Symmetry considerations in Structural Phase Transitions

J. Manuel Perez-Mato
Facultad de Ciencia y Tecnología
Universidad del País Vasco, UPV-EHU
BILBAO, SPAIN
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
```
Prologue:

we all use symmetry arguments... without mathematics

same energy for the two distortions....
Prologue:

we all use symmetry arguments... without mathematics

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

coset decomposition: $G = F' + g_2 F'$

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

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

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

the "mathematics" behind ...

Symmetry break

coset decomposition: \[ G = F + g_2 F + g_3 F + g_4 F \]

same energy for the four distortions ....

\[ \text{order of } G \]
\[ \text{order of } F \]

= 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):

\[
E = E_0 + \frac{1}{2} \kappa_1 Q_1^2 + \frac{1}{2} \kappa_2 Q_2^2 + \beta_1 Q_1^4 + \beta_2 Q_2^4 + \gamma Q_1^2 Q_2^2 + \ldots
\]

invariants for all symmetry operations of \( G \)
Example: The orthorhombic Amm2 structure of BaTiO$_3$

<table>
<thead>
<tr>
<th>index ($i_k \times i_n$)</th>
<th>N. domains</th>
<th>N. twins</th>
</tr>
</thead>
<tbody>
<tr>
<td>14/mcm</td>
<td>2x3</td>
<td>6</td>
</tr>
</tbody>
</table>

SrTiO$_3$

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

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tilting of octahedra

(it is not the one in SrTiO$_3$ !)
SrTiO$_3$

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

Possible space groups ? Apply program 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:

<table>
<thead>
<tr>
<th>N</th>
<th>Group Symbol</th>
<th>Transformation matrix</th>
<th>Group-Subgroup index</th>
<th>Symmetry operations</th>
<th>Set of subgroups*</th>
</tr>
</thead>
</table>
| 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 | | |
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$_3$? Use Structure Relations….

or PSEUDO…. same results?
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:

\[ E = E_0 + \frac{1}{2} \kappa(T) Q^2 + \ldots \]

\[ \kappa(T) < 0 \quad T < T_c \]

**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”:

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

\[ e = (e_1, e_2, e_3, e_4) \]

Normalization: \[ |e_1|^2 + |e_2|^2 + |e_3|^2 + 2 |e_4|^2 = 1 \]

(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:

\[ E = E_0 + \frac{1}{2} \sum \kappa_j(k) Q_i(k) + \ldots \]

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

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

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

Energy

\[ Q > 0 \]

\[ Q < 0 \]
Order parameter \( Q = (Q_1, Q_2) = \rho (a_1, a_2) \) with \( a_1^2 + a_2^2 = 1 \)

Irreducible representation of \( G \) (irrep) (matrices)

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

Phase Transition / Symmetry break / Order Parameter

High symmetry group \( G = \{g\} \)

Irreducible representation of \( G \) (irrep) (matrices)

g belongs to \( F \)

High symmetry

Low symmetry

F: isotropy subgroup

Group-subgroup relation:

\[ T(g) Q = Q \]

\( g \) belongs to \( F \)

\( T(g) Q = Q' \neq Q \)

g does not belong to \( F \): \( Q' \) equivalent but distinguishable state
Modes and irreducible representations (irreps)

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

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

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

Irreducible representation of $G$ (irrep) (matrices)

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

$T(g)$ : nxn matrix

distortions: Vectors in a multidimensional space

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

minimal subspaces kept invariant by $G$: irreducible
Not all possible subgroups are equally probable in a distorted structure: isotropy subgroups

We want to know the possible symmetries of a distorted phase

$$G \rightarrow ?$$

possible isotropy subgroups for a given active irrep?

---

**irreps of P4mm at k=0 (Γ point)**

<table>
<thead>
<tr>
<th>Character Table</th>
<th>C₄ᵥ(4mm)</th>
<th>#</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>mₓ</th>
<th>mᵧ</th>
<th>functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mult.</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>zₓ²₊ᵧ², z²</td>
</tr>
<tr>
<td>A₁</td>
<td>Γ₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>zₓ²₊ᵧ², z²</td>
</tr>
<tr>
<td>A₂</td>
<td>Γ₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>Jₓ</td>
</tr>
<tr>
<td>B₁</td>
<td>Γ₃</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>x²₋ᵧ²</td>
</tr>
<tr>
<td>B₂</td>
<td>Γ₄</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>xy</td>
</tr>
<tr>
<td>E</td>
<td>Γ₅</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(x,y), (xz, yz), (Jₓ₋Jᵧ)</td>
</tr>
</tbody>
</table>

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

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

Isotropy subgroup depends on the "direction" of the 2-dim order parameter.
Isotropy subgroups of an irrep

GM6-

Example: P6/mmm → ?

Isotropy subgroups of GM6-:

2-dim irrep:

Especial directions 1: Cm2m → P11m

Especial directions 2: C2mm (kernel: kernel: (common to any GM6 distortion)

Invariance equation:

\[ T[(R,m|t)] \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \rightarrow (R,m|t) \text{ is conserved by the distortion} \]

2x2 matrix of irrep mE, 1

Isotropy subgroups (kernel and epikernels) are derived by ISODISTORT
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+ (or R5-):

**isotropy subgroups of R4+ (or R5-):**

I4/mcm, (a+b, -a+b, 2c; 0,0,0) , (a,0,0)  \( \text{SrZrO}_3 \)

Imma, (a+c, 2b, -a+c; 0,0,0), (a,a,0)  \( \text{SrZrO}_3 \)

R-3c, (-a+b, -b+c, 2a+2b+2c; 0,0,0) , (a,a,a)  \( \text{CeAlO}_3 \)

C2/m, (-2c, 2b, a+c; 0,1/2,1/2), (a,b,0)  \( \text{BaPbO}_3 \)

C2/c, (-a+2b+c, -a+c,a+c; 0,1/2,1/2), (a,a,b)  \( \text{LaCoO}_3 \)

P-1, (b+c, a+c a+b; 0,0,0), (a,b,c)
SrTiO$_3$

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

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\end{pmatrix}
\] | 6=2x3 | | |
| 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 | | |

Active irrep?
use SYMMODES:
R5- with k=(1/2,1/2,1/2)

Possible symmetries resulting from a R5- distortion

Other possible symmetries for the same active irrep R5-?

Use SUBGROUPS in its option where the input can be k-vector instead of a supercell and filtered for the irrep R5-
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 R$_{5-}$:

isotropy subgroups of R$_{5-}$:

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

This type of information can also be obtained with ISODISTORT
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)
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.

\[ G = F + g_3 F + g_3 F + \ldots + g_s F \]

\[ g_n(Q_1 \ldots | Q^{(s)}_1 \ldots) \]
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

<table>
<thead>
<tr>
<th>mm mF mm 2</th>
<th>422 F 222</th>
</tr>
</thead>
<tbody>
<tr>
<td>strain</td>
<td>strain</td>
</tr>
<tr>
<td>$\varepsilon_1$ 0 0</td>
<td>$\varepsilon_1$ 0 0</td>
</tr>
<tr>
<td>0 $\varepsilon_2$ 0</td>
<td>0 $\varepsilon_2$ 0</td>
</tr>
<tr>
<td>0 0 $\varepsilon_3$</td>
<td>0 0 $\varepsilon_3$</td>
</tr>
<tr>
<td>polariz. (0,0,0)</td>
<td>(0,0,0) ferroelect.</td>
</tr>
<tr>
<td>(0,0,0)</td>
<td>(0,0,0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>mm mF 112/m</th>
<th>m-3 m F 3 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>strain</td>
<td>strain</td>
</tr>
<tr>
<td>$\varepsilon_1$ 0 0</td>
<td>$\varepsilon_4$ $\varepsilon_4$</td>
</tr>
<tr>
<td>0 $\varepsilon_2$ 0</td>
<td>$\varepsilon_4$ $\varepsilon_4$</td>
</tr>
<tr>
<td>0 0 $\varepsilon_3$</td>
<td>$\varepsilon_4$ $\varepsilon_4$ $\varepsilon_4$</td>
</tr>
<tr>
<td>polariz. (0,0,0)</td>
<td>(P,P,P)</td>
</tr>
<tr>
<td>(0,0,0) ferroelastic</td>
<td>(0,0,0)</td>
</tr>
</tbody>
</table>
Multistability: enumeration of distinct domains:

$$G \rightarrow F$$

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

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

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

Number of distinct ferroic states = \frac{\text{Order of } P_G}{\text{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) $Q$
Exercises 1, 2, 3 of SPT page
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!:
- **primary mode(s): unstable**
  - it drives the phase transition
- **secondary modes: induced by the presence of the primary one(s)**
  - much weaker in general
Hierarchy of spontaneous modes/variables

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

$$E = E_0 + \frac{1}{2} \kappa_1 Q_1^2 + \frac{1}{2} \kappa_2 Q_2^2 + \gamma Q_1^3 Q_2$$

Anharmonic allowed coupling

$$Q_2^{\text{equil.}} = - \left( \gamma / \kappa_2 \right) Q_1^3$$

Equivalent ferroic stable structures
Equivalent ferroic states

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

\[ G = F + g_1 F + g_3 F + ... + g_s F \]

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

\[ (Q_1, ..., Q_m | Q^{(s)}_1, ..., Q^{(s)}_{m_s}) \]

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

Switching a secondary small parameter will produce the switching of the large primary one …..
Amm2 – BaTiO$_3$: strain as secondary mode/variable

Proper ferroelectric
Improper ferroelastic

One can turn 90° the polarization switching the strain with a stress …
Ferroic properties Amm2- $\text{BaTiO}_3$

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarization (ferroelectric)</td>
<td>proper (order parameter)</td>
</tr>
<tr>
<td>Strain (ferroelastic)</td>
<td>improper (not order parameter)</td>
</tr>
</tbody>
</table>

One can switch a secondary mode:

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

and vice versa.
General Rules of a phase transition with symmetry break

For a given symmetry break \( G \rightarrow F \)?

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:

\[
T[g] \mathbf{Q} = \mathbf{Q}
\]

with \( g \) belonging to F

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

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

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:

\[
T[g] \mathbf{Q} = \mathbf{Q}
\]

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

$\text{P42}_1\text{m} \rightarrow \text{Pba2}$  
$(Z=2)$  
$(Z=4)$  
(cell duplication)

polar mode/polarization

$q_{M2M4} = 1.6191 \, \text{Å}$  
$q_{\Gamma3} = 0.0716 \, \text{Å}$

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

primary mode

$M_2 + M_4$

secondary mode

$\Gamma_3 (B_2)$

antiferrodistortive mode (multiplies the unit cell)

wave vector $\neq 0$
Ferroelectric Domains in Amm2 BaTiO₃

(m-3m, mm2)

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

Amm2: $Q(0, 1/\sqrt{2}, 1/\sqrt{2})$

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

Number of domains = 48/4 = 12

12 eq. directions for the order parameter:

- $(0, 1/\sqrt{2}, 1/\sqrt{2})$
- $(0, -1/\sqrt{2}, 1/\sqrt{2})$
- $(0, -1/\sqrt{2}, -1/\sqrt{2})$
- $(0, 1/\sqrt{2}, -1/\sqrt{2})$
- $(1/\sqrt{2}, 0, 1/\sqrt{2})$
- $(-1/\sqrt{2}, 0, 1/\sqrt{2})$
- $(1/\sqrt{2}, 0, -1/\sqrt{2})$
- $(1/\sqrt{2}, 0, -1/\sqrt{2})$
- $(1/\sqrt{2}, 1/\sqrt{2}, 0)$
- $(-1/\sqrt{2}, 1/\sqrt{2}, 0)$
- $(-1/\sqrt{2}, -1/\sqrt{2}, 0)$
- $(1/\sqrt{2}, -1/\sqrt{2}, 0)$
Pseudo-proper ferroic properties: the case of ferroelectric KDP

I-42d $\rightarrow$ Fdd2

( -42m ------ mm2)

No cell multiplication
(order parameter $k=0$)

Ferroic states/domains: $(P_z, \varepsilon_{xy})$, $(-P_z, -\varepsilon_{xy})$

...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).