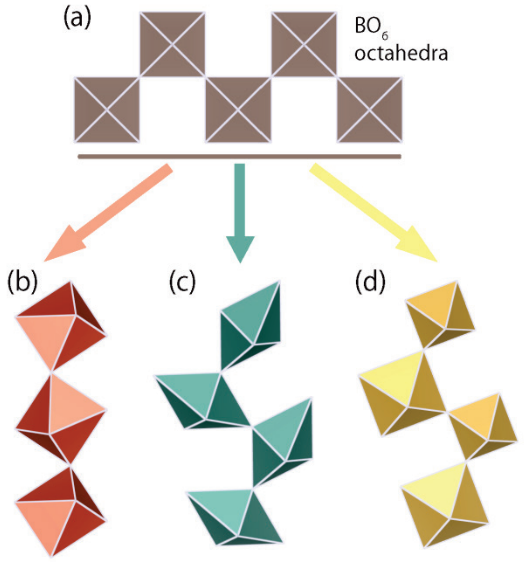
materials theory
& design group

DESIGNING ATOMIC-SCALE FUNCTION

Old challenges and new answers in complex oxides using modern theoretical tools



$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

James M Rondinelli

Department of Materials Science and Engineering
Drexel University, Philadelphia PA, 19104 USA

email – jrondinelli@coe.drexel.edu

date – August 30, 2013 | ICMR Summer School on Materials in 3D

http://mtdg.materials.drexel.edu

Research themes within our MTD group

I. Materials at the edge (of phase boundaries) – structure + properties

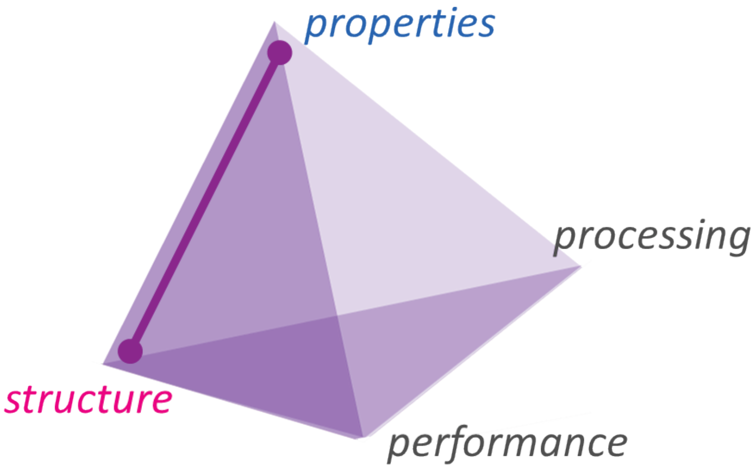
We aim to understand the functionality of materials near electronic or structural phase boundaries by correlating electronic and magnetic properties in a variety of crystal families to their basic structural units or building blocks.

II. Discovery of atomic structure directing "forces" – processing

We seek to formulate reliable "bottom-up" design strategies to control crystal structure and behavior at the unit cell level.

III. Multifunctional materials design – performance

We leverage insights derived in Themes I and II to overcome contraindicated materials properties – those that often do not coexist – and rationally harmonize them into a single structure.



The MTDG Team

- Group Members
  - UG – Adam Cordi
  - GR – Josh Young, Nenian Charles
  - PD – Antonio Cammarata, Danilo Puggioni, Prasanna Balachandran

- Collaborations/Interactions
  - Thin film growth – Steve May (Drexel); Jak Tchakhalian (Arkansas); Darrell Schlom (Cornell); Roman Engel-Hebert (PennState); Anand Bhattacharya (Argonne); Yuri Suzuki (Stanford)
  - Theory/Applied Math – Craig Fennie (Cornell); Andrew Millis, Chris Marianetti (Columbia), Bala Rajaratnam (Stanford), Gaoyang Gou (Xi' an Jiaotong Univ.)
  - Materials chemistry – Ken Poeppelmeier (Northwestern), Shiv Halasyamani (U. Houston)
  - Materials characterization – John Freeland, Phil Ryan (Argonne); Albina Borisevich, Sergei Kalinin (Oak Ridge); Venkat Gopalan (PennState)

- Support

ONR Office of Naval Research

DARPA

ACS PRF

XSEDE Extreme Science and Engineering Discovery Environment

Argonne NATIONAL LABORATORY

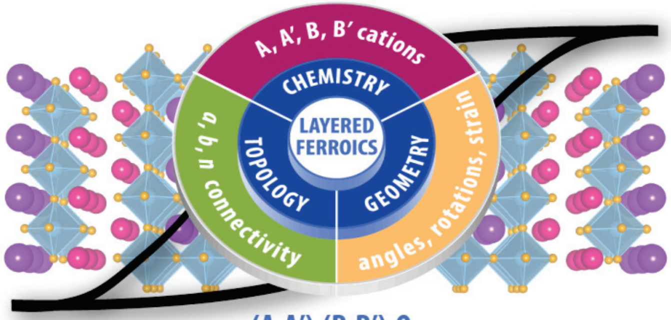
DOD HPC MODERNIZATION PROGRAM

Designing atomic-scale electronic function – Outline

- ***Foreword*** (9-10.30a)
  - Main challenges
  - Why complex oxides provide the ultimate “sand box”
  - Structure-driven properties of materials paradigm
  - Theoretical / Computational tools to formulate an understanding for design

- ***Coffee break*** (10.30-11a)

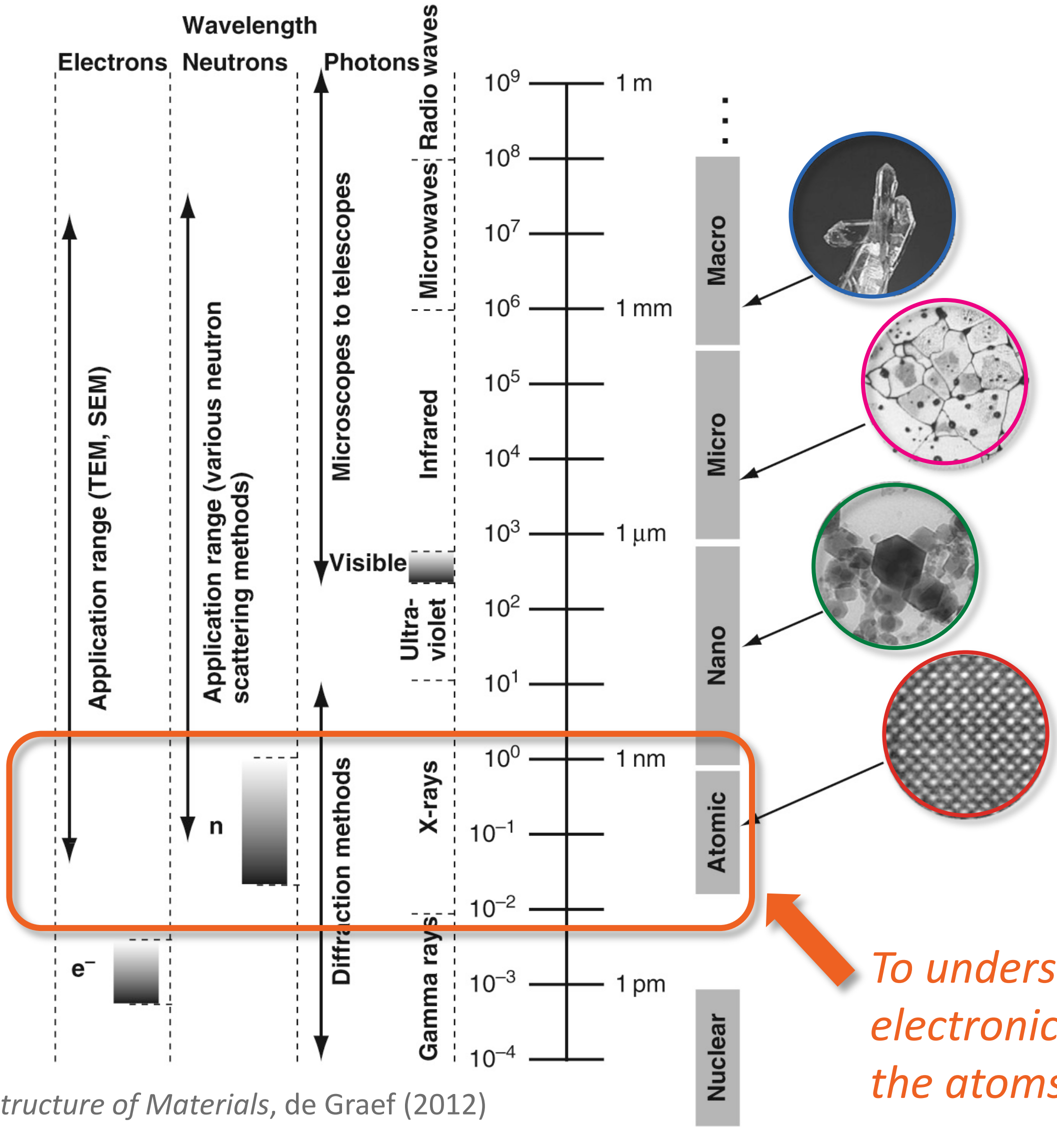
- ***Feature*** (11-12.30p)
  - *Ab initio* symmetry-based structural design protocol: confluence of group theory, electronic structure theory, and data-mining
  - Design of emergent ferroelectricity and multiferroism in artificial oxides



$(A,A')_a(B,B')_bO_n$

Structure at various length scales determines functionality

- Structures impose constraints on physical properties of materials



Quartz crystal

Grains in a $SrTiO_3$ ceramic

Nanocrystalline $Mn_{0.5}Zn_{0.5}Fe_2O_4$ particles

Atomic resolution image of $BaTiO_3$

To understand or to design materials with new electronic properties requires we understand how the atoms (electrons) are arranged

Structure of Materials, de Graef (2012)

Goals

- **Structure-driven properties.** Properties of many oxides are derived from the local structural framework or molecular motifs that comprise it
- **Computational tools to understand structure and function.** Freely available tools to rigorous analyze structures, which can be used for input to electronic structure-based calculations to explore physical mechanisms
- **Property Design Paradigms.** Examples of how first-principles calculations combined with statistical tools enable formulation of design guidelines and reduce the composition phase space for exploration

Goals

- Structure-driven properties.
- Computational tools to understand structure and function.
- Property Design Paradigms.

Some of the material presented here can be found in the following articles:

JMR and N.A. Spaldin, *Structure and properties of functional oxide thin films: Insights from electronic-structure calculations*, Advanced Materials, **23** 3363 (2011)

JMR, S. May and J.W. Freeland, *Control of octahedral connectivity in perovskite oxide heterostructures: An emerging route to multifunctional materials discovery,* MRS Bulletin, **37** 261 (2012)

Colloquium: Emergent properties hidden in plain view: Strong electronic correlations at oxide interfaces, Rev. Mod. Phys. (Forthcoming, 2014)

And other preprints located at: http://mtdg.materials.drexel.edu/Publications

If you do not have access to the articles, feel free to send me an email: jrondinelli@coe.drexel.edu

Materials design challenge – discovering new phases of matter

“Materials are traditionally something to which design is applied. ***New methods in the field of computational materials science have rendered materials as the object of design development.***

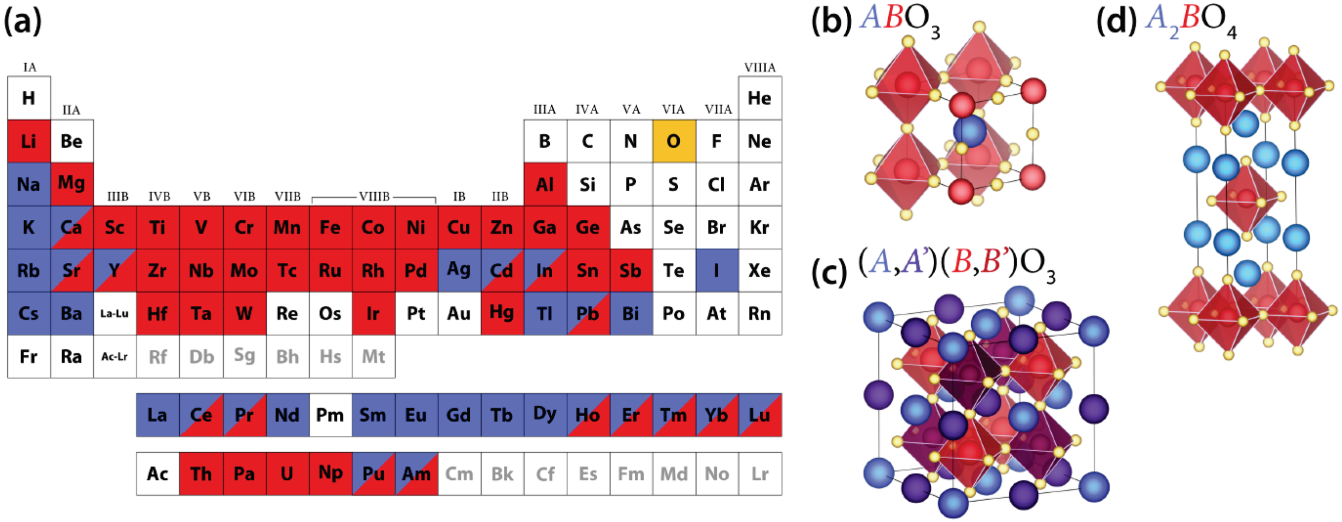
Instead of designing a thing, we design a designing thing. In the process, we have created materials with exceptional properties and collapsed the age-old boundary between the image and the object, rendering mutable the object itself.”

–Bruce Mau and the Institute without Boundaries (2004); Adapted from *Massive Change*, Phaidon Press (2004)

Materials design challenges:
Towards atomic-scale materials (properties) by design

- Of the available elements compatible with different crystal structures that can be created, what properties can arise from changes in their configurations and compositions?

- How do you activate “hidden” properties or new physics in materials through atomic scale control? And can we predict this behavior?



Can we design electronic responses by controlling the chemistry of the constituents (interactions) and the arrangement of the atomic structure (lattice geometry)?

Related practical questions

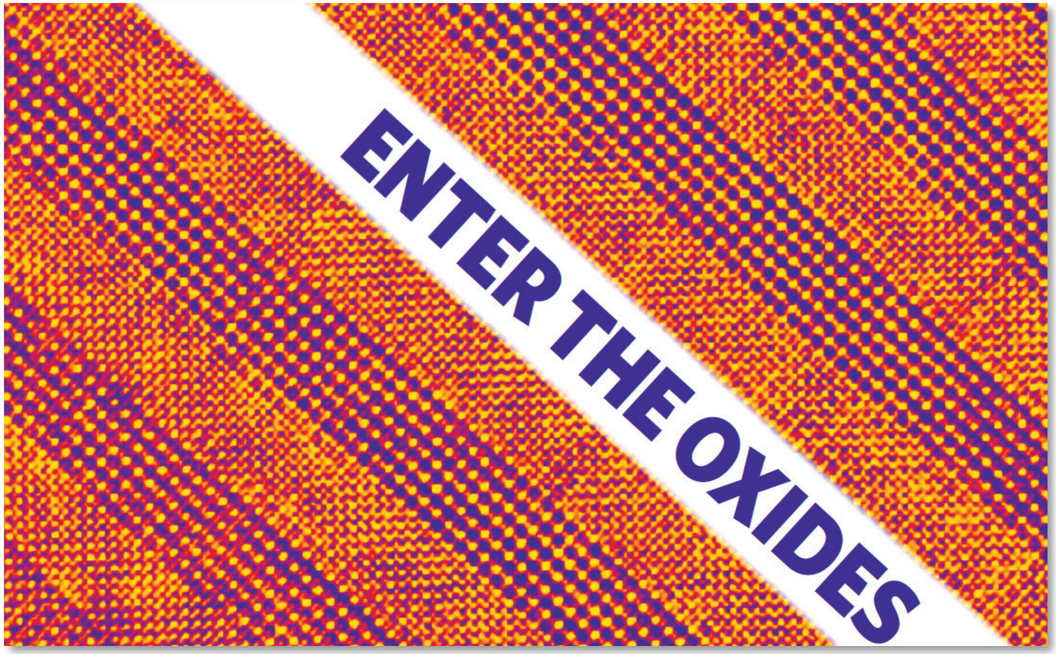
- How do you make materials with atomic level precision?
- How do you know that you have made what you wanted?
- Can you control defects and composition to the extent required for the targeted function?

- What concepts and computational tools can be used to predict new properties/behavior?

Designing atomic-scale electronic function – Outline

- ***Foreword*** (9-10.30a)
  - Main challenges
  - **Why complex oxides provide the ultimate "sand box"**
  - Structure-driven properties of materials paradigm
  - Theoretical / Computational tools to formulate an understanding for design

Provided we have the necessary, tools what kinds of materials do we want to attempt rationally design electronic properties from?

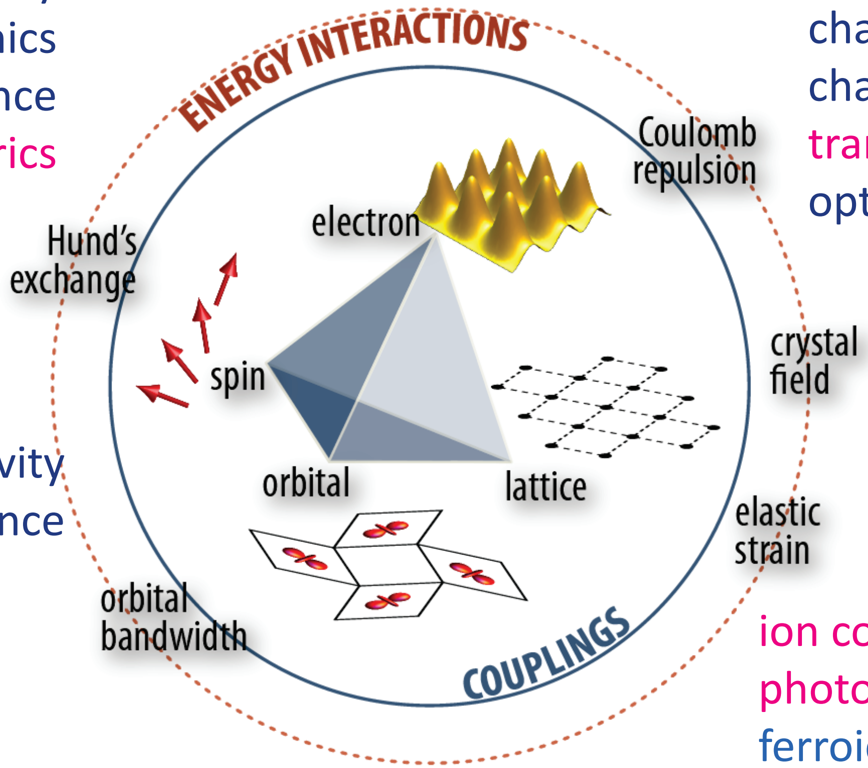


J. Heber, Nature **459**, 28 (2009)

Oxide materials support diverse interactions which are necessary to a variety of functionalities

(anti)ferromagnetism
magnetoelectricity
spintronics
giant magnetoresistance
thermoelectrics

superconductivity
colossal magnetoresistance



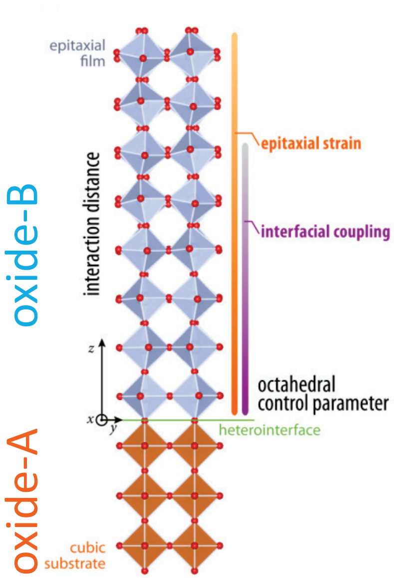
metal-insulator transitions
charge-transfer insulators
charge density waves
transparent conductors
optical absorption

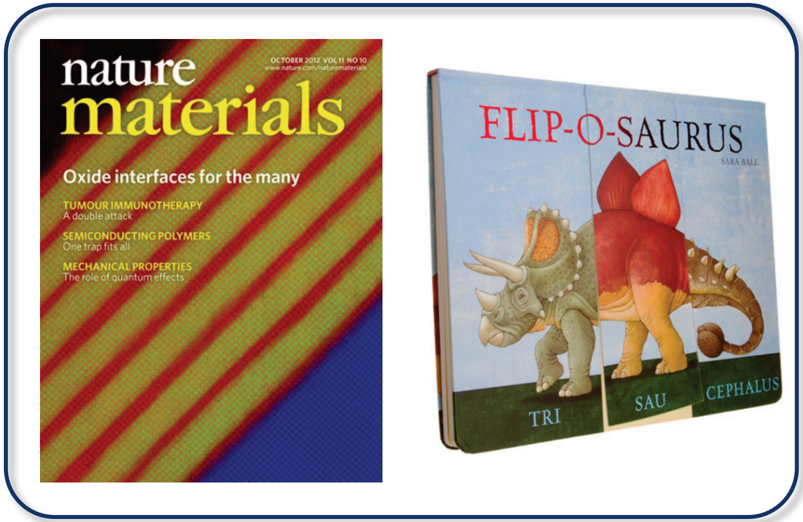
ion conduction
photocatalytic efficiency
ferroic behavior

JMR & N.A. Spaldin, Adv. Mater. **23** 3363 (2011)

Complex oxides support diverse physical properties

Function	Example
Dielectric	$CaTiO_3$
Ferroelectric	$BaTiO_3$
Magnetoelectric	$BiFeO_3$
Antiferroelectric	$PbZrO_3$
Antiferromagnetic	$LaMnO_3$
Ferromagnetic	$SrRuO_3$
Superconducting	$YBa_2Cu_3O_{7-\delta}$
Semiconducting	$CaMnO_3$





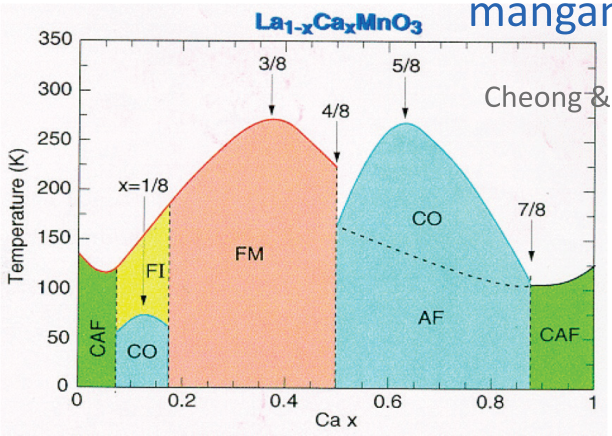
- Properties can be tailored and tuned at the (sub)-nanometer scale
  - Growth of oxides with atomic level precision comparable to semiconductors
  - Create new functionalities in layered structures
  - More “knobs” than charge density and voltages to tune from which new devices may be created

Exhibit interesting (useful) electronically ordered phases

- Close competition among electronic phases allows small changes in chemical composition, strain, or external fields to bring about dramatic phase transitions

phase diagrams

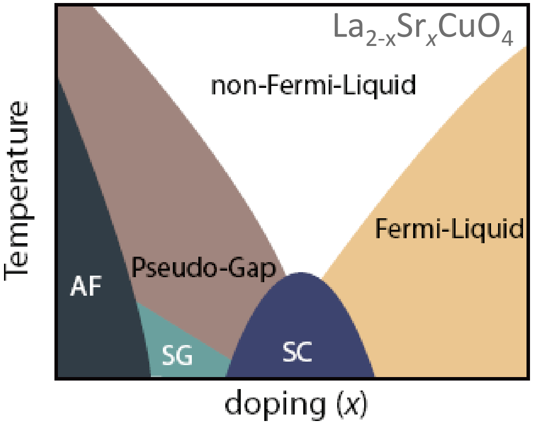
manganites



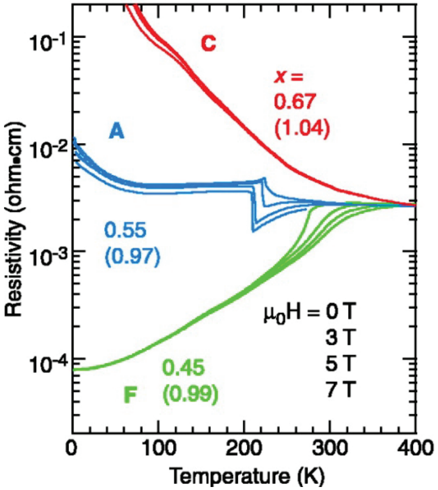
Cheong & Hwang (1999)

cuprates

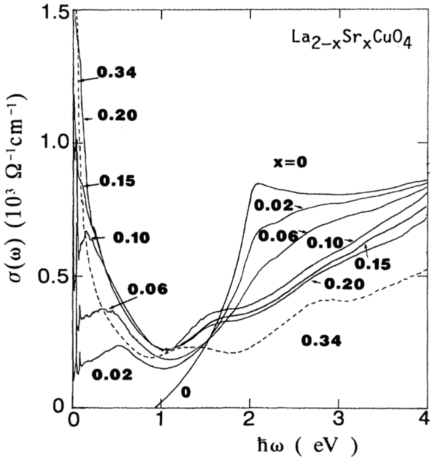
Dagotto, Science **309** 257 (2005)



behavior



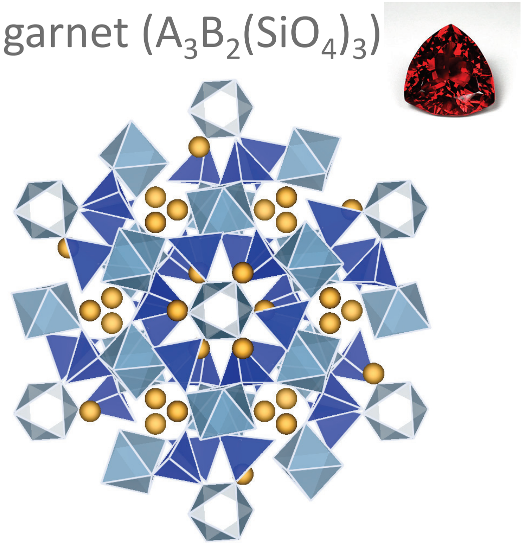
Y. Tokura et al., Science **288**, 462 -468 (2000)

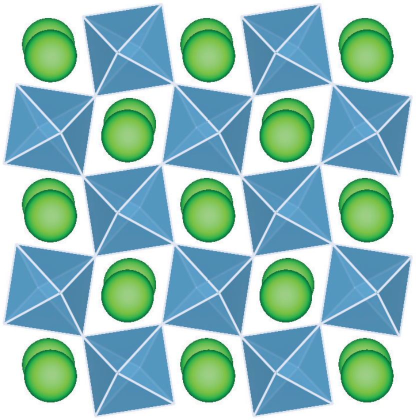


S. Uchida, Y. Tokura *et al*, PRB **43** 7942 (1990)

Flexible and adaptive structure types in complex oxides

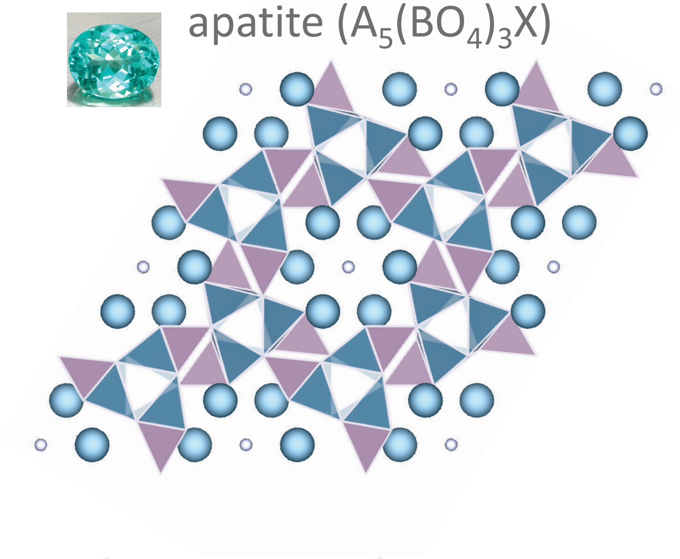
garnet ($A_3B_2(SiO_4)_3$)

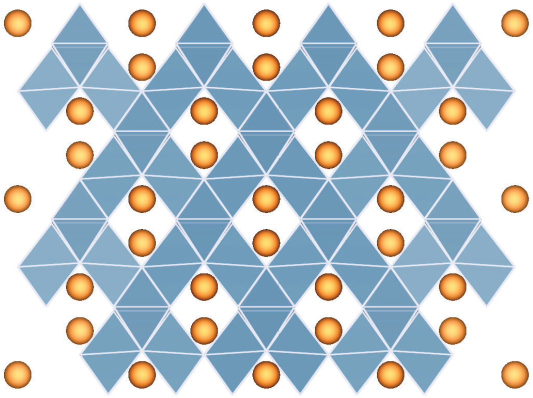




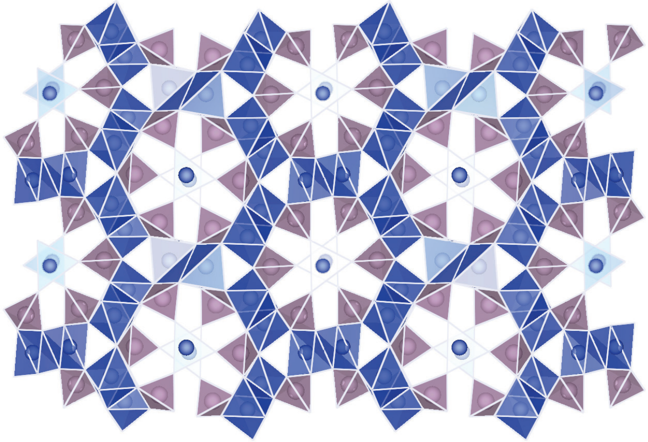
perovskite ($CaTiO_3$)

apatite ($A_5(BO_4)_3X$)





spinel ($MgAl_2O_4$)



lyonsite ($A_{16}(BO_4)_{12}$)

See J. Smit, P. Stair and K.R. Poeppelmeier, *Adaptive Solid-State Structures*. Chem. Eur. J. **12** 5944 (2006)

Designing atomic-scale electronic function – Outline

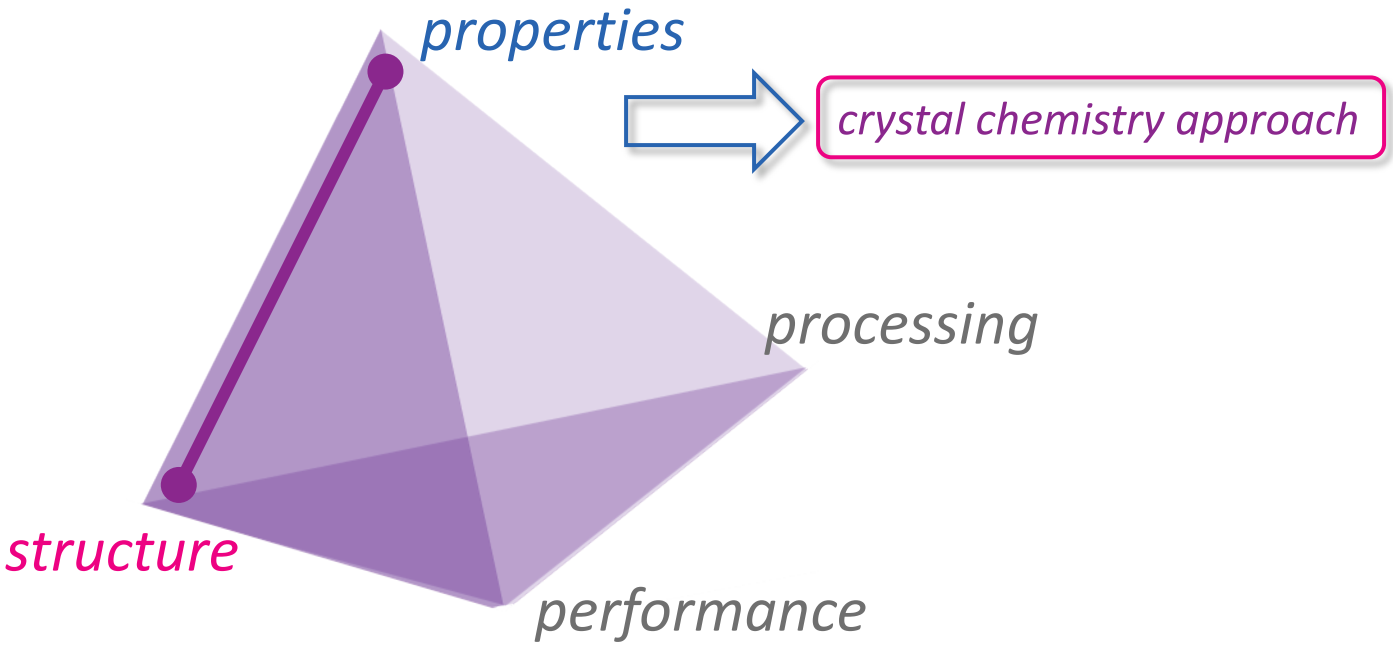
- ***Foreword*** (9-10.30a)
  - Main challenges
  - Why complex oxides provide the ultimate “sand box”
  - **Structure-driven properties of materials paradigm**
  - Theoretical / Computational tools to formulate an understanding for design

J. Heber, Nature **459**, 28 (2009)

The design challenge relies on knowing what are the key structure-property relationships and then promoting that relationship

- How to connect the atomic scale physics of the transition metal cations to nearby ligands (oxygen atoms) with materials function?

- Correlate electronic and magnetic properties to the basic structural units or building blocks

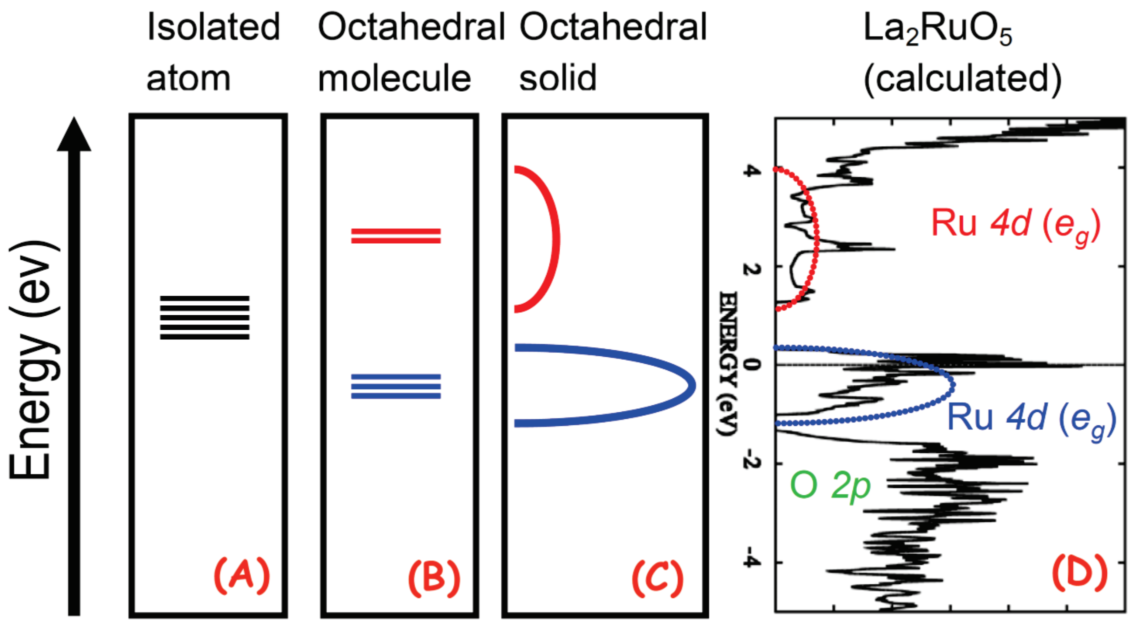


What determines the electronic properties of materials?

Figure from P. Khalifah (2013)

What determines the electronic properties of materials?

- Crystal structure → electronic structure → properties
- To first order, the electronic structure is determined by the elemental composition of a material (*need to know what elements are best*)



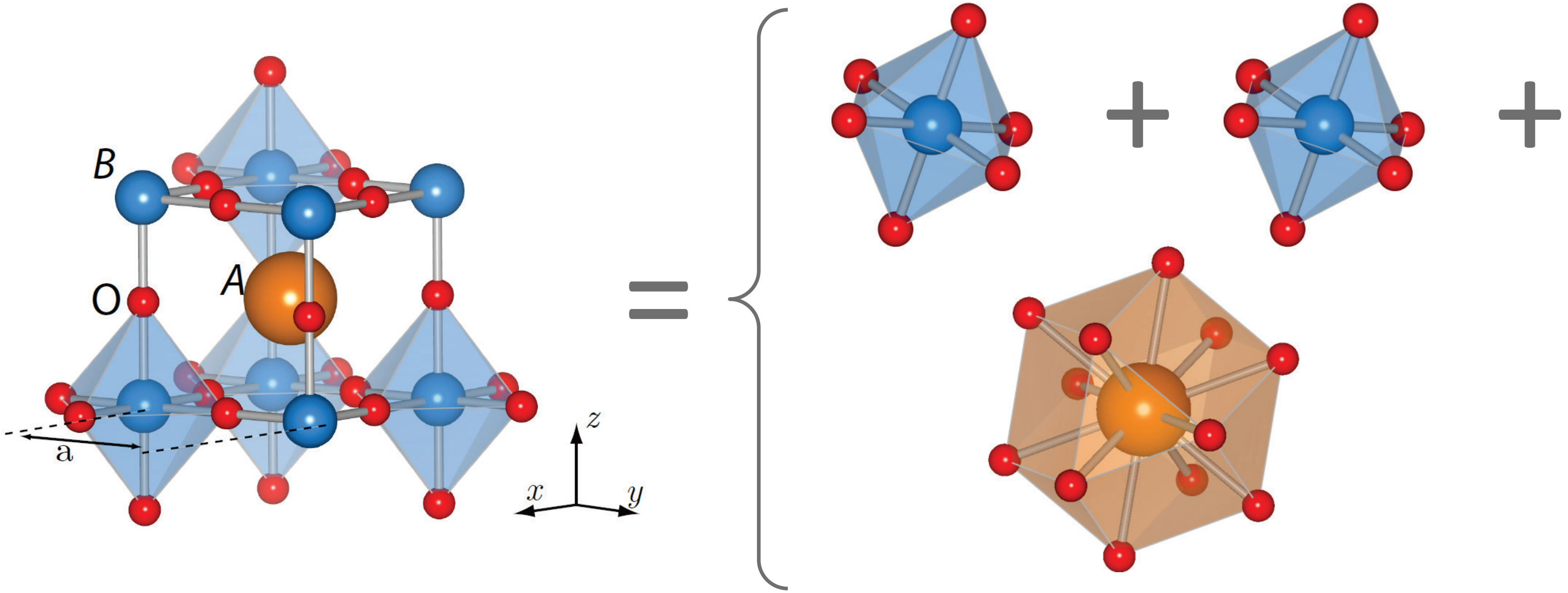
Changes occur due to:

- **Coordination environment**
- Bonding/hybridization
- Structure dimensionality
- Valence state

Figure from P. Khalifah (2013)

Polyhedra building blocks in *ABO*$_3$ perovskites

- Crystal chemistry approach to condensed matter systems
  - Crystals are supramolecular assemblies of cation-anion polyhedral building blocks

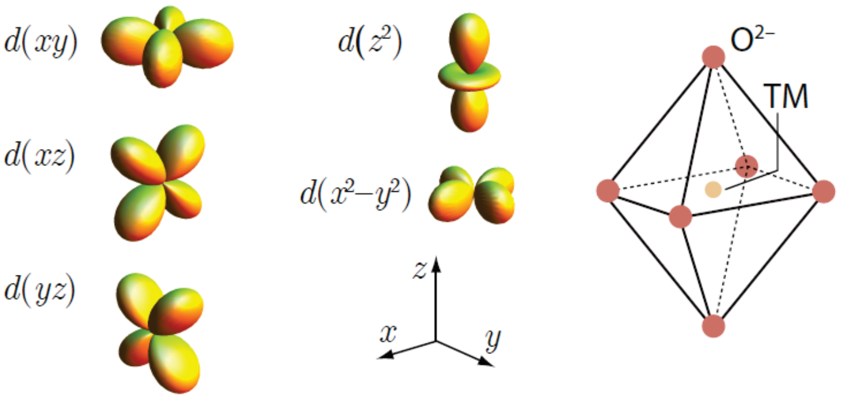


basic building blocks are BO_6 and AO_{12} polyhedra

Control over size, shape and connectivity of these units enables avenues to tailor functional material properties

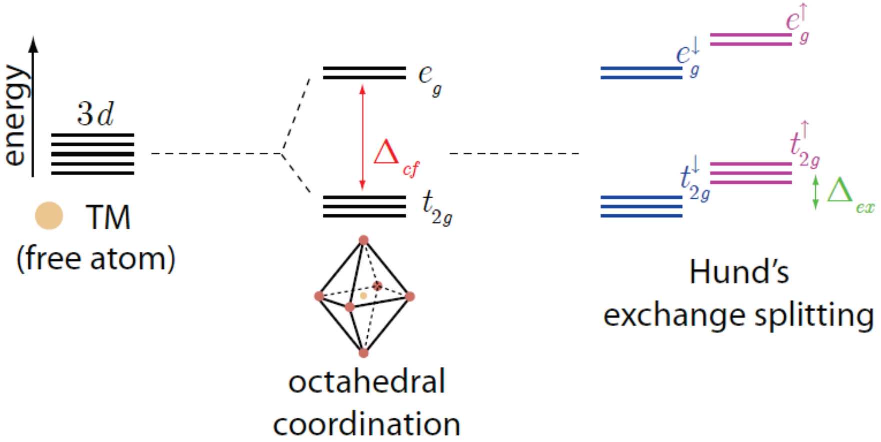
Structure-driven properties from BO_6 building blocks

- Properties are often dictated by the transition metal (TM) cation and its valence configuration—*TM chemistry is crucial*



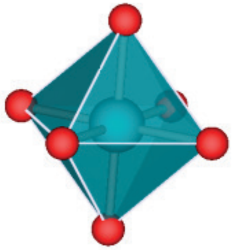
Partially filled transition metal *d*-shell supports various magnetic interactions

The active electrons producing the properties are (formally) given by the number of electrons provided by the transition metal (TM)



The BO_6 octahedron as a functional building block

- Many complex metal oxides are composed of the this simple structural unit

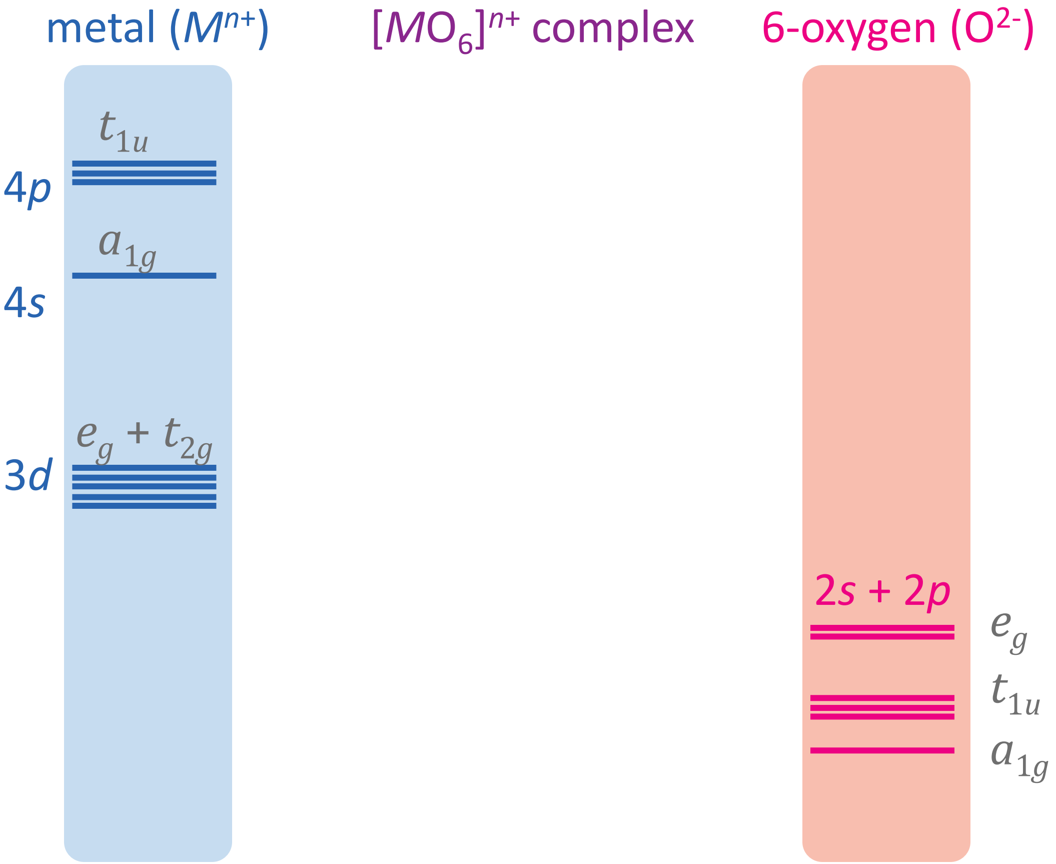


BO_6 octahedron

- The *local* electronic levels of all octahedrally coordinated cations are essentially the same

Electronic properties of the BO_6 octahedron – molecular orbitals

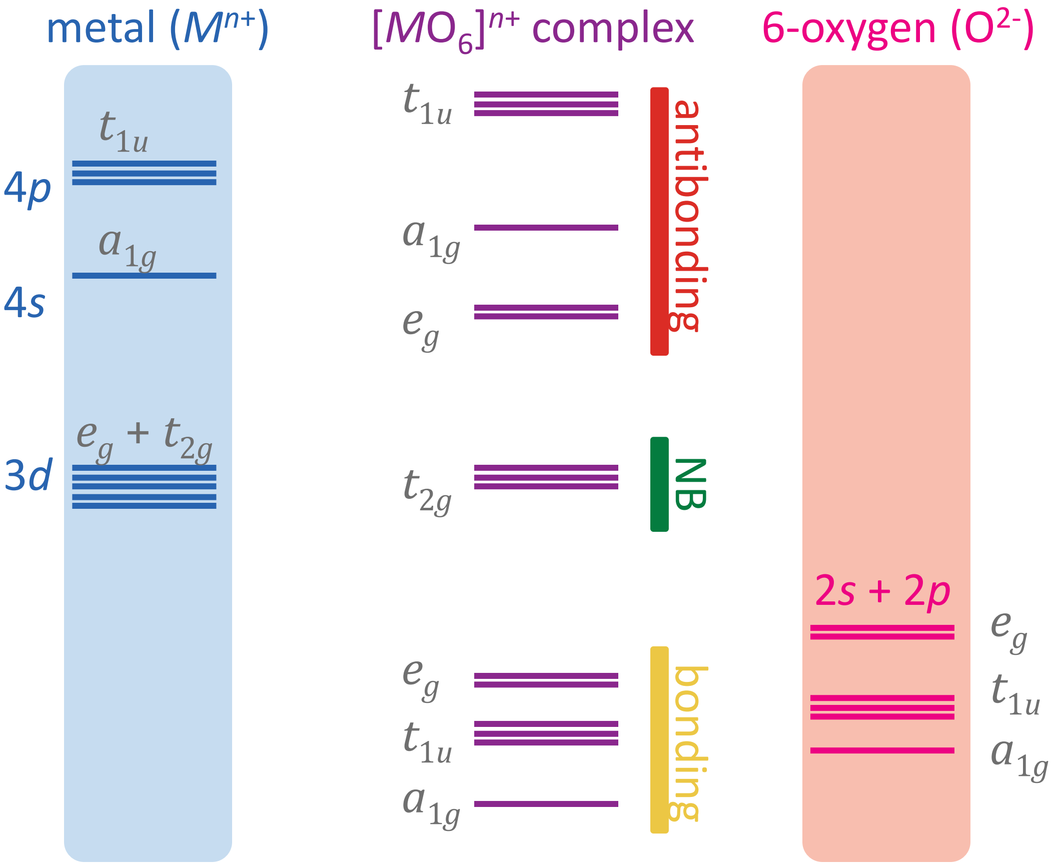
- The *local* electronic levels of all octahedrally coordinated cations are essentially the same



σ-bonding only

Electronic properties of the BO_6 octahedron – molecular orbitals

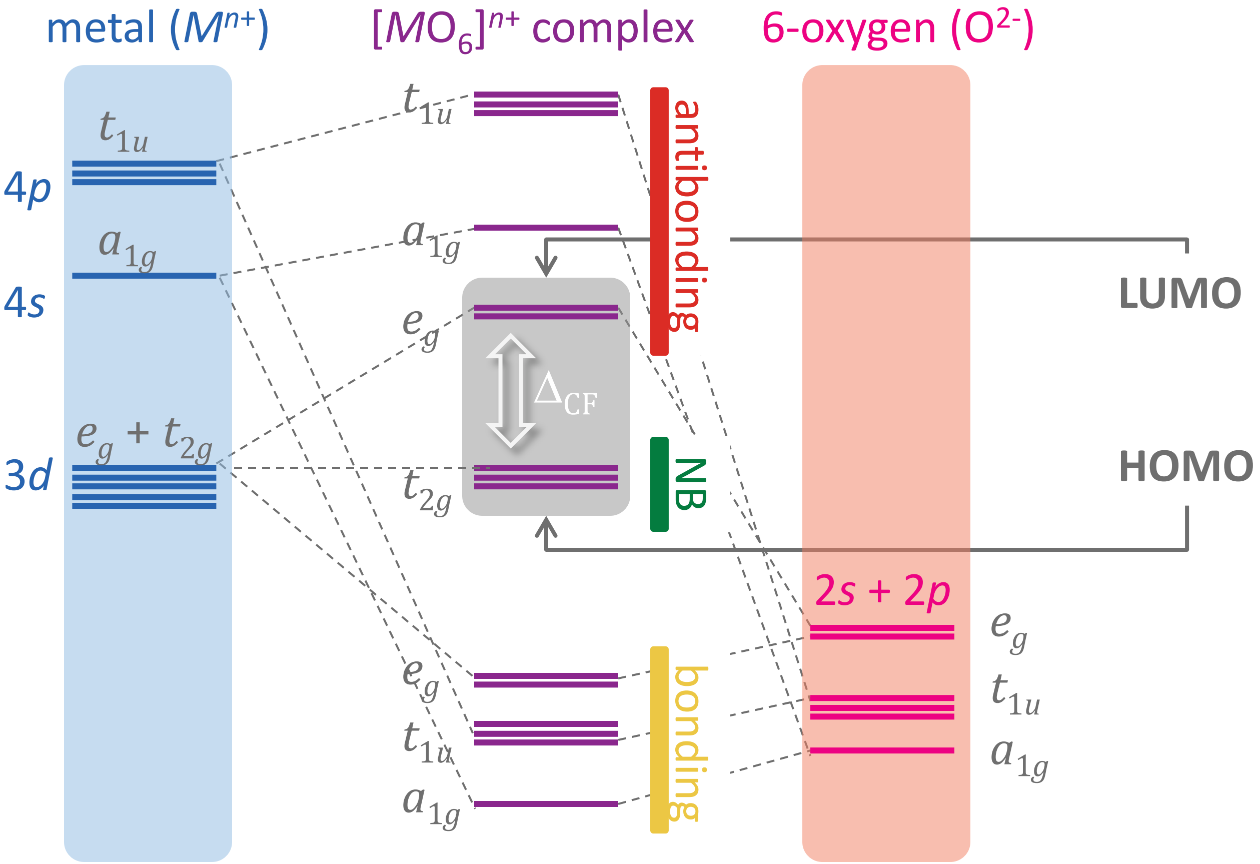
- The *local* electronic levels of all octahedrally coordinated cations are essentially the same



σ-bonding only

Electronic properties of the BO_6 octahedron – molecular orbitals

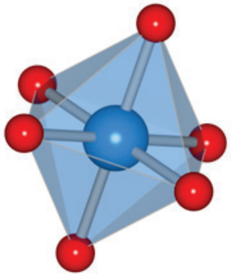
- The *local* electronic levels of all octahedrally coordinated cations are essentially the same



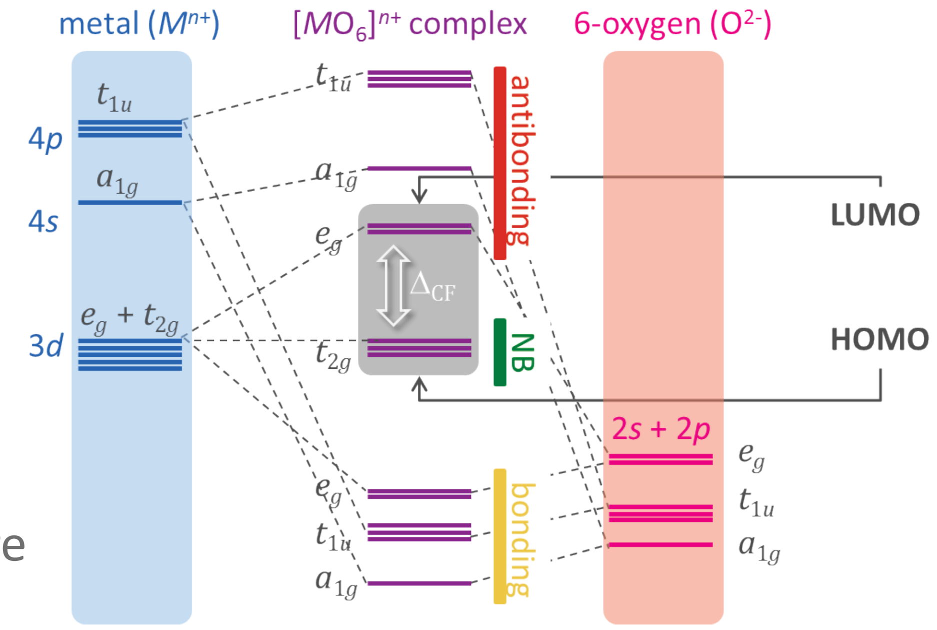
σ-bonding only

The BO_6 octahedron as a functional building block

- Many complex metal oxides are composed of the this simple structural unit



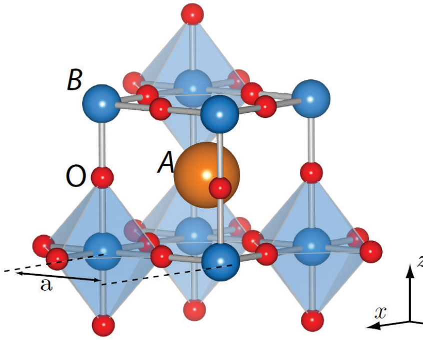
BO_6 octahedron



- The *local* electronic levels of all octahedrally coordinated cations are essentially the same

Designing properties requires control of ***electron count*** *and/or* ***extended crystal structure***

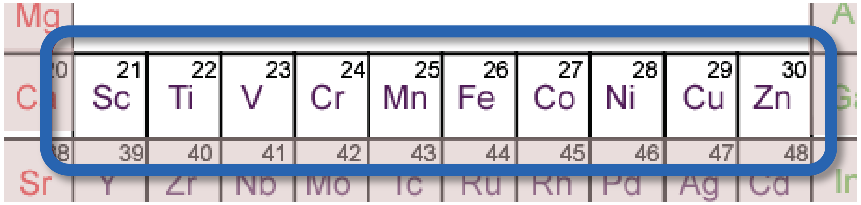
Electron counting in ABO_3 perovskites (ionic approximation)



- Oxygen is electronegative and has a formal charge of 2-
- A cation treated as a point charge [q(A) is typically 2+ or 3+]
- B-cation charge = 6-q(A), typically 3+ or 4+
  - Transition metals fill up the *d*-shell
  - Oxygen atoms grab the 2 4*s* electrons and then possibly 1 or 2 from the *d*-shell (depending on the A-site ion)

A-site = alkaline earth or rare-earth metals

B-site = TM of the 3rd or 4th row



Mg											A
0 C	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	G
8 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	Ir

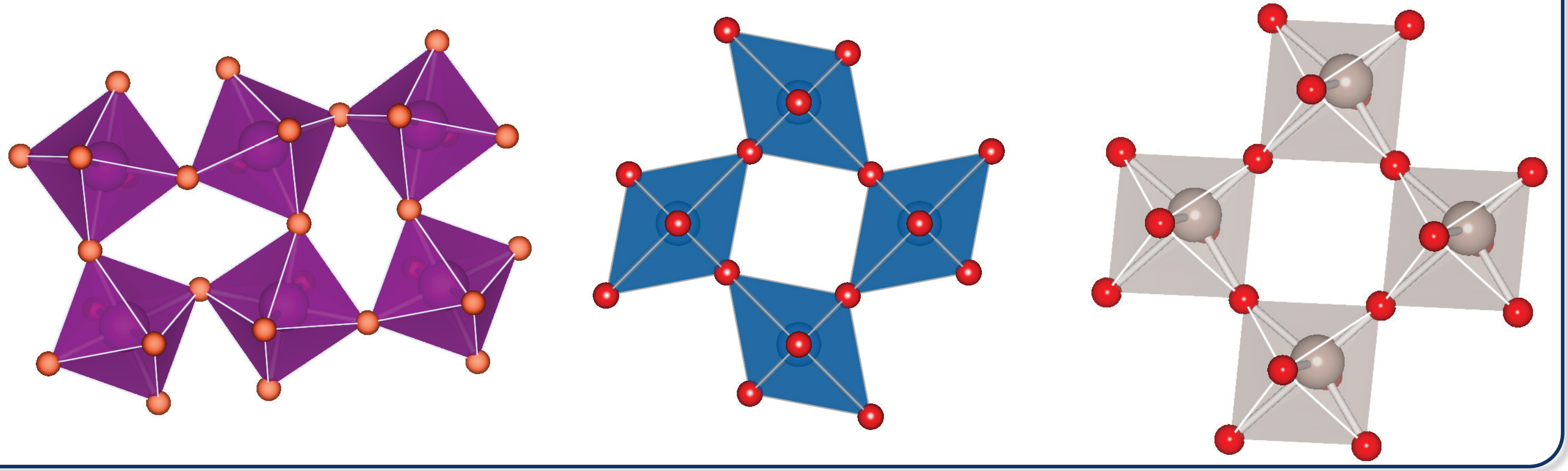
- The charge on the B-cation can be tuned by alloying on the A-site

→ Electronic and Structural effect

- Covalency between B-site and O is not always negligible

Most of the "action" originates for the transition metal center and its interaction with oxygen

- The electronic configuration of the TM can lead to
  - Geometric instabilities (Jahn-Teller distortions) , degeneracies, electron-lattice coupling interactions, etc.



structure

octahedral rotations

Jahn-Teller distortions

cation displacements

properties

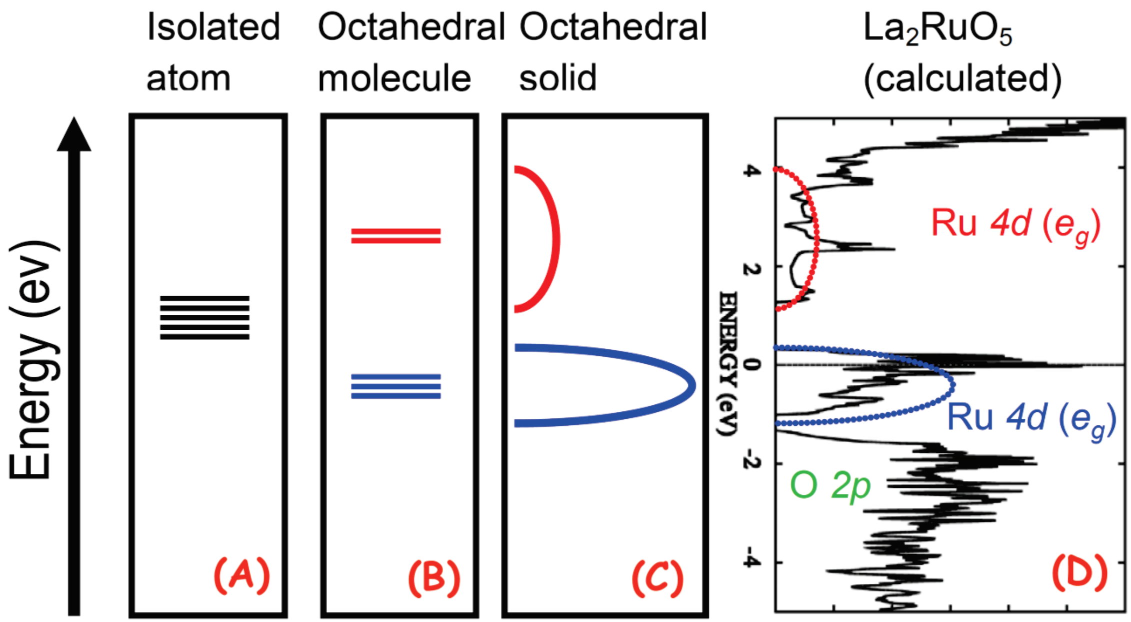
Band gaps
Magnetic exchange
Critical temperatures
Thermal conductivity

Metal-Insulator Transitions
Electronic conductivity

Ferroelectricity
Dielectric constants
Optical absorption

What determines the electronic properties of materials?

- Crystal structure → electronic structure → properties
- To first order, the electronic structure is determined by the elemental composition of a material (*need to know what elements are best*)



Changes occur due to:

- Coordination environment
- Bonding/hybridization
- **Structure dimensionality**
- Valence state

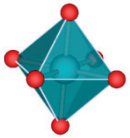
How wide are these bands?

Figure from P. Khalifah (2013)

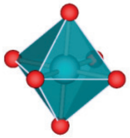
Bandwidth control through structural flexibility

- “Bottom-up” structure approach for inorganic crystalline materials

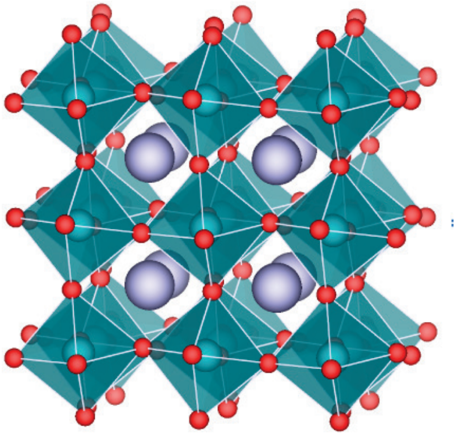
- Established that:
  - The *local* electronic levels of all octahedrally coordinated cations are essentially the same, but the way they are connected alters the bandwidth

- What happens when we make a crystal out of these units?
  - Tiling of this  in space produces a 3D or 2D crystal

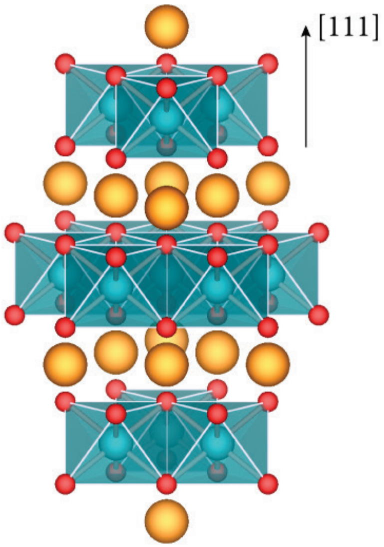
Bandwidth control through structural flexibility

- Tiling of this  in space produces a 3D or 2D crystal

Corner-to-corner: *perovskite structure*



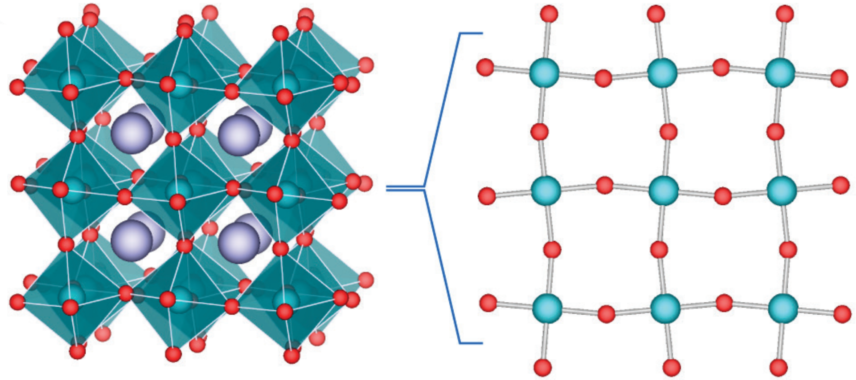
Edge-to-edge: *"stuffed"* $CdCl_2$ *structure*



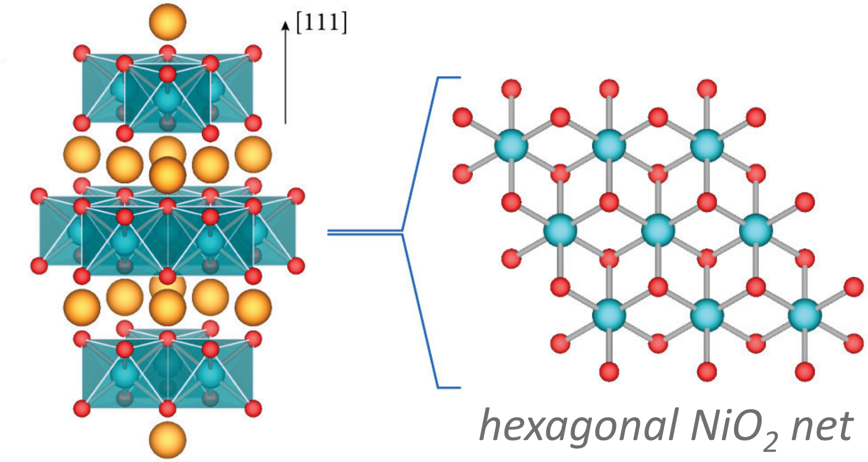
Different orbital overlap suggests the materials should behave differently since electrons move through the metal-oxygen bonds

Consequences of the octahedral connectivity – Ni^{3+} (d^7) oxides with nearly identical bond lengths

square NiO_2 net



$LaNiO_3$ (R-3c)
Paramagnetic metal
Itinerant (wide bandwidth)



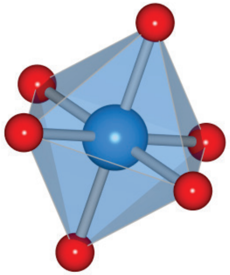
hexagonal NiO_2 net

$LiNiO_2$ (R-3m)
Ferromagnetic insulator
AFM at low-T
Localized electrons

Bandwidth control requires structural flexibility

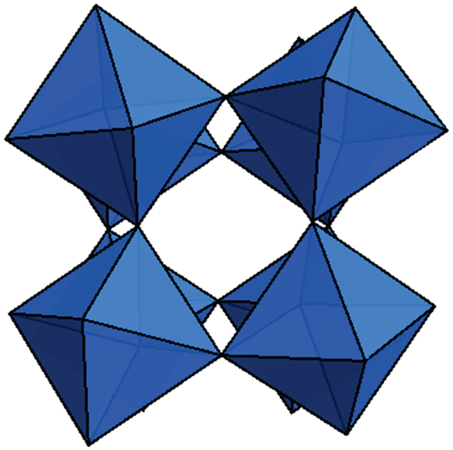
- Not so easy to completely reconfigure alignment of metal–oxygen polyhedra in most materials
- What about less dramatic changes to the structure?

Rotations of corner-connected BO_6 octahedra in perovskite oxides



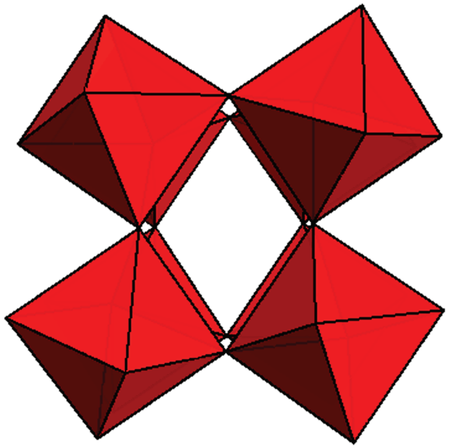
Main rotational distortions adopted by perovskite oxides

Approximately 70% of the compounds exhibit one of these rotations



rhombohedral (*a*-*a*-*a*-)

D_{3d}



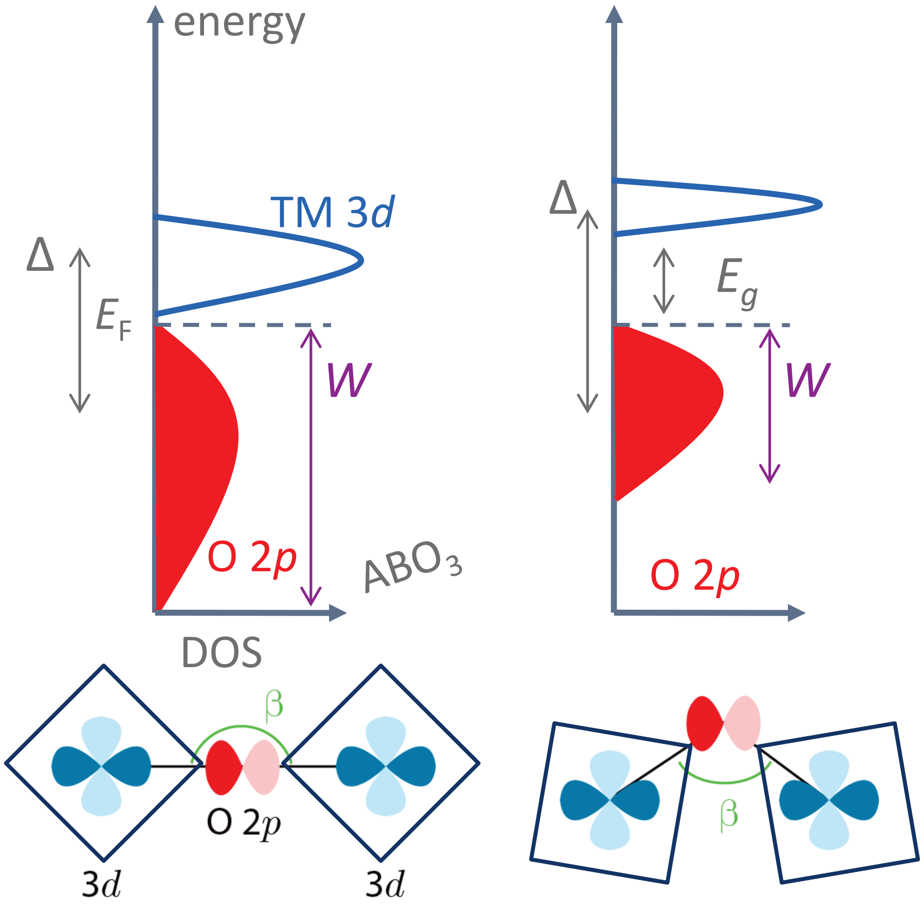
orthorhombic (*a*-*a*-*b*+)

D_{2h}

Lufaso and Woodward, *Acta Cryst*., **B57** 725 (2001)

Engineering the electronic structure

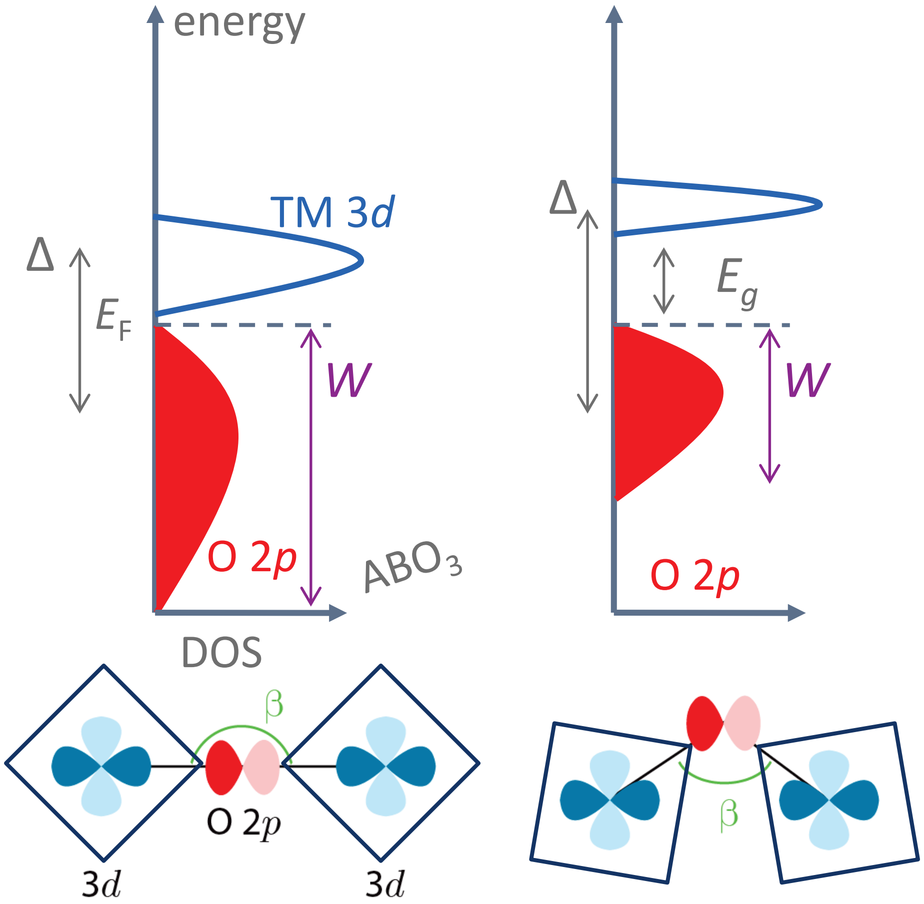
- Bandwidth is sensitive to orbital overlap in transition metal oxides



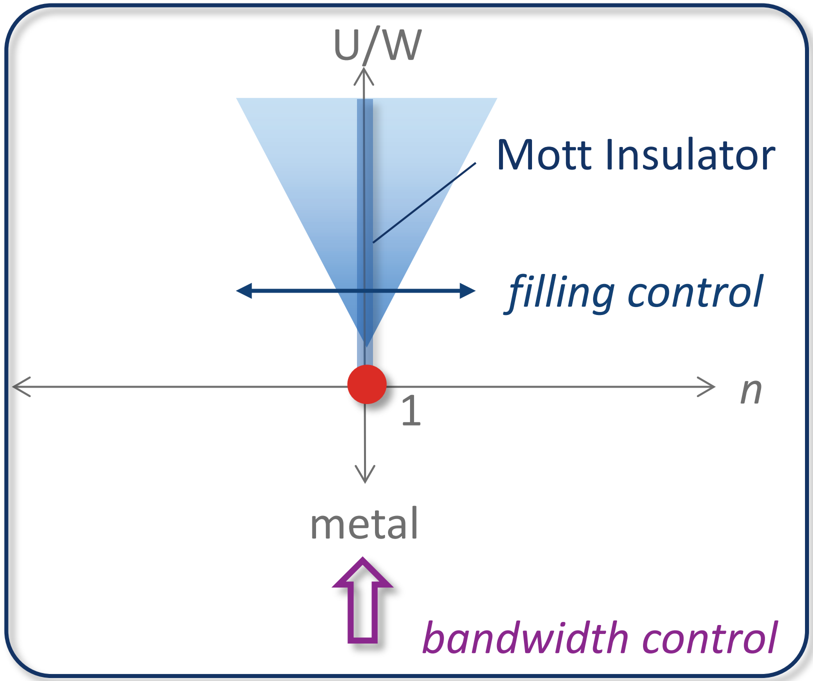
maximum hopping reduced hoping

Engineering the electronic structure through bandwidth control

- Bandwidth is sensitive to orbital overlap in transition metal oxides



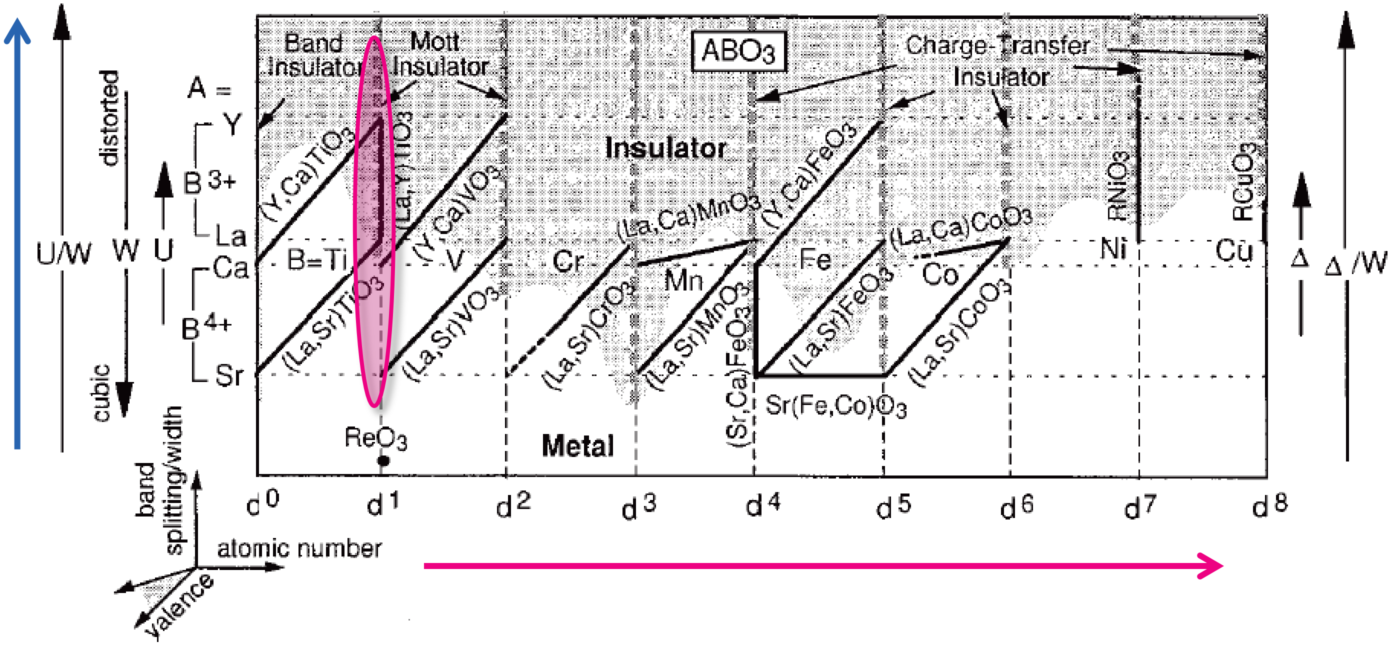
maximum hopping reduced hoping



Amenable to structure-directed design

Fujimori transition metal oxide phase diagram

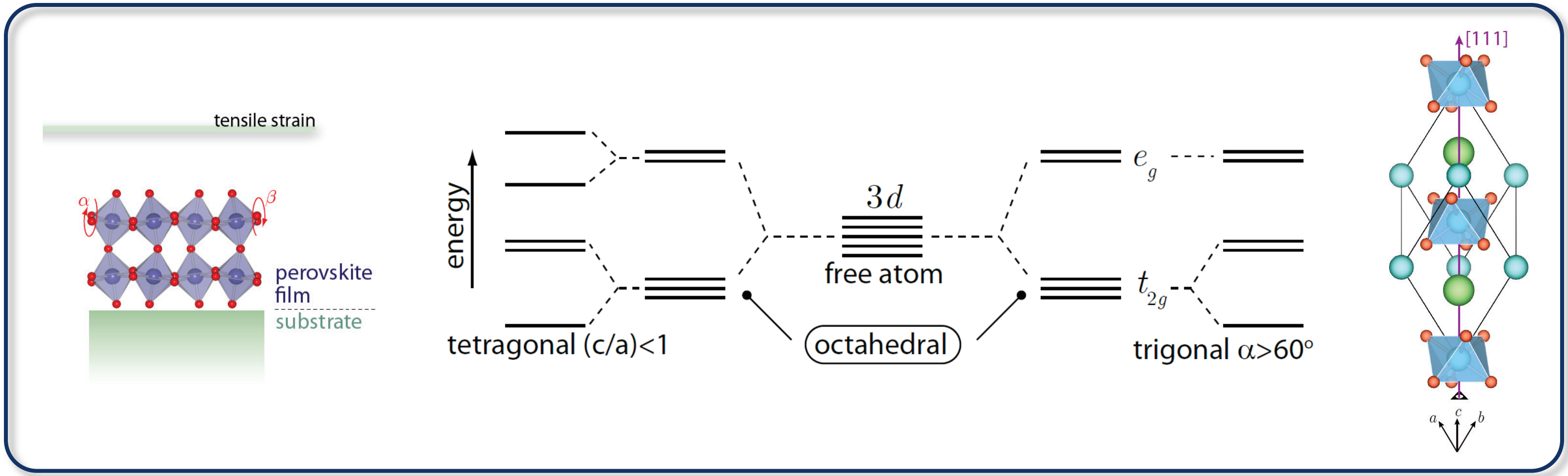
- Important ingredients are *d*-electron count and electronic bandwidth (orbital overlap)
- Insulating phases occurring at integer occupancy are incompatible with band theory (*sans* additional symmetry reductions)
  - Behavior near integer occupancy is interesting (Mott physics)

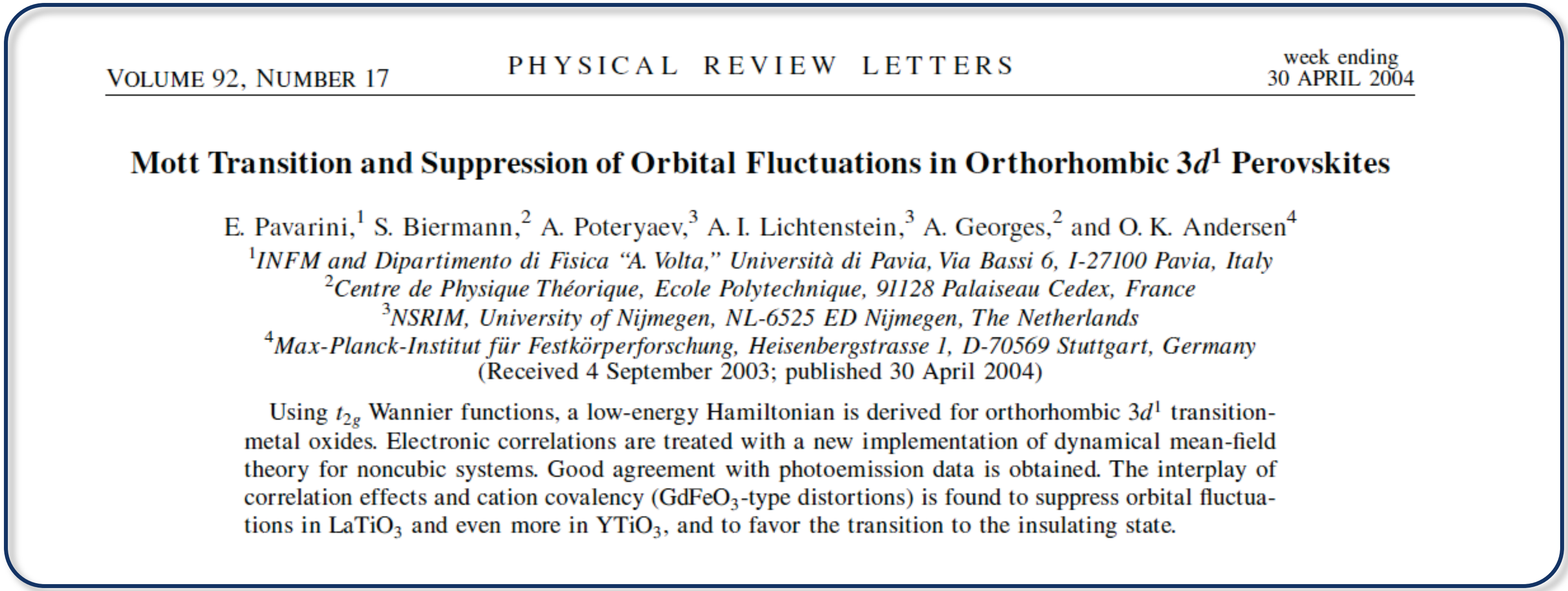


A. Fujimori J Phys Chem Sol 53 (1992)

Symmetry splitting of *d*-orbital degeneracies are electronically important

- Distortions from cubic symmetry renormalize Fujimori's phase diagram



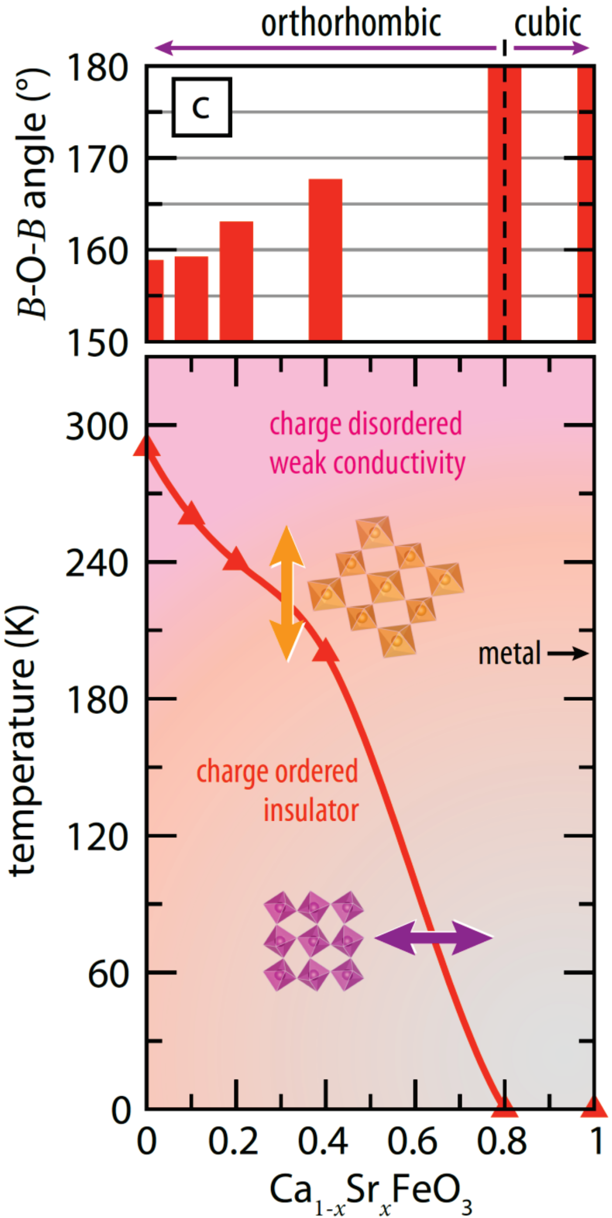

VOLUME 92, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 30 APRIL 2004

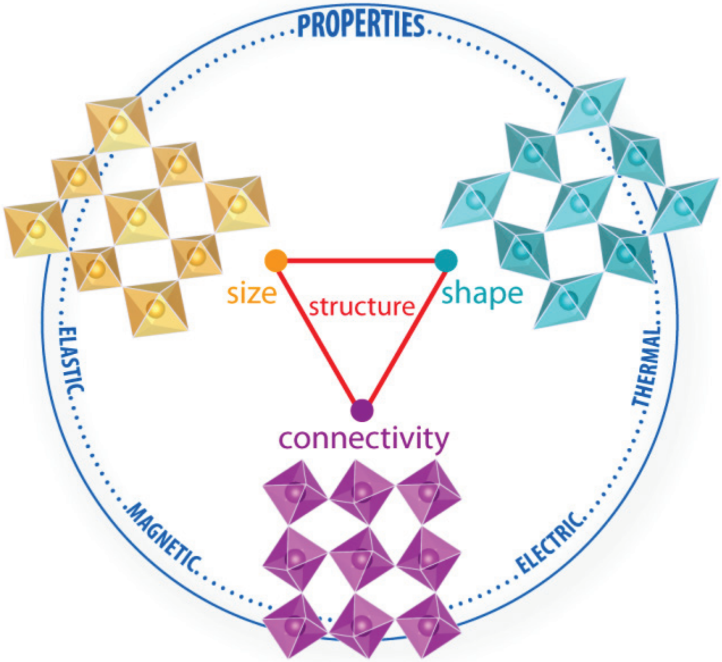
Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,[1] S. Biermann,[2] A. Poteryaev,[3] A. I. Lichtenstein,[3] A. Georges,[2] and O. K. Andersen[4]
[1]*INFM and Dipartimento di Fisica "A. Volta," Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy*
[2]*Centre de Physique Théorique, Ecole Polytechnique, 91128 Palaiseau Cedex, France*
[3]*NSRIM, University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands*
[4]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
(Received 4 September 2003; published 30 April 2004)

Using t_{2g} Wannier functions, a low-energy Hamiltonian is derived for orthorhombic $3d^1$ transition-metal oxides. Electronic correlations are treated with a new implementation of dynamical mean-field theory for noncubic systems. Good agreement with photoemission data is obtained. The interplay of correlation effects and cation covalency ($GdFeO_3$-type distortions) is found to suppress orbital fluctuations in $LaTiO_3$ and even more in $YTiO_3$, and to favor the transition to the insulating state.

Control over functional transition metal oxygen octahedra enables electronic transitions by design



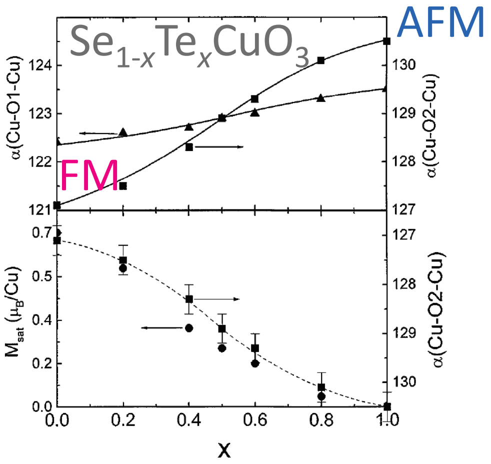


JMR, May, Freeland, MRS Bulletin **37** 261 (2012)

Structure/bandwidth engineering for other functional properties

- What’s more?

1. Produce (or destroy) collective **magnetism**
    - Exchange interactions depend on structure/connectivity

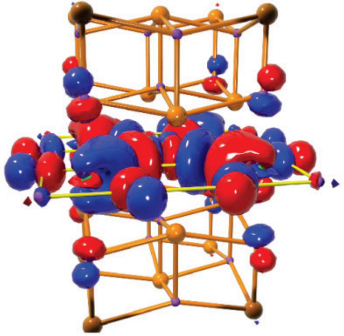


Subramanian, *et al*. PRL **82** 1558 (1999)

2. Produce (or destroy) a **conducting** state
    - Effective masses depend on band dispersion (narrower or flatter bands have larger masses)

3. Propensity to **superconductivity**
    - In single layer hole-doped cuprates, T_c scales with lattice constant along the c-axis and the apical Cu–O distance

La$_{2-x}$Sr$_x$CuO$_4$



Courtesy O. Anderson

Re-emergence of the structure-driven view for materials design

- Hoffman, Burdett, Pauling, among others…
  - Roald Hoffman, *Solids and Surfaces: A Chemists view of bonding in extended structures* (1998)
  - P.A. Cox, *The Electronic Structure and Chemistry of Solids* (1987)
  - Jeremy Burdett, *Chemical Bonding in Solids* (1995)

- Goal is to illustrate how it is possible to exploit readily available (powerful) atomic structure computational methods and this "habit of thinking" for multifunctional materials understanding and design

- Summary to here:

Control over the bandwidth, structural geometry, and transitional metal configuration (d-electron) occupancy are critical to tailoring function

Designing atomic-scale electronic function – Outline

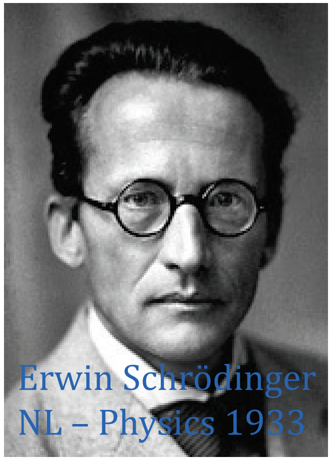
- ***Foreword*** (9-10.30a)
  - Main challenges
  - Why complex oxides provide the ultimate “sand box”
  - Structure-driven properties of materials paradigm
  - **Theoretical / Computational tools to formulate an understanding for design**

J. Heber, Nature **459**, 28 (2009)

Designing atomic-scale function using a structure-driven view of materials properties

- Main goals are to extract descriptors correlating structure to properties, enabling predictive models for new materials

Use that ***structure* descriptor** to support, promote, or suppress an interaction


Erwin Schrödinger
NL – Physics 1933

"for the discovery of new productive forms of atomic theory"

- Need to connect structure to electronic response:
  - Solid as a physical system of interacting electrons and nuclei are fully described by the theory of quantum mechanics

Schrodinger Equation

$$\mathcal{H}\Psi = E\Psi$$

This equation is sufficient to described all properties of materials

- "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that **approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.**"
  - *Paul Dirac in Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, Vol. 123, No. 792 (1929).*

for the discovery of new productive forms of atomic theory.

Quantum mechanical solutions

- Standard approach: properties are governed by a wavefunction

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N); \mathcal{H}\Psi = E\Psi$$

- We then focus on solving for the wavefunction and extract observables as expectation values of operations with this wavefunction
- For *N* electrons this is a 3*N* dimensional problem

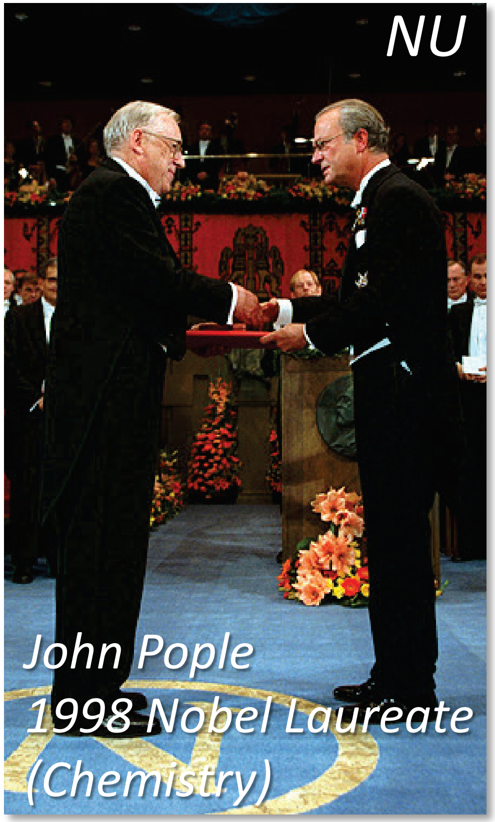
this many-body problem, with correlated many-body wavefunction is just too hard to solve

Ab initio [approximate practical] quantum mechanical (QM) methods

- Development for a reliable and efficient framework to solve the Schrodinger equation
  - WK: for the development of density functional theory
  - JP: computational methods in quantum physics

UCSB

Walter Kohn
1998 Nobel Laureate
(Chemistry)



NU

John Pople
1998 Nobel Laureate
(Chemistry)

Density functional theory approach (band theory)

- Basic Theorem (Hohenberg & Kohn)
- There exists a functional of the electron density which when minimized at the physical density of the system, one obtains the total energy of the ground state

$$E[n(\mathbf{r})] = \underbrace{F[n(\mathbf{r})]}_{\text{kinetic energy, Hartree terms, quantum mechanical (exchange-correlation) and electromagnetic terms}} + \int \underbrace{V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}}_{\text{the atomic structure and any external fields are contained in this term}}$$

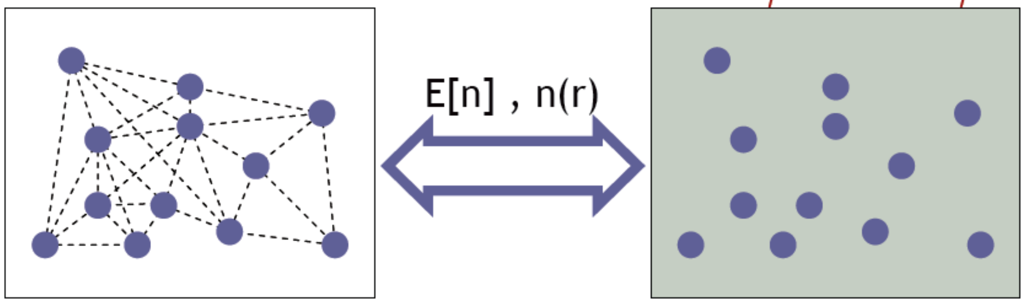
- Utility
  - Approximations (uncontrolled but often very good)
  - Efficient numerical methods to perform the minimization
  - Energy and other observables of the ground state are given as functionals of the density only (3 dimensional quantity)

P. Hohenberg & W. Kohn PR **136** B864 (1964)

Density functional theory approach (band theory)

- To minimize the functional, we solve a set of Schrodinger-like (auxiliary) equations describing single-electron problems to obtain the ground state density (and properties) of a material subjected to a self-consistency condition

$$\mathcal{H}\Psi = \mathcal{E}\Psi \qquad \hat{H}\phi = \epsilon\phi$$



interacting electrons

non-interacting electrons

$$E[n(\mathbf{r})] = \underline{F[n(\mathbf{r})]} + \int \underline{V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}}$$

kinetic energy, Hartree terms, quantum mechanical (exchange-correlation) and electromagnetic terms

$$\Rightarrow T^0[n(\mathbf{r})] + \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

P. Hohenberg & W. Kohn PR **136** B864 (1964)
W. Kohn & L. Sham PR **140** A1133 (1965)

Density functional theory approach (band theory)

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ions}}(r) + V_{\text{Hartree}}(r)\right)\psi_n(r) + V_{xc}(n(r))\psi_n(r) = E_n\psi_n(r)$$

In principle have no meaning except for self-consistency

$$n(r) = \sum_{E_n<\mu} \psi_n^\dagger(r)\psi_n(r)$$

Exchange-correlation potential is determined by the electron density and requires an iterative approach

- The XC-potential accounts for the electron–electron interactions lost during the mapping from the interacting to non-interacting system
  - It can be non-local and is also not exactly known

- 100+ approximations, the following are commonly used in CM systems
  - L(S)DA: XC-functional corresponds to the homogenous electron gas
  - GGA: generalized-gradient approximation (PBE, PBEsol, Wu-Cohen)
  - Hybrid functionals (HSE03, HSE06): include a portion of exact (Fock-type) exchange mixed with GGA

Properties available from DFT

- Enables the study of the atomic structure and electronic properties on equal footing for efficient materials design

- Allows access to different properties
  - **Electronic**: total energies, charge densities, band dispersions
  - **Lattice**: atomic structures, phonon modes (frequencies and displacements)
  - **Spin**: magnetic order, orbital orders, exchange terms
- Properties that are formally energy derivatives
  - Forces, stresses, electronic polarizations, dielectric tensors, born effective charges, elastic constants, piezoelectric tensors

- Band structure related quantities: Optical properties, excitation energies, electronic transport, etc.
  - Not fundament in DFT, but are often quite accurate
  - Inaccuracies are well-established from experience

Density functional theory approach (band theory) often successful but has difficulties with “correlated” materials

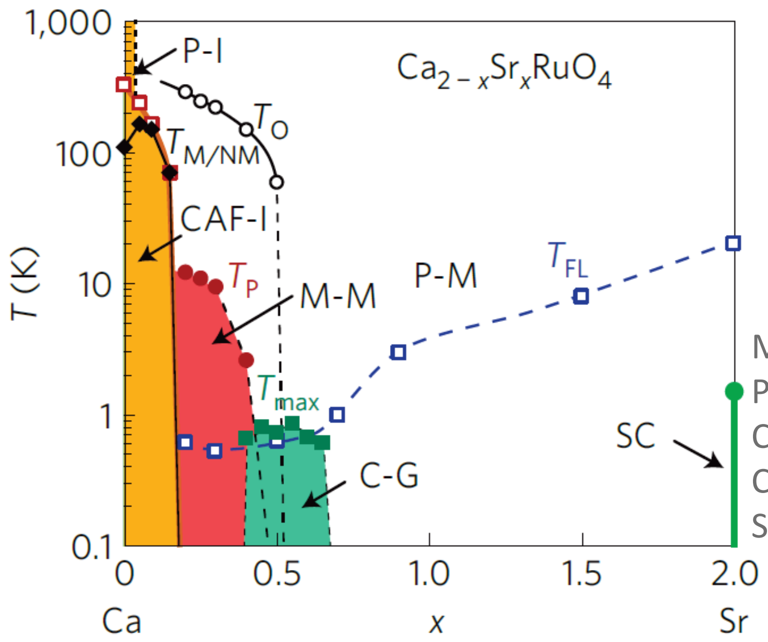
- See Wednesday’s lecture by Michell Johannes

- Most transparent explanation is that the density may not always be the optimal variable for determining the ground state phases

$$n(r) = \sum_{E_n<\mu} \psi_n^\dagger(r)\psi_n(r)$$

phases with very different physical properties can have very similar densities

Variety of “beyond”-DFT methods to *correct* band theory failures



M-M: magnetic metal
P-M: paramagnetic metal
CAF-I: commensurate antiferromagnetic insulator
C-G: Cluster glass
SC: superconductor

J.P. Carlo et al., Nat. Mater **11**, 323 (2012)

Designing atomic-scale function using a structure-driven view of materials properties

- Main goals are to extract descriptors correlating structure to properties, enabling predictive models for new materials

Density functional theory (DFT) – often very good at predicting structures

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

Provides a practical and tractable method to solve quantum mechanical equations for solids in a timely fashion while treating both the electronic and structure DOF on equally footing

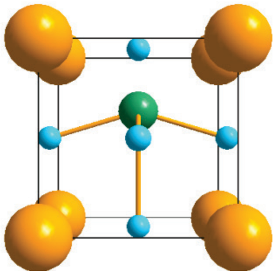
→ Test new ideas, microscopic theories, and to solicit experimental synthesis from colleagues

How do we leverage an understanding of structural distortions to create new materials?

- Across many of these phase boundaries there are changes in structure and crystallographic symmetry

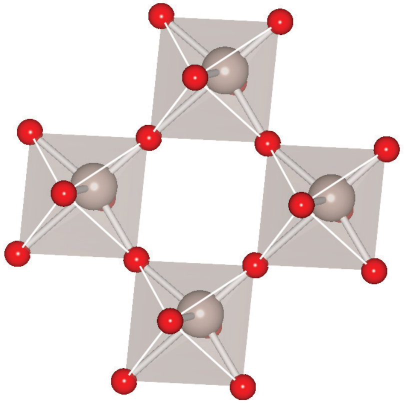
- Need to connect crystal structure to electronic function
  - Obtain equilibrium structures from DFT and evaluate total energies and electronic properties simultaneously

“out-of-center” distortion

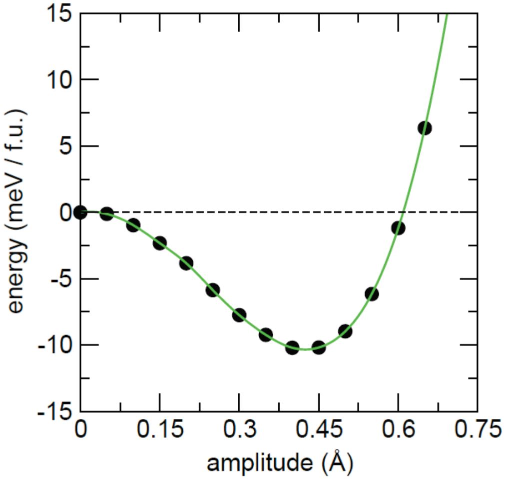


soft polar phonon

cooperative displacements



ferroelectricity



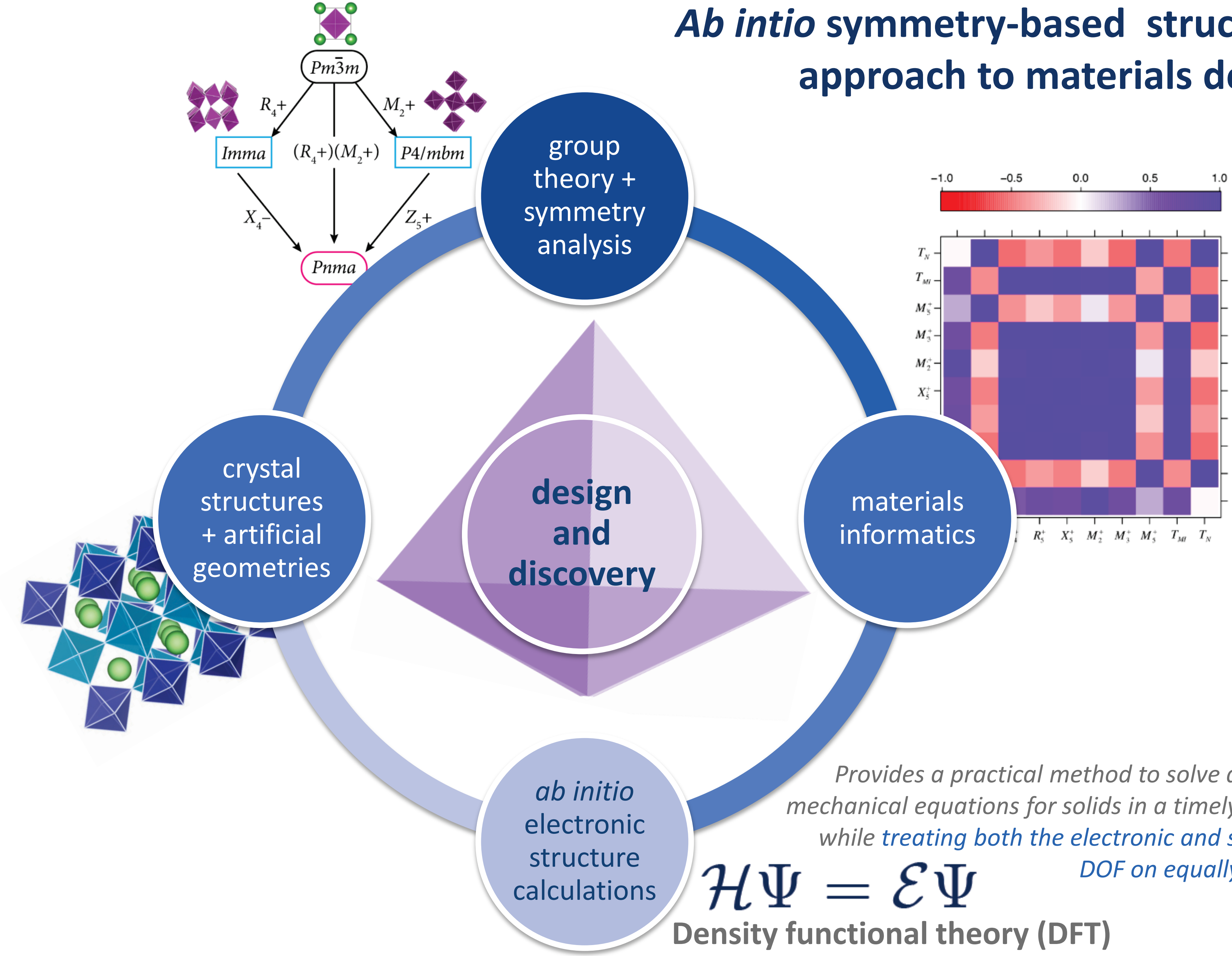
Theoretical/Computational Tools

- Symmetry analysis
  - Careful application will ensure physically correct results

- Crystallography (lattice +basis)
  - Quantitative way to represent structures of materials
  - Description includes space groups and occupied Wyckoff positions

- Electron-lattice quantities from DFT
  - Total energies (stability) and forces (structural configurations)
  - Electronic properties (band structures, magnetism, …)

Ab intio symmetry-based structural approach to materials design



group theory + symmetry analysis

crystal structures + artificial geometries

design and discovery

materials informatics

ab initio electronic structure calculations

Provides a practical method to solve quantum mechanical equations for solids in a timely fashion while treating both the electronic and structure DOF on equally footing

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

Density functional theory (DFT)

Theoretical/Computational Tools

- Symmetry analysis
  - Careful application will ensure physically correct results
- Crystallography (lattice +basis)
  - Quantitative way to represent structures of materials
  - Description includes space groups and occupied Wyckoff positions
- Electron-lattice quantities from DFT
  - Total energies (stability) and forces (structural configurations)
  - Electronic properties (band structures, magnetism, …)

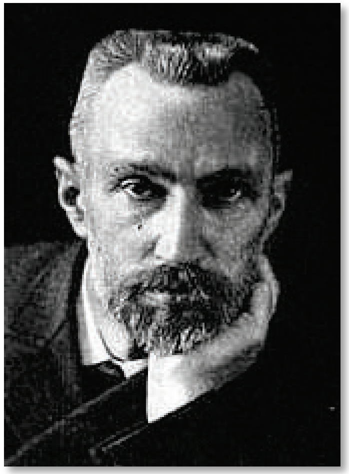
Uses of symmetry

- Provide a description of nature (condensed matter systems)

- Principles that specify particular laws or phenomena (not necessarily applied to objects)
  - Enables us to derive consequences (arguments) of particular physical situations (*sans* specific details) and properties

  - A breaking of an initial symmetry cannot happen without reason, *i.e*. an asymmetry cannot occur spontaneously

Symmetry arguments



P. Curie (1859–1906)
1903 NL in Physics

- Pierre Curie formulated one of the first explicit symmetry arguments

What are the relationships between physical properties and symmetry properties of a real system?

- Interested in the thermal, electric and magnetic properties of crystals

1. A phenomenon can exist in a medium possessing its characteristic symmetry or that of one of its subgroups. What is needed for its occurrence (i.e. for something rather than nothing to happen) is not the presence, but rather the absence, of certain symmetries: "*Asymmetry is what creates a phenomenon*".
2. The symmetry elements of the causes must be found in their effects, but the converse is not true; that is, the effects can be more symmetric than the causes – Curie's Principle

«Sur la symétrie des phénoménes physiques» Journal de Physique, **3** 118 (1894)

Curie’s symmetry arguments

- Curie’s principle provides the *necessary condition* for a given phenomenon to happen
  - Provides a *selection rule*: Behavior/properties must be compatible with specific symmetries
  - Provides a falsification criterion: if the principle is violated the physical description must be incorrect

Symmetry of physical properties

- Four symmetries to consider
  - Symmetry of the material
  - Symmetry of the external “force”
  - Symmetry of the resulting change (“displacement”)
  - Symmetry of the physical property relating displacement to external force

- All materials (including non-crystalline) show some kind of symmetry
  - Single crystals belong to one of the 32 crystal classes
  - Amorphous materials, glasses and liquids have spherical symmetry ($\infty\infty m$)
  - Polycrystalline solids with randomly oriented grains also have spherical symmetry

- Physical forces
  - Tensile stress has tetragonal (cylindrical) symmetry
  - Shear stress have orthorhombic symmetry

Structures impose constraints on physical properties of materials

- As Richard Feynman said,

  > *It would be very easy to make an analysis of any complicated chemical substance; all one would have to do would be to look at it and see where the atoms are…*

- To understand properties or to design materials with new properties requires we understand how atoms are arranged

Explained very well by Nye in *Physical Properties of Crystals (Oxford 1957), reprinted many times*

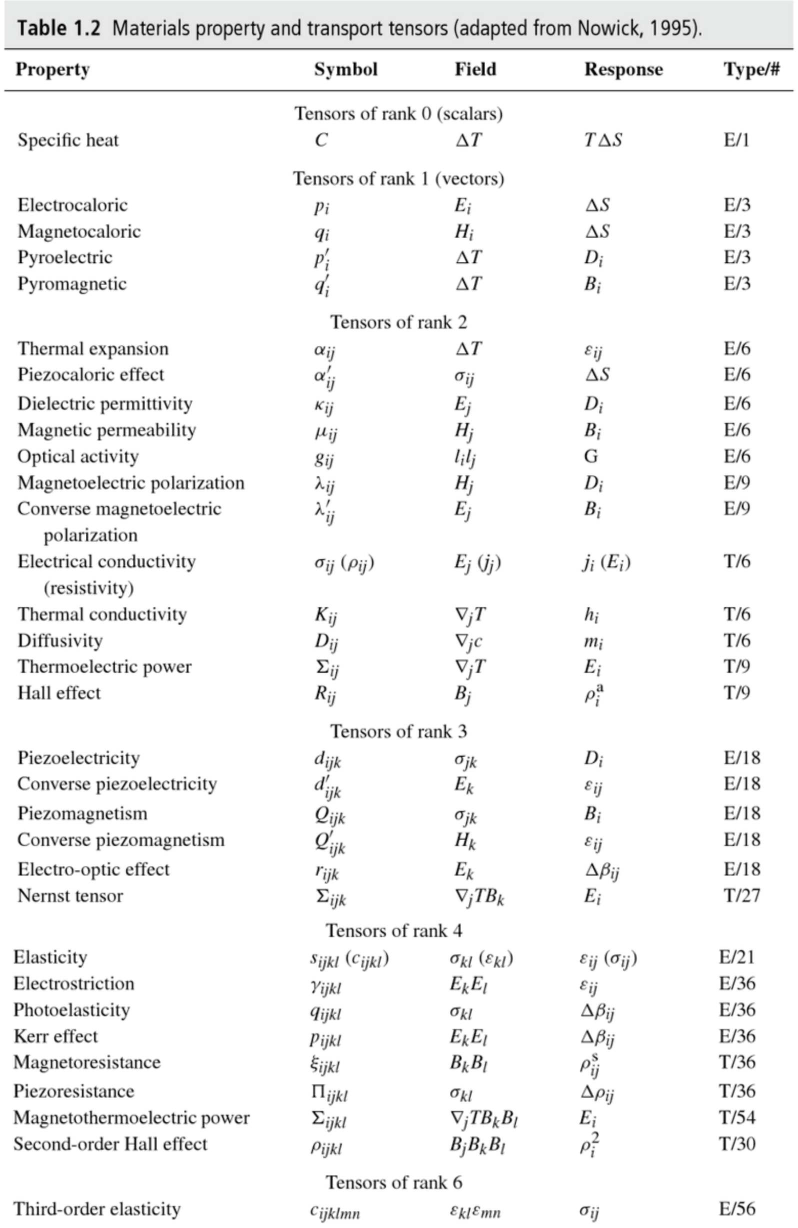


Table 1.2 Materials property and transport tensors (adapted from Nowick, 1995).

Property	Symbol	Field	Response	Type/#
Tensors of rank 0 (scalars)				
Specific heat	C	ΔT	$T\Delta S$	E/1
Tensors of rank 1 (vectors)				
Electrocaloric	p_i	E_i	ΔS	E/3
Magnetocaloric	q_i	H_i	ΔS	E/3
Pyroelectric	p'_i	ΔT	D_i	E/3
Pyromagnetic	q'_i	ΔT	B_i	E/3
Tensors of rank 2				
Thermal expansion	α_{ij}	ΔT	ε_{ij}	E/6
Piezocaloric effect	α'_{ij}	σ_{ij}	ΔS	E/6
Dielectric permittivity	κ_{ij}	E_j	D_i	E/6
Magnetic permeability	μ_{ij}	H_j	B_i	E/6
Optical activity	g_{ij}	$l_i l_j$	G	E/6
Magnetoelectric polarization	λ_{ij}	H_j	D_i	E/9
Converse magnetoelectric polarization	λ'_{ij}	E_j	B_i	E/9
Electrical conductivity (resistivity)	σ_{ij} (ρ_{ij})	E_j (j_j)	j_i (E_i)	T/6
Thermal conductivity	K_{ij}	$\nabla_j T$	h_i	T/6
Diffusivity	D_{ij}	$\nabla_j c$	m_i	T/6
Thermoelectric power	Σ_{ij}	$\nabla_j T$	E_i	T/9
Hall effect	R_{ij}	B_j	ρ_i^{a}	T/9
Tensors of rank 3				
Piezoelectricity	d_{ijk}	σ_{jk}	D_i	E/18
Converse piezoelectricity	d'_{ijk}	E_k	ε_{ij}	E/18
Piezomagnetism	Q_{ijk}	σ_{jk}	B_i	E/18
Converse piezomagnetism	Q'_{ijk}	H_k	ε_{ij}	E/18
Electro-optic effect	r_{ijk}	E_k	$\Delta\beta_{ij}$	E/18
Nernst tensor	Σ_{ijk}	$\nabla_j T B_k$	E_i	T/27
Tensors of rank 4				
Elasticity	s_{ijkl} (c_{ijkl})	σ_{kl} (ε_{kl})	ε_{ij} (σ_{ij})	E/21
Electrostriction	γ_{ijkl}	$E_k E_l$	ε_{ij}	E/36
Photoelasticity	q_{ijkl}	σ_{kl}	$\Delta\beta_{ij}$	E/36
Kerr effect	p_{ijkl}	$E_k E_l$	$\Delta\beta_{ij}$	E/36
Magnetoresistance	ξ_{ijkl}	$B_k B_l$	ρ_{ij}^{s}	T/36
Piezoresistance	Π_{ijkl}	σ_{kl}	$\Delta\rho_{ij}$	T/36
Magnetothermoelectric power	Σ_{ijkl}	$\nabla_j T B_k B_l$	E_i	T/54
Second-order Hall effect	ρ_{ijkl}	$B_j B_k B_l$	ρ_i^2	T/30
Tensors of rank 6				
Third-order elasticity	c_{ijklmn}	$\varepsilon_{kl}\varepsilon_{mn}$	σ_{ij}	E/56

From de Graef and McHenry, *Structure of Materials* (2012)

Structures impose constraints on physical properties of materials

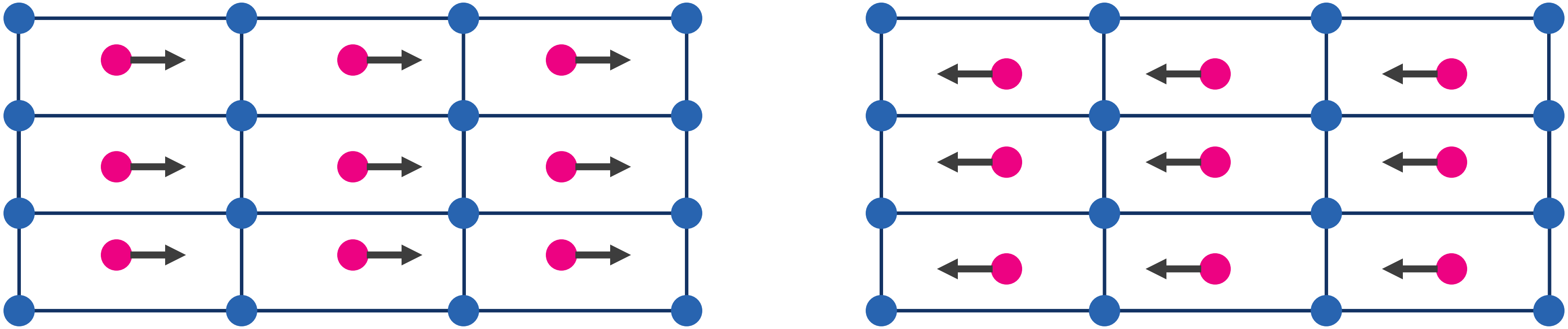
- To understand properties or to design materials with new properties requires we understand how atoms are arranged ⇒ **crystal structures**

- **CAUTION**
  - Symmetry arguments only state what properties/parameters are finite or must vanish, and how each parameter is related to another
  - The magnitude of the parameters comes from understanding the physics of materials (solid state physics, quantum mechanics, etc.), where the charge distribution is known and quantities can be computed or measured

$$\Rightarrow \mathcal{H}\Psi = \mathcal{E}\Psi$$

We often use symmetry to make arguments, but…

- To design new materials (properties) requires we are able to rigorous quantify and symmetry and have inputs for a predictive theory



two distortions have the same energy

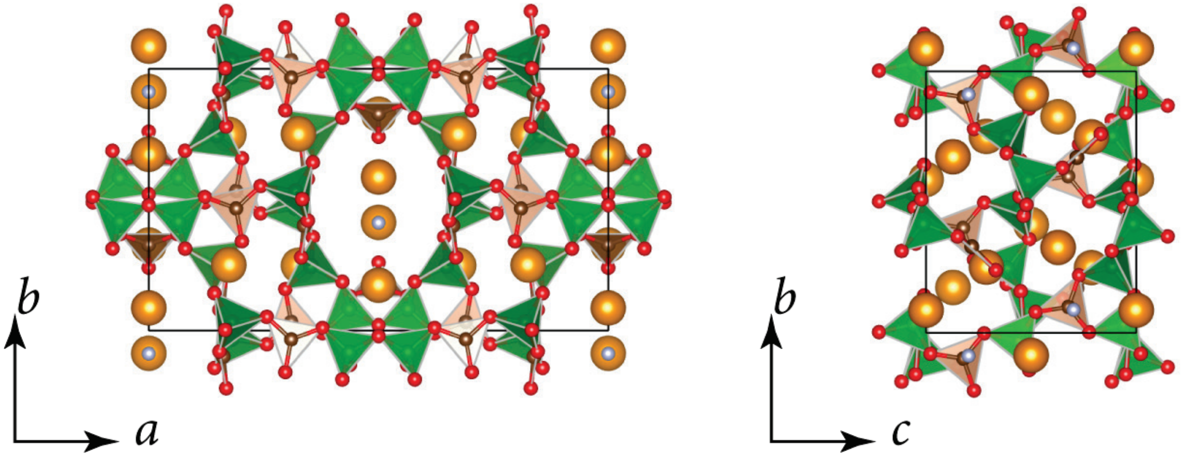
Displacement of pink atoms leads to loss of inversion symmetry

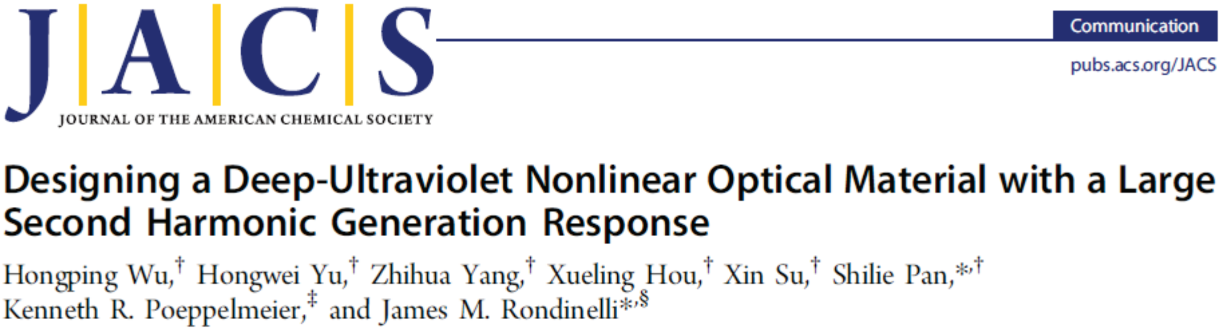
But for more complex cases, symmetry arguments are not so clear

- Need to formulate a more rigorous method…

$Ba_4B_{11}O_{20}F$ in space group $Cmc2_1$ (144 atoms in the unit cell)

How do we understand which atoms are largely responsible for the loss of inversion symmetry?





Designing a Deep-Ultraviolet Nonlinear Optical Material with a Large Second Harmonic Generation Response

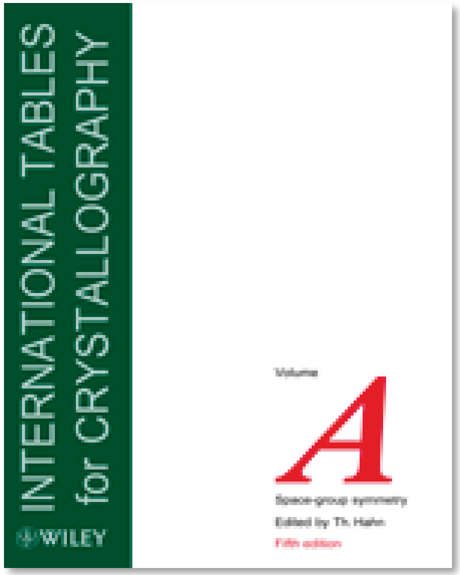
Hongping Wu,[†] Hongwei Yu,[†] Zhihua Yang,[†] Xueling Hou,[†] Xin Su,[†] Shilie Pan,[*,†] Kenneth R. Poeppelmeier,[‡] and James M. Rondinelli[*,§]

JACS **135**, 4215 (2013)

Crystal structure description

- Standard practice to state the
  - Space Group
  - Lattice Parameters
  - Wyckoff Positions of all atoms in asymmetric unit

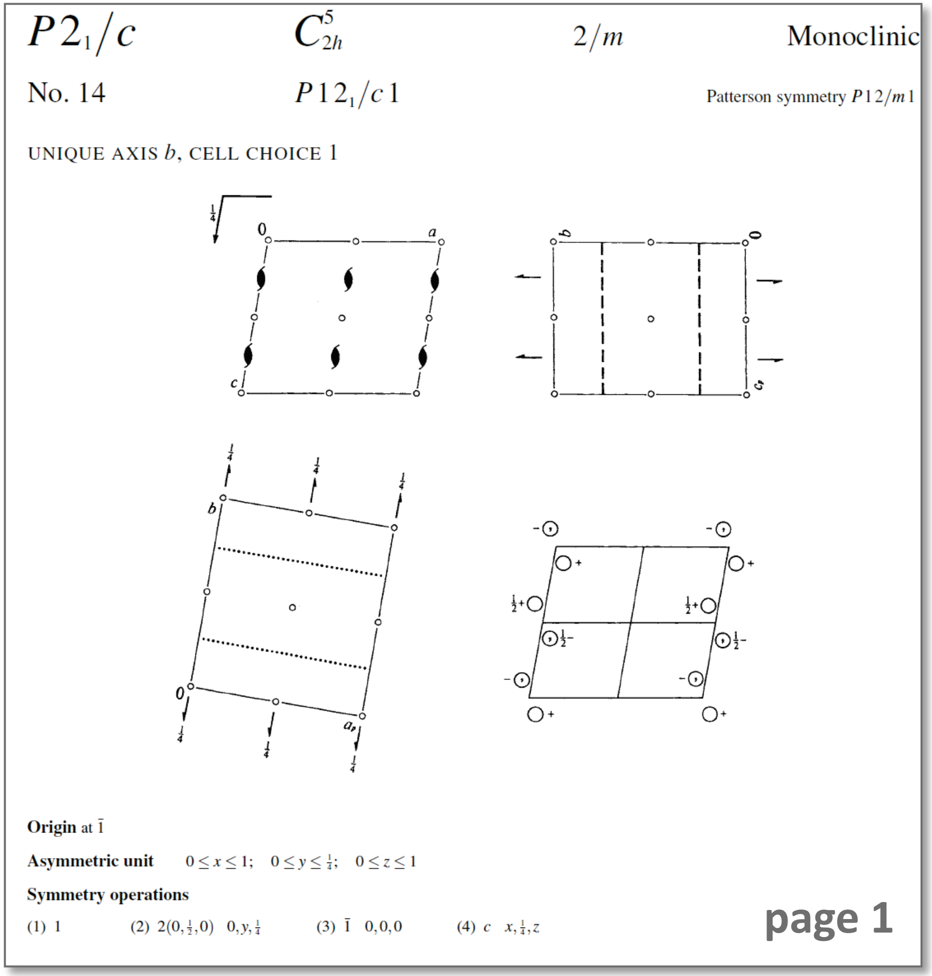
- This information and *International Tables for Crystallography* (vol A) by Th. Hahn is sufficient to unambiguously generate and describe any crystalline structure



http://dx.doi.org/10.1107/97809553602060000100

Primer on International Tables for Crystallography, Volume A

- Entry for space group $P2_1/c$ (No. 14)


$P2_1/c$ C_{2h}^5 $2/m$ Monoclinic

No. 14 $P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1

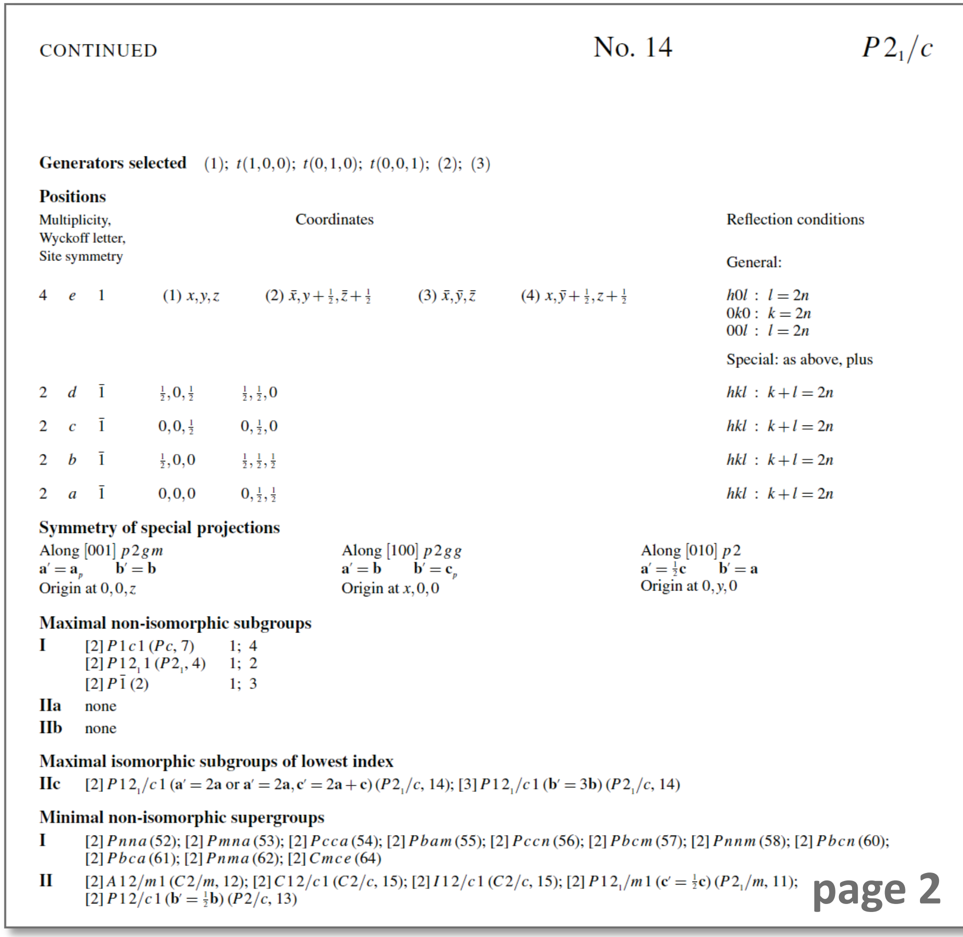
Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)\quad 0,y,\frac{1}{4}$ (3) $\bar{1}\quad 0,0,0$ (4) $c\quad x,\frac{1}{4},z$

page 1


CONTINUED No. 14 $P2_1/c$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l:\ l=2n$ $0k0:\ k=2n$ $00l:\ l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			$hkl:\ k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			$hkl:\ k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			$hkl:\ k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			$hkl:\ k+l=2n$

Symmetry of special projections

Along [001] $p2gm$	Along [100] $p2gg$	Along [010] $p2$
$\mathbf{a}'=\mathbf{a}_p\quad \mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}\quad \mathbf{b}'=\mathbf{c}_p$	$\mathbf{a}'=\frac{1}{2}\mathbf{c}\quad \mathbf{b}'=\mathbf{a}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P\,1\,c\,1$ (Pc, 7) 1; 4
[2] $P\,1\,2_1\,1$ ($P2_1$, 4) 1; 2
[2] $P\,\bar{1}$ (2) 1; 3
IIa none
IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P\,1\,2_1/c\,1$ ($\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a}, \mathbf{c}'=2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P\,1\,2_1/c\,1$ ($\mathbf{b}'=3\mathbf{b}$) ($P2_1/c$, 14)

Minimal non-isomorphic supergroups

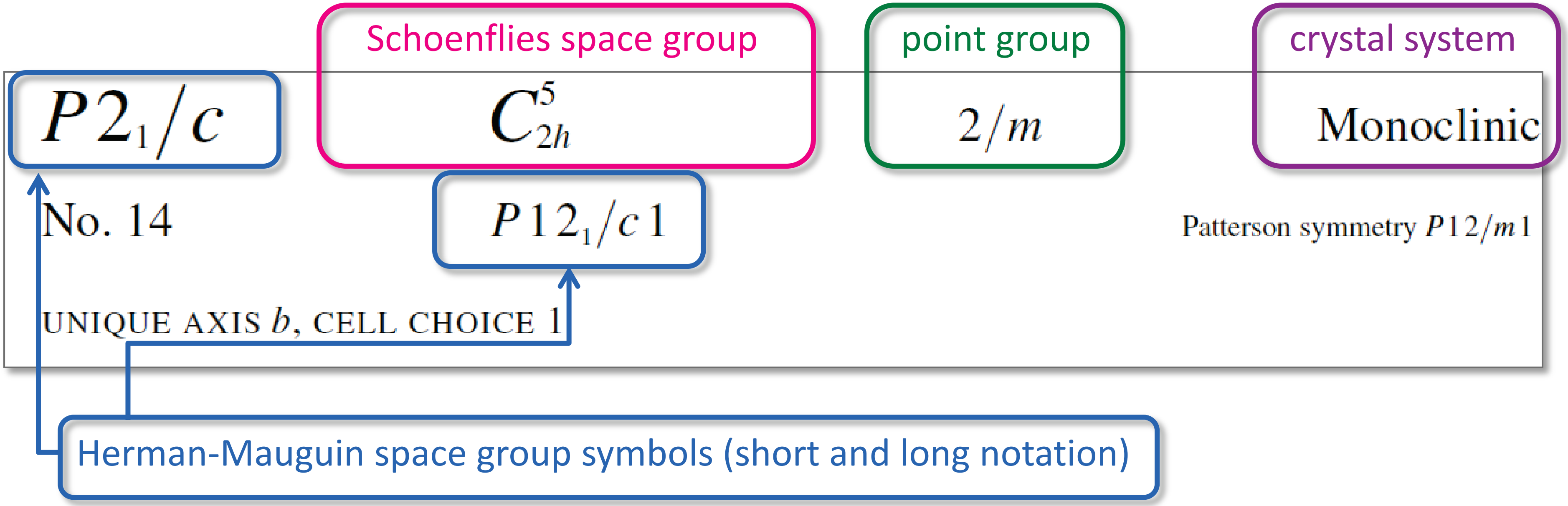
I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A\,1\,2/m\,1$ ($C2/m$, 12); [2] $C\,1\,2/c\,1$ ($C2/c$, 15); [2] $I\,1\,2/c\,1$ ($C2/c$, 15); [2] $P\,1\,2_1/m\,1$ ($\mathbf{c}'=\frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P\,1\,2/c\,1$ ($\mathbf{b}'=\frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

page 2

Primer on International Tables for Crystallography, Volume A

- Entry for space group $P2_1/c$ (No. 14)



Schoenflies space group

point group

crystal system

$P2_1/c$ C_{2h}^5 $2/m$ Monoclinic

No. 14 $P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1

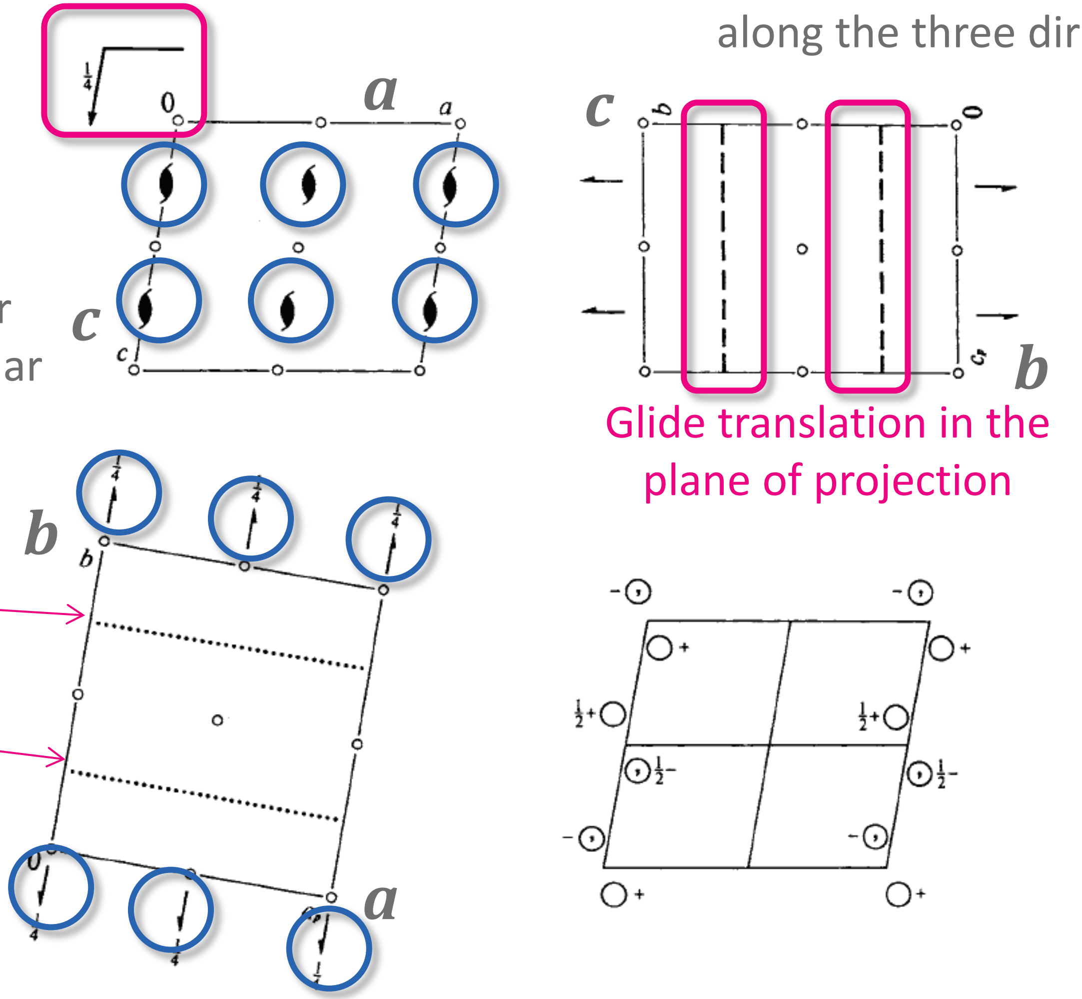
Herman-Mauguin space group symbols (short and long notation)

Space group diagrams along the three directions

UNIQUE AXIS *b*, CELL CHOICE 1

$P\;1\;2_1/c\;1$

Axes parallel to or planes perpendicular to the b-axis



Glide translation in the plane of projection

Glide translation perpendicular to the plane of projection

2_1 screw axis

inversion

Origin at $\bar{1}$

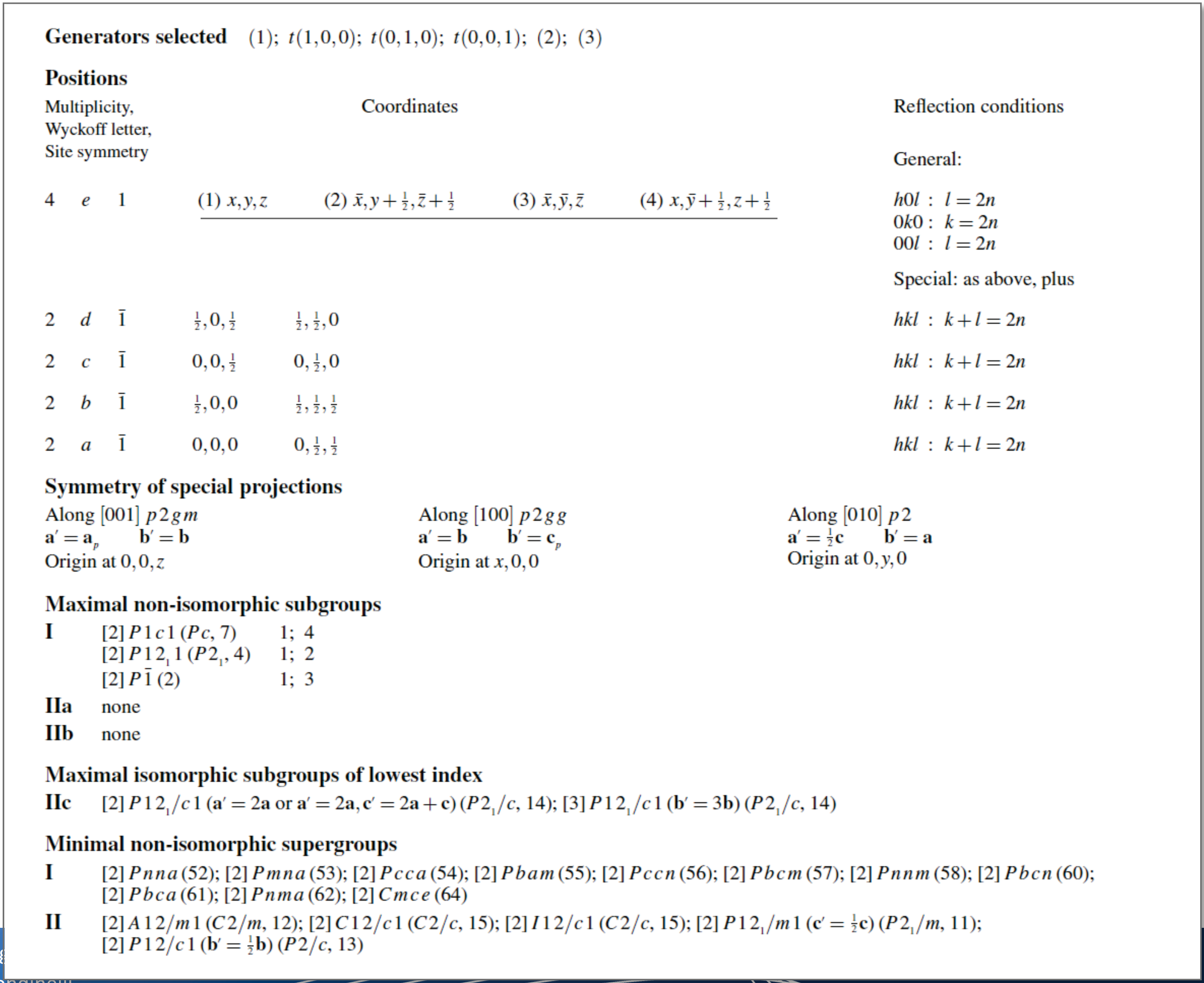
Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)\;\;0,y,\frac{1}{4}$ (3) $\bar{1}\;\;0,0,0$ (4) $c\;\;x,\frac{1}{4},z$

c glide

Entry for space group $P2_1/c$ (No. 14)



Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

Symmetry of special projections

Along [001] $p2gm$	Along [100] $p2gg$	Along [010] $p2$
$\mathbf{a}'=\mathbf{a}_p$ $\mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$	$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $0,y,0$

Maximal non-isomorphic subgroups

I	[2] $P1c1$ (Pc, 7)	1; 4
	[2] $P12_11$ ($P2_1$, 4)	1; 2
	[2] $P\bar{1}$ (2)	1; 3
IIa	none	
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [2] $P12_1/c1$ ($\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a},\mathbf{c}'=2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}'=3\mathbf{b}$) ($P2_1/c$, 14)

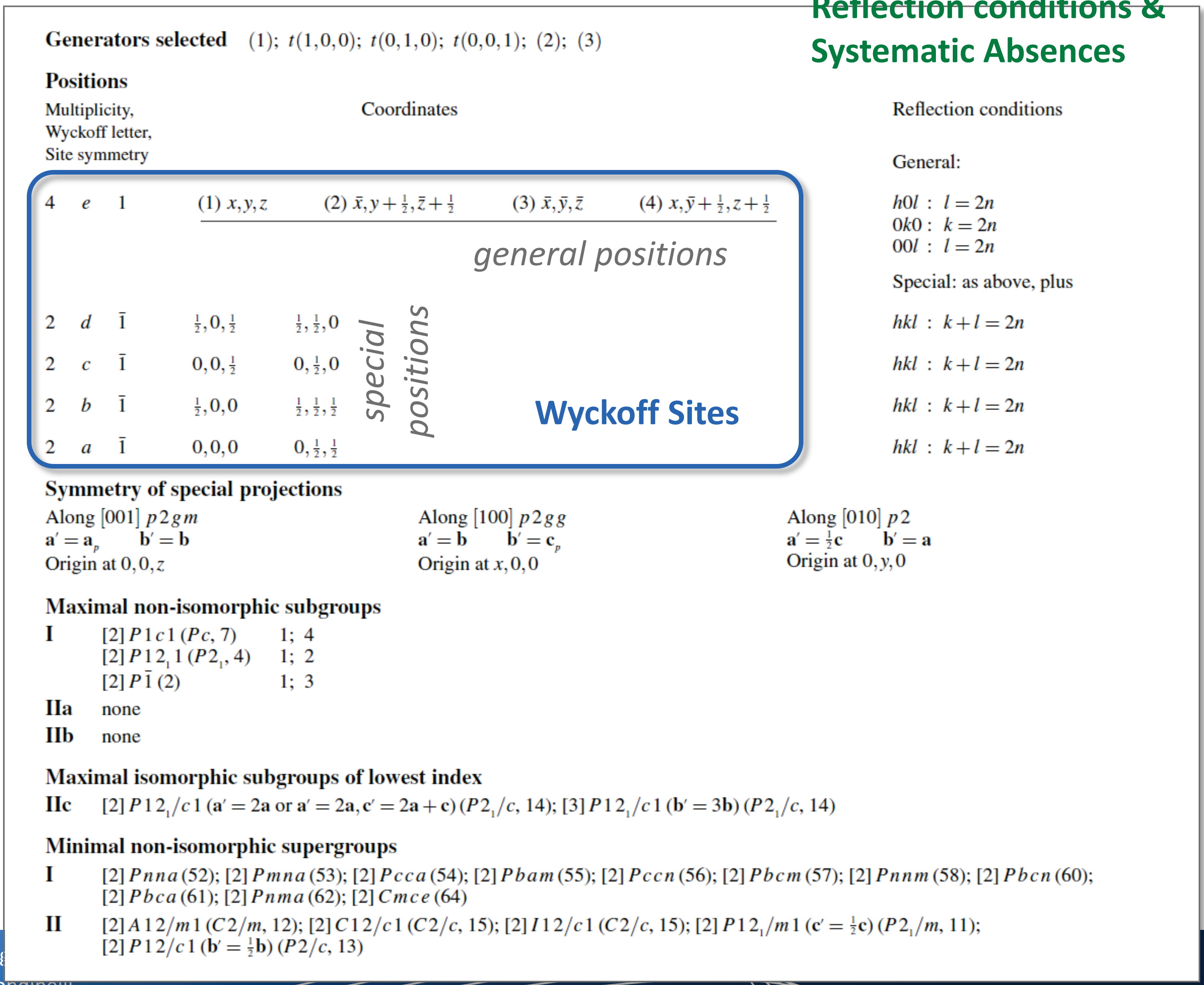
Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}'=\frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}'=\frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

Entry for space group $P2_1/c$ (No. 14)

Reflection conditions & Systematic Absences



Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

general positions

special positions

Wyckoff Sites

Symmetry of special projections

Along [001] $p2gm$
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p2gg$
$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}' = \frac{1}{2}\mathbf{c}$ $\mathbf{b}' = \mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P1c1$ (Pc, 7) 1; 4
[2] $P12_11$ ($P2_1$, 4) 1; 2
[2] $P\bar{1}$ (2) 1; 3

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

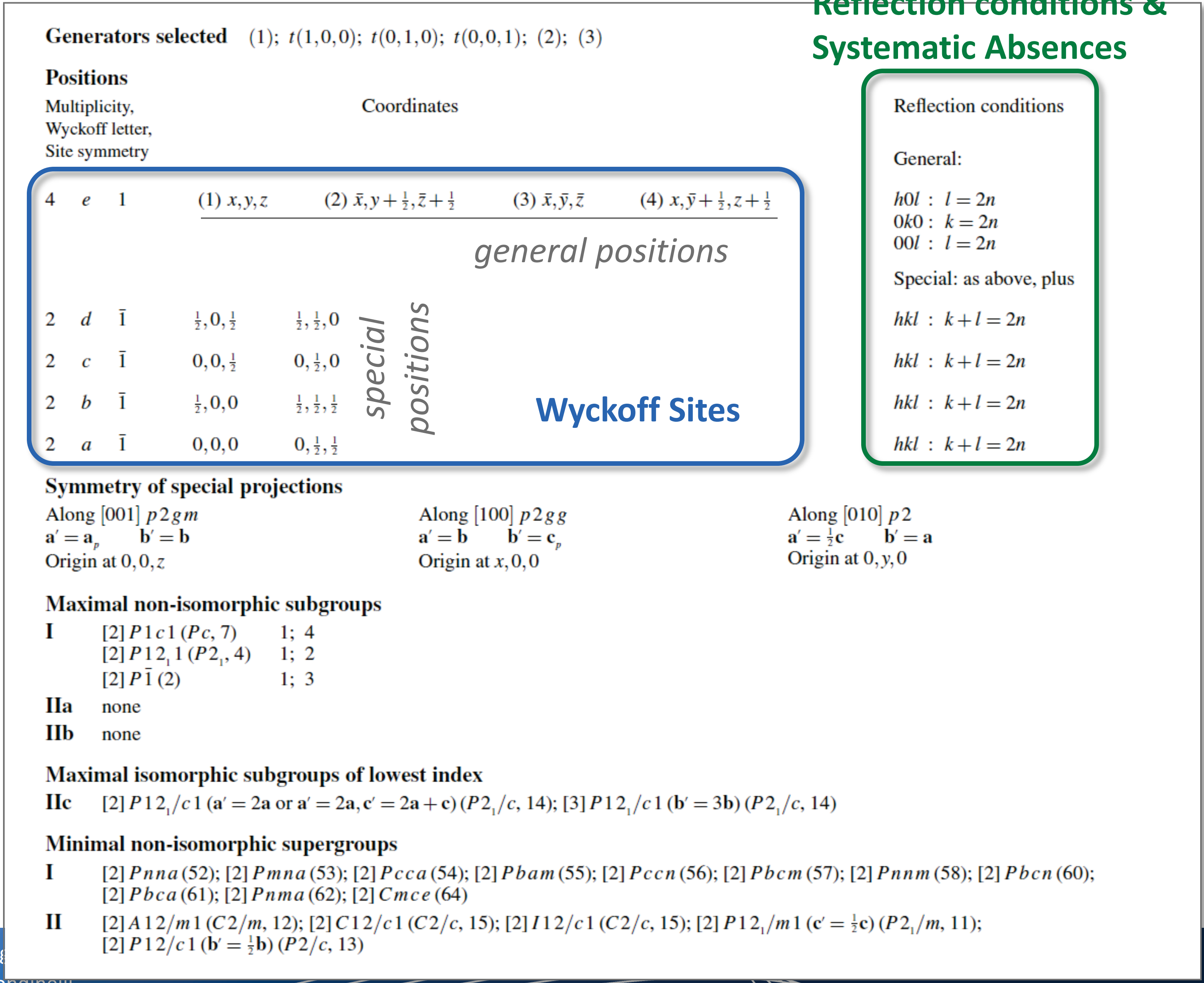
IIc [2] $P12_1/c1$ ($\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{a}' = 2\mathbf{a}, \mathbf{c}' = 2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}' = 3\mathbf{b}$) ($P2_1/c$, 14)

Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}' = \frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}' = \frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

Entry for space group $P2_1/c$ (No. 14)



Reflection conditions & Systematic Absences

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

general positions

special positions

Wyckoff Sites

Symmetry of special projections

Along [001] $p2gm$	Along [100] $p2gg$	Along [010] $p2$
$\mathbf{a}'=\mathbf{a}_p$ $\mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$	$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $0,y,0$

Maximal non-isomorphic subgroups

I	[2] $P1c1$ (Pc, 7)	1; 4
	[2] $P12_11$ ($P2_1$, 4)	1; 2
	[2] $P\bar{1}$ (2)	1; 3
IIa	none	
IIb	none	

Maximal isomorphic subgroups of lowest index

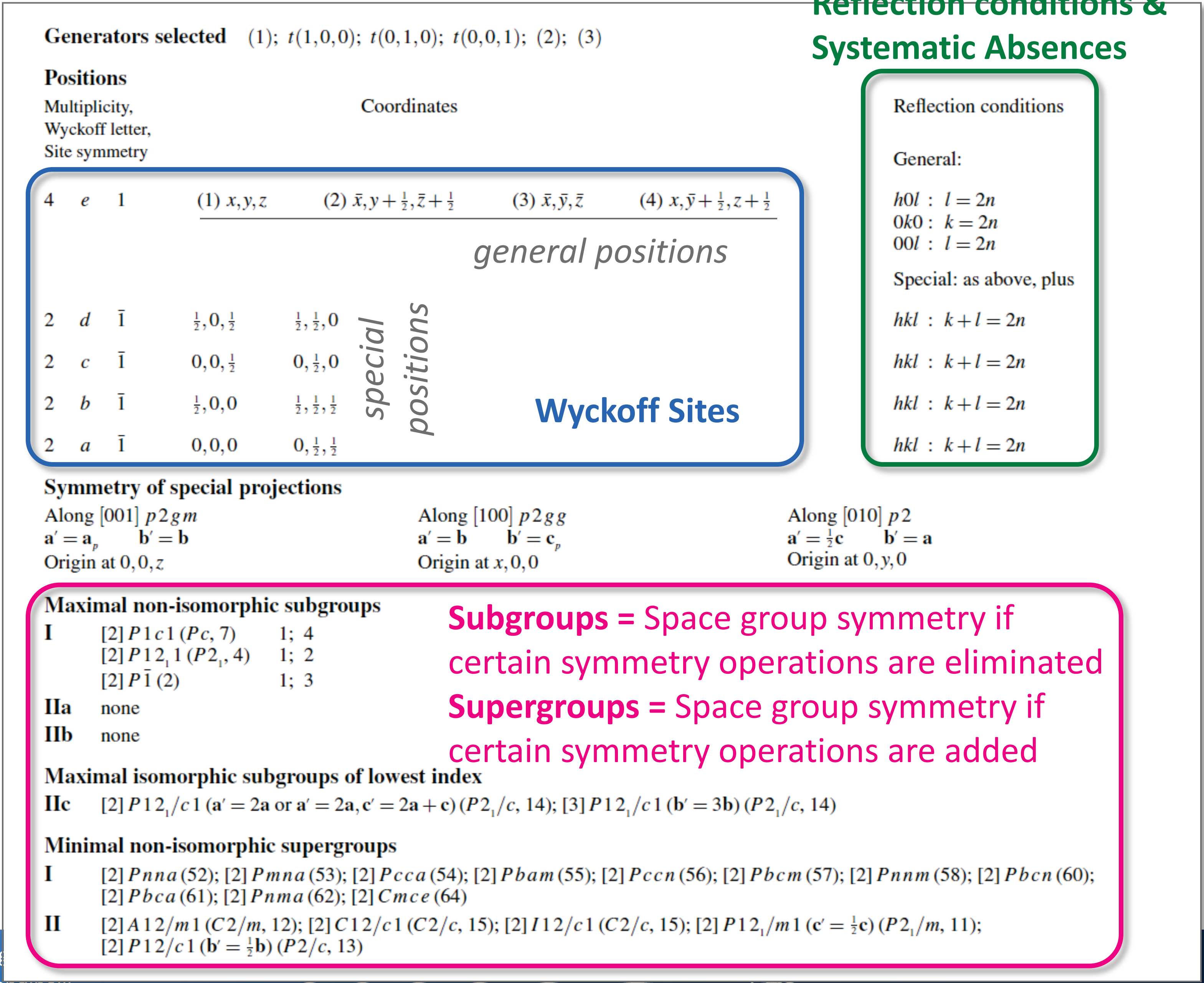
IIc [2] $P12_1/c1$ ($\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a},\mathbf{c}'=2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}'=3\mathbf{b}$) ($P2_1/c$, 14)

Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}'=\frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}'=\frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

Entry for space group $P2_1/c$ (No. 14)



Reflection conditions & Systematic Absences

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
4	*e*	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$
2	*d*	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$		
2	*c*	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$		
2	*b*	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
2	*a*	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$		

general positions

special positions

Wyckoff Sites

Reflection conditions

General:

$h0l$: $l=2n$
$0k0$: $k=2n$
$00l$: $l=2n$

Special: as above, plus

hkl : $k+l=2n$

hkl : $k+l=2n$

hkl : $k+l=2n$

hkl : $k+l=2n$

Symmetry of special projections

Along [001] $p2gm$	Along [100] $p2gg$	Along [010] $p2$
$\mathbf{a}'=\mathbf{a}_p$ $\mathbf{b}'=\mathbf{b}$	$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$	$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,0,z$	Origin at $x,0,0$	Origin at $0,y,0$

Maximal non-isomorphic subgroups

I	[2] $P1c1$ (Pc, 7)	1; 4
	[2] $P12_11$ ($P2_1$, 4)	1; 2
	[2] $P\bar{1}$ (2)	1; 3
IIa	none	
IIb	none	

Subgroups = Space group symmetry if certain symmetry operations are eliminated

Supergroups = Space group symmetry if certain symmetry operations are added

Maximal isomorphic subgroups of lowest index

IIc [2] $P12_1/c1$ ($\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a}, \mathbf{c}'=2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}'=3\mathbf{b}$) ($P2_1/c$, 14)

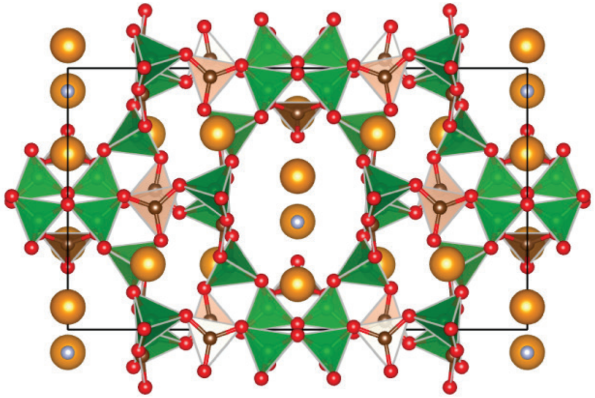
Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}'=\frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}'=\frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

$Ba_4B_{11}O_{20}F$ in space group *Cmc*2_1

- Now need to account for 21 atoms



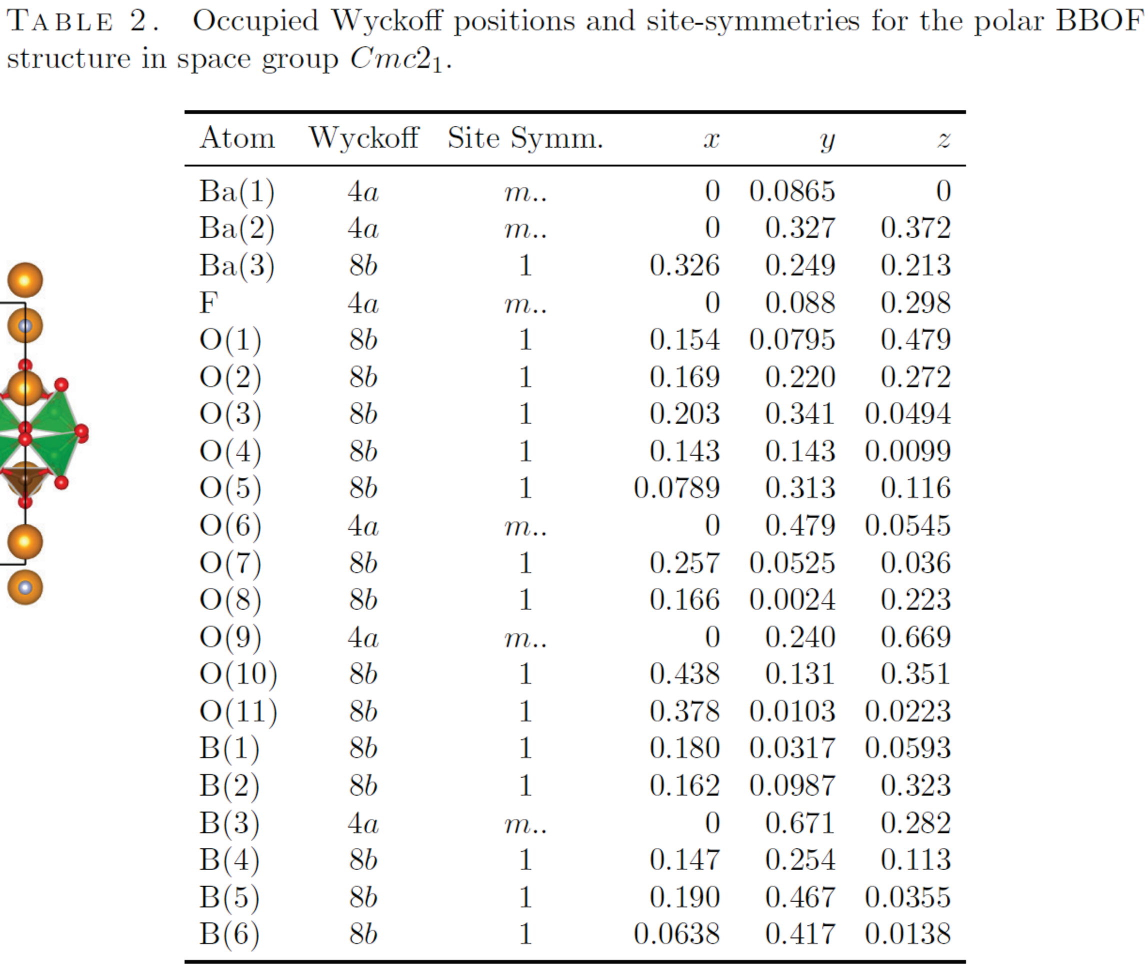


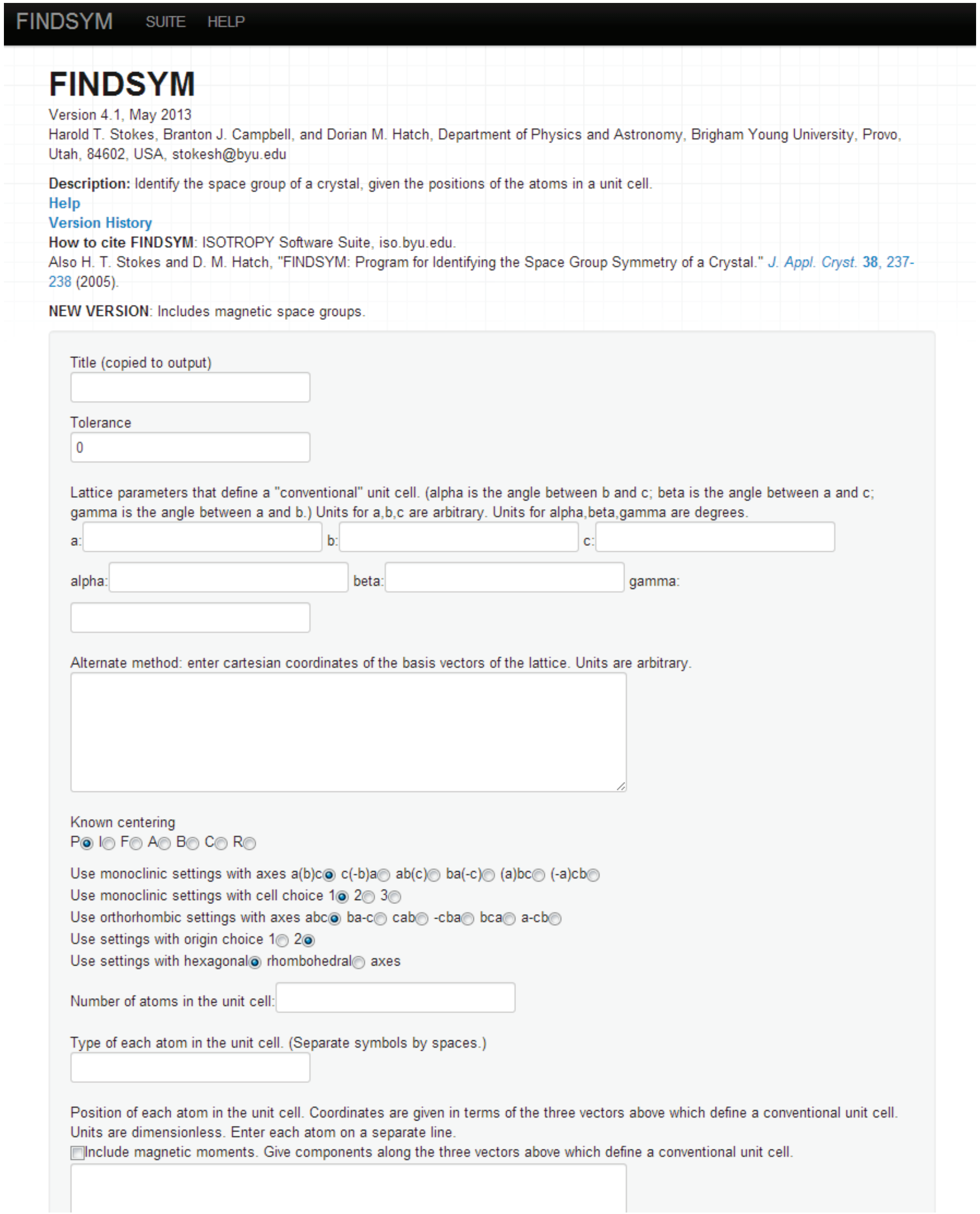
TABLE 2. Occupied Wyckoff positions and site-symmetries for the polar BBOF structure in space group $Cmc2_1$.

Atom	Wyckoff	Site Symm.	x	y	z
Ba(1)	4*a*	*m*..	0	0.0865	0
Ba(2)	4*a*	*m*..	0	0.327	0.372
Ba(3)	8*b*	1	0.326	0.249	0.213
F	4*a*	*m*..	0	0.088	0.298
O(1)	8*b*	1	0.154	0.0795	0.479
O(2)	8*b*	1	0.169	0.220	0.272
O(3)	8*b*	1	0.203	0.341	0.0494
O(4)	8*b*	1	0.143	0.143	0.0099
O(5)	8*b*	1	0.0789	0.313	0.116
O(6)	4*a*	*m*..	0	0.479	0.0545
O(7)	8*b*	1	0.257	0.0525	0.036
O(8)	8*b*	1	0.166	0.0024	0.223
O(9)	4*a*	*m*..	0	0.240	0.669
O(10)	8*b*	1	0.438	0.131	0.351
O(11)	8*b*	1	0.378	0.0103	0.0223
B(1)	8*b*	1	0.180	0.0317	0.0593
B(2)	8*b*	1	0.162	0.0987	0.323
B(3)	4*a*	*m*..	0	0.671	0.282
B(4)	8*b*	1	0.147	0.254	0.113
B(5)	8*b*	1	0.190	0.467	0.0355
B(6)	8*b*	1	0.0638	0.417	0.0138

What’s the space group of my structure?

- Need to identify symmetries for a give origin (point + translation operations) and verify lattice type cannot be reduced

- Computational tool from Harold Stokes (BYU)
- **FINDSYM**: Identifies the space group of a crystal given the atoms in the cell and vectors: http://stokes.byu.edu/iso/findsym.php



FINDSYM

Version 4.1, May 2013
Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch, Department of Physics and Astronomy, Brigham Young University, Provo, Utah, 84602, USA, stokesh@byu.edu

Description: Identify the space group of a crystal, given the positions of the atoms in a unit cell.
Help
Version History
How to cite FINDSYM: ISOTROPY Software Suite, iso.byu.edu.
Also H. T. Stokes and D. M. Hatch, "FINDSYM: Program for Identifying the Space Group Symmetry of a Crystal." *J. Appl. Cryst.* **38**, 237-238 (2005).

NEW VERSION: Includes magnetic space groups.

Title (copied to output)

Tolerance
0

Lattice parameters that define a "conventional" unit cell. (alpha is the angle between b and c; beta is the angle between a and c; gamma is the angle between a and b.) Units for a,b,c are arbitrary. Units for alpha,beta,gamma are degrees.
a: b: c:
alpha: beta: gamma:

Alternate method: enter cartesian coordinates of the basis vectors of the lattice. Units are arbitrary.

Known centering
P● I○ F○ A○ B○ C○ R○

Use monoclinic settings with axes a(b)c● c(-b)a○ ab(c)○ ba(-c)○ (a)bc○ (-a)cb○
Use monoclinic settings with cell choice 1● 2○ 3○
Use orthorhombic settings with axes abc● ba-c○ cab○ -cba○ bca○ a-cb○
Use settings with origin choice 1○ 2●
Use settings with hexagonal● rhombohedral○ axes

Number of atoms in the unit cell:

Type of each atom in the unit cell. (Separate symbols by spaces.)

Position of each atom in the unit cell. Coordinates are given in terms of the three vectors above which define a conventional unit cell. Units are dimensionless. Enter each atom on a separate line.
☐Include magnetic moments. Give components along the three vectors above which define a conventional unit cell.

Many DFT codes also provide this information but it can be less reliable

Why do we want to know the full symmetry?

- Distortions in crystal structures lead to a loss of some symmetry elements (displacive phase transitions)
  - Crystal structure of one phase is a distorted form of the crystal structure of another

- Key features
  - Transition is accomplished by small displacements of atoms
  - There exists a well-defined symmetry change
  - Physics of the transition allows us to use concepts of structure, symmetry, and lattice dynamics (energies) to connect to bonding and physical mechanisms behind material properties

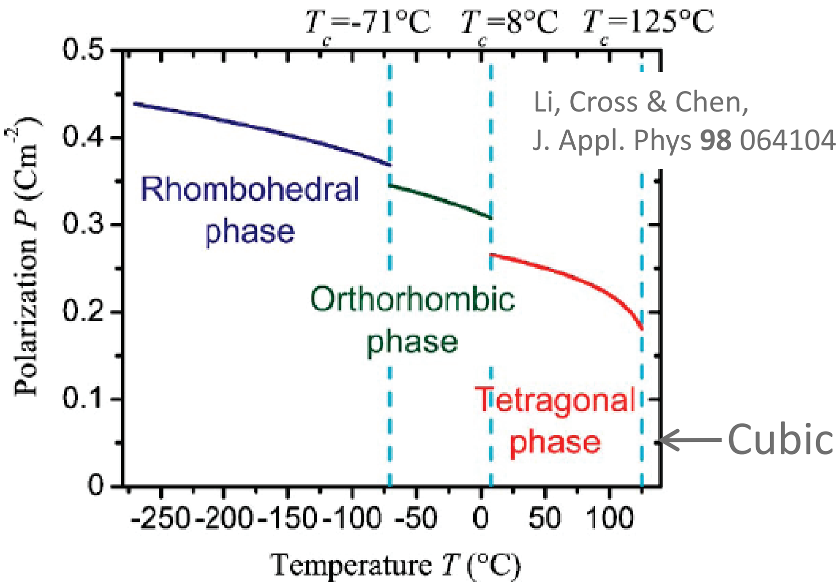
Symmetry breaks and phase transitions

- How does the crystal structure evolve during the transition from a paraelectric to ferroelectric state?

Consider the ferroelectric $BaTiO_3$ (R ⟶ O ⟶ T⟶C phase transition)

Property: *electric polarization*

Defined by a net electric dipole per unit volume



Li, Cross & Chen,
J. Appl. Phys **98** 064104 (2005)

Symmetry of the lattice is lowered as you cool $BaTiO_3$

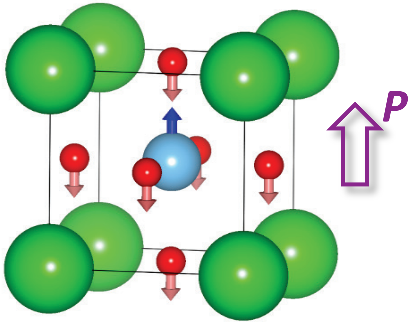
symmetry ⟺ properties

Neumann principle

A well-defined symmetry operation in a thermodynamic system must be maintained when scalar fields are changed except if a phase transition occurs

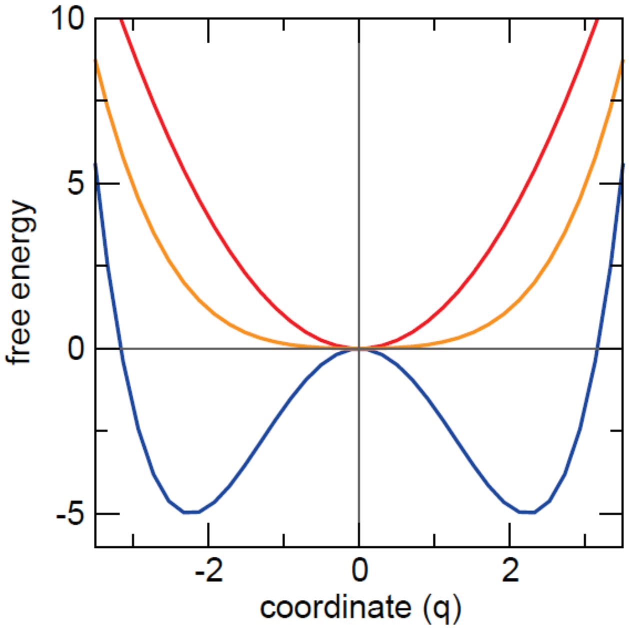
Understanding the structure–property correlations at the atomic level

- Phenomenological approach – Landau theory of phase transitions
  - Describes symmetry breaking phase transitions as due to collective modes with an order parameter



Primary order parameter (OP) is a *physical quantity, P* or an unstable collective DOF

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



$$E = E_0 + \frac{1}{2}\alpha P^2 + \beta P^4$$

$P = 0, \qquad \alpha > 0$ Paraelectric

$P = \pm\sqrt{-\frac{\alpha}{2\beta}}, \qquad a < 0$ Ferroelectric

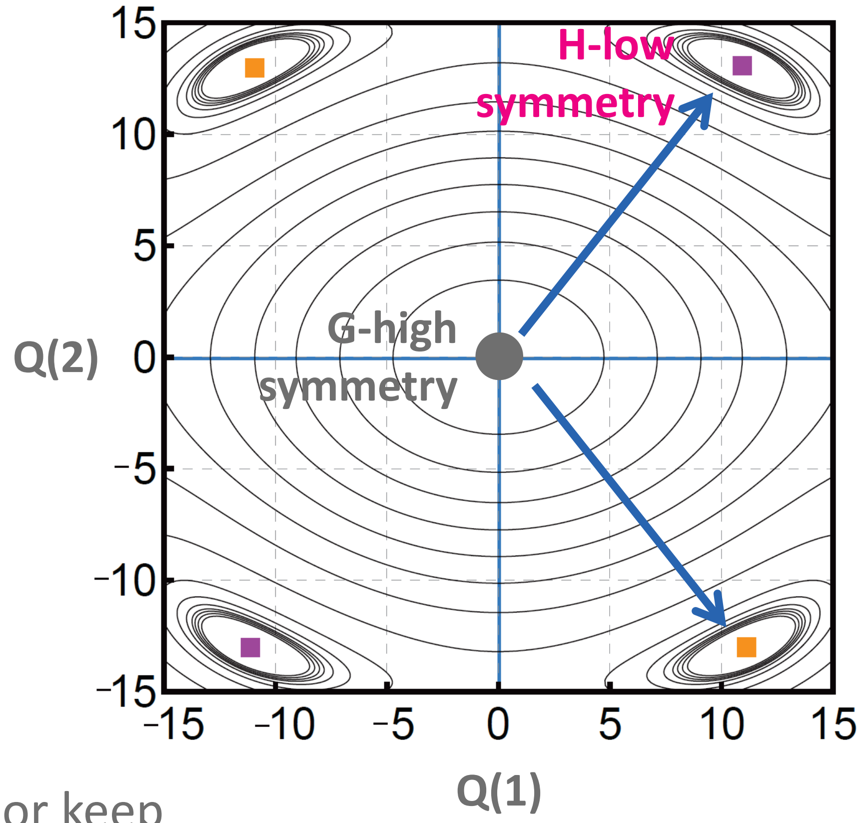
Space group relationships in crystallography across transitions

- High Symmetry Phase (**G**)

phase transition

Driven by condensation of an order parameter (**Q**) or distortion that describes the change in symmetry across the transition

- Low Symmetry Phase (**H**)



- Across a phase transition, symmetry elements are lost
- The symmetry elements that remain or keep the order parameter invariant form an **irreducible representation** (irrep) of the high symmetry space group (**G**)

The irreps can be used to represent the modes of the crystal—collective and correlated atomic displacement patterns that fulfill the symmetry of the irrep

Phase transitions and physical properties

- Implies that at least one specific physical quantity differs in the two phases, necessitating a difference in structure

Neumann principle (macroscopic phenomena)
The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of a crystal

Need a way to precisely define the difference

➡ All variables/parameters/degrees of freedom compatible with the symmetry will be present

➡ Tensor properties are constrained by the point group symmetry of the crystal (some coefficients are forced to be zero)

➡ *Converse*, any tensor property allowed by the point group will exist (be it large or small), it is allowed to be non-zero

Mode description of the static structure of a distorted phase

- Energy is expanded around the high-symmetry structure (the undistorted configuration)

$$E = E_0 + \frac{1}{2}\sum \underline{\kappa_j(\mathbf{k})}\,\underline{q_i(\mathbf{k})}^2 + \ldots$$

stiffness coefficient (“spring constant”)

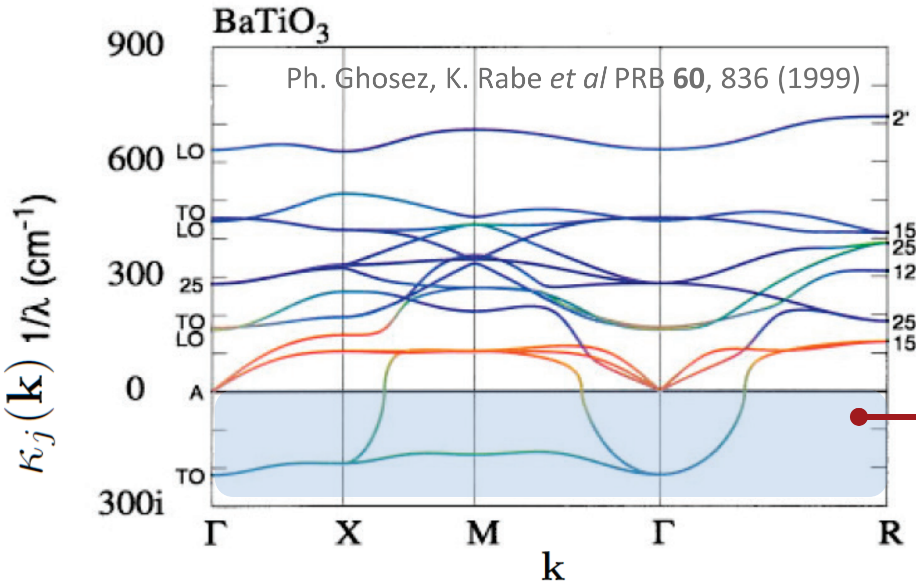
normal mode coordinates

Mode description of the static structure of a distorted phase

- Energy is expanded around the high-symmetry structure (the undistorted configuration)

$$E = E_0 + \frac{1}{2}\sum \underbrace{\kappa_j(\mathbf{k})}_{\text{stiffness coefficient (“spring constant”)}} \underbrace{q_i(\mathbf{k})}_{\text{normal mode coordinates}}^2 + \ldots$$

Ab-initio calculation of the normal modes

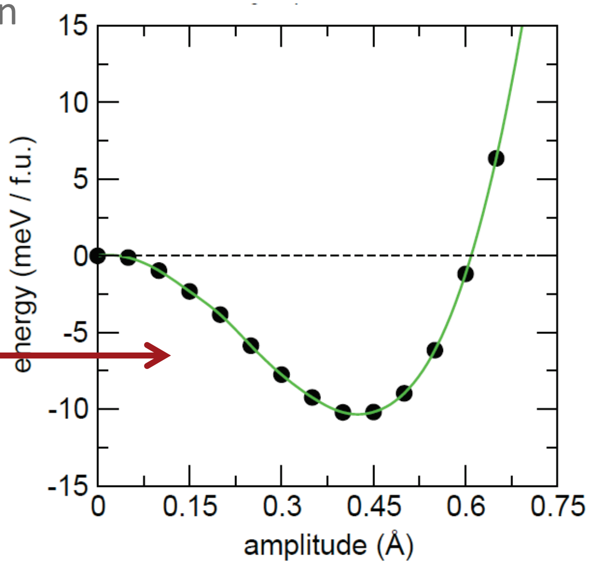


Ph. Ghosez, K. Rabe *et al* PRB **60**, 836 (1999)

Select a particular mode and map out the energy evolution

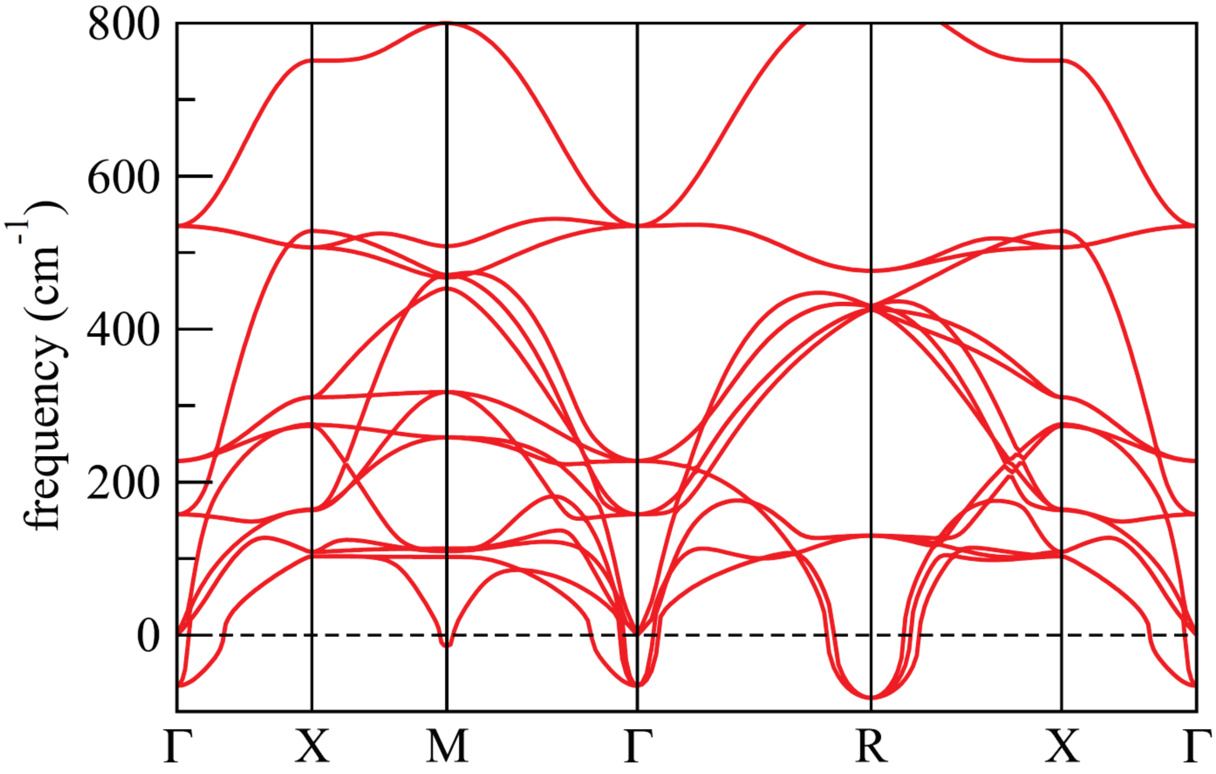
$$\omega^2 \sim \frac{\partial^2 E}{\partial u^2} < 0$$

$$\kappa_j(\mathbf{k}) < 0$$

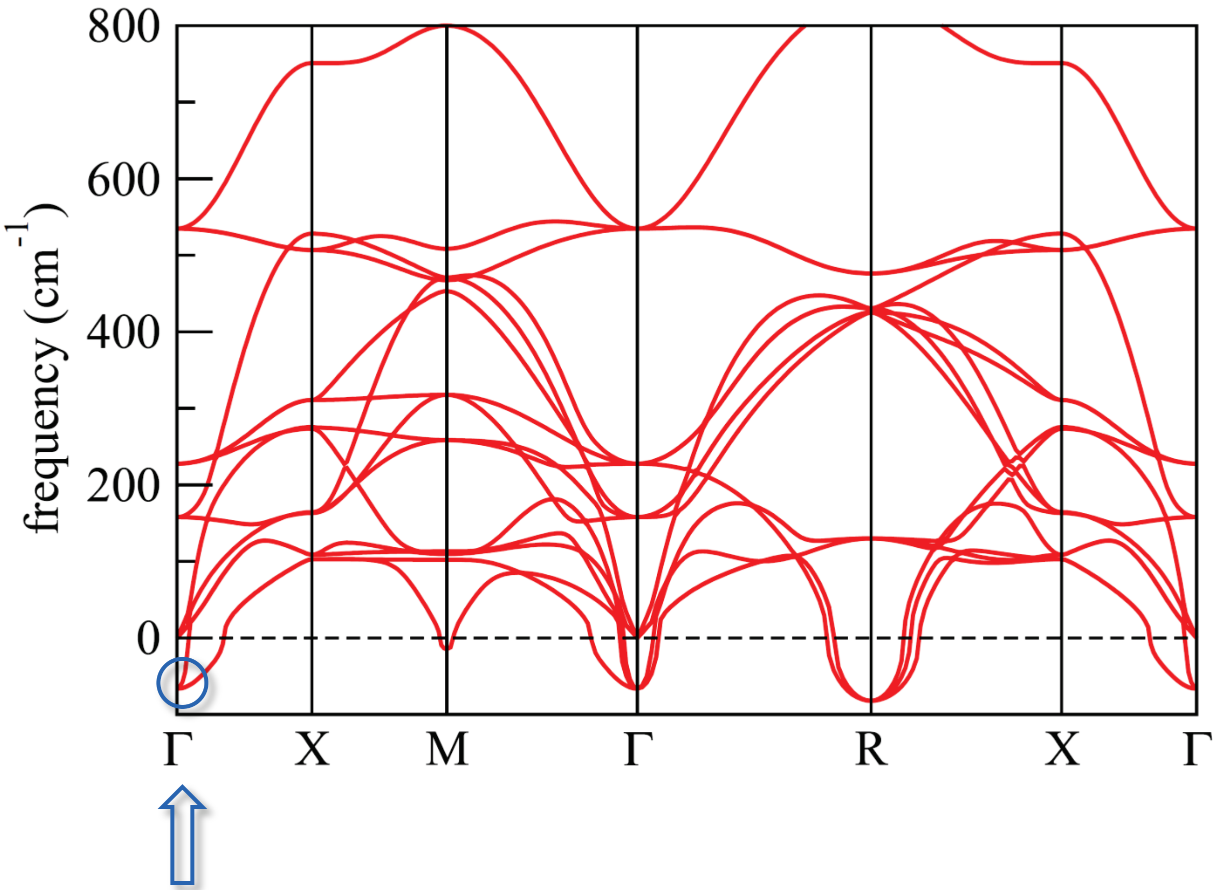


Symmetry of each mode transforms as an irrep of HS phase (group theory)

Phonon modes calculated from DFT for high-symmetry $SrTiO_3$

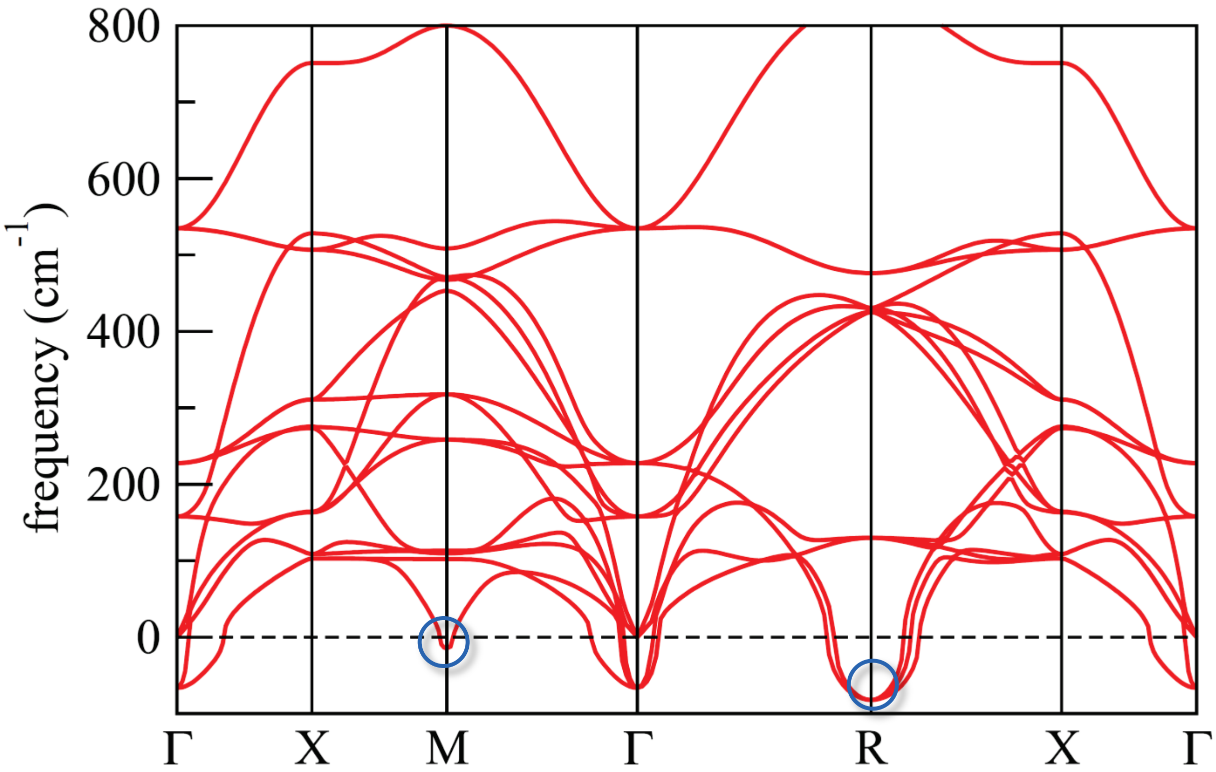


Phonon modes calculated from DFT for high-symmetry $SrTiO_3$



Triply degenerate polar mode (x, y, and z)

Phonon modes calculated from DFT for high-symmetry $SrTiO_3$



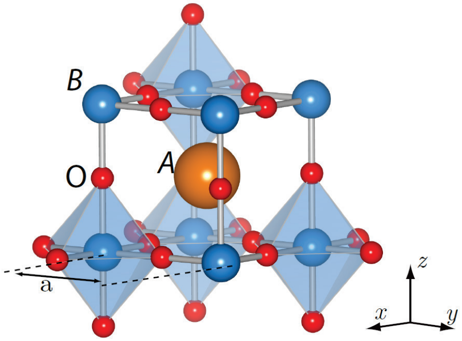
In-phase rotations of octahedra

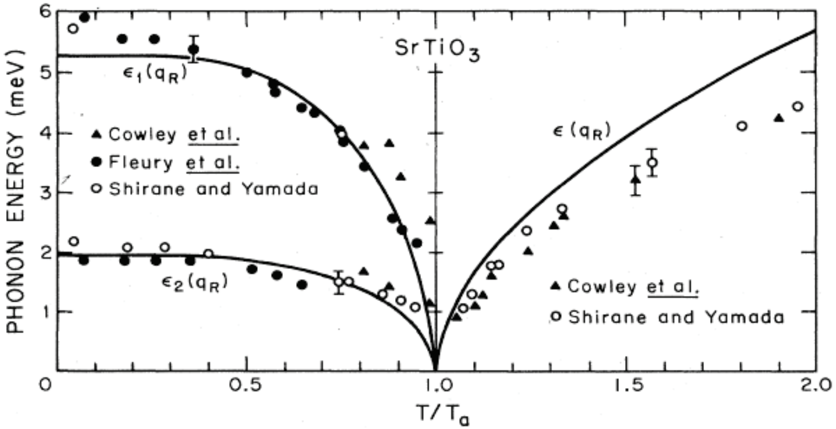
Out-of-phase rotations

Antiferrodistortive phase transition in $SrTiO_3$

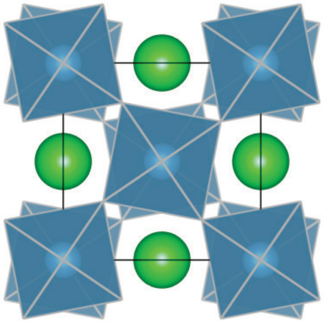
- Small rotations of BO_6 octahedra appear at a critical temperature

- $SrTiO_3$, single rotation





J.F. Scott, Rev. Mod. Phys. **46** 83 (1974)



Classify low-symmetry structures by mode content

- Von Neumann Principle
  - All modes compatible with the symmetry will be present in the total distortion
- But critically they have different weights: ***mode contributions***

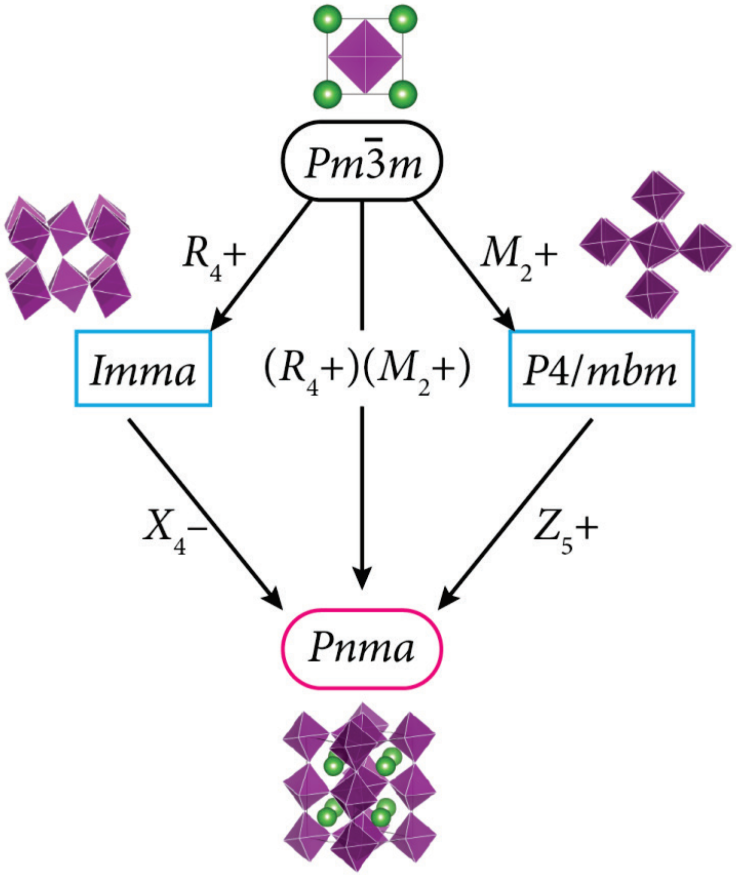
Primary modes (often most unstable):
Order parameter and drives the transition

Secondary modes (much weaker or hard)
Induced by the presence of the primary modes

- Understanding this hierarchy is critical for designing properties in new materials
  - There are free computer tools now that make this task straightforward

Complex low-symmetry structures (group theory)

- Distorted structure = high-symmetry structure + “frozen” distortion modes



- Modes are collective correlated atomic displacements fulfilling certain symmetry properties

- These modes are obtained from a higher symmetry structure that are frozen in with the correct amplitude to produce the low-symmetry geometry

- Obtained from either:
  - Structural mode decompositions or
  - Lattice phonons computed at the DFT level using total energies to obtain interatomic force constants

Mode decomposition – analogous to Fourier decomposition

- *How do you take a complex signal and describe it*: You take any function of time and describe it as a sum of sine waves each with different amplitudes and frequencies

Decompose complex function into a superposition of simpler ones

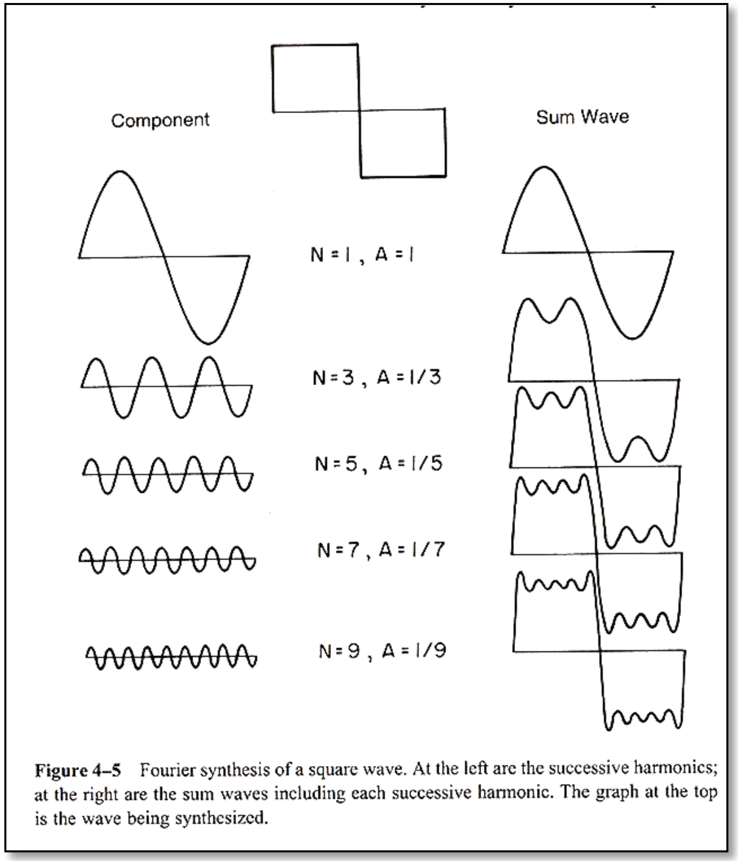


Figure 4–5 Fourier synthesis of a square wave. At the left are the successive harmonics; at the right are the sum waves including each successive harmonic. The graph at the top is the wave being synthesized.

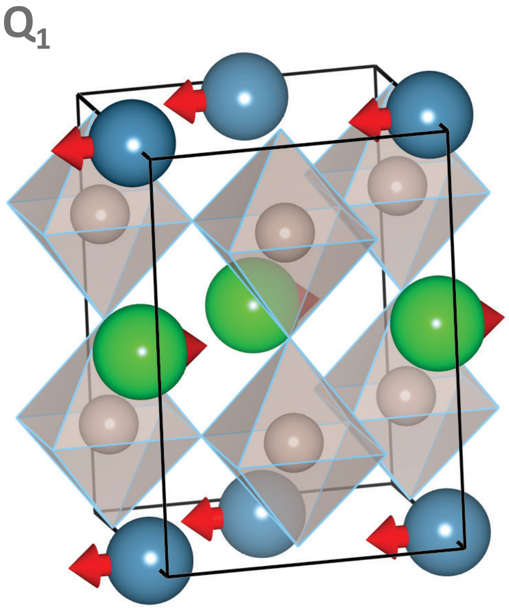
Berg & Stork, *The Physics of Sound, 3rd Edition* (2004)

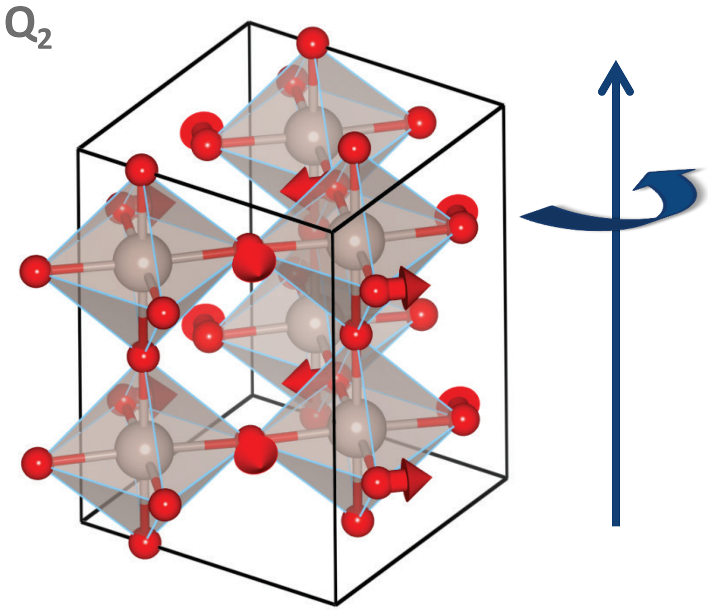
- Mode decomposition for crystal structures can exploit the complete basis set formed by irreps of the high-symmetry phase

Advantages of symmetry-adapted mode decompositions

- Irrep modes (to first order) only couple with modes of the same symmetry
  - Modes (resultant forces) of different symmetry are decoupled
  - Can be mapped onto the eigendisplacements obtained from phonon calculations

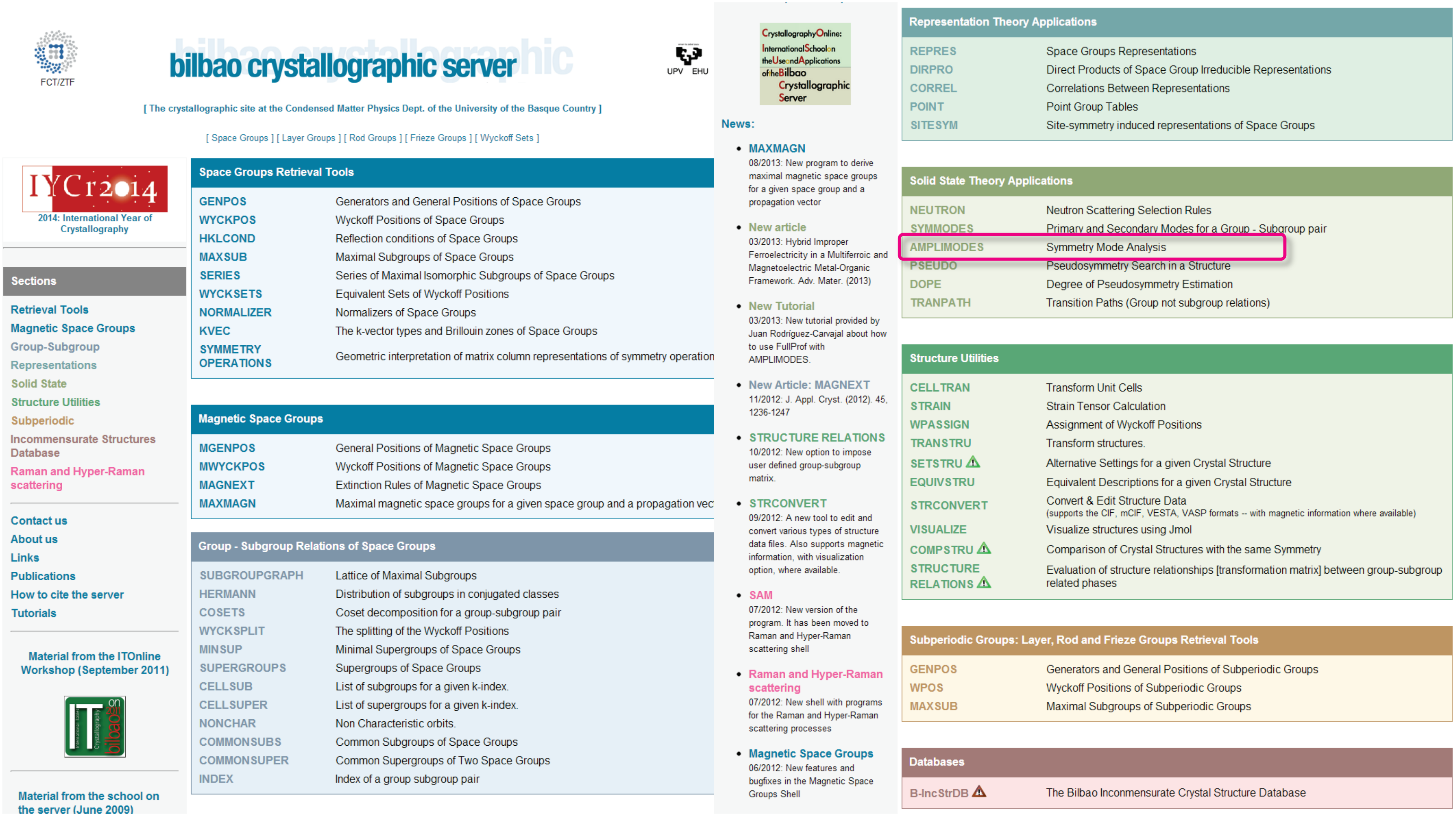
- We can compare both the amplitudes and displacement patterns of different frozen distortion modes to distinguish primary and secondary (induced) distortions, which in general have different weights in the structure





Many online resources to perform mode decompositions

- Bilbao Crystallographic Server, http://www.cryst.ehu.es



FCT/ZTF

bilbao crystallographic server

UPV EHU

[The crystallographic site at the Condensed Matter Physics Dept. of the University of the Basque Country]

[Space Groups] [Layer Groups] [Rod Groups] [Frieze Groups] [Wyckoff Sets]

IYCr2014
2014: International Year of Crystallography

Sections

- Retrieval Tools
- Magnetic Space Groups
- Group-Subgroup
- Representations
- Solid State
- Structure Utilities
- Subperiodic
- Incommensurate Structures Database
- Raman and Hyper-Raman scattering

- Contact us
- About us
- Links
- Publications
- How to cite the server
- Tutorials

Material from the ITOnline Workshop (September 2011)

Material from the school on the server (June 2009)

Space Groups Retrieval Tools

GENPOS	Generators and General Positions of Space Groups
WYCKPOS	Wyckoff Positions of Space Groups
HKLCOND	Reflection conditions of Space Groups
MAXSUB	Maximal Subgroups of Space Groups
SERIES	Series of Maximal Isomorphic Subgroups of Space Groups
WYCKSETS	Equivalent Sets of Wyckoff Positions
NORMALIZER	Normalizers of Space Groups
KVEC	The k-vector types and Brillouin zones of Space Groups
SYMMETRY OPERATIONS	Geometric interpretation of matrix column representations of symmetry operation

Magnetic Space Groups

MGENPOS	General Positions of Magnetic Space Groups
MWYCKPOS	Wyckoff Positions of Magnetic Space Groups
MAGNEXT	Extinction Rules of Magnetic Space Groups
MAXMAGN	Maximal magnetic space groups for a given space group and a propagation vec

Group - Subgroup Relations of Space Groups

SUBGROUPGRAPH	Lattice of Maximal Subgroups
HERMANN	Distribution of subgroups in conjugated classes
COSETS	Coset decomposition for a group-subgroup pair
WYCKSPLIT	The splitting of the Wyckoff Positions
MINSUP	Minimal Supergroups of Space Groups
SUPERGROUPS	Supergroups of Space Groups
CELLSUB	List of subgroups for a given k-index.
CELLSUPER	List of supergroups for a given k-index.
NONCHAR	Non Characteristic orbits.
COMMONSUBS	Common Subgroups of Space Groups
COMMONSUPER	Common Supergroups of Two Space Groups
INDEX	Index of a group subgroup pair

CrystallographyOnline: International School on the Use and Applications of the Bilbao Crystallographic Server

News:

- **MAXMAGN**
  08/2013: New program to derive maximal magnetic space groups for a given space group and a propagation vector
- **New article**
  03/2013: Hybrid Improper Ferroelectricity in a Multiferroic and Magnetoelectric Metal-Organic Framework. Adv. Mater. (2013)
- **New Tutorial**
  03/2013: New tutorial provided by Juan Rodriguez-Carvajal about how to use FullProf with AMPLIMODES.
- **New Article: MAGNEXT**
  11/2012: J. Appl. Cryst. (2012). 45, 1236-1247
- **STRUCTURE RELATIONS**
  10/2012: New option to impose user defined group-subgroup matrix.
- **STRCONVERT**
  09/2012: A new tool to edit and convert various types of structure data files. Also supports magnetic information, with visualization option, where available.
- **SAM**
  07/2012: New version of the program. It has been moved to Raman and Hyper-Raman scattering shell
- **Raman and Hyper-Raman scattering**
  07/2012: New shell with programs for the Raman and Hyper-Raman scattering processes
- **Magnetic Space Groups**
  06/2012: New features and bugfixes in the Magnetic Space Groups Shell

Representation Theory Applications

REPRES	Space Groups Representations
DIRPRO	Direct Products of Space Group Irreducible Representations
CORREL	Correlations Between Representations
POINT	Point Group Tables
SITESYM	Site-symmetry induced representations of Space Groups

Solid State Theory Applications

NEUTRON	Neutron Scattering Selection Rules
SYMMODES	Primary and Secondary Modes for a Group - Subgroup pair
AMPLIMODES	Symmetry Mode Analysis
PSEUDO	Pseudosymmetry Search in a Structure
DOPE	Degree of Pseudosymmetry Estimation
TRANPATH	Transition Paths (Group not subgroup relations)

Structure Utilities

CELLTRAN	Transform Unit Cells
STRAIN	Strain Tensor Calculation
WPASSIGN	Assignment of Wyckoff Positions
TRANSTRU	Transform structures.
SETSTRU ⚠	Alternative Settings for a given Crystal Structure
EQUIVSTRU	Equivalent Descriptions for a given Crystal Structure
STRCONVERT	Convert & Edit Structure Data (supports the CIF, mCIF, VESTA, VASP formats -- with magnetic information where available)
VISUALIZE	Visualize structures using Jmol
COMPSTRU ⚠	Comparison of Crystal Structures with the same Symmetry
STRUCTURE RELATIONS ⚠	Evaluation of structure relationships [transformation matrix] between group-subgroup related phases

Subperiodic Groups: Layer, Rod and Frieze Groups Retrieval Tools

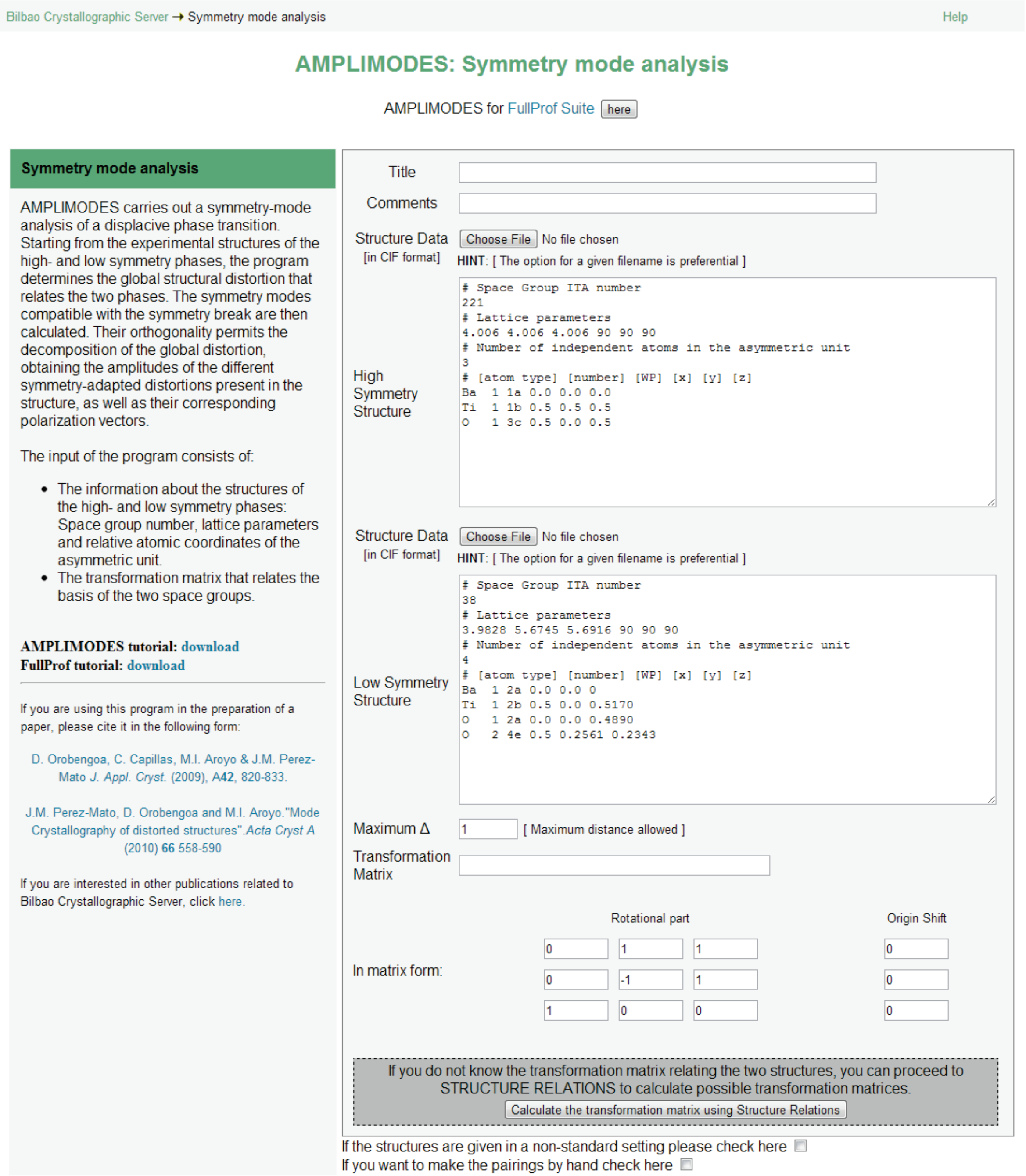
GENPOS	Generators and General Positions of Subperiodic Groups
WPOS	Wyckoff Positions of Subperiodic Groups
MAXSUB	Maximal Subgroups of Subperiodic Groups

Databases

B-IncStrDB ⚠	The Bilbao Incommensurate Crystal Structure Database

J. Appl. Crys. **A42**, 820 (2009); Acta Cryst. A **65**, 558 (2010).

AMPLIMODES



Bilbao Crystallographic Server → Symmetry mode analysis

Help

AMPLIMODES: Symmetry mode analysis

AMPLIMODES for FullProf Suite here

Symmetry mode analysis

AMPLIMODES carries out a symmetry-mode analysis of a displacive phase transition. Starting from the experimental structures of the high- and low symmetry phases, the program determines the global structural distortion that relates the two phases. The symmetry modes compatible with the symmetry break are then calculated. Their orthogonality permits the decomposition of the global distortion, obtaining the amplitudes of the different symmetry-adapted distortions present in the structure, as well as their corresponding polarization vectors.

The input of the program consists of:

- The information about the structures of the high- and low symmetry phases: Space group number, lattice parameters and relative atomic coordinates of the asymmetric unit.
- The transformation matrix that relates the basis of the two space groups.

AMPLIMODES tutorial: download
FullProf tutorial: download

If you are using this program in the preparation of a paper, please cite it in the following form:

D. Orobengoa, C. Capillas, M.I. Aroyo & J.M. Perez-Mato *J. Appl. Cryst.* (2009), A**42**, 820-833.

J.M. Perez-Mato, D. Orobengoa and M.I. Aroyo."Mode Crystallography of distorted structures".*Acta Cryst A* (2010) **66** 558-590

If you are interested in other publications related to Bilbao Crystallographic Server, click here.

Title

Comments

Structure Data [in CIF format] Choose File No file chosen
HINT: [The option for a given filename is preferential]

High Symmetry Structure

```
# Space Group ITA number
221
# Lattice parameters
4.006 4.006 4.006 90 90 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
Ba  1 1a 0.0 0.0 0.0
Ti  1 1b 0.5 0.5 0.5
O   1 3c 0.5 0.0 0.5
```

Structure Data [in CIF format] Choose File No file chosen
HINT: [The option for a given filename is preferential]

Low Symmetry Structure

```
# Space Group ITA number
38
# Lattice parameters
3.9828 5.6745 5.6916 90 90 90
# Number of independent atoms in the asymmetric unit
4
# [atom type] [number] [WP] [x] [y] [z]
Ba  1 2a 0.0 0.0 0
Ti  1 2b 0.5 0.0 0.5170
O   1 2a 0.0 0.0 0.4890
O   2 4e 0.5 0.2561 0.2343
```

Maximum Δ 1 [Maximum distance allowed]

Transformation Matrix

In matrix form:

Rotational part			Origin Shift
0	1	1	0
0	-1	1	0
1	0	0	0

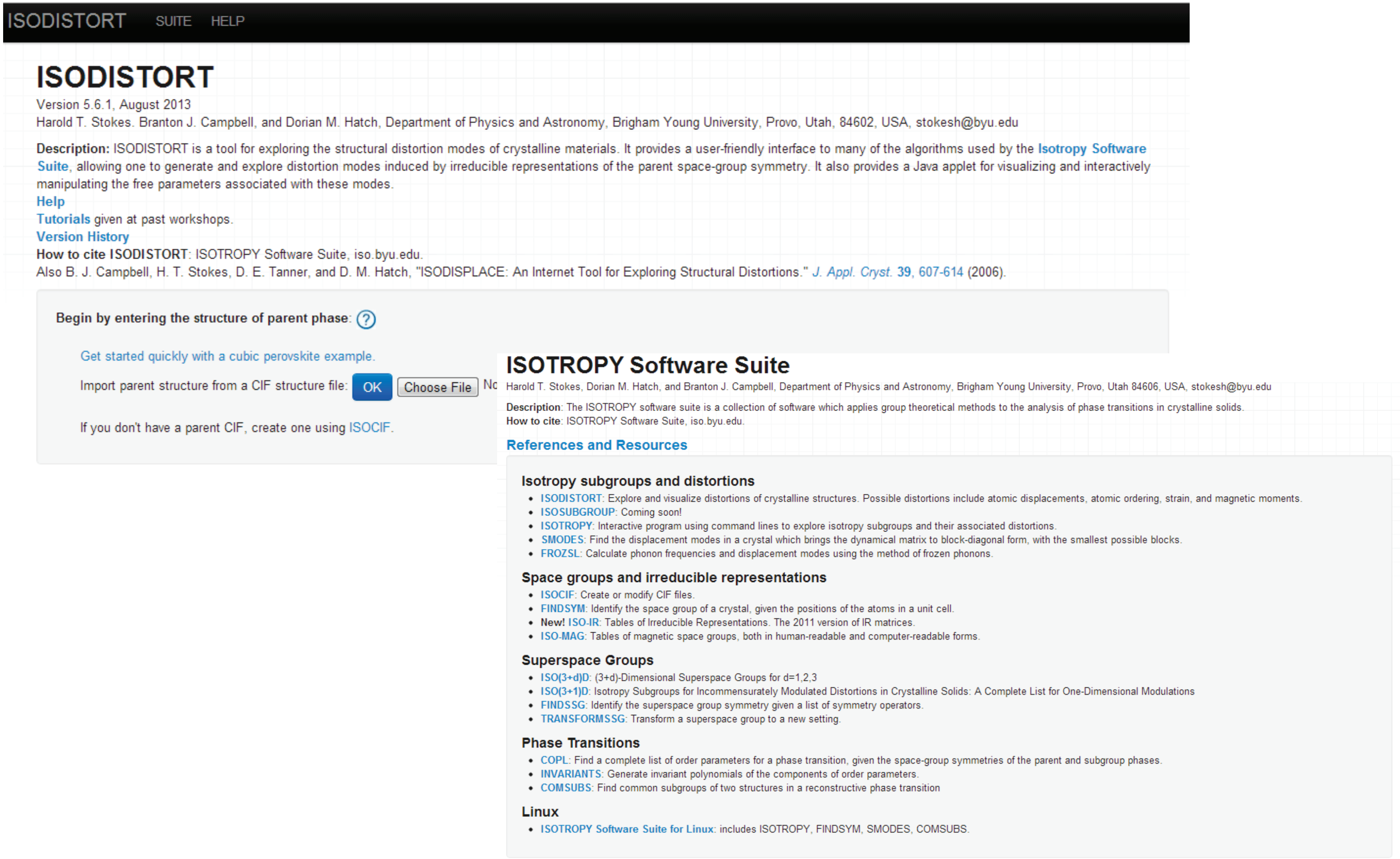
If you do not know the transformation matrix relating the two structures, you can proceed to STRUCTURE RELATIONS to calculate possible transformation matrices.

Calculate the transformation matrix using Structure Relations

If the structures are given in a non-standard setting please check here ☐
If you want to make the pairings by hand check here ☐

ISODISTORT

- From the ISOTROPY suite: http://stokes.byu.edu/iso/isodistort.php



ISODISTORT

Version 5.6.1, August 2013
Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch, Department of Physics and Astronomy, Brigham Young University, Provo, Utah, 84602, USA, stokesh@byu.edu

Description: ISODISTORT is a tool for exploring the structural distortion modes of crystalline materials. It provides a user-friendly interface to many of the algorithms used by the **Isotropy Software Suite**, allowing one to generate and explore distortion modes induced by irreducible representations of the parent space-group symmetry. It also provides a Java applet for visualizing and interactively manipulating the free parameters associated with these modes.
Help
Tutorials given at past workshops.
Version History
How to cite ISODISTORT: ISOTROPY Software Suite, iso.byu.edu.
Also B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, "ISODISPLACE: An Internet Tool for Exploring Structural Distortions." *J. Appl. Cryst.* **39**, 607-614 (2006).

Begin by entering the structure of parent phase: ?

Get started quickly with a cubic perovskite example.

Import parent structure from a CIF structure file:

If you don't have a parent CIF, create one using ISOCIF.

ISOTROPY Software Suite

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell, Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84606, USA, stokesh@byu.edu

Description: The ISOTROPY software suite is a collection of software which applies group theoretical methods to the analysis of phase transitions in crystalline solids.
How to cite: ISOTROPY Software Suite, iso.byu.edu.

References and Resources

Isotropy subgroups and distortions

- ISODISTORT: Explore and visualize distortions of crystalline structures. Possible distortions include atomic displacements, atomic ordering, strain, and magnetic moments.
- ISOSUBGROUP: Coming soon!
- ISOTROPY: Interactive program using command lines to explore isotropy subgroups and their associated distortions.
- SMODES: Find the displacement modes in a crystal which brings the dynamical matrix to block-diagonal form, with the smallest possible blocks.
- FROZSL: Calculate phonon frequencies and displacement modes using the method of frozen phonons.

Space groups and irreducible representations

- ISOCIF: Create or modify CIF files.
- FINDSYM: Identify the space group of a crystal, given the positions of the atoms in a unit cell.
- **New!** ISO-IR: Tables of Irreducible Representations. The 2011 version of IR matrices.
- ISO-MAG: Tables of magnetic space groups, both in human-readable and computer-readable forms.

Superspace Groups

- ISO(3+d)D: (3+d)-Dimensional Superspace Groups for d=1,2,3
- ISO(3+1)D: Isotropy Subgroups for Incommensurately Modulated Distortions in Crystalline Solids: A Complete List for One-Dimensional Modulations
- FINDSSG: Identify the superspace group symmetry given a list of symmetry operators.
- TRANSFORMSSG: Transform a superspace group to a new setting.

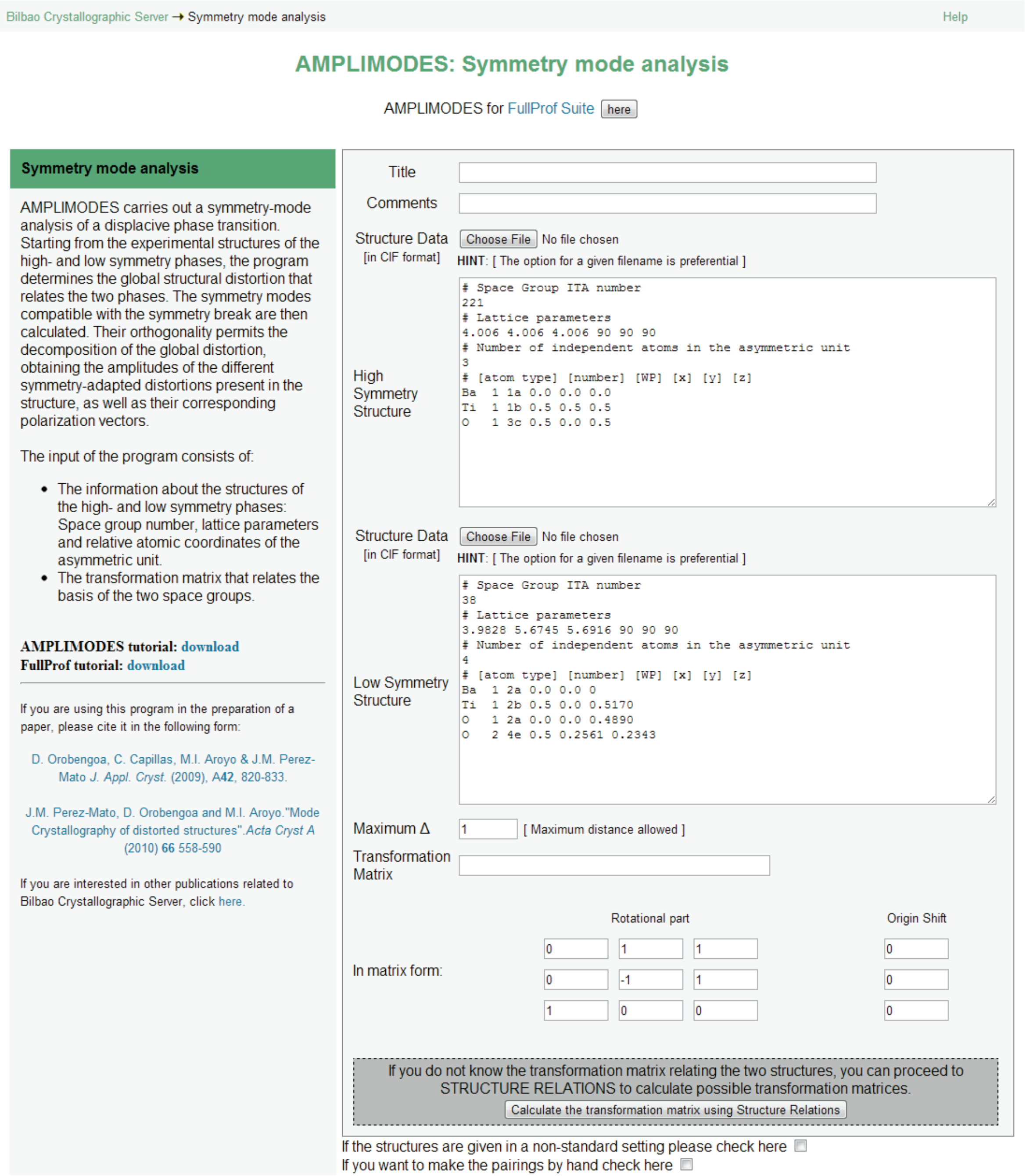
Phase Transitions

- COPL: Find a complete list of order parameters for a phase transition, given the space-group symmetries of the parent and subgroup phases.
- INVARIANTS: Generate invariant polynomials of the components of order parameters.
- COMSUBS: Find common subgroups of two structures in a reconstructive phase transition

Linux

- **ISOTROPY Software Suite for Linux**: includes ISOTROPY, FINDSYM, SMODES, COMSUBS.

AMPLIMODES



AMPLIMODES: Symmetry mode analysis

AMPLIMODES for FullProf Suite

Symmetry mode analysis

AMPLIMODES carries out a symmetry-mode analysis of a displacive phase transition. Starting from the experimental structures of the high- and low symmetry phases, the program determines the global structural distortion that relates the two phases. The symmetry modes compatible with the symmetry break are then calculated. Their orthogonality permits the decomposition of the global distortion, obtaining the amplitudes of the different symmetry-adapted distortions present in the structure, as well as their corresponding polarization vectors.

The input of the program consists of:

- The information about the structures of the high- and low symmetry phases: Space group number, lattice parameters and relative atomic coordinates of the asymmetric unit.
- The transformation matrix that relates the basis of the two space groups.

AMPLIMODES tutorial: download
FullProf tutorial: download

If you are using this program in the preparation of a paper, please cite it in the following form:

D. Orobengoa, C. Capillas, M.I. Aroyo & J.M. Perez-Mato *J. Appl. Cryst.* (2009), A**42**, 820-833.

J.M. Perez-Mato, D. Orobengoa and M.I. Aroyo."Mode Crystallography of distorted structures".*Acta Cryst A* (2010) **66** 558-590

If you are interested in other publications related to Bilbao Crystallographic Server, click here.

Title

Comments

Structure Data [in CIF format] No file chosen
HINT: [The option for a given filename is preferential]

High Symmetry Structure

```
# Space Group ITA number
221
# Lattice parameters
4.006 4.006 4.006 90 90 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
Ba  1 1a 0.0 0.0 0.0
Ti  1 1b 0.5 0.5 0.5
O   1 3c 0.5 0.0 0.5
```

Structure Data [in CIF format] No file chosen
HINT: [The option for a given filename is preferential]

Low Symmetry Structure

```
# Space Group ITA number
38
# Lattice parameters
3.9828 5.6745 5.6916 90 90 90
# Number of independent atoms in the asymmetric unit
4
# [atom type] [number] [WP] [x] [y] [z]
Ba  1 2a 0.0 0.0 0
Ti  1 2b 0.5 0.0 0.5170
O   1 2a 0.0 0.0 0.4890
O   2 4e 0.5 0.2561 0.2343
```

Maximum Δ: 1 [Maximum distance allowed]

Transformation Matrix

In matrix form:

Rotational part			Origin Shift
0	1	1	0
0	-1	1	0
1	0	0	0

If you do not know the transformation matrix relating the two structures, you can proceed to STRUCTURE RELATIONS to calculate possible transformation matrices.

If the structures are given in a non-standard setting please check here ☐
If you want to make the pairings by hand check here ☐

AMPLIMODES: Symmetry Modes Analysis

- Calculates the amplitudes and polarization vectors of all distortion modes with different symmetries (irreps) frozen into a distorted structure
  - http://www.cryst.ehu.es/cryst/amplimodes.html
  - http://www.cryst.ehu.es/cryst/tutorials/Tutorial-AMPLIMODES.pdf
  - http://www.cryst.ehu.es/html/cryst/tutorials/FullProf-Tutorial-Symmetry-Modes.pdf

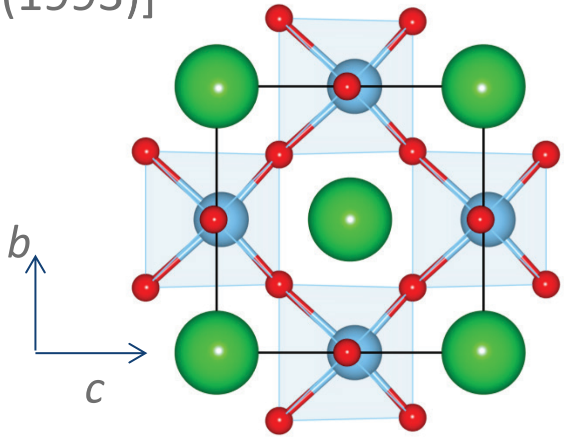
- INPUTS (**Structures can come from experiment or theory, or both**)
  - High-symmetry reference structures (some ambiguity here)
  - Low-symmetry distorted structure

- OUTPUTS
  - Algebraic form of irreps, mode amplitudes, and displacement vectors
  - Can mathematically compare structures
  - Eases identification of active/primary irrep

J. Appl. Cryst. **A42**, 820 (2009); Acta Cryst. **A66** 558 (2010)

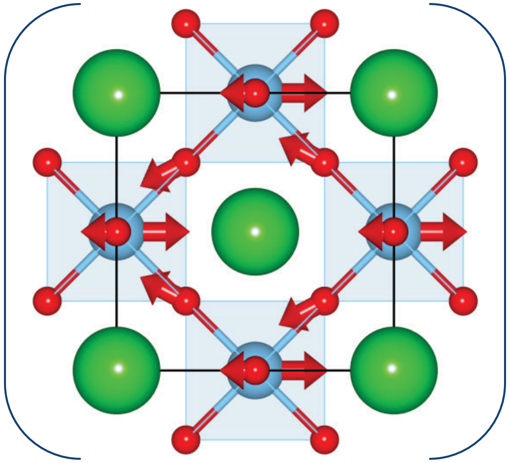
Example: $BaTiO_3$ in the orthorhombic *Amm*2 structure

- Crystal structure at 190 K [J. Phys. Chem, **97**, 2368 (1993)]

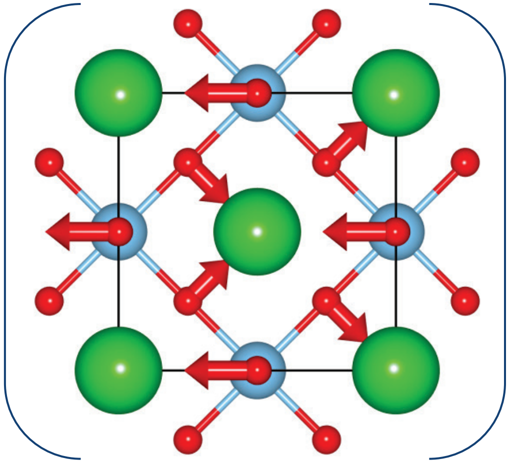


- Mode decomposition of distorted structure

$Q(\Gamma_4^-)\times$

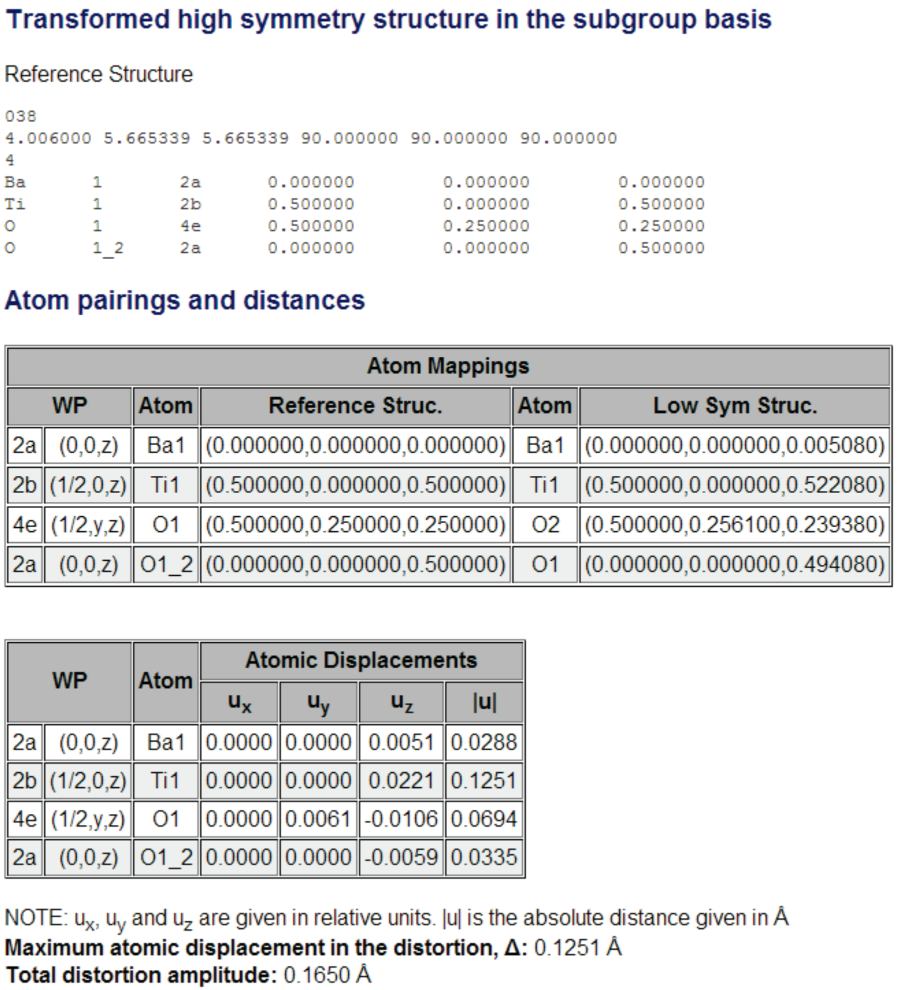


$+\ Q(\Gamma_5^-)\times$



polar (ferroelectric) mode

Quantitative data can be used for calculations and analysis



Transformed high symmetry structure in the subgroup basis

Reference Structure

```
038
4.006000 5.665339 5.665339 90.000000 90.000000 90.000000
4
Ba       1       2a      0.000000        0.000000        0.000000
Ti       1       2b      0.500000        0.000000        0.500000
O        1       4e      0.500000        0.250000        0.250000
O        1_2     2a      0.000000        0.000000        0.500000
```

Atom pairings and distances

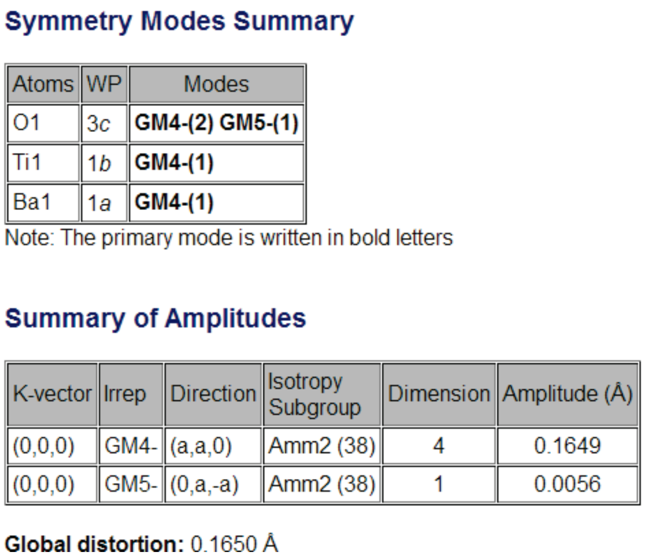
Atom Mappings					
WP		Atom	Reference Struc.	Atom	Low Sym Struc.
2a	(0,0,z)	Ba1	(0.000000,0.000000,0.000000)	Ba1	(0.000000,0.000000,0.005080)
2b	(1/2,0,z)	Ti1	(0.500000,0.000000,0.500000)	Ti1	(0.500000,0.000000,0.522080)
4e	(1/2,y,z)	O1	(0.500000,0.250000,0.250000)	O2	(0.500000,0.256100,0.239380)
2a	(0,0,z)	O1_2	(0.000000,0.000000,0.500000)	O1	(0.000000,0.000000,0.494080)

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0051	0.0288
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0221	0.1251
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0106	0.0694
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0059	0.0335

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å

Maximum atomic displacement in the distortion, Δ: 0.1251 Å

Total distortion amplitude: 0.1650 Å



Symmetry Modes Summary

Atoms	WP	Modes
O1	3*c*	**GM4-(2) GM5-(1)**
Ti1	1*b*	**GM4-(1)**
Ba1	1*a*	**GM4-(1)**

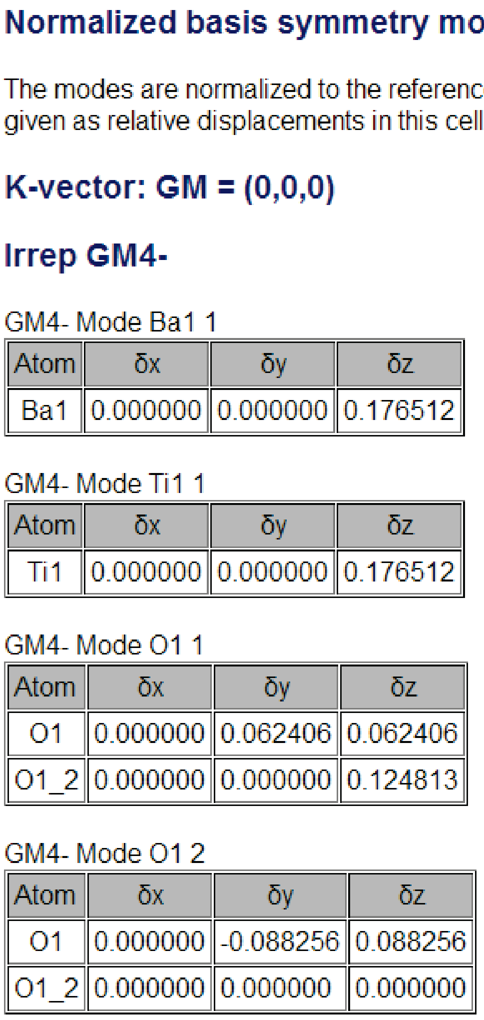
Note: The primary mode is written in bold letters

Summary of Amplitudes

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM4-	(a,a,0)	Amm2 (38)	4	0.1649
(0,0,0)	GM5-	(0,a,-a)	Amm2 (38)	1	0.0056

Global distortion: 0.1650 Å

Detailed output



Normalized basis symmetry modes

The modes are normalized to the reference structure unit cell and are given as relative displacements in this cell.

K-vector: GM = (0,0,0)

Irrep GM4-

GM4- Mode Ba1 1

Atom	δx	δy	δz
Ba1	0.000000	0.000000	0.176512

GM4- Mode Ti1 1

Atom	δx	δy	δz
Ti1	0.000000	0.000000	0.176512

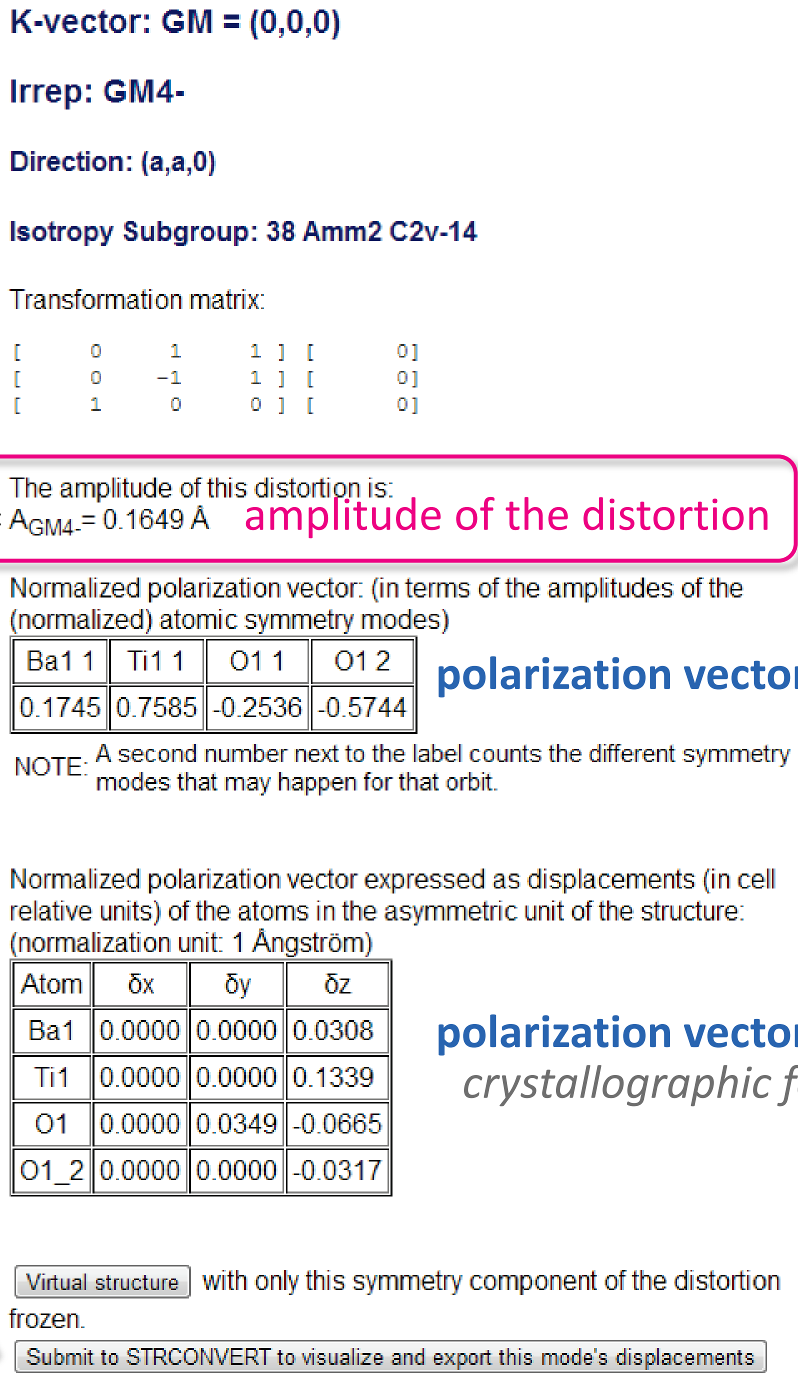
GM4- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	0.062406	0.062406
O1_2	0.000000	0.000000	0.124813

GM4- Mode O1 2

Atom	δx	δy	δz
O1	0.000000	-0.088256	0.088256
O1_2	0.000000	0.000000	0.000000

basis for the distortion vector (4 dimensional)



K-vector: GM = (0,0,0)

Irrep: GM4-

Direction: (a,a,0)

Isotropy Subgroup: 38 Amm2 C2v-14

Transformation matrix:

```
[      0      1      1 ] [        0]
[      0     -1      1 ] [        0]
[      1      0      0 ] [        0]
```

The amplitude of this distortion is:

$Q(\Gamma_4^-) =$ A_{GM4-}= 0.1649 Å amplitude of the distortion

Normalized polarization vector: (in terms of the amplitudes of the (normalized) atomic symmetry modes)

Ba1 1	Ti1 1	O1 1	O1 2
0.1745	0.7585	-0.2536	-0.5744

polarization vector (v1)

NOTE: A second number next to the label counts the different symmetry modes that may happen for that orbit.

Normalized polarization vector expressed as displacements (in cell relative units) of the atoms in the asymmetric unit of the structure: (normalization unit: 1 Ångström)

Atom	δx	δy	δz
Ba1	0.0000	0.0000	0.0308
Ti1	0.0000	0.0000	0.1339
O1	0.0000	0.0349	-0.0665
O1_2	0.0000	0.0000	-0.0317

polarization vector (v2)

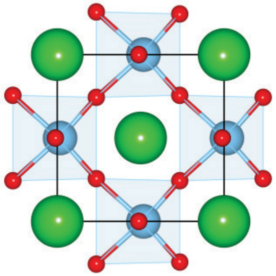
crystallographic form

Virtual structure with only this symmetry component of the distortion frozen.

Submit to STRCONVERT to visualize and export this mode's displacements

Can visualize displacement pattern

Orthorhombic (*Amm*2) $BaTiO_3$ structure



High symmetry perovskite in *Amm*2 setting without distortions

Atom	δx	δy	δz
Ba	0	0	0
Ti	0.5	0	0.5
O1	0.5	0.25	0.25
O1_2	0	0	0.5

$+$

$Q(\Gamma_4^-)\times$

(0.165 Å)

Atom	δx	δy	δz
Ba	0	0	0.0308
Ti	0	0	0.1339
O1	0	0.0349	-0.0665
O1_2	0	0	-0.0317

$+$ $Q(\Gamma_5^-)\times$

(0.006 Å)

Atom	δx	δy	δz
Ba	0	0	0
Ti	0	0	0
O1	0	0.0624	0.0624
O1_2	0	0	-0.1248

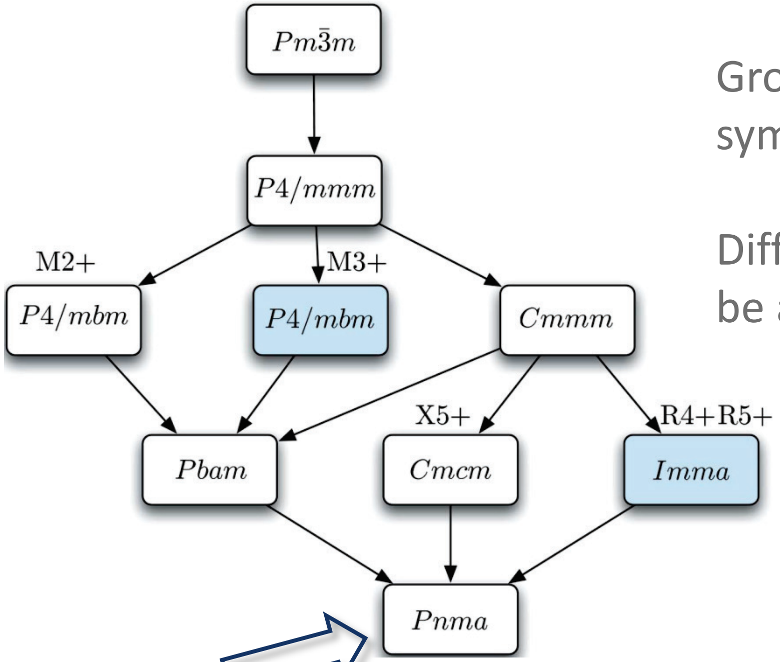
polar (ferroelectric) mode

With this information we can make correlations between structure and properties

- Able to investigate the physical mechanisms that stabilize various structures
  - Structural/Electronic phases transitions
  - Structural contribution to electronic response
    - Metal-insulator transitions
    - Ordered magnetic state
    - Non-linear optical properties
    - …

Structural phase transitions from mode decompositions in $SrZrO_3$

- Room-temperature it is *Pnma* symmetry
- Cubic structure exists above 1340 K



Group-subgroup graph displays possible intermediate symmetries

Different primary instabilities or normal modes must be active (two order parameters condense in LT)

Two-primary modes required

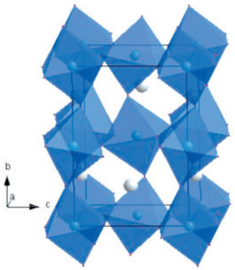


Table 13
Summary of the mode decomposition with respect to its $Pm\bar{3}m$ parent structure of the *Pnma* structure of $SrZrO_3$ at 293 K (Howard *et al.*, 2000), $NaTaO_3$ (Kennedy, Prodjosantoso & Howard, 1999) and $LaMnO_3$ at 300 K (Rodríguez-Carvajal *et al.*, 1998).

Irrep	Isotropy subgroup	Dimension	Amplitude (Å) $SrZrO_3$
R4+	*Imma*	1	1.19
R5+	*Imma*	2	0.07
X5+	*Cmcm*	2	0.34
M2+	*P4/mbm*	1	0.01
M3+	*P4/mbm*	1	0.79

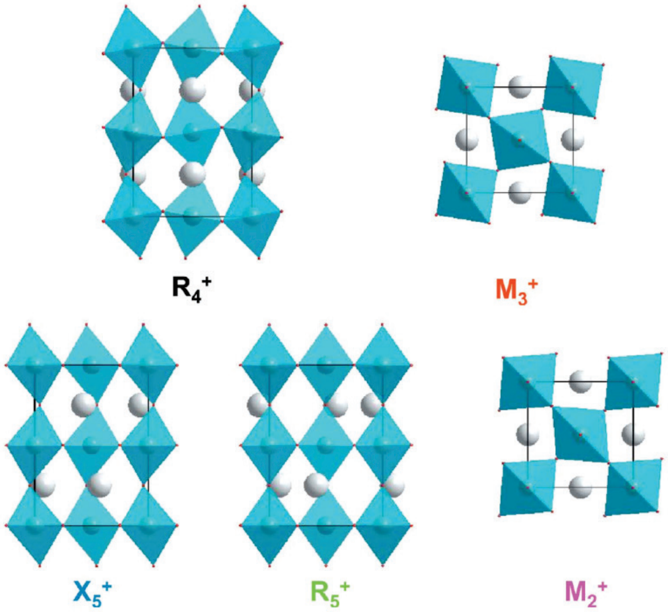
expect two phase transitions: $Pnma(M_3^+, R_4^+) \rightarrow Imma(R_4^+) \rightarrow Pm\bar{3}m$

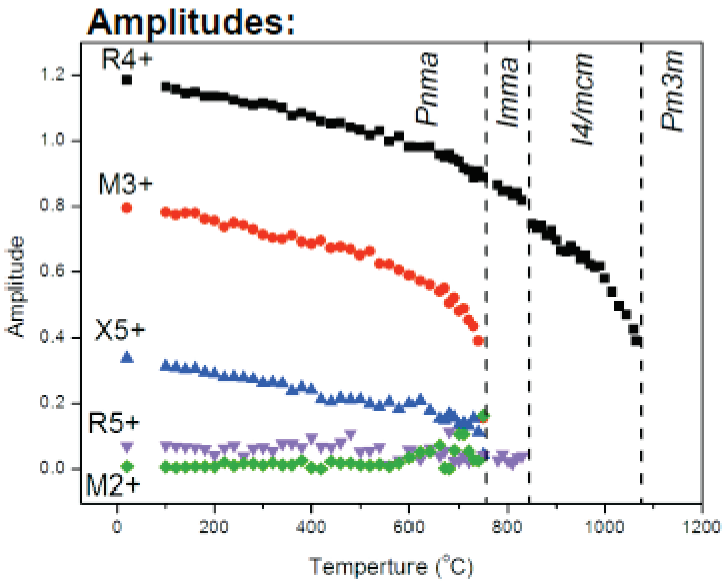
Acta Cryst. **A66** 558 (2010)

Structural phase transitions from mode decompositions in SrZrO$_3$

- Actual transition:

$$Pnma(M_3^+, R_4^+) \rightarrow Imma(R_4^+) \rightarrow I4/mcm(R_4^+) \rightarrow Pm\bar{3}m$$



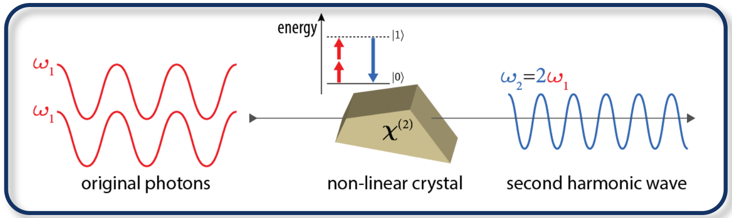


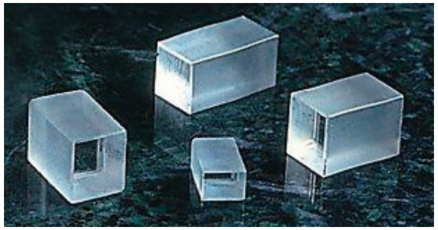
Since *R* is a multi-dimensional irrep, it remains active and simply changes direction

Figure from J.M Perez-Mato; Kennedy, Howard, Chakoumakos, PRB **59** 4023 (1999)

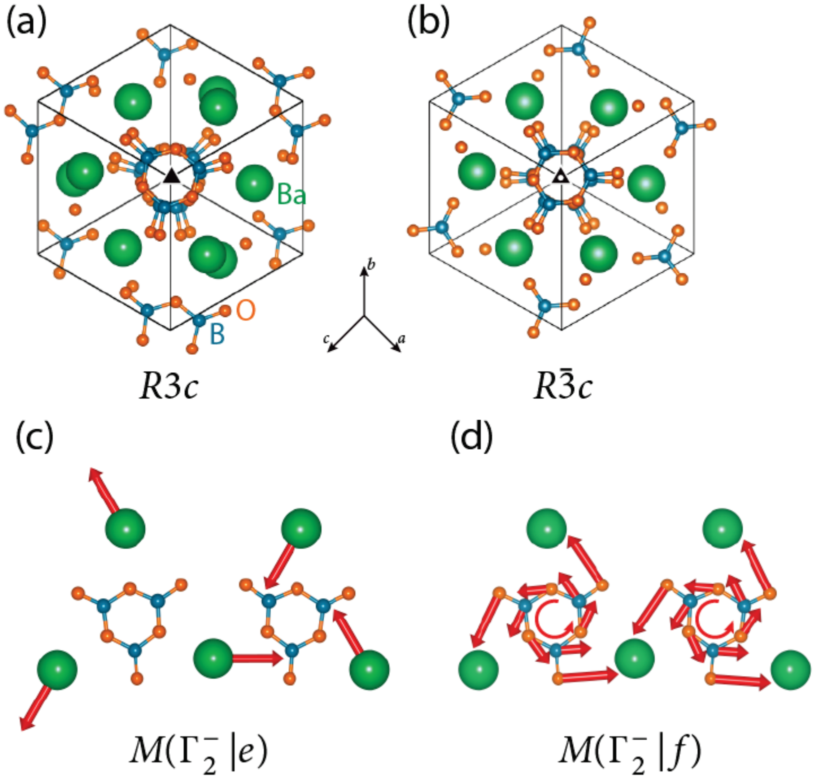
Approach can be applied to structures beyond perovskite and complex properties

- Consider the frequency doubling material β-BaB_2O_4





- Examine interaction of each mode on electronic response



$R3c$ $R\bar{3}c$

$M(\Gamma_2^-|e)$ $M(\Gamma_2^-|f)$

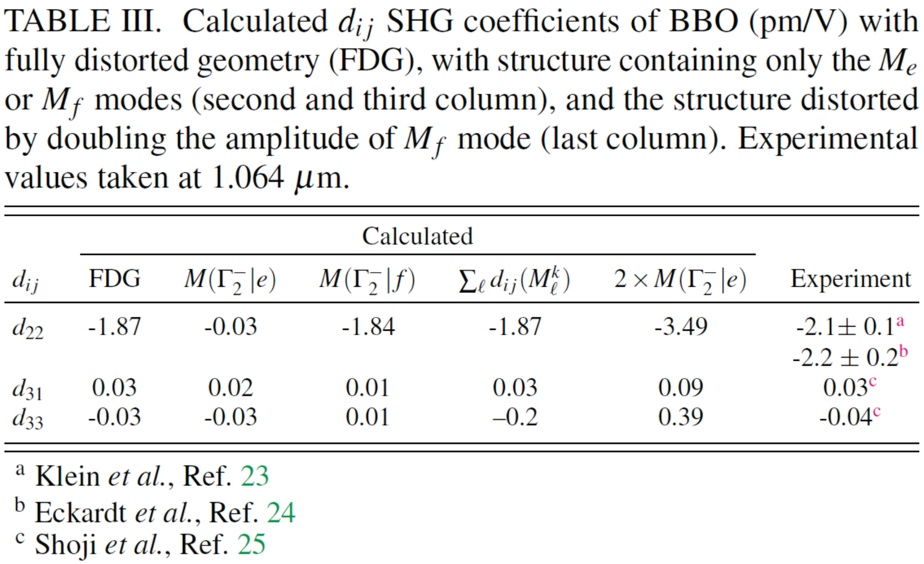


TABLE III. Calculated d_{ij} SHG coefficients of BBO (pm/V) with fully distorted geometry (FDG), with structure containing only the M_e or M_f modes (second and third column), and the structure distorted by doubling the amplitude of M_f mode (last column). Experimental values taken at 1.064 μm.

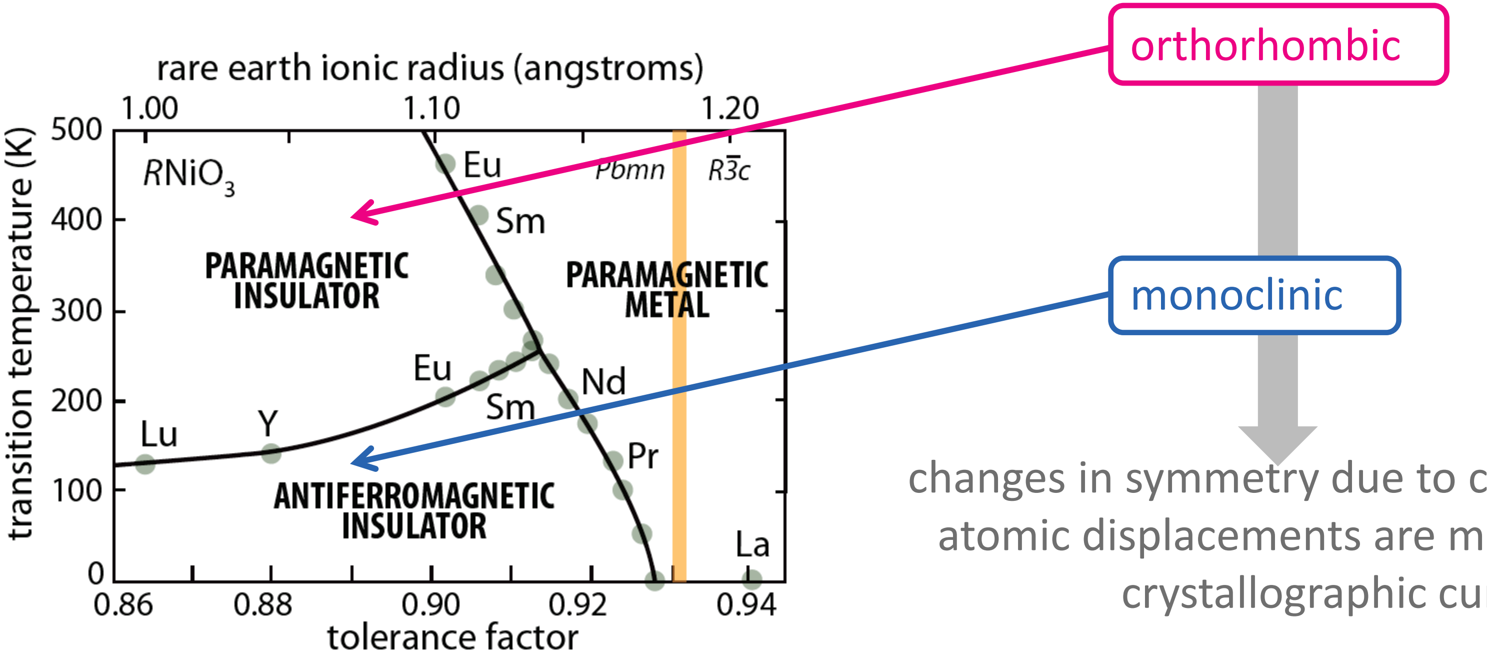
	Calculated					
d_{ij}	FDG	$M(\Gamma_2^-\|e)$	$M(\Gamma_2^-\|f)$	$\sum_\ell d_{ij}(M_\ell^k)$	$2\times M(\Gamma_2^-\|e)$	Experiment
d_{22}	-1.87	-0.03	-1.84	-1.87	-3.49	-2.1± 0.1[a] -2.2 ± 0.2[b]
d_{31}	0.03	0.02	0.01	0.03	0.09	0.03[c]
d_{33}	-0.03	-0.03	0.01	–0.2	0.39	-0.04[c]

[a] Klein *et al.*, Ref. 23
[b] Eckardt *et al.*, Ref. 24
[c] Shoji *et al.*, Ref. 25

A. Cammarata and JMR, Unpublished (2013)

Symmetry and structural effects across phase boundaries

- How can theory create structural design strategies for tailoring electronic metal-insulator phase boundaries?
  - Complex structural distortions determine electronic distribution
  - How do we rationally identify those features that are important to enhance?



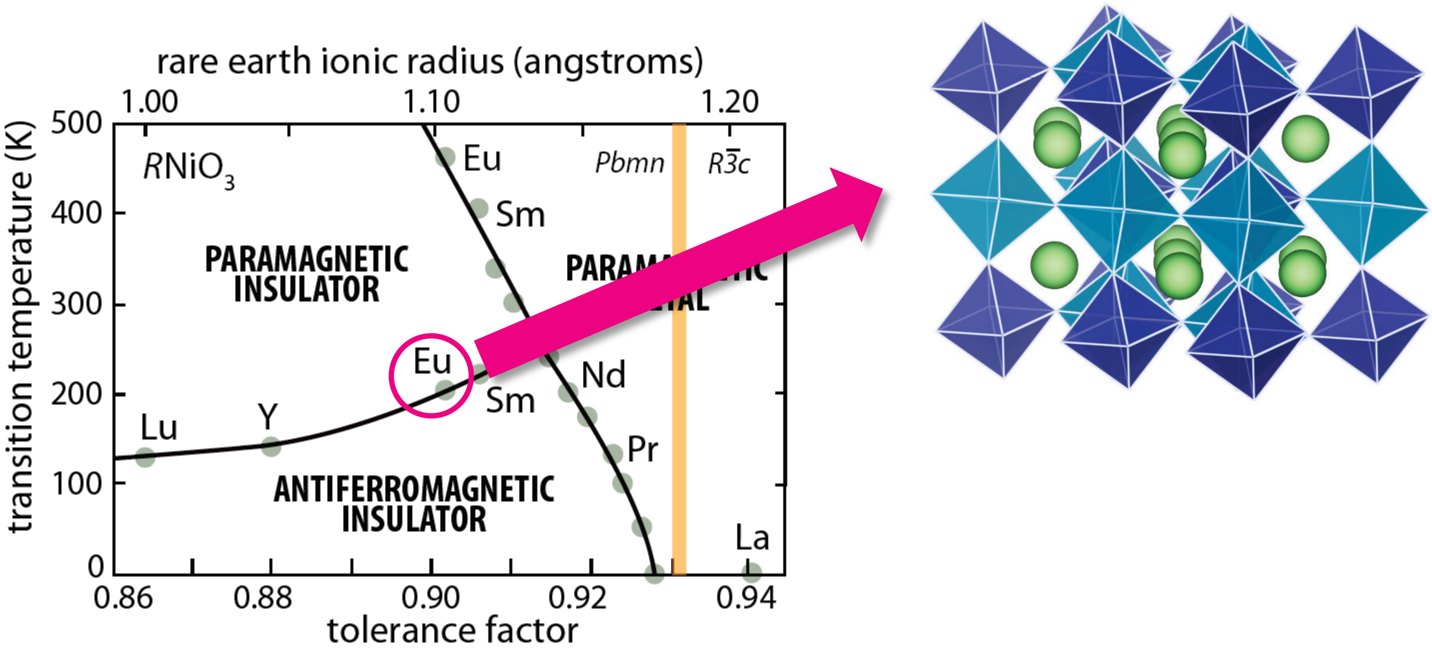
orthorhombic

monoclinic

changes in symmetry due to collective atomic displacements are more than crystallographic curiosities!

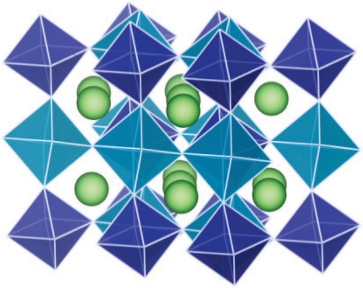
Symmetry and structural effects across phase boundaries

- How can theory create structural design strategies for tailoring electronic metal-insulator phase boundaries?
  - Take each structure in this complex phase space and decompose the displacements into a set of orthonormal symmetry modes

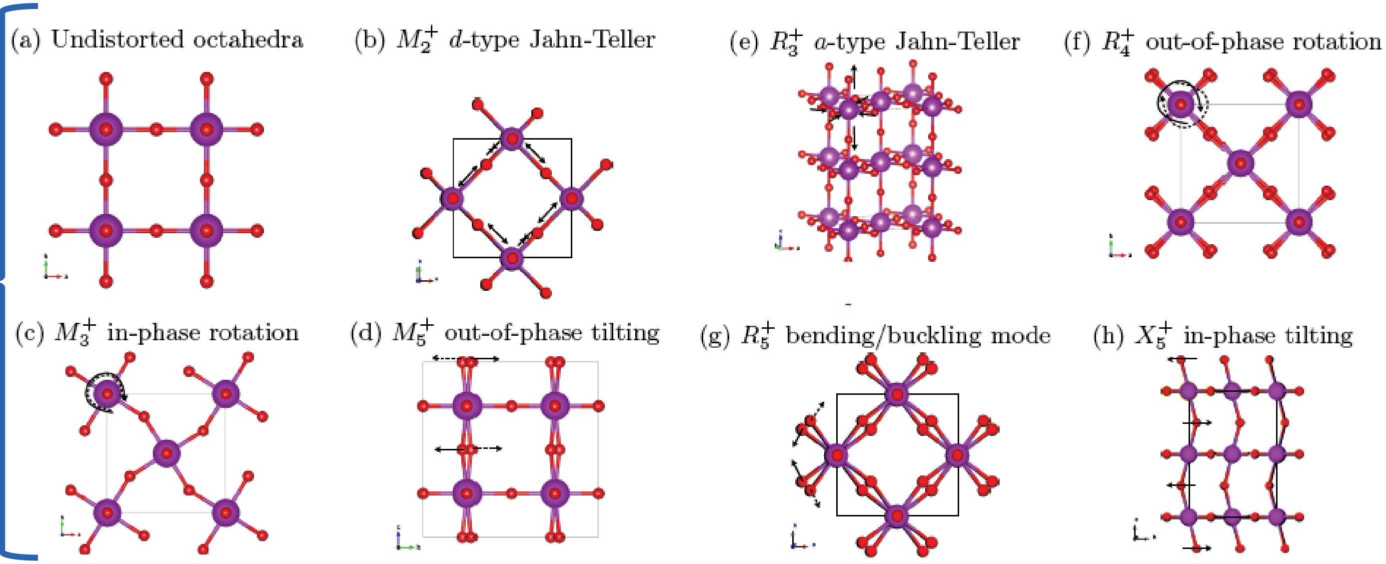


Symmetry and structural effects across phase boundaries

- Evaluate the covariance (statistical relationship) between each structural mode and the functional macroscopic response
  - T_{MI} – metal-insulator transition
  - T_N – AFM ordering transition



$$= \sum_{v=0}^{n} Cv \times (\text{displacement})$$



(a) Undistorted octahedra

(b) M_2^+ d-type Jahn-Teller

(e) R_3^+ a-type Jahn-Teller

(f) R_4^+ out-of-phase rotation

(c) M_3^+ in-phase rotation

(d) M_5^+ out-of-phase tilting

(g) R_5^+ bending/buckling mode

(h) X_5^+ in-phase tilting

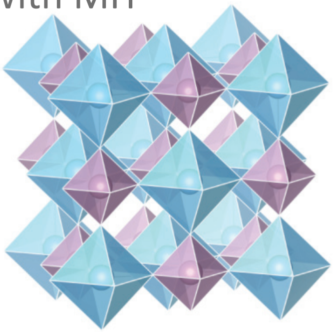
Symmetry and structural effects across phase boundaries

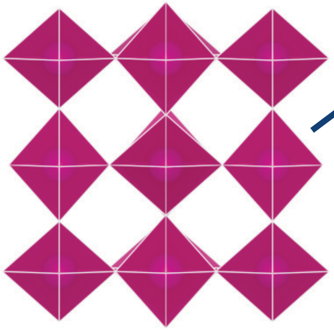
- Evaluate the covariance between each structural mode and the functional macroscopic response

T_{MI} – metal-insulator transition: correlated with rotations, breathing & bending of octahedra

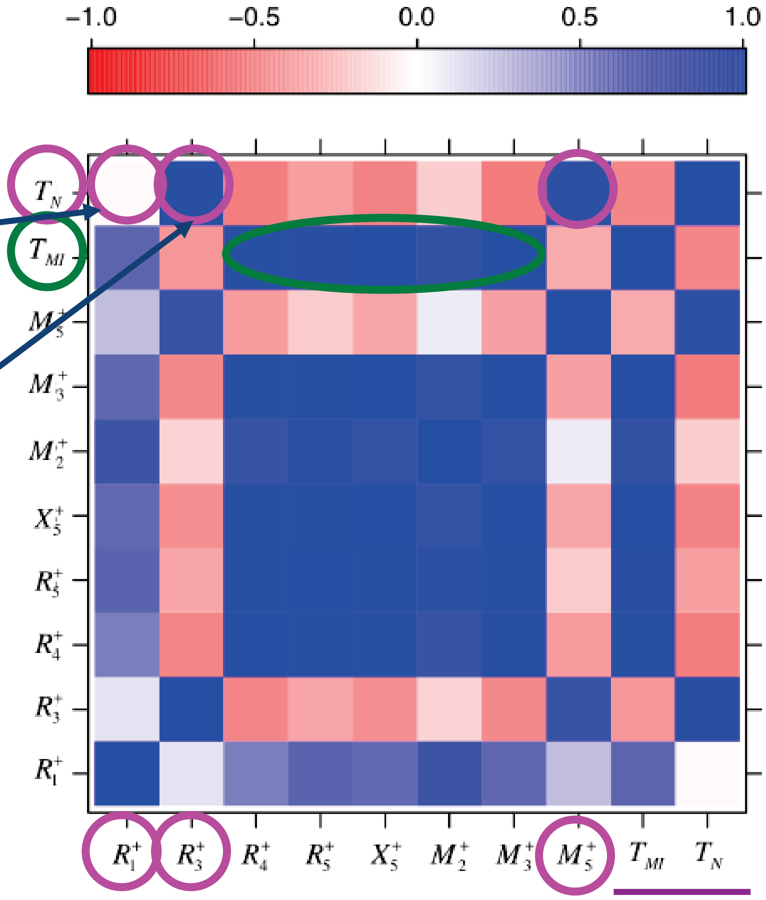
T_N – AFM ordering transition: correlated with first-order Jahn-Teller type of distortions

Breathing distortion correlated with MIT





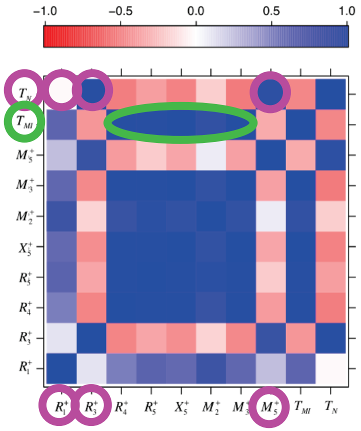
Jahn-Teller distortion correlated with magnetism



P.V. Balachandran & JMR, Phys. Rev. B, **88** 054101 (2013)

Symmetry and structural effects across phase boundaries

- Design rules to boost transition temperature begin to emerge…
  - Need to identify if the MIT in your material is magnetically mediated or not



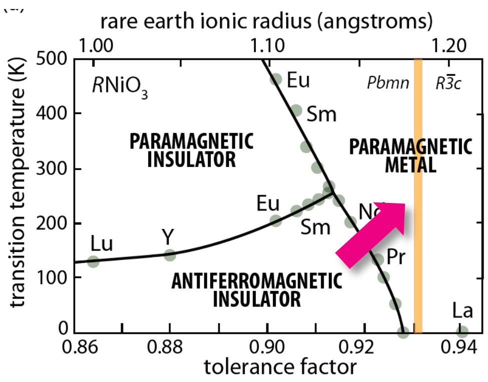
Design strategy for tailoring T_{MI}

I. Magnetic order dependent CO

➡ Promote Jahn-Teller distortions

II. CO independent of magnetism

➡ Promote BW narrowing distortions



design of afm metals?

Evaluating the microscopic origin of these correlations to extract new design rules

How do we accelerate (rational) materials discoveries?

- Extending the structure driven approach to many areas where new materials and microscopic mechanisms are needed by solving the *inverse Landau problem*

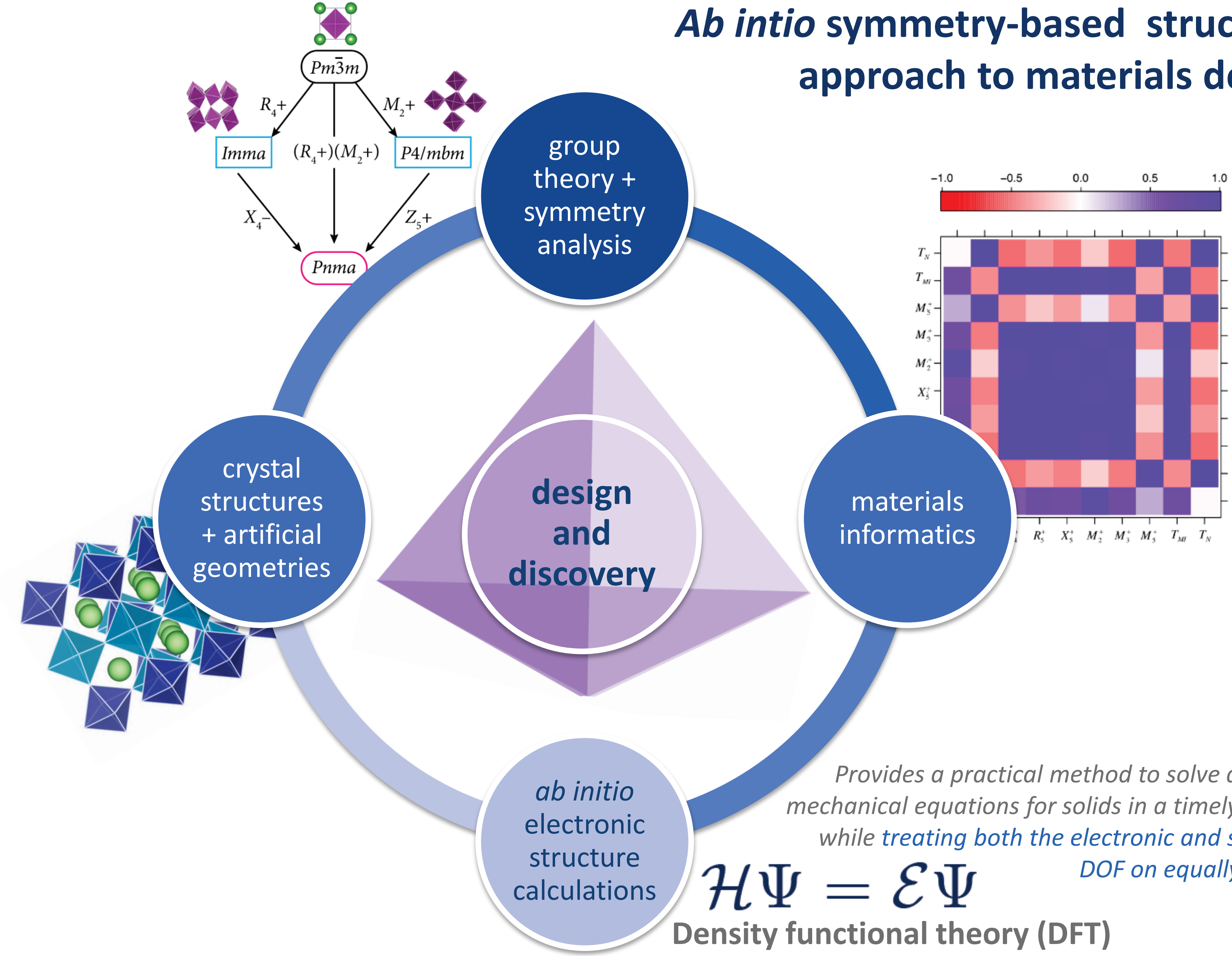
- *What distortions (atomic configurations) should I freeze into a structure to obtain a targeted property*?

  - *How can the atomic structure support the interactions I want?* *Structural Criterion*

  - *How can I choose the best chemistries to promote that interaction?* *Selection Criterion*

- Formulate a minimal theory based on atomic scale (unit cell) structure with quantitative descriptors to understand, predict, and design artificial materials

Ab intio symmetry-based structural approach to materials design



group theory + symmetry analysis

crystal structures + artificial geometries

design and discovery

materials informatics

ab initio electronic structure calculations

Provides a practical method to solve quantum mechanical equations for solids in a timely fashion while treating both the electronic and structure DOF on equally footing

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

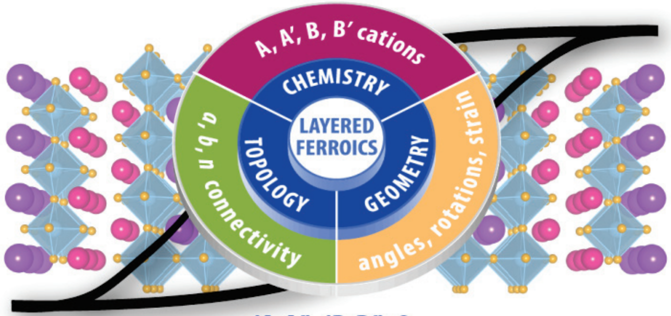
Density functional theory (DFT)

Designing atomic-scale electronic function – Outline

- ***Foreword*** (9-10.30a)
  - Main challenges
  - Why complex oxides provide the ultimate “sand box”
  - Structure-driven properties of materials paradigm
  - Theoretical / Computational tools to formulate an understanding for design

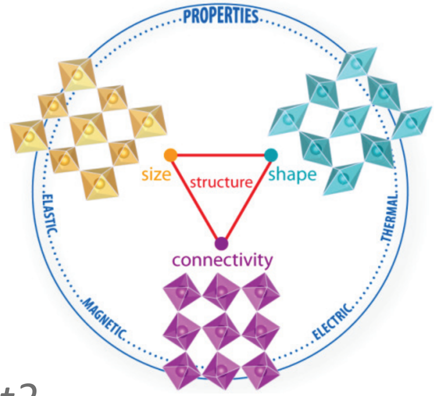
- ***Coffee break*** (10.30-11a)

- ***Feature*** (11-12.30p)
  - *Ab initio* symmetry-based structural design protocol: confluence of group theory, electronic structure theory, and data-mining
  - Design of emergent ferroelectricity and multiferroism in artificial oxides



$(A,A')_a(B,B')_bO_n$

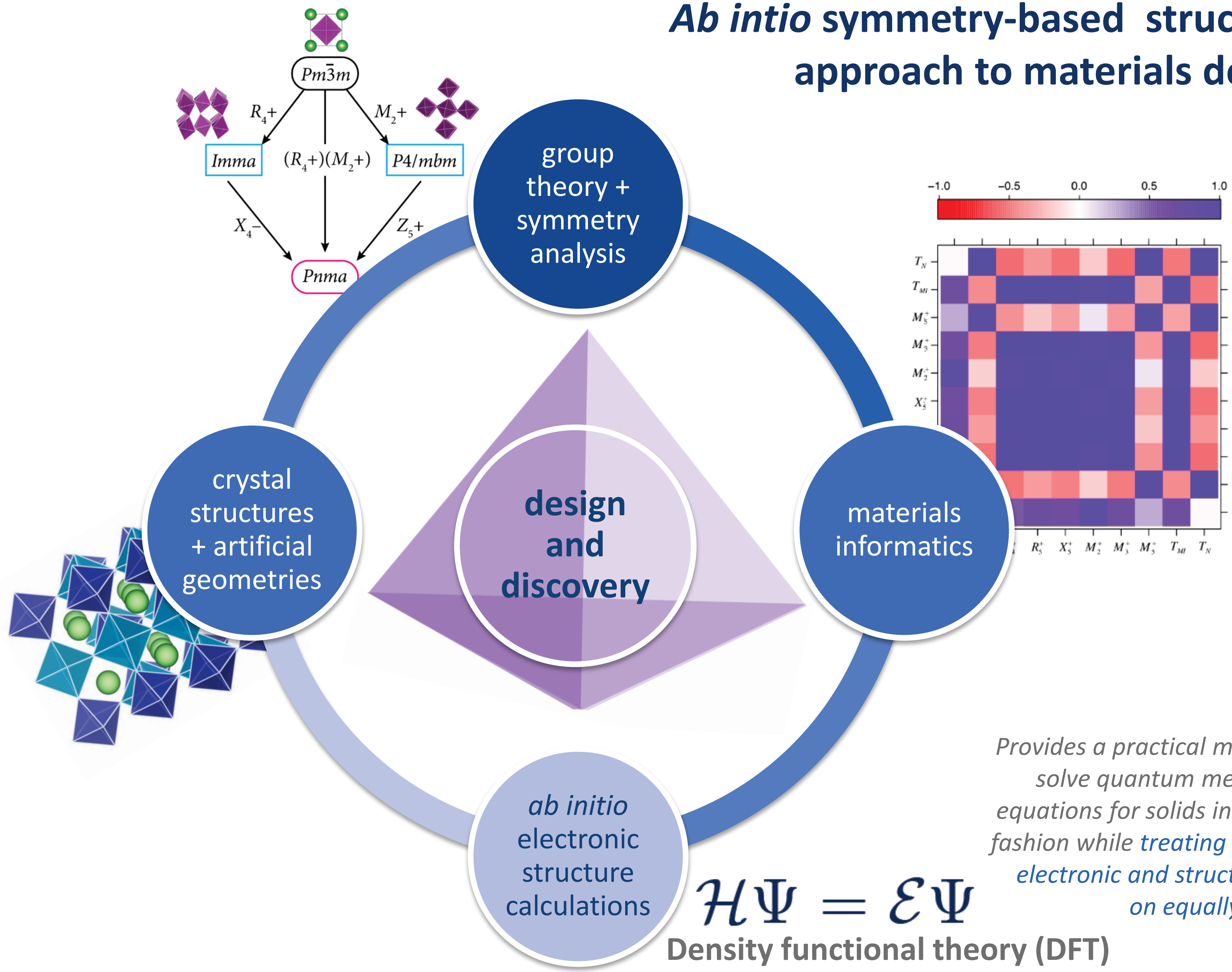
Structure-based approach for materials design



- Identify and exploit structure–property relationships
- Correlate electronic and magnetic properties to the basic structural units
  - *How can the atomic structure support the interactions I want?*
    Structural Criterion
  - *How can I choose the best chemistries to promote that interaction?*
    Selection Criterion
  - *How can I leverage additional degrees of freedom to enhance the response?*
    Response Optimization

JMR, May, Freeland, MRS Bulletin **37** 261 (2012)

Ab intio symmetry-based structural approach to materials design



group theory + symmetry analysis

materials informatics

ab initio electronic structure calculations

crystal structures + artificial geometries

design and discovery

Provides a practical method to solve quantum mechanical equations for solids in a timely fashion while treating both the electronic and structure DOF on equally footing

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

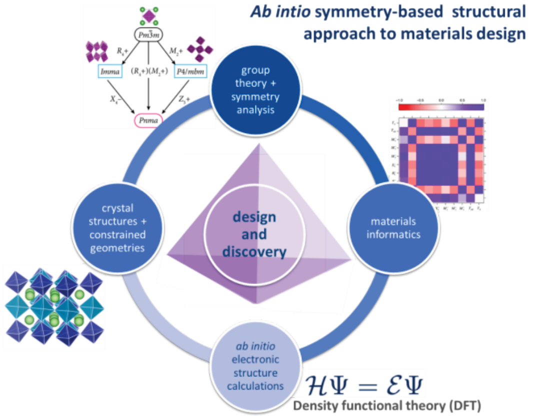
Density functional theory (DFT)

Design of a new mechanism for ferroelectricity—electric polarizations induced by non-polar displacements

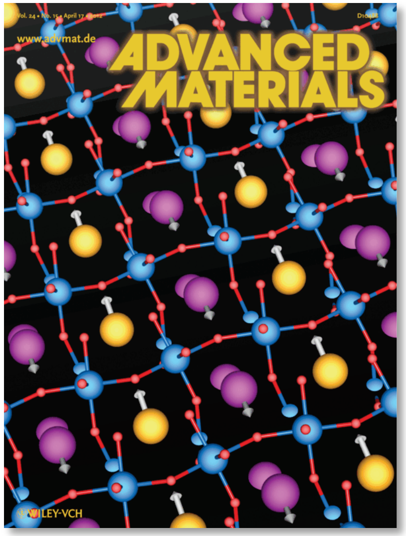
Modern Materials Design

Design modalities in materials research today

Structure-based approach to mechanistic physical property design

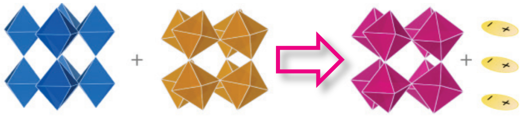


Emergent Ferroelectricity



JMR & Fennie, Adv. Mater., **24** 1961 (2012)

$$ABO_3 + A'BO_3 = (A,A')B_2O_6$$

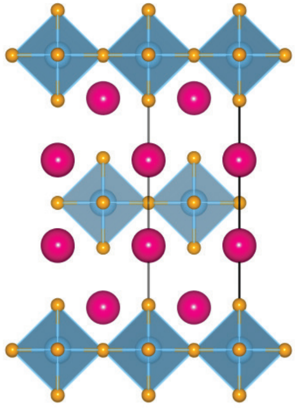


Design Dividends

Multiferroic Materials in layered Ruddlesden-Popper structures

DISCOVERY

FUNCTIONALITY



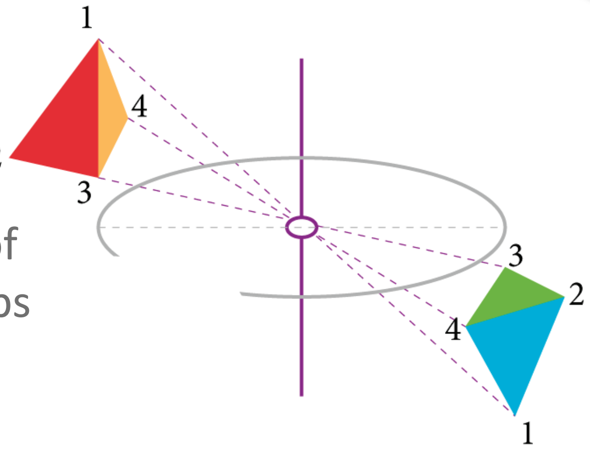
How do we rationally discover new ferroelectrics and will they have any novel properties or features?

How do we rationally discover new ferroelectrics and will they have any novel properties or features?

- **Ferroelectric** materials exhibit a macroscopic electrical polarization that can be switched with an external electric field
  - Property: Polarization
  - Definition: Spontaneous electric dipole per unit volume
  - Symmetry: Must exist in a polar point group

Structural Requirement

Absence of the parity operation of inversion; the element which maps coordinate (*x*,*y*,*z*) to (-*x*,-*y*,-*z*)



In the design process, we want to focus on microscopic mechanisms

- What mechanisms already exists to support ferroelectricity?

Microscopic mechanisms for ferroelectricity

- Second-order Jahn-Teller effect – chemistry specific
- Geometric-driven/Accidental ferroelectrics – cation size mismatch without chemical bond formation
    - $YMnO_3$, A_2CuTiO_6, $BaMF_4$ (M=Mn,Fe,Co,Ni)

Can we find an alternative route to lift inversion symmetry and create a ferroelectric?

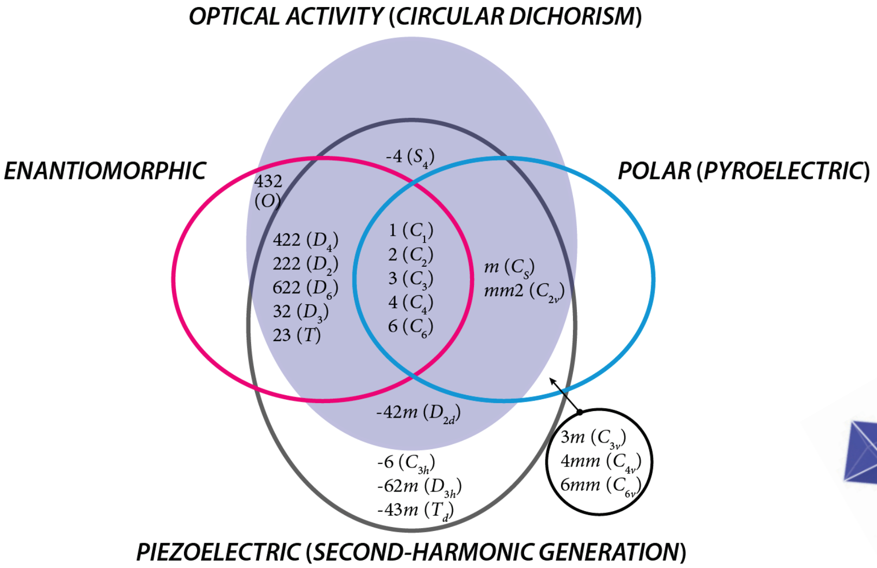
Ab intio symmetry-based structural approach to materials design

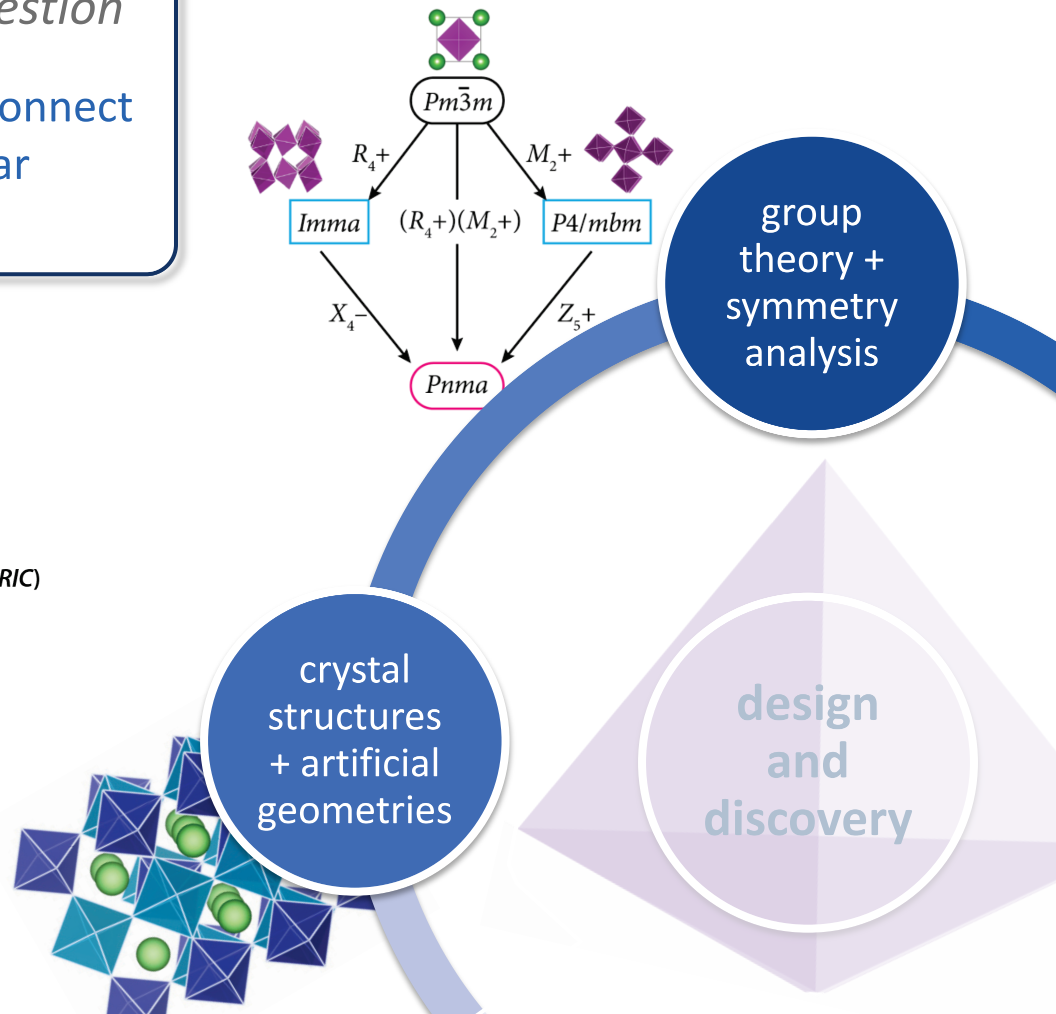
- Use applied group to perform a symmetry-based search on known structures to evaluate the microscopic displacements that remove inversion symmetry

We ask the following structural question

What types of atomic displacements connect a high-symmetry space group to a polar structure of lower symmetry?

Do we discovery anything new?



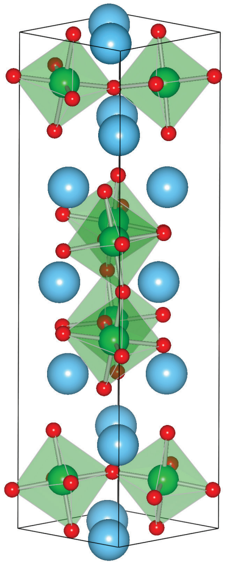


group theory + symmetry analysis

crystal structures + artificial geometries

design and discovery

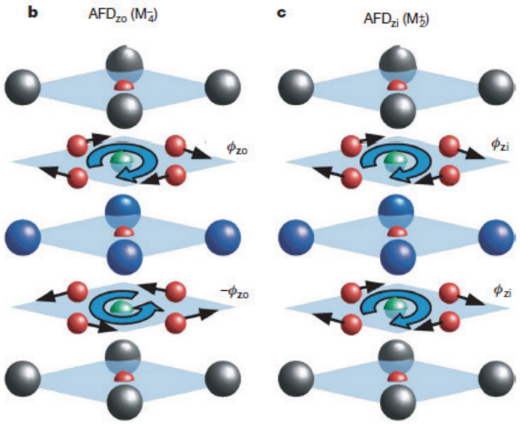
Octahedral rotations plus "layering" can lift inversion symmetry and support electric polarizations

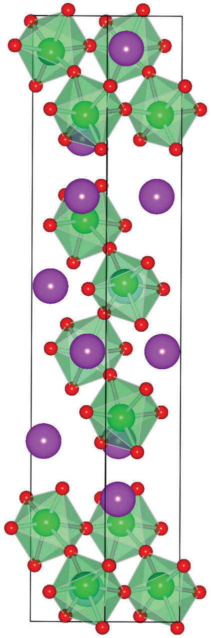


$Ca_3Ti_2O_7$
$Ca_3Mn_2O_7$

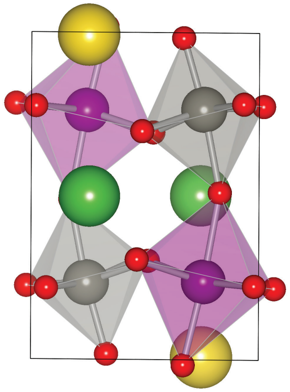
Benedek & Fennie,
PRL **106**, 107204 (2011)

$(PbTiO_3)_1(SrTiO_3)_1$
Bousquet *et al.*, Nature **452**, 732 (2008)





$La_2Ti_2O_7$
López-Pérez and Íñiguez
PRB **84**, 075121 (2011)

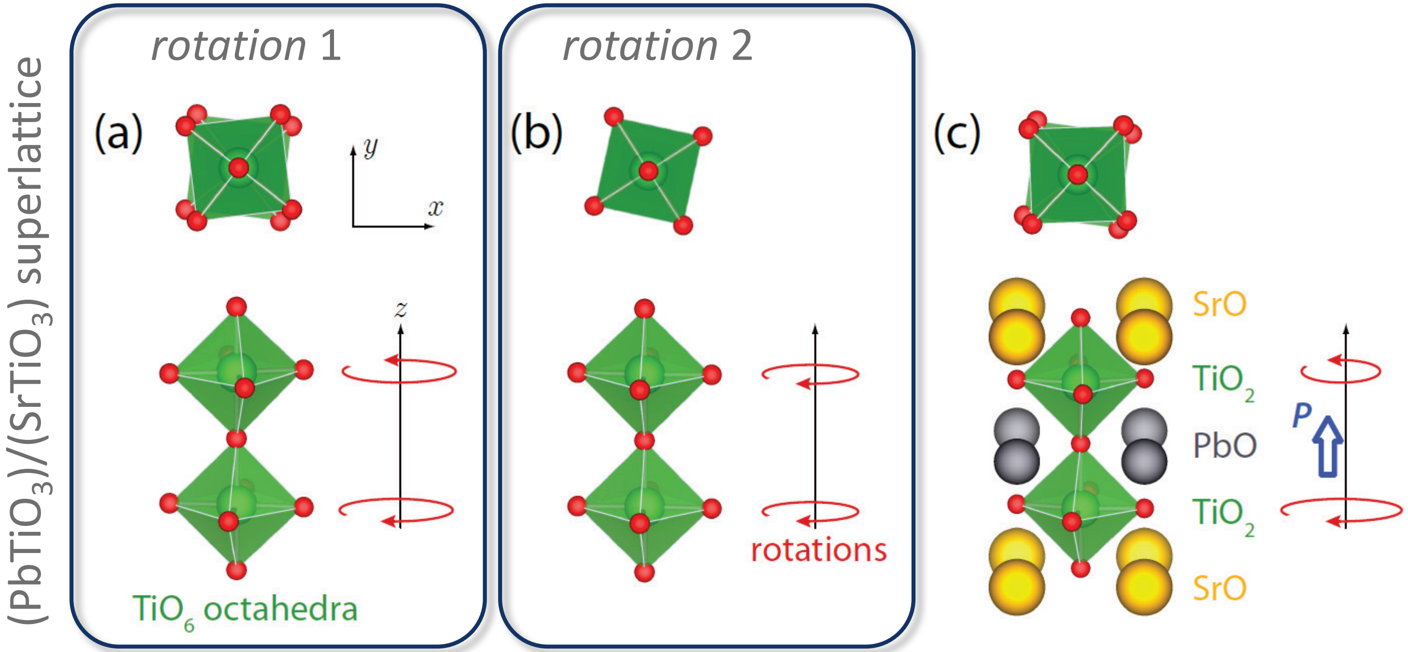


$NaLaMnWO_6$
Fukushima *et al.*, PSSP **13**
12186 (2011)

In each case, **TWO** non-polar rotations of different symmetry "freeze-in" to produce or contribute to the electric polarization

Cooperative rotations of octahedra can support electric polarizations

- It is possible to obtain a contribution to the total polarization from an "improper" contribution in a perovskite superlattice



TWO zone boundary modes freeze-in to induce a polarization

Bousquet *et al.*, Nature **452**, 732 (2008)

Can one rationally design and predict octahedral rotation-induced ferroelectrics in artificial materials?

Just because one discovers an example of a new form of ferroelectricity, doesn't mean we know how to create more…

Why do we even want to do this?

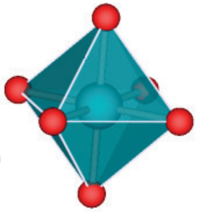
- Polyhedra connectivity in transition metal oxides largely influences the electronic and magnetic properties – new route to coupling multiple degrees of freedom

- *Chemistry-independent mechanism for ferroelectricity* – desirable compositions can transformed into ferroelectrics (multiferroics)

- New mechanisms for ferroics and classes of materials with potential applications (design dividends)
  - Isosymmetric phase transitions
  - High-temperature piezoelectric materials
  - High energy density storage materials

Where do we start the design process?

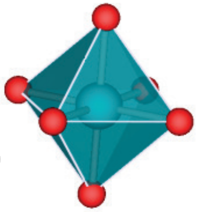
- *How can the atomic structure support the interactions I want?* *Structural Criterion*
  - Need materials with polyhedral units (octahedra)



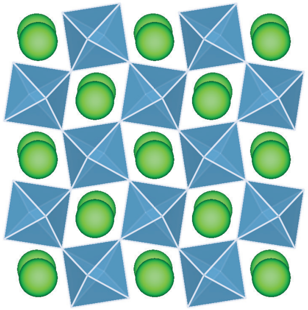
  - The octahedra should be corner-connected so they can readily rotate

Where do we start the design process?

- *How can the atomic structure support the interactions I want?*
  Structural Criterion
  - Need materials with polyhedral units (octahedra)

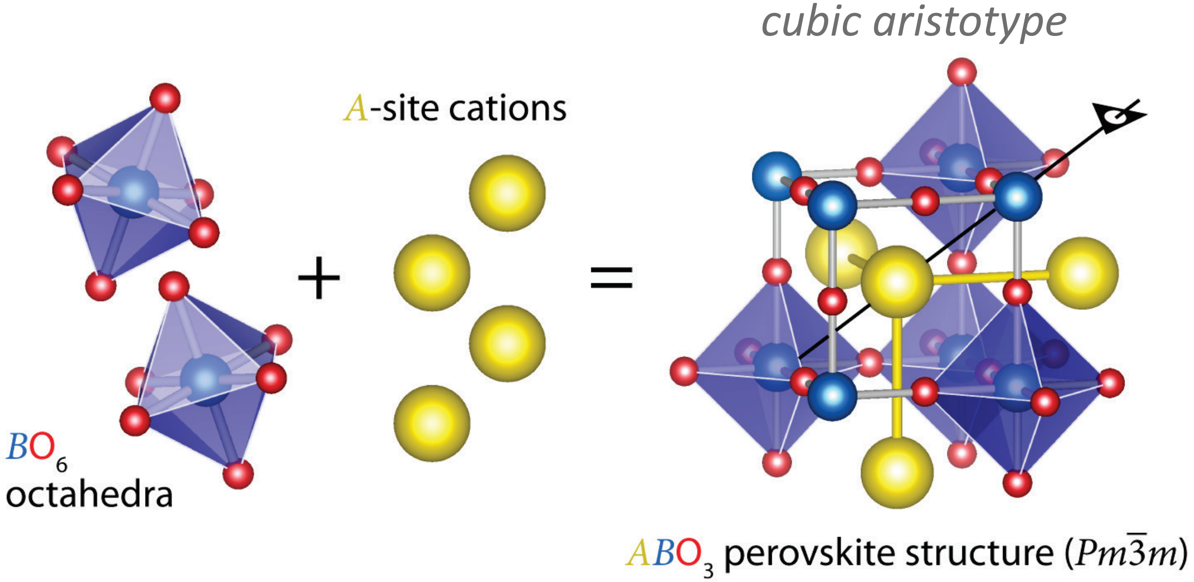


  - The octahedra should be corner-connected so they can readily rotate



perovskite ($CaTiO_3$)

What about the symmetry requirements?

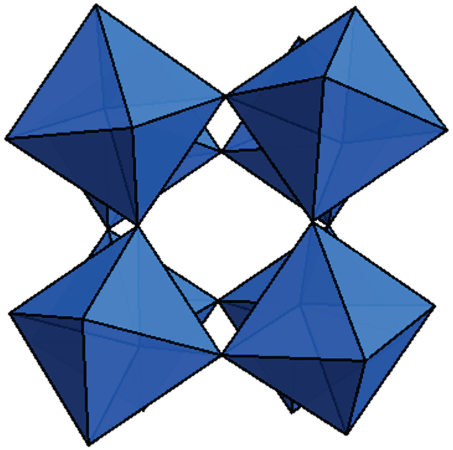


polar ⇨ absence of inversion symmetry (missing mirror)

centric octahedra ⇨ molecular BO_6 units with inversion symmetry

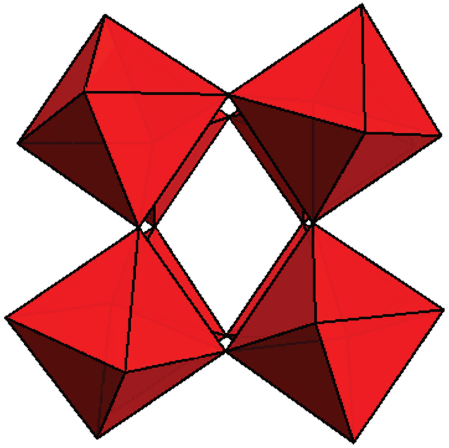
Few perovskites are cubic due to rotational distortions, yet they retain their centricity

- Two main rotational distortions in perovskites (~75% exhibit these tilts)



rhombohedral (*a-a-a-*)

D_{3d}



orthorhombic (*a-a-b+*)

D_{2h}

point symmetry at transition metal center

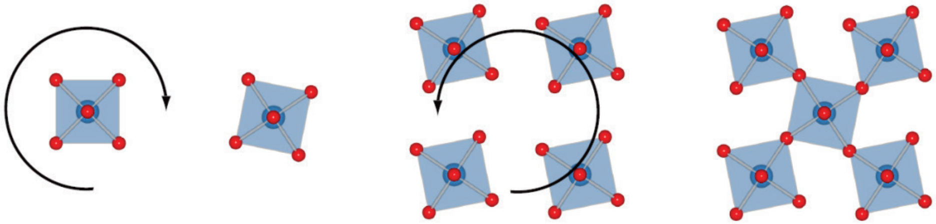
$\bar{3}$

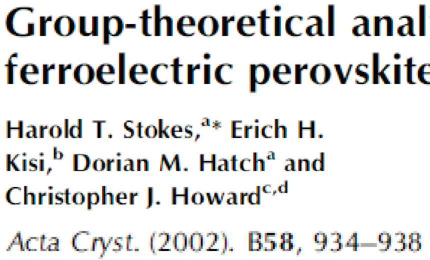
$\bar{1}$

Distortions from cubic to these lower symmetry structures preserve the octahedra centricity

Tiling of centric polyhedra in three dimensions

- No combinations of octahedral rotations in a single phase ABO_3 perovskite break inversion symmetry



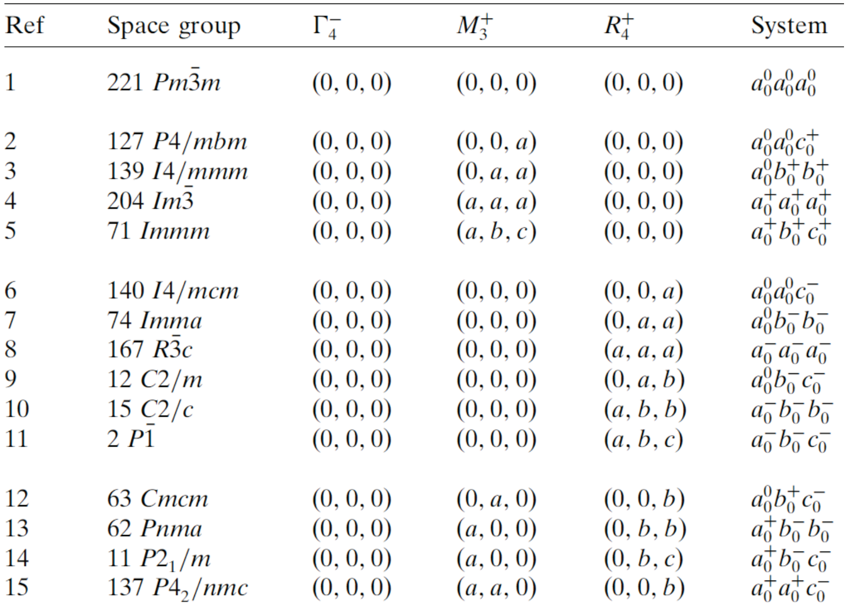


Group-theoretical analysis of octahedral tilting in ferroelectric perovskites

Harold T. Stokes,[a]* Erich H. Kisi,[b] Dorian M. Hatch[a] and Christopher J. Howard[c,d]

Acta Cryst. (2002). B58, 934–938

centrosymmetric space groups



Ref	Space group	Γ_4^-	M_3^+	R_4^+	System
1	221 $Pm\bar{3}m$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0a_0^0$
2	127 $P4/mbm$	(0, 0, 0)	(0, 0, a)	(0, 0, 0)	$a_0^0a_0^0c_0^+$
3	139 $I4/mmm$	(0, 0, 0)	(0, a, a)	(0, 0, 0)	$a_0^0b_0^+b_0^+$
4	204 $Im\bar{3}$	(0, 0, 0)	(a, a, a)	(0, 0, 0)	$a_0^+a_0^+a_0^+$
5	71 $Immm$	(0, 0, 0)	(a, b, c)	(0, 0, 0)	$a_0^+b_0^+c_0^+$
6	140 $I4/mcm$	(0, 0, 0)	(0, 0, 0)	(0, 0, a)	$a_0^0a_0^0c_0^-$
7	74 $Imma$	(0, 0, 0)	(0, 0, 0)	(0, a, a)	$a_0^0b_0^-b_0^-$
8	167 $R\bar{3}c$	(0, 0, 0)	(0, 0, 0)	(a, a, a)	$a_0^-a_0^-a_0^-$
9	12 $C2/m$	(0, 0, 0)	(0, 0, 0)	(0, a, b)	$a_0^0b_0^-c_0^-$
10	15 $C2/c$	(0, 0, 0)	(0, 0, 0)	(a, b, b)	$a_0^-b_0^-b_0^-$
11	2 $P\bar{1}$	(0, 0, 0)	(0, 0, 0)	(a, b, c)	$a_0^-b_0^-c_0^-$
12	63 $Cmcm$	(0, 0, 0)	(0, a, 0)	(0, 0, b)	$a_0^0b_0^+c_0^-$
13	62 $Pnma$	(0, 0, 0)	(a, 0, 0)	(0, b, b)	$a_0^+b_0^-b_0^-$
14	11 $P2_1/m$	(0, 0, 0)	(a, 0, 0)	(0, b, c)	$a_0^+b_0^-c_0^-$
15	137 $P4_2/nmc$	(0, 0, 0)	(a, a, 0)	(0, 0, b)	$a_0^+a_0^+c_0^-$

Tiling of centric polyhedra in three dimensions

- No combinations of octahedral rotations in a single phase *AB*O_3 perovskite break inversion symmetry

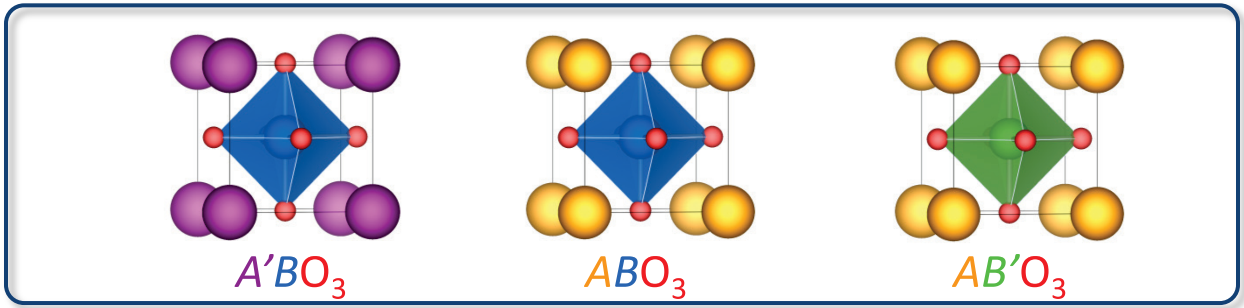
PROBLEM!

how do we formulate design rules for centric octahedral rotation-induced ferroelectricity?

Create an artificially layered perovskite to replicate the "two-dimensionality" found in the crystallographic structure search

Interleave two common dielectrics to support rotation-induced ferroelectricity

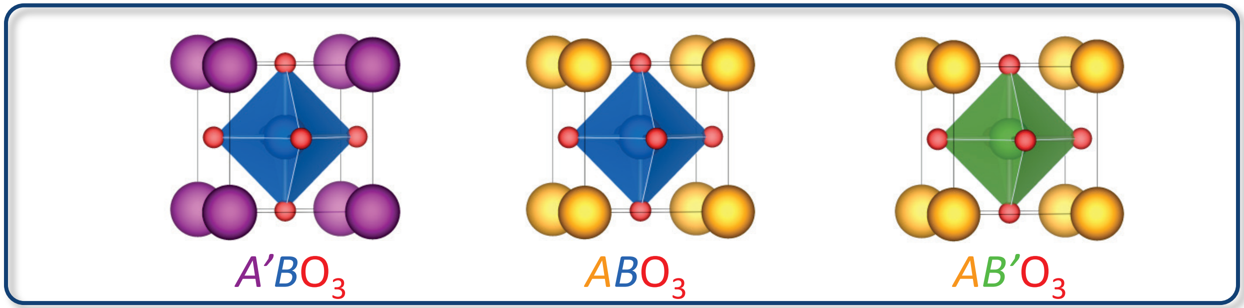
three bulk materials



Interleave two common dielectrics to support rotation-induced ferroelectricity

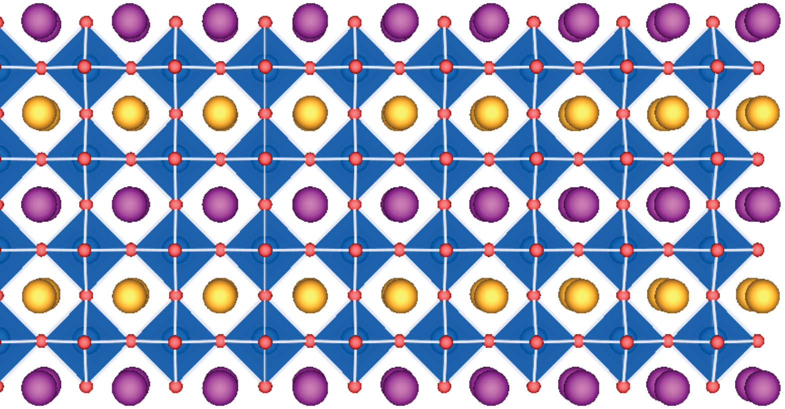
- Two possible simple cation ordering schemes

three bulk materials

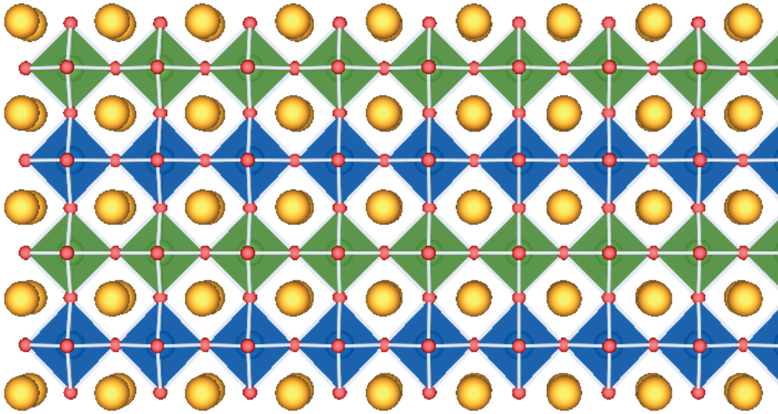


$A'BO_3$ ABO_3 $AB'O_3$

$(A',A)B_2O_6$

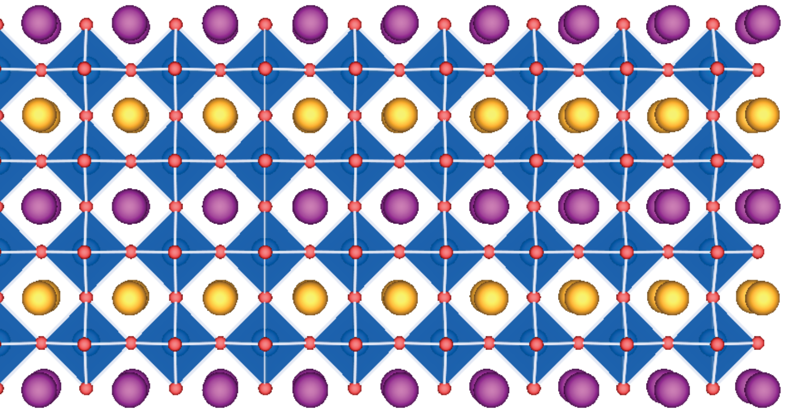


$A_2(B,B')O_6$



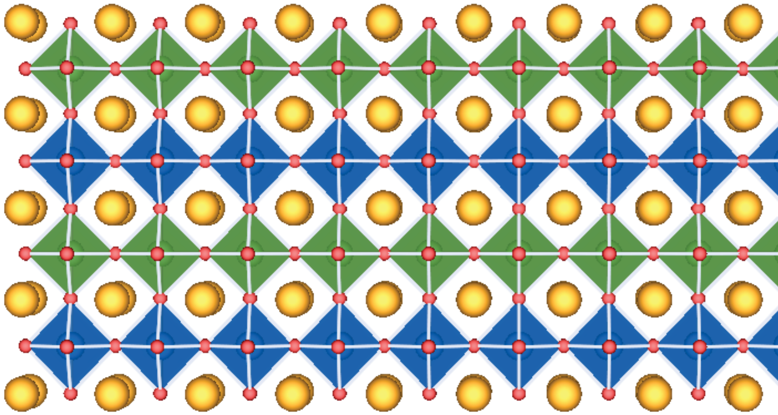
Consequences of cation order on inversion symmetry

$(A',A)B_2O_6$



Continuous *B*-site cation sublattice

$A_2(B,B')O_6$

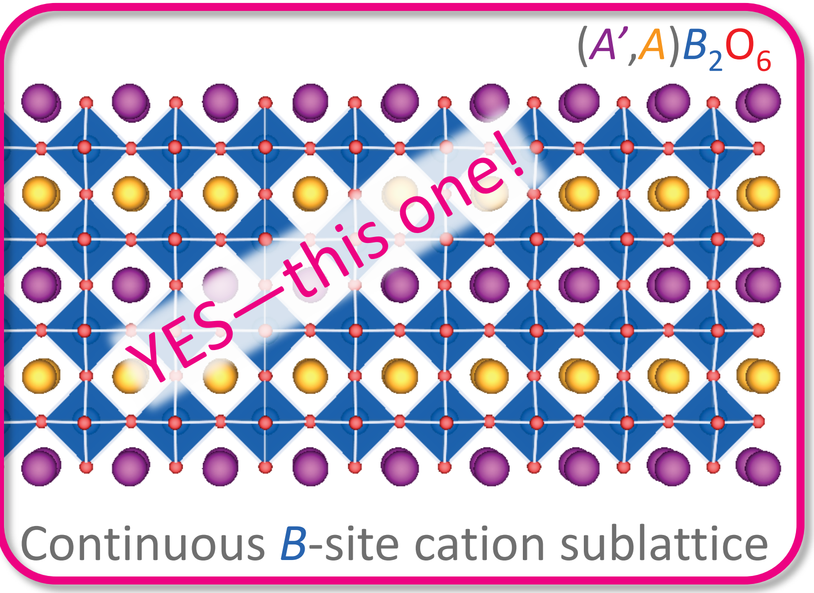


Continuous *A*-site cation sublattice

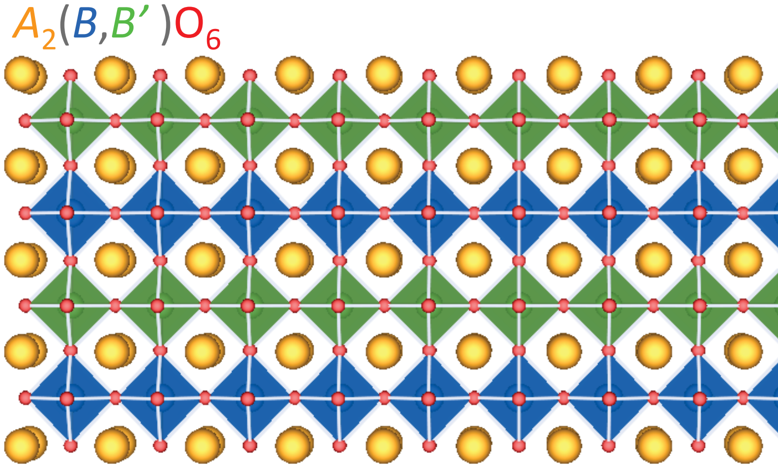
1. Cation ordering alone maintains inversion symmetry D_{4h}
2. Rotations in absence of cation ordering also preserve inversion symmetry

Is there a combination of (1) and (2) *that breaks inversion symmetry?*

Consequences of cation order and rotations on inversion symmetry



Continuous *B*-site cation sublattice

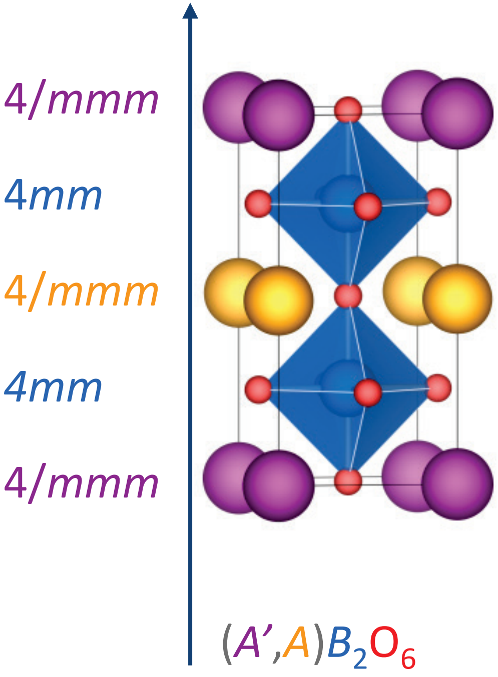


Continuous *A*-site cation sublattice

In the **absence of any polar atomic displacements** two symmetry unique BO_6 rotations and A/A′ cation order break inversion symmetry

Crystallographic origin of rotation-induced ferroelectricity

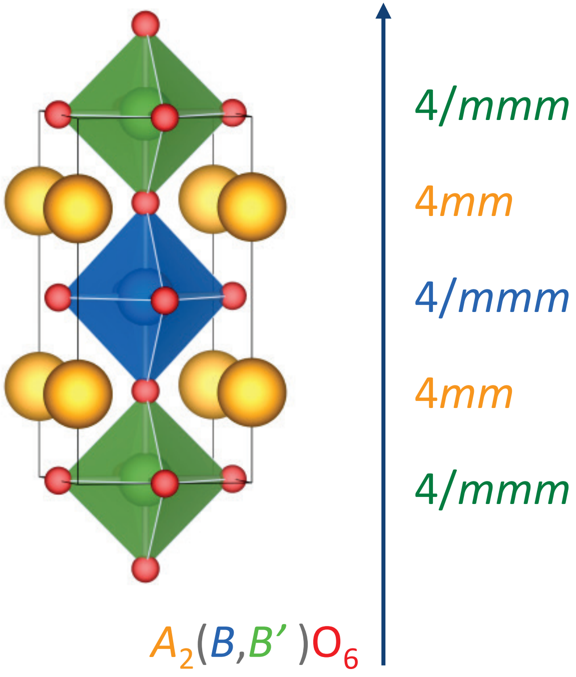
- Consider only the site symmetry at the cation-positions in the ordered structures



4/mmm
4mm
4/mmm
4mm
4/mmm

$(A',A)B_2O_6$

inversion centers on *A*-sites



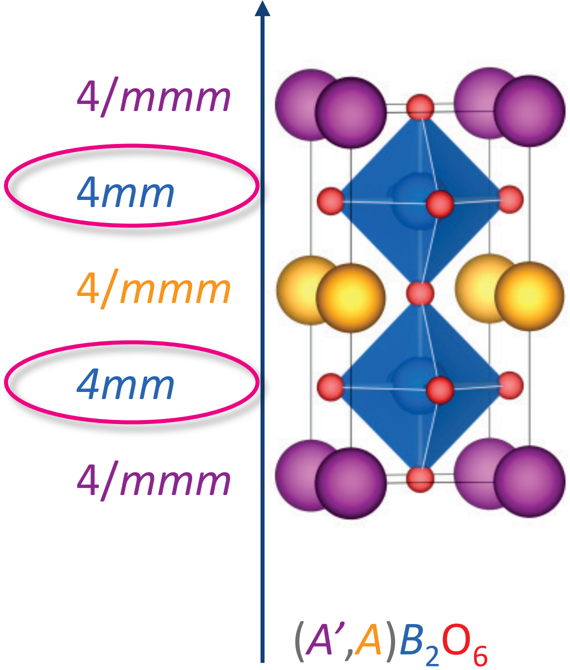
4/mmm
4mm
4/mmm
4mm
4/mmm

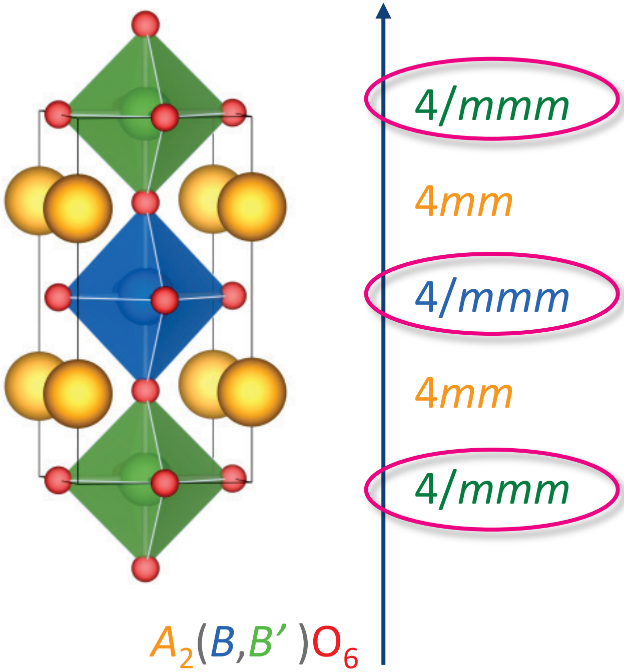
$A_2(B,B')O_6$

inversion centers on *B*-sites

Octahedral rotations remove inversion symmetry on the *A*-site

- The site symmetry at the cation-positions depends on the ordered arrangement of atoms!





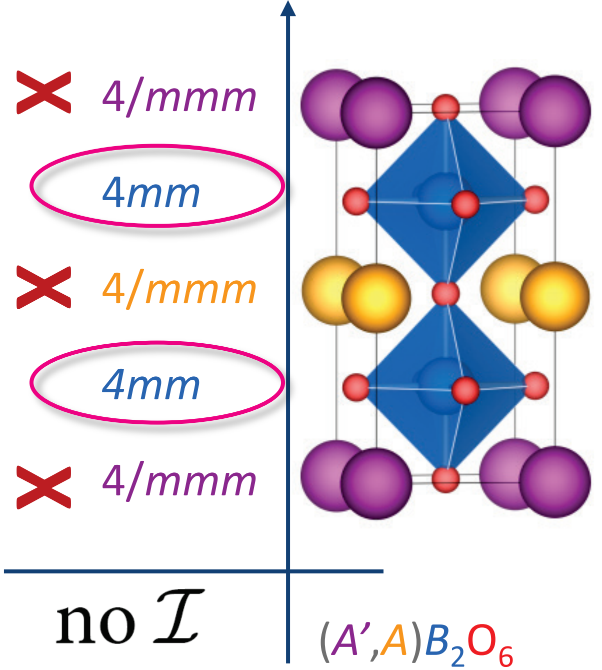
inversion centers on *A*-sites

inversion centers on *B*-sites

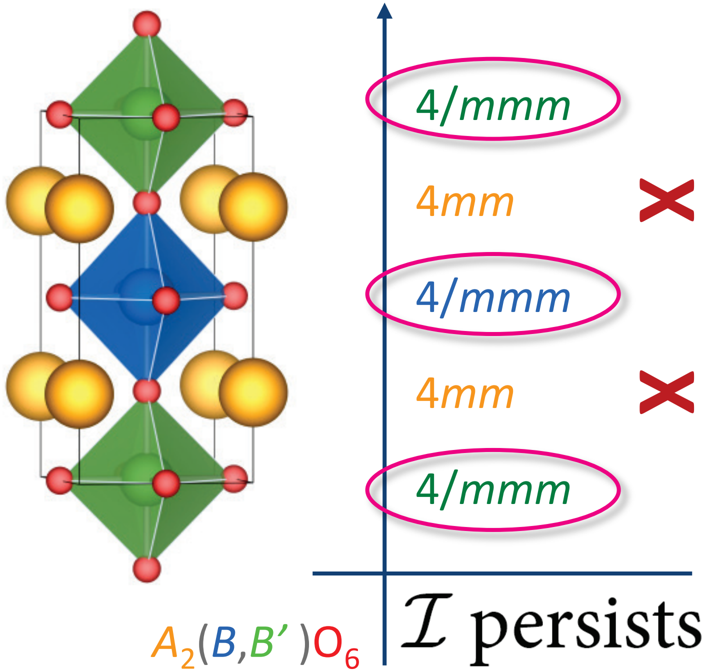
Rotations always preserve inversion on *B*-sites

Octahedral rotations remove inversion symmetry on the *A*-site

- The site symmetry at the cation-positions depends on the ordered arrangement of atoms!



inversion centers on *A*-sites



inversion centers on *B*-sites

Rotations always preserve inversion on *B*-sites

but can destroy it on A-sites

Implications for the design of new ferroelectrics

- Rotations can induce a polarization through **trilinar linear coupling** among octahedral rotations and a polar mode (hybrid-improper ferroelectricity*)

$$P \sim (\mathcal{R}_1 \cdot \mathcal{R}_2)$$

No SOJT cations are needed

chemistry independent mechanism

Leads to a number of trilinear free energy invariants coupling rotations to a polarization: $P_{xy}\phi_z^+\psi_{xy}^-$

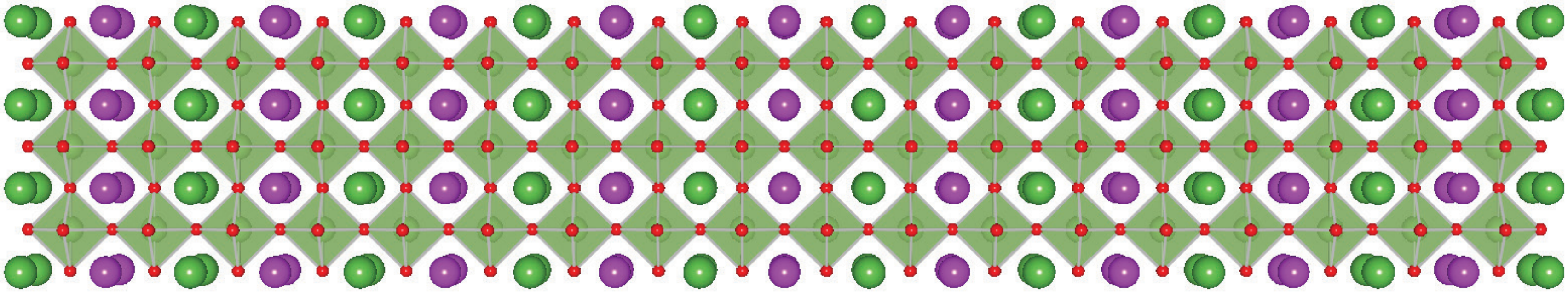
---

*Benedek & Fennie, PRL, **106** 107204 (2011)

When do the octahedral rotations *induce* polar displacements?

- Condition(s) for rotation-induced ferroelectricity

  1. *Suitable* site-symmetry: ordered *A*/*A'* sublattice } chemistry



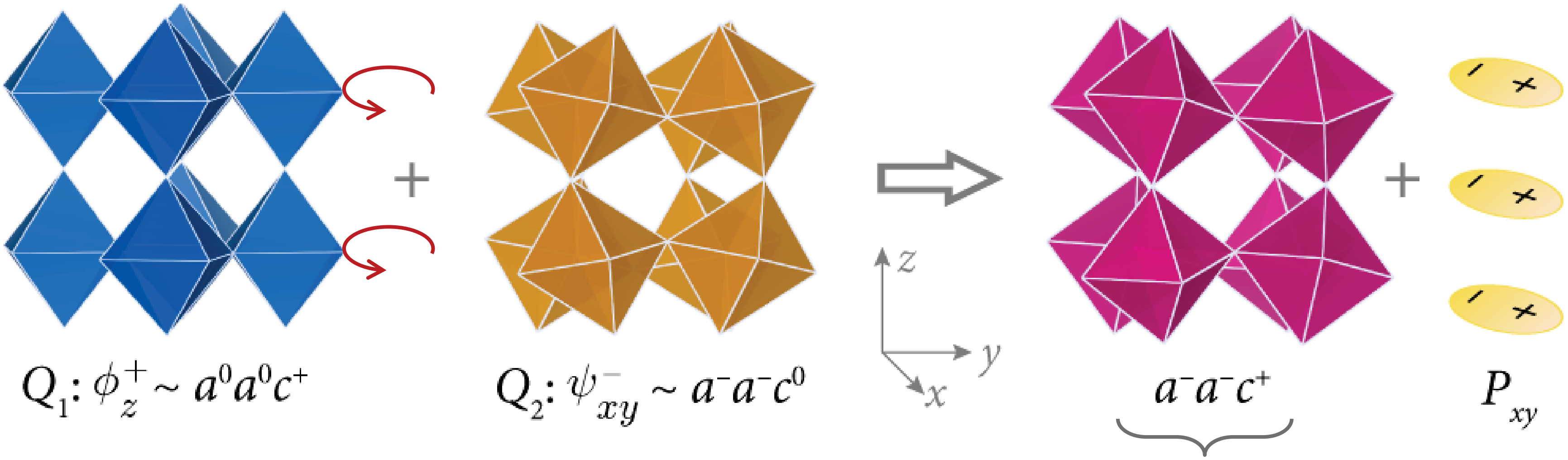
Is this condition sufficient? No…it's necessary, but insufficient.

For the rotations to induce a large ionic polarization they must dominate the energy landscape

JMR & Fennie, Adv. Mater., **24** 1961 (2012)

Validate the additional energetic criterion using the *orthorhombic* tilt pattern

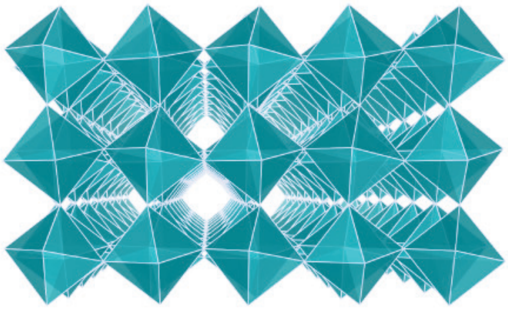
- Explore energy criterion using the invariant $P_{xy}\phi_z^+\psi_{xy}^-$



common orthorhombic perovskite tilt pattern

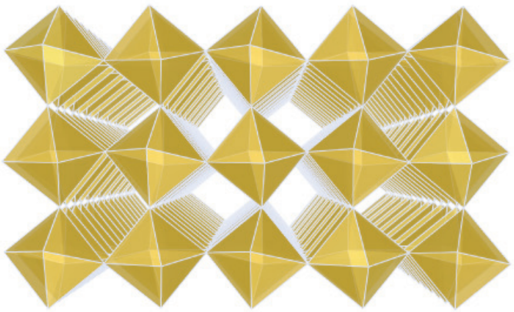
To design a ferroelectric from rotations and cation order, we also need a robust insulator

- *Structural Criterion*
  - Symmetry arguments suggest most probable structures and geometries
- *Selection Criterion*
  - Filled electronic shells guarantee insulating behavior



rhombohedral tilt $a^-a^-a^-$

$LaAlO_3$
$BiAlO_3$



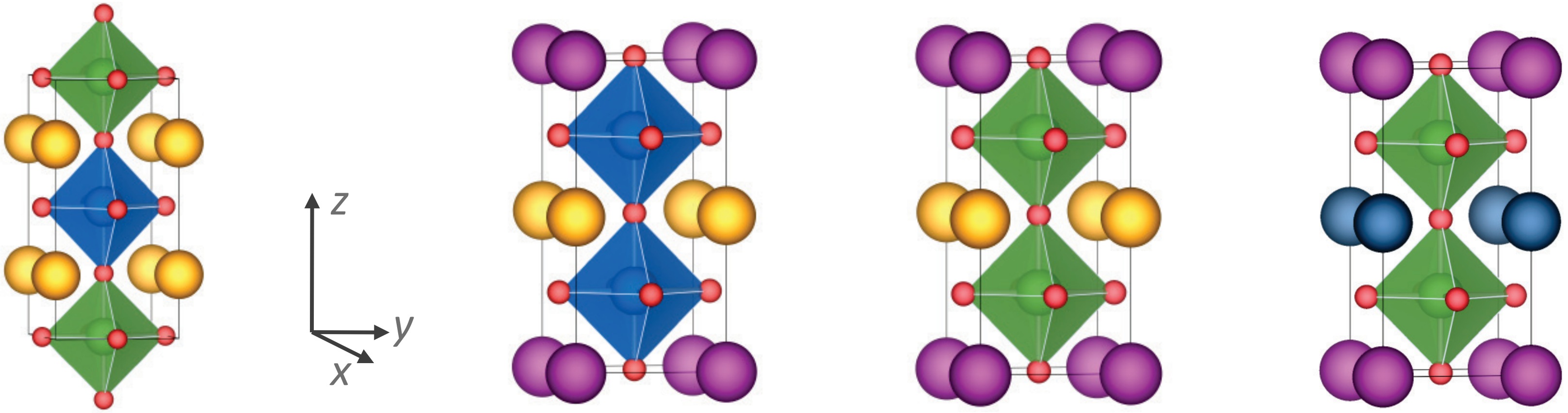
orthorhombic tilt $a^-a^-c^+$

$YAlO_3$
$YGaO_3$
$LaGaO_3$

Designing properties requires control of ***electron count*** *and the* ***extended crystal structure***

First-principles validation of materials design criteria

- Examine four ordered perovskites to identify the full materials design criteria



$YGaO_3/YAlO_3$ $LaGaO_3/YGaO_3$ $LaAlO_3/YAlO_3$ $LaAlO_3/BiAlO_3$

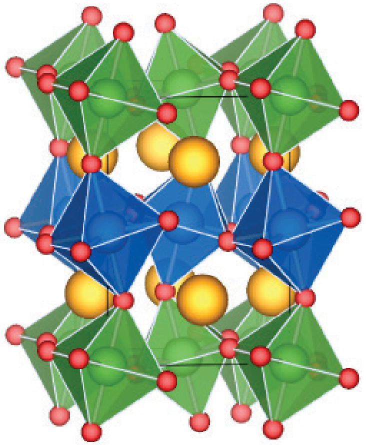
- Compute ground state structures and identify primary modes (atomic displacements) that lead to the ground state structure
  - VASP calculations, PAW pseudopotentials, 550 eV planewave energy cutoff

P.E. Blöchl, Phys. Rev. B **50** 17953 (1994); G. Kresse and J. Furthmuller, Phys. Rev. B **54** 11169 (1996)
G. Kresse and D. Joubert, Phys. Rev. B **59** 1758 (1999)

Ground state atomic structures of the ordered perovskites

- All *A*/*A’* structures are polar and have octahedral rotations, but which ones show polar distortions induced by the rotations?

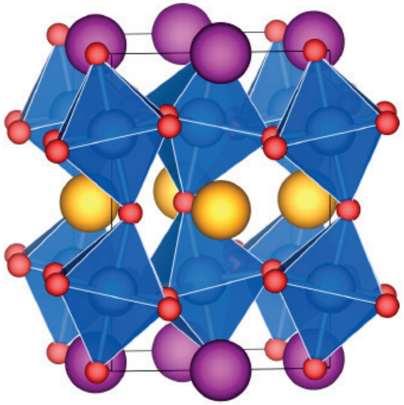
$P2_1/c$



$YGaO_3$/$YAlO_3$

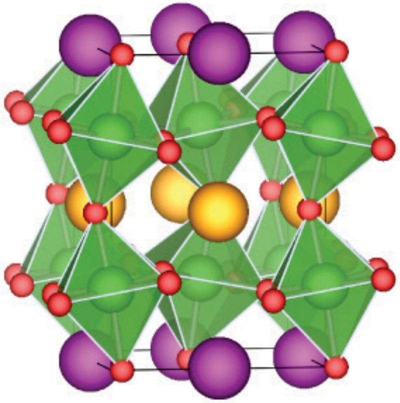
$|\mathbf{P}| = 0\ \mu\mathrm{C\ cm}^{-2}$

$Pmc2_1$



$LaGaO_3$/$YGaO_3$

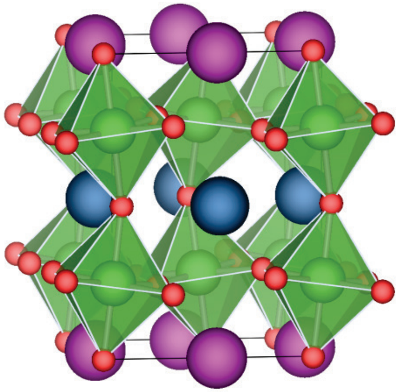
$|\mathbf{P}| = 11.8$



$LaAlO_3$/$YAlO_3$

$|\mathbf{P}| = 9.94$

Pc



$LaAlO_3$/$BiAlO_3$

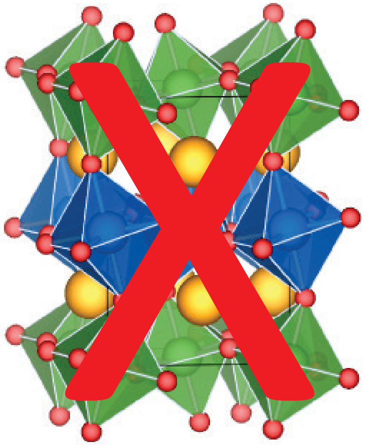
$|\mathbf{P}| = 9.62$

Atomic origin of polarization is from the non-cancelation of A and A’ cation displacements

Ground state atomic structures of the ordered perovskites

- All *A*/*A*’ structures are polar and have octahedral rotations, but which ones show polar distortions induced by the rotations?

*P*2$_1$/*c*



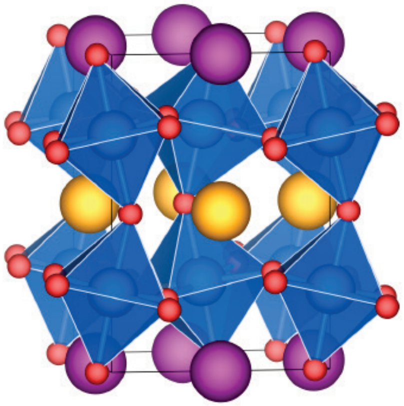
$YGaO_3/YAlO_3$

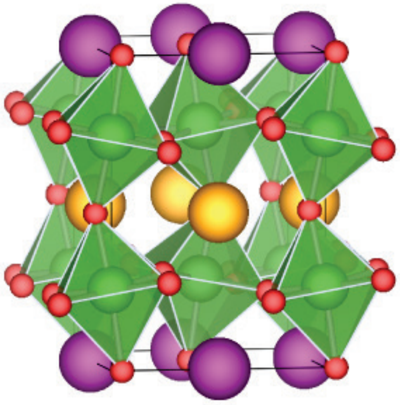
$|\mathbf{P}| = 0\ \mu\mathrm{C\ cm}^{-2}$

rotations do not break inversion

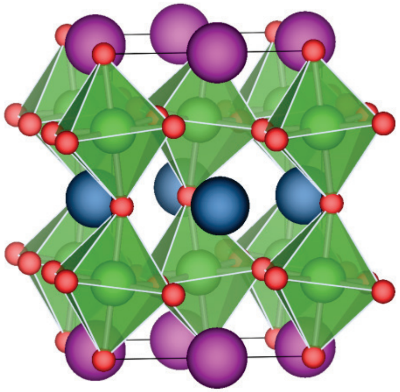
(symmetry argument)

*Pmc*2$_1$





Pc



$LaGaO_3/YGaO_3$

$|\mathbf{P}| = 11.8$

$LaAlO_3/YAlO_3$

$|\mathbf{P}| = 9.94$

$LaAlO_3/BiAlO_3$

$|\mathbf{P}| = 9.62$

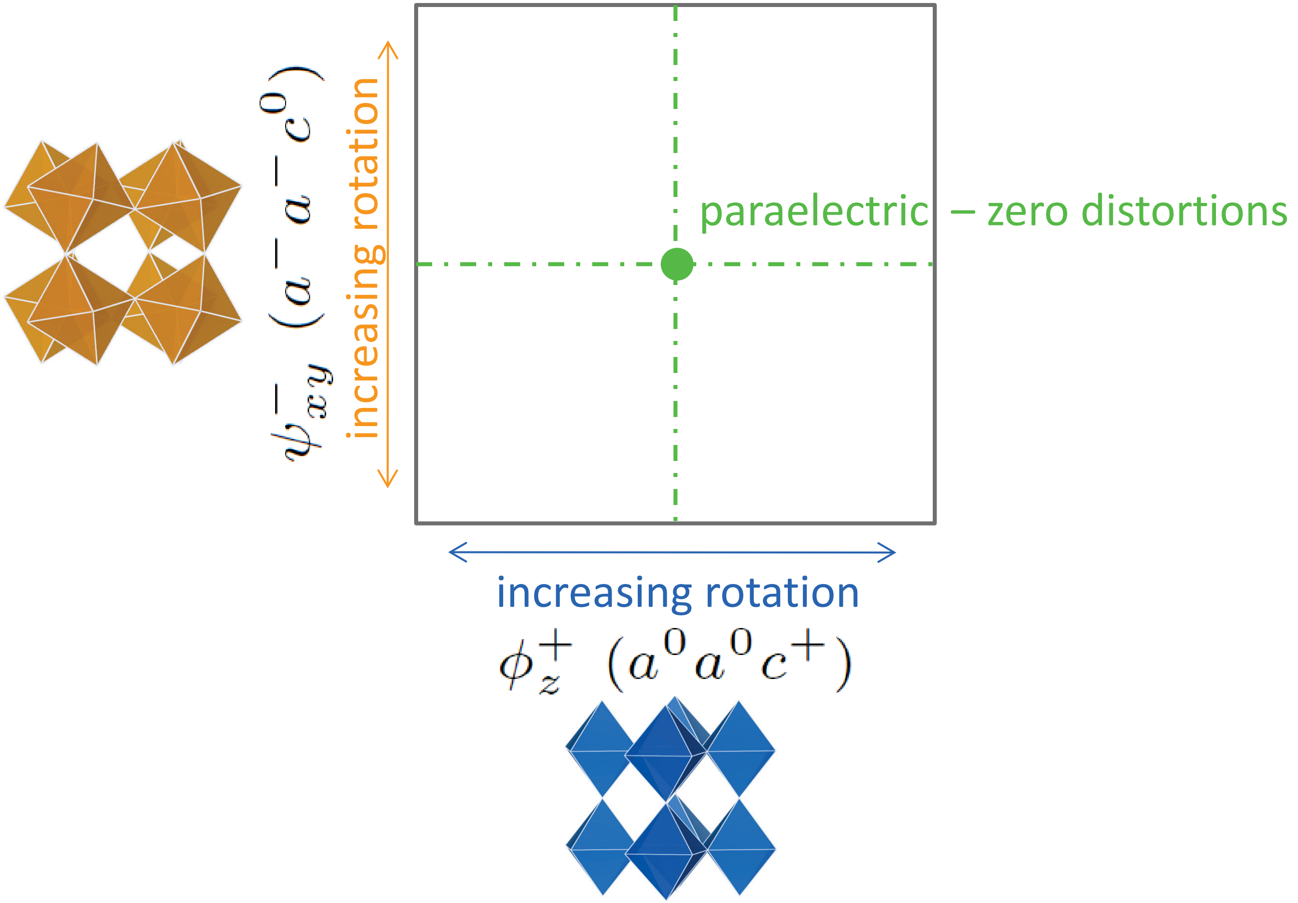
In which of these materials do the rotations drive FE?

Do the rotations induce the electric polarization?

- Evaluate how the rotations interact and alter the energy landscape

Interactions between the octahedral rotations

- Map out energy landscape with respect to the rotational modes



$\psi_{xy}^{-}\ (a^{-}a^{-}c^{0})$

increasing rotation

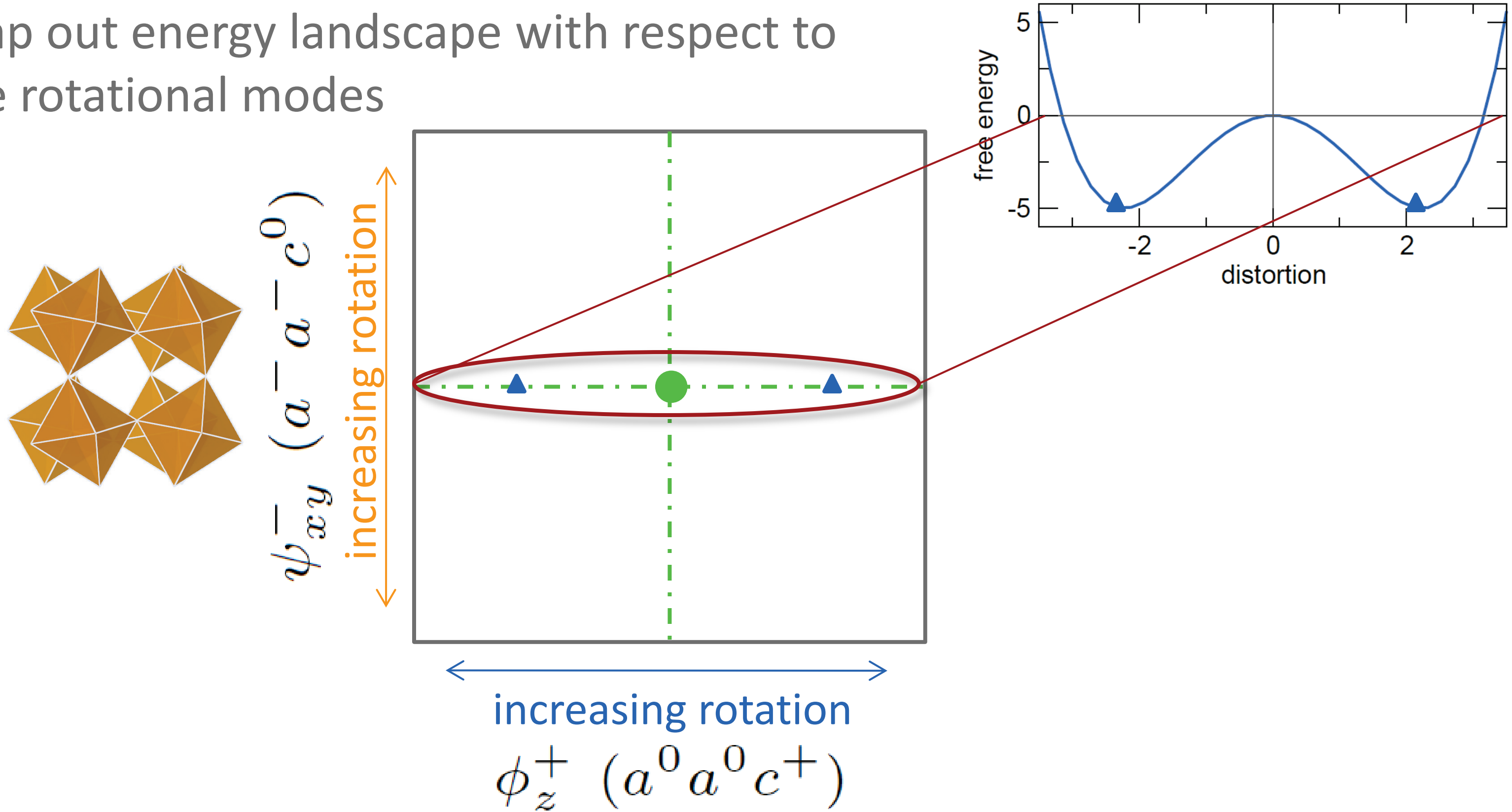
paraelectric – zero distortions

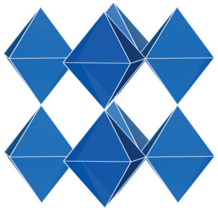
increasing rotation

$\phi_{z}^{+}\ (a^{0}a^{0}c^{+})$

Interactions between the octahedral rotations

- Map out energy landscape with respect to the rotational modes

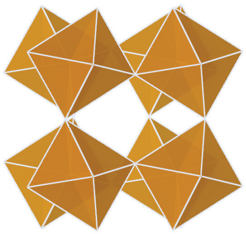


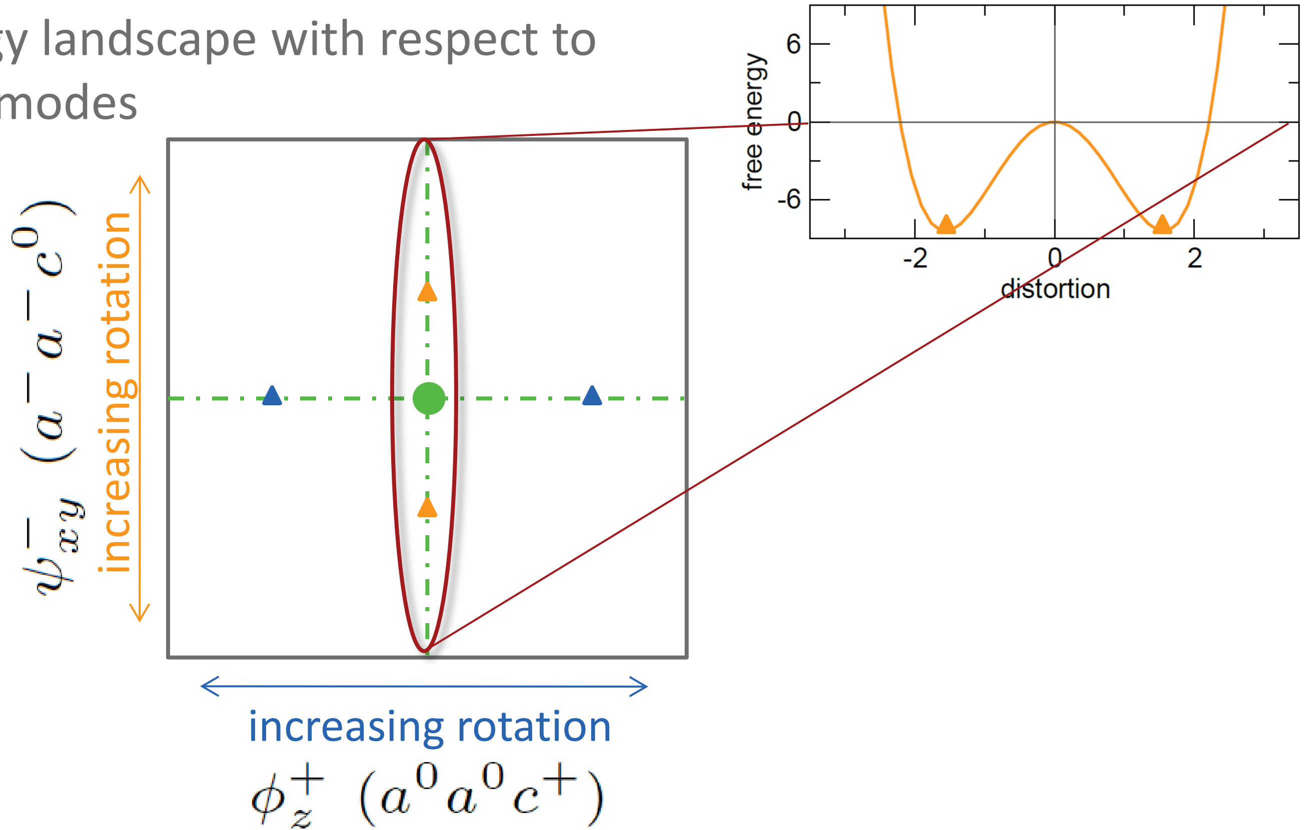


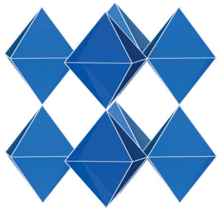
paraelectric – zero rotations
centrosymmetric – finite rotations

Interactions between the octahedral rotations

- Map out energy landscape with respect to the rotational modes

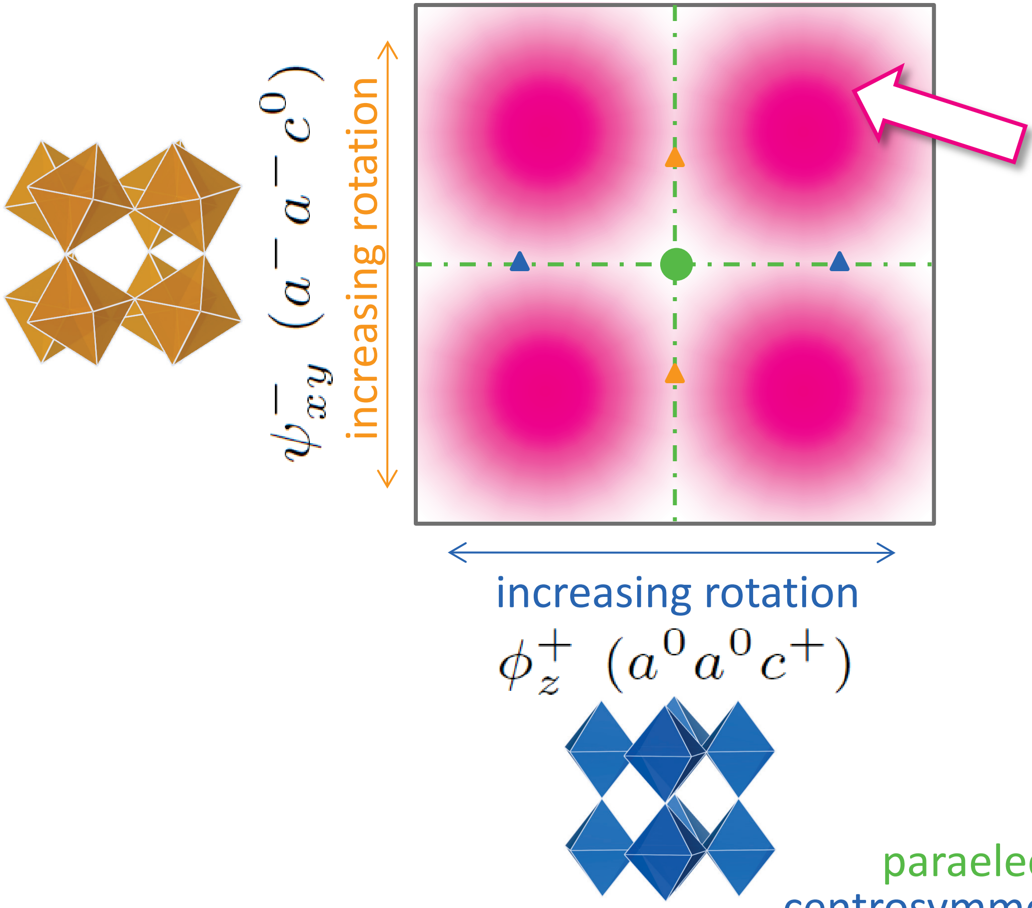






paraelectric – zero rotations
centrosymmetric – finite rotations
centrosymmetric – finite rotations

Interactions between the octahedral rotations



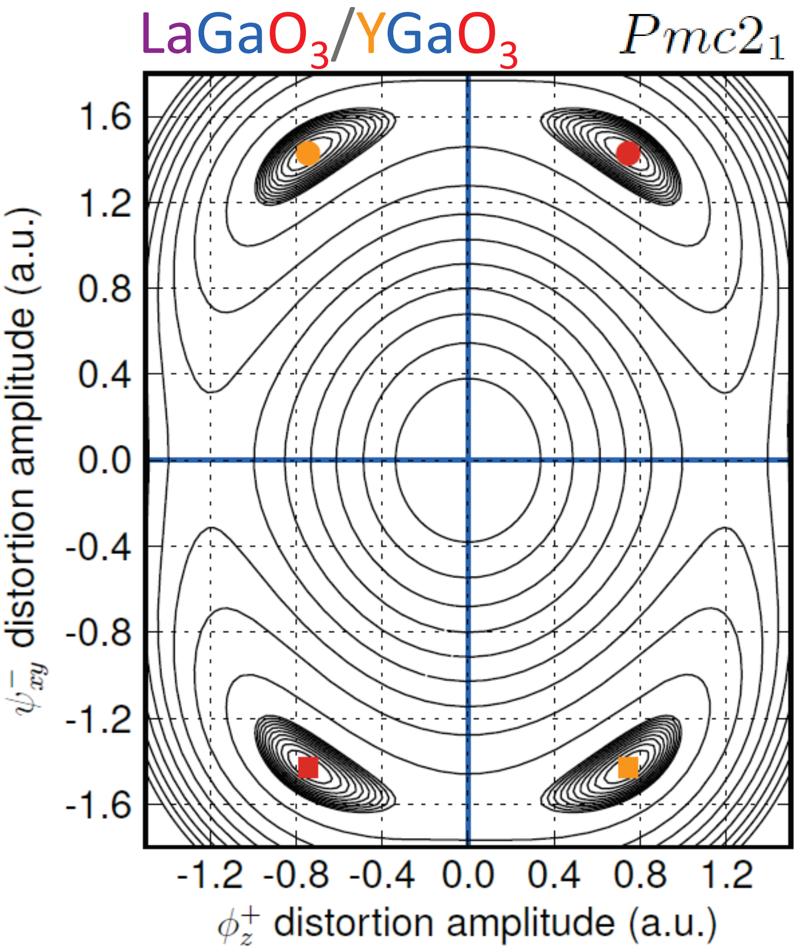
Polar crystal structure requires a minimum out here

Recall: ***TWO*** *rotation modes are needed to break inversion symmetry*

They also must energetically cooperate with one another

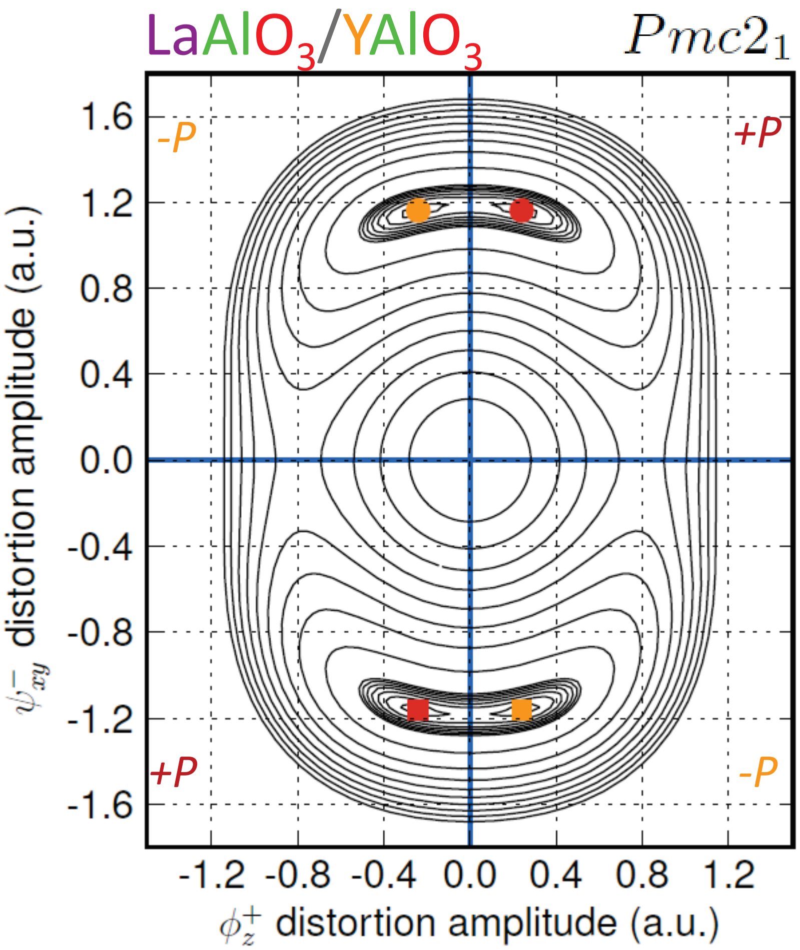
paraelectric – zero rotations
centrosymmetric – finite rotations
centrosymmetric – finite rotations

Interactions between the octahedral rotations



Modes cooperate *strongly*

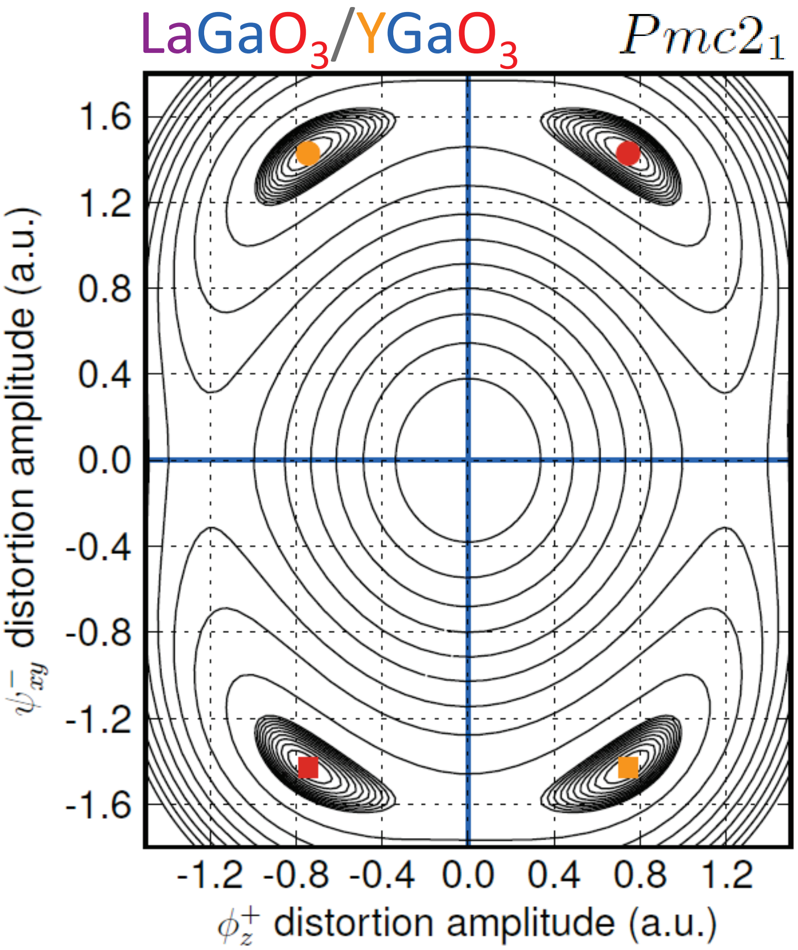
4 polar minima (twins & antiphase)



Modes cooperate *weakly*

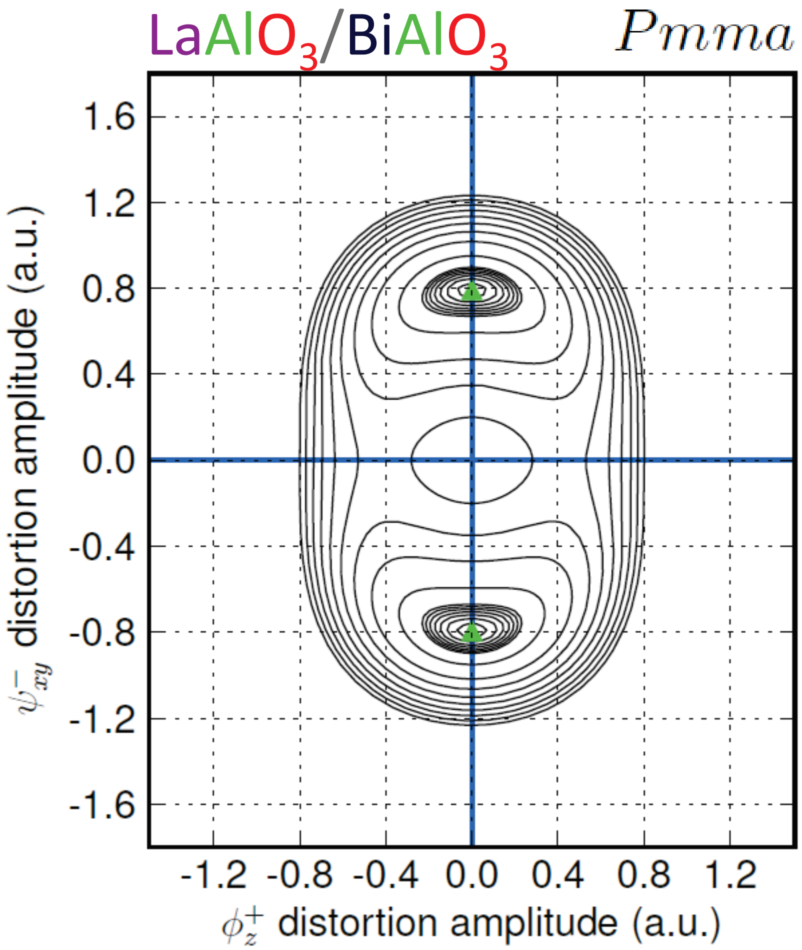
4 polar minima (twins & antiphase)

Interactions between the octahedral rotations



Modes cooperate *strongly*

4 polar minima (twins & antiphase)

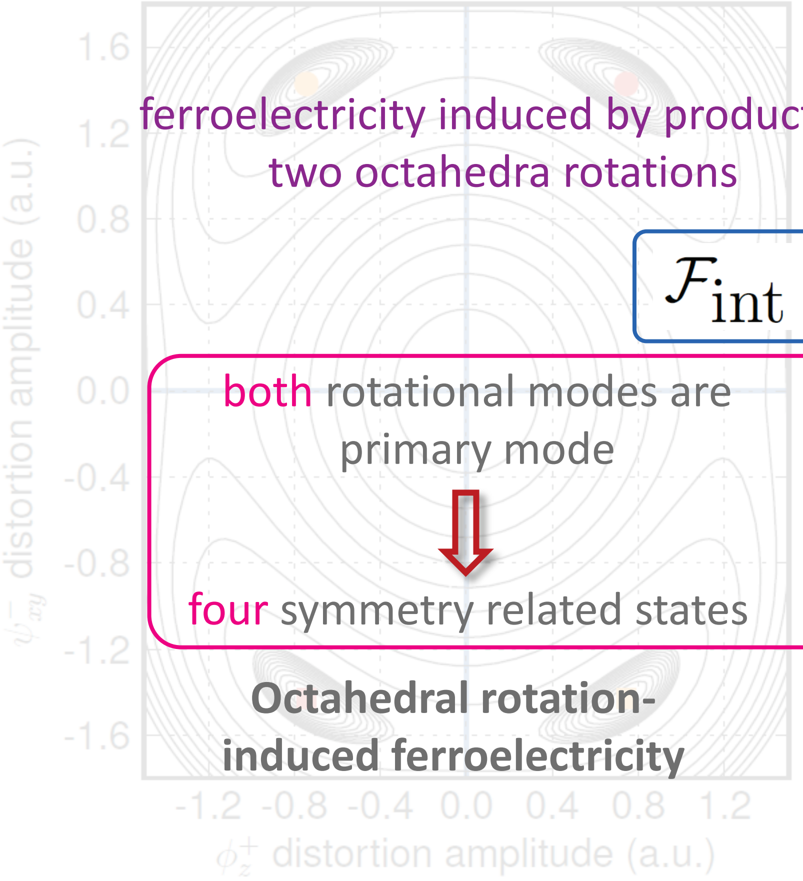


Modes COMPETE

2 non-polar minima

Interactions between the octahedral rotations

$LaGaO_3/YGaO_3$



ferroelectricity induced by product of two octahedra rotations

both rotational modes are primary mode

⇩

four symmetry related states

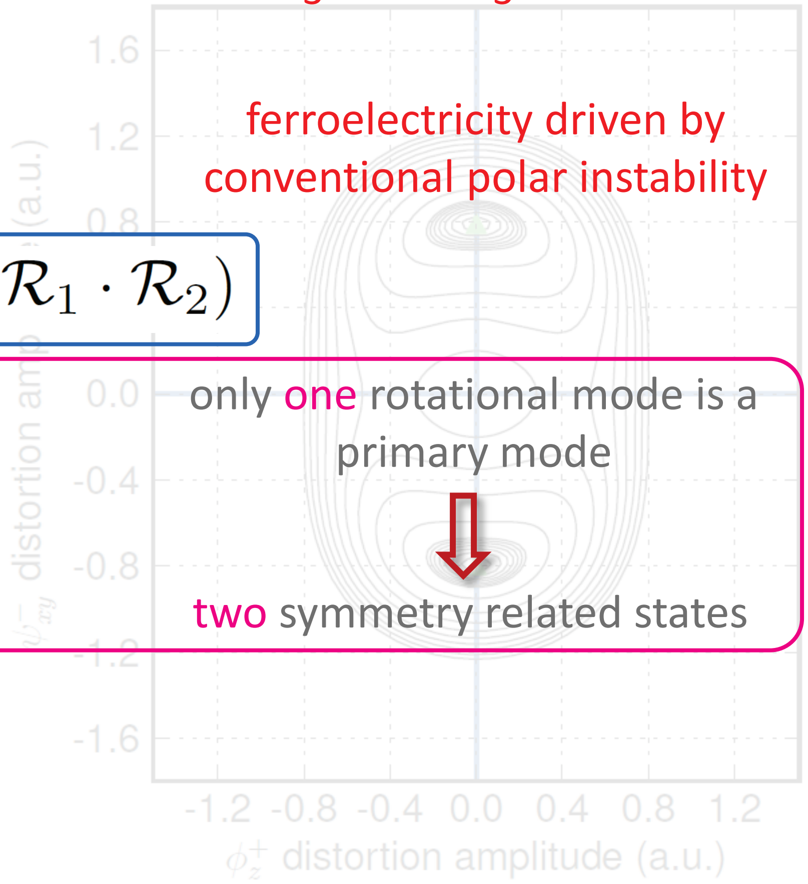
Octahedral rotation-induced ferroelectricity

Modes cooperate *strongly*

4 polar minima (twins & antiphase)

$$\mathcal{F}_{\text{int}} \sim P\,(\mathcal{R}_1 \cdot \mathcal{R}_2)$$

$LaAlO_3/BiAlO_3$



ferroelectricity driven by conventional polar instability

only one rotational mode is a primary mode

⇩

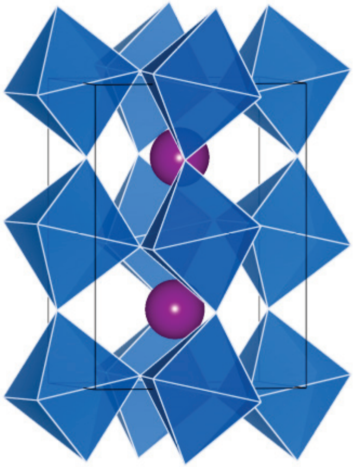
two symmetry related states

Modes COMPETE

2 non-polar minima

How to identify *a priori* if the octahedral rotations should cooperate or compete? …and induce ferroelectricity?

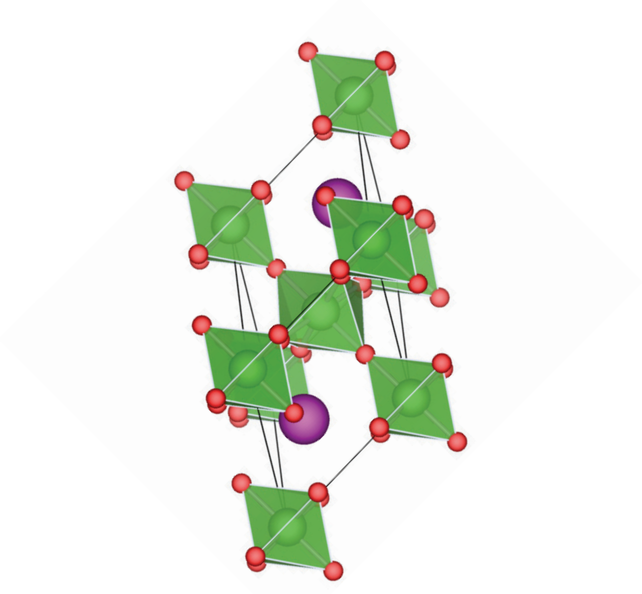
$LaGaO_3/YGaO_3$



a-a-c+

Modes cooperate because the ϕ_z^+ mode is unstable in both compounds

$LaAlO_3/BiAlO_3$



a-a-c-

Modes compete because the ϕ_z^+ mode is destabilized in bulk $LaAlO_3$

The bulk materials should exhibit the targeted structural transition driven by changes in octahedral rotations, or KNOW YOUR PHASE DIAGRAMS*

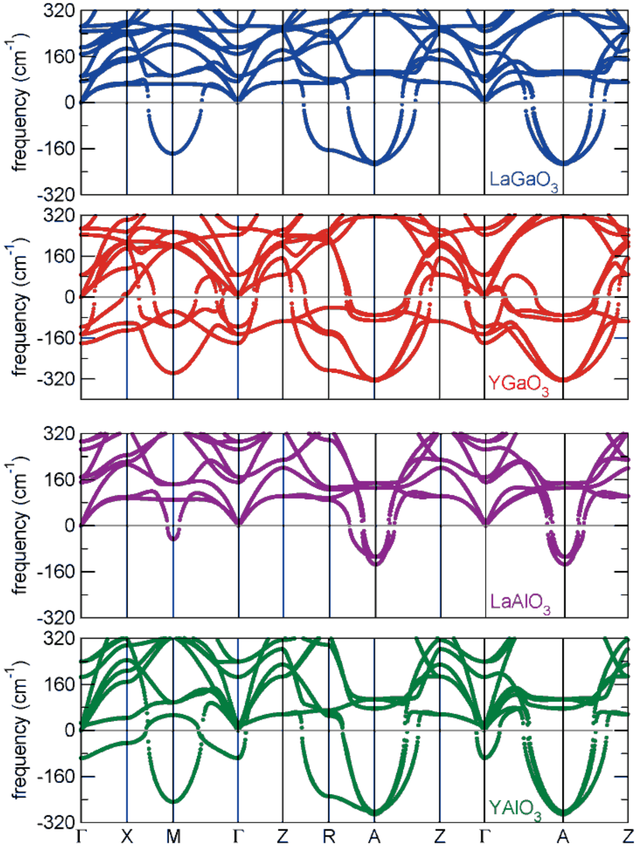
**If you are a computational scientist, one should look for soft zone-boundary phonons in the paraelectric bulk phases of each constituent*

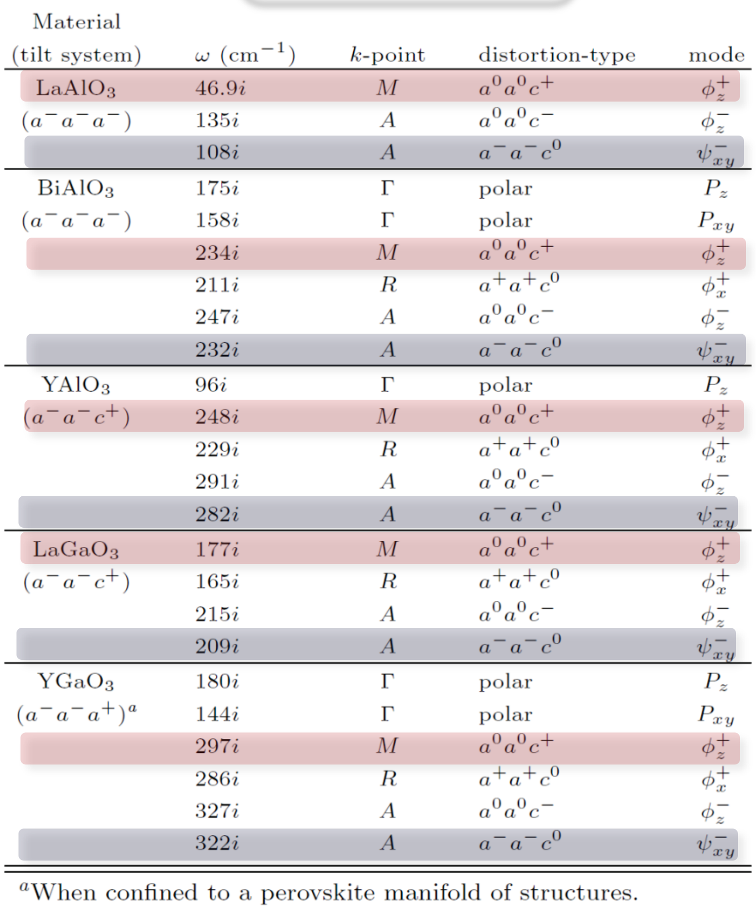
How to identify *a priori* if the octahedral rotations should cooperate or compete? …and induce ferroelectricity?

- Theparaelectric phases of the bulk materials should have unstable *zone-boundary* modes that cooperatively combine to produce stable low-symmetry rotationally distorted structures

$$\boxed{P_{xy}\phi_z^+\psi_{xy}^-}$$

tetragonal – *P4/mmm* references

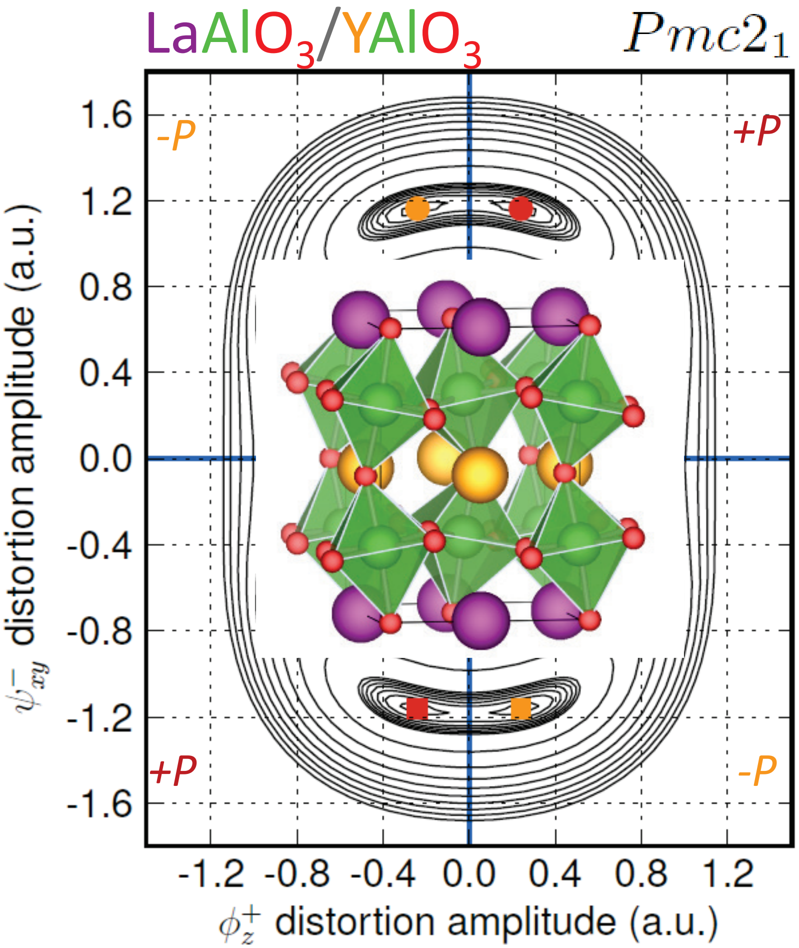




Material (tilt system)	ω (cm^{-1})	k-point	distortion-type	mode
LaAlO$_3$	$46.9i$	M	$a^0a^0c^+$	ϕ_z^+
($a^-a^-a^-$)	$135i$	A	$a^0a^0c^-$	ϕ_z^-
	$108i$	A	$a^-a^-c^0$	ψ_{xy}^-
BiAlO$_3$	$175i$	Γ	polar	P_z
($a^-a^-a^-$)	$158i$	Γ	polar	P_{xy}
	$234i$	M	$a^0a^0c^+$	ϕ_z^+
	$211i$	R	$a^+a^+c^0$	ϕ_x^+
	$247i$	A	$a^0a^0c^-$	ϕ_z^-
	$232i$	A	$a^-a^-c^0$	ψ_{xy}^-
YAlO$_3$	$96i$	Γ	polar	P_z
($a^-a^-c^+$)	$248i$	M	$a^0a^0c^+$	ϕ_z^+
	$229i$	R	$a^+a^+c^0$	ϕ_x^+
	$291i$	A	$a^0a^0c^-$	ϕ_z^-
	$282i$	A	$a^-a^-c^0$	ψ_{xy}^-
LaGaO$_3$	$177i$	M	$a^0a^0c^+$	ϕ_z^+
($a^-a^-c^+$)	$165i$	R	$a^+a^+c^0$	ϕ_x^+
	$215i$	A	$a^0a^0c^-$	ϕ_z^-
	$209i$	A	$a^-a^-c^0$	ψ_{xy}^-
YGaO$_3$	$180i$	Γ	polar	P_z
($a^-a^-a^+$)[a]	$144i$	Γ	polar	P_{xy}
	$297i$	M	$a^0a^0c^+$	ϕ_z^+
	$286i$	R	$a^+a^+c^0$	ϕ_x^+
	$327i$	A	$a^0a^0c^-$	ϕ_z^-
	$322i$	A	$a^-a^-c^0$	ψ_{xy}^-

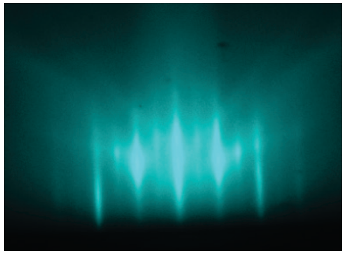
[a] When confined to a perovskite manifold of structures.

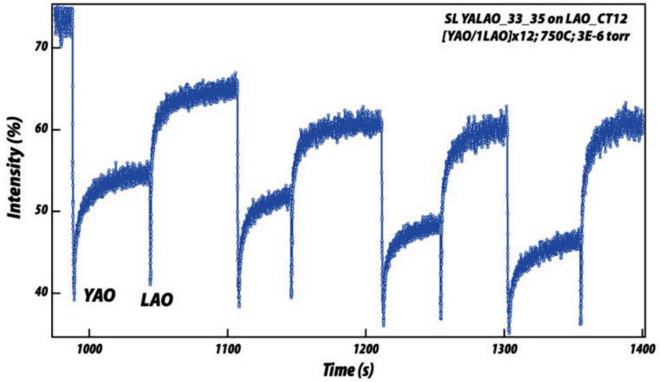
Low switching barrier (<5meV) should be experimentally accessible



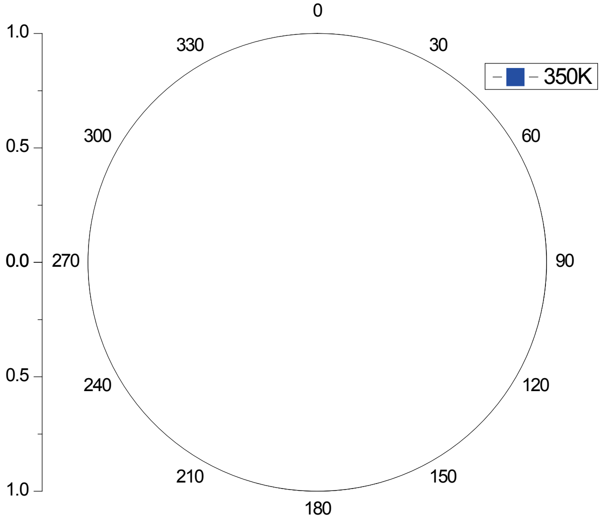
Jak Tchakhalian (U Arkansas, 2013)

Last layer LAO
View along (001)
Thin film after cooling





SHG Polar Plot



Guidelines for rotation-induced ferroelectricity in perovskites

- Guidelines for tailoring for octahedral rotation-induced ferroelectricity
  1. **Suitable cation site-symmetry:** ordered *A/A'* sublattice } chemistry
  2. **Energetic (correspondence) principle:** rotations should dominate the energy landscape, combining to break inversion symmetry. This occurs if they drive structural transitions (are primary order parameters) in the bulk constituents. } phase equilibria

	Condition 1	Condition 2	
$YAlO_3/YGaO_3$	✗	✗	Non-polar dielectric
$LaGaO_3/YGaO_3$	✓	✓	Rotation-induced FE
$LaAlO_3/YAlO_3$	✓	✓	Rotation-induced FE
$LaAlO_3/BiAlO_3$	✓	✗	Conventional ferroelectric

JMR & Fennie, Adv. Mater., **24** 1961 (2012)

Searching for functional rotation-induced ferroelectrics

- *Structural Criterion*

  A/A’ superlattices and perovskites with orthorhombic rotation

- *Selection Criterion*

  Chemistries that favor insulating band structures

- *Response Optimization*

  Can we obtain larger polarizations?
  Reduce switching barriers?
  Enhanced piezoelectricity?

  Mulder, Bendek, JMR, Fennie,
  Adv. Func. Mater.
  DOI: 10.1002/adfm.201300210

  Can we order the cations differently? → *Generalized for (A,A’)(B,B’)O_6*

  Couple with magnetism?

  Realize new transitions? → Gou & JMR, *Ferri-to-Ferroelectric Transitions with Large Piezoelectric Response* http://arxiv.org/abs/1304.4911 (2013)

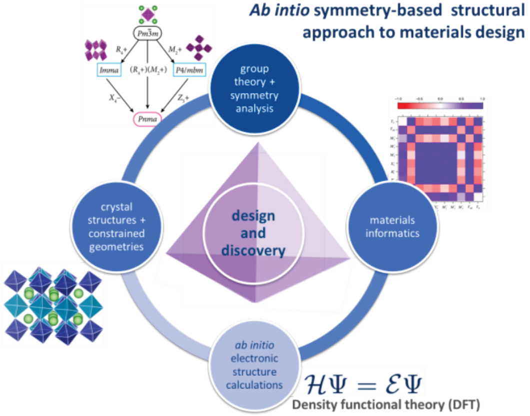
The answer to each question is YES!

Design of a new mechanism for ferroelectricity—electric polarizations induced by non-polar displacements

Modern Materials Design

Design modalities in materials research today

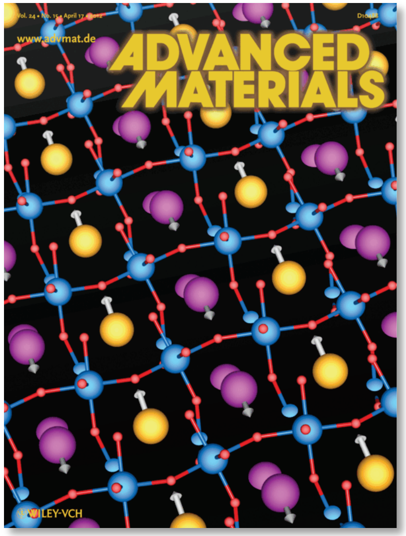
Structure-based approach to mechanistic physical property design



$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

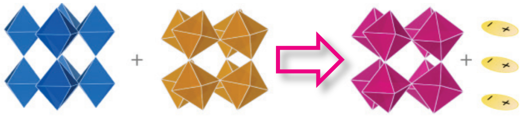
Density functional theory (DFT)

Emergent Ferroelectricity



JMR & Fennie, Adv. Mater., **24** 1961 (2012)

$$ABO_3 + A'BO_3 = (A,A')B_2O_6$$

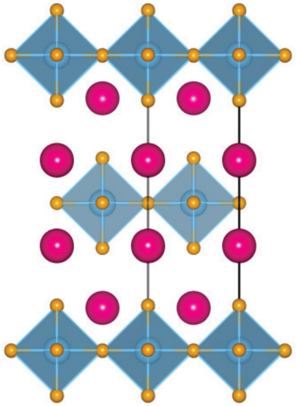


Design Dividends

Multiferroic Materials in layered Ruddlesden-Popper structures

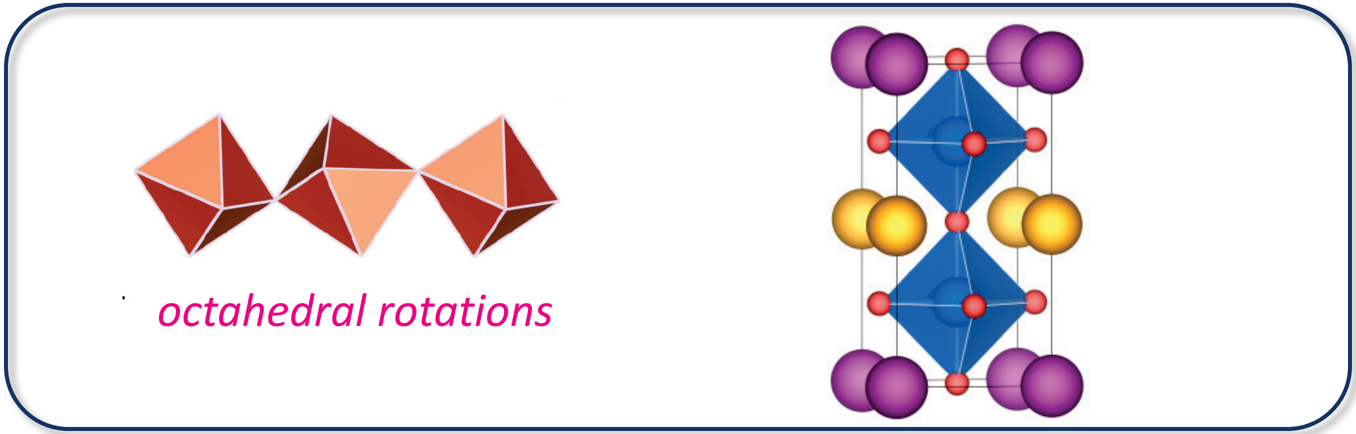
DISCOVERY

FUNCTIONALITY

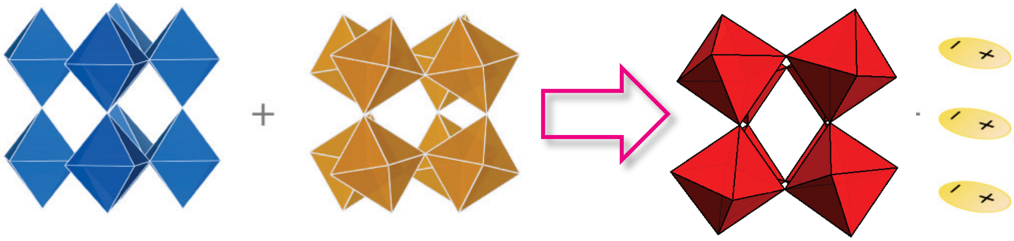


Rotation-induced ferroelectricity in perovskite oxide superlattices

- Artificial “layered” oxides (bi-color) with no tendency to polar distortions can be made polar by combining orthorhombic tilts ($a^-a^-c^+$) and cation ordering in digital superlattices



$$ABO_3 + A'BO_3 = (A,A')B_2O_6$$

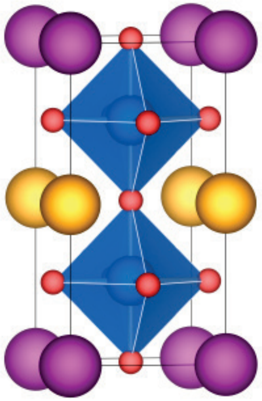


Cation ordering shifts the inversion center and enables the rotations to break all inversion elements

JMR & Fennie, Adv. Mater., **24** 1961 (2012)

Implications for the design of new ferroelectrics

- Rotations can induce a polarization through **trilinear linear coupling** among octahedral rotations and a polar mode (hybrid-improper ferroelectricity*)



$$P \sim (\mathcal{R}_1 \cdot \mathcal{R}_2)$$

No SOJT cations are needed

↓

chemistry independent mechanism

$$\boxed{\mathcal{F}_{\text{int}} \sim P\,(\mathcal{R}_1 \cdot \mathcal{R}_2)}$$

*Benedek & Fennie, PRL, **106** 107204 (2011)

Design dividends from formulating new mechanisms

DISCOVERY

- *Can we discover more ferroelectrics in alternative crystal families where the polarization is induced by other non-polar lattice modes?*

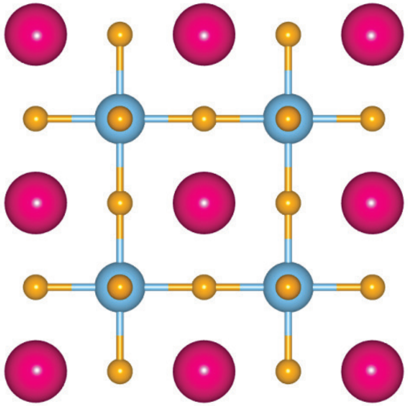
FUNCTIONALITY

- *Can we make it compatible with additional functionalities?*
- Magnetism (multiferroics/magnetoelectrics)

Layered Ruddlesden-Popper structures with disconnected BO_6 units

- Rotations of octahedra in 2D Ruddlesden-Popper structures also will not break inversion symmetry

Perovskite oxides

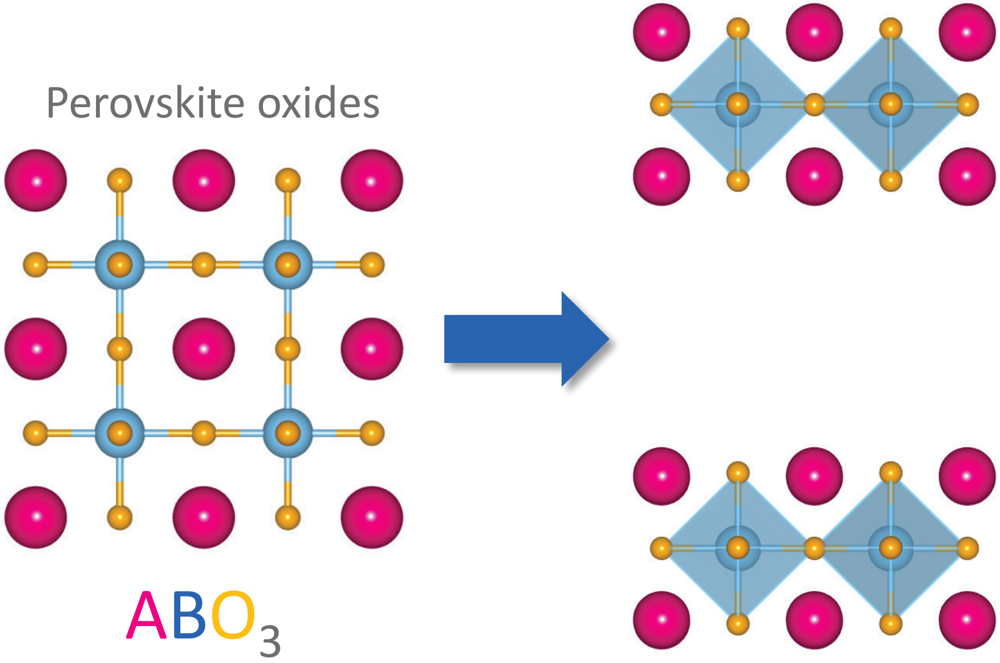


ABO_3

Ruddlesden-Popper
(n=1) oxides

Layered Ruddlesden-Popper structures with disconnected BO_6 units

- Rotations of octahedra in 2D Ruddlesden-Popper structures also will not break inversion symmetry

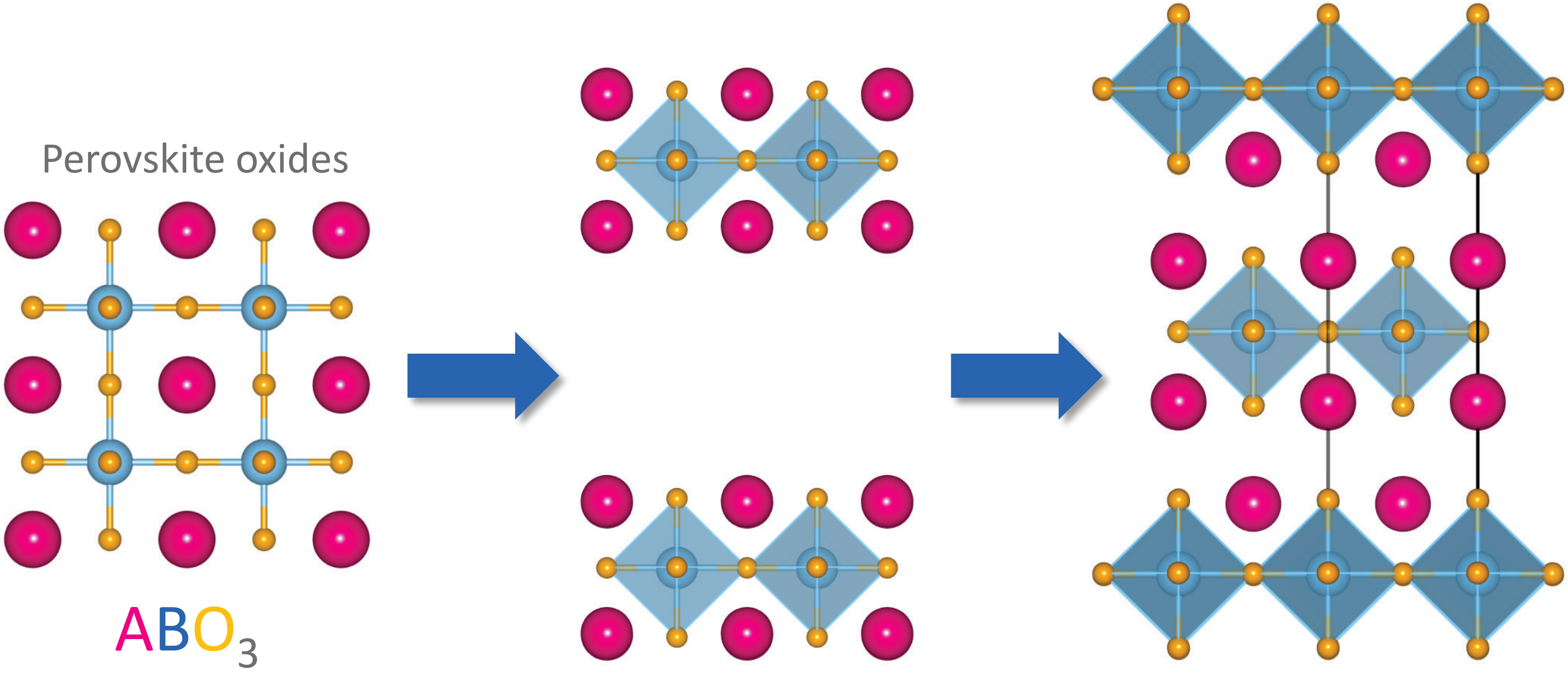


Ruddlesden-Popper (n=1) oxides

Layered Ruddlesden-Popper structures with disconnected BO_6 units

- Rotations of octahedra in 2D Ruddlesden-Popper structures also will not break inversion symmetry

$A_2BO_4 = (AO)/(ABO_3)$



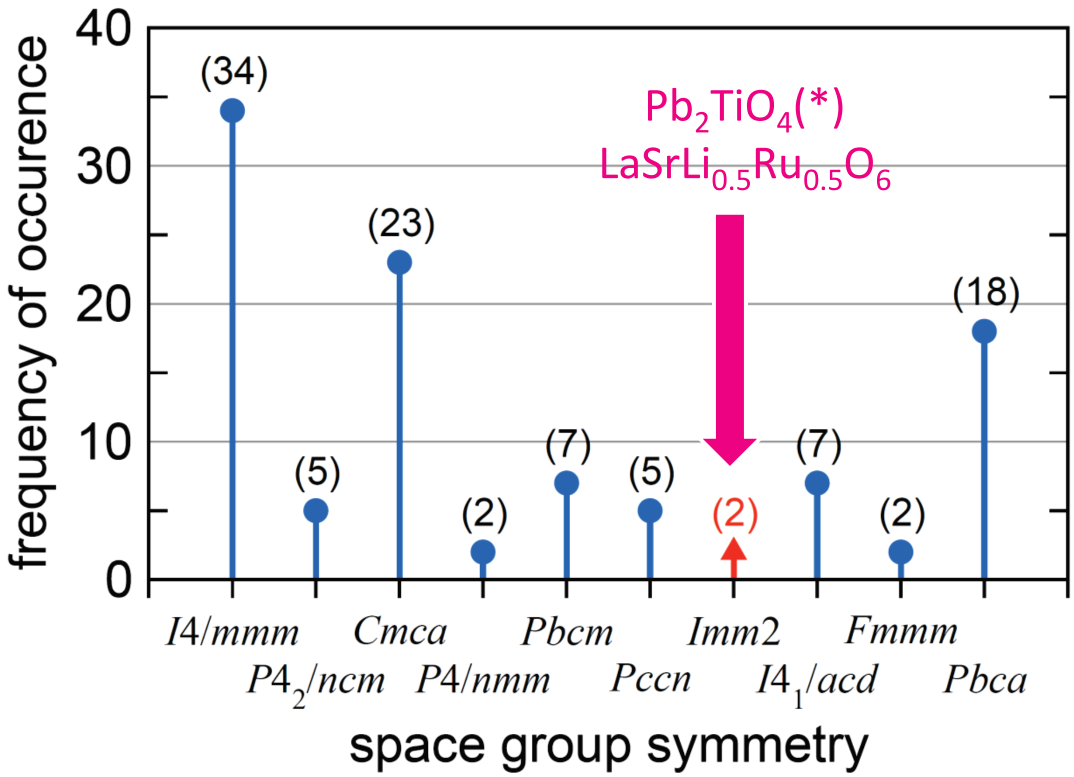
Perovskite oxides

ABO_3

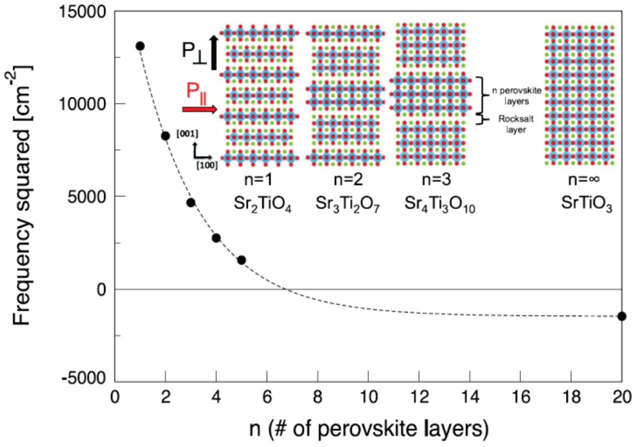
Ruddlesden-Popper (n=1) oxides

Dearth of polar oxides in “214” Ruddlesden-Popper structure

- 105 structures surveyed and there exists only 1 material that is experimentally polar



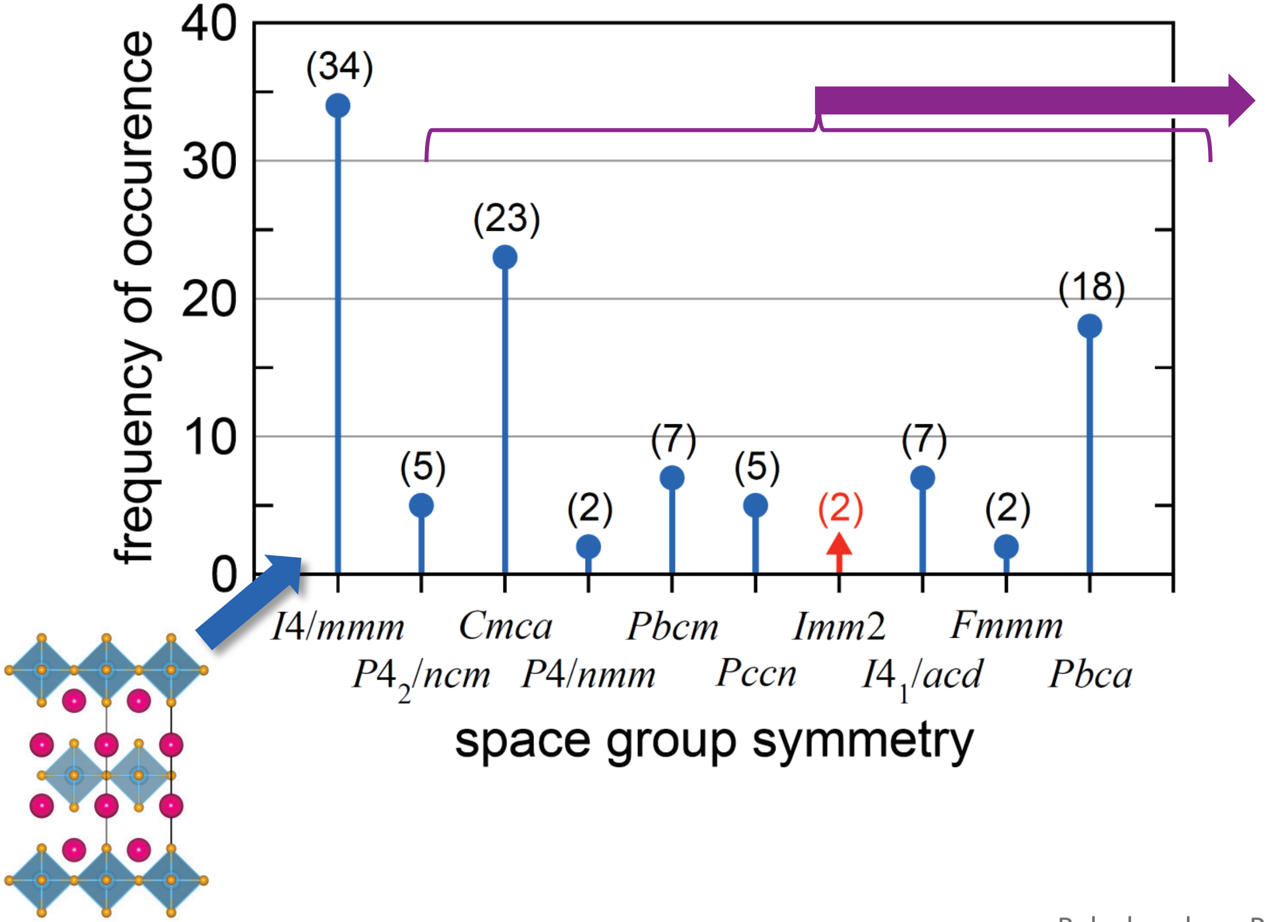
Disconnected octahedra destroy the coherency required for coherent off-centering displacements [Fennie, PRL **107**, 257602 (2011)]



*C.J. Fennie & K.M. Rabe; PRB **71**, 100102(R) (2005); P. Battle et al., Chem. Mater., **16** 4266 (2004).

Dearth of polar oxides in “214” Ruddlesden-Popper structure

- 105 structures surveyed and there exists only 1 material that is experimentally polar



All of these structures contain distorted octahedra, but no distortion mode alone is sufficient to lift inversion

Balachandran, Puggioni, JMR, (Submitted, 2013)

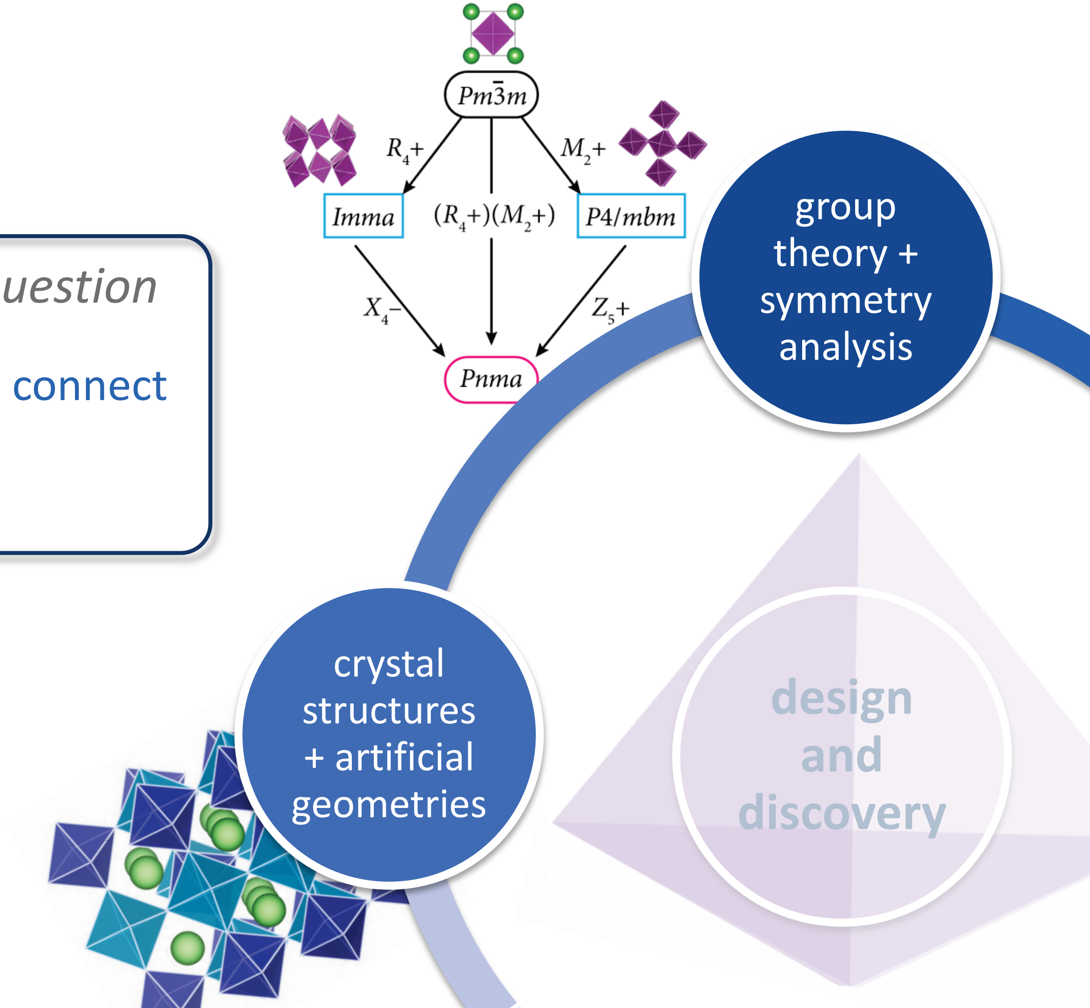
Ab intio symmetry-based structural approach to materials design

- Use applied group to perform a symmetry-based search on known structures to evaluate the microscopic displacements that lower the crystal symmetry

We ask the following structural question

What types of atomic displacements connect the high-symmetry space group to a structure of lower symmetry?

This is the inverse Landau problem:
What combinations of irreps will remove inversion symmetry



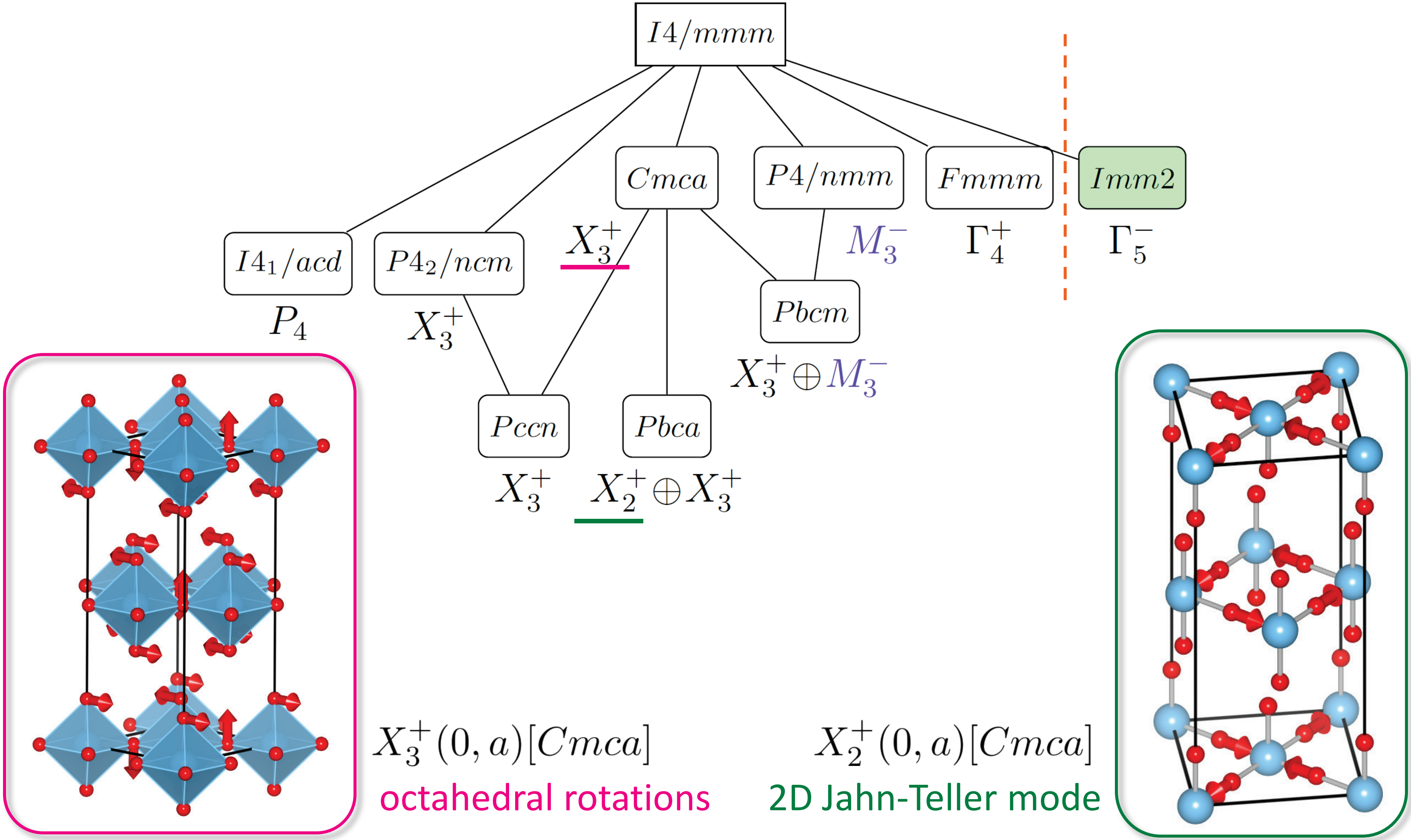
group theory + symmetry analysis

crystal structures + artificial geometries

design and discovery

Group-subgroup relationships for the experimental 214 RP phases

- No observed distortion modes lift inversion symmetry alone



$X_3^+(0,a)[Cmca]$

octahedral rotations

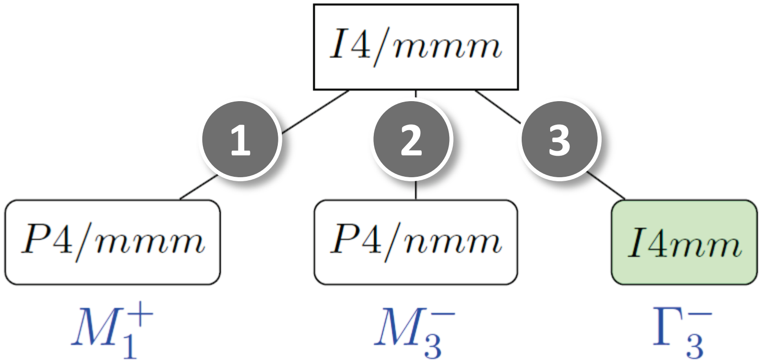
$X_2^+(0,a)[Cmca]$

2D Jahn-Teller mode

Role of cation ordering in 214 perovskites along [001]

- Three unique arrangements to order cations on the A site which keep the stoichiometry the same

$$ABO_3 + A'O = (A,A')BO_4$$

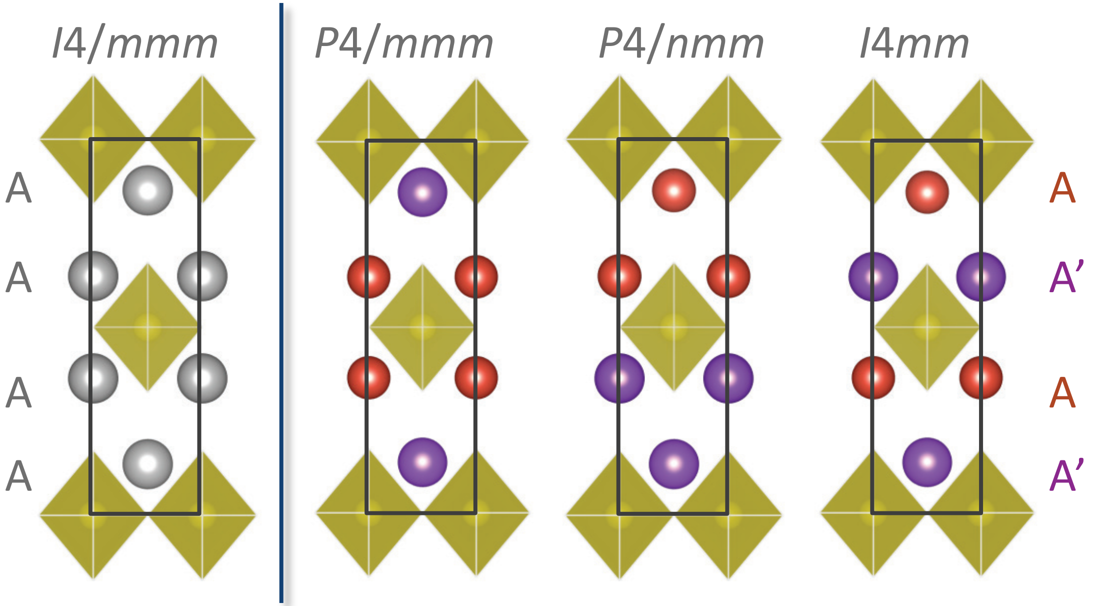


- Two arrangements do not lift inversion

① ②

- One arrangement lifts inversion trivially from compositional order alone without distortions

③

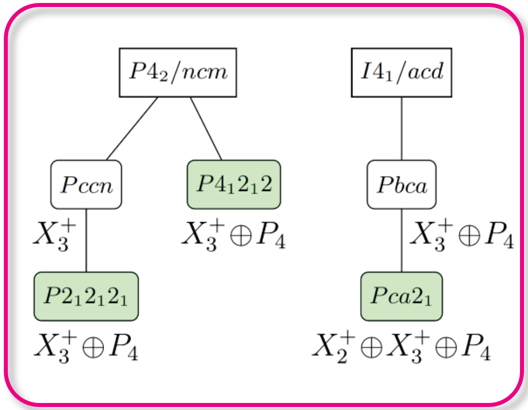


Are there combinations of non-polar displacement patterns or composition modes that lift inversion?

- Examine interplay of multiple atomic and/or compositional distortions

Are there combinations of non-polar or composition modes that lift inversion?

- Examine interplay of multiple atomic and/or compositional distortions

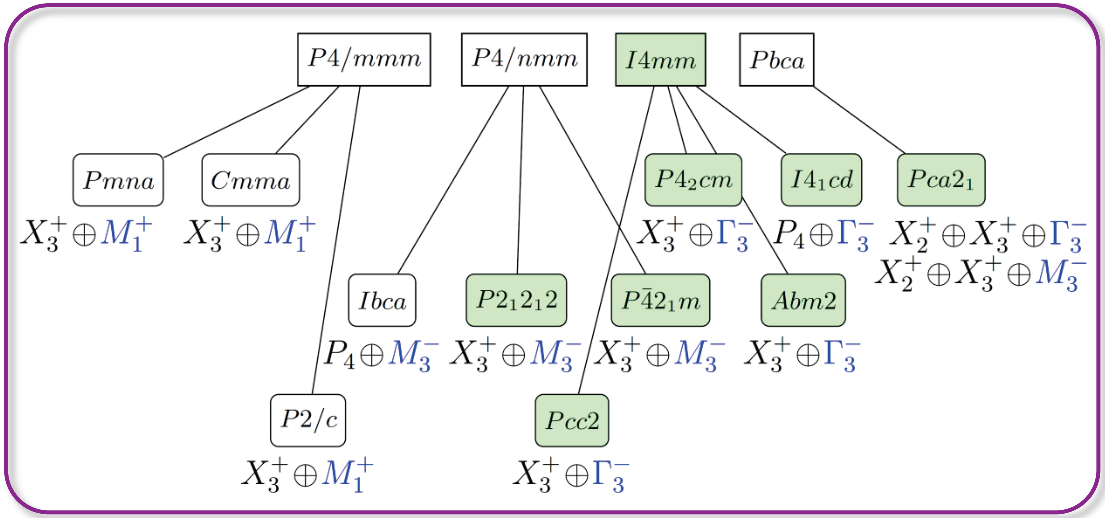


$I4/mmm$ **Route 1**

$Pca2_1$

$$X_2^+ \oplus X_3^+ \oplus P_4$$

only atomic distortion modes



$I4/mmm$ **Route 2**

$Pca2_1$

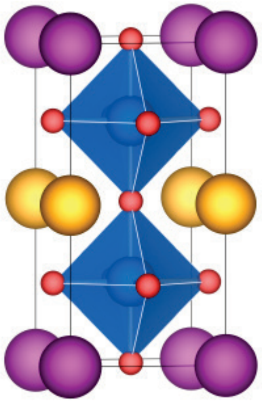
$$X_2^+ \oplus X_3^+ \oplus M_3^-$$

atomic distortions + cation order

These multiple "distortions" activate trilinear invariants capable of triggering a polarization

Polarization induced by coupling of multiple non-polar lattice modes in the presence of cation order

- Perovskite superlattice: $(A',A)B_2O_6$



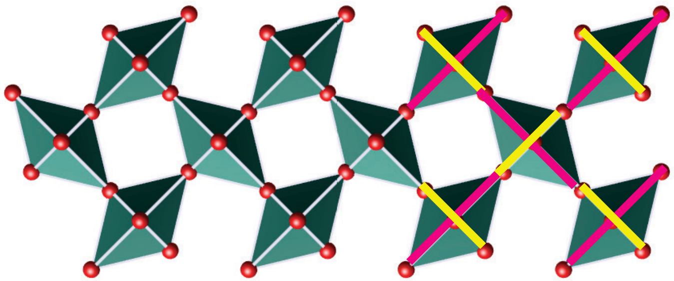
$$\mathcal{F} \sim P \cdot \underline{Q_1 \cdot Q_2}$$

octahedral rotations (in- and out-of-phase)

polar displacements

- Non-polar modes Q_1 and Q_2 may describe any zone-boundary lattice mode that does not individually lift inversion symmetry
  - Real rotations of polyhedral units
  - Berry-pseudorotations* that describe (a)symmetric bond stretching

Jahn-Teller bond elongations



*Gillespie, Ramirez *et al.*, Chem. Res. **4** 288 (1971)

Polarization induced by coupling of multiple non-polar lattice modes in the presence of cation order

- *n*=1 Ruddlesden-Popper structure (*A*,*A'*)*B*O_4

$I4/mmm$ **Route 2**

$Pca2_1$

$X_2^+ \oplus X_3^+ \oplus M_3^-$

atomic distortions

\+

cation order

$$\mathcal{F} \sim P \cdot Q_1 \cdot Q_2$$

Balachandran, Puggioni, JMR, (Submitted, 2013)

Polarization induced by coupling of multiple non-polar lattice modes in the presence of cation order

- *n*=1 Ruddlesden-Popper structure (*A*,*A'*)*B*O_4

$I4/mmm$ **Route 2**

$Pca2_1$

$X_2^+ \oplus X_3^+ \oplus M_3^-$

atomic distortions

+

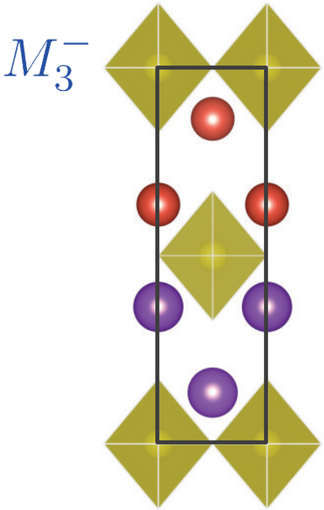
cation order

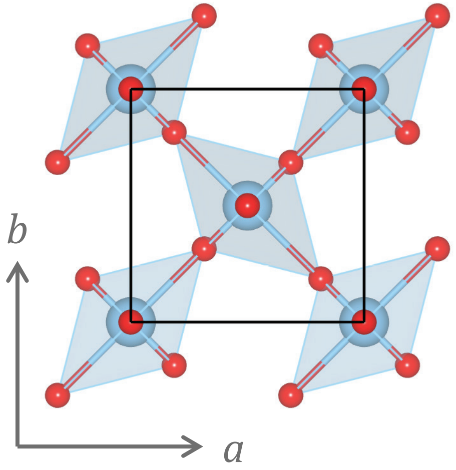
$$\mathcal{F} \sim P \cdot Q_1 \cdot Q_2$$

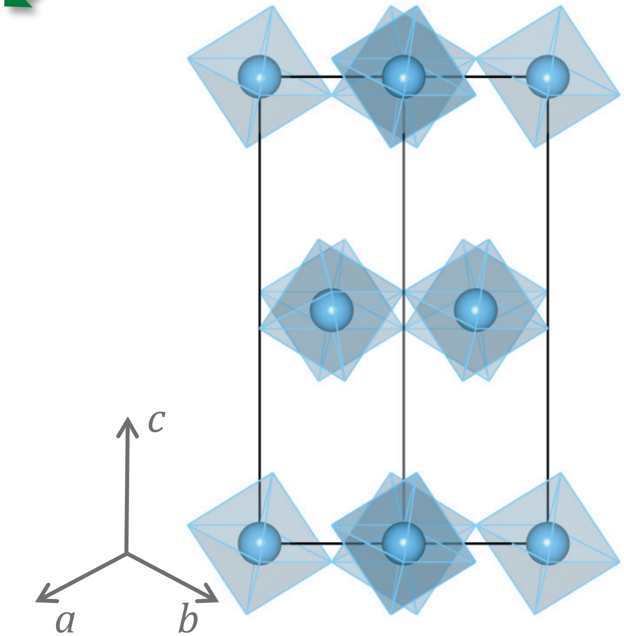
polar displacements

X_2^+ *Jahn-Teller distortions*

X_3^+ *octahedral rotations*

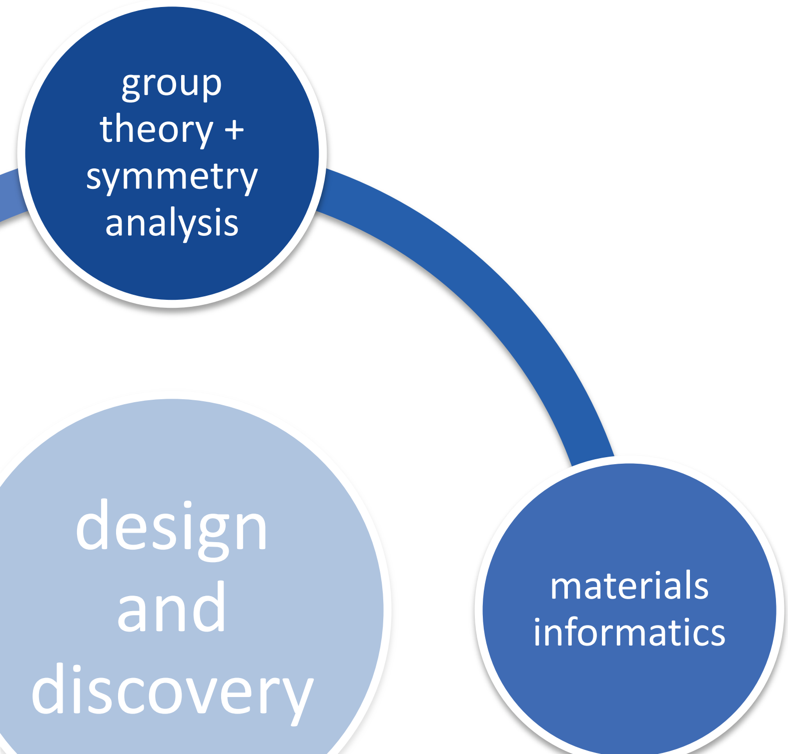






What chemistries should we choose for rotations and Jahn-Teller distortions to induce an electric polarization?

- *Structural Criterion*
  - Symmetry arguments suggest most probable structures and geometries
- *Selection Criterion*
  - Query our database of known compounds using Bayesian statistics/inference



group theory + symmetry analysis

design and discovery

materials informatics

$$\mathcal{F} \sim P \cdot (X_2^+ \cdot X_3^+)$$

Bayes' rules for making statistical inferences

- Based on an interpretation of probability as a **conditional measure of uncertainty**
  - Frequently how we use "probability" in normal language
  - Important in statistical applications but remains controversial among statisticians

- Algorithm to combine prior experience with current evidence to make an *optimistic* judgment (rational method for updating beliefs)

  Principled way of combining knowledge with belief
  Can be done iteratively as new knowledge obtained (Bayesian updating)

- Bayesian inference derives the posterior probability as a consequence of two antecedents, a prior probability and a "likelihood function" derived from a probability model for the data to be observed

posterior probability = likelihood × prior probability

Lee, *Bayesian Statistics*, Wiley (2012)

Prior probabilities

- Bayesian inference derives the posterior probability as a consequence of two antecedents, a prior probability and a "likelihood function" derived from a probability model for the data to be observed

- Example: A couple learns they are having twin boys

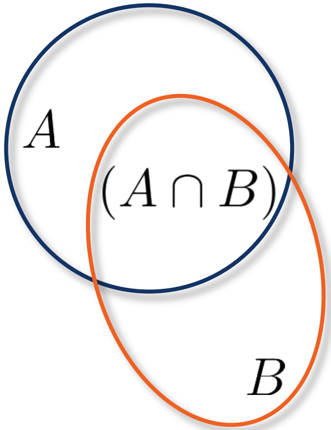
  What is the probability they are identical rather than fraternal?

- Prior probabilities
  - $P(A)$: 1/3 of all twin cases are identical
  - $P(A^c)$: 2/3 are fraternal

Efron, Science, **340** 1177 (2013)

Conditional probability / Likelihood

- Conditional probability for two events
  - Probability that under condition *A* then the event *B* occurs



$$P(B|A) = \frac{P(A \cap B)}{P(A)}$$

- If we are certain that the event A occurs, then *P*(*B*|*A*) is the probability for the event, otherwise we call it the likelihood

- Bayes Theorem says:

$$\boxed{\underbrace{P(A|B)}_{\text{posterior probability}} = \frac{\underbrace{P(B|A)}_{\text{likelihood}}\,\underbrace{P(A)}_{\text{prior probability}}}{P(B)} =}$$

posterior probability likelihood prior probability

$$P(B) = P(B|A)P(A) + P(B|A^c)P(A^c)$$

Conditional probability / Likelihood

- Bayes Theorem says:

$$P(A|B) = \frac{P(B|A)P(A)}{P(B)}$$

posterior probability likelihood prior probability

$$P(B) = P(B|A)P(A) + P(B|A^c)P(A^c)$$

A is the twins being identical
B is the sonogram shows two boys

- – *P*(*A*): 1/3 of all twin cases are identical
- – *P*(*A*^{c}): 2/3 are fraternal
- – P(*B*|*A*) = 1/2 of fraternal twins are boys
- – P(*B*|*A*^{c}) = 1/4 since it is twice as likely identical twins are boys

Efron, Science, **340** 1177 (2013)

Conditional probability / Likelihood

- Bayes Theorem says:

$$\boxed{\underbrace{P(A|B)}_{\text{posterior probability}} = \frac{\underbrace{P(B|A)}_{\text{likelihood}}\underbrace{P(A)}_{\text{prior probability}}}{P(B)} = \frac{(1/2)(1/3)}{(1/3)}}$$

$$P(B) = P(B|A)P(A) + P(B|A^c)P(A^c)$$

A is the twins being identical
B is the sonogram shows two boys

  - *P*(*A*): 1/3 of all twin cases are identical
  - *P*(A^c): 2/3 are fraternal
  - P(*B*|*A*) = 1/2 of fraternal twins are boys
  - P(*B*|A^c) = 1/4 twice as likely identical twins are boys

$$\boxed{P(A|B) = \frac{1}{2}}$$

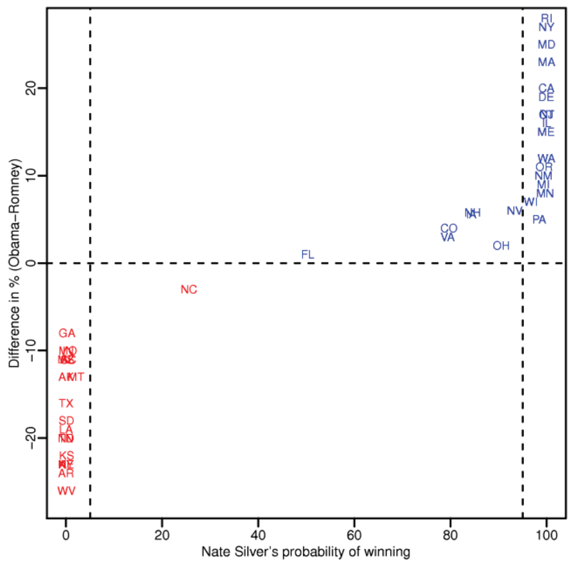
Correctly predicts the twins will have an equal probability of being fraternal or identical

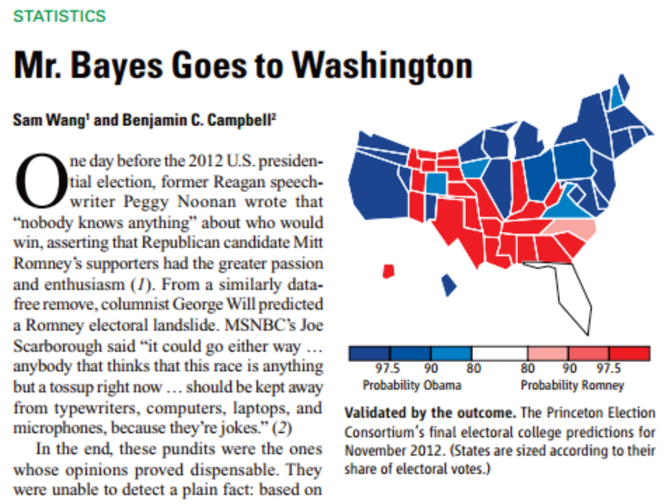
Efron, Science, **340** 1177 (2013)

Bayesian analysis examples

- Nate Silver's FiveThirtyEight blog
  - http://fivethirtyeight.blogs.nytimes.com/author/nate-silver/

- 2012 Presidential election
  - Algorithm that updated prior poll results with new data on a daily basis, correctly *predicting* the actual vote in all 50 states





STATISTICS

Mr. Bayes Goes to Washington

Sam Wang[1] and Benjamin C. Campbell[2]

One day before the 2012 U.S. presidential election, former Reagan speechwriter Peggy Noonan wrote that "nobody knows anything" about who would win, asserting that Republican candidate Mitt Romney's supporters had the greater passion and enthusiasm (*1*). From a similarly data-free remove, columnist George Will predicted a Romney electoral landslide. MSNBC's Joe Scarborough said "it could go either way … anybody that thinks that this race is anything but a tossup right now … should be kept away from typewriters, computers, laptops, and microphones, because they're jokes." (*2*)

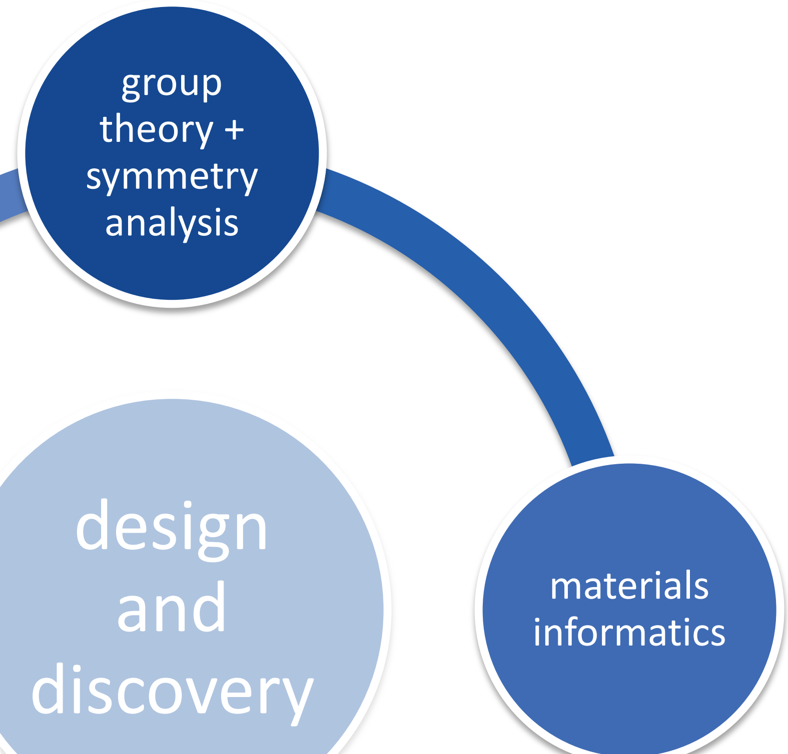
In the end, these pundits were the ones whose opinions proved dispensable. They were unable to detect a plain fact: based on

Validated by the outcome. The Princeton Election Consortium's final electoral college predictions for November 2012. (States are sized according to their share of electoral votes.)

Science, **339**. 758 (2013).

What chemistries should we choose for rotations and Jahn-Teller distortions to induce an electric polarization?

- *Structural Criterion*
  - Symmetry arguments suggest most probable structures and geometries
- *Selection Criterion*
  - Query our database of known compounds using Bayesian statistics/inference



group theory + symmetry analysis

design and discovery

materials informatics

$$\boxed{\mathcal{F} \sim P \cdot (X_2^+ \cdot X_3^+)}$$

Bayes' rules for making statistical inferences

- Specifies a method to make a statistical inference about a quantity of interest by modifying the uncertainty about its value in the light of available evidence
- Use this method to select chemistries

probability of finding an element on a site given a particular distortion among all compounds with that symmetry

probability of finding a particular distortion or active mode among all compounds

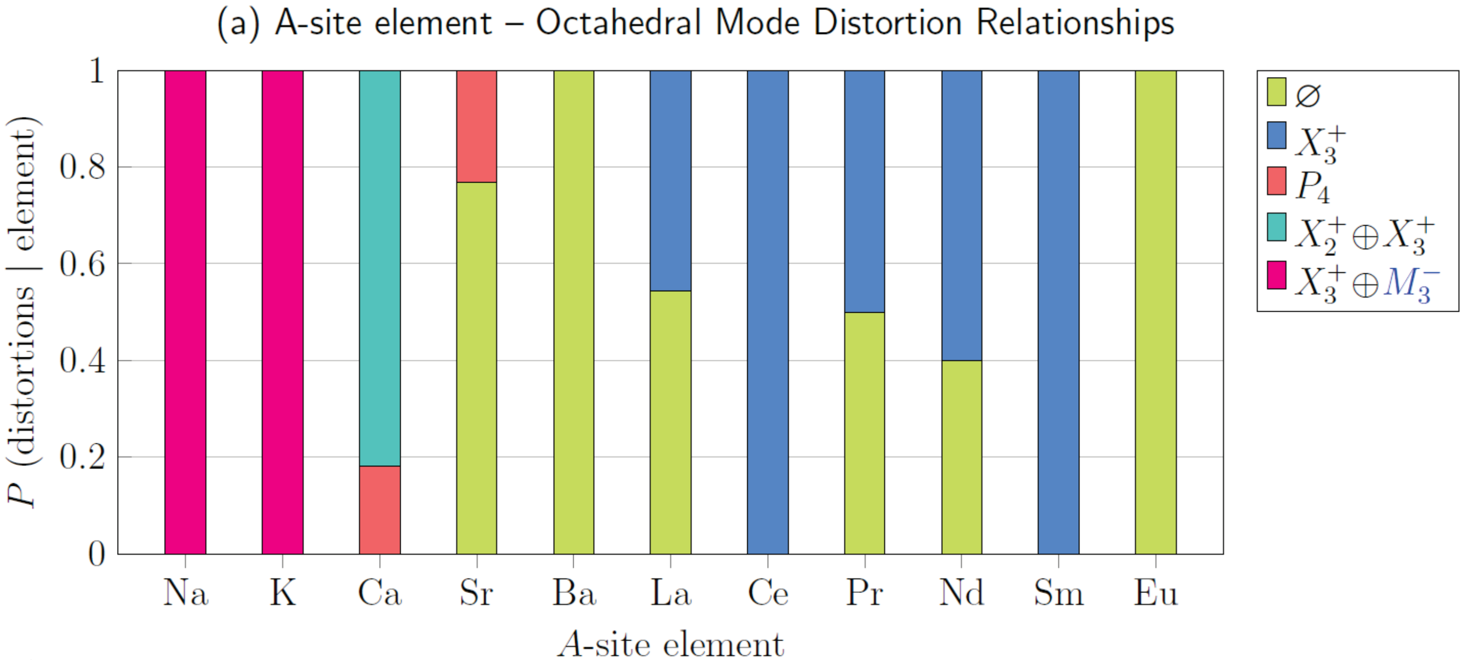
$$\underbrace{P(\text{distortions}|\text{cation})}_{\text{posterior probability}} = \frac{\overbrace{P(\text{cations}|\text{distortions})}^{\text{likelihood}} \times \overbrace{P(\text{distortions})}^{\text{prior probability}}}{\underbrace{P(\text{cation})}}$$

probability of finding a compound with the element on the correct site in the dataset

Statistical learning and data-mining for probable chemistries

- Bayesian analysis of *n*=1 RP database

$$\underline{P(\text{distortions}|\text{cation})} = \frac{\overbrace{P(\text{cations}|\text{distortions})}^{\text{likelihood}} \times \overbrace{P(\text{distortions})}^{\text{prior probability}}}{P(\text{cation})}$$



(a) A-site element – Octahedral Mode Distortion Relationships

posterior probability

Assumptions:

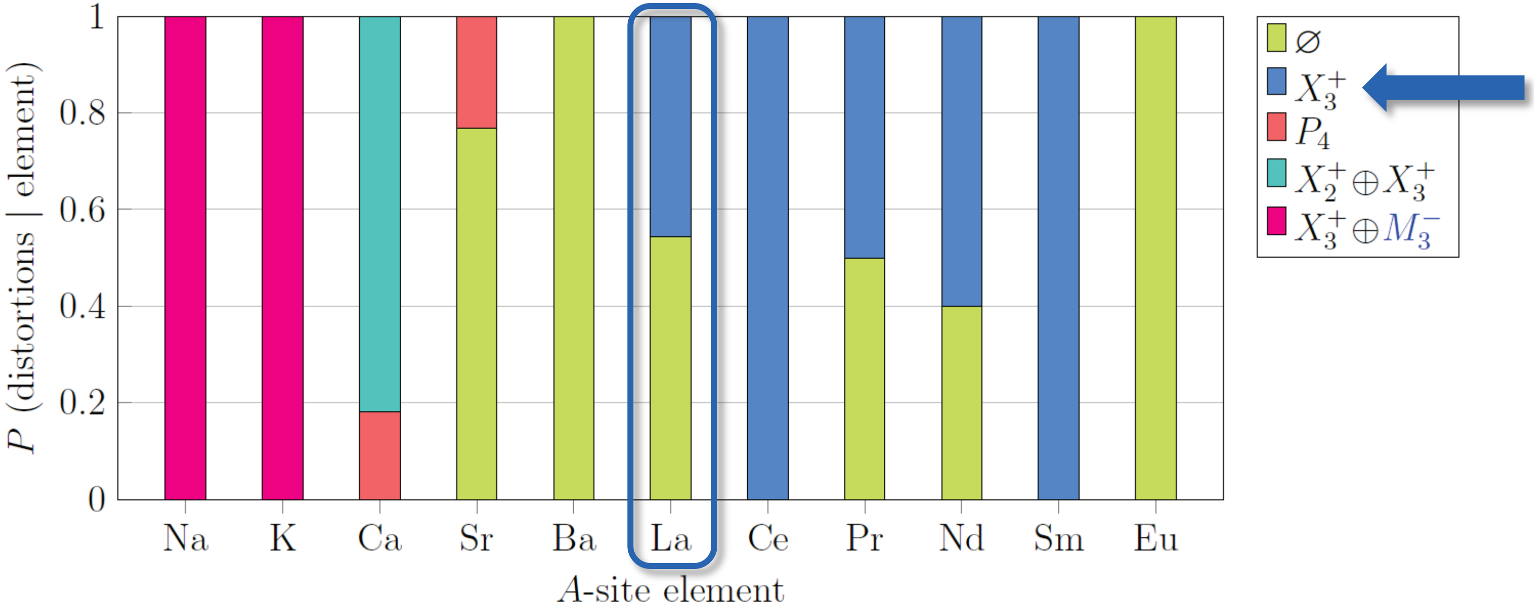
A-site, B-site, and temperature probabilities are mutual independent (non-interacting)

Balachandran, Puggioni, JMR, (Submitted, 2013)

Statistical learning and data-mining for probable chemistries

- Bayesian analysis of *n*=1 RP database

$$\underline{P(\text{distortions}|\text{cation})} = \frac{\overbrace{P(\text{cations}|\text{distortions})}^{\text{likelihood}} \times \overbrace{P(\text{distortions})}^{\text{prior probability}}}{P(\text{cation})}$$



(a) A-site element – Octahedral Mode Distortion Relationships

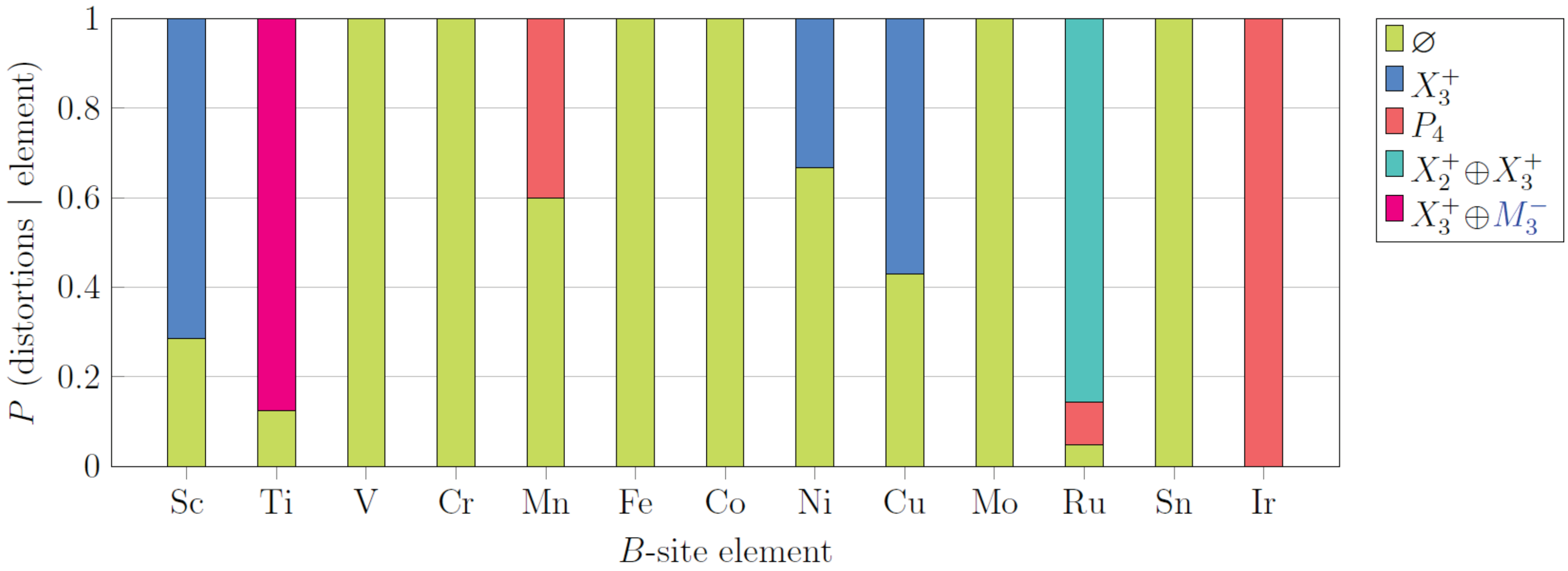
posterior probability

- *A* site cation selection

La^{3+} cation prefers to distortions with octahedral rotations of X_3^+ symmetry

Statistical learning and data-mining for probable chemistries

- *B* site selection
  - Few transition metals in the available database show Jahn-Teller distortions (X_2^+)



(b) B-site element – Octahedral Mode Distortion Relationships

posterior probability

- Valence state of Mn is the database is 4+ (d^3) – not Jahn-Teller active in octahedral crystal field

→ High spin Mn^{3+} (d^4) is Jahn-Teller active

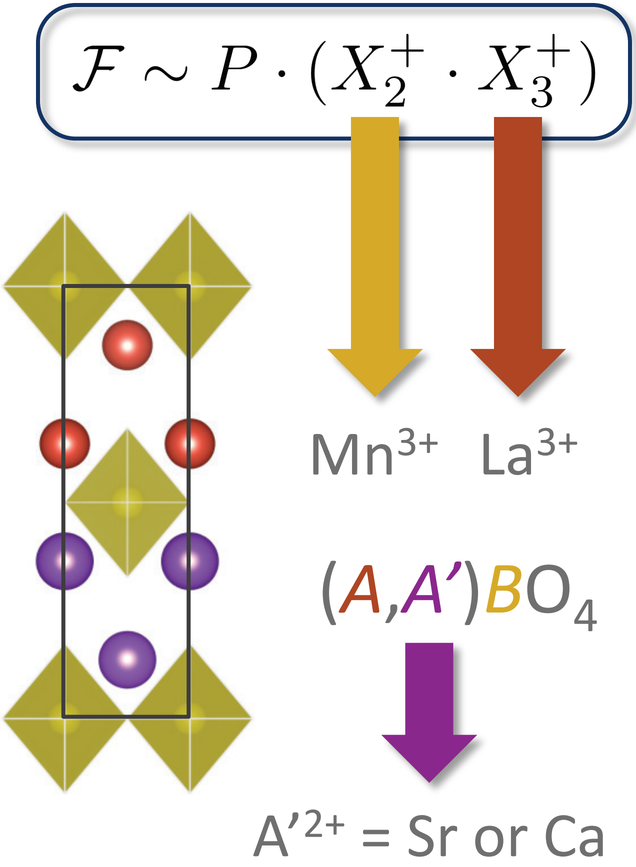
What chemistries should we choose for rotations and Jahn-Teller distortions to induce an electric polarization?

- *Structural Criterion*
  - Group theoretical approach
- *Selection Criterion*
  - Bayesian analysis

$$X_2^+ \oplus X_3^+ \oplus M_3^-$$

atomic distortions + cation order

Rotation + Berry-Pseudorotations will induce a ferroelectric polarization



$$\mathcal{F} \sim P \cdot (X_2^+ \cdot X_3^+)$$

Mn^{3+} La^{3+}

$(A,A')BO_4$

A'^{2+} = Sr or Ca

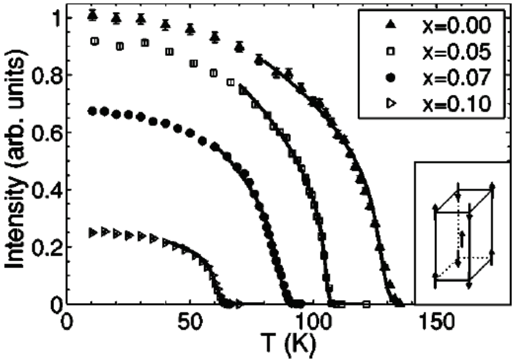
Explore energetics of down-selected $(La,Sr)MnO_4$ compound

First-principles validation of data-driven prediction

- Compute ground state structures and identify primary modes (atomic displacements) that lead to the ground state structure
  - VASP calculations, PAW pseudopotentials, 600 eV planewave energy cutoff
  - LDSA+*U* exchange-correlation functional (*U* = 5 eV, *J* = 0.5 eV)

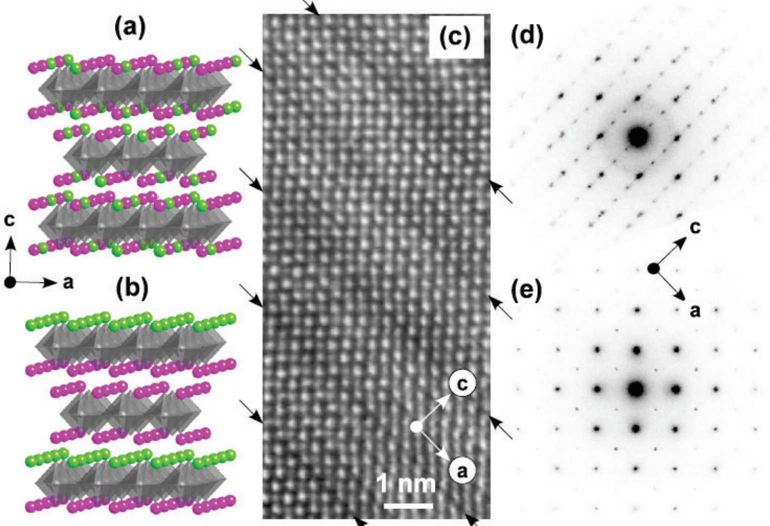
- **SANITY CHECK**
  Can this thing be made or does it exist in bulk as a solid solution?

AFM Mott insulator (T_N ~ 120K) in bulk



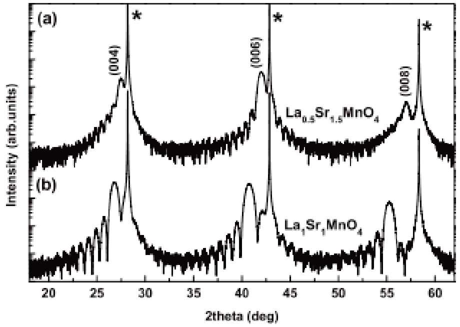
PRB **71**, 024435 (2005); JAP **113**, 053906 (2013)

$La_{2/3}Sr_{4/3}MnO_4$ STEM Image



B. Nelson-Cheeseman *et al*, APL **98** 072505 (2011)

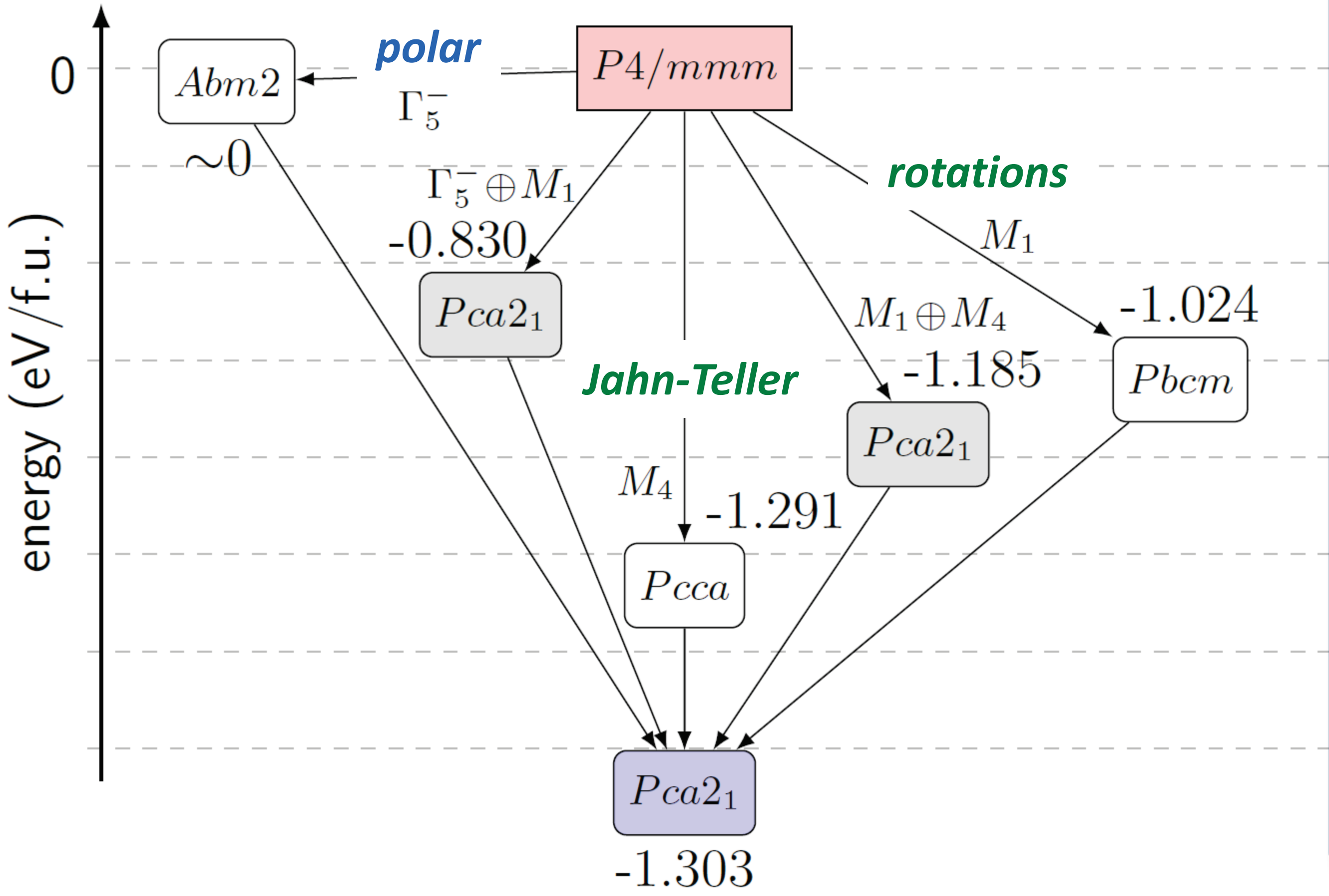
Strain-engineered



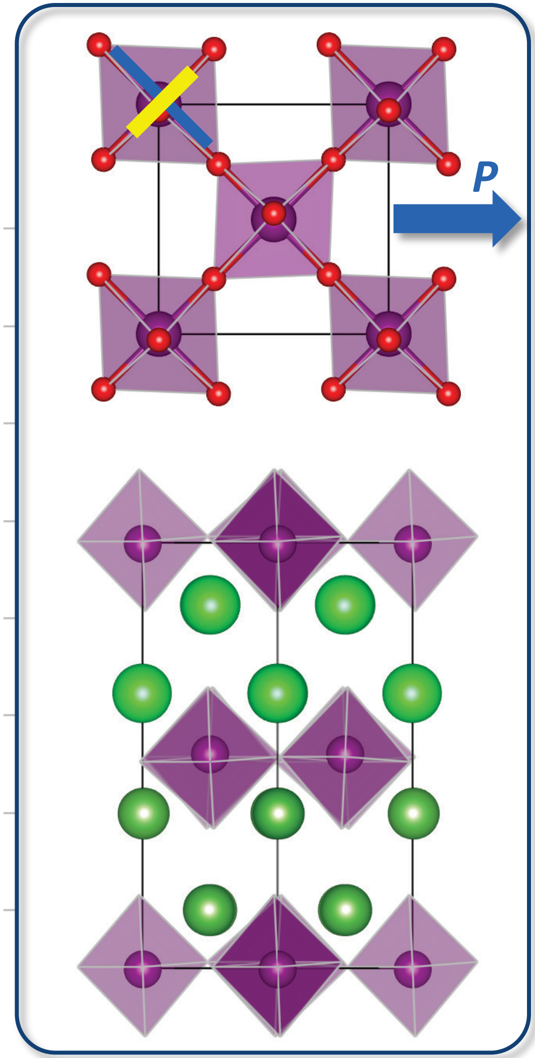
JAP **113**, 053906 (2013)

Low energy phases of (La,Sr)MnO_4

- Ground state is polar and exhibits the targeted structural distortions



$Pca2_1$, $\mathcal{P} \sim 1.25\ \mu C/cm^2$



Ground state is insulating with a 1.41 eV gap

Cammarata, JMR, (Unpublished, 2013)

Origin for the polar ground state in $LaSrMnO_4$

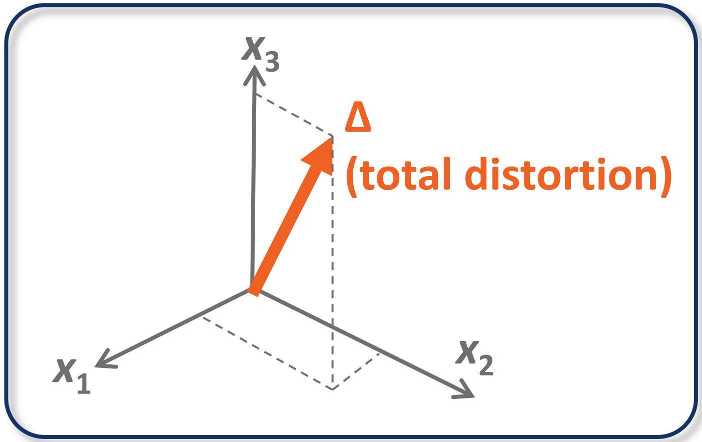
- Structural mode-decomposition reveals that the largest mode contributions come from those present in the trilinear invariant

$$\mathcal{F} \sim P \cdot Q_1 \cdot Q_2$$

P: polar displacements

$Q_1 \rightarrow X_2^+$ *Jahn-Teller distortions*

$Q_2 \rightarrow X_3^+$ *octahedral rotations*



notation is relative to *I4/mcm*

MODE	DESCRIPTION	NORM. AMP.
Γ_1^+	Anti-parallel displacements	0.65
Γ_5^-	Polar displacements along *c*	0.01
X_2^+	**Jahn-Teller distortions**	**0.26**
X_3^+	**Octahedral rotations**	**0.50**
X_3^-	La-O displacements in *ac*-plane	0.07
M_3^-	**Displacements along *b***	**0.51**

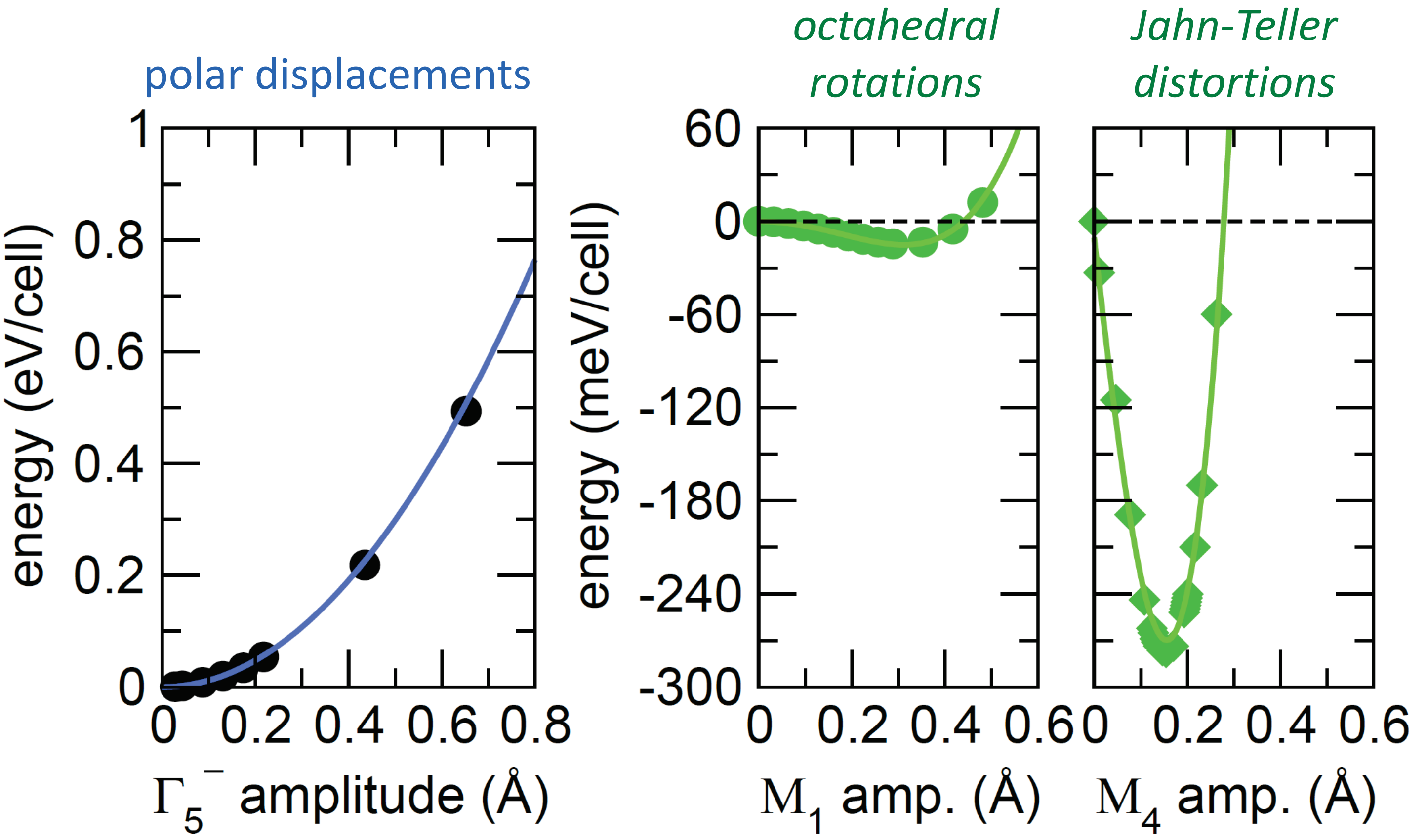
weak, secondary mode, triggered by coupling to primary modes

These two modes alone can lift inversion symmetry

$$\boxed{X_2^+ \oplus X_3^+ \oplus M_3^-}$$

Jahn-Teller and octahedral rotations provide structural stability

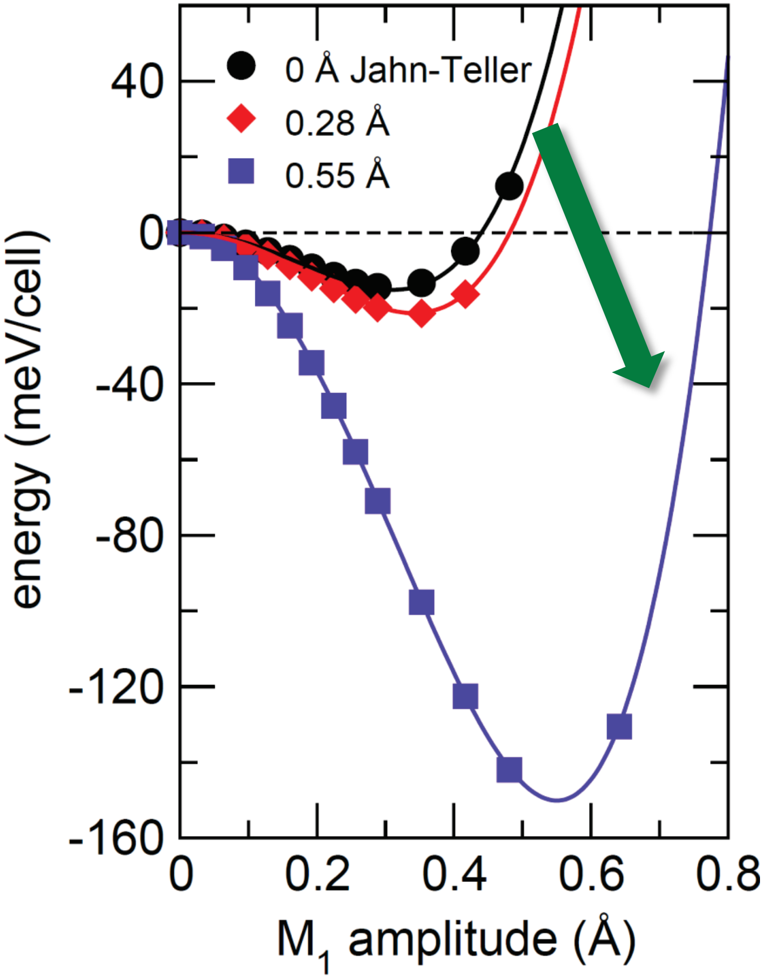
- Energetics determine the modes responsible for the induced electric polarization



- Polar mode is hard; it’s presence in the ground state is induced by the other modes

Jahn-Teller and octahedral rotations provide structural stability

- Modes cooperatively interact to stabilize the polar the structure



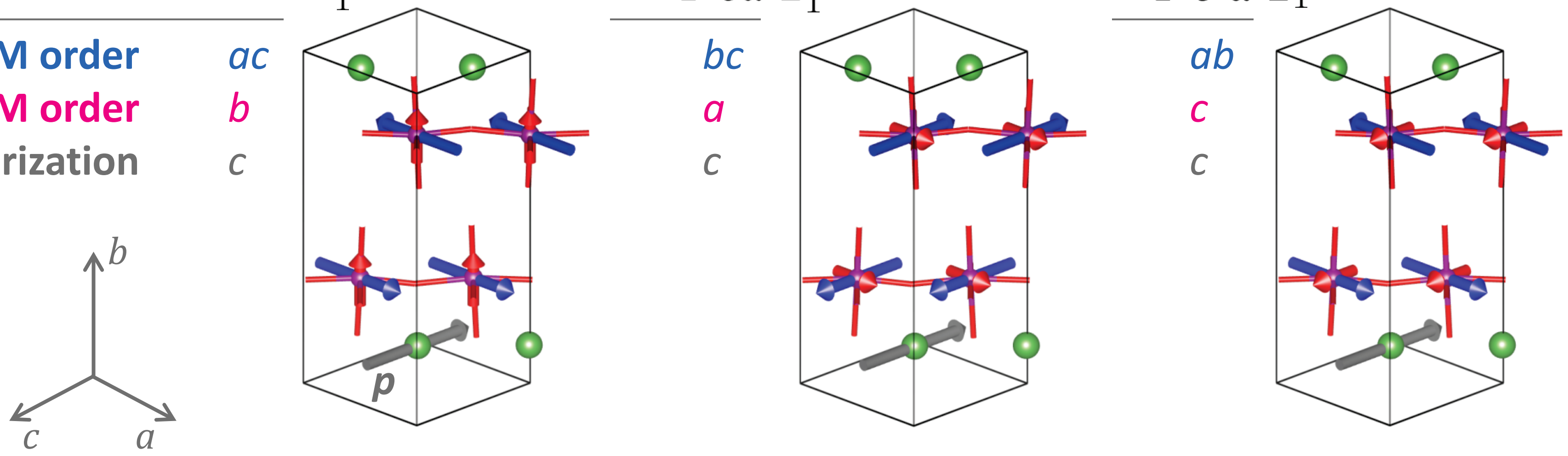
Increasing amplitude of Jahn-Teller distortions lowers the energy of the system

Cammarata, JMR, (Unpublished, 2013)

Magnetoelectricity—coupling polarization to magnetism

- Spin configuration and electric polarization allows for weak-ferromagnetism along different crystallographic directions

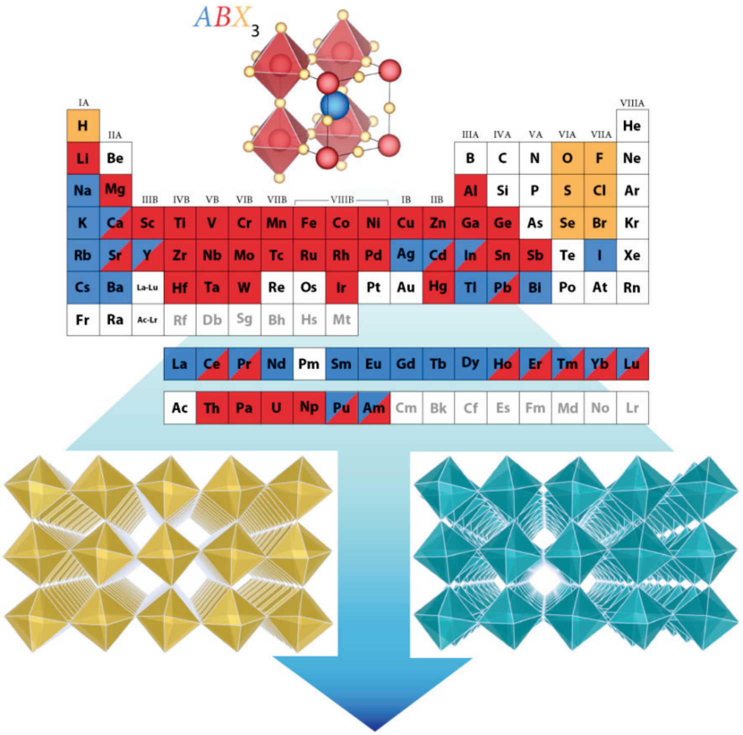
	$Pc'a2_1'$	$Pca'2_1'$	$Pc'a'2_1$
AFM order	*ac*	*bc*	*ab*
FM order	*b*	*a*	*c*
Polarization	*c*	*c*	*c*



Exploring magnetoelectric coupling

- Linear magnetoelectric effect is a direct consequence of the coupling of multiple modes to induce a polarization through terms $\sim \mathcal{M}_i\mathcal{L}_j\mathcal{P}_j$
- Investigating modes that induce weak-FM
  - Rotations suggest Dzyaloshinkskii-Moriya interaction
  - Jahn-Teller modes suggest magnetic single-ion anisotropy due SOC

Artificial design of ferroic behavior from polyhedral building blocks and cation ordering



Chemistry-independent mechanism for rotation-induced ferroelectricity

Multiple anharmonic couplings to induce ferroelectric polarizations remain to be explored

	Q_1	Q_2
☑	rotation	rotation
☑	rotation	pseudo-rotation
☐	pseudo-rotation	pseudo-rotation

Multiferroic compound from rotations and Jahn-Teller distortions

Mulder, Benedek, JMR, Fennie, Adv. Func. Mater. (2013)
JMR & Fennie, Adv. Mater., **24** 1961 (2012)
JMR, May, Freeland, MRS Bulletin **37** 261 (2012)
Gou & JMR, http://arxiv.org/abs/1304.4911 (2013)

Metal-organic framework (MOF)
Adv. Mater. **25** 2284 (2013)
Angew. Chem. Int. Ed. **50** 5847 (2011)
Chlorides:
Chem. Mater. **24** 133 (2012)

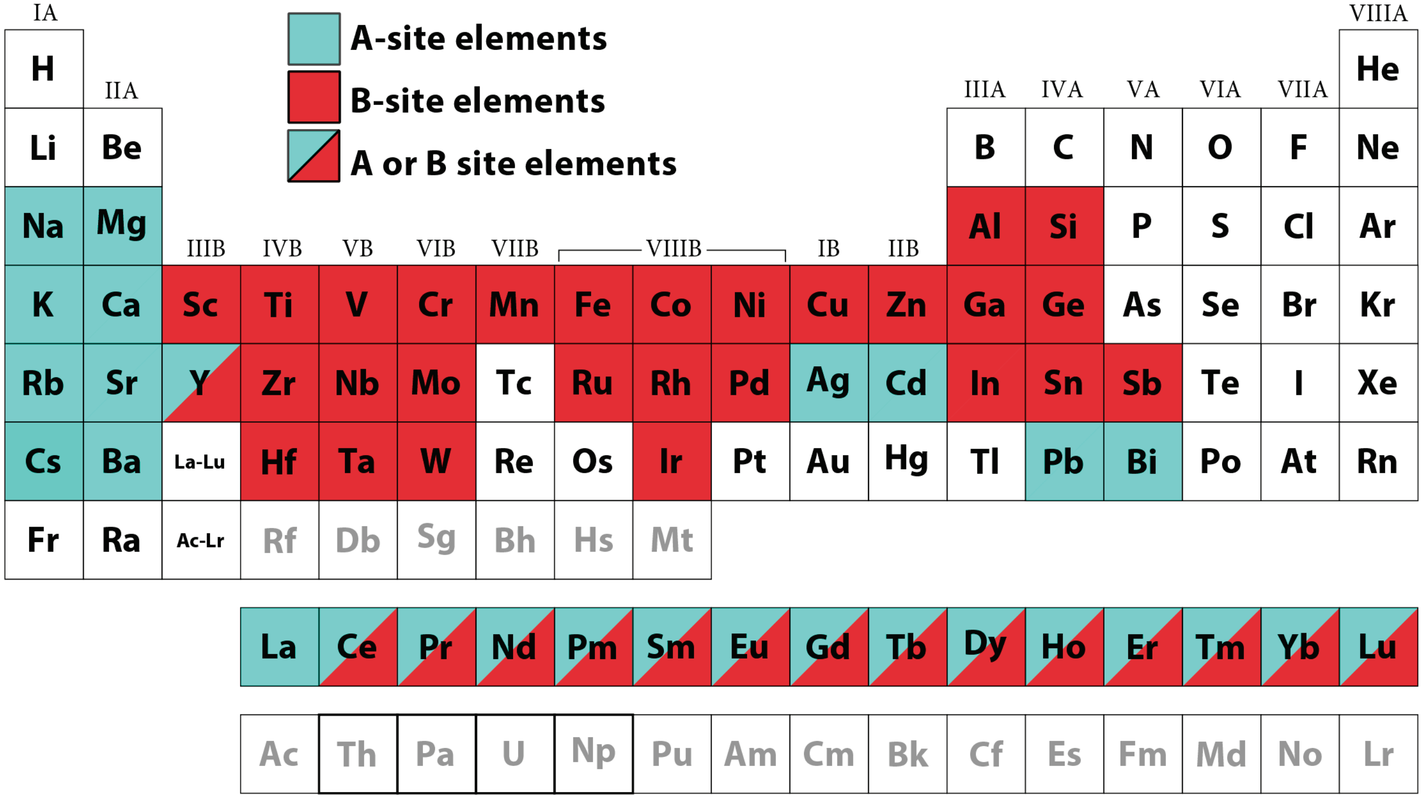
Many new reports of rotation-induced ferroelectrics

- Perovskite or perovskite-derived structures
  - E. Bousquet *et al.*, Nature 452, 732 (2008)
  - T. Fukushima *et al.*, Phys. Chem. Chem. Phys. **13**, 12186 (2011)
  - N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. **106**, 107204 (2011)
  - J. Lopez-Perez and J. Iniguez, Phys. Rev. B **84**, 075121 (2011)
  - J. M. Rondinelli and C. J. Fennie, Advanced Materials **24**, 1961 (2012)
  - G. Gou and J. M. Rondinelli, ArXiv e-prints, 1304.4911 (2013)
  - K. Yamauchi, Journal of the Physical Society of Japan **82**, 043702 (2013)
  - H. Sim, S. W. Cheong, and B. G. Kim, ArXiv e-prints, 1304.7419 (2013)

- ***Not exclusive to metal oxides***
  - A. Stroppa *et al.*, Angew. Chem. Int. Ed. **50** 5847 (2011)
  - A. Polyakov *et al.*, Chem. Mater. **24** 133 (2012)
  - A. Stroppa *et al.*, Adv. Mater. **25** 2284 (2013)

New frontiers to search for functional materials

- Combinatorial search space is immense to look for new mechanisms operative in familiar structures
- More than 1000 potential 214 Ruddlesden-Popper oxides

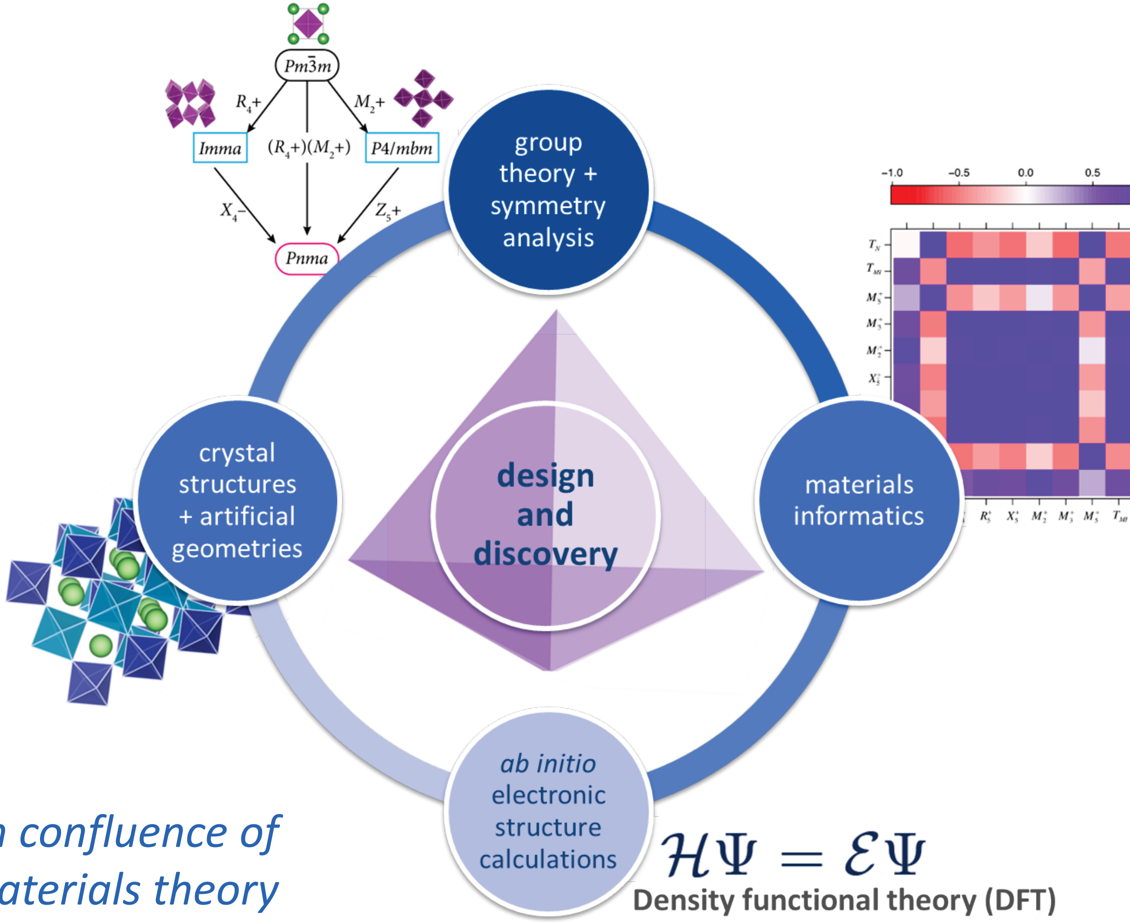


🟦 A-site elements
🟥 B-site elements
🟦🟥 A or B site elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H																	He
Li	Be											B	C	N	O	F	Ne
Na 🟦	Mg 🟦											Al 🟥	Si 🟥	P	S	Cl	Ar
K 🟦	Ca 🟦	Sc 🟥	Ti 🟥	V 🟥	Cr 🟥	Mn 🟥	Fe 🟥	Co 🟥	Ni 🟥	Cu 🟥	Zn 🟥	Ga 🟥	Ge 🟥	As	Se	Br	Kr
Rb 🟦	Sr 🟦	Y 🟦🟥	Zr 🟥	Nb 🟥	Mo 🟥	Tc	Ru 🟥	Rh 🟥	Pd 🟥	Ag 🟦	Cd 🟦	In 🟥	Sn 🟥	Sb 🟥	Te	I	Xe
Cs 🟦	Ba 🟦	La-Lu	Hf 🟥	Ta 🟥	W 🟥	Re	Os	Ir 🟥	Pt	Au	Hg	Tl	Pb 🟦	Bi 🟦	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt									
			La 🟦	Ce 🟦🟥	Pr 🟦🟥	Nd 🟦🟥	Pm 🟦🟥	Sm 🟦🟥	Eu 🟦🟥	Gd 🟦🟥	Tb 🟦🟥	Dy 🟦🟥	Ho 🟦🟥	Er 🟦🟥	Tm 🟦🟥	Yb 🟦🟥	Lu 🟦🟥
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Artificial design of ferroic behavior from polyhedral building blocks and cation ordering

- Understanding the atomic structure of the constituents *and* how building blocks are arranged, makes it possible to stabilize new phases with desirable properties



group theory + symmetry analysis

crystal structures + artificial geometries

design and discovery

materials informatics

ab initio electronic structure calculations

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

Density functional theory (DFT)

Insights obtained through confluence of multiple levels of materials theory