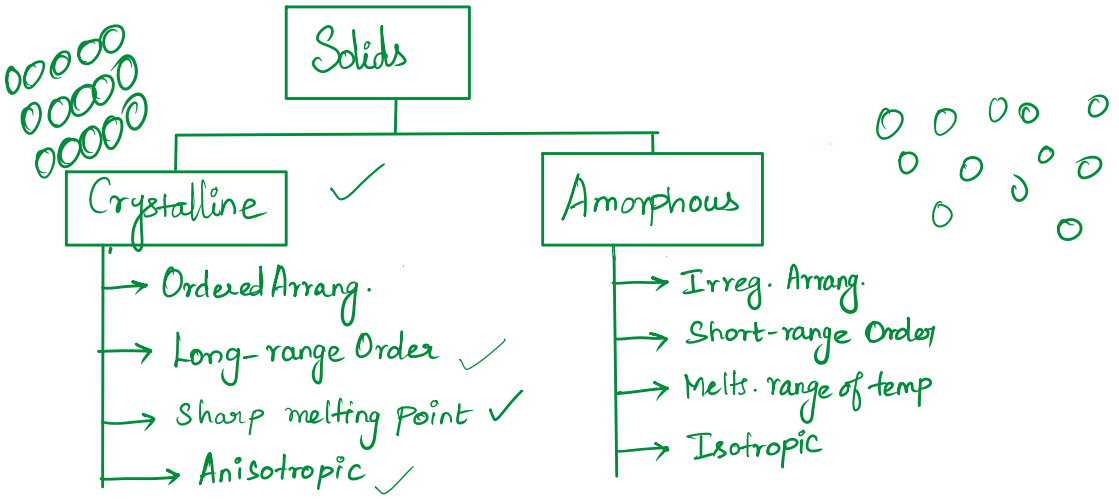
Solid state

Free Marks.

1.1 Types of Solids



1.2 Types of Crystalline Solids Based on Binding Forces

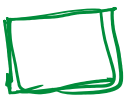
Properties	Ionic Solids	Metallic Solids	Covalent/Network Solids	Molecular Solids
Constituent Particles	Positive and negative ions	Positive ions in a 'sea' of electrons	Atoms	Molecules
Binding Force	Electrostatic attraction between ions	Electrostatic attraction between cations and sea of electrons	Strong covalent bonds	Weak van der Waals forces and dipole-dipole interactions
Hardness	Hard	Hard to very hard	Very hard (except graphite which is soft)	Very soft
Brittleness	High	Very low	Medium	Low

Melting Point	Moderate to very high	Low to very high	Very high	Low
Electrical Conductivity	Bad conductors (conductors in molten state)	Very good conductors	Bad conductors (except graphite) ↓ free e^-	Bad conductors
Solubility	Soluble in polar, insoluble in non-polar solvents	Insoluble in polar and non-polar solvents	Insoluble in polar, usually soluble in non-polar solvents	Some soluble in polar, some in non-polar, some in both
Examples	NaCl, ZnS, KNO_3, CaO, $BaCl_2$, MgO, $NaNO_3$	Metals and alloys	Diamond, graphite, S, quartz, SiO_2, SiC, AlN	CCl_4, H_2, CO_2, H_2O, N_2, I_2, sugar, Ar, CH_4

2. CRYSTAL LATTICE & UNIT CELL

2.1 Crystal Lattice

- **Definition**: Regular arrangement of an infinite set of points which describes the three-dimensional arrangement of constituent particles in space
- Also called space lattice



2.2 Unit Cell

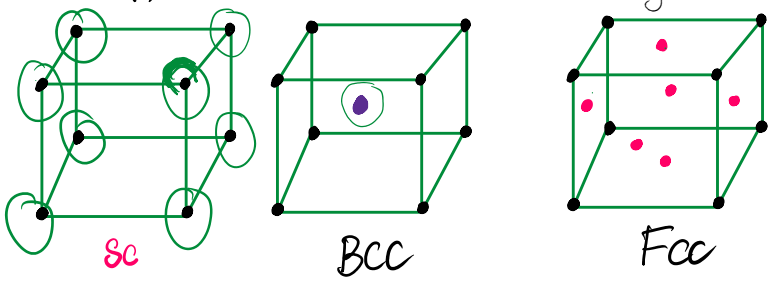
- **Definition**: Smallest repeating unit of a space lattice which, when repeated over and over in three dimensions, results into the whole crystal

- Types of Unit Cells:

1. Simple/Primitive (P): Particles only at corners

a. Face-Centered (F): Particles at corners and at center of each face

b. Body-Centered (I): Particles at corners and at body center



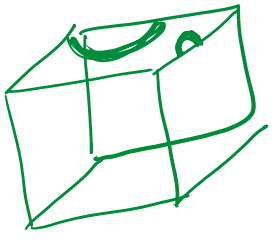
Corner - 8 Centre - 1 6 Faces

2.3 Characteristics of Different Unit Cells

Property	Simple Cubic	Face-Centered Cubic	Body-Centered Cubic
Position of particles	Only at corners ✓	At corners and center of each face	At corners and body center
No. of atoms per unit cell	1 ✓	4	2
Coordination number	6 ✓	12	8
Packing efficiency	52% ✓	74%	68%

2.4 Calculation of Number of Particles per Unit Cell

- Corner atom contribution = 1/8 per corner
- Face-centered atom contribution = 1/2 per face
- Edge atom contribution = 1/4 per edge
- Body-centered atom contribution = 1 atom



$SC = 8 \times \frac{1}{8} = 1$ $Fcc = 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

$SC = 8 \times \frac{1}{8} = 1$ $\quad Fcc = 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

$= 1 + 3 = 4$

$Bcc = 8 \times \frac{1}{8} + 1 = 1 + 1 = 2.$

2.5 Unit Cell Dimensions

- **Simple cubic:**
  - Edge length (a)
  - Atomic radius (r) = $a/2$
- **Face-centered cubic:**
  - Edge length (a)
  - Atomic radius (r) = $a/(2\sqrt{2}) = 0.3535a$
- **Body-centered cubic:**
  - Edge length (a)
  - Atomic radius (r) = $(\sqrt{3})a/4 = 0.433a$

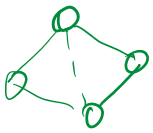
3. SEVEN CRYSTAL SYSTEMS

Crystal System	Relative Axial Length	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, CsCl, CaF_2, CaO
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	K_2PtCl_6, $PbWO_4$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	K_2SO_4, KNO_3, $BaSO_4$, $CaCO_3$ (aragonite)
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (calcite), $NaNO_3$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	AgI, SiC, HgS
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	$CaSO_4 \cdot 2H_2O$, $K_2Fe(CN)_6$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$

4. CLOSE PACKING IN CRYSTALS

4.1 Interstitial Sites in Closed Packed Structure

Void Type	Formation	Size (r/R)
Trigonal void	Formed at the center of three spheres	r = 0.155R
Tetrahedral void	Formed by covering trigonal voids by spheres of lower layer	r = 0.225R
Octahedral void	Formed at the center of six spheres	r = 0.414R
Cubic void		r = 0.732R



Where r = radius of void, R = Radius of closely packed spheres

AB AB ABCABC.

4.2 Characteristics of Voids

- If the number of closely packed spheres is N, then:
  - Number of octahedral voids = N
  - Number of tetrahedral voids = 2N

4.3 Packing Systems

- **Square close packing**: Spheres of adjacent rows one over the other
- **Hexagonal close packing**: Spheres of every second row placed in depression between spheres of first row
- **Body-centered cubic**: Not the closest system, spheres of first row slightly open and not in contact

4.4 Radius Ratio and Coordination Number

Radius Ratio (r_+/r_-)	Coordination Number	Structural Arrangement	Structure Type	Examples

		t		
0.155 – 0.225	3	Planar triangular	-	B_2O_3
0.225 – 0.414	4	Tetrahedral	Sphalerite, ZnS	CuCl, CuBr, CuI, BaS, HgS
0.414 – 0.732	6	Octahedral	Sodium chloride (Rock salt)	NaBr, KBr, MgO, MnO, CaO, CaS
0.732 – 1.000	8	Body-centered cubic	Caesium chloride	CsI, CsBr, TlBr

4.5 Packing Fraction

- Formula: $f = (Z \times \text{Volume of one sphere}) / (\text{Volume of the unit cell})$
- For elements: $f = (Z \times (4\pi r^3/3)) / a^3$
- where Z = number of atoms/unit cell (1 for simple, 2 for bcc, 4 for fcc)

4.6 Relation between Density and Edge of Cubic Crystals

- $\rho = (Z \times M) / (a^3 \times N_a)$
- where Z = number of formula units in unit cell
- M = formula mass (molecular mass) of the compound
- a = edge length of unit cell
- N_a = Avogadro's number

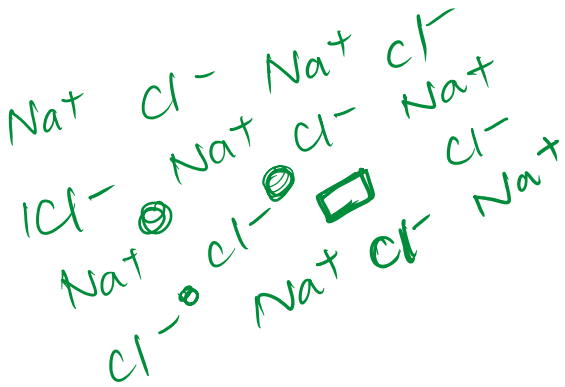
5. CHARACTERISTIC PROPERTIES OF VARIOUS TYPES OF IONIC SOLIDS

Type	Crystal Structure	Ions Forming Close Packed Structure	Ions Present in Voids	Coordination Number	No. of Formula Units	Examples
AB	ZnS type	S^{2-} ions form ccp structure	Zn^{2+} ions in	$Zn^{2+} = 4$, $S^{2-} = 4$	4	ZnS, AgI, CuCl,

			alternate tetrahedral voids			CdS, HgS, CuBr, CuI, BeS, BeO, ZnO
AB	NaCl type	Cl^- ions form ccp structure	Na^+ ions in all octahedral holes	$Na^+ = 6$, $Cl^- = 6$	4	NaCl, LiCl, KBr, AgBr, MgO, CsI, CaO, FeO, CoO, NiO
AB	CsCl type	bcc structure, Cl^- ions at corners of cube	Cs^+ ions at the center of cube	$Cs^+ = 8$, $Cl^- = 8$	1	CsCl, CsCN, CaS, CsI, TlCl, TlBr, Tll, TlCN
AB_2	CaF_2 type (Fluorite)	Ca^{2+} ions form ccp structure	F^- ions in all tetrahedral holes	$Ca^{2+} = 8$, $F^- = 4$	4	CaF_2, $BaCl_2$, PbO_2, $SrCl_2$, CdF_2
A_2B	Na_2O type (Antifluorite structure)	O^{2-} ions form ccp structure	Na^+ ions in all tetrahedral holes	$Na^+ = 4$, $O^{2-} = 8$	4	Na_2O, K_2O, Li_2O, K_2S

6. IMPERFECTIONS IN CRYSTALS

Defect	Nature of Defect
Schottky	Atom or ion missing from lattice point giving a vacancy. Density of crystal is lowered.
Interstitial	Atom or ion present in a vacant void, also called hole (or interstitial site).
Frenkel	Hybrid defect from combination of vacancy and interstitial defect. Atom or ion at lattice point displaced to an interstitial site creating a vacancy.
F-centre	Electron trapped in an anionic



	vacancy. If concentration of F-centres is high, colorless crystals (like KCl, LiCl, NaCl) develop some color.
Dislocation	Line defects called dislocations.
Non-stoichiometric	Compounds contain combining elements in ratio different from stoichiometric formulae. E.g., VO_2 (x = 0.6 to 1.3), $Fe_{0.95}O$.

7. ELECTRICAL PROPERTIES

7.1 Classification Based on Conductivity

- **Conductors**: Allow passage of electric current
  - Conductivity: $10^6 - 10^8$ ohm^{-1} cm^{-1}
- **Semiconductors**: Intermediate conductivity
  - Conductivity: $10^{-9} - 10^2$ ohm^{-1} cm^{-1}
- **Insulators**: Do not practically allow passage of electric current
  - Conductivity: 10^{-20} ohm^{-1} cm^{-1}

7.2 Types of Semiconductors

- **Intrinsic Semiconductors**: Electrical conductivity due to internal disorder without adding external substance
- **Extrinsic Semiconductors**: Show electrical conductivity due to externally added impurity
  - **n-type**: Group 14 elements doped with group 15 elements, free electron increases conductivity
  - **p-type**: Group 14 elements doped with group 13 elements, holes increase conductivity

8. MAGNETIC AND DIELECTRIC PROPERTIES

8.1 Magnetic Properties

- **Diamagnetic substances**: Weakly repelled by external magnetic field. E.g., N_2, NaCl, Zn, TiO_2
- **Paramagnetic substances**: Weakly attracted by external magnetic field.

E.g., O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}

- **Ferromagnetic substances**: Show permanent magnetism even in absence of external magnetic field. E.g., Ni, Fe, Co
- **Antiferromagnetic substances**: Have zero net dipole moment even though they have large number of unpaired electrons. E.g., MnO
- **Ferrimagnetic substances**: Possess very small net magnetic moment even though having large number of unpaired electrons. E.g., Fe_3O_4

8.2 Dielectric Properties

- **Piezoelectricity**: Electricity produced due to displacement of ions from their orderly arrangement by application of mechanical stress. E.g., $PbZrO_3$, $NH_4H_2PO_4$, quartz
- **Pyroelectricity**: Some piezoelectric crystals when heated produce a small electric current
- **Ferroelectricity**: Certain piezoelectric crystals show permanent alignment of dipoles even in absence of electric field. E.g., Rochelle salt, $BaTiO_3$
- **Antiferroelectricity**: In some crystals, equal number of dipoles are oriented in opposite directions so crystal does not possess net dipole moment. E.g., lead zirconate ($PbZrO_3$)

9. IMPORTANT POINTS FOR COMPETITIVE EXAMS

- **Bragg's equation**: $2d \sin\theta = n\lambda$
  - d = distance between atomic planes
  - λ = wavelength of X-rays used
  - θ = angle at which X-rays are incident on face of crystal
  - n = 1, 2, 3... (order of diffraction)
- **Normal spinel structure**: Structure where anions constitute ccp or fcc lattice and cations occupy voids
  - Dipositive ions present in tetrahedral voids and tripositive ions in octahedral voids. E.g., $MgAl_2O_4$, $MgCr_2O_4$
- **Inverse spinel structure**: Dipositive ions present in octahedral holes and tripositive ions equally distributed between tetrahedral and octahedral holes. E.g., Fe_3O_4
- **Isomorphism**: Phenomenon wherein crystalline solids have similar chemical composition and same crystal shape. E.g., $ZnSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 7H_2O$
- Ferromagnetic, ferrimagnetic, and antiferromagnetic substances show

paramagnetism at higher temperatures due to greater alignment of spins. E.g., Fe_3O_4 is ferrimagnetic at room temperature but becomes paramagnetic at 850 K

- **Curie temperature**: Characteristic temperature above which no ferromagnetism is observed
- Cubic is the most symmetrical crystal system, while triclinic is the most unsymmetrical
- Polonium is the only metal that crystallizes in simple cubic lattice
- On pressurizing a crystal its coordination number increases while on heating coordination number decreases

AgBr ⇒ Schottky & Frenkel defects.

Previously Asked Solid State Questions & Solutions

Question 1: JEE Main

Question: In a face-centered cubic lattice, atoms A occupy the corner positions and atoms B occupy the face-center positions. If one atom of B is missing from one of the face-centered positions, the formula of the compound is:

$8 \times \frac{1}{8} = 1$ atom

$6 \times \frac{1}{2} = 3$ atom.

B is missing. $3 - 1 = 2$ atoms.

A_2B_3

A_2B_5

A_4B_3

A_4B_4

Question 2: JEE Advanced

Question: The unit cell of an element of atomic mass 96 g/mol has an edge length of 480 pm. If the density of the element is 8.5 g/cm³, the type of cubic unit cell is:

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

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

$\ldots -10)^3 \times 6.022 \times 10^{23}$

Primitive cubic

Body-centered cubic

Face-centered cubic

End-centered cubic

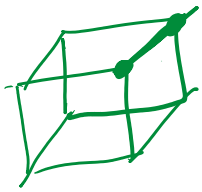
End-centered cubic

$$Z = \frac{\rho a^3 N}{M} = \frac{8.5 \times (480 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{96}$$

$$Z = 4$$

Question 3: NEET

Question: CsCl has a body-centered cubic structure. The distance between the two nearest Cs^+ ions is:



√3a

a

a/√2

a√3/2

Where 'a' is the edge length of the unit cell.

Question 4: JEE Main

Question: The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. The coordination number of Na^+ ion in NaCl crystal is:

$$\frac{r_+}{r_-} = \frac{95}{181} = 0.525$$

4

6

8

12

Question 5: JEE Advanced

Question: In a cubic close-packed structure of a compound AB_2, the anions B form the lattice and the cations A occupy only the octahedral voids. The percentage of octahedral voids occupied by the cations is:

25%
50%
75%
100%

% of Octahedral Void = $\frac{\text{No. of Cation}}{\text{No. of Oh voids}}$

$= \frac{2}{4} \times 100$

$= 50\%$

Question 6: NEET

Question: The percentage of free space in a body-centered cubic unit cell is approximately:

68%

32%
26%
48%
74%

Question 7: JEE Main

Question: The number of atoms in 100 g of an FCC crystal with density 10 g/cm^3 and cell edge 100 pm is close to:

$Z = 4$

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

$M = ?$

6 × 10^{23}

12 × 10^{23}

24 × 10^{23}

3 × 10^{23}

Question 8: JEE Advanced

Question: A metal crystallizes in a face-centered cubic lattice with a unit cell edge of 400 pm. The density of the metal is 7.2 g/cm^3. What is the molar mass of the metal?

27.4 g/mol

52.0 g/mol

104.1 g/mol

54.9 g/mol