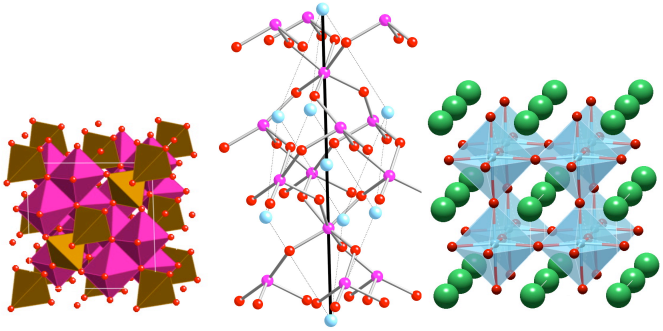
Cornell University

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

# *Competing Ferroic Orders*

## *The magnetoelectric effect*

*Craig J. Fennie*
School of Applied and Engineering Physics
fennie@cornell.edu



*Basic Training in Condensed Matter Theory 2009*

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# *Module Outline*

1. Overview and Background
    - Ferro ordering, the magnetoelectric effect
2. ME revisited, and basic oxide physics
    - ME effect revisited: Toroidal moments
    - Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry
3. Structure and Ferroelectricity
    - Basics of space groups
    - Soft mode theory, lattice dynamics, group theoretic methods
    - Competing lattice instabilities
    - microscopic mechanisms, improper FE
    - Modern theory of polarization (Berry Phase)
4. Magnetism
    - Basics, exchange interactions, superexchange, Dzyaloshinskii-Moria
    - How spins couple to the lattice! Phenomenology and microscopics (spin-phonon, spin-lattice, etc)
    - Competing magnetic orders
    - Systems: $ZnCr_2O_4$, $EuTiO_3$, $SeCuO_4$, $TeCuO_4$

## Ferroelectric and magnetic coupling

- Magneto-capacitance
- Tuning perovskites: Magnetic-induced ferroelectricity ($TbMnO_3$)
- Tuning perovskites: Colossal ME effect (strained $EuTiO_3$)
- Ferroelectric-induced ferromagnetism ($FeTiO_3$)

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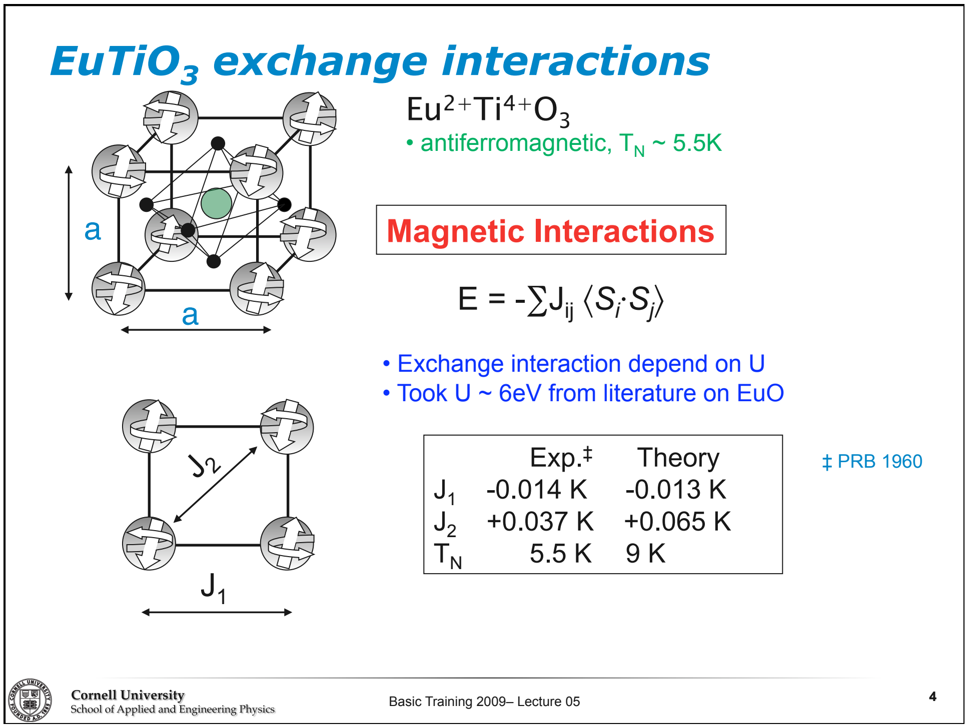


## $EuTiO_3$ exchange interactions

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

- antiferromagnetic, $T_N$ ~ 5.5K

**Magnetic Interactions**

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

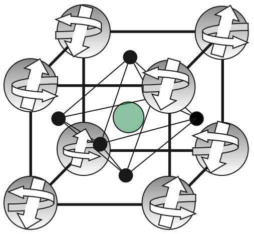
- Exchange interaction depend on U
- Took U ~ 6eV from literature on EuO

| | Exp.‡ | Theory |
|---|---|---|
| $J_1$ | -0.014 K | -0.013 K |
| $J_2$ | +0.037 K | +0.065 K |
| $T_N$ | 5.5 K | 9 K |

‡ PRB 1960

# EuTiO$_3$ magnetocapacitance

Bulk Eu$^{2+}$Ti$^{4+}$O$_3$: Ground state
antiferromagnetic paraelectric

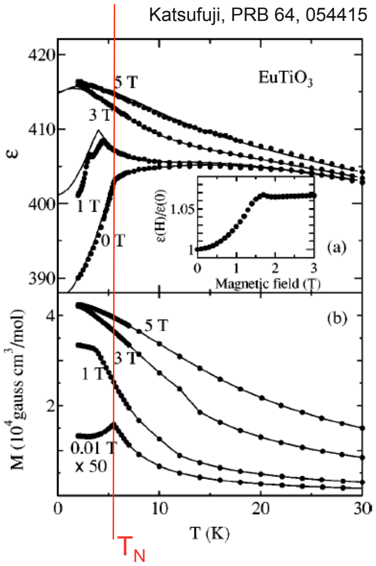


- r(Eu$^{2+}$) ~ r(Sr$^{2+}$); Cubic perovskite
- Eu$^{2+}$ → J=S=7/2; T$_n$ ~ 5.5K, G-type AFM

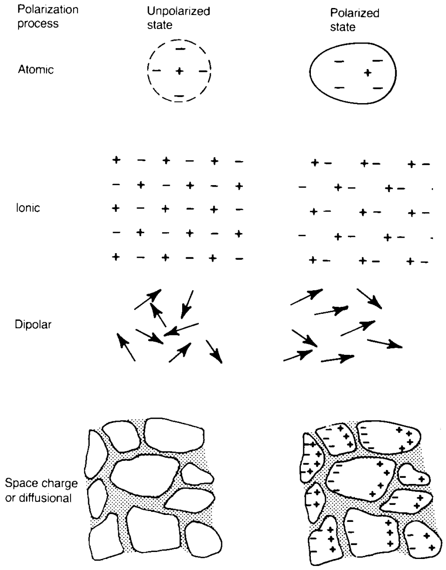
$$\Rightarrow \quad \omega^2 \propto \omega_0^2 - \partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle$$

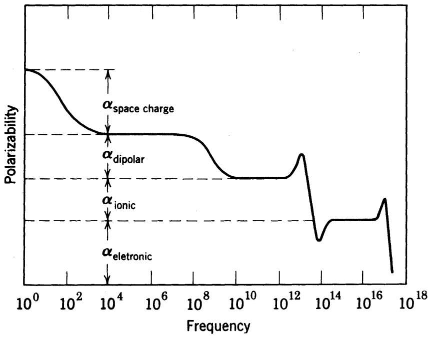
renormalized phonon — bare phonon — magnetic contribution

Katsufuji, PRB 64, 054415



# Dielectric's Response to E$_{appl}$





# Dielectric properties of insulators

Long-wavelength (q→0) behavior of crystal can be investigated by expanding ground state energy in terms of electric fields (E) and phonon displacements (u)

$$E_{tot} = -\frac{1}{2}\mathcal{E}\cdot\hat{\chi}_{\infty}\cdot\mathcal{E} + \frac{1}{2}u\cdot\hat{C}\cdot u - u\cdot\hat{Z}\cdot\mathcal{E}$$

Born and Huang, "Dynamical Theory of Crystal Lattices"
Cochran and Cowley, "Dielectric constants and lattice vibrations" J. Phys. Chem. Solids, 1962

$\mathcal{E}$: Macroscopic electric field

$u$: ion displacement

$\hat{\chi}_{\infty}$ Electronic susceptibility matrix

$\hat{C}$ Force constant matrix

$\hat{Z}$ Born effective charge tensor

---

# Born (or transverse) effect charge

Table 4, page 131; Karin M. Rabe and Philippe Ghosez, *First-principles studies of ferroelectric oxides*, Topics in Applied Physics **105**: 117-174 (2007).

$$\hat{Z} = \frac{\partial P}{\partial u}|_{\mathcal{E}=0}$$

*or equivalently*

$$\hat{Z} = \frac{\partial F}{\partial \mathcal{E}}|_{u=0}$$

Measured Values
John Axe, Phys. Rev 1967

Table III. Apparent charges of several perovskites derived from optical mode strengths.

| | $BaTiO_3$ | $SrTiO_3$ | $KTaO_3$ | $KCoF_3$ |
|---|---|---|---|---|
| $A$ | 2.9 | 2.4 | 1.2 | 0.9 |
| $B$ | 6.7 | 7.0 | 8.1 | 1.8 |
| $X_{\parallel}$ | −4.8 | −5.8 | −6.3 | −2.5 |
| $X_{\perp}$ | −2.4 | −1.8 | −1.5 | −0.1 |

Anomalous values in most perovskite ferroelectrics

| $ABO_3$ | $Z^*_A$ | $Z^*_B$ | $Z^*_{O\parallel}$ | $Z^*_{O\perp}$ | $Z^*_A/Z_A$ | $Z^*_B/Z_B$ | Method | Reference |
|---|---|---|---|---|---|---|---|---|
| nominal | 2 | 4 | −2 | −2 | | | | |
| $CaTiO_3$ | 2.58 | 7.08 | −5.65 | −2.00 | 1.29 | 1.77 | DFT (LDA) | [142] |
| $SrTiO_3$ | 2.56 | 7.26 | −5.73 | −2.15 | 1.28 | 1.82 | DFT (LDA) | [148] |
| | 2.54 | 7.12 | −5.66 | −2.00 | 1.27 | 1.78 | DFT (LDA) | [142] |
| | 2.55 | 7.56 | −5.92 | −2.12 | 1.28 | 1.89 | DFT (LDA) | [126] |
| | 2.4 | 7.0 | −5.8 | −1.8 | 1.2 | 1.8 | experiment | [149] |
| $BaTiO_3$ | 2.77 | 7.25 | −5.71 | −2.15 | 1.39 | 1.81 | DFT (LDA) | [148] |
| | 2.75 | 7.16 | −5.69 | −2.11 | 1.38 | 1.79 | DFT (LDA) | [142] |
| | 2.61 | 5.88 | −4.43 | −2.03 | 1.31 | 1.47 | Pseudo-SIC | [47] |
| | 2.9 | 6.7 | −4.8 | −2.4 | 1.45 | 1.68 | experiment | [149] |
| $BaZrO_3$ | 2.73 | 6.03 | −4.74 | −2.01 | 1.37 | 1.51 | DFT (LDA) | [142] |
| $PbTiO_3$ | 3.90 | 7.06 | −5.83 | −2.56 | 1.95 | 1.77 | DFT (LDA) | [142] |
| $PbZrO_3$ | 3.92 | 5.85 | −4.81 | −2.48 | 1.96 | 1.46 | DFT (LDA) | [142] |
| nominal | 1 | 5 | −2 | −2 | | | | |
| $NaNbO_3$ | 1.13 | 9.11 | −7.01 | −1.61 | 1.13 | 1.82 | DFT (LDA) | [142] |
| $KNbO_3$ | 0.82 | 9.13 | −6.58 | −1.68 | 0.82 | 1.83 | DFT (LDA) | [150] |
| | 1.14 | 9.23 | −7.01 | −1.68 | 1.14 | 1.85 | DFT (LDA) | [142] |
| | 1.14 | 9.37 | −6.86 | −1.65 | 1.14 | 1.87 | DFT (LDA) | [151] |
| | 1.07 | 8.12 | −5.38 | −1.80 | 1.07 | 1.62 | HF | [48, 49] |
| nominal | - | 6 | −2 | −2 | | | | |
| $WO_3$ | - | 12.51 | −9.13 | −1.69 | - | 2.09 | DFT (LDA) | [152] |

# Dielectric properties of insulators

See Umesh Waghmare and Karin Rabe, *Dielectric properties of simple and complex oxides from first principles*, in Materials Fundamentals of Gate Dielectrics, Eds Demkov and Navrotsky (Springer 2005)

**Static dielectric tensor**

Intrinsic contribution assuming centrosymmetric crystal

$$\epsilon^0_{\alpha\beta} = \epsilon^\infty_{\alpha\beta} + \sum_m \Delta\epsilon_{m,\alpha\beta}$$

**Oscillator strength**

$$\Delta\epsilon_{m,\alpha\beta} = \frac{4\pi e^2}{M_0\, V} \frac{\widetilde{Z}^*_{m\alpha}\, \widetilde{Z}^*_{m\beta}}{\omega_m^2}$$

**Effective Plasma frequency**

$$\Omega^2_{p,m} = (4\pi e^2/M_0\, V)\widetilde{Z}^*_{m\alpha}\widetilde{Z}^*_{m\beta}$$

**Born effective *mode* charge**

$$\widetilde{Z}^*_{m\alpha} = \sum_{i\gamma} \underbrace{Z^*_{\alpha\gamma}(i)}_{\text{Born effective charge}} \left(\frac{M_0}{M_i}\right)^{1/2} \xi_m(i\gamma)$$

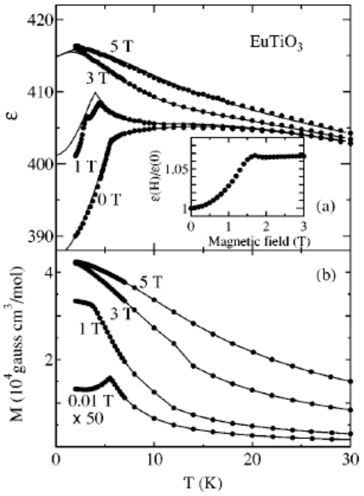
# Magnetodielectric response

- Origin of effect:
magnetic field induces change in magnetic order,
shifts polar phonon
Frequencies
(Fennie and Rabe, PRL 2006)

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

where $p_{m\alpha} = \sum_{\kappa\beta} Z_{\kappa\beta,\alpha} \xi^m_{\kappa\beta}/\sqrt{M}_\kappa$

$$\tilde{C}_{\eta,\eta'} = C_{\eta,\eta'} - \sum_{ij} \frac{\partial^2 J_{ij}}{\partial f_\eta \partial f_{\eta'}} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$



Katsufuji, PRB 64, 054415

# *Next, tuning perovskites and phase competition*

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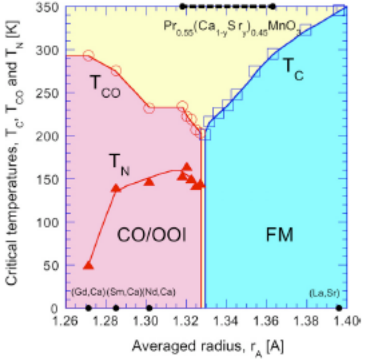
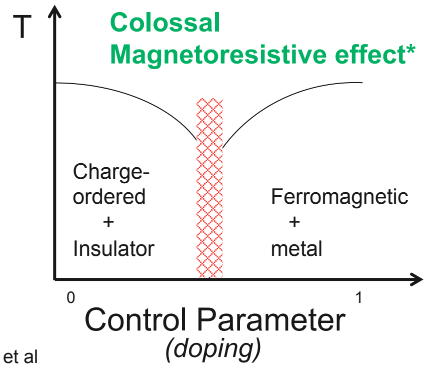
## *Phase Competition: Generic paradigm to achieve colossal effects*

$Pr(Ca_{1-y}Sr_y)_{0.45}MnO_3$



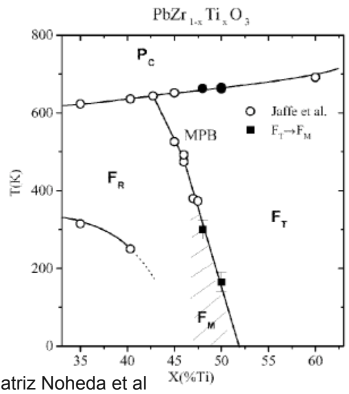
Tokura et al



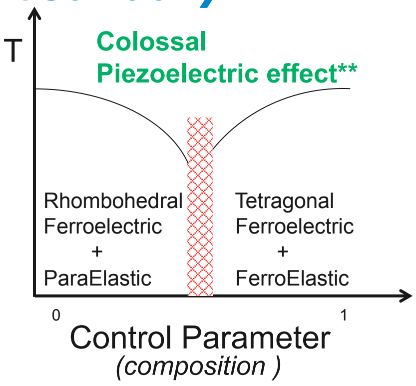
* Y. Tokura, “Critical Feature of Colossal Magnetoresistive Manganites,” Rep. Prog. Phys. 2006.
“Multiferroics - Toward Strong Coupling …,” JMMM 2007.

** R.E. Newnham, “Molecular Mechanisms in Smart Materials,” MRS Bull. 1997.

# Phase Competition and the morphotropic phase boundary



Beatriz Noheda et al



T

Colossal
Piezoelectric effect**

Rhombohedral
Ferroelectric
+
ParaElastic

Tetragonal
Ferroelectric
+
FerroElastic

0

1

Control Parameter
*(composition )*

* 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.

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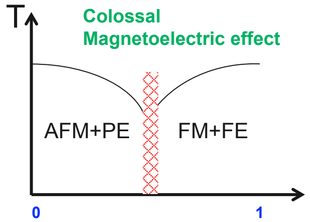
# Macroscopic property: Colossal Magnetoelectric effect



T

Colossal
Magnetoelectric effect

AFM+PE

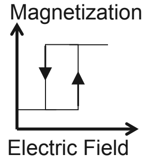
FM+FE

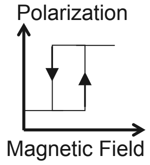
0

1

Control parameter

Tune to boundary, but stay on
AFM+PE side of phase transition





CJ Fennie and KM Rabe, Physical Review Letters 2006.

And

Y. Tokura “Multiferroics - Toward Strong Coupling …,”
JMMM 2006.

# 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

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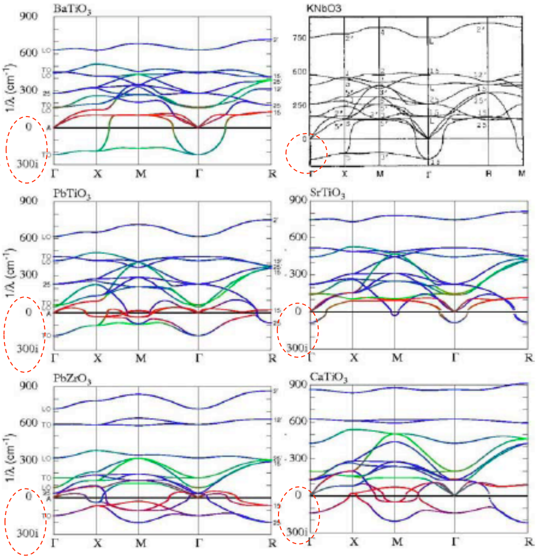
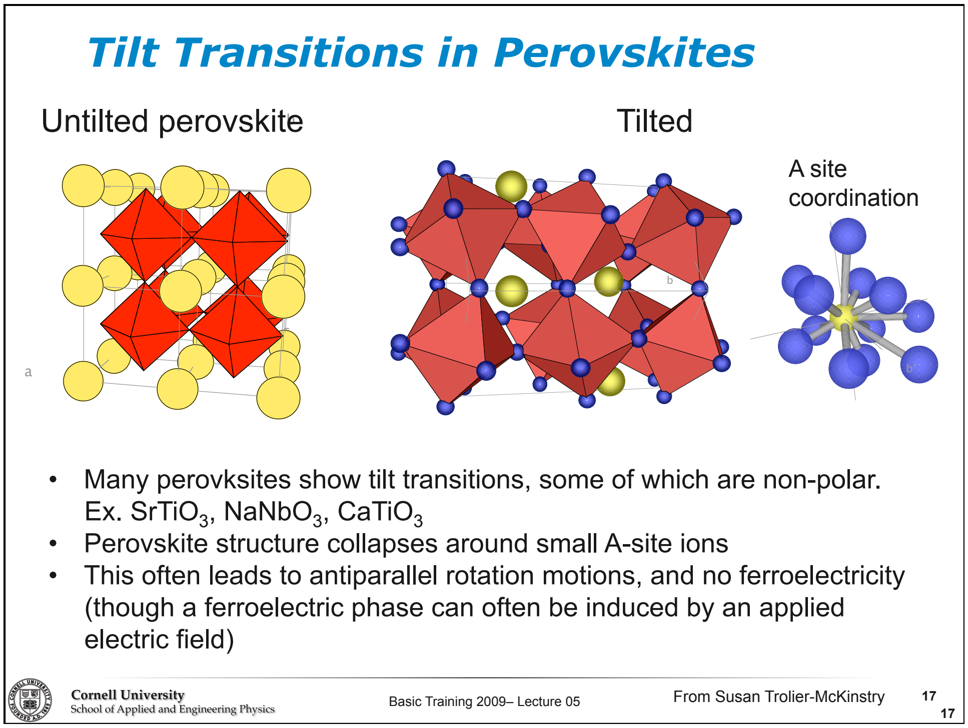
# Phonon dispersion at T=0 of cubic $ABO_3$ from first principles

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, *First-principles studies of ferroelectric oxides*, Topics in Applied Physics **105**: 117-174 (2007).



## Tilt Transitions in Perovskites

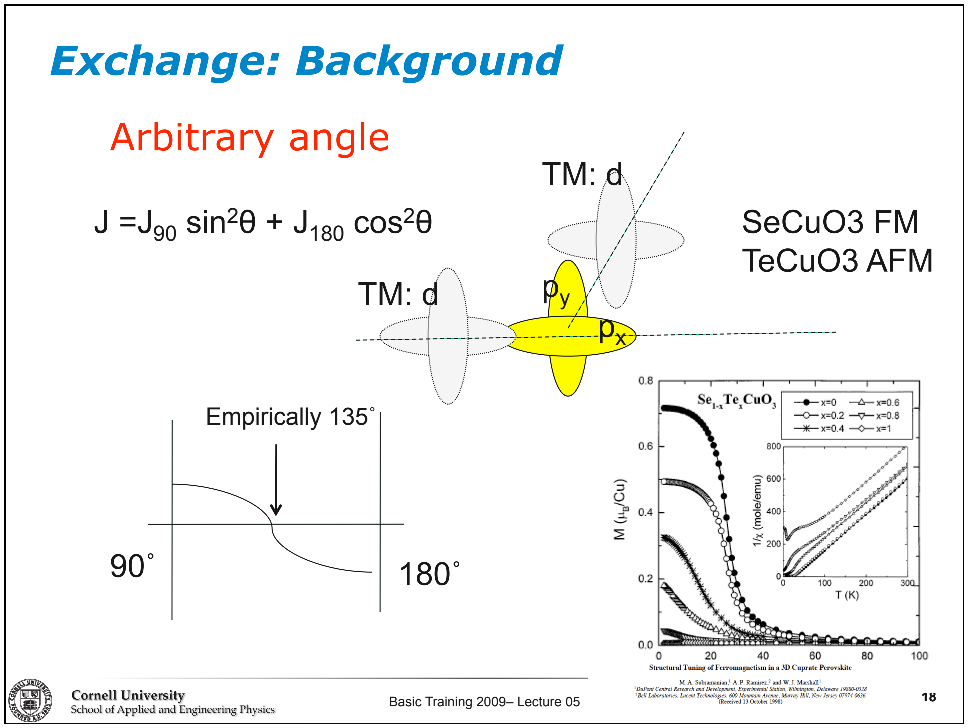
Untilted perovskite

Tilted

A site coordination

- Many perovksites show tilt transitions, some of which are non-polar. Ex. $SrTiO_3$, $NaNbO_3$, $CaTiO_3$
- Perovskite structure collapses around small A-site ions
- This often leads to antiparallel rotation motions, and no ferroelectricity (though a ferroelectric phase can often be induced by an applied electric field)

From Susan Trolier-McKinstry



## Exchange: Background

Arbitrary angle

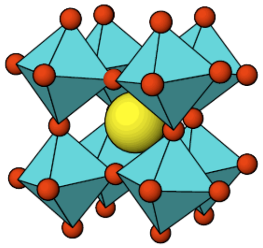
$$J = J_{90} \sin^2\theta + J_{180} \cos^2\theta$$

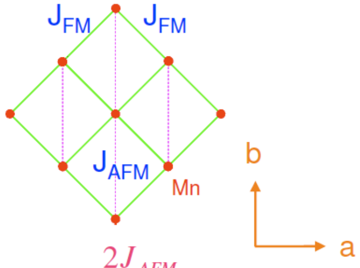
SeCuO3 FM
TeCuO3 AFM

**Structural Tuning of Ferromagnetism in a 3D Cuprate Perovskite**

M. A. Subramanian,[1] A. P. Ramirez,[2] and W. J. Marshall[1]
[1] *DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328*
[2] *Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974-0636*
(Received 13 October 1998)

# Magnetic frustration in $RMnO_3$





$$\kappa = \frac{2J_{AFM}}{J_{FM}}$$

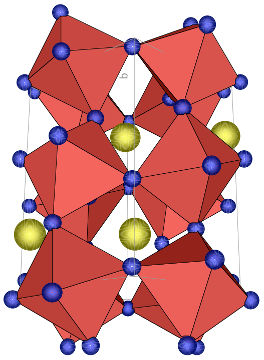
**$\kappa < 1$ Ferromagnetic**

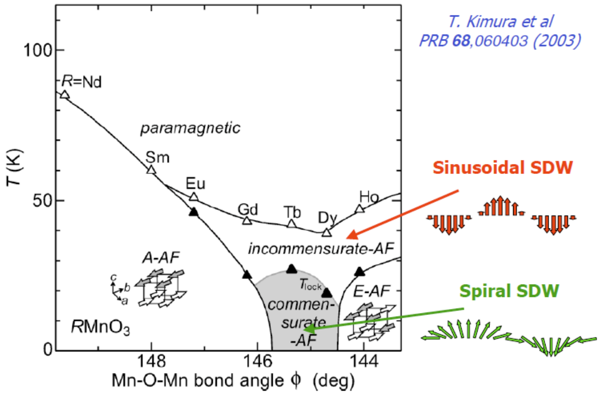
**$\kappa > 1$ Incommensurate SDW**

$$\cos\frac{Q_b}{2} = \frac{1}{\kappa}$$

# *Orthorhombic REMnO$_3$ perovskites*

## *Tuning with chemical pressure*



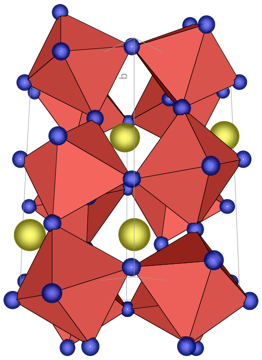


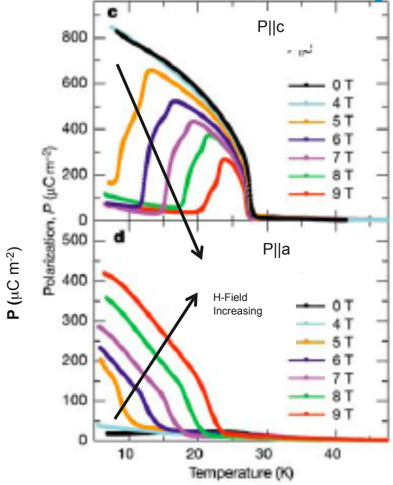
*T. Kimura et al*
*PRB **68**,060403 (2003)*

## *Magnetic field control of ferroelectricity*

First experiment: T. Kimura et al, Nature 2004
For review see
T. Kimura *Spiral Magnets as Magnetoelectrics*
*Annu. Rev. Mater. Res.* ***37****, 2007.*

e.g. $TbMnO_3$





Kimura, Nature 2003

Today's best ferroelectrics are perovskites

| | |
|---|---|
| e.g. | $PbTiO_3$: $T_c$~800K, $P_s$~70 $\mu C/cm^2$ |
| compared with | $TbMnO_3$: $T_c$~ 50K, $P_s$~0.07 $\mu C/cm^2$ |

---

## *Improper magnetic ferroelectric: Spin Spiral*

e.g. $TbMnO_3$

Primary order parameter: M
Secondary order parameter: P

(note energy expansion simplified for pedagogy)

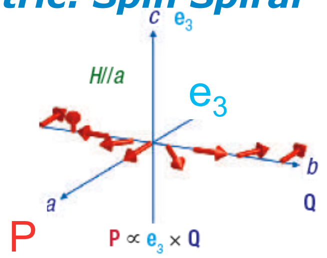
$$\mathcal{F}_{mp}(M, \mathbf{P}) = 1/\chi_e \mathbf{P}^2 + 1/\mu \mathbf{M}^2 + \gamma \mathbf{P} \cdot [\, M(\nabla \cdot M) - (M \cdot \nabla) M \,]$$

$$\boxed{\mathbf{P} = \gamma\, \chi_e\, [\, M(\nabla \cdot M) - (M \cdot \nabla) M \,]}$$

For a spin-density-wave

$M = M_1\, \mathbf{e}_1 \cos Q\cdot x + M_2\, \mathbf{e}_2 \cos Q\cdot x + M_3 \mathbf{e}_3$

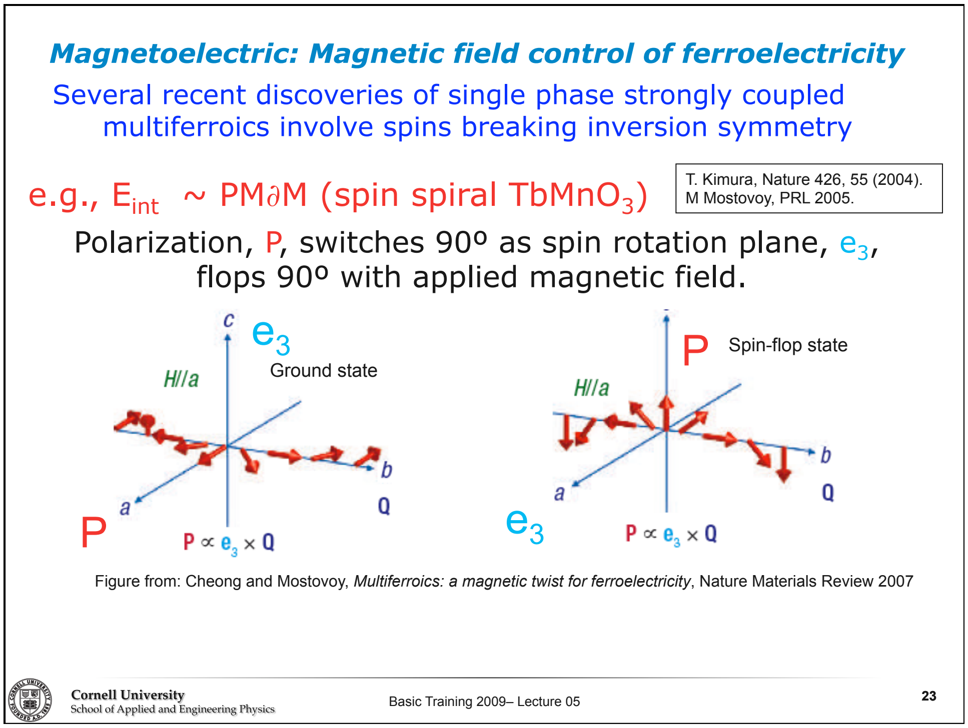
$$\rightarrow \mathbf{P} = \gamma\, \chi_e\, M_1\, M_2\, [\, \mathbf{e}_3 \times Q]$$



First experiment: T. Kimura et al, Nature 2004
For review see
T. Kimura *Spiral Magnets as Magnetoelectrics*
*Annu. Rev. Mater. Res.* ***37****, 2007.*

Simplest explanation:
Maxim Mostovoy,
Physical Review Letters **96**,
067601 (2006)

More advanced treatment see:
Brooks Harris, *Landau analysis of the symmetry of the magnetic structure and magnetoelectric interaction in multiferoics*, PRB **76**, 054447 (2007)



## Magnetoelectric: Magnetic field control of ferroelectricity

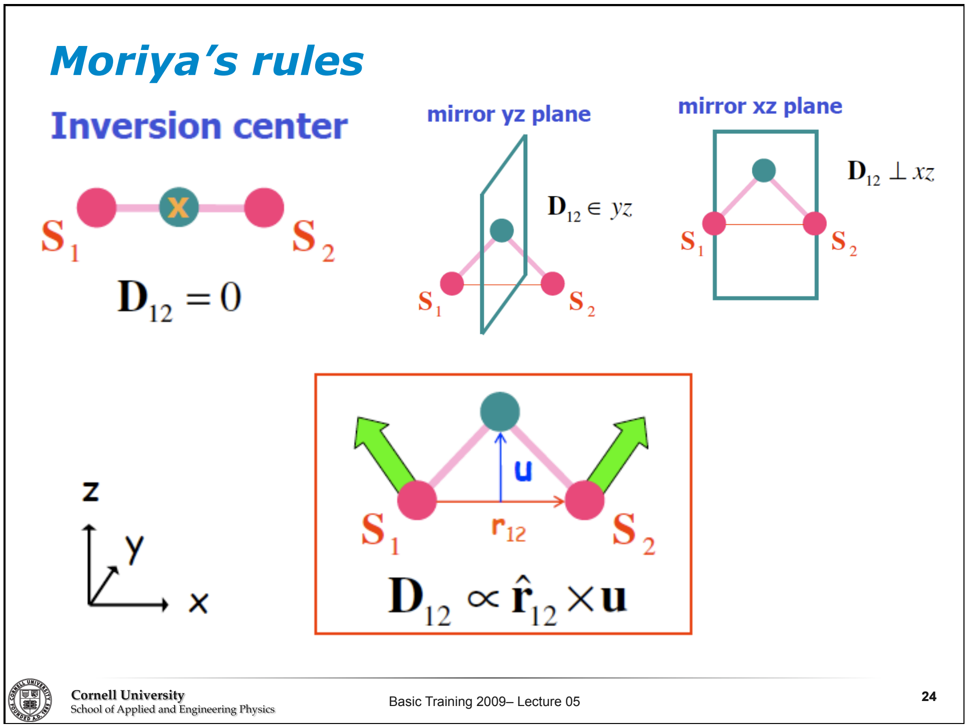
Several recent discoveries of single phase strongly coupled multiferroics involve spins breaking inversion symmetry

T. Kimura, Nature 426, 55 (2004).
M Mostovoy, PRL 2005.

e.g., $E_{int} \sim PM\partial M$ (spin spiral $TbMnO_3$)

Polarization, P, switches 90º as spin rotation plane, $e_3$, flops 90º with applied magnetic field.

Figure from: Cheong and Mostovoy, *Multiferroics: a magnetic twist for ferroelectricity*, Nature Materials Review 2007



## Moriya’s rules

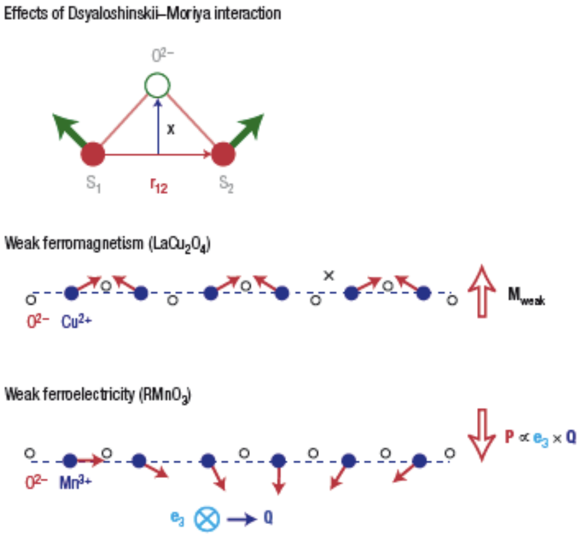
$$\mathbf{D}_{12} \propto \hat{\mathbf{r}}_{12} \times \mathbf{u}$$

# Inverse DM interaction

$$E_{DM} = D\cdot\langle S_1 \times S_2\rangle$$

$$D \propto x \times r_{12}$$

x is defined as the displacement of the oxygen atom



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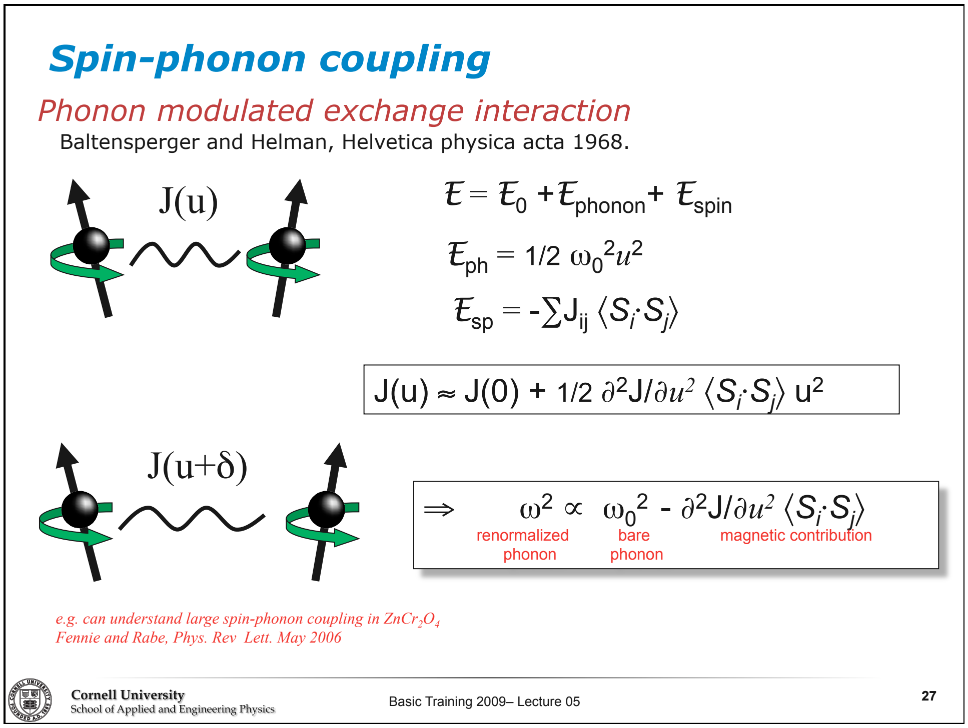
# Next, more tuning perovskites and phase competition



## Spin-phonon coupling

*Phonon modulated exchange interaction*

Baltensperger and Helman, Helvetica physica acta 1968.

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

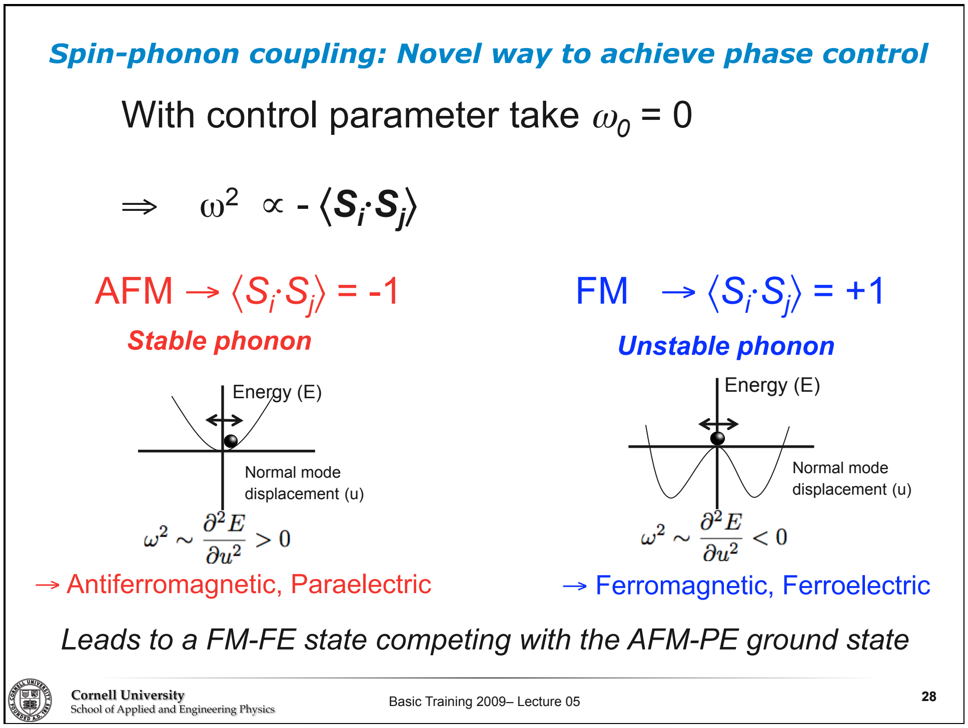
$$\mathcal{E}_{\text{ph}} = 1/2\ \omega_0^2 u^2$$

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

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

$$\boxed{\Rightarrow \quad \underbrace{\omega^2}_{\text{renormalized phonon}} \propto \underbrace{\omega_0^2}_{\text{bare phonon}} - \underbrace{\partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle}_{\text{magnetic contribution}}}$$

*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 $\omega_0 = 0$

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

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

***Stable phonon***

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

→ Antiferromagnetic, Paraelectric

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

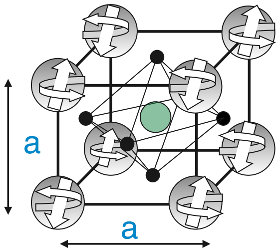
***Unstable phonon***

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

→ Ferromagnetic, Ferroelectric

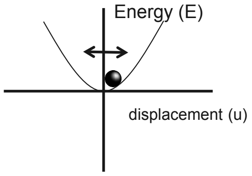
*Leads to a FM-FE state competing with the AFM-PE ground state*

## First-principles density-functional theory results



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

**Phonon frequencies**



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

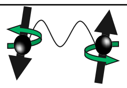
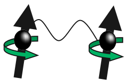
| | Theory<br>Fennie and Rabe PRL 2006 | Exp.‡<br>Kamba et al, 2007 |
|---|---|---|
| $\omega_1$ | 78 $cm^{-1}$ | 82 $cm^{-1}$ |
| $\omega_2$ | 164 $cm^{-1}$ | 153 $cm^{-1}$ |
| $\omega_3$ | 548 $cm^{-1}$ | 539 $cm^{-1}$ |

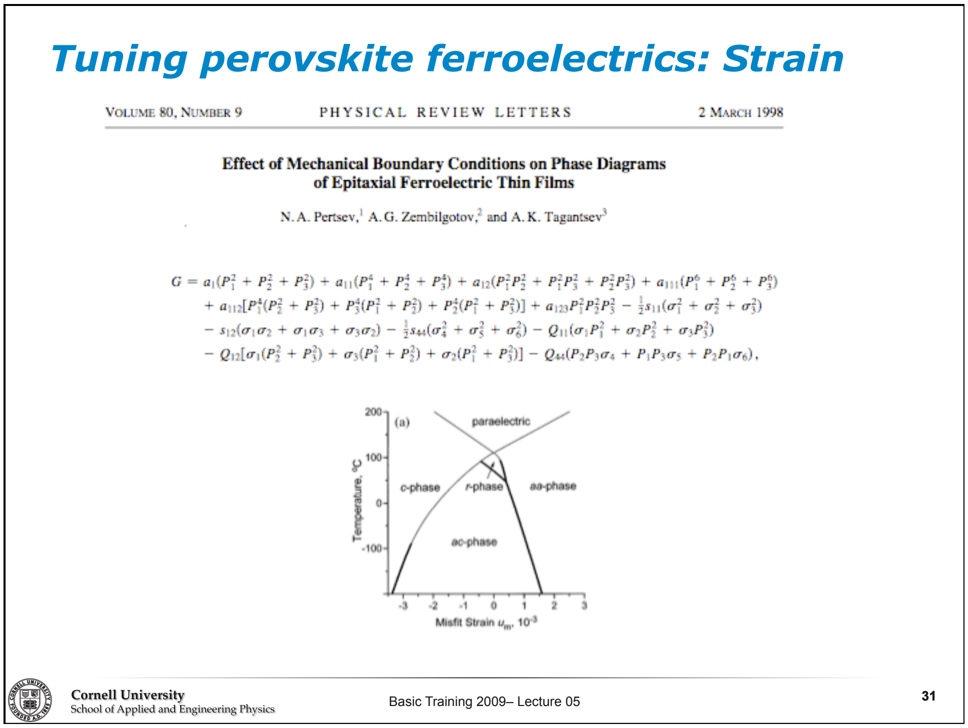
‡ Reflectivity measurements

---

## $EuTiO_3$: Spin-phonon coupling

Spin-phonon coupling $\omega \approx \omega_0 + \lambda \langle S_i \cdot S_j \rangle$

| Spin-order | | | Phonon frequencies |
|---|---|---|---|
| AFM |  | $\rightarrow \langle S_i \cdot S_j \rangle = -1$ | $\omega_1$ = 78 cm-1 |
| FM |  | $\rightarrow \langle S_i \cdot S_j \rangle = +1$ | $\omega_1$ = 71 cm-1 |



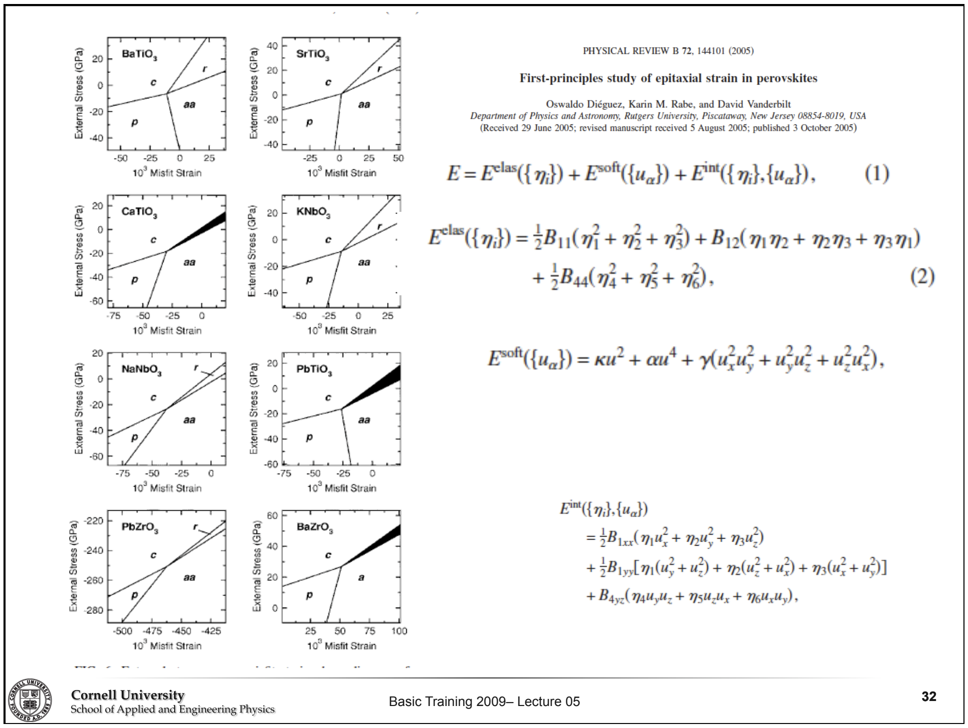
# Tuning perovskite ferroelectrics: Strain

VOLUME 80, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1998

## Effect of Mechanical Boundary Conditions on Phase Diagrams of Epitaxial Ferroelectric Thin Films

N. A. Pertsev,[1] A. G. Zembilgotov,[2] and A. K. Tagantsev[3]

$$\begin{aligned}G = {}& a_1(P_1^2+P_2^2+P_3^2) + a_{11}(P_1^4+P_2^4+P_3^4) + a_{12}(P_1^2P_2^2+P_1^2P_3^2+P_2^2P_3^2) + a_{111}(P_1^6+P_2^6+P_3^6)\\ &+ a_{112}[P_1^4(P_2^2+P_3^2) + P_3^4(P_1^2+P_2^2) + P_2^4(P_1^2+P_3^2)] + a_{123}P_1^2P_2^2P_3^2 - \tfrac{1}{2}s_{11}(\sigma_1^2+\sigma_2^2+\sigma_3^2)\\ &- s_{12}(\sigma_1\sigma_2+\sigma_1\sigma_3+\sigma_3\sigma_2) - \tfrac{1}{2}s_{44}(\sigma_4^2+\sigma_5^2+\sigma_6^2) - Q_{11}(\sigma_1P_1^2+\sigma_2P_2^2+\sigma_3P_3^2)\\ &- Q_{12}[\sigma_1(P_2^2+P_3^2) + \sigma_3(P_1^2+P_2^2) + \sigma_2(P_1^2+P_3^2)] - Q_{44}(P_2P_3\sigma_4 + P_1P_3\sigma_5 + P_2P_1\sigma_6),\end{aligned}$$



PHYSICAL REVIEW B 72, 144101 (2005)

## First-principles study of epitaxial strain in perovskites

Oswaldo Diéguez, Karin M. Rabe, and David Vanderbilt
*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA*

(Received 29 June 2005; revised manuscript received 5 August 2005; published 3 October 2005)

$$E = E^{\text{elas}}(\{\eta_i\}) + E^{\text{soft}}(\{u_\alpha\}) + E^{\text{int}}(\{\eta_i\},\{u_\alpha\}), \qquad (1)$$

$$\begin{aligned}E^{\text{elas}}(\{\eta_i\}) = {}& \tfrac{1}{2}B_{11}(\eta_1^2+\eta_2^2+\eta_3^2) + B_{12}(\eta_1\eta_2+\eta_2\eta_3+\eta_3\eta_1)\\ &+ \tfrac{1}{2}B_{44}(\eta_4^2+\eta_5^2+\eta_6^2), \qquad (2)\end{aligned}$$

$$E^{\text{soft}}(\{u_\alpha\}) = \kappa u^2 + \alpha u^4 + \gamma(u_x^2u_y^2 + u_y^2u_z^2 + u_z^2u_x^2),$$

$$\begin{aligned}&E^{\text{int}}(\{\eta_i\},\{u_\alpha\})\\ &\quad= \tfrac{1}{2}B_{1xx}(\eta_1u_x^2+\eta_2u_y^2+\eta_3u_z^2)\\ &\quad+ \tfrac{1}{2}B_{1yy}[\eta_1(u_y^2+u_z^2)+\eta_2(u_z^2+u_x^2)+\eta_3(u_x^2+u_y^2)]\\ &\quad+ B_{4yz}(\eta_4u_yu_z+\eta_5u_zu_x+\eta_6u_xu_y),\end{aligned}$$

## Tuning perovskite ferroelectrics: Strain

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

(note energy expansion simplified for pedagogy, see Dieguez et al PRB 2005 for full details )

| | |
|---|---|
| $\mathcal{F}(P, \eta) = \kappa P^2 + c_1 P^4$ | Soft-mode |
| $+ \frac{1}{2}\beta_{11}(2\eta^2 + \eta_z^2) + \frac{1}{2}\beta_{12}(\eta^2 + 2\eta\eta_z)$ | Elastic |
| $+ \beta_{1xx}(2\eta P_{xy}^2 + \eta_z P_z^2)$ | Coupling |

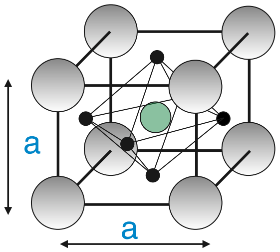
$$\partial\mathcal{F}/\partial\eta_z = \beta_{11}\ \eta_z + \beta_{12}\ 2\eta + \beta_{1xx} P_z^2$$

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

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

Soft-mode “force constant” gets renormalized by epitaxial strain

## Epitaxial strain-induced ferroelectricity



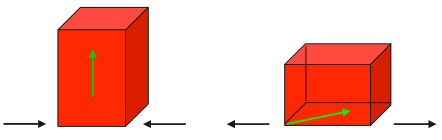
$Sr^{2+}Ti^{4+}O_3$

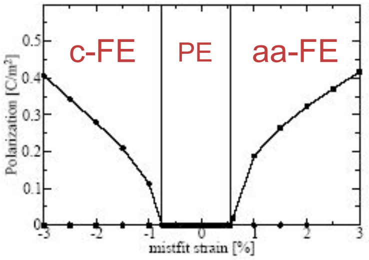
- In bulk: paraelectric (PE) ground state (cubic)

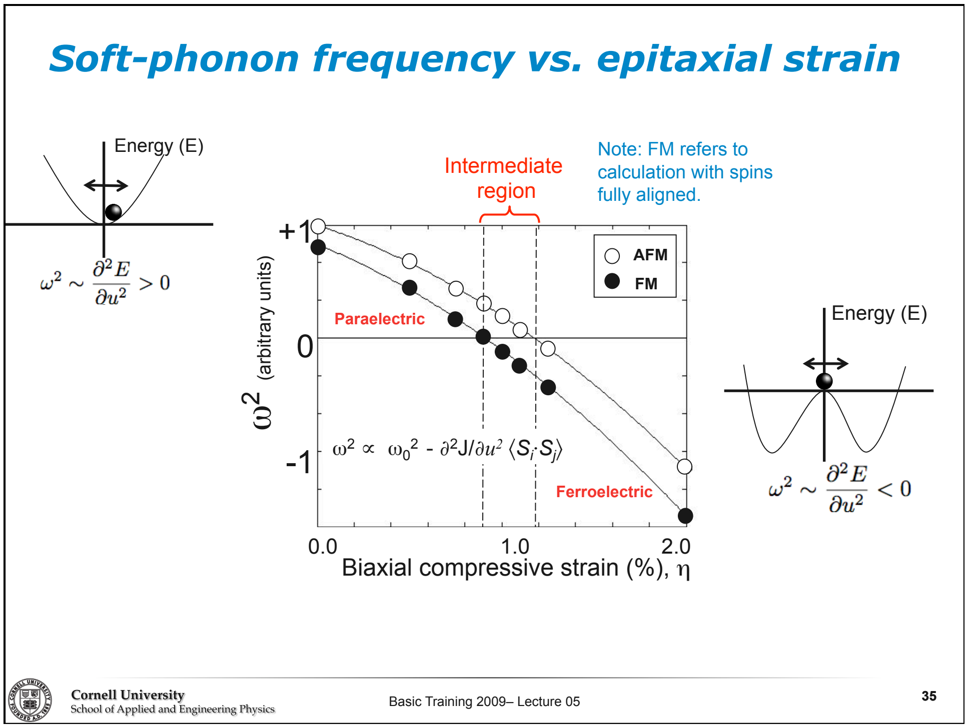
a (A) 3.863 (3.905)

- 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





# Soft-phonon frequency vs. epitaxial strain

Note: FM refers to calculation with spins fully aligned.

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

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

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

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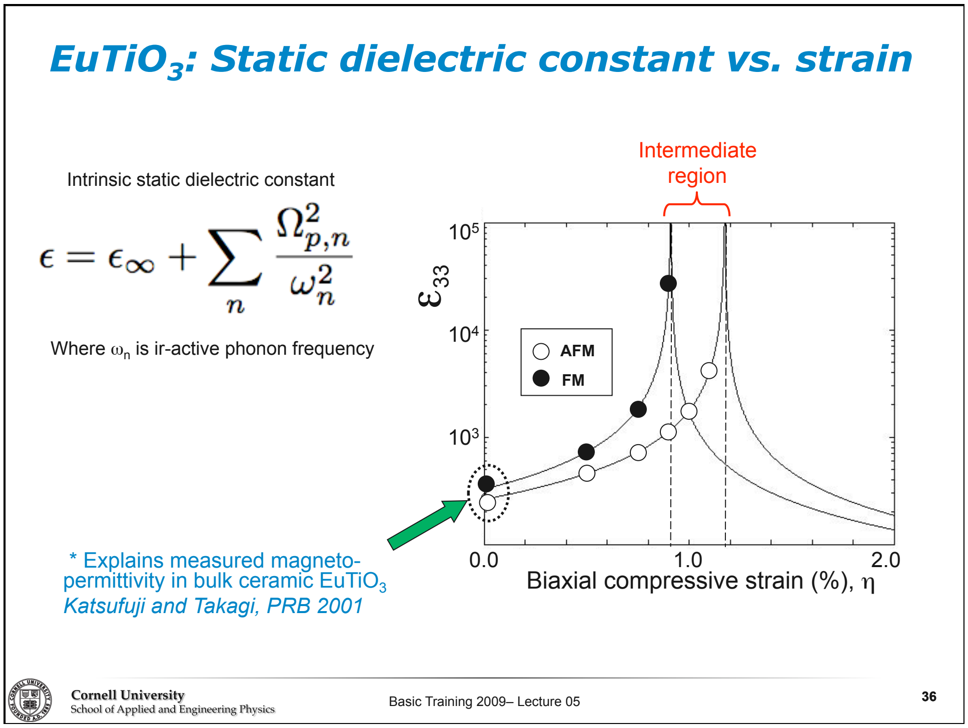

# EuTiO$_3$: Static dielectric constant vs. strain

Intrinsic static dielectric constant

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

Where $\omega_n$ is ir-active phonon frequency

* Explains measured magneto-permittivity in bulk ceramic EuTiO$_3$
*Katsufuji and Takagi, PRB 2001*

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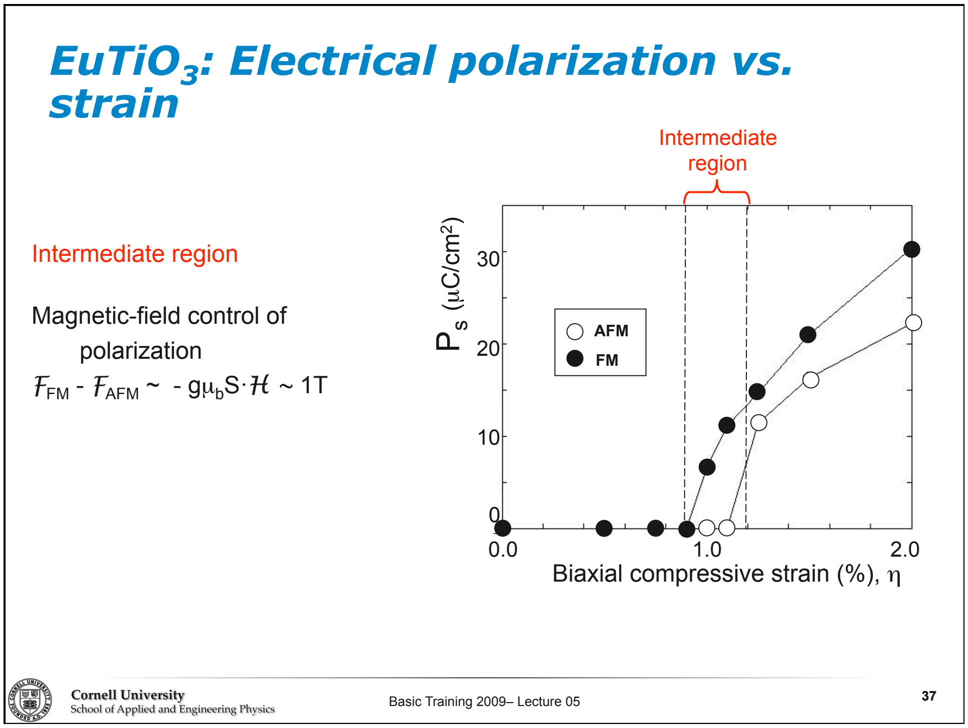
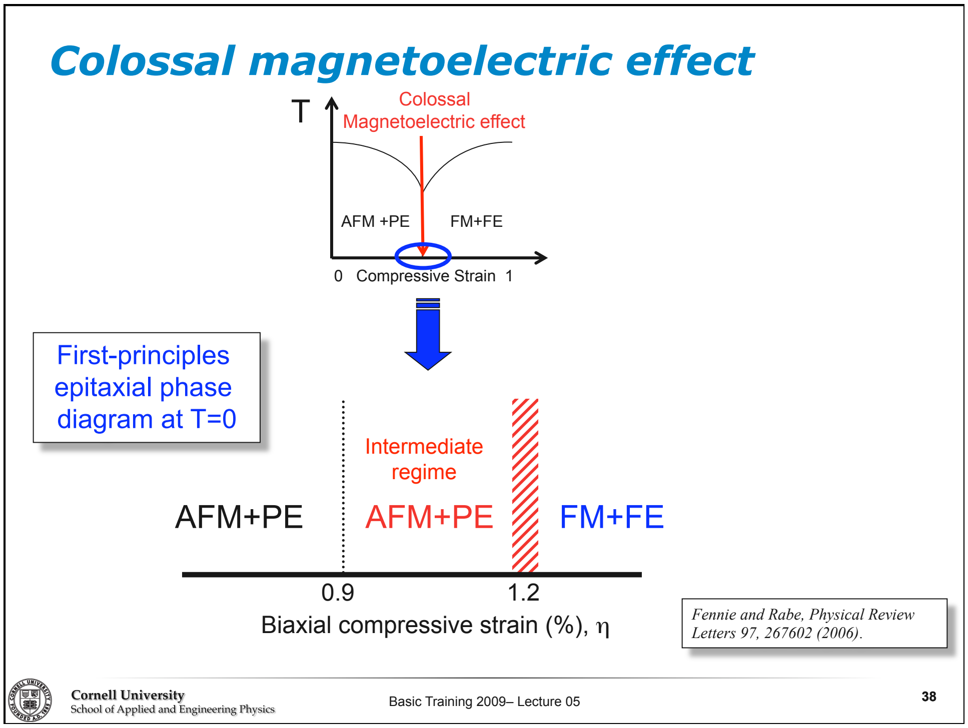


# EuTiO$_3$: Electrical polarization vs. strain

Intermediate region

Magnetic-field control of polarization

$\mathcal{F}_{FM} - \mathcal{F}_{AFM} \sim -g\mu_b S\cdot\mathcal{H} \sim 1T$



# Colossal magnetoelectric effect

First-principles epitaxial phase diagram at T=0

*Fennie and Rabe, Physical Review Letters 97, 267602 (2006).*

# *Can a ferroelectric induce magnetism?*

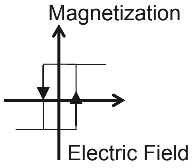
- Can an electric field be used to switch the magnetization 180°?
- What about to its time-reversed state? (are these the same thing?)

## Macroscopic property: Electric-field switching of ferromagnetism

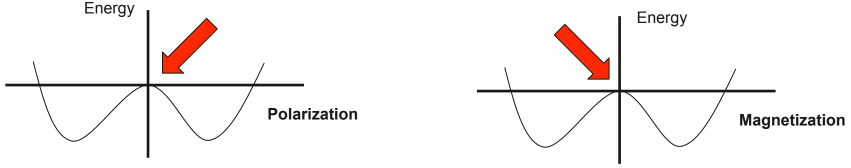
In a single phase material, the most promising route is when a ferroelectric lattice distortion induces ferromagnetism.

*in a system that is otherwise antiferromagnetically ordered!*

*Fox and Scott, J Phys. C ~1977*



*Expand about P =0, M=0*



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## Ferroelectrically induced weak-ferromagnetism

*Phenomenology: free energy of the paraelectric –antiferromagnetic phase, i.e., P=0, M=0.*

$$\mathcal{F}(P,M) = \alpha_1 P^2 + \beta_1 P^4 + \alpha_2 M^2 + \beta_2 M^4 + \gamma_{ijk} \mathsf{L}_i T_j M_k$$

*Two Cases:*

*If T is a polar vector* $I$ T = -T i.e., odd under space inversion

⇒ L must be odd under space inversion

*If T is an axial vector* $I$ T = +T i.e., even under space inversion

⇒ L must be even under space inversion

## Ferroelectrically induced weak-ferromagnetism

*Phenomenology: free energy of the paraelectric –antiferromagnetic phase, i.e., P=0, M=0.*

$$\mathcal{F}(P,M) = \alpha_1 P^2 + \beta_1 P^4 + \alpha_2 M^2 + \beta_2 M^4 + D\cdot(\mathrm{L} \times M)$$

***T*** *is an axial vector, e.g.,* ***T*** *≡ D, the Dzyaloshinskii vector*

*I* T = +T i.e., even under space inversion ⇒ L must be even under space inversion

Then regardless of the sign of $\alpha_2$, *M≠0 ⇒ weak ferromagnetism*

*But magnetoelectric effect, i.e., a coupling like ~PLM, in the paraelectric phase is zero by symmetry!*

---

## Ferroelectrically induced weak-ferromagnetism

*Phenomenology: free energy of the paraelectric –antiferromagnetic phase, i.e., P=0, M=0.*

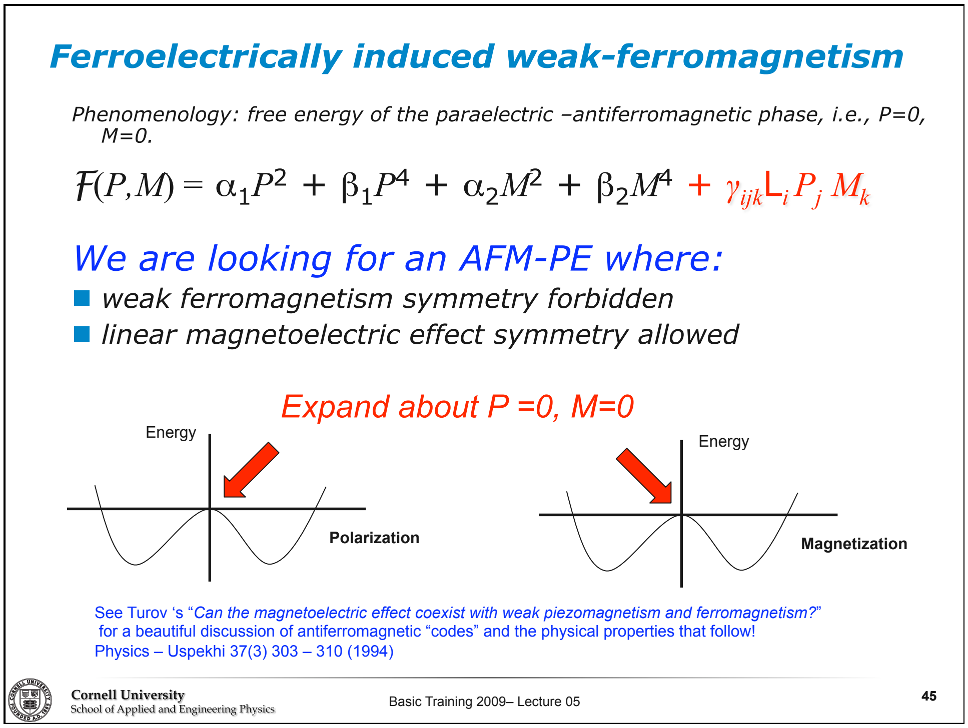
$$\mathcal{F}(P,M) = \alpha_1 P^2 + \beta_1 P^4 + \alpha_2 M^2 + \beta_2 M^4 + \gamma_{ijk}\mathrm{L}_i P_j M_k$$

***T*** *is a Polar vector, e.g., T ≡ P, the polarization vector*

*I* T = -T i.e., odd under space inversion ⇒ L must be odd under space inversion

*Weak ferromagnetism = 0 in paraelectric phase, (but ≠ 0 for nonzero P).*

*But ME effect in the paraelectric phase is ≠0 by symmetry!*



## Ferroelectrically induced weak-ferromagnetism

*Phenomenology: free energy of the paraelectric –antiferromagnetic phase, i.e., P=0, M=0.*

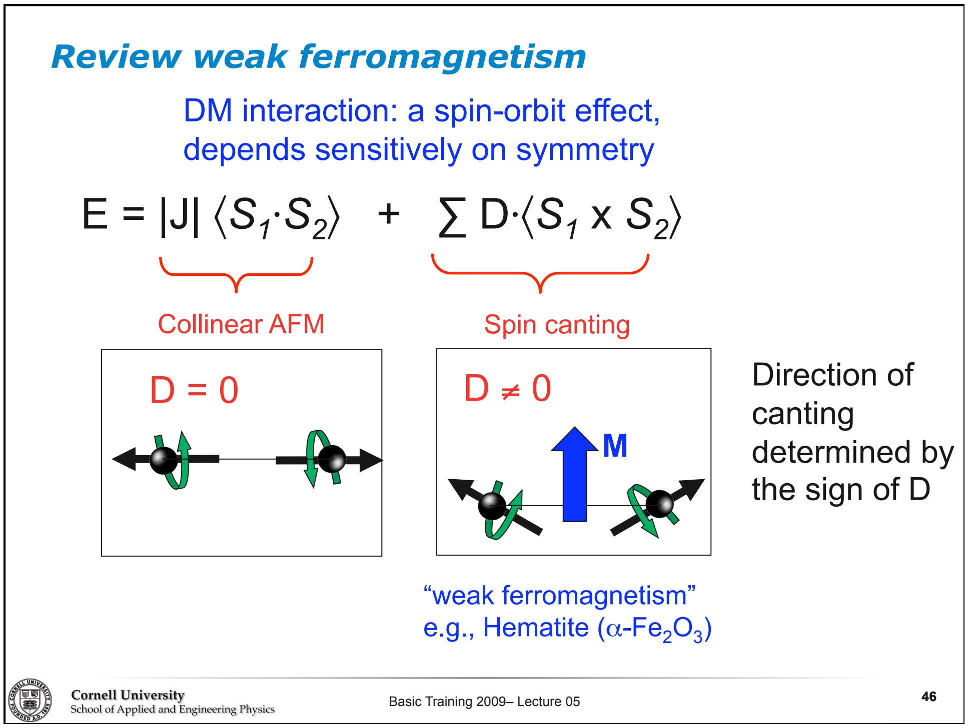
$$\mathcal{F}(P,M) = \alpha_1 P^2 + \beta_1 P^4 + \alpha_2 M^2 + \beta_2 M^4 + \gamma_{ijk} L_i P_j M_k$$

*We are looking for an AFM-PE where:*

- *weak ferromagnetism symmetry forbidden*
- *linear magnetoelectric effect symmetry allowed*

*Expand about P =0, M=0*

See Turov 's "*Can the magnetoelectric effect coexist with weak piezomagnetism and ferromagnetism?*" for a beautiful discussion of antiferromagnetic "codes" and the physical properties that follow! Physics – Uspekhi 37(3) 303 – 310 (1994)



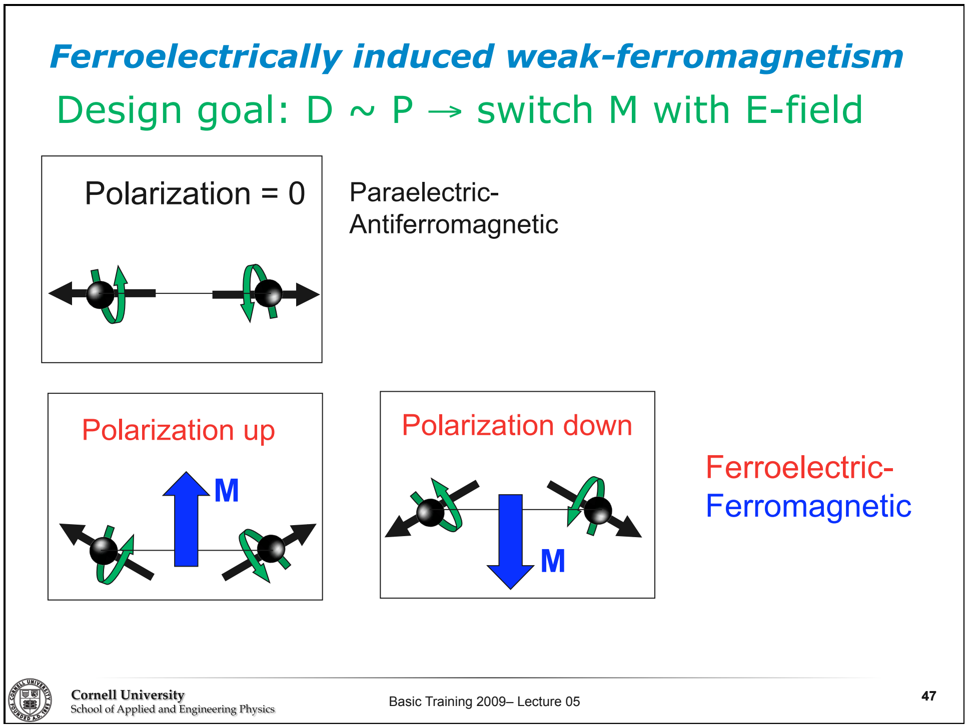
## Review weak ferromagnetism

DM interaction: a spin-orbit effect, depends sensitively on symmetry

$$E = \underbrace{|J| \langle S_1 \cdot S_2 \rangle}_{\text{Collinear AFM}} + \underbrace{\sum D \cdot \langle S_1 \times S_2 \rangle}_{\text{Spin canting}}$$

Direction of canting determined by the sign of D

"weak ferromagnetism"
e.g., Hematite ($\alpha$-$Fe_2O_3$)



## Ferroelectrically induced weak-ferromagnetism

Design goal: D ~ P → switch M with E-field

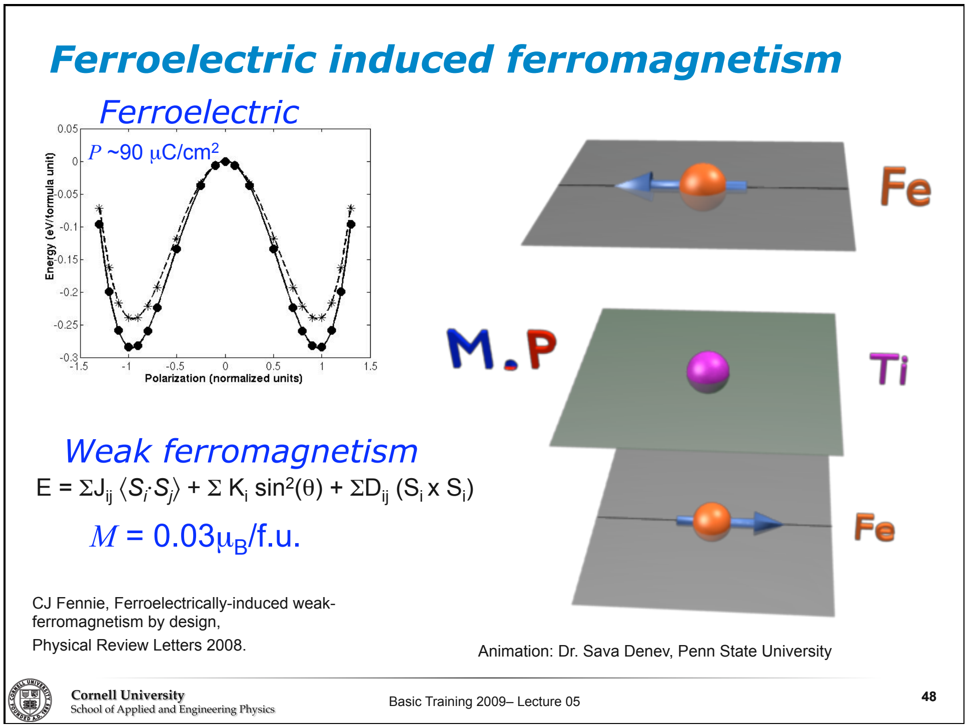
Polarization = 0

Paraelectric-
Antiferromagnetic

Polarization up

Polarization down

Ferroelectric-
Ferromagnetic



## Ferroelectric induced ferromagnetism

Ferroelectric

Weak ferromagnetism

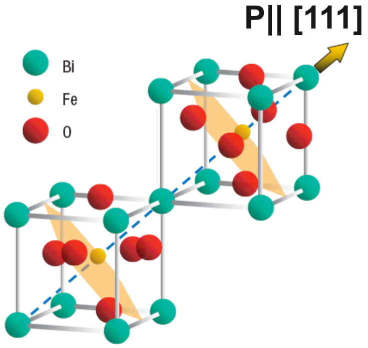
$$E = \Sigma J_{ij} \langle S_i \cdot S_j \rangle + \Sigma K_i \sin^2(\theta) + \Sigma D_{ij} (S_i \times S_i)$$

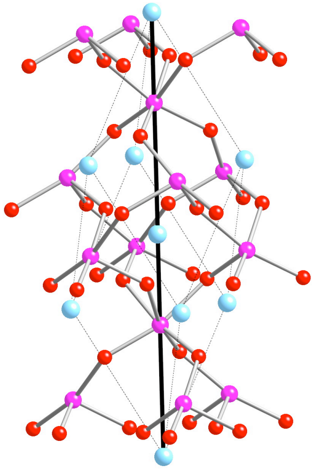
$M = 0.03\mu_B$/f.u.

CJ Fennie, Ferroelectrically-induced weak-ferromagnetism by design,
Physical Review Letters 2008.

Animation: Dr. Sava Denev, Penn State University

## $BiFeO_3$ structure and $LiNbO_3$-structure are isomorphic





$BiFeO_3$ space group R3c

$FeTiO_3$ space group R3c

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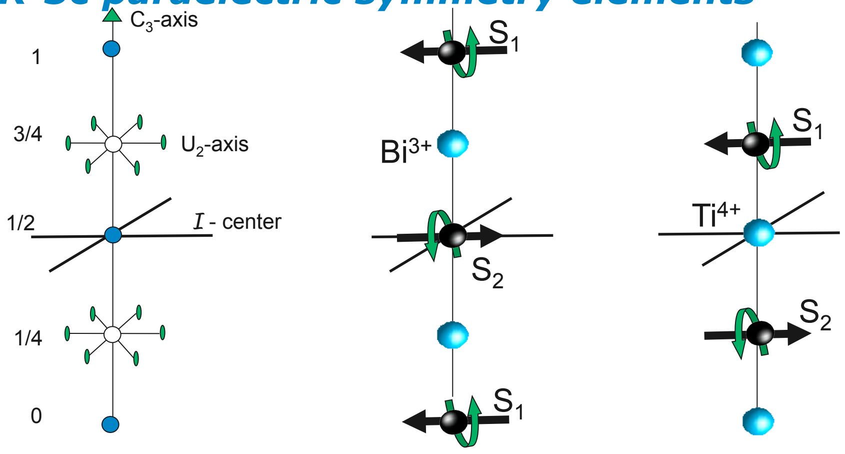
## R-3c paraelectric symmetry elements



$ABO_3$

○ A-site: (1/4,1/4,1/4) (3/4,3/4,3/4)

● B-site: (0,0,0) (1/2,1/2,1/2)

$BiFeO_3$

$L \equiv S_1\text{-}S_2$

$I\,L = I\,(S_1\text{-}S_2)$
$= (S_1\text{-}S_2)$
$= +L$

$FeTiO_3$

$L \equiv S_1\text{-}S_2$

$I\,L = I\,(S_1\text{-}S_2)$
$= (S_2\text{-}S_1)$
$= -L$

## Ferroelectrically induced weak-ferromagnetism

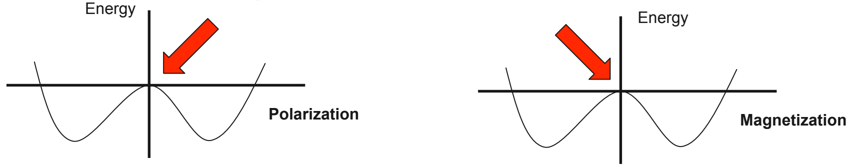
*Phenomenology: free energy of the paraelectric –antiferromagnetic phase, i.e., P=0, M=0.*

$$\mathcal{F}(P,M) = \alpha_1 P^2 + \beta_1 P^4 + \alpha_2 M^2 + \beta_2 M^4 + \gamma_{ijk} L_i P_j M_k$$

*We are looking for an AFM-PE where:*

- *weak ferromagnetism symmetry forbidden*
- *linear magnetoelectric effect symmetry allowed*

*Expand about P =0, M=0*



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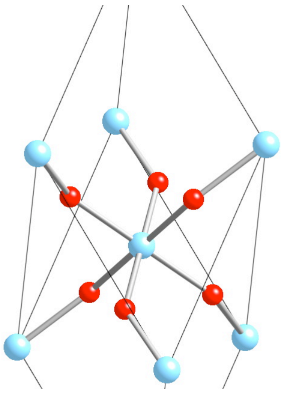
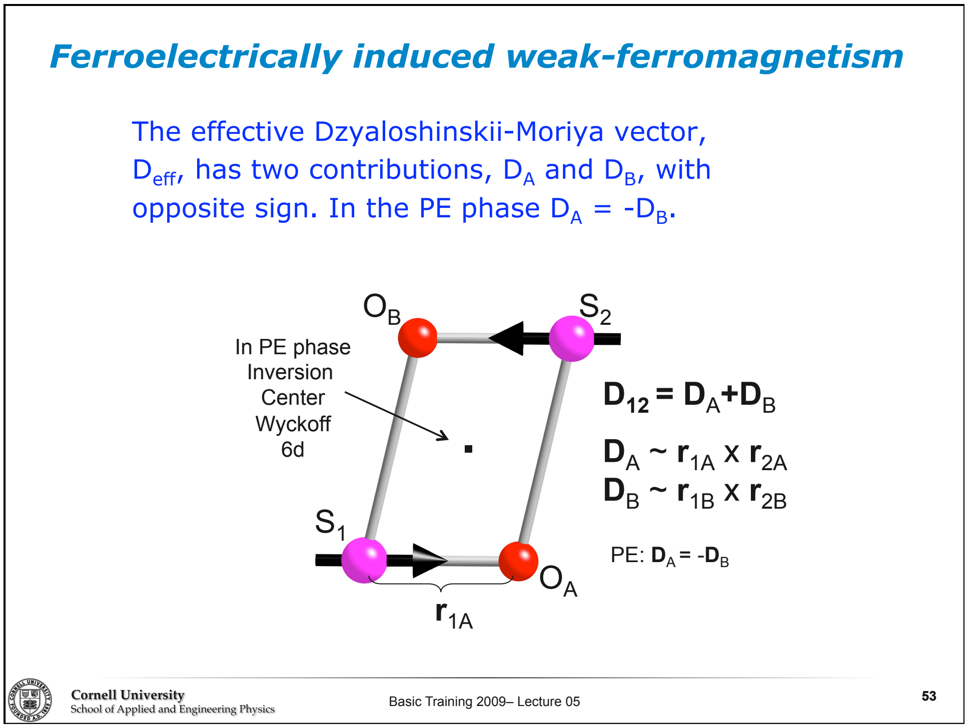
Physics – Uspekhi 37(3) 303 – 310 (1994)





## Ferroelectrically induced weak-ferromagnetism

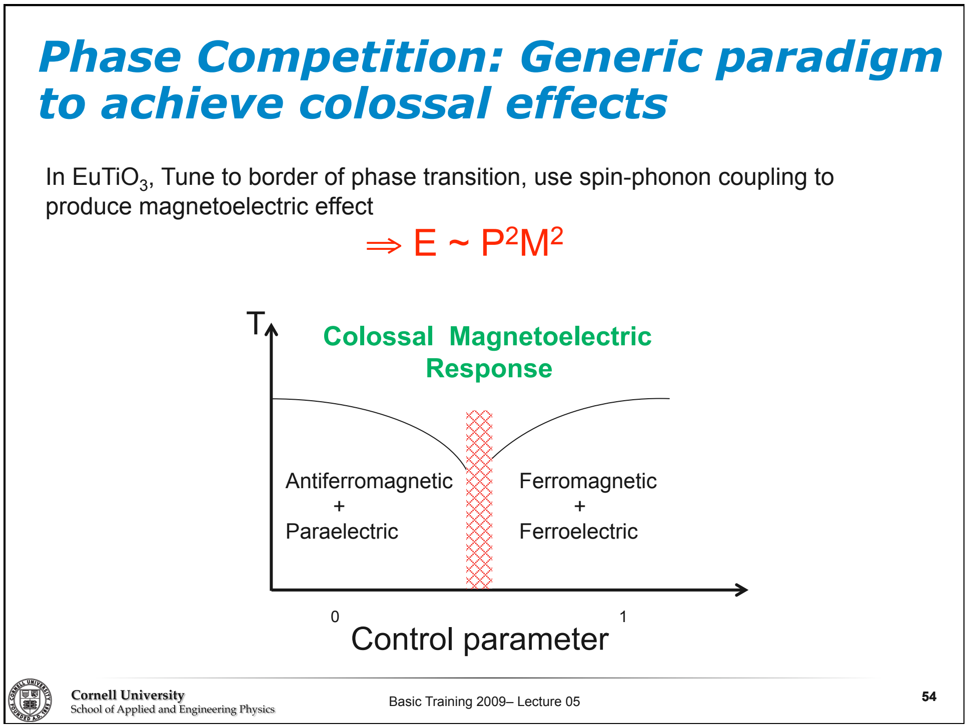
The effective Dzyaloshinskii-Moriya vector, $D_{eff}$, has two contributions, $D_A$ and $D_B$, with opposite sign. In the PE phase $D_A = -D_B$.

$\mathbf{D}_{12} = \mathbf{D}_A + \mathbf{D}_B$

$\mathbf{D}_A \sim \mathbf{r}_{1A} \times \mathbf{r}_{2A}$

$\mathbf{D}_B \sim \mathbf{r}_{1B} \times \mathbf{r}_{2B}$

PE: $\mathbf{D}_A = -\mathbf{D}_B$



## Phase Competition: Generic paradigm to achieve colossal effects

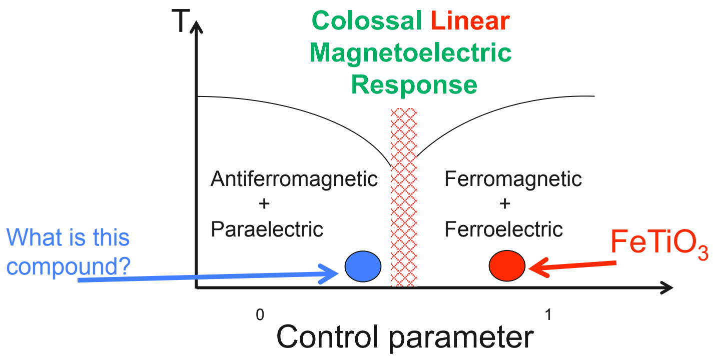
In $EuTiO_3$, Tune to border of phase transition, use spin-phonon coupling to produce magnetoelectric effect

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

## Phase Competition: Generic paradigm to achieve colossal effects

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

$$\Rightarrow E \sim P\cdot(L \times M)$$



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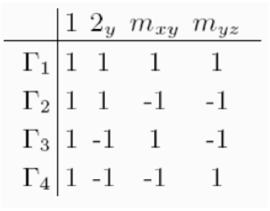
## Symmetry of magneto-electric interactions

$$\mathcal{H} = \sum_{\alpha\beta\gamma,\mathbf{q}} a_{\alpha\beta\gamma}(\mathbf{q}) M_\alpha(\mathbf{q}) M_\beta(-\mathbf{q}) P_\gamma(0)\ .$$

Trilinear Coupling of M and P is allowe

Representational Analysis: M order parameters transform to one of the four irreducible representations in $TbMnO_3$: $\Gamma_2+\Gamma_3$

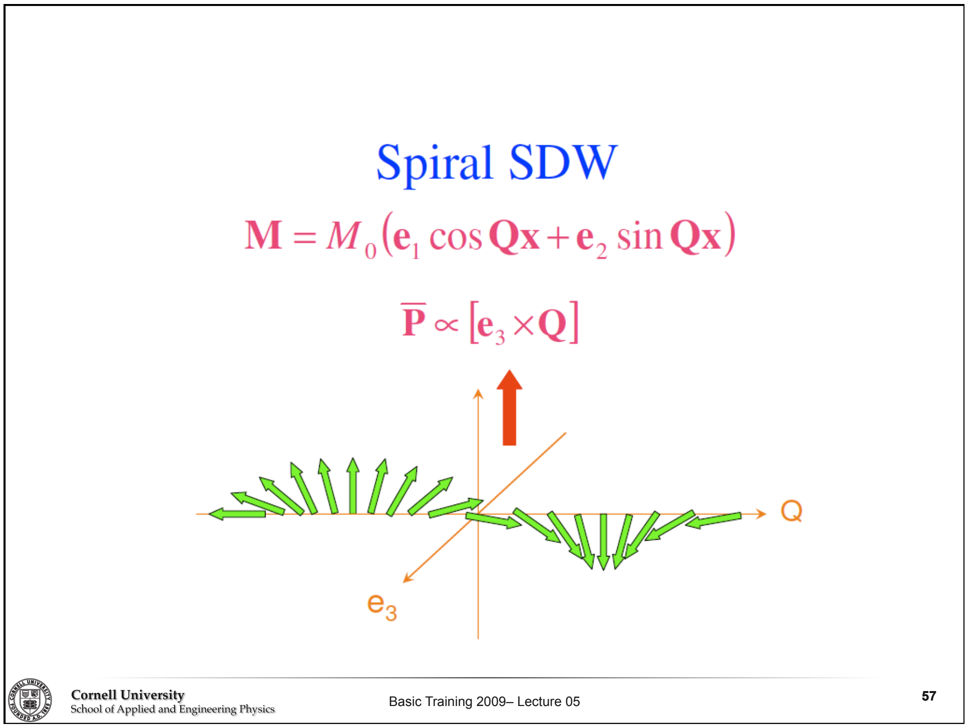


| | $1$ | $2_y$ | $m_{xy}$ | $m_{yz}$ |
|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 |
| $\Gamma_2$ | 1 | 1 | -1 | -1 |
| $\Gamma_3$ | 1 | -1 | 1 | -1 |
| $\Gamma_4$ | 1 | -1 | -1 | 1 |

→ **P** has to transform as $M_\alpha(q)\ M_\beta(-q)$

→ Electric polarization is only allowed along the c-direction as observed (P has to be even under 1 & $m_{yz}$ and odd under $2_y$ & $m_{xy}$)

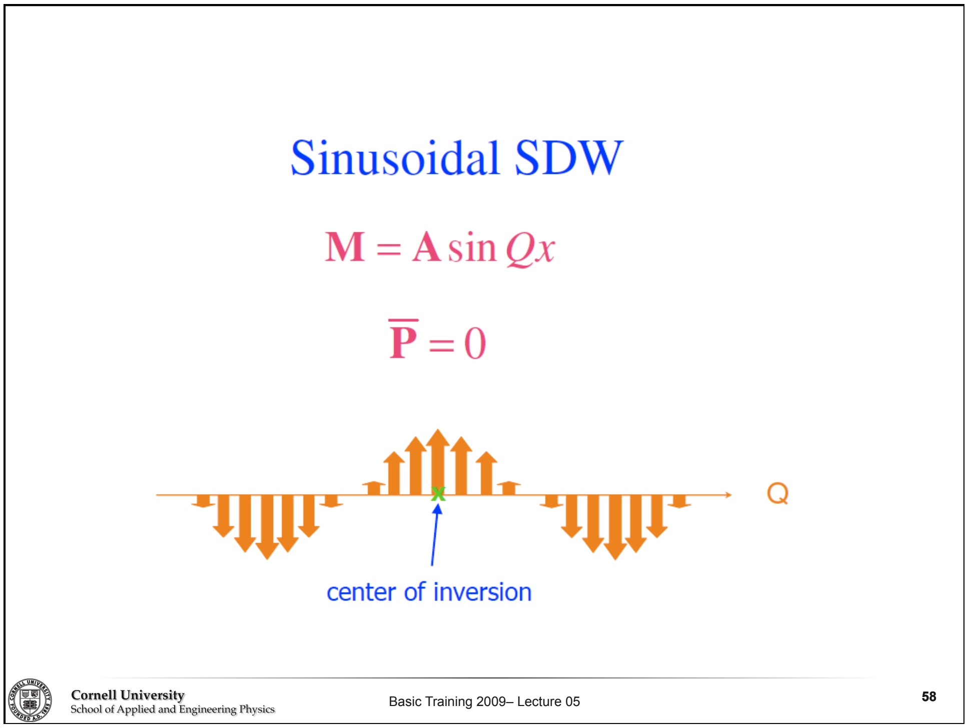
M. Kenzelmann et al, Phys. Rev. Lett. **95**, 087206 (2005)



## Spiral SDW

$$\mathbf{M} = M_0\left(\mathbf{e}_1 \cos \mathbf{Qx} + \mathbf{e}_2 \sin \mathbf{Qx}\right)$$

$$\overline{\mathbf{P}} \propto [\mathbf{e}_3 \times \mathbf{Q}]$$



## Sinusoidal SDW

$$\mathbf{M} = \mathbf{A} \sin Qx$$

$$\overline{\mathbf{P}} = 0$$

# Sinusoidal-helicoidal transition

**Ginzburg-Landau expansion**

$$\Phi_m = a_x (M^x)^2 + a_y (M^y)^2 + a_z (M^z)^2 + \frac{b}{2} M^4 + c\mathbf{M}\left(\frac{d^2}{dx^2} + Q^2\right)^2 \mathbf{M}$$

**Anisotropy:** $\boxed{a_x < a_y = a_x + \Delta < a_z}$

**1st transition: Sinusoidal SDW** $\mathbf{M} = M^x \hat{\mathbf{x}} \cos Qx$

$$a_x = \alpha (T - T_{SDW}) = 0$$

**P = 0**

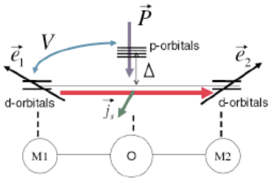
**2nd transition: Helicoidal SDW** $\mathbf{M} = M^x \hat{\mathbf{x}} \cos Qx + M^y \hat{\mathbf{y}} \sin Qx$

$$a_y = \frac{a_x}{3} \qquad \boxed{T_{SP} = T_{SDW} - \frac{3}{2}\frac{\Delta}{\alpha}}$$

**P || y**

---

**1) Spin-current**



$$\vec{P} \propto \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)$$

unit vector connecting the sites $i$ and $j$

Katsura et al, Phys. Rev. Lett. **95**, 057205 (2005)

**2) Dzyaloshinskii-Moriya interactions**

$$\mathcal{H}_{\mathrm{DM}} = \sum_i \mathbf{D}_i \cdot (\mathbf{S}_{i-1} \times \mathbf{S}_i)$$

sometimes called the
"inverse Dzyaloshinskii-Moriya effect"

Sergienko et al, Phys. Rev. B **73**, 094434 (2006)

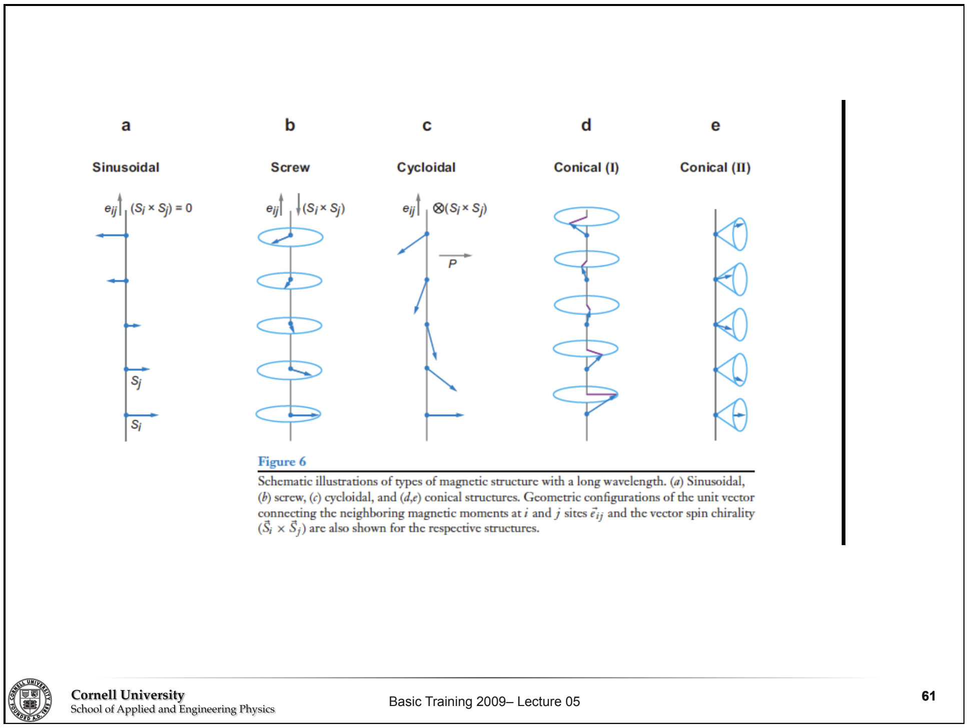
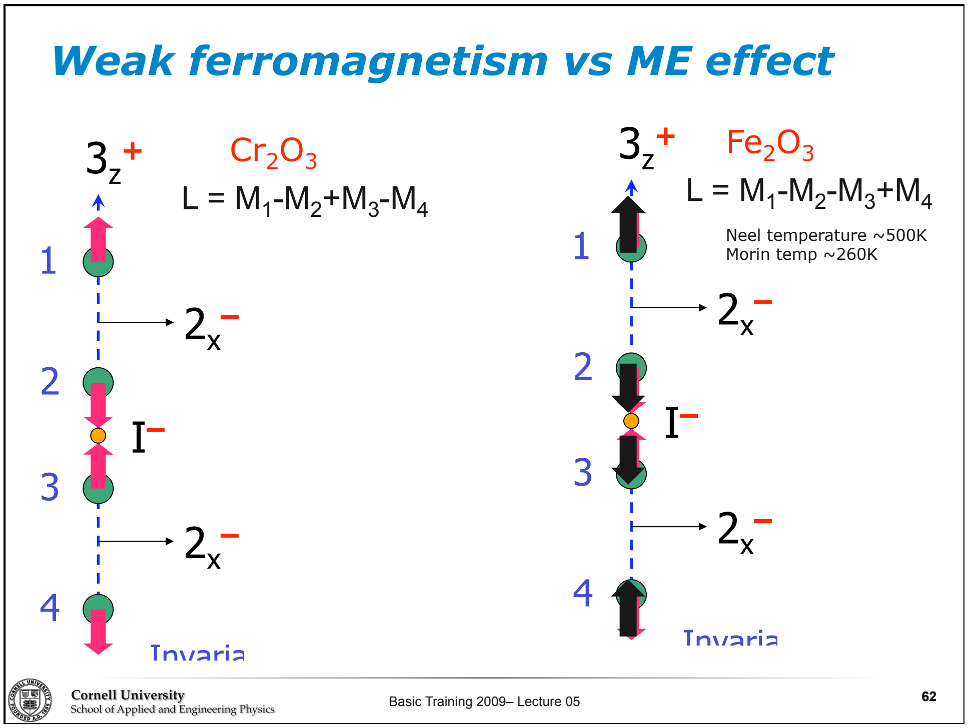


**Figure 6**

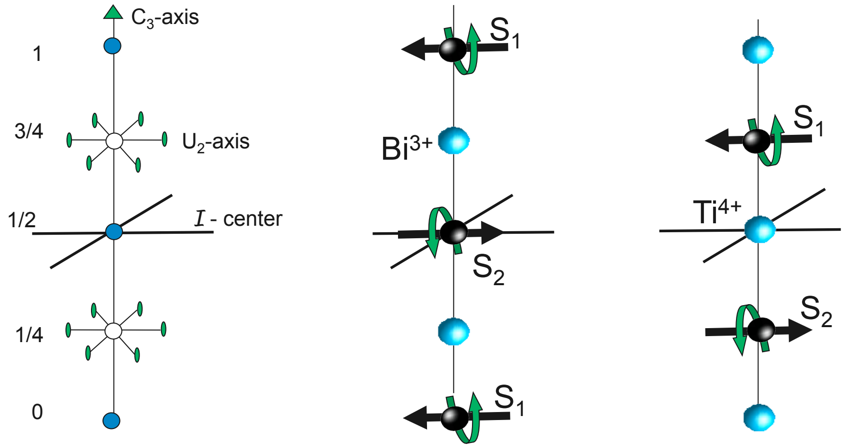
Schematic illustrations of types of magnetic structure with a long wavelength. (*a*) Sinusoidal, (*b*) screw, (*c*) cycloidal, and (*d*,*e*) conical structures. Geometric configurations of the unit vector connecting the neighboring magnetic moments at $i$ and $j$ sites $\vec{e}_{ij}$ and the vector spin chirality $(\vec{S}_i \times \vec{S}_j)$ are also shown for the respective structures.



## Weak ferromagnetism vs ME effect

Neel temperature ~500K
Morin temp ~260K

# R-3c paraelectric symmetry elements



**$ABO_3$**

○ A-site: (1/4,1/4,1/4) (3/4,3/4,3/4)

● B-site: (0,0,0) (1/2,1/2,1/2)

**$BiFeO_3$**

$L \equiv S_1 - S_2$

$$I\,L = I(S_1 - S_2) = (S_1 - S_2) = +L$$

**$FeTiO_3$**

$L \equiv S_1 - S_2$

$$I\,L = I(S_1 - S_2) = (S_2 - S_1) = -L$$

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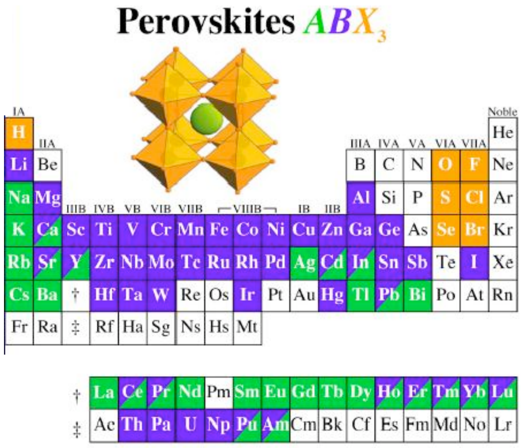
# Perovskites and the Period Table



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