Cornell University

"I would found an institution where any person can find instruction in any study."
− Ezra Cornell, 1868

Materials by Design

One theorist's perspective

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5th European School on Multiferroics, Ascona 2012

Goals: Part 1 and Part 2

To go through the thought process of two Materials by Design examples

(Symmetry, simple models, first-principles calculations of material specific compounds)

1. Phase competition a Generic paradigm to achieve colossal responses in proper ferroelectrics

2. Octahedral rotation induced antiferroelectricity as the origin hybrid improper ferroelectricity, or more accurately, ferrI-electricity

Outline: Part 1 and Part 2

A. Introduction to multifunctional materials

B. Phase Competition: a Generic paradigm to achieve colossal responses
   1. Basics of proper ferroelectricity: Landau theory phenomenology, Structural phase transitions, and Microscopic mechanism
   2. Strain tuning: controlling ferroelectricity with strain and improper ferroelastics
   3. Spin- phonon coupling → ~ P^2M^2 interaction by design
   4. Spin-lattice coupling → ~ $P \cdot L \times M$ interaction by design

C. Octahedral rotation induced antiferroelectricity as the origin hybrid improper ferroelectricity, or more accurately, ferrI-electricity (i.e., how to make Pnma perovskites useful:-)
   1. Octahedral rotations in perovskites
   2. Basics of improper ferroelectricity: primary lattice, secondary polarization
   3. hybrid improper ferroelectricity

A few useful to me review articles

- D. I. Khomskii, *Multiferroics: Different ways to combine magnetism and ferroelectricity*, J. Magnetism and Magnetic Mat. **306** (2006) 1-8.
- Y. Tokura, Multiferroics-toward strong coupling between magnetization and polarization in a solid, J. Magnetism and Magnetic Mat. **310** (2007) 1145-1150.
- *Physics of ferroelectrics - A modern perspective*, Karin M. Rabe, Charles H. Ahn, and Jean-Marc Triscone (Eds.), Topics in Applied Physics **105** (2007) Springer.
- International Tables for Crystallography (2006). Vol. D, Chapter 1.5 Magnetic properties pp. 105–149. By A. S. Borovik-Romanov† and H. Grimmer

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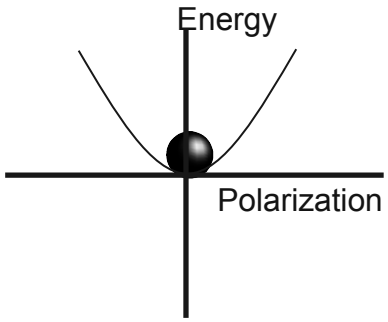
Functional Materials: Ferroelectricity

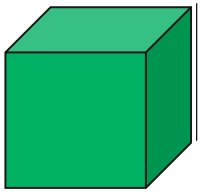
Property: Polarization

Definition: Electric dipole per unit volume

Dielectrics

$\mathrm{P} \propto E$ (small E)

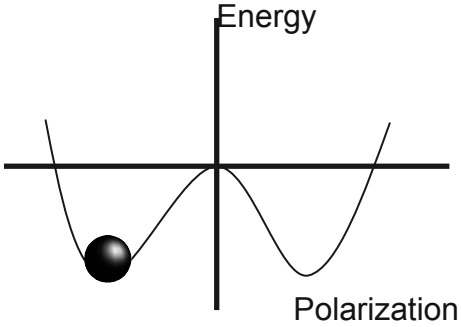


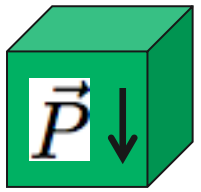


Ferroelectrics

$\mathrm{P} \neq 0$ in zero E

Switchable to another orientation by applied E



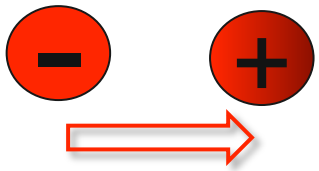


Analogous to ferromagnetism: $\mathrm{P} \rightarrow \mathrm{M}$, $E \rightarrow H$

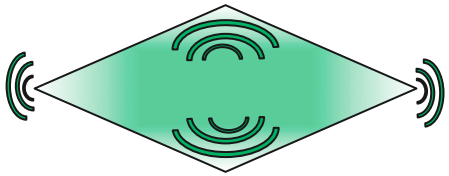
Multifunctional multiferroics

Multiferroic: combine more than one "ferro" ***property***:
Ferroelectricity, ferroelasticity, and/or magnetism

(Hans Schmid, 1973)



Polarization, P



Strain, ε

Magnetization, M

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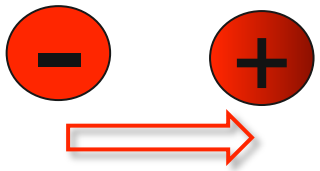
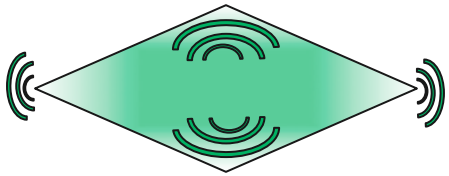


Polarization, P

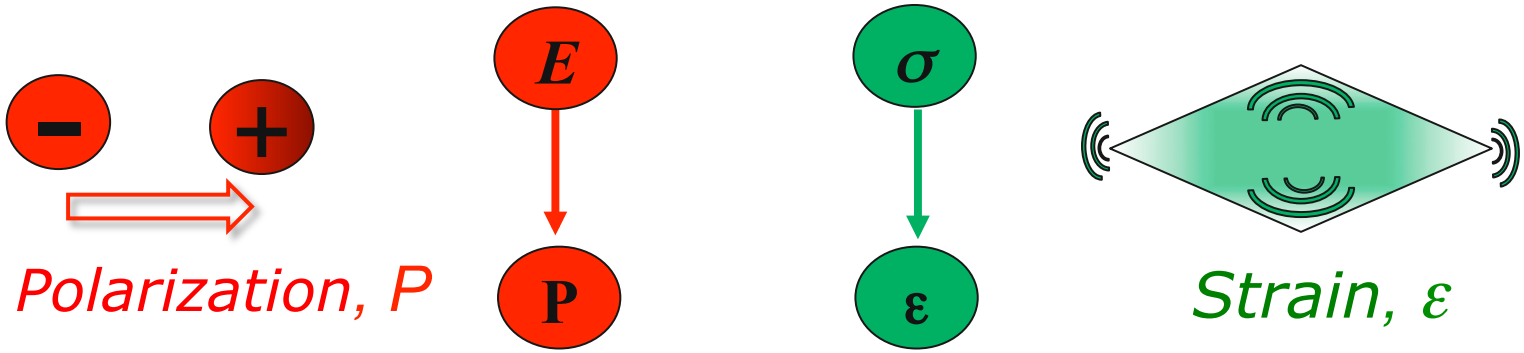


Strain, ε

e.g., ferroelectric ferroelastic

Multifunctional multiferroics

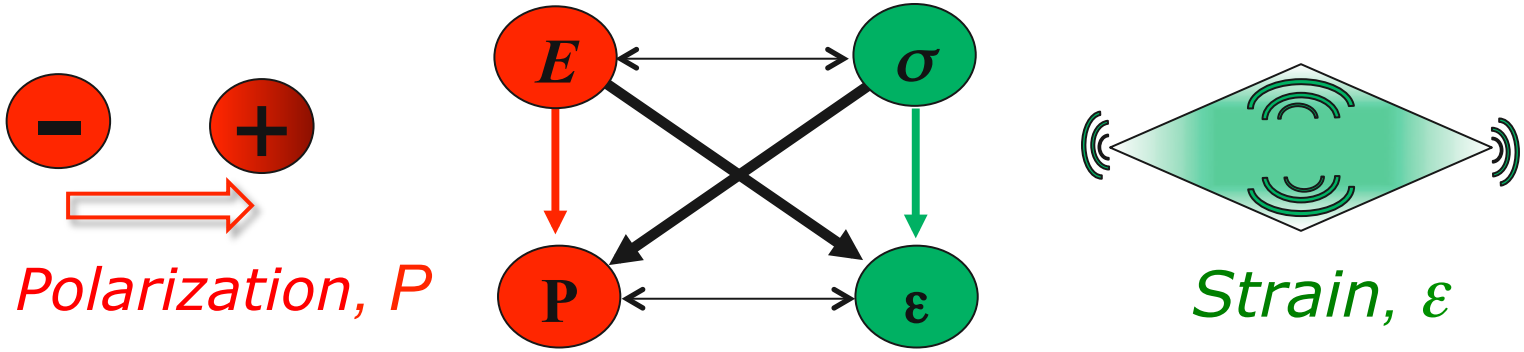
Multifunctional: response to more than one external ***perturbation***: Electric (E) and stress (σ) fields



e.g., ferroelectric ferroelastic

Multifunctional Electrostrictive materials

(Generalized) **Electrostriction**: cross coupled response to electric (*E*) and stress (σ) fields



i.e. control of the strain (electric) state with an applied electric (stress) field

The order of the coupling to strain:

$E \rightarrow$ piezoelectricity

$E^2 \rightarrow$ electrostriction

Multifunctional multiferroics

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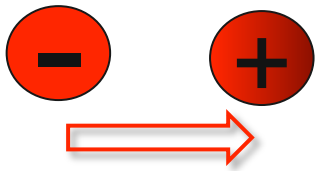
(Hans Schmid, 1973)



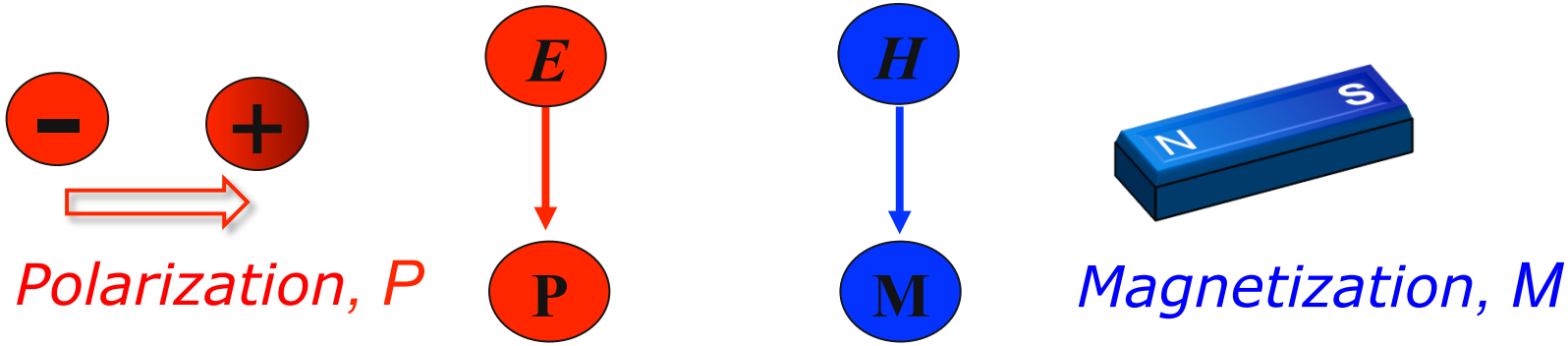
Polarization, P

Magnetization, M

e.g., ferroelectric ferromagnet

Multifunctional multiferroics

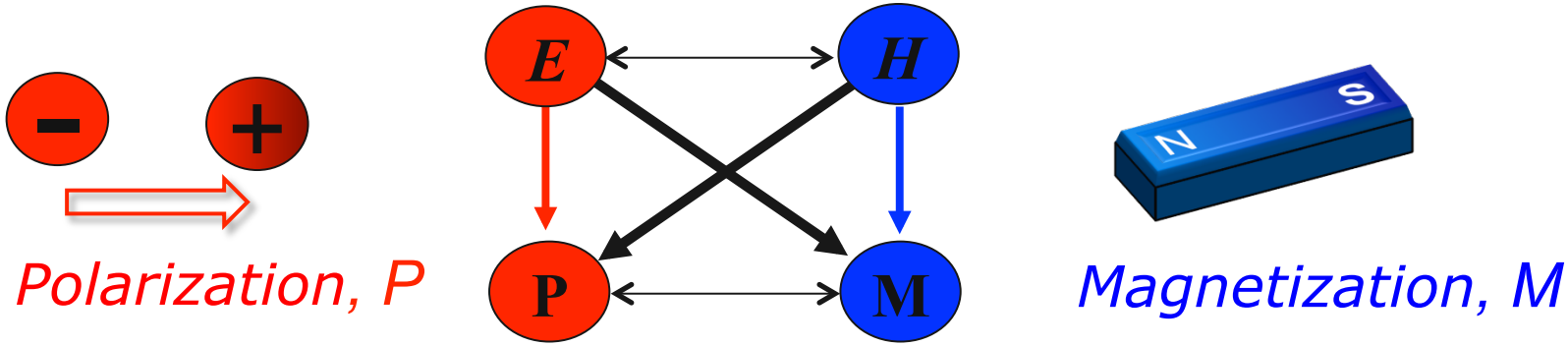
Multifunctional: response to more than one external ***perturbation***: Electric and magnetic fields



e.g., ferroelectric ferromagnet

Multifunctional magnetoelectrics

(Generalized) **Magnetoelectric**: cross coupled response to electric and magnetic fields



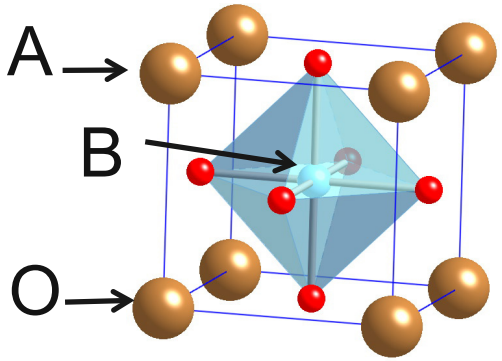
i.e. control of the magnetic **M** *(electric* **P***) phase with an applied electric* ***E*** *(magnetic* ***H****) field*

Emergence of new macroscopic phenomena

Where do we look for new phenomena and why do we look there?

More is definitely different (e.g., ABO_3 Perovskites)

Same prototypical structure



Nearly any physical property

- Dielectric — $CaTiO_3$, $SrTiO_3$, $(CaCu_3)(Ti_4)(O_4)_3$
- Ferroelectric — $BaTiO_3$, $LiNbO_3$, $PbTiO_3$
- Magnetoelectric — $TbMnO_3$, $BiFeO_3$
- Antiferroelectric — $PbZrO_3$
- Piezoelectric — $PbZr_xTi_{1-x}O_3$
- Antiferromagnetic — $LaMnO_3$
- Ferromagnetic — $SrRuO_3$
- Superconducting — doped-$SrTiO_3$
- Colossal Magneto-resistance $(La,Ca)MnO_3$

"More is Different," Phil Anderson, Science 1972

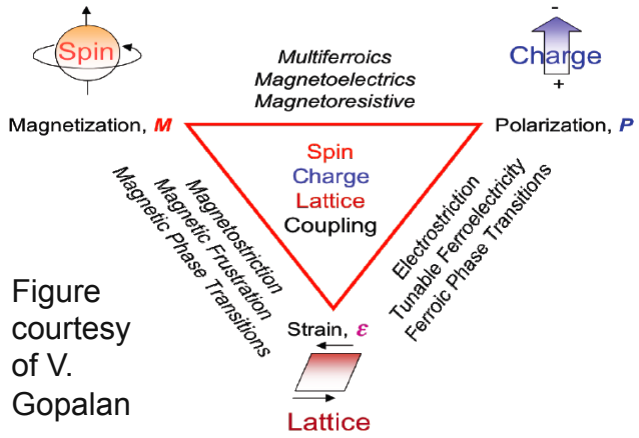
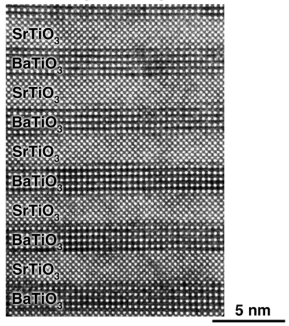


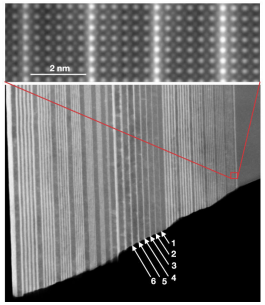
Figure courtesy of V. Gopalan

Advances in synthesis and characterization - tailoring properties at the nanoscale



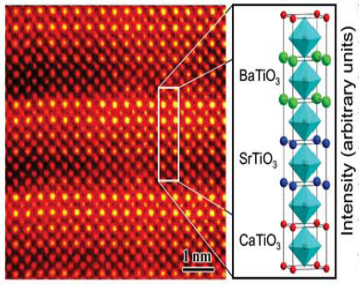
$(BaTiO_3)_6(SrTiO_3)_5$

Haeni, Schlom, Tian, & Pan (2001)



$(LaTiO_3)_1(SrTiO_3)_n$

Ohtomo, Muller, Grazul, & Hwang

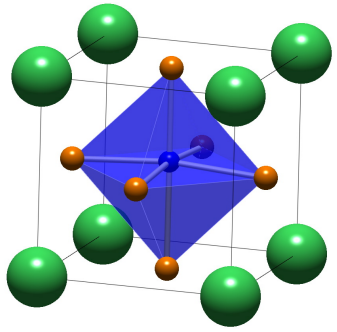


$(BaTiO_3)_n(SrTiO_3)_m(CaTiO_3)_k$

Lee, ORNL

Enormous number of tertiary and quaternary perovskites

Perovskites ABO_3



IA												IIIA	IVA	VA	VIA	VIIA	Noble
H	IIA																He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIB	⌐VIIIB¬		IB	IIB		Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	†	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	‡	Rf	Ha	Sg	Ns	Hs	Mt									

†	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
‡	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Substitutions on A, B or both $(A_{1-x}A'_x)(B_{1-y}B'_y)O_3$

Random distribution or ordered

You are not going to program a computer and calculate your way to new materials that have the physics you want them to have

Common themes: Designer Hamiltonians

1. Playing with models, symmetry, and basic principles of crystal chemistry we come up with a set of materials design rules (i.e., no calculations) that we used to identify candidate materials

2. From first principles, given A-B-X, we have access to metastable structures that may not appear in the phase diagram

The question then turns to "how to be stabilize such phases?

⇒ need growers who are willing to run with a crazy idea and be pat of a long term program that gives the freedom to do so.

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   1. Basics of proper ferroelectricity: Landau theory phenomenology, Structural phase transitions, and Microscopic mechanism
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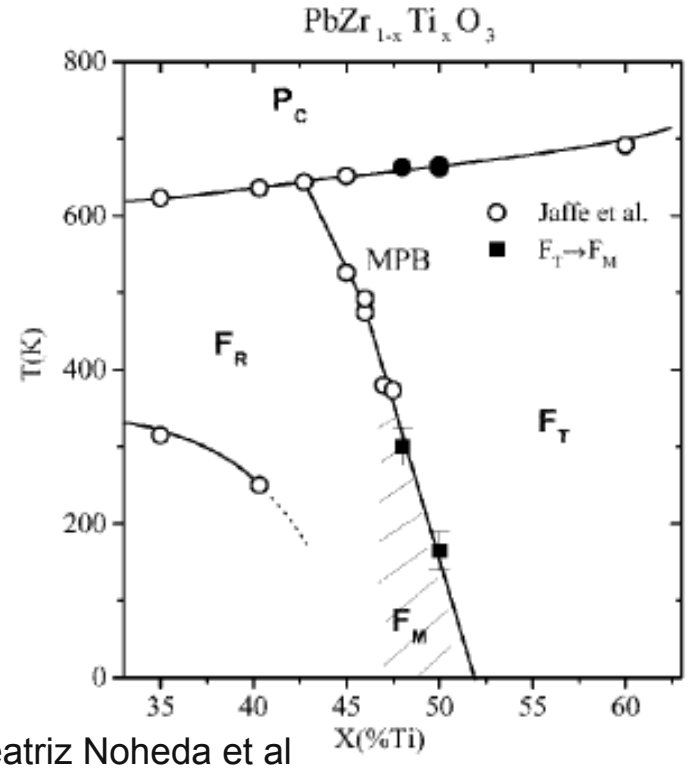
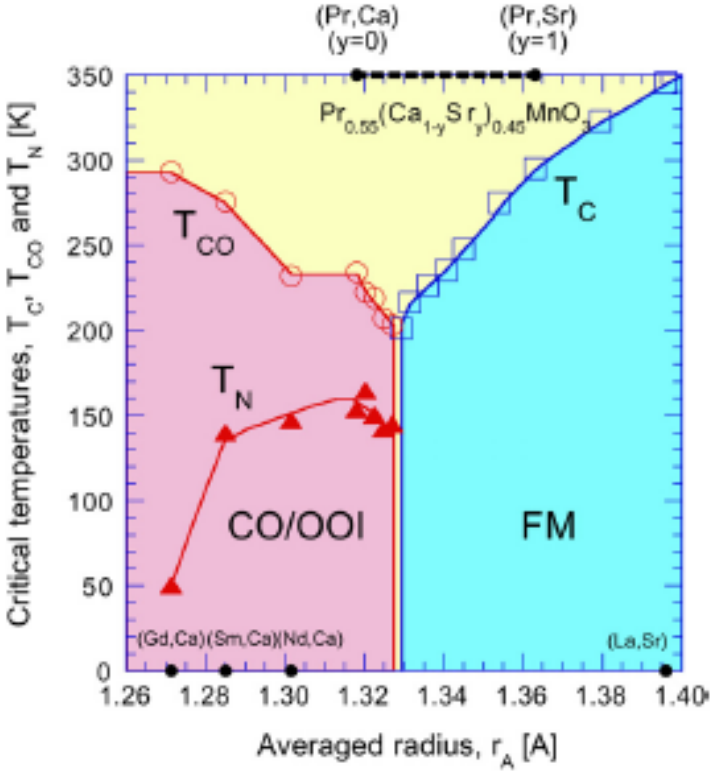
Phase Competition: Generic paradigm to achieve colossal effects

Colossal Electro-mechanical response



Beatriz Noheda et al

Colossal Magneto-resistance response



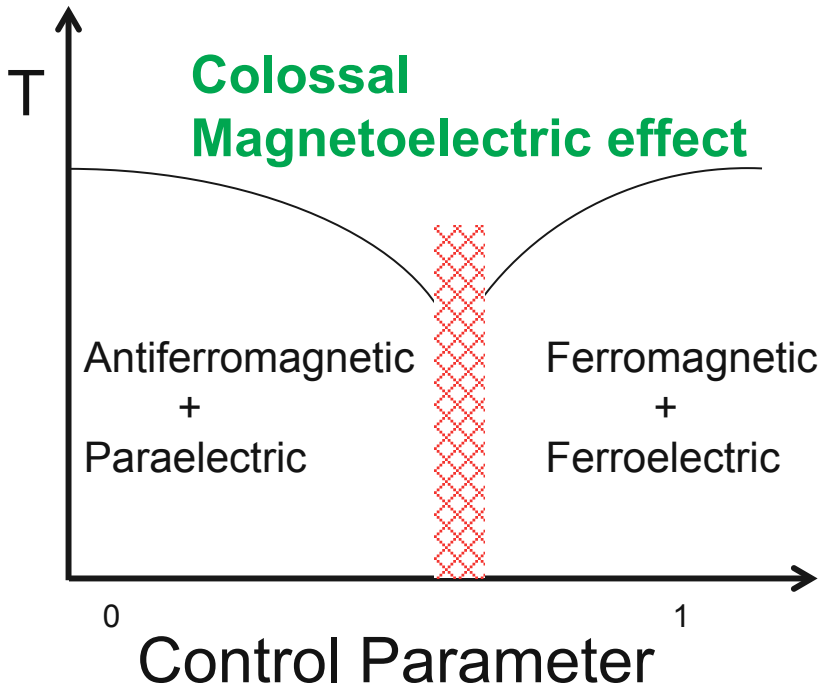
Tokura et al

* Y. Tokura, "Critical Feature of Colossal Magnetoresistive Manganites," Rep. Prog. Phys. 2006.
"Multiferroics - Toward Strong Coupling …," JMMM 2007.
* R.E. Newnham, "Molecular Mechanisms in Smart Materials," MRS Bull. 1997.

Generic paradigm to design new multiferrroic

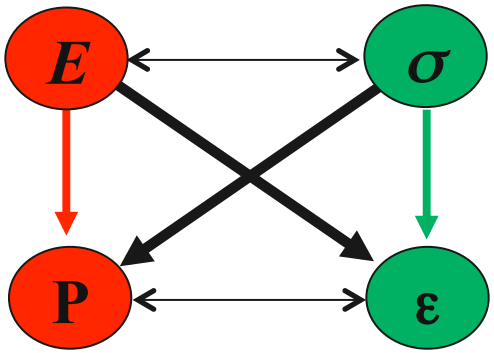
Start with AFM-PE material and tune to a FM-FE phase

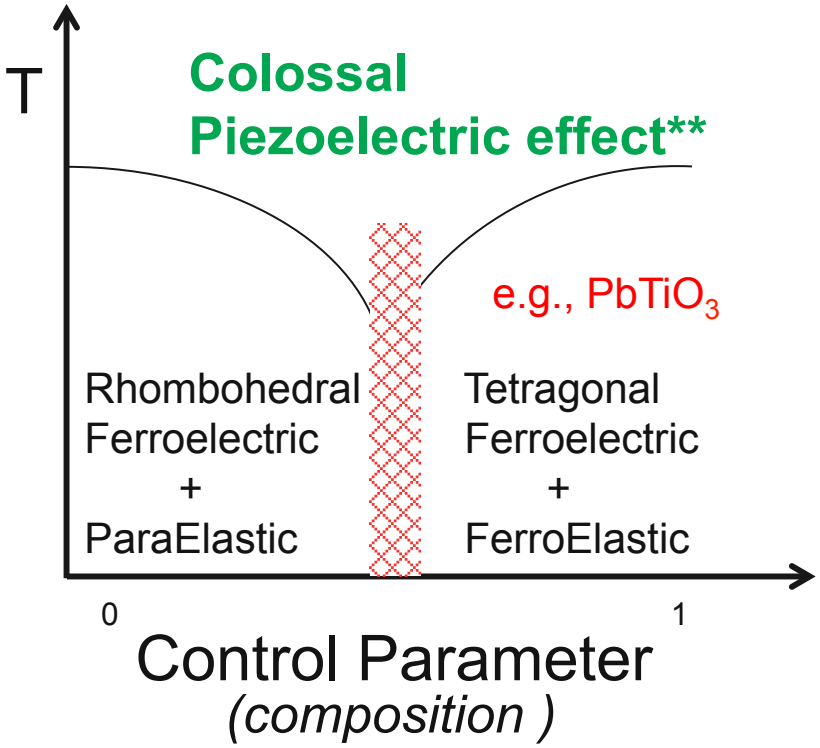
1. *Identify microscopic mechanism to achieve coupling of order parameters*



Phase Competition and the morphotropic phase boundary

Piezoelectric: cross coupled response to electric (*E*) and stress (σ) fields





In perovskite ferroelectrics such as $PbTiO_3$, there is a "natural" ***cross coupled response*** *between electric, E, and stress, σ, fields*

Why? (we will see in a bit)

Generic paradigm to design new multiferrroic

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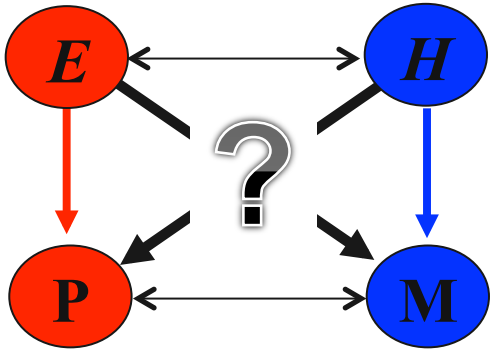
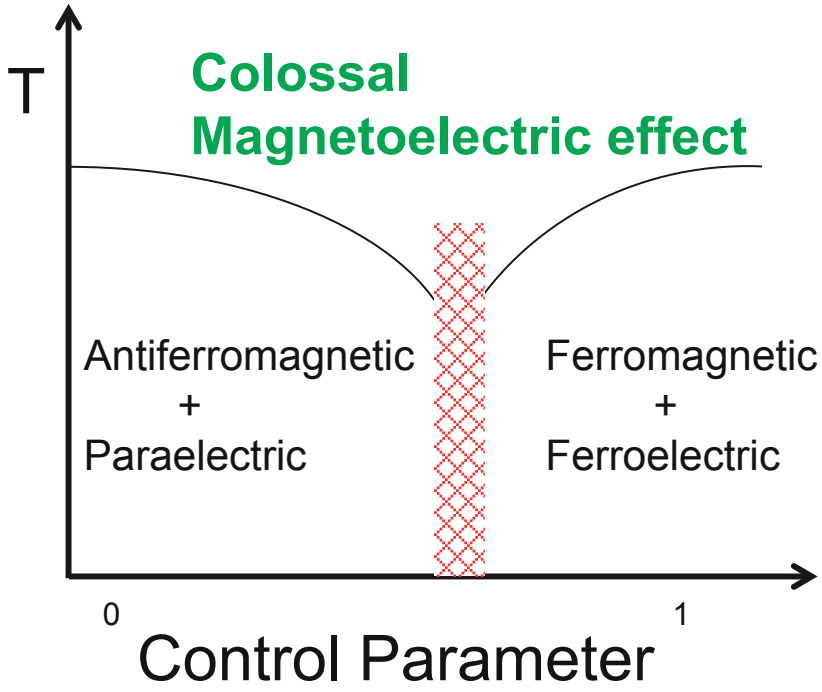
1. *Identify microscopic mechanism to achieve coupling of order parameters*

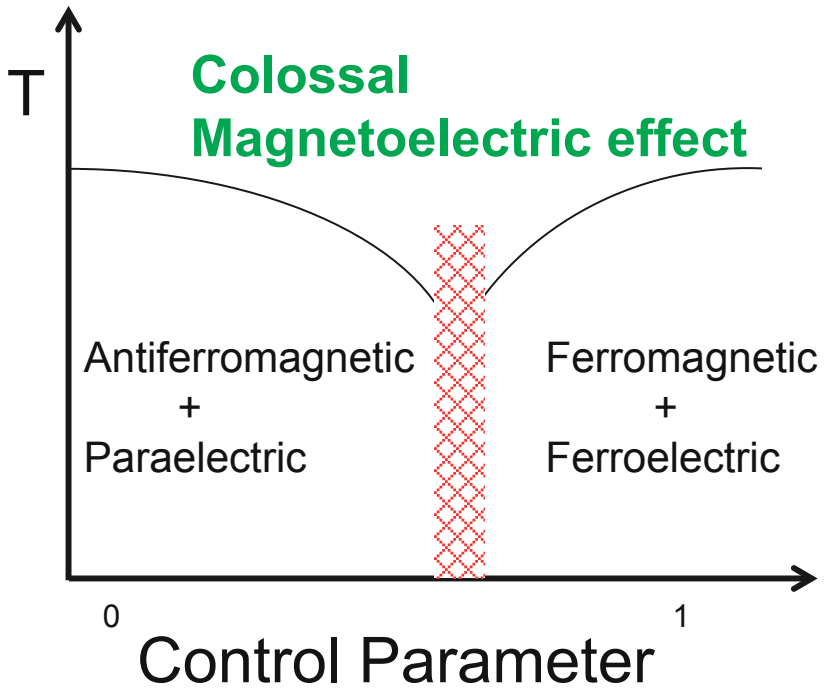




Generic paradigm to design new multiferrroic

Start with AFM-PE material and tune to a FM-FE phase

1. *Identify microscopic mechanism to achieve coupling of order parameters*
2. *Identify tuning mechanism*
3. *Identify material realization*



Theory-driven experimental pursuit of new materials-by-design: Example 1

What is our microscopic model?

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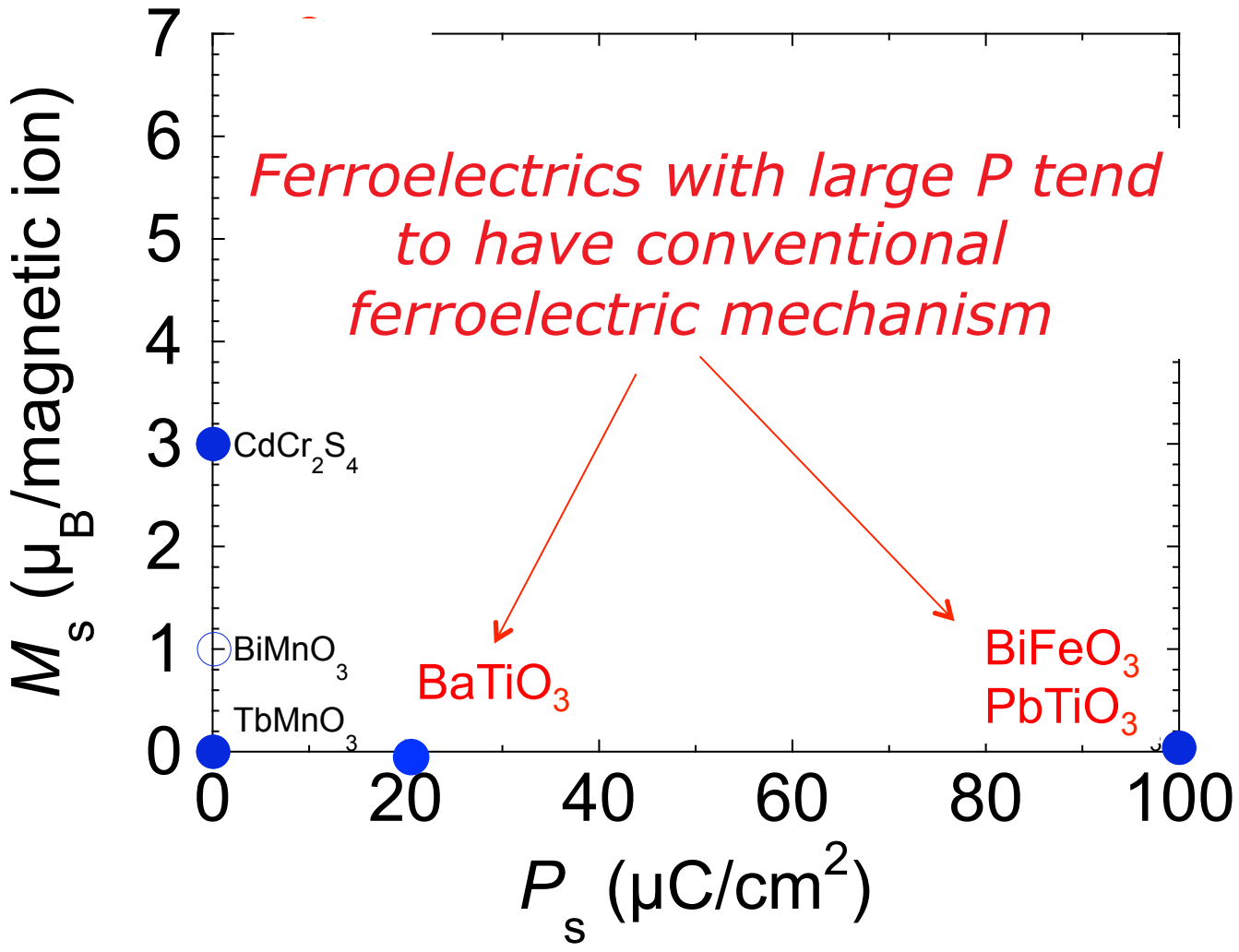
Strong ferroelectricity and ferromagnetism via spin-phonon coupling

Break the problem up into steps!

Strong Ferromagnetic Ferroelectrics



Slide from D. Schlom

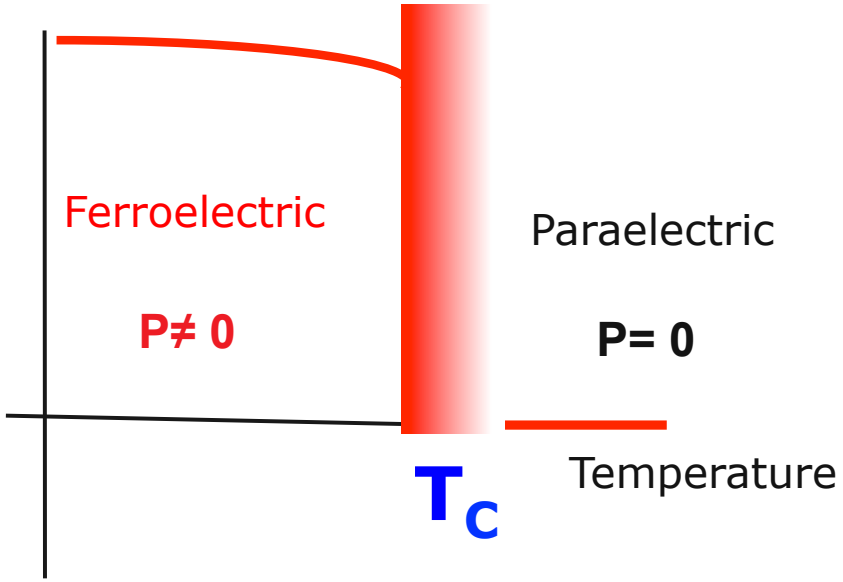
Identify primary order parameter

What do I mean by “primary”

Ferroelectricity

At the most simplest level we are trying to describe the appearance of a spontaneous polarization

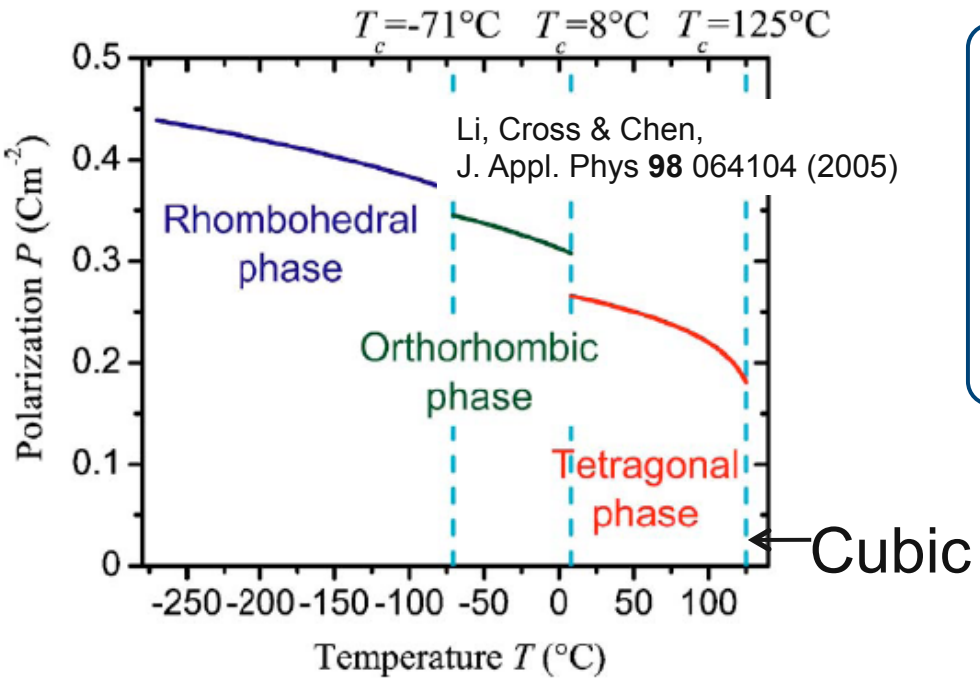
Property: *electric polarization*
Defined by a net electric dipole per unit volume



Prototypical ferroelectric

Let's ask a similar question: *how does the crystal structure evolve during the transition from a paraelectric to ferroelectric state?*

Consider the ferroelectric $BaTiO_3$ (R → O → T→ C phase transition)



Symmetry of the lattice is lowered as you cool $BaTiO_3$

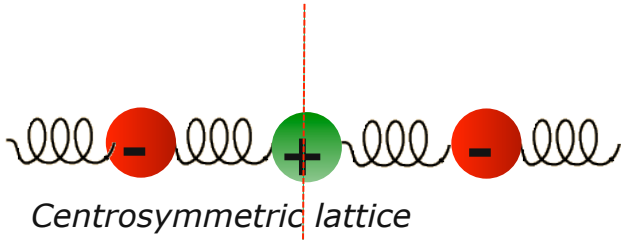
symmetry ⟺ properties

Neumann principle

Ferroelectricity

Spontaneous polarization P

⇒ Dipole moment per unit volume



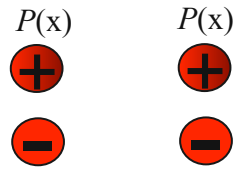
Ordering of polar mode

in many cases, this turns out to be a lattice mode

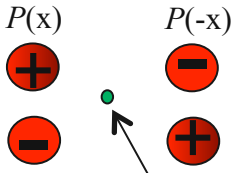
Spontaneous space-inversion, I, symmetry breaking

Symmetry properties

P(-x) = -P(x)

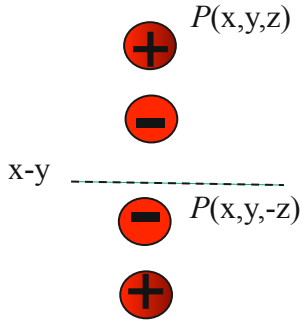


Time inversion R $t \rightarrow -t$

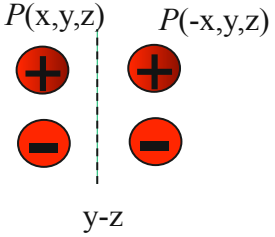


Space inversion I $r \rightarrow -r$

P and E *are Polar vectors*



Mirror reflection m



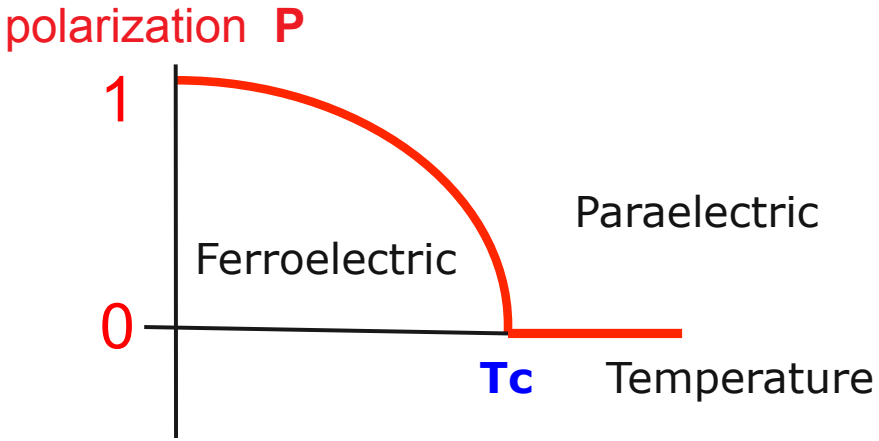
Proper ferroelectric transition: phenomenology

The primary OP accounts for the appearance of the spontaneous physical quantity, i.e., P, AND completely accounts for the ***symmetry*** lost at the phase transition

⇒ Proper ferroelectric transition. (we will see example of improper ferroelectric transitions, e.g., $YMnO_3$).

$PbTiO_3$: Primary Order Parameter
Spontaneous polarization P

Introductory: Ekhard Salje, "Crystallography and structural phase transitions, in introduction," *Acta Crystal*. A47, 453-469 (1991).
More advanced: Stokes and Hatch, "Coupled order parameters in the Landau theory of phase transitions in solids," *Phase Transitions* V34, 53-67 (1991).



Proper ferroelectric transition: phenomenology

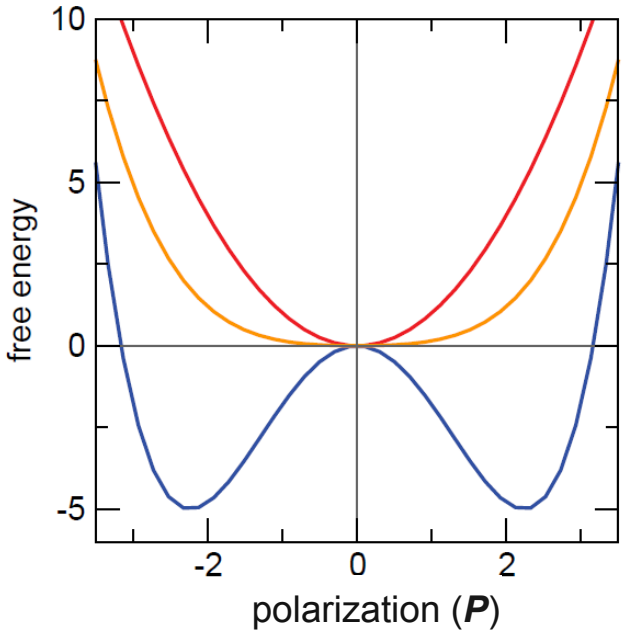
A simple example: The cubic paraelectric

• in paraelectric free energy remains invariant under space inversion, i.e., $\mathcal{F}(P) = \mathcal{F}(-P)$

⇒ only even powers of P

$$\mathcal{F}_{PE}(P) = \frac{1}{2}aP^2 + \frac{1}{4}bP^4$$

$$a = a_0(T - T_c)$$



$$\partial\mathcal{F}/\partial P|_{P_0} = aP_0 + bP_0^3 = 0$$

$$P_0 = \begin{cases} 0 & a > 0 \\ \pm\sqrt{(-\frac{a}{b})} & a < 0 \end{cases}$$

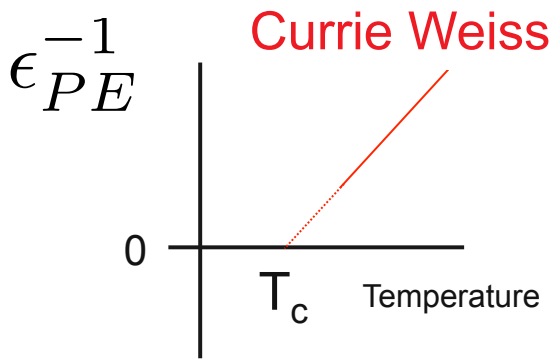
Proper ferroelectric transition: phenomenology

A simple example: The cubic paraelectric

$$\mathcal{F}_{PE}(P) = \frac{1}{2}aP^2 + \frac{1}{4}bP^4$$

The dielectric susceptibility

$$\epsilon_{PE}^{-1} = \partial^2\mathcal{F}_{PE}/\partial P\partial P|_{P=0} = a = a_0(T - T_c)$$

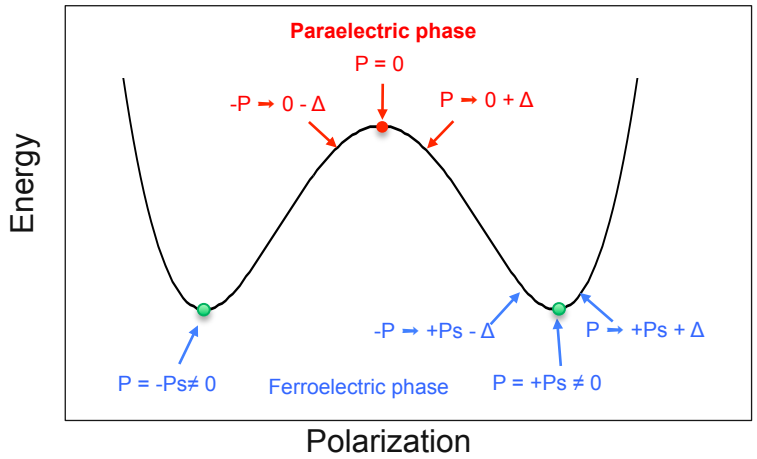


Proper ferroelectric transition: phenomenology

One can also investigate the *ferroelectric* phase within a Landau theory.

Confusion sometimes arises due to the standard notational practice of using the symbol "**P**" as the order parameter in the ferroelectric phase, i.e.,

$$\mathcal{F}_{FE}(\Delta_P) = \frac{1}{2}a'\Delta_P^2 + \frac{1}{3}c'\Delta_P^3 + \frac{1}{4}b'\Delta_P^4$$



Note, that the cubic term is allowed since there is NO symmetry that takes $\Delta_P \rightarrow -\Delta_P$

Proper ferroelectric transition: phenomenology

One can also investigate the *ferroelectric* phase within a Landau theory.

A far more pedagogical approach towards understanding the properties of the ferroelectric phase, is to *consider a reference structure* in which the primary order parameter (and all additional order parameters that have identical symmetry transformational properties) is zero, this is *the paraelectric reference structure*.

Starting with $$\mathcal{F}_{PE}(P) = \frac{1}{2}aP^2 + \frac{1}{4}bP^4$$

let $$\mathrm{P} \rightarrow P_0 \pm \Delta_P$$

$$\mathcal{F}(P) = \mathcal{F}_{PE}|_{P_0} + \frac{1}{2}a'\Delta_P^2 + \frac{1}{3}c'\Delta_P^3 + \frac{1}{4}b'\Delta_P^4$$

Proper ferroelectric transition: phenomenology

One can also investigate the *ferroelectric* phase within a Landau theory.

Confusion sometimes arises due to the standard notational practice of using the symbol "**P**" as the order parameter in the ferroelectric phase, i.e.,

$$\mathcal{F}_{FE}(P) = \frac{1}{2}a'P^2 + \frac{1}{3}c'P^3 + \frac{1}{4}b'P^4$$

Proper ferroelectric transition: phenomenology

One can also investigate the *ferroelectric* phase within a Landau theory.

$$\mathcal{F}(P) = \mathcal{F}_{PE}|_{P_0} + \frac{1}{2}a'\Delta_P^2 + \frac{1}{3}c'\Delta_P^3 + \frac{1}{4}b'\Delta_P^4$$

$$\begin{aligned} a' &= a + 3bP_0^2 \\ c' &= bP_0 \\ b' &= b \end{aligned}$$

1. P → -P implies switching from one ferroelectric well to its symmetry equivalent direction.
2. One can explicitly see that a new term, the cubic term, arises whenever the equilibrium value of the primary order parameter is non-zero, its coefficient increasing linear with P_0.
3. the response to small fields in either the paraelectric phase, i.e., $P_0 = 0$, (if it actually exists in the equilibrium phase diagram of the the ferroelectric phase of interest) or the ferroelectric phase can be calculated.

Proper ferroelectric transition: phenomenology

A intuitive way to find the susceptibility in both the paraelectric and ferroelectric phases

$$\mathcal{F}(P) = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 - \mathcal{E}P$$

$$\partial\mathcal{F}/\partial P|_P = aP + bP^3 = \mathcal{E}$$

let $\mathrm{P} \rightarrow P_0 + \Delta_P$ when $\mathrm{E} \rightarrow \Delta\mathcal{E}$

$$\Rightarrow \Delta\mathcal{E} = a(P_0 + \Delta_P) + b(P_0 + \Delta_P)^3$$

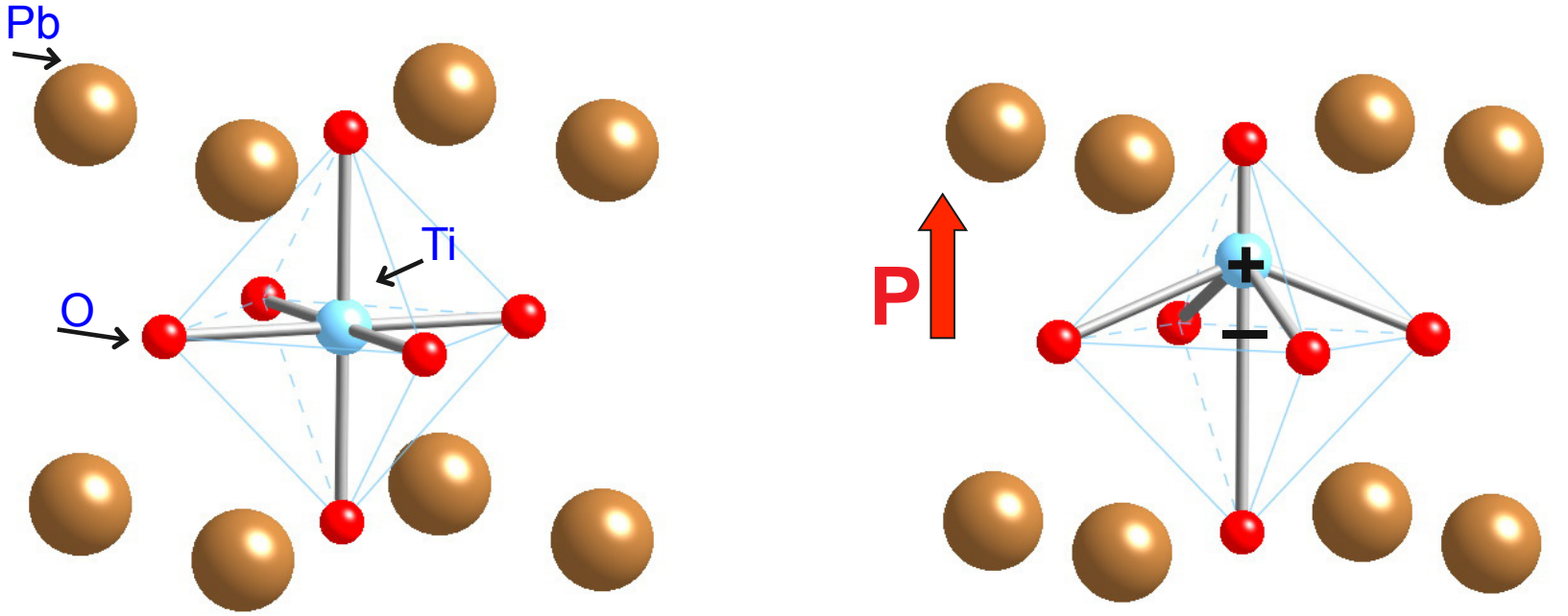
$$= \underbrace{aP_0 + bP_0^3}_{=0 \rightarrow P_0} + \underbrace{(a + 3bP_0^2)}_{\rightarrow \epsilon}\Delta_P + \mathcal{O}(\Delta_P^2)$$

$$\Rightarrow \epsilon \sim \frac{\Delta_P}{\Delta\mathcal{E}} = \frac{1}{a + 3bP_0^2}$$

Phenomenology is nice, we need to start understanding microscopic mechanism and the relevant microscopic degree of freedom.

Ferroelectricity as a lattice property

FE lattice distortion, **Q**, has identical *symmetry* properties as the polarization, i.e. **Q**∝ **P**, involve small atomic distortions



cubic-paraelectric
Space group Pm3m

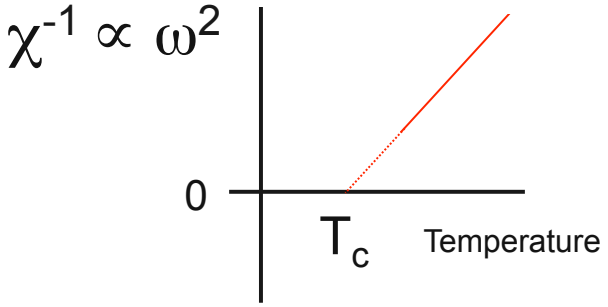
tetragonal-ferroelectric
Space group P4mm

Soft-mode theory of ferroelectricity

Born and Huang, 1954, W. Cochran, Phys. Rev. Lett. 1959

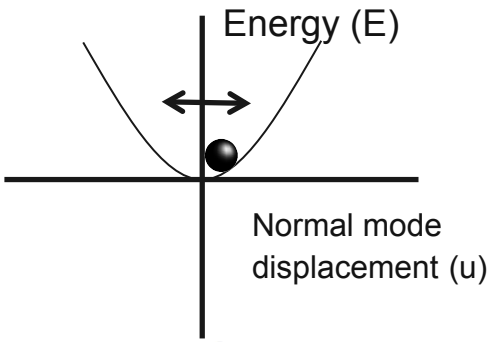
Experiments see:
Jim Scott
RMP 46, 83 (1974)

Currie Weiss



Where ω is an infrared-active phonon frequency

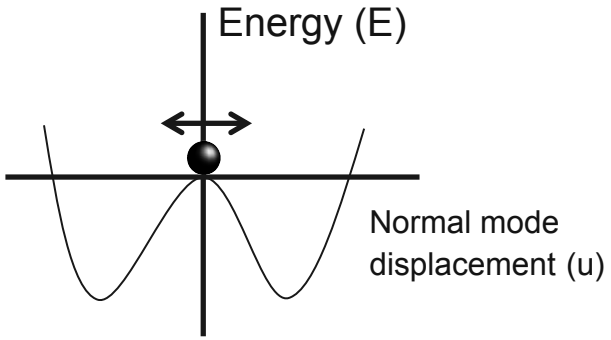
Stable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} > 0$$

→ Paraelectric

Unstable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$

→ Ferroelectric

Phonon dispersion at T=0 of cubic ABO_3 from first principles

Identify microscopic degrees of freedom from first principles

Remember: Imaginary frequencies imply lattice instability

Phonon Symmetry Labels
Γ: q=0
M: q=(1,1,0)
X: q=(1,0,0)
R: q=(1,1,1)

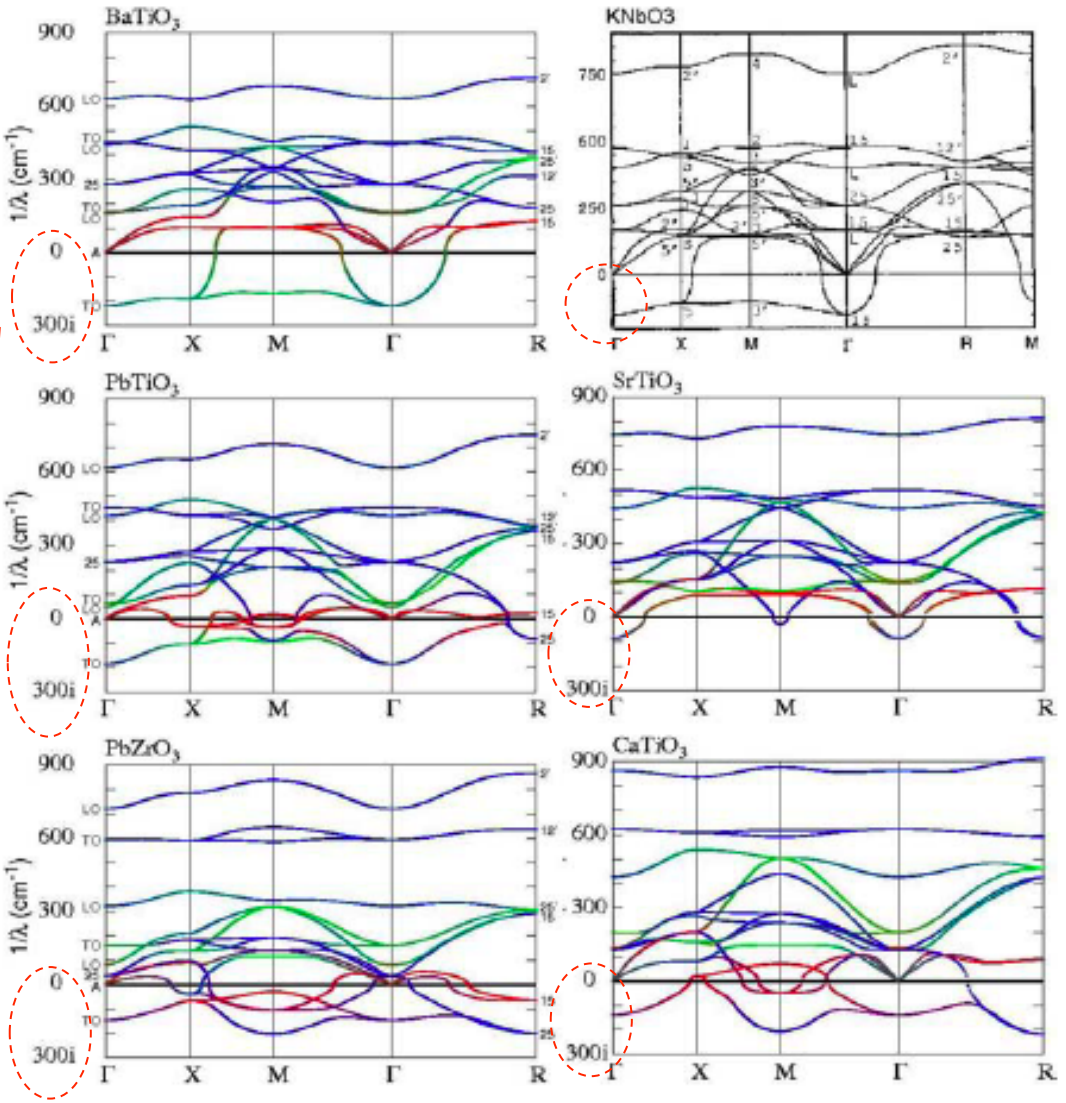


Fig 3, page 135; Karin M. Rabe and Philippe Ghosez, Topics in Applied Physics **105**: 117-174 (2007).

Soft-mode theory of ferroelectricity

- Crystal is stable against small deformations if all normal modes have *real* frequencies
- Ferroelectricity is associated with the freezeing-in (condensation) of an unstable or soft polar phonon (IR-active)

Primary distortion mode becomes the order parameter

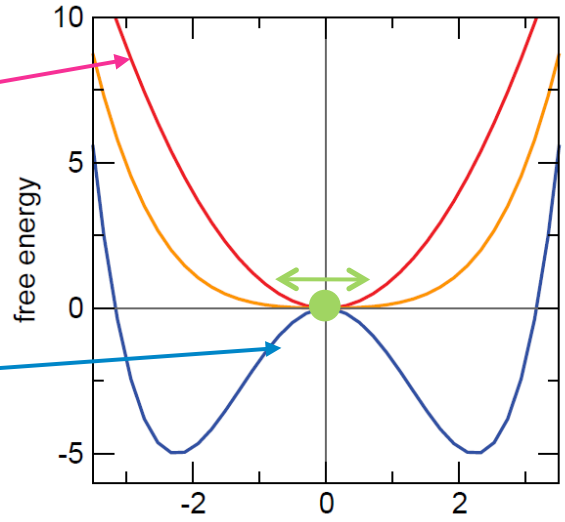
$$E = E_0 + \frac{1}{2}\alpha u^2 + \beta u^4$$

Stable phonon

$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} > 0$$

Unstable phonon

$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$



Normal mode displacement

Ferroelectric mechanisms: Chemical

(formally) d^0 transition metals e.g. $Ba^{2+}Ti^{4+}O^{2-}$ Ti^{4+}: $3d^04s^0$

Origin of FE distortion

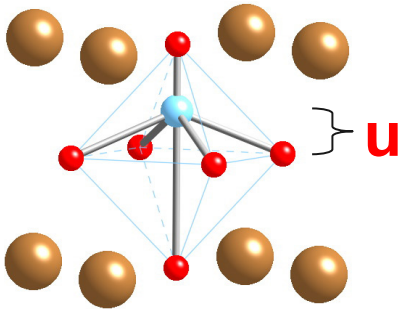
Balance between two competing forces:

- short-ranged repulsive forces favor centrosymmetric structure
- changes in chemical bonding favor ion off-centering

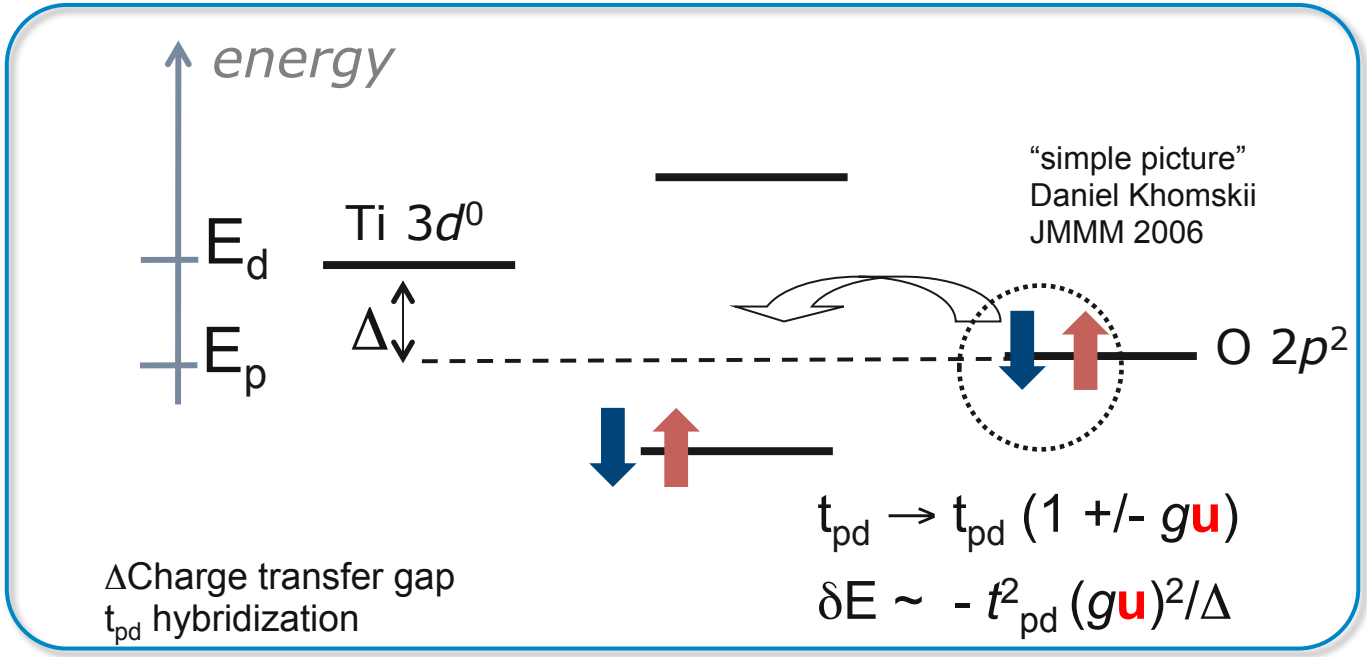
→ dipole-dipole interactions stabilize long-range order

Ron Cohen, Nature 1993

Nicola Spaldin, *Analogies and differences between ferroelectrics and ferromagnets*, in Topic in Advanced Physics V 105 (2007).



Change in hybridization of empty d-states with filled O p-states (2nd order Jahn-Teller)



Vibronic theory of ferroelectricity

- Electronic description for the local polar displacements is required
- Chemistry description via the second-order (pseudo-) Jahn-Teller Effect
  - Bersuker and Vekhter, *The vibronic theory of ferroelectricity*, Ferroelectrics, **19,** 137-150 (1978)
  - Pearson, Proc. Nat. Acad. Sci. **72**, 2104 (1975)
  - Burdett, Inorg. Chem. **20**, 1959 (1981)
  - Kunz and Brown, J. Solid State Chem. **115**, 395 (1995)

Small detour: microscopic mechanisms

Lets consider a Born-Oppenheimer system

$$H_e(r;Q) = T_e + V(r,Q)$$

$$H_e(r;Q)\psi_n(r;Q) = E_n(Q)\psi_n(r;Q)$$

$$M_I \frac{d^2 Q_I}{dt^2} = -\frac{\partial E_0(Q_j)}{\partial Q_I}$$

Vibronic theory: 1st and 2nd order Jahn-Teller

Expanding the Hamiltonian as a function of normal coordinate Q about the electronic Hamiltonian for the high symmetry reference phase,

$$E = E^{(0)} + \langle 0| \mathcal{H}^{(1)} |0\rangle Q + \frac{1}{2}[\langle 0| \mathcal{H}^{(2)} |0\rangle - 2\sum_n \frac{|\langle 0| \mathcal{H}^{(1)} |n\rangle|^2}{E^{(n)} - E^{(0)}}]Q^2 + \ldots$$

first-order JT does not give rise to FE distortions, *non-zero if orbitally degenerate*

second-order JT is a competition between two terms

Conventional mechanisms for inversion symmetry breaking

- Second-order Jahn-Teller effect

$$E = E^{(0)} + \boxed{} + \frac{1}{2}[\langle 0|\,\mathcal{H}^{(2)}\,|0\rangle - 2\sum_{n}\frac{|\,\langle 0|\,\mathcal{H}^{(1)}\,|n\rangle\,|^2}{E^{(n)} - E^{(0)}}]Q^2 + \ldots$$

second-order JT

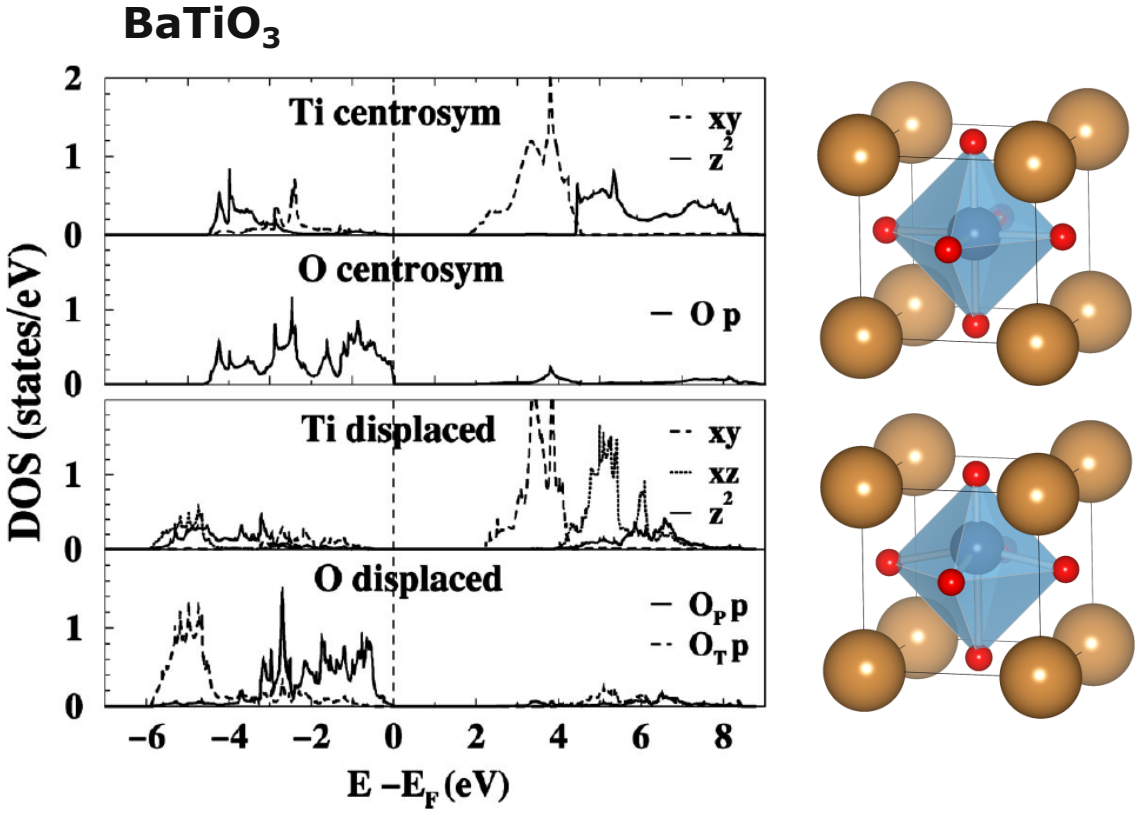
energy raising term describes the short-range repulsive forces and tends to be small in the case of d^0 cations

energy lowering term describes the relaxation of the electronic system to atomic displacements (bond formation)

polar displacements

Electronic/chemical mechanism for ferroelectricity

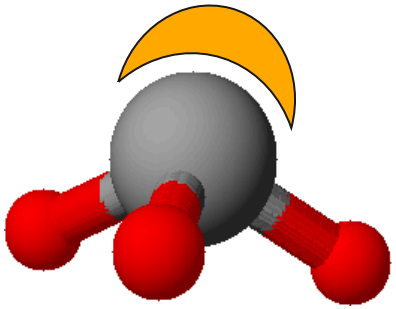
- Ti off-centering enhances cross-gap *p*-*d* hybridization



R.E. Cohen, Nature **358** 136 (1992)
A. Filippetti & N.A. Spaldin, Phys. Rev. B **65** 195120 (2002)

Electronic/chemical mechanism for ferroelectricity

- Second-order Jahn-Teller effect
  - Ligand field stabilization of empty cation *d*-orbitals by oxygen *p*-electrons
  - Polar cation displacements in d^0 metals (group 4, 5 or 6 transition metals)
  - Stereochemical lone pair activity (Tl^{+},Pb^{2+},Sn^{2+},Sb^{3+},Bi^{3+}, Se^{4+}, Te^{4+}) non-bonded electrons stabilized through *s*–*p* mixing



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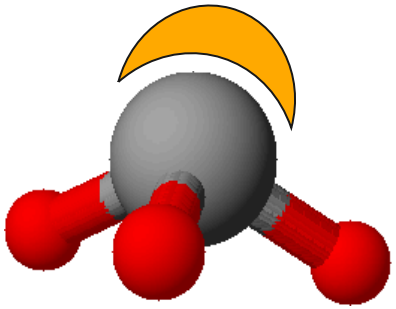


Recognized as early as 1950s by Matthias, that **large** ferroelectric polarizations require d^0-ness

B.T. Matthias, Phys. Rev. **75** 1771 (1949)

New Ferroelectric Crystals

B. T. MATTHIAS
Bell Telephone Laboratories, Murray Hill, New Jersey
April 18, 1949

THREE different groups of crystals are known which show an anomalous dielectric behavior somewhat analogous in their phenomenological aspects to ferromagnetism. The crystal groups are: Rochelle salts; KH_2PO_4 and the corresponding isomorphous crystals; and barium titanate and its solid solutions with the strontium and lead salts.

The mechanism responsible for the high dielectric constant in the first two groups is generally considered to be associated with hydrogen bonds, whereas in $BaTiO_3$ the high polarizability of the TiO_6 octahedras combined with the polarizability of BaO is thought to be responsible for the occurrence of a spontaneous polarization.[1] The latter assumption is reasonable in view of the high dielectric constants of rutile and BaO.

As expressed previously[2] the occurrence of ferroelectricity in Rochelle salt and $BaTiO_3$ seems to be of an accidental nature, insofar as none of their isomorphous crystals are ferroelectric. In the case of $BaTiO_3$ it was thought probable that crystals would be ferroelectric, regardless of valency, if the metal-oxygen octahedra were of identical size and of similar electronic configuration to the Ti-O_6 octahedra in $BaTiO_3$. From this point of view the metals columbium and tantalum appeared to be of interest. Both the Cb^{+5} and Ta^{+5} ions have a noble gas configuration similar to Ti^{+4} and have the same octahedral radii. In the fourth row of the periodic table Ga^{+3} might be considered, though it is slightly smaller and its electronic core, although having closed shells, has not a noble gas

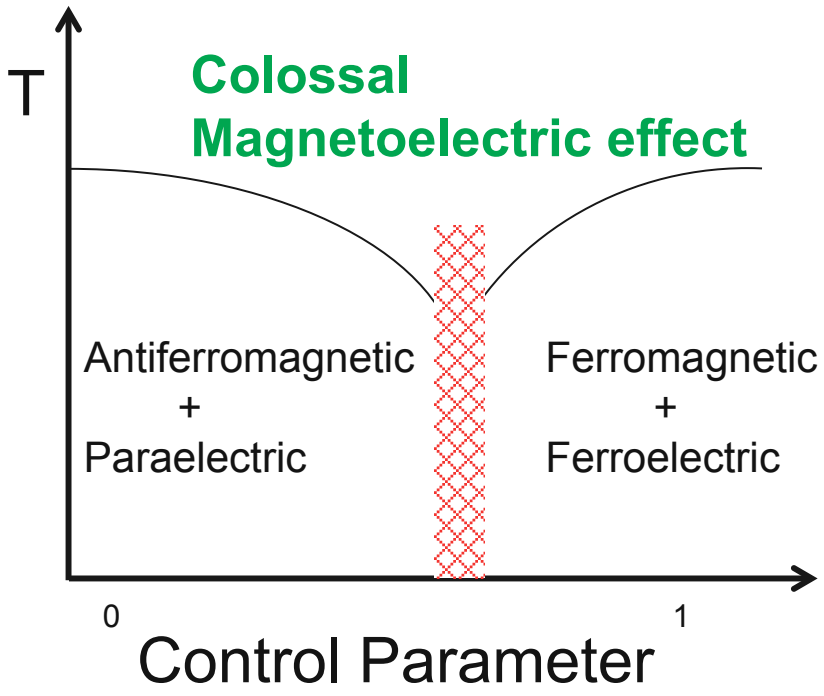
Chemistries that favor this form of ferroelectricity are problematic for magnetism and in turn M&Ms

Requires un-paired electrons. Consider: $LaMnO_3$, Mn^{3+} has $3d^4 4s^0$ electronic configuration

Generic paradigm to design new multiferrroic

Start with AFM-PE material and tune to a FM-FE phase

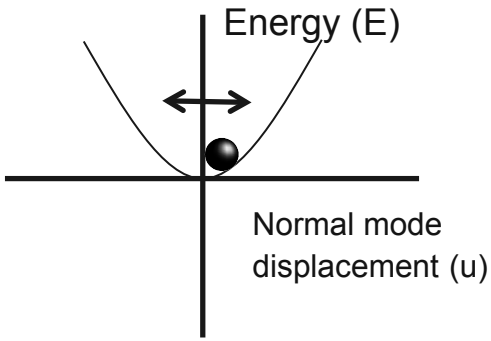
1. *Identify microscopic mechanism to achieve coupling of order parameters*
2. *Identify tuning mechanism*
3. *Identify material realization*



Soft-mode theory of ferroelectricity

Born and Huang, 1954, W. Cochran, Phys. Rev. Lett. 1959

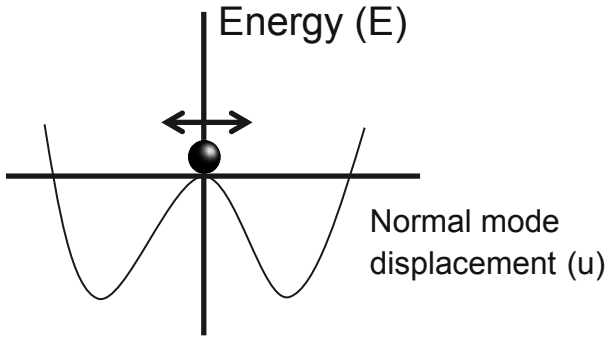
Stable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} > 0$$

→ Paraelectric
at T = 0

Unstable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$

→ Ferroelectric
at T = 0

Keep in mind we want the ground state to be PE, but also want a way of tuning to the FE border, how?

Where ω is an infrared-active phonon frequency

Outline: Part 1 and Part 2

A. Introduction to multifunctional materials

B. Phase Competition: a Generic paradigm to achieve colossal responses
   1. Basics of proper ferroelectricity: Landau theory phenomenology, Structural phase transitions, and Microscopic mechanism
   2. Strain tuning: controlling ferroelectricity with strain and improper ferroelastics
   3. Spin- phonon coupling → ~ P^2M^2 interaction by design
   4. Spin-lattice coupling → ~ $P \cdot L \times M$ interaction by design

C. Octahedral rotation induced antiferroelectricity as the origin hybrid improper ferroelectricity, or more accurately, ferrI-electricity (i.e., how to make Pnma perovskites useful:-)
   1. Octahedral rotations in perovskites
   2. Basics of improper ferroelectricity: primary lattice, secondary polarization
   3. hybrid improper ferroelectricity

Detour – Tuning perovskite ferroelectrics: Pressure

VOLUME 35, NUMBER 26 PHYSICAL REVIEW LETTERS 29 DECEMBER 1975

Important Generalization Concerning the Role of Competing Forces in Displacive Phase Transitions

G. A. Samara*
Sandia Laboratories, Albuquerque, New Mexico 87115

and

T. Sakudo
Electrotechnical Laboratory, Tanashi, Tokyo, Japan

and

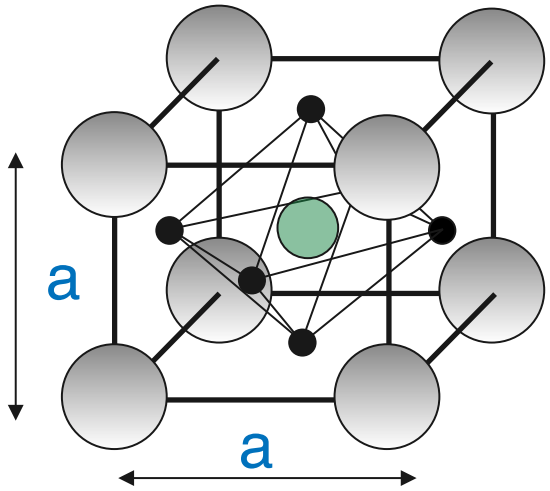
K. Yoshimitsu
Department of Physics, Kwansei Gakuin University, Nishinomiya, Japan
(Received 19 August 1975)

Positive pressure→ smaller volume

short-range repulsive forces increase faster than long range dipole-dipole interactions ⇒ FE soft-mode hardens

For a modern first-principles take see work by Ph. Ghosez on e.g., $BaTiO_3$

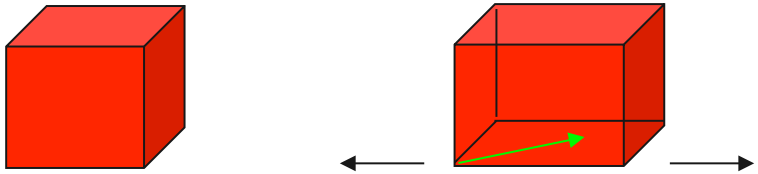
Detour – Epitaxial strain-induced ferroelectricity



$Sr^{2+}Ti^{4+}O_3$

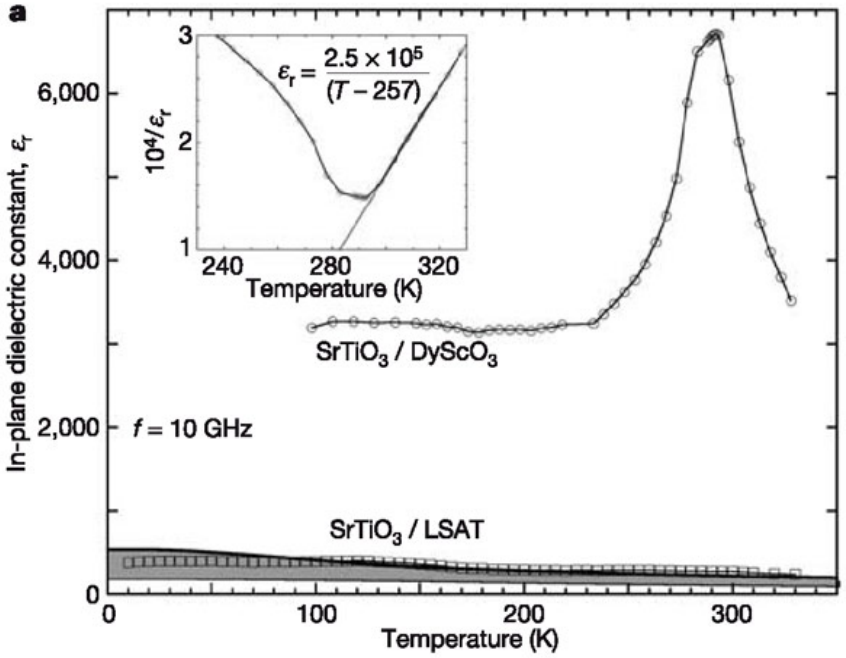
- In bulk: paraelectric (PE) ground state (cubic)

- epitaxially strained film: room temperature ferroelectric (FE) (Nature 2004, Schlom et al.)



Cubic
(Unstrained)
Paraelectric

Tensile-strain
Ferroelectric aa-phase

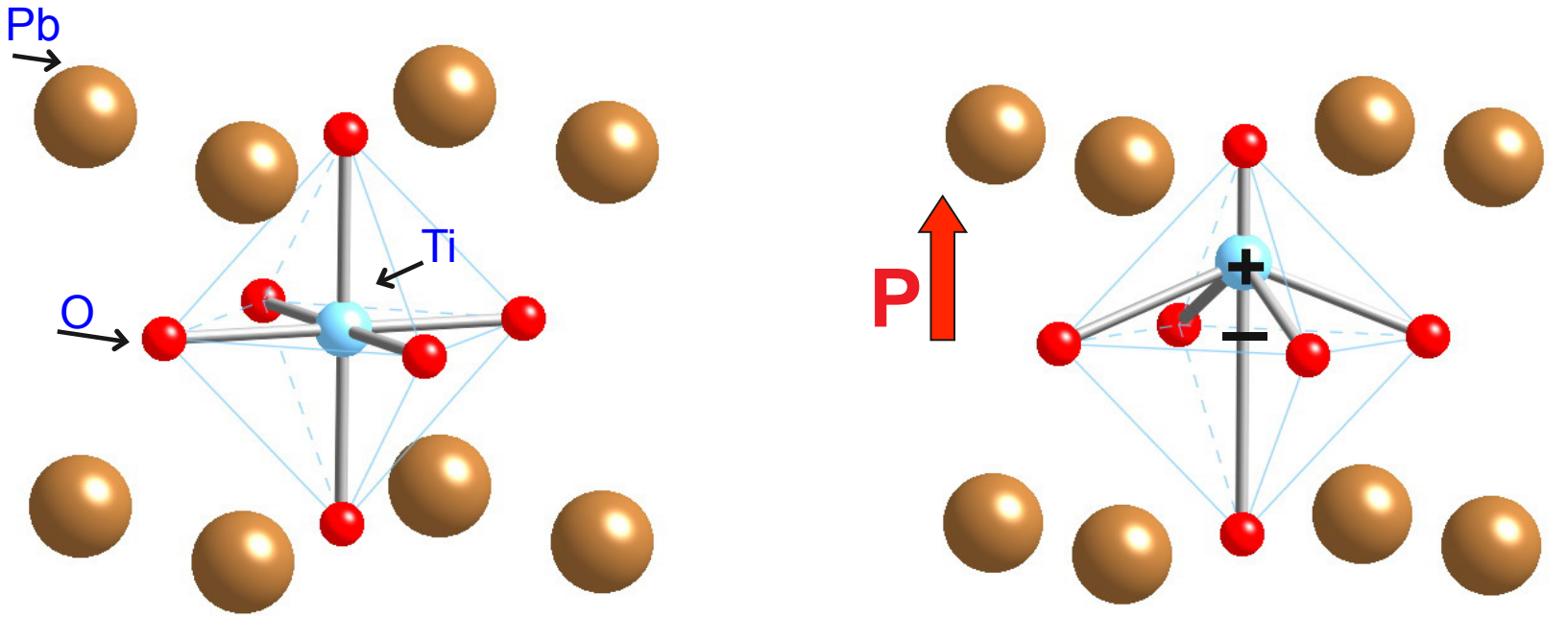


Detour – Tuning perovskite ferroelectrics

Why strain and ferroelectricity are naturally coupled and how to account for the coupling

Detour – Symmetry lost at transition

So ferroelectricity in the cubic perovskite like $PbTiO_3$ is associated with the instability of a Γ_{15} mode, i.e., a polar lattice distortion, is translational symmetry changed?



cubic-paraelectric
Space group Pm3m

tetragonal-ferroelectric
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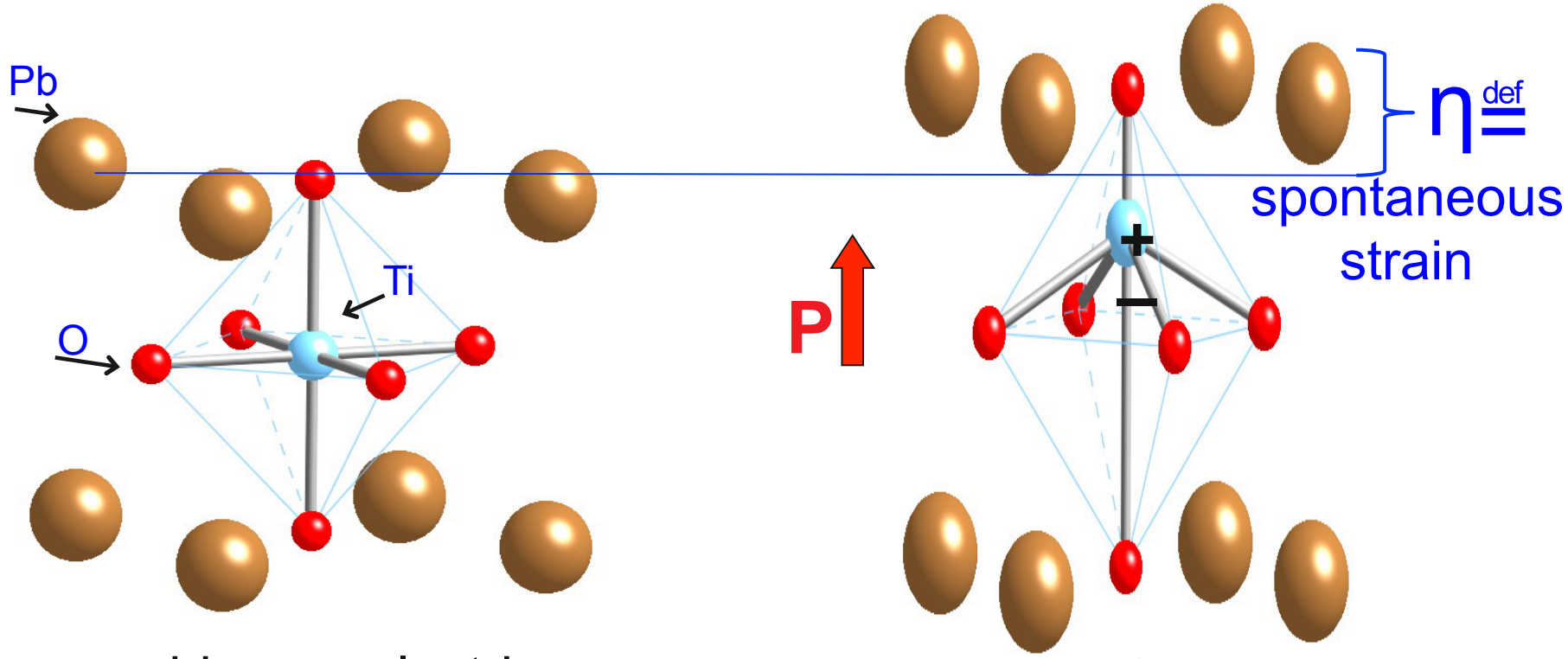
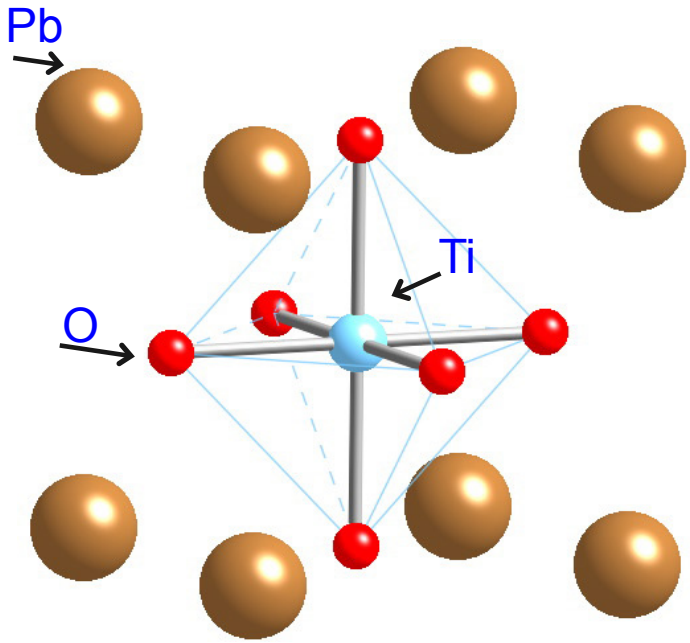
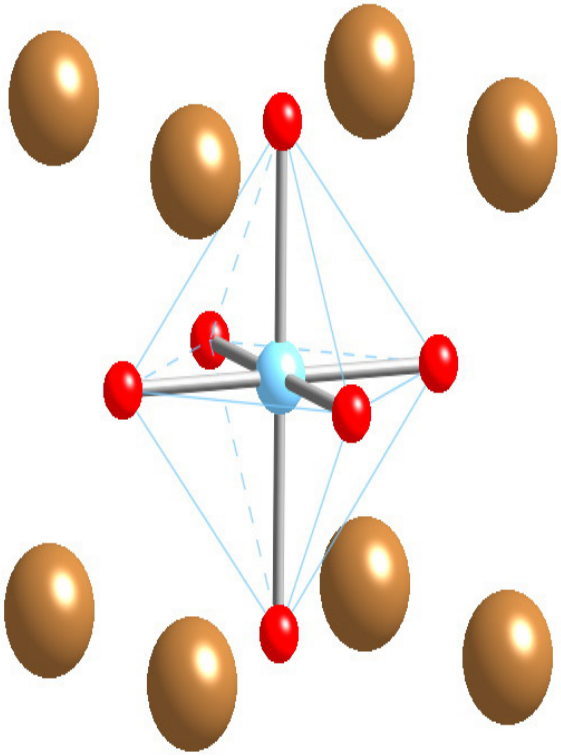


Detour – Symmetry lost at transition

So ferroelectricity in the cubic perovskite like $PbTiO_3$ is associated with the instability of a Γ_{15} mode, i.e., a polar lattice distortion, is translational symmetry changed?





cubic-paraelectric
Space group Pm3m

Tetragonal-paraelectric
Space group P4/mmm

Detour – Improper ferroelastic transition: phenomenology

$BaTiO_3$ and $PbTiO_3$ have a proper ferroelectric transition, but an improper ferroelastic transition

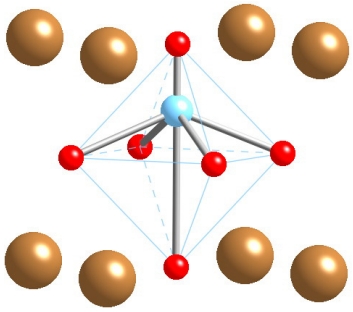
Primary order parameter	Secondary order parameter
Spontaneous polarization P	Spontaneous strain ε

(note energy expansion for cubic-to-tetragonal pt, simplified for pedagogy)

$$\mathcal{F}(P, \varepsilon) = a_1 P^2 + c_1 P^4 + a_2 \varepsilon^2 + b_1 \varepsilon P^2$$

$$\partial \mathcal{F} / \partial \varepsilon = 2 a_2 \varepsilon + b_1 P^2 = 0$$

$$\varepsilon_{eq} \sim - P^2$$



Once P becomes nonzero, a strain is induced

Internal energy from first principles

Internal energy as a function of FE distortion, u, and strain, ε

$$\mathcal{E}(u, \varepsilon) = -\omega^2_0 u^2 + Bu^4 + C\varepsilon u^2$$

Neglecting strain: Both $BaTiO_3$ and $PbTiO_3$ have rhombohedral ground states, in contradiction to experiment!

In $PbTiO_3$, polarization-strain coupling is essential to observe tetragonal ground state

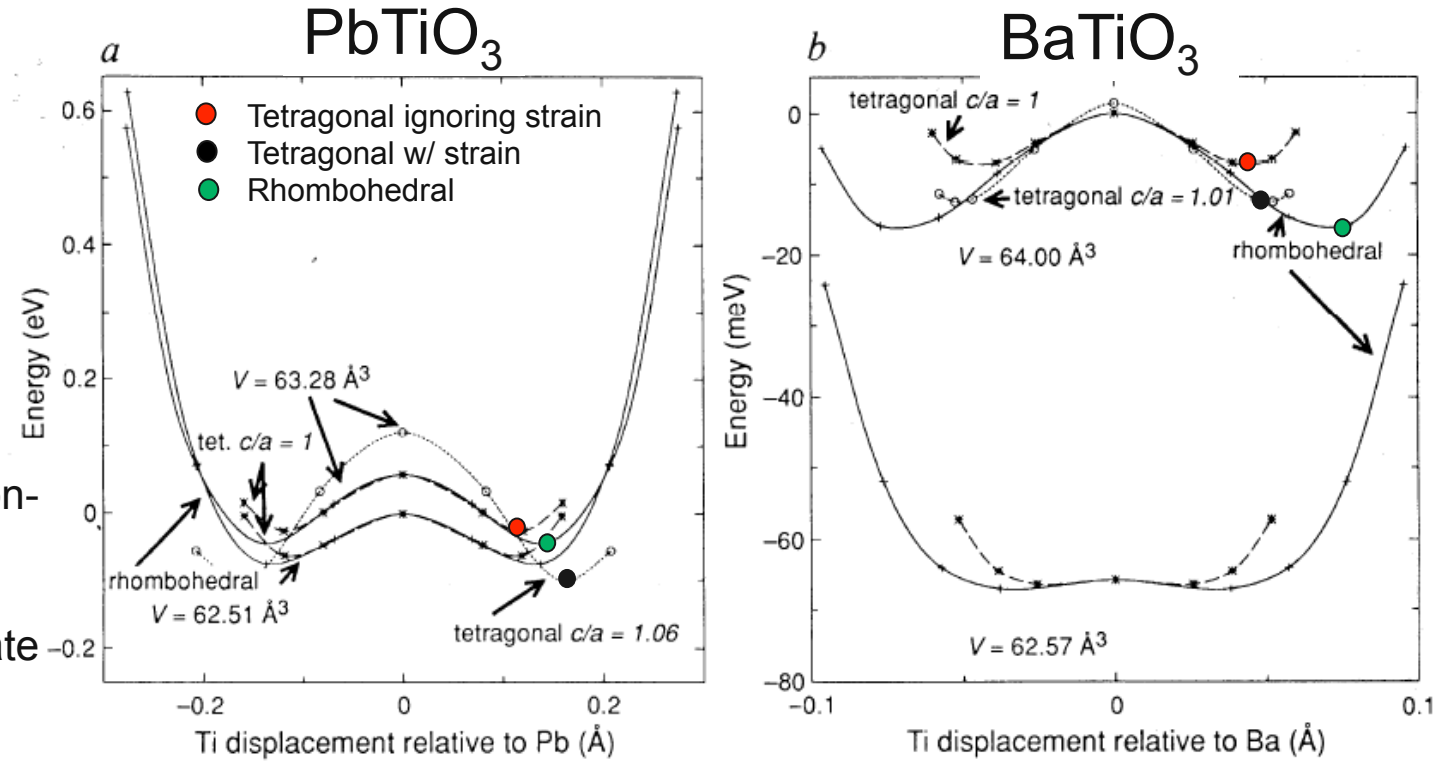
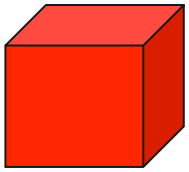


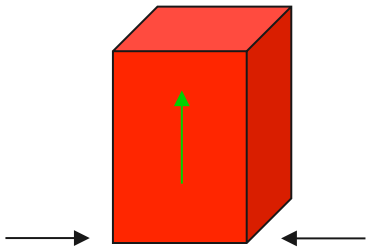
Fig 1, page 137; Ron Cohen, *Origin of ferroelectricity in perovskite oxides*, Nature **358**: 136-138 (1992).

Detour – Tuning perovskite ferroelectrics: Strain

For the case of biaxial strain, i.e., $\eta_x = \eta_y \equiv \eta$



Cubic
(Unstrained)



Compressive strain

$$\mathcal{F}(P_z, \eta) = \kappa P_z^2 + c_1 P_z^4$$ (note energy expansion simplified for pedagogy, see Dieguez et al PRB 2005 for full details) — Soft-mode

$$+ \tfrac{1}{2}\beta_{11}(2\eta^2 + \eta_z^2) + \tfrac{1}{2}\beta_{12}(\eta^2 + 2\eta\eta_z)$$ — Elastic

$$+ \beta_{1xx}(2\eta P_{xy}^2 + \eta_z P_z^2)$$ — Coupling

$$\partial\mathcal{F}/\partial\eta_z = \beta_{11}\ \eta_z + \beta_{12}\ 2\eta + \beta_{1xx}\ P_z^2$$

$$\Rightarrow \eta_z \sim -\beta_{12}/\beta_{11}\ \eta$$

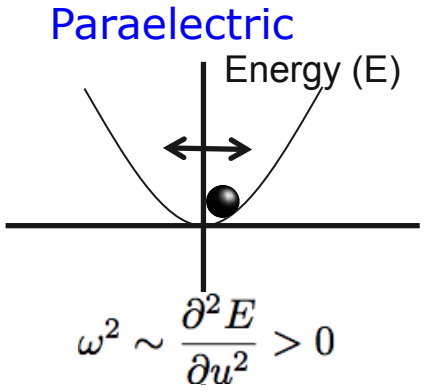
$$\Rightarrow \boldsymbol{\kappa} \longrightarrow \boldsymbol{\kappa} + -\beta_{1xx}\beta_{12}/\beta_{11}\ \boldsymbol{\eta}$$

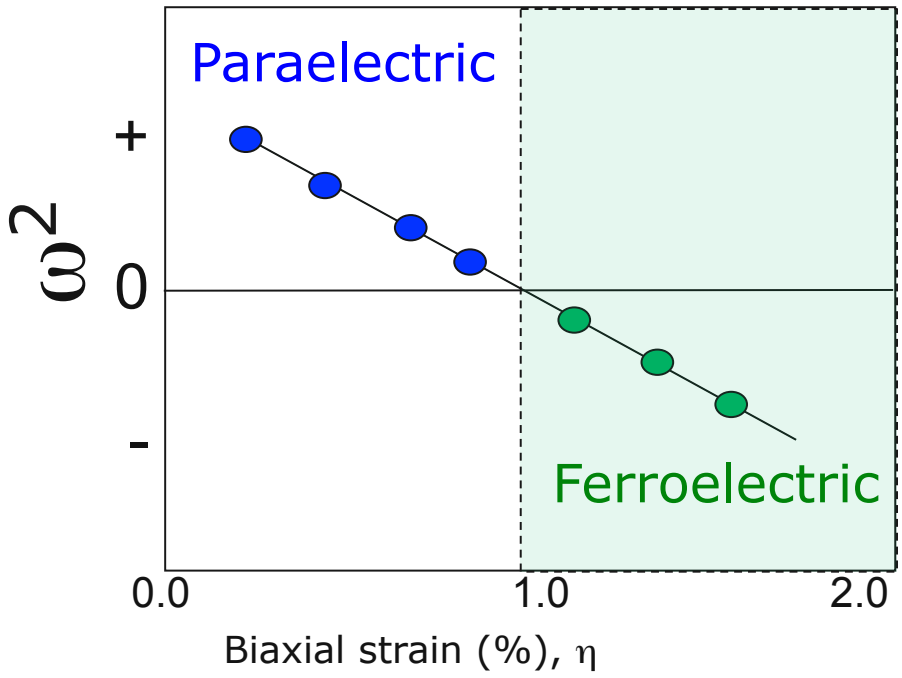
Soft-mode "frequency" gets renormalized by epitaxial strain

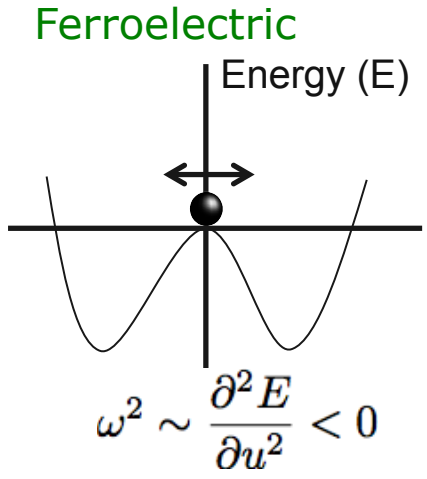
Detour – Strain-induced ferroelectricity

Strain couples strongly to the lowest polar mode "polarization-strain coupling" (Cohen, Nature 1992)

In paraelectric phase → epitaxial-strain-induced ferrroelectricity

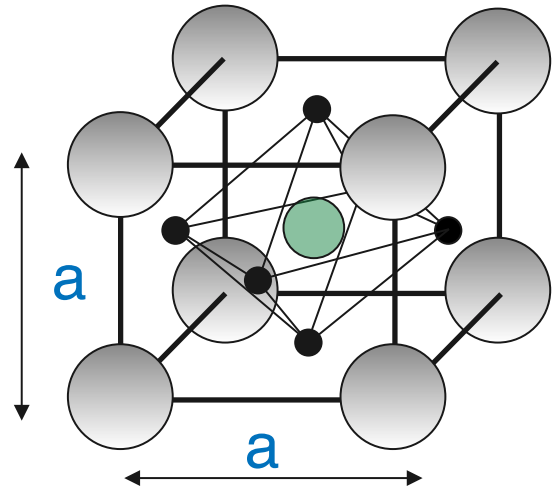






For example, Strain-induced ferroelectricity in $SrTiO_3$, *Nature* 2004, Schlom group

Detour – Epitaxial strain-induced ferroelectricity



$Sr^{2+}Ti^{4+}O_3$

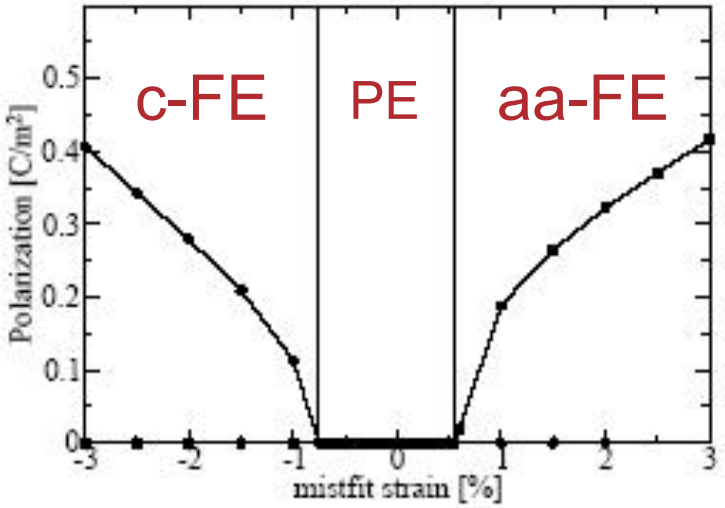
- In bulk: paraelectric (PE) ground state (cubic)

- epitaxially strained film: room temperature ferroelectric (FE) (Nature 2004, Schlom et al.)

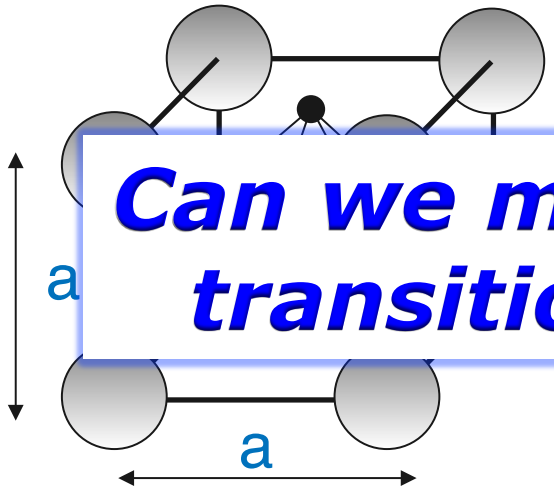
First-principles epitaxial strain-induced ferroelectricity (Antons, PRB 2004)

Compressive
Ferroelectric c-phase

Tensile
Ferroelectric aa-phase



Detour – Epitaxial strain-induced ferroelectricity



$Sr^{2+}Ti^{4+}O_3$

- In bulk: paraelectric (PE) ground state

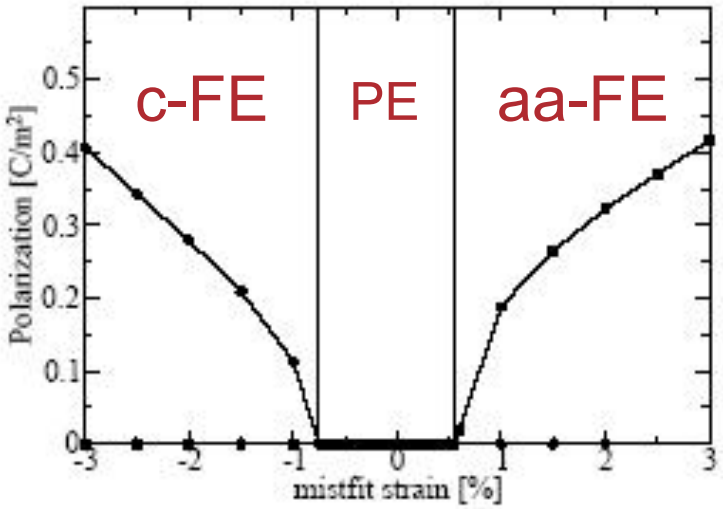
Can we make the ferroelectric transition spin dependent?

2004, Schlom et al.)

First-principles epitaxial strain-induced ferroelectricity (Antons, PRB 2004)

Compressive
Ferroelectric c-phase

Tensile
Ferroelectric aa-phase



Outline: Part 1 and Part 2

A. Introduction to multifunctional materials

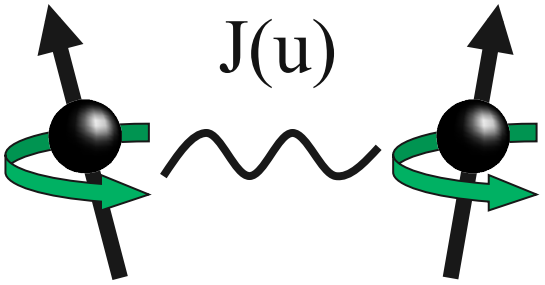
B. Phase Competition: a Generic paradigm to achieve colossal responses
   1. Basics of proper ferroelectricity: Landau theory phenomenology, Structural phase transitions, and Microscopic mechanism
   2. Strain tuning: controlling ferroelectricity with strain and improper ferroelastics
   3. Spin- phonon coupling → ~ P^2M^2 interaction by design
   4. Spin-lattice coupling → ~ P·L×M interaction by design

C. Octahedral rotation induced antiferroelectricity as the origin hybrid improper ferroelectricity, or more accurately, ferrI-electricity (i.e., how to make Pnma perovskites useful:-)
   1. Octahedral rotations in perovskites
   2. Basics of improper ferroelectricity: primary lattice, secondary polarization
   3. hybrid improper ferroelectricity

Spin-phonon coupling: Novel way to achieve phase control

Phonon modulated exchange interaction

Baltensperger and Helman, Helvetica physica acta 1968.

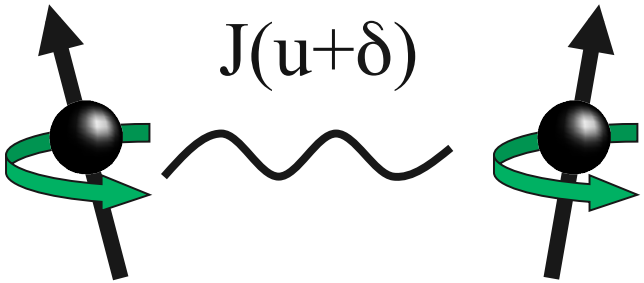


$$\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_{phonon} + \mathcal{E}_{spin}$$

$$\mathcal{E}_{ph} = 1/2\ \omega_0^2 u^2$$

$$\mathcal{E}_{sp} = -\sum J_{ij} \langle S_i \cdot S_j \rangle$$

$$J(u) \approx J(0) + 1/2\ \partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle\ u^2$$



$$\Rightarrow \quad \omega^2 \propto \omega_0^2 - \partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle$$

renormalized phonon | bare phonon | magnetic contribution

e.g. can understand large spin-phonon coupling in $ZnCr_2O_4$
Fennie and Rabe, Phys. Rev Lett. May 2006

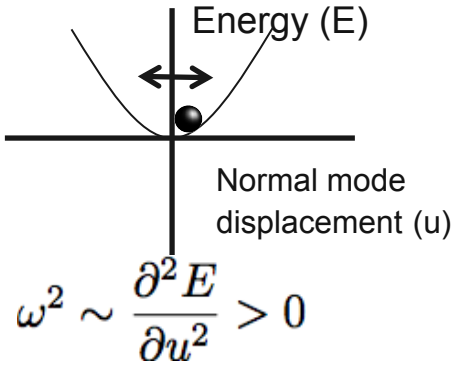
Spin-phonon coupling: Novel way to achieve phase control

With control parameter take $\omega_0 = 0$

$$\Rightarrow \quad \omega^2 \propto -\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle$$

AFM $\rightarrow \langle S_i \cdot S_j \rangle = -1$

Stable phonon

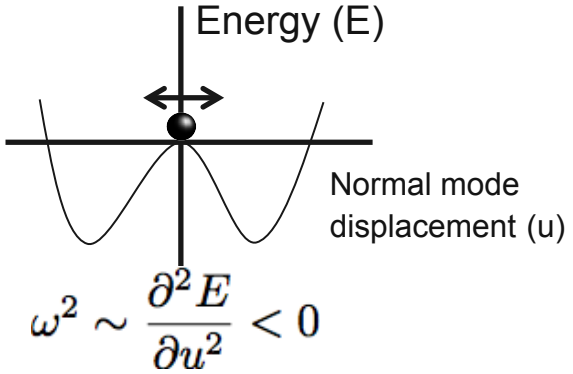


$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} > 0$$

→ Antiferromagnetic, Paraelectric

FM $\rightarrow \langle S_i \cdot S_j \rangle = +1$

Unstable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$

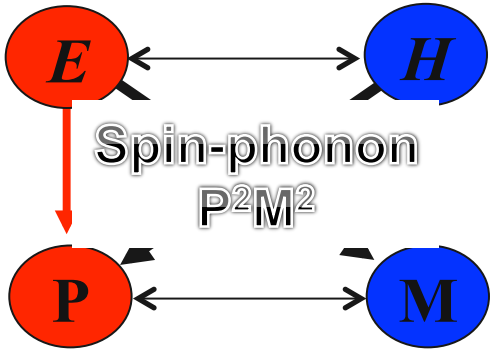
→ Ferromagnetic, Ferroelectric

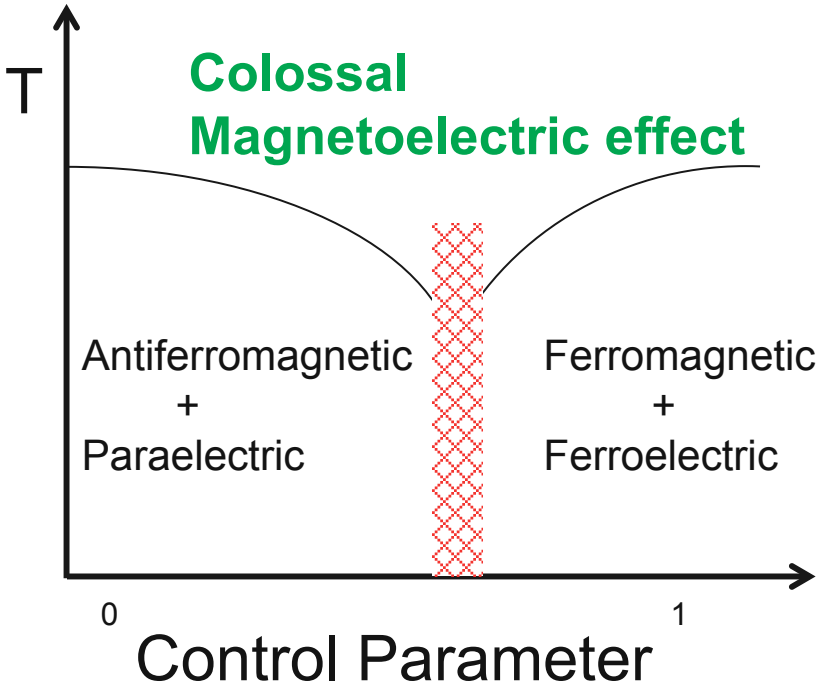
Leads to a FM-FE state competing with the AFM-PE ground state

Generic paradigm to design new multiferrroic

Start with AFM-PE material and tune to a FM-FE phase

1. *Identify microscopic mechanism to achieve coupling of order parameters*

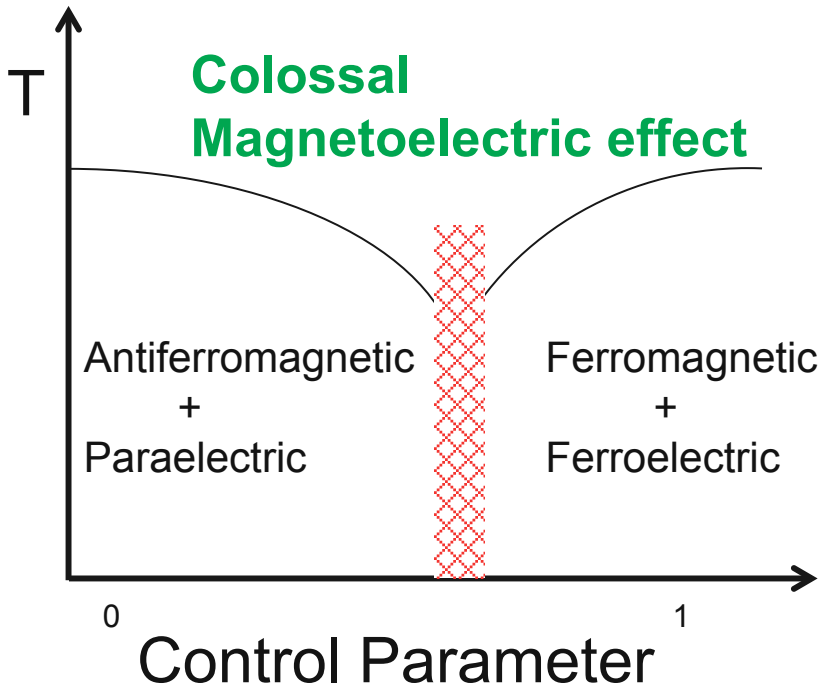




Generic paradigm to design new multiferrroic

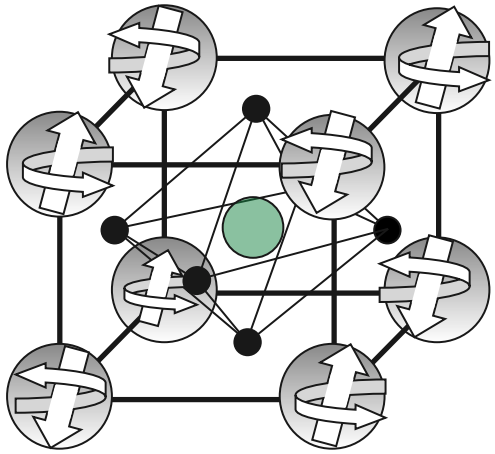
Start with AFM-PE material and tune to a FM-FE phase

1. *Identify microscopic mechanism to achieve coupling of order parameters*
2. *Identify tuning mechanism*
3. *Identify material realization*



$EuTiO_3$ magnetocapacitance

Bulk $Eu^{2+}Ti^{4+}O_3$: Ground state
antiferromagnetic paraelectric

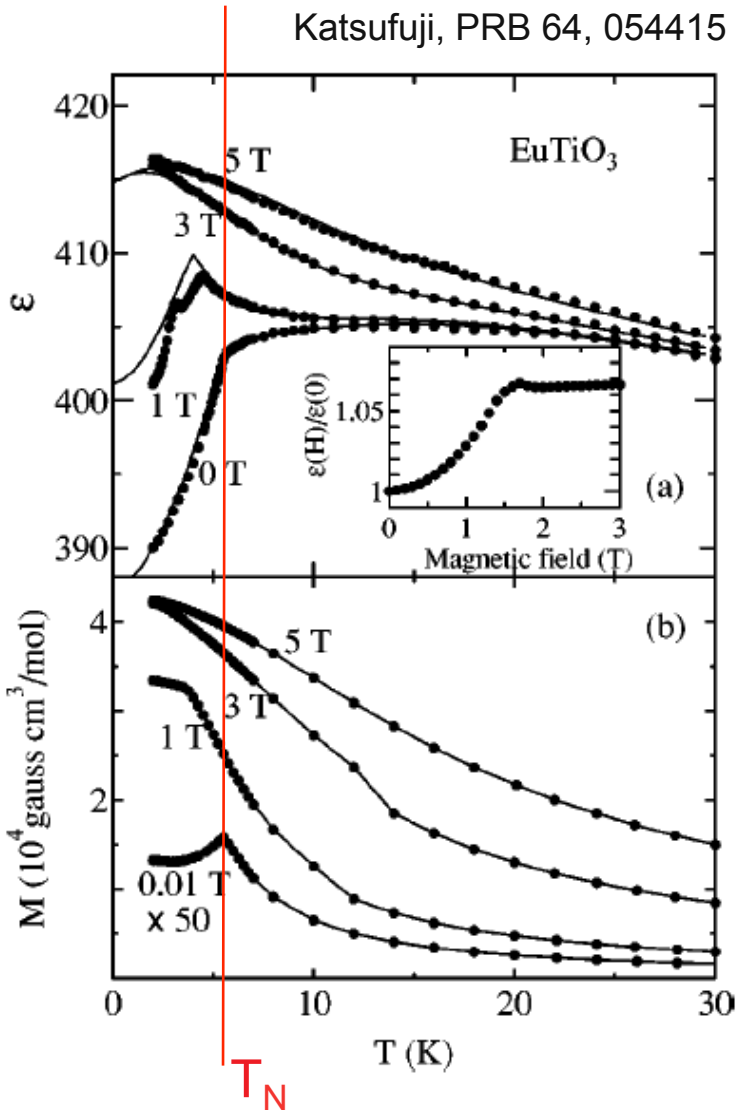


- $r(Eu^{2+}) \sim r(Sr^{2+})$; Cubic perovskite
- $Eu^{2+} \rightarrow J=S=7/2$; $T_n \sim 5.5K$, G-type AFM

$$\epsilon^0_{\alpha\beta} = \epsilon^\infty_{\alpha\beta} + \frac{4\pi}{\Omega_0} \sum_{\mathrm{m}} \frac{p_{m\alpha} \cdot p_{m\beta}}{\omega^2_{\mathrm{m}}} ,$$

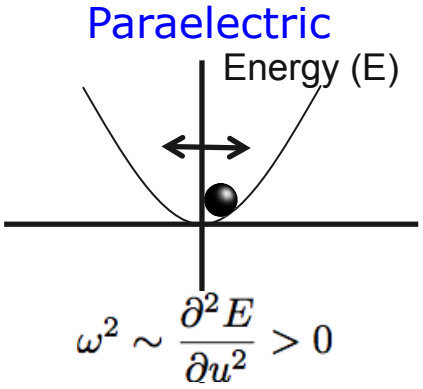
$$\text{where } p_{m\alpha} = \textstyle\sum_{\kappa\beta} Z_{\kappa\beta,\alpha} \xi^m_{\kappa\beta} / \sqrt{M_\kappa}$$

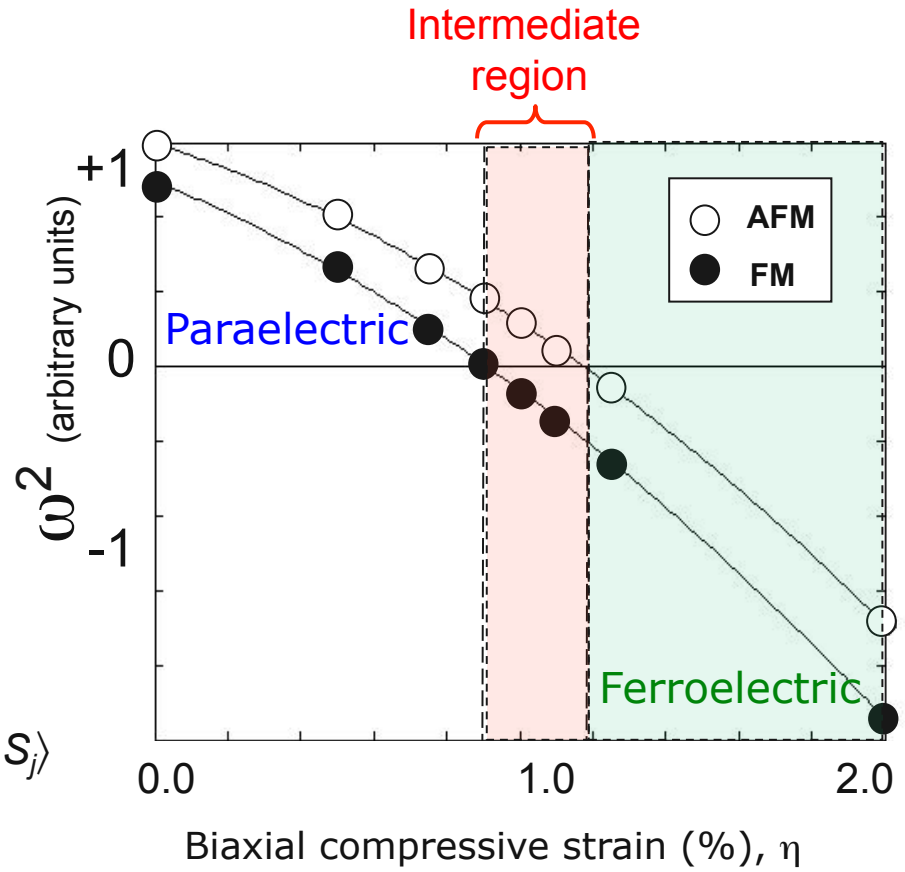
Katsufuji, PRB 64, 054415

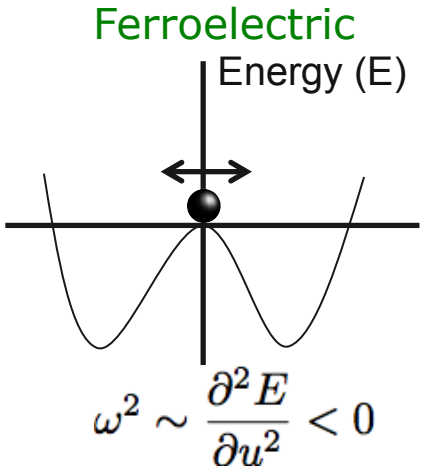


$EuTiO_3$: Soft-phonon frequency vs. epitaxial strain from first principles

C.J. Fennie and K.M. Rabe, *Physical Review Letters* **97** (2006) 267602







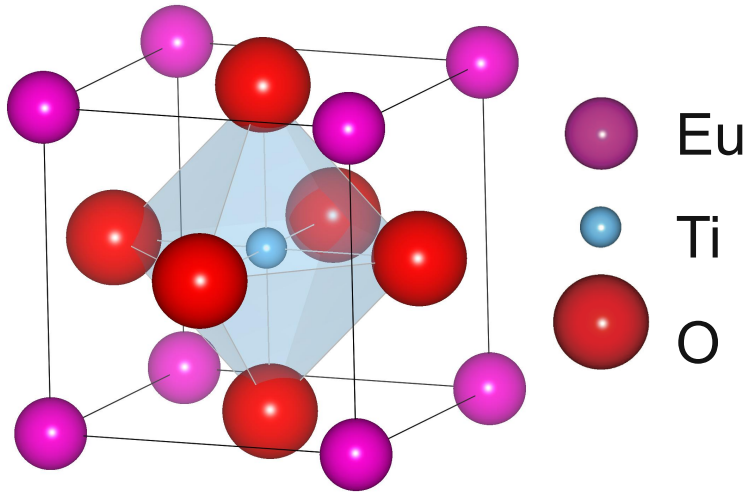
$\omega^2 \propto \omega_0^2 - \partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle$

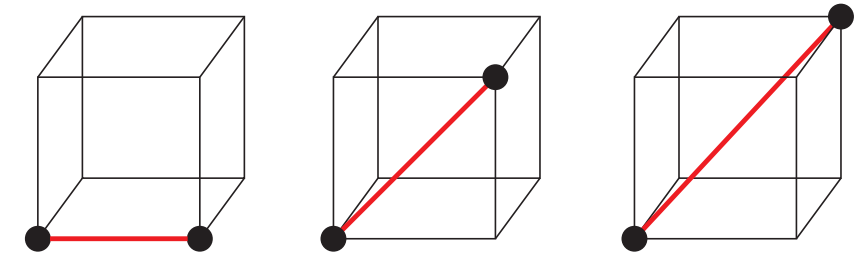
Note: FM refers to calculation with spins fully aligned.

Spin–Phonon Coupling in $EuTiO_3$

$EuTiO_3$ is an insulating antiferromagnet.

It is different from other materials with spin – phonon coupling: Polar mode involves displacement of Ti ions, while magnetization involves Eu ions.

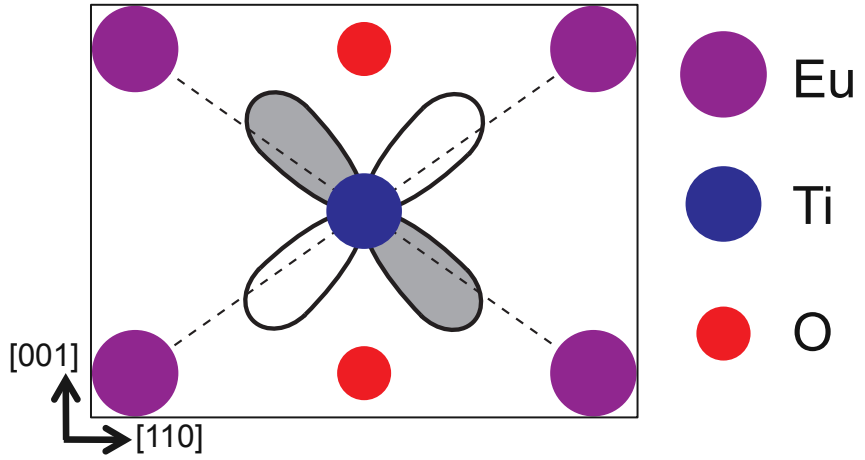


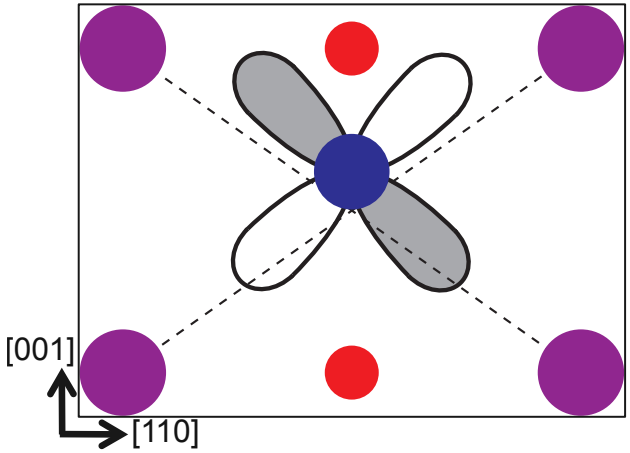


The AFM state is stabilized by a unique superexchange mechanism, which connects the first three nearest neighbors.

Spin–Phonon Coupling in $EuTiO_3$

Electrons from Eu-f orbitals are virtually excited to Ti-d orbitals and then to the f orbitals of another Eu ion, leading to an antiferromagnetic superexchange.

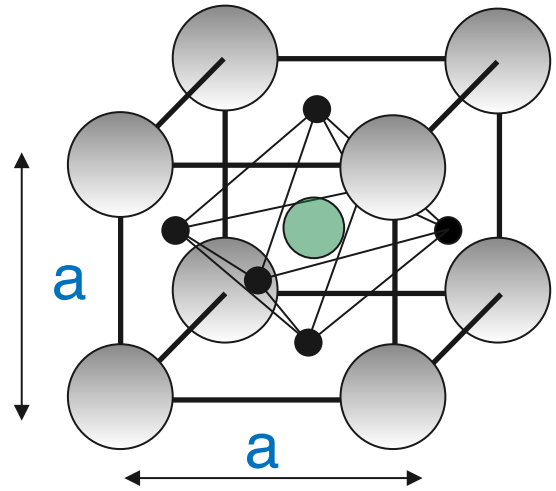




The strength of this antiferromagnetic tion-mediated superexchange depends very sensitively on the overlap of Ti-d and Eu-f orbitals, and decreases when Ti atom is displaced from the center of the cell. So, energy cost of the polar distortion is smaller when the system is FM.

Polar mode softens in the FM state.

Detour – Epitaxial strain-induced ferroelectricity



$Sr^{2+}Ti^{4+}O_3$

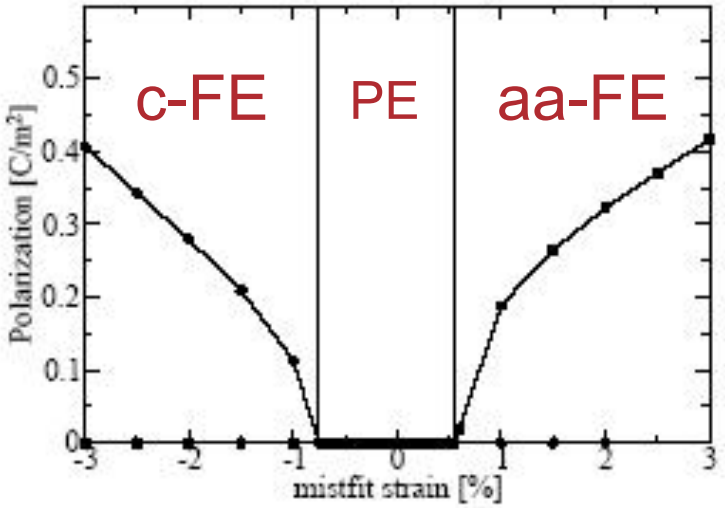
- In bulk: paraelectric (PE) ground state (cubic)

- epitaxially strained film: room temperature ferroelectric (FE) (Nature 2004, Schlom et al.)

First-principles epitaxial strain-induced ferroelectricity (Antons, PRB 2004)

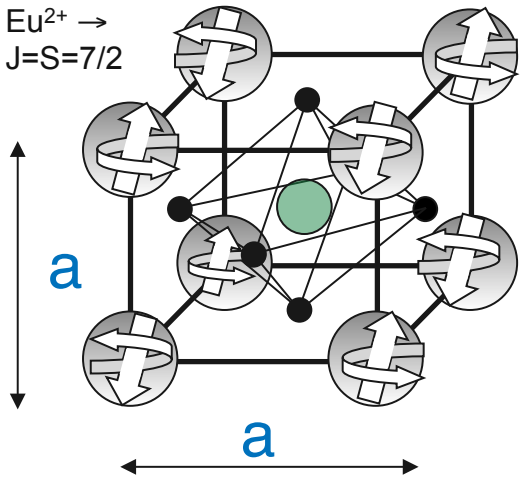
Compressive
Ferroelectric c-phase

Tensile
Ferroelectric aa-phase



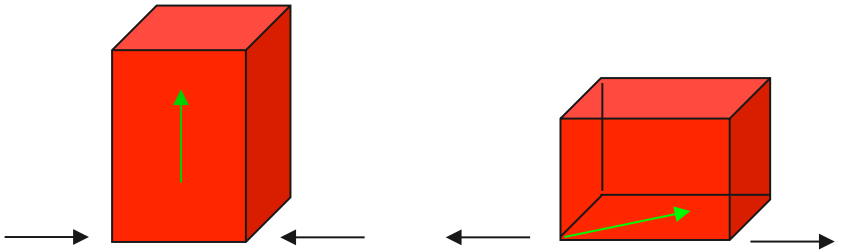
$EuTiO_3$: A new paradigm in strain-enabled multiferroics

C.J. Fennie and K.M. Rabe, *Physical Review Letters* **97** (2006) 267602



$Eu^{2+}Ti^{4+}O_3$

- In bulk: paraelectric (PE) and antiferromagnetic (AFM)
- Epitaxially strained thin film: ferroelectric (FE) and ferromagnetic (FM)



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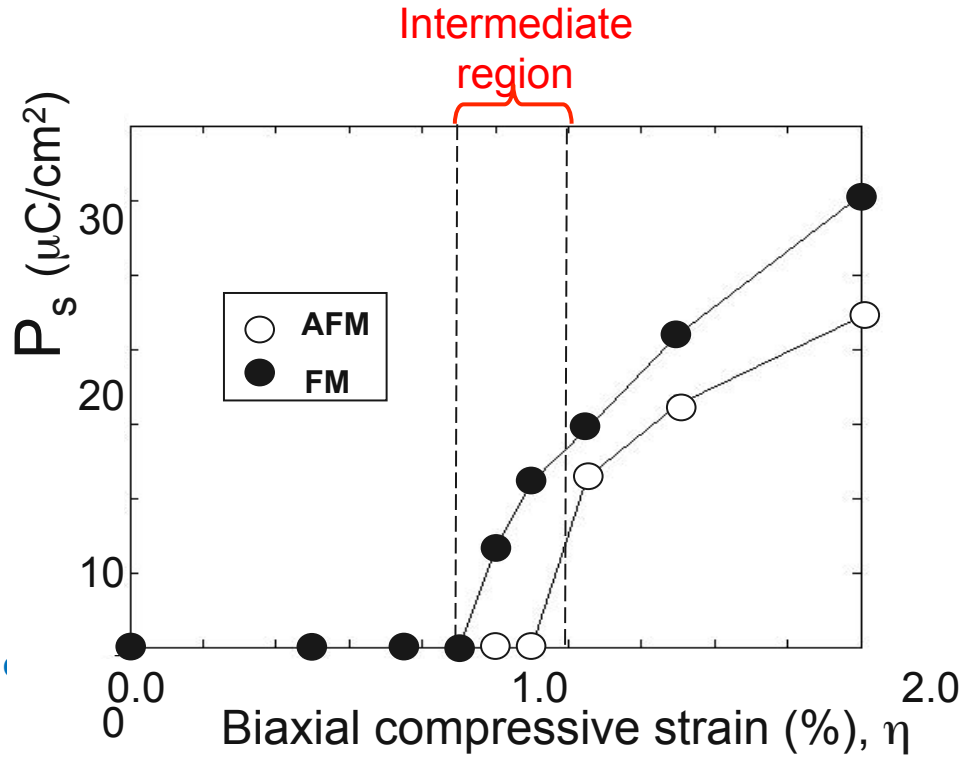
Ferroelectric c-phase

Tensile
Ferroelectric aa-phase

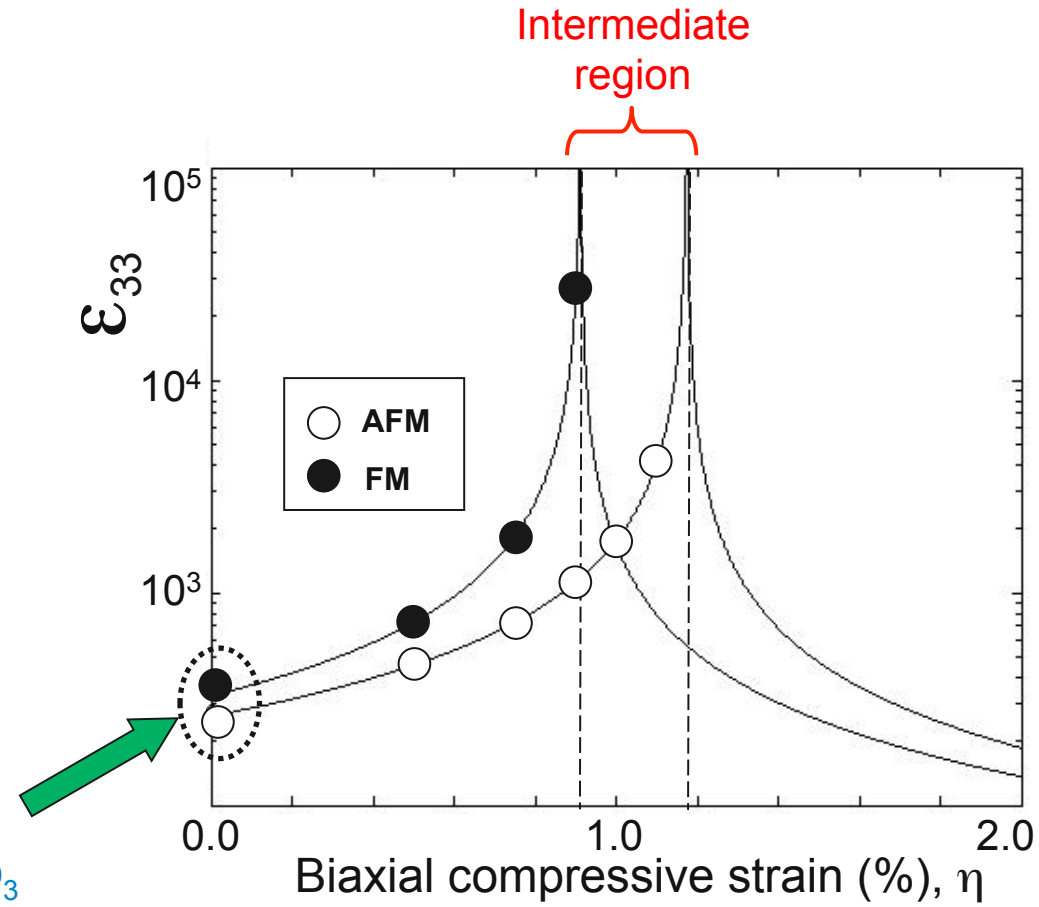


$EuTiO_3$: Static dielectric constant vs. strain

Intrinsic static dielectric constant

$$\epsilon = \epsilon_\infty + \sum_n \frac{\Omega_{p,n}^2}{\omega_n^2}$$

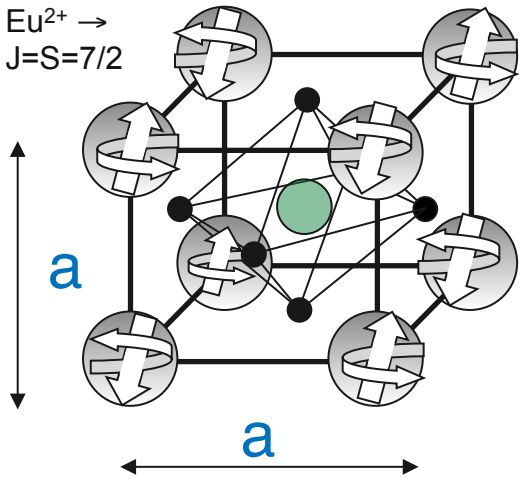
Where ω_n is ir-active phonon frequency



* Explains measured magneto-permittivity in bulk ceramic $EuTiO_3$
Katsufuji and Takagi, PRB 2001

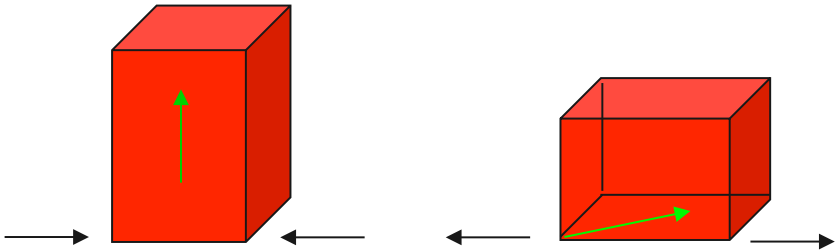
$EuTiO_3$: A new paradigm in strain-enabled multiferroics

C.J. Fennie and K.M. Rabe, *Physical Review Letters* **97** (2006) 267602



$Eu^{2+}Ti^{4+}O_3$

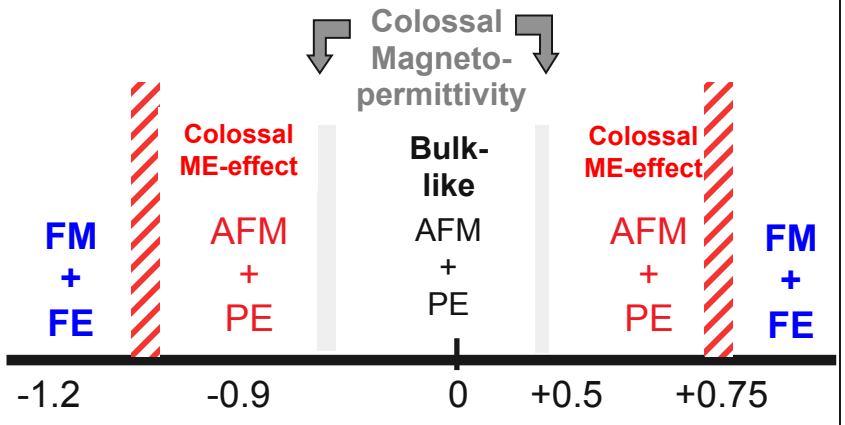
- In bulk: paraelectric (PE) and antiferromagnetic (AFM)
- Epitaxially strained thin film: ferroelectric (FE) and ferromagnetic (FM)



Compressive
Ferroelectric c-phase

Tensile
Ferroelectric aa-phase

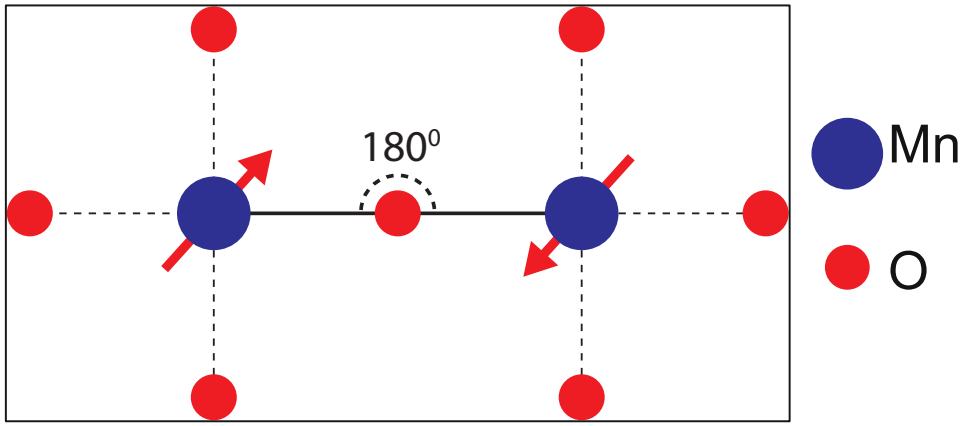
Epitaxially strained film
Rich magnetoelectric phase diagram due to spin-lattice coupling predicted from first principles

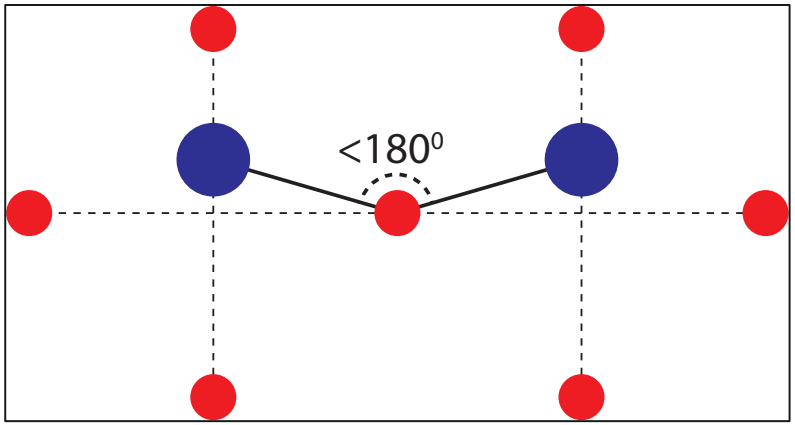


Spin–Phonon Coupling in $SrMnO_3$

$SrMnO_3$ is an insulating antiferromagnet.

Mn – O – Mn angle is 180^0 and the resulting superexchange is antiferromagnetic.





Polar distortion decreases the Mn – O – Mn angle, and weakens the AFM superexchange.

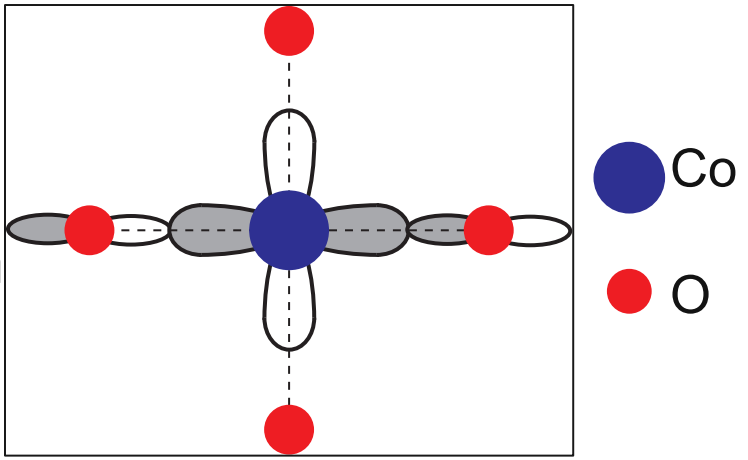
The energy cost of this displacement is lower in the FM state.

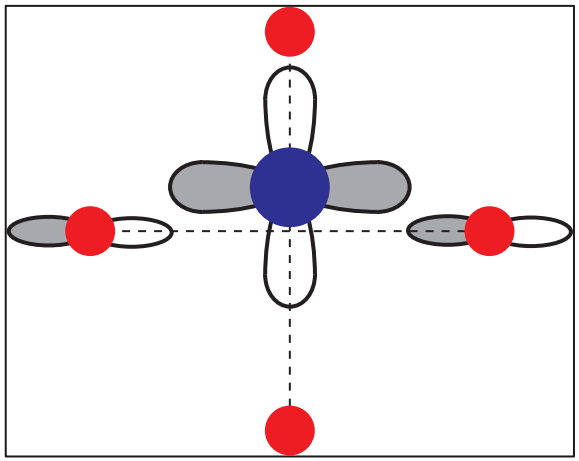
Polar mode softens in the FM state.

Spin–Phonon Coupling in $SrCoO_3$

$SrCoO_3$ is a metallic ferromagnet.

The ferromagnetic Zener double exchange depends very sensitively on the overlap between Co-d and O-p orbitals.





Polar distortion decreases the overlap between Co-d and O-p orbitals, and weakens the FM double exchange.

The energy cost of this displacement is lower in the AFM state.

Polar mode softens in the AFM state.

"it takes a village …"

"Creating a Strong Ferroelectric Ferromagnet via Spin-Lattice Coupling"
Nature 466, 954-958 (2010).

J. H. Lee[1,2], L. Fang[3], E. Vlahos[2], X. Ke[4], Y. W. Jung[3], L. Fitting Kourkoutis[5], J.W. Kim[6], P. Ryan[6], T. Heeg[1], M. Roeckerath[7], V. Goian[8], M. Bernhagen[9], R. Uecker[9], P. C. Hammel[3], K. M. Rabe[10], S. Kamba[8], J. Schubert[7], J. W. Freeland[6], D. A. Muller[5], C. J. Fennie[5], P. Schiffer[4], V. Gopalan[2], E. Johnston-Halperin[3] & D. G. Schlom[1]

1 Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853- 1501, USA
2 Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802-5005, USA
3 Department of Physics, Ohio State University, Columbus, Ohio 43210-1117, USA
4 Department of Physics and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, USA
5 School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, USA
6 Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
7 Institute of Bio and Nanosystems, JARA-Fundamentals of Future Information Technologies, Research Centre Jülich, D-52425 Jülich, Germany
8 Institute of Physics ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic
9 Institute for Crystal Growth, Max-Born-Straße 2, D-12489 Berlin, Germany
10 Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854- 8019, USA

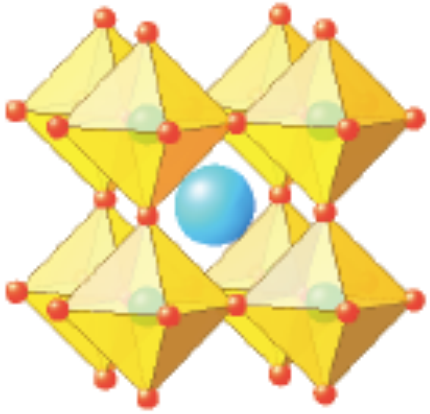
In a collaboration involving 3 MRSECs (*Cornell*, *Penn State*, *Ohio State*) and international collaborators from Germany (*Forschungszentrum Jülich* and *Institut für Kristallzüchtung*), we have shown that appropriately strained $EuTiO_3$ is simultaneously ferromagnetic and ferroelectric, with a spontaneous magnetization × spontaneous polarization product higher than any other material. The ability of strain (*i.e.* stretching or squishing) to create multiferroic $EuTiO_3$ was predicted in 2006,* but the prediction required $EuTiO_3$ to be squished far past its normal breaking point. This work shows that stretching is a viable means to dramatically alter the properties of thin films.

Village Mayor (aka Sandwich Maker): Darrell Schlom, Cornell MSE

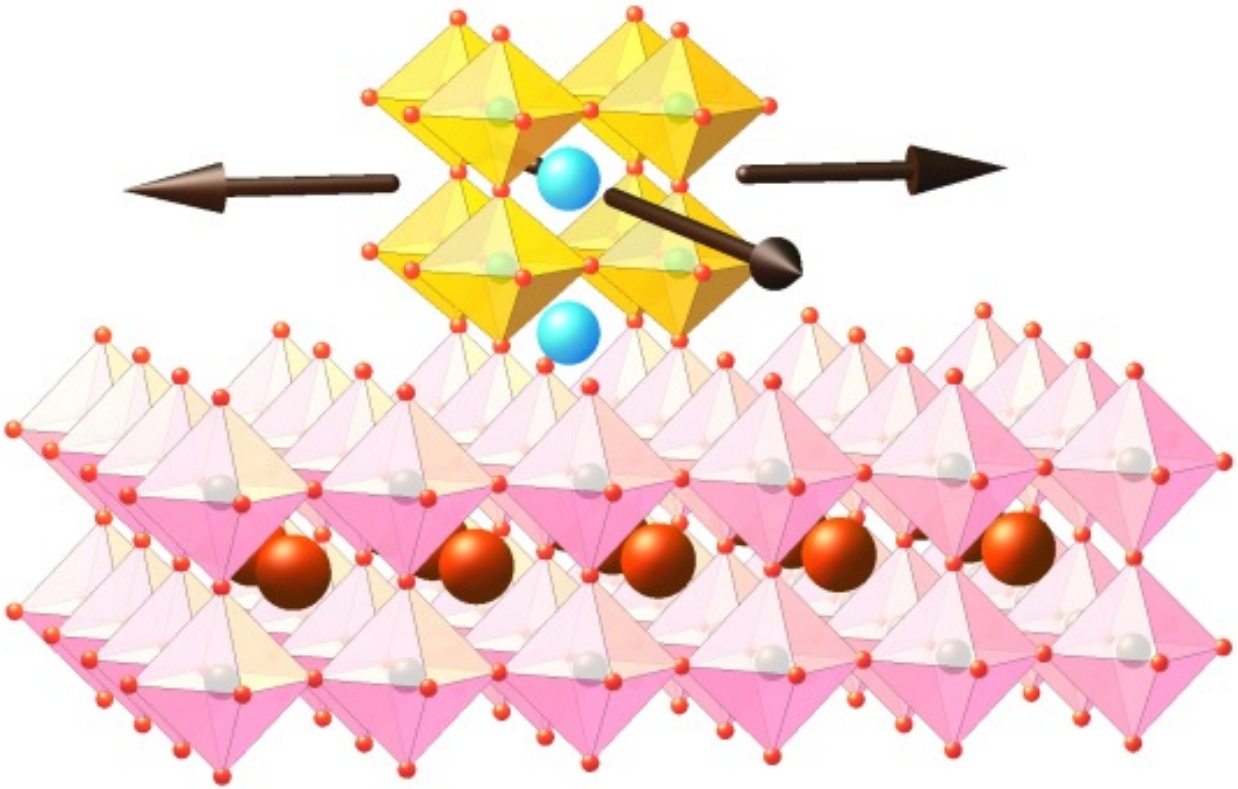
http://www.engineering.cornell.edu/faculty/new-faculty/new-faculty-2008/schlom.cfm

Biaxial Strain via Epitaxy

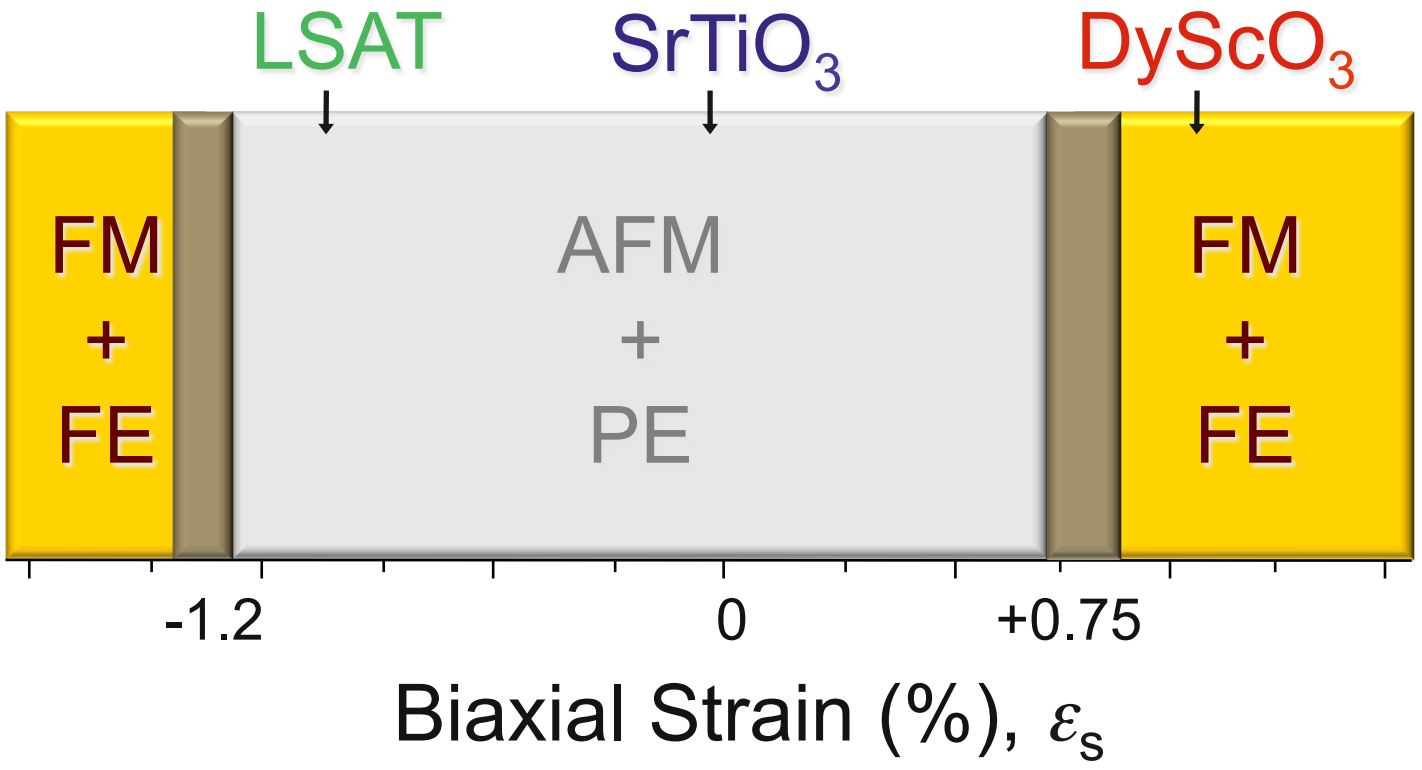
Unstrained



Strained



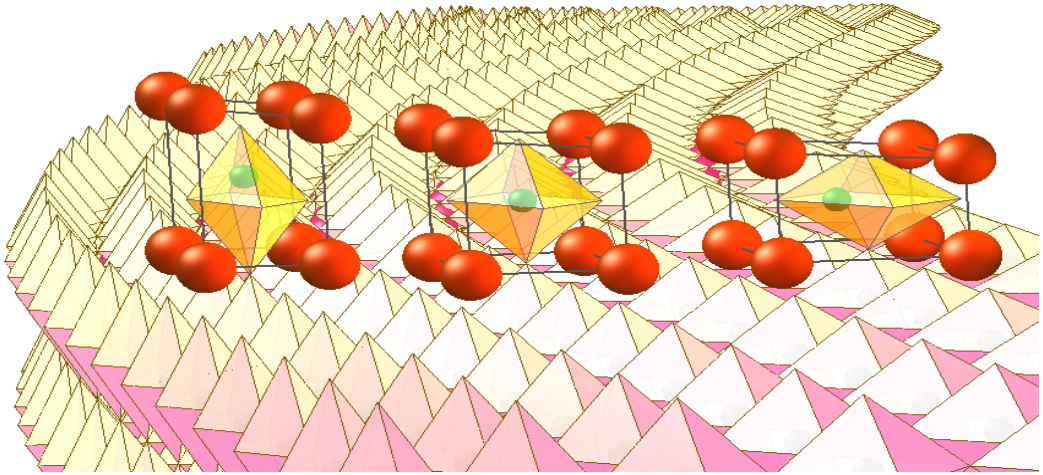
First Principles Epitaxial Phase Diagram of Strained $EuTiO_3$ (at T = 0 K)

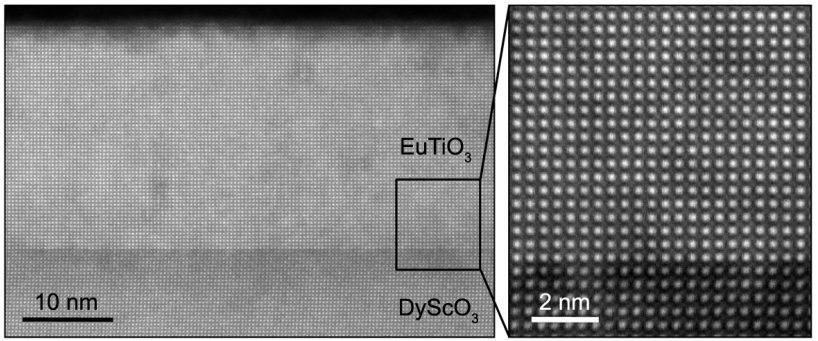


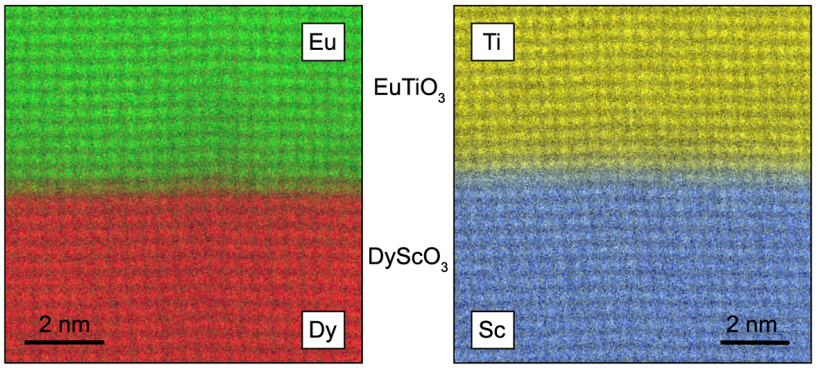
J. H. Lee, E. Vlahos, L. Fang, X. Ke, Y. W. Jung, L. Fitting Kourkoutis, P. Ryan, J.W. Freeland, T. Heeg, M. Roeckerath, C. Hammel, M. Bernhagen, R. Uecker, J. Schubert, D. A. Muller, C. J. Fennie, P. Schiffer, E. Johnston-Halperin, V. Gopalan, and D. G. Schlom,
"A Strong Ferroelectric Ferromagnet created via Spin-Phonon Coupling," *Nature* **466,** 954-958 (2010).

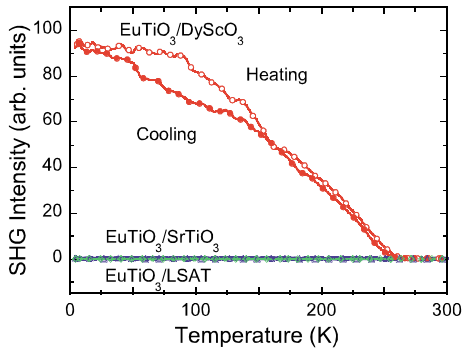
Alchemy Made Possible by Strain

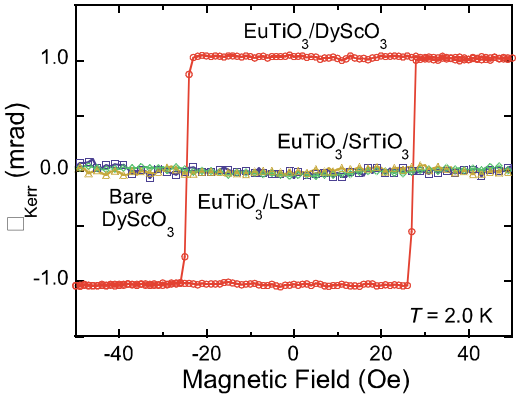
Stretching changes boring ceramic into high-tech material











Ferroelectric
P ~ 20 μC/cm2

\+

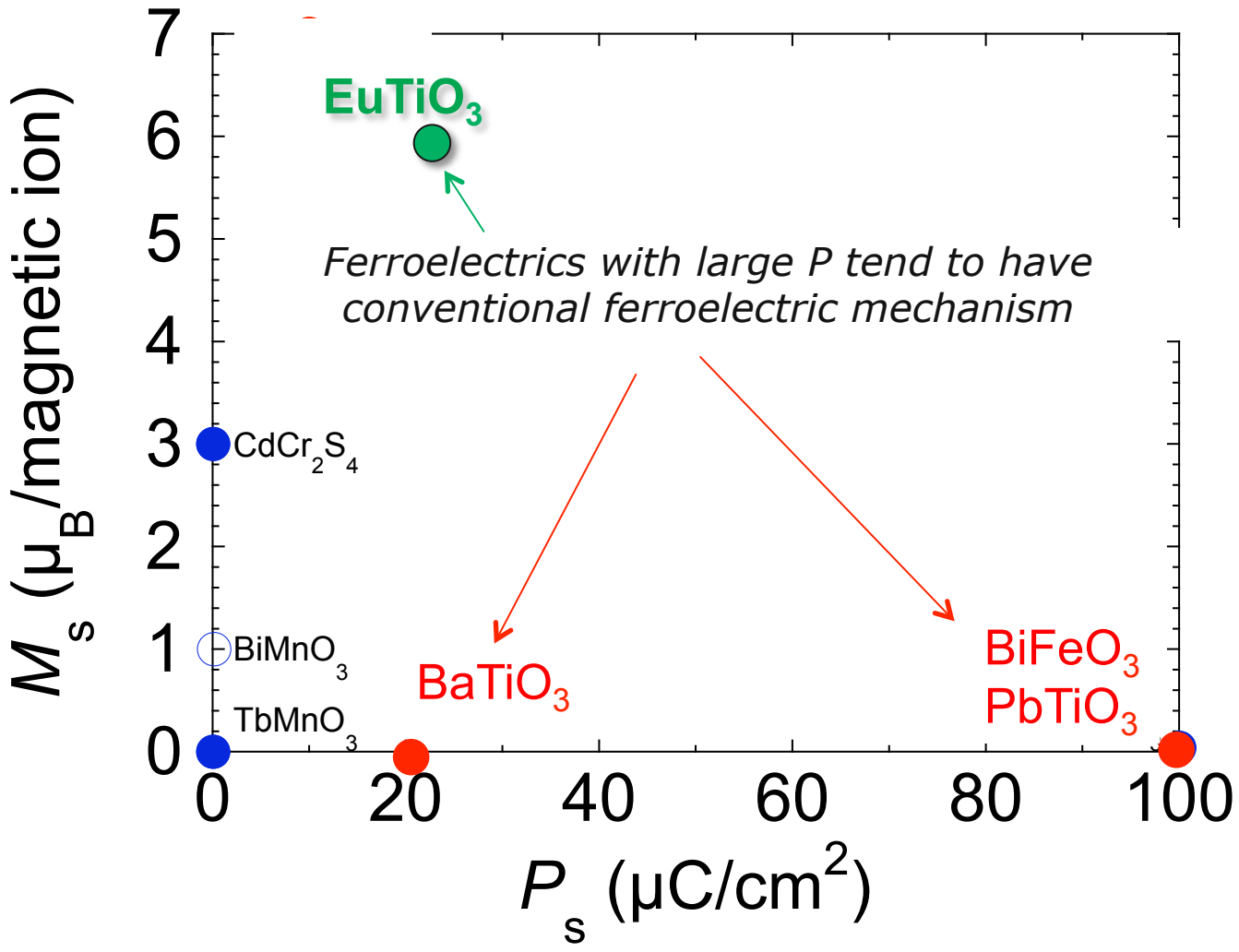
Ferromagnetic
~ 5 μ_B/Eu

=

Multiferroic (1000× stronger than prior ferromagnetic ferroelectrics)

Nature 466 (2010) 954

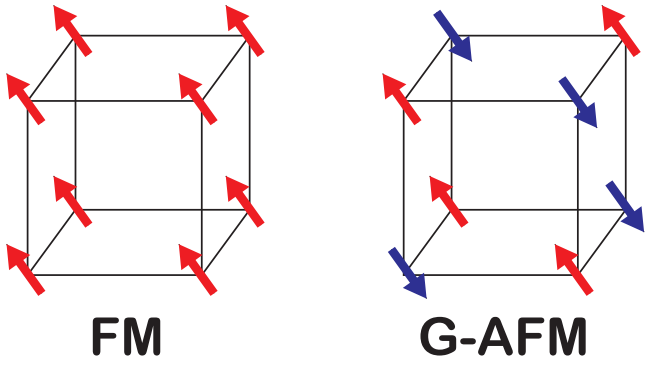
Strong Ferromagnetic Ferroelectrics



Slide from D. Schlom

Spin–Phonon Coupling in Perovskites

Frequency of the polar soft mode can depend on the magnetic state.



Soft Mode Frequency (cm^{-1})

$SrTiO_3$ (d^0)	$SrVO_3$ (d^1)		$SrCrO_3$ (d^2)	
nonmag.	*G*-AF	FM	*G*-AF	FM
130 *i*	329	290	287	187

$SrMnO_3$ (d^3)		$SrFeO_3$ (d^4)		$SrCoO_3$ (d^5)	
G-AF	FM	*G*-AF	FM	*G*-AF	FM
120	122 *i*	248	231	176 *i*	203

Note that it is not always the FM state that leads to a softer phonon mode.

[Lee & Rabe (2011)]

Spin-phonon coupling operative in other perovskites

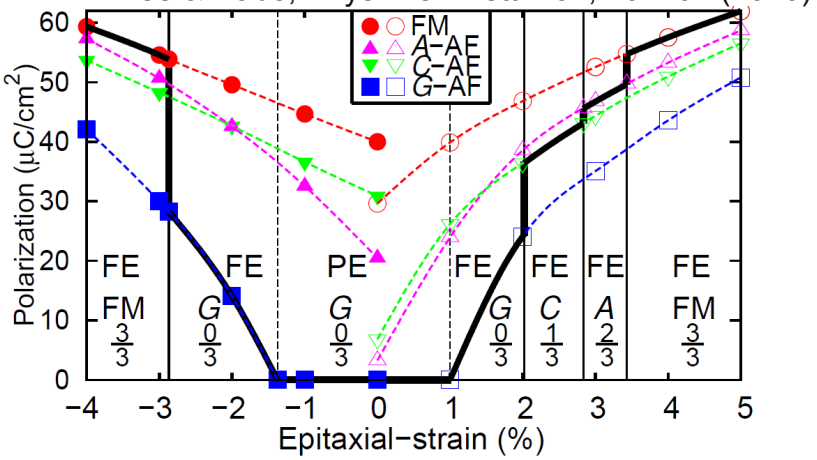
- Manganates, cobaltates and ferrates [cf. Lee & Rabe, Phys. Rev. B 84, 104440 (2011)]

$SrMnO_3$

TABLE I: Calculated lowest phonon frequencies, in cm^{-1}, of cubic $SrMnO_3$ at calculated equilibrium lattice constants with G-AFM and FM orderings for high symmetry q-points.

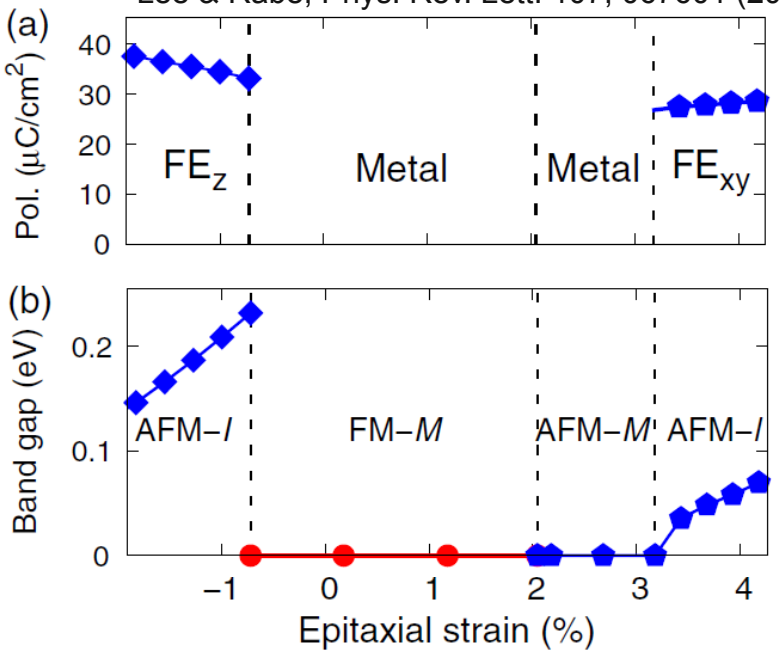
	Γ	X	R	M
G-AFM (a_0=3.845Å)	121	116	84.5i	38.1i
FM (a_0=3.845Å)	76.2i	116	114i	86.3i
FM (a_0=3.865Å)	109i	113	119i	89.9i

Lee & Rabe, Phys. Rev. Lett. 104, 207204 (2010)



$SrCoO_3$

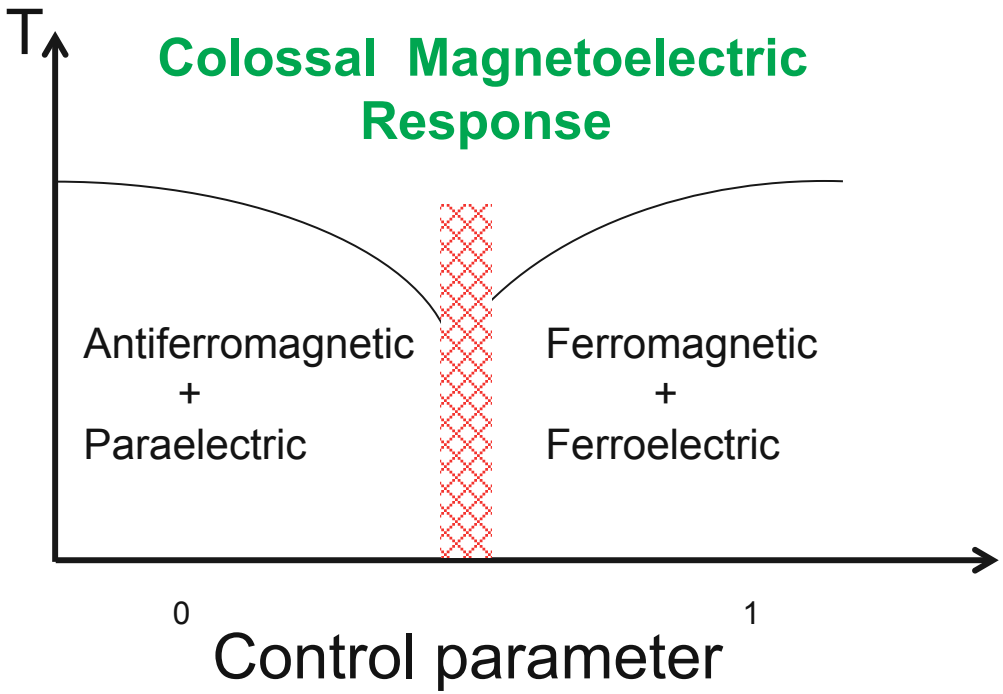
Lee & Rabe, Phys. Rev. Lett. 107, 067601 (2011)



Phase Competition: Generic paradigm to achieve colossal effects

In $EuTiO_3$, Tune to border of phase transition, use spin-phonon coupling to produce magnetoelectric effect

$$\Rightarrow E \sim P^2M^2$$



Phase Competition: Generic paradigm to achieve colossal effects

*Can we combine the physics of **ferroelectrically-induced weak-ferromagnetism** and **phase competition**?*

$$E \sim P_i L_j M_k$$