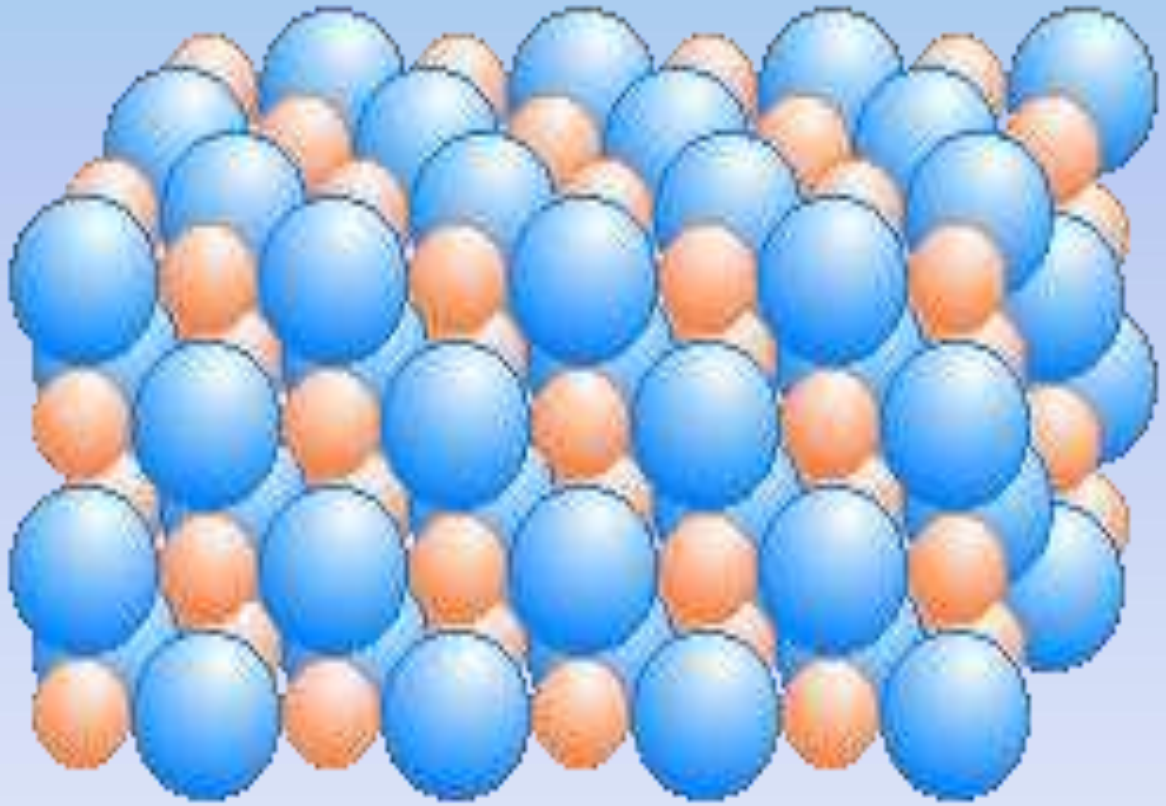
CRYSTAL STRUCTURES



Matter what is available in nature can be classified into three STATES

GASEEOUS

LIQUID

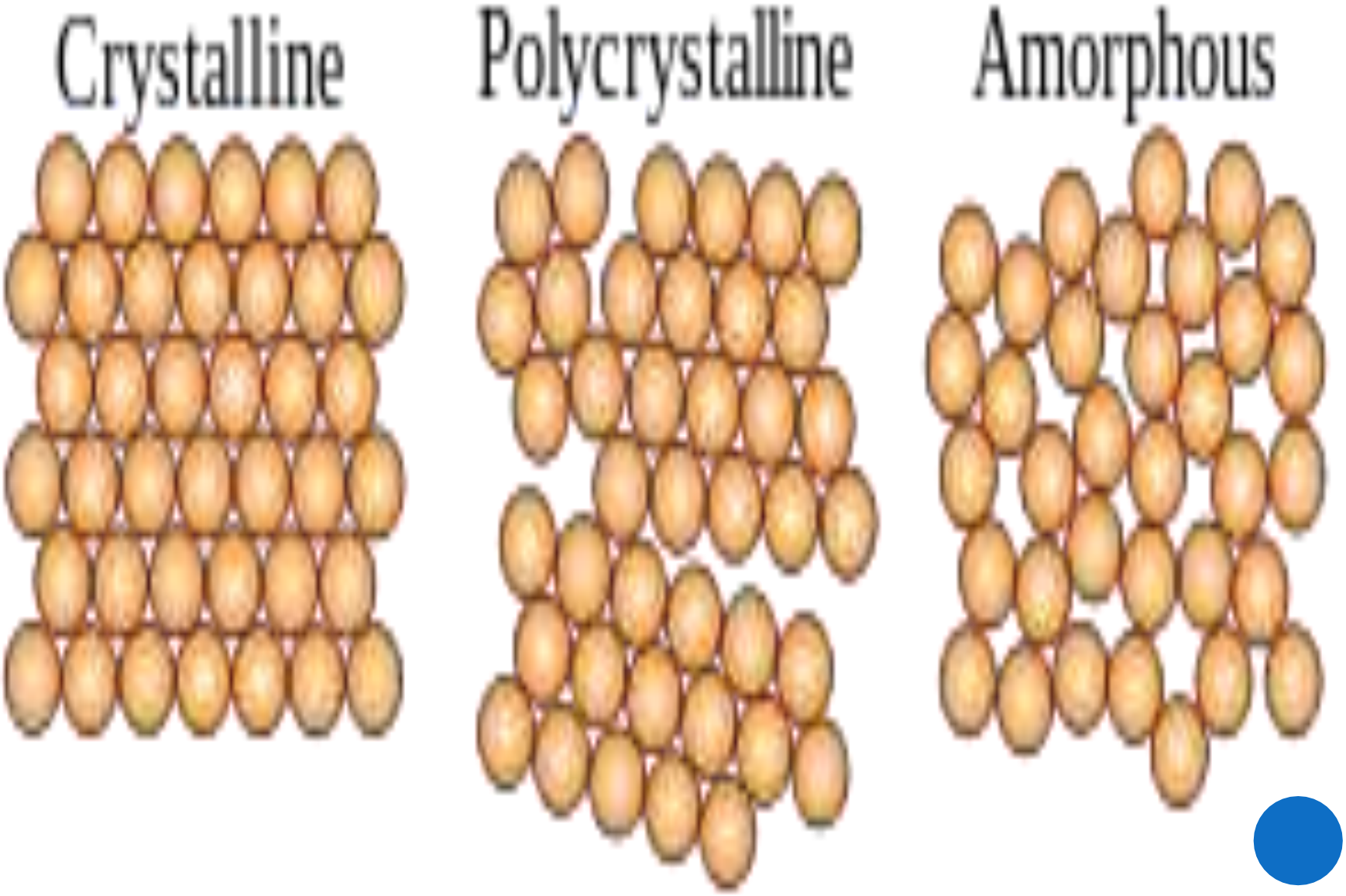
SOLID

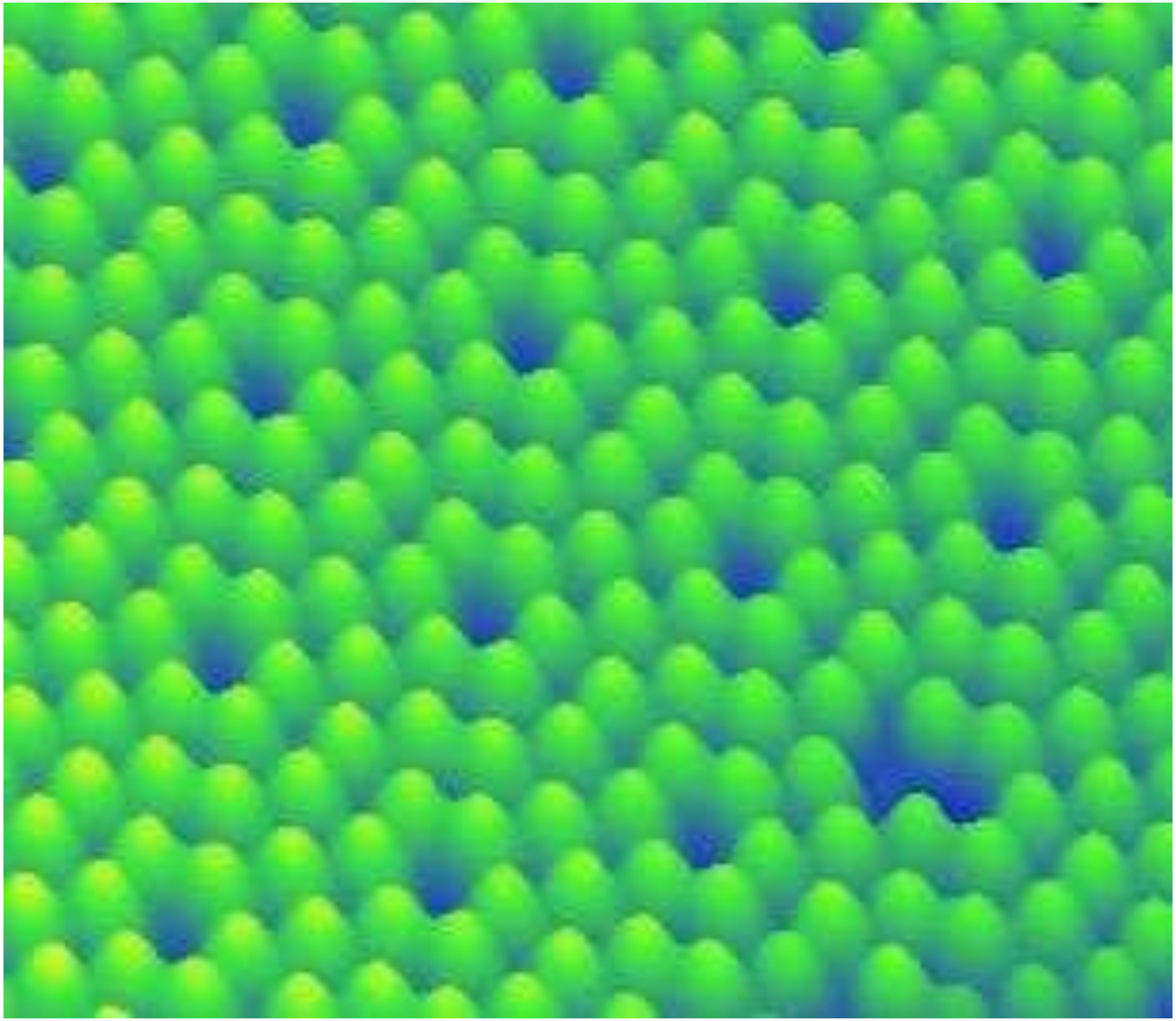
SOLID

- CRYSTALLINE SOLID
- AMORPHOUS SOLID

SOLID IN WHICH ATOMS ARE ARRANGED IN REGULAR MANNER WITH PERFECT PERIODICITY OVER A LONG RANGE ORDER, ARE CALLED CRYSTALLINE SOLID

ATOMS ARRANGED IN IRREGULAR MANNER, CALLED NON-CRYSTALLINE SOLID

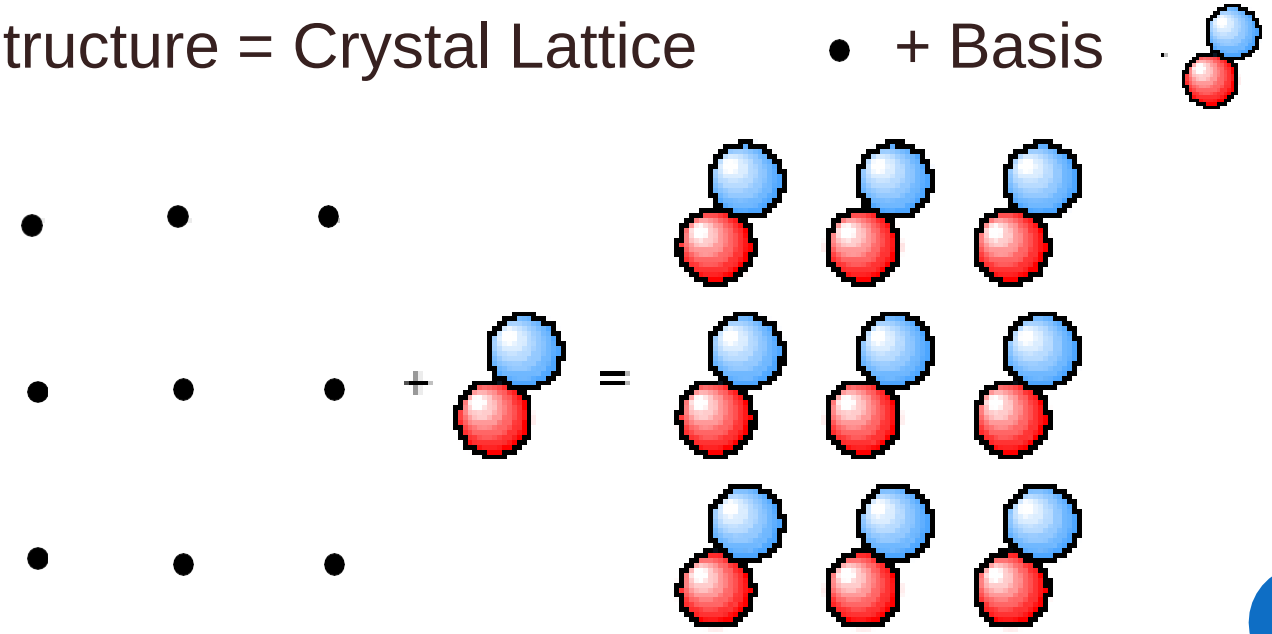

Crystalline
Polycrystalline
Amorphous



Crystal Structure

- Crystal structure 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

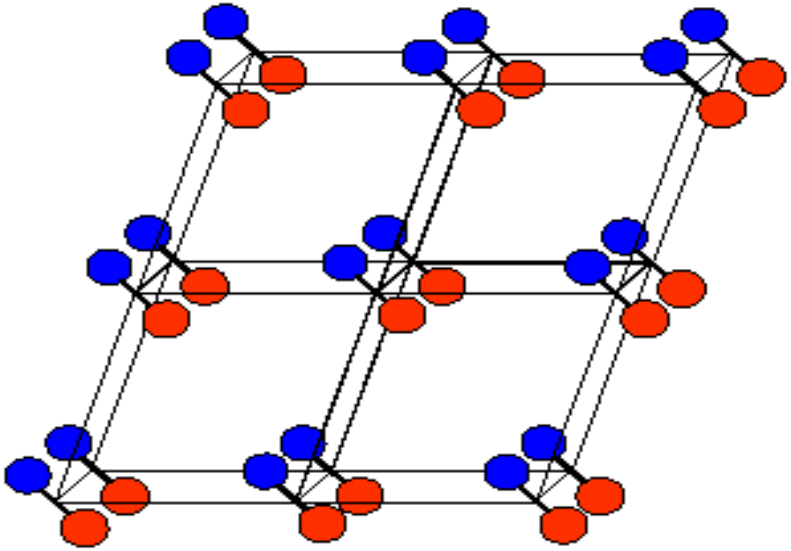


THE REGULAR ARRANGEMENT OF POINTS INSTEAD OF ATOMS IS CALLED LATTICE.
IT IS AN IMAGINARY CONCEPT
Eg: egg box

A GROUP OF ATOMS OR MOLECULE ATTACHED TO EACH LATTICE POINT WHICH ARE IDENTICAL IN COMPOSITION AND ORIENTATION IS CALLED BASIS
Eg: EGGS

Crystal structure

- Don't mix up atoms with lattice points
- Lattice points are infinitesimal points in space
- Lattice points do not necessarily lie at the centre of atoms



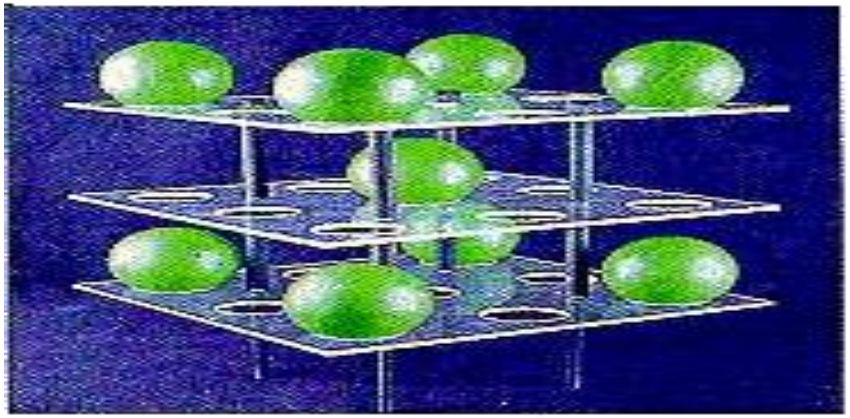
Crystal Structure = Crystal Lattice + Basis

UNIT CELL

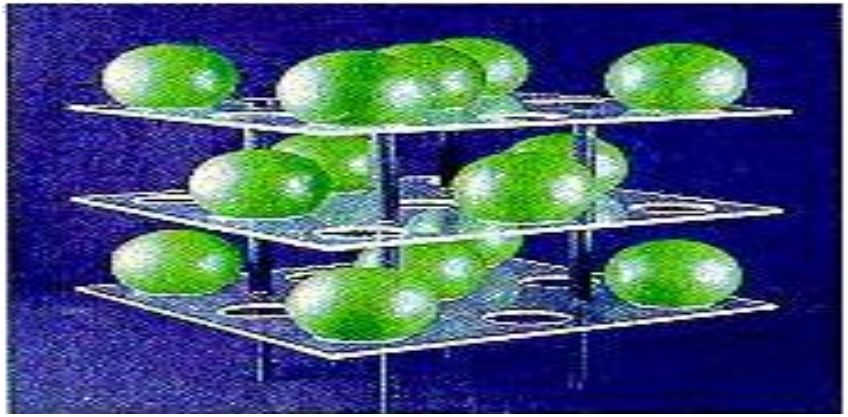
IT IS A BUILDING BLOCK OF CRYSTAL STRUCTURE

IT IS A MINIMUM NUMBER OF ATOMS
BY THE REPETATION OF IT IN THREE DIMENSION
WE CAN CONSTRUCT THE TOTAL CRYSTAL STRUCTURE

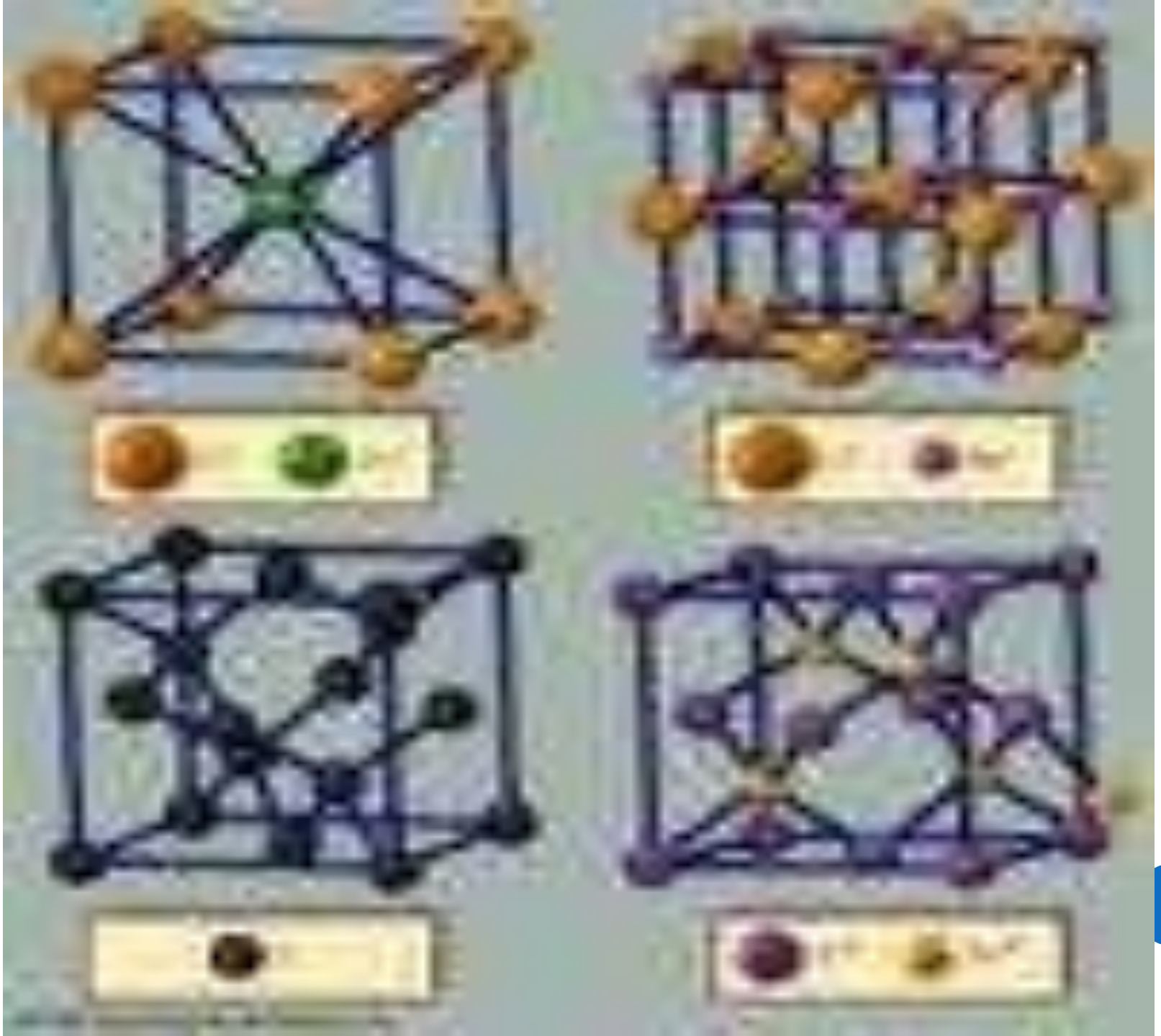
Simple Cubic



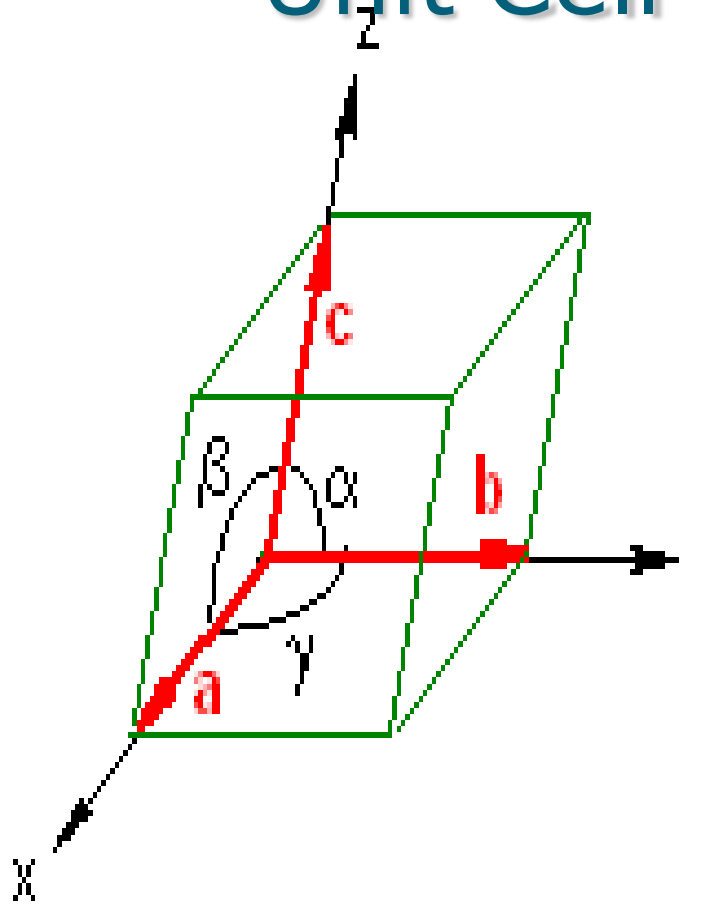
Body-Centered Cubic



Face-Centered Cubic



Unit Cell



- The unit cell and, consequently, the entire lattice, is *uniquely* determined by the six lattice constants: a, b, c, α, β and γ. These are lattice parameters

- a, b, c are axial lengths; α, β and γ. Interfacial angles

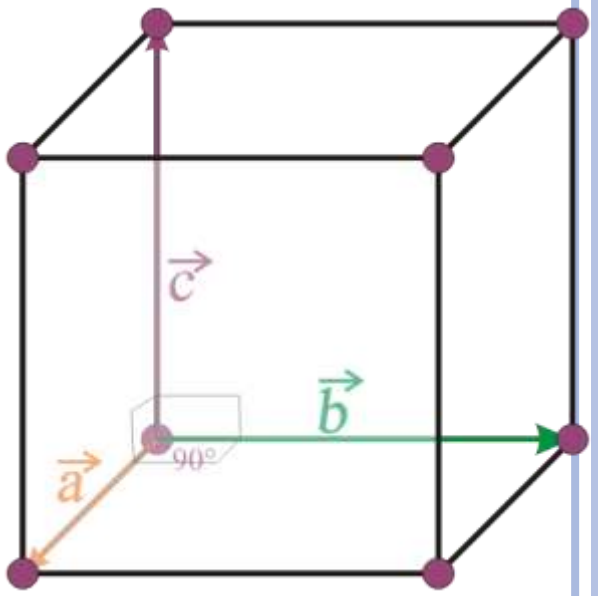
DEPEND UPON THE LATTICE PARAMETER CRYSTAL SYSTM CAN BE CLASSIFIED INTO SEVEN SYSTEMS THOSE ARE

1. **Cubic Crystal System (SC, BCC,FCC)**
2. **Hexagonal Crystal System (S)**
3. **Triclinic Crystal System (S)**
4. **Monoclinic Crystal System (S, Base-C)**
5. **Orthorhombic Crystal System (S, Base-C, BC, FC)**
6. **Tetragonal Crystal System (S, BC)**
7. **Trigonal (Rhombohedral) Crystal System (S)**

Cubic Crystals

$a = b = c$

$\alpha = \beta = \gamma = 90^{o}$



- Simple Cubic (P) - SC
- Body Centred Cubic (I) – BCC
- Face Centred Cubic (F) - FCC

SC, BCC, FCC are lattices while HCP & DC are crystals!

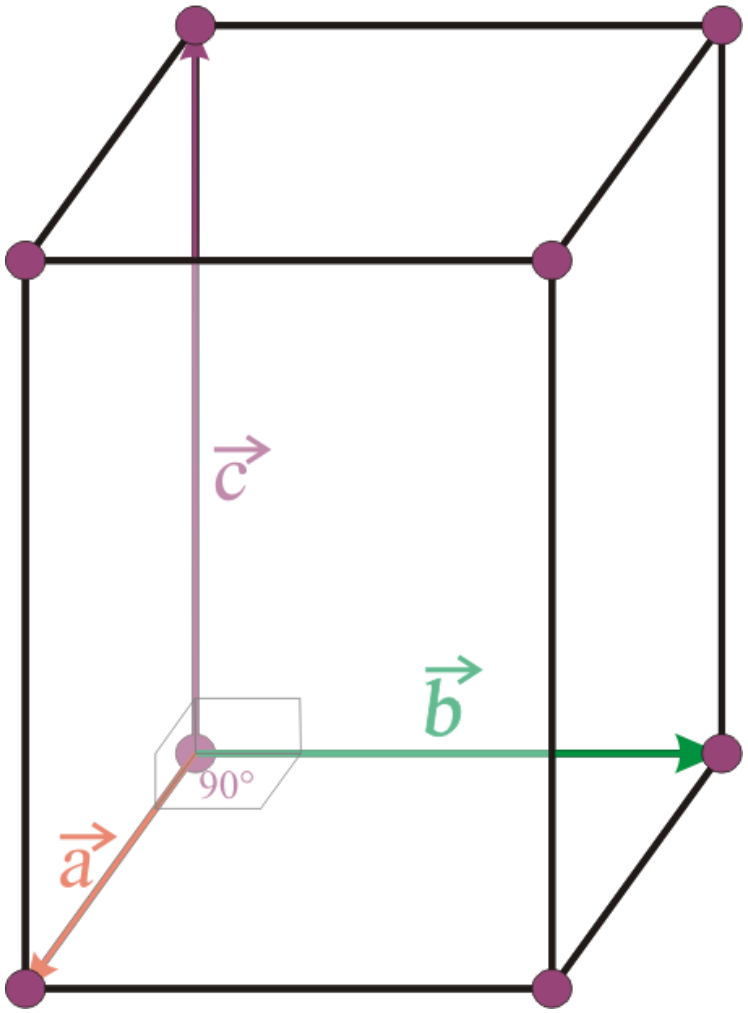
- Elements with Cubic structure → SC: F, O, Po ||
  BCC: Cr, Fe, Nb, K, W, V||
  FCC: Al, Ar, Pb, Ni, Pd, Pt, Ge

Tetragonal Crystals

$a = b \neq c$

$\alpha = \beta = \gamma = 90^{o}$

- Simple Tetragonal
- Body Centred Tetragonal -BCT

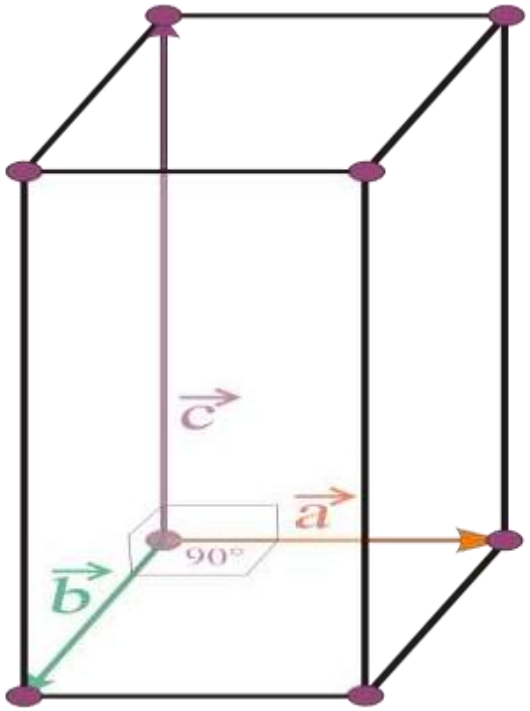


- Elements with Tetragonal structure → In, Sn

Orthorhombic Crystals

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^{o}$



- Simple Orthorhombic
- Body Centred Orthorhombic
- Face Centred Orthorhombic
- End Centred Orthorhombic

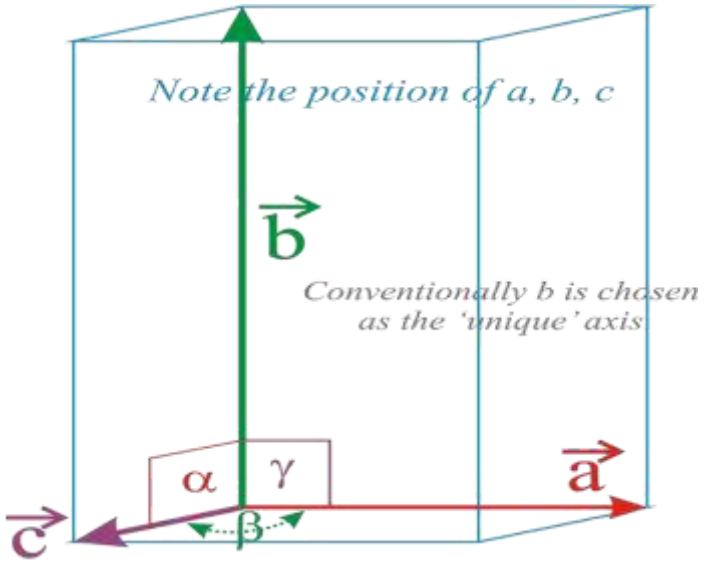
- Elements with Orthorhombic structure → Br, Cl, Ga, I, Su

Monoclinic Crystals

$a \neq b \neq c$

$\alpha = \gamma = 90^o \neq \beta$

- Simple Monoclinic
- End Centred (base centered) Monoclinic (A/C)



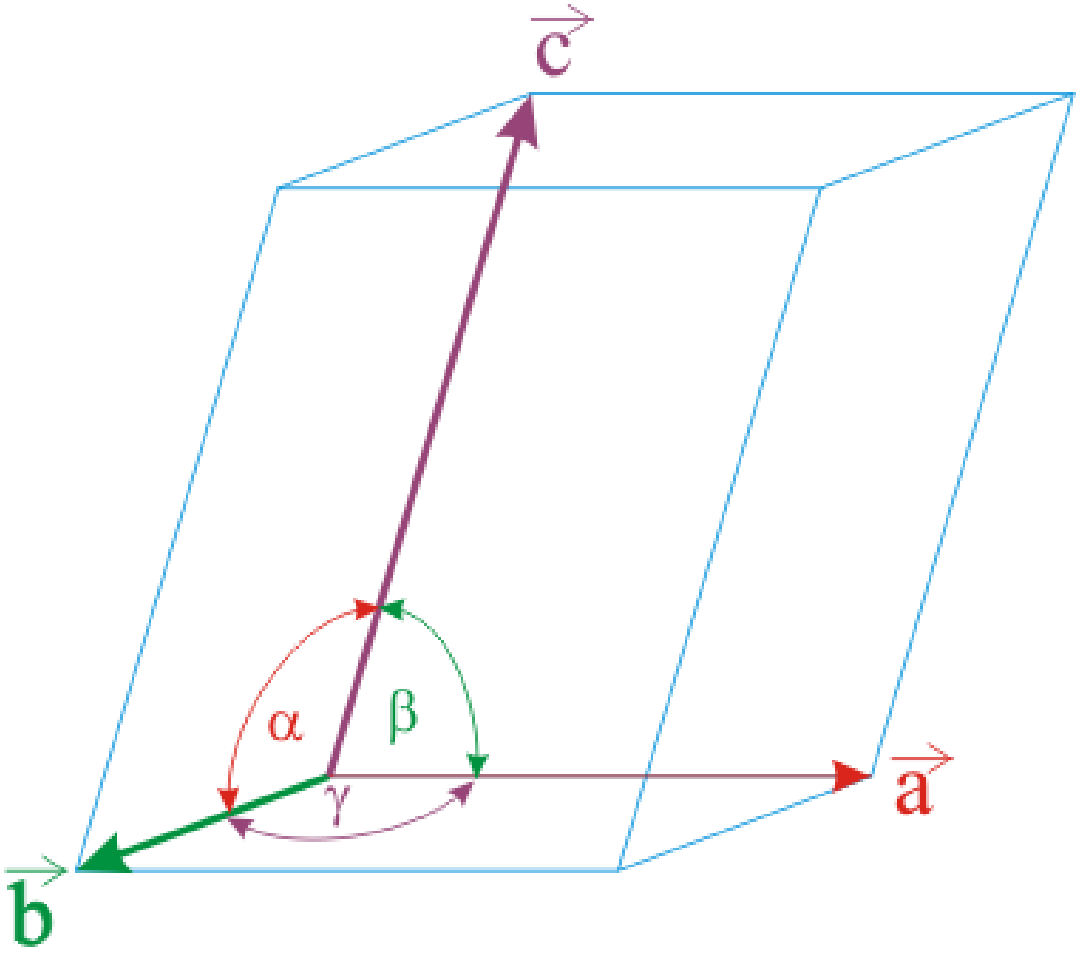
- Elements with Monoclinic structure → P, Pu, Po

Triclinic Crystals

$a \neq b \neq c$

$\alpha \neq \gamma \neq \beta$

- Simple Triclinic

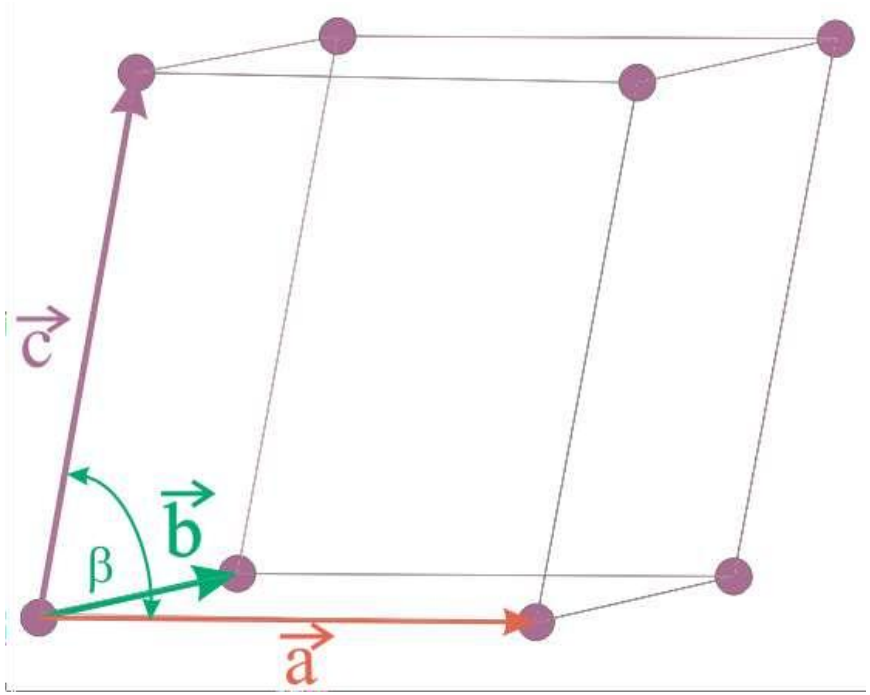


Trigonal/Rhombohedral Crystals

$a = b = c$

$\alpha = \beta = \gamma \neq 90^o$

- Rhombohedral (simple)



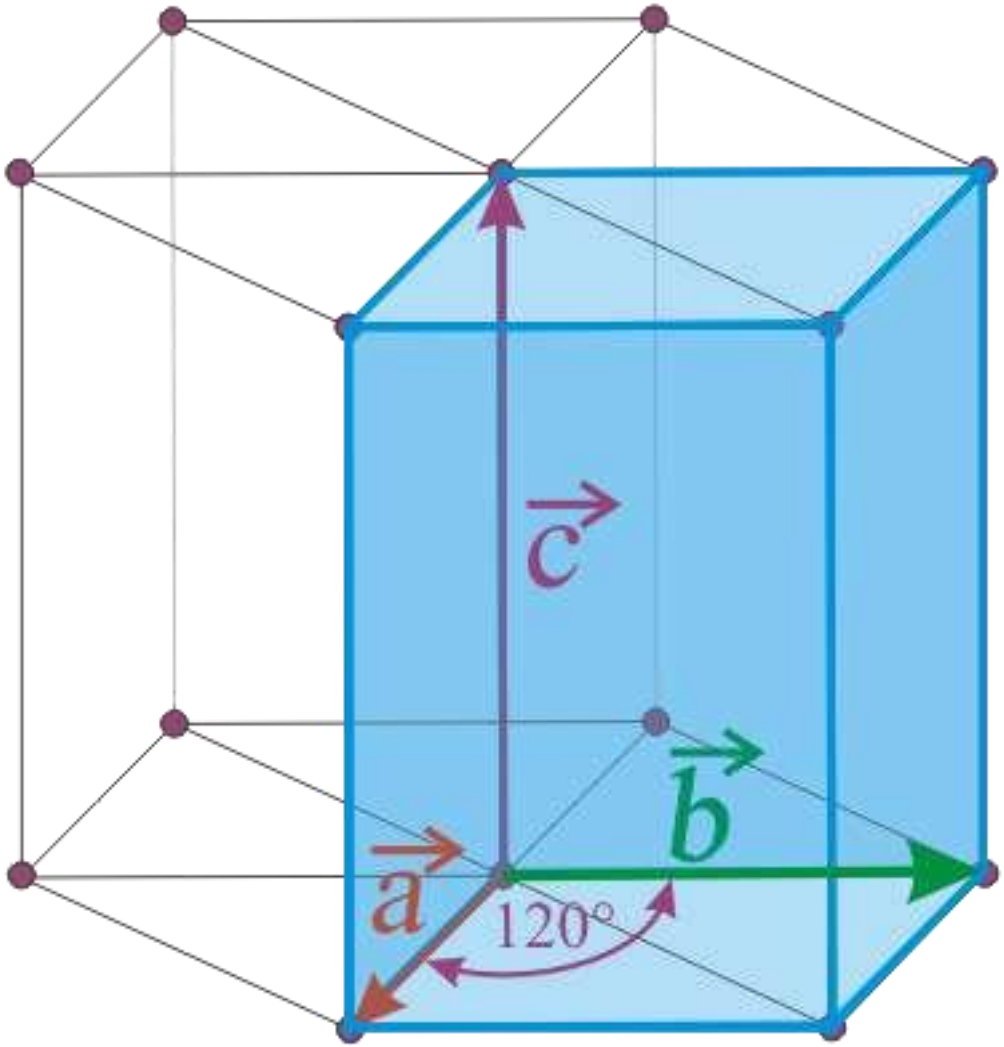
- Elements with Trigonal structure → As, B, Bi, Hg, Sb, Sm

Hexagonal Crystals

$a = b \neq c$

$\alpha = \beta = 90^o \quad \gamma = 120^o$

- Simple Hexagonal

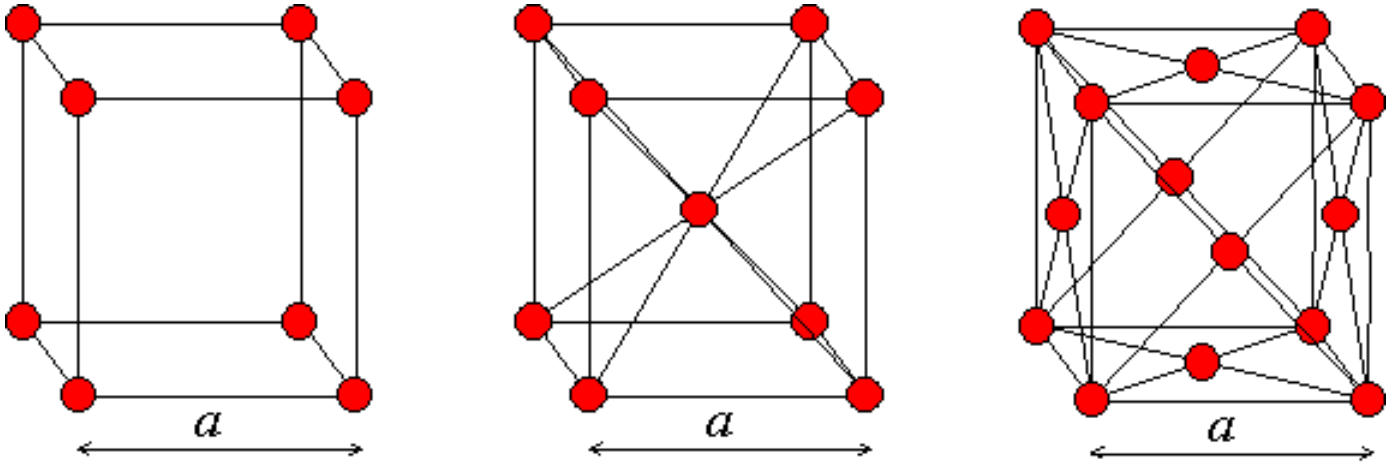


- Elements with Hexagonal structure → Be, Cd, Co, Ti, Zn

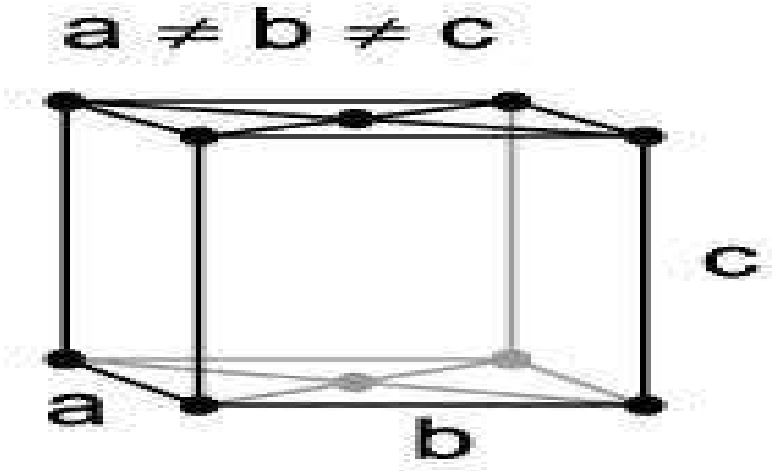
Auguste Bravais
(1811-1863)

LATTICES

- In 1848, Auguste Bravais demonstrated that in a 3-dimensional system there are fourteen possible lattices
- A Bravais lattice is an infinite array of discrete points with identical environment
- seven crystal systems + four lattice centering types = 14 Bravais lattices
- Lattices are characterized by translation symmetry



simple cubic (a) body-centered cubic (b) face centered cubic (c)

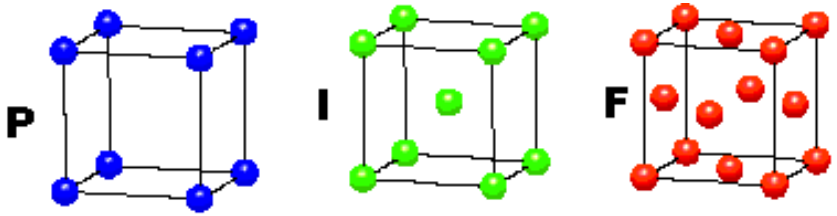


BASE CENTERED

CUBIC

$a = b = c$

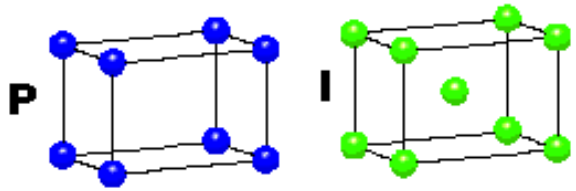
$\alpha = \beta = \gamma = 90°$



TETRAGONAL

$a = b \neq c$

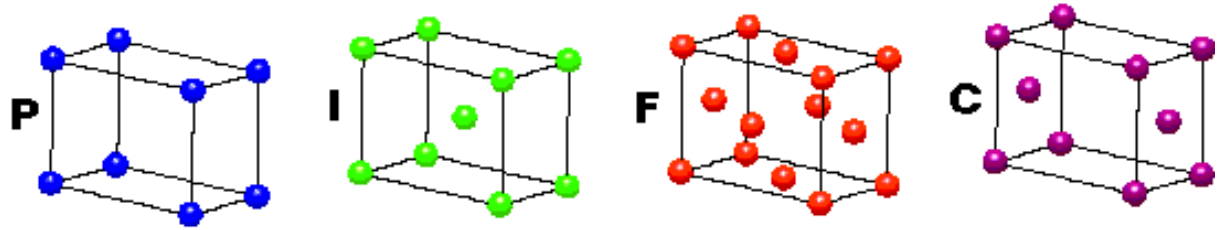
$\alpha = \beta = \gamma = 90°$



ORTHORHOMBIC

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

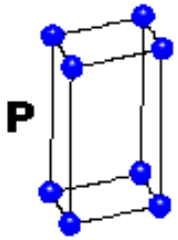


HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

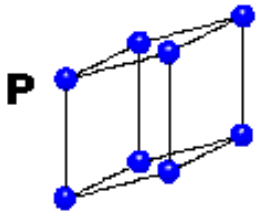
$\gamma = 120°$



TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

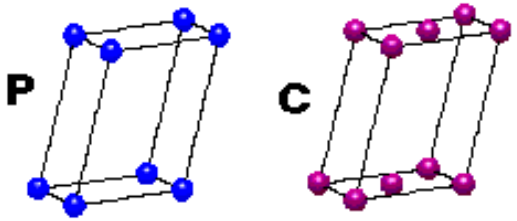


MONOCLINIC

$a \neq b \neq c$

$\alpha = \gamma = 90°$

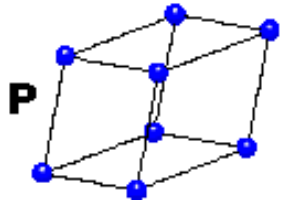
$\beta \neq 120°$



TRICLINIC

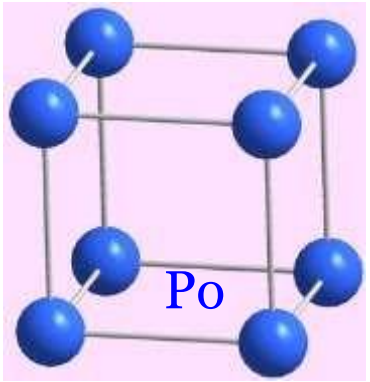
$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$

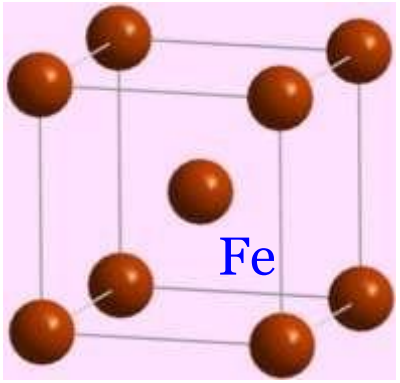


4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

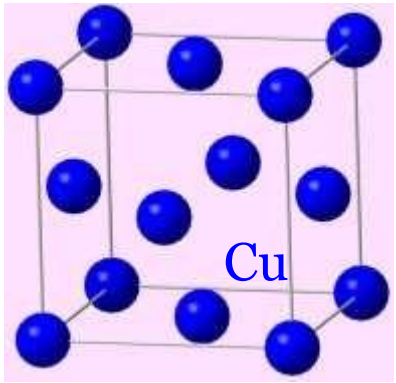
Examples of elements with Cubic Crystal Structure



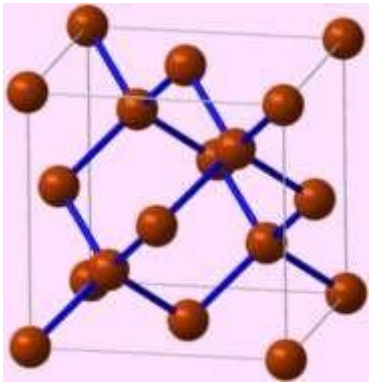
n = 1 SC



n = 2 BCC



n = 4 FCC/CCP



n = 8 DC

C (diamond)

Properties of unit cell

1. Coordination Number
2. No of Atoms Per Unit Cell
3. Lattice Constant
   Atomic Radius
   Atomic Packing Fraction

No of Atoms Per Unit Cell

Effective no of atoms per unit cell

Coordination Number

- Coordination Number (CN) : The Bravais lattice points closest to a given point are the nearest neighbours.

- Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number. It is a property of the lattice.

- A simple cubic has coordination number 6;
- A body-centered cubic lattice, 8;
- A face-centered cubic lattice, 12.

Atomic Packing Factor

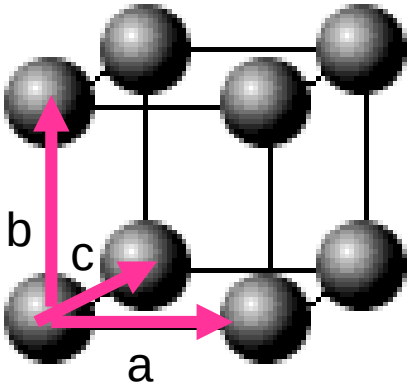
- Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

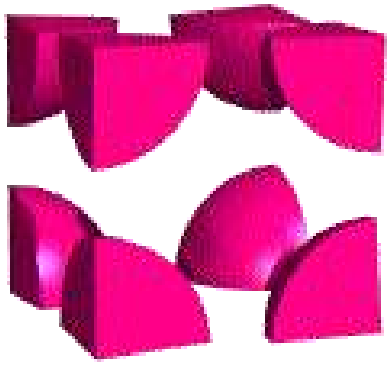
$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

1-CUBIC CRYSTAL SYSTEM

a- Simple Cubic (SC)

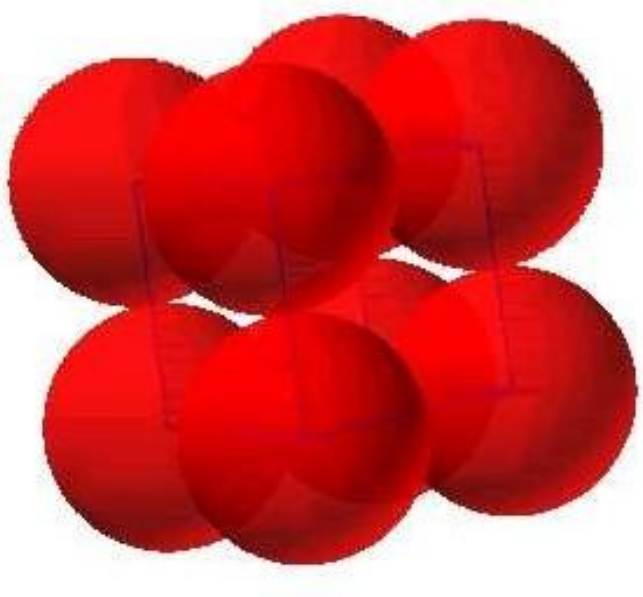
- Simple Cubic has one lattice point so its primitive cell.
- In the unit cell on the left, the atoms at the corners are cut because only a portion (in this case 1/8) belongs to that cell. The rest of the atom belongs to neighboring cells.
- Coordinatination number of simple cubic is 6.



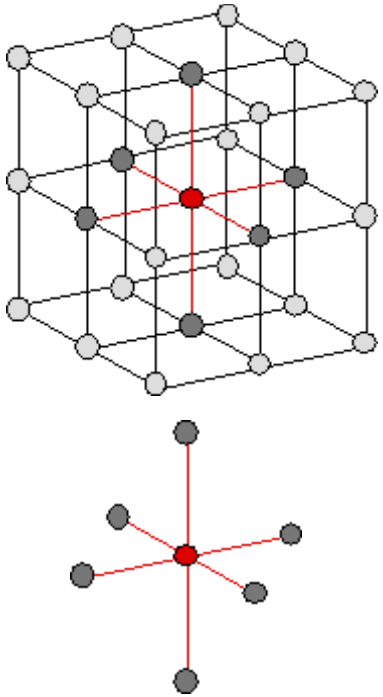


Simple Cubic Structure (SC)

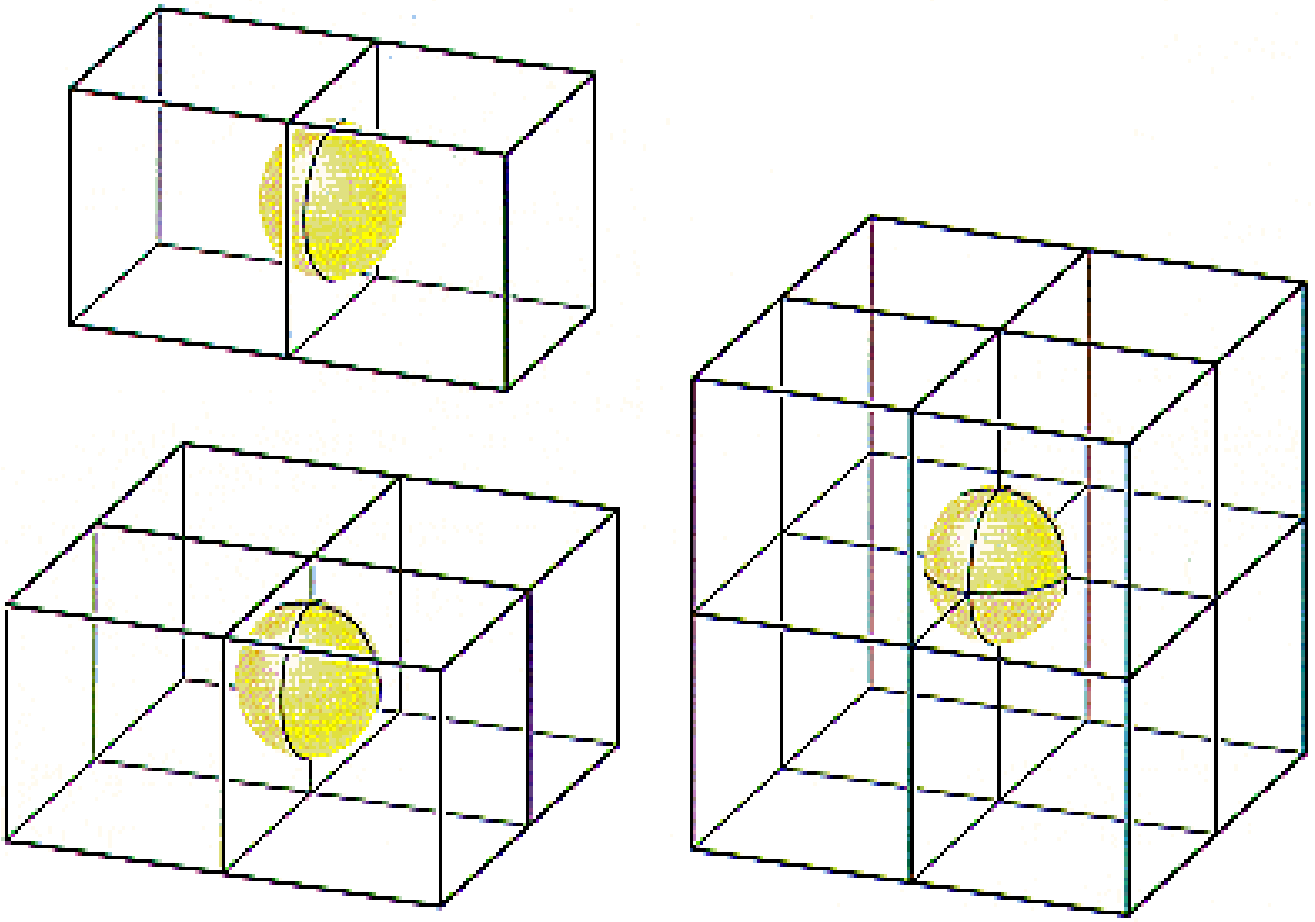
- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.



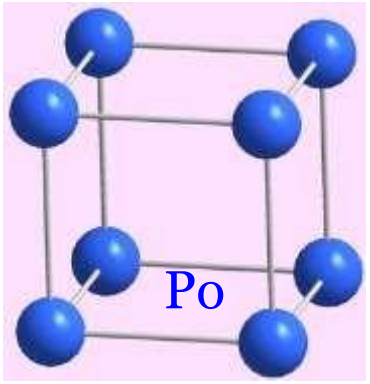
- Coordination # = 6
  (# nearest neighbors)



SHARING OF CORNER ATOM WITH EIGHT NEIGHBOURING UNIT CELLS

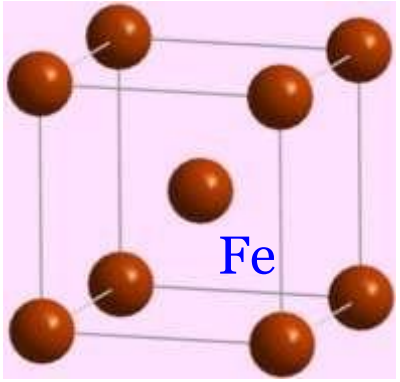


NUMBER OF ATOM PER UNIT CELL



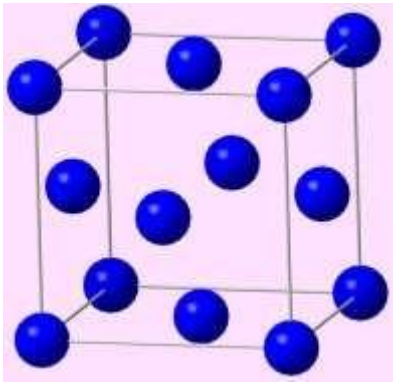
n = 1 SC

8*1/8=1



n = 2 BCC

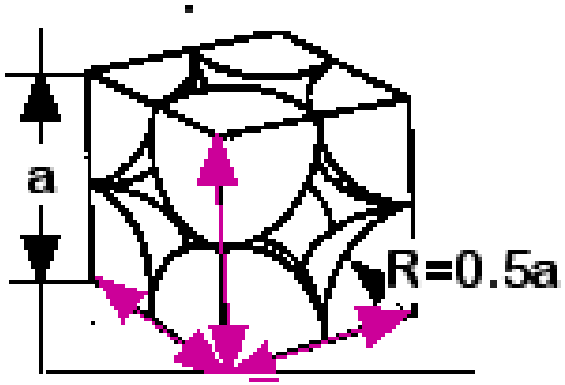
8*1/8+1=2



n = 4 FCC

8*1/8+6*1/2=4

Atomic Packing Factor of SC



contains 8 x 1/8 =
1atom/unit cell

APF = 0.52 for simple cubic

$$APF = \frac{\frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

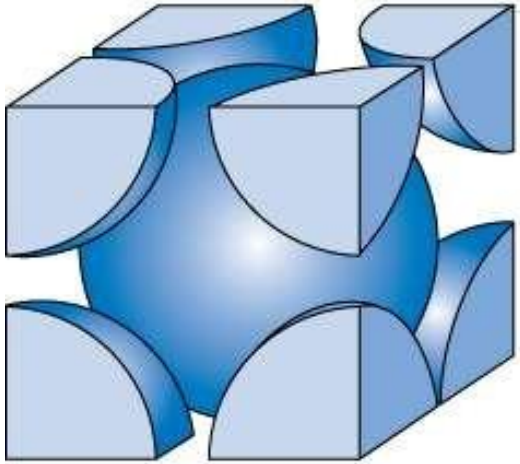
Body Centered Cubic Structure (BCC)

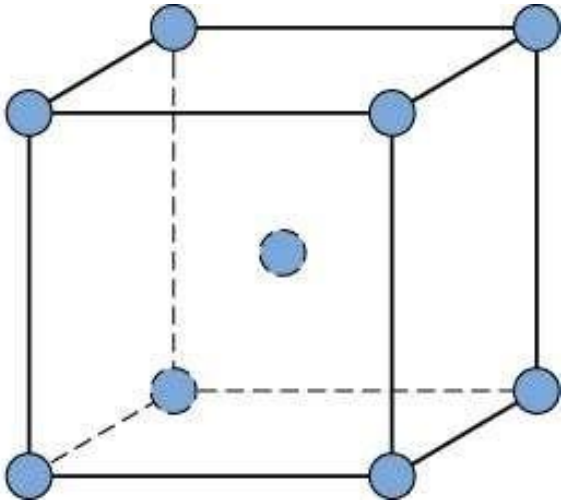
- Atoms touch each other along cube diagonals.

  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

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

- Coordination # = 8

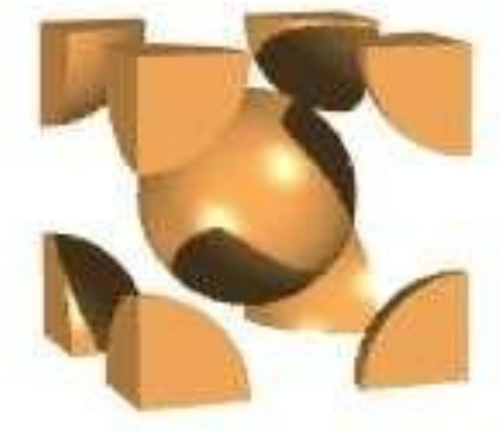


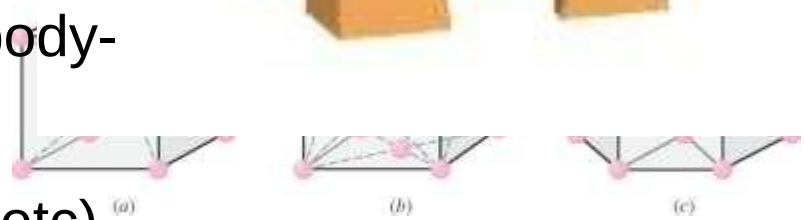


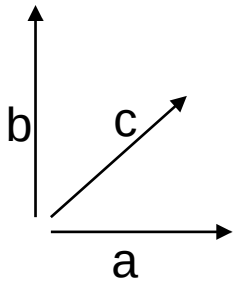
2 atoms/unit cell: 1 center + 8 corners x 1/8

B-Body Centered Cubic (BCC)

- BCC has two lattice points so BCC is a non-primitive cell.
- BCC has eight nearest neighbors. Each atom is in contact with its neighbors only along the body-diagonal directions.
- Many metals (Fe,Li,Na..etc), including the alkalis and several transition elements choose the BCC structure.

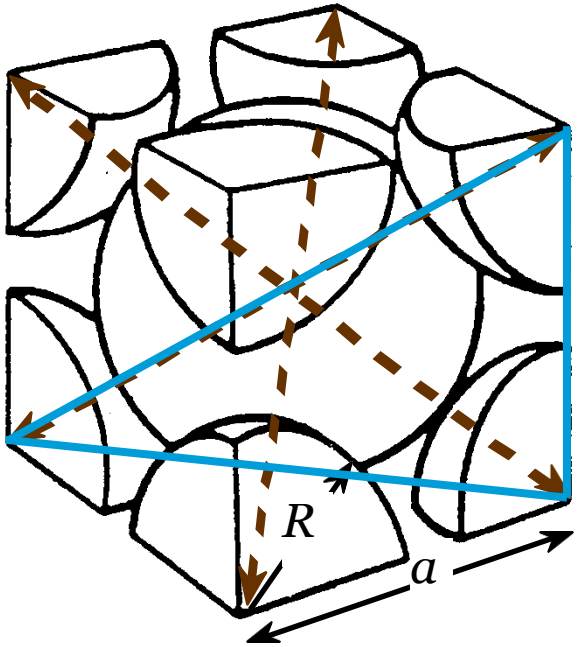


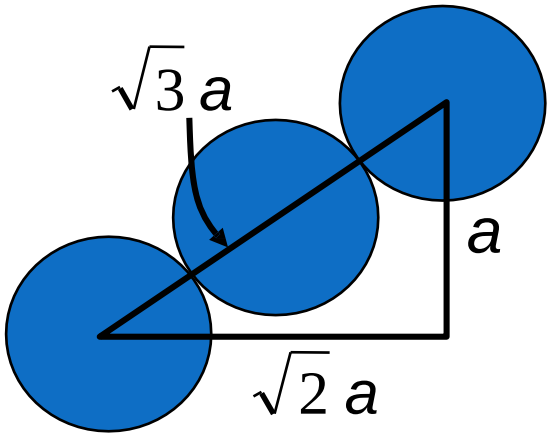




Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68





Close-packed directions:

length = $4R = \sqrt{3}\,a$

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

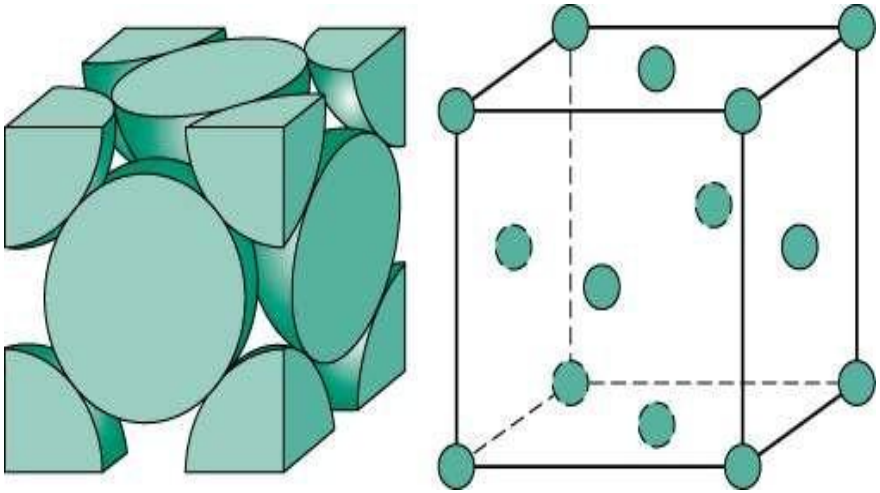
FACE CENTERED CUBIC STRUCTURE (FCC)

- Atoms touch each other along face diagonals.

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

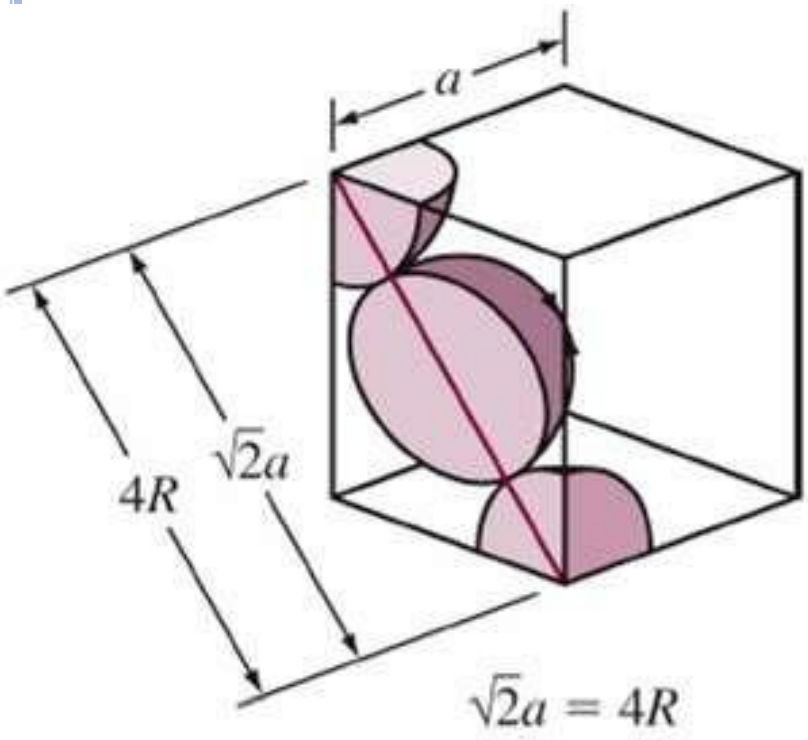
ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12



4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

Atomic Packing Factor of FCC



$$APF_{FCC} = \frac{V_{atoms}}{V_{unit\ cell}} = 0{,}74$$

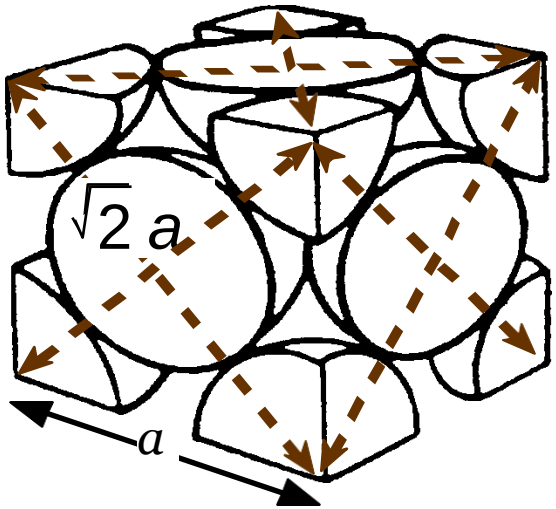
$$APF = \frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \cdot \frac{\text{volume}}{\text{unit cell}}$$

$$APF = \frac{4 \cdot \frac{4}{3}\pi(0{,}353a)^3}{a^3}$$

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74

maximum achievable APF



Close-packed directions:

length = $4R = \sqrt{2}\,a$

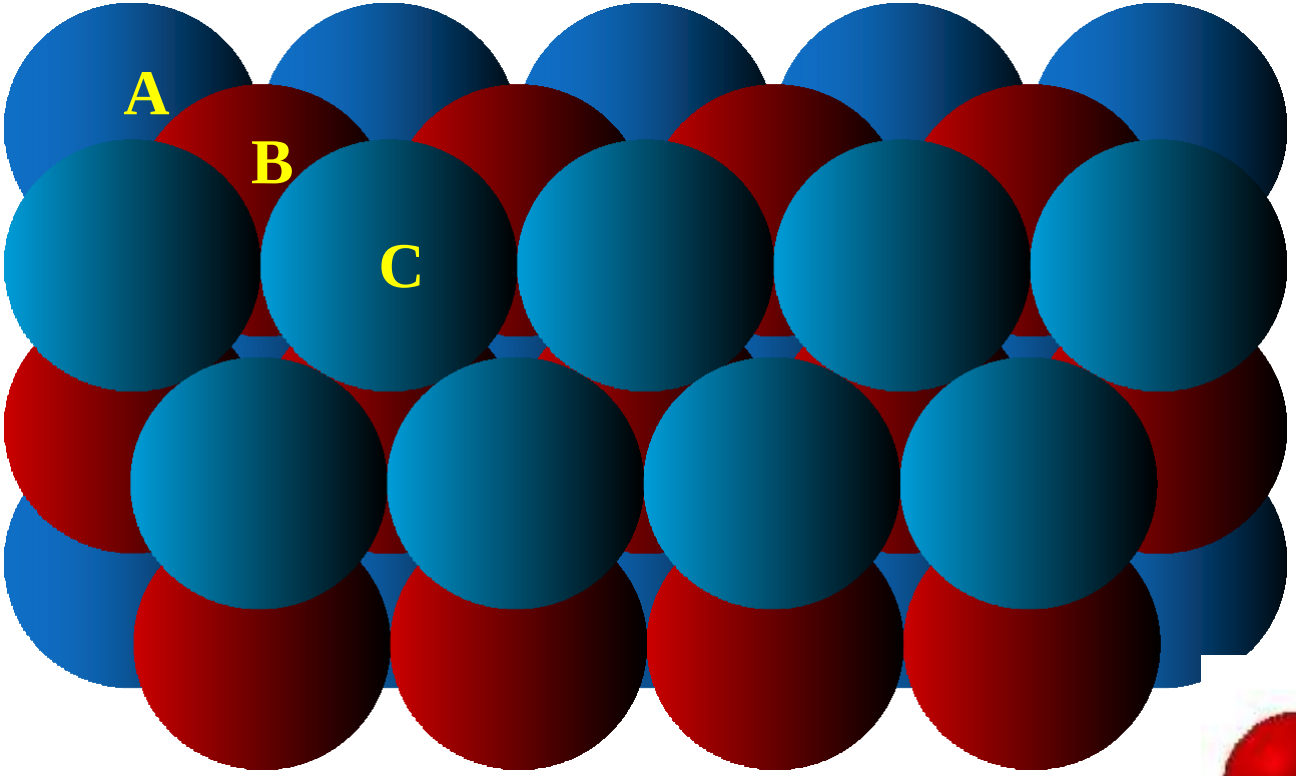
Unit cell contains:

6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

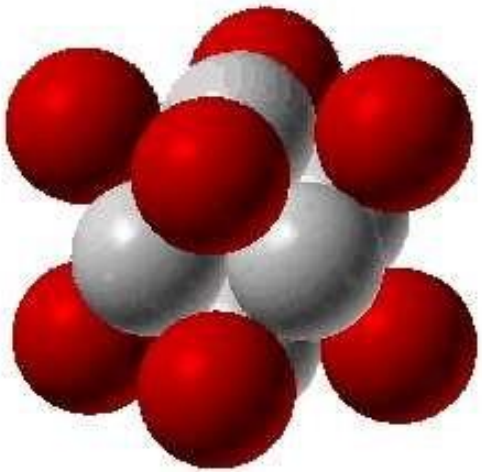
$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \leftarrow 4 \quad \dfrac{4}{3}\pi\left(\sqrt{2}\,a/4\right)^3 \leftarrow \dfrac{\text{volume}}{\text{atom}}}{a^3 \leftarrow \dfrac{\text{volume}}{\text{unit cell}}}$$

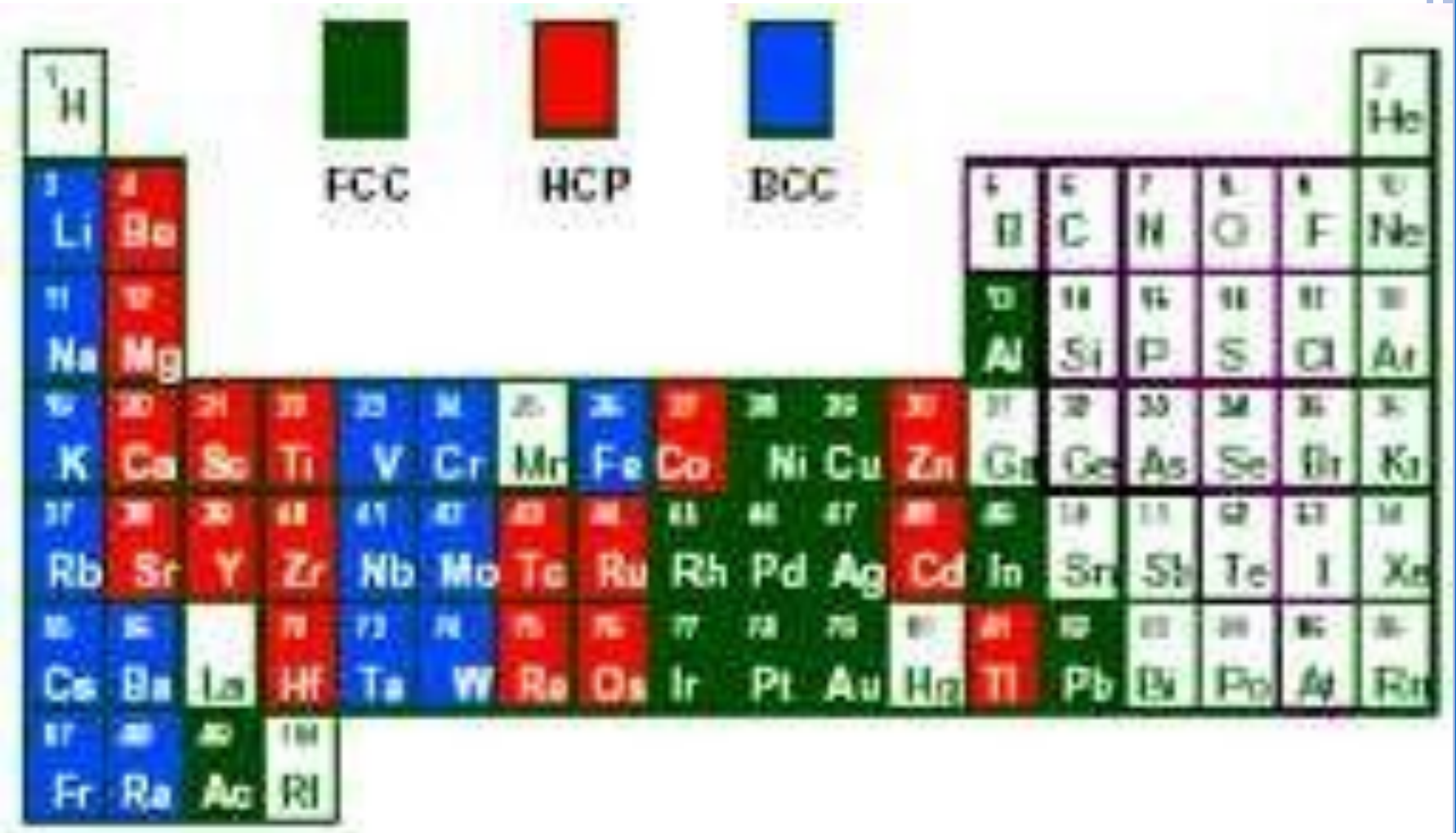
FCC Stacking



Highlighting the stacking

Highlighting the faces



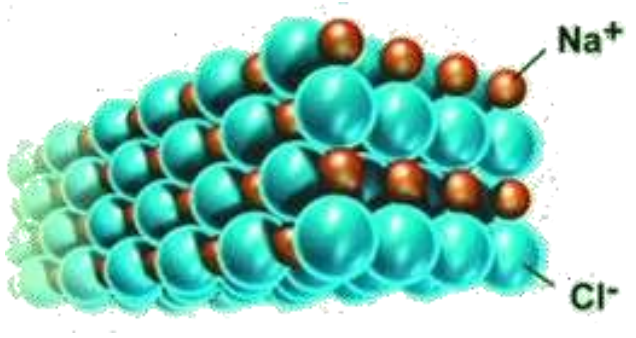

FCC
HCP
BCC
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
Ac
Rf

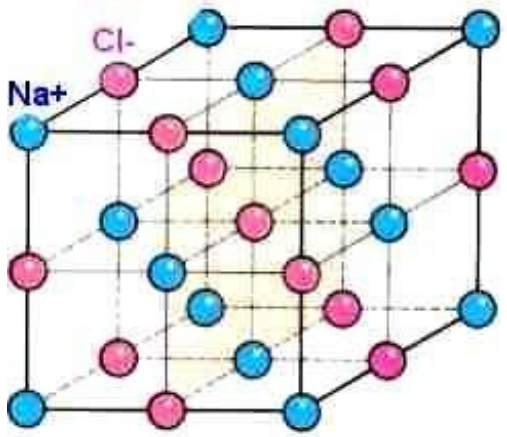
THE MOST IMPORTANT CRYSTAL STRUCTURES

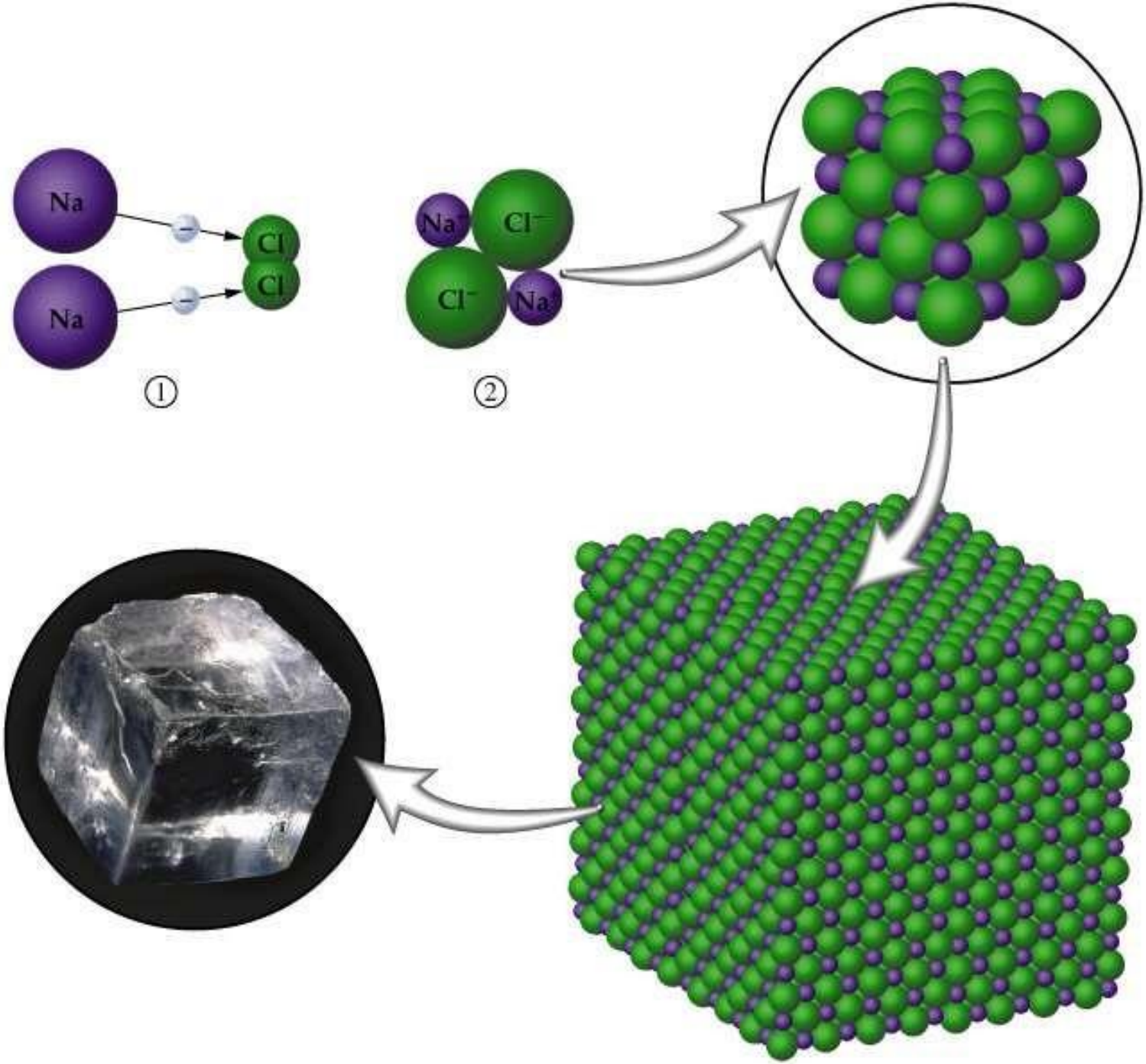
- Sodium Chloride Structure $Na^{+}Cl^{-}$
- Cesium Chloride Structure $Cs^{+}Cl^{-}$
- Hexagonal Closed-Packed Structure
- Diamond Structure
- Zinc Blende

1 – Sodium Chloride Structure

- **Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.**
- **Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice.**
- **Each ion has six of the other kind of ions as its nearest neighbours.**



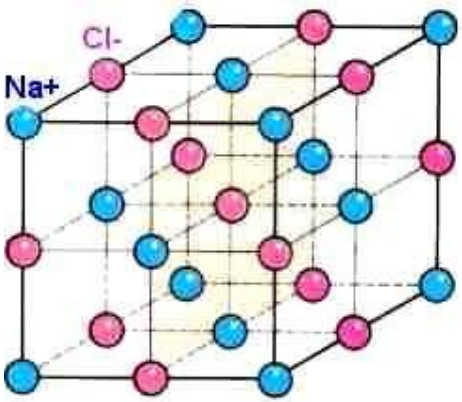



Na
Cl
Cl
Na
①
Na+
Cl−
Cl−
Na+
②

Sodium Chloride Structure

- **If we take the NaCl unit cell and remove all the red Cl ions, we are left with only the blue Na. If we compare this with the fcc / ccp unit cell, it is clear that they are identical. Thus, the Na is in a fcc sublattice.**

Sodium Chloride Structure



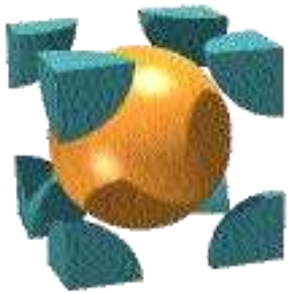
- This structure can be considered as a face-centered-cubic Bravais lattice with a basis consisting of a sodium ion at 0 and a chlorine ion at the center of the conventional cell,

$$a\ /\ 2\ (\ \vec{x} + \vec{y} + \vec{z}\ )$$

- LiF,NaBr,KCl,LiI,etc
- The lattice constants are in the order of 4-7 angstroms.

2-Cesium Chloride Structure Cs^+Cl^-

- **Cesium chloride crystallizes in a cubic lattice. The unit cell may be depicted as shown. (Cs+ is teal, Cl- is gold).**



- ***Cesium chloride consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion has eight of the other kind as its nearest neighbors.***