Module Outline

1. Overview and Background
   - Ferro ordering, the magnetoelectric effect

2. ME revisited, and basic oxide physics
   - ME effect revisited: Toroidal moments
   - Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry

3. Structure and Ferroelectricity
   - Basics of space groups
   - Soft mode theory, lattice dynamics, group theoretic methods
   - Competing lattice instabilities
   - microscopic mechanisms, improper FE
   - Modern theory of polarization (Berry Phase)


What have we done

- presented various ferro-ordering and examined their basic symmetry properties.

- Showed in systems which break both time-reversal and space-inversion symmetry, that symmetry allows a bi-linear coupling between the Electric and Magnetic fields, $F_{ME} = \alpha EH$.

- Presented a relatively new (or rediscovered) ferro-toroidal ordering. What is this? Don’t know yet, here is what I know: Electromagnetism allows the existence of some moment referred to as a toroidal moment (toroidal because it has the symmetry of of toroidal solenoid). Expanding the interaction energy between energy the magnetic density and the magnetic field, one arrives at a coupling between the toroidal moment and the field which has the same symmetry as the antisymmetrical component of the magnetolectric tensor, i.e., a toroidal moment would lead to an antisymmetric ME effect. That’s it, that is all I presently understand. Questions are plentiful.

We are we going?

- although symmetry allows the existence of a ME effect, it tells us nothing about its size. This is not a question of optimizing parameters to increase the magnitude of the effect in e.g., Cr$_2$O$_3$, but requires entirely new physical ideas.

- An idea that is prevalent in materials physics today (some would argue throughout nature) is the idea where the competition between different ordered ground states leads to new emergent phenomena (sometimes the adjective “colossal” is attached the observed effect).

- What if we have a system where ferroelectricity and (anti)ferromagnetism compete with each other, will it lead to “colossal” ME effects. Note this doesn’t mean we simply add ferroelectricity and magnetism, i.e., multiferroics, we need to think of microscopic mechanisms that would COUPLE the two order parameters in a nontrivial way.

- Can we provide this coupling through the lattice? So in the remainder of this module we will
  - Understand the origin of ferroelectricity and how it couples to the lattice
  - Understand the origin of (anti)ferromagnetism and how it couples to the lattice
  - Combine these ideas to produce the stated goal.

Perovskites are ubiquitous materials that display an amazing variety of different phenomena, let’s focus on them
Multifunctional multiferroics

Multiferroic: combine more than one “ferro” property:
Ferroelectricity, ferroelasticity, and/or magnetism

(Hans Schmid, 1973)

Polarization, $P$

\[ \begin{array}{c}
- \\
+
\end{array} \]

Magnetization, $M$

\[ \begin{array}{c}
N \\
S
\end{array} \]

e.g., ferroelectric ferromagnet

Multifunctional multiferroics

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

Polarization, $P$

\[ \begin{array}{c}
- \\
+
\end{array} \]

P

Magnetization, $M$

\[ \begin{array}{c}
N \\
S
\end{array} \]

E

H

e.g., ferroelectric ferromagnet
Multifunctional magnetoelectrics

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

Polarization, $P$  \hspace{1cm} Magnetization, $M$

\[ \begin{align*}
E & \leftrightarrow M \\
\uparrow & \leftrightarrow \uparrow \\
P & \leftrightarrow M
\end{align*} \]

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

Proper ferroelectric transition: phenomenology

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

Primary Order Parameter

Spontaneous polarization $P$

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

\[ \begin{align*}
T_1 & < T_2 \\
T_3 & < T_2 \\
T_4 & < T_3
\end{align*} \]

\[ F(P) = \alpha P^2 + \beta P^4 \]

\[ P_{eq} = 0 \text{ } \alpha > 0 \]

\[ P_{eq} = \pm \sqrt{\frac{\alpha}{2\beta}} \text{ } \alpha < 0 \]

\[ \alpha \propto \chi^{-1} \propto T-T_c \text{ Currie Weiss} \]

\[ \chi; \text{ dielectric susceptibility} \]


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

Emergence of new macroscopic phenomena

Conventional ferroelectrics
Typically, have a polar lattice instability driving the ferroelectricity

Recent novel ferroelectrics
- **Lattice** - Lattice coupling → non-polar lattice mode driving FE
- **Spin** - Lattice coupling → spin DoFs driving FE
- **Charge** - Lattice → charge DoFs driving FE
- **Orbital** - Lattice → Orbital DoFs driving FE
**Order-Disorder Ferroelectrics**

- **KDP**  \( T_c = 123K \)
- **KD\(_2\)PO\(_4\)**  \( T_c = 220K \)

**NaNO\(_2\)**  \( T_c = 456K \)

Very strong covalent bonds. Rigid molecular units

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**Displacive ferroelectrics**

Pb

\( \text{paraelectric} \rightarrow \text{ferroelectric} \)

Small displacement

Side note: transition metal oxides tend to follow the Goldilocks lemma: Not too ionic, not too covalent, just right to be perfectly floppy
Often "displacive properties of both"

After 50 years of research one can definitely say, without a doubt that the "prototype" perovskite ferroelectric $\text{BaTiO}_3$ is both:-)

Model that goes from O-D limit to displacive

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

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

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

Soft-mode theory of ferroelectricity


Where $\omega$ is an infrared-active phonon frequency

\[ \chi^{-1} \propto \omega^2 \]

\[ T_c \]

Temperature

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

Curie Weiss

Stable phonon

Energy (E)

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

$\Rightarrow$ Paraelectric

Unstable phonon

Energy (E)

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

$\Rightarrow$ Ferroelectric
Small detour: microscopic mechanisms

Let's consider a Born-Oppenheimer system

\[ H_e(r; Q) = T_e + V(r, Q) \]

\[ H_e(r; Q)\psi_n(r; Q) = E_n(Q)\psi_n(r; Q) \]

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

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

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

\[ \mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} Q + \frac{1}{2} \mathcal{H}^{(2)} Q^2 + \ldots \]

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

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

**1st order Jahn-Teller**

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

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

**2nd order Jahn-Teller**

\[ + \ldots \]
**Ferroelectric mechanisms: Chemical**

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

Origin of FE distortion

Balance between two competing forces:

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

→ dipole-dipole interactions stabilize long-range order

Ron Cohen, Nature 1993


△E

de

△E ~ - t_{pd}^2 (gu)^2/△

"simple picture"

Daniel Khomskii

JMMM 2006

△Charge transfer gap
t_{pd} hybridization

**Symmetry-breaking crystal distortions**

- Interatomic force constants: energy \( E(\{u_{i\alpha}\}) \)
  
  \[-(d^2E/du_{i\alpha}du_{j\kappa})u_{i\alpha} = \text{force on atom } j\kappa \text{ in the } \beta \text{ direction} \]
  
  produced by displacement of atom \( i\alpha \) in \( \alpha \) direction

  (j labels unit cell, \( \kappa \) labels atom in basis)

Crystal symmetries lead to

equalities and zeros for this matrix
**Symmetry-breaking crystal distortions**

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

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

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

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

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**Symmetry breaking crystal distortions**

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

Cubic perovskite example: simple cubic

- \( \Gamma \): (0,0,0)
- \( R \): \( \pi/a(1,1,1) \)
- \( X \): \( \pi/a(1,0,0) \)
- \( M \): \( \pi/a(1,1,0) \)

where \( a \) is the lattice constant of the simple cubic lattice
Cubic perovskite: symmetrized displacement patterns

- $\Gamma$: Q=0 (uniform from cell to cell)

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

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

What do we really mean when we say polar mode?

Irrep for the polar vector
Basic Training 2009– Lecture 03

**Cubic perovskite: symmetrized displacements**

- $\Gamma$: $Q=0$ (uniform from cell to cell)

Matrices become block diagonal

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

(In $\Gamma$ matrix, acoustic $\Gamma_{15}$ mode can be found by including uniform translation) Finding eigenvalues becomes much easier!
**Ferroelectricity as a lattice property**

FE lattice distortion, \( u \), has identical symmetry properties as the polarization, i.e. \( u \propto P \), involve small atomic distortions.

![Diagram of PbTiO₃ structure](image)

- **cubic-paraelectric**: Space group Pm3m
- **tetragonal-ferroelectric**: Space group P4mm

**Internal energy from first principles**

Internal energy as a function of FE distortion, \( u \), and strain, \( \varepsilon \):

\[
\mathcal{E}(u, \varepsilon) = -\omega_0^2 u^2 + B u^4 + C \varepsilon u^2
\]

Neglecting strain:

Both BaTiO₃ and PbTiO₃ have rhombohedral ground states, in contradiction to experiment!

In PbTiO₃, polarization-strain coupling is essential to observe tetragonal ground state.

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

So ferroelectricity in the cubic perovskite like PbTiO$_3$ is associated with the instability of a \( \Gamma_{15} \) mode, i.e., a polar lattice distortion, is translational symmetry changed?
**Example: cubic perovskite structure**

Crystallographic description—generally given in the literature

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

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Coordinates</th>
</tr>
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<tbody>
<tr>
<td>Pb</td>
<td>1a</td>
<td>0,0,0</td>
</tr>
<tr>
<td>Pb</td>
<td>1b</td>
<td>½,½,½</td>
</tr>
<tr>
<td>Ti</td>
<td>1b</td>
<td>½,½,½</td>
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<tr>
<td>Ti</td>
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<tr>
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<td>3c</td>
<td>0,½,½ ½,0,½ ½,½,0</td>
</tr>
<tr>
<td>O</td>
<td>3d</td>
<td>½,0,0 0,½,0 0,0,½</td>
</tr>
</tbody>
</table>

Lattice parameter $a_0$

No additional free structural parameters for this symmetry

Symmetries are manifest

Point group: governs macroscopic properties (allowed couplings)

Site symmetry groups from the table

Can easily reconstruct lattice+basis description

(eg for input into first-principles program)

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**Example: tetragonal FE phase of PbTiO$_3$**

- Primitive tetragonal lattice $a$, $a$, $c$ (P4mm #99)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
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<td>1a</td>
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</tr>
<tr>
<td>Pb</td>
<td>1b</td>
<td>½,½,$z$</td>
</tr>
<tr>
<td>Ti</td>
<td>1b</td>
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<td>0,0,$z$</td>
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<tr>
<td>O</td>
<td>2c</td>
<td>½,0,$z$ 0,½,$z$</td>
</tr>
<tr>
<td>O</td>
<td>2c</td>
<td>½,0,$z$ 0,½,$z$</td>
</tr>
</tbody>
</table>

Two lattice parameters $a$, $c$

Three nontrivial additional parameters for this symmetry

*Caution, nothing requires the lattice constants to differ*
**Improper ferroelastic transition: phenomenology**

BaTiO$_3$ and PbTiO$_3$ have a proper ferroelectric transition, but an improper ferroelastic transition

<table>
<thead>
<tr>
<th>Primary order parameter</th>
<th>Secondary order parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous polarization $P$</td>
<td>Spontaneous strain $\varepsilon$</td>
</tr>
</tbody>
</table>

(Primary order parameter)

\[
F(P, \varepsilon) = a_1 P^2 + a_2 \varepsilon^2 + b_1 \varepsilon P^2 + c_1 P^4
\]

(Secondary order parameter)

\[
\frac{\partial F}{\partial \varepsilon} = 2 a_2 \varepsilon + b_1 P^2 = 0
\]

\[
\varepsilon_{eq} \sim - P^2
\]

Once $P$ becomes nonzero, a strain is induced.

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**Caution**

- This is true for any instability, no matter its origin! Any mode (charge, orbital, spin) that removes the point group symmetries, will couple to strain!!!

- The coupling does not need to be large or even measureable, but symmetry allows it (one should consider zero coupling, an accident).
**Improper ferroelastic transition: large piezoelectric response**

In perovskite ferroelectrics such as PbTiO$_3$, there is a strong **cross coupled response** between electric, $E$, and stress, $\sigma$, fields.

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

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**Phase Competition and the morphotropic phase boundary**

**Phase Competition: Generic paradigm to achieve colossal effects**

![Diagram of phase competition](image)


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**Zone-boundary instabilities**

In general, many ferroelectrics have competing lattice instabilities
**Phonon dispersion at T=0 of cubic ABO$_3$ from first principles**

Remember:
Imaginary frequencies imply lattice instability.

Phonon Symmetry Labels

- $\Gamma$: $q=0$
- $M$: $q=(1,1,0)$
- $X$: $q=(1,0,0)$
- $R$: $q=(1,1,1)$


---

**Tilt Transitions in Perovskites**

Untilted perovskite

Tilted

- Many perovskites show tilt transitions, some of which are non-polar. Ex. SrTiO$_3$, NaNbO$_3$, CaTiO$_3$
- Perovskite structure collapses around small A-site ions
- This often leads to antiparallel rotation motions, and no ferroelectricity (though a ferroelectric phase can often be induced by an applied electric field)

From Susan Trolier-McKinstry
**Cubic perovskite symm. displacements**

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

**Distorted perovskites: mode content + Glazer notation**


<table>
<thead>
<tr>
<th>Space group</th>
<th>( \Gamma_1 )</th>
<th>( M^* )</th>
<th>( R_1^* )</th>
<th>System</th>
<th>Lattice vectors</th>
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<td>(0, 0, 0)</td>
<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
<td>(1, 0, 0; 1, 0, 0)</td>
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<tr>
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<td>(0, 0, 0)</td>
<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
<td>(1, 1, 0; 1, 0, 0)</td>
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<tr>
<td>139 P4/mmm</td>
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<td>(0, 0, 0)</td>
<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
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<tr>
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<td>(2, 0, 0; 0, 2, 0)</td>
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<tr>
<td>71 Imm</td>
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<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
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<tr>
<td>140 I4/mcm</td>
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<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
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<tr>
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<tr>
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<tr>
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<td>(0, 0, 0)</td>
<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
<td>(1, 1, 1; 1, 1, 1)</td>
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<tr>
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<td>(0, 0, 0)</td>
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<tr>
<td>8 Cm</td>
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<td>(0, 0, 0; 1, 0, 1)</td>
</tr>
<tr>
<td>1 P</td>
<td>(a, b, c)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
<td>(0, 0, 0; 0, 0, 1)</td>
</tr>
</tbody>
</table>
**R3c: LiNbO$_3$, BiFeO$_3$**

- 2 formula units (10 atoms) / cell

161 R3c:  \((a, a, a)\) \((0, 0, 0)\) \((b, b, b)\) \(a_1^a a_1^a\) \((\bar{1}, 1, 0)(0, \bar{1}, 1)(2, 2, 2)\)

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

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**Improper ferroelectric transition: phenomenology**

Primary order parameter = \(\eta\)

Secondary order parameter

Spontaneous polarization \(P\)

where \(\eta\) is "some other mode", e.g. zone-boundary lattice instability, magnetic chiral vector, etc.

\[
F(\eta, P) = \alpha_p P^2 + \alpha_\eta \eta^2 + \gamma_\eta P \eta^n + \beta P^4
\]

\[
\frac{\partial F}{\partial P} = 2\alpha_p P + \gamma_\eta \eta^n + 4 \beta P^3 = 0
\]

Once primary OP becomes nonzero, a polarization is induced

\(P_{eq} \sim - \eta^n\)
Improper structural ferroelectric: Hexagonal Manganites

RMnO₃, R = Y, Sc, Ho-Lu


Paraelectric (Z=2)

YMnO₃ Ferroelectric (Z=6)

T > ~1250K

Fennie and Rabe, Physical Review B 72, 100103 2005

Improper ferroelectric transition example: YMnO₃

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

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

$E(P) = \omega_0^2 P^2 + \beta P^4$

$P_{63/mcm}$

FE stable

$E(K) = -\omega_0^2 K^2 + \beta K^4$

FE $P_{63}c$ Z=6

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

Fennie and Rabe, Physical Review B 72, 100103 2005
**Improper ferroelectric transition example: YMnO$_3$**

Expand energy to fourth order in the primary $K_3$ and secondary $P$ order parameters:

$F(K_3, P) = \alpha_P P^2 + \alpha_K K_3^2 + \gamma P K_3^3 + \beta P^4$

$\Rightarrow P \sim \gamma K_3^3$

Also note, no anomalous Born effective charges

Recent experiments confirm the improper ferroelectric transition in the hexagonal manganites


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

**Intrinsic static dielectric constant**

$\epsilon = \epsilon_\infty + \sum_{\eta} \frac{\Omega^2_{\eta,n}}{\omega^2_{\eta,n}}$

Where $\omega_{\eta,n}$ is $\eta$-active phonon frequency

**Proper FE transition**

Currie Weiss

$\chi^{-1} \propto \omega^2$

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<table>
<thead>
<tr>
<th>$T_c$</th>
<th>Temperature</th>
</tr>
</thead>
</table>

$T_c$ Temperature

**Improper FE transition**

Specific form depends on faintness index

For example see:

- Principles and Applications of Ferroelectrics and related applications, by Lines and Glass, Oxford
- Ferroelectric Phenomena in Crystal by Strukov and Levanyuk
Crystallography: specifying crystal structures

- Textbook description: lattice + basis
- A more useful description:
  - space group + occupied Wyckoff positions
Most compact (in conjunction with Int’l Tables)
Symmetries and free structural parameters evident
(almost) unique – origin, “setting” of axes

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

Example: cubic perovskite structure

Crystallographic description—generally given in the literature

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

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1a</td>
<td>0,0,0</td>
</tr>
<tr>
<td>Pb</td>
<td>1b</td>
<td>½,½,½</td>
</tr>
<tr>
<td>Ti</td>
<td>1b</td>
<td>½,½,½</td>
</tr>
<tr>
<td>Ti</td>
<td>1a</td>
<td>0,0,0</td>
</tr>
<tr>
<td>O</td>
<td>3c</td>
<td>0,½,½</td>
</tr>
<tr>
<td>O</td>
<td>3d</td>
<td>½,0,0</td>
</tr>
<tr>
<td>O</td>
<td>3d</td>
<td>0,½,0</td>
</tr>
<tr>
<td>O</td>
<td>3d</td>
<td>0,0,½</td>
</tr>
</tbody>
</table>

Lattice parameter \(a_0\)

No additional free structural parameters for this symmetry
Basic Training 2009– Lecture 03

**Pm\(\overline{3}m\)**  
**O\(\overline{1}\)_h**  
**m\(\overline{3}m\)**  
Cubic  

| No. 221 |  
| --- | --- | --- | --- | --- |
| **P 4/m \(\overline{3} 2/m\)** |  
|  

**Symmetry operations**

1. (1) 1  
2. (2) \(0, 0, z\)  
3. (3) \(0, y, 0\)  
4. (4) \(0, x, 0\)  
5. (5) \(x, x, x\)  
6. (6) \(x, x, x\)  
7. (7) \(x, x, x\)  
8. (8) \(x, x, x\)  
9. (9) \(x, x, x\)  
10. (10) \(x, x, x\)  
11. (11) \(x, x, x\)  
12. (12) \(x, x, x\)  
13. (13) \(0, x, 0\)  
14. (14) \(0, x, 0\)  
15. (15) \(0, x, 0\)  
16. (16) \(0, x, 0\)  
17. (17) \(0, x, 0\)  
18. (18) \(0, x, 0\)  
19. (19) \(0, x, 0\)  
20. (20) \(0, x, 0\)  
21. (21) \(0, x, 0\)  
22. (22) \(0, x, 0\)  
23. (23) \(0, x, 0\)  
24. (24) \(0, x, 0\)  
25. (25) \(0, x, 0\)  
26. (26) \(0, x, 0\)  
27. (27) \(0, x, 0\)  
28. (28) \(0, x, 0\)  
29. (29) \(x, x, x\)  
30. (30) \(x, x, x\)  
31. (31) \(x, x, x\)  
32. (32) \(x, x, x\)  
33. (33) \(x, x, x\)  
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44. (44) \(x, x, x\)  
45. (45) \(x, x, x\)  
46. (46) \(x, x, x\)  
47. (47) \(x, x, x\)  
48. (48) \(x, x, x\)  
49. (49) \(x, x, x\)  
50. (50) \(x, x, x\)  

**This is the symmetry group of the cube**

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**Pm\(\overline{3}m\)**  
**O\(\overline{1}\)_h**  
**m\(\overline{3}m\)**  
Cubic  

| No. 221 |  
| --- | --- | --- | --- | --- |
| **P 4/m \(\overline{3} 2/m\)** |  
|  

| 3  | \(\frac{1}{2}, 0, 0\) | \(0, \frac{1}{2}, 0\) | \(0, 0, \frac{1}{2}\) |
| 3  | \(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\) | \(\frac{1}{2}, 0, \frac{1}{2}\) | \(0, \frac{1}{2}, \frac{1}{2}\) |
| 1  | \(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\) | \(0, \frac{1}{2}, \frac{1}{2}\) | \(\frac{1}{2}, 0, \frac{1}{2}\) |
| 1  | \(0, 0, 0\) | \(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\) | \(0, \frac{1}{2}, \frac{1}{2}\) |

These are the highest symmetry (and lowest multiplicity) Wyckoff positions in this space group. They appear in the description of the cubic perovskite structure.
What’s the space group of lattice+basis?

- "by hand:" identify the symmetries for a given origin—point symmetries + additional symmetries with nonprimitive translation?
  [doublecheck lattice type—may be lower symmetry than initial guess; for example, a primitive tetragonal lattice with c=a could initially be misidentified as simple cubic]

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

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

Example: cubic perovskite structure

- Simple cubic lattice \( a_0 x, a_0 y, a_0 z \)
- Pb at \((0,0,0)\)
- Ti at \((1/2,1/2,1/2)\)
- O at \((1/2,1/2,0)\)
- O at \((0,1/2,1/2)\)
- O at \((1/2,0,1/2)\)

Note that basis is not unique (can add lattice vector to any position(s), can put origin at Ti or, in fact, anywhere in cell)
does not have full symmetry of the crystal (and symmetries not obvious in this description)
Symmetry determines allowed couplings

- Macroscopic properties: need point group only
- Forms of tensors (zeros, equalities) determined
  (this is explained very well for nonmagnetic crystals in J. F. Nye, Physical Properties of Crystals (Oxford 1957, reprinted many times since) and for magnetic crystals in Birss, Symmetry and Magnetism).