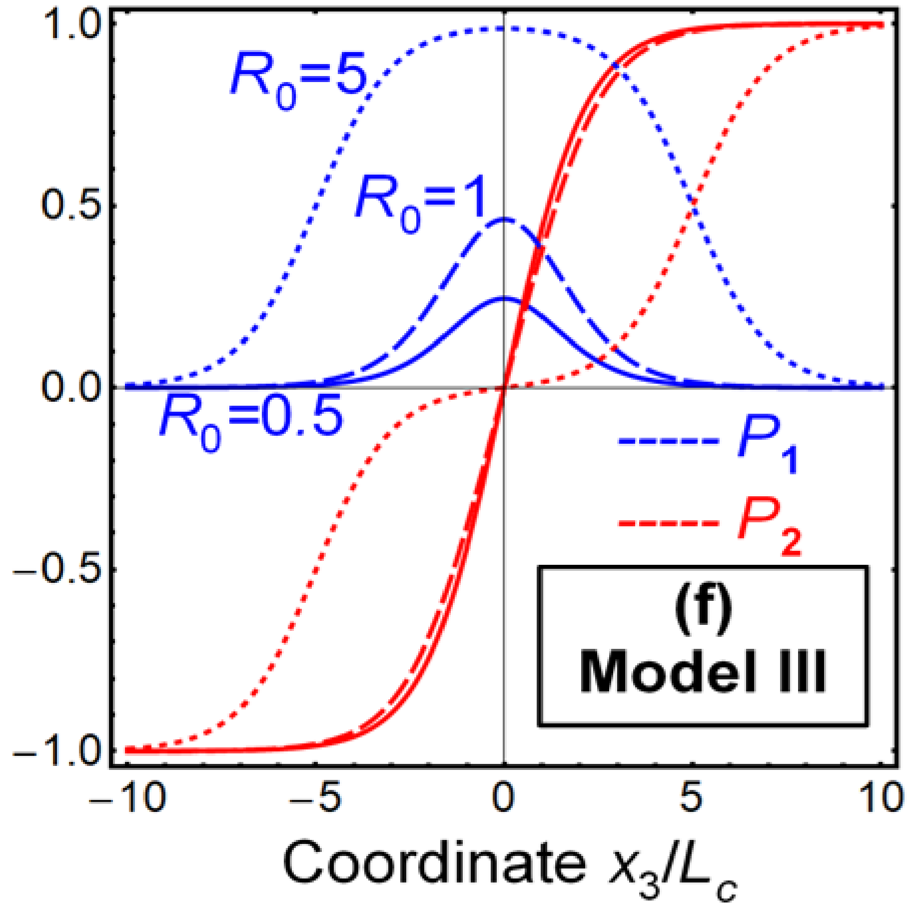


Model 2. For the ferroelectrics with the first order phase transition, the order parameter profile is more complex:

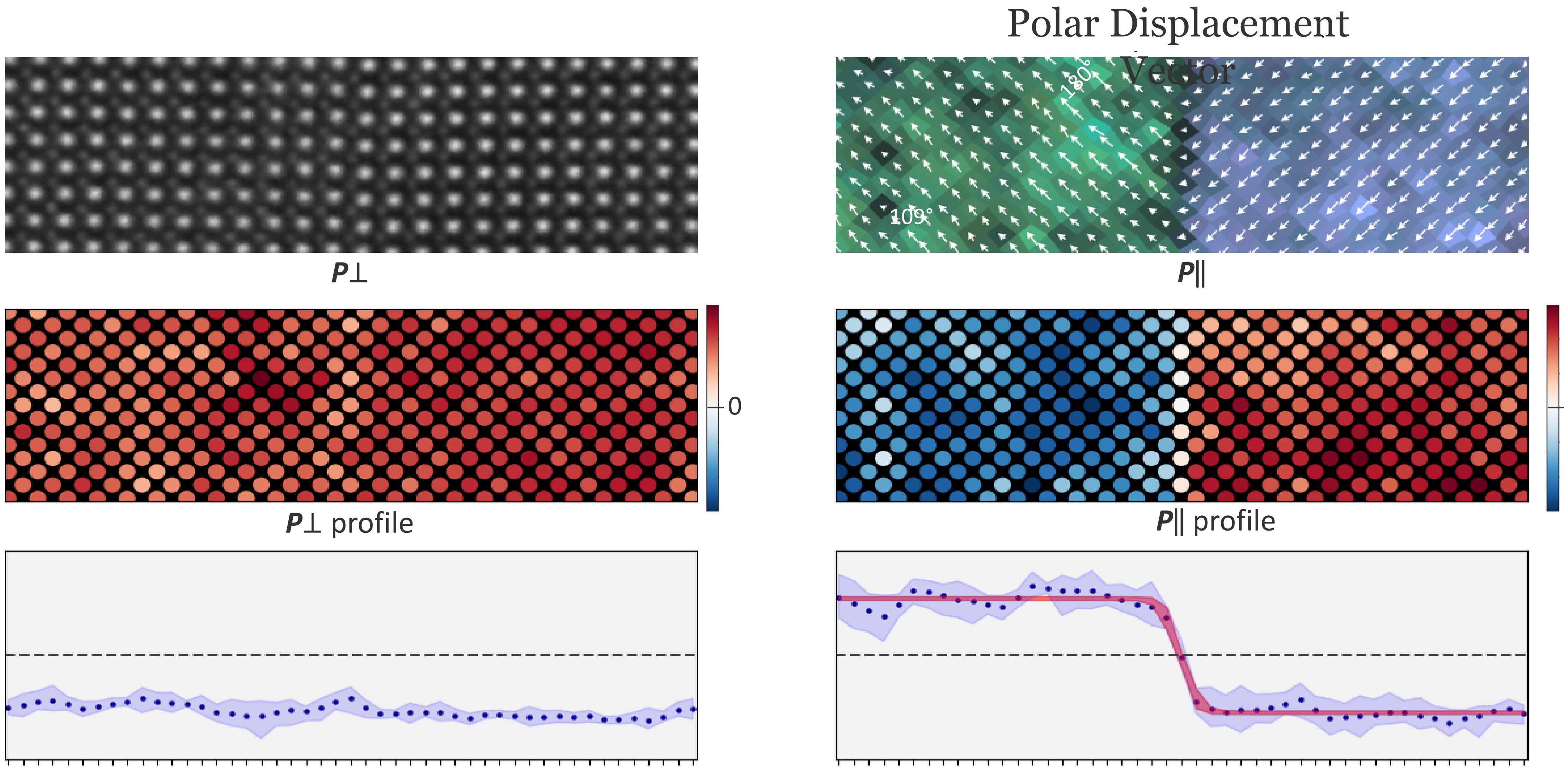
$$P_2\left(x_3\right)=\frac{P_S\cdot\sinh[\left(x_3-x_0\right)/L_c]}{\sqrt{\eta+\cosh^2\left[\left(x_3-x_0\right)/L_c\right]}},\ P_1\left(x_3\right)=0, \qquad (3b)$$

Model: Ferroelectric order parameter

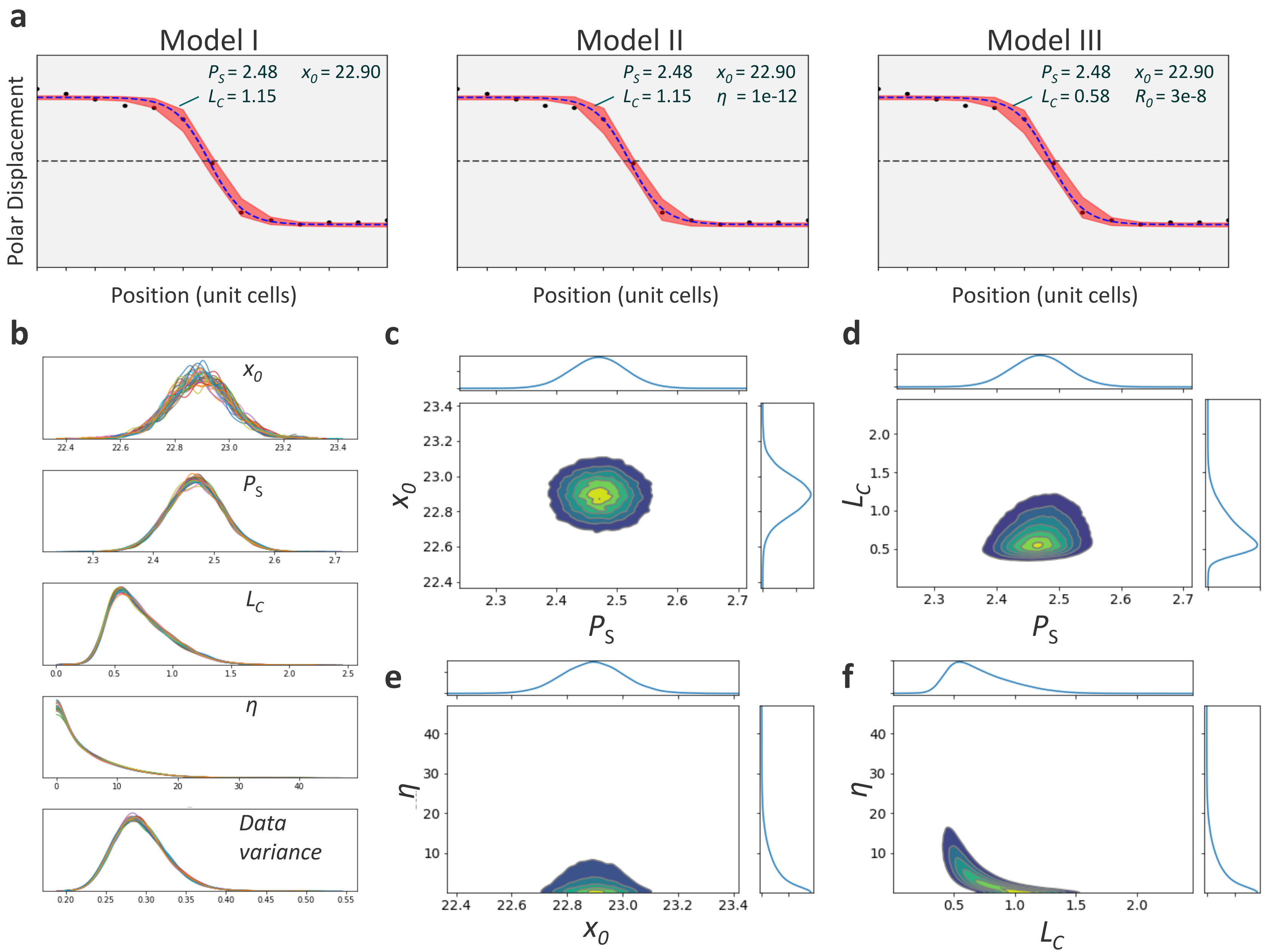




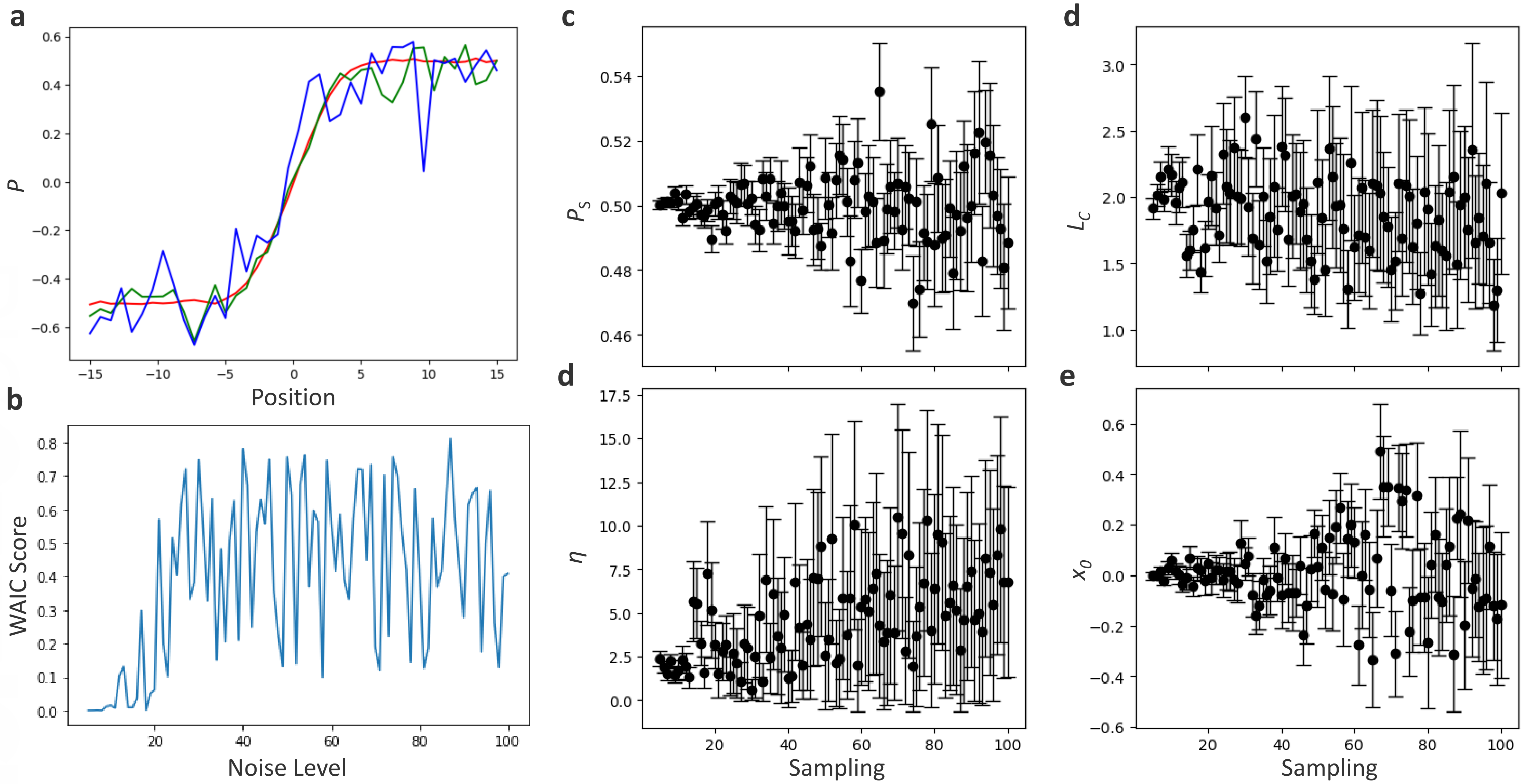
Analysis: Wall Profile



Bayesian Inference

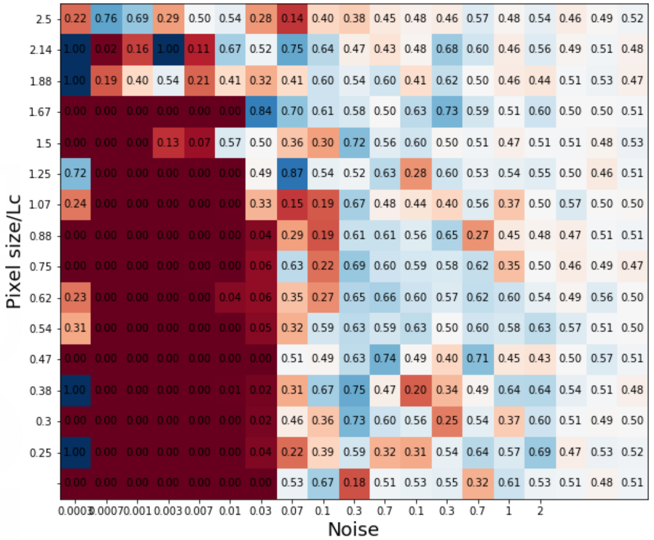


So, what microscope do we need?

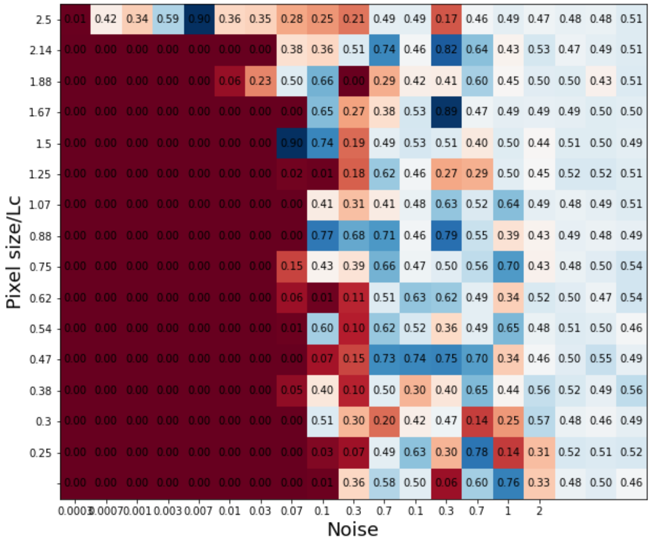


Effect of prior knowledge

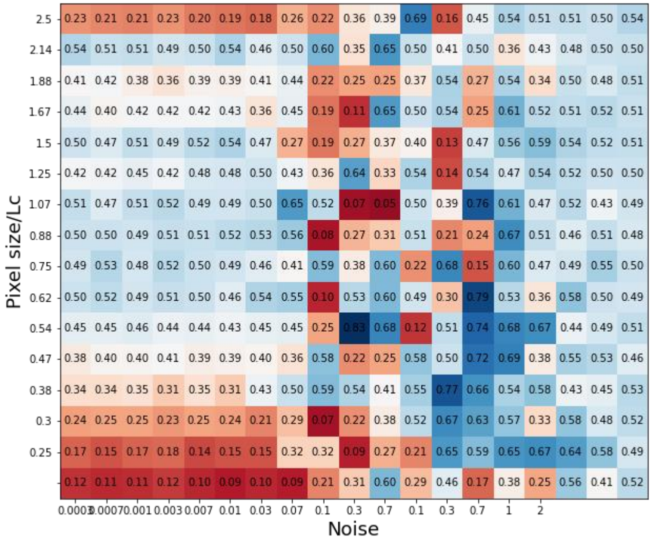
$P_s \sim U(0.4, 0.6)$, $L_c \sim U(0.5, 5.0)$



$P_s \sim U(0.49, 0.51)$, $L_c \sim U(1.9, 2.1)$



$P_s = 0.7$, $L_c \sim U(0.5, 5)$



Connecting Mesoscopic and Atomic Worlds

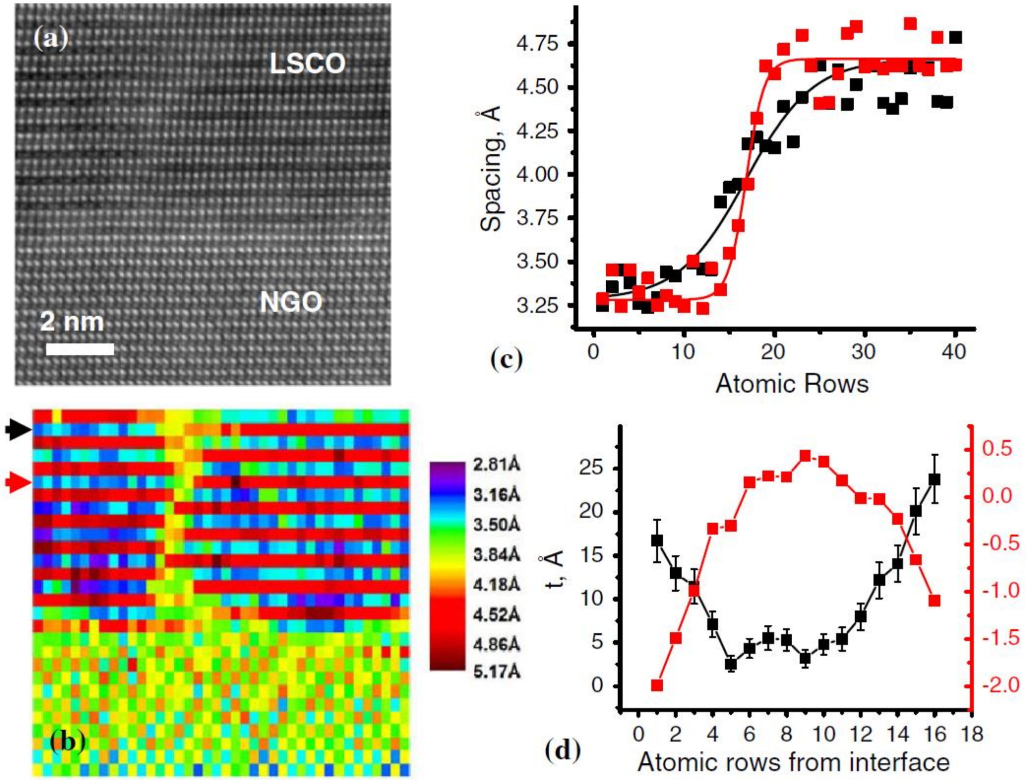
Model System: La-Sr cobaltite with topological defects and interfaces

Fitting the experimentally observed atomic profiles to the functional form of order parameter

$$\eta_{SD}(z) \approx \eta_b\left(1 - \frac{1}{1+\sqrt{2}\lambda/L_C(0)}\exp\left(-\frac{\sqrt{2}z}{L_C(0)}\right)\right)$$

Antiphase domain boundary

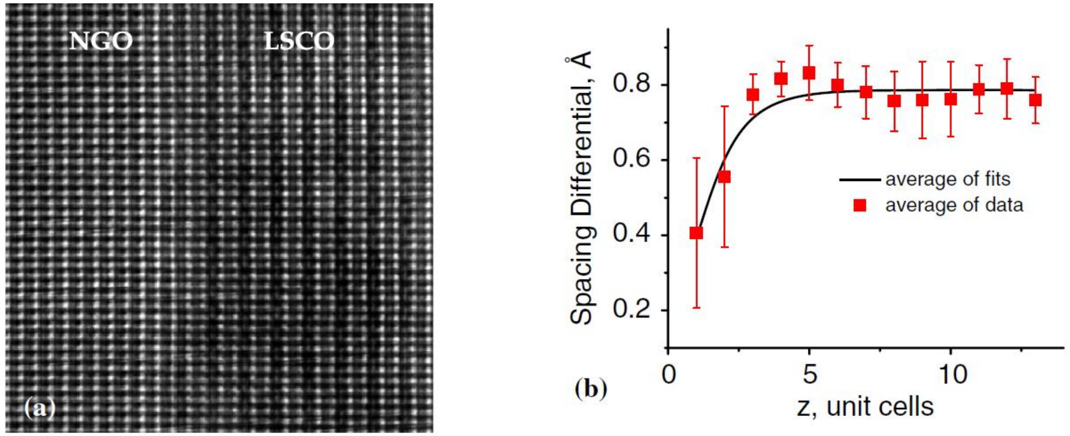
$$\eta(x, z) \approx \eta_{SD}(z)\tanh\left(\frac{x - x_0}{L_C(z)}\right)$$



A.Y. Borisevich *et al.*, *PRL* **109**, 065702 (2012)

Ordering behavior at the interfaces

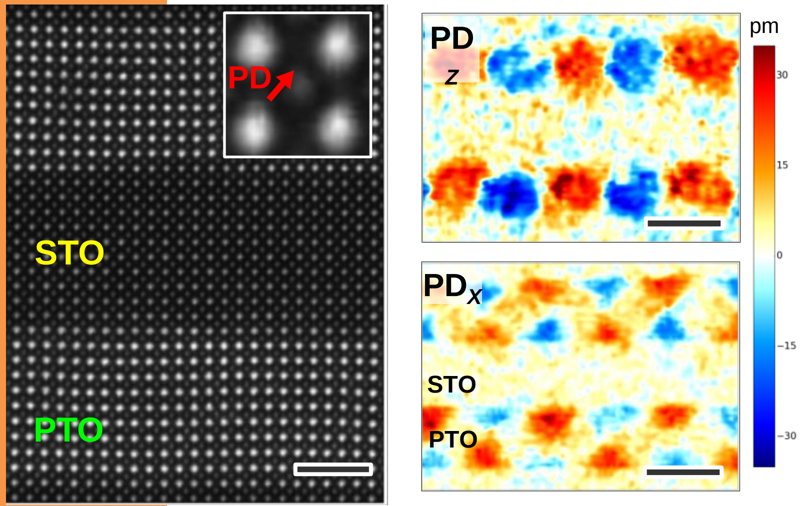
$$\eta(z) = 0.787(1 - 0.5\exp(-\tfrac{z-1}{1.1}))$$



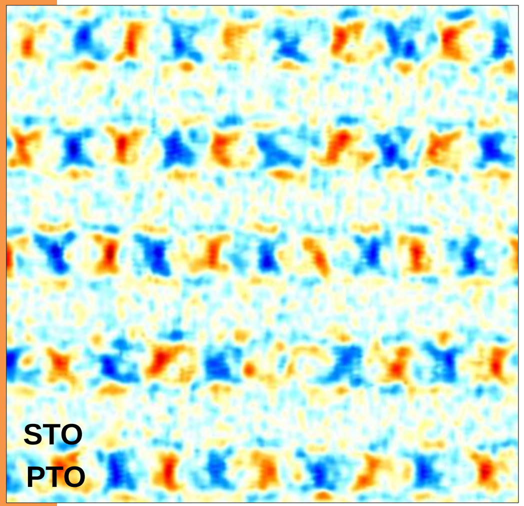
Allows to analyze the interplay between ordering, chemical composition, and mechanical effects at domain walls, interfaces and structural defects

Flexoelectricity by Computer Vision

HAADF-STEM images

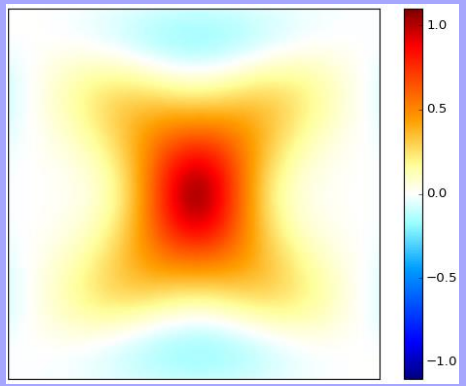


Vorticity/polar gradient

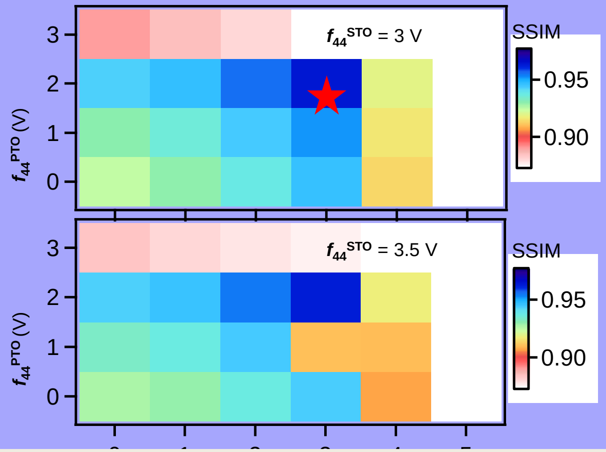


Theory-experiment matching

Model (best-fit flexo)



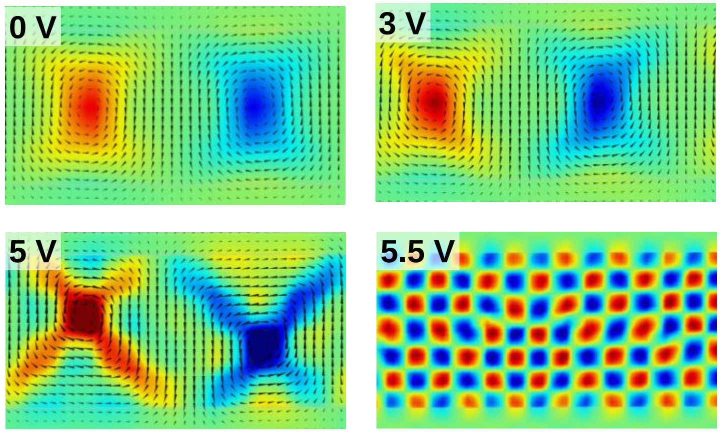
Similarity map



Effect of flexoelectricity

$$F = \alpha_{ij} P_i P_j + \alpha_{ijkl} P_i P_j P_k P_l + \alpha_{ijklmn} P_i P_j P_k P_l P_m P_n + \frac{1}{2} g_{ijkl} P_{i,j} P_{k,l} + \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - q_{ijkl} \varepsilon_{ij} P_k P_l - \frac{1}{2} \kappa_0 E_i E_i - E_i P_i + \boxed{f_{ijkl} (P_{k,l} \varepsilon_{ij} - \varepsilon_{ij,l} P_k)}$$

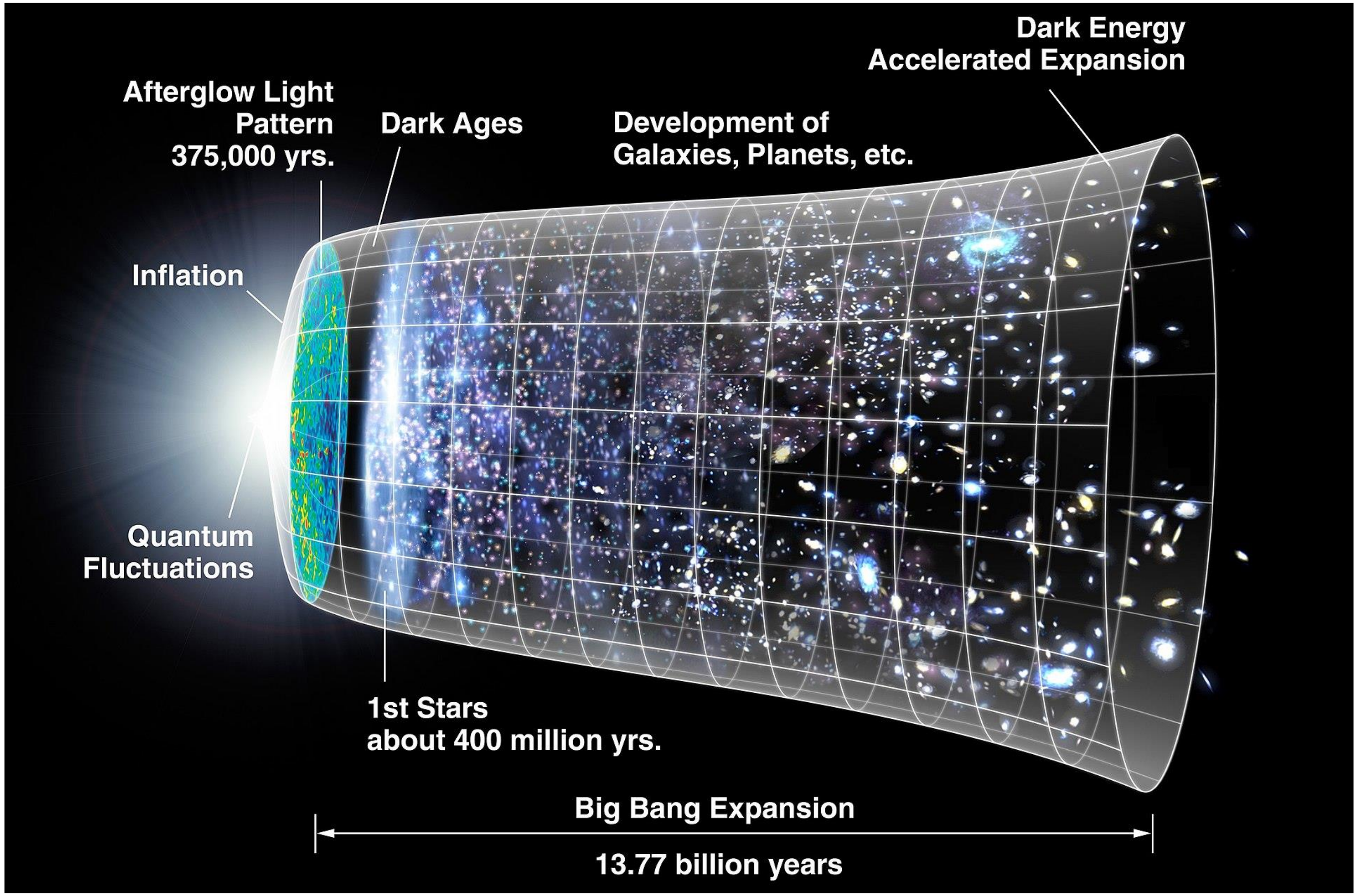
Longitudinal/transverse flexocoupling f_{11}/f_{12} ($f_{11} \sim -f_{12}$)



The flexocoupling in both PTO and STO layers is considered, revealing different modulation effects.

Li et al., Nat. Comm. 2017

- Polarization and tilt behavior at interfaces and topological defects: gradient terms and physical BCs
- Coupling with (electro)chemical boundary conditions
- Defect effects: transition from localized perturbation to collective responses



Wikipedia, NASA

Problems can be intractable combinatorically, but have simple constitutive laws

Low dimensional non-linear manifold in the very high dimensional linear spaces

Observational data: astronomy

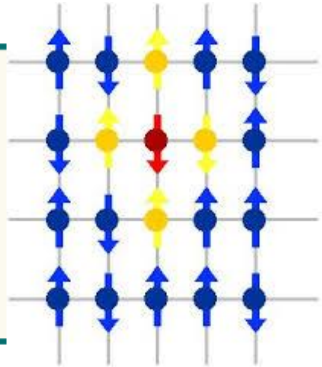
Physics from Microscopic Degrees of Freedom

Macroscopic observables:
- Property
- Average structure
- fluctuations

Macroscopic measurements
Scattering data

Can ML do it?
(Melko 2017)

Microscopic models
- Ising model
- Heisenberg model
- Kitaev model
- ….



Can ML do it?

Real material

A. Sefat

On atomistic scale, we often use lattice Hamiltonian models:

- Can we determine local interactions from STEM or SPM data
- What if some information is lost (1 << observables << degrees of freedom)

2D Ising Model

Ising model represents a system of spins (magnetic dipoles) on a lattice.

Without external magnetic field, the energy reads

$$E = -J \sum_{<ij>} s_i s_j$$

J > 0: ferromagnetic, sum over neighbors only

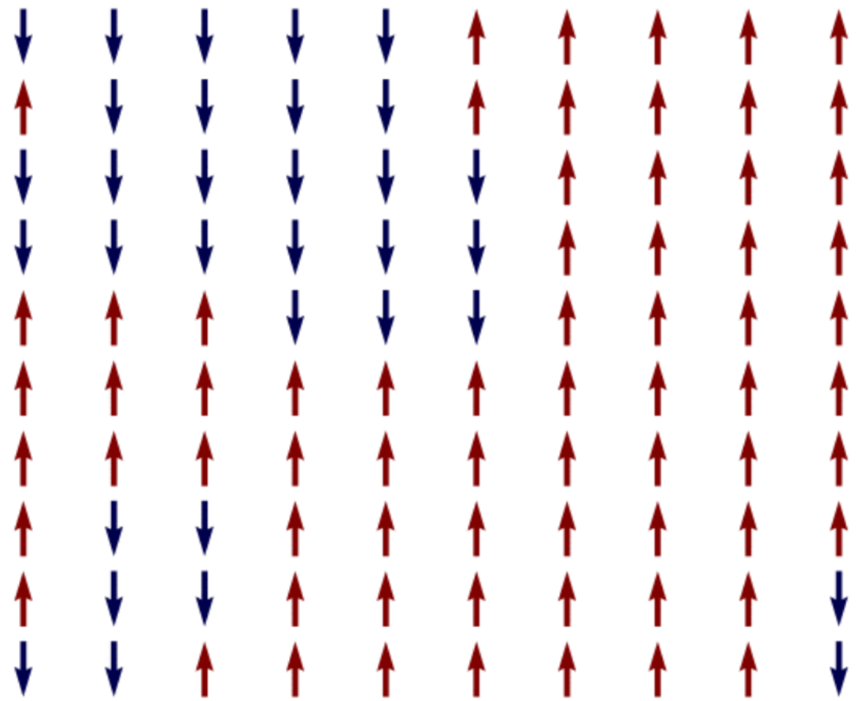
Magnetisation:

$$M = \sum_i s_i$$

Below the Curie temperature

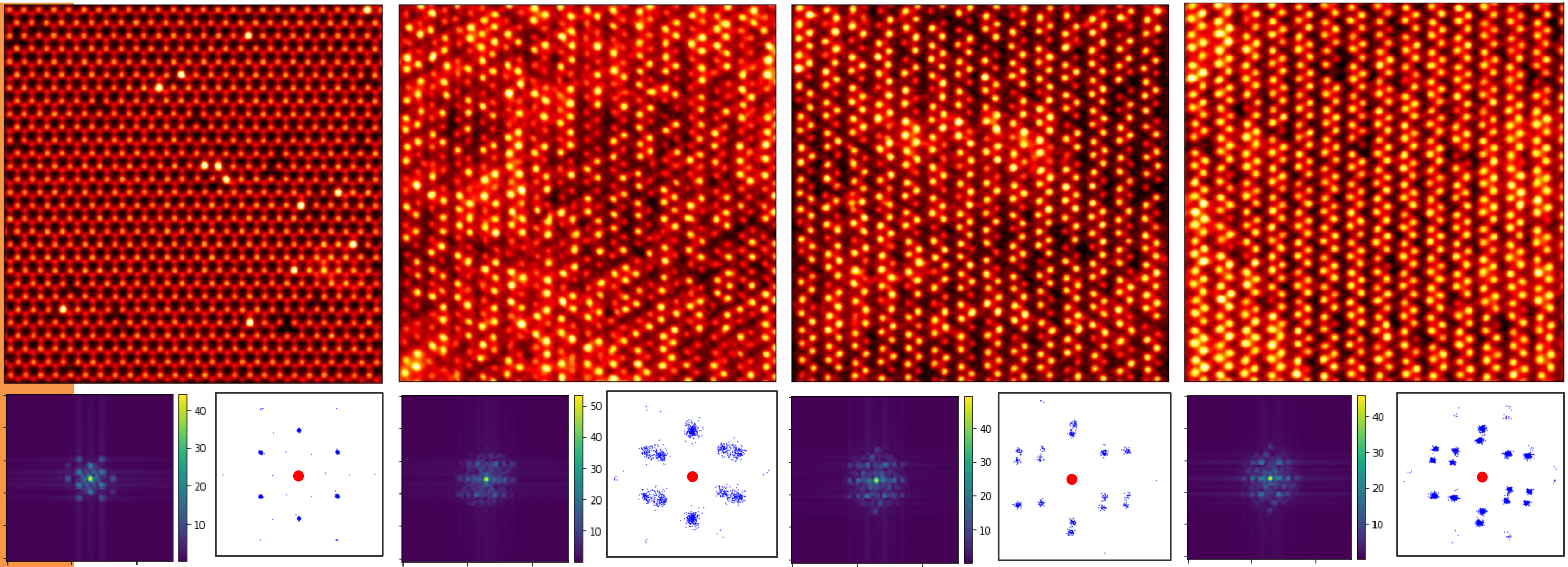
$$\frac{k_B T_C}{J} = \frac{2}{\ln(1+\sqrt{2})}$$

exhibits spontaneous magnetization |M|>0

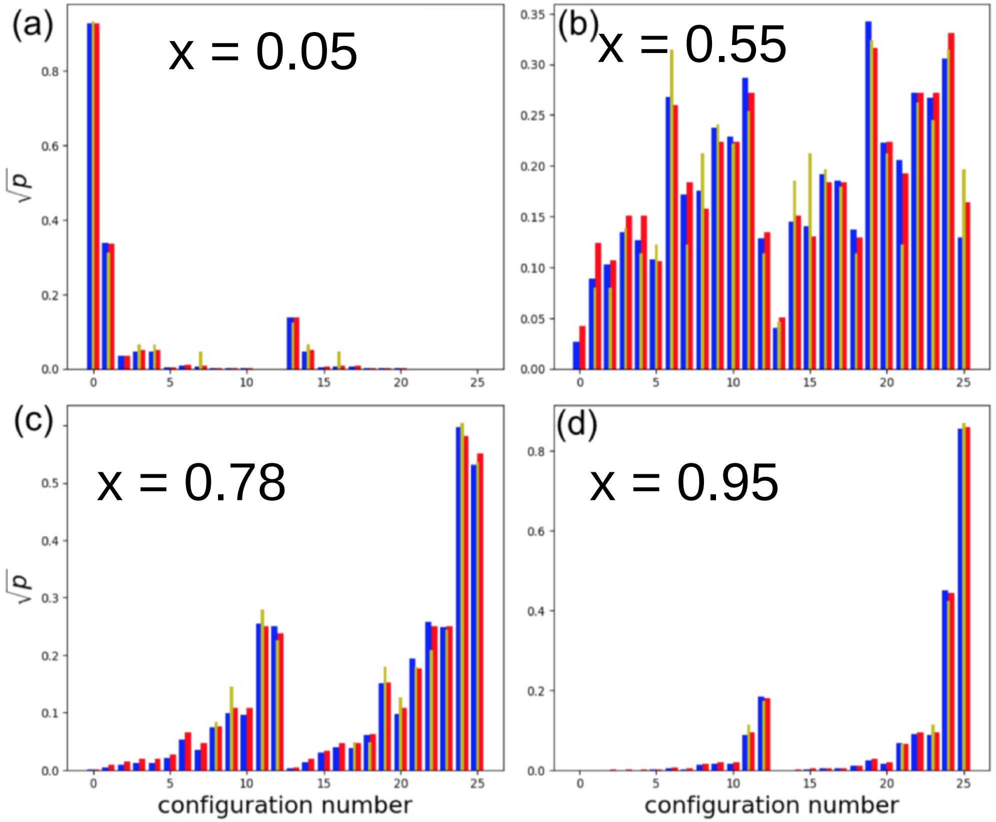


MoS_2 – ReS_2 Solid Solutions

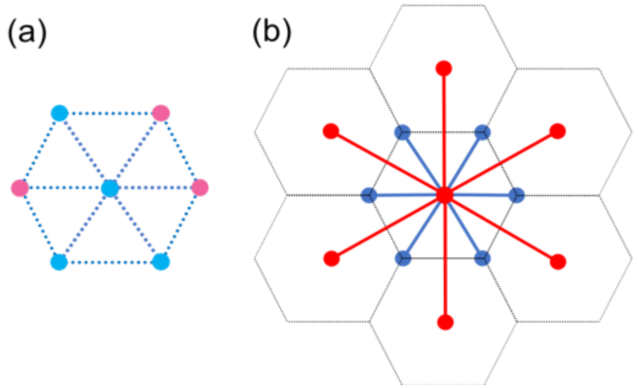
5% ReS_2 | 55% ReS_2 | 78% ReS_2 | 95% ReS_2



Thermodynamics of Solid Solution

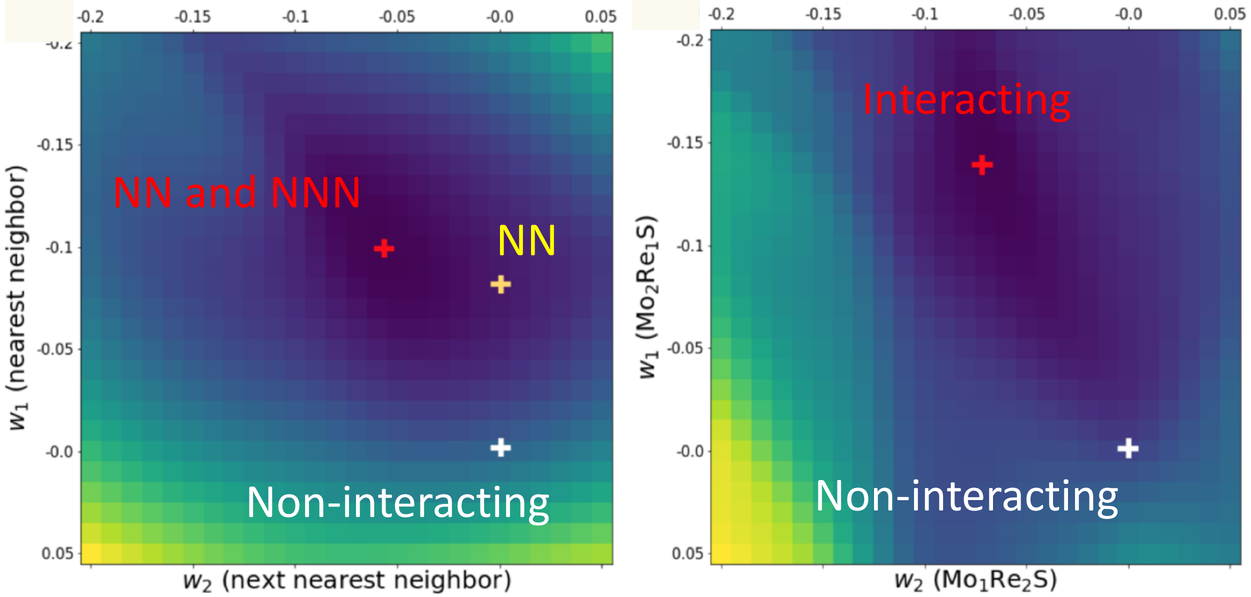


Nearest and next-nearest interactions



Pair Additive

Many Body



1. Pair-additive Model

$$u_i = w_1 \sum_{\{NN\}} \delta_{MoRe} + w_2 \sum_{\{NNN\}} \delta_{MoRe}$$

2. Many-body Model

$$u_i = w_1 \sum_{\{S\}} \delta_{MoMoRe} + w_2 \sum_{\{S\}} \delta_{MoReRe}$$

L. Vlcek, S. Yang, Y. Gong, P. Ajayan, W. Zhou, M. F. Chisholm, M. Ziatdinov, R. K. Vasudevan, S. V. Kalinin, 2019.

Colab