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IUCr Commission on Mathematical and Theoretical Crystallography

# INTERNATIONAL AUTUMN SCHOOL ON FUNDAMENTAL AND ELECTRON CRYSTALLOGRAPHY

8-13 October 2017, Sofia, Bulgaria

# SPACE GROUPS
# AND
# THEIR SYMMETRY RELATIONS

# SPACE GROUPS

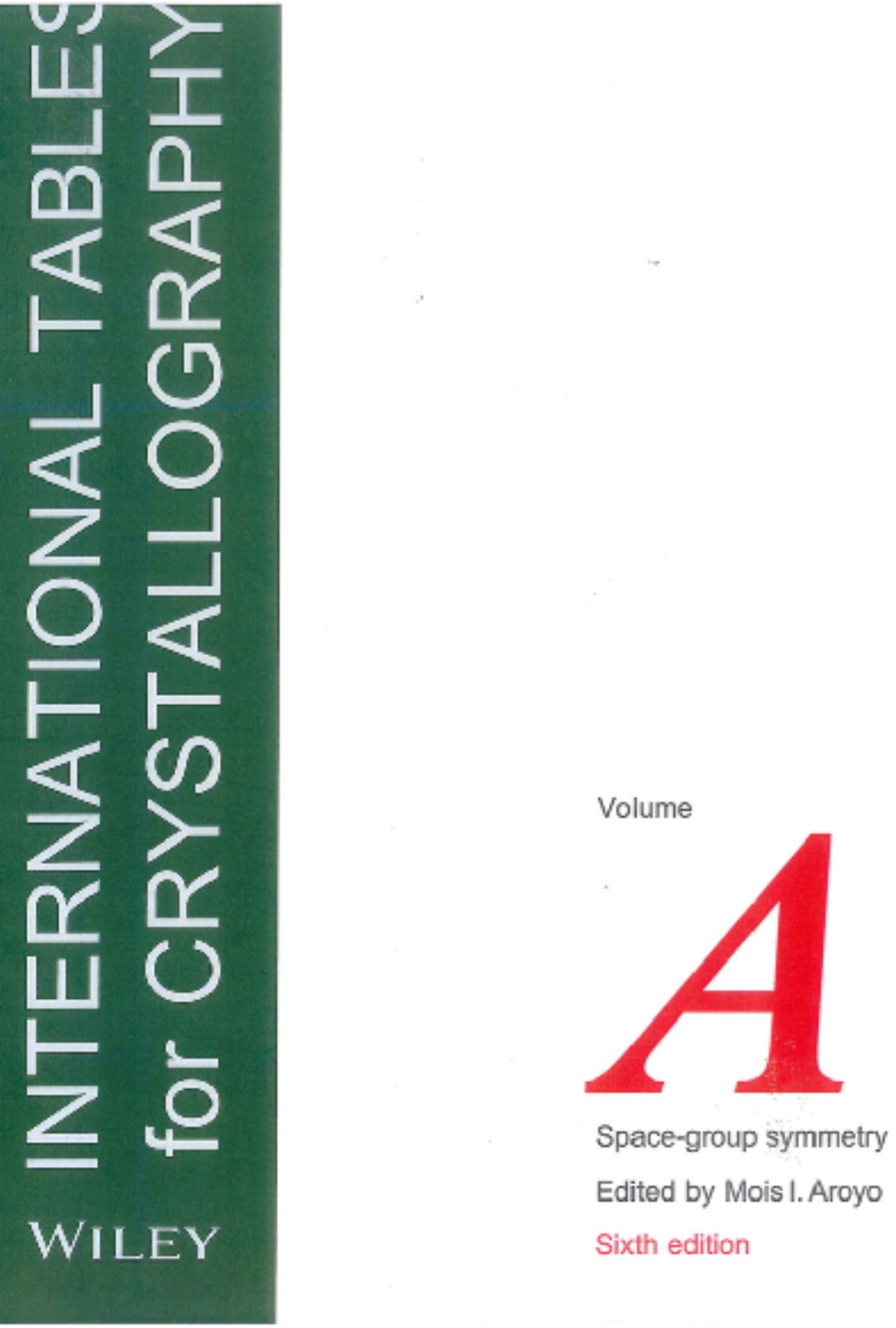
**Crystal pattern:** infinite, idealized crystal structure (without disorder, dislocations, impurities, etc.)

**Space group G:** The set of all symmetry operations (isometries) of a crystal pattern

**Translation subgroup $H \triangleleft G$:** The infinite set of all translations that are symmetry operations of the crystal pattern

**Point group of the space groups $P_G$:** The factor group of the space group G with respect to the translation subgroup T: $P_G \cong G/H$

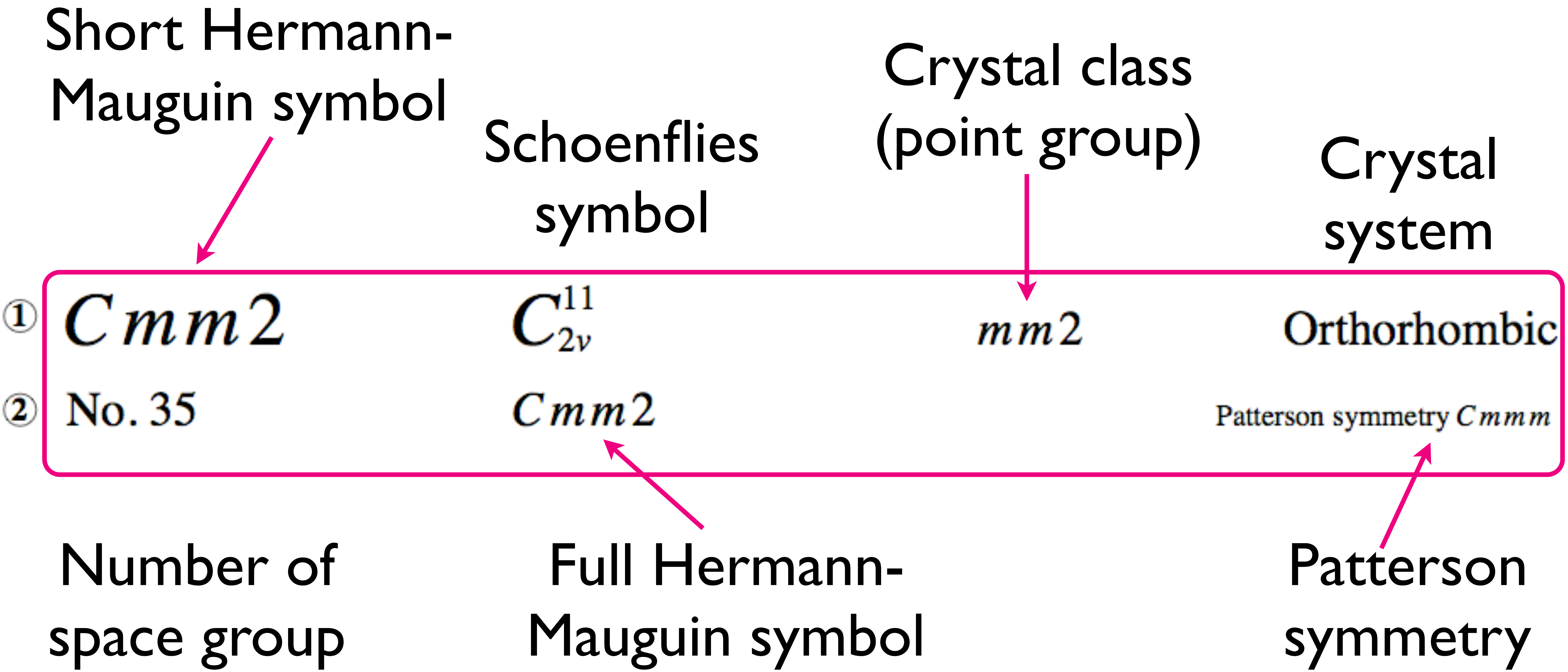
# INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY
# VOLUME A: SPACE-GROUP SYMMETRY




Extensive tabulations and illustrations of the 17 plane groups and of the 230 space groups

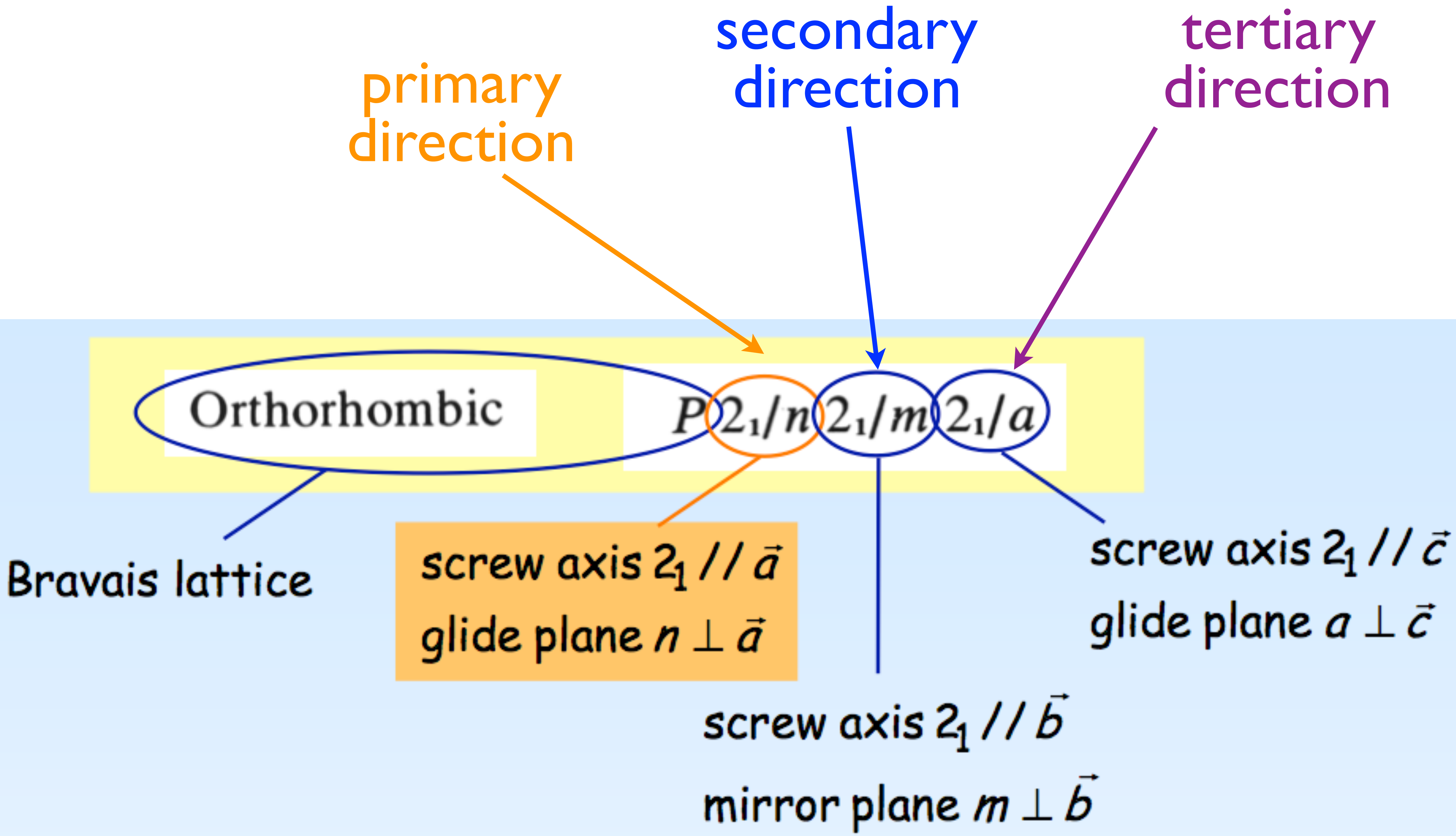
- headline with the relevant group symbols;
- diagrams of the symmetry elements and of the general position;
- specification of the origin and the asymmetric unit;
- list of symmetry operations;
- generators;
- general and special positions with multiplicities, site symmetries, coordinates and reflection conditions;
- symmetries of special projections;

# HERMANN-MAUGUIN SYMBOLISM

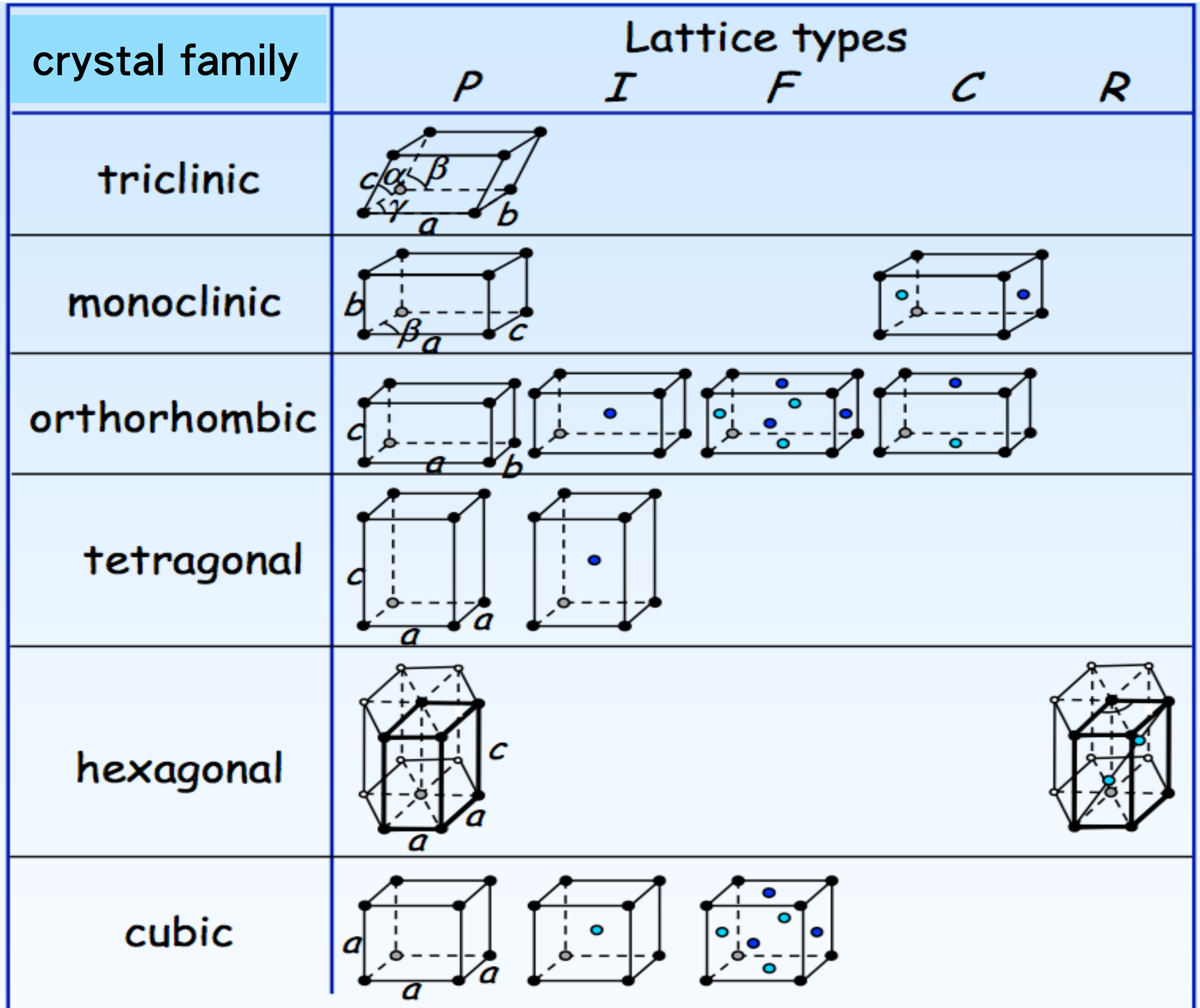


Short Hermann-Mauguin symbol
Schoenflies symbol
Crystal class (point group)
Crystal system
① $Cmm2$
$C_{2v}^{11}$
$mm2$
Orthorhombic
② No. 35
$Cmm2$
Patterson symmetry $Cmmm$
Number of space group
Full Hermann-Mauguin symbol
Patterson symmetry

# Hermann-Mauguin symbols for space groups



# 14 Bravais Lattices



# Hermann-Mauguin symbols for space groups

Directions that belong to the same set of equivalent symmetry directions are collected between braces. The first entry in each set is taken as the representative of that set.

| Lattice | Symmetry direction (position in Hermann–Mauguin symbol) | | |
|---|---|---|---|
| | Primary | Secondary | Tertiary |
| Triclinic | None | | |
| Monoclinic* | [010] ('unique axis $b$')<br>[001] ('unique axis $c$') | | |
| Orthorhombic | [100] | [010] | [001] |
| Tetragonal | [001] | $\left\{\begin{matrix}[100]\\ [010]\end{matrix}\right\}$ | $\left\{\begin{matrix}[1\bar{1}0]\\ [110]\end{matrix}\right\}$ |
| Hexagonal | [001] | $\left\{\begin{matrix}[100]\\ [010]\\ [\bar{1}\bar{1}0]\end{matrix}\right\}$ | $\left\{\begin{matrix}[1\bar{1}0]\\ [120]\\ [\bar{2}\bar{1}0]\end{matrix}\right\}$ |
| Rhombohedral (hexagonal axes) | [001] | $\left\{\begin{matrix}[100]\\ [010]\\ [\bar{1}\bar{1}0]\end{matrix}\right\}$ | |
| Rhombohedral (rhombohedral axes) | [111] | $\left\{\begin{matrix}[1\bar{1}0]\\ [01\bar{1}]\\ [\bar{1}01]\end{matrix}\right\}$ | |
| Cubic | $\left\{\begin{matrix}[100]\\ [010]\\ [001]\end{matrix}\right\}$ | $\left\{\begin{matrix}[111]\\ [1\bar{1}\bar{1}]\\ [\bar{1}1\bar{1}]\\ [\bar{1}\bar{1}1]\end{matrix}\right\}$ | $\left\{\begin{matrix}[1\bar{1}0] & [110]\\ [01\bar{1}] & [011]\\ [\bar{1}01] & [101]\end{matrix}\right\}$ |

# SPACE-GROUP SYMMETRY OPERATIONS

# Crystallographic symmetry operations

characteristics:

fixed points of isometries $(W,w)X_f=X_f$
geometric elements

## Types of isometries preserve handedness

identity: the whole space fixed

translation t: no fixed point $\tilde{\mathbf{x}} = \mathbf{x} + \mathbf{t}$

rotation: one line fixed
rotation axis
$\phi = k \times 360^\circ / N$

screw rotation: no fixed point
screw axis
screw vector

# Types of isometries do not preserve handedness

| | |
|---|---|
| roto-inversion: | centre of roto-inversion fixed<br>roto-inversion axis |
| inversion: | centre of inversion fixed |
| reflection: | plane fixed<br>reflection/mirror plane |
| glide reflection: | no fixed point<br>glide plane<br>glide vector |

# Matrix formalism

$$\begin{pmatrix}\tilde{x}\\ \tilde{y}\\ \tilde{z}\end{pmatrix} = \begin{pmatrix}W_{11} W_{12} W_{13}\\ W_{21} W_{22} W_{23}\\ W_{31} W_{32} W_{33}\end{pmatrix}\begin{pmatrix}x\\ y\\ z\end{pmatrix} + \begin{pmatrix}w_1\\ w_2\\ w_3\end{pmatrix}$$

linear/matrix part

translation column part

$$\tilde{\boldsymbol{x}} = \boldsymbol{W}\,\boldsymbol{x} + \boldsymbol{w}$$

$$\tilde{\boldsymbol{x}} = (\,\boldsymbol{W},\,\boldsymbol{w})\,\boldsymbol{x} \quad \text{or} \quad \tilde{\boldsymbol{x}} = \{\,\boldsymbol{W}\,|\,\boldsymbol{w}\}\,\boldsymbol{x}$$

matrix-column pair

Seitz symbol

# Space group *Cmm*2 (No. 35)

Diagram of symmetry elements

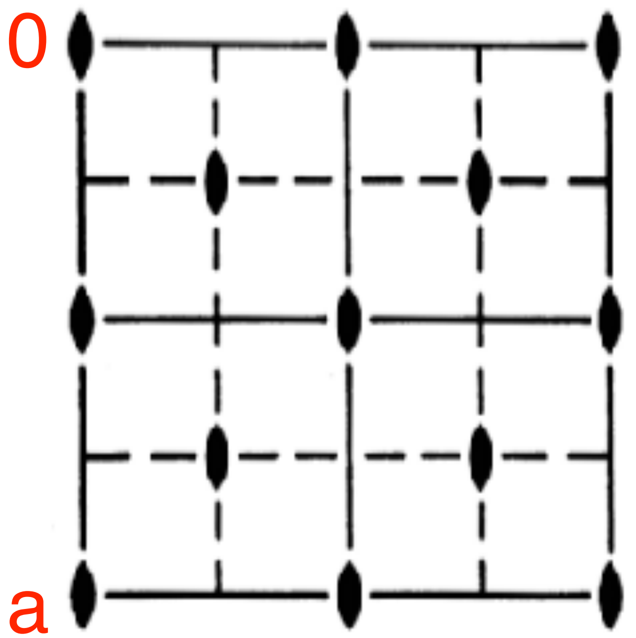
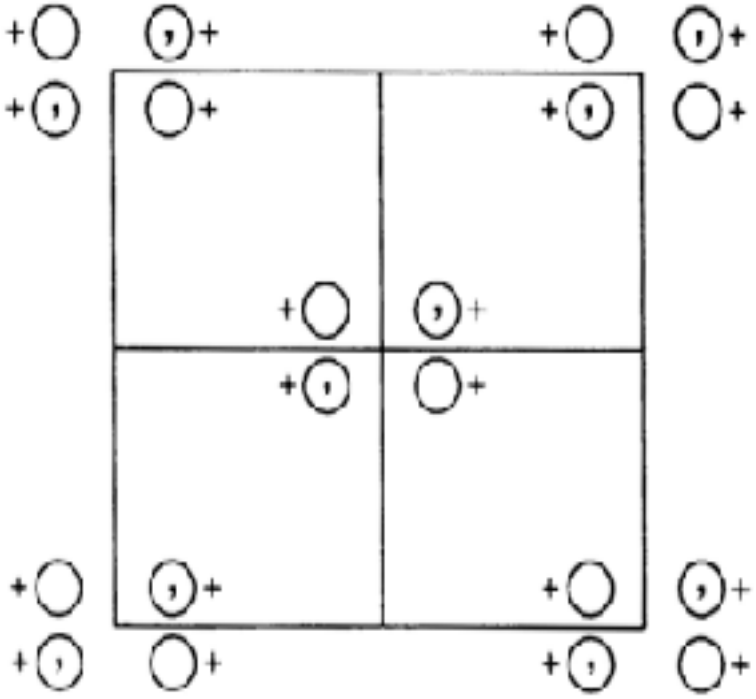



Diagram of
general position points



## How are the symmetry operations represented in ITA ?

**Symmetry operations**

For (0,0,0)+ set

(1) 1 (2) 2 0,0,$z$ (3) $m$ $x$,0,$z$ (4) $m$ 0,$y$,$z$

For ($\frac{1}{2}$,$\frac{1}{2}$,0)+ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) 2 $\frac{1}{4},\frac{1}{4},z$ (3) $a$ $x,\frac{1}{4},z$ (4) $b$ $\frac{1}{4},y,z$

## General Position

Coordinates

(0,0,0)+ ($\frac{1}{2}$,$\frac{1}{2}$,0)+

8 $f$ 1 (1) $x,y,z$ (2) $\bar{x},\bar{y},z$ (3) $x,\bar{y},z$ (4) $\bar{x},y,z$

# General position

(i) coordinate triplets of an image point $\tilde{X}$ of the original point $X = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ under (W,w) of G

-presentation of infinite image points $\tilde{X}$ under the action of (W,w) of G

(ii) short-hand notation of the matrix-column pairs (W,w) of the symmetry operations of G

-presentation of infinite symmetry operations of G
$(W,w) = (I,t_n)(W,w_0)$, $0 \leq w_{i0} < 1$

# Space Groups: infinite order

## Coset decomposition $G:T_G$

General position

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $(I,0)$ | $(W_2,w_2)$ | ... | $(W_m,w_m)$ | | ... | $(W_i,w_i)$ | |
| $(I,t_1)$ | $(W_2,w_2+t_1)$ | ... | $(W_m,w_m+t_1)$ | | ... | $(W_i,w_i+t_1)$ | |
| $(I,t_2)$ | $(W_2,w_2+t_2)$ | ... | $(W_m,w_m+t_2)$ | | ... | $(W_i,w_i+t_2)$ | |
| ... | ... | ... | ... | | ... | ... | |
| $(I,t_j)$ | $(W_2,w_2+t_j)$ | ... | $(W_m,w_m+t_j)$ | | ... | $(W_i,w_i+t_j)$ | |
| ... | ... | ... | ... | | ... | ... | |

## Factor group $G/T_G$

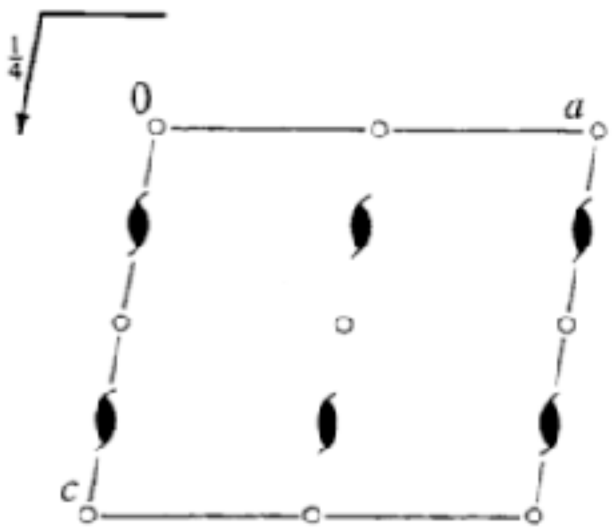
isomorphic to the point group $P_G$ of G

Point group $P_G = \{I, W_2, W_3, \ldots, W_i\}$

EXAMPLE

# Coset decomposition $P2_1/c$:T

## Point group ?




General position

(1) $x,y,z$ (2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$ (3) $\bar{x},\bar{y},\bar{z}$ (4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$

| | | | |
|---|---|---|---|
| (1,0) | (2,0 ½ ½) | ($\bar{1}$,0) | (m,0 ½ ½) |
| (1,$t_1$) | (2,0 ½ ½+$t_1$) | ($\bar{1}$,$t_1$) | (m,0 ½ ½ +$t_1$) |
| (1,$t_2$) | (2,0 ½ ½ +$t_2$) | ($\bar{1}$,$t_2$) | (m,0 ½ ½ +$t_2$) |
| ... | ... ... | ... | ... ... |
| (1,$t_j$) | (2,0 ½ ½ +$t_j$) | ($\bar{1}$,$t_j$) | (m,0 ½ ½ +$t_j$) |
| ... | ... ... | ... | ... ... |

inversion centers

($\bar{1}$,p q r): $\bar{1}$ at p/2,q/2,r/2

$2_1$ screw axes

(2,u ½+v ½ +w) → (2,0 ½+v ½)

(2,u ½+v ½ +w) → (2,u ½ ½ +w)

*International Tables for Crystallography* (2006). Vol. A, Space gro

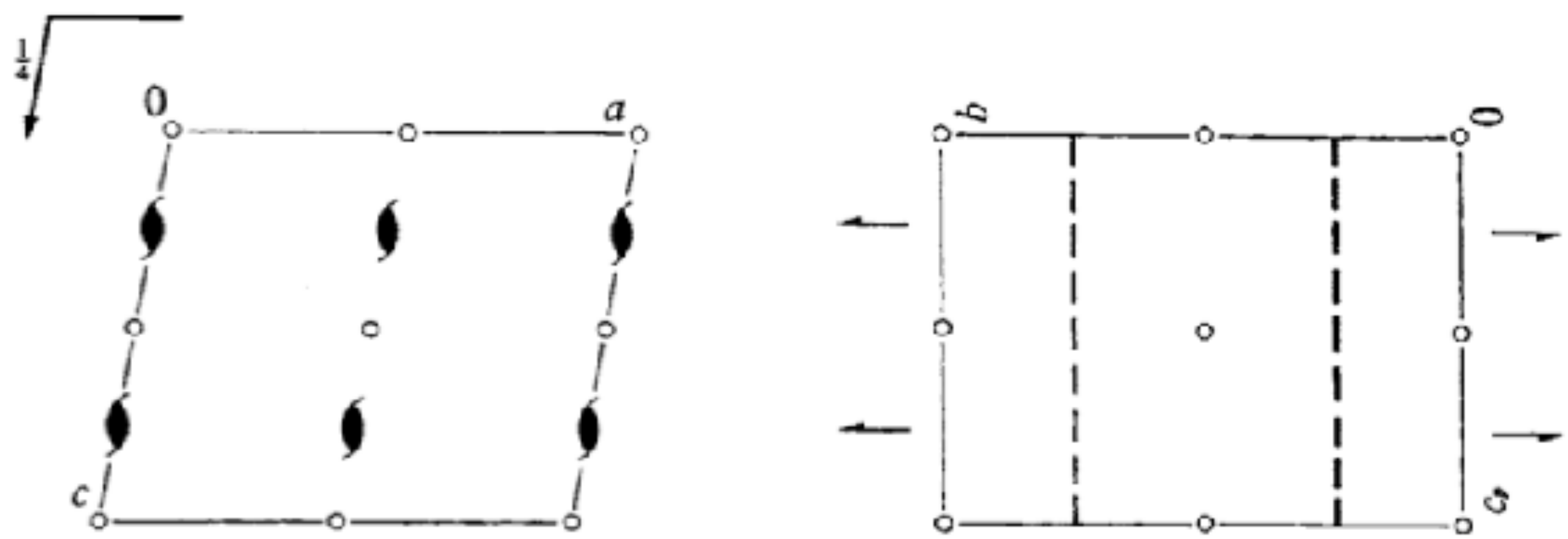
# Space group $P2_1/c$ (No. 14)

$P2_1/c$ $\qquad$ $C_{2h}^5$ $\qquad$ $2/m$ $\qquad$ I

No. 14 $\qquad$ $P12_1/c1$ $\qquad$ Patterson sy

UNIQUE AXIS $b$, CELL CHOICE 1

EXAMPLE




**Generators selected** (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

**Positions**

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Matrix-column presentation

4 $e$ 1 $\qquad$ (1) $x,y,z$ $\qquad$ (2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$ $\qquad$ (3) $\bar{x},\bar{y},\bar{z}$ $\qquad$ (4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$

Geometric interpretation

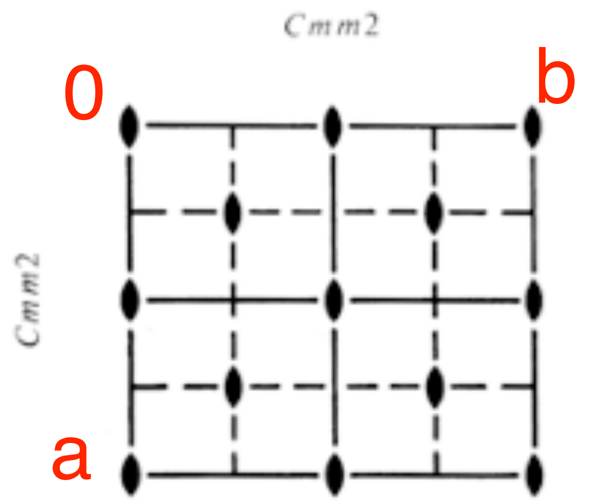
**Symmetry operations**

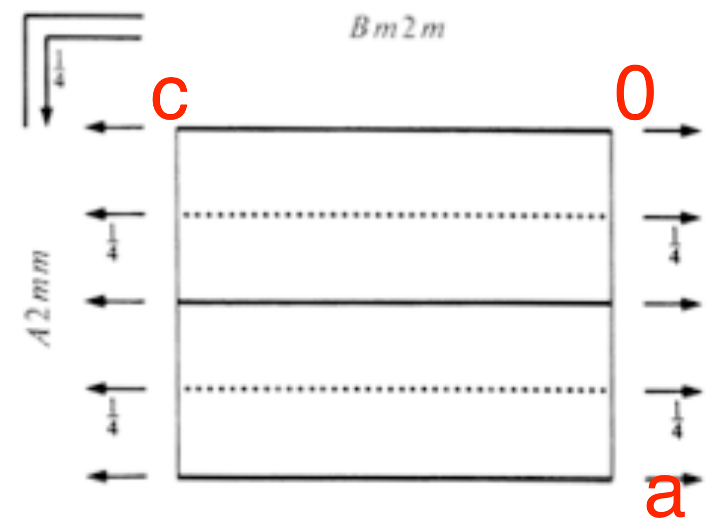
(1) 1 $\qquad$ (2) $2(0,\frac{1}{2},0)$ $\;0,y,\frac{1}{4}$ $\qquad$ (3) $\bar{1}$ $\;0,0,0$ $\qquad$ (4) $c$ $\;x,\frac{1}{4},z$

# SPACE-GROUP DIAGRAMS

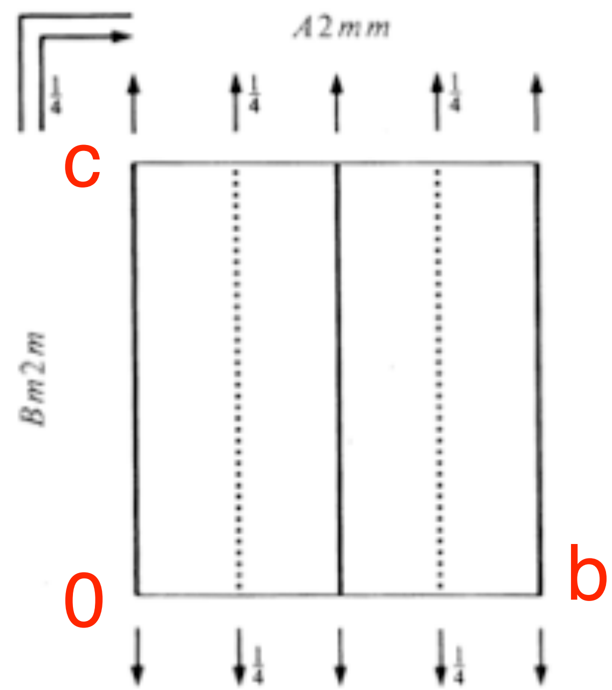
# Diagrams of symmetry elements

three different settings




permutations of ***a*,*b*,*c***



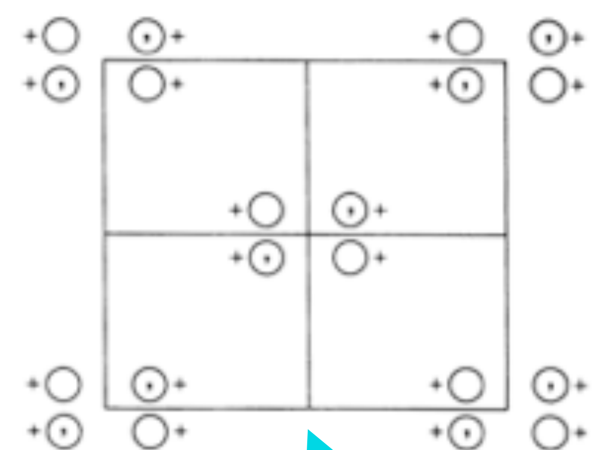
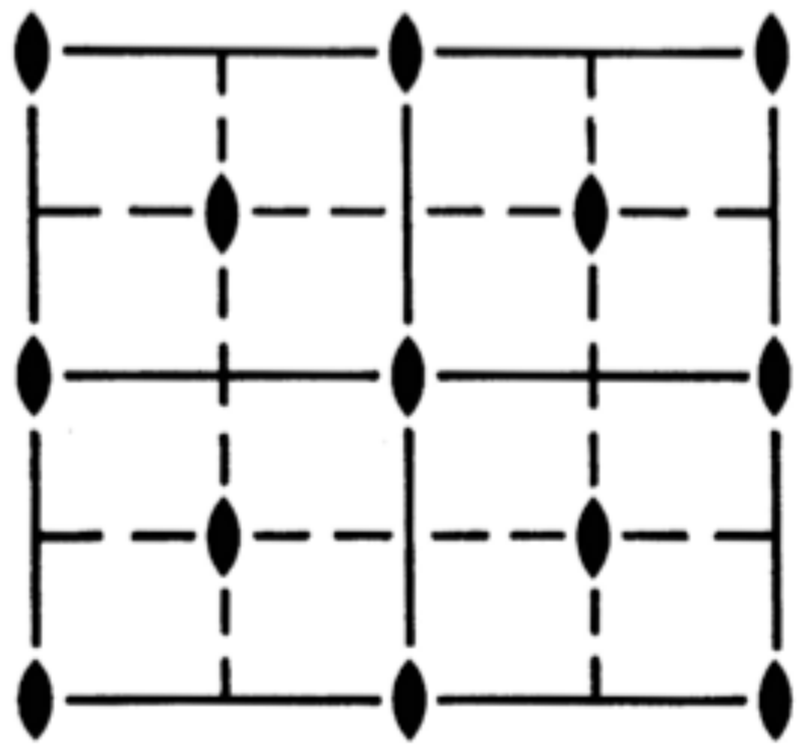



Diagram of general position points

# ORIGINS
# AND
# ASYMMETRIC UNITS

# Space group *Cmm*2 (No. 35): left-hand page ITA

| | | | |
|---|---|---|---|
| *Cmm*2 | $C_{2v}^{11}$ | *mm*2 | Orthorhombic |
| No. 35 | *Cmm*2 | | Patterson symmetry *Cmmm* |



**Origin** on *mm*2

## Origin statement

The site symmetry of the origin is stated, if different from the identity.
A further symbol indicates all symmetry elements (including glide planes and screw axes) that pass through the origin, if any.

## Space groups with two origins

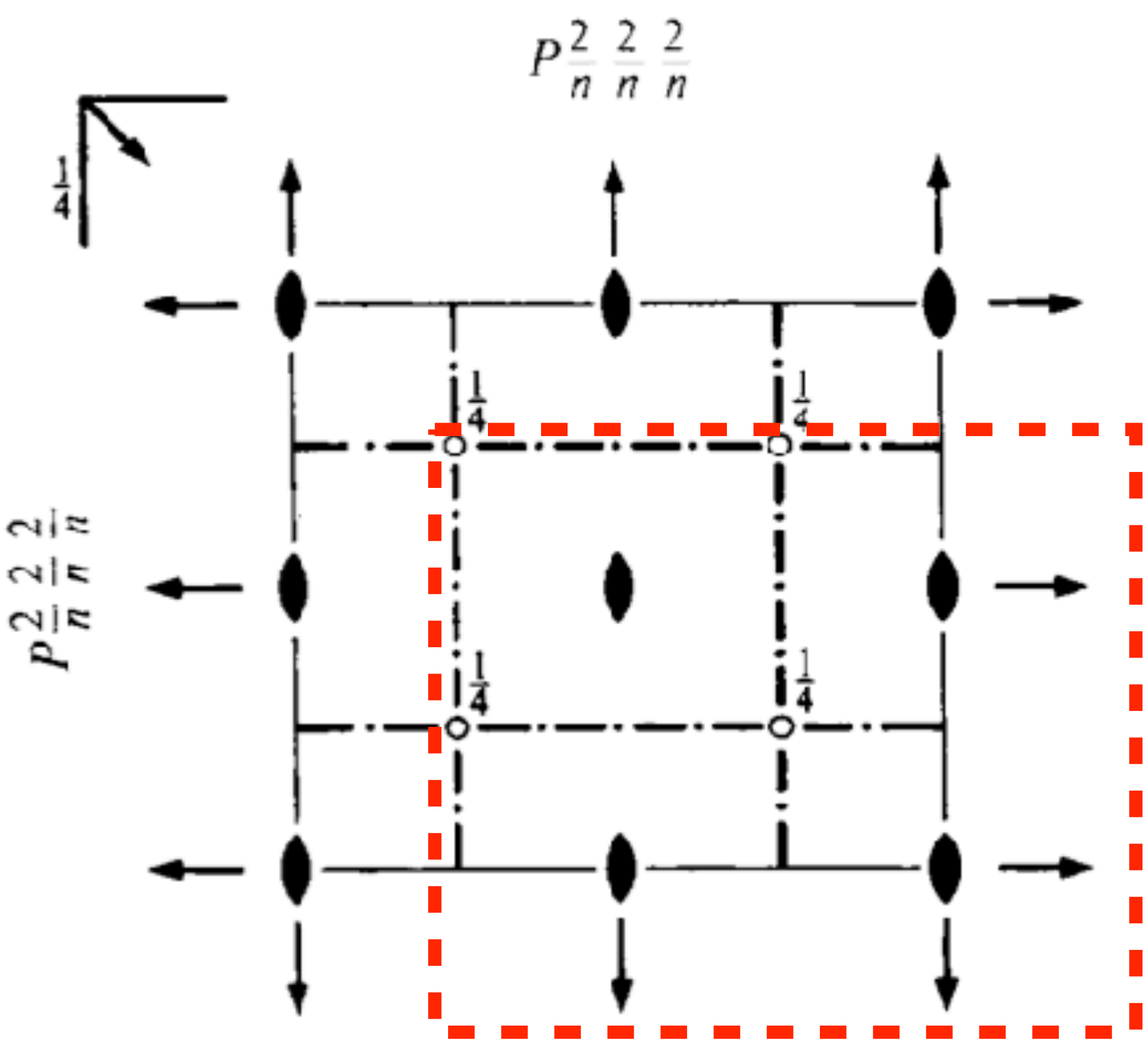
For each of the two origins the location relative to the other origin is also given.

# Example: Different origins for *Pnnn*

$Pnnn$ $D_{2h}^{2}$ $mmm$ Orthorhombic

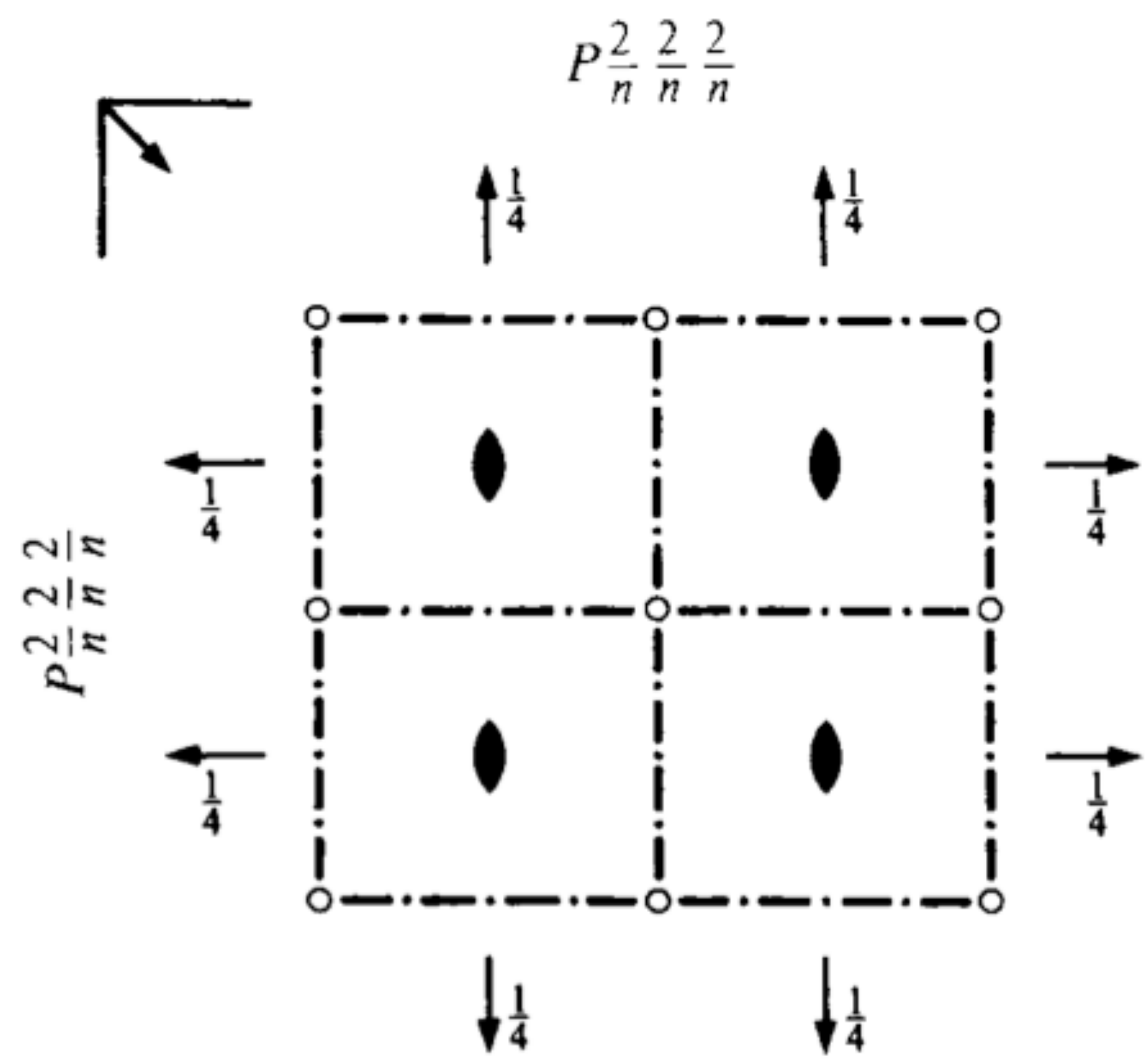
No. 48 $P\ 2/n\ 2/n\ 2/n$ Patterson symmetry $Pmmm$

ORIGIN CHOICE 1




**Origin** at 222, at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ from $\bar{1}$

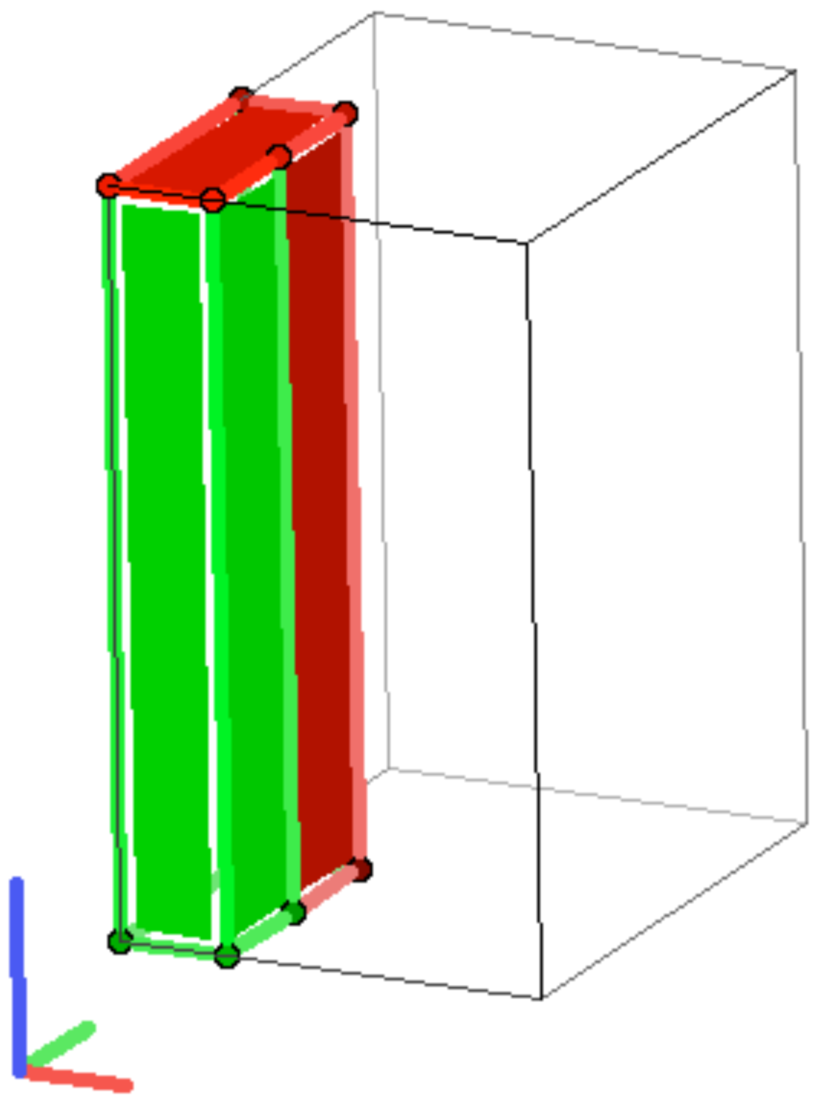
ORIGIN CHOICE 2




**Origin** at $\bar{1}$ at $nnn$, at $-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}$ from 222

# Example: Asymmetric unit *Cmm*2 (No. 35)

ITA: **Asymmetric unit** $0 \le x \le \frac{1}{4}; \quad 0 \le y \le \frac{1}{2}; \quad 0 \le z \le 1$



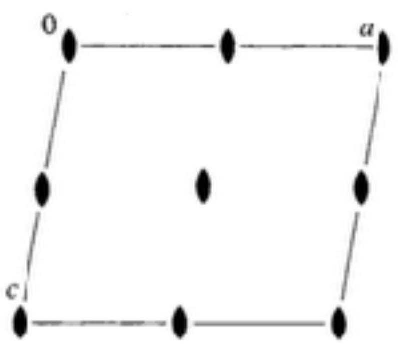
Surface area: green = inside the asymmetric unit, red = outside
Basis vectors: a = red, b = green, c = blue

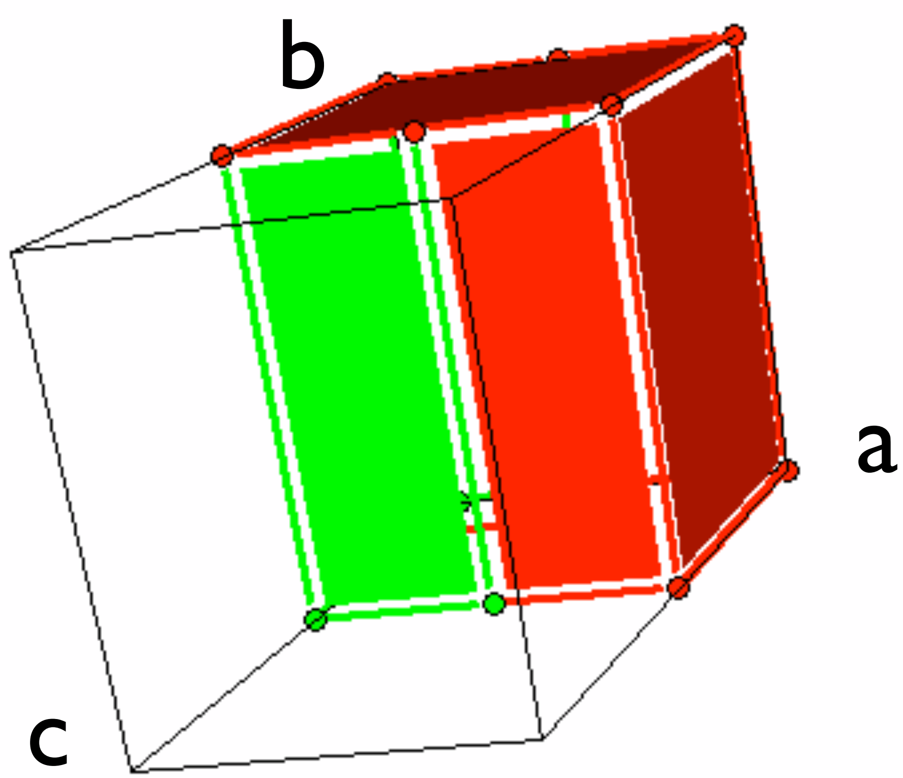
| Number of vertices: 8 | Number of facets: 6 |
|---|---|
| 0, 1/2, 0 | x>=0 |
| 0, 1/2, 1 | x<=1/4 [y<=1/4] |
| 1/4, 1/2, 1 | y>=0 |
| 1/4, 0, 1 | y<=1/2 |
| 0, 0, 0 | z>=0 |
| 1/4, 1/2, 0 | z<1 |
| 0, 0, 1 | |
| 1/4, 0, 0 | [Guide to notation] |

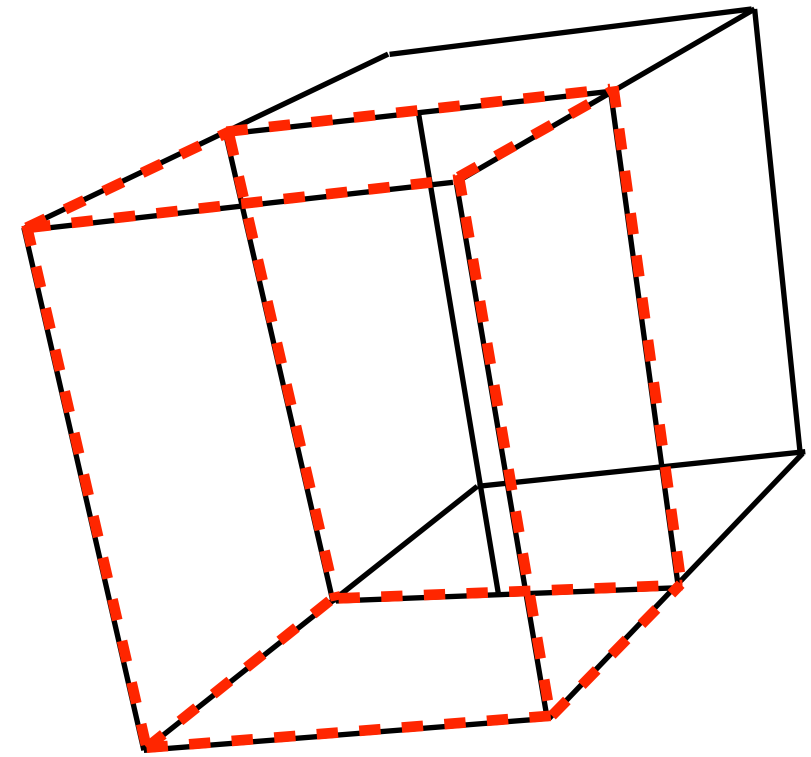
(output cctbx: Ralf Grosse-Kustelve)

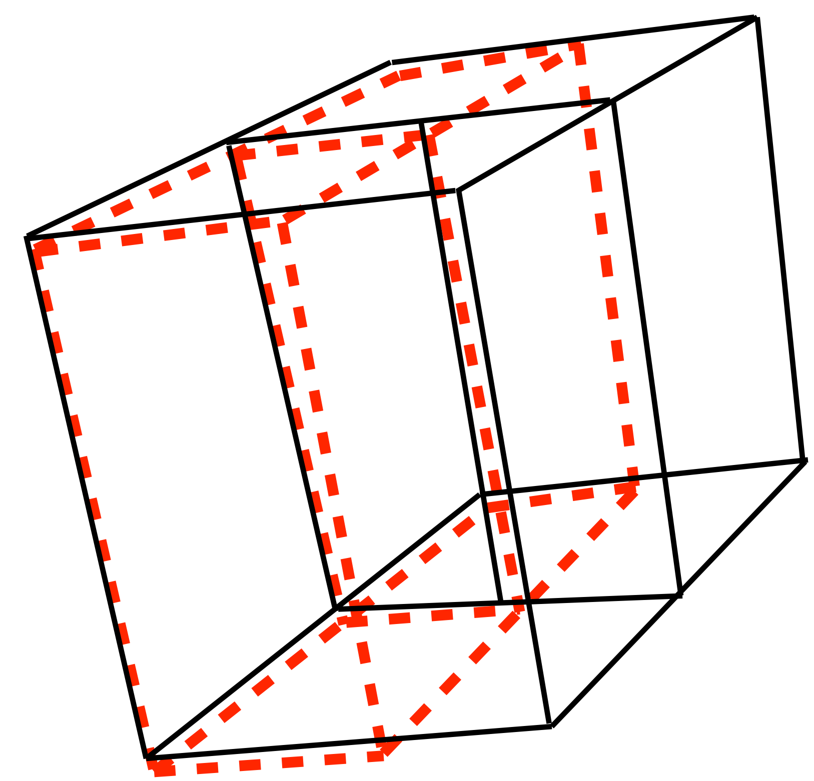
ITA: An asymmetric unit of a space group is a (simply connected) smallest closed part of space from which, by application of all symmetry operations of the space group, the whole of space is filled.

# Example: Asymmetric units for the space group P121





```
Number of vertices: 8
   0, 1, 1/2
   1, 1, 0
   1, 0, 0
   0, 0, 1/2
   1, 0, 1/2
   0, 0, 0
   0, 1, 0
   1, 1, 1/2
```

```
Number of facets: 6
   x>=0
   x<1
   y>=0
   y<1
   z>=0  [x<=1/2]
   z<=1/2  [x<=1/2]
```

[Guide to notation]

(output cctbx: Ralf Grosse-Kustelve)

# GENERAL AND SPECIAL WYCKOFF POSITIONS SITE-SYMMETRY

# Group Actions

## Group Actions

. A *group action* of a group $\mathcal{G}$ on a set $\Omega = \{\omega \mid \omega \in \Omega\}$ assigns to each pair $(g, \omega)$ an object $\omega' = g(\omega)$ of $\Omega$ such that the following hold:

(i) applying two group elements $g$ and $g'$ consecutively has the same effect as applying the product $g'g$, *i.e.* $g'(g(\omega)) = (g'g)(\omega)$

(ii) applying the identity element $e$ of $\mathcal{G}$ has no effect on $\omega$, *i.e.* $e(\omega) = \omega$ for all $\omega$ in $\Omega$.

## Orbit and Stabilizer

The set $\omega^{\mathcal{G}} := \{g(\omega) \mid g \in \mathcal{G}\}$ of all objects in the orbit of $\omega$ is called the *orbit of $\omega$ under $\mathcal{G}$*.

The set $S_{\mathcal{G}}(\omega) := \{g \in \mathcal{G} \mid g(\omega) = \omega\}$ of group elements that do not move the object $\omega$ is a subgroup of $\mathcal{G}$ called the *stabilizer* of $\omega$ in $\mathcal{G}$.

## Equivalence classes

Often, two objects $\omega$ and $\omega'$ are regarded as equivalent if there is a group element moving $\omega$ to $\omega'$.

*Via* this equivalence relation, the action of $\mathcal{G}$ partitions the objects in $\Omega$ into equivalence classes

# General and special Wyckoff positions

**Orbit of a point $X_o$** under G: $G(X_o)=\{(W,w)\ X_o, (W,w)\in G\}$

Multiplicity

**Site-symmetry group** $S_o=\{(W,w)\}$ of a point $X_o$

$$(W,w)X_o = X_o$$

$$\left(\begin{array}{ccc|c} a & b & c & w_1 \\ d & e & f & w_2 \\ g & h & i & w_3 \end{array}\right)\begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} = \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix}$$

Multiplicity: $|P|/|S_o|$

**General position $X_o$**

$S=\{(I,\mathbf{o})\}\simeq \mathbf{1}$

Multiplicity: $|P|$

**Special position $X_o$**

$S>\mathbf{1}=\{(I,\mathbf{o}),...,\}$

Multiplicity: $|P|/|S_o|$

Site-symmetry groups: oriented symbols

# General position

(i) coordinate triplets of an image point $\tilde{X}$ of the original point $X = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ under (W,w) of G

-presentation of infinite image points $\tilde{X}$ under the action of (W,w) of G

(ii) short-hand notation of the matrix-column pairs (W,w) of the symmetry operations of G

-presentation of infinite symmetry operations of G

$(W,w) = (I,t_n)(W,w_0)$, $0 \leq w_{i0} < 1$

# General Position of Space groups

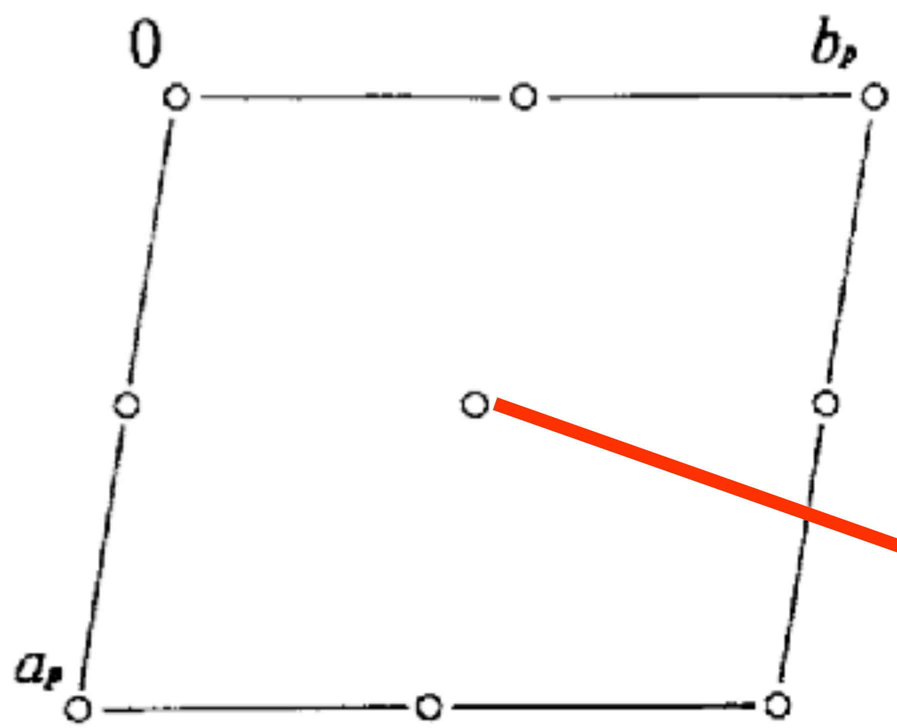
As coordinate triplets of an image point $\tilde{X}$ of the original point $X=\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ under $(W,w)$ of G

General position

| | | | | | | |
|---|---|---|---|---|---|---|
| $(I,0)X$ | $(W_2,w_2)X$ | ... | $(W_m,w_m)X$ | ... | $(W_i,w_i)X$ |
| $(I,t_1)X$ | $(W_2,w_2+t_1)X$ | ... | $(W_m,w_m+t_1)X$ | ... | $(W_i,w_i+t_1)X$ |
| $(I,t_2)X$ | $(W_2,w_2+t_2)X$ | ... | $(W_m,w_m+t_2)X$ | ... | $(W_i,w_i+t_2)X$ |
| ... | ... | ... | ... | ... | ... |
| $(I,t_j)X$ | $(W_2,w_2+t_j)X$ | ... | $(W_m,w_m+t_j)X$ | ... | $(W_i,w_i+t_j)X$ |
| ... | ... | ... | ... | ... | ... |

# Example: Calculation of the Site-symmetry groups

## Group P-1




**Positions**

| Multiplicity, | Wyckoff letter, | Site symmetry | Coordinates | |
|---|---|---|---|---|
| 2 | $i$ | 1 | (1) $x, y, z$ | (2) $\bar{x}, \bar{y}, \bar{z}$ |
| 1 | $h$ | $\bar{1}$ | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ | |
| 1 | $g$ | $\bar{1}$ | $0, \frac{1}{2}, \frac{1}{2}$ | |
| 1 | $f$ | $\bar{1}$ | $\frac{1}{2}, 0, \frac{1}{2}$ | |
| 1 | $e$ | $\bar{1}$ | $\frac{1}{2}, \frac{1}{2}, 0$ | |
| 1 | $d$ | $\bar{1}$ | $\frac{1}{2}, 0, 0$ | |
| 1 | $c$ | $\bar{1}$ | $0, \frac{1}{2}, 0$ | |
| 1 | $b$ | $\bar{1}$ | $0, 0, \frac{1}{2}$ | |
| 1 | $a$ | $\bar{1}$ | $0, 0, 0$ | |

$S=\{(W,w), (W,w)X_o = X_o\}$

$$\left(\begin{bmatrix} -1 & & \\ & -1 & \\ & & -1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}\right) \begin{bmatrix} 1/2 \\ 0 \\ 1/2 \end{bmatrix} = \begin{bmatrix} -1/2 \\ 0 \\ -1/2 \end{bmatrix}$$

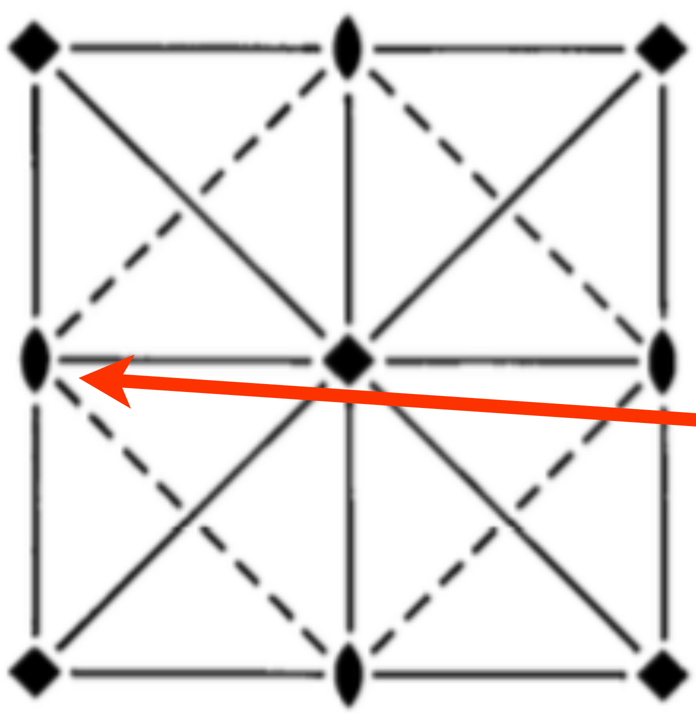
$S_f=\{(1,0), (-1,101)X_f = X_f\}$

$S_f \simeq \{1, -1\}$ isomorphic

EXERCISES

# General and special Wyckoff positions of P4mm

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | *g* | 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{y},x,z$ | (4) $y,\bar{x},z$ |
| | | | (5) $x,\bar{y},z$ | (6) $\bar{x},y,z$ | (7) $\bar{y},\bar{x},z$ | (8) $y,x,z$ |
| 4 | *f* | . *m* . | $x,\frac{1}{2},z$ | $\bar{x},\frac{1}{2},z$ | $\frac{1}{2},x,z$ | $\frac{1}{2},\bar{x},z$ |
| 4 | *e* | . *m* . | $x,0,z$ | $\bar{x},0,z$ | $0,x,z$ | $0,\bar{x},z$ |
| 4 | *d* | . . *m* | $x,x,z$ | $\bar{x},\bar{x},z$ | $\bar{x},x,z$ | $x,\bar{x},z$ |
| 2 | *c* | 2 *m m* . | $\frac{1}{2},0,z$ | $0,\frac{1}{2},z$ | | |
| 1 | *b* | 4 *m m* | $\frac{1}{2},\frac{1}{2},z$ | | | |
| 1 | *a* | 4 *m m* | $0,0,z$ | | | |



**Symmetry operations**

| | | | |
|---|---|---|---|
| (1) 1 | (2) 2 $0,0,z$ | (3) $4^+$ $0,0,z$ | (4) $4^-$ $0,0,z$ |
| (5) *m* $x,0,z$ | (6) *m* $0,y,z$ | (7) *m* $x,\bar{x},z$ | (8) *m* $x,x,z$ |

# MAXIMAL SUBGROUPS OF SPACE GROUPS

# I. MAXIMAL TRANSLATIONENGLEICHE SUBGROUPS

# 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

# Coset decomposition G:H

## Group-subgroup pair H < G

left coset decomposition

$G=H+g_2H+...+g_mH$, $g_i \notin H$,
m=index of H in G

right coset decomposition

$G=H+Hg_2+...+Hg_m$, $g_i \notin H$
m=index of H in G

**Normal subgroups**

$Hg_j= g_jH$, for all $g_j=1, ..., [i]$

# Subgroups of Space groups

## Coset decomposition $G:T_G$

| | | | | | |
|---|---|---|---|---|---|
| $(I,0)$ | $(W_2,w_2)$ | ... | $(W_m,w_m)$ | ... | $(W_i,w_i)$ |
| $(I,t_1)$ | $(W_2,w_2+t_1)$ | ... | $(W_m,w_m+t_1)$ | ... | $(W_i,w_i+t_1)$ |
| $(I,t_2)$ | $(W_2,w_2+t_2)$ | ... | $(W_m,w_m+t_2)$ | ... | $(W_i,w_i+t_2)$ |
| ... | ... | ... | ... | ... | ... |
| $(I,t_j)$ | $(W_2,w_2+t_j)$ | ... | $(W_m,w_m+t_j)$ | ... | $(W_i,w_i+t_j)$ |
| ... | ... | ... | ... | ... | ... |

## Factor group $G/T_G$

isomorphic to the point group $P_G$ of $G$

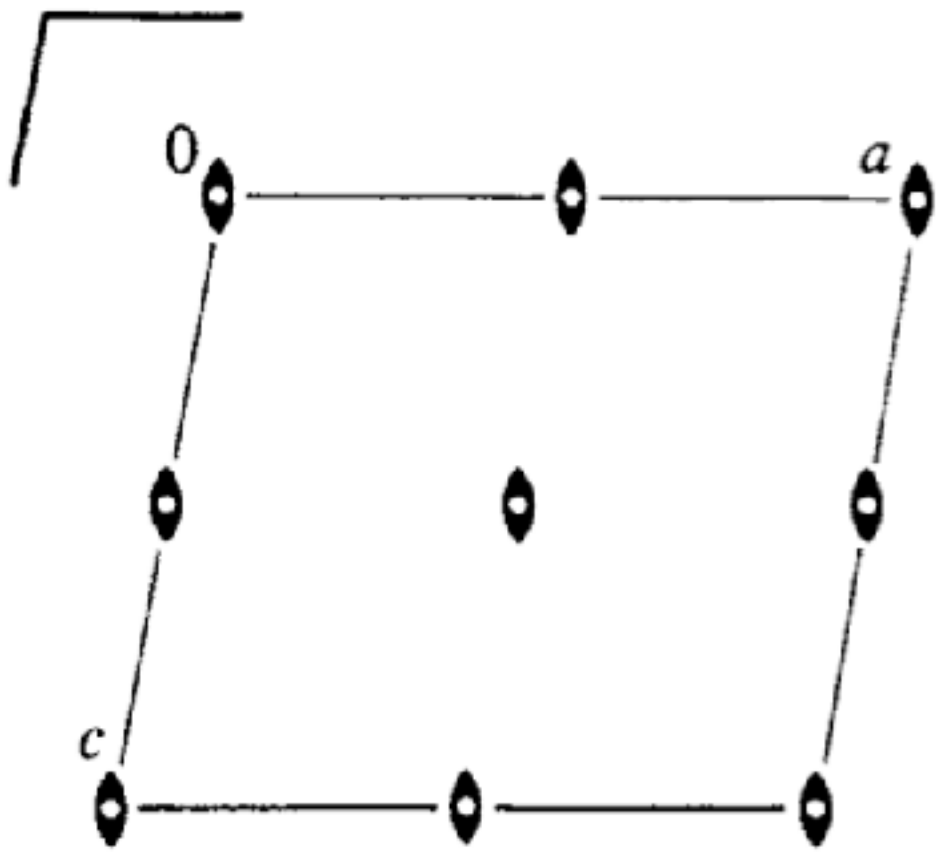
Point group $P_G = \{I, W_2, W_3, \ldots, W_i\}$

# Example: P12/m1

## Coset decomposition G:$T_G$

## Factor group $G/T_G \simeq P_G$

$P_G = \{1, 2, \bar{1}, m\}$




| $T_G$ | $T_G\,2$ | $T_G\,\bar{1}$ | $T_G\,m$ |
|---|---|---|---|
| $(1,0)$ | $(2,0)$ | $(\bar{1},0)$ | $(m,0)$ |
| $(1,t_1)$ | $(2,t_1)$ | $(\bar{1}, t_1)$ | $(m, t_1)$ |
| $(1,t_2)$ | $(2,t_2)$ | $(\bar{1}, t_2)$ | $(m,t_2)$ |
| ... | ... | ... | ... |
| $(1,t_j)$ | $(2,t_j)$ | $(\bar{1}, t_j)$ | $(m, t_j)$ |
| ... | ... | ... | ... |

inversion centres $(\bar{1},t)$:

$$\left(\begin{array}{ccc} -1 & & \\ & -1 & \\ & & -1 \end{array}\right) \left(\begin{array}{c} n_1 \\ n_2 \\ n_3 \end{array}\right) \xrightarrow{\bar{1}\ \text{at}} \left(\begin{array}{c} n_1/2 \\ n_2/2 \\ n_3/2 \end{array}\right)$$

## Translationengleche subgroups H<G: $\begin{cases} T_H = T_G \\ P_H < P_G \end{cases}$

### Example: P12/m1

Coset decomposition

| $T_G$ | $T_G\,2$ | $T_G\,\bar{1}$ | $T_G\,m$ |
|---|---|---|---|
| $(1,0)$ | $(2,0)$ | $(\bar{1},0)$ | $(m,0)$ |
| $(1,t_1)$ | $(2,t_1)$ | $(\bar{1}, t_1)$ | $(m, t_1)$ |
| $(1,t_2)$ | $(2,t_2)$ | $(\bar{1}, t_2)$ | $(m,t_2)$ |
| ... | ... | ... | ... |
| $(1,t_j)$ | $(2,t_j)$ | $(\bar{1}, t_j)$ | $(m, t_j)$ |
| ... | ... | ... | ... |

*t*-subgroups:

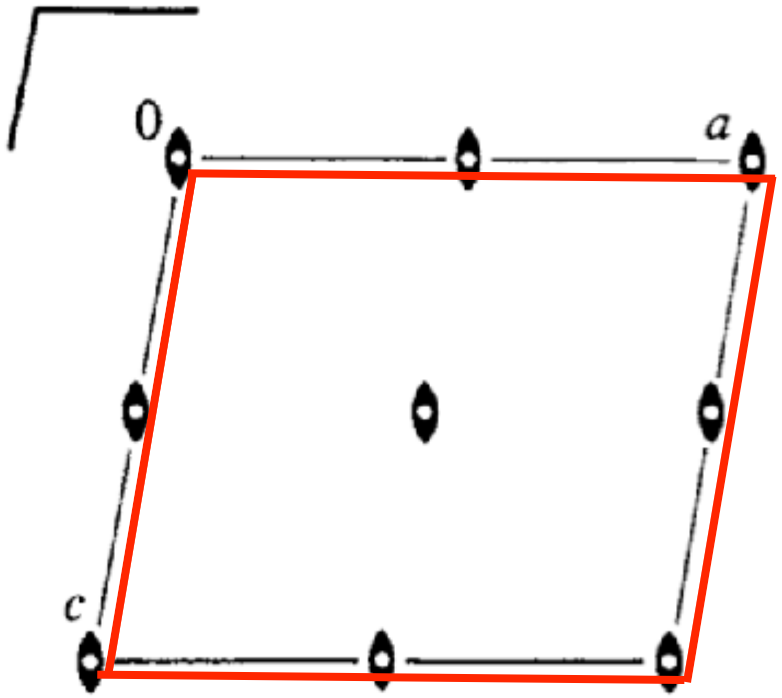
$H_1 = T_G \cup T_G 2$
P121

$H_2 = T_G \cup T_G \bar{1}$

$H_3 = T_G \cup T_G\, m$
Pm

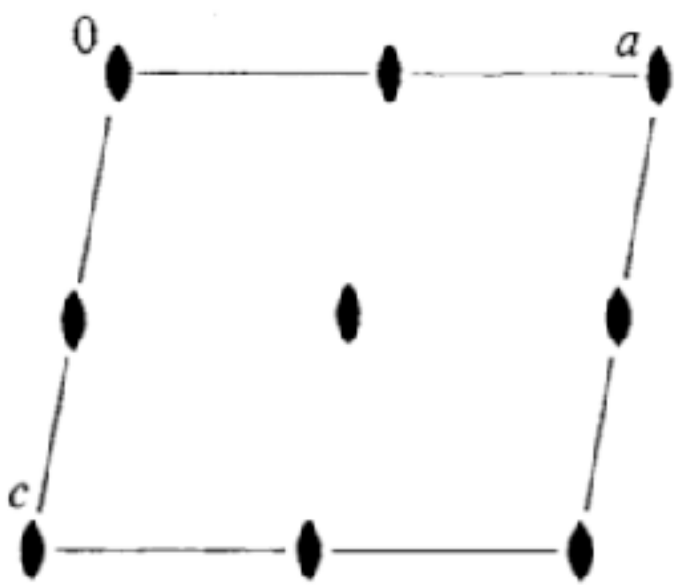
Example: P12/m1

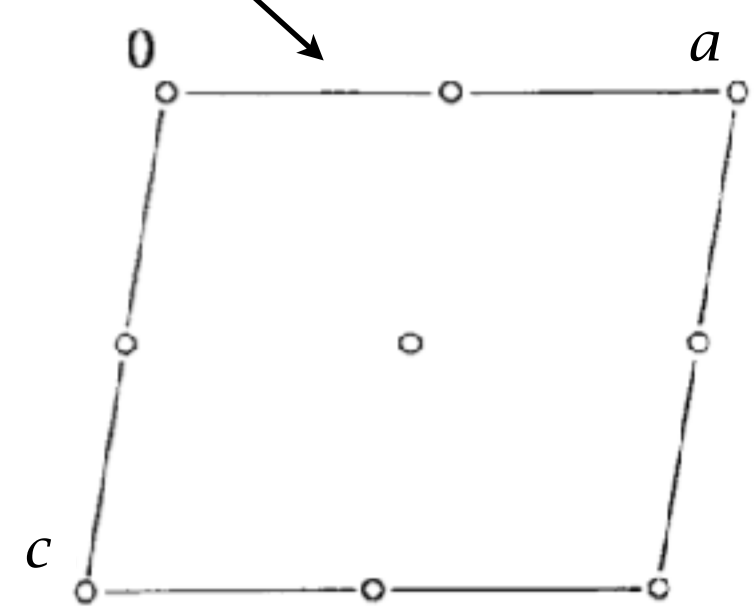
Translationengleche subgroups H<G:




$P\bar{1} = T_G \cup T_G \bar{1}$

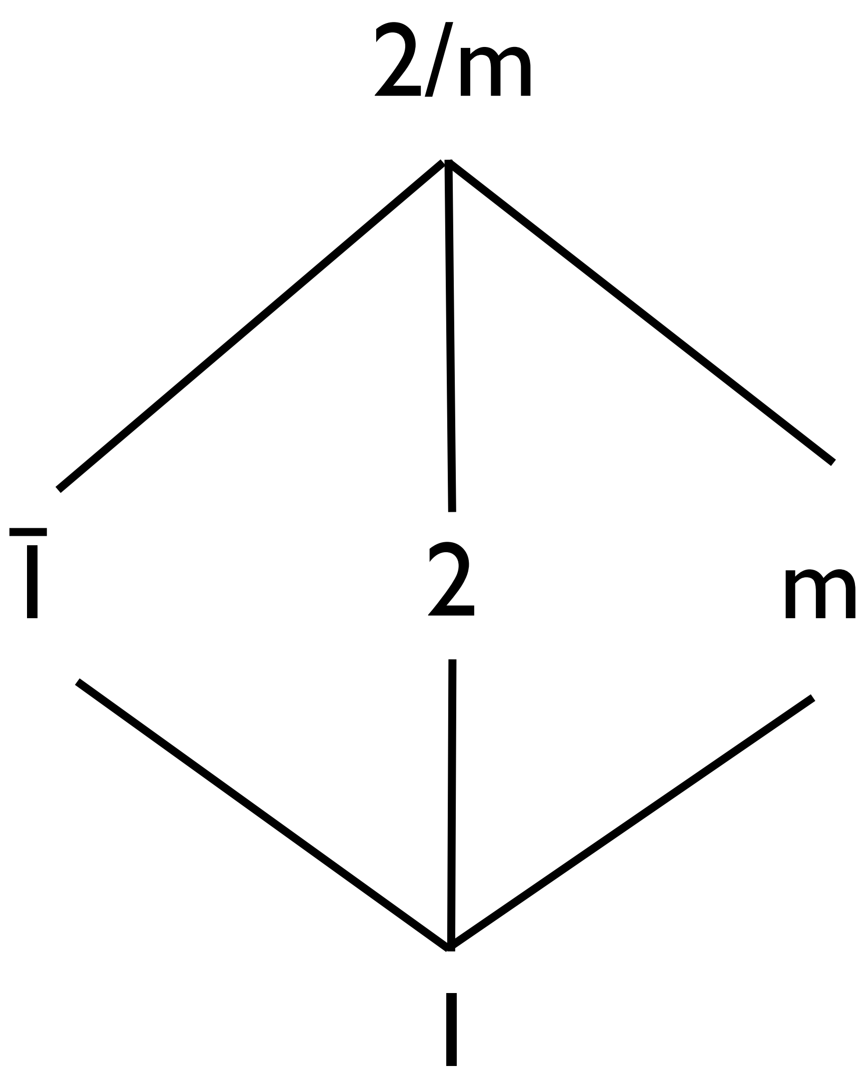
P121 $= T_G \cup T_G 2$



## Example: P12/m1

## Translationengleche subgroups H<G:

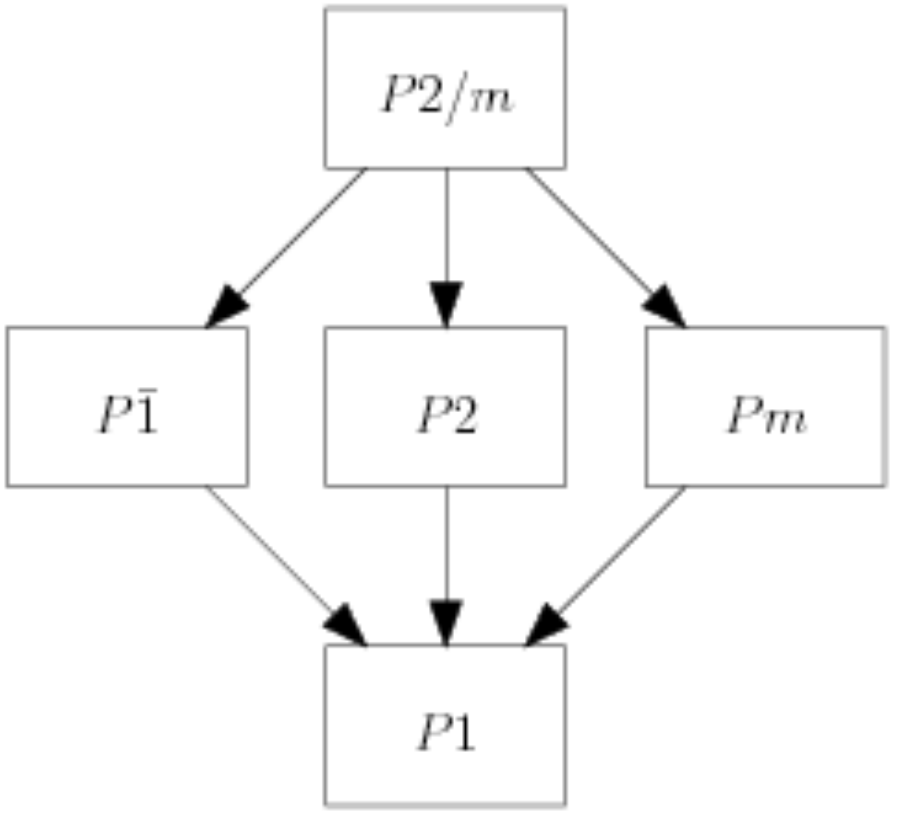



index

[1]

[2]

[4]




Subgroup diagram of point group 2/m

*Translationengleiche* subgroups of space group *P*2/m

# EXERCISES

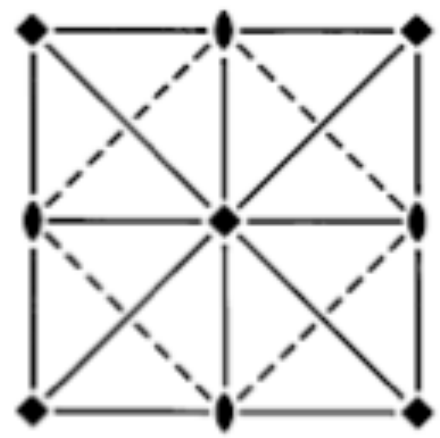
## Problem 2.3.1(a)

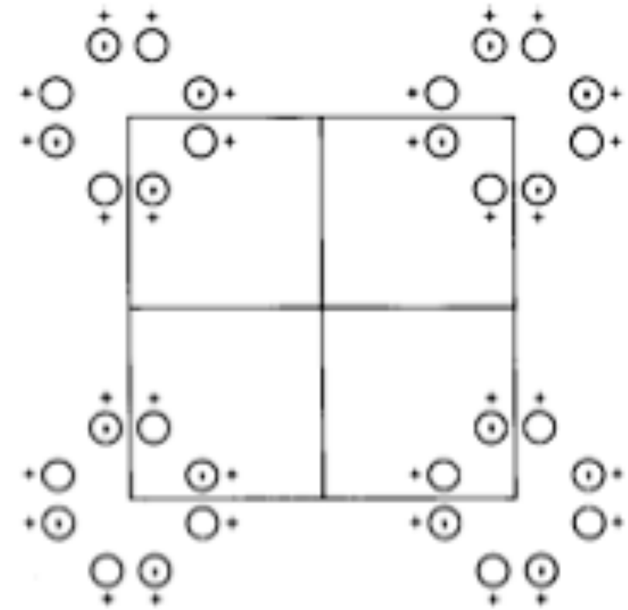
Construct the diagram of the *t*-subgroups of *P*4*mm* using the 'analogy' with the subgroup diagram of 4*mm*

*International Tables for Crystallography* (2006). Vol. A, Space group 99, pp. 382–383.

# *P*4*mm* $C_{4v}^1$ 4*mm* Tetragonal

No. 99 *P*4*mm* Patterson symmetry *P*4/*mmm*





**Origin** on 4*mm*

**Asymmetric unit** $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le 1$; $x \le y$

**Symmetry operations**

| | | | |
|---|---|---|---|
| (1) 1 | (2) 2 $0,0,z$ | (3) $4^+$ $0,0,z$ | (4) $4^-$ $0,0,z$ |
| (5) *m* $x,0,z$ | (6) *m* $0,y,z$ | (7) *m* $x,\bar{x},z$ | (8) *m* $x,x,z$ |

**Generators selected** (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

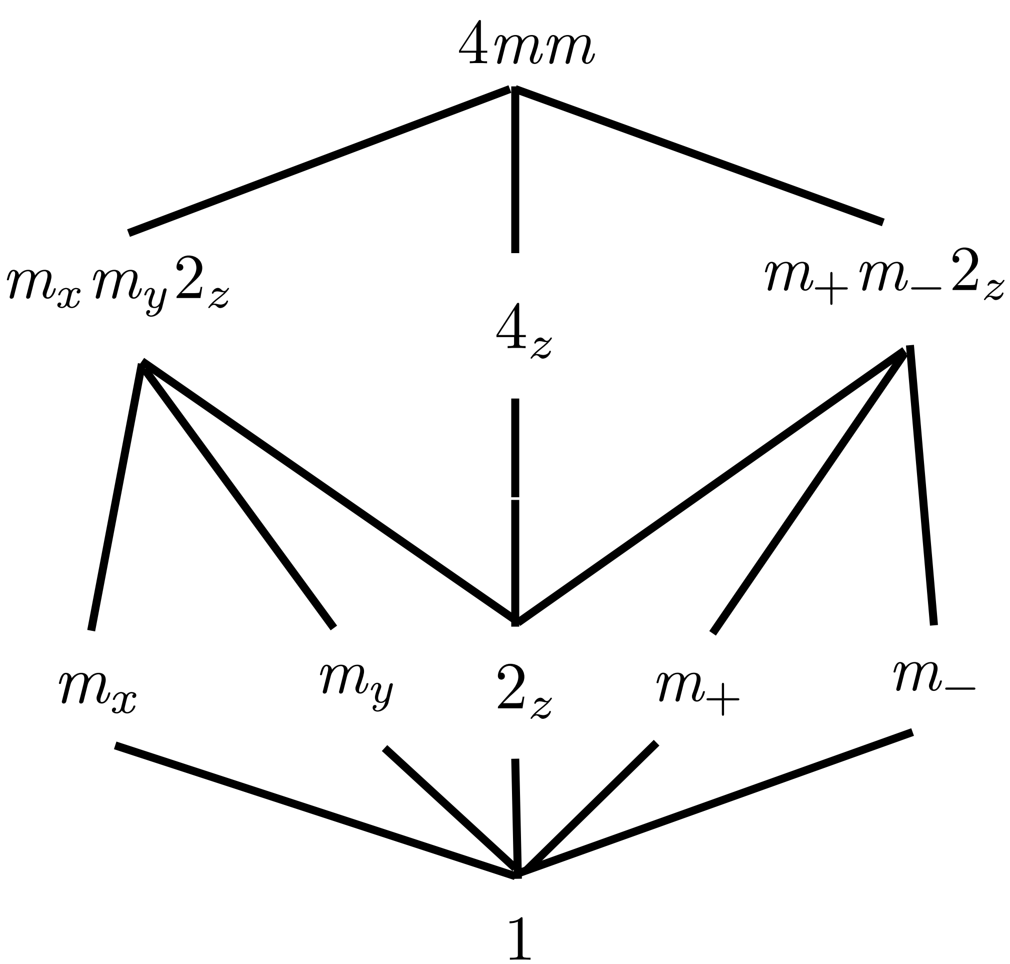
**Positions**

Multiplicity, Wyckoff letter, Site symmetry — Coordinates

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | *g* | 1 | (1) $x,y,z$ | (2) $\bar{x},\bar{y},z$ | (3) $\bar{y},x,z$ | (4) $y,\bar{x},z$ |
| | | | (5) $x,\bar{y},z$ | (6) $\bar{x},y,z$ | (7) $\bar{y},\bar{x},z$ | (8) $y,x,z$ |

# Problem 2.3.1

# SOLUTION



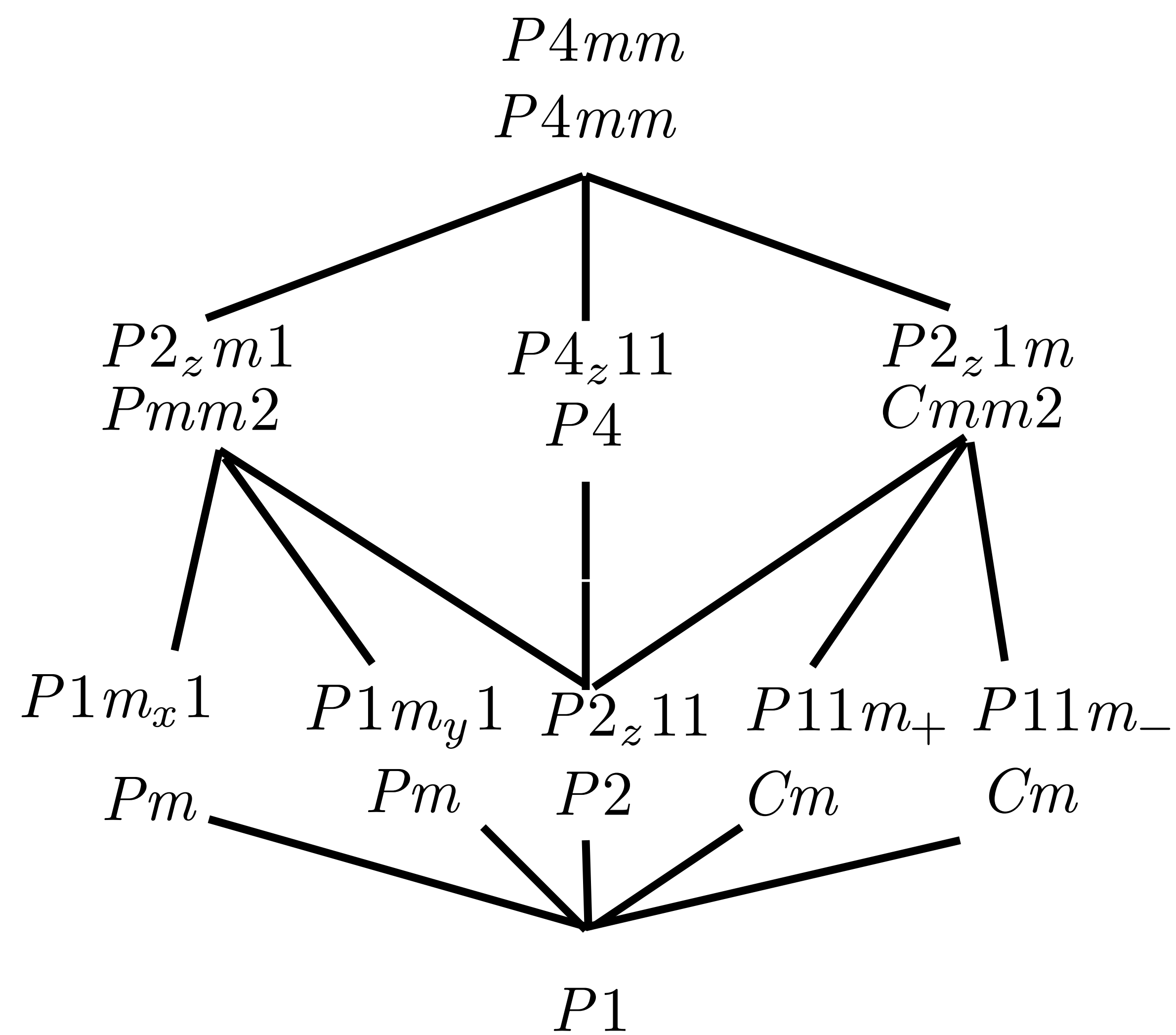

index

[1]

[2]

[4]

[8]

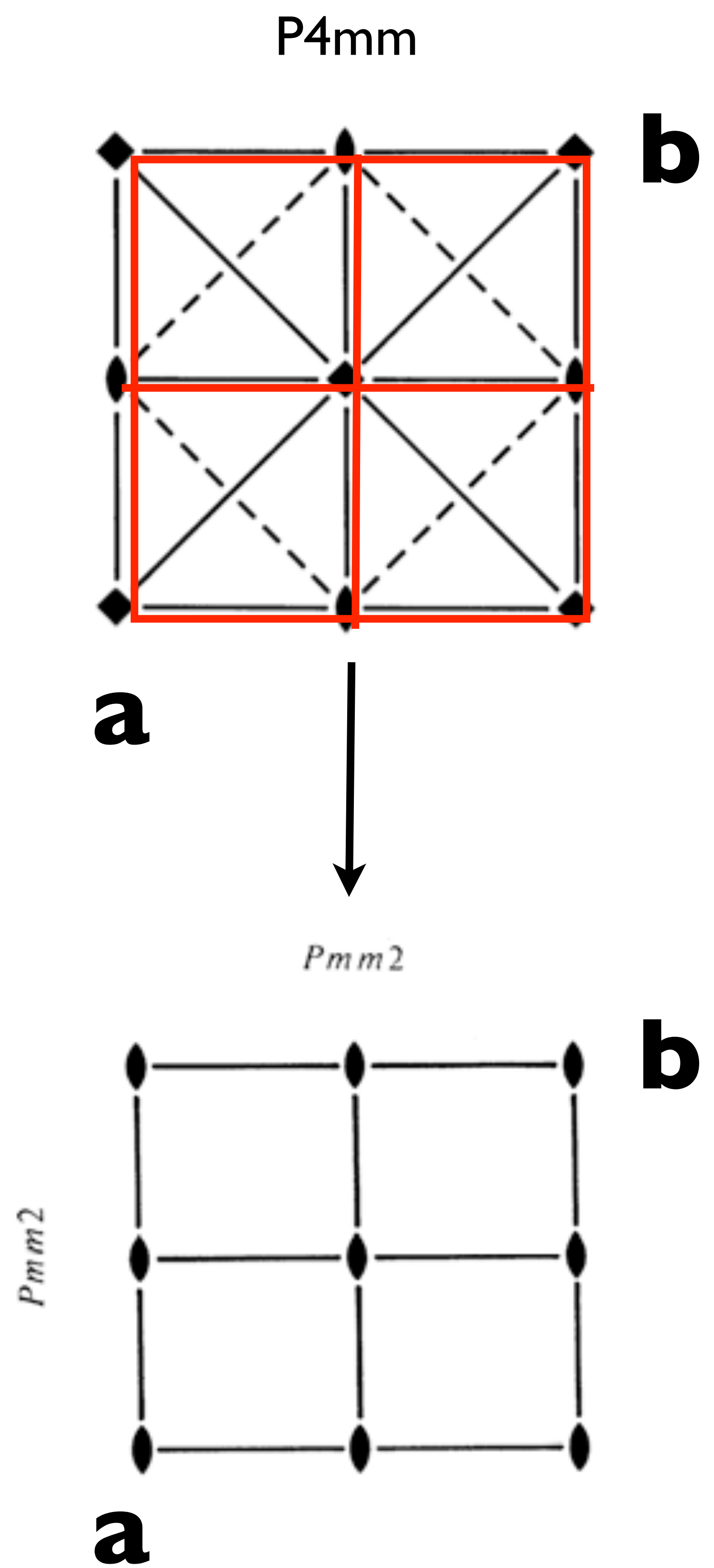


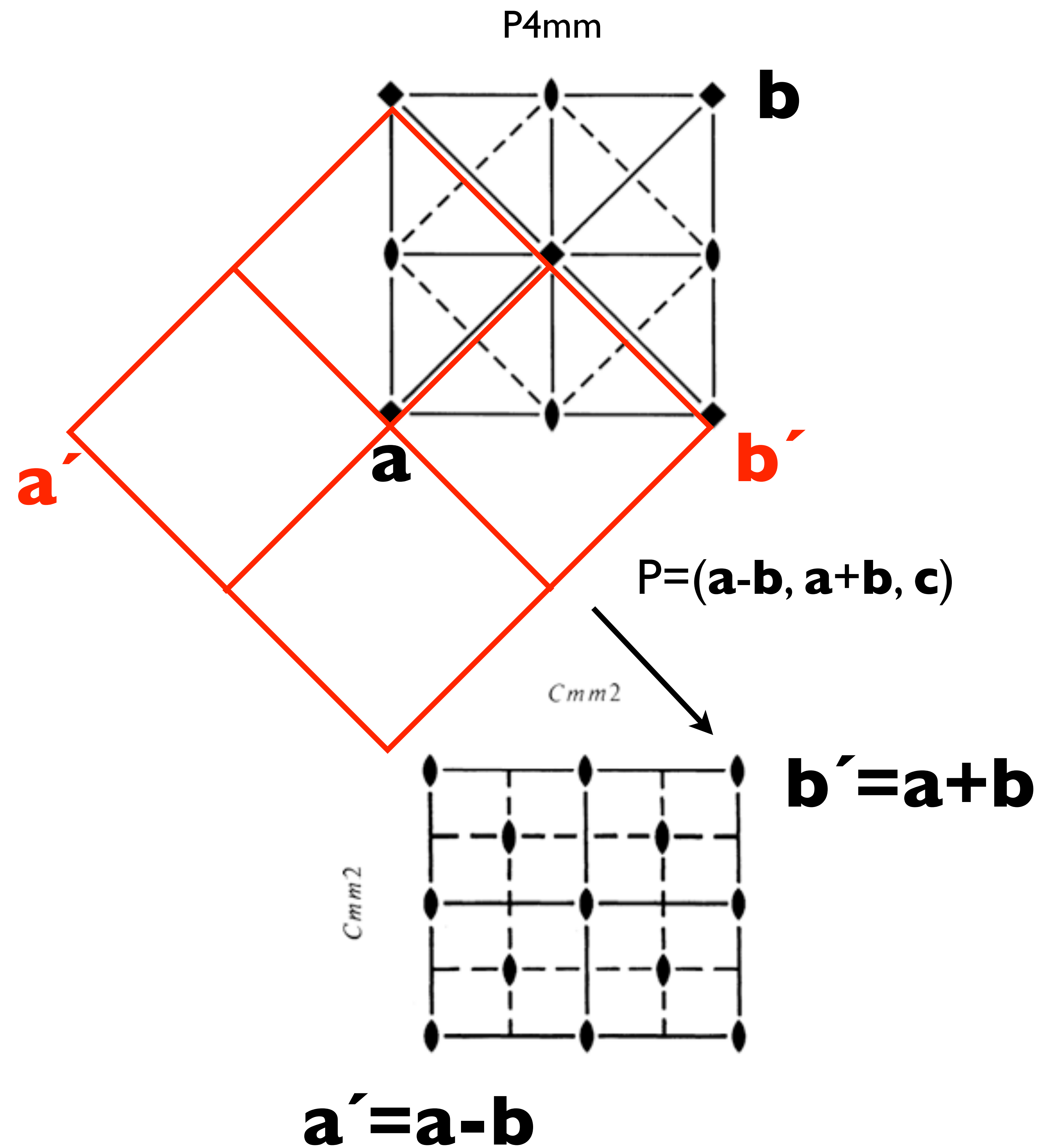

Subgroup diagram of point group *4mm*

*Translationengleiche* subgroups of space group *P4mm*

# Problem 2.3.1

# SOLUTION

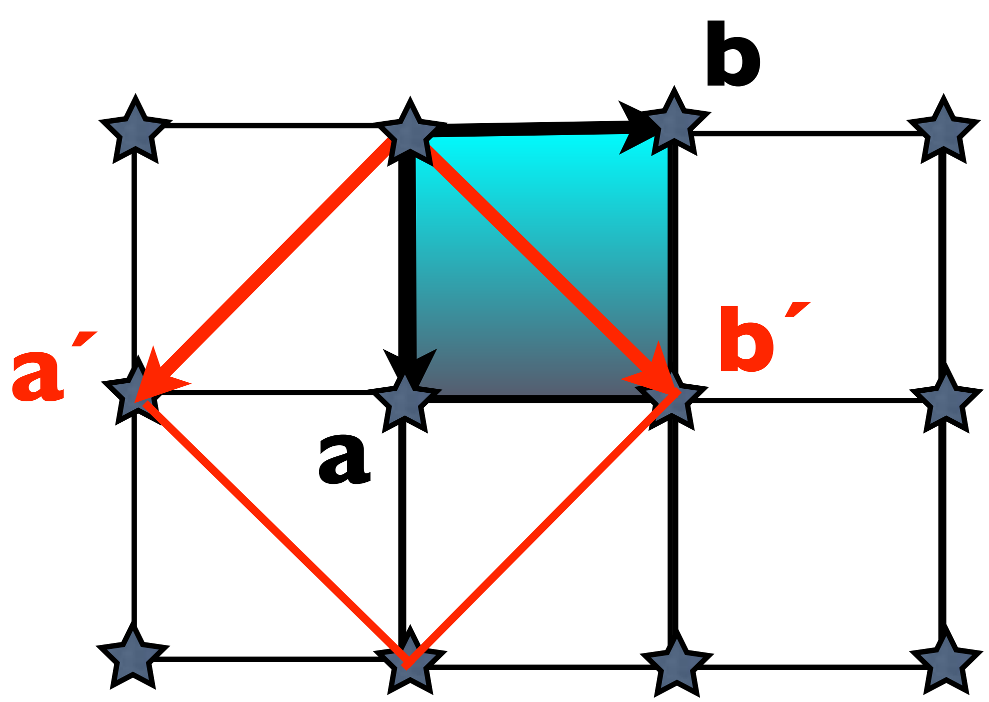


# Problem 2.3.1

# SOLUTION

*Remark 1.* Due to the convention to choose the basis vectors parallel to the rotation axes, $C$-centered cells appear although the translation lattice has not changed. If the retained twofold axes are diagonal, the conventional basis vectors **a',b',c'** of the subgroup are **a' = a-b, b' = a+b, c' = c** with respect to the basis vectors **a,b,c** of $P4mm$. Referred to **a',b',c'** the cell is $C$-centered.




**P**rimitive

**a'=a-b**

**b'=a+b**

**C**entred

*International Tables for Crystallography*, Vol. A1

eds. H. Wondratschek, U. Mueller

Example: P4mm

## Maximal subgroups of space groups

$C_{4v}^{1}$ | $P4mm$ | No. 99 | $P4mm$

**I Maximal *translationengleiche* subgroups**

| | | |
|---|---|---|
| [2] $P411$ (75, $P4$) | 1; 2; 3; 4 | |
| [2] $P21m$ (35, $Cmm2$) | 1; 2; 7; 8 | $\mathbf{a}-\mathbf{b}, \mathbf{a}+\mathbf{b}, \mathbf{c}$ |
| [2] $P2m1$ (25, $Pmm2$) | 1; 2; 5; 6 | |

**II Maximal *klassengleiche* subgroups**

- **Enlarged unit cell**

[2] $\mathbf{c}' = 2\mathbf{c}$

| | | |
|---|---|---|
| $P4_2mc$ (105) | $\langle 2;\ 5;\ 3+(0,0,1)\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |
| $P4cc$ (103) | $\langle 2;\ 3;\ 5+(0,0,1)\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |
| $P4_2cm$ (101) | $\langle 2;\ (3;\ 5)+(0,0,1)\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |
| $P4mm$ (99) | $\langle 2;\ 3;\ 5\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |

- **Series of maximal isomorphic subgroups**

[$p$] $\mathbf{c}' = p\mathbf{c}$

| | | | |
|---|---|---|---|
| $P4mm$ (99) | $\langle 2;\ 3;\ 5\rangle$<br>$p > 1$<br>no conjugate subgroups | $\mathbf{a}, \mathbf{b}, p\mathbf{c}$ | |

[$p^2$] $\mathbf{a}' = p\mathbf{a}$, $\mathbf{b}' = p\mathbf{b}$

| | | | |
|---|---|---|---|
| $P4mm$ (99) | $\langle 2+(2u,2v,0);\ 3+(u+v,-u+v,0);\ 5+(0,2v,0)\rangle$<br>$p > 2;\ 0 \le u < p;\ 0 \le v < p$<br>$p^2$ conjugate subgroups for the prime $p$ | $p\mathbf{a}, p\mathbf{b}, \mathbf{c}$ | $u, v, 0$ |

DATA ITA1: Maximal Subgroups

## Transformation matrix: (P,p)

group G $\{e, g_2, g_3, \ldots, g_i, \ldots, g_{n-1}, g_n\}$

subgroup H<G
non-conventional $\{e, \ldots\ldots, g_3, \ldots, g_i, \ldots\ldots\ldots, g_n\}$

**(P,p)**

subgroup H<G $\{e, h_2, h_3, \ldots, h_m\}$

Subgroup specification: HM symbol, [i], (P,p)

# MAXIMAL SUBGROUPS OF SPACE GROUPS

# II. MAXIMAL KLASSENGLEICHE SUBGROUPS

# Klassengleiche subgroups H<G:

$\begin{cases} T_H < T_G \\ P_H = P_G \end{cases}$

## Example: P1

$\boldsymbol{t}$=u$\boldsymbol{a}$+v$\boldsymbol{b}$+w$\boldsymbol{c}$

Coset decomposition

$T_e = \{\boldsymbol{t}(u=2n,v,w)\}$

$\boldsymbol{t}_a(a,0,0)$

| $T_e$ | $T_e\, t_a$ |
|---|---|
| (I,0) | (I,$t_a$) |
| (I,$t_1$) | (I,$t_1+t_a$) |
| (I,$t_2$) | (I,$t_2+t_a$) |
| ... | ... |
| (I,$t_j$) | (I,$t_j+t_a$) |
| ... | ... |

$H=T_e$

## isomorphic *k*-subgroups:

P1(2$\boldsymbol{a}$,$\boldsymbol{b}$,$\boldsymbol{c}$)

## Klassengleiche subgroups H<G:

## Subgroups of space groups

$$\begin{cases} T_H < T_G \\ P_H = P_G \end{cases}$$

**Example: P1**

$\boldsymbol{t} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$

$H = T_e \qquad t_a(1,0,0)$

## Coset decomposition

$P1 = T_e + T_e t_a$

$T_e = \{t(u = 2n, v, w)\}$

| $T_e$ | $T_e t_a$ |
|---|---|
| (I,0) | $(I, t_a)$ |
| $(I, t_1)$ | $(I, t_1 + t_a)$ |
| $(I, t_2)$ | $(I, t_2 + t_a)$ |
| ... | ... |
| $(I, t_j)$ | $(I, t_j + t_a)$ |
| ... | ... |

## Isomorphic *k*-subgroup:

$P1(2\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$

## Series of isomorphic *k*-subgroups:

$P1(p\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$: p>1, prime

$P1(\boldsymbol{a}, q\boldsymbol{b}, \boldsymbol{c})$: q>1, prime

... *etc.*

**INFINITE** number of maximal isomorphic subgroups

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Example: P-1

# Series of maximal isomorphic subgroups

$P\bar{1}$ No. 2 $P\bar{1}$

• **Series of maximal isomorphic subgroups**

[$p$] $\mathbf{a}' = p\mathbf{a}$, $\mathbf{b}' = q\mathbf{a}+\mathbf{b}$, $\mathbf{c}' = r\mathbf{a}+\mathbf{c}$

| | | | |
|---|---|---|---|
| $P\bar{1}$ (2) | $\langle 2+(2u,0,0)\rangle$<br>$p>2$; $0\le q<p$; $0\le r<p$; $0\le u<p$<br>$p$ conjugate subgroups for each triplet of $q$, $r$, and prime $p$ | $p\mathbf{a}, q\mathbf{a}+\mathbf{b}, r\mathbf{a}+\mathbf{c}$ | $u,0,0$ |

[$p$] $\mathbf{b}' = p\mathbf{b}$, $\mathbf{c}' = q\mathbf{b}+\mathbf{c}$

| | | | |
|---|---|---|---|
| $P\bar{1}$ (2) | $\langle 2+(0,2u,0)\rangle$<br>$p>2$; $0\le q<p$; $0\le u<p$<br>$p$ conjugate subgroups for each pair of $q$ and prime $p$ | $\mathbf{a}, p\mathbf{b}, q\mathbf{b}+\mathbf{c}$ | $0,u,0$ |

[$p$] $\mathbf{c}' = p\mathbf{c}$

| | | | |
|---|---|---|---|
| $P\bar{1}$ (2) | $\langle 2+(0,0,2u)\rangle$<br>$p>2$; $0\le u<p$<br>$p$ conjugate subgroups for the prime $p$ | $\mathbf{a}, \mathbf{b}, p\mathbf{c}$ | $0,0,u$ |

# Klassengleiche subgroups H<G: **non-isomorphic**

$$\begin{cases} T_H < T_G \\ P_H = P_G \end{cases}$$

## Example: C2

## Coset decomposition

$C2 = T_c + T_c 2$

$(T_i + T_i t_c)$

$t_i$=integer

$t_c$=1/2,1/2,0

| $T_i$ | $T_i t_c$ | $T_i\,2$ | $T_i t_c\,2$ |
|---|---|---|---|
| (1,0) | $(1,t_c)$ | (2, 0) | $(2,t_c)$ |
| $(1,t_1)$ | $(1,t_1+t_c)$ | $(2, t_1)$ | $(2, t_1+t_c)$ |
| $(1,t_2)$ | $(1,t_2+t_c)$ | $(2, t_2)$ | $(2, t_2+t_c)$ |
| ... | ... | ... | ... |
| $(1,t_j)$ | $(1,t_j+t_c)$ | $(2, t_j)$ | $(2, t_j+t_c)$ |
| ... | ... | ... | ... |

## non-isomorphic *k*-subgroups:

$H_1 = T_i \cup T_i 2$

P2

$H_2 = T_i \cup T_i t_c\,2$

$P2_1$

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# Example: P4mm

## Maximal subgroups of space groups

$C_{4v}^1$ | $P4mm$ | No. 99 | $P4mm$

**I Maximal *translationengleiche* subgroups**

| | | |
|---|---|---|
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| [2] $P21m$ (35, $Cmm2$) | 1; 2; 7; 8 | $\mathbf{a}-\mathbf{b}, \mathbf{a}+\mathbf{b}, \mathbf{c}$ |
| [2] $P2m1$ (25, $Pmm2$) | 1; 2; 5; 6 | |

**II Maximal *klassengleiche* subgroups**

- **Enlarged unit cell**

[2] $\mathbf{c}' = 2\mathbf{c}$

| | | |
|---|---|---|
| $P4_2mc$ (105) | $\langle 2;\ 5;\ 3+(0,0,1)\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |
| $P4cc$ (103) | $\langle 2;\ 3;\ 5+(0,0,1)\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |
| $P4_2cm$ (101) | $\langle 2;\ (3;\ 5)+(0,0,1)\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |
| $P4mm$ (99) | $\langle 2;\ 3;\ 5\rangle$ | $\mathbf{a}, \mathbf{b}, 2\mathbf{c}$ |

- **Series of maximal isomorphic subgroups**

[$p$] $\mathbf{c}' = p\mathbf{c}$

| | | | |
|---|---|---|---|
| $P4mm$ (99) | $\langle 2;\ 3;\ 5\rangle$<br>$p > 1$<br>no conjugate subgroups | $\mathbf{a}, \mathbf{b}, p\mathbf{c}$ | |

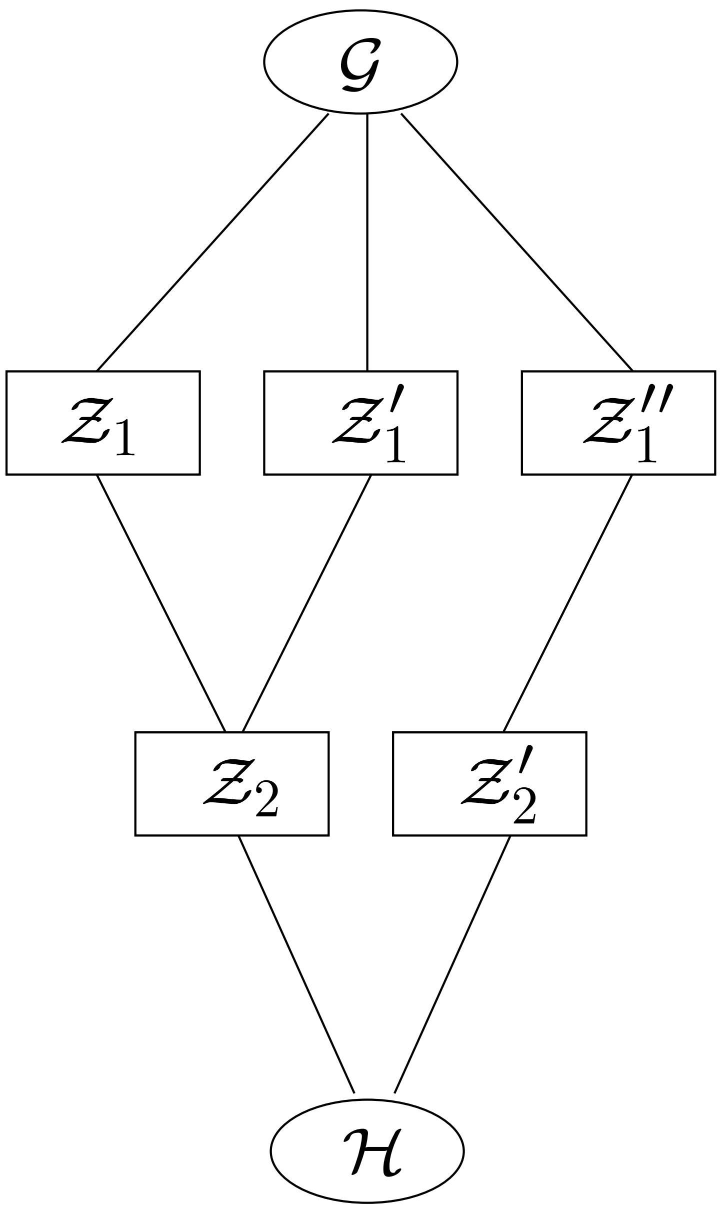
[$p^2$] $\mathbf{a}' = p\mathbf{a}$, $\mathbf{b}' = p\mathbf{b}$

| | | | |
|---|---|---|---|
| $P4mm$ (99) | $\langle 2+(2u,2v,0);\ 3+(u+v,-u+v,0);\ 5+(0,2v,0)\rangle$<br>$p > 2;\ 0 \le u < p;\ 0 \le v < p$<br>$p^2$ conjugate subgroups for the prime $p$ | $p\mathbf{a}, p\mathbf{b}, \mathbf{c}$ | $u, v, 0$ |

# GENERAL SUBGROUPS OF SPACE GROUPS

# General subgroups H<G:

## Graph of maximal subgroups




Group-subgroup pair

$$\mathcal{G} > \mathcal{H} \,:\, \mathcal{G},\ \mathcal{H},\ [i],\ (\mathrm{P},\mathbf{p})$$

Pairs: group - maximal subgroup

$$\mathcal{Z}_k > \mathcal{Z}_{k+1},\ (\mathrm{P},\mathbf{p})_k$$

$$(\mathrm{P},\mathbf{p}) = \prod_{k=1}^{n} (\mathrm{P},\mathbf{p})_k$$

# General subgroups H<G:

$$\begin{cases} T_H < T_G \\ P_H < P_G \end{cases}$$

## Theorem Hermann, 1929:

For each pair G>H, there exists a uniquely defined intermediate subgroup M, G ≧ M ≧ H, such that:

$$G \xrightarrow{i_P} M \xrightarrow{i_L} H$$

M is a *t*-subgroup of G

H is a *k*-subgroup of M

$$[i]=[i_P].[i_L]$$

## Corollary

A maximal subgroup is either a *t*- or *k*-subgroup

**PROBLEM:** **Domain-structure analysis**

$$G \xrightarrow{[i]} H$$

number of domain states

twins and antiphase domains states

twinning operation

symmetry groups of the domain states; multiplicity and degeneracy

# Phase transitions domain structures

Homogeneous (parent) phase G —symmetry reduction→ H Deformed (daughter) phase

Domain structure

**Domain**

A connected homogeneous part of a domain structure or of a twinned crystal is called a *domain*. Each domain is a single crystal.

The number of such crystals is not limited; they differ in their locations in space, in their orientations, in their shapes and in their space groups but all belong to the same space-group type of H.

**Domain states**

The domains belong to a finite (small) number of *domain states*.

Two domains belong to the same *domain state* if their crystal patterns are identical, *i.e.* if they occupy different regions of space that are part of the *same* crystal pattern.

The number of domain states which are observed after a phase transition is limited and determined by the group-subgroup relations of the space groups G and H.

# SUBGROUPS CALCULATIONS: HERMANN

## Hermann, 1929:

For each pair $\mathcal{G}>\mathcal{H}$, index [i], there exists a uniquely defined intermediate subgroup $\mathcal{M}$, $\mathcal{G} \geqq \mathcal{M} \geqq \mathcal{H}$, such that:

$\mathcal{M}$ is a *t-subgroup* of $\mathcal{G}$

$\mathcal{H}$ is a *k-subgroup* of $\mathcal{M}$

$\mathcal{G}$

↓ $i_P$

$\mathcal{M}$

↓ $i_L$

$\mathcal{H}$

with $[i]=[i_P].[i_L]$

$i_P=P_G/P_H$ twins

$i_L=Z_{H,p}/Z_{G,p}=V_{H,p}/V_{G,p}$ antiphase

EXAMPLE

Index [i] for a group-subgroup pair G>H

Lead vanadate $Pb_3(VO_4)_2$

INDEX: $[i]=[i_P].[i_L]$

$\mathcal{R}\text{-}3m$

$i_P=P_G/P_H$ ↓ **$[i_P]=3$**

$C2/m$

$i_L=Z_{H,p}/Z_{G,p}$ ↓ **$[i_L]=2$**

$\mathcal{P}2_1/c$

High-symmetry phase R-3m

**$Z_{G,p}=1$ $|P_G|=12$**

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb   1   3a   0.000000   0.000000   0.000000
Pb   2   6c   0.000000   0.000000   0.207100
PV   3   6c   0.000000   0.000000   0.388400
O    4   6c   0.000000   0.000000   0.324000
O    5   18i  0.842400   0.157600   0.430100
```

⇓

Low-symmetry phase $P2_1/c$

**$|P_H|=?$**

**$Z_{H,p}=?$**

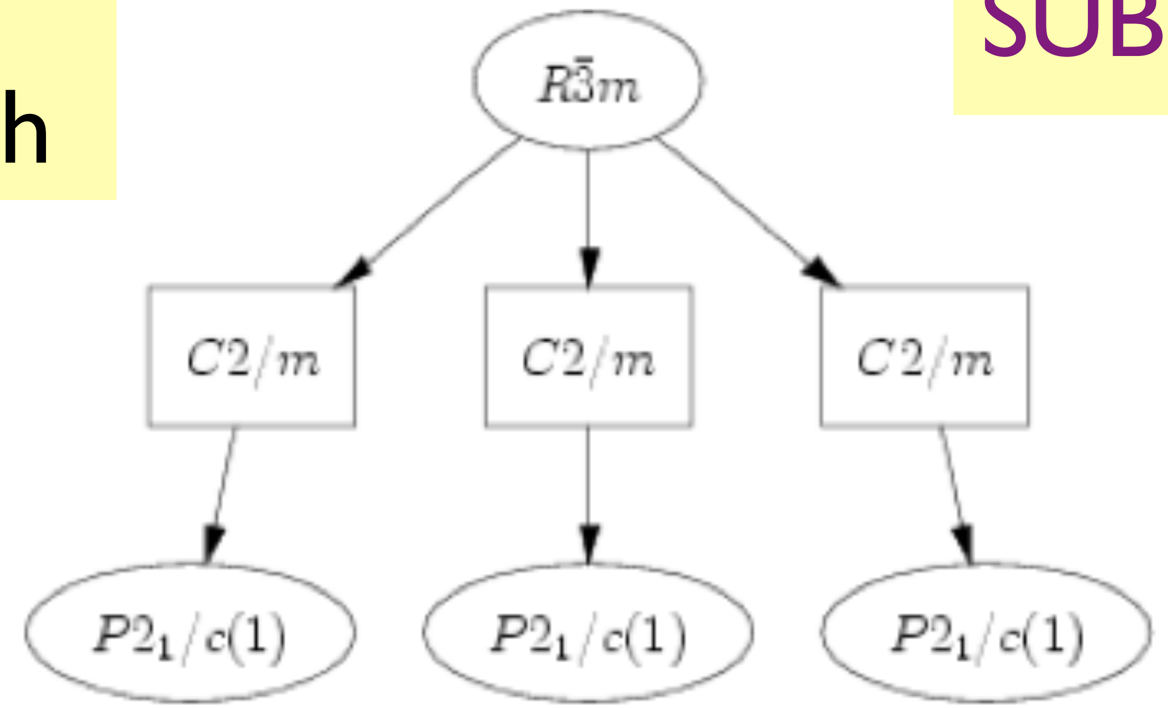
```
14
7.5075 6.0493 9.4814 90. 115.162 90.
7
Pb 1 2a 0 0 0
Pb 2 4e 0.3835 0.5815 0.2879
PV 1 4e 0.2071 0.0143 0.3999
O  1 4e 0.2872 0.2559 0.0159
O  2 4e 0.2598 0.7979 0.0216
O  3 4e 0.3194 0.9784 0.2823
O  4 4e 0.0335 0.5431 0.2091
```

# $Pb_3(VO_4)_2$: Ferroelastic Domains in $P2_1/c$ phase

## Group-Subgroup Lattice

Maximal-subgroup graph

SUBGROUPGRAPH



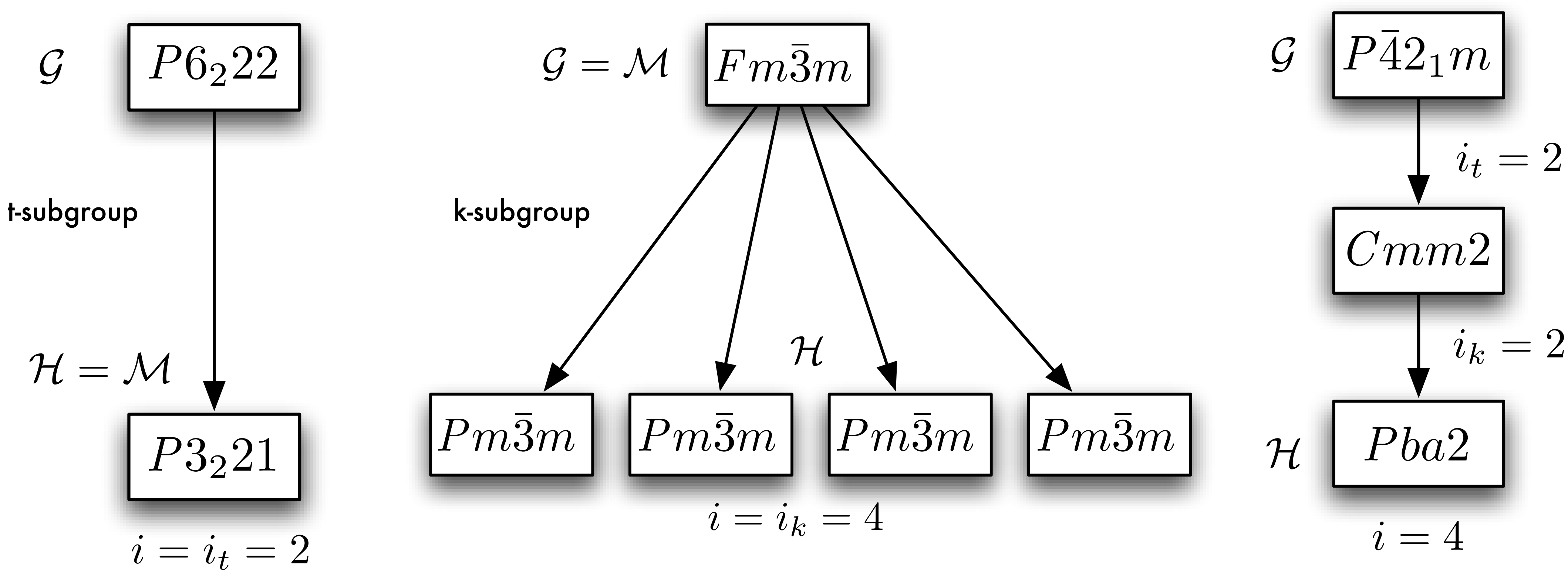

number of domain states= index [i] = $[i_P].[i_L]$=6

number of ferroelastic domain states: $i_P$ = 12:4=3

number of different subgroups $P2_1/c$: 3

# Problem: CLASSIFICATION OF DOMAINS — **HERMANN**

Quartz | $Cu_3Au$ | $Gd_2(MoO_4)_3$




twin domains

antiphase domains

twin and antiphase domains

EXERCISES

# Problem 2.3.3

(A) High symmetry phase: P2/m

Low symmetry phase: P1, small unit-cell deformation

How many and what kind of domain states?

*Hint*: Determine the index $[i]=[i_P].[i_L]$

(B) High symmetry phase: P2/m

Low symmetry phase: P1, duplication of the unit cell

How many and what kind of domain states?

(C) High symmetry phase: P4mm

Low symmetry phase: P2, index 8

How many and what kind of domain states?

(D) High symmetry phase: $P4_2bc$

Low symmetry phase: $P2_1$, index 8

How many and what kind of domain states?