

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
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CHEMICAL SCIENCES

CODE:01

2.12. Solid State

At a glance

Various types solids and their physical properties, 3D appearance, Unity cells and structural properties, packing, structure of ionic solids, Miller and Weises indices, Primitive, BCC, CCP type of crystals, HCP, CCP type of crystal, density etc.



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Key Statements

Basic Key statements: True solids or crystalline solids (2.12.1), Ionic solids (2.12.3), Isomorphism and polymorphism (2.12.7), Characteristics of seven types of crystal system (2.12.11), Unit cell (2.12.16), Structures of ionic compounds (2.12.19), Density of crystal (2.12.26)

Standard Key statements: Laws of crystallography (2.12.8), Interplanar distance (2.12.12), Packing fraction (2.12.17), Characteristics of different unit cells (2.12.18), Characteristics properties of various types of ionic solids (2.12.30),

Advance Key statements: Miller indices (2.12.9), Bragg's equation (2.12.21), Close packing in crystals (2.12.22/23/24/25)



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Key Facts

2.12.1. True solids or crystalline solids:

In crystalline solids, constituent units are arranged in an ordered manner. A crystalline solid is characterized by a definite crystal structure, a definite melting point and a definite heat of fusion.

2.12.2. Pseudo solids or amorphous solids:

Substances which look like solids but actually are not solids are called pseudo solids. These do not have definite geometrical structure because the constituent particles are not arranged in an order manner but in a random manner. These are actually regarded as **super cooled liquids**. These lose their shape on standing and flow under their own weight, e.g., glass, pitch, rubber etc.

2.12.3. Ionic solids:

Here constituent units are ions of opposite charges and interparticle forces are ionic forces, e.g., NaCl, BaCl₂ etc.

2.12.4. Covalent solids:

Here the constituent particles are atoms which are held together by covalent bonds. These solids are very hard because of strong interparticle covalent bonds, e.g., quartz, diamond etc.

2.12.5. Metallic solids:

Here the constituent units are positively charged kernels which are held together by metallic bonds, e.g., Na, Cu etc.

2.12.6. Molecular solids:

Here the constituent units are molecules and the interparticle forces are hydrogen bonds or Van der Waals forces, e.g., dry ice, CO₂, S₈ etc.

2.12.7. Isomorphism and polymorphism:

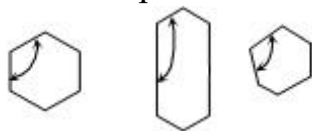
If two substances possess a similar crystalline form and similar chemical composition, these are called isomorphs, e.g., Na_2SeO_4 and Na_2SO_4 .

On the other hand certain substances can exist in more than one crystalline form (polymorphism), e.g., rhombic and monoclinic sulphur.

2.12.8. Laws of crystallography:

Crystallography is the branch of science which deals with the geometry properties and structure of crystals and crystalline substances. It is based on three fundamental laws.

- **The law of constancy of interfacial angles:** This law states that angle between the adjacent corresponding faces is the interfacial angles of the crystal of the particular substance is always constant in spite of having different shapes and sizes and mode of growth of crystal. The size and shape of the crystal depend upon the conditions of the crystallisation. This law is also called as Steno's Law.



- **Laws of rotational indices (Haüy's law):** This law describes that the ratio of intercepts of the different faces of a crystal with the three axes are constant and can be expressed by the rational numbers that the intercepts of any face of the crystal along the crystallographic axes are either equal to unit intercepts (which means intercepts made by the unit cell) a, b, c or various simple whole number multiples of them such as $na, n'b, n''c$, where n, n' and n'' are the simple whole numbers. The whole numbers n, n' and n'' are known as **Weiss indices**.

- **The law of constancy of symmetry:** In accordance to this law, all the crystals of a substance have the same elements of the symmetry is the plane of symmetry, the axis of symmetry and the centre of symmetry.

2.12.9. Miller indices: The planes in the crystals are described by a set of integers (such as h , k and l) known as Miller indices. The Miller indices of the plane are reciprocals of the fractional intercepts of that plane on the a variety of crystallographic axes. For calculating the Miller indices, a reference plane, generally known as parametral plane, is selected having the intercepts of a , b and c along the y , x and z -axes, respectively. Then, the intercepts of the unknown plane are given with respect to the a , b and c of parametral plane.

Therefore, the Miller indices are:

$$h = \frac{a}{\text{intercept of the plane along } x - \text{axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y - \text{axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z - \text{axis}}$$

2.12.10. Crystal systems:

In first sight there seems to be infinite number of shapes of crystals. However careful examination of several thousand crystals of various substances has revealed that only seven possible crystals symmetries are possible. The 7 different combinations of symmetry elements are called crystal system.

Images

2.12.11. Characteristics of seven types of crystal system:

System	Number of Bravais lattice (14)	Maximum symmetry elements	Axis and angles	Examples
1. Cubic	3	9 planes 13 axes	$a=b=c$ $\alpha=\beta=\gamma=90^\circ$	NaCl, KCl
2. Tetragonal	2	5 planes 5 axes	$a=b \neq c$ $\alpha=\beta=\gamma=90^\circ$	SnO ₂ , ZnO ₂
3. Hexagonal	1	7 planes 7 axes	$a=b \neq c$ $\alpha=\beta=90^\circ$ $\gamma=120^\circ$	ZnO, HgS
4. Trigonal or rhombohedral	1	7 planes 7 axes	$a=b=c$ $\alpha=\beta=\gamma \neq 90^\circ$	CaSO ₄ , Calcite
5. Orthorhombic	4	3 planes 3 axes	$a \neq b \neq c$ $\alpha=\beta=\gamma=90^\circ$	K ₂ SO ₄ , KNO ₃
6. Monoclinic	2	1 plane 1 axis	$a \neq b \neq c$ $\alpha=\gamma=90^\circ$ $\beta \neq 90^\circ$	Na ₂ SO ₄ .10H ₂ O, CaSO ₄ .2H ₂ O
7. Triclinic	1	No plane No axis	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , H ₃ BO ₃

2.12.12. Interplanar distance:

The distance between the parallel planes in a crystal are designated as d_{hkl} .

For different cubic lattices these interplanar spacing are given by

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

2.12.13. Lattice energy:

It is defined as the energy released in the process flow in the constituent ions are placed in their respective positions in the crystal lattice for this experimentally measured from the born Haber cycle data.

$$U = - \frac{N_0 A Z_+ Z_- e^2}{4\pi\epsilon_0 r} \left(1 - \frac{1}{n}\right)$$

2.12.14. Dulong - Petit's law:

This law states that the product of the specific heat capacity of a solid element and its mass per mole is constant.

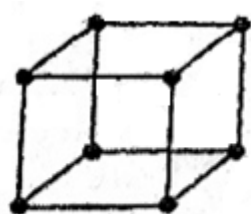
2.12.15. Space lattice:

The regular arrangement of infinite set of points in space is called lattice or space lattice.

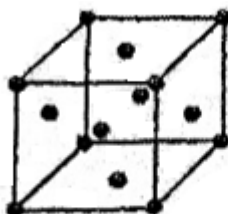
2.12.16. Unit cell: The smallest three dimensional motion of a complete space lattice when repeated over again and again in different directions produces the complete space lattice is called unit cell.

The shape of may be of following kinds:-

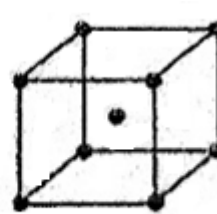
- ❖ Simple or primitive cell: In this type points are present only at the corner of the unit cell.
- ❖ Face – centered (FCC): In this type, points were present at the corners as well as centre of each of the six faces.
- ❖ Body – centered (BCC): In This type points are present at the corners and an additional. Each present at the centre of the unit cell.
- ❖ End face – centered: In this type points are present at the corners and at centre of two endfaces.



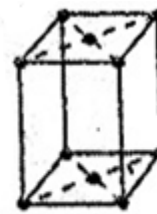
(a) simple



(b) Face-centred



(c) Body-centred



(d) End-centred

2.12.17. Packing fraction: It is defined as the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

$$P.F = \frac{\text{Total volume occupied by the molecules}}{\text{Volume of the unit cell}}$$

2.12.18. Characteristics of different unit cells:

Cubic unit cell	No of atoms per unit cell	Relation between edge length (a) and radius of atom (r)	Packing efficiency	Area cover by the atoms	Void space
Simple or Primitive	1	$a = 2r$	0.524	52.4%	47.6%
BCC	2	$a\sqrt{3} = 4r$	0.68	68%	32%
FCC	3	$a\sqrt{2} = 4r$	0.74	74%	26%

2.12.19. Structures of ionic compounds:

Normally each ion is surrounded by the largest possible number of oppositely charged ions which is known as coordination number. The coordination number can be predicted by knowing the radius ratio of cation to anion. Simple ionic compounds are of two types AB and AB₂. From the knowledge of close packed structure and white space developed therein, we can have any idea about the structure of simple and compounds.

- If the anions (B⁻) constituted the crystal lattice and all the octahedral voids are occupied by the cation (A⁺) then the formula of the ionic solids should be A⁺B⁻.
- Similarly if half of the tetrahedral voids are occupied by cation (A⁺) then the formula of the solid crystal becomes A⁺B⁻.
- The anions (B⁻) are consisting space lattice and all the tetrahedral voids are occupied by the cation (A⁺) then the formula of the solid crystal should be A₂B.

- (d) When the anions (B^-) are present at the lattice point and all the octahedral voids are occupied by the cation (A^+) then the formula of crystalline solid will become A_2B .

2.12.20. Characteristics properties of various types of ionic solids:

Structure	Ions forming the closed packed structure	Ions present in voids	Coordination number	Number of formula per unit cell	Examples
ZnS type	S^{2-} ions form CCP	Zn^{2+} ion in alternate tetrahedral void	$Zn^{2+} = 4$ $S^{2-} = 4$	4	ZnS, AgI, HgS etc.
NaCl type	Cl^- form CCP structure	Na^+ ions in all octahedral holes	$Na^+ = 6$ $Cl^- = 6$	4	NaCl, KBr etc.
CsCl type	BCC structure Cl^- ion at cube	Cs^+ ion at the centre of the cube	$Cs^+ = 8$ $Cl^- = 8$	1	CsCl, CsCN etc.
CaF_2 type	Ca^{2+} ions at CCP	F^- ions in all tetrahedral holes	$Ca^{2+} = 8$ $F^- = 4$	4	CaF_2 , PbO_2 etc.
Li_2O type	O^{2-} ions form CCP structure	Li^+ ions are in all tetrahedral holes	$Li^+ = 4$ $O^{2-} = 8$	4	K_2O , Na_2O

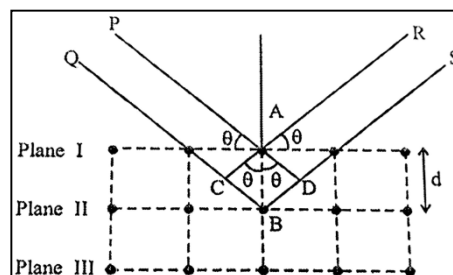
2.12.21. Bragg's equation:

The key to the Bragg analysis is the realization that the different rays striking the two layers of atoms are in phase initially but can be increase after reflection only if the extra distance $BC + CB'$ equal to a whole number of wavelength, $n\lambda$, where n is an integer (1, 2, 3...).

Imposing this requirement on a proper way with a angle θ , the Bragg equation:

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

Where, n = order of X – ray diffraction, λ be the wavelength, d is the distance between two layer.

**2.12.22. Close packing in crystals:**

The arrangement of atoms or molecules in three dimensional spaces with properly ordered arrangement give arises to the crystal structure with maximum density, which type of packing is called close packing.

The types of close packing are—

2.12.23. 1D – Packing:

Atoms are been packed in a horizontal line one by one.

2.12.24. 2D – Packing:

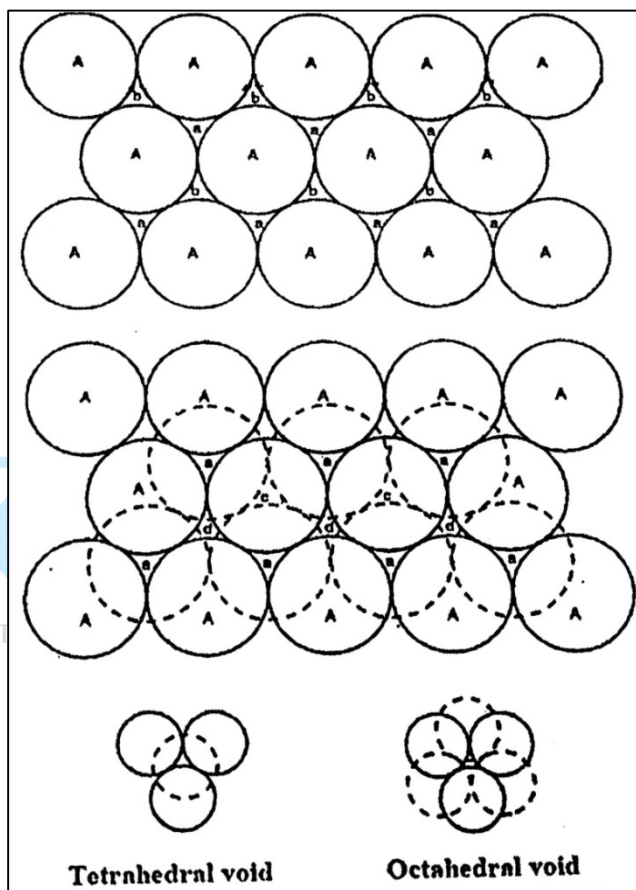
Atoms are been packed in a two dimensional plane. This can be done by two way—

- The particles when placed in the adjacent rows, shows horizontal as well as vertical alignment and forms square. This type of packing is called square close packing.
- The particles in every next row are placed in the dispersion force between the particles of the first row. The particles in the third row in a vertically aligned with those in the first row. This type of packing leaves a hexagonal pattern and is called hexagonal close packing.

2.12.25. 3D – Packing:

For two different types of 2D – packing, hexagonal close packing is more efficient. No another layer in 3D can attributes in two ways—

- When second layer is placed with spheres vertically aligned with those in the first layer, its voids will come above the voids in the first layer. This is an inefficient way of filling the space.
- When the secondary is placed in such a way that its spheres find place in the 'a' voids of the first layer, the 'b' voids will be left on occupied seems under this arrangement no sphere can be placed in them.
- Now there are two types of voids in the second layer. These are marked as 'c' and 'd'. The voids 'c' are ordinary points which lie above the spheres of the first layer where is the voids 'd' Leon the voice of the first layer and hence are combinations of two voids, one of the first layer and second of the second layer.
- For HCP crystal due to presence 'n' no of atoms, total no of Octahedral voids are 'n' and tetrahedral voids are '2n'.
- For CCP crystal due to presence 'n' no of atoms, total no of Octahedral voids are 'n' and tetrahedral voids are '2n'.



2.12.26. Density of crystal:

$$\rho = \frac{ZM}{Na^3}$$

Z = No of atoms per atoms per unit cell, M = Molecular weight, a = edge length.



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Q. In a cubic crystal, the plane [100] is equally inclined to the planes

- (a) [010] and [011] (b) [010] and [110]
(c) [001] and [101] (d) [110] and [011]

Ans. Angle between [100] and [010]

$$\cos \theta = \frac{0+0+0}{\sqrt{1}\sqrt{1}} \text{ i.e., } \theta = 90^\circ$$

Again, angle between [100] and [011]

$$\cos \theta = \frac{0+0+0}{\sqrt{1}\sqrt{2}} \text{ i.e., } \theta = 90^\circ$$

Correct option is (a).

Q. For a simple cubic lattice, the ratio between the unit cell length and the separation of two adjacent parallel crystal planes can NOT have a value of

- (a) $5^{1/2}$ (b) $7^{1/2}$ (c) $11^{1/2}$ (d) $13^{1/2}$

Ans. $d = \frac{a}{\sqrt{h^2+k^2+l^2}}; \Rightarrow \frac{a}{d} = \sqrt{h^2+k^2+l^2}$

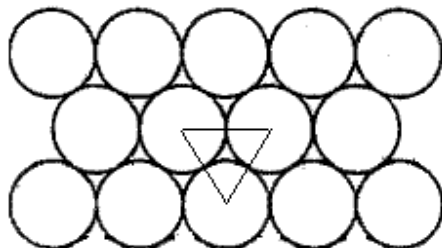
Correct option is (b).

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Q. Each void in a two dimensional hexagonal close-packed layer of circles is surrounded by

- (a) six circles (b) three circles (c) four circles (d) twelve circles

Ans.



Correct option is (b).

Q. The $\sin^2 \theta$ values obtained from X-ray powder diffraction pattern of a solid are $2x$, $4x$, $6x$, $8x$ where x is equal to 0.06. The wavelength of X-ray used to obtain this pattern is 1.54 \AA . The unit cell and the unit cell length, respectively are

- (a) BCC, 3.146 \AA (b) FCC, 3.146 \AA
(c) SCC, 6.281 \AA (d) BCC, 1.544 \AA

Ans. $x^2 = \frac{\lambda^2}{4a^2}; \Rightarrow a = \frac{1.54}{2\sqrt{x}} = \frac{1.54}{2\sqrt{0.06}} = 3.14 \text{ \AA}$

Correct option is (a).

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Q. Metallic silver crystallizes in face-centred-cubic lattice structure with a unit cell of length 40 nm. The first order diffraction angle of X-ray beam from (2, 1, 0) plane of silver is 30° . The wavelength of X-ray used is close to

- (a) 11 nm (b) 18 nm (c) 25 nm (d) 32 nm

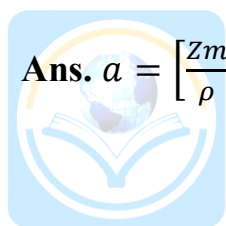
Ans. We have, $2 \frac{a}{\sqrt{h^2+k^2+l^2}} \sin \theta = n\lambda$, $\lambda = 18\text{nm}$

Correct option is (b).

Q. Polonium is the only metal known to exist in a simple cubic lattice form. The density of polonium at 0°C is measured to be 10.00 g/cm^3 . The atomic radius of polonium would then be (assume the mass of a polonium atom = $2.7 \times 10^{-22} \text{ g}$)

- (a) 1.1 Å (b) 1.9 Å (c) 1.5 Å (d) 2.3 Å

Ans. $a = \left[\frac{zm}{\rho} \right]^{1/3} = 3\text{\AA}$; $r = \frac{a}{2} = 1.5\text{\AA}$; **Correct option is (c).**



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Q. If the atoms/ions in the crystal are taken to be hard spheres touching each other in the unit cell, then the fraction of volume occupied in the body centered cubic structure is

- (a) $\sqrt{3}\pi$ (b) $\frac{\sqrt{2}\pi}{6}$ (c) $\frac{\pi}{6}$ (d) $\frac{\sqrt{3}\pi}{8}$

Ans. P. F = $\frac{4}{3}Z\pi\left(\frac{r}{a}\right)^3 = \frac{\sqrt{3}\pi}{8}$; **Correct option is (d).**

Q. The separation of the (123) planes of an orthorhombic unit cell is 3.12 nm. The separation of (246) and (369) planes are, respectively,

- (a) 1.56 nm and 1.04 nm (b) 1.04 nm and 1.56 nm
(c) 3.12 nm and 1.50 nm (d) 1.04 nm and 3.12 nm

Ans. $d_{246} = \frac{d_{123}}{2} = 1.56\text{nm}$; $d_{369} = \frac{d_{123}}{3} = 1.04\text{nm}$

Correct option is (a).

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Q. If all the lattice points of an FCC structure are occupied by uniform hard spheres that touch each other, the fraction of volume occupied is

- (a) $\frac{\pi\sqrt{2}}{6}$ (b) $\frac{\pi\sqrt{3}}{6}$ (c) $\frac{\pi}{6}$ (d) $\frac{2\pi}{6}$

Ans. For FCC, packing fraction = $\frac{4 \times \frac{4}{3}\pi r^3}{a^3} = \frac{\pi\sqrt{2}}{6}$, $a\sqrt{2} = 4r$

Correct option is (a).

Q. The (002) plane of an elemental FCC crystal diffract X – rays ($\lambda = 0.154 \text{ nm}$) at Bragg angle 90° . The density of the crystal is $4 \times 10^4 \text{ kg m}^{-3}$. The atomic weight of the elemental solid is

- (a) 22 (b) 44 (c) 88 (d) 66

Ans. $2 \frac{a}{\sqrt{h^2+k^2+l^2}} \sin 90^\circ = 1 \times 0.154; a=0.154 \text{ \AA}$

$$\rho = \frac{zM}{Na^3}; M = \frac{\rho Na^3}{Z} = 22$$

Correct option is (a).



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