Tutorial on the application of the tools of the Bilbao Crystallographic Server in the study of group-subgroup phase transitions
(Version from 2010 with some updating comments added in 2018)

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1. In a phase transition, not all symmetry-breaks are *equally possible*!

Isotropy Subgroups

The Landau theory of symmetry-breaking structural phase transitions is based on the basic postulate that the symmetry break taking place in such transitions is due to the condensation (i.e. the change from zero to a non-zero amplitude) of one or a set of collective degrees of freedom that transform according to a single irreducible representation (irrep) of the space group of the high-symmetry phase (the so-called active irrep). These amplitudes $\{Q_i, i=1,\ldots,n\}$ that become spontaneously non-zero in the low-symmetry phase, constitute the so-called order parameter, and the n-dimensional irrep describing its transformation properties is usually called the active irrep of the transition.

Although Landau theory may not reproduce accurately the thermodynamic behaviour close to the transition points, its symmetry aspects and resulting restrictions are of much general validity. Its basic postulate of a single active irrep is fulfilled in most cases by group-subgroup phase transitions, even if they are discontinuous (for which its validity is not ensured).

That the symmetry change in a transition is fully determined by a single active irrep, independently of the condensation of other degrees of freedom, is a very restrictive condition, which can be very powerful in the analysis and prediction of the structural and symmetry properties of these systems.

Basic problem to solve: we know the high symmetry group and the active irrep, and we want to know the possible symmetries of the low symmetry phase.

$$G \longrightarrow \text{?}$$

possible isotropy subgroups for a given active irrep?

Let us call G the space group of the high-symmetry phase, and τ the (n-dimensional) active irrep for a certain low-symmetry phase, and let be $Q=(Q_1,\ldots,Q_n)$ the n-dimensional order parameter transforming according to the irrep τ. By definition, if an operation g of the space group G is applied to the low-symmetry distorted structure, the amplitudes $Q=(Q_1,\ldots,Q_n)$ will change/transform according to the irrep τ:

$$T_\tau(g)\, \mathbf{Q} = \mathbf{Q'} \qquad\qquad (1)$$

where the $T_\tau(g)$ is the nxn matrix associated by the irrep τ to the operation g. The system will keep the operation g among its symmetry operations, i.e. g will belong to the low-symmetry distorted phase, if the system is undistinguishable after the operation is applied, i.e. $\mathbf{Q'}=\mathbf{Q}$.

Hence, all possible space groups, H (subgroups of G), for the low-symmetry phase, resulting from an active irrep τ, can be obtained from the condition that the space group operations h belonging to H should fulfill:

$$T_\tau(h)\, \mathbf{Q} = \mathbf{Q} \qquad\qquad (2)$$

The possible subgroups of G, H, that can satisfy this invariance equation, and therefore be the symmetry of a distorted phase with τ as active irrep, are usually called ***isotropy subgroups*** (for the irrep τ).

The "lost" operations g, such that:

$$T_\tau(g)\, \mathbf{Q} = \mathbf{Q'} \neq \mathbf{Q} \qquad\qquad (3)$$

transform the structure into configurations which are distinguishable from the original one, but energetically equivalent, and represent domain-related structures.

In the case of a 1-dim irrep, eq. (2) is rather trivial, and only a single isotropy subgroup exists. It is formed by all operations of G for which $T_\tau(g)=1$. The symmetry of the low-symmetry phase is therefore fully determined by the 1-dim irrep, and very simple to derive.

Let us consider for instance the example of a material having I4/mmm symmetry and consider the possible phase transitions/symmetry breaks that the material can suffer, without changing its unit cell, i.e. without loosing any lattice translation.

By definition, the matrix $T_\tau(\{E,l\})$ associated to a lattice translation $\{E,l\}$ by an irrep τ is a diagonal matrix of the form:

$$
\begin{bmatrix}
e^{ik_1 \cdot l} & & & & \\
& \cdot & & & \\
& & \cdot & & \\
& & & \cdot & \\
& & & & e^{ik_s \cdot l}
\end{bmatrix}
$$

where $\{\mathbf{k}_1,\dots\mathbf{k}_s\}$ are the wave vectors of the star of the irrep. Therefore, according to eq. (2), if we want all lattice translations $\{E,l\}$ maintained in the isotropy subgroup, the

wave vectors $\mathbf{k}_i$ should be zero, i.e. the active irrep should have null wave vector, or in other words correspond to the point Γ of the Brillouin zone.

The irreps of a space group at the Brillouin zone center are equivalent to those of the corresponding point group. The lattice translations have associated identity operators. We get then to the irreps of I4/mmm at the Γ point by looking at the irreps of the point group 4/mmm in the program POINT of this server:

Table 1: Character table of the irreps of the point group 4/mmm obtained with the server tool POINT

Character Table											
D_{4h}(4/mmm)	#	1	2	4	2_h	$2_{h'}$	-1	m_z	-4	m_v	m_d	functions
Mult.	-	1	1	2	2	2	1	1	2	2	2	_
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	x^2+y^2,z^2
A_{2g}	Γ_2^+	1	1	1	-1	-1	1	1	1	-1	-1	J_z
B_{1g}	Γ_3^+	1	1	-1	1	-1	1	1	-1	1	-1	x^2-y^2
B_{2g}	Γ_4^+	1	1	-1	-1	1	1	1	-1	-1	1	xy
E_g	Γ_5^+	2	-2	0	0	0	2	-2	0	0	0	$(xz,yz),(J_x,J_y)$
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	_
A_{2u}	Γ_2^-	1	1	1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	Γ_3^-	1	1	-1	1	-1	-1	-1	1	-1	1	_
B_{2u}	Γ_4^-	1	1	-1	-1	1	-1	-1	1	1	-1	_
E_u	Γ_5^-	2	-2	0	0	0	-2	2	0	0	0	(x,y)

To determine the space groups resulting from each 1-dim irrep acting as active irrep, we have just to keep the operations with character 1:

Table 2: Isotropy subgroups of I4/mmm for onedimensional irreps with $\mathbf{k}$=0

irrep	Operations conserved	Isotropy subgroup
A_{1g}	all operations	I4/mmm
A_{2g}	1, 2z, 4z, -1, mz, -4	I4/m
B_{1g}	1, 2z, 2h (2x, 2y), -1, mz, mv (mx, my)	Immm
B_{2g}	1, 2z, 2h' (2xy, 2x-y), -1, mz, md (mxy, mx-y)	Fmmm
A_{2u}	1, 2z, 4z, mh(mx, my), md(mxy,mx-y)	I4mm
B_{1u}	1, 2z, 2h (2x, 2y), -4, md(mxy, mx-y)	I-42m
B_{2u}	1, 2z, 2h'(2xy, 2x-y), -4, mv (mx, my)	I-4m2

The irrep A_{1g} is trivial and does not break the symmetry. We have taken into account that the columns in Table 1 correspond to equivalence classes with several operations. The lattice is labelled as F in the case of the irrep B_{2g}, despite that the lattice is not changed, because in this case the operations of the orthorhombic group mmm are defined along the diagonal directions on the plane xy of the tetragonal I lattice. The I lattice described in a unit cell with (110) and (-110) as basic translations becomes an F lattice.

Table1 contains a final column, headed with "functions", which contains useful additional information. It lists functions of the coordinates x,y,z of a polar vector, or the coordinates J_x, J_y and J_z, of an axial vector, that transform according to the corresponding irrep. For instance, the product xy transforms according to the irrep B_{2g}. But a shear strain ε_{xy} of the crystal transforms as a function xy. Therefore a shear strain ε_{xy} is a crystal magnitude of the I4/mmm crystal transforming according to B_{2g}, and could be the order parameter for a phase transition I4/mmm --- Fmmm, i.e. a proper ferroelastic transition, with a switchable spontaneous strain.

In general irreps of dimension n > 1 have more than one isotropy subgroup depending on the direction taken by the order parameter Q within its n-dimensional space.

In our example, we have two 2-dim irreps, E_g and E_u. Let us consider the irrep E_g, whose matrices can be chosen in the following form (it straightforward to derive them from the fact that they should correspond to the transformation properties of the pair of functions xz, yz):

Table 3: matrices of the irrep E_g of the point group 4/mmm, for a certain choice of the basis in the irrep space.

	1,-1	2z, mz	4z+, -4z+	4z-, -4z-	2x, mx	2y, my	2xy, mxy	2x-y, mx-y
Eg	1 0 0 1	-1 0 0 -1	0 -1 1 0	0 1 -1 0	-1 0 0 1	1 0 0 -1	0 -1 -1 0	0 1 1 0

As the inversion -1 has associated the identity matrix, operations g and -1.g have the same matrix. Identity and inversion will always fullfill eq. (2) and operations 2_z, mz, 4z+, -4z+, 4z- and -4z- will never fullfill it, independently of the direction of **Q**. The conservation of the other operations depends on the direction of **Q**. For instance if we consider that the E_g order parameter is of the form (0,Q), i.e. takes the direction (0,1) in the irrep space, 2_x and m_x will be conserved in the distorted structure, and the resulting isotropy subgroup is P2/m11.

It is easy to check, considering the matrices above that the whole set of possible isotropy subgroups for E_g, depending on the order parameter direction, are:

Table 4: Isotropy subgroups of the irrep E_g of I4/mmm, depending on the direction within the irrep space

direction	operations	space group
(0,1)	1, 2x, -1, mx	C2/m (**-b-c**, **a**, **c** ; 0 0 0)
(1,0)	1, 2y, -1, my	C2/m (**-a-c**, **b**, **c**; 0 0 0)
(1,1)	1, 2xy, -1, mxy	C2/m (**a-b+c**, **a+b**, c; 0 0 0)
(-1,1)	1, 2x-y, -1, mx-y	C2/m (**a+b+c**, **-a+b**, **c**; 0 0 0
arbitrary	1,-1	P-1 (**a**, **b**, **a**/2+**b**/2+**c**/2; 0 0 0)

The I centred unit cell must be transformed to a C centred cell for the monoclinic space groups and to a primitive unit cell for the tricilinic one, if expressed in a conventional setting. The b-axis is the monoclinic unique axis in the conventional setting used. The lattice does not change, it is only expressed in a conventional unit cell consistent with the direction of the monoclinic axis.

The directions (0,1) and (1,0) for the order parameter are equivalent: they correspond to domain related directions. The four equivalent order parameter values obtained by applying the matrices of the lost operations are {(Q,0), (0,Q), (-Q,0), (0,-Q)}. This means mathematically that the isotropy subgroups corresponding to the order parameter directions (0,1) and (1,0) belong to the same conjugacy class.

In general the number of domain-related configurations is equal to the index of the subgroup (4 in this case). Similarly for the solutions of type (1,1), there are four equivalent order parameter directions {(a,a), (-a,a), (-a,-a), (a,-a)}.
We have then three possible isotropy subgroups for the irrep Eγ, which are not equivalent: C2/m (with monoclinic axis along x or y), C2/m (with monoclinic axis along the oblique directions (110) or (1-10)) and P-1.

With a a similar analysis for E$_u$ we can complete the set of isotropy subgroups of I4/mmm for irreps with k=0:

Table 5: Non-equivalent isotropy subgroups of I4/mmm for irreps with **k**=0

irrep	Isotropy subgroup
A1g	I4/mmm
A2g	I4/m
B1g	Immm
B2g	Fmmm
A2u	I4mm
B1u	I-42m
B2u	I-4m2
Eg	C2/m
	C2/m
	P-1
Eu	Imm2
	Fmm2
	Cm

It is interesting to compare this table with the set of all subgroups of I4/mmm that maintain the lattice, which can be obtained with the program CELLSUB of the Bilbao Crystallographic Server. **An alternative more powerful and versatile program for this kind of calculations with the name SUBGROUPS is now available.**

The program CELLSUB:
    CELLSUB lists all possible subgroups of a given space group for a given k-index (or for a k-index smaller than a certain value). The program lists first the space group types, and then, for each space group type, it can distinguish the different conjugacy classes. The k-index i$_k$ is the "klassengleich" index, and indicates the multiplication factor relating the volume of the primitive cell of the subgroup with

respect to the primitive cell of the original structure. Thus, $i_k=1$ implies conservation of the primitive unit cell, and therefore of the whole lattice.

For $i_k=1$, CELLSUB lists for I4/mmm the following subgroups:

Table 6: Subgroups of I4/mmm with $i_k=1$

List of subgroups of space group *I4/mmm*(139) for a given k-index = 1

NOTE: The program uses the default choice for the group settings.

In the following table a list of t-subgroups, k-subgroups and general subgroups is given for a given k-index. Click over "show..." to obtain the classification in conjugate classes of subgroups.

k-index i_k = 1

N. of subgroups (for k-index 1) found: 18

t-subgroups of space group *I4/mmm* (139)

N	HM Symbol	ITA	index	t-index	k-index	More info
1	I-42m	121	2	2	1	show...
2	I-4m2	119	2	2	1	show...
3	I4mm	107	2	2	1	show...
4	I422	097	2	2	1	show...
5	I4/m	087	2	2	1	show...
6	I-4	082	4	4	1	show...
7	I4	079	4	4	1	show...
8	Immm	071	2	2	1	show...
9	Fmmm	069	2	2	1	show...
10	Imm2	044	4	4	1	show...
11	Fmm2	042	4	4	1	show...
12	I222	023	4	4	1	show...
13	F222	022	4	4	1	show...
14	C2/m	012	4	4	1	show...
15	Cm	008	8	8	1	show...
16	C2	005	8	8	1	show...
17	P-1	002	8	8	1	show...
18	P1	001	16	16	1	show...

Clicking over each of them we can see the non-equivalent subgroups of each type. Thus for C2/m, we obtain:

Table 7: Conjugacy classes of subgroups of I4/mmm of type C2/m with index $i_k=1$

Classification of the subgroups of type *C2/m*(12) of group *I4/mmm*(139) with index 4

For the group G = *I4/mmm* there are 5 different subgroups H_j isomorphic to H = *C2/m* of index 4. These subgroups are distributed in 3 classes of conjugate subgroups with respect to the group G.

In the tables below each table corresponds to one class. For each class are given the chains corresponding to the different subgroups in the class, and the obtained transformation matrices.

The list with the chains and transformation matrices that give identical subgroups can be seen by clicking on the button in the column **Identical** of the table.

Class 1

Check	Chain [indices]	Chain with HM symbols	Transformation	Identical
◉ 1	139 069 012 [2 2]	I4/mmm > Fmmm > C2/m	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$	to group 1

(Show graph)

Class 2

Check	Chain [indices]	Chain with HM symbols	Transformation	Identical
◉ 2	139 069 012 [2 2]	I4/mmm > Fmmm > C2/m	$\begin{pmatrix} 1 & 1 & -1/2 & 0 \\ -1 & 1 & 1/2 & 0 \\ 0 & 0 & 1/2 & 0 \end{pmatrix}$	--
○ 3	139 069 012 [2 2]	I4/mmm > Fmmm > C2/m	$\begin{pmatrix} -1 & 1 & 1/2 & 0 \\ -1 & -1 & 1/2 & 0 \\ 0 & 0 & 1/2 & 0 \end{pmatrix}$	--

(Show graph)

Class 3

Check	Chain [indices]	Chain with HM symbols	Transformation	Identical
◉ 4	139 071 012 [2 2]	I4/mmm > Immm > C2/m	$\begin{pmatrix} -1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$	--
○ 5	139 071 012 [2 2]	I4/mmm > Immm > C2/m	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$	--

(Show graph)

There are therefore 3 conjugacy classes of space groups of type C2/m. Classes 2 and 3 in the list correspond to the two non-equivalent isotropy subgroups discussed above. On the other hand, class 1 has the monoclinic axis along the z direction of the tetragonal setting, and it is not an isotropy subgroup. (**Warning:** the ordering and numbering of the classes done by the program is not fixed. Different runs can order the classes differently!)

Inspecting the classes for all subgroup types, the number of non-equivalent subgroups with i_k=1 is then 26, while the number of non-equivalent isotropy subgroups is only 13.

Therefore, not all subgroups of I4/mmm compatible with its lattice can be reached through a phase transition with a single active irrep, as demanded by the Landau postulate. The Landau postulate restricts the number of possible symmetries to 13 of the 26 possible subgroups.

The restriction of the possible symmetry break to only isotropy subgroups is very demanding, and can provide very valuable information. For instance, if a symmetry change between two phases does not comply with this condition, it indicates that the distorted phase contains at least two active irreps, i.e. the symmetry break can

only be explained considering at least two different order parameters transforming according to different irreps. It will therefore be highly probable that a sequence of at least two phase transitions will exist, due to the separate condensation of the two order parameters, and an intermediate phase is most likely (see below for an example).

Some predictive power about the phase diagram of a compound or that of similar compounds can be achieved from the knowledge of the isotropy subgroups of a certain irrep. If a mutidimensional irrep is known to be active in a certain material, it may exhibit several phases with different symmetries corresponding to different isotropy subgroups of this active irrep, depending on the thermodynamic stabilization of the order parameter along different directions. Similarly, if the same irrep is active in a family of isomorphous compounds, the distorted symmetries observed in different compounds may be different, but will correspond to different isotropy subgroups of the same irrep.

Let us consider for instance the example of the perovskites. Perovskites are known to have an intrinsic instability due to the softness of three degenerate rigid unit modes (modes tilting the octahedral framework and keeping the BX_6 octahedra approximately rigid), which transform according to the 3-dim irrep R_4+ of the parent symmetry Pm-3m. The isotropy subgroups of Pm-3m for irrep R_4+ are the following:

Table 8: Isotropy subgroups of Pm-3m for irrep 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)	

This example is now discussed in detail in the tutorial of the program SUBGROUPS

In this list, the last triad for each space group indicates the restricted direction of the order parameter in its 3-dim space. For each of the possible isotropy subgroups, we have listed one perovskite compound that is known to have this symmetry in one particular phase. One can see that any of the possible symmetries is realized in some perovskite compound, except the lowest one, which corresponds to an arbitrary direction of the order parameter.

There are perovskites, as $CeAlO_3$, where the following phase transition sequence takes place as temperature is increased:

I4/mcm --- Imma ---- R-3c ----- Pm3m
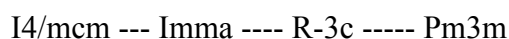
Thus, the system is changing the direction of its R_4+ order parameter from one phase to the next, through first-order phase transitions, yielding symmetries given by different isotropy subgroups of the list above.

The determination by hand of the isotropy subgroups for a given irrep is time consuming and tedious. The Bilbao Crystallographic Server does not have a tool to do this job directly, but the isotropy subgroup are listed (with some restrictions) in the book: **This is no longer true: the new program SUBGROUPS can provide the isotropy subgroups of any irrep (among many other things. See the tutorial of this program)**

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

or they can be obtained automatically using the program **ISOTROPY** (H. T. Stokes, D. M. Hatch, and B. J. Campbell, (2007), stokes.byu.edu/isotropy.html) , or some accompanying programs, all available in http://stokes.byu.edu/isotropy.html

The use of ISOTROPY requires getting familiar with some specific program commands, which are necessary for running the program. A more direct form to get the information about the isotropy subgroups is to run the associated programs INVARIANTS or ISODISPLACE, which are more user-friendly, and can be executed by filling some self-evident menus. These two programs yield the list of isotropy subgroups of a chosen irrep as a preliminary result. The information is more complete in ISODISPLACE, but running this program, requires the ntroduction of some structure for the high-symmetry phase (which can be a fake one, since for deriving the list of isotropy subgroups the structure is not used at all). **The name of ISODISPLACE is now ISODISTORT**

Some variations on the same problem: **(obsolete example)**
In many practical cases, we ignore the active irrep of the transition, but we may know some restrictive conditions on the symmetry of the distorted phase, which can be sufficient for deriving a restricted set of possible space groups H, and possible active irreps.

Let us consider as an example a real case. Recently crystals that include both molecules of fullerene and cubane have been synthetized. They are known to crystallize at high temperatures in the Fm-3m space group with the disordered fullerenes centred at the site 4a (0 0 0) and disordered cubane molecules at 4b (½ ½ ½) (Nature Mat. 4, 764 (2005)). At low temperature the system exhibits a couple of phase transitions, as the molecules become ordered. From powder diffraction experiments, the symmetry of the final phase has been reported to be a primitive orthorhombic structure, with its lattice parameters satisfying the approximate relations a and b ≈ $a_c/\sqrt{2}$, while c ≈ 2c, but its space group, and therefore its structure could not be determined (J. Phys. Chem B 113 2042 (2009)). Obviously, if we could restrict the symmetry of this phase to a minimal set of possible/probable space groups, we could have a better chance for succeeding in the interpretation and analysis of the diffraction diagram of this phase.

We can start by determining all possible primitive orthorhombic subgroups of Fm-3m, fulfilling the unit cell relation that has been observed. We can use for that CELLSUB, provided that we know the k-index of the subgroup we are searching. This index can be derived in a straightforward manner comparing the volumes of the primitive unit cell of the two space groups:

Fm3m: $a_c^3/4$ **This example has become obsolete and can be treated**
Orthorhombic phase: a_c^3 **much more efficiently with the program**
SUBGROUPS. It is discussed as a first example in the
tutorial of this program.

This means, the orthorhombic space group keeps only ¼ of the lattice translations, or in other words the primitive orthorhombic unit cell contains 4 formula units, while the Fm-3m structure only one. Hence $i_k = 4$. The point group of the searched orthorhombic space groups can be 222, mm2 or mmm. To simplify the example, we are going to assume that this point group symmetry is the maximal mmm (but we could proceed similarly with the other two possible point groups).

Restricted for $i_k=4$, point group mmm, and no centring, CELLSUB lists a quite long list of subgroups:

Table 9: Subgroups (types) of Fm-3m with point group mmm, $i_k=4$ and no centring.

N	HM Symbol	ITA	index	t-index	k-index	More info
1	Pnma	062	24	6	4	show...
2	Pbca	061	24	6	4	show...
3	Pbcn	060	24	6	4	show...
4	Pmmn	059	24	6	4	show...
5	Pnnm	058	24	6	4	show...
6	Pbcm	057	24	6	4	show...
7	Pccn	056	24	6	4	show...
8	Pbam	055	24	6	4	show...
9	Pcca	054	24	6	4	show...
10	Pmna	053	24	6	4	show...
11	Pnna	052	24	6	4	show...
12	Pmma	051	24	6	4	show...
13	Pban	050	24	6	4	show...
14	Pccm	049	24	6	4	show...
15	Pnnn	048	24	6	4	show...
16	Pmmm	047	24	6	4	show...

But not all of them will have unit cell parameters consistent with the experimental values. By clicking on "show" we get the different non-equivalent classes of subgroups of this type. For instance, for Pbca, there is a single class as shown by the output of CELLSUB (**warning:** the ordering of the classes is not fixed, and different runs of the program will yield in general different orderings):

Table 10: conjugacy classes of subgroups of Fm-3m of type Pbca

 Classification of the subgroups of type *Pbca*(61) of group *Fm*-3*m*(225) with index 24
For the group G = *Fm*-3*m* there are 2 different subgroups H$_j$ isomorphic to H = *Pbca* of index 24. These subgroups are distributed in 1 <u>class of conjugate subgroups</u> with respect to the group G.
In the tables below each table corresponds to one class. For each class are given the chains corresponding to the different subgroups in the class, and the obtained <u>transformation matrices</u>.
The list with the chains and transformation matrices that give identical subgroups can be seen by clicking on the button in the column **Identical** of the table.

Class 1

Check		Chain [indices]	Chain with HM symbols	Transformation	Identical
⦿	1	225 139 069 064 061 [3 2 2 2]	*Fm-3m > I4/mmm > Fmmm > Cmce > Pbca*	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$	to group 1
○	2	225 139 069 064 061 [3 2 2 2]	*Fm-3m > I4/mmm > Fmmm > Cmce > Pbca*	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	to group 2

The transformation matrix relating the two groups is then (-b,-c,a; 0 0 0) or equivalent ones, with the unit cell parameters coinciding with those of the cubic cell. Therefore this space group can be discarded.

On the other hand, if we consider subgroups of type Pnma, there are four classes of Pnma subgroups, and one of these classes is listed as:

Table 11: One of the conjugacy classes of subgroups of Fm-3m of type Pnma

Check		Chain [indices]	Chain with HM symbols	Transformation	Identical
⦿	31	225 139 137 059 062 [3 2 2 2]	*Fm-3m > I4/mmm > P4$_2$/nmc > Pmmn > Pnma*	$\begin{pmatrix} 0 & 1/2 & 1/2 & 1/4 \\ 2 & 0 & 0 & 3/4 \\ 0 & 1/2 & -1/2 & 1/2 \end{pmatrix}$	to group 31
○	32	225 139 071 059 062 [3 2 2 2]	*Fm-3m > I4/mmm > Immm > Pmmn > Pnma*	$\begin{pmatrix} 0 & 1/2 & 1/2 & 1/4 \\ 0 & -1/2 & 1/2 & 0 \\ 2 & 0 & 0 & 3/4 \end{pmatrix}$	to group 32
○	33	225 139 137 059 062 [3 2 2 2]	*Fm-3m > I4/mmm > P4$_2$/nmc > Pmmn > Pnma*	$\begin{pmatrix} 0 & 1/2 & -1/2 & 1/2 \\ 0 & 1/2 & 1/2 & 1/4 \\ 2 & 0 & 0 & 1/4 \end{pmatrix}$	to group 33
○	34	225 139 137 059 062 [3 2 2 2]	*Fm-3m > I4/mmm > P4$_2$/nmc > Pmmn > Pnma*	$\begin{pmatrix} 0 & 1/2 & -1/2 & 1/2 \\ 0 & 1/2 & 1/2 & 1/4 \\ 2 & 0 & 0 & 3/4 \end{pmatrix}$	to group 34

○	35	225 139 137 059 062 [3 2 2 2]	Fm-3m > I4/mmm > P4₂/nmc > Pmmn > Pnma	$\begin{pmatrix} 0 & 1/2 & 1/2 & 1/2 \\ 0 & -1/2 & 1/2 & 1/4 \\ 2 & 0 & 0 & 1/4 \end{pmatrix}$	to group 35
○	36	225 139 129 059 062 [3 2 2 2]	Fm-3m > I4/mmm > P4/nmm > Pmmn > Pnma	$\begin{pmatrix} 2 & 0 & 0 & 3/4 \\ 0 & 1/2 & -1/2 & 1/4 \\ 0 & 1/2 & 1/2 & 0 \end{pmatrix}$	to group 36
○	37	225 139 071 059 062 [3 2 2 2]	Fm-3m > I4/mmm > Immm > Pmmn > Pnma	$\begin{pmatrix} 2 & 0 & 0 & 3/4 \\ 0 & 1/2 & 1/2 & 1/4 \\ 0 & -1/2 & 1/2 & 0 \end{pmatrix}$	to group 37
○	38	225 139 137 059 062 [3 2 2 2]	Fm-3m > I4/mmm > P4₂/nmc > Pmmn > Pnma	$\begin{pmatrix} 2 & 0 & 0 & 1/4 \\ 0 & 1/2 & -1/2 & 1/2 \\ 0 & 1/2 & 1/2 & 1/4 \end{pmatrix}$	to group 38
○	39	225 139 137 059 062 [3 2 2 2]	Fm-3m > I4/mmm > P4₂/nmc > Pmmn > Pnma	$\begin{pmatrix} 2 & 0 & 0 & 1/4 \\ 0 & 1/2 & 1/2 & 1/2 \\ 0 & -1/2 & 1/2 & 1/4 \end{pmatrix}$	to group 39
○	40	225 139 129 059 062 [3 2 2 2]	Fm-3m > I4/mmm > P4/nmm > Pmmn > Pnma	$\begin{pmatrix} 0 & 1/2 & 1/2 & 0 \\ 2 & 0 & 0 & 1/4 \\ 0 & 1/2 & -1/2 & 1/4 \end{pmatrix}$	to group 40
○	41	225 139 129 059 062 [3 2 2 2]	Fm-3m > I4/mmm > P4/nmm > Pmmn > Pnma	$\begin{pmatrix} 0 & -1/2 & 1/2 & 0 \\ 2 & 0 & 0 & 1/4 \\ 0 & 1/2 & 1/2 & 1/4 \end{pmatrix}$	to group 41
○	42	225 139 071 059 062 [3 2 2 2]	Fm-3m > I4/mmm > Immm > Pmmn > Pnma	$\begin{pmatrix} 0 & -1/2 & 1/2 & 0 \\ 2 & 0 & 0 & 3/4 \\ 0 & 1/2 & 1/2 & 1/4 \end{pmatrix}$	to group 42

The parameters of the Pnma orthorhombic cell for this class are therefore a=2a$_c$, b= c=a$_c$/√2, which are consistent with the orthorhombic cell observed, if a permutation of the parameter labels is done.

Inspecting the classes for all the subgroups in the list, it is straightforward to conclude that only six symmetries Pnma, Pmmn, Pccn, Pmma, Pccm and Pmmm with transformations matrices listed below (or equivalent), are consistent with the experimental observation.

Table 12: Possible centrosymmetric orthorhombic subgroups of Fm-3m fulfilling the lattice metrics observed in the orthorhombic phase of fullerene-cubane crystals.

Pnma (2**a**, **b**/2+**c**/2, -**b**/2+**c**/2; ¾, ¼ , 0)
Pmmn (**a**/2-**b**/2, **a**/2+**b**/2, 2**c**; ¼ , 0, ¾)
Pccn (**a**/2-**b**/2, **a**/2+**b**/2, 2**c**; ¼ , 0, ¾)
Pmma (2**a**, **b**/2+**c**/2, -**b**/2+**c**/2; ½ , 0 , 0)
Pccm (**a**/2-**b**/2, **a**/2+**b**/2, 2**c**; 0, 0, 1/2)

Pmmm (**a**/2-**b**/2, **a**/2+**b**/2, 2c; 0, 0, 0)

This list could be further reduced if we assume that the searched symmetry should correspond to an isotropy subgroup (see exercise 2 below), i.e. an active irrep can explain the corresponding symmetry break, but this lead us into a new type of problem, which we treat in the following section.

Exercise 1: A structure has symmetry Pnma. At lower temperatures, a phase transition happens, and diffraction experiments show that superstructure reflections at points (h, k, l+ ½) appear, indicating the duplication of the c parameter, while keepin an orthorhombic lattice. Assuming a group-subgroup related transition and using CELLSUB, predict the only possible space group of this low-temperature phase, and the transformation matrix relating it with the parent space group Pnma.
(The use of SUBGROUPS is again here more efficient. This is the second example explained in its tutorial)

2. The inverse Landau problem:

The problem: We know the symmetry break and we want to identify the active irrep

From the discussion above, it should be clear that the most important information required for the characterization of a certain phase transition is the identification of its active irrep. In most cases it is sufficient to know the high and low space groups to identify it, but for some symmetry breaks this may not be sufficient.

The ISOTROPY website (stokes.byu.edu/isotropy.html) includes the program COPL, which does this identification, and also provides the irreps of all additional spontaneous secondary variables.

In the Bilbao Crystallographic Server, the program SYMMODES can also give this information as a by-product.

Secondary spontaneous variables:
In the low symmetry phase, apart from the order parameter and quantities transforming according to the active irrep, variables or degrees of freedom transforming according to other irreps can also condense or become spontaneous. The only requirement is that they are compatible with the low-symmetry space group. This is the realization of the Von Neumann principle: *any variable/degree of freedom compatible with the symmetry of the crystal is allowed and will therefore in general have a non-zero value.*
Using the concept of isotropy subgroup, we can say that any quantity with transformation properties given by an irrep having an isotropy subgroup containing the group H of the distorted phase will be spontaneous in the transition (i.e. it will change from zero to non-zero values in the distorted phase). Therefore, while the active irrep

must have H as an isotropy subgroup, the irreps associated to spontaneous secondary variables have in general an isotropy subgroup which is a supergroup H.

Let us consider the following case:

I4/mmm -------- C2/m (-**b-c**, **a**, **c** ; 0 0 0)
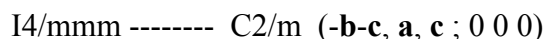
From the example discussed above, we know that the active irrep for this symmetry change is Eg (**k**=0).

If introduce this symmetry change, including the transformation matrix, in the program COPL (stokes.byu.edu/isotropy.html), the following result is obtained:

Table 13: Output of COPL for the symmetry break I4/mmm --- C2/m (-**b-c**,**a**,**c**; 000)

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

Parent: 139 D4h-17, I4/mmm, I4/m2/m2/m
Subgroup: 12 C2h-3, C2/m, C12/m1, unique axis b, cell choice 1
Lattice vectors:
0 -1 -1
1 0 0
0 0 1
origin: 0 0 0

Irrep	Dir	Subgroup	Size
GM1+	(a)	139 I4/mmm	1
GM2+	(a)	71 Immm	1
GM5+	(a,0)	12 C2/m	1

The program lists a set of irreps, a "direction" or subspace within the irrep space and their isotropy subgroup. The final column headed "size" indicates the multiplication of the primitiva unit cell of the corresponding isotropy subgroup relative to the parent high-symmetry space group (i.e. the klassengleiche index i_k).

We have then the irrep GM_5+ as the active irrep with the actual observed symmetry as isotropy subgroup, and then a secondary irrep GM_2+ with an isotropy subgroup Immm, which necessarily must be a supergroup of C2/m. In addition, the trivial irrep GM_1+ always appear as possible symmetry of secondary variables that are allowed to have non-zero values both at the distorted phase, and also at the parent phase. The label GM is being used to indicate that they are irreps at the Brillouin zone centre (Gamma point)), as the translational symmetry is not broken. GM_5+ must be the irrep labelled Eg in the Table above, while GM_2+ should be the irrep labelled above as B_{1g}.

There are now in the Bilbao Crystallographic Server a program called Get_irreps with a similar function to COPL, and more complete information. It can be directly called from the program SUBGROUPS, for any of the listed subgroups.

The reason for the existence of secondary spontaneous quantities transforming according to the irrep B_{1g} becomes obvious if we use SUBGROUPGRAPH or CELLSUB to construct the graph of minimal subgroups connecting the two end space groups:

Figure 1: Graph of minimal subgroups connecting the space group I4/mmm and its subgroup C2/m (-**b-c**, **a**, **c** ; 0 0 0) (or equivalent), obtained with SUBGROUPGRAPH. (*to obtain this graph one has to choose the correct conjugacy class among the three classes given by the program*)
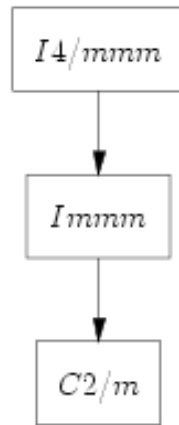
SUBGROUPS can also be be used here. See its tutorial

The group Immm, which is the isotropy subgroup of B_{1g}, as shown in the previous section, is indeed a supergroup of C2/m. Therefore, B_{1g} variables are compatible with the symmetry of the distorted phase, and therefore can be non-zero in this phase. They will be secondary spontaneous variables.

Table 1 indicates that x^2-y^2 and (xz, yz) transform according to B_{1g} and E_g, respectively. This means that the shear strain components (ε_{xz}, ε_{yz}) have the symmetry properties of the active irrep, and could in principle be identified with the order parameter of the transition, while the strain difference ε_{xx}-ε_{yy} transforms according to B_{1g}, being zero in the parent phase, and becoming spontaneous, as a secondary variable, in the C2/m phase. We have then a proper or pseudoproper ferroelastic transition (i.e. some strain component(s) have the symmetry of the order parameter), and we expect the softness at the transition of the stiffness coefficients corresponding to ε_{xz} and ε_{yz}, i.e. the elastic constants C_{55} and C_{66}. The shear strain ε_{yz} (direction (0,1) in E_g) should become spontaneous in the C2/m phase, deviating the monoclinic angle from 90º, as a primary order parameter effect. [Equivalently we could consider the domain related distortion with ε_{xz} (direction (1,0) in E_g)]. On the other hand, the quantity ε_{xx}-ε_{yy} is zero in the parent phase (cell parameters a and b are equal), while in the C2/m phase ε_{xx}-$\varepsilon_{yy} \neq 0$ (cell parameter a and b become different), but as a secondary (weaker) effect.

As the index of C2/m is 4, four equivalent domain-related structures must exist. These domains should be distinguishable by the value of the order parameter (see eq. (3) above). From the structure having a spontaneous shear strain yz ε^o and zero shear strain xz: $(0,\varepsilon^o)$, we obtain the values of the spontaneous shear strains ε_{xz} and ε_{yz} in the other domains applying lost symmetry operations according to the matrices listed in

Table 3: $\{2_z|000\} \rightarrow (0,-\varepsilon^o)$, $\{4_z\text{-}|000\} \rightarrow (\varepsilon^o, 0)$, $\{4_z\text{+}|000\} \rightarrow (-\varepsilon^o, 0)$. Therefore, the primary spontaneous monoclinic strain can have opposite values in different domains, and can also have two different orientations with respect to the parent tetragonal phase, corresponding to the monoclinic axis being along x or y, as listed in Table 4 above.

Note: One must be take into account that the computer-adapted irrep labels used by COPL and ISOTROPY differ from those used in some programs of the Bilbao server, but they coincide with those employed by the programs SYMMODES and AMPLIMODES of the Bilbao server, as both of them use an adapted version of COPL kindly provided by H. Stokes.

The program SYMMODES (J. Appl. Cryst. (2003). 36, 953)**:**

SYMMODES is designed to provide a basis of symmetry-adapted displacive modes for describing any displacive distortion relating a group-subgroup-related pair of phases. These modes, which are allowed to condense in the distorted phase are both primary (with their symmetry given by the active irrep) and secondary (with their symmetry given by secondary irreps having isotropy subgroups containing the observed space group). The program has been developed in collaboration with H. Stokes (Brigham Young University), and uses the program COPL.

For each allowed irrep (either active/primary or secondary), and restricted to the necessary irrep subspace, SYMMODES lists a complete set of symmetry-adapted displacive modes for the Wyckoff orbit types chosen by the user. In contrast with COPL, the program only requires as initial input the space group types of the high and low symmetry phase, G and H, and their index. The program then determines all the different classes of subgroups H of G, and the user has to choose the one relevant for the problem. A direct link to SUBGROUPGRAPH to obtain the graph of minimal subgroups is also available.

Once the relevant class of subgroups H is decided, the user chooses the set of Wyckoff positions, for which the basis of symmetry-adapted modes is desired. Note that the choice of unit cell for the H-group done by the program may not coincide with the one wished, but an equivalent one should appear on the list.

The program also allows to introduce a specific desired matrix transformation (If the matrix is not consistent with the subgroup, the program will write a warning and will stop). For our I4/mmm example, we use this option to introduce the specific matrix transformation we have been considering above for C2/m, and the following menu appears:

Table 14: First Menu of SYMMODES for the pair I4/mmm --- C2/m (**-b-c**, **a**, **c** ; 0 0 0)

Wyckoff positions of group *I4/mmm*(139)

Select Wyckoff Positions		
The Wyckoff Positions of the group *I4/mmm*(139) are listed on the following table. Select the Wyckoff Positions corresponding to the occupied orbits of atoms in the structure.		

Check	WP	Representatives
☐	32o	x,y,z
☐	16n	0,y,z
☐	16m	x,x,z
☐	16l	x,y,0
☐	16k	x,x+1/2,1/4
☐	8j	x,1/2,0
☑	8i	x,0,0
☐	8h	x,x,0
☐	8g	0,1/2,z
☐	8f	1/4,1/4,1/4
☐	4e	0,0,z
☐	4d	0,1/2,1/4
☐	4c	0,1/2,0
☐	2b	0,0,1/2
☐	2a	0,0,0

To see the primary and secondary symmetry modes for the symmetry break G>H_j click **Show modes** button. (Please note , the number and the patterns of the symmetry modes, in general, depend on the chosen class of conjugate subgroups.)

The splitting of Wyckoff positions during the symmetry change G>H_j is shown after clicking the corresponding button. (Please note, that, in general, the splitting of the Wyckoff Positions depends on the chosen subgroup H_j.)

(Show modes) (Show splitting)

We choose the Wyckoff position 8i to see the displacive modes that will be triggered by the transition for atoms on sites of this type. The output is the following:

Table 15: Output of SYMMODES for the pair I4/mmm -- C2/m (**-b-c,a,c**;000) and the Wyckoff positions 8i.

Symmetry Modes for group - subgroup pair *I4/mmm*(139)>*C2/m*(12)

Initial Data:

Group	*I4/mmm* (139)
Subgroup	*C2/m* (12)
Transformation Matrix	-b-c, a, c (read it by colums)
Wyckoff Positions	8i

Symmetry Modes Summary

WP	Modes
8i	GM1+(1) GM2+(1) **GM5+(1)**

Note: The primary mode is written in bold letters

K vector: GM = (0,0,0)

Irrep GM1+
Order Parameter (a)
Isotropy Subgroup H 139 I4/mmm D4h-17

Transformation Matrix
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

WP 8i	Displacements
(x,0,0)	(1,0,0)
(-x,0,0)	(-1,0,0)
(0,-x,0)	(0,-1,0)
(0,x,0)	(0,1,0)

Irrep GM2+
Order Parameter (a)
Isotropy Subgroup H 71 Immm D2h-25

Transformation Matrix
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

WP 8i	Displacements
(x,0,0)	(1,0,0)
(-x,0,0)	(-1,0,0)
(0,-x,0)	(0,1,0)
(0,x,0)	(0,-1,0)

Irrep GM5+
Order Parameter (a,0)
Isotropy Subgroup H 12 C2/m C2h-3

Transformation Matrix
$$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

WP 8i	Displacements
(x,0,0)	(0,0,0)
(-x,0,0)	(0,0,0)
(0,-x,0)	(0,0,1)
(0,x,0)	(0,0,-1)

(Show splitting)

This ouput gives first a "Symmetry Modes Summary" listing the irreps corresponding to the displacive modes allowed for the chosen Wyckoff position(s), and highlighting in bold letters the active irrep, i.e. the one having C2/m as isotropy subgroup. We can see that modes of symmetry GM_1+, GM_2+ and GM_5+ are allowed for 8i sites in the distorted structures, in agreement with Table 13.

The output then lists for each irrep the corresponding isotropy subgroup with its transformation matrix, the eventual restriction on the direction within the irrep space (this is the data headed as "order parameter"), and a set of linearly independent modes having this irrep as symmetry.

The form of the modes are given as a column of triads indicating the correlated displacements of the atoms of the Wyckoff orbit extended to the primitive unit cell of the distorted phase. As the distorted phase in our example has the same primitive unit cell ($i_k = 1$) than the parent phase, the set of listed atomic positions is limited to 4. The other atoms in the structure belonging to the same orbit are related by lattice translations to those listed in the output and their mode displacements will have the same displacements.

The components of the atomic displacements describing the modes are given in the setting of the parent structure. Modes are not normalized and, in the case of existing several modes for the same irrep, they are not orthogonalized.

We can see in Table 15 that for 8i atoms, there is only a single mode with the symmetry of the active irrep. It involves displacements along the z-axis of only 2 of the 4 atoms within a primitive unit cell. Only atoms with non-zero y-component have non-zero displacements. Atoms with opposite y-components have opposite displacements along z.

Modes GM_1+ and GM_2+ are restricted to the xy plane. As it should be, GM_1+ displaces the atoms in such a way that their components will maintain the I4/mmm symmetry relation described in the first column. In contrast, the mode GM_2+ mode breaks this relationship: (x,0,0) and (0,x,0) sites have (0,1,0) and (0,-1,0) displacements respectively.

From this output one expects that the atoms 8i of type (0,x,0) in the I4/mmm structure and their related ones by the I centring will suffer displacements along the c axis much stronger than along the y axis, the only two directions allowed (always working in the tetragonal setting), because the z-displacements correspond to the primary mode with the symmetry of the active irrep, and will be in principle related with the transitions mechanism. The atoms with positions (x,0,0) and the related ones by the I centring, on the other hand, will only have secondary displacements along the x-direction, that maintain the symmetry relation among them.

SYMMODES also allows to examine the splitting of the Wyckoff orbit due to the symmetry decrease, by means of a link to the program WYCKSPLIT of the server:

Table 16 : Splitting of orbits 8i for the symmetry break I4/mmm -- C2/m (**-b-c**,**a**,**c**;000)

		Wyckoff position(s)	
	Group	Subgroup	More...
1	8i	4g 4i	Relations

Table 17: Detailed splitting of orbits 8i for the symmetry break I4/mmm -- C2/m (-b-c,a,c;000)

No	Representative group basis	Representative subgroup basis	Subgroup Wyckoff position name[n]	Subgroup Wyckoff position representative
1	$(x, 0, 0)$	$(0, x, 0)$		$(0, y_1, 0)$
2	$(-x, 0, 0)$	$(0, -x, 0)$		$(0, -y_1, 0)$
3	$(x+1/2, -1/2, -1/2)$	$(1/2, x+1/2, 0)$	$4g_1$	$(1/2, y_1+1/2, 0)$
4	$(-x+1/2, -1/2, -1/2)$	$(1/2, -x+1/2, 0)$		$(1/2, -y_1+1/2, 0)$
5	$(0, x, 0)$	$(-x, 0, -x)$		$(x_2, 0, z_2)$
6	$(0, -x, 0)$	$(x, 0, x)$		$(-x_2, 0, -z_2)$
7	$(1/2, x-1/2, -1/2)$	$(-x+1/2, 1/2, -x)$	$4i_1$	$(x_2+1/2, 1/2, z_2)$
8	$(1/2, -x-1/2, -1/2)$	$(x+1/2, 1/2, x)$		$(-x_2+1/2, 1/2, -z_2)$

The last column in Table 17 describes the generic positions of the two splitted orbits in the subgroup basis, while the third column indicates the corresponding position in the higher I4/mmm structure. One can see that the first 4 positions forming the $4g_1$ orbit do not really break the tetragonal symmetry; their only allowed variation of the y component (in the subgroup basis) is also compatible with the tetragonal space group. On the other hand, the other four positions forming the $4i_1$ orbit introduce an additional degree of freedom by breaking the correlation between the x and z components (in the subgroup basis). The number of symmetry free components in the two orbits is 3. This should coincide with the number of distinct modes listed in Table 15. In general, the number of modes should be equal to the number of degrees of freedom for the 8i atomic positions in the subgroup, and this is the number of free parameters in the resulting Wyckoff orbits in the subgroup symmetry.

Even if we are not interested in the displacive modes present in the distorted phase, SYMMODES can still be used to obtain important information on the active and secondary irreps relevant for a given symmetry break. The information is more complete than in COPL as the transformation matrices for each isotropy subgroup are also listed. But a caution note should be added: SYMMODES only lists the compatible irreps which can be associated to displacive modes of the Wyckoff positions chosen. If we are interested in all the irreps compatible with the symmetry reduction, it is convenient to choose a general Wyckoff orbit, in order to have as many symmetry allowed displacive modes as possible. In most cases this will be sufficient to get all compatible irreps, but in some cases some compatible irreps may not be involved in any atomic displacements, and then it will not be listed by SYMMODES.

Exercise 2: Using SYMMODES show that only two of the six space groups listed in Table 12 are isotropy subgroups of Fm-3m, and therefore only for these two subgroups a single active irrep can be identified. These two space groups should be therefore the two first obvious choices for the symmetry of the orthorhombic phase of the fullerene-cubane crystals.

Exercise 3: As a continuation of exercise 1, check using SYMMODES that the space group you have determined in exercise 1 is an isotropy subgroup. Identify the wave vector and the label of the active irrep of the transition, and check by hand that indeed this irrep yields the superlattice that has been observed.

Exercise 4: A compound with parent symmetry Pmmm exhibits a sequence of phase transitions into two phases with superstructures having their parameter b multiplied by 4 and 3, respectively. The two phases are due to a distortion which varies its wave vector along **b***, but keeps the same rotational symmetry given by the same small irrep (only the modulus of the wave vector changes). The space group of the phase with b-parameter = 4b has been identified as Pmmb keeping the same setting (or Pmma in conventional setting). The experiments indicate that the phase with the b-parameter = 3b is also orthorhombic. Using SYMMODES and CELLSUB predict the space group of this second phase. Show that it will be ferroelectric with the polar axis along the z axis (in the original setting).

Exercise 5: Monoclinic phase of the system $PbZr_{1-x}Ti_xO_3$
Consider the perovskite-like ferroelectric system $PbZr_{1-x}Ti_xO_3$ (PZT). Some measurements have revealed a monoclinic phase (with no cell multiplication) between the previously established tetragonal (P4mm) and rhombohedral (R3m) regions in its phase diagram as a function of x. Both phases, P4mm and R3m, are ferroelectric distorted phases of the perovskite, due to the condensation of a polar mode of symmetry at **k**=0. The perfect perovskite structure $PbBO_3$ is cubic Pm-3m (Z=1) with positions: pb 1b, B 1a, O 3d.

(i) If you have difficulties to derive directly the index of the subgroups P4mm and R3m with respect to their parent space group Pm-3m, use POINT to obtain the order of the point groups m-3m, 4mm and 3m, and from them, obtain the t-index. This t-index multiplied by the relevant k-index will give you the necessary index to use in SYMMODES.
(ii) Using SYMMODES obtain a valid transtormation matrix for the pairs Pm-3m -- P4mm, and Pm-3m -- R3m, and check that indeed the two phases, P4mm and R3m, can be assigned to the same active irrep, for two different directions of the order parameter. Take notice of the active irrep and these directions.
(iii) A reasonable assumption about the detected monoclinic structure is that it must be some bridging phase with the order parameter changing between the two special directions obtained in (ii). Its symmetry would then be given by a common subgroup of the tetragonal and rhomboedral space groups. Use COMMONSUBS to predict under this assumption the space group of the monoclinic phase. Take notice of the transformation matrix relating it with the space group P4mm.
(v) From the transformation matrices for the pairs Pm-3m --- P4mm and P4mm --- monoclinic space, obtain the transformation matrix relating Pm-3m and the monoclinic space group. Using SYMMODES again demonstrate that the active irrep of the postulated monoclinic space group is indeed the same as for the other two phases. Compare the order parameter direction with those obtained in (ii)
(vi) Use TRANSTRU to derive a starting structural model of the monoclinic phase (with a single mixed site for the Zr/Ti atoms), which you could use as the starting point for a refinement of the structure.

3. Symmetry breaks with several active irreps

As already mentioned above, there may be some symmetry breaks that do not fulfill the Landau postulate of having a single active irrep. In other words, the symmetry reduction cannot be explained by a single irrep, as the symmetry of the distorted phase is not an isotropy subgroup of the parent space group. If the transition is discontinuous or first order, there are indeed mechanisms that can explain the breaking of the Landau postulate and predict the simultaneous condensation of two irreps. However, these situations are rare, and the most plausible explanation for such cases is that the condensation of the two active irreps is in fact stepwise and an intermediate phase has been overlooked

Independently of the existence or not of an intermediate phase, the existence of two active irreps implies a scenario, where several degrees of freedom of the structure are independently unstable in the high-symmetry configuration. This is bound to produce rich phase diagrams.

Let us consider the example of the Aurivillius compound $SrBi_2Ta_2O_9$. The compound is known to have a tetragonal I4/mmm phase at high-temperatures with Z=2, and at room temperature crystallizes in the subgroup $Cmc2_1$ (c, a-b,a+b; ¼,¼,0) with Z=4. Using SYMMODES we can obtain the following information about the intermediate subgroups relating this group-subgroup pair (note that there are two $Cmc2_1$ classes with the same type of cell transformation, and only distinguishable by the origin shift. So one has to take care of choosing the correct one)

Figure 2: Graph of minimal subgroups connecting the space group I4/mmm and its subgroup $Cmc2_1$ (**c**, **a-b**,**a+b**; ¼,¼,0) (or equivalent), obtained with SUBGROUPGRAPH.
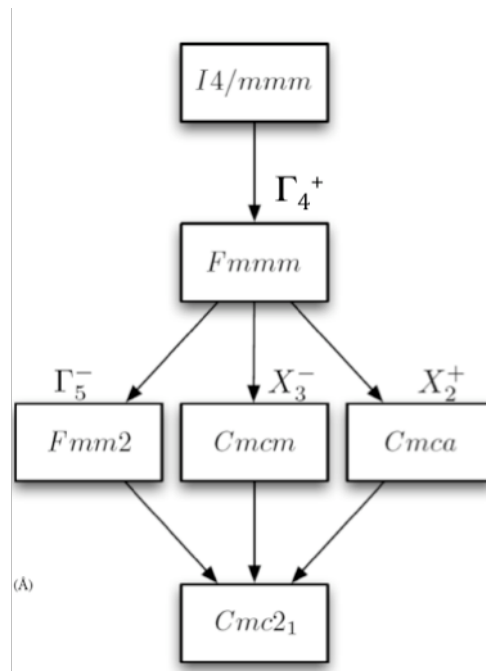
Again here the new program SUBGROUPS can speed up the analysis

(Note: The group Cmca (N. 64) is labelled Cmce in the new convention of the last version of the International Tables of Crystallography)

For each of the subgroups, we have indicated in Figure 2 the corresponding active irrep, if existing. The graph shows then that all subgroups are isotropy subgroups for some irrep, except for the actual observed symmetry. The room temperature phase requires therefore several active irrep. How many? Just two. The effective symmetry resulting from the presence of two of the distortions is the intersection of the two corresponding isotropy subgroups, and this is given in the graph by their first common subgroup. Hence, it is sufficient to consider any pair of the distortions Γ_5^-, X_3^- and X_2^+, to reach the symmetry Cmc2_1. Only the irrep Γ_4+ cannot be relevant for producing the observed symmetry Cmc2_1. i.e. its addition to any of the other ones, does not decrease further the symmetry.

We have therefore three possible irreps among which two must be the active ones. Symmetry considerations cannot go further. Only a quantitative analysis of the structure, ab-initio calculations, or the thermal behaviour of the system can indicate which of the three irreps are really the active irreps in this specific case. The distortions having the symmetry of the active irrep are expected to have larger amplitudes, and be the ones that are unstable in the high-symmetry configuration. For instance, a decomposition of the Cmc2_1 structure of $SrBi_2Ta_2O_9$ in terms of symmetry-modes, done with AMPLIMODES, shows that the distortions of symmetry Γ_5^- and X_3^- have much larger amplitude than the one for the irrep X_2^+. Furthermore, the X_3^- distortion is significantly larger than the Γ_5^-. Therefore we can identify X_3^- and Γ_5 as the active irreps. The additional X_2^+ spontaneous distortion present in the experimental structure can be considered a secondary effect, essentially induced by the presence of the other two primary distortion modes

As the X_3^- distortion is the largest one we expect it to be the one that thermalizes to zero value at higher temperatures, and therefore we can infer that an intermediate phase with symmetry Cmcm is highly probable, corresponding to the presence of only this active irrep. Indeed this intermediate phase has been observed! The other mode Γ_5^- is the irrep E_u in the notation of the Tables of the program POINT. It corresponds to the symmetry properties of a vector on the plane xy, and therefore is a polar instability, that can produce a spontaneous polarization (its isotropy subgroup Fmm2 is polar along the (1,1,0) direction in the tetragonal setting). This Γ_5^- polar distortion is then the fundamental mechanism causing the lost of the inversion centre in the room-temperature structure, and the ferroelectric properties of the room temperature phase

Exercise 6: A compound has *Pnma* symmetry at high temperatures and has space group *P12$_1$1* at low temperatures, keeping essentially the same lattice, except for some strain. Using SYMMODES obtain the graph of minimal subgroups relating both symmetries. Check that at least two irreps must be active to explain the symmetry of the distorted structure. Indicate the possible pairs of active irreps in the distorted phase. Indicate the possible (alternative) symmetries of a probable intermediate phase.

Exercise 7: The multiferroic $BiFeO_3$ has symmetry R3c with Z=6 at room-temperature, having at high temperatures the cubic perovskite configuration (Fe: 1a, Bi: 1b, O: 3d).
(i) Using SYMMODES, show that the room temperature phase of $BiFeO_3$ has two active irreps, one being the usual R4+ mentioned above, and the other one is the one discussed in exercise 5, present in BaTiO3.

(ii) Some publications have reported an intermediate phase with symmetry I4/mcm. Crosscheck the consistency of this intermediate symmetry with your previous results.
(iii) With TRANSTRU produce a starting structural model to refine the structures I4/mcm and R3c of BiFeO3, indicating the refinable coordinates of the constructed asymmetric unit.