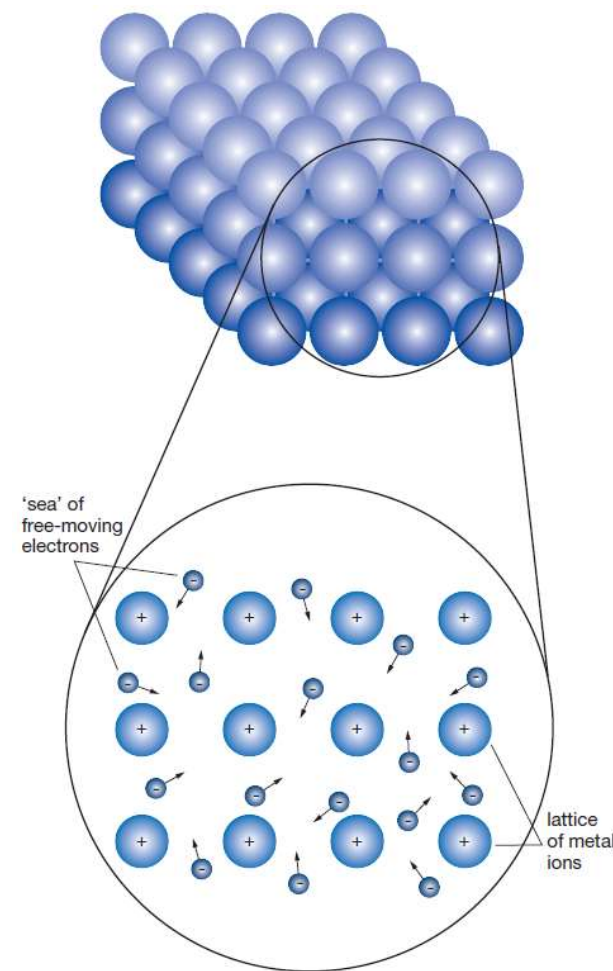


*Most inorganic compounds exist as solids whose structures are regular, space-filling arrangements of the metal atoms. This happens through metallic bonding, which occurs in metals when each atom loses one or more electrons to a common 'sea' of electrons. i.e. delocalization of  $e^-$ s throughout the solid. This accounts for malleability and ductility, common characteristics of a metal. Metallic bonding is non-directional. Lustre of metals is due to reflection of an incident wave of electromagnetic radiation.*

*Ionic bonding occurs between different elements arranged in rigid, symmetrical arrays due to attraction between their opposite charges.*

*Both ionic and metallic bonding are nondirectional, leading to optimal space-filling models that maximize, the quantity and quality of the electrostatic interactions between the ions. The regular patterns of atoms, ions, or molecules in solids in terms of the repeating units that are produced as a result of the efficient methods of filling space.*

*A crystal of an element or compound is defined as a regularly repeating structural unit, comprising atoms, molecules, or ions. The 'crystal lattice' is the pattern formed by the points.*



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	Db	Sg	Bh	Hs	Mt	Ds	Rg							

A metallic bond is the (electrostatic) force of attraction between **positively charged metal ions** and **negatively charged free or mobile (delocalized) electrons**.

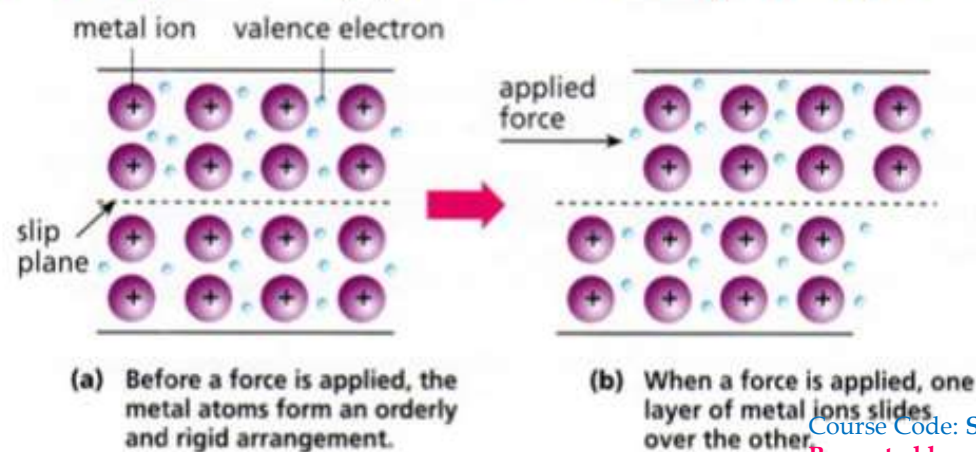
Positive ions immersed in a sea of electrons

- Low ionization energies cause electrons to be loosely held
- So valence electrons move among the atoms and around the many kernels
- “Mobile sea of electrons”

Properties

- Good conductors of electricity and heat as a solid or liquid
- Moderately to very hard (Au vs Zr)
- Lustrous since electrons absorb and emit light as they move around
- Malleable (not brittle)
- High melting point

When a force is applied to a metal, the layers of atoms

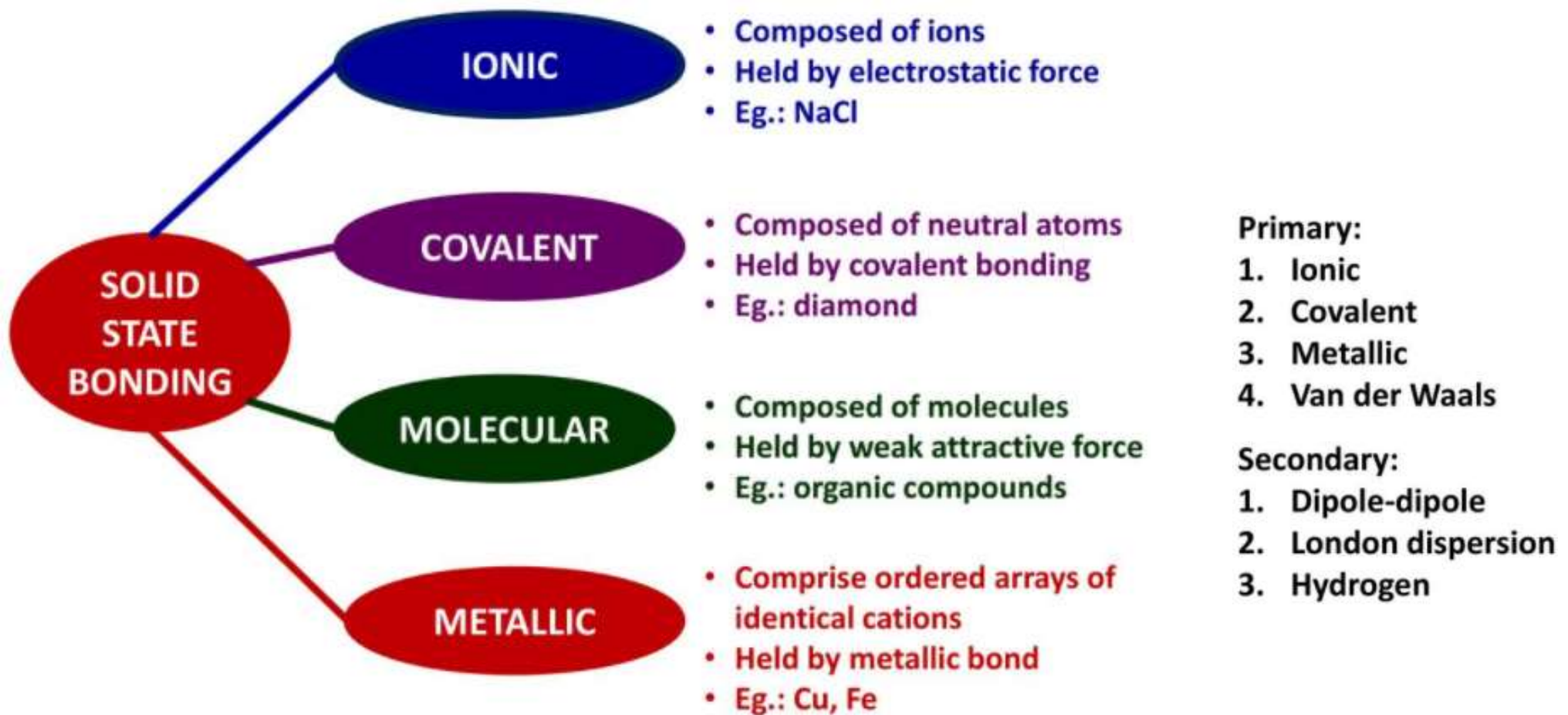


Effect of force being applied on a metal lattice

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Type	Structural Unit	Bonding	Characteristics	Examples
Ionic	Cations and anions	Electrostatic, nondirectional	Hard, brittle, high m.p.; moderate insulators, melts are conducting	alkali metal halides
Extended covalent array	Atoms	Mainly covalent	Strong, hard crystals high m.p.	diamond, silica
Molecular	Molecules	Mainly covalent between atoms in a molecule, van der Waals or H-bonding between molecules	Soft crystals of low m.p.; large coefficient of expansion; insulators	ice, organic compounds
Metallic	Metal atoms	Band model	m.p. varies, good conductors	Fe, Al

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- ❖ Repulsive interaction between atoms is primarily due to electrostatic repulsion of overlapping charge distributions and Pauli principle
- ❖ Several types of attractive forces:
  - Ionic crystals – electrostatic forces between "+" and "-" ions
  - Covalent bond: overlap of charge distributions with antiparallel spin
  - Metals: reduction of kinetic energy of electrons in free state compared to the localized state of a single atom
  - Secondary forces (Van der Waals, hydrogen) become significant when the other bonds are impossible, e.g. in inert gases
- ❖ Physical properties are closely related to the type of bonding

Due to the movement of delocalized electrons  
When heated, the delocalized electrons gain more energy and move faster, colliding with neighbouring electrons. Heat is transferred in these collisions.

Metals are good conductors of:

- **heat** – the free electrons can take in heat energy, which makes them move faster. They can then transfer the energy throughout the lattice.
- **electricity** – the free electrons can carry an electrical charge.

**zinc** , **magnesium** and **copper** are added to **aluminium** to create an alloy that is light but very strong. This is used in building aircraft.

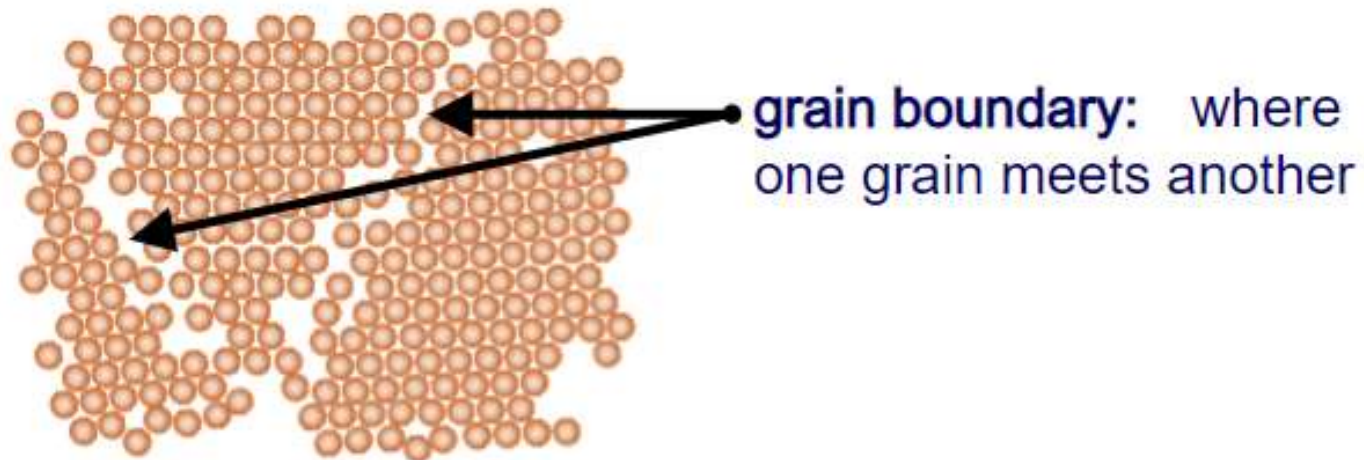
**chromium** and **nickel** are added to **iron** to make **stainless steel** , which is resistant to corrosion.

**tin** and **lead** are mixed together to create **solder** , which has a low melting point and is used to join other metals together.



Metal ions form a lattice which is more tightly packed and **denser** than the lattices in ionic compounds. They form crystals called **grains**.

Layers of atoms can slip over each other in metal grains when a force is applied, but this slippage stops at grain boundaries.



The smaller the grains, the shorter the distance the atom layers can move. This means that metals with smaller grains are stronger and harder than metals with larger grains.

The faster that molten metal is cooled, the smaller the grain size.

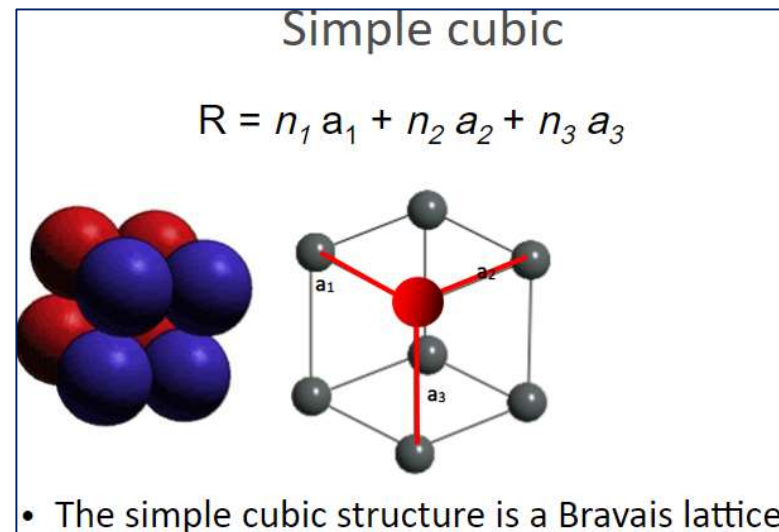
*A crystal of an element or compound is defined as a regularly repeating structural unit, comprising atoms, molecules, or ions. The 'crystal lattice' is the pattern formed by the points.*

*The lattice is defined as a network of three-dimensional, infinite array of identical points, lattice points, each of which is surrounded in an identical way by neighbouring points, that has the translational symmetry of a structure.*

*A unit cell is an imaginary parallel-sided subdivision of a crystal that, when stacked together without rotation or reflection, can reproduce the entire crystal from which it is formed.*

*The relationship between the lattice parameters in three dimensions as a result of the symmetry of the structure gives rise to the seven crystal systems.*

*The angles ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) & lengths ( $a$ ,  $b$ ,  $c$ ) are the unit cell parameters/lattice parameters which define the size and shape of a unit cell; the angle between  $a$  and  $b$  is  $\gamma$ , that between  $b$  and  $c$  is  $\alpha$ , and that between  $a$  and  $c$  is  $\beta$ .*

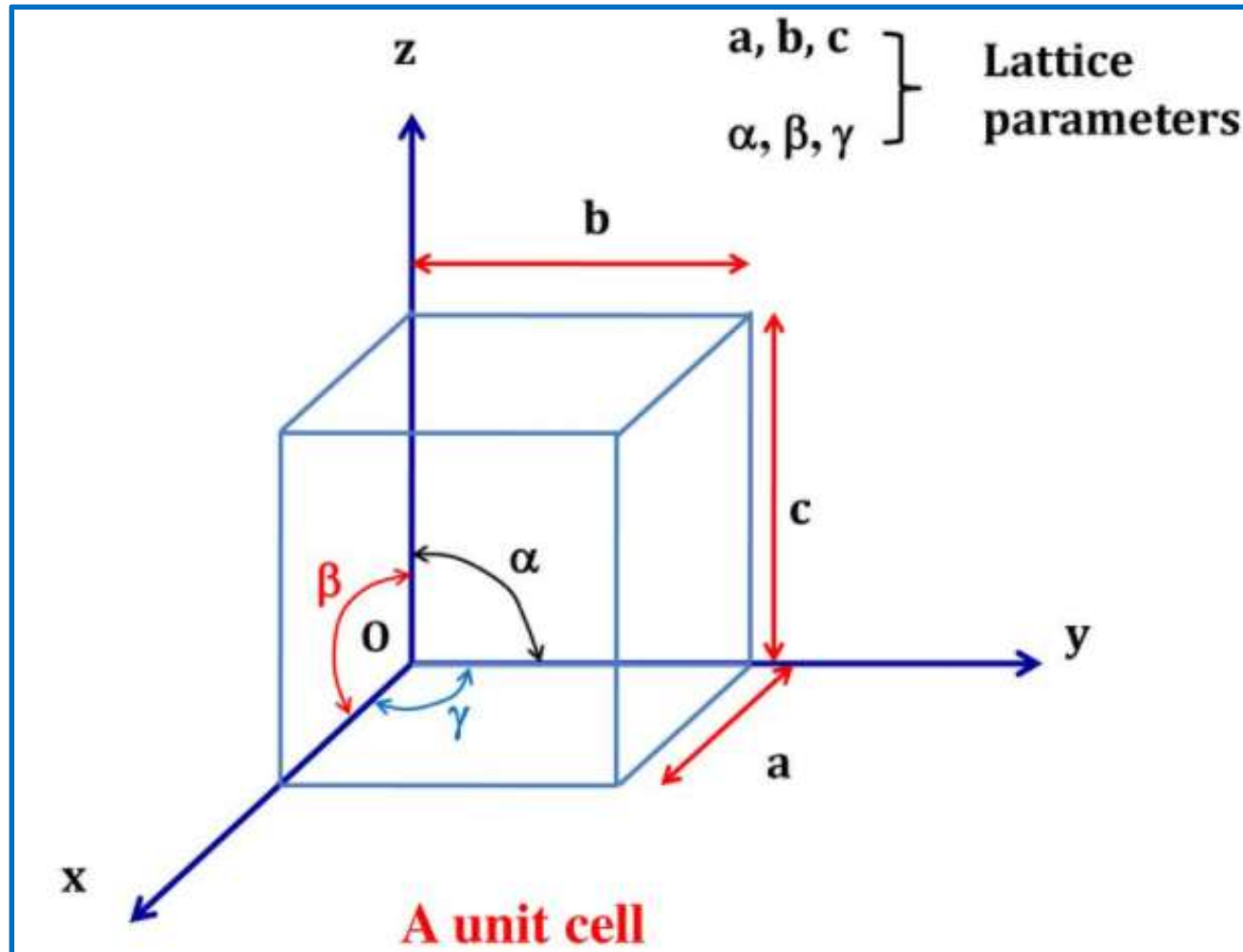


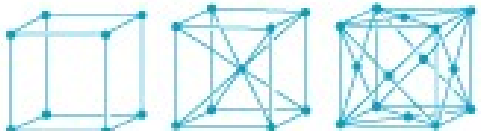

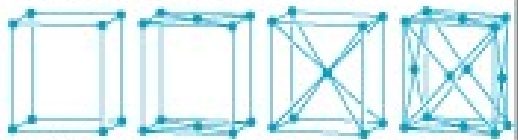

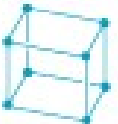

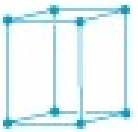
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Bravais lattice cells	Axes and interaxial angles	Examples
 Cubic P    Cubic I    Cubic F	<p>Three axes at right angles; all equal: <math>a = b = c; \alpha = \beta = \gamma = 90^\circ</math></p>	Copper (Cu), silver (Ag), sodium chloride (NaCl)
 Tetragonal P    Tetragonal I	<p>Three axes at right angles; two equal: <math>a = b \neq c; \alpha = \beta = \gamma = 90^\circ</math></p>	White tin (Sn), rutile (TiO <sub>2</sub> ), $\beta$ -spodumene (LiAlSi <sub>2</sub> O <sub>6</sub> )
 P    C    I    F Orthorhombic	<p>Three axes at right angles; all unequal: <math>a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ</math></p>	Gallium (Ga), perovskite (CaTiO <sub>3</sub> )
 Monoclinic P    Monoclinic C	<p>Three axes, one pair not at right angles, of any lengths: <math>a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta</math></p>	Gypsum (CaSO <sub>4</sub> • 2H <sub>2</sub> O)
 Triclinic P	<p>Three axes not at right angles, of any lengths: <math>a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ</math></p>	Potassium chromate (K <sub>2</sub> CrO <sub>7</sub> )
 Trigonal R (rhombohedral)	<p>Rhombohedral: three axes equally inclined, not at right angles; all equal: <math>a = b = c; \alpha = \beta = \gamma \neq 90^\circ</math></p>	Calcite (CaCO <sub>3</sub> ), arsenic (As), bismuth (Bi)
 Trigonal and hexagonal C (or P)	<p>Hexagonal: three equal axes coplanar at 120°, fourth axis at right angles to these: <math>a_1 = a_2 = a_3 \neq c;</math> <math>\alpha = \beta = 90^\circ, \gamma = 120^\circ</math></p>	Zinc (Zn), cadmium (Cd), quartz (SiO <sub>2</sub> ) [P]

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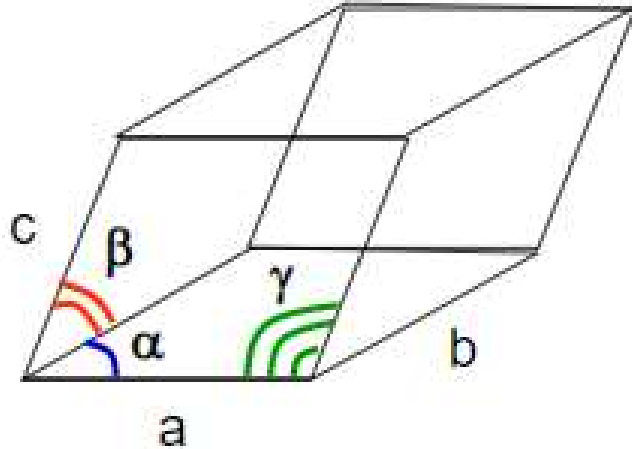
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## Crystal systems



System	Axes	Min sym
<b>Triclinic (1)</b>	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	$1, \bar{1}$
<b>Monoclinic (2)</b>	$a \neq b \neq c, \alpha = \beta = 90^\circ \neq \gamma$	$2, m, 2/m$
<b>Orthrhombic (4)</b>	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	$mm, 22$
<b>Trigonal (1)</b>	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	3
<b>Tetragonal (2)</b>	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	4
<b>Hexagonal (1)</b>	$a = b \neq c, \alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	6
<b>Cubic (3)</b>	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four-3

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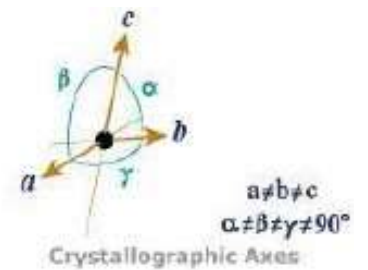
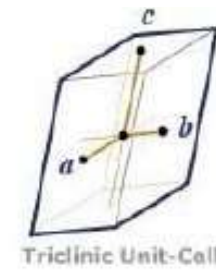
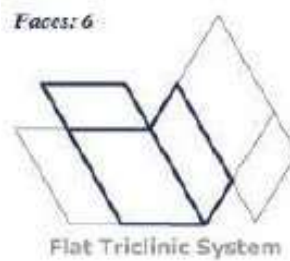
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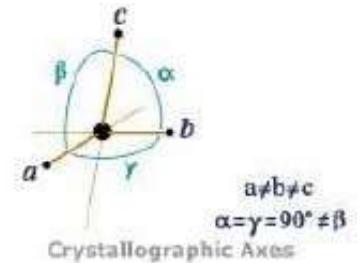
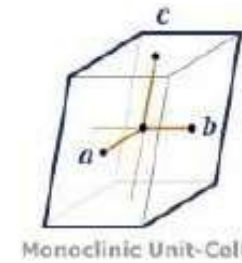
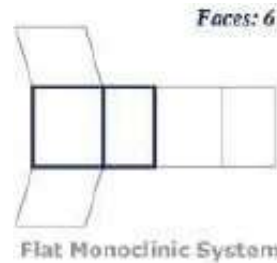
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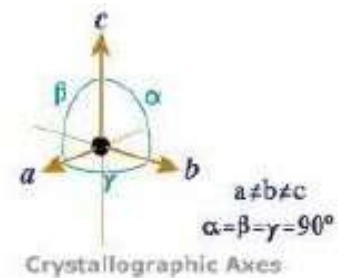
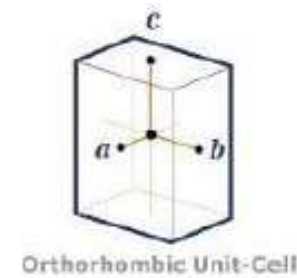
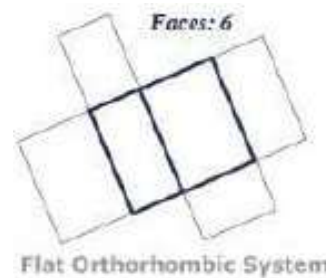
1. *Triclinic: crystals have three unequal sides, intersecting at oblique angles. They have no symmetry axis and no mirrored or prismatic planes.*



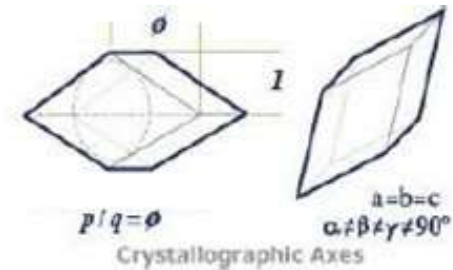
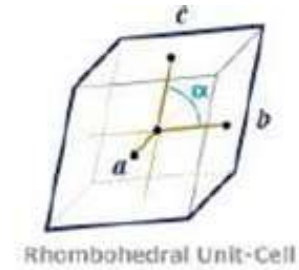
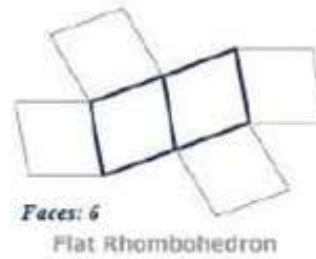
2. *Monoclinic: crystals have three unequal axes. It has three unequal sides, and one two-fold (rotation axis) or one mirror plane called the ortho axis.*



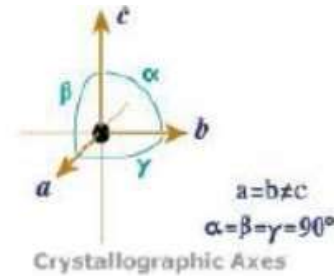
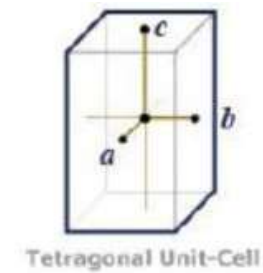
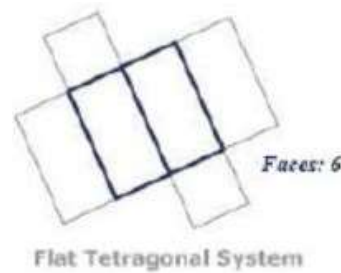
3. *Orthorhombic: crystals have three unequal sides, intersecting at right angles, 3 twofold axes of rotation or, 1 twofold axis of rotation and two mirror planes.*



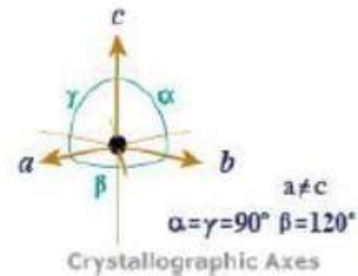
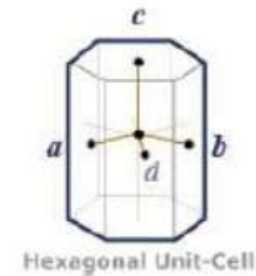
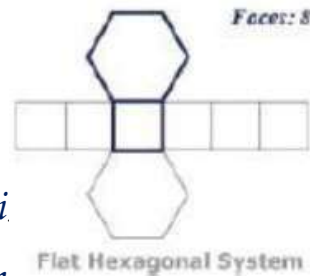
4. Rhombohedral: (trigonal) system has a 1 threefold axis of rotation . If all of the non-obtuse internal angles of the faces are equal it is called a trigonal-trapezohedron.



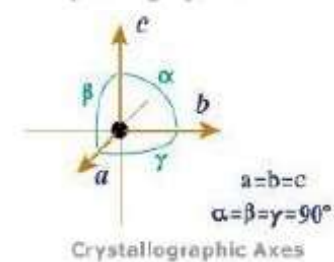
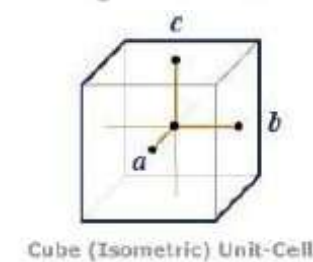
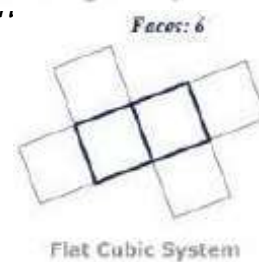
5. Tetragonal: A tetragonal crystal is a 1 fourfold axis of rotation. The tetragonal crystal will have a square base and top, but a height which is taller.



6. Hexagonal: The hexagonal crystal system has one six-fold rotation axis.



7. Cubic: The cubic (Isometric) crystal system is characterized by its total symmetry. It has three equal sides and orthogonal four threefold rotation axes.



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How many different ways can we put atoms into these 7 crystal systems and get distinguishable point environment?

**AUGUST BRAVAIS** (1848) mathematically proved that there are 14 distinct ways to arrange points in space



### 14 BRAVAIS LATTICES

#### The Fourteen Bravais Lattices

<i>Type of symmetry</i>	<i>Lattice</i>	<i>Corresponding crystal system</i>
Cubic	Cube	Regular
	Body-centred cube	
	Face-centred cube	
Tetragonal	Square prism	Tetragonal
	Body-centred square prism	
Orthorhombic	Rectangular prism	Orthorhombic
	Body-centred rectangular prism	
	Rhombic prism	
	Body-centred rhombic prism	
Monoclinic	Monoclinic parallelepiped	Monoclinic
	Clinorhombic prism	
Triclinic	Triclinic parallelepiped	Triclinic
Rhomboidal	Rhombohedron	Trigonal
Hexagonal	Hexagonal prism	Hexagonal

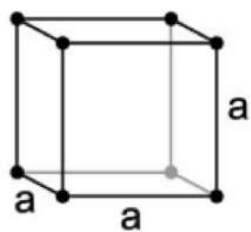
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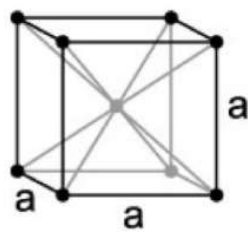


1



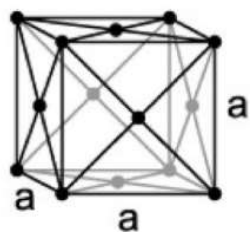
Simple cubic

2



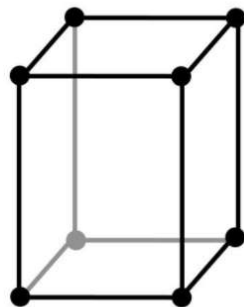
Body-centered cubic

3



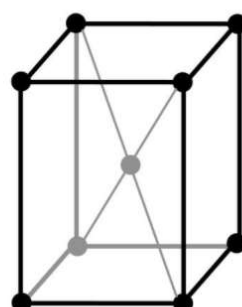
Face-centered cubic

4



Simple tetragonal

5



Body-centered tetragonal

6



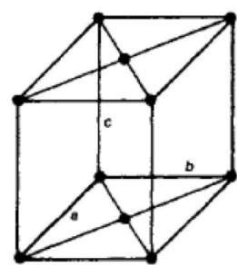
Simple orthorhombic

7

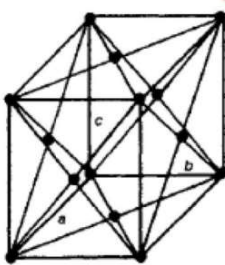


Body-centered orthorhombic

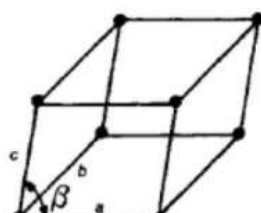
8

BASE-CENTERED  
ORTHORHOMBIC  
(C)

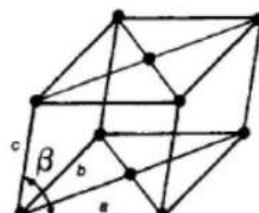
9

FACE-CENTERED  
ORTHORHOMBIC  
(F)

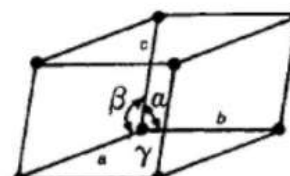
10

SIMPLE  
MONOCLINIC (P)

11

BASE-CENTERED  
MONOCLINIC (P)

12

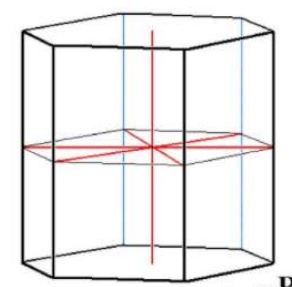


TRICLINIC (P)

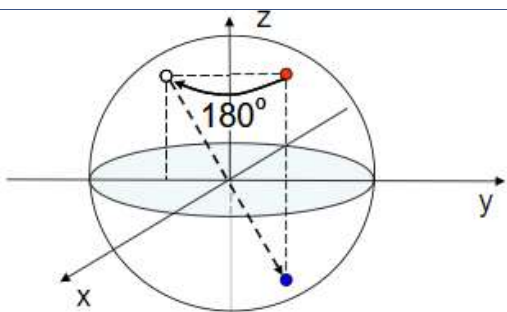
13

RHOMBOHEDRAL  
(R)

14



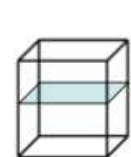
Hexagonal



## Symmetry symbols

$$\bar{2} = m \quad (360^\circ/2 + \text{inversion})$$

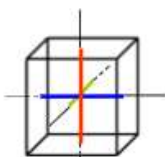
## Symmetry of a cube



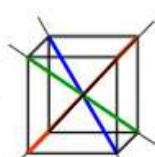
$m$  planes parallel to the faces (3)



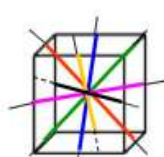
$m$  diagonal planes (6)



4 tetrad axes (3)



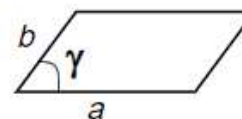
3 triad axes (4)



2 diad axes (6)

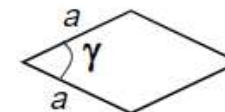
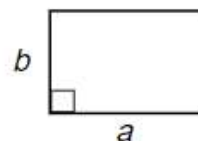
## Symmetry symbols

parallelogram



$$2 \quad (360^\circ/2)$$

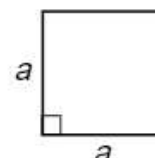
rectangle



rhombus

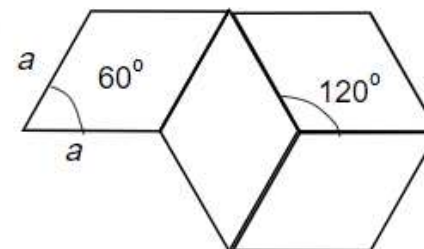
$$2mm \quad (360^\circ/2 - \text{two reflexion})$$

square

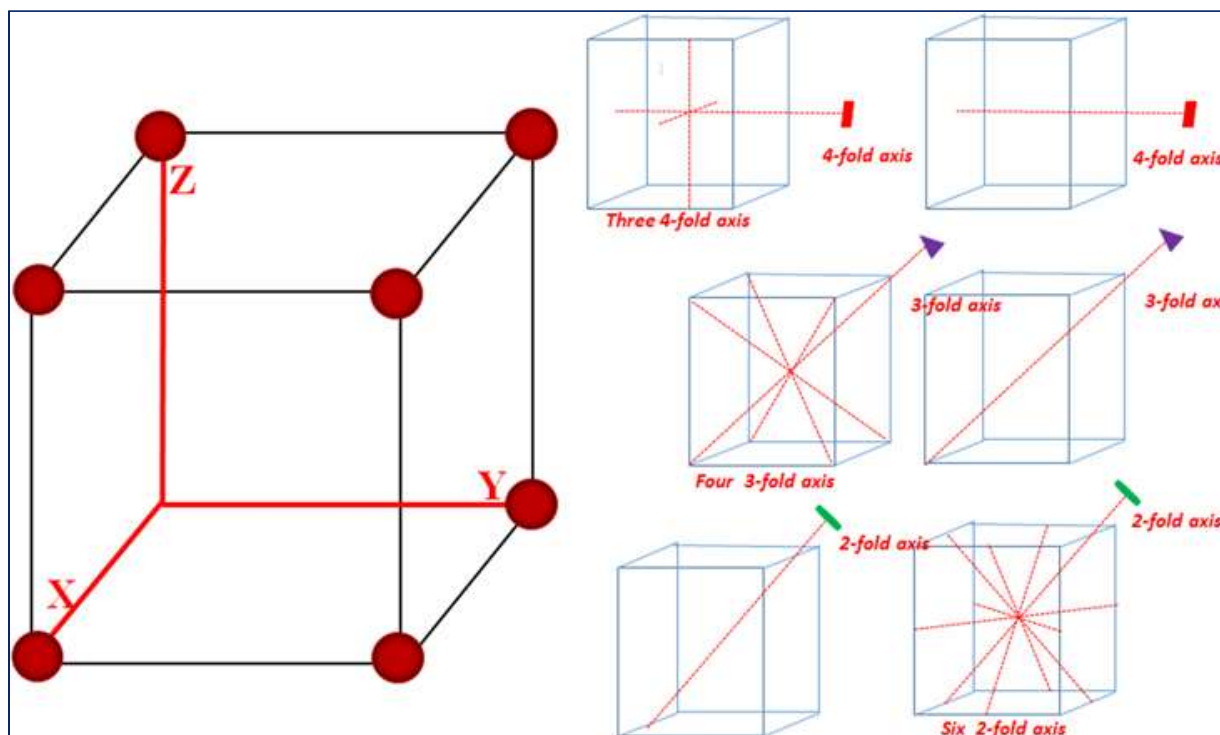


$$4mm$$

triangular net



$$6mm$$



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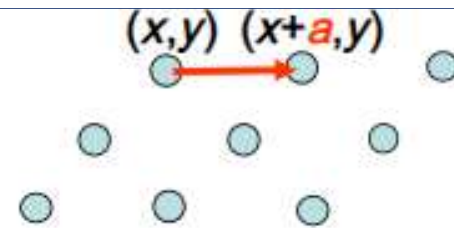
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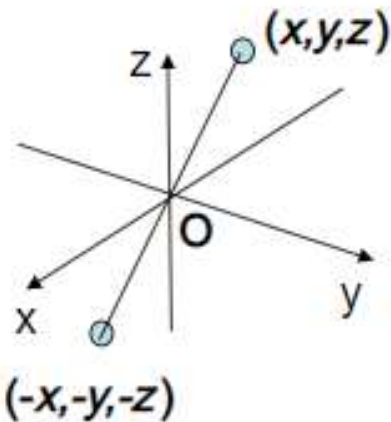
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Crystals possess translation symmetry :  
it remains identical to itself after shifting  
by  $\vec{a}$

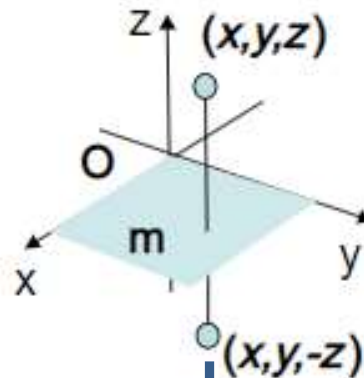


Crystals can possess point group symmetry :

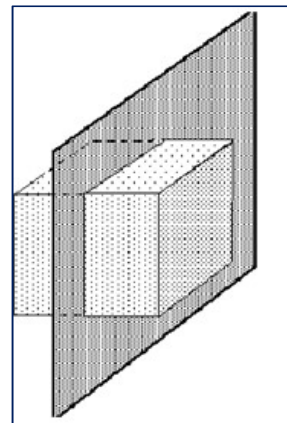
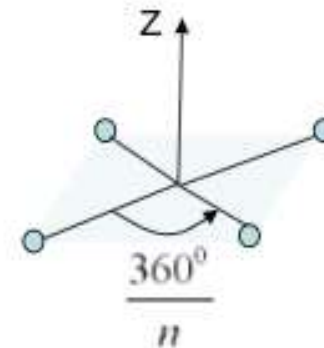
inversion  
 $(x, y, z) \rightarrow (-x, -y, -z)$



reflexion  
 $(x, y, z) \rightarrow (x, y, -z)$



rotation  
 $(x, 0, z) \rightarrow (x \cos \phi, x \sin \phi, z)$   
 $\phi = 360/n, n=1, 2, 3, 4, 6$





## Symmetry

Symmetry is useful when it comes to describing the shapes of both individual molecules and regular repeating structures.

**Point symmetry** - is the symmetry possessed by a single object that describes the repetition of identical parts of the object

**Symmetry operations** - are actions such as rotating an object or molecule ( $\hat{C}_n$ )

**Symmetry elements** - are the rotational axes, mirror planes, etc., possessed by objects

**Schoenflies**- useful in describing the point symmetry of individual molecules (spectroscopists)

**Hermann-Mauguin** - can describe the point symmetry of individual molecules, and also the relationship of different atoms to one another in space (space symmetry)

## Elements of symmetry

In addition to periodicity (translation) each lattice can have other symmetry properties:

- Inversion center  $i$
- Reflection (mirror) plane
- Rotation axes. Only 2-, 3-, 4-, and 6-fold rotations are compatible with translation invariance
- Rotation-inversion axes

## Point symmetry

Every crystal lattice may be described by a particular combination of symmetry operations determined by symmetry of the basis and the symmetry of the Bravais lattice.

There are **32 crystal classes (point groups)**

Combining with translational symmetries, one obtains 230 **space groups**

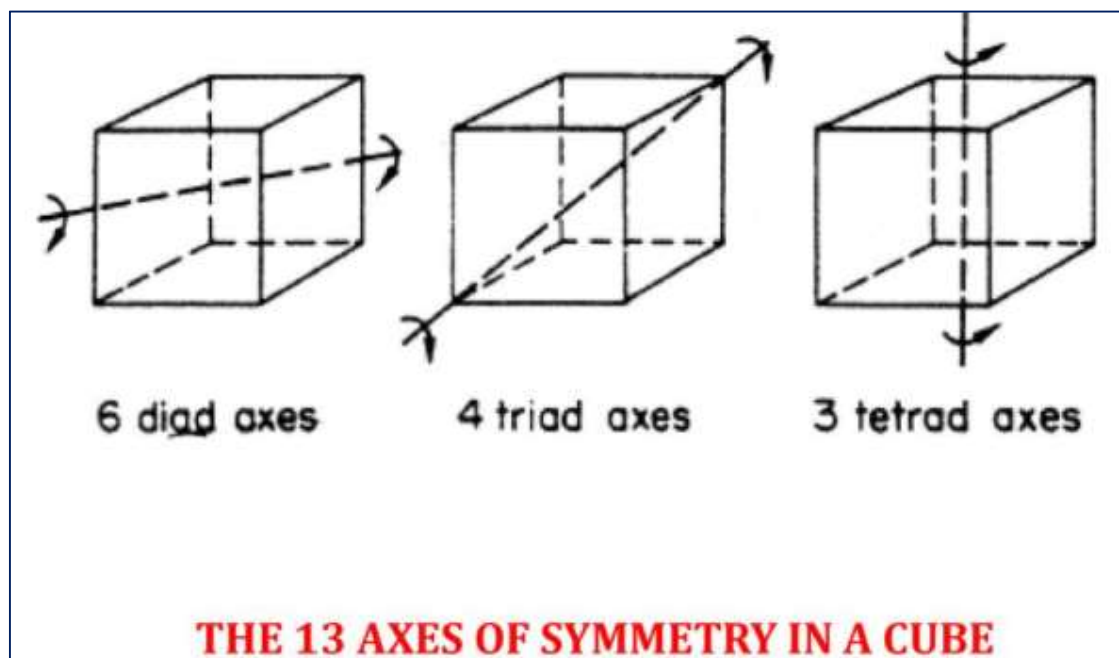
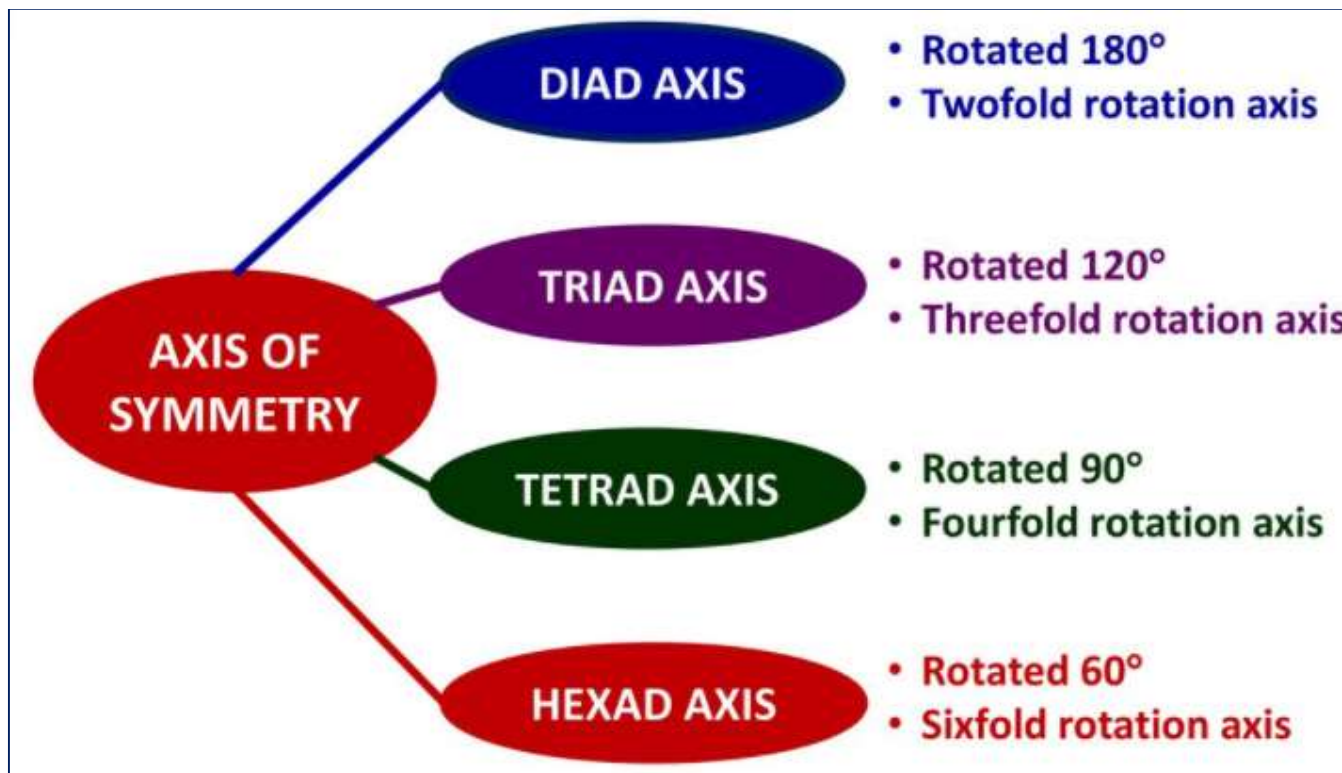
### The three elements of symmetry:

- Symmetry about a point (a center of symmetry)
- Symmetry about a line (an axis of symmetry)
- Symmetry about a plane (a plane of symmetry)

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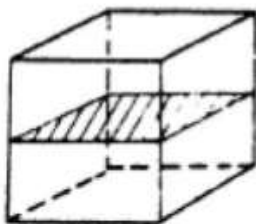
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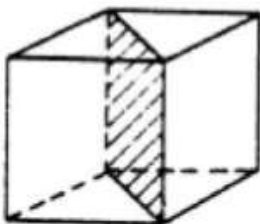
**SYMMETRY ABOUT A PLANE**

A plane of symmetry bisects a solid object in a such manner that one half becomes the mirror image of the other half in the given plane.

A cube has 9 planes of symmetry:



3 rectangular planes



6 diagonal planes

**THE 9 PLANES OF SYMMETRY IN A CUBE**

Cube (hexahedron) is a highly symmetrical body as it has 23 elements of symmetry (a center, 9 planes, and 13 axis)





**ELEMENTS OF SYMMETRY**

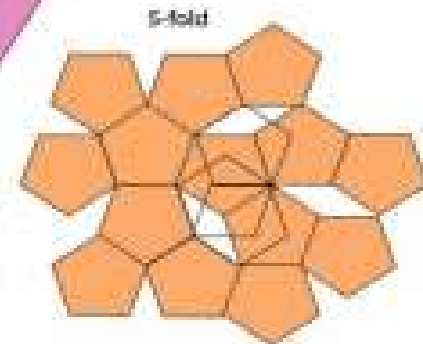
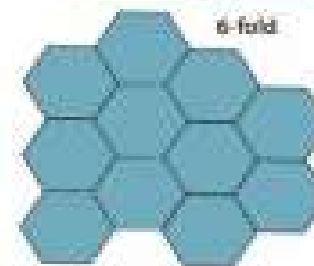
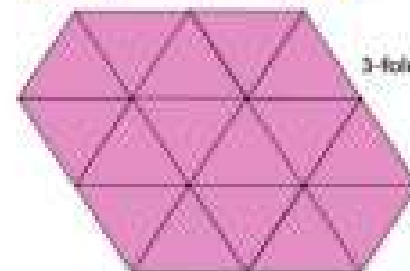
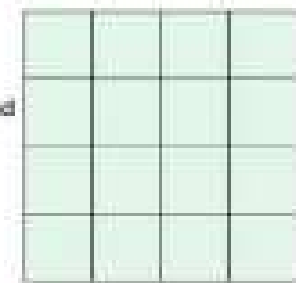
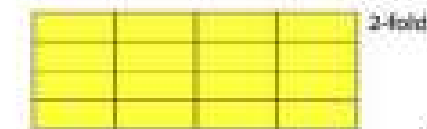
System	Minimum Symmetry Elements
Cubic	Four threefold rotation axes
Tetragonal	One fourfold rotation (or rotation-inversion) axis
Rhombohedral	Three perpendicular twofold rotation (or rotation-inversion) axes
Hexagonal	One sixfold rotation (or rotation-inversion) axis
Monoclinic	One twofold rotation (or rotation-inversion) axis
Triclinic	None



# Symmetry elements with respect to an axis

Rotation angle  $\theta = 360^\circ / X$ ,  
 $X$  = # of rotations

$\theta$	Symbol
1-fold axis: $360^\circ$	1
2-fold axis: $180^\circ$	2 
3-fold axis: $120^\circ$	3 
4-fold axis: $90^\circ$	4 
6-fold axis: $60^\circ$	6 



5-fold, 7-fold, 8-fold, 10-fold (...) axes  
 are not possible in 3 dimensional space.\*

Schoenflies and <u>international</u> symbols of point groups			
System	Schoenflies symbol	International symbol	p
triclinic	$C_1$	1	1
	$C_i$	-1	2
monoclinic	$C_2$	2	2
	$C_{1h}$	m	2
	$C_{2h}$	2/m	4
orthorhombic	$D_2$	222	4
	$C_{2v}$	mm2	4
	$D_{2h}$	2/m 2/m 2/m = mmm	8
tetragonal	$C_4$	4	4
	$S_4$	-4	4
	$C_{4h}$	4/m	8
	$D_4$	422	8
	$C_{4v}$	4mm	8
	$D_{2d}$	-42m	8
	$D_{4h}$	4/m 2/m 2/m = 4/mmm	16
	$C_3$	3	3
trigonal	$C_{3i}$	-3	6
	$D_3$	32	6
	$C_{3v}$	3m	6
	$D_{3d}$	-3 2/m = -3m	12
	$C_6$	6	6
hexagonal	$C_{3h}$	-6	6
	$C_{6h}$	6/m	12
	$D_6$	622	12
	$C_{6v}$	6mm	12
	$D_{3h}$	-62m	12
	$D_{6h}$	6/m 2/m 2/m = 6/mmm	24
	T	23	12
cubic	$T_h$	2/m -3 = m-3	24
	O	432	24
	$T_d$	-43m	24
	$O_h$	4/m -3 2/m = m-3m	48

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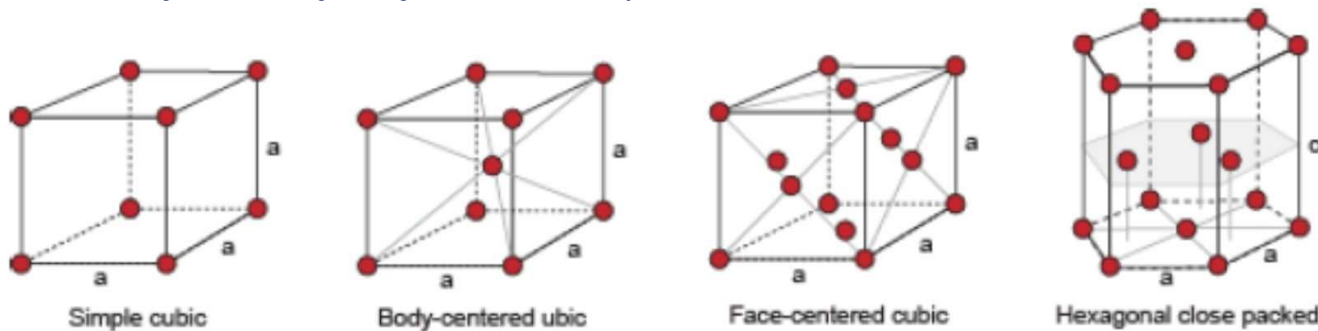
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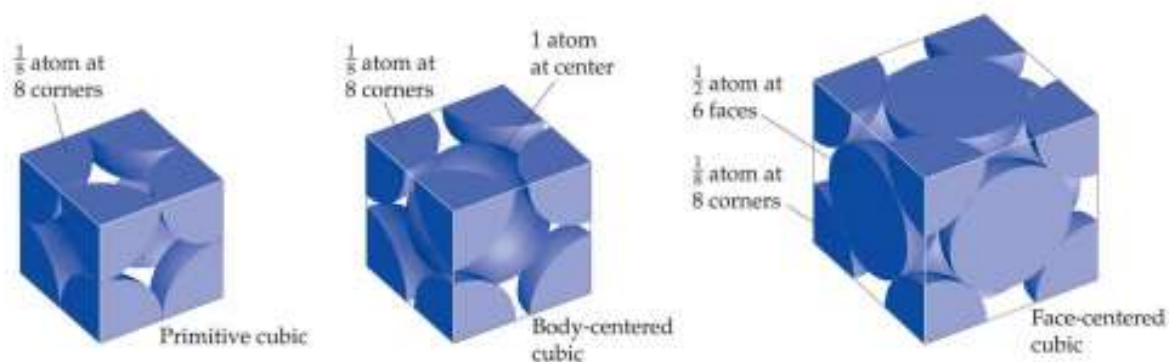
A primitive unit cell  $P$  (simple cubic) has just 1 lattice point in the unit cell. More complex lattice types are body-centred and face-centred (F) with 2 and 4 lattice points in each unit cell, respectively, with additional translational symmetry beyond that of unit cell.

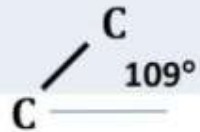


The rules to work out the number of lattice points in a three-dimensional unit cell are:

1. A lattice point in the body of, that is fully inside, a cell belongs entirely to that cell and counts as 1.
2. A lattice point on a face is shared by two cells and contributes  $1/2$  to the cell.
3. A lattice point on an edge is shared by four cells and hence contributes  $1/4$ .
4. A lattice point at a corner is shared by eight cells that share the corner, and so contributes  $1/8$ .

Thus, for face-centred cubic lattice [fcc] the total number of lattice points in the unit cell is  $(8 \times 1/8) + (6 \times 1/2) = 4$ . For the body-centred cubic lattice [bcc], the number of lattice points is  $(1 \times 1) + (8 \times 1/8) = 2$ .



BRAVAIS LATTICE	BASIS	CRYSTAL STRUCTURE	EXAMPLE
FCC	atom	FCC	Au, Al, Cu, Pt
	molecule	FCC	CH <sub>4</sub>
	ion pair (Na <sup>+</sup> and Cl <sup>-</sup> )	Rock salt	NaCl
	Atom pair 	DC (diamond crystal)	Diamond, Si, Ge

### CHARACTERISTIC OF CUBIC LATTICES

	SC	BCC	FCC
Unit cell volume	$a^3$	$a^3$	$a^3$
Lattice point per cell	1	2	4
Nearest neighbor distance	$a$	$a\sqrt{3} / 2$	$a/\sqrt{2}$
Number of nearest neighbors (coordination no.)	6	8	12
Second nearest neighbor distance	$a\sqrt{2}$	$a$	$a$
Number of second neighbor	12	6	6
$a = f(r)$	$2r$	$4/\sqrt{3} r$	$2\sqrt{2} r$
or $4r =$	$a\sqrt{4}$	$a\sqrt{3}$	$a\sqrt{2}$
Packing density	0.52	0.68	0.74

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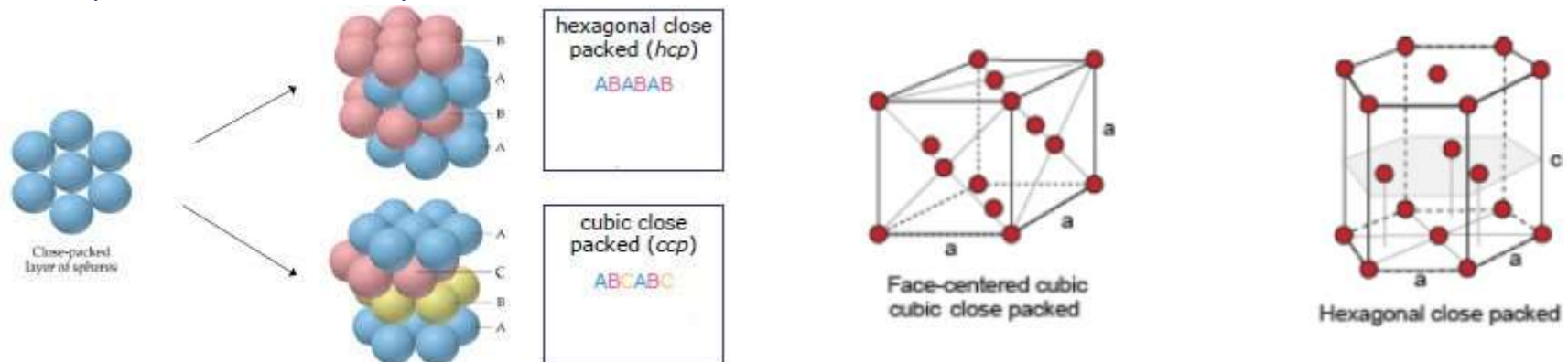


## Fractional atomic coordinates and projections

The position of an atom in a unit cell is normally described in terms of fractional coordinates, coordinates expressed as a fraction of the length of a side of the unit cell. Thus, the position of an atom located at  $x$ a parallel to  $a$ ,  $y$ b parallel to  $b$ , and  $z$ c parallel to  $c$  is denoted  $(x,y,z)$ , with  $0 \leq x, y, z \leq 1$ .

The close packing of spheres can result in a variety of polytypes, of which hexagonal (hcp) and cubic close-packed (ccp) structures are the most common. In absence of covalent bonding, the spheres are free to adopt a close-packed structure, a structure in which there is least unfilled space. The coordination number (CN) of a sphere in a close-packed arrangement of ccp or hcp (the 'number of nearest neighbours') is 12, the greatest number that is allowed by geometry. A non close-packed metal structure of body-centred cubic crystal has CN of 8. e.g. NaCl crystal

Because each ccp unit cell has a sphere at one corner and one at the centre of each face, a ccp unit cell is sometimes referred to as face-centred cubic (fcc) unit cell.

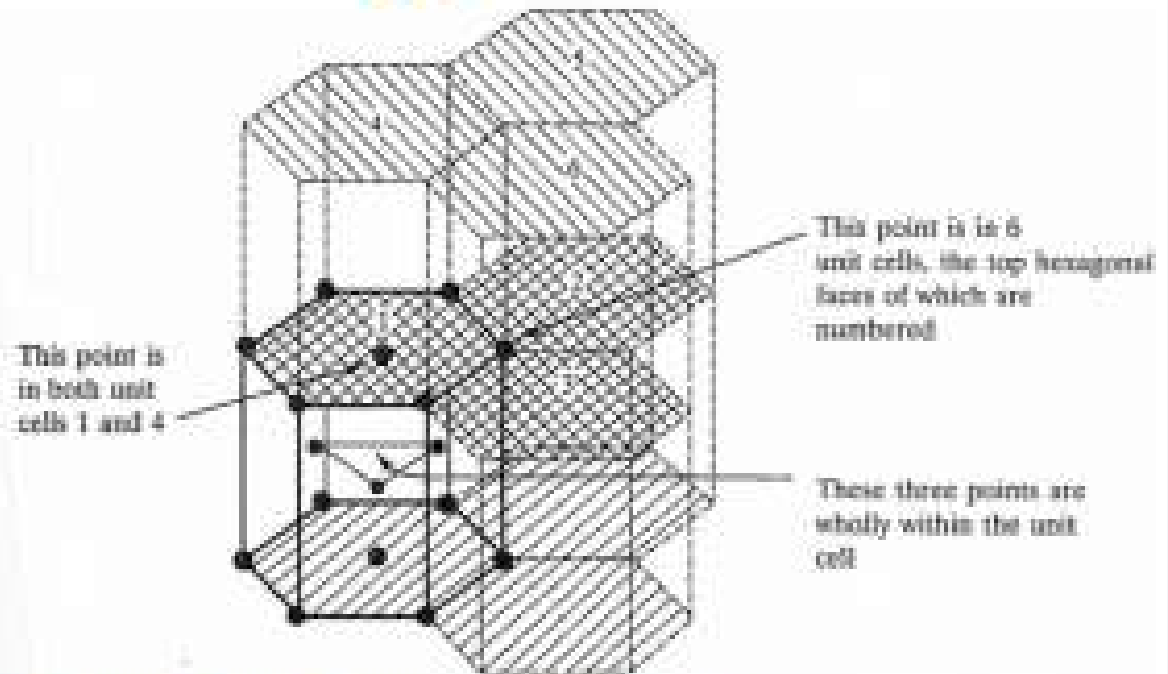
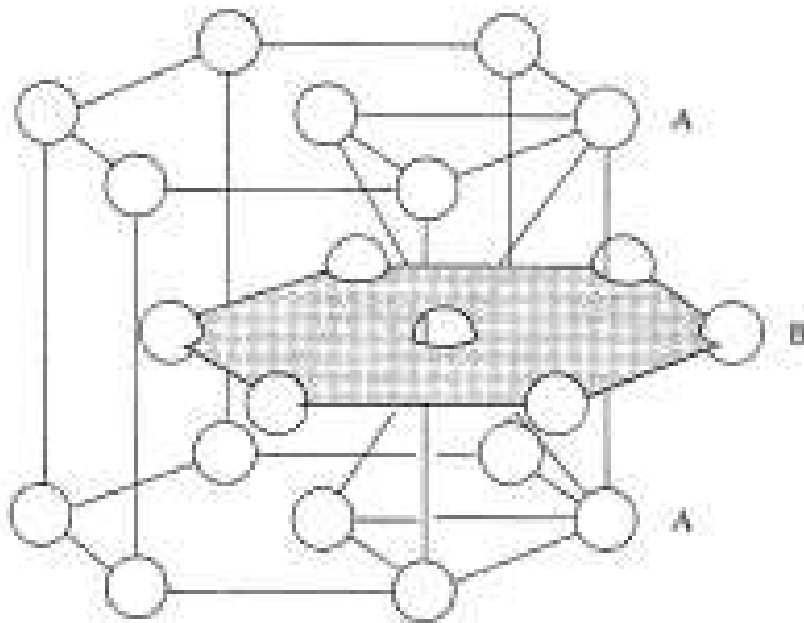
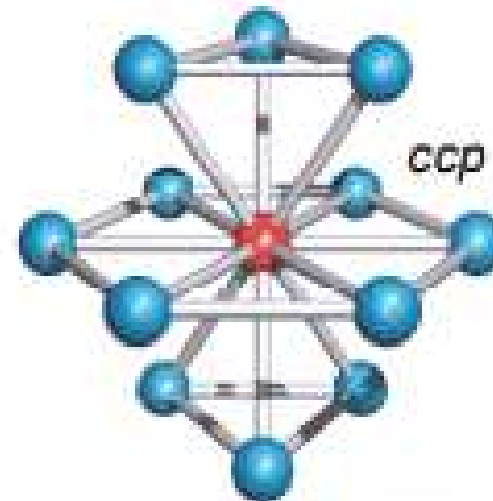
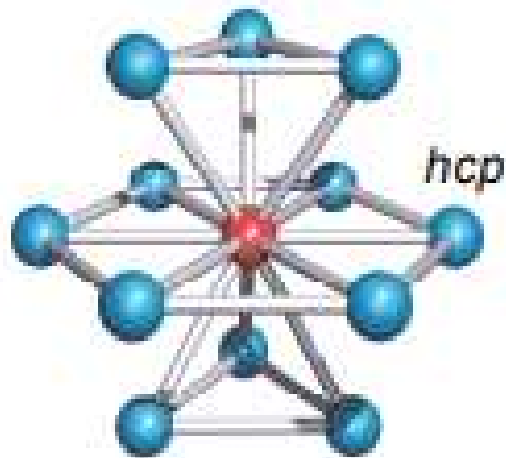


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# Coordination Number



The coordination number of each atom is 12.

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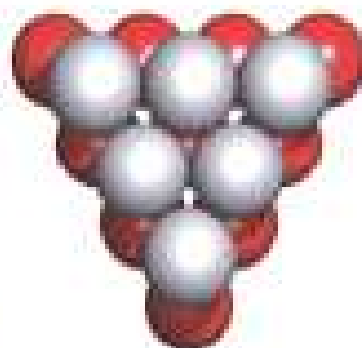
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Layer A  
(a)

Place one sphere  
over every other  
hollow in layer A

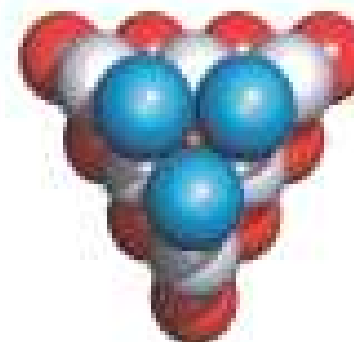


Layer A (red spheres)  
Layer B (grey spheres)

Layer B contains two  
different types of  
hollow (see text)

By placing spheres in  
one or other of these  
different hollows, two  
new layers of spheres  
can be produced.

(b)



Layer A (red spheres)  
Layer B (grey spheres)  
Layer C (blue spheres)

(c)

**ccp**

*cubic  
close  
packed*



Layer A (red spheres)  
Layer B (grey spheres)  
Layer A (red spheres)

(d)

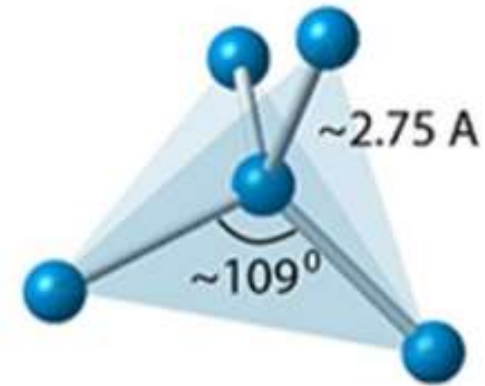
**hcp**

*hexagonal  
close  
packed*

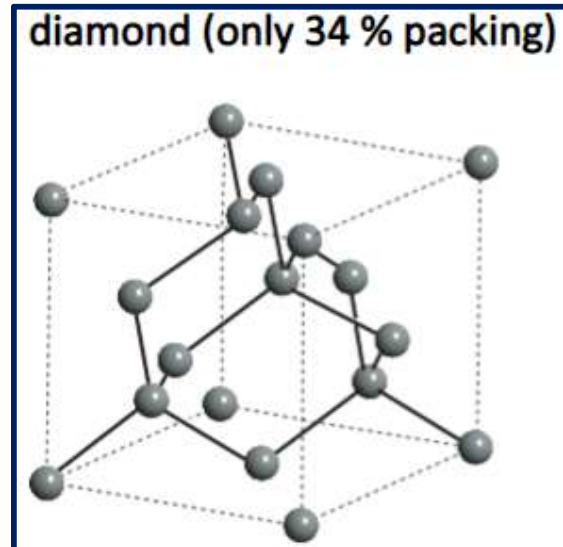
# Simple Crystal Structures

## Diamond

Crystal class  $T_d$  (tetrahedral)  
- Each atom has 4 nearest-neighbors (nn).



Crystal	$a$ ( $\text{\AA}$ )
C (diamond)	3.57
Si	5.43
Ge	5.66
$\alpha$ -Sn (grey)	6.49





## Calculation of unoccupied space in a close-packed structure (ccp or hcp):

The geometrically simpler structure, ccp has spheres of radius  $r$  in contact across the face of the cube and so the length of this diagonal is  $r+2r+r = 4r$ .

The side of such a cell is  $(8^{1/2})r$  [Pythagoras' theorem]  $2Xa^2 = (4r)^2$   $a = 8^{1/2}r$

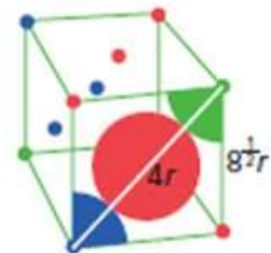
Cell volume =  $a^3 = (8^{1/2}r)^3 = 8^{3/2}r^3$ .

The unit cell contains  $1/8$  of a sphere at each corner ( $8 \times 1/8 = 1$ ) and half a sphere on each face ( $6 \times 1/2 = 3$ )  $1 + 3 = 4$ .

Volume of each sphere =  $4/3 \pi r^3$ , thus total volume of 4 spheres =  $16/3 \pi r^3$ . The occupied fraction =  $(16/3 \pi r^3)/(8^{3/2}r^3) = 16/3 \pi/8^{3/2}, = 0.740$ .

Thus, unoccupied fraction =  $1 - 0.740$

=  $0.260 \equiv 26\%$ .



	SC	BCC	FCC
Volume of conventional cell	$a^3$	$a^3$	$a^3$
# of atoms per cubic cell	1	2	4
Volume, primitive cell	$a^3$	$\frac{1}{2} a^3$	$\frac{1}{4} a^3$

Packing Efficiency:  
ratio of space occupied  
by spheres to that of  
the unit cell

Packing fraction =  $\frac{(4/3)\pi(a/2)^3}{(a^3)}$   
(atomic volume)/  
(bravais unit cell  
volume)  
 $= \pi / 6$

Packing fraction =  $\frac{(4/3)\pi(\sqrt{3}a/4)^3}{(a^3/2)}$   
(atomic volume)/  
( bravais unit cell  
volume)  
 $= \sqrt{3}\pi / 8$

Packing fraction =  $\frac{(4/3)\pi(a/2)^3}{(a^3/4)}$   
(atomic volume)/  
(bravais unit cell  
volume)  
 $= \sqrt{2}\pi / 6$

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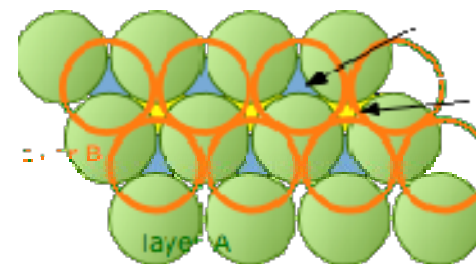
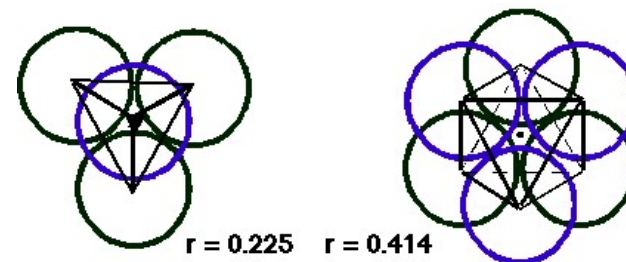
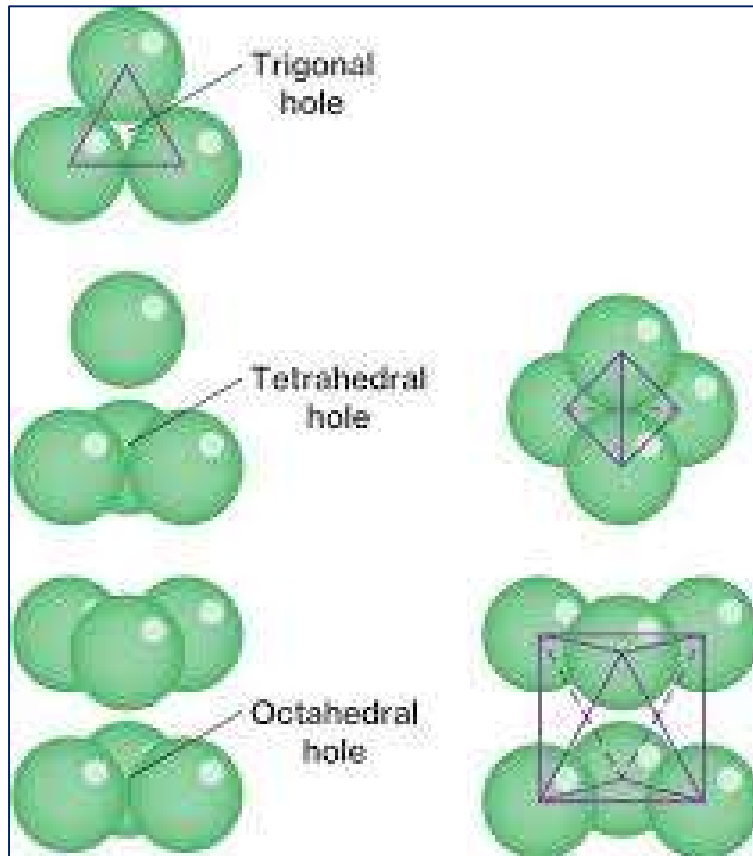
## Holes in close-packed structures

A hole is an unoccupied space between the spheres. Two types of holes are the tetrahedral or octahedral holes are occupied by other atoms or ions.

An octahedral hole lies between two triangles of spheres on adjoining layers.

A tetrahedral hole, T, is formed by a planar triangle of touching spheres capped by a single sphere lying in the dip between them.

The ratio of spheres to octahedral holes to tetrahedral holes in a close-packed structure is 1:1:2.



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### Calculation of density in a close-packed structure:

*In a cubic close-packed array of gold atoms of molar mass  $M = 196.97 \text{ g mol}^{-1}$  and cubic lattice parameter  $a = 409 \text{ pm}$ , calculate density.*

*Density of the unit cell is the same as the density of any macroscopic sample (intensive property). Close-packed structure has an arrangement as a face-centred lattice with one sphere at each lattice point there are four spheres in a unit cell.*

*Mass of an atom =  $M/N_A$ ,  $N_A$ : Avogadro's constant*

*Thus, total mass of unit cell =  $4 \times M/N_A$*

*The volume of the cubic unit cell =  $a^3$  Density=Mass/Volume*

*Thus mass density of the cell =  $4M/N_A a^3$ .*

$$\text{Density of gold } \rho = \frac{4 \times 196.97 \times 10^{-3} \text{ (kg/mol)}}{(6.022 \times 10^{23} \text{ mol}^{-1})(409 \times 10^{-12} \text{ m})^3} = 1.91 \times 10^4 \text{ kg/m}^3 = 19.1 \text{ g/cm}^3$$

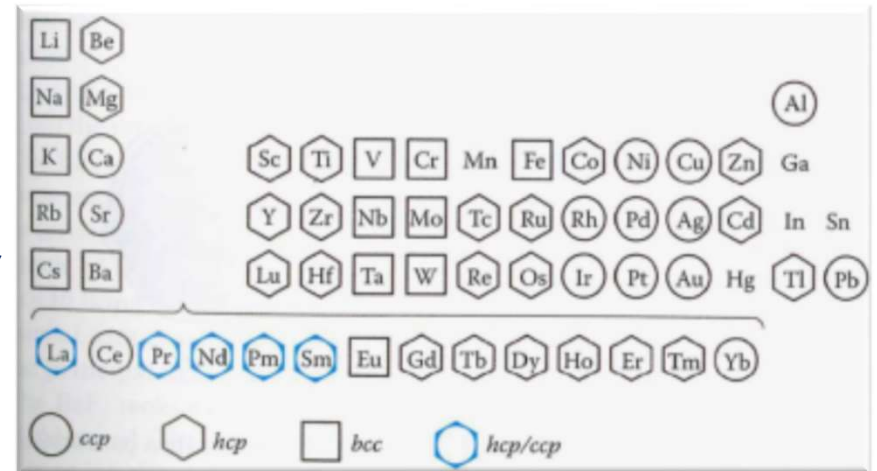
## Polytypism

*Polytypes involves complex stacking arrangements of close-packed layers in case of some metals.*

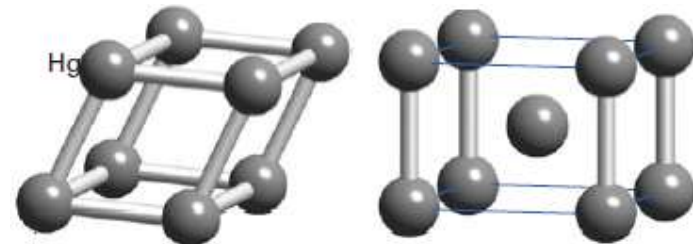
## Non close-packed structures

*A common non close-packed metal structure is body-centred cubic or a primitive cubic structure. Metals can have structures more complex than those described and are regarded as slightly distorted versions of simple structures.*

<i>Type of crystal</i>	<i>Elements</i>
<i>Hexagonal close-packed (hcp)</i>	<i>Be, Ca, Co, Mg, Ti, Zn</i>
<i>Cubic close-packed (ccp)</i>	<i>Ag, Al, Au, Cd, Cu, Ni, Pb, Pt Ba,</i>
<i>Body-centred cubic (bcc)</i>	<i>Cr, Fe, W, alkali metals</i>
<i>Primitive cubic (cubic-P)</i>	<i>Po (<math>\alpha</math>-polymorph of Polonium)</i>



*Solid mercury ( $\alpha$ -Hg), is obtained from the cubic-P arrangement by stretching the cube along one of its body diagonals; a second form of solid mercury ( $\beta$ -Hg) has a structure based on the bcc arrangement but compressed along one cell direction.*



Other sequences include ABAC (La, Pr, Nd, Am), and ABACACBCB (Sm). Actinides are more complex.

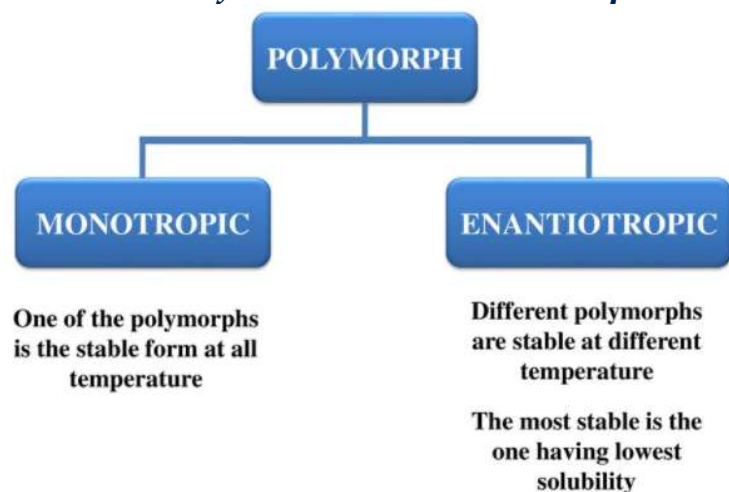


*Polymorphism is the ability to form different crystal structures under different conditions of pressure and temperature. Iron (Fe) shows several solid–solid phase transitions:  $\alpha$ -Fe, which is bcc, occurs up to 906°C,  $\gamma$ -Fe, which is ccp, occurs up to 1401°C, and then  $\alpha$ -Fe occurs again up to the melting point at 1530°C.*

*The hcp polymorph,  $\beta$ -Fe, is formed at high pressures and was believed to be the form that exists at the Earth's core, but recent studies indicate that a bcc polymorph  $\alpha$ -Fe is more likely to exist at the core.*

*Atomic radii of metals: The Goldschmidt correction converts atomic radii of metals to the value they would have in a close-packed structure with 12-fold coordination. The atomic radius of a metallic element generally increases with the coordination number of the lattice.*

*The empirical atomic radius of Na is 185 pm, but that is for the bcc structure where the coordination number is 8. To adjust to 12-coordination  $1/0.97 = 1.03$ ,  $\times 185 = 191$  pm as the radius that a Na atom would have if it were in a close-packed structure.*



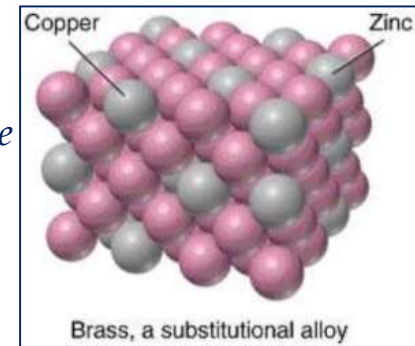
Crystal	c/a
He	1.633
Be	1.581
Mg	1.623
Ti	1.586
Zn	1.861
Cd	1.886
Co	1.622
Y	1.570
Zr	1.594
Gd	1.592
Lu	1.586

Coordination no.	Relative radius
12	1
8	0.97
6	0.96
4	0.88

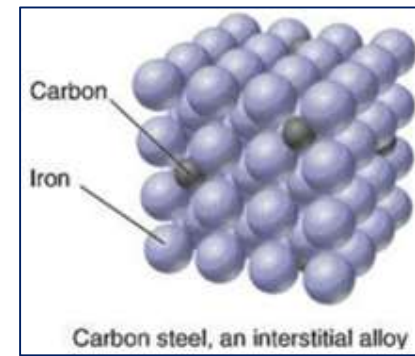
**Alloys**: An alloy is a blend of metallic elements prepared by mixing the molten components and then cooling the mixture to produce a metallic solid. Alloys may be homogeneous solid solutions, in which the atoms of one metal are distributed randomly among the atoms of the other, or they may be compounds with a definite composition and internal structure. Alloys typically form from two electropositive metals.

Solid solutions are classified as either 'substitutional' or 'interstitial'.

A substitutional solid solution is a solid solution in which atoms of the solute metal occupy some of the locations of the solvent metal atoms. E.g. brass



An interstitial solid solution is a solid solution in which the solute atoms occupy the interstices (the holes) between the solvent atoms. A substitutional solid solution involves the replacement of one type of metal atom in a structure by another. E.g. carbon steel



Substitutional solid solutions must fulfil these three criteria:

1. The atomic radii of the elements are within about 15 per cent of each other.
2. The crystal structures of the two pure metals are the same; this similarity indicates that the directional forces between the two types of atom are compatible with each other.
3. The electropositive characters of the two components are similar; otherwise compound formation, where electrons are transferred between species, would be more likely.

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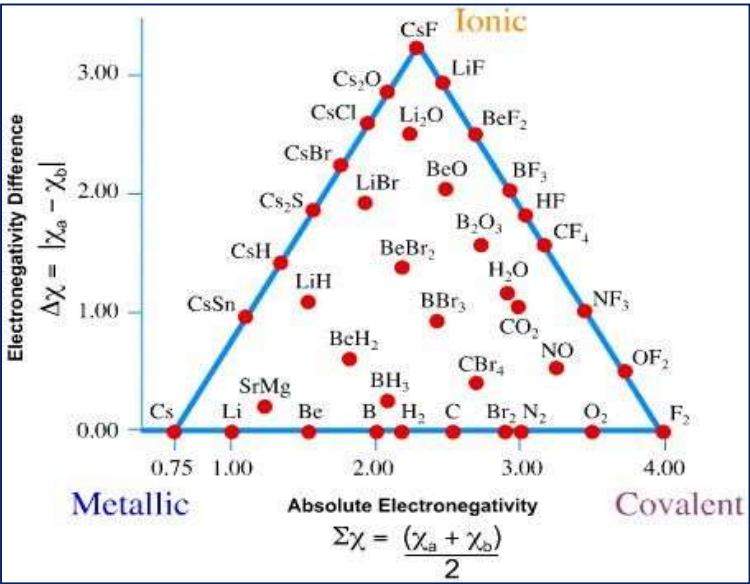
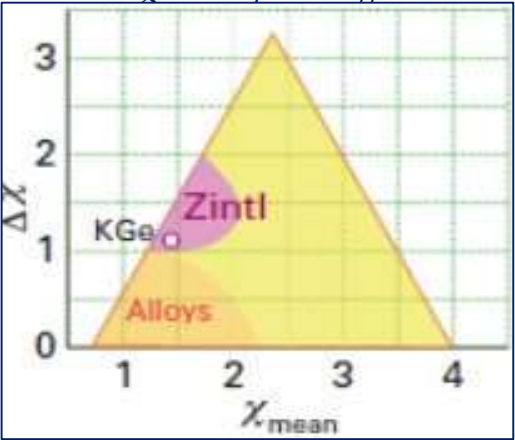
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**Intermetallic compounds:** The third type of alloy are those in which the structure adopted is different from the structures of either component metal. E.g.  $\beta$ -brass ( $\text{CuZn}$ ) and compounds of composition  $\text{MgZn}_2$ ,  $\text{Cu}_3\text{Au}$ ,  $\text{NaTl}$ , and  $\text{Na}_5\text{Zn}_{21}$ . Intermetallic compounds containing a very electropositive metal in combination with a less electropositive metal (for example, Na and Zn), and in a Ketelaar triangle lie above the true alloys are called Zintl phases. These compounds are not fully ionic. E.g.  $\text{KGe}$ .

The Ketelaar triangle is an equilateral triangle with vertices designated metallic (M), ionic (I), and covalent (C), which quantifies the Periodic

Table based on types of chemical bonding plotted with mean electronegativity vs. difference in electronegativity.



- **Brass**
  - 67% Cu
  - 33% Zn
- **Stainless Steel**
  - 80.6% Fe
  - 0.4% C
  - 18% Cr
  - 1% Ni
- **Gold (14K)**
  - 58% Au
  - 42% Cu
- **Sterling Silver**
  - 92.5% Ag
  - 7.5% Cu
- **Bronze**
  - 88% Cu
  - 12% Sn

**Ionic solids:** The ionic solid is an assembly of oppositely charged spheres that interact by nondirectional electrostatic forces (Coulombic forces) and repulsions between complete shells in contact; if the calculated thermodynamic properties of the solid match with experiment, then the compound is considered to be ionic. In  $\text{NaCl}$  and  $\text{KNO}_3$ , electrons made available by cation formation which are localized on a neighbouring anion instead of an adaptable, mobile electron sea. Binary ionic materials have large electronegativity differences, typically  $\Delta\chi > 3$ , thus found at the top corner of Ketelaar triangle.

Characteristic structures of ionic solids: are normally of two types:

Binary phases,  $AX_n$

Structures expressed w.r.t. holes are the rock-salt, caesium-chloride, sphalerite, fluorite, wurtzite, nickel-arsenide, and rutile structures.

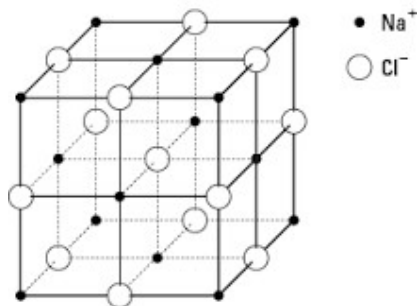
Ternary phases  $A_aB_bX_n$

The perovskite and spinel structures adopted by many compounds with stoichiometries  $ABO_3$  and  $AB_2O_4$ , respectively have ternary phases.

The simple structures come from the arrangement of the anions /cations) in the positions of the spheres in the fcc or hcp lattices, and cations go into some or all of the octahedral and tetrahedral holes within the lattices.

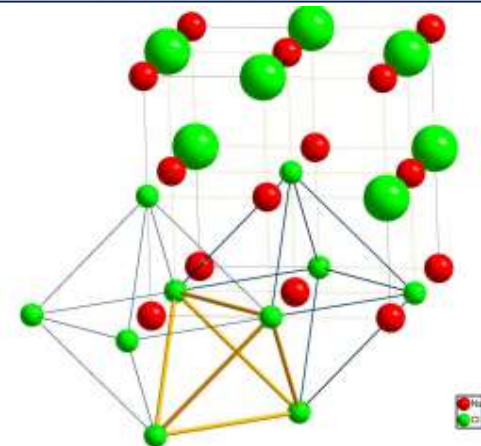
**The Rock Salt structure:** is adopted by Sodium Chloride, NaCl. It is based on the fcc array of the large chloride anions, and the sodium cations occupy all the octahedral holes in the fcc lattice.

However, it could also be seen as an fcc array of sodium ions, with the anions in all the octahedral holes. Each ion is octahedrally coordinated by six counterions, so this structure has (6,6)-coordination where the first number refers to the coordination of the cation and the second to anion.



Crystal	a
LiH	4.08 Å
MgO	4.20
MnO	4.43
NaCl	5.63
AgBr	5.77
PbS	5.92
KCl	6.29
KBr	6.59

Close-packing type	Hole filling	Structure
Cubic (ccp)	All octahedral	Rock salt (NaCl)
	All tetrahedral	Fluorite ( $CaF_2$ )
	Half octahedral	$CdCl_2$
	Half tetrahedral	Sphalerite (ZnS)
Hexagonal (hcp)	All octahedral	Nickel arsenide (NiAs); with some distortion from perfect hcp $CdI_2$
	Half octahedral	Rutile ( $TiO_2$ ); with some distortion from perfect hcp
	All tetrahedral	No structure exists: tetrahedral holes share faces
	Half tetrahedral	Wurtzite (ZnS)



NaCl showing edge-sharing of octahedra and an enclosed tetrahedral space.

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**The Sphalerite structure:** adopted by ZnS, is also known as zinc blende structure.

In an fcc array of sulphide anions, and the zinc cations occupy half the tetrahedral holes.

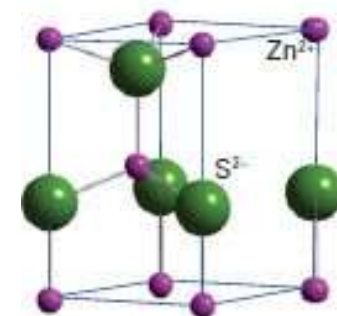
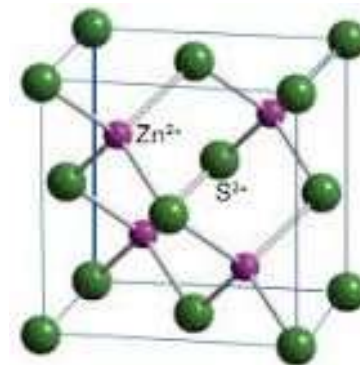
The cations are tetrahedrally coordinated by anions, and the anions are surrounded by eight tetrahedral sites, of which half are occupied, and hence the anions

are also four-coordinate. The zinc blende structure therefore has (4,4)-coordination.

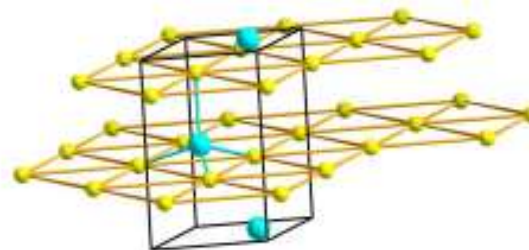
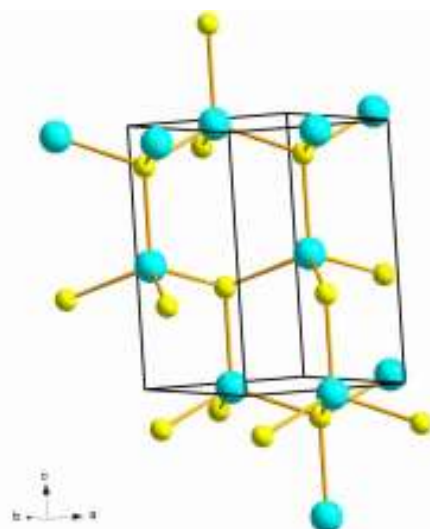
Structures based on hexagonal close packed lattices **Wurtzite**

This is another structure adopted by ZnS, the difference from Zinc Blende being that the ions now occupy the sites in an hcp lattice. In an hcp array of sulphide anions, the zinc cations occupy half the tetrahedral holes. There are two tetrahedral holes for each atom in the hcp array, and so the stoichiometry of the compound dictates that only half of them be occupied, so that there are the same number of cations as anions.

It has (4,4)-coordination.



The Wurtzite structure type is composed of an hcp array of sulfide ions with alternate tetrahedral holes occupied by zinc ions.



BeO, ZnO, NH<sub>4</sub>F also adopt this structure type.

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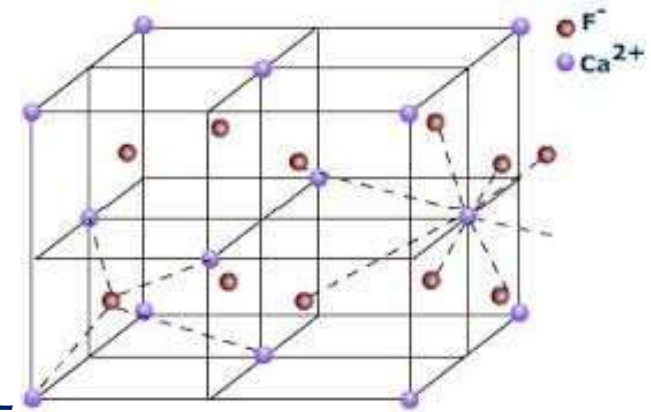
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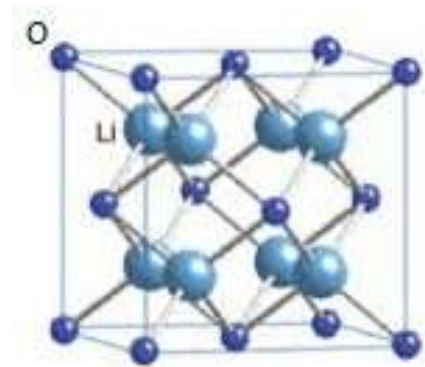
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**The Fluorite structure:** is the structure of Calcium Fluoride,  $\text{CaF}_2$ .

There is now an fcc array of calcium cations, and the fluoride anions occupy all of the tetrahedral holes. The anions are tetrahedrally coordinated by cations, and the cations are surrounded by eight tetrahedral sites, all of which are occupied, and hence cations are eight-coordinate, thus (8,4)-coordination.



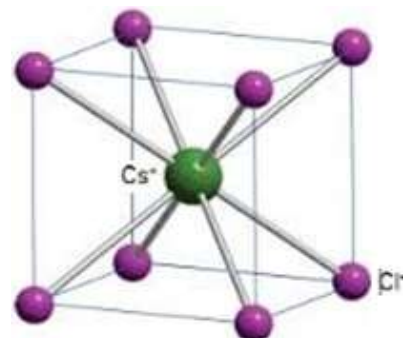
**The Antifluorite structure:** is the inverse of the fluorite structure where the locations of cations and anions are reversed. E.g.  $\text{Li}_2\text{O}$ . Cations are twice the number of anions. In a ccp array of anions, cations occupy all the tetrahedral holes. The coordination is (4,8).



## Structures based on other cubic lattices

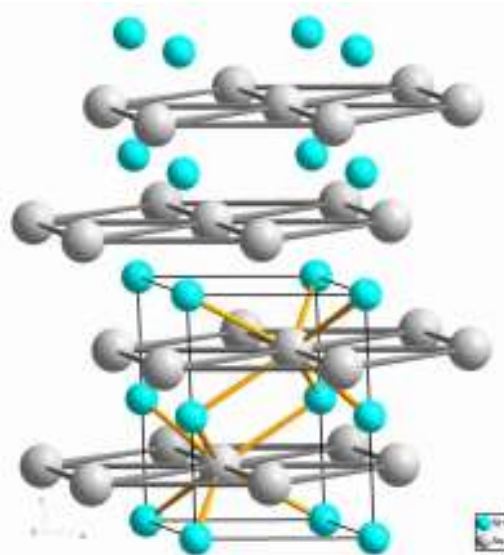
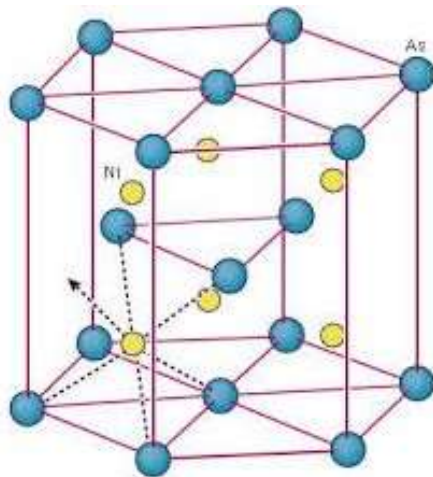
**The Caesium Chloride structure:** also adopted by CsBr and CsI, is formed when the anion and cation have similar sizes. It has interleaved bcc lattice of cations and anions.

The anions, at the corners of the cube, are coordinated to eight cations at the centers of each of the surrounding cubes, and the cations are surrounded by the eight anions at the corners of the cube. The cesium chloride structure therefore has (8,8)-coordination.



Crystal	a
BeCu	2.70 Å
AlNi	2.88
CuZn	2.94
CuPd	2.99
AgMg	3.28
LiHg	3.29
NH <sub>4</sub> Cl	3.87
TlBr	3.97
CsCl	4.11
TlI	4.20

**The Nickel Arsenide Structure:** is the structure of NiAs, and is based on a distorted hcp array of Arsenide anions. By contrast with the wurtzite structure, however, which is also of formula AB, the cations now occupy all the octahedral sites rather than half the tetrahedral holes. This structure type lies in the 'polarized ionic salt area' of a Ketelaar triangle.



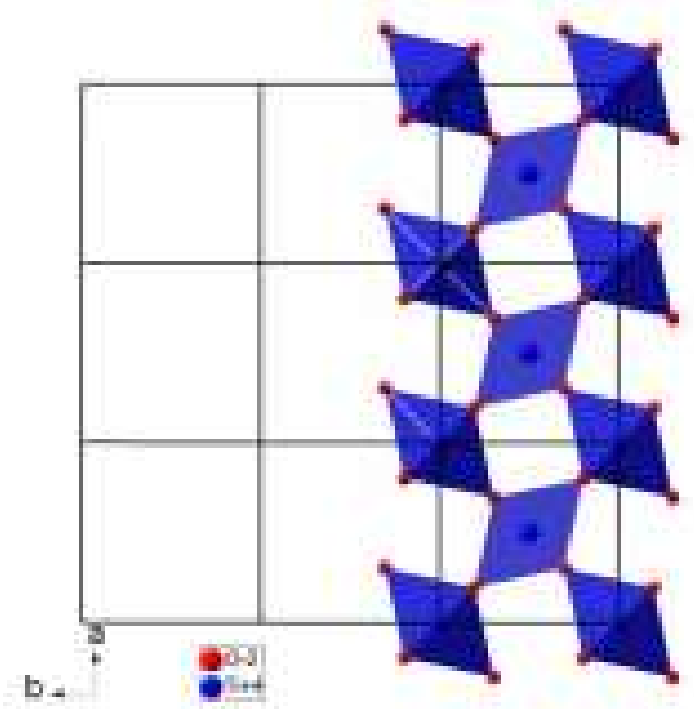
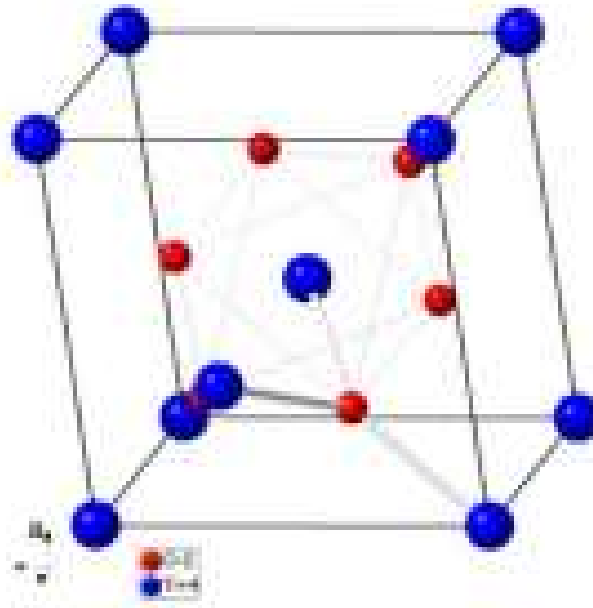
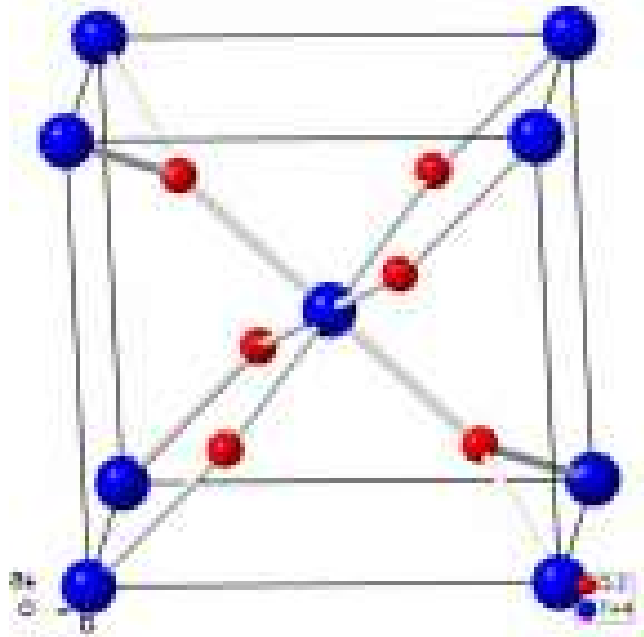
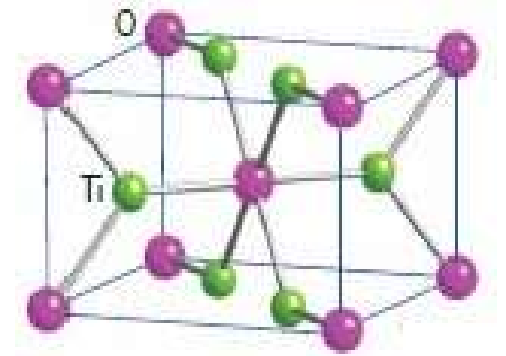
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**The Rutile Structure:** is the structure of Titanium Oxide,  $\text{TiO}_2$ .

Here, the anions occupy the hcp lattice, and the cations occupy half of the octahedral holes. The arrangement of the anions and cations leads to the (6,3)-coordination.



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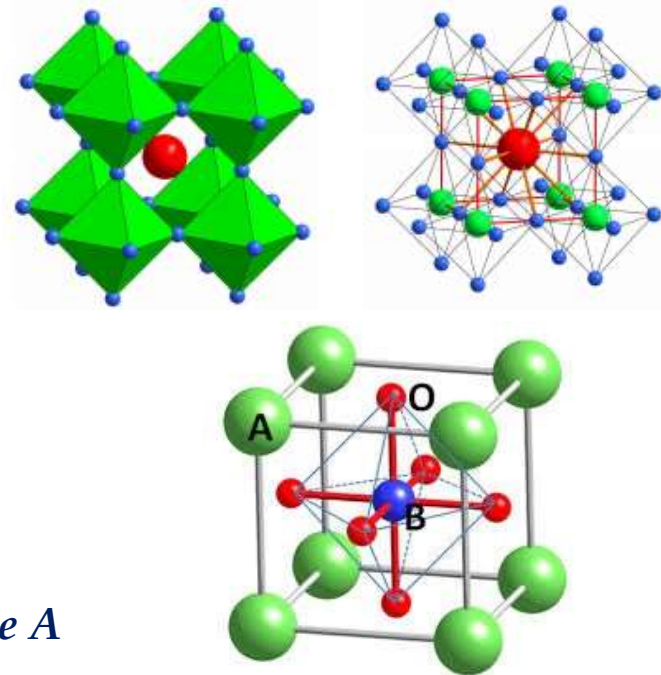
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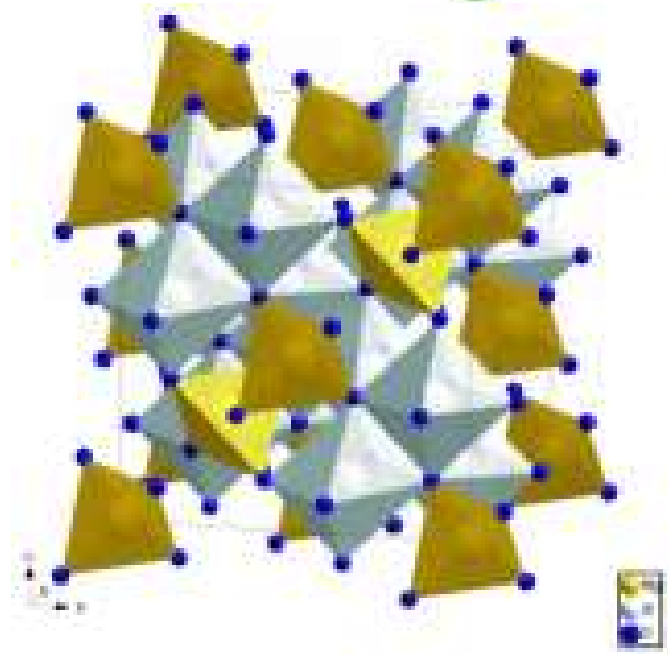
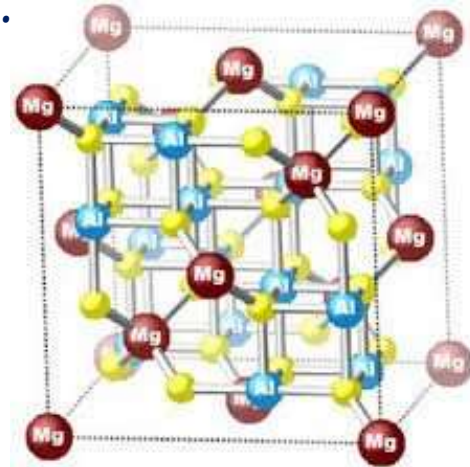
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**The Perovskite Structure:** The mineral perovskite, Calcium Titanate,  $\text{CaTiO}_3$  has a simple cubic array of A atoms (Ca), B atoms (Ti), occupying the center of the cube, as in CsCl, and the X atoms (O) being sited at the centre of the 6 faces of the simple cube. The central A ion is coordinated by 12 X ions; the B ion is octahedrally coordinated by 6 X ions; and the X ion is linearly coordinated by 2 B ions. The coordination number of Ca is 12, Ti is 6 and O is 2.



**The Spinel Structure:**  $\text{MgAl}_2\text{O}_4$  has a ccp array of  $\text{O}^{2-}$  ions in which the A (Mg) cations occupy one-eighth of the tetrahedral holes and the B (Al) cations occupy half the octahedral holes. Coordination is A (Mg) 4 tetrahedral coordination, B (Al) 6 octahedral coordination X (O) 4 distorted tetrahedral coordination.



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Structure map: is a variation in crystal structure plotted with the difference in electronegativity between the elements vs. the average principal quantum number of the valence shells of the two atoms to depict the character of the bond.

Lattice enthalpy for a compound is calculated from the Born-Haber cycle: Refer Chem. Thermodynamics.

Born-Mayer equation: is used to determine lattice enthalpy for an ionic lattice, taking into account Coulombic attractions and repulsions between the ions and the repulsive interactions when the electron densities of the ions overlap.

For the lattice enthalpy at  $T = 0$ , the eqn. is

$$\Delta H_L^\circ = \frac{N_A |z_A z_B| e^2}{4\pi\epsilon_0 d} \left(1 - \frac{d^*}{d}\right) A$$

where  $N_A$ : Avogadro's constant,  $z_A$  and  $z_B$  the charge of the cation and anion,  $\epsilon_0$  the vacuum permittivity,  $d^*$ : constant = 34.5 pm, representing the repulsion between ions at short range,  $A$ : Madelung constant

The Madelung constant reflects the effect of the geometry of the lattice on the basis of the net Coulombic interaction. It is derived from the molar contribution of Coulomb potential energy of the ions

$$V = \frac{N_A e^2}{4\pi\epsilon_0 d} A$$

$$E_C = -\frac{e^2}{4\pi\epsilon_0 r} \left( \frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} \dots \right)$$

The term (series) inside the brackets is known as the **Madelung constant,  $A$** . For one mole of NaCl, the energy due to the coulombic interactions is:

$$E_C = -\frac{N_A A e^2}{4\pi\epsilon_0 r}$$

$N_A$  = Avogadro's number

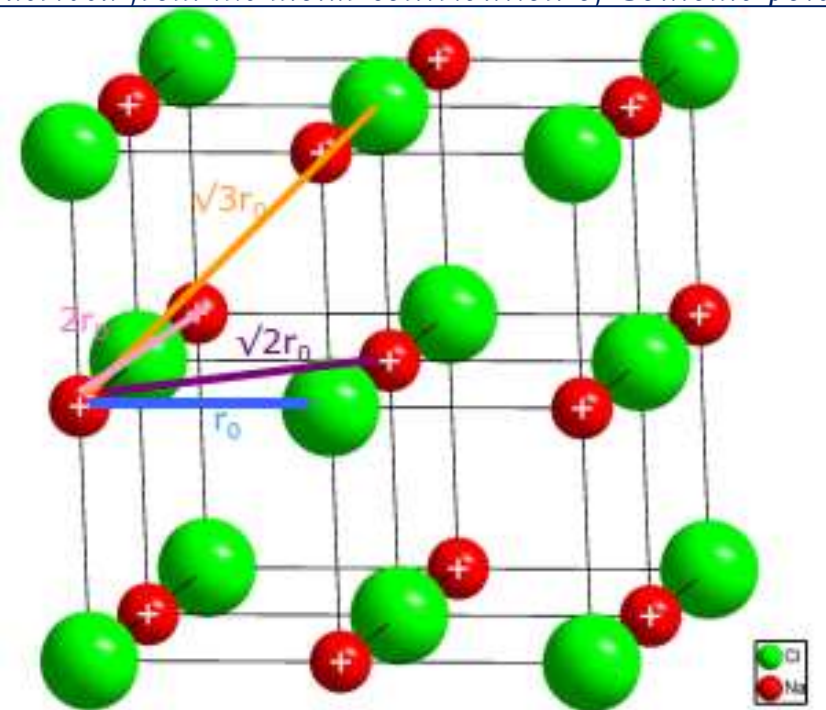
From a  $\text{Na}^+$ ,

Six  $\text{Cl}^-$  at a distance of  $r_0$

Twelve  $\text{Na}^+$  at a distance of  $\sqrt{2}r_0$

Eight  $\text{Cl}^-$  at a distance of  $\sqrt{3}r_0$

Six  $\text{Na}^+$  at a distance of  $2r_0$



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Structure	Madelung Constant, $A$	Number of ions in formula unit, $v$	$A/v$	Coordination
Cesium chloride, CsCl	1.763	2	0.882	8:8
Sodium chloride, NaCl	1.748	2	0.874	6:6
Fluorite, $\text{CaF}_2$	2.519	3	0.840	8:4
Zinc Blende, ZnS	1.638	2	0.819	4:4
Wurtzite, ZnS	1.641	2	0.821	4:4
Corundum, $\text{Al}_2\text{O}_3$	4.172	5	0.835	6:4
Rutile, $\text{TiO}_2$	2.408	3	0.803	6:3

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## Structures related to close-packed arrangements of anions

Formula	Cation:anion Coordination	Type and number of holes occupied	Examples: Cubic close packing	Examples: Hexagonal close packing
MX	6:6	All octahedral	Sodium chloride: NaCl, FeO, MnS, TiC	Nickel arsenide: NiAs, FeS, NiS
	4:4	Half tetrahedral; every alternate site occupied	Zinc blende: ZnS, CuCl, $\gamma$ -AgI	Wurtzite: ZnS, $\beta$ -AgI
MX <sub>2</sub>	8:4	All tetrahedral	Fluorite: CaF <sub>2</sub> , ThO <sub>2</sub> , ZrO <sub>2</sub> , CeO <sub>2</sub>	None
	6:3	Half octahedral; alternate layers have fully occupied sites	Cadmium chloride: CdCl <sub>2</sub>	Cadmium iodide: CdI <sub>2</sub>
MX <sub>3</sub>	6:2	One-third octahedral; alternate pairs of layers have two-thirds of the octahedral sites occupied.		Bismuth iodide: BiI <sub>3</sub> , FeCl <sub>3</sub> , TiCl <sub>3</sub> , VCl <sub>3</sub> .
M <sub>2</sub> X <sub>3</sub>	6:4	Two-thirds octahedral		Corundum: $\alpha$ - Al <sub>2</sub> O <sub>3</sub> , $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>3</sub> , Ti <sub>2</sub> O <sub>3</sub> , $\alpha$ - Cr <sub>2</sub> O <sub>3</sub>
ABO <sub>3</sub>		Two-thirds octahedral		Ilmenite: Fe <sub>2</sub> O <sub>3</sub>
AB <sub>2</sub> O <sub>4</sub>		One-eighth tetrahedral and one-half octahedral		Olivine: Mg <sub>2</sub> SiO <sub>4</sub>

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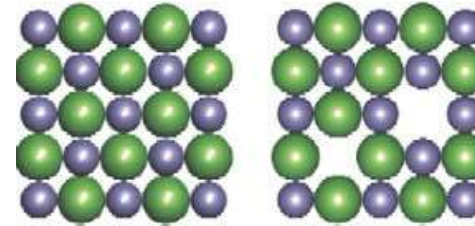
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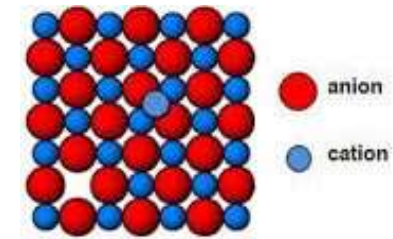
Defects and their types: defects are formed because they introduce disorder into the lattice and the entropy rises. Formation of defects is endothermic and increases as the melting points of solids are reached. Defects are of two types:

**1. Intrinsic point defects:**

Schottky defect is a point defect in which an atom or ion is missing from its normal site in the structure. They occur in more ionic materials.



Frenkel defect is a point defect in which an atom or ion has been displaced onto an interstitial site. They occur in more covalent materials with low coordination numbers.



A third type is an atom-interchange or anti-site defect, which consists of an interchanged pair of atoms: neutral atoms exchange metal atoms in metal alloys.

**2. Extrinsic point defects:** are defects introduced into a solid due to doping with an impurity atom. E.g. introduction of As into Si to enhance the latter's semiconducting properties.

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**Band formation, Insulators & Semiconductors:** The overlap of atomic orbitals in solids gives rise to bands of energy levels separated by energy gaps, called band gaps, which are values of energy for which there is no molecular orbital.

The Fermi level is the highest occupied energy level in a solid at  $T = 0$  K & lies near the centre of the band. When the band is not completely full, the electrons close to the Fermi level can easily be promoted to nearby empty levels, as in a conductor. A metallic conductor is a substance with an electric conductivity that decreases with increasing temperature.

A **semiconductor** is a substance with an electric conductivity that increases with increasing temperature. They are of two types- intrinsic & extrinsic.

**Intrinsic semiconductor:** Some electrons from the valence band move to the empty upper band introducing +ve holes, equivalent to an absence of electrons, into the lower band, and as a result the solid is conducting.

A solid insulator is a substance with a very low electrical conductivity. It is a semiconductor with a large band gap. The band of highest energy in an insulator, containing electrons (at  $T = 0$ ) is called the valence band. The next higher band (empty at  $T = 0$ ) is called the conduction band.

**Superconductors** are a special class of materials that have zero electrical resistance below a critical temperature.



*Extrinsic semiconductors: are formed due to intentionally added impurities/dopants. p-Type semiconductors are solids doped with atoms that remove electrons from the valence band (Boron B doped in Si); n-type semiconductors are solids doped with atoms that supply electrons to the conduction band (Phosphorous P doped in Si).*

