Unit wise Marks Distribution of 10+2 Syllabus

S.No	Unit	Name	Marks
1	I	Solid State	4
2	II	Solutions	5
3	III	Electro Chemistry	5
4	IV	Chemical Kinetics	5
5	V	Surface Chemistry	4
6	VI	General Principles and Process or Isolation of Elements	3
7	VII	p-Block Elements	8
8	VIII	d and f-Block Elements	5
9	IX	Coordination Compounds	3
10	X	Haloalkanes and Haloarenes.	4
11	XI	Alcohols, Phenols and Ethers	4
12	XII	Aldehydes, Ketones and Carboxylic Acids	6
13	XIII	Organic compounds containing Nitrogen	4
14	XIV	Biomolecules	4
15	XV	Polymers	3
16	XVI	Chemistry in everyday life	3

Schedule for special classes

Date	Time (am)	Topic	R/Person (Dr.Mr.)
06-06-09	8.00-8.40	Classification of Solids, Unit cells, Determination of density.	Anand Gupta
	8.40-9.20		Mahesh Kapil
	9.20-9.40	BREAK	
	9.40-10.20	Imperfection in solids, Electrical and Magnetic properties of solids. Typical Questions	Anand Gupta
	10.20-11.00		Mahesh Kapil
07-06-09	8.00-8.40	Solutions; types and methods to express the strength of solutions	Anand Gupta
	8.40-9.20		Mahesh Kapil
	9.20-9.40	BREAK	
	9.40-10.20	Colligative properties and Abnormal Molar Masses Typical Questions	Anand Gupta
	10.20-11.00		Mahesh Kapil

Date	Time (am)	Topic	R/Person (Dr.Mr.)
08-06-09	8.00-8.40	Redox reactions; Electrochemical cell, Nernst Equations	Anand Gupta
	8.40-9.20		Mahesh Kapil
	9.20-9.40	BREAK	
	9.40-10.20	Commercial cells; corrosion;	Anand Gupta
	10.20-11.00		Mahesh Kapil
09-06-09	8.00-8.40	Electrolysis; factors affecting electrolytic conduction.	Anand Gupta
	8.40-9.20		Mahesh Kapil
	9.20-9.40	BREAK	
	9.40-10.20	Chemical Kinetics.; Rate of Reaction; Factors	Anand Gupta
	10.20-11.00		Mahesh Kapil
10-06-09	8.00-8.40	Effect of Temperature on rate of reaction	Anand Gupta
	8.40-9.20	Adsorption	Mahesh Kapil
	9.20-9.40	BREAK	
	9.40-10.20	Catalysis	Anand Gupta
	10.20-11.00	Colloids	Mahesh Kapil

Solid State

By

Dr Anand Gupta **Mr. Mahesh Kapil**
09356511518 **09888711209**
anandu71@yahoo.com **mkapil_foru@yahoo.com**

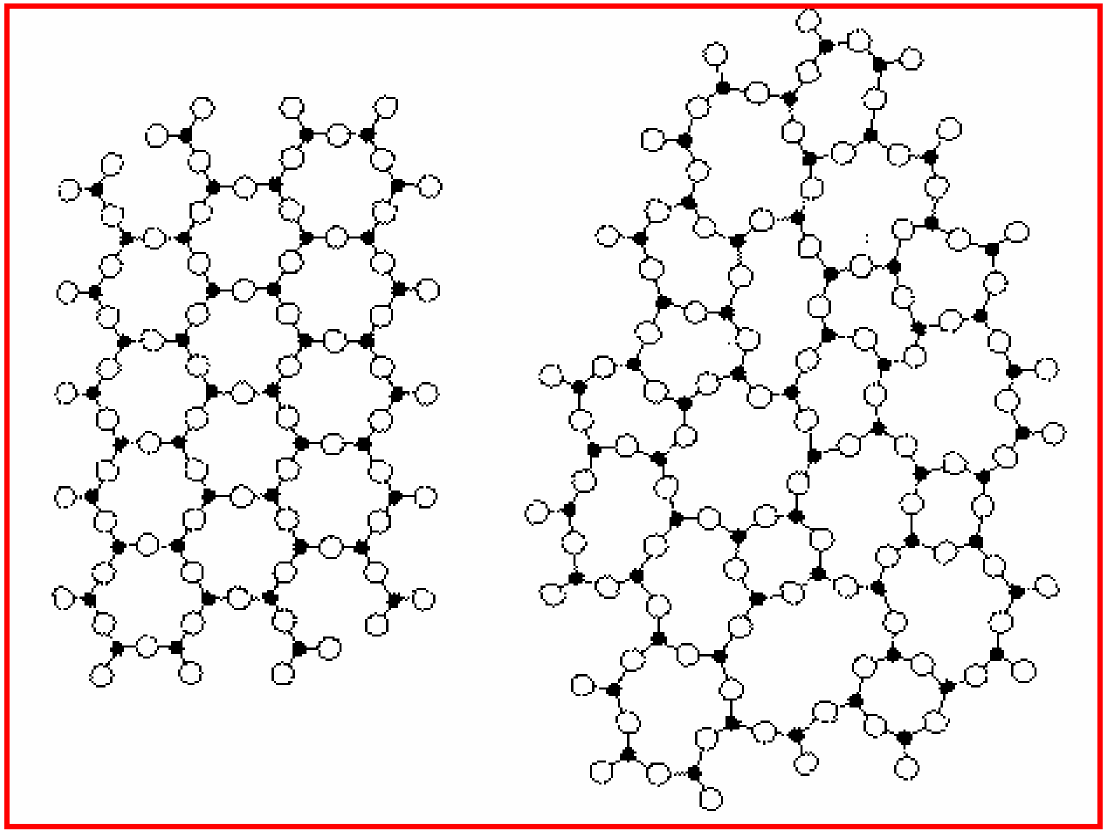
Solids

- Solids have "resistance" to changes in both shape and volume
- Solids can be Crystalline or Amorphous
- Crystals are solids that consist of a periodic array of atoms, ions, or molecules
  - If this periodicity is preserved over "large" (macroscopic) distances we call it **"Long Range Order"**
- **Amorphous solids** do not have Long-Range Order
  - Short Range Order

Solids

- **Crystals Solids:**
  - Short Range Order
  - Long Range Order

- **Amorphous solids:**
  - Short Range Order
  - **No** Long-Range Order



Distinction between Crystalline and Amorphous solids

- Regular arrangement
- Sharp melting point
- Anisotropic nature
- True solids

- Irregular arrangement
- Diffused melting point
- Isotropic nature
- Super cooled liquids

Crystals

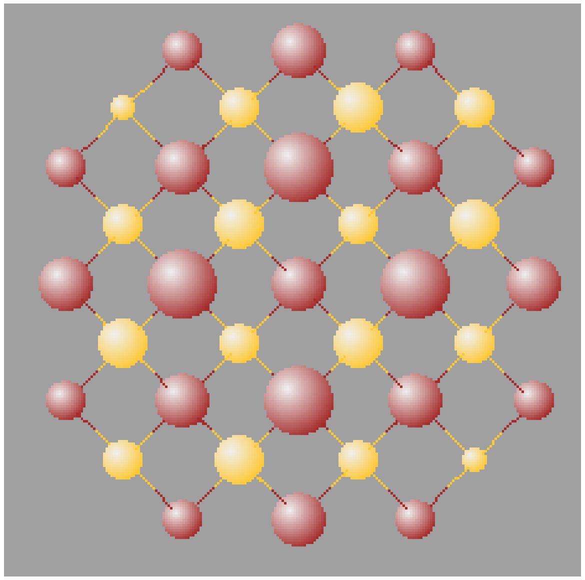
- **The periodic array of atoms, ions, or molecules that form the solids is called Crystal Structure**

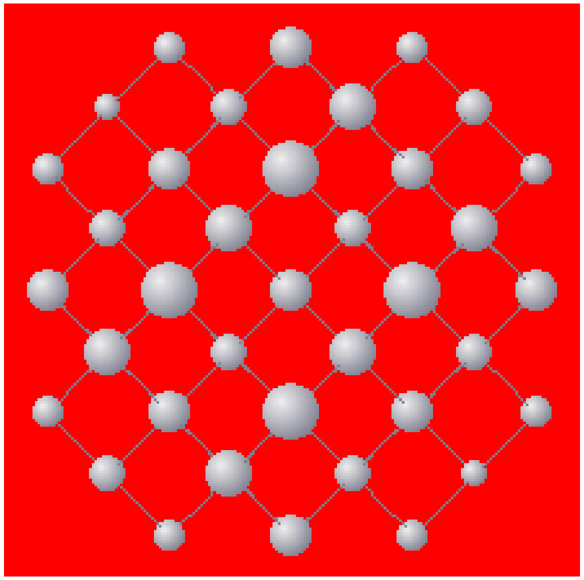
Crystal Structure = Space (Crystal) Lattice + Basis

- **Space (Crystal) Lattice** is a **regular periodic** arrangement of ***points*** in space, and is purely ***mathematical abstraction***
- **Crystal Structure** is formed by "putting" the identical atoms (group of atoms) in the points of the space lattice
- This group of atoms is called **Basis**

Solids

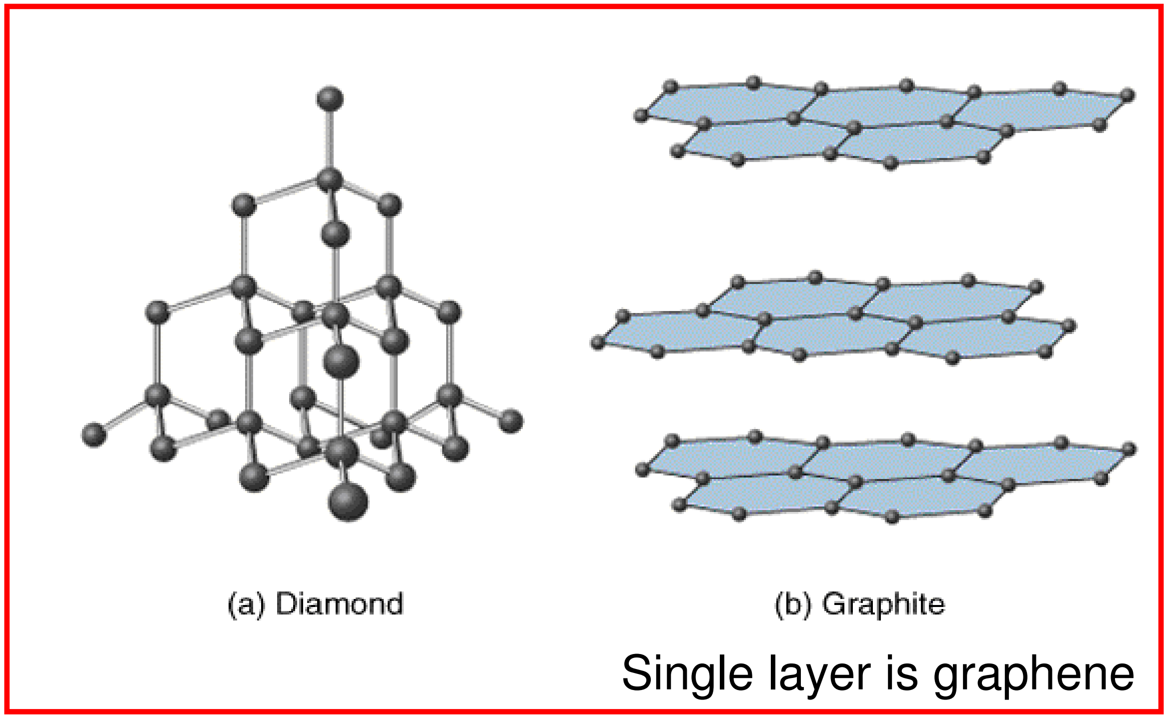
- **Different solids can have the same geometrical arrangements of atoms**
  - *Properties are determined by crystal structure, i.e. both crystal lattice and basis are important*
- Example:
  - Si, Diamond (C), GaAs, ZnSe have the same geometry
  - Si and C (Diamond) Form "Diamond Structure"
  - GaAs or ZnSe form a structure called "Zinc Blende"





Solids

- **Different arrangements of atoms (even the same atoms) give different properties**



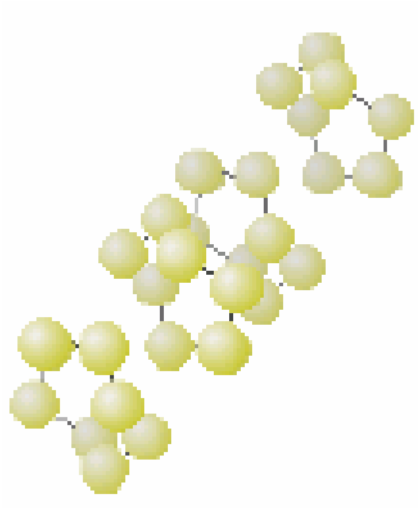
Classification of Solids

- Since we know the structure of atoms that form solids, we can classify them via the type of bonds that hold solids together

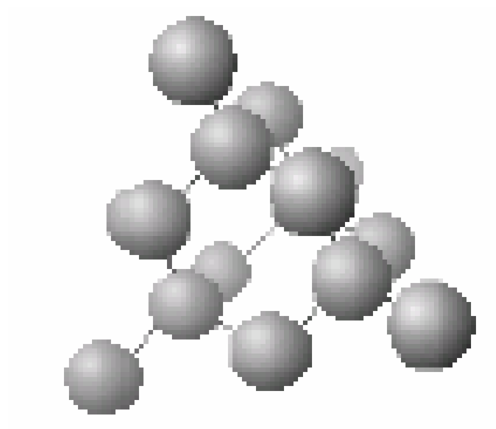
  - **In this case we say that we classify solids according to the nature of bonding**

  - There are four classes of solids:
    - **metallic, ionic, covalent, and molecular**
  - All the forces holding solids together have electrostatic origin

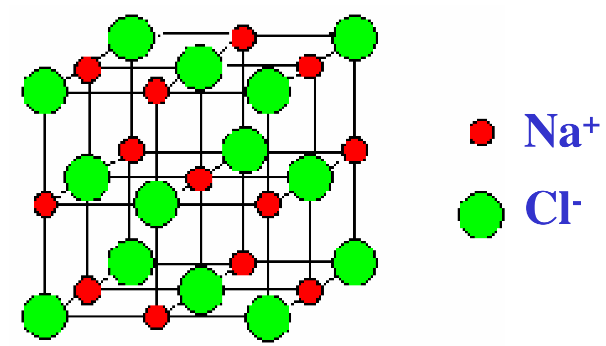
STRUCTURES OF CRYSTALLINE SOLID TYPES



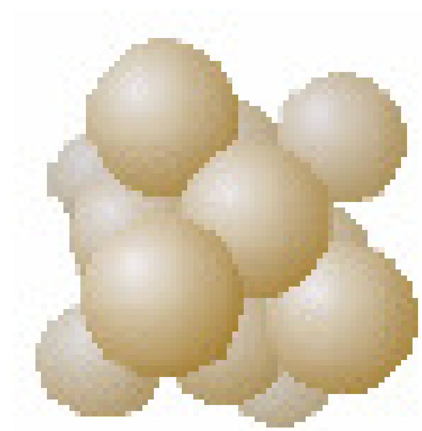
Molecular Solids



Covalent Solids



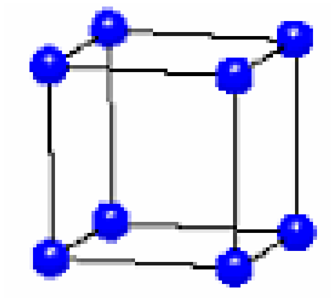
Ionic solids



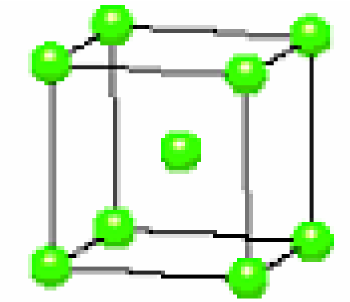
Metallic solids

Crystal Type	Particles	Interparticle Forces	Physical Behaviour	Examples
Molecular	Molecules	Dispersion Dipole-dipole H-bonds	➢ Fairly soft ➢ Low to moderate mp ➢ Poor thermal and electrical conductors	O_2, P_4, H_2O, Sucrose
Metallic	Atoms	Metallic bond	❑ Soft to hard ❑ Low to very high mp ❑ Mellable and ductile ❑ Excellent thermal and electrical conductors	Na, Cu, Fe
Ionic	Positive and negative ions	Ion-ion attraction	❖ Hard and brittle ❖ High mp ❖ Good thermal and electrical conductors in molten condition	NaCl, CaF_2, MgO
Network	Atoms	Covalent	• Very hard • Very high mp • Poor thermal and electrical conductors	SiO_2(Quartz) C (Diamond)

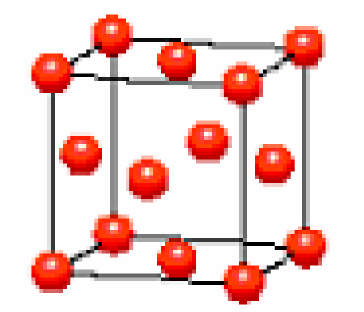
LATTICE TYPES



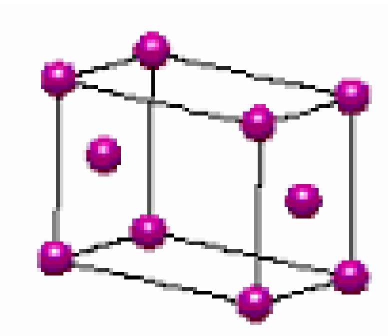
Primitive (**P**)



Body Centered (**I**)



Face Centered (**F**)

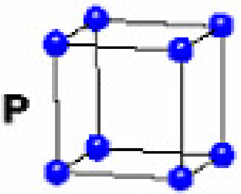


End Centered (**C**)

THREE DIMENTIONAL UNIT CELLS / UNIT CELL SHAPES

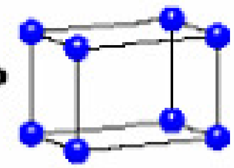
1 CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$

P



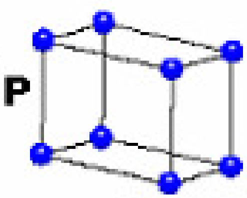
2 TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

P



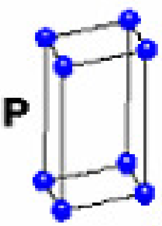
3 ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

P



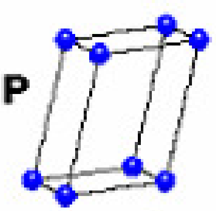
4 HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

P



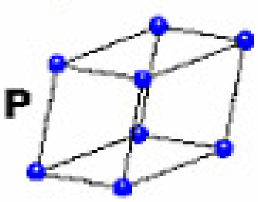
5 MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

P



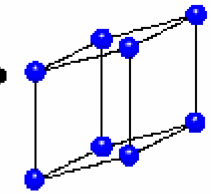
6 TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

P

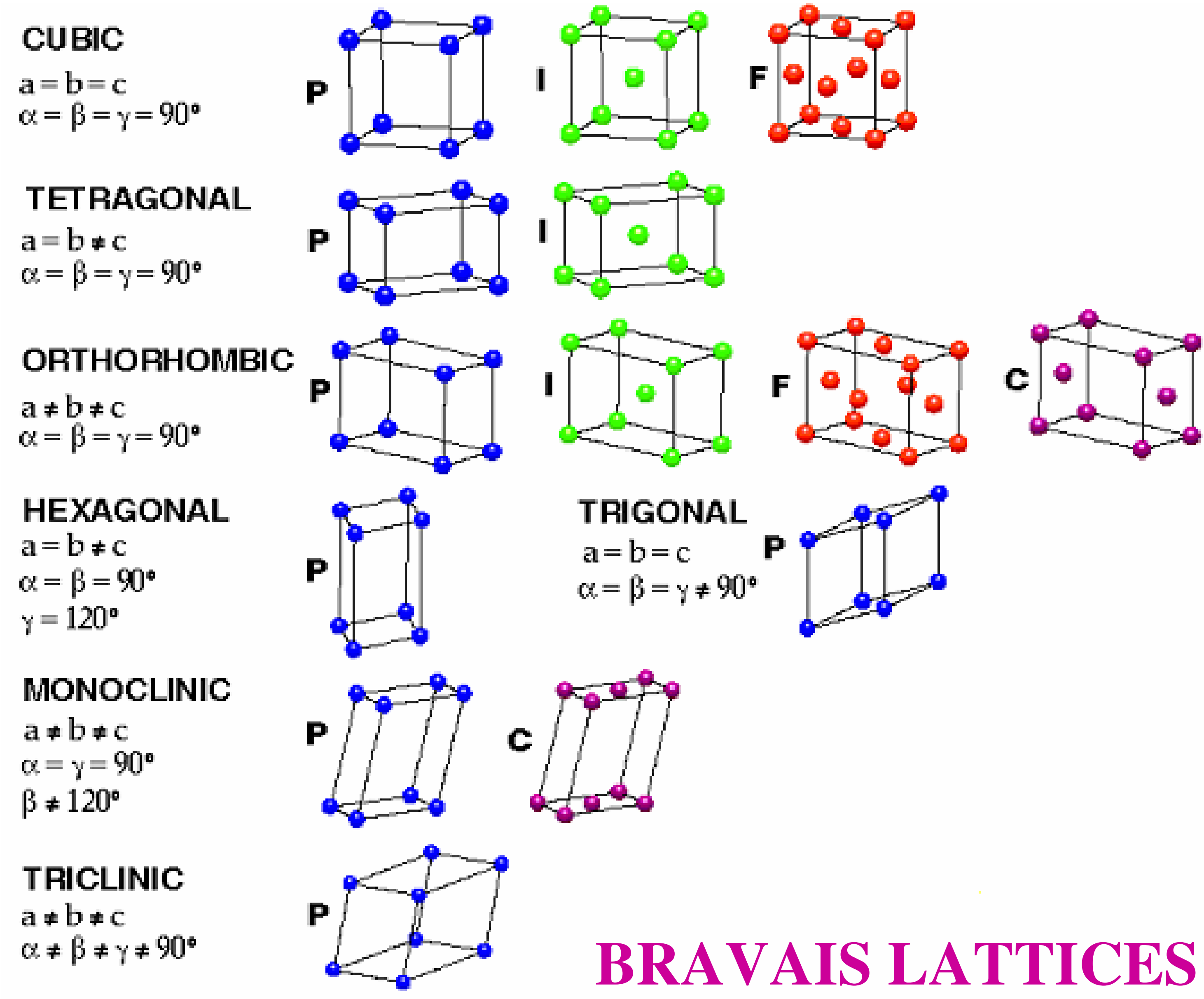


7 TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

P



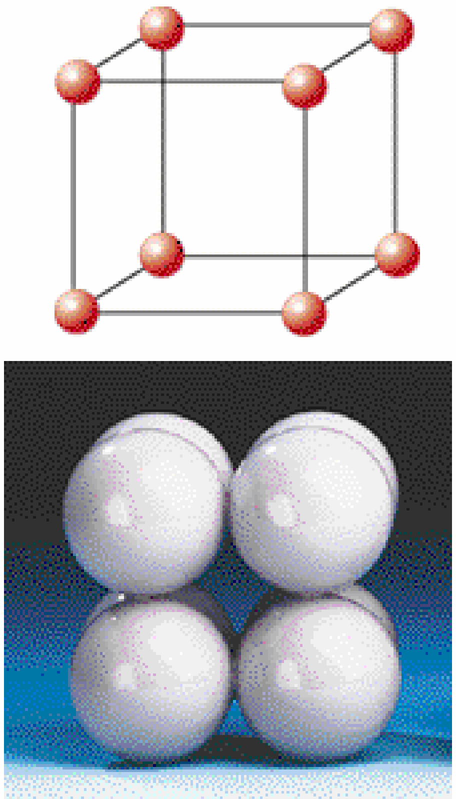
7 UNIT CELL TYPES + 4 LATTICE TYPES = 14 BRAVAIS LATTICES



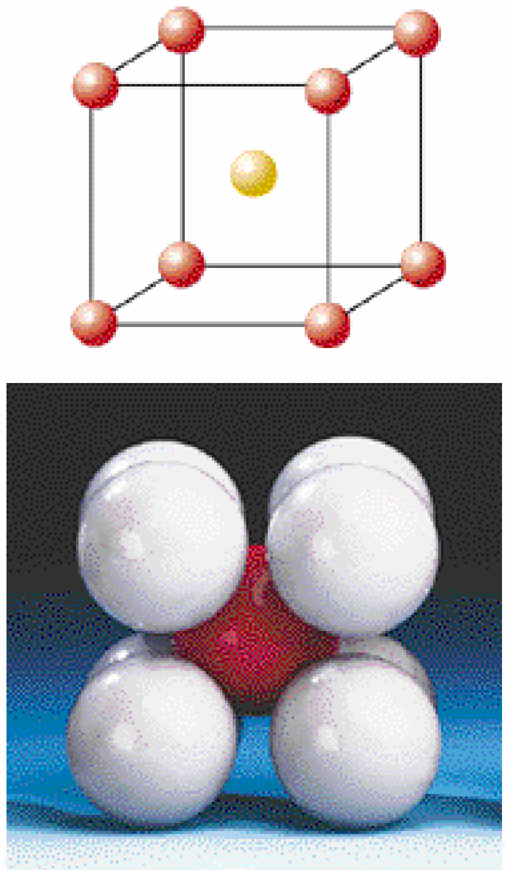
BRAVAIS LATTICES

Structures of Solids

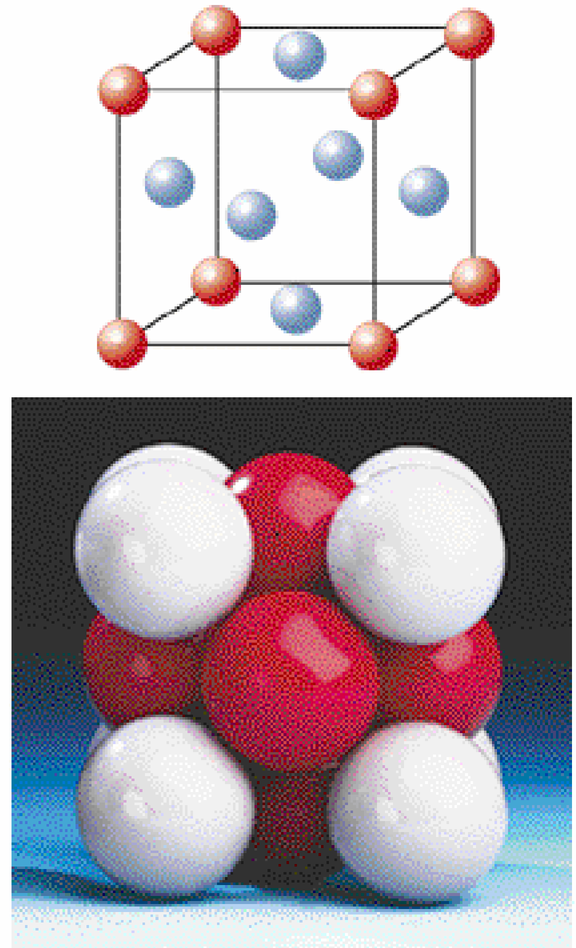
Unit Cells



simple cubic

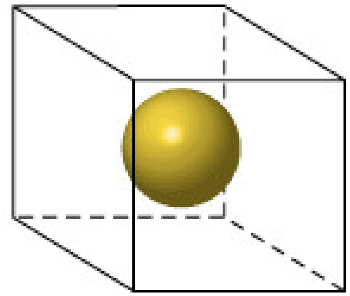


body-centered cubic

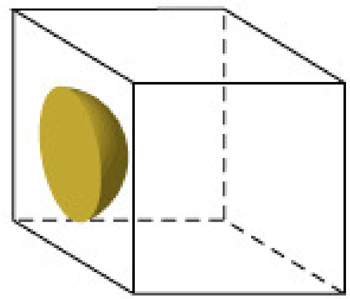


face-centered cubic

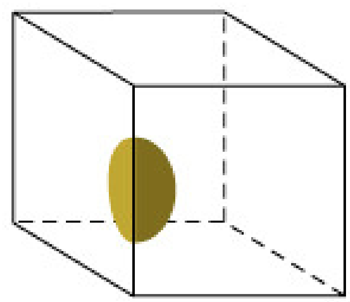
Body Center = 1 unit



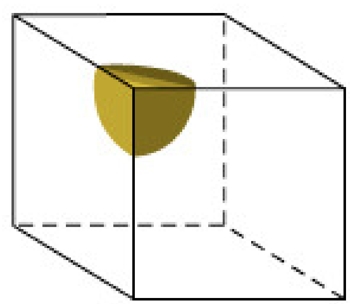
Face Center = 1/2 unit



Edge = 1/4 unit



Corner = 1/8 unit



QUESTIONS

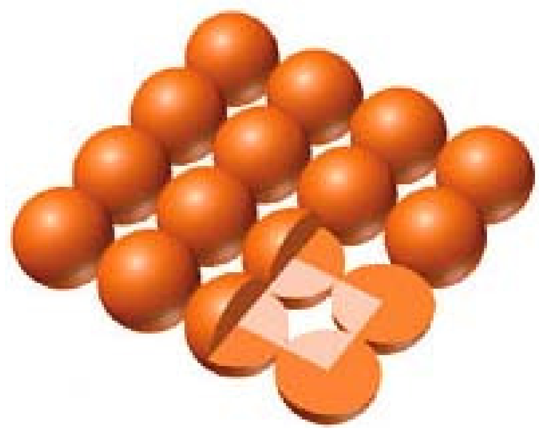
A unit cell consists of a cube in which there are A atoms are at the corners and B atoms at the face centres and A atoms from 2 corners are missing what is the simplest formula of compound

Calculate no. atoms present in unit if points are present at the corners all the edges of cube.

Packing Arrangements

How do these packing arrangements arise?

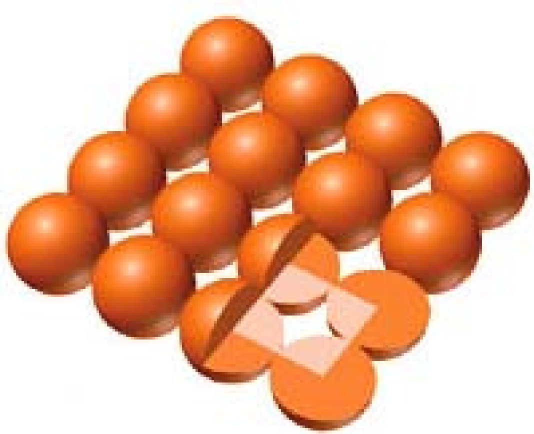
Start always with a layer of atoms, separated center to center by the lattice parameter, a.



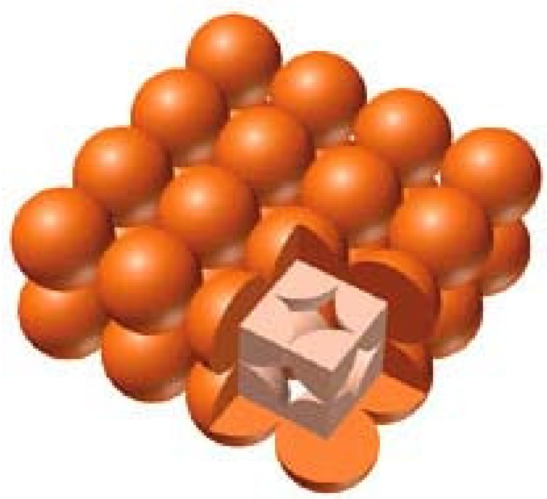
Then, place a layer on top, over atoms or over spaces.

Thus, for a simple cubic lattice (SC):

The first layer is spaced with a = 2R



Then the second layer is placed with every atom directly atop the one below

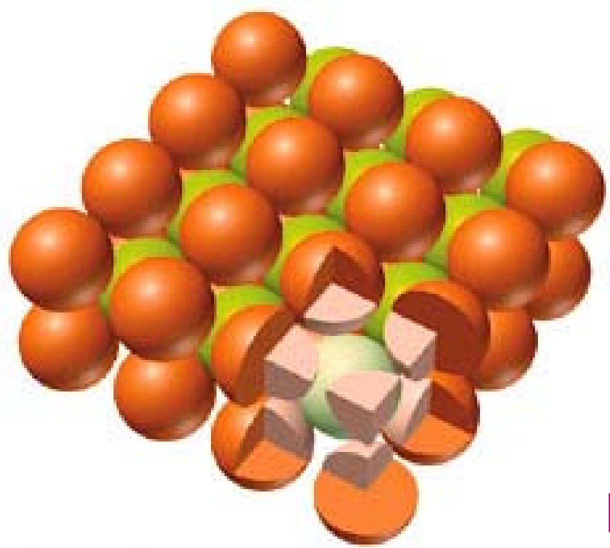


Not a close-packed structure.

Packing fraction = 54%

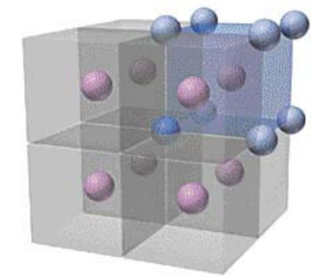
For a body-centered cubic lattice (BCC):

The first layer is spaced with $a = \frac{4}{\sqrt{3}} R$



Still not a close-packed structure.

Coordination number = 8 (bi-prism)



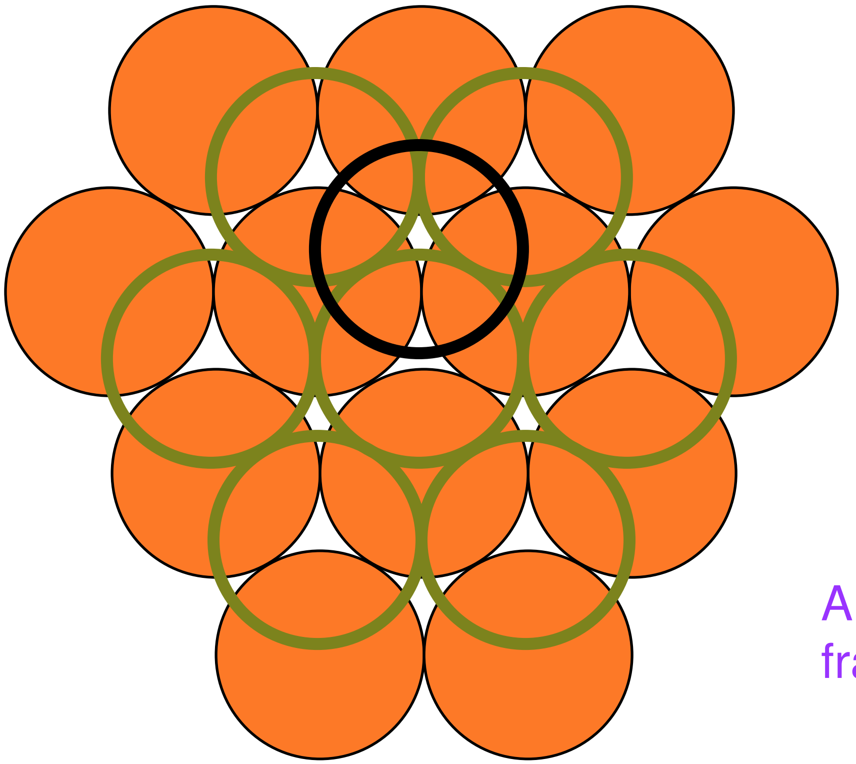
Packing fraction = 68%

Then, the second layer is placed over the spaces between atoms.

Finally, a third layer lines up directly over the atoms in the first.

The close-packed crystal systems

Cubic closest packing or face-centered cubic, FCC



Shift every other row in the first layer to compress packing

Place second layer over triangular spaces

Third layer over gaps that remain

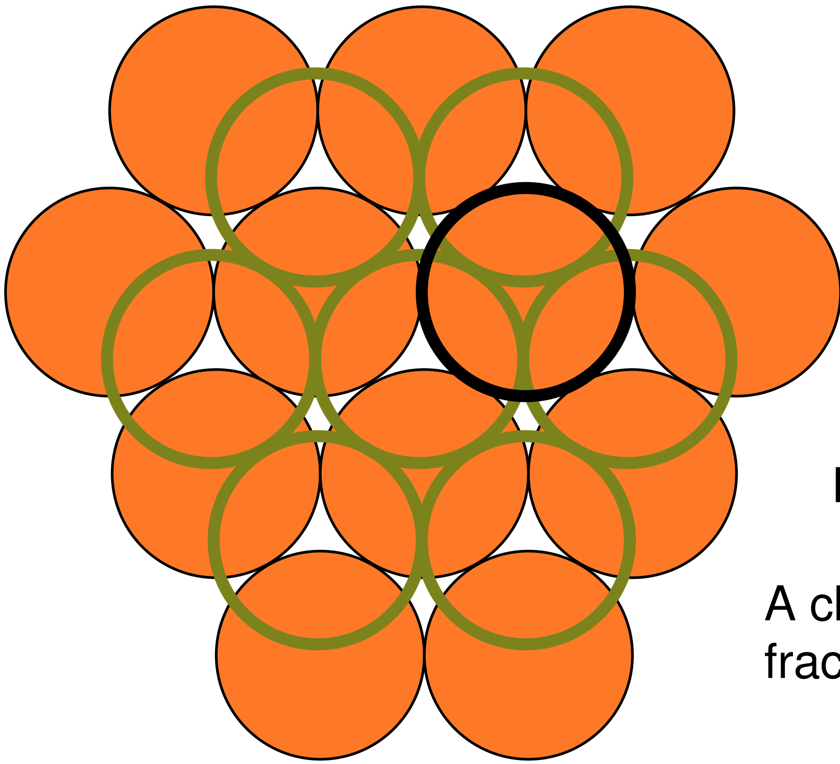
Tilt to find unit cell

A close-packed structure with a packing fraction of 74%

abcabc…

The close-packed crystal systems

Hexagonal closest packing, HCP



Shift every other row in the first layer to compress packing

Place second layer over triangular spaces

Third layer directly over the atoms of the first

Rhombic unit cell

A close-packed structure with a packing fraction of 74%

Coordination # = 12

(3 above, 6 in the plane, 3 below)

abab…

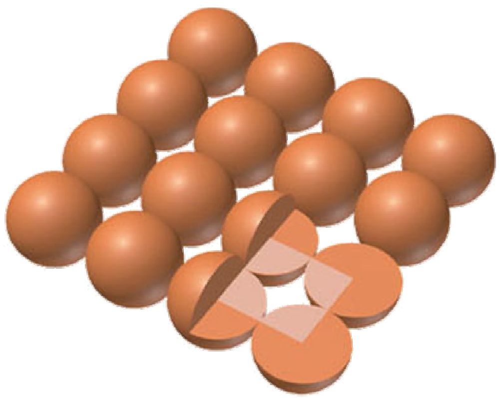
Packing efficiency

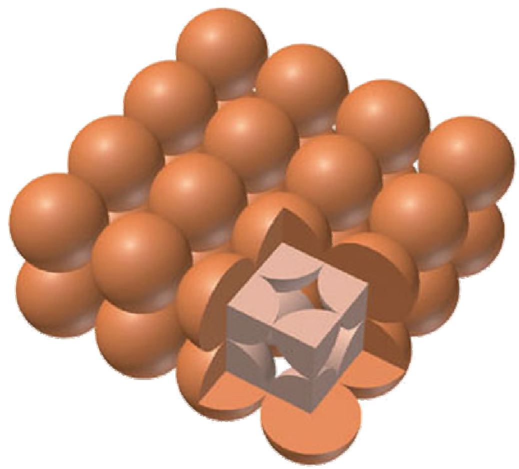
For a given atom radius, the higher the coordination, the higher the packing efficiency:

Cell Type	Coordination #	Packing Efficiency
Simple cubic	6	52%
Body-centered cubic	8	68%
Face-centered cubic (cubic closest packing)	12	74%
Hexagonal	12	74%

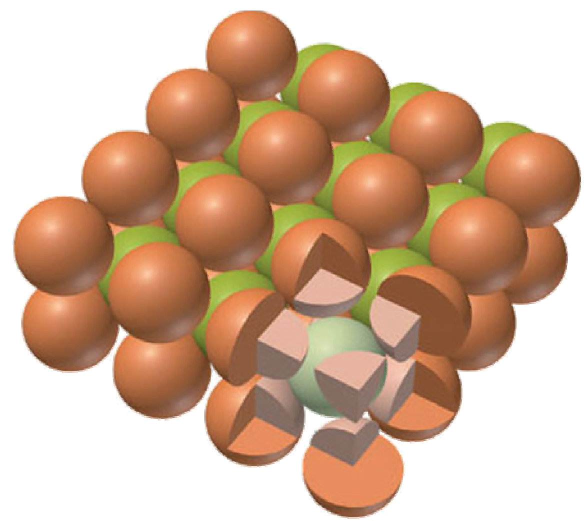
Most metallic elements pack in hexagonal closest packing lattice.
Many ionic compounds are fcc. (NaCl – two interspersed fcc lattices.)

Packing of spheres.

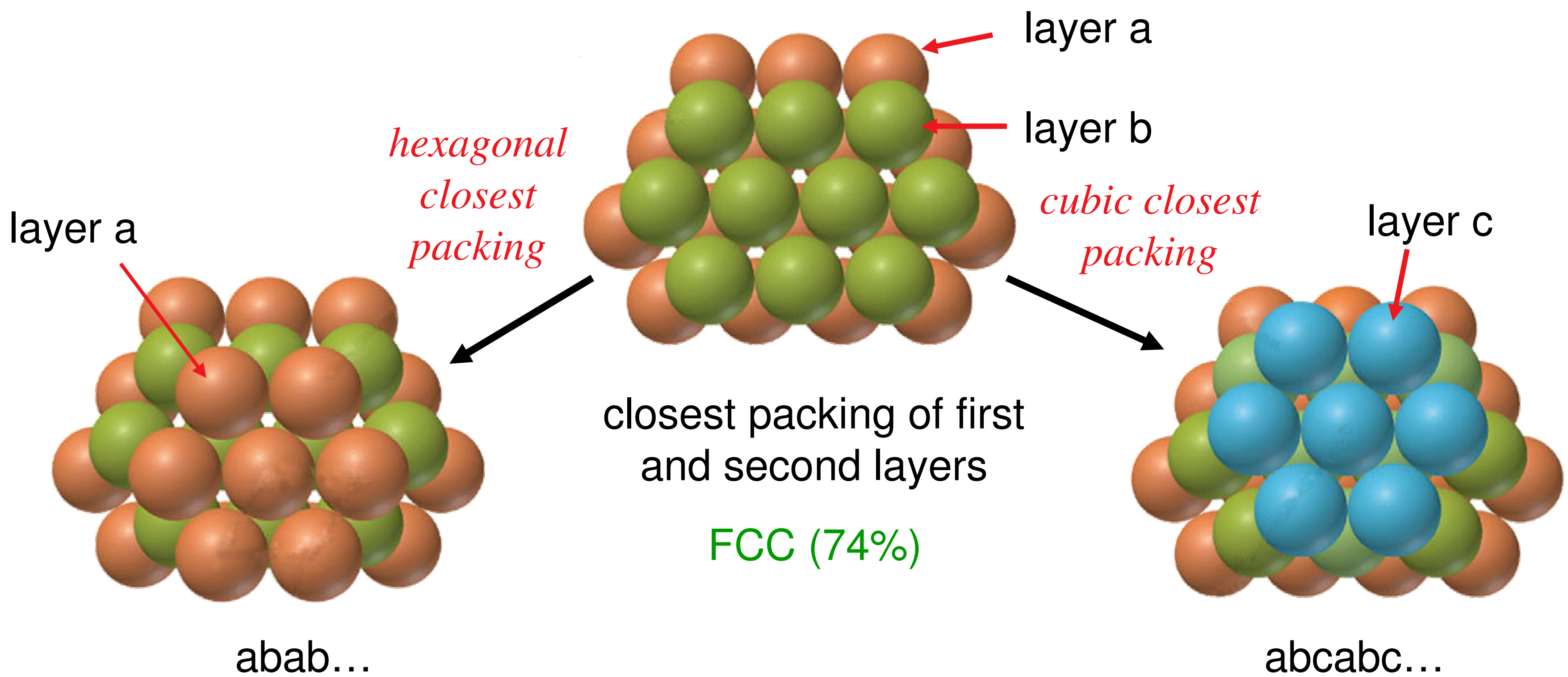




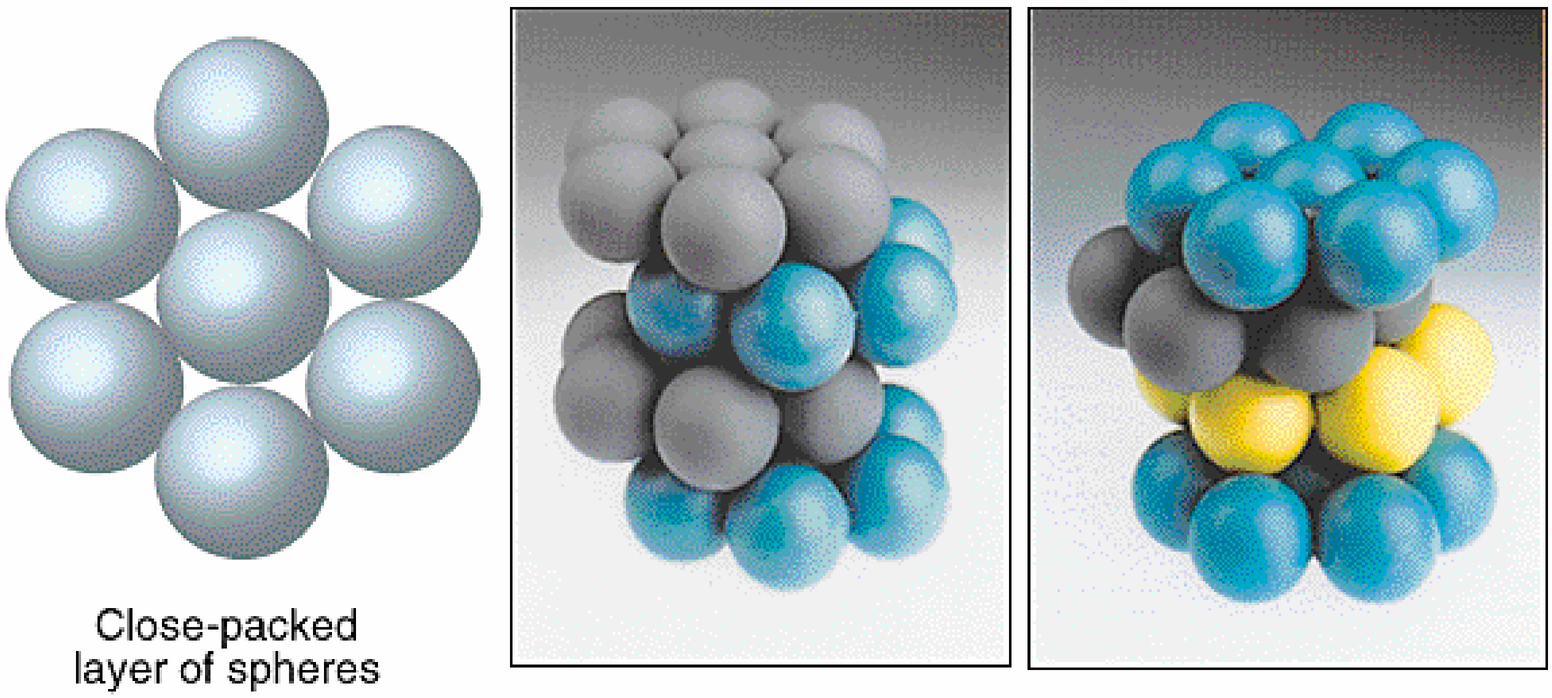
simple cubic(52%)



BCC (68%)

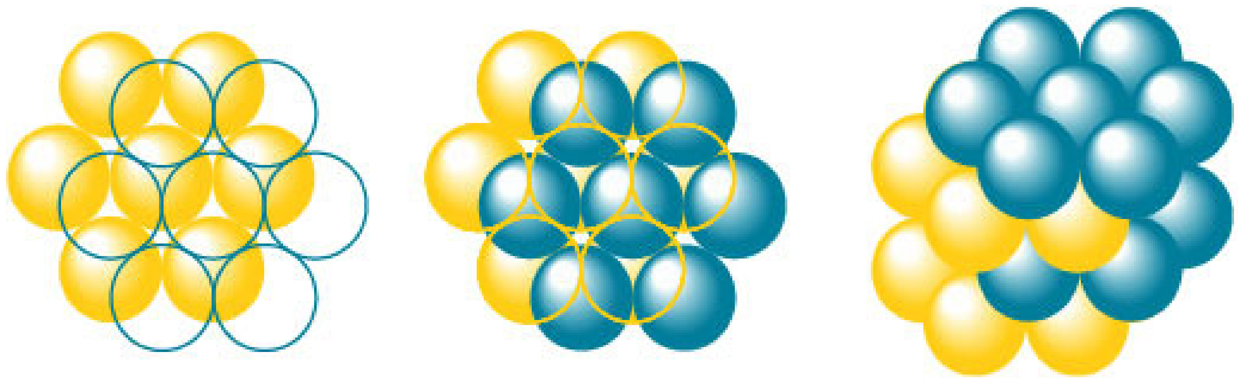

layer a
layer b
hexagonal closest packing
cubic closest packing
layer a
layer c
closest packing of first and second layers
FCC (74%)
abab…
abcabc…

Close Packing of Spheres



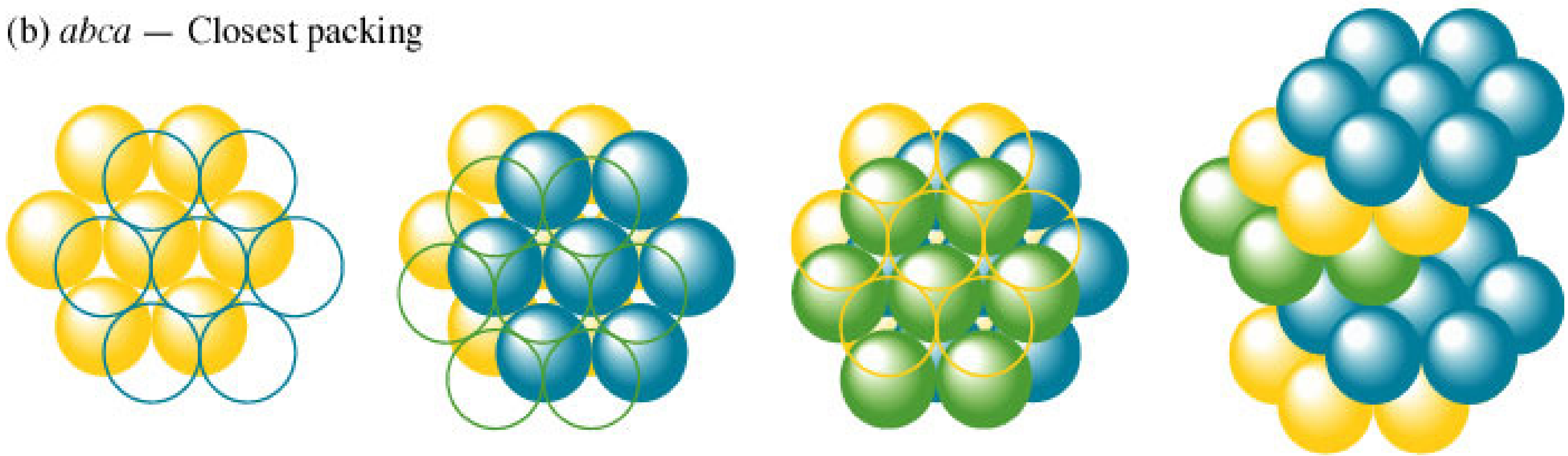
(a) (b) (c)

(a) *abab* — Closest packing



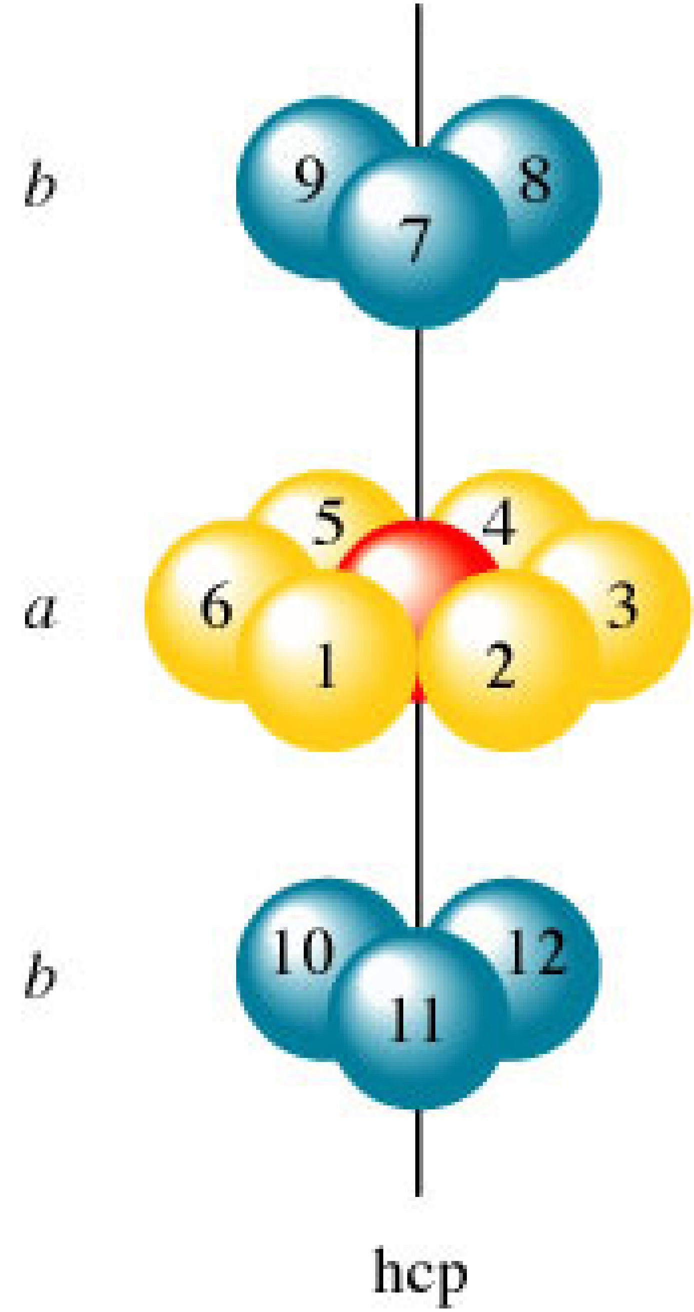
Top view Top view Side view

(b) *abca* — Closest packing



Top view Top view Top view Side view

The Indicated Sphere Has 12 Nearest Neighbors



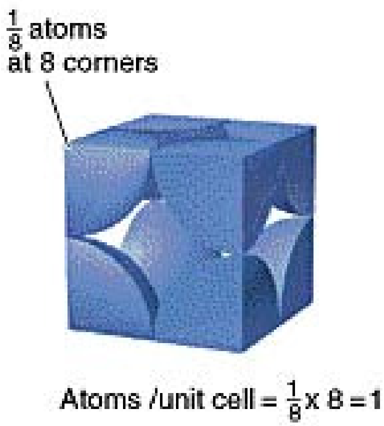
Structures of Solids

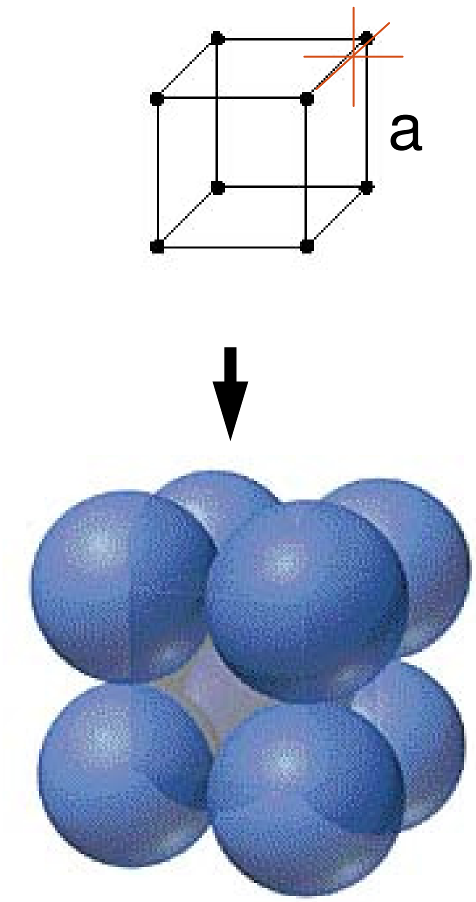
Close Packing of Spheres

- Each sphere is surrounded by 12 other spheres (6 in one plane, 3 above and 3 below).
- Coordination number: the number of spheres directly surrounding a central sphere.
- If unequally sized spheres are used, the smaller spheres are placed in the interstitial holes.

Simple Cubic (SC)

- SC lattice and crystal structure





Coordination number = 6

SC

$$a = 2R$$

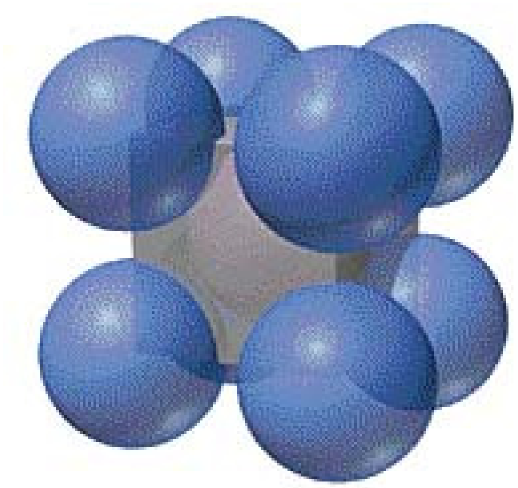
Where:

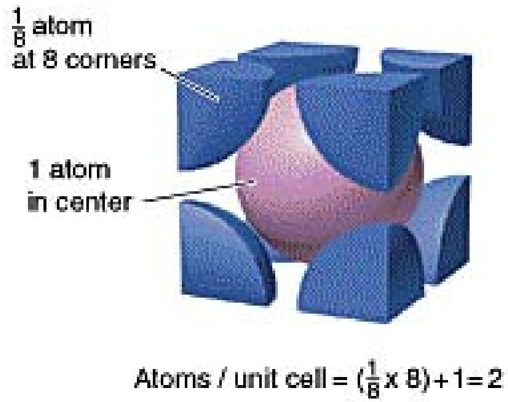
R = atomic radius

a = lattice parameter

Packing fraction = 54%

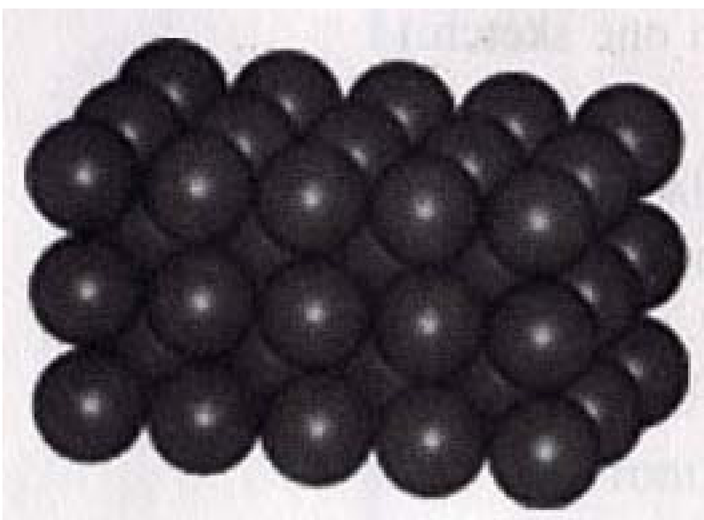
Body Centered Cubic (BCC)





Coordination number = 8

Packing fraction = 68%

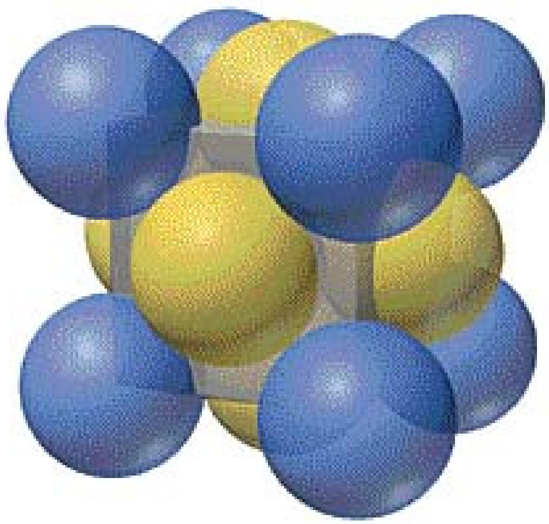


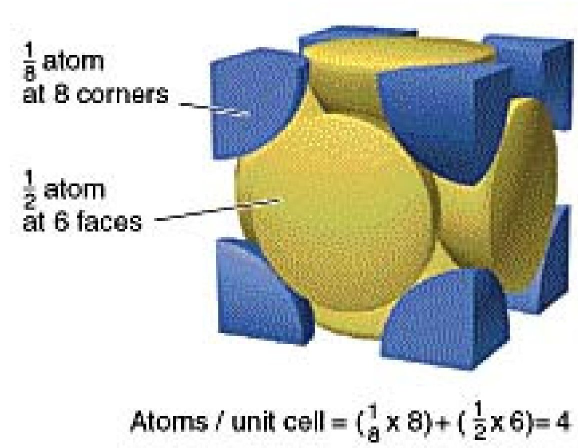
BCC

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

Where:
- R = atomic radius
- a = lattice parameter

Face Centered Cubic (FCC)





Coordination number = 12

A close-packed structure
with a packing fraction of 74%

FCC

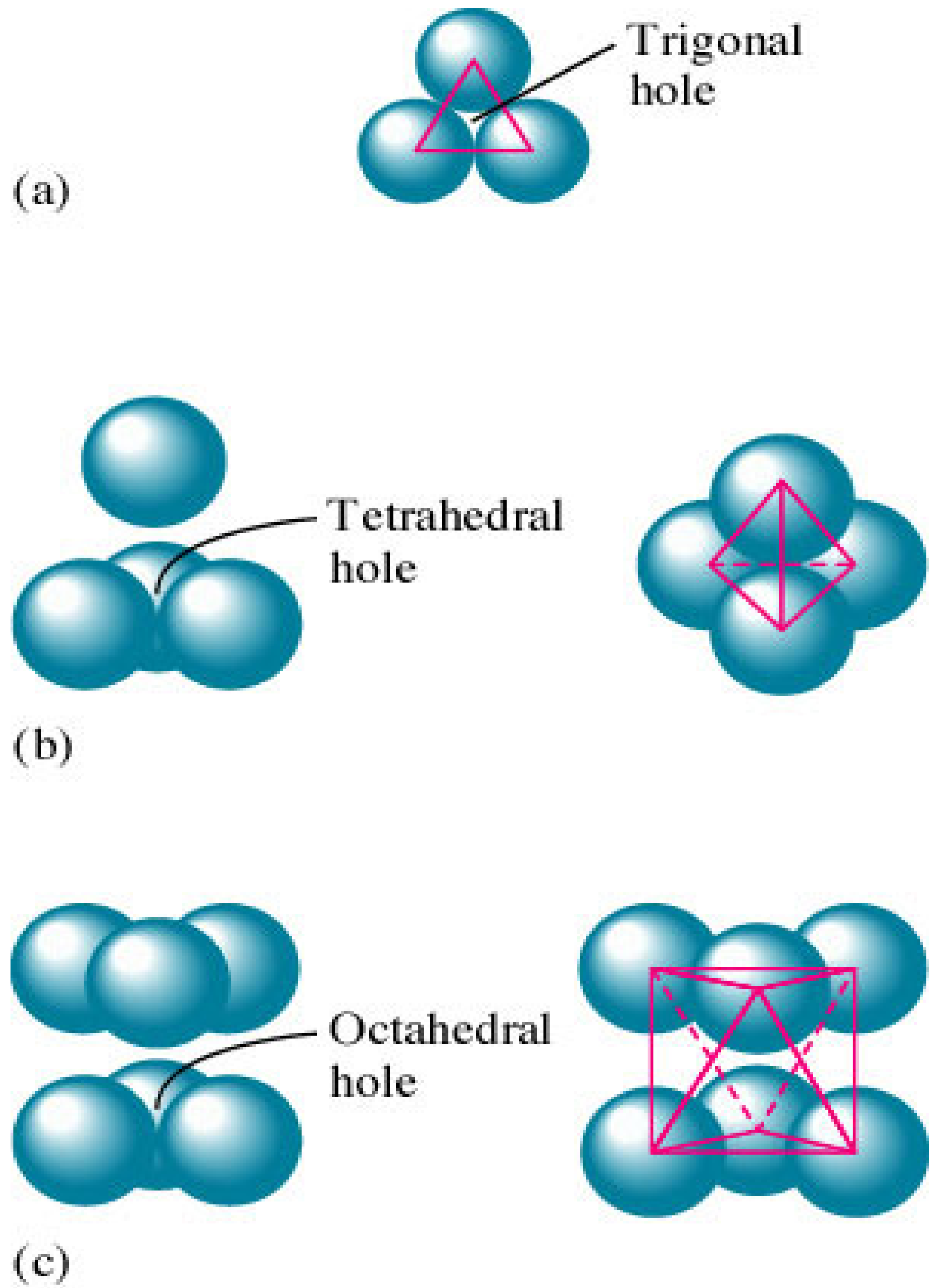
$$a = \frac{4R}{\sqrt{2}}$$

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

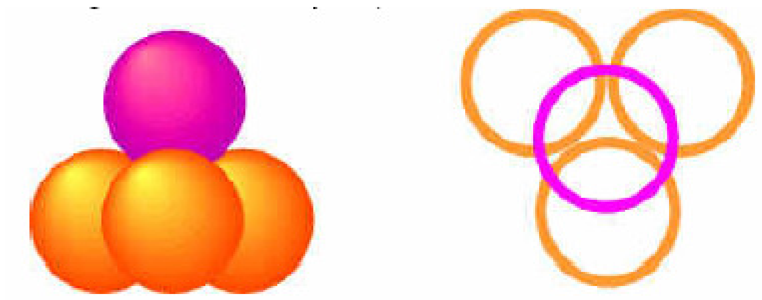
Where:
R = atomic radius
a = lattice parameter

The Holes that Exist Among Closest Packed

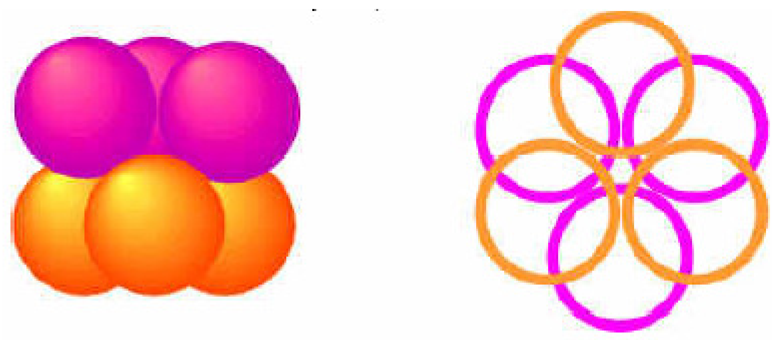
Uniform Spheres



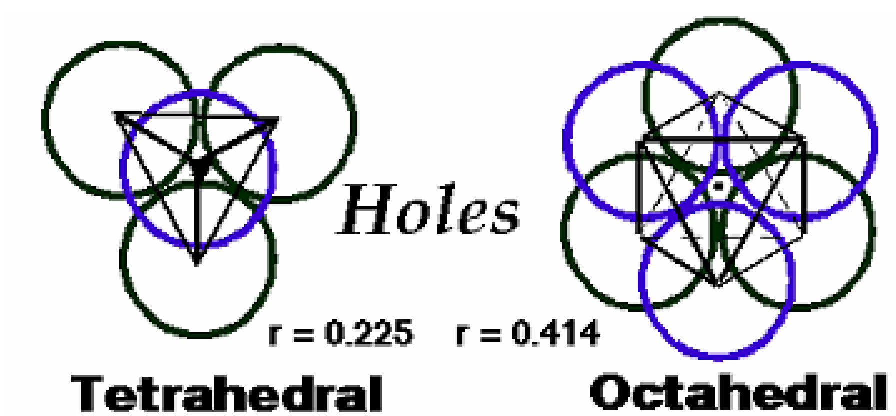
TYPE OF HOLES IN CLOSE PACKING



TETRAHEDRAL HOLES



OCTAHEDRAL HOLES

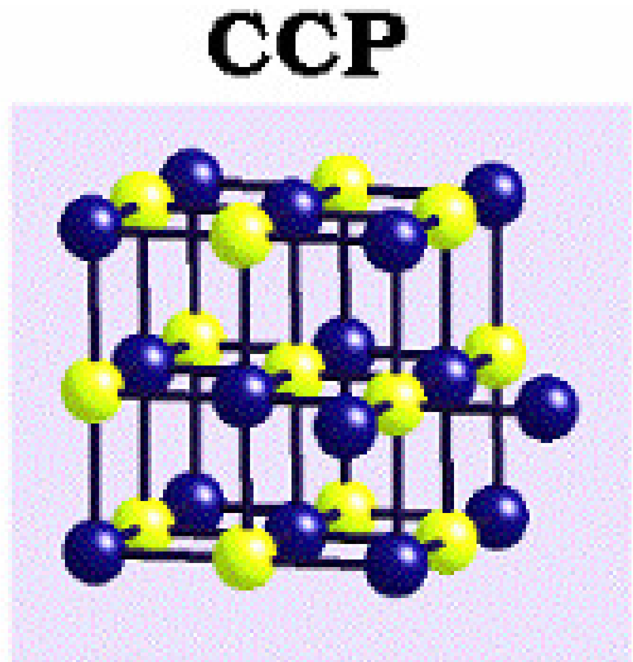


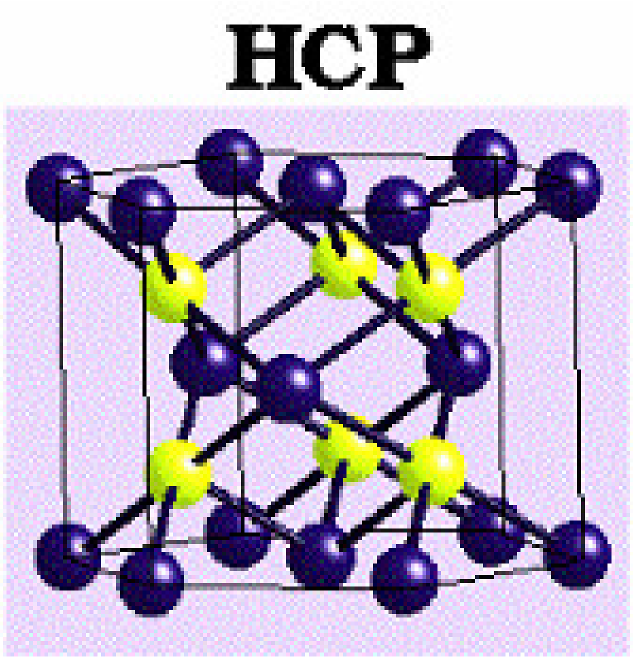
QUESTIONS

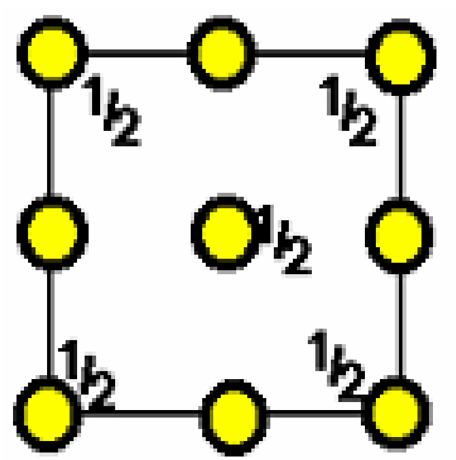
A compound is formed by two elements M & N. The element N forms ccp & atoms of of M occupy 1/3rd of octahedral voids. What is formula of compound

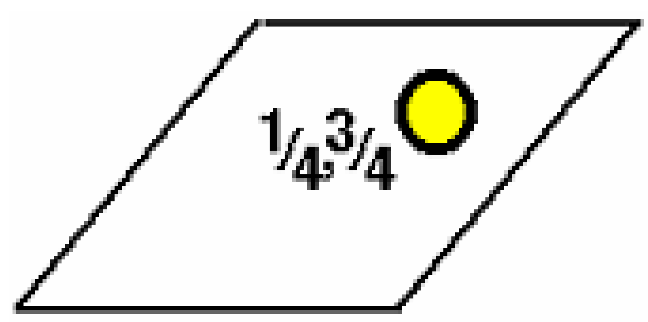
A compound forms hcp structure what is total number of voids in 0.5 moles of it?

LOCATION OF OCTAHEDRAL HOLES IN CLOSE PACKING

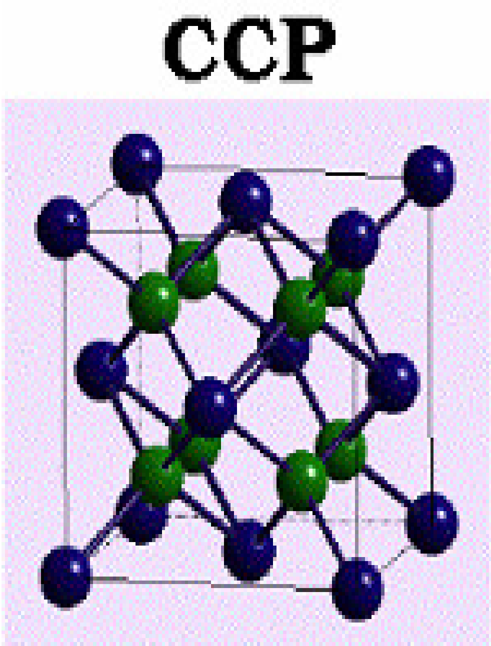


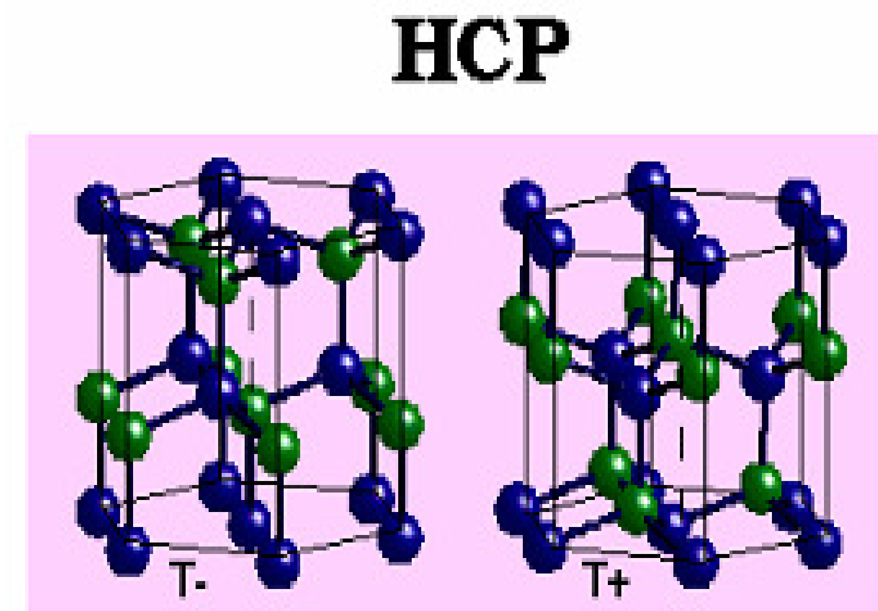


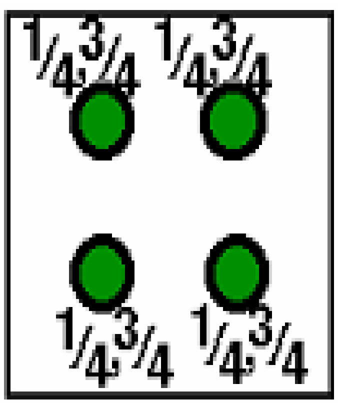


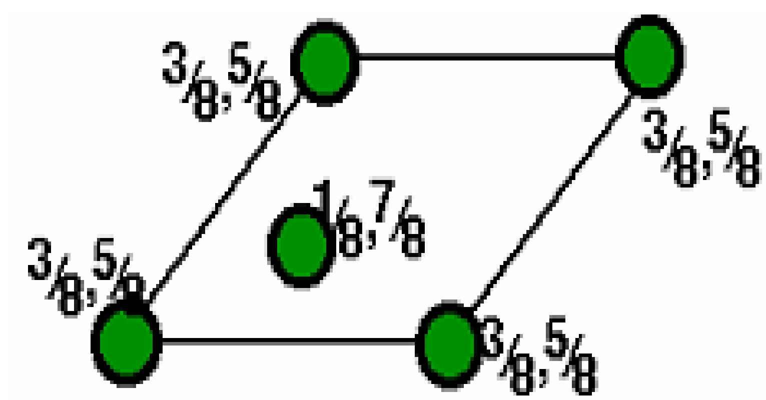


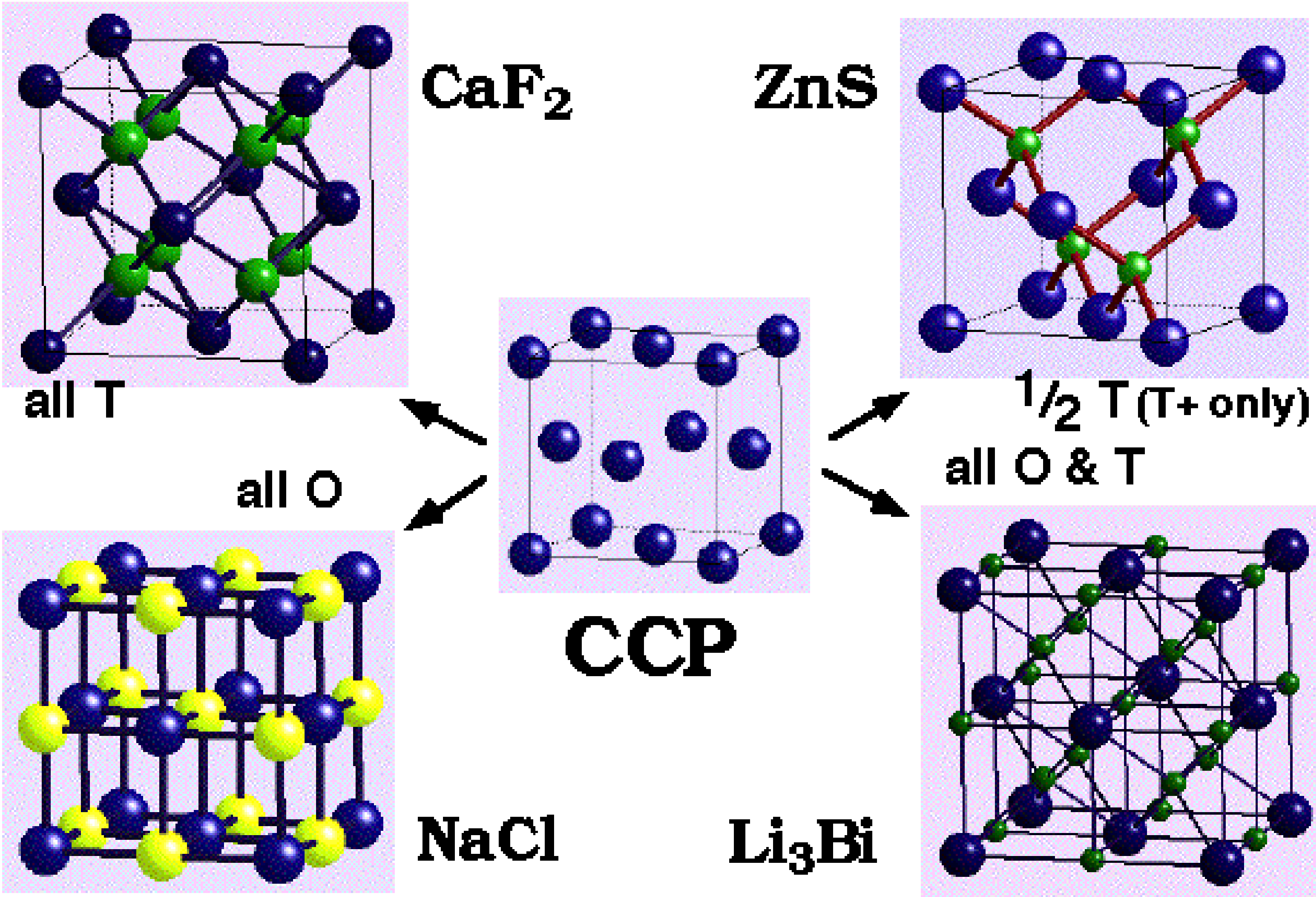
Location Of Tetrahedral Holes In Close Packing











HOLE FILLING IN CCP

RADIUS RATIO RULE

$$\text{Radius ratio} = \frac{\text{Radius of the positive ion}}{\text{Radius of the negative ion}}$$

Radius ratio	Coordination number	Structural Arrangement
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 1	8	BCC

Density Calculation

$$\text{Density} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= Z \times M / a^3 \times N_o$$

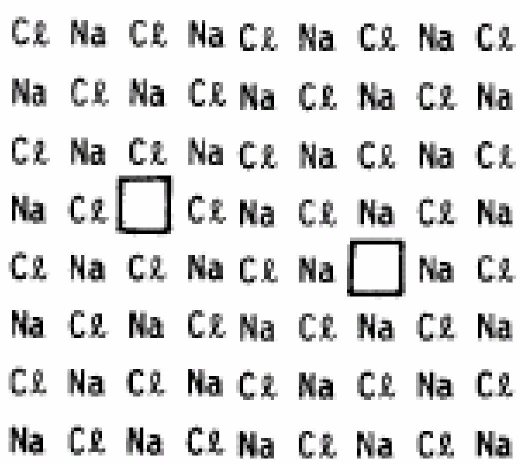
Z = No. of particles per unit cell
M= Gram molecular mass
a = edge length
N_o = Avogadro number

Questions

- CsCl has bcc structure if the edge length is 400pm Calculate its density. GMM of CsCl is 168.5 gm/mole.

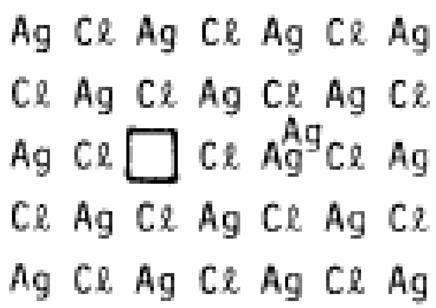
Any departure from perfect orderly arrangement of atoms in a crystal constitutes a defect

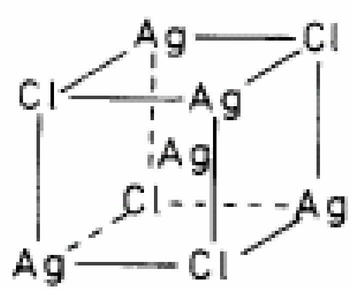
- Stoichiometric defects
- Impurity defects
- Non Stoichiometric defects



Schottky defects

-200 kJmol^{-1} creation energy





Frenkel defects

-130 kJmol^{-1} creation energy

Schottky Defect & Frenkel Defect

Schottky Defect

- Missing of some atoms or ions from their normal sites
- Cations & anions are of same sizes
- High co-ordination no.
- NaCl KCl

Frenkel Defect

- Ion is missing from from normal position and occupies an interstitial site
- Anions are of much larger size than cations
- Low coordination no.
- AgCl AgBr

Effects of Stoichiometric Defect

- Increase in electrical conductivity
- Change in density
- Stability

Extrinsic defects (due to impurities)

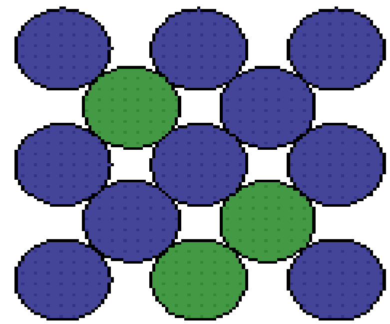
Impurities or ***dopants*** in a solid are any atom(s) of a type that do not belong in the perfect crystal structure (see 'extrinsic semiconductors')

The host crystal with impurities is called a ***solid solution***

Substitutional solid solutions

Impurity atoms occupy the same sites of the **host atoms**

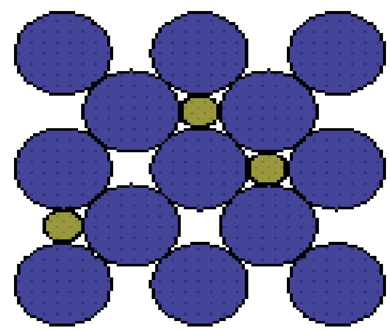
Impurities "substitute" for the host atoms



Interstitial solid solutions

Impurity atoms occupy interstices in the **host crystal** structure

Impurities usually have a small size compared to the host atoms



NON-STOICHIOMETRIC COMPOUNDS

Non-stoichiometric compounds are characterised by non-integer stoichiometric indices in their chemical formula

Non-stoichiometric compounds usually exhibit a *range of compositions*

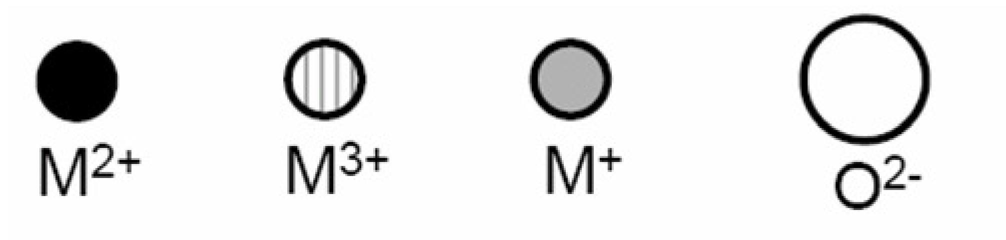
$Zr_{1-x}Ca_xO_{2-\delta}$ $0.1 \leq \mathbf{x} \leq 0.2$

$La_{1-x}A_xMnO_3$ with A = Ca^{2+}, Sr^{2+}, Ba^{2+} and $0 \leq \mathbf{x} \leq 1$

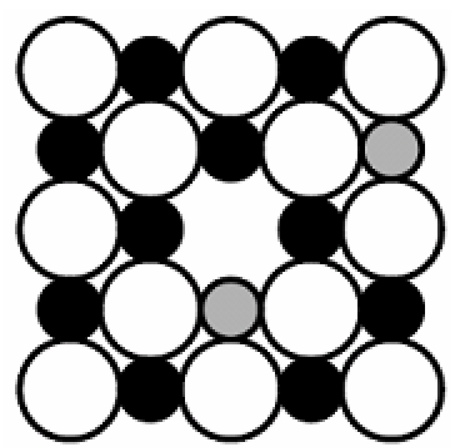
$La_{2-x}A_xCuO_4$ with A = Ca^{2+}, Sr^{2+}, Ba^{2+} and $0 \leq \mathbf{x} \leq 2$

Compounds containing transition metals are likely to show non-stoichiometry, due to the variable oxidation state of the transition metal cations

There are four types of non-stoichiometry in transition metal monoxides

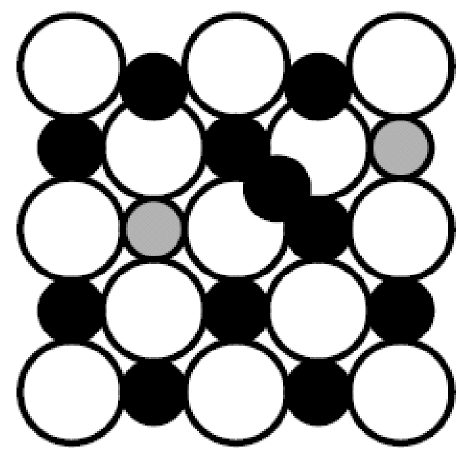


1. Anion vacancies MO_{1-x}



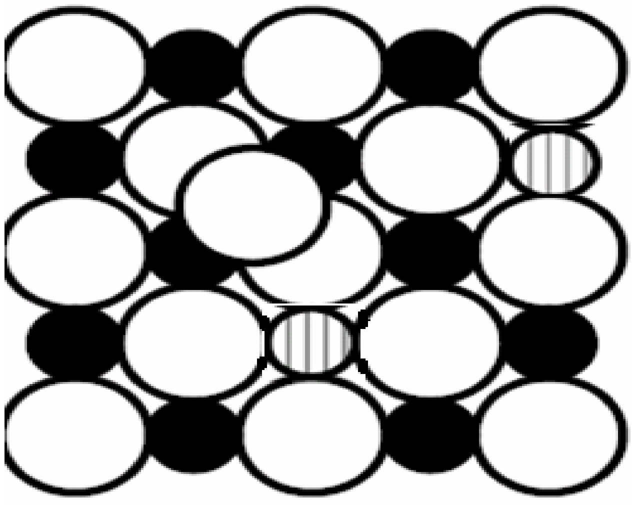
1 O^{2-} vacancy ⟶ 2 M^{2+} reduced to M^{+}

2. Interstitial cations $M_{1+x}O$



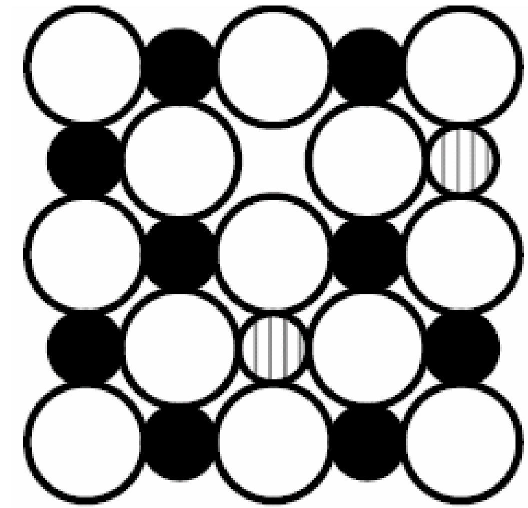
1 interstitial M^{2+} ⟶ 2 M^{2+} reduced to M^{+}

3. Interstitial anion MO_{1+x}

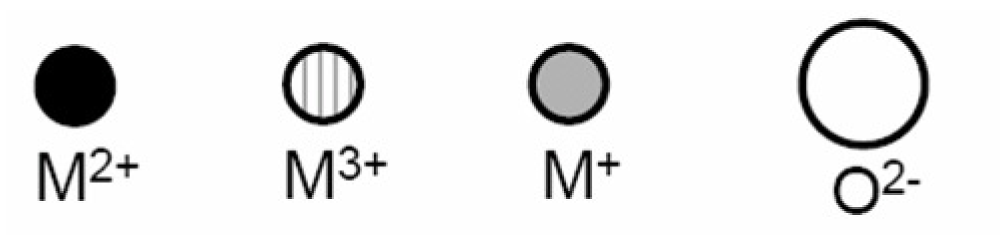


1 interstitial O^{2-} → 2 M^{2+} oxidised to M^{3+}

4. Cation vacancies $M_{1-x}O$



1 M^{2+} vacancy → 2 M^{2+} oxidised to M^{3+}



NON-STOICHIOMETRY IN WUSTITE

FeO is always deficient in iron: this deficiency can be originated in two ways

1. Fe vacancies $Fe_{1-x}O$
2. O excess FeO_{1+x}

A comparison of theoretical and measured densities distinguishes between the alternatives

Example of calculations to establish the nature of defects

A crystal of FeO was found to have a unit cell dimension of 430.1 pm, a measured density of 5.728×10^3 Kg m^{-3} and an iron to oxygen ratio of 0.945. Determine whether the defect in this sample is due to iron vacancies or interstitial oxides

$$V_{UC} = (430.1)^3 = 79562482.9\,pm^3 = 7.9562\times10^{-29}\,m^3$$

$$1\,pm = 10^{-12}\,m; (1\,pm)^3 = 10^{-36}\,m^3$$

Mass of contents for iron vacancies

The content of the unit cell is 4 oxide anions and 4 × 0.945 iron cations.

$$[(4\times 55.86\times 0.945)+(4\times 16.00)]/(N_A\times 10^3)kg = 4.5691\times 10^{-25}kg$$

$$\frac{4.5691\times 10^{-25}kg}{7.9562\times 10^{-29}m^3} = 5.7428\times 10^3 kg\cdot m^{-3}$$

Mass of contents for oxygen interstitial

The content of the unit cell is 1/0.945 oxide anions and 4 iron cations.

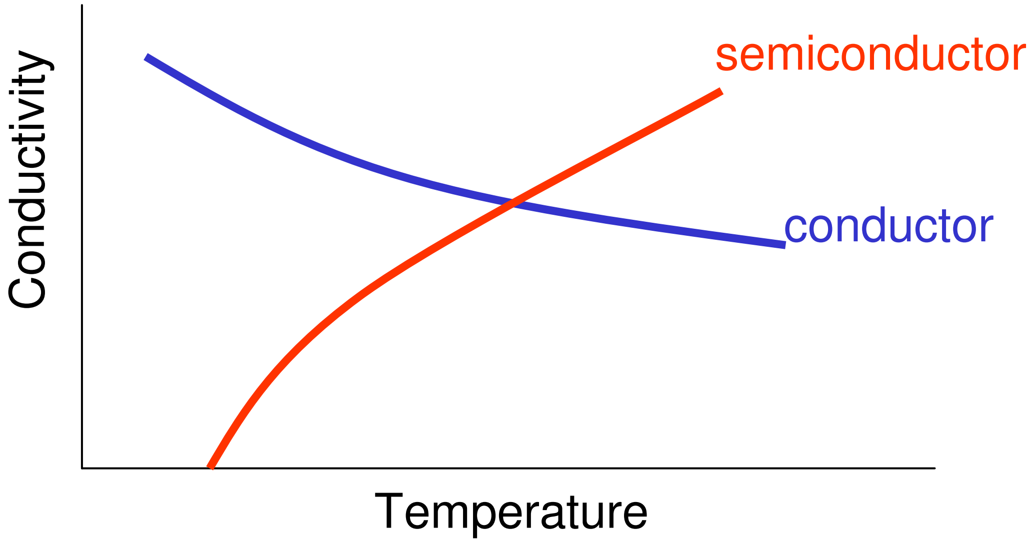
$$\left[(4\times 55.86)+\left(4\times 16.00\times {}^{1}\!/_{0.945}\right)\right]/(N_A\times 10^3)kg = 4.8350\times 10^{-25}kg$$

$$\frac{4.8350\times 10^{-25}kg}{7.9562\times 10^{-29}m^3} = 6.0770\times 10^3 kg\cdot m^{-3}$$

Answer: comparing the density calculated assuming that the defects are due to cation deficiency with the density calculated assuming that the defects are due to interstitial oxygen, it is clear that the defects are due to cation deficiency

Chemical formula is $Fe_{0.945}O$

CONDUCTIVITY IN INORGANIC SOLIDS



Semiconductors: a substance with an electric conductivity that increases with temperature

Metallic Conductor: a substance with an electric conductivity that decreases with temperature

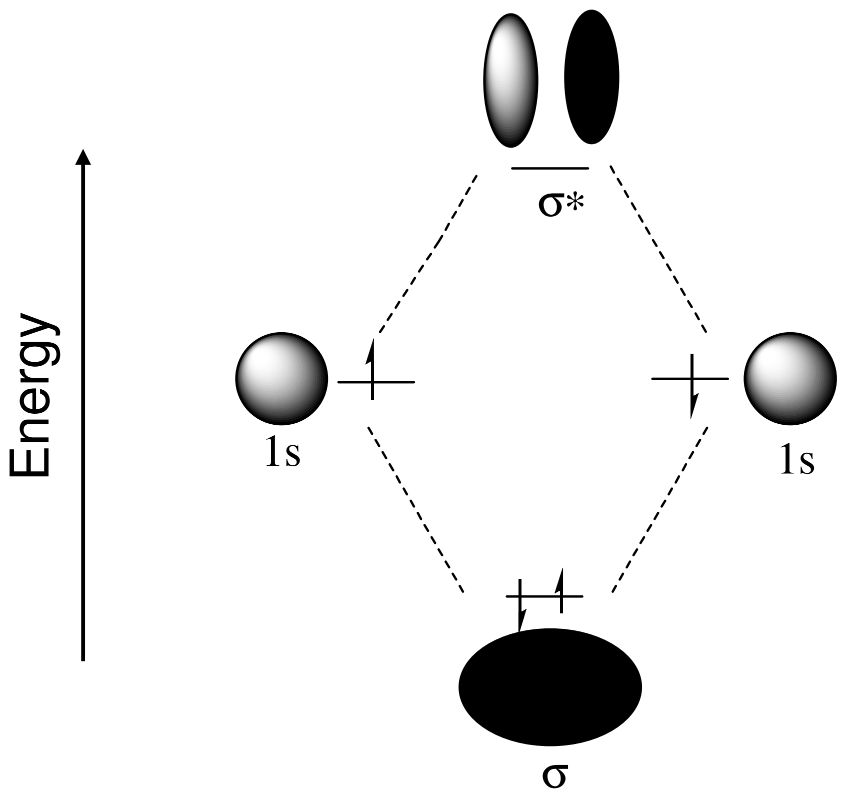
Insulator: a substance with a very low electrical conductivity

Superconductors: special class of materials which show electrical conductivity with zero resistance

BAND THEORY

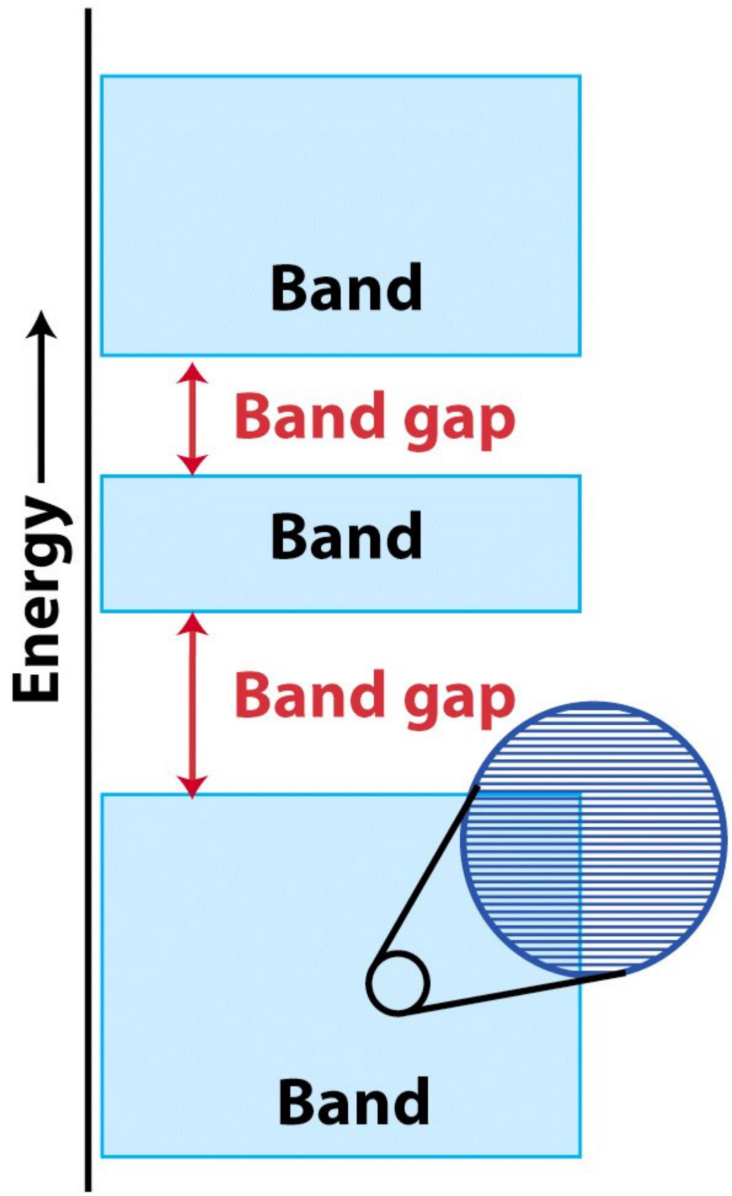
Extension of **Molecular Orbital theory** (tight-binding approximation)

Molecular orbitals are formed by overlapping of atomic orbitals



MO for H_2

The overlap of atomic orbitals in solids gives rise to **bands** of energy levels separated by energy **gaps**



If N atoms are brought together, **BANDS** of energy levels are generated rather than a few well spaced orbitals

The bands are separated by **GAPS** at energies at which orbitals do not occur

s bands are formed by *s* atomic orbitals

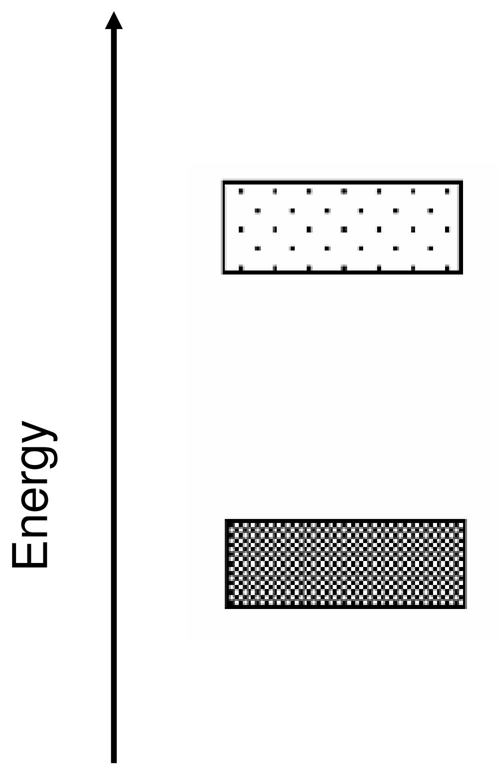
p bands are formed by *p* atomic orbitals

d bands are formed by *d* atomic orbitals

There may or may not be a ***Band Gap*** between s bands and p bands

Band structure for insulators, conductors and semiconductors

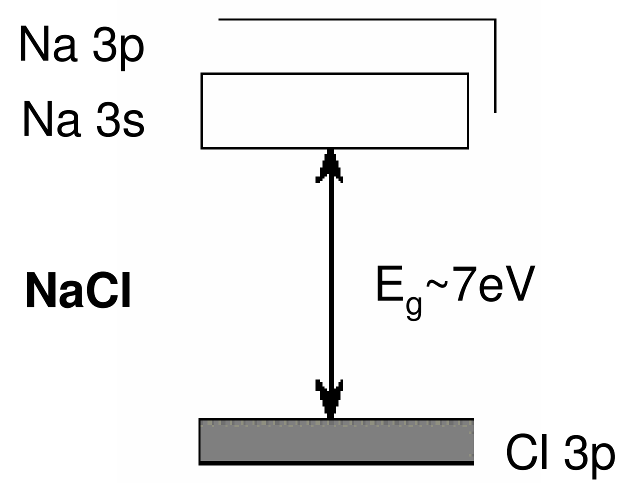
Insulators



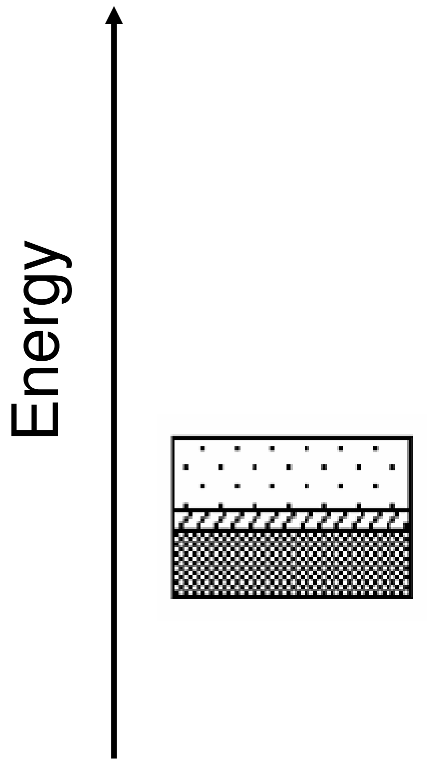
Large gap between lower and upper band

Electrons in the occupied levels do not have any access to unoccupied levels

Conductivity is very low

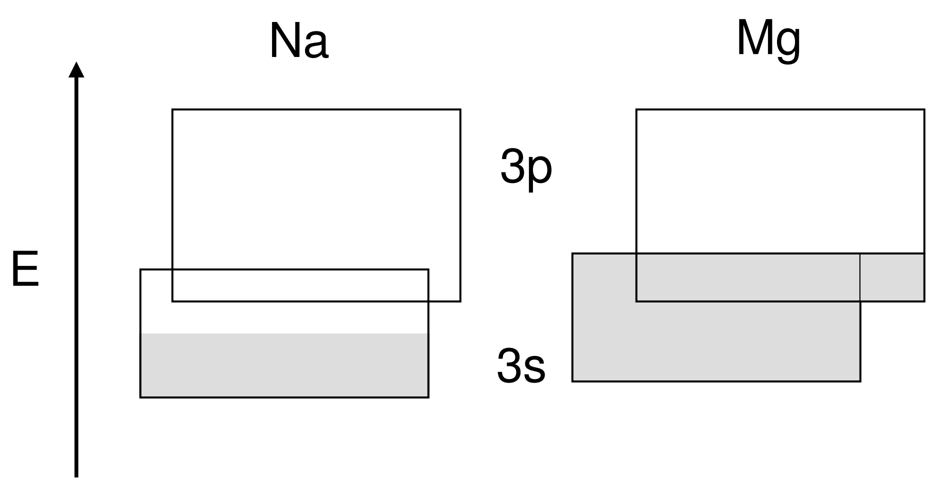


Conductors

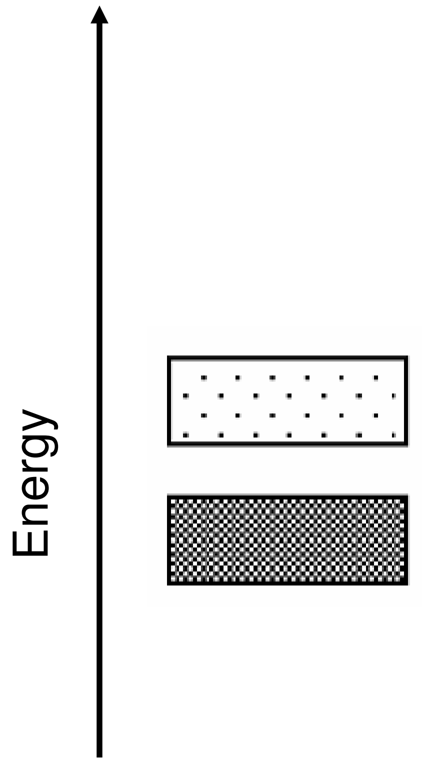


Conductors are characterised by an overlapping between the lower and upper bands

Metals



Semiconductors



Small energy gap between the valence and the conduction bands

A portion of electrons can promoted into the conducting band

⇩

Conductivity

Conductivity can be achieved by temperature or doping

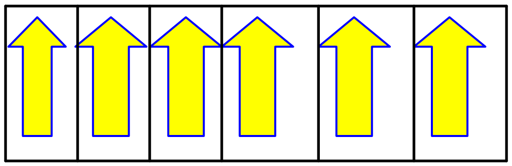
There are two types of semiconductors:

Intrinsic semiconductors

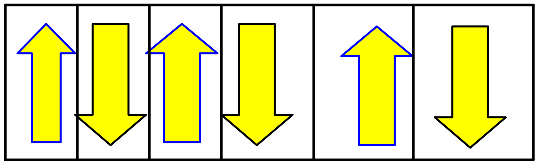
Extrinsic semiconductors

Magnetic Properties

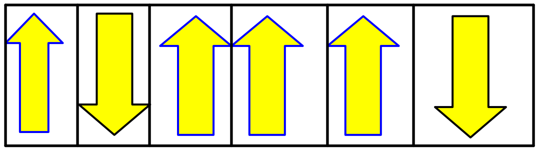
- Diamagnetic : H_2O, NaCl
- Paramagnetic : Fe^{3+}, O_2
- Ferromagnetic : CrO_2, Ni



- Anti-Ferromagnatic : MnO



- Ferrimagnetic : Fe_3O_4



Questions

- Why $CdCl_2$ added to AgI increases its conductance?
- Zinc oxide is white but it turns yellow on heating?
- Why alkali metal halides don't show Frenkel defect?
- Analysis shows that a metal oxide has formula $M_{0.96}O_{1.00}$. Calculate the % of M^{2+} and M^{3+} ions in the crystal system.