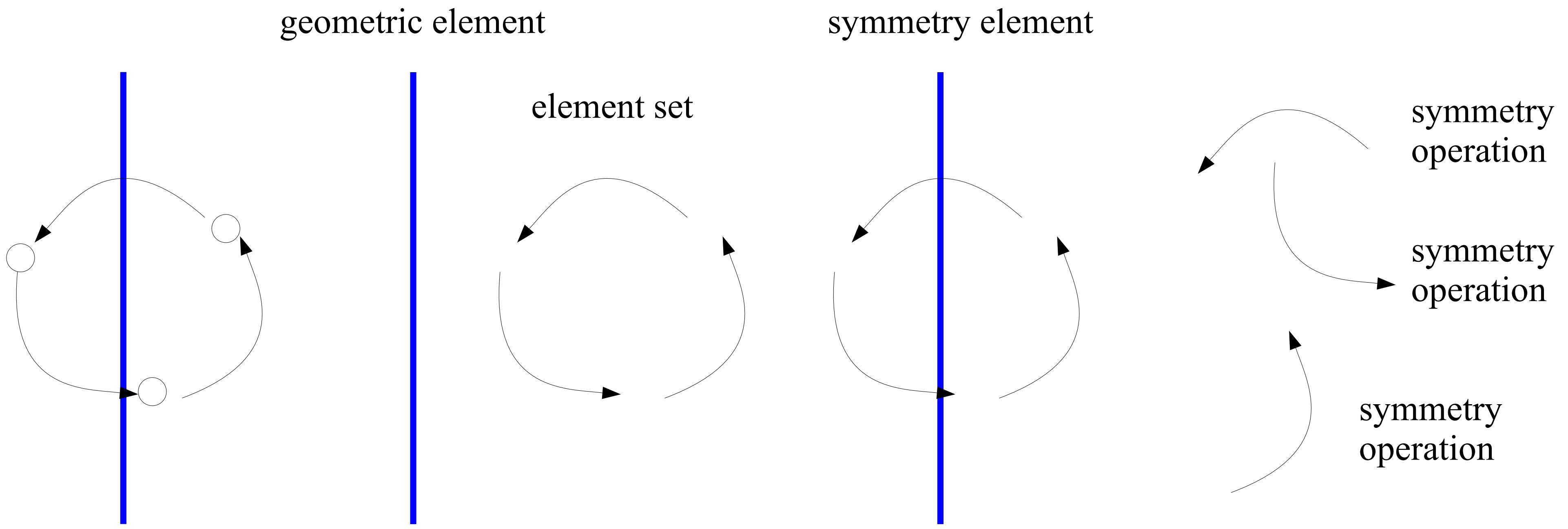
Introduction to space-group symmetry

Didactic material for the MaThCryst schools

Massimo Nespolo, Université de Lorraine, France
massimo.nespolo@univ-lorraine.fr

Elements and operations

- **geometric element** : the point, line or plane left invariant by the symmetry operation.
- **symmetry element**: the geometric element defined above together with the set of operations (called **element set**) that leave in invariant.
- **symmetry operation** : an isometry that leave invariant the object to which it is applied.



The operation that share a given geometric element differ by a lattice vector. The one characterized by the shortest vector is called **defining operation**.

Finding the geometric element

- Remove the intrinsic translation part (screw or glide component).
- Impose that the coordinates of the geometric element are fixed by the operation.

$$\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & \bar{1} & 1/2 \end{array}\right)$$

Intrinsic part: screw component

Location part: the element does not pass through the origin

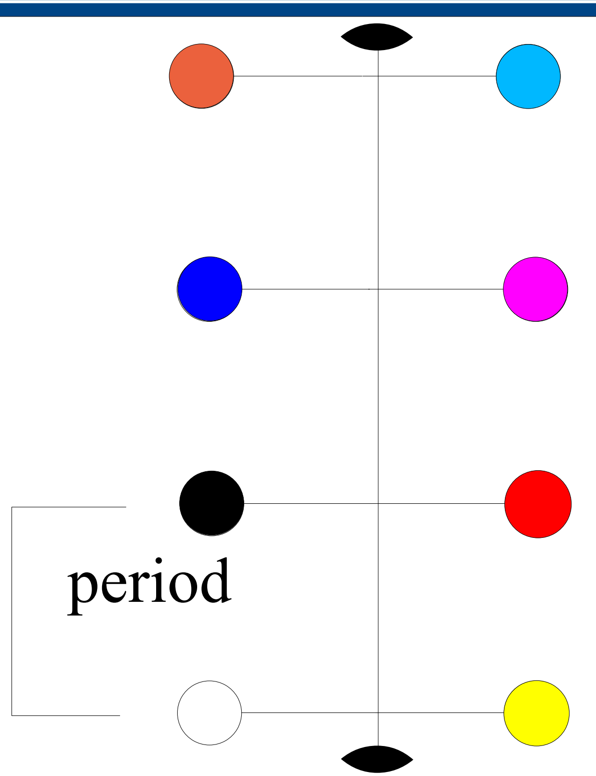
Linear part: twofold rotation about [010]

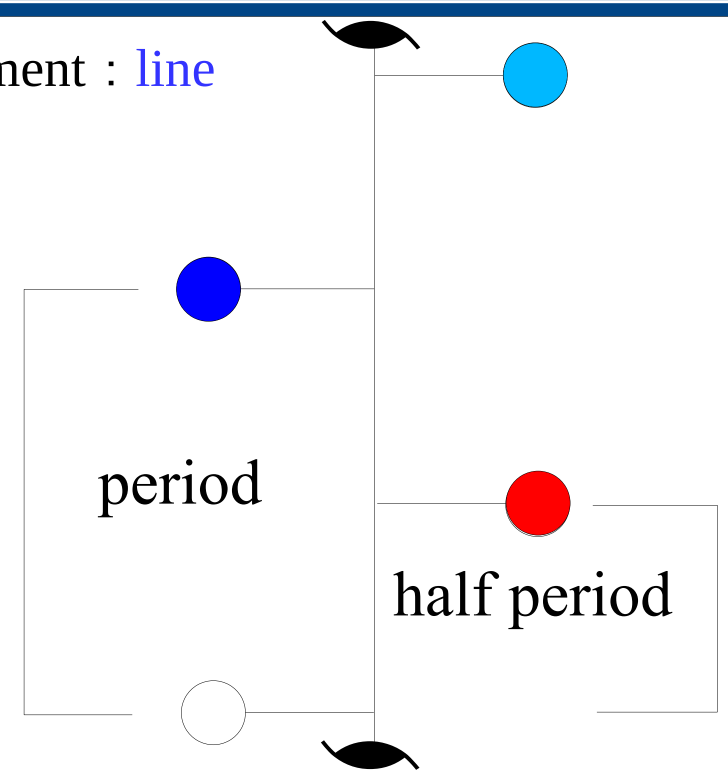
$$\left(\begin{array}{ccc|c} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 1/2 \end{array}\right)\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} u \\ v \\ w \end{pmatrix} \qquad \begin{cases} -u = u \\ v = v \\ -w + 1/2 = w \end{cases} \qquad \begin{cases} u = 0 \\ \forall v \\ w = 1/4 \end{cases} \qquad 0,y,\tfrac{1}{4}$$

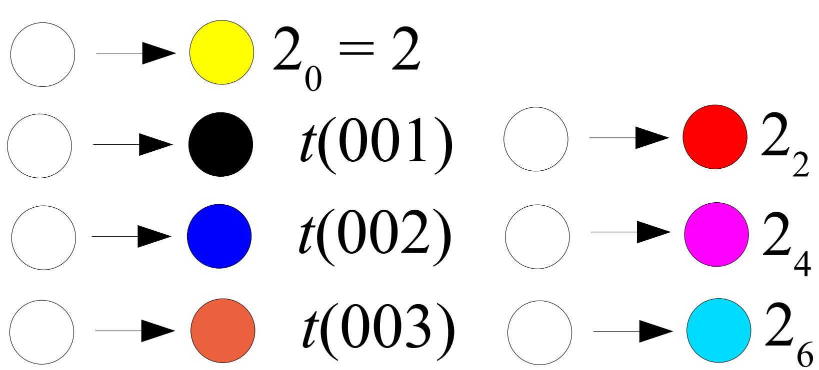
Screw axes n_p (screw component: p/n)

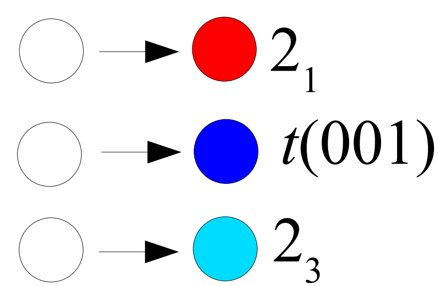
http://dx.doi.org/10.1002/crat.201600129

Geometric element : line









Defining operation : twofold rotation
Symmetry element : rotation axis

Defining operation : twofold screw rotation
Symmetry element : screw axis

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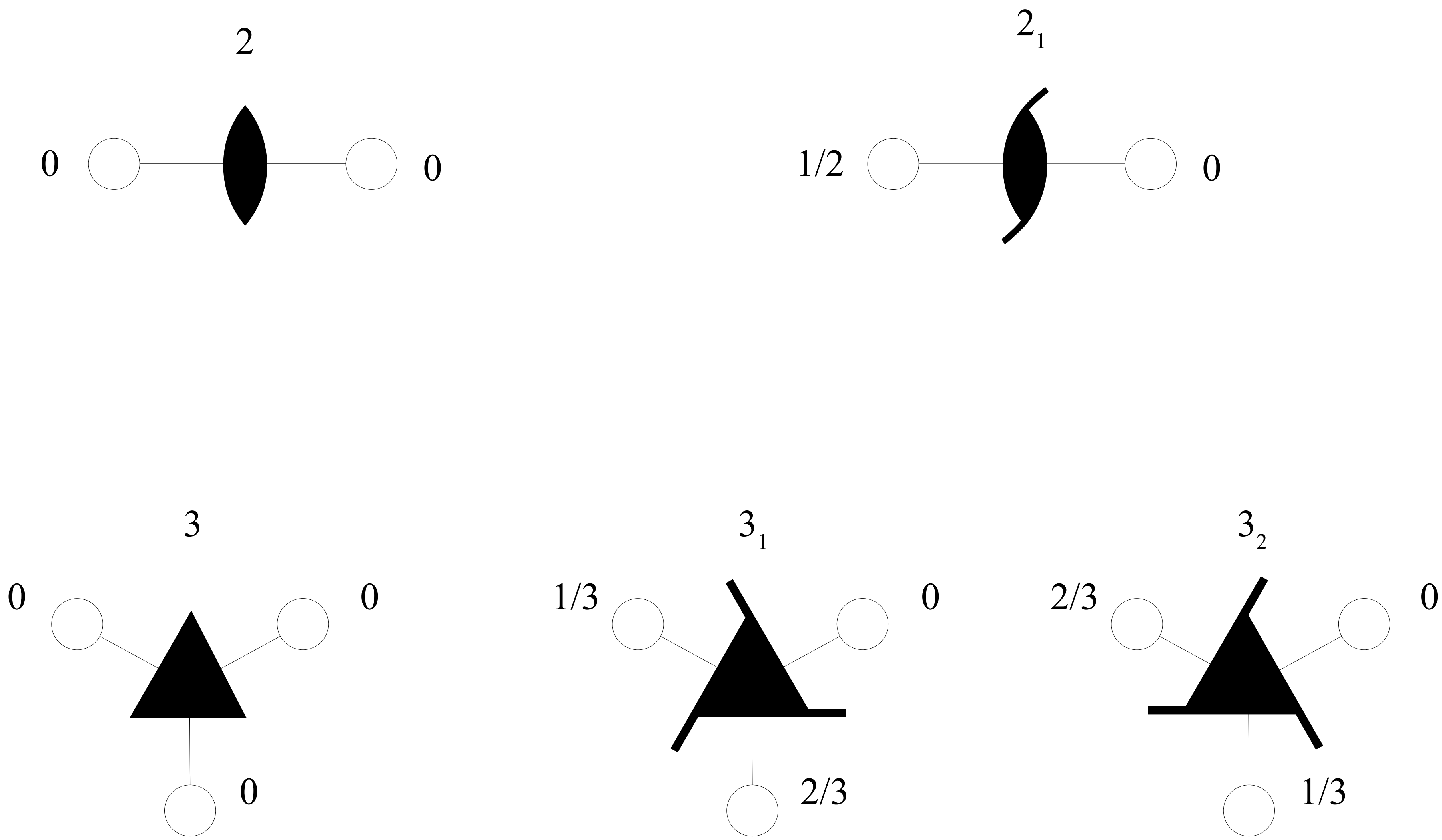
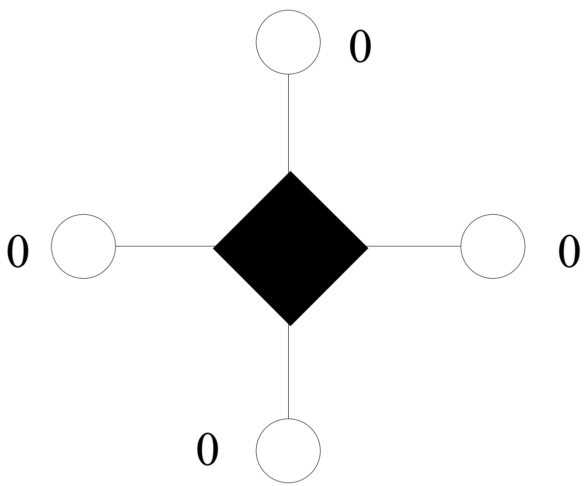
Screw axes

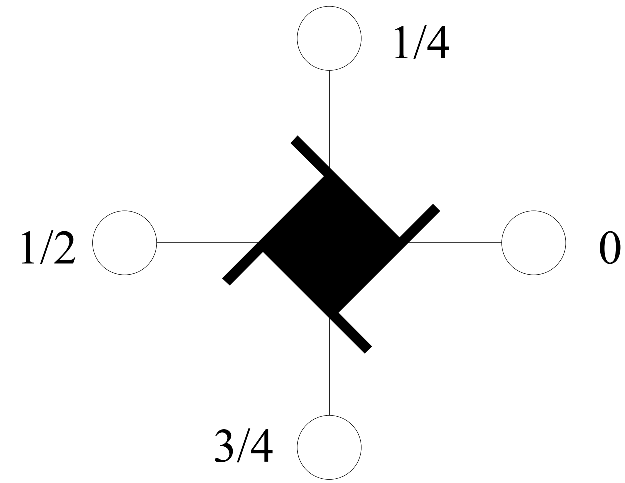


Screw axes

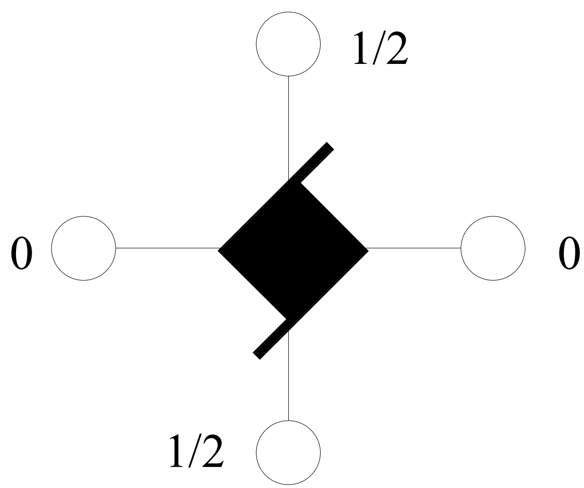
4



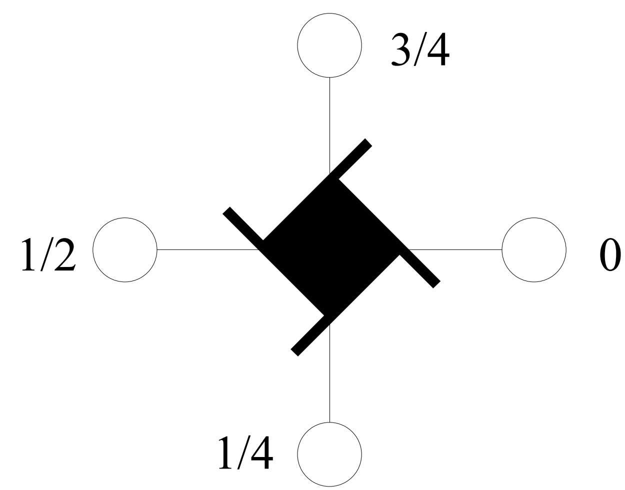
$4_1 \supset 2_1$



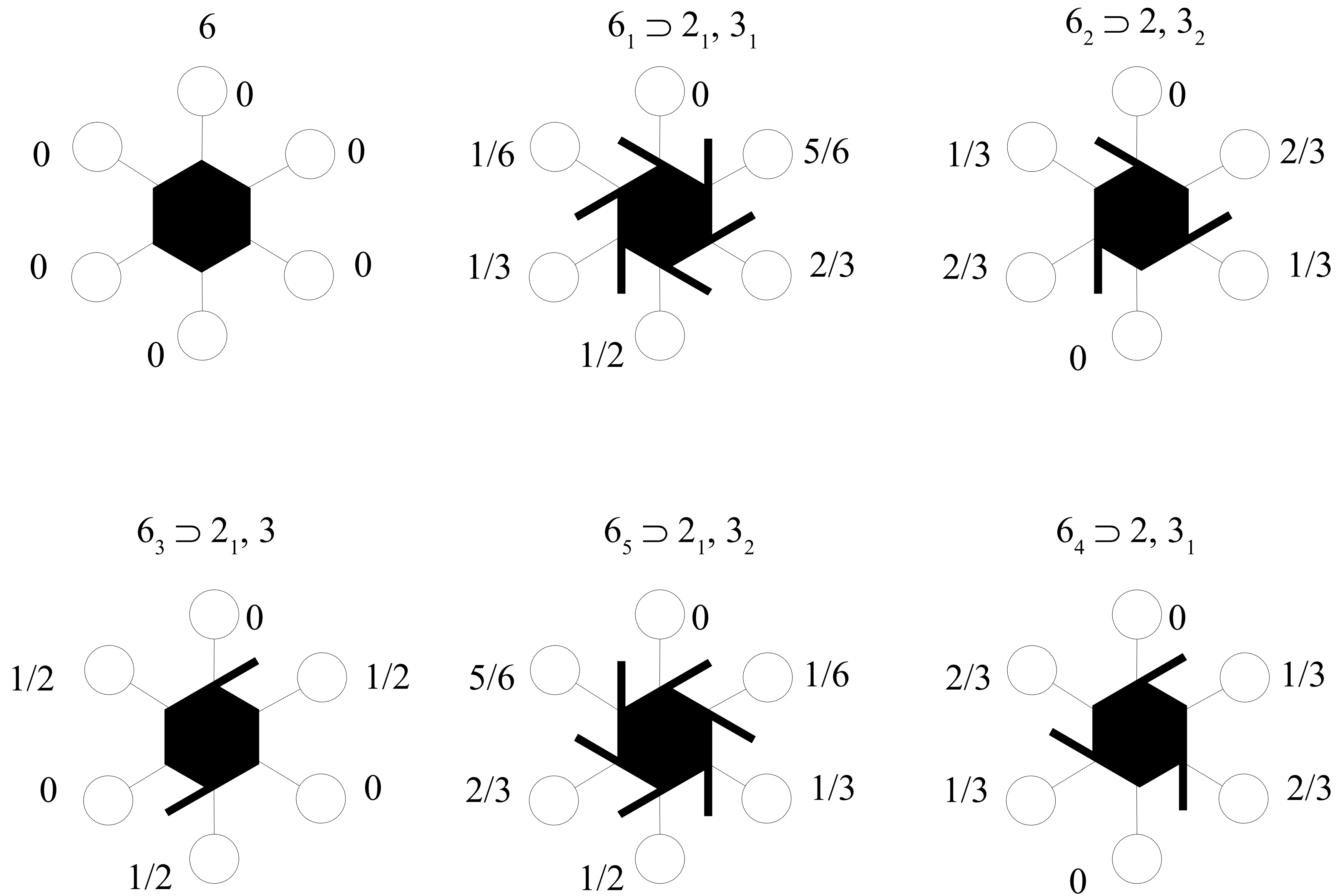
$4_2 \supset 2$



$4_3 \supset 2_1$



Screw axes


6
0
0
0
0
0
0
$6_1 \supset 2_1, 3_1$
0
1/6
5/6
1/3
2/3
1/2
$6_2 \supset 2, 3_2$
0
1/3
2/3
2/3
1/3
0
$6_3 \supset 2_1, 3$
0
1/2
1/2
0
0
1/2
$6_5 \supset 2_1, 3_2$
0
5/6
1/6
2/3
1/3
1/2
$6_4 \supset 2, 3_1$
0
2/3
1/3
1/3
2/3
0

Screw axes

n_p

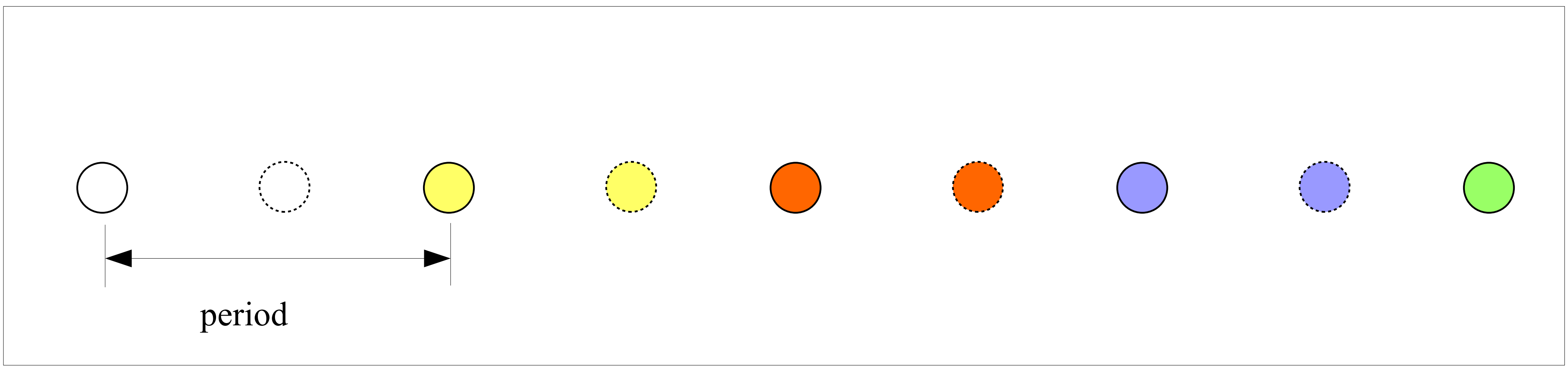
n_{n-p}

Glide planes *g*

http://dx.doi.org/10.1002/crat.201600129

Geometric element : plane

[001]



g (½ ½,0) *x,x,z* — *t*(1,1,0)

g (3/2,3/2,0) *x,x,z* — *t*(2,2,0)

g (5/2,5/2,0) *x,x,z* — *t*(3,3,0)

g (7/2,7/2,0) *x,x,z* — *t*(4,4,0)

[110]

Special cases

g (0,0,0): *m*
g (½,0,0): *a*
g (0,½,0): *b*
g (0,0,½): *c*
g (half-diagonal): *n*
g (quarter-diagonal): *d*

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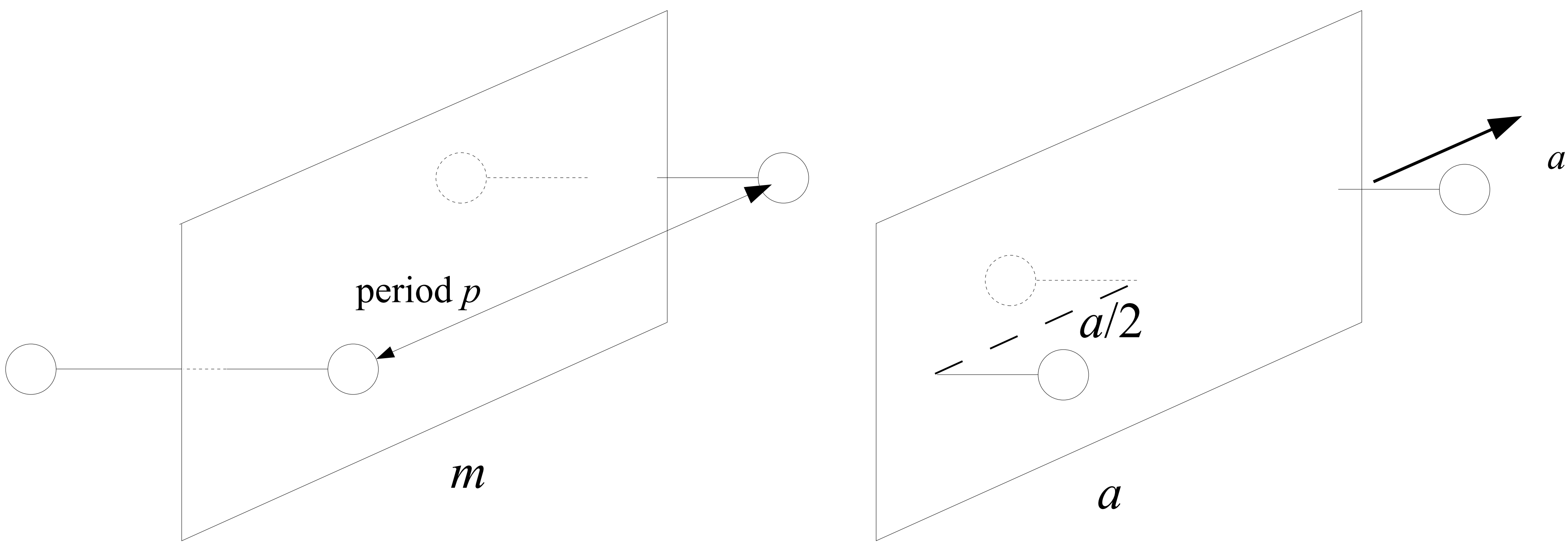
Glide planes *g*

Geometric element: plane

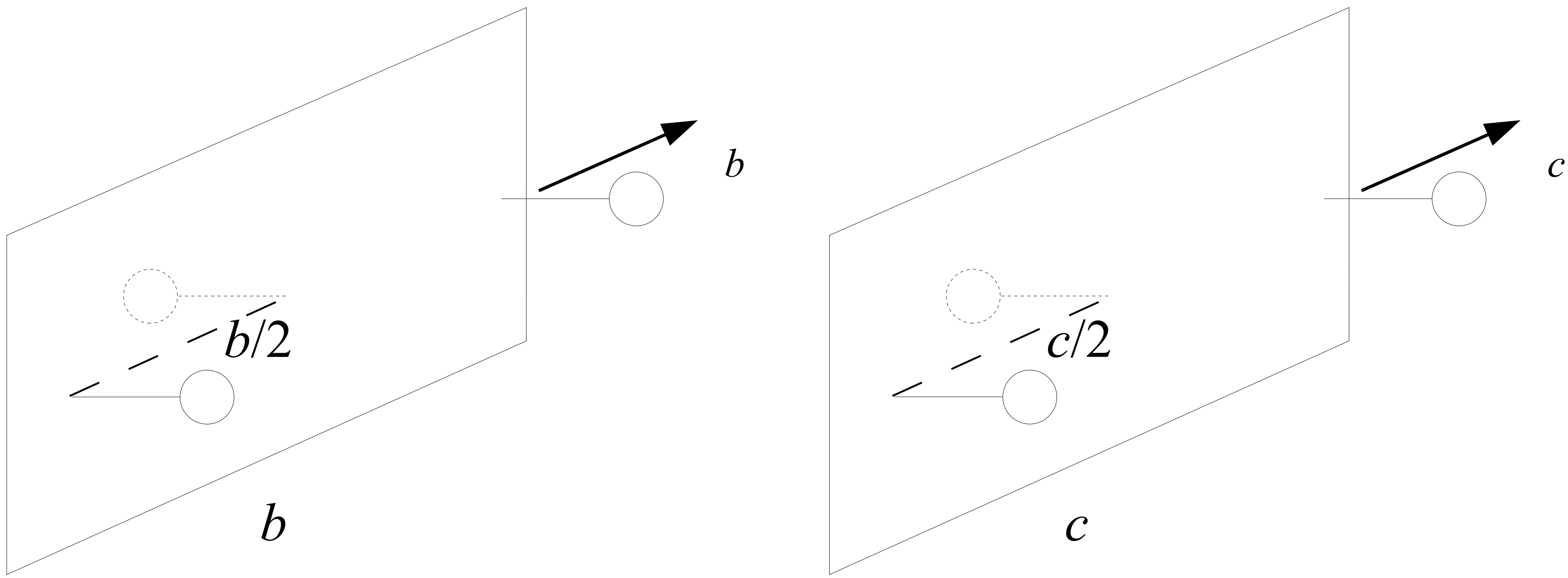


Defining operation: reflection
Symmetry element: mirror plane

Defining operation: glide reflection
Symmetry element: glide plane

Glide planes *g*

Geometric element: plane



Defining operation: glide reflection
Symmetry element: glide plane

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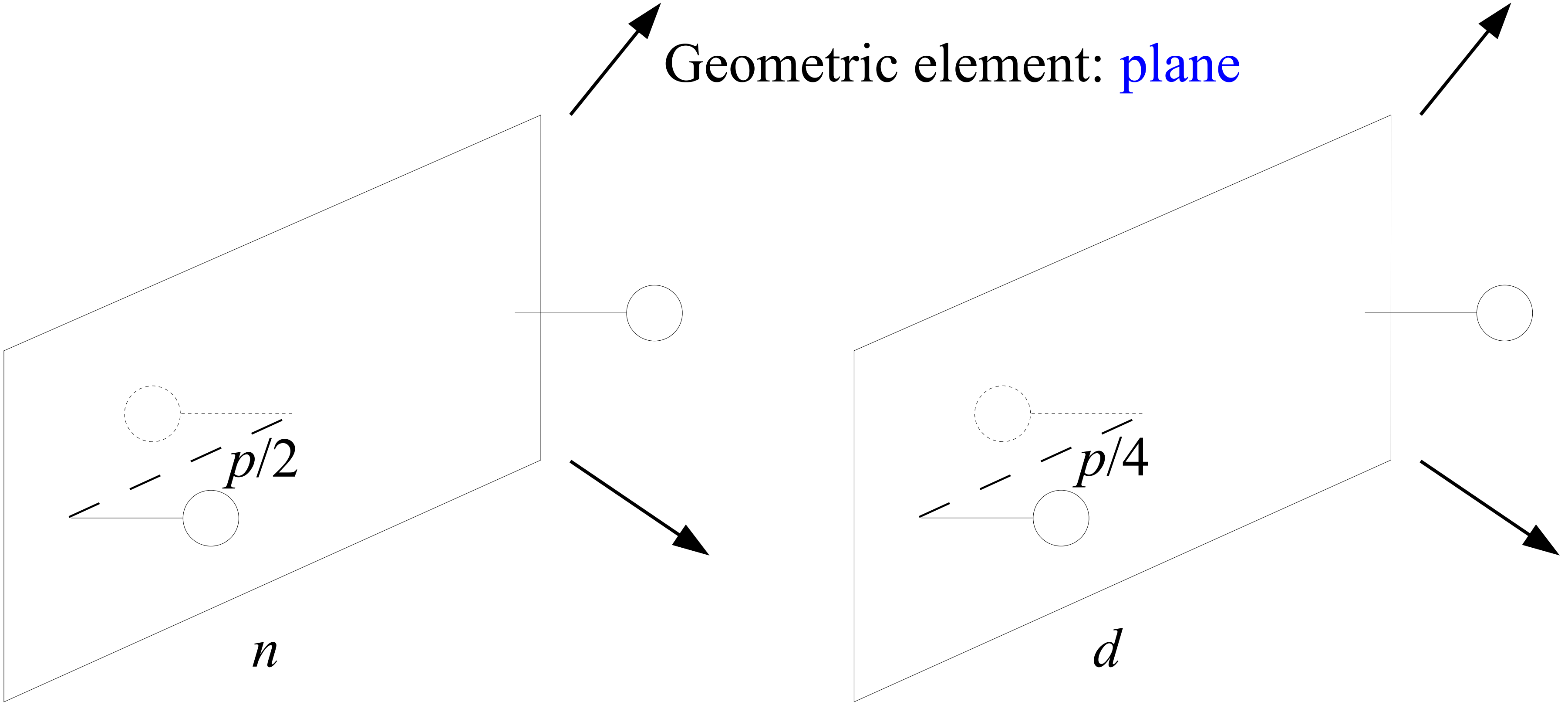
Glide planes *g*

Geometric element: plane



Defining operation: glide reflection
Symmetry element: glide plane

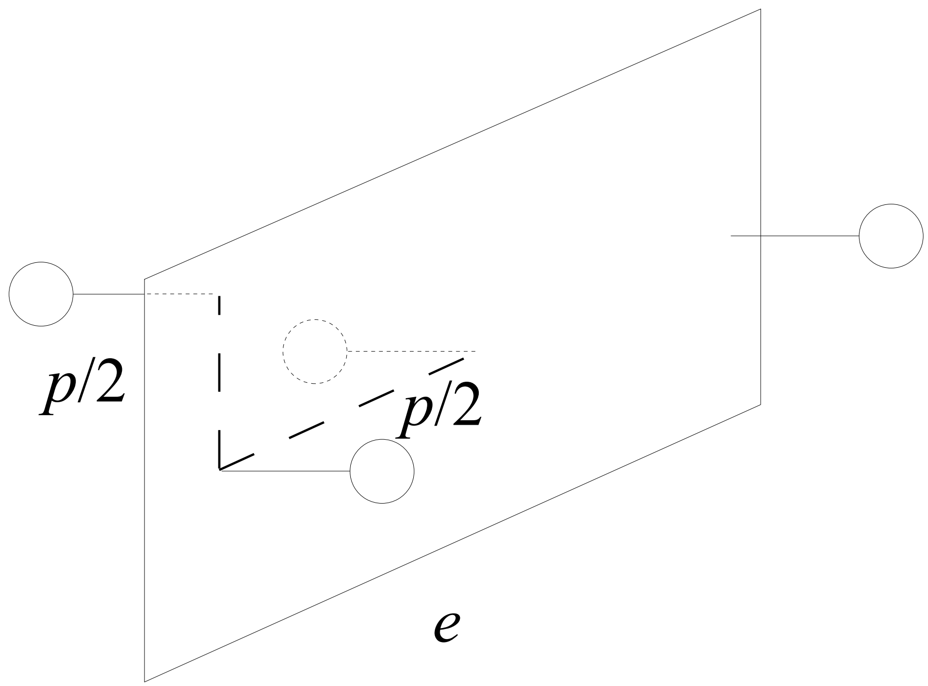
diagonal

Diamond structure glide plane

2D glide line; 3D glide plane with “unusual' glide

Glide planes *g*

Geometric element: plane

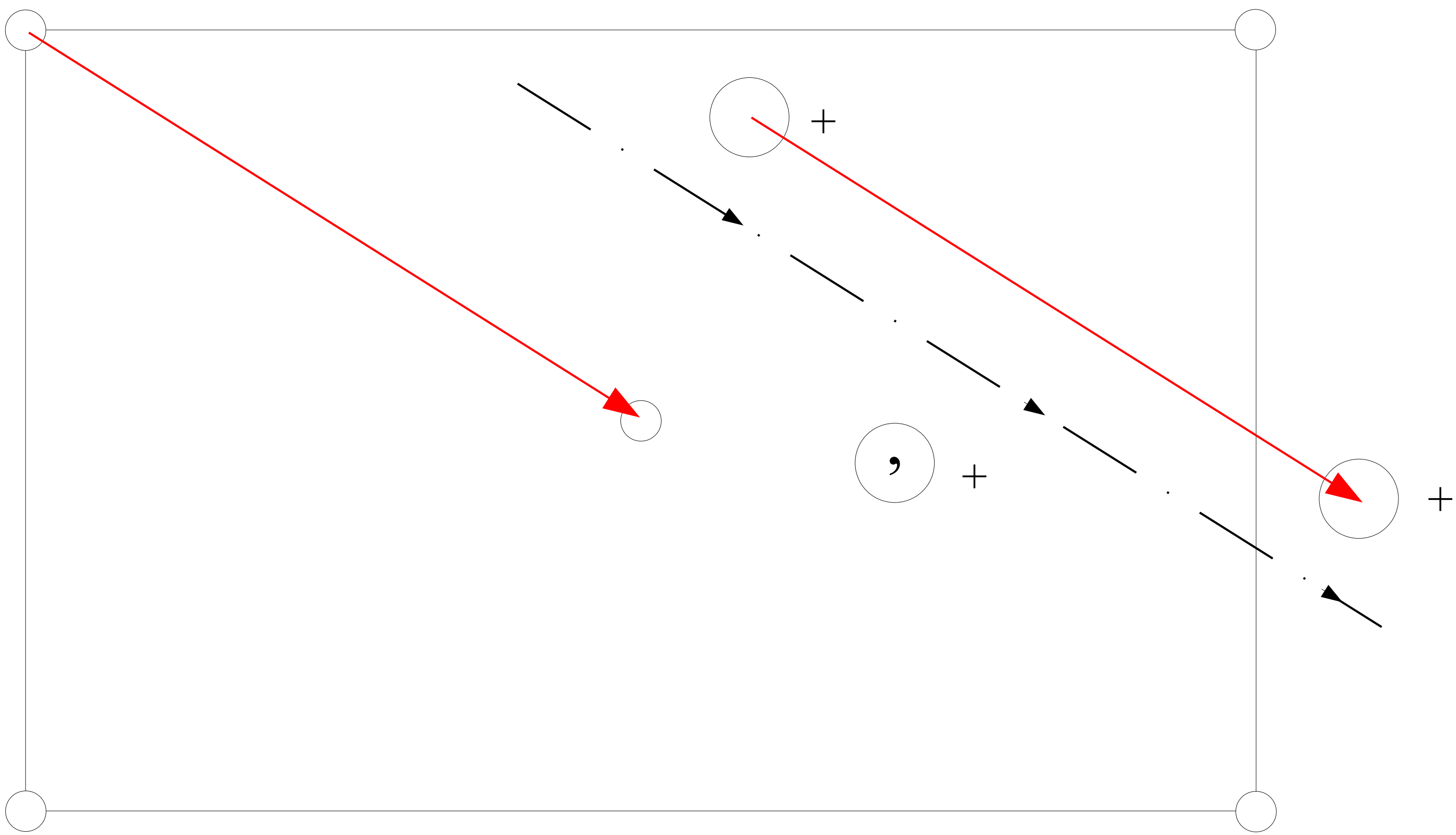


Defining operation: glide reflection
Symmetry element: glide plane

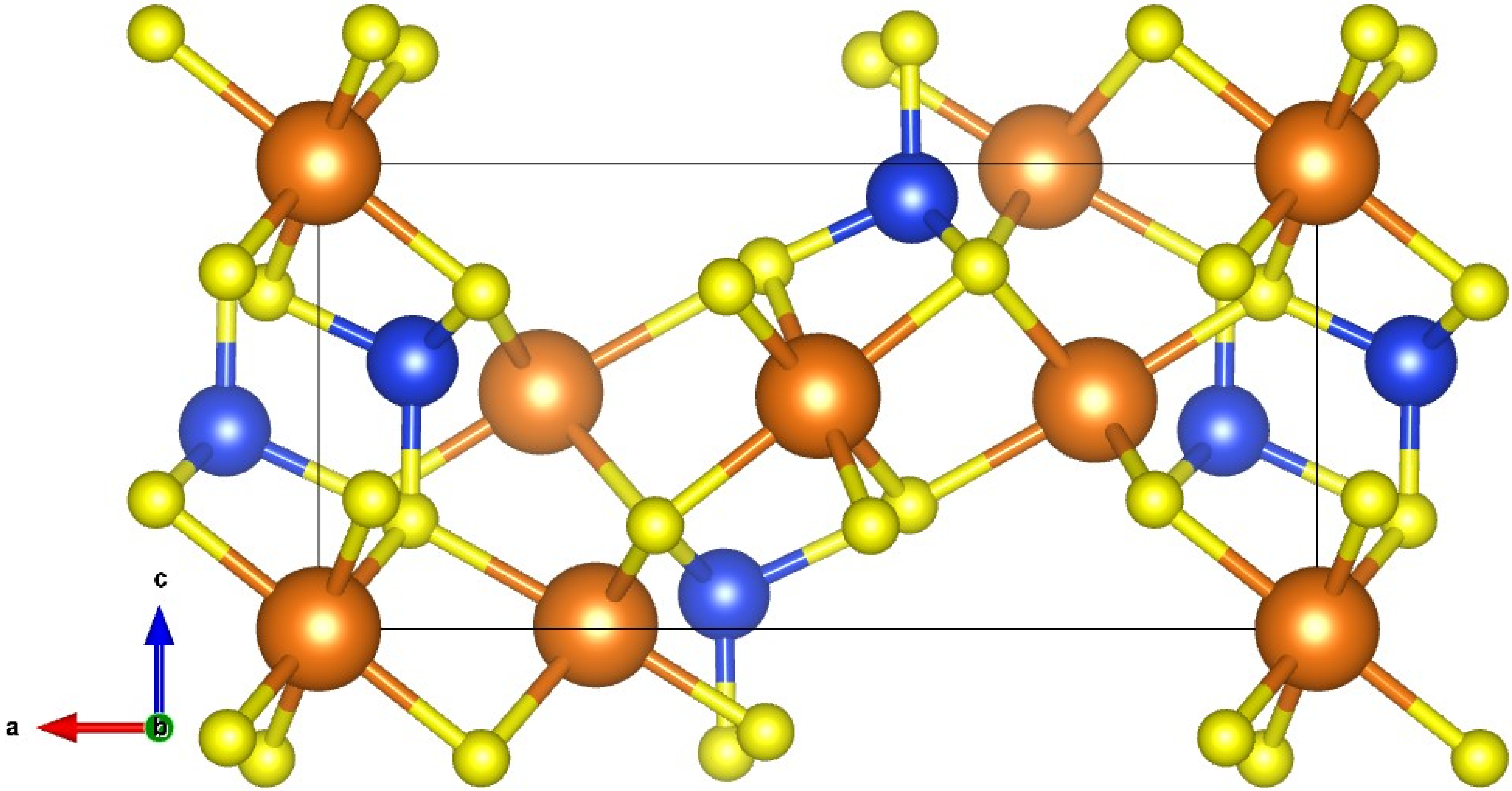
How can we have a glide of ¼ if the reflection is an operation of order 2 ?

If the unit cell is centred !

Vector centring the unit cell, with a norm *p*/2

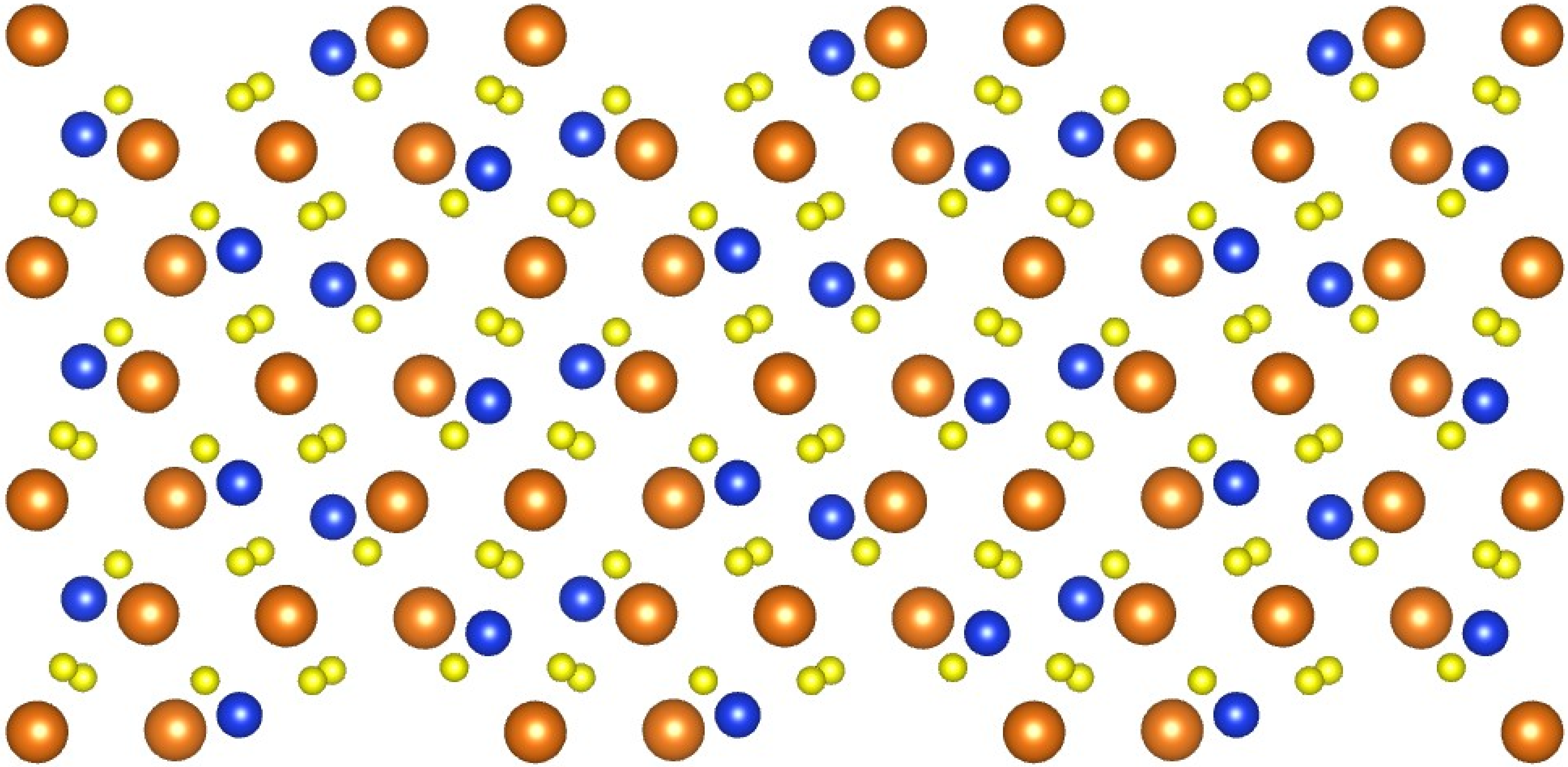


Example of crystal structure



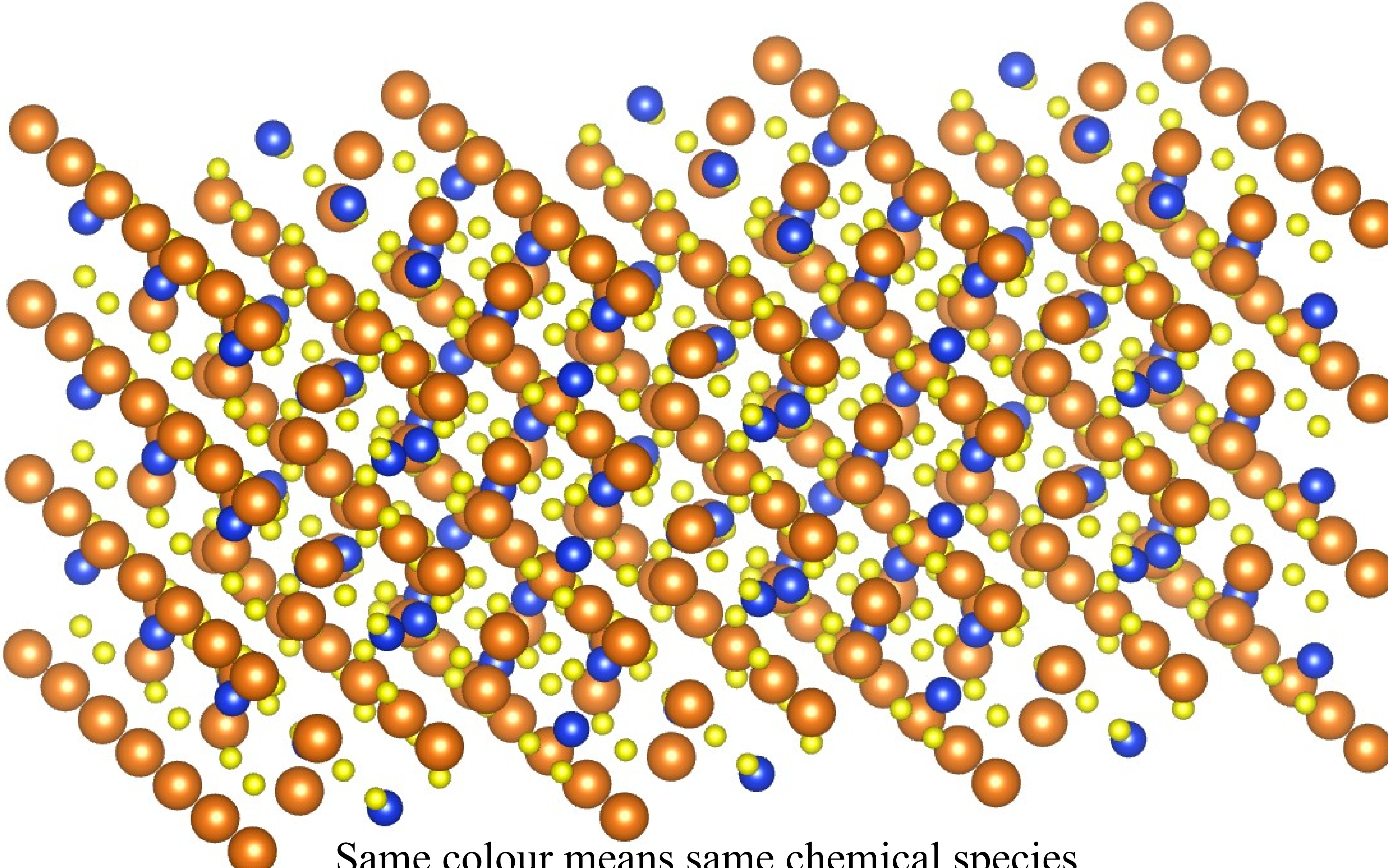
Same colour means same chemical species

Example of crystal structure



Same colour means same chemical species

Example of crystal structure



Same colour means same chemical species

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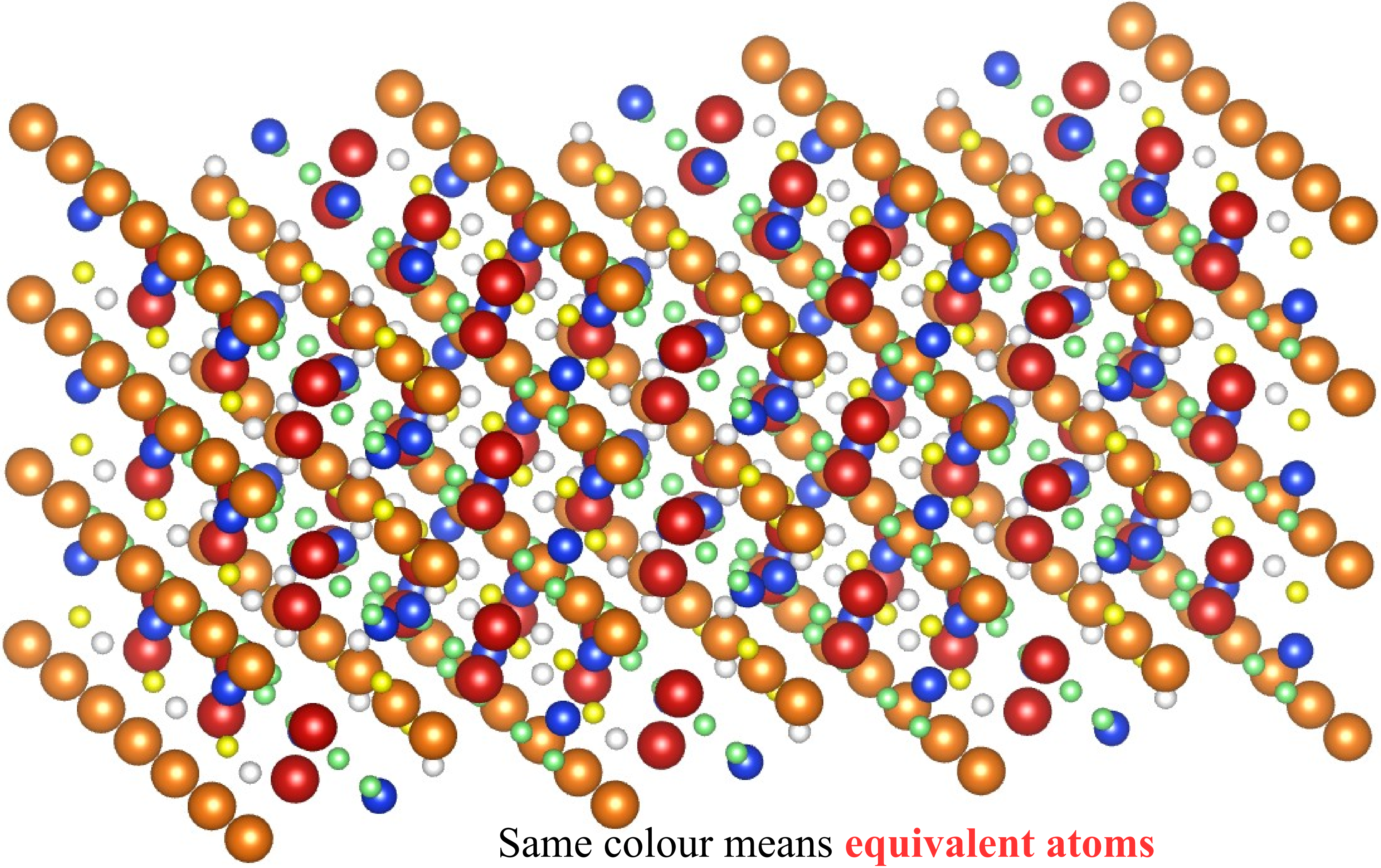
Example of crystal structure



Same colour means **equivalent atoms**

Equivalent atoms

- The atoms of an infinite[†] set in a crystal structure are equivalent if the fulfil two conditions:
  - they all correspond to the same chemical species;
  - they can be related by global isometries.

Each set of atoms that fulfils the above conditions constitute **crystallographic orbit**.

The whole set of isometries that maps atoms belonging to the same crystallographic orbit constitutes the **eigensymmetry** of that orbit.

The whole set of atoms building up a solid[‡] can be divided into a finite number of crystallographic orbits. The solid is a crystal and the atoms define its crystal structure.

[†]The surface of a crystal is treated as a defect and ignored.

[‡]This definition ignores static and dynamic defects.

Crystal structure, fractional atomic coordinates, crystallographic orbits, Wyckoff positions

Crystal structure atomic distribution in space that complies with the order and periodicity of the crystal

Fractional atomic coordinates : atomic coordinates *x*,*y*,*z* within a unit cell with respect to the basis vectors **a**,**b**,**c**.

a,**b**,**c** (bold) : basis vectors

a,*b*,*c* (italics) : reference axes and cell parameters

x,*y*,*z* (italics) : fractional atomic coordinates

Don't forget the translations!

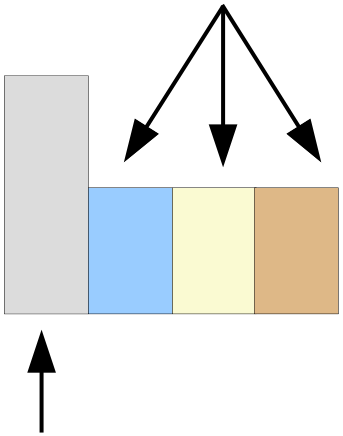
crystallographic orbit : the infinite set of atoms obtained by applying all the symmetry operations of the space group to a given atom in the unit cell.

Wyckoff positions : classification of the crystallographic orbits on the basis of the symmetry of the atomic positions (site-symmetry group)（N to 1 mapping）

Hermann-Mauguin symbols for space groups

Up to three numbers or low-case letters (italics): symmetry **elements** along the symmetry directions of the lattice

Placeholders



Capital italics letter: type of unit cell

Example: $C2/c$, $Pbam$, $I4_1/acd$, $Fd\bar{3}c$ etc.

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Hermann-Mauguin symbols for space groups

Procedure to read the symbol:

- remove the capital letter
- replace screw axes n_p (if any) with rotation axes n
- replace glide planes (if any) with mirror planes *m*

Obtain the point group of the space group

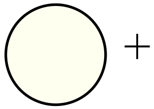
Obtain the crystal system and the conventional unit cell

Interpret the symbol of the space group

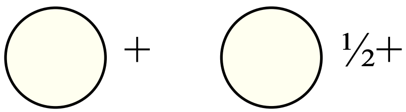
Example: $C2/c$, $Pbam$, $I4_1/acd$, $Fd\bar{3}c$ etc.

Graphical symbols for atoms projected in the unit cell

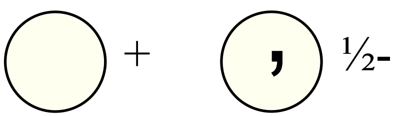
Direction of projection *c* → vertical coordinate *z*.



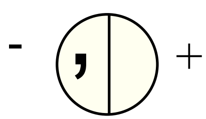
An atom with coordinate $z > 0$ (“+”).



Two atoms mapped by an operation of the first kind (handedness preserving operation) with coordinates z (> 0) and ½+z respectively.

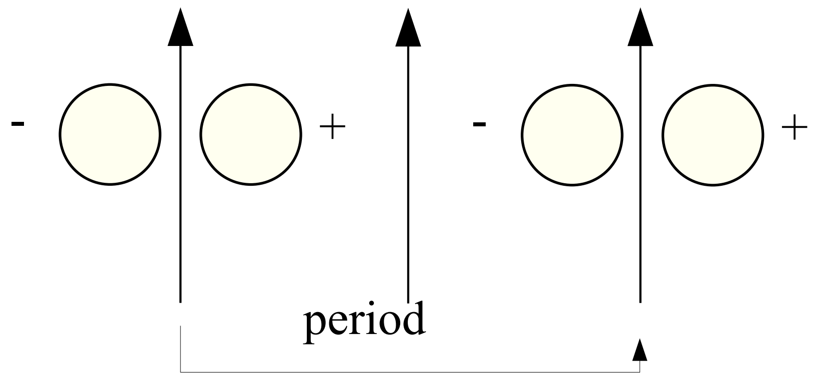


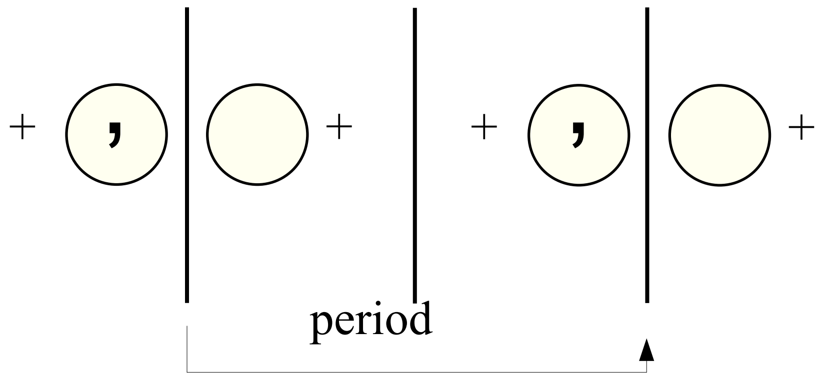
Two atoms mapped by an operation of the second kind (handedness reversing operation: note the “comma”) with coordinates z (> 0) and ½-z respectively.

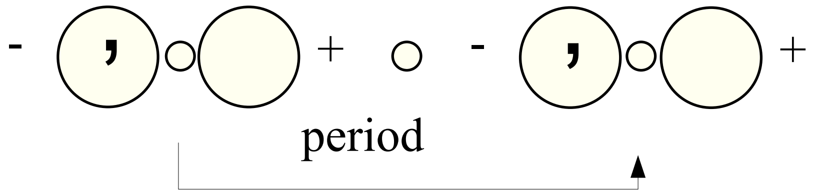


Two atoms mapped by an operation of the second kind (handedness reversing operation: note the “comma”) with coordinates x,y,z and $x,y,\bar{z}$ respectively, overlapped in projection. The vertical segment represents a “cut” of the atom above (left) which allows to see half of the atom below (right).

Symmetry elements corresponding to involutions occur every half period







Site-symmetry groups (stabilizers) and Wyckoff positions of space groups

Let G be a space group (thus, **infinite**) and X a point in space.

The **infinite** set of points $\{GX\} = \{X, X', X''\ldots\}$ is the **crystallographic orbit** of X under the action of G.

A finite subgroup S of G ($S \subset G$) leaves X invariant, *i.e*. it "stabilizes" X: $SX = X$

S is called the **site-symmetry group** (or **stabilizer**) of X.

Crystallographic orbits for which $S = \{1\}$ are called **general orbits**.

Crystallographic orbits for which $S \supset \{1\}$ are called **special orbits**.

Two points X and X' belonging to the same crystallographic orbit, whose site-symmetry groups S and S' are conjugate under G, belong the same class, which is known as **Wyckoff position**.

$s \in S, sX = X$ $\qquad$ $s' \in S', s'X' = X'$ $\qquad$ $g \in G, gX = X'$ $\qquad$ $s' = gsg^{-1}$

X, X' belong to the same Wyckoff position.

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Site-symmetry groups (stabilizers) and Wyckoff positions of space groups

The number of points belonging to a crystallographic orbit is infinite.

The number of points of a given crystallographic orbit within a single unit cell is known as the **multiplicity** of the Wyckoff position.

The multiplicity M of the **general** Wyckoff position is obtained as:

$$\text{M(general)} = \text{O(P)} \times \text{M(U)}$$

Order of the point group P of G

Multiplicity of the unit cell U of G

The multiplicity M of a **special** Wyckoff position is obtained as:

$$\text{M(special)} = \text{M(general)} / \text{O(S)}$$

Order of the site-symmetry group of the special position