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Sandia National Laboratories

A Phase-field Model of Substrate Anisotropy Effects in BiFeO3 Thin Films

Ben Winchester

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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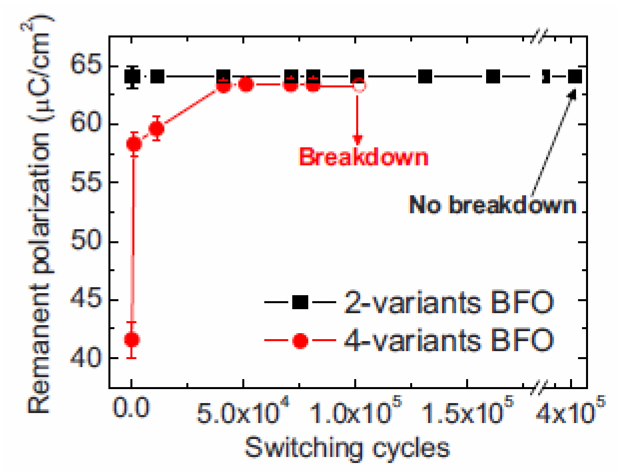
Outline

- Introduction: the importance of ferroelectric domain structures and one way we might control them
- The Approach: a Phase Field model
- Results
- Conclusions & future work

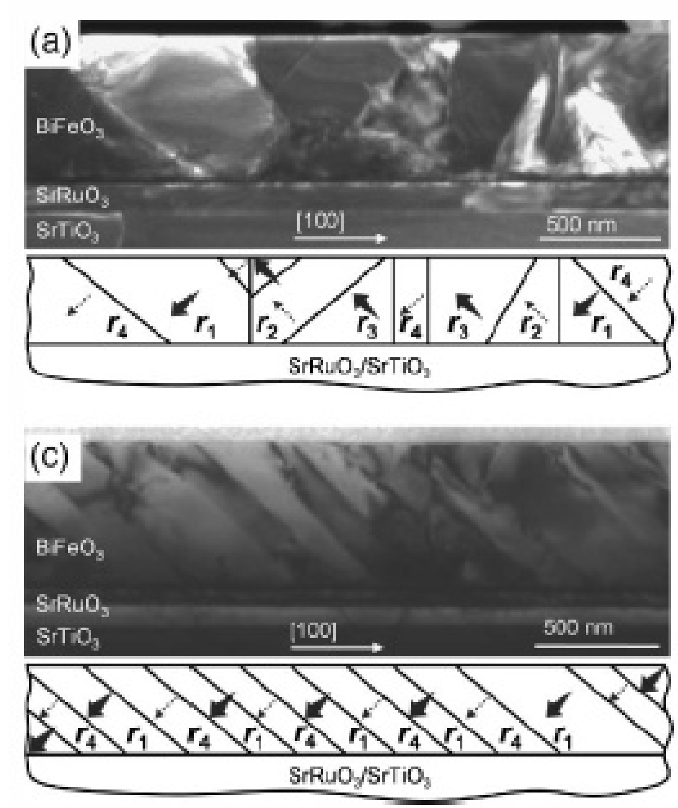
The importance of domain structure

Between bulk and interfacial properties, that's just about everything.



Breakdown behaviors of 2-variant and 4-variant BFO films.

- Two versus four variants in $BiFeO_3$.
- Four-variant film has decreased $P_{r,}$ decreased switching lifetime.

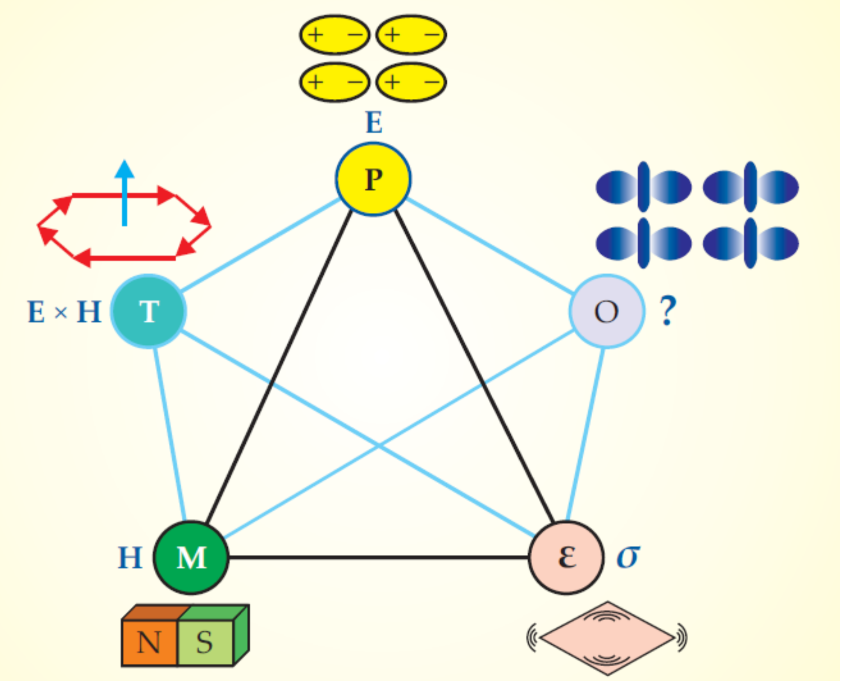


Cross-sectional TEM images of $BiFeO_3$ films 600nm thick on a), exact, and c), miscut $SrTiO_3$.

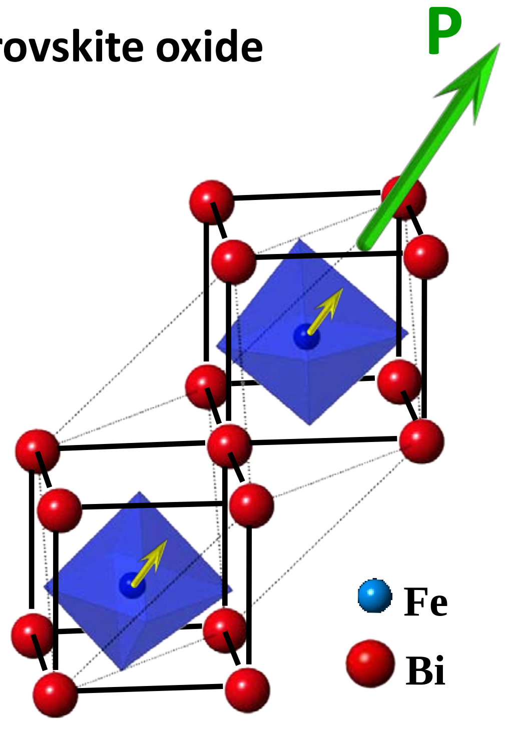
* J.W. Park, et al., *Appl. Phys. Lett*. **97**, 212904 (2010)

Multiferroic $BiFeO_3$

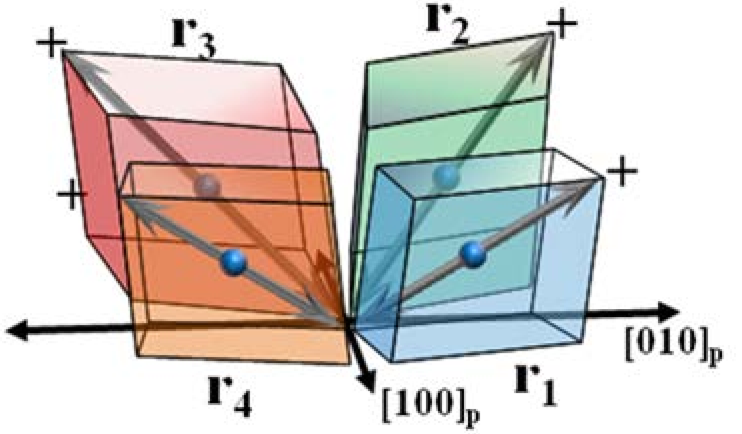
Multiferroicity:



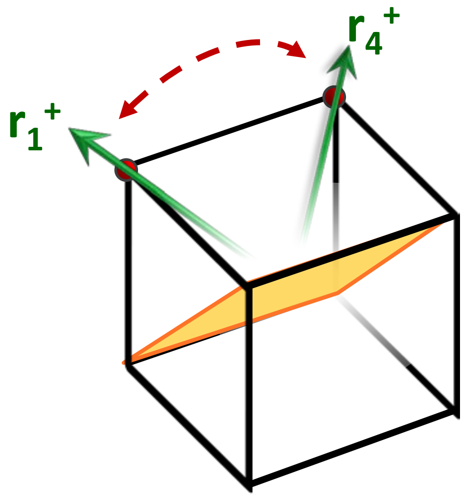
Perovskite oxide

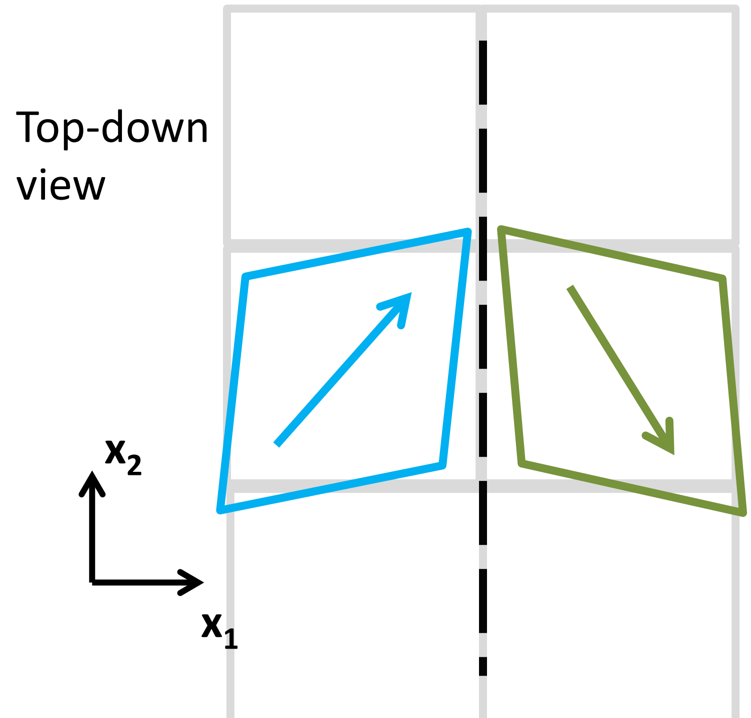


Four ferroelastic variants

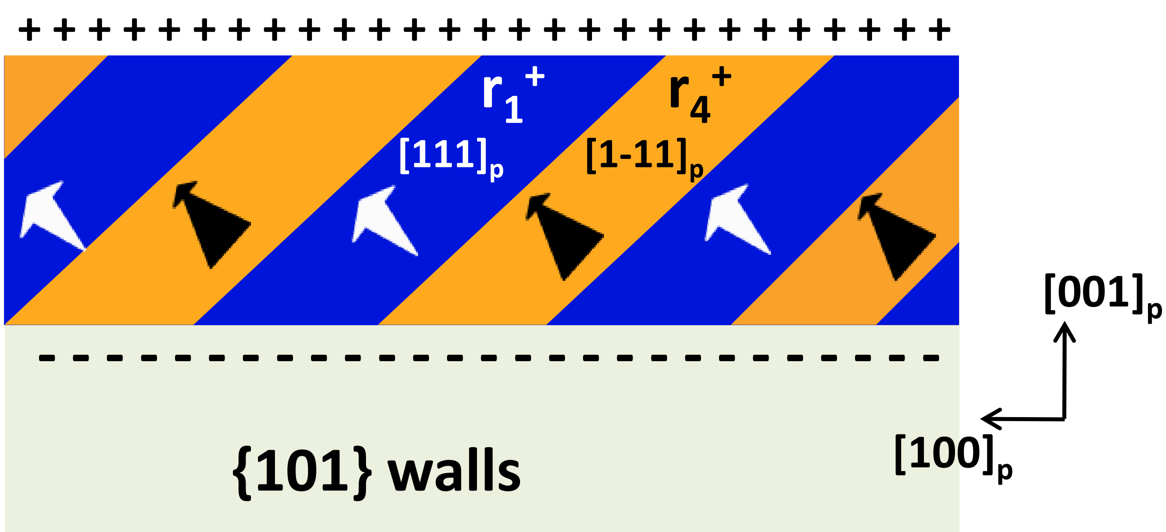


71° Domain Wall

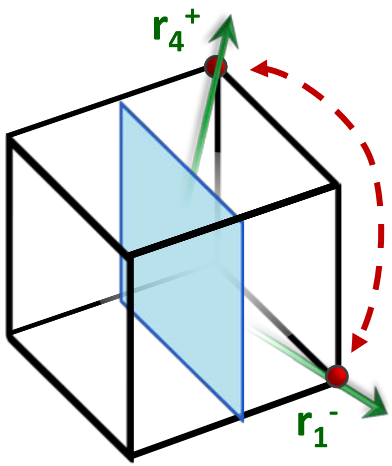


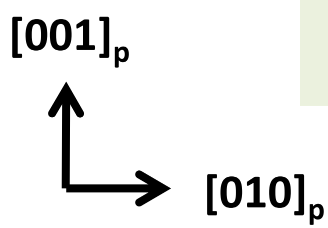


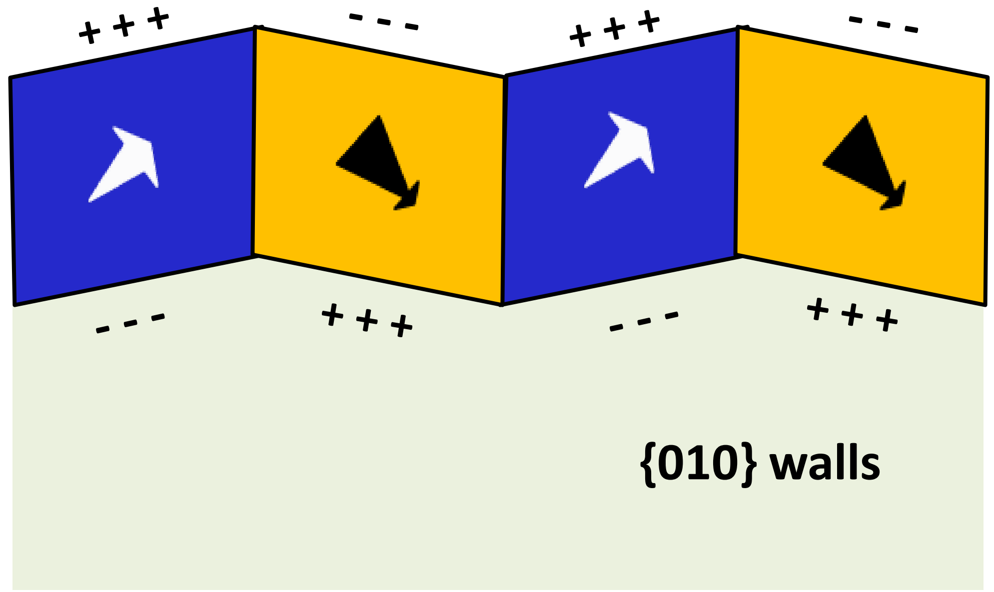
Compensates in-plane stresses, but leaves surfaces charged.



109° Domain Wall



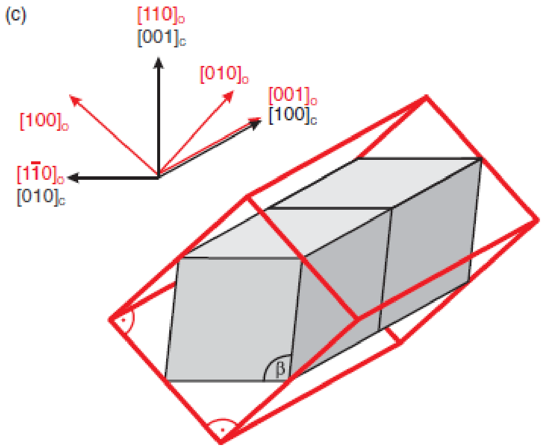




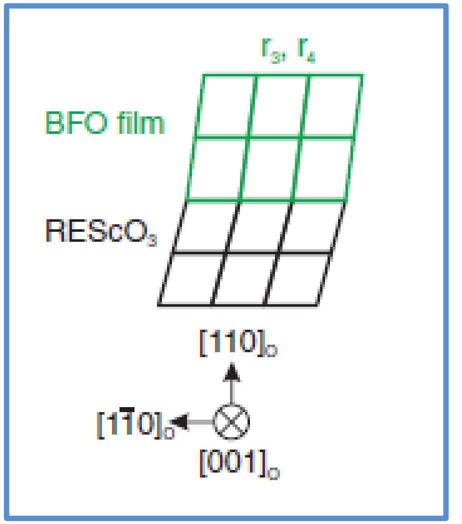
Compensates electrical charge, but creates out-of-plane stresses.

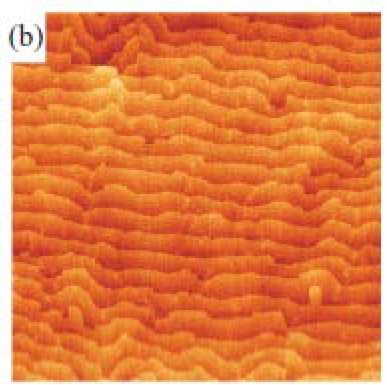
Why do some substrates tend to produce certain variants?

Orthorhombic rare-earth scandates (TbScO3, $DyScO_3$, $GdScO_3$, etc.)

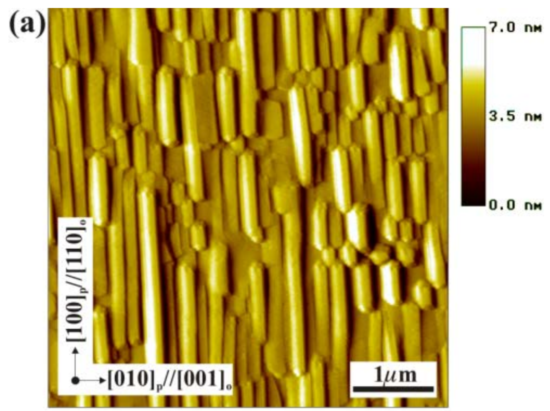


Interfacial effect, or…



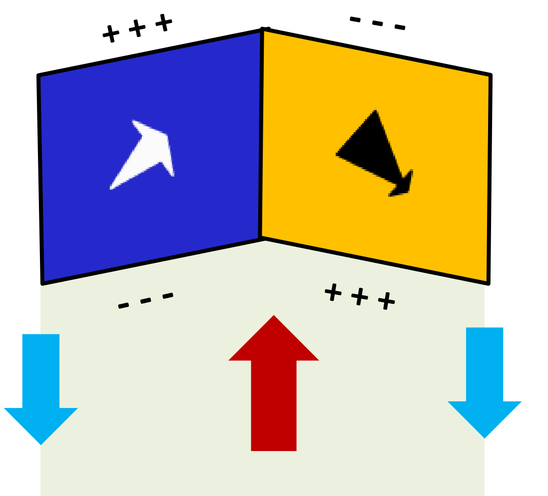


AFM image of BiFeO3 on DyScO3



AFM images of 109° walls on $TbScO_3$

Substrate anisotropy?



[1] F. Johann *et al.*, Phys. Rev. B **84**, 094105 (2011)
[2] C. M. Folkman *et al.*, Appl. Phys. Lett **94**, 251911 (2009)

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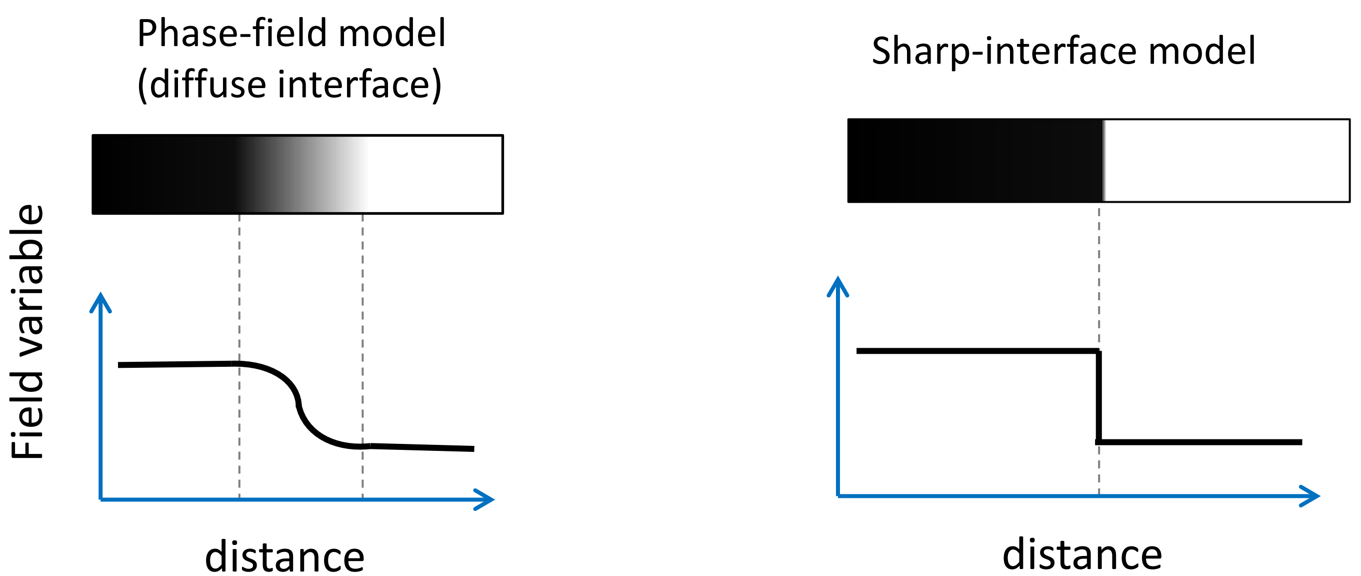
About the phase-field method

- A meso/continuum-scale method based on thermodynamics
- Uses phenomenological data from experiments and other models.
- Takes some macro "order parameter" that varies in space (superconductivity, magnetism, etc.) and solves its evolution by a variational method.
- We treat the parameter as a continuous variable.



The Ginzburg-Landau model

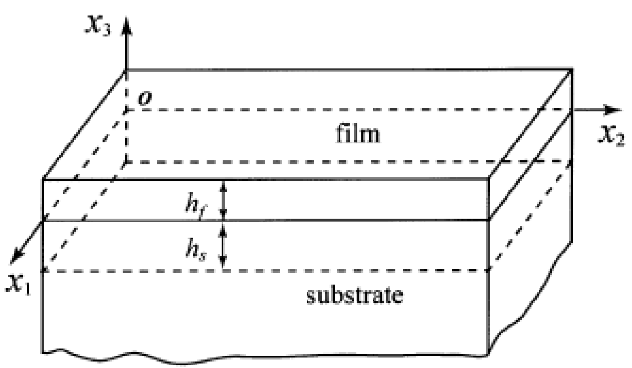
$$F = \int_V \left(f_{Landau} + f_{elastic} + f_{gradient} + f_{electric}\right) dV$$

Time-dependent Ginzburg-Landau equation:

$$\frac{\partial P_i(x)}{\partial t} = -L \frac{\delta F}{\delta P_i(x)}$$

Gradient energy

$$f_{gradient} = \frac{1}{2} g_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}$$



Landau (bulk) energy

$$\begin{aligned} f_{Landau} = {} & \alpha_1\left(P_1{}^2 + P_2{}^2 + P_3{}^2\right) \\ & + \alpha_{11}\left(P_1{}^4 + P_2{}^4 + P_3{}^4\right) \\ & + \alpha_{12}\left(P_1{}^2 P_2{}^2 + P_2{}^2 P_3{}^2 \right. \\ & \left. + P_3{}^2 P_1{}^2\right) + \cdots \end{aligned}$$

Electric energy

$$f_{electric} = -E_i \left(\frac{1}{2} \epsilon_r \epsilon_0 E_i + P_i\right)$$

Elastic energy

$$\begin{aligned} f_{elastic} &= \frac{1}{2} c_{ijkl} e_{ij} e_{kl} \\ &= \frac{1}{2} c_{ijkl} \left[\varepsilon_{ij} - \varepsilon_{ij}{}^0\right] \left[\varepsilon_{kl} - \varepsilon_{kl}{}^0\right] \end{aligned}$$

Coupling term (eigenstrain):

$$\varepsilon_{ij}{}^0 = Q_{ijkl} P_k P_l$$

Microstructural evolution with adaptive meshing

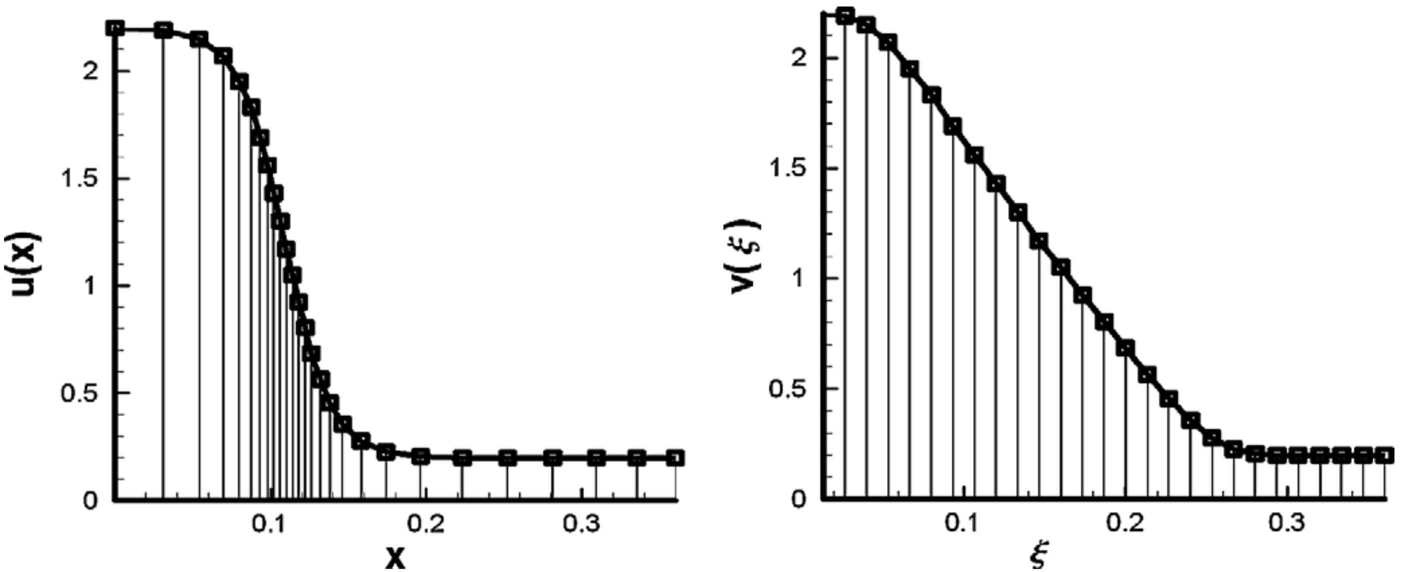
Mesh moves to where the monitor function ω is highest.

Variational eq'n

$$I[\xi] = \int \sum_{i=1}^{3} \frac{\nabla_x \xi^i \cdot \nabla_x \xi^i}{\omega} dx$$

Monitor function

$$\omega \cong \sqrt{1 + \beta^2 |\nabla_x u|^2}$$



Physical domain (left) and computational domain (right)[1].

[1] W.M. Feng *et al.*, J. Comp. Phys. **220** (2006) 498-510

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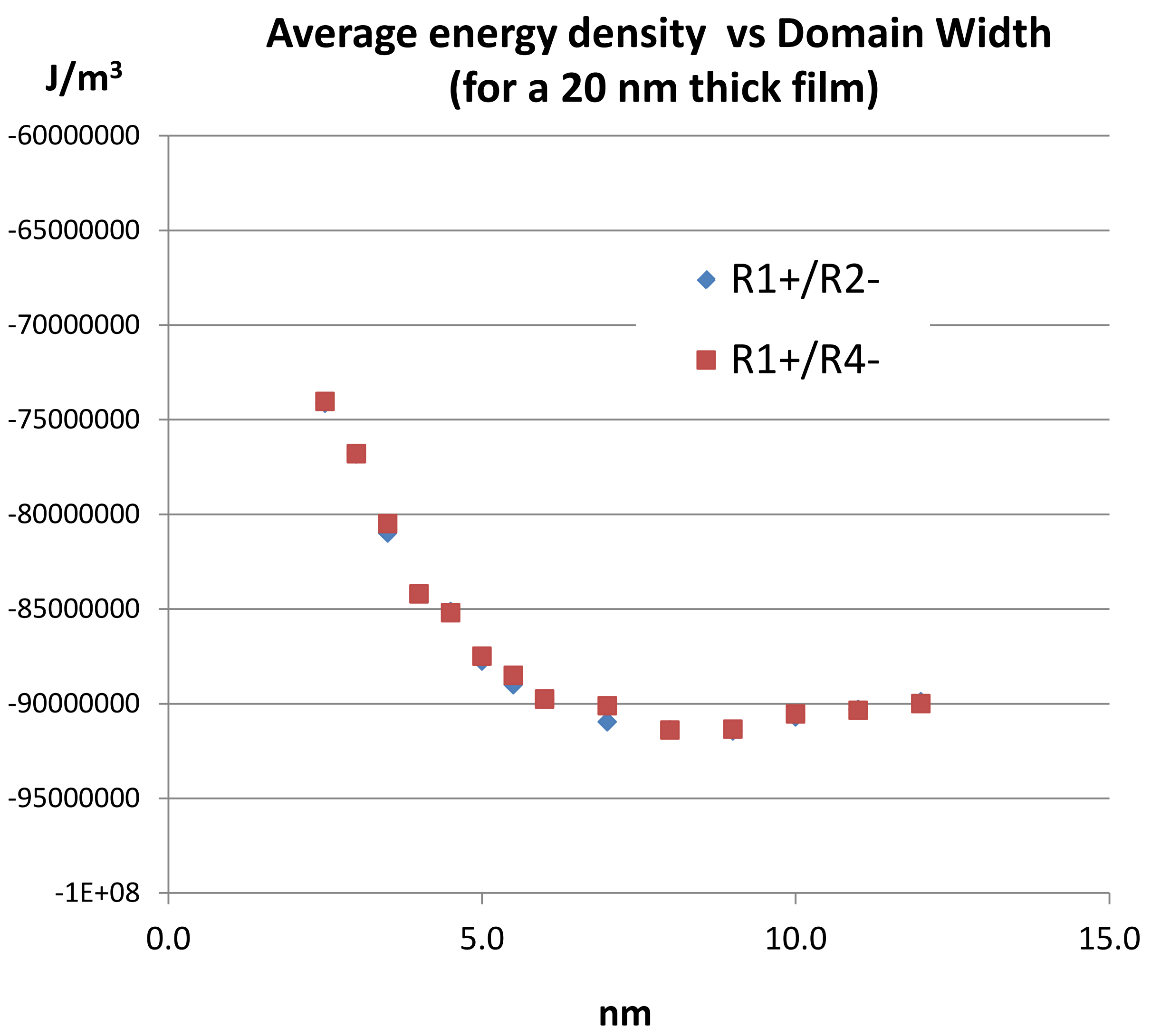
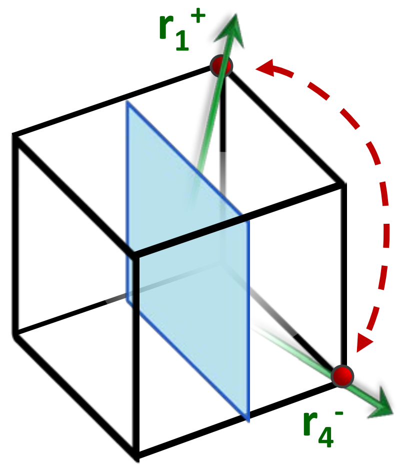
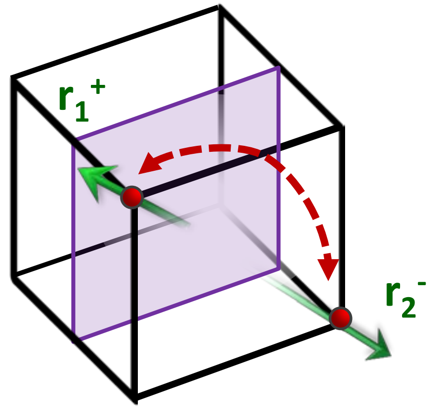
Examining domain orientation's affect on energy:

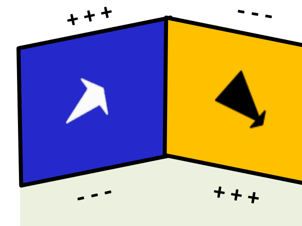




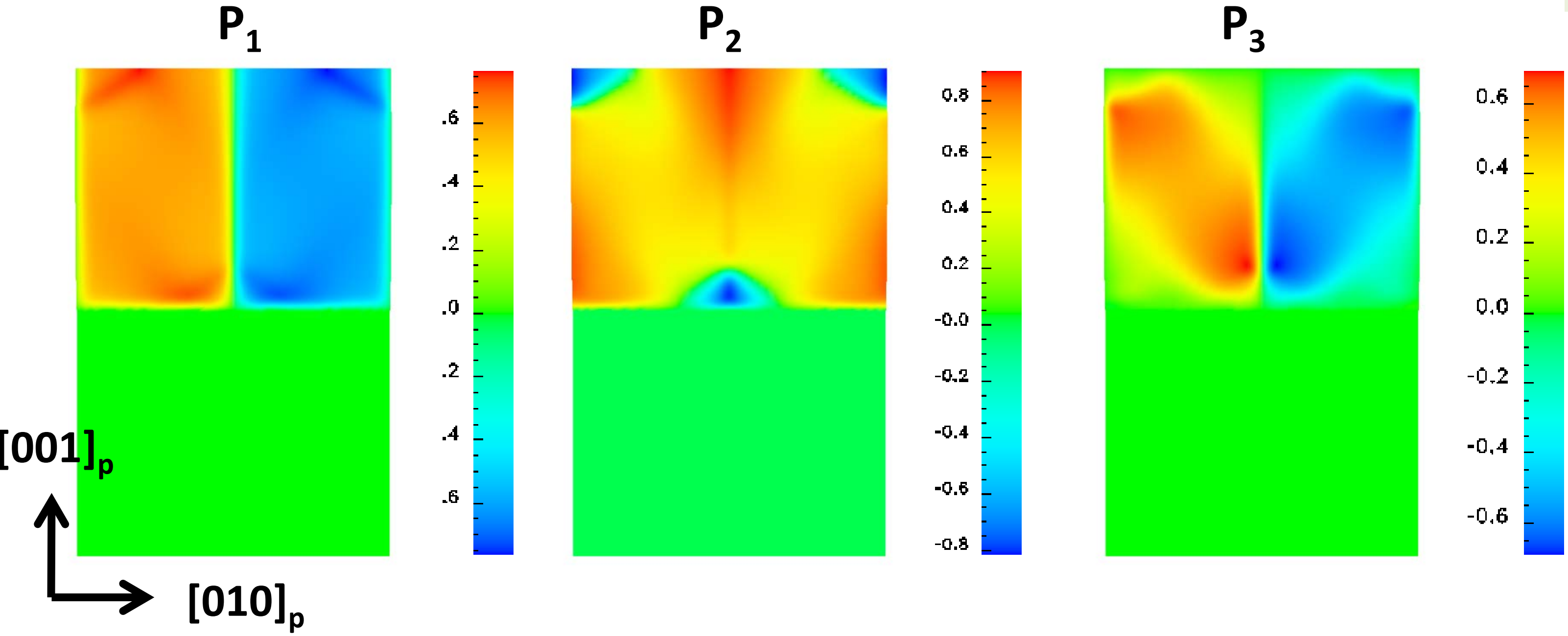


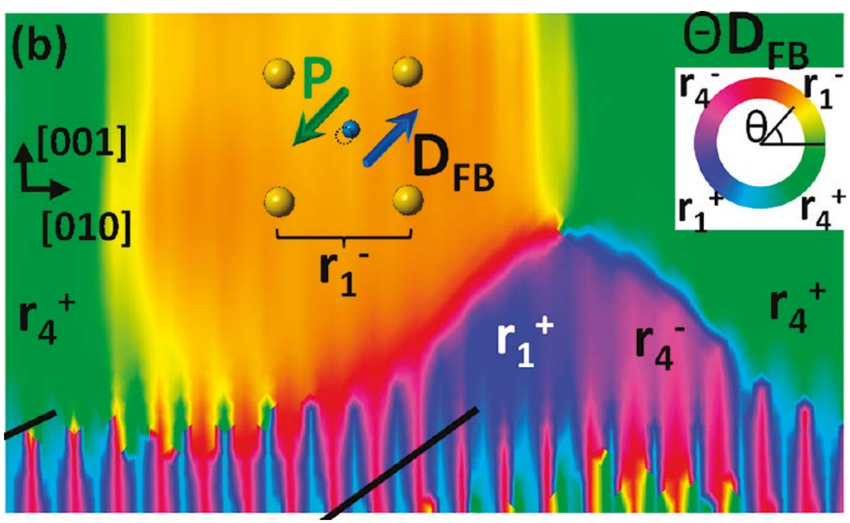
Conclusion: very little energy difference between the two orientations. Why is that?

What's going on? A look at some plots.



Polarization components ($\mu C/m^2$):

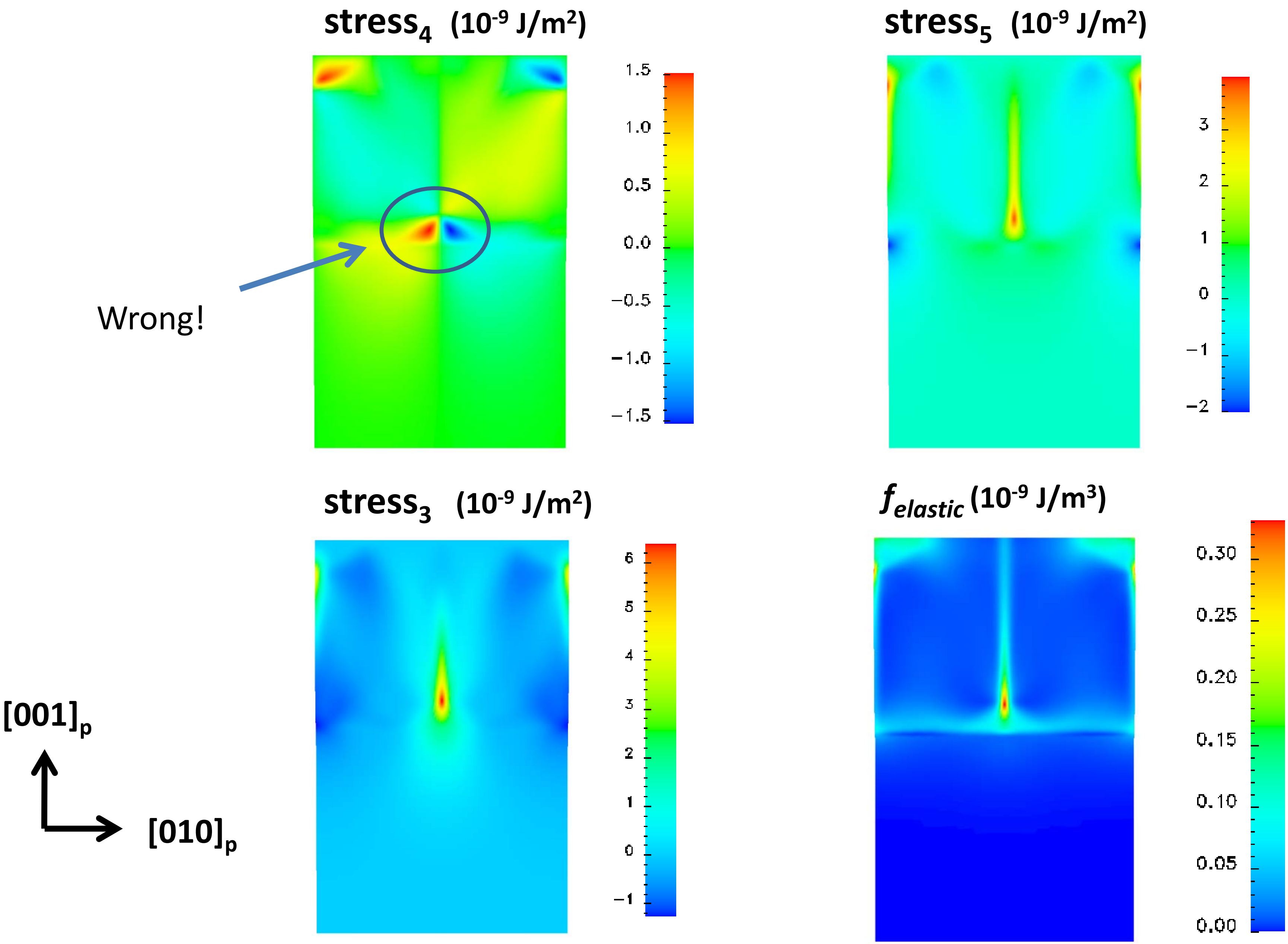




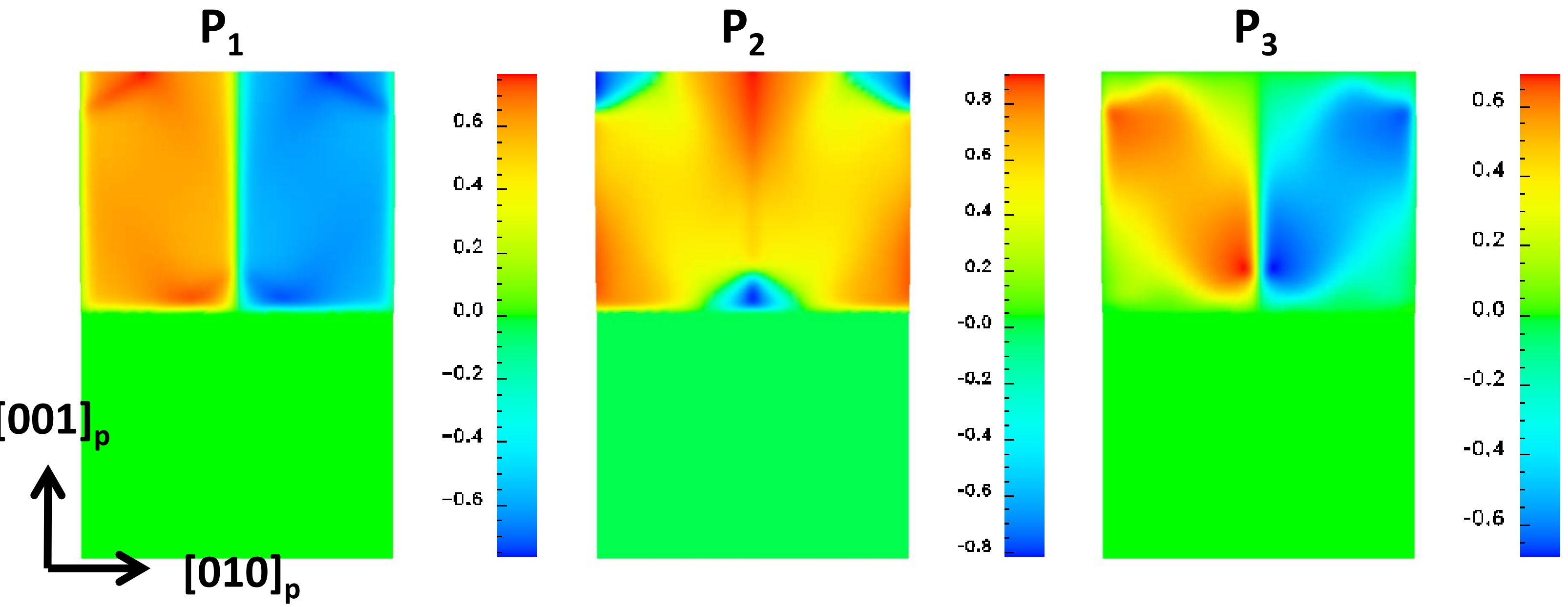
Z-constrast STEM image of two 109° domain walls.

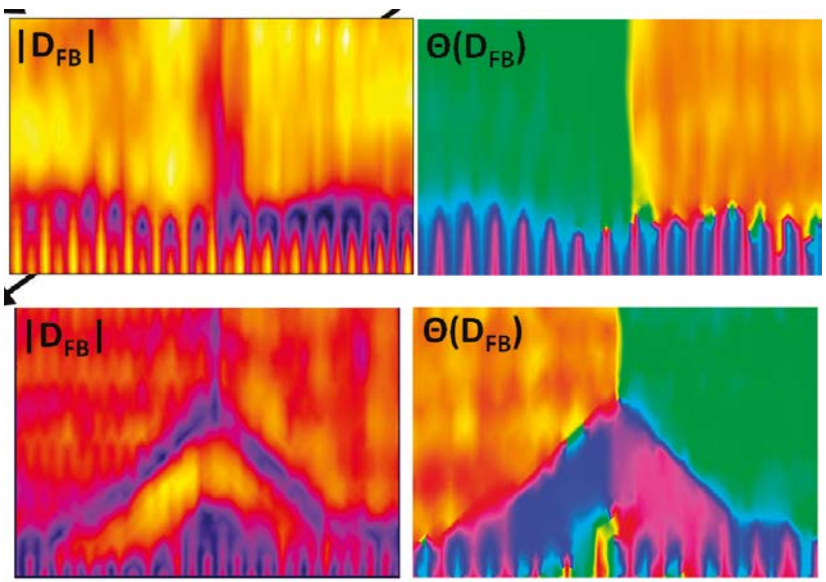
C. T. Nelson *et al.*, Nano Lett. **11**, (2011) 828-834

What's going on? A look at more plots.



Comparing experimental and simulation polarizations in more depth.





Z-constrast STEM image of the two different 109° domain walls, showing magnitude, $|D_{FB}|$, and angle, $\theta(D_{FB})$, of ferroelectric ion displacement.

Note the difference in domain wall sharpness between experiment and simulation.

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

Conclusions

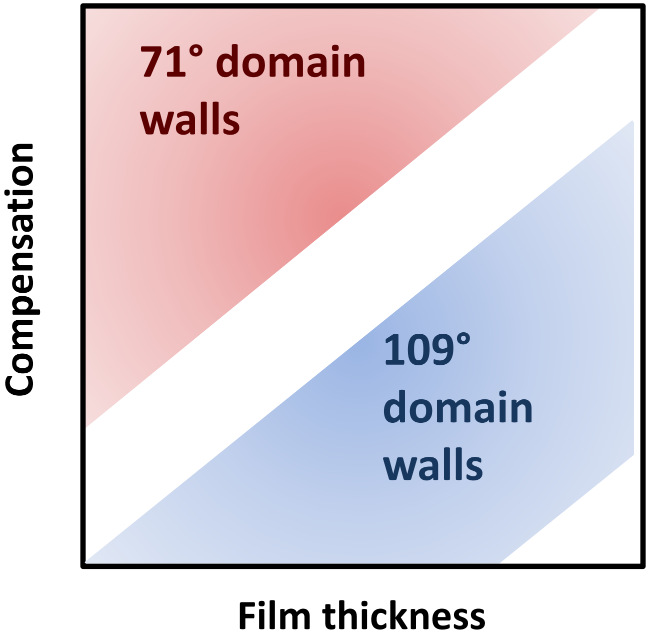
- We developed an adaptive mesh phase-field model to look at the effects of substrate anisotropy on domain structure.
- The results did *not* indicate that the substrate anisotropy is responsible for the preferential selection of two ferroelastic variants in these films.
- However, the results leave questions as to why.

Future Work

- Continue to examine potential discrepancies between simulation and experiment.

- Comparison of energetics, for film thickness vs electrical compensation. Where are the different domain structures favored?

(Hypothetical) Electrical Surface Compensation vs. Film Thickness



Acknowledgements

Sandia National Laboratories

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Elastic anisotropy

Typical elastic stiffness tensor for these rare-earth scandates

(in *Pbnm* notation)

300	130	130	0	0	0
130	300	130	0	0	0
130	130	250	0	0	0
0	0	0	115	0	0
0	0	0	0	90	0
0	0	0	0	0	80

(convert to pseudo-cubic lattice)

(with $[001]_o \parallel [010]_p$)

295.	130.	135.	0.	0.	0.
130.	250.	130.	0.	0.	0.
135.	130.	295.	0.	0.	0.
0.	0.	0.	102.5	0.	12.5
0.	0.	0.	0.	85.	0.
0.	0.	0.	12.5	0.	102.5

(with $[001]_o \parallel [100]_p$)

250.	130.	130.	0.	0.	0.
130.	295.	135.	0.	0.	0.
130.	135.	295.	0.	0.	0.
0.	0.	0.	85.	0.	0.
0.	0.	0.	0.	102.5	12.5
0.	0.	0.	0.	12.5	102.5