Theorem: A group containing type II operations ($\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{6}$) is of even order with an equal no. of Type I and Type II operations.

$\bar{1}$ = centre of inversion; $\bar{2} \equiv m$

Lec 21 08.04.2024

Crystallographic Symmetry in 3D

3D Point Groups

122]

	2D	3D
Crystal Systems	4	7
Bravais Lattices	5	14
Point Groups	10	32
Space "	17	230

Symmetry operations		2D	3D
		1, 2, 3, 4, 6	1, 2, 3, 4, 6
	Point	m	$\bar{1}$, $\bar{2}=m$, $\bar{3}$, $\bar{4}$, $\bar{6}$
		$\bar{a}$, $\bar{b}$	$\bar{a}$, $\bar{b}$, $\bar{c}$
	space operation	g	a, b, c, d, e, n

123] **Crystallographic Restriction in 3D:**

Only possible rotations compatible with lattice translations in 3D are 1, 2, 3, 4 and 6.

(1) A rotation is represented by a rotation matrix in a given basis.

$P, \; Q = P^{-1}$ $\qquad \mathcal{B} \xrightarrow{Q} \mathcal{B}'$

$(\bar{a}' \, \bar{b}' \, \bar{c}') = (\bar{a}, \bar{b}, \bar{c}) P$ $\qquad W \qquad W'$

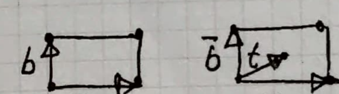
$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = Q \begin{pmatrix} x \\ y \\ z \end{pmatrix} = P^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad \boxed{W' = Q W Q^{-1}}$$

$$\begin{array}{ccc} \mathcal{B} & & \mathcal{B}' \\ \bar{x} & \xrightarrow{Q} & \bar{x}' = Q\bar{x} \\ W \downarrow & & \downarrow W' \\ \tilde{x} & \xrightarrow{Q} & \tilde{x}' = Q\tilde{x} \end{array}$$

(2) Rotation in $\mathcal{B}$ = Primitive Basis for lattice

All lattice translations have Integer components

$\tilde{t} = W^{\mathcal{B}}(t)$



Primitive $\qquad$ Non primitive

$\tilde{t} = n\bar{a} + m\bar{b} \qquad \tilde{t} = \frac{1}{2}\bar{a} + \frac{1}{2}\bar{b}$

$$\begin{pmatrix} \tilde{t}_1 \\ \tilde{t}_2 \\ \tilde{t}_3 \end{pmatrix} = (W^{\mathcal{B}}) \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix}$$

integers

$W^{\mathcal{B}}$ is a matrix of integer element

$W^{\mathcal{B}}_{ij}$ = integers.

$$\begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \underbrace{\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}}_{\text{Lattice translation } a} \leftarrow \bar{a} \quad = \underbrace{\begin{pmatrix} W_{11} \\ W_{21} \\ W_{31} \end{pmatrix}}_{\text{Rotated Lattice translation}}$$

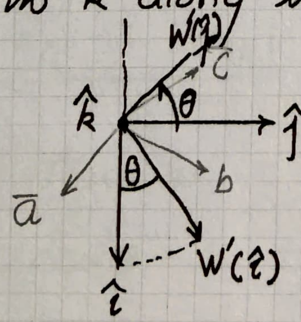
$\Rightarrow$ 1st colum is integers

Choose $\bar{b}$ and $\bar{c}$ $\Rightarrow$ 2nd. and 3rd col. integers

$W =$ integers.

$$\text{Trace} = \sum_{i=1}^{3} W_{ii} = W_{ii} = \text{integer}.$$

(3) Let us change the basis to $\mathcal{B}'$ which is an orthonormal basis $\mathcal{B}' = \{\hat{i}, \hat{j}, \hat{k}\}$ with $\hat{k}$ along the rotation axis



Matrix for rotation by angle θ in this basis

$$W' = \begin{array}{c} \begin{matrix} W'(\hat{i}) & W'(\hat{j}) & W'(\hat{k}) \end{matrix} \\ \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

$$\text{Trace } W' = \cos\theta + \cos\theta + 1 = 2\cos\theta + 1$$

(4) Trace of any operation is indepent of Basis Chosen. (!)

$$W' = QWQ^{-1}$$

$$W'_{ii} = (QWQ^{-1})_{ii}$$

$$= Q_{ij} W_{jk} Q^{-1}_{ki}$$ from matrix mult.

$$= (Q^{-1}_{ki} Q_{ij}) W_{jk}$$ as the three numbers are scalars

$$= (Q^{-1}Q)_{kj} W_{jk}$$

$$= I_{kj} W_{jk}$$

$$= (IW)_{kk}$$

$$\boxed{W'_{ii} = W_{kk}}$$ Trace $W' =$ Trace W

(5) Trace W' = Trace W

$2\cos\theta + 1$ = Integer

$\Rightarrow$ $2\cos\theta$ = Integer = N (say.)

$$\cos\theta = \frac{N}{2}$$

$$-1 \leq \frac{N}{2} \leq 1$$

$$\Rightarrow \quad -2 \leq N \leq 2$$

N	$N/2 = \cos\theta$	θ	Fold $n = 360/\theta$
-2	-1	180°	2
-1	$-\frac{1}{2}$	120°	3
0	0	90°	4
1	$\frac{1}{2}$	60°	6
2	1	360°	1

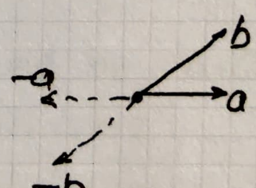
124]

Presence of $\bar{1}$ in 3D

Why is $\bar{1}$ absent in 2D ?

$$\bar{1}(\bar{r}) = -\bar{r} \quad \text{for inversion in origin.}$$

$$\bar{1}_{2D} = \begin{array}{cc} -a & -b \\ \multicolumn{2}{c}{\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}} \end{array}$$

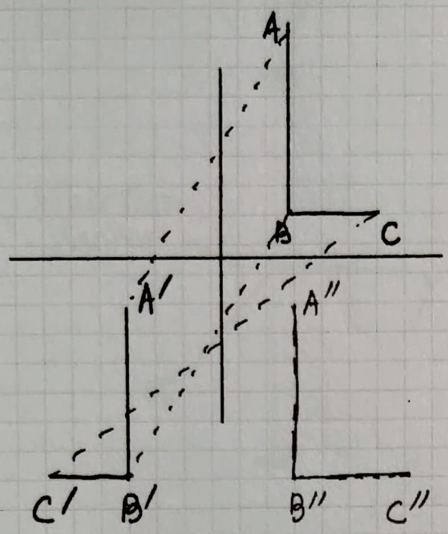


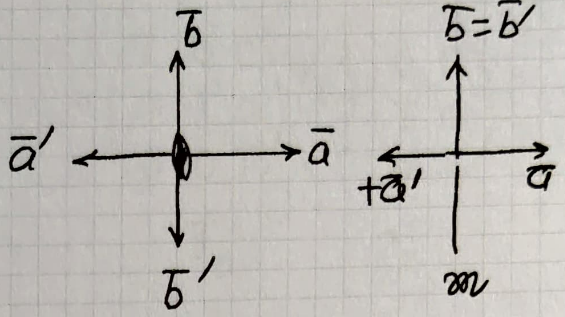
Det $= +1 \Rightarrow$ Type 1

$\Rightarrow$ Rotation !

$$2\cos\theta = -2 \Rightarrow \cos\theta = -1 \Rightarrow \theta = 180^\circ$$
$$= 2 \text{ fold!}$$

2)





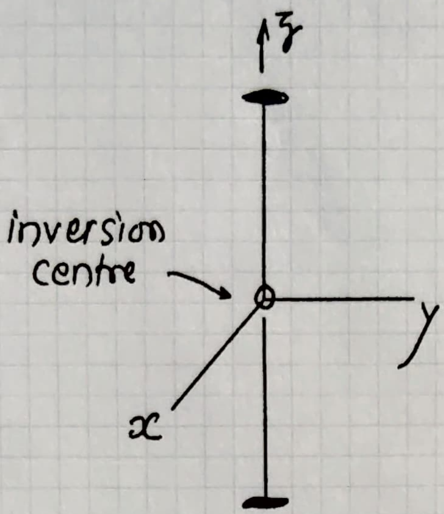
$\bar{1}$ = Inversion centre is a new operation in 3D

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{Det} = -1 \quad \text{Type II}.$$

125] Rotoinversion Rotation followed by inversion on a point on the rotation axis.

$\bar{1}$ = 1 fold rotation followed by an "

$\bar{2}$ = 2-fold rotation followed by inversion



$$\bar{2}_z = \underset{\bar{1}_0}{\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}} \underset{2_z}{\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}}$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$

$$= m_{xy}$$

$\bar{2} = m \perp$ to rotation axis and passing through inversion centre.

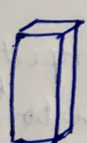
{ Lecture Sheets Attached }

LECTURE 22 (15/04/2024)

Q→ Find all centrosymmetric groups (containing $\bar{1}$)

$\bar{1}$: centrosymmetric
m: not centrosymmetric (although not chiral)

NOTE: The point group of a duster (or any cuboid)



is given as:
mm2
(in 3D) ⇒ ∴ It is Orthorhombic

* { In 2D we would call it : 2mm }

(we write mm2 instead of 2mm, just by convention)

{ In orthorhombic the convention is :

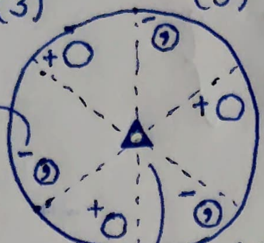
m m 2
x y z
(the unique axis is placed in z) }

NOTE: $\bar{3}$ contains 3 as a subgroup

$(\bar{3} = 3 \cup \bar{1})$

$\bar{3}^{-} = (\bar{3})^2$ $\qquad (\bar{3})^3 = \bar{1}$

(-ve sign to show below the equatorial plane)



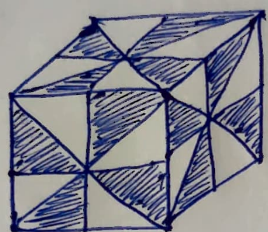
$\bar{3}^{+} = \bar{3}$ $\qquad (\bar{3})^4 = 3^{+}$ $\qquad (\bar{3})^5 = \bar{3}^{-}$

1

From here we also see that $\bar{3}$ is a cyclic group

 : represents 3-fold rotation along with inversion

NOTE: Example:



For something to be cubic

↓

it must have four 3-fold symmetries

↓

⇒ Here that condition is satisfied (body diagonals)

Possibilities are:

432 $\quad \cancel{23} \quad \cancel{m\bar{3}} \quad \cancel{\bar{4}3m} \quad m\bar{3}m \equiv \frac{4}{m}\bar{3}\frac{2}{m}$

these are centrosymmetric

Another property we see is that the object has 4-fold ~~diagonals~~

NOTE:

432	O
23	T
$m\bar{3}$	T_h
$\bar{4}3m$	T_d
$m\bar{3}m$	O_h
[IUCr]	[Schoenflies]

⇒ A useful property of the international notation is:

eg: 432

along [100] [111] [110]

* Also, operations included in the international symbol of a point group are generators of the point group.

From here we see that only
432 and $m\bar{3}m$ have a 4-fold

Next, there is also a 2-fold (through opposite edge centres)

Now, interestingly, if we carefully see the object, we observe that it does not have a $\bar{1}$
$\Downarrow$
thus, it cannot have a $\bar{3}$ too
(so, $m\bar{3}m$ is also rejected)

Hence, we get: $\boxed{432}$

{ *NOTE: $\frac{3}{m} = \bar{6}$ }

LECTURES 23 & 24 ⇝ Involved solving on Tutorial questions (on 15[th] and 18[th] April respectively)

L25 18·04·2025

126] Space Groups $G = \{(W, w)\}$ ← 230 Space Groups

Location Screw glide

Translation Subgroup $T = \{(I, t)\}$

Lattice translations
Lattice.

New operations in 3D: Screw and glide

127] Point Groups : Group of operations that leave a point fixed.
No translations
for molecules, for a point a crystal
(site symmetry)

<u>Space Group</u> : Group of all operations (including translations) ~~that leave~~ bring a crystal into self-coincidence.

$$G = \{(W, w), \dots\}$$

Linear or matrix part — vector or translation part.

128] <u>Identity</u>

$$G = \{(I, 0), \dots\}$$

$$(I, 0)(W, w) = (IW, Iw + 0)$$
$$= (W, w)$$

$$G = \{(W, w), \dots\}$$

location | screw | glide | pure translation

For pure translation $W = I$

(I, t) : No rotation
$\Rightarrow t$ = pure translation

$t =$ lattice translations

~~Imper~~ Images of an initial ~~so~~ choosen point under all lattice translations t' is called the lattice.

$$\mathcal{T} = \{(W, w) \mid W = I\}$$

$\mathcal{T}$ is the translation subgroup of $\mathcal{G}$

identity $(I, 0) \in \mathcal{T}$, $\quad (I, t)^{-1} = (I^{-1}, -I^{-1}t)$

inverse $(I, t) \in \mathcal{T} \Rightarrow (I, t)^{-1} \in \mathcal{T} \quad = (I, -t)$

Closure $(I, t)(I, t') = (I^2, It' + t)$

$$= (I, t' + t) \in \mathcal{T}$$

$\Rightarrow$ Translations form a subgroup of the space group called the translation group.

Point group of plane group

p2gm $\longrightarrow$ Point group 2mm

<u>In 3D</u> | Glide $\rightarrow$ mirror
Screw $\rightarrow$ pure rotation

129] **Definition of a Point Group of a Space Group:**

$$(W, w) \in G$$

We define a the point group of a space group G

as $P = \{ W \mid (W, w) \in G \}$

Is P a group?

identity $(I, 0) \in G \Rightarrow I \in P$

Closure $(W, w), (W', w') \in G \Rightarrow W, W' \in P$

$$(W, w)(W', w') \in G$$

$$\Rightarrow (WW', Ww' + w) \in G$$

$$\Rightarrow WW' \in P$$

Inverse $(W, w) \in G \Rightarrow W \in P$

$$\Rightarrow (W, w)^{-1} \in G$$

$$\Rightarrow (W^{-1}, -W^{-1}w) \in G$$

$$\Rightarrow W^{-1} \in P$$

P is a Group

Is P a subgroup of G ?

$\Rightarrow$ No (Diff. types of operations)

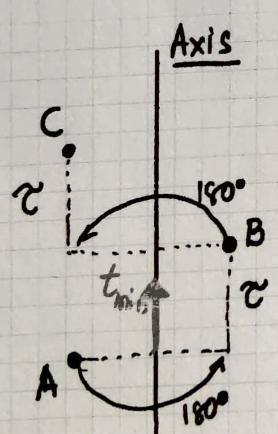
Two <u>new</u> kinds of operations in 3D Space Group

Screw operations

Rotation about an axis with translation parallel to the axis.

130]

Types of crystallographic screw axes



τ = screw translation

s = screw operation

$s^2 = 2\tau$

$$(2, \tau)^2 = (2, \tau)(2, \tau)$$
$$= (2^2, 2\tau + \tau)$$
$$= (I, \tau + \tau)$$
$$= (I, 2\tau)$$

$2\tau = \tau$ as $\tau \parallel$ rotation axis.

$(I, 2\tau) \in \mathcal{T} \Rightarrow 2\tau$ is a lattice translation.

Let t_{min} be the shortest lattice translation along the rotation axis

$$2\tau = m\, t_{min}$$

$$\Rightarrow \boxed{\tau = \frac{m}{2} t_{min}}$$

$\Rightarrow$

Don't give me new operation.

$m = 0 \Rightarrow$ no translation $\Rightarrow$ pure rotation.

$m = 2 \quad \tau = t_{min}$ combination of rotation with a full lattice translation

$$0 < m < 2 \Rightarrow m = 1$$

For a two-fold screw $m = 1$

$$\boxed{\tau = \frac{1}{2} t_{min}} \Rightarrow 2_1 \text{ Screw axis}$$

rotation fold

translation part $\tau = \frac{1}{2} t_{min}$

Generalization of screw axes for different folds of rotation

$$(n, \tau)^n = (I, n\tau) \Rightarrow n\tau = \text{lattice translation}$$

$n\tau = m t_{min}$ where t_{min} is the shortest lattice translation along the rotation axis.

$$\Rightarrow \boxed{\tau = \frac{m}{n} t_{min}}$$

Symbol for the corresponding screw axis

n_m

$0 < m < 1$ for the reasons discussed above for two-fold screw.

131] Possible screw axes in crystals (n_m, $0<m<n$)

2_1

3_1, 3_2

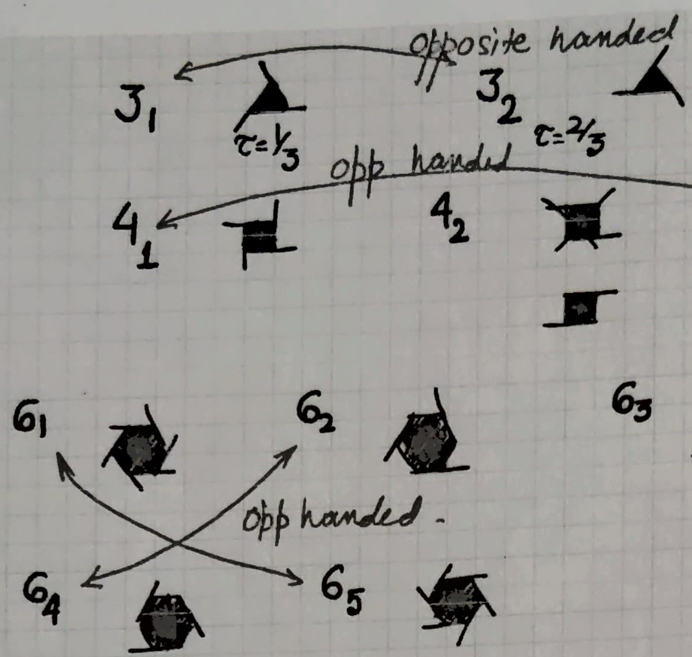
4_1, 4_2, 4_3

6_1, 6_2, 6_3, 6_4, 6_5

// Possible Screw Rotation Axes.

<u>Diagrammatic Symbols</u>

2_1  $\xrightarrow{\text{(half arrow)}}$ 2_1 || the projection plane.

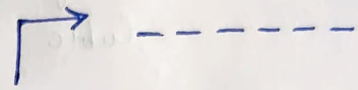
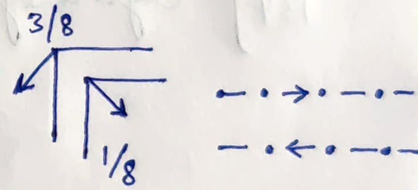
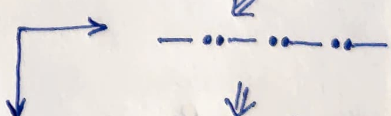


NOTE: This was followed by Galois skit by Samyak and

The next lecture, Lec 26 was by Prof. Aroyo, on Bilbao Crystallographic Server

LECTURE 27 (25/04/2024)

132]

Glide Plane	Glide Translation	Symbols
a (a glide)	$\pm \frac{1}{2} \vec{a}$	
b (b glide)	$\pm \frac{1}{2} \vec{b}$	
c (c glide)	$\pm \frac{1}{2} \vec{c}$	. . . .
d (diamond glide)	$\frac{1}{4}(\vec{a} \pm \vec{b})$ $\frac{1}{4}(a \pm b \pm c)$	
e (double glide)	$\frac{1}{2}\vec{a}$, $\frac{1}{2}\vec{b}$	
n (diagonal glide)	$\frac{1}{2}(\vec{a}+\vec{b})$	

a glide: Glide is in the projection plane (perpendicular lines represent the plane & arrow represents glide direction); Glide is ⊥ to proj. plane

c glide: (dots show the direction of the glide) glide plane is ⊥ ; & glide dirⁿ is also ⊥ to proj. plane

d glide: (these two parallel planes are at different heights)

e glide: (double dot) (one is in the plane, & one is into the plane)

133] **7 Crystal Systems** | **32 Point Groups** | **Bravais Lattices**

7 Crystal Systems	32 Point Groups	Bravais Lattices
Triclinic	$1, \bar{1}$	aP
Monoclinic	$2, m, 2/m$	mP, mS
Orthorhombic	$222, mm2, mmm$	oP, oI, oF, oS
Tetragonal	$4, \bar{4}, 4/m, 422, \bar{4}m2, 4mm, 4/m\,mm$	tP, tI
Trigonal	$3, \bar{3}, 3m, 32, \bar{3}m$	hP, hR
Hexagonal	$6, \bar{6}, 6/m, 622, \bar{6}m2, 6mm, 6/m\,mm$	hP
Cubic	$23, 432, m\bar{3}, \bar{4}3m, m\bar{3}m$	cP, cI, cF

* **NOTE**: The $a, b, c, \alpha, \beta, \gamma$ based definitions of crystal systems (that are commonly found in textbooks)

↓ are inaccurate

↓ the actual definitions are based on symmetries.

134] Crystal systems are defined by <u>their characteristic symmetry</u>

↓ and NOT by relations b/w the lattice parameters

eg: Cubic crystal system → does not mean $a = b = c$, etc.

⇓ instead it implies 4 three-fold axes

Bravais Lattice Notations

a = anorthic ≡ triclinic

{ **NOTE**: "aP" — a → family system, P → centering system }

m = monoclinic

P = primitive (lattice points at corners)

S = end-centered (Base-centred)

{ S ≡ A, B, C }

o = Orthorhombic

t = tetragonal

h = hexagonal

c = cubic

I ≡ Body-centred
("I" comes from the german word for body-centred
↓
Schoenflies was German)

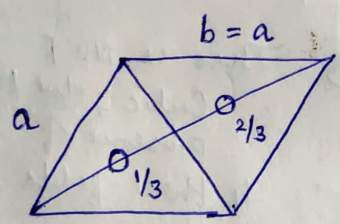
F ≡ Face-centred

* NOTE: In the trigonal crystal system
↓
there is no trigonal bravais lattice!
(99% textbooks make this mistake)

{ Earlier, Rhombohedral was used equivalently to Trigonal
↓
but this is not the case now }

Trigonal actually has 2 lattices: Primitive, Rhombohedral

R = Rhombohedral centering



(two points are drawn at $1/3^{rd}$ and $2/3^{rd}$ distance on the diagonal
↓
these points are centroids of the two triangles)

* NOTE: From the table you can see
↓
hP is the ONLY lattice which belongs to two crystal systems ⇒ To emphasize this point
↓
* 6 Crystal Families are created
↓
where Trigonal and Hexagonal crystal systems both come under the same "Hexagonal Crystal family"

6 Crystal Families	7 Crystal Systems
Triclinic	Triclinic
Monoclinic	Monoclinic
Orthogonal	Orthogonal
Tetragonal	Tetragonal
Hexagonal	{ Trigonal, Hexagonal
Cubic	Cubic

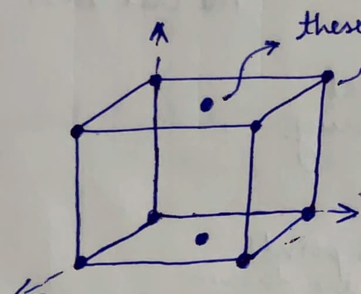
135] Also we have

7 Lattice systems

aP	Triclinic
mP, mS	Monoclinic
oP, oI, oF, oS	Orthorhombic
tP, tI	Tetragonal
hP, hR	Hexagonal
hP	Rhombohedral
cP, cI, cF	cubic

136] <u>Why some lattices appear to be missing :</u>

Why cS → cC (C-centred cubic) is not present as a Bravais lattice



these two points are actually identical in the 3D lattice

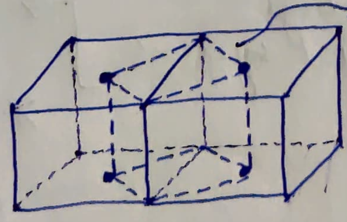
⇒ This is NOT Cubic, due to absence of 4 three-folds

⇓

We can see that there is a 4-fold along the centred points

⇓

This is Tetragonal



choosing this ↓ we see that we get a primitive tetragonal lattice

Similarly, anything else we can construct will fall into one of the 14 Bravais lattices

137] **Space Groups Construction**

Combine Bravais lattice with point group

Crystal = Lattice + Motif
(How to repeat) (What to repeat)
⇓
14 types

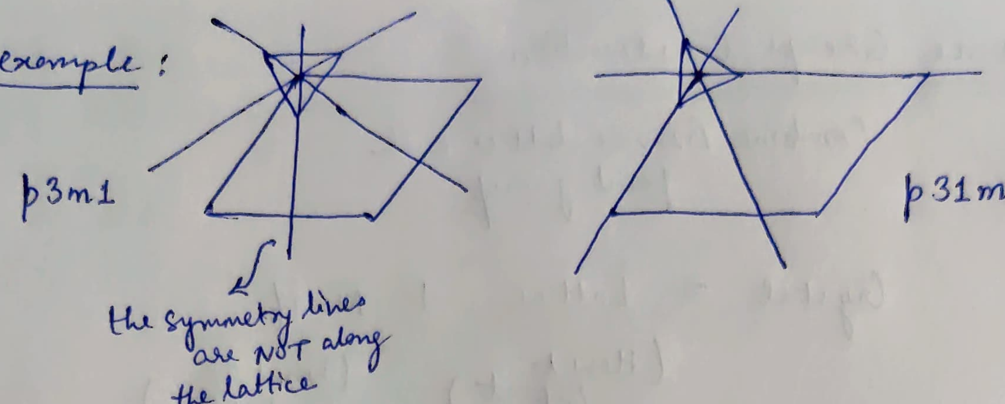
Space Group Symmetry = Translation Symmetry + Point Group Symmetry

Combination of 14 Bravais lattices with 32 point groups result in 73 symmorphic space groups

	Bravais Lattice	Point Groups	Symmorphic Groups
Triclinic	1 (aP)	2 (1, $\bar{1}$) this tells the symmetry of the motif	$1 \times 2 = 2$ P1, P$\bar{1}$
Monoclinic	2 (mP, mC)	3 (2, m, 2/m)	$2 \times 3 = 6$ P2, Pm, P2/m, C2, Cm, C2/m
Orthorhombic	4	3	$4 \times 3 = 12$
Tetragonal	2	7	$2 \times 7 = 14$
Trigonal	2	5	$2 \times 5 = 10$
Hexagonal	1	7	$1 \times 7 = 7$
Cubic	3	5	$3 \times 5 = 15$
			66

⇙
here 7 groups are missing (from the total 73)
↓
this is because of the possibility of orienting the point groups with the lattice

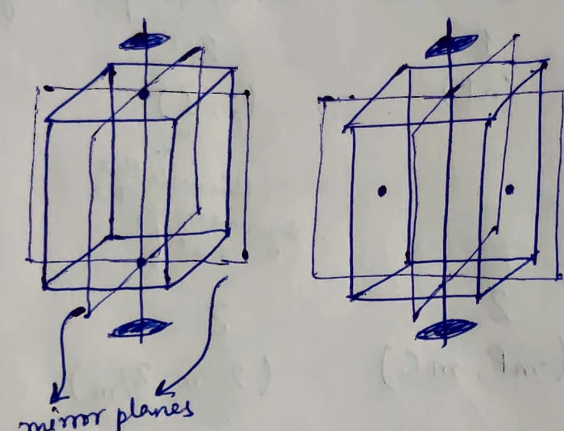
2D example :



{ Here,  has a 3m point group } ⇒ this exists in a hp lattice

Taking a 3D example

mm2 point group
on oS lattice



* **NOTE:** These 73 symmorphic space groups
↓
* did NOT require any screw or glide plane to generate them
{ thus, it is not present in the symbol }
↓
* But some symmorphic space groups may contain screw or glide

The remaining 230 − 73 = 157 space groups are Non-symmorphic
↓
i.e., they require screw or glide as generators ⇒ their symbols have screw or glide

eg: We can create non-symmorphic groups from symmorphic groups :

$$P2 \longrightarrow P2_1$$

Symmorphic   Non-symmorphic

$$Pm \longrightarrow Pc$$

LECTURE 28 (26/04/2024)

[This covered only doubts and summary]

END OF DEGREE