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Magnetostructural coupling in multiferroics, part 1

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First principles investigations
Microscopics: atomic and electronic arrangements

Multiferroics: crystal distortions/phonons

- Dynamical and static (symmetry lowering distortions)
- Atoms move – couples to magnetic ordering

Phonons freeze in at structural phase transitions—modify magnetic order

Magnetic phase transitions lead to anomalies in phonon frequencies

Coupling includes strain and elastic constants

Spin-phonon coupling, magnetodielectric response..

[electromagnons]

- Crystallography – where the atoms are
- Symmetry analysis of phonon modes
- Modulation of exchange interactions by displacements

(includes both striction and DM)

Overview of the two lectures

- Space groups and crystal structures—

especially important for complex structures!

- Symmetry-breaking distortions—phonons, strain
- Classification of low-symmetry phases by mode content
- The effect of magnetism on symmetry analysis
- Magnetically-induced phonon anisotropy
- Modulation of exchange by distortions

- Examples: rocksalt MnO
- Perovskites $BaTiO_3$, double perovskites, $BiFeO_3$, $FeTiO_3$
- hexagonal $YMnO_3$

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)

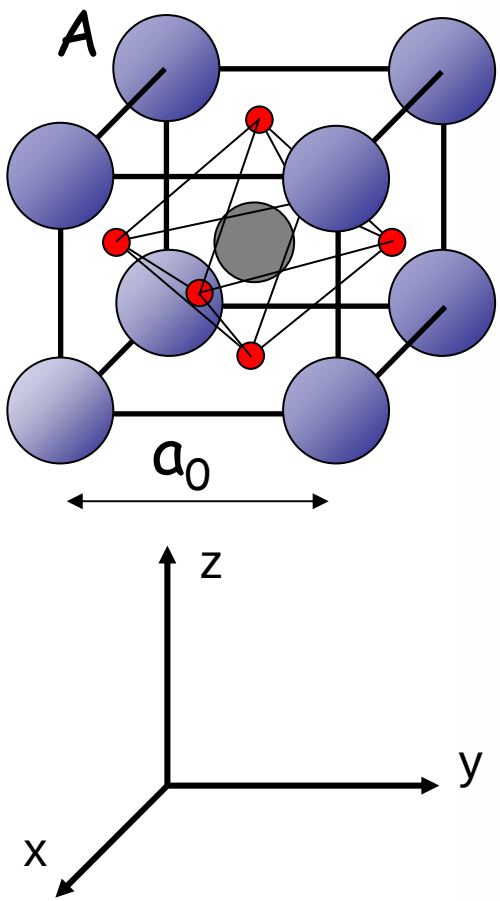
Symmetries and free structural parameters evident

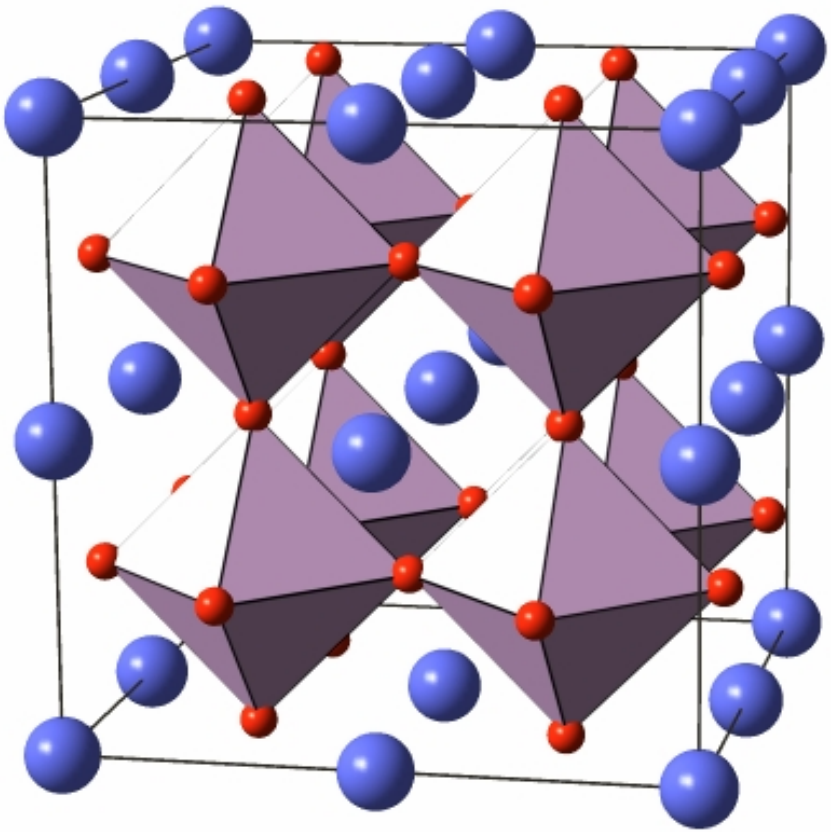
(almost) unique – origin, "setting" of axes

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

Example: cubic perovskite structure

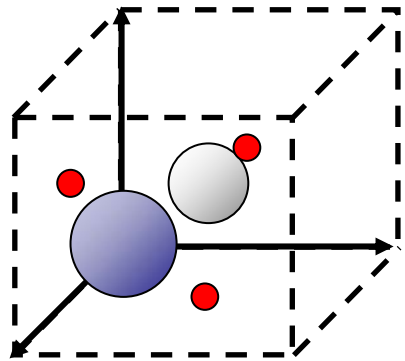
- Simple cubic lattice a_0x, a_0y, a_0z





Example: cubic perovskite structure

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



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

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

Example: cubic perovskite structure

Crystallographic description—generally given in the literature

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

Pb 1a 0,0,0 Pb 1b ½,½,½

Ti 1b ½,½,½ Ti 1a 0,0,0

O 3c 0,½,½ ½,0,½ ½,½,0 O 3d ½,0,0 0,½,0 0,0,½

Lattice parameter a_0

No additional free structural parameters for this symmetry

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

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

Symmetry operations

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

this is the symmetry group of the cube

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

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

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

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

Example: cubic perovskite structure

Crystallographic description—generally given in the literature

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

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

Lattice parameter a_0

No additional free structural parameters for this symmetry

Symmetries are manifest

Point group: governs macroscopic properties (allowed couplings)

Site symmetry groups from the table

Can easily reconstruct lattice+basis description

(eg for input into first-principles program)

What's the space group of lattice+basis?

- "by hand:" identify the symmetries

for a given origin—point symmetries +

additional symmetries with nonprimitive translation?

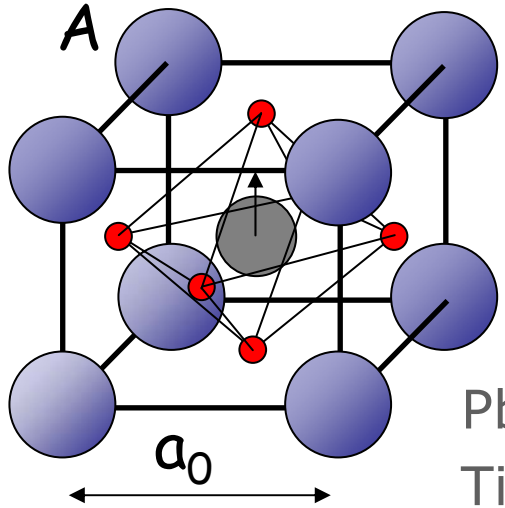
[doublecheck lattice type—may be lower symmetry than initial guess; for example, a primitive tetragonal lattice with c=a could initially be misidentified as simple cubic]

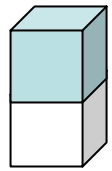
- A useful computational tool: ISOTROPY
- http://stokes.byu.edu/isotropy.html
- **FINDSYM**: Identify the space group of a crystal, given the positions of the atoms in a unit cell.

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

Example: tetragonal FE phase of $PbTiO_3$

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





Point symmetries are those of this object

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

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

Two lattice parameters a, c

Three nontrivial additional parameters for this symmetry

Creating a crystal structure

- Pick a space group (Example: P4mm #99)
- Occupy selected Wyckoff positions with chosen elements

8	*g*	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
			(5) $x,\bar{y},z$	(6) $\bar{x},y,z$	(7) $\bar{y},\bar{x},z$	(8) y,x,z	
							Special:
4	*f*	. *m* .	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$	$\frac{1}{2},x,z$	$\frac{1}{2},\bar{x},z$	no extra conditions
4	*e*	. *m* .	$x,0,z$	$\bar{x},0,z$	$0,x,z$	$0,\bar{x},z$	no extra conditions
4	*d*	. . *m*	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,z$	$x,\bar{x},z$	no extra conditions
2	*c*	2 *m m* .	$\frac{1}{2},0,z$	$0,\frac{1}{2},z$			hkl : $h+k=2n$
1	*b*	4 *m m*	$\frac{1}{2},\frac{1}{2},z$				no extra conditions
1	*a*	4 *m m*	$0,0,z$				no extra conditions

Creating a crystal structure

- Pick a space group
- Occupy selected Wyckoff positions with chosen elements
-  avoid a “common” mistake –

your crystal may have higher symmetry than the starting space group!

More symmetry than you thought…

- Example #1:

1a (0,0,0)

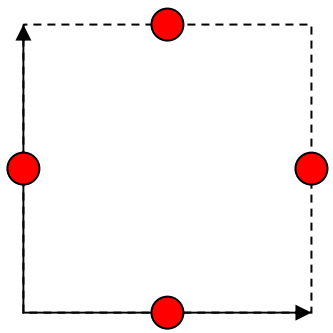
Monoatomic primitive tetragonal Bravais lattice P4/mmm

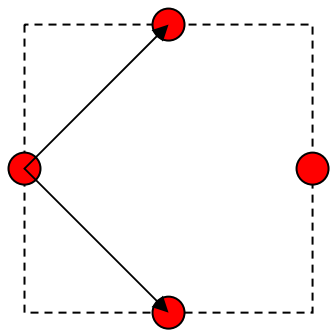
- Example #2

2c (0,1/2,z) (1/2,0,z)

Monoatomic primitive tetragonal BL P4/mmm

ADDITIONAL TRANSLATIONAL SYMMETRIES!



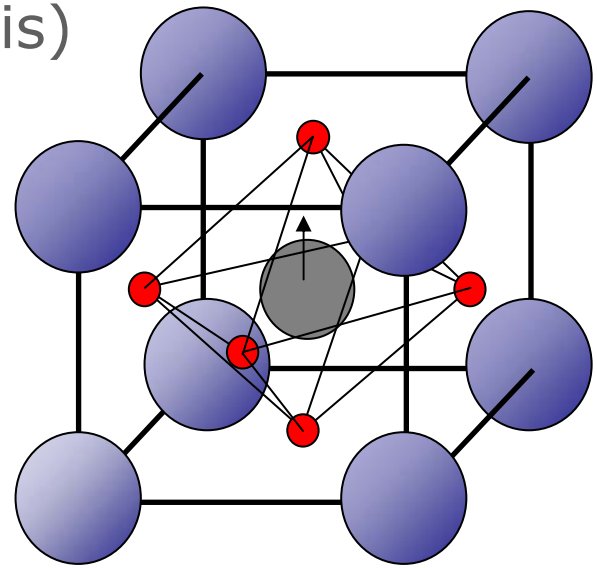


Symmetry-breaking crystal distortions

- Interatomic force constants: energy $E(\{u_{i\tau\alpha}\})$

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

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



Crystal symmetries lead to equalities and zeros for this matrix

Symmetry-breaking crystal distortions

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

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

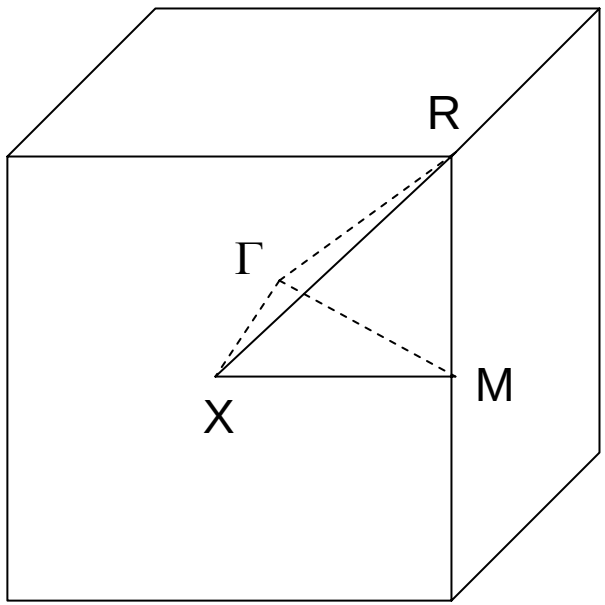
The force constant matrix (and dynamical matrix) are block diagonal with nonzero elements only between patterns with same transformation under crystal symmetry operations (that belong to same row of same irrep)

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

Symmetry breaking crystal distortions

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

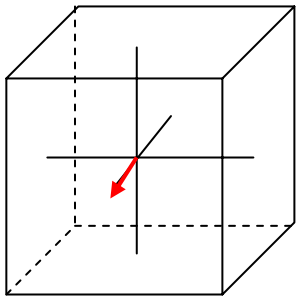
Cubic perovskite example: simple cubic



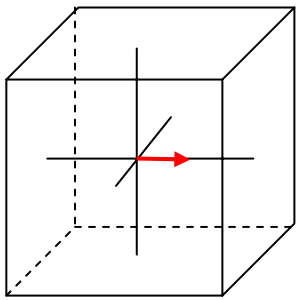
Γ: (0,0,0)
R: π/a(1,1,1)
X: π/a(1,0,0)
M: π/a(1,1,0)
where a is the lattice constant of the simple cubic lattice

Cubic perovskite: symmetrized displacement patterns

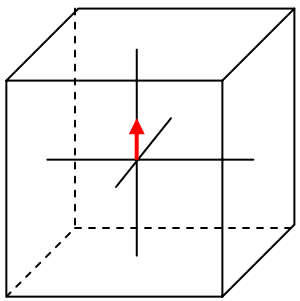
- Γ: Q=0 (uniform from cell to cell)



x



y

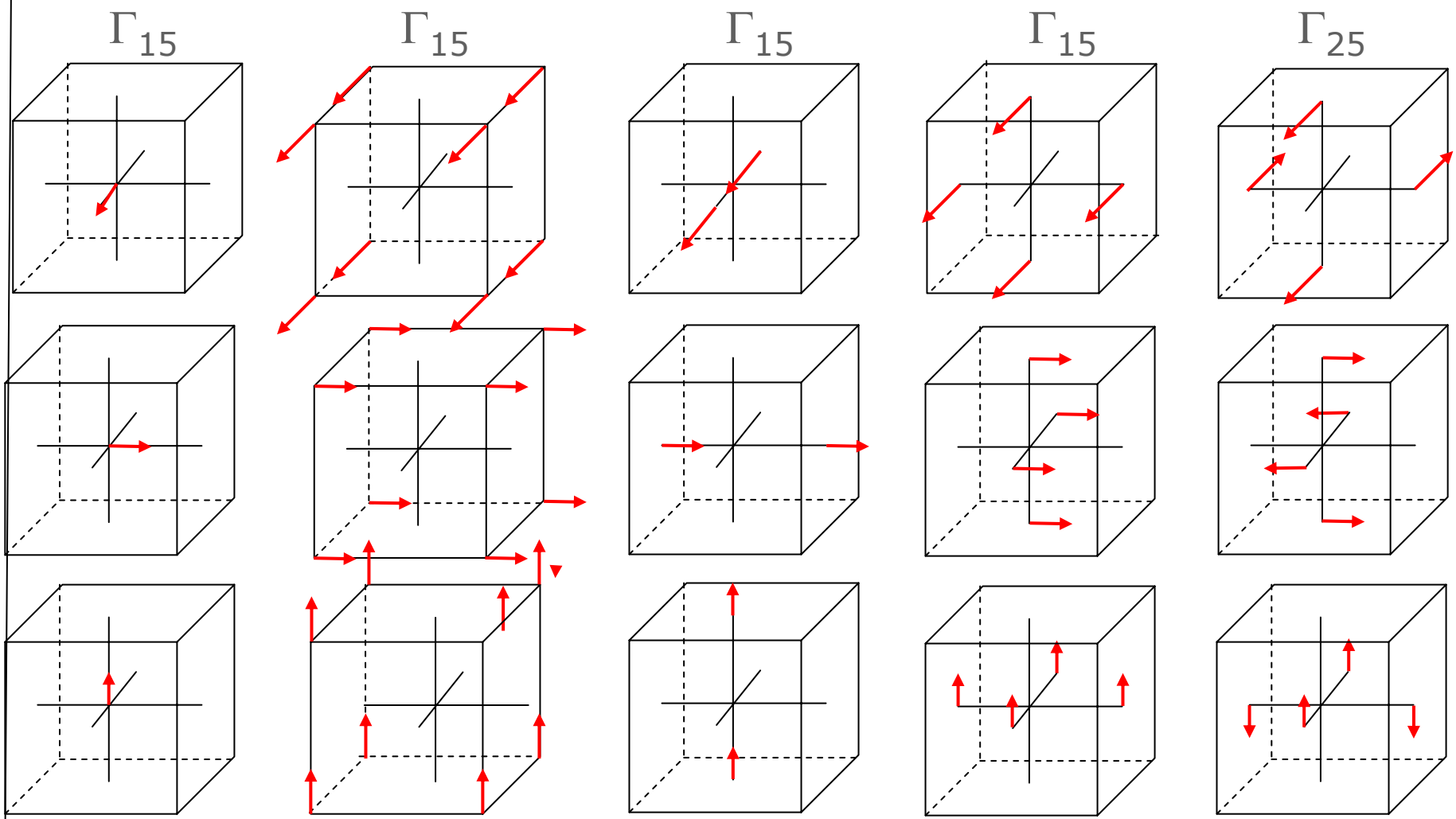


z

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

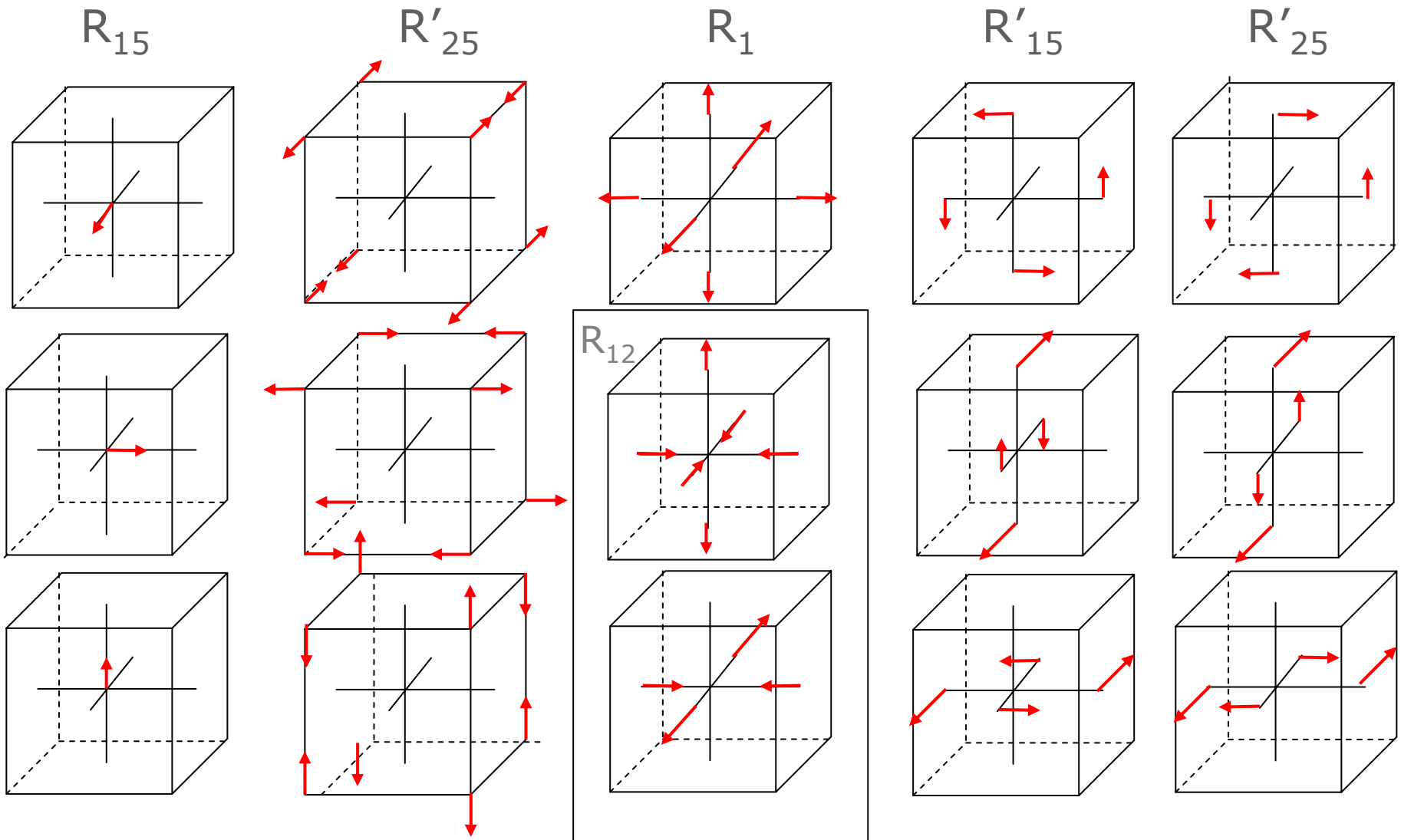
Cubic perovskite: symmetrized displacements

- Γ: Q=0 (uniform from cell to cell)



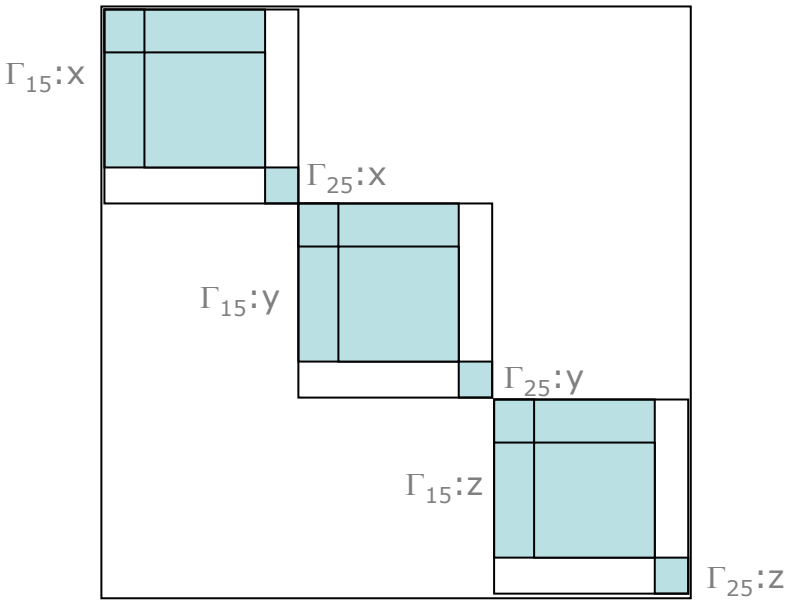
Cubic perovskite symm. displacements

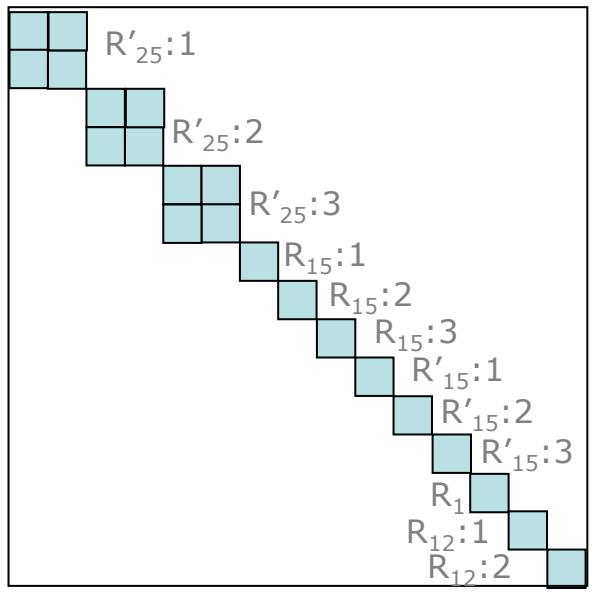
- R: Q=π/a(1,1,1) (changes sign from cell to cell)



Matrices become block diagonal

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





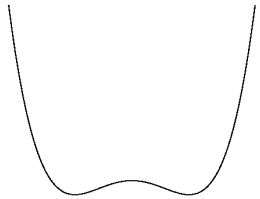
(In Γ matrix, acoustic Γ_{15} mode can be found by including uniform translation)
Finding eigenvalues becomes much easier!

Unstable modes

- Negative eigenvalue $\omega^2 < 0$

indicates energy-lowering distortion

(energy vs amplitude)



$BaTiO_3$ – unstable zone-center polar phonon

freezes in to produce low-temperature ferroelectric phases

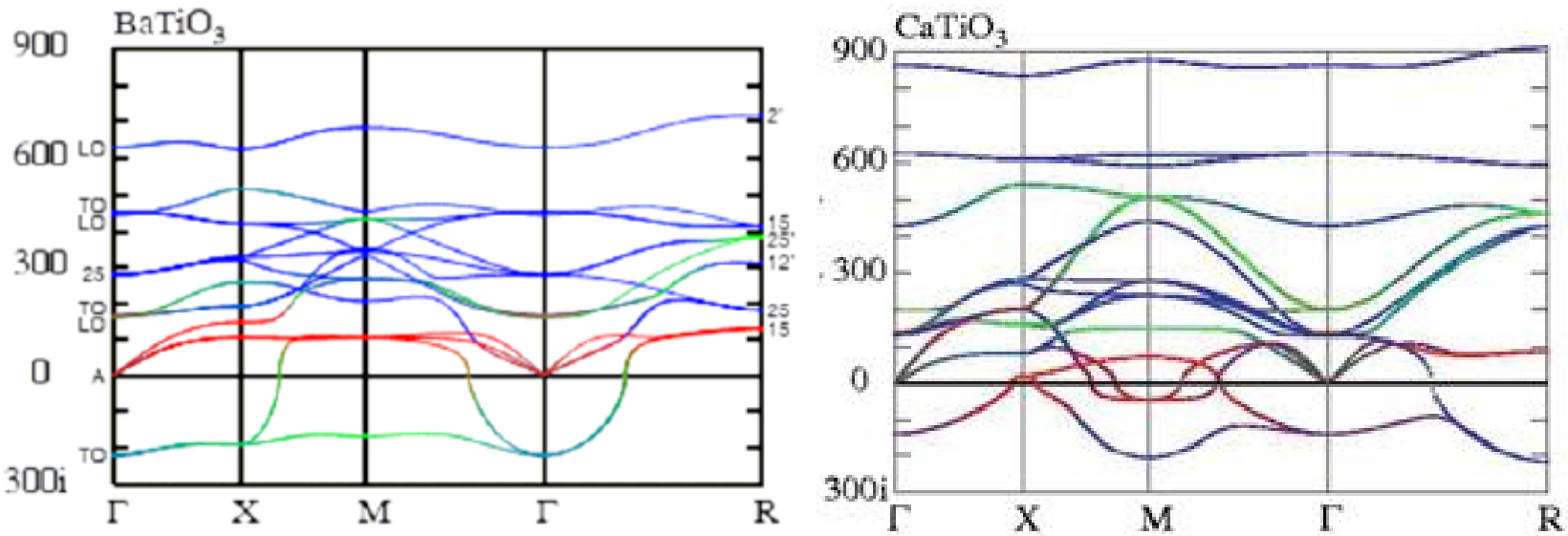
couples to strain of same symmetry

(tetragonal, orthorhombic, rhombohedral)

Symmetry breaking distortions/phonons

- Full phonon dispersion relation, with unstable modes

(note zone center includes LO/TO splitting – nonanalyticity depends on Z* and epsilon)



Symmetry breaking distortions/phonons

- Classification of low-symmetry structures by specification of mode content

Single modes

More than one mode (with coupling)

Q≠0 modes reduce translation symmetry

Reduction of point symmetry $\rightarrow$ nonzero strain

Of particular interest: oxygen octahedron rotations

M_3^+: sense of rotation same along axis of rotation

R_4^+: sense of rotation alternates along axis of rotation

Distorted perovskites: mode content+Glazer notation

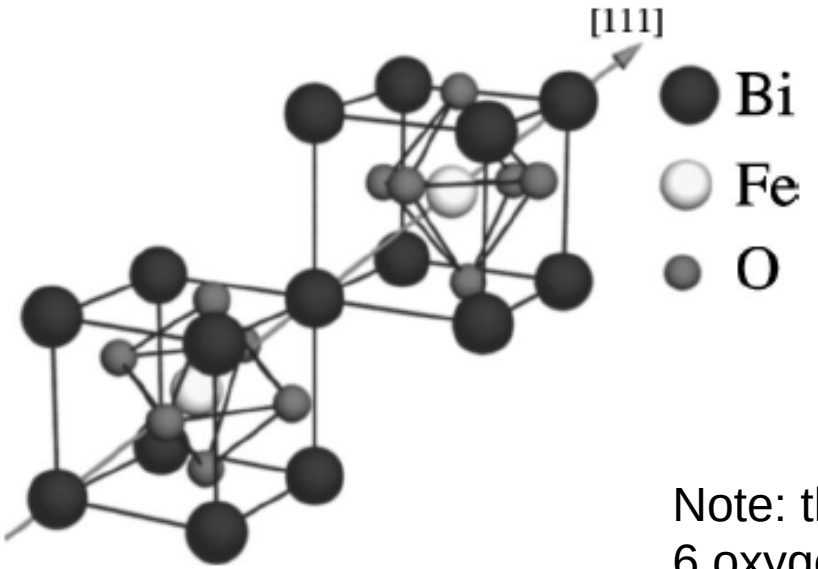
H. T. Stokes, et al, "Group theoretical analysis of octahedral tilting in ferroelectric perovskites," Acta Cryst. B58, 934 (2002)

Space group	Γ_4^-	M_3^+	R_4^+	System	Lattice vectors
221 $Pm\bar{3}m$	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0a_0^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)
127 $P4/mbm$	(0, 0, 0)	(0, 0, a)	(0, 0, 0)	$a_0^0a_0^0c_0^+$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)
139 $I4/mmm$	(0, 0, 0)	(0, a, a)	(0, 0, 0)	$a_0^0b_0^+b_0^+$	(0, 2, 0)(0, 0, 2)(2, 0, 0)
204 $Im\bar{3}$	(0, 0, 0)	(a, a, a)	(0, 0, 0)	$a_0^+a_0^+a_0^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)
71 $Immm$	(0, 0, 0)	(a, b, c)	(0, 0, 0)	$a_0^+b_0^+c_0^+$	(2, 0, 0)(0, 2, 0)(0, 0, 2)
140 $I4/mcm$	(0, 0, 0)	(0, 0, 0)	(0, 0, a)	$a_0^0a_0^0c_0^-$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 2)
74 $Imma$	(0, 0, 0)	(0, 0, 0)	(0, a, a)	$a_0^0b_0^-b_0^-$	(0, 1, 1)(2, 0, 0)(0, 1, $\bar{1}$)
167 $R\bar{3}c$	(0, 0, 0)	(0, 0, 0)	(a, a, a)	$a_0^-a_0^-a_0^-$	(1, 1, 0)(0, $\bar{1}$, 1)(2, 2, 2)
12 $C2/m$	(0, 0, 0)	(0, 0, 0)	(0, a, b)	$a_0^0b_0^-c_0^-$	(0, $\bar{2}$, 0)(2, 0, 0)(0, 1, 1)
15 $C2/c$	(0, 0, 0)	(0, 0, 0)	(a, b, b)	$a_0^-b_0^-b_0^-$	(2, $\bar{1}$, $\bar{1}$)(0, 1, $\bar{1}$)(0, 1, 1)
2 $P\bar{1}$	(0, 0, 0)	(0, 0, 0)	(a, b, c)	$a_0^-b_0^-c_0^-$	(0, 1, 1)(1, 0, 1)(1, 1, 0)
63 $Cmcm$	(0, 0, 0)	(0, a, 0)	(0, 0, b)	$a_0^0b_0^+c_0^-$	(2, 0, 0)(0, 0, $\bar{2}$)(0, 2, 0)
62 $Pnma$	(0, 0, 0)	(a, 0, 0)	(0, b, b)	$a_0^+b_0^-b_0^-$	(0, 1, 1)(2, 0, 0)(0, 1, $\bar{1}$)
11 $P2_1/m$	(0, 0, 0)	(a, 0, 0)	(0, b, c)	$a_0^+b_0^-c_0^-$	(0, $\bar{1}$, 1)(2, 0, 0)(0, 1, 1)
137 $P4_2/nmc$	(0, 0, 0)	(a, a, 0)	(0, 0, b)	$a_0^+a_0^+c_0^-$	(2, 0, 0)(0, 2, 0)(0, 0, 2)
99 $P4mm$	(0, 0, a)	(0, 0, 0)	(0, 0, 0)	$a_0^0a_0^0c_+^0$	(1, 0, 0)(0, $\bar{1}$, 0)(0, 0, 1)
38 $Amm2$	(a, a, 0)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0c_0^0$	(0, 0, 1)(1, $\bar{1}$, 0)(1, 1, 0)
160 $R3m$	(a, a, a)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0a_+^0$	(1, $\bar{1}$, 0)(0, 1, $\bar{1}$)(1, 1, 1)
6 Pm	(a, b, 0)	(0, 0, 0)	(0, 0, 0)	$a_+^0b_+^0c_0^0$	(0, 1, 0)(0, 0, 1)(1, 0, 0)
8 Cm	(a, a, b)	(0, 0, 0)	(0, 0, 0)	$a_+^0a_+^0c_+^0$	(1, 1, 0)($\bar{1}$, 1, 0)(0, 0, 1)
1 $P1$	(a, b, c)	(0, 0, 0)	(0, 0, 0)	$a_+^0b_+^0c_+^0$	(1, 0, 0)(0, 1, 0)(0, 0, 1)

R3c: $LiNbO_3$, $BiFeO_3$

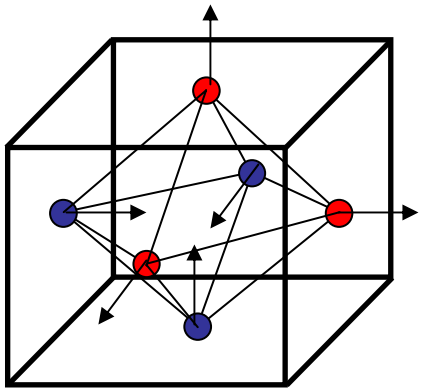
- 2 formula units (10 atoms) / cell

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



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

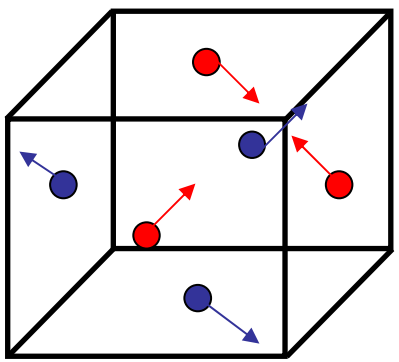
R3c: closer look at polar mode along [111]

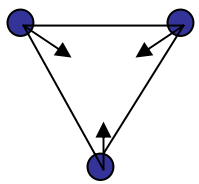


A and B atoms displace along [111]

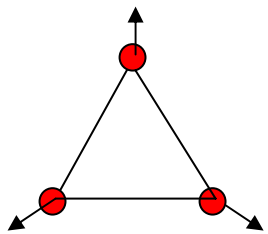
O atoms have lower site symmetry
Displacement not along [111] in general

View along [111]





In and up



Out and up

160 *R*3*m* (a,a,a) $(0,0,0)$ $(0,0,0)$ $a^0_+a^0_+a^0_+$ $(1,\bar{1},0)(0,1,\bar{1})(1,1,1)$

1 formula unit per cell

Positions

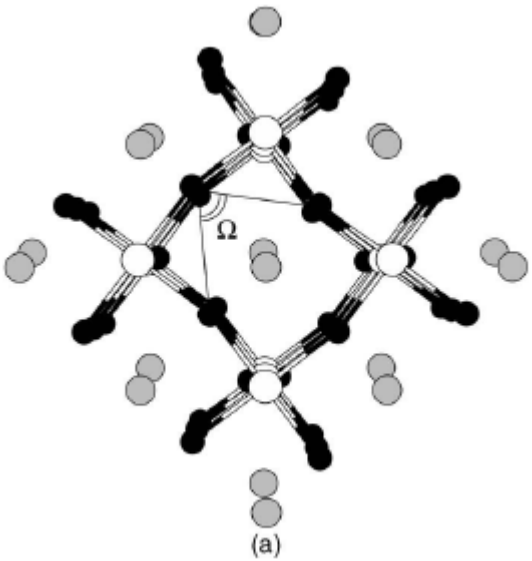
Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
						General:
6	*b*	1	(1) x,y,z (4) $z+\frac{1}{2},y+\frac{1}{2},x+\frac{1}{2}$	(2) z,x,y (5) $y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$	(3) y,z,x (6) $x+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2}$	hhl : $l=2n$ hhh : $h=2n$
						Special: as above, plus
2	*a*	3 .	x,x,x	$x+\frac{1}{2},x+\frac{1}{2},x+\frac{1}{2}$		hkl : $h+k+l=2n$

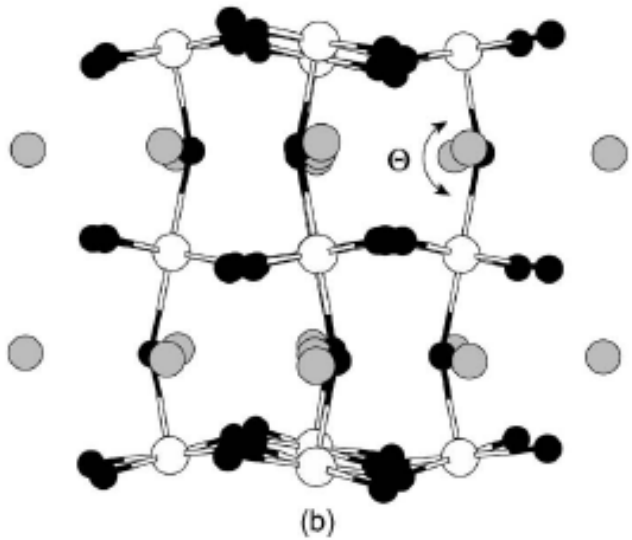
For $BiFeO_3$:

Bi 2a
Fe 2a
O 6b

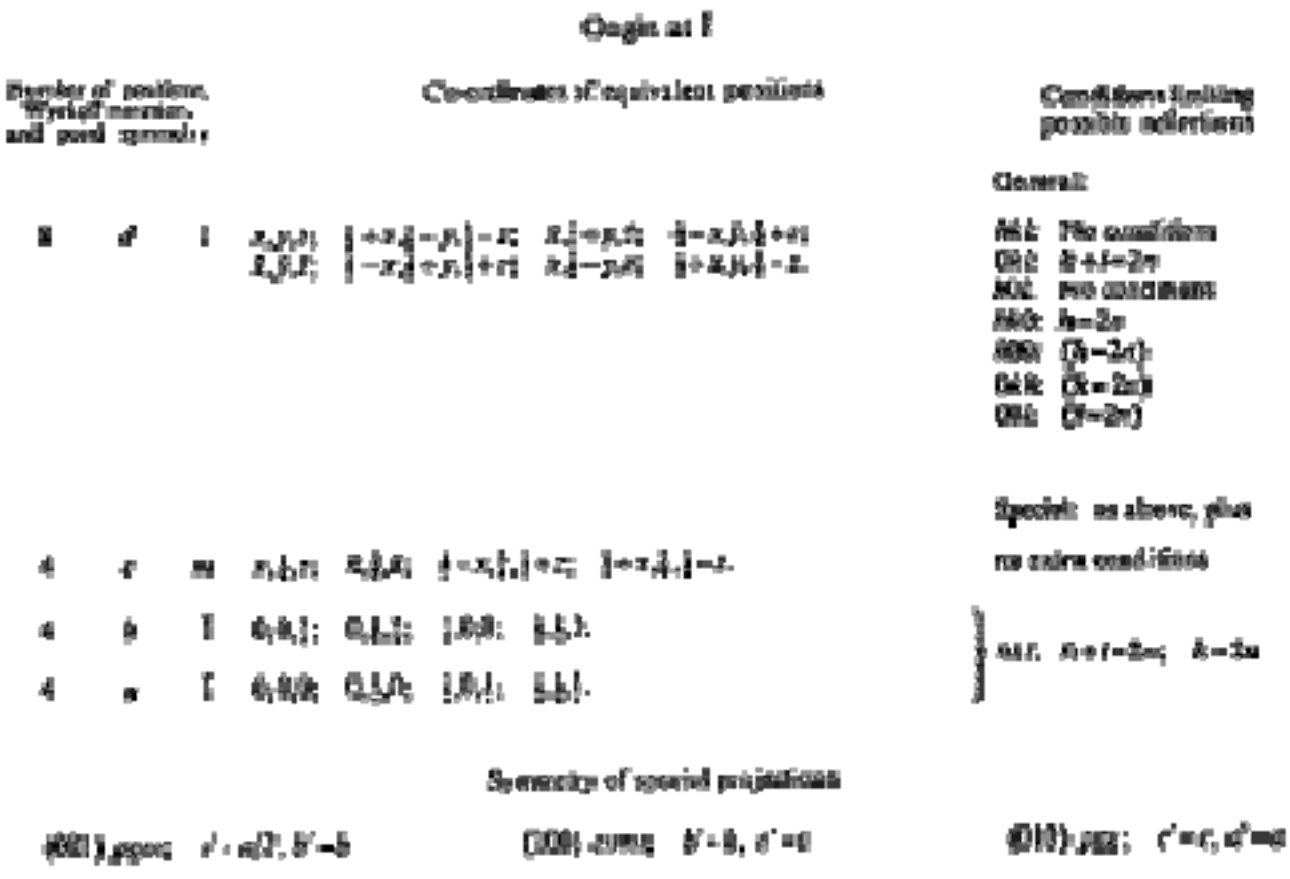
Orthorhombic perovskites ($CaTiO_3$…) : Pnma

13	62 *Pnma*	$(0, 0, 0)$	$(a, 0, 0)$	$(0, b, b)$	$a_0^+ b_0^- b_0^-$	$(0, 1, 1)(2, 0, 0)(0, 1, \bar{1})$





View along [100]



This space group is often specified using a different “setting” (choice of axes) as Pbnm

Not just the perovskite structure

- Spinels
- Pyrochlore
- Layered perovskites (Ruddlesden-Popper, Dion-Jacobson…)
- Rutile

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).

Of particular interest:

- Piezoelectric tensor
- Nonlinear optical properties--SHG (see also lectures by Thomas Lottermoser)