Why ferroelectrics are usually not magnetic and magnets are usually not polar

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Outline

Definition of “multiferroic” (formal and working)

Why are magnetism and ferroelectricity “contra-indicated”?

How can we combine magnetism and ferroelectricity?

What is a multiferroic?

FORMAL DEFINITION: A multiferroic is a material in which two or more of the primary ferroic order parameters co-exist in a single phase (Hans Schmid)

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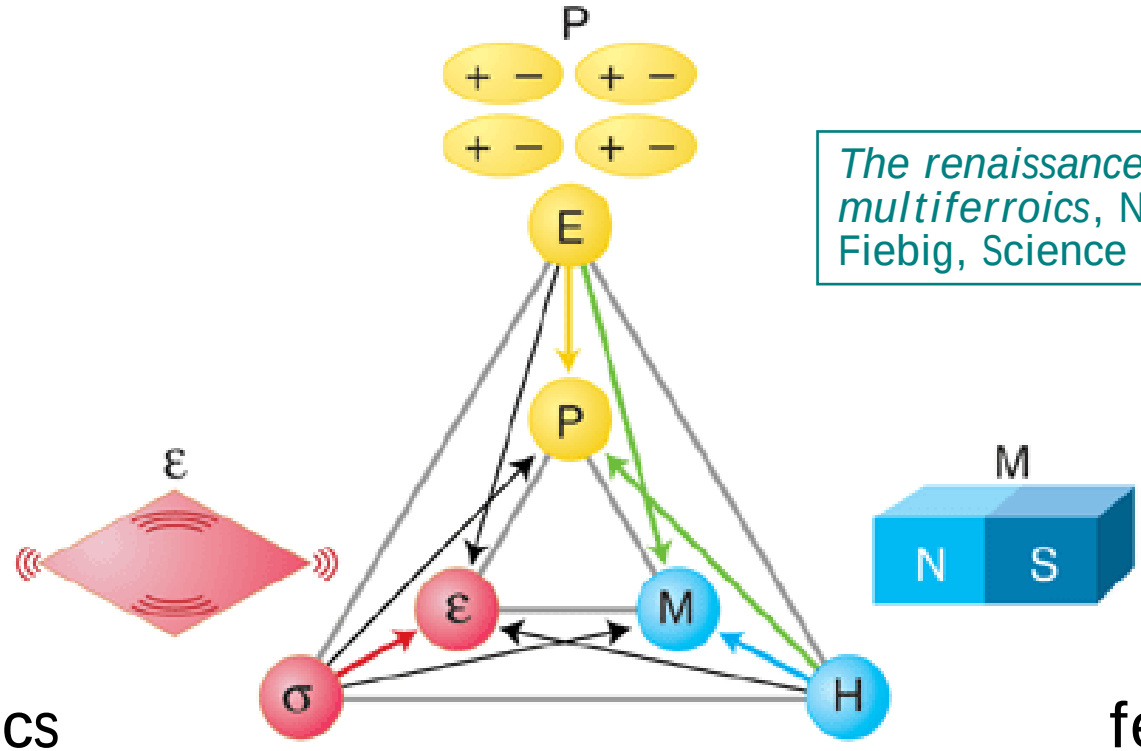
ferroelectrics



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

ferroelastics

ferromagnets

OPEN QUESTION: Should *ferrotoroidics* – materials that have a spontaneous and switchable toroidal moment – be included in the group of primary ferroics?

What is a multiferroic?

FORMAL DEFINITION: A multiferroic is a material in which two or more of the primary ferroic order parameters co-exist in a single phase (Hans Schmid)

If we stick strictly to this definition:

- Ferroelastic ferroelectrics and ferroelastic ferromagnets are multiferroics
- Antiferromagnetic ferroelectrics are not multiferroics
- Composites are not multiferroics

Often we use the term “multiferroic” to refer to anything with both ferroelectric and magnetic ordering

Also:

- “Multiferroic” does not require coupling between the order parameters

Outline

Definition of “multiferroic” (formal and working)

Why are magnetism and ferroelectricity “contra-indicated”?

How can we combine magnetism and ferroelectricity?

What are the chemistries associated with magnetism and ferroelectricity?

Magnetism:

partially filled shells of localized electrons, usually transition metal *d* electrons

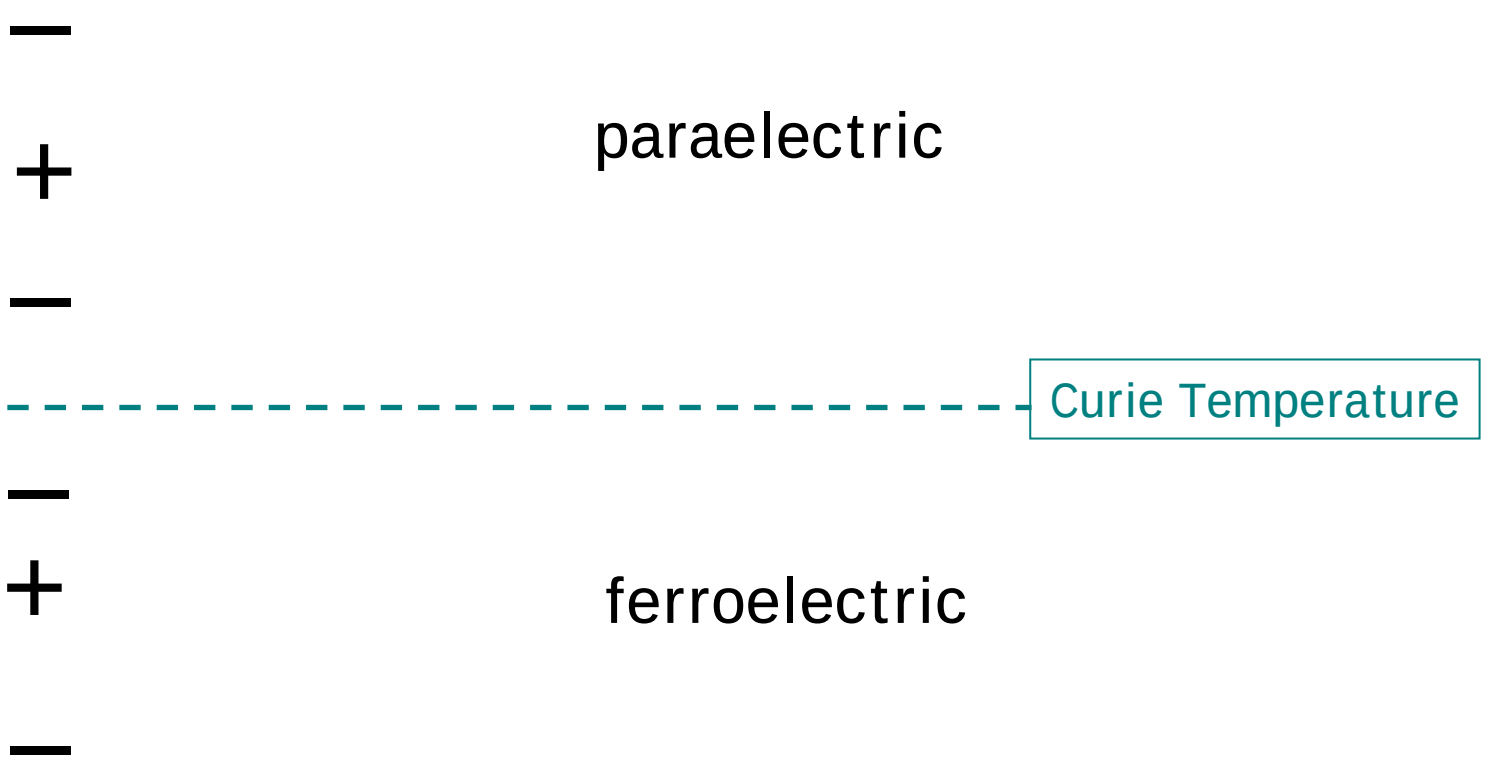
Ferroelectricity:

Transition metals with formally empty *d* shells

the CHEMISTRY that promotes one functionality disfavors the other

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

What is the conventional mechanism for ferroelectricity?



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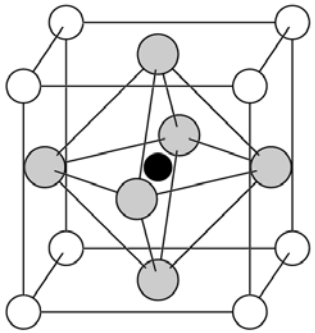
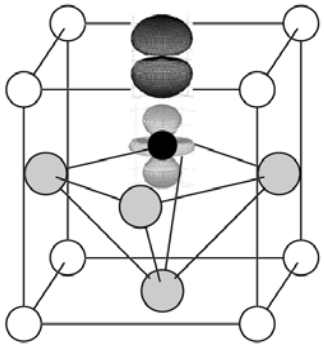


paraelectric

Curie Temperature



ferroelectric

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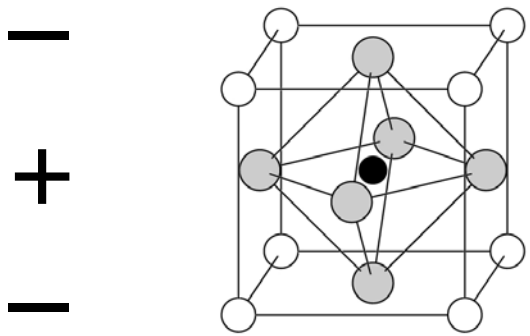
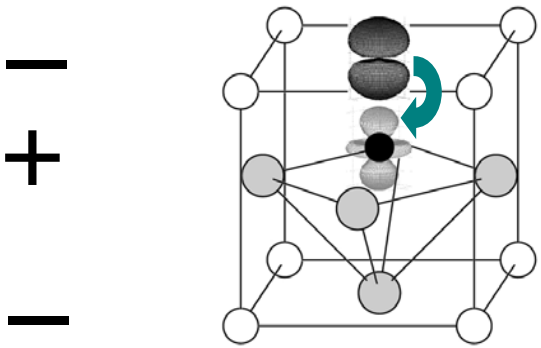


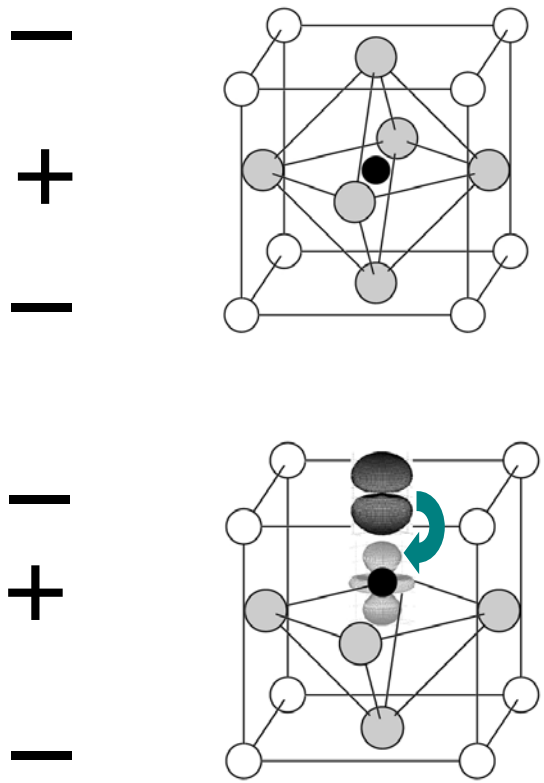
paraelectric

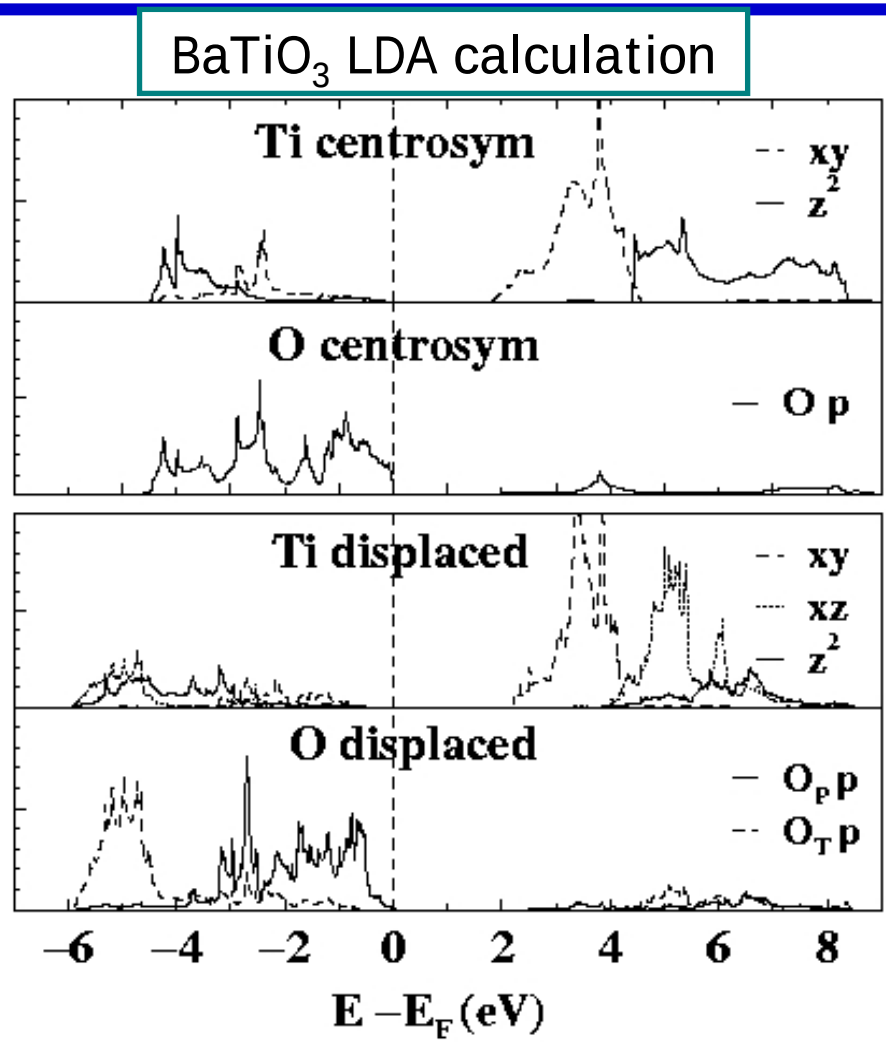


ferroelectric

Chemistry language: Ligand field stabilization of *empty* cation d orbitals by oxygen p electrons:

What does this look like in an energy band picture?





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

Perturbation theory (rigorous)

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

$$H = H^{(0)} + H^{(1)}Q + \frac{1}{2}H^{(2)}Q^2$$

where

$$H^{(1)}Q = (\delta H/\delta Q)_0 Q$$
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|0>, |n> are ground, nth excited electronic state at Q=0

then

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

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1st-order Jahn-Teller effect

Second-order Jahn-Teller effect

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1st-order JT
Non-zero for orbitally degenerate states
want this to be zero
NOT d1, d2, d4, etc.!

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1st-order JT
Non-zero for orbitally degenerate states
want this to be zero
NOT d1, d2, d4, etc.!

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

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

Second-order Jahn-Teller effect

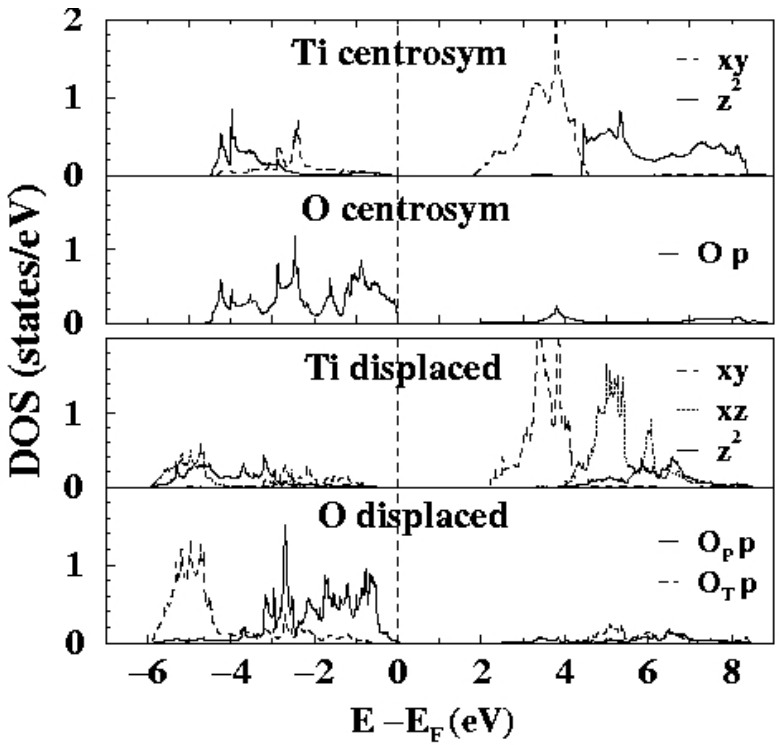
2nd order terms (slightly hand-waving single-particle picture)

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

$BaTiO_3$ (d^0)

Repulsive term small

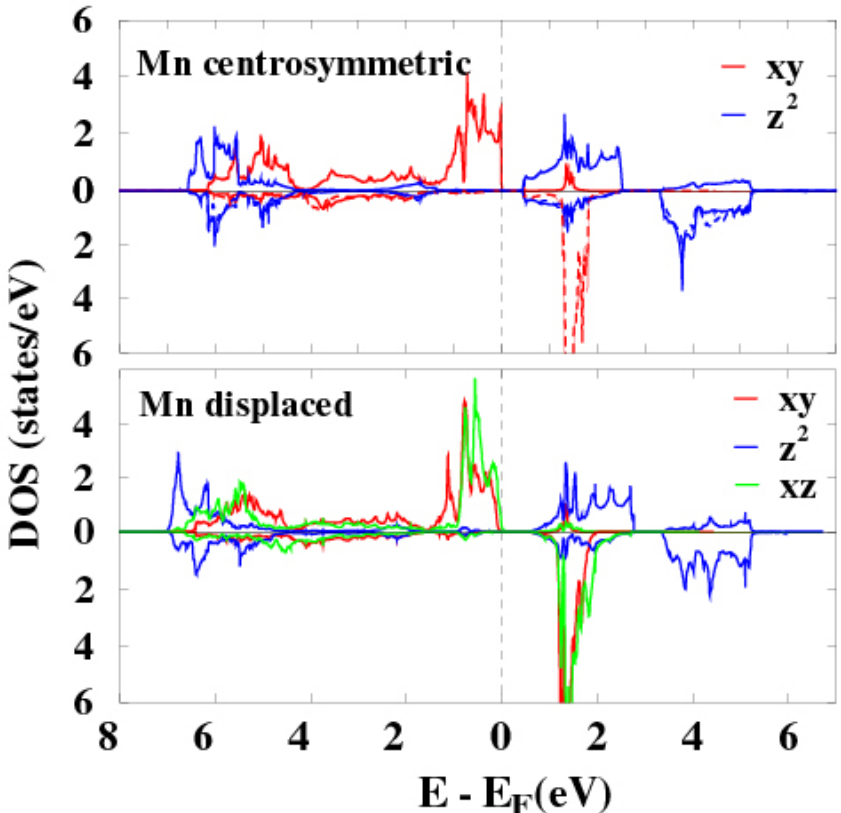
Energy-lowering term non-zero



$CaMnO_3$ (d^3)

Repulsive term large

Energy-lowering term small 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.

Chemical contra-indication

Conventional magnetism requires *d* electrons
Atoms with *d* electrons tend not to off center

DISCLAIMER

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

2nd order Jahn-Teller effect is a *balance* between two competing terms!

Off-centering is dis-favored by the presence of *d* electrons but not dis-allowed!

Perovskite oxides exhibit many structural distortions from the ideal cubic structure; disabling one (e.g. rotations) can tip the balance towards another (e.g. off-centering)

(Singh, Rabe)

How to combine M and P?

either

1) use an alternative mechanism for P

or

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OPEN QUESTION: Introducing novel types of magnetism (d^0 magnetism!?) into conventional ferroelectrics

Two challenges:

1. Combining ferromagnetism and ferroelectricity

   Large M and P
   Room temperature

2. Coupling the ferromagnetism and ferroelectricity

   Large magnetoelectric coefficients
   Switching M with E field

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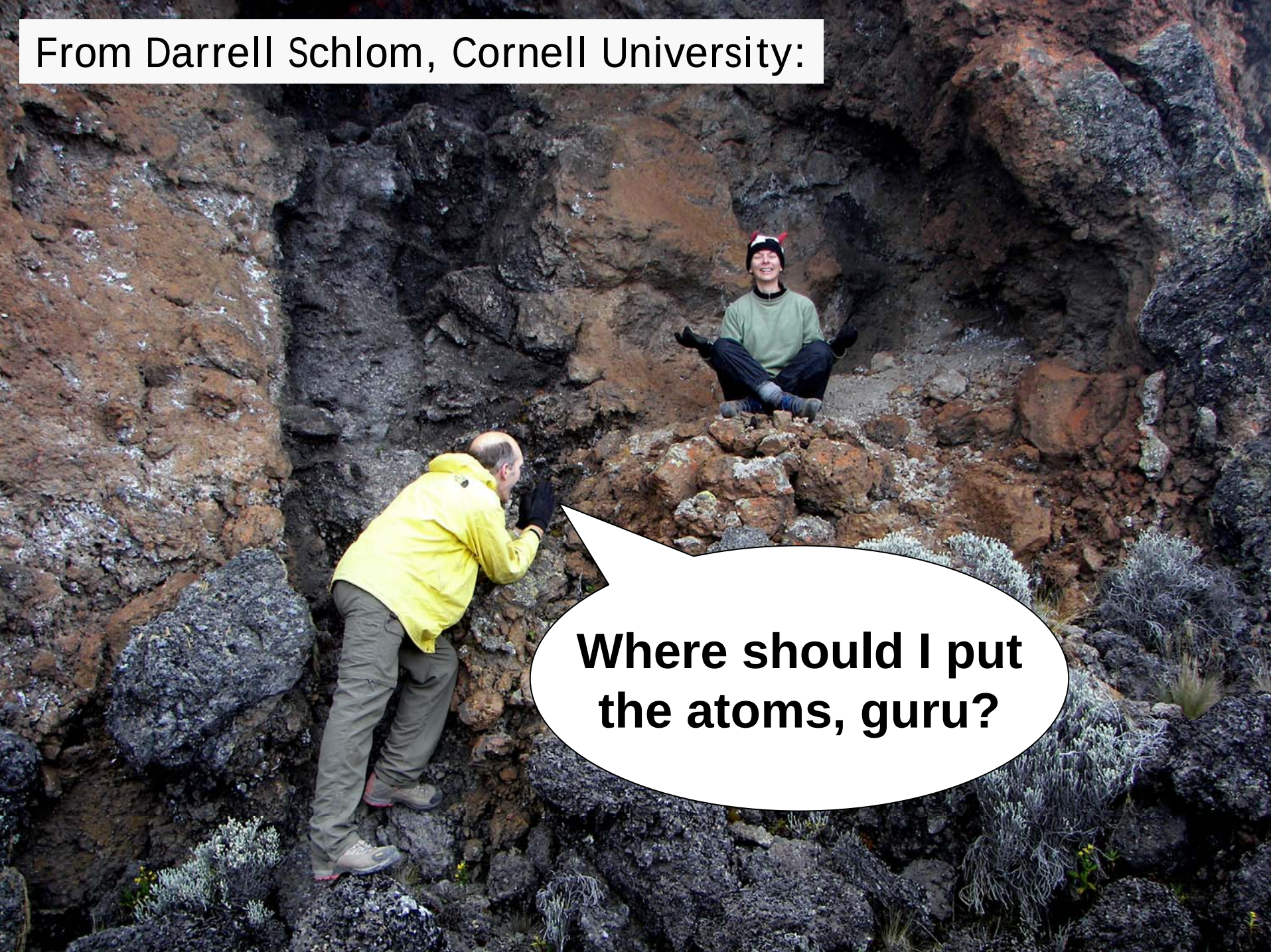
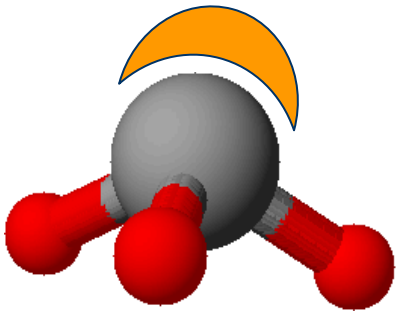

From Darrell Schlom, Cornell University:
Where should I put the atoms, guru?


Put the
Bi on the *A*-site,
grasshopper.

Classification of known types of multiferroics

Lone pair active

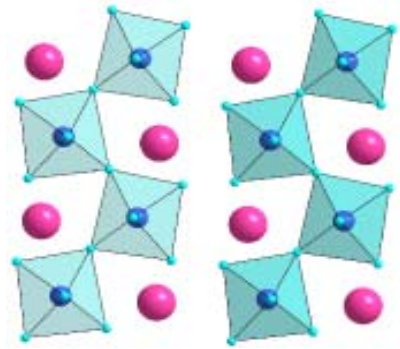
e.g. $BiMnO_3$, $BiFeO_3$



Geometric ferroelectricity

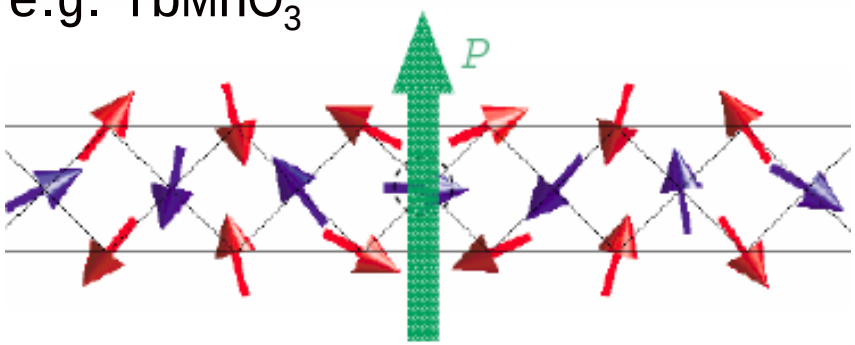
e.g. $BaNiF_4$

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



Magnetically driven

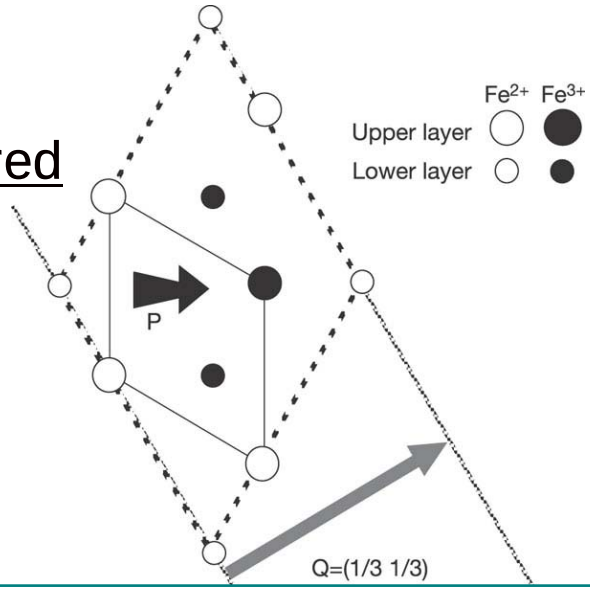
e.g. $TbMnO_3$



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

Charge ordered

e.g. $LuFe_2O_4$



N. Ikeda et al., *Ferroelectricity from iron valence ordering in the charge-frustrated system $LuFe_2O_4$,* Nature 436, 1136 (2005)

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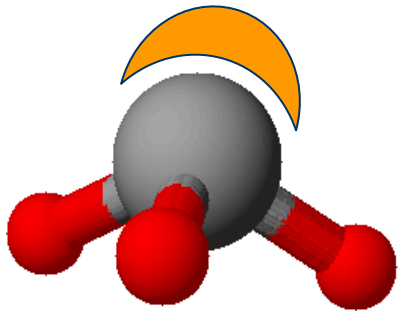

OPEN QUESTION: Will the “lone pairs” align or anti-align?

Summary

Progress in making new multiferroics (with novel mechanisms for ferroelectricity)

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

Routes still to be explored:

non-oxide multiferroics

alternative mechanisms for magnetism

Many, many open questions…