Multiferroics – Review of Classification

(and where to look for a room temperature multiferroic with large, robust and coupled M and P)

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How to combine M and P?

either

1) use an alternative mechanism for P

or

2) use an alternative mechanism for M

Or play tricks to tip the energy balance in the Second-Order-Jahn-Teller effect

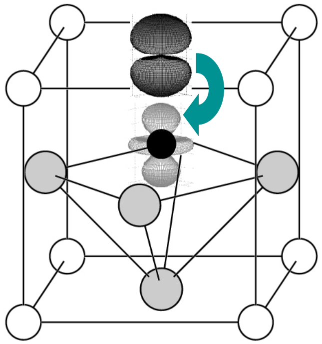
Outline

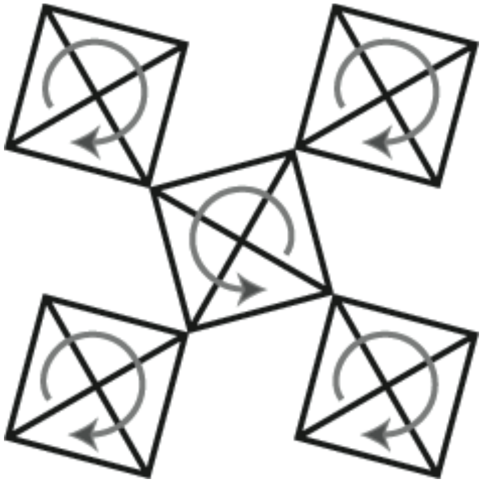
Mechanisms for ferroelectricity that are compatible with magnetism

- Tricking SOJT
- Unconventional mechanisms for ferroelectricity
- Non-transition-metal magnets

Tricking perturbation theory

Perovskites have many possible instabilities from the ideal cubic phase



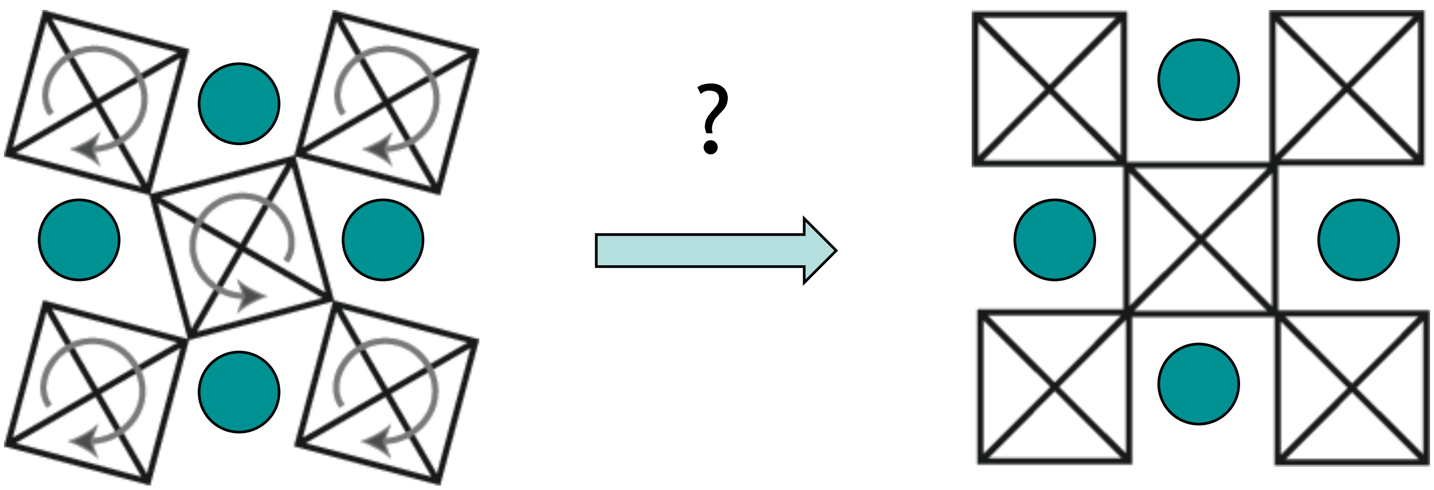


Unless the ions happen to pack exactly, rotations will occur

Can disabling one instability favor another?

Plan: turn off tiltings to see if non-d^0 transition metals off-center!

How can we disable tiltings?



Need to increase lattice constant, e.g. with strain or chemical pressure

An example: $BaMnO_3$

Ghosez, Bousquet et al.: $CaMnO_3$ shows a tendency to ferroelectricity at *negative pressure* and under strain

<u>Perovskite $BaMnO_3$:</u>

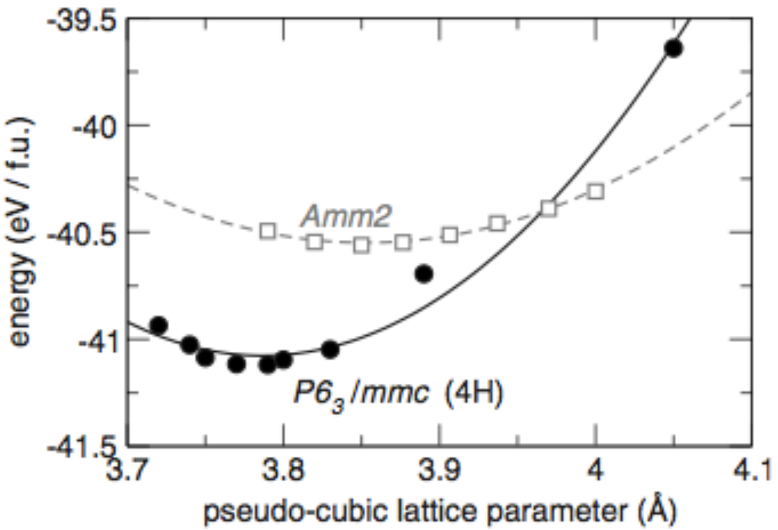
Cubic phase: strongly unstable (200i cm^{-1}) polar zone center phonon

Structural optimization ⟶ *Amm2* structure, P=12.8 $\mu C/cm^2$

$Z^*_{Mn} = 9$

G-type AFM

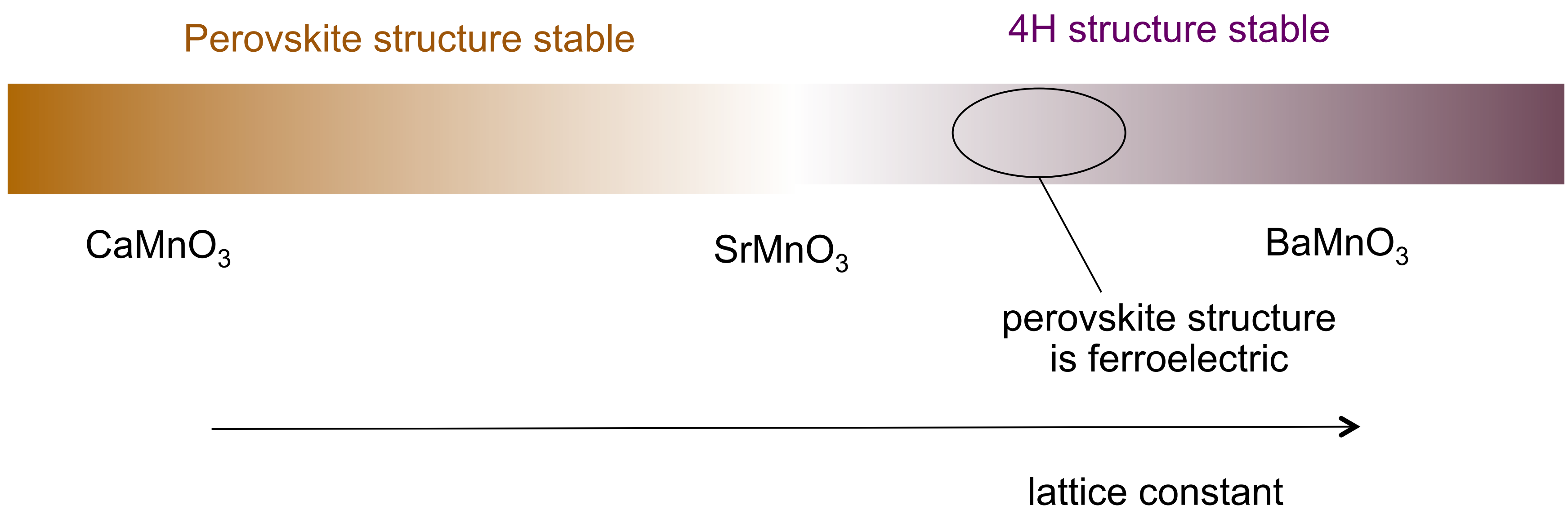
J. Rondinelli, A. Eidelson and N.A. Spaldin, Non-d^0 Mn-driven ferroelectricity in BaMnO3, PRB **79**, 205119 (2009)



Recently synthesized by Tokura et al. and shows predicted properties

An example: $BaMnO_3$

More generally, pushing materials close to or beyond their region of stability induces interesting behavior!



Outline

Mechanisms for ferroelectricity that are compatible with magnetism

- Tricking SOJT
- **Unconventional mechanisms for ferroelectricity**
- Non-transition-metal magnets

Interesting new/ongoing directions (blatant one-sided view)

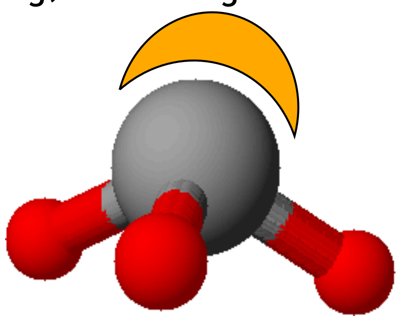
- Novel behavior at interfaces (phase boundaries/domain walls)
- Applications in high-energy physics and cosmology

REMINDER – START CHART ON BLACKBOARD

Zoology of multiferroics with unconventional ferroelectricity

Lone pair active

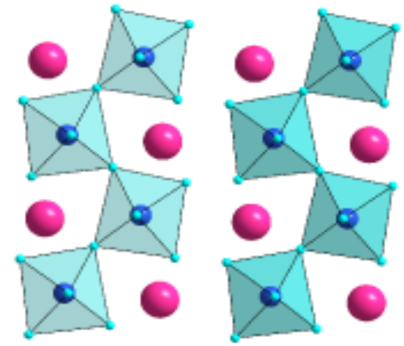
e.g. $BiMnO_3$, $BiFeO_3$



Geometric ferroelectricity

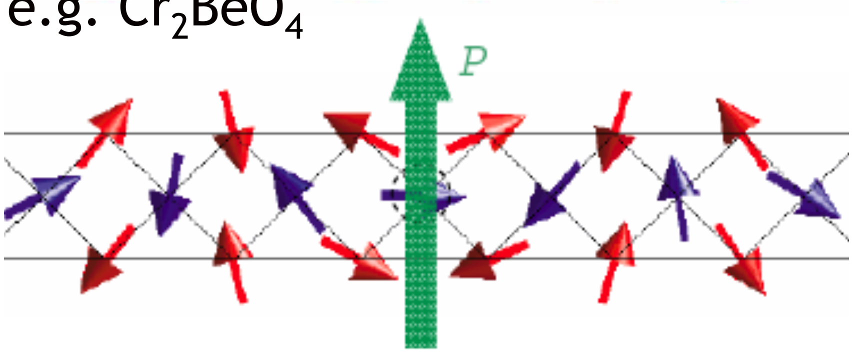
e.g. $BaNiF_4$

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



Magnetically driven

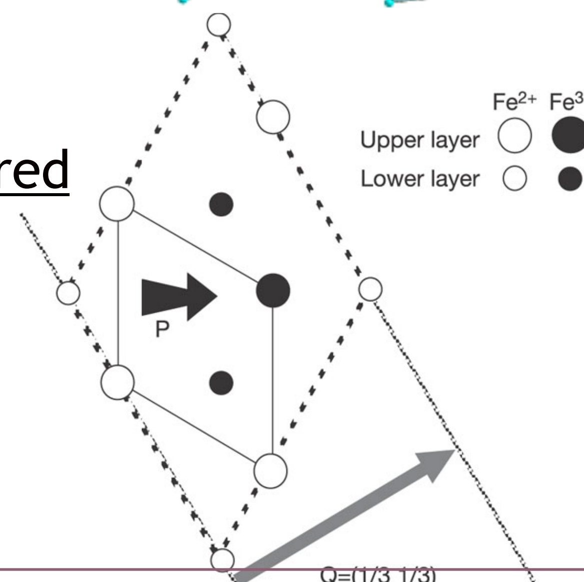
e.g. Cr_2BeO_4



R. E. Newnham et al., *Magnetoferroelectricity in Cr_2BeO_4*, J. Appl. Phys. **49**, 6088 (1978)

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)

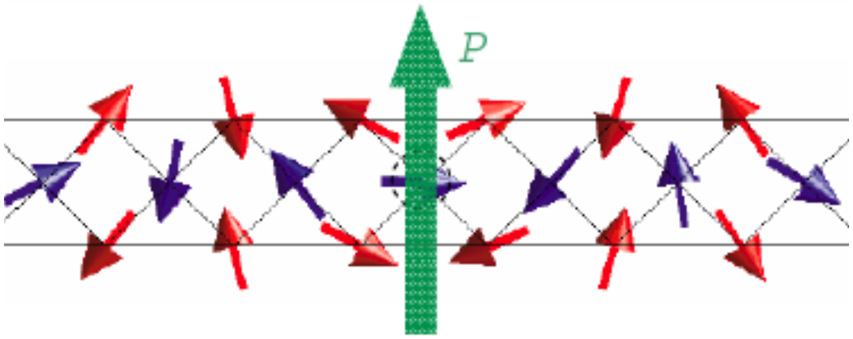
Magnetically-driven (I) Spiral magnets

e.g. chromium chrysoberyl

R. E. Newnham et al., *Magnetoferroelectricity in Cr_2BeO_4*, J. Appl. Phys. 49, 6088 (1979)

magnetic structure at 4.5K is a cycloidal spiral without an inversion center

spontaneous polarization around 1000 times smaller than in conventional ferroelectrics



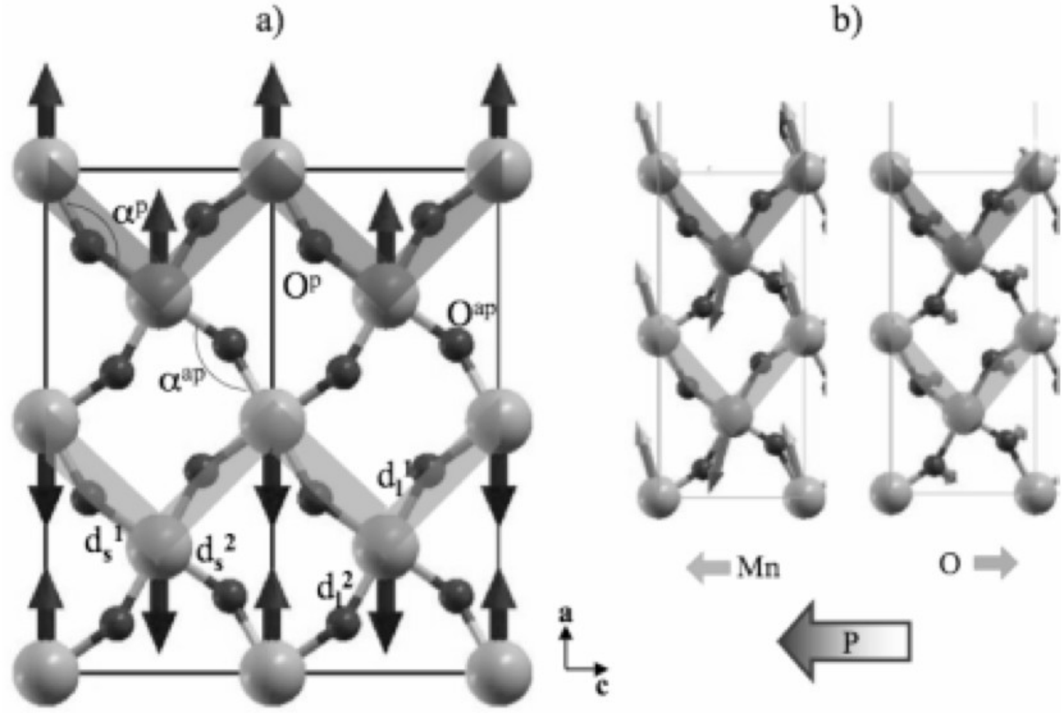
"Magnetoferroelectrics might be termed the ultimate impropriety"

Recently rediscovered in $TbMnO_3$

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

Magnetically-driven II: Superexchange

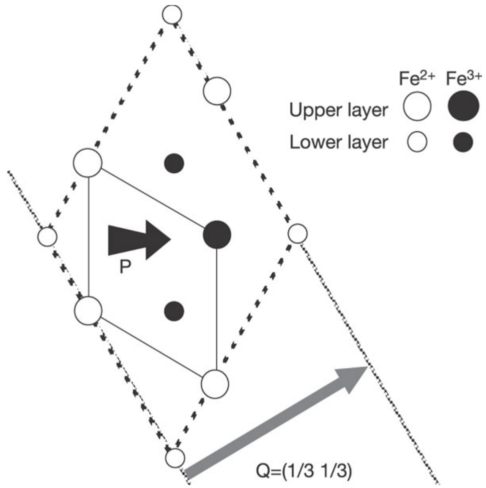
e.g. $HoMnO_3$



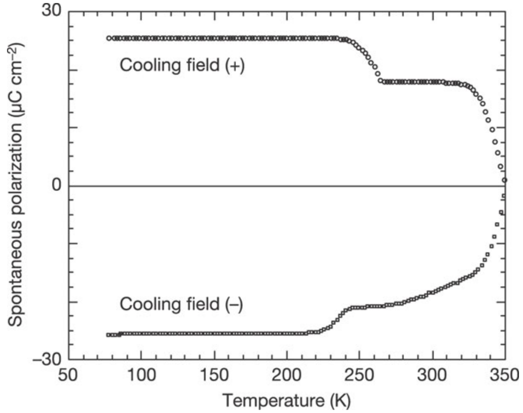
S. Picozzi et al., *Dual nature of improper ferroelectricity in a magnetoelectric multiferroic*, Phys. Rev. Lett. **99**, 227201 (2007)

Charge-ordered multiferroics

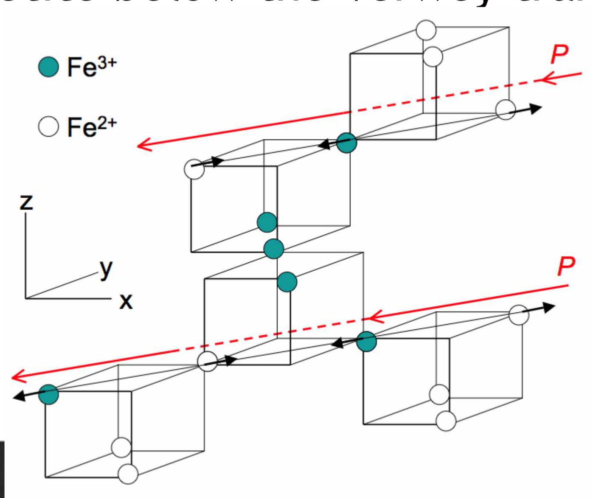
e.g. $LuFe_2O_4$



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



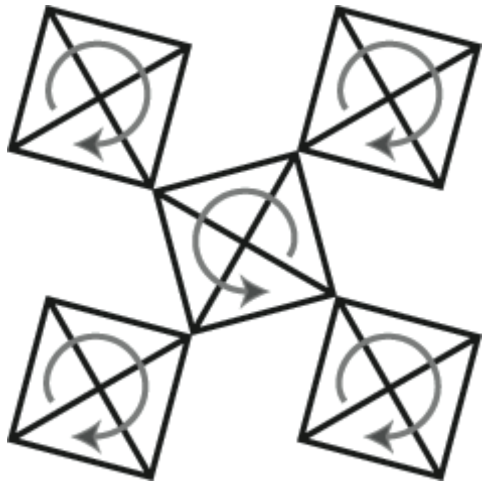
Intriguing open question:
Is magnetite below the Verwey transition a charge-ordered ferroelectric?



J. van den Brink and D. Khomskii, *Multiferroicity due to charge ordering*, arXiv:0803.2964

Geometric ferroelectrics

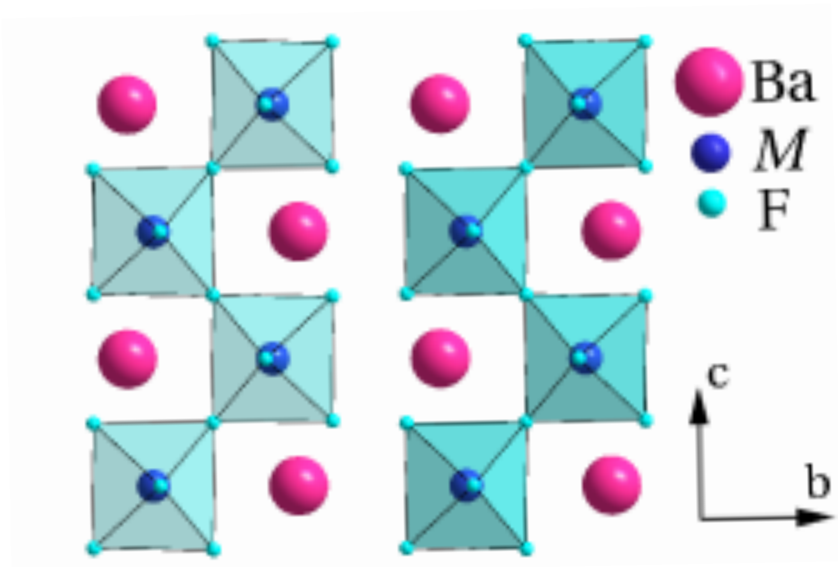
Tiltings in 3-dimensionally connected structures are non-polar



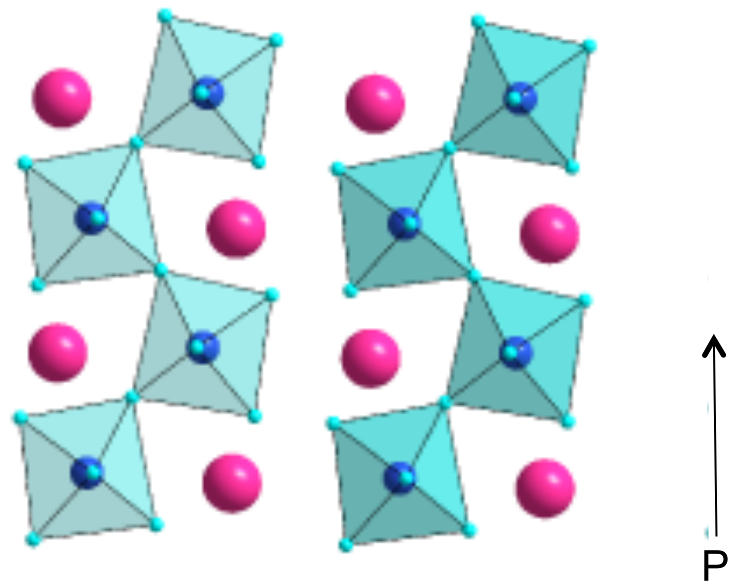
BUT 2-D connectivities can have polar tilt modes!

Geometric ferroelectrics: $BaNiF_4$

reference structure



polar ground state



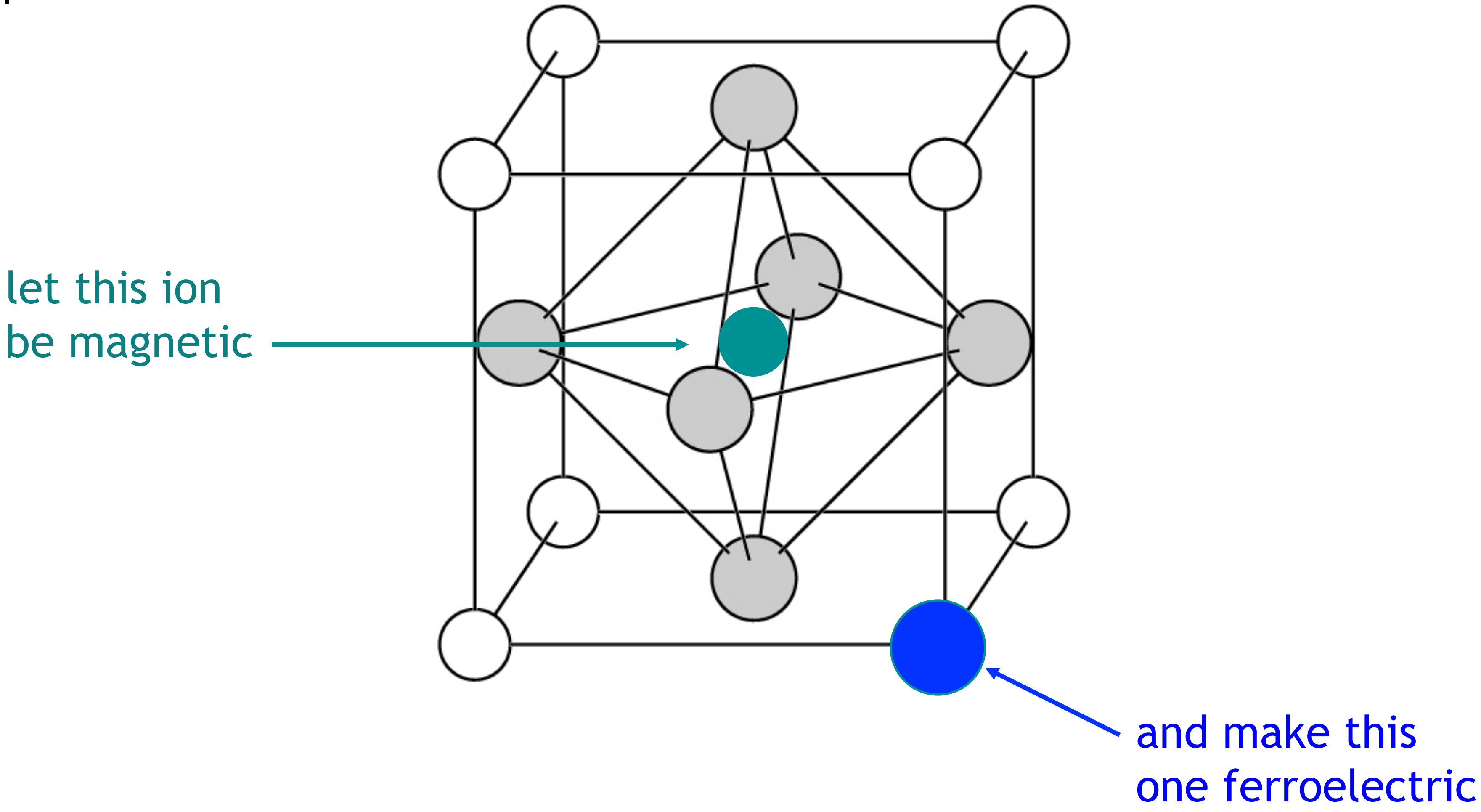
Also $YMnO_3$ although IMPROPER

Z*s?

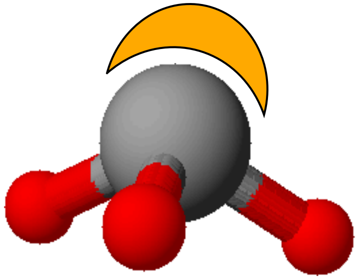
C. Ederer and N.A. Spaldin, Orgin of ferroelectricity in the multiferroic barium fluorides $BaMF_4$: A first principles study, Phys Rev B **74**, 024102 (2006)

Lone-pair active ferroelectrics

Exploit two different chemistries



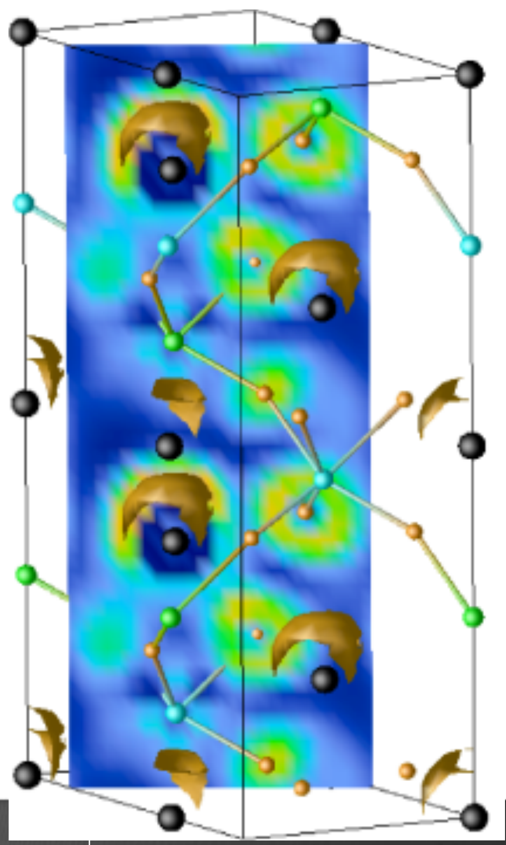
Lone-pair active multiferroics: $BiFeO_3$



Idea:

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

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



Find:

Calculate and measure P = 90 $\mu C/cm^2$ (huge!)

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

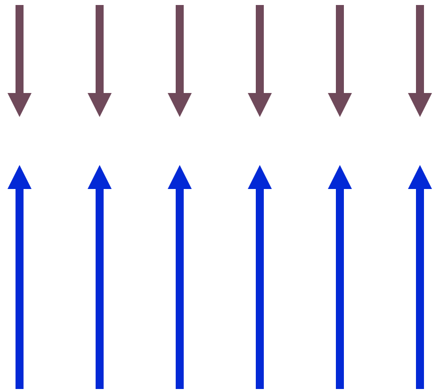
BUT: *anti*-ferromagnetic alignment of Fe^{3+} ions

How to introduce a net magnetization?

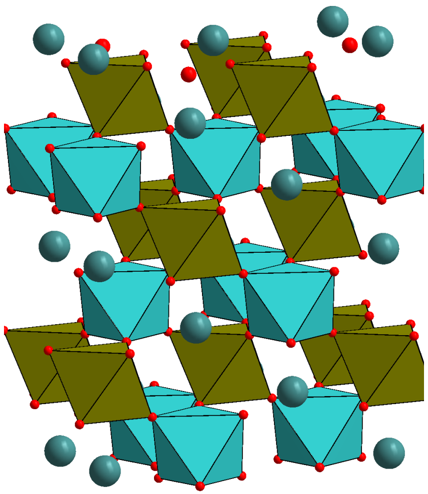
Magnetic moments in insulating oxides usually anti-align

so...

try ferr *i* magnetic ferroelectrics



Ferr *i* magnetic ferroelectrics?



Materials Choice:

Double perovskites

Lone pair-active Bi^{3+} on the A-site

Two different *3d* transition-metal cations on B-site:

e.g. Fe^{3+} (d^5) and Cr^{3+} (d^3)

Mn^{4+} (d^3) and Ni^{2+} (d^8)

Results (Theory and Experiment):

often obtain a ferroelectric polarization (competing rotational instabilities)

reports of ferr*i*magnetic moments BUT best T_cs around 100K

P. Baettig and N.A. Spaldin, *Ab initio prediction of a multiferroic with large polarization and magnetization*, APL **86**, 012505 (2005).

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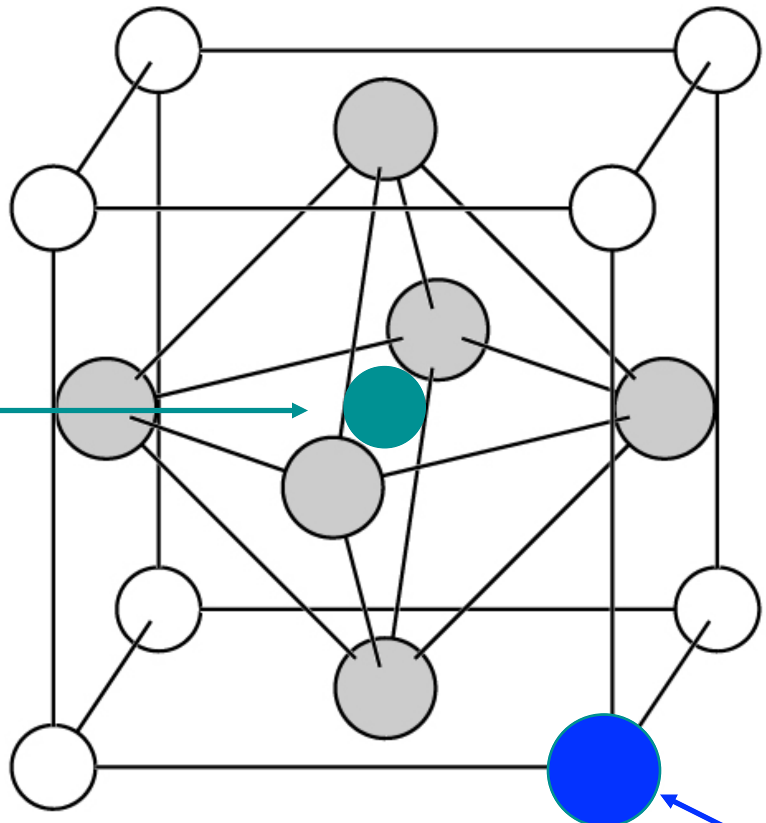
Exploit two different chemistries

let this ion be ferroelectric



and make this one magnetic

e.g. strained $EuTiO_3$ (Fennie and Rabe); $(Eu,Ba)TiO_3$

Summary of our discussions