The Wacky World of Perovskites

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The mineral perovskite:
$CaTiO_3$
"A minor ore of Ti"

Image from www.mindat.org: (mineral from Chelyabinsk, Russia)

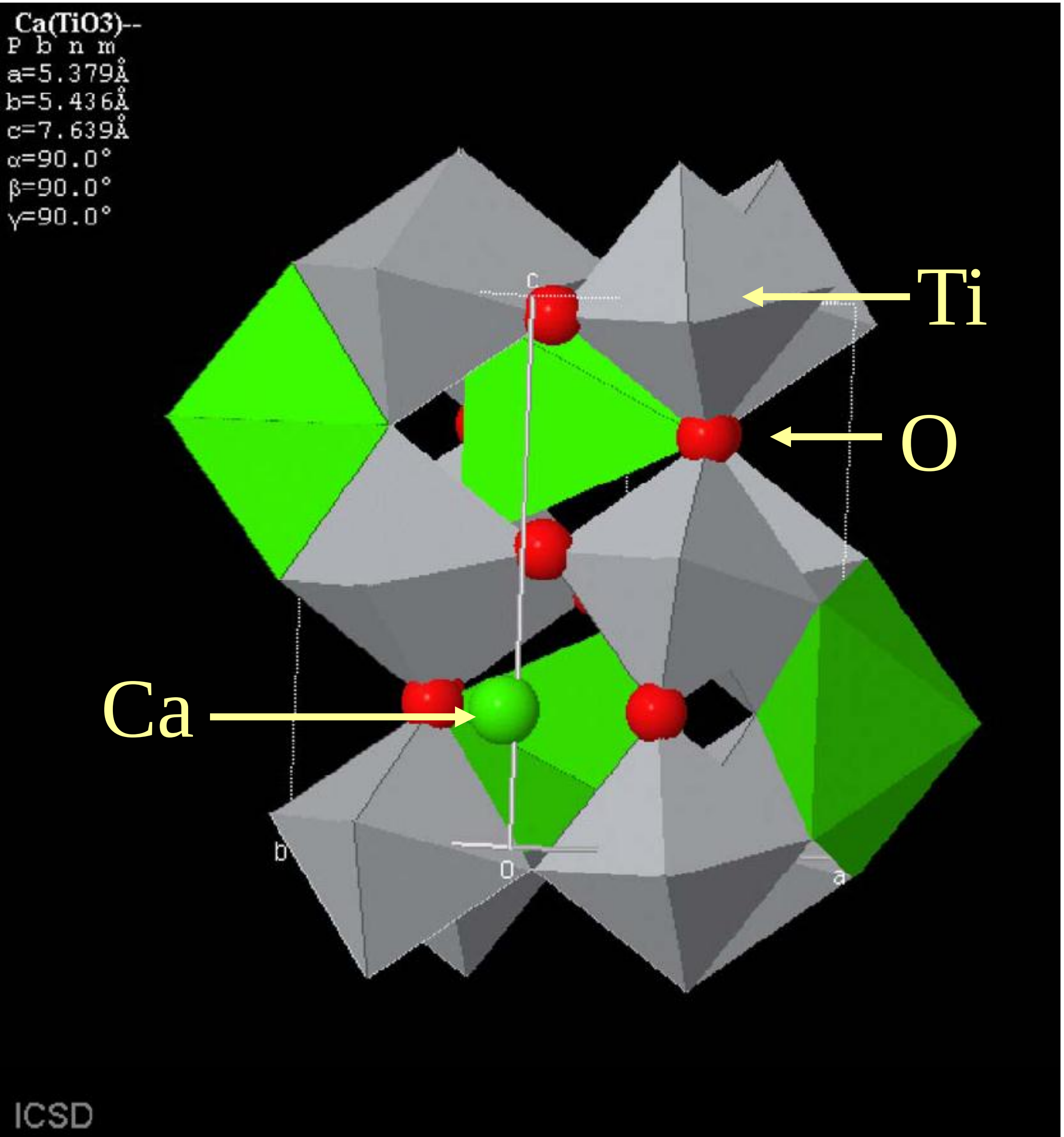
Supported by DOE, BES, Materials Sciences and Engineering and the S3TEC EFRC.

WARNING

If you do not ask questions, I will.

(corollary) If you do not contradict me, I will.

Structure of $CaTiO_3$

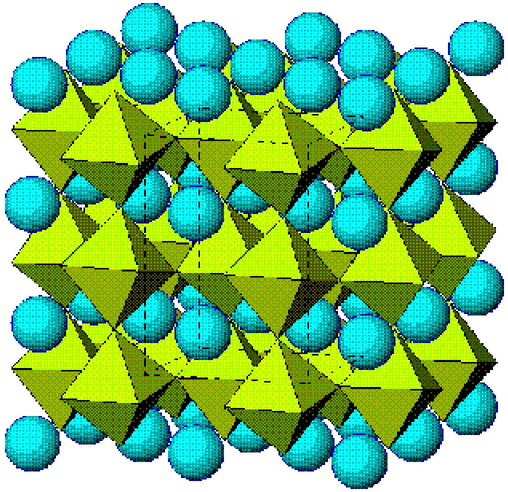


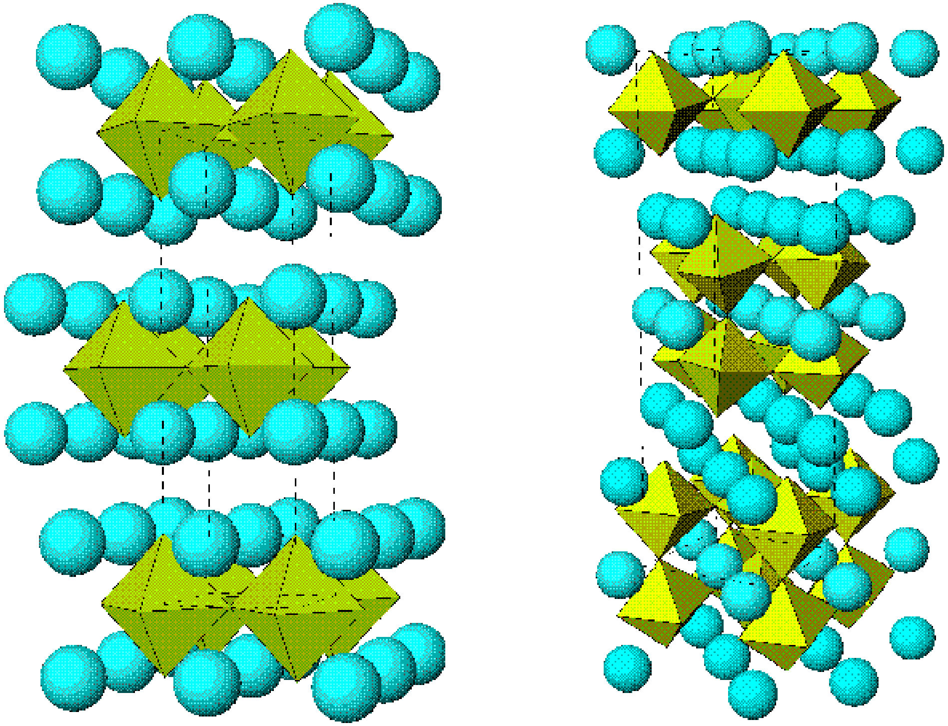
Key structural feature is corner sharing TiO_6 octahedra.

$CaTiO_3$ is pseudocubic (orthorhombic, a distortion of a cubic structure).

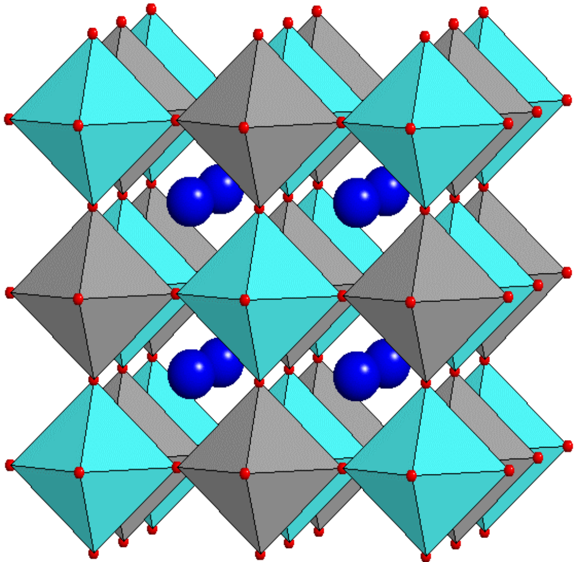
Perovskite Variants

Cubic Perovskite





Layered Perovskites

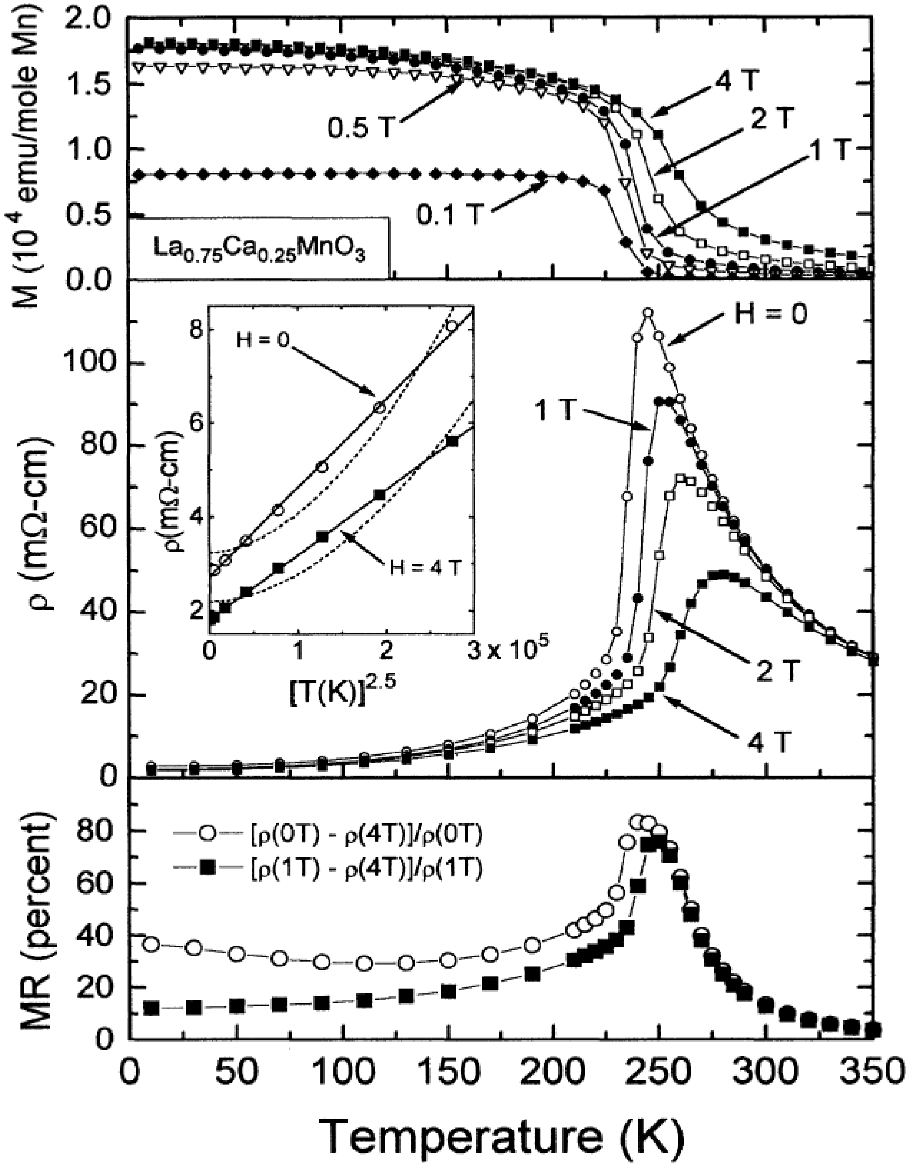


Double Perovskite, e.g. Sr_2YRuO_6

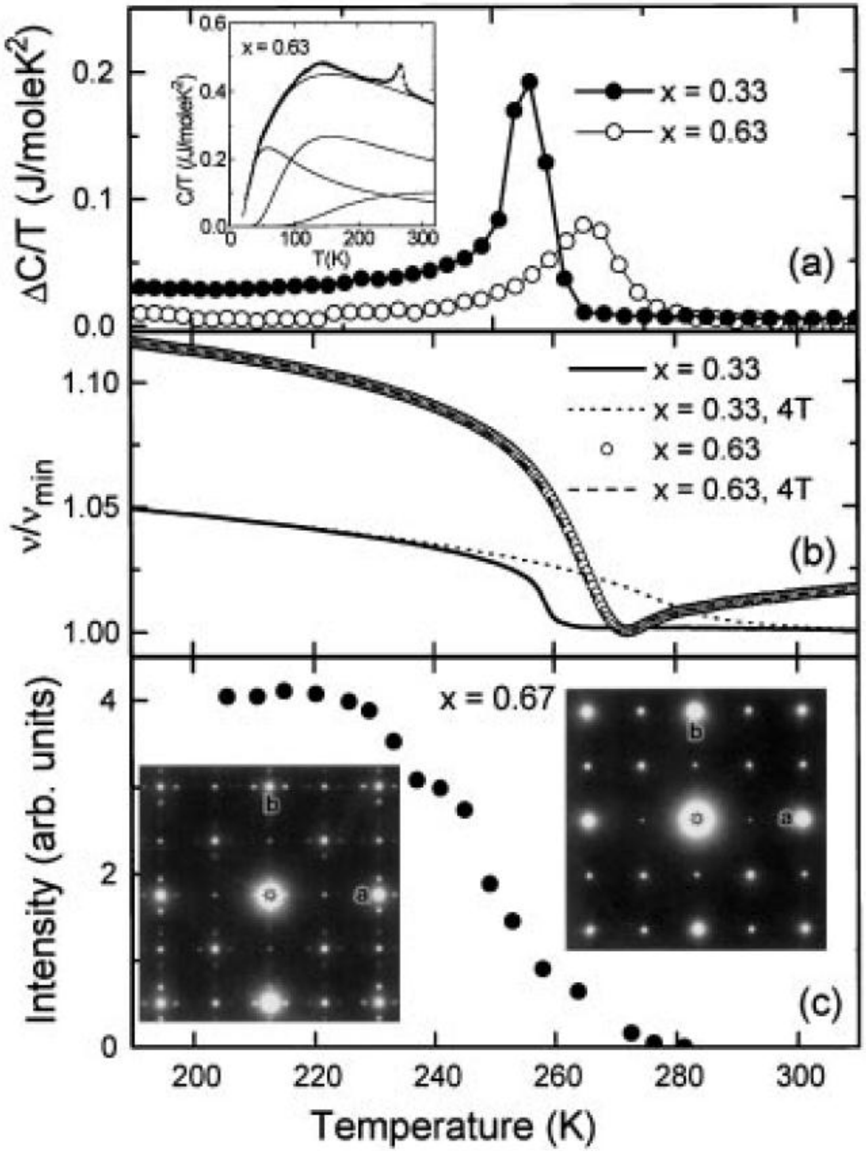
What’s Interesting

- Tendency towards sometimes complex structure distortions (as in e.g. $CaTiO_3$.
- Many perovskites are metallic and many are not. Sometimes one can tune between metallic and insulating states by “small” perturbations.
- Many perovskites exist with magnetic ions both on the Ca site, such as various rare earth’s and the B-site, such as various 3d transition elements e.g. $GdFeO_3$.
- There is often strong coupling between degrees of freedom in perovskites – structure – magnetism – electronic properties.
- The perovskite family allows wide chemical flexibility – many compounds can be formed.

Example: CMR Manganites

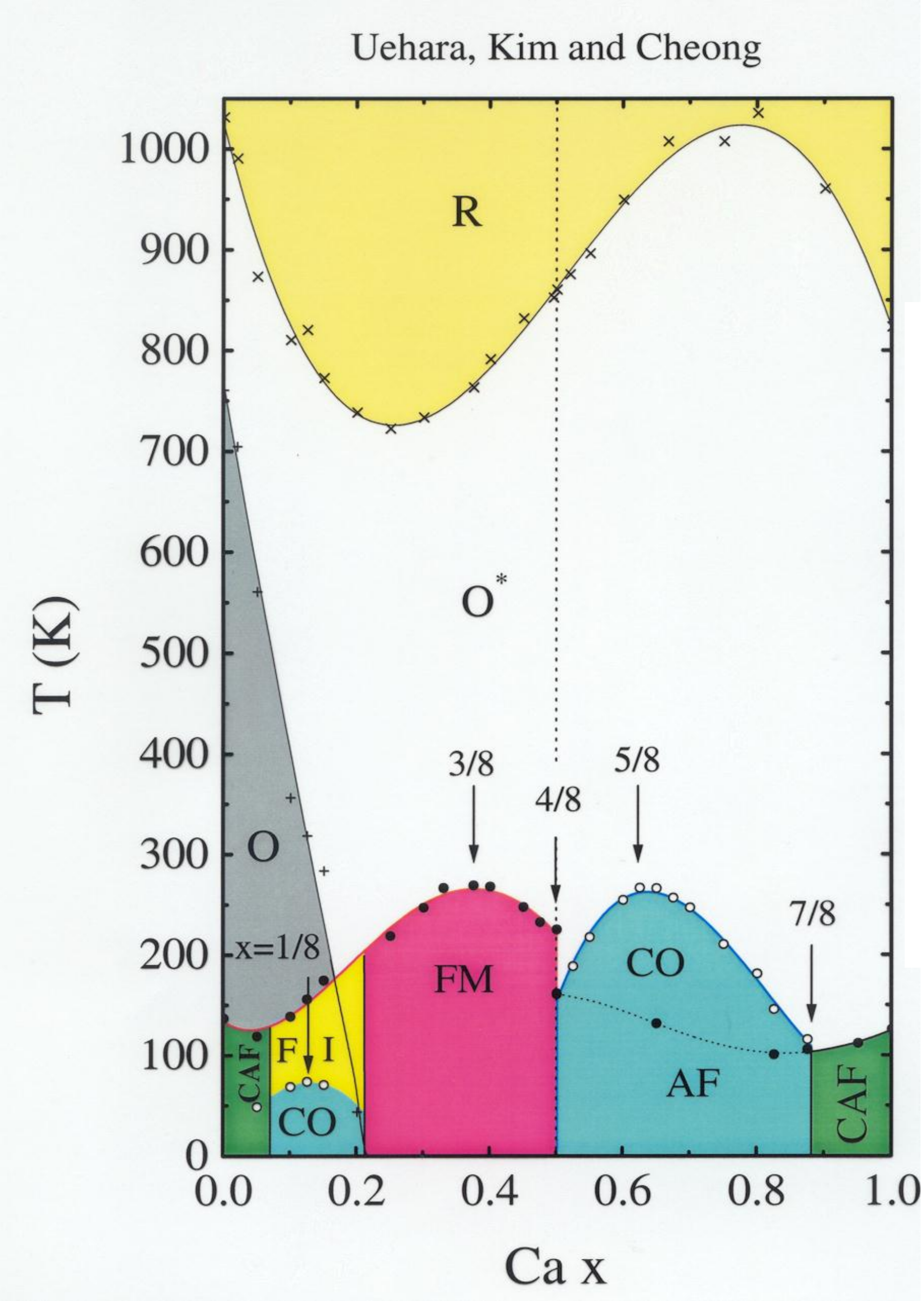


Schiffer et al. (1995)



Ramirez et al. (1996)

$La_{1-x}Ca_xMnO_3$ Phase Diagram



All phases show local moment magnetism as expected for 3*d* high spin ion due to Hund’s coupling.

Wide variety of magnetic phases: coupled metal insulator transitions, orbital orderings, spin orderings.

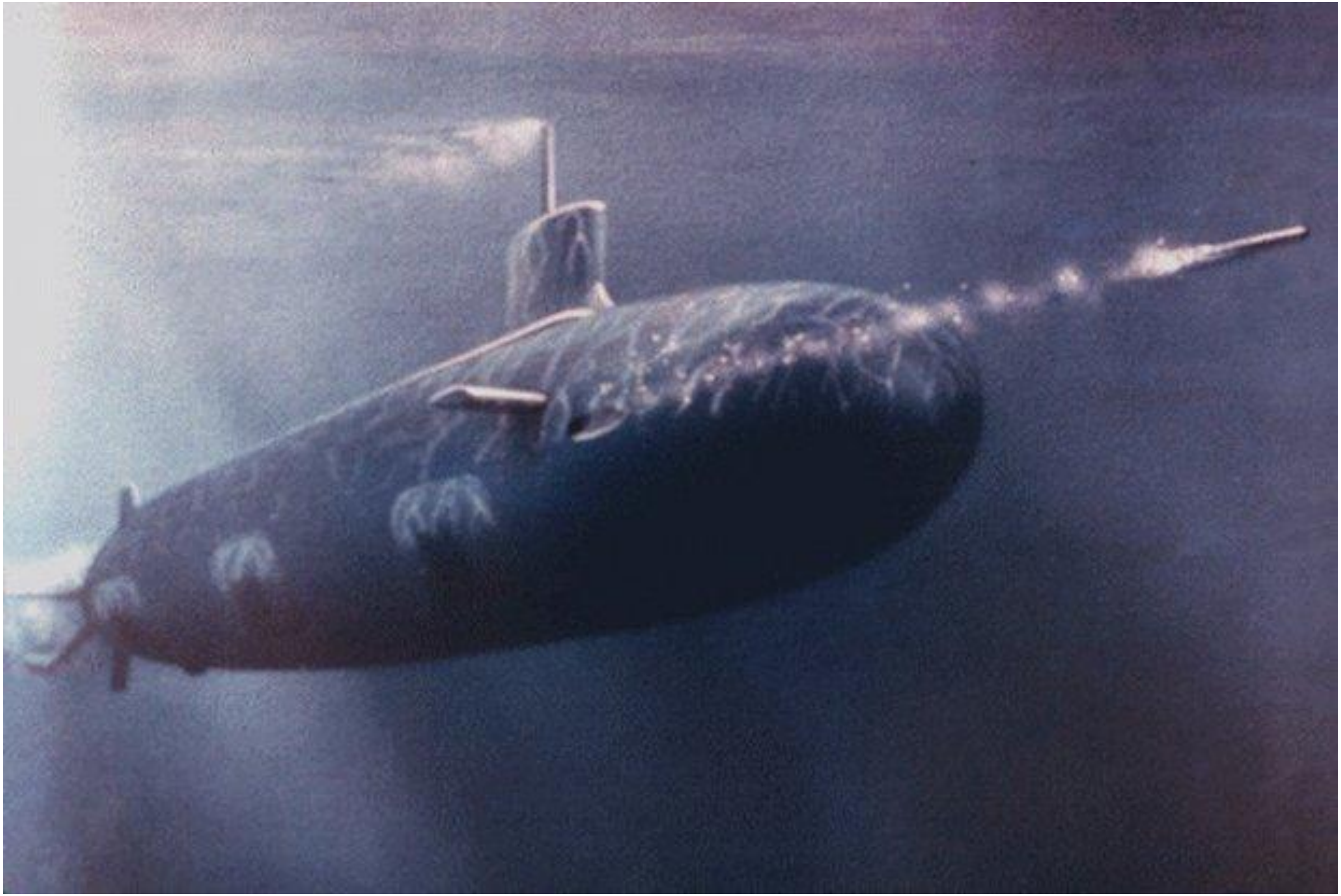
Properties

- Main families of ferroelectrics used in applications – $Pb(Zr,Ti)O_3$, $BaTiO_3$, $(K,Na)NbO_3$, $(Ba,Sr)TiO_3$ etc.
  - Electronics, medical ultrasound, actuators, sonars, microwave devices, motion detectors …
- Colossal magnetoresistance (manganites).
- High T_C half-metal ferromagnets: Sr_2MoFeO_6 …
- High-T_c superconductors: Cuprates, $(Ba,K)BiO_3$.
- ….

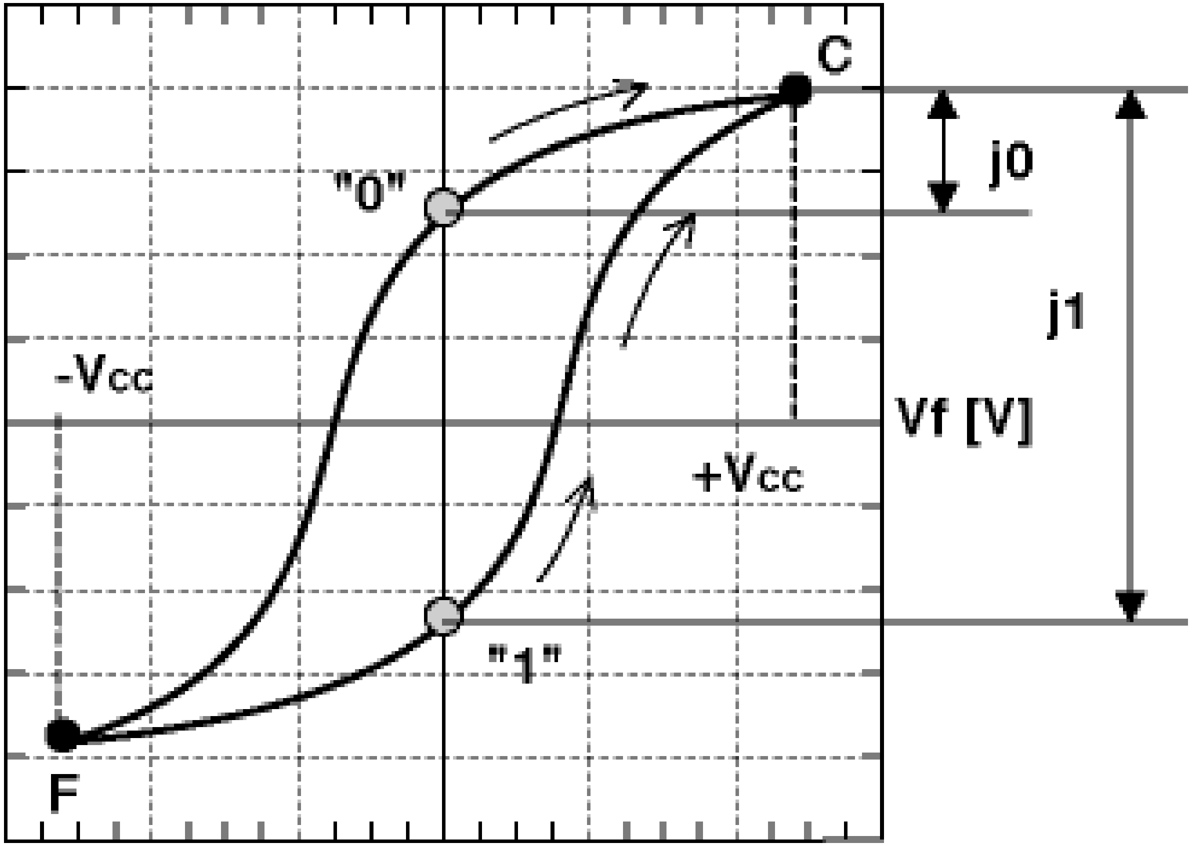
STRUCTURE AND IONIC SIZE

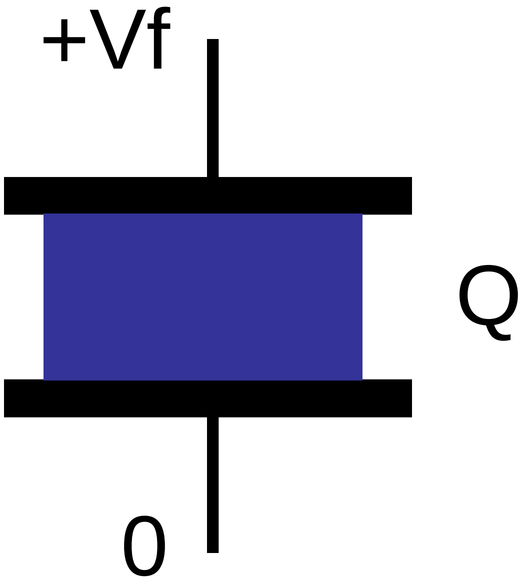
(Ferroelectrics)

SSN21 Seawolf



What are Ferroelectrics?

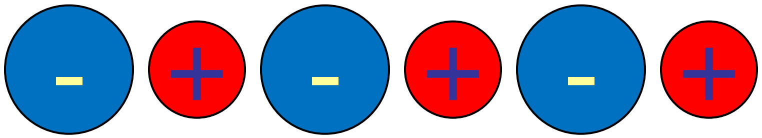


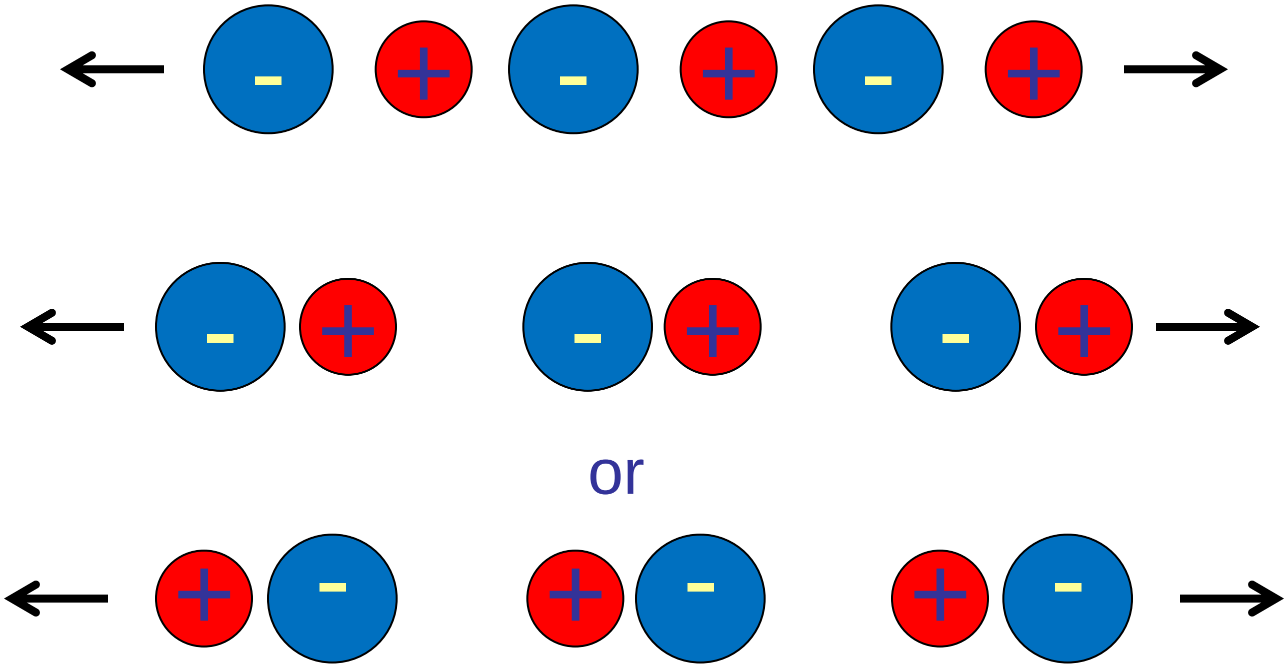


Note analogy with Ferromagnets

Producing a Ferroelectric

Linear chain of charged atoms (e.g. H and F)



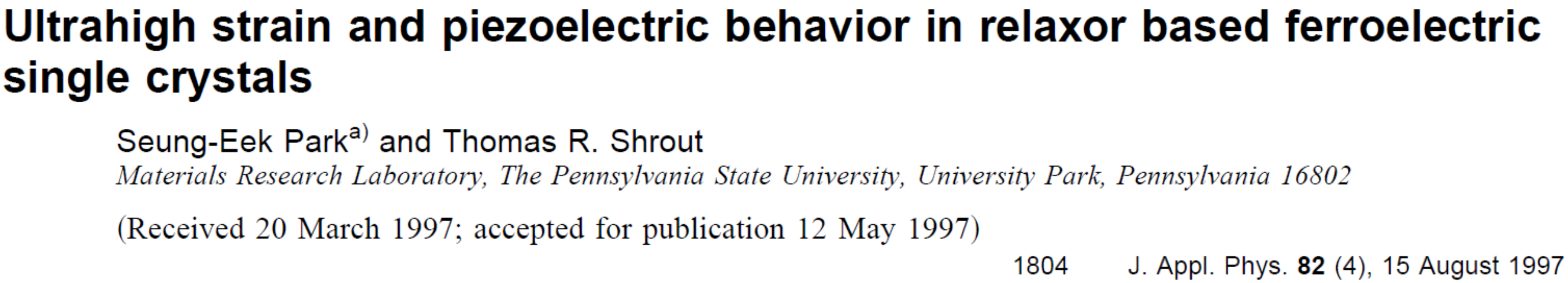


Tensile strain
➔ Symmetry breaking

Coulomb interactions and covalent bonds favor ferroelectric

Closed shell repulsion oppose ferroelectric

Medical Imaging



Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals

Seung-Eek Park[a] and Thomas R. Shrout

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 20 March 1997; accepted for publication 12 May 1997)

1804 J. Appl. Phys. **82** (4), 15 August 1997

Materials discovery to commercial products in less than seven years

Live 3D imaging enables clear visualization of thickened ventricular cardiomyopathy and pericardial effusion, while also providing valve, chamber and muscle detail.

PHILIPS

sense and simplicity

Electronics and Others

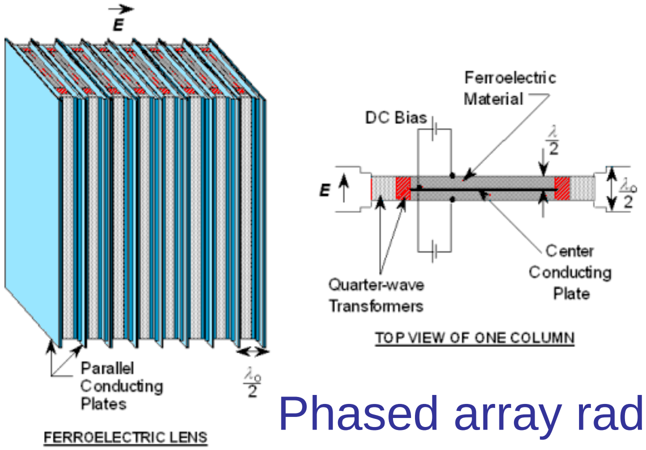
Ferroelectric memories:

- Ramtron
- Fujitsu
- Samsung

Passive components:

- EPCOS and many others

Microwave/Radar:



Phased array radar lens
J.B.L. Rao et al.

Actuators:

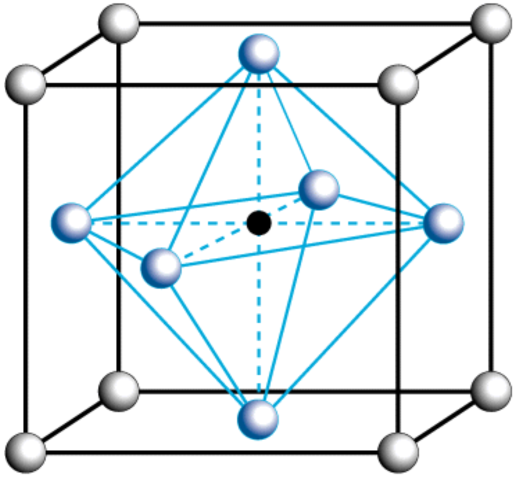
Piezoelectric fuel injector (Bosch)

Pyroelectric Effect

Motion detectors,
X-ray generators
Neutron generators

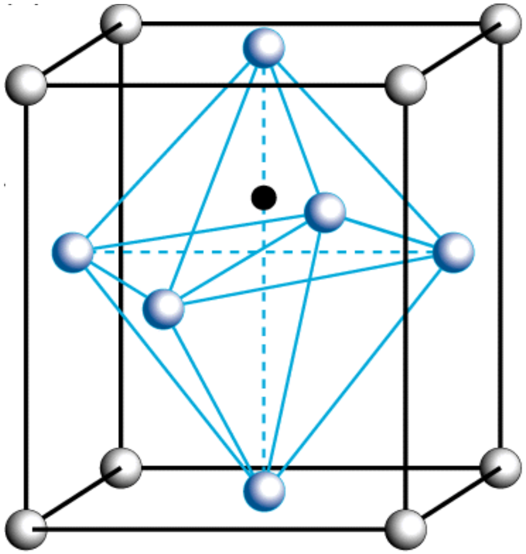
How Does PZT Work?

Cubic Perovskite Structure

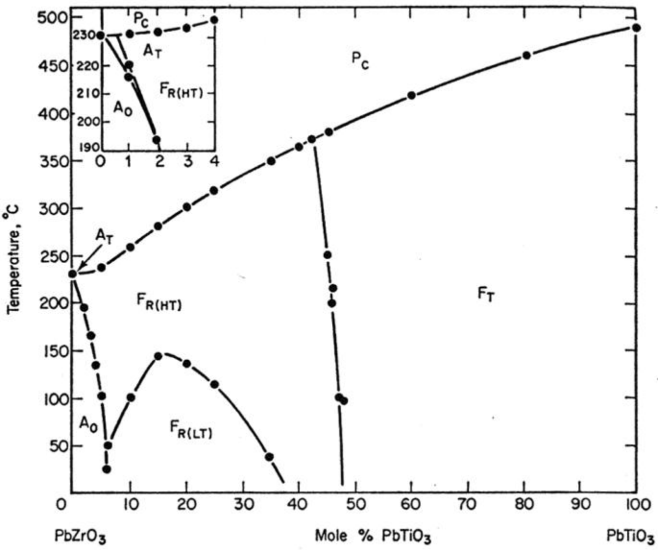


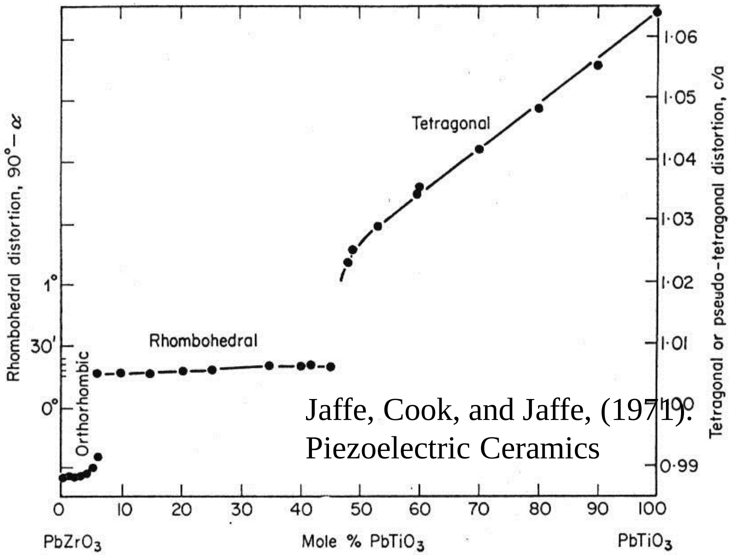
TO(Γ) unstable phonon (Ferroelectric)

Tetragonal FE



Ground state can be tetragonal, orthorhombic, rhombohedral or monoclinic.

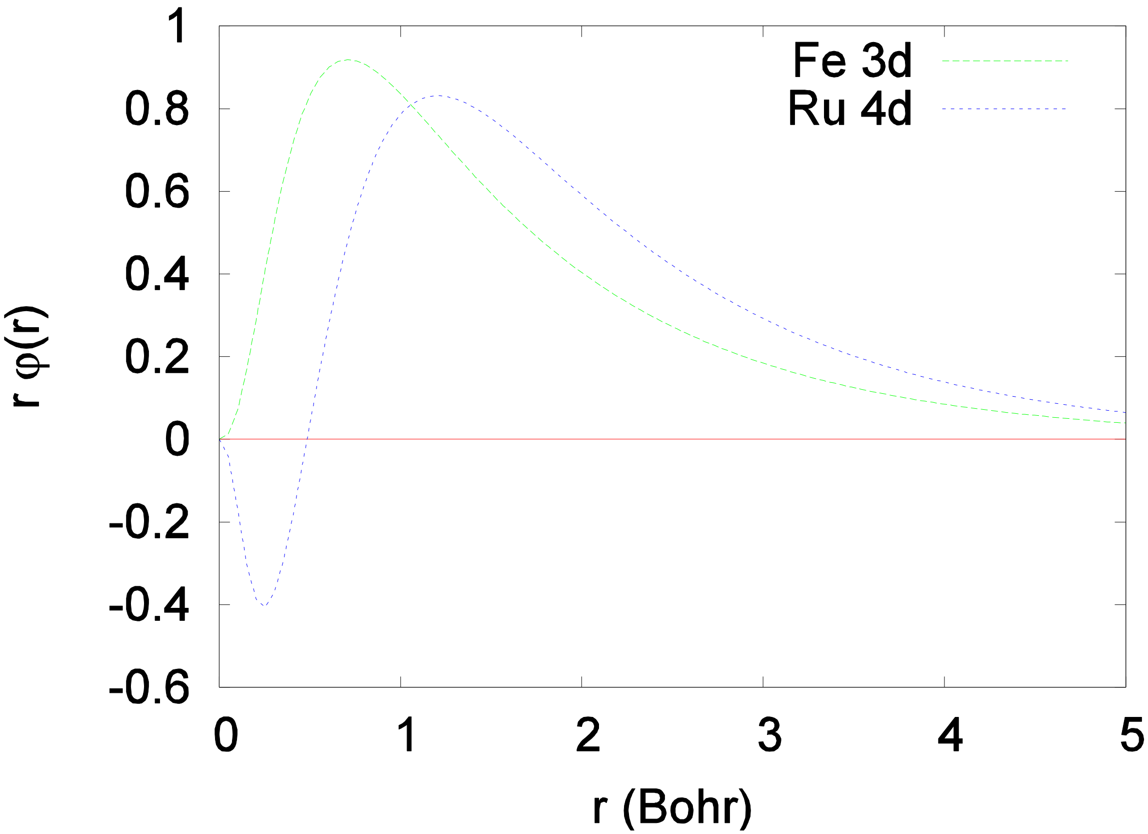


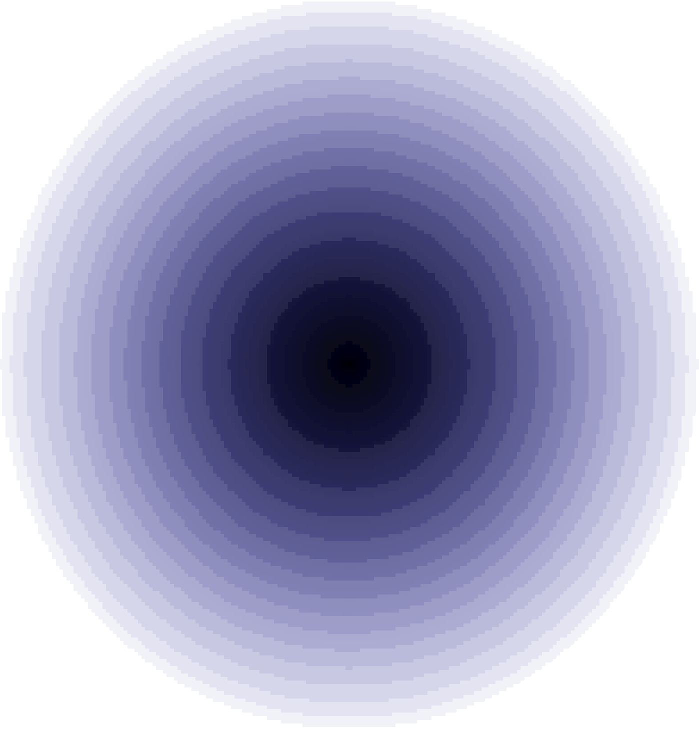


Jaffe, Cook, and Jaffe, (1971). Piezoelectric Ceramics

PZT near the morphotropic phase boundary is the basis of current devices

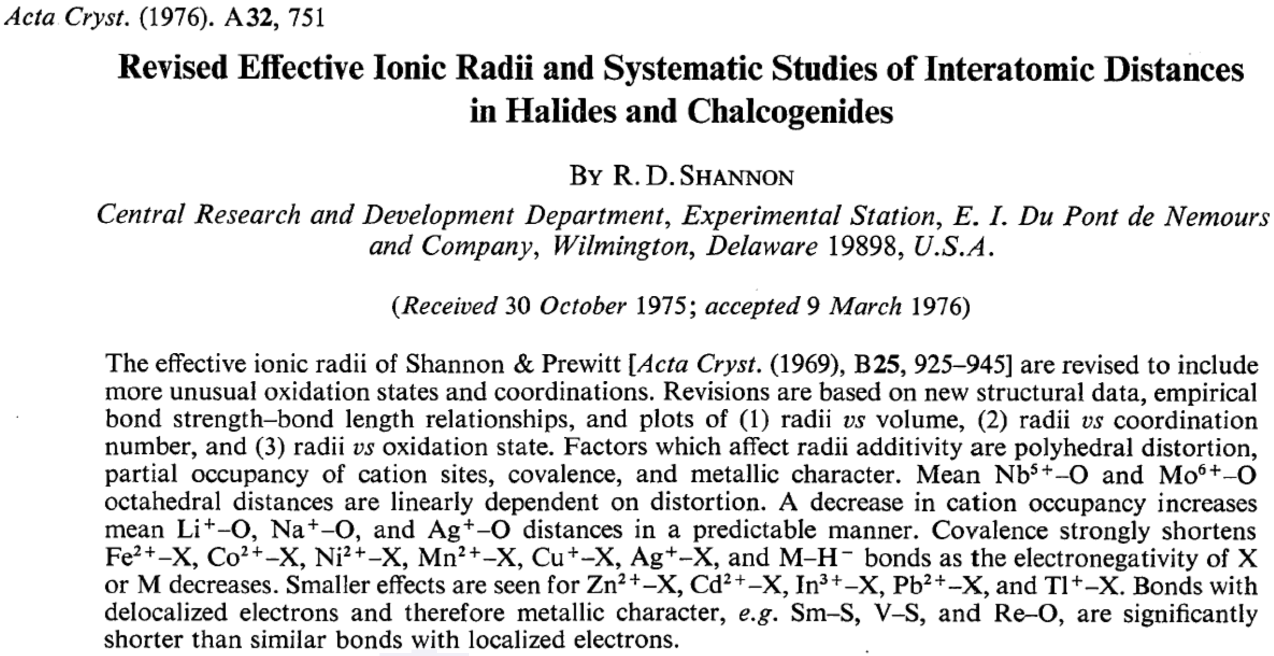
What is the Size of an Atom?





The Size of an Atom

- Goldschmidt; Pauling; Shannon and Prewitt



Acta Cryst. (1976). A**32**, 751

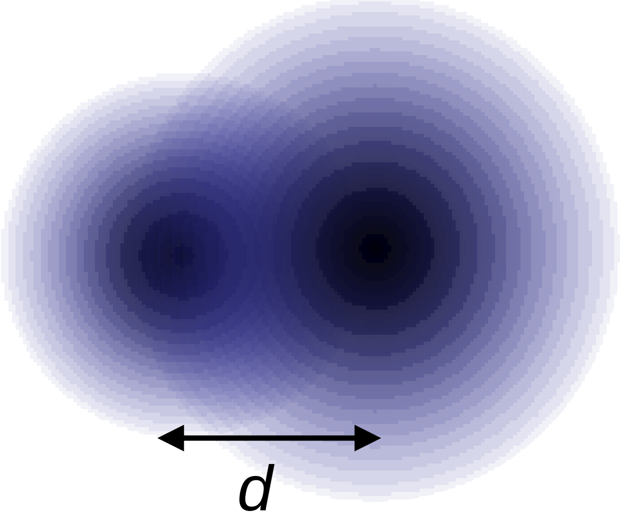
Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides

By R. D. Shannon

Central Research and Development Department, Experimental Station, E. I. Du Pont de Nemours and Company, Wilmington, Delaware 19898, *U.S.A.*

(*Received* 30 *October* 1975; *accepted* 9 *March* 1976)

The effective ionic radii of Shannon & Prewitt [*Acta Cryst.* (1969), B**25**, 925–945] are revised to include more unusual oxidation states and coordinations. Revisions are based on new structural data, empirical bond strength–bond length relationships, and plots of (1) radii *vs* volume, (2) radii *vs* coordination number, and (3) radii *vs* oxidation state. Factors which affect radii additivity are polyhedral distortion, partial occupancy of cation sites, covalence, and metallic character. Mean Nb^{5+}–O and Mo^{6+}–O octahedral distances are linearly dependent on distortion. A decrease in cation occupancy increases mean Li^+–O, Na^+–O, and Ag^+–O distances in a predictable manner. Covalence strongly shortens Fe^{2+}–X, Co^{2+}–X, Ni^{2+}–X, Mn^{2+}–X, Cu^+–X, Ag^+–X, and M–H^- bonds as the electronegativity of X or M decreases. Smaller effects are seen for Zn^{2+}–X, Cd^{2+}–X, In^{3+}–X, Pb^{2+}–X, and Tl^+–X. Bonds with delocalized electrons and therefore metallic character, *e.g.* Sm–S, V–S, and Re–O, are significantly shorter than similar bonds with localized electrons.

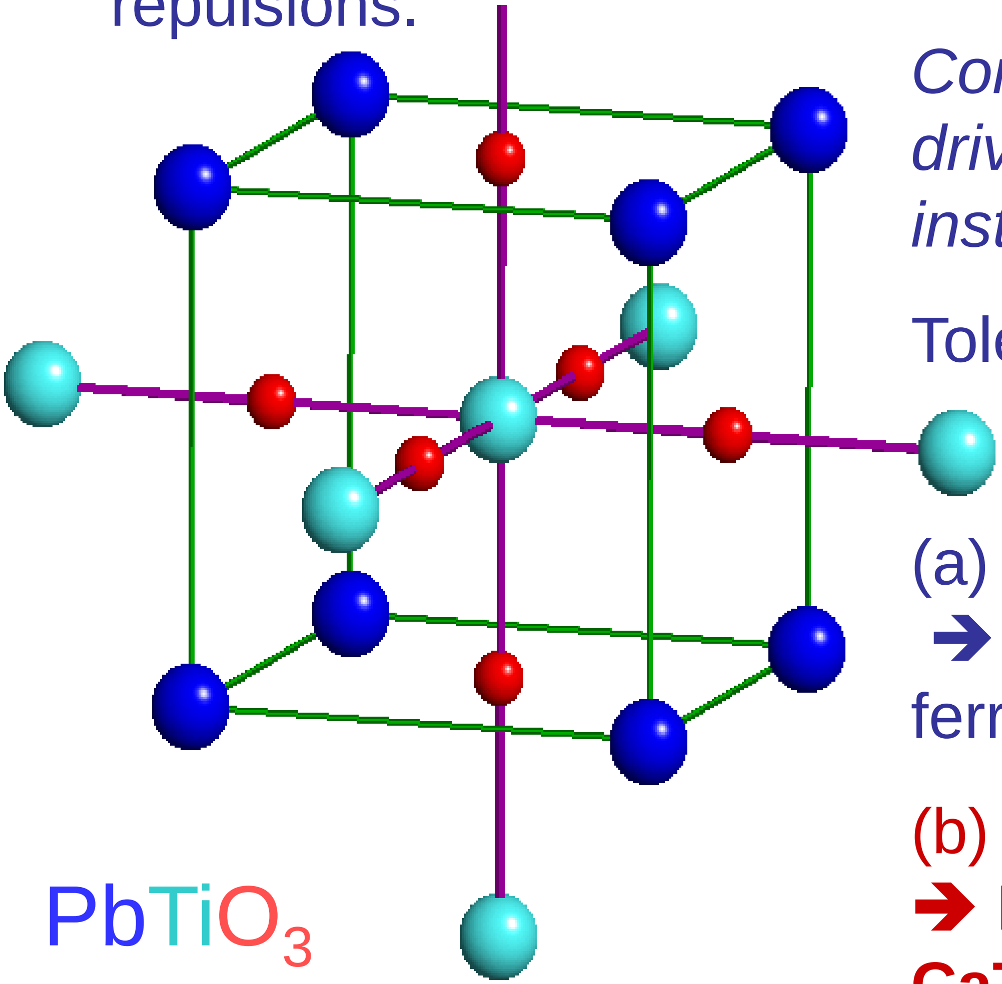


Inter-atomic distance,
$d = r_A + r_B$
Crystallographic data “defines” the “sizes” of atoms.

INSTABILITIES OF PEROVSKITES

Chemical Understanding:

- Main interactions are (1) Coulomb (ionic) and (2) Closed shell repulsions.



$PbTiO_3$

Competition of bond lengths drives most perovskite instabilities.

Tolerance Factor:

$$t = (r_A+r_O)/\sqrt{2}(r_B+r_O)$$

(a) *t*>1 (B ion [Ti] is too small)
➔ B site off-centering and ferroelectricity ($BaTiO_3$, $KNbO_3$)

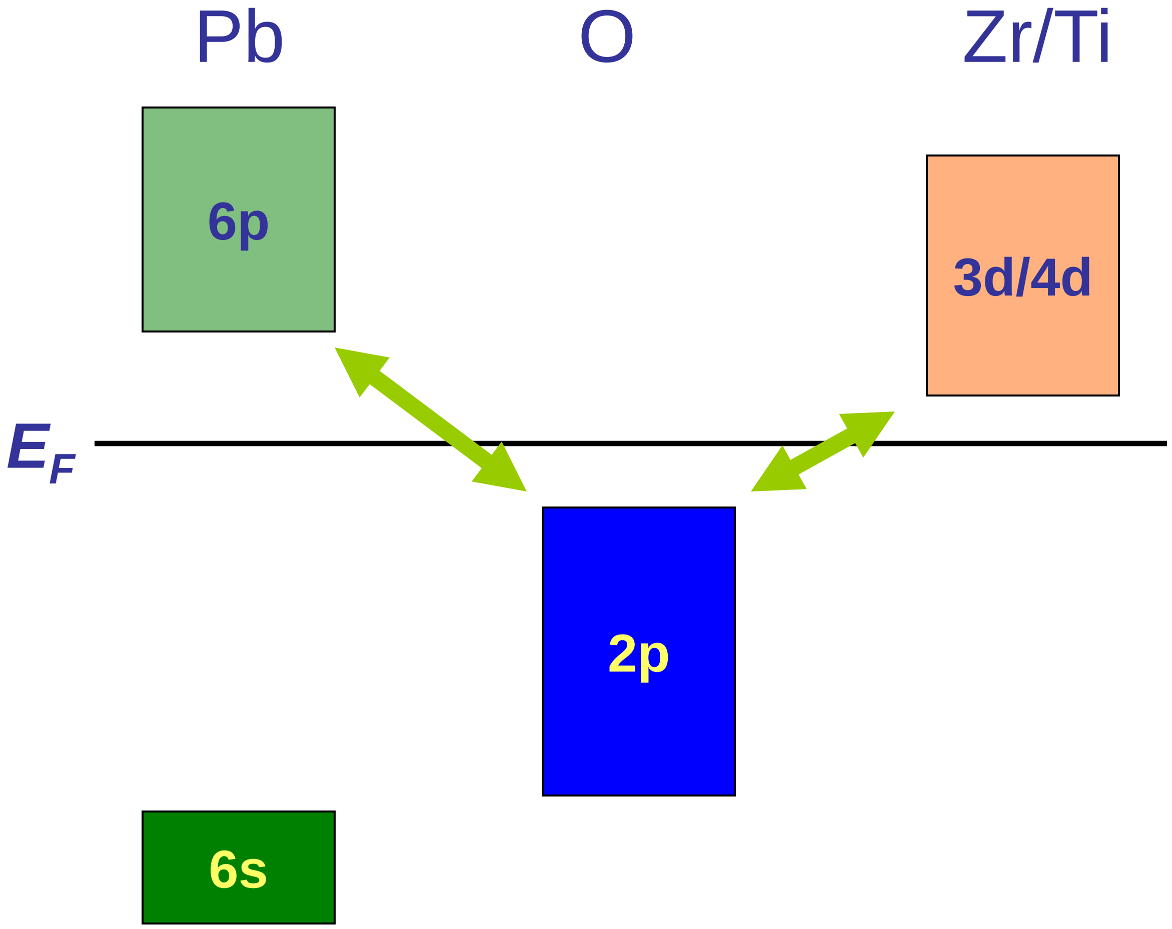
(b) ***t*<1 (A ion [Pb] is too small)**
➔ Rotation of octahedra, e.g. $CaTiO_3$, $GdFeO_3$, $LaMnO_3$… (the great majority of perovskites).

Role of Pb on the Perovskite A-Site

- **Pb allows *t*<1 perovskites to be ferroelectric instead of *Pnma* or similar.**

Electronic Structure:

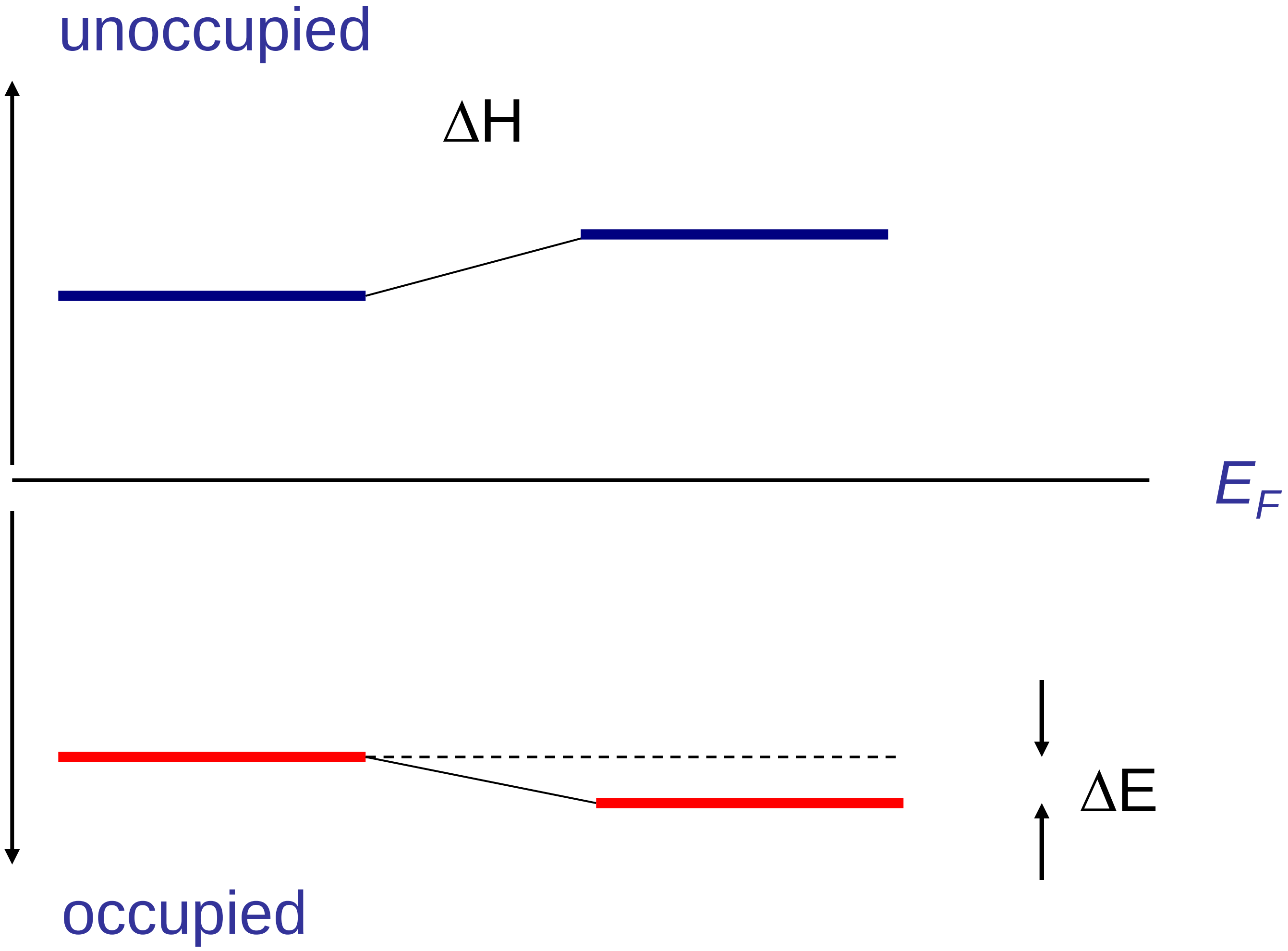
R.E. Cohen, 1992



Cross-gap hybridization:

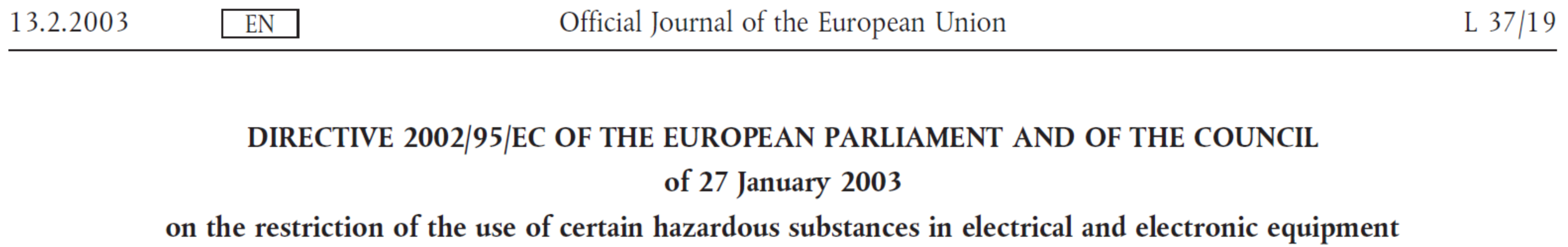
- Increases Z*
- Softens interactions
- Increases polarizability
- Favors Ferroelectricity

What’s going on here?



Occupied states decrease in energy → a chemical bond

n.b. mixing of occupied states is not a bond!



13.2.2003 EN Official Journal of the European Union L 37/19

DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 27 January 2003

on the restriction of the use of certain hazardous substances in electrical and electronic equipment

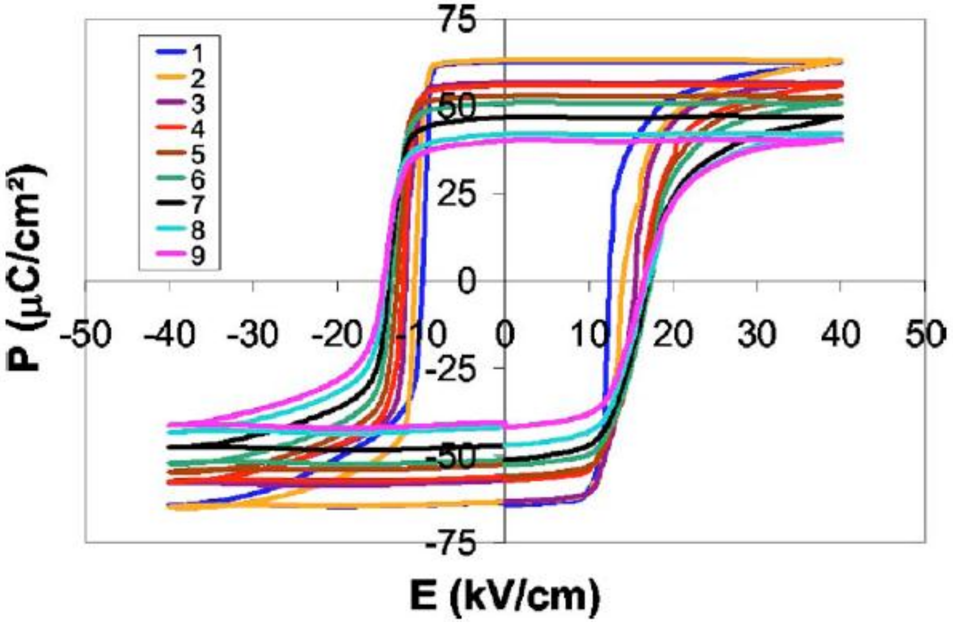
Are there Pb-free materials that are as good as or even better than the Pb-based materials, e.g. PZT?

Answer was long thought to be no…

… but results in the last decade for materials such as $BiFeO_3$ suggest a closer look.

$BiFeO_3$:

- A very high polarization material based on structure (Tomashpol'skii, 1967), but not usable due to conductivity.



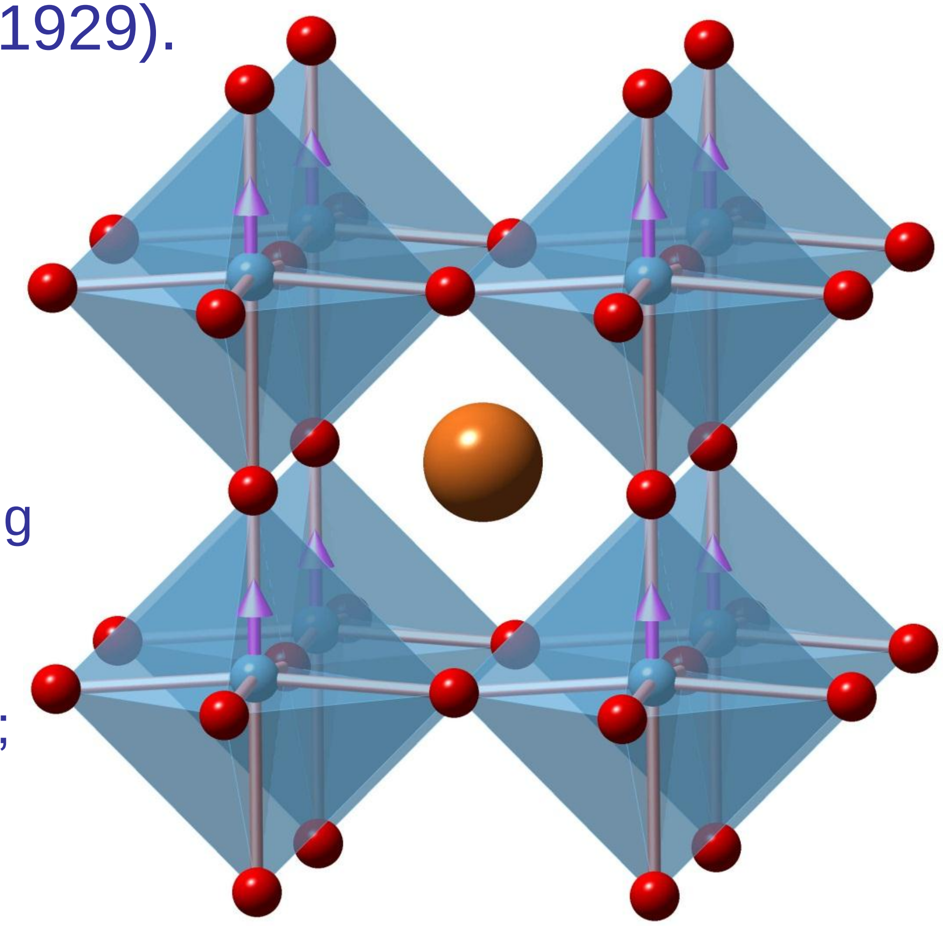
Lebeugle et al., APL 2007, room temp.

How Much of a Good Thing is Enough?

The Perovskite Structure

Pauling Rules - JACS **51**, 1010 (1929).

1. “the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio”
2. “charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching it”
3. “shared edges and particularly shared faces … decreases stability; this effect is large for cations with large valence …”



from www.crystalmaker.co.uk

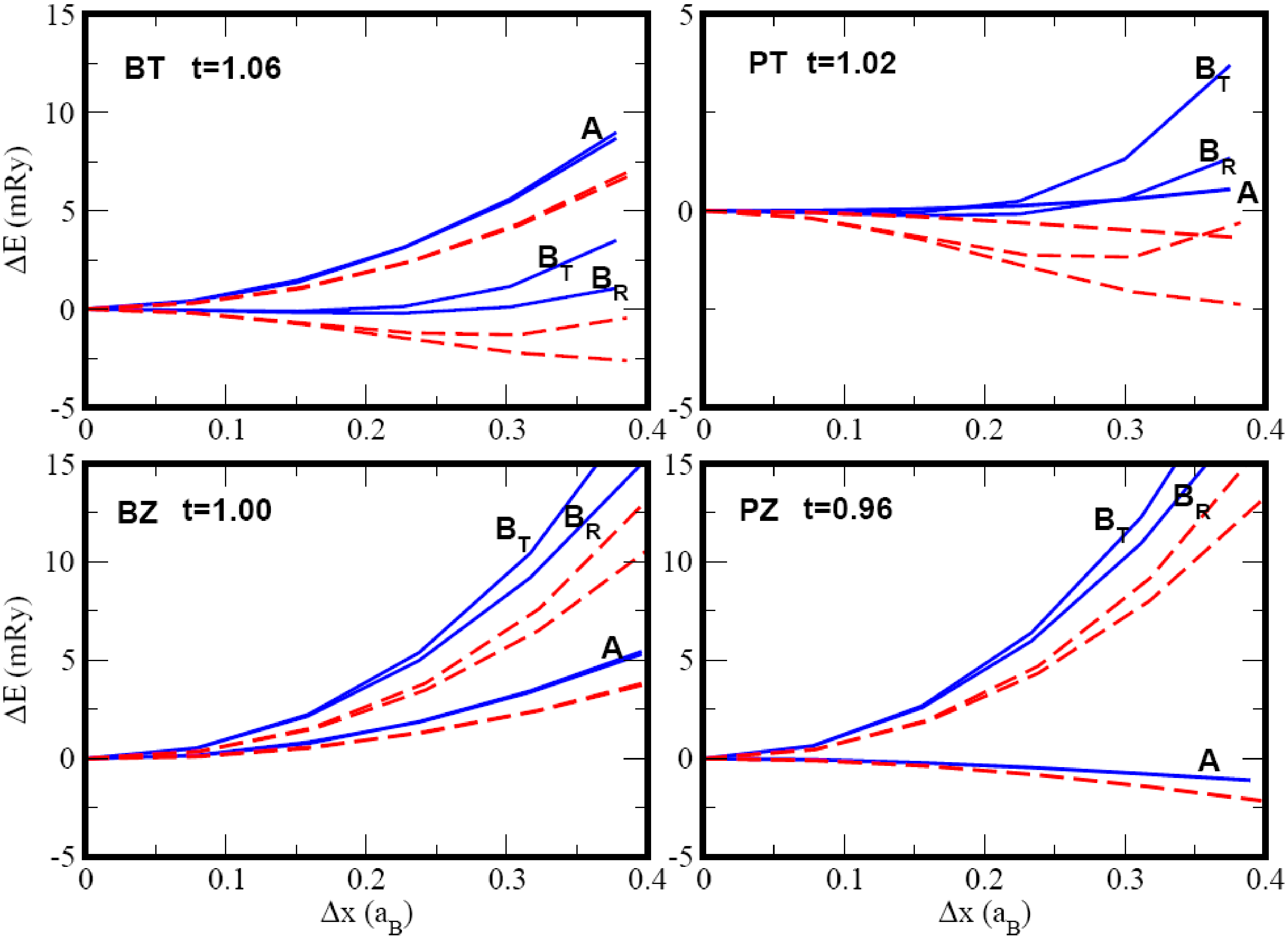
Problem:

- Bi^{3+} vs. Pb^{2+} implies lower average B-site charge.
- Bi^{3+} has c.r.~1.3 Å << Pb^{2+} (1.63 Å).

➔***Bi perovskites are often difficult to make.***

INSTABILITIES OF PEROVSKITES

Single sub-lattice off-centering (LDA):



Expt. Volume: ———

6% Expansion: — — — — —

INSTABILITIES OF PEROVSKITES

Classification:

1. U_A : Unstable against *A*-site off-centering (PZ).
- $t<1$
- also unstable against rotation.

2\. U_B: Unstable against *B*-site off-centering (BT).
- $t>1$

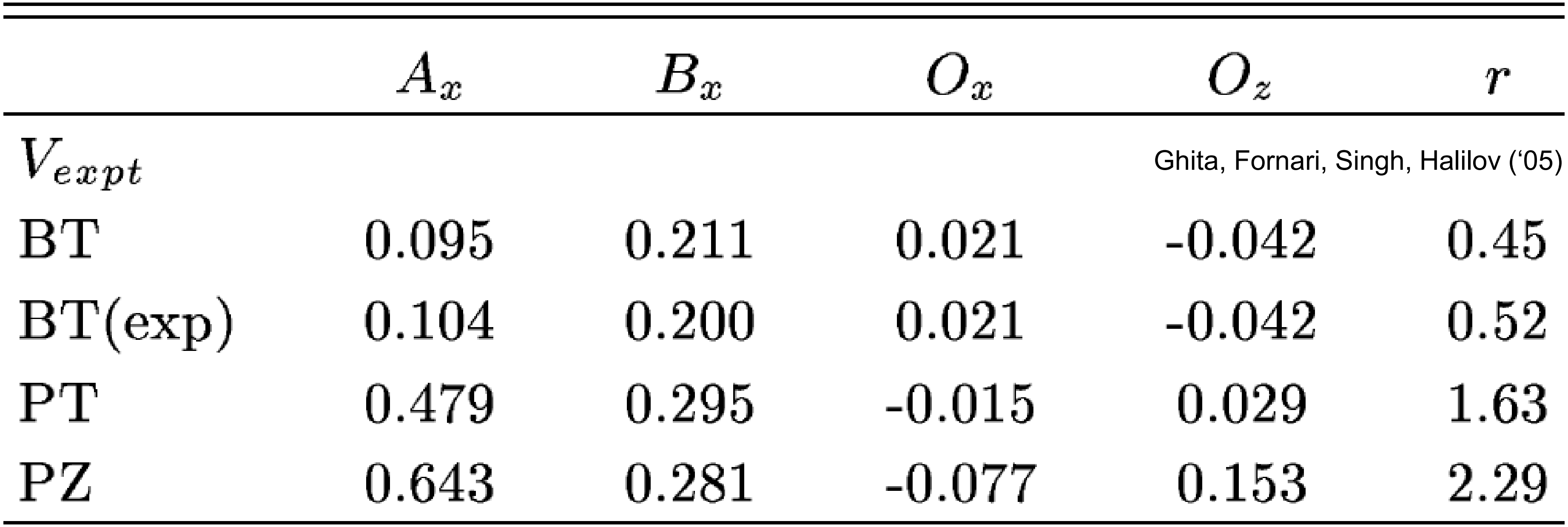
3\. U_{AB}: Unstable against both *A*- and *B*-site off-centering (PT).
- $t \sim 1$
- Instability not driven by tolerance factor.

4\. S: Stable against sub-lattice off-centering (BZ), $t \sim 1$, or ferroelectrics like KTN.

PZT is an alloy between U_A and U_{AB} end-points.
Not understood by tolerance factor alone.

INSTABILITIES OF PEROVSKITES

LDA calculations constrained to rhombohedral ferroelectric
Displacements in Bohr along *x* direction (0.529 √3 ➔ Ang. disp.)

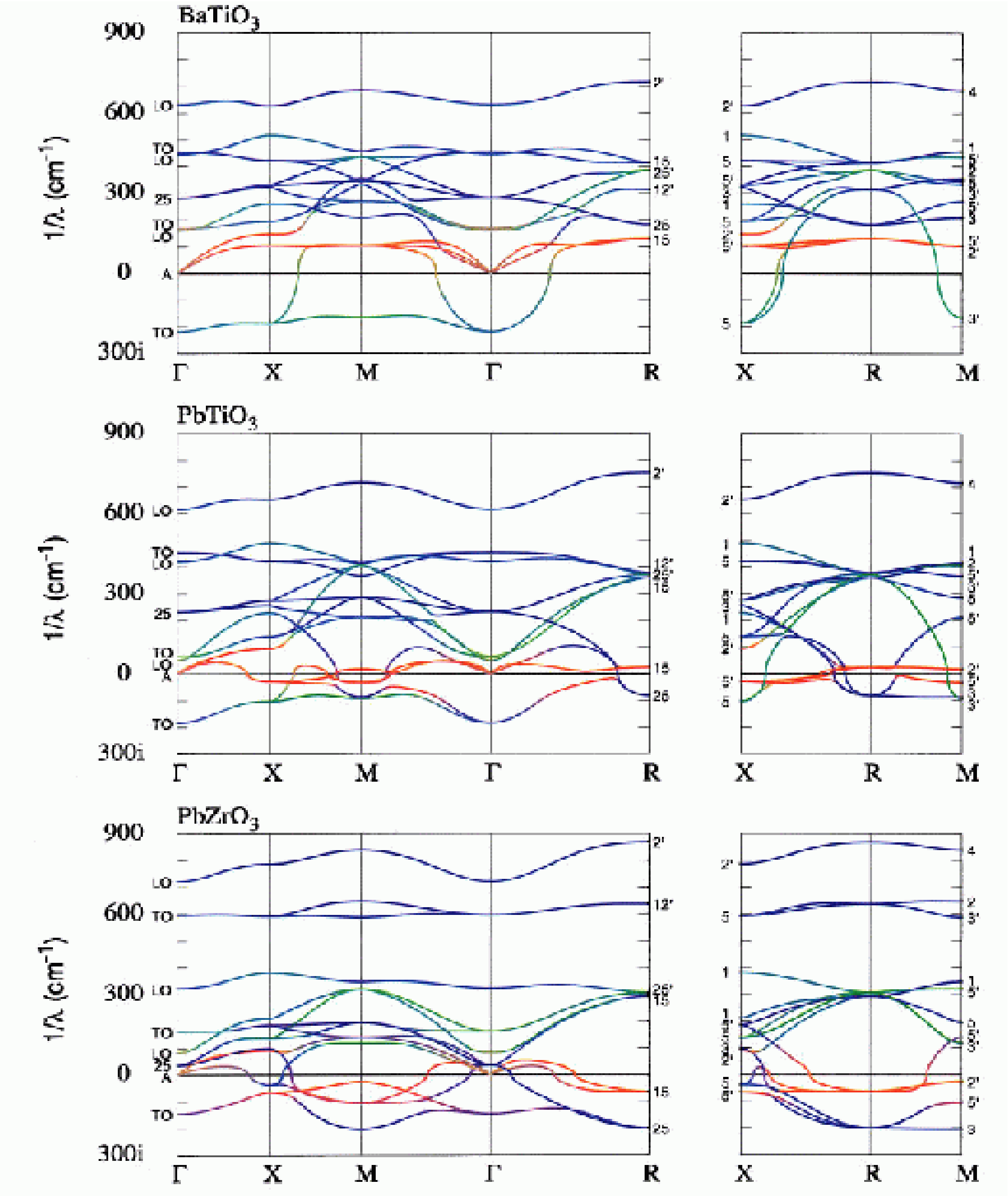


	A_x	B_x	O_x	O_z	r
V_{expt}					
BT	0.095	0.211	0.021	-0.042	0.45
BT(exp)	0.104	0.200	0.021	-0.042	0.52
PT	0.479	0.295	-0.015	0.029	1.63
PZ	0.643	0.281	-0.077	0.153	2.29

Ghita, Fornari, Singh, Halilov ('05)

Cooperative A-site and B-site displacements characterize good perovskite ferroelectrics

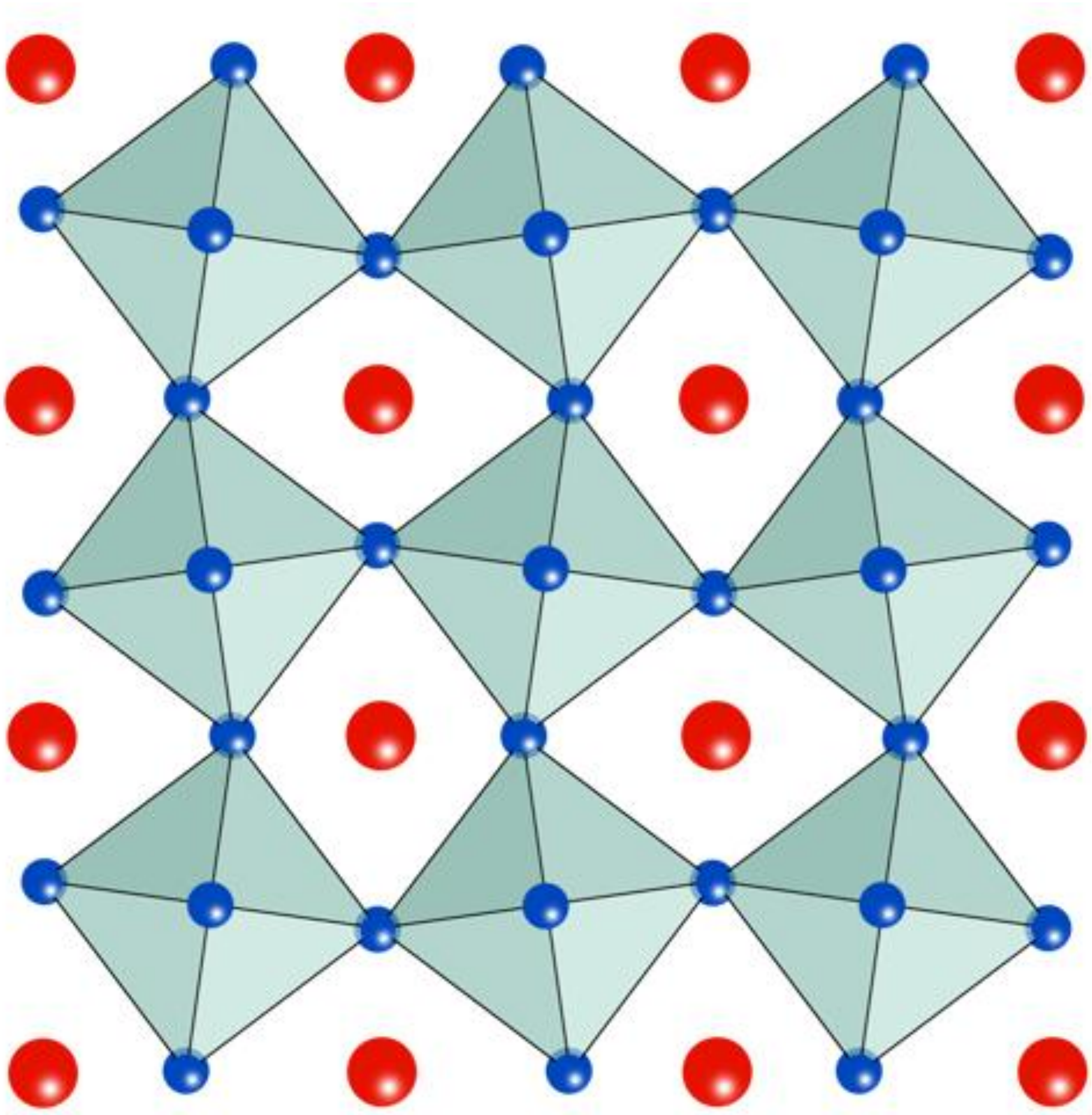
Phonons In Ferroelectric Perovskites



First Principles Calculations of Ghosez et al. (1999):

- note R point instabilities in PZ *and PT* but not BT.
- Note different coherence lengths for zone center and zone boundary instabilities.

ROTATIONAL (TILT) MODES

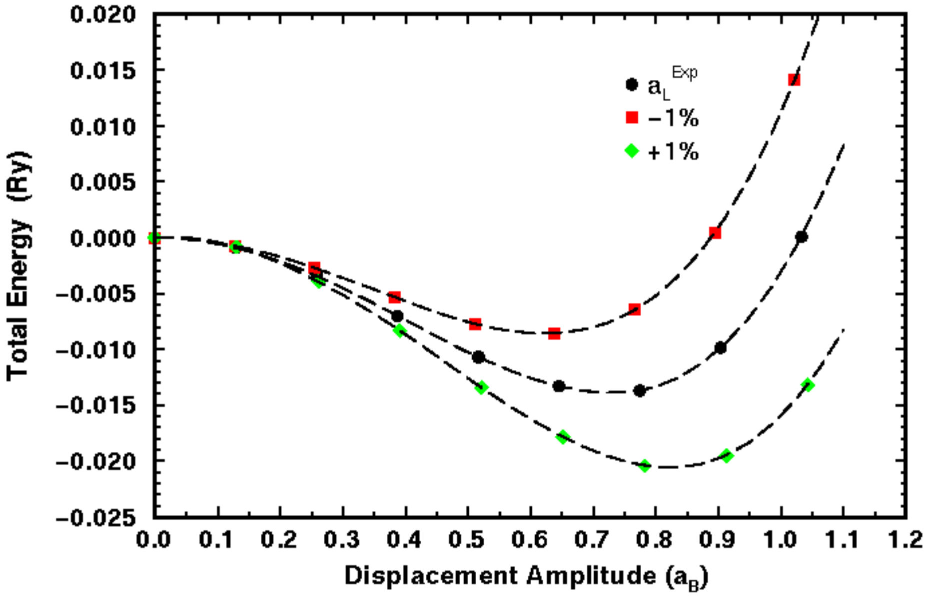


- Distortion around *A* (*A*-O bond lengths)
- Bends *B*-O-*B* bonds but only bond lengths in second order. (*n.b*. breathing mode is usually stiff).
- Driven by pressure and/or tolerance factor ***if octahedra are stiff***.
- Alternate is *A*-site off-centering (Pb).

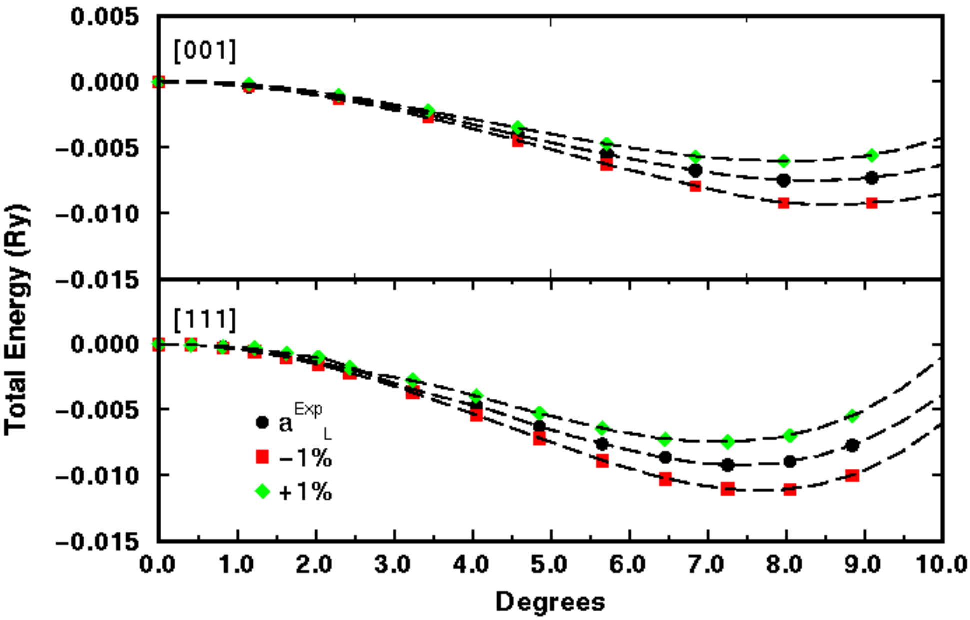
Volume Dependence of Modes (50-50 PZT)

- Fornari and Singh, 2000.

Ferroelectric Mode (Γ)



Rotational Mode (R)



- Volume dependence of FE and Rotational Instabilities is large and opposite.
- Implies co-existence in disordered alloys due to local stress fields.

- Confirmed, Ranjan et al, PRB 2002 (neutron scattering).

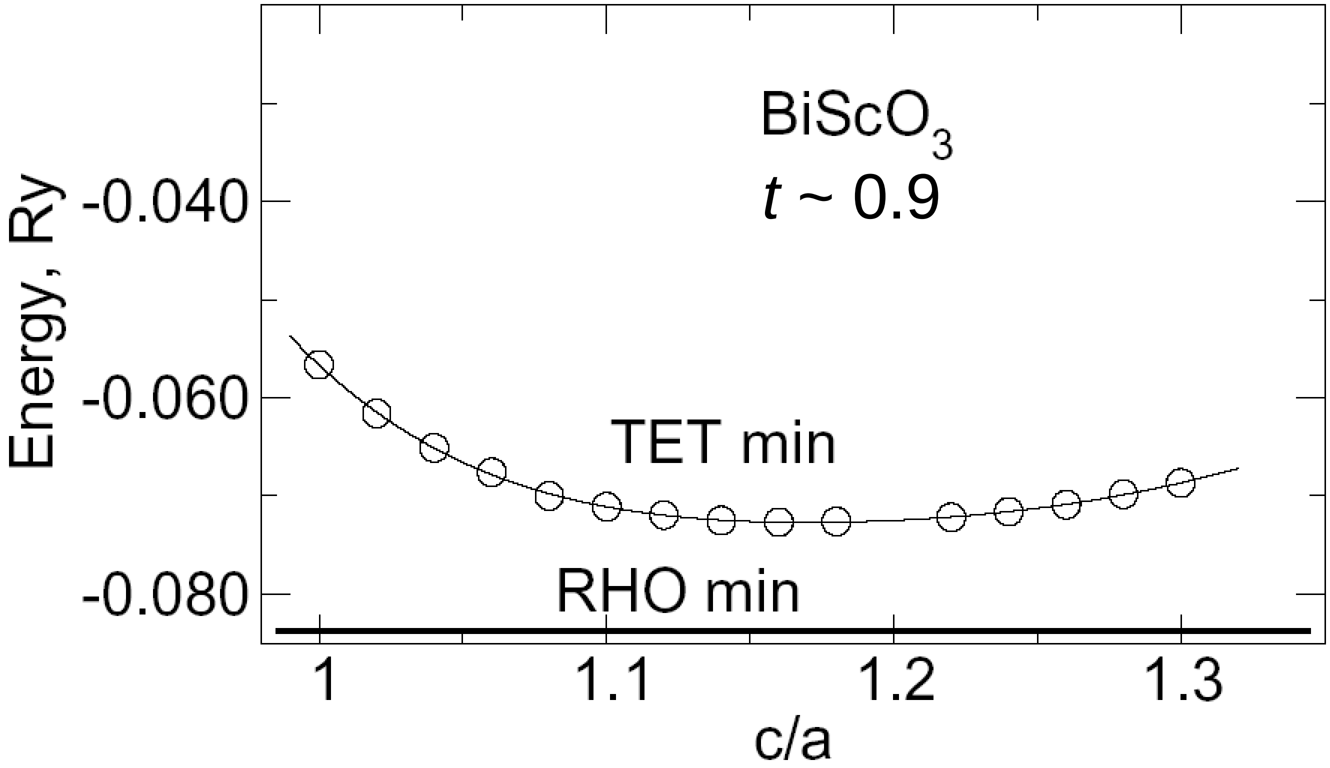
What If …

… we could eliminate the tilt instability from arbitrary $t<1$ perovskites?

First principles ➔ get ferroelectricity

Strain Coupling

Allowing only ferroelectric states & at the LDA lattice parameter:

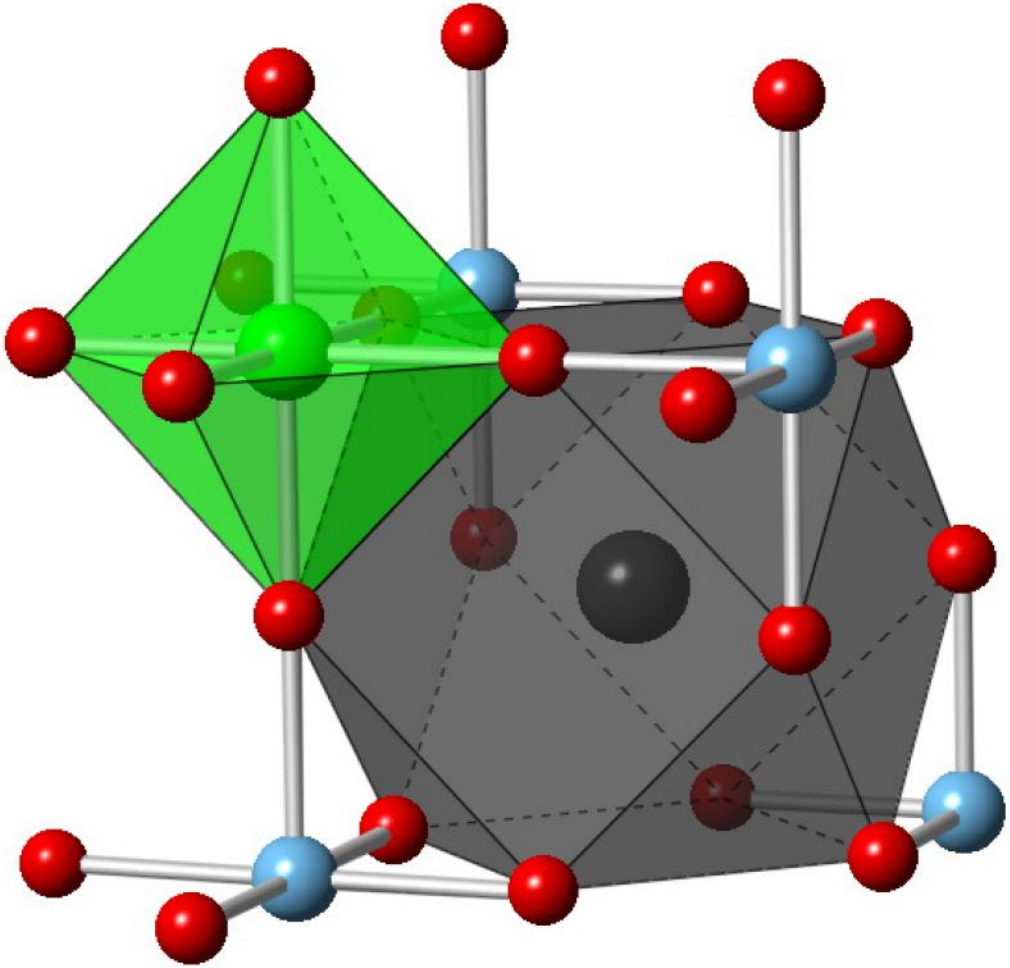


Why are these so different

- Note rhombohedral ferroelectric phase is very much more stable than tetragonal.
- Note large ferroelectric energy.
- Also note the large *c/a* of the tetragonal.

R-FE vs. T-FE LDA ENERGETICS

- A site ion is 12-fold coordinated (very isotropic).
- B site ion is 6-fold (octahedral).



Expectation:

Without strain A-site driven materials (t<1) should be isotropic. With strain they should all be tetragonal.

B-site driven materials (t>1) should be rhombohedral unless strain is very important.

Not true: Reason is cooperativity involving B-site.

Concept of Bond Valence

- I.D. Brown based on crystallography (c.f. ionic radius).
- For a given valence a sum involving bond lengths is nearly constant → A sum involving bond lengths yields valence.

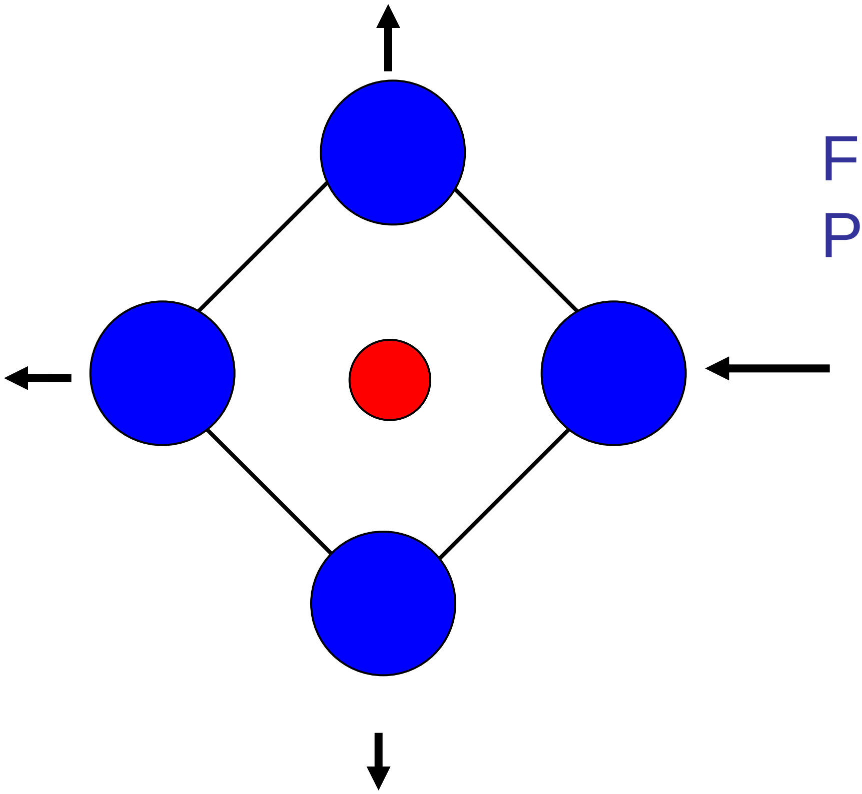
$$V = \sum (v_i) \qquad v_i = \exp\left(\frac{R_0 - R_i}{b}\right)$$

Tables of R_0 and b are in various sources:

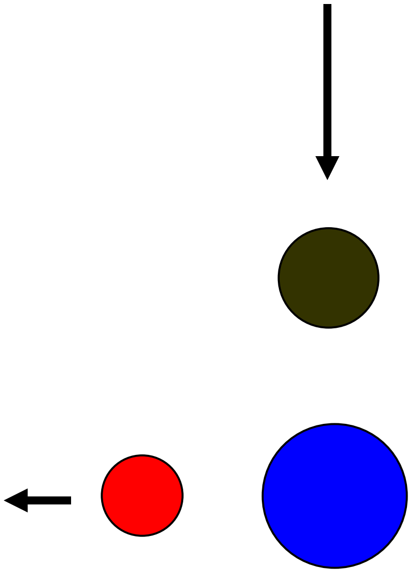
Brown, I. D.; The Chemical Bond in Inorganic Chemistry - The Bond Valence Model. IUCr monographs on Crystallography 12, Oxford University Press, (2002).

Brown, I. D.; in Structure and Bonding in Crystals, edited by M. O'Keeffe & A. Navrotsky, Vol. II, pp. 1-30. New York; Academic Press (1981).

Some Consequences of Bond Valence



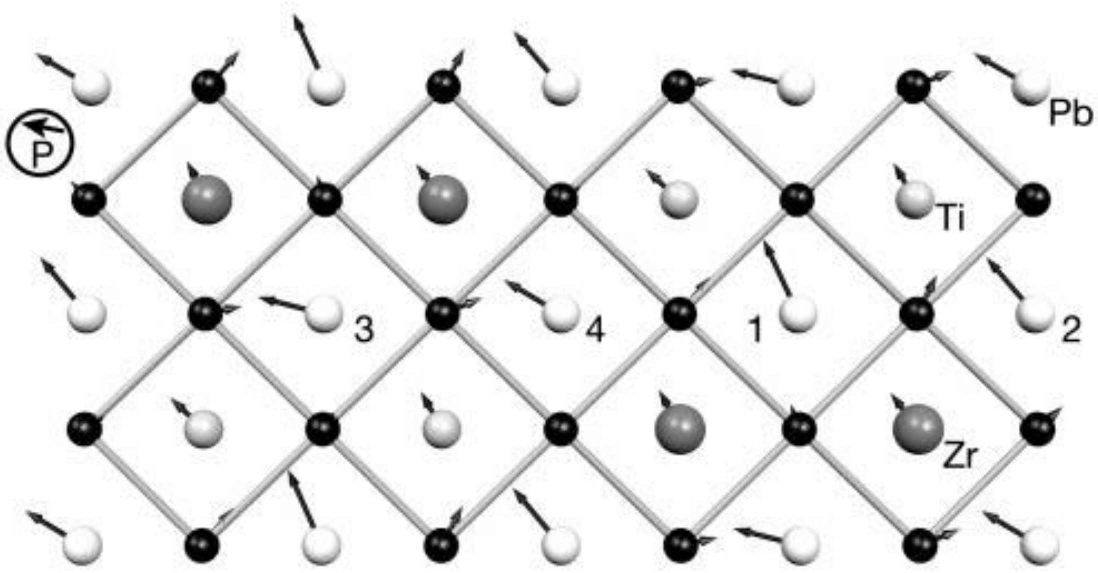
Focusing on metal site:
Push an O in and the others go out.



Focusing on O sites:
Mechanism for interplay of A and B site displacements and local correlations of cation displacements.

Application to Ferroelectrics

- Grinberg, Cooper, Rappe, Nature (2002).
- Structure relaxation of large supercells of PZT.



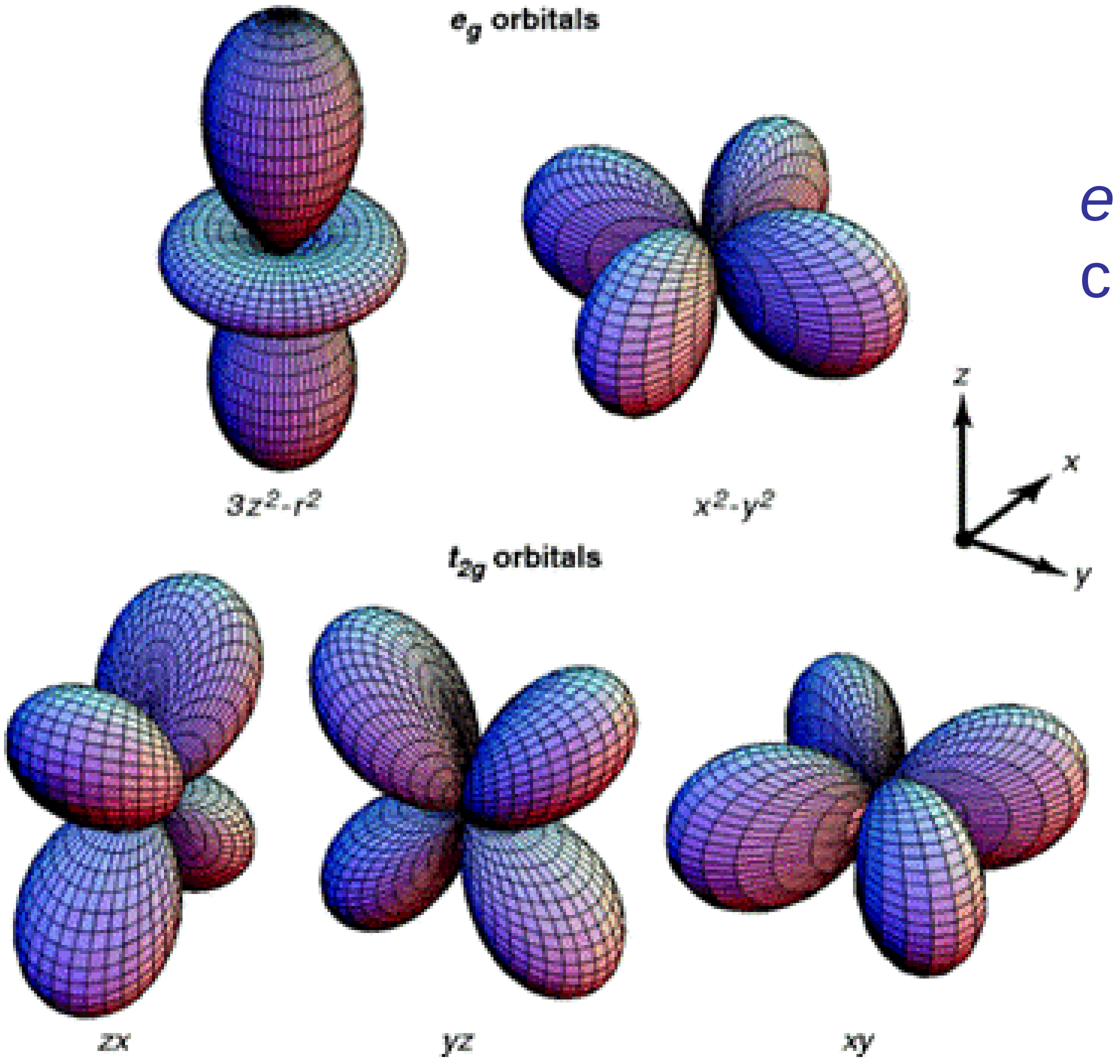
Pb displacements avoid Zr rich directions.

Complex structures with non-collinear cation displacements could be understood in terms of bond valence. Potential model based on this was made and used to study very large cells – PDF’s agree with experiment.

CRYSTAL FIELD AND

JAHN-TELLER DISTORTIONS

The d Orbitals

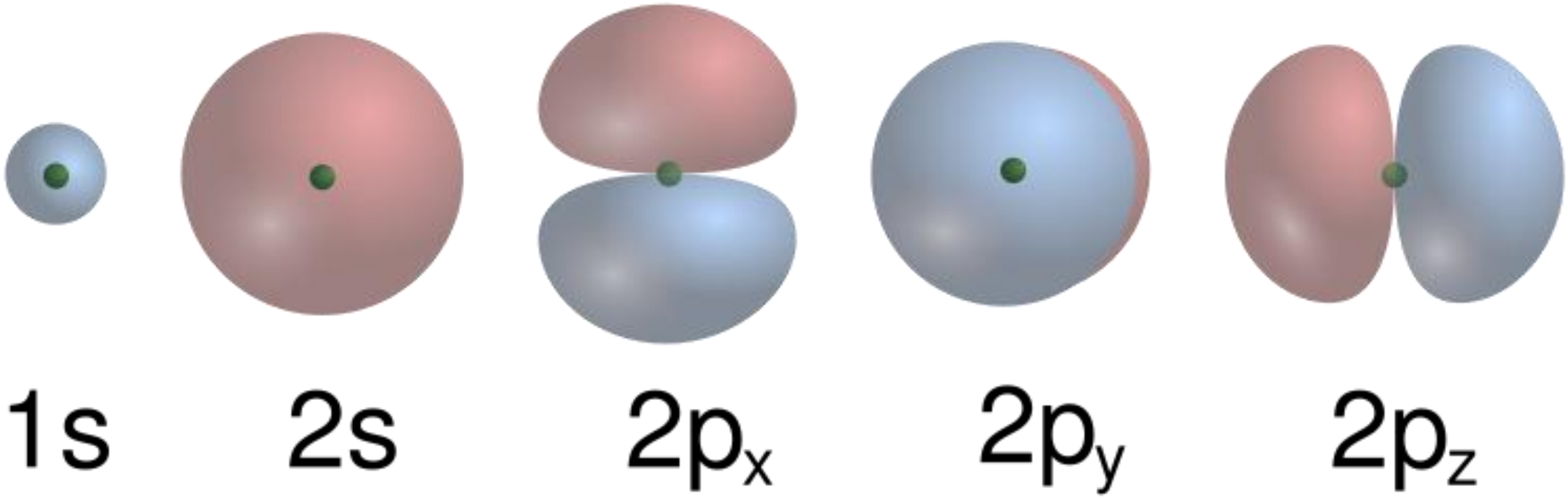


From Vinobalan Durairaj web site

e_g orbitals point at the corners of the octahedron

t_{2g} orbitals do not.

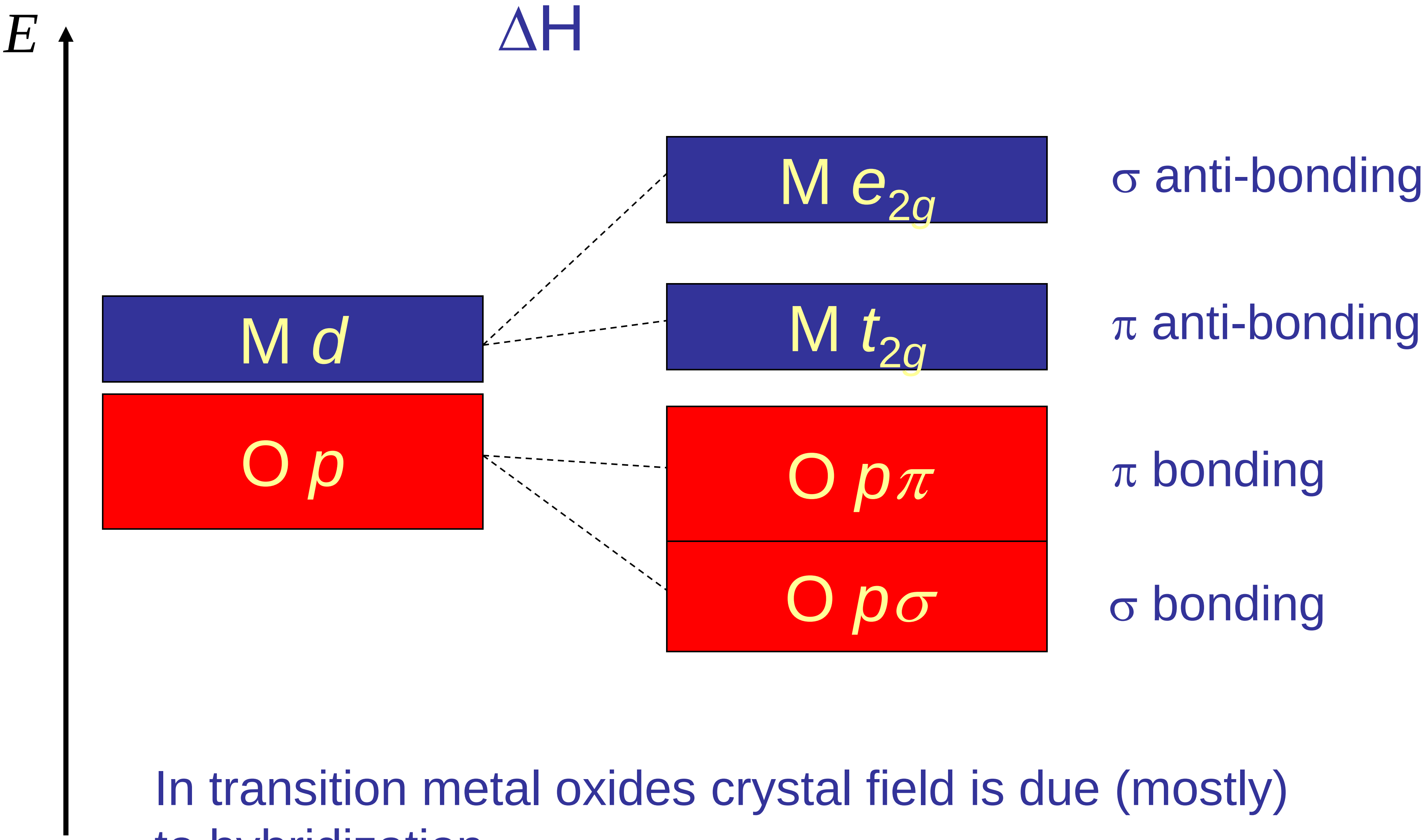
The O p Orbitals



From wikipedia

- One of these (p_σ) points at the center of the octahedron.
- The other two (p_π) are perpendicular.

The Octahedral Crystal Field



E

ΔH

M d

O p

M e_{2g}

M t_{2g}

O $p\pi$

O $p\sigma$

σ anti-bonding

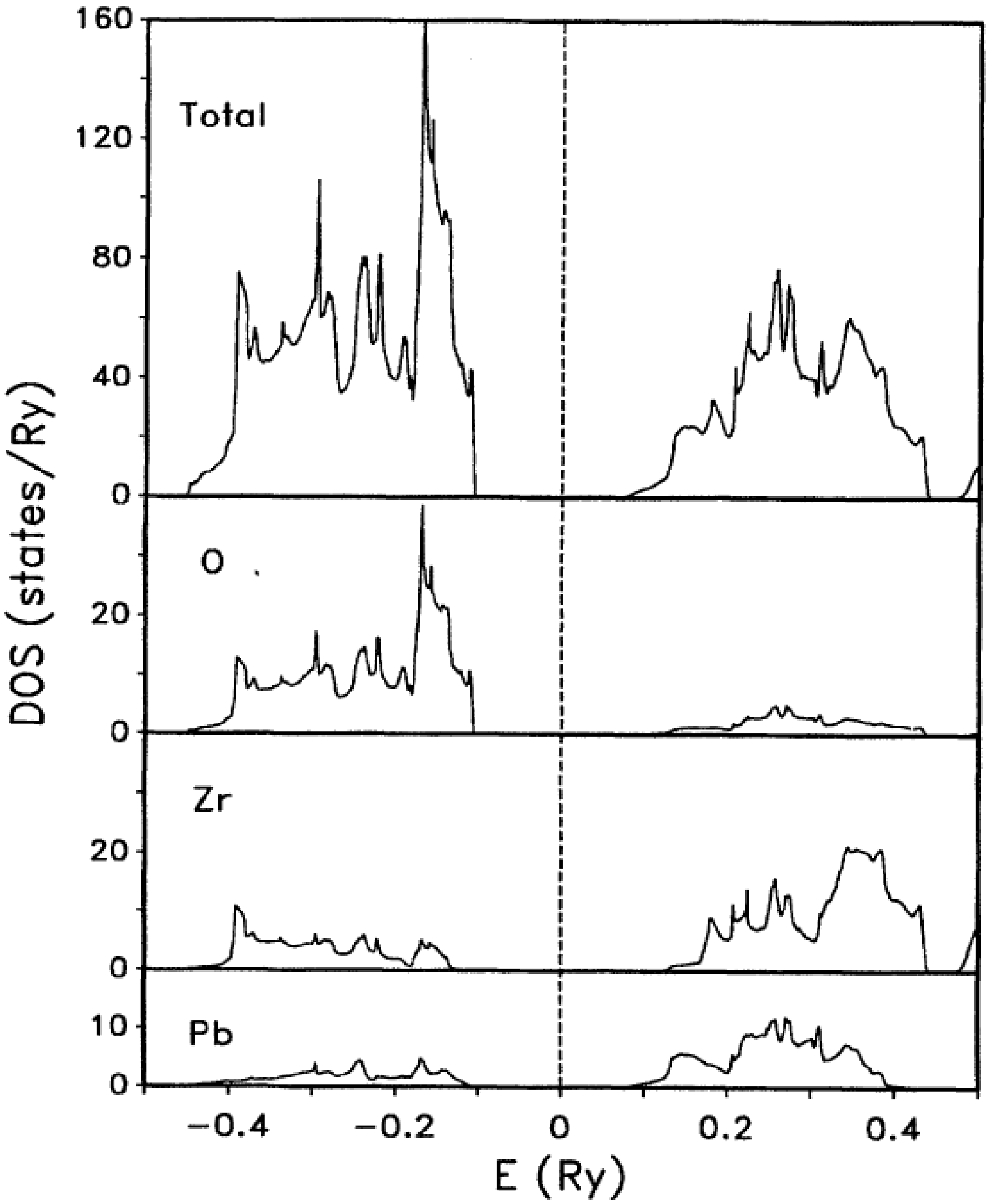
π anti-bonding

π bonding

σ bonding

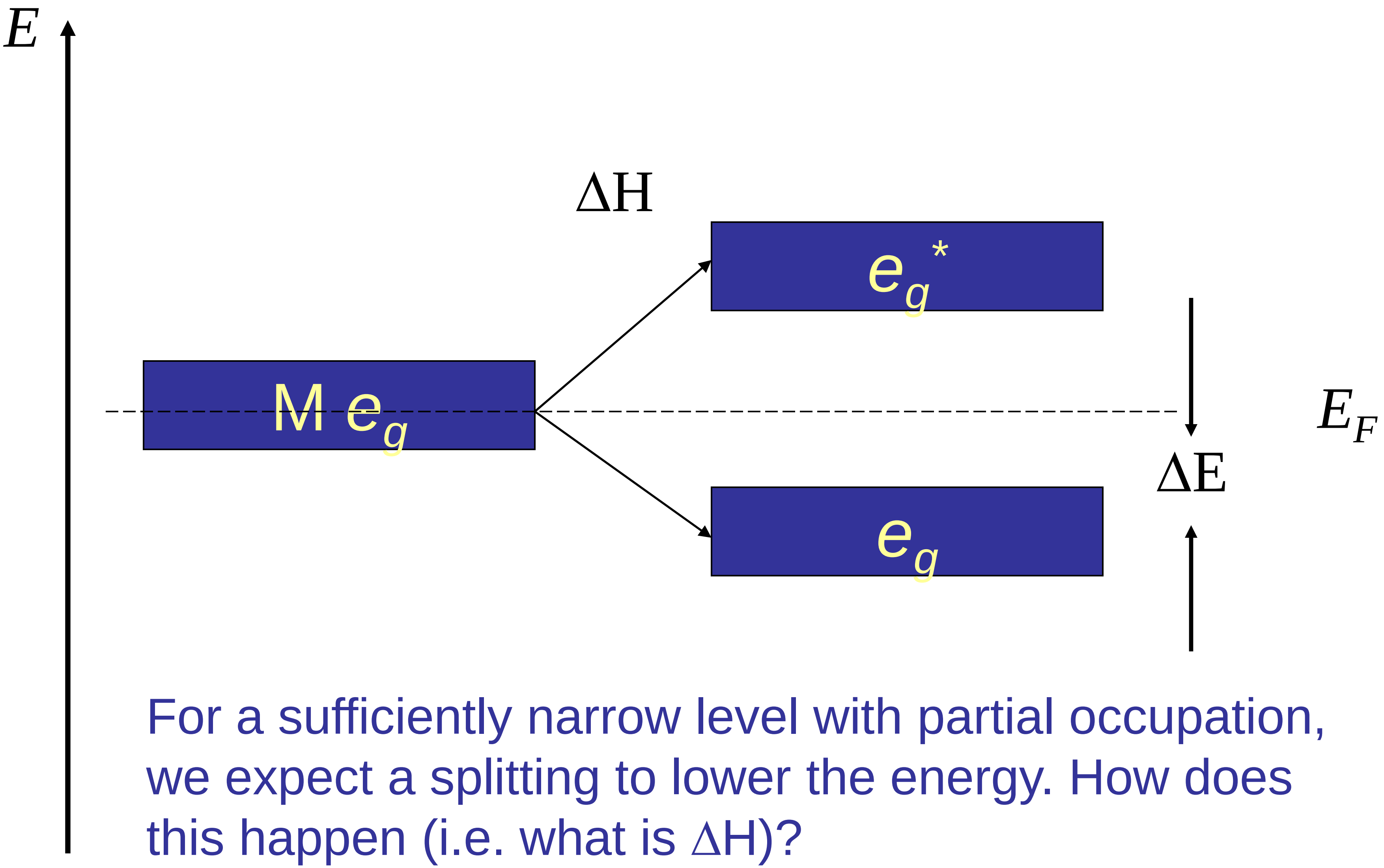
In transition metal oxides crystal field is due (mostly) to hybridization

An Example: $PbZrO_3$ (cubic)



Note Zr d contribution at bottom of O bands

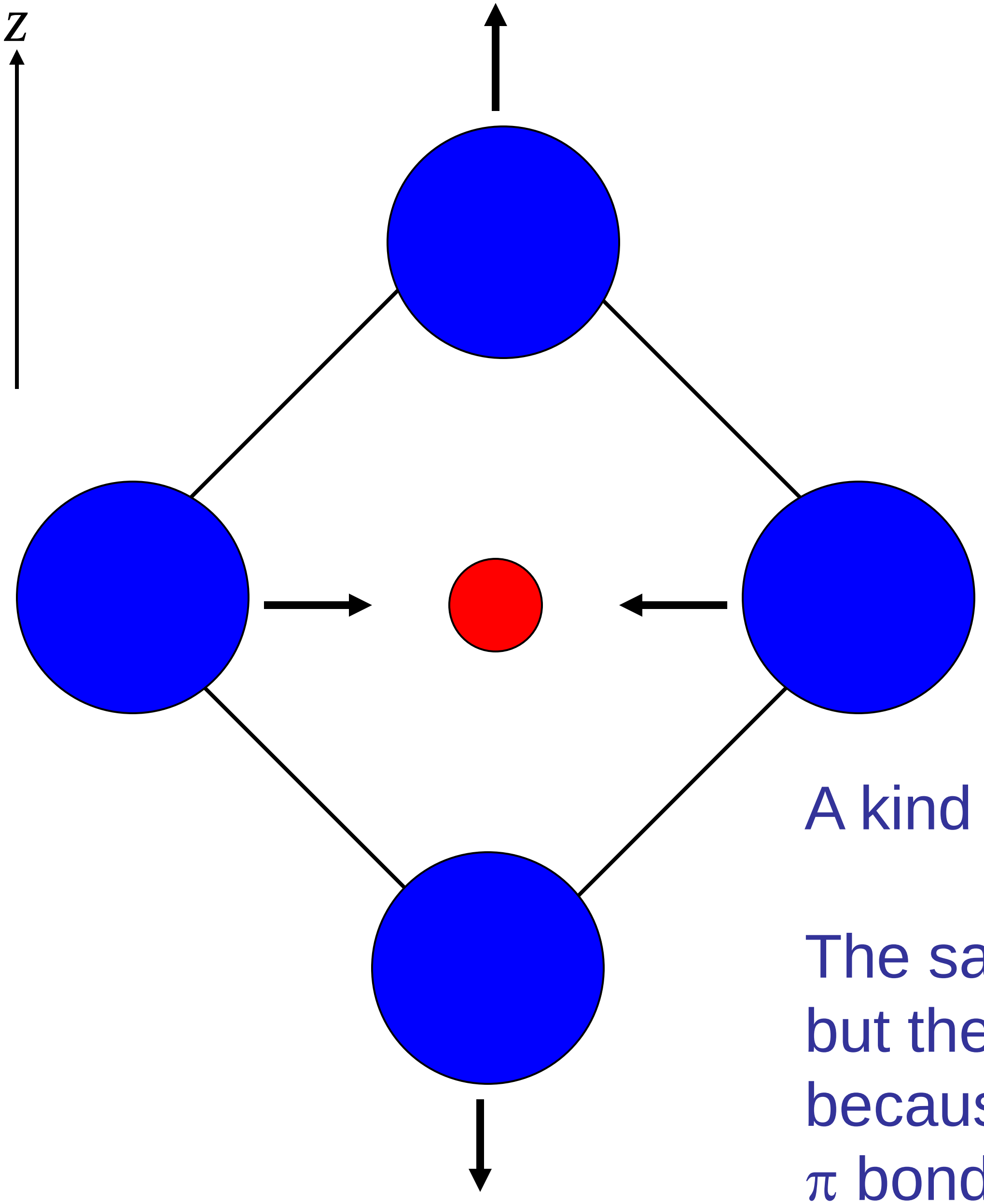
Jahn-Teller Effect

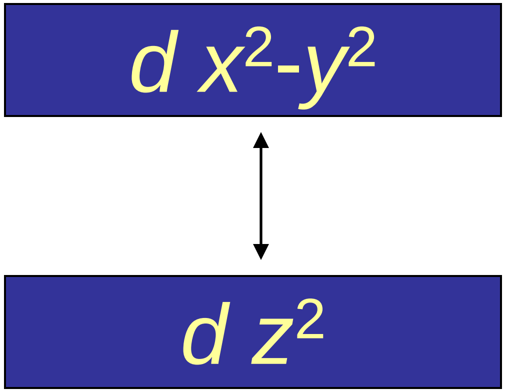


For a sufficiently narrow level with partial occupation, we expect a splitting to lower the energy. How does this happen (i.e. what is ΔH)?

Large band-width works against this.

Jahn-Teller Effect





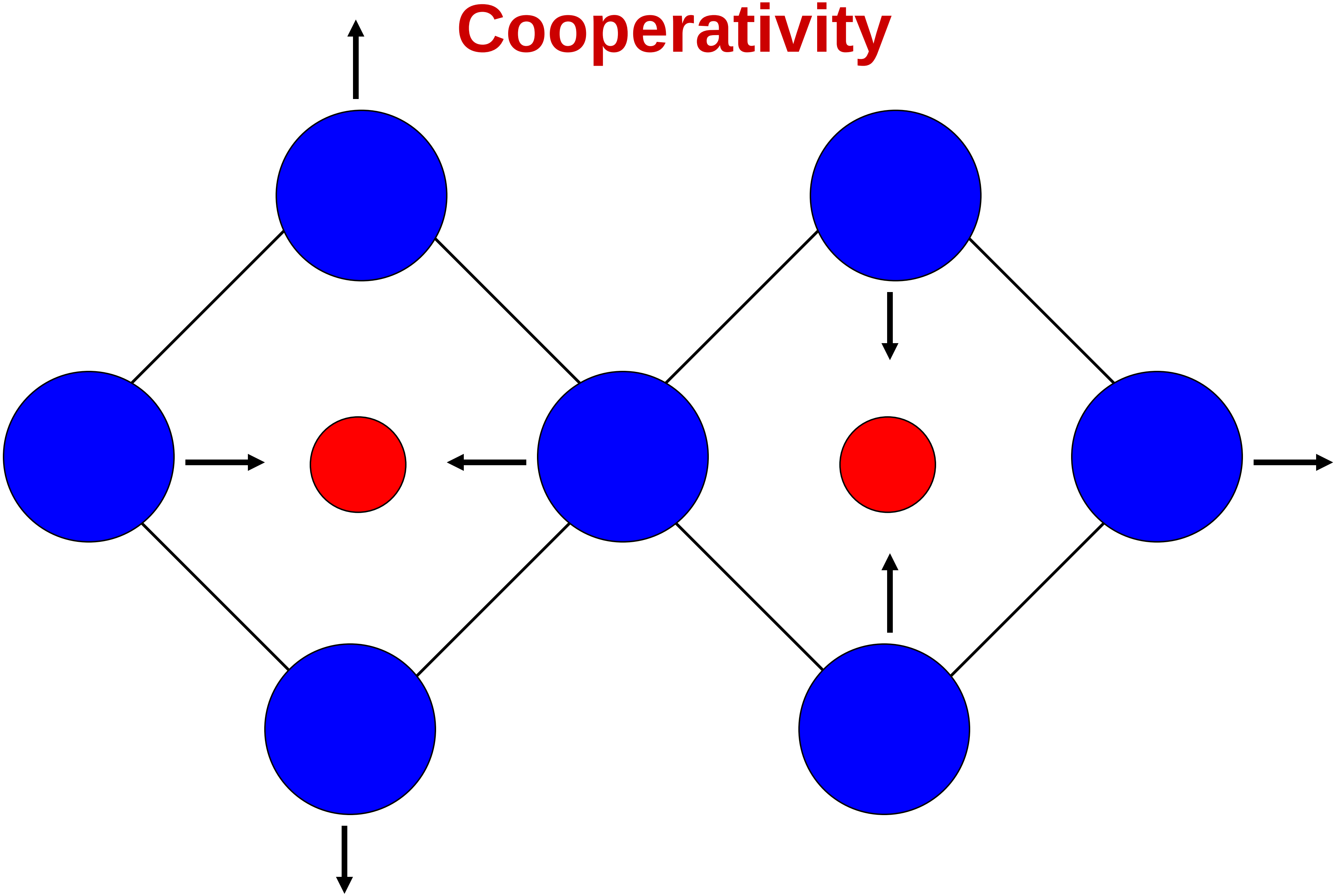
$d\ x^2\text{-}y^2$

$d\ z^2$

A kind of orbital ordering.

The same thing works for t_{2g} orbitals but the effect is (much) smaller because these are involved in weak π bonds instead of strong σ bonds

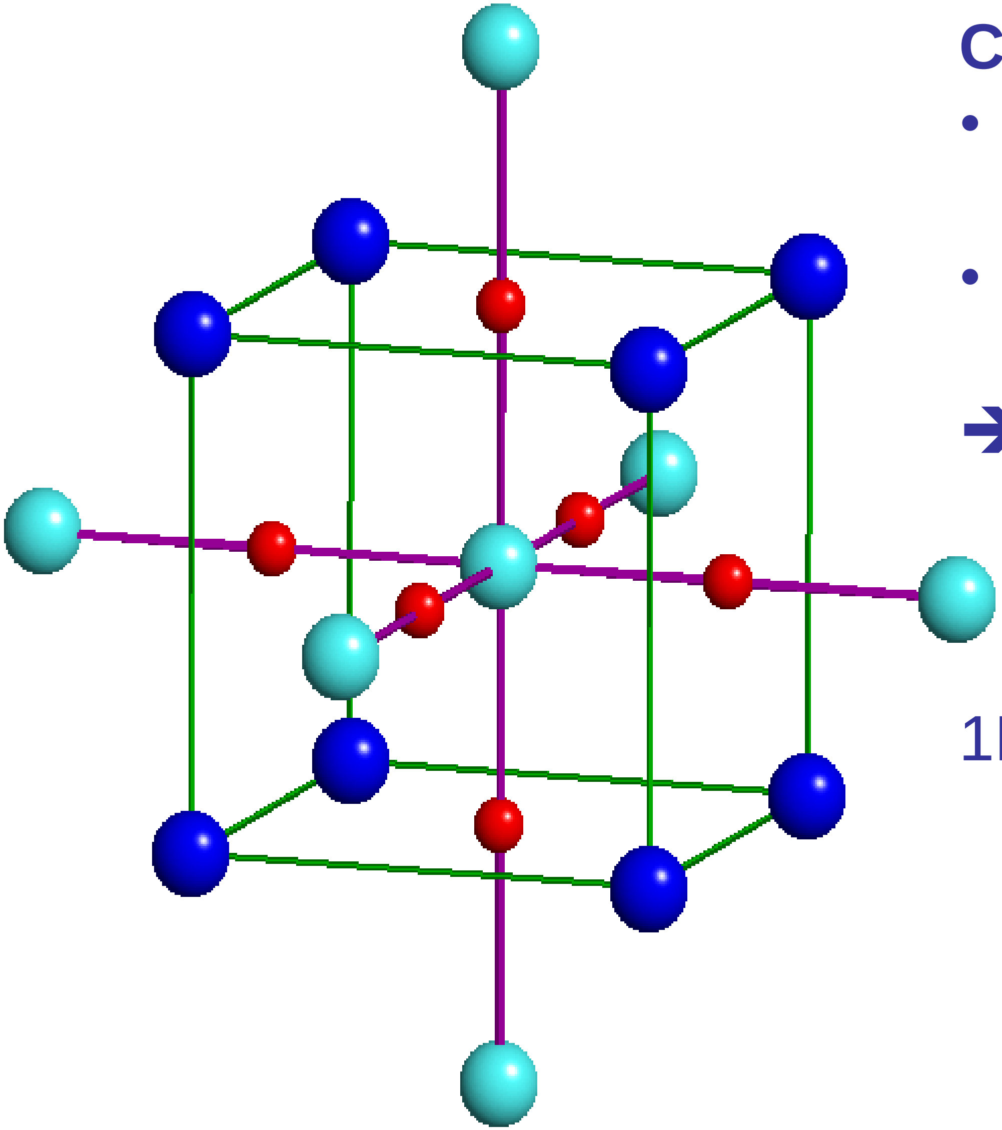
Cooperativity



Jahn-Teller is long range – corresponding zone boundary modes have long coherence length (zone center also possible – ferroelastic)

BAND FORMATION (e_g and t_{2g})

Geometric Considerations (O and B-site)



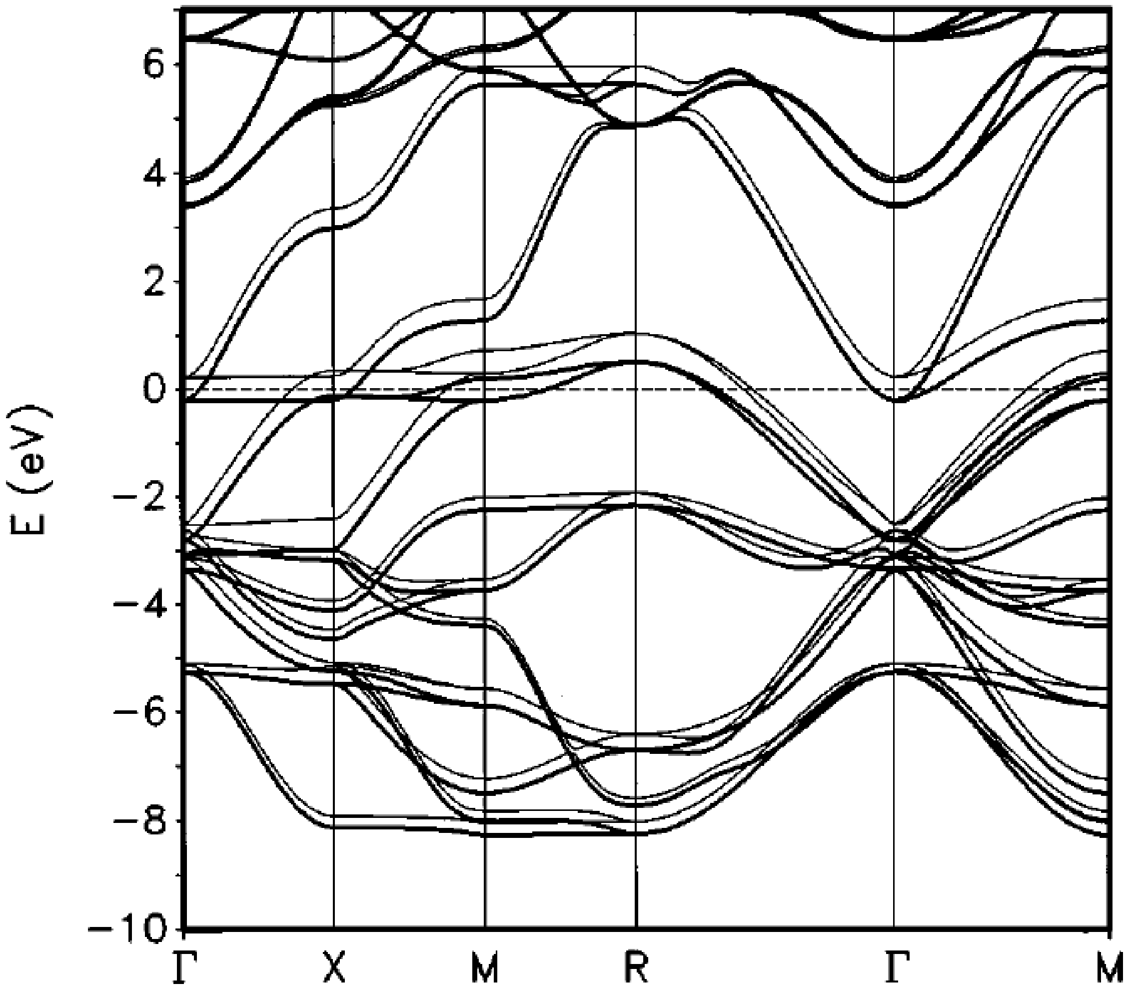
Cubic structure:

- O – O distance is *a*/√2 (can have direct hopping)
- B – B distance is *a* (too far for much direct hopping).

➔Metal bands are formed via hopping through O.

1D linear chains along Cartesian directions ➔ 1D and 2D bands.

Geometric Considerations (O and B-site)

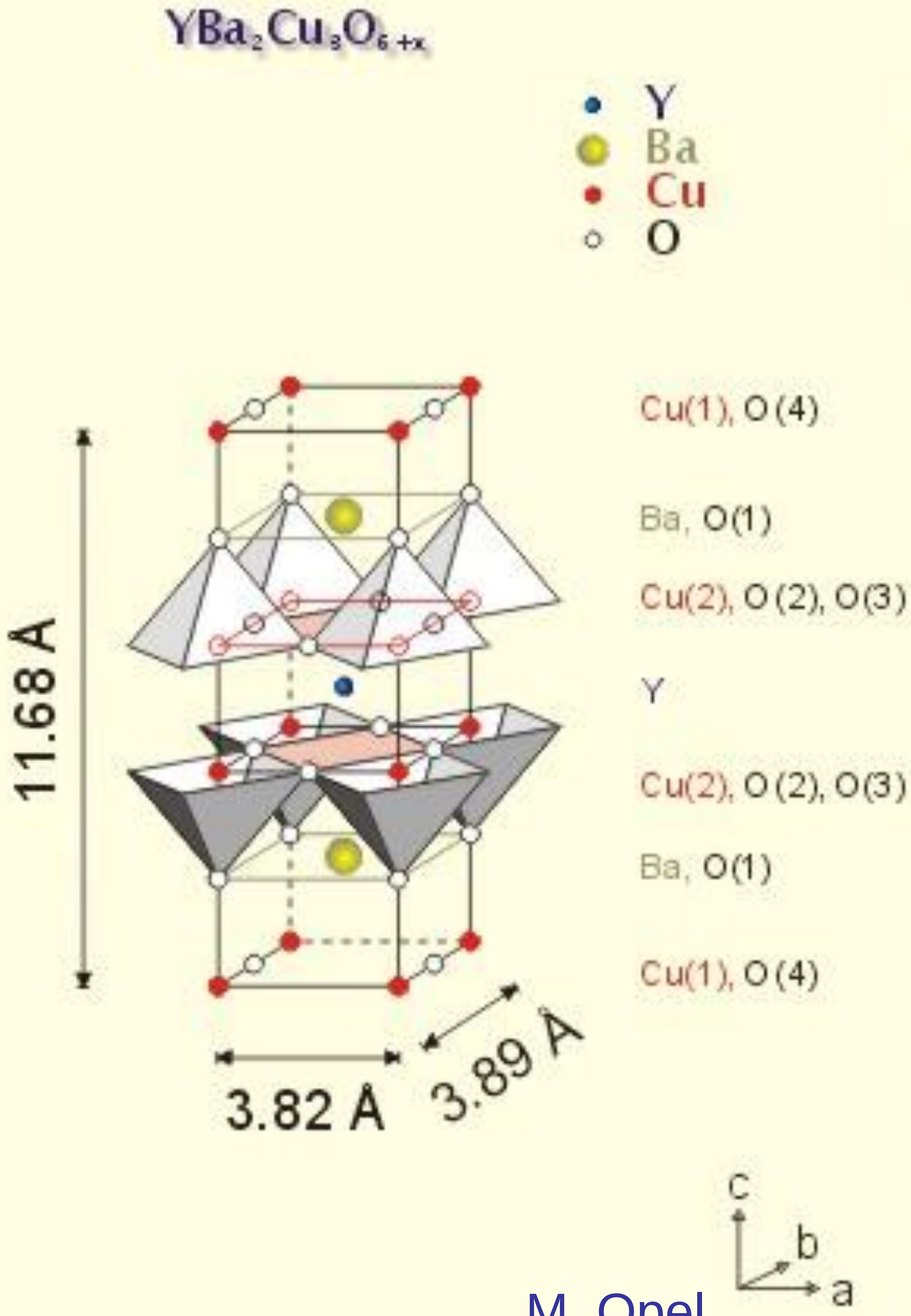


Cubic SrRuO$_3$

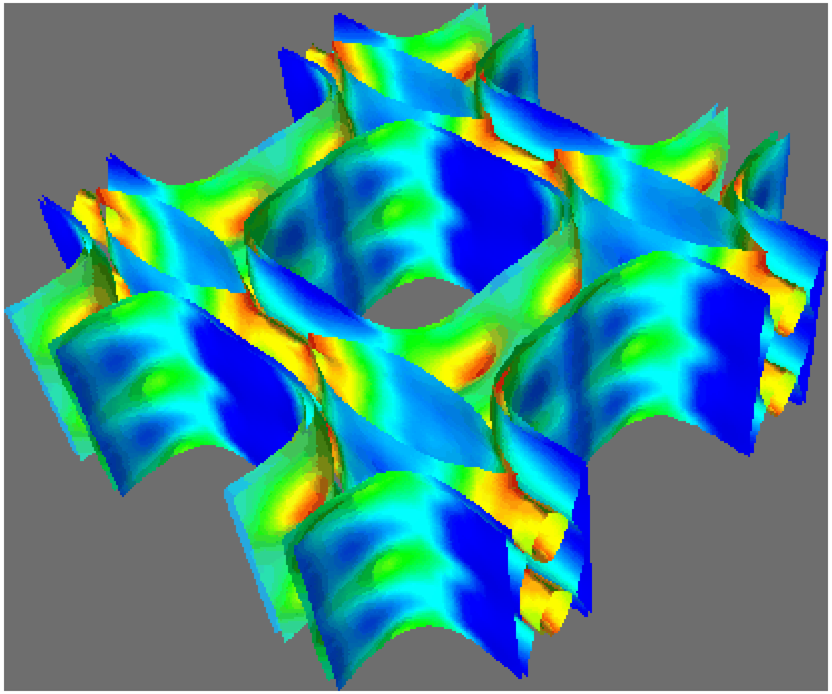
Flat bands

Planar Fermi surfaces (e.g. cubes rather than spheres).

High-T_c Electronic Structures are 2D



M. Opel

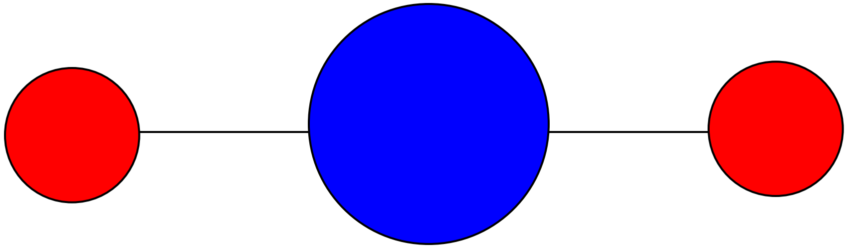


Pickett, Cohen, Krakauer, Singh

Hopping Through O

O p_x,p_y,p_z point along Cartesian directions (90 degrees apart):

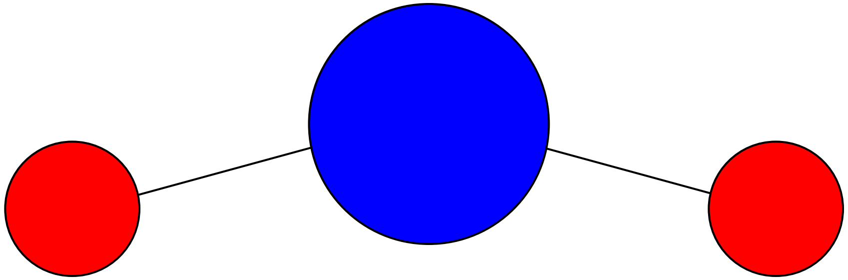
Cubic:



- Maximum $pd\sigma$ hopping.
- Wide e_g bands.

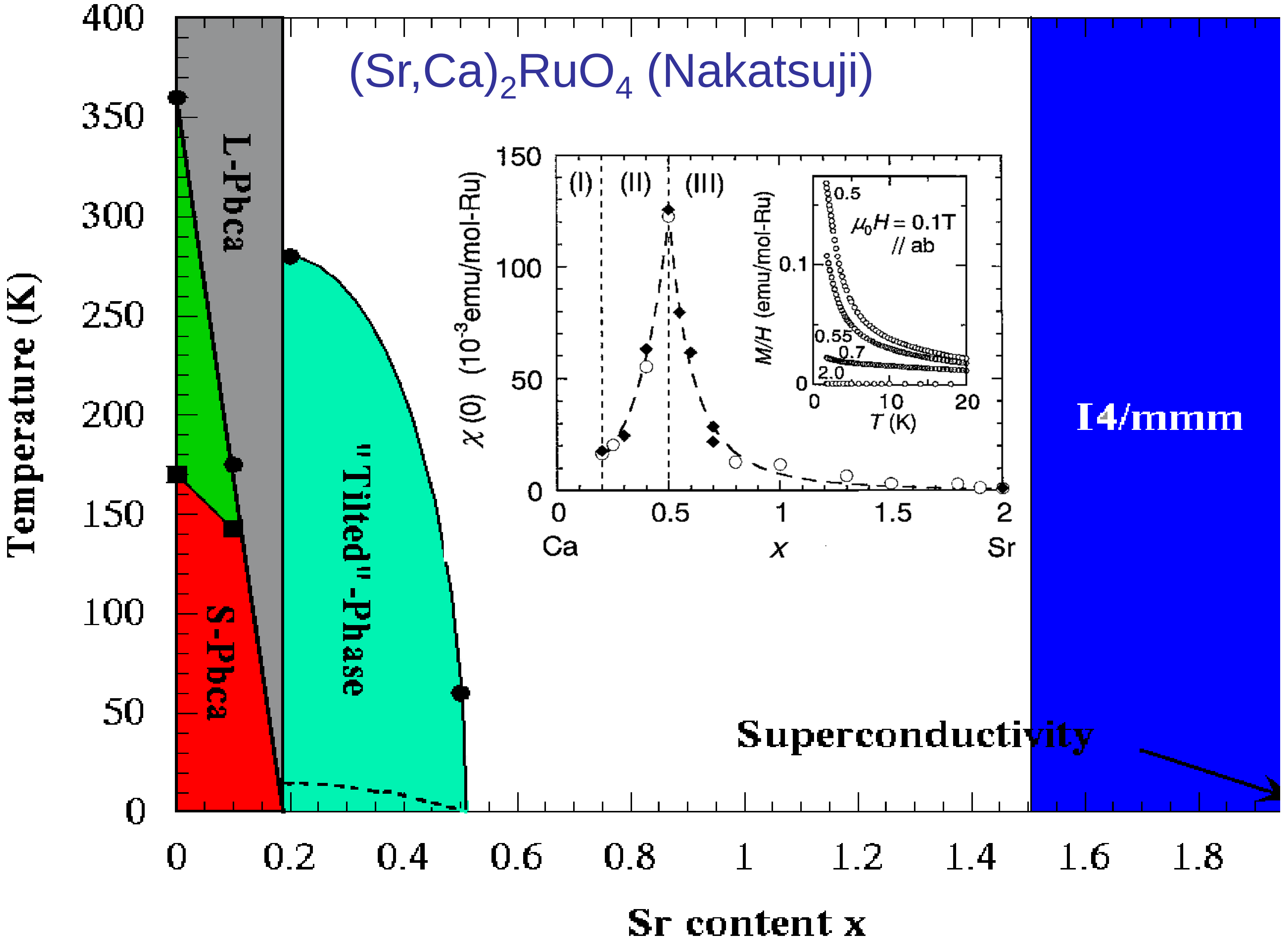
Tilts reduce band width but do not reduce hybridization (i.e. crystal field).

Tilted:



- Reduced $pd\sigma$ hopping.
- Narrower e_g bands.
- Additional splittings due to symmetry lowering.
- Can broaden t_{2g} bands depending on details.
- Direct m-m hopping.

Tilts and Hopping Through O



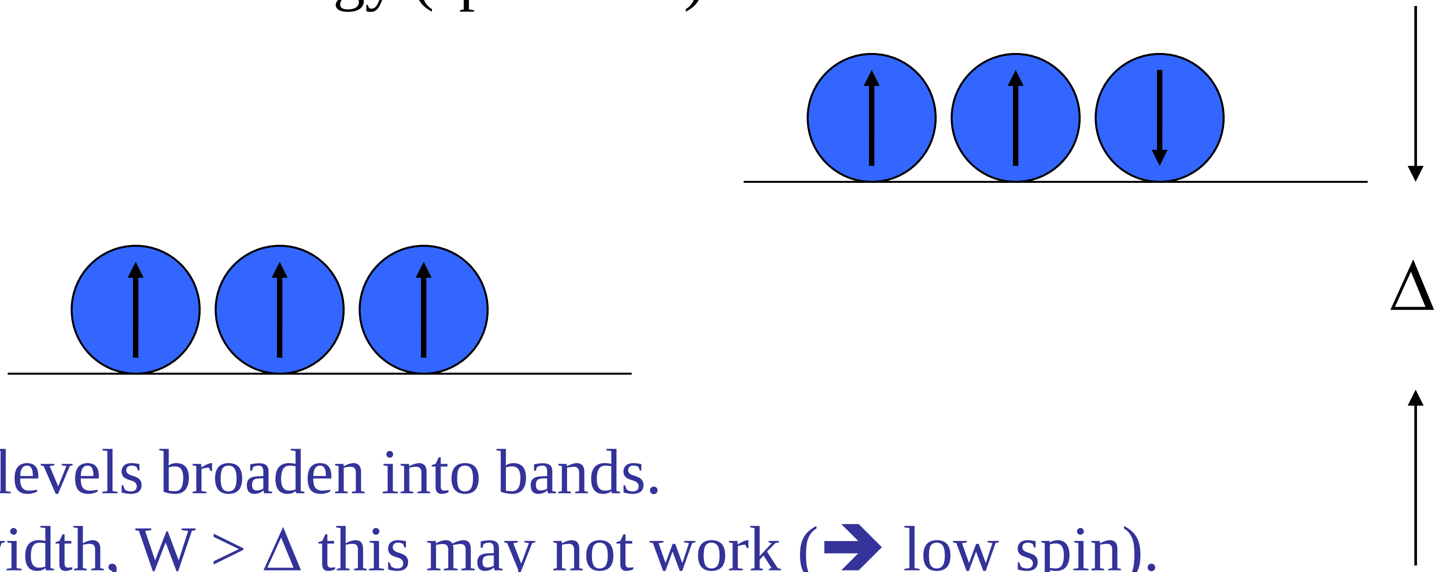
$(Sr,Ca)_2RuO_4$ (Nakatsuji)

MAGNETISM: Moment Formation

Local Atomic Moments (Hund's Rules)

1. For a given electron configuration, the term with maximum multiplicity (maximum *S*) has the lowest energy (exchange / Coulomb correlation).
2. For a given multiplicity, the term with the largest value of *L* has the lowest energy (Coulomb correlation).
3. For a given term, in an atom with outermost sub-shell half-filled or less, the level with the lowest value of *J* lies lowest in energy. If the outermost shell is more than half-filled, the level with highest value of *J* is lowest in energy (spin-orbit).

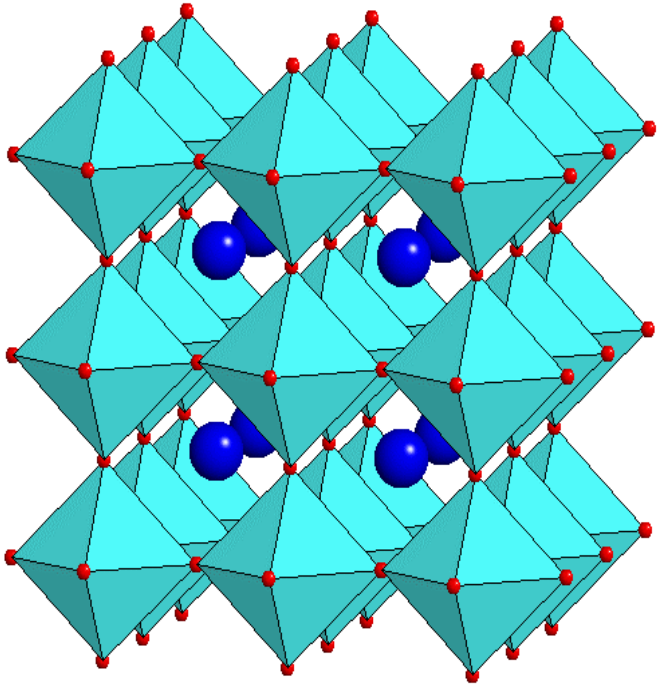
1st Rule:

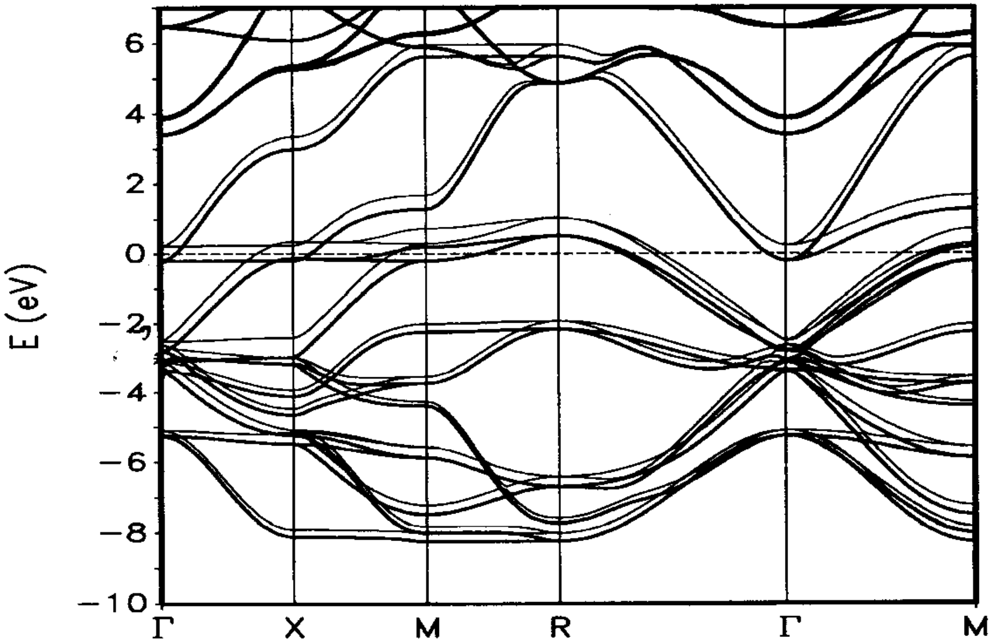


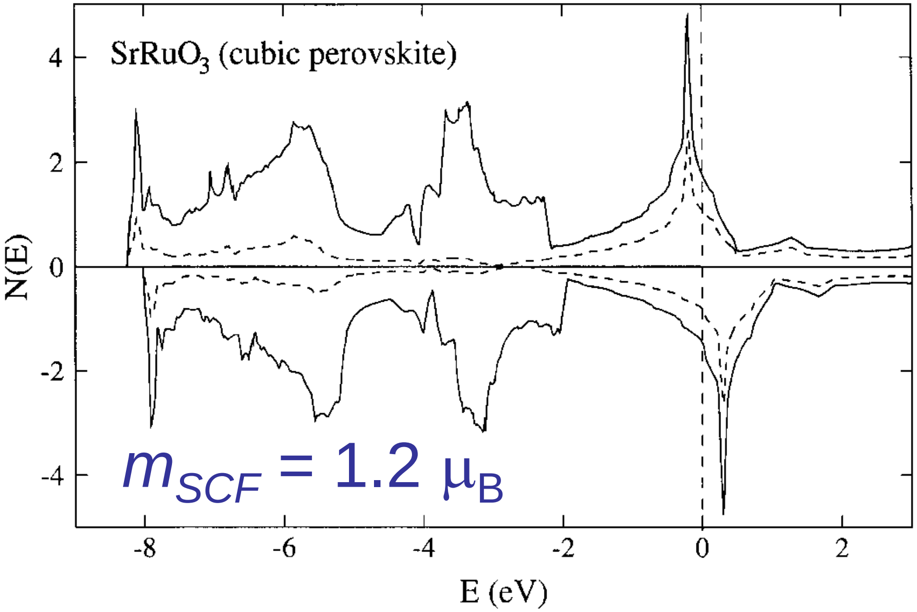
In solids levels broaden into bands.

If band width, W > Δ this may not work (➔ low spin).

Stoner Model (Itinerant Magnets)







$m_{SCF} = 1.2\ \mu_B$

Band structure effects can lead to high degeneracy near E_F → magnetic instability and energy lowering.

Stoner Criterion:

$N(E_F)I > 1$

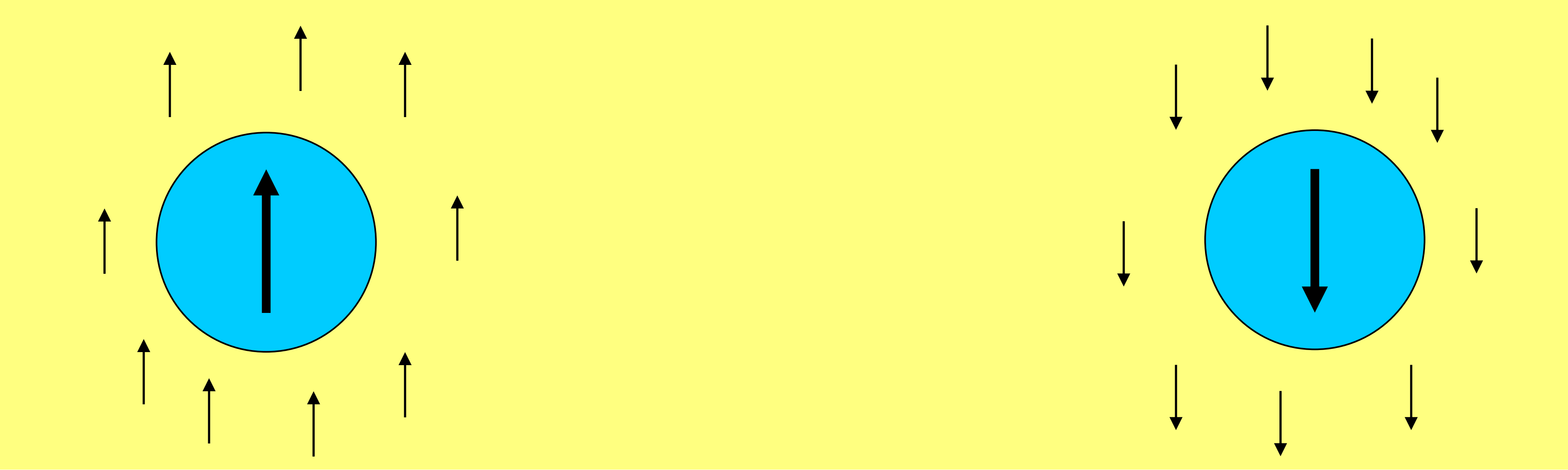
$I \sim 0.7 – 0.9$ eV for d elements.

Interaction Between Moments (Exchange)

- Moment formation by itself is not magnetism. Ordering is required, and therefore interactions between moments on different sites are what underlie magnetism.

- Some Mechanisms:
  - Direct exchange – two atoms are touching (or very close) so that their wavefunctions overlap. The interaction is like that which gives rise to Hund’s first rule. It can be positive or negative depending on the separation of the atoms, but it falls off very strongly with distance.
  - Super Exchange – coupling of spins through spin dependent overlap typically involving other atoms.
  - Conduction electron mediated exchange: e.g. RKKY, magnetic semiconductors … Moments interact with conduction electrons which mediate the coupling.

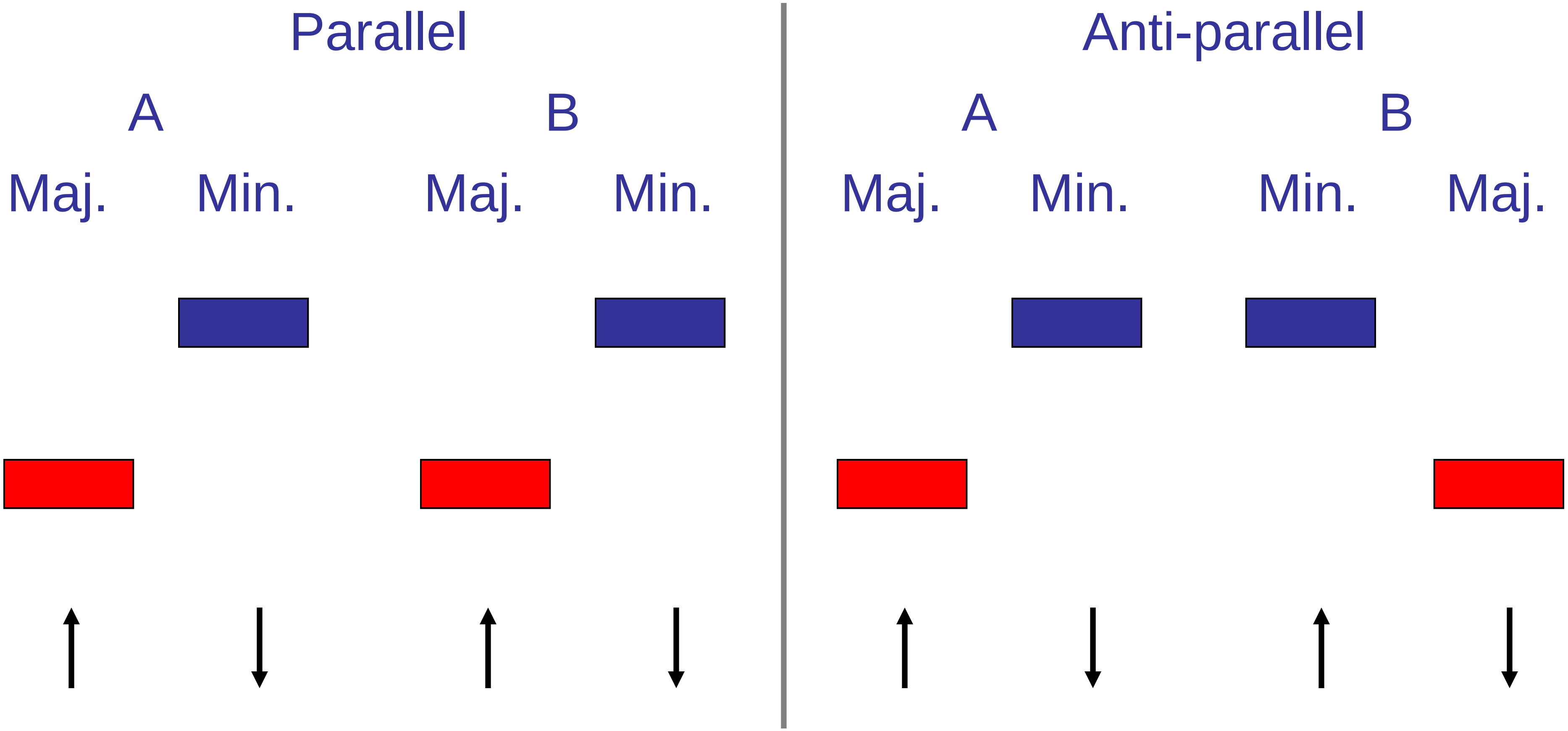
Conduction Electron Mediated Exchange



In weak interacting limit medium has some response, $\chi(\mathbf{q})$, which defines the interaction through $\chi(\mathbf{r}_i-\mathbf{r}_j)$. More generally the response may differ for strong interactions at short range but at long distance would still take RKKY type form in a metal.

Super Exchange and Related

Consider two magnetic ions which interact via O and consider parallel and anti-parallel alignments of the moments:



Parallel

A

Maj. Min.

B

Maj. Min.

Anti-parallel

A

Maj. Min.

B

Min. Maj.

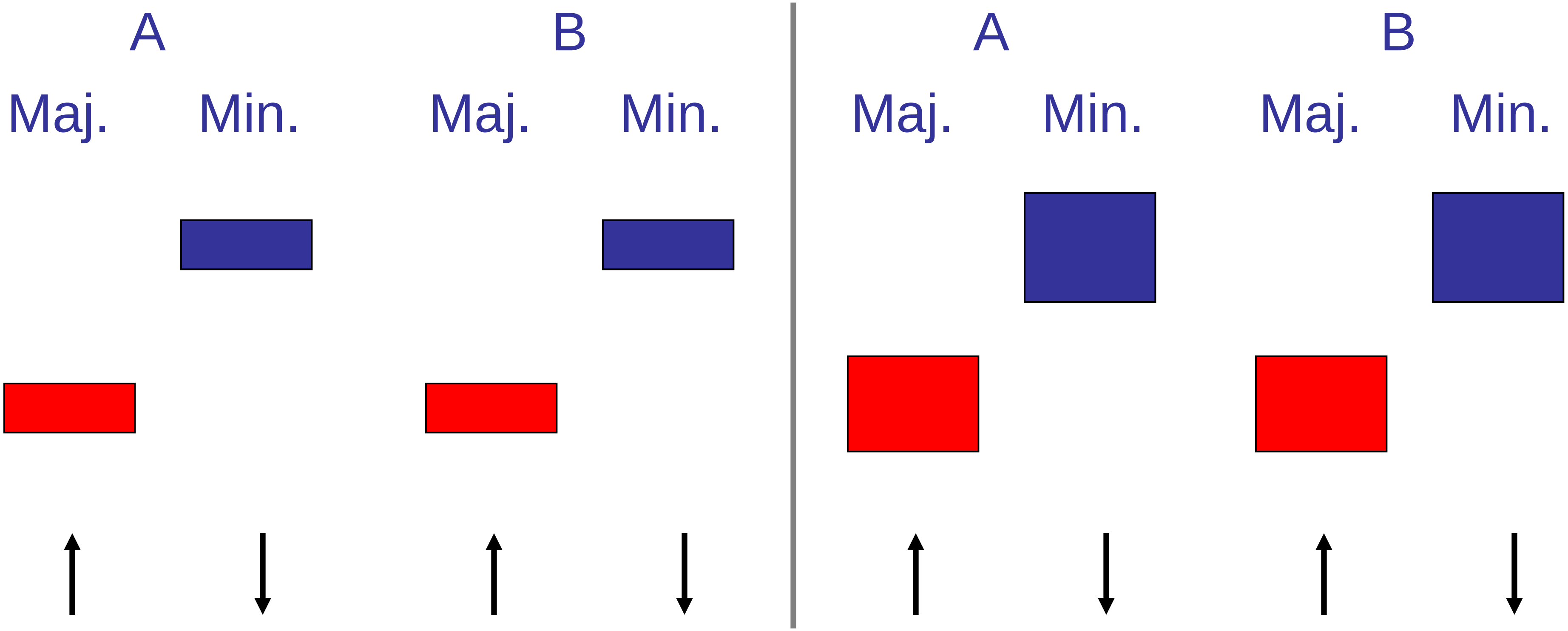
Global Spin Direction

Band Formation

In the absence of spin orbit and non-collinear structures hopping is separate for spin up and spin down.

Parallel Case:

Parallel Case with hopping:



A

B

Maj. Min. Maj. Min.

A

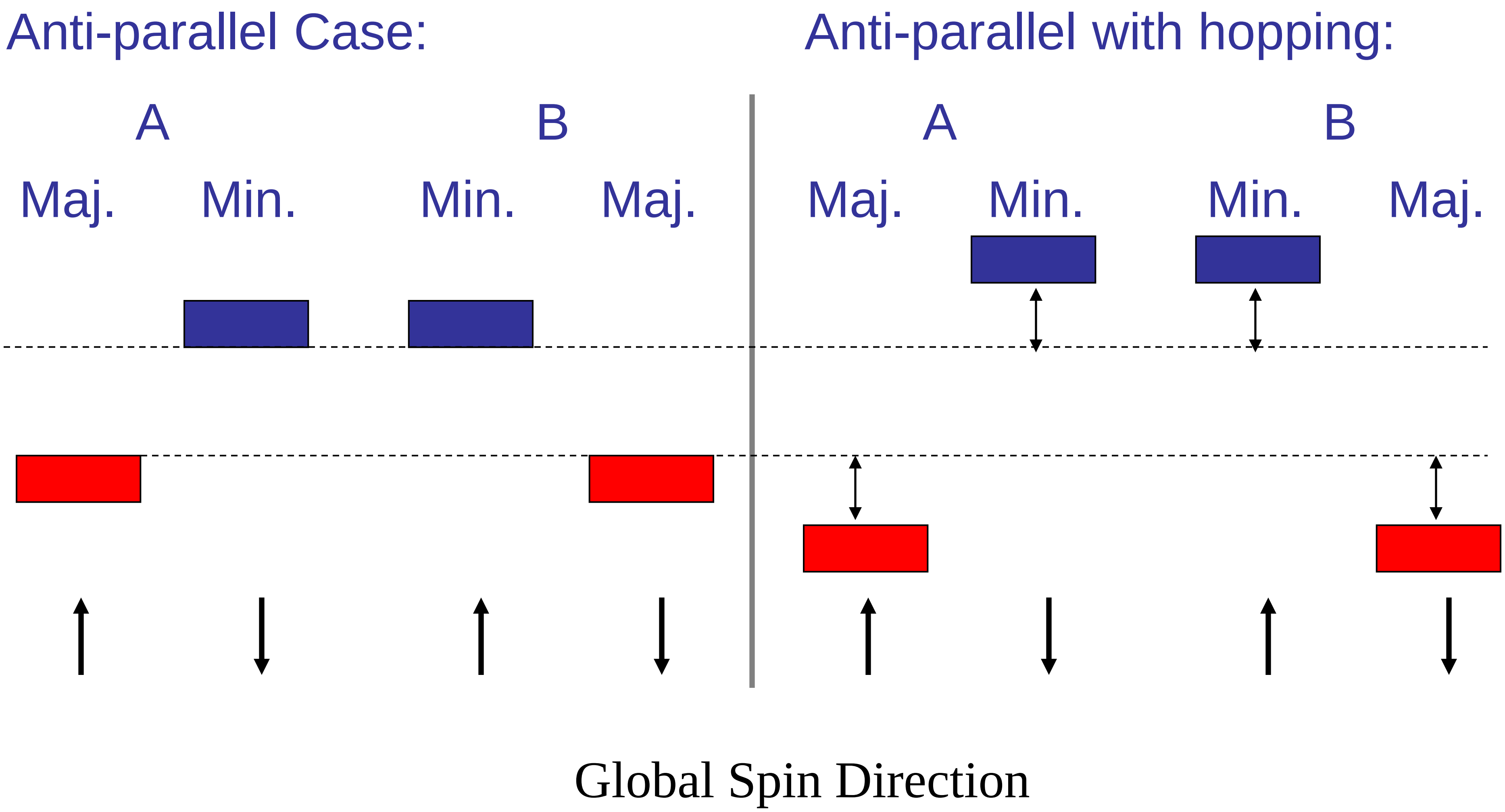
B

Maj. Min. Maj. Min.

Global Spin Direction

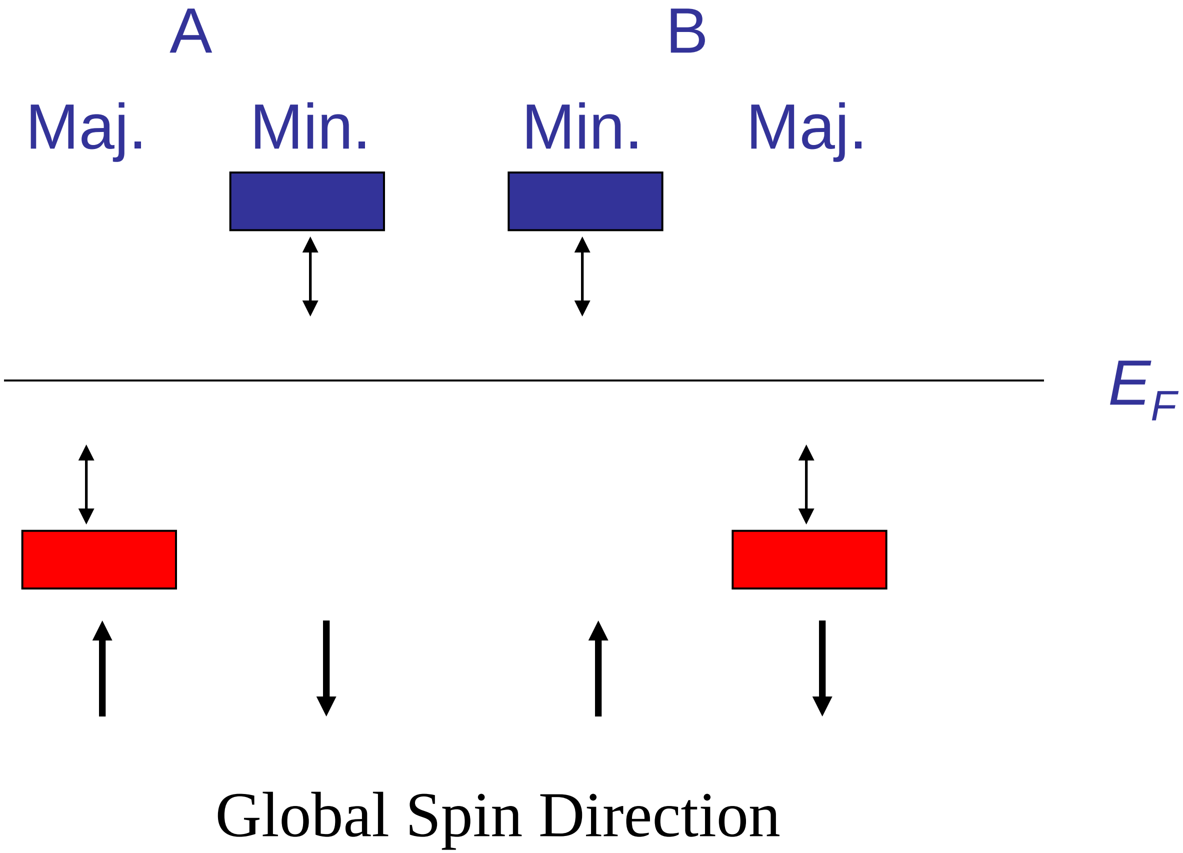
Band Formation

In the absence of spin orbit and non-collinear structures hopping is separate for spin up and spin down.



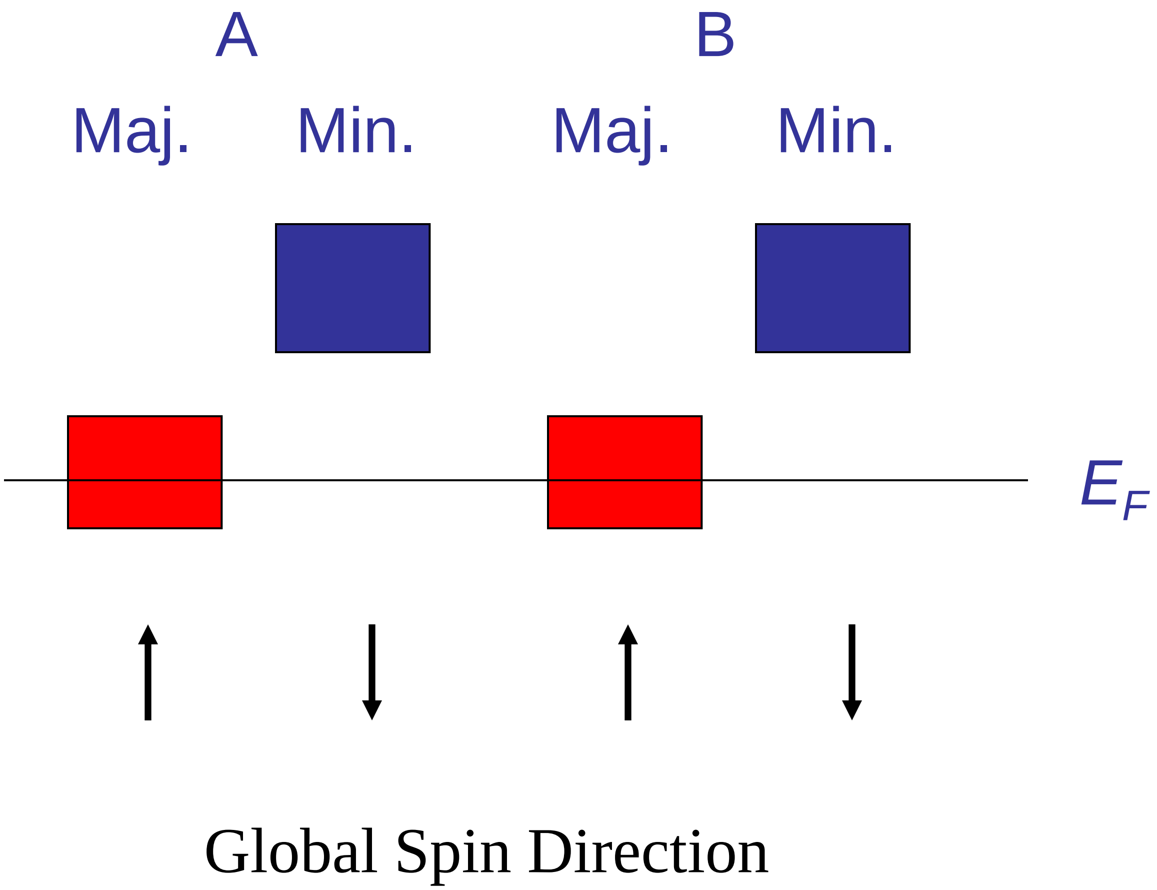
Antiferromagnetic Super Exchange

Anti-parallel with hopping:



Average energy of ***occupied states*** is lowered. Favors antiferromagnetic alignment (super exchange)

Ferromagnetic Exchange



A

B

Maj. Min. Maj. Min.

E_F

↑ ↓ ↑ ↓

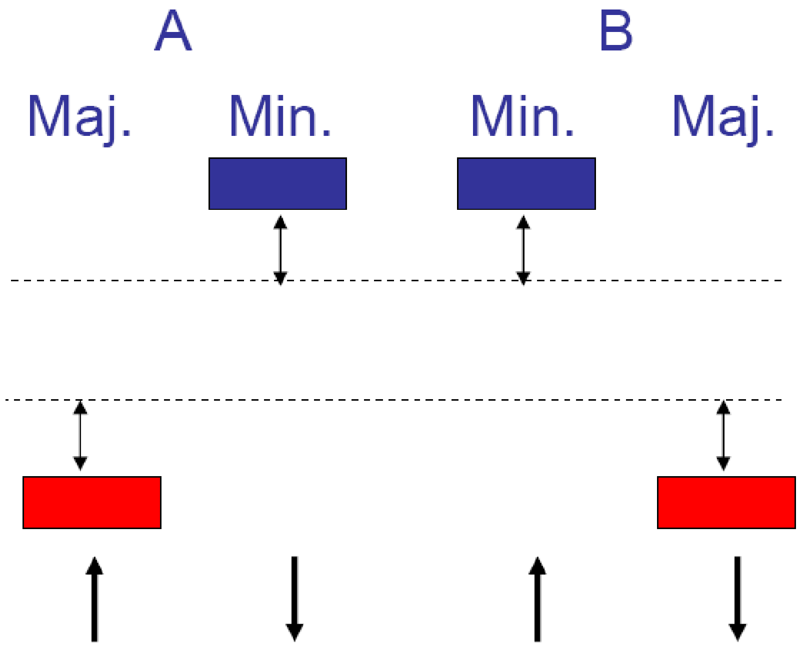
Global Spin Direction

Average energy of ***occupied states*** is lowered. Favors ferromagnetic alignment (super exchange).

This is the nature of the double exchange in manganites: It competes with Jahn-Teller, which would split the e_g level.

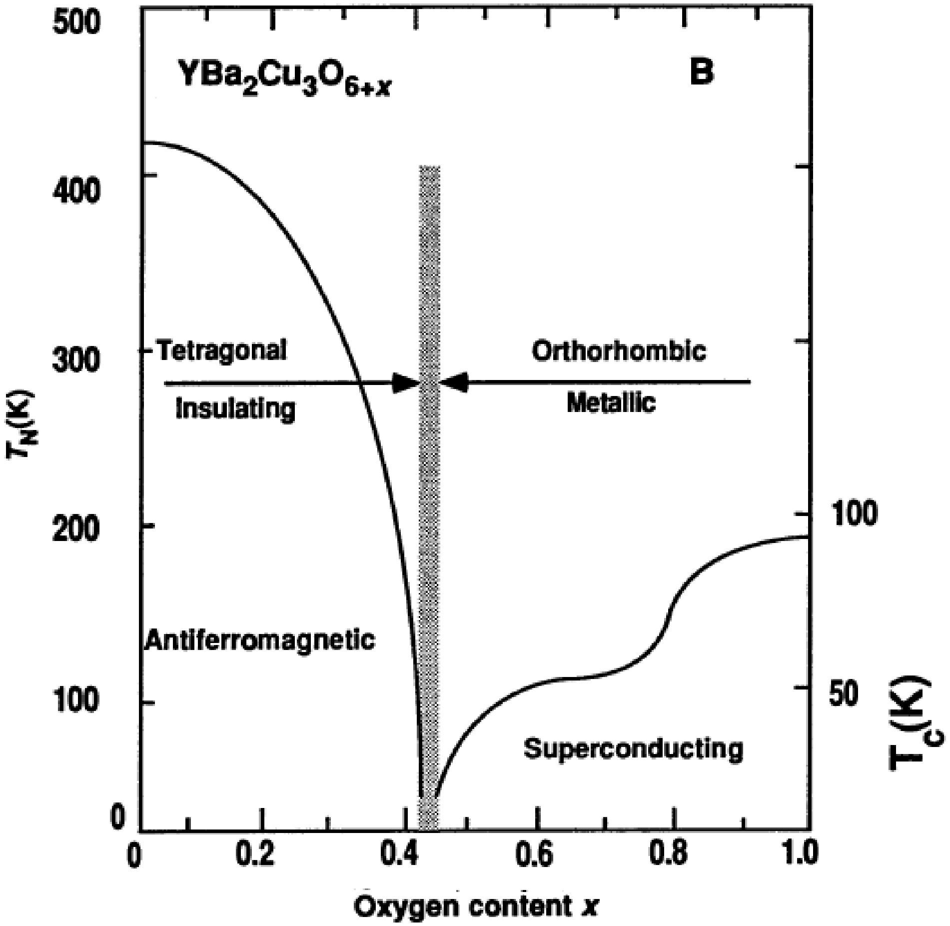
What Favors Strong Super Exchange?

1. High spin state.
2. Bond angles that favor M – O – M hopping (i.e. 180º for e_g).
3. Strong hybridization with O.
    - Large orbitals that overlap strongly with O (e_g much better than t_{2g}).
    - Short M-O neighbor distances.
    - *d*-states that are close in energy to the O *p* states (e.g. high metal valence states like Cu^{2+}).

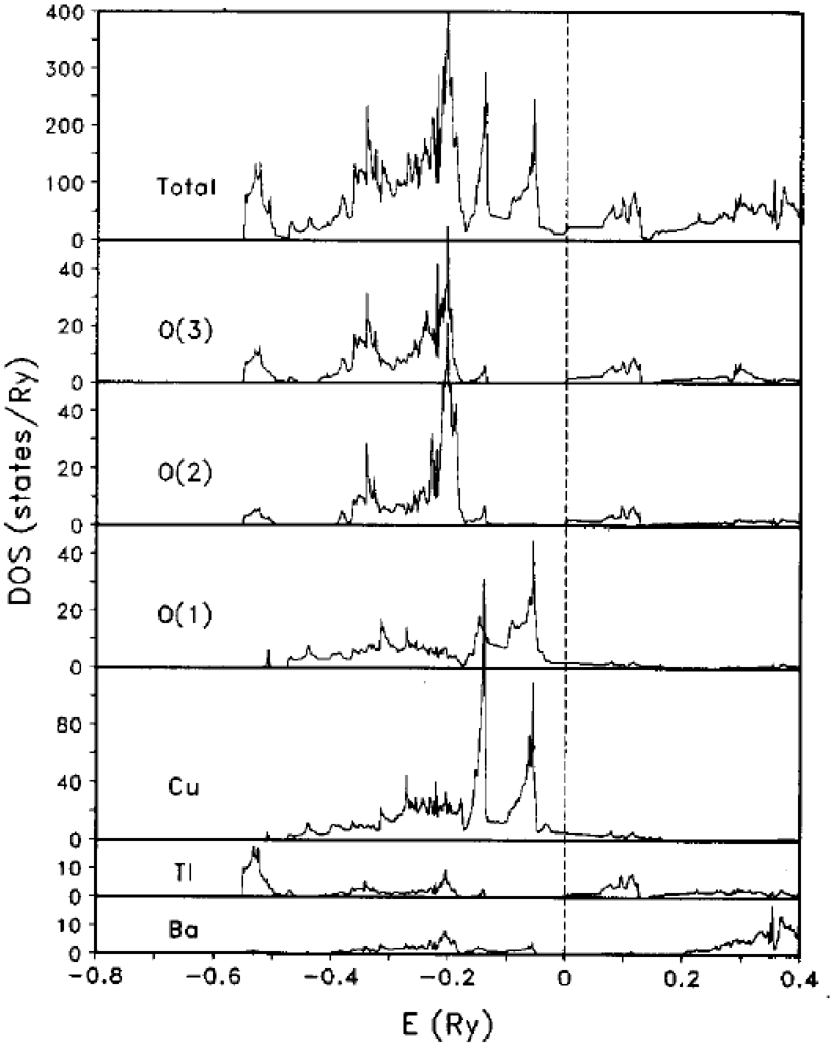


- In perovskites the interaction proceeds through O.

Example: Cuprate Superconductors (Spin ½)



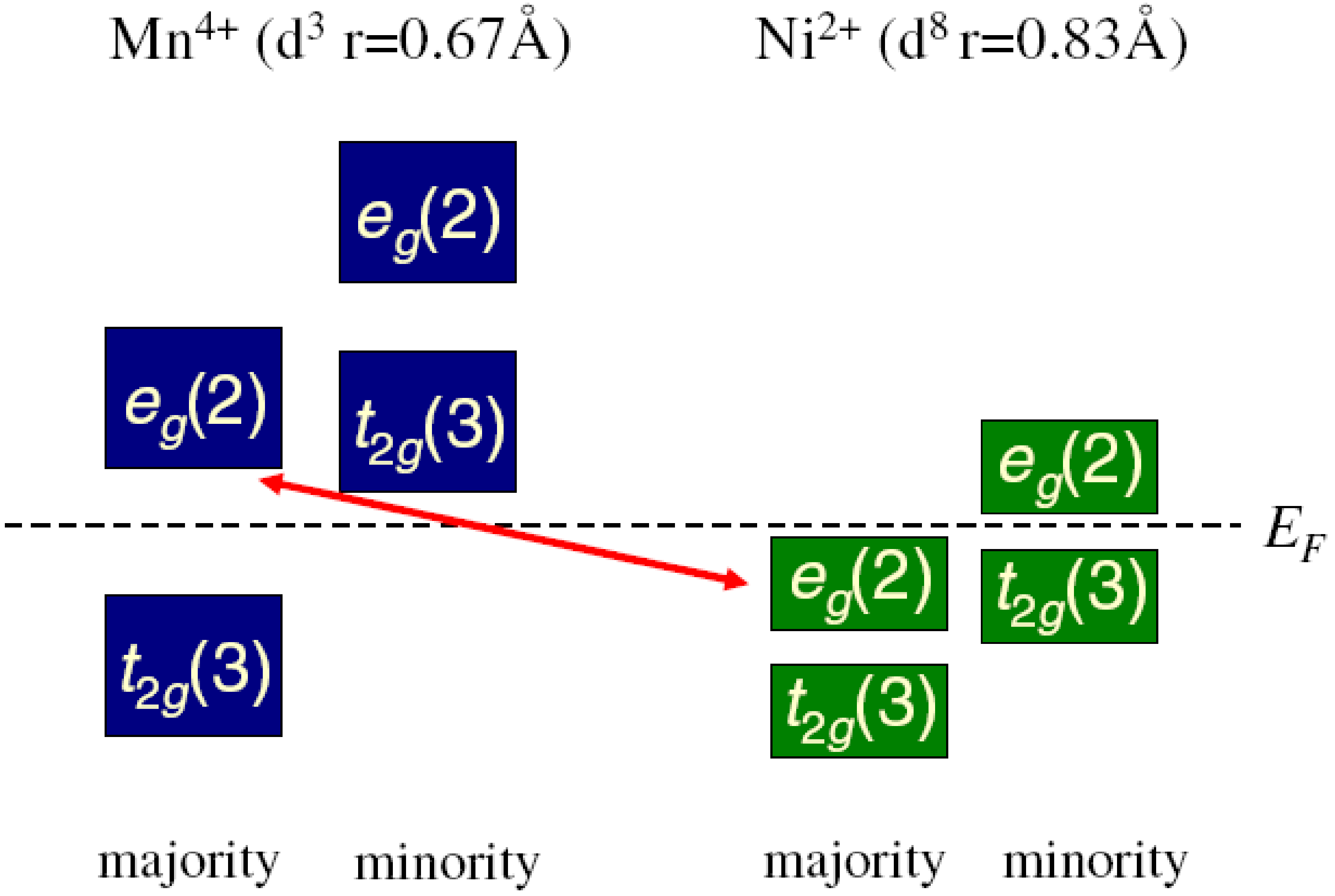
$Tl_2Ba_2CuO_6$ Note hybridization of Cu and in-plane O(1)



Highest T_c cuprates have long apical O bond (and short in plane bonds), are hole doped and have flat CuO_2 planes (straight bonds).

An Example (R_2NiMnO$_6$) Double Perovskite

Azuma et al., Oratani et al., Mater et al., DJS et al.



A ferromagnet via standard Anderson super exchange.

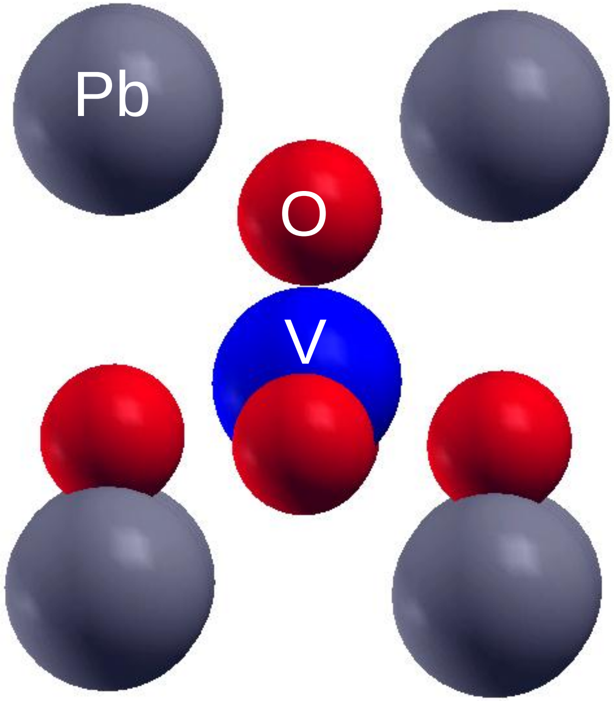
Another Example $PbVO_3$

Perovskite, polar tetragonal structure *P*4*mm*; extreme *c*/*a* ~ 1.23.

Shpanchenko (2004), Belik (2005), Uratani (2005), DJS (2006).

Ionic model: $Pb^{2+}V^{4+}(O^{2-})_3$

- Two stereochemically active ions:
- Pb^{2+} on *A*-site
- V^{4+} on B-site (also magnetic)
- No transition with *T* up to 570K
- Tetragonal to Cubic transition at *P*~2 GPa.



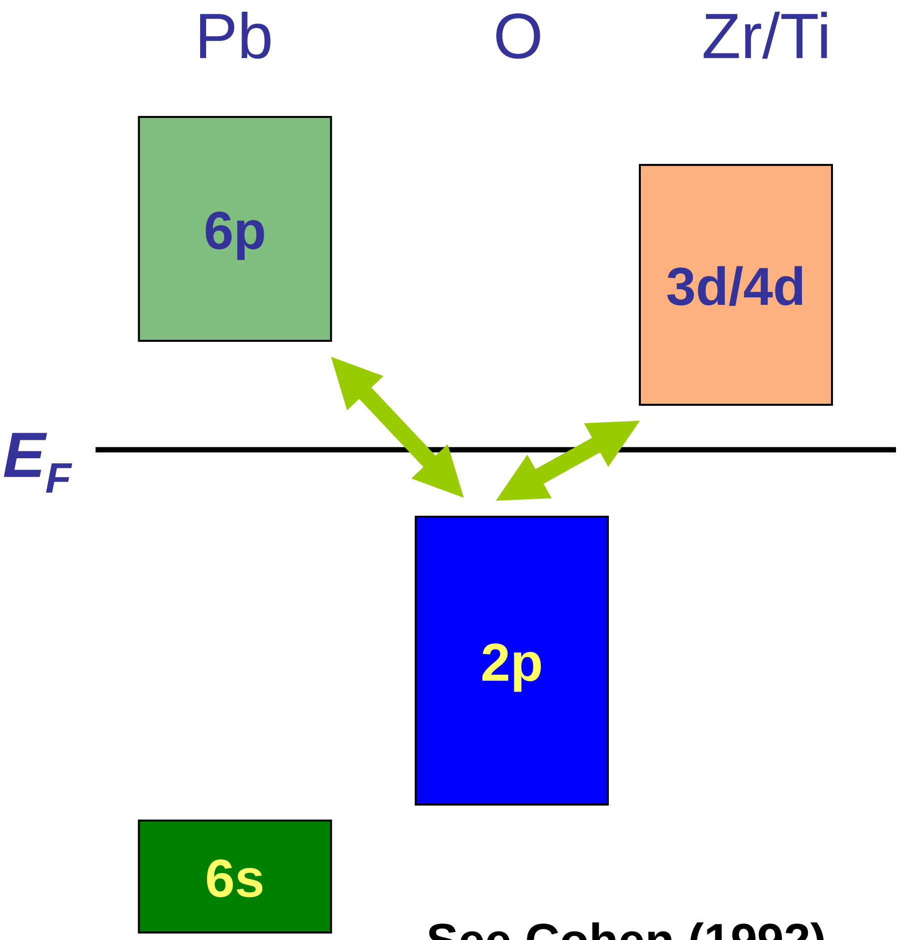
Perovskite Instabilities

- *B*-site driven:
  - Classic ferroelectrics (*e.g.* $BaTiO_3$)
  - *B*-site – O hybridization is important.
- *A*-site driven:
  - Tilted structures (*e.g.* $CaTiO_3$)
  - *A*-site stereochemical activity (Pb – O hybridization) can give strong ferroelectricity (*e.g.* PZT).
  - Morphotropic phase boundaries (piezoelectrics).
  - Short FE coherence length → interesting nanostructures and high temperature relaxors.
- $PbVO_3$ has strong stereochemical activity on both *A*- and *B*-site positions. *Super properties?*

Hybridization Schemes

PZT

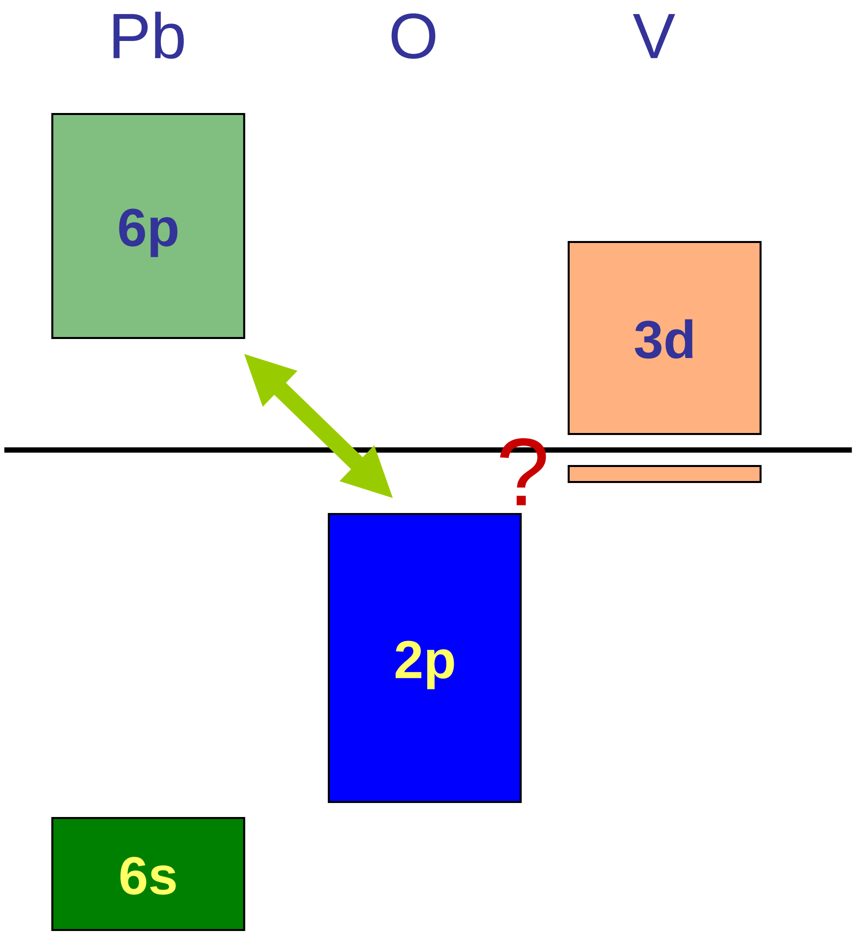
c/*a* ~ 1.015 – 1.06, T_C ~ 250 – 450 °C



See Cohen (1992).

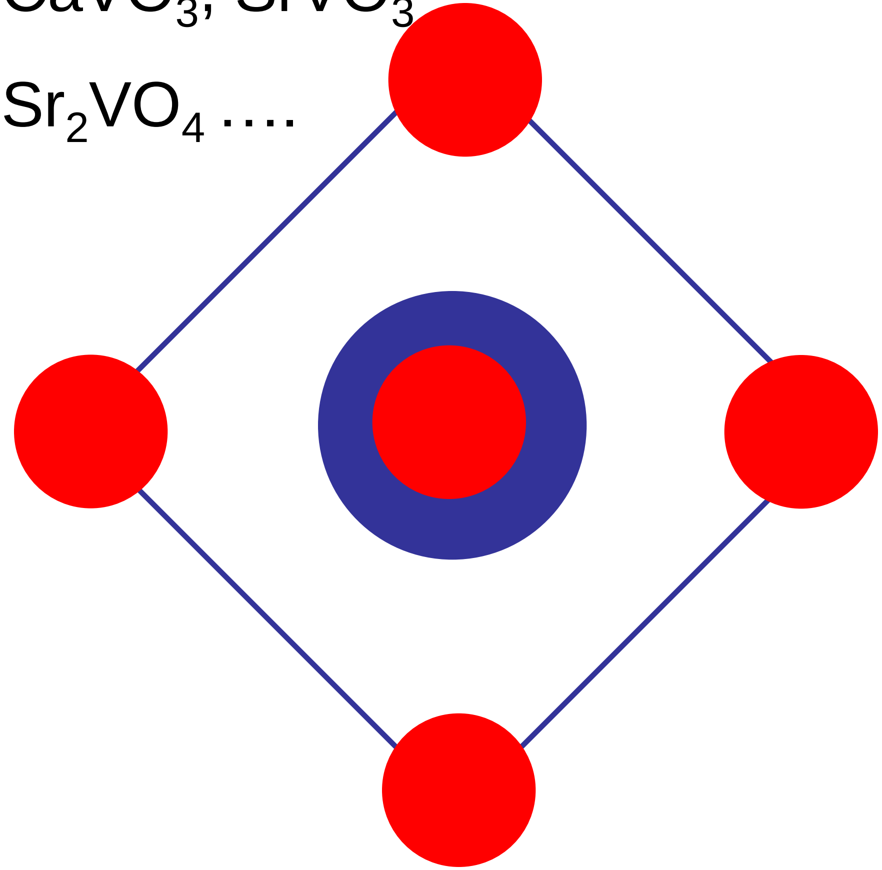
$PbVO_3$

c/*a* ~ 1.23, T_C *unknown*



V^{4+} in Oxides

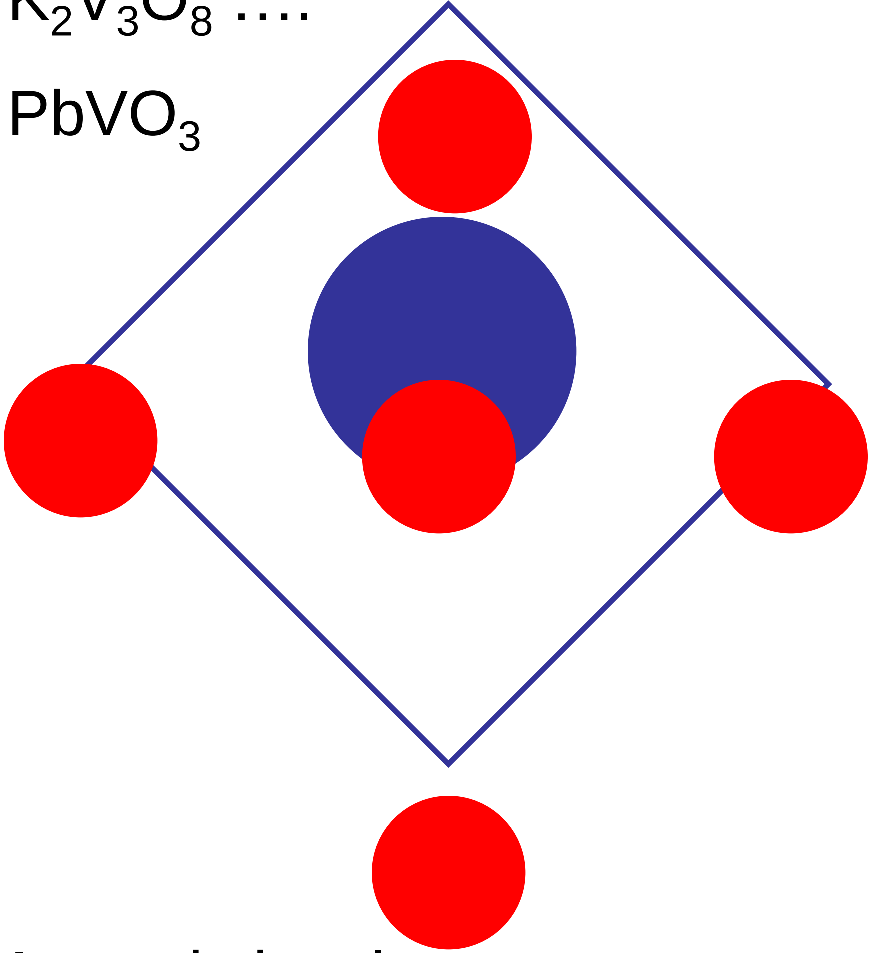
Two normal configurations:



$CaVO_3$, $SrVO_3$

Sr_2VO_4 ….

Metal or Mott Insulator.



$K_2V_3O_8$ ….

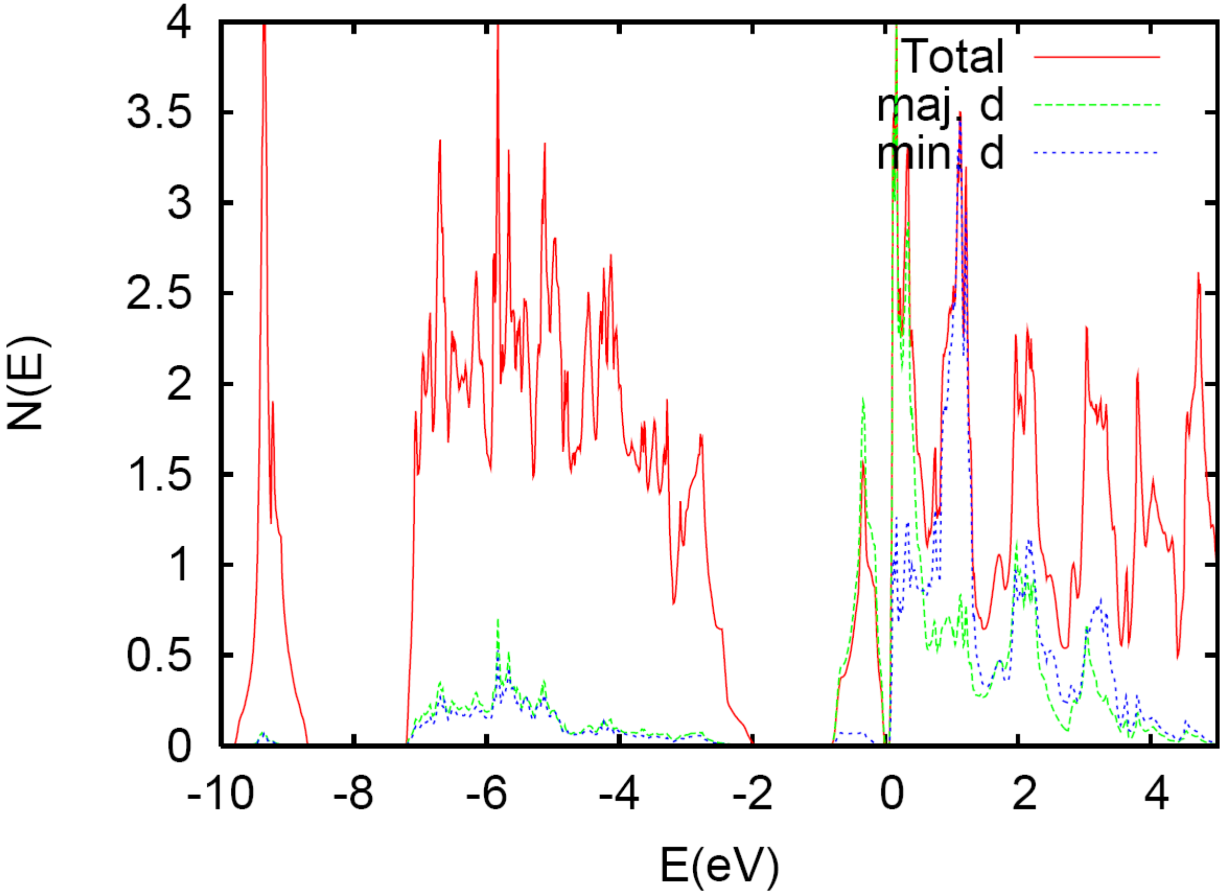
$PbVO_3$

Magnetic insulator.

Short bond (1.55 – 1.60 Å)

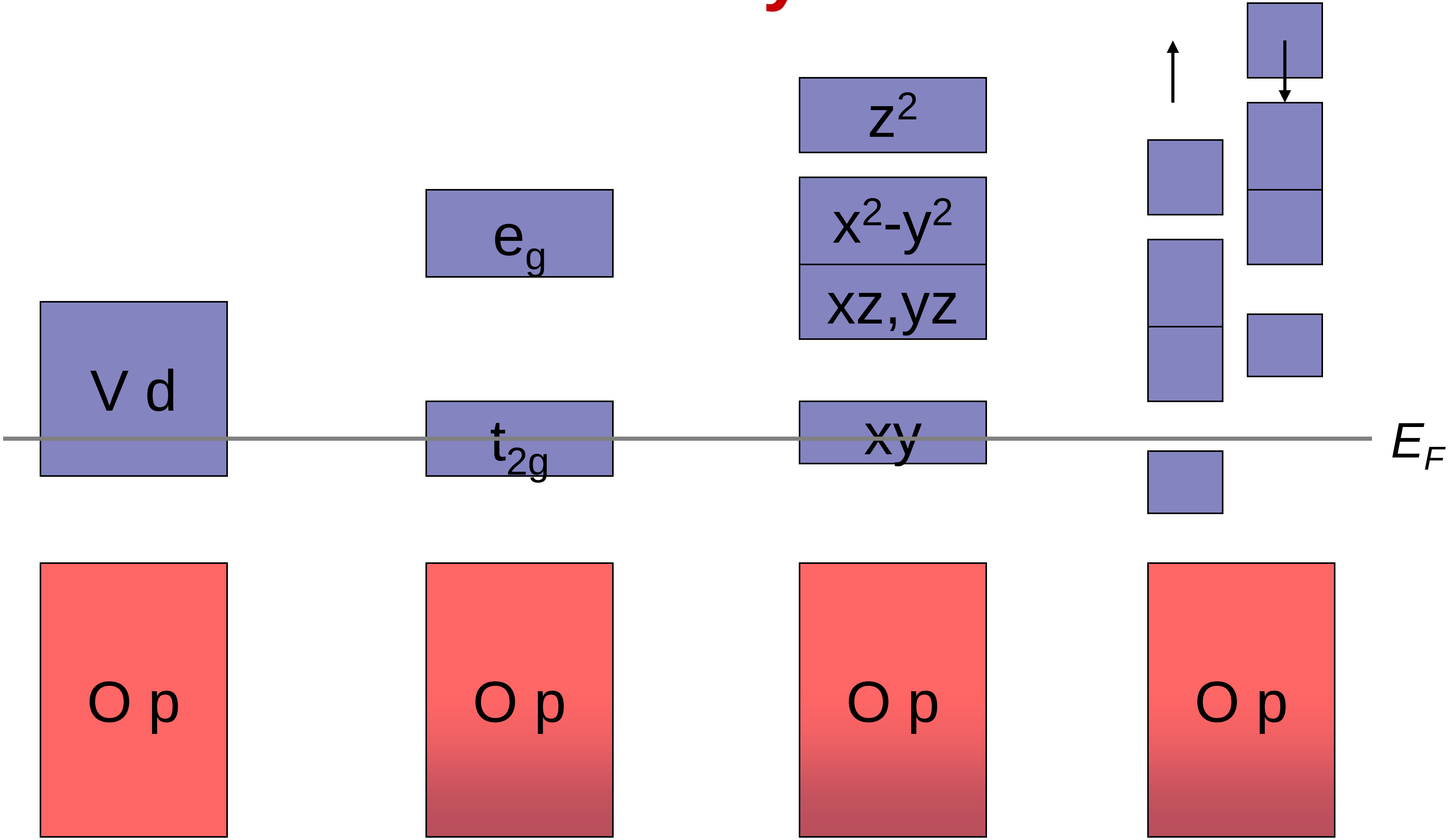
Moment Formation in $PbVO_3$

- LDA Calculations with LAPW method, *c.f.* Shpanchenko, Uratani.
- Stable local moments on V ($m_s = 1\mu_B$).
- Ground state is AF C-type.



Conf.	***E*(meV)**
NSP	0
F	-111.2
G	-127.3
A	-91.8
C	**-127.8**

The Vanadyl Bond



V d

e_g

t_{2g}

z^2

x^2-y^2

xz,yz

xy

E_F

O p

O p

O p

O p

Isotropic

Octahedral
$SrVO_3$, $CaVO_3$

Vanadyl

Hund’s
$PbVO_3$

Structure of $PbVO_3$

Why does $PbVO_3$ form a highly tetragonal structure with short V-O bond, while $SrVO_3$ and $CaVO_3$ do not?

Not ion size (*c.f.* Sr, Ca).

Metastable structure that could be made with e.g. $CaVO_3$?

- LDA Structure Relaxation (FM $PbVO_3$):

	LDA	Expt.
z_V	0.5689	0.5668
z_{O1}	0.2158	0.2102
z_{O2}	0.6872	0.6889

V-O bond length = 1.67Å.

$\omega(a_g)$=190, 408, 838 cm^{-1}

Structure of $PbVO_3$

Does the V-O vanadyl bond form because of ionic forces?

LDA calculations for hypothetical $CaVO_3$ in the $PbVO_3$ structure.

	$PbVO_3$(FM)	$CaVO_3$(FM)
$M(\mu_B)$	1.0	0.88
$F_V(\mathrm{mRy}/a_0)$	0^*	80

Large force pushing vanadyl bond apart

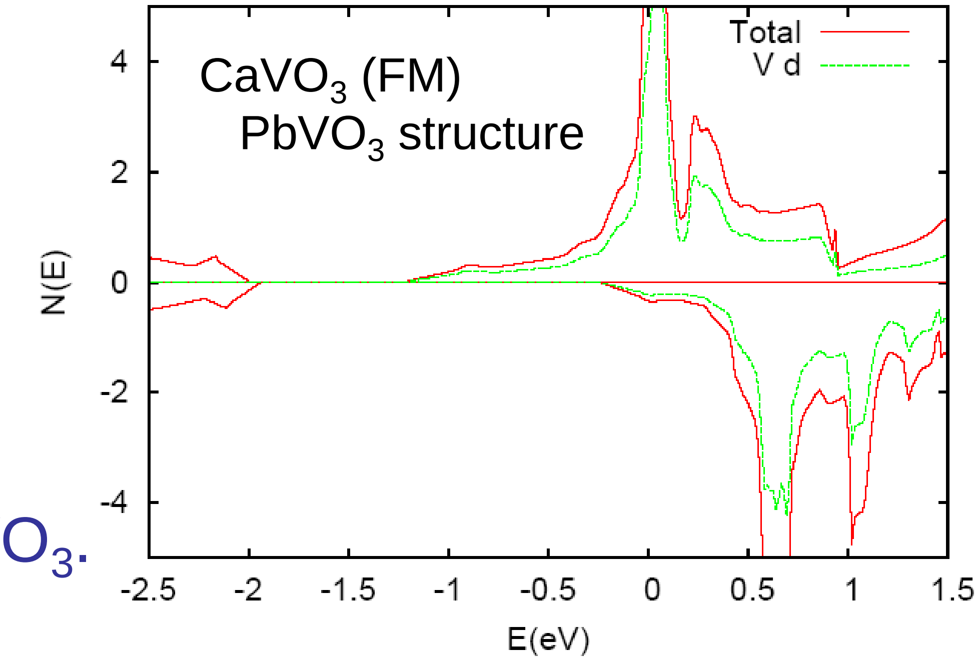
V moment is reduced

Vanadyl destabilized.

t_{2g} bands broadened.

V moment is reduced.

Reason is competition of V-O and Pb-O hybridization in $PbVO_3$.



MAGNETOELASTIC COUPLINGS

Why is Magnetism Coupled to the Lattice?

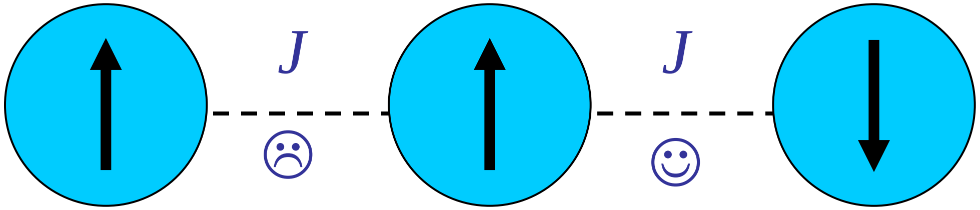
1. Moment formation affects bonding.
    - Difference in size of high spin and low spin ions (Shannon).
    - Moment formation competes with bonding (bonds have paired electrons in normal cases) -- Invar
2. Exchange interactions depend on structure through hopping integrals and on-site terms (relative shifts in levels).
3. Relativistic effects (spin orbit and Dzyaloshinsky-Moria) couple spin directions to the lattice – magnetostriction, moment canting.

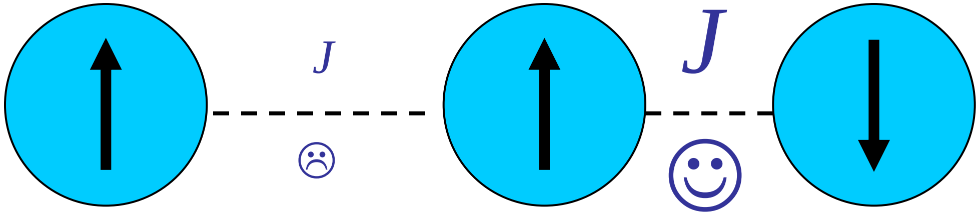
How Does It Work?

Heisenberg Model $J \sim t^2/\Delta E$

$$\mathcal{H} = -\sum_{i,j} \mathcal{J}_{ij}\vec{s}_i \cdot \vec{s}_j$$

But both ΔE and t depend on position – The hopping t is from wave function overlap, which is very strongly dependent on distance (exponential) and bond angles. $J \rightarrow J(\mathbf{r}_i-\mathbf{r}_j,\theta)$





“Spin-Dimer”

A kind of bonding

Can accomplish the same thing with M – O – M bond angles in perovskites or by lattice strain (e.g. MnO).

Big Effects

Ibarra et al.,PRL (1995).

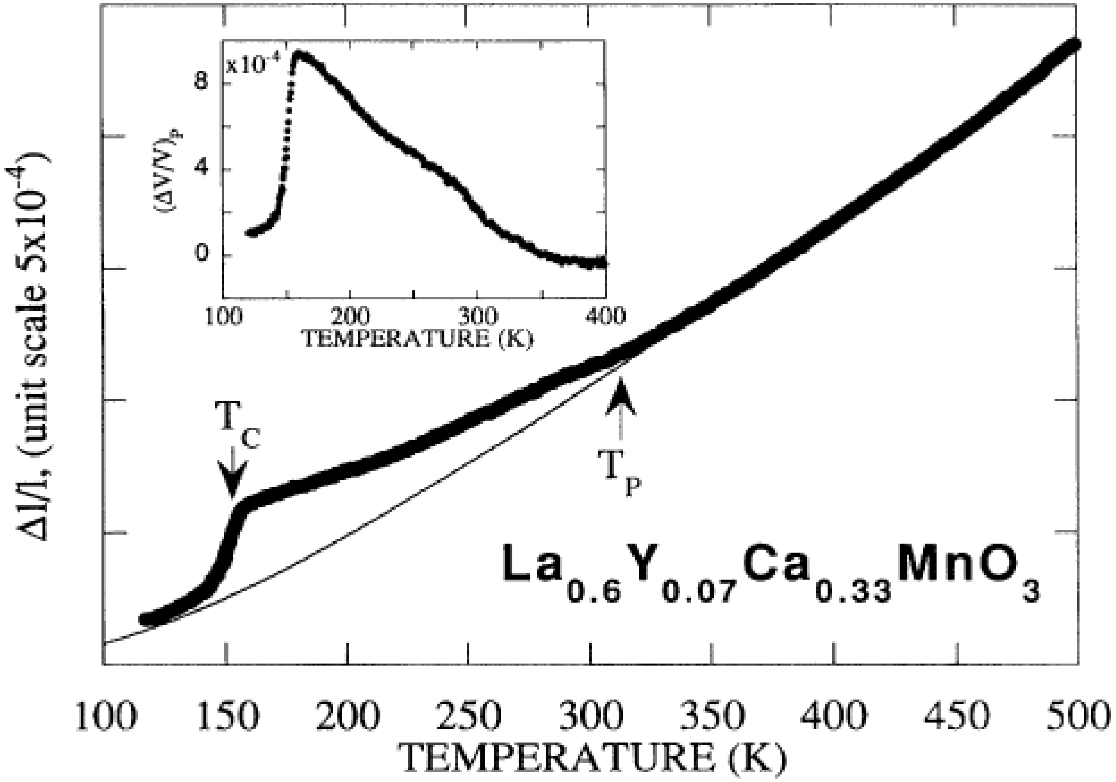


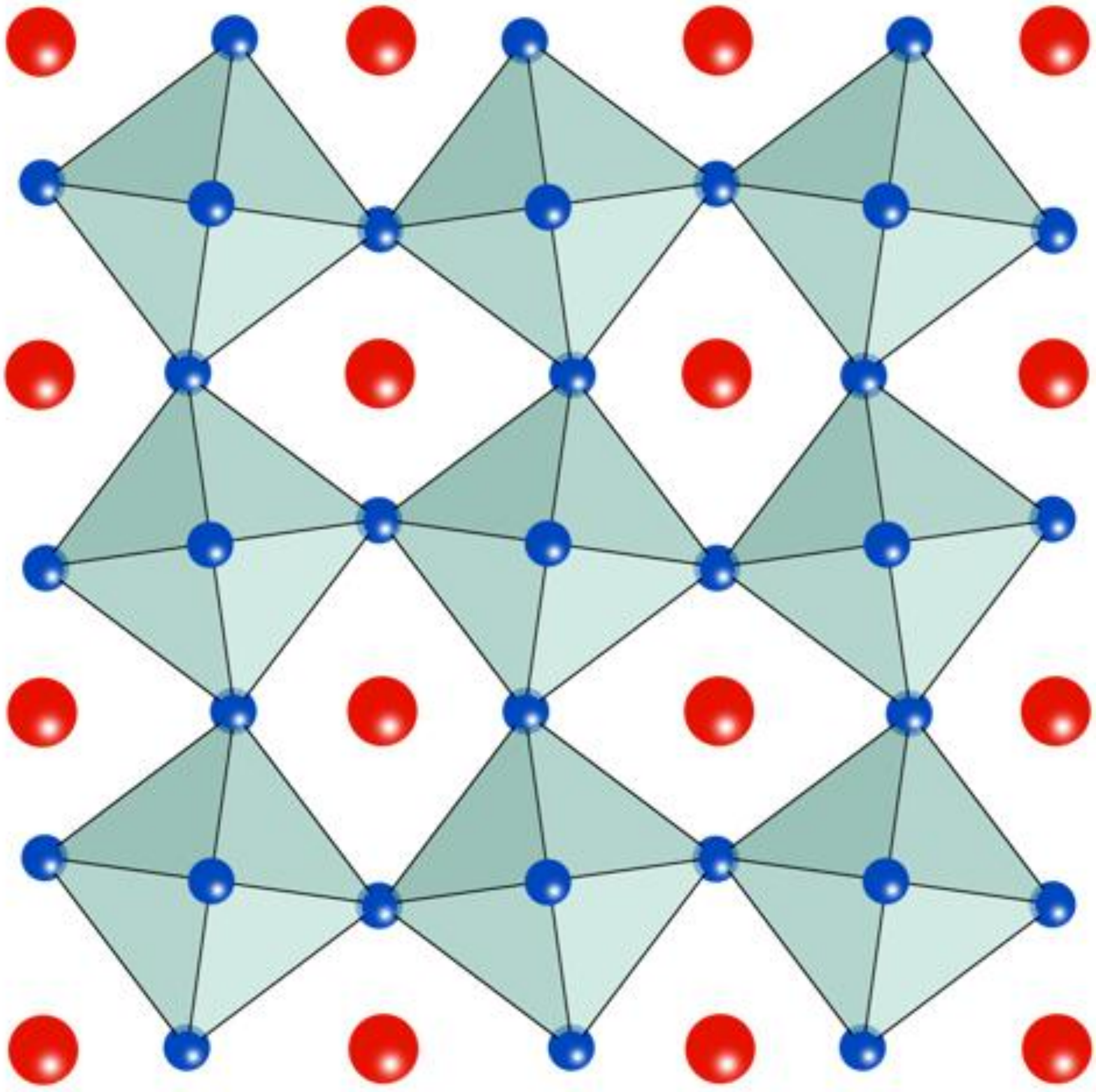
FIG. 2. Linear thermal expansion of $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$. Inset: anomalous thermal expansion contribution $(\Delta l/l)_P$.

Large lattice signatures of changes in magnetic order with e_g electrons.

SOMETHING NEW:

A-Site Disorder

ROTATIONAL MODE



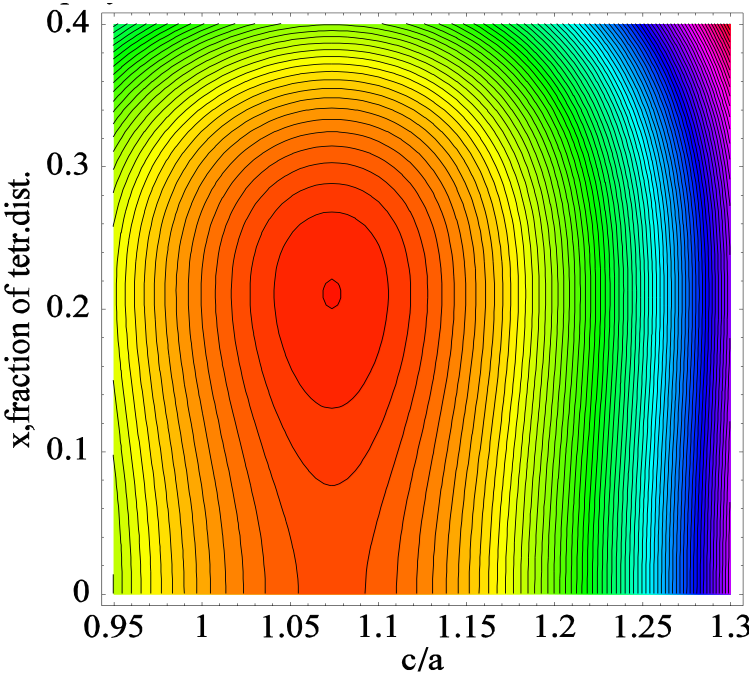
- Distortion around *A* (*A*-O bond lengths)
- Bends *B*-O-*B* bonds but only bond lengths in second order. (*n.b*. breathing mode is usually stiff).
- Driven by pressure and/or tolerance factor ***if octahedra are stiff***.
- Alternate is *A*-site off-centering (Pb).

What If …

… we could eliminate the tilt instability from arbitrary $t<1$ perovskites?

$CdTiO_3$ and Alloys with $PbTiO_3$

Density functional calculations for $CdTiO_3$ (small tolerance factor, possibly interesting chemistry)

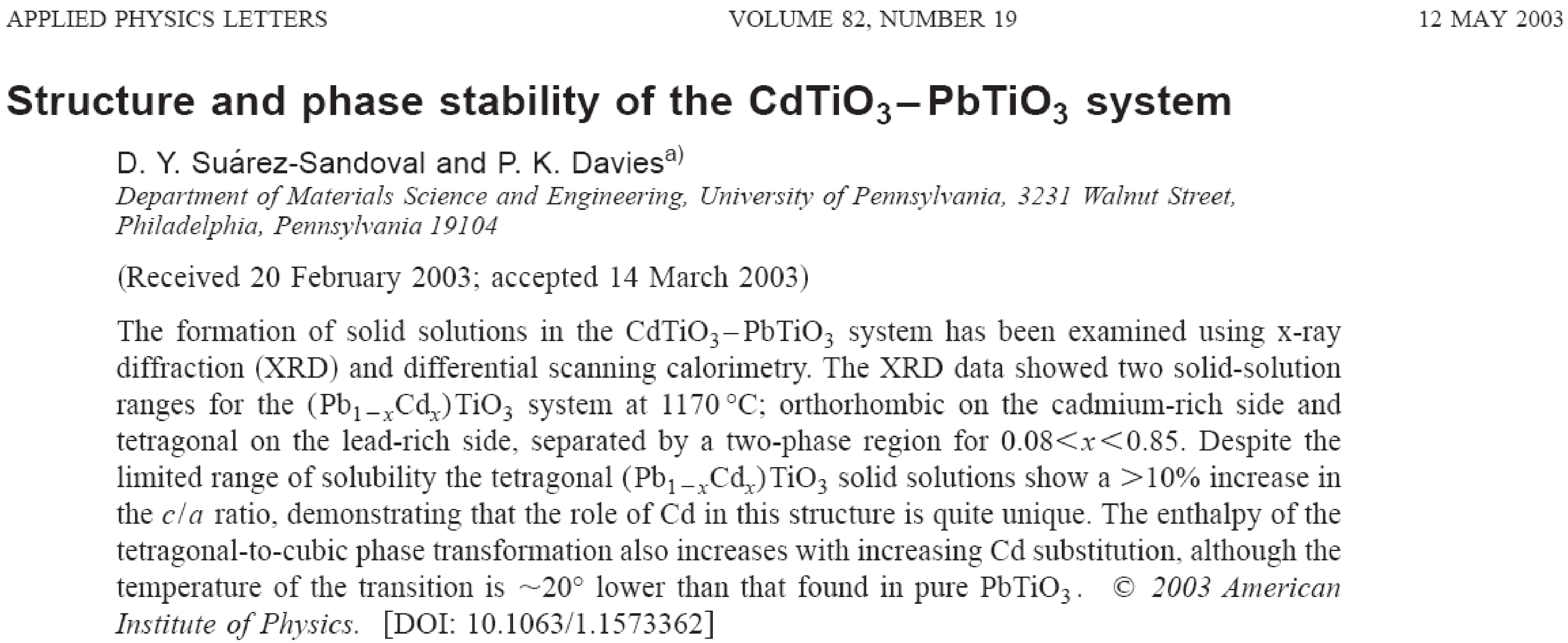


“Ferroelectric $CdTiO_3$”

- $CdTiO_3$ has antiferroelectric ground state.
- If forced ferroelectric it has a large tetragonal strain in the tetragonal FE state, and high energy scale.
- Supercells for 50-50 $CdTiO_3$-$PbTiO_3$ are borderline ferroelectric and tetragonal and have a large c/a~1.08 (higher than $PbTiO_3$).

S.V. Halilov, M. Fornari and D.J. Singh, Appl. Phys. Lett. **81**, 3443 (2002).

Experimental Confirmation



APPLIED PHYSICS LETTERS VOLUME 82, NUMBER 19 12 MAY 2003

Structure and phase stability of the $CdTiO_3-PbTiO_3$ system

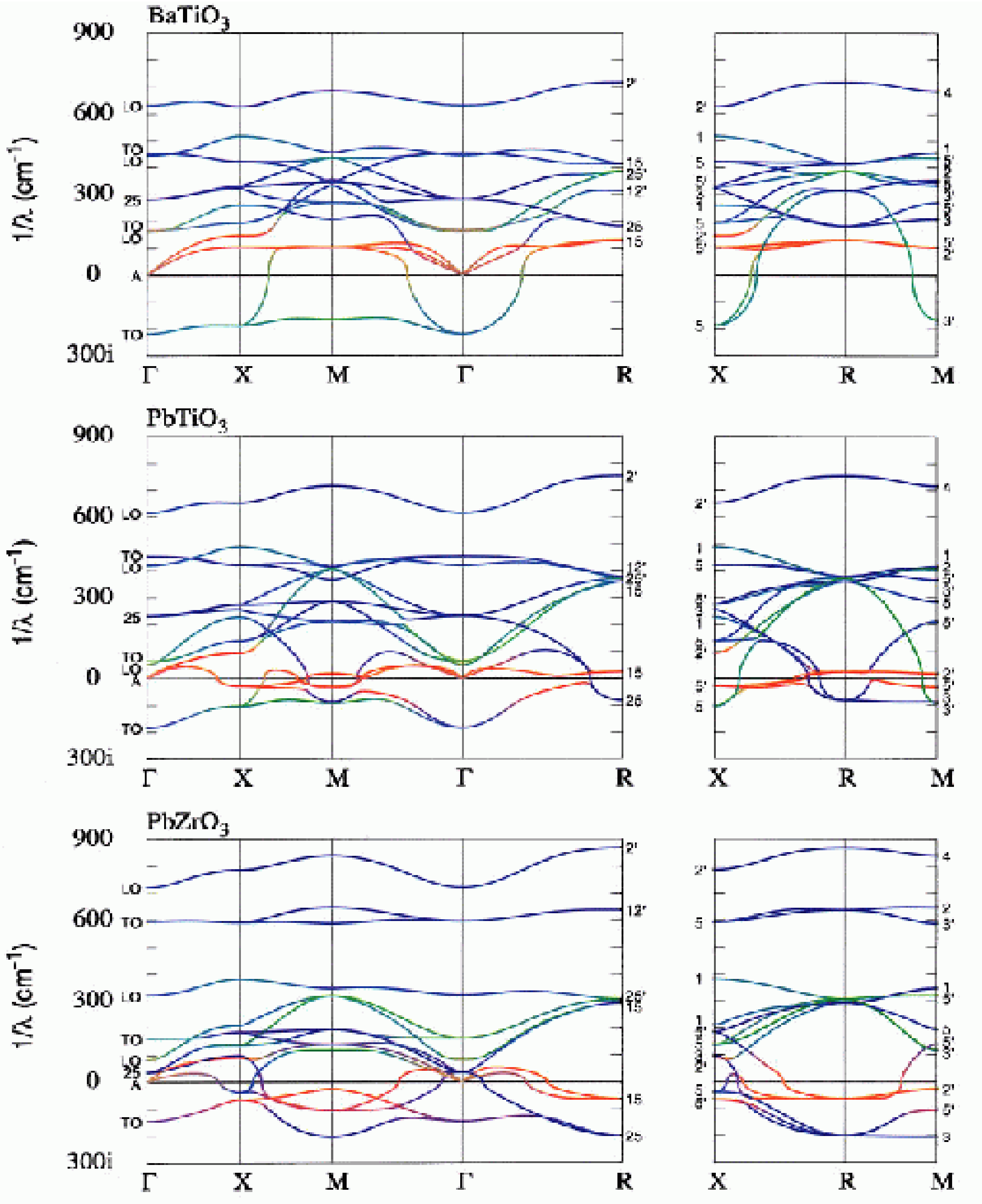
D. Y. Suárez-Sandoval and P. K. Davies[a)]
Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104

(Received 20 February 2003; accepted 14 March 2003)

The formation of solid solutions in the $CdTiO_3-PbTiO_3$ system has been examined using x-ray diffraction (XRD) and differential scanning calorimetry. The XRD data showed two solid-solution ranges for the $(Pb_{1-x}Cd_x)TiO_3$ system at 1170 °C; orthorhombic on the cadmium-rich side and tetragonal on the lead-rich side, separated by a two-phase region for $0.08<x<0.85$. Despite the limited range of solubility the tetragonal $(Pb_{1-x}Cd_x)TiO_3$ solid solutions show a >10% increase in the c/a ratio, demonstrating that the role of Cd in this structure is quite unique. The enthalpy of the tetragonal-to-cubic phase transformation also increases with increasing Cd substitution, although the temperature of the transition is ~20° lower than that found in pure $PbTiO_3$. [DOI: 10.1063/1.1573362]

This was the second example of an alloy with $PbTiO_3$ that increases c/a.

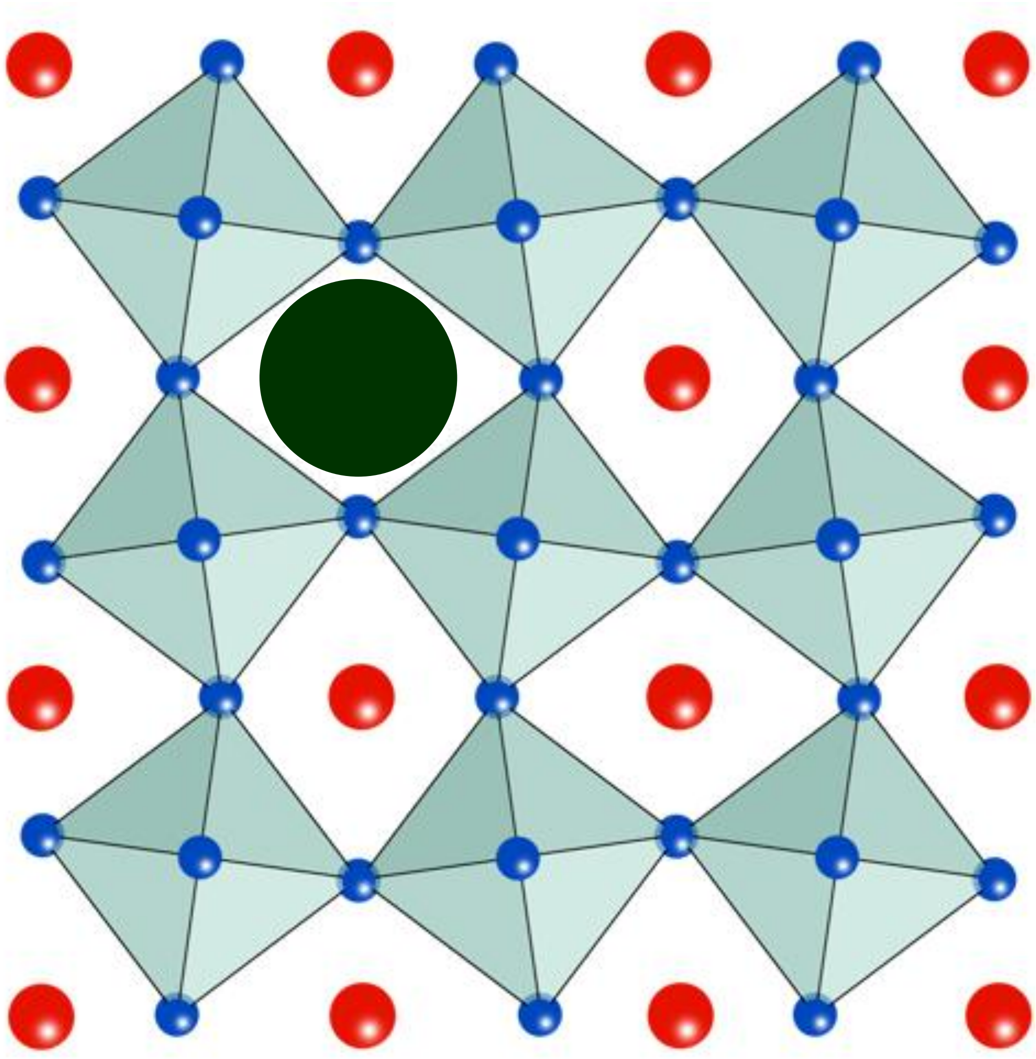
Phonons In Ferroelectric Perovskites



First Principles Calculations of Ghosez et al. (1999):

- note R point instabilities in PZ *and PT* but not BT.
- Note different coherence lengths for zone center and zone boundary instabilities.

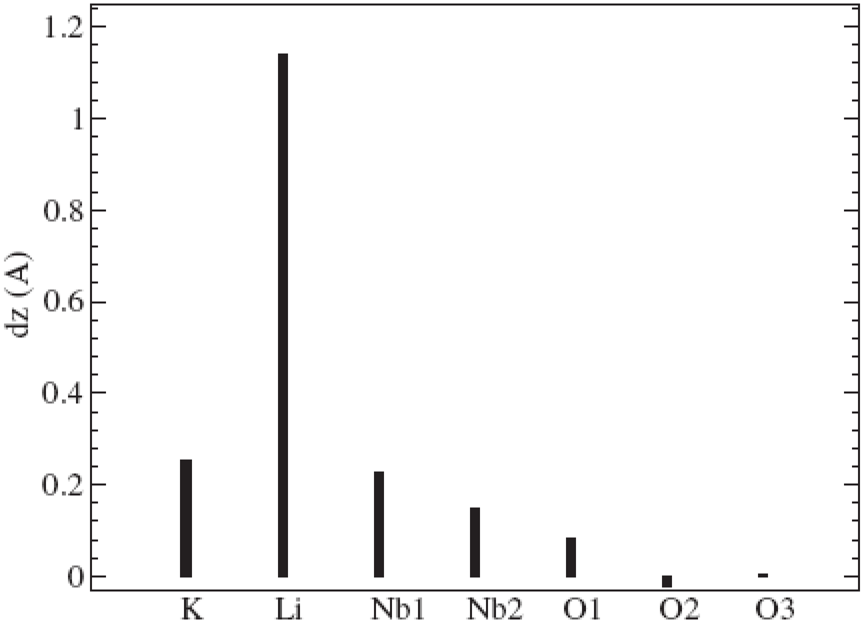
ROTATIONAL MODE

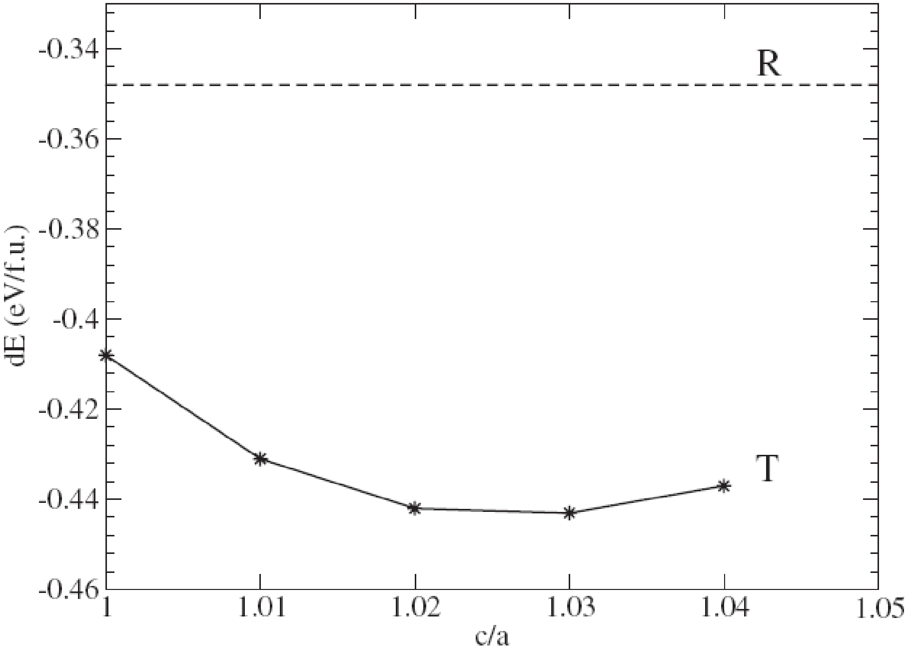


Can we use disorder to exploit the difference in coherence length between rotational and ferroelectric instabilities?

Hypothetical Perovskite: $K_{0.5}Li_{0.5}NbO_3$

- K and Li have very different sizes (1.8Å vs. 1.1Å).
- What if we make a perovskite alloying K and Li on the A-site?

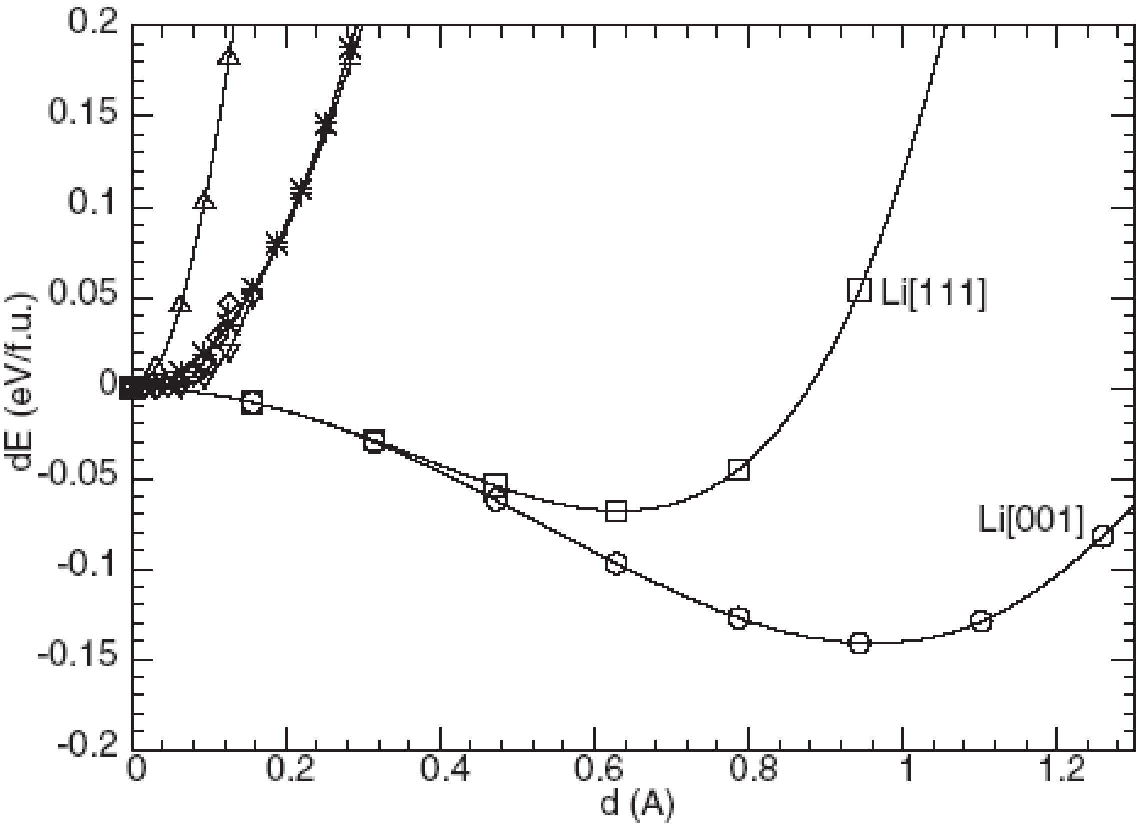




- Strong off-centering of Li (A-site driven ferroelectric) – Tilt does not happen.

D.I. Bilc and D.J. Singh, PRL **96**, 147602 (2006).

Single ion off-centering



- Reason for tetragonal state is the very large displacement of Li.

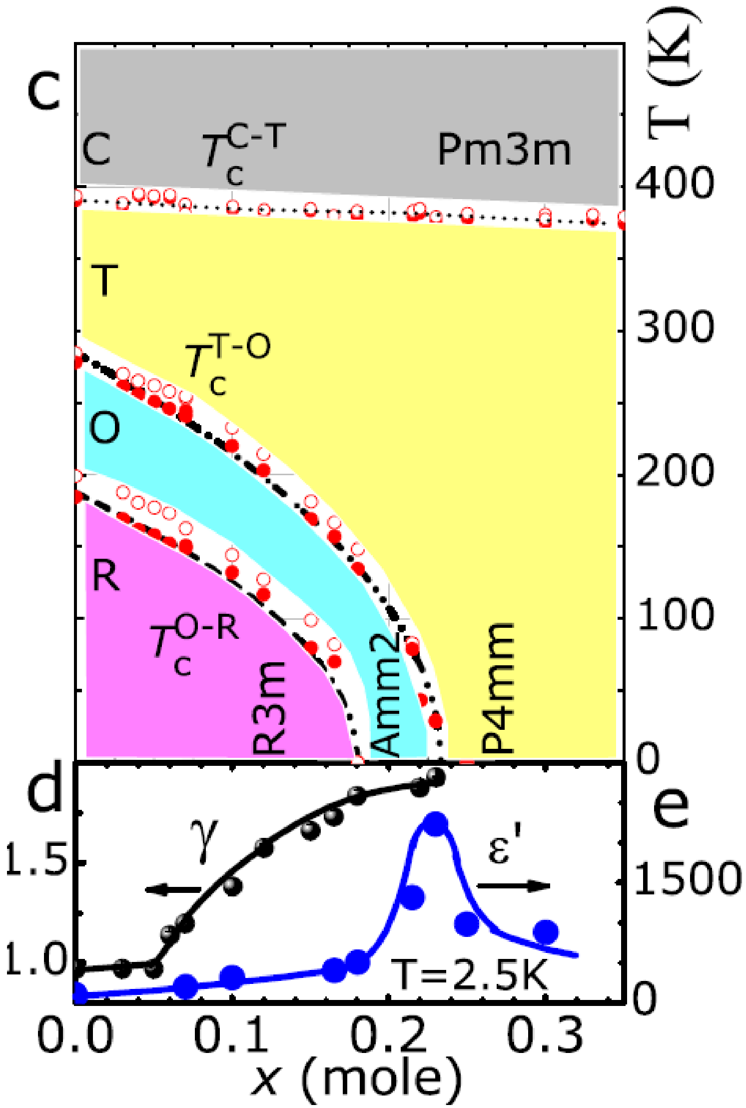
LATTICE INSTABILITIES IN PEROVSKITES (Design Rules)

1. Hybridization between unoccupied A-site states and O 2p states favors ferroelectricity in t<1 perovskites.
2. Alloying small A-site ions favor large tetragonality if ferroelectricity can be obtained – e.g. $CdTiO_3$ - PT
3. ***In materials with stiff octahedra, frustration due to a mixture of large and small A-site ions, can stabilize ferroelectricity due to the short coherence length of the ferroelectric instability and the long rotational coherence length.***
4. The balance between tetragonal and rhombohedral ground states (i.e. the MPB) can be controlled via the BO_6 polarizability – e.g. NbO_6 vs. TaO_6

PRL **100,** 227601 (2008) PHYSICAL REVIEW LETTERS week ending 6 JUNE 2008

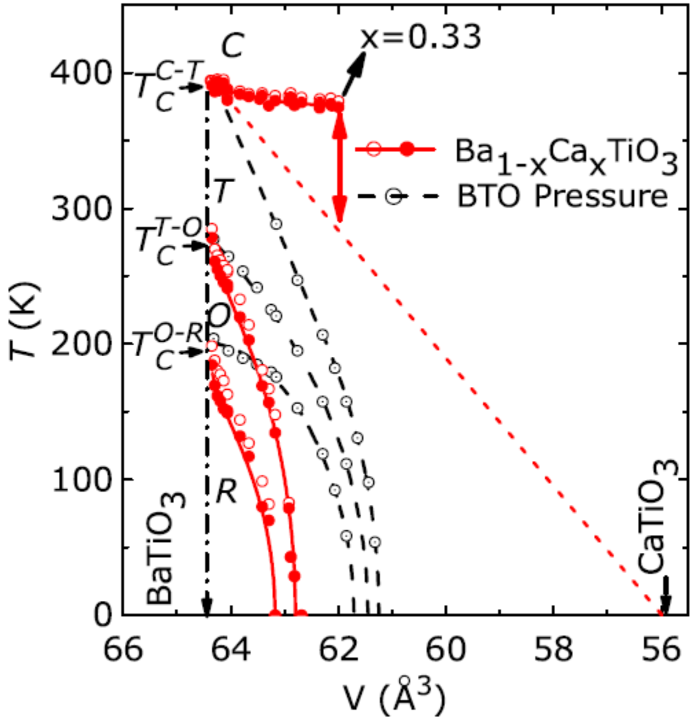
Anomalous Phase Diagram of Ferroelectric (Ba, Ca)TiO_3 Single Crystals with Giant Electromechanical Response

Desheng Fu,[1,2] Mitsuru Itoh,[2] Shin-ya Koshihara,[1,3,4] Taichi Kosugi,[5] and Shinji Tsuneyuki[5]



1) T_c is maintained high under Ca alloying even though the average tolerance factor is strongly decreasing.

2) The system becomes much more tetragonal as Ca is added.



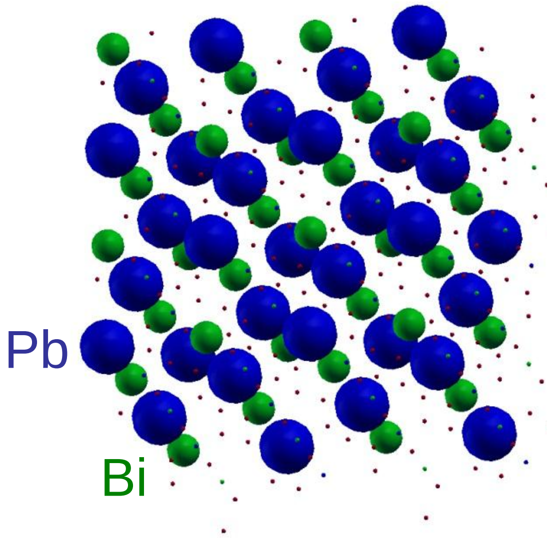
$Ba_{1\text{-}x}Ca_xTiO_3$

A-Site Alloys with Bi

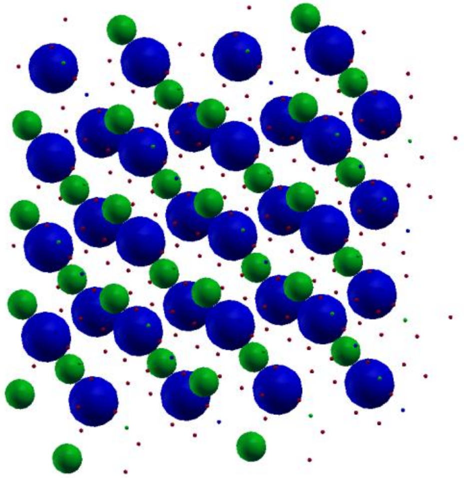
- $Bi_{0.5}Sr_{0.5}Zn_{0.5}Nb_{0.5}O_3$ was reported in perovskite structure by Kosyachenko *et al.* [Neorg. Mater. **18**, 1352 (1982)] and evidence pointing towards ferroelectricity was found.
- $Bi_{0.5}Pb_{0.5}Zn_{0.5}Nb_{0.5}O_3$ would be the 50-50 solid solution of PZN with hypothetical $BiZn_{2/3}Nb_{1/3}O_3$.
- $(Na,Bi)TiO_3$ is a known material that has been investigated alone and in alloys with $PbTiO_3$ and $KNbO_3$.
- $Bi(Zn_{0.5}Ti_{0.5})O_3$ was shown to be a super tetragonal ferroelectric with very high polarization by Suchomel and Davies [APL **86**, 262905 (2005)].

$(Bi,Pb)_2ZnNbO_6$ Supercells

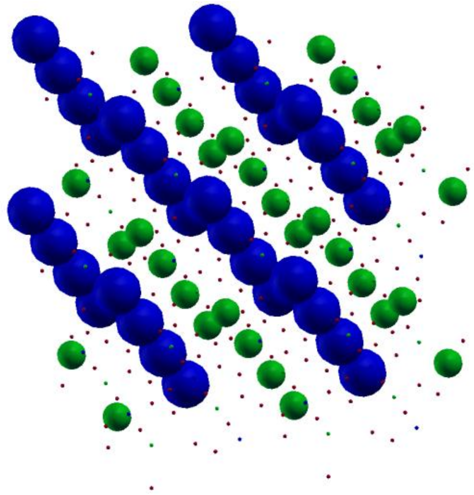
NaCl (111) layers



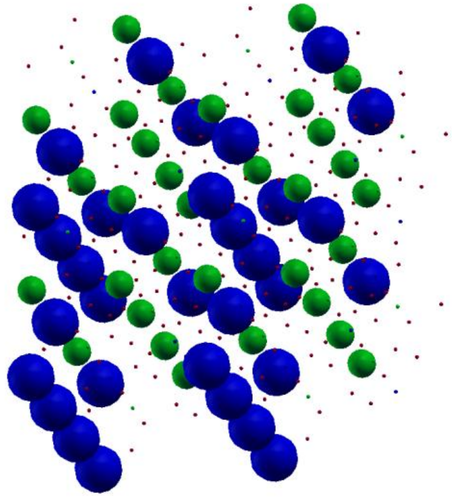
A-type (100) layers



C-type [001] chains



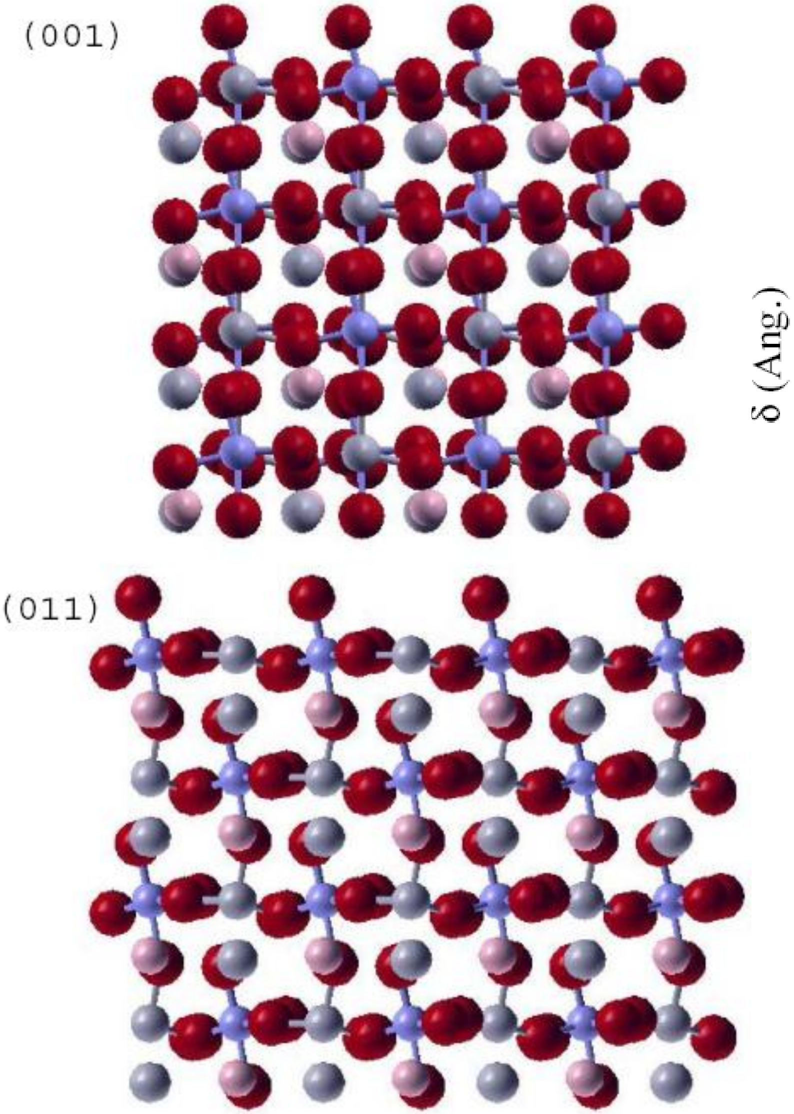
Clusters

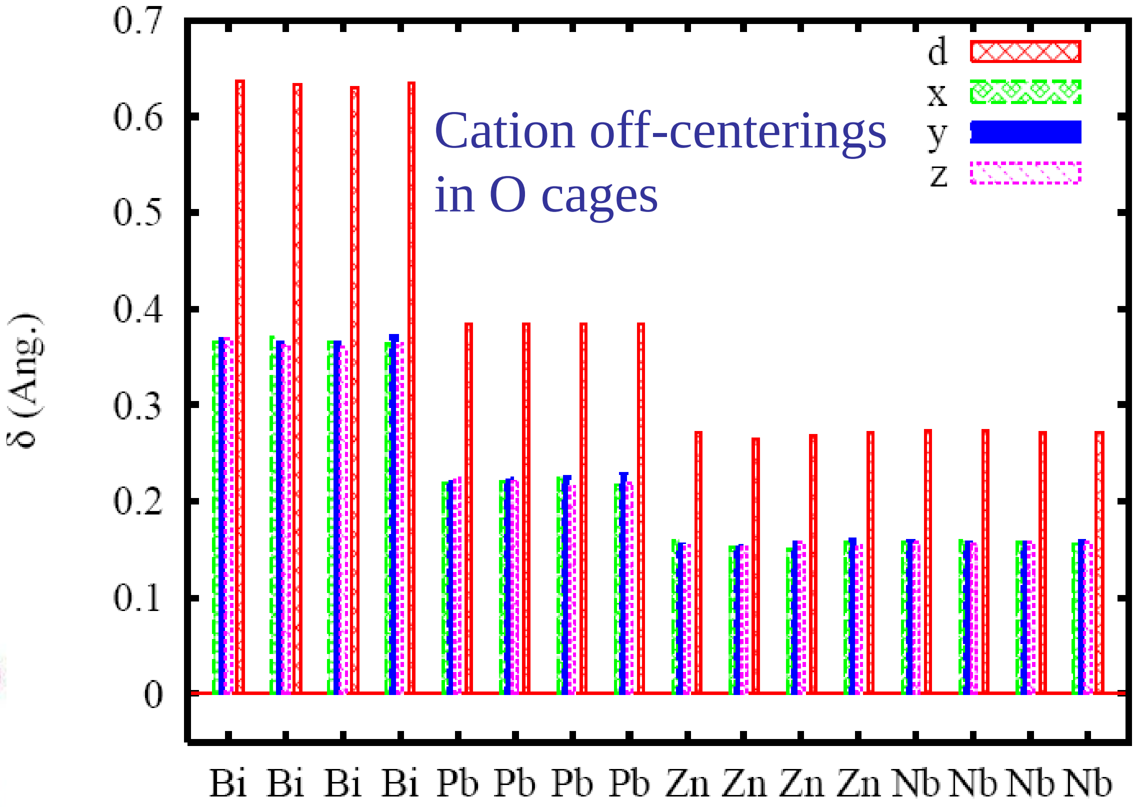


- Charge difference of Nb^{5+} and Zn^{2+} is 3 ➔ favors chemical ordering.
- $PbZn_{1/3}Nb_{2/3}O_3$ (PMN) has a two sub-lattice (double perovskite based) structure ➔ should be stronger for Zn:Nb ratio at 1:1.
- Done at LDA lattice parameter ➔ somewhat compressed [3.99 Å for Pb and 3.97 Å for Sr]
- LDA calculations for 40-atom double perovskite supercells with various Bi/Pb orderings and rocksalt Bi/Sr ordering.

$BiPbZnNbO_6$

Relaxed G-type cell at LDA lattice parameter (3.99 Å), pseudo-cubic



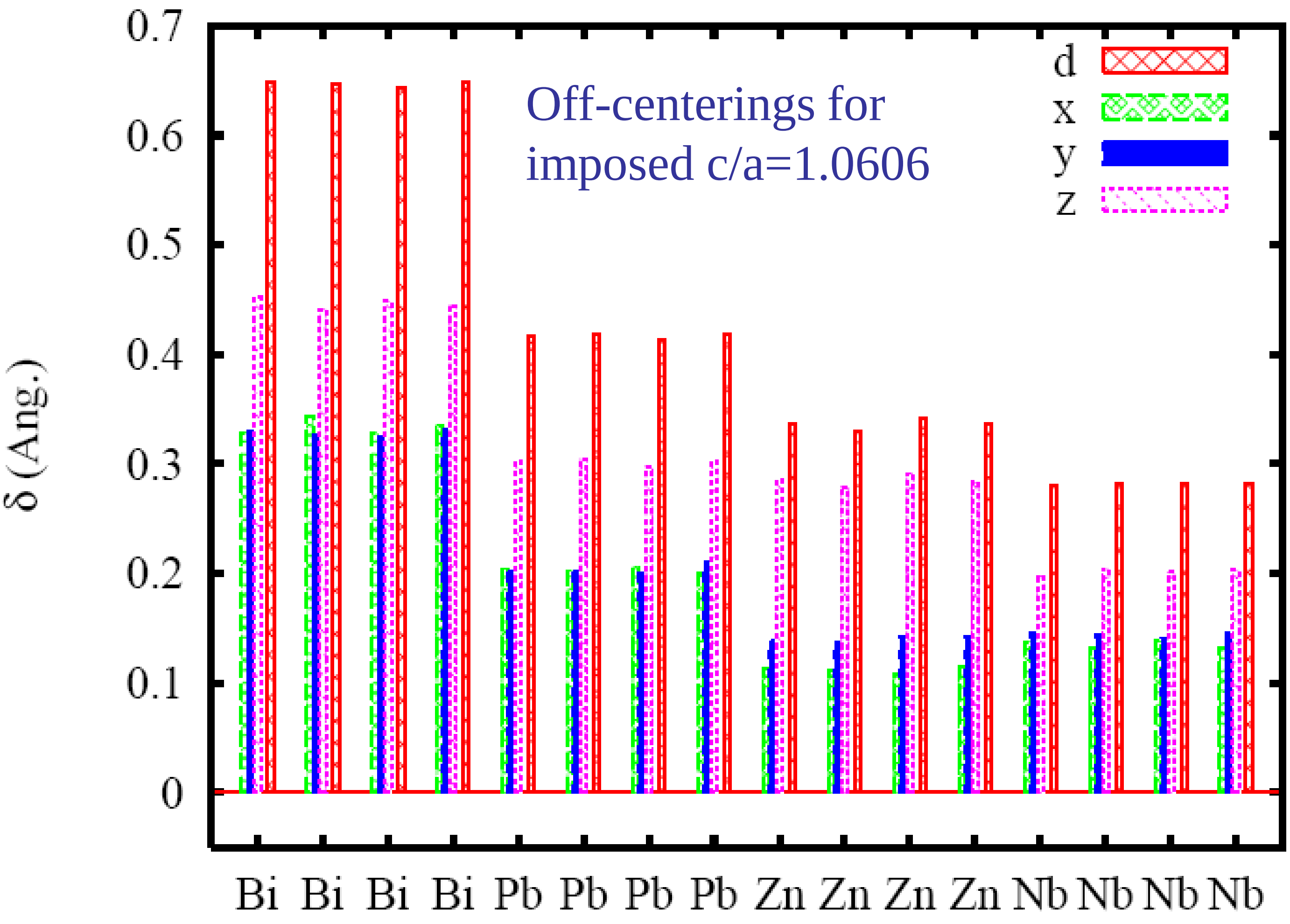


- Large off-centerings of Bi, but also substantial for other ions, including Nb.
- Off-centering is along [111].
- Similar results for other three supercells.

S. Takagi, A. Subedi, D.J. Singh and V.R. Cooper, Phys. Rev. B **81**, 134106 (2010)

$BiPbZnNbO_6$

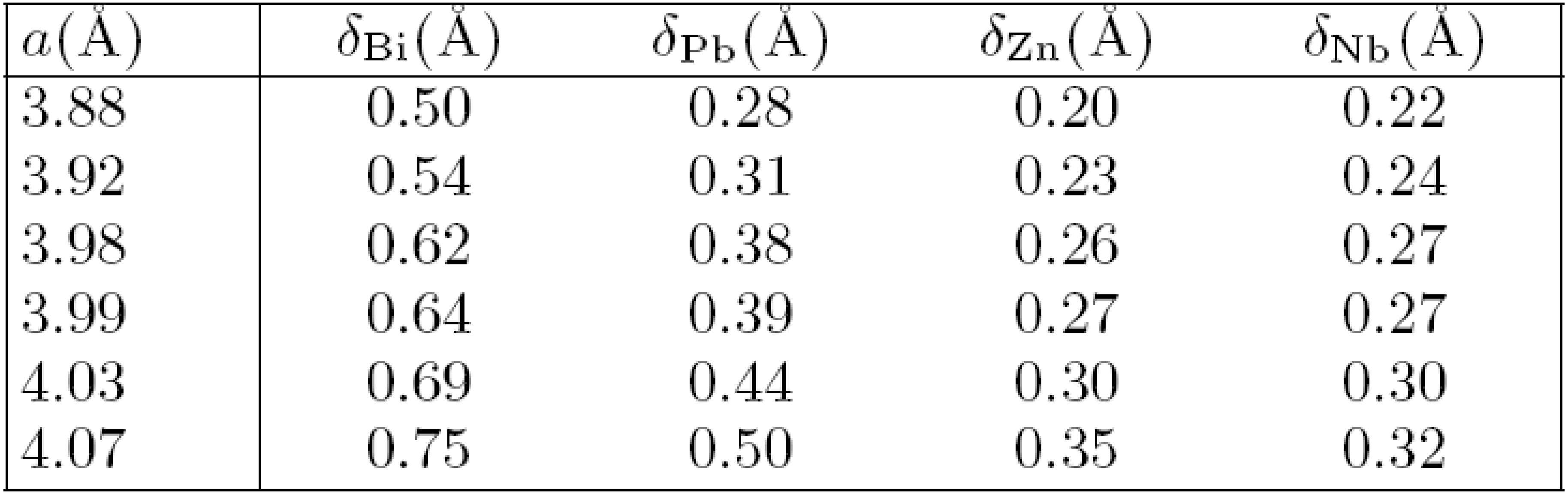
- G-type cell was relaxed as a function of tetragonal strain
- Minimum energy was at a c/a ratio of ~1.015, but this appears to be due to tilts, not ferroelectricity (supercell artifact)



Note that off-centering does not switch to [001] even with large imposed strain.

BiPbZnNbO$_6$

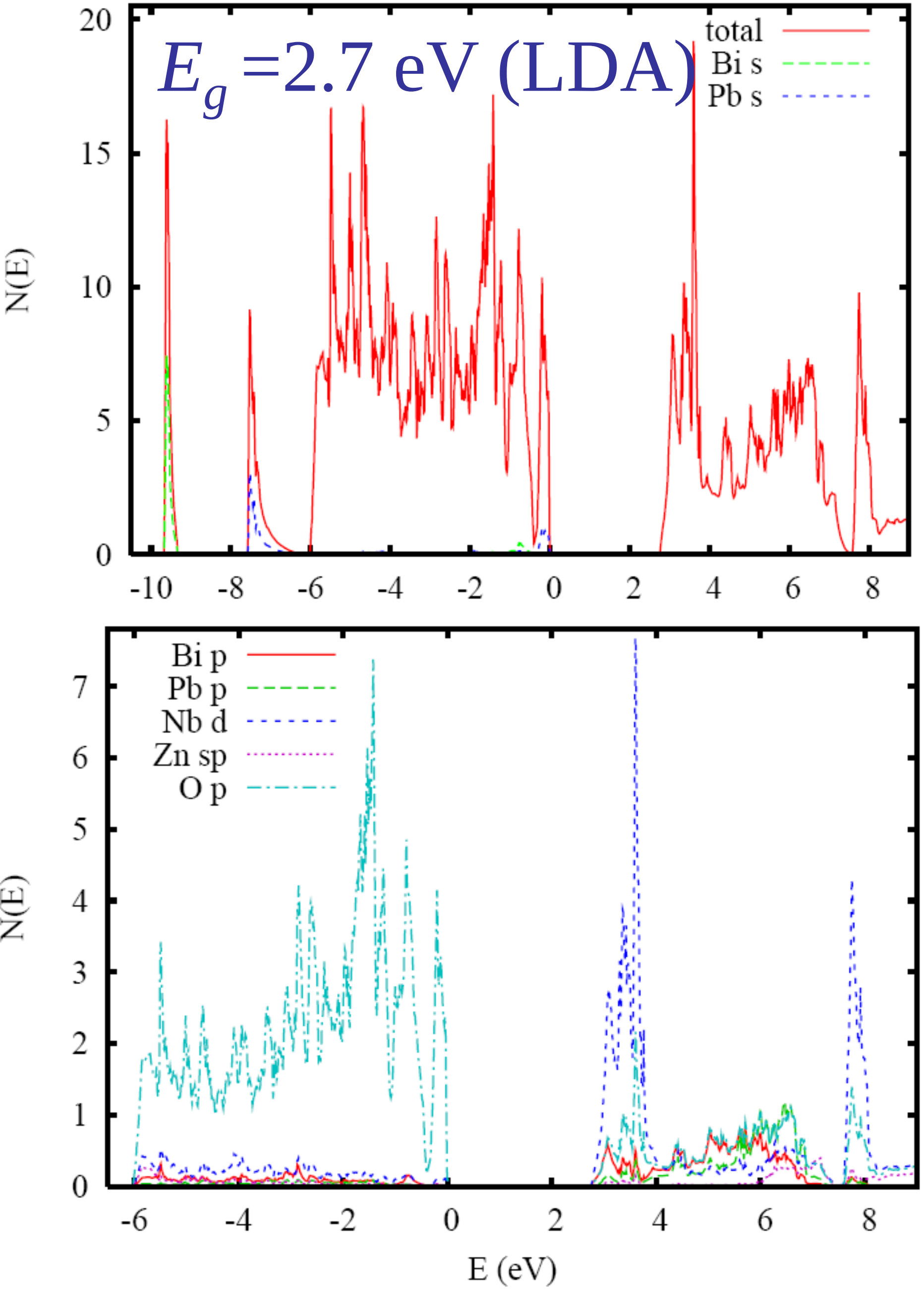
G-type supercell as a function of pseudo-cubic lattice parameter:



$a(\text{Å})$	$\delta_{\text{Bi}}(\text{Å})$	$\delta_{\text{Pb}}(\text{Å})$	$\delta_{\text{Zn}}(\text{Å})$	$\delta_{\text{Nb}}(\text{Å})$
3.88	0.50	0.28	0.20	0.22
3.92	0.54	0.31	0.23	0.24
3.98	0.62	0.38	0.26	0.27
3.99	0.64	0.39	0.27	0.27
4.03	0.69	0.44	0.30	0.30
4.07	0.75	0.50	0.35	0.32

- Increasing off-centering with increasing volume, as usual (LDA may underestimate).
- Substantial off-centerings of Nb.

Electronic Structure



E_g =2.7 eV (LDA)

- Note sizable band gap even at the LDA level. Also note ions in stable valence configurations for oxides ➔ consistent with good insulating behavior.
- Substantial hybridization of O 2p states with Bi p, Pb p, Nb d.

Polarization: $BiSrZnNbO_6$ and the Role of Pb

	$BiPbZnNbO_6$	$BiSrZnNbO_6$
a(LDA)	3.99 Å	3.97 Å
δ(Bi)	0.64 Å	0.62 Å
z^* (Bi)	4.4	4.4
δ(Pb/Sr)	0.39 Å	0.33 Å
z^* (Pb/Sr)	3.6	2.6
δ(Zn)	0.27 Å	0.25 Å
z^* (Zn)	2.9	2.8
δ(Nb)	0.27 Å	0.25 Å
z^* (Nb)	5.8	5.8
P(111)	85 μC/cm^2	79 μC/cm^2

$BiSrZnNbO_6$

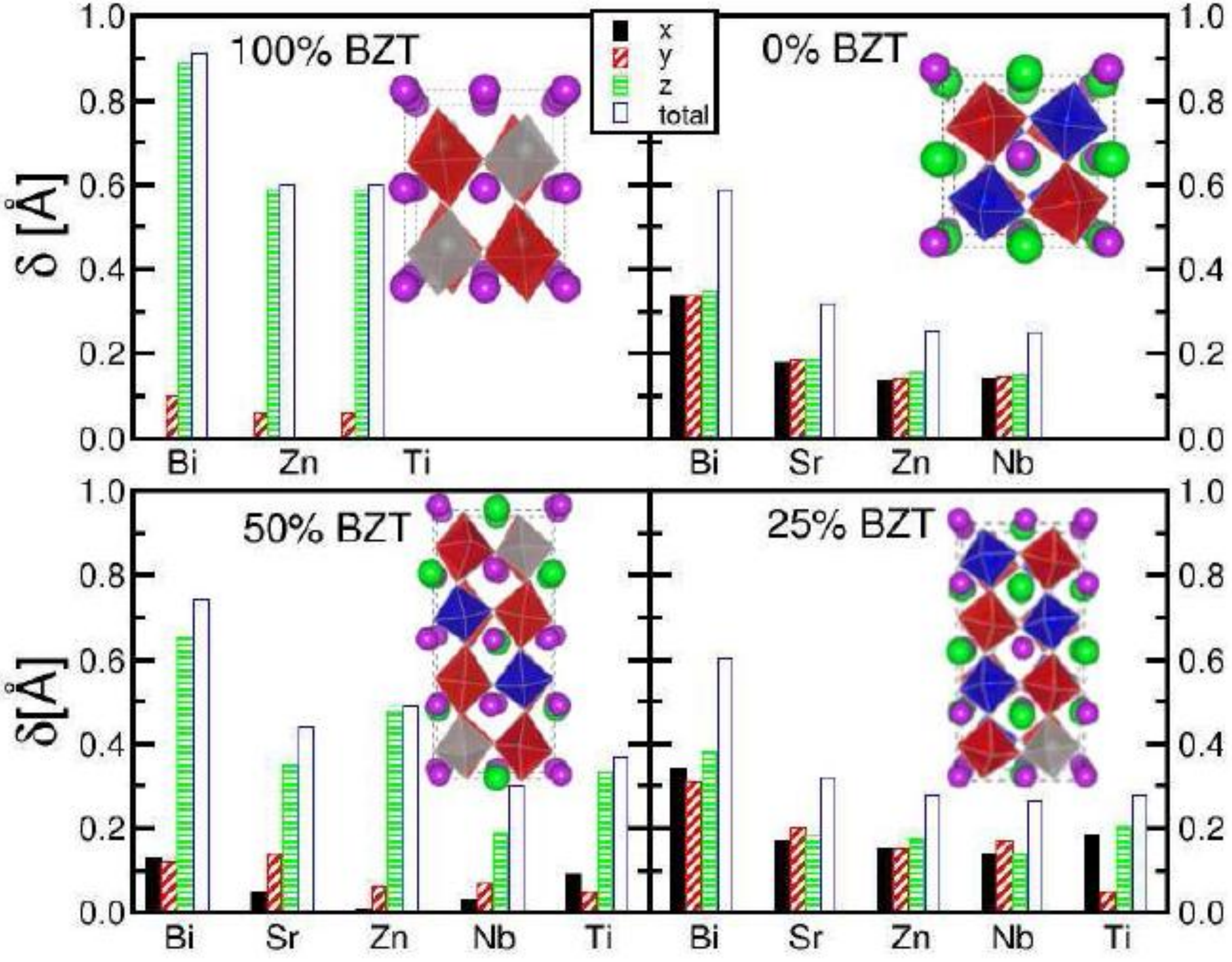
- Known compound that readily forms in perovskite structure.
- Average A-site charge is +2.5 → Av. B-site is +3.5 (better for stability of perovskite).
- Polarization is comparable to pure Bi compounds even though there is only 50% Bi.
- Reason is large Bi displacement & Nb off-centering.

$BiSrZnNbO_6$ – Bi_2ZnTiO_6 Solid Solution

- $Bi(Zn,Ti)O_3$ has a very large polarization ~150 μC/cm^2 but is essentially non-switchable due to super-tetragonality, c/a ~ 1.2 (Suchomel, 2006).
- Can we produce a useful MPB by alloying – key may be to alloy with a strongly R material that produces an MPB far from the BZT end so that it can be switchable.
- We did supercell calculations for the pseudo-binary solid solution with $BiSrZnNbO_6$.
- We used 40 and 80 atom cells with Zn and (Ti,Nb) on separate sublattices (i.e. double perovskite).

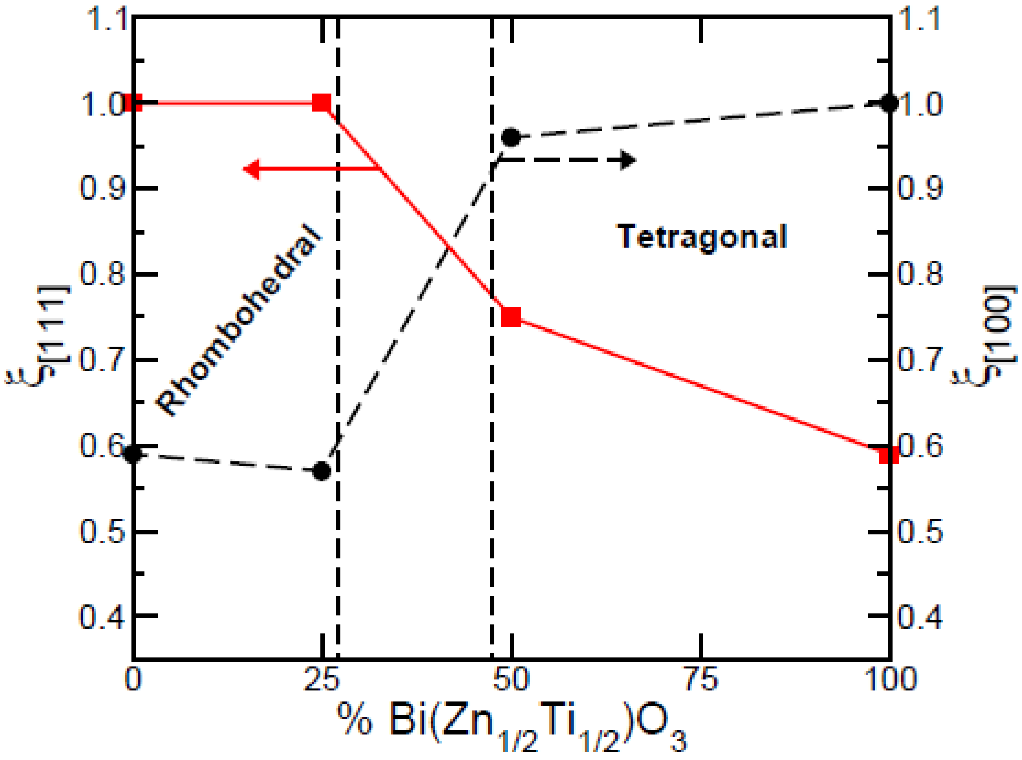
$BiSrZnNbO_6$ – Bi_2ZnTiO_6 Solid Solution

Average cation off-centerings in supercells:



Proposed Phase Diagram

Direction of *P* relative to 111 and 100:



% BZT	a [Å]	c/a	P [μC/cm^2]
100	3.74	1.22	142
50	3.84	1.11	114
25	3.95	1.01	81
0	3.95	1.01	77

- We find a region with a possible MPB and high polarization, although the tetragonality on the T side is still very high.

Summary

The mineral perovskite:
$CaTiO_3$
“A minor ore of Ti”

… pretty interesting physics though

Image from www.mindat.org: (mineral from Chelyabinsk, Russia)