The Abdus Salam International Centre for Theoretical Physics

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10 - 12 January 2013

From transition metal oxides to cosmology with electronic structure calculations

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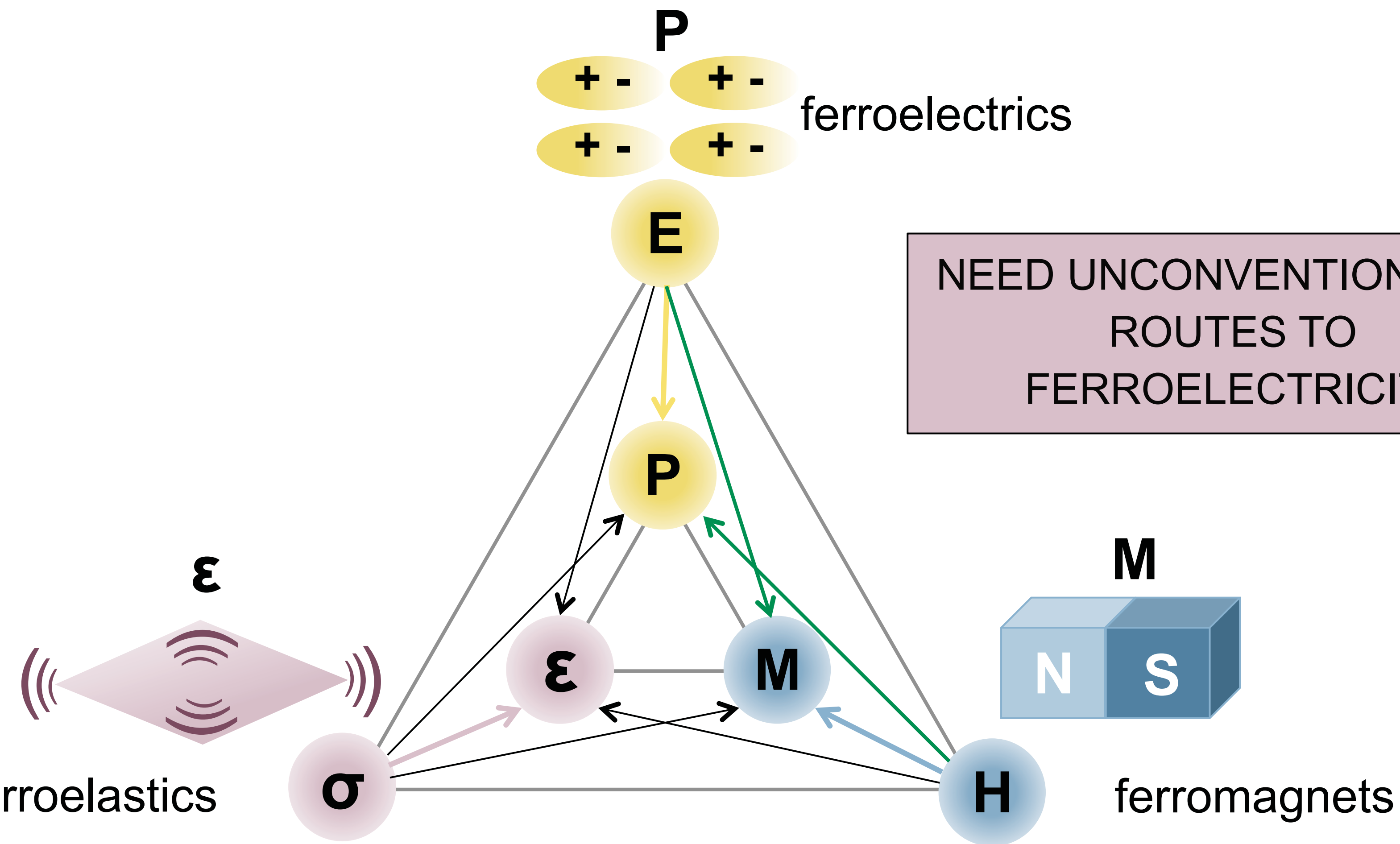
MATERIALS THEORY

From Multiferroics to Cosmology with Electronic Structure calculations

Nicola Spaldin
Materials Theory
Department of Materials, ETH Zürich

Magnetoelectric multiferroics



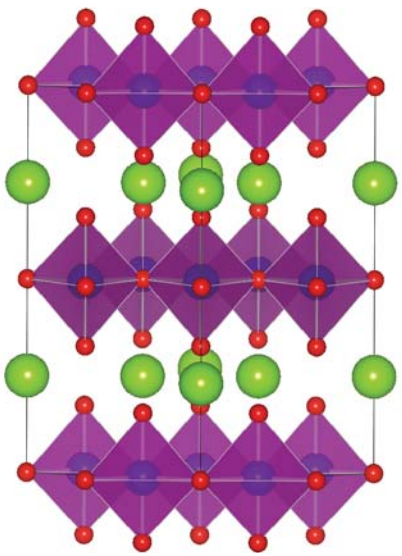
NEED UNCONVENTIONAL ROUTES TO FERROELECTRICITY

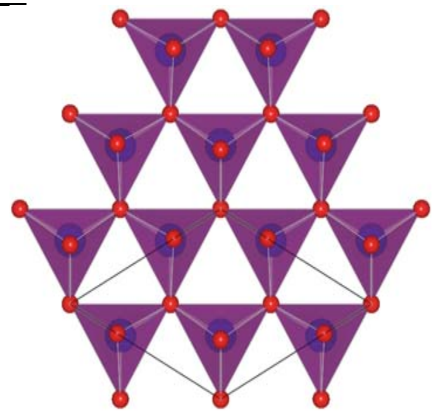
The renaissance of magnetoelectric multiferroics, N.A. Spaldin and M. Fiebig, Science 15, 5733 (2005)
N.A. Hill, *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B 104, 6694 (2000)

An unconventional ferroelectric: $YMnO_3$

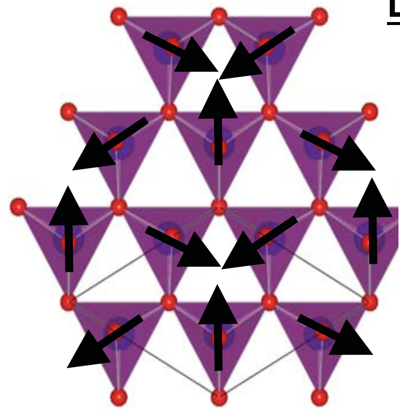
High temperature

P6₃/mmc



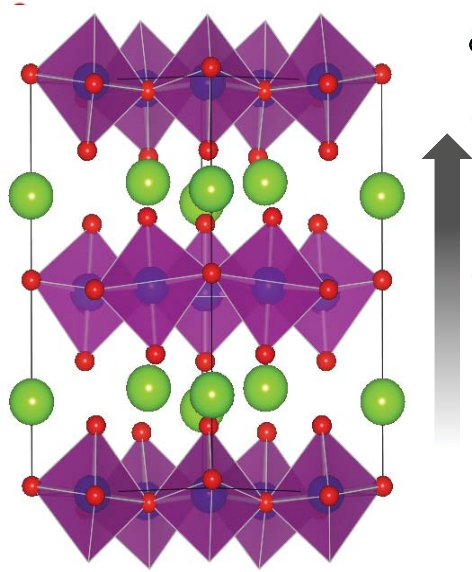


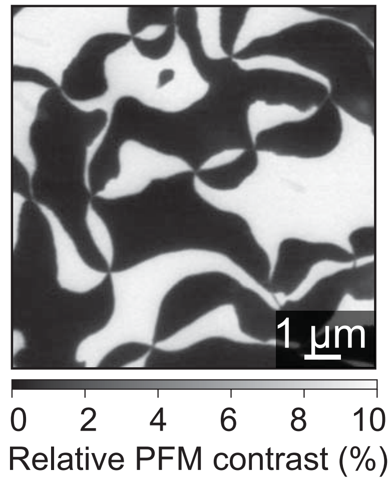
~1000K



Low temperature

P6₃cm





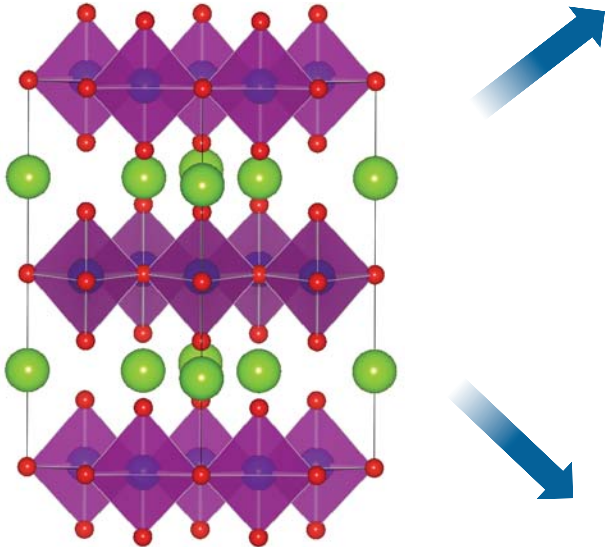
Polarization (5.6 μC/cm²)

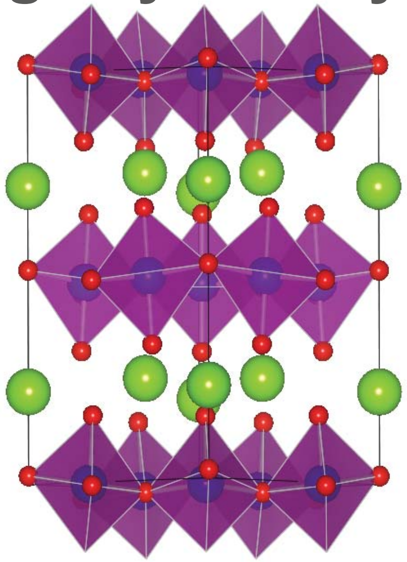
paraelectric

ferroelectric

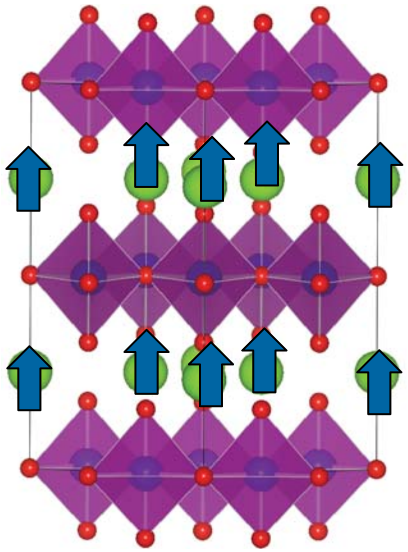
Calculate phonons for high symmetry structure

We find that 2 phonon modes of the high symmetry structure take us to the low symmetry structure





Trimerization (K_3)



Y displacements (Γ_2)

We can then map out the energy surface for these phonons

DFT calculations show us that the ferroelectricity is *improper*:

The trimerization (K3) mode is the energy-lowering primary order parameter

An improper geometric ferroelectric

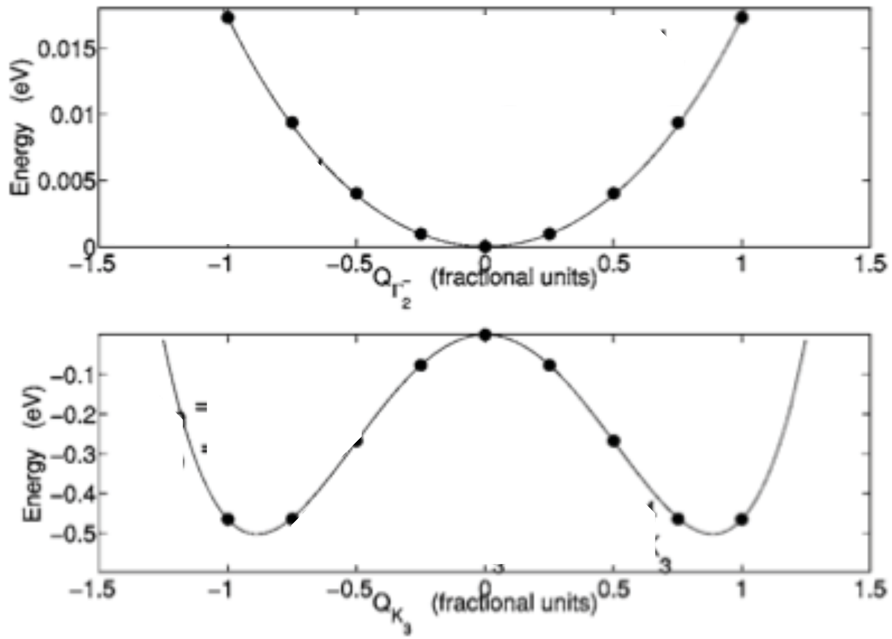
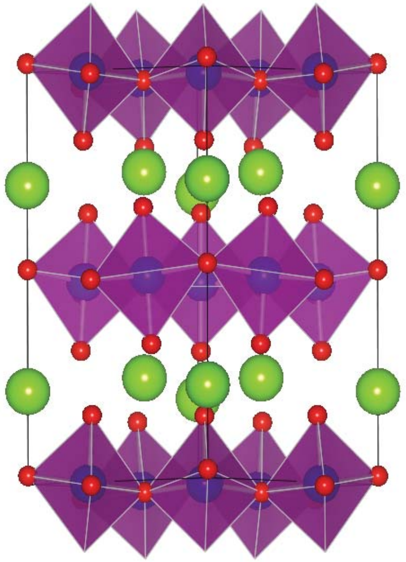
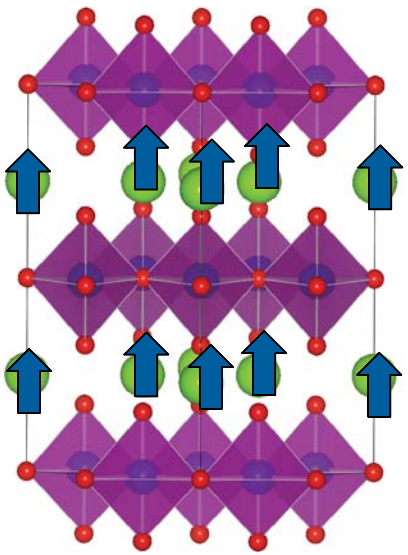


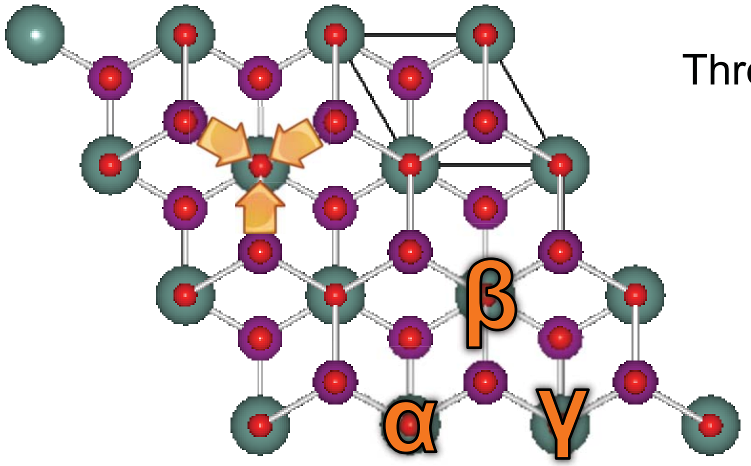
FIG. 2. Energy as a function of (top) $Q_{\Gamma_2^-}$ and (bottom) Q_{K_3}.

B.B. van Aken, T.T.M. Palstra, A. Filippetti and NAS, *The origin of ferroelectricity in magnetoelectric YMnO3,* Nat. Mater. 3, 164(2004)
C.J. Fennie and K.M. Rabe, *Ferroelectric phase transition in YMnO3 from first principles* Phys. Rev. B 72, 100103 (2005)

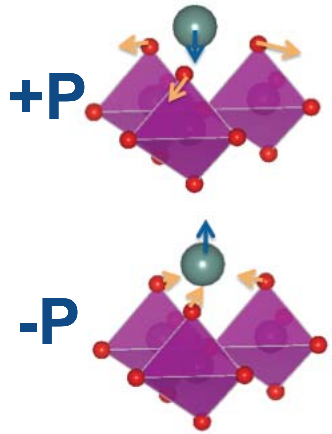
Look at these distortions in more detail:





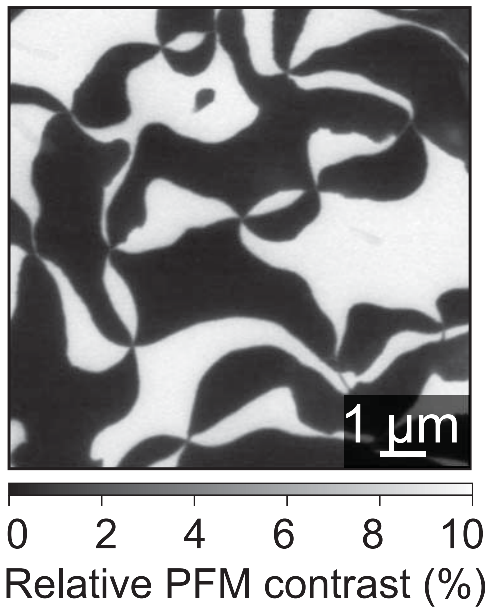


Three possible origins

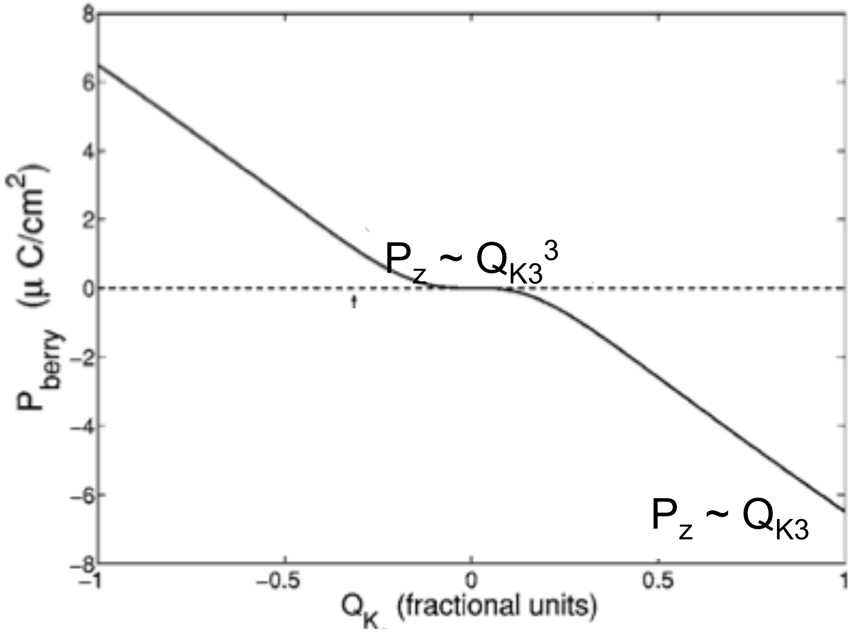


Two possible orientations

Expect six domains!



We can calculate how the polarization depends on the trimerization amplitude:



Near the phase transition the ferro-electric polarization is effectively zero

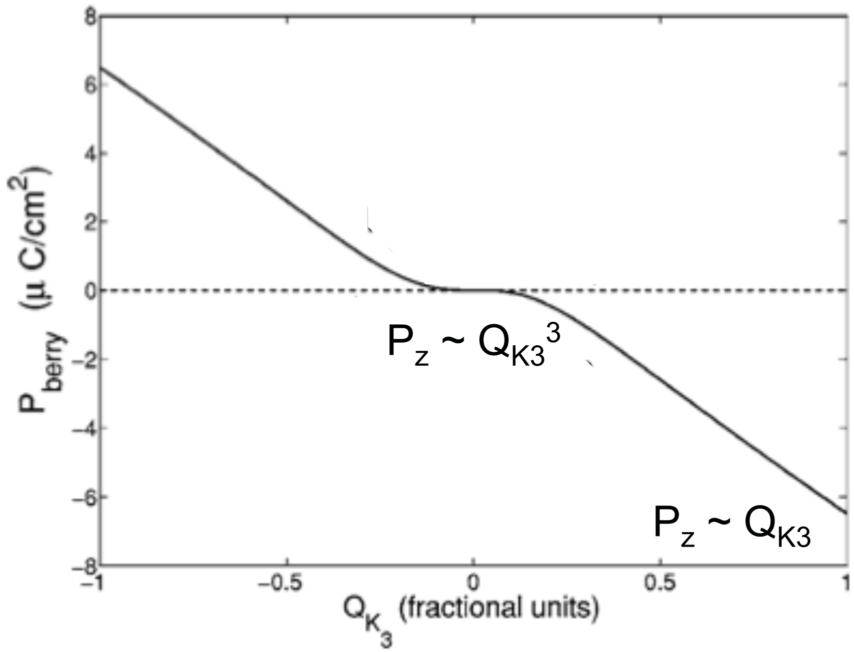
Landau free energy

$$f_{\mathrm{u}} = \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{Q^6}{6}\left(c + c' \cos 6\Phi\right) - gQ^3 P_z \cos 3\Phi + \frac{g'}{2}Q^2 P_z^2 + \frac{P_z^2}{2\chi_0}$$

S. Artyukhin, K.T. Delaney, NAS and M. Mostovoy, *Landau theory of topological defects in multiferroic hexagonal manganites*, arXiv:1204.4126

C.J. Fennie and K.M. Rabe, *Ferroelectric phase transition in YMnO3 from first principles* Phys. Rev. B 72, 100103 (2005)

Consequences of "zero" polarization at small trimerization amplitude:



1) Domain formation at the transition is not dominated by minimization of the depolarizing field

2) Effective continuous symmetry at the phase transition

Combine to allow application of $YMnO_3$ to cosmological problems

S. Artyukhin, K.T. Delaney, NAS and M. Mostovoy, *Landau theory of topological defects in multiferroic hexagonal manganites*, arXiv:1204.4126

C.J. Fennie and K.M. Rabe, *Ferroelectric phase transition in YMnO3 from first principles* Phys. Rev. B 72, 100103 (2005)

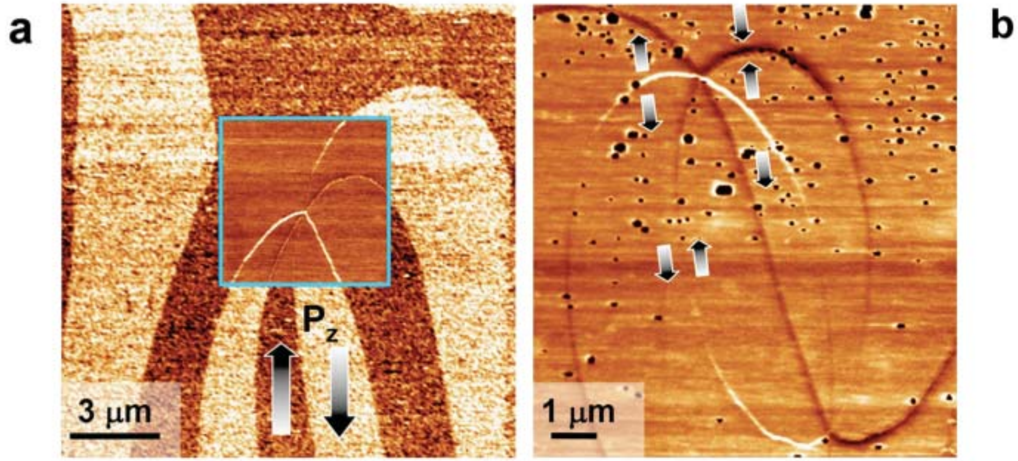
Outline

Analogy between the structural phase transition in $YMnO_3$ and the Grand Unification Transition

Show that the symmetry of the phase transition in $YMnO_3$ results in one-dimensional “topologically protected” defects (Kibble)

Test whether the formation of these defects follows the so-called “Kibble-Zurek” scaling (number of defects as a function of cooling rate) proposed for such a transition

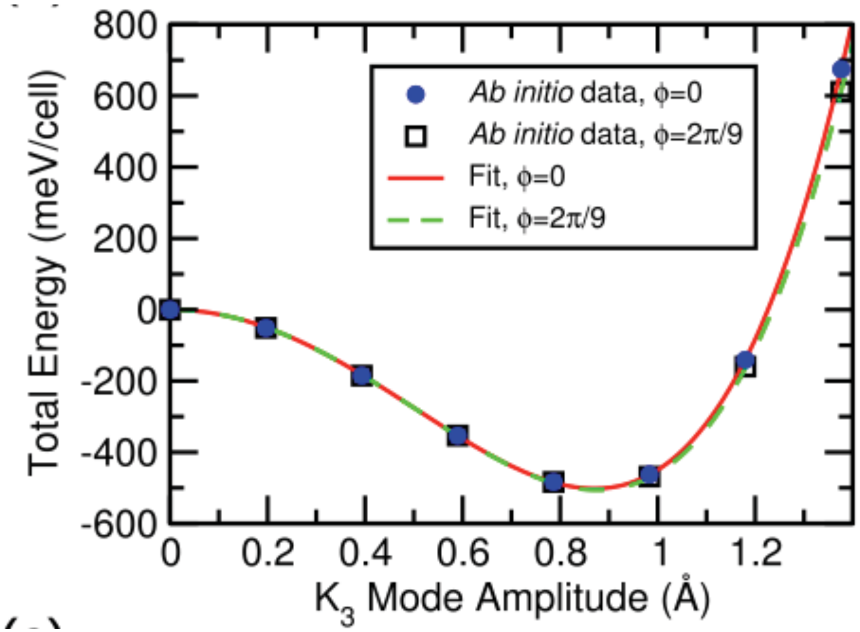
Ferroelectric polarization does not determine domain structure:
Formation of head-to-head and tail-to-tail domain walls



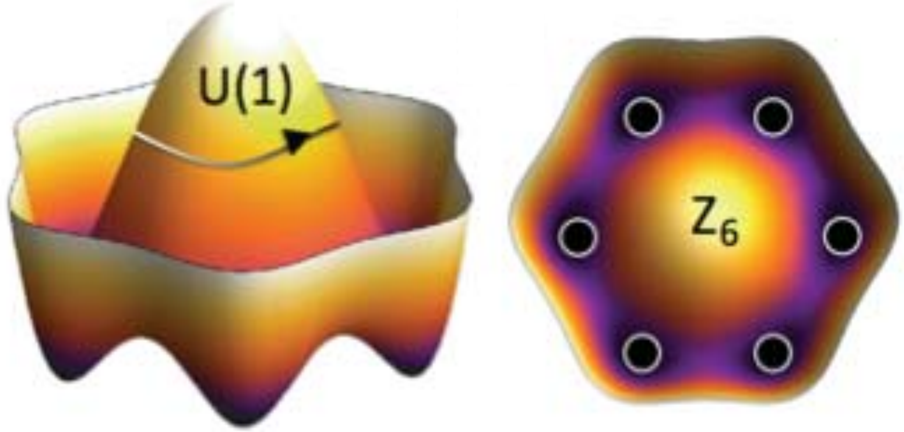
D. Meier, Yu Kumagai, R. Ramesh, NAS et al., *Ferroelectric domain walls as functional oxide interfaces,* Nat. Mater. 11, 284 (2012)

Effective continuous symmetry at the phase transition:

When P=0, the energy is (surprisingly) independent of the trimerization angle:



And the potential is a Mexican hat with a smooth peak and six minima in the brim:



S. Artyukhin, K.T. Delaney, NAS and M. Mostovoy, *Landau theory of topological defects in multiferroic hexagonal manganites*, arXIv:1204.4126

Early universe processes

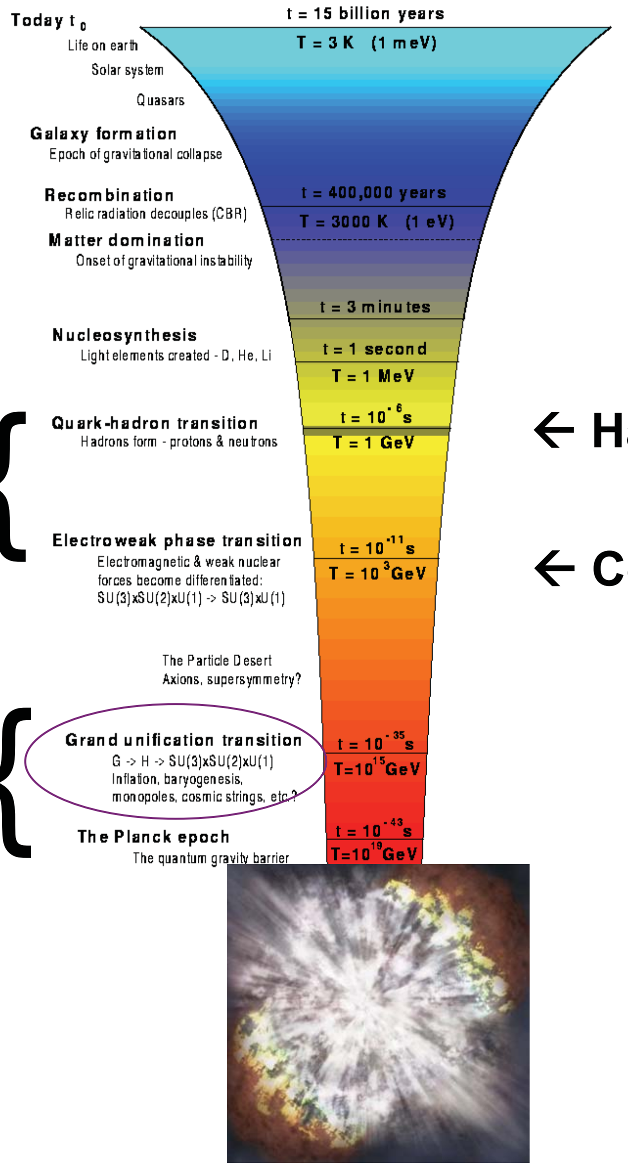
Today

Time

Very long time ago

Very expensive

Inaccessible?



← Hadron Colliders

← Cosmic Microwave Background

Low

Temperature

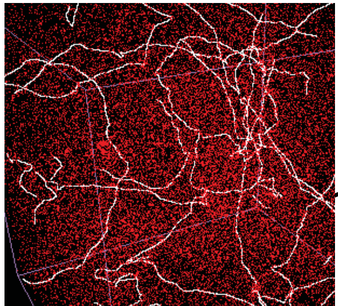
High

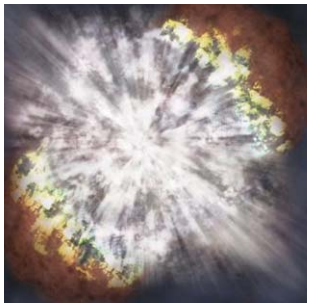
Analogy between $YMnO_3$ and the physics proposed for the GUT?

spontaneous symmetry breaking described by a non-trivial homotopy group

Results in formation of *topological defects* (Kibble)

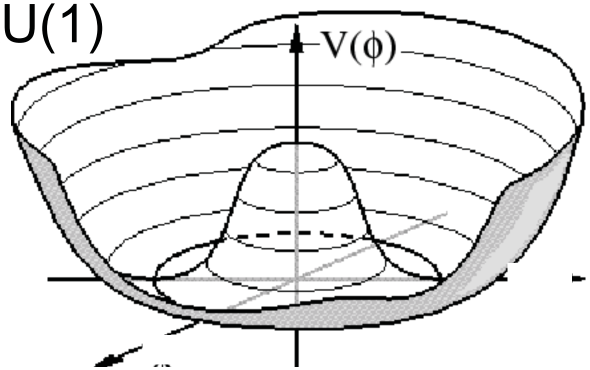
Universe





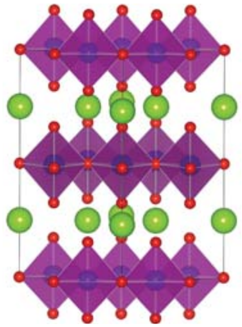
SU(3)xSU(2)xU(1)

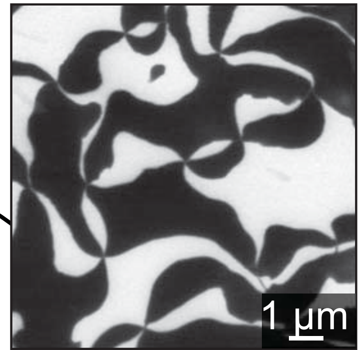
The Particle Desert



$YMnO_3$

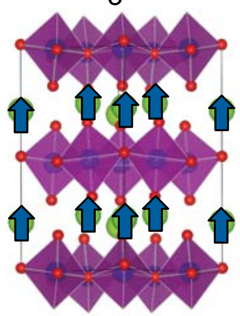
P6_3*/mmc*



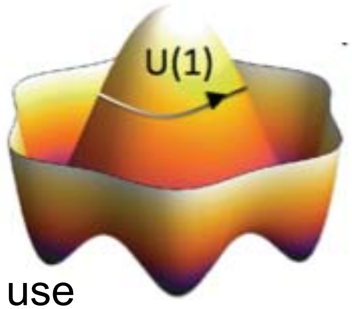


U(1)

P6_3*cm*



We can show formally that the $YMnO_3$ phase transition produces one-dimensional topological defects:

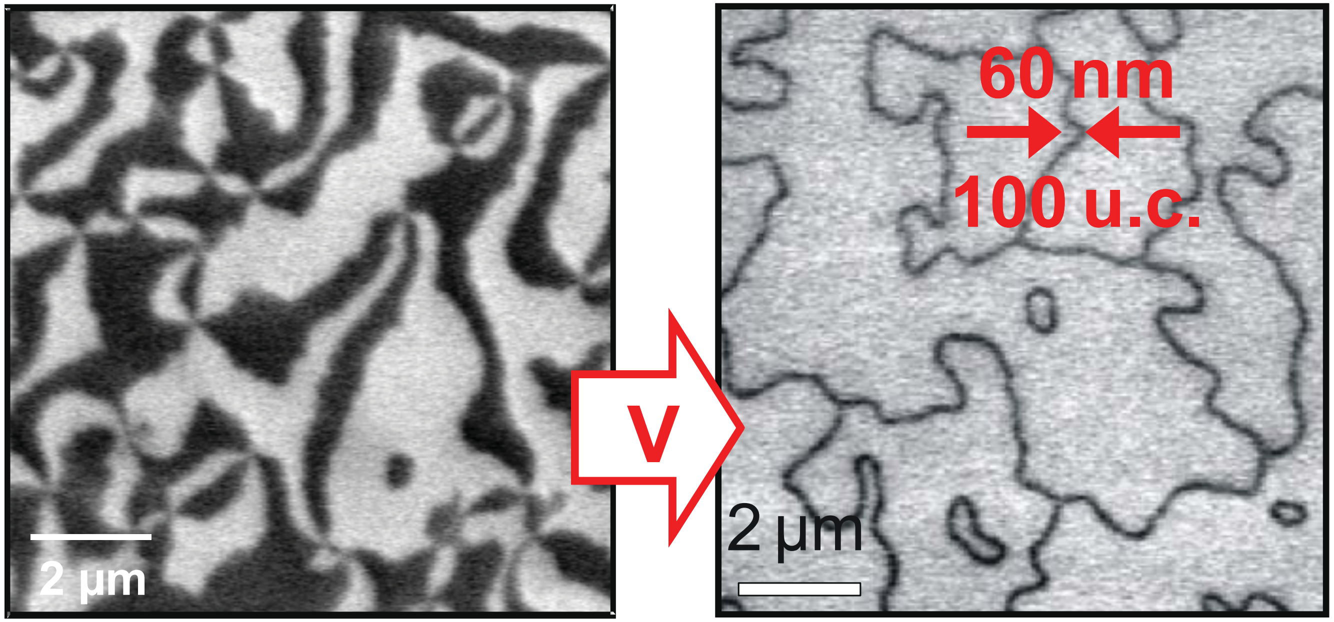


Since the symmetry near the phase transition is effectively continuous, we can use established results of homotopy theory to assess the topology of transition:

1) Map the symmetry characteristic of the order parameter – U(1) – onto an n-dimensional sphere: one-dimensional circle S^1
2) Look up in a topology textbook whether the homotopy group π of S^1 is non-trivial or not
3) In fact $\pi_1(S^1)$ is non-trivial and produces 1-dimensional topologically protected singularities!

The domain intersections in YMnO3 are formally mathematically topologically protected

"Protected" domain structure can't be poled:



Early universe processes

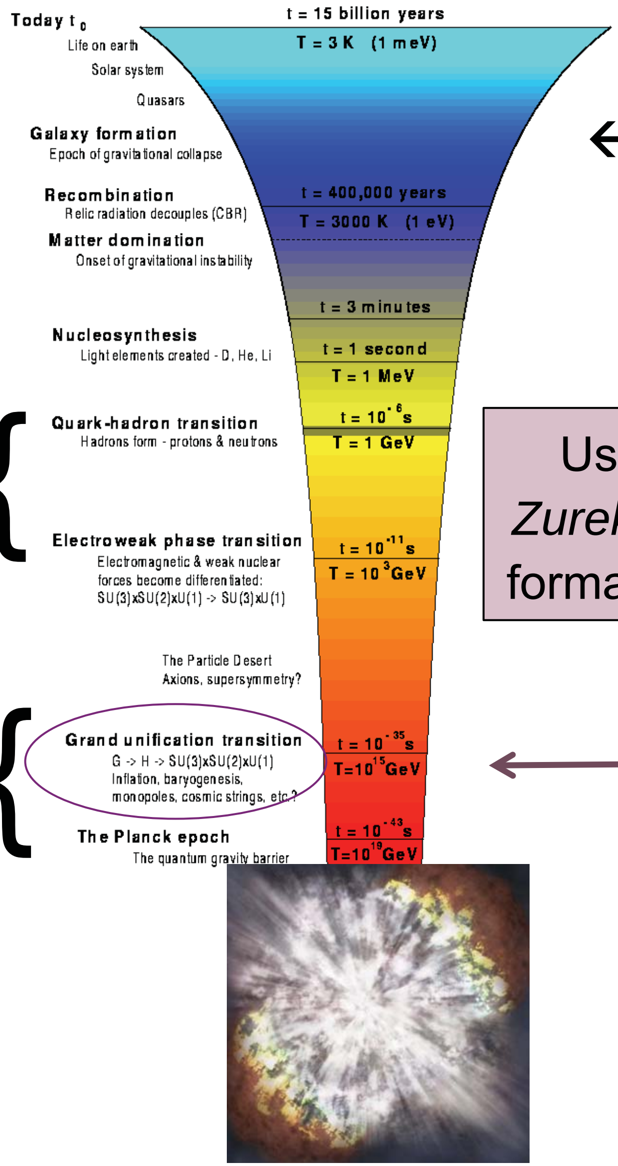
Today

Time

Very long time ago

Very expensive

Inaccessible?



← **Multiferroics !!**

Use $YMnO_3$ to test *Kibble-Zurek scaling law* proposed for formation of topological defects

Low

Temperature

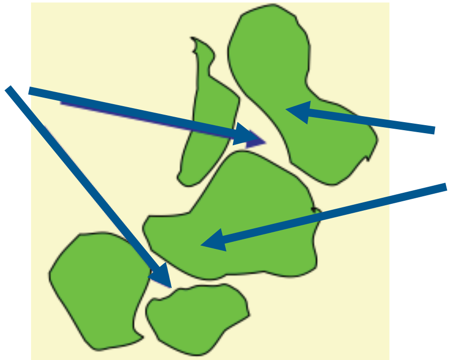
High

Kibble-Zurek scenario

Kibble: Spontaneous symmetry breaking described by non-trivial homotopy group yields topologically-protected defects

Zurek:

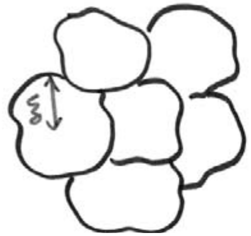
defects form when they meet



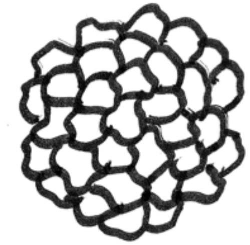
isolated low-symmetry regions fluctuate

How many defects depends on time spent at the transition temperature

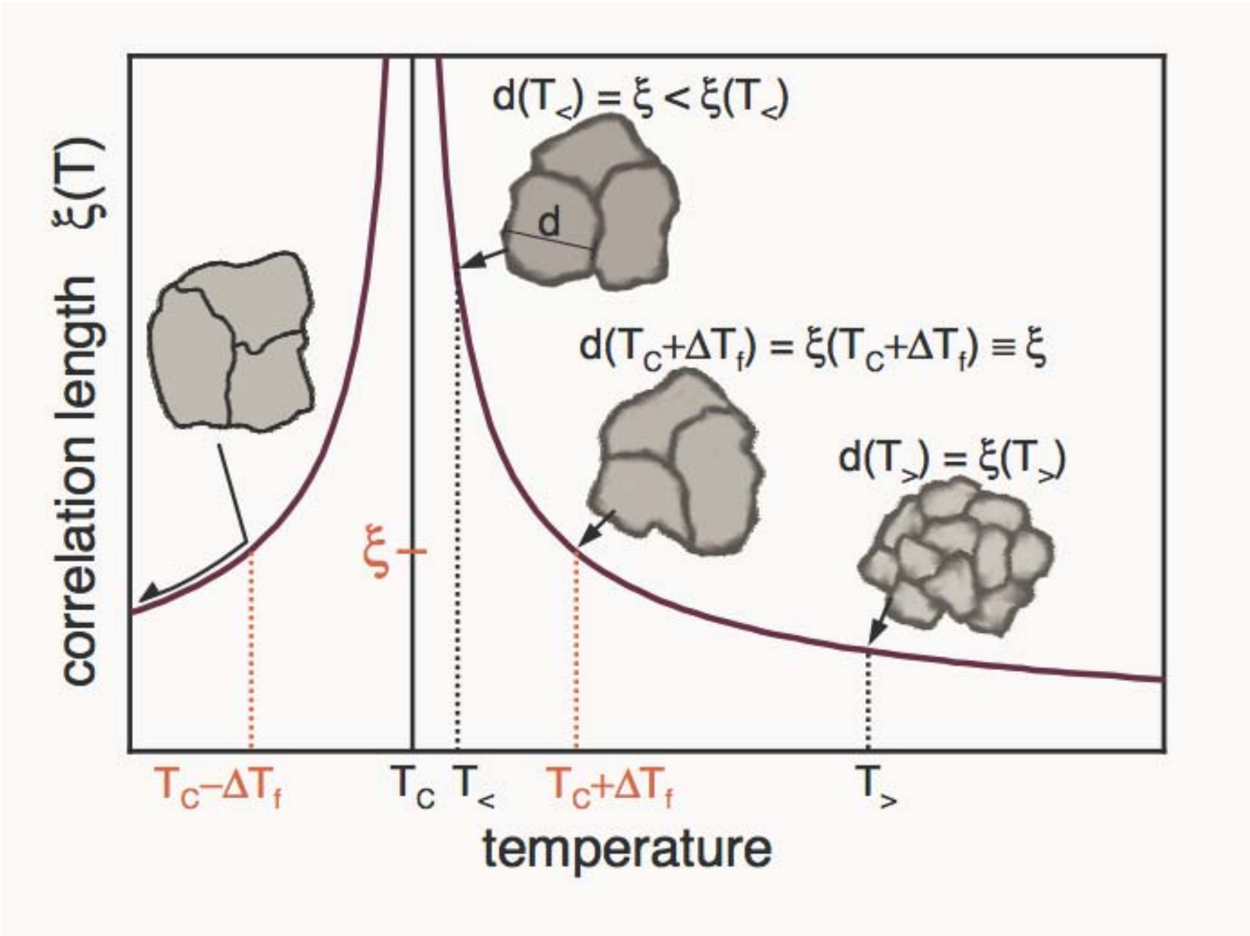
Cool slowly: Different regions can communicate their choice of phase
→ **Large regions of the same choice**
→ **Low density of defects**



Cool quickly: Not much time to communicate choice of phase
→ **Many smaller regions with different choice of phase**
→ **High density of defects**



A bit more rigorously



Quantitatively

domain size,

defined as Tc (1400K) / cooling rate

$$d = \xi_0 \left(\frac{\tau_q}{\tau_0} \right)^{\frac{\nu}{1+\mu}}$$

Critical exponents: $\nu = 0.6717$

$\mu = 1.3132$

from MC simulations for 3D XY model

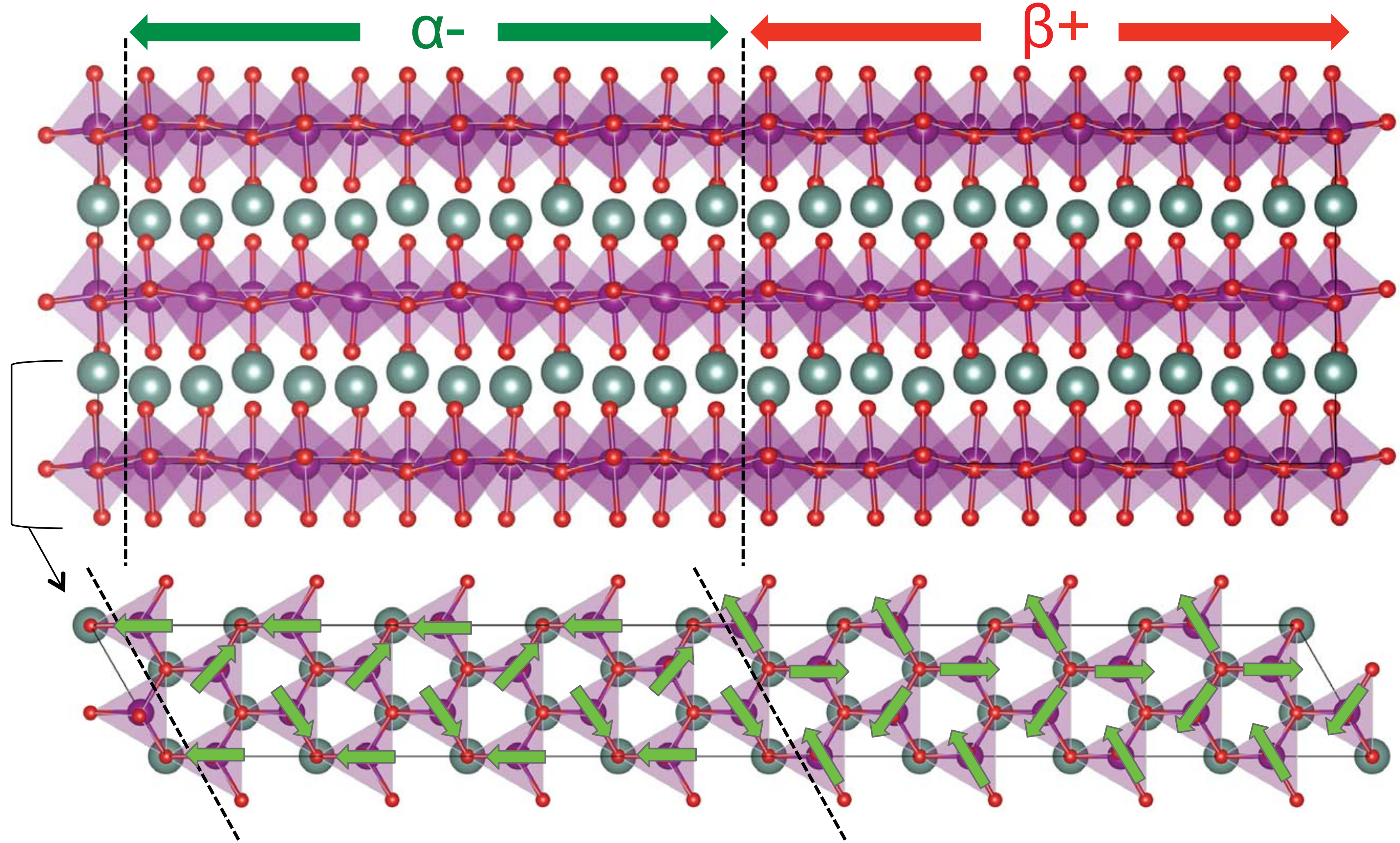
M. Campostrini et al., Phys. Rev. B **74**, 144506 (2006)

zero-temperature correlation length
~ domain wall width in ferroelectrics
(DFT)

zero-temperature relaxation time
= ξ_0 / speed of sound

speed of sound = 640 m/s (DFT)

DFT calculations of domain walls in $YMnO_3$

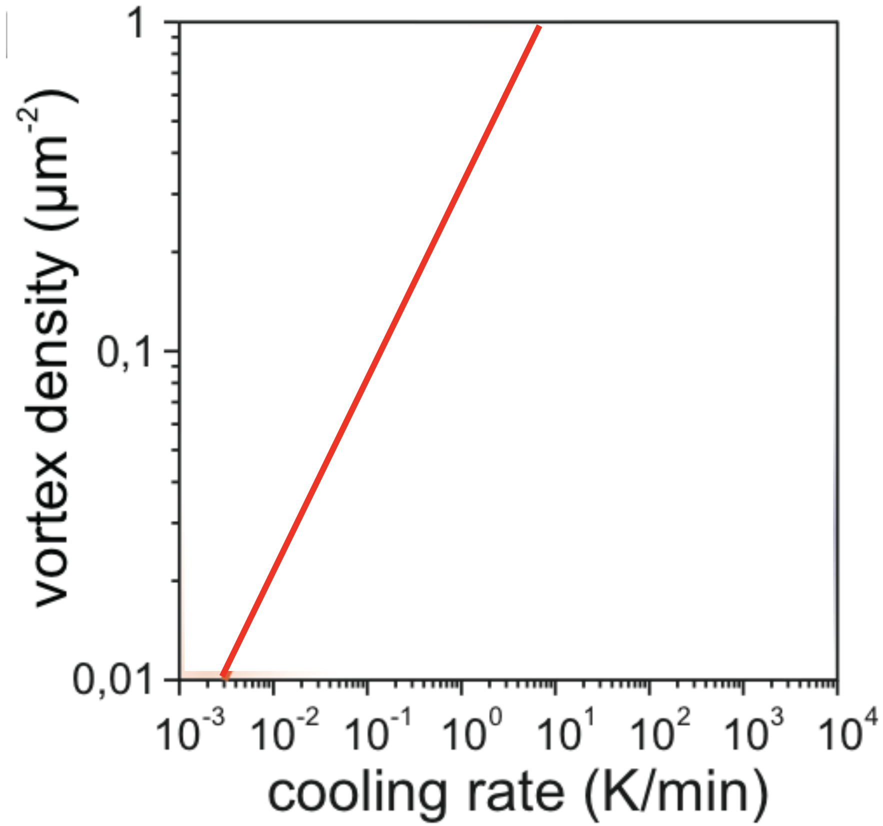


Domain wall width effectively zero!

Y. Kumagai and NAS, *Structural domain walls in polar hexagonal manganites*, Nat. Communications, in press

Comparison of KZ theory (DFT parameters) with experiment

Red line: our calculations
with ξ_0 = 0.06 A



Comparison of KZ theory (DFT parameters) with experiment

Red line: our calculations

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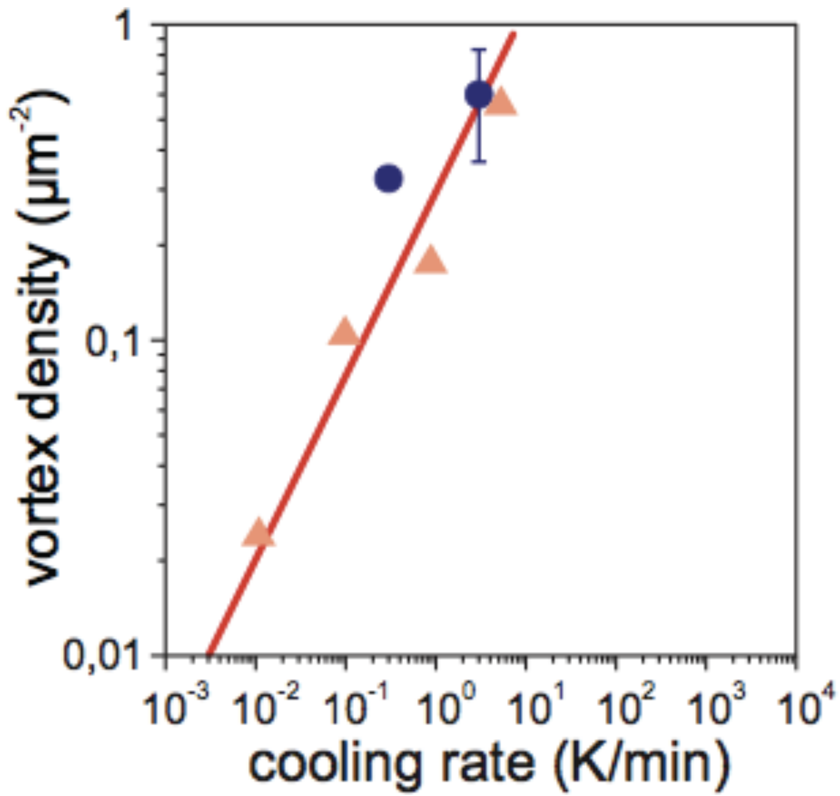
Red circles: measured by Chae et al.

Blue circles: measured by Fiebig et al.

REMARKABLE AGREEMENT!



S. C.. Chae et al., *Direct observation of the proliferation of ferroelectric loop domains and vortex-antivortex pairs,* PRL **108**, 167603 (2012)

Comparison of KZ theory (DFT parameters) with experiment

Red line: our calculations
with ξ_0 = 0.06 A

Red circles: measured by Chae et al.

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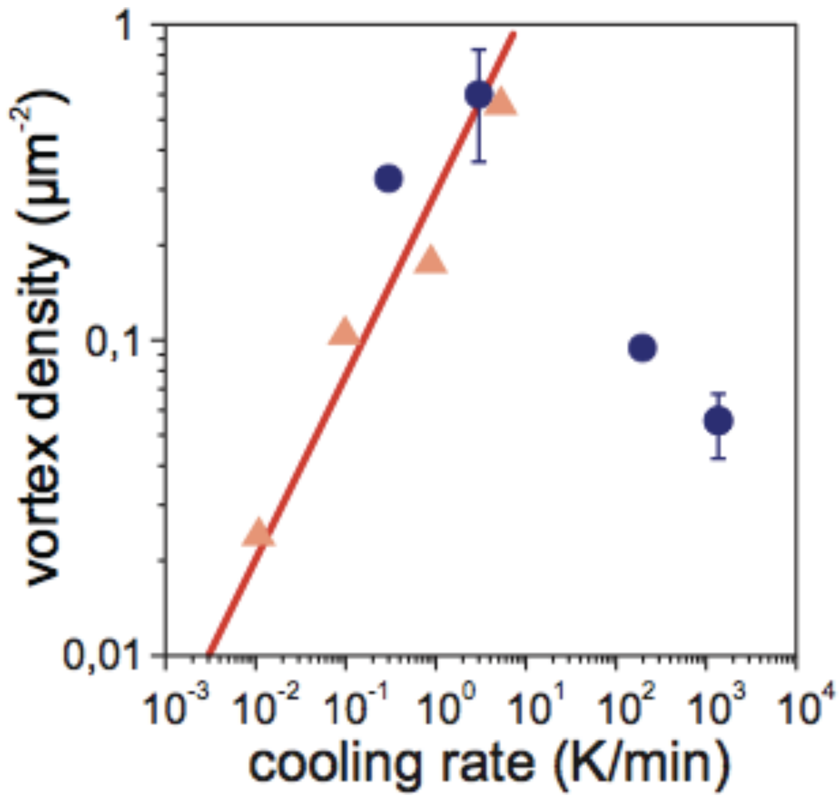
REMARKABLE AGREEMENT
AT SLOW COOLING RATES!



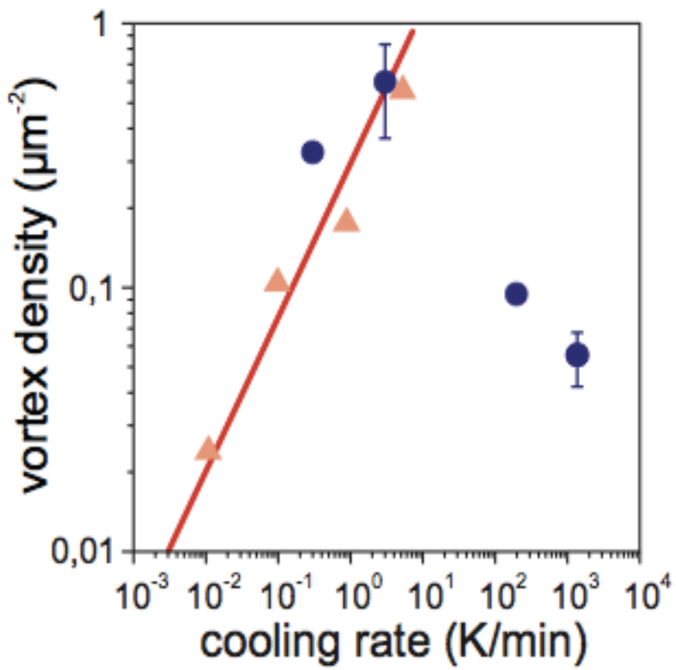
S. Griffin, M. Lilienblum, K. Delaney, Y. Kumagai, M. Fiebig and N. A. Spaldin, *Scaling behaviour and beyond equilibrium in the hexagonal manganites*, PRX **2**, 041022 (2012)

Open questions:

Are we now able to explore the "beyond-Kibble-Zurek" regime?

If so, what is the origin of the turnaround?

Or do we not have K-Z behavior at all?



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The Materials Theory group

Yu Kumagai

Sinead Griffin

The Multifunctional Ferroic Materials group

Manfred Fiebig and Martin Lilienblum


Kris Delaney, UC Santa Barbara

Summary

$YMnO_3$ displays rich physics beyond its multiferroism

Electronic structure calculations are helpful in unraveling some of this physics

$YMnO_3$ seems to provide the first example of Kibble-Zurek scaling in a condensed matter system

Use of condensed matter systems to explore questions in other areas of physics is a lot of fun

K. Rushchanskii, NAS et al., *A multiferroic material to search for the permanent electric dipole moment of the electron,* Nature Materials 9, 649 (2010)


Universe's Existence May Be Explained by New Material 2010-08-05 12.17

NATIONAL GEOGRAPHIC Daily News

Universe's Existence May Be Explained by New Material

A new material could help physicists explain the existence of matter, such as this astronaut seen above Earth.

Photograph courtesy NASA