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# Symmetry Aspects of Structural Phase Transitions (I)

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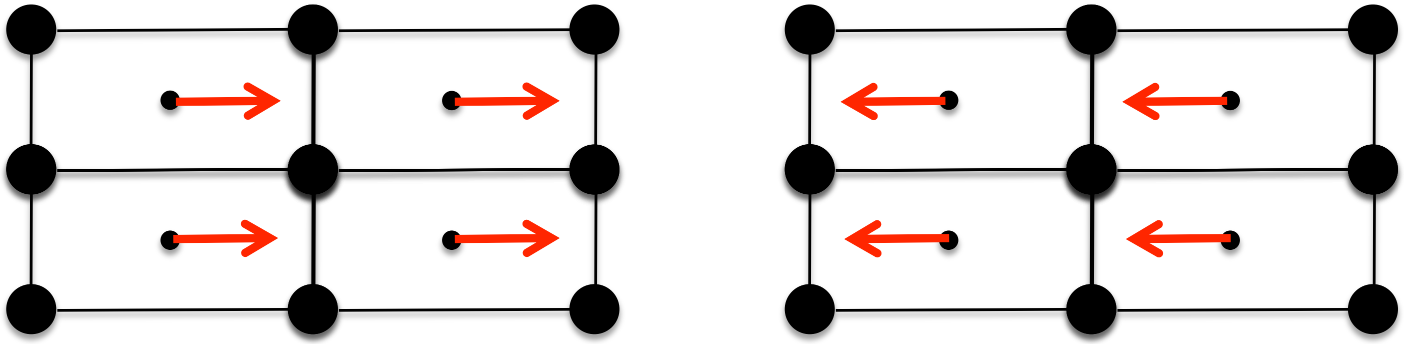
## Prologue:

we all use symmetry arguments... without mathematics



same energy for the two distortions....

## Prologue:

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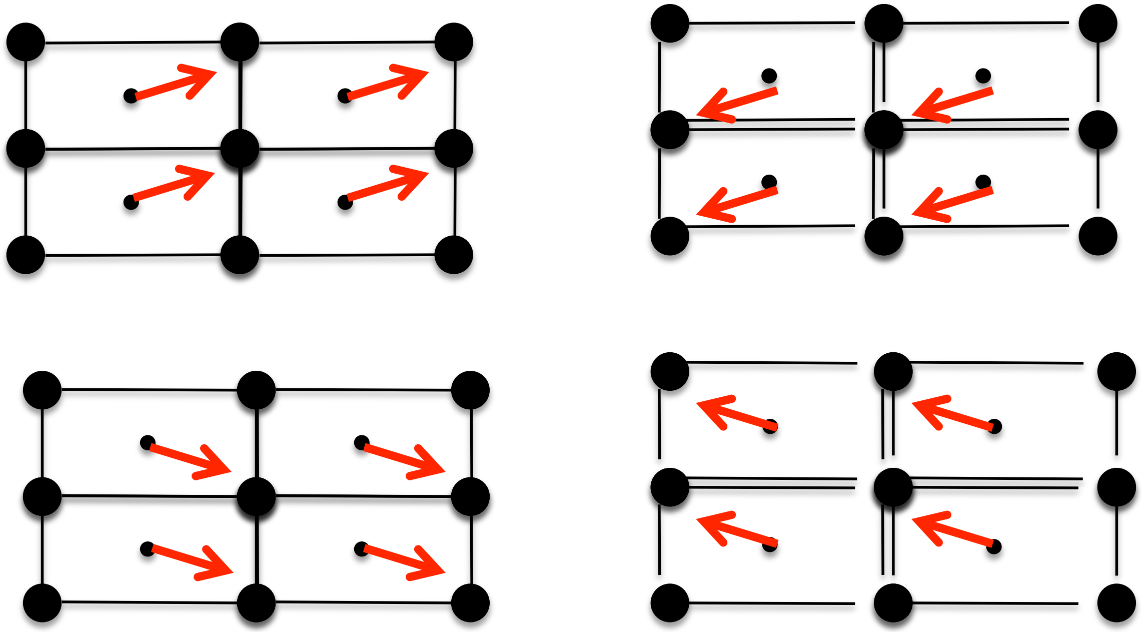
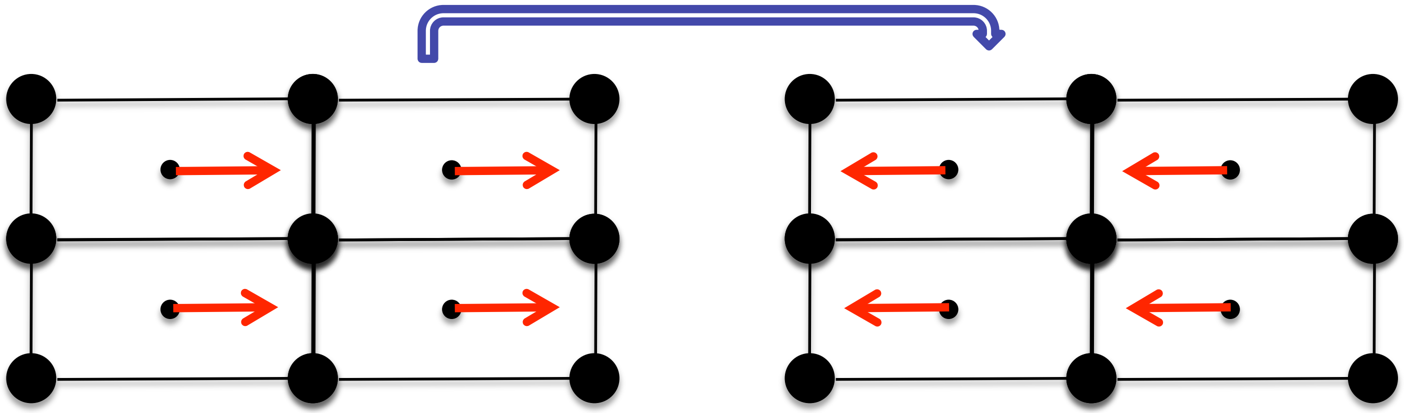


same energy for the four distortions ....

# Prologue:

## the "mathematics" behind ...



transformation by "lost" symmetry operation

**same energy for the two distortions...**

In fact, half of the symmetry operations have been lost and all of them transform from one structure into the other:

**Symmetry break**

symmetry group without distortion $G \rightarrow F'$ symmetry group with the distortion (a subset of G)

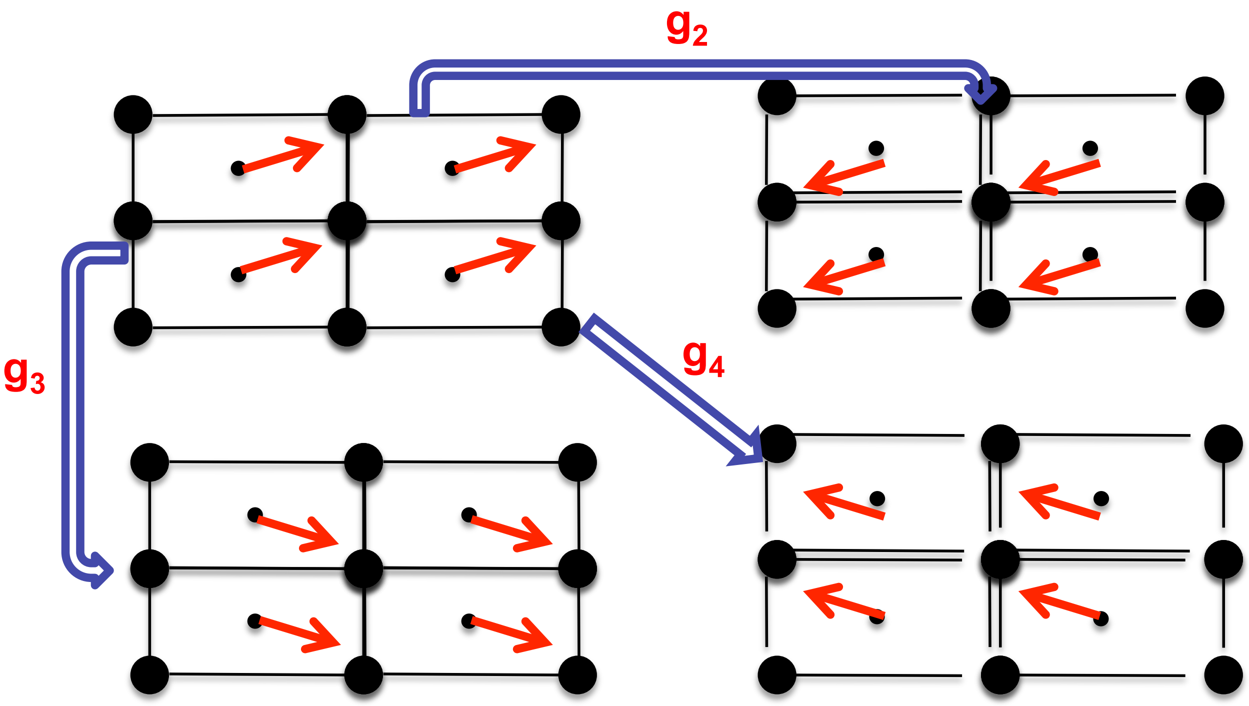
**coset decomposition:** $G = F' + g_2F'$

$$\frac{\text{order of } G}{\text{order of } F'} = \text{index} = 2$$

F' has half the number of operations of G: 2 equivalent configurations

# Prologue:

## the "mathematics" behind ...



same energy for the four distortions ....

**Symmetry break**

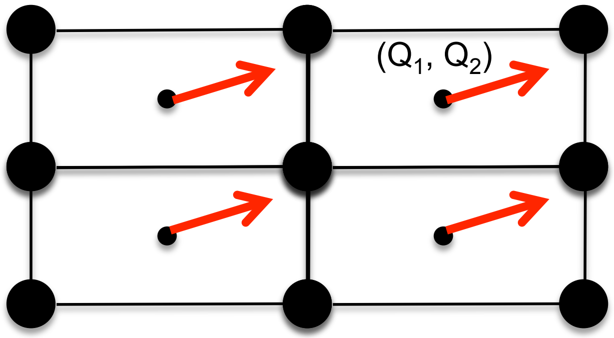
$G \rightarrow F$

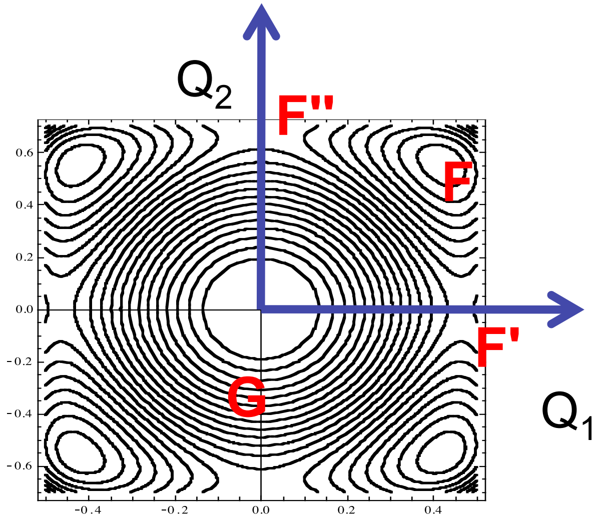
**coset decomposition:** $G = F + g_2F + g_3F + g_4F$

$\frac{\text{order of G}}{\text{order of F}}$ = index= 4

F has one fourth of the operations of G: 4 equivalent configurations

# The energy map:





- Multistability depending on the symmetry break:
  energetically equivalent configurations/domains – switching properties
- Energy is extremal (maximum or minimum for symmetry breaking distortions)
- Taylor expansion of the energy (restricted by symmetry) :

invariants for all symmetry operations of G

$$\mathbf{E = Eo + ½\ \kappa_1 Q_1^2 + ½\ \kappa_2 Q_2^2 + \beta_1 Q_1^4 + \beta_2 Q_2^4 + \gamma Q_1^2 Q_2^2 + ....}$$

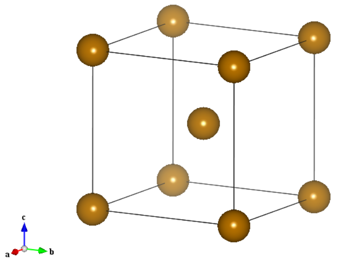
# Symmetry and Physics

## Symmetry break → Phase Transition

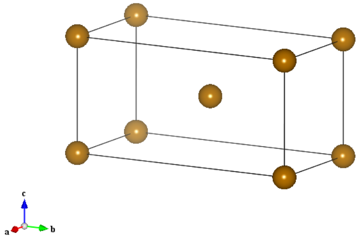
A symmetry property in a solid is NOT ONLY a certain geometric or transformation condition!

A well defined symmetry operation in a thermodynamic system must be maintained when scalar fields (temperature, pressure,…) are changed, except if a phase transition takes place.

The break of a symmetry condition (without external fields) **necessarily implies** a thermodynamic phase transition.



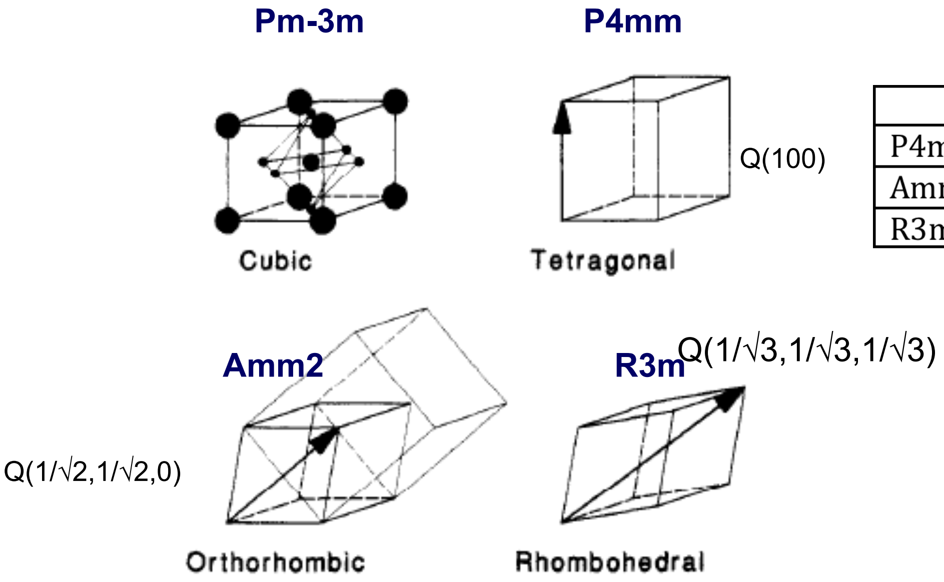
a=b=c symmetry property



a = c
b = 2a

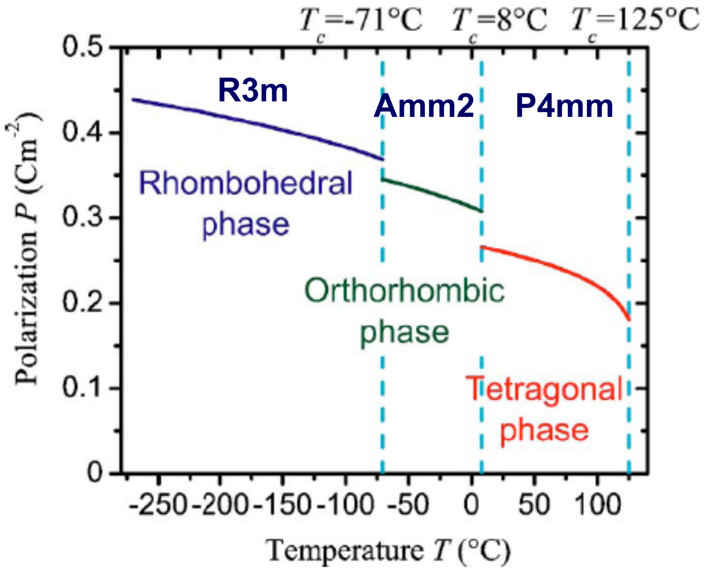
"nice" but not a symmetry property

# Example: The orthorhombic Amm2 structure of $BaTiO_3$

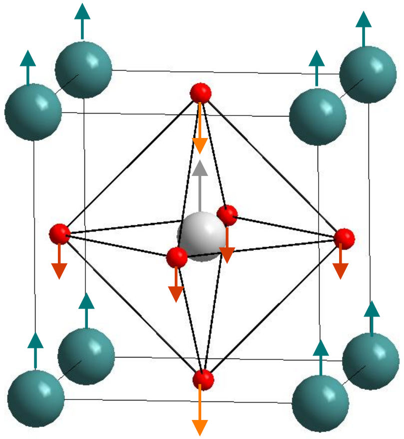


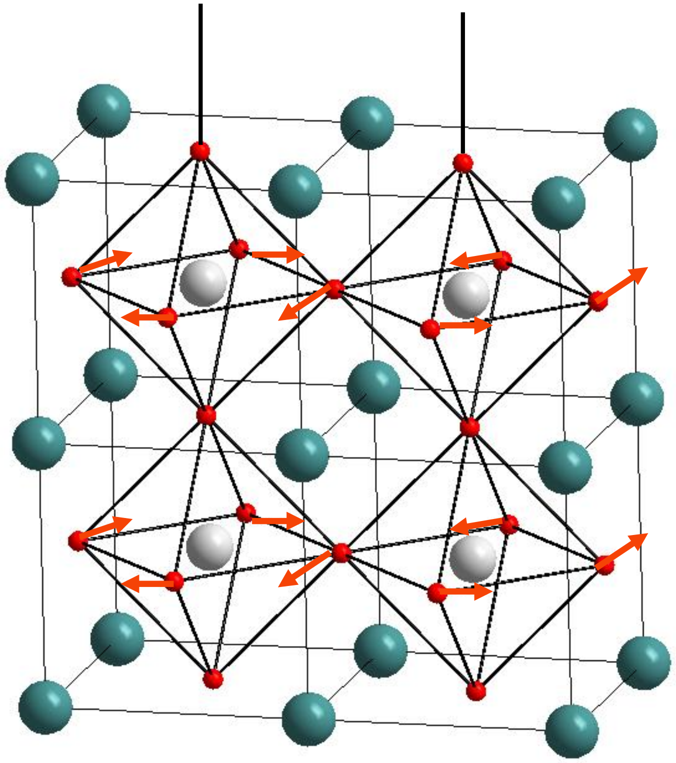
number of domains:

| | index($i_k$ x $i_p$) | N. domains | N. twins |
|---|---|---|---|
| P4mm | 1 x 6 | 6 | 6 |
| Amm2 | 1 x 12 | 12 | 12 |
| R3m | 1 x 8 | 8 | 8 |



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





tilting of octahedra

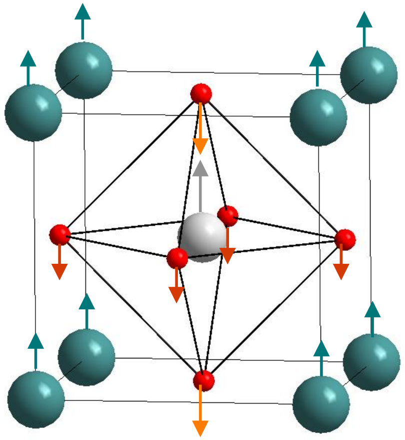
# $\mathbf{SrTiO_3}$

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

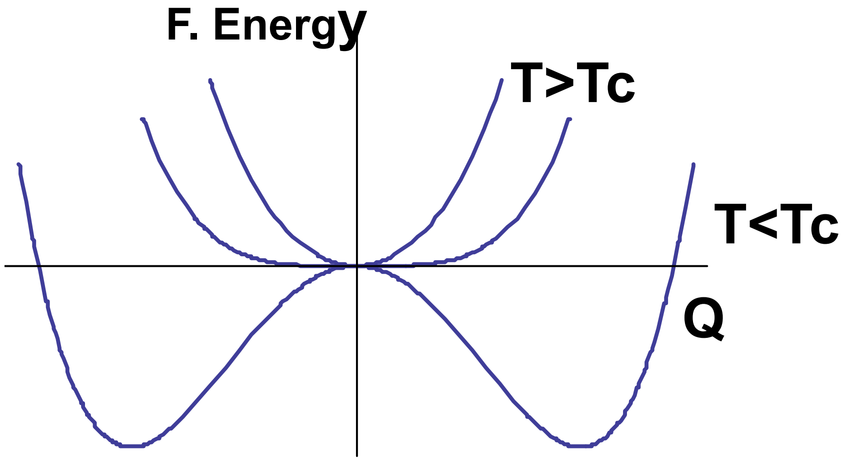
| | index($i_k$ x $i_p$) | N. domains | N. twins |
|---|---|---|---|
| I4/mcm | 2 x 3 | 6 | 3 |

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

**Amplitude(s) of primary distortion mode : order parameter**



Unstable collective degree of freedom:



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

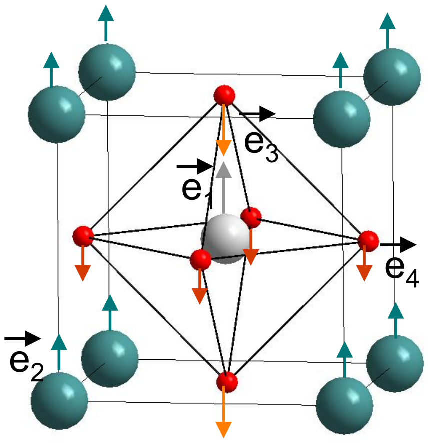
$$\kappa(T)<0 \quad T < Tc$$

**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 phase:

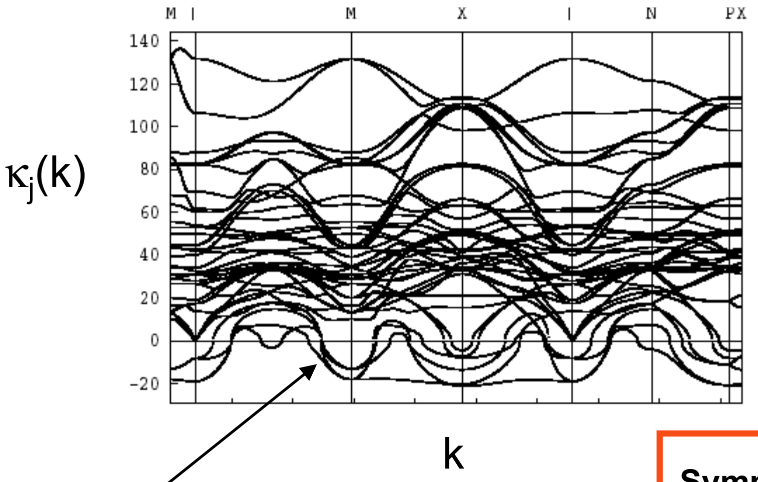
**(Free) Energy around the high-symmetry non-distorted configuration:**

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

stiffness coefficients

Normal (static) coordinates

Ab-initio calculation of static normal modes in the high-symmetry configuration



$\kappa_j(k)<0$

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

Q

$\kappa<0$

E

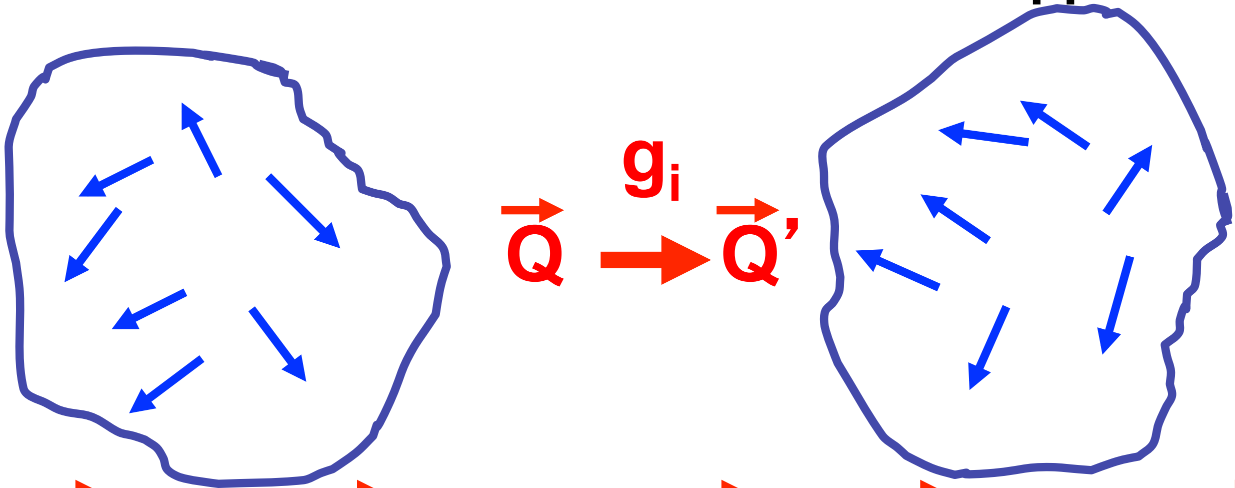
**Symmetry of distortion modes: irreducible representations (group theory)**

# Phase Transition / Symmetry break / Order Parameter

**High symmetry group $G_o = \{g_i\}$**

Key concept of a symmetry break: order parameter

**Distortion in the structure** **Distortion after application of $g_i$**



$$\vec{Q} \xrightarrow{g_i} \vec{Q}'$$

$$\vec{Q} = Q_1\vec{e}_1+\ldots+Q_n\vec{e}_n \qquad \vec{Q}' = Q'_1\vec{e}_1+\ldots+Q'_n\vec{e}_n$$

Irreducible representation of G (irrep) (matrices)

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

**T(g)** : one nxn matrix for each operation g of **G**

**distortions: Vectors in a multidimensional space**

# Modes and irreducible representations (irreps)

High symmetry group $G = \{g\}$ $F < G$

$$u(\text{atoms}) = \sum Q_i\, e_i \xrightarrow{g} u'(\text{atoms}) = \sum Q'_i\, e_i$$

$$\vec{Q}=\{Q_1, Q_2,\ldots, Q_n\} \qquad \vec{Q'}=\{Q'_1, Q'_2,\ldots, Q'_n\}$$

Irreducible representation of G (irrep) (matrices)

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

$T(g)$ : nxn matrix

**distortions:** Vectors in a multidimensional space

Action of the operations of G = linear transformations (matrices- a repres. of G)

matrices of minimal dimension: irreducible representation of G

# Phase Transition / Symmetry break / Order Parameter

High 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

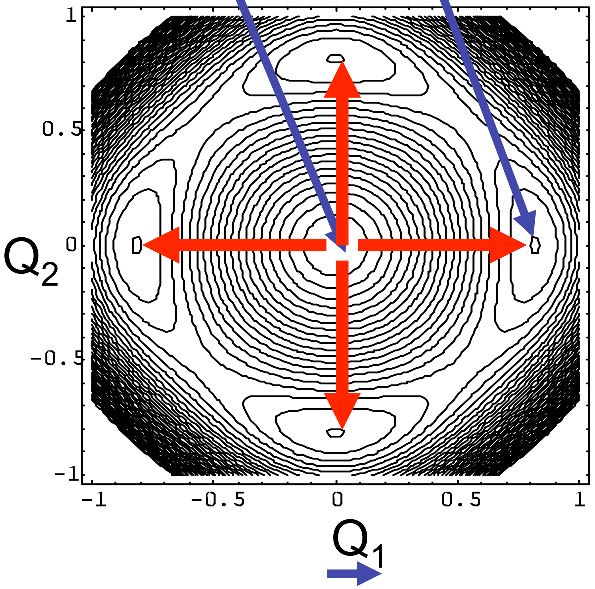
group-subgroup relation:

$\mathbf{G} \rightarrow \mathbf{F}$

**F: isotropy subgroup**

High symmetry

Low symmetry



Key concept of Landau theory:
It defines the type of symmetry break

**Order parameter** $\vec{\mathbf{Q}} = (Q_1,Q_2) = \rho\,(a_1,a_2)$

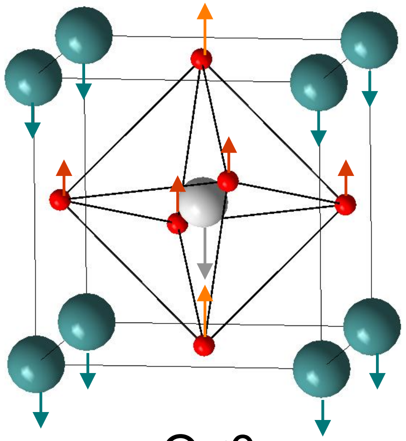
amplitude

$a_1^2+a_2^2 = 1$

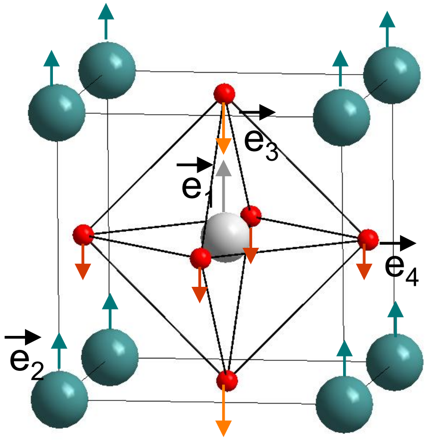
# Multistability:

**Energy**

**Q**

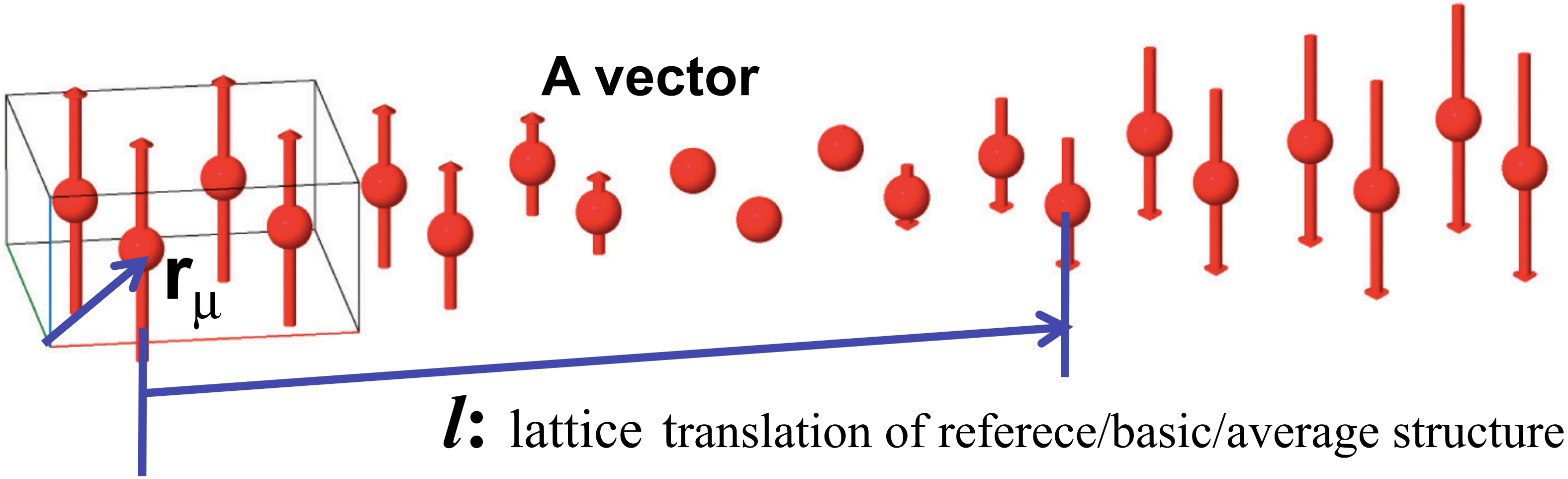


Q<0



Q >0

# distortion wave with wave vector k:



$\boldsymbol{l}$: lattice translation of referece/basic/average structure

**Harmonic Modulation with propagation vector k of "quantity" A of atom μ:**

$$A(\boldsymbol{l},\mu)= A_\mu\, e^{i2\pi \mathbf{k}.(\boldsymbol{l}+\mathbf{r}\mu)}+A^*_\mu\, e^{-i2\pi \mathbf{k}.(\boldsymbol{l}+\mathbf{r}\mu)}$$

If **k** = 0 or a reciprocal lattice vector **K** the distortion:

exp(**i**2π**K.*l***)= 1 for all lattice vectors ***l***: this means the lattice is conserved

a wave vector **k** and **k'** = **k+K** are equivalent

If **k** ≠ 0 and from a reciprocal lattice vector **K** the distortion:

if exp(**i**2π**k.*l***)= 1 ***l*** is conserved

if exp(**i**2π**k.*l***)≠ 1 ***l*** is lost

they form the lattice conserved by the distortion ( subgroup of the original lattice)

# Not all possible subgroups are equally probable in a distorted structure: isotropy subgroups (epikernels and kernel of a single irrep)

We want to know the possible symmetries of a distorted phase

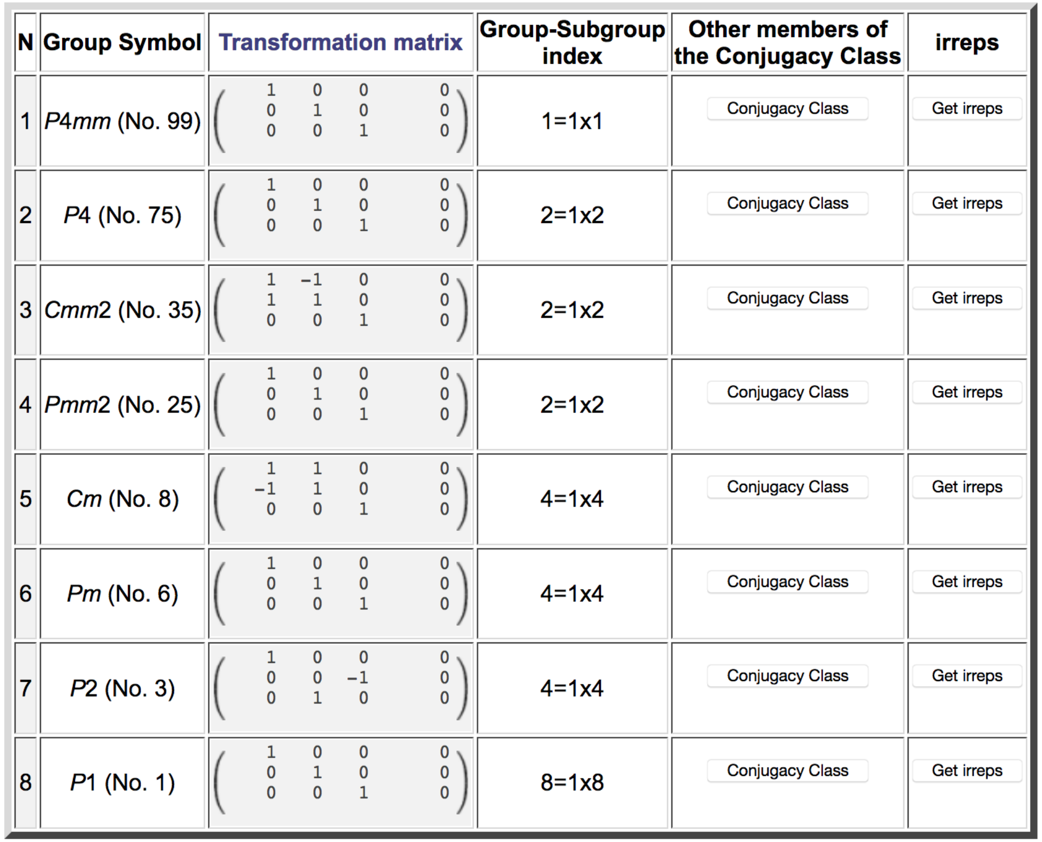
$$G \longrightarrow ?$$

**Example:** $P4mm \longrightarrow ?$ **k=0**

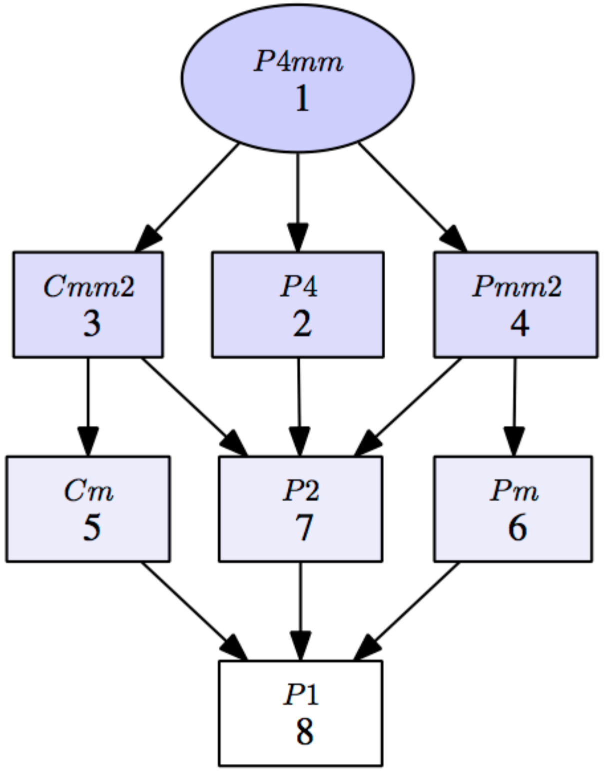
## *P4mm* → ? k=0

Use of program SUBGROUPS:

all subgroups for k=0:



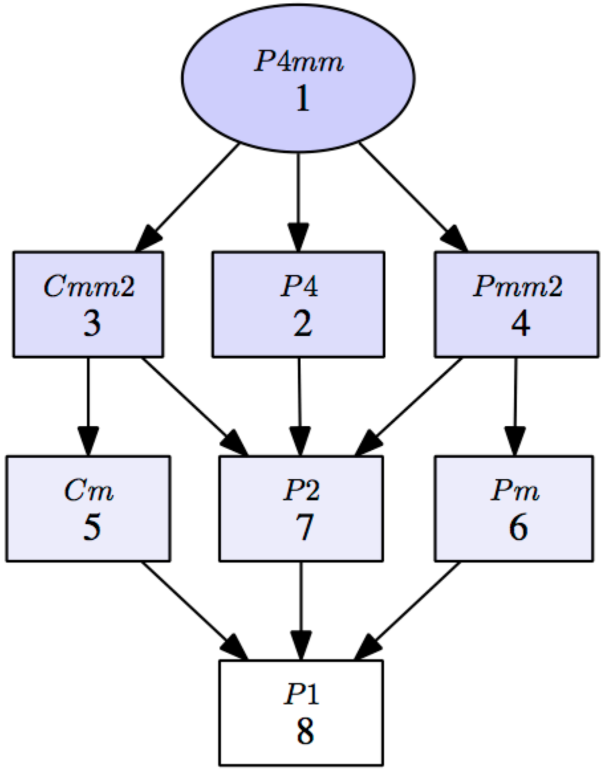
| N | Group Symbol | Transformation matrix | Group-Subgroup index | Other members of the Conjugacy Class | irreps |
|---|---|---|---|---|---|
| 1 | *P4mm* (No. 99) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 1=1x1 | Conjugacy Class | Get irreps |
| 2 | *P4* (No. 75) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 2=1x2 | Conjugacy Class | Get irreps |
| 3 | *Cmm2* (No. 35) | $\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 2=1x2 | Conjugacy Class | Get irreps |
| 4 | *Pmm2* (No. 25) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 2=1x2 | Conjugacy Class | Get irreps |
| 5 | *Cm* (No. 8) | $\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 4=1x4 | Conjugacy Class | Get irreps |
| 6 | *Pm* (No. 6) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 4=1x4 | Conjugacy Class | Get irreps |
| 7 | *P2* (No. 3) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$ | 4=1x4 | Conjugacy Class | Get irreps |
| 8 | *P1* (No. 1) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ | 8=1x8 | Conjugacy Class | Get irreps |



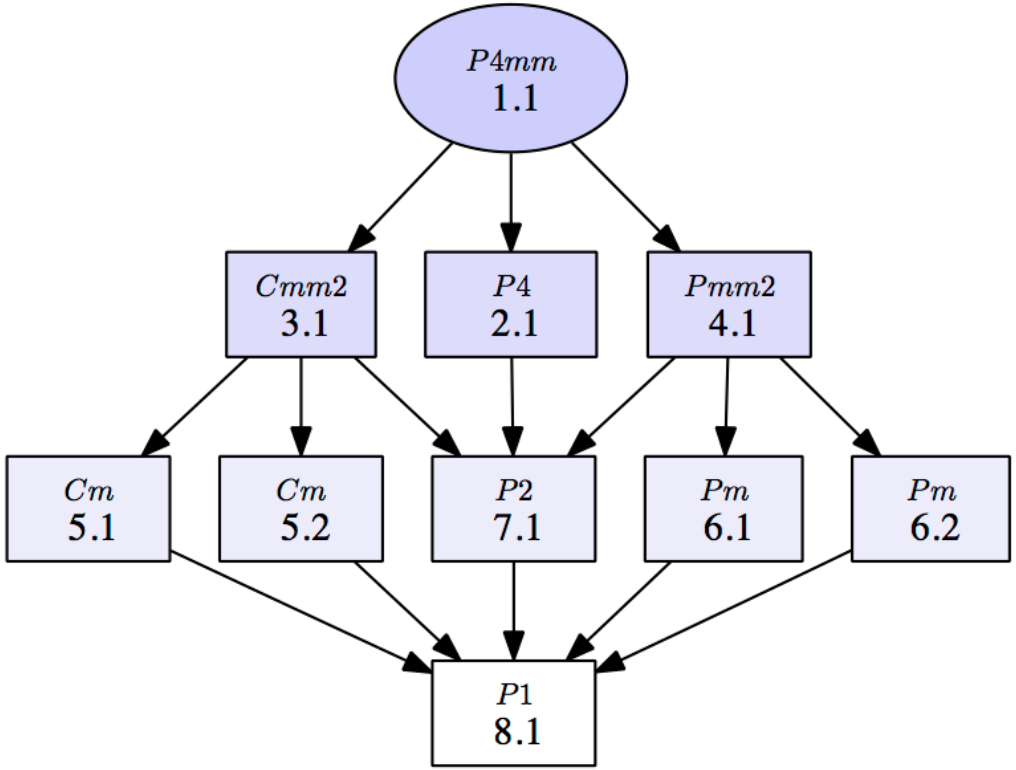
**_P4mm_ → ?** **k=0**

Use of program SUBGROUPS:

ALL subgroups (as conjugacy classes):



ALL distinct subgroups:



# Not all possible subgroups are equally probable in a distorted structure: isotropy subgroups (epikernels and kernel of a single irrep)

**We want to know the possible symmetries of a distorted phase**

$$G \longrightarrow ?$$

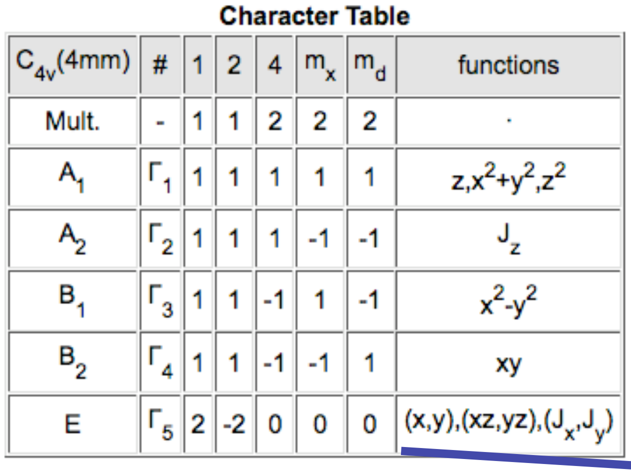
**k=0**

possible isotropy subgroups for a given active irrep?

**Example:**

$$P4mm \longrightarrow ?$$

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 | . |
| $A_1$ | $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | $z,x^2+y^2,z^2$ |
| $A_2$ | $\Gamma_2$ | 1 | 1 | 1 | -1 | -1 | $J_z$ |
| $B_1$ | $\Gamma_3$ | 1 | 1 | -1 | 1 | -1 | $x^2-y^2$ |
| $B_2$ | $\Gamma_4$ | 1 | 1 | -1 | -1 | 1 | $xy$ |
| E | $\Gamma_5$ | 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**

**Cm**

**P1**

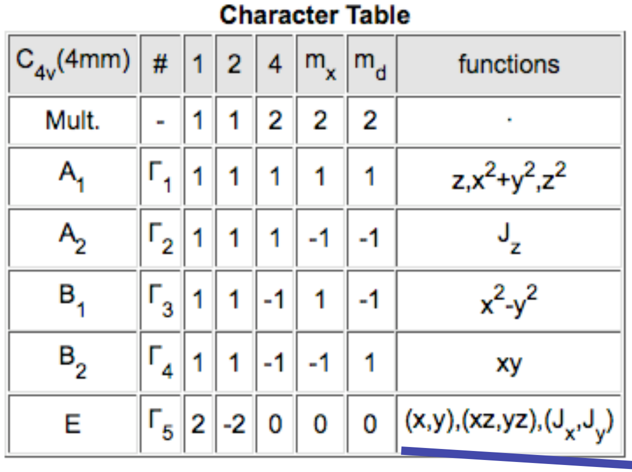
$T[g]\ Q=Q \qquad \{g\}=F$

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

**possible isotropy subgroups for a given active irrep?**

$P4mm \longrightarrow ?$

irreps of P4mm at k=0 ($\Gamma$ point)



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| $A_2$ | $\Gamma_2$ | 1 | 1 | 1 | -1 | -1 | $J_z$ |
| $B_1$ | $\Gamma_3$ | 1 | 1 | -1 | 1 | -1 | $x^2-y^2$ |
| $B_2$ | $\Gamma_4$ | 1 | 1 | -1 | -1 | 1 | xy |
| E | $\Gamma_5$ | 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**

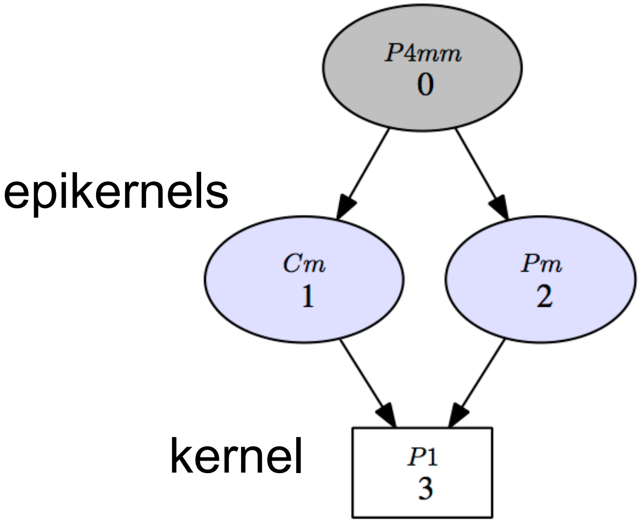
**Cm**

**P1**

$T[g]\,Q=Q \qquad \{g\}=F$

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

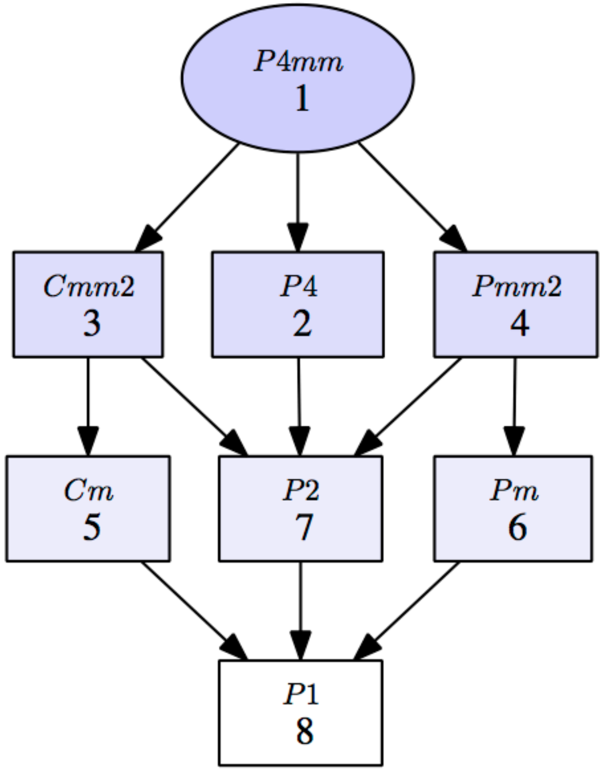
**irrep GM5 (k=0)**



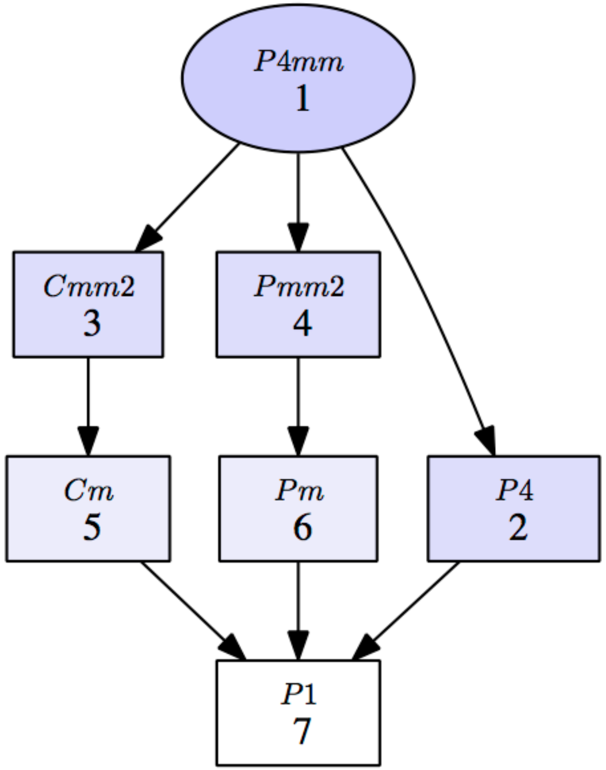
## *P4mm* ⟶ ?   k=0

Use of program SUBGROUPS:

all subgroups
(conjugacy classes):

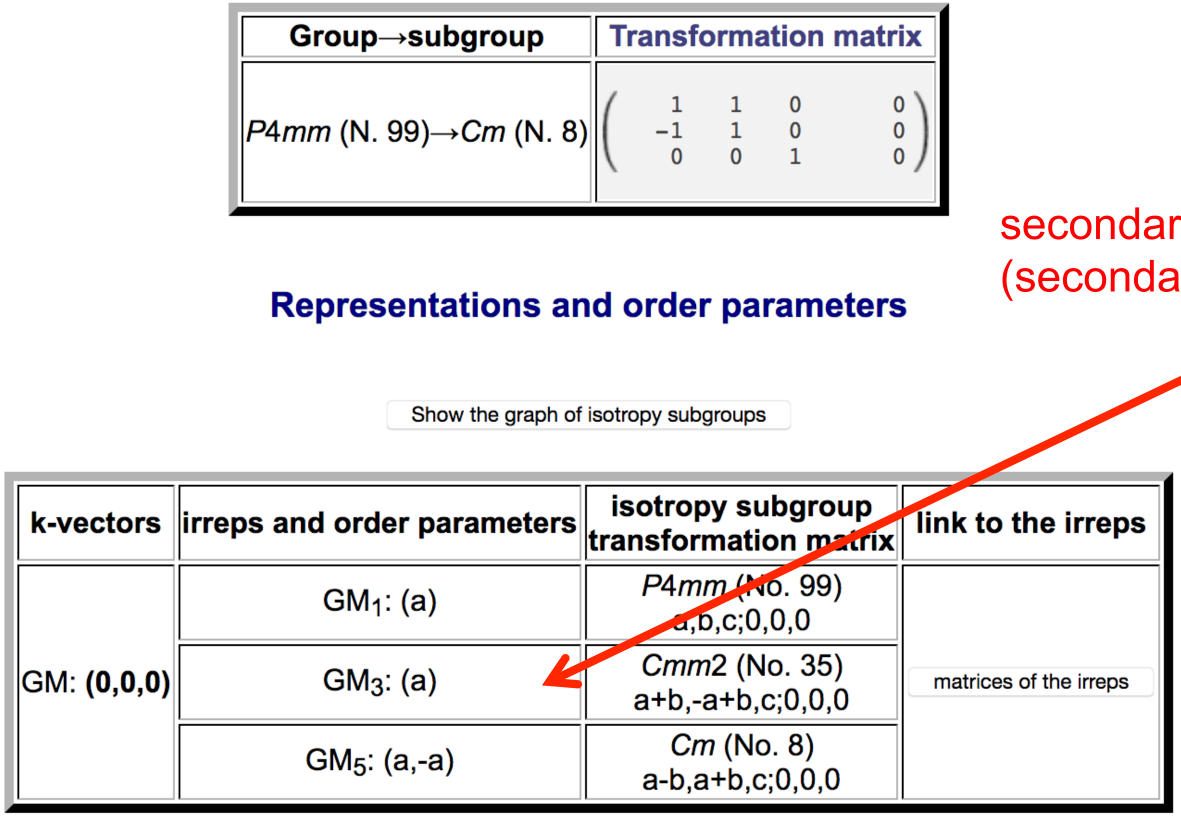


only “Landau”
(conjugacy classes):



## $P4mm \xrightarrow{\text{irrep GM5}} Cm$

Get_irreps output:



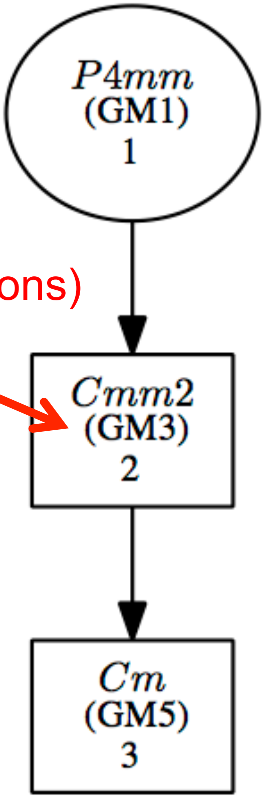
| **Group→subgroup** | **Transformation matrix** |
|---|---|
| *P4mm* (N. 99)→*Cm* (N. 8) | $\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ |

**Representations and order parameters**

Show the graph of isotropy subgroups

| **k-vectors** | **irreps and order parameters** | **isotropy subgroup transformation matrix** | **link to the irreps** |
|---|---|---|---|
| GM: **(0,0,0)** | $GM_1$: (a) | *P4mm* (No. 99)<br>a,b,c;0,0,0 | matrices of the irreps |
| | $GM_3$: (a) | *Cmm2* (No. 35)<br>a+b,-a+b,c;0,0,0 | |
| | $GM_5$: (a,-a) | *Cm* (No. 8)<br>a-b,a+b,c;0,0,0 | |

secondary irrep
(secondary irrep distortions)



Use SYMMODES as an alternative if the subgroup label is known, but without transformation relation

# Isotropy subgroups of an irrep

**Example:** P6/mmm $\xrightarrow{\text{GM6-}}$ ?

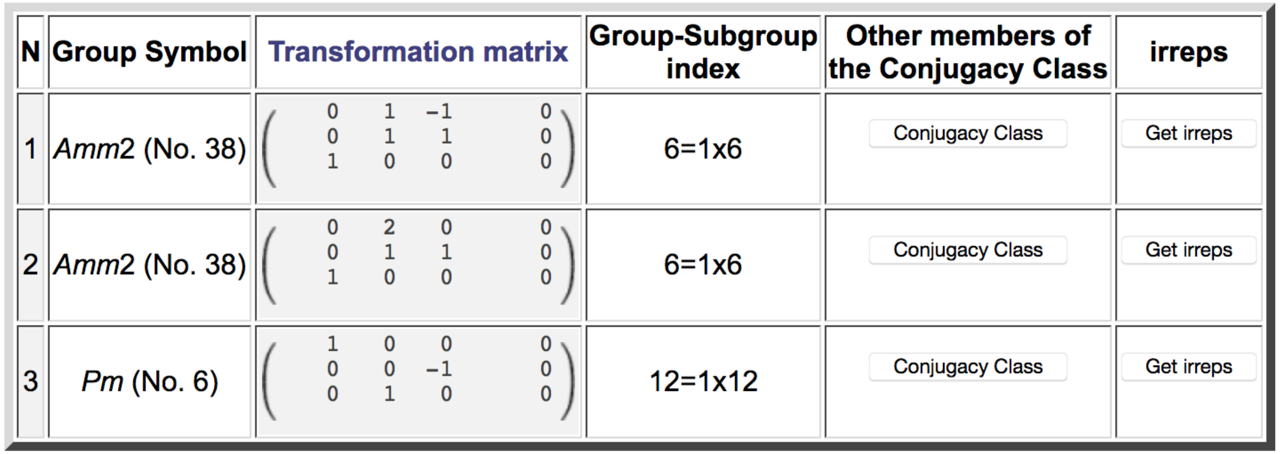
**Isotropy subgroups of GM6-?**

# Isotropy subgroups of an irrep

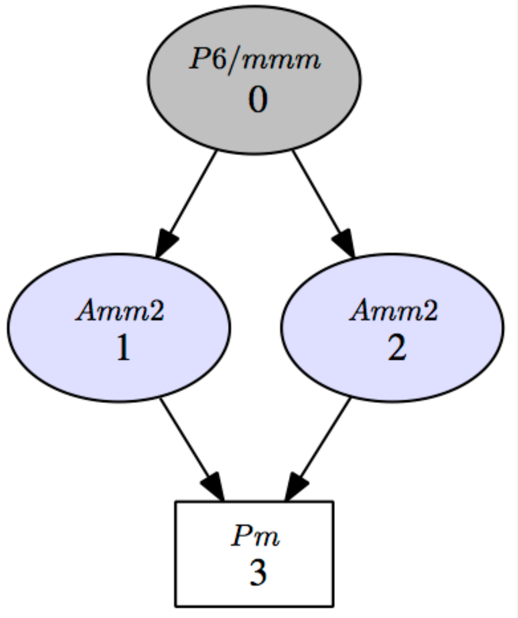
**GM6-**

**Example:** **P6/mmm** $\longrightarrow$ **?**

**Isotropy subgroups of GM6-?**



| N | Group Symbol | Transformation matrix | Group-Subgroup index | Other members of the Conjugacy Class | irreps |
|---|---|---|---|---|---|
| 1 | *Amm*2 (No. 38) | $\begin{pmatrix} 0 & 1 & -1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$ | 6=1x6 | Conjugacy Class | Get irreps |
| 2 | *Amm*2 (No. 38) | $\begin{pmatrix} 0 & 2 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$ | 6=1x6 | Conjugacy Class | Get irreps |
| 3 | *Pm* (No. 6) | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$ | 12=1x12 | Conjugacy Class | Get irreps |



# Isotropy subgroups of an irrep

Example: *P6/mmm* $\xrightarrow{\text{GM6-}}$ ?

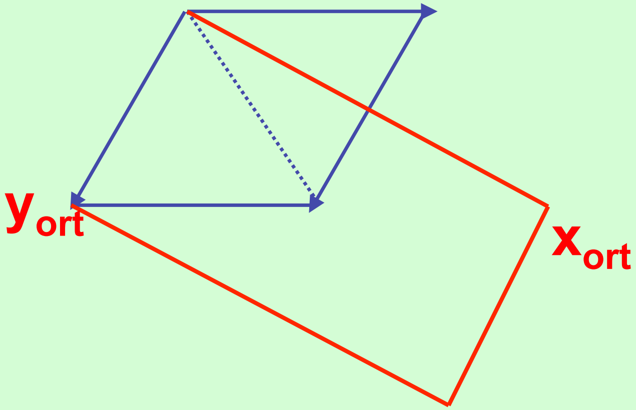
**Isotropy subgroups of GM6-:**

**2-dim irrep:**

Especial directions 1: ***Amm2*** **(*Cm2m*)** → **P11m**

Especial directions 2: ***Amm2*** **(*C2mm*)** → **P11m**

kernel(common to any GM6- distortion)



## Invariance equation:

$$T[(R|t)] \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \rightarrow$$

(R|t) is conserved by the distortion

2x2 matrix of irrep $mE_1$