UNIVERSITÉ DE LORRAINE

CRM² Cristallographie, Résonance Magnétique et Modélisations

cnrs

Institut Jean Barriol

Modular structures, partial operations and groupoids

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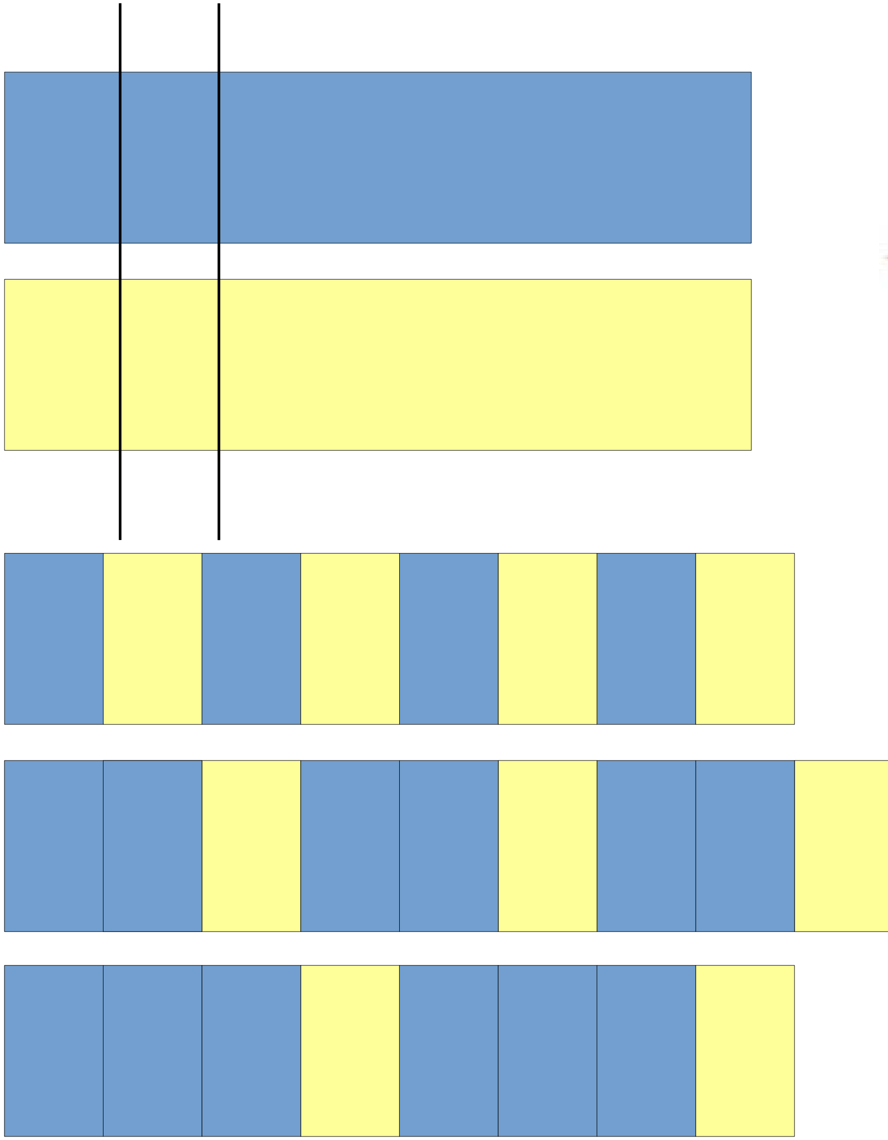
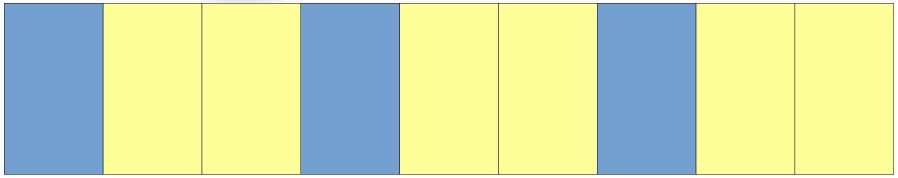
The basic idea of modular structures



Polyarchetypal modular structures

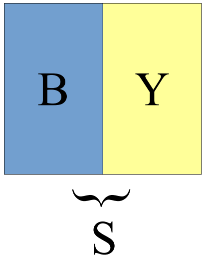


etc ...

Series of structures

Polysomatic series (πολύς + σῶμα)

Homologous series



Classifications of modular structures

Monoarchetypal vs. polyarchetypal modular structures: the modules are obtained from one or more (real or fictitious) archetype.

Periodicity of the building modules:

- 0-periodic: bricks or blocks
- 1-periodic: chains or rods
- 2-periodic: sheets or layers

In the following, modules are called **substructures** and the modular structures **superstructures**.

Periodic and subperiodic groups

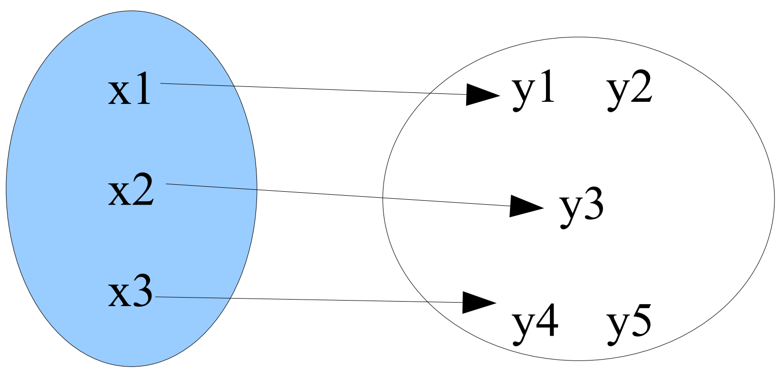
G^n_m n-dimensional space, m-dimensional periodicity

m = 0: **point groups**; n = m: **space groups**; 0 < m < n: **subperiodic groups**

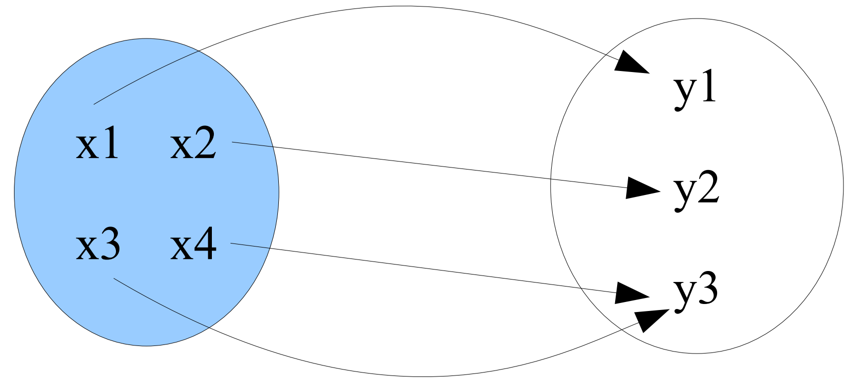
n	m	No. of types of groups	Name
1	0	2	1-dimensional **point groups**
	1	2	Line groups : **1-dimensional space groups**
2	0	10	2-dimensional **point groups**
	1	7	**Frieze groups**
	2	17	Plane groups, wallpaper groups: **2-dimensional space groups**
3	0	32	3-dimensional **point-groups**
	1	75	**Rod groups**
	2	80	**Layer groups**
	3	230	(3-dimensional) **Space groups**

Total functions

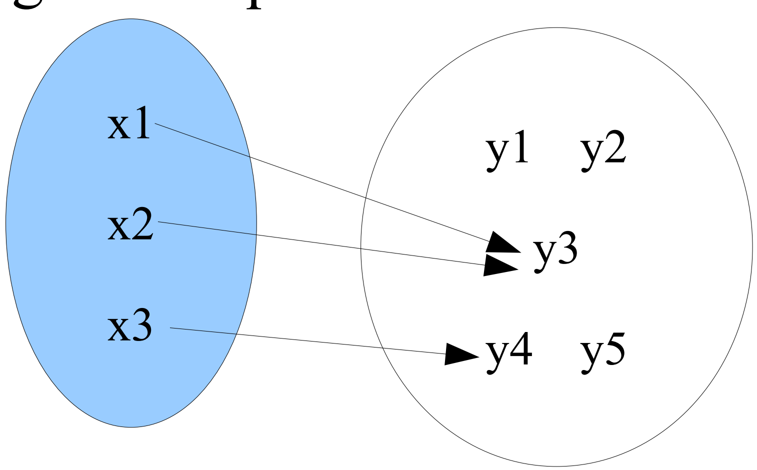
A total function *f* from X to Y (X → Y) is a mapping from each element X to some or all element of Y



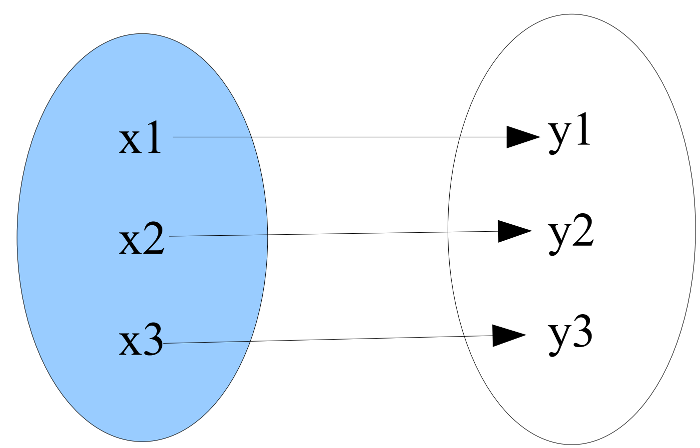
Injection: not all elements y of Y are the image of *f*, but if they are, then the full preimage is unique



Surjection: all elements y of Y are images of *f*, but the full preimage of each y is not necessarily unique.



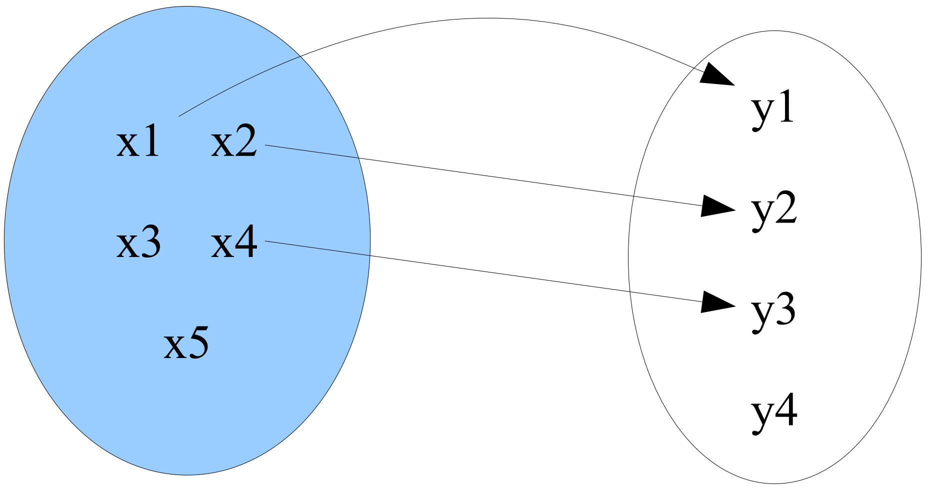
Neither injection nor surjection



Bijection: both injection and surjection

Partial functions

A **partial** function *f* from X to Y (X ⇸ Y) is a mapping from some but (not all) element x of X to some or all elements y of Y



Reminder: conjugation

When we apply an isometry ton an object O, the position/orientation of the object is changed ($O \rightarrow O'$)

$gO = O', g \notin H,H'$ $hO = O, h \in H$ $h'O' = O', h' \in H'$

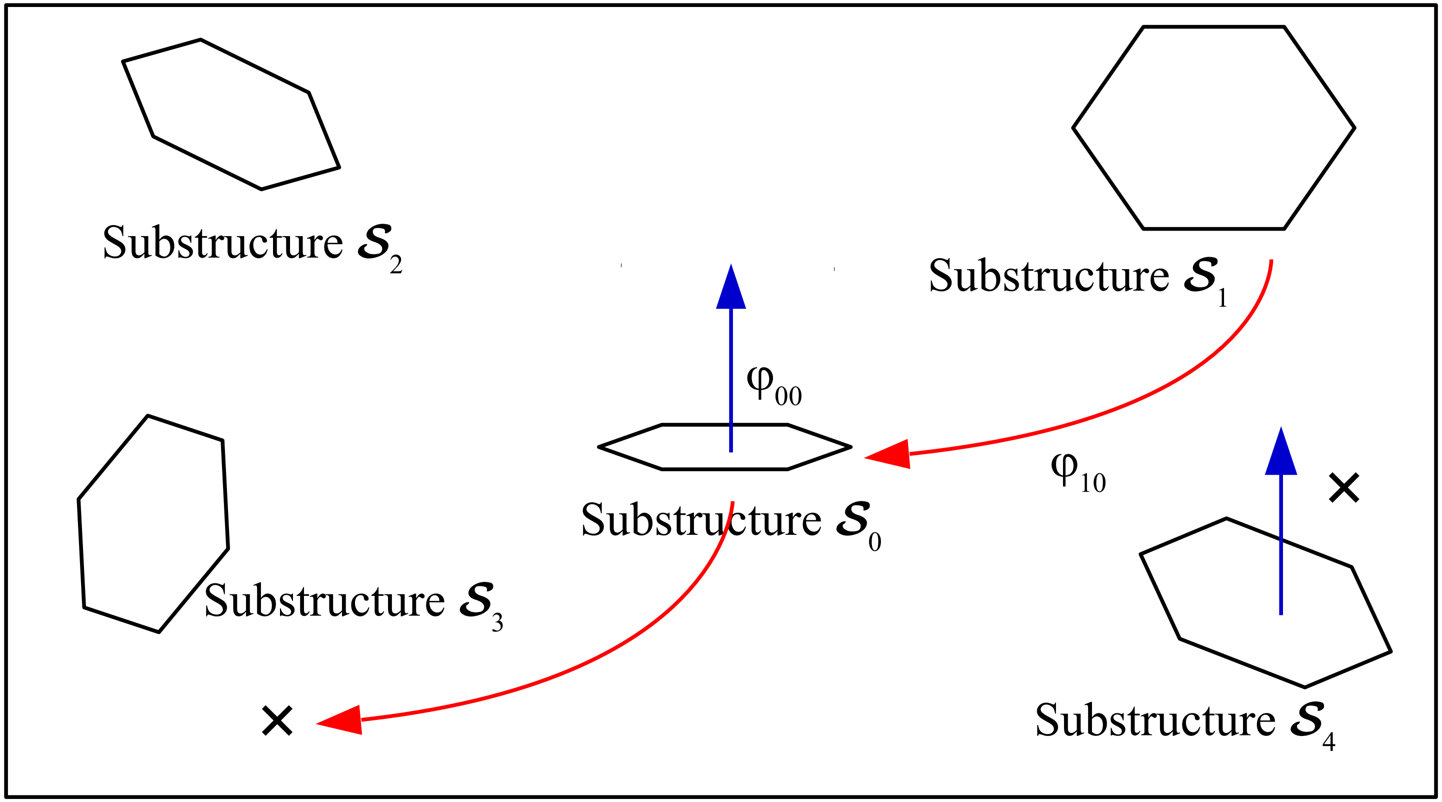
$$h'O' = O' = gO = g(hO) = ghO = gh(g^{-1}O') = ghg^{-1}O'$$

$$h' = ghg^{-1}$$

$$H' = gHg^{-1}$$

The symmetry group of the object is transformed by conjugation

Partial functions in crystallography



Superstructure

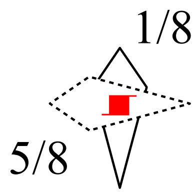
φ_{pq} partial operations: relate only a specific pair of substructures

φ_{pp} local operations: special case of partial operations, which act only on a specific substructure

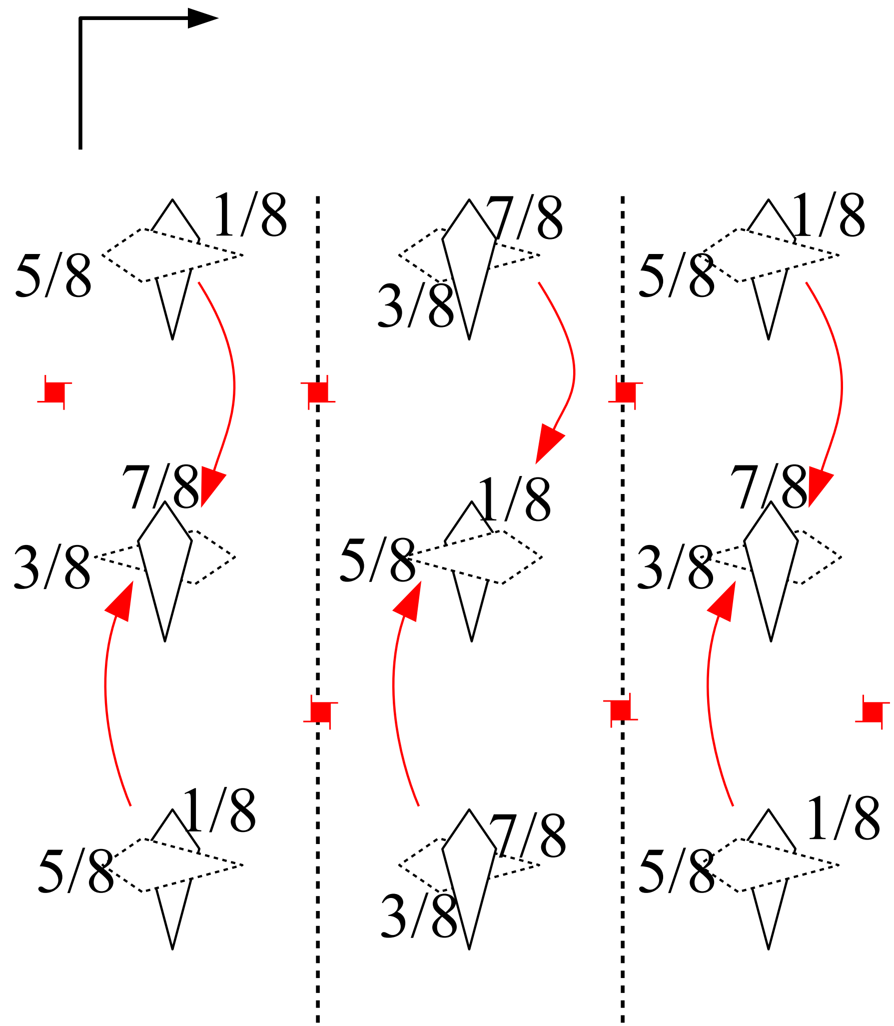
Global (total) operations : that subset of local and partial operations that actually act on the whole structure

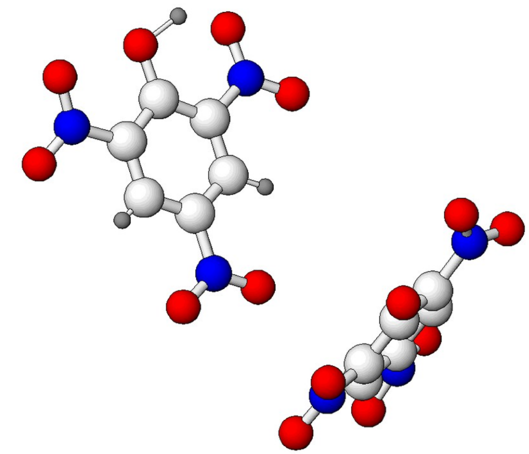
https://doi.org/10.2465/gkk1952.14.Special2_215https://doi.org/10.2465/gkk1952.14.Special2_215

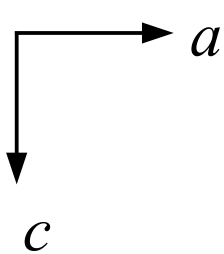
Examples of of partial operations



The substructure contains partial operations

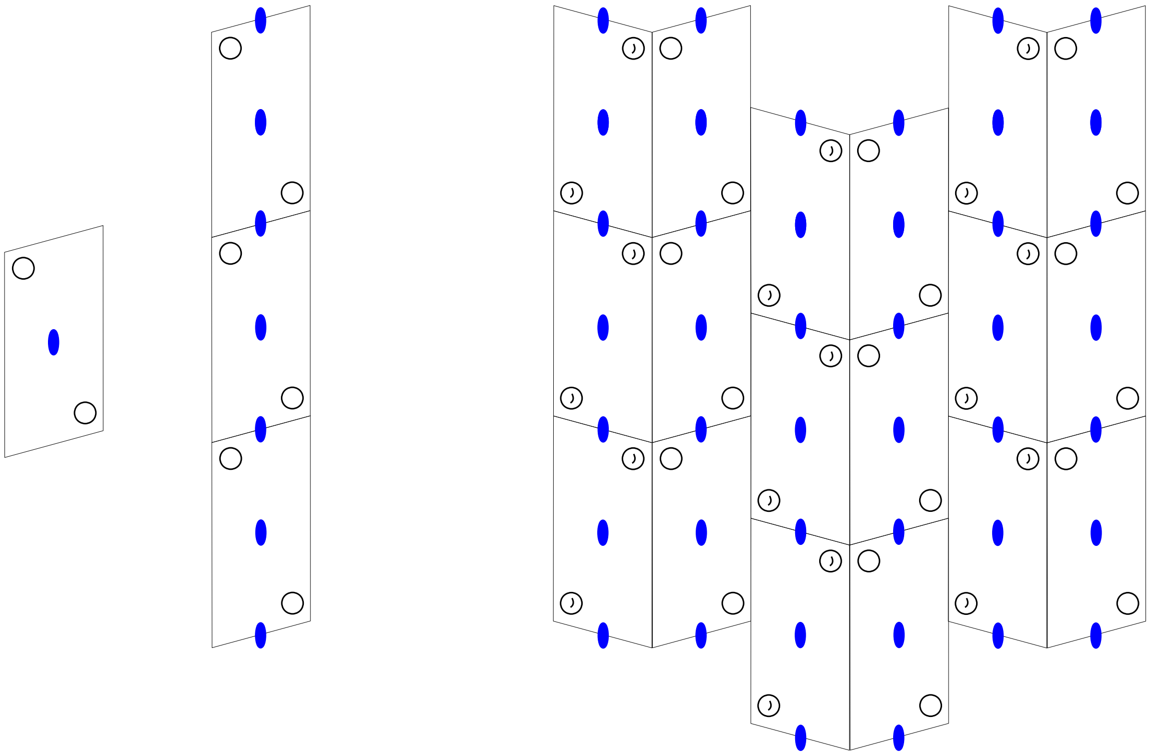






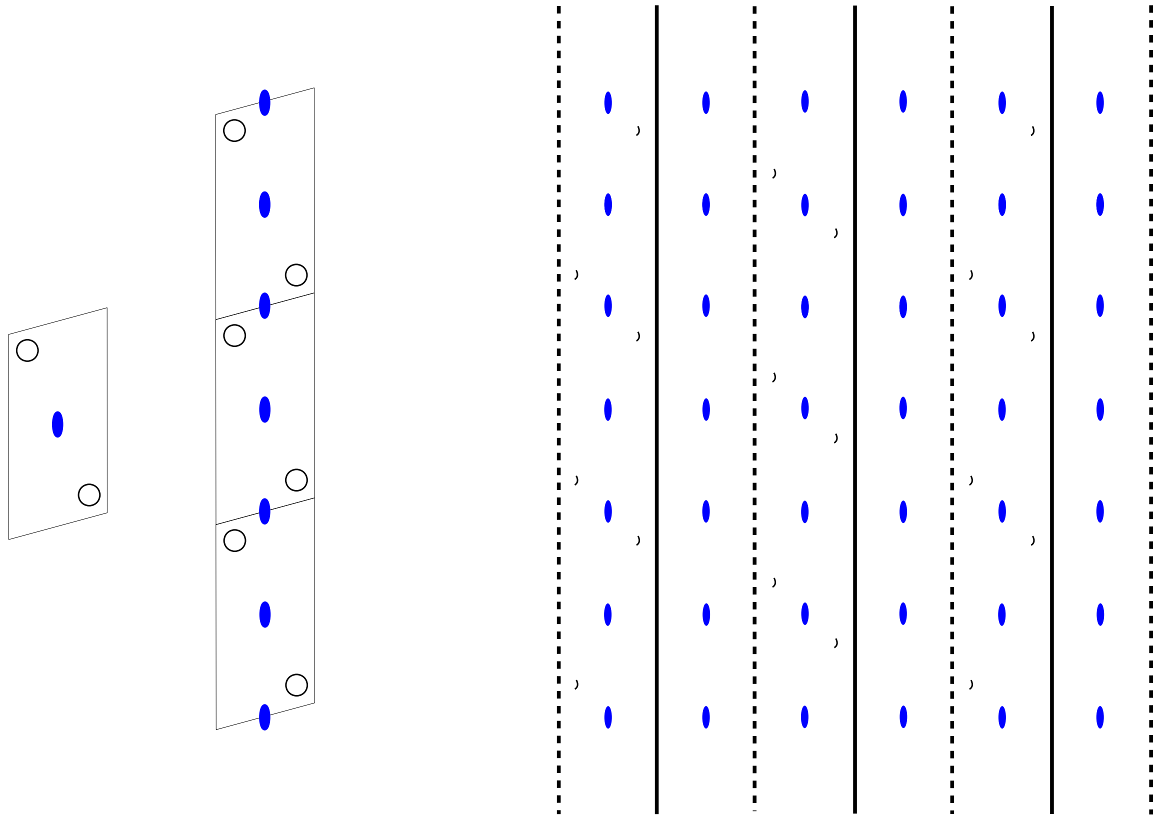
The space group of the structure is of type $Pca2_1$ and does not show the partial operations.

Examples of of partial operations

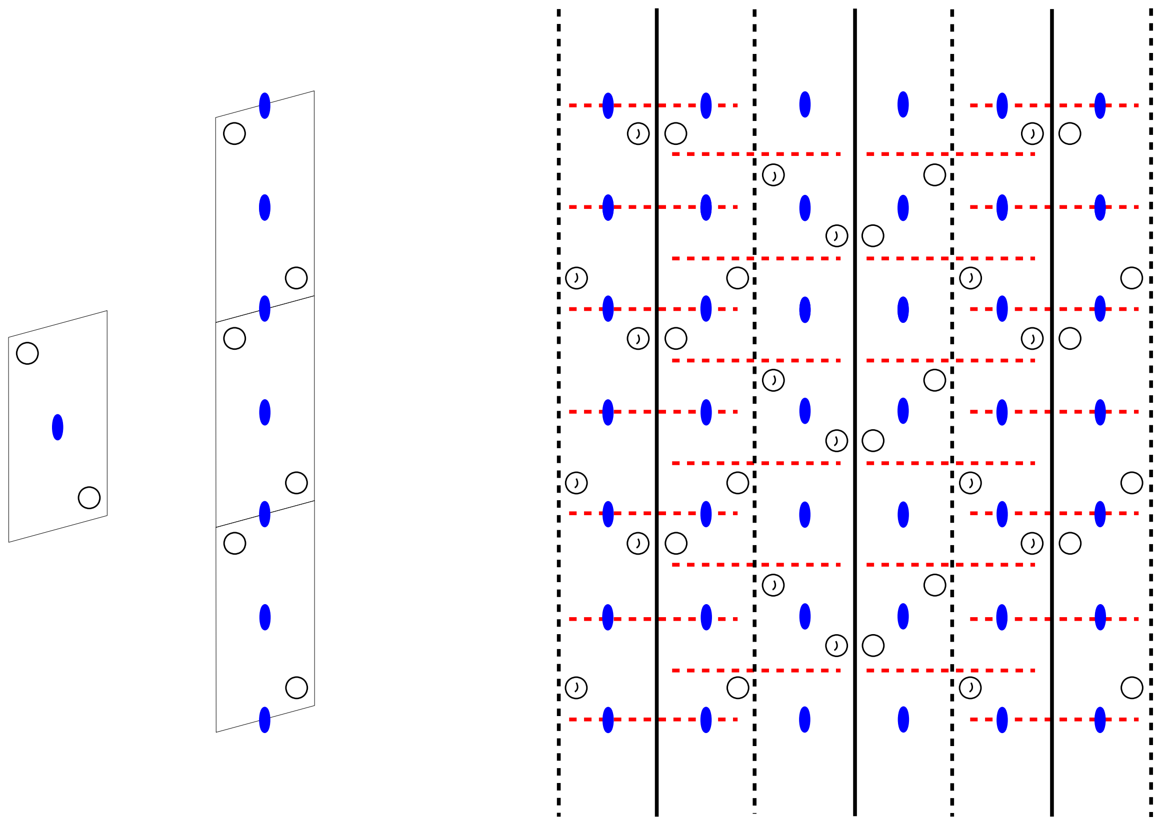


The substructure contains local operations

Examples of of partial operations

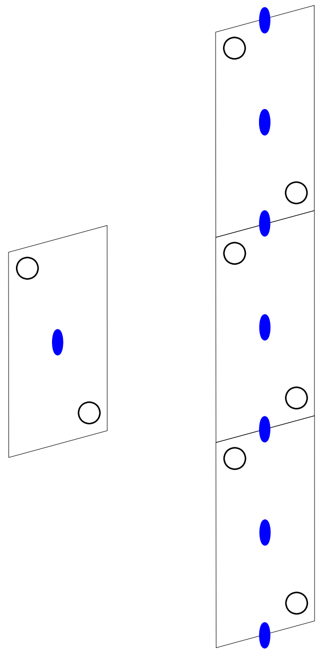


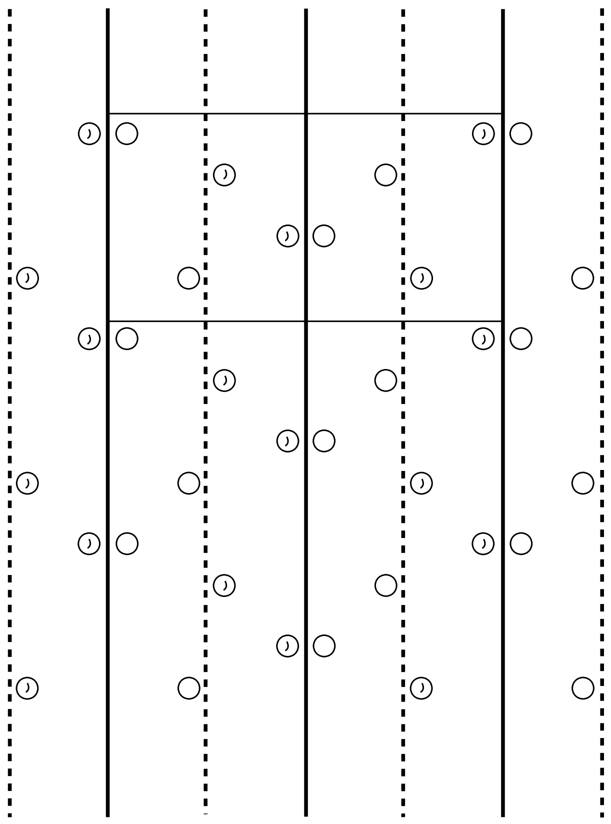
Examples of of partial operations



The combination of local operations of the substructure with global operations of the superstructure generates partial operations.

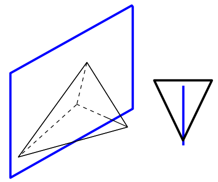
Examples of of partial operations



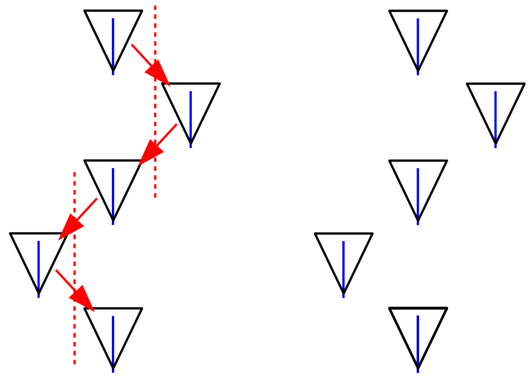


If one looks at global operations only,
the conclusion is *cm* with Z' = 2

OD structures



The substructure contains local operations



The ***structure-building operations*** are **partial**.

The OD ("Order-Disorder") theory has been developed to deal with layer structures, although some attempt to generalize it to rod structures have been later introduced.

The nucleus of a substructure

A partial operation φ_{qp} (σ-PO in the OD language) maps $\mathcal{S}_p$ to $\mathcal{S}_q$: $\varphi_{qp}\mathcal{S}_p = \mathcal{S}_q$.

The special case q = p corresponds to a local operation (λ-PO in the OD language): $\varphi_{pp}\mathcal{S}_p = \mathcal{S}_p$.

The set $\Phi_{pp} = \{\varphi_{pp}\}$ of local operations forms the group of symmetry operations of the p-th substructure $\mathcal{S}_p$ and is by definition a subperiodic group:

- point group (limiting case of subperiodic group) if $\mathcal{S}_p$ is a brick or block;
- rod group if $\mathcal{S}_p$ is a rod or chain;
- layer group if $\mathcal{S}_p$ is a sheet or layer.

We call it the **nucleus** of $\mathcal{S}_p$ and indicate it as N_p.

Composition of partial operations

The set of partial operations $\Phi_{qp} = \{\varphi_{qp}\}$ contains all the operations mapping $\mathcal{S}_p \nrightarrow \mathcal{S}_q$ and does not form a group.

We take p = 0 as the reference structure (fixed target) and consider the set $M_0 \cup_p \Phi_{0p} = \cup_p \{\varphi_{0p}\}$ of all the operations mapping any source $\mathcal{S}_p$ to the target $\mathcal{S}_0$. M_0 is called the mixed group of $\mathcal{S}_0$. Although it is not a group, we can decompose it in right cosets with respect to N_0 exactly as we would to for groups.

$$M_0 = \cup_p N_0\varphi_{0p} = N_0 \cup N_0\varphi_{01} \cup N_0\varphi_{02} \cup N_0\varphi_{03} \cdots$$

φ_{0p} is one coset representative of $\Phi_{0p} = \{\varphi_{0p}\}$. In particular, we can take $\varphi_{00} = 1$ (identity).

Composition of partial operations

The composition of two local operations of the same substructure is still a local operation of that substructure

$$\varphi_{pp}\varphi'_{pp} = \varphi''_{pp}$$

The composition of a partial and a local operation in either order is another partial operation with the same source and target

$$\varphi_{00}\varphi_{0p} = \varphi'_{0p} \qquad \varphi_{0p}\varphi_{pp} = \varphi''_{0p}$$

The composition of two partial operations is possible if the target of the first operation and the source of the second coincide; the result is a partial or local operation depending on the source of the first and target of the second

$$\varphi_{q0}\varphi_{0p} = \varphi_{qp} \qquad \varphi_{p0}\varphi_{0p} = \varphi_{pp} \qquad \varphi_{rq}\varphi_{0p} = \text{undefined}$$

The inverse of a partial or local operation is defined and belongs to the same set as the direct operation

$$\varphi_{qp}^{-1} = \varphi_{pq};\ \ \varphi_{qp}, \varphi_{pq} \in \Phi_{qp}$$

The composition of local operations of two different substructures is undefined

$$\varphi_{qq}\varphi_{pp} = \text{undefined}$$

Conjugating N_0 with partial operations

$\varphi_{0q}^{-1}N_0\varphi_{0q}$ is the conjugation of the nucleus N_0 (symmetry group of $\mathcal{S}_0$) by a partial operation φ_{0q}. It represents the nucleus N_q of $\mathcal{S}_q$, $q \neq 0$, isomorphic to N_0.

$$N_q = \varphi_{0q}^{-1}N_0\varphi_{0q} \rightarrow N_0 = \varphi_{0q}N_q\varphi_{0q}^{-1}$$

$\varphi_{0q}^{-1}N_0\varphi_{0p}$ is a composite operation mapping $\mathcal{S}_p$ to $\mathcal{S}_q$ via $\mathcal{S}_0$.

$$\varphi_{0q}^{-1}M_0 = \varphi_{0q}^{-1}\cup_p N_0\varphi_{0p} = \varphi_{0q}^{-1}\cup_p[\varphi_{0q}N_q\varphi_{0q}^{-1}]\varphi_{0p} = \cup_p\varphi_{0q}^{-1}\varphi_{0q}N_q\varphi_{q0}\varphi_{0p} = \cup_p N_q\varphi_{qp} = M_q$$

$\varphi_{0q}^{-1}M_0 = M_q$ is the mixed group of the substructure $\mathcal{S}_q$, i.e. the set of all the partial operations having $\mathcal{S}_q$ as target (including the special case when $\mathcal{S}_q$ is also the source, i.e. the local operations of $\mathcal{S}_q$).

From mixed group to groupoid

Definition

$$D = \cup_q \varphi_{0q}{}^{-1} M_0 = \cup_{q,p} \varphi_{0q}{}^{-1} N_0 \varphi_{0p}$$

is the (Brandt's) **space groupoid** fully describing the structure built by substructures of the same kind.

The number of substructures building the superstructure is infinite (as usual, the surface of the crystal is treated as a defect).

The number of substructures not related by full-period translations is however finite. In the following, this number is indicated as n+1 so that the running indices (p, q…) go from 0 to n.

Decomposition of the groupoid D in terms of N_0

$$
\begin{array}{r|llllll}
M_0 & N_0 \cup & N_0\varphi_{01} \cup & \ldots\ldots\cup & N_0\varphi_{0p} \cup & \ldots\ldots\cup & N_0\varphi_{0n} \cup \\
M_1 = \varphi_{01}{}^{-1}M_0 & \varphi_{01}{}^{-1}N_0 \cup & \varphi_{01}{}^{-1}N_0\varphi_{01} \cup & \ldots\ldots\cup & \varphi_{01}{}^{-1}N_0\varphi_{0p} \cup & \ldots\ldots\cup & \varphi_{01}{}^{-1}N_0\varphi_{0n} \cup \\
 & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\
M_p = \varphi_{0p}{}^{-1}M_0 & \varphi_{0p}{}^{-1}N_0 \cup & \varphi_{0p}{}^{-1}N_0\varphi_{01} \cup & \ldots\ldots\cup & \varphi_{0p}{}^{-1}N_0\varphi_{0p} \cup & \ldots\ldots\cup & \varphi_{0p}{}^{-1}N_0\varphi_{0n} \cup \\
 & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\
M_n = \varphi_{0n}{}^{-1}M_0 & \varphi_{0n}{}^{-1}N_0 \cup & \varphi_{0n}{}^{-1}N_0\varphi_{01} \cup & \ldots\ldots\cup & \varphi_{0n}{}^{-1}N_0\varphi_{0p} \cup & \ldots\ldots\cup & \varphi_{0n}{}^{-1}N_0\varphi_{0n}
\end{array}
$$

Diagonal terms $\varphi_{0p}{}^{-1}N_0\varphi_{0p}$ map $\mathcal{S}_p$ and are **local** operations.

$$\varphi_{0p}{}^{-1}N_0\varphi_{0p} = N_p \text{ isomorphic to } N_0$$

Extra-diagonal terms $\varphi_{0q}{}^{-1}N_0\varphi_{0p}$ map $\mathcal{S}_q$ to $\mathcal{S}_p$ and are **partial** operations.

Decomposition of the groupoid D in terms of N_0

$N_0 \cup$	$N_0\varphi_{01} \cup$	$\ldots\cup$	$N_0\varphi_{0p} \cup$	$\ldots\cup$	$N_0\varphi_{0n} \cup$
$\varphi_{01}^{-1}N_0 \cup$	$N_1 \cup$	$\ldots\cup$	$\varphi_{01}^{-1}N_0\varphi_{0p} \cup$	$\ldots\cup$	$\varphi_{01}^{-1}N_0\varphi_{0n} \cup$
....	....	....	....	....	....
$\varphi_{0p}^{-1}N_0 \cup$	$\varphi_{0p}^{-1}N_0\varphi_{01} \cup$	$\ldots\cup$	$N_p \cup$	$\ldots\cup$	$\varphi_{0p}^{-1}N_0\varphi_{0n} \cup$
....	....	....	....	....	....
$\varphi_{0n}^{-1}N_0 \cup$	$\varphi_{0n}^{-1}N_0\varphi_{01} \cup$	$\ldots\cup$	$\varphi_{0n}^{-1}N_0\varphi_{0p} \cup$	$\ldots\cup$	N_n

Local and **partial** operations that occur in *each and every* mixed group act on the whole crystal space become **global** operations and form the **space group** of the structure.

The expression of the groupoid above contains only operation obtained by applying to N_0 partial operations acting on substructures assigned to a single unit cell. The result $\varphi_{0p}^{-1}N_0\varphi_{0q}$ may well act on substructures outside the unit cell → the global nature has to be evaluated modulo full translations.

Application to the investigation of the symmetry of twinned crystals

https://doi.org/10.1107/S2053273319000664

Definition

A twinned crystal (twin) is a heterogeneous crystalline edifice composed by two or more homogeneous individuals / domain states of the same chemical composition and crystal structure, differing in their orientation.

A twin can be seen as the extreme case of modular structure, in which the whole individual / domain state is itself a module.

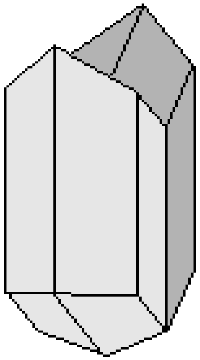
The number of individuals / domain states is finite.

The "local operations" become the symmetry operation of the point group of the individual / domain state.

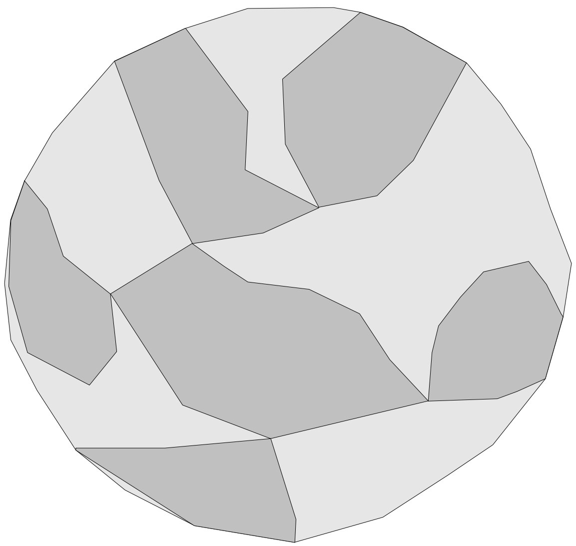
The "partial operations" become the operations mapping different individuals / domain states in the twin.

The groupoid describing the whole symmetry of the twin is a **point groupoid**.

Basic definitions



Two individuals



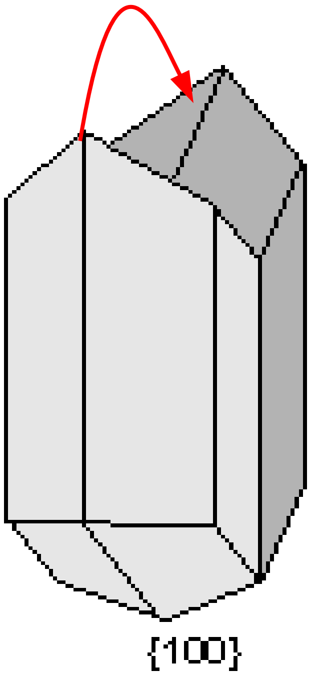
Two orientation domains (domain states, variants) with N domains

Twin operation, twin element, twin law

- **Twin operation**: the isometry mapping the orientation of one individual onto the orientation of another individual.
- **Twin element**: the geometrical element in *direct space* (plane, axis, centre) about which the twin operation is performed.
  - Correspondingly, twins are classified as reflection twins, rotation twins and inversion twins
- **Twin law**: the set of twin operations equivalent under the point group of the individual, obtained by coset decomposition.

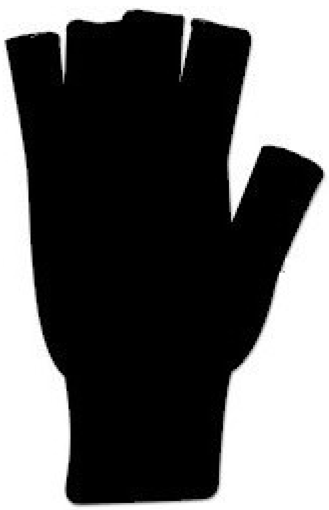
Operations mapping individuals as chromatic operations

The difference of orientation can be seen as a difference of colour if assigns a different colour to each individual / domain state. The operation mapping different individuals / domain states can then be seen as an operation that changes the colour (chromatic operation) and the orientation.

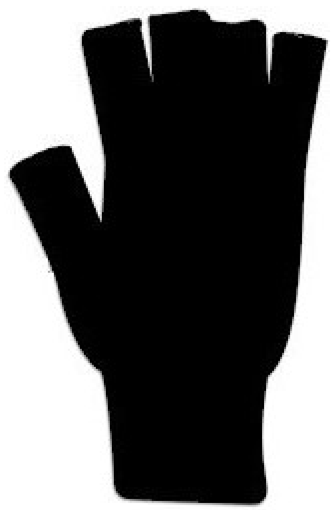


Dichromatic operations

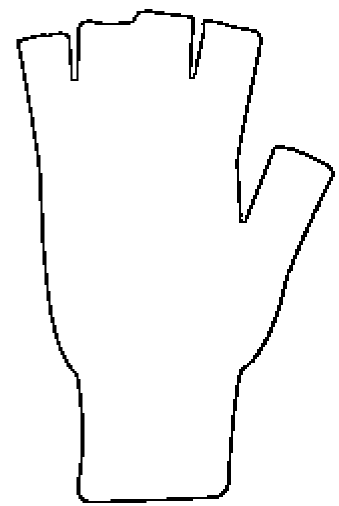
Identity



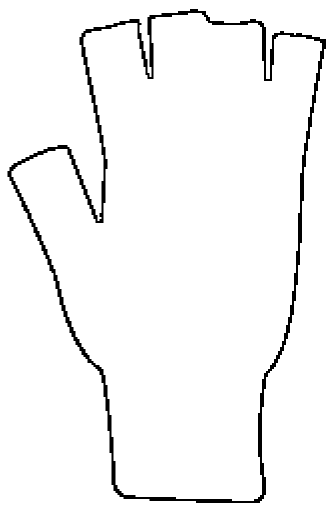
Reflection



Anti-identity



Anti-reflection



Chromaticity and neutral groups

A polychromatic group is indicated as $\mathcal{K}^{(p)}$

p shows the chromaticity (number of colours)

Let $\mathcal{H}$ be an achromatic subgroup of $\mathcal{K}^{(p)}$

$1^{(p)} = \{1, 1', 1'' \ldots, 1^{p}\}$ is the colour identification group: it permutes the p colours

The direct product $\mathcal{H}\, 1^{(p)}$ results in 320 neutral point groups

$(\mathcal{H}, 1^{(1)}) = \mathcal{H} \times \{1\}$:
32 achromatic (monochromatic) groups

$(\mathcal{H}, 1^{(2)}) = \mathcal{H} \times \{1, 1'\}$:
32 neutral dichromatic ("grey") groups

$(\mathcal{H}, 1^{(p>2)}) = \mathcal{H} \times \{1, 1', 1'' \ldots\}$:
256 polychromatic neutral groups

Classification of polychromatic point groups

- Dichromatic invariant extensions of point groups: dichromatic (Shubnikov) groups $\mathcal{K}^{(2)} = \{\mathcal{H} \times n^{(p=2)}\} = \{\mathcal{H} \times n'\}$
- Polychromatic invariant extensions of point groups (Koptsik groups) $\mathcal{K}^{(p>2)}$
- Polychromatic non-invariant extensions of point groups (Van der Waerden-Burckhardt groups) $\mathcal{K}_{\mathcal{WB}}{}^{(p>2)}$

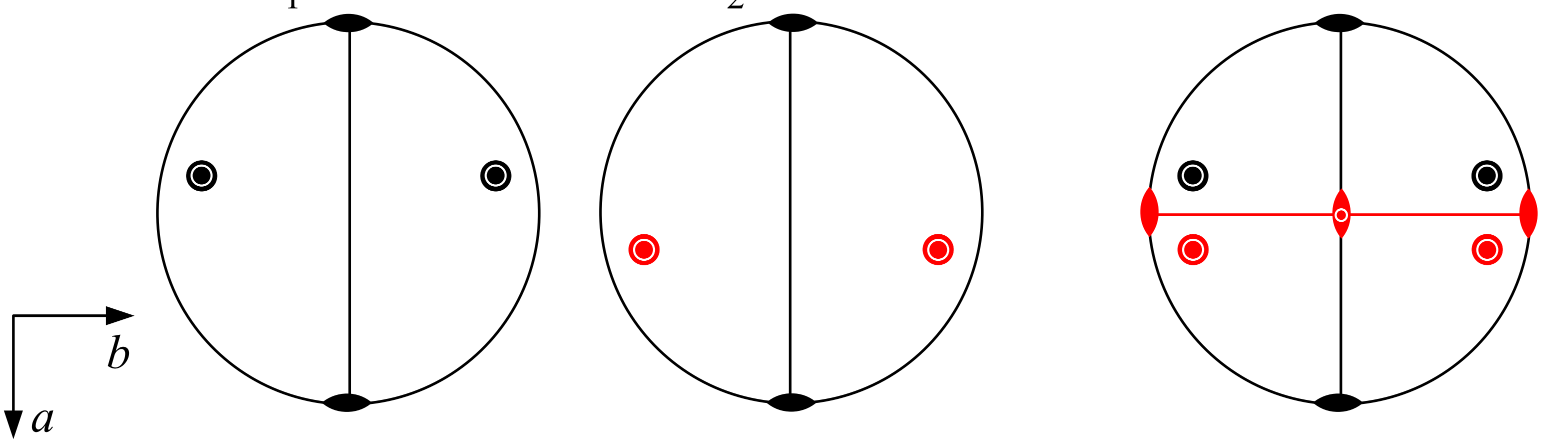
n = achromatic operation	Operation that fixes (leaves invariant) the colours
$n^{(p)}$ = chromatic operation	Operation that exchanges p colours (if the group contains only operations for which p = 2, p is replaced by ')
$n^{(p1,p2)}$ = partially chromatic operation	Operation that exchanges p_1 colours while fixing (leaving invariant) p_2 colours.

Example of Shubnikov groups

$\mathcal{H}_1 = 2mm$	$\{1, 2_{[100]}, m_{[010]}, m_{[001]}\}$	$\{1, 2_{[100]}, m_{[010]}, m_{[001]}\}\bar{1}$	Individual 2 → Individual 1
Individual 1 → Individual 2	$\bar{1}\{1, 2_{[100]}, m_{[010]}, m_{[001]}\}$	$\bar{1}\{1, 2_{[100]}, m_{[010]}, m_{[001]}\}\bar{1}$	$\mathcal{H}_2 = t^{-1}(2mm)t$

$\{1, 2_{[100]}, m_{[010]}, m_{[001]}\}$	$\{\bar{1}, m_{[100]}, 2_{[010]}, 2_{[001]}\}$
$\{\bar{1}, m_{[100]}, 2_{[010]}, 2_{[001]}\}$	$\{1, 2_{[100]}, m_{[010]}, m_{[001]}\}$

$t = \bar{1}$ $\quad \mathcal{H}_1 = 2mm$ $\quad \mathcal{H}_2 = 2mm$ $\quad \mathcal{K}^{(2)} = 2/m'\, 2'/m\, 2'/m$



Example of Koptsik groups: $\mathcal{H} = mm2$, $t_1 = \bar{1}$, $t_2 = 4_{[001]}$

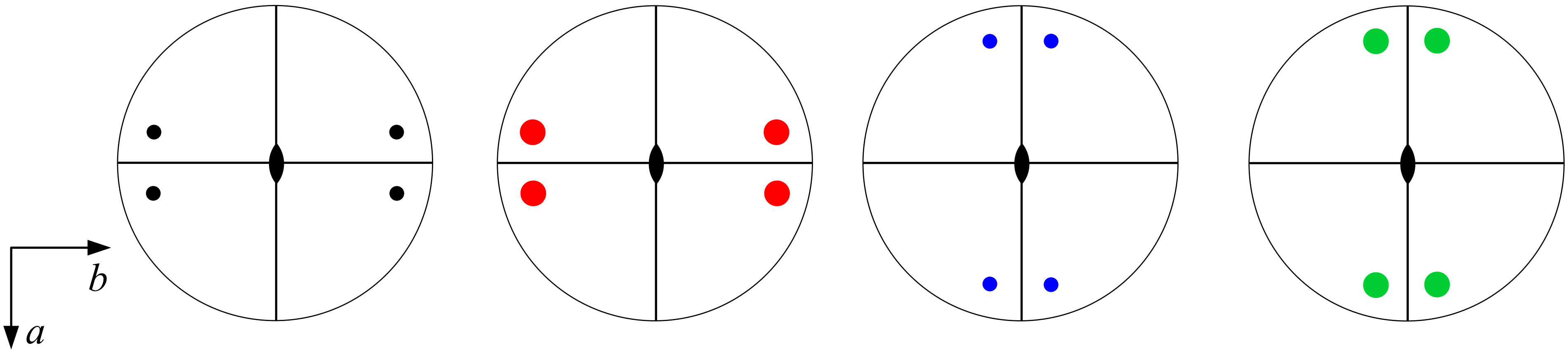
$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{1}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$
$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]]}\}\bar{1}$	$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$
$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{1}$	$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$
$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{1}$	$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$

$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$	$\{4_{[001]},m_{[1\bar{1}0]},m_{[110]},4^{-1}_{[001]}\}$	$\{\bar{4}_{[001]},2_{[1\bar{1}0]},2_{[110]},\bar{4}^{-1}_{[001]}\}$
$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{\bar{4}_{[001]},2_{[1\bar{1}0]},2_{[110]},\bar{4}^{-1}_{[001]}\}$	$\{4_{[001]},m_{[1\bar{1}0]},m_{[110]},4^{-1}_{[001]}\}$
$\{4^{-1}_{[001]},m_{[1\bar{1}0]},m_{[110]},4_{[001]}\}$	$\{\bar{4}^{-1}_{[001]},2_{[1\bar{1}0]},2_{[110]},\bar{4}_{[001]}\}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$
$\{\bar{4}^{-1}_{[001]},m_{[1\bar{1}0]},m_{[110]},\bar{4}_{[001]}\}$	$\{4^{-1}_{[001]},m_{[1\bar{1}0]},m_{[110]},4_{[001]}\}$	$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}$

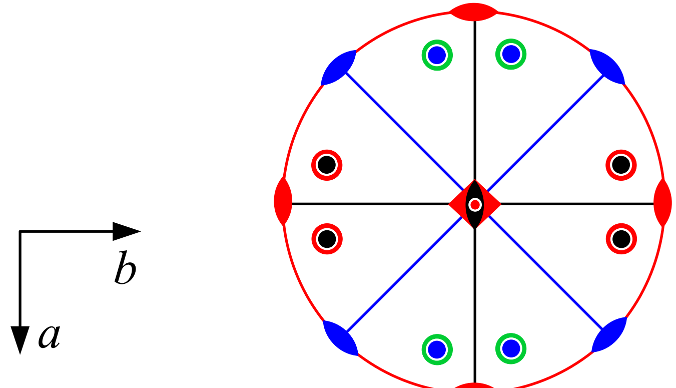
Four individuals, 12 twin operations divided into 3 twin laws

Example of Koptsik groups: $\mathcal{H} = mm2$, $t_1 = \bar{1}$, $t_2 = 4_{[001]}$

$\mathcal{H}_1 = mm2$ $\quad$ $\mathcal{H}_2 = mm2$ $\quad$ $\mathcal{H}_3 = mm2$ $\quad$ $\mathcal{H}_4 = mm2$



$$\mathcal{K}^{(4)} = (4^{(2)}/m^{(2)}\ 2^{(2)}/m\ 2^{(2)}/m^{(2)})^{(4)}$$



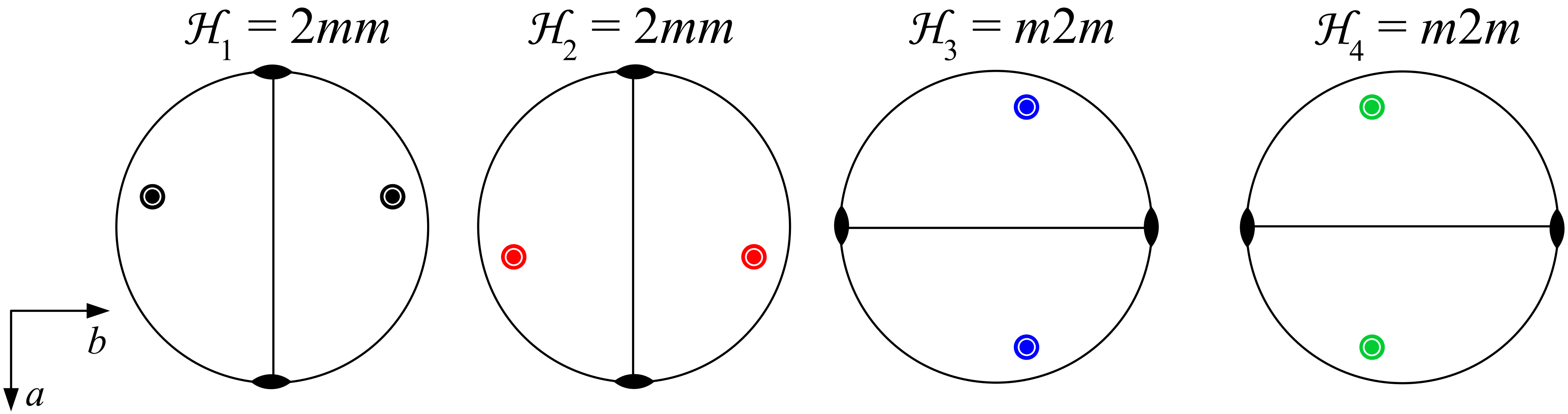
Example of Van der Waerden-Burckhardt groups: $\mathcal{H}$ = $2mm$, $t_1 = \bar{1}$, $t_2 = 4_{[001]}$

$\{1,2_{[100]},m_{[010]},m_{[001]}\}$	$\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{1}$	$\{1,2_{[100]},m_{[010]},m_{[001]}\}4_{[001]}$	$\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{4}_{[001]}$
$\bar{1}\{1,2_{[100]},m_{[010]},m_{[001]}\}$	$\bar{1}\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{1}$	$\bar{1}\{1,2_{[100]},m_{[010]},m_{[001]}\}4_{[001]}$	$\bar{1}\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{4}_{[001]}$
$4^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}$	$4^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{1}$	$4^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}4_{[001]}$	$4^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{4}_{[001]}$
$\bar{4}^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}$	$\bar{4}^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{1}$	$\bar{4}^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}4_{[001]}$	$\bar{4}^{-1}_{[001]}\{1,2_{[100]},m_{[010]},m_{[001]}\}\bar{4}_{[001]}$

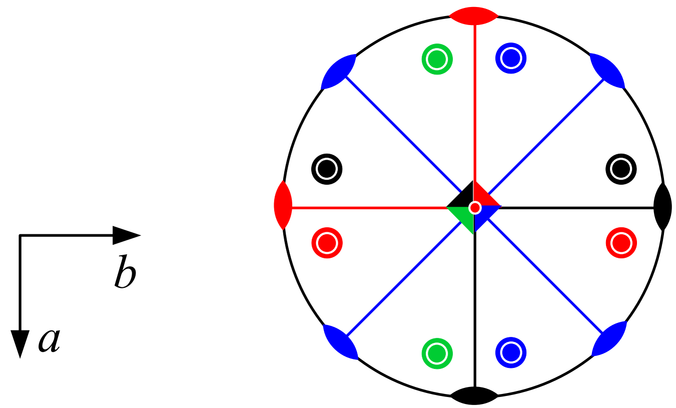
$\{1,2_{[100]},m_{[010]},m_{[001]}\}$	$\{\bar{1},m_{[100]},2_{[010]},2_{[001]}\}$	$\{4_{[001]},2_{[1\bar{1}0]},m_{[110]},\bar{4}^{-1}_{[001]}\}$	$\{\bar{4}_{[001]},m_{[1\bar{1}0]},2_{[110]},4^{-1}_{[001]}\}$
$\{\bar{1},m_{[100]},2_{[010]},2_{[001]}\}$	$\{1,2_{[100]},m_{[010]},m_{[001]}\}$	$\{\bar{4}_{[001]},m_{[1\bar{1}0]},2_{[110]},4^{-1}_{[001]}\}$	$\{4_{[001]},2_{[1\bar{1}0]},m_{[110]},\bar{4}^{-1}_{[001]}\}$
$\{4^{-1}_{[001]},2_{[1\bar{1}0]},m_{[110]},\bar{4}_{[001]}\}$	$\{\bar{4}^{-1}_{[001]},m_{[1\bar{1}0]},2_{[110]},4_{[001]}\}$	$\{1,2_{[010]},m_{[100]},m_{[001]}\}$	$\{\bar{1},m_{[100]},2_{[010]},2_{[001]}\}$
$\{\bar{4}^{-1}_{[001]},m_{[1\bar{1}0]},2_{[110]},4_{[001]}\}$	$\{4^{-1}_{[001]},2_{[1\bar{1}0]},m_{[110]},\bar{4}_{[001]}\}$	$\{\bar{1},m_{[100]},2_{[010]},2_{[001]}\}$	$\{1,2_{[010]},m_{[100]},m_{[001]}\}$

Four individuals, 12 twin operations divided into 3 twin laws

Example of Van der Waerden-Burckhardt groups: $\mathcal{H} = 2mm$, $t_1 = \bar{1}$, $t_2 = 4_{[001]}$



$$\mathcal{K}_{WB}{}^{(4)} = (4^{(4)}/m\ 2^{(2,2)}/m^{(2,2)}\ 2^{(2)}//m^{(2)})^{(4)}$$



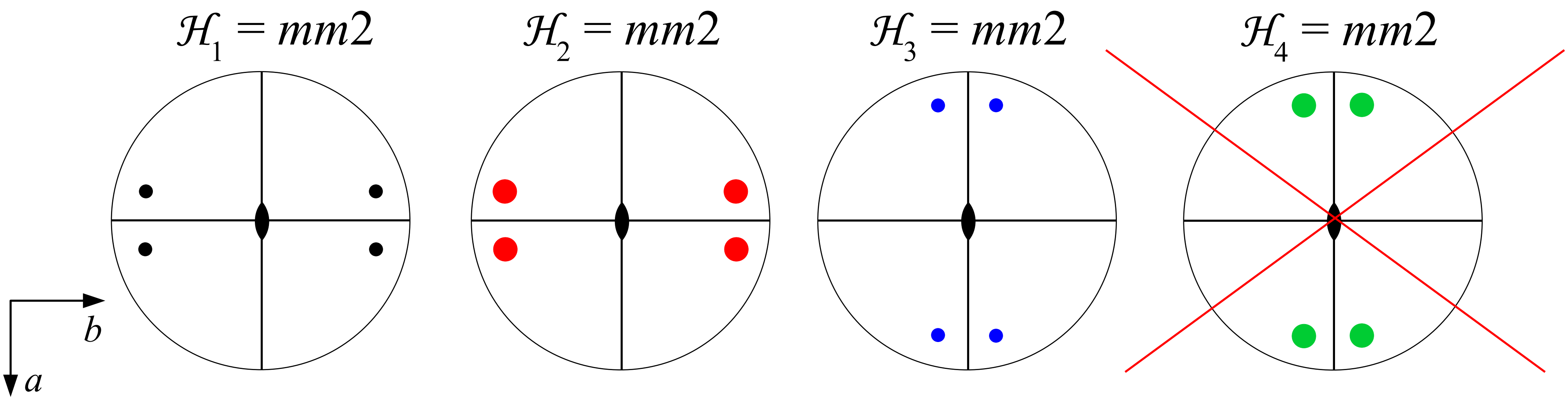
Incomplete twins

A twin in which as many individuals as the number of twin laws appear is called a **complete twin**.

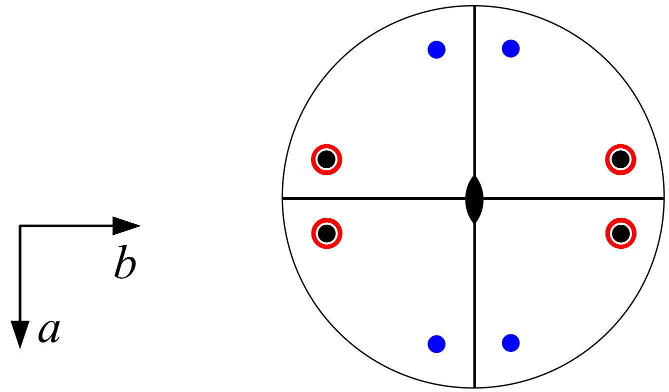
If one or more individuals are missing (not developed, broken off), the twin is twin **incomplete**.

To describe the symmetry an incomplete twin one needs the point groupoid.

Example of incomplete twin: $\mathcal{H} = mm2$, $t_1 = \bar{1}$, $t_2 = 4_{[001]}$



A group containing only total operations, this incomplete twin cannot be described by a chromatic group.



Example of incomplete twin: $\mathcal{H} = mm2$, $t_1 = \bar{1}$, $t_2 = 4_{[001]}$

$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{1}$	$\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	~~$\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$~~ **missing**
$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]]}\}\bar{1}$	$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	~~$\bar{1}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$~~ **missing**
$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{1}$	$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$	~~$4^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$~~ **missing**
~~$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}$~~ **missing**	~~$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{1}$~~ **missing**	~~$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}4_{[001]}$~~ **missing**	~~$\bar{4}^{-1}_{[001]}\{1,m_{[100]},m_{[010]},2_{[001]}\}\bar{4}_{[001]}$~~ **missing**

$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$ **partial**	$\{4_{[001]},m_{[1\bar{1}0]},m_{[110]},4^{-1}_{[001]}\}$ **partial**	~~$\{\bar{4}_{[001]},2_{[1\bar{1}0]},2_{[110]},\bar{4}^{-1}_{[001]}\}$~~ **missing**
$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$ **partial**	$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	$\{\bar{4}_{[001]},2_{[1\bar{1}0]},2_{[110]},\bar{4}^{-1}_{[001]}\}$ **partial**	~~$\{4_{[001]},m_{[1\bar{1}0]},m_{[110]},4^{-1}_{[001]}\}$~~ **missing**
$\{4^{-1}_{[001]},m_{[1\bar{1}0]},m_{[110]},4_{[001]}\}$ **partial**	$\{\bar{4}^{-1}_{[001]},2_{[1\bar{1}0]},2_{[110]},\bar{4}_{[001]}\}$ **partial**	$\{1,m_{[100]},m_{[010]},2_{[001]}\}$	~~$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$~~ **missing**
~~$\{\bar{4}^{-1}_{[001]},m_{[1\bar{1}0]},m_{[110]},\bar{4}_{[001]}\}$~~ **missing**	~~$\{4^{-1}_{[001]},m_{[1\bar{1}0]},m_{[110]},4_{[001]}\}$~~ **missing**	~~$\{\bar{1},2_{[100]},2_{[010]},m_{[001]}\}$~~ **missing**	~~$\{1,m_{[100]},m_{[010]},2_{[001]}\}$~~ **missing**

Application to the investigation of modular structures

From point to space groupoids

A crystallographic point group is a finite group. In a crystallographic point groupoid, the number of substructures is also finite.

A crystallographic point groupoid contains a finite number of partial operations. With respect to a suitable coordinate system, they are represented by square matrices.

A space group is an infinite group. In a space groupoid, the number of substructures is also infinite.

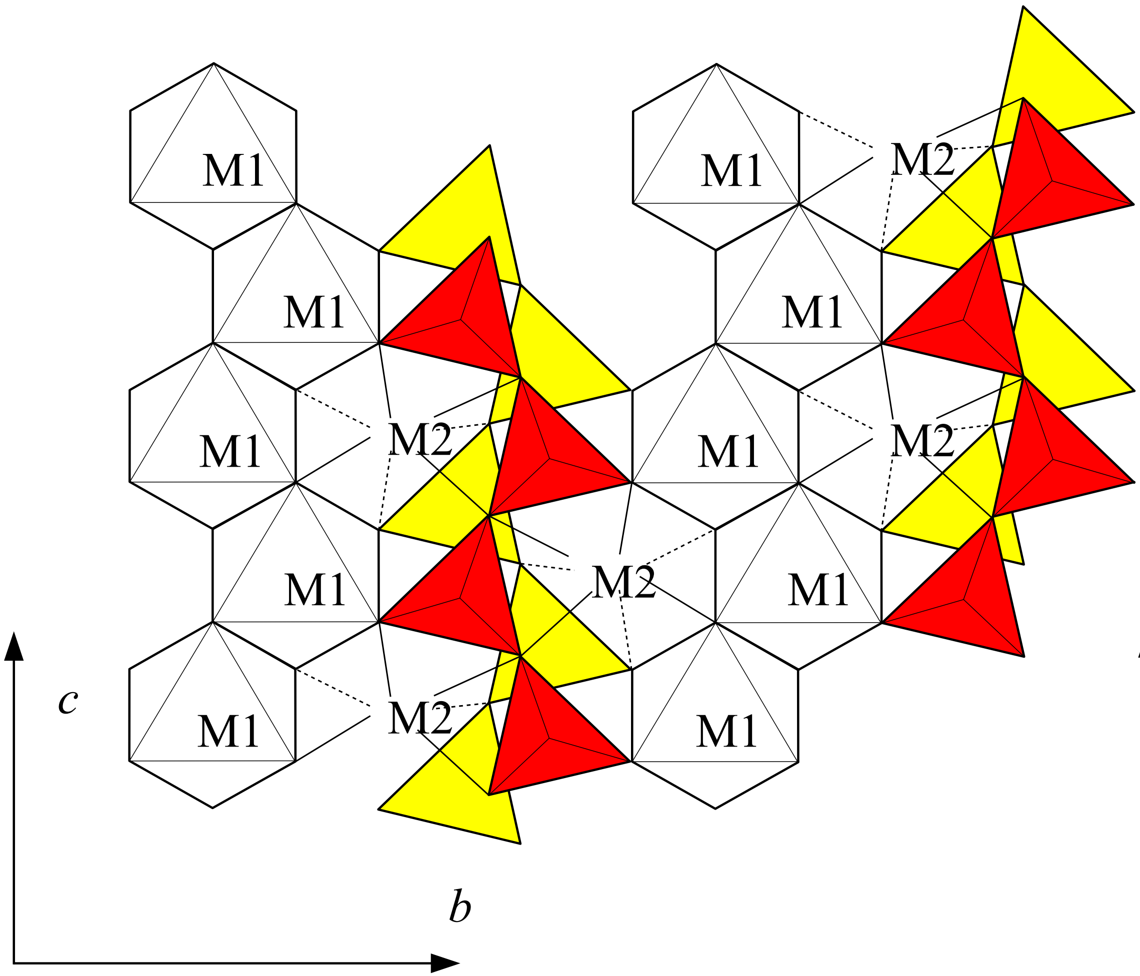
A space groupoid contains an infinite number of partial operations. With respect to a suitable coordinate system, they are represented by square matrices (linear part) and vectors (translation part). One can select as representatives those operations whose translation part is shorter than one period.

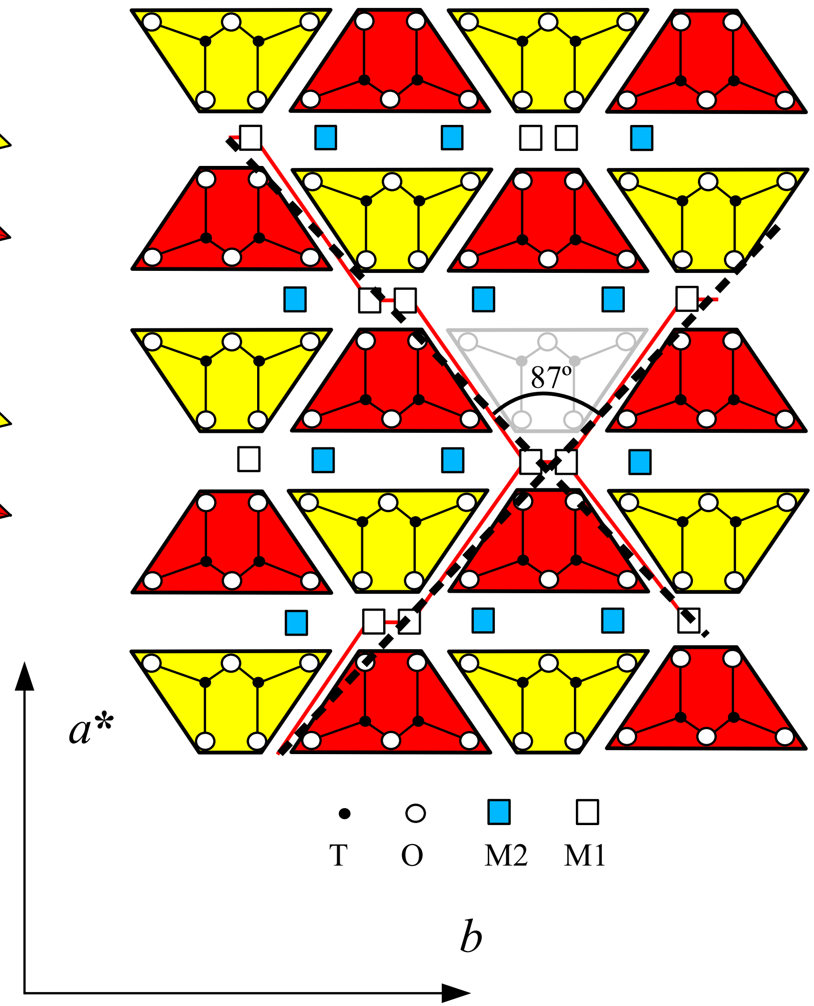
Dealing with modular crystal structures

A crystal structure is composed by a finite number of infinite crystallographic orbits. The number of atomic positions of an orbit inside a unit cell is finite and corresponds to the multiplicity of the Wyckoff position. The other, infinitely many atomic positions of the same orbit are obtained by applying translations.

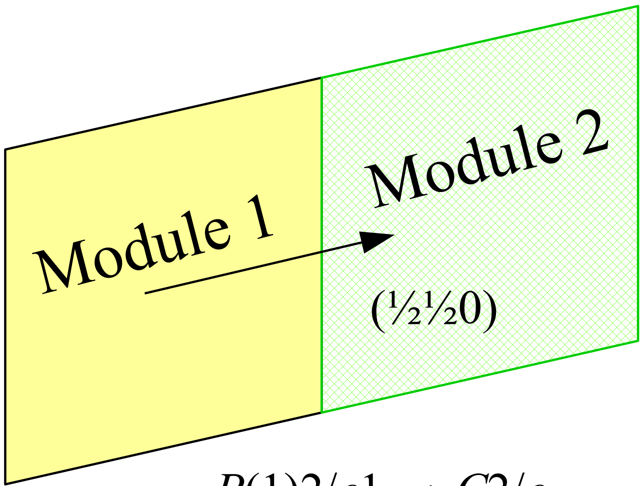
A modular structure is composed by an infinite number of modules, classified in a finite (usually small, often 1) number of *types*. The number of modules that can be *assigned* to a unit cell is finite. The other, infinitely many modules are obtained by applying translations.

Example. The modular structure of pyroxenes

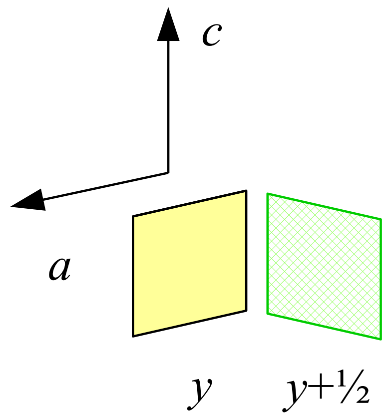


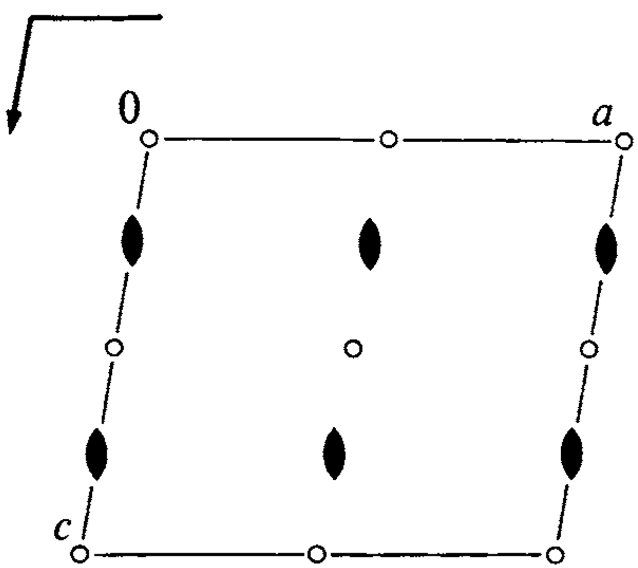


Monoclinic pyroxenes



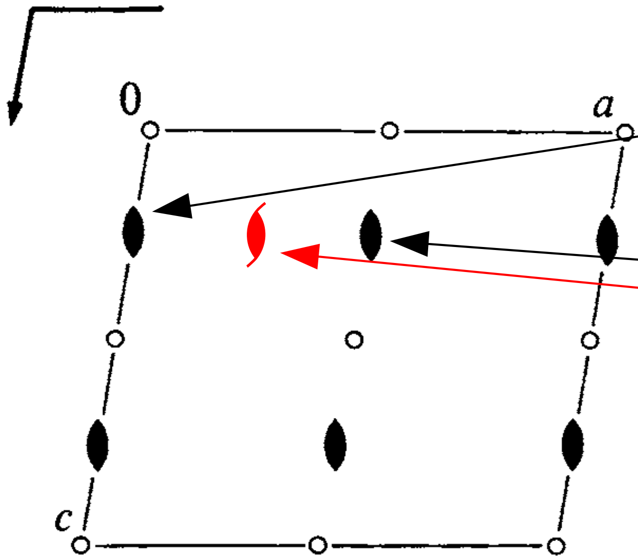
$P(1)2/c1 \rightarrow C2/c$





$P(1)2/c1$	$P(1)2/c1\ t^{-1}(½½0)$
$t(½½0)P(1)2/c1$	$t(½½0)P(1)2/c1\ t^{-1}(½½0)$

Monoclinic pyroxenes: two-fold rotation



$2_{[010]},0y\frac{1}{4}$ Matrix representation $\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right)$

$$t(\tfrac{1}{2}\tfrac{1}{2}0)\cdot 2_{[010],0y\frac{1}{4}} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right)$$

$2_{1[010],\frac{1}{4}y\frac{1}{4}}$ 2-fold screw rotation

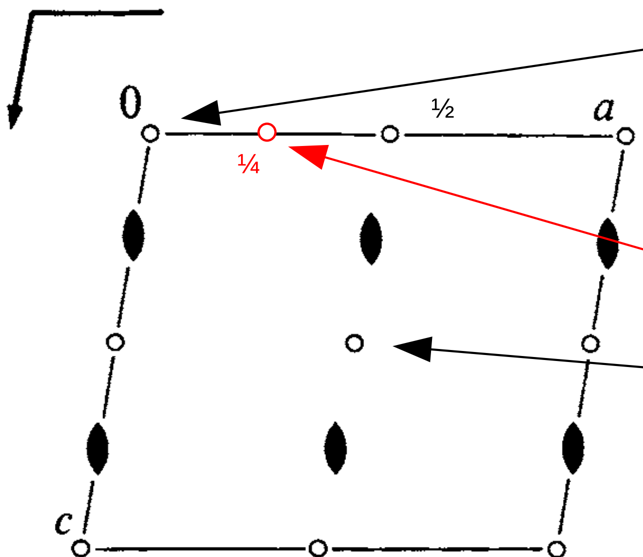
$$2_{[010],0y\frac{1}{4}}\cdot t^{-1}(\tfrac{1}{2}\tfrac{1}{2}0) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{\bar{1}}{2} \\ 0 & 1 & 0 & \frac{\bar{1}}{2} \\ 0 & 0 & 1 & 0 \end{array}\right) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{\bar{1}}{2} \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right)$$

$2_{1[010],\frac{1}{4}y\frac{1}{4}}$ 2-fold screw rotation

$$t(\tfrac{1}{2}\tfrac{1}{2}0)\cdot 2_{[010],0y\frac{1}{4}}\cdot t^{-1}(\tfrac{1}{2}\tfrac{1}{2}0) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{\bar{1}}{2} \\ 0 & 1 & 0 & \frac{\bar{1}}{2} \\ 0 & 0 & 1 & 0 \end{array}\right) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & \frac{1}{2} \end{array}\right)$$

$2_{[010],\frac{1}{2}y\frac{1}{4}}$ 2-fold rotation

Monoclinic pyroxenes: inversion



$\bar{1}_{000}$

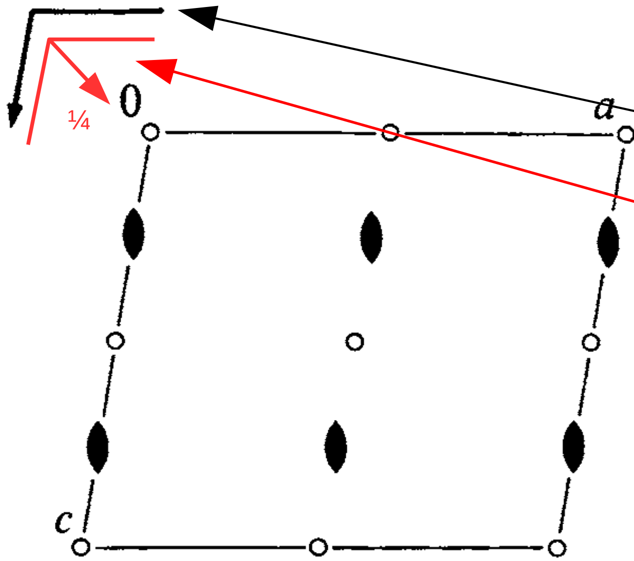
Matrix representation $\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \end{array}\right)$

$$t(\tfrac{1}{2}\tfrac{1}{2}0)\cdot\bar{1}_{000} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \tfrac{1}{2} \\ 0 & 1 & 0 & \tfrac{1}{2} \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \end{array}\right) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & \tfrac{1}{2} \\ 0 & \bar{1} & 0 & \tfrac{1}{2} \\ 0 & 0 & \bar{1} & 0 \end{array}\right) \quad \bar{1}_{\frac{1}{4}\frac{1}{4}0}$$

$$\bar{1}_{000}\cdot t^{-1}(\tfrac{1}{2}\tfrac{1}{2}0) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & \bar{1}/2 \\ 0 & 1 & 0 & \bar{1}/2 \\ 0 & 0 & 1 & 0 \end{array}\right) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & \tfrac{1}{2} \\ 0 & \bar{1} & 0 & \tfrac{1}{2} \\ 0 & 0 & \bar{1} & 0 \end{array}\right) \quad \bar{1}_{\frac{1}{4}\frac{1}{4}0}$$

$$t(\tfrac{1}{2}\tfrac{1}{2}0)\cdot\bar{1}_{000}\cdot t^{-1}(\tfrac{1}{2}\tfrac{1}{2}0) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \tfrac{1}{2} \\ 0 & 1 & 0 & \tfrac{1}{2} \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & \bar{1}/2 \\ 0 & 1 & 0 & \bar{1}/2 \\ 0 & 0 & 1 & 0 \end{array}\right) = \left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 1 \\ 0 & \bar{1} & 0 & 1 \\ 0 & 0 & \bar{1} & 0 \end{array}\right) \quad \bar{1}_{\frac{1}{2}\frac{1}{2}0}$$

Monoclinic pyroxenes: glide reflection



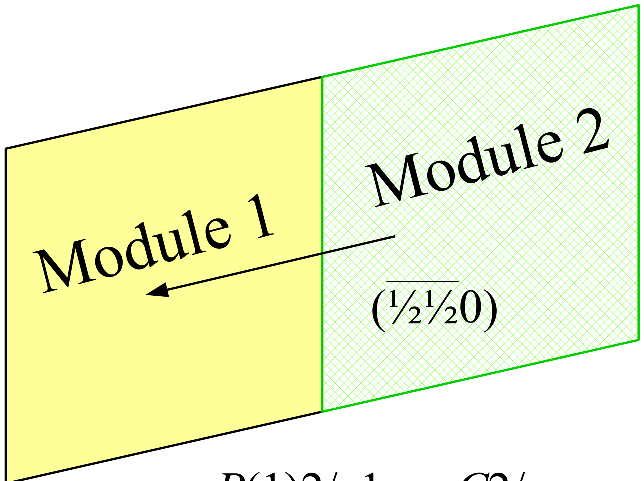
c_{0y0} Matrix representation: $\left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right)$

$$t(\tfrac{1}{2}\tfrac{1}{2}0)\cdot c_{x0z} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & 0 & \frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right) \quad n_{x\frac{1}{4}z}$$

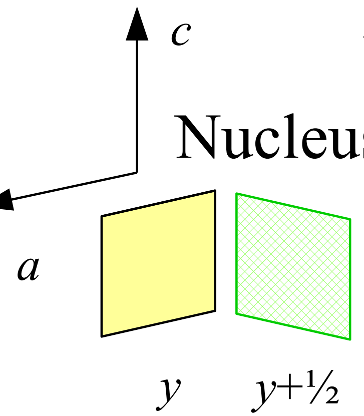
$$c_{x0z}\cdot t^{-1}(\tfrac{1}{2}\tfrac{1}{2}0) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{\bar{1}}{2} \\ 0 & 1 & 0 & \frac{\bar{1}}{2} \\ 0 & 0 & 1 & 0 \end{array}\right) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{\bar{1}}{2} \\ 0 & \bar{1} & 0 & \frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right) \quad n_{x\frac{1}{4}z}$$

$$t(\tfrac{1}{2}\tfrac{1}{2}0)\cdot c_{x0z}\cdot t^{-1}(\tfrac{1}{2}\tfrac{1}{2}0) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right)\left(\begin{array}{ccc|c} 1 & 0 & 0 & \frac{\bar{1}}{2} \\ 0 & 1 & 0 & \frac{\bar{1}}{2} \\ 0 & 0 & 1 & 0 \end{array}\right) = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 1 \\ 0 & 0 & 1 & \frac{1}{2} \end{array}\right) \quad c_{x\frac{1}{2}z}$$

Monoclinic pyroxenes



$P(1)2/c1 \rightarrow C2/c$

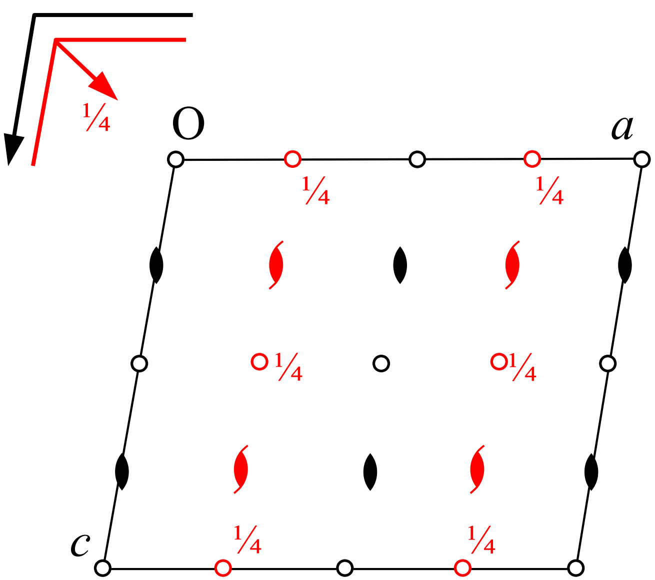


Nucleus of module 1: $P(1)2/c1$

Nucleus of module 2: $t(\tfrac12\tfrac12 0)\ P(1)2/c1\ t(\overline{\tfrac12\tfrac12}0)$

$= P(1)2/c1$ conjugate by the translation vector

$P(1)2/c1$	$P(1)2/c1\ t(\overline{\tfrac12\tfrac12}0)$
$t(\tfrac12\tfrac12 0)P(1)2/c1$	$t(\tfrac12\tfrac12 0)P(1)2/c1\ t(\overline{\tfrac12\tfrac12}0)$



$t(\tfrac12\tfrac12 0)\cdot 1 = t(\tfrac12\tfrac12 0)$ $\quad 1\cdot t(\overline{\tfrac12\tfrac12}0) = t(\overline{\tfrac12\tfrac12}0) = t(\tfrac12\tfrac12 0)$ Same

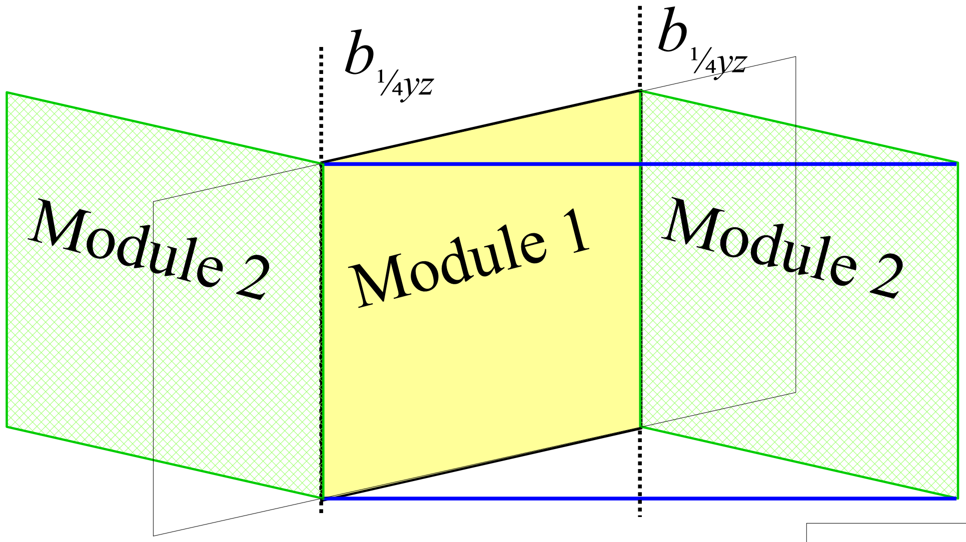
$t(\tfrac12\tfrac12 0)\cdot 2_{[010],0y\frac14} = 2_{1,[010],\frac14 y\frac14}$ $\quad 2_{[010],0y\frac14}\cdot t(\overline{\tfrac12\tfrac12}0) = 2_{1,[010],\frac14 y\frac14}$ Same

$t(\tfrac12\tfrac12 0)\cdot \bar{1}_{000} = \bar{1}_{\frac14\frac14 0}$ $\quad \bar{1}_{000}\cdot t(\overline{\tfrac12\tfrac12}0) = \bar{1}_{\frac14\frac14 0}$ Same

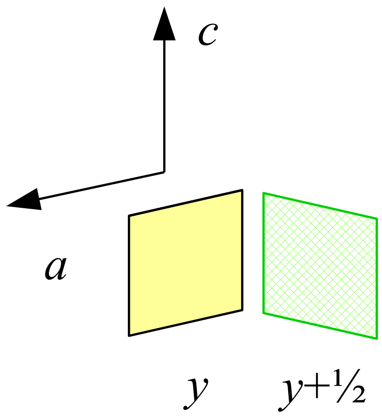
$t(\tfrac12\tfrac12 0)\cdot c_{x0z} = n_{x\frac14 z}$ $\quad c_{x0z}\cdot t(\overline{\tfrac12\tfrac12}0) = n_{x\frac14 z}$ Same

All the partial operations become total → the groupoid degenerates into a group

Protopyroxenes



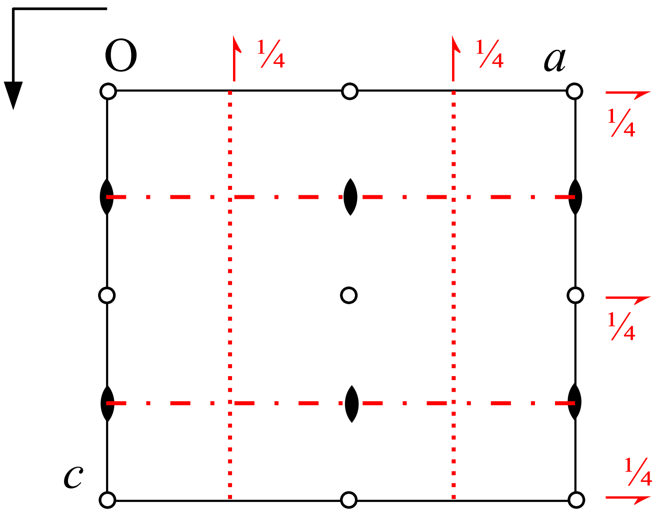
$P(1)2/c1 \rightarrow Pbcn$



Nucleus of module 1: $P(1)2/c1$

Nucleus of module 2: $b_{¼yz}\ P(1)2/c1\ b_{¼yz}^{-1}$ = $P(1)2/c1$ conjugate by *b*-glide

$P(1)2/c1$	$P(1)2/c1\ b_{¼yz}^{-1}$
$b_{¼yz}\ P(1)2/c1$	$b_{¼yz}\ P(1)2/c1\ b_{¼yz}^{-1}$



$b_{¼yz}\cdot 1 = b_{¼yz}$ $\quad 1\cdot b_{¼yz}^{-1} = b_{¼yz}^{-1} = b_{¼yz}$ Same

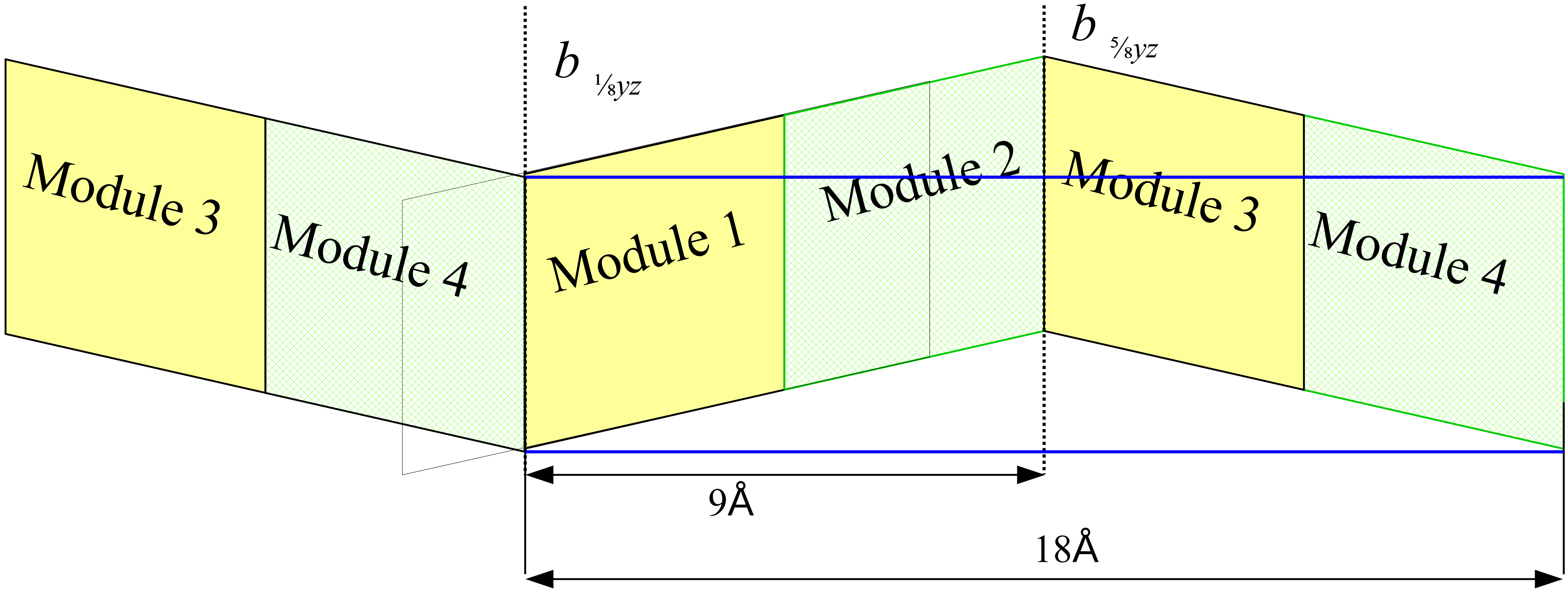
$b_{¼yz}\cdot 2_{[010],0y¼} = n_{x¼z}$ $\quad 2_{[010],0y¼}\cdot b_{¼yz}^{-1} = n_{x¼z}$ Same

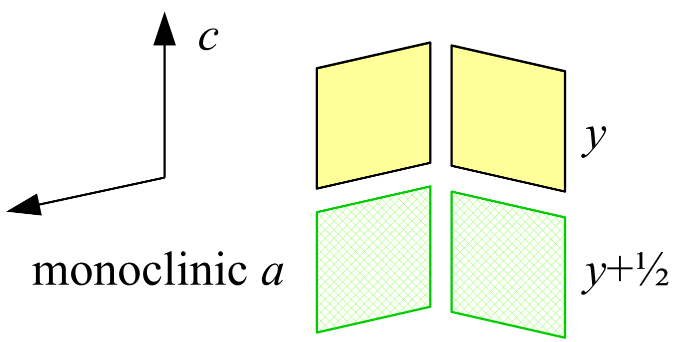
$b_{¼yz}\cdot \bar{1}_{000} = 2_{1,[100],x¼0}$ $\quad \bar{1}_{000}\cdot b_{¼yz}^{-1} = 2_{1,[100],x¼0}$ Same

$b_{¼yz}\cdot c_{x0z} = 2_{1,[001],¼¼z}$ $\quad c_{x0z}\cdot b_{¼yz}^{-1} = 2_{1,[001],¼¼z}$ Same

All the partial operations become total → the groupoid degenerates into a group

Orthopyroxenes



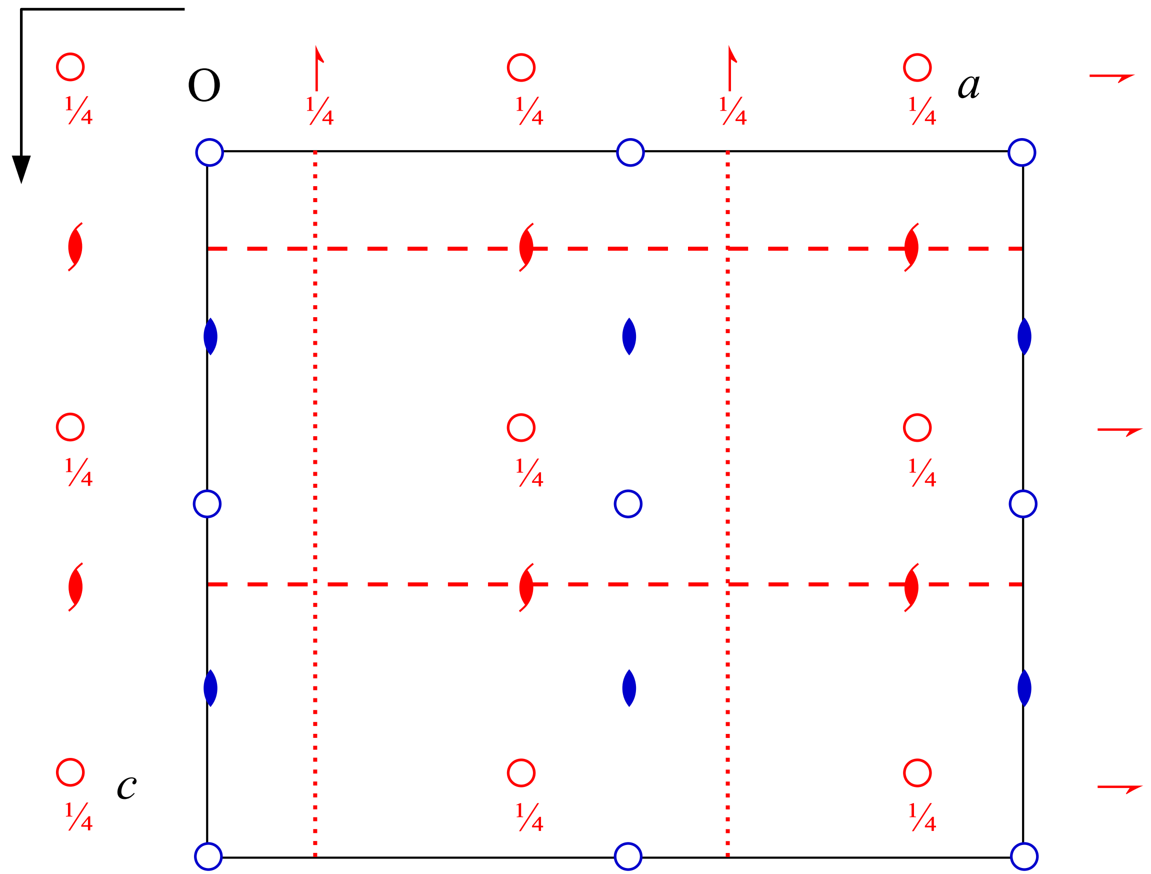


$2 \rightarrow 1$: $t(\overline{\tfrac{1}{2}\tfrac{1}{2}0})_{clino}$, $(\overline{\tfrac{1}{4}\tfrac{1}{2}\tfrac{1}{4}})_{ortho}$ **2a-c,b,c**

$3 \rightarrow 1$: $b_{\frac{1}{8}yz}$

$4 \rightarrow 1$: $(\overline{\tfrac{1}{4}\tfrac{1}{2}\tfrac{1}{4}})\cdot b_{\frac{1}{8}yz}$

Orthopyroxenes

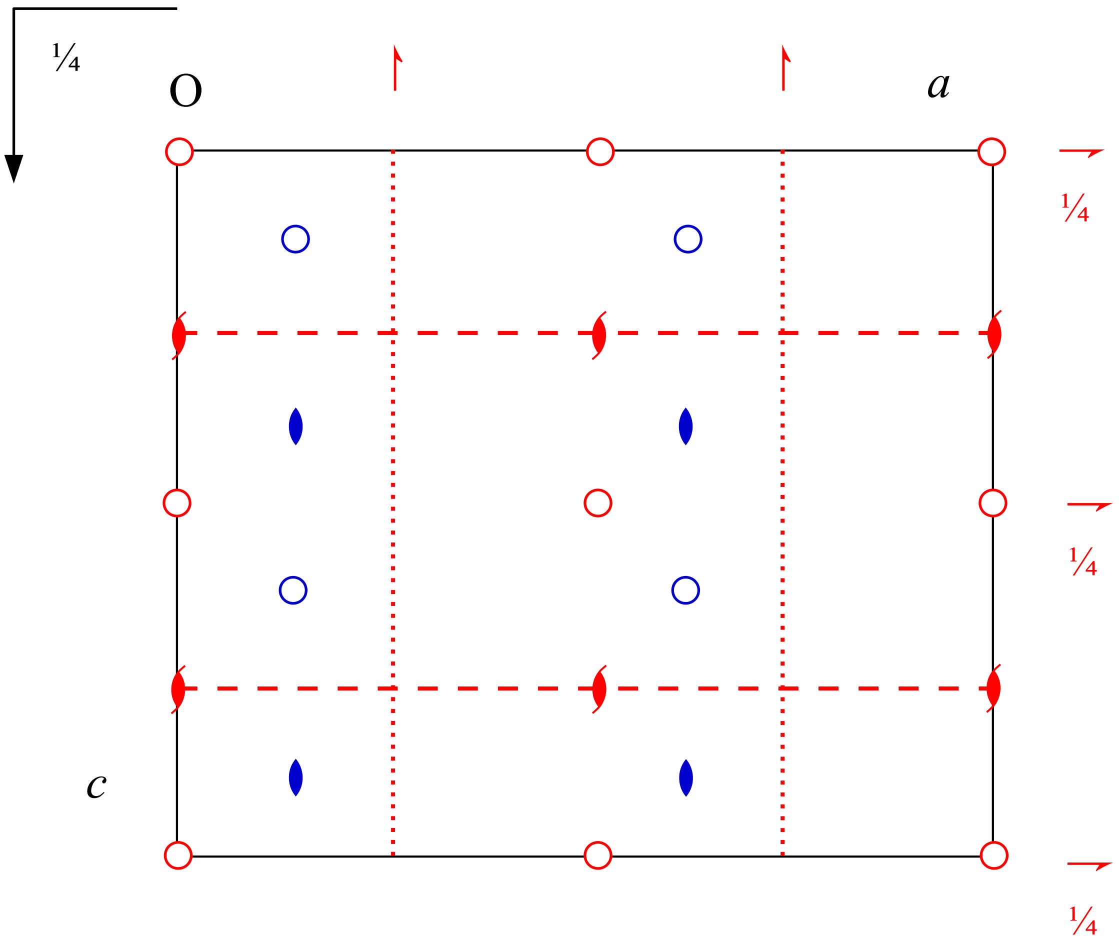


Black: symmetry element of the layer which remains as symmetry element of the orthopyroxene

Blue: symmetry elements of the layer are lost in the orthopyroxene

Red: symmetry elements of the orthopyroxene generated by the stacking operation

Orthopyroxenes



After a shift of the origin

$$P(1)2/c1 \rightarrow Pbca$$