Symmetry-mode analysis: Solutions

Exercise 1. Identity symmetry modes : Solution

How the identity symmetry-modes for an orbit of atoms belonging to the 6*h* Wyckoff position of a $P6_3/mmc$ structure can be directly derived from the set of coordinate triplets is evident from the results given in Table 1. The 6*h* Wyckoff position is described by one variable parameter, so there is one identity mode for the atoms occupying this position. Such a mode follows directly from the coordinates of the 6*h* equivalent atoms and is listed in Table 1.

Similarly, one could write down the modes for the atoms occupying an orbit belonging to the general Wyckoff position 2*l* of $P6_3/mmc$. In this case there are three independent displacive modes and they can be chosen following the variable parameters in the coordinates of the 2*l* atoms, *i.e.* along the **a**, **b,** and **c** axes.

There are no displacive modes compatible with $P6_3/mmc$ symmetry for atoms occupying the 2*a* Wyckoff position and this is evident from the fact that the 2*a*-coordinate triplets are described with no variable parameters.

Table 1. Identity symmetry mode for 6*h* atoms of $P6_3/mmc$. The factor is due to normalization with respect to the unit cell of $P6_3/mmc$.

atoms labels	Coordinates of 6*h* atoms of $P6_3/mmc$			identity mode x	y	z
1	x	2x	1/4	1	2	0
2	-2x	-x	1/4	-2	-1	0
3	x	-x	1/4	1	-1	0
4	-x	-2x	3/4	-1	-2	0
5	2x	x	3/4	2	1	0
6	-x	x	3/4	-1	1	0
	normalization factor			1/24		

Exercise 2. Chain-adapted modes for a group-subgroup chain with a maximal subgroup: Solution

(i). Consider the group-subgroup chain $P6_3/mmc > P\bar{3}m1$. In the transition to the $P\bar{3}m1$ symmetry the orbits belonging to the 6*h* Wyckoff position of $P6_3/mmc$ do not split, their site symmetry is reduced and they become orbits of the 6*i* position for the subgroup $P\bar{3}m1$which symbolically can be written as:

6*h*(mm2) x,2x,1/4 → 6*i*(m) x,2x,z

Here, each Wyckoff position orbit is presented by its multiplicity, Wyckoff letter, site symmetry group (in brackets) and a coordinate triplet in the asymmetric unit. The $P\bar{3}m1$-identity modes for the 6*i*-atoms are listed in Table 2. Their relations with the corresponding $P6_3/mmc$ identity mode for the 6*h*-atoms (Table 1) is evident. Obviously, the $P\bar{3}m1$-identity mode (which we call $P\bar{3}m1$-mode for short) along the **c**-axis is a primary distortion for an hypothetical displacive $P6_3/mmc > P\bar{3}m1$ phase transition. The xy-plane mode of $P\bar{3}m1$symmetry is a secondary one as it is also invariant with respect to $P6_3/mmc$. In this case the chain-adaptation matrix is the unit matrix.

Table 2. Identity modes for 6i atoms of $P\bar{3}m1$.The factors are due to normalization with respect to the unit cell of $P\bar{3}m1$.

atom labels	Coordinates of 6*i* atoms of $P\bar{3}m1$			plane-mode			z-mode		
				x	y	z	x	y	z
1	x	2x	z	1	2	0	0	0	1
2	-2x	-x	z	-2	-1	0	0	0	1
3	x	-x	z	1	-1	0	0	0	1
4	-x	-2x	-z	-1	-2	0	0	0	-1
5	2x	x	-z	2	1	0	0	0	-1
6	-x	x	-z	-1	1	0	0	0	-1
	normalization factors			√1/24			√1/6		

(ii). Consider the group-subgroup chain $P\bar{3}m1 > C2/m$, where $C2/m$ is a maximal *translationengleiche* subgroup of index 3. There are three different subgroups $[C2/m]_i$, i=1,...3, forming a conjugate set. An orbit belonging to 6*i*-Wyckoff position of $P\bar{3}m1$splits into two C2/m-orbits:

6*i*(mm2) x,2x,z → 8*j*(1) x',y',z' ∪ 4*i*(m) x'',0,z''

The splitting of the Wyckoff positions is the same for the three conjugated subgroups of $P\bar{3}m1$. However, it is very important to note that the distribution of the atoms of $P\bar{3}m1$-orbit into orbits of $C2/m$ depends on the individual subgroup: it is different for the three

subgroups $[C2/m]_i$, i=1,...,3. The distribution of the 6*i* atoms among the two orbits of each of the *C*2/*m* -subgroups is easily obtained after the transformations of the coordinates of the 6i-atoms to the conventional bases of the subgroups: If we choose the transformation matrix $\boldsymbol{P}_1=\begin{pmatrix}-1 & -1 & 0\\ 1 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}$ for one of the subgroups, say $[C2/m]_1$, then atoms 1,2,4 and 5 form the representative set of the 8*j*-orbit, and atoms 3 and 6-the representative set for 4*i*-orbit of $[C2/m]_1$.

Consider the two $[C2/m]_1$ modes along **c**-axis which are listed under identity $[C2/m]_1$-modes in Table 3. The fact that they originated from one $P\bar{3}m1$-mode shows that there exists a linear combination of them which is compatible with the $P\bar{3}m1$-symmetry. Comparing with the $P\bar{3}m1$-mode in Table 2 it is clear that this mode should be the one listed as chain-adapted $P\bar{3}m1$mode in Table 3, *i.e.* a linear combination of the two $[C2/m]_1$ modes, and therefore, the chain adaptation matrix in this case is as follows:

$$\boldsymbol{X}^{\mathrm{H}}_{\mathrm{G}}=\begin{pmatrix}\sqrt{2/3} & \sqrt{1/3}\\ \sqrt{1/3} & -\sqrt{2/3}\end{pmatrix}$$

The coefficients in the first column of $\boldsymbol{X}^{\mathrm{H}}_{\mathrm{G}}$ determine the linear combination of $[C2/m]_1$ modes compatible with the $P\bar{3}m1$ symmetry; the other column is forced by the orthogonality condition and corresponds to the chain-adapted *C*2/*m* mode, *i.e.* to the primary mode for a hypothetical symmetry break $P\bar{3}m1>[C2/m]_1$.

Table 3. Chain-adapted z-modes of the 6*i* atoms for $P\bar{3}m1>[C2/m]_1$. The coordinates of the atoms and the symmetry modes are given with respect to the basis of $[C2/m]_1$. The sequence of 6*i* atoms has been changed so that the orbit splitting is easily followed. The chain-adapted modes for are given in the last two columns of the table. The secondary mode is compatible with $P\bar{3}m1$symmetry.

atoms	$P\bar{3}m1$ Coordinates of 6*i*-atoms				$[C2/m]_1$ Orbit Splitting				z-symmetry modes			
									identity $[C2/m]_1$ modes		Chain-adapted modes	
											$P\bar{3}m1$	$[C2/m]_1$
1	6*i*	x/2	-3/2x	z	8*j*	x’	-y’	z’	1	0	1	1
2		x/2	3/2x	z		x’	y’	z’	1	0	1	1
4		-x/2	3/2x	-z		-x’	y’	-z’	-1	0	-1	-1
5		-x/2	-3/2x	-z		-x’	-y’	-z	-1	0	-1	-1
3		-x	0	z	4*i*	x’’	0	z’’	0	1	1	-2
6		x	0	-z		-x’’	0	-z’’	0	-1	-1	2
					normalization factors				1/2	√1/2	√1/6	√1/12

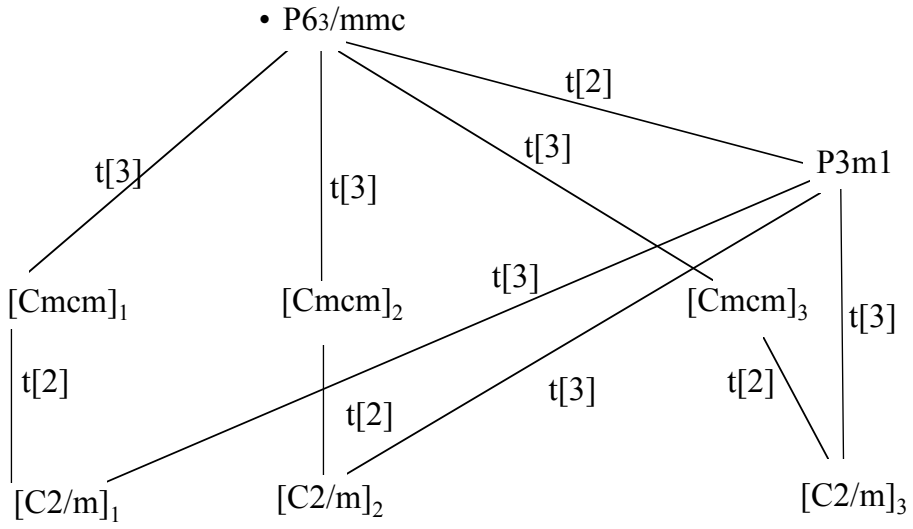
Exercise 3. Chain-adapted modes for the symmetry break $P6_3/mmc > C2/m$: Solution

In the following, the example of $P6_3/mmc > C2/m$ symmetry break is considered. It is present for example in the α–β phase transitions of $CsCrCl_3$ and $RbCrCl_3$ (Perez-Mato, Mañes and Tello, 1980). The chain-adapted modes for atoms occupying 2a-, 2d- and 6h-orbits of $P6_3/mmc$ are considered.

(i) Graph of maximal subgroups *for $P6_3/mmc > C2/m$ (Fig. 1.)*

$C2/m$ is a *translationengleiche* subgroup of $P6_3/mmc$ of index 6. The possible orientational domain structure of the low symmetry phase is due to the three conjugate $C2/m$ subgroups. There are two chains of maximal subgroups for each of the C2/m subgroups: one over subgroup $P\bar{3}m1$ of index 2, and a second one over a *Cmcm* subgroup of index 3.

Fig. 1. Graph of maximal subgroups for $P6_3/mmc > C2/m$ The symbols t[i] indicate the *translationengleiche* type and the index of the corresponding maximal subgroups.



(ii) Splitting of Wyckoff positions

The splitting of the 2*a*-, 2*d*-, and 6*h*-Wyckoff positions for the two possible chains of maximal subgroups for $C2/m$ are given in Fig.2, Fig.3 and Fig.4, respectively. Orbits belonging to 2*d*-Wyckoff position do not split, only their site symmetry is reduced. In the case of 6*h* Wyckoff position, the orbits split into two and their site symmetries are reduced. As it was mentioned before, the distribution of the atoms into subgroup orbits is different for the different subgroups $C2/m$ and is easily obtained if the coordinates of the atoms are transformed to the conventional basis of the subgroup. In our case, the transformation matrix $\boldsymbol{P}_1$ (Exercise 2.) is used for the case of $[C2/m]_1$. The following

two matrices have been applied for the subgroups $[C2/m]_2$ and $[C2/m]_3$ (cf. ITA1):

$$\boldsymbol{P}_2=\begin{pmatrix} -1 & 1 & 0 \\ -2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \boldsymbol{P}_3=\begin{pmatrix} 2 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

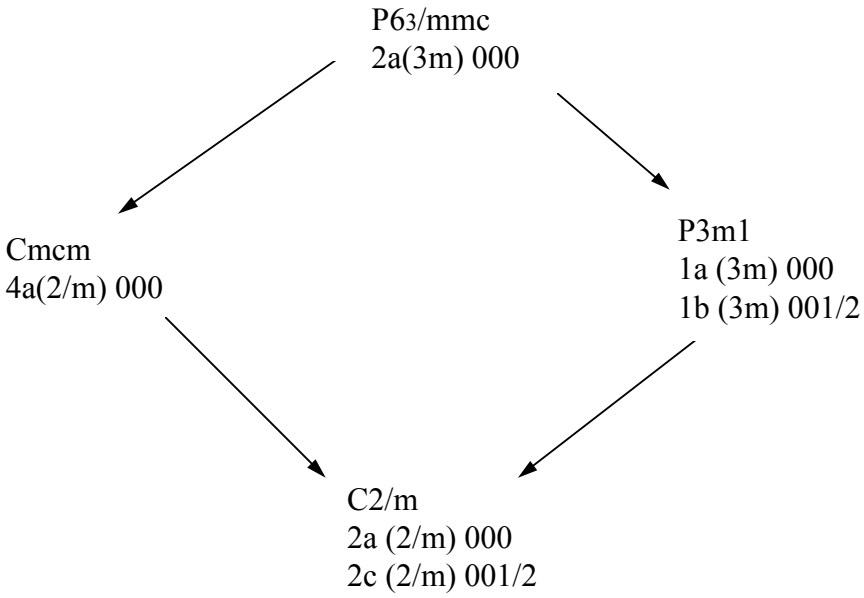


Fig. 2. Splitting of the 2*a* Wyckoff position for the two chains of maximal subgroups for $P6_3/mmc > C2/m$. No displacive modes.

There are no symmetry-modes for atoms occupying 2*a*-orbits of $P6_3/mmc$ as the coordinate triplets of the 2*a*- and 2*c*-orbits of *C*2/*m* into which the 2*a* orbit splits, contain no variable parameters.

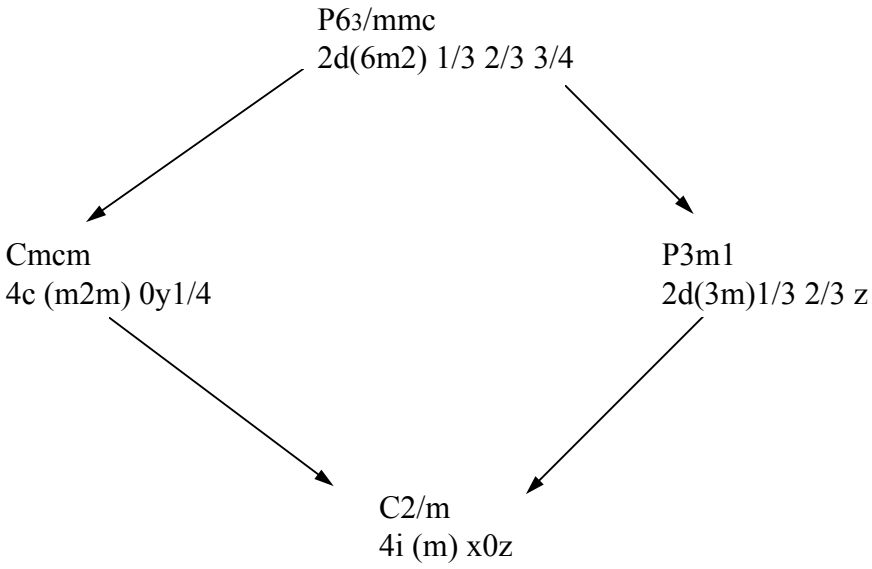


Fig. 3. Splitting of the 2*d* Wyckoff position for the two chains of maximal subgroups for $P6_3/mmc > C2/m$.

There are two modes for the 2*d*-atoms and both are secondary. One is compatible with *Cmcm* while the other is a $P\bar{3}m1$-mode.

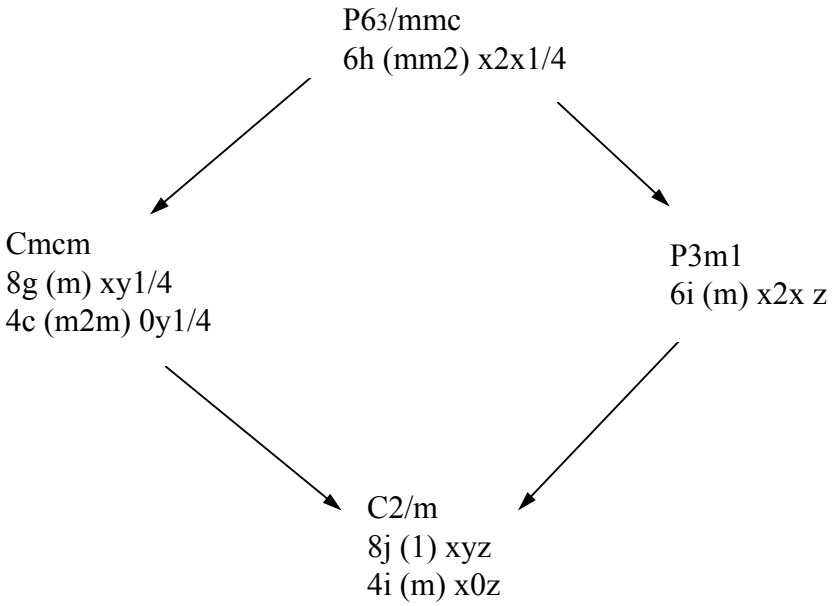


Fig. 4. Splitting of the 6*h*Wyckoff position for the two chains of maximal subgroups for $P6_3/mmc > C2/m$.

Due to the splitting of the 6*h* Wyckoff position of $P6_3/mmc$ into two orbits of $C2/m$ (Fig. 4) there are five symmetry-modes compatible with $C2/m$ symmetry: three xy-plane modes and two z-modes. All xy-plane modes are secondary ones. One of the two z-modes for the 6*h*-atoms is a primary one and the other is compatible with the $P\bar{3}m1$ symmetry.

(iii) Chain-adapted symmetry-modes for 2*d*-atoms of $P6_3/mmc > C2/m$

As already pointed out, there are two modes for the 2*d*-atoms and both are secondary. One is compatible with *Cmcm* while the other is a $P\bar{3}m1$-mode. In that case the chain-adaptation matrix is the unit one, *i.e*. the $C2/m$ identity modes coincide with the chain-adapted modes.

Table 4. Chain-adapted modes of the 2*d* atoms $P6_3/mmc > [C2/m]_1$. The coordinates of the atoms and modes are given with respect to the basis of $[C2/m]_1$. In this case the $[C2/m]_1$-identity modes coincide with the listed chain-adapted modes which are secondary: the z-mode is compatible with *Cmcm* and the x-mode with $P\bar{3}m1$.

	$P6_3/mmc$ Coordinates of 2*d*-atoms	$P\bar{3}m1$	*Cmcm*	$[C2/m]_1$	Chain-adapted modes	
		Orbit description	Orbit description	Orbit description	Cmcm	$P\bar{3}m1$
1	2/3 0 3/4	2*d* 2/3 0 z	4*c* x 0 3/4	4*i* x 0 z	100	001
2	1/3 0 1/4	1/3 0 -z	-x 0 1/4	-x 0 -z	-100	00-1
				normalization factors	√1/2	√1/2