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CRYSTALLOGRAPHIC POINT GROUPS I
(basic facts)

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GROUP THEORY
(few basic facts)
The equilateral triangle allows six symmetry operations: rotations by $\theta$ and $2\theta$ around its centre, reflections through the three thick lines intersecting the centre, and the identity operation.
Mirror symmetry operation

Mirror line \( m_y \) at \( 0,y \)

Matrix representation

Fixed points

\[
m_y \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix}
\]

\[
\begin{pmatrix} \begin{array}{c} x \\ y \end{array} & -x \\ y \end{pmatrix} = \begin{pmatrix} -1 & x \\ 1 & y \end{pmatrix}
\]

\[
\det \begin{pmatrix} -1 & x \\ 1 & y \end{pmatrix} = ? \quad \text{tr} \begin{pmatrix} -1 & x \\ 1 & y \end{pmatrix} = ?
\]
Symmetry operations in the plane
Matrix representations

2-fold rotation

\[ 2_z \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -x \end{pmatrix} = \begin{pmatrix} -1 & x \\ -1 & y \end{pmatrix} \]

\[ \text{det} \begin{pmatrix} -1 & x \\ -1 & y \end{pmatrix} = ? \]

\[ \text{tr} \begin{pmatrix} -1 & x \\ -1 & y \end{pmatrix} = ? \]

3-fold rotation

\[ 3^+ \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -y \\ x-y \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} \]

\[ \text{det} \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} = ? \]

\[ \text{tr} \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} = ? \]
2. Group axioms

**DEFINITION.** The symmetry operations of an object constitute its *symmetry group.*

**DEFINITION.** A group is a set \( G = \{e, g_1, g_2, g_3 \ldots \} \) together with a product \( \circ \), such that

i) \( G \) is "closed under \( \circ \)"; if \( g_1 \) and \( g_2 \) are any two members of \( G \) then so are \( g_1 \circ g_2 \) and \( g_2 \circ g_1 \);

ii) \( G \) contains an identity \( e \): for any \( g \) in \( G \), \( e \circ g = g \circ e = g \);

iii) \( \circ \) is associative: \( (g_1 \circ g_2) \circ g_3 = g_1 \circ (g_2 \circ g_3) \);

iv) Each \( g \) in \( G \) has an inverse \( g^{-1} \) that is also in \( G \): \( g \circ g^{-1} = g^{-1} \circ g = e \).
GROUP AXIOMS

1. CLOSURE
\[ g_1 \circ g_2 = g_12 \quad g_1, g_2, g_12 \in G \]

2. IDENTITY
\[ g \circ e = e \circ g = g \]

3. INVERSE ELEMENT
\[ g \circ g^{-1} = e \]

4. ASSOCIATIVITY
\[ (g_1 \circ g_2) \circ g_3 = g_1 \circ (g_2 \circ g_3) = g_1 \circ g_2 \circ g_3 \]
1. **Order of a group** \(| G |\): number of elements
   - Crystallographic point groups: \(1 \leq |G| \leq 48\)
   - Space groups: \(|G| = \infty\)

2. **Abelian group** \(G\):
   \[g_i \cdot g_j = g_j \cdot g_i \quad \forall g_i, g_j \in G\]

3. **Cyclic group** \(G\):
   \[G = \{g, g^2, g^3, \ldots, g^n\}\]
   - Finite: \(|G| = n, g^n = e\)
   - Infinite: \(G = \langle g, g^{-1} \rangle\)

   Order of a group element: \(g^n = e\)
4. How to define a group

**Multiplication table**

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>E</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
<td>B</td>
<td>E</td>
</tr>
<tr>
<td>B</td>
<td>B</td>
<td>E</td>
<td>A</td>
</tr>
</tbody>
</table>

**Group generators**

a set of elements such that each element of the group can be obtained as a product of the generators
Crystallographic Point Groups in 2D

Point group $\mathbb{2} = \{1, 2\}$

Motif with symmetry of $\mathbb{2}$

Where is the two-fold point?

\[
\begin{align*}
2_z & \quad \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} \\
\text{det} & = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = ? \\
\text{tr} & = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = ?
\end{align*}
\]

drawing: M.M. Julian
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Point group \(2 = \{1, 2\}\)

- Group axioms?
- Order of 2?
- Multiplication table
- Generators of 2?

Motif with symmetry of 2

Where is the two-fold point?

drawing: M.M. Julian
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Crystallographic symmetry operations in the plane

Mirror symmetry operation

Mirror line $m_y$ at 0,y

Where is the mirror line?

Matrix representation

$$m_y = \begin{pmatrix} x & -x \\ y & y \end{pmatrix} = \begin{pmatrix} -1 & x \\ 1 & y \end{pmatrix}$$

$$\det \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix} = ? \quad \text{tr} \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix} = ?$$

drawing: M.M. Julian

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Crystallographic Point Groups in 2D

Point group $\mathbf{m} = \{1, \mathbf{m}\}$

Motif with symmetry of $\mathbf{m}$

- group axioms?

$\mathbf{m} \times \mathbf{m} = \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$

- order of $\mathbf{m}$?

- multiplication table

- generators of $\mathbf{m}$?
Isomorphic groups

- groups with the same multiplication table
Isomorphic groups

\[ G = \{ g \} \quad \Phi^{-1}(g') = g \]

\[ \Phi : G \rightarrow G' \quad \Phi^{-1} : G' \rightarrow G \]

Homomorphic condition

\[ \Phi(g_1)\Phi(g_2) = \Phi(g_1g_2) \]

-Groups with the same multiplication table
Crystallographic Point Groups in 2D

Point group $\mathbf{1} = \{1\}$

Motif with symmetry of $\mathbf{1}$

- group axioms?

$1 \times 1 = \begin{array}{|c|c|c|} \hline \cline{1-3} 1 & 1 & 1 \\ \hline \end{array} \begin{array}{|c|} \hline 1 \\ \hline \end{array} = \begin{array}{|c|} \hline 1 \\ \hline \end{array}$

-order of $\mathbf{1}$?

-multiplication table

-generators of $\mathbf{1}$?

drawing: M.M. Julian

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Problem 2.1

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

Determine:

- symmetry operations: matrix and $(x,y)$ presentation
- generators
- multiplication table
Problem 2.2

Consider the symmetry group of the square. Determine:

- symmetry operations: matrix and \((x,y)\) presentation
- generators
- multiplication table
Visualization of Crystallographic Point Groups

- general position diagram
- symmetry elements diagram

Stereographic Projections

Points P in the projection plane
EXAMPLE

Stereographic Projections of $mm2$

Point group $mm2 = \{1, 2, m_x, m_y\}$

Molecule of pentacene

Stereographic projections diagrams

general position  symmetry elements
Problem 2.2 (cont.)

Stereographic Projections of $4mm$

general position diagram

symmetry elements diagram
Problem 2.3 (additional)

Consider the symmetry group of the equilateral triangle. Determine:

- symmetry operations: matrix and $(x,y)$ presentation
- general-position and symmetry-elements stereographic projection diagrams;
- generators
- multiplication table
Conjugate elements

$4^+$  
$m_x \sim m_y$

$4mm$
**Conjugate elements**

Conjugate elements: \[ g_i \sim g_k \text{ if } \exists g: g^{-1}g_i g = g_k, \]
where \( g, g_i, g_k, \in G \)

**Classes of conjugate elements**

Classes of conjugate elements: \[ L(g_i) = \{ g_j \mid g^{-1}g_i g = g_j, g \in G \} \]

**Conjugation-properties**

(i) \( L(g_i) \cap L(g_j) = \{ \emptyset \} \), if \( g_i \notin L(g_j) \)

(ii) \( |L(g_i)| \) is a divisor of \( |G| \)

(iii) \( L(e) = \{ e \} \)

(iv) if \( g_i, g_j \in L \), then \( (g_i)^k = (g_j)^k = e \)
Example (Problem 2.2):

The group of the square $4mm$

Classes of conjugate elements:

- $\{1\}$,
- $\{2\}$,
- $\{4, 4^{-1}\}$,
- $\{m_x, m_y\}$,
- $\{m_+, m_-\}$

Classes of conjugate elements

Multiplication table of $4mm$
Distribute the symmetry elements of the group \( \text{mm2} = \{1, 2_z, m_x, m_y\} \) in classes of conjugate elements.

\[
\begin{array}{c|cccc}
\times & 1 & 2 & m_x & m_y \\
\hline
1 & 1 & 2 & m_x & m_y \\
2 & 2 & 1 & m_y & m_x \\
m_x & m_x & m_y & 1 & 2 \\
m_y & m_y & m_x & 2 & 1 \\
\end{array}
\]
GROUP-SUBGROUP RELATIONS

I. Subgroups: index, coset decomposition and normal subgroups

II. Conjugate subgroups

III. Group-subgroup graphs
Subgroups: Some basic results (summary)

Subgroup $H < G$

1. $H = \{e, h_1, h_2, \ldots, h_k\} \subset G$
2. $H$ satisfies the group axioms of $G$

Proper subgroups $H < G$, and

trivial subgroup: $\{e\}$, $G$

Index of the subgroup $H$ in $G$: $[i] = |G|/|H|$

(order of $G$)/(order of $H$)

Maximal subgroup $H$ of $G$

NO subgroup $Z$ exists such that:

$H < Z < G$
Example

Molecule of pentacene

Subgroups of point groups

Subgroups of \textbf{mm2}

\{1, 2_z\} \rightarrow \{1, 2_z, m_x, m_y\} \rightarrow \{1, m_x\} \rightarrow \{2_z, m_x\}

Subgroup graph

mm2 = \{1, 2_z, m_x, m_y\}

Index

4 \{1, 2_z, m_x, m_y\} \rightarrow \{1, m_x\} \rightarrow \{1, m_y\} \rightarrow \{1\} \rightarrow 1

2 \{1, 2_z\} \rightarrow \{1, m_x\} \rightarrow 2

1 \{1\} \rightarrow 4
Problem 2.4

Consider the group of the square and determine its subgroups

Multiplication table of 4mm
Problem 2.5 (additional)

(i) Consider the group of the equilateral triangle and determine its subgroups;

(ii) Distribute the subgroups into classes of conjugate subgroups;

(iii) Construct the maximal subgroup graph of 3m

Multiplication table of 3m
Coset decomposition $G: H$

Group-subgroup pair $H < G$

left coset decomposition

$G = H + g_2 H + ... + g_m H$, $g_i \not\in H$, $m =$ index of $H$ in $G$

right coset decomposition

$G = H + Hg_2 + ... + Hg_m$, $g_i \not\in H$, $m =$ index of $H$ in $G$

Coset decomposition-properties

(i) $g_i H \cap g_j H = \{\emptyset\}$, if $g_i \not\in g_j H$

(ii) $|g_i H| = |H|$

(iii) $g_i H = g_j H$, $g_i \in g_j H$
Theorem of Lagrange

A group $G$ of order $|G|$ and a subgroup $H < G$ of order $|H|$ implies that $|H|$ is a divisor of $|G|$ and $[i] = |G:H|$.

Corollary

The order $k$ of any element $g$ of $G$, $g^k = e$, is a divisor of $|G|$.
Problem 2.6

Consider the subgroup \{e, 2\} of 4mm, of index 4:

- Write down and compare the right and left coset decompositions of 4mm with respect to \{e, 2\};

- Are the right and left coset decompositions of 4mm with respect to \{e, 2\} equal or different? Can you comment why?

Problem 2.7

Demonstrate that H is always a normal subgroup if |G:H|=2.
Conjugate subgroups

Let $H_1 < G$, $H_2 < G$

then, $H_1 \sim H_2$, if $\exists g \in G: g^{-1}H_1g = H_2$

(i) Classes of conjugate subgroups: $L(H)$

(ii) If $H_1 \sim H_2$, then $H_1 \cong H_2$

(iii) $|L(H)|$ is a divisor of $|G|/|H|$

Normal subgroup

$H \triangleleft G$, if $g^{-1}Hg = H$, for $\forall g \in G$
Problem 2.4 (cont)

Distribute the subgroups of the group of the square into classes of conjugate subgroups.

**Hint:** The stereographic projections could be rather helpful.

**Multiplication table of 4mm**
Complete and contracted group-subgroup graphs

Complete graph of maximal subgroups

Contracted graph of maximal subgroups
Fig. 10.1.3.2. Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. Solid lines indicate maximal normal subgroups; double or triple solid lines mean that there are two or three maximal normal subgroups with the same symbol. Dashed lines refer to sets of maximal conjugate subgroups. The group orders are given on the left. Full Hermann–Mauguin symbols are used.
Factor group

product of sets: \[ G = \{ e, g_2, \ldots, g_p \} \]

\[ K_j \cap K_k = \{ g_{jp} g_{kq} = g_r \mid g_{jp} \in K_j, g_{kq} \in K_k \} \]

Each element \( g_r \) is taken only once in the product \( K_j \cap K_k \).

factor group \( G/H \):

\[ H \triangleleft G \]

\[ G = H + g_2 H + \ldots + g_m H, \quad g_i \not\in H, \]

\[ G/H = \{ H, g_2 H, \ldots, g_m H \} \]

group axioms:

(i) \( (g_i H)(g_j H) = g_{ij} H \)

(ii) \( (g_i H) H = H(g_i H) = g_i H \)

(iii) \( (g_i H)^{-1} = (g_i^{-1}) H \)
Consider the normal subgroup \( \{e,2\} \) of \( 4mm \), of index 4, and the coset decomposition \( 4mm: \{e,2\} \):

(3) Show that the cosets of the decomposition \( 4mm: \{e,2\} \) fulfil the group axioms and form a factor group

(4) Multiplication table of the factor group

(5) A crystallographic point group isomorphic to the factor group?
Let $G_1$ and $G_2$ are two groups. The set of all pairs $\{(g_1,g_2), \, g_1 \in G_1, \, g_2 \in G_2\}$ forms a group $G_1 \times G_2$ with respect to the product: $(g_1,g_2) \cdot (g'_1,g'_2) = (g_1g'_1, \, g_2g'_2)$.

The group $G = G_1 \times G_2$ is called a **direct-product** group.

Properties of $G_1 \times G_2$

(i) $G_1 \times G_2 \supset \{(g_1,e_2), \, g_1 \in G_1\} \cong G_1$

(ii) $\{(g_1,e_2), \, g_1 \in G_1\} \cap \{(e_1,g_2), \, g_2 \in G_2\} = \{(e_1,e_2)\}$

(iii) $\forall (g_1,g_2) \in G_1 \times G_2: \, (g_1,g_2) = (g_1,e_2) \cdot (e_1,g_2)$
GENERAL AND SPECIAL WYCKOFF POSITIONS
General and special Wyckoff positions

Site-symmetry group $S_0 = \{W\}$ of a point $X_0$

$WX_0 = X_0$

\[
\begin{array}{ccc|ccc}
  a & b & c & x & x \\
  d & e & f & y & y \\
  g & h & i & z & z \\
\end{array}
\]

General position $X_0$

$S = 1 = \{1\}$

Special position $X_0$

$S > 1 = \{1, \ldots, \}$

Site-symmetry groups: oriented symbols
General and special Wyckoff positions

Point group \( \mathbf{2} = \{1, 2z\} \)

Site-symmetry group \( S_\circ = \{W\} \) of a point \( X_\circ = (0,0,z) \)

\[ S_\circ = \mathbf{2} \]

\[ WX_\circ = X_\circ \]

Example

\[
\begin{array}{ccc}
2 & b & 1 \\
1 & a & 2 \\
\end{array}
\]

\[
\begin{array}{ccc}
(x,y,z) & (-x,-y,z) & (0,0,z) \\
\end{array}
\]
General and special Wyckoff positions

Point group $\text{mm2} = \{1, 2z, m_x, m_y\}$

Site-symmetry group $S_0 = \{W\}$ of a point $X_0 = (0,0,0)$

$S_0 = \text{mm2}$

$WX_0 = X_0$

Example:

- $2z$: $\begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}$
  $\begin{pmatrix} 0 \\ 0 \\ z \end{pmatrix}$

- $m_y$: $\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}$
  $\begin{pmatrix} 0 \\ 0 \\ z \end{pmatrix}$

- $4d$: $1$ $\begin{pmatrix} x, y, z \end{pmatrix}$ $\begin{pmatrix} -x, -y, z \end{pmatrix}$ $\begin{pmatrix} x, -y, z \end{pmatrix}$ $\begin{pmatrix} -x, y, z \end{pmatrix}$

- $2c$: $\begin{pmatrix} 0, y, z \end{pmatrix}$ $\begin{pmatrix} 0, -y, z \end{pmatrix}$

- $2b$: $\begin{pmatrix} x, 0, z \end{pmatrix}$ $\begin{pmatrix} -x, 0, z \end{pmatrix}$

- $1a$: $\text{mm2}$. $\begin{pmatrix} 0, 0, z \end{pmatrix}$
Consider the symmetry group of the square \textit{4mm} and the point group \textit{422} that is isomorphic to it.

Determine the general and special Wyckoff positions of the two groups.

\textit{Hint}: The stereographic projections could be rather helpful.
Group-subgroup pair $mm2 > 2, [i]=2$

Wyckoff positions splitting schemes:

$4 \ d \ 1$

$(x, y, z)$
$(-x, -y, z)$
$(x, -y, z)$
$(-x, y, z)$

$x, y, z = x_1, y_1, z_1$
$-x, -y, z = -x_1, -y_1, z_1$

$x, -y, z = x_2, y_2, z_2$
$-x, y, z = -x_2, -y_2, z_2$
Consider the general and special Wyckoff positions of the symmetry group of the square 4mm and those of its subgroup mm2 of index 2.

Determine the splitting schemes of the general and special Wyckoff positions for 4mm > mm2.

*Hint:* The stereographic projections could be rather helpful.