

POSSIBLE SYMMETRIES OF A DISTORTED PHASE WITH A KNOWN SUPERCELL (OR KNOWN MODULATION WAVE VECTOR(S)). TUTORIAL ON THE USE OF THE PROGRAM *SUBGROUPS* AT THE BILBAO CRYSTALLOGRAPHIC SERVER (www.ehu.es):

L. Elcoro, J.M. Perez-Mato and M.I. Aroyo

Depto. Física de la Materia Condensada, Fac. de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apdo. 644, Bilbao, Spain.

SUBGROUPS is a freely available program at the Bilbao Crystallographic Server (www.cryst.ehu.es), which allows to determine and explore online all possible symmetries of a structure that can result from the distortion of a parent structure of higher symmetry, if the relation of its lattice with respect to the one of the parent structure is known (or alternatively, the modulation wave vector(s) present in the distortion are given).

The minimal input required is the space group of the parent structure (parent space group) and the supercell defining the lattice of the distorted structure with respect to the one of the parent space group. The program then provides all possible symmetries consistent with the given supercell, defined as subgroups of the parent space group, and it can show their complete group-subgroup hierarchy. The set of physically equivalent subgroups within each conjugacy class, which are compatible with the given supercell, can also be retrieved. The irreducible representations (irreps) of the parent space group compatible with each of the listed possible symmetries can also be obtained.

Alternatively, instead of a supercell, the relation of the lattice of the distorted structure with respect to the lattice of the parent structure can be given introducing the set of wave vectors, which can describe all the extra superstructure reflections (commensurate *satellite reflections*) observed in the diffraction diagram, when compared with the one of the parent structure (if the lattice is maintained a zero wave vector should be given).

The possible subgroups provided by the program can be filtered according to different criteria, the most important ones being:

- i) Subgroups that are possible for displacive distortions if the atoms of the parent structure only occupy some specific special Wyckoff positions.
- ii) Subgroups down to a given crystalline class or a given point group.
- iii) Subgroups that can be the result of an order parameter fulfilling the Landau condition of transforming according to a single irreducible representation (irrep) of the parent space group.
- iv) In the case that the input includes the definition of the active wave vectors: subgroups that can be realized by the action of an order parameter transforming according to one (or several) chosen irrep(s) of the parent space group for the input wave vector(s).

Additionally the possible subgroups can be restricted considering some particular property of the distorted phase, as for instance being polar or non-polar, centrosymmetric or non-centrosymmetric, proper ferroelastic, etc.

Below a set of examples on the use of the program are discussed in detail. In order to minimize overlapping and redundancies, these examples are in general presented and explained assuming that they are read one after the other in the order that are presented, so that in general the features that are discussed in one example are not explained again in the subsequent ones. Therefore, it is convenient to read the examples below in the given order.

Example 1: Possible symmetries of the low temperature phase of a fullerene-cubane crystal.

Crystals that include both molecules of fullerene and cubane 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 the disordered cubane molecules at 4b (1/2 1/2 1/2) (Nature Mat. 4, 764 (2005)). At low temperature, as the molecules become ordered, the system exhibits a couple of phase transitions. From powder diffraction experiments, the symmetry of the final phase has been reported to be an orthorhombic structure, with the lattice parameters of its primitive orthorhombic unit cell satisfying the approximate relations: $a \approx b \approx a_c/\sqrt{2}$, while $c \approx 2a_c$. However, the phase 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 or most probable space groups, we could have a better chance of succeeding in the interpretation and analysis of its diffraction diagram. The program SUBGROUPS is designed to deal with such type of problems, and can be used for this specific example in the following way:

Subgroups: Subgroups compatible with a given supercell or some propagation vector(s).

Subgroups

The program *Subgroups* provides the possible subgroups of a space group which are possible for a given **supercell**. The program provides a list of the set of space groups or a graph showing the group-subgroup hierarchy, grouped into conjugacy classes. More optional information about the classes or subgroups is also given.

Other alternatives for the input of the program:

Instead of the whole set of subgroups, the output can be limited to subgroups having a chosen common subgroup of lowest symmetry, common point group of lowest symmetry, or groups which belong to a specific crystal class.

Enter the serial number of the space group:

Alternatively give the operations of the space group in a non-standard setting

Introduce the supercell

Alternatively give the modulation wave-vectors

$a_s =$	$b_s =$	$c_s =$	
<input type="text" value="1/2"/> a	<input type="text" value="1/2"/> a	<input type="text" value="0"/> a	
+	+	+	The supercell is centred:
<input type="text" value="-1/2"/> b	<input type="text" value="1/2"/> b	<input type="text" value="0"/> b	<input type="button" value="P"/>
+	+	+	
<input type="text" value="0"/> c	<input type="text" value="0"/> c	<input type="text" value="2"/> c	

a) Introduce in the first input page of SUBGROUPS the parent space group $Fm-3m$ (N. 225) and the lattice supercell, which must be $a_s=1/2a-1/2b$, $b_s=1/2a+1/2b$, $c_s=2c$, and set this supercell as primitive in the corresponding centering option (the basis of the supercell must keep the assumed right-handedness of the parent basis). Leave all additional options in their default values (notice that the *Bilbao crystallographic server* in general, and this program in particular, follows the convention of the *International Tables for Crystallography*, and consequently, the transformed vectors defining the unit cell basis, when expressed in the form of a 3x3 matrix, are the columns of the matrix, and not the rows). By clicking the "submit" button at the bottom with "List of subgroups" chosen by default, a list of all possible subgroups of $Fm-3m$ (actually conjugate classes of subgroups) consistent with the observed supercell is obtained.

The list of subgroups provided by the program for these conditions is very numerous (99 subgroups) as it goes down up to the minimal symmetry of P1. This number is still workable, and the program can deal with up to several hundreds,

but it must be warned that, if the supercell is very large with respect to the parent one, the number of subgroups may increase so much that the maximum running time allocated for the program will be reached and the program will stop without yielding any result.

In our example, let us reduce the list by going back to the page of the previous menu and set the option “*Lowest crystal system to consider*” to *orthorhombic*. The list is now reduced to 62 subgroups. Most of them can still be discarded, as the observed diffraction symmetry is orthorhombic, and the list includes all subgroups belonging to crystal systems of higher symmetry. Being orthorhombic, the point group of the possible space group within the list can only be *222*, *mm2* or *mmm*. To simplify, we are going to assume that the relevant point group symmetry is the maximal one: *mmm* (we could proceed similarly with the other two possible point groups if necessary).

b) In order to select from the whole set of possible subgroups those with point group *mmm*, go back to the first input page and select the option: “Lowest point group to consider” and introduce the point group “*mmm*”.

Optional:

refine further the subgroups of the output giving the Wyckoff positions of the atoms

Give the Wyckoff positions Wyckoff

Optional: Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter).

Possible limitations of the subgroup list.

(Check only one option on the left and the specific value on the right)

(Check only one option on the left and the specific value on the right)

Lowest space group to consider choose it 1

Lowest point group to consider 8: mmm

Lowest crystal system to consider -----

Only maximal subgroups

The list is then reduced to 20 subgroups, which are shown as an interactive list or, if the button “Graph of subgroups” is clicked, as a graph showing the group-subgroup hierarchy of these 20 subgroups:

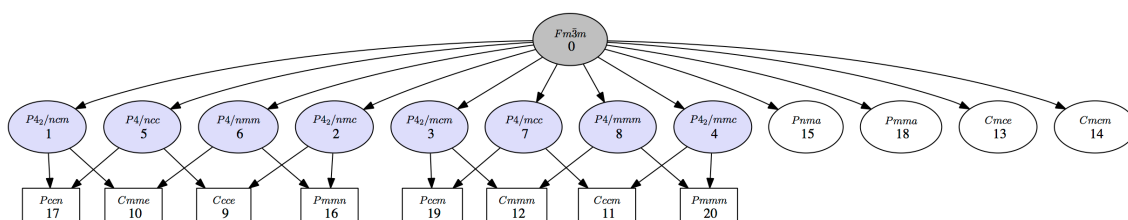


Figure 1.1. Graph obtained with SUBGROUPS showing the group-subgroup hierarchy of all possible symmetries of a structure resulting from the distortion of a cubic structure with space group *Fm-3m*, restricted to those having a primitive supercell ($1/2a-1/2b$, $1/2a+1/2b$, $2c$) or equivalent, and with a point group *mmm* or higher.

The list includes all subgroups with point group *mmm* or higher. The tetragonal groups can be discarded, and the orthorhombic ones that are C centred can also be dropped: the unit cell is known to be primitive, with the orthorhombic axes along the oblique supercell basis vector directions, while the C centered groups have their orthorhombic symmetry axes along the parent cubic *a,b,c* directions, instead of the desired oblique directions (notice that these subgroups have been correctly included by the program in the previous list because they have as primitive unit cell the one that we have introduced). We are then left with 6 possible symmetries, shown in Figure 1.2.

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps
15	<i>Pnma</i> (No. 62)	$\begin{pmatrix} 0 & 1/2 & -1/2 & 0 \\ 0 & 1/2 & 1/2 & 1/4 \\ 2 & 0 & 0 & -1/4 \end{pmatrix}$	24=4x6	Conjugacy Class	Get irreps
16	<i>Pmmn</i> (No. 59)	$\begin{pmatrix} 1/2 & -1/2 & 0 & 0 \\ 1/2 & 1/2 & 0 & 1/4 \\ 0 & 0 & 2 & -1/4 \end{pmatrix}$	24=4x6	Conjugacy Class	Get irreps
17	<i>Pccn</i> (No. 56)	$\begin{pmatrix} 1/2 & -1/2 & 0 & 0 \\ 1/2 & 1/2 & 0 & 1/4 \\ 0 & 0 & 2 & -1/4 \end{pmatrix}$	24=4x6	Conjugacy Class	Get irreps
18	<i>Pmma</i> (No. 51)	$\begin{pmatrix} 0 & 1/2 & -1/2 & 0 \\ 0 & 1/2 & 1/2 & 0 \\ 2 & 0 & 0 & 1/2 \end{pmatrix}$	24=4x6	Conjugacy Class	Get irreps
19	<i>Pccm</i> (No. 49)	$\begin{pmatrix} 1/2 & -1/2 & 0 & 0 \\ 1/2 & 1/2 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	24=4x6	Conjugacy Class	Get irreps
20	<i>Pmmm</i> (No. 47)	$\begin{pmatrix} 1/2 & -1/2 & 0 & 0 \\ 1/2 & 1/2 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	24=4x6	Conjugacy Class	Get irreps

Figure 1.2. Fragment of the list of subgroups obtained with SUBGROUPS, showing the possible space group symmetries of a structure with point group *mmm*, resulting from the distortion of a cubic structure with space group *Fm-3m*, and having as primitive unit cell a supercell (1/2a-1/2b, 1/2a+1/2b, 2c) or equivalent. The symmetries are described as subgroups of the space group *Fm-3m*. Each subgroup is a representative of a set of subgroups that are physically equivalent and belong to the same conjugacy class (see text).

In the third column of the tabulated list a transformation (**P,p**) is given for each subgroup, where **P** is a 3x3 matrix and **p** = (p₁, p₂, p₃) a column vector. This transformation indicates in each case a choice of unit cell and origin, for which the subgroup acquires the standard setting of the corresponding space group type indicated in the second column. This means that the symmetry operations of this subgroup of the parent space group, when described using this unit cell and origin, take the form used for this space group type in the International Tables for Crystallography, vol. A (ITA), which we take as the standard setting of this space group (see www.cryst.ehu.es/cgi-bin/cryst/programs/nph-def-choice for more information on the standard settings chosen in the Bilbao crystallographic server in the case of space groups where several choices are allowed in the ITA). The transformation (**P,p**) is defined with respect to the unit cell (**a_p,b_p,c_p**) and origin **O_p** of the parent space group, in the following form:

$$(\mathbf{a}^s, \mathbf{b}^s, \mathbf{c}^s) = (\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p) \cdot \mathbf{P} \quad , \quad \mathbf{O}^s = \mathbf{O}_p + p_1 \mathbf{a}_p + p_2 \mathbf{b}_p + p_3 \mathbf{c}_p$$

where $(\mathbf{a}^s, \mathbf{b}^s, \mathbf{c}^s)$ and \mathbf{O}^s are the unit cell basis vectors and origin for which the subgroup operations take the form of the standard setting of its space group type. This means, as stressed above, that the transformed basis vectors are given by the columns of the matrix (not the rows).

The fourth column in the output list of subgroups indicates the subgroup index, i.e. the factor relating the number of operations in the parent space group with the one in the subgroup. The subgroup index is separated in two factors, the first one relating the two lattices, and the second one the two point groups. Thus in this case, the first factor is always 4, as it is the approximate volume ratio between the primitive unit cells of the parent and the searched distorted structure, while the second factor is 6, which is the index or reduction factor of the mmm point group (with 8 operations) as subgroup of the parent cubic point group $m-3m$ (with 48 operations). This subgroup index defines the number of distinct domains that can be expected in a distorted phase with this subgroup symmetry. The first factor determines the number of distinct antiphase domains related by lattice translations (not distinguishable in diffraction experiments), while the second one defines the number of distinct twins or domains associated with lost rotational or roto-inversion symmetry operations.

A button in the fifth column allows to obtain a listing of the conjugacy class of subgroups, from which the one listed in the Table is a representative. It is very important to stress that in general this listing does not include the whole conjugacy class, as **it is restricted to the conjugate subgroups that are compatible with the supercell introduced in the input. Conjugate subgroups belonging to the conjugacy class but with orientations such that their supercell does not coincide with the one of the input, are NOT shown.** In general, all subgroups within a conjugacy class are physically equivalent, and one can select arbitrarily any of them to describe the distorted phase. The program makes an arbitrary choice of the class representative and this is the subgroup given in the output list shown in Figure 1.2. Therefore, the first list provided by the program can be considered a list of conjugacy classes of subgroups, which are compatible with the sublattice defined by the input supercell.

It is important to stress that the hierarchical group-subgroup graph that can optionally be retrieved, as the one shown in Figure 1.1, represents group-subgroup relations between pairs of unspecified subgroups belonging to the corresponding conjugacy classes labelled by their representatives. Therefore, in general they do NOT imply a group-subgroup relation between the specific subgroups that are listed as conjugacy class representatives in the accompanying list. In order to obtain more detailed graphs of group-subgroup relations between specific subgroups, one has to use instead the graph options appearing when the corresponding conjugacy class is listed by clicking in the fifth column on this list. We will keep these options unused in this example.

The last column in the listing shown in Figure 1.2 with the button “*Get irreps*” links directly with a separate program of the *Bilbao Crystallographic Server* with this name, which can help to limit further the most probable symmetry of the investigated structure, as shown in the next steps.

c) Click the button “Get_irreps” for the first of the subgroups in Figure 1.2, the one of type *Pnma*. By clicking on this button one gets the irreducible representations (irreps) of the parent structure that are compatible with this specific symmetry for the distorted structure. This means that one gets the irreps that can characterize the degrees of freedom allowed by this symmetry, and that in accordance with Von Neumann principle are set free in a distorted structure with its symmetry described by this subgroup. The output is organized in the form of a Table. Its first column indicates the star of wave vectors of the irrep. The wave vector(s) that are involved with the chosen symmetry are highlighted in bold. The second column indicates the label of the irrep, and in parenthesis the subspace within the irrep space into which the irrep distortion (order parameter) must be constrained.

List of physically irreducible representations and order parameters between a parent group and a given subgroup.

Input data

Group→subgroup	Transformation matrix
$Fm\bar{3}m$ (N. 225)→ $Pnma$ (N. 62)	$\begin{pmatrix} 0 & 1/2 & -1/2 & 0 \\ 0 & 1/2 & 1/2 & 1/4 \\ 2 & 0 & 0 & -1/4 \end{pmatrix}$

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)	$Fm\bar{3}m$ (No. 225) a,b,c;0,0,0	matrices of the irreps
	GM ₃ ⁺ : (a,0)	$I4/mmm$ (No. 139) a/2-b/2,a/2+b/2,c;0,0,0	
	GM ₅ ⁺ : (a,0,0)	$Immm$ (No. 71) a/2+b/2,-a/2+b/2,c;0,0,0	
DT: (0,1/2,0)(1/2,0,0) (0,0,1/2)	DT ₅ : (0,0,0,0,0,0,0,0,a,0,0,a)	$Pnma$ (No. 62) 2c,a/2+b/2,-a/2+b/2;0,1/4,-1/4	matrices of the irreps
X: (0,1,0)(1,0,0) (0,0,1)	X ₂ ⁻ : (0,0,a)	$P4_2/nmc$ (No. 137) a/2-b/2,a/2+b/2,c;0,1/4,1/4	matrices of the irreps
	X ₃ ⁻ : (0,0,a)	$P4/nmm$ (No. 129) a/2-b/2,a/2+b/2,c;1/4,0,1/4	

Figure 1.3. Output when calling to the program “Get_irreps” for the subgroup of *Fm-3m* of type *Pnma* indicated in Figure 1.2. One can see that the actual *Pnma* subgroup is among the listed compatible irrep isotropy subgroups, and therefore this symmetry can be attained by an order parameter associated with the corresponding irrep, namely DT5. The wave vector (0,0,1/2), shown in bold, within the set of wave vectors of the irrep (irrep star) is the only one involved in the necessary irrep distortion.

The actual irrep matrices, which are being chosen for the description of the relevant irreps, can be consulted by clicking in the corresponding button “matrices

of the irreps" in the last column of the table. This is a direct link to the database REPRESENTATIONS SG, where the matrix form that is being used for the irrep can be retrieved.

The irrep labels are those being also used by the ISOTROPY suite (iso.byu.edu), but the specific matrix form of the irreps, which depends on the choice of basis, may differ from the one chosen in that reference. Therefore it is important to stress that the symbol for the order parameter direction in the second column, which depends on the matrix choice for the irrep, is not necessarily the same as in ISOTROPY. Finally, in the third column one can consult the so-called isotropy subgroup associated with each of the listed compatible irreps. These *irrep isotropy subgroups* of the parent space group, also expressed as a space group type and a transformation (P,p) to its standard setting, are the symmetries that would result from the only presence in the structure of an order parameter transforming according to the corresponding irrep (restricted to the indicated subspace). By definition, all these subgroups must be strict supergroups of the actual subgroup being analysed, or coincide with it.

Distorted phases very often comply with the Landau assumption that their symmetry is the result of an order parameter transforming according to a single irrep. Thus, symmetries that can be reached by the onset of a single irrep are more probable. In Figure 1.3, one can see that the isotropy subgroup of one of the compatible irreps, namely DT5, coincides with the actual subgroup of type $Pnma$ that is being analyzed. This implies that the symmetry break $Fm-3m \rightarrow Pnma$ ($2c, -1/2a+1/2b, -1/2a-1/2b; 0, \frac{1}{4}, -\frac{1}{4}$) can be realized through a Landau type phase transition, with an order parameter having the transformation properties of the DT5 irrep (within the specified direction). This is clearly seen if one clicks on the option "show the graph of isotropy subgroups" available in the Get_irreps output, as we do in the next step.

d) Click on the graph button of the output represented in Figure 1.3.

This provides a graph of the group-subgroup hierarchy between the parent space group and the analysed subgroup, with all intermediate subgroups included, as shown in Figure 1.4. The isotropy subgroups in the list are highlighted in the graph by adding the associated irrep or irreps in parenthesis below their label. In the present case, the end node of the graph, which is the analysed subgroup $Pnma$, includes an irrep label, showing that it can be directly reached by the onset of an order parameter associated with the indicated irrep.

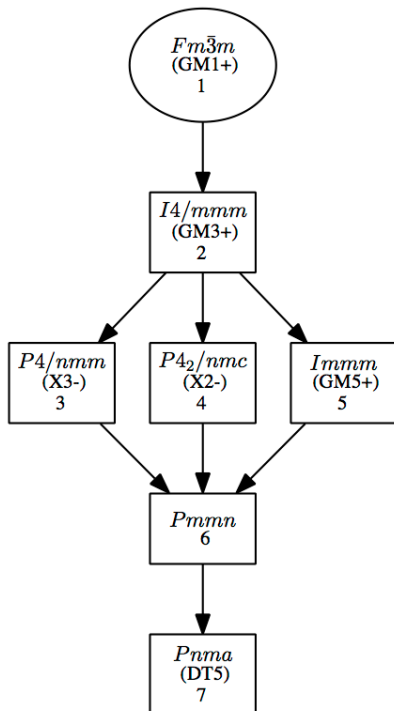


Figure 1.4. Output of the graph option in the output of “Get_irreps” for the subgroup of $Fm\bar{3}m$ of type $Pnma$ indicated in Figure 1.2. One can see that this $Pnma$ subgroup is among the listed irrep isotropy subgroups, with the relevant irrep DT5 shown in parenthesis below the space group label. Therefore this symmetry can be attained by an order parameter associated with this single irrep, in accordance with Landau theory.

e) Use the “Get irreps” option for the other possible symmetries shown in Figure 1.2. You will then see that only two of the six possible symmetries shown in Figure 1.2 can be the result of a single irrep order parameter and therefore fulfill the Landau condition, i.e. they can be the result of a Landau-type phase transition. These are namely those of type $Pnma$ and $Pmma$. The listings that you will obtain show that both of them can be the result of the condensation of an order parameter characterized by the irrep DT5:

DT5

$Fm\bar{3}m \dashrightarrow Pnma (2c, -1/2a+1/2b, -1/2a-1/2b; 0, 1/4, -1/4)$

DT5

$Fm\bar{3}m \dashrightarrow Pmma (2c, -1/2a+1/2b, -1/2a-1/2b; 0, 0, 1/2)$

These two symmetry breakings are therefore the two first choices to explore for the investigated phase. Of course, the other four orthorhombic symmetries are also possible but they necessarily require the action of more than one irrep, i.e. the presence of at least two order parameters. For instance, the “Get irreps” output for the symmetry $Pmnn (1/2a+1/2b, -1/2a+1/2b, 2c; 0, 1/4, -1/4)$ is shown in Figure 1.5. One can see that this symmetry is not realized by any of the listed compatible irreps, and this particular symmetry break requires more than one irrep.

List of physically irreducible representations and order parameters between a parent group and a given subgroup.

Input data

Group→subgroup	Transformation matrix
$Fm\bar{3}m$ (N. 225)→ $Pmnn$ (N. 59)	$\begin{pmatrix} 1/2 & -1/2 & 0 & 0 \\ 1/2 & 1/2 & 0 & 1/4 \\ 0 & 0 & 2 & -1/4 \end{pmatrix}$

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)	$Fm\bar{3}m$ (No. 225) a,b,c;0,0,0	matrices of the irreps
	GM ₃ ⁺ : (a,0)	$I4/mmm$ (No. 139) a/2-b/2,a/2+b/2,c;0,0,0	
	GM ₅ ⁺ : (a,0,0)	$Immm$ (No. 71) a/2+b/2,-a/2+b/2,c;0,0,0	
DT: (0,1/2,0)(1/2,0,0)(0,0,1/2)	DT ₁ : (0,0,0,0,a,a)	$P4/nmm$ (No. 129) a/2+b/2,-a/2+b/2,2c;0,1/4,-1/4	matrices of the irreps
	DT ₃ : (0,0,0,0,a,-a)	$P4_2/nmc$ (No. 137) a/2+b/2,-a/2+b/2,2c;0,1/4,-1/4	
X: (0,1,0)(1,0,0)(0,0,1)	X ₂ ⁻ : (0,0,a)	$P4_2/nmc$ (No. 137) a/2-b/2,a/2+b/2,c;0,1/4,1/4	matrices of the irreps
	X ₃ ⁻ : (0,0,a)	$P4/nmm$ (No. 129) a/2-b/2,a/2+b/2,c;1/4,0,1/4	

Figure 1.5. Output when calling to the program “Get_irreps” for the subgroup of $Fm\bar{3}m$ of type $Pmnn$ indicated in Figure 1.2. One can see that the $Pmnn$ subgroup is absent from the listed irrep isotropy subgroups compatible with this subgroup, and therefore this symmetry cannot be associated with a distorted phase resulting from a Landau-type phase transition.

f) Click on the graph button of the output represented in Figure 1.5 to show graphically the group-subgroup relations among the listed isotropy subgroups. The program then provides a list and a graph of all intermediate subgroups up to the chosen $Pmnn$. The list includes by definition all irrep isotropy subgroups listed in Figure 1.5, but also all other ones that are subgroup of the parent one and supergroup of the specific $Pmnn$. One can clearly see that all compatible irreps give place to intermediate subgroups, but none of them can be associated with the final symmetry being considered. In this case the symmetry break cannot be achieved with a single irrep, and the location of the irrep isotropy subgroups in this graph allows to identify which irreps can be relevant for the set of primary order parameters.

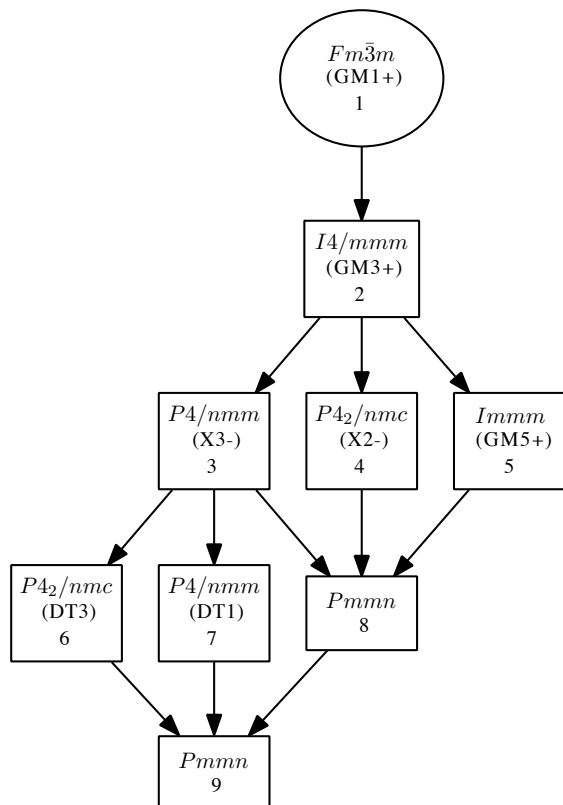


Figure 1.6. Part of the output obtained with the graph option after calling the program “Get_irreps” for the subgroup of $Fm\bar{3}m$ of type $Pmnn$ indicated in Figure 1.5. One can see that this subgroup can only be reached as the intersection of at least two isotropy subgroups for two different irreps

From Figure 1.6, one can derive the subgroup that is realized by the presence of any chosen pair of the irreps under scrutiny, namely, it is just the maximal subgroup in the graph that is a common subgroup of the isotropy subgroups corresponding to the two irreps. Hence, inspecting the graph shown in Figure 1.6, one can see that the $Pmnn$ symmetry, could be consequence of the presence of two order parameters transforming according to the irreps DT3 and DT1. But the following pairs of irreps could also do the same job: DT3 and X2-, DT1 and X2-, DT3 and GM5+, DT1 and GM5+. What is clear is that two irreps are sufficient for this specific symmetry break.

g) Do the same process as in the previous step for the other three possible symmetries not associated with a single irrep. Graphs of similar topology to the one of Figure 1.6 are to be obtained, showing also the need of two primary order parameters for these symmetry breaks. Similarly as in the case discussed above, identify the possible pairs of active irreps for the corresponding symmetry breakings.

h) Come back to the main menu of SUBGROUPS and choose the option “Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter)”, cancelling the previous limit of the lowest symmetry that had been introduced.

Optional: Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter).

Possible limitations of the subgroup list.

(Check only one option on the left and the specific value on the right)

(Check only one option on the left and the specific value on the right)

- Lowest space group to consider choose it 1
- Lowest point group to consider
- Lowest crystal system to consider
- Only maximal subgroups

This option allows to discard all possible symmetries that cannot be reached by the action of a single irrep distortion, and therefore cannot be the result of a phase transition fulfilling the basic condition of Landau theory: the onset of an order parameter transforming according to single irrep of the parent space group. This “Landau-type” filter allows to obtain directly all possible symmetries under this condition. In our case, one can see that this condition reduces the number of possible distinct symmetries from 99 to 31. The obtained list of 31 subgroups includes, as it should be, the subgroups $Pnma$ and $Pmma$, that we had already determined, in the previous steps, as possible symmetries for a Landau type transition. Thus, this filter allows to reach much rapidly the same conclusion. The other possible symmetries with point group mmm , which require more than one order parameter, are automatically excluded.

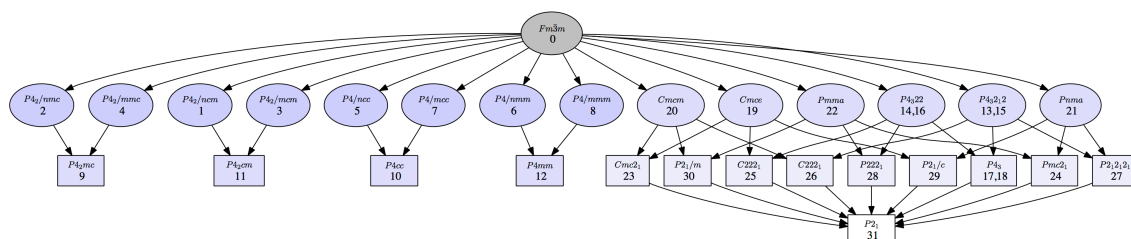


Figure 1.7. Graph obtained with SUBGROUPS showing the group-subgroup hierarchy of all possible symmetries of a structure resulting from the distortion of a cubic structure with space group $Fm-3m$, restricted to those having a primitive supercell ($1/2a-1/2b$, $1/2a+1/2b$, $2c$) or equivalent, and adding the condition that the symmetry should be possible for a Landau-type phase transition, i.e. the symmetry can be the result of the onset of an order parameter transforming according to a single irrep of the parent space group. From the six non-centered subgroups with point group mmm , appearing in Figures 1.1 and 1.2, only the subgroups of type $Pnma$ and $Pmma$ appear here, as they are the only ones that fulfill the Landau condition.

Summarizing, using the program SUBGROUPS we have been able to identify two possible space groups for the phase under investigation, which would be consistent with a Landau-type phase transition. Four additional possible space group symmetries have also been determined, but these alternative space groups require the action of two irreps, and therefore imply a more complex transition mechanism with two order parameters, either concomitant in a single transition or becoming spontaneous in two consecutive phase transitions.

Example 2. Possible symmetries with parent space group *Pnma* and a cell multiplication (a,b,2c)

Let us suppose that we observe a structure with symmetry *Pnma*, which exhibits when lowering the temperature a phase transition. Diffraction experiments in the low temperature phase give evidence of superstructure reflections, which can be indexed as (h, k, l+ 1/2). This additional diffraction peaks indicate a distortion which implies a duplication of the c parameter, while keeping an orthorhombic lattice, or equivalently a distortion with a modulation wave vector (0,0,1/2), when expressed in the basis of the parent reciprocal lattice. We wish to know the possible space group symmetries that this low temperature phase can have, in order to construct structural models that could fit the diffraction data.

a) Introduce in the input webpage of SUBGROUPS the space group *Pnma* N. 62 , as symmetry of the parent phase, and the supercell (a,b,2c), as primitive unit cell, of the observed distorted phase. Without any additional restriction the program lists 11 possible space group symmetries (Figure 2.1) given by the 11 possible subgroups of *Pnma* (in general, they are actually representatives of conjugacy classes of subgroups), which are consistent with the sublattice defined by the observed supercell. The format of this list was explained in the previous example of this tutorial.

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps
1	<i>Pca2</i> ₁ (No. 29)	$\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 1/4 \\ 2 & 0 & 0 & -1/4 \end{pmatrix}$	4=2x2	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
2	<i>Pmc2</i> ₁ (No. 26)	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1/4 \\ 0 & 2 & 0 & -1/4 \end{pmatrix}$	4=2x2	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
3	<i>P2</i> ₁ /c (No. 14)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	4=2x2	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
4	<i>P2</i> ₁ /m (No. 11)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	4=2x2	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
5	<i>Pc</i> (No. 7)	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & -1/4 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
6	<i>Pc</i> (No. 7)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
7	<i>Pm</i> (No. 6)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
8	<i>P2</i> ₁ (No. 4)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
9	<i>P2</i> ₁ (No. 4)	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 1/4 \\ 0 & 0 & 2 & -1/4 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
10	<i>P</i> $\bar{1}$ (No. 2)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
11	<i>P1</i> (No. 1)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	16=2x8	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>

Figure 2.1. List obtained with SUBGROUPS, showing the possible space group symmetries resulting from the distortion of a structure with space group *Pnma*, and having a supercell (a, b, 2c). The symmetries are described as subgroups of the space group *Pnma*. Each subgroup is a representative of a set of subgroups that are physically equivalent and belong to the same conjugacy class (see text).

We only repeat here the meaning of the third column information, where a transformation (\mathbf{P}, \mathbf{p}) is given for each subgroup, with \mathbf{P} being a 3x3 matrix and $\mathbf{p} = (p_1, p_2, p_3)$ a column vector. This transformation indicates in each case a choice of unit cell and origin, for which the subgroup being listed acquires the standard setting of the corresponding space group type, given by the label in the second column. This means that the symmetry operations of this subgroup, when described using this unit cell and origin, take the form used for the symmetry operations of this space group type in the International Tables for Crystallography vol. A (ITA), which we take as the standard setting for this space group type (see www.cryst.ehu.es/cgi-bin/cryst/programs/nph-def-choice for more information on the standard settings chosen in the Bilbao server in the case of space groups where several choices are allowed by the ITA). The transformation (\mathbf{P}, \mathbf{p}) is defined with respect to the unit cell $(\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p)$ and origin \mathbf{O}_p of the parent space group, in the following form

$$(\mathbf{a}^s, \mathbf{b}^s, \mathbf{c}^s) = (\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p) \cdot \mathbf{P} \quad , \quad \mathbf{O}^s = \mathbf{O}_p + p_1 \mathbf{a}_p + p_2 \mathbf{b}_p + p_3 \mathbf{c}_p$$

where $(\mathbf{a}^s, \mathbf{b}^s, \mathbf{c}^s)$ and \mathbf{O}^s are the unit cell vectors and origin for which the subgroup operations take the form of the standard setting of its space group type. This means, as stressed above, that the transformed basis vectors are given by the columns of the matrix (not the rows!).

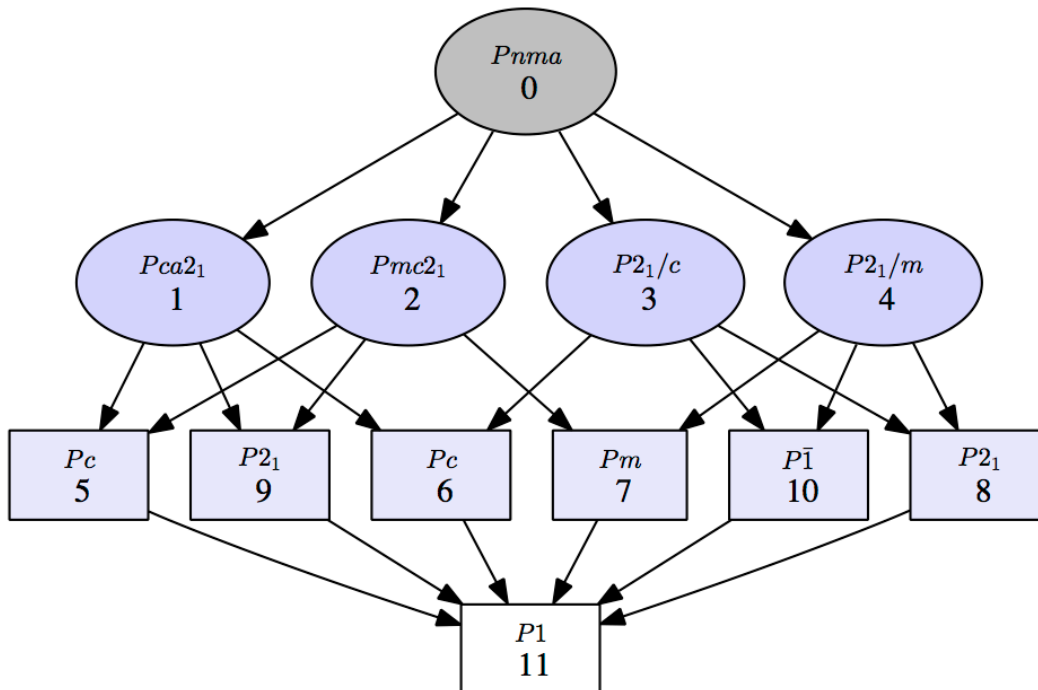


Figure 2.2. Graph obtained with SUBGROUPS, showing the possible space group symmetries resulting from the distortion of a structure with space group $Pnma$, and having a supercell $(a, b, 2c)$. The symmetries are described as subgroups of the space group $Pnma$. Each subgroup is in general a representative of a set of subgroups that are physically equivalent and belong to the same conjugacy class (see text). The numbers below the space group labels correspond to the sequential numbering used in the list shown in Figure 2.1. If desired, a graph without these numbering can also be retrieved.

b) Click on the “get group-subgroup graph” button on the output list obtained in the previous step. The group-subgroup hierarchy of the listed possible subgroups is shown graphically. The four subgroups of maximal symmetry, i.e. those not having intermediate subgroups between them and the parent space group, are those with the minimal symmetry break. Empirically these maximal subgroups can be considered more probable as symmetries of a distorted structure. The program allows restricting the list of subgroup from the start to these maximal subgroups by choosing on the first input page the option “only maximal subgroups”. Then the list and graph would be reduced to the groups $Pca2_1$, $Pmc2_1$, $P2_1/c$ and $P2_1/m$.

c) Come back to the main input webpage and use the appropriate additional filter to restrict the possible subgroups to those that are polar. The list is then reduced to 8 subgroups, which using the graphical option they are shown in Figure 2.3. This means that most of the possible symmetries are polar, implying in the case of an insulator an improper ferroelectric phase.

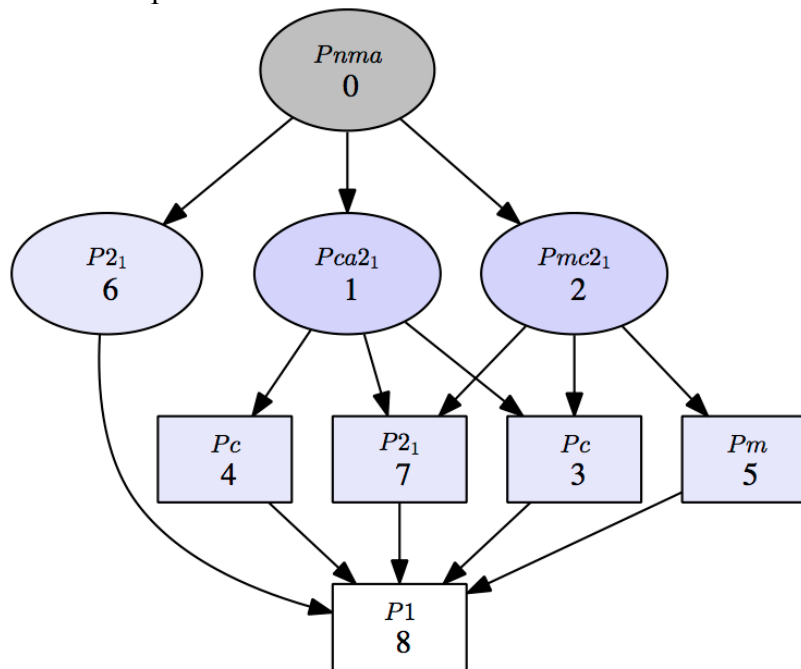


Figure 2.3. Graph obtained with SUBGROUPS, showing the possible space group symmetries resulting from the distortion of a structure with space group $Pnma$, having a supercell $(a, b, 2c)$, and restricted to those being polar. The numbers below the space group labels correspond to the sequential numbering used in the corresponding listing.

d) Come back to the main input page, cancel the filter “only polar” and produce again the full list of subgroups shown in Figure 2.2. By clicking on “Get_irreps” explore, in a similar form as in the previous example of this tutorial, which of those symmetries can be reached by the onset of a single irrep order parameter, and therefore, be the result of a symmetry breaking in accordance with the assumption of a Landau type phase transition. Check that all maximal subgroups can be result of a Landau type transition, while from the remaining ones, only some of them satisfy the condition.

Optional: Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter).

e) Come back to the main input page and apply the filter available there to reduce directly the listed symmetries to those that are possible for a Landau type phase transition, i.e. those corresponding to the symmetry break associated with a single irrep order parameter (Figure 2.4). Check that the subgroups provided now by the program coincide with those that you selected in step d).

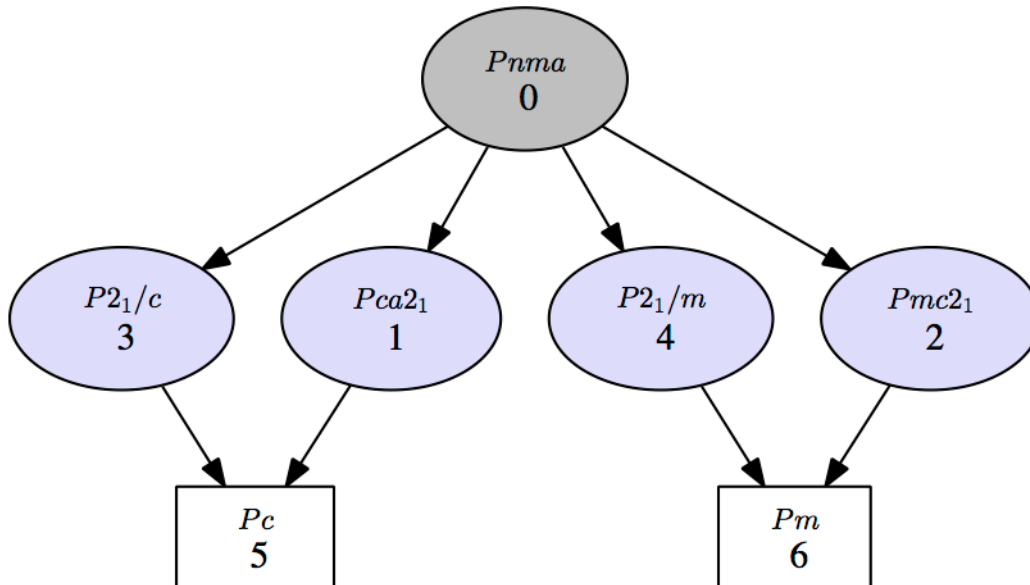


Figure 2.4. Graph obtained with SUBGROUPS, showing the possible space group symmetries resulting from the distortion of a structure with space group $Pnma$, having a supercell $(a, b, 2c)$, and restricted to those that are possible for a Landau-type phase transition, i.e. having a single irrep associated with its order parameter. The numbers below the space group labels correspond to the sequential numbering used in the corresponding listing.

We are now going to show that the possible symmetry breakings resulting from the onset of a distortion according to a single or to several irreps can be fully characterized if we use an alternative input option, introducing the wave vectors of the observed distortion instead of the supercell,

f) Come back to the first input page and click on the button “Alternatively give the modulation wave-vectors” in order to change the input webpage, such that instead of a supercell, now one or more wave vectors can be introduced. The duplication of unit cell in this example implies a primary modulation wave vector of type $(0, 0, 1/2)$, and this is the modulation wave vector that we must introduce in the corresponding window. It is important to note that wave vector components should be given using the basis of the conventional or standard reciprocal unit cell. This means that in the case of a parent space group with centring, the program assumes that the reciprocal basis of the conventional centered unit cell is being used for the wave vector components (always in the form of fractions n/m or integers).

Subgroups

The program *Subgroups* provides the possible subgroups of a space group which are possible for a given supercell. The program provides a list of the set of space groups or a graph showing the group-subgroup hierarchy, grouped into conjugacy classes. More optional information about the classes or subgroups is also given.

Other alternatives for the input of the program:

Enter the serial number of the space group:

choose it
62

Alternatively give the operations of the space group in a non-standard setting

Introduce the wave vector(s)

(Give the components of the wave vectors in a fractional form, n/m)

k_{1x} 0 k_{1y} 0 k_{1z} 1/2

Show the independent vectors of the star

Choose the whole star of the propagation vector

More wave-vectors needed

g) Check that the list and graph of possible subgroups provided by the program introducing the wave vector $(0,0,1/2)$ for the distortion, is fully identical to the one that we have obtained previously introducing the supercell (Figure 2.1), as both conditions are fully equivalent. But now, we can further filter the possible symmetries depending on the irrep or irreps associated with the wave vector $(0,0,1/2)$ that are active in the symmetry breaking.

h) Come back to the first input page with the input wave vector and click on the button “representations”

Optional: refine further the subgroups of the output giving a set of irreps

Choose the irreps

Representations

Then the program provides an extensive information, shown in Figure 2.5, which includes the standard label associated with the input wave vector, the irrep decomposition of the space of possible displacive distortions, showing the possible irreps that can describe such type of distortions. As we have not specified the Wyckoff positions occupied by the atoms in the structure (button “Wyckoff”), the program considers the irrep decomposition corresponding to an atom in a general position, and all irreps for the given wave vector are possible.

Space group: (No. 62)

Choose the irreducible representation(s) for each modulation vector

If no Wyckoff position has been given, a general position will be assumed

Possible irreducible representations

Wave-vectors of the star (1 vector):

Z:(0,0,1/2)

Decomposition of the mechanical representation(s) into irreps.

8d:(x,y,z) \rightarrow 6×Z1(2) \oplus 6×Z2(2)

Choose the representation(s)

irreps: Z1(2) Z2(2)

(In parentheses, the dimensions of the irreducible representations of the little group of k)

Submit

Figure 2.5. Output and input page of SUBGROUPS when “representations” is clicked, indicating the label Z associated with the input wave vector $(0,0,1/2)$, and the irrep decomposition of the space of displacive distortions associated with an atom in a general position for the parent space group $Pnma$. One can then choose one or more irreps and reduce the listing of possible symmetries to those resulting from the onset of order parameter(s) associated with the chosen irrep(s).

i) Choose the irrep Z1 and submit. The input first page is now modified and the choice of the Z1 irrep for the symmetry breaking distortion is included and fixed in the input page. Submit. The list of possible symmetries is now reduced to three, and their graphical representation is shown in Figure 2.3. They correspond to half of the symmetries obtained in step e) (Figure 2.4). The other three possible symmetries correspond to the other possible irrep Z2, as it can be observed if one goes back and chooses instead Z2 as the active irrep in the irrep filter shown in Figure 2.5.

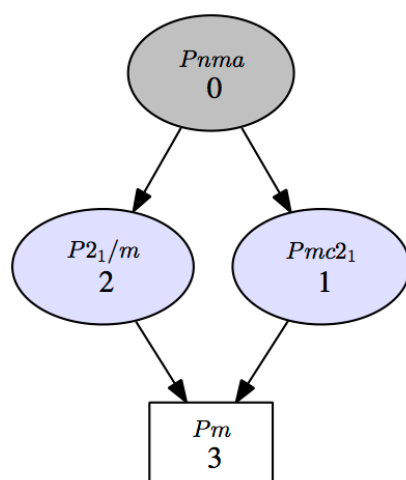


Figure 2.6. Graph obtained with SUBGROUPS, showing the possible space group symmetries resulting from the distortion of a structure with space group $Pnma$, with active wave vector $(0,0,1/2)$, and restricted to those resulting from the onset of an order parameter transforming according to the irrep Z1. The numbers below the space group labels correspond to the sequential numbering used in the corresponding listing.

Thus, using these optional irrep filters, one can determine the possible subgroups that can be reached by the action of any possible single irrep, and we recover the 6 possible symmetries associated with Landau-type phase transitions. The other possible subgroups require the concomitant presence of distortions according to the two possible irreps. The irrep filter allows to choose more than one irrep and by default provides the possible symmetries associated with the simultaneous presence of distortions transforming according to all the irreps chosen. Using the button “more options”, one can change the filter so that the listed symmetries listed are all those possible by the onset of one or more of the chosen irreps.

j) Come back to the menu that allows to choose the possible active irreps (Figure 2.5), choose now both possible irreps Z1 and Z2, submit, and submit the resulting input page. Check that the the resulting list of subgroups is reduced to the 5 subgroups (conjugacy classes) that were not listed when choosing separately Z1 and Z2 as single active irreps. These symmetries are only reachable by the simultaneous action of both irreps.

k) Click on the “more options” button and choose the option “at least one of the irreps should be active to reach the subgroup”. The listing now changes to all possible subgroups that can be reached by either the action of Z_1 , Z_2 or both. As there are only two possible irreps, this second listing should include in this case all the 11 subgroups that were obtained without any irrep filter. Thus in this case this option implies in practice no filter at all, but in more complex cases with several possible irreps, this option can be used to extract possible symmetries with some particular set of irreps involved.

Example 3. Possible distorted perovskite structures resulting from the onset of a degenerate unstable mode.

The cubic parent structure of many perovskite-related structures of composition ABO_3 is unstable for some so-called *rigid-unit modes* (RUMs), which involve correlated rotations of their octahedral framework, while maintaining in a first approximation the rigidity of their constituent octahedral units. A RUM, which is soft or fully unstable in many perovskites, is for instance the one that becomes frozen in $SrTiO_3$ below 105K, and results in a phase with space group $I4/mcm$, its standard unit cell being related with the cubic perovskite unit cell in the form $(a_p+b_p, -a_p+b_p, 2c; 0,0,0)$ [the second part of the transformation indicates the required origin shift, which is null for a choice of origin in the cubic perovskite such that Zr lies at the origin]. In this example we will explore using SUBGROUPS all the possible symmetries that can occur in a perovskite as the result of a distortion due to this kind of unstable RUMs.

a) Introduce in the main input webpage of SUBGROUPS the parent perovskite space group $Pm-3m$ (N. 221) and the supercell of the low temperature phase of $SrTiO_3$. Change also the centering information indicating that this supercell is I centered and submit. (Note that the transformed basis vectors are always the columns of the transformation matrices in the BCS, in accordance with the convention of the International Tables for Crystallography)

Enter the serial number of the space group:

[Alternatively give the operations of the space group in a non-standard setting](#)

Introduce the supercell

$a_s=$	$b_s=$	$c_s=$	
<input type="text" value="1"/> a	<input type="text" value="-1"/> a	<input type="text" value="0"/> a	
+	+	+	
<input type="text" value="1"/> b	<input type="text" value="1"/> b	<input type="text" value="0"/> b	The supercell is centred:
+	+	+	<input type="text" value="I"/> <input type="button" value="v"/>
<input type="text" value="0"/> c	<input type="text" value="0"/> c	<input type="text" value="2"/> c	

Include the subgroups compatible with intermediate cells.
(It is not applied when only the maximal subgroups are calculated)

Optional: [refine further the subgroups of the output giving the Wyckoff positions of the atoms](#)

Give the Wyckoff positions

We can then see that the list of possible subgroups under this condition is rather

large. Up to 98 non-equivalent subgroups are possible. Remember that this output lists a representative for each possible conjugacy class of subgroups. The set of subgroups belonging to each class, but limited to those that keep the lattice defined by the input supercell, can be seen when clicking on the button “conjugacy class”.

Do not try the group-subgroup graphical option for this list, because with so many subgroups the graph will have no utility. The fact that the atoms in the perovskite structure are located in special Wyckoff positions of very high symmetry can make that many of these symmetries cannot be reached through displacement of the atoms. If we are only searching for symmetries resulting from displacive modes, we should then discard these subgroups. This filtering can be done with the button “Wyckoff”, as shown in the next step.

b) Come back to the input main page and click additionally on “Wyckoff”. This will make appear an input menu, where one can introduce the type of Wyckoff positions that are being occupied in the parent structure. Submit after clicking on the occupied Wyckoff positions.

<input type="checkbox"/>	o	g	$(x,-x,-x),(-x,x,-x),(-x,-x,x),(-x,-x,-x)$
<input type="checkbox"/>	6	f	$(x,1/2,1/2),(1/2,1/2,-x),(1/2,1/2,x)$ $(1/2,x,1/2),(1/2,-x,1/2),(-x,1/2,1/2)$
<input type="checkbox"/>	6	e	$(x,0,0),(0,0,-x),(0,0,x)$ $(0,x,0),(0,-x,0),(-x,0,0)$
<input checked="" type="checkbox"/>	3	d	$(1/2,0,0),(0,0,1/2),(0,1/2,0)$
<input type="checkbox"/>	3	c	$(0,1/2,1/2),(1/2,1/2,0),(1/2,0,1/2)$
<input checked="" type="checkbox"/>	1	b	$(1/2,1/2,1/2)$
<input checked="" type="checkbox"/>	1	a	$(0,0,0)$

We consider here the origin of the perovskite structure such that the B atom occupies the origin, atom A the unit cell center, and the oxygen atoms are on the cell edge centers, i.e. $(1/2,0,0)$ and equivalent. It is important to note that the labels of the irreps describing the symmetry of the modes and order parameters depend on this origin choice. An equally valid description shifting the origin by $(1/2,1/2,1/2)$ implies a change of the irrep labels of the modes, although obviously physically the relevant modes to be discussed will be the same. The reason for this label change is that the irrep labels depend on the origin chosen for the description of the symmetry operations.

Having introduced the $1a$, $1b$ and $3d$ Wyckoff positions occupied by the atoms in the parent perovskite structure, the list of possible non-equivalent subgroups reduces to 68. Nevertheless, this number is still very large. We can go back however to the main input menu and click on the appropriate button to restrict the list to the maximal subgroups.

c) Come back to the main input webpage and click on the restriction “only maximal subgroups”. The list is then reduced to 10 subgroups (conjugacy

classes):

Input data

Subgroups of the space group : $Pm\bar{3}m$ (N. 221)
 Only maximal subgroups should be shown
 Supercell given by: (1,1,0),(-1,1,0),(0,0,2)
 Centred supercell: I
 Wyckoff positions occupied by the atoms 3d:(1/2,0,0)
 1b:(1/2,1/2,1/2)
 1a:(0,0,0)

List of possible subgroups assuming the given wyckoff positions

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps
1	$Fm\bar{3}c$ (No. 226)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	2=2x1	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
2	$Fm\bar{3}c$ (No. 226)	$\begin{pmatrix} 2 & 0 & 0 & 1/2 \\ 0 & 2 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	2=2x1	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
3	$Fm\bar{3}m$ (No. 225)	$\begin{pmatrix} 2 & 0 & 0 & 1/2 \\ 0 & 2 & 0 & 1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	2=2x1	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
4	$Fm\bar{3}m$ (No. 225)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	2=2x1	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
5	$I4/mcm$ (No. 140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & -2 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix}$	6=2x3	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
6	$I4/mcm$ (No. 140)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ 0 & 0 & -2 & 1/2 \\ -1 & 1 & 0 & 1/2 \end{pmatrix}$	6=2x3	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
7	$I4/mmm$ (No. 139)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & -2 & 1/2 \\ -1 & 1 & 0 & 0 \end{pmatrix}$	6=2x3	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
8	$I4/mmm$ (No. 139)	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ 0 & 0 & -2 & 0 \\ -1 & 1 & 0 & 1/2 \end{pmatrix}$	6=2x3	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
9	$Imma$ (No. 74)	$\begin{pmatrix} 0 & -1 & 1 & 1/2 \\ 0 & 1 & 1 & 0 \\ -2 & 0 & 0 & 0 \end{pmatrix}$	12=2x6	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
10	$Imma$ (No. 74)	$\begin{pmatrix} 0 & 1 & 1 & 1/2 \\ 0 & 1 & -1 & 0 \\ -2 & 0 & 0 & 1/2 \end{pmatrix}$	12=2x6	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>

Figure 3.1. List obtained showing the possible maximal space group symmetries for a distorted perovskite structure having an I-centered unit cell (a+b, -a+b, 2c), or equivalent, with respect to the cubic perovskite unit cell. The symmetries are described as subgroups of the space group $Pm\bar{3}m$. Each subgroup is a representative of a set of subgroups that are physically equivalent and belong to the same conjugacy class (see text).

Among these 10 maximal symmetries, the conjugacy class corresponding to the symmetry of the low temperature phase of $SrTiO_3$ is present. It is the one numbered as 5 in the list. To be noted that there are two conjugacy classes with subgroups of type $I4/mcm$, and they are distinguished by the position of its standard origin with respect to the one of the parent structure.

d) Click on the button “conjugacy class”. One can see then that the conjugacy class numbered as 5 includes 3 subgroups, the third one corresponds to the specific one mentioned above for SrTiO₃. The three subgroups of this class are physically equivalent and correspond to different equivalent orientations of the structure of SrTiO₃ with respect to the cubic parent perovskite, representing the three possible orientational domains of this phase.

**Subgroups that belong to the same conjugacy class,
limited to those compatible with the given supercell or the
supercell determined by the given wave vector(s).**

N	Group Symbol	Transformation matrix	Group-Subgroup index	Symmetry operations	Set of subgroups*	irreps
5.1	<i>I4/mcm</i> (No. 140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & -2 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix}$	6=2x3	<input type="button" value="Plain text format"/> <input type="button" value="Matrix form"/>	<input type="button" value="List of subgroups"/> <input type="button" value="Graph of subgroups"/>	<input type="button" value="Get irreps"/>
5.2	<i>I4/mcm</i> (No. 140)	$\begin{pmatrix} 0 & 0 & -2 & 0 \\ -1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}$	6=2x3	<input type="button" value="Plain text format"/> <input type="button" value="Matrix form"/>	<input type="button" value="List of subgroups"/> <input type="button" value="Graph of subgroups"/>	<input type="button" value="Get irreps"/>
5.3	<i>I4/mcm</i> (No. 140)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	6=2x3	<input type="button" value="Plain text format"/> <input type="button" value="Matrix form"/>	<input type="button" value="List of subgroups"/> <input type="button" value="Graph of subgroups"/>	<input type="button" value="Get irreps"/>

* List or graph of subgroups that are related with the chosen group through group-subgroup relation.

Figure 3.2. List of subgroups belonging to the conjugacy class with space group type *I4/mcm* with unit cell unit cell (a+b, -a+b, 2c) and having as representative the first one of the list, which is the one included in the list of Figure 3.1.

e) For the specific orientation/subgroup listed as N. 3 in the list of Figure 3.2, click on “Get irreps”. This subgroup and the parent group is then directly communicated to the program Get_irreps, which provides the irreducible representations (irreps) of the parent structure that are compatible with this specific symmetry for the distorted structure. This means that one gets the irreps of the parent structure that can characterize the degrees of freedom allowed in a distorted structure with this symmetry and, in accordance with Von Neumann principle are set free in this structure. The information is completed for each irrep with the information on the subspace within the irrep space into which the irrep distortion (order parameter) must be constrained and the so-called isotropy subgroup associated with this irrep (restricted to the indicated subspace).

Figure 3.3 shows the output for our particular example. For each irrep, the list includes the relevant wave vector(s) (in bold) and the irrep label, the irrep subspace in parenthesis, the isotropy subgroup and a link called “*matrices of the irreps*” to the database REPRESENTATIONS SG, where the matrix form of the irrep can be retrieved. This latter information is relevant for the description of the relevant irrep subspace. The irrep labels used in this program are those used by the ISOTROPY suite (iso.byu.edu), but the specific matrix form of the irreps, which depends on the choice of basis, may differ from the one used in that reference. Therefore it is important to stress that the symbol for the order parameter direction in the second column, which depends on the matrix choice for the irrep,

is not necessarily the same as in ISOTROPY. The irrep isotropy subgroups of the parent space group $Pm\bar{3}m$, are expressed, as usual, as a space group type and a transformation (P,p) from the standard basis of the parent space group to its standard setting.

It can be seen in Figure 3.3 that the isotropy subgroup of one of the compatible irreps, namely R_4^+ with wave vector $R(1/2,1/2,1/2)$, coincides with the actual subgroup of type $I4/mcm$ that is being considered. This implies that the symmetry break $Pm\bar{3}m \rightarrow I4/mcm(a+b, -a+b; 0, 0, 0)$ can be realized through a Landau type phase transition, with an order parameter having the transformation properties of this irrep (and the direction specified). The irrep is 3-dimensional and the restricted direction within this 3-dimensional irrep space is specified as $(a,0,0)$ in the basis used.

Group→subgroup	Transformation matrix
$Pm\bar{3}m$ (N. 221)→ $I4/mcm$ (N. 140)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$

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)	$Pm\bar{3}m$ (No. 221) a,b,c;0,0,0	matrices of the irreps
	GM_3^+ : (a,0)	$P4/mmm$ (No. 123) a,b,c;0,0,0	
R: $(1/2,1/2,1/2)$	R_4^+ : (a,0,0)	$I4/mcm$ (No. 140) a+b,-a+b,2c;0,0,0	matrices of the irreps

Figure 3.3. Output obtained in step e, when Get_irreps is applied for the relevant subgroup. The set of irreps and corresponding irrep subspaces compatible with the subgroup are listed, together with the corresponding isotropy subgroups (i.e. the symmetry maintained by the corresponding irrep distortion restricted to the indicated subspace).

f) Come back to the list of subgroups of the conjugacy class, shown in Figure 3.2, and check that the call to Get_irreps for any of these subgroups gives an analogous output, but with the direction changed for the R_4^+ subspace. This means that the other subgroups are attained by the same 3-dimensional order parameter, directed along different, but physically equivalent directions within the 3-dim R_4^+ irrep space.

Figure 3.4 depicts the R_4^+ distortion mode present in the structure of $SrTiO_3$, showing its rigid unit mode (RUM) character. Obviously, physically equivalent distortions are realized when the axis of the octahedra rotations is changed to the other symmetry equivalent directions on the xy plane, which in the tetragonal setting of the figure are along $a+b$ and $a-b$. These equivalent distortions correspond to the other two possible subgroups of the conjugacy class listed in

Figure 3.2, with different but equivalent directions for the R_4^+ 3-dim order parameter.

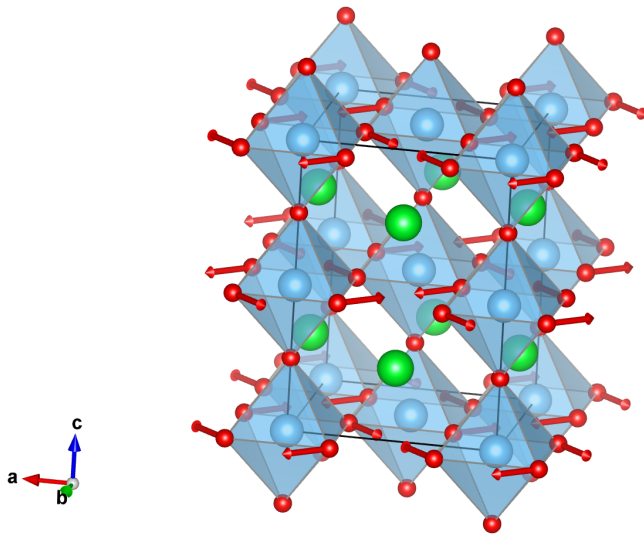


Figure 3.4. Graphical representation of the R_4^+ distortion mode present in tetragonal structure of SrTiO_3 (obtained from its experimental structure using AMPLIMODES and VESTA). The distortion mode is clearly a rigid unit mode involving antiphase rotations of the octahedra around the z cubic axis. The a, b, c basis is the figure is the tetragonal one. (For more information on methods to visualize distortion mode see the tutorial on this matter on the webpage of AMPLIMODES).

The three degenerate modes of the type shown in Figure 3.4 span a 3-dim space and an arbitrary combination of them will produce a general R_4^+ distortion, represented by an arbitrary direction (a, b, c) in the R_4^+ irrep space. The only symmetry operations that will be preserved by a R_4^+ distortion of general type (a, b, c) , are those to which the irrep R_4^+ associates the 3×3 identity matrix. These operations form a subgroup of the parent space group, the so-called kernel of the irrep, which is then the minimal symmetry that will be maintained by an arbitrary R_4^+ distortion. For special combinations of the three degenerate modes, i.e. special directions of the 3-dim R_4^+ order parameter, the preserved symmetry can be higher, corresponding to supergroups of the mentioned kernel, the so-called irrep epikernels or irrep isotropy subgroups. One example is the $(a, 0, 0)$ direction, corresponding to the presence of only one of the modes and resulting in a subgroup of type $I4/mcm$ discussed above. But there are other possible special directions or combinations of the three RUMs, yielding other possible isotropy subgroups, and the program can provide a list of all of them, as shown in the next steps.

g) Come back to the first input page and click on the button “Alternatively give the modulation wave-vectors” in order to change the input webpage, such that instead of a supercell, now one or more wave vectors can be introduced. From the result above we know that the relevant wave vector of the distortion mode in SrTiO_3 is $(1/2, 1/2, 1/2)$. We introduce then this vector, set again the Wyckoff positions that are occupied and click on “representations”.

Space group: $Pm\bar{3}m$ (No. 221)

Set of chosen modulation wave-vectors
 $k_1=(1/2,1/2,1/2)$

Include the subgroups compatible with intermediate cells.
 (It is not applied when only the maximal subgroups are calculated)

Wyckoff positions of the atoms
 3d:(1/2,0,0)
 1b:(1/2,1/2,1/2)
 1a:(0,0,0)

Optional: refine further the subgroups of the output giving a set of irreps
 Choose the irreps

Optional: possible limitations of the subgroup list
 (Check only one option on the left and the specific value on the right)
 (Check only one option on the left and the specific value on the right)
 Lowest space group to consider

The program provides then a second input page, shown in Figure 3.5, which includes the irrep decomposition of the space of possible displacive distortions, showing the possible irreps that can describe them.

Space group: $Pm\bar{3}m$ (No. 221)
Choose the irreducible representation(s) for each modulation vector

If no Wyckoff position has been given, a general position will be assumed

Non bolded irreps are incompatible with the given Wyckoff positions
Bolded irreps are compatible with at least one given Wyckoff position
Red colored irreps are compatible with all the Wyckoff positions given

Possible irreducible representations

Wave-vectors of the star (1 vector):
 R:(1/2,1/2,1/2)

Decomposition of the mechanical representation(s) into irreps.
 3d:(1/2,0,0) → $1 \times R1+(1) \oplus 1 \times R3+(2) \oplus 1 \times R4+(3) \oplus 1 \times R5+(3)$
 1b:(1/2,1/2,1/2) → $1 \times R5+(3)$
 1a:(0,0,0) → $1 \times R4-(3)$

Choose the representation(s)
 irreps: **R1+(1)** R1-(1) R2+(1) R2-(1) **R3+(2)** R3-(2) **R4+(3)** R4-(3) **R5+(3)** R5-(3)

(In parentheses, the dimensions of the irreducible representations of the little group of k)

Figure 3.5. Output and input page of SUBGROUPS when “representations” is clicked, indicating the irrep decomposition the space of displacive distortions (mechanical representation) associated with the chosen Wyckoff positions of the parent space group $Pm\bar{3}m$, for the wave vector R (1/2,1/2,1/2). One can then choose one or more of the listed possible irreps and reduce the listing of possible symmetries to those resulting from the onset of order parameter(s) associated with the chosen irrep(s).

The page indicates the irrep decomposition of the mechanical representation of the displacements of the atoms associated with each of the occupied Wyckoff positions. One can then see that only 4 of the 10 possible irreps are relevant for a perovskite structure, and among them, as expected, the R_4^+ irrep is present. The user can now choose one or several of these possible irreps and see the possible symmetries resulting from the presence of distortions corresponding to these irreps. we are interested in possible symmetries resulting from the freezing of some combination of the RUMs corresponding to the R_4^+ irrep.

h) Choose the R_4^+ irrep and submit.

The program then lists all possible distinct space group symmetries (subgroups of the parent $Pm\bar{3}m$) that can result from an order parameter with R_4^+ symmetry, i.e., in our case, from the combination of the three degenerate RUMs of the type shown in Figure 3.4. The output is shown in Figure 3.6.

Input data

```

Subgroups of the space group :           $Pm\bar{3}m$  (N. 221)
Lowest space group to consider:         $P1$  (N. 1)
Modulation wave-vectors                (1/2,1/2,1/2)
Wyckoff positions occupied by the atoms 3d:(1/2,0,0)
                                          1b:(1/2,1/2,1/2)
                                          1a:(0,0,0)

Reducible representations                $R_4^+$ 
R:(1/2,1/2,1/2)

```

List of possible subgroups assuming the given wyckoff positions and that have as primary irreps all the irreps given

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps
1	$R\bar{3}c$ (No. 167)	$\begin{pmatrix} -1 & 0 & 2 & 0 \\ 0 & -1 & -2 & 0 \\ 1 & -1 & 2 & 0 \end{pmatrix}$	8=2x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
2	$I4/mcm$ (No. 140)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & -2 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix}$	6=2x3	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
3	$Imma$ (No. 74)	$\begin{pmatrix} 0 & 1 & 1 & 1/2 \\ 0 & 1 & -1 & 0 \\ -2 & 0 & 0 & 1/2 \end{pmatrix}$	12=2x6	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
4	$C2/c$ (No. 15)	$\begin{pmatrix} 1 & -1 & -1 & 0 \\ 2 & 0 & 0 & 1/2 \\ -1 & -1 & 1 & 1/2 \end{pmatrix}$	24=2x12	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
5	$C2/m$ (No. 12)	$\begin{pmatrix} 0 & 0 & 1 & 1/2 \\ -2 & 0 & -1 & 0 \\ 0 & -2 & 0 & 1/2 \end{pmatrix}$	24=2x12	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>
6	$P\bar{1}$ (No. 2)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 1 & 0 & 1 & 0 \end{pmatrix}$	48=2x24	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>

Figure 3.6. List obtained with SUBGROUPS showing the possible space group symmetries for a distorted structure derived from a $Pm\bar{3}m$ parent structure, as the result of a distortion according to the R_4^+ irrep. The symmetries are described as subgroups of $Pm\bar{3}m$. Each subgroup is a representative of a set of subgroups that are physically equivalent and belong to the same conjugacy class.

One can see in Figure 3.6 that the possible subgroups (strictly, conjugacy classes of subgroups) are six, $P\bar{1}$ being the minimal symmetry possible, being the kernel of the chosen irrep.

i) In order to see the group-subgroup hierarchy of these six different possible symmetries click on the “get the subgroup-graph” button. The result shown in Figure 3.7, where for each symmetry the particular special direction required for the R_4^+ order parameter is also indicated. This additional information can be retrieved by clicking on the “Get_irreps” button of the Table shown in Figure 3.6, which provides for each possible subgroup an output analogous to the

one of Figure 3.3.

Figure 3.7 shows all the possible symmetries that a perovskite can acquire as the result of the freezing of some combination of the three R4+ distortions of the type shown in Figure 3.4. These distortion modes, being RUMS, are expected to cost little energy, or even be unstable and become frozen. One therefore expects that the symmetries shown in Figures 3.6 and 3.7 are realized in some perovskite-like materials, and indeed this is the case. We indicate in Figure 3.7 for each of the space groups (except for the minimal kernel) a specific compound where this particular symmetry has been observed.

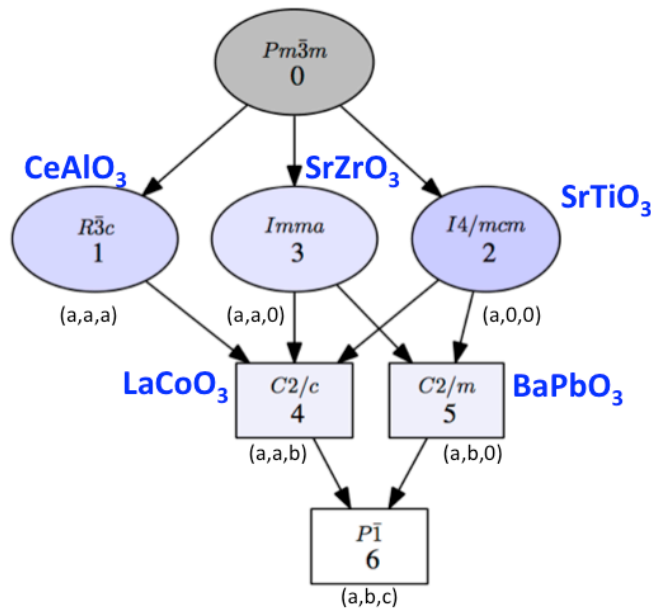


Figure 3.7. Graph obtained with SUBGROUPS showing the possible space group symmetries for a distorted structure derived from a $Pm\bar{3}m$ parent structure, as the result of a distortion according to the R4+ irrep. The appropriate direction of the order parameter within the 3-dimensional irrep space is also indicated below each subgroup. In addition, we have added in blue besides each subgroup an example of material, if existing, where this symmetry is realized.

For instance, the compound CeAlO_3 exhibits a phase with space group R-3c as the result of a combination with equal amplitudes of the three R4- distortion modes of the type shown in Figure 3.4 (direction (a,a,a)). The R4- distortion mode involved in such structure is depicted in Figure 3.8. The relation between the distortion mode shown in this figure and the one in Figure 3.4, both corresponding to the same R4+ irrep, but associated with different directions or combinations of the three basis modes, can be intuitively guessed, but if one goes to lower symmetries, the relationships among the different structures is far from obvious. Figure 3.9 depicts for instance the R4- distortion mode with direction (a,a,b), which is observed in LaCoO_3 .

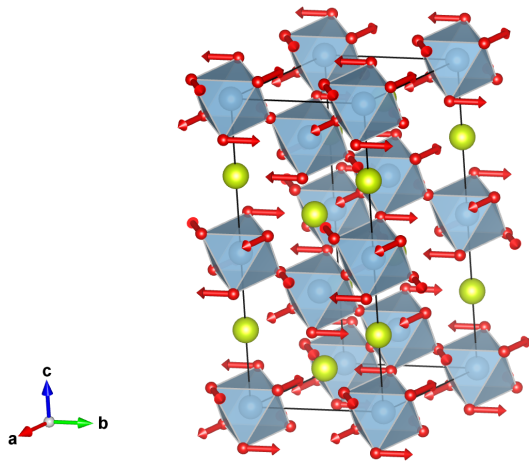


Figure 3.8. Graphical representation of the R4+ distortion mode present in the rhombohedral R-3c structure of CeAlO_3 (obtained from the experimental structure using AMPLIMODES and VESTA). The unit cell in the figure is the rhombohedral one. The distortion mode is clearly a rigid unit mode involving antiphase rotations of the octahedra around the z rhombohedral axis (direction (111) in the cubic setting).

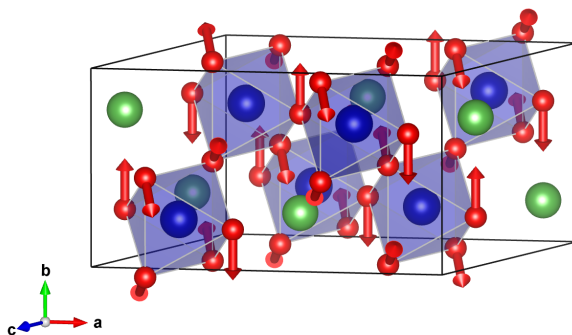


Figure 3.8. Graphical representation of the R4+ distortion mode present in the monoclinic C2/c structure of LaCoO_3 (obtained from the experimental structure using AMPLIMODES and VESTA). The unit cell in the figure is the monoclinic one. The distortion mode is a rigid unit mode involving rotations of the octahedra around some direction on the monoclinic plane, according to a linear combination of type (a,a,b) of the three basis R4+ modes representing rotations around the three cubic axes (see Figure 3.4).

SUBGROUPS can be combined with the program TRANSTRU, also in the Bilbao Crystallographic Server, to create an initial structural model of a distorted structure under one or more of the symmetries obtained with SUBGROUPS. These structural models can then be transported in CIF format for their eventual fit with any refinement program to experimental data. Let us see for instance how this CIF file is created for the C2/c structure observed in LaCoO_3 .

k) Open the program TRANSTRU and load the structure of LaCoO_3 in its parent cubic configuration. The structure can be an experimental or a virtual

idealized one, and can be loaded either manually on the available window, or as a CIF file:

Transform Structure

Structure Data Examinar... No se ha seleccionado ningún archivo.
 [in CIF format] **HINT:** [The option for a given filename is preferential]

```

221
3.82 3.82 3.82 90. 90. 90.
3
La 1 1b 0.500000 0.500000 0.500000
Co 1 1a 0.000000 0.000000 0.000000
O 1 3d 0.500000 0.000000 0.000000
    
```

High Symmetry Structure

Transform structure to a subgroup basis
 Transform structure with an arbitrary matrix

Show

This gives place to a second webpage where the subgroup under consideration must be defined.

I) We introduce in this second menu the subgroup C2/c as defined in listing obtained with SUBGROUPS and shown in Figure 3.6:

Transform Structure

```

221
3.82 3.82 3.82 90. 90. 90.
3
La 1 1b 0.500000 0.500000 0.500000
Co 1 1a 0.000000 0.000000 0.000000
O 1 3d 0.500000 0.000000 0.000000
    
```

Structure

Low symmetry Space Group *ITA* number

Transformation Matrix:

	Linear part			Origin Shift
In matrix form:	<input type="text" value="1"/>	<input type="text" value="-1"/>	<input type="text" value="-1"/>	<input type="text" value="0"/>
	<input type="text" value="2"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="1/2"/>
	<input type="text" value="-1"/>	<input type="text" value="-1"/>	<input type="text" value="1"/>	<input type="text" value="1/2"/>

m) On the resulting output click on the button to download a CIF file of the input structure transformed in a description under the input C2/c subgroup, termed “low symmetry structure”:

Transform structure

Transformation matrix: $a+2b-c, -a-c+1/2, -a+c+1/2$

High symmetry structure

```
221
3.82 3.82 3.82 90. 90. 90.
3
Ia      1      1b      0.500000      0.500000      0.500000
Co      1      1a      0.000000      0.000000      0.000000
O       1      3d      0.500000      0.000000      0.000000
```

Low symmetry structure

```
015
9.357051 5.402296 5.402296 90.000000 125.264397 90.000000
4
Ia      1      4e      0.000000      0.750000      0.750000
Co      1      4c      0.750000      0.250000      0.500000
O       1      8f      0.750000      0.000000      0.250000
O       1_2    4e      0.000000      0.250000      0.750000
```

We have now a CIF file with the atomic positions corresponding to the ideal perovskite structure, but subject to the lower symmetry described by the input subgroup of $Pm-3m$, which is ready for refinement using any refinement program.