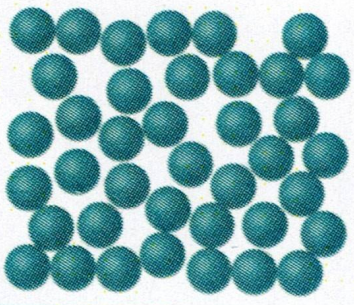
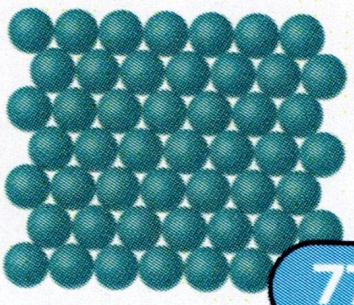
SOLID STATE

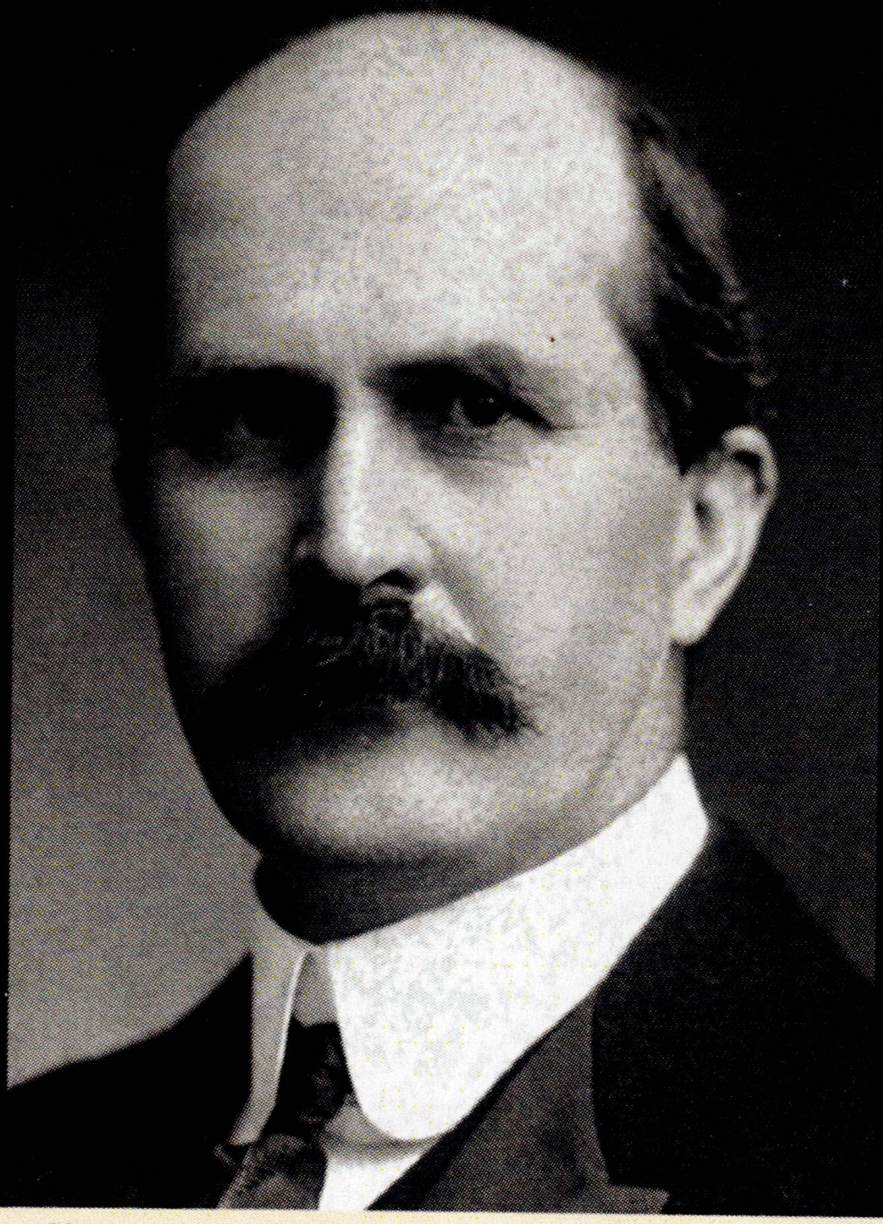
Types of Crystals

Comparison	Amorphous solids	Crystalline solids
Repeating Units	Irregular	Regular
Shapes	No shape	Exist
Melting Point	Not defined	Fixed
Chemical Nature	Isotropic	Anisotropic
Physical Nature	Pseudo Solids	True Solids
Symmetry Order	Unsymmetrical	Symmetrical
Range	Short Range	Long Range
Example	Glass, wax, Rubber, Plastic etc	Diamond, NaCl, Quartz, ZnS etc.

Looks something like this







Broadly speaking, the discovery of X-rays has increased the keenness of our vision ten thousand times, and we can now 'see' the individual atoms and molecules.

William Bragg

Solids on basis of constituent particles

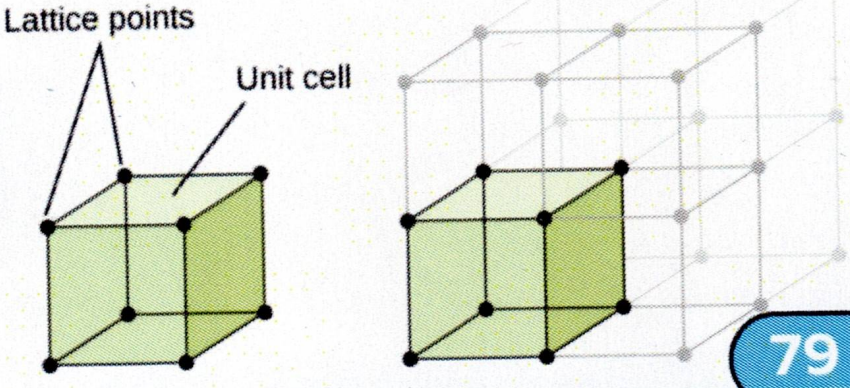
Types	Particles	Forces	Example
IONIC	Ions	Electrostatic	KCl, Na_2SO_4, NaF
COVALENT	Atoms	Covalent	Diamond, Graphite
METALLIC	Metal	Metallic	Fe(s), Zn(s)
MOLECULAR	Molecule	London Dispersion	NH_3(s), SO_2(s), I_2 (s), He(s)

Molecular Solids Classified

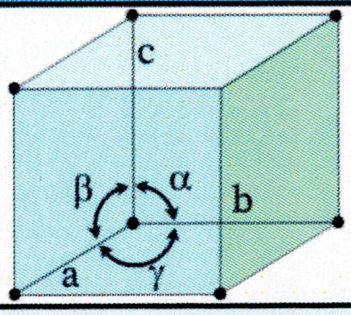
Types	Nature	Forces	Example
Non-Polar	Soft	London	Ar, CCl_4, H_2, I_2, CO_2
Polar	Soft	Dipole-Dipole	HCl, SO_2
H-Bonding	Hard	H-Bonding	H_2O (ice)

- Only Metallic Solids, ionic solids in molten states & Graphite (Covalent) are electrically conducting.
- **M.P. order** : Covalent > Metallic > Ionic > Molecular

UNIT CELL



Classification of unit cell : On basis of shape



Six parameters used to define lattice

- a,b,c : Defining dimensions of sides
- α, β, γ : Defining angles between sides.

7 Crystal Systems and 14 Bravais Lattices

Cubic, Tetragonal, Orthorhomic, Monoclinic, Triclinic, Rhombohedral, Hexagonal

- Hexagonal has 8 faces (others have 2)

Remember as C TOM THeRe (**SEE TOM THERE**)

Crystal	Sides	Angles	Type
Cubic	a=b=c	$\alpha=\beta=\gamma=90°$	P,B,F
Tetragonal	a=b≠c	$\alpha=\beta=\gamma=90°$	P,B
Orthorhombic	a≠b≠c	$\alpha=\beta=\gamma=90°$	P,B,F,E
Monoclinic	a≠b≠c	$\alpha=\gamma=90°;\beta\neq90°$	P,E
Triclinic	a≠b≠c	$\alpha\neq\beta\neq\gamma\neq90°$	P
Rhombohedral	a=b=c	$\alpha=\beta=\gamma\neq90°$	P
Hexagonal	a=b≠c	$\alpha=\beta=90;\ \gamma=120°$	P

14 B.L.

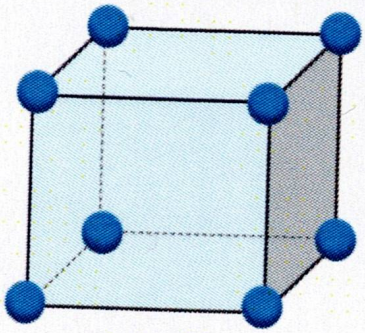
P = Primitive Centred; B = Body Centred ;
F = Face Centred ; E = End Centred

Lattice Points

- 1 Corner is shared by 8 unit cells (1/8 Contribution)
- 1 Face Centred shared by 2 unit cells (1/2 Cont.)
- 1 Body centred is shared by 2 unit cells (1/2 Cont.)
- 1 Edge Centred is shared by 4 unit cells

Types of Unit cells

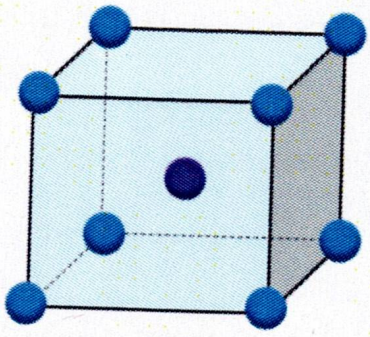
- $2r = a$
- Packing Fraction = 0.52 or $\pi/6$
- Void Fraction = 0.48
- Coordination Number = 6
- Size of body centre void = 0.732r
- Size of Face Center Void = 0.414r
- Nearest Neighbor Distance = a
- Next Nearest Neighbor = $a\sqrt{2}$
- e.g. Pollonium



Primitive

Z=1

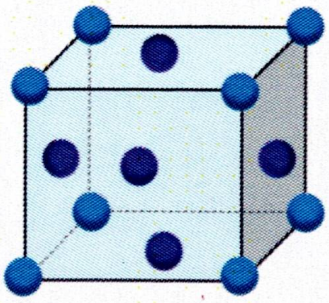
- $4r = a\sqrt{3}$
- Packing Fraction = 0.68 or $\sqrt{3}\pi/8$
- Void Fraction = 0.32
- Coordination Number = 8
- Size of edge centre void = 0.155r
- Size of Face Center Void = 0.155r
- Nearest Neighbor Distance = $a\sqrt{3}/2$
- Next Nearest Neighbor = a
- e.g. Iron, Sodium Etc.



Body Centred

Z=2

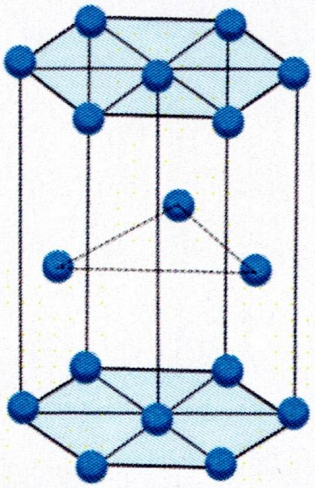
- $4r = a\sqrt{2}$
- Packing Fraction = 0.74 or $\sqrt{2}\pi/6$
- Void Fraction = 0.26
- Coordination Number = 12
- Size of edge centre void = 0.414r
- Size of Face Center Void = 0.414r
- Nearest Neighbor Distance = $a/\sqrt{2}$
- Next Nearest Neighbor = a
- e.g. Al, Ni, Fe, Pd, all solid noble gases



Face Centred
Z=4

- $2r = a$
- Height = $4r\sqrt{2/3}$
- Packing Fraction = 0.74
- Void Fraction = 0.26
- Coordination Number = 12

Hexagonal Closed Packaging (HCP) Z=6



For Diamond	Z = 8	P.E. = 34%	Dist. b/w C-C $2r = \sqrt{3}a/4$

Density of a unit cell

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$

Z = No. of Atoms per unit cell
a = Edge length in pm
M = Molar Mass (g/mol)
N_A= Avogadro's no.

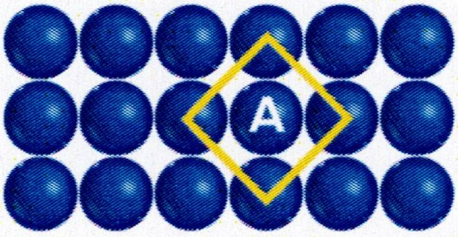
Types of Packing of Crystals

1-D Packing or Packing Along x-axis

Coordination Number = 2

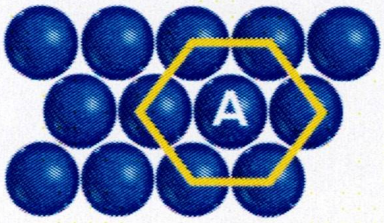
2-D Packing

Possibility 1



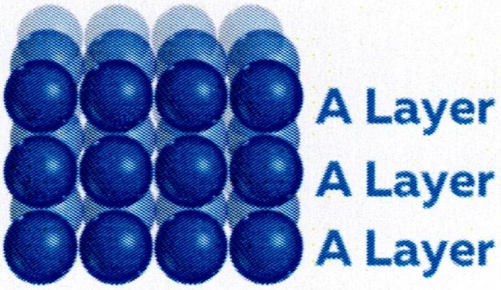
Square Closed Packing (SCP)
Packing Efficiency = 74.8%
Coordination Number = 4

Possibility 2



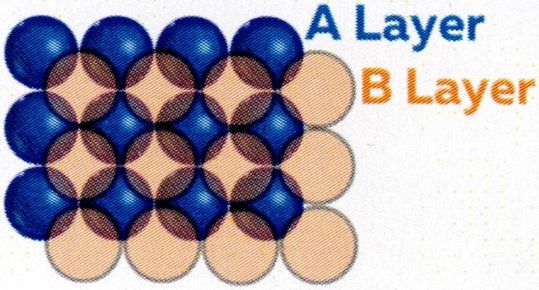
Hexagonal Closed (HCP)
Packing Efficiency = 91%
Coordination Number = 6

3-D Packing : Case 1



Possibility 1

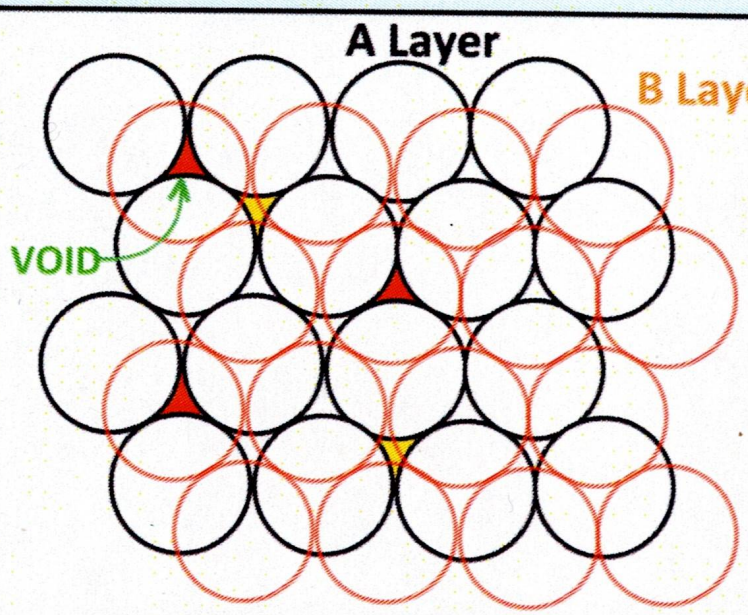
Simple Cubic Cell (SCC)
Packing Efficiency = 74.8%
A.A.A.A.A. Arrangement



Possibility 2

Body Centre Unit cell (BCC)
Packing Efficiency = 68%
A.B.A.B.A. Arrangement

3-D Packing : Case 2 (Hexagonal)



For n atoms,

▲ n Octahedral

▲ 2n Tetrahedral

NOTE

A third layer over the structure will exhibit more options

Third Layer over Td Void	Third Layer over Oh Void
• Hexagonal Closed (HCP)	• Cubic Closed (CCP)
• Hexagonal Unit Cell	• Face Centred Unit Cell
• Packing Efficiency = 74%	• Packing Efficiency = 74%
• **A.B.A.B.A.** Arrangement	• **A.B.C.A.B.C.** Arrange
• Coordination no. = 12	• Coordination no. = 12

C.N. may vary depending upon location of atom in cell

Formula of a compound

- Element 'B' forms ccp structure
- 'A' occupies half of the octahedral voids
- Oxygen atoms occupy all tetrahedral voids

$n_B = 4$ (ccp structure)

Octahedral voids $= n_B$

$n_A = 2$ (Half of n_B)

Tetrahedral voids $= 2 \times n_B$

$n_O = 8$ (Twice of n_B)

$2 : 4 : 8 \rightarrow 1 : 2 : 4$

Answer : $\mathbf{AB_2O_4}$

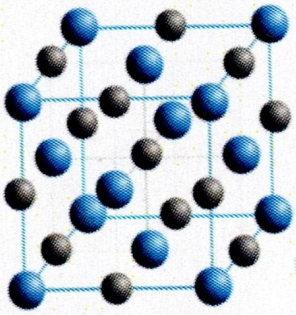
Radius Ratio Table

R.R.	C.N.	Structure	Type	Examples
0-0.155	2	Linear	-	-
0.155-0.225	3	Triangular	-	-
0.225-0.414	4	Tetrahedral	ZnS	CuCl, CuBr, HgS
0.414-0.732	6	Octahedral	NaCl	MgO, NaBr,CaS
0.732-1	8	Cubic	CsCl	CsI,NH_4Br,TiBr
1	12	FCC or HCP	-	-

Different Ionic Crystals

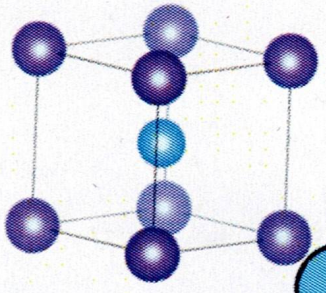
AB : NaCl Rock Salt Type

- Na^+ : Octahedral Sites
- Cl^- : CCP Arrangement
- **CN** of Na = 6 & Cl = 6.
- $Z_{eff} = 4$
- Tetrahedral Voids Are Empty
- Halides of Li, Rb, AgF, AgBr, NH_4Cl, NH_4Br, NH_4I



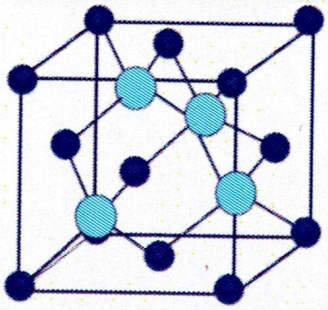
AB : Caesium Chloride (CsCl) Type

- Cs^+ : Body Center
- Cl^- : Corners of the cube
- **CN** of Cs = 8 & Cl = 8.
- $Z_{eff} = 1$
- CsCl, CsBr, CsI, TlI, TlBr, TlCN



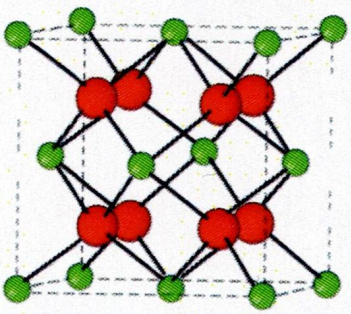
AB : ZnS Blende Type

- Zn^{+} : Alternate Td Sites
- S^{2-} : CCP Arrangement
- **CN** of Zn = 4 & S = 4.
- Z_{eff} = 4
- CuCl , CuBr, AgI



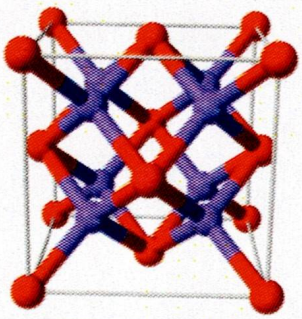
AB_2 : CaF_2 : Fluorite Type

- Ca^{2+} : CCP Arrangement
- F^{-} : All Tetrahedral sites
- **CN** of Ca = 8 & F = 4.
- Z_{eff} = 4
- BaF_2, $BaCl_2$, CdF_2, $SrCl_2$, PbF_2



A_2B : Anti-Fluorite Type

- Na^{+} : All Tetrahedral sites
- O^{2-} : CCP Arrangement
- CN of Na = 4 & O = 8.
- Z_{eff} = 4
- Na_2O, Li_2O



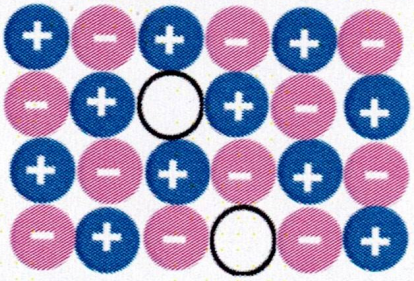
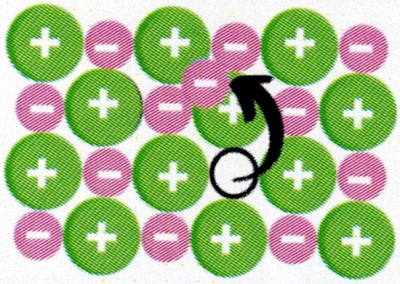
Rutile Structure (TiO_2) : O^{2-} forming HCP while Ti^{4+} ions occupy tetrahedral Voids

Pervoskite Structure ($CaTiO_3$) : Ca^{2+} in corner of the cube, O^{2-} in the face centre & Ti^{4+} at the centre of the cube

Defects in Solids

Stoichiometric Defects	Non-Stoichiometric Defects
The formula of the compound doesn't change	The formula of the compound changes

Stoichiometric Defects

Shottky Defect	Frenkel Defect
• Equal Cations and anions Missing • Density Decreases • Similar size of ions • NaCl, KCl, AgBr • Compounds with Low Coordination number.	• Some Ions leave their Normal Site • Density Same • Different size of ions • AgCl, AgBr • Compounds with high Coordination number.
	

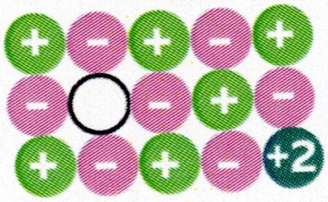
Non-Stoichiometric Defects

Metal Deficiency	Metal Excess Defects

Can be due to Anion Vacancies or Extra cations in interstitial site

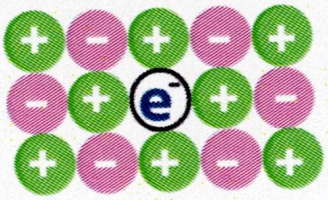
Metal Deficiency Defect

- FeO shows this defect which is mostly found in the composition of Fe (O.95). E.g. $Fe_{0.98}O$
- Fe^{2+} goes missing and Fe^{3+} appears



Metal Excess Defect due to Anion Vacancy

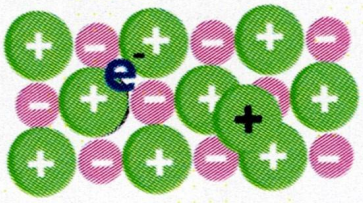
- Negative ion missing.
- Electron occupy empty space.
- These are called F-Centers
- E.g. NaCl heated in Na Vapours gives yellow color. LiCl gives Pink Color & KCl gives Violet Color



- F-Centers Present
- e^- in interstitial sites cause colors

Metal Excess Defect due to Cation Vacancy

- Extra cations present in the interstitial sites of the crystal.
- Electrons in other sites maintain electrical neutrality.



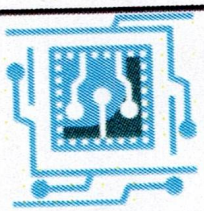
Extra cations on Heating

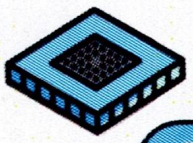
- Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow

$$ZnO \rightleftharpoons Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Yellow Colour due to 2 Electrons

- Crystals with either type of metal excess defect act as semiconductors



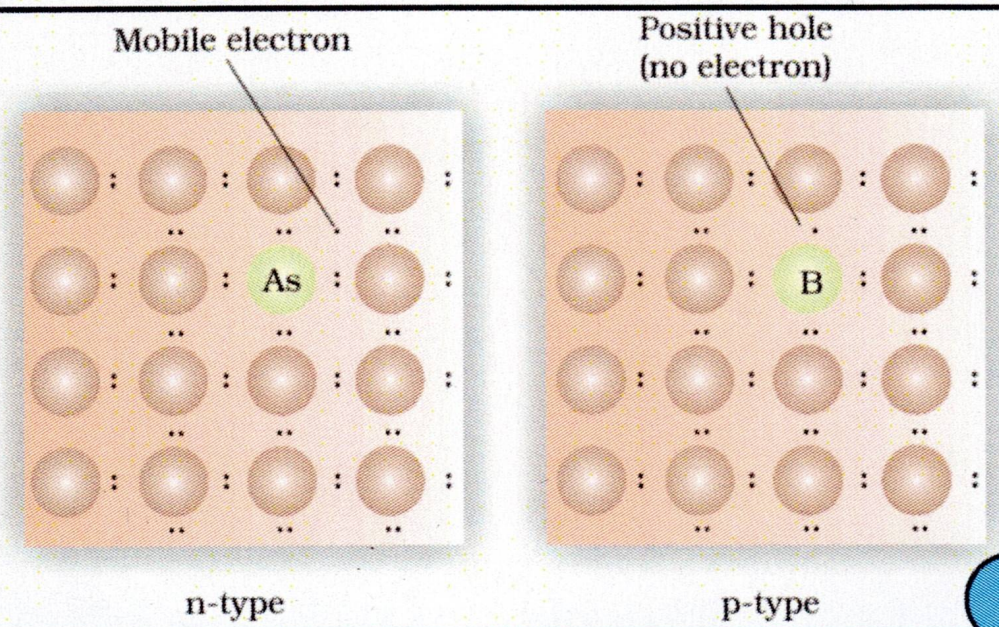


Electrical Properties of Solids

Property	Conductors	Insulators	Semiconductors
Conductivity Range	10^4-10^7	10^{-20} to 10^{-10}	10^{-6} to 10^4
Band Gap of V.B. and C.B.	Overlap	HIGH	Low

Semiconductors

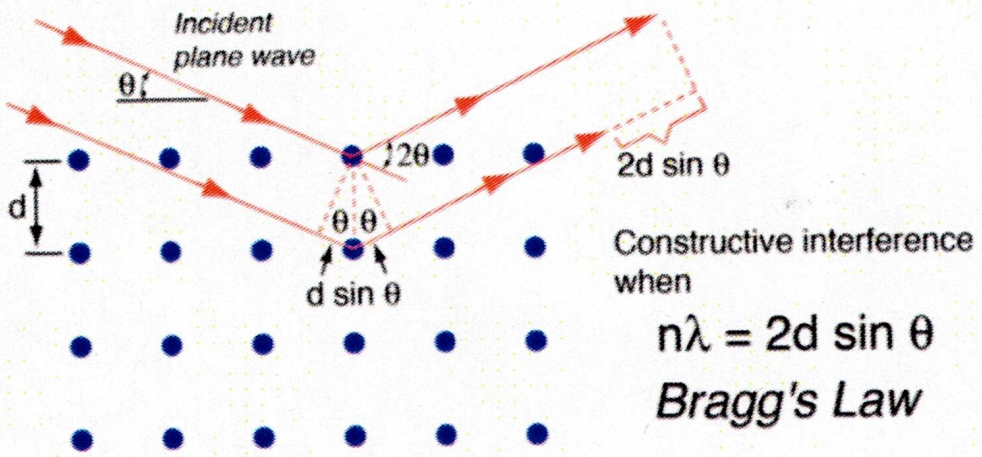
- On Heating, Some elctrons can jump from V.B. to C.B. in Pure Semiconductors (Intrinsic).
- Very Low Conductivity, Conductivity increases with doping **(Extrinsic) - 2 types**
- **n-type semiconductor :** Electron rich impurities added (G-14, Se or Ge doped with G-15 P or As)
- **p-type semiconductor** : Electron rich impurities added (G-14, Se or Ge doped with G-13 B or Al)



Some Common Magnetic and Dielectric Substance

Type of Substance	Examples
Diamagnetic	N_2, NaCl, Zn, Cd, Cu^+, TiO_2
Paramagnetic	Transition Metals (Cr, Mn, Ni, Co), metal ions (Cu^{2+}, Ni^{2+}), M-oxides (CuO, VO_2), molecules (NO & O_2)
Ferromagnetic	Ni, Fe, Co, CrO_2
AntiFerromagnetic	MnO, Mn_2O_3, MnO_2
Ferrimagnetic	Fe_3O_4 and pyrites
Ferroelectric	Rochelle salt, KH_2PO_4
Anti-Ferroelectic	$PbZrO_3$

Bragg's Law



Constructive interference when

$$n\lambda = 2d \sin \theta$$

Bragg's Law