

Difference between Crystalline and Amorphous Solids :

Crystalline solids

They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three-dimensional space.

Amorphous solids

They do not have any pattern of arrangement of atoms, ions or molecules and, thus do not have any definite geometrical shape.

TYPES OF CRYSTALLINE SOLIDS :

	Ionic	Metallic	Covalent	molecular
Particles occupying lattice points	Anions, cations	Metal ions in electron cloud	Atoms	Molecules (or atoms)
Binding force	Electrostatic attraction	Metallic bonds	Covalent bonds	Van der waals dipole-dipole
Properties	Hard, Brittle, poor thermal and electrical conductors	Soft to very hard, good thermal and electrical conductors	Very hard, poor thermal and electrical conductors	Soft, poor thermal and electrical conductors
Example	NaCl, CaBr ₂ , KNO ₂ , etc	Li, K, Ca, Cu, Na, etc.	C(diamond) SiO ₂ (quartz), etc	H ₂ O, H ₂ , CO ₂ , Ar etc

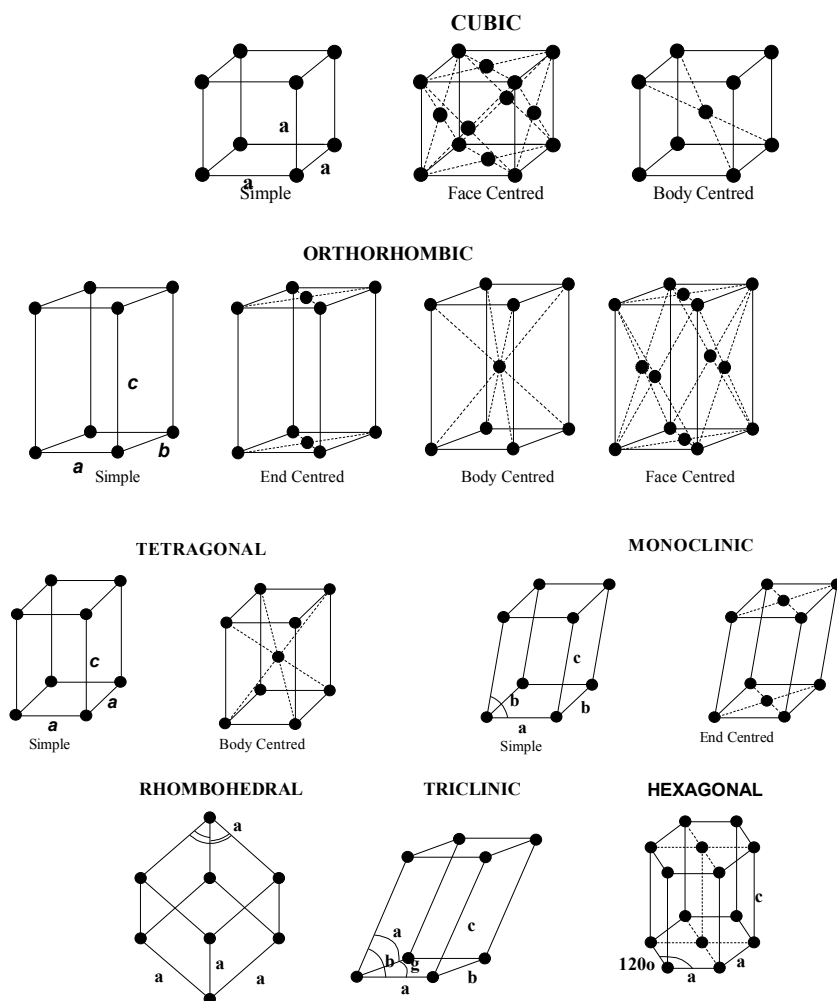
Space lattice or crystal lattice :

It may be defined as a regular three dimensional arrangement of identical points in space.

Seven Crystal Systems :

Crystal System	Bravais Lattices	Parameters of Unit Cell		Example
		Intercepts	Interfacial angle	
1. Cubic	Primitive, Face Centered, Body Centered = 3	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Pb, Hg, Ag, Au Diamond, NaCl, ZnS
2. Tetragonal	Primitive, Body Centered = 2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ , SnO ₂
3. Orthorhombic	Primitive, Face Centered, Body Centered, End Centered = 4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO ₃ , K ₂ SO ₄
4. Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Mg, SiO ₂ , Zn, Cd
5. Rhombohedral	Primitive = 1	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	As, Sb, Bi, CaCO ₃
6. Monoclinic	Primitive, End Centered = 2	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	CaSO ₄ ·2H ₂ O
7. Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CaSO ₄ ·5H ₂ O
Total = 14 (Total 14 type of lattices are called Bravais lattices)				

Seven Crystal Systems and Fourteen Bravais Lattice :



Type of Lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face-center	1/2
Body Center	1

Calculation of number of particles in a unit cell

Type of unit cell	Lattice points at corners	Lattice points at face-centered	Lattice points at body centered	Z = no. of lattice points per unit cell
SCC	8	0	0	$8 \times \frac{1}{8} = 1$
BCC	8	0	1	$8 \times \frac{1}{8} + 1 \times 1 = 2$
FCC	8	6	0	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Relation between edge length of unit cell and radius of atoms :

Simple cubic or Primitive : edge length of unit cell $a = 2 r$

Body centre cubic : atomic radius, $r = \frac{\sqrt{3} a}{4}$

Face centre cubic/cubic close packed : atomic radius $r = \frac{\sqrt{2} a}{4}$

Fraction of volume occupied by atoms in a cube :

Packing Fraction = Volume of atoms in the cube/Total volume of cube)

	Item	Primitive	BCC	FCC
1.	Atoms occupy :	8 corners	8 corners, 1 centre	8 corners, 6 face centres
2.	Each atom contributes			
	(a) corner atom :	$\frac{1}{8} \text{th} \times 8$	$\frac{1}{8} \text{th} \times 8$	$\frac{1}{8} \text{th} \times 8$
	(b) Face centre atom :	nil	nil	$\frac{1}{6} \times 6$
	(c) Body centre atom :	nil	one \times one	nil
3.	\therefore No. of atoms in the cube (Z):	one	two	four
4.	Radius of the atom :	r	r	r
5.	Total volume of atoms :	$1 \times \frac{4}{3} \pi r^3$	$2 \times \frac{4}{3} \pi r^3$	$4 \times \frac{4}{3} \pi r^3$
6.	Edge of the cube :	a	a	a
7.	Edge of the cube in terms of r :	$a = 2r$	$a = \frac{4}{\sqrt{3}} r$	$a = \frac{4r}{\sqrt{2}}$
8.	Total volume of the cube, a^3 :	$(2r)^3$	$\left(\frac{4}{\sqrt{3}} r\right)^3$	$\left(\frac{4}{\sqrt{2}} r\right)^3$
9.	Fraction of volume occupied :	$\frac{4}{3} \pi r^3$	$\frac{8}{3} \pi r^3$	$\frac{16}{3} \pi r^3$
	$= \frac{\text{Total volume of atoms}}{\text{Total volume of cube}}$	$8r^3$	$\frac{64}{3\sqrt{3}} r^3$	$\frac{64}{2\sqrt{2}} r^3$
10.	(or) packing fraction :	$\frac{\pi}{6}$	$\frac{\sqrt{3}}{8} \pi$	$\frac{\sqrt{2}}{6} \pi$
11.	(or) volume occupied by atoms :	0.52	0.6802	0.7405
12.	% volume occupied by atoms :	52%	68.02 %	74.05%
13.	Fraction of void volume :	0.48	0.3198	0.2595
14.	% of void volume in cube :	48%	31.98%	25.95%
15.	% of empty space in cube :	48%	31.98%	25.95%

Density of unit cell :

$$\text{Density of unit cell (and hence density of a crystal)} \rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}}$$

where a is edge of unit cell in pm

N_0 = Avogadro number (6.02×10^{23})

M = Atomic mass of element or formula mass of the compound

Z = No. of atoms present per unit cell or formula units. e.g.

for fcc, Z = 4, for bcc, Z = 2, for simple cubic, Z = 1

Close packing in crystals :

Close packing in three dimensions

When the third layer is placed over the second layer. This arrangement is called ABAB,... pattern or hexagonal (HCP) close packing.

(a) For HCP geometry Coordination number = 12

(b) For HCP geometry no. of atoms per unit cell

$$= 12 \text{ (corners)} \times \frac{1}{6} + 2 \text{ (face centres)} \times \frac{1}{2} + 3 \text{ (inside the body)} \times 1 = 6$$

(c) For HCP geometry packing efficiency = 74 %

The ABC ABC peaking has cubic symmetry and is known as cubic close packing (ccp). The cubic close packing close packing has face centered cubic (fcc) unit cell.

Types of Voids

Triangular : $\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.155$

Tetrahedral : $\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.225$

Octahedral : $\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.414$

cubical void : $\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.732$

Common coordination numbers are 3, 4, 6 and 8.

Limiting $\frac{r_a}{r_c}$ radius ratio	Co-ord. No.	Shape	
Example			
< 0.155	2	Linear	BeF_2
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS
0.414–0.732	4	square planar	PtCl_4^{-2}
0.414–0.732	6	octahedral	NaCl
0.732 – 0.999	8	B.C.C.	CsCl

Structure of ionic compounds :

Structures of Type AB :

1. Rock salt (NaCl) type
2. Cesium chloride (CsCl) type
3. Zinc blende (ZnS) type

Rock salt structure (NaCl) :

(a) Cl^- is forming a FCC unit cell in which Na^+ is in the octahedral voids. The co-ordination number of Na^+ is 6 and that of Cl^- would also be 6.

(b) Ratio of ionic radii = $\left(\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.525 \right)$

(c) No. of sodium ions = $12 \text{ (At edge centre)} \times \frac{1}{4} + 1 \text{ (At body centre)} \times 1 = 4$

No. of chloride ions = $8 \text{ (At corners)} \times \frac{1}{8} + 6 \text{ (At face centres)} \times \frac{1}{2} = 4$ (Thus formula is Na_4Cl_4 i.e. NaCl)

Caesium chloride structure (CsCl) :

(a) CsCl has body-centered cubic (bcc) arrangement. This structure has 8 : 8 co-ordination, i.e., each Cs^+ ion is touching eight Cl^- ions and each Cl^- ions in touching eight Cs^+ ions. (bcc)

(b) No. of Cl^- ions = $8 \text{ (At corners)} \times \frac{1}{8} = 1$

No. of Cs^+ ions = $1 \text{ (At the body centre)} \times 1 = 1$

No. of CsCl unit per unit cell = 1

Zinc blende structure or sphalerite structure (ZnS) :

(a) Sulphite ions are face centered and zinc is present in alternate tetrahedral voids.

(b) $\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.40 \quad \therefore \text{No. of ZnS units per unit cell} = 4$

Fluorite structure (CaF_2) : The cations are arranged in cubic close packing (ccp) while the anion occupy all the tetrahedral voids. Calcium fluoride has 8 : 4 co-ordination. (ccp)

\therefore No. of CaF_2 units per unit cell = 4

Antifluorite structure : In antifluorite structure e.g., (Na_2O)

(a) The anions are arranged in cubic close packing (ccp) while the cations occupy all the tetrahedral voids.

(b) Na_2O has 4 : 8 co-ordination

WURTZITE structure : Sulphide ions have hcp arrangement and zinc ions occupy tetrahedral voids.

Spinal structure : General formula of compound is AB_2O_4 e.g., MgAl_2O_4 , ZnFe_2O_4

Oxide ions are arranged in ccp arrangement. Divalent cations are in tetrahedral sites and trivalent ions are in octahedral sites.

Imperfections or defects in solids :

Stoichiometric point defects :

(a) **Schottky Defects :** This type of defect is created when one positive ion and one negative ion are missing from their respective positions leaving behind a pair of holes. Schottky defects are more common in ionic compounds with high co-ordination number.

(b) **Frenkel Defect –** This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site. Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions.

Non Stoichiometric defects :

Metal excess Defects due to Anion Vacancies. A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality.

Metal Deficiency due to cations vacancies. The non-stoichiometric compounds may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge.