Cornell University

"I would found an institution where any person can find instruction in any study."
– Ezra Cornell, 1868

Competing Ferroic Orders

The magnetoelectric effect

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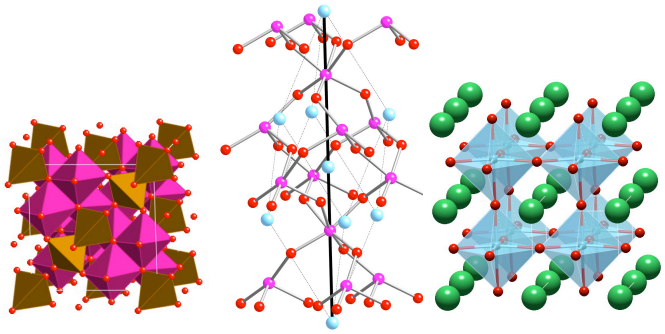


Basic Training in Condensed Matter Theory 2009

Module Outline

1. Overview and Background
   - Ferro ordering, the magnetoelectric effect
2. ME revisited, and basic oxide physics
   - ME effect revisited: Toroidal moments
   - Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry
3. Structure and Ferroelectricity
   - Basics of space groups
   - Soft mode theory, lattice dynamics, group theoretic methods
   - Competing lattice instabilities
   - microscopic mechanisms, improper FE
   - Modern theory of polarization (Berry Phase)

What have we done

- *presented various ferro-ordering and examined their basic symmetry properties.*
- *Showed in systems which break both time-reversal and space-inversion symmetry, that symmetry allows a bi-linear coupling between the Electric and Magnetic fields, $F_{ME} = \alpha EH$.*
- *Presented a relatively new (or rediscovered) ferro-toroidal ordering. What is this? Don't know yet, here is what I know: Electromagnetism allows the existence of some moment referred to as a toroidal moment (toroidal because it has the symmetry of of toroidal solenoid). Expanding the interaction energy between energy the magnetic density and the magnetic field, one arrives at a coupling between the toroidal moment and the field which has the same symmetry as the antisymmetrical component of the magnetoelectric tensor, i.e., a toroidal moment would lead to an antisymmetric ME effect. That's it, that is all I presently understand. Questions are plentiful.*

We are we going?

- *although symmetry allows the existence of a ME effect, it tells us nothing about its size. This is not a question of optimizing parameters to increase the magnitude of the effect in e.g., Cr_2O_3, but requires entirely new physical ideas.*
- *An idea that is prevalent in materials physics today (some would argue throughout nature) is the idea where the competition between different ordered ground states leads to new emergent phenomena (sometimes the adjective "colossal" is attached the observed effect).*
- *What if we have a system where ferroelectricity and (anti)ferromagnetism compete with each other, will it lead to "colossal" ME effects. Note this doesn't mean we simply add ferroelectricity and magnetism, i.e., multiferroics, we need to think of microscopic mechanisms that would COUPLE the two order parameters in a nontrivial way .*
- *Can we provide this coupling through the lattice? So in the remainder of this module we will*
  - *Understand the origin of ferroelectricity and how it couples to the lattice*
  - *Understand the origin of (anti)ferromagnetism and how it couples to the lattice*
  - *Combine these ideas to produce the stated goal.*

Perovskites are ubiquitous materials that display an amazing variety of different phenomena, lets focus on them

Multifunctional multiferroics

Multiferroic: combine more than one "ferro" ***property***:
Ferroelectricity, ferroelasticity, and/or magnetism

(Hans Schmid, 1973)

Polarization, P

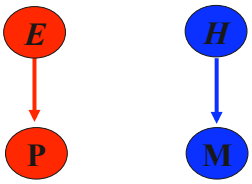
Magnetization, M

e.g., ferroelectric ferromagnet

Multifunctional multiferroics

Multifunctional: response to more than one external
perturbation: Electric and magnetic fields

Polarization, P

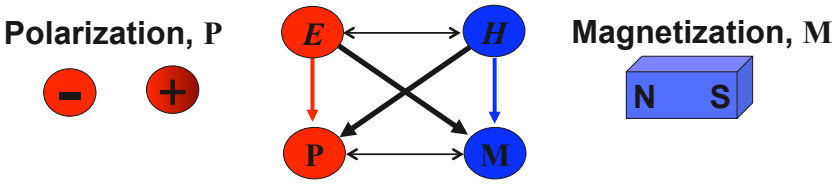


Magnetization, M

e.g., ferroelectric ferromagnet

Multifunctional magnetoelectrics

(Generalized) **Magnetoelectric**: cross coupled response to electric and magnetic fields



i.e. control of the magnetic **M** *(electric* **P***) phase with an applied electric* ***E*** *(magnetic* ***H****) field*

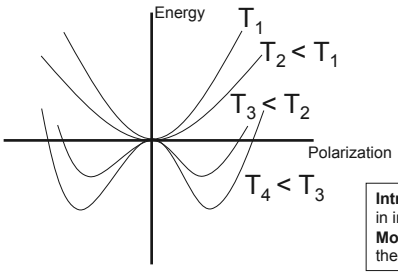
Proper ferroelectric transition: phenomenology

Proper and improper refer to the *transition*. Technically "(im)proper ferroelectric" or "(im)proper ferroelectricity" terminology is incorrect.

Primary Order Parameter
Spontaneous polarization P

$$\mathcal{F}(P) = \alpha P^2 + \beta P^4$$

The primary OP completely accounts for the ***symmetry*** lost at the phase transition



$$P_{eq} = 0 \qquad \alpha > 0$$
$$P_{eq} = \pm\sqrt{-\frac{\alpha}{2\beta}} \qquad \alpha < 0$$

$\alpha \propto \chi^{-1} \propto T\text{-}T_c$ Currie Weiss
χ: dielectric susceptibility

Introductory: Ekhard Salje, "Crystallography and structural phase transitions, in introduction," *Acta Crystal.* A47, 453-469 (1991).
More advanced: Stokes and Hatch, "Coupled order parameters in the Landau theory of phase transitions in solids," *Phase Transitions* V34, 53-67 (1991).

Phenomenology is nice, we need to start understanding microscopic mechanism and the relevant microscopic degree of freedom.

Emergence of new macroscopic phenomena

Conventional ferroelectrics

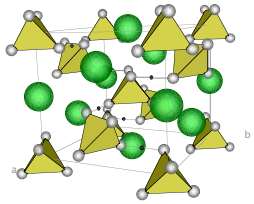
Typically, have a polar lattice instability driving the ferroelectricity

Recent novel ferroelectrics

- *Lattice* - Lattice coupling → non-polar lattice mode driving FE
- *Spin* - Lattice coupling → spin DoFs driving FE
- *Charge* - Lattice → charge DoFs driving FE
- *Orbital* - Lattice → Orbital DoFs driving FE

Order-Disorder Ferroelectrics

KDP KH_2PO_4 T_c = 123K
KD_2PO_4 T_c = 220K



Potassium dihydrogen phosphate

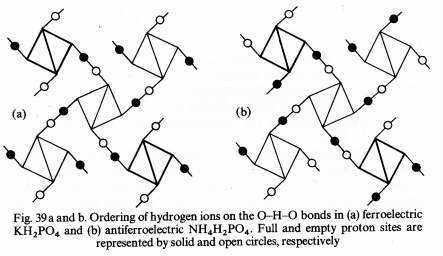
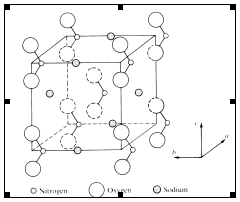
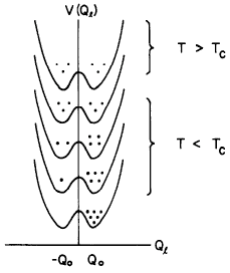


Fig. 39 a and b. Ordering of hydrogen ions on the O–H–O bonds in (a) ferroelectric KH_2PO_4 and (b) antiferroelectric $NH_4H_2PO_4$. Full and empty proton sites are represented by solid and open circles, respectively

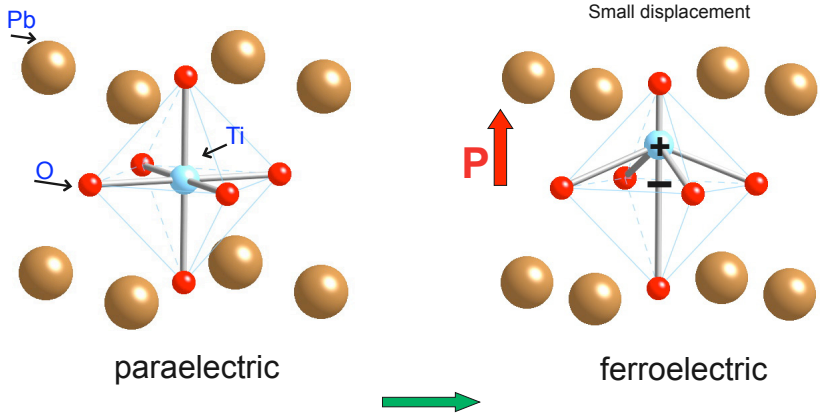
$NaNO_2$ T_c = 456K



Very strong covalent bonds. Rigid molecular units



Displacive ferroelectrics



Side note: transition metal oxides tend to follow the Goldilocks lemma: Not to ionic, not too covalent, just right to be perfectly floppy

Often "displacive properties of both

After 50 years of research one can definitely say, without a doubt that the "prototype" persovskite ferroelectric $BaTiO_3$ is both:-)

Model that goes from O-D limit to displacive

$$V = \sum_n v(Q_n) + \frac{1}{2}\sum_{n,n'} C(Q_n - Q'_n)^2$$

$$v(Q_n) = E_0(Q_n^2 - 1)^2$$

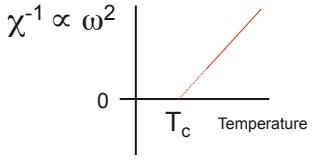
Limit $C/E_0 \rightarrow \infty$ ⇒ pure displacive
Limit $C/E_0 \rightarrow 0$ ⇒ pure O-D (Ising)

Soft-mode theory of ferroelectricity

Experiments see:
Jim Scott
RMP 46, 83 (1974)

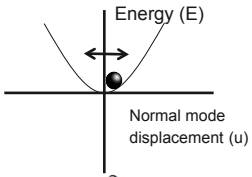
Born and Huang, 1954, W. Cochran, Phys. Rev. Lett. 1959

Currie Weiss



Where ω is an infrared-active phonon frequency

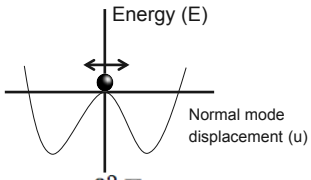
Stable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} > 0$$

→ Paraelectric

Unstable phonon



$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$

→ Ferroelectric

Small detour: microscopic mechanisms

Lets consider a Born-Oppenheimer system

$$H_e(r;Q) = T_e + V(r,Q)$$

$$H_e(r;Q)\psi_n(r;Q) = E_n(Q)\psi_n(r;Q)$$

$$M_I \frac{d^2 Q_I}{dt^2} = -\frac{\partial E_0(Q_j)}{\partial Q_I}$$

Vibronic theory: 1st and 2nd order Jahn-Teller

Expanding the Hamiltonian as a function of normal coordinate Q about the electronic Hamiltonian for the high symmetry reference phase,

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}Q + \frac{1}{2}\mathcal{H}^{(2)}Q^2 + \ldots \quad ,$$

$$\mathcal{H}^{(1)} = \left.\frac{\delta \mathcal{H}}{\delta Q}\right|_{Q=0} \text{ and } \mathcal{H}^{(2)} = \left.\frac{\delta^2 \mathcal{H}}{\delta Q^2}\right|_{Q=0}$$

capture the vibronic coupling between the displacements of the ions from their positions in the high symmetry phase and the electrons.

1st order Jahn-Teller

$$E = E^{(0)} + \langle 0|\mathcal{H}^{(1)}|0\rangle Q$$

2st order Jahn-Teller

$$+ \frac{1}{2}[\langle 0|\mathcal{H}^{(2)}|0\rangle - 2\sum_n \frac{|\langle 0|\mathcal{H}^{(1)}|n\rangle|^2}{E^{(n)} - E^{(0)}}]Q^2$$

$$+ \ldots$$

Ferroelectric mechanisms: Chemical

(formally) d^0 transition metals e.g. $Ba^{2+}Ti^{4+}O^{2-}$ Ti^{4+}: $3d^04s^0$

Origin of FE distortion

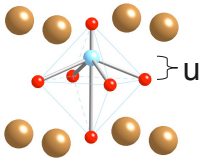
Ron Cohen, Nature 1993

Balance between two competing forces:

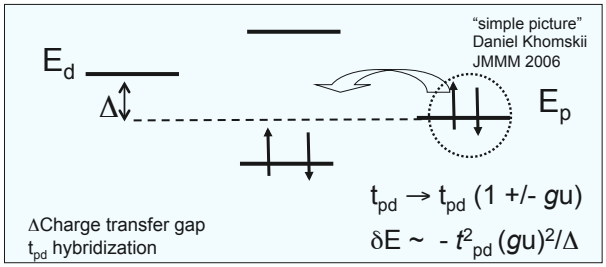
- short-ranged repulsive forces favor centrosymmetric structure
- changes in chemical bonding favor ion off-centering

→ dipole-dipole interactions stabilize long-range order

Nicola Spaldin, *Analogies and differences between ferroelectrics and ferromagnets*, in Topic in Advanced Physics V 105 (2007).



Change in hybridization of empty d-states with filled O p-states (2nd order Jahn-Teller)



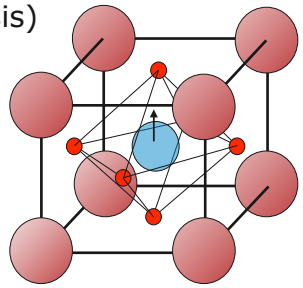
Symmetry-breaking crystal distortions

- Interatomic force constants: energy $E(\{u_{ita}\})$

$-(d^2E/du_{i\tau\alpha}du_{j\kappa\beta})u_{i\tau\alpha}$ = force on atom $j\kappa$ in the β direction produced by displacement of atom $i\tau$ in α direction

(j labels unit cell, κ labels atom in basis)

Crystal symmetries lead to equalities and zeros for this matrix



Symmetry-breaking crystal distortions

Interatomic force constant matrix has full symmetry of the crystal space group

Transform to basis of symmetrized displacement patterns (these transform according to irreducible representations of the space group) →

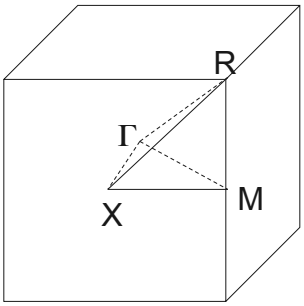
The force constant matrix (and dynamical matrix) are block diagonal with nonzero elements only between patterns with same transformation under crystal symmetry operations (that belong to same row of same irrep)

Displacement patterns for some irreps may even be uniquely determined by symmetry!

Symmetry breaking crystal distortions

- Labels for space group irreps: wavevector Q in irreducible Brillouin zone + irrep of little group of Q

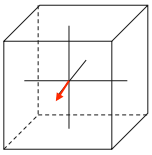
Cubic perovskite example: simple cubic



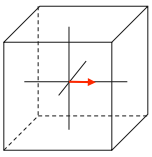
Γ: (0,0,0)
R: π/a(1,1,1)
X: π/a(1,0,0)
M: π/a(1,1,0)
where a is the lattice constant of the simple cubic lattice

Cubic perovskite: symmetrized displacement patterns

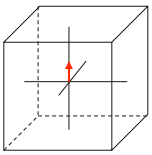
- Γ: Q=0 (uniform from cell to cell)



x



y



z

3-dimensional irreducible representation (irrep) Γ_{15} (this is the vector representation)
Three rows: x, y, z

Character Table for Pm3m, i.e., the cube

Bilbao Crystallographic Server → Ir and Raman Modes

IR and Raman Modes for P m -3 m (221)

Character Table

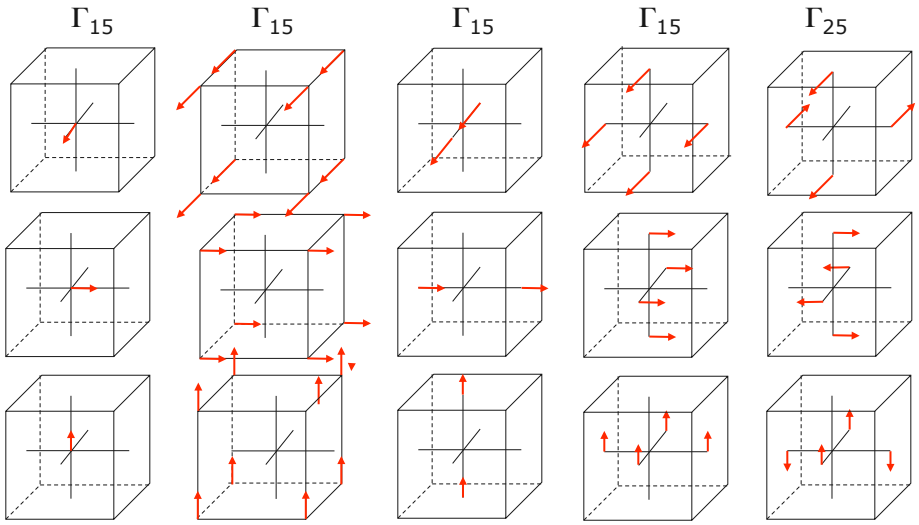
O_h(m-3m)	1	4	2	3	2'	-1	-4	m	-3	m'	functions
Mult.	1	6	3	8	6	1	6	3	8	6	·
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	·
A_{2g}	1	-1	1	1	-1	1	-1	1	1	-1	·
A_{2u}	1	-1	1	1	-1	-1	1	-1	-1	1	·
E_g	2	0	2	-1	0	2	0	2	-1	0	$(2z^2-x^2-y^2, x^2-y^2)$
E_u	2	0	2	-1	0	-2	0	-2	1	0	·
T_{2u}	3	-1	-1	0	1	-3	1	1	0	-1	·
T_{2g}	3	-1	-1	0	1	3	-1	-1	0	1	(xy,xz,yz)
T_{1u}	3	1	-1	0	-1	-3	-1	1	0	1	(x,y,z)
T_{1g}	3	1	-1	0	-1	3	1	-1	0	-1	(J_x,J_y,J_z)

What do we really mean when we say polar mode?

Irrep for the polar vector

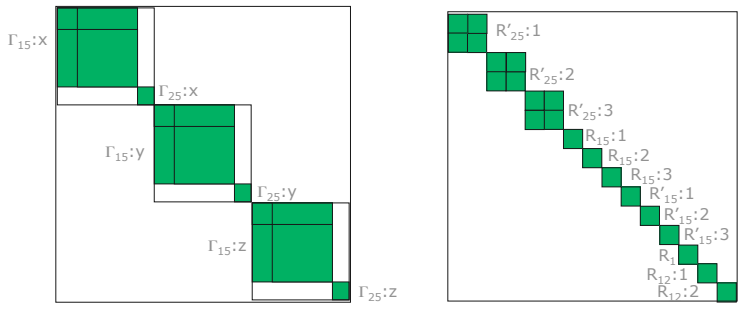
Cubic perovskite: symmetrized displacements

- Γ: Q=0 (uniform from cell to cell)



Matrices become block diagonal

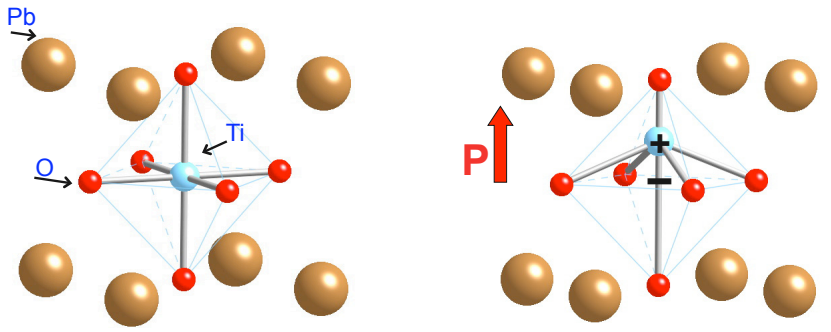
Matrix elements are nonzero only between symmetrized displacements that transform according to the same row of the same irrep for ideal perovskite structure, 15x15 dynamical matrices



(In Γ matrix, acoustic Γ_{15} mode can be found by including uniform translation) Finding eigenvalues becomes much easier!

Ferroelectricity as a lattice property

FE lattice distortion, **u**, has identical *symmetry* properties as the polarization, i.e. **u**∝ **P**, involve small atomic distortions



cubic-paraelectric
Space group Pm3m

tetragonal-ferroelectric
Space group P4mm

Internal energy from first principles

Internal energy as a function of FE distortion, u, and strain, ε

$$\mathcal{E}(u, \varepsilon) = -\omega^2_0 u^2 + Bu^4 + C\varepsilon u^2$$

Neglecting strain: Both $BaTiO_3$ and $PbTiO_3$ have rhombohedral ground states, in contradiction to experiment!

In $PbTiO_3$, polarization-strain coupling is essential to observe tetragonal ground state

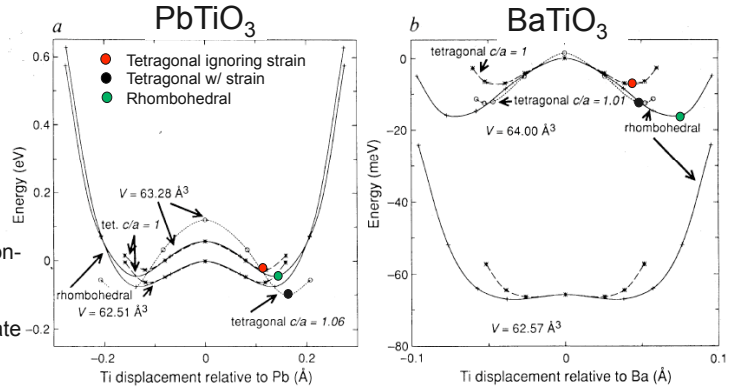
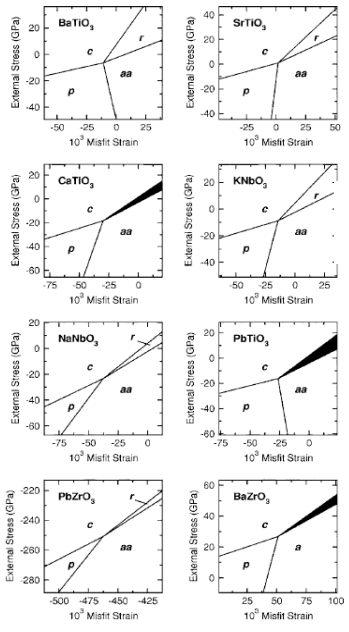


Fig 1, page 137; Ron Cohen, *Origin of ferroelectricity in perovskite oxides*, Nature **358**: 136-138 (1992).



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First-principles study of epitaxial strain in perovskites

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(Received 29 June 2005; revised manuscript received 5 August 2005; published 3 October 2005)

$$E = E^{\text{elas}}(\{\eta_i\}) + E^{\text{soft}}(\{u_\alpha\}) + E^{\text{int}}(\{\eta_i\},\{u_\alpha\}), \qquad (1)$$

$$E^{\text{elas}}(\{\eta_i\}) = \tfrac{1}{2}B_{11}(\eta_1^2+\eta_2^2+\eta_3^2) + B_{12}(\eta_1\eta_2+\eta_2\eta_3+\eta_3\eta_1) + \tfrac{1}{2}B_{44}(\eta_4^2+\eta_5^2+\eta_6^2), \qquad (2)$$

$$E^{\text{soft}}(\{u_\alpha\}) = \kappa u^2 + \alpha u^4 + \gamma(u_x^2u_y^2+u_y^2u_z^2+u_z^2u_x^2),$$

$$E^{\text{int}}(\{\eta_i\},\{u_\alpha\}) = \tfrac{1}{2}B_{1xx}(\eta_1u_x^2+\eta_2u_y^2+\eta_3u_z^2) + \tfrac{1}{2}B_{1yy}[\eta_1(u_y^2+u_z^2)+\eta_2(u_z^2+u_x^2)+\eta_3(u_x^2+u_y^2)] + B_{4yz}(\eta_4u_yu_z+\eta_5u_zu_x+\eta_6u_xu_y),$$

Symmetry lost at transition

So ferroelectricity in the cubic perovskite like $PbTiO_3$ is associated with the instability of a Γ_{15} mode, i.e., a polar lattice distortion, is translational symmetry changed?

Example: cubic perovskite structure

Crystallographic description—generally given in the literature

Space group Pm3barm (#221) (out of 230 space groups total)

Pb	1a	0,0,0			Pb	1b	½,½,½	
Ti	1b	½,½,½			Ti	1a	0,0,0	
O	3c	0,½,½	½,0,½	½,½,0	O	3d	½,0,0	0,½,0	0,0,½

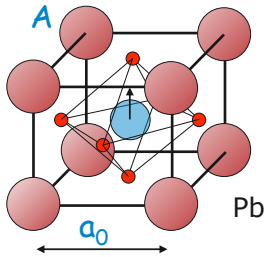
Lattice parameter a_0

No additional free structural parameters for this symmetry

Symmetries are manifest
Point group: governs macroscopic properties (allowed couplings)
Site symmetry groups from the table
Can easily reconstruct lattice+basis description
(eg for input into first-principles program)

Example: tetragonal FE phase of $PbTiO_3$

- Primitive tetragonal lattice a x, a y, c z (P4mm #99)



Point symmetries are those of this object

Pb	1a	0,0,z			Pb	1b	½,½,z	
Ti	1b	½,½,z			Ti	1a	0,0,z	
O	1b	½,½,z			O	1a	0,0,z	
O	2c	½,0,z	0,½,z		O	2c	½,0,z	0,½,z

Two lattice parameters a, c

Three nontrivial additional parameters for this symmetry

Caution, nothing requires the lattice constants to differ

Improper ferroelastic transition: phenomenology

$BaTiO_3$ and $PbTiO_3$ have a proper ferroelectric transition, but an improper ferroelastic transition

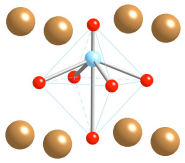
Primary order parameter	Secondary order parameter
Spontaneous polarization P	Spontaneous strain ε

(note energy expansion for cubic-to-tetragonal pt, simplified for pedagogy)

$$\mathcal{F}(P, \varepsilon) = a_1 P^2 + a_2 \varepsilon^2 + b_1 \varepsilon P^2 + c_1 P^4$$

$$\partial \mathcal{F} / \partial \varepsilon = 2 a_2 \varepsilon + b_1 P^2 = 0$$

$$\varepsilon_{eq} \sim - P^2$$



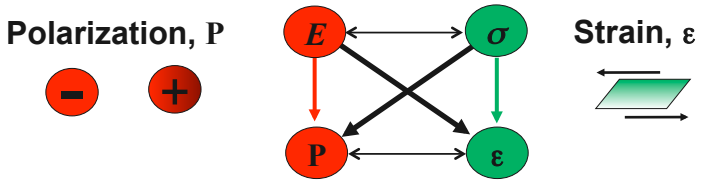
Once P becomes nonzero, a strain is induced

Caution

- This is true for any instability, no matter its origin! Any mode (charge, orbital, spin) that removes the point group symmetrs, will couple to strain!!!
- The coupling does not need to be large or even measureable, but symmetry allows it (one should consider zero coupling, an accident).

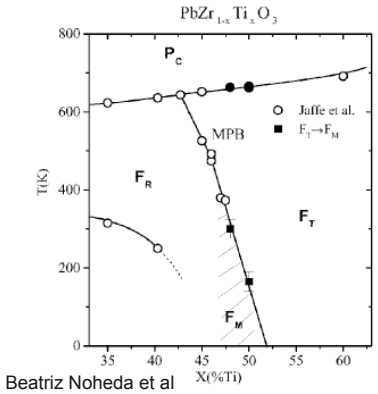
Improper ferroelastic transition: large piezoelectric response

In perovskite ferroelectrics such as $PbTiO_3$, there is a strong **cross coupled response** between electric, E, and stress, σ, fields

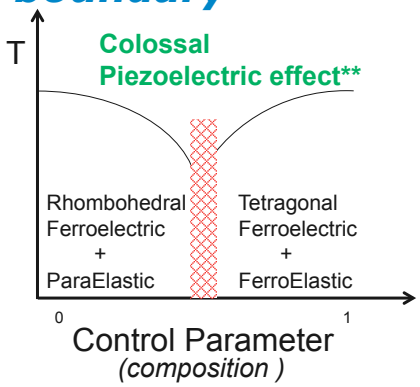


Why? Or better question, why should they be coupled at all?

Phase Competition and the morphotropic phase boundary



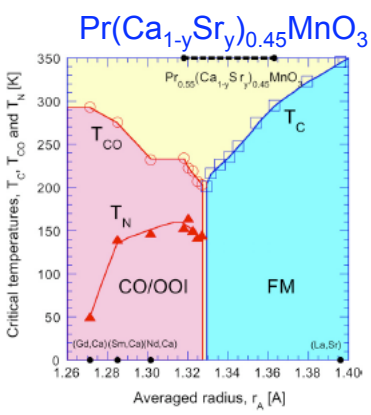
Beatriz Noheda et al

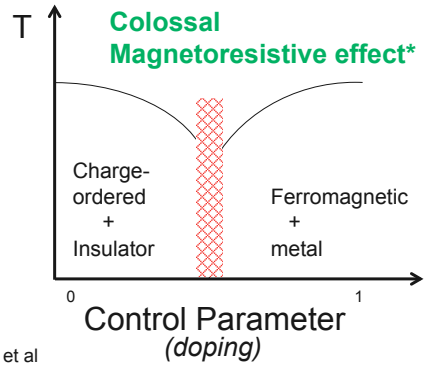


* Y. Tokura, "Critical Feature of Colossal Magnetoresistive Manganites," Rep. Prog. Phys. 2006.
"Multiferroics - Toward Strong Coupling …," JMMM 2007.

** R.E. Newnham, "Molecular Mechanisms in Smart Materials," MRS Bull. 1997.

Phase Competition: Generic paradigm to achieve colossal effects





Tokura et al

* Y. Tokura, "Critical Feature of Colossal Magnetoresistive Manganites," Rep. Prog. Phys. 2006.
"Multiferroics - Toward Strong Coupling …," JMMM 2007.

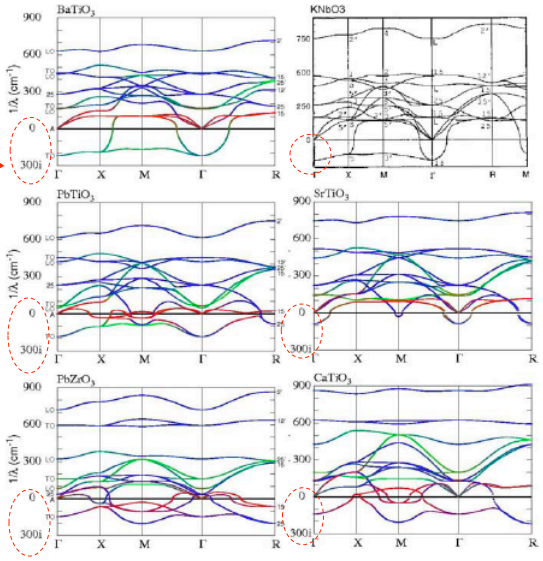
** R.E. Newnham, "Molecular Mechanisms in Smart Materials," MRS Bull. 1997.

Zone-boundary instabilities

In general, many ferroelectrics have competing lattice instabilities

Phonon dispersion at T=0 of cubic ABO_3 from first principles

Remember:
Imaginary frequencies imply lattice instability

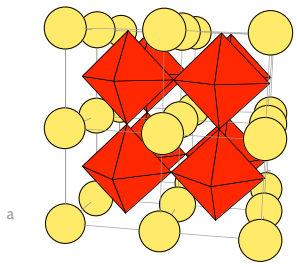


Phonon Symmetry Labels
Γ: q=0
M: q=(1,1,0)
X: q=(1,0,0)
R: q=(1,1,1)

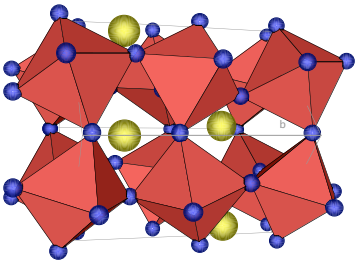
Fig 3, page 135; Karin M. Rabe and Philippe Ghosez, *First-principles studies of ferroelectric oxides*, Topics in Applied Physics **105**: 117-174 (2007).

Tilt Transitions in Perovskites

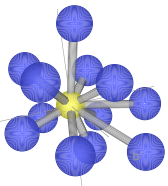
Untilted perovskite



Tilted



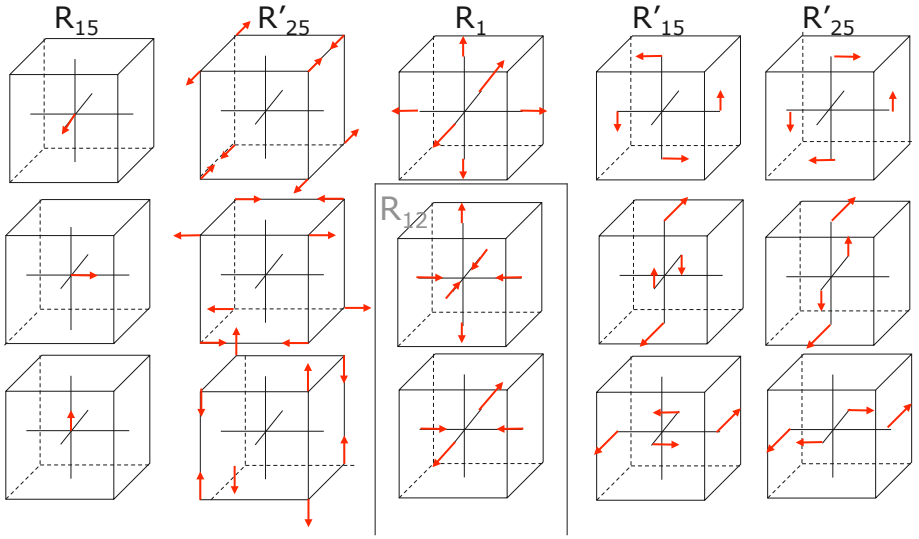
A site coordination



- Many perovksites show tilt transitions, some of which are non-polar. Ex. $SrTiO_3$, $NaNbO_3$, $CaTiO_3$
- Perovskite structure collapses around small A-site ions
- This often leads to antiparallel rotation motions, and no ferroelectricity (though a ferroelectric phase can often be induced by an applied electric field)

Cubic perovskite symm. displacements

- R: Q=π/a(1,1,1) (changes sign from cell to cell)



Distorted perovskites: mode content+Glazer notation

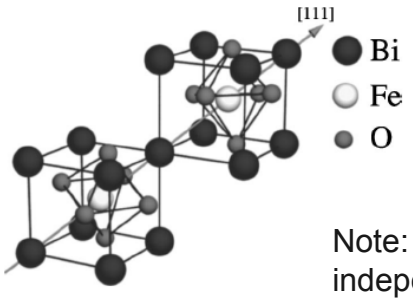
H. T. Stokes, et al, "Group theoretical analysis of octahedral tilting in ferroelectric perovskites," Acta Cryst. B58, 934 (2002)

Space group	Γ_4^-	M_3^+	R_4^+	System	Lattice vectors
221 $Pm\bar{3}m$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0a_0^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)
127 $P4/mbm$	(0, 0, 0)	(0, 0, a)	(0, 0, 0)	$a_0^0a_0^0c_0^+$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)
139 $I4/mmm$	(0, 0, 0)	(0, a, a)	(0, 0, 0)	$a_0^0b_0^+b_0^+$	(0, 2, 0)(0, 0, 2)(2, 0, 0)
204 $Im\bar{3}$	(0, 0, 0)	(a, a, a)	(0, 0, 0)	$a_0^+a_0^+a_0^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)
71 $Immm$	(0, 0, 0)	(a, b, c)	(0, 0, 0)	$a_0^+b_0^+c_0^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)
140 $I4/mcm$	(0, 0, 0)	(0, 0, 0)	(0, 0, a)	$a_0^0a_0^0c_0^-$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 2)
74 $Imma$	(0, 0, 0)	(0, 0, 0)	(0, a, a)	$a_0^0b_0^-b_0^-$	(0, 1, 1)(2, 0, 0)(0, 1, $\bar{1}$)
167 $R\bar{3}c$	(0, 0, 0)	(0, 0, 0)	(a, a, a)	$a_0^-a_0^-a_0^-$	($\bar{1}$, 1, 0)(0, $\bar{1}$, 1)(2, 2, 2)
12 $C2/m$	(0, 0, 0)	(0, 0, 0)	(0, a, b)	$a_0^0b_0^-c_0^-$	(0, $\bar{2}$, 0)(2, 0, 0)(0, 1, 1)
15 $C2/c$	(0, 0, 0)	(0, 0, 0)	(a, b, b)	$a_0^-b_0^-b_0^-$	(2, $\bar{1}$, $\bar{1}$)(0, 1, $\bar{1}$)(0, 1, 1)
2 $P\bar{1}$	(0, 0, 0)	(0, 0, 0)	(a, b, c)	$a_0^-b_0^-c_0^-$	(0, 1, 1)(1, 0, 1)(1, 1, 0)
63 $Cmcm$	(0, 0, 0)	(0, a, 0)	(0, 0, b)	$a_0^0b_0^+c_0^-$	(2, 0, 0)(0, 0, $\bar{2}$)(0, 2, 0)
62 $Pnma$	(0, 0, 0)	(a, 0, 0)	(0, b, b)	$a_0^+b_0^-b_0^-$	(0, 1, 1)(2, 0, 0)(0, 1, $\bar{1}$)
11 $P2_1/m$	(0, 0, 0)	(a, 0, 0)	(0, b, c)	$a_0^+b_0^-c_0^-$	(0, $\bar{1}$, 1)(2, 0, 0)(0, 1, 1)
137 $P4_2/nmc$	(0, 0, 0)	(a, a, 0)	(0, 0, b)	$a_0^+a_0^+c_0^-$	(2, 0, 0)(0, 2, 0)(0, 0, 2)
99 $P4nm$	(0, 0, a)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0c_+^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)
38 $Amm2$	(a, a, 0)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0c_0^0$	(0, 0, 1)(1, $\bar{1}$, 0)(1, 1, 0)
160 $R3m$	(a, a, a)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0a_+^0$	(1, $\bar{1}$, 0)(0, 1, $\bar{1}$)(1, 1, 1)
6 Pm	(a, b, 0)	(0, 0, 0)	(0, 0, 0)	$a_+^0b_+^0c_0^0$	(0, 1, 0)(0, 0, 1)(1, 0, 0)
8 Cm	(a, a, b)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0c_+^0$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)
1 $P1$	(a, b, c)	(0, 0, 0)	(0, 0, 0)	$a_+^0b_+^0c_+^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)

R3c: $LiNbO_3$, $BiFeO_3$

- 2 formula units (10 atoms) / cell

161 *R3c* (a, a, a) $(0, 0, 0)$ (b, b, b) $a_+^- a_+^- a_+^-$ $(\bar{1}, 1, 0)(0, \bar{1}, 1)(2, 2, 2)$



Note: the two octahedra are not independent!
6 oxygen atoms – related by translation in pairs

Improper ferroelectric transition: phenomenology

Primary order parameter ≡ η

where η is "some other mode", e.g. zone-boundary lattice instability, *magnetic chiral vector*, etc.

Secondary order parameter

Spontaneous polarization $\mathbf{P}$

$$\mathcal{F}(\eta, P) = \alpha_P P^2 + \alpha_\eta \eta^2 + \gamma_\eta P \eta^n + \beta P^4$$

n ≡ faintness index

$$\partial \mathcal{F} / \partial P = 2\alpha_p P + \gamma_\eta \eta^n + 4\,\beta P^3 = 0$$

$P_{eq} \sim -\eta^n$

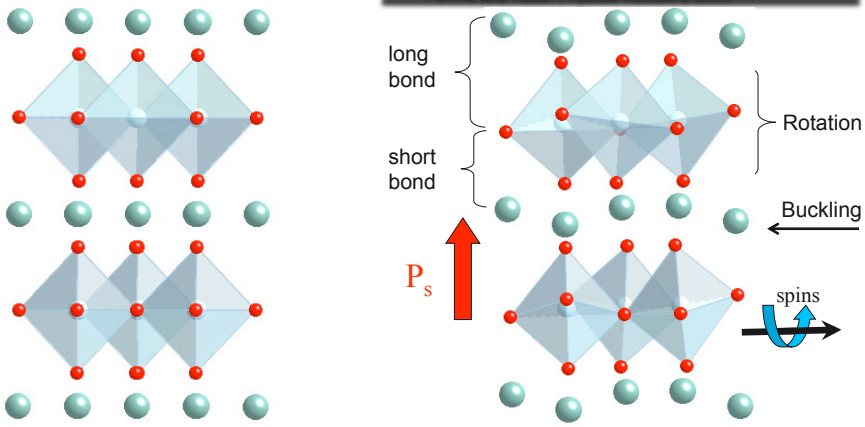
Once primary OP becomes nonzero, a polarization is induced

Improper structural ferroelectric: Hexagonal Manganites

$RMnO_3$, R = Y, Sc, Ho-Lu

Identified as geometric ferroelectric:
vanAken, Palstra, Fillipetti, Spaldin, Nature Materials 2004.

correctly Identified the improper ferroelectric transition
Fennie and Rabe, Physical Review B 2005



Paraelectric *(Z=2)* *T > ~1250K*

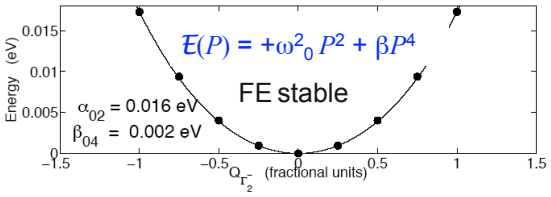
$YMnO_3$

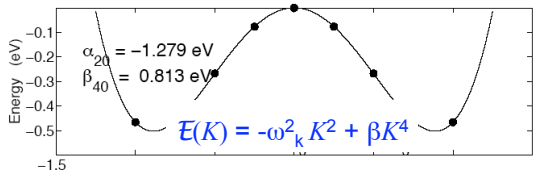
Ferroelectric *(Z=6)* *T: 0K → ~1250K*

Improper ferroelectric transition example: $YMnO_3$

The internal Energy can be calculated as a function of the primary and secondary order parameters from first principles

Primary order parameter: zone-boundary lattice instability **K_3**
Secondary order parameter: Spontaneous polarization **P**





Zone boundary K-mode, double well

PE
$P6_3/mcm$
Z=2

FE
$P6_3cm$
Z=6

A single OP, the zone-boundary K-mode, accounts for symmetry loss from PE to FE

Fennie and Rabe, Physical Review B 72, 100103 2005

Improper ferroelectric transition example: $YMnO_3$

Expand energy to fourth order in the primary K_3 and secondary $\mathbf{P}$ order parameters:

Fennie and Rabe, Physical Review B 72, 100103 2005

(note energy expansion simplified for pedagogy)

$$\mathcal{F}(K_3, \mathbf{P}) = \alpha_P \mathbf{P}^2 + \alpha_k K_3^2 + \gamma_\eta \mathbf{P} K_3^3 + \beta \mathbf{P}^4$$

$$\Rightarrow P \sim \gamma_\eta K_3^3$$

Also note, no anomalous Born effective charges

Recent experiments confirm the improper ferroelectric transition in the hexagonal manganites

I.-K. Jeong, N.Hur, and Th. Proffen, *High-temperature structural evolution of hexagonal multiferroic $YMnO_3$ and $YbMnO_3$*, J. Appl. Crystall, **40**, 730-735 (2007).

G. Nenert, *Mechanism for ferroelectricity in hexagonal $RMnO_3$*, in Orbital Ordering and Multiferroics, Chapter 4, Ph.D. thesis, University of Groningen, 2007.

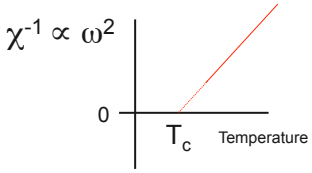
Note, the dielectric constant does not diverge at an improper ferroelectric transition!

Intrinsic static dielectric constant

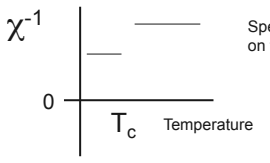
$$\epsilon = \epsilon_\infty + \sum_n \frac{\Omega_{p,n}^2}{\omega_n^2}$$

Where ω_n is ir-active phonon frequency

Proper FE transition
Currie Weiss



Improper FE trasition



Specific form depends on faintness index

For example see:

- *Principles and Applications of Ferroelectrics and related applications*, by Lines and Glass, Oxford
- *Ferroelectric Phenomena in Crystal* by Strukov and Levanyuk

Crystallography: specifying crystal structures

- Textbook description: lattice + basis
- A more useful description:
  space group + occupied Wyckoff positions

Most compact (in conjunction with Int'l Tables)
Symmetries and free structural parameters evident
(almost) unique – origin, "setting" of axes

Proper knowledge and careful application of crystallographic analysis will ensure physically correct results and allow you to avoid embarrassing mistakes!

Example: cubic perovskite structure

Crystallographic description—generally given in the literature

- Space group Pm3barm (#221) (out of 230 space groups total)
- which Wyckoff positions are occupied by which atoms

Pb 1a 0,0,0 Pb 1b ½,½,½
Ti 1b ½,½,½ Ti 1a 0,0,0
O 3c 0,½,½ ½,0,½ ½,½,0 O 3d ½,0,0 0,½,0 0,0,½
Lattice parameter a_0

No additional free structural parameters for this symmetry

$Pm\bar{3}m$ O_h^1 $m\bar{3}m$ Cubic

No. 221 $P\ 4/m\ \bar{3}\ 2/m$ Patterson symmetry $Pm\bar{3}m$

Symmetry operations

(1) 1	(2) 2 0,0,z	(3) 2 0,y,0	(4) 2 x,0,0
(5) 3^+ x,x,x	(6) 3^+ $\bar{x},x,\bar{x}$	(7) 3^+ $x,\bar{x},\bar{x}$	(8) 3^+ $\bar{x},\bar{x},x$
(9) 3^- x,x,x	(10) 3^- $x,\bar{x},\bar{x}$	(11) 3^- $\bar{x},\bar{x},x$	(12) 3^- $\bar{x},x,\bar{x}$
(13) 2 $x,x,0$	(14) 2 $x,\bar{x},0$	(15) 4^- 0,0,z	(16) 4^+ 0,0,z
(17) 4^- x,0,0	(18) 2 0,y,y	(19) 2 0,$y,\bar{y}$	(20) 4^+ x,0,0
(21) 4^+ 0,y,0	(22) 2 x,0,x	(23) 4^- 0,y,0	(24) 2 $\bar{x}$,0,x
(25) $\bar{1}$ 0,0,0	(26) m x,y,0	(27) m x,0,z	(28) m 0,y,z
(29) $\bar{3}^+$ x,x,x; 0,0,0	(30) $\bar{3}^+$ $\bar{x},x,\bar{x}$; 0,0,0	(31) $\bar{3}^+$ $x,\bar{x},\bar{x}$; 0,0,0	(32) $\bar{3}^+$ $\bar{x},\bar{x},x$; 0,0,0
(33) $\bar{3}^-$ x,x,x; 0,0,0	(34) $\bar{3}^-$ $x,\bar{x},\bar{x}$; 0,0,0	(35) $\bar{3}^-$ $\bar{x},\bar{x},x$; 0,0,0	(36) $\bar{3}^-$ $\bar{x},x,\bar{x}$; 0,0,0
(37) m $x,\bar{x},z$	(38) m x,x,z	(39) $\bar{4}^-$ 0,0,z; 0,0,0	(40) $\bar{4}^+$ 0,0,z; 0,0,0
(41) $\bar{4}^-$ x,0,0; 0,0,0	(42) m $x,y,\bar{y}$	(43) m x,y,y	(44) $\bar{4}^+$ x,0,0; 0,0,0
(45) $\bar{4}^+$ 0,y,0; 0,0,0	(46) m $\bar{x},y,x$	(47) $\bar{4}^-$ 0,y,0; 0,0,0	(48) m x,y,x

this is the symmetry group of the cube

$Pm\bar{3}m$ O_h^1 $m\bar{3}m$ Cubic

No. 221 $P\ 4/m\ \bar{3}\ 2/m$ Patterson symmetry $Pm\bar{3}m$

3	d	$4/m\,m\,.\,m$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$
3	c	$4/m\,m\,.\,m$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
1	b	$m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
1	a	$m\bar{3}m$	0,0,0		

These are the highest symmetry (and lowest multiplicity) Wyckoff positions in this space group.
They appear in the description of the cubic perovskite structure.

What's the space group of lattice+basis?

- "by hand:" identify the symmetries

for a given origin—point symmetries +

additional symmetries with nonprimitive translation?

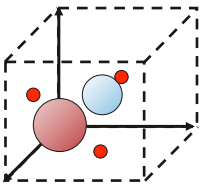
[doublecheck lattice type—may be lower symmetry than initial guess; for example, a primitive tetragonal lattice with c=a could initially be misidentified as simple cubic]

- A useful computational tool: ISOTROPY
- http://stokes.byu.edu/isotropy.html
- **FINDSYM**: Identify the space group of a crystal, given the positions of the atoms in a unit cell.

Note: many first-principles packages include space-group identification, but less reliable

Example: cubic perovskite structure

- Simple cubic lattice a_0x, a_0y, a_0z
- Pb at (0,0,0)
- Ti at (1/2,1/2,1/2)
- O at (1/2,1/2,0)
- O at (0,1/2,1/2)
- O at (1/2,0,1/2)



Note that basis is not unique (can add lattice vector to any position(s), can put origin at Ti or, in fact, anywhere in cell)

does not have full symmetry of the crystal (and symmetries not obvious in this description)

Symmetry determines allowed couplings

- Macroscopic properties: need point group only
- Forms of tensors (zeros, equalities) determined

(this is explained very well for nonmagnetic crystals in J. F. Nye, Physical Properties of Crystals (Oxford 1957, reprinted many times since) and for magnetic crystals in Birss, Symmetry and Magnetism).