Why are magnetism and ferroelectricity contra-indicated?

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<u>Outline</u>

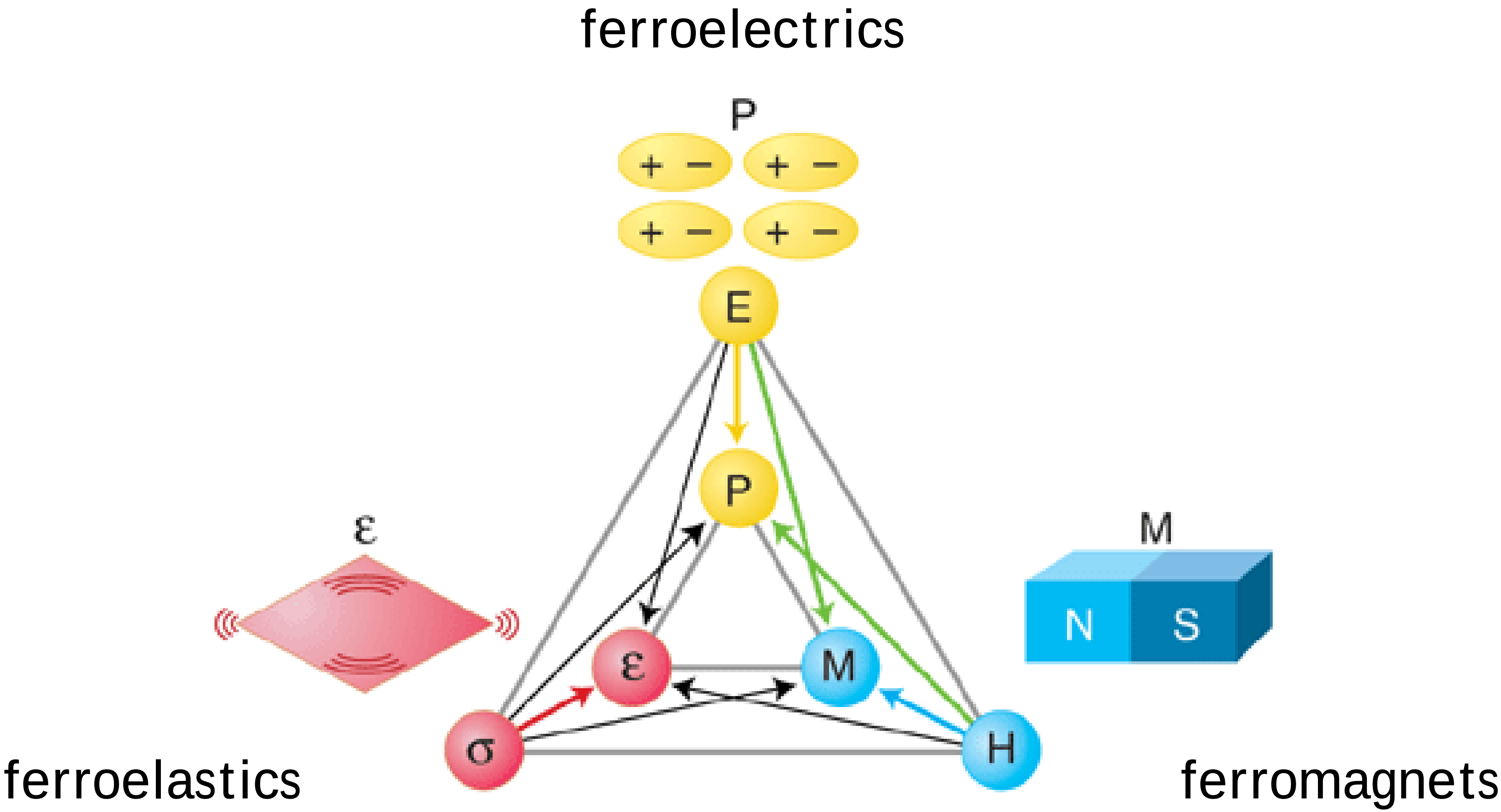
Multiferroics: definition

Conventional mechanism for ferroelectricity ("d^0-ness")

Combining magnetism and ferroelectricity

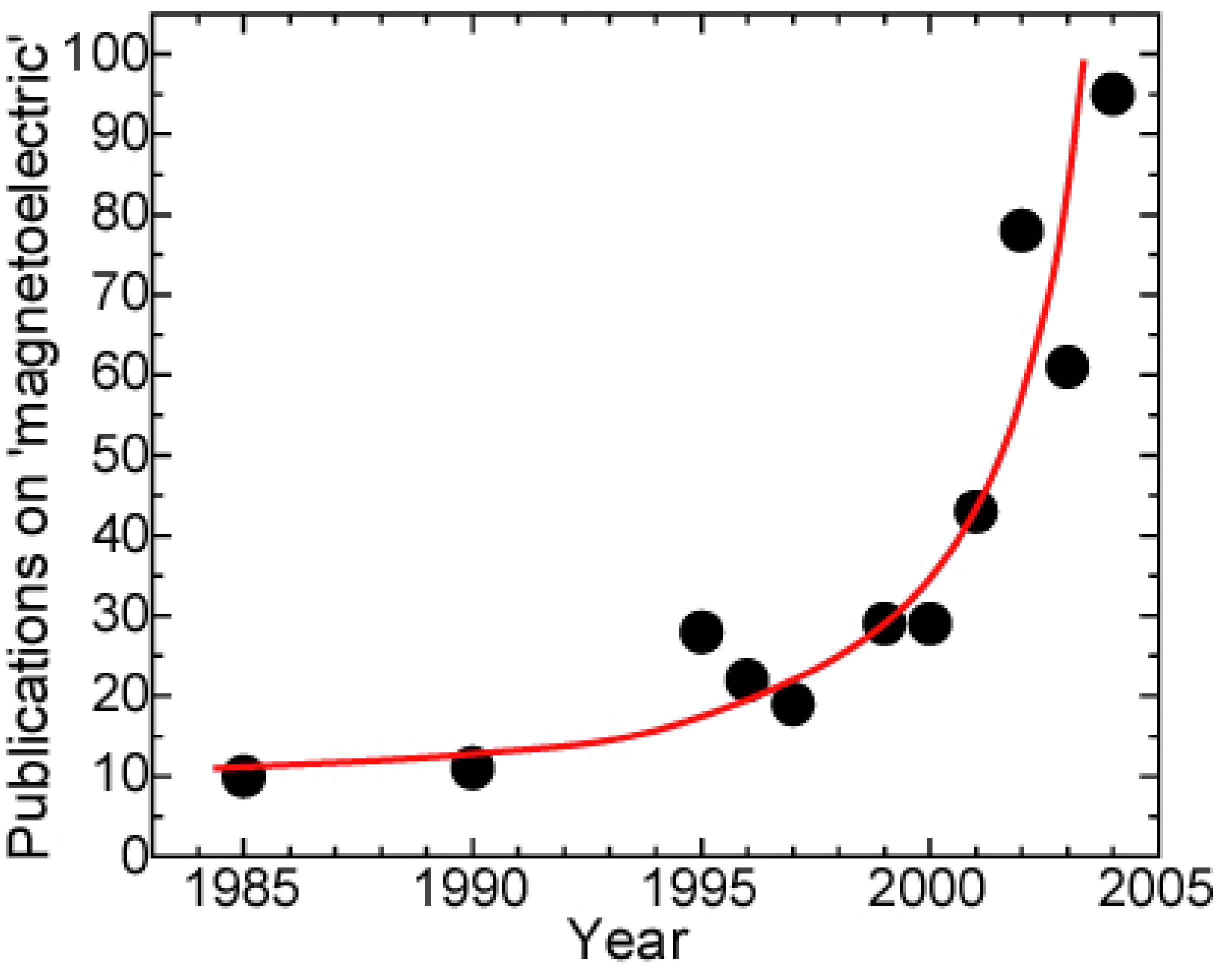
- alternative mechanisms for ferroelectricity
- non-d-electron magnets

Multiferroics



The renaissance of magnetoelectric multiferroics,
N. A. Spaldin and M. Fiebig, Science **15**, 5733 (2005)

Increasing interest in magnetoelectric multiferroics



The revival of the magnetoelectric effect, M. Fiebig, J. Phys. D **38**, R123 (2005)

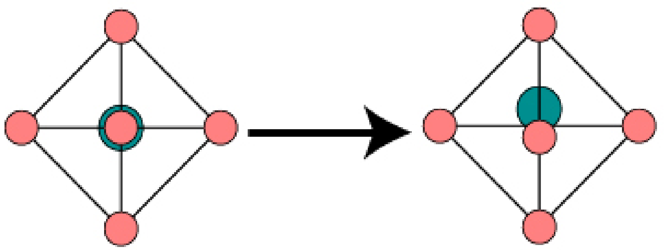
Problem

There are (almost) no magnetic ferroelectrics

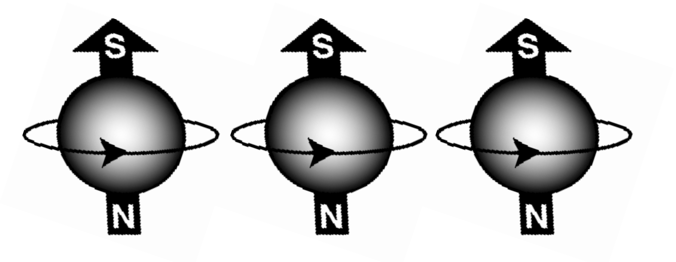
Magnetism and ferroelectricity are *chemically contra-indicated*:

Magnetism requires localized (transition metal *d*) electrons

Atoms with localized *d* electrons don't off-center to form polar ferroelectric states



Ferroelectricity
requires empty *d* orbitals
Second-order Jahn-Teller effect



Ferromagnetism
requires filled *d* orbitals
Stoner instability

N.A. Hill, *Why are there so few magnetic ferroelectrics?*
J. Phys. Chem. B **104**, 6694-6709 (2000)

Conventional ferroelectricity mechanism I. Hand-waving explanation of “d^0-ness”

−

paraelectric

+

−

−

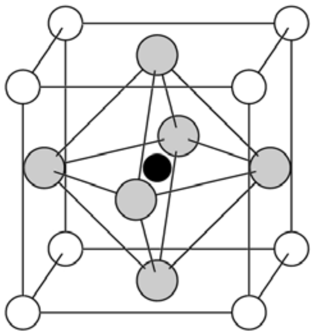
+

ferroelectric

−

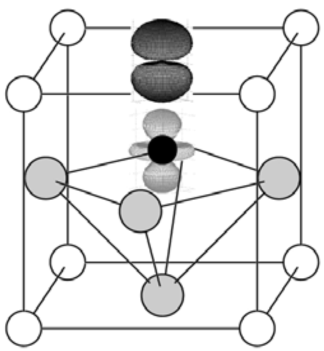
Conventional ferroelectricity mechanism I.
Hand-waving explanation of “d^0-ness”

–
+
–



paraelectric

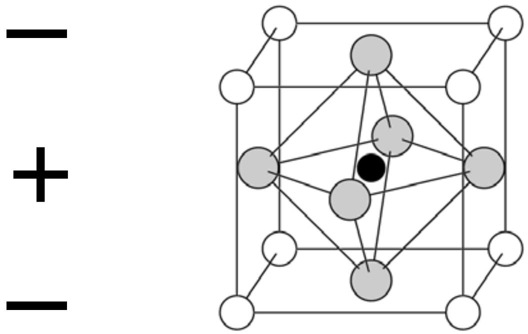
–
+
–



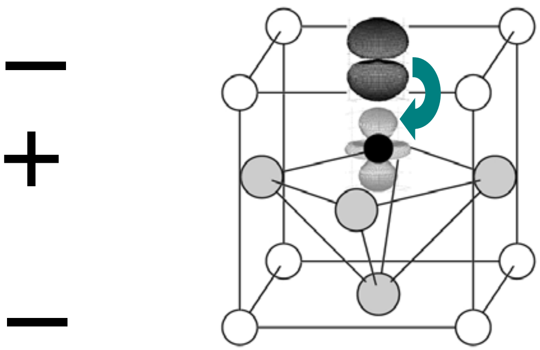
ferroelectric

Unfavorable Coulomb repulsion between oxygen and transition metal valence electrons

Conventional ferroelectricity mechanism I.
Hand-waving explanation of “d^0-ness”



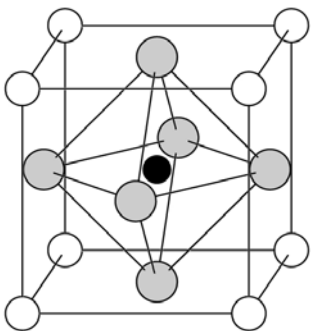
paraelectric

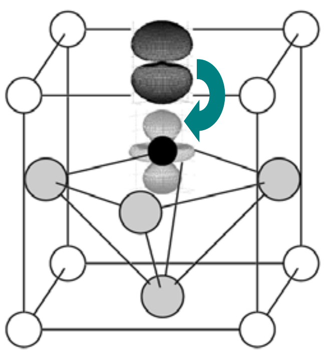


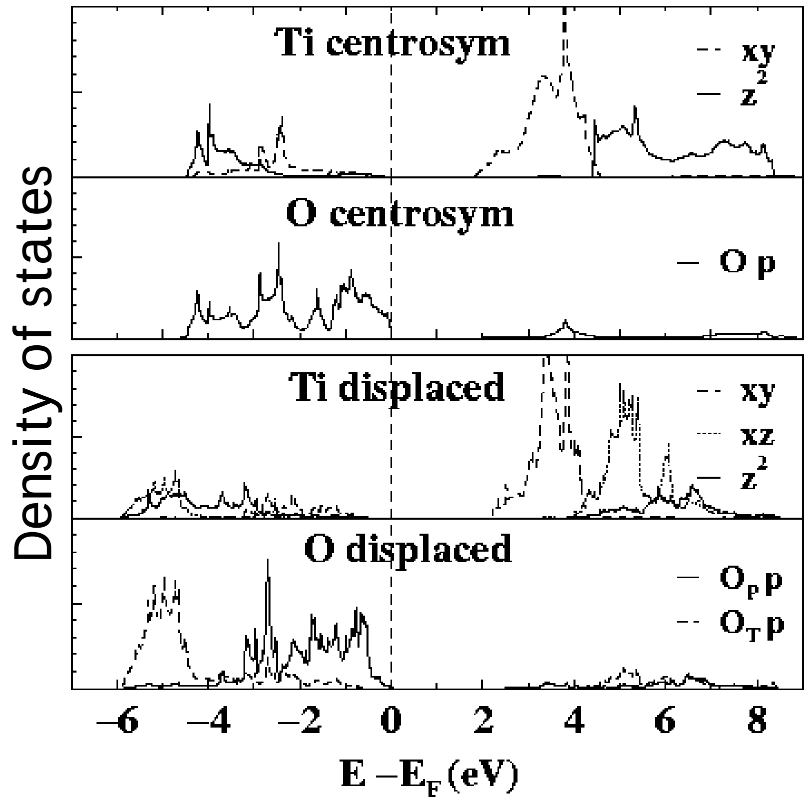
ferroelectric

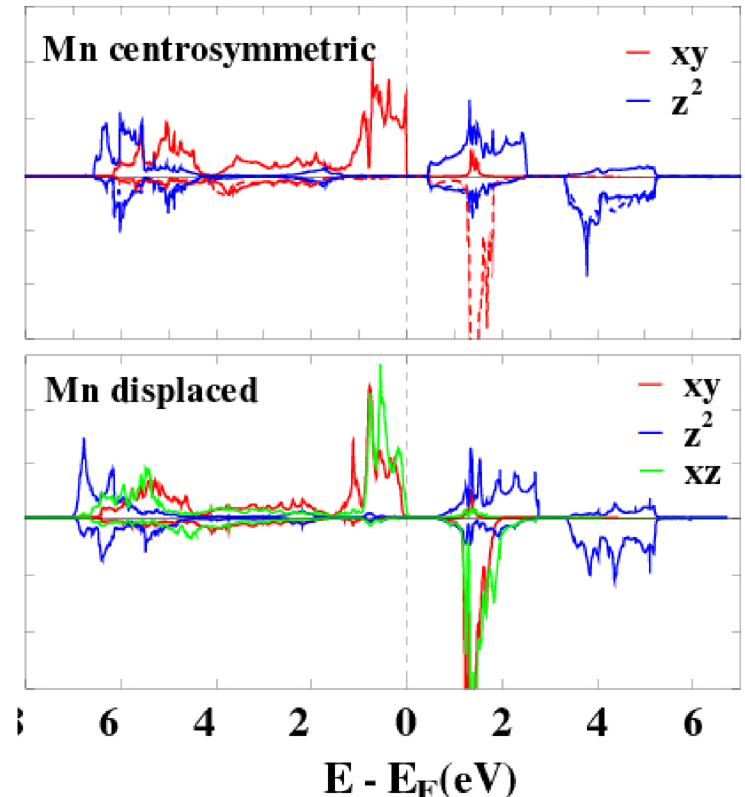
Favorable “ligand field stabilization” of *empty* cation *d* orbitals by oxygen *p* electrons

Illustration within LDA









$BaTiO_3$ (d^0)
small Coulomb repulsion
good bond formation

$CaMnO_3$ (d^3)
large Coulomb repulsion
poor bond formation

A. Filippetti and N.A. Hill, *Coexistence of magnetism and ferroelectricity in perovskites*, PRB **65**, 195120 (2002).

Perturbation theory

Expand Hamiltonian as function of atomic distortion (normal coordinate), Q:

$$H = H^{(0)} + H^{(1)}Q + \frac{1}{2}H^{(2)}Q^2 \quad \text{where} \quad \begin{aligned} H^{(1)}Q &= (\delta H/\delta Q)_0 Q \\ H^{(2)}Q^2 &= (\delta^2 H/\delta Q^2)_0 Q^2 \end{aligned}$$

then

$$E(Q) = E(0) + < 0|(\delta H/\delta Q)_0|0 > Q + \frac{1}{2}\left(< 0|(\delta^2 H/\delta Q^2)_0|0 > -2\Sigma_n' \frac{|< 0|(\delta H/\delta Q)_0|n >|^2}{E_n - E(0)} \right) Q^2 + \ldots$$

1st-order JT
Non-zero for orbitally degenerate states

always positive (moving nuclei with fixed electrons); want this to be small

always negative (relaxation of electron distribution); want this to be large
1) need a non-zero matrix element;
2) need En close to E(0)

Second-order Jahn-Teller effect

Perturbation theory (slightly hand-waving)

$$+\frac{1}{2}\left(<0|(\delta^2 H/\delta Q^2)_0|0> - 2\Sigma'_n \frac{|<0|(\delta H/\delta Q)_0|n>|^2}{E_n - E(0)}\right) Q^2$$

$BaTiO_3$ (d^0)

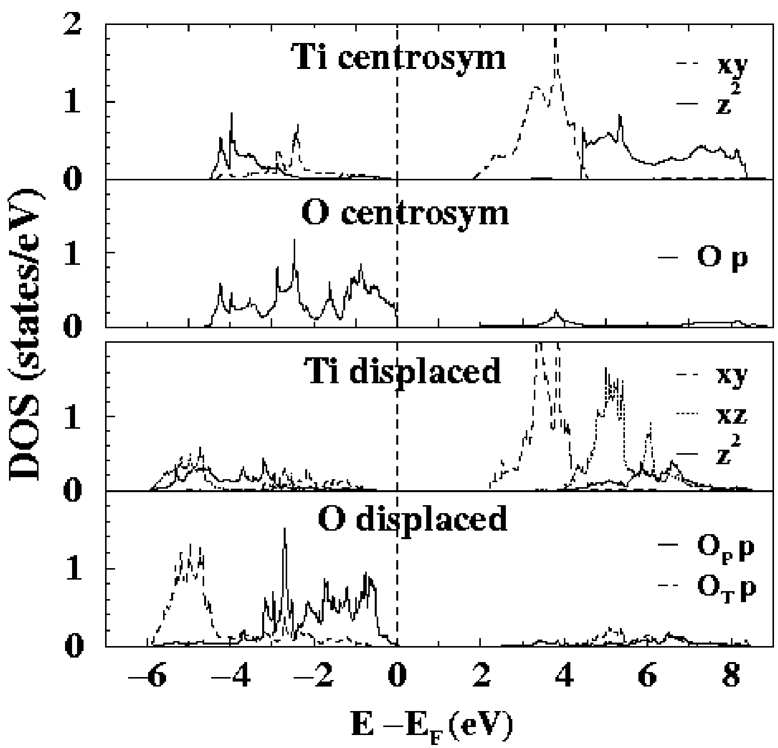
Repulsive term small

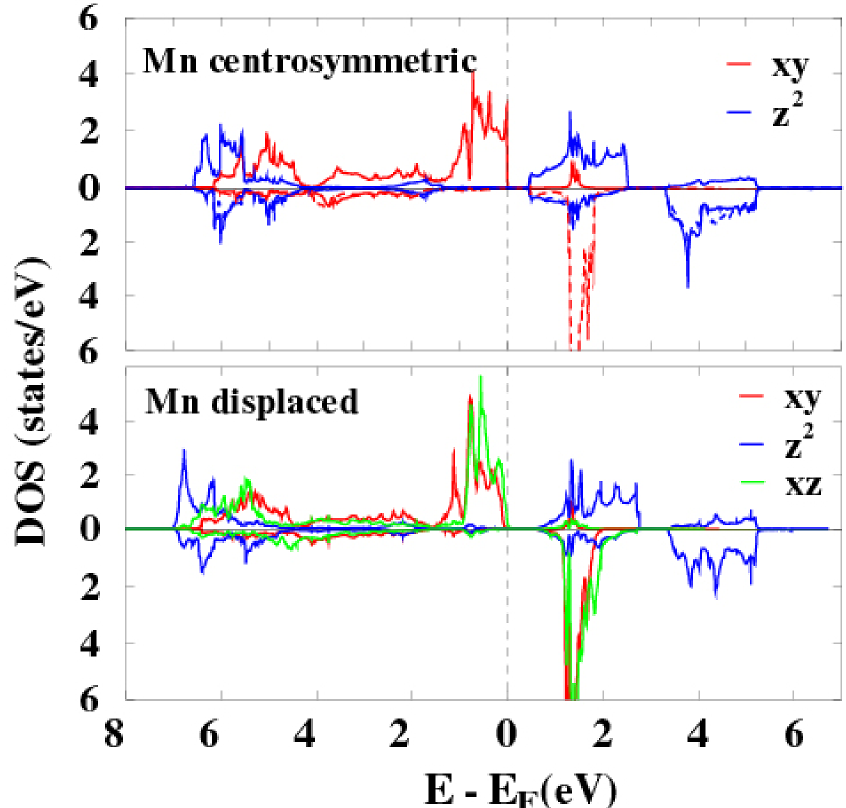
Energy-lowering term non-zero

$CaMnO_3$ (d^3)

Repulsive term large

Energy-lowering term 0 by symmetry





BUT magnetism requires localized electrons!

In perovskite structure oxides the source of magnetic, localized electrons is usually the transition metal *d* electrons e.g. $LaMnO_3$, $SrRuO_3$, etc.

Photo: Anna Karin-Axelsson, Imperial College, London

How to combine M and P?

either

1) use an alternative mechanism for P

or

2) use an alternative mechanism for M

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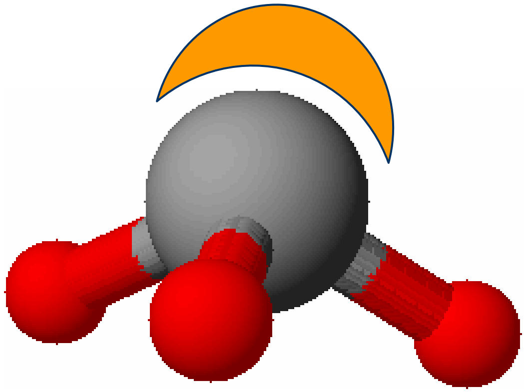
"Lone-pair active" multiferroics

Ferroelectricity from the "stereochemically active lone pair" on Bi^{3+} (cf ammonia, NH_3)

Magnetism from a 3d transition metal (Mn^{3+} or Fe^{3+})



<u>$BiMnO_3$:</u>

Ferromagnetic
Polar instability from Bi lone pairs
Anti-polar? (C2/c)

P. Baettig, R. Seshadri and N. A. Spaldin, *Anti- polarity in ideal $BiMnO_3$*, JACS **129**, 9854-9855 (2007).

<u>$BiFeO_3$:</u>

Ferroelectric, P = 90 $\mu C/cm^2$
Polar instability from Bi lone pairs
Anti-ferromagnetic (weak FM)

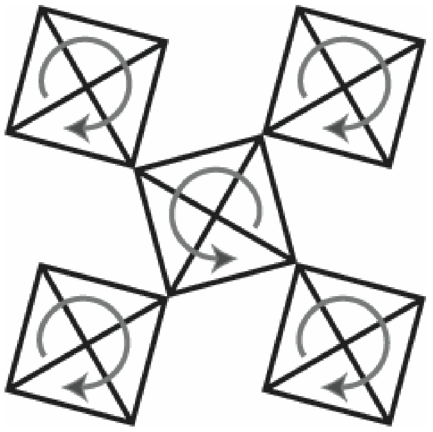
Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Wang, Spaldin, Ramesh et al., Science 299, 1719 (2003)

<u>Another idea:</u> Combining ferroelectricity with ferromagnetism is HARD!
ferr *i* magnetism might be easier…

P. Baettig, C. Ederer and N.A. Spaldin, PRB **72**, 214105 (2005)

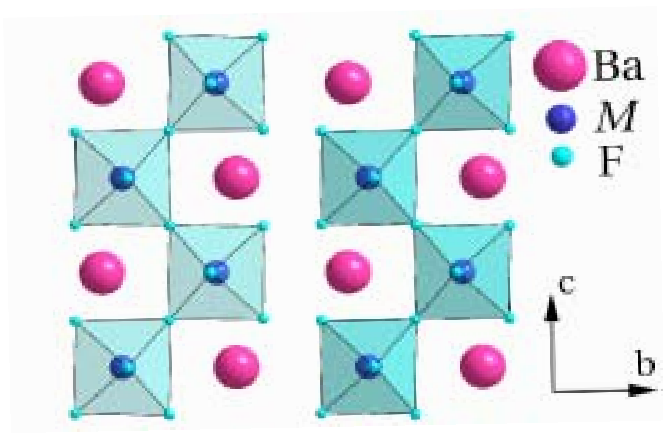
Geometric ferroelectrics

rotations driven by non-ideal ion packing doesn't yield a net P with 3D connectivity

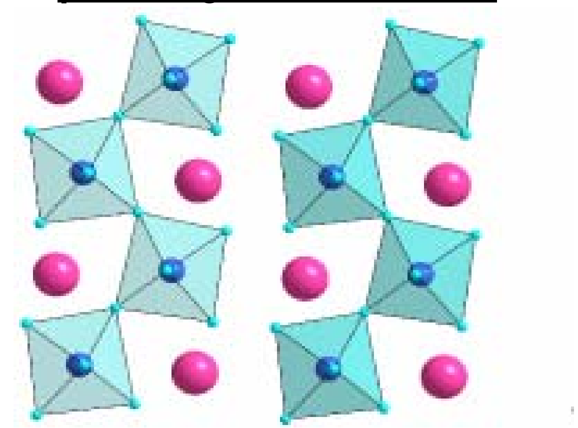


in 2D, inversion center can be lifted
e.g. $BaNiF_4$ (FE T_C = 1200K; AFM, T_N = 60K)

reference structure



polar ground state



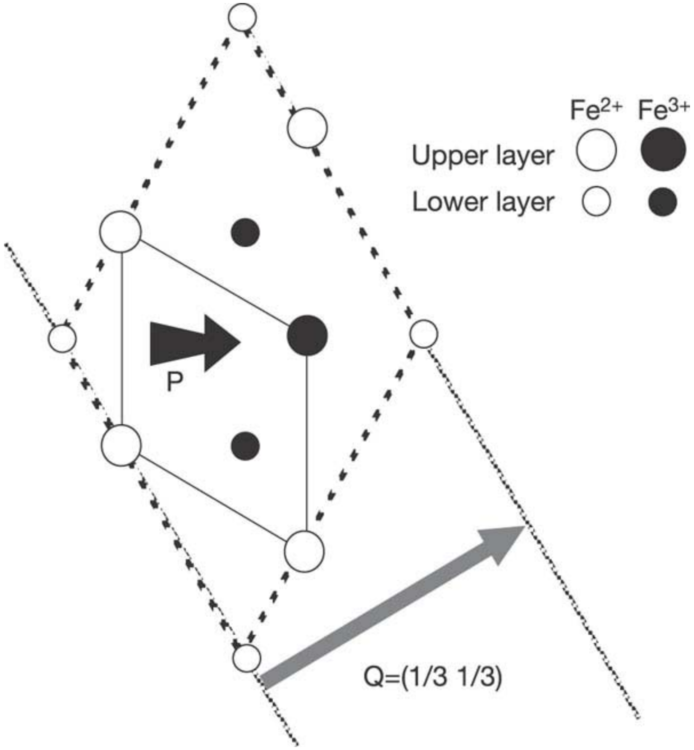
C. Ederer and N.A. Spaldin, Electric-field switchable magnets: The case of $BaNiF_4$, PRB **74**, 020401(R) (2006)

Charge ordered

e.g. $LuFe_2O_4$ (FE, T_C = 330K; frustrated magnet)

Asymmetric charge ordering of Fe^{2+} and Fe^{3+} causes polarization

Proposed structure:

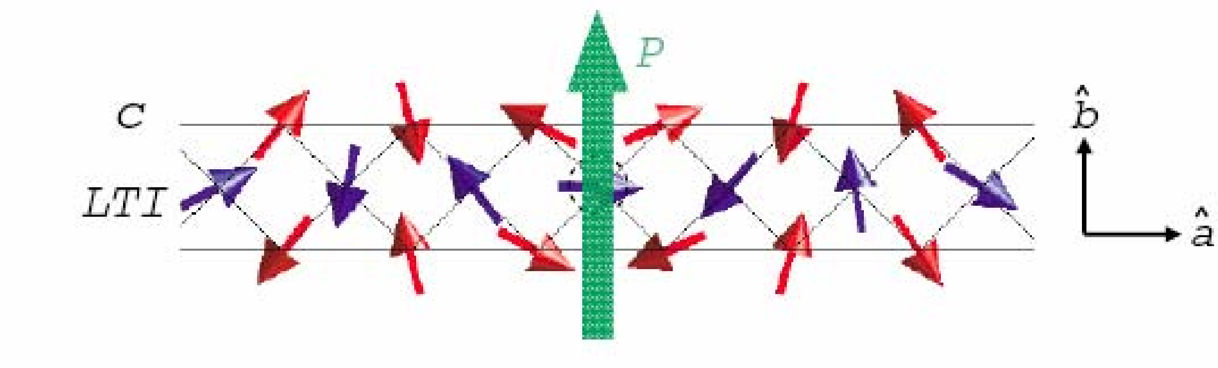


N. Ikeda et al., Nature 436, 1136 (2005)

Magnetically-driven (spiral) ferroelectricity

e.g. $TbMnO_3$

P very small BUT coupled to magnetic axis



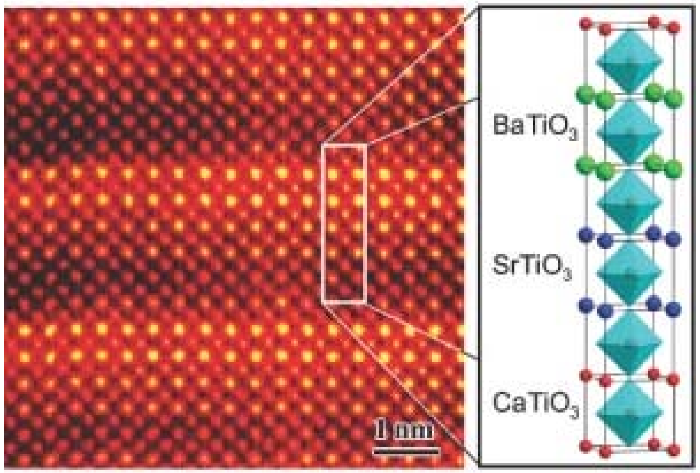
T. Kimura et al., *Magnetic control of ferroelectric polarization,* Nature **426**, 55 (2004).

Another idea

Inversion symmetry breaking by three-component layering

Strong polarization enhancement in asymmetric three-component ferroelectric superlattices, H. N. Lee et al., Nature 433, 395 (2005).

A.J. Hatt and N.A. Spaldin, Tri-layer superlattices: A route to magnetoelectric multiferroics? APL **90**, 242916 (2007)



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or

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<u>*f* electron magnetism</u>

$EuTiO_3$ (Eu^{2+}; Ti^{4+} is d^0)

prediction (Fennie and Rabe): FM under strain

Summary

d^0 cations can provide ferroelectricity but not magnetism

Alternative mechanisms for ferroelectricity are compatible with magnetism

f electron magnetism is compatible with d^0 ferroelectricity

Multiferroic with large magnetization and large polarization at room temperature not yet achieved

Magnetoelectric coupling an additional challenge