Why are there so few magnetic ferroelectrics?

and a review of tricky things like the Born Effective Charge

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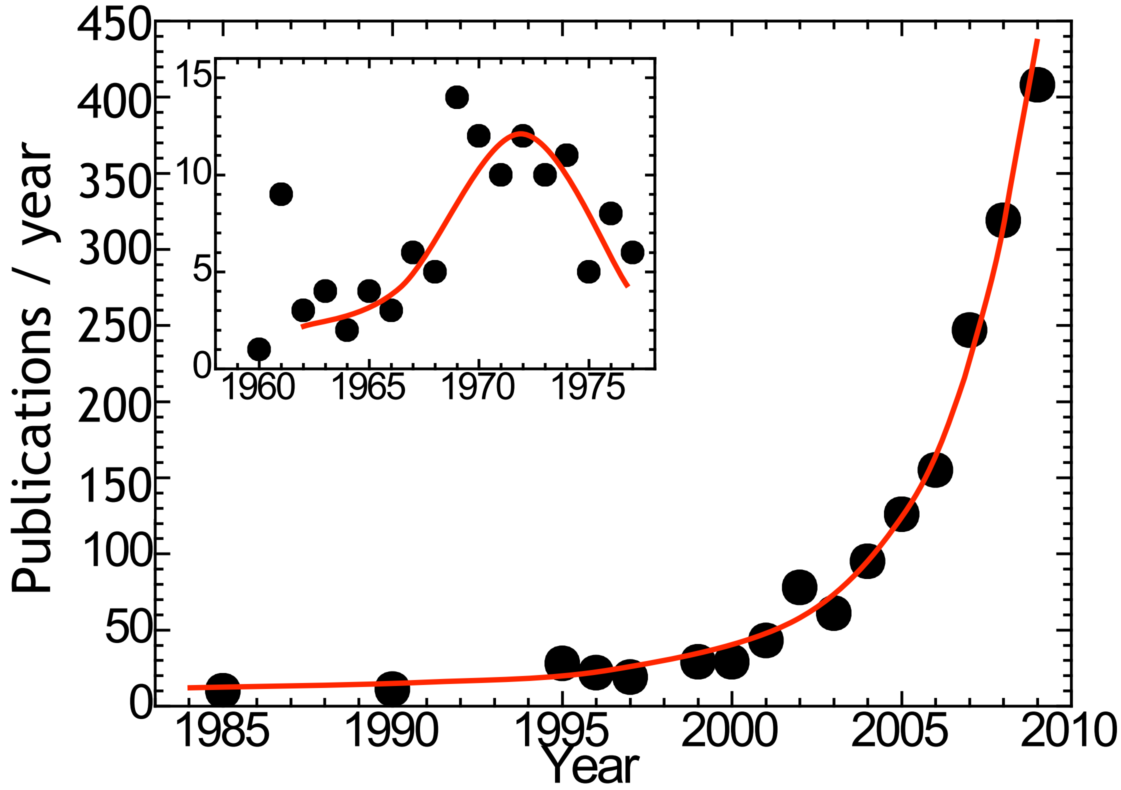
History of multiferroics

1960s: Fundamental work in FSU and Japan

1970s – 1990s: Activity in FSU, Japan and at U. Geneva

1993: Ascona “MEIPIC” meeting – introduced term “multiferroic” – virus unleashed

2000: End of virus incubation period: Practical routes to multiferroics

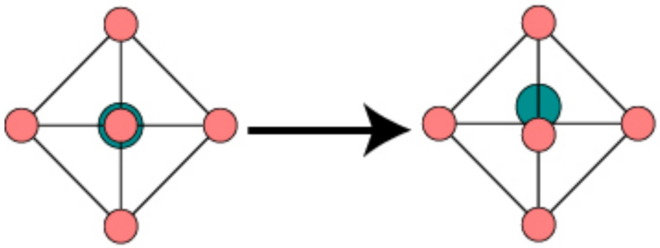


N.A. Hill, *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B 104, 6694 (2000)

Why are there so few magnetic ferroelectrics?

the CHEMISTRY that promotes one functionality often prohibits another

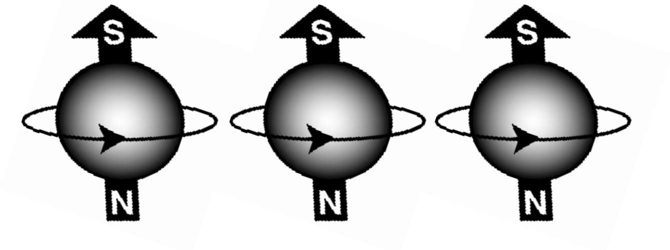
Ferroelectricity



"Matthias rule": requires diamagnetic ions (empty *d* orbitals)

Second-order Jahn-Teller effect

Ferromagnetism



Requires partially filled *d* orbitals

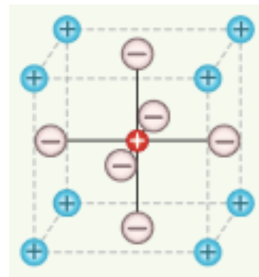
CHEMICALLY CONTRA-INDICATED!

B.T. Matthias, *New ferroelectric crystals*, Phys. Rev. (1949)
N.A. Hill, *Why are there so few magnetic ferroelectrics?* J. Phys. Chem. B 104, 6694 (2000)

“Conventional” Ferroelectrics

Fundamental size limits in ferroelectricity.
N.A. Spaldin, Science 304, 1606 (2004)

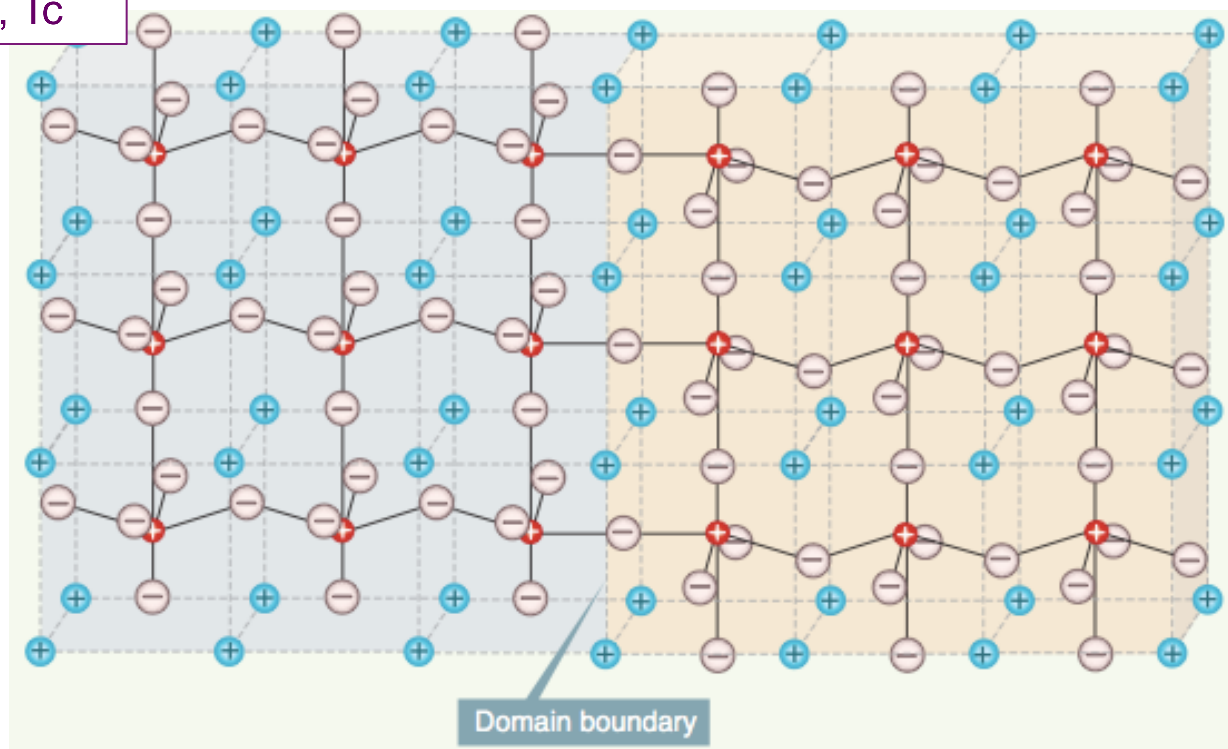
high temperature



high symmetry

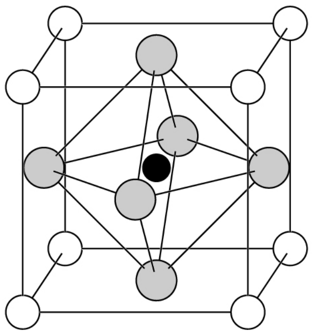
Transition (Curie) temperature, Tc

low temperature

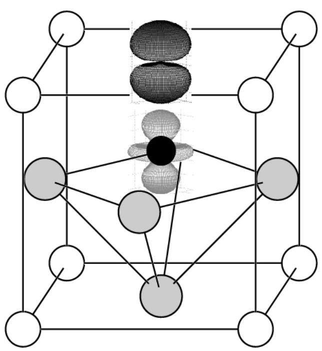


low symmetry

Conventional mechanism for ferroelectricity:

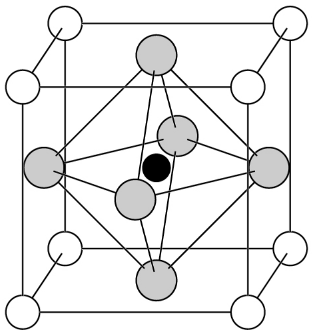


paraelectric

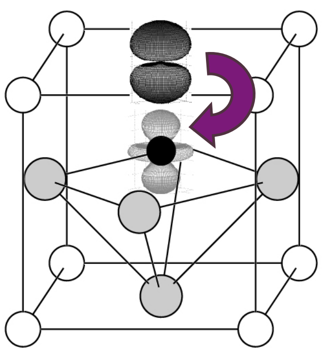


ferroelectric

Conventional mechanism for ferroelectricity:



paraelectric



ferroelectric

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

Perturbation theory

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

Then $H = H^{(0)} + H^{(1)}Q + \frac{1}{2}H^{(2)}Q^2$ where $H^{(1)}Q = (\delta H/\delta Q)_0 Q$

$H^{(2)}Q^2 = (\delta^2 H/\delta Q^2)_0 Q^2$

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

1^{st}-order JT
Non-zero for orbitally degenerate states
centrosymmetric

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

Perturbation theory

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

$BaTiO_3$ (d^0)

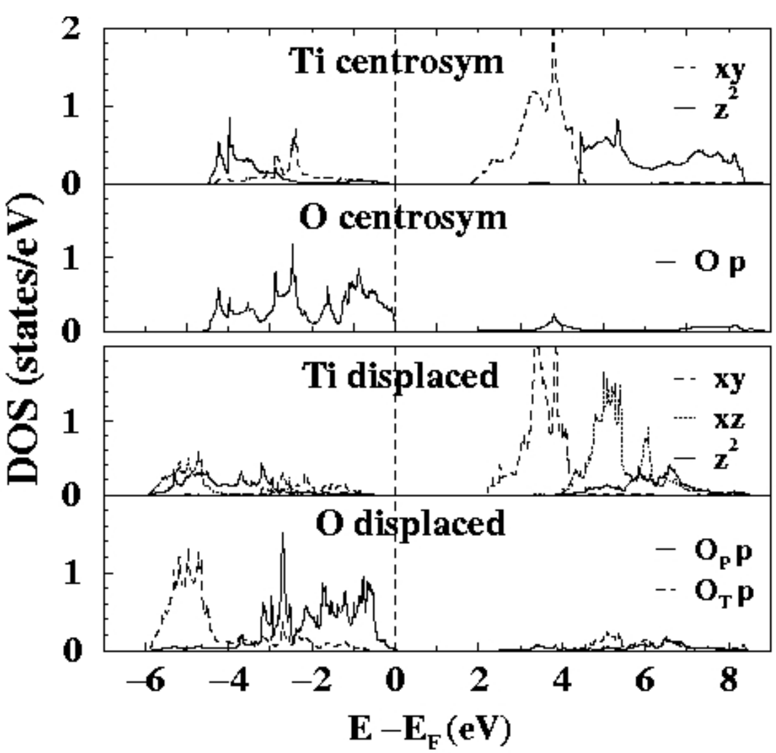
Repulsive term small

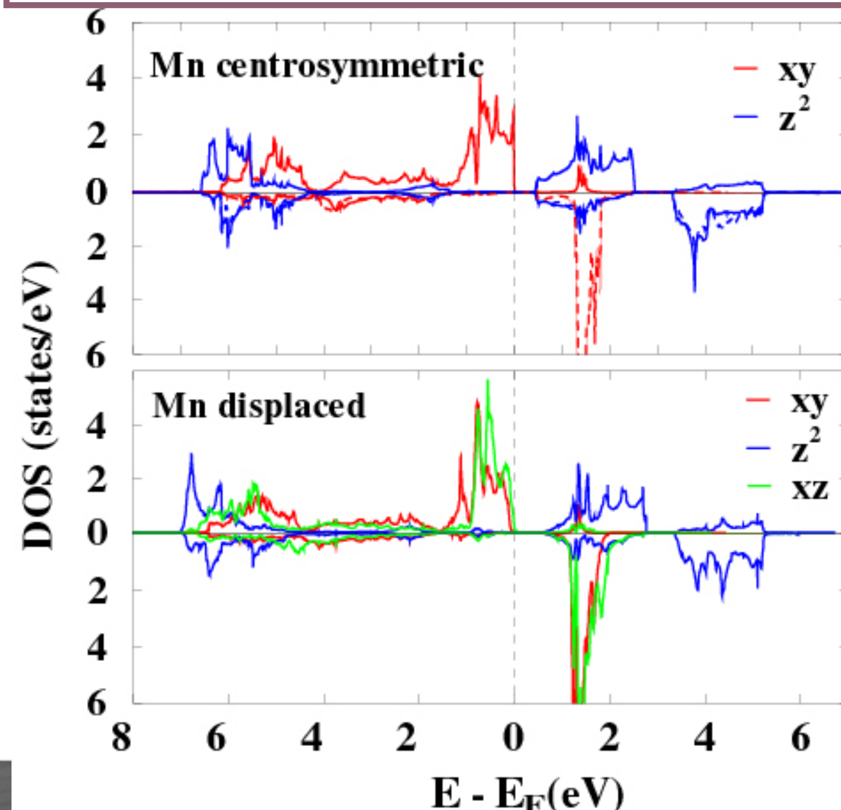
Energy-lowering term non-zero

$CaMnO_3$ (d^3)

Repulsive term large

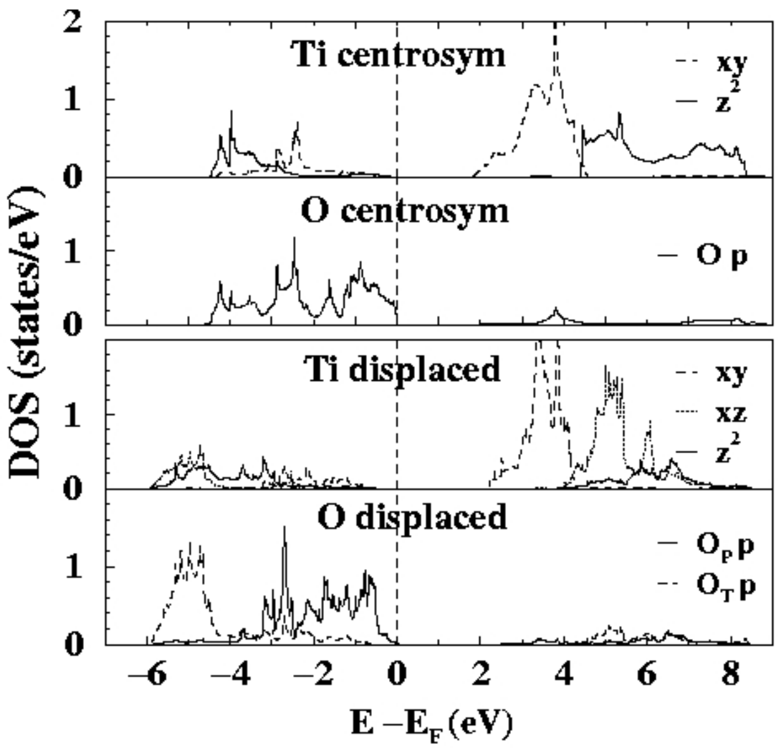
Energy-lowering term 0 by symmetry





Formal charge, ionic charge and Born effective charge

$BaTiO_3$, FORMALLY d^0



Born Effective Charge derived and discussed on blackboard

Chemical contra-indication

Conventional ferromagnetism requires *d* electrons

Conventional ferroelectricity is favored by "d^{0}-ness"

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