

**Relations between crystal structures. Bärnighausen trees of crystal families.
Computer tools on BCS for the study of crystal-structure relationships.**

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Abstract

Relations between structure types specified by their space group and occupied Wyckoff positions. Definitions of the aristotype and hettotypes for a given crystal family. Relations between the space group, structure type and structure. Construction of a descending Bärnighausen tree beginning with an aristotype and an ascending tree beginning with a hettotype. Determination of archetypes as the dead ends of the ascending Bärnighausen tree. Hettotypes with non-characteristic orbits. Equivalent structure types. Bärnighausen trees for two cases: symmetry relationships between different phases of a given compound, symmetry relationships between different structures with varied composition derived from a given parent crystal. Computer tools on the Bilbao Crystallographic server: [MAXSUB](#), [MINSUP](#), [CELLSUB](#), [CELLSUPER](#), [WYCKPOS](#), [WYCKSPLIT](#), [WYCKSETS](#), [SUBGROUPGRAPH](#).

Main concepts and definitions

- 1) Space group and subgroup
- 2) Point subgroup ([POINT](#))
- 3) Wyckoff positions ([WYCKPOS](#))
- 4) Index of a group-subgroup relation ([POINT](#), [SUPERGROUPS](#))
 - a) k-index (*klassengleich* index)
 - b) t-index (*translationgleich* index)

EXERCISE 1

INPUT DATA:

ANATASE structure type

Space group G141 (I4₁/amd)

Tetragonal crystal system

Origin choice 1:

Ti: 4a (000), (0 ½ ¼) + (½ ½ ½)

O: 8e (0 0 z) (0 ½ z+¼) (½ 0 - z+¾) (½ ½ -z + ½) + (½ ½ ½)

Origin choice 2:

Ti: 4a (0 ¾ ⅛), (½ ¾ ¾) + (½ ½ ½)

O: 8e (0 ¼ z) (0 ¾ z+¼) (½ ¼ - z+½) (½ ¾ -z+¼) + (½ ½ ½)

- **a) Find the minimal supergroups of the anatase space group and show that it is the “dead end” of the tree.**

Step 1.

Click [MINSUP](#) (Minimal Supergroups of Space Groups) on the first page of the site of the Bilbao Crystallographic Server.

Enter the space group number.

Step 2

Click the button [SHOW MINIMAL SUPERGROUPS](#).

Step 3

In the list of minimal supergroups, mark one of the supergroup and click the button [FIND THE SUPERGROUPS](#).

Step 4

Click the button [WP splitting](#).

Step 5

Check, are there Wyckoff positions (WP) in the supergroup which split ONLY into the occupied WP in the group

Step 6

If the WP in the supergroup split into occupied and non-occupied positions of the group, the corresponding transformation could not be of the displacive type.

- **b) Find maximal subgroups of the anatase space group, occupied WP splittings, structure types with non-characteristic orbits.**

Step 1.

Click [MAXSUB](#) (Maximal Subgroups of Space Groups)
Enter the space group number.
Mark the field “[Show WP Splittings?](#)”.

Step 2

Click the button [SHOW MAXIMAL SUBGROUPS](#)

Step 3

In the list of maximal subgroups, choose one of the supergroups and click the button [SHOW...](#) in the last column.

Step 4

Click the button [WP splitting](#).

Step 5

You will see the table of WP splitting for group-subgroup pair. For the occupied WP (4a, 8e) in the anatase structure, click the button [Relation](#).

Step 6.

Check the coordinates of the splitted WP in the subgroup basis. If the crystal system is not changed (tetragonal for anatase) and coordinates of the subgroup WP are like in the group basis, the atoms “physically” do not change their positions in space. Thus the orbits occupied by atoms in the subgroup are non-characteristic for this subgroup: the system in fact has higher symmetry.

Step 7

Return to Step 3 and check the WP splittings for all the subgroups from the list. You will obtain the first level of the descending Bärnighausen tree.

- c) Find possible paths to the cottunite structure type G62 (Pnma) (4c, 4c+4c).

Cotunnite structure type

Space group G62 (Pnma)

Ti: 4c $(x_1 \ 1/4 \ z_1) \ (-x_1 + 1/2 \ 3/4 \ z_1 + 1/2) \ (-x_1 \ 3/4 - z_1) \ (x_1 + 1/2 \ 1/4 - z_1 + 1/2)$

O1: 4c $(x_2 \ 1/4 \ z_2) \ (-x_2 + 1/2 \ 3/4 \ z_2 + 1/2) \ (-x_2 \ 3/4 - z_2) \ (x_2 + 1/2 \ 1/4 - z_2 + 1/2)$

O2: 4c $(x_3 \ 1/4 \ z_3) \ (-x_3 + 1/2 \ 3/4 \ z_3 + 1/2) \ (-x_3 \ 3/4 - z_3) \ (x_3 + 1/2 \ 1/4 - z_3 + 1/2)$

Step 1.

Click [SUBGROUPGRAPH](#) (Lattice of Maximal Subgroups)

Enter the supergroup number, subgroup number and index of transformation.

Space group numbers can be found in Table of Space Group Symbols (click button "Space groups" at the top of the first page of the site).

t-index of transformation can be found clicking [POINT](#) (Point Group Tables) and $O_h(m-3m)$.

Step 2.

You will see chains of maximal subgroups from the supergroup to the subgroup. Click [Draw the lattice](#) and find the possible group-subgroup paths.

Step 3.

Using [MAXSUB](#) check are the occupied WP of the supergroup structure type split into the occupied WP of the subgroup structure type.

Exercise 2.

INPUT DATA:

WURZITE structure type as the parent structure type

Space group G186 (P6₃mc)

Hexagonal system

Ga: 2b ($\frac{1}{3}$ $\frac{2}{3}$ z₁) ($\frac{2}{3}$ $\frac{1}{3}$ z₁ + $\frac{1}{2}$)

N: 2b ($\frac{1}{3}$ $\frac{2}{3}$ z₂) ($\frac{2}{3}$ $\frac{1}{3}$ z₂ + $\frac{1}{2}$)

- a) For the wurtzite parent structure type, find possible (GaN)_m(AlN)_n superlattice families specified by one of the maximal subgroups in the Bärnighausen tree.

Step 1.

Click [MAXSUB](#) (Maximal Subgroups of Space Groups).

Enter the space group number.

Mark the field “[Show WP Splittings?](#)”.

Step 2

Click the button: [SHOW MAXIMAL SUBGROUPS](#)

Step 3

In the list of maximal subgroups, choose one of the supergroups and click the button [SHOW...](#) in the last column. You will see the Transformation Matrix that relates the basis of the group with that of the subgroup.

- b) Choose the superlattice growth direction, i.e. the direction of the unit cell multiplication.

Step 1.

Analyze the Transformation Matrix

Step 2.

Choose among the subgroups those which correspond to the desired direction of the unit cell multiplication.

For example, for the multiplication along the z-direction, the Transformation Matrix is of the following form:

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & p & 0 \end{bmatrix}$$

Step 5

For a subgroup with the desired Transformation Matrix, click the button [WP Splitting](#).

Step 6.

You will see the table of WP splitting for the group-subgroup pair. For the occupied WP (2b, 2b) in the wurtzite structure, click the button [Relation](#).

- **c) Find the possible combinations of occupations of the splitted Wyckoff positions.**

Step 1.

Click the button [Relation](#) and check the relation of coordinates of atoms in the parent structure to the coordinates of atoms in the subgroup structure at the occupied WP.

Step 2.

Change the composition of the subgroup structure filling the splitted WP by different atoms. Determine how the new structure would look like.