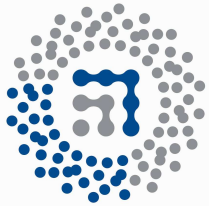

ZTF-FCT
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Symmetry considerations in structural phase transitions

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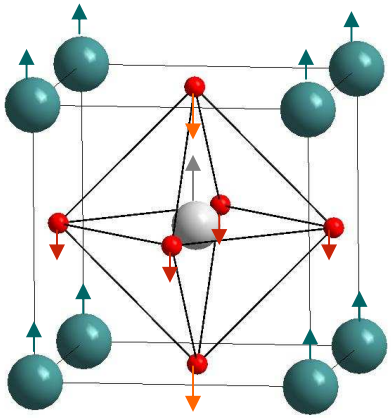
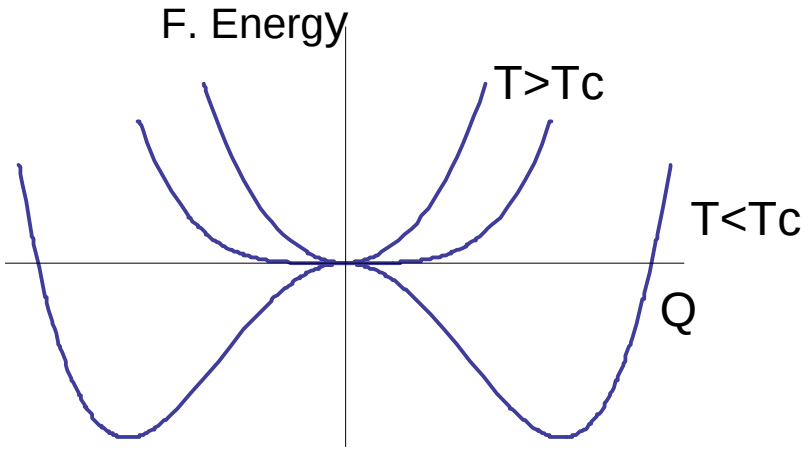
BILBAO, SPAIN

The natural language to describe a symmetry break/phase transition is the one of collective symmetry-adapted modes (Landau Theory)



primary distortion mode : order parameter

Unstable collective degree of freedom:



$E = Eo + 1/2\ \kappa(T)\ Q^2 + \ldots$

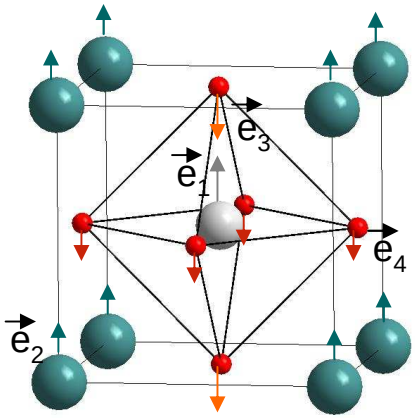
$\kappa(T)<0 \quad T<Tc$

distortion modes:

- displacive type: local variable =atomic displacements
- order-disorder type: local variable: site occupation probabilities
- magnetic type: local variable: atomic magnetic moments

Distorted Structure = High-symmetry Struct + “frozen” distortion modes

distortion mode = Amplitude * polarization vector



Description of a displacive “mode”:

$\vec{u}(\text{atoms}) = Q\ \vec{e}$

amplitude — polarization vector

$\mathbf{e} = (\vec{e}_1, \vec{e}_2, \vec{e}_3, \vec{e}_4)$

normalization: $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2\,|\vec{e}_4|^2 = 1$
(within a unit cell)

Modes in the description of the statics (STRUCTURE) of a distorted solid:

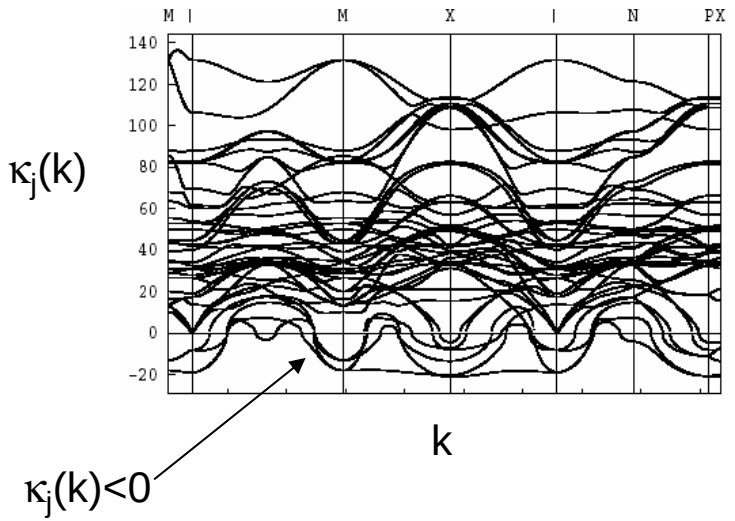
(Free) Energy around the high-symmetry non-distorted configuration:

$$E = Eo + 1/2 \sum \kappa_j(k)\, Q_i^2(k) + \ldots$$

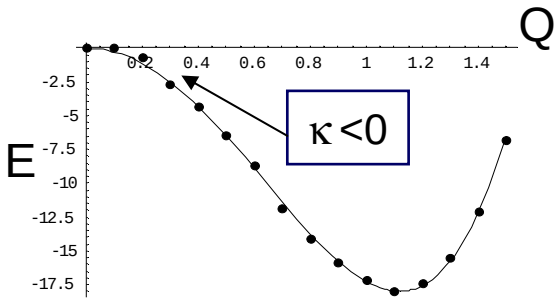
stiffness coefficients

Normal (static) coordinates

Ab-initio calculation of static normal modes in a ferroic:

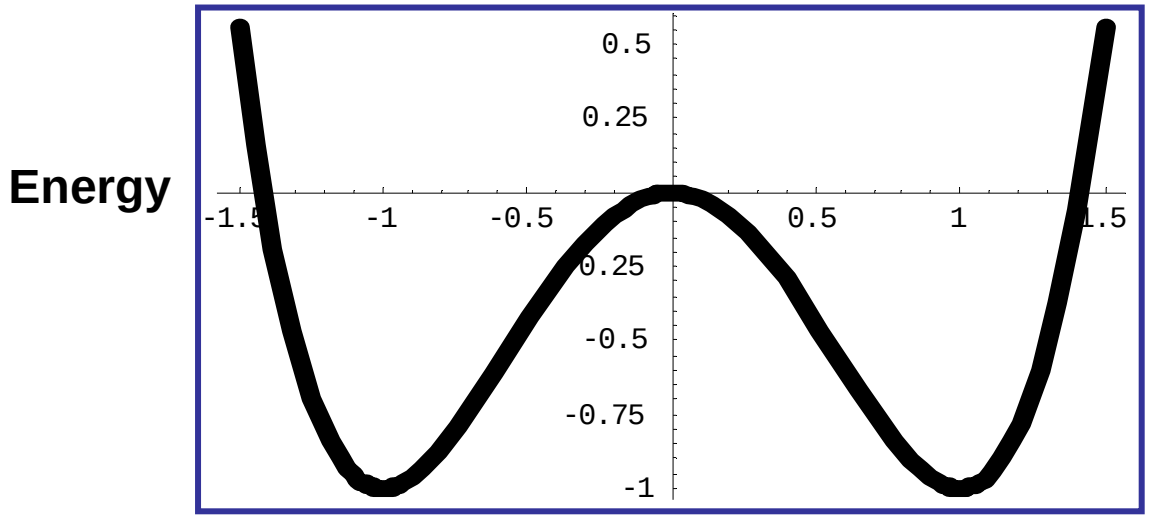


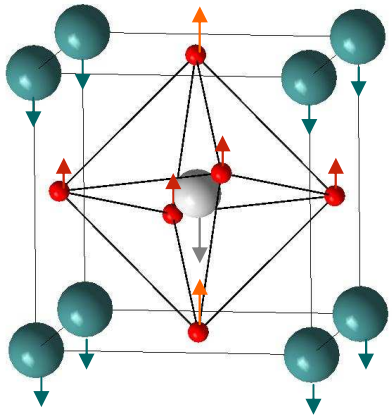
Energy as a function of the amplitude of an unstable Q:



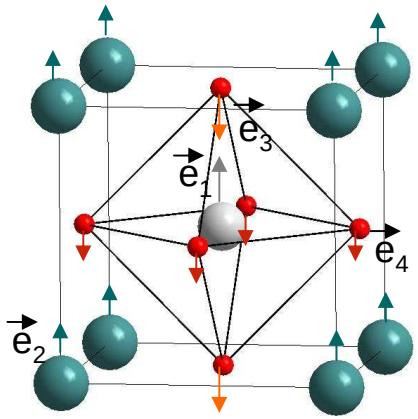
Symmetry of distortion modes:
irreducible representations (group theory)

Multistability:





Q<0



Q >0

Phase Transition / Symmetry break / Order Parameter

Symmetry group **G** = {g}

Irreducible representation of G (irrep) (matrices)

$T(g)\,\vec{Q} = \vec{Q}$

g belongs to F

$T(g)\,\vec{Q} = \vec{Q}' \neq \vec{Q}$

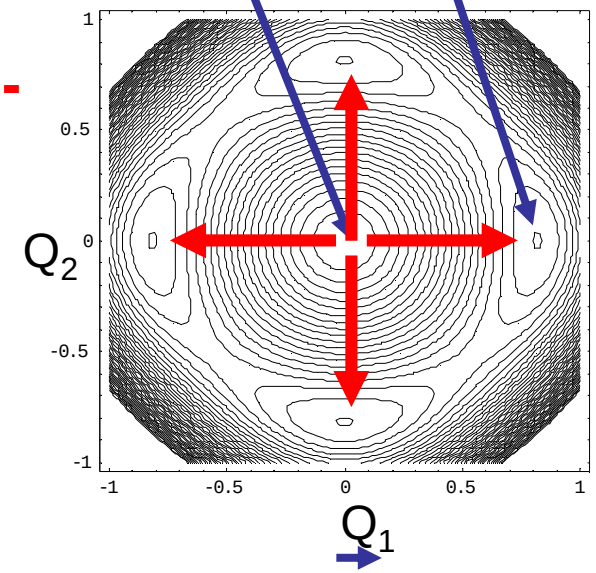
g does not belong to F: $\vec{Q}'$ equivalent but distinguishable state

Symmetry break

G → **H**

G contains **H**

High symmetry — Low symmetry



Key concept! (Landau):
It defines the type of symmetry break

Order parameter **Q** = (Q_1,Q_2) = Q (a_1,a_2)

$a_1^2+a_2^2 = 1$

Switchable quantities are those that were zero in G ("spontaneous" in F)

Multistability: contability of distinct domains:

G → H

We need to know the irrep of the order parameter

distinct domains/states: $\{\vec{Q}'\}$ $T(g)\,\vec{Q} = \vec{Q}'$

Number of distinct equivalent states = $\dfrac{\textbf{Order of G}}{\textbf{Order of H}}$ = n (index of H)

coset decomposition: $G = H + g_2H + \ldots + g_nH$

distinct Ferroic states: only if the symmetry operations g contain different rotational parts:

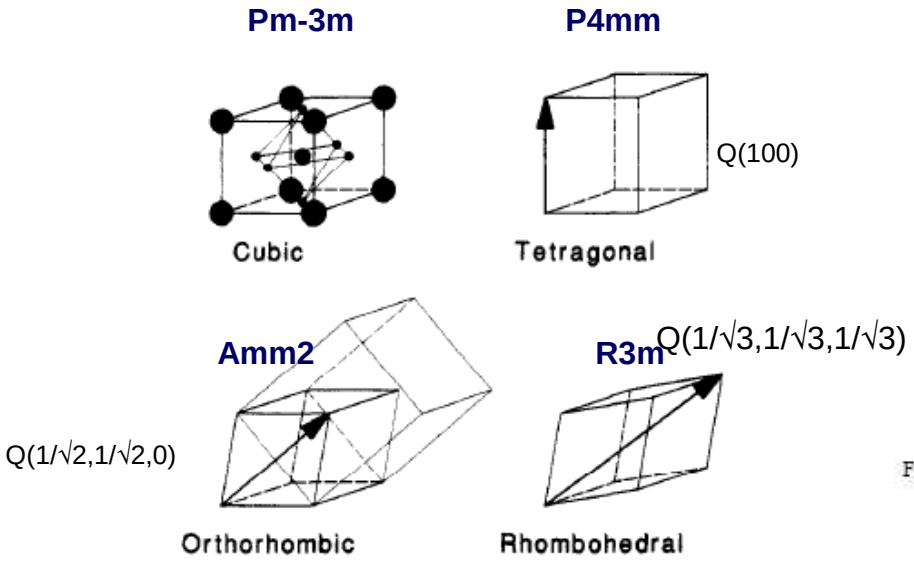
Number of distinct ferroic states = $\dfrac{\textbf{Order of } P_G}{\textbf{Order of } P_H}$ = i_t (t-index)

Two levels of knowledge of the symmetry of a distorted phase:

1) pair of points groups: **(P_G, P_H)**

2) space group **G** + active irrep(s) + plus direction order parameter(s) $\vec{Q}$

Example: The orthorhombic Amm2 structure of $BaTiO_3$



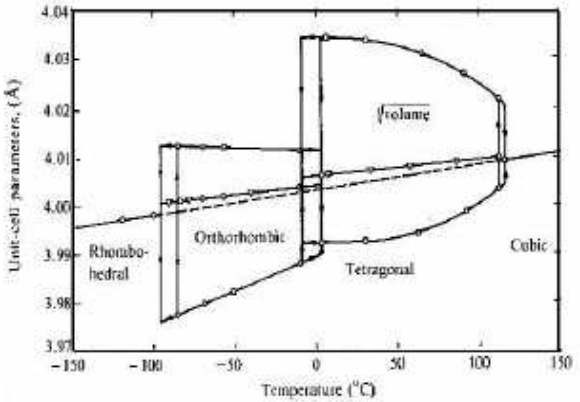
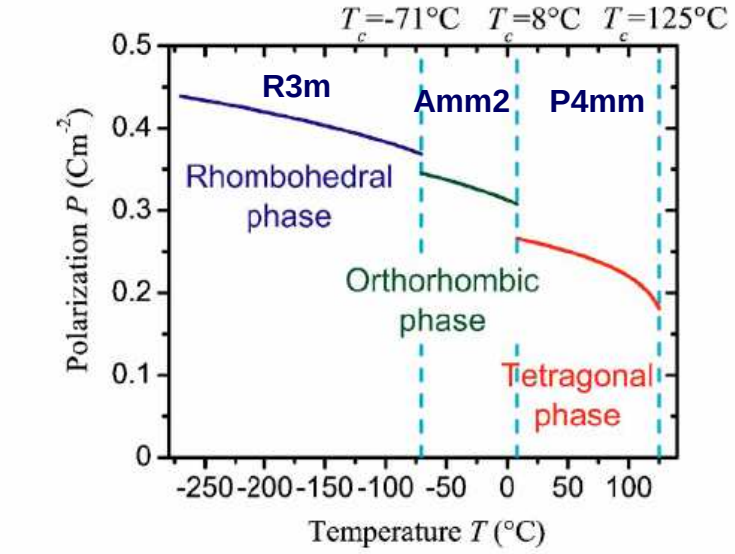
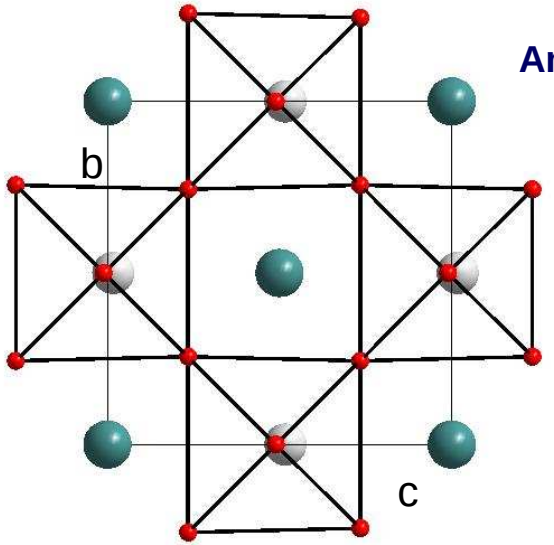


Figure 2. Lattice parameters of $BaTiO_3$ as a function of temperature [11].



Li et al. J. Appl. Phys. (2005)



Polarization

Ferroelectric Domains in Amm2 $BaTiO_3$

(m-3m, mm2)

high symmetry Pm-3m
order parameter:
irrep T_{1u} (vector representation)

Amm2: Q(0,1/√2,1/√2)

Order of m-3m = 48
Order of mm2 = 4

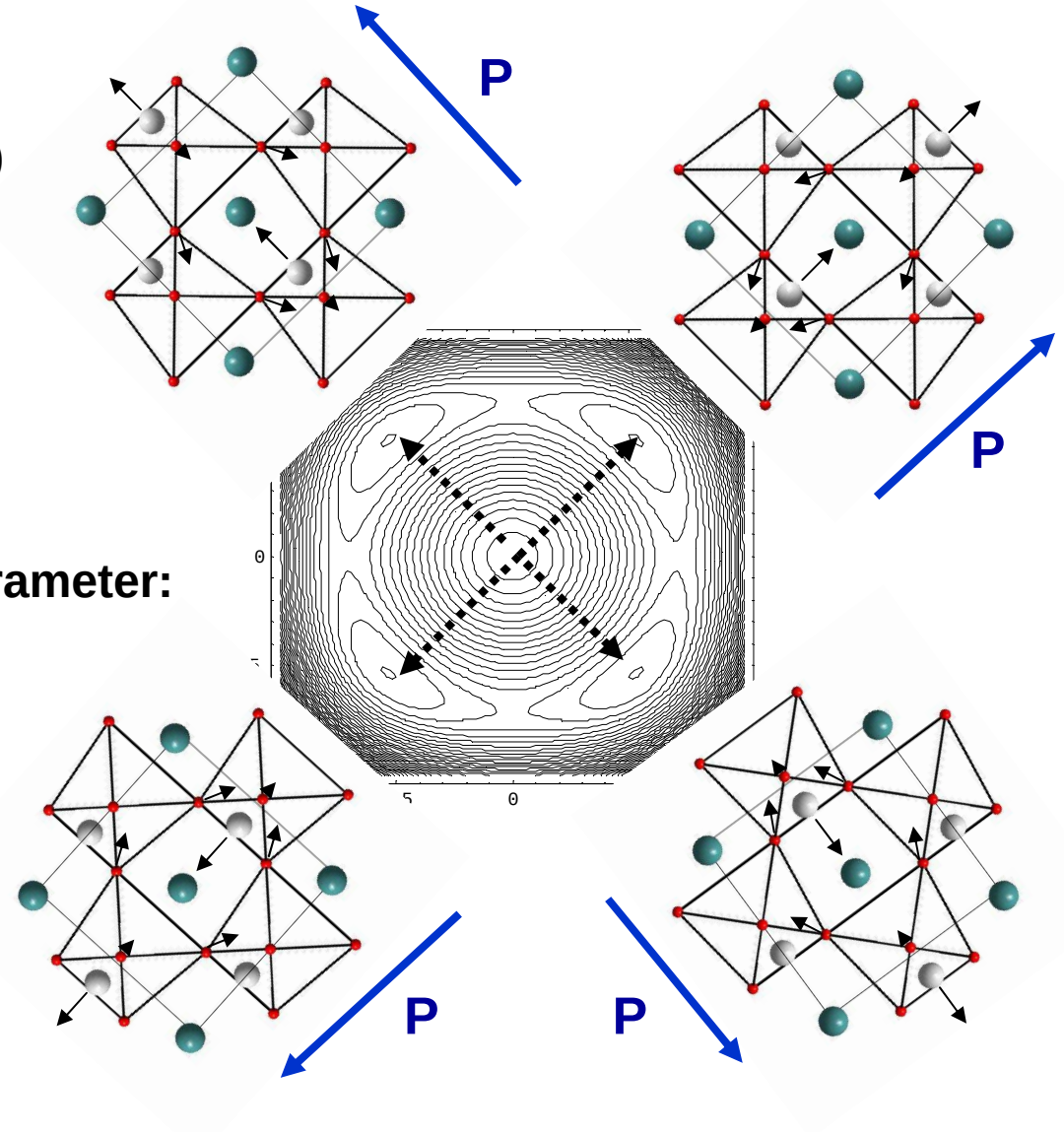
Number of domains = 48/4=12

12 eq. directions for the order parameter:

(0,1/√2,1/√2)
(0,-1/√2,1/√2)
(0,-1/√2,-1/√2)
(0,1/√2,-1/√2)

(1/√2,0,1/√2)
(-1/√2,0,1/√2)
(1/√2,0,-1/√2)
(1/√2,0,-1/√2)

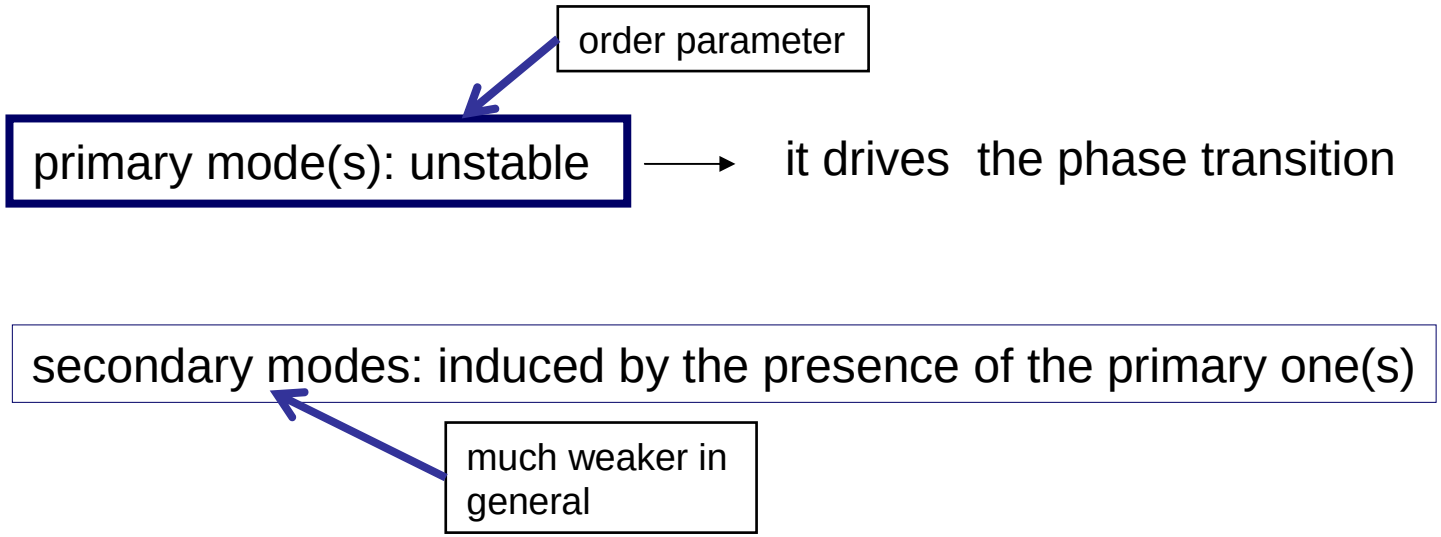
(1/√2,1/√2,0)
(-1/√2,1/√2,0)
(-1/√2,-1/√2,0)
(1/√2,-1/√2,0)



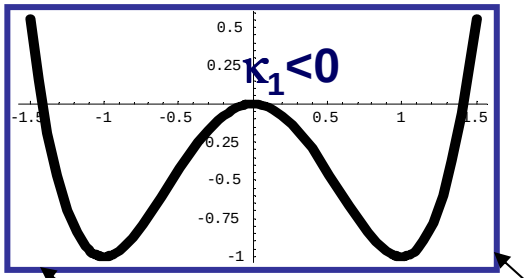
Hierarchy of modes:

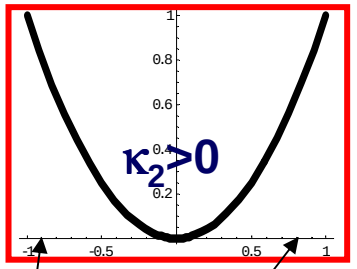
Von Neumann principle:
all modes/variables compatible with the symmetry
will be present in the total distortion ….

But not all with the same weight!:

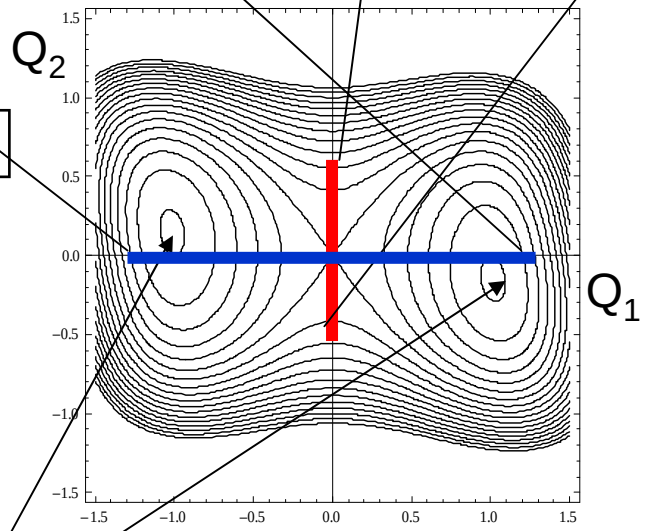


Hierarchy of spontaneous modes/variables





Example of a (free) energy map with primary (Q_1) and secondary (Q_2) distortion modes:



faintness index

$\kappa_1<0$ $\kappa_2>0$

$$E = Eo + \tfrac{1}{2}\ \kappa_1 Q_1^2 + \tfrac{1}{2}\ \kappa_2 Q_2^2 + \gamma Q_1^3 Q_2 +$$

Anharmonic allowed coupling

$$Q_2^{\text{equil.}} = -(\gamma / k_2)\, Q_1^3$$

Equivalent ferroic stable structures

Secondary spontaneous strain in Amm2-$BaTiO_3$

Secondary spontaneous modes/variables:

everything that is allowed by symmetry in the distorted phase !

Order parameter (polar mode): (Q_x,Q_y,Q_z) – irrep T_{1u}

shear strains: $(\varepsilon_{xy}, \varepsilon_{xz}, \varepsilon_{yz})$ – irrep T_{2g}

Lowest coupling term allowed by symmetry in the (free) energy (symmetry invariant):

$\gamma\,(Q_x,Q_y\varepsilon_{xy}+ Q_xQ_z\,\varepsilon_{xz}+ Q_yQ_z\varepsilon_{yz})$ ← linear in the secondary variable

γ: System-dependent coefficient: symmetry cannot tell us the magnitude of the coupling – only if it is possible

In addition, the usual elastic energy: $\frac{1}{2}\, C_{44}\,(\varepsilon_{xy}^2+\varepsilon_{xz}^2+\varepsilon_{yz}^2)$

Then energy minimum for:

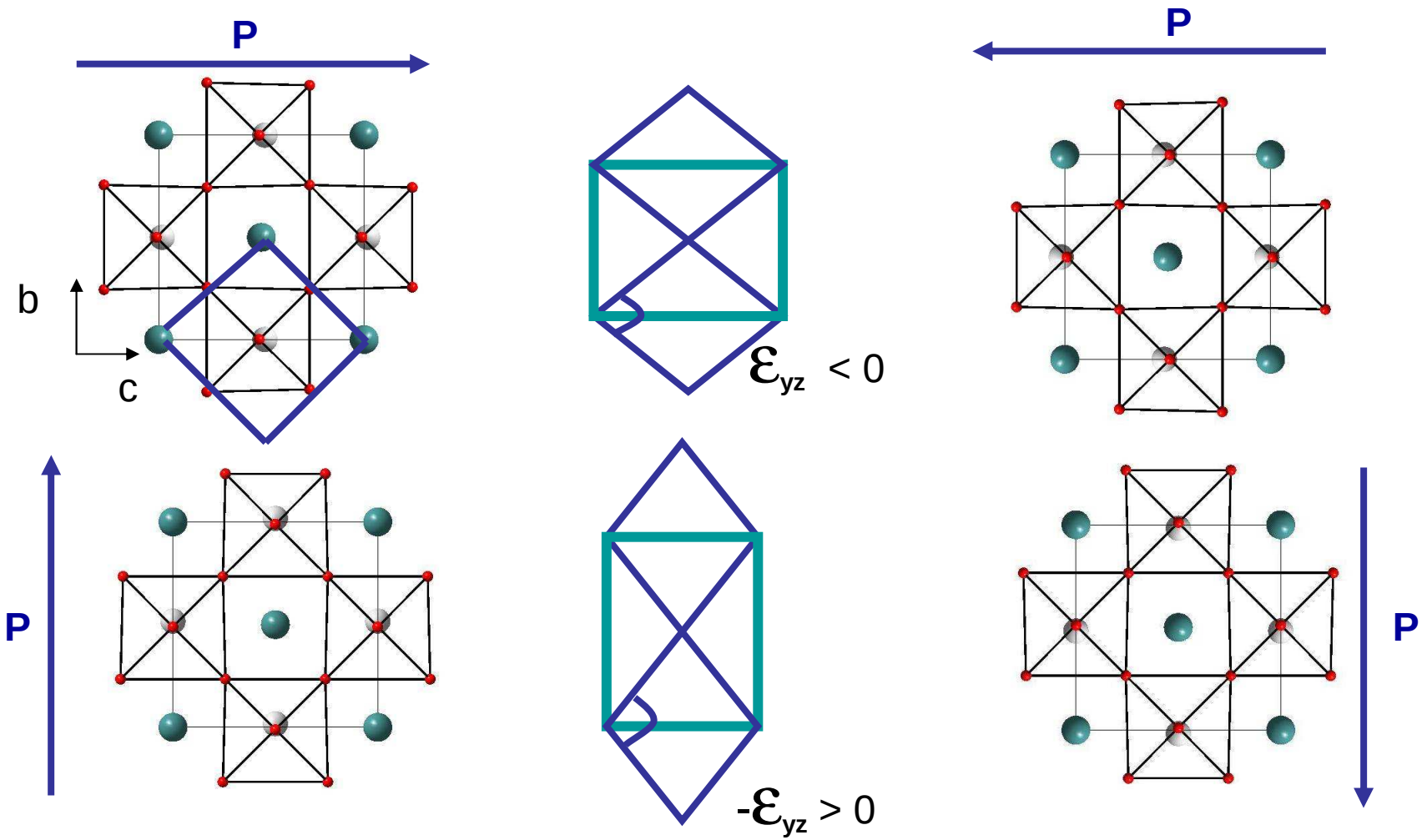
$$\varepsilon_{xy} = -\frac{\gamma}{C_{44}} Q_xQ_y$$
$$\varepsilon_{xz} = -\frac{\gamma}{C_{44}} Q_xQ_z$$
$$\varepsilon_{yz} = -\frac{\gamma}{C_{44}} Q_yQ_z$$

Ferroic states/domains →

(Q_x,Q_y,Q_z)	$(\varepsilon_{xy}, \varepsilon_{xz}, \varepsilon_{yz})$
$Q(0,1/\sqrt{2},1/\sqrt{2})$	$(0,0, \varepsilon^o_{yz})$
$Q(0,-1/\sqrt{2},1/\sqrt{2})$	$(0, 0, -\varepsilon^o_{yz})$
$Q(0,-1/\sqrt{2},-1/\sqrt{2})$	$(0,0, \varepsilon^o_{yz})$
$Q(0,1/\sqrt{2},-1/\sqrt{2})$	$(0,0, -\varepsilon^o_{yz})$

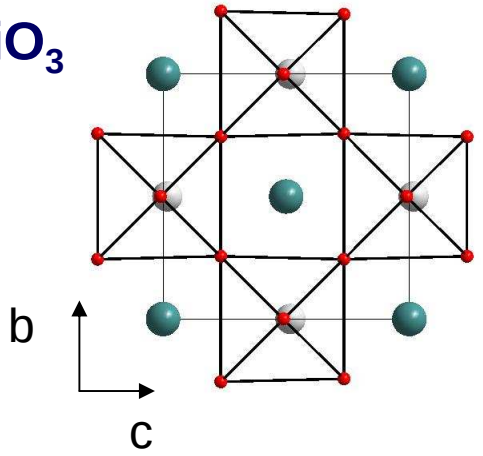
Amm2 – $BaTiO_3$: strain as secondary mode/variable

Proper ferroelectric
Improper ferroelastic



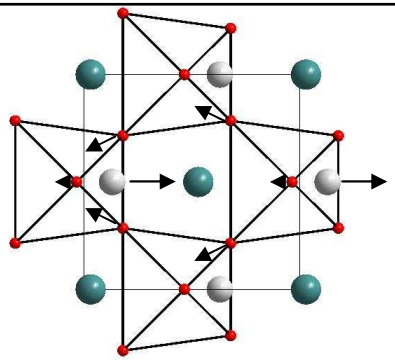
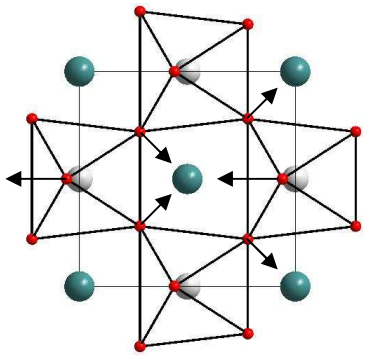
One can turn 90º the polarization switching the strain with a stress …

Secondary mode in the Amm2 structure of $BaTiO_3$



Mode decomposition of structure distortion:

primary mode-order parameter:

Q_{T1u} x  + Q_{T2u} x 

T_{1u} - mode

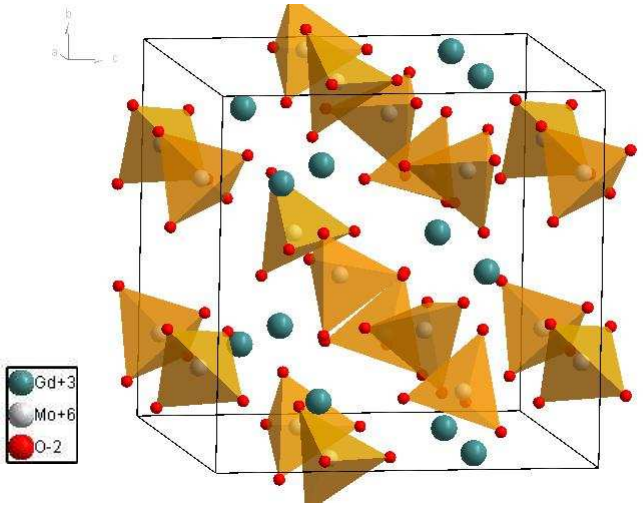
T_{2u} - mode

secondary mode

$Q_{T1u} >> Q_{T2u}$

$Q_{T2u} \sim Q_{T1u}^{3}$ ← faintness index

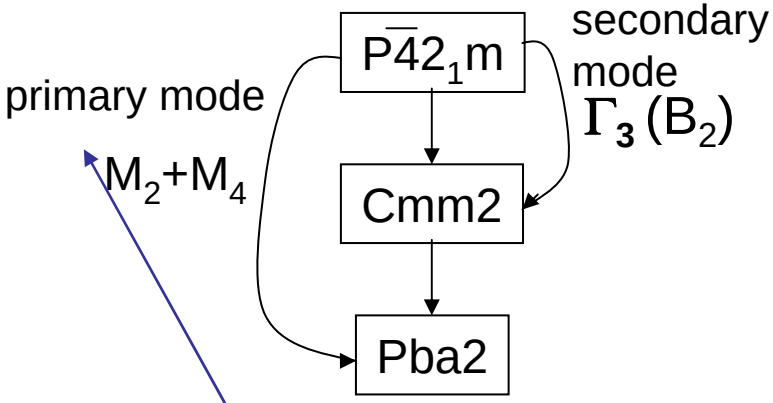
An “improper” ferroelectric (and ferroelastic) - $Gd_2(MoO_4)_2$



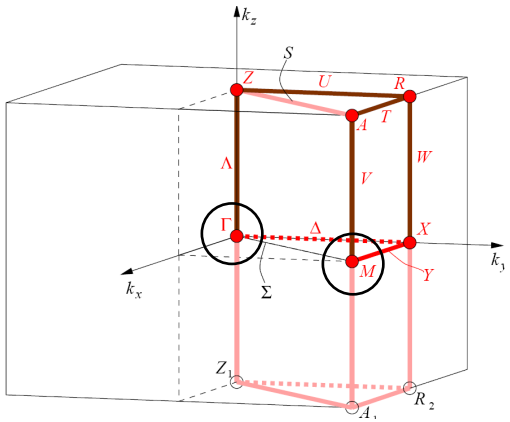
A Polar (ferroelectric) mode as a secondary mode

$P\bar{4}2_1m$ (Z=2) $\xrightarrow{160\ C}$ Pba2 (Z=4) ($\bar{4}$2m ------ mm2) cell duplication

polar mode/polarization



antiferrodistortive mode (multiplies the unit cell)
wave vector ≠ 0



M=(1/2, 1/2, 0)

Q_{M2M4}= 1.6191 Å

$Q_{\Gamma 3}$ = 0.0716 Å

General Rules

for a given symmetry break $G \longrightarrow H?$

To know which is the “proper” ferroic property, one has to identify the order parameter symmetry (irrep or irreps of G)

To know which is the symmetry F of the distorted phase, one can then use the invariance equation:

matrix irrep → $T[g]\,\vec{Q} = \vec{Q}$ → g belongs to **H**

H

secondary spontaneous ferroic variables (“improper” ferroic properties):

Polynomial of order n (faintness index) → $X \sim F^{(n)}[Q_1,\ldots,Q_n]$

energy coupling: $X.F^{(n)}[Q_1,\ldots Q_n]$

Knowing the pair of symmetries (G,F) is sufficient to predict all ferroic properties (but not their magnitudes!).

Distinct ferroic states obtained by: $T[g]\,\vec{Q} = \vec{Q}'$ with g belonging to G, but not H

A practical guide:

case 1: **We know a structure with space group F and we want to know/predict if it can have ferroic properties and/or have some phase transition at higher temperatures**

pseudosymmetry search

Program PSEUDO

We search for a structure with space group G (supergroup of F) such that:

Structure G = Structure F + small (symmetry-breaking) distortion

A practical guide:

case 2: **We know the high symmetry and the active irrep or order parameter and we want to know the possible symmetries of the distorted phase**

$$G \longrightarrow ?$$

possible isotropy subgroups for a given active irrep?

irreps of P4mm at k=0 (Γ point)

Character Table

C_{4v}(4mm)	#	1	2	4	m_x	m_d	functions
Mult.	-	1	1	2	2	2	.
A_1	Γ_1	1	1	1	1	1	z,x^2+y^2,z^2
A_2	Γ_2	1	1	1	-1	-1	J_z
B_1	Γ_3	1	1	-1	1	-1	x^2-y^2
B_2	Γ_4	1	1	-1	-1	1	xy
E	Γ_5	2	-2	0	0	0	$(x,y),(xz,yz),(J_x,J_y)$

for 1-dim irreps rather trivial, for n-dim one must apply the matrix equations or use some group theoretical "tricks"

P4mm

P4

Pmm2

Cmm2

Pm

C

m

P1

T[g] Q=Q {g}=F

isotropy subgroup depends on the "direction" of the 2-dim order parameter.

case 2: $G \longrightarrow ?$

possible isotropy subgroups for a given active irrep?

Relax.... computers can do it for you!: http://stokes.byu.edu/isotropy.html

ISOTROPY

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ISOTROPY is a software package which applies group theoretical methods to the analysis of phase transitions in crystalline solids.

When this software is used in research that results in published papers, please include a reference which contains the following information:

H. T. Stokes, D. M. Hatch, and B. J. Campbell, (2007). ISOTROPY, stokes.byu.edu/isotropy.html.

Documentation

ISOTROPY User's Manual
ISOTROPY Tutorial
Introduction to Isotropy Subgroups and Displacive Phase Transitions (unpublished)

New! ISO(3+1)D: Isotropy Subgroups for Incommensurately Modulated Distortions in Crystalline Solids: A Complete List for One-Dimensional Modulations

Internet Versions

ISOTROPY: Main interactive program.

ISODISPLACE: Explore and visualize displacive distortions of a crystalline structure associated with space group irreducible representations.

ISOCIF: Create or modify CIF files.

FINDSYM: Identify the space group of a crystal, given the positions of the atoms in a unit cell.

COPL: Find a complete list of order parameters for a phase transition, given the space-group symmetries of the parent and subgroup phases.

INVARIANTS: Generate invariant polynomials of the components of order parameters.

SMODES: Find the displacement modes in a crystal which brings the dynamical matrix to block-diagonal form, with the smallest possible blocks.

FROZSL: Calculate phonon frequencies and displacement modes using the method of frozen phonons.

COMSUBS: Find common subgroups of two structures in a reconstructive phase transition

There is also a book of isotropy subgroups:

H. T. Stokes and D. M. Hatch, Isotropy Subgroups of the 230 Crystallographic Space Groups (World Scientific, Singapore, 1988).

case 2: $G \longrightarrow ?$

possible isotropy subgroups for a given active irrep?

Program INVARIANTS gives the isotropy subgroups as a by-product:

HELP

Invariants Step 4

Space Group: 99 P4mm C4v-1
Point in first Brillouin zone: GM, k17 (0,0,0)
Irreducible Representation: GM5, k17t5
Choose a direction of the order parameter:
Each direction determines a structure with different symmetry (isotropy subgroup), also given in the list below.
for the direction chosen. If you want the complete invariant polynomials, choose the general direction (last item

P1 (a,0) 6 Pm Cs-1

Next Step

case 2: $G \longrightarrow ?$

possible isotropy subgroups for a given active irrep?

Prediction of probable symmetries for compounds of a family, or for the same compound at different conditions due to a common active irrep, with the order parameter taking different directions:

Example: Perovskites are known to have systematically a soft or unstable mode with irrep R4+:

isotropy subgroups of R4+:

I4/mcm, (a+b, -a+b ,2c; 0,0,0) , (a,0,0)	$SrZrO_3$
Imma, (a+c, 2b, -a+c; 0,0,0), (a,a,0)	$SrZrO_3$
R-3c, (-a+b, -b+c, 2a+2b+2c; 0,0,0) , (a,a,a)	$CeAlO_3$
C2/m, (-2c, 2b, a+c; 0,1/2,1/2), (a,b,0)	$BaPbO_3$
C2/c, (-a+2b-c, -a+c,a+c; 0,1/2,1/2), (a,a,b)	$LaCoO_3$
P-1, (b+c, a+c a+b; 0,0,0), (a,b,c)	

A practical guide:

case 3: We know the symmetry break and we want to identify the active irrep (inverse Landau problem)

$G \longrightarrow H$

active irrep?

comparison of the unit cells → k-vector(s) of the active irrep: star of the active irrep

$e^{ik.T}=1$, transl. T belongs to F

$k.T=2\pi n$

irreps of P4mm at k=0 (Γ point)

Character Table

C_{4v}(4mm)	#	1	2	4	m_x	m_d	functions
Mult.	-	1	1	2	2	2	·
A_1	Γ_1	1	1	1	1	1	z, x^2+y^2, z^2
A_2	Γ_2	1	1	1	-1	-1	J_z
B_1	Γ_3	1	1	-1	1	-1	x^2-y^2
B_2	Γ_4	1	1	-1	-1	1	xy
E	Γ_5	2	-2	0	0	0	$(x,y),(xz,yz),(J_x,J_y)$

P4mm
P4
Pmm2
Cmm2
Pm
C
m
P1

from the possible isotropy subgroups,
identify possible active irrep with the known k-vector

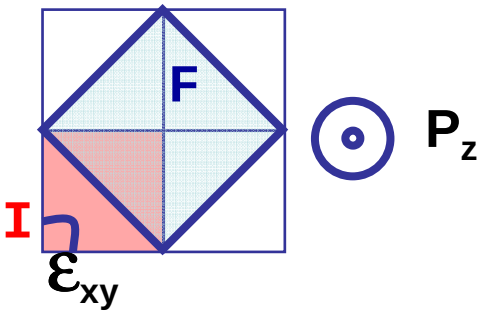
via computer:
COPL (isotropy)
SYMMODES (Bilbao server) --- as by-product
AMPLIMODES (Bilbao server) --- as by product

Pseudo-proper ferroic properties: the case of ferroelectric KDP

I4-2d → Fdd2 **(42m ------ mm2)**

No cell multiplication

(order parameter **q**=0)



Character Table

D_{2d}(-42m)	#	1	2	-4	2_x	m_d	functions
Mult.	-	1	1	2	2	2	·
A_1	Γ_1	1	1	1	1	1	x^2+y^2,z^2
A_2	Γ_2	1	1	1	-1	-1	J_z
B_1	Γ_3	1	1	-1	1	-1	x^2-y^2
B_2	Γ_4	1	1	-1	-1	1	z,xy
E	Γ_5	2	-2	0	0	0	(x,y),(xz,yz),(J_x,J_y)

faintness index n=1

$\varepsilon_{xy} \sim P_z$

two possibilities:

bilinear coupling: $P_z\ \varepsilon_{xy}$

P_z order parameter – ε_{xy} secondary

Proper ferroelect. –pseudo proper ferroelast.

P_z secondary – ε_{xy} order parameter

Pseudo-proper ferroelect. – proper ferroelast.

Ferroic states/domains: (P_z , ε_{xy}), (-P_z , -ε_{xy})

….A stress can change sign of the polarization
…An electric field can change sign of the strain

$P6_3/mmc \rightarrow P6_3cm$ (a+2b, -2a-b,c; 0 0 0)

active irrep?

case 3:

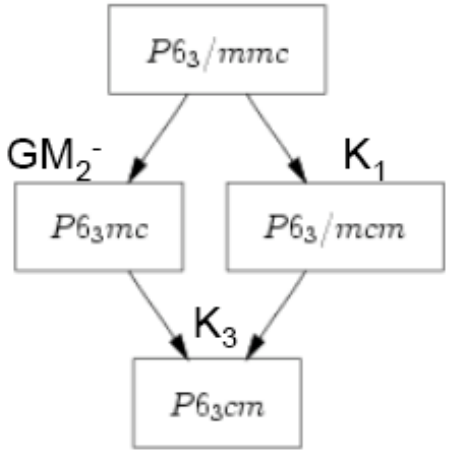
from COPL:

```
COPL, Version 1.0, August 2001
Written by Harold T. Stokes and Dorian M. Hatch
Brigham Young University

Parent: 194 D6h-4, P6_3/mmc, P6_3/m2/m2/c
Subgroup: 185 C6v-3, P6_3cm, P6_3cm
Lattice vectors:
1 2 0
-2 -1 0
0 0 1
origin: 0 0 0

Irrep Dir     Subgroup       Size
GM1+  (a)     194 P6_3/mmc     1
GM2-  (a)     186 P6_3mc       1
K1    (a,0)   193 P6_3/mcm     3
K3    (a,0)   185 P6_3cm       3
```

secondary irreps/modes

active irrep

from SYMMODES and SUBGROUPGRAPH (Bilbao server):



spontaneous crystal tensor quantities that transform according to GM2-: Polarization along z

→ Improper ferroelectric

coupling of secondary variables/modes with order parameter (faintness index)? : program INVARIANTS (Isotropy)

case 3: $P6_322$ → $P2_1$ (c,-a-2b,a; 3/4 0 3/4)

active irrep?

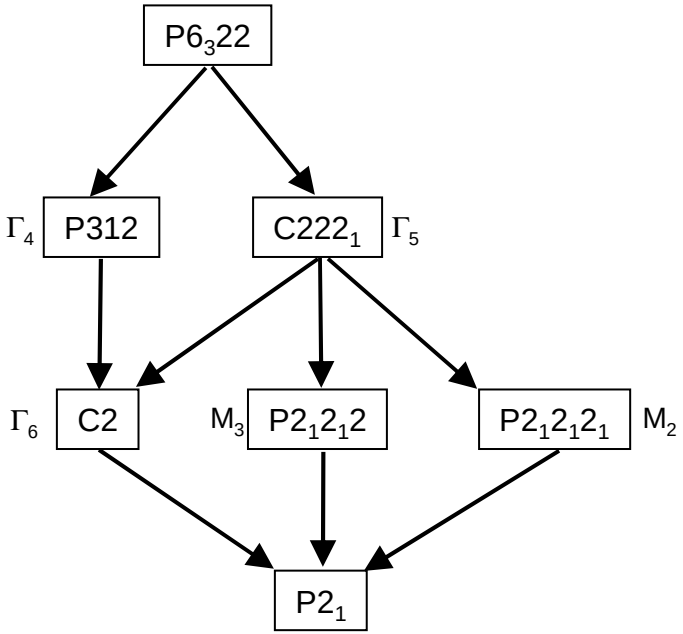
F is not an isotropy subgroup: two active irreps are necessary ....

```
COPL, Version 1.0, August 2001
Written by Harold T. Stokes and Dorian M. Hatch
Brigham Young University

Parent: 182 D6-6, P6_322, P6_322
Subgroup:   4 C2-2, P2_1, P12_11, unique axis b
Lattice vectors:
0 0 1
-1 -2 0
1 0 0
origin: 3/4 0 3/4

Irrep Dir          Subgroup          Size
GM1   (a)          182 P6_322          1
GM4   (a)          149 P312            1
GM5   (a,1.732a)    20 C222_1          1
GM6   (a,1.732a)     5 C2              1
M2    (0,0,a)       19 P2_12_12_1      2
M3    (0,0,a)       18 P2_12_12        2
```

$P2_1$ is not an isotropy subgroup: more than one active irrep necessary.

probable intermediate phase !

from SYMMODES and SUBGROUPGRAPH (Bilbao server):



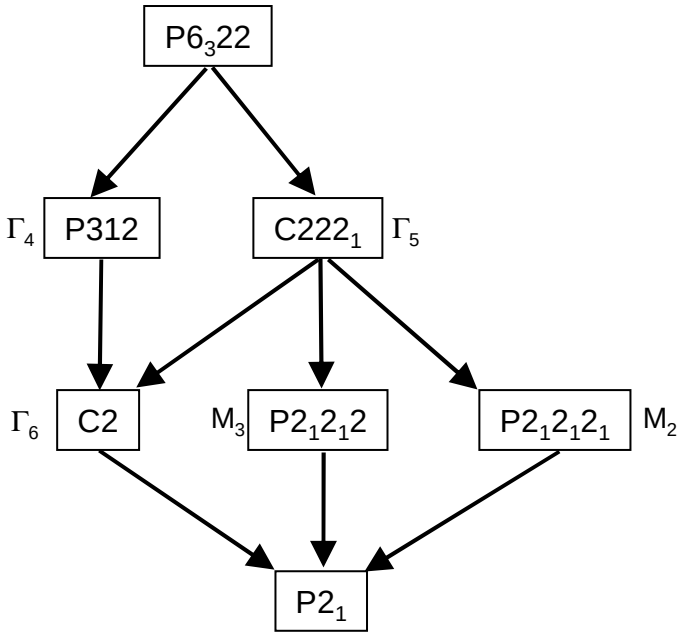
In this case, two active irreps are necessary. which ones?

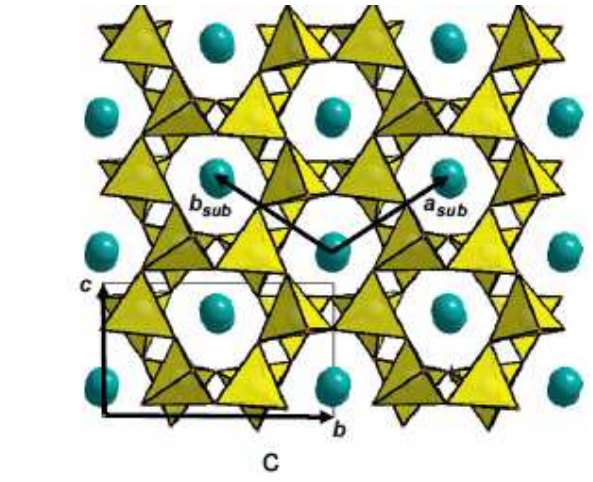
GM6: responsible of polarization along the monoclinic axis: it can be a primary or secondary effect. Only experiment or simulations can tell.

2 order parameters : Pseudo-proper ferroelasticity of $SrAl_2O_4$

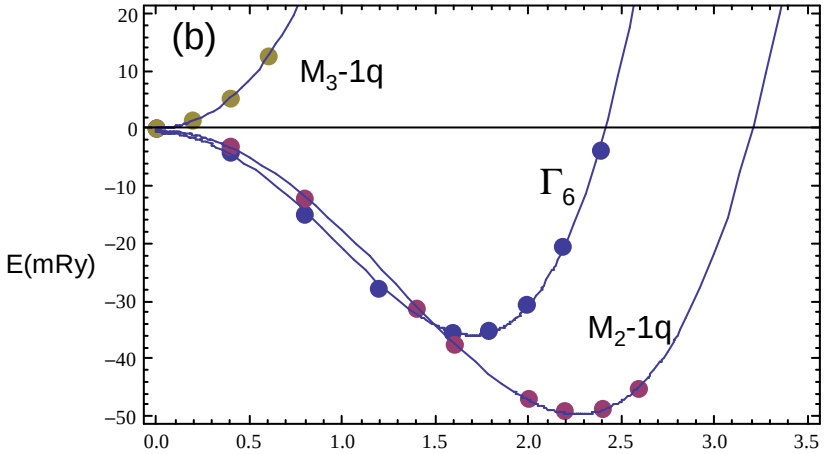
(Larsson et al. 2008)

$P6_322 \longrightarrow P2_1$

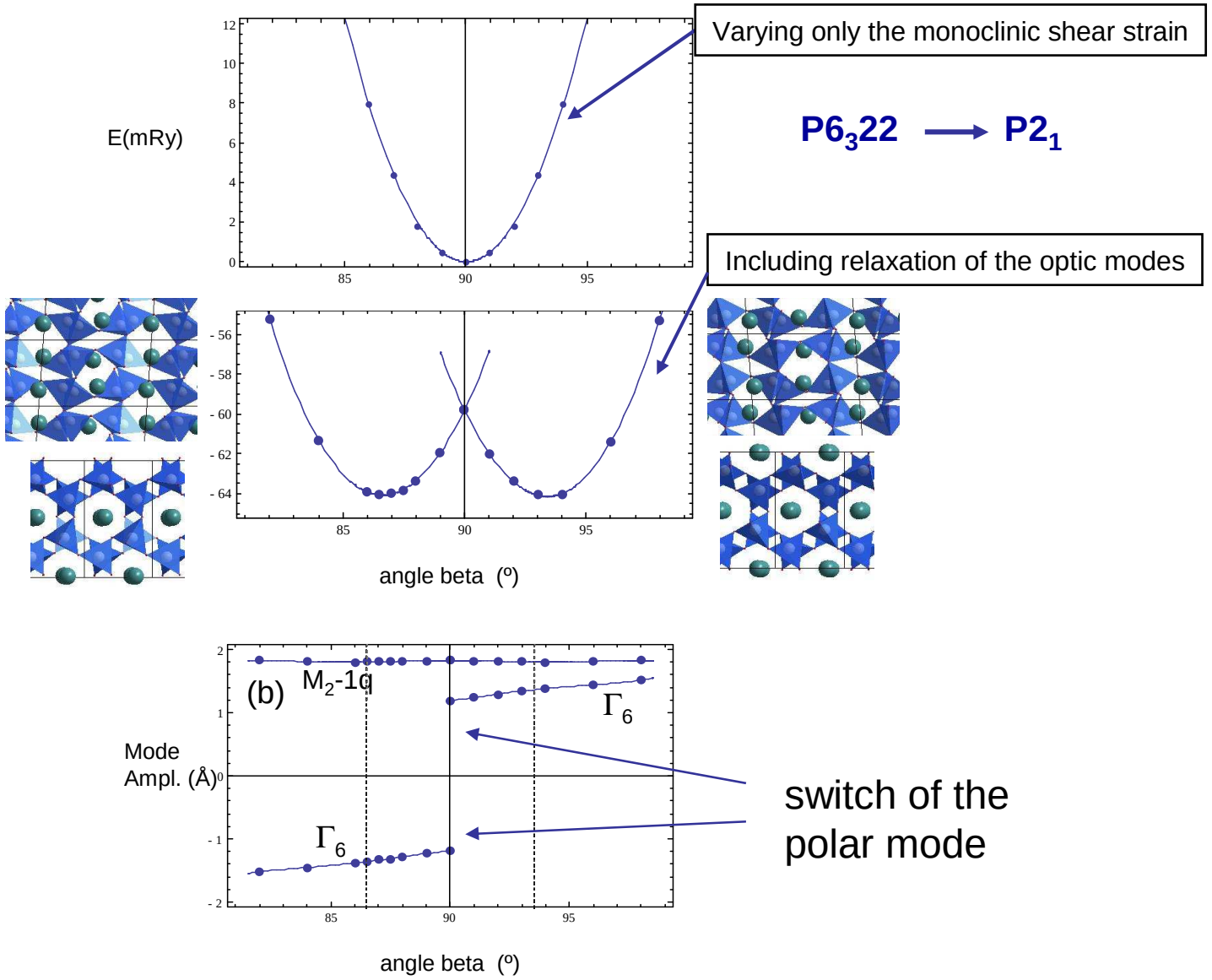




two unstable irrep distortions:



Pseudo-proper ferroelasticity of $SrAl_2O_4$ seen in ab-initio calculations



A practical guide:

case 4: We know the symmetry break and active irrep and want to derive further "consequences".

- spontaneous ferroic (switchable) quantities – only ferroic species needed

POINT COSETS

- primary and secondary spontaneous degrees of freedom/modes: transition mechanism.

COPL (Isotropy) SYMMODES

- separation of structural parameters into collective modes with very different weigth in the distorted structure.

ISODISPLACE (Isotropy) AMPLIMODES Amplimodes+ FullProf= direct struct. refinement

- temperature/pressure dependence of variables/modes: Landau analysis

INVARIANTS (isotropy)

- Domain structure: orientational relations, domain walls, domain related equivalent structures

COSETS NORMALIZER