

Magnetostructural coupling in multiferroics, part 2

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First principles investigations

Microscopics: atomic and electronic arrangements

Multiferroics: crystal distortions/phonons

Displacement of atoms:

dynamical (phonons) & static (symmetry lowering distortions)

Displacement of atoms is coupled to magnetic ordering
(spin-phonon coupling)

Magnetic order affects phonons:

- magnetic phase transitions lead to anomalies in phonon frequencies
- magnetically-induced phonon anisotropy
- magnetodielectric response

Phonons/symmetry-lowering distortions affect magnetic ordering:

- structural phase transitions modify magnetic order—
example of ferroelectrically-induced ferromagnetism

Discussion also includes strain and elastic constants

- Crystallography – where the atoms are
- Symmetry analysis of phonon modes in magnetic space groups
- Modulation of magnetic interactions by displacements
(includes both striction and DM)

Overview of the second lecture: distortions of magnetic crystals

- The effect of magnetism on symmetry analysis
- First-principles calculation of J 's
- Magnetically-induced phonon anisotropy
- Dielectric anomalies at magnetic transitions
- Modulation of J 's by distortions
- Symmetry criterion for FM canting of AFM—ferroelectrically-induced ferromagnetism

- Examples: rocksalt MnO
- BiFeO_3 , EuTiO_3 , double perovskites, FeTiO_3
- [hexagonal YMnO_3]

Time-reversal symmetry

- Reversal of spin (currents, etc)
- Combine TR with crystallographic operations to get magnetic groups

Groups in which TR does not appear

Groups in which TR is a symmetry

Groups in which TR appears only in combination with nontrivial crystallographic operations

Point groups: $32 + 32 + 58 = 122$

Space groups: $230 + 230 + 1191 = 1651$

Point operations and spin

- How do spins transform under the action of crystallographic point operations?

No spin-orbit

Spin space and real space decoupled

Spin-polarized DFT calcs: spin is a scalar

Including spin-orbit

Transformation according to matrix:

Symmetry is lowered

Eg no ferromagnetic crystal can have a cubic magnetic space group

Note: spatial inversion leaves spin UNCHANGED

Magnetically-induced phonon anisotropy

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Noncubic Behavior of Antiferromagnetic Transition-Metal Monoxides with the Rocksalt Structure

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(Received 9 April 1998)

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Structural, electronic, and magnetic properties of MnO

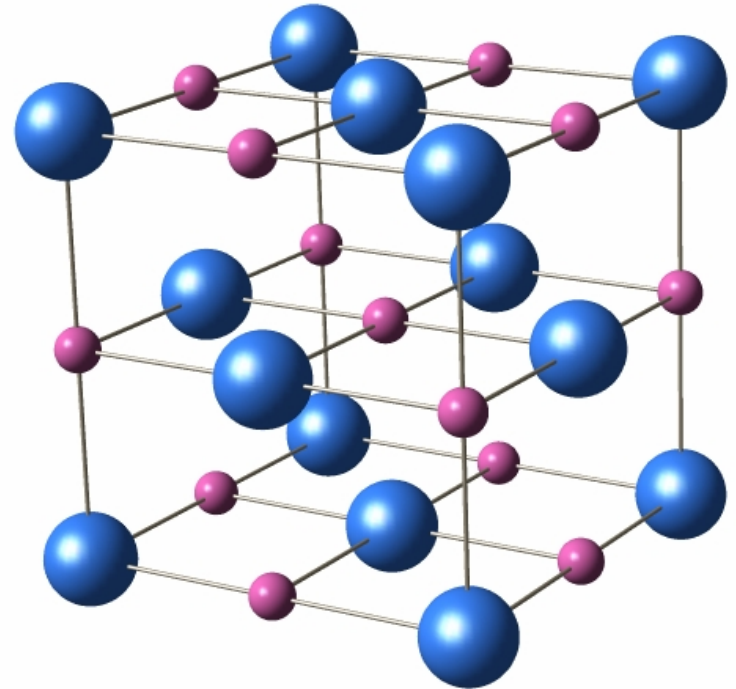
J. E. Pask, D. J. Singh, I. I. Mazin, C. S. Hellberg, and J. Kortus

Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375

(Received 13 December 2000; published 11 June 2001)

Magnetically-induced phonon anisotropy in MnO

- Mott insulators
- Paramagnetic: rocksalt
- fcc lattice, two atoms/cell
- $Q=0$ phonons:
acoustic mode (3-fold vector);
optic mode (3-fold vector;
LO/TO splitting to 1+2 fold)



Magnetically-induced phonon anisotropy in MnO

- first-principles computation of J 's (Singh 2001):

Energy differences of magnetically-ordered structures ($S = 5/2$)
AFI[001], AFII[111]

$$H = \sum_{NN} J_1 \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{NNN} J_2 \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1)$$

Considering a single formula unit, the above Hamiltonian reduces to

$$H^{\text{FM}} = (6J_1 + 3J_2)S^2, \quad (2)$$

$$H^{\text{AFI}} = (-2J_1 + 3J_2)S^2, \quad (3)$$

and

$$H^{\text{AFII}} = -3J_2S^2, \quad (4)$$

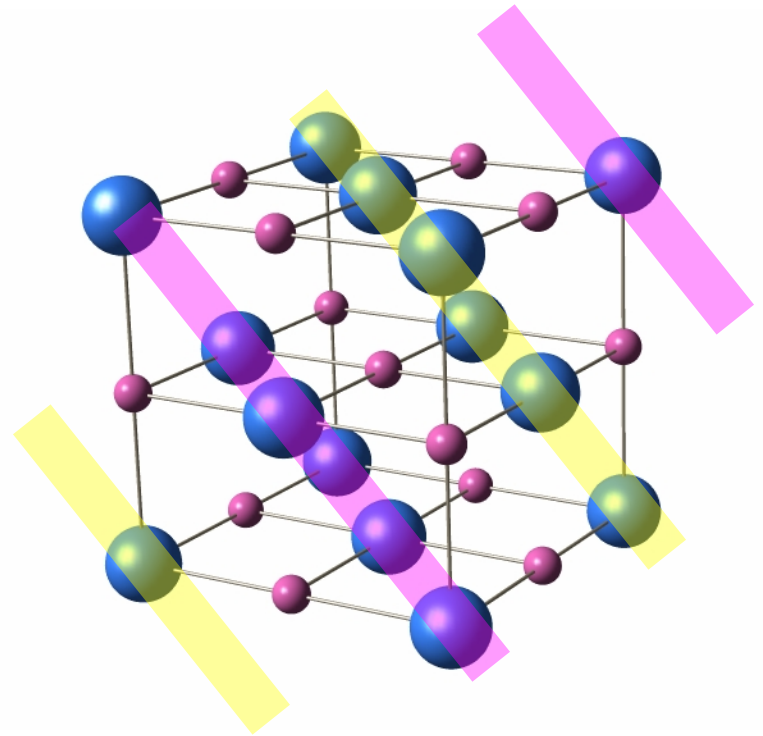
Results (in K)

	LAPW	
	LDA	GGA
J_1	9.8	18.8
J_2	24.5	33.0

(there is also another method, based on calculating exchange integrals from orbitals—Das et al 2008)

Magnetically-induced phonon anisotropy in MnO

- Antiferromagnetic:
Ordering along $\langle 111 \rangle$
 $T_N = 117$ K for MnO, 523 K for NiO
+ small rhombohedral distortion
(0.624 deg, 0.100 deg)
- Magnetic space group:
Unit cell doubles
ABCABC -> **AuBdCuAdBuCd**



Magnetically-induced phonon anisotropy in MnO

- Antiferromagnetic:

Ordering along $\langle 111 \rangle$

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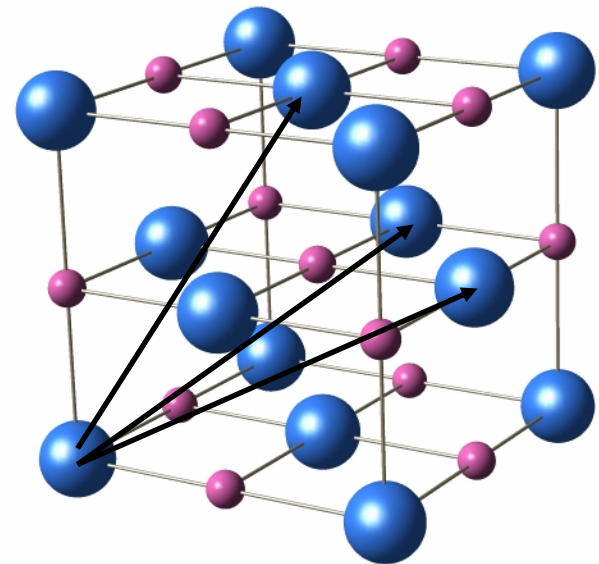
Unit cell doubles

Lattice vectors 112, 121, 211

Mn \uparrow at 000, Mn \downarrow at $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$

O at $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$ and $\frac{3}{4}$ $\frac{3}{4}$ $\frac{3}{4}$

Additional symmetry: TR + translation by $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$



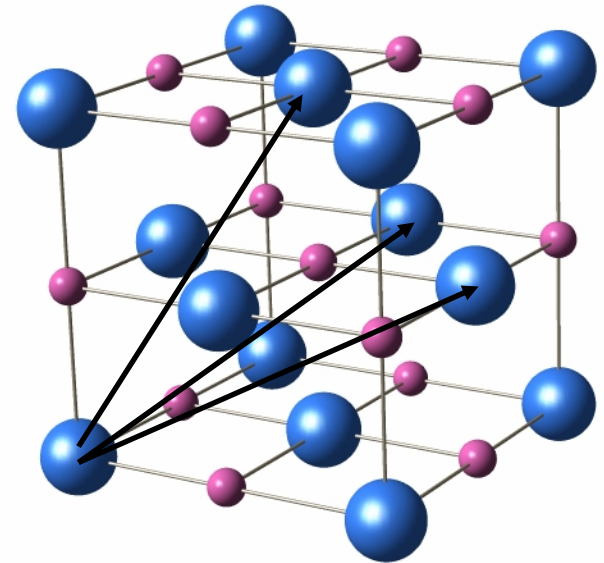
Magnetically-induced phonon anisotropy in MnO

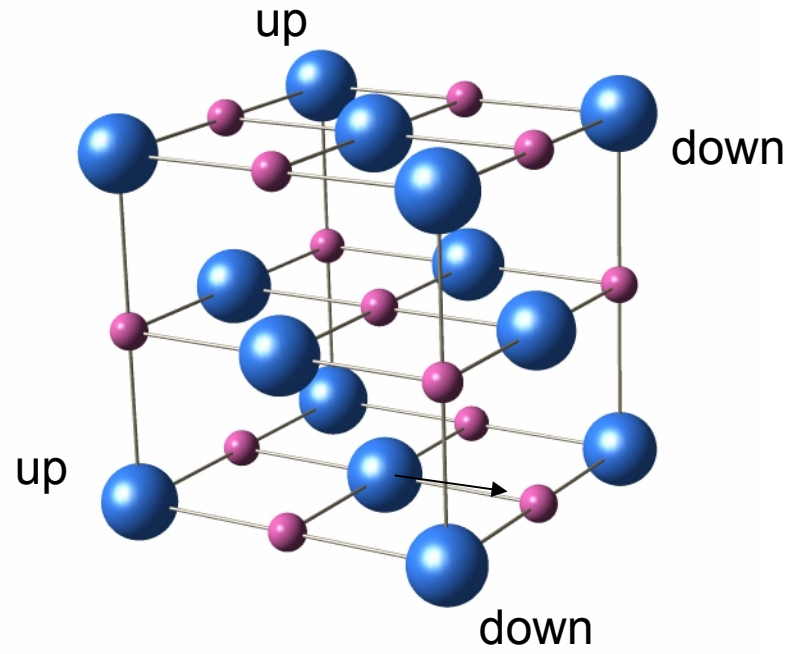
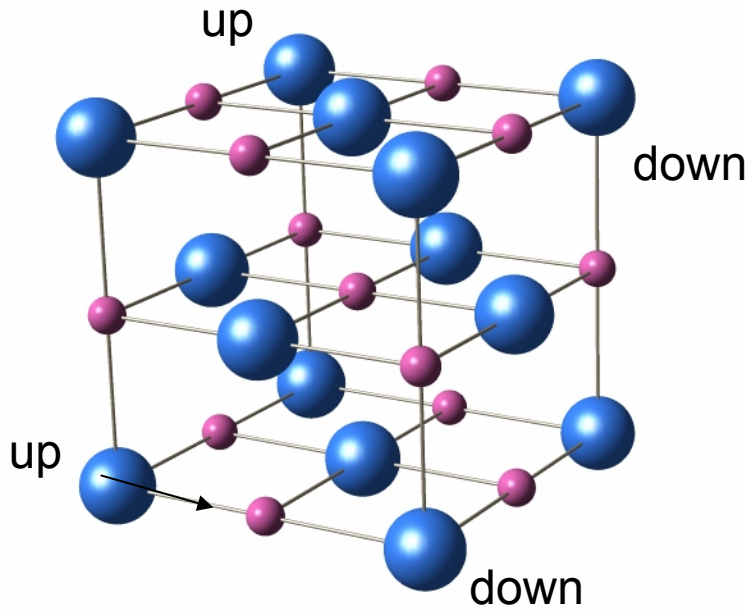
What happens to the phonons?

You might think that doubling of the unit cell leads to mixing of $Q=0$ and $Q=\pi/a(111)$ ($=G$)

BUT

The magnetic space group includes pure translation symmetry combined with TR; equivalent to pure translation symmetry for force constant matrix





Energy, pattern of forces on all atoms are the same whether we displace a spin up atom or spin down

Magnetically-induced phonon anisotropy in MnO

If spin-orbit coupling is **not included**
full rhombohedral point symmetry

Vector rep \rightarrow 1-fold (along $[111]$)
+2-fold (perpendicular to $[111]$)

[if spin-orbit coupling were included,
symmetry would be lowered further
and would depend on the direction
of the moments]

MnO anisotropy: results

- 8.27 THz along [111]
- 6.97 THz perpendicular to [111]
- Average 7.40 THz (compare expt 7.40 THz)
- Born effective charge tensor shows comparable anisotropy
- Splitting observed expt'ly?
- Strain has little effect: anisotropy is not primarily strain-mediated

Magnetically-induced phonon anisotropy

The origin of this effect:

The dependence of J 's on atomic positions $J_{ij}(r_1, r_2, \dots, r_N)$
("exchange striction")

Not just the separation of the magnetic ions –

effect would be zero for optic mode in MnO!

Importance of oxygen bond lengths and bond angles
already emphasized

Magnetically-induced phonon anisotropy

from Fennie & Rabe, PRL 2006

$$E = E_0 + E_{\text{ph}} + E_{\text{spin}}$$

$$E_{\text{ph}} = \frac{1}{2} \sum_{\eta\eta'} C_{\eta,\eta'} f_{\eta} f_{\eta'}, \quad E_{\text{spin}} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j.$$

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

Calculations and comparison with experiment for spinel ZnCr_2O_4

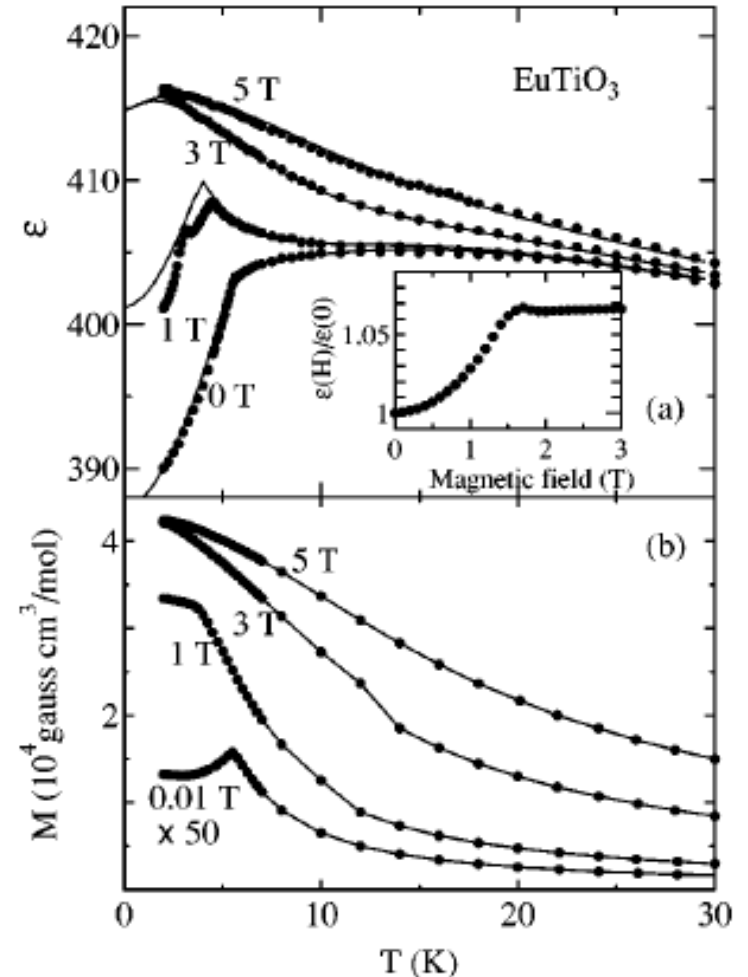
Magnetodielectric response

- Origin of effect: magnetic field induces change in magnetic order, shifts polar phonon frequencies

$$\epsilon_{\alpha\beta}^0 = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{p_{m\alpha} \cdot p_{m\beta}}{\omega_m^2},$$

where $p_{m\alpha} = \sum_{\kappa\beta} Z_{\kappa\beta,\alpha} \xi_{\kappa\beta}^m / \sqrt{M_{\kappa}}$

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



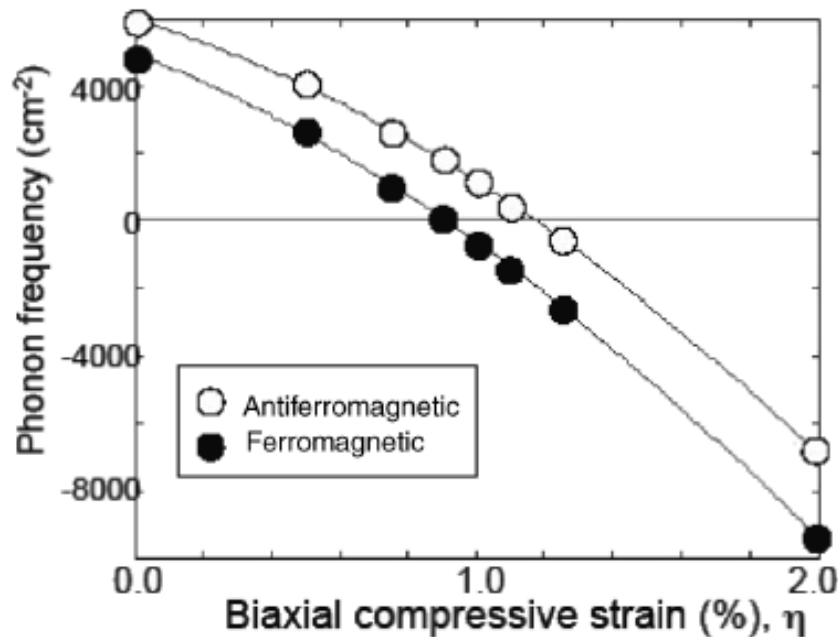
Katsufuji, PRB 64, 054415

(most recent application to $\text{La}_2\text{MnNiO}_6$, H. Das et al. arxiv 0805.1112)

Magnetic and electric phase control in epitaxial EuTiO_3 from first principles

Fennie and Rabe, PRL 2006

Bulk EuTiO_3 is an AFM cubic perovskite (paraelectric)



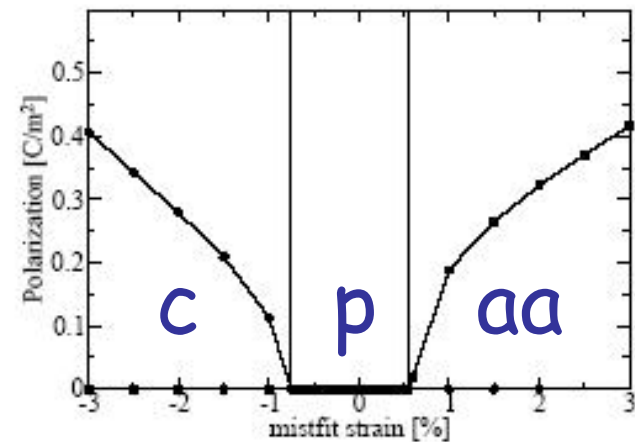
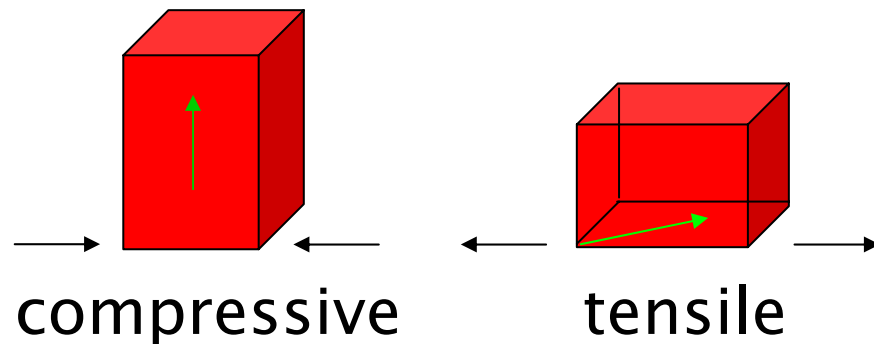
Polar phonon that generates the FE structure is softer with FM ordering

What happens to the paraelectric AFM cubic phase as η is increased?

Strain-induced FE in a ferro/ferrimagnetic system?

First principles investigation of phase boundaries

Example: epitaxial-strain-induced ferroelectricity in SrTiO_3



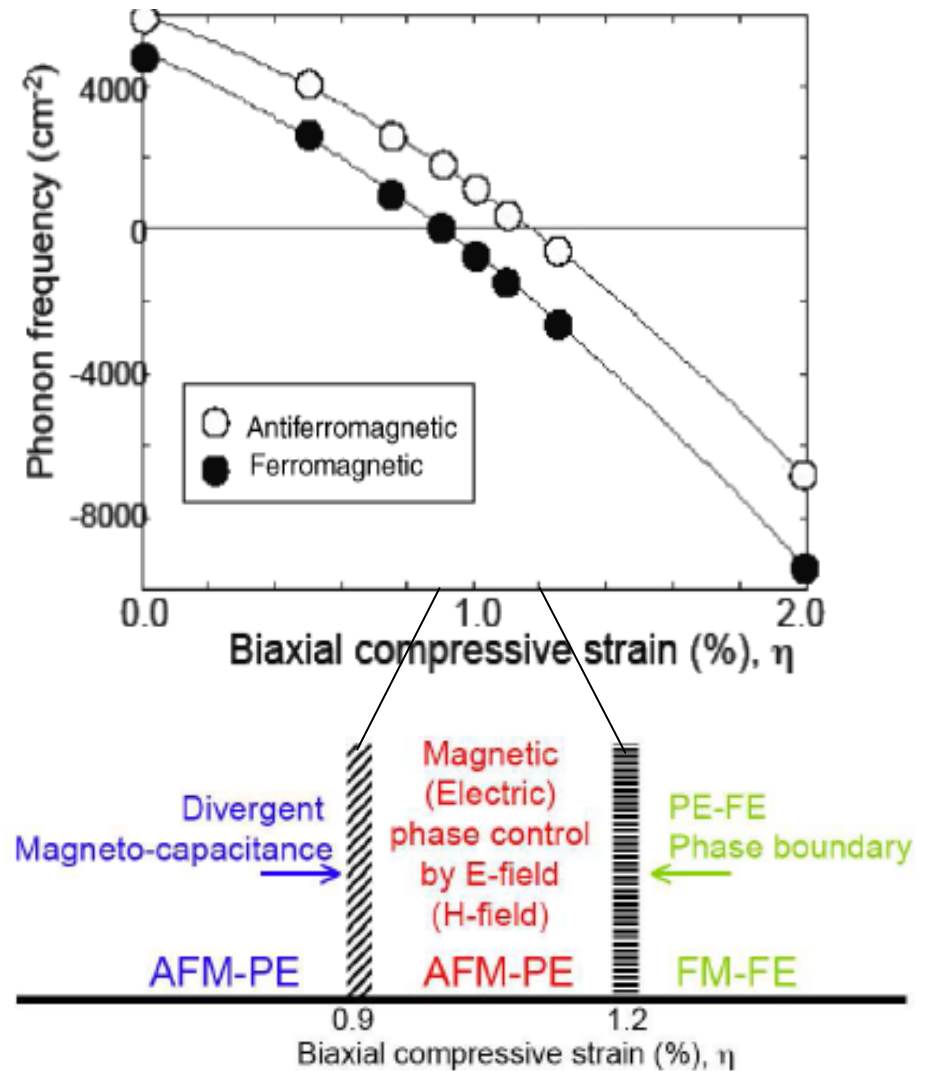
Compare experiments on strained SrTiO_3 films:
ferroelectric $T_c > 300$ K (Schlom 2004).

(Antons, Neaton, Rabe and Vanderbilt PRB 2004)

EuTiO₃:

Transition from **AFM-PE** to **FM-FE phase** at 1.2 % strain
--energy gain from FE distortion becomes larger than AFM-FM energy splitting

Near phase boundary,
magnetic field lowers
AFM-FM energy splitting
and drives transition to FE phase:
*can induce electric polarization
by magnetic field*



Phonon/symmetry-lowering distortion effect on exchange coupling and magnetic order

The origin of this effect is THE SAME:

The dependence of J's on atomic positions $J_{ij}(r_1, r_2, \dots, r_N)$

Anomalies in magnetic quantities (magnetization, susceptibility) at structural phase transition temperature

Phonon/symmetry-lowering distortion effect on magnetic interactions

(from Ederer & Fennie, arxiv 0806.0589)

“the basic idea is that a ferroelectric distortion in an antiferromagnetic material can “switch on” the Dzyaloshinskii-Moriya interaction which leads to a canting of the antiferromagnetic sublattice magnetizations and thus to a net magnetization”

“ferroelectrically-induced ferromagnetism”

Counterpart to

“magnetically-induced ferroelectricity

Inherent coupling

[proposed by Scott in study of BaMnF_4 , 1974]

Phonon/symmetry-lowering distortion effect on magnetic interactions

(from Ederer & Fennie, arxiv 0806.0589)

“if the symmetry of the purely antiferromagnetic state is such that the appearance of a magnetization does not lead to a further symmetry lowering,” then in general a nonzero (though perhaps small) magnetization will be present

Canting / “weak” ferromagnetism

If this symmetry criterion is met due to a polar distortion of a higher-symmetry state, the polarization will be coupled to the magnetization

(inversion symmetry is not the one to break!)

Phonon/symmetry-lowering distortion effect on magnetic interactions

- First principles calculations

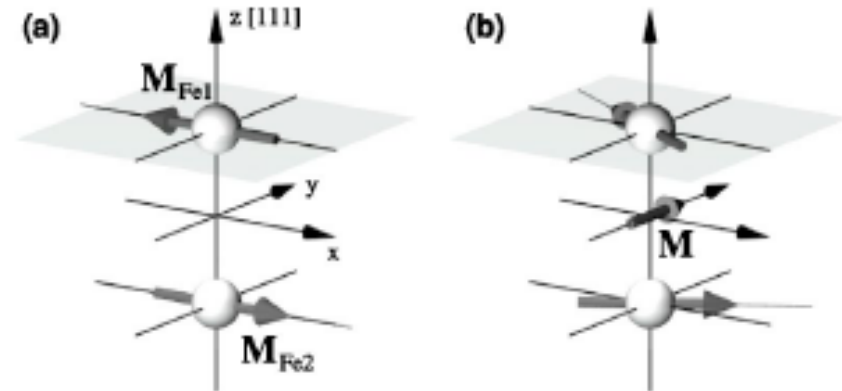
Need spin-orbit coupling

* DM interaction

$$E_{ij}^{\text{DM}} = \vec{d}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) \quad ,$$

Without spin-orbit, extra symmetries that can
(spuriously) forbid the weak ferromagnetism

Noncollinear spins



BiFeO₃

(from Ederer & Spaldin PRB 71 060401(R) (2005))

In R3c structure, compute
moment $0.1 \mu_B$ / unit cell

Recall that R3c structure is
produced by two distortions:

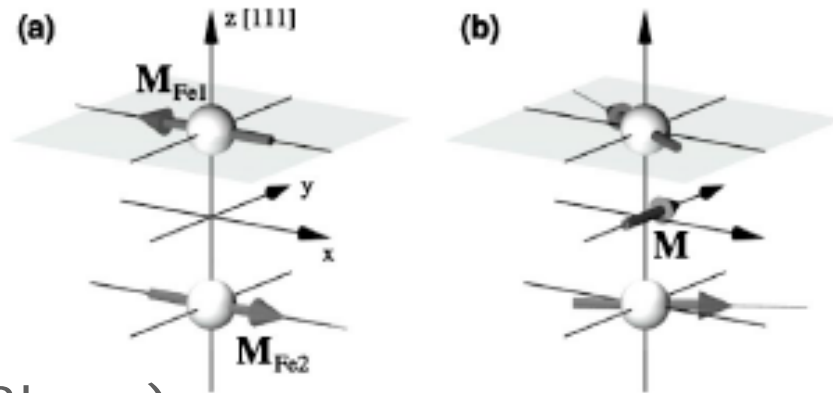
Oxygen octahedron rotation (R3barc)

Polar mode (P along [111]) (R3m)

In BiFeO₃, weak FM is induced

by the oxygen octahedron rotation

Reversing the direction of the rotations, keeping AFM
order (L) fixed, reverses M.



MnTiO₃, FeTiO₃, NiTiO₃

(from Fennie PRL 100 167203 (2008))

Magnetic ion on the A site

In R3c structure, compute polarization 80-100 $\mu\text{C}/\text{cm}^2$

Computed J's: estimate

TN = 100 K for FeTiO₃ and MnTiO₃

TN = 250 K for NiTiO₃

Recall that R3c structure is produced by two distortions:

Oxygen octahedron rotation (R3barc)

Polar mode (P along [111]) (R3m)

In ATiO₃, weak FM is induced **by the polar mode**

0.002, 0.03, 0.25 μ_B/fu for A = Mn, Fe, Ni

Reversing the direction of the polar distortion,

keeping AFM order (L) fixed, reverses M.

Lowered symmetry by cation ordering

- Superlattice?
- nanocheckerboard? (see Lucia Palova's poster on BiFeO₃/BiMnO₃)
- Cation-ordered perovskite (eg double)?

Look for nonzero trilinear invariant

$$\vec{P} \cdot (\vec{M} \times \vec{L})$$

Magnetic unit cell has to be identical to the crystallographic unit cell

L has to be odd under spatial inversion

For further discussion, see Ederer & Fennie

Overview of the second lecture: distortions of magnetic crystals

- The effect of magnetism on symmetry analysis
- First-principles calculation of J 's
- Magnetically-induced phonon anisotropy
- Dielectric anomalies at magnetic transitions
- Modulation of J 's by distortions
- Symmetry criterion for FM canting of AFM—ferroelectrically-induced ferromagnetism

- Examples: rocksalt MnO
- BiFeO_3 , EuTiO_3 , double perovskites, FeTiO_3
- [hexagonal YMnO_3] left as EXERCISE