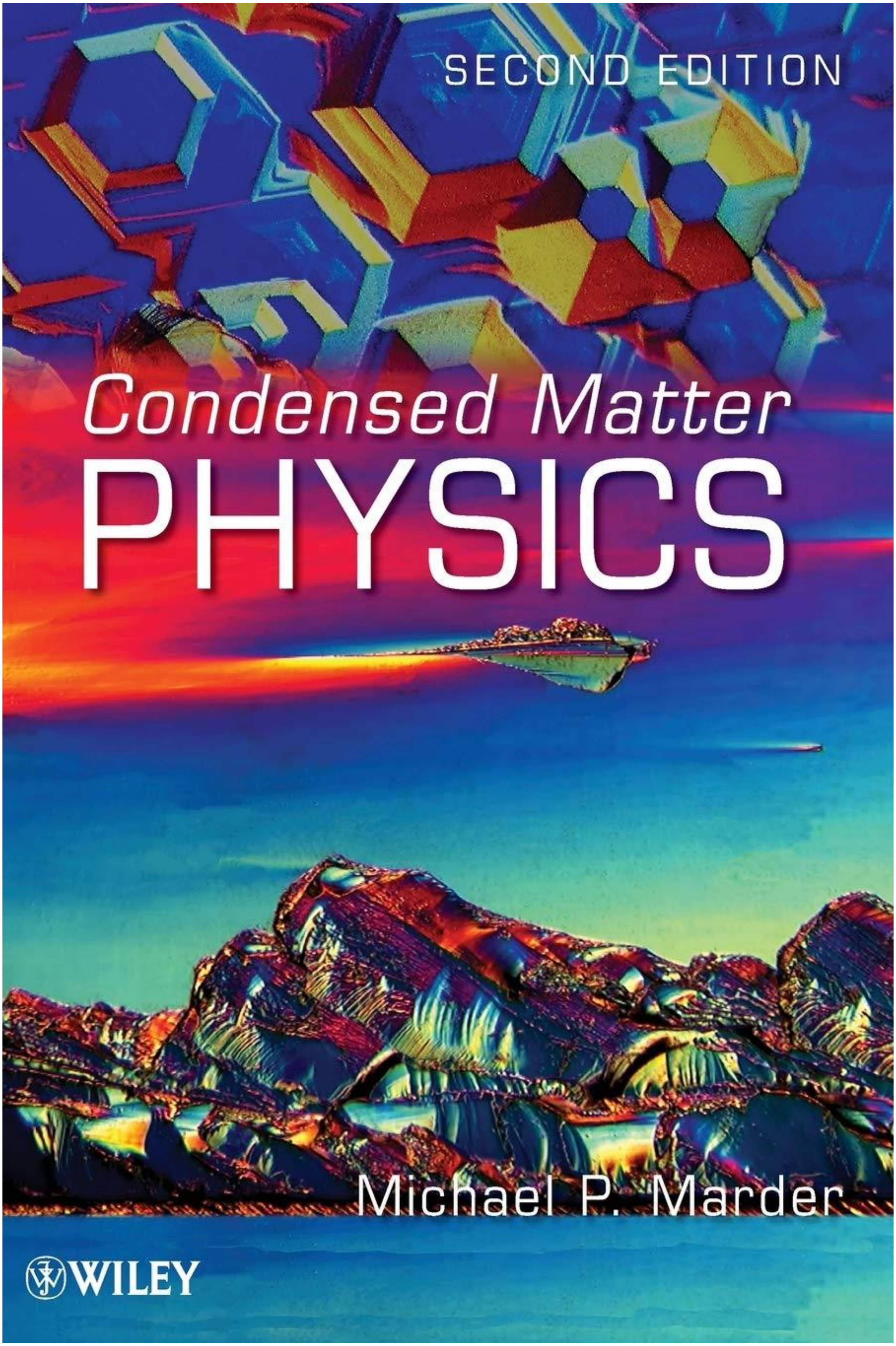

SECOND EDITION
Condensed Matter
PHYSICS
Michael P. Marder
WILEY

Condensed Matter physics

Phys (771)

Dr. Gassem Alzoubi

<u>Textbook</u>: Condensed Matter Physics, 2^{nd} edition, (2010)

by Michael Marder

Publisher: John wiley and Sons, New Jersey, USA

CMP is the study of materials in solid and Liquid phases

This includes the study of ordered crystalline phases of solids, as well as disordered phases such as amorphus and glassy phases of solids.

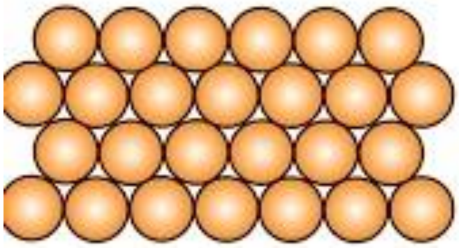
- solids are classified into 3 categories

i) crystalline solids: form a repeating (Periodic) pattern

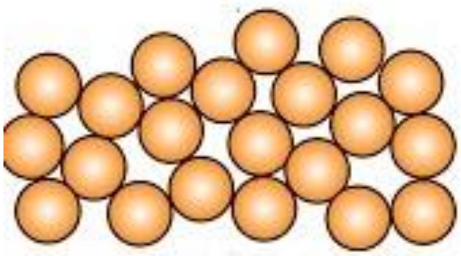
ii) Amorphus solids: No repeating pattern

iii) Polycrystalline solids: made up of large # of small crystals, called crystallits. Regular pattern in each crystallits. size and orientation are varying from one crystallite to another.

Crystalline Solid

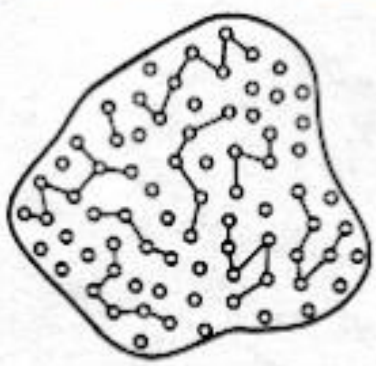


Amorphous Solid

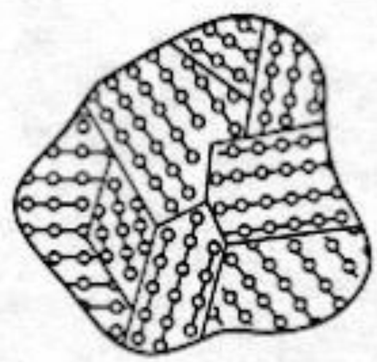


Crystalline Solid

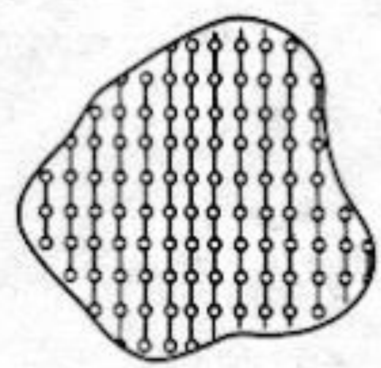
Amorphous Solid



Amorphous Solid



Polycrystalline Solid



Crystalline Solid

Sources
https://www.pinterest.com/

https://www.shutterstock.com/

http://www.jhaj.net/

In this course, we will mainly focus on crystalline solids, where we shall assume infinite and perfectly periodic crystals

Part I

Atomic Structure

Chapter 1: The idea of crystals

A crystal is a solid where the atoms are arranged in the form of a lattice.

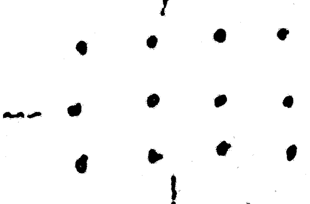
Key point is

Lattice + Basis = Crystal structure

A lattice: is an arrangement of points where the same pattern repeats over and over again.

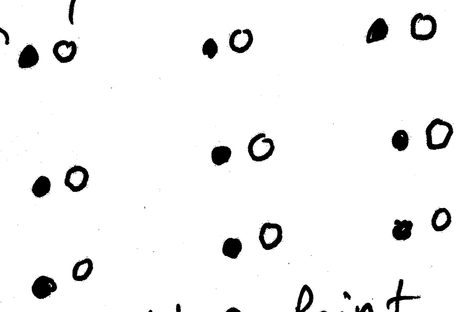
Basis: Atoms that reside on lattice points

Example:



an infinite array

lattice points occupied by one atom



each lattice point occupied by two atoms A and B

How to describe a lattice?

to describe a lattice, we need the following

- conventional cell
- primitive unit cell
- primitive lattice vectors $\vec{a_1}$, $\vec{a_2}$, and $\vec{a_3}$
- translational vector $\vec{R}$

- Two-dimensional lattices:

Q: how many possible lattices can one have in 2D?

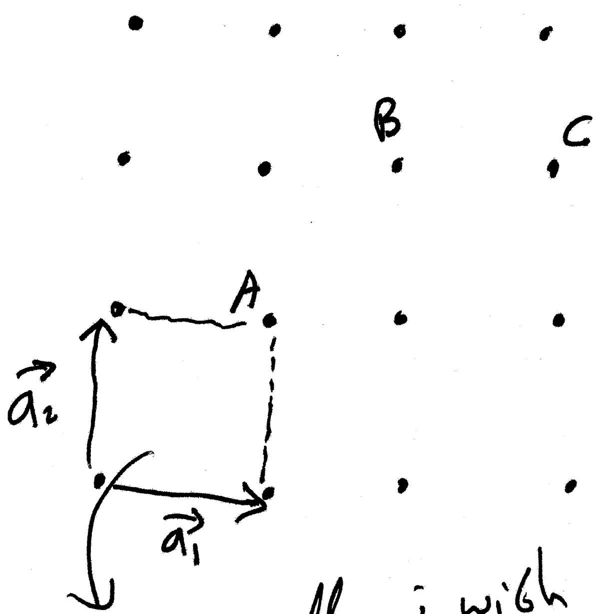
A: many many lattices. however, there are special types of lattices that are stable and occur naturally; these lattices are called Bravais lattices.

so a 2D Bravais lattice is an infinit array of discrete points that can be connected or generated by a positive lattice vector that takes the form

$$\vec{R} = n_1 \vec{a_1} + n_2 \vec{a_2} \; ; \quad n_1, n_2 : \text{integers } 0, \pm 1, \pm 2, \cdots$$
$$\vec{a_1}, \vec{a_2} : \text{primitive lattice vectors}$$

where $\vec{a_1}$, $\vec{a_2}$ are not unique and can be chosen by different ways. furthermore, they are not necessary to be perpendicular to each others.

Example: 2D square lattice



A, B, C are equivalent position

- A and B are connected by $\vec{a}_1 + \vec{a}_2$ to move from $A \to B$
- A and C are connected by $2\vec{a}_1 + \vec{a}_2$; to move from $A \to C$

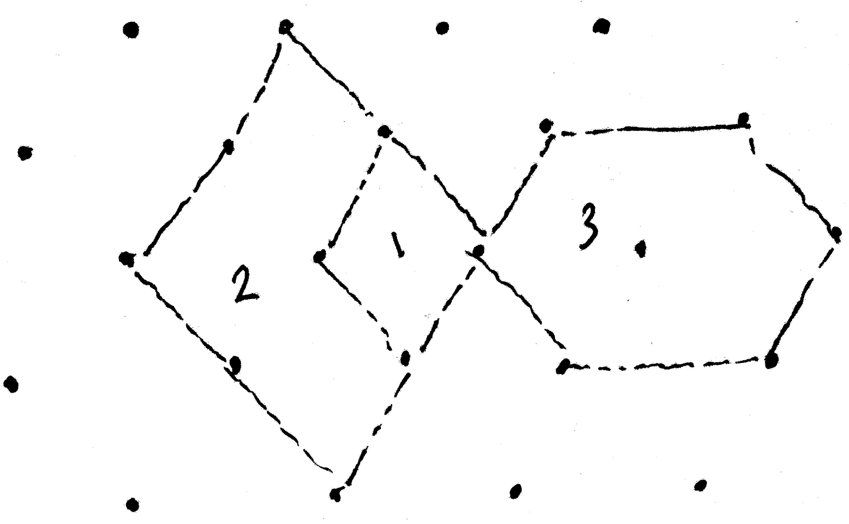
unit cell ; with $a_1 = a_2$; area $= |\vec{a}_1 \times \vec{a}_2|$

1 Lattice point / unit cell

- primitive unit cell contains only one lattice point; i.e there are lattice points only at every corner of the unit cell, but not inside the cell or at the faces or edges.

the primitive unit cell is the smallest possible unit cell.

Ex!



1: primitive

2, 3: are non-primitive

by connecting primitive cells, one can fill all space with no voids and overlaps.

a 2D Bravais lattice is charcterized by

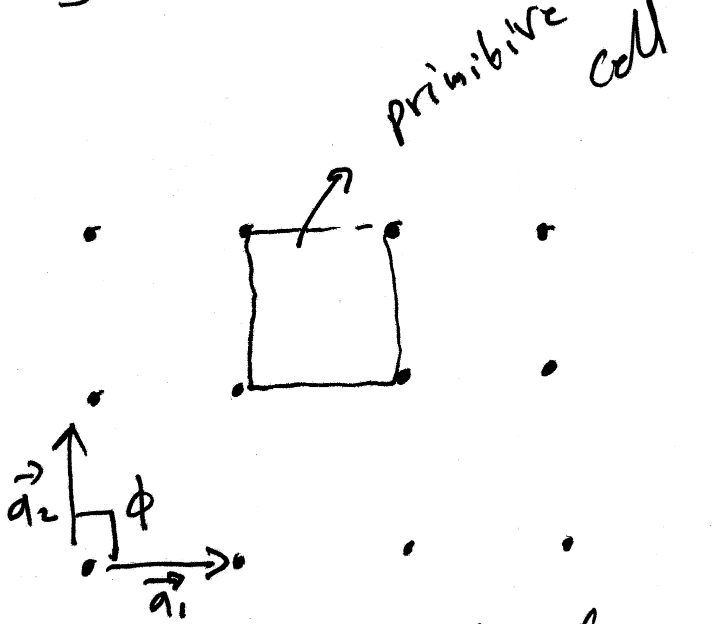
- all atoms are of the same type (monoatomic)
- all lattice points are equivalent.

in 2D and based on symmetry, there are 5 Bravais lattices, where each type of lattice has its specific symmetry elements.

① square lattice

$|\vec{a}_1| = |\vec{a}_2|$

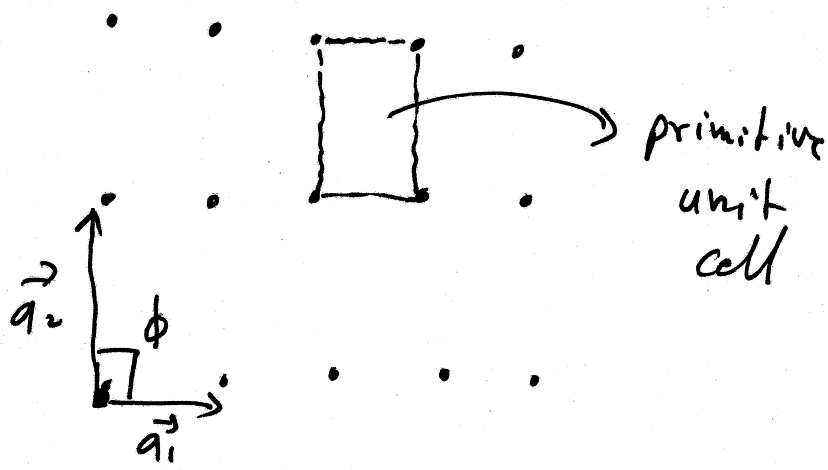
and $\phi = \frac{\pi}{2}$



Note that each unit cell is shared with four others, giving one lattice point per unit cell, and hence primitive.

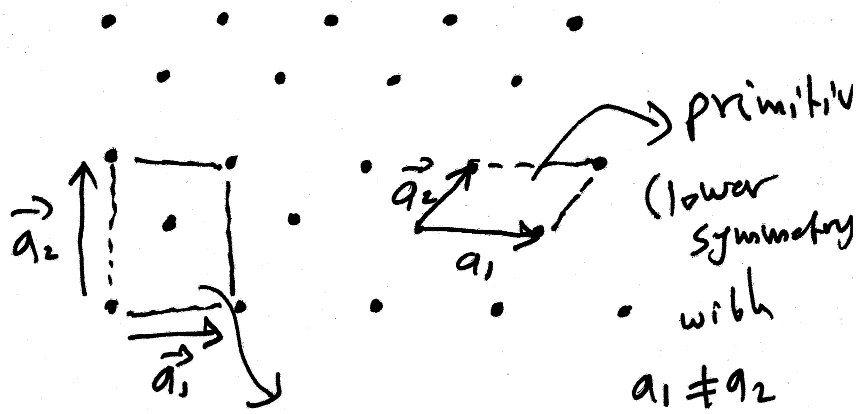
② Rectangular lattice $|\vec{a}_1| \neq |\vec{a}_2|$ and $\phi = \pi/2$

1 LP/cell



③ Centered Rectangular lattice

can be set up in two ways, perimitive and non-premitive (see fig)



(lower symmetry with $a_1 \neq a_2$ and $\phi \neq \frac{\pi}{2}$)

1 LP/cell

non-primitive unit cell (more symmetric)

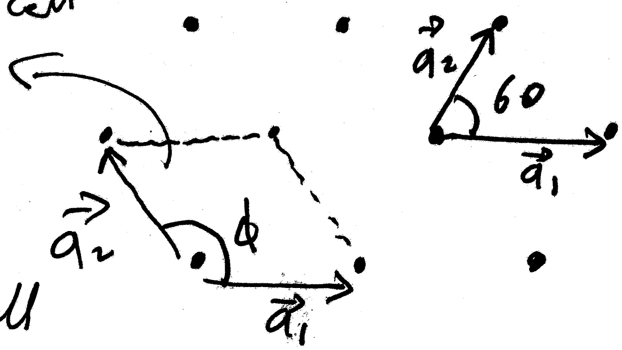
2LP/cell

$a_1 \neq a_2$ and $\phi = \pi/2$

④ Hexagonal $|\vec{a}_1| = |\vec{a}_2|$; and $\phi = 120°$

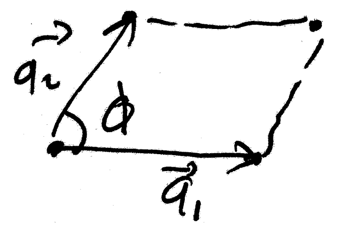
primitive unit cell

the primitive cell is shared with four other surronding cells, giving 1 lattice point / P. unit cell



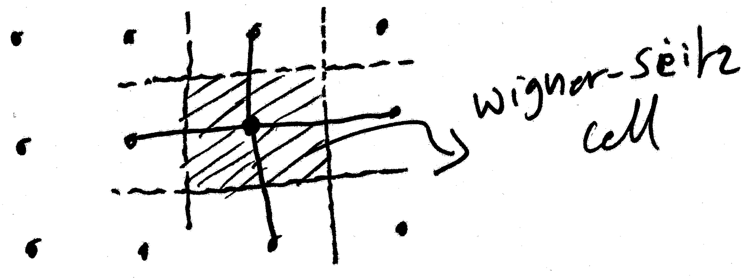
⑤ oblique lattice ; $|\vec{a_1}| \neq |\vec{a_2}|$ and $\phi \neq \pi/2$

1 LP/cell

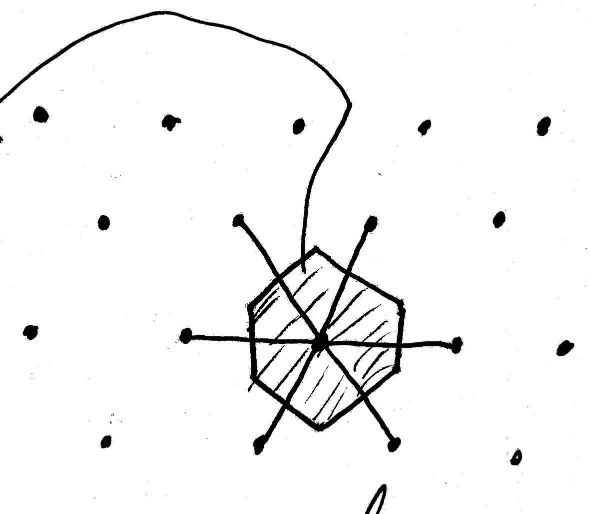


So All crystal structures in 2D, must belong to one of these five types of lattices.

<u>Wigner-Seitz cell:</u> it is a special primitive unit cell that reflects the full symmetry of the Bravais lattice. it is constructed by the following steps i) take a lattice point and draw lines connecting the point to all nearby lattice points, ii) Bisect these lines with orthogonal planes, iii) construct the the smallest area (volume in 3D) that contains the lattice point



square lattice



Hexagonal lattice

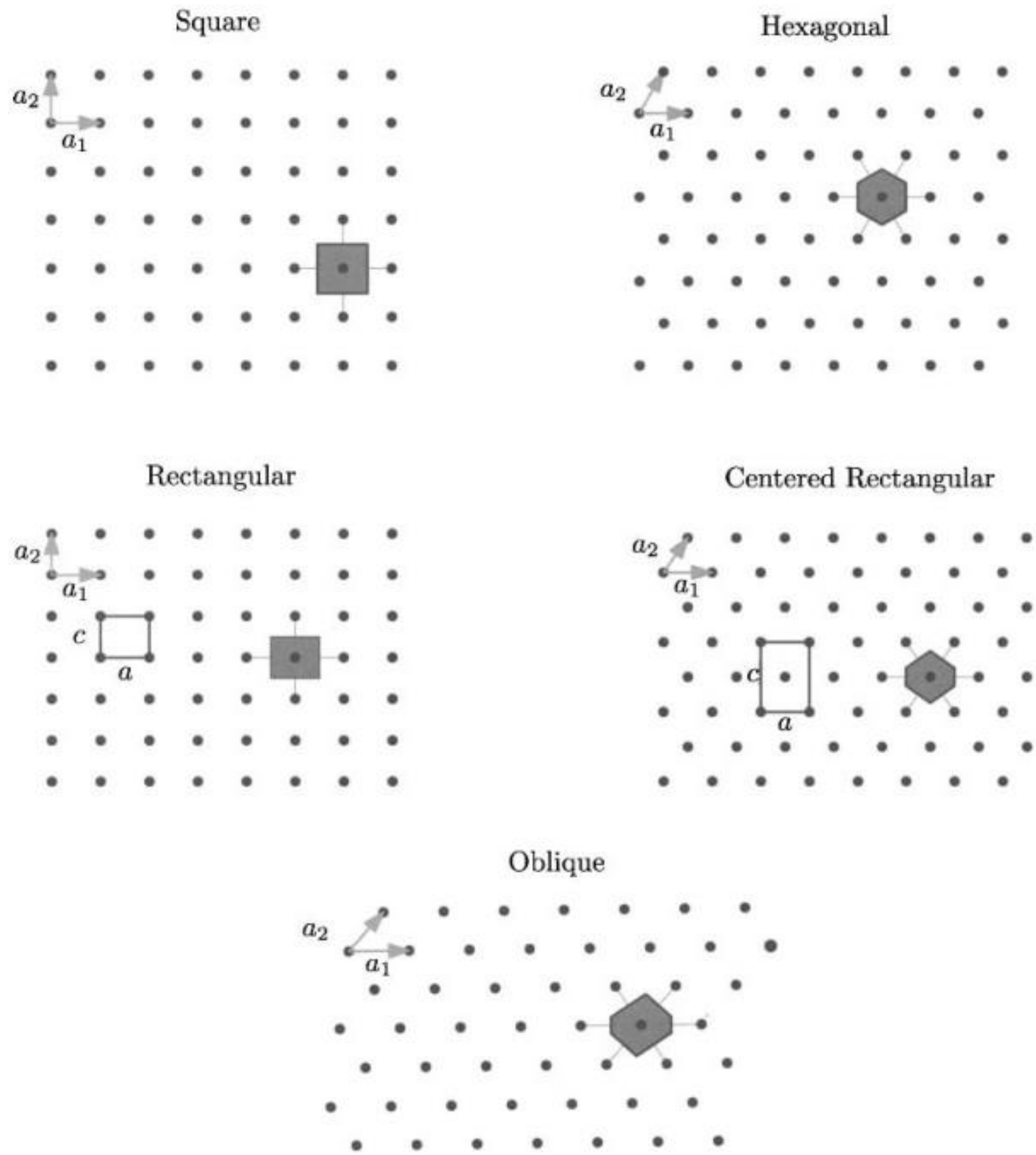


Figure 1.4. The five two-dimensional Bravais lattices. Note that the centered rectangular lattice can be built by repetition of the structure in the hollow box, which shows how it obtains its name. The figure also shows Wigner–Seitz cells for each lattice. One constructs them by choosing some point 0 in the lattice and then drawing the perpendicular bisector of the line between 0 and each of its neighbors. The Wigner–Seitz cell is the region surrounding 0 contained within all these perpendicular bisectors.

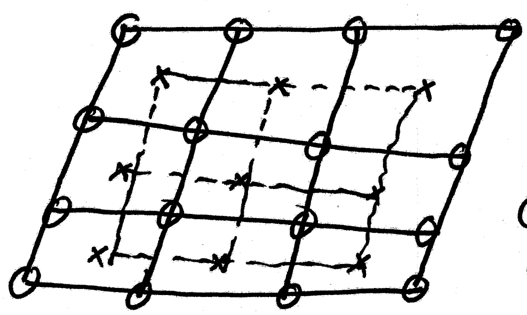
Recall that for Bravais lattice (BL)

- all atoms are the same kind as well as all lattice points are equivalent.

and for non-Bravais lattice, atoms are of different types and/or some lattice points are not equivalent

However, most lattices occuring in nature are not BL, but called lattices with basis. furthermore, any non-BL can be written as a sum of two or more BL's

<u>Ex 1:</u>



2D- non BL

atom 1 : o
atom 2 : x

two different atoms

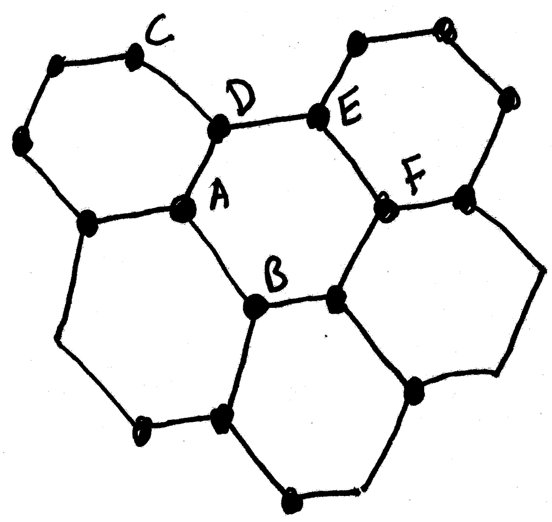
can be decomposed into two BL

—— 1^{st} BL

- - - 2^{nd} BL

<u>Ex 2:</u> <u>Honeycomb lattice!</u>

(Graphene)



2D- non BL

one type of atoms (carbon atoms)

- but some lattice points are not equivalent

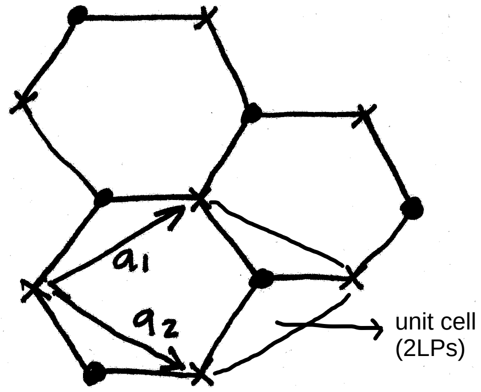
A, C, E equivalent

B, D, F are equivalent

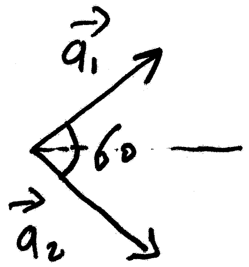
but for example A and B are not equivalent

Again the honeycomb lattice (Graphene lattice) can be decomposed into two BLs

A, C, E, --- 1^{st} BL and B, D, E, -- 2^{nd} BL
represented by ($\bullet$) represented by ($\times$)



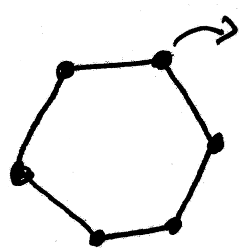
- Now to construct lattice vectors, Recall they must connect equivalent lattice points and the best choice is to take them as



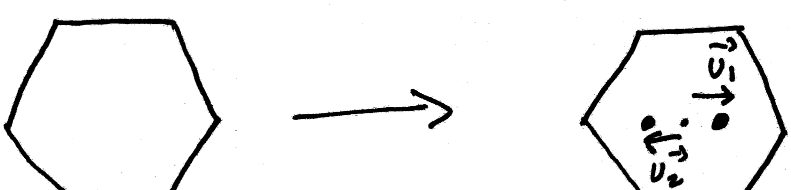
$$\vec{a_1} = a\cos 30\,\hat{i} + a\sin 30\,\hat{j} = a\left(\tfrac{\sqrt{3}}{2} \quad \tfrac{1}{2}\right)$$
$$\vec{a_2} = a\cos 30\,\hat{i} - a\sin 30\,\hat{j} = a\left(\tfrac{\sqrt{3}}{2} \quad -\tfrac{1}{2}\right)$$

Note that there are 2 lattice point / unit cell as each lattice point is shared with 3 hexagons, so

$$6 \times \frac{1}{3} = 2$$



- the graphene lattice can be constructed by starting with a hexagonal lattice and replacing the single point in the center of each cell by a pair of points



See Fig 1.5 in textbook

with $\vec{v_1} = a\left(\underbrace{\tfrac{1}{2\sqrt{3}}} \quad 0\right)$ and $\vec{v_2} = a\left(-\tfrac{1}{2\sqrt{3}} \quad 0\right)$

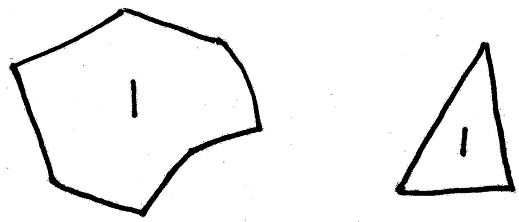
$$\frac{1}{3}(a_1)_x = \frac{1}{3}\frac{\sqrt{3}}{2} = \frac{1}{3}\frac{\sqrt{3}}{2}\frac{\sqrt{3}}{\sqrt{3}} = \frac{1}{2\sqrt{3}}$$

This choice is not unique

Rotational symmetry of the 5-2D Bravais lattice

if an object can be rotated about an axis and repeat itself **n**-times during a rotation of 360° (2π), then it is said to have an axis of n-fold rotational symmetry.
the following types of rotational symmetry axes are allowed in the 5-2D Bravais lattices:

- 1-fold rotation axis:

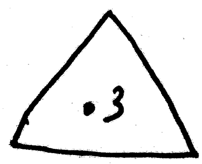


the lattice or the object repeats itself once during 360° rotation i.e $n = \frac{360°}{\theta}$; $\theta = 360 \Rightarrow n = 1$

- 2-fold rotation axis:

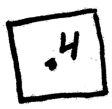
the lattice repeats itself twice during the 360° rotation. i.e repeats itself every 180° rotation $\Rightarrow n = \frac{360°}{180°} = 2$

- 3-fold rotation axis:



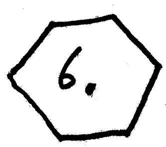
repeats itself every 120° rota $\Rightarrow n = \frac{360°}{120} = 3$

- 4-fold rotation axis:



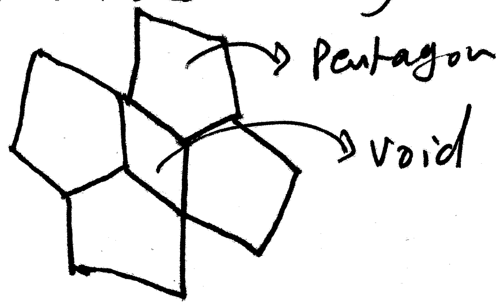
repeats itself every 90° rot $n = \frac{360}{90} = 4$

- 6-fold rotation axis:

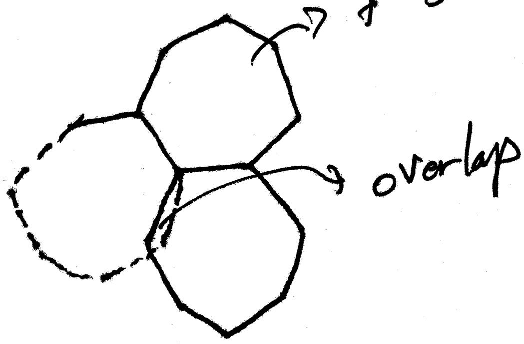


repeats itself every 60° rot $n = \frac{360}{60} = 6$

so, there are only 1, 2, 3, 4, 6 fold rotation axes in these 2D Bravais lattices. Note that the 5-fold rotational symmetry is not allowed as it can not fill all space without leaving voids. i.e objects with 5-fold symmetry axes can not be combined in such away they completely fill all space.



- similarly, the 7-fold rotational symmetry is not allowed as it can not fill all space without overlaps



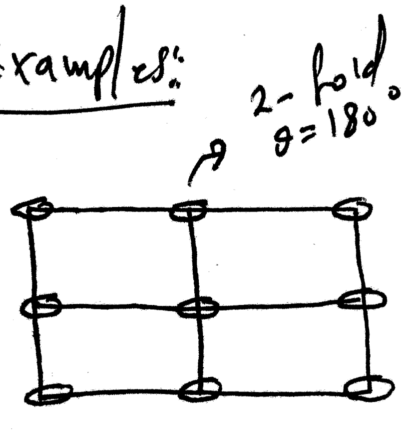
- symbols used to describe rotational symmetry are:

1-fold ○ 4-fold □

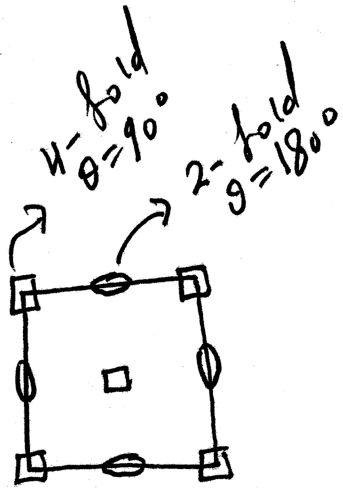
2-fold ⬭ 6-fold ⬡

3-fold △

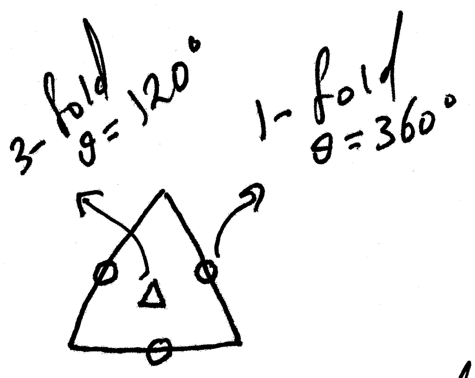
Examples:



rectangular lattice



square lattice



part of Hexagonal lattice

Symmetries in crystalline solids

A symmetry operation is an operation that leaves the crystal invariant. That is, after symmetry operation, the positions of the lattice points (or particles attached) in the new lattice ~~con~~ coinside with the positions of similar lattice points in the original lattice.

- Typical symmetry operations in 3-dimensions are:

① Translation group operation which is defined by the general translation vector $\vec{R}$

$$\vec{R} = \sum_{i=1}^{d} n_i \vec{a_i} \quad ; \quad d: \text{dimensionality}$$

in 2D $\vec{R} = n_1 \vec{a_1} + n_2 \vec{a_2}$.

in 3D $\vec{R} = n_1 \vec{a_1} + n_2 \vec{a_2} + n_3 \vec{a_3}$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$: primitive vectors

n_1, n_2, n_3 ; integers $\quad n_i = 0, \pm 1, \pm 2, \pm 3, \cdots$

② Point group operations: called Point group as it keeps at least one point fixed. This includes:

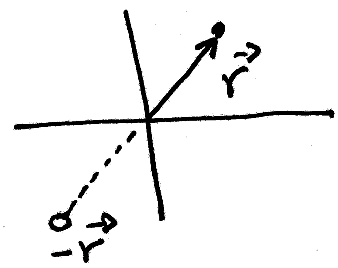
a) Rotation around an axis ($\vec{n}$) through angle θ which is an integer multiple of $\frac{2\pi}{n}$; $n = 1, 2, 3, 4, 6$

$R(\vec{n}, \theta)$; $\vec{n}$: axis of rotation ; θ: angle of rotation ; some times denoted by C_n

b) Inversion: takes every point $\vec{r}$ into the point $-\vec{r}$

$\vec{r} \longrightarrow -\vec{r}$ i.e $(x, y, z) \rightarrow (-x, -y, -z)$

denoted by I

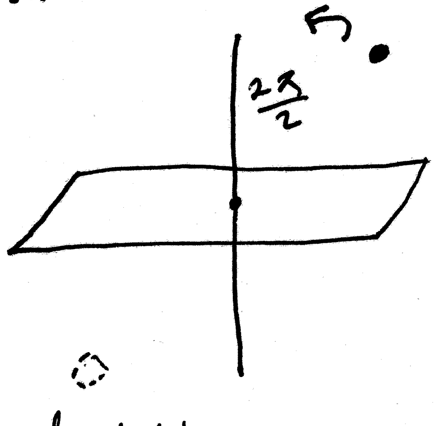


c) Reflection: takes every point into its mirror image with respect to a plane (mirror plane)

- denoted by σ

d) Rotation Reflection: rotation about an axis through an angle $\left(\theta = \frac{2\pi}{n} ; n = 1, 2, 3, 4, 6\right)$, followed by reflection in a plane perpendicular to the axis

- denoted by S_n



in the example, we have S_2 which is rotation by π, followed by reflection in the plane perpendicular to the axis of rotation

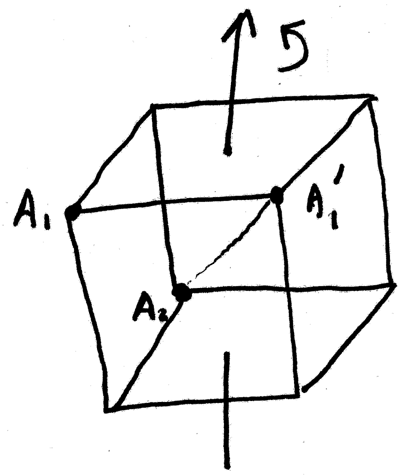
e) Rotation - Inversion: rotation by $\frac{2\pi}{n}$ $(n = 1, 2, 3, 4, 6)$ around an axis followed by inversion around the origin

in the example, we have

rotation by $\frac{2\pi}{4} = \pi/2$

$(A_1 \to A_1')$, followed by inversion about the origin

$(A_1' \to A_2)$



③ Glide planes: a glide plane operation is a reflection in a plane, followed by a translation parallel with that plane.

④ screw axes: a screw axis operation is a rotation about an axis, followed by a translation along the direction of the axis

---

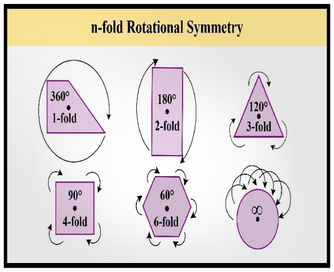
As demonstrated in 1890, only 230 combinations of the above mentioned symmetry operations are possible, yeilding 230 space groups. A crystal can be assigned to one of these groups.

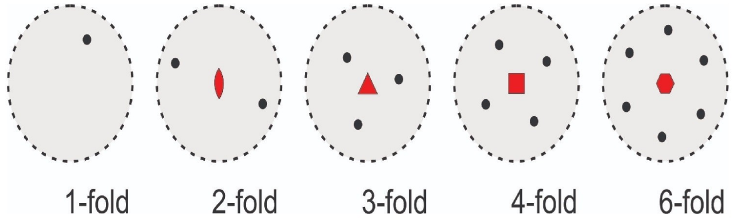
The translational group and the point group operations can be described by the formulla

$\vec{y} = \vec{a} + R\vec{x}$; where $\vec{x}$ is an arbitrary vector in the lattice ; R is an operator that could be Rotation, Reflection, and inversion; $\vec{a}$ is a translation vector. This eqn can be understood as follows: the operator R first rotates (or reflects or inverses) the vector $\vec{x}$, and then a translation by a vector $\vec{a}$ is applied; yeilding the new vector y. The above eqn applies only to Bravais lattices.

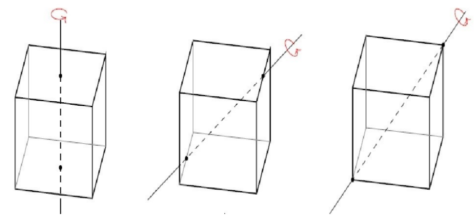
However, the general lattice with a basis has symmetry operations that are not included in the above equation such as glide planes and screw axes. So as a result, the space group of Bravais lattice can be represented simply as a product of translation group and point group.

a) Rotation



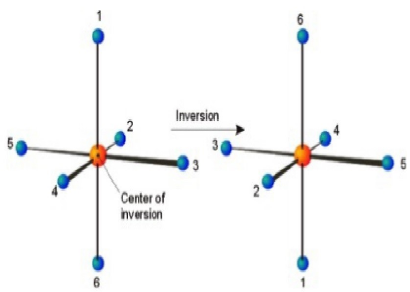


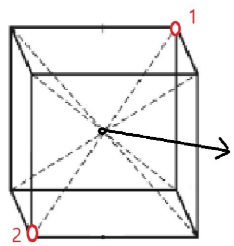
0 or 360° | 180° | 120° | 90° | 60°



4-fold (90°) | 2-fold (180°) | 3-fold (120°)

b) inversion (x, y, z) ⟹ (-x, -y, -z)

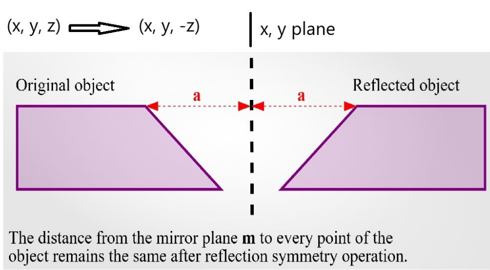




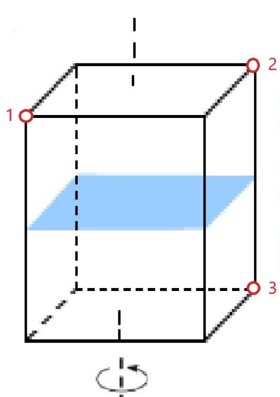
Inversion center:

1 to 2

c) Reflection



d) Rotation-reflection (Improper rotation)

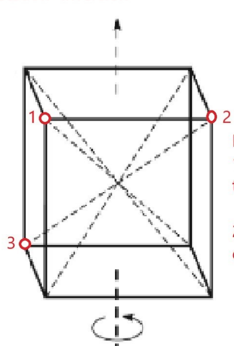


Rotation-reflection example in a cube:

1 to 2 rotation by 180° about the axis shown

2 to 3 reflection about the plane shown

e) Rotation- inversion



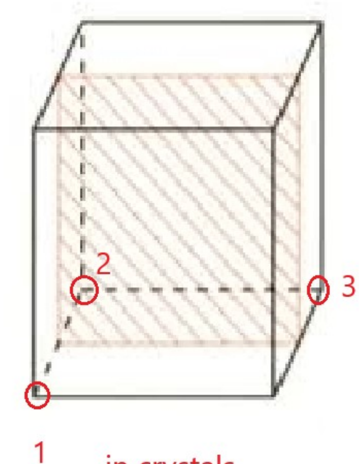
Rotation-Inversion example:
1 to 2 rotation by 90° about the axis shown

2 to 3 inversion about the center of the cube

Glide Planes

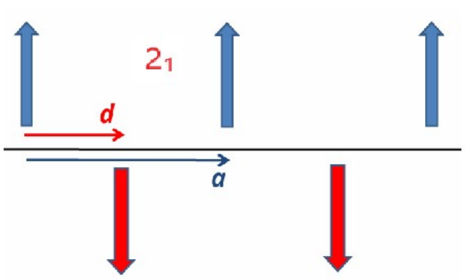
1- reflect through the glide plane (just like a mirror)

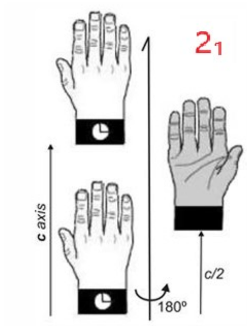
2- translate parallel to the glide plane



in crystals

Screw axes:





A 2_1 screw axis in the c direction. A rotation of 180 followed by a translation of c/2 along the c axis.

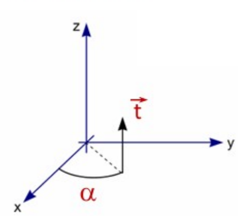
- Screw Axis n_m ; where m < n

⟶ rotation by an angle α of 360°/n

⟶ n = order of the axis = 360° / n

⟶ translation of m/n of the whole unit cell parallel to the screw axis

screw axes : z



$\vec{t}$ = translation element = m / n

α = rotation angle

Example:

Screw axis n_m , where m<n
3_2 screw axis (n=3, m=2) means

rotation by 360/3 = 120 deg,
and translation of m/n = 2/3 of the whole unit cell parallel to the screw axes

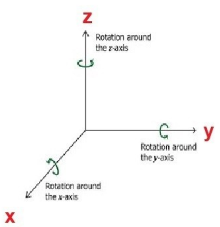
the possible screw axes are 2_1, 3_1, 4_1, 4_2, 6_1, 6_2, 3_2, 4_3, 6_4, 6_5

Matrix Representations of Symmetry operations:

The Identity: A point (x,y,z) does not change under this operation. Therefore, the identity operation is represented by a unit matrix.

$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

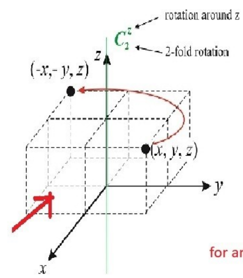
Rotation: counterclockwise: (to obtain matrices of clockwise rotation just replace θ by -θ



$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\vartheta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \sin\theta \end{pmatrix}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



Rotation around z axis by 180°

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

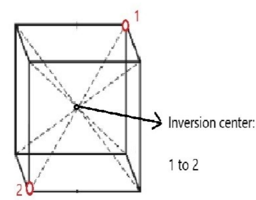
for any rotational matrix Tr (R)= -1 and det (R)= +1

Inversion:

This operation results simply the change of signs of all the coordinates. Clearly we need a negative unit matrix to represent inversion operation.

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

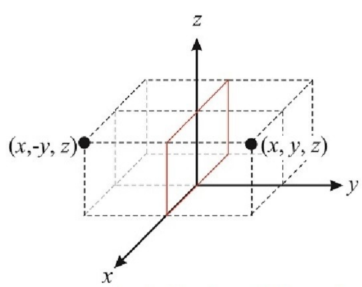
i.e (x, y, z) ⇨ (-x, -y, -z)



Reflection:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

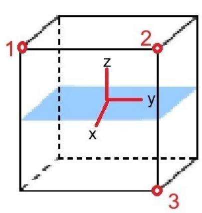
σ_{xz}



A reflection through the xz plane

for any reflection matrix Tr (R)= +1 and det (R)= -1

Rotation-reflection



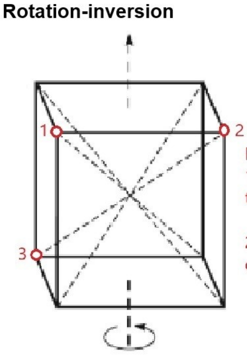
Rotation about z-axis by 90° followed by reflection about xy plane

$$\sigma_{xy}\, R_z(\pi/2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -y \\ x \\ -z \end{pmatrix}$$

for example point 1 (1,-1,1) goes to point 3 (1,1,-1)

Rotation-inversion



Rotation-Inversion example:
1 to 2 rotation by 90° about the axis shown

2 to 3 inversion about the center of the cube

$$Inversion \times R_z(\pi/2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} y \\ -x \\ -z \end{pmatrix}$$ x goes to y, y goes to -x, and z goes to -

for example point 1 (1,-1,1) goes to point 3 (-1,-1,-1)