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EXERCISES

INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY
Volume A: Space-group Symmetry
Volume A1: Symmetry Relations between Space Groups

THE BILBAO CRYSTALLOGRAPHIC SERVER
Short Practical Course

Mois I. Aroyo
Departamento Física de la Materia Condensada
Universidad del País Vasco, UPV/EHU, Bilbao, Spain
mois.aroyo@ehu.es
1 Space-group symmetry data in *International Tables for Crystallography*, Volume A and Volume A1: Basic concepts and notation

1.1 Crystallographic Symmetry Operations

In order to describe the symmetry operations analytically one introduces a coordinate system \( \{O, \mathbf{a}, \mathbf{b}, \mathbf{c}\} \), consisting of a set of basis vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) and an origin \( O \). A symmetry operation can be regarded as an instruction of how to calculate the coordinates \( \tilde{x}, \tilde{y}, \tilde{z} \) of the image point \( \tilde{X} \) from the coordinates \( x, y, z \) of the original point \( X \).

The equations are

\[
\tilde{x} = W_{11}x + W_{12}y + W_{13}z + w_1 \\
\tilde{y} = W_{21}x + W_{22}y + W_{23}z + w_2 \\
\tilde{z} = W_{31}x + W_{32}y + W_{33}z + w_3,
\]

(1.1.1)

These equations can be written using the matrix formalism:

\[
\tilde{x} = Wx + w = (W, w)x \quad \text{where}
\]

the symmetry operations \((W, w)\) are given in a matrix-column form consisting of a \((3 \times 3)\) matrix (linear) part \( W \) and a \((3 \times 1)\)-column (translation) part \( w \):

\[
(W, w) = \begin{pmatrix}
W_{11} & W_{12} & W_{13} \\
W_{21} & W_{22} & W_{23} \\
W_{31} & W_{32} & W_{33}
\end{pmatrix}
\begin{pmatrix}
w_1 \\
w_2 \\
w_3
\end{pmatrix}
\]

(1.1.2)

Apart from the matrix-column pair presentation of \((W, w)\) often the so-called short-hand notation for the symmetry operations is used. It is obtained from the left-hand side of equ. (1.1.1) by omitting the terms with coefficients 0 and writing in one line the three different rows of equ.(1.1.1), separated by commas.

For example, consider the symmetry operation under No. 30 in the list of general positions obtained by GENPOS for the space group \( Pn\bar{3}n \), No. 222 (origin choice 2):

\[
\tilde{x} = (W, w)x = \begin{pmatrix}
0 & 0 & -1 \\
1 & 0 & 0 \\
0 & 1 & 0
\end{pmatrix}
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
+ \begin{pmatrix}
0 \\
1/2 \\
1/2
\end{pmatrix}
\]

would be

\[
\tilde{x} = 0x + 0y - 1z, \quad \tilde{y} = 1x + 0y + 0z + 1/2, \quad \tilde{z} = 0x + 1y + 0z + 1/2.
\]

The shorthand notation of \((W, w)\) reads: \( \tau, x + 1/2, y + 1/2 \).

1.2 Crystallographic Symmetry Operations and Their Representations by Matrices

Geometric meaning of matrix-column pairs \((W, w)\)

The geometric meaning of a matrix-column pair \((W, w)\) can be determined only if the reference coordinate system is known. The following procedure indicates the necessary steps for the complete geometric characterization of \((W, w)\).

Procedure for the geometric interpretation of \((W, w)\)

1. \( W \)-information
(a) Type of isometry: the types 1,2,3,4,6 or 1̅,2̅,3̅,4̅,6̅ can be determined by the matrix invariants: \( \det(W) \) and \( \text{tr}(W) \)

<table>
<thead>
<tr>
<th>( \text{tr}(W) )</th>
<th>( \det(W) = +1 )</th>
<th>( \det(W) = -1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>type 1</td>
<td>3 2 1 0 -1</td>
<td>-3 -2 -1 0 1</td>
</tr>
<tr>
<td>type 2</td>
<td>1 6 4 3 2</td>
<td>1 6 4 3 2</td>
</tr>
<tr>
<td>order 1</td>
<td>2 6 6 6 2</td>
<td>1 6 4 3 2</td>
</tr>
<tr>
<td>order 2</td>
<td>1 6 4 3 2</td>
<td>1 6 4 3 2</td>
</tr>
</tbody>
</table>

(b) Direction of \( u \) the rotation or rotoinversion axis or the normal of the reflection plane

i. Rotations: Calculate the matrix \( Y(W) = W^{k-1} + W^{k-2} + \ldots + W + I \). The elements of any non-zero column of \( Y \) give the components of the vector \( u \) with respect to the reference co-ordinate system.

ii. Rotoinversions: Calculate the matrix \( Y(-W) \). The elements of any non-zero column of \( Y \) give the components of the vector \( u \) with respect to the reference co-ordinate system. For \( \bar{2} = m \), \( Y(-W) = -W + I \).

(c) Sense of rotation (for rotations or rotoinversions with \( k > 2 \)): The sense of rotation is determined by the sign of the determinant of the matrix \( Z \), given by \( Z = [u|x|(\det W)w] \), where \( u \) is the vector of 1b and \( x \) is a non-parallel vector of \( u \), e.g. one of the basis vectors.

2. \( w \) -information

(a) Intrinsic translation part (screw or glide component) \( t/k \)

i. Screw rotations

\[
\frac{t}{k} = \frac{1}{k} Y w, \text{ where } W^k = I 
\]

(1.2.3)

ii. Glide reflections

\[
\frac{t}{k} = \frac{1}{2} (W + I) w
\]

(1.2.4)

(b) Location of the symmetry elements (fixed points \( x_F \))

i. \( t/k = 0 \)

\[
(W, w)x_F = x_F.
\]

(1.2.5)

ii. \( t/k \neq 0 \)

\[
(W, w_{lp})x_F = x_F.
\]

(1.2.6)

The column \( w_{lp} = w - t/k \) is the so-called location part as it determines the position of the rotation or screw-rotation axis or of the reflection or glide-reflection plane in space.

The formulæ of this section enable the user to find the geometric contents of any symmetry operation. In reality, ITA have provided the necessary information for all symmetry operations which are listed in the plane–group or space–group tables. The entries of the General position are numbered. The geometric meaning of these entries is listed under the same number in the block Symmetry operations in the tables of ITA. The explanation of the symbols for the symmetry operations is found in Sections 2.9 and 11.2 of ITA.
1.3 Symmetry Operations and Symmetry Elements

The definitions of symmetry elements, geometric elements and the related element sets of symmetry operations for crystallographic space groups and point groups are summarised in the following table.

<table>
<thead>
<tr>
<th>Name of symmetry element</th>
<th>Geometric element</th>
<th>Defining operation (d.o)</th>
<th>Operations in element set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mirror plane</td>
<td>Plane A</td>
<td>Reflection in A</td>
<td>D.o. and its coplanar equivalents*</td>
</tr>
<tr>
<td>Glide plane</td>
<td>Plane A</td>
<td>Glide reflection in A; 2ν (not ν) a lattice translation</td>
<td>D.o. and its coplanar equivalents*</td>
</tr>
<tr>
<td>Rotation axis</td>
<td>Line b</td>
<td>Rotation around b, angle $2\pi/n$, $n = 2, 3, 4$ or 6</td>
<td>1st, ..., $(n-1)$th powers of d.o. and their coaxial equivalents†</td>
</tr>
<tr>
<td>Screw axis</td>
<td>Line b</td>
<td>Screw rotation around b, angle $2\pi/n$, $u = j/n$ times shortest lattice translation along b, right-hand screw, $n = 2, 3, 4$ or 6, $j = 1, \ldots, (n-1)$</td>
<td>1st, ..., $(n-1)$th powers of d.o. and their coaxial equivalents†</td>
</tr>
<tr>
<td>Rotoinversion axis</td>
<td>Line b and point P on b</td>
<td>Rotoinversion: rotation around b, angle $2\pi/n$, and inversion through P, $n = 3, 4$ or 6</td>
<td>D.o. and its inverse</td>
</tr>
<tr>
<td>Center</td>
<td>Point P</td>
<td>Inversion through P</td>
<td>D.o. only</td>
</tr>
</tbody>
</table>

* That is, all glide reflections with the same reflection plane, with glide vectors $\mathbf{v}$ differing from that of d.o. (taken to be zero for reflections) by a lattice translation vector. The glide planes $a, b, c, d$ and $e$ are distinguished.

† That is, all rotations and screw rotations with the same axis $b$, the same angle and sense of rotation and the same screw vector $u$ (zero for rotation) up to a lattice translation vector.

1.4 Site symmetry: General and Special positions

The concept of Site symmetry, i.e. the set of symmetry operations that leave a given point fixed, allows to define General and Special positions for space groups.

Let $\mathcal{G}$ be a space group and $X$ a point. The subgroup $\mathcal{S}_X = \{(\mathbf{W}, w)\}$ of all $(\mathbf{W}, w) \in \mathcal{G}$ that leave $X$ fixed, i.e. for which $(\mathbf{W}, w)X = X$ holds, is called the site symmetry group $\mathcal{S}_X$ of $\mathcal{G}$ for the point $X$. The group $\mathcal{S}_X < \mathcal{G}$ is of finite order. If $\mathcal{S}_X = \{I\}$, i.e. only the identity operation maps $X$ onto itself, $X$ is called a point of General position. Otherwise, if $\mathcal{S}_X > \{I\}$, $X$ is called a point of Special position.

Each point $X_i$ of a $\mathcal{G}$-orbit has its site symmetry group $\mathcal{S}_i < \mathcal{G}$. The site symmetry groups $\mathcal{S}_i$ and $\mathcal{S}_j$ of two points $X_i$ and $X_j$ of the same $\mathcal{G}$-orbit are conjugate subgroups of $\mathcal{G}$: if $X_j = (\mathbf{W}, w)X_i$, $(\mathbf{W}, w) \in \mathcal{G}$, then $\mathcal{S}_j = (\mathbf{W}, w)\mathcal{S}_i(\mathbf{W}, w)^{-1}$. For this reason, all points of one special position in ITA are described by the same site-symmetry symbol.

In ITA the so-called oriented site-symmetry symbols are used to show how the symmetry elements at a site are related to the symmetry elements of the crystal lattice. The oriented site-symmetry symbols of the site-symmetry groups display the same sequence of symmetry directions as the space-group symbol. Sets of equivalent symmetry directions that do not contribute any element to the site-symmetry group are represented by a dot.
1.5 Coordinate Transformations: basic results

Let a coordinate system be given with a basis \((a_1, a_2, a_3)\) and an origin \(O\). The general transformation (affine transformation) of the coordinate system consists of two parts, a linear part and a shift of the origin. The transformation is uniquely defined by the \((3 \times 3)\) matrix \(P\) of the linear part and the \((3 \times 1)\) column matrix \(p\) containing the components of the shift vector \(p\).

1. The linear part is described by a \((3 \times 3)\) matrix

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

i.e. the matrix which relates the new basis \((a'_1, a'_2, a'_3)\) to the old basis \((a_1, a_2, a_3)\) according to

\[
(a'_1, a'_2, a'_3) = (a_1, a_2, a_3) \begin{pmatrix}
P_{11} & P_{12} & P_{13} \\
P_{21} & P_{22} & P_{23} \\
P_{31} & P_{32} & P_{33}
\end{pmatrix}
\]

(1.5.7)

2. A shift of the origin is defined by the shift vector

\[
p = (p_1a_1, p_2a_2, p_3a_3)
\]

The basis vectors \(a_1, a_2, a_3\) are fixed at the origin \(O\); the new basis vectors \((a'_1, a'_2, a'_3)\) are fixed at the new origin \(O'\) that has the coordinates \((p_1, p_2, p_3)\) in the old coordinate system.

The general affine transformation of the coordinates of a point \(X\) in direct space (given by the column \(x = (x_1, x_2, x_3)\)) is given by the following formula:

\[
x' = (P, p)^{-1}x = P^{-1}x - P^{-1}p = P^{-1}(x - p).
\]

(1.5.8)

The metric tensor \(G\) of the unit cell in direct lattice is transformed by the matrix \(P\) as follows:

\[
G' = P^t GP
\]

(1.5.9)

where \(P^t\) is the transposed matrix of \(P\).

The volume of the unit cell \(V\) changes with the transformation. The volume of the new unit cell \(V'\) is obtained by

\[
V' = \det(P)V
\]

(1.5.10)

with \(\det(P)\) being the determinant of the matrix \(P\).

Also, the matrix-column pairs of the symmetry operations are changed by a change of the coordinate system. If a symmetry operation is described in the \(\text{“old”}\) (unprimed) coordinate system by the matrix-column pair \((W, w)\) and in the \(\text{“new”}\) (primed) coordinate system by the pair \((W', w')\), then the relation between the pairs \((W, w)\) and \((W', w')\) is given by:

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

(1.5.11)

The coordinate systems of the space groups used by the programs and database on the Bilbao Crystallographic Server (referred to as \textit{standard} or \textit{default} settings) for the presentation of the space-group data coincide with the conventional space-group descriptions found in ITA. For space groups with more than one description in ITA, the following settings are chosen as standard: \textit{unique axis b} setting, \textit{cell choice 1}
1.6 Group-subgroup relations of space groups

1.6.1 Basic definitions

A subset \( \mathcal{H} \) of elements of a group \( \mathcal{G} \) is called a subgroup of \( \mathcal{G} \), \( \mathcal{G} > \mathcal{H} \) if it fulfills the group postulates with respect to the law of composition of \( \mathcal{G} \). In general, the group \( \mathcal{G} \) itself is included among the set of subgroups of \( \mathcal{G} \), i.e. \( \mathcal{G} \geq \mathcal{H} \). If \( \mathcal{G} > \mathcal{H} \) is fulfilled, then the subgroup \( \mathcal{H} \) is called a proper subgroup of \( \mathcal{G} \).

In a relation \( \mathcal{G} \geq \mathcal{H} \) or \( \mathcal{G} > \mathcal{H} \), \( \mathcal{G} \) is called a supergroup of \( \mathcal{H} \). A subgroup \( \mathcal{H} < \mathcal{G} \) is a maximal subgroup if no group \( \mathcal{Z} \) exists for which \( \mathcal{H} < \mathcal{Z} < \mathcal{G} \) holds. If \( \mathcal{H} \) is a maximal subgroup of \( \mathcal{G} \), then \( \mathcal{G} \) is a minimal supergroup of \( \mathcal{H} \).

Let \( \mathcal{H} < \mathcal{G} \) be a subgroup of \( \mathcal{G} \) of order \( |\mathcal{H}| \). Because \( \mathcal{H} \) is a proper subgroup of \( \mathcal{G} \) there must be elements \( g_i \in \mathcal{G} \) which are not elements of \( \mathcal{H} \). Let \( g_2 \in \mathcal{G} \) be one of them. Then the set of elements \( g_2 \mathcal{H} = \{g_2 h_j \mid h_j \in \mathcal{H}\} \)
\footnote{The formulation \( g_2 \mathcal{H} = \{g_2 h_j \mid h_j \in \mathcal{H}\} \) means: \( g_2 \mathcal{H} \) is the set of the products \( g_2 h_j \) of \( g_2 \) with all elements \( h_j \in \mathcal{H} \).} is a subset of elements of \( \mathcal{G} \) with the property that all its elements are different and that the sets \( \mathcal{H} \) and \( g_2 \mathcal{H} \) have no element in common. Thus, also the set \( g_2 \mathcal{H} \) contains \( |\mathcal{H}| \) elements of \( \mathcal{G} \). If there is another element \( g_3 \in \mathcal{G} \) which does belong neither to \( \mathcal{H} \) nor to \( g_2 \mathcal{H} \), one can form another set \( g_3 \mathcal{H} = \{g_3 h_j \mid h_j \in \mathcal{H}\} \). All elements of \( g_3 \mathcal{H} \) are different and no one occurs already in \( \mathcal{H} \) or in \( g_2 \mathcal{H} \). This procedure can be continued until each element \( g_i \in \mathcal{G} \) belongs to one of these sets. In this way the group \( \mathcal{G} \) can be partitioned, such that each element \( g \in \mathcal{G} \) belongs to exactly one of these sets.

The partition just described is called a decomposition (\( \mathcal{G} : \mathcal{H} \)) into left cosets of the group \( \mathcal{G} \) relative to the group \( \mathcal{H} \).

\[
\mathcal{G} = \mathcal{H} \cup g_2 \mathcal{H} \cup \cdots \cup g_i \mathcal{H} \tag{1.6.12}
\]

The sets \( g_i \mathcal{H} \), \( i = 1, \ldots, \) are called left cosets, because the elements \( h_j \in \mathcal{H} \) are multiplied with the new elements from the left-hand side. The procedure is called a decomposition into right cosets \( \mathcal{H} g_i \) if the elements \( h_j \in \mathcal{H} \) are multiplied with the new elements \( g_i \) from the right-hand side.

\[
\mathcal{G} = \mathcal{H} \cup \mathcal{H} g_2 \cup \cdots \cup \mathcal{H} g_i \tag{1.6.13}
\]

The elements \( g_p \) or \( g_s \) are called the coset representatives. The number of cosets is called the index \( [\mathcal{G}] = |\mathcal{G} : \mathcal{H}| \) of \( \mathcal{H} \) in \( \mathcal{G} \).

Two subgroups \( \mathcal{H}_j, \mathcal{H}_k < \mathcal{G} \) are called conjugate if there is an element \( g_q \in \mathcal{G} \) such that \( g_q^{-1} \mathcal{H}_j g_q = \mathcal{H}_k \) holds. In this way, the subgroups of \( \mathcal{G} \) are distributed into classes of conjugate subgroups that are also called conjugacy classes of subgroups. Subgroups in the same conjugacy class are isomorphic and thus have the same order. Different conjugacy classes of subgroups may contain different numbers of subgroups, i.e. have different lengths.

A subgroup \( \mathcal{H} \) of a group \( \mathcal{G} \) is a normal subgroup \( \mathcal{H} \triangleleft \mathcal{G} \) if it is identical with all of its conjugates, \( g_q^{-1} \mathcal{H} g_q = \mathcal{H} \), for all \( g_q \in \mathcal{G} \), i.e. if its conjugacy class consists of the one subgroup \( \mathcal{H} \) only.

1.6.2 Subgroups of space groups

The set of all symmetry operations of a three-dimensional crystal pattern forms its symmetry group, which is the space group of this crystal pattern. An essential feature of a crystal pattern is its periodicity which

for monoclinic groups, hexagonal axes setting for rhombohedral groups, and origin choice 2 (origin in \( T \)) for the centrosymmetric groups listed with respect to two origins in ITA. Optionally certain applications allow the usage of the so-called ITA settings which include all conventional settings applied in ITA (e.g. rhombohedral axes setting for rhombohedral groups, and origin choice 1 for the centrosymmetric groups) and the great variety of about 530 settings of monoclinic and orthorhombic groups listed in Table 4.3.2.1 of ITA. Settings different from the standard ones and the ITA settings are designated as non-conventional.
The following types of subgroups of space groups are to be distinguished:

- **Point groups** \( \mathcal{P}_G \)
- **Linear parts**, represented by the set of matrices \( \mathcal{W}_G \)

Each coset in the decomposition \( \mathcal{G} = \mathcal{H} \mathcal{P}_G \)

Obviously, the coset representatives of the decomposition \( \mathcal{G} = \mathcal{H} \mathcal{P}_G \) represent in a clear and compact way the infinite number of elements of the space group \( \mathcal{G} \). And this is one of the ways of presenting the space groups in ITA and also in the Bilbao Crystallographic Server, i.e. by the matrices of the coset representatives of \( \mathcal{G} = \mathcal{H} \mathcal{P}_G \) listed in the General position.

Each coset in the decomposition \( \mathcal{G} = \mathcal{H} \mathcal{P}_G \) is characterized by its linear part. One can show that the set of linear parts, represented by the set of matrices \( \mathcal{W}_G \), forms a group which is called the point group \( \mathcal{P}_G \) of the space group \( \mathcal{G} \). The point groups which can belong to space groups are called **crystallographic point groups**.

The following types of subgroups of space groups are to be distinguished [?]:

- A subgroup \( \mathcal{H} \) of a space group \( \mathcal{G} \) is called a **translationengleiche subgroup** or a \( t \)-subgroup of \( \mathcal{G} \) if the set \( \mathcal{T}(\mathcal{G}) \) of translations is retained, i.e. \( \mathcal{T}(\mathcal{H}) = \mathcal{T}(\mathcal{G}) \), but the number of cosets of the decomposition \( \mathcal{G} = \mathcal{H} \mathcal{P}_G \) is reduced.

- A subgroup \( \mathcal{H} < \mathcal{G} \) of a space group \( \mathcal{G} \) is called a **klassengleiche subgroup** or a \( k \)-subgroup if the set \( \mathcal{T}(\mathcal{G}) \) of all translations of \( \mathcal{G} \) is reduced to \( \mathcal{T}(\mathcal{H}) < \mathcal{T}(\mathcal{G}) \) but all linear parts of \( \mathcal{G} \) are retained. Then the number of cosets of the decompositions \( \mathcal{G} = \mathcal{H} \mathcal{P}_G \) and \( \mathcal{G} = \mathcal{H} \mathcal{P}_H \) is the same, i.e. the order of the point group \( \mathcal{P}_H \) is the same as that of \( \mathcal{P}_G \).

- A **klassengleiche** or \( k \)-subgroup \( \mathcal{H} < \mathcal{G} \) is called **isomorphic** or an **isomorphic subgroup** if it belongs to the same affine space-group type (isomorphism type) as \( \mathcal{G} \) does.

- A subgroup of a space group is called **general** or a **general subgroup** if it is neither a **translationengleiche** nor a **klassengleiche** subgroup. It has lost translations as well as linear parts, i.e. point-group symmetry.

Any subgroup \( \mathcal{H} \) of a group \( \mathcal{G} \) is related to a specific subset of elements of \( \mathcal{G} \) and this subset defines the subgroup uniquely: different subgroups of \( \mathcal{G} \), even those isomorphic to \( \mathcal{H} \), correspond to different subsets of the elements of \( \mathcal{G} \). For example, the listing of the maximal \( t \)-subgroups of the space groups in ITA is based on this fact: apart from the space-group type and index, each \( t \)-subgroup \( \mathcal{H} \) is specified by the set of coordinate triplets of the general position of \( \mathcal{G} \) which are retained in \( \mathcal{H} \).

In the Bilbao Crystallographic Server any subgroup \( \mathcal{H} \) of a space group \( \mathcal{G} \) is specified by its ITA-number, the index in the group \( \mathcal{G} \) and the transformation matrix-column pair \((\mathbf{P}, \mathbf{p})\) that relates the standard bases \((\mathbf{a}, \mathbf{b}, \mathbf{c})_\mathcal{H}\) of \( \mathcal{H} \) and \((\mathbf{a}, \mathbf{b}, \mathbf{c})_\mathcal{G}\) of \( \mathcal{G} \):

\[
(a, b, c)_\mathcal{H} = (a, b, c)_\mathcal{G} \mathbf{P}
\]

(1.6.14)

The column \( \mathbf{p} = (p_1, p_2, p_3) \) of coordinates of the origin \( O_\mathcal{H} \) of \( \mathcal{H} \) is referred to the coordinate system of \( \mathcal{G} \).
1.6 Group-subgroup relations of space groups

The subgroup data listed in the server, i.e. the space-group type of $\mathcal{H}$ and the transformation matrix $(P, p)$, are completely sufficient to define the subgroup uniquely: the transformation of the coordinate triplets of general-position of $\mathcal{H}$ (in standard setting) to the coordinate system of $\mathcal{G}$ by $(P, p)^{-1}$ yields exactly the subset of elements of $\mathcal{G}$ corresponding to $\mathcal{H}$.

A very important result on group-subgroup relations between space groups is given by Hermann’s theorem: For any group–subgroup chain $\mathcal{G} \supset \mathcal{H}$ between space groups there exists a uniquely defined space group $\mathcal{M}$ with $\mathcal{G} \supseteq \mathcal{M} \supseteq \mathcal{H}$, where $\mathcal{M}$ is a translationengleiche subgroup of $\mathcal{G}$ and $\mathcal{H}$ is a klassengleiche subgroup of $\mathcal{M}$. The decisive point is that any group–subgroup chain between space groups $\mathcal{G} \supset \mathcal{H}$ of index $[i]$ can be split into a translationengleiche subgroup chain between the space groups $\mathcal{G}$ and $\mathcal{M}$ of index $[i_L]$ and a klassengleiche subgroup chain between the space groups $\mathcal{M}$ and $\mathcal{H}$ of index $[i_L]$ where $[i] = [i_P] \cdot [i_L]$.

The first one, also called $t$-chain $\mathcal{G} [i_P] \supset \mathcal{M}$, is related to the reduction of the point-group symmetry in the subgroup. The second one $\mathcal{M} [i_L] \supset \mathcal{H}_j$ is known also as $k$-chain and it takes account of the loss of translations.

If the maximal subgroups are known for each space group, then in principle each non-maximal subgroup of a space group is either a translationengleiche subgroup or a klassengleiche subgroup, never a general subgroup.

If the maximal subgroups are known for each space group, then in principle each non-maximal subgroup of a space group $\mathcal{G}$ with finite index can be obtained from the data on maximal subgroups. A non-maximal subgroup $\mathcal{H} < \mathcal{G}$ of finite index $[i]$ is connected with the original group $\mathcal{G}$ through a chain $\mathcal{H} = Z_k < Z_{k-1} < \cdots < Z_1 < Z_0 = \mathcal{G}$, where each group $Z_j < Z_{j-1}$ is a maximal subgroup of $Z_{j-1}$, with the index $[i_j] = [Z_{j-1} : Z_j], j = 1, \ldots, k$. The number $k$ is finite and the relation $i = \prod_{j=1}^{k} i_j$ holds, i.e. the total index $[i]$ is the product of the indices $i_j$.

In a similar way, one can express the transformation matrix $(P, p)$ for the symmetry reduction $\mathcal{G} \rightarrow \mathcal{H}$ as a product of the transformation matrices $(P, p)_j$ characterizing each of the intermediate steps $Z_{j-1} > Z_j$: $(P, p) = (P, p)_1(P, p)_2 \cdots (P, p)_k$ (here the matrices $(P, p)_j$ relate the bases of $Z_{j-1}$ and $Z_j$, i.e. $(a, b, c)_j = (a, b, c)_{j-1} P_j$).
2 Exercises

2.1 Group theory in crystallography (basic concepts)

- **Exercise 2.1.** Symmetry group of the pentacene molecule

Consider the model of the molecule of the organic semiconductor pentacene ($C_{22}H_{14}$):

1. Determine all symmetry operations and their matrix and the short-hand $(x, y)$ presentation;
2. Draw up the general-position and the symmetry-elements stereographic-projection diagrams;
3. Find a set of generators;
4. Construct the multiplication table of the group of the pentacene molecule;
5. Distribute the elements of the group into classes of conjugate elements.

- **Exercise 2.2.** Symmetry group of the square

Consider the symmetry group of the square:

1. Determine all symmetry operations and their matrix and the short-hand $(x, y)$ presentation;
2. Draw up the general-position and the symmetry-elements stereographic-projection diagrams;
3. Find a set of generators;
4. Construct the multiplication table of the group of the square;
5. Distribute the elements of the group into classes of conjugate elements.
2.1 Group theory in crystallography (basic concepts)

- **Exercise 2.3.** Symmetry group of the equilateral triangle

  Consider the symmetry group of the equilateral triangle:
  
  1. Determine all symmetry operations and their matrix and the short-hand \((x, y)\) presentation;
  2. Draw up the general-position and the symmetry-elements stereographic-projection diagrams;
  3. Find a set of generators;
  4. Construct the multiplication table of the group of the equilateral triangle;
  5. Distribute the elements of the group into classes of conjugate elements.

- **Exercise 2.4.** Consider the symmetry group of the square \(4mm\), cf. Exercise 2.2.

  1. Which are the possible orders of the subgroups of \(4mm\)?
  2. Determine the subgroups of \(4mm\) and construct the complete subgroup graph of point group \(4mm\), see Remarks.
  3. Which of these subgroups are conjugate (symmetrically equivalent) in \(4mm\) and which are normal subgroups?

*Remarks*

In a subgroup diagram each, subgroup is located at a level which is determined by its index (the original group with index \([1]\) on top, subgroups of index \([2]\) next lower level, etc.). Each of these groups is connected with its maximal subgroups by straight lines.

- **Exercise 2.5.** Consider the symmetry group of the equilateral triangle \(3m\), cf. Exercise 2.3.

  1. Determine the subgroups of \(3m\);
  2. Distribute the subgroups into classes of conjugate subgroups;
  3. Construct the graph of maximal subgroups of \(3m\).

- **Exercise 2.6.** Consider the subgroup \(2 = \{1, 2\}\) of \(4mm\).

  1. Write down the left and right coset decomposition of the group \(4mm\) with respect to the subgroup \(2\).
  2. Are the right and the left coset decompositions equal or different? Why?
  3. Show that the cosets of the decomposition \(4mm\) with respect to \(2\) satisfy the group axioms and the set of cosets forms a factor group.
  4. Construct the multiplication table of the factor group.
  5. Indicate a crystallographic point group isomorphic to the factor group.

- **Exercise 2.7.** Show that \(H \triangleleft G\) holds always for \(|G : H| = 2\), i.e. subgroups of index 2 are always normal subgroups.
• **Exercise 2.8.** Consider the symmetry group of the square 4mm (cf. Exercise 2.2) and the point group 422 that is isomorphic to it. Determine the general and special Wyckoff positions for the two groups.

• **Exercise 2.9.** Consider the general and the special Wyckoff positions of the symmetry group of the square 4mm (cf. Exercise 2.8) and those of its subgroup mm2 (cf. Exercise 2.4). Determine the splitting schemes of the Wyckoff positions for the pair 4mm > mm2.

• **Exercise 2.10.** Consider the group 4mm and its subgroups of index 4 (cf. Exercise 2.4). Determine their normalizers in 4mm. Distribute the subgroups of 4mm of index 4 into conjugacy classes with the help of their normalizers in 4mm.

• **Exercise 2.11.** Point groups isomorphic to 4mm Consider the following three pairs of stereographic projections. Each of them correspond to a crystallographic point group isomorphic to 4mm:

1. Determine the point groups isomorphic to 4mm by indicating their symbols, symmetry operations and possible sets of generators;

2. Construct the corresponding multiplication tables;

3. For each of the isomorphic point groups indicate the one-to-one correspondence with the symmetry operations of 4mm;

4. Distribute the elements of the point groups isomorphic to 4mm into classes of conjugate elements.

• **Exercise 2.12.** Determine the symmetry elements and the corresponding point groups for each of the following models of molecules:
2.2 Space-group symmetry data

Exercise 2.13. Explain the terms composition series and solvable groups. Write down the composition series for the point groups $4/mmm$, $m\overline{3}m$ and $6/mmm$. Generate the symmetry operations of the groups $4/mmm$ and $\overline{3}m$ following their composition series.

2.2 Space-group symmetry data

Exercise 2.14. Matrix-column presentation of symmetry operations

1. Referred to an ‘orthorhombic’ coordinate system ($a \neq b \neq c; \alpha = \beta = \gamma = 90$) two symmetry operations are represented by the following matrix-column pairs: $(W_1, w_1) = \left( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \right)$ and $(W_2, w_2) = \left( \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1/2 \\ 0 \\ 1/2 \end{pmatrix} \right)$.

(a) Determine the images $X_i$ of a point $X = \begin{pmatrix} 0.7 \\ 0.31 \\ 0.95 \end{pmatrix}$ under the action of the symmetry operations.

(b) Can you guess what is the ‘geometric nature’ of $(W_1, w_1)$ and $(W_2, w_2)$?

(c) Determine the determinant and the trace of $W_1$.

(d) Determine the sets of fixed points of $(W_1, w_1)$ and $(W_2, w_2)$.  

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(c) Determine the determinant and the trace of $W_1$.

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(a) Determine the images $X_i$ of a point $X = \begin{pmatrix} 0.7 \\ 0.31 \\ 0.95 \end{pmatrix}$ under the action of the symmetry operations.

(b) Can you guess what is the ‘geometric nature’ of $(W_1, w_1)$ and $(W_2, w_2)$?

(c) Determine the determinant and the trace of $W_1$.

(d) Determine the sets of fixed points of $(W_1, w_1)$ and $(W_2, w_2)$.
2. Consider the matrix-column pairs of the two symmetry operations \((W_1, w_1) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}\)

and \((W_2, w_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \end{pmatrix}\).

(a) Determine and compare the matrix-column pairs of the combined symmetry operations:
\((W, w) = (W_1, w_1)(W_2, w_2)\) and \((W, w)' = (W_2, w_2)(W_1, w_1)\).

(b) Determine the inverse symmetry operations \((W_1, w_1)^{-1}\) and \((W_2, w_2)^{-1}\).

(c) Determine the inverse symmetry operation \((W, w)^{-1}\) if \((W, w) = (W_1, w_1)(W_2, w_2)\).

3. Consider the matrix-column pairs \((A, a) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \end{pmatrix}\)

and \((B, b) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}\).

(a) What are the matrix-column pairs resulting from: \((A, a)(B, b) = (C, c)\) and \((B, b)(A, a) = (D, d)\).

(b) Determine \((A, a)^{-1}\), \((B, b)^{-1}\), \((C, c)^{-1}\) and \((D, d)^{-1}\). What is \((B, b)^{-1}(A, a)^{-1}\)?

**Exercise 2.15.** The General position of a space group is listed as: (1) \(x, y, z\) (2) \(\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}\)

1. Construct the matrix-column pairs of these ‘coordinate triplets’. Write down the corresponding \((4 \times 4)\) matrix representation.

2. Characterize geometrically the matrices if they refer to a monoclinic basis with unique axis \(b\) (type of operation, glide (screw) component, fixed points, nature and location of the symmetry element).

3. Use the program SYMMETRY OPERATIONS for the geometric interpretation of the matrix-column pairs of the symmetry operations.

**Exercise 2.16.** The following matrix-column pairs \((W, w)\) are determined with respect to a basis \((a,b,c)\): (1) \(x, y, z\) (2) \(\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}\) (3) \(\bar{x}, \bar{y}, \bar{z}\) (4) \(x, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}\).

- Determine the corresponding matrix-column pairs \((W', w')\) with respect to the basis \((a', b', c') = (a, b, c)P\), with \(P = c, a, b\).

- The coordinates of a point \(X = \begin{pmatrix} 0.70 \\ 0.31 \\ 0.95 \end{pmatrix}\) are determined with respect to the basis \((a,b,c)\).

What would be the coordinates \(X'\) referred to the basis \((a', b', c')\)?

**Exercise 2.17.**

(a) Consider the General position data given in ITA for the space group \(Cmm2\) (No. 35):

1. Characterize geometrically the matrix-column pairs listed under General position of the space group \(Cmm2\). Compare the results with the data listed under Symmetry operations.

2. Consider the diagram of the symmetry elements of \(Cmm2\). Try to determine the matrix-column pairs of the symmetry operations whose symmetry elements are indicated on the unit-cell diagram.

3. Compare your results with the results of the program SYMMETRY OPERATIONS for the geometric interpretation of the matrix-column pairs of the symmetry operations considered in this exercise.

(b) The same for the space group \(P4mm\) (No.99).
2.2 Space-group symmetry data

**Attachments:** Copies of the ITA pages with the space-group data of Cmm2, No. 35.
Copies of the ITA pages with the space-group data of P4mm, No. 99.

- **Exercise 2.18.** Consider the special Wyckoff positions of the the space group P4mm (No. 99)

  1. Determine the site-symmetry groups of Wyckoff positions 1a and 1b. Compare the results with the listed data of P4mm in ITA.
  2. The coordinate triplets \((x, 1/2, z)\) and \((1/2, x, z)\), belong to Wyckoff position 4f. Compare their site-symmetry groups.
  3. Compare your results with the output of the program WYCKPOS for the space group P4mm.
  4. Use the option *Non-conventional settings* of the program WYCKPOS to determine the coordinate triplets of the Wyckoff positions of the space group P4mm referred to a non-conventional setting with the four-fold rotation axes parallel to \(a\) axis.

**Attachments:** Copies of the ITA pages with the space-group data of P4mm, No. 99.

- **Exercise 2.19.** Consider the Wyckoff-position data given in ITA for the space group P42/mbc (No. 135):

  1. Determine the site-symmetry groups of the following Wyckoff positions: 4(a); 4(c); 4(d); 8(g). Construct the corresponding oriented site-symmetry symbols and compare them with those listed in ITA. Compare your results with the results listed by the program WYCKSPLIT.
  2. Characterize geometrically the isometries (3), (8), (12), (15) and (16) as listed under General Position. Compare the results with the corresponding geometric descriptions listed under Symmetry operations in ITA.
  3. Compare the calculated geometric descriptions of the isometries by the program SYMMETRY OPERATIONS

**Attachments:** Copies of the ITA pages with the space-group data of P42/mbc, No. 135.

- **Exercise 2.20.** ITA -conventional settings of space groups

  1. Consider the space group P21/c (No. 14). Show that the relation between the General and Special position data of P1121/a (setting unique axis \(c\)) can be obtained from the data P121/c1 (setting unique axis \(b\)) applying the transformation \((a, b, c)_c = (a, b, c)_b P\), with \(P = c, a, b\).
  2. Use the retrieval tools GENPOS (generators and general positions) and WYCKPOS (Wyckoff positions for accessing ITA data. Get the data on general and special positions in different settings either by specifying transformation matrices to new bases, or by selecting one of the 530 settings of the monoclinic and orthorhombic groups listed in ITA (cf. Table 4.3.2.1).

**Attachments:** Copies of the ITA pages with the space-group data of P21/c (No. 14).

- **Exercise 2.21.** ITA and Non-conventional settings of space groups

  1. Use the retrieval tools GENPOS (generators and general positions), WYCKPOS (Wyckoff positions and HKLCOND (reflection conditions) for accessing ITA data. Get the data on general and special positions in different settings either by specifying transformation matrices to new bases, or by selecting one of the 530 settings of the monoclinic and orthorhombic groups listed in ITA (cf. Table 4.3.2.1).
2. Consider the General position data of the space group $Im\overline{3}m$ (No. 229). Using the option Non – conventional setting obtain the matrix-column pairs of the symmetry operations with respect to a primitive basis $(a_p, b_p, c_p)$, applying the transformation $a_p, b_p, c_p = \frac{1}{2}(-a + b + c), \frac{1}{2}(a - b + c), \frac{1}{2}(a + b - c)$ (where $(a, b, c)$ is the conventional basis).

2.3 Group-subgroup relations of space groups

- **Exercise 2.22.** Construct the diagram of the $t$-subgroups of $P4mm$ using the ‘analogy’ with the subgroup diagram of the group $4mm$, cf. Exercise 2.4. Give the standard Hermann-Mauguin symbols of the $t$-subgroups of $P4mm$.

- **Exercise 2.23.** The retrieval tool MAXSUB gives an access to the database on maximal subgroups of space groups as listed in ITA1. Consider the maximal subgroups of the group $P4mm$, (No. 99) and compare them with the maximal subgroups of $P4mm$ derived in Problem 2.17 (ITA Exercises). Comment on the differences, if any.

- **Exercise 2.24.** Study the group–subgroup relations between the groups $G = P4_12_12$, No. 92, and $H = P2_1$, No. 4 using the program SUBGROUPGRAPH. Consider the cases with specified (e.g. $[i] = 4$) and unspecified index of the group-subgroup pair.

- **Exercise 2.25.** Translationengleiche subgroups of $P4mm$

  (a) Explain the difference between the contracted and complete graphs of the $t$-subgroups of $P4mm$ (No. 99) obtained by the program SUBGROUPGRAPH. Compare the complete graph with the results of Problems 2.4 and 2.17 of ITA Exercises.

  (b) Explain why the $t$-subgroup graphs of all 8 space groups from No. 99 ($P4mm$) to No. 106 ($P4_2bc$) have the same ‘topology’ (i.e. the same type of ‘family tree’), only the corresponding subgroup entries differ.

- **Exercise 2.26.** Phase transitions in BaTiO$_3$

  The crystal structure of BaTiO$_3$ is of perovskite type. Above 120°C BaTiO$_3$ has the ideal paraelectric cubic structure (space group $Pm\overline{3}m$) shown in Figure 1. Below 120°C BaTiO$_3$ assumes three structures with slightly deformed unit cells, all three being ferroelectric with different directions of the axis of spontaneous polarisation (polar axis). The three ferroelectric polymorphs differ in the direction of displacement of the Ti-atoms from the centres of the octahedra (and the accompanying lattice distortion):

  (a) No displacement: cubic structure

  (b) Displacement parallel to a cube edge: <100>, symmetry group $P4mm$;

  (c) Displacement parallel to face diagonal of the cube: <110>, symmetry group $Amm2$;

  (d) Displacement parallel to a body diagonal of the cube: <111>, symmetry group $R3m$.

  (i) Which subgroup indices do the three space groups of the ferroelectric polymorphs display with respect to the cubic group $Pm\overline{3}m$?

  (ii) How many orientation states of the twin domains occur for each polymorph? Which mutual orientation do the domains exhibit for case (b)?
2.3 Group-subgroup relations of space groups

Figure 1: (1) Perovskite structure (undistorted); (2) Distorted perovskite structure: Ti displacements and lattice distortion parallel to a cube edge, and the related dipole generation in BaTiO$_3$

- **Exercise 2.27.** SrTiO$_3$ has the cubic perovskite structure, space group $Pm\bar{3}m$. Upon cooling below 105K, the coordination octahedra are mutually rotated and the space group is reduced to $I4/mcm$; $c$ is doubled and the unit cell is increased by the factor of four. Can we expect twinned crystals of the low symmetry form? If so, how many kinds of domains?

Determine the number and type of domains of the low-symmetry form of SrTiO$_3$ using the computer tools of the Bilbao Crystallographic server.

- **Exercise 2.28.** Study the splittings of the Wyckoff positions for the group-subgroup pair $P4mm$ (No. 99) $>$ $Cm$ (No. 4) of index 4 by the program WYCKSPLIT.

- **Exercise 2.29.** Consider the group–supergroup pair $\mathcal{H} \lhd \mathcal{G}$ with $\mathcal{H} = P222$, No. 16, and the supergroup $\mathcal{G} = P422$, No. 89, of index $[\mathcal{i}] = 2$. Using the program MINSUP determine all supergroups $P422$ of $P222$ of index $[\mathcal{i}] = 2$. How does the result depend on the normalizer of the supergroup and/or that of the subgroup.
3 Symmetry relations between crystal structures

Structure data for the exercises:
http://www.cryst.ehu.es/resources/Varanasi2014

• Exercise 3.1. Structure descriptions for different space-group settings (Wondratschek, 2002)

(a) In R. W. G. Wyckoff, Crystal structures, vol. II, Ch. VIII, one finds the important mineral zircon $ZrSiO_4$ and a description of its crystal structure. Many rare-earth phosphates, arsenates, and vanadates belong to the same structure type.

Structural data: Space group $I4_1/amd = D_{19}^{14}$, No. 141;
lattice constants $a = 6.60$ Å; $c = 5.88$ Å.

The origin choice is not stated explicitly. However, Wyckoff’s Crystal Structures started to appear in 1948, when there was one conventional origin only (the later ORIGIN CHOICE 1, i.e. Origin at $\bar{4}m\bar{2}$).

$Zr$: ($a$) $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0$;

$Si$: ($b$) $0, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0$

$O$: ($h$) $(0, u, v; 0, \bar{u}, \bar{v}; u, 0, \bar{v}; 0, \frac{1}{2} + u, \frac{1}{2} - v; 0, \frac{1}{2} - u, \frac{1}{2} + v; \frac{1}{2}, v + \frac{1}{4}; u, \frac{1}{2}, v + \frac{1}{4})$ [and the same with $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$].

The parameters $u$ and $v$ are listed with $u = 0.20$ and $v = 0.34$.

(b) In the Structure Reports, vol. 22, (1958), p. 314 one finds:

‘$a = 6.6164(5)$ Å, $c = 6.0150(5)$ Å’

‘Atomic parameters. Origin at center (2/m) at $0, \frac{1}{4}, \frac{1}{8}$ from $4m2$.

‘Oxygen: (0, y, z) with $y = 0.067, z = 0.198.’

Compare the two structure descriptions and check if they belong to the same structure type. Which of the structure tools of the Bilbao Crystallographic Server could help you to solve the problem?

Hint: In order to compare the different data, the parameters of Wyckoff’s book are to be transformed to ‘origin at center 2/m’, i.e. ORIGIN CHOICE 2.

• Exercise 3.2. Equivalent structure descriptions

(a) CsCl is cubic, space group $Pm\bar{3}m$, with the following co-ordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1a</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td>Cs</td>
<td>1b</td>
<td>0.5 0.5 0.5</td>
</tr>
</tbody>
</table>

How many equivalent sets of co-ordinates can be used to describe the structure? What are their co-ordinates?

Hint: The number of different equivalent descriptions of CsCl is equal to the index of its space group $Pm\bar{3}m(a, b, c)$ in the Euclidean normalizer $I\bar{m}\bar{3}m(a, b, c)$, i.e. $|i| = 2$. The two different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group.
(b) $P(C_6C_5)_4[MoNCl_4]$ is tetragonal, space group $P4/n$, with the following co-ordinates:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2b</td>
<td>0.25 0.75 0</td>
</tr>
<tr>
<td>Mo</td>
<td>2c</td>
<td>0.25 0.25 0.121</td>
</tr>
<tr>
<td>N</td>
<td>2c</td>
<td>0.25 0.25 -0.093</td>
</tr>
<tr>
<td>C1</td>
<td>8g</td>
<td>0.362 0.760 0.141</td>
</tr>
<tr>
<td>C2</td>
<td>8g</td>
<td>0.437 0.836 0.117</td>
</tr>
<tr>
<td>Cl</td>
<td>8g</td>
<td>0.400 0.347 0.191</td>
</tr>
</tbody>
</table>

(H and C3 to C6 omitted)

How many equivalent sets of co-ordinates can be used to describe the structure? What are their co-ordinates?

**Hint:** The number of different equivalent descriptions of $P(C_6C_5)_4[MoNCl_4]$ is equal to the index of its space group $P4/n$ in the Euclidean normalizer. The different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group. In the special case of $P(C_6C_5)_4[MoNCl_4]$ such equivalent descriptions can be generated, for example, by the translations $t(0,0,1/2)$ and $t(1/2,1/2,0)$, and by a reflection through a mirror plane at $(x,x,z)$ represented by the coordinate triplet $(y,x,z)$.

**Exercise 3.3. Isoconfigurational structure types (Koch & Fischer, 2002)**

Do the following three structures belong to the same structure type? Try to find analogous coordinate descriptions for all three crystal structures.

1. KAsF$_6$ (ICSD: 59413)

| Unit Cell | 7.348(1) | 7.348(1) | 7.274(8) | 90. 90. 120 |
| Space group | R-3h |

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>3b</td>
<td>0.33333 0.66667 0.166667</td>
</tr>
<tr>
<td>As</td>
<td>3a</td>
<td>0 0 0</td>
</tr>
<tr>
<td>F</td>
<td>18f</td>
<td>0.1292(2) 0.2165(2) 0.1381(2)</td>
</tr>
</tbody>
</table>

2. BaIrF$_6$ (ICSD: 803188)

| Unit Cell | 7.3965(1) | 7.3965(1) | 7.2826(1) | 90. 90. 120 |
| Space group | R-3h |

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>3b</td>
<td>0.33333 0.6666 0.166666</td>
</tr>
<tr>
<td>Ir</td>
<td>3a</td>
<td>0 0 0</td>
</tr>
<tr>
<td>F</td>
<td>18f</td>
<td>0.0729(2) 0.2325(2) 0.1640(2)</td>
</tr>
</tbody>
</table>

3. BaSnF$_6$ (ICSD: 33788)

| Unit Cell | 7.4279(2) | 7.4279(2) | 7.418(2) | 90. 90. 120 |
| Space group | R-3h |

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>3b</td>
<td>0.33333 0.6666 0.166666</td>
</tr>
<tr>
<td>Sn</td>
<td>3a</td>
<td>0 0 0</td>
</tr>
<tr>
<td>F</td>
<td>18f</td>
<td>0.0729(2) 0.2325(2) 0.1640(2)</td>
</tr>
</tbody>
</table>
Atom  Wyckoff  Coordinate triplets
     position  x       y       z
Ba    3a     0       0       0
Sn    3b     0       0       0.5
F     18f    0.2586(3) 0.8262(3) 0.0047(3)

Hint: Consider the Euclidean normalizer of symmetry group \( R_3^3 \) (hex) of KAsF\(_6\). The number of different equivalent descriptions of KAsF\(_6\) is equal to the index of its space group in the Euclidean normalizer. The different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group. In the special case of KAsF\(_6\) such equivalent descriptions can be generated, for example, by the translation \( t(0,0,1/2) \), by a reflection through a mirror plane at \((x,-x,z)\) represented by the coordinate triplet \((-y,-x,z)\), etc.

Exercise 3.4. Crystal structure descriptions

In Inorganic Crystal Structure Database can be found several structure data sets of \( \epsilon\)-Fe\(_2\)O\(_3\), all of them of symmetry \( Pna2_1 \) (No.33). Compare the two structure descriptions listed in the Exercise Data file and check if they belong to the same structure type.

Exercise 3.5. Cristobalite phase transitions

At low temperatures, the space-group symmetry of cristobalite is given by the space group is \( P4_12_12 \) (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), 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 \( Fd\bar{3}m \) (227), \( a = 7.147 \text{Å} \). It is listed in the space-group tables with two different origins.

1. 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-centering 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 lattice distortion accompanying the transition.

2. Repeat the calculations for the characterization of the phase transition using the Origin-choice 1 description of the high-symmetry phase (cf. Exercise Data file for the structure data).

Exercise 3.6. Ferroelastic phase transitions

(a) Lead phosphate Pb\(_3\)(PO\(_4\))\(_2\) shows a phase transition from a paraelastic high-temperature phase with symmetry \( R\bar{3}m \) (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:

(a) characterize the symmetry reduction between the high- and low-symmetry phases (index and transformation matrix);
(b) 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.

(b) Lead phosphate-vanadate Pb\(_3\)(PVO\(_4\))\(_2\) shows a phase transition from a paraelastic high-temperature phase with symmetry \( R\bar{3}m \) (No.166) to a ferroelastic phase of symmetry \( P2_1/c \)
Using the structure data given in the ExerciseData file and the tools of the Bilbao Crystallographic Server 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.

**Exercise 3.7.** Order-disorder phase transitions in CuAu alloy

(i) A high-temperature form where Au and Cu are distributed statistically over the sites of an fcc packing; i.e. symmetry Fm3m, Wyckoff position 4a m3m 0,0,0 and a lattice parameter \(a_c = 3.83\text{Å};\)

(ii) A low temperature phase where Au and Cu are ordered in layers perpendicular to one of the four-fold axes of Fm3m: the positions 0,0,0 and 1/2,1/2,0 are occupied by Cu, and 1/2,0,1/2 and 0,1/2,1/2 by Au. The symmetry is reduced to \(P4/mmm\), with lattice parameters \(a_t = 2.86\text{Å}, c_t = a_c.\)

(a) characterize the symmetry reduction between the high- and low-symmetry phases (index and transformation matrix);
(b) 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.

**Exercise 3.8.** CoU hetotype of the β-brass structure

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.

**Exercise 3.9.** (Müller, 2008): Crystal-structure relationships

1. \(HT\)-quartz and \(LT\)-quartz

Upon heating above 573 C the \(LT\)-quartz transforms to its \(HT\) form. Set up the corresponding Bärnighausen 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 data of \(LT\)-quartz are:

| Unit Cell: | 4.91 4.91 5.41 90. 90. 120 |
| Space group: | \(P3_2\overline{2}1\) |

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Coordinate</th>
<th>triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3a</td>
<td>0.470</td>
</tr>
<tr>
<td>O</td>
<td>6c</td>
<td>0.414</td>
</tr>
</tbody>
</table>

| Unit Cell: | 5 5 5.46 90. 90. 120 |
| Space group: | \(P6_2\overline{2}2\) |

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Coordinate</th>
<th>triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3c</td>
<td>0.5</td>
</tr>
<tr>
<td>O</td>
<td>6j</td>
<td>0.416</td>
</tr>
</tbody>
</table>

2. \(\alpha\)-AlPO\(_4\)

The crystal data of \(\alpha\)-AlPO\(_4\):
Unit Cell: 4.94 4.94 10.95 90. 90. 120
Space group: \(P3_121\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Coordinate triplets</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3a</td>
<td>0.466 0 0.33333</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>3b</td>
<td>0.467 0 5/6</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>6c</td>
<td>0.417 0.292 0.398</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>6c</td>
<td>0.417 0.257 0.883</td>
<td></td>
</tr>
</tbody>
</table>

What is the symmetry relation of \(\alpha\)-AlPO\(_4\) to quartz?

**Exercise 3.10.** Hettotypes of the fluorite structure (Hahn & Wondratschek, 1984)

The structure of \(\alpha\)-XOF (X=La, Y, and Pu) can be derived from that of cubic CaF\(_2\) (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.

The conventional basis \(a', b', c'\) of \(\alpha\)-XOF is \(a' = \frac{1}{2}(a - b), b' = \frac{1}{2}(a + b), c' = c\) where \(a, b, c\) is the basis of CaF\(_2\). Moreover, the conventional origin of \(\alpha\)-XOF is shifted by \(p = \frac{1}{4}, 0, \frac{1}{4}\) relative to that of \(\alpha\)-XOF (symmetry group \(P4/nmm\) (129)).

The coordinates of CaF\(_2\) are:

Ca 4\(a\) \(m3m\) 0,0,0 \(\frac{1}{2}, \frac{1}{2}, 0\) \(\frac{1}{2}, 0\frac{1}{2}\) \(0, \frac{1}{2}, \frac{1}{2}\)

F 8\(c\) \(43m\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)

\(\frac{1}{4}, \frac{1}{4}, 0\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)

\(\frac{1}{4}, \frac{1}{4}, 0\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)

\(\frac{1}{4}, \frac{1}{4}, 0\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\) \(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)

Questions

(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 CaF\(_2\) 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 CaF\(_2\) 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 CaF\(_2\)? (structure data of \(\alpha\)-LaOF in Exercise Data file)

**Exercise 3.11.** Structural pseudosymmetry of Pb\(_2\)MgWO\(_6\)

Analyse the structural pseudosymmetry of Pb\(_2\)MgWO\(_6\) using the program PSEUD0, cf. structure data in Exercise Data file: (i) Try to determine the maximal possible pseudosymmetry stepwise, i.e. \textit{climbing} via the minimal supergroups (applying Option 1 of the program); (ii) Apply Option 3 of PSEUD0 (Pseudosymmetry search for a specific supergroup given by a transformation matrix \((P, p)\)) to confirm the flagged maximal pseudosymmetry in (i).

**Exercise 3.12.** Structural pseudosymmetry of a \(C222_1\) structure

Using the program PSEUD0, Option1, analyse the structural pseudosymmetry of a hypothetical \(C222_1\) (No. 20) structure stepwise, i.e. \textit{climbing} via the minimal supergroups (cf. structure data in Exercise Data file). Compare the results if different minimal-supergroup paths are followed.
Exercise 3.13. Apparently complex phase Ga-II of Ga under pressure
Analyze the structural pseudosymmetry of the orthorhombic phase Ga-II of Ga under pressure using the program PSEUDO (structure data in Exercise Data file).

Hint: As a first step check the structural pseudosymmetry with respect to an isomorphic supergroup of index 13 (can you guess why?), specified by the transformation matrix: a,b,13c, Option 3.

Exercise 3.14. Tetragonal phase of GeF$_2$
The compound GeF$_2$, of symmetry $P2_12_12_1$ (No. 19) (cf. structure data in Exercise Data file), is reported to have at high temperatures an unknown tetragonal phase, with the primitive unit cell volume being essentially maintained. Using PSEUDO, with the option 2, which allows to check supergroups with a fixed k-index (multiplication of the primitive unit cell), postulate a probable space group or groups and a starting structural model for this high-temperature phase.

Exercise 3.15. Non-polar phases of NaSb$_3$F$_{10}$
The compound NaSb$_3$F$_{10}$ whose room-temperature phase is polar, space group $P6_3$, has been predicted to be ferroelectric (cf. structure data in Exercise Data file). The symmetries $P6_3$22 and $P6_3/mmc$ had been proposed for two successive non-polar phases at high temperature. Applying the pseudosymmetry approach confirm the predictions for the non-polar phases of NaSb$_3$F$_{10}$. Show that apart from $P6_3$22 phase, there are two more appropriate candidates for the intermediate phases between the polar phase $P6_3$ and the non-polar one of maximal symmetry, $P6_3/mmc$.

Exercise 3.16. Structural pseudosymmetry of Nd$_4$GeO$_8$
The compound Nd$_4$GeO$_8$ is reported to have polar $Pmc2_1$ symmetry (Doklady Akademii Nauk SSSR (1978) 241, 353-356) (cf. structure data in Exercise Data file).

(i) Using PSEUDO (Option 1), show that this structure can be considered a small distortion of a $Cmcm$ structure.

(ii) Using SUBGROUPGRAPH show the graph of maximal subgroups connecting the two symmetries.

(iii) Using again PSEUDO (Option 3) obtain the atomic displacements relating the two structures.

Exercise 3.17. Overlooked symmetry of Ca$_2$Ge$_7$O$_{16}$
According to a structural model for Ca$_2$Ge$_7$O$_{16}$ published in Doklady Akademii Nauk SSSR (1979) 245, 110-113, the symmetry group of the compound is $Pba2$.

Despite the 4/mmm Laue symmetry of the diffraction diagram the authors of this publication were unable to find an appropriate tetragonal structural model, and refined the compound in $Pba2$ symmetry.

Using PSEUDO, demonstrate that this structure differs from a tetragonal one with space group $P4b2$, by atomic displacements which are practically negligible or within experimental accuracy, so that in fact this structure file should be considered incorrect, being a case of overlooked symmetry. The pseudosymmetry of the structure was reported in (Acta Cryst. B (2002) 58, 921) and the compound has been recently confirmed to have $P4b2$ symmetry by a new study of the structure (Acta Cryst. C (2007) 63, i47).

Exercise 3.18. Pseudosymmetry search in monoclinic structures
(a) Lead phosphate Pb$_2$(PO$_4$)$_2$ shows a phase transition from a paraelectric high-temperature phase with symmetry $R3m$ (No.166) to a ferroelectric phase of symmetry $C2/c$ (No.15). Using the structure data of the low-symmetry monoclinic phase given in the ExerciseData file (cf.
Problem 6a) analyze its structural pseudosymmetry with respect to the symmetry group of the high-symmetry phase. Using the program COMPSTRU evaluate the difference between the experimentally determined $R\bar{3}m$ structure and the idealized high-symmetry structure proposed by PSEUDO.

(b) Lead phosphate-vanadate Pb$_3$(PVO$_4$)$_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry $P2_1/c$ (No.14). Using the structure data of the low-symmetry monoclinic phase given in the ExerciseData file (cf. Problem 6b) analyze its structural pseudosymmetry with respect to the symmetry group of the high-symmetry phase. Using the program COMPSTRU evaluate the difference between the experimentally determined $R\bar{3}m$ structure and the idealized high-symmetry structure proposed by PSEUDO.

- **Exercise 3.19.** Determine the isotropy subgroups of the irreducible representations of $P4mm$ with wave vector $\mathbf{k}=\mathbf{0}$.

- **Exercise 3.20.** A structure has symmetry $Pnma$. At lower temperatures, a phase transition happens, and diffraction experiments show that superstructure reflections at points $(h, k, l + \frac{1}{2})$ appear, indicating the duplication of the $c$ parameter, while keeping an orthorhombic lattice.

  1. Assuming a group-subgroup related transition and using CELLSUB, predict the only two possible space groups of this low-temperature phase, and the transformation matrix relating it with the parent space group $Pnma$.

  2. Using SYMMODES determine if the space groups determined in i. (i) are isotropy subgroups or not. For the isotropy subgroups, identify the wave vector and the label of the active irreps of the transitions, and check by hand that indeed the irreps yield the superlattice that has been observed.

- **Exercise 3.21.** The following centrosymmetric orthorhombic subgroups of $Fm\bar{3}m$ fulfilling the lattice metrics observed in the orthorhombic phase of fullerene-cubane crystals have been determined by CELLSUB:

  $Pnma(2a, \frac{b}{2} + \frac{c}{2}, -\frac{b}{2} + \frac{c}{2}; \frac{3}{4}, \frac{1}{4}, 0)$;

  $Pmmn(\frac{a}{2}, -\frac{b}{2}, \frac{b}{2}; 0, \frac{1}{4}, 0, \frac{3}{4})$;

  $Pcnn(\frac{a}{2}, -\frac{b}{2}, \frac{b}{2}; \frac{1}{4}, 0, \frac{3}{4})$;

  $Pnma(2a, \frac{b}{2} + \frac{c}{2}, -\frac{b}{2} + \frac{c}{2}; 0, 0, 0)$;

  $Pccm(\frac{a}{2} - \frac{b}{2}, \frac{a}{2} + \frac{b}{2}, 2c; 0, 0, 0)$;

  $Pmmm(\frac{a}{2} - \frac{b}{2}, \frac{a}{2} + \frac{b}{2}, 2c; 0, 0, 0)$.

Using SYMMODES show that only two of the six space groups are isotropy subgroups of $Fm\bar{3}m$, and therefore only for these two subgroups a single active irrep can be identified. These two space groups should be therefore the two first obvious choices for the symmetry of the orthorhombic phase of the fullerene-cubane crystals.

- **Exercise 3.22.** Monoclinic phase of the system PbZr$_{1-x}$Ti$_x$O$_3$

Consider the perovskite-like ferroelectric system PbZr$_{1-x}$Ti$_x$O$_3$ (PZT). Some measurements have revealed a monoclinic phase (with no cell multiplication) between the previously established tetragonal ($P4mm$) and rhombohedral ($R3m$) regions in its phase diagram as a function of $x$. Both phases, $P4mm$ and $R3m$, are ferroelectric distorted phases of the perovskite, due to the condensation of a polar mode of symmetry at $\mathbf{k}=\mathbf{0}$. The perfect perovskite structure PbBO$_3$ is cubic $Pm\bar{3}m$ ($Z=1$) with positions: Pb 1b, B 1a, O 3d.
(a) Using **SYMMODES** obtain a valid transformation matrix for the pairs $Pm\bar{3}m \rightarrow P4mm$, and $Pm\bar{3}m \rightarrow R\bar{3}m$, and check that indeed the two phases, $P4mm$ and $R\bar{3}m$, can be assigned to the same active irrep, for two different directions of the order parameter. Take notice of the active irrep and these directions.

(b) A reasonable assumption about the detected monoclinic structure is that it must be some bridging phase with the order parameter changing between the two special directions obtained in (a). Its symmetry would then be given by a common subgroup of the tetragonal and rhombohedral space groups. Use **COMMONSUBS** to predict under this assumption the space group of the monoclinic phase. Take notice of the transformation matrix relating it with the space group $P4mm$.

(c) From the transformation matrices for the pairs $Pm\bar{3}m \rightarrow P4mm$ and $P4mm$ — monoclinic phase, obtain the transformation matrix relating $Pm\bar{3}m$ and the monoclinic space group. Using **SYMMODES** again demonstrate that the active irrep of the postulated monoclinic space group is indeed the same as for the other two phases. Compare the order parameter direction with those obtained in (a).

(d) Use **TRANSTRU** to derive a starting structural model of the monoclinic phase (with a single mixed site for the Zr/Ti atoms), which you could use as the starting point for a refinement of the structure.

**Exercise 3.23.** A compound has $Pnma$ symmetry at high temperatures and has space group $P12_11$ at low temperatures, keeping essentially the same lattice, except for some strain. Using **SYMMODES** obtain the graph of minimal subgroups relating both symmetries. Check that at least two irreps must be active to explain the symmetry of the distorted structure. Indicate the possible pairs of active irreps in the distorted phase. Indicate the possible (alternative) symmetries of a probable intermediate phase.

**Exercise 3.24.**

The multiferroic BiFeO$_3$ has symmetry $R3c$ with $Z=6$ at room-temperature, having at high temperatures the cubic perovskite configuration (Fe: 1$a$, Bi: 1$b$, O: 3$d$).

1. Using **SYMMODES**, show that the room temperature phase of BiFeO$_3$ has two active irreps, one being the usual $R4+$ mentioned above, and the other one is the one discussed in exercise 3.22, present in BiFeO$_3$.

2. Some publications have reported an intermediate phase with symmetry $I4/mcm$. Crosscheck the consistency of this intermediate symmetry with your previous results.

3. With **TRANSTRU** produce a starting structural model to refine the structures $I4/mcm$ and $R3c$ of BiFeO$_3$, indicating the refinable coordinates of the constructed asymmetric unit.

**Exercise 3.25.** Apply the program **AMPLIMODES** for the symmetry-mode analysis of the ferroelectric phase transition to the orthorhombic $Amm2$ structure of BaTiO$_3$. Consider carefully the output of the program and find the relevant information for the characteristics of the symmetry-adapted modes, such as wave vectors, irreducible representations (irreps), directions in irrep space, isotropy subgroups. What are the polarization vectors and the amplitudes of the irrep distortions that have non-zero contribution into the global distortion of the symmetry break $Pm\bar{3}m \rightarrow Amm2$? Which is the primary dominant distortion?

The ferroelectric phase transition to the orthorhombic $Amm2$ structure of BaTiO$_3$ is the default online example of the program **AMPLIMODES** and the necessary INPUT data is available on the web page of the program on the Bilbao Crystallographic Server.

1. Obtain with AMPLIMODES that the ferroelectric structure has two distortion modes, a primary one that yields the $P1c1$ space group, i.e. the order parameter distortion, and a secondary one compatible with the parent symmetry.

2. Change arbitrarily some of the coordinates of $P12_1/c1$, but displacing the positions only a small amount (below 1 Å). Check that AMPLIMODES gives the same results (amplitude and polarization vector) for the symmetry-breaking mode, changing only the form of the fully symmetric mode GM1.

3. Which atoms are moving more strongly in the transition? Derive the atomic positions of the Sn atoms in two virtual $P1c1$ structures having only the experimental primary ferroelectric mode with an amplitude of 0.1 Å and of 0.2 Å. One could use such virtual structures in an \textit{ab-initio} calculation to characterize the energy variation of the system as a function of the ferroelectric mode.

Exercise 3.27. Carry out a symmetry mode analysis of the room-temperature phase $P6_3cm$ of $\text{KNiCl}_3$, considering this phase as a distortion from a virtual parent phase of symmetry $P6_3/mmc$ (the structures are given in the Exercise Data file).

There are different types of symmetry-adapted modes contributing to the global distortion. What symmetry modes could be related to the primary order parameter, and which are related to the secondary effects? Is it correct to classify the room-temperature form of $\text{KNiCl}_3$ as proper ferroelectric?

\textit{Hint}: Use the databases and computer tools on the Bilbao Crystallographic Server to determine the transformation matrix $(P, p)$ for the symmetry break: $P6_3/mmc \rightarrow P6_3cm$. 