AITS Advance Preparatory Guide

Solid State

Advanced Level for IIT JEE Advanced

All India Test Series (AITS)

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Contents

1 Introduction

Solid State is a crucial chapter for IIT JEE Advanced, focusing on the structural and physical properties of crystalline solids. This guide offers deeply expanded theoretical discussions, advanced examples with solutions, rigorous exercises, and JEE-style MCQs, enriched with illustrative diagrams to clarify complex concepts. The vibrant format, complete solutions, and focus on multi-step problem-solving ensure aspirants master topics like crystal structures, defects, and magnetic properties, preparing them for the exams challenges.

2 Classification of Solids and Crystal Structures

2.1 Theory

Solids are broadly classified into **crystalline** and **amorphous** solids based on their atomic arrangement. Crystalline solids exhibit a long-range order with atoms arranged in a repeating 3D pattern, forming a **crystal lattice**, whereas amorphous solids lack such order, resembling liquids structurally (e.g., glass). Crystalline solids are further categorized into ionic, covalent, molecular, and metallic solids, each with distinct properties: ionic solids (e.g., NaCl) have high melting points due to strong electrostatic forces; covalent solids (e.g., diamond) are hard due to directional covalent bonds; molecular solids (e.g., ice) are soft with weak van der Waals forces; and metallic solids (e.g., copper) conduct electricity due to delocalized electrons.

The **unit cell** is the smallest repeating unit of a crystal lattice, characterized by lattice parameters: edge lengths (a, b, c) and angles (α, β, γ). There are seven crystal systems (cubic, tetragonal, orthorhombic, etc.), and 14 Bravais lattices, with cubic systems (simple cubic, BCC, FCC) being most relevant for JEE. The number of atoms per unit cell (Z) is calculated as:

$$Z = \frac{\text{Number of atoms at corners}}{8} + \frac{\text{Number of atoms at faces}}{2} + \frac{\text{Number of atoms at edges}}{4} + \text{Number of atoms a}$$

For example, in FCC, $Z = \frac{8}{8} + \frac{6}{2} = 4$. Coordination number (number of nearest neighbors) and atomic radius relationships (e.g., $a = 2r$ for simple cubic) are critical for JEE problems involving density or lattice parameter calculations. The diagram below illustrates a simple cubic unit cell.

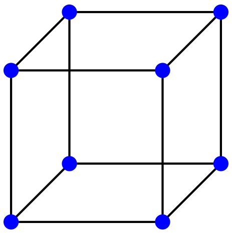

Figure 1: Simple cubic unit cell, showing atoms at corners (shared by 8 unit cells).

2.2 Example 1: Number of Atoms in BCC Unit Cell

Calculate the number of atoms per unit cell in a body-centered cubic (BCC) structure.

Solution: In a BCC unit cell, there are 8 atoms at the corners and 1 atom at the body center. Each corner atom is shared by 8 unit cells, and the body-centered atom is fully within the unit cell. Thus:

$$Z = \frac{8}{8} + 1 = 1 + 1 = 2$$

So, the number of atoms per BCC unit cell is 2.

2.3 Example 2: Coordination Number of FCC

Determine the coordination number of an atom in a face-centered cubic (FCC) structure.

Solution: In an FCC unit cell, consider an atom at the center of a face. It is surrounded by 4 atoms in the same face (in-plane), 4 atoms from the 4 edges of adjacent faces, and 4 atoms from the corners of adjacent unit cells. Alternatively, consider a corner atom: it has 4 face-centered atoms in its own unit cell and 4 in adjacent unit cells, plus 4 from edges, totaling 12 nearest neighbors. Thus, the coordination number of FCC is 12.

2.4 Example 3: Density of Simple Cubic Crystal

A simple cubic crystal has a lattice parameter $a = 3\,\text{Å}$ and atomic mass 50 g/mol. Calculate its density ($N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$).

Solution: For a simple cubic unit cell, $Z = 1$ (8 corner atoms, each shared by 8 unit cells: $\frac{8}{8} = 1$). Volume of the unit cell: $V = a^3 = (3 \times 10^{-8}\,\text{cm})^3 = 27 \times 10^{-24}\,\text{cm}^3$. Mass of one atom: $m = \frac{50}{6.022\times10^{23}} \approx 8.303 \times 10^{-23}\,\text{g}$. Mass of the unit cell: $Z \cdot m = 1 \cdot 8.303 \times 10^{-23} = 8.303 \times 10^{-23}\,\text{g}$. Density:

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{8.303 \times 10^{-23}}{27 \times 10^{-24}} \approx 3.075\,\text{g/cm}^3$$

Thus, the density is approximately 3.08 g/cm^3.

3 Close Packing in Solids

3.1 Theory

Close packing refers to the efficient arrangement of spherical particles (atoms) to minimize empty space in a crystal lattice, maximizing packing efficiency. In one dimension, spheres touch along a line. In two dimensions, **hexagonal close packing** (HCP) arranges spheres in a hexagonal pattern, with each sphere touching 6 others (coordination number 6). In three dimensions, close packing occurs in two primary forms: **cubic close packing** (CCP, equivalent to FCC) and **hexagonal close packing** (HCP). Both have a packing efficiency of 74% and a coordination number of 12.

In CCP/FCC, layers are stacked in an ABCABC pattern: the third layer (C) is offset from the first (A) and second (B). In HCP, layers follow an ABAB pattern, where the third layer aligns with the first. The packing efficiency is calculated as:

$$\text{Packing efficiency} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} \times 100$$

For FCC: $Z = 4$, and the relationship between lattice parameter a and atomic radius r is $a = 2\sqrt{2}r$, yielding a packing efficiency of $\frac{\pi\sqrt{2}}{6} \approx 74\%$. Voids in close-packed structures include **tetrahedral** (coordination number 4) and **octahedral** (coordination number 6) voids, which are critical for understanding ionic solids in JEE problems. The diagram below shows the ABC stacking in FCC.

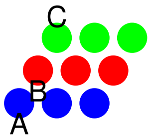

Figure 2: ABC stacking in FCC (cubic close packing), showing layer arrangement.

3.2 Example 1: Packing Efficiency of FCC

Calculate the packing efficiency of an FCC unit cell (atomic radius r).

Solution: In FCC, $Z = 4$. The relationship between lattice parameter a and radius r is $a = 2\sqrt{2}r$. Volume of the unit cell: $V = a^3 = (2\sqrt{2}r)^3 = 8\sqrt{8}r^3$. Volume of one atom: $v = \frac{4}{3}\pi r^3$. Total volume of atoms: $Z \cdot v = 4 \cdot \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$. Packing efficiency:

$$\text{Efficiency} = \frac{\frac{16}{3}\pi r^3}{8\sqrt{8}r^3} \times 100 = \frac{16\pi}{3 \cdot 8 \cdot 2\sqrt{2}} \times 100 = \frac{16\pi}{48\sqrt{2}} \times 100 \approx 74\%$$

Thus, the packing efficiency of FCC is 74%.

3.3 Example 2: Radius of Tetrahedral Void in FCC

Find the radius of a tetrahedral void in an FCC lattice with atomic radius r.

Solution: In an FCC lattice, a tetrahedral void is formed by one corner atom and three face-centered atoms. The corner atom is at $(0,0,0)$, and face-centered atoms are at $(a/2, a/2, 0)$, $(a/2, 0, a/2)$, and $(0, a/2, a/2)$. The distance from the corner to a face-centered atom is $a\sqrt{3}/2$. Since $a = 2\sqrt{2}r$, this distance is $(2\sqrt{2}r)\sqrt{3}/2 = r\sqrt{6}$. The center of the tetrahedral void is at the centroid, at a distance of $\frac{3}{4}$ of this from the corner atom: $d = \frac{3}{4} \cdot r\sqrt{6} = r\sqrt{\frac{3}{2}}$. The radius of the void R satisfies $R + r = d$, so:

$$R = r\sqrt{\frac{3}{2}} - r = r(\sqrt{\frac{3}{2}} - 1) \approx r(1.225 - 1) = 0.225r$$

Thus, the radius of the tetrahedral void is $0.225r$.

3.4 Example 3: Number of Octahedral Voids in HCP

Determine the number of octahedral voids in an HCP unit cell.

Solution: In an HCP unit cell, there are 6 atoms (2 atoms in the basal planes, each contributing $\frac{1}{3}$ of 6 atoms, and 3 atoms in the middle plane). Each HCP unit cell has one octahedral void per atom in the close-packed structure. However, considering the unit cell definition, there are 2 octahedral voids fully within the HCP unit cell: one formed between the bottom A layer and middle B layer, and another between the middle B layer and top A layer. Thus, the number of octahedral voids in an HCP unit cell is 2.

4 Imperfections in Solids

4.1 Theory

Real crystals deviate from perfect order due to **imperfections** or defects, which significantly affect their properties. Defects are classified into **point defects** (involving single atomic sites) and **line defects** (dislocations). Point defects include **vacancy defects** (missing atoms), **interstitial defects** (extra atoms in interstitial sites), and **substitutional defects** (foreign atoms replacing host atoms). In ionic solids, point defects maintain charge neutrality, leading to **Schottky defects** (equal number of cation and anion vacancies, e.g., in NaCl) and **Frenkel defects** (cation displaced to an interstitial site, e.g., in AgCl).

The concentration of defects increases with temperature, following the Arrhenius equation: $n_d \propto e^{-\frac{E_d}{kT}}$,