DESIGNING ATOMIC-SCALE FUNCTION

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

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date – August 30, 2013 | ICMR Summer School on Materials in 3D
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\[
E[n(r)] = F[n(r)] + \int \nabla V(r)n(r)dr
\]
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**
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
Structure at various length scales determines functionality

- Structures impose constraints on physical properties of materials

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


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

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

(anti)ferromagnetism
magnetoelectricity
spintronics
giant magnetoresistance
thermoelectrics

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

superconductivity
colossal magnetoresistance

ion conduction
photocatalytic efficiency
ferroic behavior

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

<table>
<thead>
<tr>
<th>Function</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric</td>
<td>CaTiO$_3$</td>
</tr>
<tr>
<td>Ferroelectric</td>
<td>BaTiO$_3$</td>
</tr>
<tr>
<td>Magnetoelectric</td>
<td>BiFeO$_3$</td>
</tr>
<tr>
<td>Antiferroelectric</td>
<td>PbZrO$_3$</td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td>LaMnO$_3$</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>SrRuO$_3$</td>
</tr>
<tr>
<td>Superconducting</td>
<td>YBa$_2$Cu$<em>3$O$</em>{7-\delta}$</td>
</tr>
<tr>
<td>Semiconducting</td>
<td>CaMnO$_3$</td>
</tr>
</tbody>
</table>
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 diagram for manganites](image1)

![Phase diagram for cuprates](image2)

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


Cheong & Hwang (1999)

Flexible and adaptive structure types in complex oxides

- garnet ($A_3B_2(SiO_4)_3$)
- perovskite ($CaTiO_3$)
- spinel ($MgAl_2O_4$)
- apatite ($A_5(BO_4)_3X$)
- lyonsite ($A_{16}(BO_4)_{12}$)

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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

![Diagram showing relationships between structure, processing, properties, and performance]
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

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 this simple structural unit.

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

$BO_6$ octahedron
Electronic properties of the $BO_6$ octahedron – molecular orbitals

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

- **metal ($M^{n+}$)**
  - $4p$
  - $4s$
  - $3d$

- **$[MO_6]^{n+}$ complex**
  - $t_{1u}$
  - $a_{1g}$
  - $e_g + t_{2g}$

- **6-oxygen ($O^{2-}$)**
  - $2s + 2p$
  - $e_g$
  - $t_{1u}$
  - $a_{1g}$

$\sigma$-bonding only
Electronic properties of the $BO_6$ octahedron – molecular orbitals

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

<table>
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<th>$[MO_6]^{n+}$ complex</th>
<th>6-oxygen ($O^{2-}$)</th>
</tr>
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<tbody>
<tr>
<td>$4p$</td>
<td>$t_{1u}$</td>
<td>antibonding</td>
</tr>
<tr>
<td>$4s$</td>
<td>$a_{1g}$</td>
<td></td>
</tr>
<tr>
<td>$3d$</td>
<td>$e_g + t_{2g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$t_{2g}$</td>
<td>NB</td>
</tr>
<tr>
<td></td>
<td>$e_g$</td>
<td>bonding</td>
</tr>
<tr>
<td></td>
<td>$t_{1u}$</td>
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<td>$a_{1g}$</td>
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$\sigma$-bonding only
Electronic properties of the $BO_6$ octahedron – molecular orbitals

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

The diagram shows the electronic levels of the metal ($M^{n+}$), the $[MO_6]^{n+}$ complex, and the 6-oxygen ($O^{2-}$) ions. The electronic levels are divided into bonding and antibonding states, with $t_{1u}$, $e_g$, $t_{2g}$, and $a_{1g}$ orbitals depicted. The $\Delta_{CF}$ is the charge transfer splitting. The $\sigma$-bonding only is highlighted, showing the bonding and antibonding states for the metal and oxygen ions.
The $BO_6$ octahedron as a functional building block

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

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

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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 4s 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 3$^{rd}$ or 4$^{th}$ row

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

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.

![Diagram showing octahedral rotations, Jahn-Teller distortions, and cation displacements.](image)

- 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*)

**Figure from P. Khalifah (2013)**

Changes occur due to:
- Coordination environment
- Bonding/hybridization
- **Structure dimensionality**
- Valence state

**How wide are these bands?**

Designing atomic-scale function...
James Rondinelli
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

- \(\text{LaNiO}_3\) (R-3c)
  - Paramagnetic metal
  - Itinerant (wide bandwidth)

- \(\text{LiNiO}_2\) (R-3m)
  - Ferromagnetic insulator
  - AFM at low-T
  - Localized electrons

\(\text{square NiO}_2\) net

\(\text{hexagonal NiO}_2\) net
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 ($a$-$a$-$b^+$)
  - $D_{2h}$

Engineering the electronic structure

- **Bandwidth** is sensitive to orbital overlap in transition metal oxides

![Diagram showing energy levels and orbital overlap](image)
Engineering the electronic structure through bandwidth control

- **Bandwidth** is sensitive to orbital overlap in transition metal oxides

\[ \begin{align*}
\text{DOS} & \quad \text{O} 2p \\
\text{TM} 3d & \quad E_F \\
\Delta & \quad W \\
\Delta & \quad E_g
\end{align*} \]

\[ \text{ABO}_3 \]

- **Amenable to structure-directed design**

\[ \begin{align*}
\text{U/W} & \quad \text{filling control} \\
1 & \quad \text{metal} \\
& \quad \text{bandwidth control}
\end{align*} \]

- Maximum hopping
- Reduced hoping
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).

Fujimori transition metal oxide phase diagram

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

- Distortions from cubic symmetry renormalize Fujimori’s phase diagram

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

E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen

INFM and Dipartimento di Fisica “A. Volta,” Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy
Centre de Physique Théorique, Ecole Polytechnique, 91128 Palaiseau Cedex, France
NSRIM, University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands
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

![Graph showing the relationship between B-O-B angle and Ca₁₋ₓSrₓFeO₃ structure.](image1)

![Diagram illustrating the properties of materials with different structures.](image2)

Structure/bandwidth engineering for other functional properties

- What’s more?
  1. Produce (or destroy) collective **magnetism**
     - Exchange interactions depend on structure/connectivity
  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

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

- Hoffman, Burdett, Pauling, among others...

- 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

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.

- 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.

Schroedinger 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.”

Quantum mechanical solutions

- Standard approach: properties are governed by a wavefunction

\[ \Psi(r_1, r_2, \ldots, r_N); \mathcal{H}\Psi = E\Psi \]

- 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 \( 3N \) 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

Walter Kohn 1998 Nobel Laureate (Chemistry)
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

\[ E[n(r)] = F[n(r)] + \int V_{\text{ext}}(r)n(r)\,dr \]

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

- 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.

\[
\mathcal{H}\Psi = \mathcal{E}\Psi
\]

\[
\hat{\mathcal{H}}\phi = \epsilon\phi
\]

interacting electrons

non-interacting electrons

\[
E[n(r)] = F[n(r)] + \int V_{\text{ext}}(r)n(r)dr
\]

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

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

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

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

- 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

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

### Figure

- **Ca\(_{2-x}\)Sr\(_x\)RuO\(_4\)**
- **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

\[ H\Psi = \varepsilon\Psi \]

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

- Graph showing energy (meV/f.u.) vs. amplitude (Å)
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 initio symmetry-based structural approach to materials design

Density functional theory (DFT)
\[ H \Psi = E \Psi \]

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.
Theoretical/Computational Tools

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Designing atomic-scale function...
James Rondinelli
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

- 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 phénomènes 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 (∞∞m)
  - Polycrystalline solids with randomly oriented grains also have spherical symmetry

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Field</th>
<th>Response</th>
<th>Type/#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat</td>
<td>$C$</td>
<td>$\Delta T$</td>
<td>$T \Delta S$</td>
<td>E/1</td>
</tr>
<tr>
<td>Electrocaloric</td>
<td>$\rho_i$</td>
<td>$E_i$</td>
<td>$\Delta S$</td>
<td>E/3</td>
</tr>
<tr>
<td>Magnetocaloric</td>
<td>$q_i$</td>
<td>$H_i$</td>
<td>$\Delta S$</td>
<td>E/3</td>
</tr>
<tr>
<td>Pyroelectric</td>
<td>$p'_i$</td>
<td>$\Delta T$</td>
<td>$D_i$</td>
<td>E/3</td>
</tr>
<tr>
<td>Pyromagnetic</td>
<td>$q'_i$</td>
<td>$\Delta T$</td>
<td>$B_i$</td>
<td>E/3</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>$\alpha_{ij}$</td>
<td>$\Delta T$</td>
<td>$\epsilon_{ij}$</td>
<td>E/6</td>
</tr>
<tr>
<td>Piezoelectric effect</td>
<td>$\alpha'_{ij}$</td>
<td>$\sigma_{ij}$</td>
<td>$\Delta S$</td>
<td>E/6</td>
</tr>
<tr>
<td>Dielectric permittivity</td>
<td>$\kappa_{ij}$</td>
<td>$E_j$</td>
<td>$D_i$</td>
<td>E/6</td>
</tr>
<tr>
<td>Magnetic permeability</td>
<td>$\mu_{ij}$</td>
<td>$H_j$</td>
<td>$B_i$</td>
<td>E/6</td>
</tr>
<tr>
<td>Optical activity</td>
<td>$k_{ij}$</td>
<td>$l_{ij}$</td>
<td>$G$</td>
<td>E/6</td>
</tr>
<tr>
<td>Magnetoelastic polarization</td>
<td>$\lambda_{ij}$</td>
<td>$H_j$</td>
<td>$D_i$</td>
<td>E/9</td>
</tr>
<tr>
<td>Converse magnetoelastic polarizaton</td>
<td>$\lambda'_{ij}$</td>
<td>$E_j$</td>
<td>$B_i$</td>
<td>E/9</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>$\sigma_{ij}$</td>
<td>$(\rho_{ij})$</td>
<td>$E_j \left(j_i \right)$</td>
<td>$j_i \left(E_i \right)$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$K_{ij}$</td>
<td>$V_jT$</td>
<td>$h_i$</td>
<td>T/6</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$D_{ij}$</td>
<td>$V_jc$</td>
<td>$m_i$</td>
<td>T/6</td>
</tr>
<tr>
<td>Thermoelectric power</td>
<td>$\Sigma_{ij}$</td>
<td>$V_jT$</td>
<td>$E_i$</td>
<td>T/9</td>
</tr>
<tr>
<td>Hall effect</td>
<td>$R_{ij}$</td>
<td>$B_j$</td>
<td>$\rho_i^2$</td>
<td>T/9</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>$d_{ijk}$</td>
<td>$\sigma_{jk}$</td>
<td>$D_i$</td>
<td>E/18</td>
</tr>
<tr>
<td>Converse piezoelectricity</td>
<td>$d'_{ijk}$</td>
<td>$E_k$</td>
<td>$\epsilon_{ij}$</td>
<td>E/18</td>
</tr>
<tr>
<td>Piezomagnetism</td>
<td>$Q_{ijk}$</td>
<td>$\sigma_{jk}$</td>
<td>$B_i$</td>
<td>E/18</td>
</tr>
<tr>
<td>Converse piezomagnetism</td>
<td>$Q'_{ijk}$</td>
<td>$H_k$</td>
<td>$\epsilon_{ij}$</td>
<td>E/18</td>
</tr>
<tr>
<td>Electro-optic effect</td>
<td>$\tau_{ijk}$</td>
<td>$E_k$</td>
<td>$\Delta \beta_{ij}$</td>
<td>E/18</td>
</tr>
<tr>
<td>Nernst tensor</td>
<td>$\Sigma_{ijk}$</td>
<td>$V_jT B_k$</td>
<td>$E_i$</td>
<td>T/27</td>
</tr>
<tr>
<td>Elasticity</td>
<td>$s_{ijkl}$</td>
<td>$(C_{ijkl})$</td>
<td>$\sigma_{ij}$</td>
<td>$(\epsilon_{ij})$</td>
</tr>
<tr>
<td>Electrostriction</td>
<td>$\gamma_{ijkl}$</td>
<td>$E_k E_l$</td>
<td>$\epsilon_{ij}$</td>
<td>E/36</td>
</tr>
<tr>
<td>Photoelasticity</td>
<td>$q_{ijkl}$</td>
<td>$\sigma_{ij}$</td>
<td>$\Delta \beta_{ij}$</td>
<td>E/36</td>
</tr>
<tr>
<td>Kerr effect</td>
<td>$p_{ijkl}$</td>
<td>$E_k E_l$</td>
<td>$\rho_i^2$</td>
<td>T/36</td>
</tr>
<tr>
<td>Magnetoresistance</td>
<td>$\xi_{ijkl}$</td>
<td>$B_k B_l$</td>
<td>$\rho_i^2$</td>
<td>T/36</td>
</tr>
<tr>
<td>Piezo-resistance</td>
<td>$\Omega_{ijkl}$</td>
<td>$\sigma_{ij}$</td>
<td>$\Delta \beta_{ij}$</td>
<td>E/36</td>
</tr>
<tr>
<td>Magnetothermoelastic power</td>
<td>$\Sigma_{ijkl}$</td>
<td>$V_jTB_k B_l$</td>
<td>$E_i$</td>
<td>T/54</td>
</tr>
<tr>
<td>Second-order Hall effect</td>
<td>$\rho_{ijkl}$</td>
<td>$B_j B_l B_i$</td>
<td>$\rho_i^2$</td>
<td>T/30</td>
</tr>
<tr>
<td>Third-order elasticity</td>
<td>$C_{ijklmn}$</td>
<td>$\epsilon_{ijklmn}$</td>
<td>$\sigma_{ij}$</td>
<td>E/56</td>
</tr>
</tbody>
</table>
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

\[ \mathcal{H}\Psi = E\Psi \]
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...

$\text{Ba}_4\text{B}_{11}\text{O}_{20}\text{F}$ in space group $\text{Cmc}_{21}$ (144 atoms in the unit cell)

*How do we understand which atoms are largely responsible for the loss of inversion symmetry?*
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
Entry for space group $P2_1/c$ (No. 14)

**CONTINUED**

**positions**

<table>
<thead>
<tr>
<th>Multiplicity, Wyckoff letter, Site symmetry</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 e 1</td>
<td>(1) x, y, z</td>
</tr>
<tr>
<td>2 d 1</td>
<td>(2) x, y + \frac{1}{2}, z + \frac{1}{2}</td>
</tr>
<tr>
<td>2 c 1</td>
<td>(3) x, y, z</td>
</tr>
<tr>
<td>2 b 1</td>
<td>(4) x, y + \frac{1}{2}, z + \frac{1}{2}</td>
</tr>
</tbody>
</table>

**reflection conditions**

- General: $h0l : l = 2n$
- $0k0$ : $k = 2n$
- $00l$ : $l = 2n$
- Special: as above, plus $hk0 : k+i+l = 2n$
- $0k0$ : $k = 2n$
- $h0l : k+i+l = 2n$
- $0k0$ : $k = 2n$
- $h0l : k+i+l = 2n$

**symmetry of special projections**

Along [001] $p2$  
\[a' = a, \quad b' = b, \quad c' = c] 

Origin at 0, 0, 1

**maximal non-isomorphic subgroups**

I  
1. $[2]P1/c1 (P6_3, 7)$; 1: 4  
2. $[2]P2_1/c2 (P2_1, 4)$; 1: 2  
3. $[2]P2_1 (2)$; 1: 3

II  
4. none

**maximal isomorphic subgroups of lowest index**

Ic  
1. $[2]P12_1/c1 (a = 2a, c = 2a + c) (P2_1/c, 14)$; 1: 4  
2. $[2]P12_1/c1 (b = 3b) (P2_1/c, 14)$

**minimal non-isomorphic supergroups**

I  
1. $[2]Pnaa (52); \quad [2]Pnma (53); \quad [2]Pcca (54); \quad [2]Pbam (55); \quad [2]Pbcm (56); \quad [2]Pnma (57); \quad [2]Pnma (58); \quad [2]Pbcn (60)$
2. $[2]Pnaa (61); \quad [2]Pnma (62); \quad [2]Pmna (64)$

II  
1. $[2]P12_1/m1 (C2/m, 12); \quad [2]P12_1/c1 (C2/c, 15); \quad [2]P12_1/c1 (C2/c, 15); \quad [2]P12_1/c1 (C2/c, 15); \quad [2]P12_1/m1 (C2/m, 15)$; 1: 4  
2. $[2]P12_1/c1 (b = 3b) (P2_1/c, 13)$
Entry for space group $P2_1/c$ (No. 14)
Designing atomic-scale functions...

James Rondinelli

Space group diagrams along the three directions

Axises parallel to or planes perpendicular to the b-axis

Glide translation in the plane of projection

2₁ screw axis

Glide translation perpendicular to the plane of projection

Origin at $\bar{1}$

Asymmetric unit

\[ 0 \leq x \leq 1; \ 0 \leq y \leq \frac{1}{2}; \ 0 \leq z \leq 1 \]

Symmetry operations:

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

Inversion 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

<table>
<thead>
<tr>
<th>Multiplicity, Wyckoff letter, Site symmetry</th>
<th>Coordinates</th>
<th>Reflection conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 e 1</td>
<td>(1) $x,y,z$</td>
<td>General:</td>
</tr>
<tr>
<td></td>
<td>(2) $\bar{x},y+\frac{1}{2},z+\frac{1}{2}$</td>
<td>$h0l : l = 2n$</td>
</tr>
<tr>
<td></td>
<td>(3) $\bar{x},\bar{y},\bar{z}$</td>
<td>$0k0 : k = 2n$</td>
</tr>
<tr>
<td></td>
<td>(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$</td>
<td>$00l : l = 2n$</td>
</tr>
</tbody>
</table>

#### Symmetry of special projections

- Along [001] $p2gm$
  - $a' = a$, $b' = b$
  - Origin at $0,0,z$

- Along [100] $p2gg$
  - $a' = b$, $b' = c$
  - Origin at $x,0,0$

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

#### Maximal non-isomorphic subgroups

- I [2] $P1c1$ ($Pc$, 7)
- I [2] $P12_1$ ($P2_1$, 4)
- I [2] $P1$ (2)
- IIa none
- IIb none

#### Maximal isomorphic subgroups of lowest index

- IIC [2] $P12_1/c1$ ($a' = 2a$ or $a' = 2a$, $c' = 2a + c$) ($P2_1/c$, 14);
- [3] $P12_1/c1$ ($b' = 3b$) ($P2_1/c$, 14)

#### Minimal non-isomorphic supergroups

- II [2] $A12/m1$ ($C2/m$, 12);
- [2] $C12/m1$ ($C2/c$, 15);
- [2] $I12_1/c1$ ($C2/c$, 15);
- [2] $P12_1/m1$ ($c' = \frac{1}{2}c$) ($P2_1/m$, 11);
- [2] $P12_1/c1$ ($b' = \frac{1}{2}b$) ($P2/c$, 13)
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

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 e 1</td>
<td>(1) $x,y,z$ (2) $x,y+\frac{1}{2},z+\frac{1}{2}$ (3) $x,y,z$ (4) $x,y+\frac{1}{2},z+\frac{1}{2}$</td>
</tr>
</tbody>
</table>

#### Wyckoff Sites

**General positions**

- $d$ 1
  - $\frac{1}{2},0,\frac{1}{2}$
  - $\frac{1}{2},\frac{1}{2},0$

- $c$ 1
  - $0,0,\frac{1}{2}$
  - $0,\frac{1}{2},0$

- $b$ 1
  - $\frac{1}{2},0,0$
  - $\frac{1}{2},\frac{1}{2},0$

- $a$ 1
  - $0,0,0$
  - $0,\frac{1}{2},\frac{1}{2}$

#### Special positions

**Reflection conditions & Systematic Absences**

- 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] $p 2gm$
  - Origin at $0,0,z$
- Along [100] $p 2gg$
  - Origin at $0,0,0$
- Along [010] $p 2$
  - Origin at $0,0,0$

### Maximal non-isomorphic subgroups

I

- [2] $P1c1 (Pc, 7)$
  - 1; 4
- [2] $P12_1, 1 (P2_1, 4)$
  - 1; 2
- [2] $P1 \bar{1} (2)$
  - 1; 3

IIa none

IIb none

### Maximal isomorphic subgroups of lowest index

IIc

- [2] $P12_1/c1 (a' = 2a$ or $a' = 2a, c' = 2a + c) (P2_1/c, 14)$
- [3] $P12_1/c1 (b' = 3b) (P2_1/c, 14)$

### Minimal non-isomorphic supergroups

I


II

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

<table>
<thead>
<tr>
<th>4 e 1</th>
<th>(1) $x, y, z$</th>
<th>(2) $\bar{x}, y + \frac{1}{2}, z + \frac{1}{2}$</th>
<th>(3) $\bar{x}, y, \bar{z}$</th>
<th>(4) $x, y + \frac{1}{2}, z + \frac{1}{2}$</th>
</tr>
</thead>
</table>

**Wyckoff Sites**
- General positions
- Special positions

**Symmetry of special projections**
- Along [001] $p 2_{gm}$
- Along [100] $p 2 gg$
- Along [010] $p 2$

**Maximal non-isomorphic subgroups**
- I [2] $P 1 c 1 (P c, 7)$; (2) $P 1 2, 1 (P 2_1, 4)$; (2) $P \bar{1} (2)$
- IIa none
- IIb none

**Maximal isomorphic subgroups of lowest index**
- IIC [2] $P 1 2_1 / c 1 (a' = 2a$ or $a' = 2a, c' = 2a + c) (P 2_1 / c, 14)$; [3] $P 1 2_1 / c 1 (b' = 3b) (P 2_1 / c, 14)$

**Minimal non-isomorphic supergroups**
- II [2] $A 1 2 / m 1 (C 2 / m, 12)$; [2] $C 1 2 / c 1 (C 2 / c, 15)$; [2] $I 1 2 / c 1 (C 2 / c, 15)$; [2] $P 1 2_1 / c 1 (e' = \frac{1}{2}c) (P 2_1 / c, 11)$; [2] $P 1 2 / c 1 (b' = \frac{1}{2}b) (P 2_1 / c, 13)$

**Reflection conditions & Systematic Absences**
- General:
  - $h0l; l = 2n$
  - $0k0; k = 2n$
  - $00l; l = 2n$
- Special: as above, plus
  - $hkl; k + l = 2n$
  - $hkl; k + l = 2n$
  - $hkl; k + l = 2n$
  - $hkl; k + l = 2n$
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

<table>
<thead>
<tr>
<th>Wyckoff letter</th>
<th>Multiplicity</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$</td>
<td>1</td>
<td>$(1) x, y, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(2) \bar{x}, y + \frac{1}{2}, z + \frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(3) \bar{x}, \bar{y}, z$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(4) x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$</td>
</tr>
</tbody>
</table>

#### General positions

<table>
<thead>
<tr>
<th>Position</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2d$</td>
<td>$\frac{1}{2}, 0, \frac{1}{2}$</td>
</tr>
<tr>
<td>$2c$</td>
<td>$0, 0, \frac{1}{2}$</td>
</tr>
<tr>
<td>$2b$</td>
<td>$\frac{1}{2}, 0, 0$</td>
</tr>
<tr>
<td>$2a$</td>
<td>$0, 0, 0$</td>
</tr>
</tbody>
</table>

#### Special positions

### Reflection conditions & Systematic Absences

**Reflection conditions**

**General:**
- $h0l : l = 2n$
- $0k0 : k = 2n$
- $00l : l = 2n$

**Special:** as above, plus
- $hkl : k + l = 2n$
- $hkl : k + l = 2n$
- $hkl : k + l = 2n$
- $hkl : k + l = 2n$

### Subgroups

Space group symmetry if certain symmetry operations are eliminated

### Supergroups

Space group symmetry if certain symmetry operations are added

### Symmetry of special projections

#### Along [001] $p2gm$

- $a' = a$
- $b' = b$

Origin at $0, 0, z$

#### Along [100] $p2gg$

- $a' = b$
- $b' = c$

Origin at $x, 0, 0$

#### Along [010] $p2$

- $a' = \frac{1}{2} c$
- $b' = a$

Origin at $0, y, 0$

### Maximal non-isomorphic subgroups

<table>
<thead>
<tr>
<th>$I$</th>
<th>$[2] P1c1$ ($Pc$, 7)</th>
<th>1; 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[2] P12, 1$ ($P2_1/c$, 4)</td>
<td>1; 2</td>
<td></td>
</tr>
<tr>
<td>$[2] P\bar{1}$ ($2$)</td>
<td>1; 3</td>
<td></td>
</tr>
<tr>
<td>$IIa$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>$IIb$</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

### Maximal isomorphic subgroups of lowest index

| $IIC$     | $[2] P12, 1/c$ ($a' = 2a$ or $a' = 2a, c' = 2a + c$) ($P2_1/c$, 14); $[3] P12, 1/c$ ($b' = 3b$) ($P2_1/c$, 14) |

### Minimal non-isomorphic supergroups

<table>
<thead>
<tr>
<th>$I$</th>
<th>$[2] P\overline{n}a2$ ($52$); $[2] P\overline{m}n(a2)$ ($53$); $[2] P\overline{c}ca$ ($54$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pbam (55)$; $Pccn (56)$; $Pbcn (57)$; $Pnnm (58)$; $Pbcn (60)$; $P\overline{ca} (61)$; $P\overline{n}ma (62)$; $Cmce (64)$</td>
<td></td>
</tr>
<tr>
<td>$II$</td>
<td>$[2] A12/m1$ ($C2/m$, 12); $[2] C12/c1$ ($C2/c$, 15); $[2] I12/c1$ ($C2/c$, 15); $[2] P12, 1/m1$ ($c' = \frac{1}{2} c$) ($P2_1/m$, 11); $[2] P12/c1$ ($b' = \frac{1}{2} b$) ($P2_1/c$, 13)</td>
</tr>
</tbody>
</table>
**Ba$_4$B$_{11}$O$_{20}$F in space group $Cmc2_1$**

- Now need to account for 21 atoms

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

<table>
<thead>
<tr>
<th>Atom</th>
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<th>Site Symm.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
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<tbody>
<tr>
<td>Ba(1)</td>
<td>4a</td>
<td>m..</td>
<td>0</td>
<td>0.0865</td>
<td>0</td>
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<tr>
<td>Ba(2)</td>
<td>4a</td>
<td>m..</td>
<td>0</td>
<td>0.327</td>
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<tr>
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<td>8b</td>
<td>1</td>
<td>0.326</td>
<td>0.249</td>
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</tr>
<tr>
<td>F</td>
<td>4a</td>
<td>m..</td>
<td>0</td>
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<td>0.298</td>
</tr>
<tr>
<td>O(1)</td>
<td>8b</td>
<td>1</td>
<td>0.154</td>
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<td>0.479</td>
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<tr>
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<td>B(2)</td>
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<td>0.162</td>
<td>0.0987</td>
<td>0.323</td>
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<tr>
<td>B(3)</td>
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<td>m..</td>
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<td>0.671</td>
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<tr>
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<td>0.0355</td>
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<tr>
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<td>8b</td>
<td>1</td>
<td>0.0638</td>
<td>0.417</td>
<td>0.0138</td>
</tr>
</tbody>
</table>
What’s the space group of my structure?

- Need to identify symmetries for a given 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

- 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 BaTiO₃ ($R \rightarrow O \rightarrow T \rightarrow C$ phase transition)

**Property:** electric polarization

- Defined by a net electric dipole per unit volume

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

**Symmetry of the lattice is lowered as you cool BaTiO₃**

**Neumann principle**
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

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

\[
P = 0, \quad \alpha > 0 \quad \text{(Paraelectric)}
\]

\[
P = \pm \sqrt{-\frac{\alpha}{2\beta}}, \quad \alpha < 0 \quad \text{(Ferroelectric)}
\]
Space group relationships in crystallography across transitions

- **High Symmetry Phase** \((G)\)
  
  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

- 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

Need a way to precisely define the difference
Mode description of the static structure of a distorted phase

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

\[ E = E_0 + \frac{1}{2} \sum \kappa_{ij}(\mathbf{k}) q_i(\mathbf{k})^2 + \ldots \]

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)

\[ E = E_0 + \frac{1}{2} \sum \kappa_{ij}(\mathbf{k}) q_i(\mathbf{k})^2 + \ldots \]

stiffness coefficient ("spring constant") normal mode coordinates

*Ab-initio* calculation of the normal modes

Select a particular mode and map out the energy evolution

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.

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

  

  ![Figure 4-5](image)

  **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.

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

**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:


If you are interested in other publications related to Bilbao Crystallographic Server, click [here](#).

<table>
<thead>
<tr>
<th>Structure Data (in CIF format)</th>
</tr>
</thead>
<tbody>
<tr>
<td># Space Group III number 221</td>
</tr>
<tr>
<td># Lattice parameters 6.000 4.006 6.006 90 90 90</td>
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<tr>
<td># Number of independent atoms in the asymmetric unit 8</td>
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<tr>
<td># [atom type] [number] [WPI] [x] [y] [z]</td>
</tr>
<tr>
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</tr>
<tr>
<td>O 1.36 0.5 0.5 0.5</td>
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<table>
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<tr>
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<table>
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<tr>
<th>Maximum Δ</th>
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<td>1 [Maximum distance allowed]</td>
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<table>
<thead>
<tr>
<th>Transformation Matrix</th>
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<tr>
<td>0</td>
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<tr>
<td>1</td>
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</table>

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


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

[Image of AMPLIMODES interface with text boxes and input fields for symmetry mode analysis, structure data, and transformation matrix inputs.]

Maximum Δ: 1  [Maximum distance allowed]

Transformation Matrix:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
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<td>1</td>
</tr>
<tr>
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<td>0</td>
</tr>
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</table>

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/amplimodes.html)

- **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

Example: BaTiO$_3$ in the orthorhombic $Amm2$ 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

D3h
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 0.300000 0.000000 0.000000
O 1 4e 0.500000 0.250000 0.250000
O 1 2a 0.000000 0.000000 0.000000

Atom pairings and distances

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<th></th>
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</thead>
<tbody>
<tr>
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<td>Ba1 (0.000000,0.000000,0.005080)</td>
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<tr>
<td>2b</td>
<td>(1/2,0,z)</td>
<td>Ti1 (0.500000,0.000000,0.500000)</td>
<td>Ti1 (0.500000,0.000000,0.522080)</td>
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</tr>
<tr>
<td>4e</td>
<td>(1/2,y,z)</td>
<td>O1 (0.500000,0.250000,0.250000)</td>
<td>O2 (0.500000,0.256100,0.239380)</td>
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<tr>
<td>2a</td>
<td>(0,0,z)</td>
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Symmetry Modes Summary

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<tr>
<th>Atoms</th>
<th>WP</th>
<th>Modes</th>
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<tr>
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<td>GM4-(2) GM5-(1)</td>
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<td>Ti1</td>
<td>1b</td>
<td>GM4-(1)</td>
</tr>
<tr>
<td>Ba1</td>
<td>1a</td>
<td>GM4-(1)</td>
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</table>

Note: The primary mode is written in bold letters

Summary of Amplitudes

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<tr>
<th>K-vector</th>
<th>Irrep</th>
<th>Direction</th>
<th>Isotropy Subgroup</th>
<th>Dimension</th>
<th>Amplitude (Å)</th>
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</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>GM4-</td>
<td>(a,a,0)</td>
<td>Amm2 (38)</td>
<td>4</td>
<td>0.1649</td>
</tr>
<tr>
<td>(0,0,0)</td>
<td>GM5-</td>
<td>(0,a,-a)</td>
<td>Amm2 (38)</td>
<td>1</td>
<td>0.0056</td>
</tr>
</tbody>
</table>

Global distortion: 0.1850 Å

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, $\Delta$: 0.1251 Å
Total distortion amplitude: 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-

Direction: (a,a,0)
Isotropy Subgroup: 38 Amm2 C2v-14

Transformation matrix:

\[
\begin{bmatrix}
0 & 0 & 1 & 1 \\
0 & -1 & 0 & 0 \\
1 & 0 & 0 & 0
\end{bmatrix}
\]

The amplitude of this distortion is:
\[Q(\Gamma^-_4) = 0.1649 \text{ Å} \]

Normalized polarization vector (v1):

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \delta x )</th>
<th>( \delta y )</th>
<th>( \delta z )</th>
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<tbody>
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<td>0.176512</td>
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<tr>
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<td>0.062406</td>
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<tr>
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Normalized polarization vector (v2):

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<th>( \delta y )</th>
<th>( \delta z )</th>
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<td>0.0308</td>
</tr>
<tr>
<td>Ti1</td>
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<td>0.1339</td>
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<td>O1</td>
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<td>-0.0665</td>
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<tr>
<td>O1_2</td>
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<td>0.000000</td>
<td>-0.0317</td>
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</table>

Can visualize displacement pattern

Submit to STRCONVERT to visualize and export this mode's displacements.
Orthorhombic (*Amm2*) BaTiO$_3$ structure

High symmetry perovskite in *Amm2* setting without distortions

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\delta x$</th>
<th>$\delta y$</th>
<th>$\delta z$</th>
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<tbody>
<tr>
<td>Ba</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
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<tr>
<td>O1</td>
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<td>0.25</td>
<td>0.25</td>
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<tr>
<td>O1_2</td>
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<td>0</td>
<td>0.5</td>
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</table>

$Q(\Gamma_4^-) \times (0.165 \text{ Å})$

polar (ferroelectric) mode

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\delta x$</th>
<th>$\delta y$</th>
<th>$\delta z$</th>
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</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0</td>
<td>0</td>
<td>0.0308</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
<td>0</td>
<td>0.1339</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
<td>0.0349</td>
<td>-0.0665</td>
</tr>
<tr>
<td>O1_2</td>
<td>0.0349</td>
<td>0</td>
<td>-0.0665</td>
</tr>
</tbody>
</table>

$Q(\Gamma_5^-) \times (0.006 \text{ Å})$

<table>
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<tr>
<th>Atom</th>
<th>$\delta x$</th>
<th>$\delta y$</th>
<th>$\delta z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
<td>0.0624</td>
<td>0.0624</td>
</tr>
<tr>
<td>O1_2</td>
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<td>0</td>
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</tr>
</tbody>
</table>
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
    - ...

With this information we can make correlations between structure and properties
Structural phase transitions from mode decompositions in \( \text{SrZrO}_3 \)

- Room-temperature it is \( \text{Pnma} \) 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)

**Table 13**
Summary of the mode decomposition with respect to its \( Pm\bar{3}m \) parent structure of the \( \text{Pnma} \) structure of \( \text{SrZrO}_3 \) at 293 K (Howard et al., 2000), \( \text{NaTaO}_3 \) (Kennedy, Prodjosantoso & Howard, 1999) and \( \text{LaMnO}_3 \) at 300 K (Rodríguez-Carvajal et al., 1998).

<table>
<thead>
<tr>
<th>Irrep</th>
<th>Isotropy subgroup</th>
<th>Dimension</th>
<th>( \text{SrZrO}_3 ) amplitude (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4+</td>
<td>( \text{Imma} )</td>
<td>1</td>
<td>1.19</td>
</tr>
<tr>
<td>R5+</td>
<td>( \text{Imma} )</td>
<td>2</td>
<td>0.07</td>
</tr>
<tr>
<td>X5+</td>
<td>( \text{Cmcm} )</td>
<td>2</td>
<td>0.34</td>
</tr>
<tr>
<td>M2+</td>
<td>( \text{P4/mmb} )</td>
<td>1</td>
<td>0.01</td>
</tr>
<tr>
<td>M3+</td>
<td>( \text{P4/mmb} )</td>
<td>1</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Expect two phase transitions: \( \text{Pnma}(M^+_3, R^+_4) \rightarrow \text{Imma}(R^+_4) \rightarrow Pm\bar{3}m \)
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 $\beta$-BaB$_2$O$_4$

- Examine interaction of each mode on electronic response

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 $\mu$m.

| $d_{ij}$ | FDG  | $M(\Gamma_2^- | e)$ | $M(\Gamma_2^- | f)$ | $\sum_i d_{ij} | M_f^2 |$ | $2 \times M(\Gamma_2^- | e)$ | Experiment |
|---------|------|-----------------|-----------------|-----------------|-----------------|------------|
| $d_{22}$ | -1.87 | -0.03 | -1.84 | -1.87 | -3.49 | -2.1 $\pm$ 0.1$^a$ |
| $d_{34}$ | 0.03 | 0.02 | 0.01 | 0.03 | 0.09 | 0.03$^c$ |
| $d_{35}$ | -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
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?

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
  - $T_{\text{MI}}$ – metal-insulator transition
  - $T_N$ – AFM ordering transition

\[
\sum_{v=0}^{n} C_v \times \text{(displacement)}
\]

- (a) Undistorted octahedra
- (b) $M_2^+$ d-type Jahn-Teller
- (c) $M_3^+$ in-phase rotation
- (d) $M_5^+$ out-of-phase tilting
- (e) $R_3^+$ a-type Jahn-Teller
- (f) $R_4^+$ out-of-phase rotation
- (g) $R_5^+$ bending/buckling mode
- (h) $X_6^+$ 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

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

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 initio symmetry-based structural approach to materials design

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)

- Crystal structures + artificial geometries
- Ab initio electronic structure calculations
- Design and discovery
- Materials informatics
- Group theory + symmetry analysis

Designing atomic-scale 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

- **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
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*

Ab initio symmetry-based structural approach to materials design

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.

\[ H \Psi = E \Psi \]

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


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 exist 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$_2$CuTiO$_6$, Ba$M$F$_4$ ($M$=Mn,Fe,Co,Ni)

*Can we find an alternative route to lift inversion symmetry and create a ferroelectric?*
**Ab initio** 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 discover anything new?*

---

**OPTICAL ACTIVITY (CIRCULAR DICHORISM)**

- ENANTIOMORPHIC
  - 432 (O)
  - 422 (D)
  - 222 (D)
  - 622 (D)
  - 32 (D)
  - 23 (T)
  - -4 (S)

- POLAR (PYROELECTRIC)
  - m (C)
  - m2 (C)
  - -42m (D)
  - -6 (C)
  - -62m (D)
  - -43m (T)

**PIEZOELECTRIC (SECOND-HARMONIC GENERATION)**

- 3m (C)
- 4mm (C)
- 6mm (C)

**Group theory + symmetry analysis**

- Crystal structures + artificial geometries

**Design and discovery**
Octahedral rotations plus “layering” can lift inversion symmetry and support electric polarizations

\((\text{PbTiO}_3)_1(\text{SrTiO}_3)_1\)


\(\text{Ca}_3\text{Ti}_2\text{O}_7\)
\(\text{Ca}_3\text{Mn}_2\text{O}_7\)

Benedek & Fennie, PRL 106, 107204 (2011)

\(\text{La}_2\text{Ti}_2\text{O}_7\)

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

\(\text{NaLaMnWO}_6\)

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

\[ \frac{\text{rotation 1}}{\text{rotation 2}} \]

**TWO** zone boundary modes freeze-in to induce a polarization

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 (CaTiO₃)*
What about the symmetry requirements?

$BO_6$ octahedra + $A$-site cations = $ABO_3$ perovskite structure ($Pm\bar{3}m$)

- polar $\iff$ absence of inversion symmetry (missing mirror)
- centric octahedra $\iff$ 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)

- 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 $\text{ABO}_3$ perovskite break inversion symmetry

---

### Group-theoretical analysis of octahedral tilting in ferroelectric perovskites

<table>
<thead>
<tr>
<th>Ref</th>
<th>Space group</th>
<th>$\Gamma^-_4$</th>
<th>$M^+_3$</th>
<th>$R^+_4$</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>221 $Pm\bar{3}m$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>$a_0^3d_0^3d_0^3$</td>
</tr>
<tr>
<td>2</td>
<td>127 $P4/mnbm$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, a)</td>
<td>(0, 0, 0)</td>
<td>$a_0^3d_0^3e_0^3$</td>
</tr>
<tr>
<td>3</td>
<td>139 $I4/mmm$</td>
<td>(0, 0, 0)</td>
<td>(0, a, a)</td>
<td>(0, 0, 0)</td>
<td>$a_0^3b_0^3b_0^3$</td>
</tr>
<tr>
<td>4</td>
<td>204 $Im\bar{3}$</td>
<td>(0, 0, 0)</td>
<td>(a, a, a)</td>
<td>(0, 0, 0)</td>
<td>$a_0^3a_0^3a_0^3$</td>
</tr>
<tr>
<td>5</td>
<td>71 $I\bar{m}nn$</td>
<td>(0, 0, 0)</td>
<td>(a, b, c)</td>
<td>(0, 0, 0)</td>
<td>$a_0^3b_0^3c_0^3$</td>
</tr>
<tr>
<td>6</td>
<td>140 $I4/mcm$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, a)</td>
<td>$a_0^3d_0^3e_0^3$</td>
</tr>
<tr>
<td>7</td>
<td>74 $Imma$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, a, a)</td>
<td>$a_0^3b_0^3b_0^3$</td>
</tr>
<tr>
<td>8</td>
<td>167 $R\bar{3}c$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(a, a, a)</td>
<td>$a_0^3a_0^3a_0^3$</td>
</tr>
<tr>
<td>9</td>
<td>12 $C2/m$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(a, b, a)</td>
<td>$a_0^3b_0^3c_0^3$</td>
</tr>
<tr>
<td>10</td>
<td>15 $C2/c$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(a, b, b)</td>
<td>$a_0^3b_0^3b_0^3$</td>
</tr>
<tr>
<td>11</td>
<td>2 $P1$</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(a, b, c)</td>
<td>$a_0^3b_0^3c_0^3$</td>
</tr>
<tr>
<td>12</td>
<td>63 $Cnma$</td>
<td>(0, 0, 0)</td>
<td>(0, a, 0)</td>
<td>(0, 0, b)</td>
<td>$a_0^3b_0^3c_0^3$</td>
</tr>
<tr>
<td>13</td>
<td>62 $Pnma$</td>
<td>(0, 0, 0)</td>
<td>(0, a, 0)</td>
<td>(0, b, b)</td>
<td>$a_0^3b_0^3b_0^3$</td>
</tr>
<tr>
<td>14</td>
<td>11 $P2_1/m$</td>
<td>(0, 0, 0)</td>
<td>(a, a, 0)</td>
<td>(0, 0, b)</td>
<td>$a_0^3b_0^3c_0^3$</td>
</tr>
<tr>
<td>15</td>
<td>137 $P4_2/nnm$</td>
<td>(0, 0, 0)</td>
<td>(a, a, 0)</td>
<td>(0, 0, b)</td>
<td>$a_0^3a_0^3c_0^3$</td>
</tr>
</tbody>
</table>
Tiling of centric polyhedra in three dimensions

- No combinations of octahedral rotations in a single phase $ABO_3$ 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
Interleave two common dielectrics to support rotation-induced ferroelectricity

- Two possible simple cation ordering schemes

three bulk materials

\[ A'B'O_3 \]

\[ A'B'O_3 \]

\[ A'B'O_3 \]

\[ (A',A)B_2O_6 \]

\[ A_2(B,B')O_6 \]
Consequences of cation order on inversion symmetry

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

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

$\frac{1}{4}(A',A)B_2O_6$

inversion centers on $A$-sites

$\frac{1}{4}A_2(B,B')O_6$

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!

\[(A',A)B_2O_6\]

inversion centers on $A$-sites

\[A_2(B,B')O_6\]

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!

\[ (A', A)B_2O_6 \quad \text{no } I \]

inversion centers on A-sites

\[ A_2(B, B')O_6 \quad I \text{ persists} \]

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

*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

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

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

\[ Q_1: \phi_z^+ \sim a^0 a^0 c^+ \]

\[ Q_2: \psi_{xy}^- \sim a^- a^- c^0 \]

$P_{xy}$

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

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

<table>
<thead>
<tr>
<th>Rhombohedral Tilt $a^{-}a^{-}a^{-}$</th>
<th>Orthorhombic Tilt $a^{-}a^{-}c^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaAlO$_3$</td>
<td>YAIO$_3$</td>
</tr>
<tr>
<td>BiAlO$_3$</td>
<td>YGaO$_3$</td>
</tr>
<tr>
<td></td>
<td>LaGaO$_3$</td>
</tr>
</tbody>
</table>
First-principles validation of materials design criteria

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

- 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

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?

$\begin{align*}
P2_1/c \\
YGaO_3/YAlO_3 & : |P| = 0 \ \mu C \ \text{cm}^{-2} \\
LaGaO_3/YGaO_3 & : |P| = 11.8 \\
LaAlO_3/YAlO_3 & : |P| = 9.94 \\
LaAlO_3/BiAlO_3 & : |P| = 9.62
\end{align*}$

Atomic origin of polarization is from the non-cancelation of $A$ and $A'$ cation displacements.
Designing atomic-scale function...

James Rondinelli

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?

$P2_1/c$

- $YGaO_3/YAIO_3$
  - $|P| = 0 \mu C \text{ cm}^{-2}$
  - Rotations do not break inversion (symmetry argument)

$Pmc2_1$

- $LaGaO_3/YGaO_3$
  - $|P| = 11.8$

- $LaAlO_3/YAlO_3$
  - $|P| = 9.94$

- $LaAlO_3/BiAlO_3$
  - $|P| = 9.62$

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
Interactions between the octahedral rotations

- Map out energy landscape with respect to the rotational modes

\[ \psi_{xy} (a - a \cdot c^0) \]

\[ \phi^+ (a^0 a^0 c^+) \]

paraelectric – zero rotations
centrosymmetric – finite rotations
Interactions between the octahedral rotations

- Map out energy landscape with respect to the rotational modes

\[
\psi_{x,y} \left( a - a - c^0 \right)
\]

increasing rotation

increasing rotation

\[
\phi_{z}^+ \left( a^0 a^0 c^+ \right)
\]

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
Interactions between the octahedral rotations

LaGaO$_3$/YGaO$_3$  

Modes cooperate strongly  
4 polar minima (twins & antiphase)

LaAlO$_3$/YAlO$_3$  

Modes cooperate weakly  
4 polar minima (twins & antiphase)
Interactions between the octahedral rotations

LaGaO$_3$/YGaO$_3$  \(Pmc2_1\)

- Modes cooperate strongly
- 4 polar minima (twins & antiphase)

LaAlO$_3$/BiAlO$_3$  \(Pmna\)

- Modes COMPETE
- 2 non-polar minima

Designing atomic-scale function...
James Rondinelli
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)**

**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**

\[ F_{\text{int}} \sim P (R_1 \cdot R_2) \]
How to identify *a priori* if the octahedral rotations should cooperate or compete? ...and induce ferroelectricity?

LaGaO$_3$/YGaO$_3$

Modes **cooperate** because the $\phi^+$ mode is unstable in both compounds.

LaAlO$_3$/BiAlO$_3$

Modes **compete** because the $\phi^+$ 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?

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

![Graphical representation of vibrational modes](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>(tilt system)</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$k$-point</th>
<th>distortion-type</th>
<th>mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaAlO$_3$</td>
<td></td>
<td>108i</td>
<td>$A$</td>
<td>$a^0 a^0 c^0$</td>
<td>$\phi_+^-$</td>
</tr>
<tr>
<td>(a$^-$ a$^-$ a$^-$)</td>
<td>135i</td>
<td>$A$</td>
<td>$a^0 a^0 c^-$</td>
<td>$\phi_+^-$</td>
<td></td>
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<td>$R$</td>
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<tr>
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<td>$M$</td>
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<td>$\phi_+^-$</td>
<td></td>
</tr>
<tr>
<td>YAIO$_3$</td>
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<td>232i</td>
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<td>$a^0 a^0 c^-$</td>
<td>$\phi_+^-$</td>
</tr>
<tr>
<td>(a$^-$ a$^-$ c$^+$)</td>
<td>282i</td>
<td>$A$</td>
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<td>$\phi_+^-$</td>
<td></td>
</tr>
<tr>
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<td>165i</td>
<td>$R$</td>
<td>$a^+ a^+ c^0$</td>
<td>$\phi_+^-$</td>
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<tr>
<td>(a$^-$ a$^-$ c$^+$)</td>
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<td>$a^0 a^0 c^-$</td>
<td>$\phi_+^-$</td>
<td></td>
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<tr>
<td>YAIO$_3$</td>
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<td>307i</td>
<td>$A$</td>
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<td>$\phi_+^-$</td>
</tr>
<tr>
<td>(a$^-$ a$^-$ a$^+$)</td>
<td>309i</td>
<td>$A$</td>
<td>$a^0 a^0 c^+$</td>
<td>$\phi_+^-$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$When confined to a perovskite manifold of structures.
Low switching barrier (<5meV) should be experimentally accessible

LaAlO$_3$/YAlO$_3$ $Pmc2_1$

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

SHG Polar Plot

Jak Tchakhalian (U Arkansas, 2013)
Guidelines for rotation-induced ferroelectricity in perovskites

- Guidelines for tailoring for octahedral rotation-induced ferroelectricity
  
  1. **Suitable cation site-symmetry**: ordered $A/A'$ sublattice

  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.

<table>
<thead>
<tr>
<th></th>
<th>Condition 1</th>
<th>Condition 2</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{YAlO}_3/\text{YGaO}_3$</td>
<td>$\times$</td>
<td>$\times$</td>
<td>Non-polar dielectric</td>
</tr>
<tr>
<td>$\text{LaGaO}_3/\text{YGaO}_3$</td>
<td>$\checkmark$</td>
<td>$\checkmark$</td>
<td>Rotation-induced FE</td>
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<tr>
<td>$\text{LaAlO}_3/\text{YAIO}_3$</td>
<td>$\checkmark$</td>
<td>$\checkmark$</td>
<td>Rotation-induced FE</td>
</tr>
<tr>
<td>$\text{LaAlO}_3/\text{BiAlO}_3$</td>
<td>$\checkmark$</td>
<td>$\times$</td>
<td>Conventional ferroelectric</td>
</tr>
</tbody>
</table>

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?  
  Can we order the cations differently?  
  Couple with magnetism?  
  Realize new transitions?


**Generalized for (A,A’)(B,B’)O₆**

*Gou & JMR, Ferri-to-Ferroelectric Transitions with Large Piezoelectric Response*


_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

Emergent Ferroelectricity


\[ AB_2O_3 + A'B_2O_3 = (A,A')B_2O_6 \]

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.

\[
\begin{align*}
\text{ABO}_3 + \text{A'}\text{BO}_3 & = (A,A')\text{B}_2\text{O}_6 \\
\end{align*}
\]

*octahedral rotations*

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

Implications for the design of new ferroelectrics

- Rotations can induce a polarization through \textit{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

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

*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/magnetoelcetrics)
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

$\text{ABO}_3$

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.
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)]

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.
**Ab initio 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-subgroup relationships for the experimental 214 RP phases

- No observed distortion modes lift inversion symmetry alone

\[ X_3^+ (0, a) [Cmca] \]
\[ X_2^+ (0, a) [Cmca] \]

octahedral rotations

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

**Route 1**

- **I4/mmm**
  - $P_{42/1}$
  - $X_2^+ \oplus X_3^+ \oplus P_4$
- **Pca2**

**Route 2**

- **I4/mmm**
  - $P_{ca21}$
  - $X_2^+ \oplus X_3^+ \oplus M_3^-$

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: \((A',A)B_2O_6\)

\[ \mathcal{F} \sim P \cdot Q_1 \cdot Q_2 \]

- 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

*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 $(A,A')BO_4$

\[ F \sim P \cdot Q_1 \cdot Q_2 \]

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 $(A,A')BO_4$

Diagram:
- $I4/mmm$ crystal class
- $Pca2_1$ space group
- $X_2^+ \oplus X_3^+ \oplus M_3^-$ atomic distortions
- + cation order

Mathematical expression:

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

- $X_3^+$ octahedral rotations
- Polar displacements
- Jahn-Teller distortions

Diagram labels:
- Route 2
- $M_3^-$
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

\[ F \sim P \cdot (X_2^+ \cdot X_3^+) \]
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

\[
\text{posterior probability} = \text{likelihood} \times \text{prior probability}
\]
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

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:
  \[ P(A|B) = \frac{P(B|A)P(A)}{P(B)} = \]
  **posterior probability** \hspace{1cm} **likelihood** \hspace{1cm} **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

Bayes Theorem says:

\[ P(A|B) = \frac{P(B|A)P(A)}{P(B)} = \frac{(1/2)(1/3)}{(1/3)} \]

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
- \( P(B|A^c) = 1/4 \) twice as likely identical twins are boys

\[ P(A|B) = \frac{1}{2} \] Correctly predicts the twins will have an equal probability of being fraternal or identical

Bayesian analysis examples

- Nate Silver’s FiveThirtyEight blog

- 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

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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

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

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

\[
P(\text{distortions}|\text{cation}) = \frac{P(\text{cations}|\text{distortions}) \times P(\text{distortions})}{P(\text{cation})}
\]

- 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
- 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

\[
P(\text{distortions} | \text{cation}) = \frac{P(\text{cations} | \text{distortions}) \times P(\text{distortions})}{P(\text{cation})}
\]

Assumptions:
A-site, B-site, and temperature probabilities are mutual independent (non-interacting)
Statistical learning and data-mining for probable chemistries

- Bayesian analysis of $n=1$ RP database

$$P(\text{distortions}|\text{cation}) = \frac{P(\text{cations}|\text{distortions}) \times P(\text{distortions})}{P(\text{cation})}$$

- 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 ($X_2^+$).

![Diagram of B-site element-Octahedral Mode Distortion Relationships]

- 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

\[ F \sim P \cdot (X_2^+ \cdot X_3^+) \]

Rotation + Berry-Pseudorotations will induce a ferroelectric polarization

Explore energetics of down-selected \((\text{La,Sr})\text{MnO}_4\) compound

\(X_2^+ \oplus X_3^+ \oplus M_3^-\)

atomic distortions + cation order

Mn\(^{3+}\)  La\(^{3+}\)

\((A,A')\text{BO}_4\)

A\(^{2+}\) = Sr or Ca
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
  - LSDA+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 ($T_N \approx 120$K) in bulk**

La$_{2/3}$Sr$_{4/3}$MnO$_4$ STEM Image

Strain-engineered

---

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

B. Nelson-Cheeseman et al, APL 98 072505 (2011)
Low energy phases of (La, Sr)MnO$_4$

- Ground state is polar and exhibits the targeted structural distortions

Ground state is insulating with a 1.41 eV gap

\[ P_{ca21}, \mathcal{P} \sim 1.25 \mu C/cm^2 \]

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

\[ \mathcal{F} \sim P \cdot Q_1 \cdot Q_2 \]

- Polar displacements
- Jahn-Teller distortions
- Octahedral rotations

MODE DESCRIPTION | NORM. AMP.
--- | ---
$\Gamma_1^+$ | Anti-parallel displacements | 0.65
$\Gamma_5^-$ | 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

These two modes alone can lift inversion symmetry

\[ X_2^+ \oplus X_3^+ \oplus M_3^- \]

The weak, secondary mode, triggered by coupling to primary modes

notation is relative to $I4/mcm$
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
Spin configuration and electric polarization allows for weak-ferromagnetism along different crystallographic directions.

**AFM order**
- $ac$
- $b$
- $c$

**FM order**
- $bc$
- $a$
- $c$

**P polarization**
- $c$

---

Exploring magnetoelectric coupling

- Linear magnetoelectric effect is a direct consequence of the coupling of multiple modes to induce a polarization through terms $\sim M_i L_j P_j$
- Investigating modes that induce weak-FM
  - Rotations suggest Dzyaloshinskii-Moriya interaction
  - Jahn-Teller modes suggest magnetic single-ion anisotropy due SOC
Artificial design of ferroic behavior from polyhedral building blocks and cation ordering

Multiple anharmonic couplings to induce ferroelectric polarizations remain to be explored

<table>
<thead>
<tr>
<th>$Q_1$</th>
<th>$Q_2$</th>
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<tbody>
<tr>
<td>rotation</td>
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<td>pseudo-rotation</td>
</tr>
<tr>
<td>pseudo-rotation</td>
<td>pseudo-rotation</td>
</tr>
</tbody>
</table>

Multipferroic compound from rotations and Jahn-Teller distortions


Metal-organic framework (MOF)
Angew. Chem. Int. Ed. 50 5847 (2011)
Chlorides:
Many new reports of rotation-induced ferroelectrics

- **Perovskite or perovskite-derived structures**

- **Not exclusive to metal oxides**
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
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.

**Insights obtained through confluence of multiple levels of materials theory**