

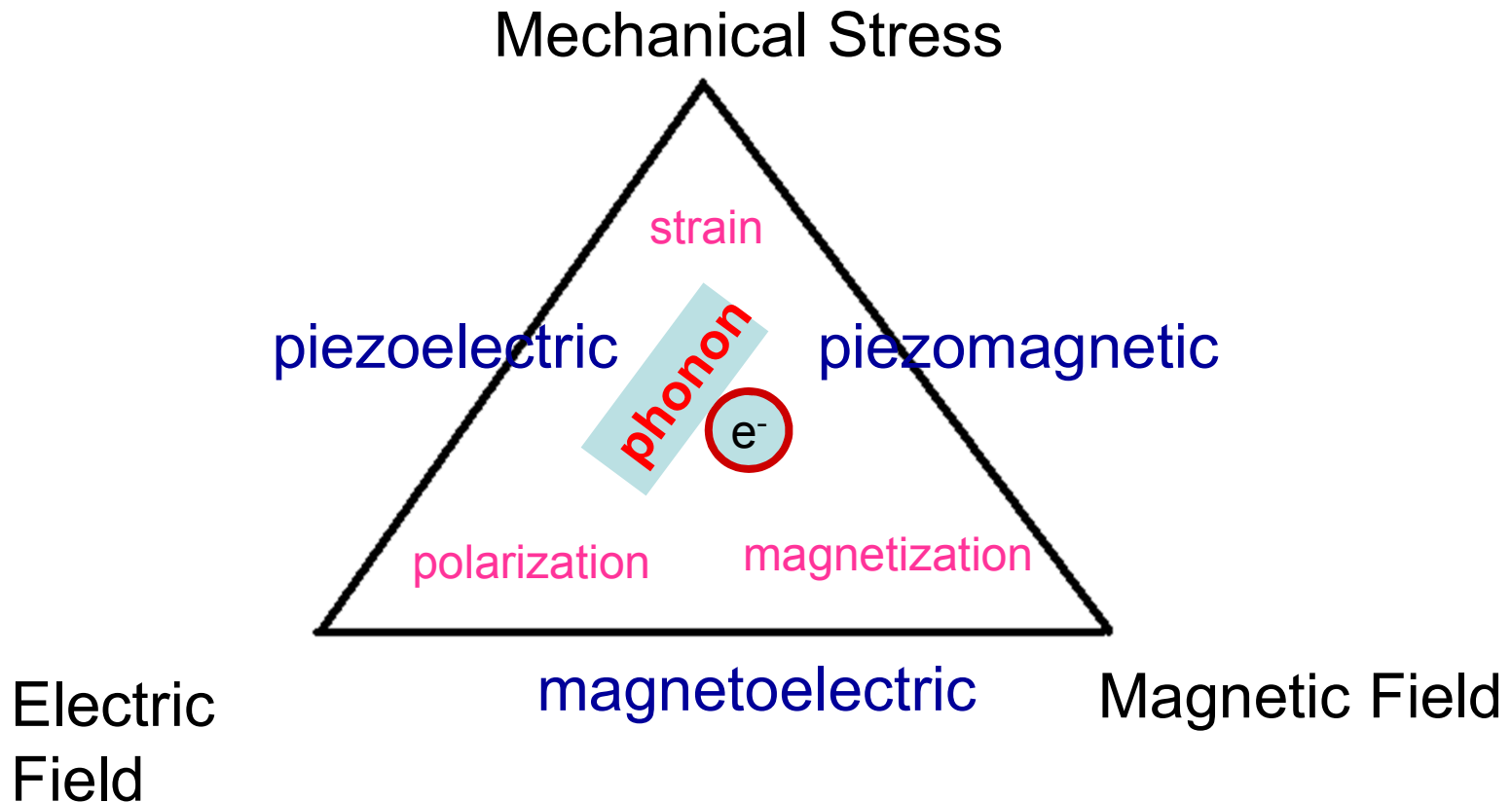
Functional Materials II:
Ferroics and Multiferroics

Umesh V Waghmare

Theoretical Sciences Unit
J. Nehru Centre for Advanced Scientific Research
Bangalore 560 064, INDIA
<http://www.jncasr.ac.in/waghmare>

JAKS-2012

Important Fields and Couplings in *smart functional materials*



A material that executes a nontrivial action through coupling with chemical, electrical, magnetic or mechanical stress field (s).

Ferroics and Multiferroics

- Smart materials:

Sense external stimulus (*sensor*)

Actuate a controlled response (*actuator*)

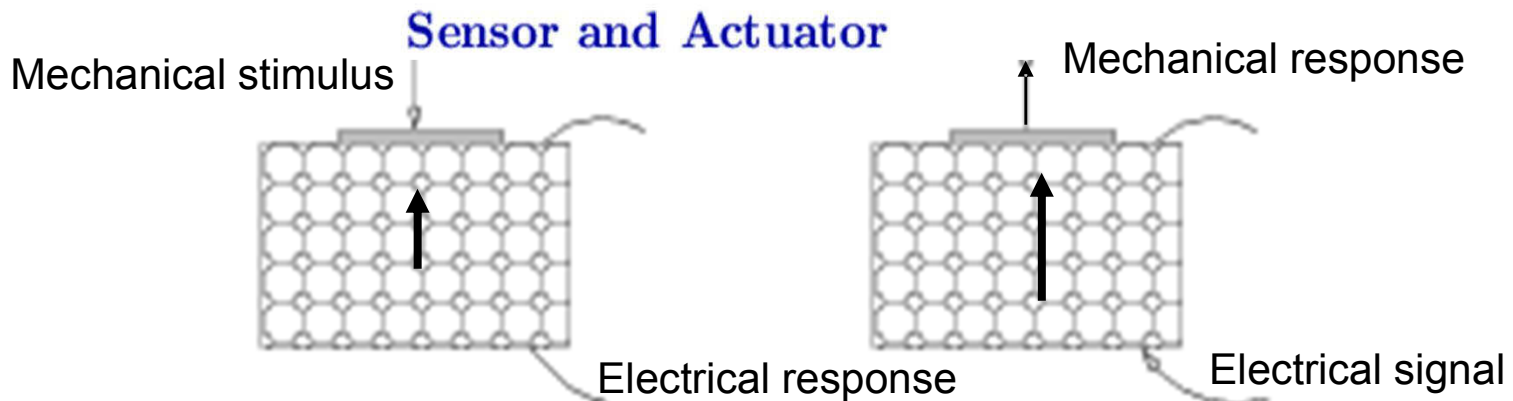
- Memory effects

Switchability between different states

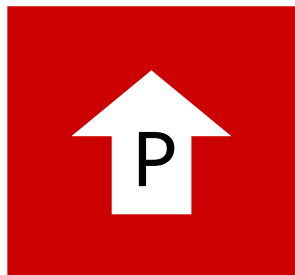
They exhibit interesting phase transitions

INTRODUCTION

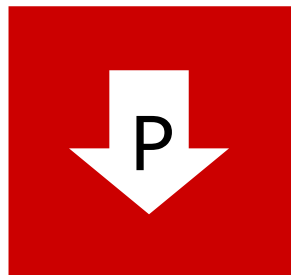
“Smart” Materials: Piezoelectrics



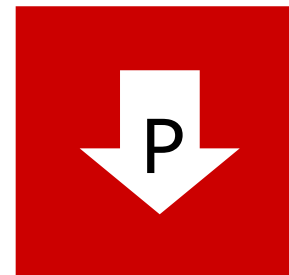
Subclass: Ferroelectrics ↔ switchability: a kind of “Ferroic”



$$E = 0$$



$$E = -E_0$$



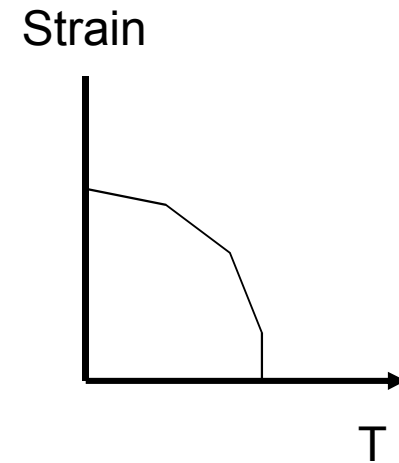
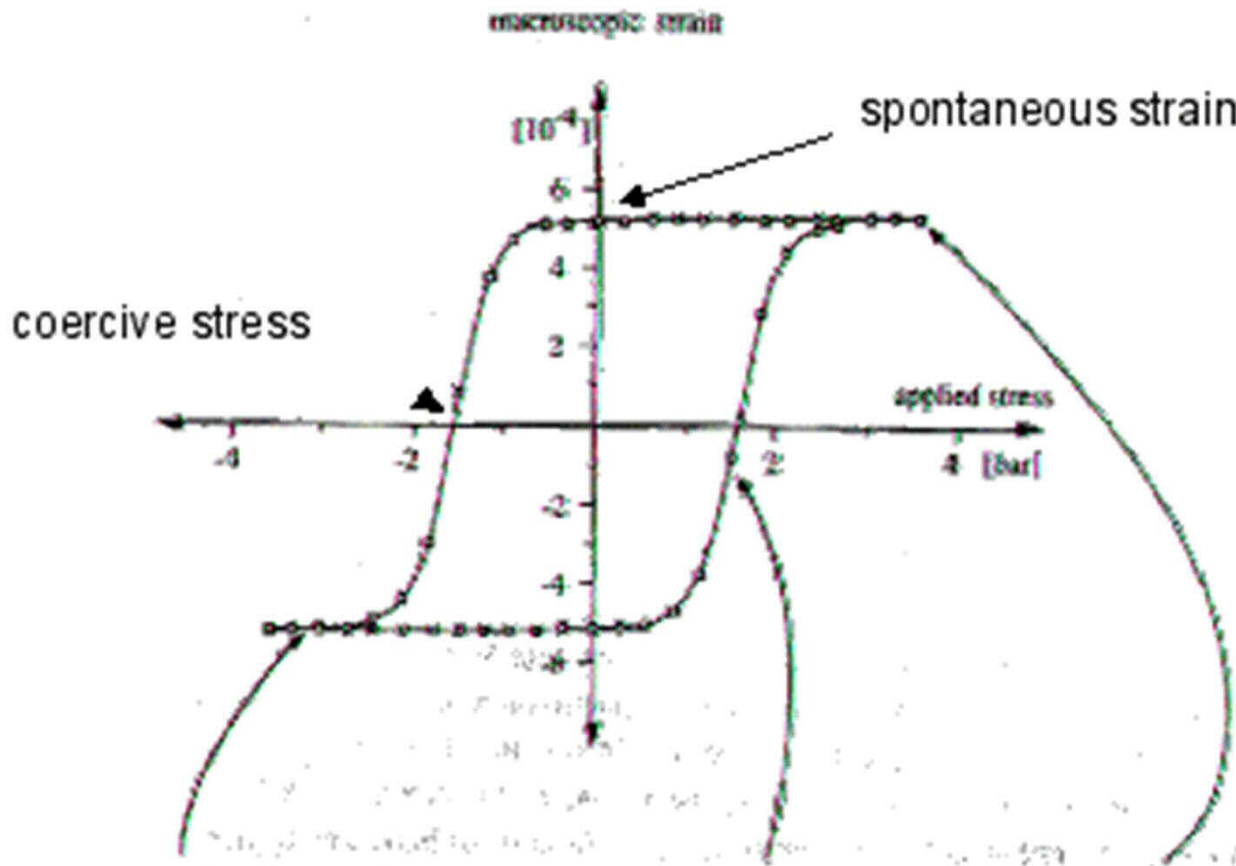
$$E = 0$$

Many technological applications

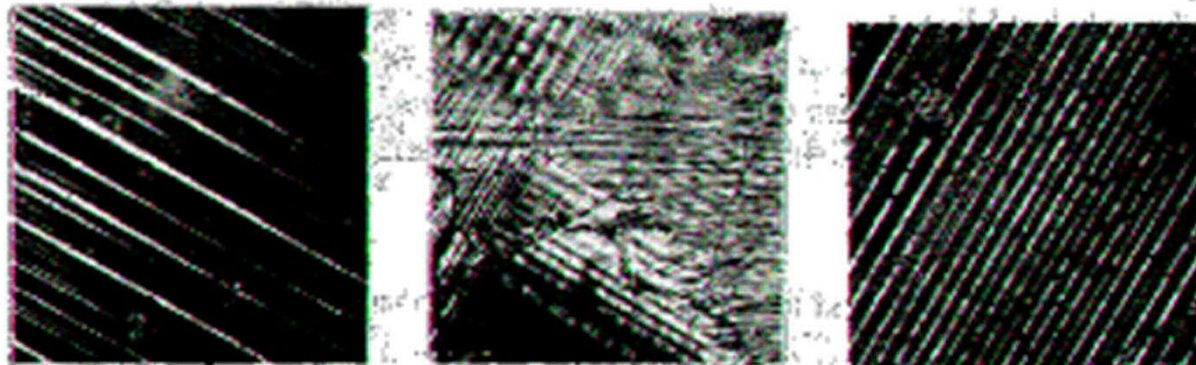
non-volatile memories, micro-electro-mechanical systems (MEMS),
micromachines, **Lots of applications**

Camouflage: acoustic waves-based detection; IR-detectors

Ferroelastic Material

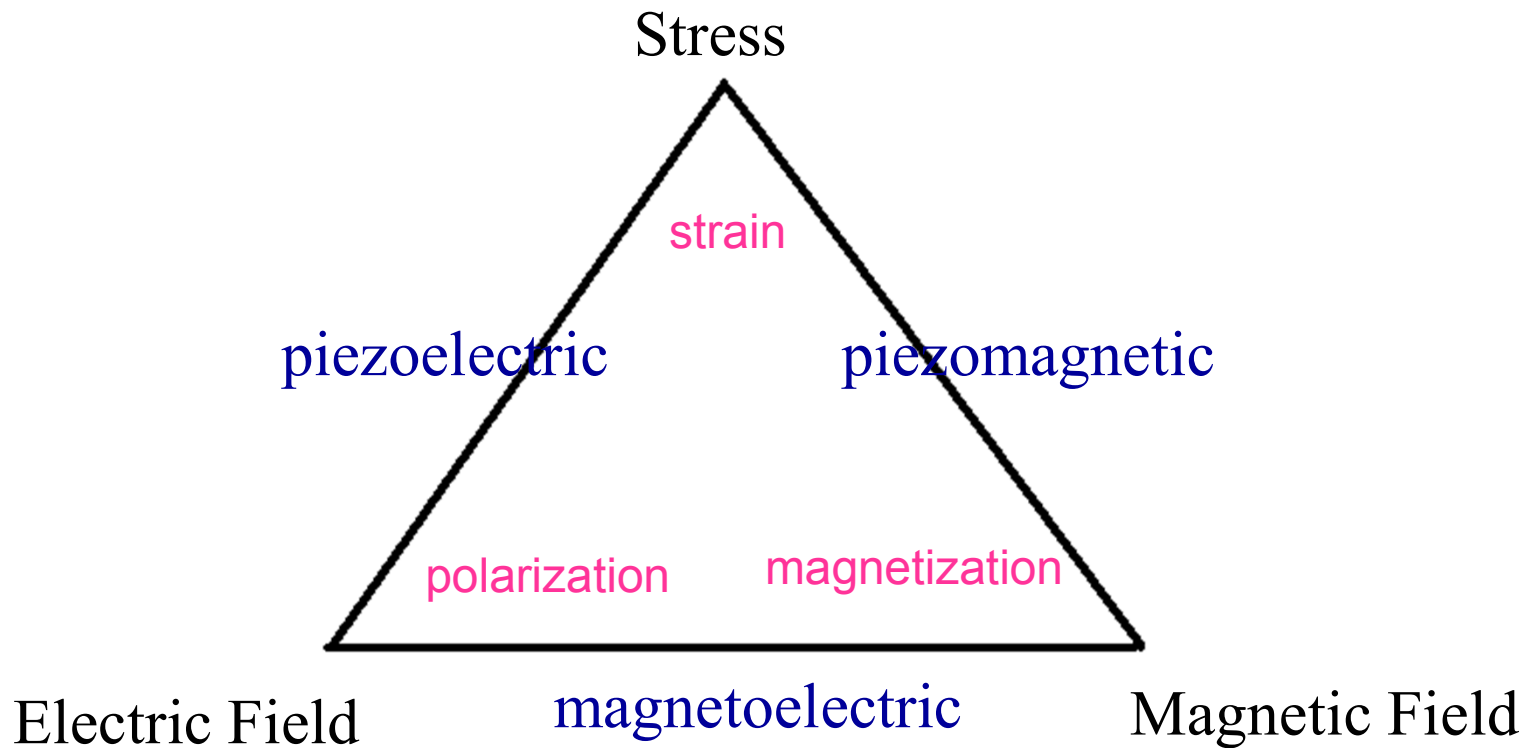


Eg. Lead Ortho Phosphate



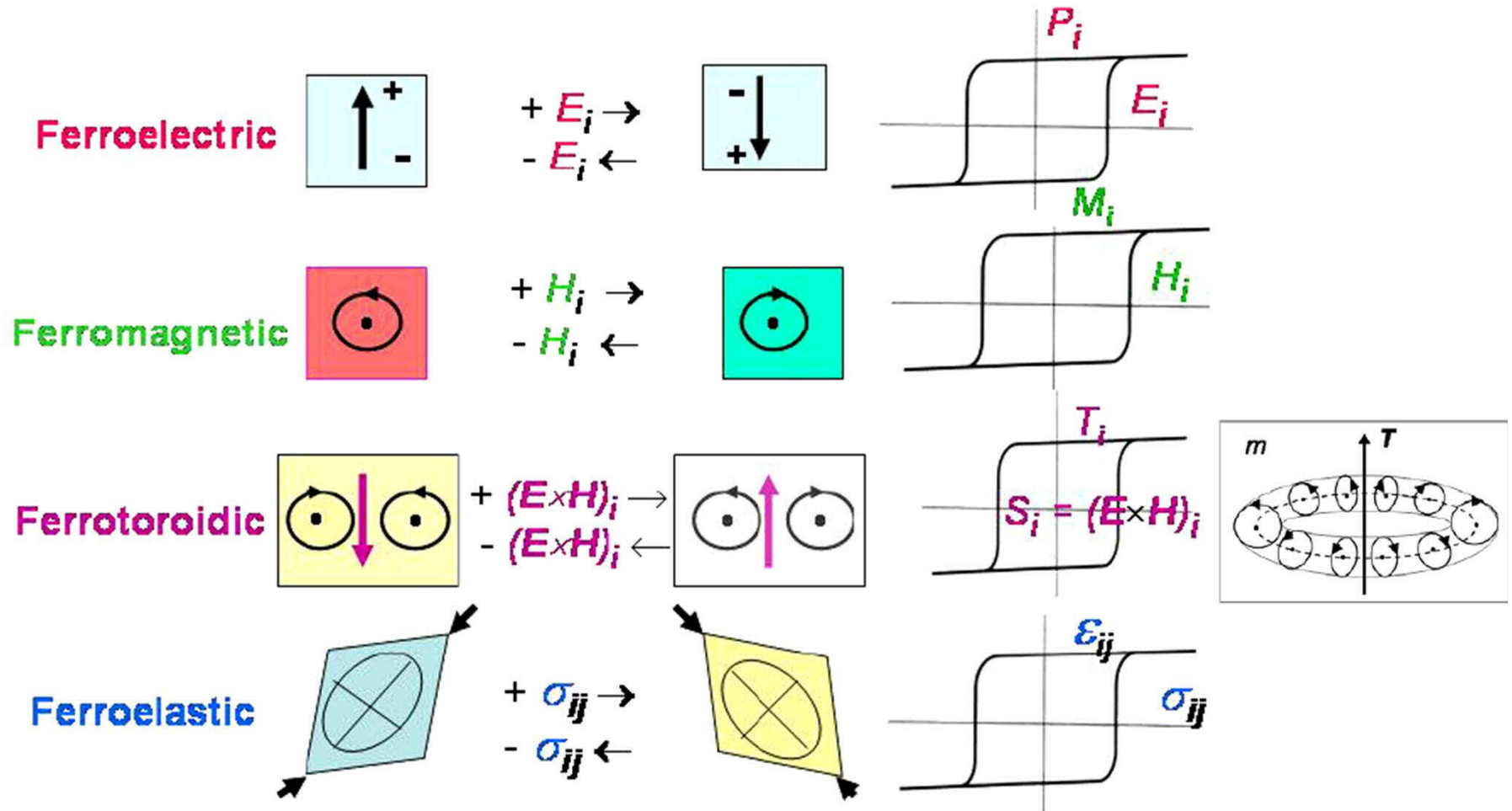
Shape Memory
Alloys: Nitinol
Superelasticity

Important Fields and Couplings in Materials: *smart materials*



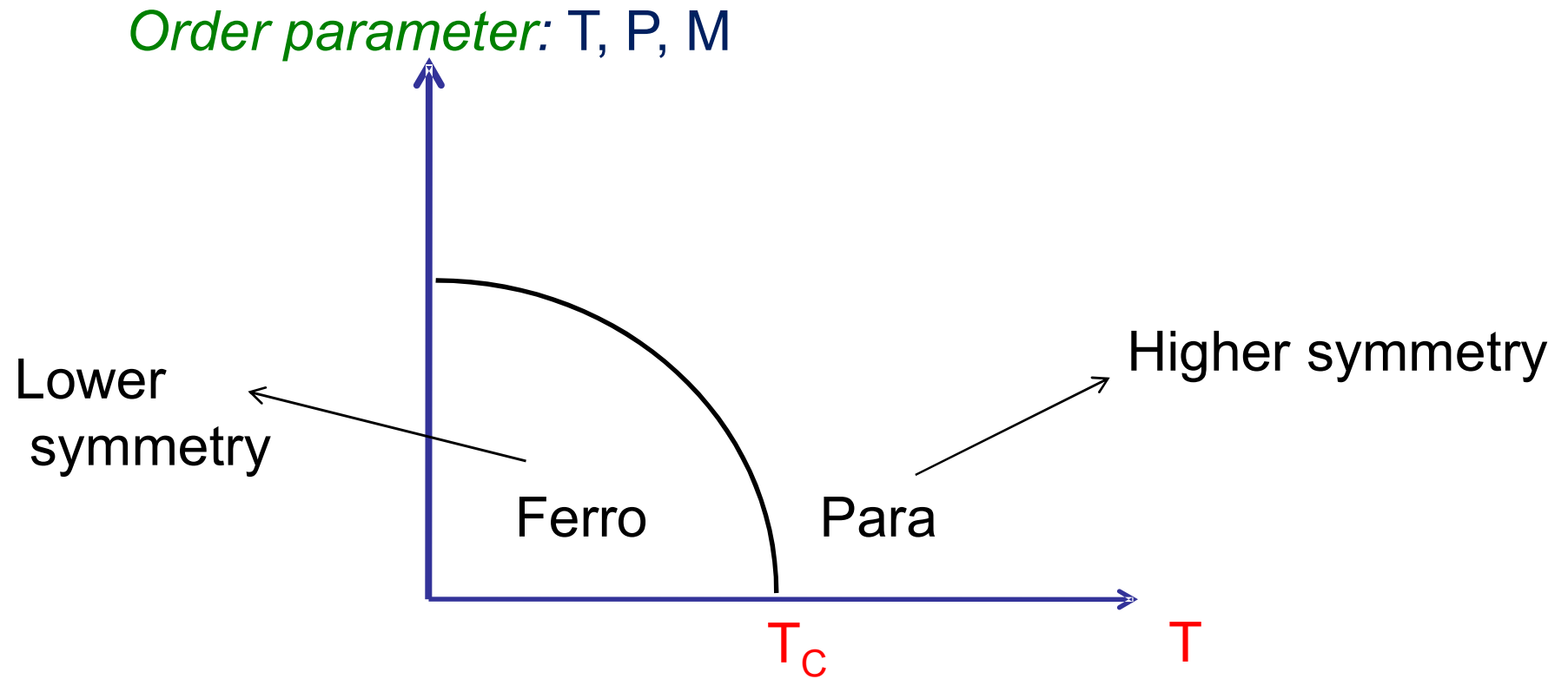
Symmetry Properties: Ferroics

The field breaking symmetry of the high-T phase



H Schmid, J of Physics Cond Mat 20, 434201 (2008).

Phase Transition in Ferroics



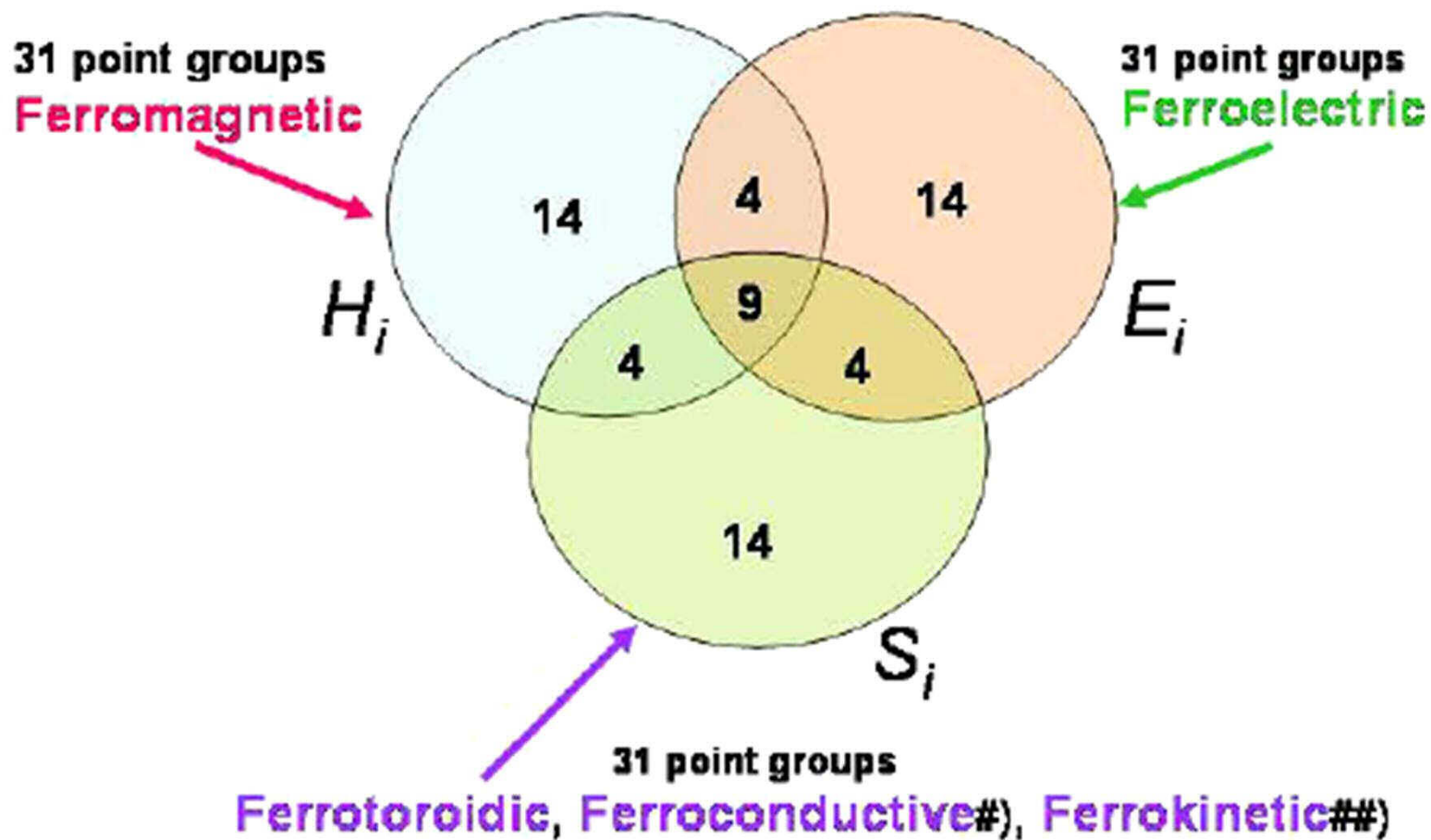
Symmetry Properties: Ferroics

Symmetry of the field breaking symmetry of the high-T phase

Ascher (1966a)				Ascher (1974)			
1	$\bar{1}$	1'	$\bar{1}'$				
1	1	1	1	ρ	$\partial M / \partial t$, grad P		ϵ
1	-1	1	-1	P	P , $\partial v / \partial t$		P
1	1	-1	-1	M	M , grad v		M
1	-1	-1	1	j	j , v , p , A , $\partial P / \partial t$, grad M		T

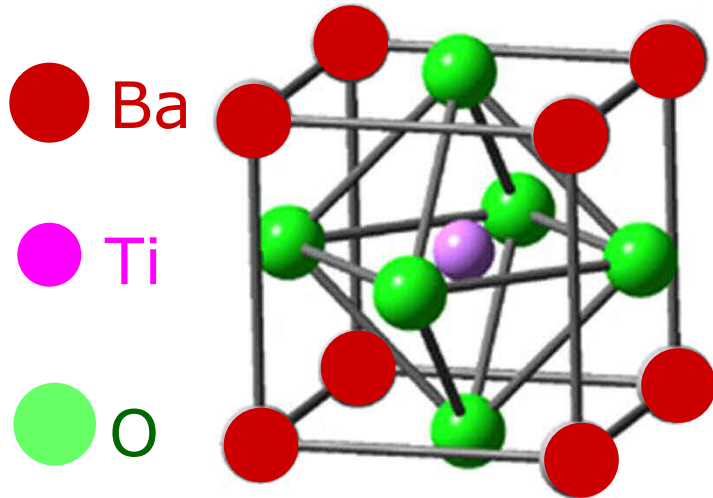
1: identity, $\bar{1}$: inversion, 1': time reversal, $\bar{1}'$: Inv*TR

For a material to be a ferroic of given type, its symmetry group can not include the corresponding symmetries



H Schmid, J of Physics Cond Mat 20, 434201 (2008).

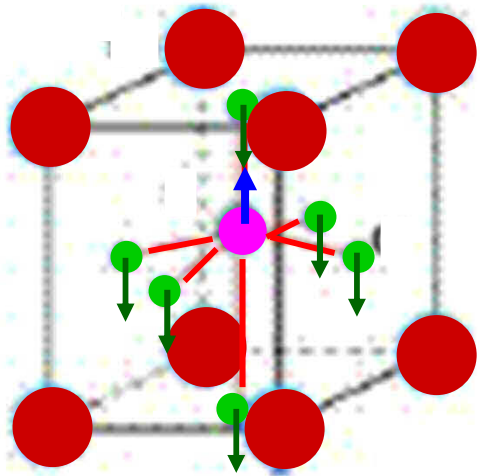
➤ Ferroelectric BaTiO₃



➤ High Temperature

➤ CUBIC Structure:
PARAELECTRIC

➤ $a = b = c$



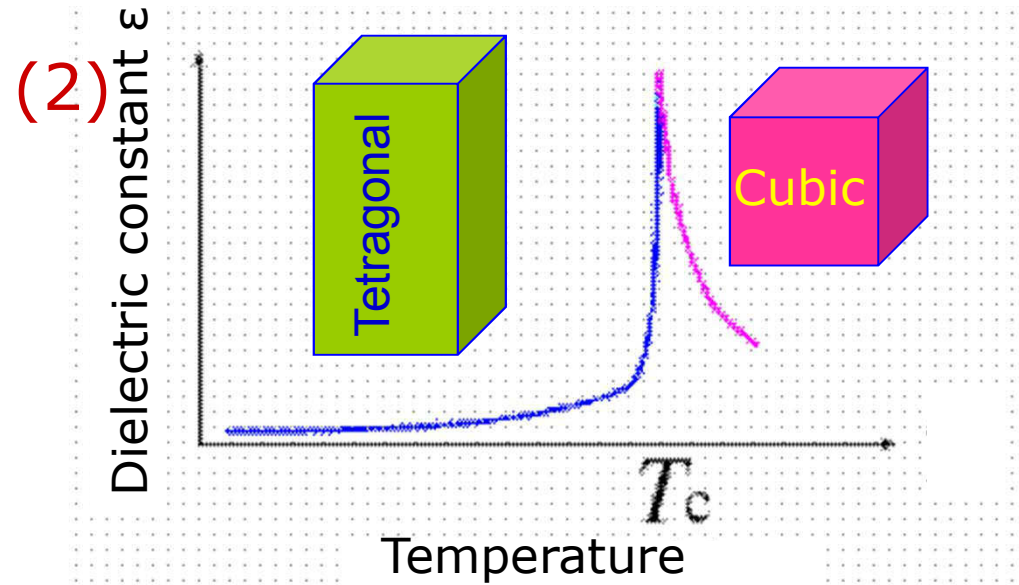
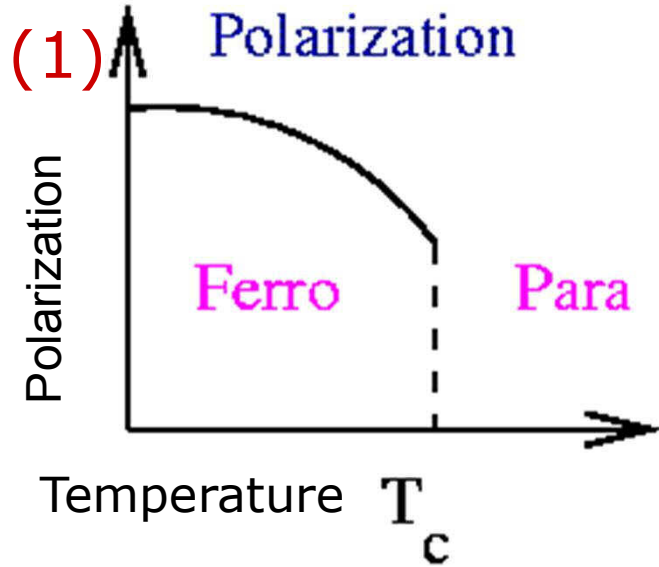
➤ Room Temperature

➤ TETRAGONAL Structure:
FERROELECTRIC

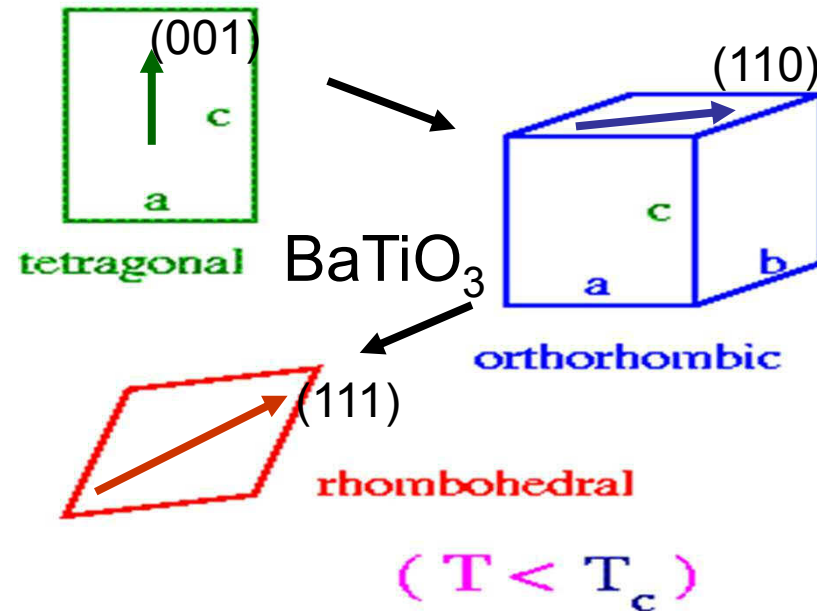
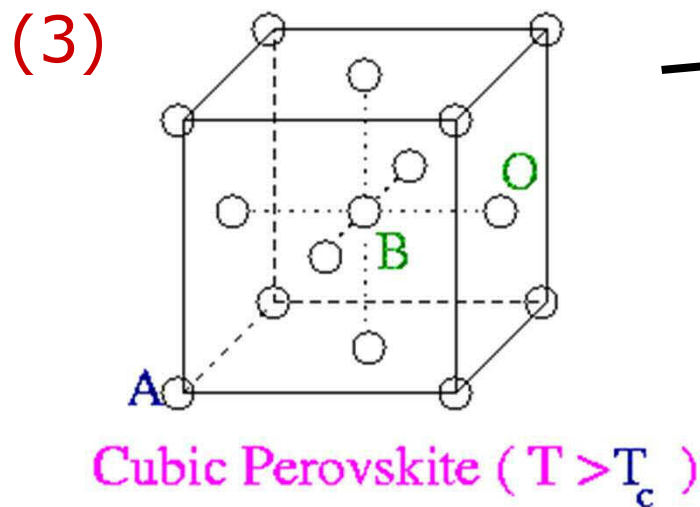
➤ $a = b \neq c$: strain

❖ Ti⁴⁺ and Ba²⁺ shifted wrt O²⁻ →
finite dipole moment: polar phonon

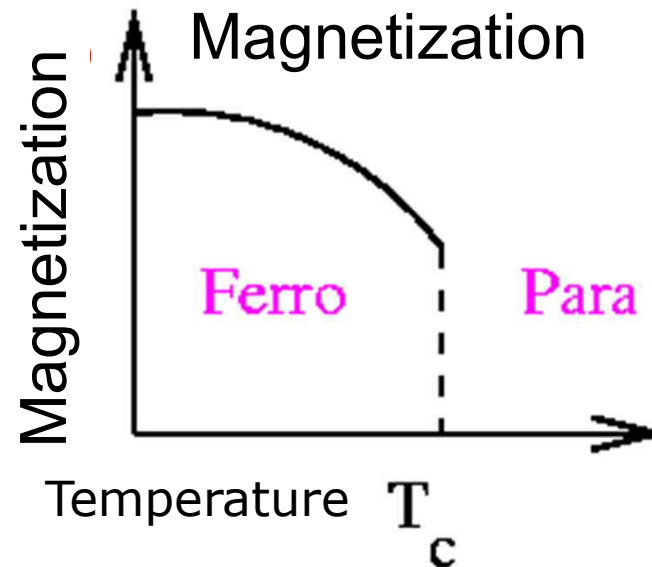
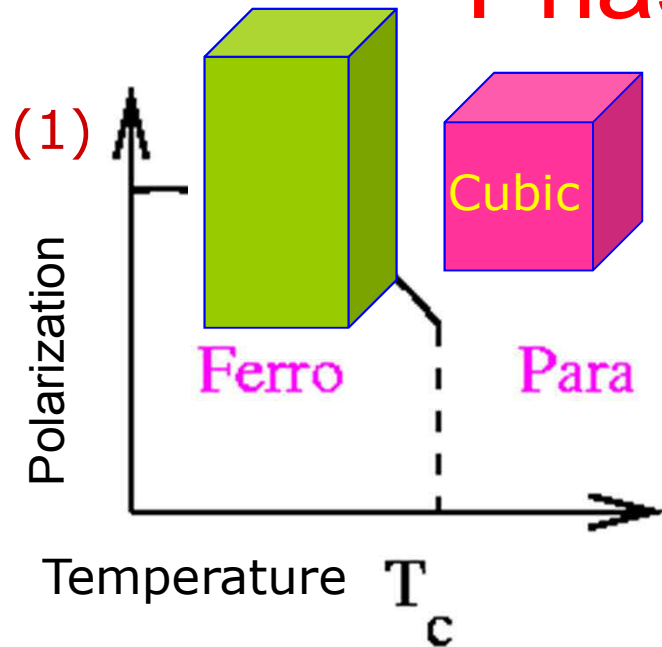
➤ Ferroelectric Phase transition(s)



Perovskite Ferroelectrics



Landau Theory: Phase Transitions



Change in symmetry at T_c :

inversion symmetry broken in (a)

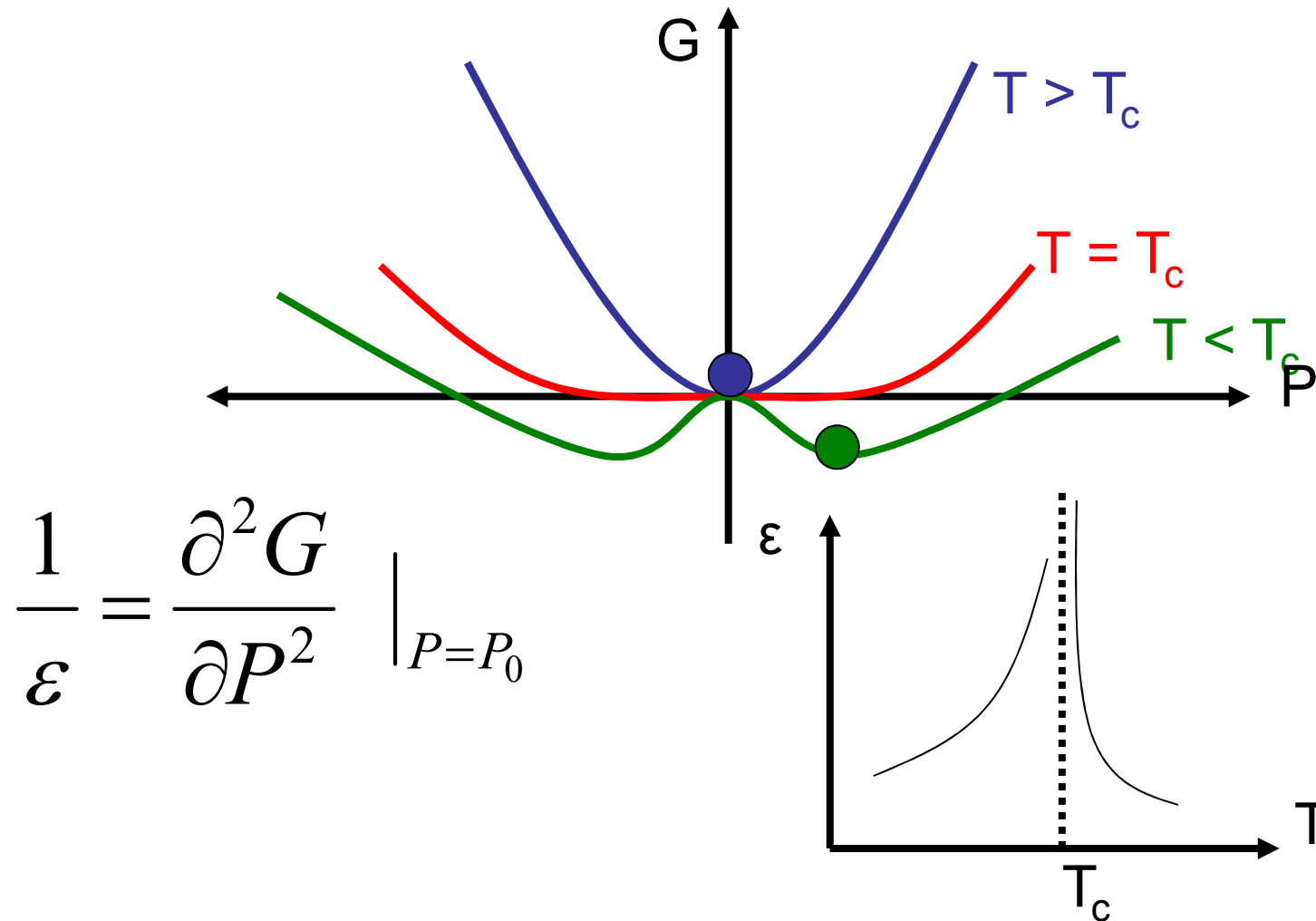
time reversal symmetry broken in (b)

Low-T state is connected with the high-T state: **order parameter P and M .**

$$\text{Landau free energy: } G = G_0 + A (T - T_c) P^2 + B P^4$$

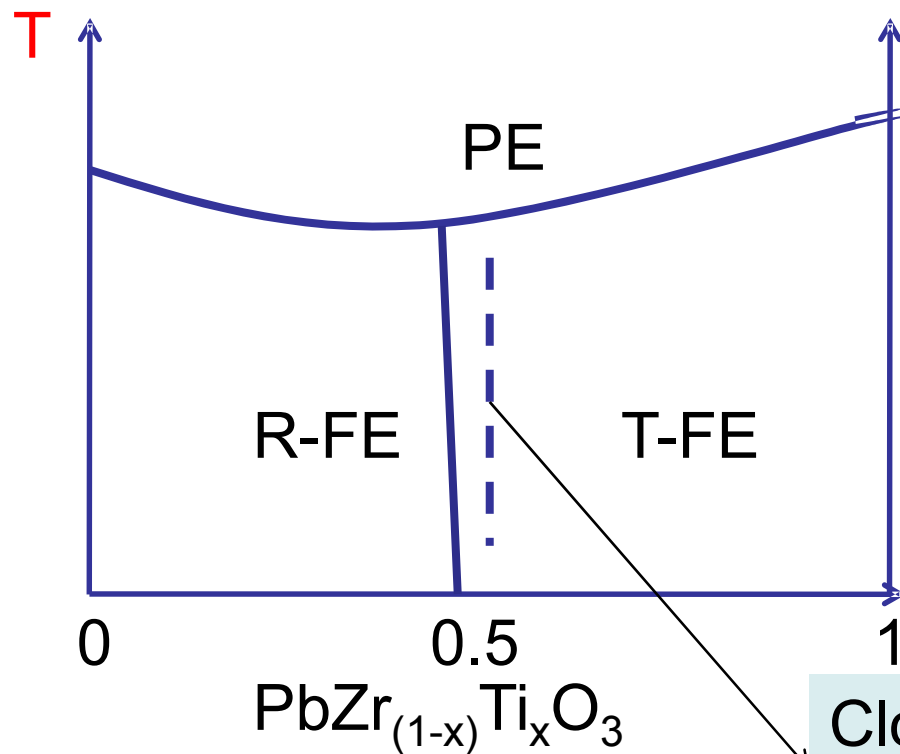
Landau Theory:

Form of the free energy G is completely determined by symmetry.



Near a transition, susceptibility diverges: important to technology

Why PZT is one of the best ferroelectrics?



It helps to be close to a phase transition: large fluctuations

Close to a phase transition at all T (upto T_c)!
> Large response

Energy or the Free Energy

u: atomic displacement, E: electric field, S: spin (or strain!),
Z: effective charge of the atom displacing, L: S-phonon coupl.

$$F = \frac{1}{2}Ku^2 - ZEu - LSu + JS^2$$
$$K = \alpha\omega^2,$$

$$F_{eff} = -\frac{Z^2}{2K}E^2 + \left(J - \frac{L^2}{2K}\right)S^2 - \frac{ZL}{K}ES$$

Dielectric
constant

Renormalized Piezoelectric
Elastic or
Exchange
constant

or
Magnetolectric
coupling

$$K \propto (T - T_c)$$

$$L \propto (T - T_c)^{1/2}$$

Dielectric response of phonons

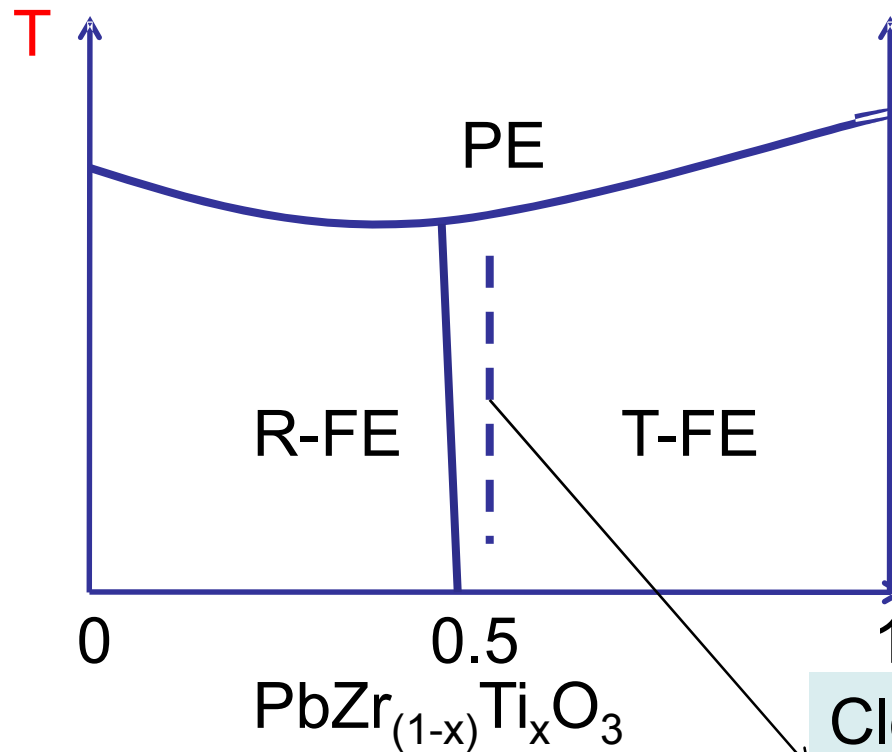
$$\epsilon \propto \frac{1}{K} = \frac{1}{T - T_c}$$

Piezo or Magneto-electric response of phonons

$$\gamma \propto \frac{L}{K} = \frac{1}{(T - T_c)^{1/2}}$$

Being close to a phase transition helps: A Large Response

Why PZT is one of the best ferroelectrics?



$$\epsilon \propto \frac{1}{K} = \frac{1}{x - x_c}$$

It helps to be close to a phase transition: large fluctuations

Close to a phase transition at all T (upto T_c)!
> Large response

Unifying Concept[s] in Materials

Total Energy Function

Chemistry: Z_i : Atomic numbers of atoms in a given material
Structure: R_i : Atomic positions of atoms in a given materia

Quantum Mechanics

Electrostatic Energy

$$E_{tot}(Z_I, R_I) = E_G^{el}(Z_I, R_I) + E_{Coulomb}^{ion}(Z_I, R_I)$$

Minimum energy state of electrons

- Interatomic potential
- Hamiltonian of a collection of atoms

Born-Oppenheimer Approximation

If I had access to an *infinite* computer, I would solve H quantum mechanically:

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

~~$$- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$~~

$H_e(Z_I, R_I)$

Very small, because $M_I \gg m_e$.

Classical term: $E_c(R_I)$

e: Ground state

$$H_e(Z_I, R_I) \Psi_G(Z_I, R_I) = E_G(Z_I, R_I) \Psi_G(Z_I, R_I)$$

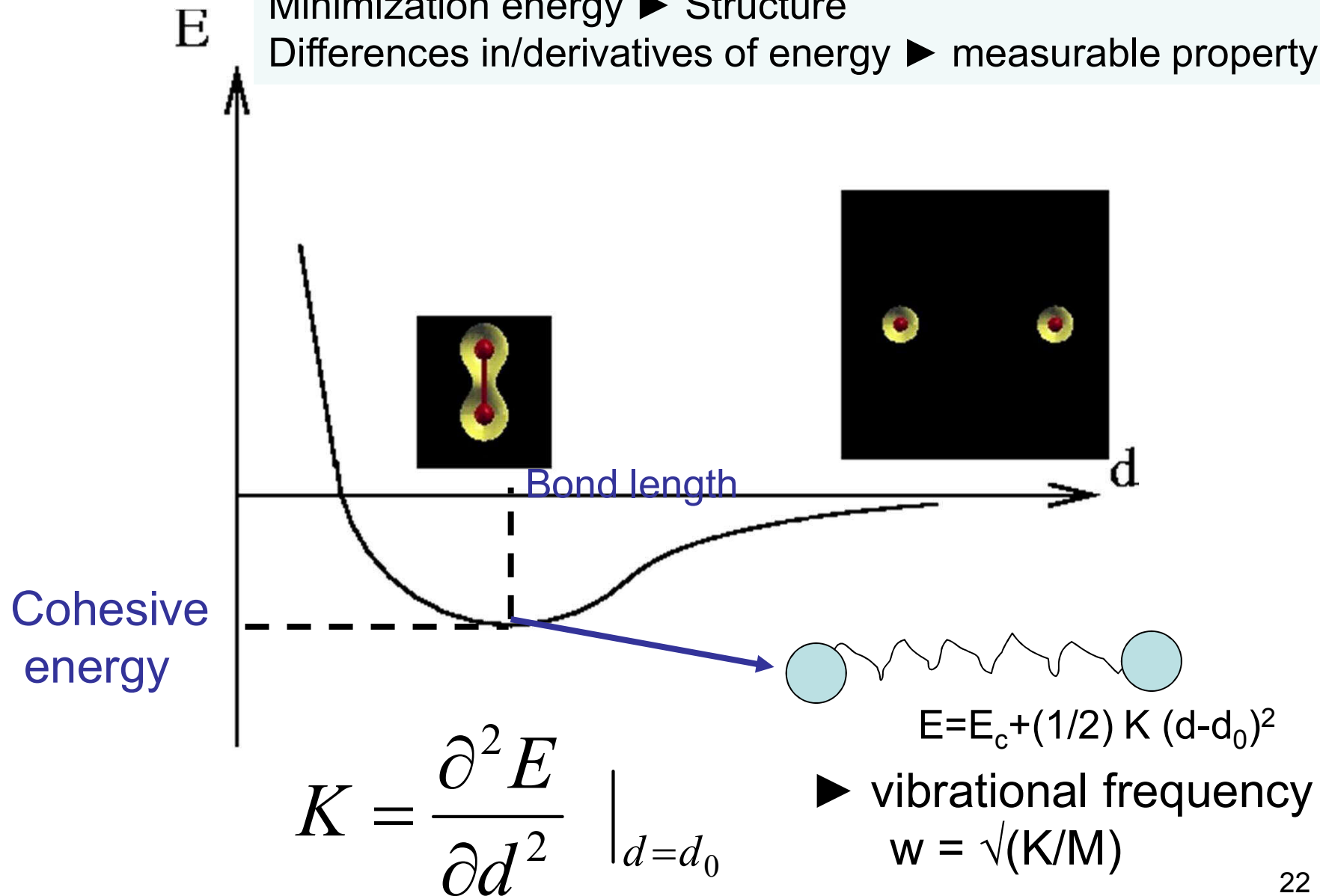
$$E_{\text{total}}(Z_I, R_I) = E_G(Z_I, R_I) + E_c(Z_I, R_I)$$

E_{total} has all the material-specific information *except for electronic excitations*.
 E_G is the part that is hard to determine!

Example: O₂ molecule

Minimization energy ► Structure

Differences in/derivatives of energy ► measurable property



Energy Function: $E_{\text{total}}(d_i, Z_i) = E_G + E_c$

$T \neq 0$: $E_{\text{total}} \rightarrow$ tools of statistical mechanics \rightarrow free energy F

Second derivative of E_{tot} or F wrt

Physical property

d_j, d_i (atomic displacement)

Force spring const: phonons

E, E (E-field)

Dielectric constant

ε, ε (strain)

Elastic constant

E, ε

Piezo-electric constant

E, d_i

Born Dynamical charge

ε, d_i

Strain-phonon coupling

H, H (magnetic field)

Magnetic susceptibility

E, H

Magneto-electric constant

H, ε

Piezo-magnetic constant

Energy Function: $E(R_i, Z_i)$ (contd)

$T \neq 0$ properties: statistical mechanics

Free energy [use Molecular Dynamics, Monte Carlo]

$$F(T, V) = -k_B T \text{Log} \int dR_i \text{Exp}(-E_{\text{total}}(Z_i, R_i)/k_B T)$$

Derivatives of Free energy \leftrightarrow Physical properties at finite T

It seems that E_{total} should be adequate to determine all the macroscopic properties of a material!

Except those which involve excitation of electrons (eg. Optical spectra)

How to access $E_{\text{total}}(Z_i, R_i) = E_G + E_c$?

- 1. Empirical approach: Have Nature solve all the equations!*
- 2. First-principles approach: Have a computer solve all the equations!*

Generalized Landau Theory: a real ferroelectric

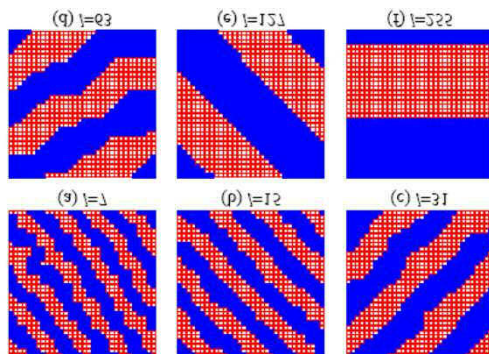
$$G(\vec{P}, T) = G_0 + A(T) \int dr |\vec{P}(r)|^2 + B_1(T) \int dr [P_x^4(r) + P_y^4(r) + P_z^4(r)] \\ + B_2(T) \int dr |\vec{P}(r)|^4 + C \int dr |\vec{P}(r)|^6 + D \int dr |\vec{P}(r)|^8$$

$$+ U \int dr |\nabla \cdot \vec{P}(r)|^2 + V \int dr |\nabla \times \vec{P}(r)|^2 \\ + \frac{1}{2\epsilon^\infty} \int dr dr' \frac{|\nabla \cdot \vec{P}(r) \parallel \nabla' \cdot \vec{P}(r')|}{|r - r'|}$$

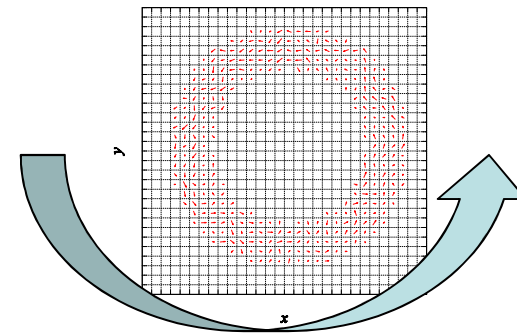
**Energetics of
fluctuations in P**

Anil Kumar and U Waghmare, Phys Rev B 82, 054117 (2010)

Applicable to bulk and nano-forms of a ferroelectric



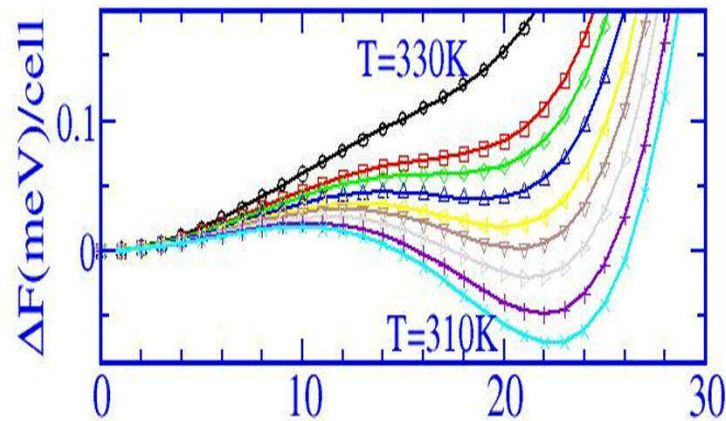
Stripe domains in
Films
Chiral ordering on
Nanotubes



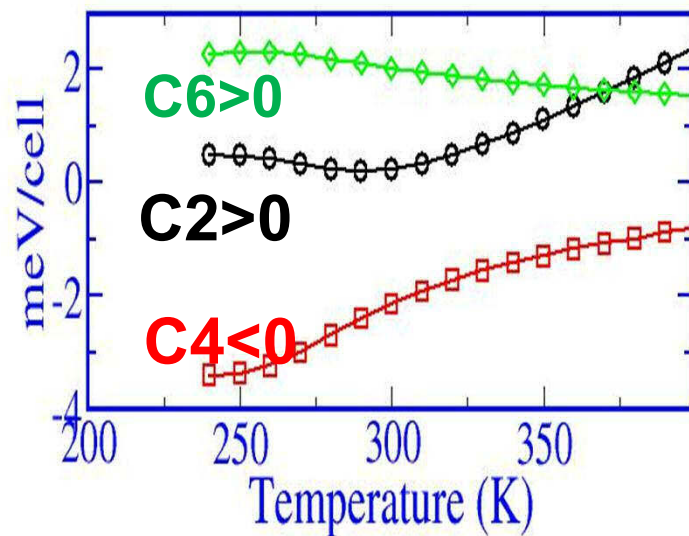
Nishimatsu, Waghmare, Kawazoe and Vanderbilt, PRB (2008); Editor's suggestion.

Lecture I breaks here

Order of Phase Transition



First-order transition!



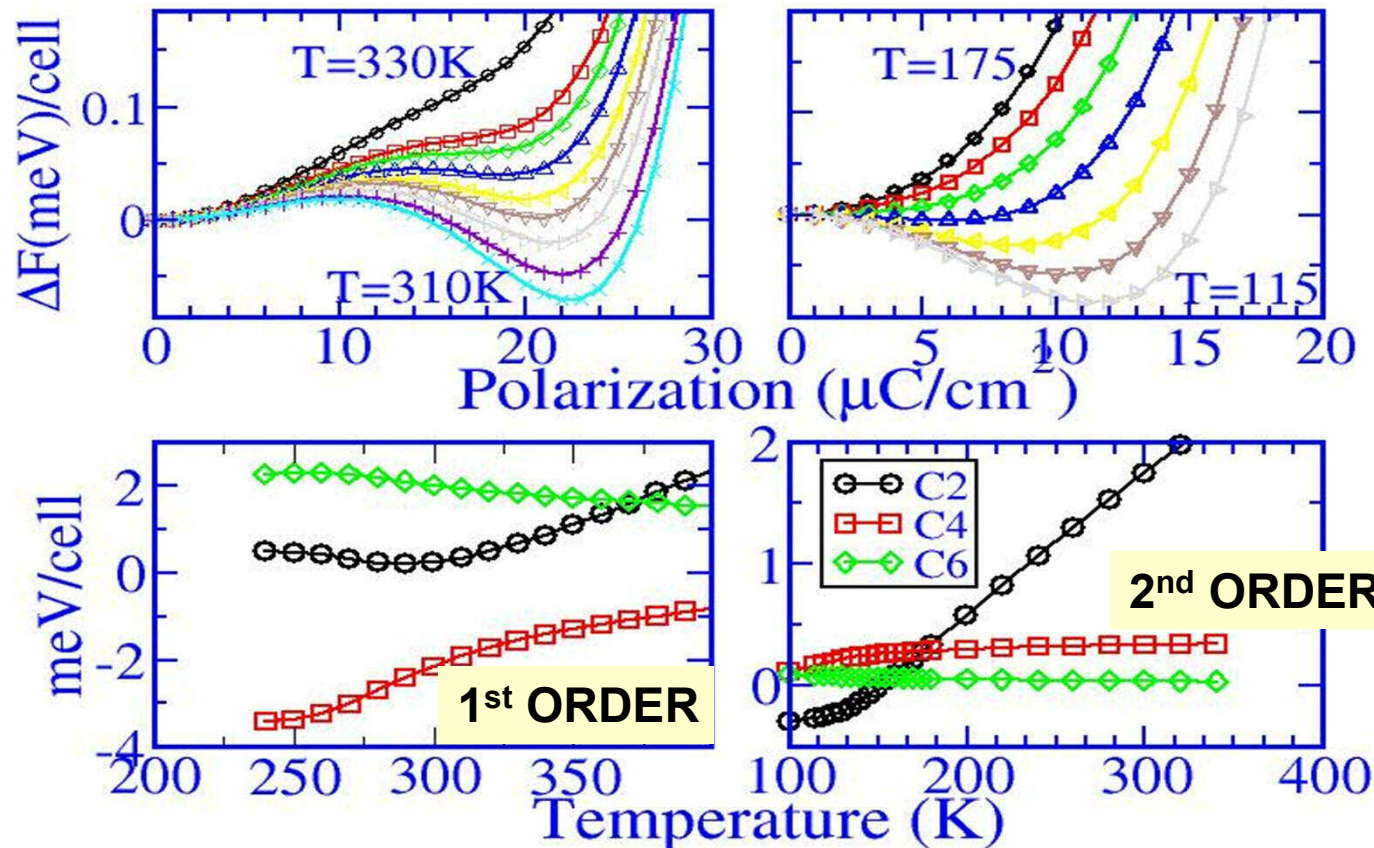
$$\Delta F = C_2 P^2 + C_4 P^4 + C_6 P^6$$

Which coupling drives first-order transition?

Order of Phase Transition: Strain Coupling

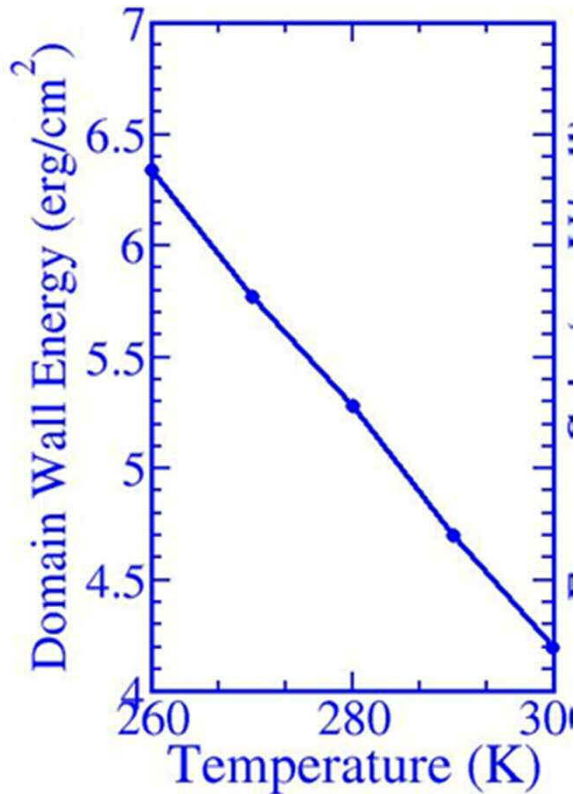
Strain-P coupling **ON**

OFF $H_{sp} = g P^2 \eta$

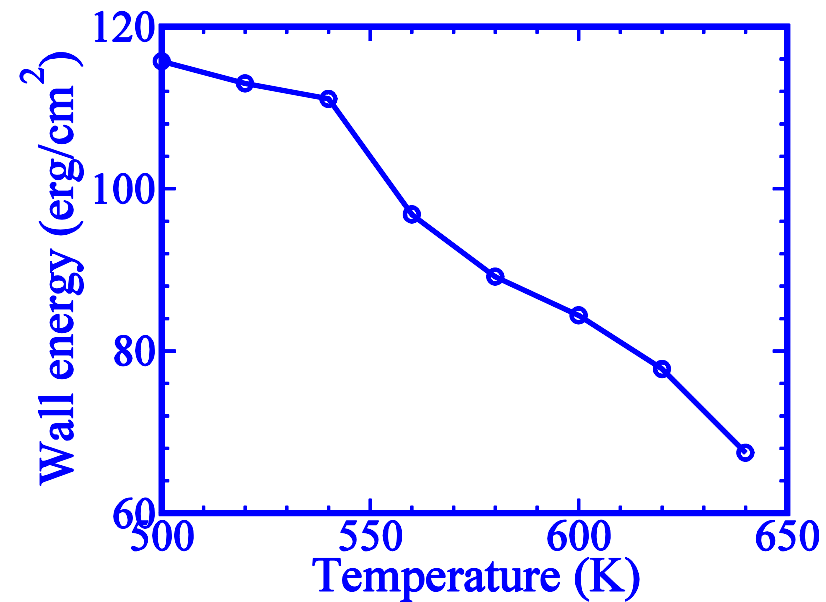
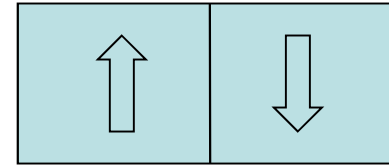


Strain-P coupling is responsible for **first-order phase transition** in ferroelectrics!

Domain wall energies of Ferroelectrics: (from first-principles simulations)



BaTiO₃



PbTiO₃

It is evident that chemistry and Temperature affect the FE properties greatly!

Magnetolectrics

INTRODUCTION

Multiferroics

- **Ferroids: spontaneous property in the absence of conjugate field**
 - Ferroelectric (FE): electric polarization (P) when $\vec{E} = 0$
 - Ferromagnetic (FM): magnetization (M) when $\vec{H} = 0$
 - Ferroelastic (FS): strain (ϵ) when $\vec{\sigma} = 0$
 - **Domains: spontaneous property in different orientation:**
Symmetry-related, equi-energy states
 - **Multiferroics: more than one spontaneous property**
Ascher (1966): $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$
 - **Magic Trinity of Symmetry, Ascher (1966): 9 point groups**
Kineto-electric, Kineto-magnetic effects! (out of 122)
-

History

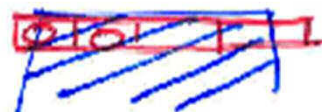
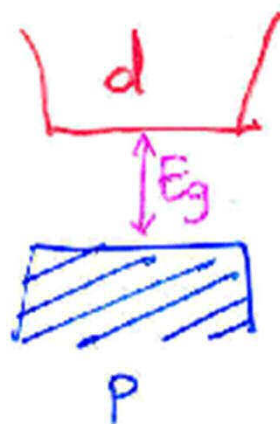
Magnetoelectric Effects

- **Pierre Curie (1894) conjecture:**
electric dipole induced by magnetic field and vice versa
 - **Peter Debye (1926):** “Magnetoelectric (ME)”
 - **Wigner (1932):** Time Reversal Symmetry R
 $R\vec{v} = -\vec{v}$, $R\vec{H} = -\vec{H}$, $R\vec{\rho} = \vec{\rho}$, $R\vec{E} = \vec{E}$
 - **Landau (1937):** Symmetry of a crystal \leftrightarrow physical property
phase transitions \leftrightarrow change in symmetry
 - **Dzyaloshinsky (1959) predicted:**
 Cr_2O_3 (antiferromagnetic) \rightarrow linear ME effect $\mathbf{M} = \chi \mathbf{E}$
 - **Astrov (1960) expt:** Confirmed the linear ME property of Cr_2O_3
-

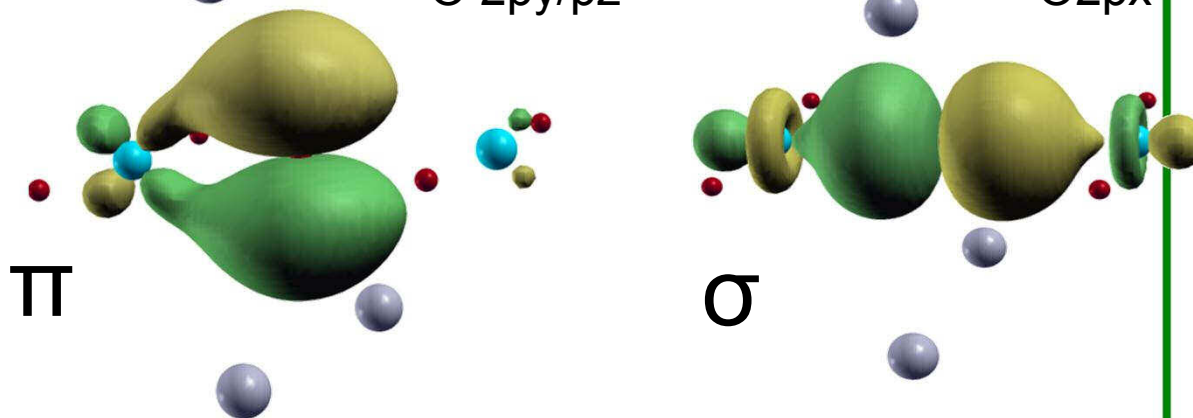
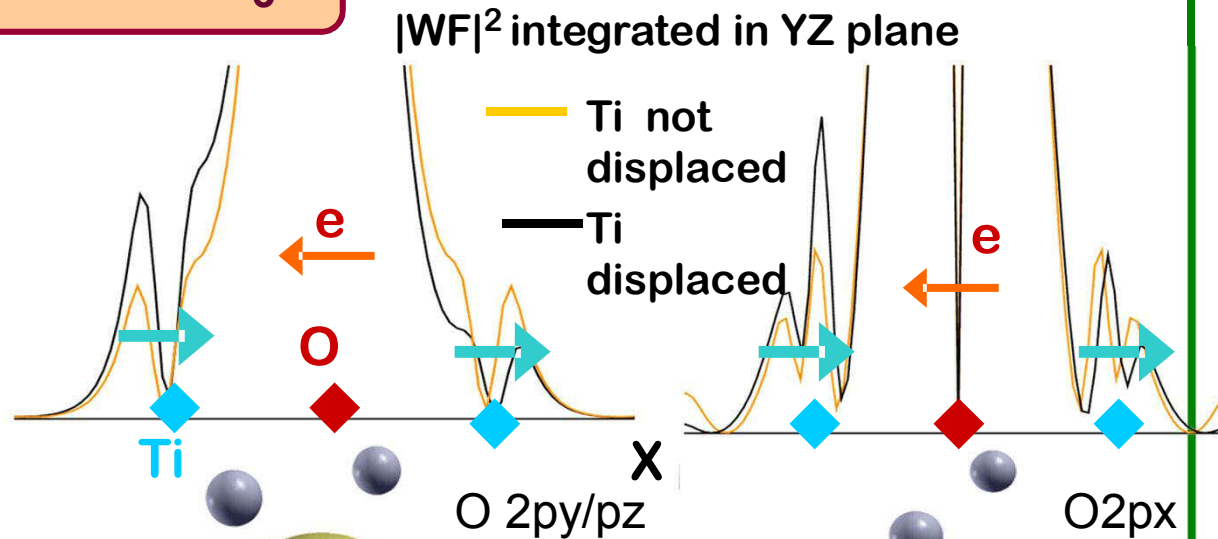
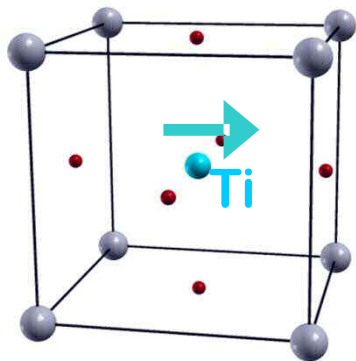
- **Ginzburg (1984):** 31 point groups of ferrotoroids: linear ME e

Why multiferroics are rare?

- **Ferroelectrics (FE):** KNbO_3 , BaTiO_3 , PbTiO_3
 $1+, 5+, 2^-$ $2+, 4+, 2^-$ $2+, 4+, 2^-$
 - valence (occupied) bands: p electrons of O
 - conduction (unoccupied) bands: d electrons of TM
 - d^0 -ness of TM
- **Ferromagnets (FM):** eg. $(\text{LaCa})\text{MnO}_3$
 - d electrons of TM: local magnetic moment
- **Conflicting d -electron occupation**
metal (FM) vs insulator (FE)

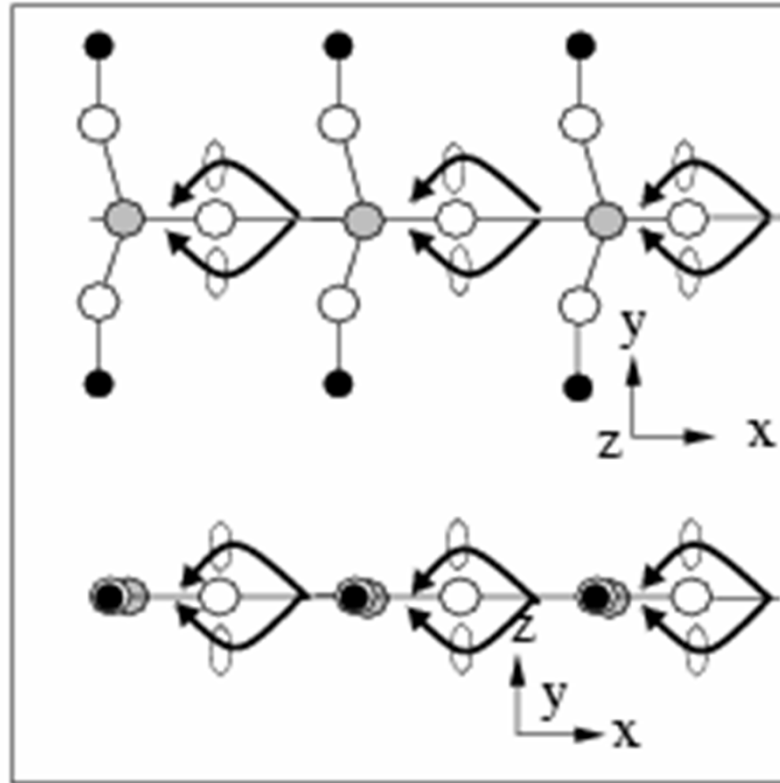


Tetragonal PbTiO_3 & BaTiO_3



	$Z^*x(\text{Ti})$		
PbTiO_3 :	7.02 a.u.	+1.40	+0.82
BaTiO_3 :	7.13 a.u.	+1.43	+0.81

Inter atomic charge transfer through π like orbitals



Local charges
remain the same

Mechanism of anomalous effective charge:

Transfer of a small fraction of electrons from one Ti to the neighboring one is facilitated by the oxygen p orbitals perpendicular to the -Ti-O-Ti- chain.

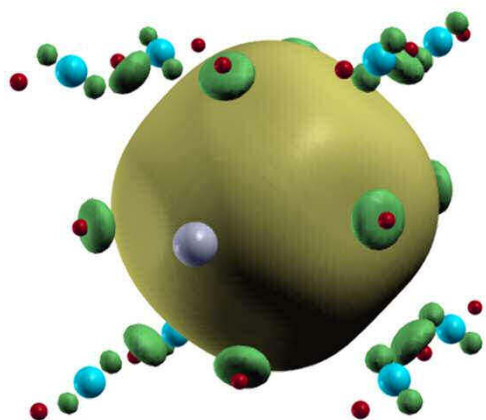
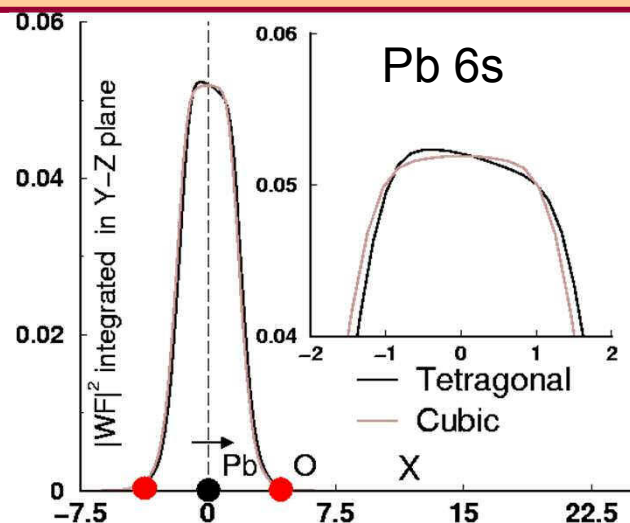
Bhattacharjee,
Waghmare (2010)

Like “*charge superexchange*”

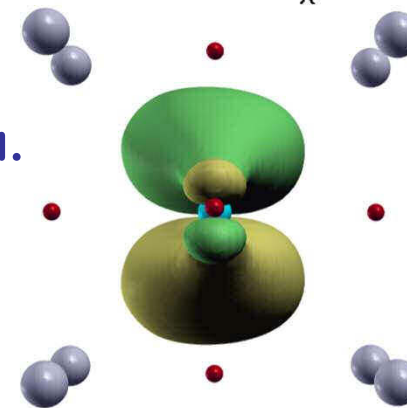
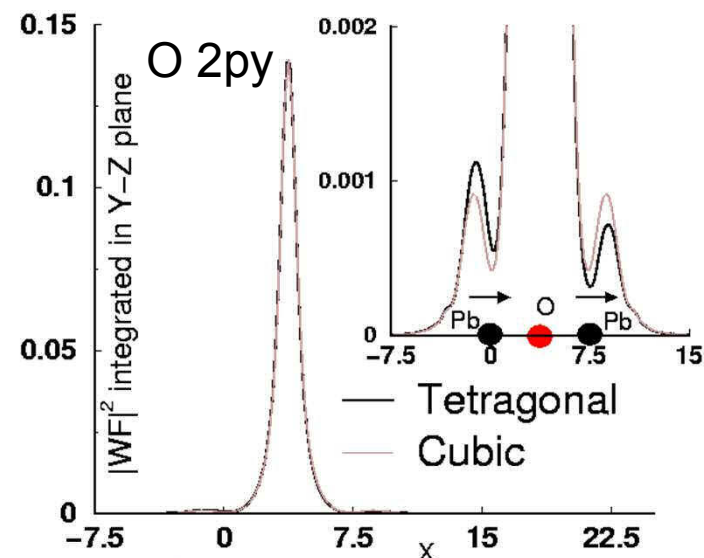
Mechanisms in multiferroic ((A)FM+FE)

- 1. Lone pair of A atom: FE and d electrons of B atom: FM
Eg. BiMnO_3 , BiFeO_3
(Ref. Wang et al, Science 299, 1719 (2003))
2. Geometric (Structural) ferroelectricity in a magnetic compound, Eg. YMnO_3 , InMnO_3 (hexagonal)
(Ref. Van Aken et al, Nature Mat. 3, 164 (2004)).
3. Magnetoelastic structural modulation to give FE in a magnetic compound. Eg. TbMnO_3 , DyMnO_3 , TbMn_2O_5
(Ref. Kimura et al, Nature 426, 55 (2003)).
4. Proposed Mechanism: Superposition of two different charge-ordered states to give a dipole moment.
Eg. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x < 0.5$
(Ref. Efremov et al, Nature Mat 3, 853 (2004)).

PbTiO₃ Pb displaced



0.59 a.u.



0.49 a.u.

$Z^*x(\text{Pb}) = 3.86 \text{ a.u.}$

$Z_n = 2 \text{ a.u.}$

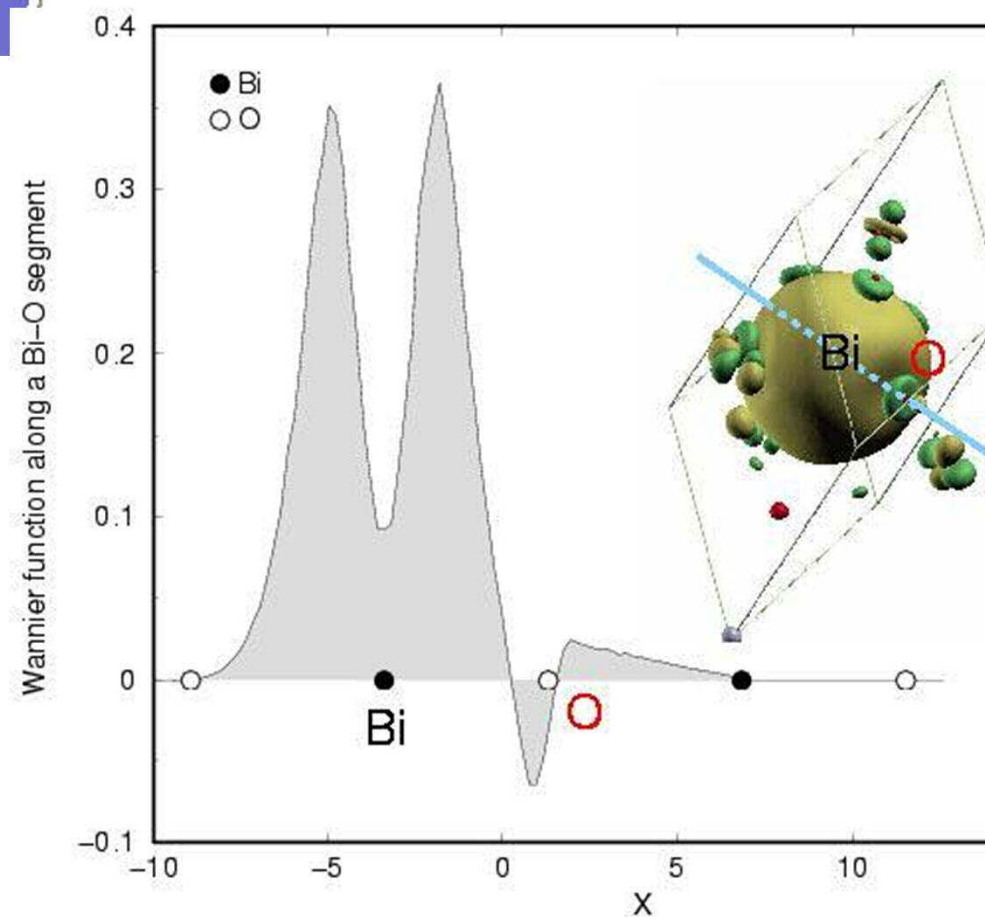
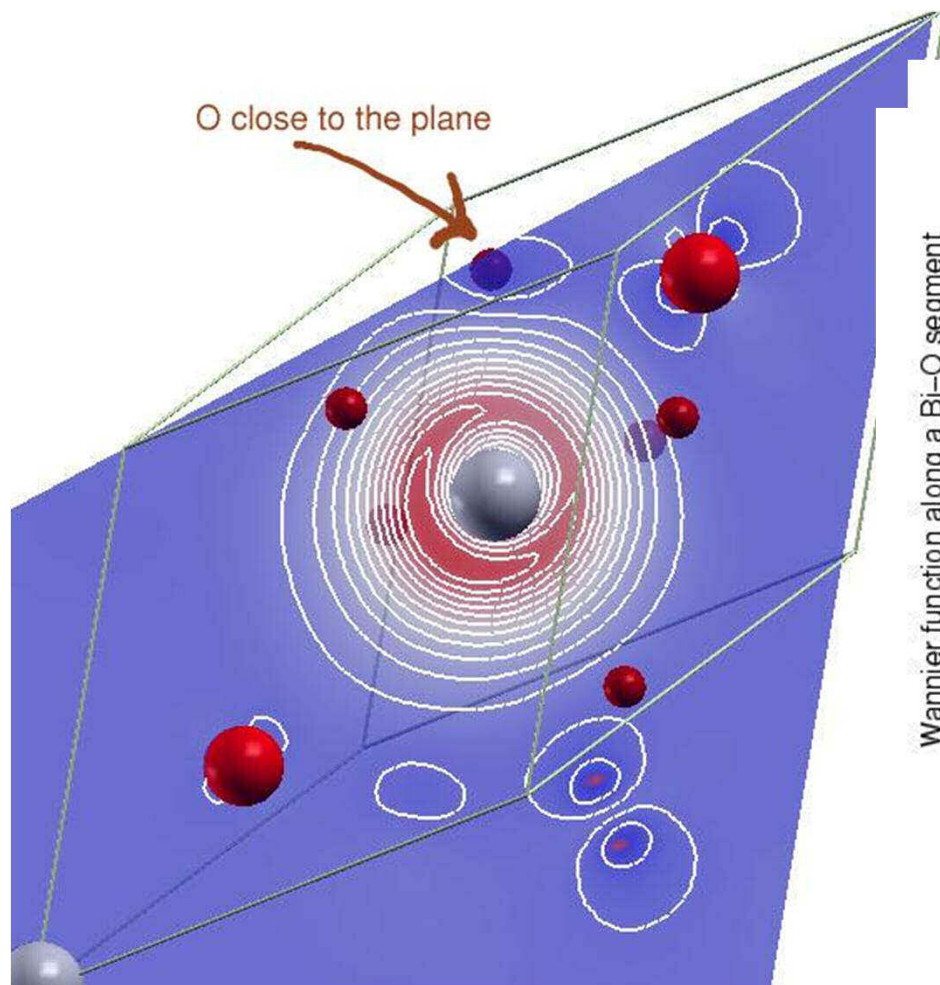
$Z_a = 1.86 \text{ a.u.}$

**Strong Pb(6s)-O(2p) coupling:
Stereochemically Active Lone pair e on Pb and Bi**

Chemical origin of FE in BiFeO_3

(with Joydeep Bhattacharjee)

Wannier functions



Why is P so small ?

Mechanisms in multiferroic ((A)FM+FE)

1. Lone pair of A atom: FE and d electrons of B atom: FM

Eg. BiMnO_3 , BiFeO_3

(Ref. Wang et al, Science 299, 1719 (2003))

→ 2. Geometric (Structural) ferroelectricity in a magnetic compound, Eg. YMnO_3 , InMnO_3 (hexagonal)

(Ref. Van Aken et al, Nature Mat. 3, 164 (2004)).

3. Magnetoelastic structural modulation to give FE in a magnetic compound. Eg. TbMnO_3 , DyMnO_3 , TbMn_2O_5

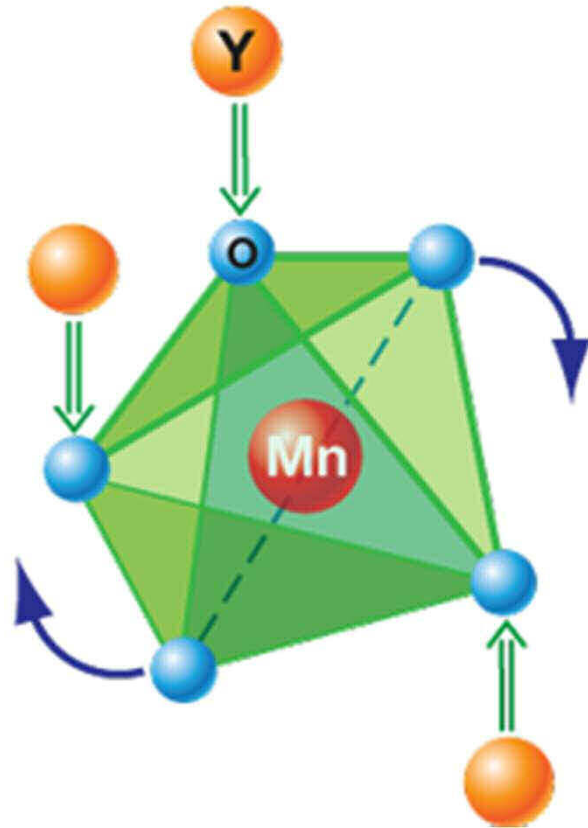
(Ref. Kimura et al, Nature 426, 55 (2003)).

4. Proposed Mechanism: Superposition of two different charge-ordered states to give a dipole moment.

Eg. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x < 0.5$

(Ref. Efremov et al, Nature Mat 3, 853 (2004)).

InMnO₃, YMnO₃: Improper ferroelectric (Geometric FE)



Primary order parameter involves rotation of the MnO polyhedra

It induces polarization as a secondary order parameter

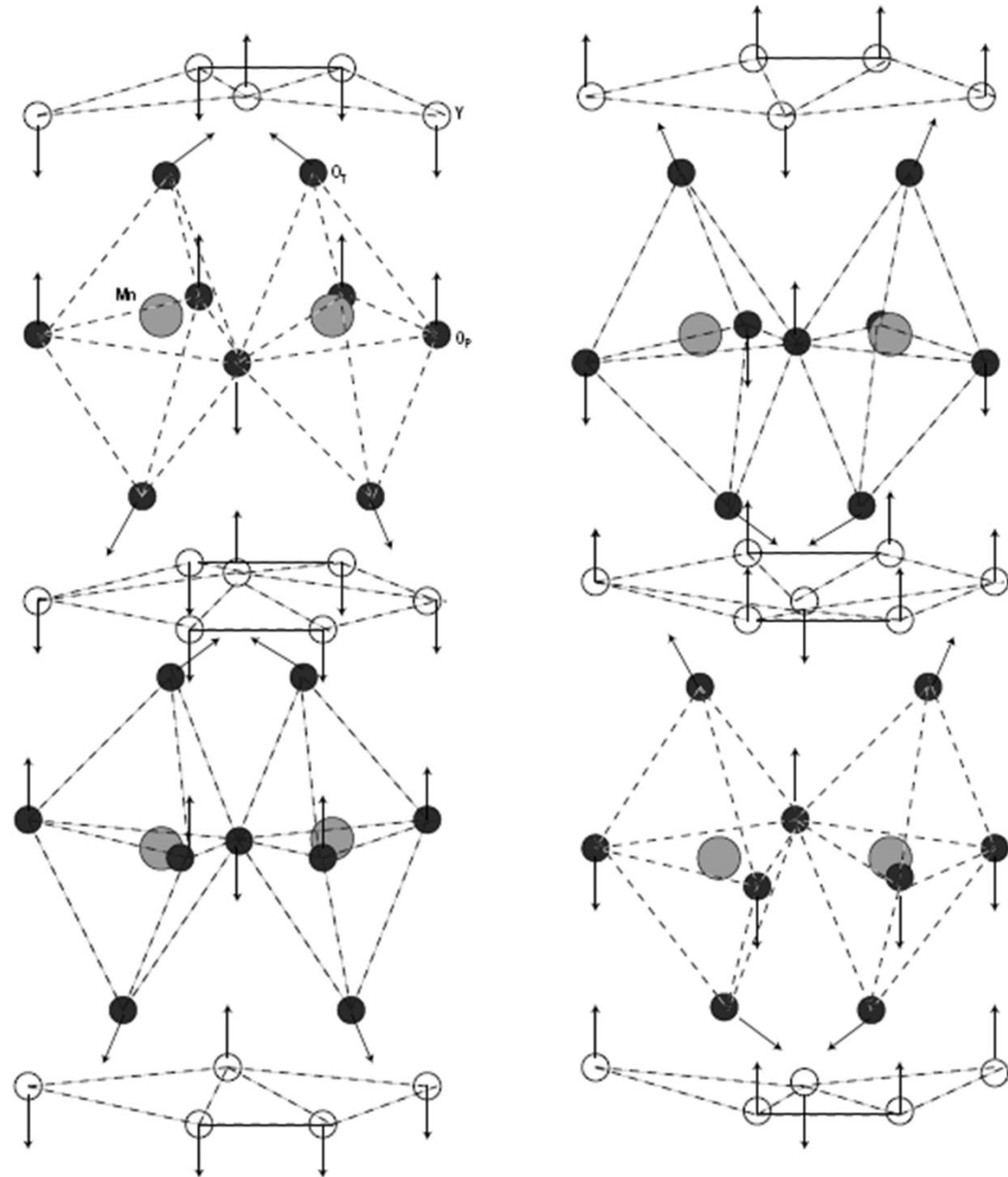
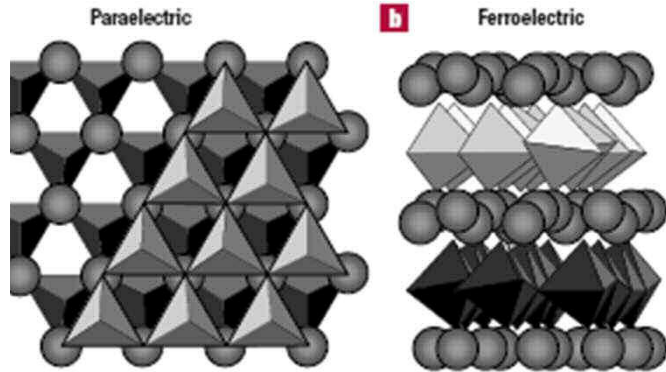
Consequences:
Weak dielectric response,
P-switching is difficult!

Spaldin et al, Nature Mater. 3, 164-170 (2004).

CNR Rao et al, J of Appl. Phys 100, 076104 (2006).

YMnO₃

Van Aken et al, Nat. Mat. 3, 164 (2004).



Phonons at Γ and K points involved

Purely geometry and electrostatics effect: FE
*No anomalous Z**

$P=6 \mu\text{C}/\text{cm}^2$

InMnO₃

- $P=19 \mu\text{C}/\text{cm}^2$ (as obtained from Berry phase)

But the reference paraelectric str:

$$P = \text{half integer quantum} = 27 \mu\text{C}/\text{cm}^2$$

$$P(1) - P(0) = \int_0^1 \frac{\partial P}{\partial \lambda} d\lambda$$

- ▶ Measured $P = 8 \mu\text{C}/\text{cm}^2$
- Energy difference (FE-PE) = 0.368 eV/f.u.
eg. For PbTiO₃ $dE=0.1$ eV/f.u.

P -switching expected to be a lot harder.

InMnO₃: Origin of ferroelectricity (geometric)

$$F = \alpha Q_{\Gamma}^2 + \alpha' (T - T_c) Q_K^2 + \beta Q_{\Gamma}^4 + \beta' Q_K^4 + \\ + \gamma Q_K^3 Q_{\Gamma} + \mu Q_K^2 Q_{\Gamma}^2$$

Q_K: Tilting of MnO₅ polyhedra (unstable)

Q_Γ: Ferroelectric mode (stable)

Born charges: Nominal (In, 3+), (Mn, 3+).

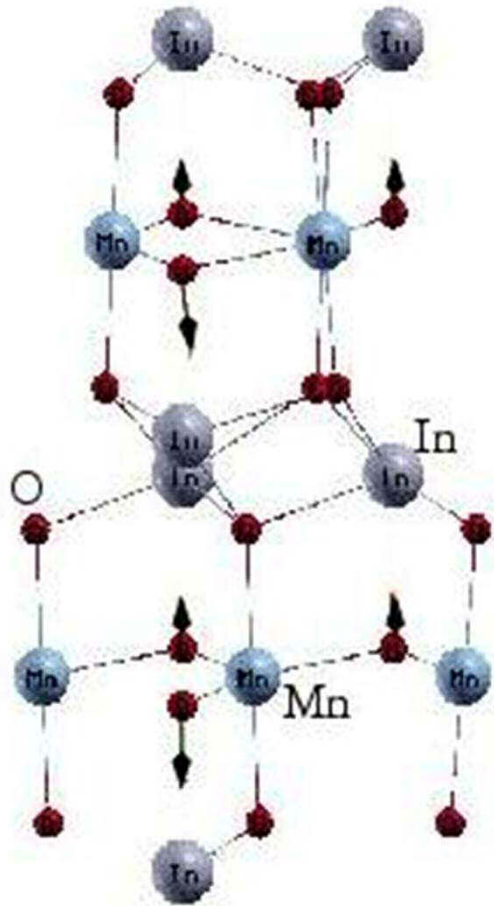
Off-centering of In and Mn is not favored

~ 8 and 15 eV/Å² (very stable)

K₃ mode: is the *primary instability* (electrostatics)

Γ mode feels a force once K₃ is frozen in.

InMnO₃: Response to Strain



Main structural response is through the K_3 mode which is the primary instability (soft mode)

Hence, the piezoelectric response is relatively weak $\sim 0.15 \text{ C/m}^2$

The same is expected in the dielectric response

“Geometric” ferroelectricity would *not* yield properties good for technology.

Mechanisms in multiferroic ((A)FM+FE)

1. Lone pair of A atom: FE and d electrons of B atom: FM

Eg. BiMnO_3 , BiFeO_3

(Ref. Wang et al, Science 299, 1719 (2003))

2. Geometric (Structural) ferroelectricity in a magnetic compound, Eg. YMnO_3 , InMnO_3 (hexagonal)

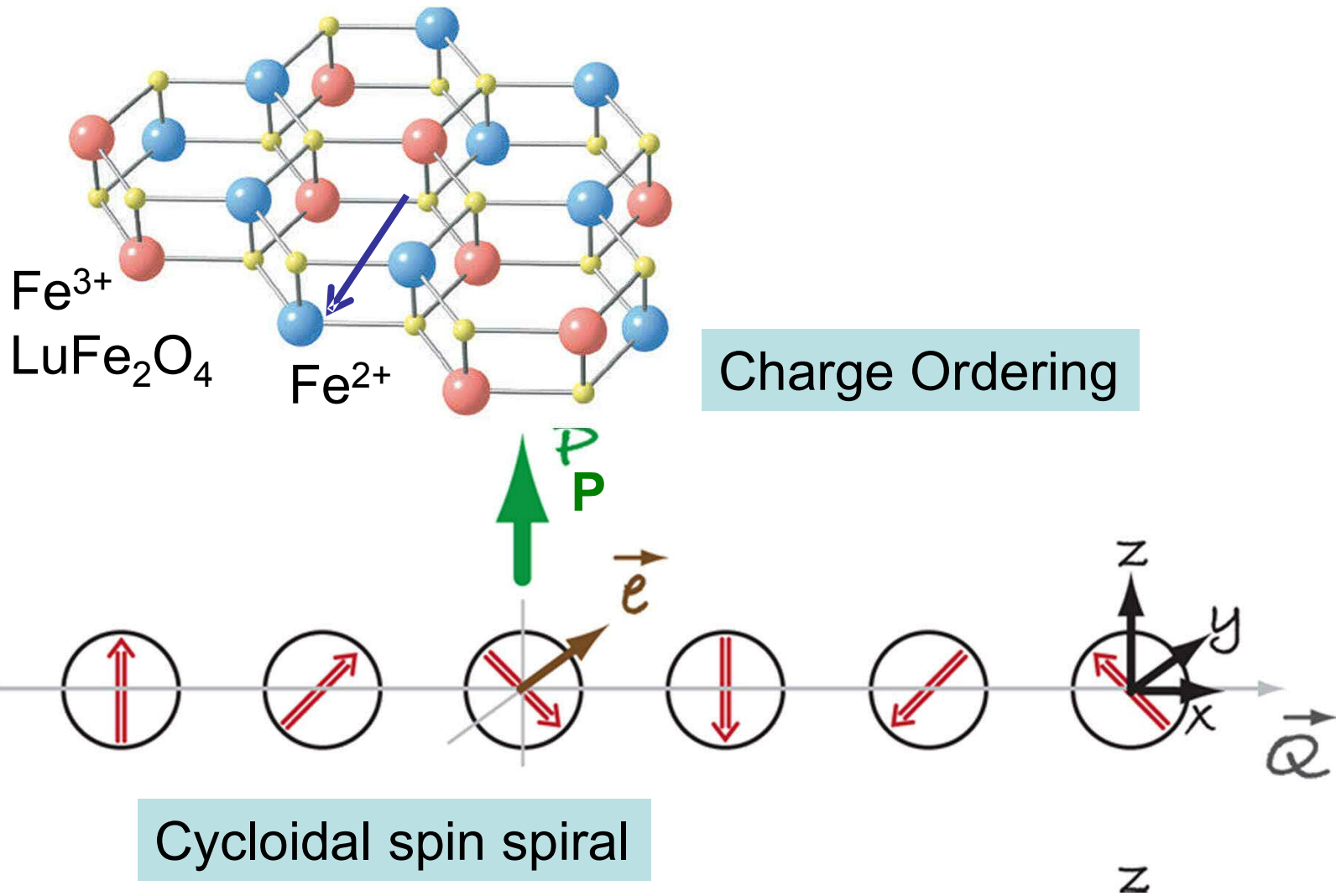
(Ref. Van Aken et al, Nature Mat. 3, 164 (2004)).

→ 3. Magnetoelastic structural modulation to give FE in a magnetic compound. Eg. TbMnO_3 , DyMnO_3 , TbMn_2O_5
(Ref. Kimura et al, Nature 426, 55 (2003)).

→ 4. Proposed Mechanism: Superposition of two different charge-ordered states to give a dipole moment.

Eg. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x < 0.5$

(Ref. Efremov et al, Nature Mat 3, 853 (2004)).



Khomskii, Physics 2, 20 (2009).

Cheong and Mostovoy, Nature Materials 6, 13 (2007)

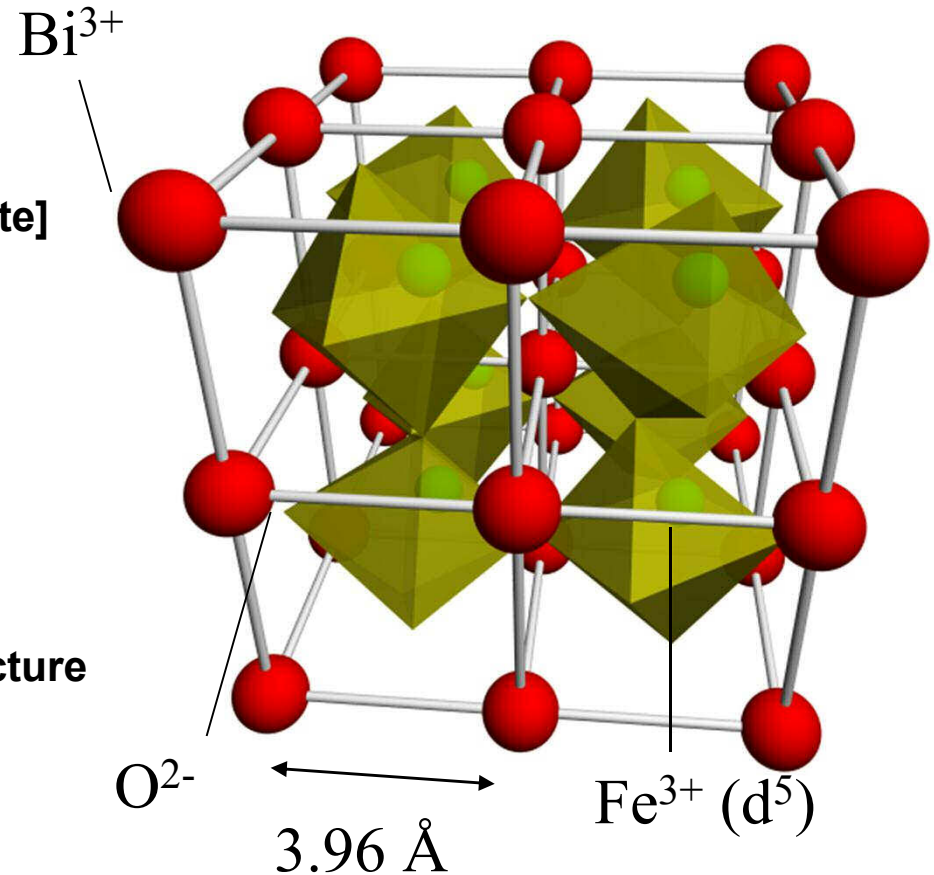
Multiferroic BiFeO₃

BiFeO₃

What is known about multiferroic BiFeO₃?

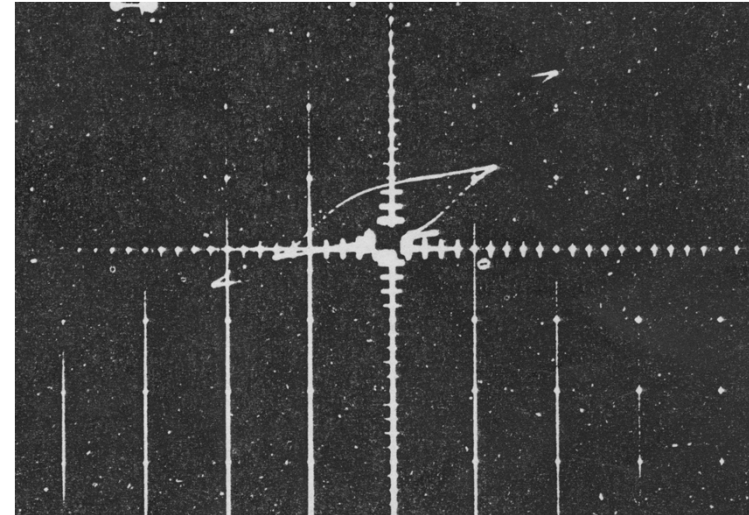
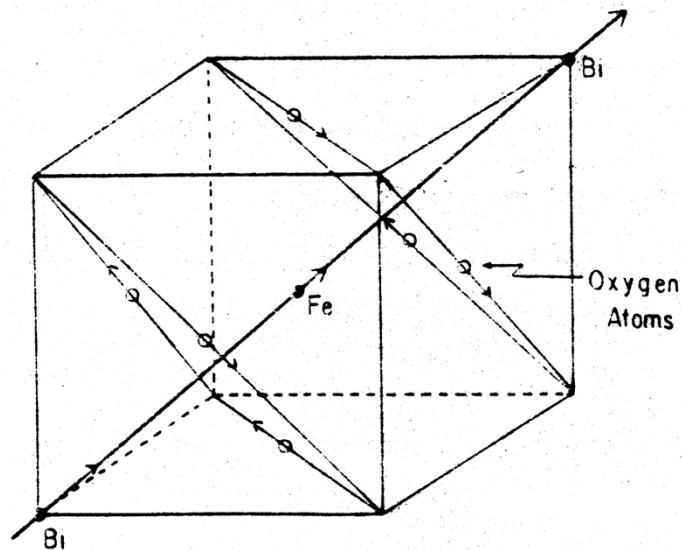
Perovskite: Bi A sites; FeO₆ octahedra

- Rhombohedral *R3c* (10 atoms/cell)
- [Large distortions from cubic perovskite]
- Ferroelectric: $P_s \sim 6 \mu\text{C}/\text{cm}^2$, $T_c \sim 1120 \text{ K}$
- $\text{Bi}^{3+}(6s^26p^0)$, $\text{Fe}^{3+}(3d^5)$ states
- Weak FM insulator, $T_{\text{AFM}} \sim 650 \text{ K}$
- G-type, rock-salt spin order + spiral structure (~620 Å period)
- No optical measurements available
- Kubel & Schmid (1991), Teague *et al* (1970), Sosnowska *et al* (1982).





Properties of Bulk BiFeO_3



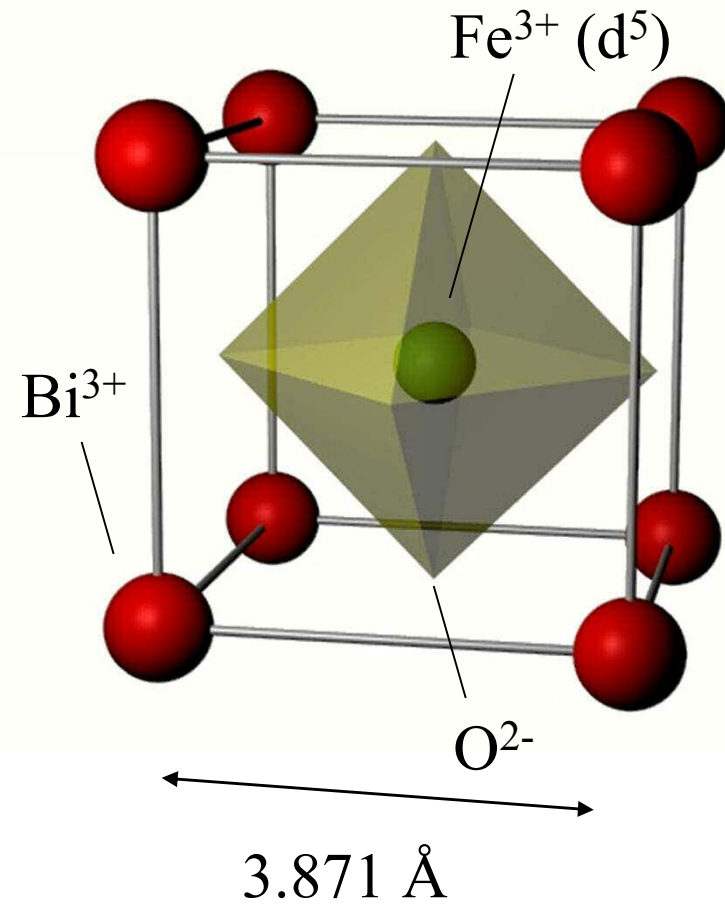
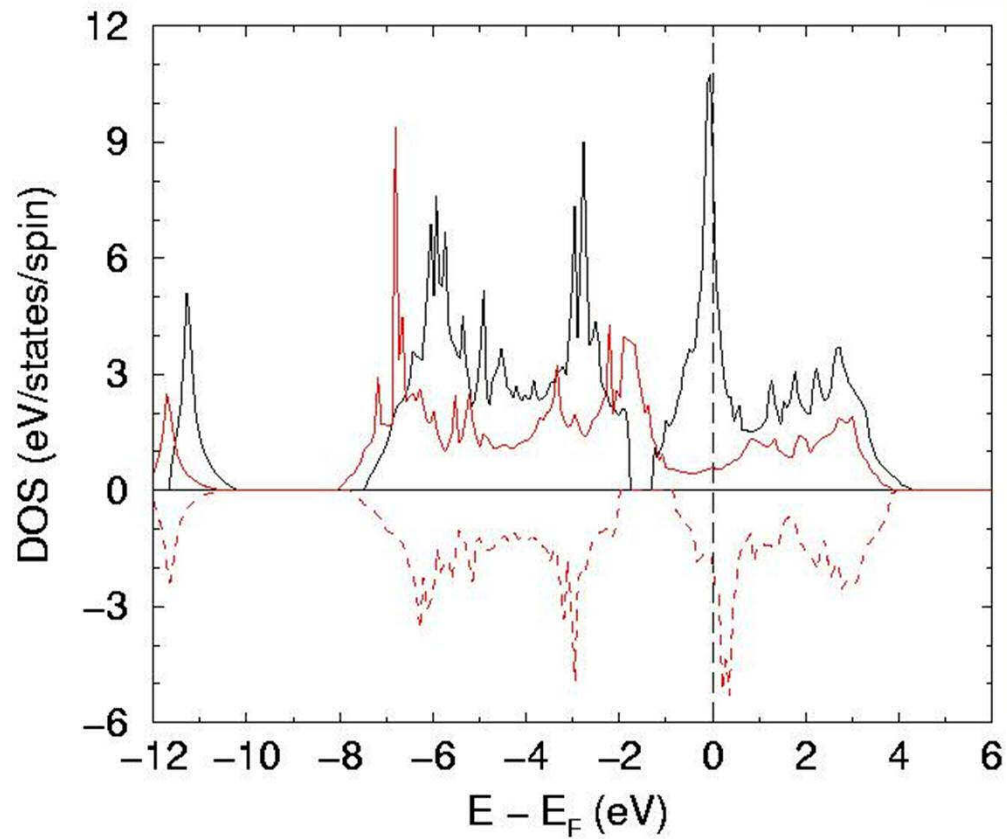
Bi: 0.62\AA along (111)
Fe: 0.23\AA along (111)
O: 0.30\AA rotating about (111)

C. Michel et al,
Solid State Communications, 1969

Spontaneous Polarization
 $P_s = 6.2\mu\text{C}/\text{cm}^2$, $E_c = 20\text{kV}/\text{cm}$
Measured at liquid nitrogen T

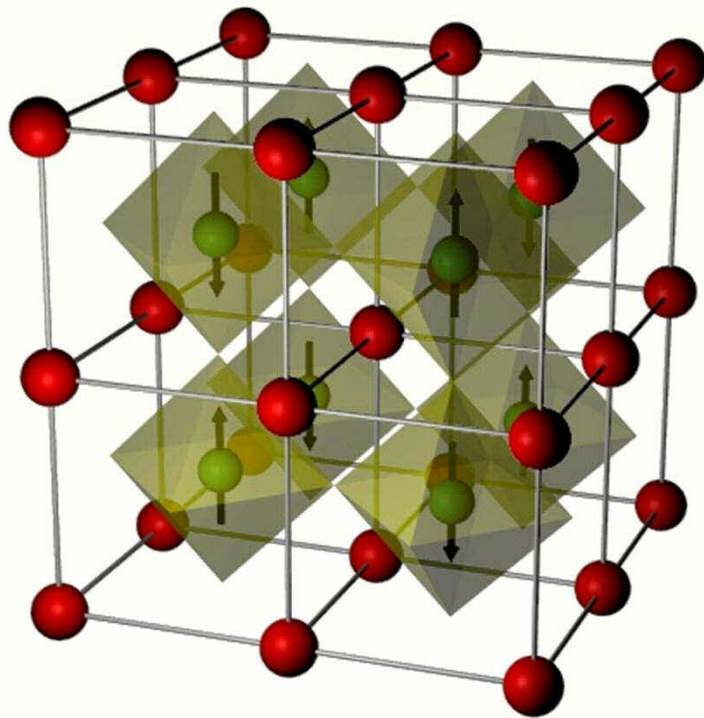
J. R. Teague, et al.
Solid State Communications, 8, 1970

Metallic nonmagnetic & ferromagnetic cubic perovskite structure

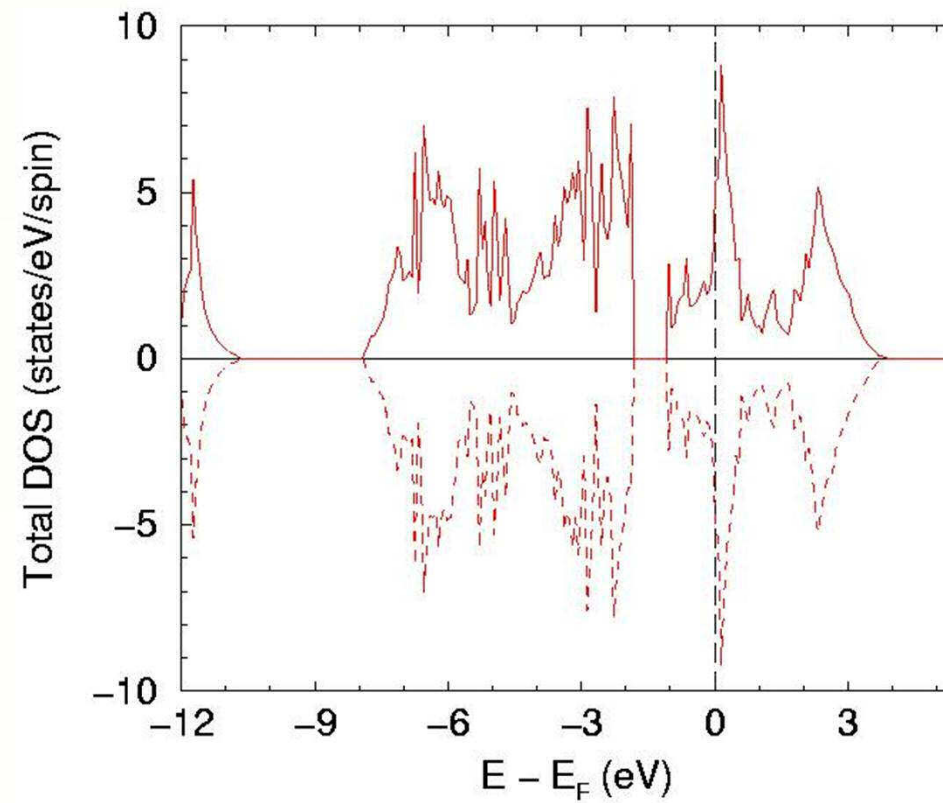


G-type antiferromagnetism in the cubic phase

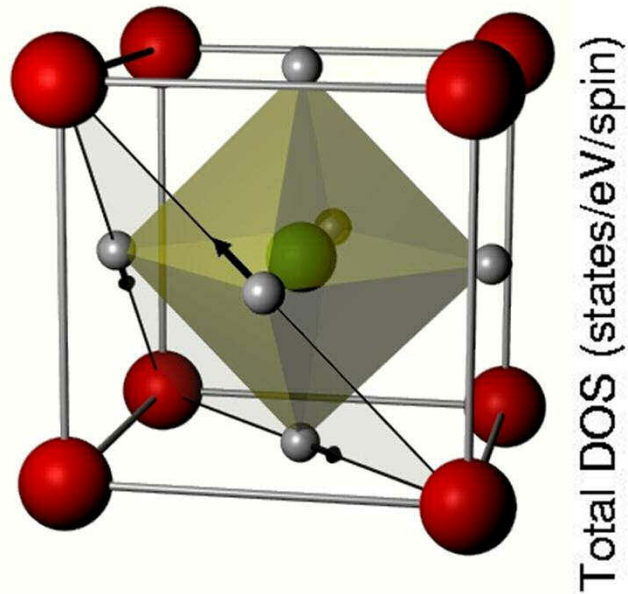
Spins are rock-salt ordered



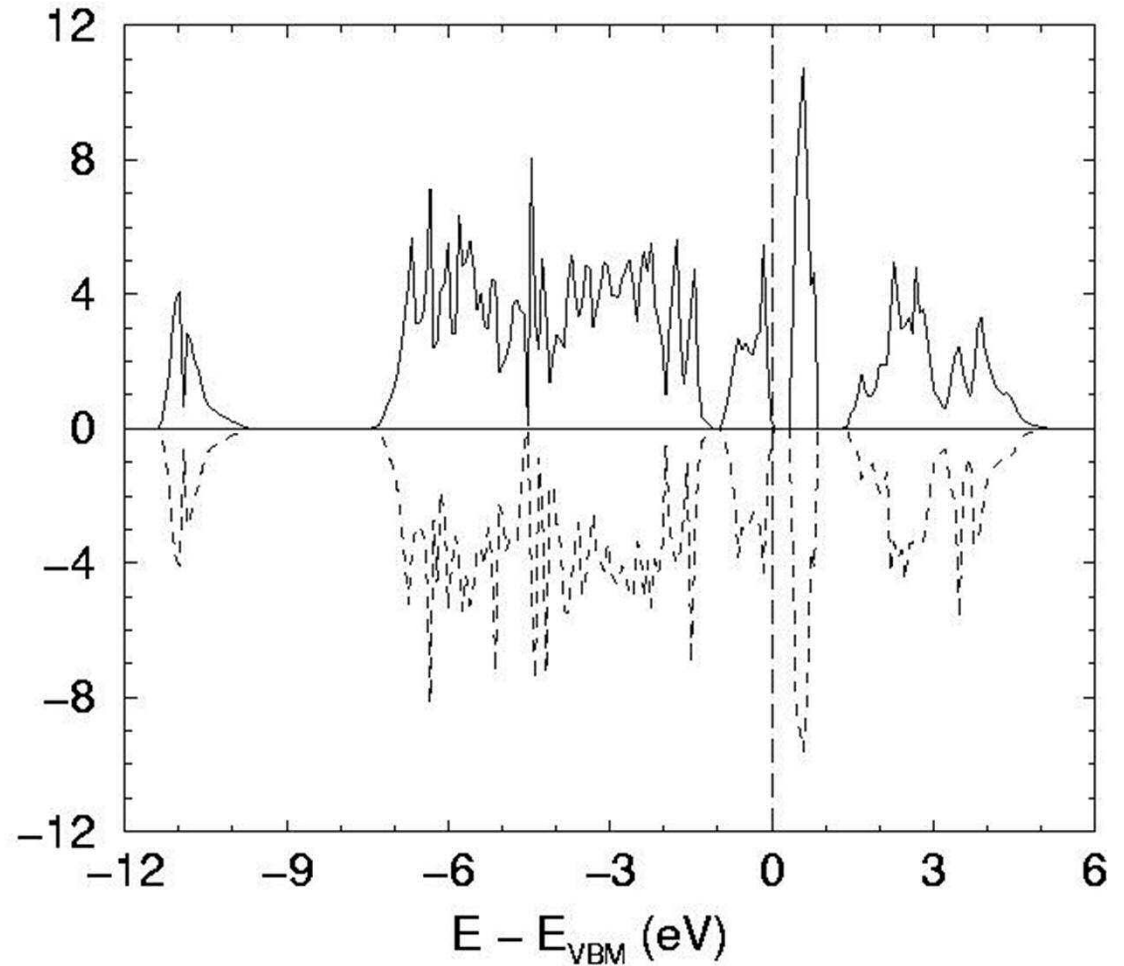
DOS remains high at E_F



Rotation about the [111] axis opens the band gap

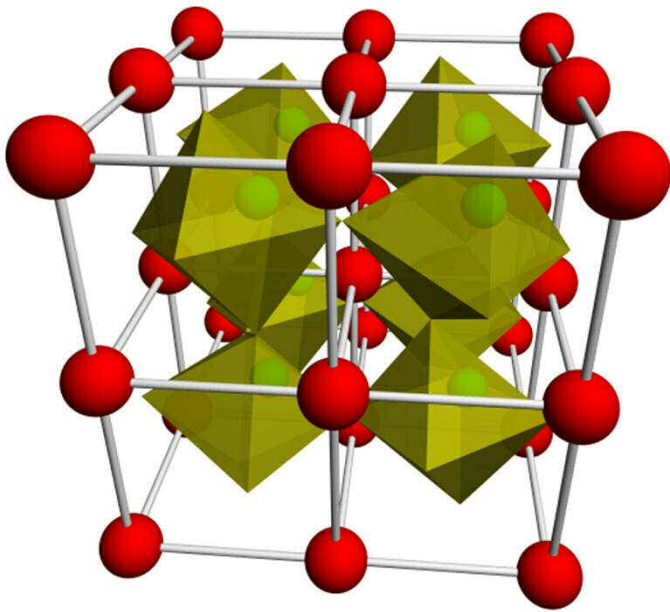


Rotation results in
a centrosymmetric
R-3c phase

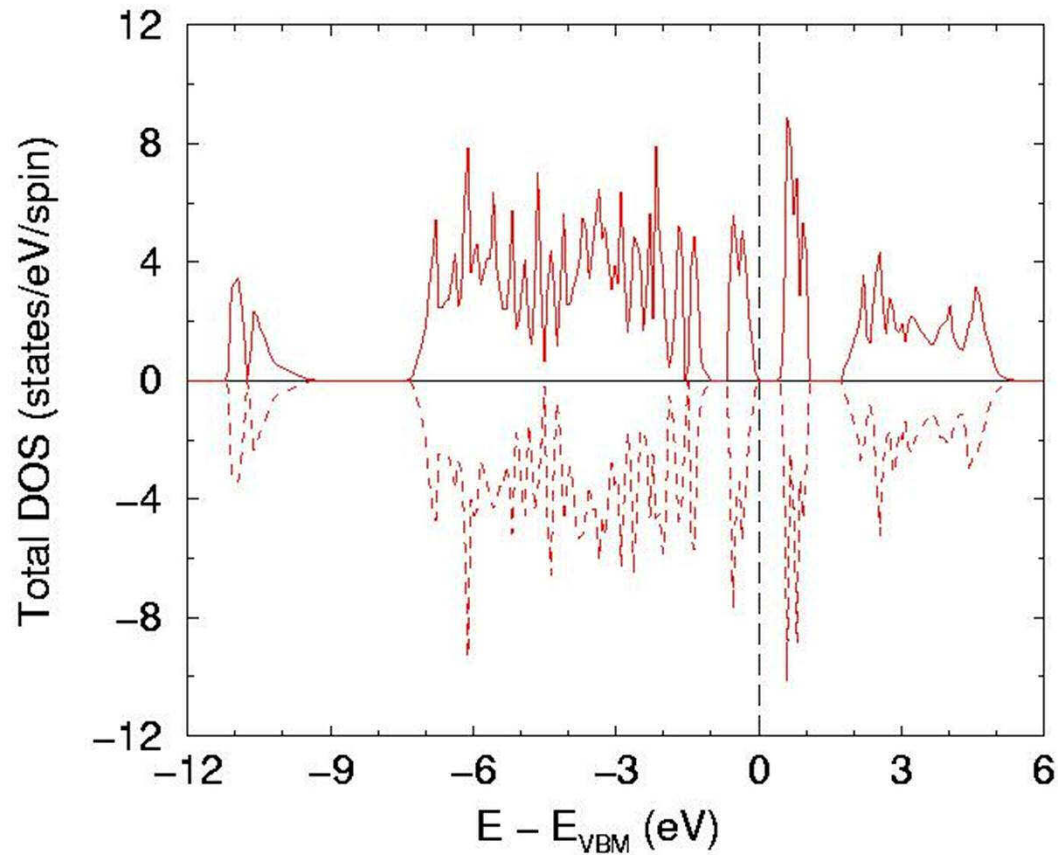


Cubic \longrightarrow R-3c

Breaking inversion symmetry lowers energy



R3c phase
 $E_g \sim 0.4$ eV (LSDA)



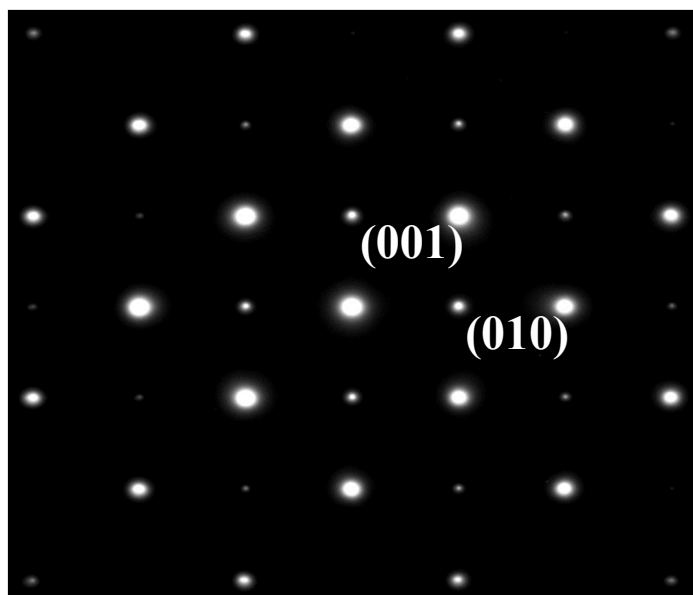
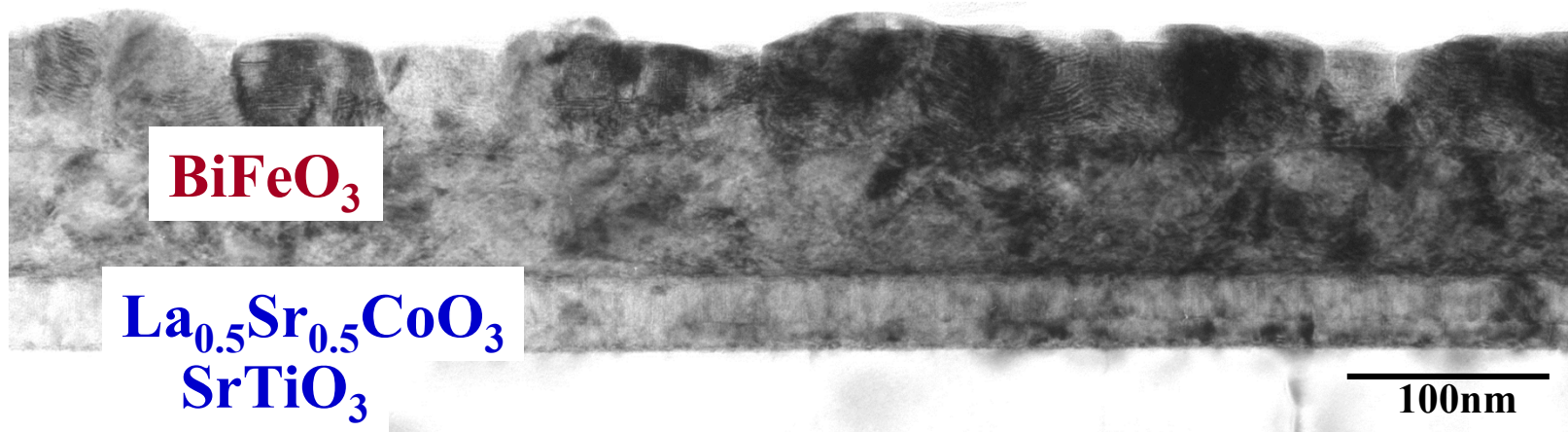
R-3c $\xrightarrow{P = .07 \text{ C/m}^2}$ R3c

Perovskite design by epitaxy

- Are epitaxial thin films better materials?
- Perovskite oxides:
 - Unparalleled variety of electronic properties
 - Structural consistency
- Why epitaxy?
 - Atomic-level manipulation and control of structure
 - Order can be a good thing (fundamentals & applications)
 - Experiment and theory at the same length scale
- An example of previous success:
 - BST superlattices with enhanced polarization



A tetragonal phase of BiFeO_3 ?



R Ramesh s group

Experiment finds:

$$a=3.935 \text{ \AA}$$

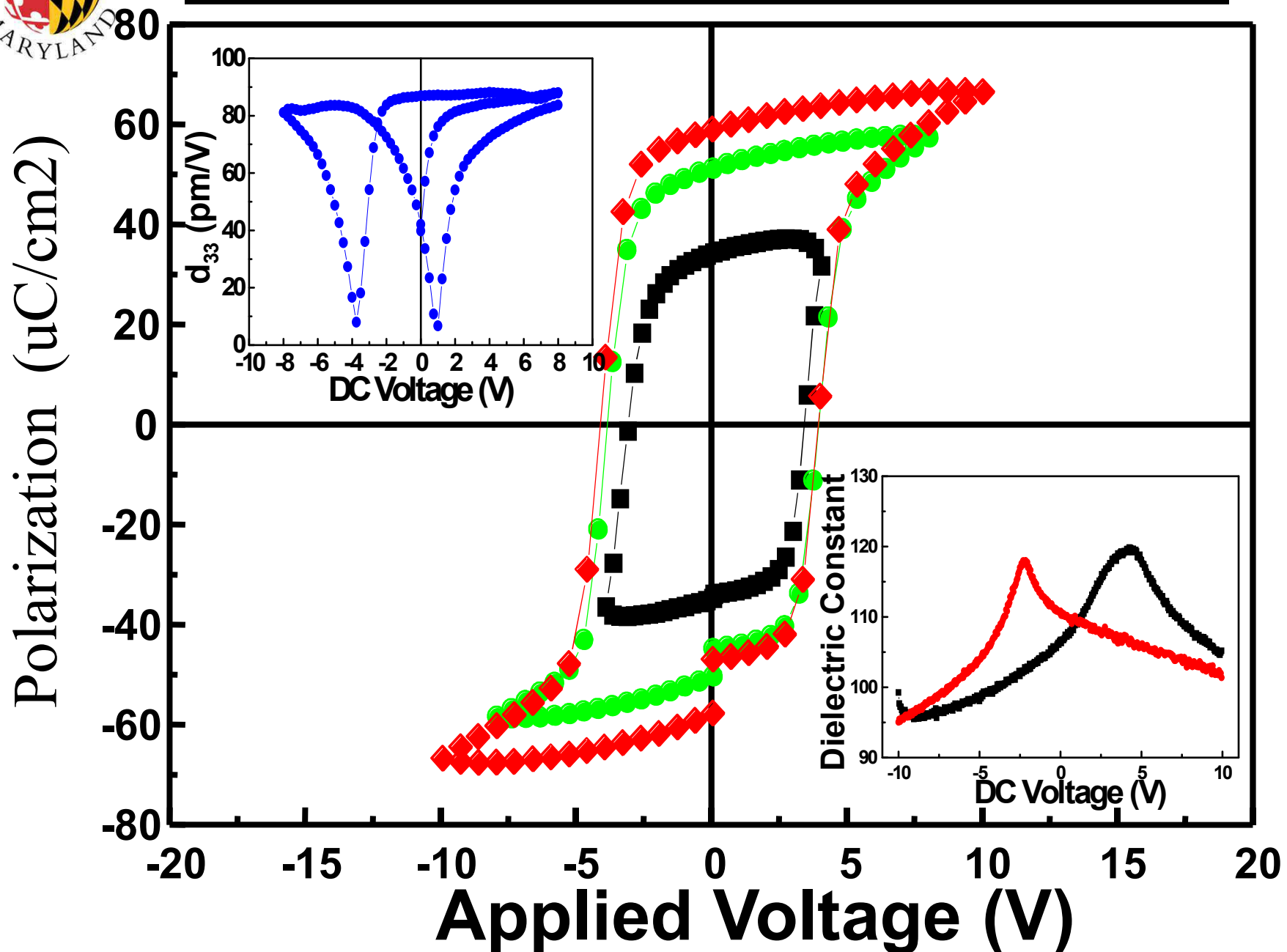
$$c/a = 1.01 \sim 1.02.$$

$$\alpha = 90 \pm 0.1^\circ.$$

Film could be tetragonal
or monoclinic.

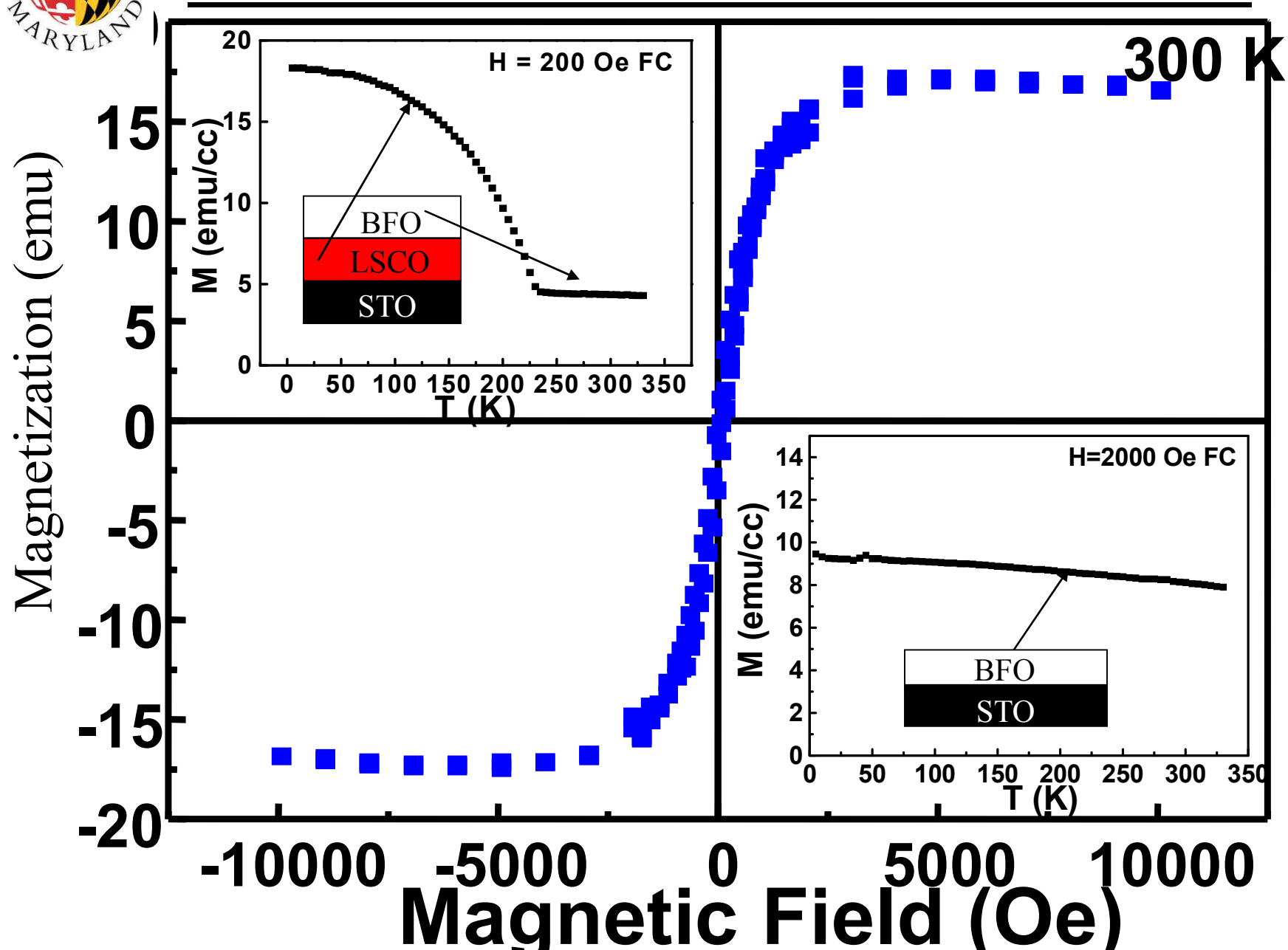


Properties of Epitaxial BiFeO₃





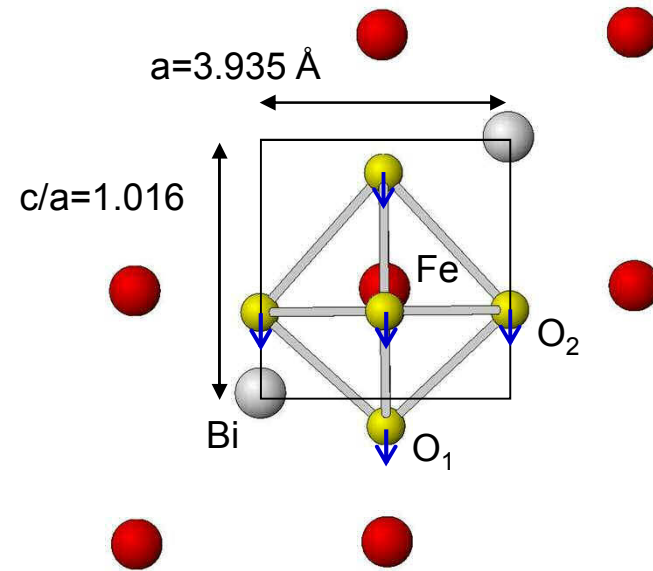
Magnetic Property of Epitaxial BiFeO_3



Hypothetical tetragonal phase

Tetragonal P4mm ($P_s \parallel [001]$)

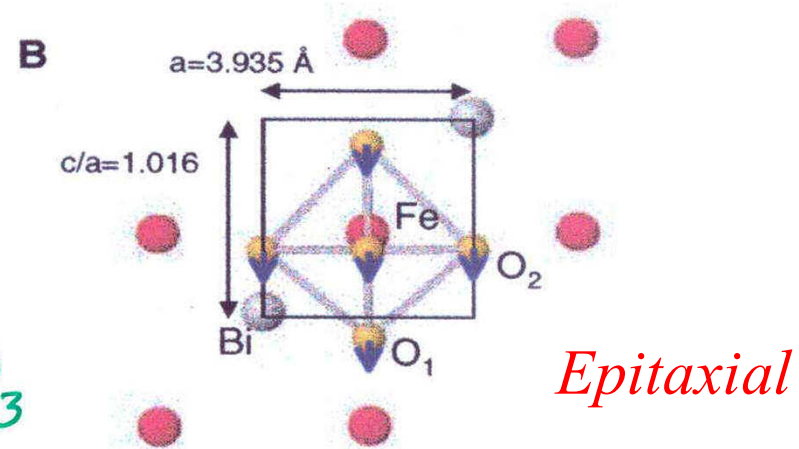
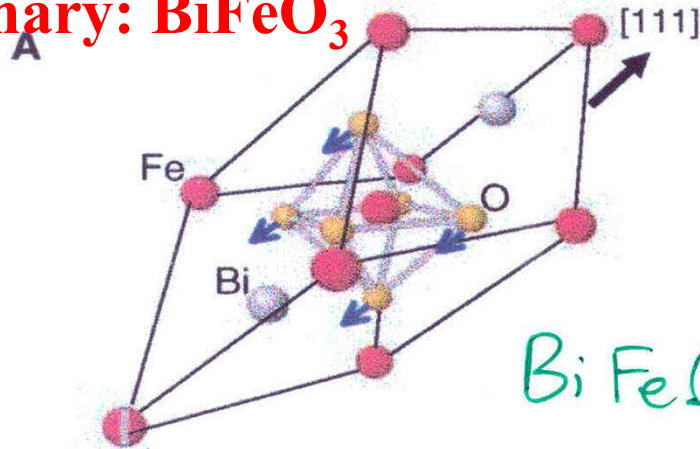
	LSDA	Expt
Bi (1a) z	0	
Fe (1b) z	0.41	
O ₁ (1b) z	-0.101	
O ₂ (2c) z	0.367	
a (Å)	3.935*	3.935
c/a	1.016*	1.016
V (Å ³)	61.91*	61.91
P_s(mC/cm²)	63.2	50-60



But: a polarization path is yet to be identified

Summary: BiFeO₃

Bulk



C

Rhombohedral R3c ($P_s \parallel [111]$)

	LSDA	Expt
Bi (2a) x	0	0
Fe (2a) x	0.2308	0.22077
O (6b) x	0.5423	0.5279
y	0.9428	0.9333
z	0.3980	0.3948
a (Å)	5.4590	5.6343
α (°)	60.36	59.348
V (Å ³)	115.98	124.601
P_s (μC/cm ²)	6.61	6.1

D

Tetragonal P4mm ($P_s \parallel [001]$)

	LSDA	Expt
Bi (1a) z	0	
Fe (1b) z	0.41	
O ₁ (1b) z	-0.101	
O ₂ (2c) z	0.367	
a (Å)	3.935*	3.935
c/a	1.016*	1.016
V (Å ³)	61.91*	61.91
P_s (μC/cm ²)	63.2	50-60

Fig. 3. Schematic of the prototypical rhombohedral (A) and tetragonal (B) BiFeO₃ unit cells. (It that computations were performed with a 10-atom body-centered tetragonal unit cell, which doubled to accommodate the G-type antiferromagnetic ordering.) The corresponding atomic positions and spontaneous polarizations from first-principles calculations are shown in (C) and respectively. Structural parameters for the rhombohedral R3c phases were taken from (13), asterisks in (D) indicate that lattice parameters were fixed to the experimental values of 200-nm film.

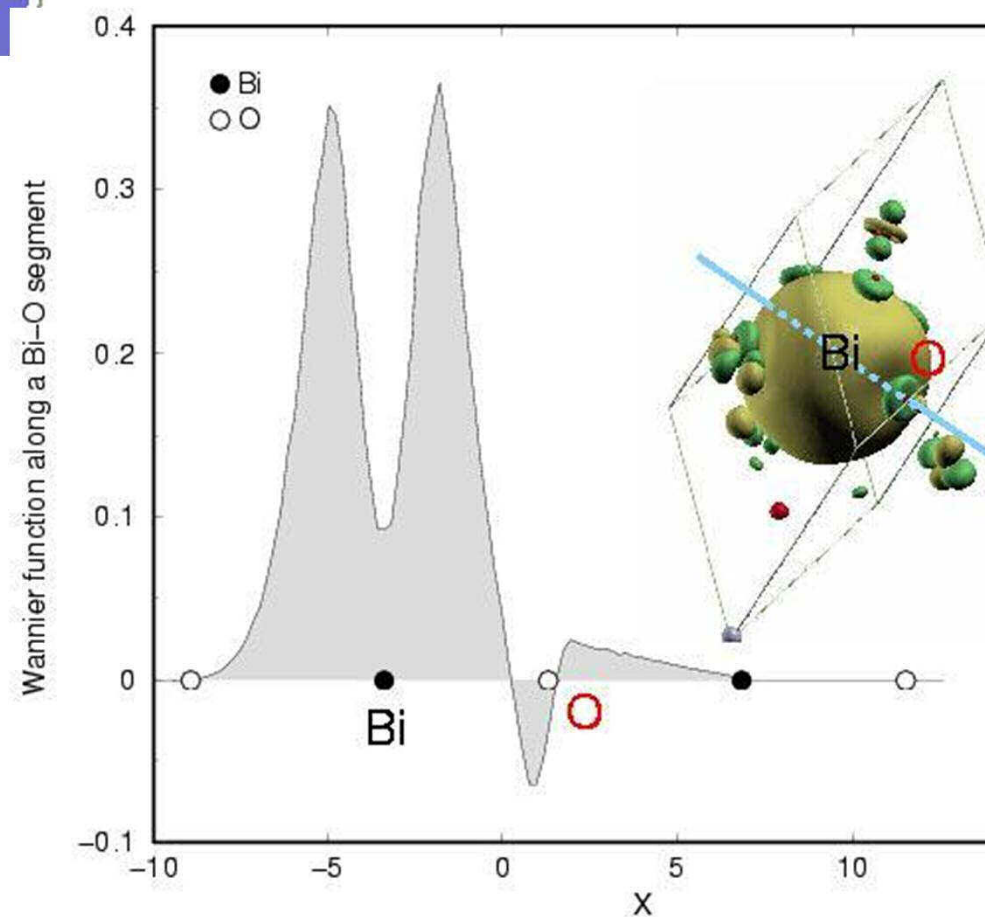
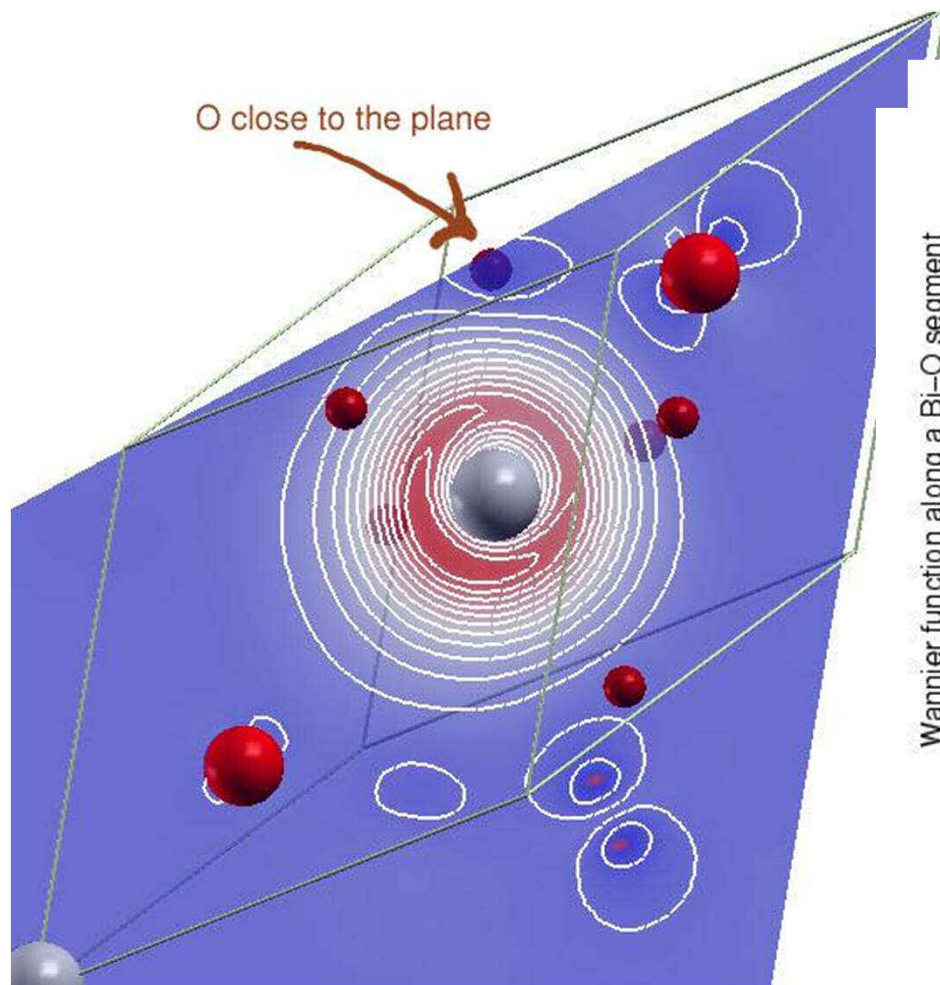
With

Neaton, Spaldin, Rabe, Ramesh *et al*, *Science* 299, 1719 (2003)

Chemical origin of FE in BiFeO_3

(with Joydeep Bhattacharjee)

Wannier functions



Why is P so small ?

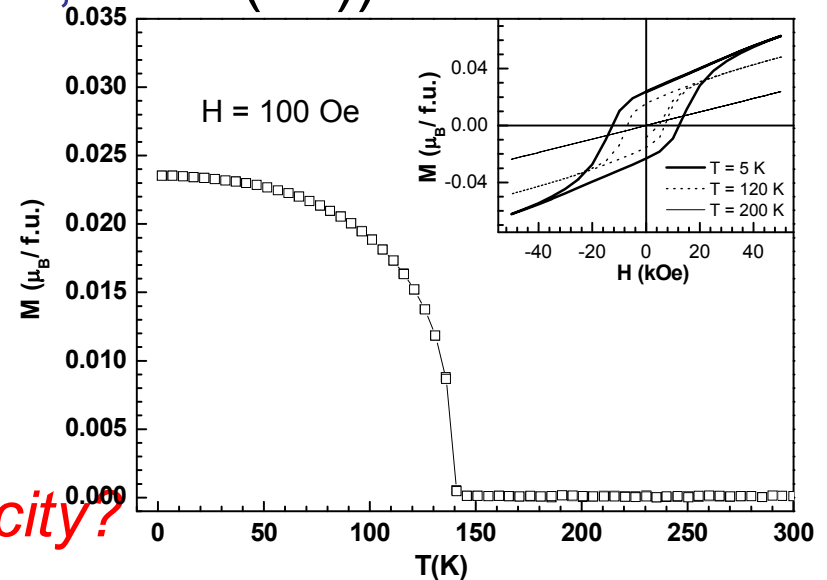
YCrO₃

(with Serrao, Kundu, Krupanidhi and C. N. R. Rao, Phys. Rev. B 72, 220101 (R) 2005).

- Known since 1955 (Katz, Acta Cryst. 55)
- Monoclinic structure P2₁/n (spg no: 14):
Centrosymmetric!
- An AFM with weak ferromagnetism
(T_N=140 K) (Judin and Sherman, SSC (66)).
- Experiments at JNCASR:
Signs of ferroelectricity with
a *weak polarization*.
0.01 C/m²
T_c ~ 425 K.

Questions: *Is it ferroelectric?*

What drives its ferroelectricity?



First-principles Determination of Structure

Lattice constants kept fixed at the experimental values.

Two paths:

A Initial structure: $P2_1/n$

Break inversion symmetry and relax.

B Initial structure: cubic perovskite

Break symmetry with small random atomic displacements

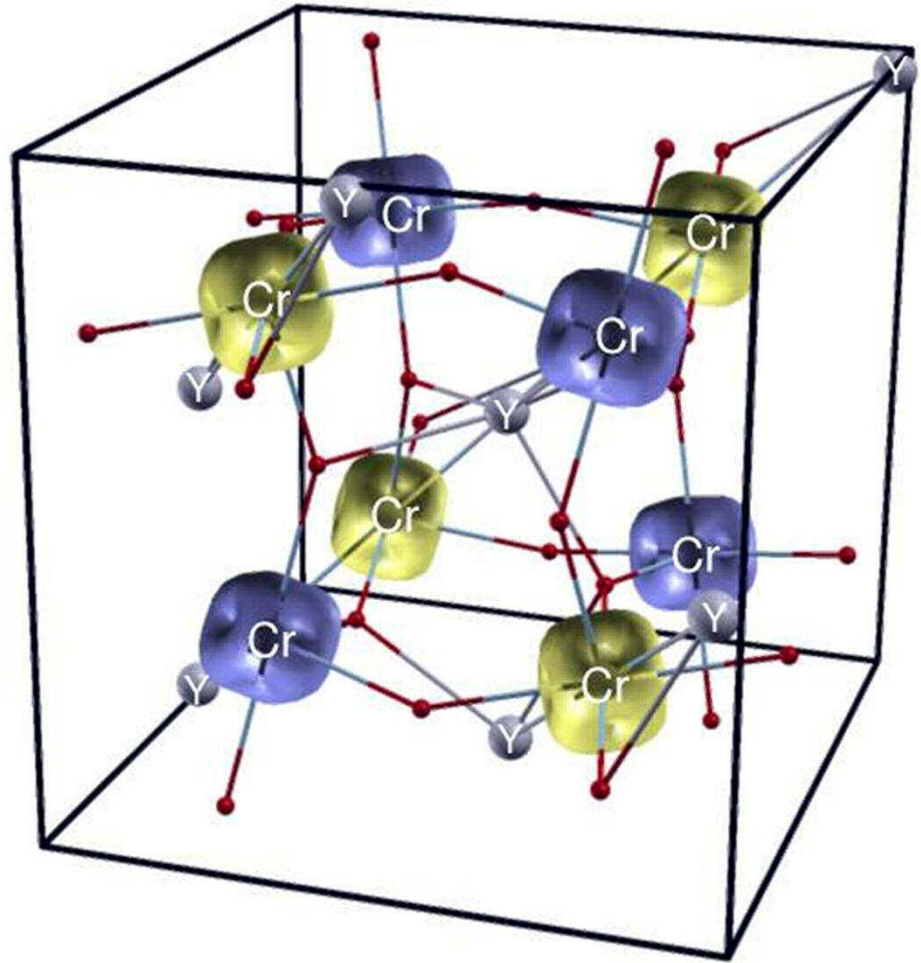
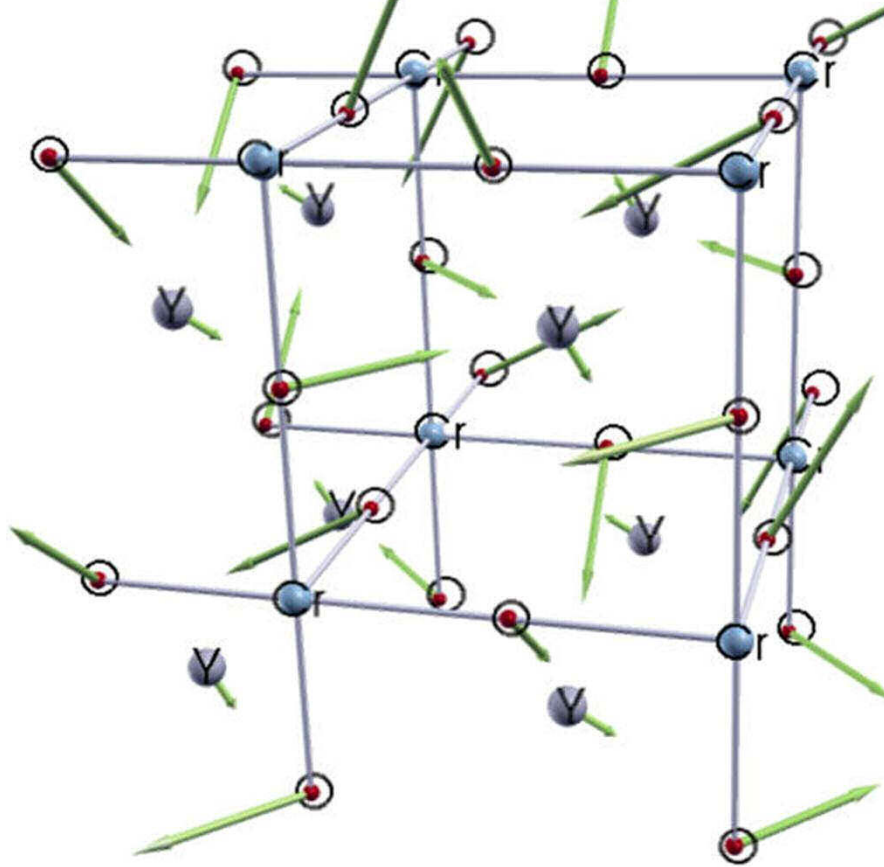
Relax the structure.

We get the same structure with inversion symmetry and
space group no. 1.

This structure is *lower* in energy than $P2_1/n$
by 0.025 eV/fmu.

YCrO₃: Structure

Distortions of cubic structure:



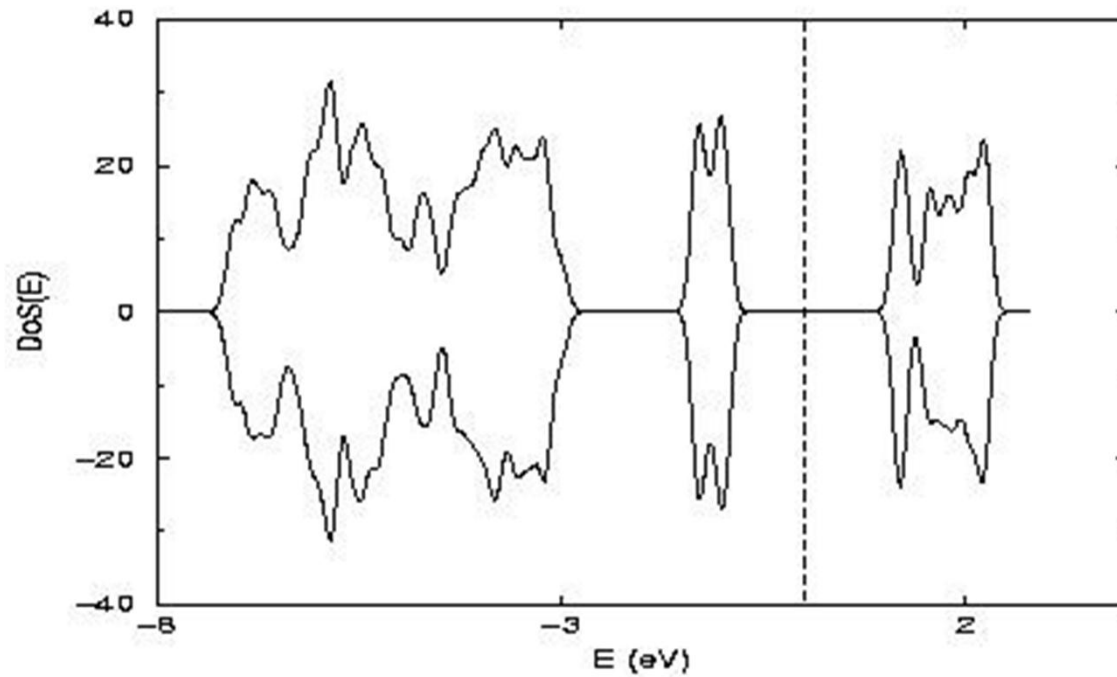
No displacements of Cr.

R₂₅ and M₃ modes dominate (O)
(octahedral rotations)

Weak component of X₅', M₅' and Γ_{15} (Y and O) -> **Ferroelectricity**

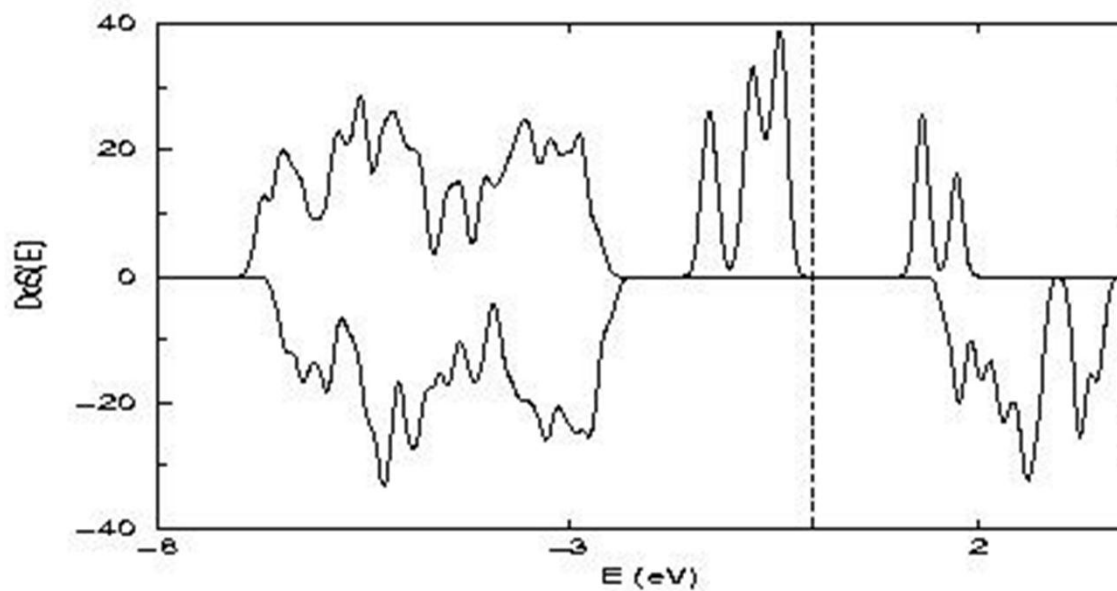
Phys. Rev. B 72, 220101 (R) 2005

Electron Density of States: YCrO_3



AFM

Large crystal field
and
exchange
splitting: d^3



FM

YCrO₃: Born effective charges

Y: 4.52 (compare with 3.9 of Pb in PbTiO₃)

Cr: 3.52

O: -3.64, -2.24

Y at A-site drives ferroelectricity.

> We distorted cubic perovskite structure (G-AFM) with only Y displacements and find energy lowering of 0.09 eV/fmu!

Unstable phonons of the double-cubic structure:

~ 300 i cm⁻¹ (R25, octahedral rotation)

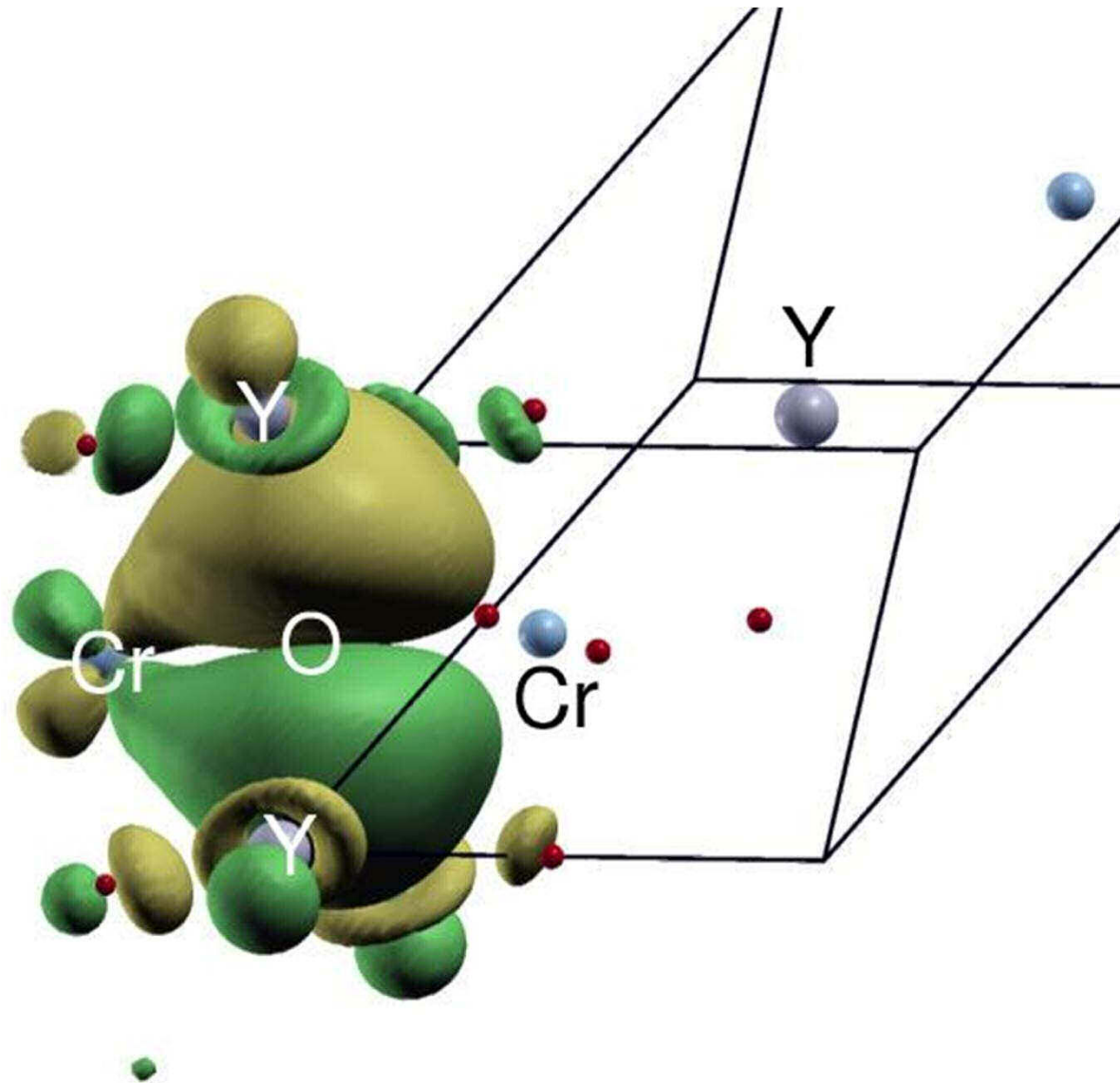
~ 100 i cm⁻¹ (Γ15, ferroelectric mode with Y-O distortions)

Ferroelectricity is quite weak (0.03 C/m²).

(with Serrao, Kundu, Krupanidhi and C. N. R. Rao, Phys. Rev. B 72, 220101 (R) 2005).

YCrO₃: interaction between Y and O

p and *d* states
of Y couple with
p states of O



Mechanisms in multiferroic ((A)FM+FE)

1. Lone pair of A atom: FE and d electrons of B atom: FM
Eg. BiMnO_3 , BiFeO_3
(Ref. Wang et al, Science 299, 1719 (2003))
2. Geometric (Structural) ferroelectricity in a magnetic compound, Eg. YMnO_3 , InMnO_3 (hexagonal)
(Ref. Van Aken et al, Nature Mat. 3, 164 (2004)).
3. Magnetoelastic structural modulation to give FE in a magnetic compound. Eg. TbMnO_3 , DyMnO_3 , TbMn_2O_5
(Ref. Kimura et al, Nature 426, 55 (2003)).
4. Proposed Mechanism: Superposition of two different charge-ordered states to give a dipole moment.
Eg. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x < 0.5$
(Ref. Efremov et al, Nature Mat 3, 853 (2004)).
- 5. Defects (vacancies) in a ferroelectric

Oxygen Vacancies in BaTiO₃

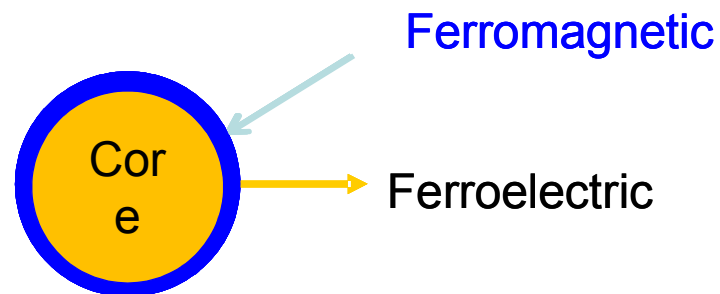
Mangalam RVK, Ray N, Waghmare UV, A Sundaresan, CNR Rao,
Sol. St. Comm 149, 1 (2009)

Multiferroic nature of BaTiO_3 nanoparticles

Multiferroic?

Materials that exhibit coupled electric and magnetic order

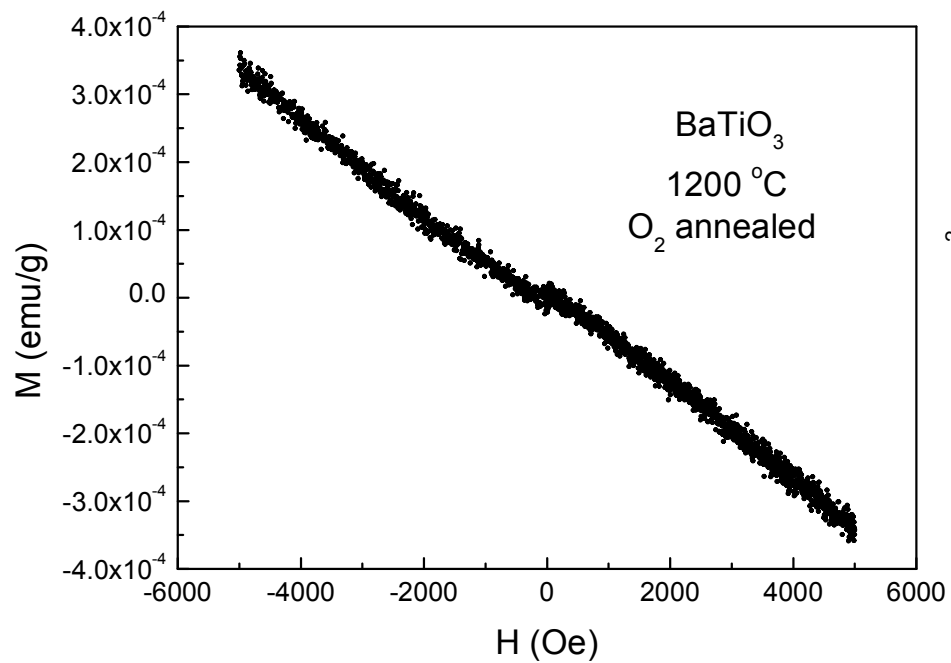
Surface ferromagnetism & core ferroelectricity



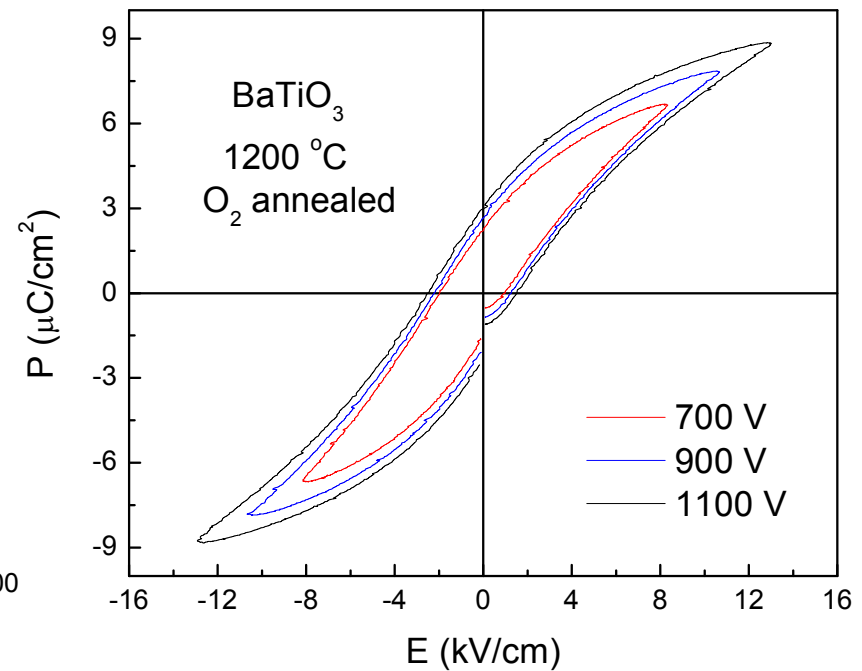
With V. K. Mangalam, N. Ray, A. Sundaresan, U. V. Waghmare and C. N. R. Rao

Bulk BaTiO₃

Prepared by sintering nanoparticles at 1200 °C in O₂ atmosphere



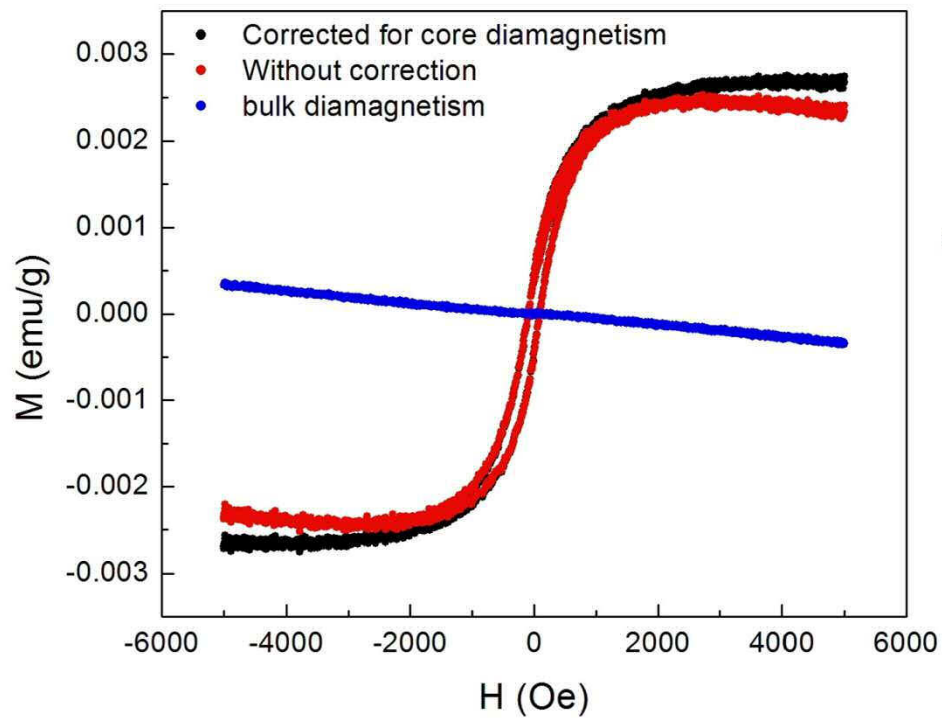
Magnetization



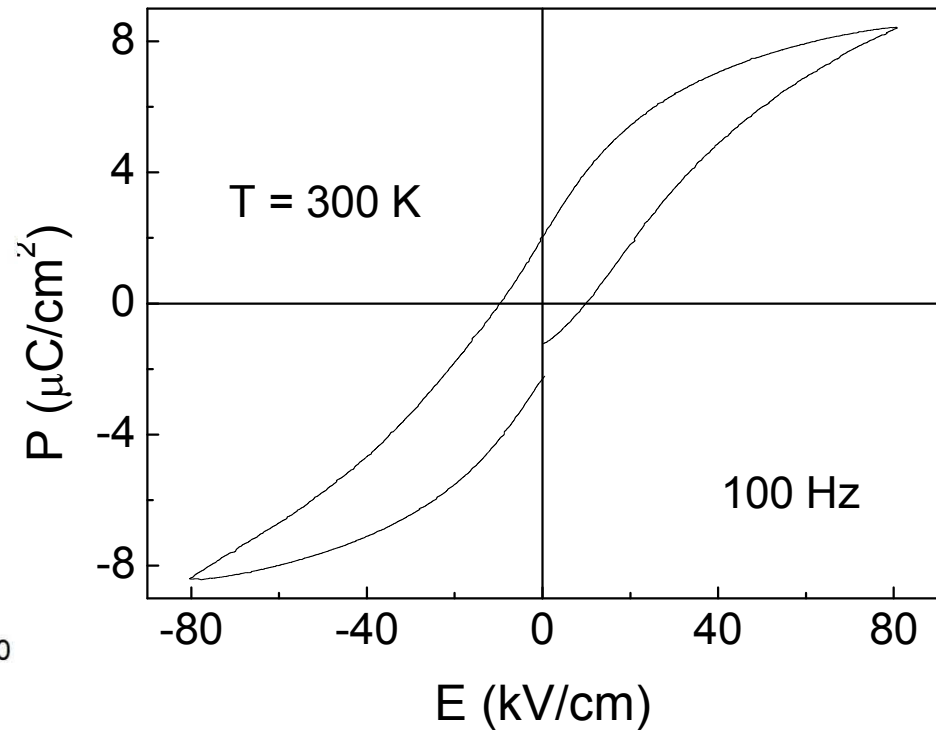
P-E Hysteresis

BaTiO₃ Nanoparticles (50 nm)

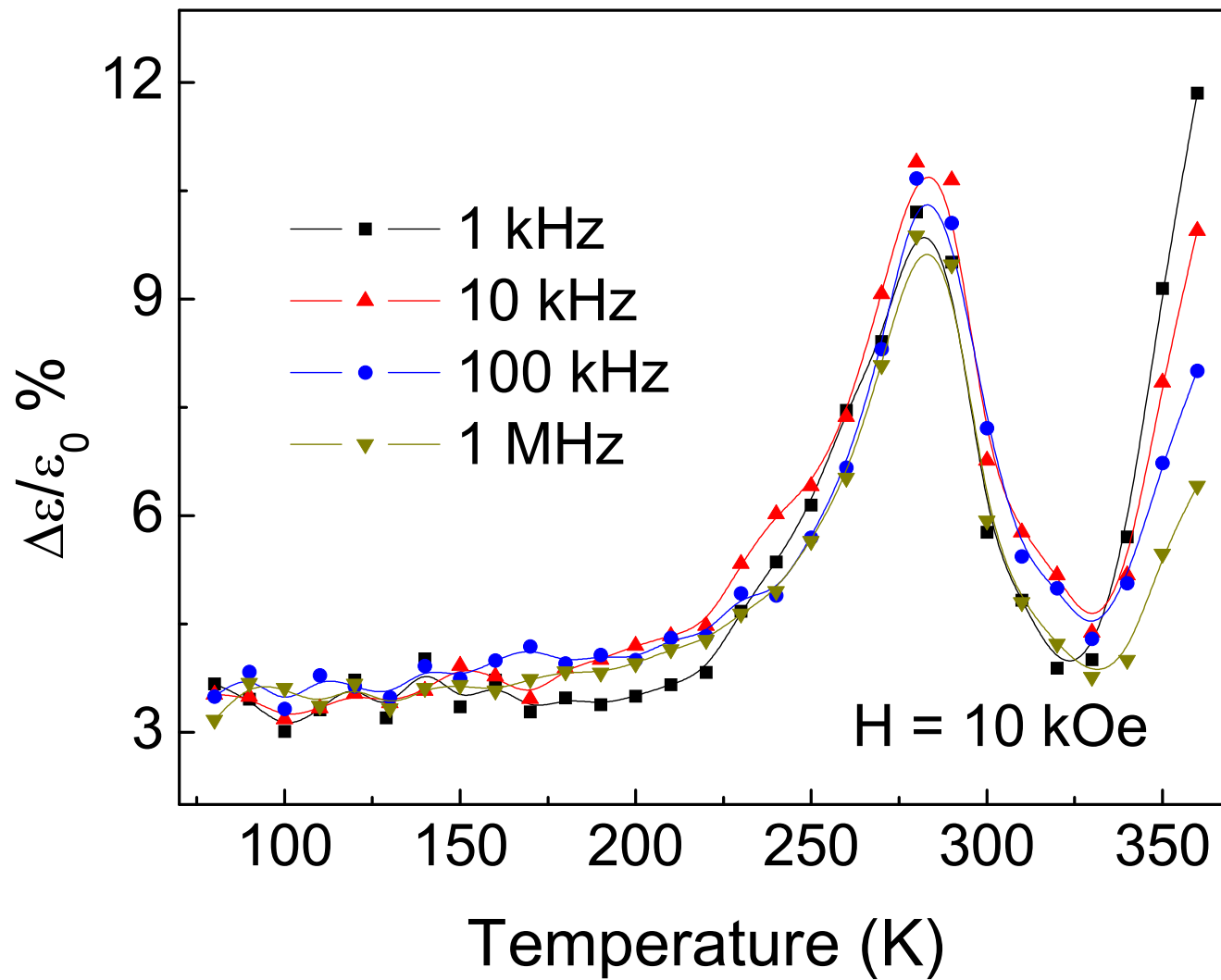
Prepared by sintering nanoparticles at 500 °C in O₂ atmosphere

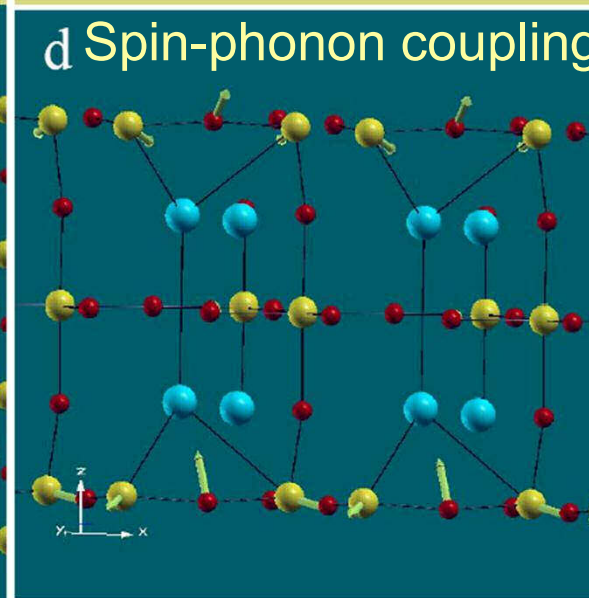
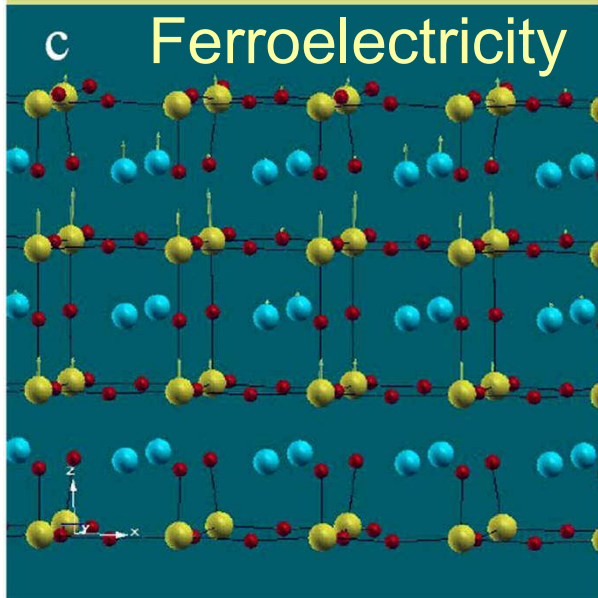
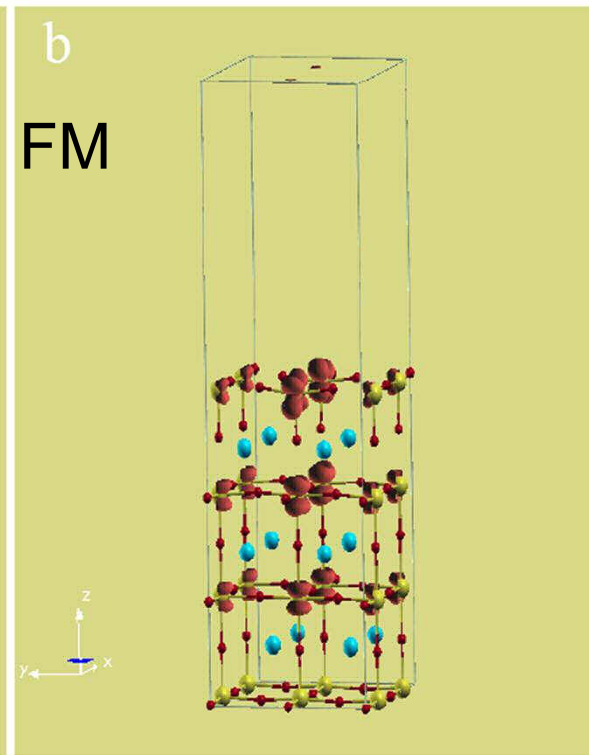
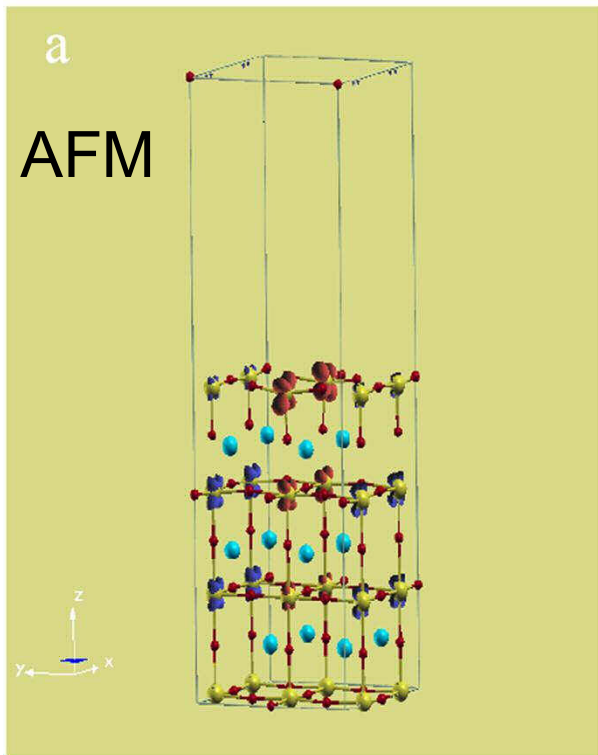


Magnetization



P-E Hysteresis

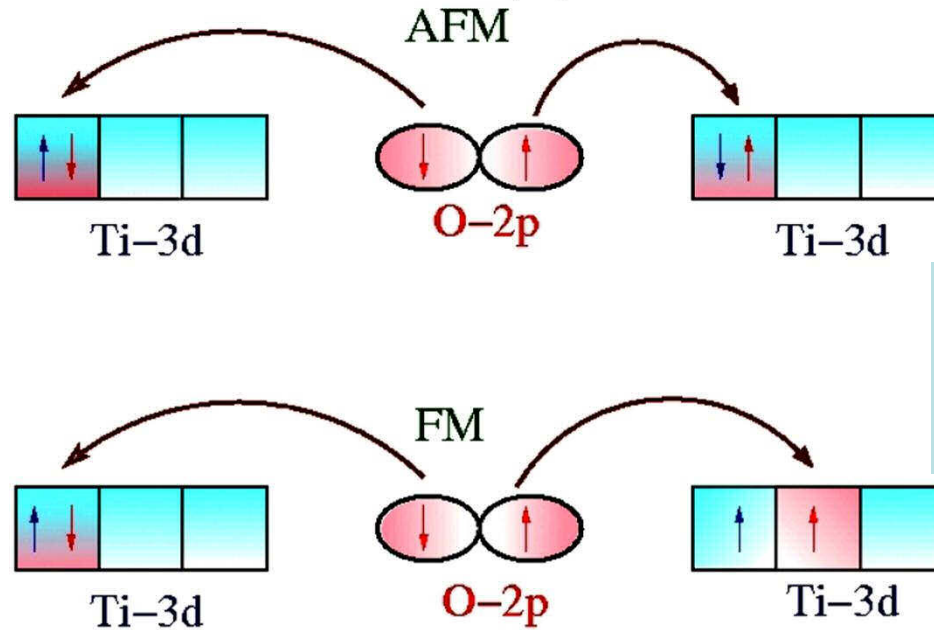
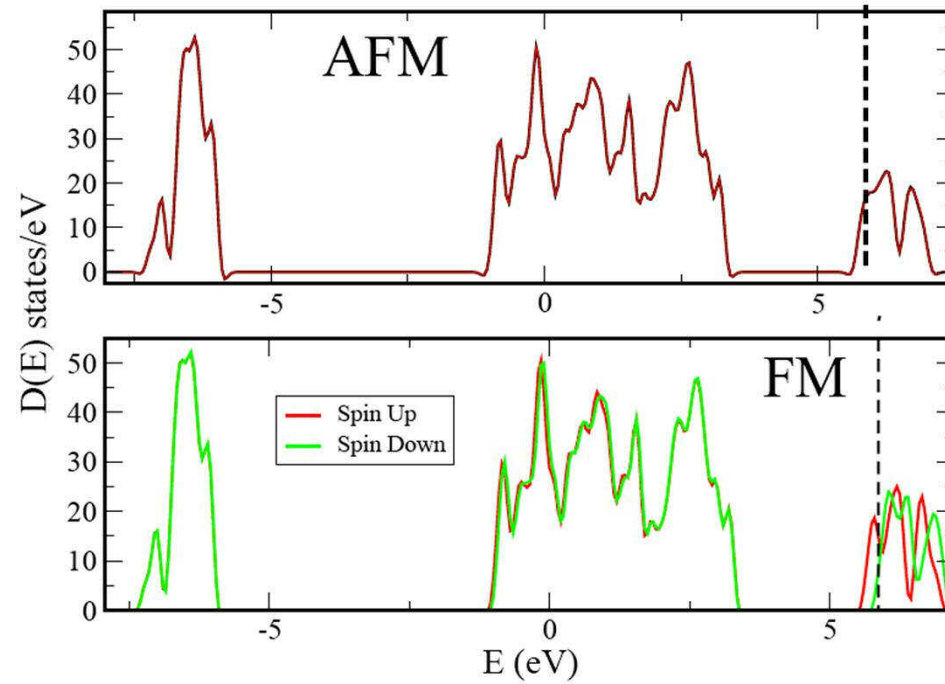




We consider 1.2 nm thick slab of BaTiO_3

- Seven [100] atomic planes terminated with TiO_2 planes
- Periodic supercell consisting of slab and vacuum layers with 2×2 unit cells periodicity of in-plane

FM state is lower in energy, FE arises from the core, spin-phonon coupling is at the surface



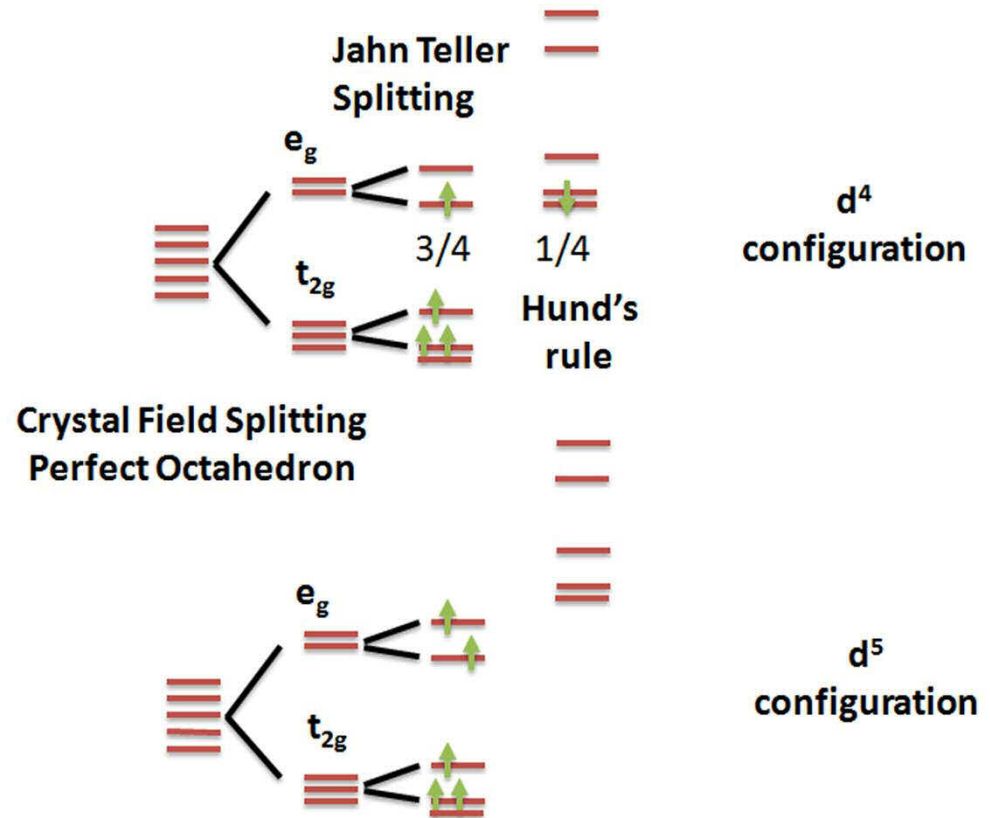
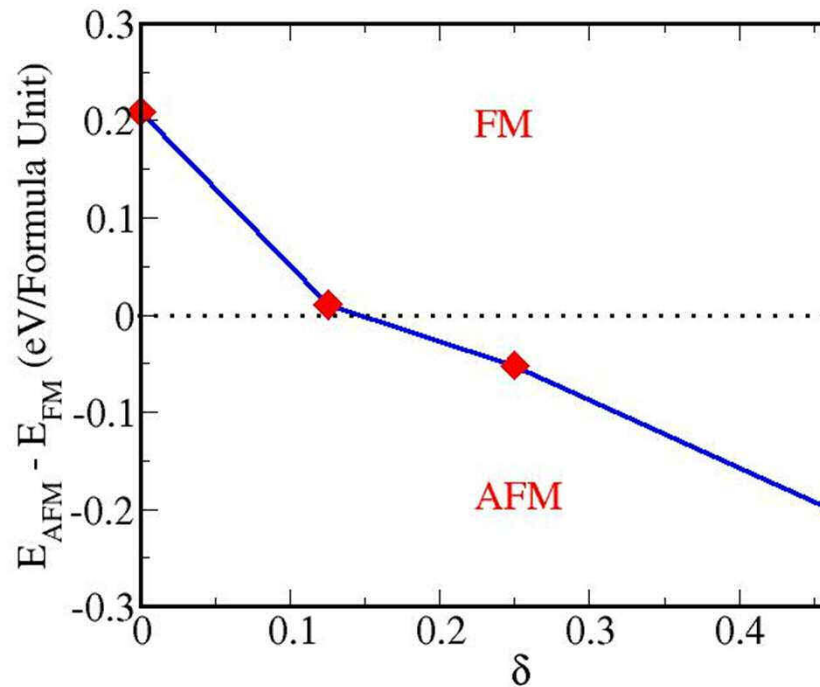
Hunds' coupling stabilizes FM state

Result

- Oxygen vacancies at the **surface** has lower energy by about 1.2 eV per vacancy than **bulk**
- Ferromagnetic state is lower in energy by more than 10 meV with $2 \mu_B$ per vacancy
- Ferroelectricity is weak at the surface
- Spin-phonon coupling: magnetocapacitance

Opposite example: $\text{BaFeO}_{3-\delta}$

See Poster 69 by Pan, Bhowmik and Waghmare



BaFeO_3 transforms from FM state to AFM state with increasing oxygen vacancies (δ)

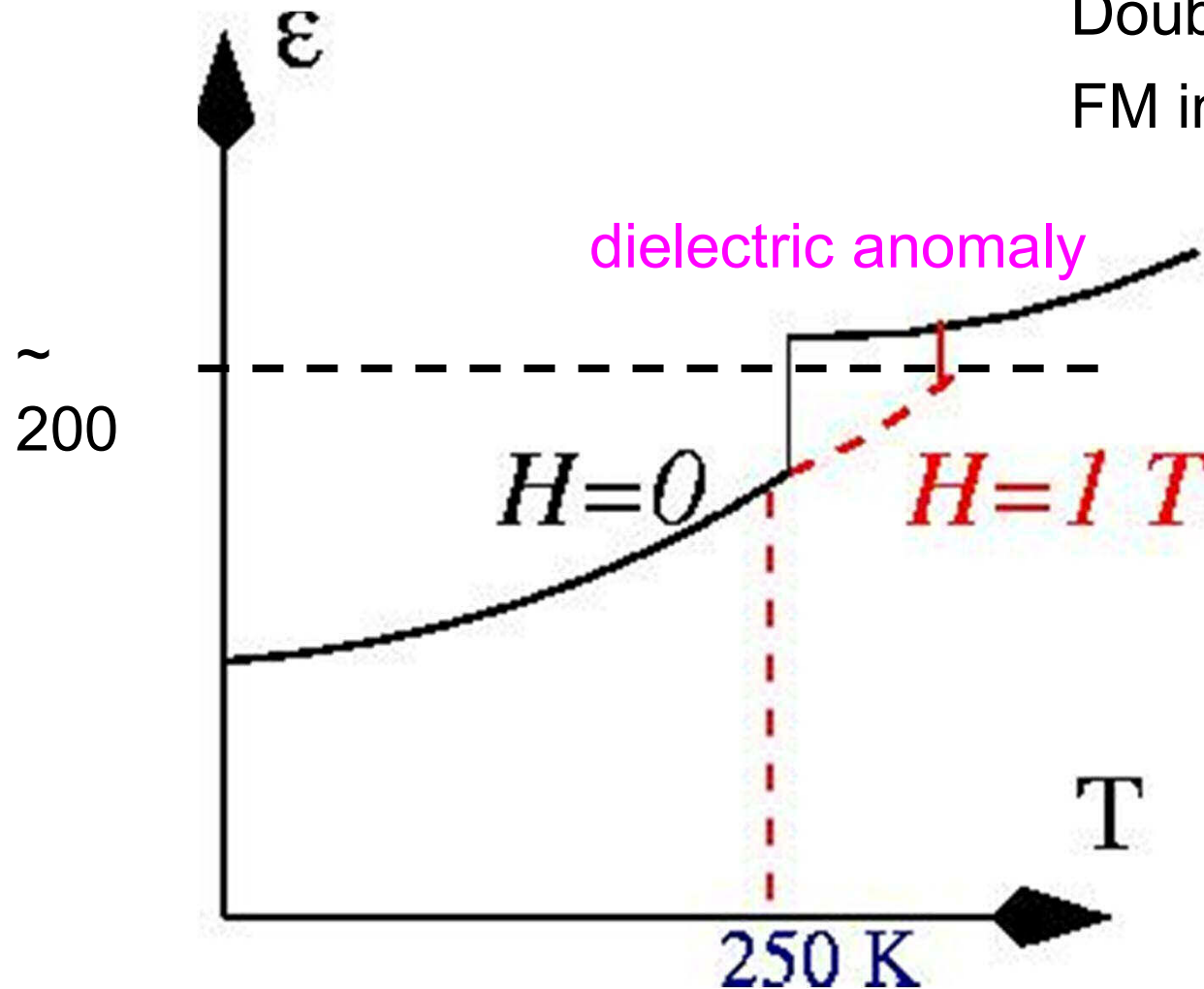
Other Materials with Magneto-electric Couplings



Room temperature magneto-capacitance of $\text{La}_2\text{NiMnO}_6$

Double perovskite

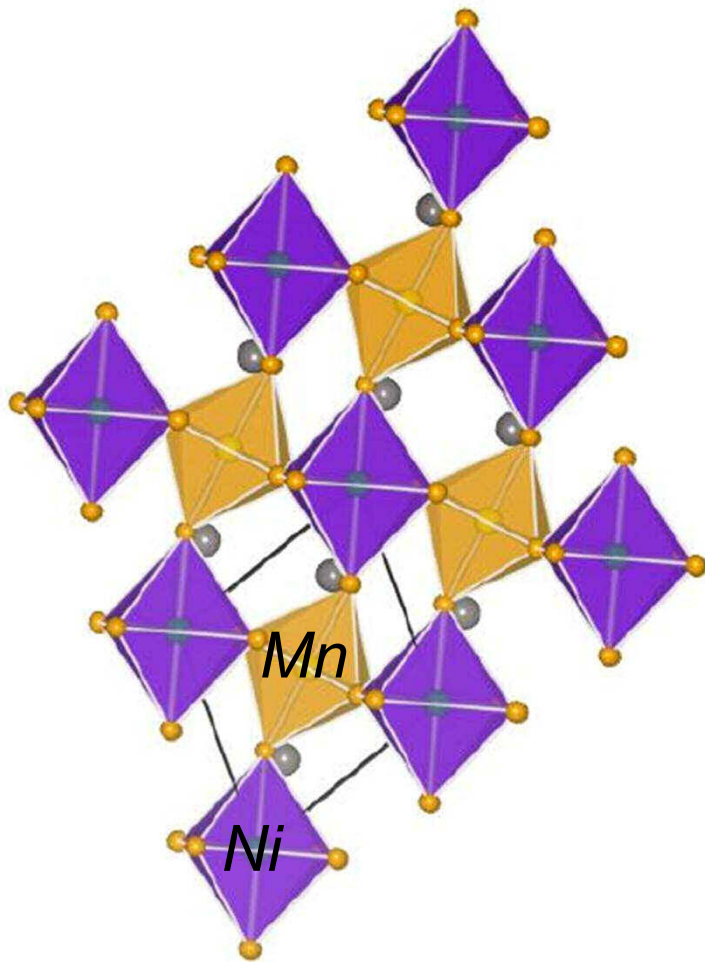
FM insulator $T_c \sim 280 \text{ K}$



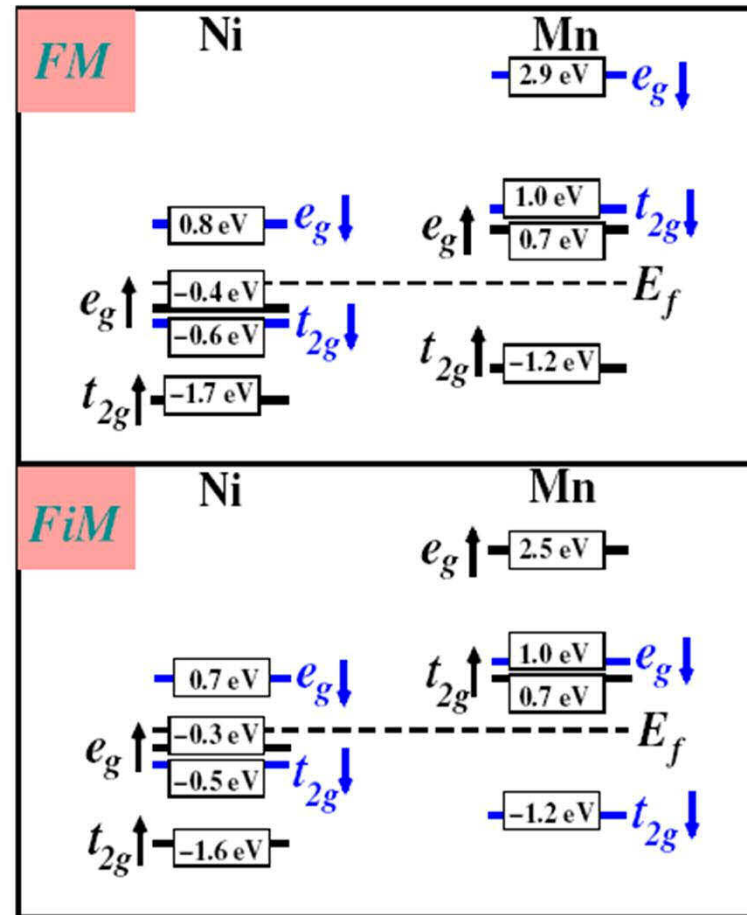
M A Subramanian et al, Advanced Materials 17, 2225 (2005).

La₂NiMnO₆: a ferromagnetic insulator

a



b

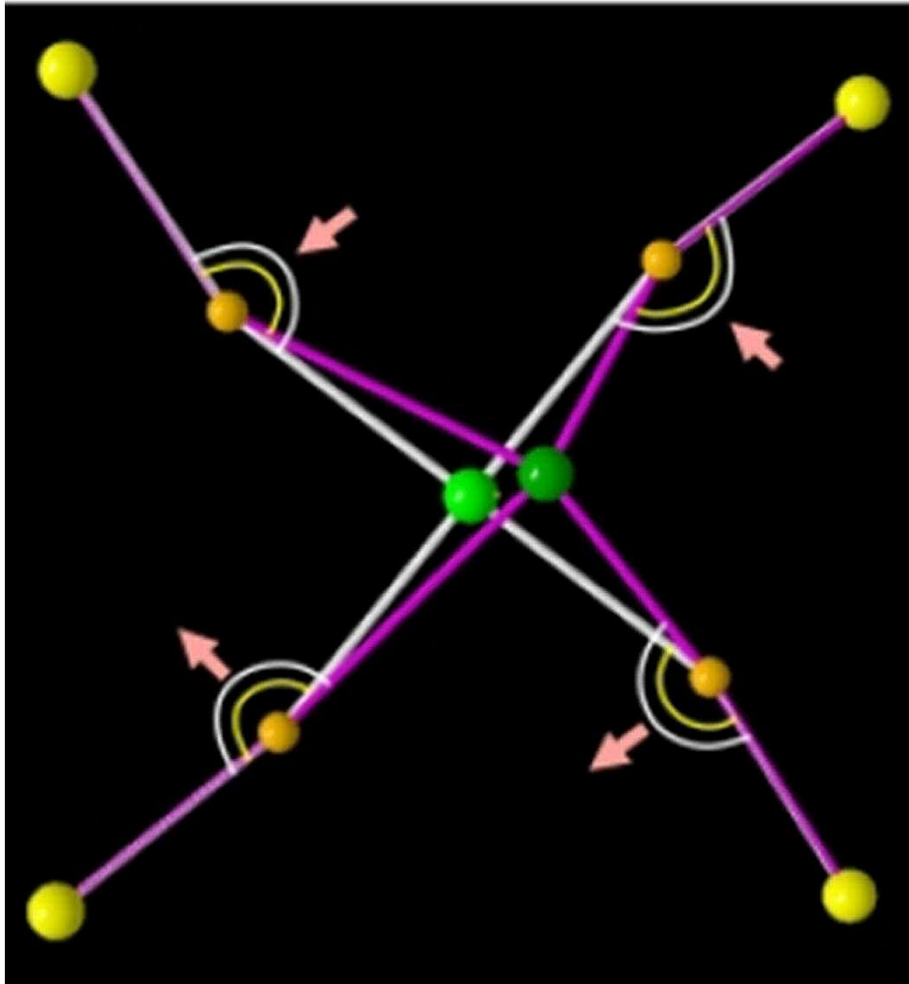


Superexchange interaction:

FM between e_g^2 of Ni²⁺ and e_g^0 of Mn⁴⁺ -25 meV

AFM between e_g^2 of Ni²⁺ and t_{2g}^3 of Mn⁴⁺ 19 meV

Spin-phonon Coupling



Vibrational motion
results in change in
Ni-O-Mn bond angles

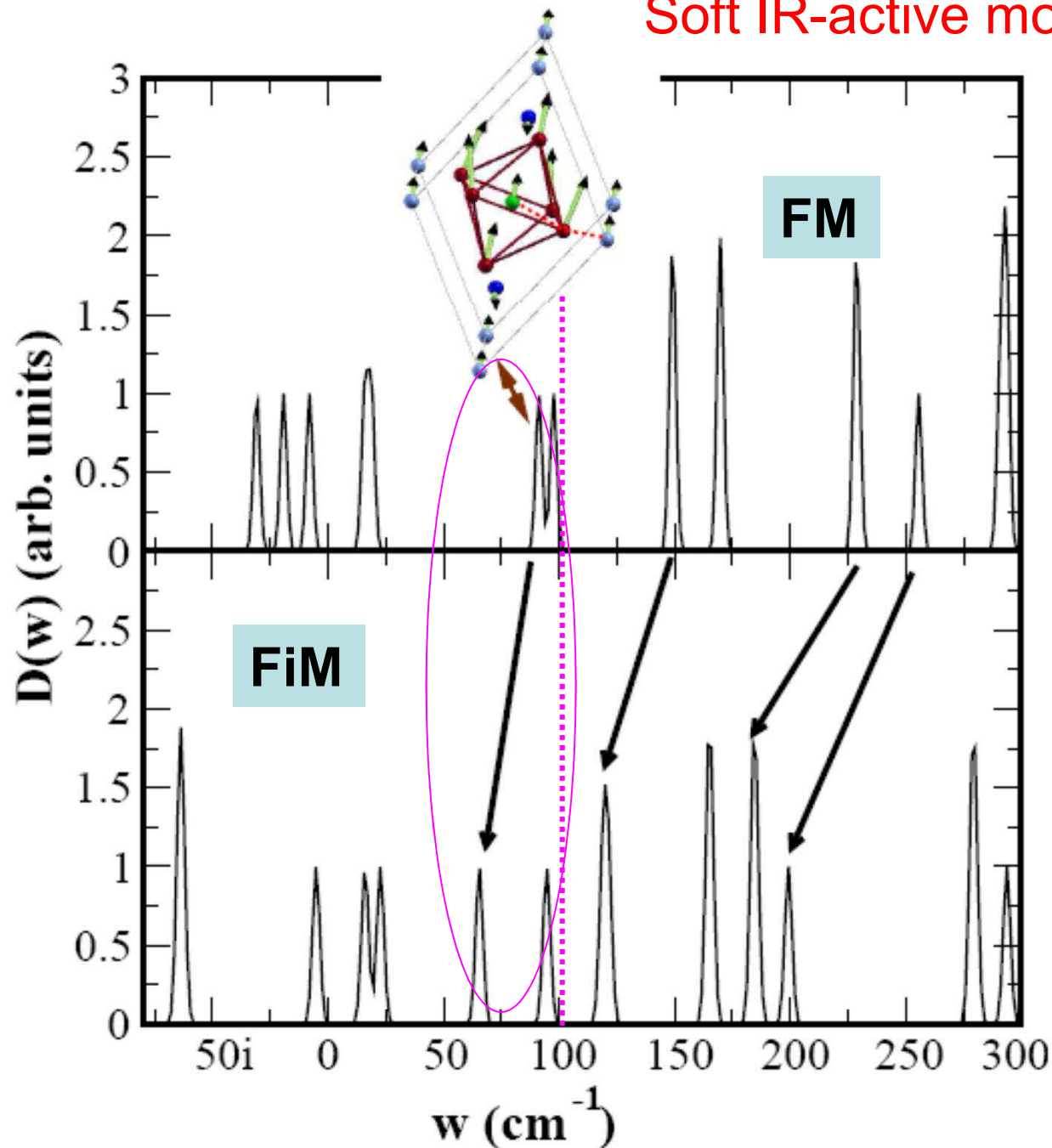


Changes in super-exchange
interaction energy

Change in magnetic
ordering

- ▶ Change in force constant
between Ni, Mn and O
- ▶ Change in ω

Soft IR-active modes upon change in magnetic ordering



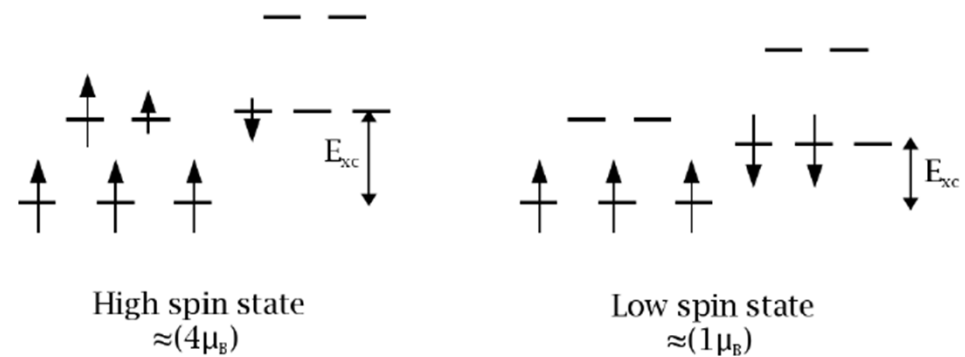
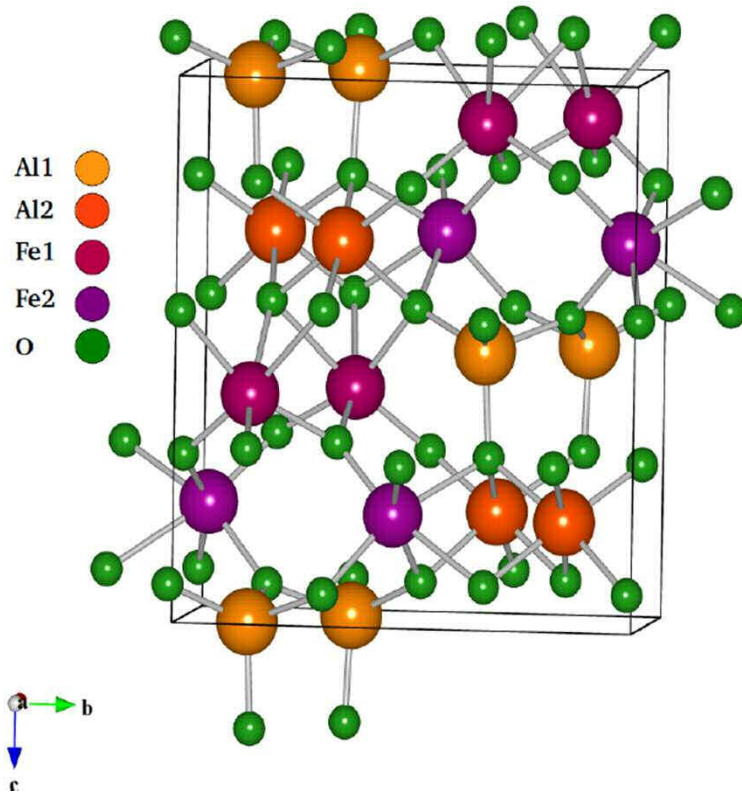
Super-exchange
Strong coupling
between spin and
soft phonon:
Magnetocapacitance
~ 20-40 %

$$\epsilon \propto \frac{1}{\omega^2}$$

Das, Waghmare,
Saha-Dasgupta, Sarma,
Phys Rev Lett (2008).

FeAlO₃

Anti-site disorder between Fe and Al:
difference in ionic size
change in the spin state



With out disorder: FeAlO₃ is AFM

Disorder > *Ferrimagnetism*

Size mismatch Al:Fe

► *Spin-phonon coupling*

Experiments of CNR Rao and A Sundaresan: magneto-capacitance
Work with Sharmila Shirodkar (2010)

SUMMARY

- Interesting Physics of Magnetoelectrics
Different routes to *multiferroics*
Spin-phonon coupling
- *Sensitivity to*
Chemistry, Structure (strain), Disorder, Vacancies
Vicinity to different instabilities, phase transitions
- **Challenge:**
To develop a material with significant ME-coupling at RT