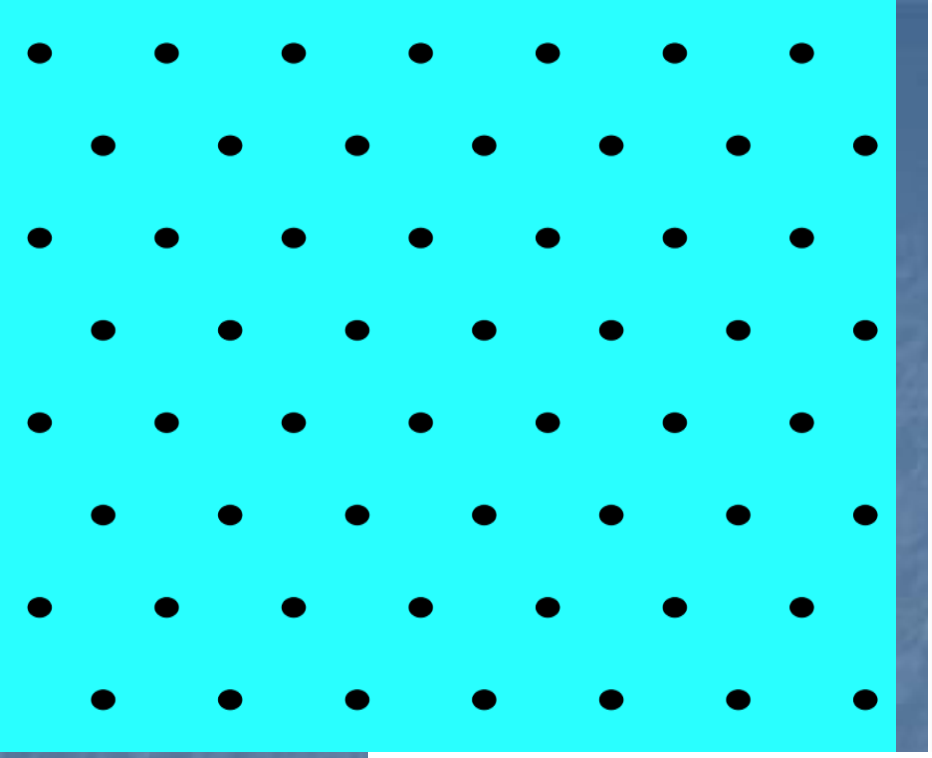
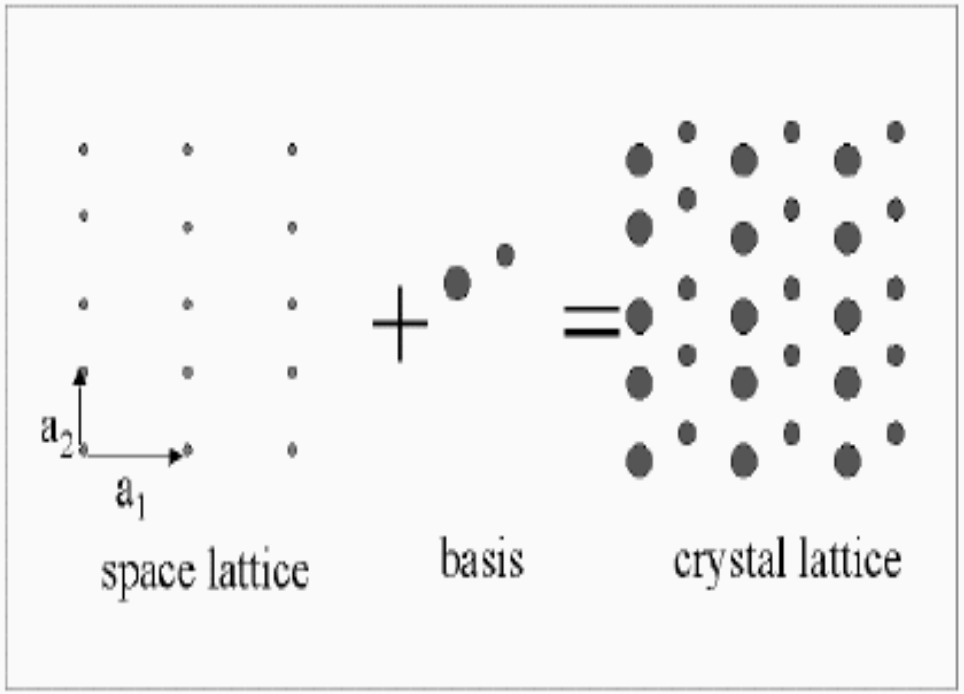
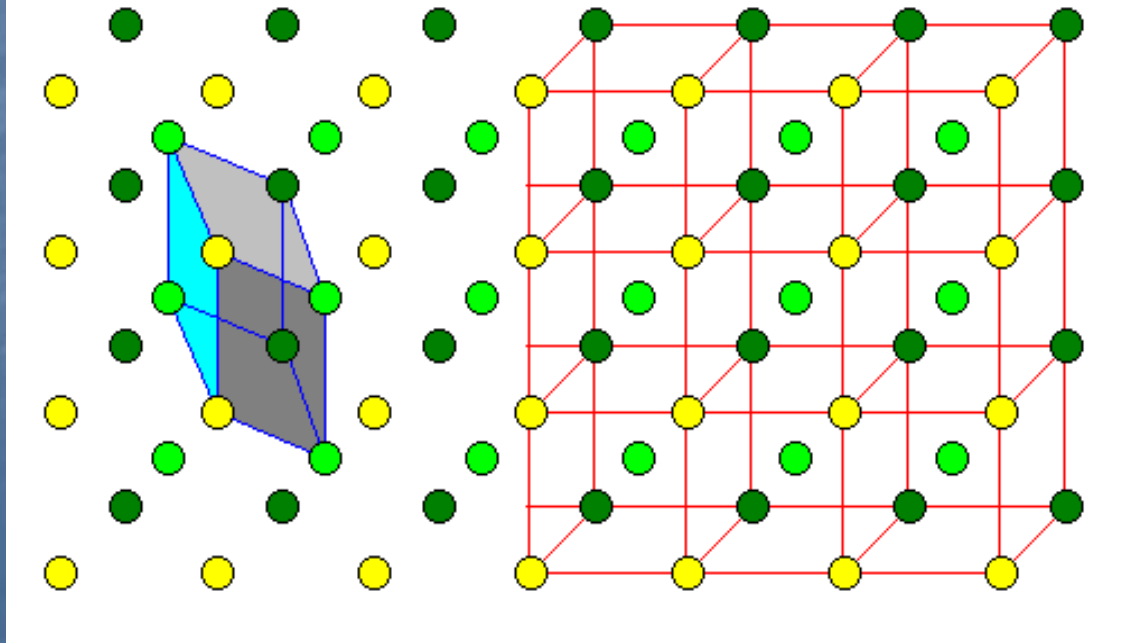
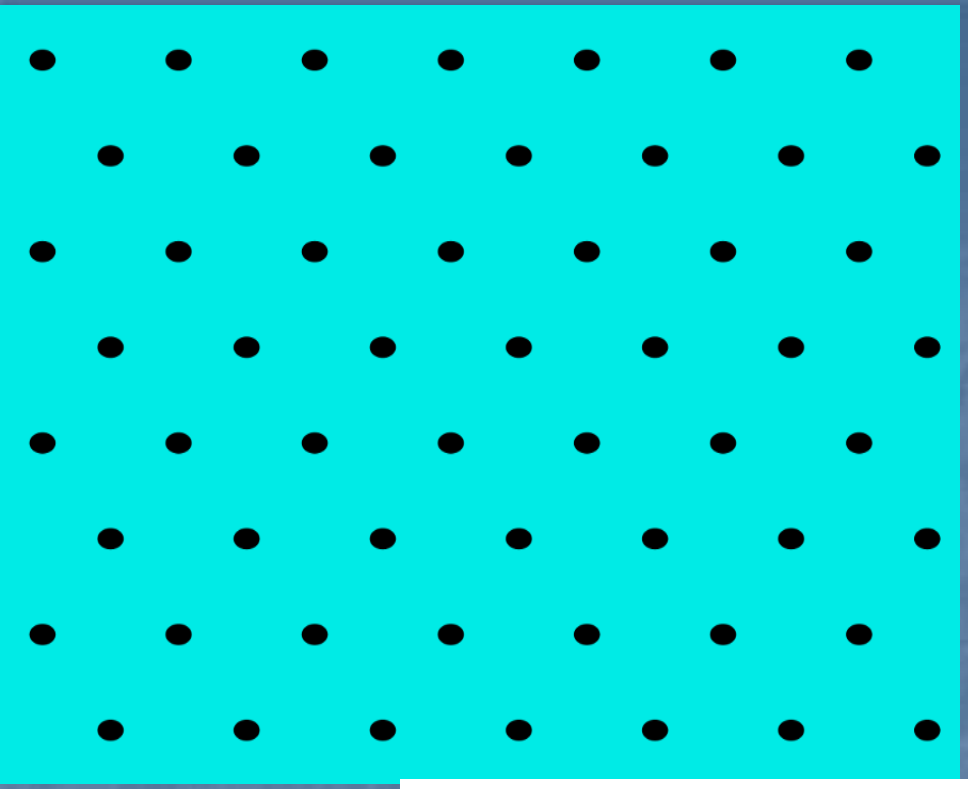
CRYSTALLOGRAPHY

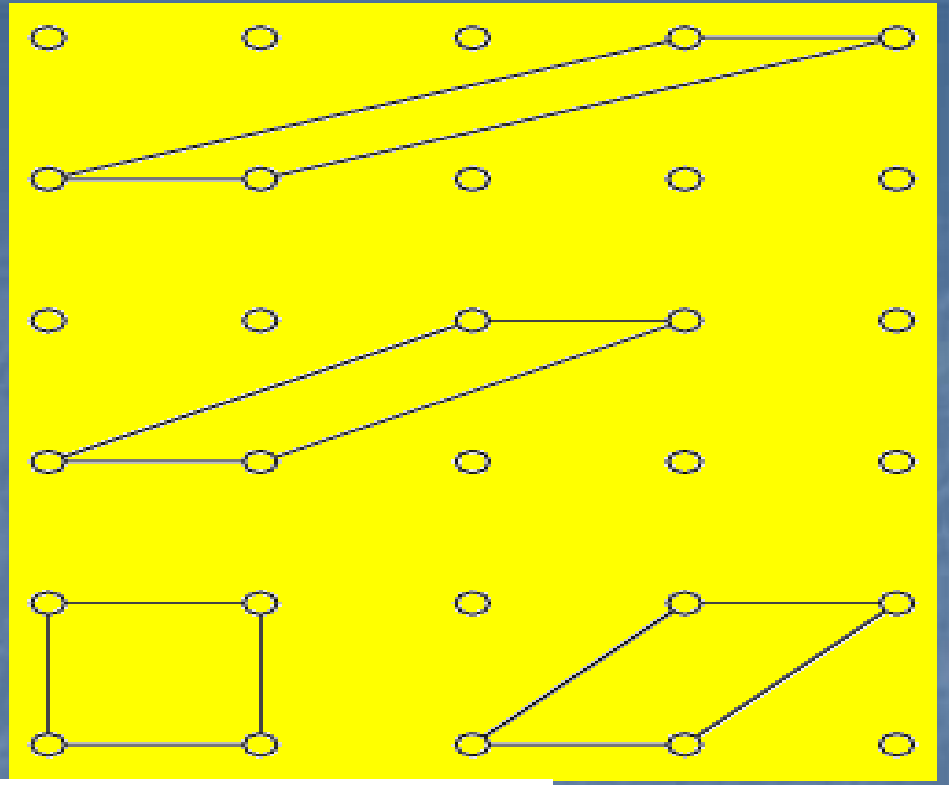
Dr.S.R. Jigajeni

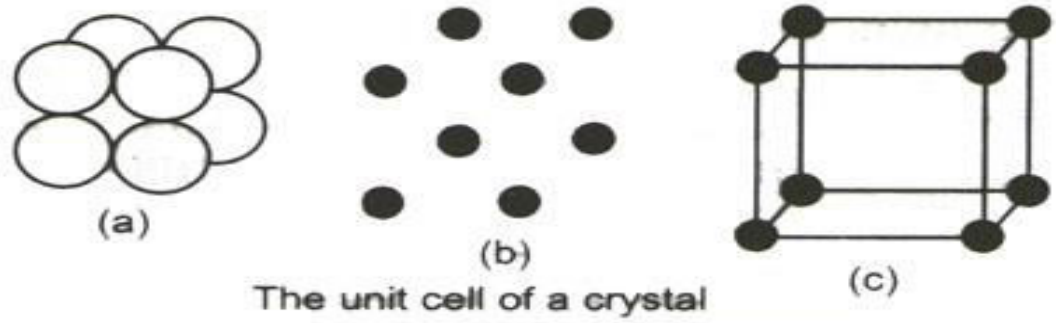



a2
a1
space lattice
basis
crystal lattice

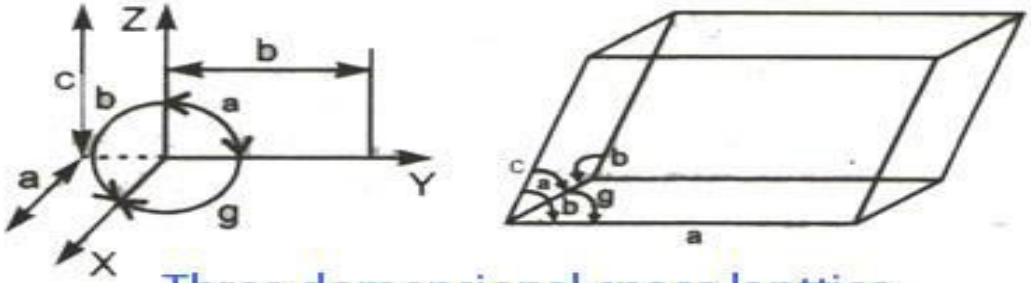








The unit cell of a crystal

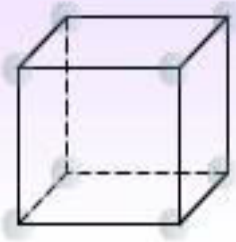


Three domensional space lanttice

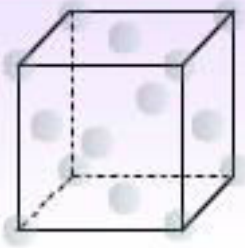
Unit Cells Types

A unit cell is the smallest component of the crystal that reproduces the whole crystal when stacked together with purely translational repetition.

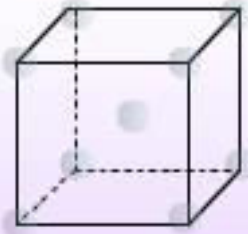
- Primitive (P) unit cells contain only a *single lattice point*.
- Internal (I) unit cell contains an atom in the *body center*.
- Face (F) unit cell contains atoms in the *all faces of the planes* composing the cell.
- Centered (C) unit cell contains atoms *centered on the sides* of the unit cell.



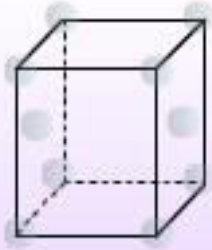
Primitive



Face-Centered

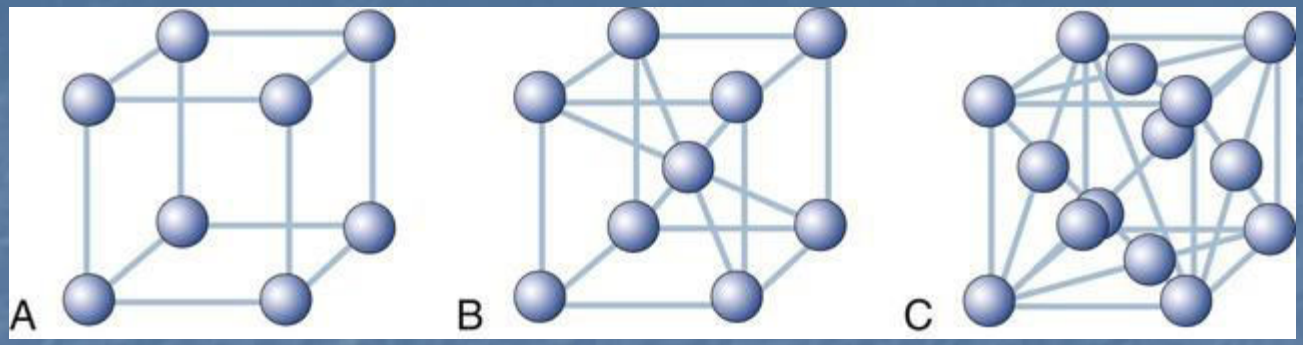


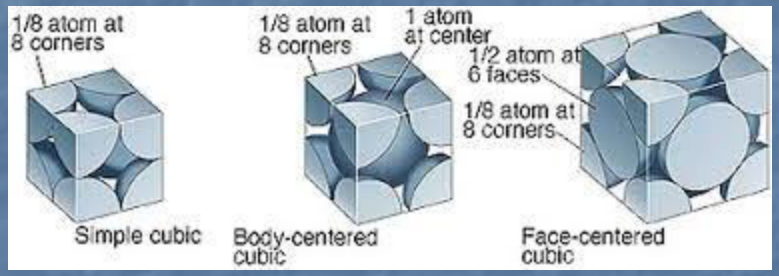
Body-Centered



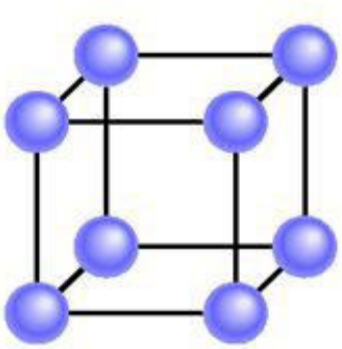
End-Centered

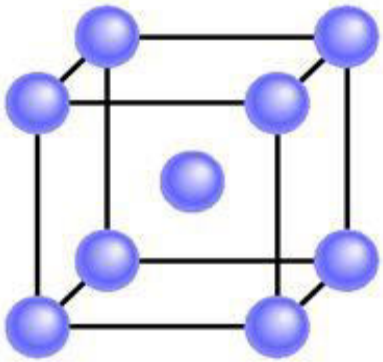
KNOW THIS!

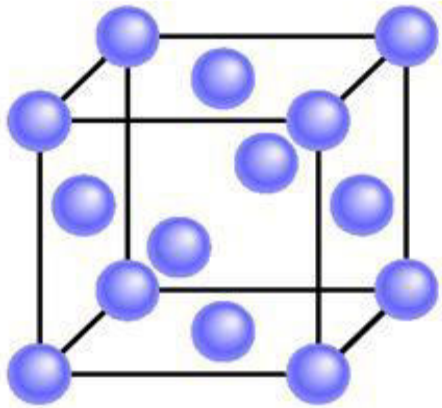

A
B
C

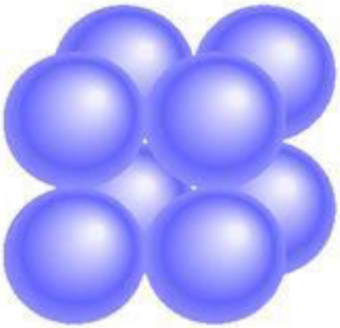

1/8 atom at 8 corners
Simple cubic
1/8 atom at 8 corners
1 atom at center
Body-centered cubic
1/2 atom at 6 faces
1/8 atom at 8 corners
Face-centered cubic

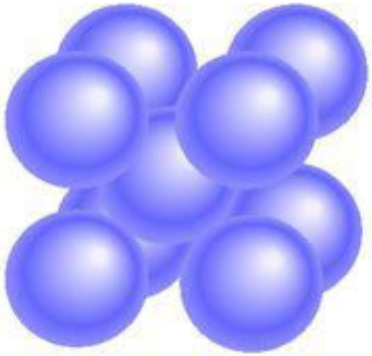
Number of Atoms Per Unit Cell

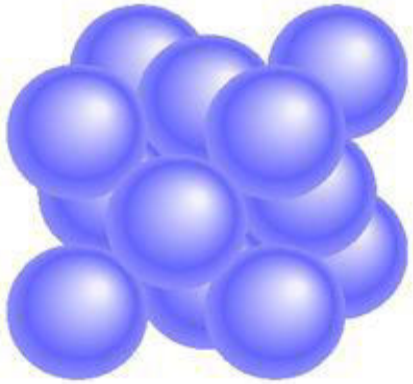












Simple cubic

1 atom/unit cell

(8 x 1/8 = 1)

Body-centered cubic

2 atoms/unit cell

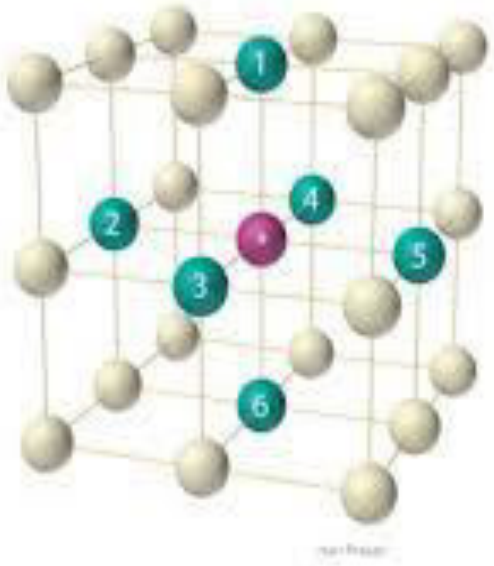
(8 x 1/8 + 1 = 2)

Face-centered cubic

4 atoms/unit cell

(8 x 1/8 + 6 x 1/2 = 4

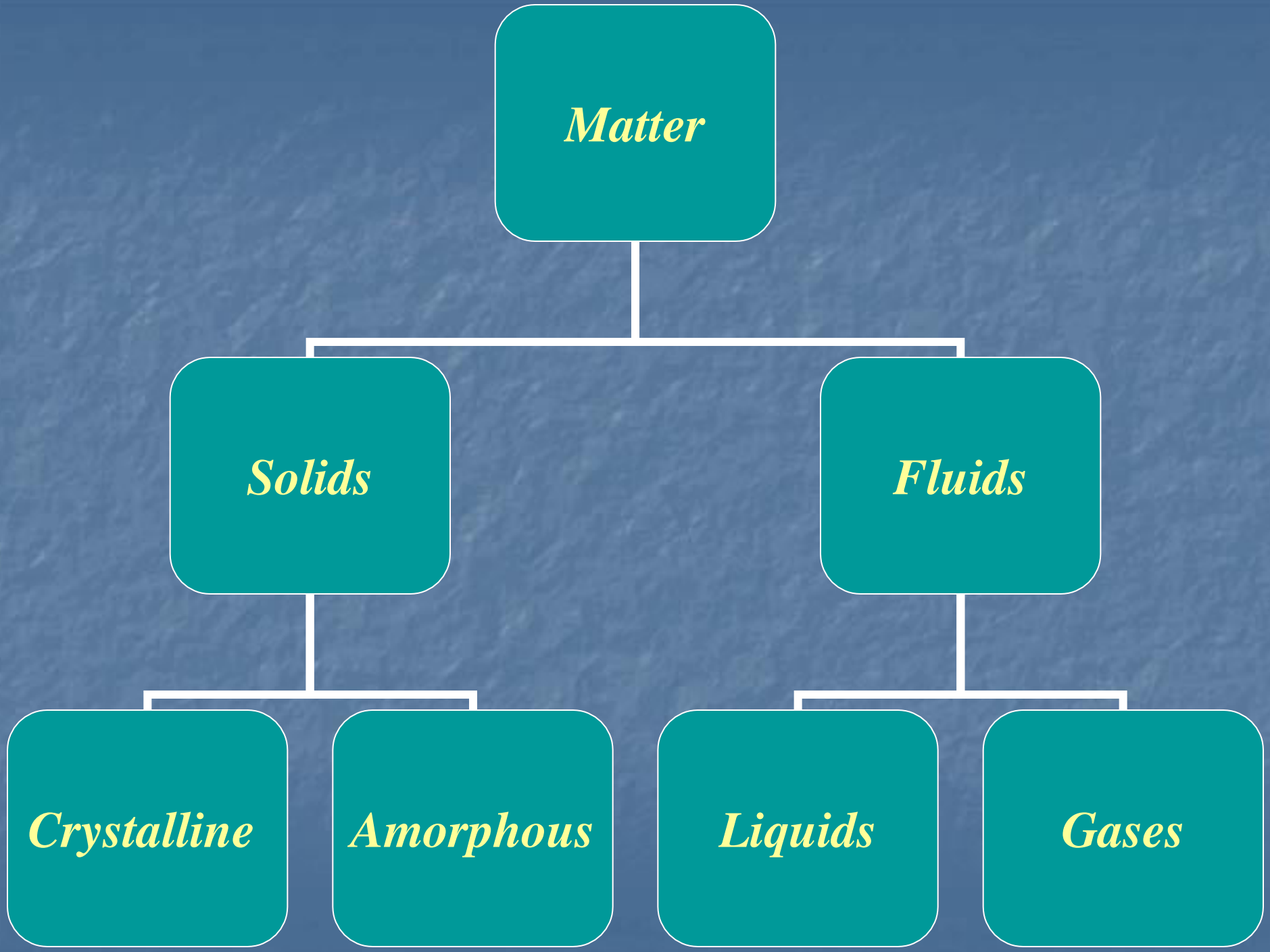
SC-coordination number



6

Crystallography

The study of geometric form and other physical properties of crystalline solids by using X-rays, electron beams and neutron beams constitutes the science of crystallography.


Matter
Solids
Fluids
Crystalline
Amorphous
Liquids
Gases

Crystal Structure and Periodicity

Crystalline Materials

Atoms are in an ordered 3-D periodic array

Single crystal or polycrystalline solids

(metals, ceramics, semiconductors, some polymers)

Amorphous Materials

short range order

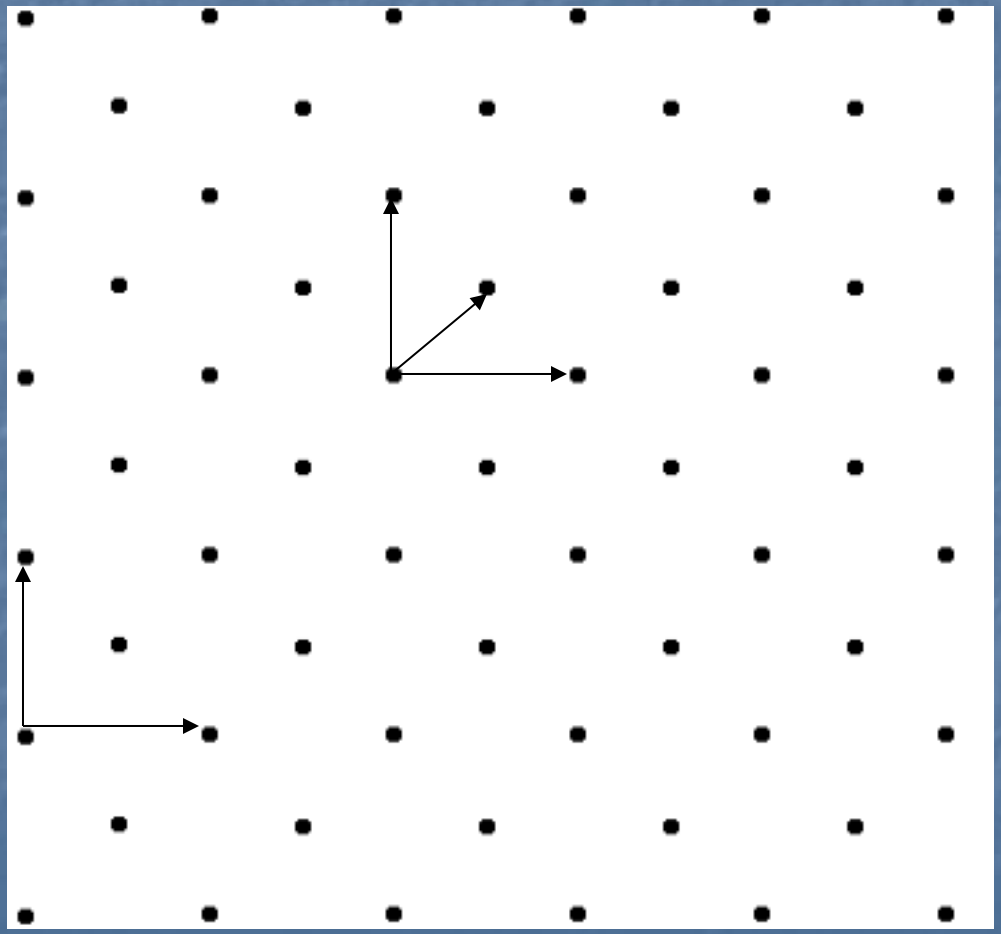
(glasses, many polymers)

Intermediates

Lattice

- *A lattice is a set of points or grid lines that possess the translational periodicity of the crystal --imaginary construct*
- *The environment of each lattice point should be identical.*
- *The lattice defines the coordinate system for atoms or molecules in a crystal.*

Lattice of NaCl



The translational vectors in two dimension is given by

$$\vec{r}=n_1\vec{a}+n_2\vec{b}$$

The translational vectors in three dimension is given by

$$\vec{r}=n_1\vec{a}+n_2\vec{b}+n_3\vec{c}$$

The translational vectors $\vec{a}$, $\vec{b}$, $\vec{c}$, are called the basis vectors or the primitive vectors of the lattice or lattice parameters.

Crystal Lattice and unit cell

A crystal lattice is a space lattice in which the lattice sites are occupied by atoms or clusters of atoms.

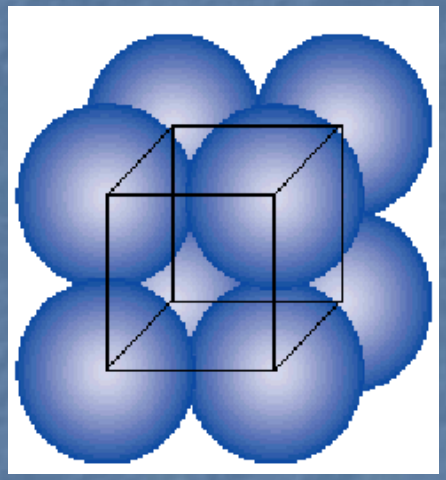
Each lattice point is associated with the same unit of groups of atoms, called 'Basis'.

Mathematically,

Space lattice + Basis = Crystal structure.

Unit Cell

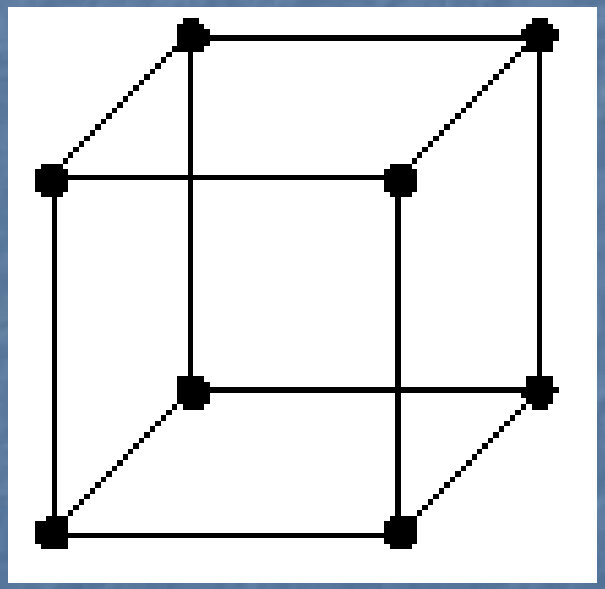
Unit Cell - *The smallest repeat unit which defines the crystal structure*

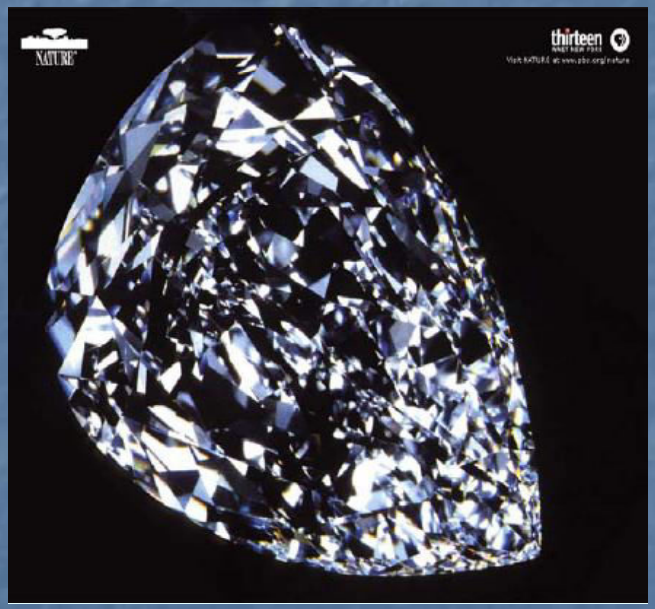


A three dimensional unit cell.

Some features of the crystal-

*1. **Faces**: A number of flat surfaces are present in crystal may be like or unlike.*





*2. **Forms**: The crystals may present in different forms 1. Simple form*

2. Combinational form

*3. **Edges and Interstitial angles:***

The intersection of two adjacent faces of the crystal forms the edges of the crystals.

The relation between plane faces, straight edges, and interfacial angle is given by,

$$f+c = e+2$$

Cubic Systems - Based on a Cubic unit Cell

Simple Cubic (SC)

One atom on each corner

Coordination number of 6

Body-centered Cubic (BCC)

One atom on each corner and one in the center

Coordination number of 8

Face-centered Cubic (FCC)

One atom on each corner and on each face

Coordination number of 12

$a=b=c$, $\alpha=\beta=\gamma=90°$

Simple Cubic (SC)

SC lattice and crystal structure

Lattice

↓

Hang 1 atom on each lattice point

↓

Crystal Structure

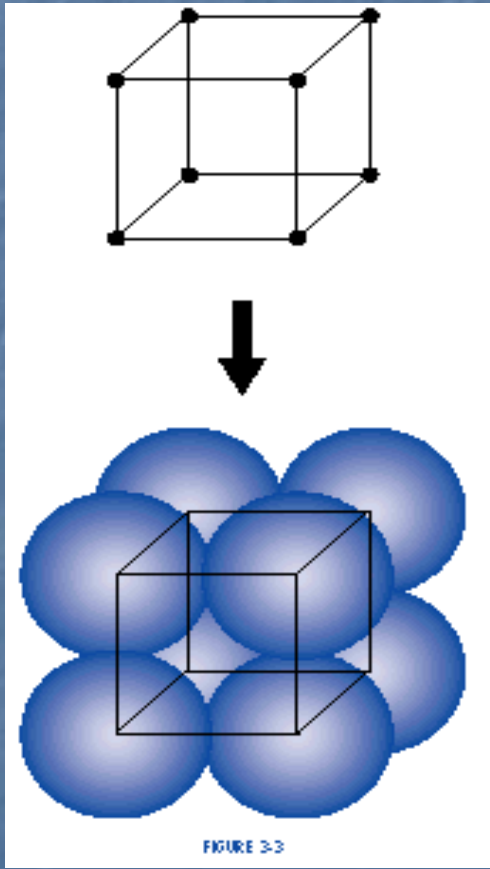


FIGURE 3-3

a = 2R

Where:

R = atomic radius

a = lattice parameter

Body Centered Cubic (BCC)

- *BCC lattice and crystal structure*

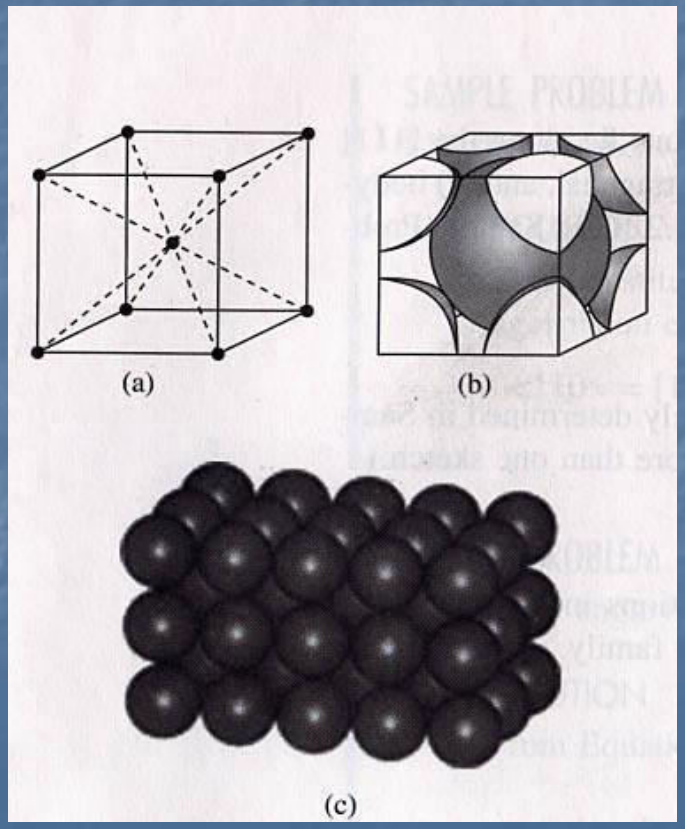
One atom is at each corner and one is at the center of cube.

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

where:

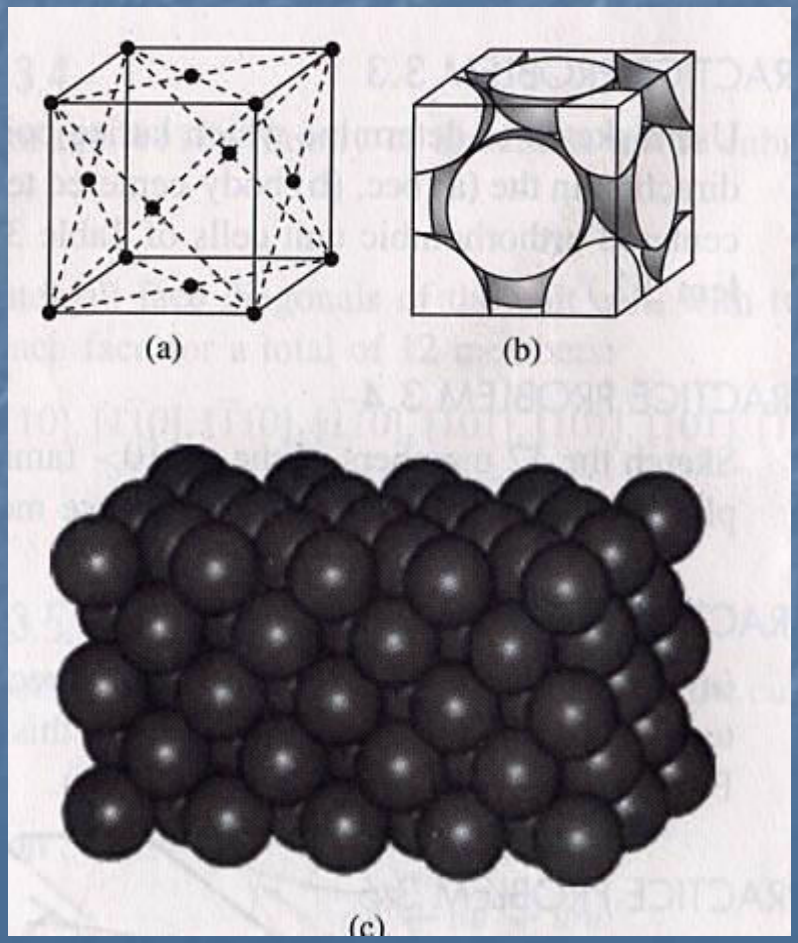
R = atomic radius

a = lattice parameter



Face Centered Cubic (FCC)

One atom is at every corner and one atom is at the center of each face of the cube.



$a = 4R/\sqrt{2}$

where:

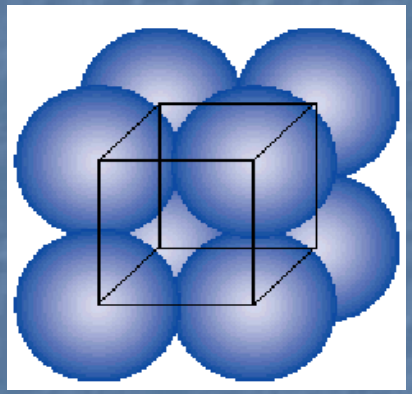
R = atomic radius atom

a = lattice parameter

No. of atoms per unit cell

Simple Cubic: There are 8 corner atoms and each corner atom is shared by 8 surrounding cubes so share of each atom is

8 X 1/8 = 1atom



Body centered cube: It has eight corner atoms at the corner and one center atom.

No. of atoms are

1 X 1/8 + 8 X 1\8 = 1+1= 2

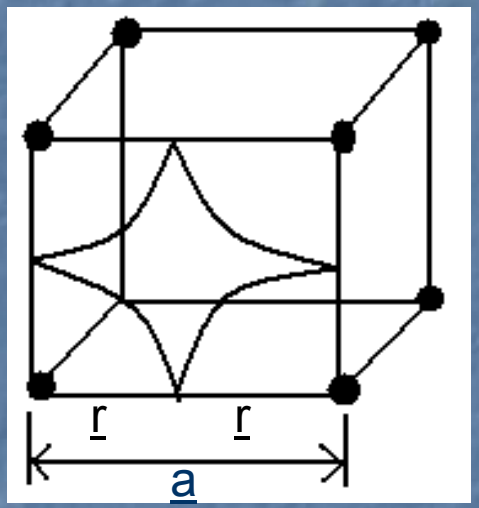
Face centered cube: *It has 8 atoms at corner and 6 face centered atoms. Each face centered atom is shared by 2 cubes and corner atom by 8, so total no. of atoms per unit cell is:*

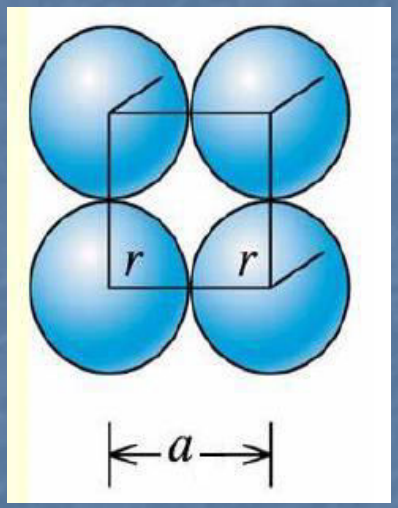
6 X 1/2=3 and 8 X 1/8=1

3+1=4

Atomic Radius: *It is defined as half the distance between nearest neighbors in a crystal, of a pure element. It is expressed in cube edges a.*

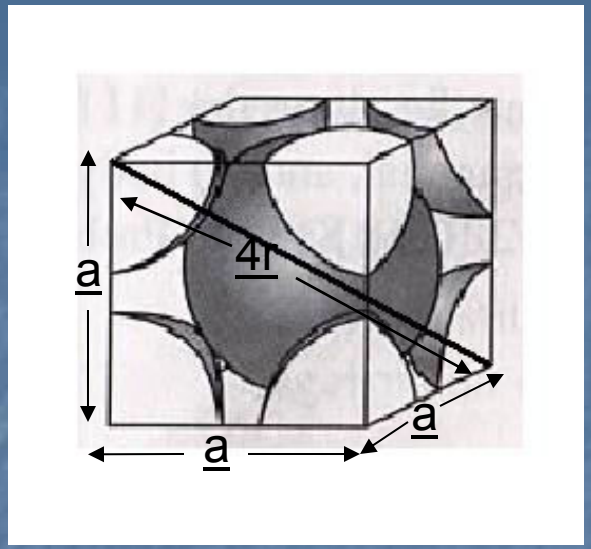
For SC structure: $r = a/2$

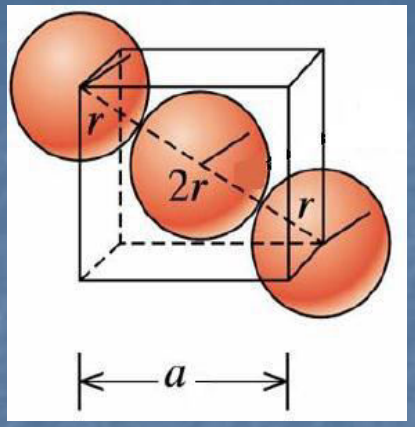




For BCC structure:

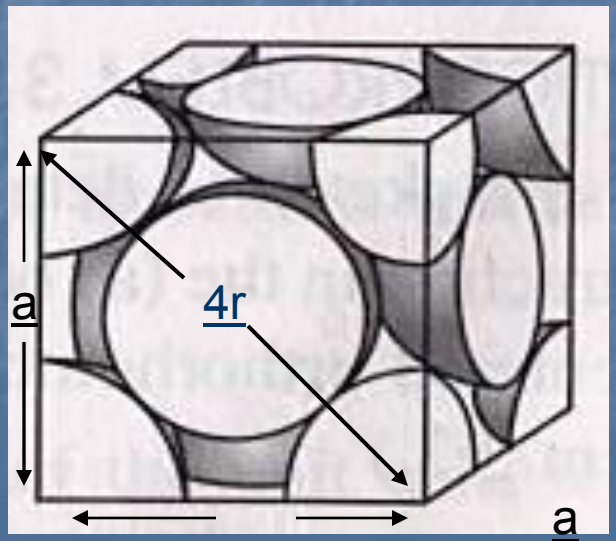
$$r = \frac{\sqrt{3}a}{4}$$

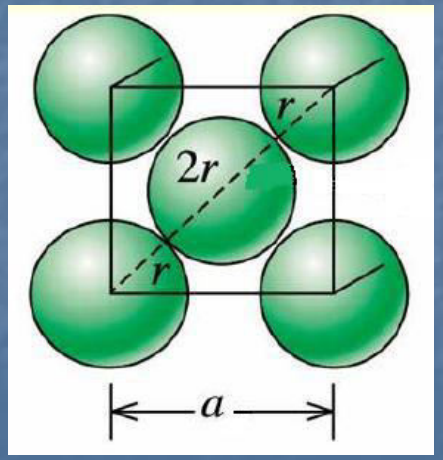




For FCC structure:

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





Atomic Packing Factor OR Packing Density:

Atomic packing factor is the ratio of volume occupied by the atoms in an unit cell (v) to the total volume of the unit cell (V).

Packing factor $= v / V$

$$APF = \frac{\text{volume of atoms per unit cell}}{\text{Volume of the unit cell}}$$

For SC:

Atoms per unit cell = 1

Volume of one atom = 4\3ΠR³

Here, R = a/2

Volume of atom = 4/3 Π(a/2)³ = Πa³ / 6

Volume of cube = V = a³

Atomic packing fraction = v / V

$$= \frac{\Pi a^3/6}{a^3}$$

$$= \Pi/6$$

$$= 0.52$$

For BCC:

Atoms per unit cube $= 2$

Volume of two atoms $= 2 \times 4\backslash 3\Pi R^3$

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

Volume of atom = v $= 2 \times 4/3\Pi (\sqrt{3}a/4)^3$

$= \sqrt{3}/8\ \Pi\ a^3$

Volume of cube = V $= a^3$

Atomic packing fraction $= v / V$

$$= \frac{\sqrt{3}/8\ \Pi\ a^3}{a^3}$$

$= \sqrt{3}/8\ \Pi$

$= 0.68$

For FCC:

Atoms per unit cube $= 4$

Volume of four atoms $= 4 \times 4\backslash 3\Pi R^3$

Here $R = \sqrt{2}a/4$

Volume of atom = v $= 4 \times 4/3\Pi (\sqrt{2}a/4)^3$

$= \sqrt{2}/6\ \Pi\ a^3$

Volume of cube = V $= a^3$

Atomic packing fraction $= v / V$

$$= \frac{\sqrt{2}/6\ \Pi\ a^3}{a^3}$$

$= \sqrt{2}/6\ \Pi$

$= 0.74$

Co-ordination Number:

It is the number of nearest neighbors which an atom has in the unit cell of any crystal structure.

For SC: 6 For BCC: 8 For FCC: 12

Void Space:

The void space in the unit cell is the vacant space left utilized in the cell.

It is expressed as percentage also known as interstitial space.

Void space = (1-APF) X 100

For SC: 48% For BCC: 32% For FCC: 26%

Density:

It is defined as mass per unit volume of the crystal.

$$\rho = \frac{ZM}{N_A V}$$

For SC: $\rho = \frac{M}{N_A a^3}$

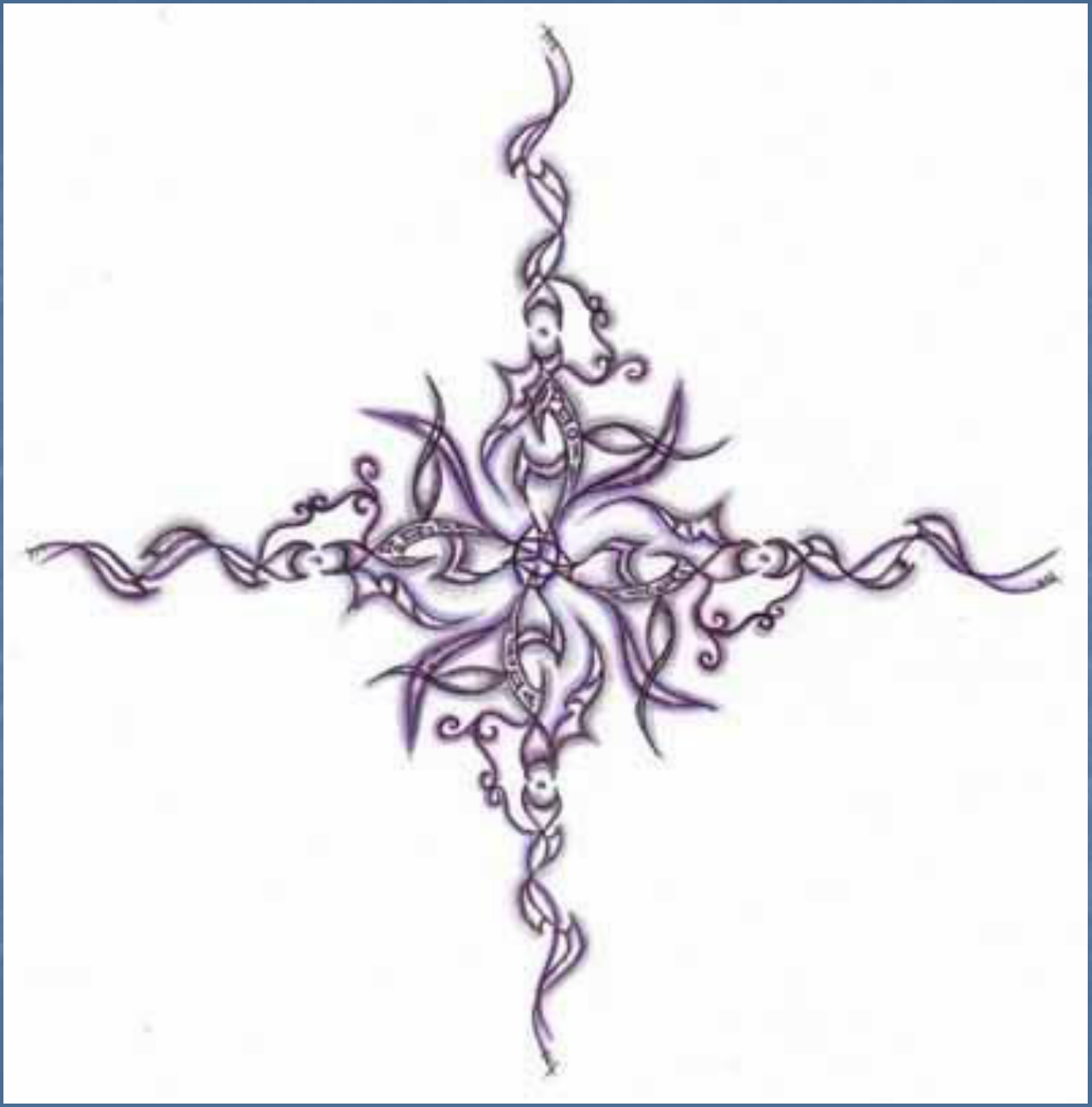
For BCC: $\rho = \frac{2M}{N_A a^3}$

For FCC: $\rho = \frac{4M}{N_A a^3}$

SYMMETRY


COMMON BROWN


Phili



A Symmetry operation is an operation that can be performed either physically or imaginatively that results in no change in the appearance of an object.

It is emphasized that in crystals, the symmetry is internal, that is it is an ordered geometrical arrangement of atoms and molecules on the crystal lattice.

There are 3 types of symmetry operations:

Rotation, Reflection, and Inversion.

Crystal Symmetry

The main symmetry elements of crystalline solid are:

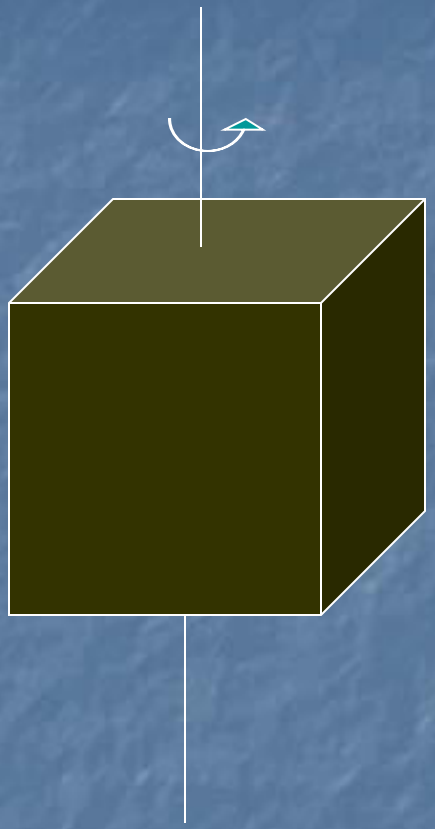
1. ***Axis** of symmetry*
2. ***Plane** of symmetry*
3. ***Centre** of symmetry*

Axis of symmetry

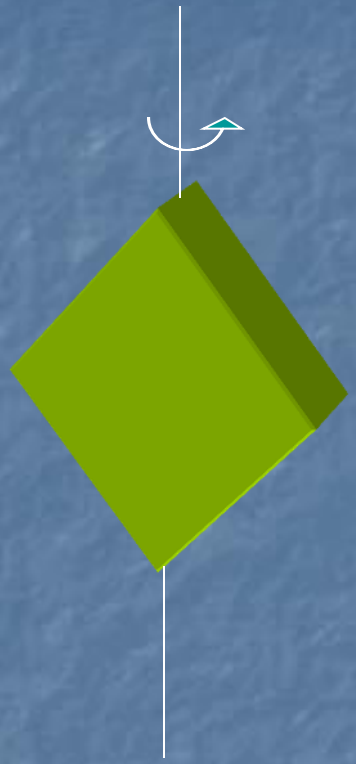
An axis of symmetry is defined as a line about which the crystal may be rotated such that after a definite angular rotation about this axis the crystal comes in congruent position.

The axis of symmetry is given by angle 2Π/n radians or 360/n degrees and is called as n-fold symmetry.

Order of 'n'	*Angle for congruent position*	*Axis called as*
1	*360*	*Identity*
2	*180*	*Diad*
3	*120*	*Triad*
4	*90*	*Tetrad*
6	*60*	*Hexad*



$\theta = 90^0$



$\theta = 180^0$

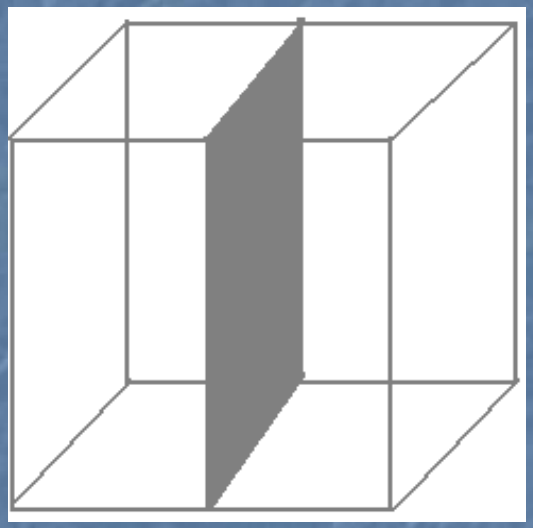
Plane of Symmetry

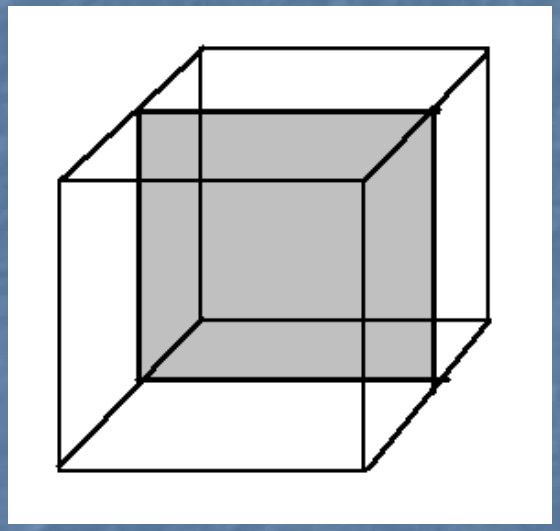
When an imaginary plane can divide the crystal in two equal parts such that each part is exact mirror image of the other then the crystal is said to have a plane of symmetry.

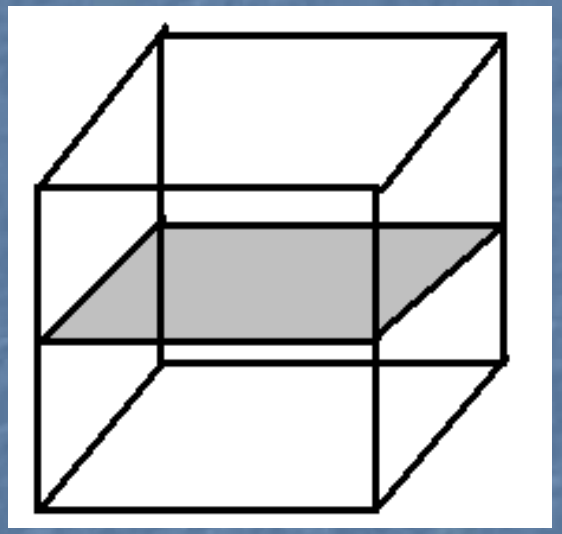
There are two types:

1. *The plane forms mirror images.*
2. *The plane form congruent images.*

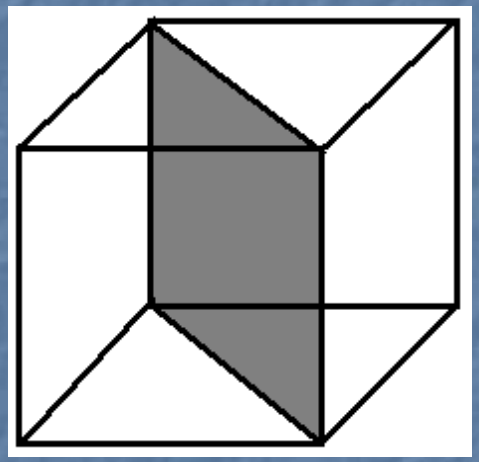
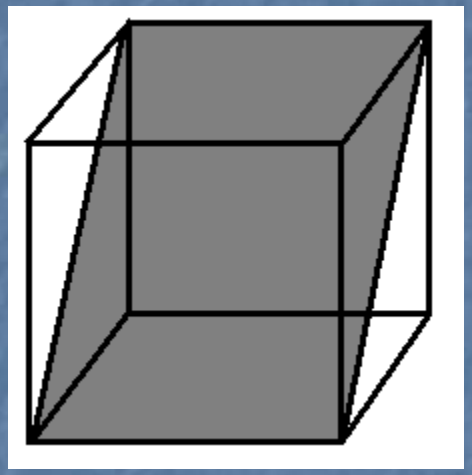
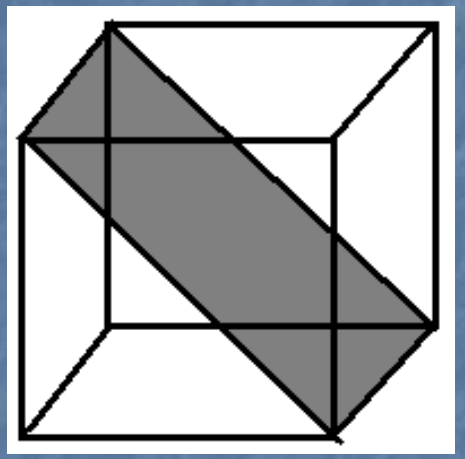
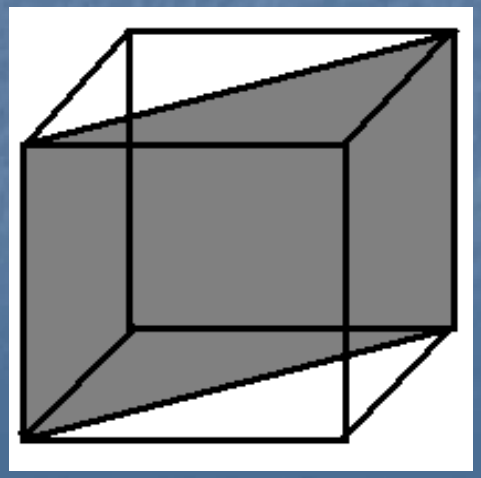
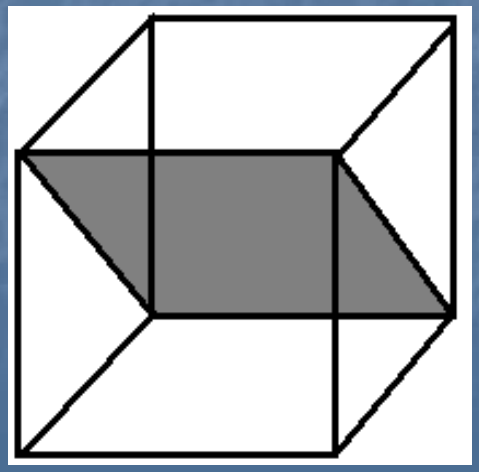
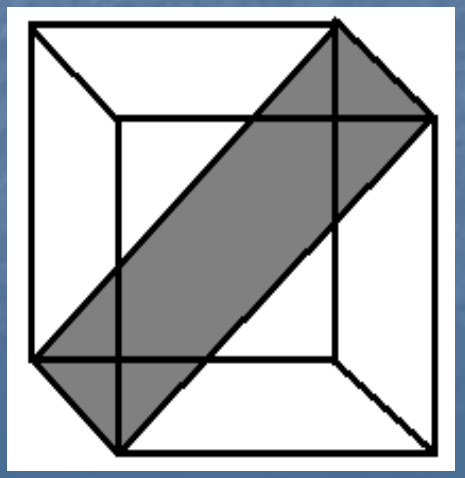
In cube there are three planes of symmetry ***parallel to face of cube.***





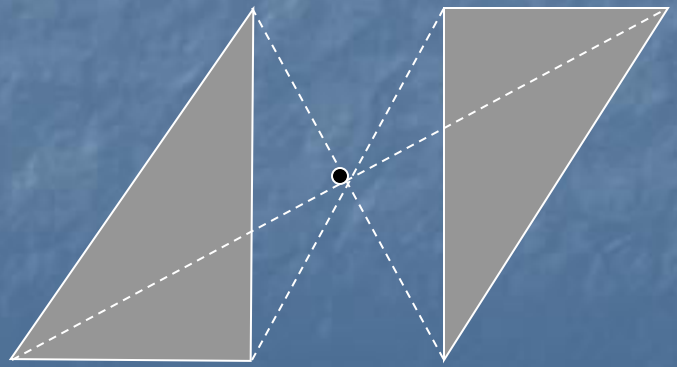


In cube there are six more planes of symmetry formed by a pair of ***opposite parallel edges.***

Centre of symmetry

A centre of symmetry is such a point that any straight point drawn through this point intersects the crystal surface at equal distances in both directions joins identical points in crystal also known as Inversion centre.



Classification of solids

The requirement is that a lattice should be invariant (all points have identical surrounding) under the rotation operation $2\Pi/n$, where n=1,2,3,4,6 or under mirror operation places restrict the primitive vectors a and b. Lattice thus obtained are called "Bravais Lattices".

In three dimensions point symmetry groups require 14 different lattice types: one general and thirteen special.

These 14 lattices are divided in to seven different groups.

Key things to know to describe a crystal Also---initial Steps in the Crystal Structural Determination

- *Unit Cell Parameters (a, b, c, α, β, γ)*
- *Lattice Types (P, I, F, C,...)*
- *Space Groups*
- *Positions of atoms not related by symmetry in unit cell ---asymmetric unit*

A space group consists of a set of symmetry elements that completely describes the symmetry of a crystal.

The important characteristics of seven different crystal systems

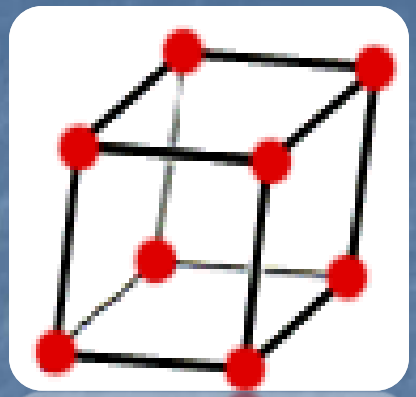
Sr. No.	Crystal System	Bravais Lattices	No. of lattice in the system	Lattice Symbols	Nature of the unit cell
1	Triclinic	Simple	1	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
2	Monoclinic	Simple, Base centered	2	P, C	$a \neq b \neq c$ $\alpha = \gamma = 90^0 \neq \beta$
3	Orthorhombic	Simple, Base centered, BCC,FCC	4	P, C, I, F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^0$
4	Tetragonal	Simple, BCC	2	P, I	$a = b \neq c$ $\alpha = \beta = \gamma = 90^0$

The important characteristics of seven different crystal systems

Sr. No.	Crystal System	Bravais Lattices	No. of lattice in the system	Lattice Symbol	Nature of the unit cell
5	Cubic	Simple, BCC, FCC	3	P, I, F	$a = b = c$ $\alpha = \beta = \gamma = 90^0$
6	Trigonal	Simple	1	P	$a = b = c$ $\alpha = \beta = \gamma < 120^0, \neq 90^0$
7	Hexagonal	Simple	1	P	$a = b \neq c$ $\alpha = \beta = 90^0, \gamma = 120^0$

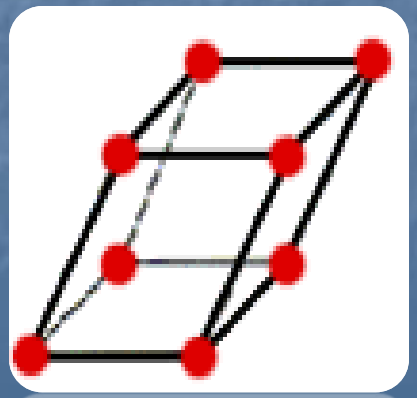
Triclinic

Simple

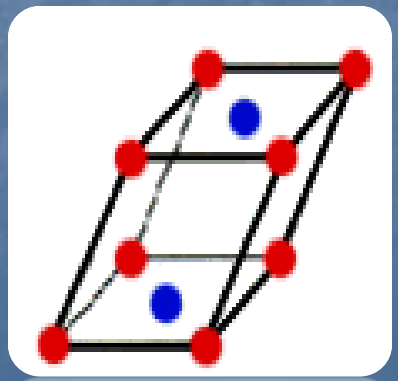


Monoclinic

Simple

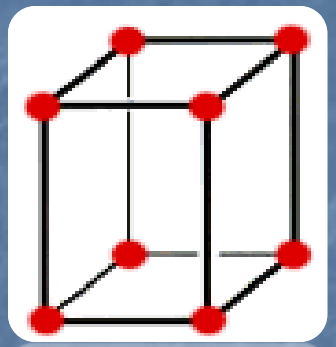


BCC

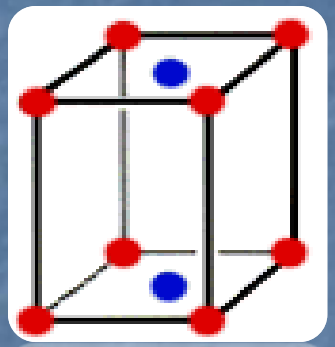


Orthorhombic

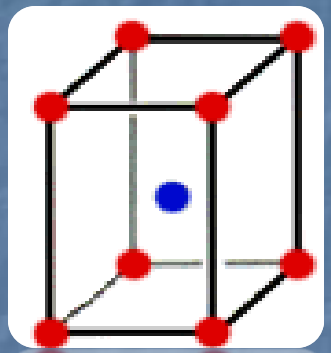
Simple



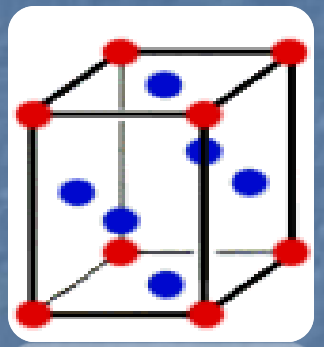
Base centered



BCC

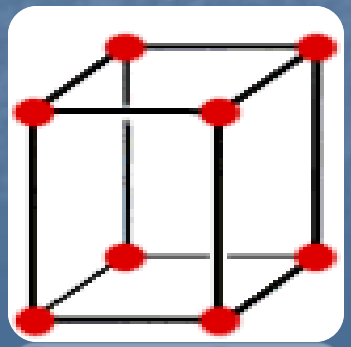


FCC

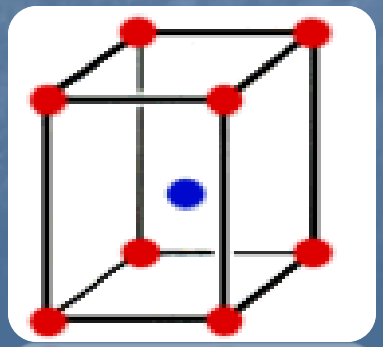


Tetragonal

Simple

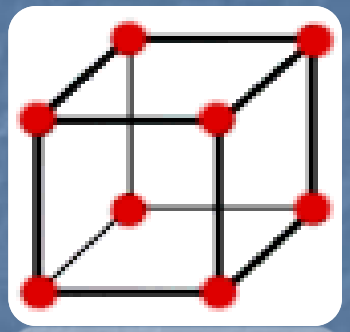


BCC

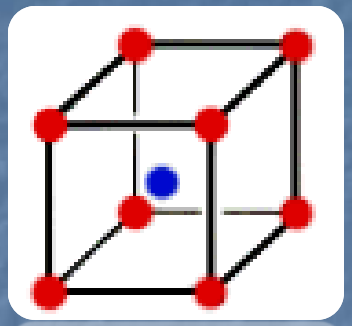


Cubic

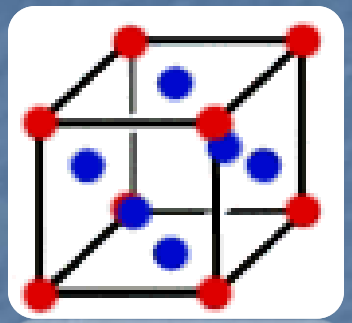
Simple



BCC

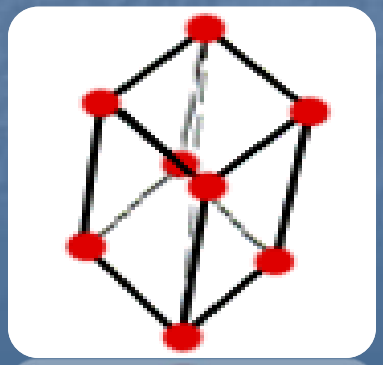


FCC



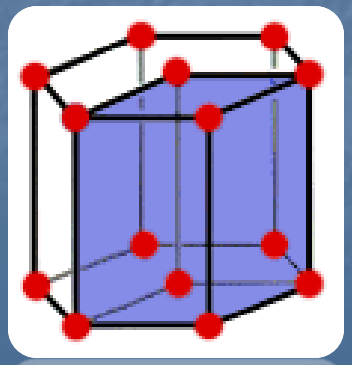
Trigonal

Simple



Hexagonal

Simple



Sr. No.	Characteristics	Types of cubic cell		
		SC	BCC	FCC
1.	No. of atoms per unit cell	1	2	4
2.	Atomic radius	$a/2$	$\sqrt{3}a/4$	$\sqrt{2}a/4$
3.	Co ordination number	6	8	12
4.	Atomic packing fraction	$\Pi/6$	$\sqrt{3}\Pi/8$	$\sqrt{2}\Pi/6$
5	Void space	48%	32%	26%
6.	Density	$\frac{M}{N_A a^3}$	$\frac{2M}{N_A a^3}$	$\frac{4M}{N_A a^3}$

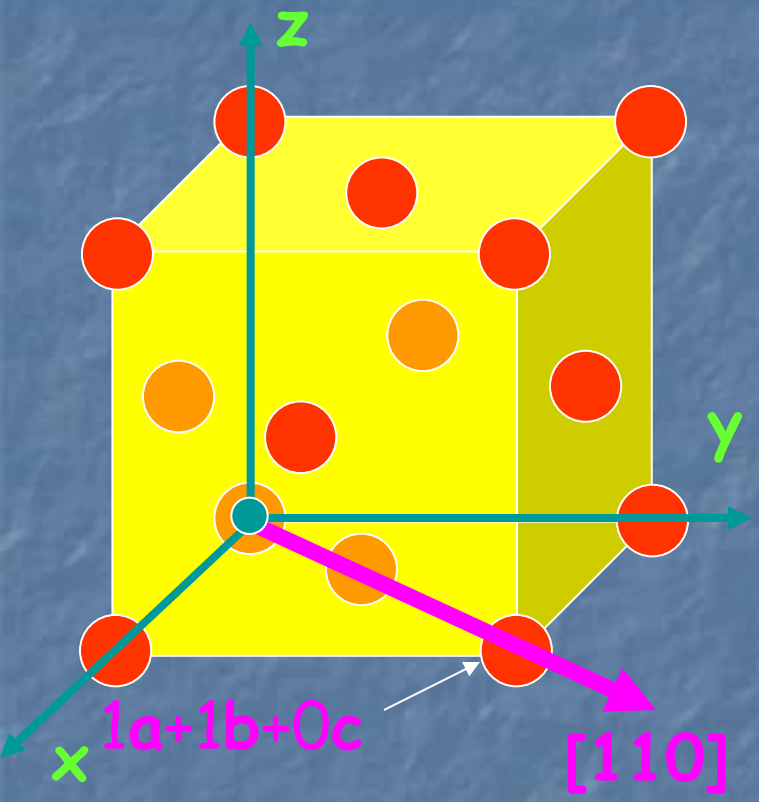
Miller Indices

The Miller Indices are the smallest possible integers which have the same ratios as the reciprocal of the intercepts of the planes concerned on three axes.

Method of finding Miller Indices:

- *Determine the intercept of the plane along X, Y and Z axis in terms of lattice constant a, b, c.*
- *Determine the reciprocal of these intercepts.*
- *Find LCM and multiply each by LCM.*
- *Write the result in the form of (hkl), called as Miller Indices.*

Miller Indices of Directions



1. Choose a lattice point on the direction as the origin

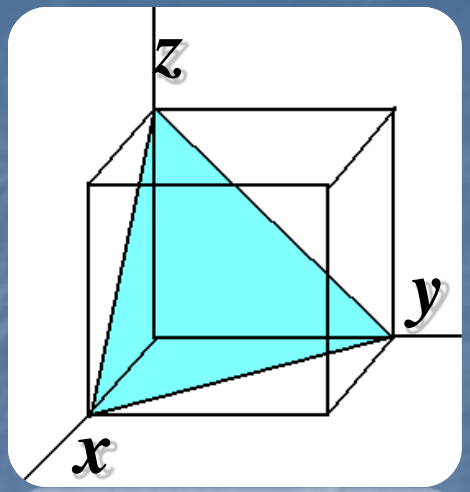
2. Choose a crystal coordinate system with axes parallel to the unit cell edges

3. Find the coordinates, in terms of the respective lattice parameters a, b and c, of another lattice point on the direction.

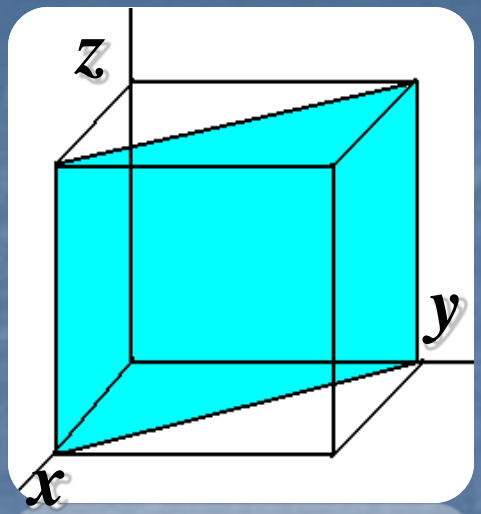
4. Reduce the coordinates to smallest integers.

5. Put in square brackets [...]

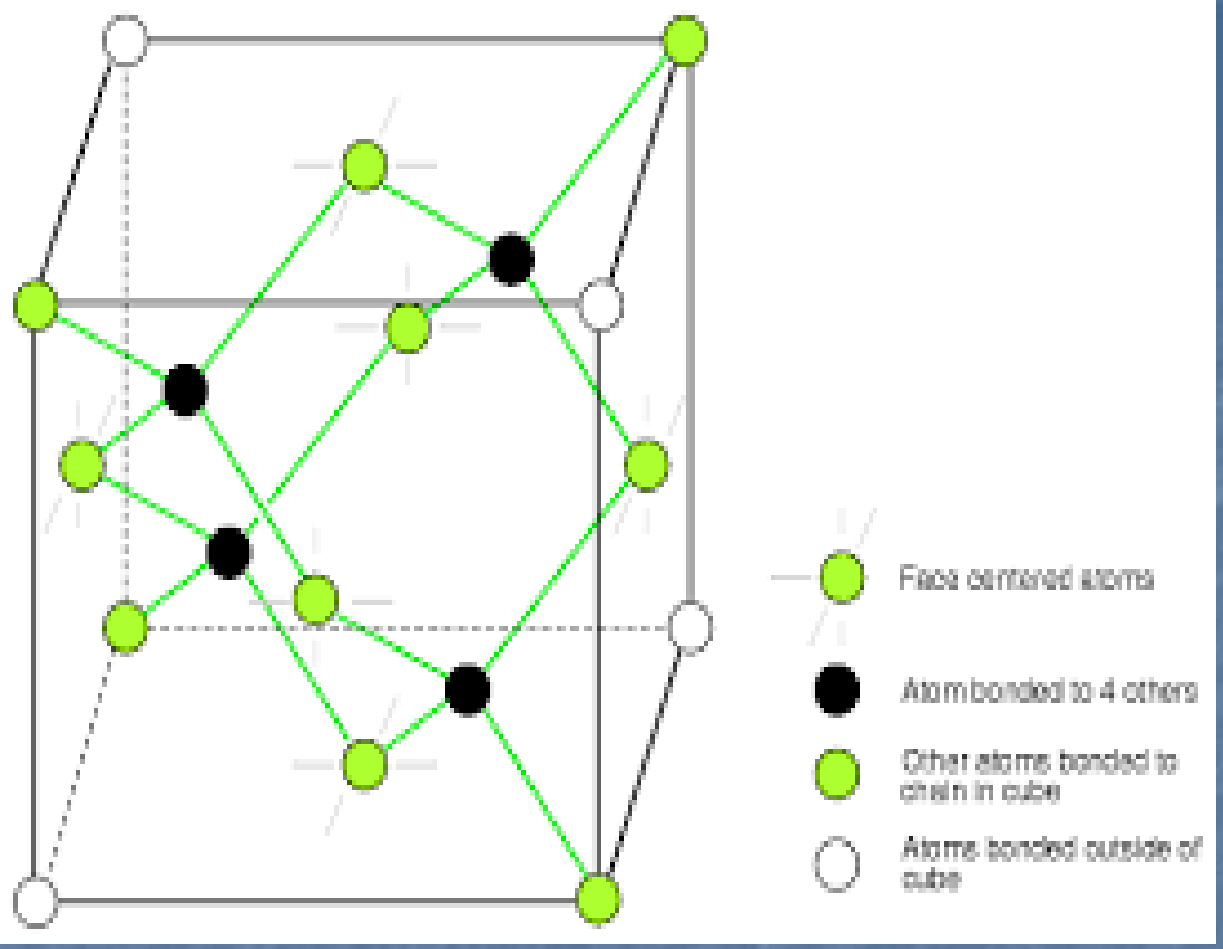
Miller Indices are (111)



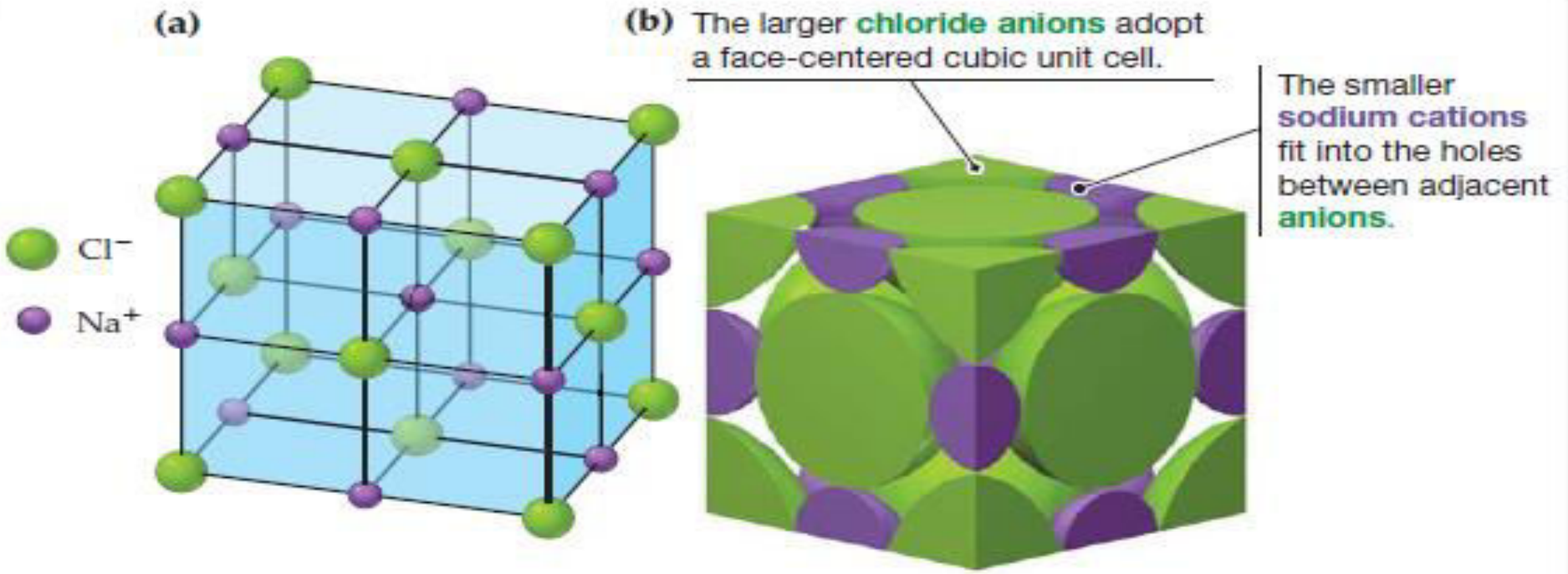
The Miller Indices are (110)



For an intercept at infinity the index is zero.



- **Diamond** unit cell is F.C.C type with four additional C atoms tetrahedrally bonded(black ones). Corner atoms contributes to 1/8th of the atom to the unit cell , Face centered atoms contributes 1/2 of the atom .Now, Total atom in one cell can be summed up to :



Structure of NaCl (Rock salt)

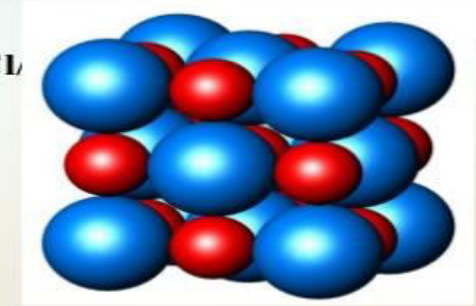
- FCC type.
- Co-ordination number 6:6.
- **Calculation of no. of atoms of NaCl/ cell:**

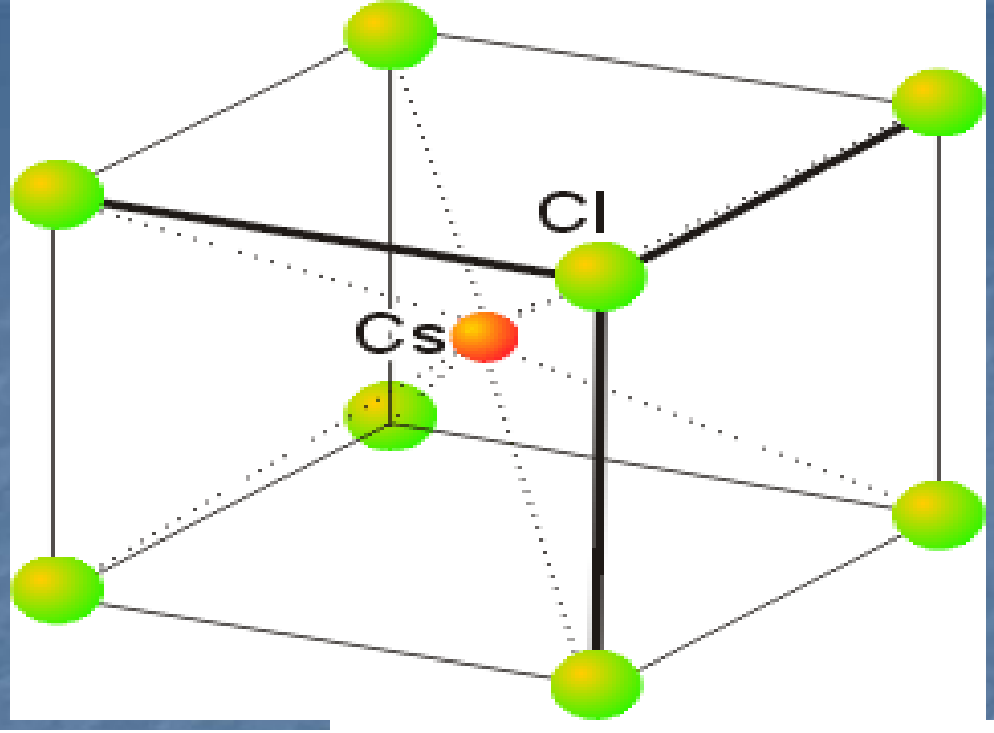
Cl at corners: $(8 \times 1/8) = 1$
Cl at face centres $(6 \times 1/2) = 3$

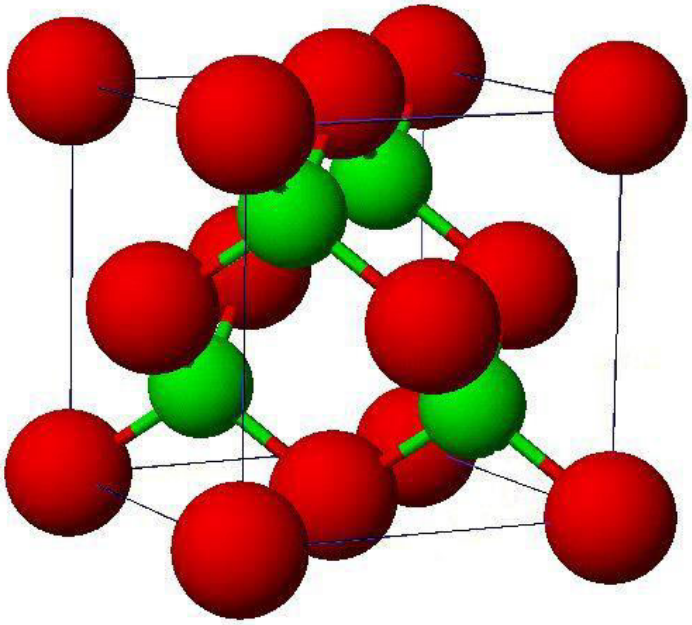
Na at edge centres $(12 \times 1/4) = 3$
Na at body centre $= 1$

Unit cell contents are $4(Na^+Cl^-)$

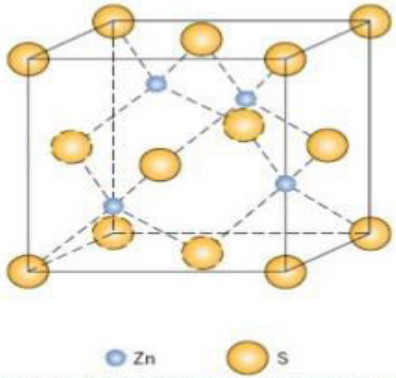
i.e. per each unit cell, 4 NaCl units will be present







Zinc Blende (闪锌矿) Structure



A unit cell for ZnS structure

- **Coordination number: 4**
  All ions are tetrahedrally coordinated.
- **All corner and face positions of the cubic cell are occupied by S atoms, while the Zn atoms fill interior tetrahedral positions. Vise versa.**
- **ZnS, ZnTe, and SiC**

THANK YOU!!