

Revision Notes on Solid State

Classification of solids:

Crystalline and Amorphous solids:

S.No.	Crystalline Solids	Amorphous solids
1	Regular internal arrangement of particles	irregular internal arrangement of particles
2	Sharp melting point	Melt over a range of temperature
3	Regarded as true solids	Regarded as super cooled liquids or pseudo solids
4	Undergo regular cut	Undergo irregular cut.
5	Anisotropic in nature	Isotropic in nature

Based on binding forces:

Crystal Classification	Unit Particles	Binding Forces	Properties	Examples
Atomic	Atoms	London dispersion forces	Soft, very low melting, poor thermal and electrical conductors	Noble gases
Molecular	Polar or non – polar molecules	Vander Waal's forces (London dispersion, dipole – dipole forces, hydrogen bonds)	Fairly soft, low to moderately high melting points, poor thermal and electrical conductors	Dry ice (solid, methane)
Ionic	Positive and negative ions	Ionic bonds	Hard and brittle, high melting points, high heats of fusion, poor thermal and electrical conductors	NaCl, ZnS
Covalent	Atoms that are connected in covalent bond network	Covalent bonds	Very hard, very high melting points, poor thermal and electrical conductors	Diamond, quartz, silicon
Metallic Solids	Cations in electron cloud	Metallic bonds	Soft to very hard, low to very high melting points, excellent thermal and electrical conductors, malleable and ductile	All metallic elements, for example, Cu, Fe, Zn

Bragg Equation:

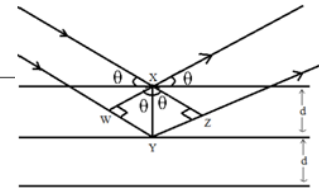
$$n\lambda = 2d\sin\theta,$$

Where

- d = distance between the planes
- n = order of refraction
- θ = angel of refraction
- λ = wavelength

Crystal Systems:

- Total number of crystal systems: 7
- Total number of Bravais Lattices: 14

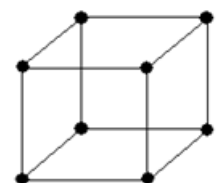


Crystal Systems	Bravais Lattices	Intercepts	Crystal angle	Example
Cubic	Primitive, Face Centered, Body Centered	$a = b = c$	$a = b = c = 90^\circ$	Pb, Hg, Ag, Au Diamond, NaCl, ZnS
Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$a = b = c = 90^\circ$	$\text{KNO}_3, \text{K}_2\text{SO}_4$
Tetragonal	Primitive, Body Centered	$a = b \neq c$	$a = b = c = 90^\circ$	$\text{TiO}_2, \text{SnO}_2$
Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$a = c = 90^\circ, b \neq 90^\circ$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$a \neq b \neq c \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7, \text{CaSO}_4 \cdot 5\text{H}_2\text{O}$
Hexagonal	Primitive	$a = b \neq c$	$a = b = 90^\circ, c = 120^\circ$	Mg, SiO_2 , Zn, Cd
Rhombohedral	Primitive	$a = b = c$	$a = c = 90^\circ, b \neq 90^\circ$	As, Sb, Bi, CaCO_3

Number of atoms in unit cells.

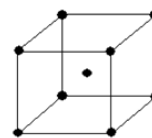
Primitive cubic unit cell:

- Number of atoms at corners = $8 \times \frac{1}{8} = 1$
- Number of atoms in faces = 0
- Number of atoms at body-centre = 0
- Total number of atoms = 1



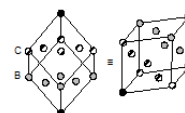
Body-centred cubic unit cell:

- Number of atoms at corners = $8 \times 1/8 = 1$
- Number of atoms in faces = 0
- Number of atoms at body-centre: = 1
- Total number of atoms = 2



Face-centred cubic or cubic-close packed unit cell:

- Number of atoms at corners = $8 \times 1/8 = 1$
- Number of atoms in faces = $6 \times 1/2 = 3$
- Number of atoms at body-centre: = 0
- Total number of atoms = 4



Packing Efficiency

Packing Efficiency = (Volume occupied by all the atoms present in unit cell / Total volume of unit cell) $\times 100$

Close structure	Number of atoms per unit cell 'z'.	Relation between edge length 'a' and radius of atom 'r'	Packing Efficiency
hcp and ccp or fcc	4	$r = a/(2\sqrt{2})$	74%
bcc	2	$r = (\sqrt{3}/4)a$	68%
Simple cubic lattice	1	$r = a/2$	52.4%

Density of crystal lattice:

$$r = (\text{Number of atoms per unit cell} \times \text{Mass number}) / (\text{Volume of unit cell} \times N_A)$$

$$r = \frac{\text{Number of unit cells} \times \text{Mass number}}{\text{Volume of Unit Cells} \times N_A}$$

or

$$r = \frac{z \times M}{V \times N_A}$$

Octahedral and Tetrahedral Voids:

Number of octahedral voids = Number of effective atoms present in unit cell

Number of tetrahedral voids = $2 \times$ Number of effective atoms present in unit cell

So, Number of tetrahedral voids = $2 \times$ Number of octahedral voids.

Coordination numbers and radius ratio:

Coordination numbers	Geometry	Radius ratio (x)	Example
2	Linear	$x < 0.155$	BeF ₂
3	Planar Triangle	$0.155 \leq x < 0.225$	AlCl ₃
4	Tetrahedron	$0.225 \leq x < 0.414$	ZnS
4	Square planar	$0.414 \leq x < 0.732$	PtCl ₄ ²⁻
6	Octahedron	$0.414 \leq x < 0.732$	NaCl
8	Body centered cubic	$0.732 \leq x < 0.999$	CsCl

Classification of Ionic Structures:

Structures	Descriptions	Examples
Rock Salt Structure	Anion(Cl ⁻) forms fcc units and cation(Na ⁺) occupy octahedral voids. Z=4 Coordination number =6	NaCl, KCl, LiCl, RbCl
Zinc Blende Structure	Anion (S ²⁻) forms fcc units and cation (Zn ²⁺) occupy alternate tetrahedral voids Z=4 Coordination number =4	ZnS, BeO
Fluorite Structures	Cation (Ca ²⁺) forms fcc units and anions (F ⁻) occupy tetrahedral voids Z= 4 Coordination number of anion = 4 Coordination number of cation = 8	CaF ₂ , UO ₂ , and ThO ₂
Anti- Fluorite Structures	Oxide ions are face centered and metal ions occupy all the tetrahedral voids.	Na ₂ O, K ₂ O and Rb ₂ O.
Cesium Halide Structure	Halide ions are primitive cubic while the metal ion occupies the center of the unit cell. Z=2 Coordination number of = 8	All Halides of Cesium.
Pervoskite Structure	One of the cation is bivalent and the other is tetravalent. The bivalent ions are present in primitive cubic lattice with oxide ions on the centers of all the six square faces. The tetravalent cation is in the center of the unit cell occupying octahedral void.	CaTiO ₃ , BaTiO ₃
Spinel and Inverse Spinel Structure	Spinel :M ²⁺ M ₂ ³⁺ O ₄ , where M ²⁺ is present in one-eighth of tetrahedral voids in a FCC lattice of oxide ions and M ³⁺ ions are present in half of the octahedral voids. M ²⁺ is usually Mg, Fe, Co, Ni, Zn and Mn; M ³⁺ is generally Al, Fe, Mn, Cr and Rh.	MgAl ₂ O ₄ , ZnAl ₂ O ₄ , Fe ₃ O ₄ , FeCr ₂ O ₄ etc.

Defects in crystal:

Stoichiometric Defects

1. Schottky Defects

- Some of the lattice points in a crystal are unoccupied.
- Appears in ionic compounds in which anions and cations are of nearly same size.

- Decreases the density of lattice
- Examples: NaCl and KCl

2. Frenkel Defects

- Ion dislocate from its position and occupies an interstitial position between the lattice points
- Appears in crystals in which the negative ions are much larger than the positive ion.
- Does not affect density of the crystal.
- Examples: AgBr, ZnS

Non-Stoichiometric Defects

1. Metal Excess defect:

Metal excess defect occurs due to

- anionic vacancies or
- presence of extra cation.
- F-Centres: hole produced due to absence of anion which is occupied by an electron.

2. Metal deficiency defect:

Metal deficiency defect occurs

- due to variable valency of metals
- when one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one