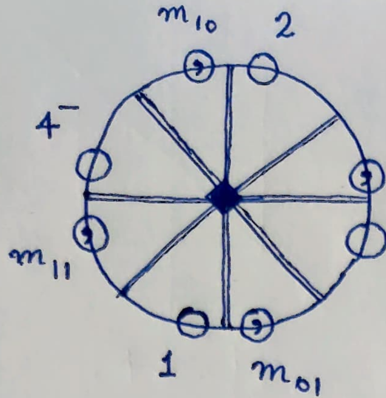
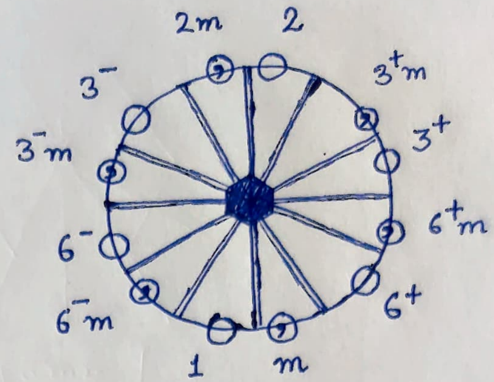
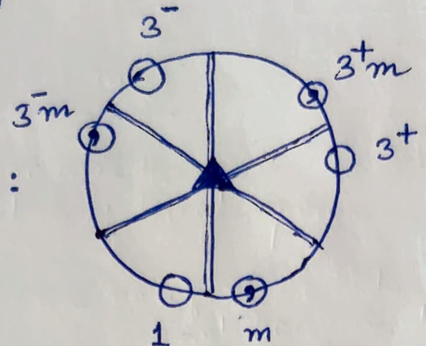
4mm:





: 6mm

3m:



H.W.: Establish Group-subgroup relations between point groups.

LECTURE 18 (01/04/2024)

L18

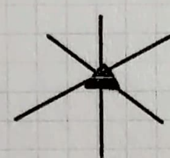
Plane Groups III

1. Group-Subgroup relations in 2D point groups
2. 2D Crystal System
3. 2D Bravais lattices
4. Symmorphic plane groups
5. Non-symmorphic " "
6. International Tables — Next Class.

92]

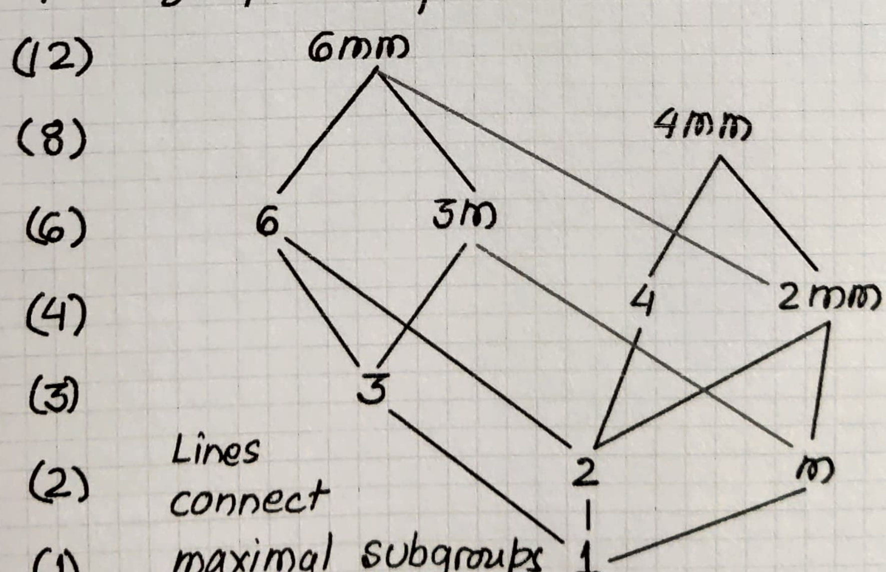
10 2D Crystallographic Point Groups (For 2D Periodic Patterns)

	Hermann-Mauguin (International)		Schoenflies	Order
Type I	1		C_1	1
Chiral group	2		C_2	2
Enantiomorphic Group	3	$=\{1, 3^+, 3^-\}$	C_3	3
	4	$\{1, 4^+, 2, 4^-\}$	C_4	4
F ꟻ	6		C_6	6
	m	Spiegel = mirror	C_s	2
Achiral	2 mm		C_{2v}	4
A	3m		C_{3v}	6
	4mm		C_{4v}	8
	6mm		C_{6v}	12



93]

Group-Subgroup tree of 2D Point Groups



Lines connect maximal subgroups

94]

2D Crystal System

Classification of 10 point groups

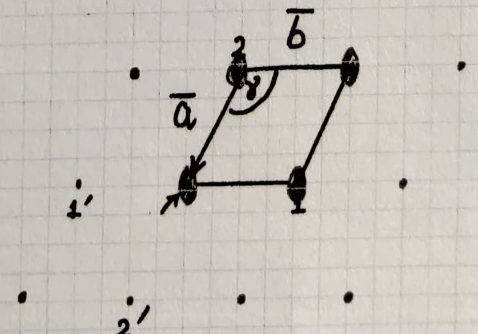
Oblique	1, 2
Rectangular	m, 2mm
Square	4, 4mm
Hexagonal	3, 6, 3m, 6mm

95]

2D Bravais Lattices (Five Bravais lattices)

1 : always possible (does not put any restriction on $\vec{a}, \vec{b}, \gamma$)

2 :



$|\vec{a}| \neq |\vec{b}|$

γ : arbitrary

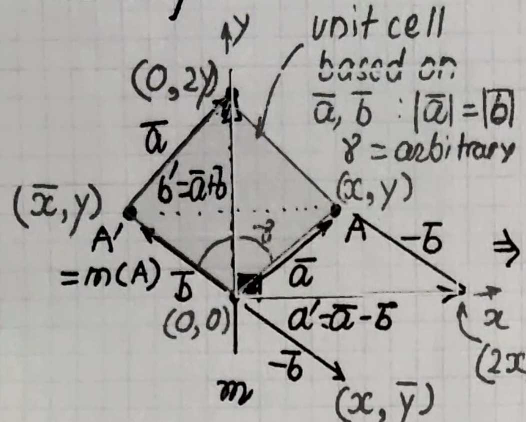
$\boxed{\text{Oblique lattice}}$

mp
monoclinic primitive

⬮ does not put any restriction of $\vec{a}, \vec{b}$ and γ.

96]

Rectangular lattice



• Lattice points

$\bar{a}$ is arbitrary wrt m

$\bar{b}$ is image of $\bar{a}$ in m

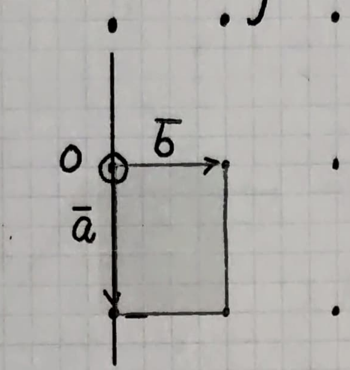
$$\left.\begin{array}{l}\Rightarrow \bar{a} + \vec{b} \text{ along } m \\ \vec{x} \quad \bar{a} - \vec{b} \perp m.\end{array}\right\}$$

Centred ↘ ↙ ortho rhombic

OC

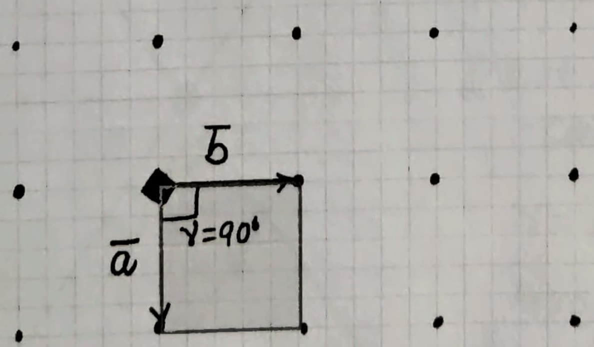
We choose $\bar{a}' = \bar{a} - \bar{b}$ and $\bar{b}' = \bar{a} + \bar{b}$ as our basis vectors to get $\boxed{\text{centred rectagular lattice}}$

97] Primitive Rectangular (op)



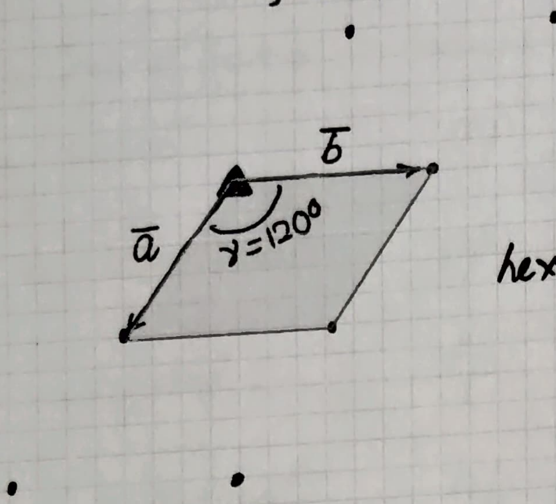
Primitive Rectangular

98] Point group 4 in a lattice



$|\bar{a}|=|\bar{b}|$, $\gamma = 90°$ primitive square (tp)

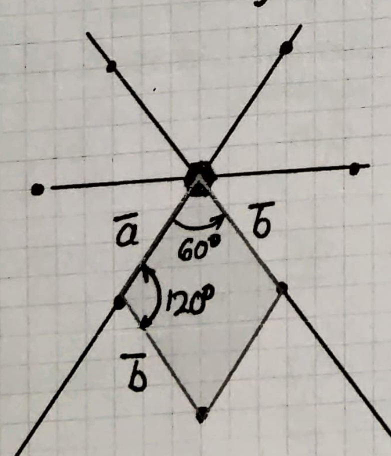
99] 3 (Hexagonal lattice) hp



$|\bar{a}| = |\bar{b}|$
$\gamma = 120^0$

hexagonal primitive hp

100] 6 hexagonal primitive hp



$|\bar{a}| = |\bar{b}|$ $\cancel{\gamma = 60^0}$

Insist on $\gamma \geq 90^0$ by convention.

$\gamma = 120^0$

hexagonal p lattice

101]

Five 2D Bravais Lattices

Crystal System	Bravais Lattices	Point Groups
oblique	mp	1, 2
Rectangular	op, oc	m, 2mm
square	tp	4, 4mm
Hexagonal	hp	3, 6, 3m, 6mm

102]

Plane Groups

13 symmorphic Plane Groups

Crystal System	Bravais Lattices	Point Groups	Plane Groups
oblique	mp	1, 2	p1, p2
Rectangular	op, oc	m, 2mm	pm, p2mm cm, c2mm
square	tp	4, 4mm	p4, p4mm
Hexagonal	hp	3, 6, 3m, 6mm	p3, p6, p6mm, p31m, p3m1

4 missing groups are nonsymmorphic plane groups.

Groups generated by glides.

Replace m by g. 4 Non-symmorphic plane groups

pm → pg

p2mm → p2gg also p2gm

p4mm → p4gm

cm and c2mm replacement of m by g does not generate new groups. (They already have glides).

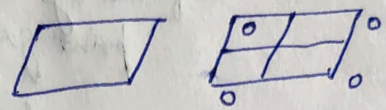
LECTURE 19 (04/04/2024)

104] International Table for Crystallography
↓
draws the plane groups through two separate diagrams

Symmetry element diagram

General position diagram

eg: p1 ⇝ H-M short symbol



1 ⇝ Point Group

No.1 ⇝ Plane group number ⇒ {these no.s are arbitrary}

p1 ⇝ H-M Full symbol

105] Plane Group Symbol to Point group

p1 ⟶ ① Cross out the letter symbol for lattice

~~p~~1 ⇒ 1

② Change any g to m

1 ⇒ 1

Thus, the point group of Plane group p1 is 1

NOTE: Once you know the point group you can also find the crystal system

eg: Point group 1 ⇒ Crystal system: Oblique

106] Patterson Symmetry

this is actually needed when solving for crystal system in case of XRD

Here we will just study the formula to find it

Patterson symmetry of any plane group is found by replacing its point group by another point group derived from the original point group by adding 2

eg: $p1 \rightarrow$ Point group = 1

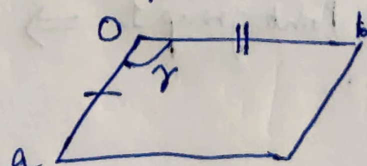
$\underbrace{1+2}_{\text{Combining 2 with identity gives 2}} = 2$

$\therefore$ Patterson symmetry of $p1$ is $p2$

107] Symmetry element diagram

A diagram showing all symmetry elements by their graphic symbols within a conventional unit cell

$p1 \longrightarrow$ Oblique $\longrightarrow mp \longrightarrow a \neq b$, γ = arbitrary

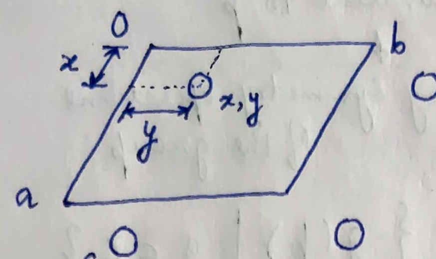


No other symmetry element for $p1$ thus, this is the symmetry element diagram

*

108] <u>General Position Diagram</u>

Here, we take some arbitrary ("general") position from the origin
{i.e. at some x and y coordinate}

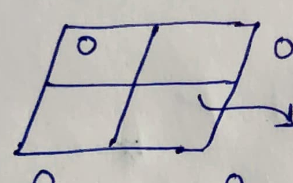


this comes from 'b' translation

this comes from 'a' translation

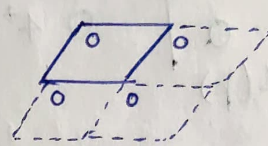
⇓

Here we may show it as:



these are guidelines

{ NOTE: Actually these 3 points outside are NOT part of the unit cell
↓
these are part of their respective unit cells
↓
But we draw these points by convention anyways }



109] <u>Asymmetric unit</u> : This is a region of the pattern
+
which generates the entire pattern when repeated by <u>ALL</u> symmetry operations of the group.

{ <u>NOTE:</u> <u>Unitcell</u> : A region of the pattern which generates the entire pattern
↓
when repeated by <u>translations</u>

(i.e., in other words, these are "periodic repetitions")

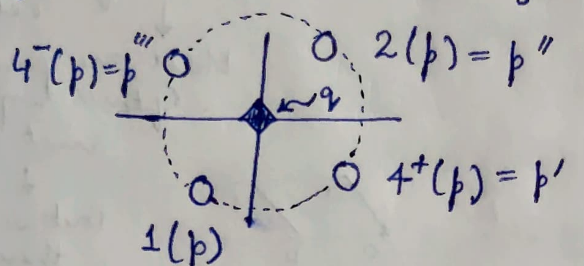
eg: For $p1$ → the unit cell itself is the asymmetric unit

10] Positions

Orbit : Orbit of a point p
↓
refers to all points equivalent to p
↓
by symmetry operations of the group

$$Orb(p) = \{ g(p) \mid g \in G \}$$

eg: $G = 4 = \{1, 4^+, 2, 4^-\}$



$Orbit(p) = \{ p, p', p'', p''' \}$
$Orbit(q) = \{ q \}$

* (Thus, orbit depends on where the point is located w.r.t. symmetry operations)

11] Stabilizer of a point

Set of all symmetry operations of G
↓
that leave a point p fixed
↓
is called the Stabilizer of p

$$Stab(p) = \{ g \in G \mid g(p) = p \}.$$

* NOTE: Stabilizer must always contain identity operation (since that always leaves point unchanged)

In the above example :

$$Stab(p) = \{1\} = 1$$
$$Stab(q) = \{1, 4^+, 2, 4^-\} = 4$$

Stabilizer $Stab(p)$ is a subgroup of G

we can see this as follows :

(i) Closure : $g(p) = p$, $h(p) = p$
$\Rightarrow gh(p) = g(p) = p$

(ii) Associative from G

(iii) Identity : $1(p) = p \Rightarrow$ 1 will always belong to $Stab(p)$

{i.e. $1 \in Stab(p)$ }

(iv) Inverse : $g(p) = p$

$$\Rightarrow g^{-1}g(p) = g^{-1}(p)$$
$$\Rightarrow e(p) = g^{-1}(p)$$
$$\Rightarrow p = g^{-1}(p)$$

Thus $g^{-1} \in Stab(p)$, $\forall g \in Stab(p)$

112] General Position

A position is called a general position

if its stabilizer is the trivial group 1

i.e. $Stab(p) = 1$

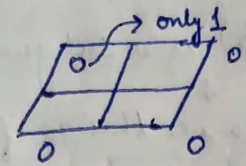
113] Special position

If $Stab(p) \neq 1 \Rightarrow p$ is a special position

* {thus, this will occur for points lying on some geometrical symmetry element }

114] Positions

Multiplicity : No. of general positions lying within a unit cell

eg: $p1$  $\Rightarrow$ Multiplicity = 1

Wyckoff letter : Arbitrarily chosen letter designating the position

'a' is used for highest symmetry position

{ eg: For $p1 \Rightarrow$ Only one type, so we use 'a'

For 4-fold $\Rightarrow$ There are two types, one general and one special → 'a' and 'b' }

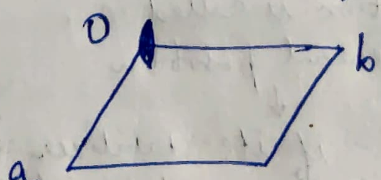
Site symmetry : Site symmetry of a position is the symmetry group of the stabilizer of that position

*** NOTE:** All these concepts that we have studied for Plane groups will actually be the same (i.e. same definitions) for Space groups.

Example : $p2$

Point group $\rightarrow \cancel{p}2 \rightarrow 2 \Rightarrow$ Crystal system: Oblique

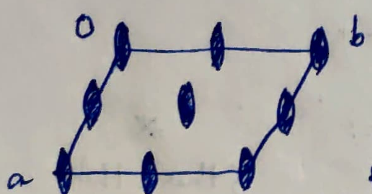
$\Rightarrow$ Lattice : mp



$\Downarrow$

But by translations the other corners are also 2-fold

thus



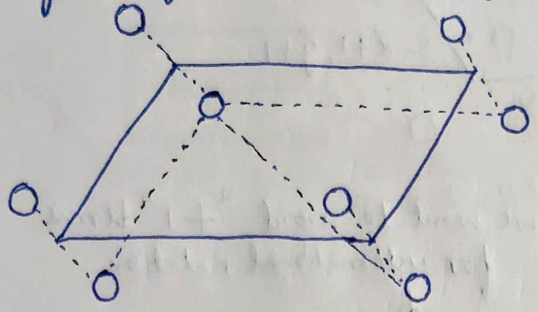
Symmetry element diagram of $p2$

{ NOTE: For $p1$ the choice of origin was arbitrary → But here, it makes sense to select the origin at the 2-fold }

* { However, we must remember that 2-fold + translation $\vec{a}$ gives a 2-fold at $\vec{a}/2$ }

LECTURE 20 (06/04/2024)

115] Creating the general position diagram:



After constructing this
↓
we see that the center 2-fold and the edge 2-folds are automatically satisfied

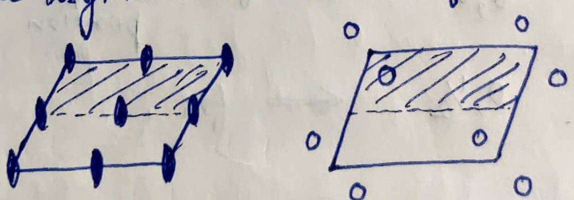
Thus, this is the General position diagram of p2

No. of general positions in the unit cell = 2

So now we have the information:

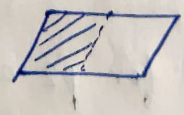
Short symbol : p2
point group : 2
Crystal sys. : Oblique
Full symbol : p2
No. 2 ⟶ International no.

Here, we see that we can take the asymmetric unit to be half the unit cell itself

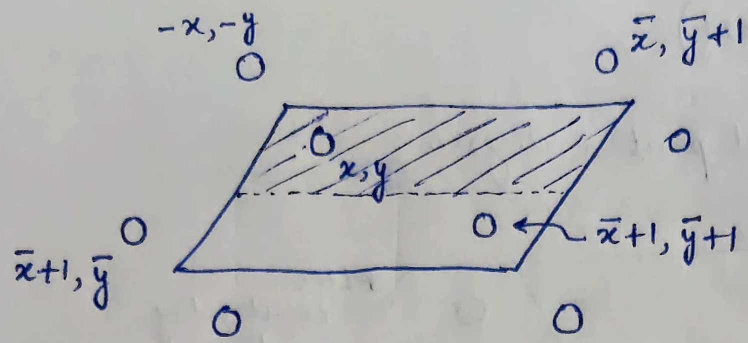


Since it generates the whole pattern by using the middle 2-fold

NOTE: Alternatively, we could choose the left/right half as asymmetric unit:



116] General positions in p2
↓
We can obtain general positions as follows:



Generally, we want to avoid "+1" terms for international notation

↓

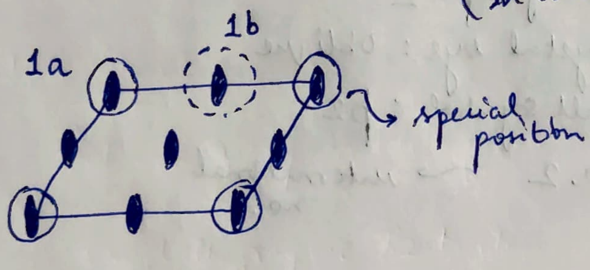
So, for instance, we use $(-x,-y)$ instead of $(\bar{x}+1, \bar{y}+1)$

↓

Since they are translationally equivalent

∴ <u>General positions</u> : $x, y \quad \bar{x}, \bar{y}$

<u>Special positions</u> : Lying on geometrical symmetry elements (in this case, 2)



Mult., Wyck.lett., Site symm.

1 a 2 0,0 ⟸ for 0,0 special position

for reference: (symbol: O in above diagram)

1 b 2 0,½ ⟵ for ◌

NOTE: We also see that:

Multiplicity × |Site symmetry| = |Point group|

NOTE: The generators for p2 are:

$(1),\ t(1,0),\ t(0,1),\ (2)$

here (2) does NOT mean 2-fold necessarily ⟸ the bracketed notation actually means ⟵ "2nd symmetry operation in the list of symm. operations"

117]

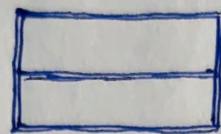
pm $\longrightarrow$ m Rectangular

#3

p1m1 $\rightarrow$ m $\perp$ to x

1-fold rotation

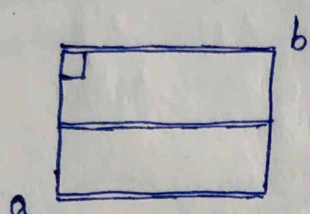
Nothing $\perp$ to y



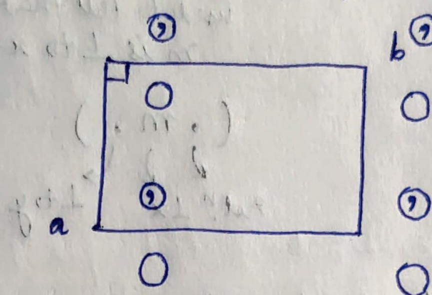
(p1m1 is the full H-M symbol)

all these doubled lines are denoting mirror operations

(alternatively, another colour can be used for this)



Symm. operation diagram



*[<u>NOTE:</u> From here we can also see geometrically that:

$$a\, m^{0,0}_{\perp x} = m^{a/2,0}_{\perp x}$$

mirror $\perp$ to x, passing through 0,0

Algebraically we see this:

$$\{I, \vec{a}\}\left\{\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}, \vec{0}\right\}$$

$$= \left\{\underbrace{\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}, \vec{a}}\right\}$$

$\Downarrow$ from this:

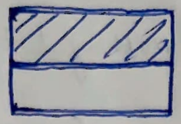
$$(am)^2 = \left\{\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}, \begin{pmatrix}0\\ 0\end{pmatrix}\right\} \Rightarrow \therefore \vec{w}_g = \frac{\vec{0}}{2} = \vec{0}$$

$$\therefore \vec{w}_l = \vec{a}$$

$$\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}x_F\\ y_F\end{pmatrix} + \begin{pmatrix}a\\ 0\end{pmatrix} = \begin{pmatrix}x_F\\ y_F\end{pmatrix} \Rightarrow \begin{matrix}2x_F = a\\ y_F = y_F\end{matrix}$$

$\therefore$ Mirror is at the line : $x = a/2$]

Again we can take the asymmetric unit as half of the unit cell:



	Mult.	Wyck. lett.	Site symm.	
Also:	1	b	.m.	$\frac{1}{2}, y$
	1	a	.m.	$0, y$

this notation is used to tell that m is $\perp$ to x

$$(\underset{\text{rot}^n}{.}\ \underset{\perp x}{m}\ \underset{\perp \text{ to } y}{.})$$

LECTURE 21 (13/04/2024)

[118] 3D Point Groups

What rotations are possible for a 3D lattice?

From Crystallographic Restriction Theorem: 1, 2, 3, 4, ~~5~~, 6, ~~7~~, ~~8~~, ...

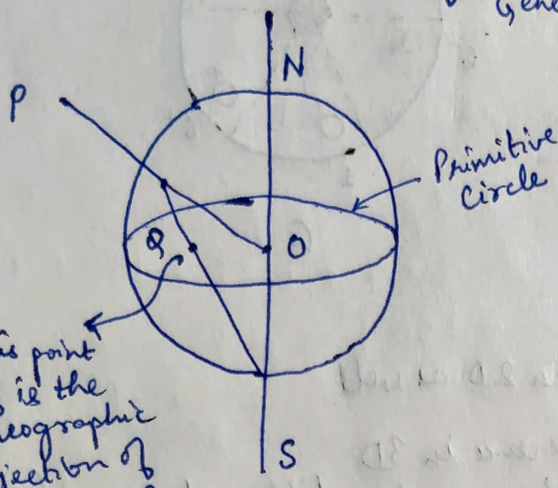
Also, five monoaxial (Cyclic) groups of proper rotations are:

$$1 = \{1\}, \quad 2 = \{1, 2\}, \quad 3 = \{1, \underset{+120^\circ}{3^+}, \underset{-120^\circ}{3^-}\}$$

$$4 = \{1, \underset{\substack{90^\circ \\ (+90^\circ)}}{4^+}, \underset{180^\circ}{2}, \underset{\substack{270^\circ \\ (-90^\circ)}}{4^-}\}, \quad 6 = \{1, 6^+, 3^+, 2, 3^-, 6^-\}$$

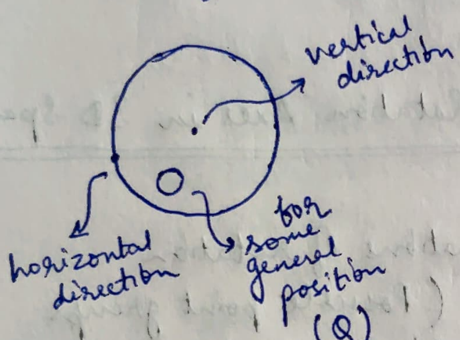
119] Stereographic Representation of 3D Point Group :

Symmetry elements and General Positions

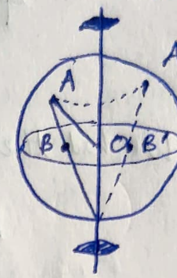


this point Q is the stereographic projection of direction OP

⇓



For the case of 2-fold rotation :

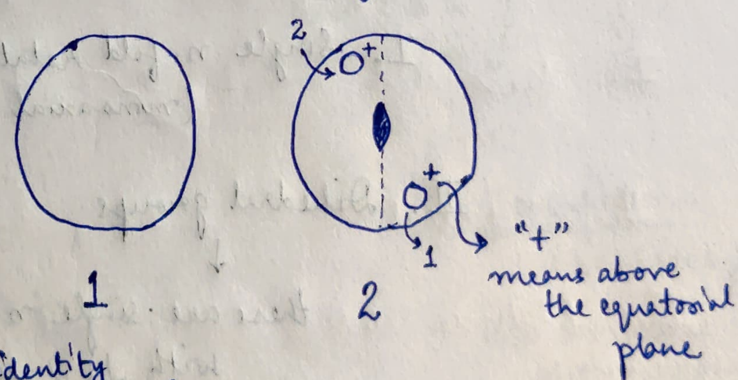


Here A is a general position (lies on the surface of the sphere)

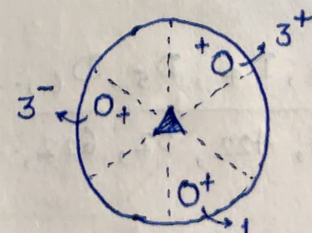
and B is its stereographic projection

{ A′ is rotated A, and B′ is the projection of A′ }

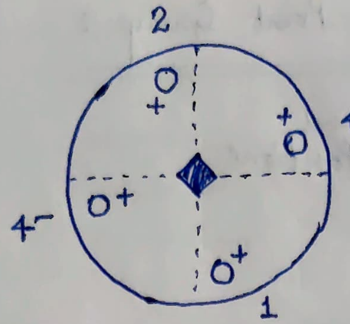
⇓



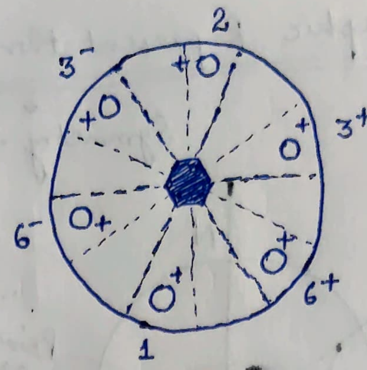
1 (identity operation) 2



3



4



6

* NOTE: We had these rotations in 2D as well

↓

but the difference in 3D is that there can be different possible orientations of the rotation axis

120] Possible Combinations of Proper Rotation Axes in 3D Spaces

Theorem: Only possible combinations of rotation axes in 3D (Possible point groups of proper rotations in 3D):

I. Single n-fold rotation axes : 1, 2, 3, 4, 5, 6, 7, ...
(monoaxial or cyclic groups) ⇓

$\{C_1, C_2, C_3, C_4, C_5, \ldots\}$ in Schoenflies notation

II. Dihedral groups

↓

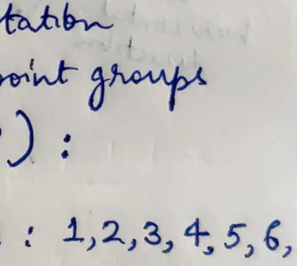
these are: single n-fold axis with $\perp$ 2-fold axes n in no. spaced $\frac{360°}{2n}$

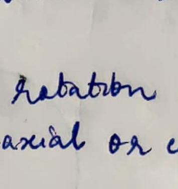
$C_2 = \cancel{D_1}, D_2, D_3, D_4, D_5, D_6, \ldots$

222, 32, 422, 52, 622, ...

⇒ International Notation

eg:



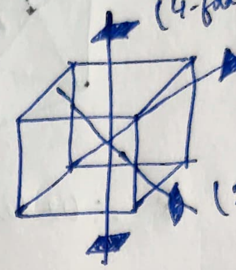


III. Five Platonic Solid Groups

We can see some unique combinations in the

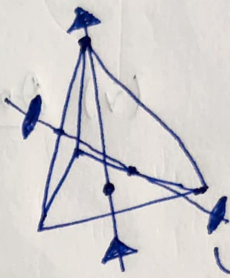
* Five Platonic solids:

(i) Cube:



{ * Order of rotation group of cube is 24 }

(ii) Tetrahedron:

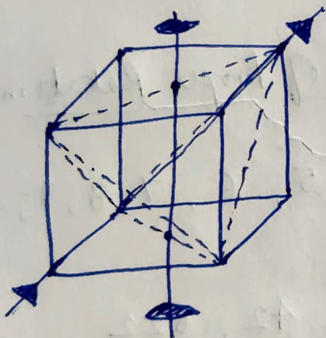


(2-fold axis exist between the mid-pts. formed by one set of corners and the other 2 corners)

{ * NOTE: Actually this is $\bar{4}$, but since we are only counting proper rotations, so we have degraded it to 2-fold

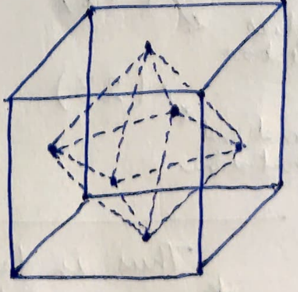
since 2 is a subgroup of $\bar{4}$ }

We can see how the tetrahedron is embedden in a cube:



* { Order of rotation group of tetrahedron: 12 }

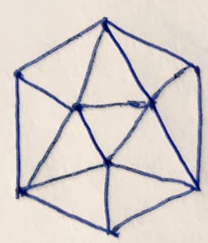
(iii) Octahedron:



* (this group is equivalent to the cube group)

(iv) Icosahedron (20-faces)

the top view is shown below:

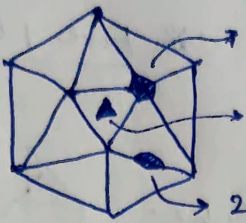


(12 vertices, 20 faces, 30 edges)

* NOTE: Euler's Polyhedron Formula:

$$\boxed{V - E + F = 2}$$

We can see the rotation axes :



5-fold (6 in no.)

3-fold (10 in no.)

2-fold (15 in no.)

$(5^-)^2$
$\equiv$
$\underbrace{\{1, 5^+, (5^+)^2, (5^+)^{-2}, 5^-\}}$
count 4 (ignoring 1 since that is already counted separately)

* ∴ Order of icosahedral point group

$$= 6 \times 4 + 10 \times 2 + 15 \times 1 + 1$$
$$= \boxed{60}$$

size of groups (ignoring element 1 in them)

(v) Dodecahedron

this is actually just a dual of the icosahedron

121] Now, from Crystallographic restriction

we get the Crystallographic Groups of Proper Rotation !

I. Monoaxial : 1, 2, 3, 4, ~~5~~, 6, ~~7~~, ~~8~~, ~~9~~, ~~-----~~

II. Dihedral : 222, 32, 42, 622

III. Platonic Solids : Tetrahedral, Octahedral ≡ Cube, ~~Icosahedral~~

Schoenflies notation : (Td) (O) (I_h)

International notation : (23) (432) (532)

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* Thus, in total there are only $\boxed{11}$ Chiral or Enantiomorphic or Proper crystal Groups