Bilbao Crystallographic Server II. Computer tools in phase-transition problems

Exercises

Exercise 1. Phase transitions with group-subgroup relation between the two phases (SYMMODES)

(i). Study the symmetry break $P6_3/mmc > C2/m$, index 6, and determine the primary and the secondary modes for atoms in $2a$, $2d$ and $6h$ Wyckoff positions. Compare the results with those obtained in the exercise on Symmetry-modes analysis.

(ii). Study the symmetry break $P422 > P1$, index 8, atoms in $1a$ and $1c$ Wyckoff positions of $P422$. Identify the primary and the secondary modes and the corresponding isotropy groups. Determine the number of the primary and the secondary symmetry modes for the same case by the symmetry-modes approach and compare the results with the SYMMODES output. (To carry out the symmetry-modes analysis, use the programs SUBGROUPGRAPH (or MAXSUB) and WYCKSPLIT.)

Exercise 2. The use of Bilbao Crystallographic Server in the search of symmetry transition paths in phase-transitions with no group-subgroup relation between the two phases

As an example we will study the transition mechanisms of the pressure-induced phase transformations between cinnabar and zincblende structure types in CdTe using the Bilbao Crystallographic Server databases and tools.

The symmetry relations between cinnabar $P3_121(152)$ and zincblende $F-43m(216)$ structure types are discussed by H. Sowa (J. Appl. Cryst. (2005) 38, 537-543, and the references therein). The transition involves a hypothetical intermediate configuration with $P3_1$ space group. From a symmetry point of view, the transition can be studied by the two symmetry breaks $F-43m > P3_1$ and $P3_121 > P3_1$ with indices 24 and 2 for the corresponding branches.
The main symmetry conditions for a transition path are:

1. $P_{31}(144)$ is a common subgroup of $F\overline{4}3m$ (216) and $P_{3}121(152)$ with indices required by the diffusionless character of the transformation.

2. The Wyckoff-position splitting schemes of the occupied orbits are compatible in the intermediate subgroups.

The aim of the exercise is to check these symmetry conditions with the help of the Bilbao Crystallographic Server.

(i). The diffusionless character of the studied transformations imposes the following relationship between the indices of the common subgroups along the two branches:

$$i_2 = i_1 \cdot \frac{Z_{1p}}{Z_{2p}} \cdot \frac{|P_{G_2}|}{|P_{G_1}|}$$

Here, $Z_{1p}$ and $Z_{2p}$ are the number of formula units per primitive unit cell and $|P_{G_1}|$ and $|P_{G_2}|$ are the orders of the point groups of $G_1$ and $G_2$.

Verify the relation of the index relation for the zincblende-to-cinnabar transformation with $P_{31}$ as a common subgroup.
(ii). Calculate the common subgroups of the space groups of the two end phases. How many common subgroups are there for a maximum cell multiplication of the subgroup equal to 4?

HINT: Use **COMMONSUBS** program for obtaining the list of common subgroups of two space groups

(iii). Use the **CELLSUB** program to verify the list of common subgroups obtained in the previous problem (ii). (CELLSUB returns the subgroups with a given cell multiplication index, $i_k$.)

(iv). Examine the group-subgroup breaks $P3_121 > P3_1$, index 2 (cinnabar branch) and $F-43m > P3_1$, index 24 (zincblende branch): obtain the different subgroups, the corresponding graphs and transformation matrices

HINT: Use **SUBGROUPGRAPH** program

(v). Check the Wyckoff-position splitting schemes for the transformation matrices obtained in the previous problem.

HINT: Use **WYCKSPLIT** program

(vi). Compare the transformed structures in the basis of the common subgroup. What is the final transformation between the structures? Is it unique? What are the internal degrees of freedom (the so-called reaction coordinates) of the studied transformation and how they change during the transformation?

**Exercise 3. Following the instructions of Exercise 2, examine the zincblende-to-rocksalt transformation in SiC. Find the possible transition paths for $(i_k)_{\text{max}}=2$.**

Structure data: Zincblende $F-43m$ (216), Z=4
Si 4$a$ (0,0,0), C 4$c$ (1/4,1/4,1/4)

Rocksalt $Fm-\overline{3}m$ (225), Z=4
Si 4$a$ (0,0,0), C 4$b$ (1/2,1/2,1/2)