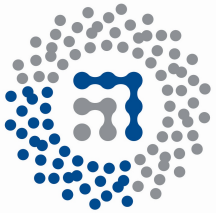

ZTF-FCT
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eman ta zabal zazu

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Symmetry Aspects of Structural Phase Transitions (II)

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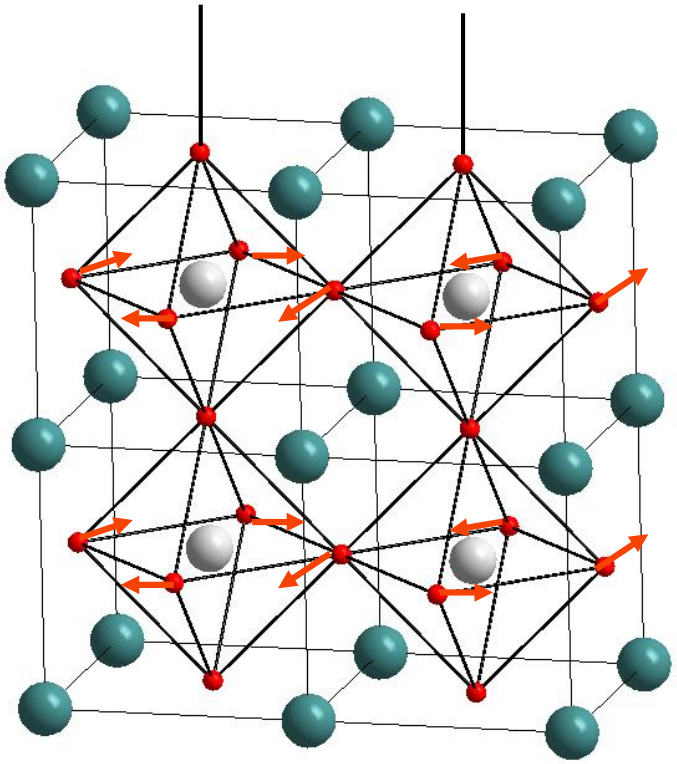


tilting of octahedra

$SrTiO_3$

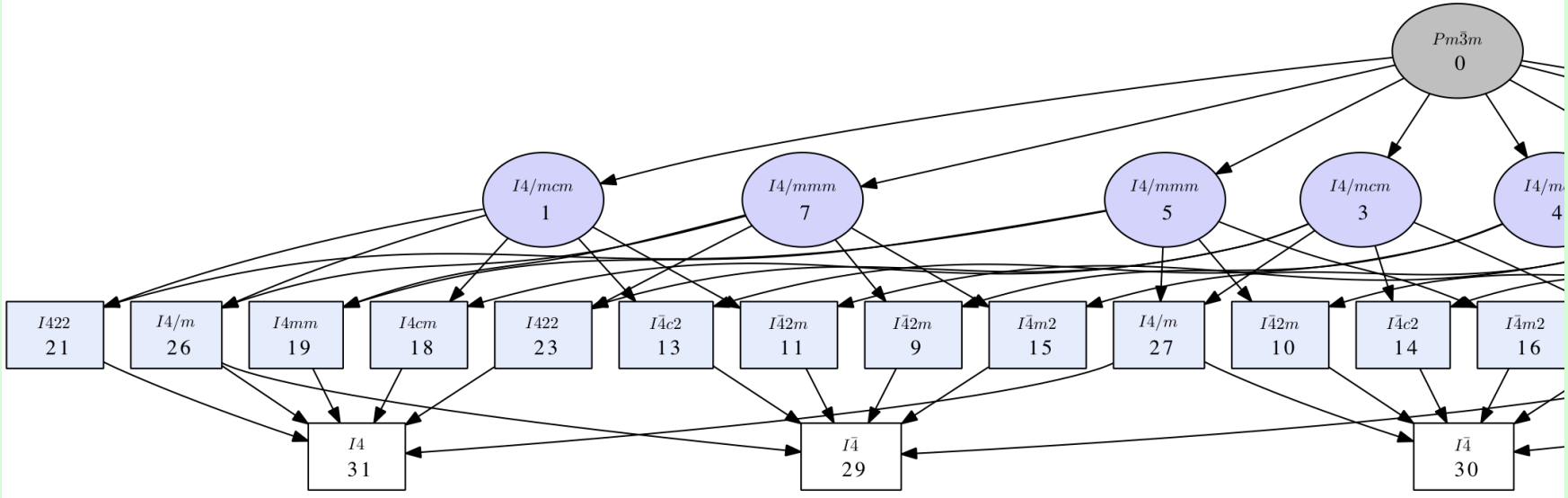
Pm-3m --- I4/mcm (**a**+**b**, -**a**+**b**,2**c**;1/2,1/2,1/2)

	index(i_k x i_p)	N. domains	N. twins
I4/mcm	2 x 3	6	3

$SrTiO_3$

Pm-3m --- tetragonal, centered I and supercell (a+b, -a+b, 2c)

Possible space groups ? Let us apply program SUBGROUPS….



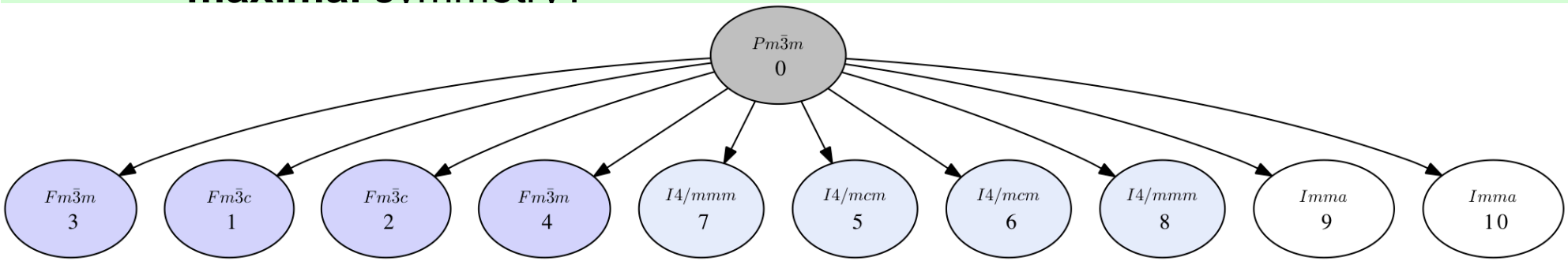
(example 2 in the Tutorial of SUBGROUPS)

$SrTiO_3$ *As in many other cases, the symmetry is maximal for the supercell observed…*

Pm-3m --- tetragonal, centered I and supercell (a+b, -a+b,2c)

Possible space groups of **maximal** symmetry?

Apply program SUBGROUPS….



There are four different tetragonal space groups of maximal symmetry, two of them of type I4/mcm:

N	Group Symbol	Transformation matrix	Group-Subgroup index	Symmetry operations	Set of subgroups*
5.1	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	6=2x3		
5.2	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 1 & -1 & 0 & 0 \end{pmatrix}$	6=2x3		

N	Group Symbol	Transformation matrix	Group-Subgroup index	Symmetry operations	Set of subgroups*
6.1	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups
6.2	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \\ 1 & -1 & 0 & 1/2 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups

$SrTiO_3$

Pm-3m --- tetragonal, centered I and supercell (a+b, -a+b,2c)

Which subgroup
of type I4/mcm is
the one realized in $SrTiO_3$?

Let us use Structure Relations….

N	Group Symbol	Transformation matrix	Group-Subgroup index	Symmetry operations	Set of subgroups*
5.1	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups
5.2	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & \\ 1 & -1 & 0 & \end{pmatrix}$		Plain text format	List of subgroups

N	Group Symbol	Transformation matrix	Group-Subgroup index	Symmetry operations	Set of subgroups*
6.1	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups
6.2	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \\ 1 & -1 & 0 & 1/2 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups

or use PSEUDO…. same results?

$SrTiO_3$

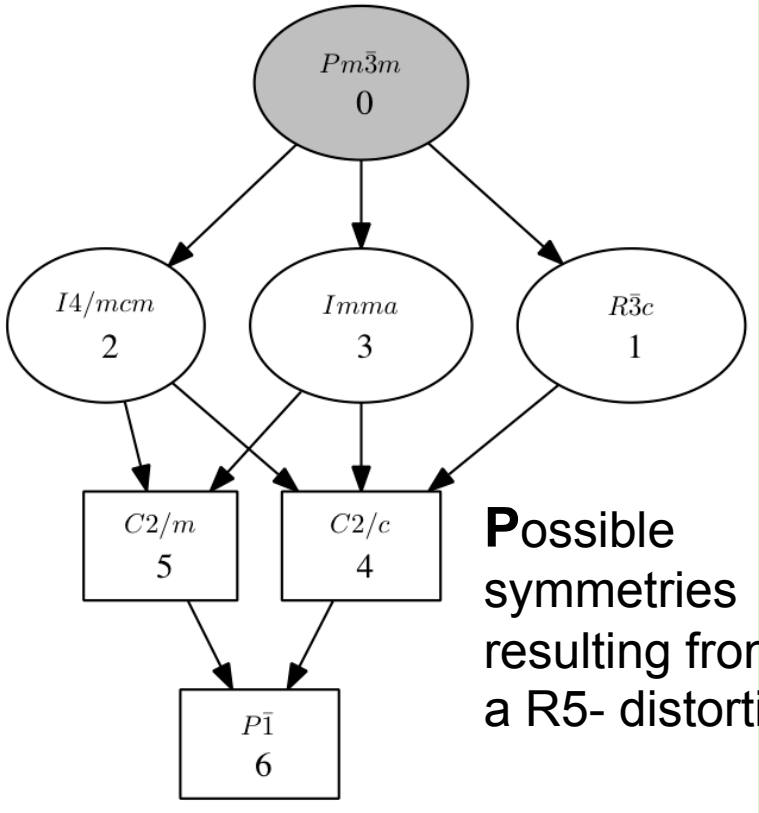
Pm-3m → tetragonal, centered I and supercell (a+b, -a+b,2c; 1/2,1/2,1/2)

N	Group Symbol	Transformation matrix	Group-Subgroup index	Symmetry operations	Set of subgroups*
6.1	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups
6.2	*I4/mcm* (#140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \\ 1 & -1 & 0 & 1/2 \end{pmatrix}$	6=2x3	Plain text format Matrix form	List of subgroups Graph of subgroups

Active irrep?
use link to Get_irreps in SUBGROUPS output:
R5- with **k=**(1/2,1/2,1/2)

Other possible symmetries for the same active irrep R5-?

Use SUBGROUPS in its option where the input can be a k-vector
instead of a supercell and filtered for the irrep R5-



Possible symmetries resulting from a R5- distortion

G ⟶ ?

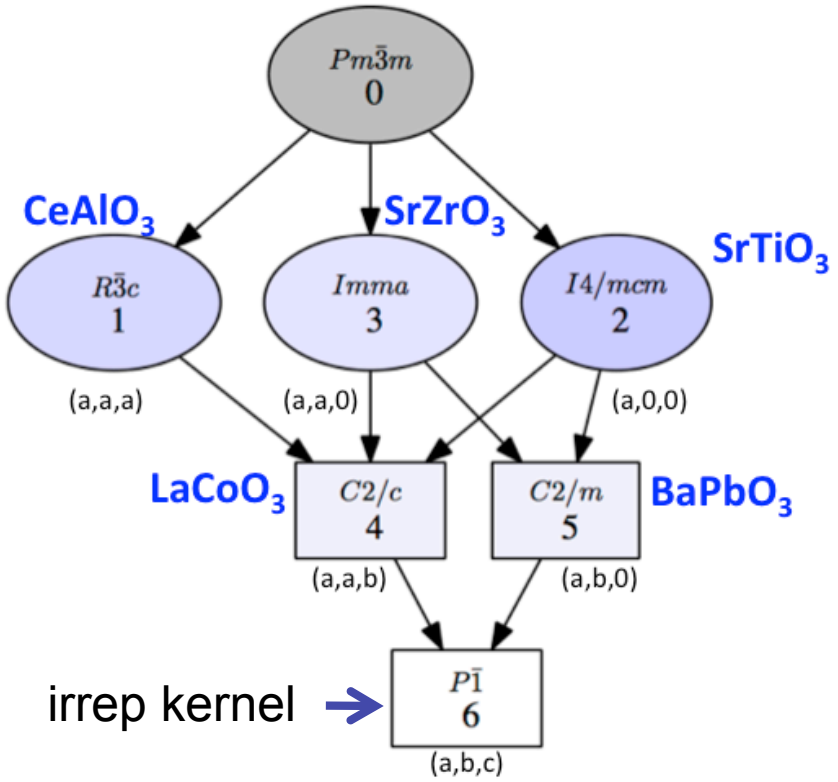
possible isotropy subgroups for a given active irrep?

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 R5-:

isotropy subgroups of R

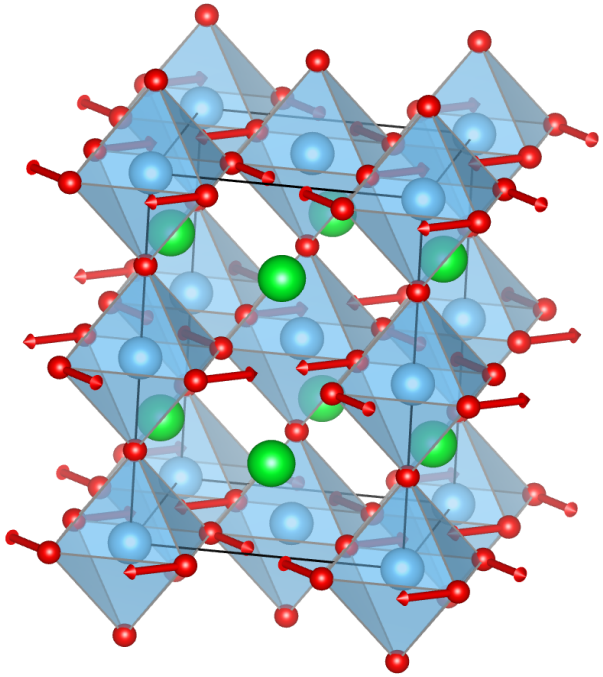
irrep epikernels



irrep kernel ⟶

Phases resulting from different combinations of R5- modes (different OP directions)

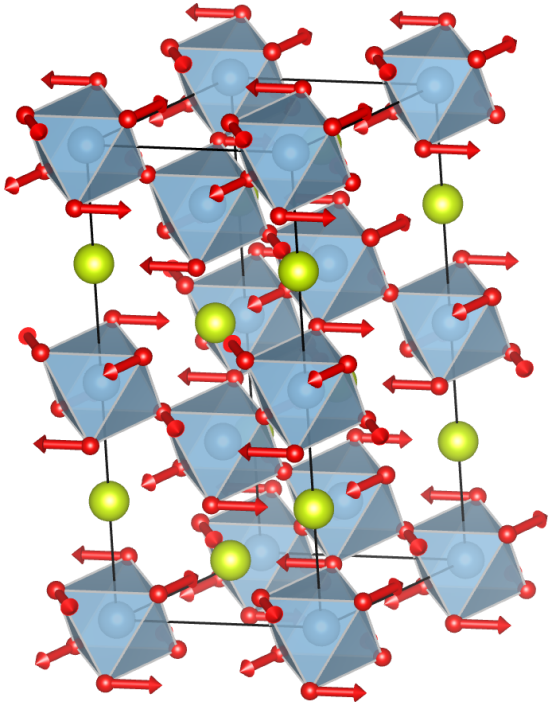
$SrTiO_3$



I4/mcm (a+b,-a+b,2c;1/2,1/2,1/2)

OP direction: (a,0,0)

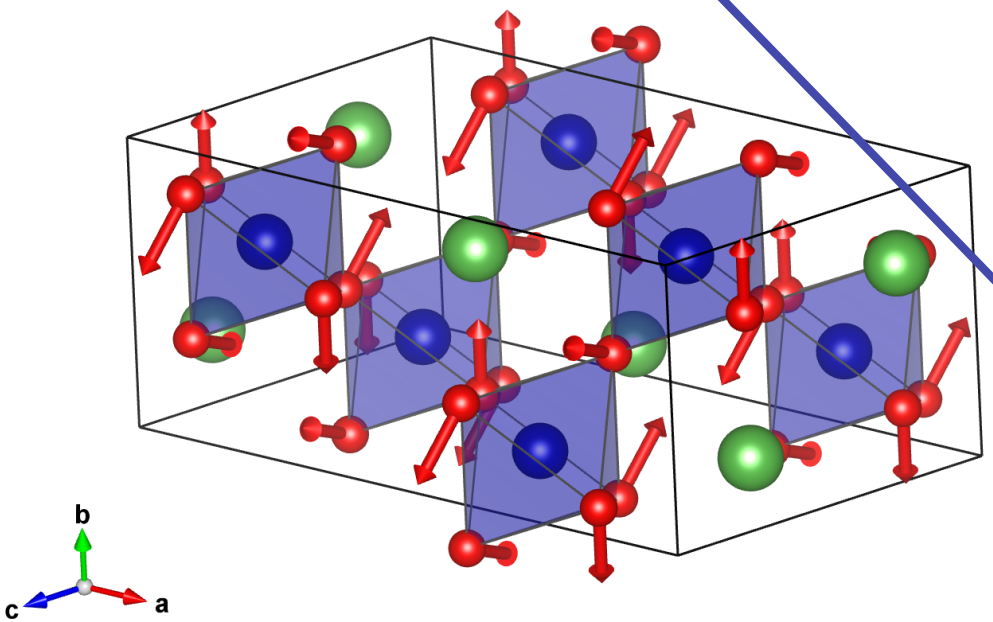
$CeAlO_3$



R-3c (a-c,-a+b,2a+2b+2c;1/2,1/2,1/2)

OP direction: (a,a,a)

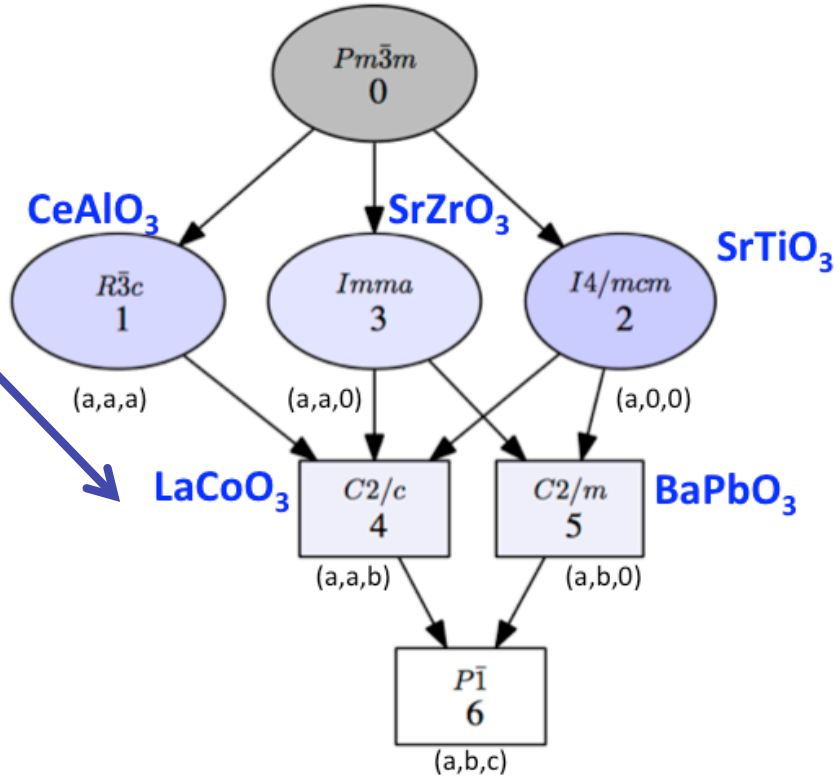
$LaCoO_3$



C2/c (a+2b+c,a-c,a+c;1/2,0,0)

OP direction: (a,a,b)

isotropy subgroups of irrep R5- (irrep epikernels and kernels)



let us obtain a starting structural model of LaCoO3 with TRANSTRU…

Consequences of symmetry

Von Neumann principle:

- all variables/parameters/degrees of freedom compatible with the symmetry will be present in the total distortion

- Tensor crystal properties are constrained by the point group symmetry of the crystal
  (some coefficients can be forced to be identically cero).

- Reversely: any tensor property allowed by the point group symmetry can exist (large or small, but it is not forced to be cero)

Origin of ferroic properties: multistability

Ferroic structure:

"distorted" structure with respect to a configuration

with a higher **point group** symmetry

Ferroic domains:

equivalent crystal tensors with different orientations

related by lost point group operations

Ferroic properties:

require the symmetry break of the point-group

symmetry between distorted and undistorted configurations

FERROIC SPECIES:

The characterization of the ferroic properties requires to know the two point group symmetries: the one of the ferroic structure, and also of the related high-symmetry configuration.

EXAMPLE: mmmFmm2

Some examples of ferroic species and corresponding switchable spontaneous crystal tensor quantities

mmmFmm2

strain $\begin{matrix}\varepsilon_1 & 0 & 0\\ 0 & \varepsilon_2 & 0\\ 0 & 0 & \varepsilon_3\end{matrix}$ $\begin{matrix}\varepsilon_1 & 0 & 0\\ 0 & \varepsilon_2 & 0\\ 0 & 0 & \varepsilon_3\end{matrix}$

polariz. **(0,0,0)** **(0,0,P_z)**

ferroelect.

mmmF112/m

strain $\begin{matrix}\varepsilon_1 & 0 & 0\\ 0 & \varepsilon_2 & 0\\ 0 & 0 & \varepsilon_3\end{matrix}$ $\begin{matrix}\varepsilon_1 & \varepsilon_6 & 0\\ \varepsilon_6 & \varepsilon_2 & 0\\ 0 & 0 & \varepsilon_3\end{matrix}$

polariz. **(0,0,0)** **(0,0,0)**

ferroelastic

422F222

strain $\begin{matrix}\varepsilon_1 & 0 & 0\\ 0 & \varepsilon_1 & 0\\ 0 & 0 & \varepsilon_3\end{matrix}$ $\begin{matrix}\varepsilon_1 & 0 & 0\\ 0 & \varepsilon_2 & 0\\ 0 & 0 & \varepsilon_3\end{matrix}$ spont. strain: $\varepsilon_s = \varepsilon_1 - \varepsilon_2$

polariz. **(0,0,0)** **(0,0,0)**

ferroelastic

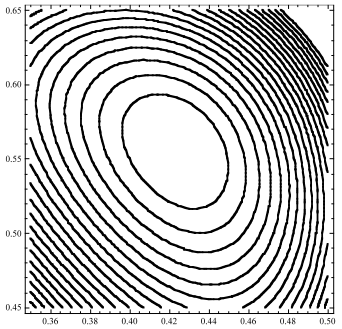
m-3mFR3m

strain $\begin{matrix}\varepsilon & 0 & 0\\ 0 & \varepsilon & 0\\ 0 & 0 & \varepsilon\end{matrix}$ $\begin{matrix}\varepsilon & \varepsilon_4 & \varepsilon_4\\ \varepsilon_4 & \varepsilon & \varepsilon_4\\ \varepsilon_4 & \varepsilon_4 & \varepsilon\end{matrix}$

polariz. **(0,0,0)** **(P,P,P)**

ferroelectric
and ferroelastic

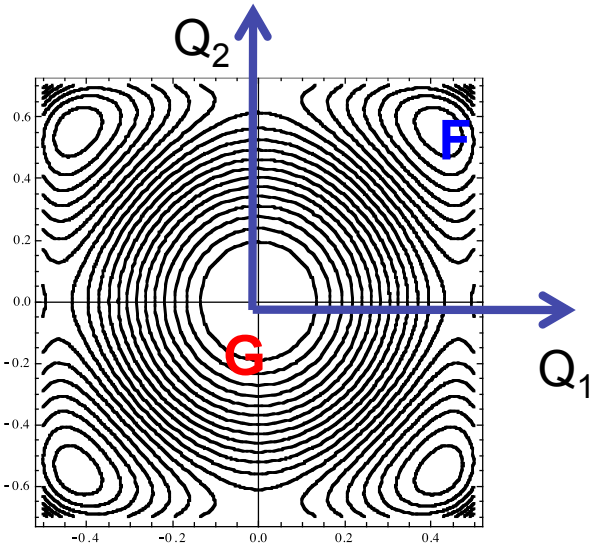
Not to confuse in a ferroic phase !:



- Linear response properties (giant or not!)

We need to know only the symmetry of the phase.

- switching properties (necessarily non-linear)



We need to know also the symmetry of the "parent" phase.

$$\mathbf{G = F + g_3F + g_3F + ... + g_sF}$$

$$\mathbf{g_n}(Q_1 \ldots \mid Q^{(s)}{}_1 \ldots.)$$

Multistability: enumeration of distinct domains:

G → F

We need to know the irrep of the order parameter

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

$$\textbf{Number of distinct equivalent states} = \frac{\textbf{Order of G}}{\textbf{Order of F}}$$

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

$$\textbf{Number of distinct ferroic states} = \frac{\textbf{Order of } P_G}{\textbf{Order of } P_F}$$

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

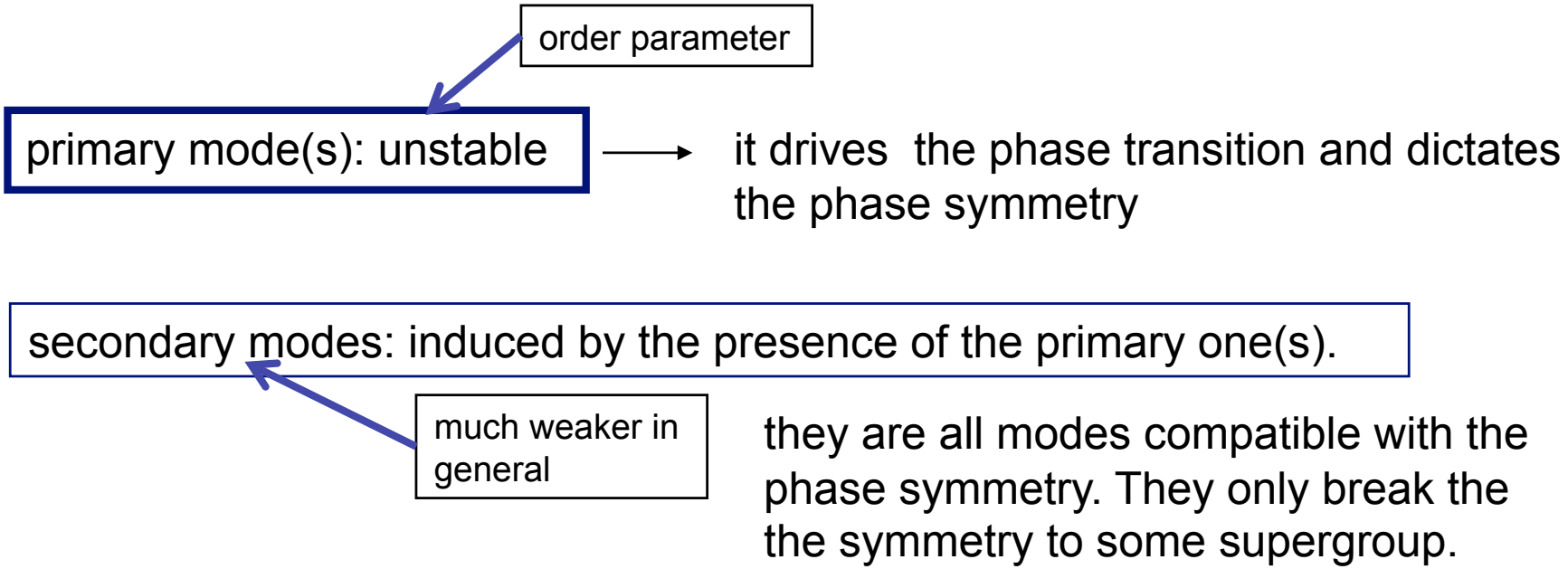
1) pair of points groups: (P_G, P_F) (Ferroic species)

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

Hierarchy of distortion modes:

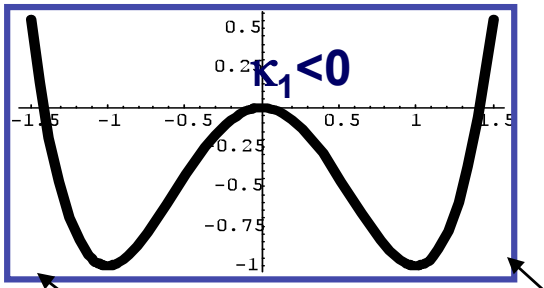
Von Neumann principle:
all modes compatible with the symmetry will be present in the total distortion ….

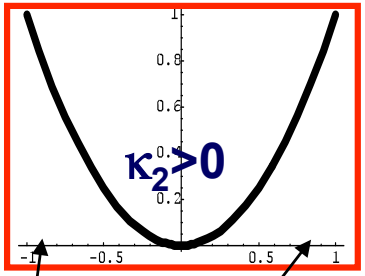
But not all with the same weight !:



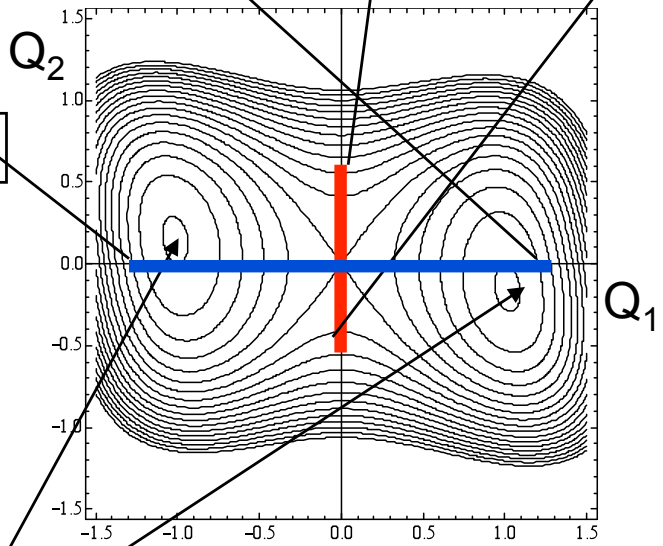
secondary distortion modes are in general not unstable!

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

Equivalent ferroic states

Coset decomposition for a symmetry break with respect to a parent phase of symmetry G:

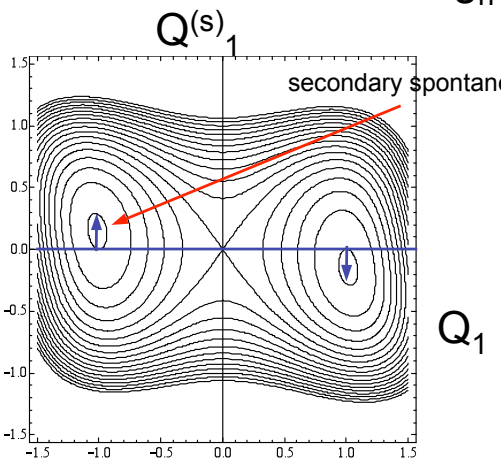
$$G = F + g_3F + g_3F + \ldots + g_sF$$

In general a ferroic state (domain) is given by the values of all spontaneous quantities:

order parameter(s) secondary spontaneous parameters

$$(Q_1,\ldots,Q_m \mid Q^{(s)}{}_1,\ldots,Q^{(s)}{}_{ms})$$

$$g_n \longrightarrow g_n(Q_1,\ldots,Q_m \mid Q^{(s)}{}_1,\ldots,Q^{(s)}{}_{ms})$$



$$g_n(Q_1 \ldots \mid Q^{(s)}{}_1 \ldots.) = (-Q_1 \ldots \mid -Q^{(s)}{}_1 \ldots.)$$

(point groups)

$$\text{Number of macroscopically distinct ferroic states} = \text{index} = \frac{\text{Order of } P_G}{\text{Order of } P_F}$$

Switching a secondary small parameter will produce
in this case the switching of the large primary one …..

Exercise 1 (Example 2 of tutorial of SUBGROUPS)

A structure has symmetry Pnma. At lower temperatures, a phase transition happens, and diffraction experiments show that superstructure reflections at points (h, k, l + 1/2) appear, indicating the duplication of the c parameter, while keeping an orthorhombic lattice.

(i). Assuming a group-subgroup related transition and using SUBGROUPS, predict the only two possible space groups of this low-temperature phase, and the transformation matrix relating it with the parent space group Pnma.

(ii). What is the wave vector associated with the order parameter of this transition?

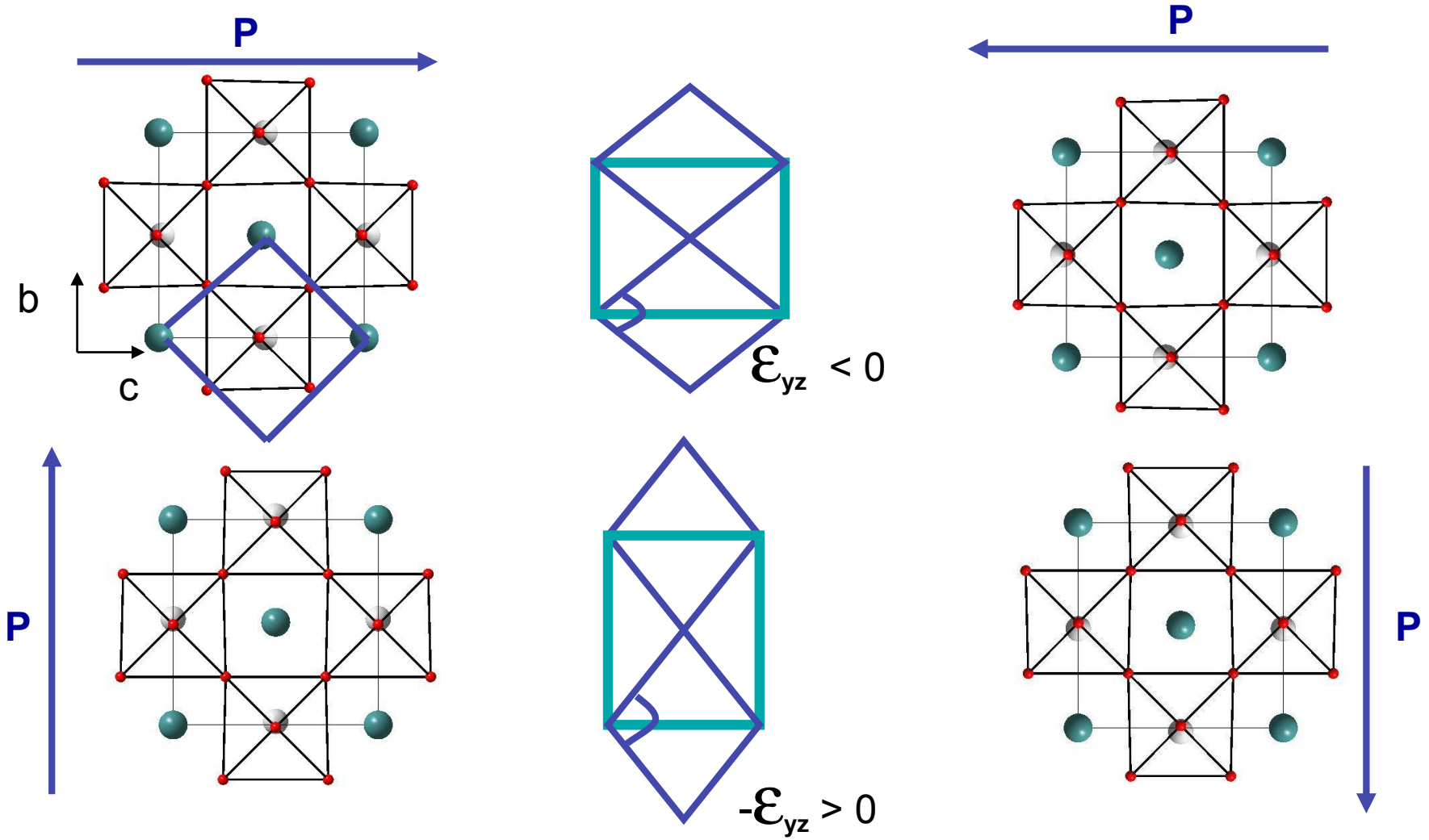
(iii) Using the Get_irreps link within SUBGROUPS determine if the space groups determined in (i) are isotropy subgroups of an irrep, and in each case, identify the label of the active primary irrep of the transition.

(iv) From the output of Get_irreps, in both cases identify the irrep associated with a secondary polar distortion mode.

(v) Determine using SUBGROUPS all the possibles symmetries that could happen in a phase transition with this wave vector, under the constraint that the Landau assumption is fulfilled (the order parameter transforms according to a single irrep).

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

Proper ferroelectric
Improper ferroelastic



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

Ferroic properties Amm2- $BaTiO_3$

Spontaneous quantities (with respect to cubic Pm-3m) in macroscopic tensors:

Polarization (ferroelectric) – proper (order parameter)
Strain (ferroelastic) – improper (not order parameter)

One can switch a secondary mode:

By means of an electric field, we switch a non-polar degree of freedom....

and viceversa.

General Rules of a phase transition with symmetry break

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

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

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

matrix irrep

$T[g]\,\vec{Q} = \vec{Q}$ $\longrightarrow$ g belongs to **F**

secondary spontaneous ferroic variables ("improper" ferroic properties):

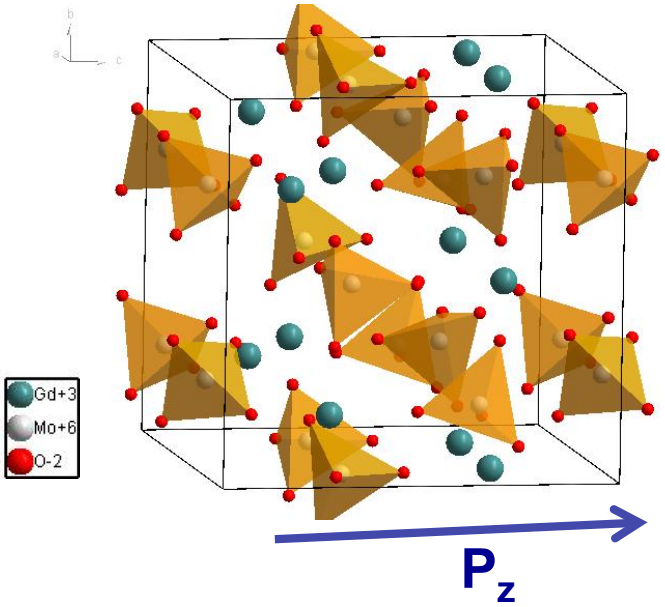
Polynomial of order n (faintness index)

$X \sim F^{(n)}[Q_1,\ldots,Q_n]$ 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 F

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

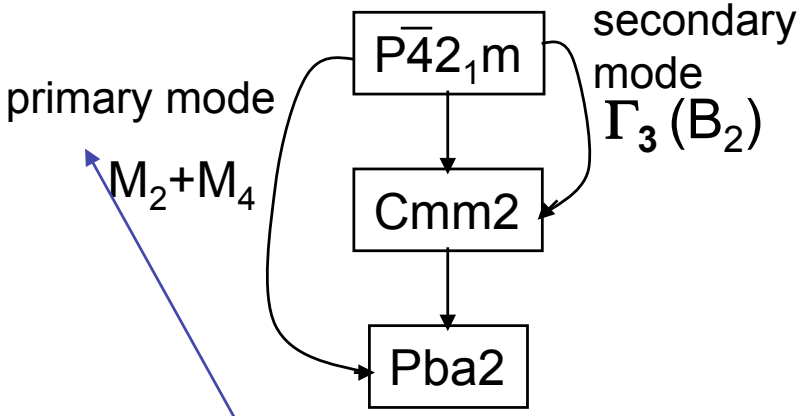


A Polar (ferroelectric) mode as a secondary mode

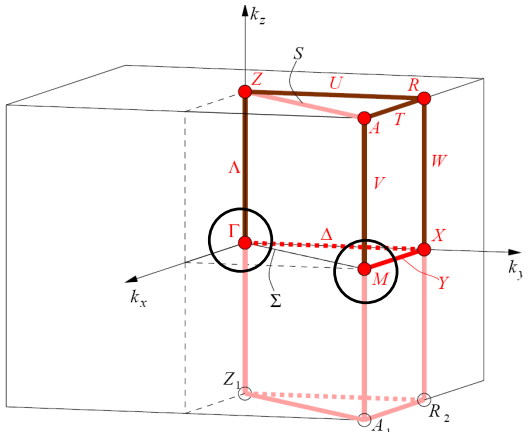
$P\bar{4}2_1m \xrightarrow{160\ C} Pba2$ **($\bar{4}$2m ------ mm2)**

(Z=2) (Z=4) cell duplication

polar mode/polarization



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



Q_{M2M4}= 1.6191 Å

$Q_{\Gamma3}$ = 0.0716 Å

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

Ferroelectric Domains in Amm2 $BaTiO_3$

(m-3m, mm2)

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

Amm2: Q(0,1/√2,1/√2)

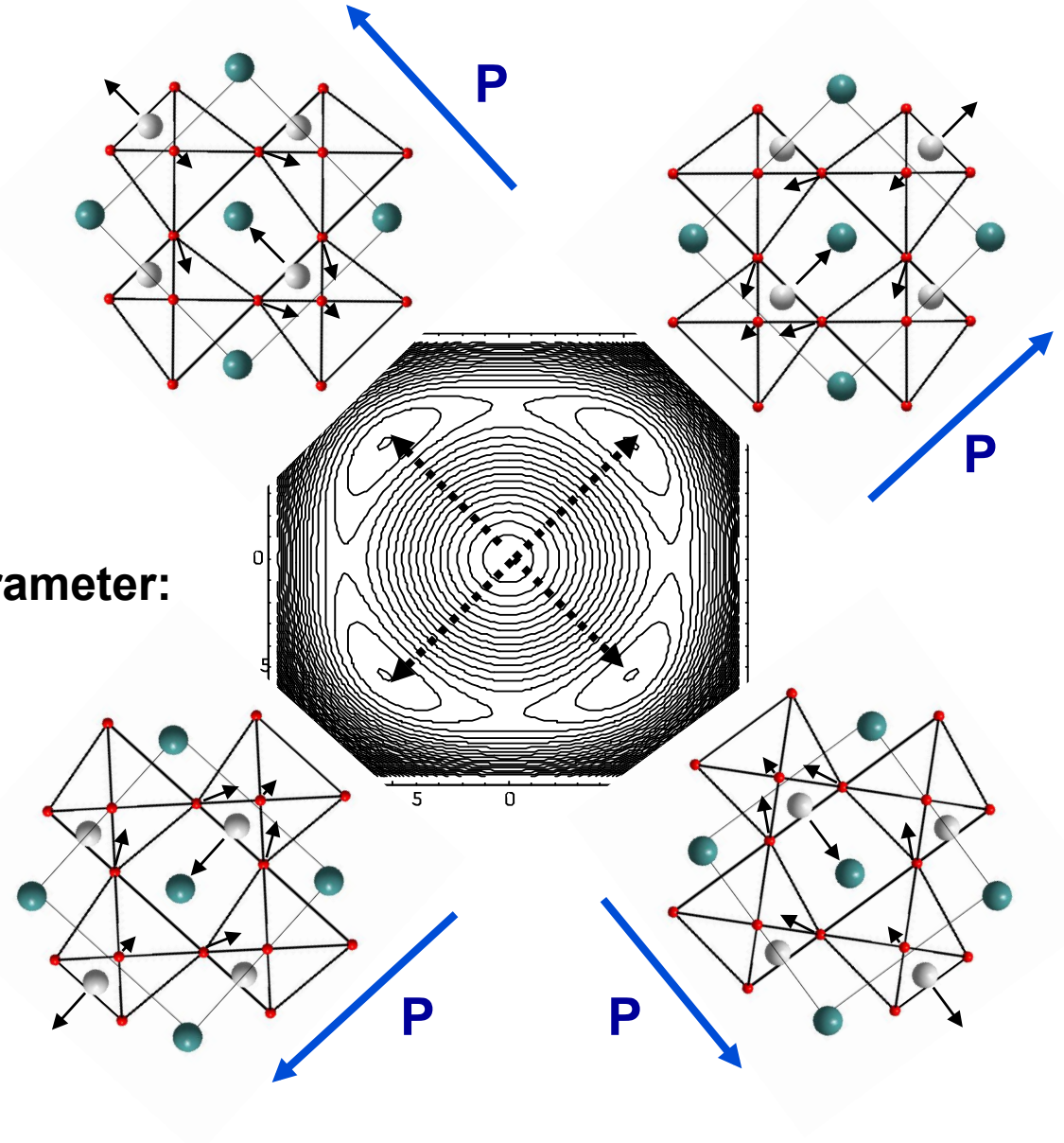
Order of m-3m = 48
Order of mm2 = 4

Number of domains = 48/4=12

12 eq. directions for the order parameter:

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

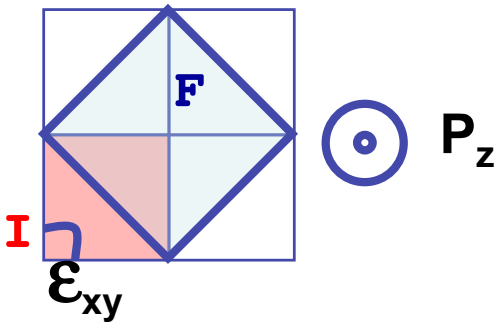


Pseudo-proper ferroic properties: the case of ferroelectric KDP

I-42d → Fdd2 **(-42m ------ mm2)**

No cell multiplication

(order parameter **k**=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

CONCLUSION:

SYMMETRY CONSIDERATIONS ARE NOT ONLY USEFUL, BUT NECESSARY FOR A FULL CHARACTERIZATION OF STRUCTURAL PHASE TRANSITIONS

EPILOGUE:

NOWADAYS THERE ARE FREE COMPUTER TOOLS THAT MAKE THIS TASK RATHER STRAIGHTFORWARD

INCOMMENSURATE MODULATED STRUCTURES HAVE ALSO SYMMETRY (and a point group)