

Crystal Structure



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Classification of solids

Solids can be classified as :

- **Crystalline Materials:**
- A crystalline material is one in which the atoms are situated in a repeating or periodic array over large atomic distances; that is, **long-range order** exists
- **Amorphous Materials:** The **long-range atomic order is absent**; There is no periodic arrangement in *noncrystalline* or *amorphous* materials

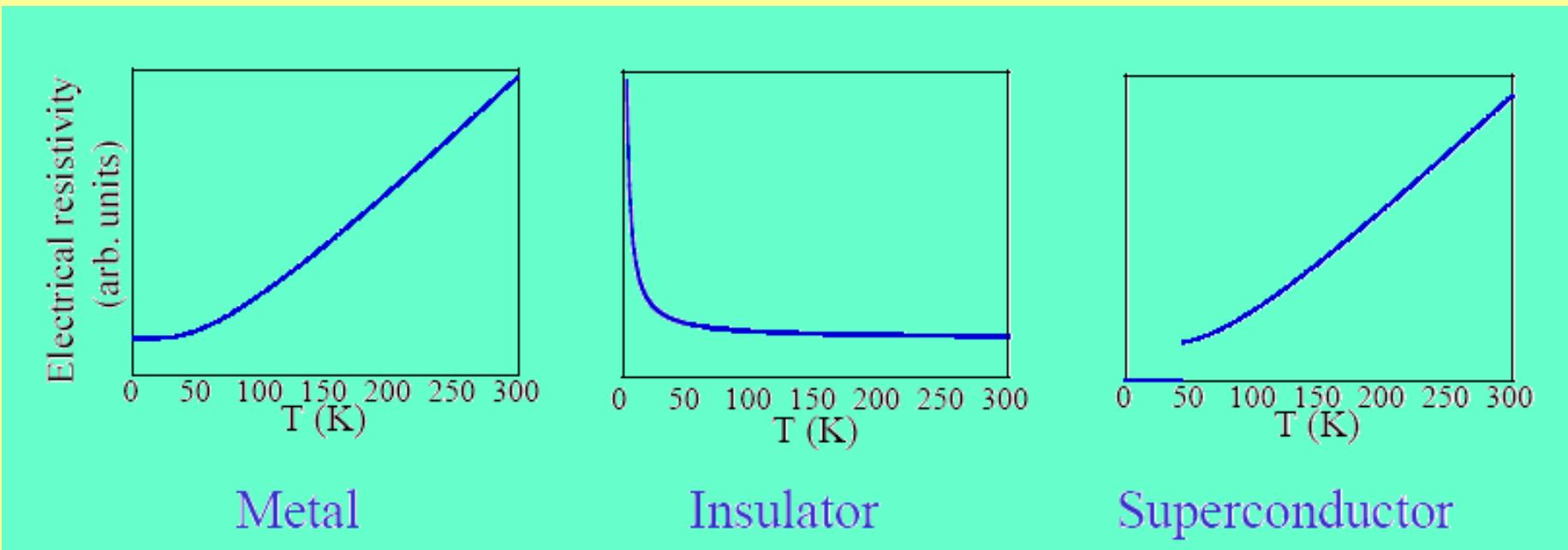
Crystalline Materials

- The majority of all solids are **crystalline**.
- The **properties of crystalline solids** depend on the crystal structure of the material, the manner in which atoms, ions, or molecules are spatially arranged.
- There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by solids.
- More progress has been made in understanding the behavior of crystalline solids than that of non-crystalline materials **since the calculation are easier** in crystalline materials.

Example: Electrical resistivity of three solid Carbon Allotropes

- How can this be? After all, they each contain a system of atoms and especially electrons of similar density. : graphite is **metal**, diamond is an **insulator** and buckminster-fullerene is a **superconductor**.

They are all just carbon!



CRYSTAL STRUCTURES

- Elementary Crystallography
 - Solid materials (crystalline, polycrystalline, amorphous)
 - Crystallography
 - Crystal Lattice
 - Crystal Structure
 - Types of Lattices
 - Unit Cell
- Typical Crystal Structures
(3D– 14 Bravais Lattices and the Seven Crystal System)

CLASSIFICATION OF SOLIDS

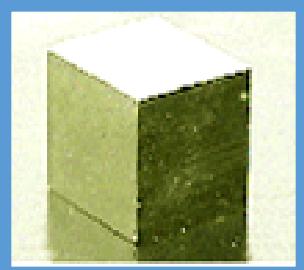
SOLID MATERIALS

CRYSTALLINE

POLYCRYSTALLINE

**AMORPHOUS
(NON-CRYSTALLINE)**

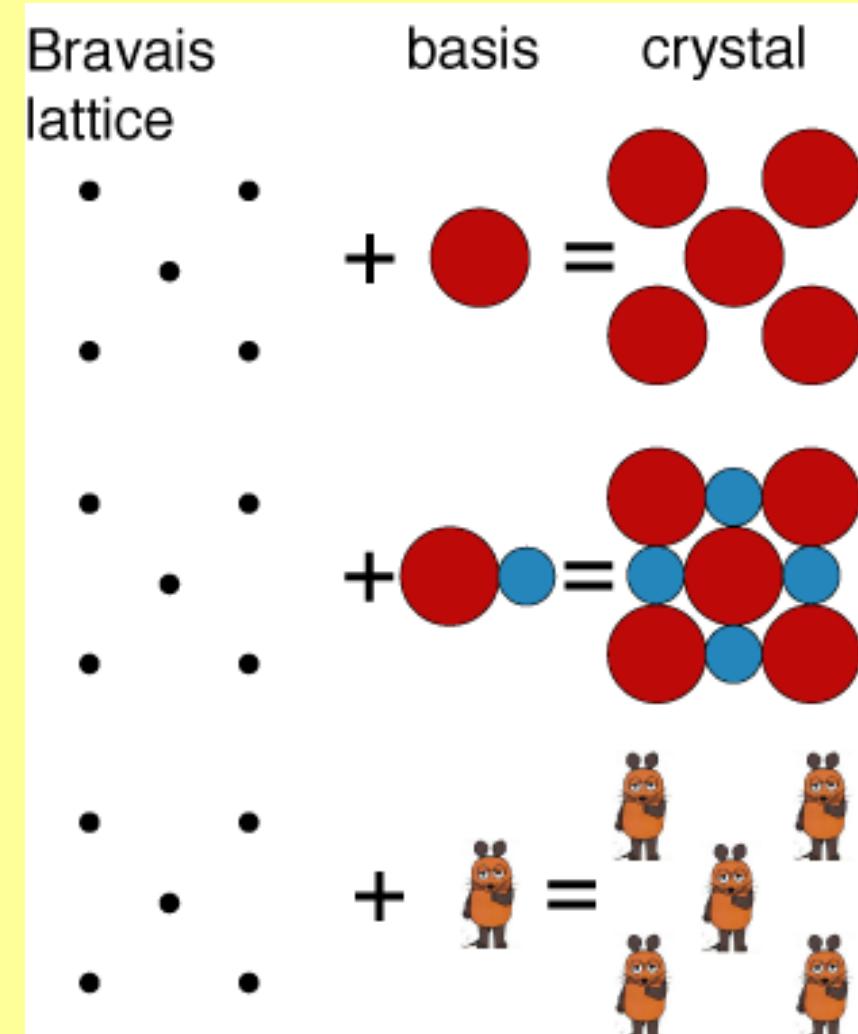
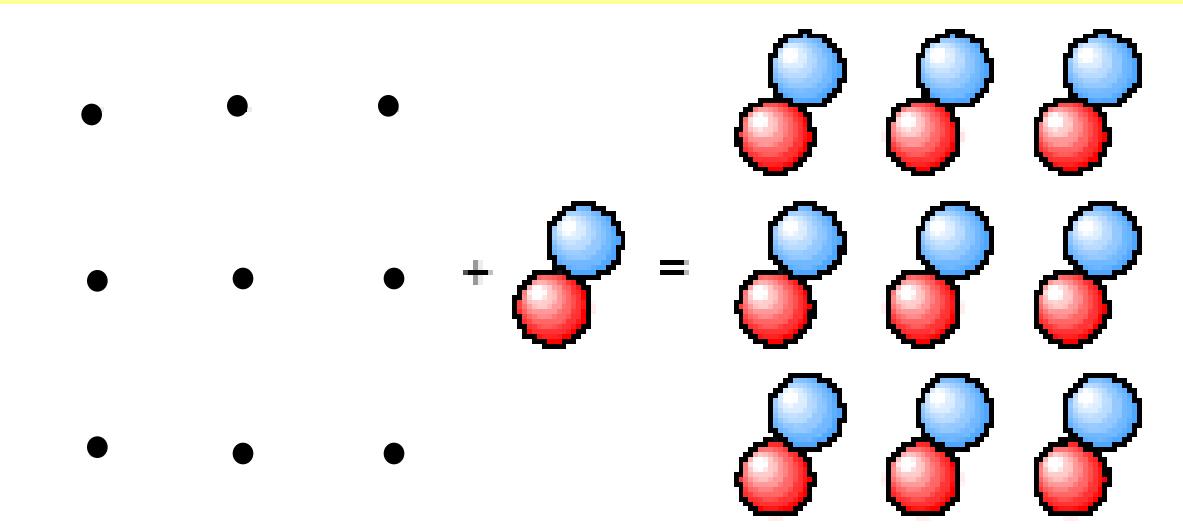
Single Crystal



Crystal Structure

- Crystal structures can be obtained by attaching atoms, **groups of atoms or molecules which are called basis (motif)** to the lattice sides of the lattice point.

Crystal Structure = Crystal Lattice + Basis



Crystal Structure = Lattice + Basis

- **Lattice:** A lattice is a hypothetical regular and periodic arrangement of points in space. It is used to describe the structure of a crystal.
- **Basis:** A basis is a collection of atoms in particular fixed arrangement in space. We could have a basis of a single atom as well as a basis of a complicated but fixed arrangement of hundreds of atoms. Below we see a basis of two atoms inclined at a fixed angle in a plane.



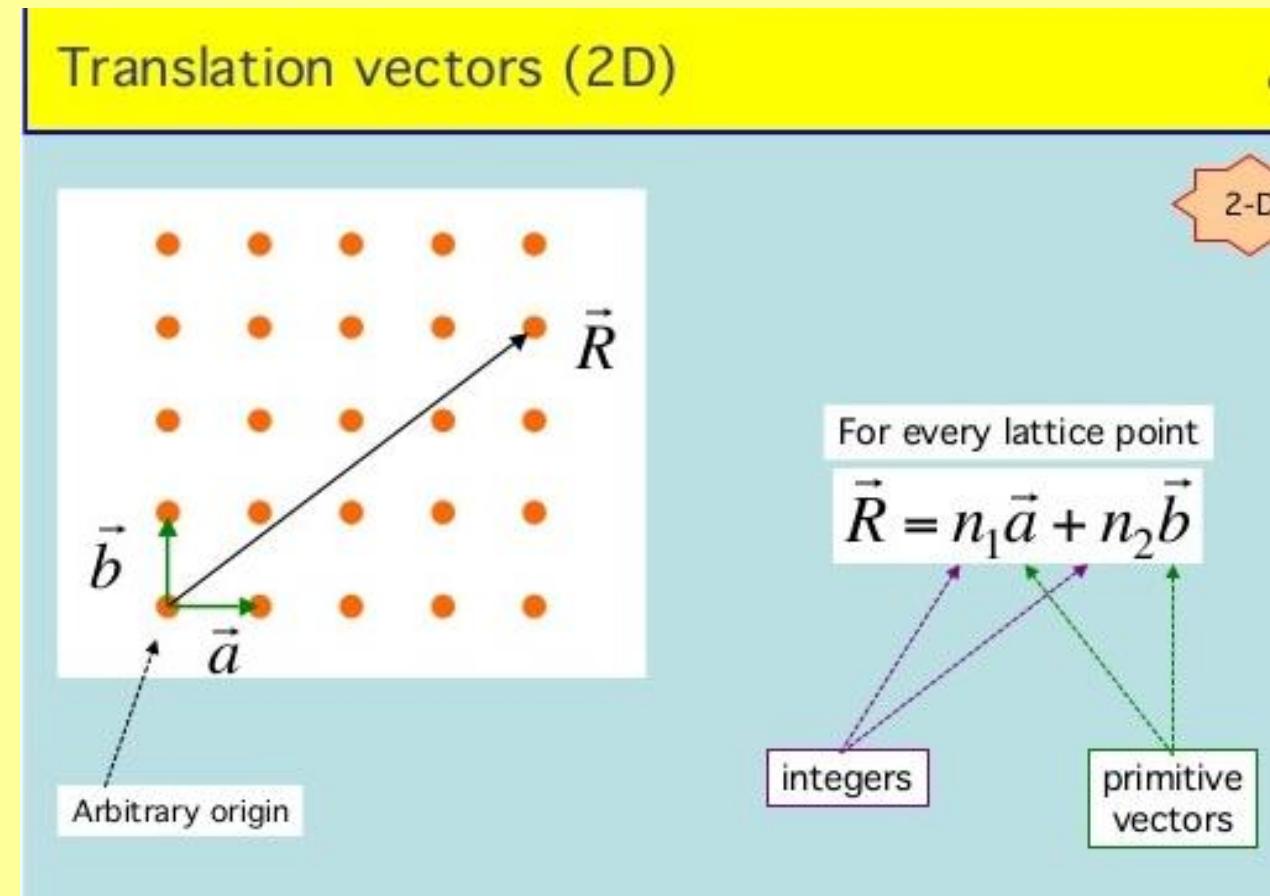
Mathematical Representation

A lattice is a periodic array of points generated by translation vectors.

- A crystal translation vector is a vector that moves (or translates) one lattice point to another identical lattice point in the crystal.

Translation symmetry:
Lattice
is *invariant* under
group of translation
expressed by the above
equation.

Thus the lattice has
translational symmetry
under all
displacements
specified by lattice
vectors R.



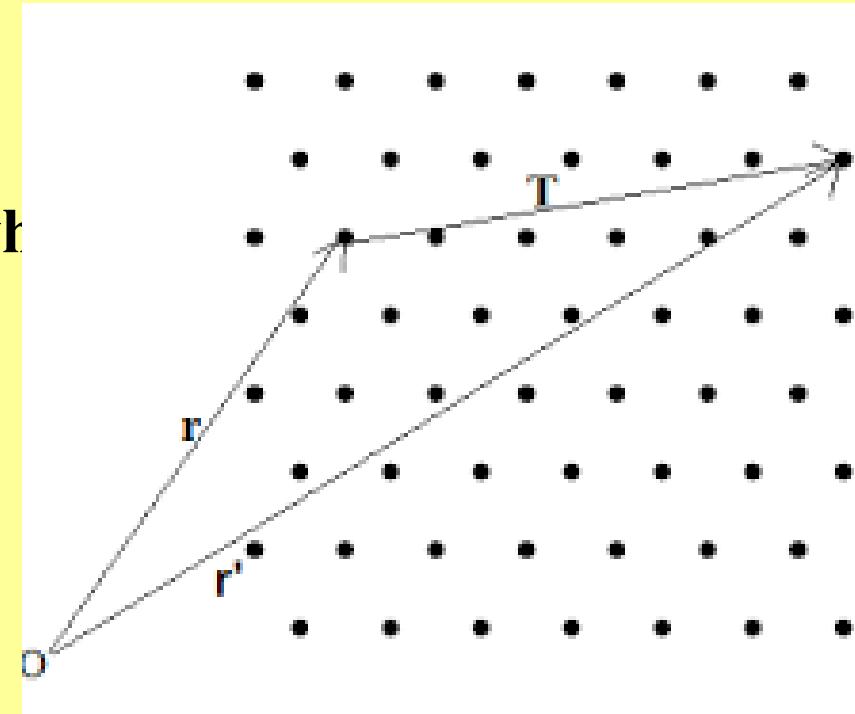
3 Dimensional Translation Vector

If \mathbf{r} be the coordinates of a lattice point from any origin,
then if we apply a lattice translation thought the lattice translation vector (\mathbf{T})

$$\mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

then we would arrive at any other lattice point \mathbf{r}' around which
the Environment would look exactly the same as around \mathbf{r} .

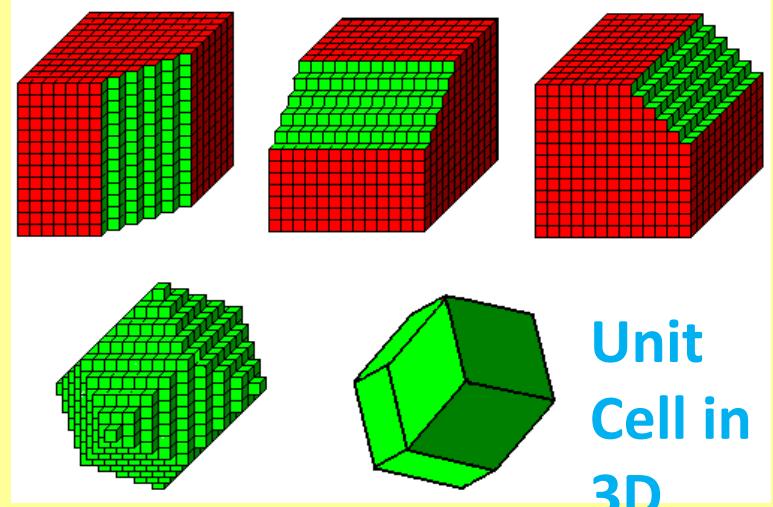
$$\begin{aligned}\mathbf{r}' &= \mathbf{r} + \mathbf{T} \\ &= \mathbf{r} + u\mathbf{a} + v\mathbf{b} + w\mathbf{c}\end{aligned}$$



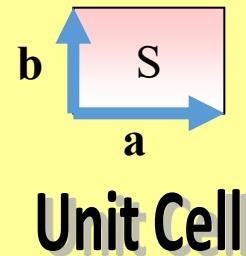
\mathbf{a} , \mathbf{b} and \mathbf{c} are the primitive translation vectors or basis vectors
which form the primitive cell of the lattice and u, v, w are integers.

Unit Cell

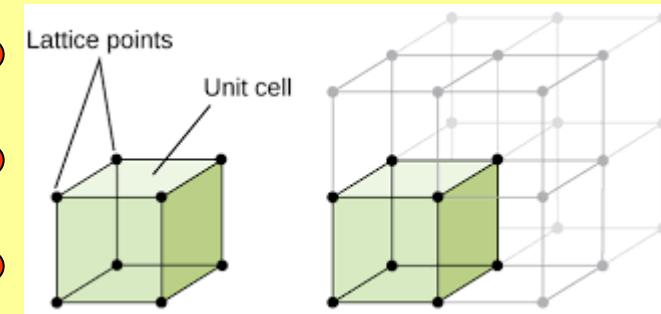
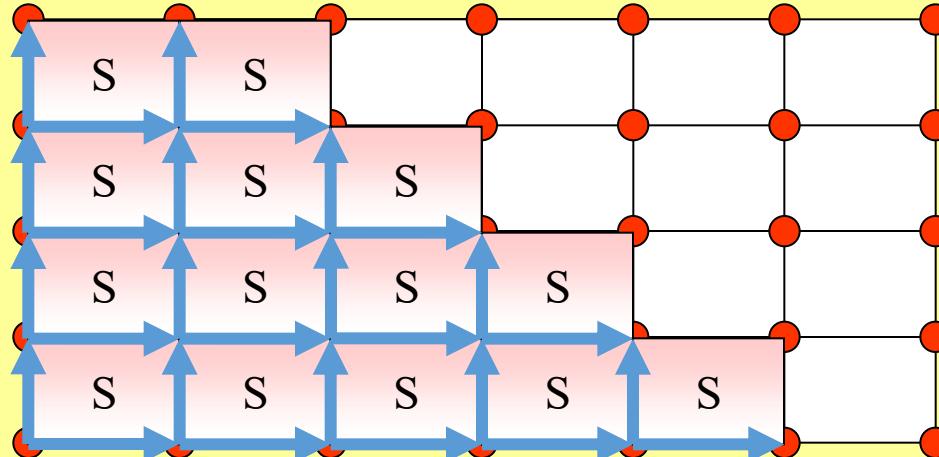
- The smallest component of the crystal (group of atoms, ions or molecules), which when stacked together with pure translational repetition reproduces the whole crystal.



Unit
Cell in
3D



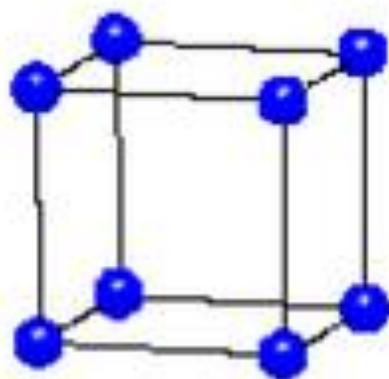
2D-Crystal



Unit Cell

Primitive

- Single lattice point (atom) per cell
- Smallest volume



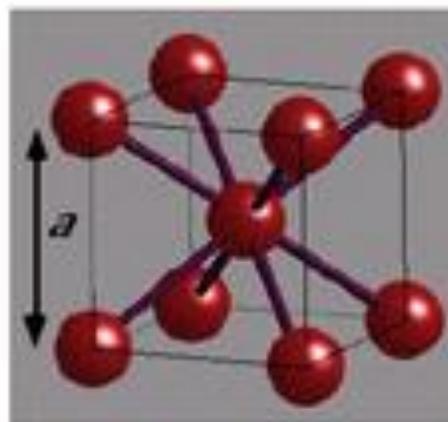
Simple cubic(sc)

Conventional = Primitive cell

Each atom at the corner is shared by 8 cells

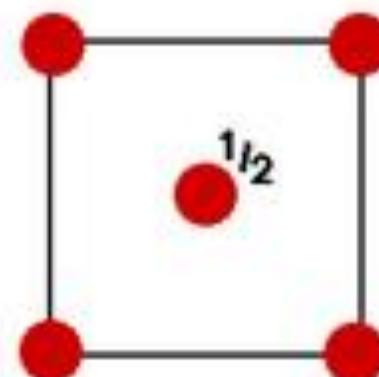
conventional

- More than one lattice point (atom) per cell
- Integral multiples of the primitive volume



Body centered cubic(bcc)

Conventional \neq Primitive cell

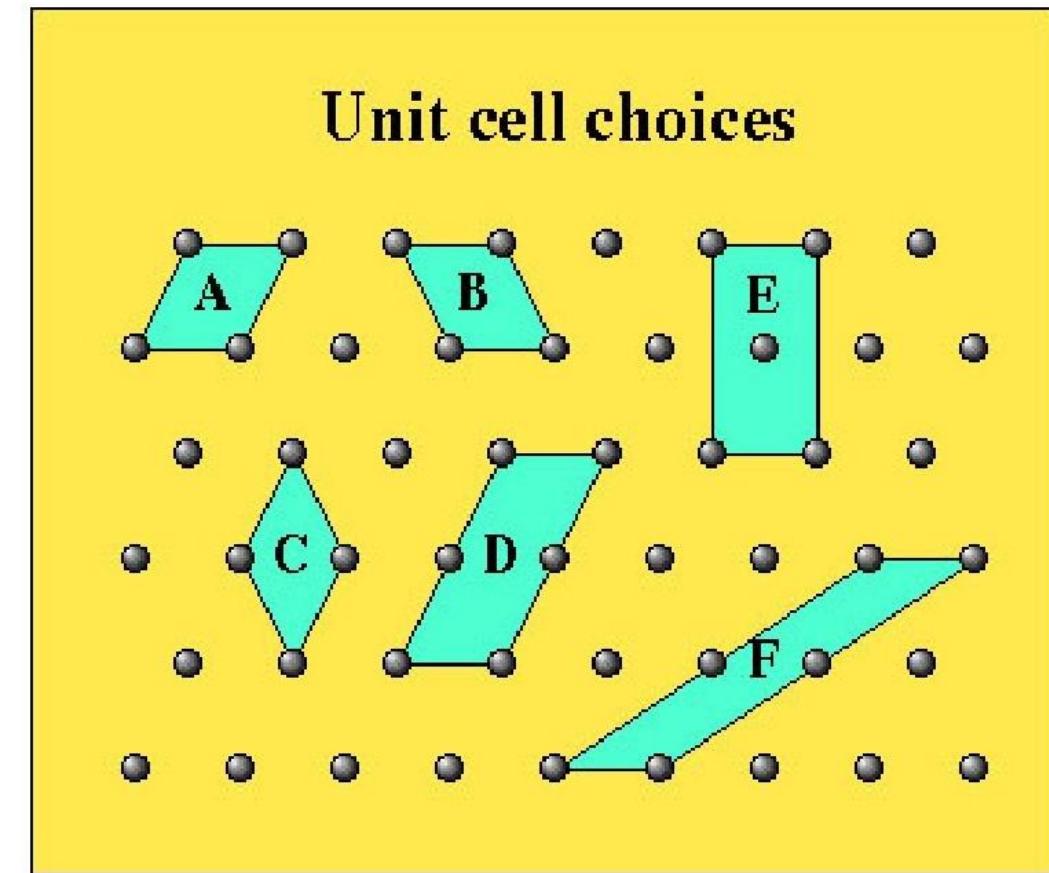


Primitive Lattice (Primitive cell)

- Primitive lattice vectors are **the shortest lattice vectors possible**.
- Primitive unit cells contain **only one lattice point**, which is made up from the lattice points at each of the corners.
- **Non-primitive unit cells** contain **additional lattice points**, either on a face of the unit cell or within the unit cell, and so have more than one lattice point per unit cell.

Choice of Primitive unit cell

- Which unit cell is a good choice?
- A, B, and C are primitive unit cells. Why?
- D, E, and F are not. Why?
- Notice: the volumes of A, B, and C are the same. Also, the choice of origin is different, but it doesn't matter
- Also: There is only one lattice point in the primitive unit cells.

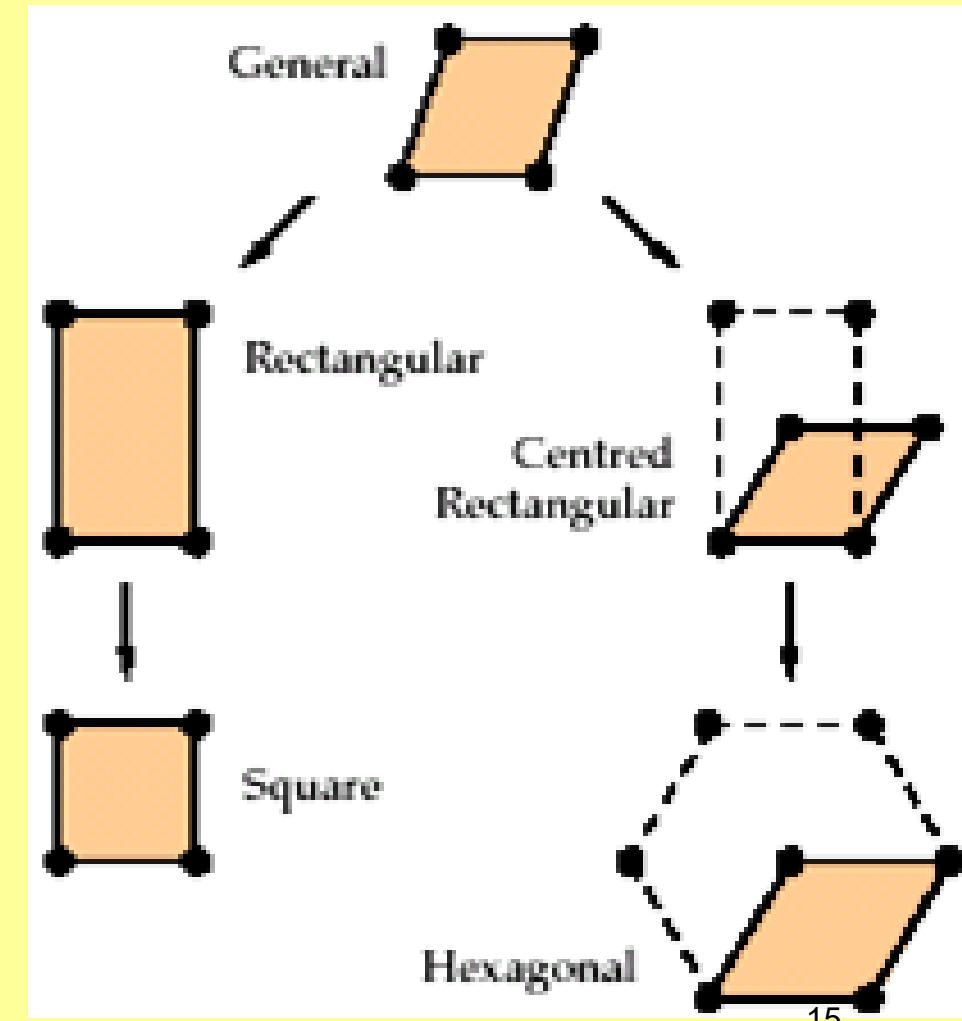


Bravais Lattices

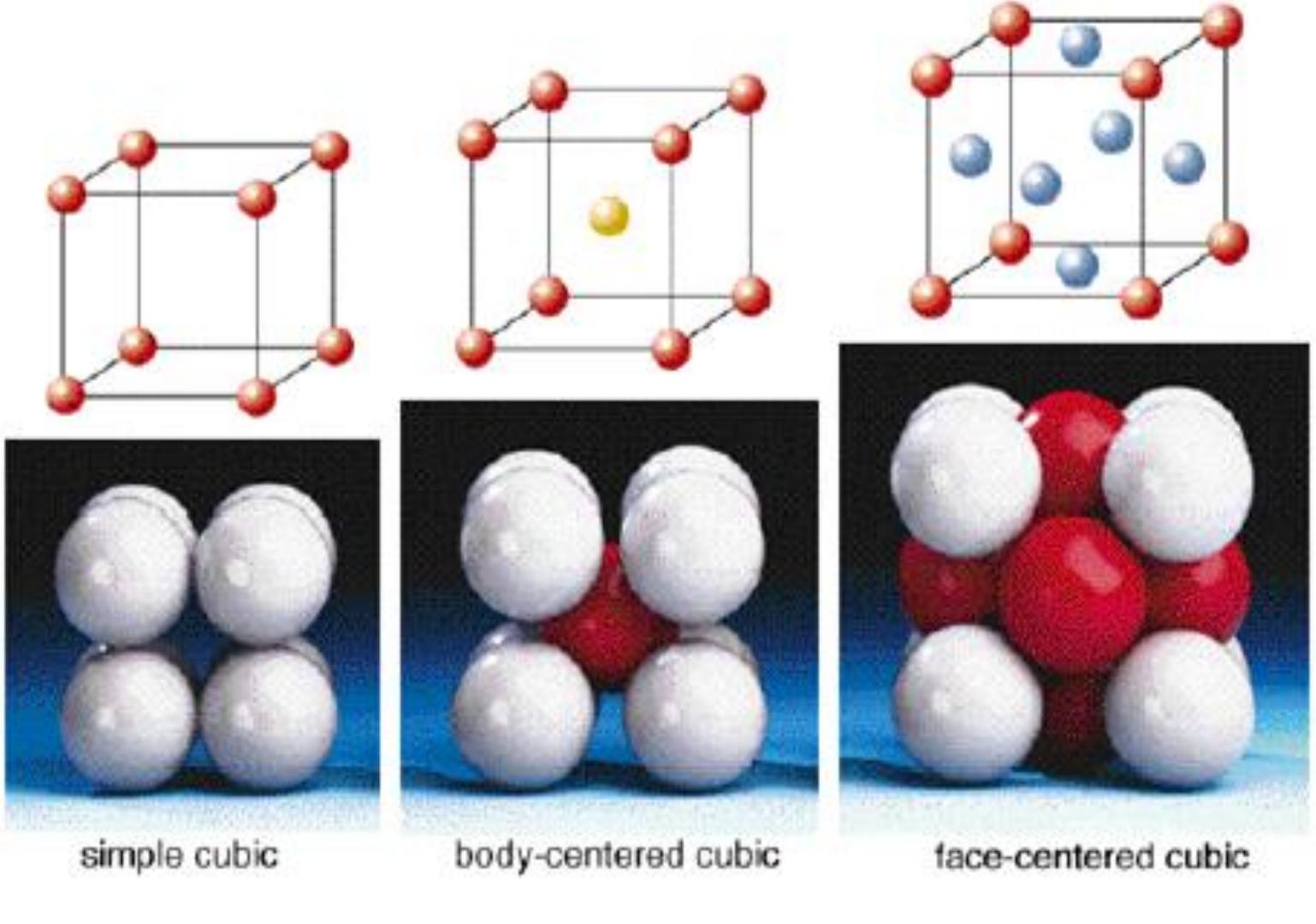
The number of lattices that can fill two- or three-dimensional space with periodically repeating units without leaving gaps or causing overlaps is limited. Lattices which fill space without gaps are called **Bravais lattices**.

**Five (5) Bravais Lattices
in 2D**

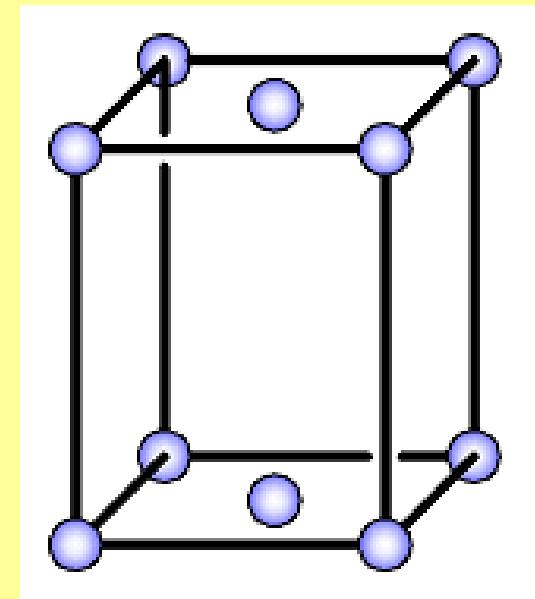
**14 Bravais Lattices
in 3D**



Three common Unit Cells in 3D



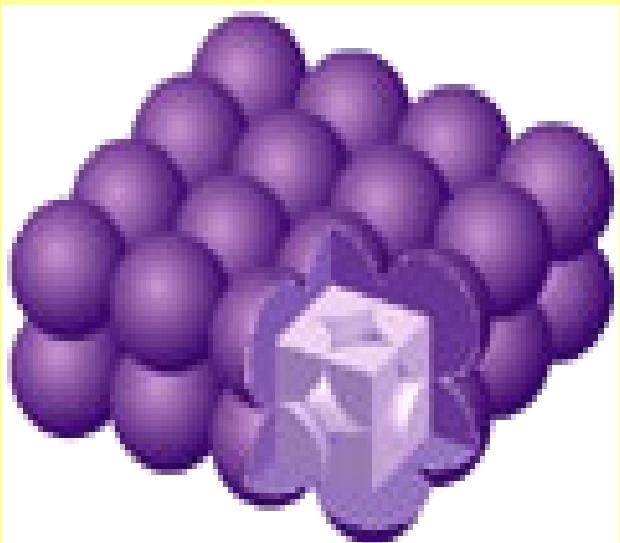
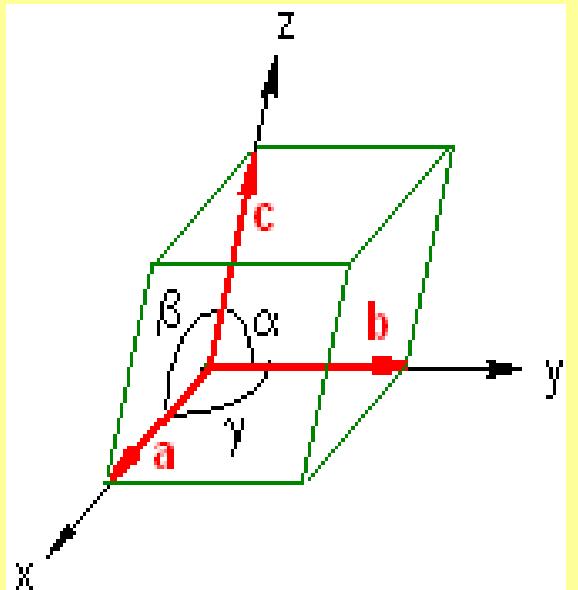
Base centered cubic



Unit Cell and Lattice Parameters

Elements of Unit Cell

- Lattice points: Positions occupied by atoms.
- Edges (a , b , c): Lengths of cell along x , y , z axes.
- Angles (α , β and γ)
- The **unit cell** and, consequently, the entire lattice, is *uniquely determined* by the **six lattice constants**: a , b , c , α , β and γ .
- Only **1/8** of each lattice point in a unit cell can actually be assigned to that cell.
- Each unit cell in the figure can be associated with $8 \times 1/8 = 1$ lattice point.

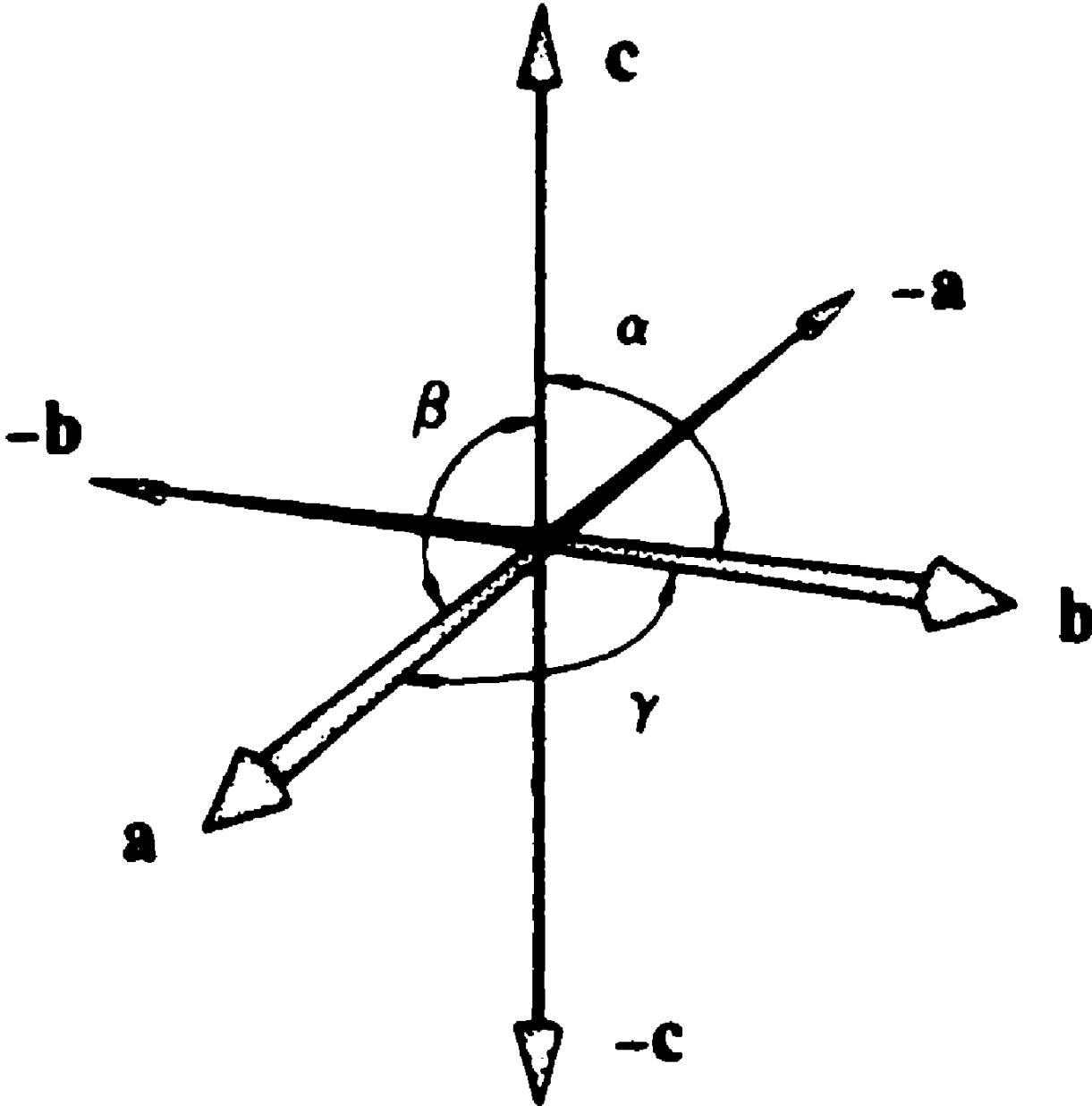


TYPICAL CRYSTAL STRUCTURES

IN 3 DIMENSION(3D) – 14 BRAVAIS LATTICES AND SEVEN CRYSTAL TYPES

- **Cubic Crystal System (P, BCC,FCC)**
- **Hexagonal Crystal System (P)**
- **Triclinic Crystal System (P)**
- **Monoclinic Crystal System (P, Base-C)**
- **Orthorhombic Crystal System (P, Base-C, BC, FC)**
- **Tetragonal Crystal System (P, BC)**
- **Trigonal (Rhombohedral) Crystal System (P)**

**Set of Axes and
Interaxial angles**



Symmetry operations

- Symmetry defines the order resulting from how atoms are arranged and oriented in a crystal
- symmetry operators : actions which result in no change to the order of atoms in the crystal structure
- Combining different operators gives point groups – which are geometrically unique units.
- Every crystal falls into some point group, which are segregated into 7 crystal systems

Crystal Symmetry: Symmetry operations in crystals

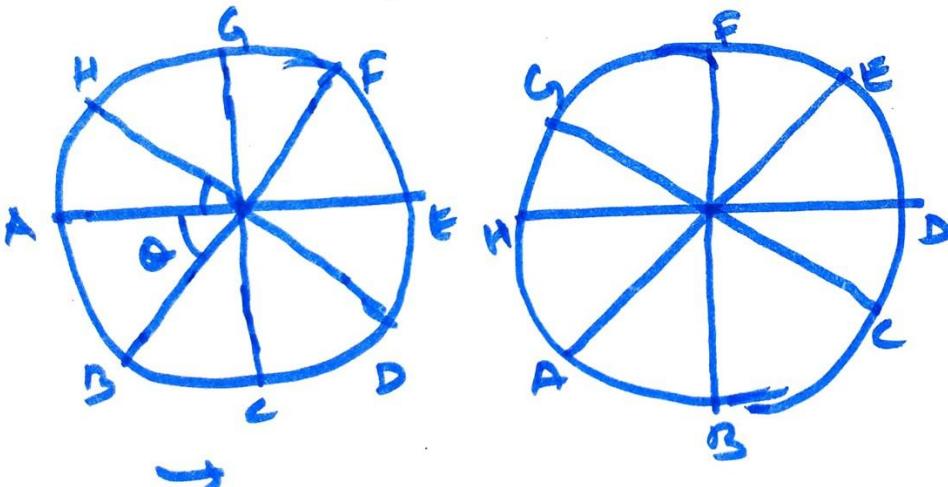
A symmetry operation is one that leaves the crystal and its environment invariant.

Types of Symmetry operations:

- ① Rotational Symmetry
- ② Reflection symmetry
- ③ Inversion "
- ④ Translation symmetry.

① Rotational Symmetry: Denoted by C_n

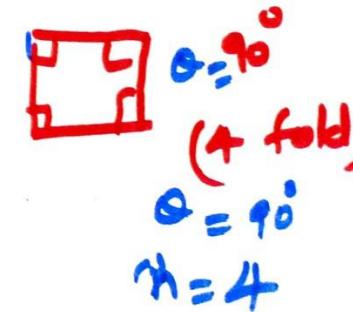
It is expressed by whole numbers from 1 to ∞ .
How many times - rotate to find original structure.



$$n\theta = 360^\circ$$
$$\theta = \frac{360}{n}$$

In this case

$$n = 8, \quad \underline{\left(\frac{360^\circ}{45^\circ}\right) = 8}$$



Reflection Symmetry

An object has **reflection symmetry** (or **mirror symmetry**) if it is **identical to its mirror image** across a **line** (in 2D) or a **plane** (in 3D).

In other words, one half of the object is a **mirror reflection** of the other half.

Let a point on an object be at coordinates (x,y) . If the object has reflection symmetry across the y -axis, then there exists a corresponding point at $(-x,y)$.

Types of Reflection Symmetry:

Type	Description	Example
Vertical symmetry	Symmetry across a vertical line	Letter A , butterfly
Horizontal symmetry	Symmetry across a horizontal line	Letter B
Diagonal symmetry	Symmetry across a diagonal line	Square, letter X
Mirror plane (3D)	Symmetry across a flat plane in space	Cubes, molecules like benzene

Reflection Symmetry:

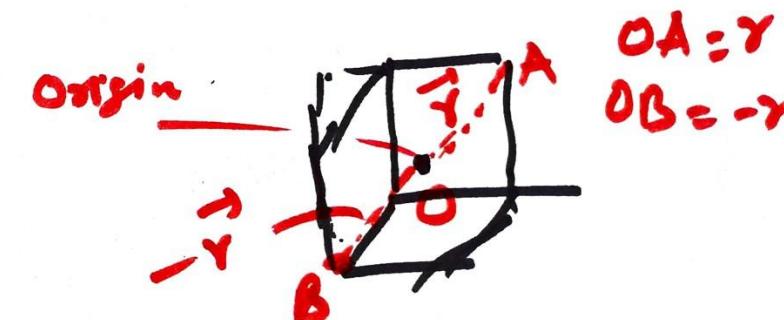
of a plane can be drawn in a body dividing it in exactly similar parts.
(denoted by m, mm)



2D - Line
3D - Plane



Inversion Symmetry: Only in 3D - A crystal is said to possess inversion symmetry if for every lattice point ' γ ' there exist a lattice point at position ' $-\gamma$ '
(denoted by i) Or bar $\bar{1}$ ($= i$)



Translation Symmetry: $\vec{\gamma} + T = \vec{\gamma}'$

$$T = n\vec{a} + n\vec{b} + n\vec{c} \quad (3D)$$

T (translation vector).

An object has **inversion symmetry** if every point at a position (x, y, z) has an equivalent point at $(-x, -y, -z)$ relative to a central point called the **inversion center**.



2-fold rotation: 180° rotation



3-fold rotation: 120° rotation



4-fold rotation: 90° rotation



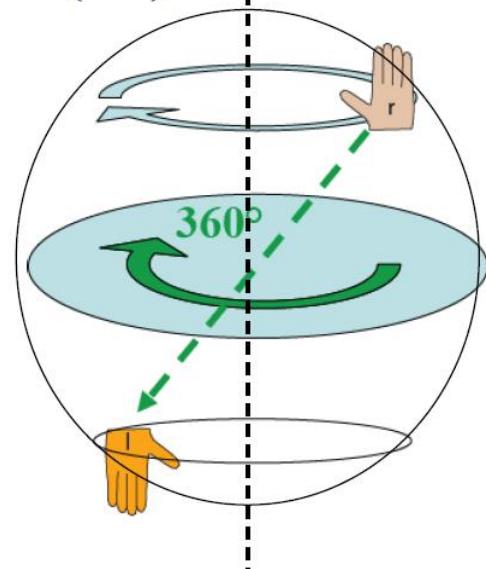
6-fold rotation: 60° rotation



mirror plane

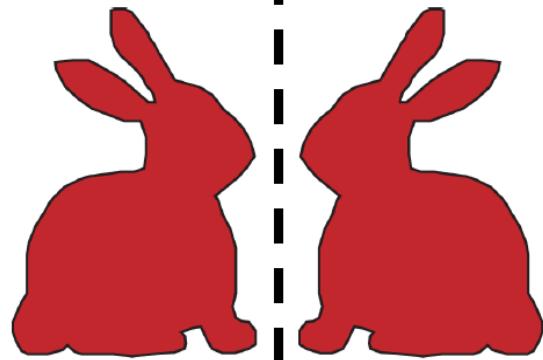
$\bar{1}$ ($= i$)

360°



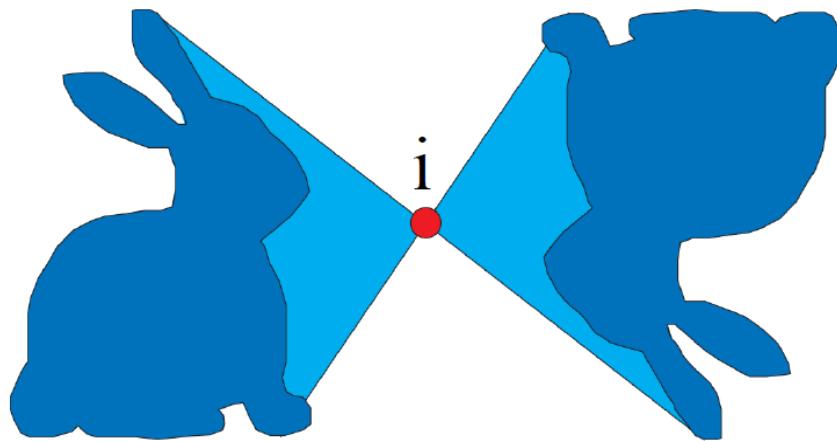
m

Reflection versus Inversion



Let us look at this purely in 2 dimensions.

Reflection of a 2-dimensional object occurs across a plane (m)



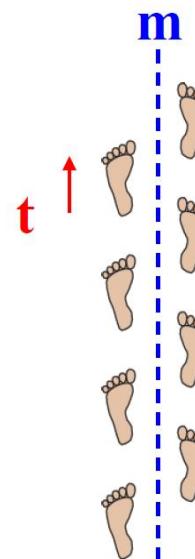
After inversion everything is an equal and opposite distance through a single point i .

Results in congruent pairs.

The combining of the single operations, rotation and inversion, generates a ***rotoinversion operation***.

Glide/

A two-step operation: reflection followed by translation (g)



Combination of Symmetry Operations:

Glide/

⊗ Slide → Reflection + translational

⊗ Screw → Rotational + Translational

These two (slide and screw) operations are called Compound operation.

⊗ Point Groups: Group of symmetry operations at a point.

2D →

10 Point Groups

3D →

32 " "

⊗ Space Group:

3D - 230 point groups

⊗ Bravais Lattices: Lattices consistent w/ with point group operations.

In 1848, Bravais categorized the 14 Bravais lattices.
(3D Case)

Why a crystal can't have five fold symmetry

Let us consider P, Q, R, S four lattice points connected with the lattice translational vector ' t '. Let space has ϕ fold symmetry. Now rotate from Q and R in either clockwise or anticlockwise direction.

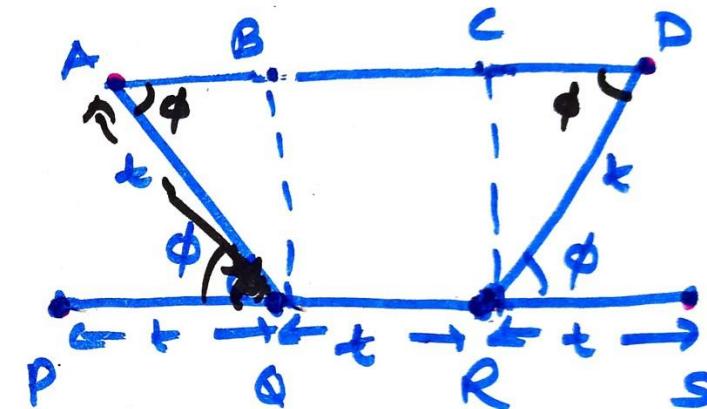
In ΔABQ ,

$$\text{Co } \phi = \frac{AB}{AQ} = \frac{AB}{t}$$

$$\text{or } AB = t \text{ Co } \phi \quad \dots \text{①}$$

From ΔCDR

$$\begin{aligned} \text{Co } \phi &= \frac{CD}{RD} = \frac{CD}{t} \quad \dots \text{②} \\ CD &= t \text{ Co } \phi \end{aligned}$$



$$\therefore AQ = RD = t$$

A to D is related with translation vector

$AD = mt$, where $m = \text{integer}$

$$AB + BC + CD = mt \quad \dots \text{③}$$

$$t \text{ Co } \phi + t + t \text{ Co } \phi = mt$$

$$2t \text{ Co } \phi = mt - t = \frac{mt}{m-1}$$

$$\text{or } 2 \text{ Co } \phi = (m-1) \quad \dots \text{④}$$

$$\text{or } \text{Co } \phi = \left(\frac{m-1}{2} \right) = \frac{N}{2}$$

where, N is any integer

or $\cos \theta = \frac{N}{2}$. ④ $\because \cos \theta$ varies from +1 to -1.

If $\cos \theta = +1$, $N=2$
 $\cos \theta = -1$; $N=-2$, N can vary from -2 to +2.

Therefore, $-2 \leq N \leq 2$

or $-2, -1, 0, 1, 2$, N have five values

From eq. ④ :

N	$\cos \phi$	ϕ	$n = \frac{360^\circ}{\phi}$
-2	-1	180°	2
-1	$-\frac{1}{2}$	120°	3
0	0	90°	4
1	$\frac{1}{2}$	60°	6
2	1	360°	1

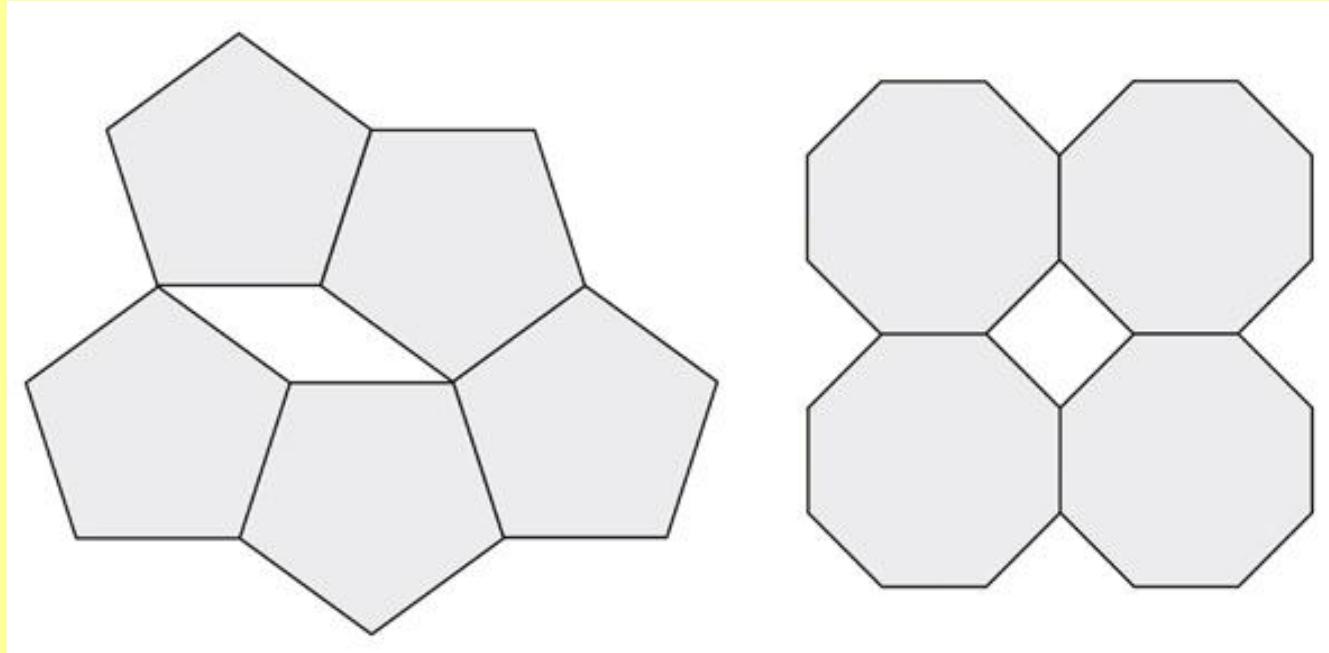
Permitted values of n .

This table shows that 5 and 7 fold symmetry doesn't exist.

Geometrically also if you put pentagons or hexagons to fill full there are voids/gaps.

Geometrically: Full space is not filled in 5, 7 fold symmetry in crystals

Mathematically, we have seen these are not permitted .



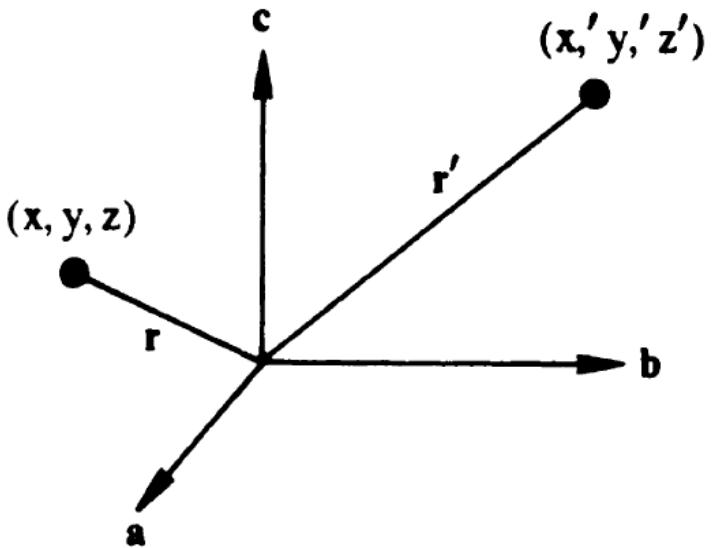


Fig. 1-2 A point in space before (x, y, z) and after (x', y', z') a symmetry operation.

Vector and Matrix representation

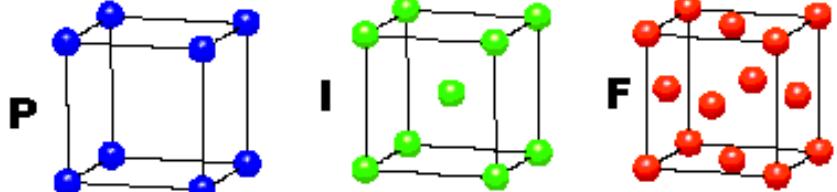
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\mathbf{r}' = \mathbf{R} \mathbf{r}$$

\mathbf{R} is transformation matrix

CUBIC

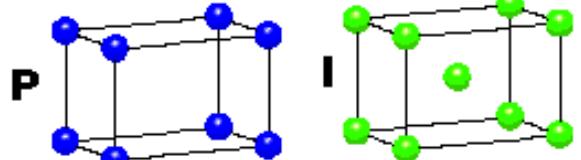
$a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



Cubic is highly symmetric and triclinic least symmetric

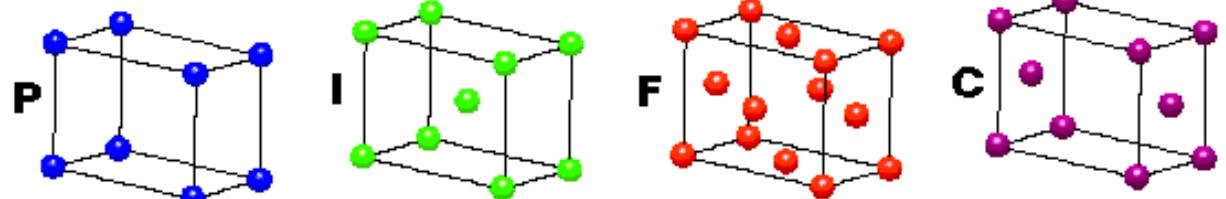
TETRAGONAL

$a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



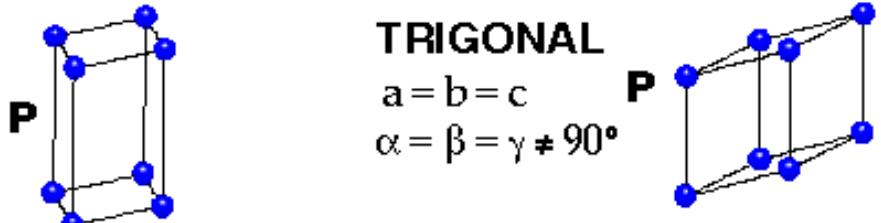
ORTHORHOMBIC

$a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



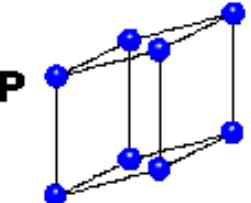
HEXAGONAL

$a = b \neq c$
 $\alpha = \beta = 90^\circ$
 $\gamma = 120^\circ$



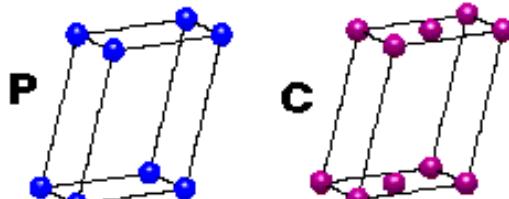
TRIGONAL

$a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



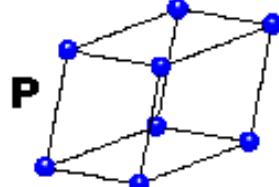
MONOCLINIC

$a \neq b \neq c$
 $\alpha = \gamma = 90^\circ$
 $\beta \neq 120^\circ$



TRICLINIC

$a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes
→ 14 Bravais Lattices

Volume of Unit Cell

System	Lengths and angles
triclinic	$a \neq b \neq c, \alpha \neq 90^\circ, \beta \neq 90^\circ, \gamma \neq 90^\circ$
monoclinic	$a \neq b \neq c, \alpha = 90^\circ, \beta \neq 90^\circ, \gamma = 90^\circ$
orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
rhombohedral	$a = b = c, \alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$

Since the primitive cell is defined by the primitive axes (vectors) $\vec{a}_1, \vec{a}_2, \vec{a}_3$, the volume V_p of the primitive cell is given by the parallelepiped from the above axes as:

$$V_p = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$$

Or

$$V = a \cdot (b \times c)$$

Volume of the unit cell = $abc (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$

For triclinic

There are many choices for the primitive vectors in the triclinic system.

So we are taking

$$a = a_x \hat{i} + a_y \hat{j} + a_z \hat{k}$$

$$b = b_x \hat{i} + b_y \hat{j} + b_z \hat{k}$$

$$c = c_x \hat{i} + c_y \hat{j} + c_z \hat{k}$$

Then,

$$V = a \cdot b \times c = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

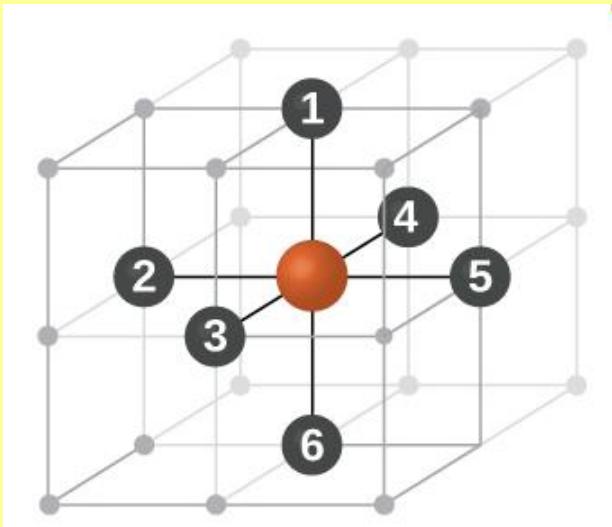
Homework: Find the unit cell volume for all the seven crystal system.

Unit cell volume for different Unit Cells

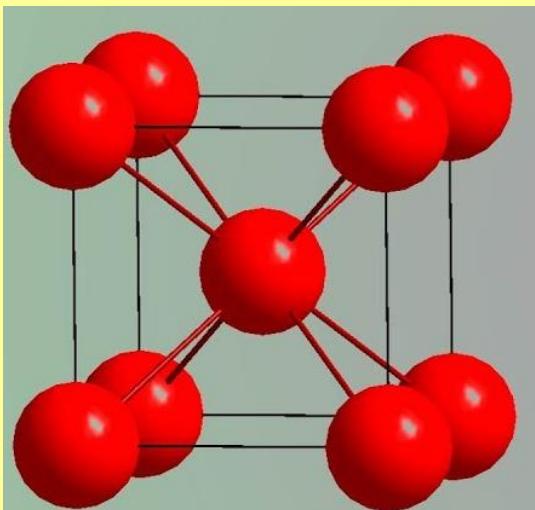
System	Unit cell volume Ω
triclinic	$abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$
monoclinic	$abc \sin \beta$
orthorhombic	abc
tetragonal	$a^2 c$
cubic	a^3
rhombohedral	$a^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$
hexagonal	$\frac{\sqrt{3}}{2} a^2 c$

Coordination Number

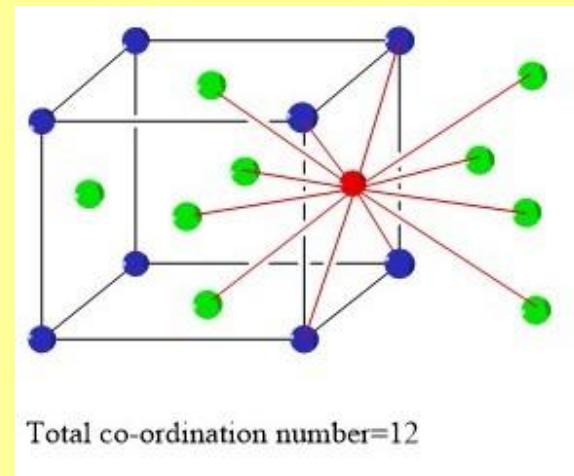
Coordination Number(CN): the number of nearest neighbor atoms or ions surrounding an atom or ion.



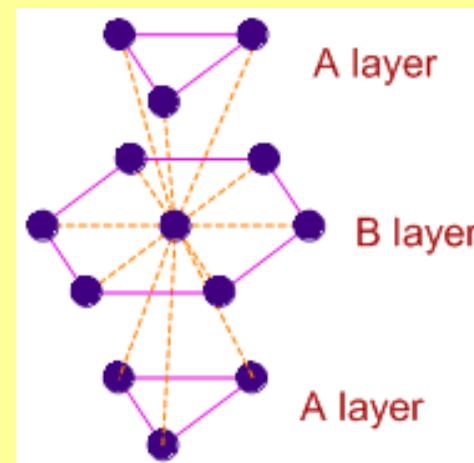
Simple Cubic (SC)
CN = 6



BCC , CN = 8

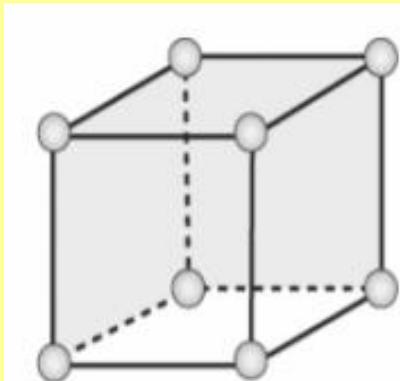


FCC, CN = 12

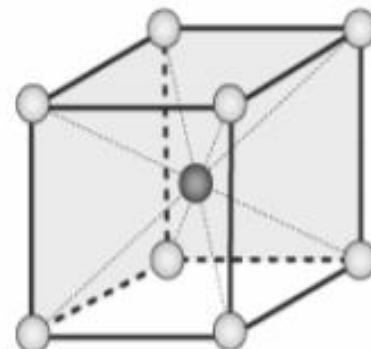


HCP, CN = 12

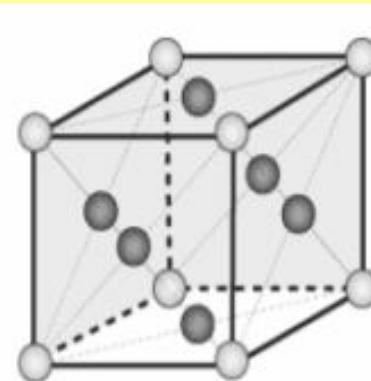
Number of Atoms Per Unit Cell



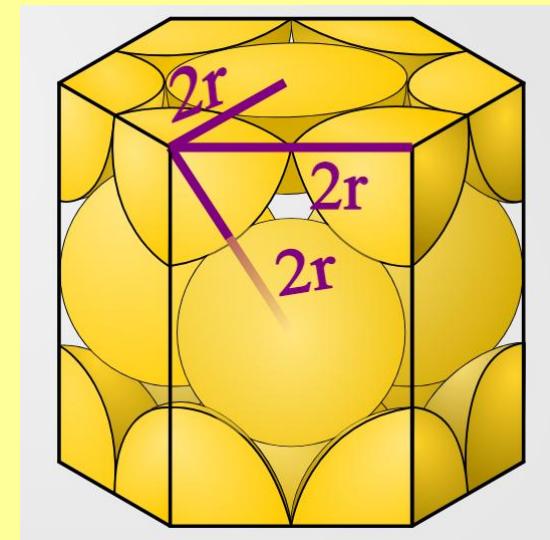
Simple cubic



Body-centred
Cubic Unit Cell
(BCC)



Face-centred
Cubic Unit Cell
(FCC)



Hexagonal closed packed (hcp)

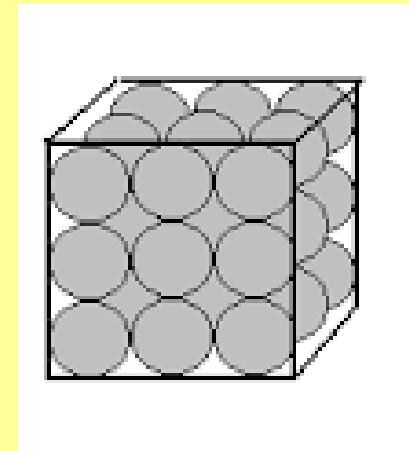
• Number of Atoms Per Unit Cell

– Determine Total Number of Atom Fraction Shared by Unit Cell, e.g.,

- SC: 8 (corner atoms) / 8 (shared by 8 unit cells) = 1
- BCC: $[8/8] + [1$ (atom inside unit cell) / 1 (shared by 1 unit cell)] = 2
- FCC: $[8/8] + [6$ (atom on unit cell faces) / 2 (shared by 1 unit cell)] = 4
- HCP: $[2 \times (6/6)] + [2 / 2] + [3 / 1] = 6$

Atomic Packing Factor (APF)

- The fraction of space occupied by atoms in a unit cell is known as atomic packing fraction.
- It is the ratio of volume of effective number of atoms in a unit cell to total volume of unit cell.
- It is like some hard balls are closely packed in a box.
- Mathematical Expression:

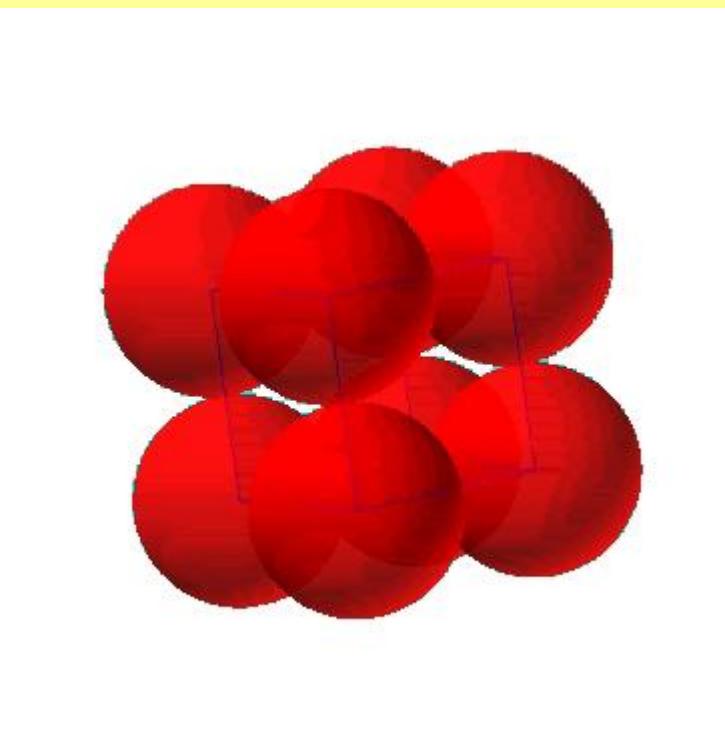
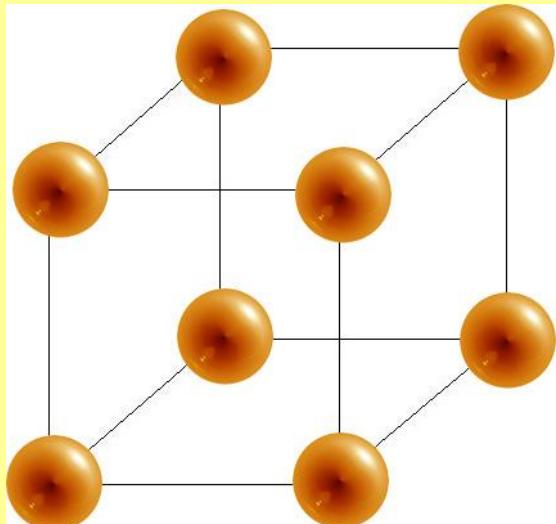


$$APF = \frac{N_{atoms} \left(\frac{4}{3}\right)\pi R^3}{a^3}$$

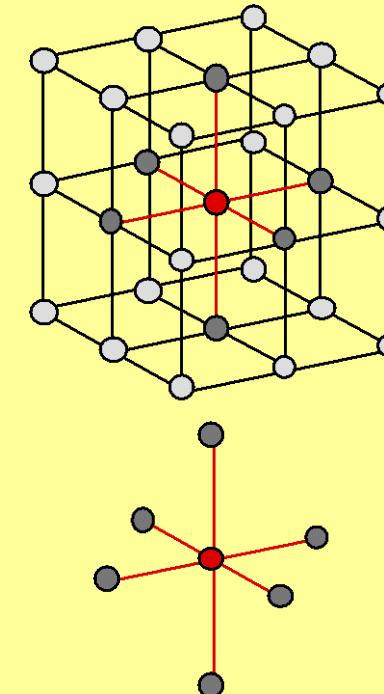
a³ is the volume for cubic unit cell

SIMPLE CUBIC STRUCTURE (SC)

- It is Rare structure due to poor packing (Example: Po (polonium))
- Close-packed directions are cube edges.



- Coordination # = 6
(# nearest neighbors)



Packing Factor
= 52%

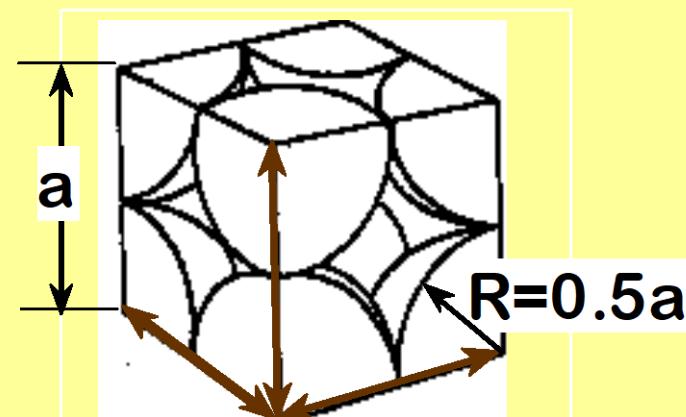
(Image Courtesy P.M. Anderson)
Book

ATOMIC PACKING FACTOR (SC structure)

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

$$APF = \frac{N_{atoms} \left(\frac{4}{3}\right)\pi R^3}{a^3}$$



close-packed directions
contains $8 \times 1/8 =$
1 atom/unit cell

Total no. of atom per simple cubic cell is $8(1/8) = 1$ atom

$$\text{Volume of one atom} = (4/3)\pi R^3$$

For calculation of Radius of atom (R), $2R = a$,
Or,

$$R = a / 2 = 0.5a$$

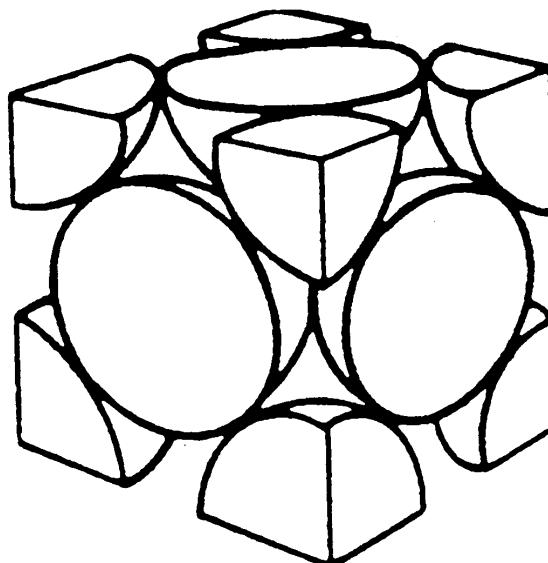
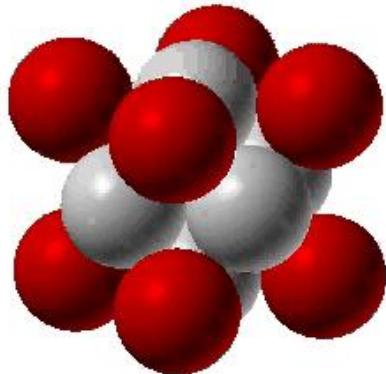
$$APF = \frac{\frac{atoms}{unit\ cell} \cdot \frac{4}{3}\pi (0.5a)^3}{\frac{volume}{atom} \cdot \frac{volume}{unit\ cell}} = 0.52$$

Adapted from Fig. 3.19,
Callister 6e.

- APF for a simple cubic structure = $0.52 = 52\%$

FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are face diagonals.
 - Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.



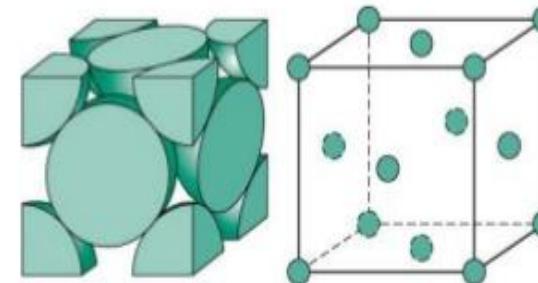
(Image Courtesy: P.M. Anderson)

Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.
 - Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12

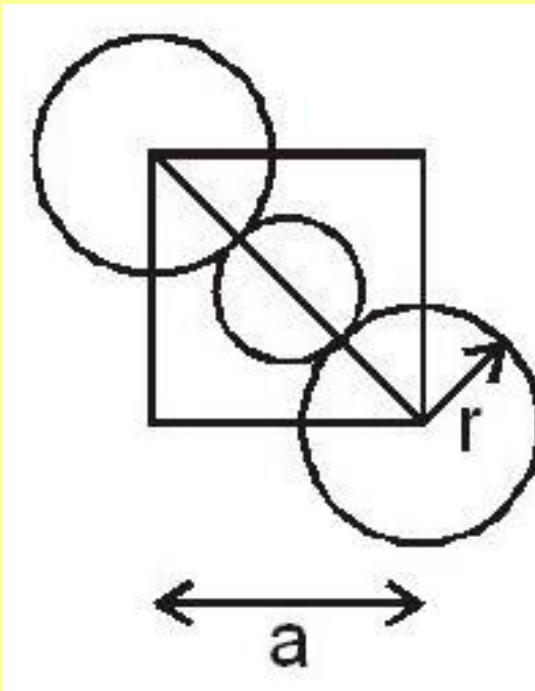
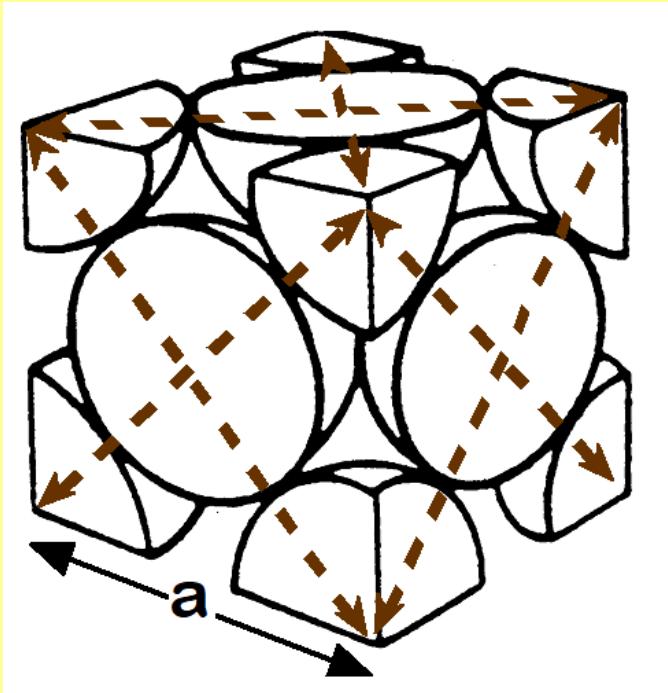


Adapted from Fig. 3.1, Callister & Rethwisch 3e.

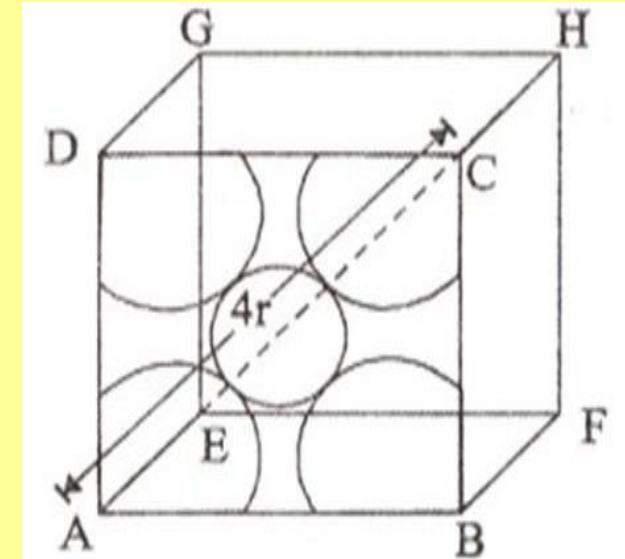
4 atoms/unit cell: $6 \text{ face} \times 1/2 + 8 \text{ corners} \times 1/8$

(Courtesy P.M. Anderson)

FCC, Radius of atom



Face diagonal = $4r$,
a is unit cell edge or lattice parameter



Consider the triangle ABC,

$$AC^2 = AB^2 + BC^2$$

$$(4r)^2 = a^2 + a^2$$

$$16 r^2 = 2a^2$$

$$r^2 = \frac{2a^2}{16}$$

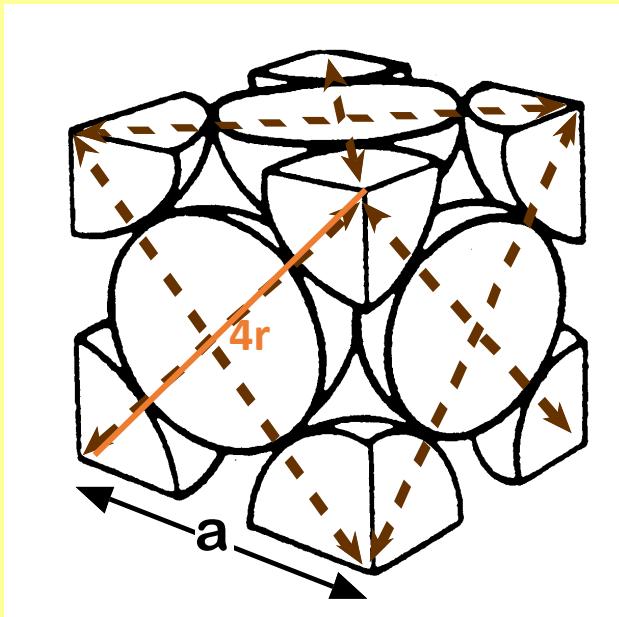
Taking square root on both sides,

$$\sqrt{r^2} = \frac{\sqrt{2a^2}}{\sqrt{16}}$$

$$r = \frac{a\sqrt{2}}{4}$$

ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74 = 74%



Unit cell contains:

$$6 \times 1/2 + 8 \times 1/8 \\ = 4 \text{ atoms/unit cell}$$

Total no. of atom per fcc unit cell = 4

Radius of one atom $r = a\sqrt{2}/4$

$$APF = \frac{N_{atoms} \left(\frac{4}{3}\right)\pi r^3}{a^3}$$

Adapted from Fig. 3.1(a), Callister 6e.

$$APF = \frac{\frac{atoms}{unit\ cell} \cdot 4 \cdot \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3 \cdot \frac{volume}{unit\ cell}}$$

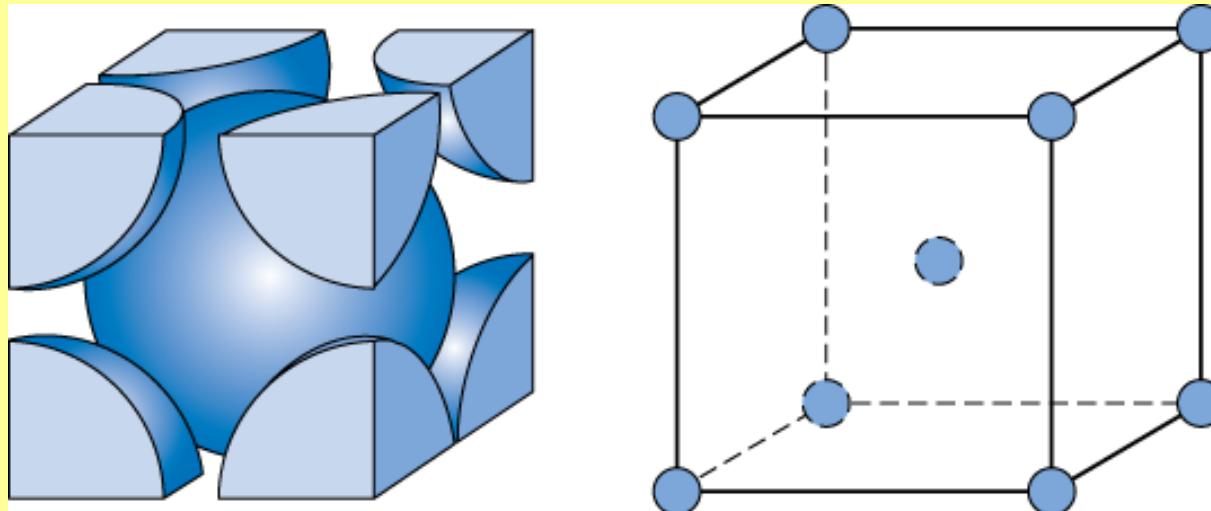
= 0.74

Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube diagonals.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8



2 atoms/unit cell: 1 center + 8 corners $\times \frac{1}{8}$

ATOMIC PACKING FACTOR: BCC

- APF for a body-centered cubic structure = 0.68

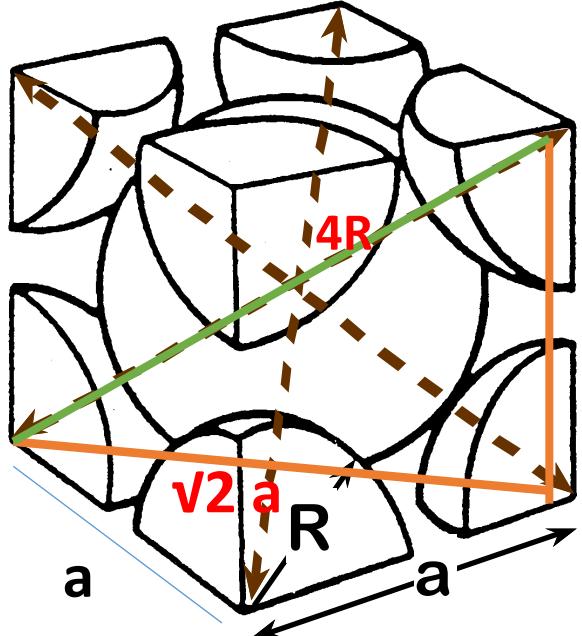


Figure Adapted from
Fig. 3.2,
Callister 6e. (book)

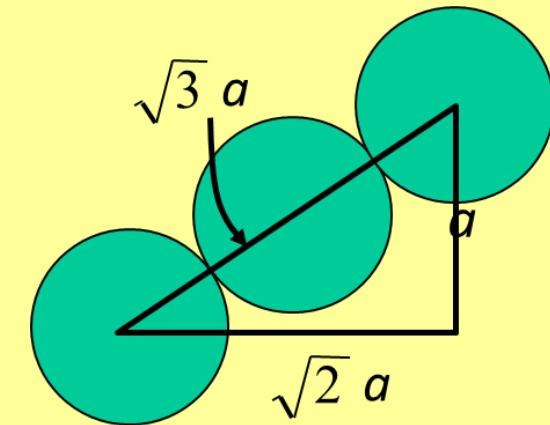
Close-packed directions:

$$\begin{aligned}\text{Diagonal length} &= 4R \\ &= \sqrt{3} a\end{aligned}$$

$$R = a\sqrt{3}/4$$

Unit cell contains:

$$\begin{aligned}1 + 8 \times 1/8 \\ = 2 \text{ atoms/unit cell}\end{aligned}$$



$$APF = \frac{N_{atoms} \left(\frac{4}{3}\right)\pi R^3}{a^3}$$

$$APF = \frac{\frac{atoms}{unit\ cell}}{\frac{volume}{unit\ cell}}$$

$\frac{4}{3} \pi (\sqrt{3}a/4)^3$ ← volume atom

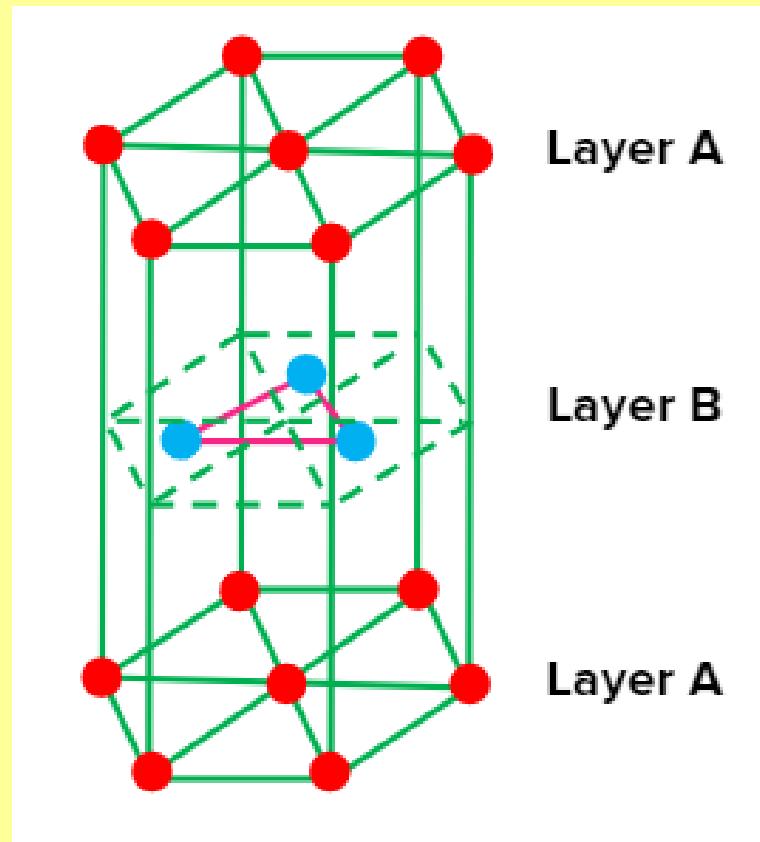
a^3 ← volume unit cell

= 0.68 or 68%

What is HCP Structure?

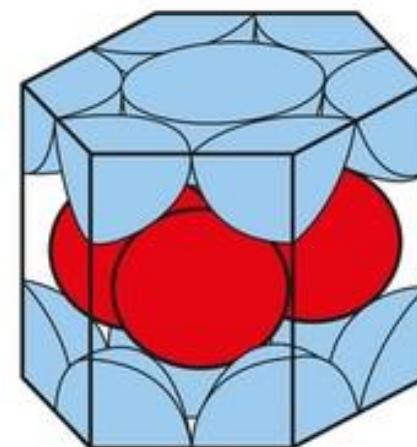
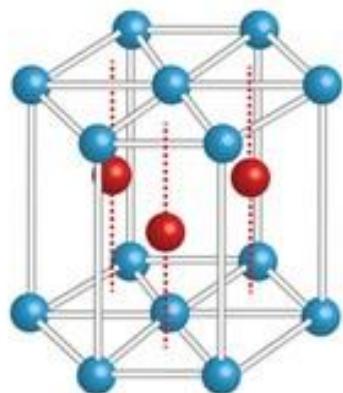
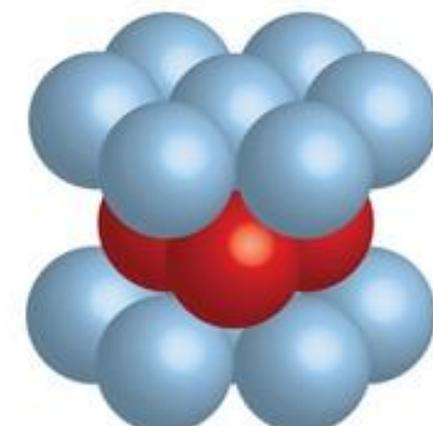
- HCP = Hexagonal Close-Packed
- One of the most efficient ways atoms can pack in 3D.
- Found in metals like Mg, Zn, Ti, Co.

Hexagonal Close Packing (HCP) is a way to arrange atoms in a crystal structure where layers of atoms are stacked in an ABAB... Pattern.



Atoms in HCP Unit Cell

- Total atoms per unit cell: 6
- - 12 corner atoms: each contributes $1/6 = 2$ atoms
- - 2 face atoms (top and bottom): each contributes $1/2 = 1$ atom
- - 3 atoms fully inside middle layer = 3 atoms
- Total = $2 + 1 + 3 = 6$ atoms



APF of HCP Unit cell

Volume of HCP unit cell

Volume of HCP unit cell(Figure 4.11 a) = Base area × height
= $6 \times \text{area of } \Delta ABC \times c$

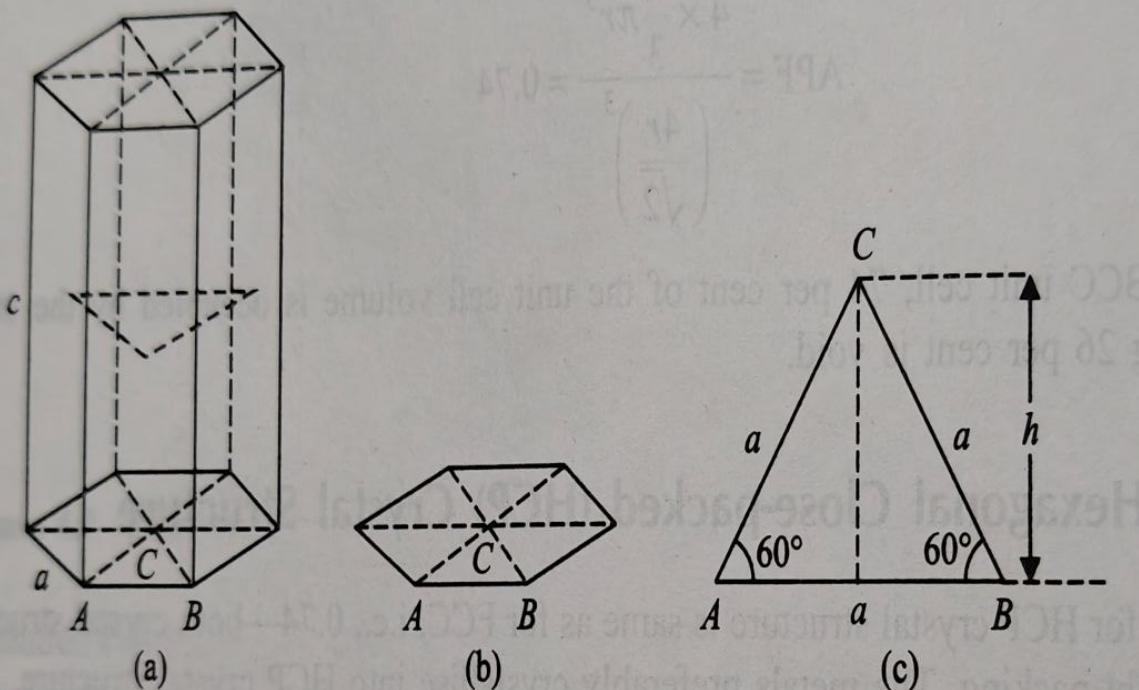


Figure 4.11 (a) HCP unit cell, (b) Basal face and (c) Triangle ABC of the base.

$$\text{Area of triangle } ABC = \frac{1}{2} \text{Base} \times \text{Height}$$

$$= \frac{1}{2} a (a \sin 60^\circ)$$

$$= \frac{1}{2} a (a \frac{\sqrt{3}}{2}) = \frac{a^2 \sqrt{3}}{4}$$

Volume of HCP unit cell

$$V = 6 \times \text{area of } \Delta ABC \times c$$

$$V = 6 \times \frac{a^2 \sqrt{3}}{4} \times c$$
$$= \frac{3 \sqrt{3}}{2} a^2 c$$

Atomic Packing Factor (APF) for HCP

For hcp unit cell: $N = 6$

$$a = 2r, \text{ or } r = a/2$$

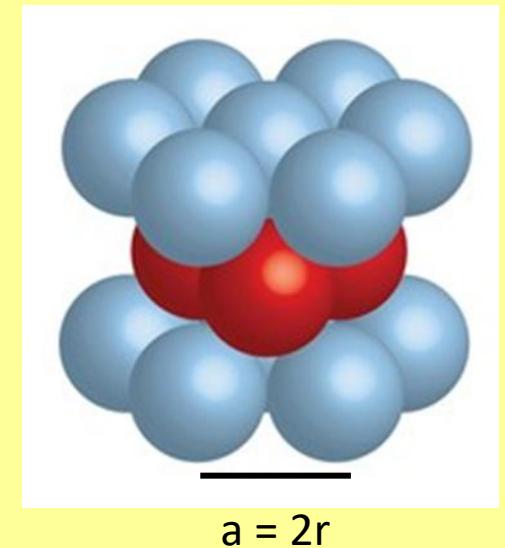
$$\frac{c}{a} = 2 \sqrt{\frac{2}{3}} = 1.63 \quad (\text{for ideal hcp crystal})$$

$$\text{And volume, } V = \frac{3\sqrt{3}}{2} a^2 c$$

$$\text{APF} = \frac{N_{\text{atoms}} V_{\text{atom}}}{V_{\text{unit cell}}} = \frac{6 \cdot \frac{4}{3} \pi r^3}{\frac{3\sqrt{3}}{2} a^2 c}$$

$$= 6 \times \frac{\frac{4}{3} \pi (\frac{a}{2})^3}{\frac{3\sqrt{3}}{2} a^2 c} \quad (\text{Put } c = \sqrt{\frac{8}{3}} a = 1.63 a)$$

$$= \frac{\pi}{\sqrt{18}} = \frac{\pi}{3\sqrt{2}} \approx 0.74048048.$$



APF = 0.74 or 74%

Diamond and Zincblende Structures

Many common semiconductors have Diamond Cubic (DC) or Zincblende crystal structures (Basically FCC type of structure).

- These structures can be seen as interpenetration of two FCC lattices with their origins at $(0,0,0)$ and $(1/4,1/4, 1/4)$.
- It can be thought of basis of two atoms in a fcc structure.

Both are Carbon (C)

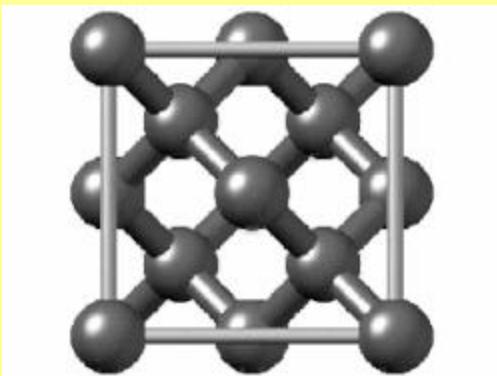
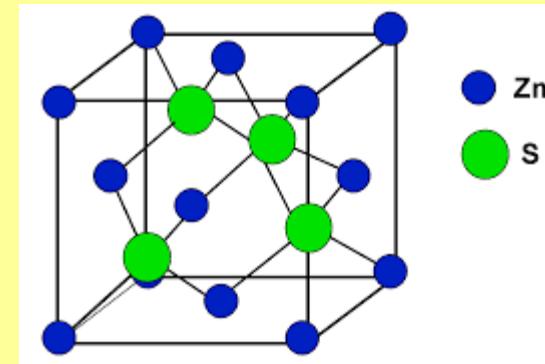


Image courtesy: From Wikipedia

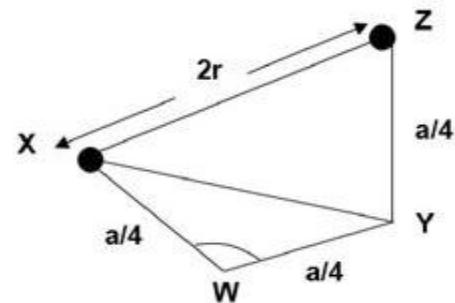
Diamond is a crystal structure with a face centered cubic Bravais lattice and two atoms in the basis. Carbon, silicon germanium, and α -tin form this crystal structure.

Zinc Blende (ZnS)



ZnS, CdS, GaAs etc

Packing Factor of Diamond Structure (34%)



$$XY^2 = XW^2 + WY^2$$

$$XZ^2 = XY^2 + YZ^2$$

$$\begin{aligned} XZ^2 &= XW^2 + WY^2 + YZ^2 \\ &= \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 \end{aligned}$$

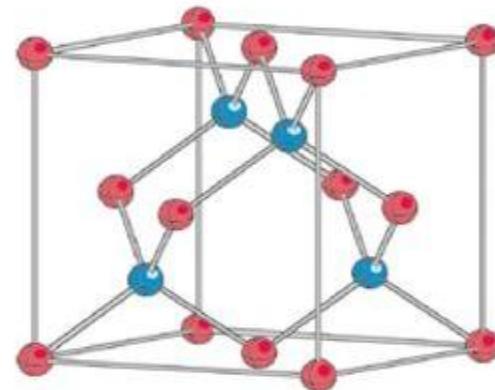
But $XZ = 2r$

$$\therefore (2r)^2 = \frac{3a^2}{16}$$

$$4r^2 = \frac{3a^2}{16}$$

$$r^2 = \frac{3a^2}{64}$$

$$\therefore \text{Atomic radius } r = \frac{\sqrt{3}}{8} a$$



Therefore number of carbon atoms per unit cell
 $= 8 \times \frac{1}{8} (\text{Corners}) + 6 \times \frac{1}{2} (\text{Face centered}) + 4 \text{ full atoms at Tetrahedral positions} = 8$

of atoms in unit cell: 8 ($= \frac{1}{8} \times 8 + \frac{1}{2} \times 6 + 4$)

$$\begin{aligned} \text{APF} &= \frac{V}{V} \\ V &= 8 \times \frac{4}{3} \pi r^3 = 8 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{8}\right)^3 \end{aligned}$$

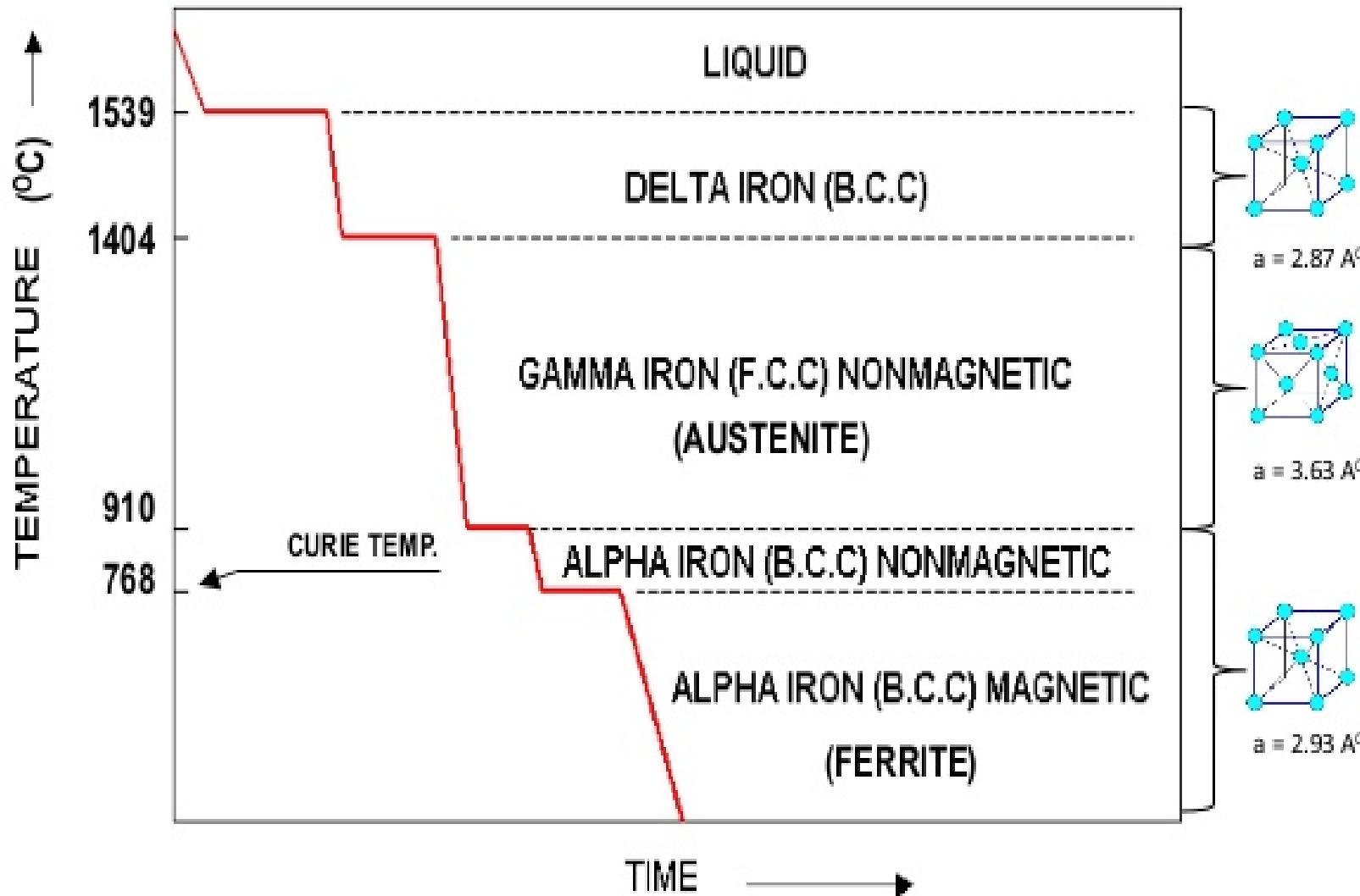
$$\begin{aligned} \text{APF} &= \frac{8 \times 4\pi \times 3 \sqrt{3} a^3}{3 \times 8^3 \times a^3} \\ &= 0.34 \quad (34\%) \end{aligned}$$

Thus it is a loosely packed structure.

Summary

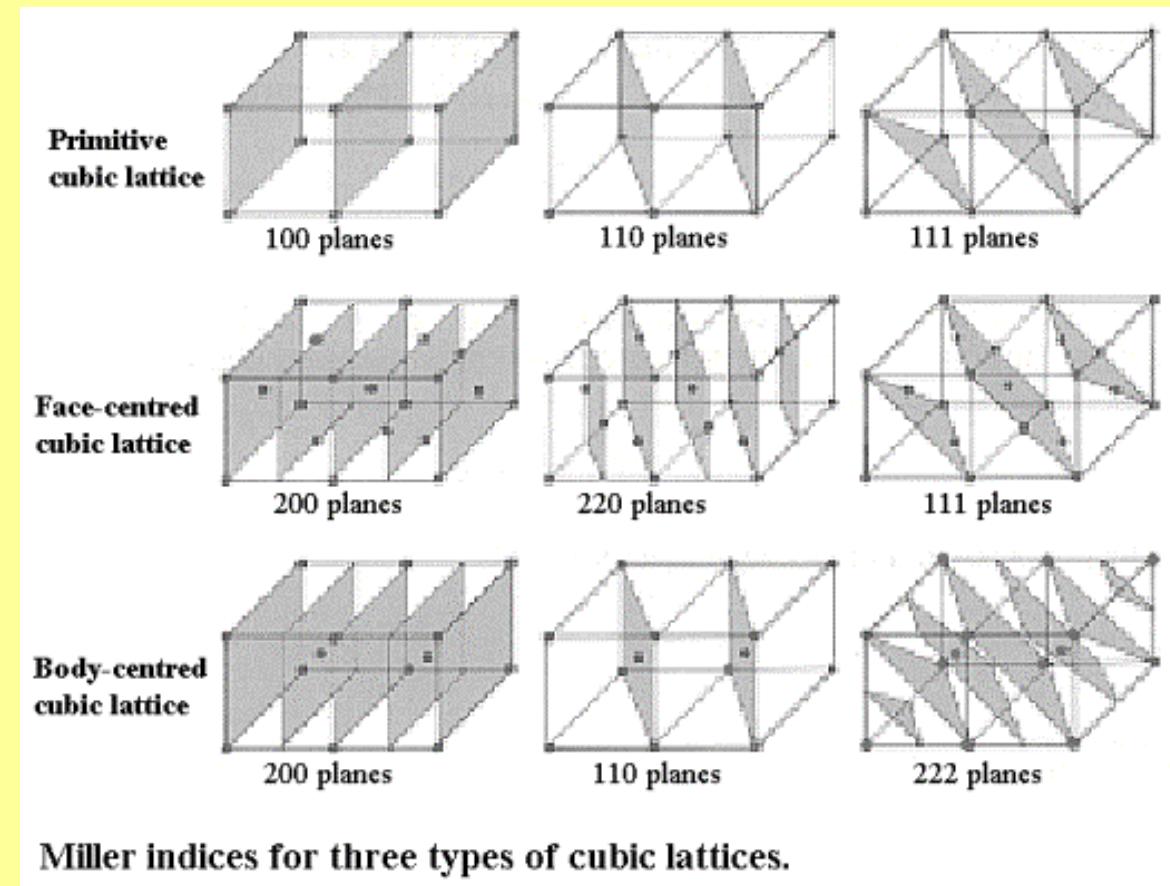
	SC	BCC	FCC	HCP	DC
No. of atoms per unit cell	1	2	4	6	8
Co-ordination no.	6	8	12	12	4
Packing fraction	52%	68%	74%	74%	34%
Atomic radii	$\frac{a}{2}$	$\frac{\sqrt{3}a}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{8}$
Volume	a^3	a^3	a^3	$V = \frac{3\sqrt{3}}{2} a^2 c$	
Example	Polonium α -Mn	Na, Li, Cr	Al, Cu, Ag, Pb	Zn	Ge, Si, C

Allotropy of Pure Iron



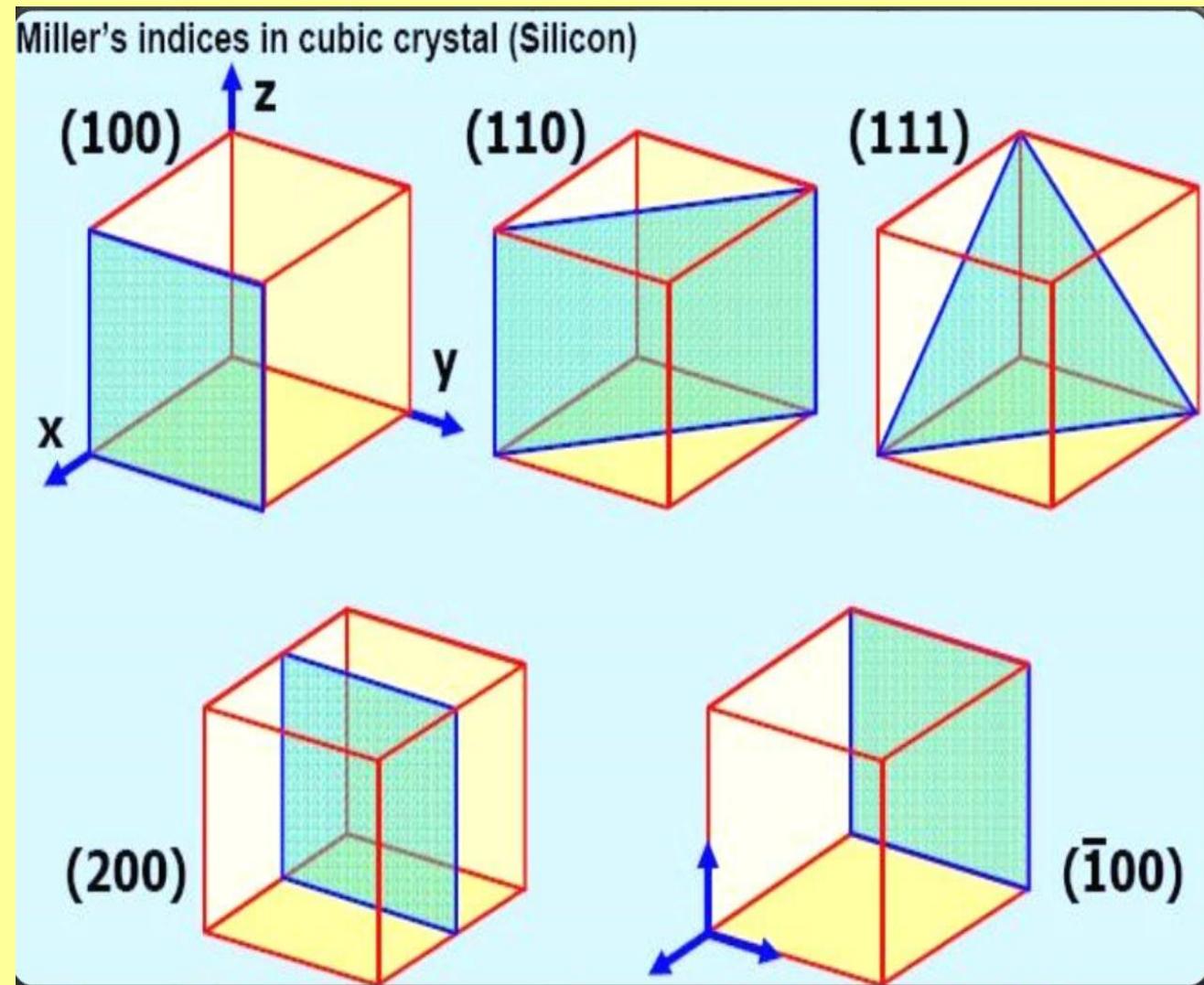
Crystallographic directions, and planes

- Crystallographic directions and planes are geometric concepts used to describe the arrangement of atoms in a crystal lattice.
- Directions = lines,
- Planes = surfaces in a crystal (defined by Miller indices).



Crystal Morphology

- A **face (or plane)** is designated by **Miller indices** in parentheses, e.g. **(100) (111)** etc.
- A **form** is a face plus its symmetric equivalents (in curly brackets) or **set of planes** e.g **{100}, {111}**.
- A **direction in crystal space** is given in square brackets e.g. **[100], [111]**.

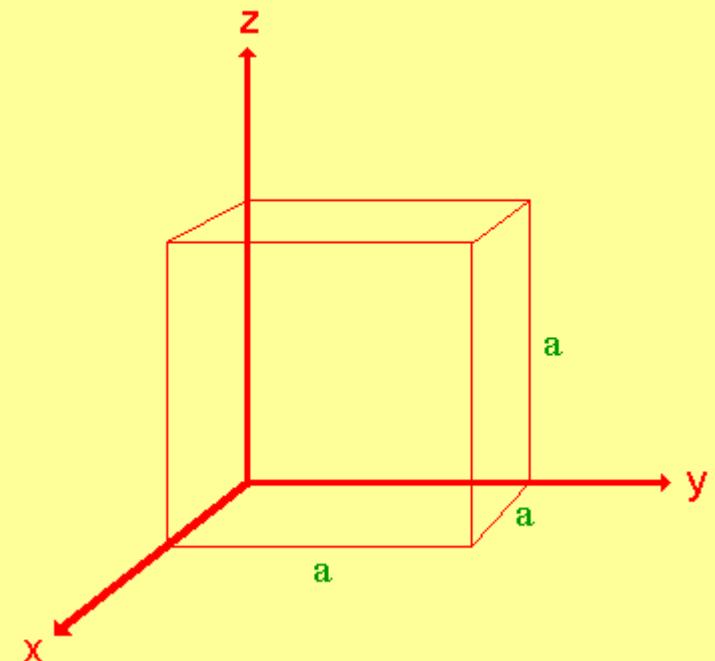


Miller Indices (hkl)

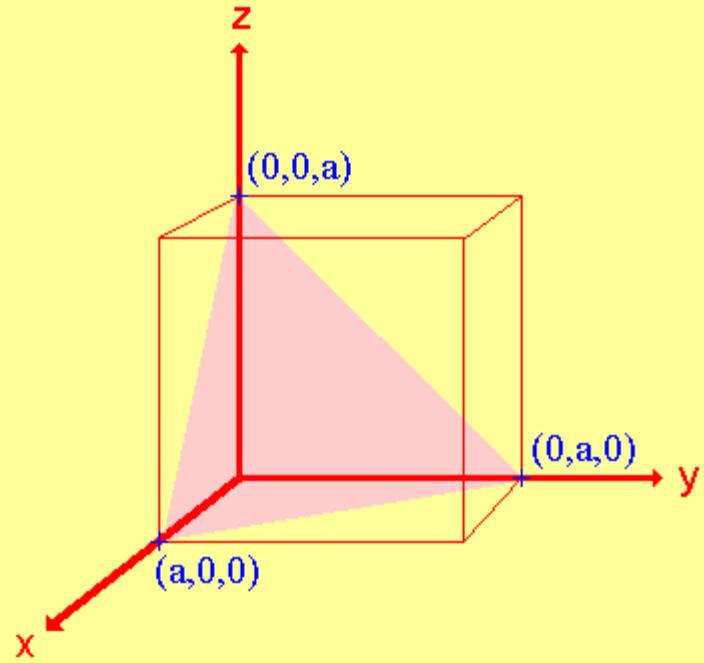
- The orientation of a surface or a crystal plane may be defined by considering how the plane intersects the main crystallographic axes of the solid.
- The application of a set of rules leads to the assignment of the Miller Indices (hkl), which are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

Procedure to find Miller indices:

- 1: Identify the intercepts on the x-, y- and z- axes.
- 2: Specify the intercepts in fractional co-ordinates
- 3: Take the reciprocals of the fractional intercepts
- 4: Make the smallest set of integral numbers and enclose them in brackets.



Miller Indices (hkl)



Intercepts: a , a , a

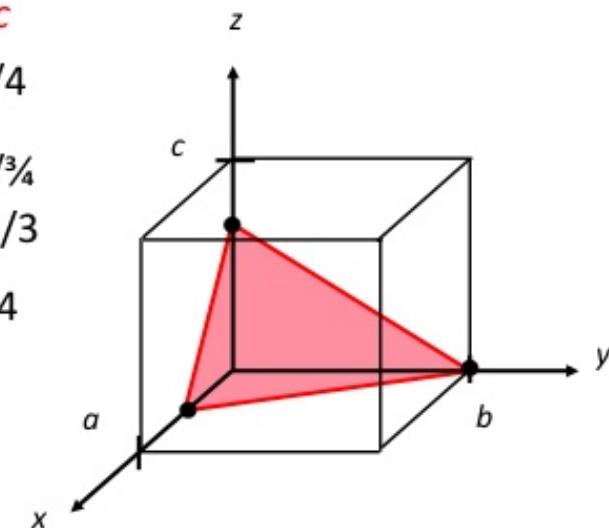
Fractional intercepts: 1 , 1 , 1

Miller Indices: **(111)**

Crystallographic Planes

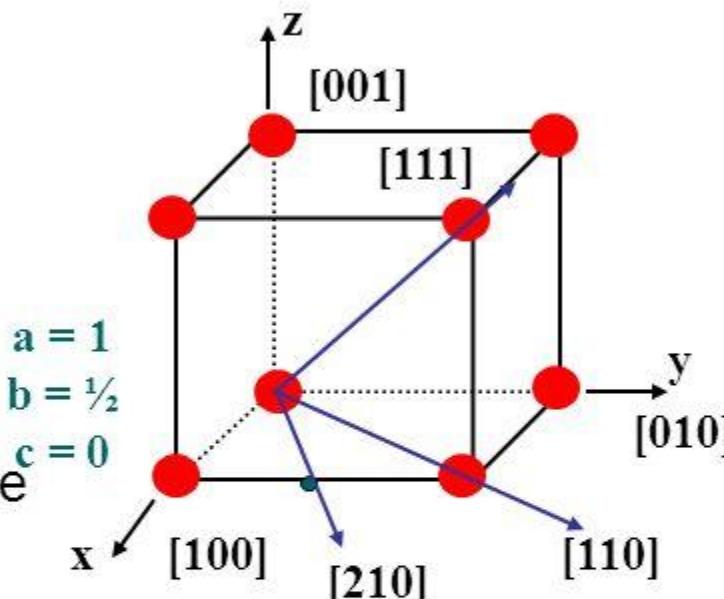
example

	a	b	c
1. Intercepts	$1/2$	1	$3/4$
2. Reciprocals	$1/\frac{1}{2}$	$1/1$	$1/\frac{3}{4}$
	2	1	$\frac{4}{3}$
3. Reduction	6	3	4
4. Miller Indices	(634)		



Crystallographic Directions

- Determining direction indices
 - Start vector at crystal axis
 - Draw to any point in the 3-D crystal
 - Project vector on each xyz axes
 - measure a in x-direction
 - measure b in y-direction
 - measure c in z-direction
 - Multiply by common factor to achieve smallest integer value
 - Enclose in [] without commas
- Negative directions indicated with -
- Family of directions indicated by $\langle \rangle$
- Hexagonal crystals have 4 indices



In a cubic crystal, $[100], [\bar{1}00], [010], [0\bar{1}0], [001], [00\bar{1}]$ are all in the $\langle 100 \rangle$ family.

Family of Planes

- Planes that are **crystallographically equivalent** have the same atomic packing.
- Also, in cubic systems only, planes having the same indices, regardless of order and sign, are equivalent.
- Ex: {111}

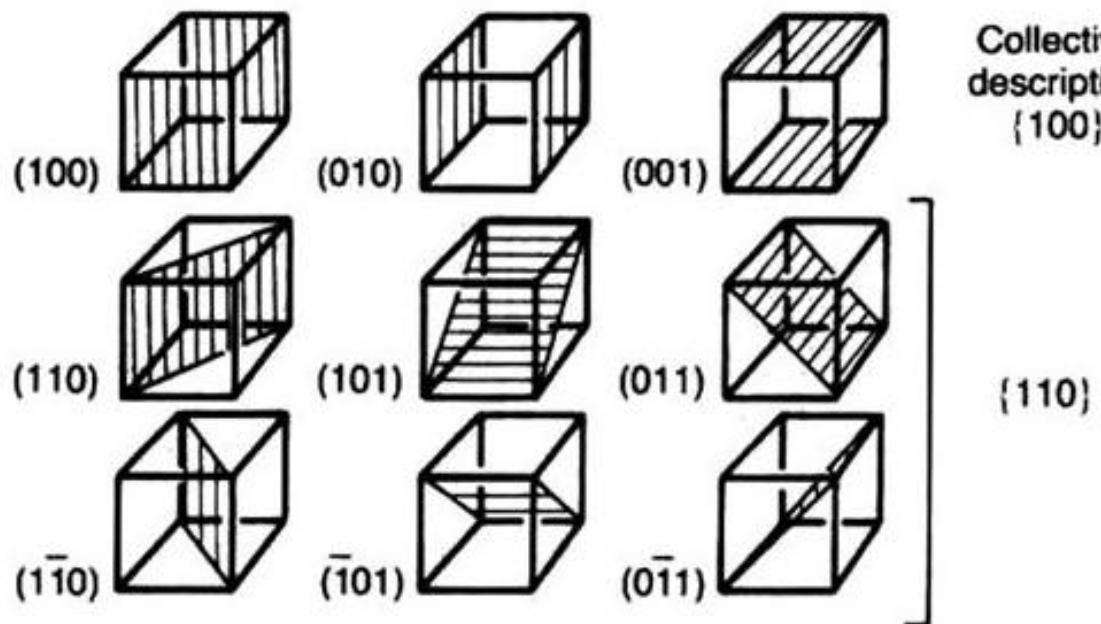
$$= (111), (\bar{1}11), (1\bar{1}1), (11\bar{1}), (\bar{1}\bar{1}\bar{1}), (\bar{1}\bar{1}1), (\bar{1}1\bar{1}), (1\bar{1}\bar{1})$$

Ex: {100} = (100), (010), (001), ($\bar{1}$ 00), (0 $\bar{1}$ 0), (00 $\bar{1}$)

FAMILIES of PLANES

- Crystallographically EQUIVALENT **PLANES** → {Curly Braces} notation
 - e.g., in a cubic system,

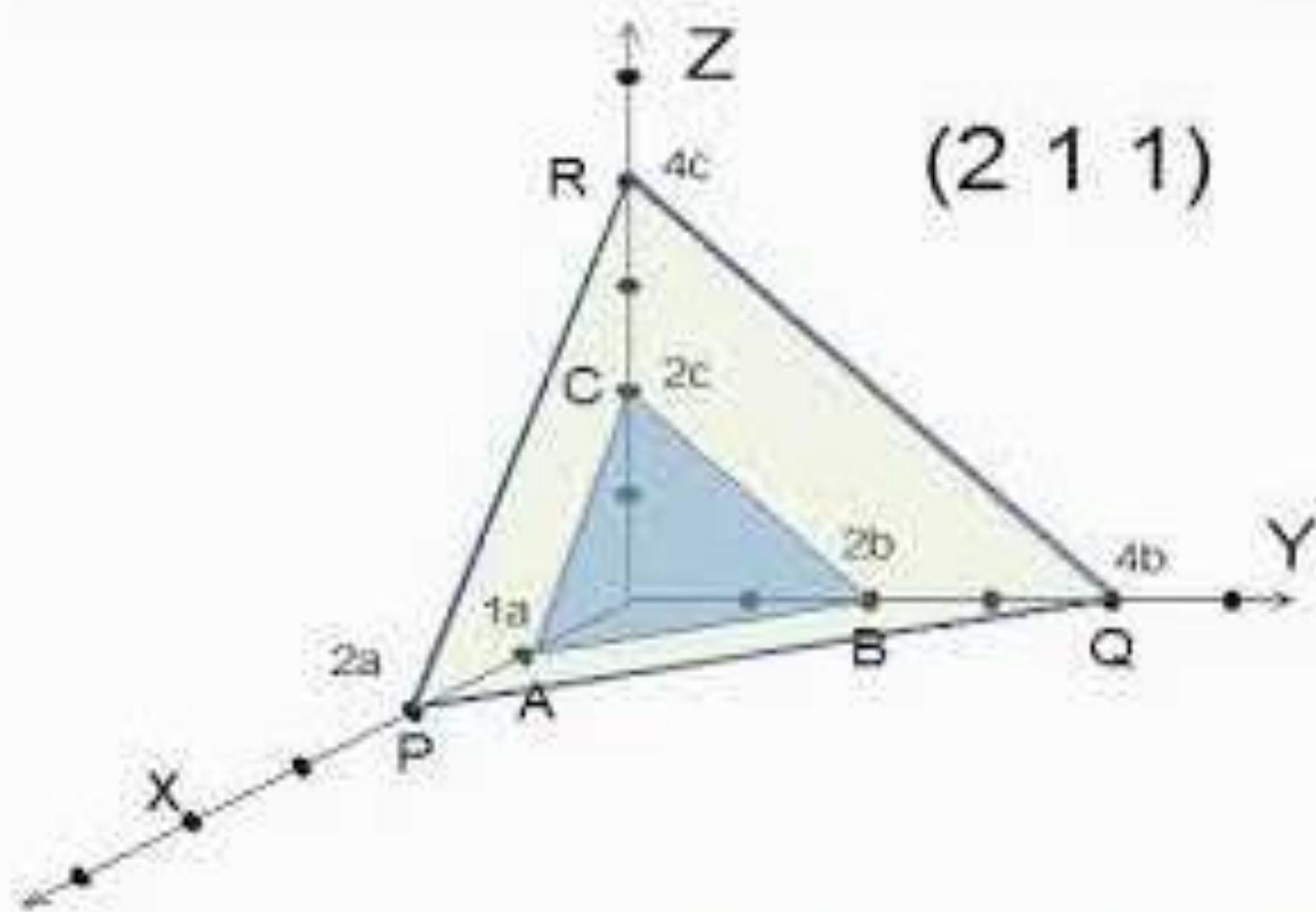
$$(110) = (\bar{1}10) = (101) = (\bar{1}\bar{0}1) = (011) = (0\bar{1}0) \rightarrow \{110\}$$



- Family of {110} planes:
SAME ATOMIC ARRANGEMENTS within all those planes



Miller Indices of Parallel planes are same (Example)



plane ABC	X	Y	Z
Intercepts	$1a$	$2b$	$4c$
Multiples of basis vectors	1	2	2
Reciprocals	1	$1/2$	$1/2$
Miller Indices	2	1	1

plane PQR	X	Y	Z
Intercepts	$2a$	$4b$	$4c$
Multiples of basis vectors	2	4	4
Reciprocals	$1/2$	$1/4$	$1/4$
Miller Indices	2	1	1