Second South African School on Fundamental Crystallography
Satellite meeting of the 21st Meeting of the International Mineralogical Union

Bloemfontein, South Africa, 25-29 August 2014

UNIVERSITY OF THE FREE STATE
UNIVERSITEIT VAN DIE VRYSTAAT
YUNIVESITHI YA FREISTATA

2014 international year of crystallography
CRYSTAL-STRUCTURE TOOLS

BILBAO CRYSTALLOGRAPHIC SERVER
PRACTICAL EXERCISES

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Universidad del Pais Vasco, Bilbao, Spain
Bilbao Crystallographic Server

http://www.cryst.ehu.es

STRUCTURE UTILITIES

- CELLTRAN: Transform Unit Cells
- STRAIN: Strain Tensor Calculation
- WPASSIGN: Assignment of Wyckoff Positions
- TRANSTRU: Transform structures.
- SETSTRU: Alternative Settings for a given Crystal Structure
- EQUIVSTRU: Equivalent Descriptions for a given Crystal Structure
- VISUALIZE: Visualize structures using Jmol
- COMPSTRU: Comparison of Similar Structures with the same Symmetry
- STRUCTURE RELATIONS: Finds the transformation matrix that relates the two given group-subgroup related structures within a tolerance.
Bilbao Crystallographic Server

http://www.cryst.ehu.es

Structure Data for the Exercises:

http://www.cryst.ehu.es/resources/LaPlata2014
CRYSTAL-STRUCTURE DESCRIPTIONS

Conventional and ITA settings of space groups

Non-conventional settings of space groups

Equivalent structure descriptions
Crystal Structure Descriptions

<table>
<thead>
<tr>
<th>Title</th>
<th>Redetermination of the oxygen parameters in zircon (Zr Si O4).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Authors</td>
<td>Krstanovic, I.R.</td>
</tr>
<tr>
<td>Reference</td>
<td>Acta Crystallographica (1958) 11, 896-897</td>
</tr>
<tr>
<td>Compound</td>
<td>Zr (Si O4) - [Zircon] Zirconium silicate [ABX4] [t124] [h b a] [ZrSiO4]</td>
</tr>
<tr>
<td>Cell</td>
<td>6.6164(5), 6.6164, 6.0150(5), 90., 90., 90. I41/AMDZ (141) V=263.32</td>
</tr>
<tr>
<td>Remarks</td>
<td>R=0.070000 : PDC =01-073-6646 : PDF =6-266 : TYP =ZrSiO4 : XDS MIN =Zircon : At least one temperature factor missing in the paper. hk0- and 0kl-data, crystals not metamict</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom (site)</th>
<th>Oxid.</th>
<th>x, y, z, B, Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr1</td>
<td>(4a)</td>
<td>4</td>
</tr>
<tr>
<td>Si1</td>
<td>(4b)</td>
<td>4</td>
</tr>
<tr>
<td>O1</td>
<td>(16h)</td>
<td>-2</td>
</tr>
</tbody>
</table>

# Space Group ITA number
141
# Lattice parameters
6.6164 6.6164 6.0150 90 90 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
Zr 1 4a 0 0.75 0.125
Si 1 4b 0 0.75 0.625
O 1 16h 0 0.067 0.198

Inorganic Crystal Structure Database

Bilbao Crystallographic Server
Problem: BASIS TRANSFORMATION

\((a, b, c)\), origin \(O\): point \(X(x, y, z)\)

\((P, p) \downarrow \n\)

\((a', b', c')\), origin \(O'\): point \(X(x', y', z)\)

(i) linear part: change of orientation or length

\((a', b', c') = (a, b, c)P\)

\[
\begin{pmatrix}
P_{11} & P_{12} & P_{13} \\
P_{21} & P_{22} & P_{23} \\
P_{31} & P_{32} & P_{33}
\end{pmatrix}
\]

\(= (a, b, c)\left(\begin{array}{ccc}
P_{11} & a + P_{21} b + P_{31} c, \\
P_{21} & a + P_{22} b + P_{32} c, \\
P_{31} & a + P_{23} b + P_{33} c.
\end{array}\right)\)

(ii) origin shift by a shift vector \(p(p_1, p_2, p_3)\):

\[O' = O + p\]

the origin \(O'\) has coordinates \((p_1, p_2, p_3)\) in the old coordinate system
Transformation of the coordinates of a point \(X(x,y,z)\):

\[
\begin{pmatrix}
    x' \\
    y' \\
    z'
\end{pmatrix}
= Q
\begin{pmatrix}
    x \\
    y \\
    z
\end{pmatrix} + q
\]

with

\[
Q = P^{-1}
\]
\[
q = -P^{-1}p.
\]

Transformation of symmetry operations \((W,w)\):

\[
(W',w') = (P,p)^{-1}(W,w)(P,p)
\]

Transformation of the metric tensor \(G\):

\[
G' = P^T(G)P
\]
Problem: ITA SETTINGS STRUCTURE DESCRIPTIONS

ITA-settings for the space group C2/c (No.15)

Choose the initial and final space groups symbols

\[ X_f = (P, p)^{-1} X_i \]

Initial setting structure description

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>Setting</th>
<th>P</th>
<th>p (^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1 2/c1</td>
<td></td>
<td>a,b,c</td>
<td>a,b,c</td>
<td></td>
</tr>
<tr>
<td>A 1 2/n1</td>
<td></td>
<td>-a,c,b,a</td>
<td>c,b,-a-c</td>
<td></td>
</tr>
<tr>
<td>I 1 2/a1</td>
<td></td>
<td>c,b,-a-c</td>
<td>-a,c,b,a</td>
<td></td>
</tr>
<tr>
<td>A 1 2/a1</td>
<td></td>
<td>c,-b,a</td>
<td>c,-b,a</td>
<td></td>
</tr>
<tr>
<td>C 1 2/n1</td>
<td></td>
<td>a,-b,a-c</td>
<td>a,-b,a-c</td>
<td></td>
</tr>
<tr>
<td>I 1 2/c1</td>
<td></td>
<td>-a,c,-b,c</td>
<td>-a,c,-b,c</td>
<td></td>
</tr>
<tr>
<td>A 1 2/a1</td>
<td></td>
<td>c,a,b</td>
<td>b,c,a</td>
<td></td>
</tr>
<tr>
<td>B 1 1 2/n</td>
<td></td>
<td>a,-a,c,b</td>
<td>a,c,-a-b</td>
<td></td>
</tr>
<tr>
<td>I 1 1 2/b</td>
<td></td>
<td>-a,c,b,c</td>
<td>-a,b,c,b</td>
<td></td>
</tr>
<tr>
<td>B 1 1 2/b</td>
<td></td>
<td>a,c,-b</td>
<td>a,c,-b</td>
<td></td>
</tr>
<tr>
<td>A 1 1 2/n</td>
<td></td>
<td>a,-c,a,-b</td>
<td>b,-c,-a-b</td>
<td></td>
</tr>
<tr>
<td>I 1 1 2/a</td>
<td></td>
<td>c,-a,-c,b</td>
<td>-a,b,-c,a</td>
<td></td>
</tr>
<tr>
<td>B 2/b 11</td>
<td></td>
<td>c,b,a</td>
<td>c,a,b</td>
<td></td>
</tr>
<tr>
<td>C 2/n 14</td>
<td></td>
<td>b,c,a</td>
<td>c,a,b</td>
<td></td>
</tr>
</tbody>
</table>

final setting structure description
Problem 3.1

Compare the two structure descriptions and check if they belong to the same structure type.
Structure 1: Space group $I4_1/amd$ (141)  
origin choice 1 at 4m2  
$a=6.60 \, \text{Å} \quad c=5.88 \, \text{Å}$

Structure 2: Space group $I4_1/amd$ (141)  
origin choice 2 at 2/m at 0,-1/4,1/8 from 4m2  
$a=6.616 \, \text{Å} \quad c=6.015 \, \text{Å}$

Compare the two structure descriptions and check if they belong to the same structure type.

Use the tools of Bilbao Crystallographic server: SETSTRU

Hint: In order to compare the different data, the parameters of Structure 1 are to be transformed to ‘origin at center 2/m’, i.e. ORIGIN CHOICE 2.
Problem: UNIT CELL TRANSFORMATION

Bilbao Crystallographic Server

G' = P^TGP

Lattice parameters
hexagonal cell

Lattice parameters
monoclinic cell

Transform Unit Cell

Cell Parameters: 5.6748 5.6748 20.3784 90 90 120

Please, define the rotational part of the transformation matrix that relates the group and the subgroup bases
in abc form:

Ex: c,a,b (read by columns)

Rotational part:

<table>
<thead>
<tr>
<th>2/3</th>
<th>0</th>
<th>-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>1/3</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Transformation matrix

(P, p)
Problem: STRUCTURE TRANSFORMATION

**Transform Structure**

**TRANSTRU** can transform a structure in two ways:

- To a lower symmetry space group. The transformed structure is given in the low symmetry space group basis, taking care of all possible splittings of the Wyckoff positions.
- With an arbitrary matrix. The structure, including the cell parameters and the atoms in the unit cell, is transformed with an arbitrary matrix introduced by the user.

Only the default choice for the conventional setting of the space groups is used.

**Structure Data**

HINT: [The option for a given filename is preferential]

<table>
<thead>
<tr>
<th>H</th>
<th>166</th>
<th>5.6748</th>
<th>5.6748</th>
<th>20.3784</th>
<th>90</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>3a</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>2</td>
<td>6c</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.20710</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>3</td>
<td>6c</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.38480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>4</td>
<td>6c</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.32400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td>18i</td>
<td>0.84240</td>
<td>0.15760</td>
<td>0.43010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Default Settings**

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

**Subgroup Basis**

**Asymmetric Unit**

**Arbitrary Transformation**
High symmetry structure

Example TRANSTRU: Pb₃(VO₄)₂

R-3m structure
(Pₚ, p)

P₂₁/c structure

Pb₁(3a) Pb₂(6c) PV(6c) O₁(6c) O₂(18h)

WP splitting

Pb₁(2a) Pb₂(4e) PV(4e) O₁(4e) O₂₁(4e) O₂₂(4e)

Low symmetry structure

View Structure (with Jmol applet)
Apply the program **TRANSTRU** in order to check if the two structure descriptions belong to the same structure type.

**Structure 1:** Space group $\textit{l4}_1/\textit{amd}$ (141) $a=6.60 \ \text{Å} \ c=5.88 \ \text{Å}$  
origin choice 1 at $\bar{4}m2$

**Structure 2:** Space group $\textit{l4}_1/\textit{amd}$ (141) $a=6.616 \ \text{Å} \ c=6.015 \ \text{Å}$  
origin choice 2 at $2/m$ at $0,-1/4,1/8$ from $\bar{4}m2$

---

**Origin choice 2**  
P=0, 1/4, -1/8
Problem: EQUIVALENT DESCRIPTIONS

How to find all possible equivalent descriptions of a crystal structure?

Number of equivalent descriptions = |N(G)|/|G|

index of the group in its Euclidean normalizer
Problem 3.2a

Bilbao Crystallographic Server

Equivalent descriptions: CsCl  EQUIVSTRU

Equivalent Descriptions of Crystal Structures

Equivalent Structures

Given a space group ITA number, the cell parameters (separated with spaces) and the atom positions, the program EQUIVSTRU transforms the corresponding structure with the elements of the euclidean normalizer of the space group. All the transformed structures are equivalent symmetry descriptions of the given initial structure. The atom positions are identified generating the Wyckoff sets.

Only the default choice for the conventional setting of the space groups is used.

Structure Data
[in CIF format]

HINT: [The option for a given filename is preferential]

# Space Group ITA number
221
# Lattice parameters
5.3 5.3 5.3 90 90 90
# Number of independent atoms in the asymmetric unit
2
# [atom type] [number] [WP] [x] [y] [z]
Cs 1 1a 0 0 0
Cl 1 1b 0.5 0.5 0.5

space group in default setting
Example EQUIVSTRU: CsCl

Equivalent Descriptions of Crystal Structures

**Equivalent Structures**

Given a space group ITA number, the cell parameters (separated with spaces) and the atom positions, the program EQUIVSTRU transforms the corresponding structure with the elements of the euclidean normalizer of the space group. All the transformed structures are equivalent symmetry descriptions of the given initial structure. The atom positions are identified generating the Wyckoff sets.

**Structure Data**

Structure Data [in CIF format]

```
#Exercise 3.2a(CsCl)
# Space Group ITA number
221
# Lattice parameters
4.12599 4.12599 4.12599 90.0 90.0 90.0
# Number of independent atoms in the asymmetric unit
2
# [atom type] [number] [WP] [x] [y] [z]
Cl  1  1a  0.000000 0.000000 0.000000
Cs  1  1b  0.500000 0.500000 0.500000
```

**Structure**

**Structure number 1**

- Normalizer coset representative: $x,y,z$
- Transformed unit cell:
  - 4.1260 4.1260 4.1260 90.00 90.00 90.00
- Transformed structure:

<table>
<thead>
<tr>
<th>AT.</th>
<th>WP</th>
<th>SS</th>
<th>Representative</th>
<th>Atomic orbit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1a</td>
<td>m-3m</td>
<td>(0.000000, 0.000000, 0.000000)</td>
<td>(0.000000, 0.000000, 0.000000)</td>
</tr>
<tr>
<td>Cs</td>
<td>1b</td>
<td>m-3m</td>
<td>(0.500000, 0.500000, 0.500000)</td>
<td>(0.500000, 0.500000, 0.500000)</td>
</tr>
</tbody>
</table>

**Structure number 2**

- Normalizer coset representative: $x+1/2,y+1/2,z+1/2$
- Transformed unit cell:
  - 4.1260 4.1260 4.1260 90.00 90.00 90.00
- Transformed structure:

<table>
<thead>
<tr>
<th>AT.</th>
<th>WP</th>
<th>SS</th>
<th>Representative</th>
<th>Atomic orbit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1b</td>
<td>m-3m</td>
<td>(0.500000, 0.500000, 0.500000)</td>
<td>(0.500000, 0.500000, 0.500000)</td>
</tr>
<tr>
<td>Cs</td>
<td>1a</td>
<td>m-3m</td>
<td>(0.000000, 0.000000, 0.000000)</td>
<td>(0.000000, 0.000000, 0.000000)</td>
</tr>
</tbody>
</table>
Additional Generators for the Normalizer of the Group 221 \((Pm-3m)\)

Additional generators of Euclidean normalizer \((lm-3m)\) \(a,b,c\)

\[
\begin{array}{ccc}
\begin{bmatrix} x+1/2, y+1/2, z+1/2 \\
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\end{array}
\]

Wyckoff Sets of Space Group 221 \((Pm-3m)\)

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

<table>
<thead>
<tr>
<th>Letter</th>
<th>Mult</th>
<th>SS</th>
<th>Rep.</th>
<th>Equivalent Positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>48</td>
<td>1</td>
<td>((x, y, z))</td>
<td>n</td>
</tr>
<tr>
<td>m</td>
<td>24</td>
<td>..m</td>
<td>((x, x, z))</td>
<td>m</td>
</tr>
<tr>
<td>f</td>
<td>6</td>
<td>4m.m</td>
<td>((x, 1/2, 1/2))</td>
<td>ef</td>
</tr>
<tr>
<td>e</td>
<td>6</td>
<td>4m.m</td>
<td>((x, 0, 0))</td>
<td>ef</td>
</tr>
<tr>
<td>d</td>
<td>3</td>
<td>4/mm.m</td>
<td>((1/2, 0, 0))</td>
<td>cd</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>4/mm.m</td>
<td>((0, 1/2, 1/2))</td>
<td>cd</td>
</tr>
<tr>
<td>b</td>
<td>1</td>
<td>m-3m</td>
<td>((1/2, 1/2, 1/2))</td>
<td>ab</td>
</tr>
<tr>
<td>a</td>
<td>1</td>
<td>m-3m</td>
<td>((0, 0, 0))</td>
<td>ab</td>
</tr>
</tbody>
</table>
**EXERCISES**

Problem 3.2b

Equivalent structure descriptions
Space group: P4/n

Exercise 6.4. \( P(C_6C_5)_4[MoNCl_4] \) is tetragonal, spac

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate ( x )</th>
<th>Coordinate ( y )</th>
<th>Coordinate ( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2b</td>
<td>0.25</td>
<td>0.75</td>
<td>0</td>
</tr>
<tr>
<td>Mo</td>
<td>2c</td>
<td>0.25</td>
<td>0.25</td>
<td>0.121</td>
</tr>
<tr>
<td>N</td>
<td>2c</td>
<td>0.25</td>
<td>0.25</td>
<td>-0.093</td>
</tr>
<tr>
<td>Cl1</td>
<td>8g</td>
<td>0.362</td>
<td>0.760</td>
<td>0.141</td>
</tr>
<tr>
<td>Cl2</td>
<td>8g</td>
<td>0.437</td>
<td>0.836</td>
<td>0.117</td>
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<tr>
<td>Cl1</td>
<td>8g</td>
<td>0.400</td>
<td>0.347</td>
<td>0.191</td>
</tr>
</tbody>
</table>

\[ N(P4/n) = P4/mmm \ (a',b',1/2c) \]

\[ a' = 1/2(a-b), \ b' = 1/2(a+b) \]
Space-group symmetry: R-3
Euclidean normalizer: R-3m(-a,-b, 1/2c)
Coset representatives:  x,y,z; x,y,z+1/2; -y,-x,z; -y,-x,z+1/2;
CRYSTAL-STRUCTURE RELATIONSHIPS

Comparison of crystal structures

Phase transitions

Symmetry relations between crystal structures
Crystal-structure relationships

COMPARISON OF CRYSTAL STRUCTURES
Different descriptions of the same structure

**PROBLEM:**
Two descriptions of the same structure with respect to the same space group, specified by unit-cell parameters and atomic coordinates data.

Search for a mapping of the two descriptions such that the global distortion accompanying the mapping is tolerably small.
Problem: Similarity of the descriptions

Description 1: \(a_1, b_1, c_1 \quad (x_1, y_1, z_1)\)

Description 2: \(a_2, b_2, c_2 \quad (x_2, y_2, z_2)\)

How to measure the similarity between two descriptions?

- **Degree of lattice distortion**
  \[ S = \frac{1}{3} \sqrt{\sum_i \eta_i^2} \]
  \(\eta_i\)-eigenvalues of the Lagrangian strain tensor

- **Average atomic displacements**
  \[ d_{av} = \frac{1}{n} \sum_i m_i u_i \]
  \(u_i\)-atomic displacements

- **Maximal atomic displacements**
  maximal displacements of the paired atoms
Problem: Similarity of the descriptions

Description 1
\( a_1, b_1, c_1 \)  
\( (x_1, y_1, z_1) \)

How to measure the similarity between two descriptions?

Description 2
\( a_2, b_2, c_2 \)  
\( (x_2, y_2, z_2) \)

\[ \Delta = [\sqrt{2\Delta(c) + 1}] \Delta(d) - 1 \]


\[ \sum_i m[(x_i - y_i)^2]^{1/2} / \sum m \]

structural descriptor

weighted mean difference between atomic coordinates

\[ \frac{[(b_1/a_1)(c_1/a_1)]}{[(b_2/a_2)(c_2/a_2)]} \]

relation between axial ratios
**Problem:** COMPARISON OF STRUCTURES

**Comparison of crystal structures of the same symmetry**

<table>
<thead>
<tr>
<th>Structure Data [in CIF format]</th>
<th>Examinar...</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HINT:</strong> The option for a given filename is preferential</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>12.800 5.691 9.420 90.0 102.3 90.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Pb 1 4e 0.0000 0.2910 0.2500</td>
<td></td>
</tr>
<tr>
<td>Pb 2 8f 0.3170 0.3900 0.3520</td>
<td></td>
</tr>
<tr>
<td>P 1 8f 0.5990 0.2410 0.4470</td>
<td></td>
</tr>
<tr>
<td>Pb 2 8f 0.6430 0.0300 0.3920</td>
<td></td>
</tr>
<tr>
<td>O 2 8f 0.6340 0.4640 0.3740</td>
<td></td>
</tr>
<tr>
<td>O 3 8f 0.6420 0.2800 0.6120</td>
<td></td>
</tr>
<tr>
<td>O 4 8f 0.4910 0.2220 0.4200</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure Data [in CIF format]</th>
<th>Examinar...</th>
</tr>
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<tbody>
<tr>
<td><strong>HINT:</strong> The option for a given filename is preferential</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>13.967 5.560 40.778 90.0 166.7 90.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Pb 1 4e 0.0000 0.0000 0.0000 0.7500</td>
<td></td>
</tr>
<tr>
<td>Pb 2 8f 0.0000 0.0000 0.0000 0.8563</td>
<td></td>
</tr>
<tr>
<td>P 1 8f 0.0000 0.0000 0.0000 0.9511</td>
<td></td>
</tr>
<tr>
<td>Pb 2 8f 0.2715 0.7285 0.8885</td>
<td></td>
</tr>
<tr>
<td>O 2 8f 0.9570 0.5000 0.1170</td>
<td></td>
</tr>
<tr>
<td>O 3 8f 0.7285 0.2715 0.6115</td>
<td></td>
</tr>
<tr>
<td>O 4 8f 0.2715 0.6115</td>
<td></td>
</tr>
</tbody>
</table>

Enter the maximum distance allowed between the paired atoms: 1 Å

Enter the allowed tolerance (a b c α β γ): .5 .5 .5 .5 .5 .5
Example COMPSTRU: $\text{Pb}_3(\text{PO}_4)_2$

Evaluation of the structure similarity

<table>
<thead>
<tr>
<th>S</th>
<th>$d_{\text{max.}}$ (Å)</th>
<th>$d_{\text{av.}}$ (Å)</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0116</td>
<td>0.3386</td>
<td>0.1430</td>
<td>0.066</td>
</tr>
</tbody>
</table>

structural descriptor $\Delta = 0.066$

maximal displacement $d_{\text{max}} = 0.34$ Å

Additional Generators for the Normalizer of the Group 221 ($Pm\text{-}3m$)

Additional generators of Euclidean normalizer ($I\text{-}m\text{-}3m$) $a, b, c$

$\begin{bmatrix} x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2} \\ 1/2 \end{bmatrix}$
Problem 3.4

In ICSD can be found several structure data sets of $\varepsilon$-Fe$_2$O$_3$, all of them of symmetry Pna2$_1$ (No. 33). Compare the following two descriptions and check if they belong to the same structure type.
Problem 3.4

ICSD data for $\varepsilon$-Fe$_2$O$_3$, 

<table>
<thead>
<tr>
<th>Atom (site)</th>
<th>Oxid.</th>
<th>$x$, $y$, $z$, B, Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O2</td>
<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O3</td>
<td>(4a)</td>
<td>-2</td>
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<tr>
<td>O4</td>
<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O5</td>
<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O6</td>
<td>(4a)</td>
<td>-2</td>
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<tr>
<td>Fe1</td>
<td>(4a)</td>
<td>3</td>
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<tr>
<td>Fe2</td>
<td>(4a)</td>
<td>3</td>
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<tr>
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<td>3</td>
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<td>Fe4</td>
<td>(4a)</td>
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<tr>
<td>O1</td>
<td>(4a)</td>
<td>-2</td>
</tr>
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<td>O2</td>
<td>(4a)</td>
<td>-2</td>
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<tr>
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<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O4</td>
<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O5</td>
<td>(4a)</td>
<td>-2</td>
</tr>
<tr>
<td>O6</td>
<td>(4a)</td>
<td>-2</td>
</tr>
</tbody>
</table>

Cell parameters:
- $a = 5.0715(2)$, $b = 8.7359(4)$, $c = 9.4178(4)$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 423.14$
Problem: Isoconfigurational Structure Types

Lima-de Faria et al. Acta Cryst. (1990), A46, 1

Isopointal structure types
- Space group
- Wyckoff position sequence
- Pearson symbol

Isoconfigurational structure types
- Isopointal
- Crystallographic orbits
- Geometrical interrelationships

Inorganic Crystal Structure Database (2009)
http://icsdweb.fiz-karlsruhe.de

isoconfigurational structure types?

Composition type (ANX formula)
- Range of c/a ratio
- β-range
- Atomic coordinates
- Chemical properties
Isoconfigurational (configurationally isotypic) Structure Types

PROBLEM:
Consider two isopointal structures specified by their space-group symmetry, unit-cell parameters and atomic coordinates data. We search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.

Structure 2 → (Structure 2)$_G$ → Structure 1

- symmetry controlled mapping
- most similar configuration
- global distortion of the mapping

atomic species correspondence scheme
Lattice deformation Atomic displacement field

COMPSTRU
How to measure the similarity between two isopointal structures?

degree of lattice distortion

\[ S = \frac{1}{3} \sqrt{\sum_{i} \eta_i^2} \]

\( \eta_i \)-eigenvalues of the Lagrangian strain tensor

average atomic displacements

\[ d_{av} = \frac{1}{n} \sum_{i} m_i u_i \]

\( u_i \)-atomic displacements

structural descriptor

\[ \Delta = [\sqrt{2} \Delta(c) + 1] \Delta(d) - 1 \]

Do these compounds belong to the same structure type?

KAsF₆  BaIrF₆  BaSnF₆

Example: STRUCTURE TYPES

STUDY OF THE FAMILY **ABF6**

<table>
<thead>
<tr>
<th>KCrF6</th>
<th>LiNbF6</th>
<th>VNbF6</th>
<th>HgRhF6</th>
<th>MgPbF6</th>
<th>InAsF6</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbCrF6</td>
<td>LiRuF6</td>
<td>CoZrF6</td>
<td>NiRhF6</td>
<td>ZnPbF6</td>
<td>CsNbF6</td>
</tr>
<tr>
<td>KAsF6</td>
<td>LiRhF6</td>
<td>PdPtF6</td>
<td>CaCrF6</td>
<td>NiPbF6</td>
<td>HgCrF6</td>
</tr>
<tr>
<td>RuAsF6</td>
<td>LiTaF6</td>
<td>FeNbF6</td>
<td>MgCrF6</td>
<td>MgPdF6</td>
<td>CoSnF6</td>
</tr>
<tr>
<td>CsAsF6</td>
<td>LiOsF6</td>
<td>CaSnF6</td>
<td>CdCrF6</td>
<td>CaPdF6</td>
<td>CsNbF6</td>
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<tr>
<td>RbSbF6</td>
<td>LiIrF6</td>
<td>FeZrF6</td>
<td>MnSnF6</td>
<td>ZnPdF6</td>
<td>MnPtF6</td>
</tr>
<tr>
<td>BaSnF6</td>
<td>LiPtF6</td>
<td>CuZrF6</td>
<td>FeSnF6</td>
<td>CdPdF6</td>
<td>CdRhF6</td>
</tr>
<tr>
<td>CsBrF6</td>
<td>LiAuF6</td>
<td>CaPtF6</td>
<td>ZnSnF6</td>
<td>LiSbF6</td>
<td>NaBiF6</td>
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<tr>
<td>CsSbF6</td>
<td>NiPtF6</td>
<td>ZnPtF6</td>
<td>NiSnF6</td>
<td>BalrF6</td>
<td>TIAsF6</td>
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<tr>
<td>CsBiF6</td>
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<tr>
<td>CsUF6</td>
<td>LiPF6</td>
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<td>KOsF6</td>
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<td>CdTiF6</td>
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<td>ZnRhF6</td>
<td>LiBiF6</td>
<td>KPF6</td>
<td></td>
</tr>
</tbody>
</table>
STUDY OF THE FAMILY ABF6

Reference structure: CaCrF₆

maximal distance Δ [Å]

MnPtF₆ 0.1282
NiPtF₆ 0.1802
NiRhF₆ 0.2005

Type: LiSbF₆

CsBrF₆ 1.0731
CsUF₆ 1.1397
BrIrF₆ 1.4067

Type: KOsF₆
STUDY OF THE FAMILY ABX₃

R-3 (148); WP sequence: fc²; Pearson: hR10

<table>
<thead>
<tr>
<th>Mg₂O</th>
<th>Co₂O₃</th>
<th>FeSbO₃</th>
<th>MnO</th>
<th>NiO</th>
<th>Ni₃O₃</th>
<th>MnO</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>Sr₂O₃</th>
<th>CaO</th>
<th>Sr₂O₃</th>
<th>CaO</th>
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<td>0.1</td>
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<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
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<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
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<td>0.6</td>
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<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
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<tr>
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<td>0.1</td>
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<td>0.3</td>
<td>0.6</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
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<tr>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
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<td>0.3</td>
<td>0.6</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.6</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ICSD (c/a)</th>
<th>Bergerhoff (structure descriptor)</th>
<th>Bilbao Server (global distortion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTiO₃</td>
<td></td>
<td>0.3 FeTiO₃ (NaSbO₃)</td>
</tr>
<tr>
<td>FePSe₃</td>
<td></td>
<td>0.4 FePSe₃</td>
</tr>
</tbody>
</table>
Crystal-structure relationships

STRUCTURAL PHASE TRANSITIONS
PROBLEM:
Consider two phases of the same compound (specified by their unit-cell parameters and atomic coordinates) with group-subgroup related symmetry groups $G > H$.

Search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.

**Structure Relationships**

- **High-symmetry phase**
  - symmetry controlled mapping
  - $G > H$ relationship
  - Wyckoff positions schemes

- **(High-symmetry phase)$_{Low}$**
  - most similar configuration
  - $G_H$ transformation

- **Low-symmetry phase**
  - global distortion of the mapping
  - Lattice deformation
  - Atomic displacement field

**Structure Relations**
Given the high- and low-symmetry phases:

1. Characterize the symmetry reduction between the high- and low-symmetry phases
   - index of the group-subgroup pair: INDEX
   - group-subgroup graph, (P,p): SUBGROUPGRAPH

2. Domain-structure analysis

3. Determine the so-called *reference* structure, i.e. high-symmetry structure in the low-symmetry basis
   - lattice parameters: CELLTRANS
   - atomic coordinates: TRANSTRU or WYCKSPLIT

4. Evaluate the lattice strain and the atomic displacements accompanying the phase transitions:
   STRAIN, COMPSTRU
At low temperatures, the space-group symmetry of cristobalite is given by the space group is \( \text{P4}_12_12 \) (92) with lattice parameters \( a=4.9586\text{Å}, c=6.9074\text{Å} \). The four silicon atoms are located in Wyckoff position 4(a) ..2 with the coordinates \( x, x, 0; -x, -x, 1/2; 1/2-x,1/2+x, 1/4; 1/2+x,1/2-x,3/4, x = 0.3028 \).

During the phase transition, the tetragonal structure is transformed into a cubic one with space group \( \text{Fd}-3\text{m} \) (227), \( a=7.147\text{Å} \). It is listed in the space-group tables with two different origins. If ‘Origin choice 2’ setting is used (with point symmetry -3m at the origin), then the silicon atoms occupy the position 8(a) -43m with the coordinates \( 1/8, 1/8, 1/8; 7/8, 3/8, 3/8 \) and those related by the face-centring translations.

Describe the structural distortion from the cubic to the tetragonal phase by the determination of (i) the displacements if the Si atoms in relative and absolute units, and (ii) the changes on the lattice parameters during the transition.
Example: $\alpha$-Cristobalite $\rightarrow$ $\beta$-Cristobalite

<table>
<thead>
<tr>
<th>Origin choice 2:</th>
<th>Si 8a 1/8,1/8,1/8 7/8,3/8,3/8</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Atom (site) Oxid.</th>
<th>x, y, z, B, Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1 (4a)</td>
<td>0.3028 0.3028 0.3028 0 0 1</td>
</tr>
<tr>
<td>O1 (8b)</td>
<td>0.2383 0.1093 0.1816 0 0 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom (site) Oxid.</th>
<th>x, y, z, B, Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1 (8a)</td>
<td>0 0 0 0 0 1</td>
</tr>
<tr>
<td>O1 (96h)</td>
<td>0.125 0.081 0.169 0 0.1667</td>
</tr>
</tbody>
</table>
1. Characterize the symmetry break between the high- and low-symmetry phases
   - index of the group-subgroup pair: INDEX
   - transformation matrix: SUBGROUPGRAPH

2. Calculate the lattice parameters of the low-symmetry phase: CELLTRANS

3. Calculate the atomic coordinates of the low-symmetry phase: TRANSFORM (or WYCKSPLIT)

4. Evaluate the lattice strain and the atomic displacements accompanying the phase transitions: STRAIN, COMPSTRU
Step 1. Determination of the index of the group-subgroup pair

INDEX: Index of a group-subgroup pair

Please, enter the sequential number of group as given in *International Tables for Crystallography, Vol. A*:

- Option A: Introduce the formula units (conventional) of the high and low symmetry structure.

The formula units (conventional) on the high symmetry structure:

The formula units (conventional) on the low symmetry structure:

- Option B: Introduce the lattice parameters of the high and low symmetry structure.

The lattice parameters on the high symmetry structure: 7.12637 7.12637 7.12637 90. 90. 90.

The lattice parameters on the low symmetry structure: 4.9501 4.9501 6.8760 90. 90. 90.

Show index

\[ [i_L] = 2 \]
\[ [i_P] = 6 \]

\[ [i] = 12 \]
Step 2. Study of the group-subgroup symmetry break

### SUBGROUPGRAPH

<table>
<thead>
<tr>
<th>Check</th>
<th>Chain [indices]</th>
<th>Chain with HM symbols</th>
<th>Transformation</th>
<th>Identical</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>227 210 098 092 [2 3 2]</td>
<td>Fd-3m &gt; F4_132 &gt; I4_122 &gt; P4_12_12</td>
<td>((-\frac{1}{2} \ 1/2 \ 0 \ 3/8)) (0 \ 0 \ 1 \ 3/8) (1/2 \ 0 \ 5/8) (1/2 \ 0 \ 5/8)</td>
<td>to group 1</td>
</tr>
<tr>
<td>2</td>
<td>227 141 098 092 [3 2 2]</td>
<td>Fd-3m &gt; I4_1/amd &gt; I4_122 &gt; P4_12_12</td>
<td>((-\frac{1}{2} \ 1/2 \ 0 \ 3/8)) (1/2 \ 1/2 \ 0 \ 3/8) (1/2 \ 1/2 \ 0 \ 3/8) (1/2 \ 1/2 \ 0 \ 3/8)</td>
<td>to group 2</td>
</tr>
<tr>
<td>3</td>
<td>227 141 098 092 [3 2 2]</td>
<td>Fd-3m &gt; I4_1/amd &gt; I4_122 &gt; P4_12_12</td>
<td>((-\frac{1}{2} \ 1/2 \ 0 \ 3/8)) (0 \ 0 \ 1 \ 3/8) (1/2 \ 0 \ 5/8) (1/2 \ 0 \ 5/8)</td>
<td>to group 3</td>
</tr>
</tbody>
</table>

**Show graph**

Which of the three matrices corresponds to the cristobalite case?
Step 3. Lattice parameters of the reference structure

**CELLTRANS**

- **High-symmetry phase** $G$
- $G \rightarrow H$ relationship
- **(High-symmetry phase)**$_{Low}$ $(G)_H$

**Transform Unit Cell**

<table>
<thead>
<tr>
<th>Cell Parameters:</th>
<th>7.147 7.147 7.147 90 90 90</th>
</tr>
</thead>
</table>

Please, define the rotational part of the transformation matrix that relates the group and the subgroup bases in $abc$ form: Ex: $c,a,b$ (read by columns)

<table>
<thead>
<tr>
<th>Rotational part</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/2$ $1/2$ $0$</td>
</tr>
<tr>
<td>$-1/2$ $1/2$ $0$</td>
</tr>
<tr>
<td>$0$ $0$ $1$</td>
</tr>
</tbody>
</table>

or in matrix form:

| 5.053 5.053 7.147 90 90 90 |

**lattice parameters of the reference structure**
Step 3. Atomic coordinates of the reference structure

High-symmetry phase $\xrightarrow{G > H}$ (High-symmetry phase)$_{Low}$

Transform Structure

Structure

Low symmetry Space Group

Transformation Matrix:

In matrix form:

Rotational part

| 1/2 | 1/2 | 0   |
| -1/2| 1/2 | 0   |
| 0   | 0   | 1   |

Origin Shift

| 5/8  |
| 3/8  |
| 3/8  |

Space Group: 92
Lattice Parameters: 5.053692 5.053692 7.147000 90 90 90

<table>
<thead>
<tr>
<th>AT</th>
<th># WP</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1</td>
<td>4a 3/4 1/4 3/4</td>
</tr>
</tbody>
</table>
Step 4. Characterization of the global distortion

Symmetry break:
Fd-3m→P4₁2₁2, index 12
aₜ=1/2(a_c−b_c), bₜ=1/2(a_c+b_c), cₜ=c_c
origin shift: (5/8,3/8,3/8)

Experiment:

**Cubic phase:**
a=7.147 Å
Si 8a 1/8 1/8 1/8
7/8 3/8 3/8

**Tetragonal phase:**
a=4.9586 Å, c=6.9074
Si 4a 0.3028 0.3028 0

Calculated:

**Reference description:**
a=5.053 Å, c=7.147 Å
Si 4a 0.75 0.25 0.75
0.25 0.25 0

affine deformation?
atomic displacements?
Step 4a. Determination of the affine deformation

Symmetry break:
Fd-3m → P4₁2₁2, index 12

\[ a_t = \frac{1}{2}(a_c - b_c), \quad b_t = \frac{1}{2}(a_c + b_c), \quad c_t = c_c \]

origin shift: (5/8, 3/8, 3/8)

Experiment:
**Cubic phase:**
\[ a = 7.147 \text{ Å} \]

**Tetragonal phase:**
\[ a = 4.9586 \text{ Å}, \quad c = 6.9074 \text{ Å} \]

Calculated:
**Reference description:**
\[ a = 5.053 \text{ Å}, \quad c = 7.147 \text{ Å} \]

**CELLTRANS**

\[
P = \begin{bmatrix}
\frac{1}{2} & \frac{1}{2} & 0 \\
-\frac{1}{2} & \frac{1}{2} & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\]

**STRAIN**

**affine deformation**
Step 4a. Determination of the affine deformation

\[(G)_{H}\]

Unit cell 1:
\[
\begin{array}{cccc}
[a_1] & [b_1] & [c_1] & [\alpha_1] [\beta_1] [\gamma_1] \\
5.053 & 5.053 & 7.147 & 90 \hspace{1mm} 90 \hspace{1mm} 90 \\
\end{array}
\]

Unit cell 2:
\[
\begin{array}{cccc}
4.9586 & 4.9586 & 6.9074 & 90 \hspace{1mm} 90 \hspace{1mm} 90 \\
\end{array}
\]

STRAIN

\[S = \frac{1}{3} (\sum \eta_i^2)^{1/2}\]
Problem: LATTICE STRAIN CALCULATION

\[ X_1 = R_1 \cdot x_1 \quad X_2 = R_2 \cdot x_2 \]

\[ R_i = \begin{pmatrix}
  a_i \sin(\beta_i) \sin(\gamma_i^*) & 0 & 0 \\
  -a_i \sin(\beta_i) \cos(\gamma_i^*) & b_i \sin(\alpha_i) & 0 \\
  a_i \cos(\beta_i) & b_i \cos(\alpha_i) & c_i
\end{pmatrix} \]

Strain definition:

\[ X_2 - X_1 = e \cdot X_1 \quad \text{with} \quad e = R_2^{-1} R_1 - I \]

\[ M_i = \begin{pmatrix}
  \vec{a}_i \cdot \vec{a}_i & \vec{a}_i \cdot \vec{b}_i & \vec{a}_i \cdot \vec{c}_i \\
  \vec{b}_i \cdot \vec{a}_i & \vec{b}_i \cdot \vec{b}_i & \vec{b}_i \cdot \vec{c}_i \\
  \vec{c}_i \cdot \vec{a}_i & \vec{c}_i \cdot \vec{b}_i & \vec{c}_i \cdot \vec{c}_i
\end{pmatrix} \]

Finite Lagrangian strain tensor:

\[ \eta = \frac{1}{2} (e + e^T + e^T e) = \frac{1}{2} R_1^{-T} (M_1 - M_2) R_1^{-1} \]

Degree of lattice distortion:

\[ S = \frac{1}{3} (\sum \eta_i^2)^{1/2} \]

Valid for linear and non-linear strains!
Step 4b. Atomic displacement field

Symmetry break:

Fd-3m $\rightarrow$ P4$_1$2$_1$2, index 12

Experiment:

Cubic phase:

- $a = 7.147 \, \text{Å}$
- Si: 8a 1/8 1/8 1/8 7/8 3/8 3/8

Calculated:

Reference description:

- $a = 5.053 \, \text{Å}, c = 7.147 \, \text{Å}$
- Si: 4a 0.75 0.25 0.75 0.25 0.25 0

Tetragonal phase:

- $a = 4.9586 \, \text{Å}, c = 6.9074$
- Si: 4a 0.3028 0.3028 0

**TRANSTRU**

**COMPSTRU**

atomic displacement field
Step 4b. Atomic displacement field

Reference structure

<table>
<thead>
<tr>
<th>Structure #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Experimental data

<table>
<thead>
<tr>
<th>Structure #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Evaluation of the structure similarity

<table>
<thead>
<tr>
<th>S</th>
<th>$d_{\text{max}}$ (Å)</th>
<th>$d_{\text{av}}$ (Å)</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0149</td>
<td>0.3774</td>
<td>0.7548</td>
<td>0.122</td>
</tr>
</tbody>
</table>

Most similar configuration

<table>
<thead>
<tr>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Affine normalizer

$\Delta = 0.122$

Structural descriptor

Atom pairings and distances

| WP | Atom | Atomic Displacements | $|u|$ |
|----|------|-----------------------|------|
| 4a | (x,x,0) | Si1                   | 0.3774 |
|    |       | $u_x$ | $u_y$ | $u_z$ |     |
|    |       | -0.0528 | 0.0528 | 0.0000 | 0.3774 |

Maximal displacement

$d_{\text{max}} = 0.377$ Å
PROBLEM: Structural Relationship between two structures with group-subgroup related symmetry groups $G \rightarrow H$

High-symmetry phase: $G$

- Symmetry reduction
- Group-subgroup relation $G > H$
- Wyckoff positions splittings

Reference description: $(G)_H$

- Affine transformation
- Lattice deformation
- Atomic displacement field

Low-symmetry phase: $H$

INDEX
SUBGROUP
HERMANN
WYCKOFF
SYMMETRY
STRAIN
COMPSTRU
**Problem 3.5**

**SOLUTION**

High-symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

<table>
<thead>
<tr>
<th>Structure Data [CIF format]</th>
</tr>
</thead>
<tbody>
<tr>
<td>227 7.147 7.147 7.147 90 90 90</td>
</tr>
<tr>
<td>BCS Format</td>
</tr>
<tr>
<td>Si 1 8a 0.125 0.125 0.125</td>
</tr>
</tbody>
</table>

Low-symmetry structure:

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

<table>
<thead>
<tr>
<th>Structure Data [CIF format]</th>
</tr>
</thead>
<tbody>
<tr>
<td>92 4.9586 4.9586 6.9074 90 90 90</td>
</tr>
<tr>
<td>BCS Format</td>
</tr>
<tr>
<td>Si 1 4a 0.3028 0.3028 0</td>
</tr>
</tbody>
</table>

Enter the allowed tolerance (a b c α β γ): 2.2 2.2 2.2 2.2

Enter the maximum distance allowed between the paired atoms: 1.5 Å
Cristobalite phase transition

Fd-3m High-symmetry phase

\[(P, p) = \begin{pmatrix} 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \end{pmatrix} \]

Symmetry-controlled mapping

(High-symmetry phase)\(_{P4\bar{1}212}\)

Global distortion

Lattice deformation

Atomic displacement field

P\(_{4\bar{1}212}\) Low-symmetry phase
Cristobalite phase transition

**Problem 3.5**

**SOLUTION**

- **Fd-3m** High-symmetry phase
  \[
  (P,p) = \begin{pmatrix}
  1/2 & 1/2 & 0 & 5/8 \\
  -1/2 & 1/2 & 0 & 3/8 \\
  0 & 0 & 1 & 3/8 
  \end{pmatrix}
  \]

- Alternative transformation matrices
  \[
  (P,p)_1 = \quad \text{and} \quad (P,p)_2 =
  \]

- **P4_12_2** low-symmetry phase

**Global distortion**

- Average distance
  \[
  d_{av} = \frac{1}{n} \sum_{i} m_i u_i
  \]

- Structural descriptor
  \[
  \Delta = \left[ \sqrt{2} \Delta(c) + 1 \right] \Delta(d) - 1
  \]

**Evaluation of the Global Distortion**

<table>
<thead>
<tr>
<th>S</th>
<th>d_{max.} (Å)</th>
<th>d_{av.} (Å)</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0149</td>
<td>0.3774</td>
<td>0.7548</td>
<td>0.122</td>
</tr>
</tbody>
</table>

**Lattice deformation**

- Maximal distance
  \[
  S = \frac{1}{3} \sqrt{\sum_{i} \eta_i^2}
  \]

**Atomic Displacements**

<table>
<thead>
<tr>
<th>WP</th>
<th>Atom</th>
<th>Atomic Displacements</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>(x,x,0) Si1</td>
<td>[ux, uy, uz,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0528, -0.0528, 0.0000, 0.3774</td>
</tr>
</tbody>
</table>
Problem 3.5

**SOLUTION**

- High-symmetry structure
- Origin choice 1
- Cristobalite phase transition
- Low-symmetry structure
- Tolerances
- **NON-standard settings**

**STRUCTURE RELATIONS**

**NON-STANDARD settings**

### High symmetry structure

Enter the formula units in the high symmetry structure.

(Leave blank for auto-detection via the volume information)

<table>
<thead>
<tr>
<th>Structure Data [CIF format]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

Exercise 3.5 (cristobalite):

- **Space Group ITA number (high-symmetry phase):** 227
- **BCS Format:**
  - **Si 1 8a 0.0 0.0 0.0 0.0**

### Low symmetry structure

Enter the formula units in the low symmetry structure.

(Leave blank for auto-detection via the volume information)

<table>
<thead>
<tr>
<th>Structure Data [CIF format]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

- **Space Group ITA number (low-symmetry phase):** 92
- **BCS Format:**
  - **Si 1 4a 0.3028 0.3028 0.0**

Enter the allowed tolerance \((a b c \alpha \beta \gamma)\):

- 2 2 2 2 2 2

Enter the maximum distance allowed between the paired atoms: 1.5 Å

**One or both of the structures are given in a non-standard setting?**

- No
- Yes
Problem 3.5

**SOLUTION**

**STRUCTURE RELATIONS**

**NON-STANDARD** settings

---

**high-symmetry structure**

- **Origin choice 1**

---

**low-symmetry structure**

---

**Cristobalite phase transition**

---

Please choose the setting in which the high symmetry structure is given:

- **Setting**
  - \(F d -3 m [\text{origin 2}]\) \(a, b, c\) \(a, b, c\)
  - **\(F d -3 m [\text{origin 1}]\)** \(a-1/8, b-1/8, c-1/8\) \(a+1/8, b+1/8, c+1/8\)

Please choose the setting in which the low symmetry structure is given:

(You can choose one of the ITA settings or define your own setting introducing a label and the transformation matrix to the standard setting)

<table>
<thead>
<tr>
<th>Setting</th>
<th>(P)</th>
<th>(P^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P 4_1 2_1 2)</td>
<td>(a, b, c)</td>
<td>(a, b, c)</td>
</tr>
</tbody>
</table>

- **User defined setting:**
  - **Label**
  - **Transformation Matrix**
    - Rotational part:
      - 1 0 0
      - 0 1 0
      - 0 0 1
    - Origin shift:
      - 0
      - 0
Lead phosphate $\text{Pb}_3(\text{PO}_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R-3m$ (No. 166) to a ferroelastic phase of symmetry $C2/c$ (No. 15).

Using the structure data given in the ExerciseData file and the tools of the Bilbao Crystallographic Server:

(i) characterize the symmetry reduction between the high- and low-symmetry phases (index, graph of maximal subgroups, etc.);

(ii) describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.
Problem 3.6

SOLUTION

**High Symmetry Structure**

Pb$_3$(PO$_4$)$_2$

Ferroelastic Phase Transition

**Low Symmetry Structure**

Tolerances
Study of the group-subgroup symmetry break

INDEX: \([i]=[i_P].[i_L]\)
\([i]=3.2=6\)

Input for SUBGROUPGRAPH

Please, enter the sequential numbers of group and subgroup as given in International Tables for Crystallography, Vol. A:

Enter supergroup number (G) or choose it: 166
Enter subgroup number (H) or choose it: 15
Enter the index [G:H] (optional): 6

Construct the lattice

Group-subgroup graph for \(\text{Pb}_3(\text{PO}_4)_2\)
Lead phosphate Pb$_3$(VO$_4$)$_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R-3m$ (No. 166) to a ferroelastic phase of symmetry $P2_1/c$ (No. 14).

Using the structure data given in the ExerciseData file and the tools of the Bilbao Crystallographic Server:

(i) characterize the symmetry reduction between the high- and low-symmetry phases (index, graph of maximal subgroups, etc.);

(ii) describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.
Problem 3.6(b) SOLUTION

**High symmetry structure**

Pb₃(VO₄)₂ ferroelastic phase transition

**Low symmetry structure**

higher tolerances

STRUCTURE RELATIONS

formula units

[Formula units for high symmetry structure: 3]

[Formula units for low symmetry structure: 2]

[Enter the allowed tolerance (a b c b a v): 0.2 5 5 2 2 2]

[Enter the maximum distance allowed between the paired atoms: 1.5 Å]
Problem 3.6(b)

SOLUTION

R-3m High-symmetry phase

(P,p)=
\[
\begin{pmatrix}
-1/3 & -1 & 1 & 0 \\
1/3 & -1 & -1 & 0 \\
1/3 & 0 & 0 & 0
\end{pmatrix}
\]

P2₁/c low-symmetry phase

Ferroelastic phase transition Pb₃(VO₄)₂

Atom pairings and distances

<table>
<thead>
<tr>
<th>Atom Mappings</th>
<th>Atom</th>
<th>Coordinates in S₁</th>
<th>Atom</th>
<th>Coordinates in S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP</td>
<td>Atom</td>
<td>Coordinates in S₁</td>
<td>Atom</td>
<td>Coordinates in S₂</td>
</tr>
<tr>
<td>2a</td>
<td>(0,0,0)</td>
<td>Pb₁</td>
<td>(0.000000,0.000000,0.000000)</td>
<td>Pb₁</td>
</tr>
<tr>
<td>4e</td>
<td>(x,y,z)</td>
<td>Pb₂</td>
<td>(0.378700,0.500000,0.292900)</td>
<td>Pb₂</td>
</tr>
<tr>
<td>4e</td>
<td>(x,y,z)</td>
<td>PV₁</td>
<td>(0.165200,0.000000,0.388400)</td>
<td>PV₁</td>
</tr>
<tr>
<td>4e</td>
<td>(x,y,z)</td>
<td>O₅₁</td>
<td>(0.290300,0.263600,0.008900)</td>
<td>O₁</td>
</tr>
<tr>
<td>4e</td>
<td>(x,y,z)</td>
<td>O₅₂</td>
<td>(0.290300,0.736400,0.008900)</td>
<td>O₂</td>
</tr>
<tr>
<td>4e</td>
<td>(x,y,z)</td>
<td>O₅</td>
<td>(0.290300,0.000000,0.272500)</td>
<td>O₃</td>
</tr>
<tr>
<td>4e</td>
<td>(x,y,z)</td>
<td>O₄</td>
<td>(0.028000,0.500000,0.176000)</td>
<td>O₄</td>
</tr>
</tbody>
</table>

Evaluation of the Global Distortion

<table>
<thead>
<tr>
<th>S</th>
<th>d_max. (Å)</th>
<th>d_avg (Å)</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0236</td>
<td>0.4981</td>
<td>0.2536</td>
<td>0.105</td>
</tr>
</tbody>
</table>
Step 1. Determination of the index of the group-subgroup pair

Example: Pb$_3$(VO$_4$)$_2$

High-symmetry phase

Low-symmetry phase

INDEX: $[i] = [i_P] \cdot [i_L]$

$[i] = 3.2 = 6$

R-3m

$i_P = P_G / P_H = 3$

C2/m

$i_L = Z_H / Z_G = 2$

P2$_1$/c
Step 2. Study of the group-subgroup symmetry break

Input for SUBGROUPGRAPH

Please, enter the sequential numbers of group and subgroup as given in International Tables for Crystallography, Vol. A:

Enter supergroup number (G) or choose it: 166
Enter subgroup number (H) or choose it: 14
Enter the index [G:H] (optional): 6

Construct the lattice

Group-subgroup graph for Pb$_3$(VO$_4$)$_2$

\[ R^{5m} \]

\[ C^{2/m} \]

\[ P_{21}/c(1) \]

\[ P_{21}/c(1) \]

\[ P_{21}/c(1) \]
Transformation matrix \((P,p)\) for \(G>H\)

Subgroups \(P2_1/c\) of \(R-3m\) of index 6 (data ITA1)

<table>
<thead>
<tr>
<th>Check</th>
<th>Chain [indices]</th>
<th>Chain with HM symbols</th>
<th>Transformation</th>
<th>Identical</th>
</tr>
</thead>
</table>
|   1   | 166 012 014 [3 2] | \(R-3m > C2/m > P2_1/c\) | \[
\begin{pmatrix}
0 & -1 & 1/3 & 0 \\
0 & -1 & -1/3 & 0 \\
1 & 0 & 2/3 & 0
\end{pmatrix}
\] | -- |
|   2   | 166 012 014 [3 2] | \(R-3m > C2/m > P2_1/c\) | \[
\begin{pmatrix}
0 & 1 & 1/3 & 0 \\
0 & 0 & 2/3 & 0 \\
1 & 0 & 2/3 & 0
\end{pmatrix}
\] | -- |
|   3   | 166 012 014 [3 2] | \(R-3m > C2/m > P2_1/c\) | \[
\begin{pmatrix}
0 & 0 & -2/3 & 0 \\
0 & 1 & -1/3 & 0 \\
1 & 0 & 2/3 & 0
\end{pmatrix}
\] | -- |

Arbitrariness of \((P,p)\)

\[\left(\begin{array}{c}
(P,p)_{\text{exp}}\end{array}\right)^{-1} (P,p)_{\text{ITA1}} = N(P2_1/c)\]

\[(P,p)_{\text{exp}} = \begin{pmatrix}
-1/3 & -1 & 1 & 0 \\
1/3 & -1 & -1 & 0 \\
1/3 & 0 & 0 & 0
\end{pmatrix}\]
1/2(a_c√2) = 1/2√2 3.83Å = 0.707 3.83Å = 2.708Å
Problem 3.7

Order-disorder phase transition CuAu

Modified structure data
Order-disorder phase transition CuAu

Fm-3m  High-symmetry phase

\[
a = 3.83\text{Å}
\]

\[
(P,p) = \begin{pmatrix}
1/2 & 1/2 & 0 & 0 \\
-1/2 & 1/2 & 0 & 0 \\
0 & 0 & 1 & 0
\end{pmatrix}
\]

Reference structure

\[(Fm-3m)_{P4/mmm}\]

\[
a = 2.71\text{Å}, \, c = 3.83\text{Å}
\]

P4/mmm  Low-symmetry phase

\[
a = 2.86\text{Å}, \, c = 3.66\text{Å}
\]

Atom pairings and distances

<table>
<thead>
<tr>
<th>WP</th>
<th>Atom</th>
<th>Coordinates in $S_1$</th>
<th>Atom</th>
<th>Coordinates in $S_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>Cu12</td>
<td>(0.500000, 0.500000, 0.500000)</td>
<td>Cu1</td>
<td>(0.500000, 0.500000, 0.500000)</td>
</tr>
<tr>
<td>1a</td>
<td>Cu1</td>
<td>(0.000000, 0.000000, 0.000000)</td>
<td>Cu2</td>
<td>(0.000000, 0.000000, 0.000000)</td>
</tr>
</tbody>
</table>

Atom Mappings

<table>
<thead>
<tr>
<th>WP</th>
<th>Atom</th>
<th>Atomic Displacements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$u_x$</td>
</tr>
<tr>
<td>1d</td>
<td>Cu12</td>
<td>0.0000</td>
</tr>
<tr>
<td>1a</td>
<td>Cu1</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Strain Calculation

\[
\eta = \frac{1}{2}(e + e^T + e^Te) = \frac{1}{2}R_1^{-1} T (M_1 - M_2) R_1^{-1}
\]
High-symmetry disordered phase

Space group: Fm-3m
Symmetry break: Fm-3m → P4/mmm

\[ a_t = \frac{1}{2}(a_c - b_c), \quad b_t = \frac{1}{2}(a_c + b_c), \quad c_t = c_c \]
Low-symmetry ordered phase

Space group: P4/mmm

<table>
<thead>
<tr>
<th>AT.</th>
<th>WP</th>
<th>SS</th>
<th>Representative</th>
<th>Atomic orbit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au1</td>
<td>1a (0,0,0)</td>
<td>4/mmm</td>
<td>(0.000000, 0.000000, 0.000000)</td>
<td>(0.000000, 0.000000, 0.000000)</td>
</tr>
<tr>
<td>Cu1</td>
<td>1d (1/2,1/2,1/2)</td>
<td>4/mmm</td>
<td>(0.500000, 0.500000, 0.500000)</td>
<td>(0.500000, 0.500000, 0.500000)</td>
</tr>
</tbody>
</table>
SYMMETRY RELATIONS BETWEEN CRYSTAL STRUCTURES
Problem: Symmetry Relations between Crystal Structures
Baernighausen Trees

Pyrite
Structural family

Hettotypes
Derivative structures

Aristotyple
Basic structure

Pyrite parameters:
- FeS$_2$
- NiAsS

Lattice parameters in pm:
- Pyrite: 541.8, 541.8, 541.8
- NiAsS: 568.9, 568.9, 568.9
- PdS$_2$: 546.0, 554.1, 753.1
- PtGeSe: 607.2, 601.5, 599.2

U. Mueller, Gargnano 2008
Modul design of crystal symmetry relations

Scheme of the general formulation of the smallest step of symmetry reduction connecting two related crystal structures

Hermann–Mauguin symbol of the higher symmetric space group \( G \rightarrow P6/m2/m2/m \)

Symbol designating the higher symmetric crystal structure, *e.g.*, the chemical formula or mineral name

Type and index of the subgroup \( H \rightarrow \)

Basis transformation* → \( \mathbf{k2} \)

Origin shift* → \( 0, 0, -\frac{1}{2} \)

Hermann–Mauguin symbol of the maximal subgroup \( H \rightarrow P6_3/m2/m2/c \)

Symbol designating the lower symmetric crystal structure

* mentioned only if there is a change

<table>
<thead>
<tr>
<th>Element symbol</th>
<th>Wyckoff position</th>
<th>Site symmetry</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al: 1a</td>
<td>( 6/mm )</td>
<td>0</td>
<td>( \frac{1}{3} \frac{2}{3} \frac{1}{4} )</td>
</tr>
<tr>
<td>B: 2d</td>
<td>( \bar{6}m2 )</td>
<td>0</td>
<td>( \frac{1}{3} \frac{2}{3} \frac{1}{4} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element symbol</th>
<th>Wyckoff position</th>
<th>Site symmetry</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca: 2b</td>
<td>( 6m2 )</td>
<td>0</td>
<td>0.455</td>
</tr>
<tr>
<td>In: 4f</td>
<td>( 3m )</td>
<td>0</td>
<td>( \frac{1}{3} \frac{2}{3} \frac{1}{4} )</td>
</tr>
</tbody>
</table>

U. Mueller, Gargnano 2008
Family tree of hettotypes of ReO$_3$
Consider two structures (specified by their unit-cell parameters and atomic coordinates) with group-subgroup related symmetry groups \( G \geq H \).

Search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.
Show that the crystal structure of CoU maybe interpreted as a slightly distorted CsCl (or β-brass, CuZn)-type structure. Using the structural data in the Exercise Data file, characterize the structural relationship between the CoU structure and CsCl structure.
Problem 3.8

**High symmetry structure**

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

| Structure Data [CIF format] | Examinar...
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#CuZn (CsCl type)</td>
<td></td>
</tr>
<tr>
<td>#V=25.67</td>
<td></td>
</tr>
<tr>
<td>2.959 2.959 2.959 90. 90. 90.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cu 1 1a 0 0 0</td>
<td></td>
</tr>
<tr>
<td>Zn1 1 1b 0.5 0.5 0.5</td>
<td></td>
</tr>
</tbody>
</table>

**Low symmetry structure**

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

| Structure Data [CIF format] | Examinar...
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>199 #I213</td>
<td></td>
</tr>
<tr>
<td>#V=256.74</td>
<td></td>
</tr>
<tr>
<td>6.3557 6.3557 6.3557 90. 90. 90.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Co 1 8a 0.294 0.294 0.294</td>
<td></td>
</tr>
<tr>
<td>U 1 8a 0.0347 0.0347 0.0347</td>
<td></td>
</tr>
</tbody>
</table>

**Atomic species correspondence scheme**

Co ↔ Cu

U ↔ Zn

Enter the allowed tolerance (a b c α β γ): 111555

Enter the maximum distance allowed between the paired atoms: 1.5 Å

One or both of the structures are given in a non-standard setting? No | Yes
Problem 3.9

Problem: Symmetry relations between crystal structures

HT-quartz and LT-quartz

(i) Upon heating above 573 °C the LT-quartz transforms to its HT form. Set up the corresponding Baernighausen tree that describes the symmetry relations between the two quartz forms. Which additional degree of freedom are present in the lower symmetry form? (The crystal structures of HT-quartz and LT-quartz can be found in the ExerciseData file.)

(ii) Consider the structure data of AlPO₄ listed in the ExerciseData file. Describe its structural relationship to quartz and construct the corresponding Baernighausen tree.

Hint: In order to find the structural relationship between quartz and AlPO₄ consider the splitting of Si positions into two: one for Al and one for P.
Problem 3.10

Problem: Symmetry relations between crystal structures

The structure of α-XOF (X=La, Y, and Pu) can be derived from that of cubic CaF₂ (fluorite structure) by splitting the fluorine positions into two: one for oxygen and one for fluorine, and by shifting the metal positions along c. By these changes the space-group symmetry is reduced.

\[ \mathbf{a}' = \frac{1}{2}(\mathbf{a} - \mathbf{b}), \quad \mathbf{b}' = \frac{1}{2}(\mathbf{a} + \mathbf{b}); \quad \mathbf{p} = (1/4, 0, 1/4) \]

\[
\begin{align*}
G &= \text{Fm}-3m(225) \\
(P,p) &
\end{align*}
\]

\[
\begin{align*}
H &= \text{P4}/nmm(129) \\
\end{align*}
\]

The coordinates of CaF₂ are:

- Ca: \(4a\ m\bar{3}m\) 
  
  \[
  \begin{array}{cccc}
  0,0,0 & \frac{1}{2},\frac{1}{2},0 & \frac{1}{2},0\frac{1}{2} & 0,\frac{1}{2},\frac{1}{2} \\
  \end{array}
  \]

- F: \(8c\ \bar{4}3m\) 
  
  \[
  \begin{array}{cccc}
  \frac{1}{4},\frac{1}{4},\frac{1}{4} & \frac{1}{4},\frac{3}{4},\frac{3}{4} & \frac{3}{4},\frac{1}{4},\frac{3}{4} & \frac{3}{4},\frac{3}{4},\frac{1}{4} \\
  \frac{3}{4},\frac{3}{4},\frac{3}{4} & \frac{3}{4},\frac{1}{4},\frac{3}{4} & \frac{1}{4},\frac{3}{4},\frac{3}{4} & \frac{1}{4},\frac{1}{4},\frac{3}{4} \\
  \end{array}
  \]

(i) Display the relation between the old \((a,b,c)\) and the new \((a',b',c')\) unit cell by means of a drawing.

(ii) Which is the crystal system of the new unit cell? Which is its centring type? (The lattice of CaF2 is F-centred cubic(fcc), \(a=b=c, \alpha=\beta=\gamma\).)

(iii) Construct the transformation matrix \(P\) describing the change of the basis.

(iv) What is the volume of the new unit cell compared to that of the old one?

(v) What are the coordinates of the atoms of the CaF2 structure referred to the new coordinate system?

(vi) Can the structure of \(\alpha\)-LaOF be considered as a hettotype (derivative structure) of the aristo-type (basic) structure of CaF2? (structure data of \(\alpha\)-LaOF in Exercise Data file)