SOLIDS

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Frenkel defect:
- Ions(cations) missing from their lattice site occupy interstitial sites
- No effect on density
- There is a large difference in the size of the ions (cation or anions).

Interstitial defect:
- When some of the atoms occupy interstitial sites.
- It increases the density of a substance.

Vacancy defect:
- When some of the lattice sites are vacant.
- Decreases the density of the substances
- It develops on heating.

Schottky defect:
- Cations and anions are missing equally
- Density decreases
- It is shown by ionic substances in which ions (cations or anion) having almost similar sizes.

Non-ionic solids

Ionic solids

Stoichiometric defects: This defects do not disturb the stoichiometry of the solid
- They are also called intrinsic defects
- It increases with the increase in temperature (thermodynamic defects)

Due to presence of extra cations at interstitial sites e.g.,

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

Zn^{2+} ions and the electrons occupy interstitial sites.

Due to anionic vacancy (F-centres)
When holes created by anions are occupied by electrons, these sites are called F-centres and are responsible for colour in the crystal. e.g., NaCl

Metal deficiency defects: It is due to missing of a cation from its lattice site and the presence of a cation having higher charge in the adjacent lattice site e.g., FeO

Metal excess defects

Impurity defects: Foreign atoms are present at the lattice site in place of host atoms or at vacant interstitial sites.

Non-Stoichiometric defects: The ratio of (+)ve and (–)ve ions present in the compound differs from that required by ideal formula.

Line defects: Deviation in entire rows of lattice point.

Point defects: Deviation around a point or an atom in a solid

Unit cell: Smallest repeating pattern

Unit cell dimensions:

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

Z = no. of atoms per unit cell
d = density of solid
a =edge length
M = molar mass
N_A = Avogadro's number

Number of atoms per unit cell:

Primitive cubic $\Rightarrow 8 \times \frac{1}{8} = 1$

Body-centred cubic

$\Rightarrow 8 \times \frac{1}{8} + 1 = 2$

Face-centred cubic

$\Rightarrow 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Body-centred: It contains one constituent particle at its body centre, besides the ones that are at its corners.

Face centred: One constituent particles is present at the centre of each face.

End-centred: One constituent particles is present at the centre of any two opposite faces.

Primitive unit cell: Constituent particles (atom, molecules or ions) are present on the corner positions only

Centred unit cell: Constituent particles are present on the corner position along with some other positions.

Crystal system e.g.	Axial distances or edge lengths	Axial angles	Example
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$	Zinc blend, KCl, NaCl, Cu
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90°$	Sn (white tin), TiO_2, $CaSO_4$, SnO_2
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $CaSO_4$
Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90°; \beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4.10H_2O$
Hexagonal	a = b ≠ c	$\alpha = \gamma = 90°; \beta = 120°$	Graphite, CdS, ZnO
Rhombohedral or Trigonal	a = b = c	$\alpha = \gamma = \beta \neq 90°$	$CaCO_3$ (calcite), HgS (cinnabar)
Triclinic	a ≠ b ≠ c	$\alpha \neq \gamma \neq \beta \neq 90°$	$CuSO_4.5H_2O$, H_3BO_3, $K_2Cr_2O_7$

Close packing in one dimension: Lattice point arranged in a row C.N. = 2

Close packing in two dimension:
(a) Square close packaging: (A–A–A)…type C.N. = 4
(b) Hexagonal close packing: (A – B – A – B type) C.N. = 6

Close packing in three dimension:
(a) Primitive cubic unit cell: AAA … type arrangement, CN = 6, P.F. = 52.4%
(b) *hcp* = ABAB … type pattern, C.N. = 12 PF = 74%
(c) *ccp* or *fcc:* ABCABC … type pattern, CN = 12 PF = 74%

Type of solids

Imperfection in solids

Properties of solids

Structure of solids

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Close packed structure

Crystalline solids:
- Definite characteristics
- Geometrical shape
- Long range order
- Anisotropic in nature e.g., NaCl, KNO_3, LiF, etc.

Amorphous solids:
- Irregular in shape
- Short range order
- Isotropic in nature e.g., plastic, glass, etc.

Type of solid	Intermolecular forces	Properties
Ionic	Ion-Ion forces	Brittle, hard, high melting point, insulator in solid but conductors in both fused and aqueous solutions e.g, NaCl
Molecular	Dispersion forces/dipole dipole/H-bonds	Soft, low melting point, Insulators e.g H_2O, Br_2, CO_2, CH_4
Covalent	Covalent bonds	Hard, very high melting point e.g C-diamond, SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, malleable and ductile, Conducting e.g Na, Zn, Cu, Fe

Doping: The conductivity of an intrinsic semiconductor increases by adding an impurity which is electron rich or electron deficient as compared to Si or Ge. This process is called doping.

Radius ratio rules:
- The coordination number is a function of the sizes of the ions.
- Ionic radius ratios of cation and anion is very important in the determination of the crystal structures of an ionic substances.

Radius ratio = Radius of cation (r_+)/Radius of anion (r_-)

Radius ration	C.N.	shape	Example
0.155-0.255	3	Planar triangle	B_2O_3
0.255-0.414	4	Tetrahedral	ZnS
0.414-0.732	6	Octahedral	NaCl
0.732-1.0	8	Body-centred cubic	CsCl

Magnetic Properties:
- Paramagnetic substances are weakly attracted by a magnetic field. e.g., O_2, Cu^{2+}, Cr^{3+}.
- Diamagnetic substances are weakly repelled by a magnetic field. e.g. H_2O, C_6H_6 and NaCl.
- Ferromagnetic substances are those which show permanent magnetism even in the absence of magnetic field e.g., Fe, Ni, Co, CrO_2 etc.
- Anti-ferromagnetic substances are those which are expected to possess paramagnetism or ferromagnetism but actually have zero net magnetic magnetic moment due to equal number of domains in opposite directions, e.g., MnO.
- Ferrimagnetic substances are those expected to have large magnetism but actually have small net magnetic moment

↑ ↑ ↑ ↑ ↑ ↑ Ferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ Antiferromagnetic ↑ ↑ ↓ ↑ ↑ ↓ Ferrimagnetic

Electrical Properties
- Conductors: Valence band is partially filled or it overlaps with a higher energy unoccupied conduction band
- Semiconductors: Small energy gap between valence and conduction band
- Insulators: Large energy gap between valence and conduction band

p-type semiconductor (by doping electron deficient impurities)
n-type semiconductor (by doping electron rich impurities)

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