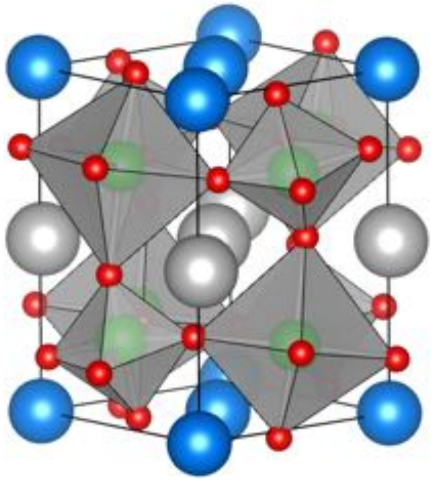
First principles design of new multiferroic materials

Nick Bristowe

Functional Materials Group, University of Kent, UK



WCPM/CSC, Warwick, May 15th 2017

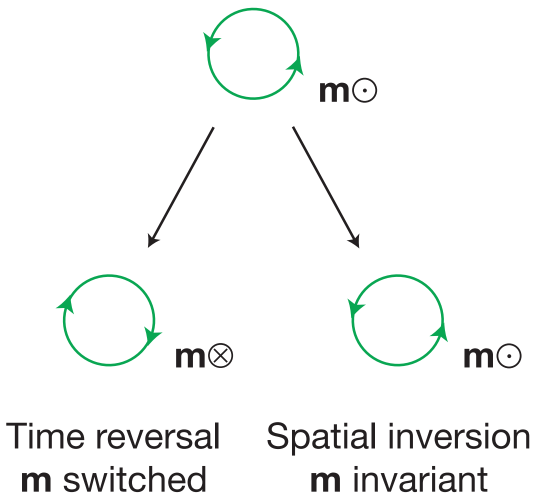
Ferroelectricity vs ferromagnetism

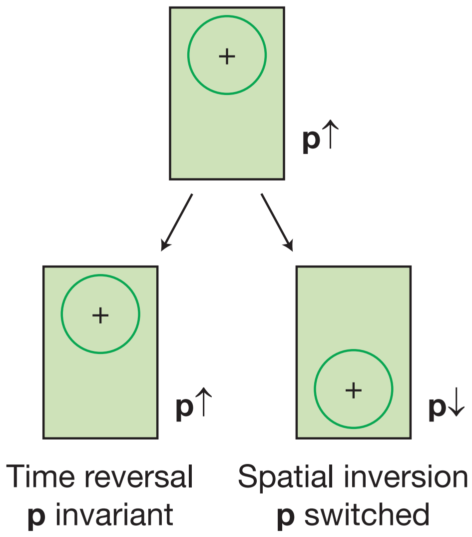
Both are types of "ferroics"

Ferroelectricity – spontaneous polarization **P** (switchable with an electric field **E**)

Ferromagnetism – spontaneous magnetization **M** (switchable with a magnetic field **H**)

Classed by symmetry:



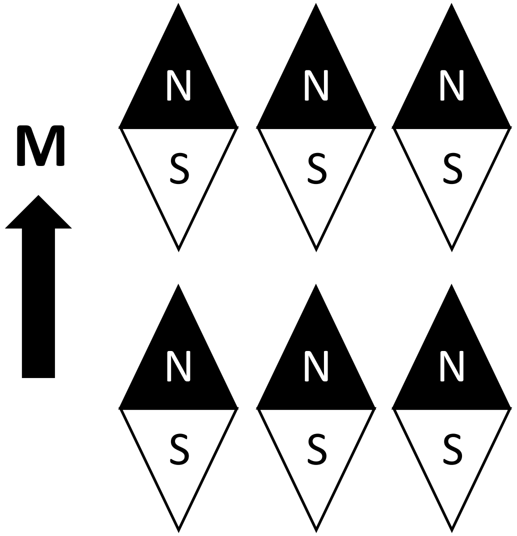


Eerenstein, Mathur & Scott Nature 442, 759 (2006)

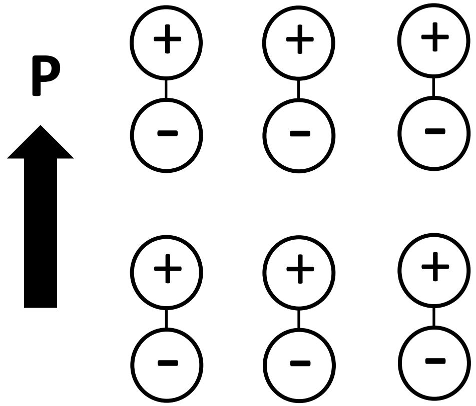
Multiferroics

Multiferroic: material combining two or more ferroic parameters

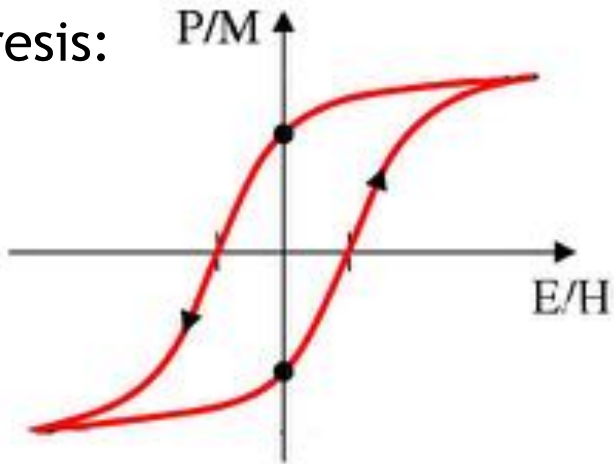
Ferromagnetic:



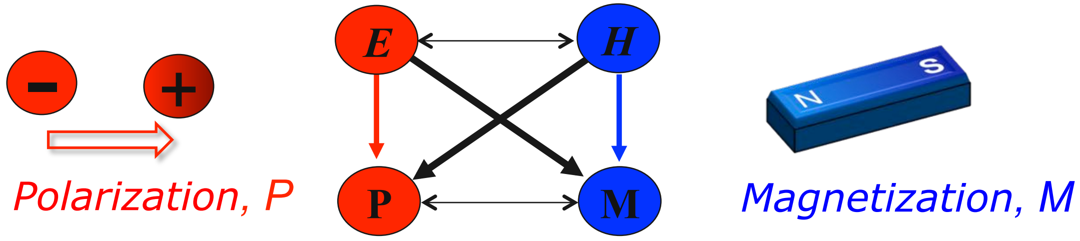
Ferroelectric:



- Hysteresis:



Magnetoelectric:

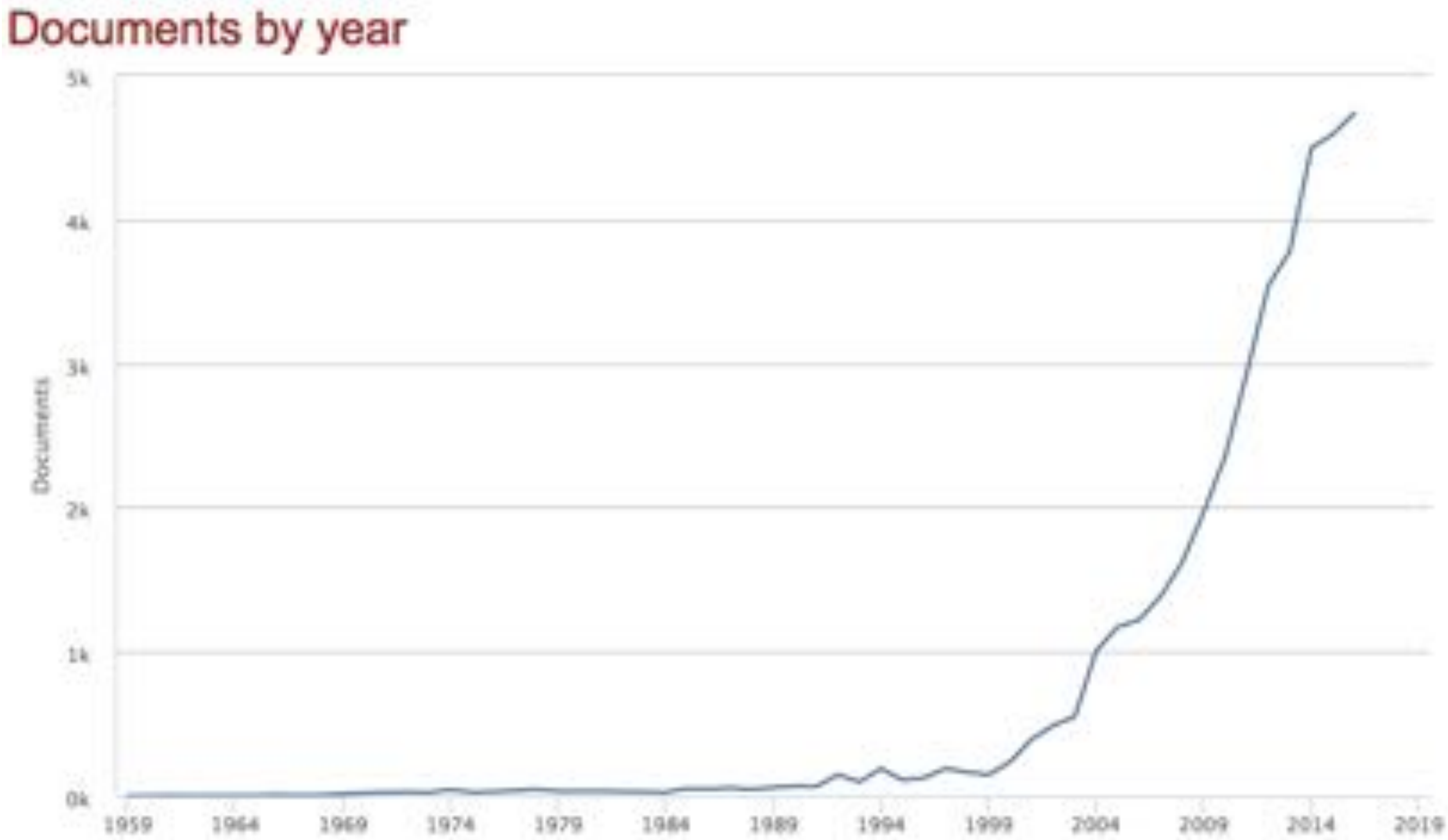


Possible applications:

- Magnetoelectric RAM: electric write / magnetic read
- 4-state memory

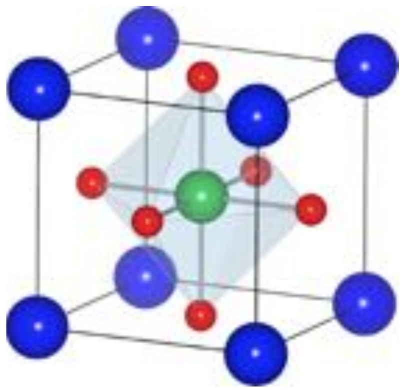
Research Activity

Scopus result for papers published with “multiferroic” OR “magnetoelectric” mentioned in any field

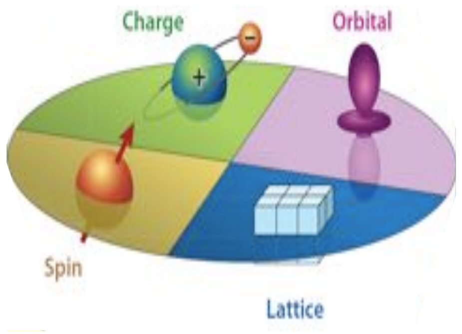


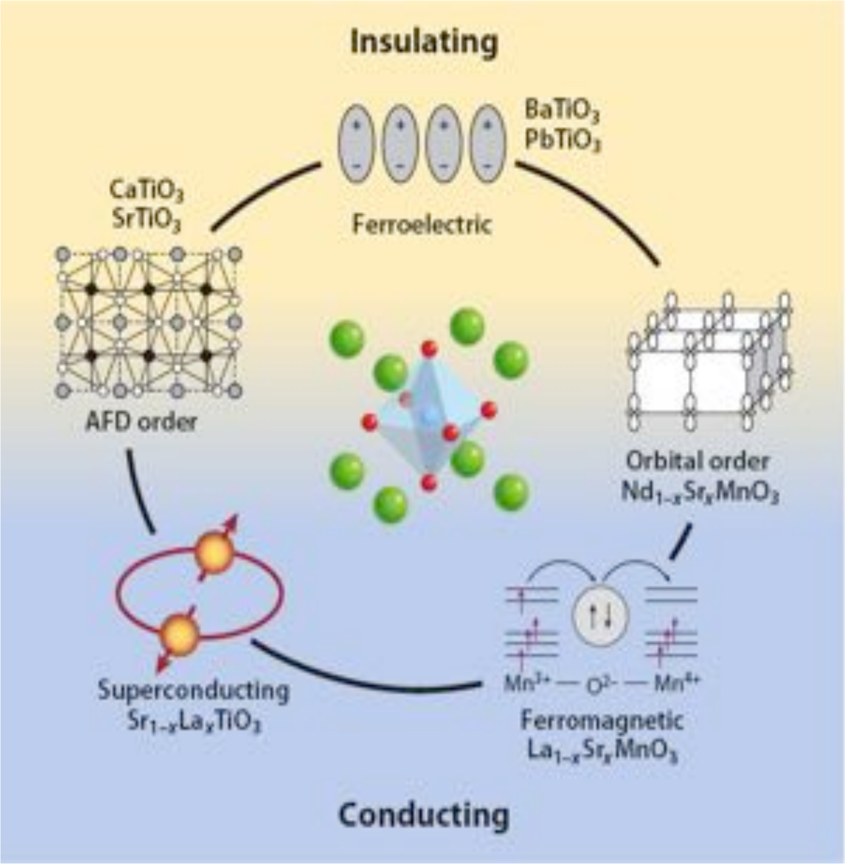
Perovskites

ABX$_3$



Wide range of properties
Due to coupling degrees of freedom

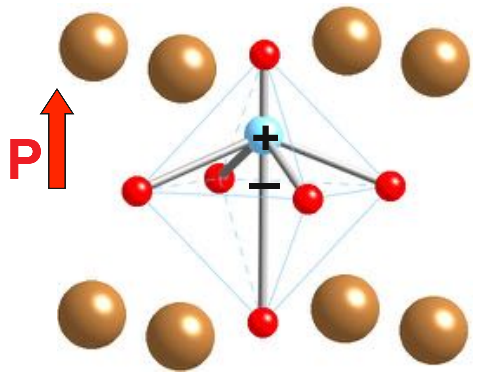




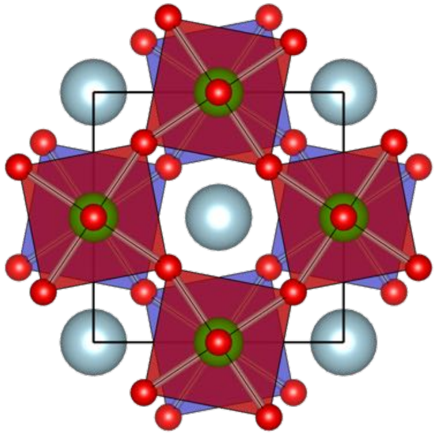
P. Zubko et al. Annu. Rev. Condens. Matter Phys. **2**, 141 (2011).

Why are most perovskites NOT FE?

$PbTiO_3$
Pure FE ground state



$CaTiO_3$
Purely tilted ground state



Why are most perovskites NOT FE?

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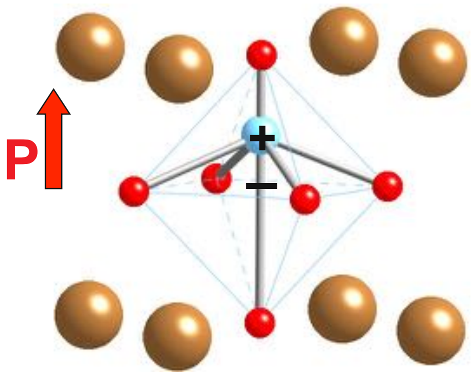
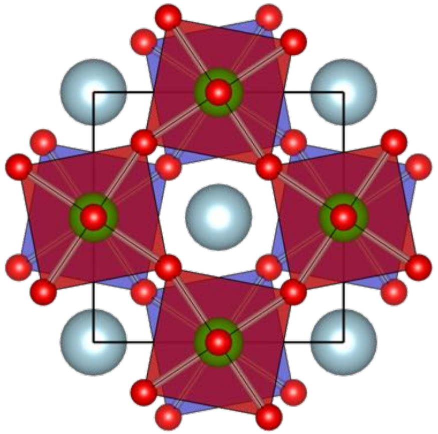
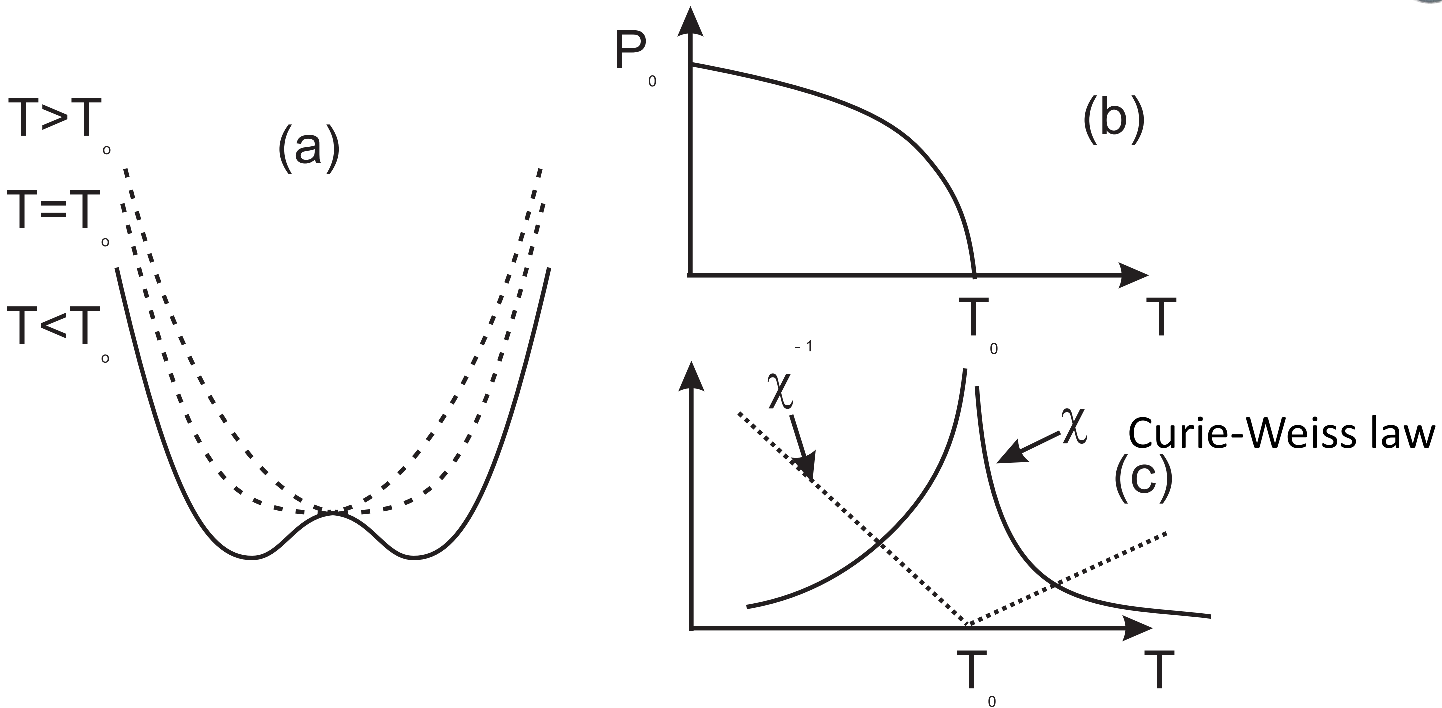


$CaTiO_3$
Purely tilted ground state



Proper phase transition (Landau)

$$f(T,P) = a_1 P^2 + a_{11} P^4 \qquad a_1 = \alpha(T - T_0)$$

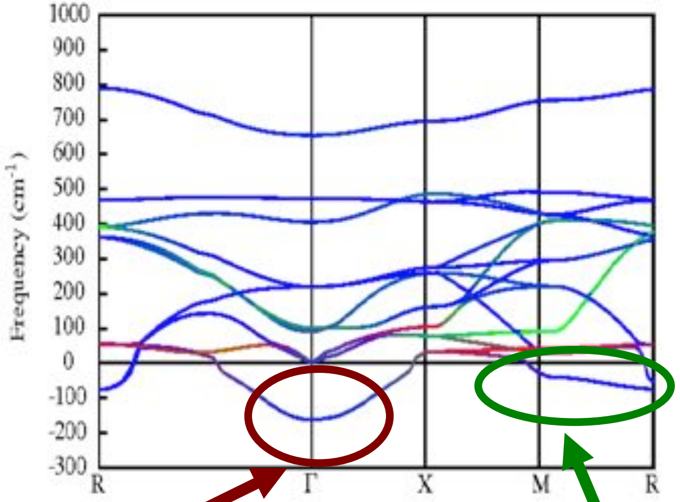


Why are most perovskites NOT FE?

Structural instabilities from simple cubic

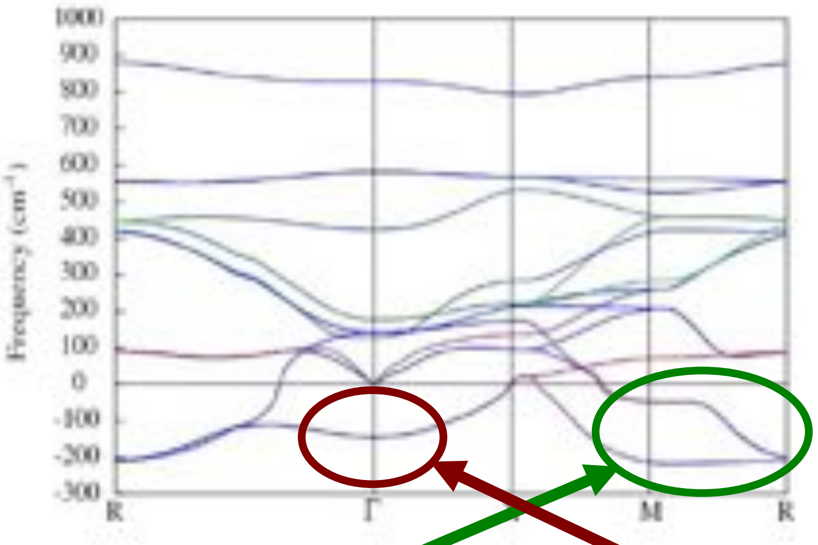
$PbTiO_3$

Pure FE ground state



$CaTiO_3$

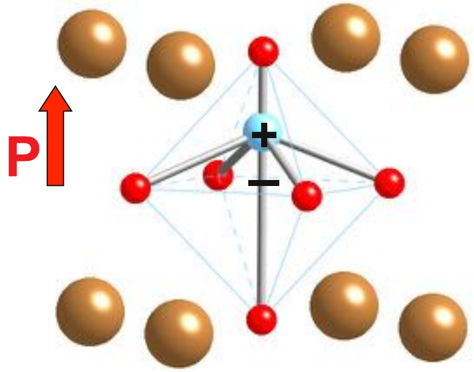
Purely tilted ground state



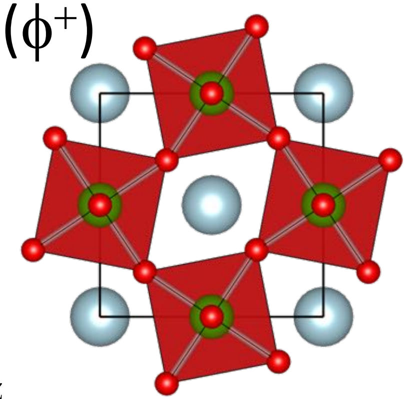
FE (ferroelectric) polar distortion

Oxygen Octahedral Tilts

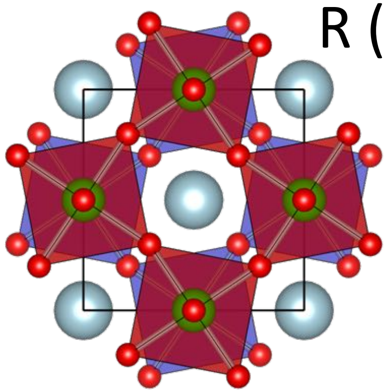
FE (ferroelectric) polar distortion

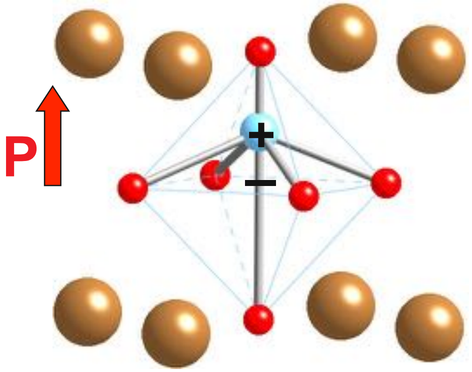


M (ϕ^+)



R (ϕ^-)

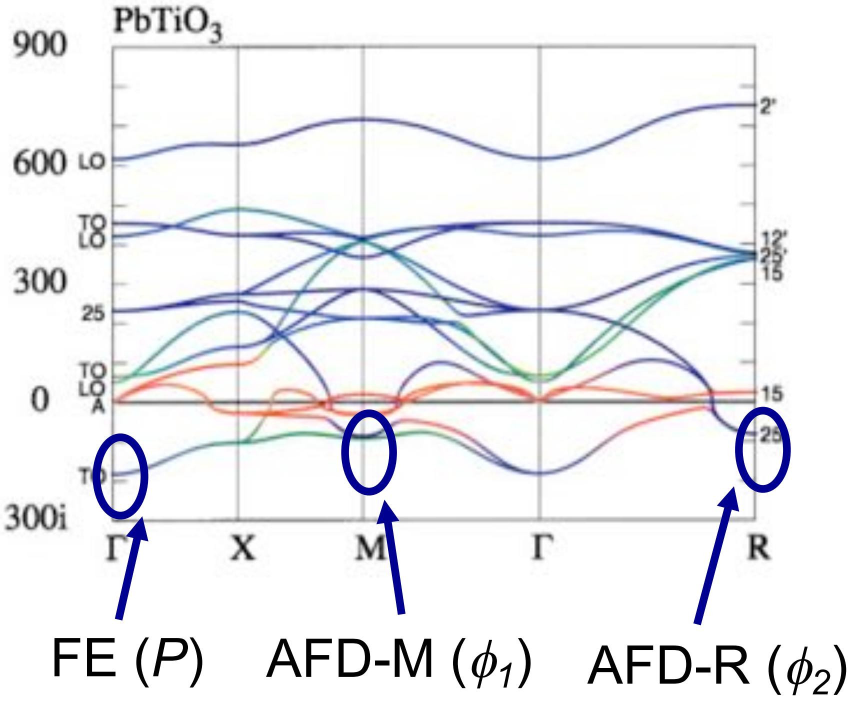




Phonons courtesy of Ph Ghosez

Why are most perovskites NOT FE?

Competing FE and AFD lattice instabilities



Tilting often wins!

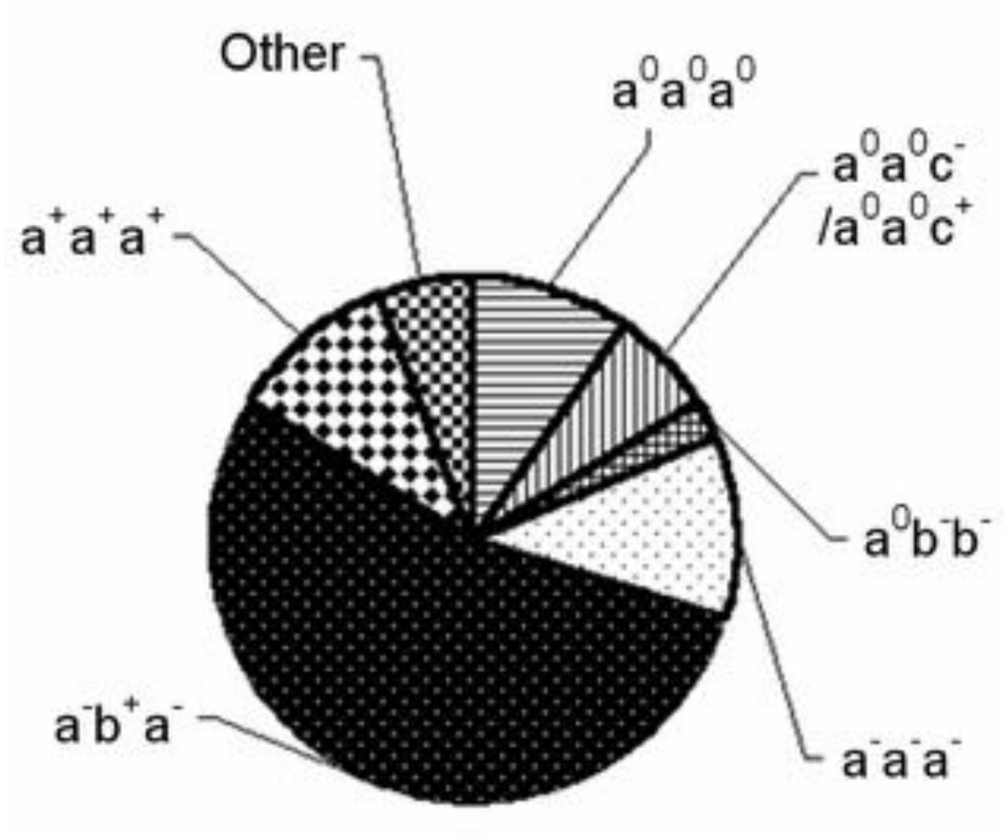
Energy landscape

$$E = \frac{1}{2}A_0P^2 + \frac{1}{4}B_0P^4 + C_{12}\phi_1^2\phi_2^2$$
$$+\frac{1}{2}A_1\phi_1^2 + \frac{1}{4}B_1\phi_1^4 + C_{01}\phi_1^2P^2$$
$$+\frac{1}{2}A_2\phi_2^2 + \frac{1}{4}B_2\phi_2^4 + C_{02}\phi_2^2P^2$$

FE and AFD usually competing through bi-quadratic coupling (C_{01},C_{02}>0)

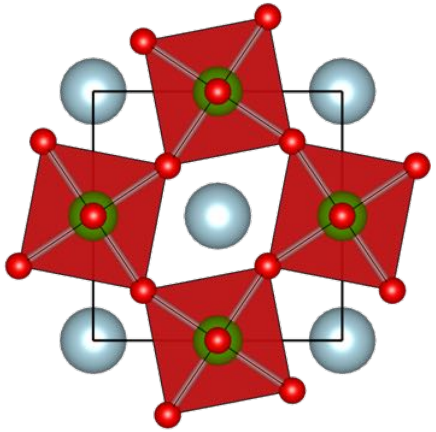
Why are most perovskites NOT FE?

They often tilt instead

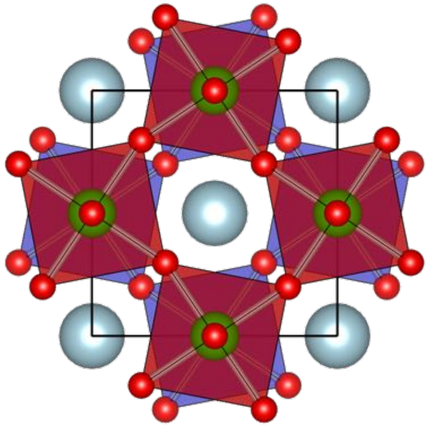


Lufaso and Woodward Acta Cryst. B57 725 (2001)

AFD (M-point) : ϕ^+



AFD (R-point) : ϕ^-



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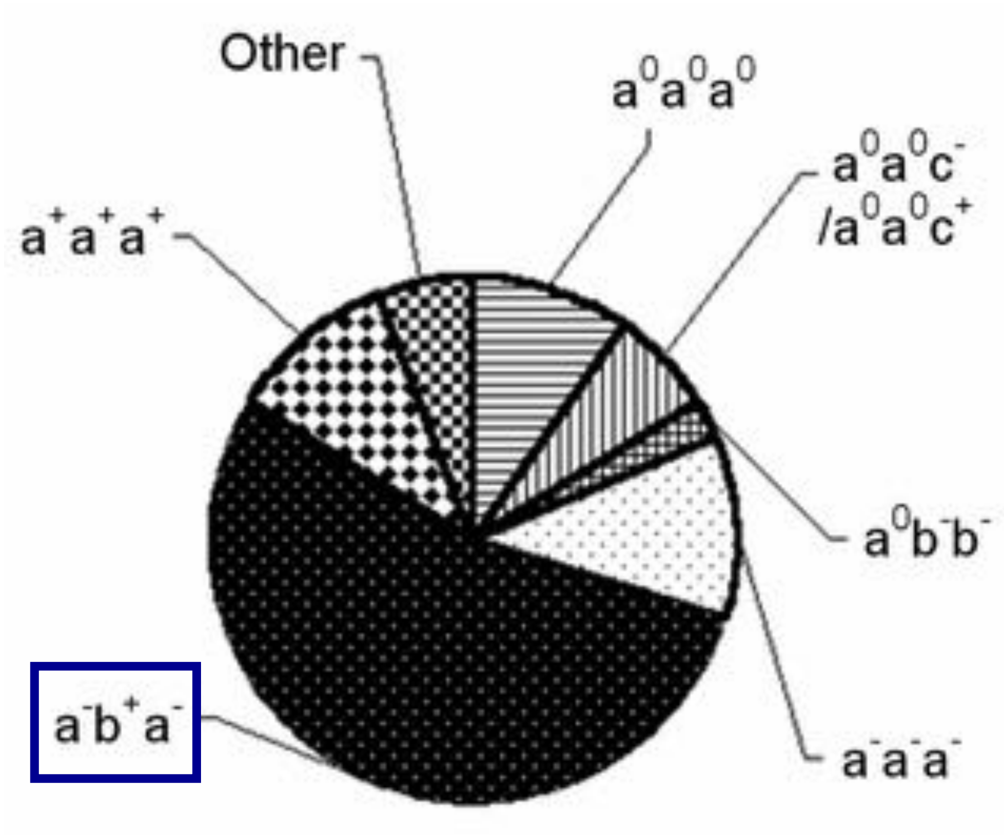
They often tilt instead



Lufaso and Woodward Acta Cryst. B57 725 (2001)

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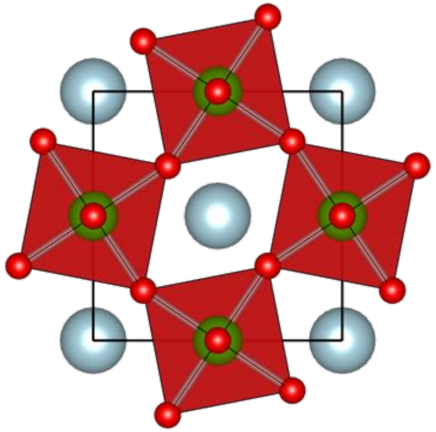
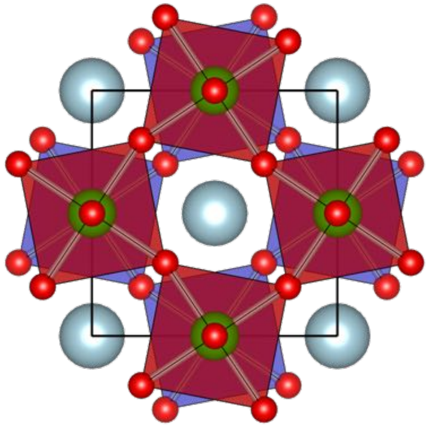
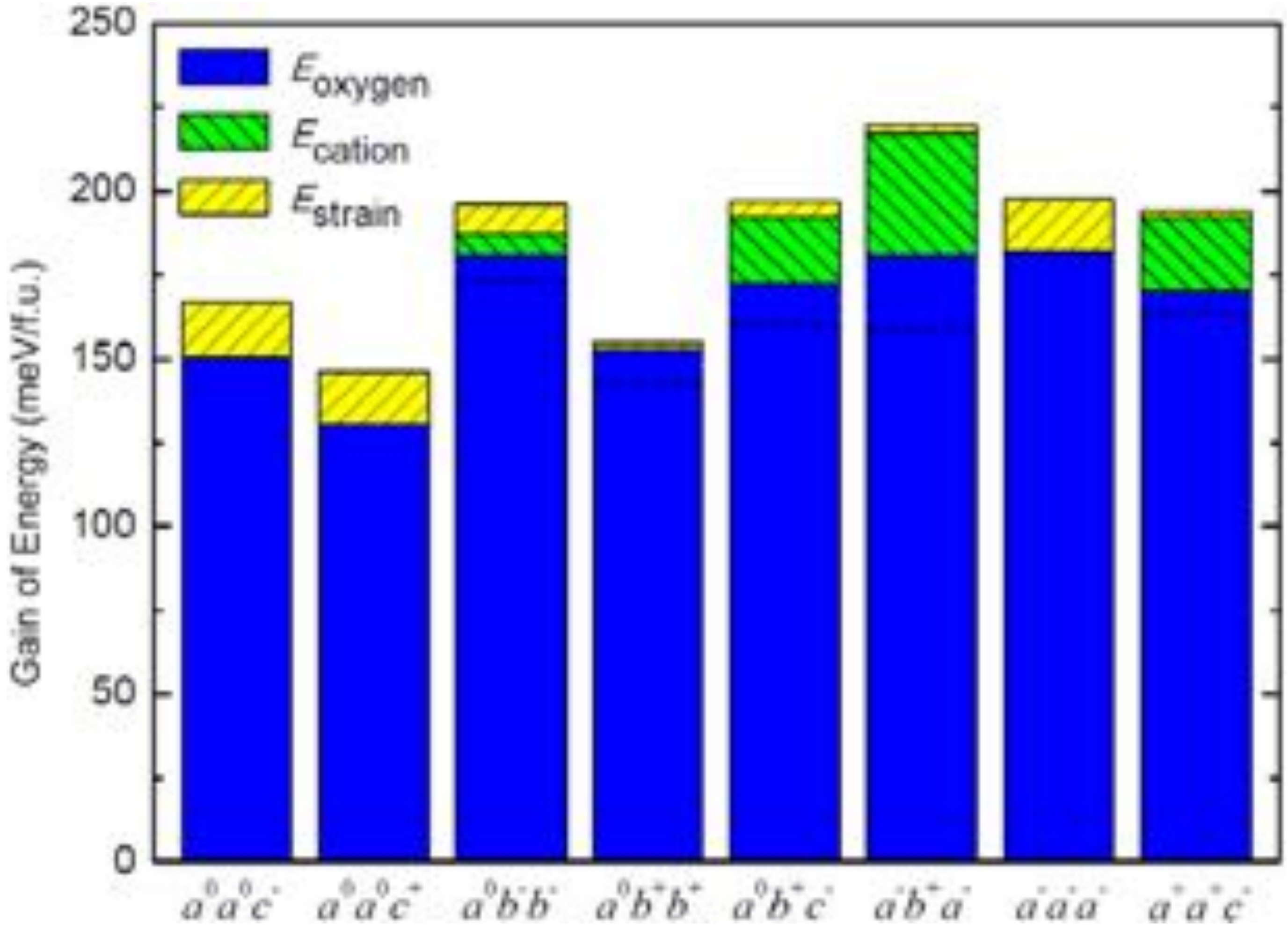


AFD (R-point) : ϕ^-



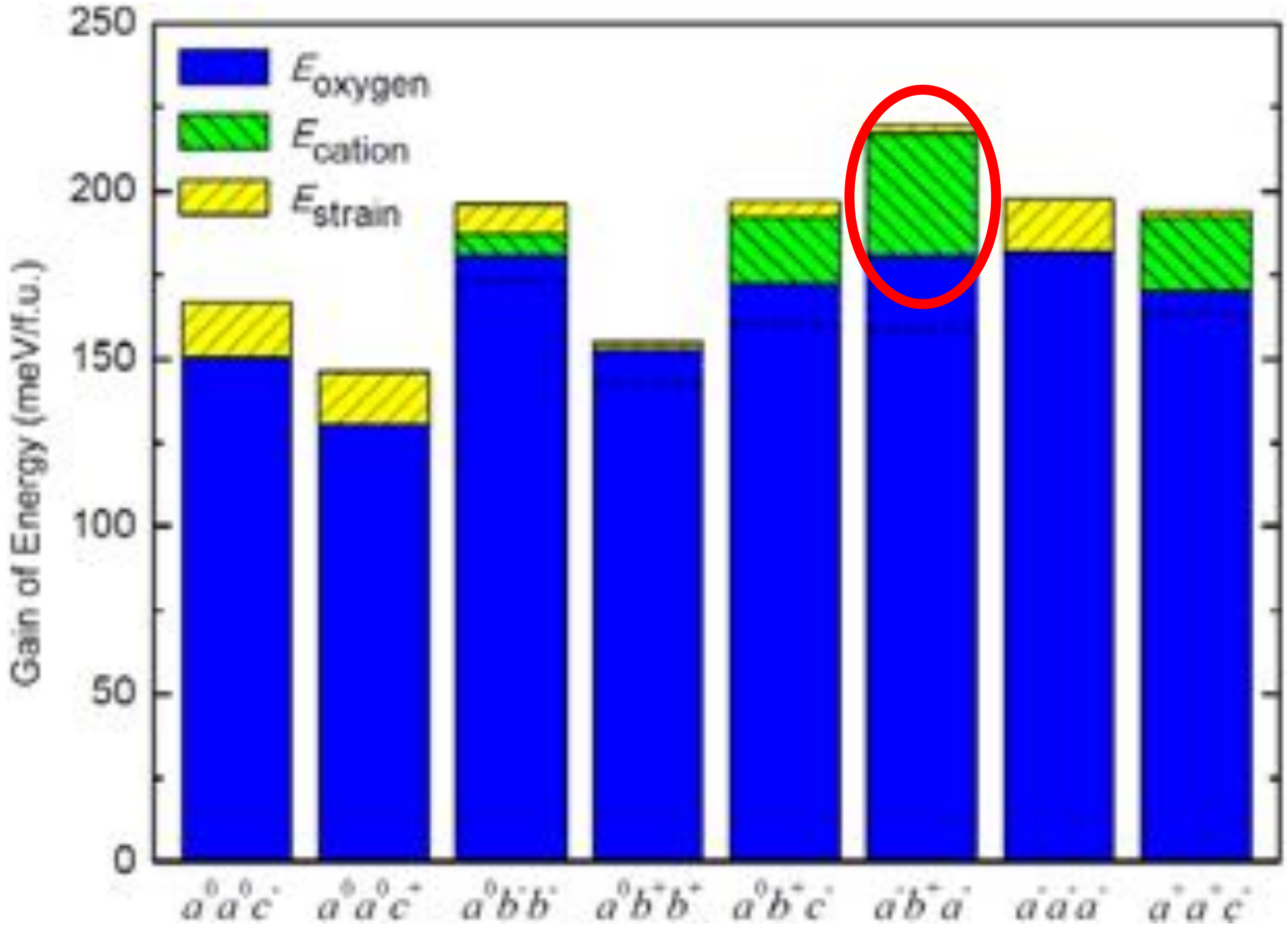
Detour: Why is *Pnma* most common?

Pnma most stable



Miao, Bristowe et al JPCM 26 035401 (2014)

Pnma most stable

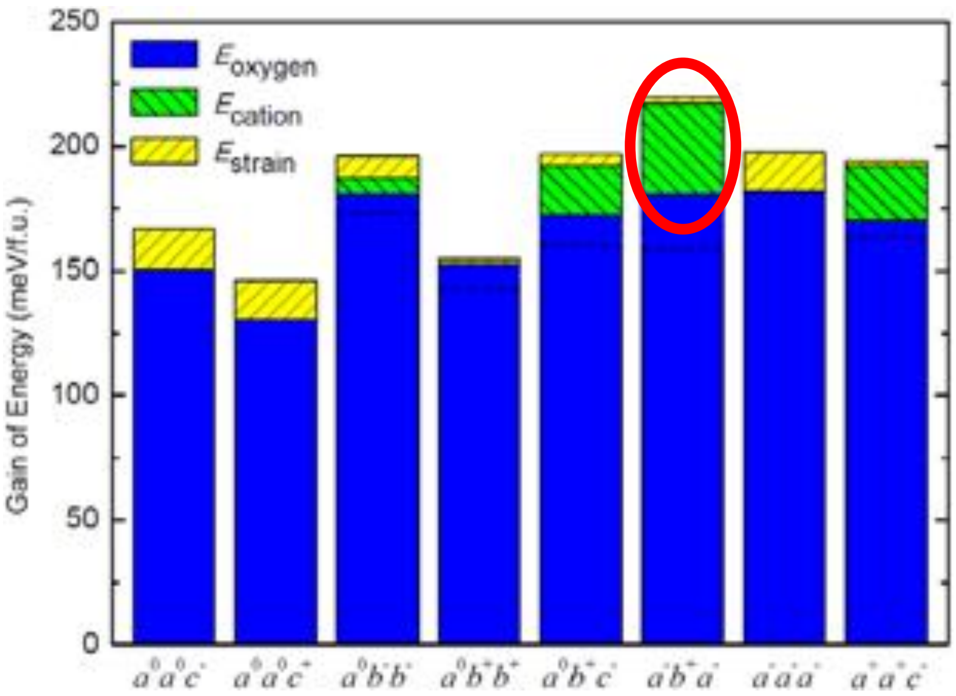


Due to other motions (not tilts!)

-> couplings at play?

Miao, Bristowe et al JPCM 26 035401 (2014)

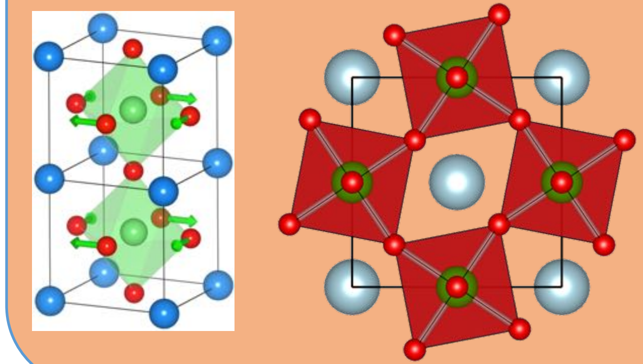
Trilinear terms



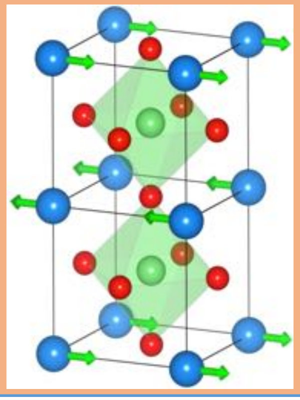
$$\mathcal{F}(X_5^-, \phi_z^+, \phi_{xy}^-) \propto \lambda \phi_z^+ \phi_{xy}^- X_5^-$$

Miao, Bristowe et al JPCM 26 035401 (2014)

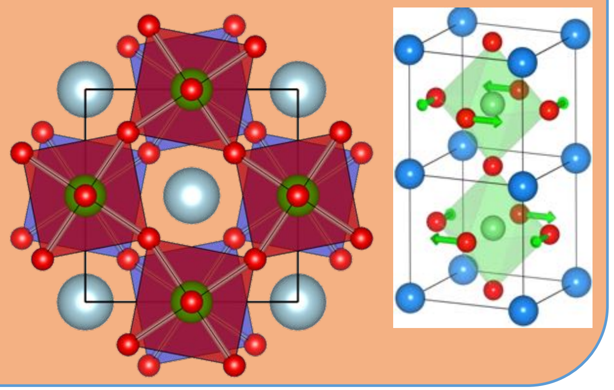
AFD (M-point) : ϕ_z^+



Anti-polar : X_5^-



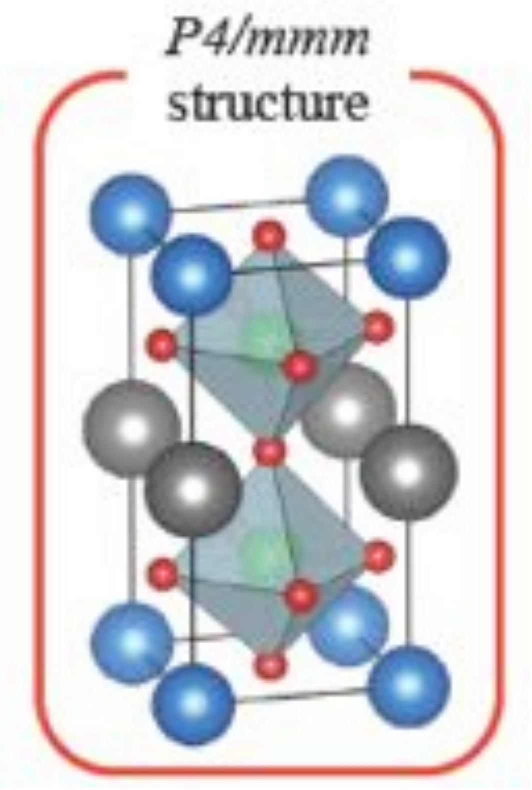
AFD (R-point) : ϕ_x^-



Can we cooperatively couple AFD with FE?

$$\mathcal{F}(X_5^-, \phi_z^+, \phi_{xy}^-) \propto \lambda \phi_z^+ \phi_{xy}^- X_5^-$$

Turn anti-polar *X* mode to polar mode?



Consider digital superlattice

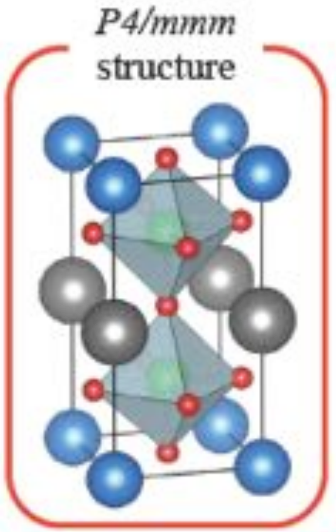
Layers of **A** and A’ in alternate (001) planes

can be grown layer-by-layer (e.g. PLD MBE)

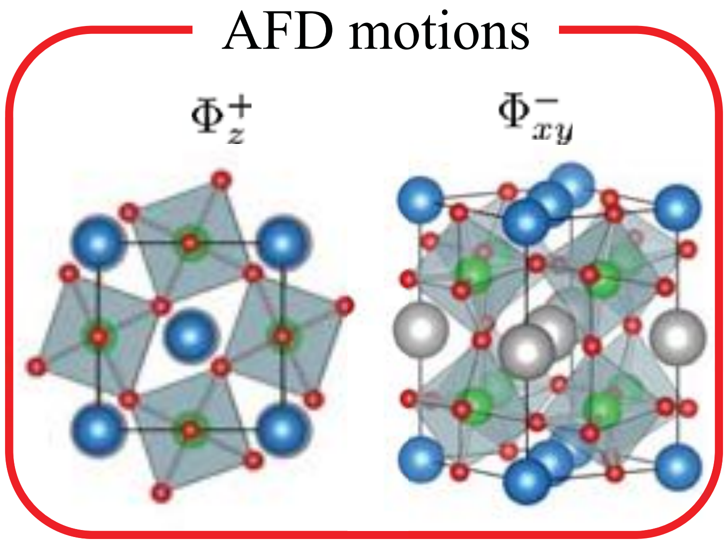
or naturally ordered (e.g. double perovskites)

(the same concept will work on thicker superlattices, and other layered materials e.g. RP, DJ, Aurivilius)

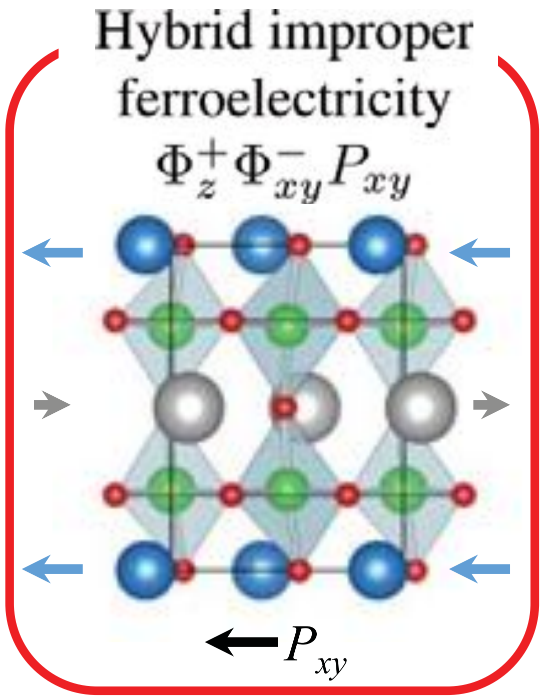
Rotationally driven ferroelectricity



digital superlattice



$$E = \lambda \phi_{xy}^- \phi_z^+ P_{xy}$$

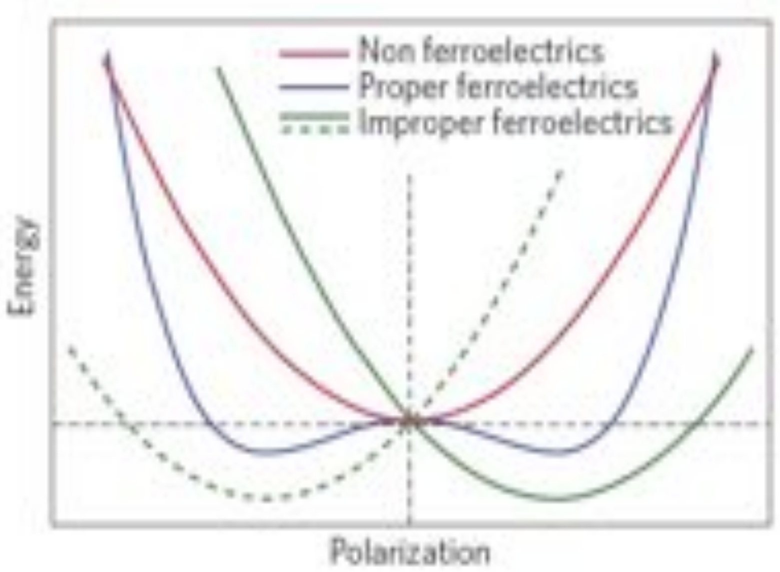


Only ingredient is *Pnma* type rotations and layering

Bousquet et al Nature 452 732 (2008), Fukushima et al PCCP 13 12186 (2011), Rondinelli et al Adv Materials 24 1961 (2012)

(Hybrid) Improper Ferroelectricity

Shift the well to lower energy through the coupling with other phonon modes



"Hybrid" = requires two independent order parameters belonging to a different subspaces

Hybrid improper ferroelectricity

$$E = \frac{1}{2}A_0P^2 + \frac{1}{4}B_0P^4 + C_{12}\phi_1^2\phi_2^2$$
$$+\frac{1}{2}A_1\phi_1^2 + \frac{1}{4}B_1\phi_1^4 + C_{01}\phi_1^2P^2$$
$$+\frac{1}{2}A_2\phi_2^2 + \frac{1}{4}B_2\phi_2^4 + C_{02}\phi_2^2P^2$$
$$+\lambda\phi_1\phi_2P$$

Trilinear coupling term

- $\lambda\phi_1\phi_2$ acts as an effective field shifting P well to lower energy
- **Switching P requires reversing either ϕ_1 or ϕ_2 (and perhaps M)**

Figure courtesy of Ph Ghosez

Experimental signatures

nature materials
ARTICLES
PUBLISHED ONLINE: 12 JANUARY 2015 | DOI: 10.1038/NMAT4168

Experimental demonstration of hybrid improper ferroelectricity and the presence of abundant charged walls in $(Ca,Sr)_3Ti_2O_7$ crystals

Yoon Seok Oh[1,2†], Xuan Luo[3], Fei-Ting Huang[1,2], Yazhong Wang[1,2] and Sang-Wook Cheong[1,2,3★]

PRL **114,** 035701 (2015) PHYSICAL REVIEW LETTERS week ending 23 JANUARY 2015

Negative Thermal Expansion in Hybrid Improper Ferroelectric Ruddlesden-Popper Perovskites by Symmetry Trapping

M. S. Senn,[1,2,*] A. Bombardi,[1] C. A. Murray,[1] C. Vecchini,[3] A. Scherillo,[4] X. Luo,[5] and S. W. Cheong[5,6]

nature Vol 452|10 April 2008|**doi:10.1038/nature06817**

LETTERS

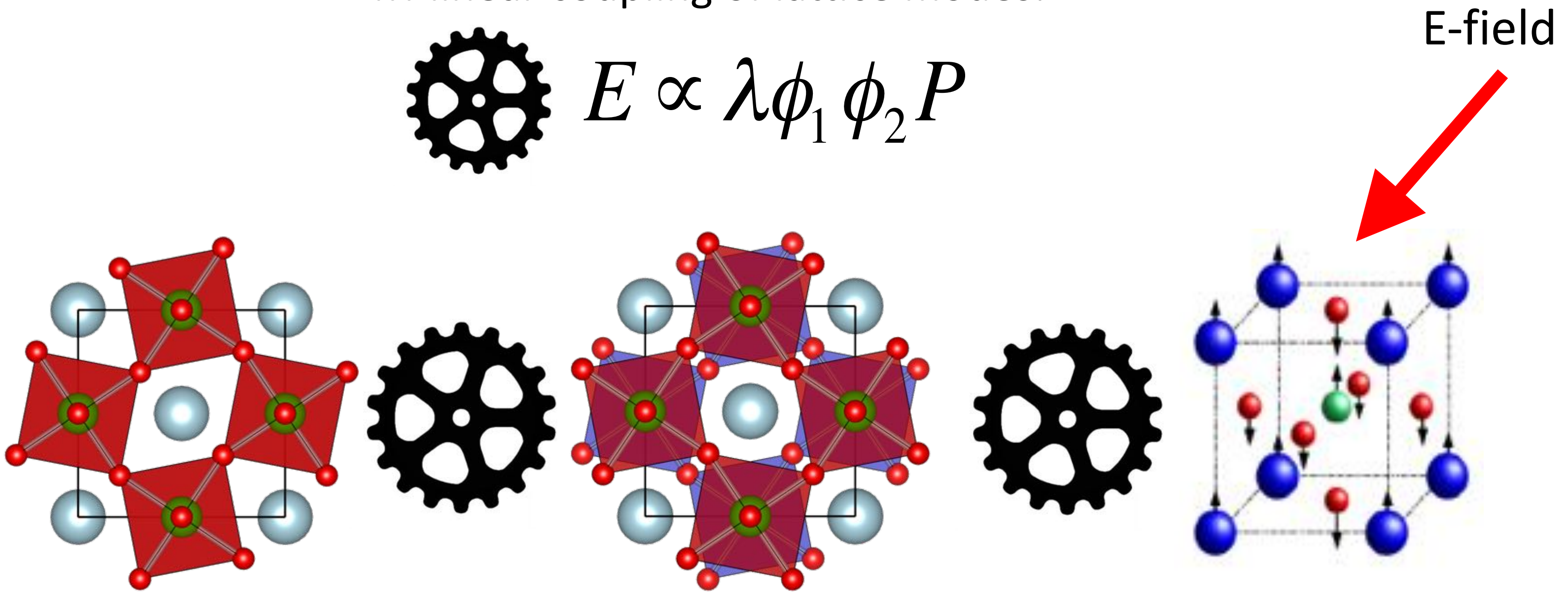
Improper ferroelectricity in perovskite oxide artificial superlattices

Eric Bousquet[1]*, Matthew Dawber[2]*†, Nicolas Stucki[2], Céline Lichtensteiger[2], Patrick Hermet[1], Stefano Gariglio[2], Jean-Marc Triscone[2] & Philippe Ghosez[1]

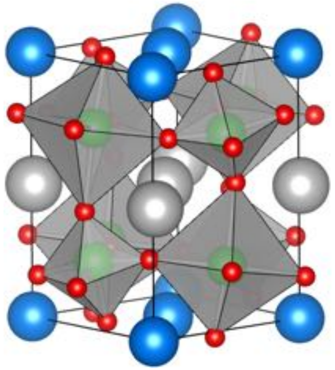
Hybrid Improper Ferroelectricity

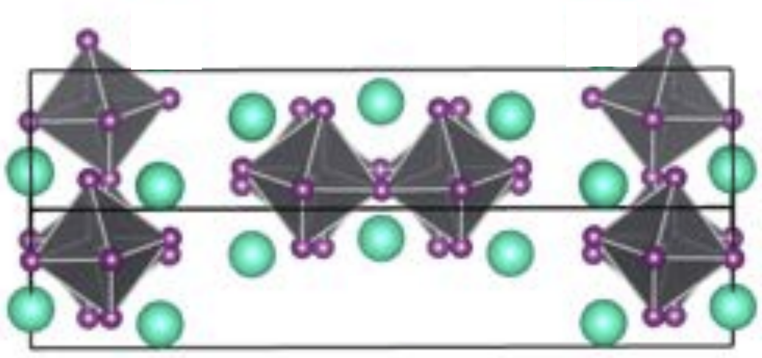
Tri-linear coupling of lattice modes:

$$E \propto \lambda \phi_1 \phi_2 P$$



Typically in *layered* perovskites with $a^-a^-c^+$ tilt pattern:





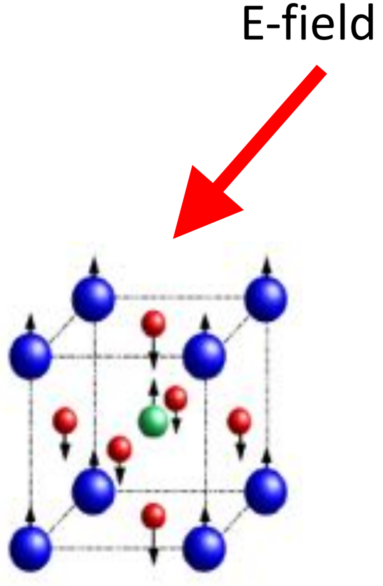
Bousquet et al Nature **452** 732 (2008), Fukushima et al PCCP **13** 12186 (2011), Benedek et al PRL **106** 107204 (2011)

Alternative to tilts?

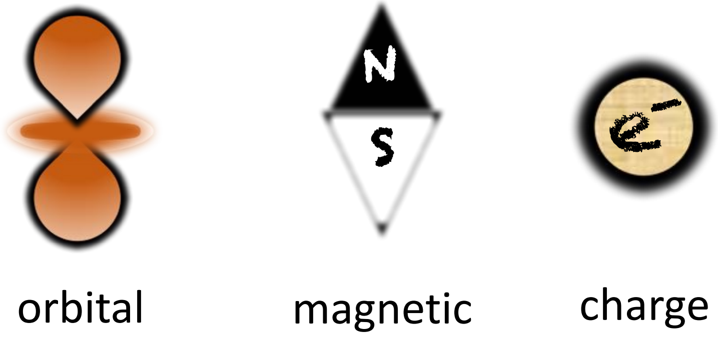
Tri-linear coupling of lattice modes:

$$E \propto \lambda R_1 R_2 P$$

R_1? R_2?



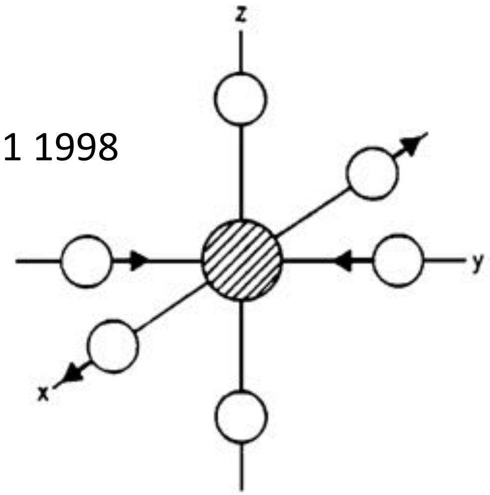
Want R to strongly couple to electronic degrees of freedom:



Jahn-Teller distortion

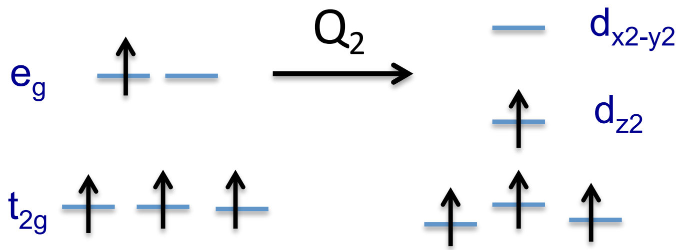
The “Q_2” distortion:

Goodenough, Annu. Rev. Mater. Sci. 28 1 1998



Orthorhombic with two short, medium and long bond lengths

e.g. Mn^{3+}



Jahn-Teller distortion

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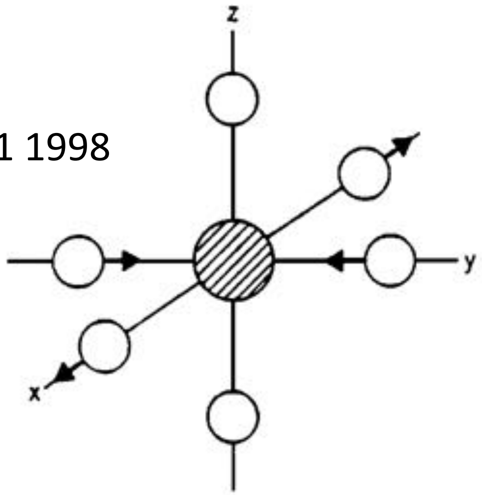
Goodenough, Annu. Rev. Mater. Sci. 28 1 1998

Orthorhombic with two short, medium and long bond lengths

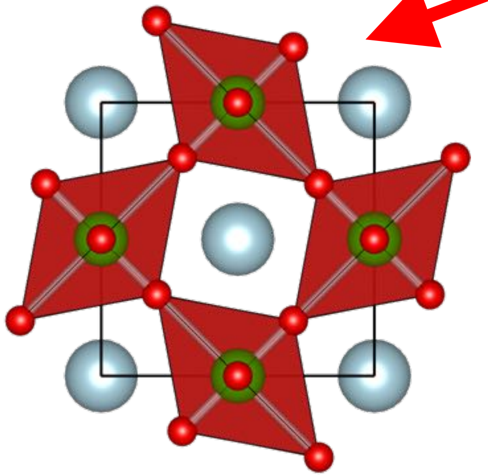
M_{JT}

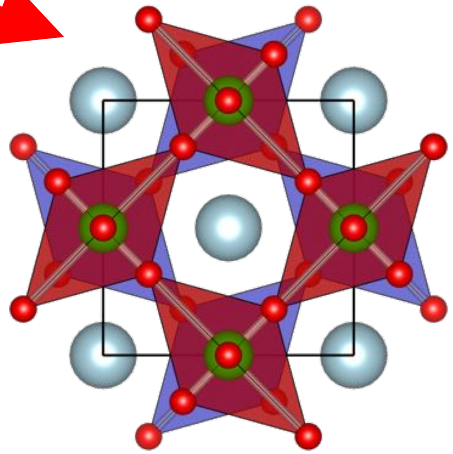
M-point

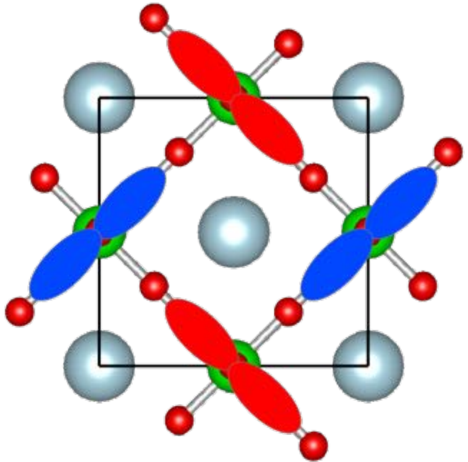


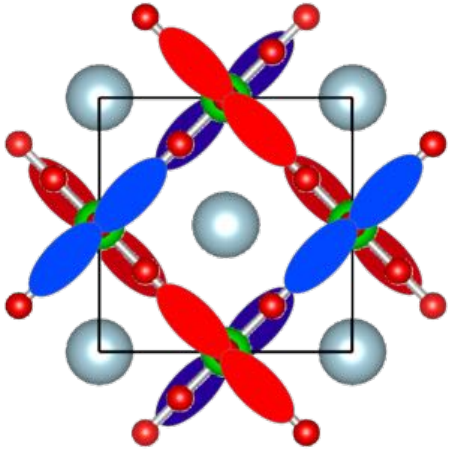
R-point

R_{JT}

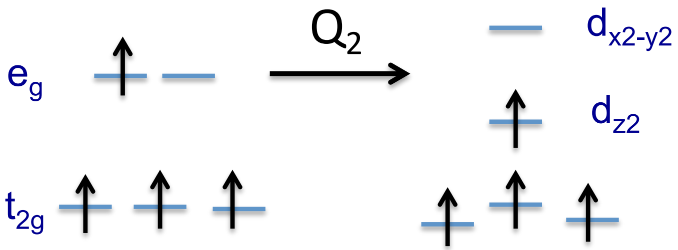








e.g. Mn^{3+}

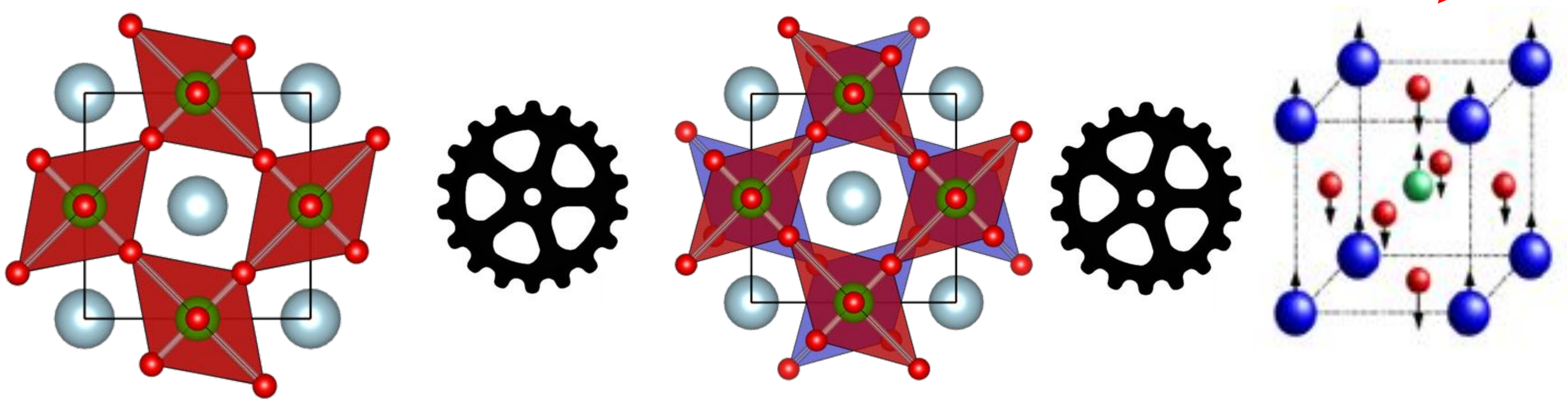


Produces different orbital orderings, and hence spin orderings

Alternative to tilts – Jahn-Teller distortion

Tri-linear coupling of lattice modes:

$$E \propto \lambda R_1 R_2 P$$



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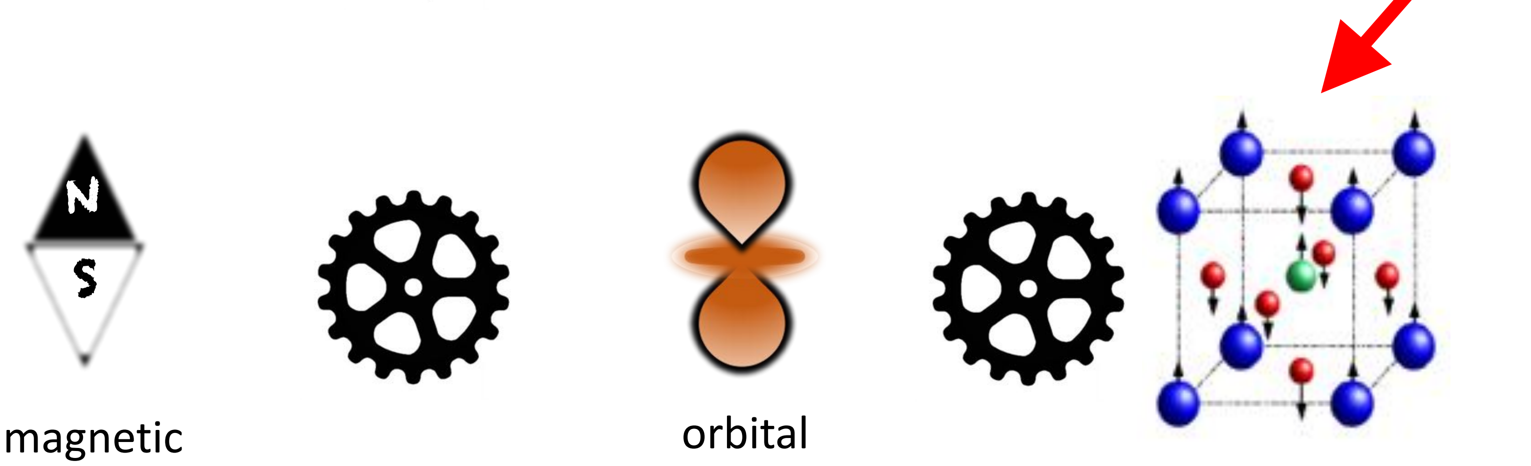
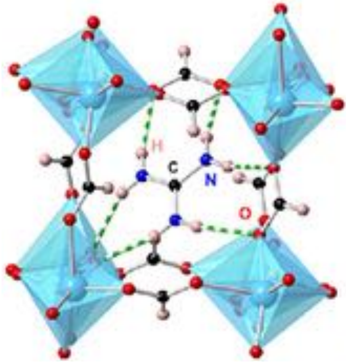


Potential applications: magnetoelectrics, electrochromic, MITs, transistors …. ??

Similar mechanism proposed in related MOFs for multiferroic magnetoelectric applications



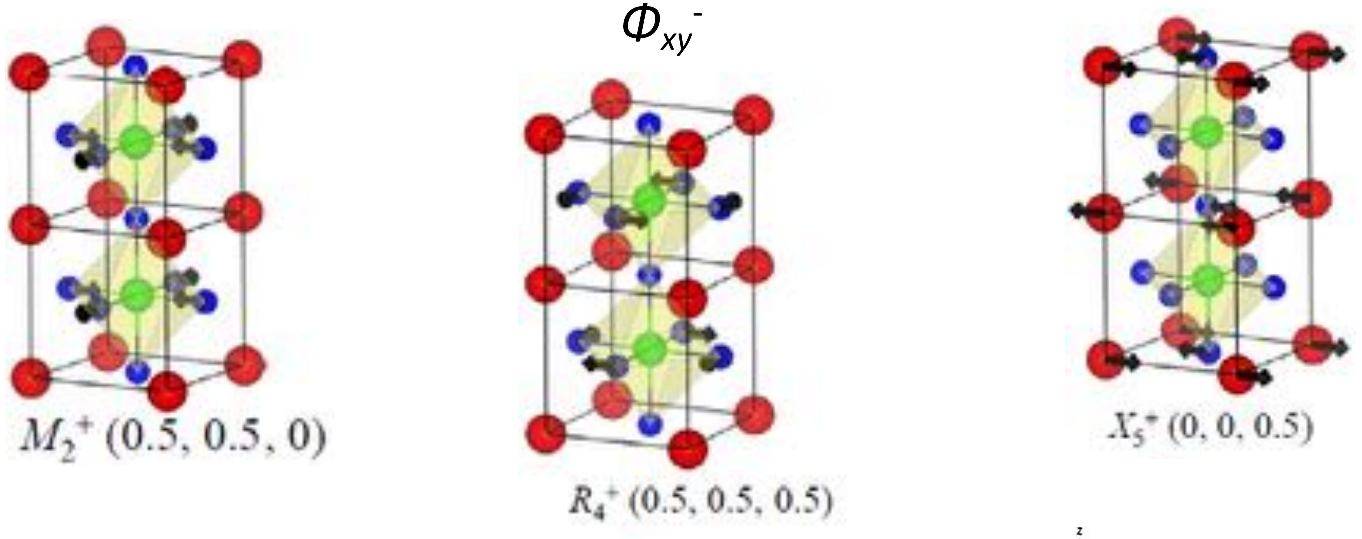
[1] Stroppa *et al.*, Adv. Mater. **25**, 2284 (2013)
[2] Tian *et al.*, Phys. Status Solidi RRL **9**, 62 (2015)

Lattice-driven Jahn-Teller distortion

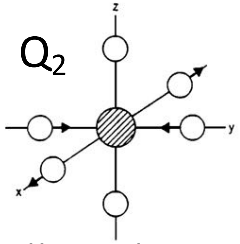
M_{JT} is allowed, and always appears, in *Pnma* perovskites [1,2]

$$E \propto \lambda M_{JT} \phi_{xy}^{-} A_{xy}$$

M_{JT} Φ_{xy}^{-} A_{xy}



Does not have to appear as an electronic instability!



Here we define a Jahn-Teller *distortion*:
by the symmetry of the mode (Q_2), whether it is electronically or lattice driven

[1] Carpenter & Howard, Acta Cryst. B **65,** 134 (2009)
[2] Miao, Bristowe, Xu, Verstraete & Ghosez, JPCM **26** 035401 (2014)

Highlight three P-JT couplings

Symmetry analysis supported by first principles calculations (PBEsol+U and/or B1WC)

1) Superlattices (d^1-d^0)
Titanates: $ATiO_3$-$RTiO_3$

$$E \propto \lambda M_{JT} \phi^{-}_{xy} P_{xy}$$

Bristowe, Varignon, Fontaine, Bousquet & Ghosez,
Nat. Commun. **6**, 6677 (2015)

2) Superlattices (d^2-d^2)
Vanadates: RVO_3-$R'VO_3$

$$E \propto \lambda M_{JT} P_z R_{JT}$$

Varignon, Bristowe, Bousquet & Ghosez,
Sci Reports **5**, 15364 (2015)

3) Epitaxial bulk (all d fillings)
ferrites, titanates, manganites …

$$E \propto \lambda M_{JT} P_{xy} A_{xy}$$

Varignon, Bristowe & Ghosez,
Phys. Rev. Lett **116**, 057602 (2016)

Collaborators

Theoretical Materials Physics, University of Liege, BELGIUM

Philippe Ghosez

Julien Varignon

Now at CNRS, Thales, France

Eric Bousquet

Denis Fontaine

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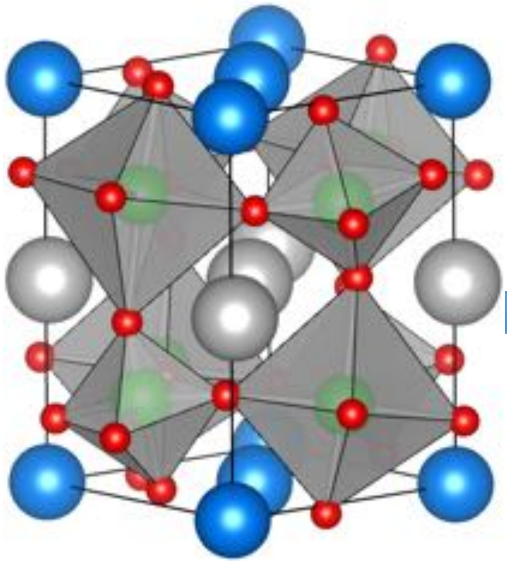
Varignon, Bristowe & Ghosez,
Phys. Rev. Lett **116**, 057602 (2016)

$ATiO_3$-$RTiO_3$ superlattice

A^{2+} = Sr, Ba, (Ca)

$Ti^{3.5+}$ = Ti

R^{3+} = La, Pr, Sm Y, Tm, (Lu)



Ground-state

(In all cases!)

- Monoclinic $P2_1$ symmetry
- Insulating
- Ferroelectric
- Ferromagnetic

Symmetry adapted mode analysis

R, A	Q					P	Δ	ΔE
	Φ_z^+	Φ_{xy}^-	P_{xy}	B	M_{JT}			
Sm, Sr	0.96	1.19	0.56	0.10	0.04	14.9	0.46	20.1
Y, Sr	1.10	1.30	0.66	0.11	0.04	16.7	0.57	18.0
Tm, Sr	1.18	1.36	0.72	0.11	0.03	18.2	0.63	16.4
Sm, Ba	0.75	0.96	0.48	0.13	0.07	18.6	0.50	18.5
Y, Ba	0.95	1.08	0.59	0.14	0.07	21.2	0.60	13.9
Tm, Ba	1.05	1.16	0.65	0.16	0.07	23.4	0.66	10.5

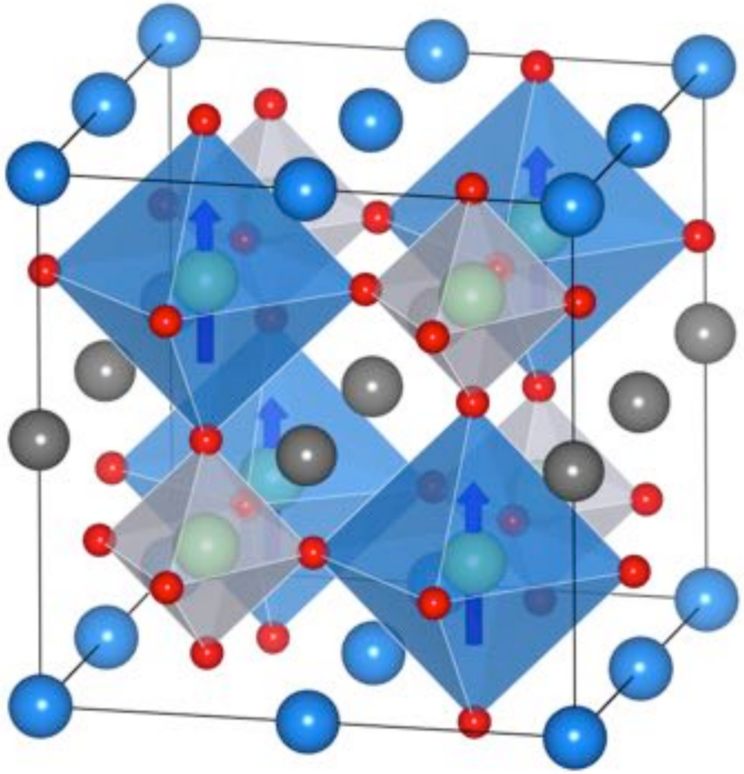
$(a^0a^0c^+)(a^-a^-c^0)$

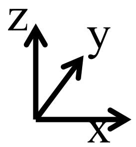
Pnma-like ($a^-a^-c^+$) ground state

$$E = \lambda \phi_{xy}^- \phi_z^+ P_{xy}$$

Ferroelectric: Amplification of P through dissimilar Z*

System remains insulating





R, A	Q					P	Δ	ΔE
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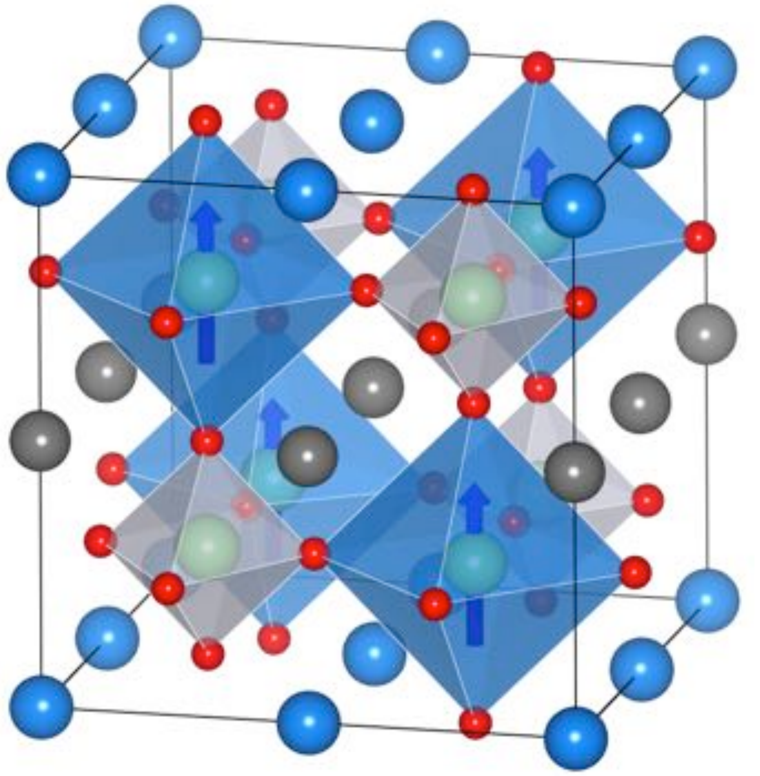
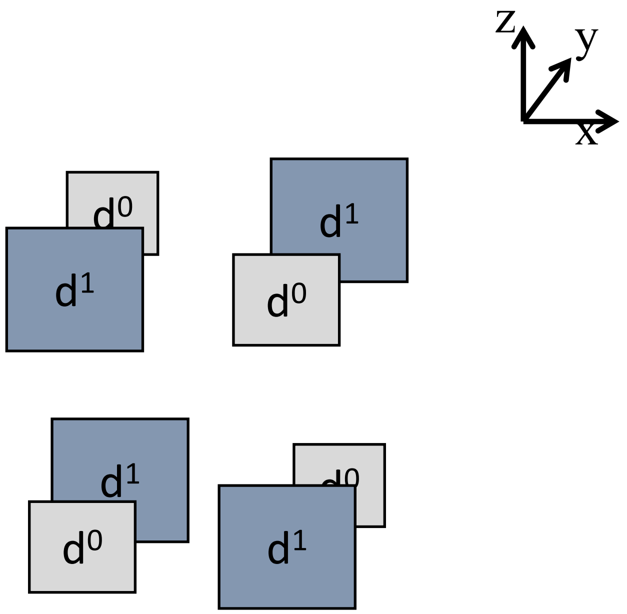
System remains insulating





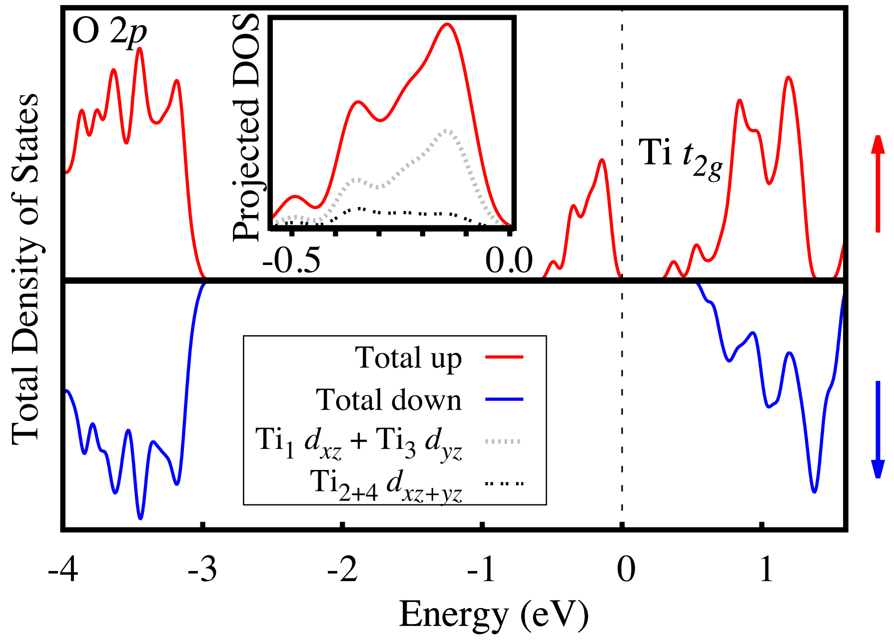
Charge ordered (d^1- d^0) state associated with a Breathing distortion

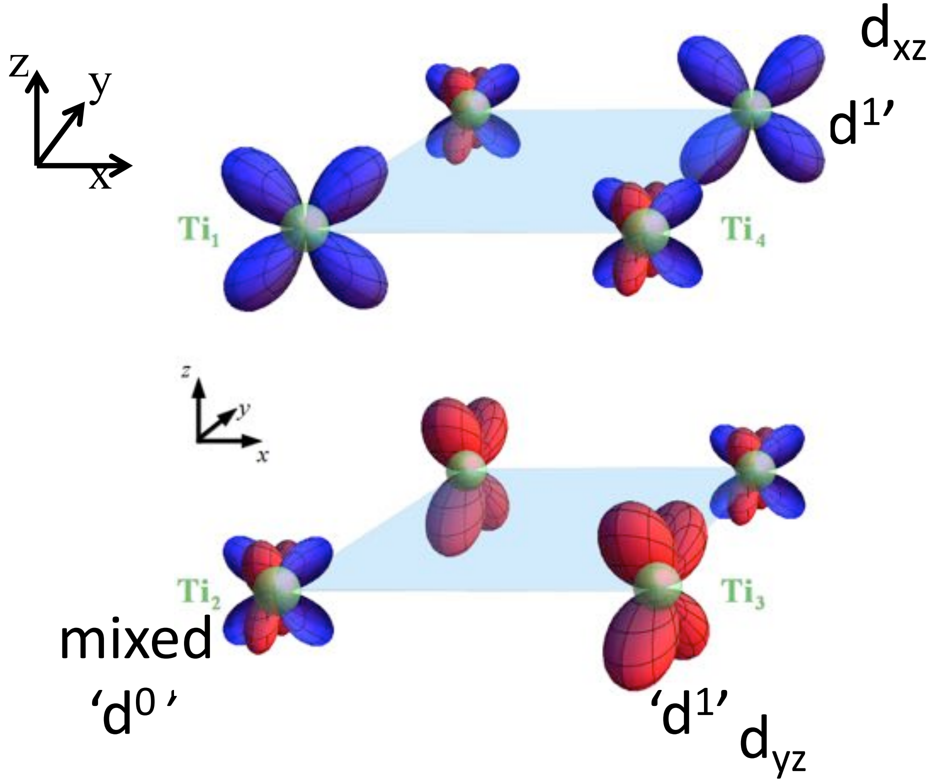
Lifts the degeneracy between neighboring Ti sites

Charge order reported in similar systems:

R. Pentcheva and W.E. Pickett, Phys. Rev. Lett. **99**, 016802 (2007)
A.C. Komarek *et al.*, arXiv:1109.0234 (2012)

Electronic structure – charge+ orbital ordering





- Spin-polarized split-off d^1 band
- Not the ideal d^1–d^0 occupancy
- <u>d^1 site</u> : orbital ordering d_{xz} – d_{yz}
- <u>d^0 site</u> : orbital mixing

Origin of orbital ordering

M_{JT} distortion allowed by symmetry
(equivalent to the coupling in *Pnma*)

$$\mathscr{F} \propto P_{xy}\phi_z^+\phi_{xy}^- + P_{xy}M_{JT}\phi_{xy}^-$$

R, A	Q					P	Δ	ΔE
	Φ_z^+	Φ_{xy}^-	P_{xy}	B	M_{JT}			
Sm, Sr	0.96	1.19	0.56	0.10	0.04	14.9	0.46	20.1
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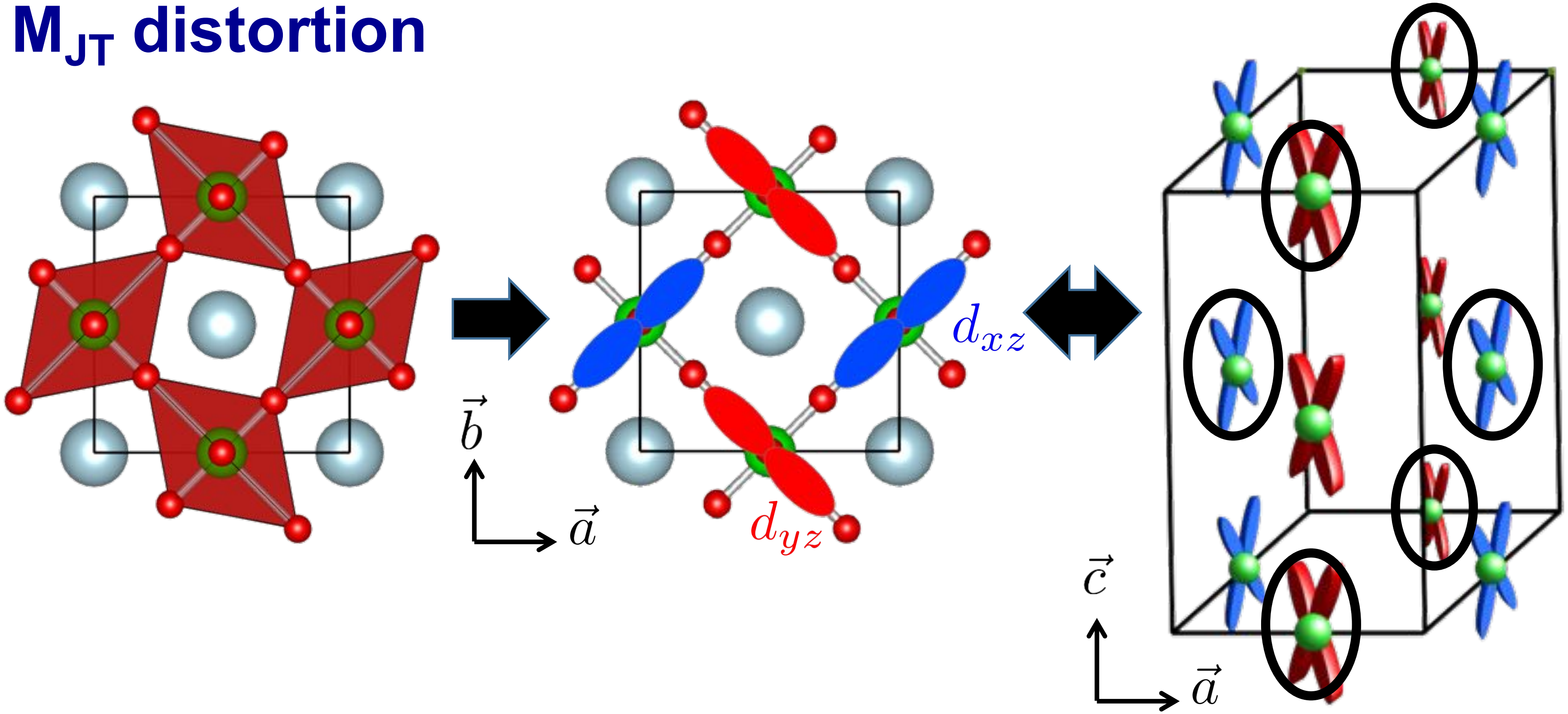
Tm, Ba	1.05	1.16	0.65	0.16	0.07	23.4	0.66	10.5

Origin of orbital ordering

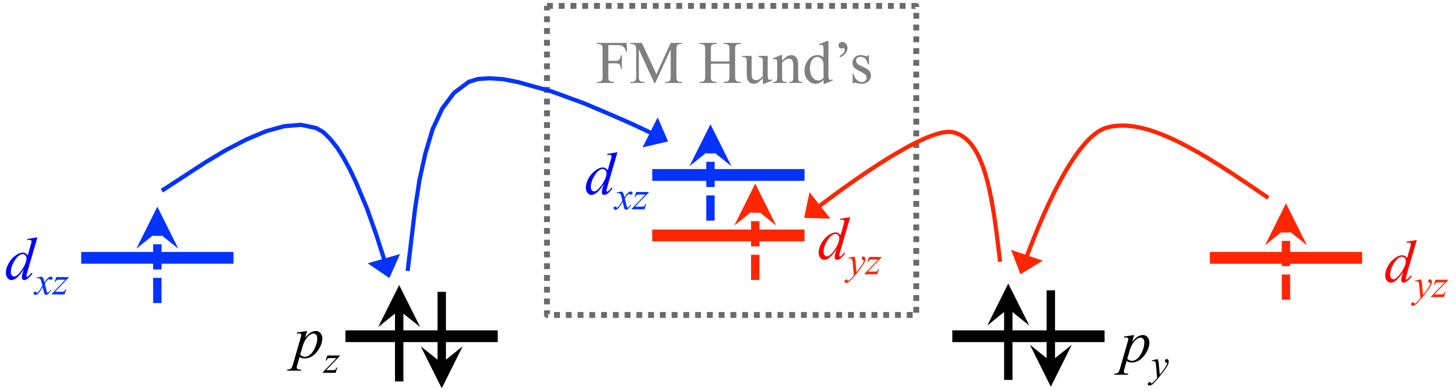
M_{JT} distortions produces the C-type orbital ordering

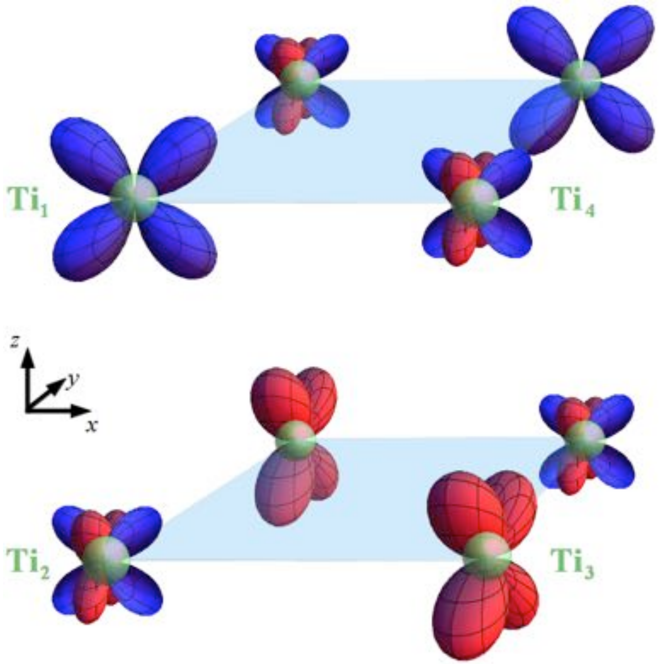
$$\mathscr{F} \propto P_{xy}\phi_z^+\phi_{xy}^- + \boxed{P_{xy}M_{JT}\phi_{xy}^-}$$

M_{JT} distortion



FM due to intrasite Hund’s





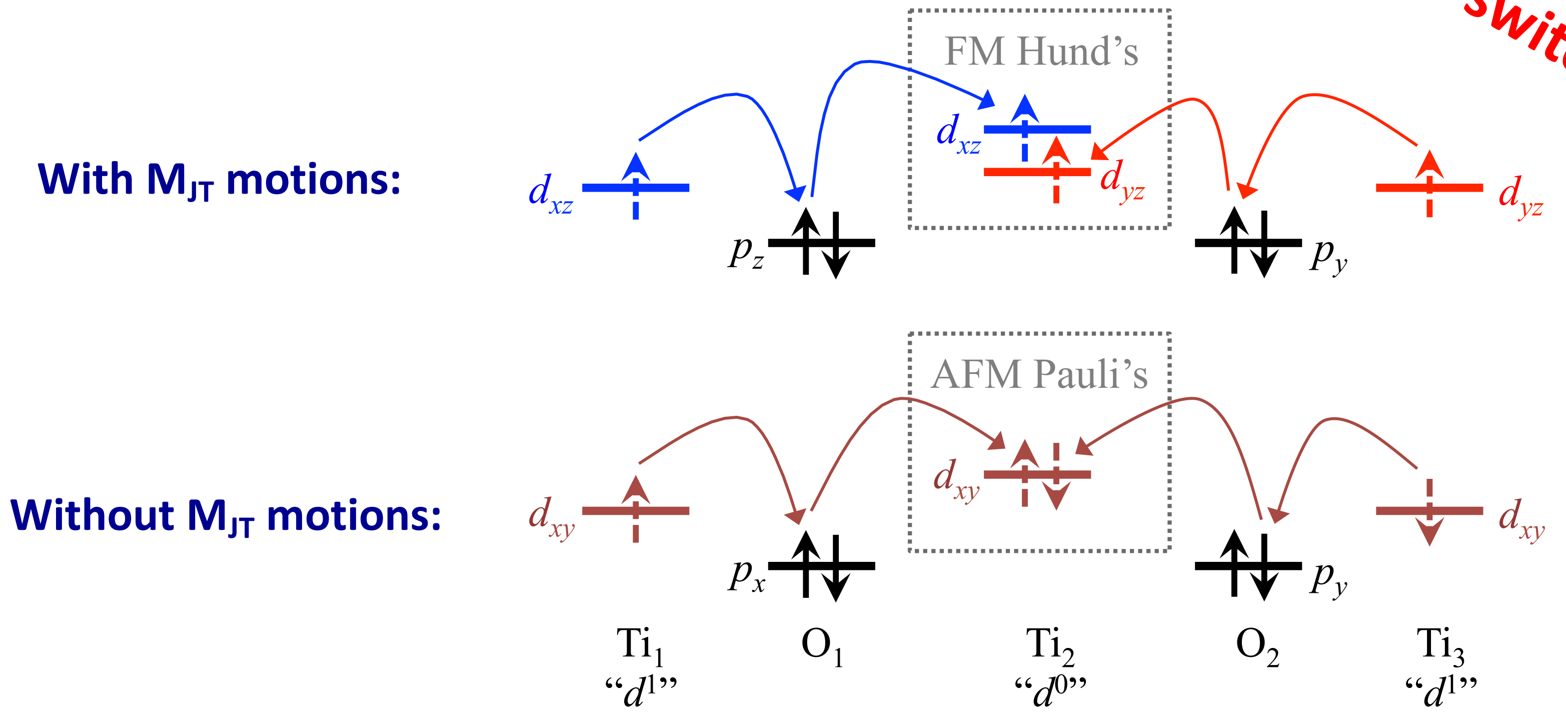
M_{JT} crucial for FM

If we artificially suppress AFD motions and hence M_{JT}

$$E \propto \lambda M_{JT} \phi^{-}_{xy} P_{xy}$$

- No orbital ordering: d_{xy} occupancy everywhere
- AFM GS
- Pauli's exclusion principle

E-field switching of FM?



Highlight three P-JT couplings

Symmetry analysis supported by first principles calculations (PBEsol+U and/or B1WC)

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Bristowe, Varignon, Fontaine, Bousquet & Ghosez,
Nat. Commun. **6**, 6677 (2015)

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Varignon, Bristowe, Bousquet & Ghosez,
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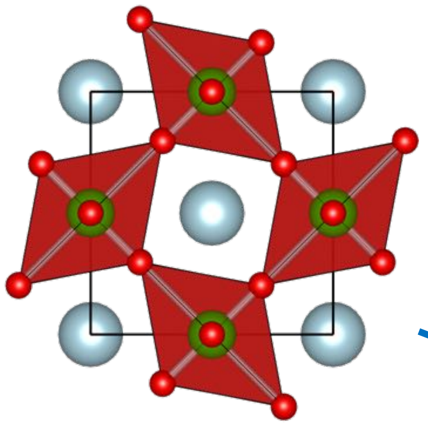
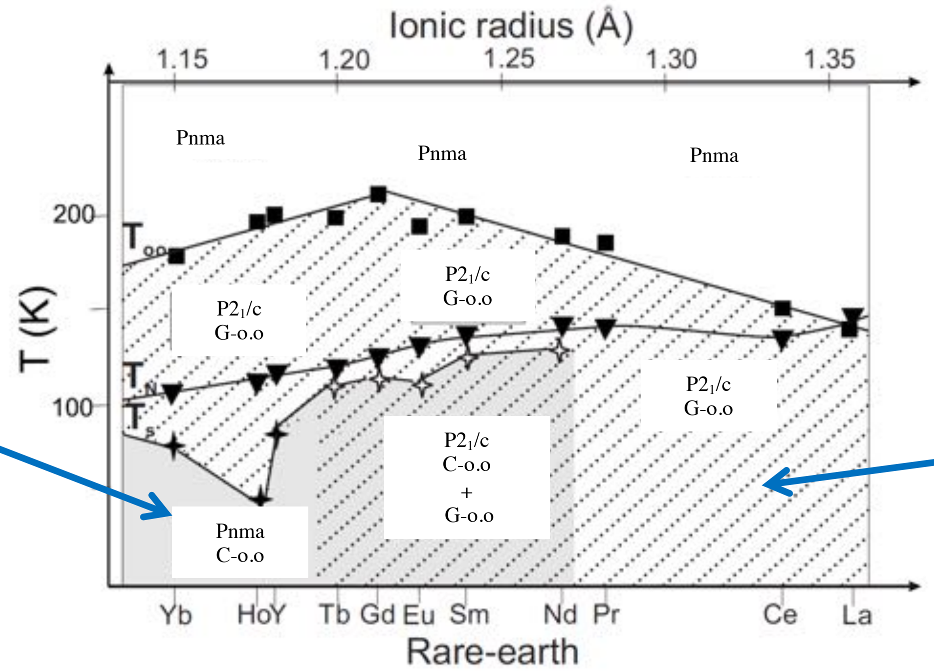
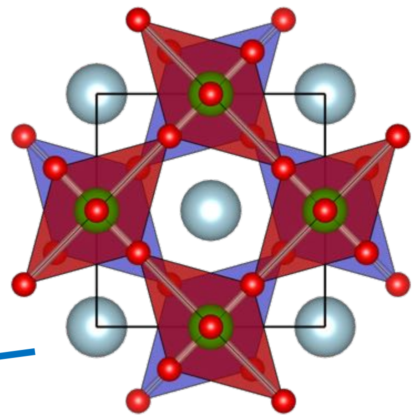
Varignon, Bristowe & Ghosez,
Phys. Rev. Lett **116**, 057602 (2016)

RVO_3



G-type AFM





C-type AFM

Rare-earth vanadates *Pnma* at room T, and with decreasing T appearance of:

- C and G type orbital orderings
- G and C type AFM orderings
- Structural phase transition to $P2_1/c$ for C-AFM

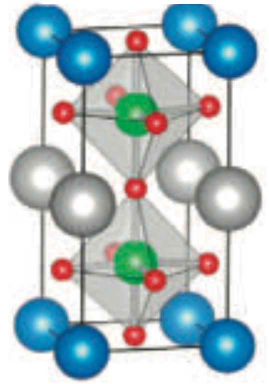
Sage *et al*, PRB **76** 195102 (2007)

RVO_3-$R'VO_3$ Superlattices

- Ground state:

	AFMG $Pb2_1m$	AFMC Pb
YVO/LaVO	0 meV	+7.76 meV
PrVO/YVO	0 meV	-0.87 meV
PrVO/LaVO	0 meV	-3.72 meV
	(“Pnma”)	(“$P2_1/c$”)

P4/mmm ref



(“$Pm\bar{3}m$”)

- Symmetry mode analysis of ground states (Å)

		Φ_{xy}^-	Φ_z^+	Φ_z^-	R_{JT}	M_{JT}	P_z	P_{xy}
YVO/LaVO	*Pb*2$_1$*m* AFMG	1.58	1.14			0.12		0.77
PrVO/YVO	*Pb* AFMC	1.61	1.16	0.01	0.10	0.04	0.01	0.81
PrVO/LaVO	*Pb* AFMC	1.36	0.94	0.01	0.10	0.01	0.00(4)	0.59
		($a^-a^-c^0$)	($a^0a^0c^+$)					

“Pnma”-like tilt pattern

***Pb* phases have additional P_z component, and combination of both Jahn-Tellers**

$R'VO_3$-RVO_3 couplings

$(RVO_3)_1/(R'VO_3)_1$ superlattice expansion

$$\Phi^-_{xy}\,\Phi^+_z\,\Phi^-_z\,\mathbf{P_{xy}}\,\mathbf{P_z}\,M_{jt}\,R_{jt}$$

[2]

$$\mathcal{F} \propto \mathbf{P_{xy}}\Phi^+_z\Phi^-_{xy} + \mathbf{P_{xy}}M_{jt}\Phi^-_{xy} + \mathbf{P_z}\Phi^+_z\Phi^-_z + \boxed{\mathbf{P_z}M_{jt}R_{jt}}$$

[1]

- *Pb2₁m* (*Pnma* in bulk)
- *Pb* (*P2₁/c* in bulk)

New trilinear coupling identified

Out-of-plane polarization coupled to Jahn-Teller !

[1] Bousquet *et al*, Nature **452** (2008)

[2] Fukushima *et al*, Phys. Chem. Chem. Phys **13** (2011); Rondinelli *et al*, Adv. Materials **24** (2012)

Magnetoelectric application?

Electric field driven magnetic transition ?

YVO/LaVO: ΔE(AFMG-AFMC) = -7.76 meV

Ground-state: *$Pb2_1m$ ("Pnma")* – *AFMG* phase:

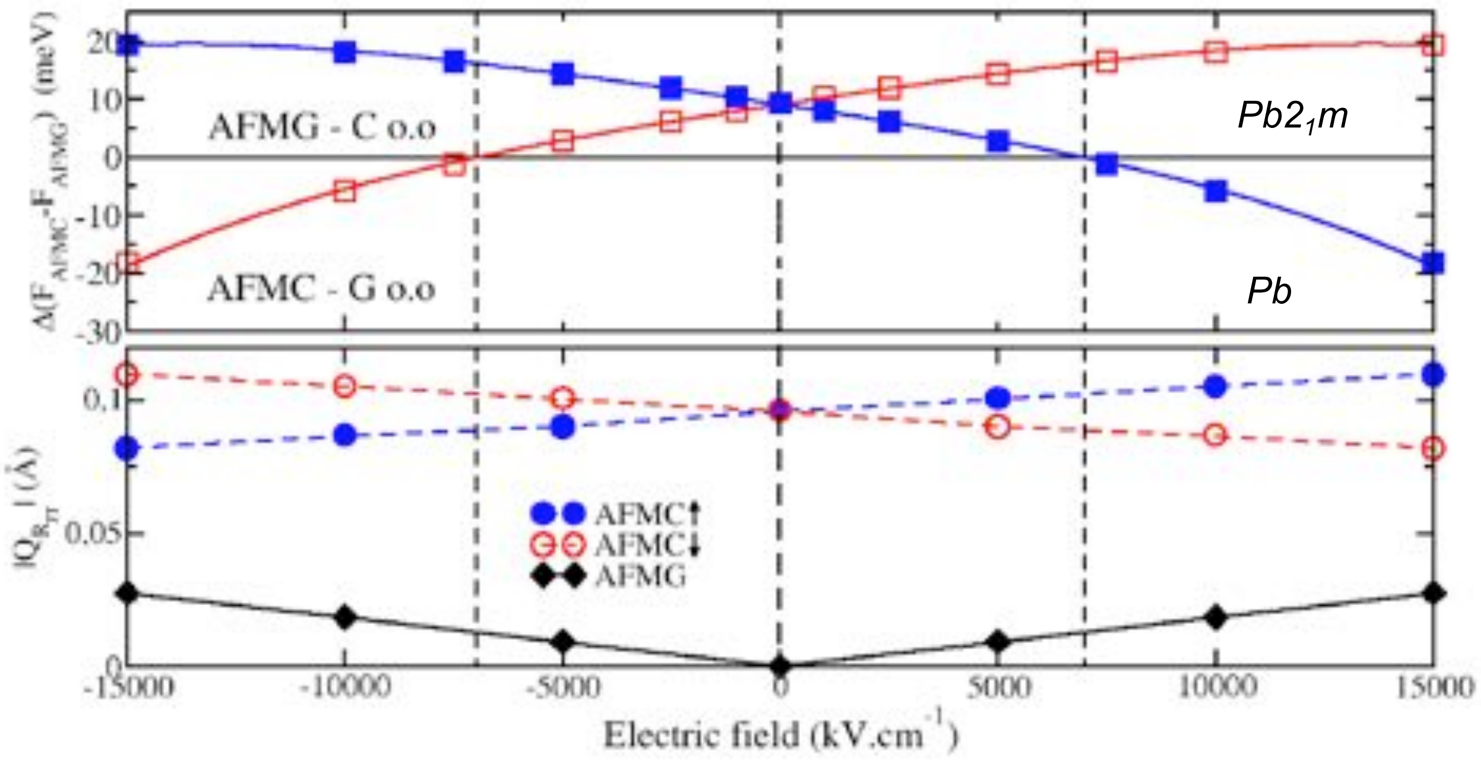
$$\mathcal{F} \propto P_{xy} M_{jt} \Phi^-_{xy} + P_{xy} \Phi^+_z \Phi^-_{xy} + P_z M_{jt} R_{jt} + P_z \Phi^+_z \Phi^-_z$$

$\vec{E}$ // z

Change of orbital and AFM orderings !

Electric field driven magnetic transition

Finite electric field method (transition at 0.55 V / bilayer)



E-field directly controls R_{JT} distortion amplitude!
In turn, this induces M transition

Highlight three P-JT couplings

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Varignon, Bristowe & Ghosez,
Phys. Rev. Lett **116**, 057602 (2016)

Can couplings appear in general bulk ABO_3?

Strain engineering?

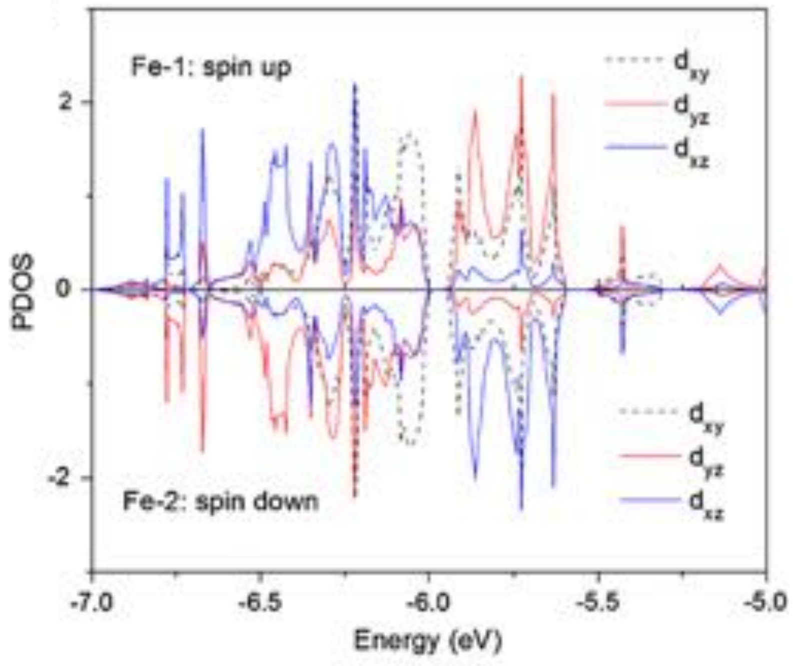
Can couplings appear in general bulk ABO_3?

Strain engineering?

Unusual *Pmc*21 phase (equivalently $Pb2_1m$) under tensile strain:

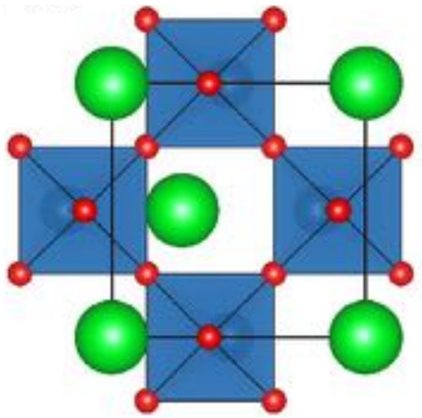
Ground state for $BiFeO_3$, $PbTiO_3$, $BaMnO_3$, $EuTiO_3$, $CaTiO_3$ (+?) at about 5% [1]

"Orbital ordering" observed for $BiFeO_3$ [1]
(though no Jahn-Teller distortion mentioned)



Tri-linear coupling found [2]:
(but not involving Jahn-Teller?)

$$E \propto \lambda A_{xy} \phi_z^+ P_{xy}$$



A_{xy}
(M_5^+)

[1] Yang *et al.,* Phys. Rev. Lett. **109** 057602 (2012)

[2] Yang *et al.,* Phys. Rev. Lett. **112** 057202 (2014)

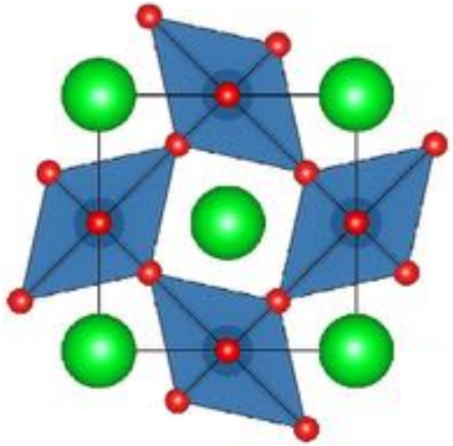
Reinvestigate *Pmc*21 phase

Truly general? Test on a range of d-fillings

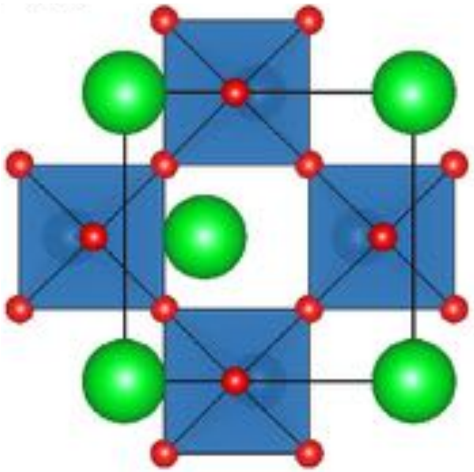
		d^0	d^3	d^5	d^4
		$SrTiO_3$	$BaMnO_3$	$BiFeO_3$*	$YMnO_3$*
Strain	(%)	+7.35 [61]	+6.1 [61]	+5.8 [61]	+4.0 [61]
Magnetism		NM	FM	AFMG	AFMG
P (Γ_5^-)	(Å)	0.615	0.421	0.346	0.753
	($\mu C\,cm^{-2}$)	76	45	29	7 [62]
M_{JT} (M_3^+)	(Å)	0.232	0.190	0.644	0.737
A (M_5^+)	(Å)	0.558	0.217	1.072	0.940
ϕ_z^+ (M_2^+)	(Å)	0.640	0.059	1.668	1.733
Gap	(eV)	3.02	0.28	1.88	1.88

* Also develop Φ_{xy}^-

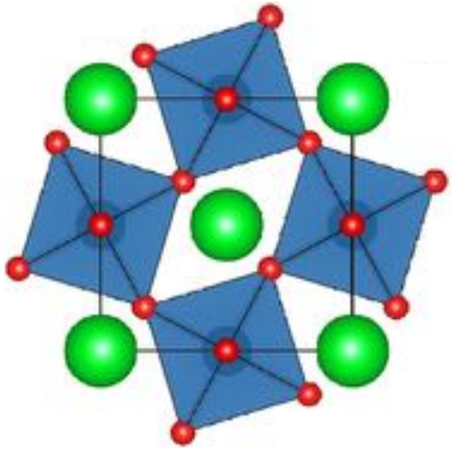
4th mode found: M_{JT}
Very large!



Invariants analysis

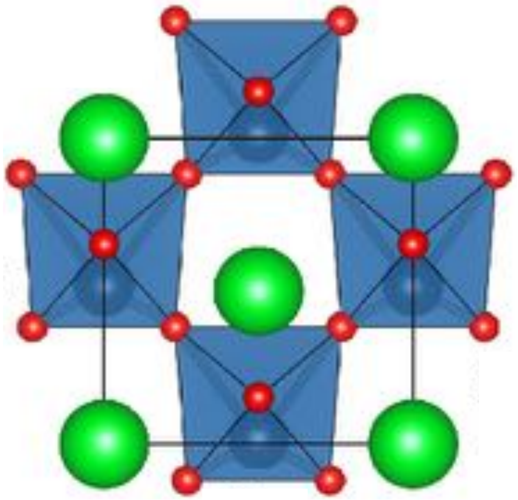


A_{xy} (M_5^+)

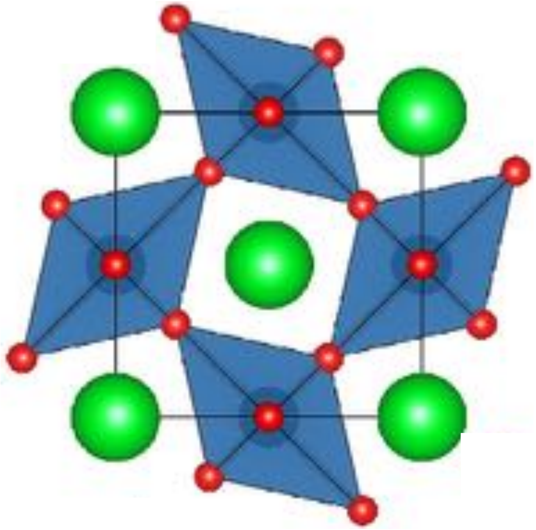


Φ_z^+ (M_2^+)

$$E \propto \lambda A_{xy}\phi_z^+ P_{xy} + \lambda A_{xy} M_{JT} P_{xy}$$



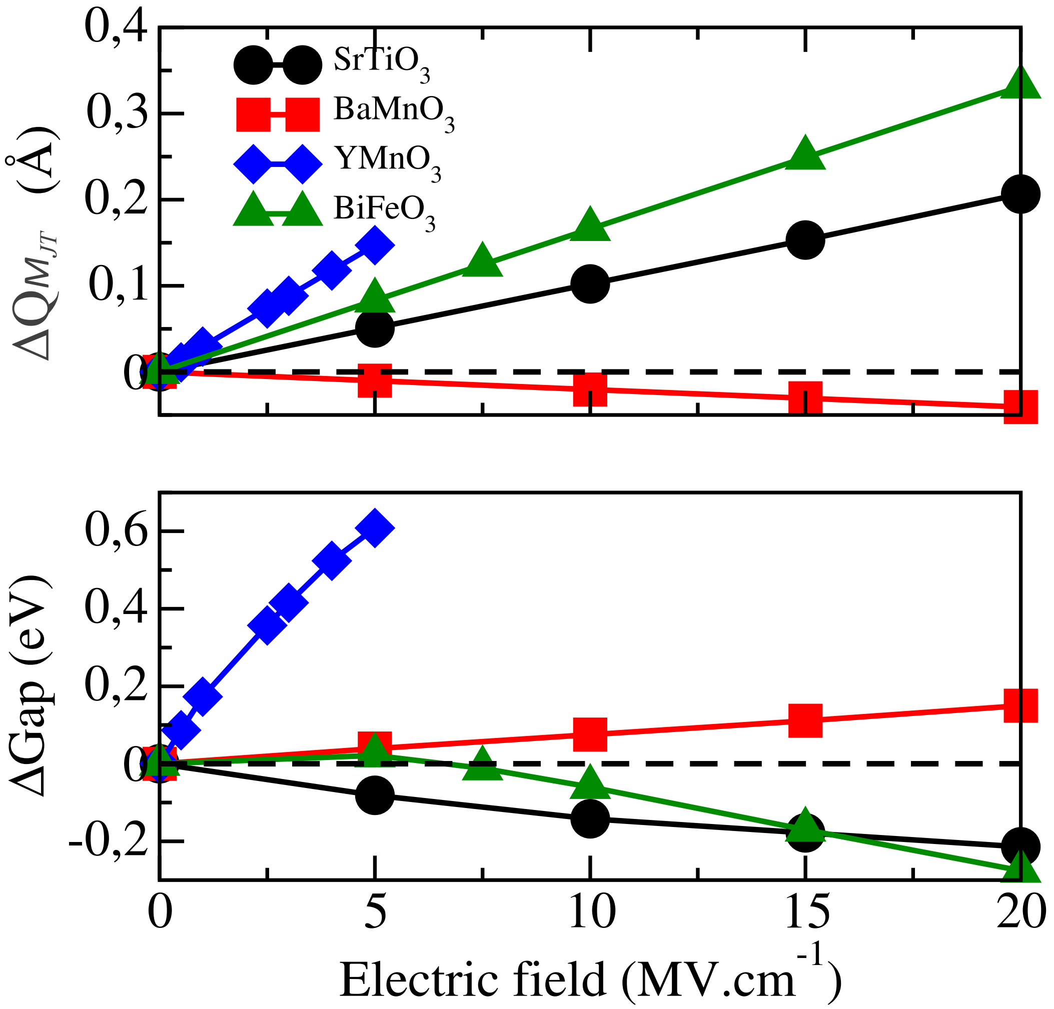
P_{xy} (GM_5^-)



M_{JT} (M_3^+)

E-field control of gap via JT

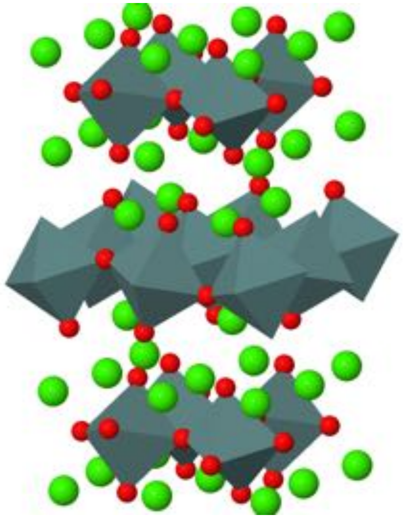
YMnO$_3$ largest effect since it is JT active



On-going/Future research in my group

Emergent phenomena at perovskite interfaces:

Negative thermal expansion
In naturally layered perovskites

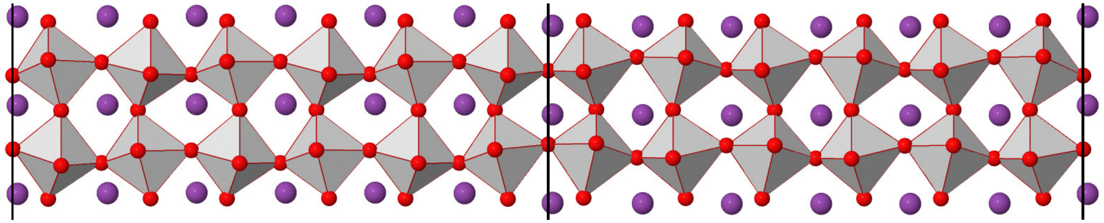


Chris Ablitt

$$\gamma_i = -\left(\frac{\partial \ln(\omega_i)}{\partial \ln(V)}\right)$$

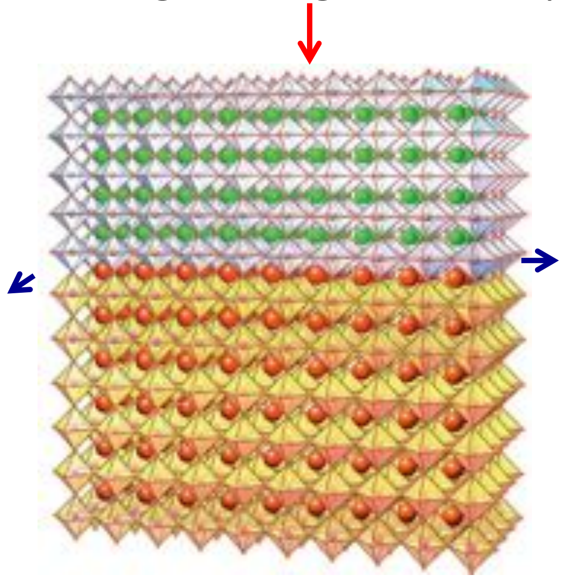
Andrew Warwick

Emergent ferroic orders at domain walls



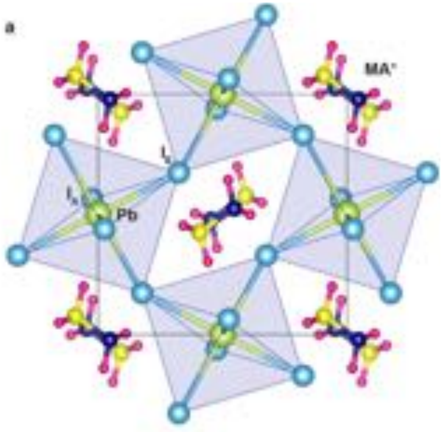
Khang Le

Strain engineering structural phases



Jordan Cowell

Photoferroicity in layered hybrid perovskites



Methodology

"Effective potential" for lattice dynamics

Wojdel *et al.*, *JPCM* **25** 305401 (2013)

Energy changes around *reference structure* due to distortions:

$$E_{\rm eff}(\{\boldsymbol{u}_i\},\boldsymbol{\eta}) = E_{\rm p}(\{\boldsymbol{u}_i\}) + E_{\rm s}(\boldsymbol{\eta}) + E_{\rm sp}(\{\boldsymbol{u}_i\},\boldsymbol{\eta})$$

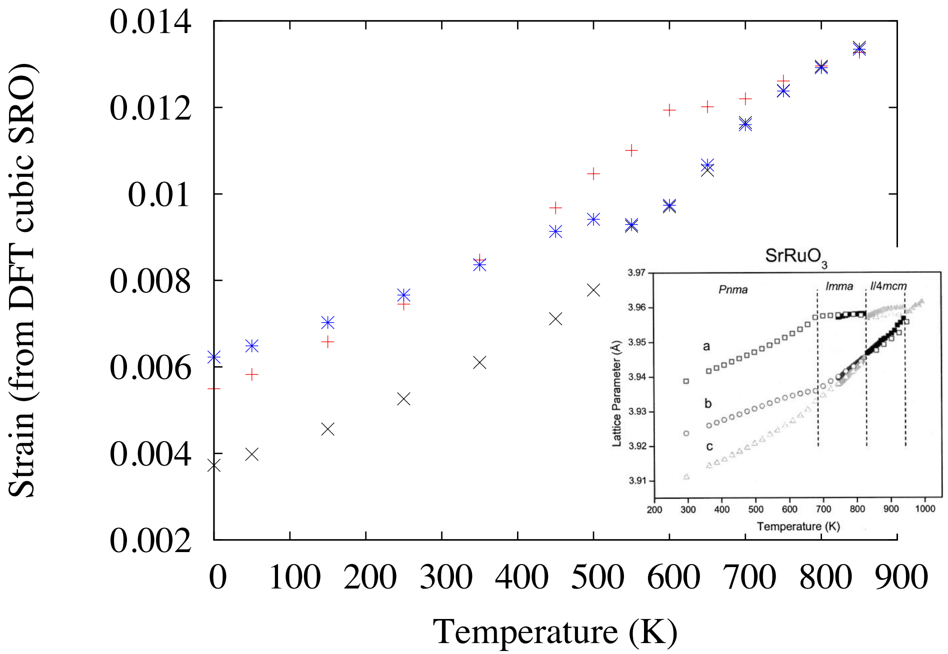
(1) Energy change from atomic displacements (p: phonons), with:

$$E_{\rm p}(\{\boldsymbol{u}_i\}) = E_{\rm har}(\{\boldsymbol{u}_i\}) + E_{\rm anh}(\{\boldsymbol{u}_i\})$$

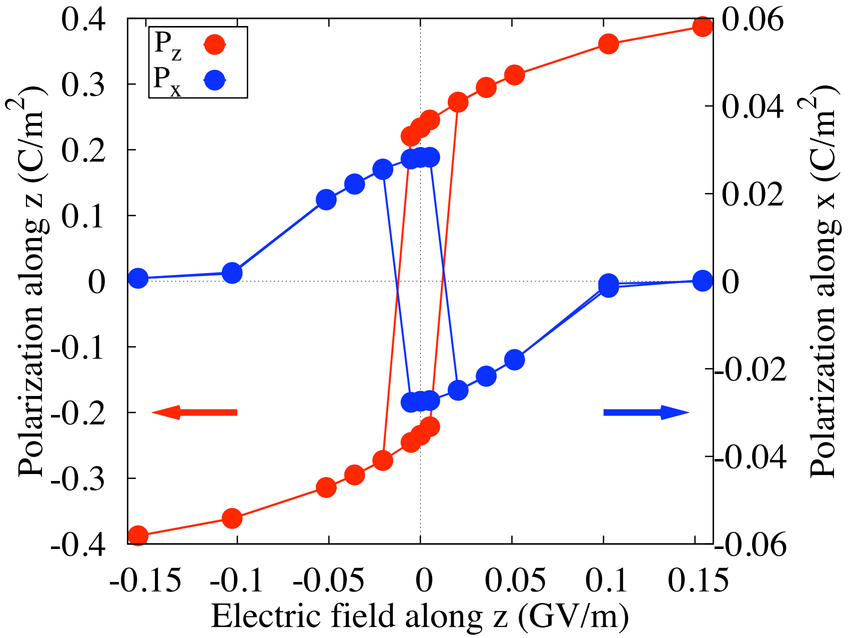
(2) Energy change due to strain only

(3) Strain-phonon coupling term

Finite T: $SrRuO_3$



Finite E: $PbTiO_3$-$SrTiO_3$



Thanks for your attention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