Crystal Structures

- **Monocrystalline and Polycrystalline Crystal Structures**
- Materials, on the basis of their structure, may be classified into two groups viz.

1. Crystalline materials, and
2. Non-crystalline (or amorphous) materials

- Generally metals are crystalline, and non-metals are non-crystalline.
- But this is not a rule.
- Plastics, a non-metal may be obtained in almost crystalline form.
- Crystalline solids have periodically repeating arrangement of atoms.
- Such solids can be further sub-classified as follows.

i. Monocrystalline, and

ii. Polycrystalline.

- Most of materials in engineering applications are polycrystalline.
- Monocrystalline material has a single crystal.

Crystal Structures

- **Monocrystalline and Polycrystalline Crystal Structures**

Monocrystalline materials	Quartz, Single crystal Ti, Single crystal garnet, Single crystal Si, etc.
Polycrystalline materials	Steel and iron, Nickel, Copper, Magnesium, Zinc, Tungsten, Gold, etc.

- **Construction of a solid**
- The smallest visible part of a material is made up of a large number of *crystals*, Fig. 2.7*a*.
- These crystals may be of different shapes and sizes.
- They generally have random orientation.
- Each crystal is further composed of basic structural item called unit cell, Fig. 2.7b.

Crystal Structures

- Unit cells are of different types.
- These unit cells contain atoms arranged in a very systematic pattern.
- The details of an atom has already been discussed earlier.
- Thus the complete system of solid materials may be summarily shown as in fig below

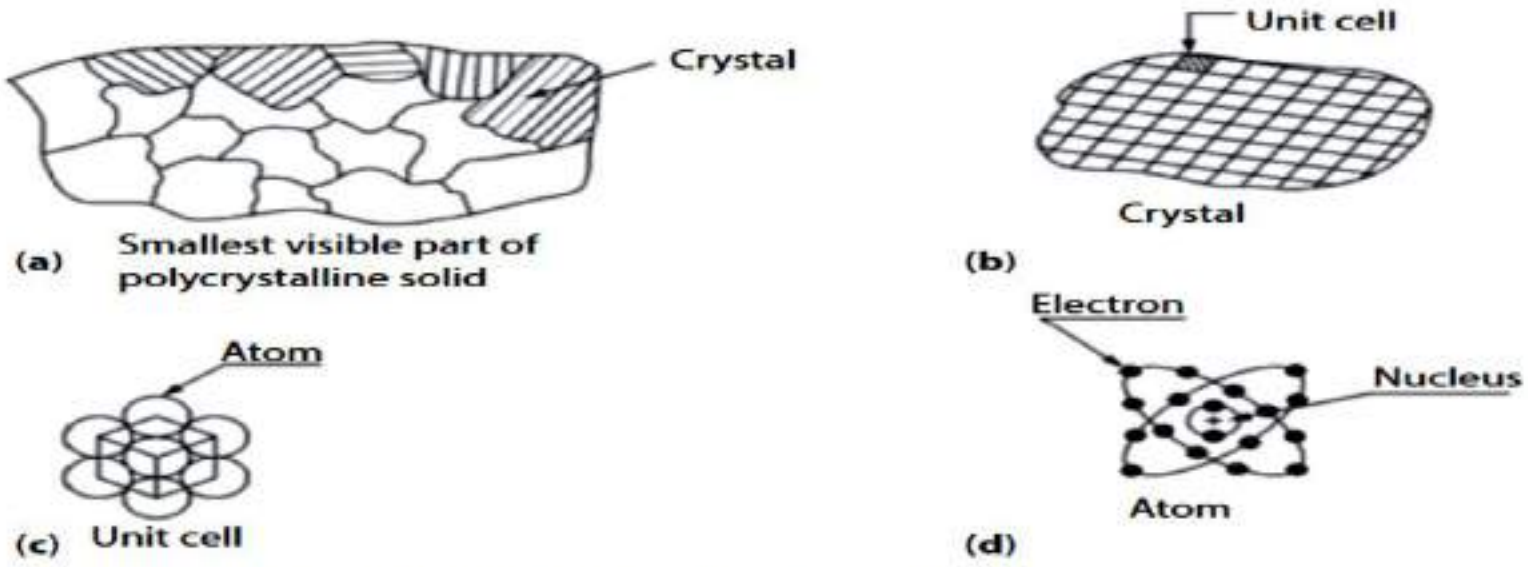


Figure 2.7 Constructional details of a solid material.

Crystal Structures

- **Space Lattice:**
- A space lattice is defined as an infinite array of points in three-dimensional space in which each point is identically located with respect to the other.
- Concept of space lattice is helpful in understanding the crystal structure of existing materials,
- and also those materials which are likely to be developed in future.

Crystal Structures

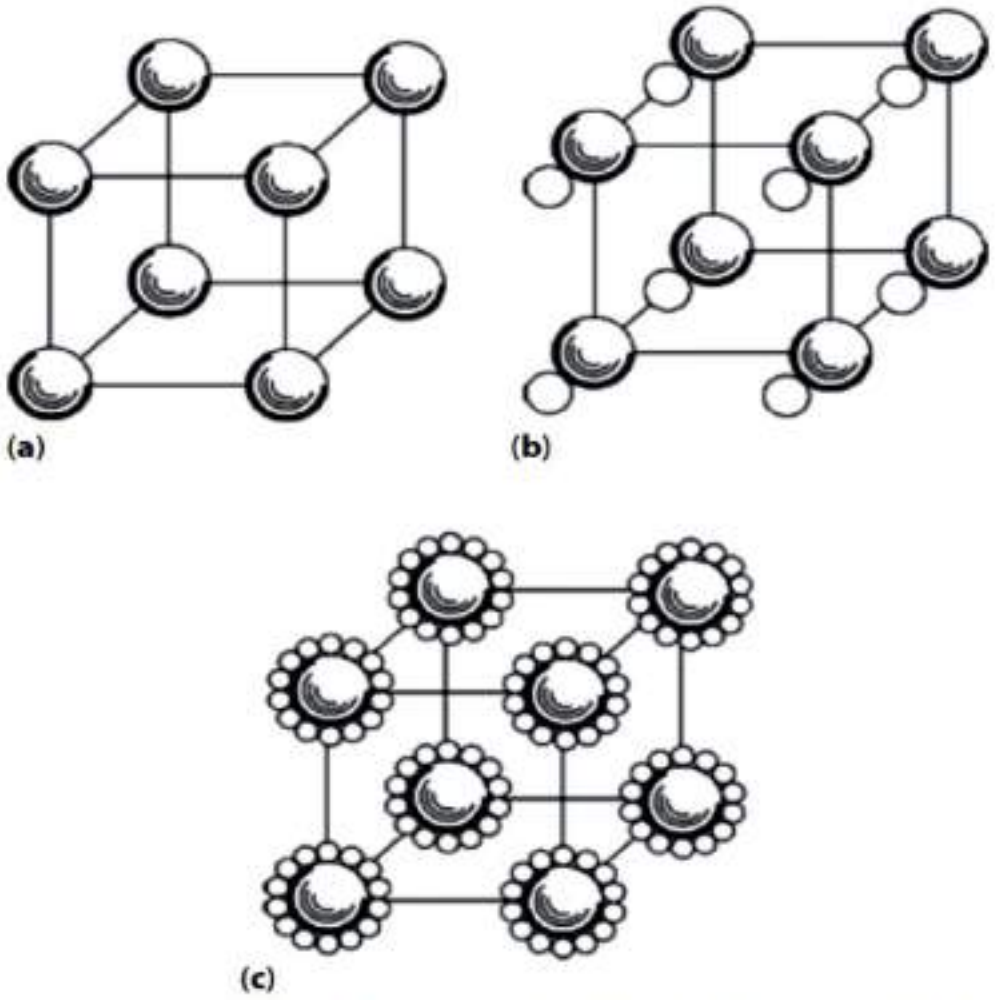
- **Basis:**
- The way of filling-up of points in a space lattice by the atoms is known as Basis.
- Each point may be occupied by one, two or many atoms in different solids.
- The space lattice when combines with the basis generates a unit cell.
- Thus **space lattice + basis = unit cell**
- The unit cell will be called monoatomic if one atom occupies a lattice point.
- When two atoms occupy a lattice point, it will make a diatomic unit cell.

Crystal Structures

- **Basis:**
- Similarly the unit cell will be known as multiatomic when too many atoms occupy a lattice point.
- These types of unit cells are shown in Figs.2.8a-b-c.
- Here the atoms are shown separated from each other for clarity, which in actual materials are not separated.
- In diatomic (Fig. 2.8b) and multiatomic (Fig. 2.8c) unit cells, the centre of larger atom coincides with the lattice point.
- In **manganese**, there are 29 atoms at each corner and 29 atoms at centre of the cube.
- Thus its unit cell contains 58 atoms.

Crystal Structures

- **Basis:**



Arrangement of atoms are different on different unit cells

Figure 2.8 Types of unit cells according to the basis (a) monoatomic, (b) diatomic, and (c) multiatomic

Crystal Structures

- **Unit Cell and Crystal:**
- **Definition:** *After developing the concept of unit cell, we now proceed to define it.*
- "A unit cell is defined as the basic structural part in the composition of materials."
- It is analogous to a brick used in the building construction.
- When many unit cells repeat in a three-dimensional space, a crystal is obtained.
- The structure of a crystal is same as that of a repeating unit cell.
- Hence crystal structure may be classified as:

1. monoatomic crystal,
2. diatomic crystal, and
3. multiatomic crystal.

Crystal Structures

- **Molecular crystal:**
- Diatomic and multiatomic crystals are also known as molecular crystals.
- There exist thousands of varieties of crystal structures.
- Many of them have complex nature.
- Complex crystal structure has two or more types mixed together, such as in

• Sulphur
• Phosphorous
• Gallium
• Uranium, etc.

Crystal Structures

- **Bravais Crystal System:**
- Crystals have unit cells of various geometries.
- The geometries are defined in terms of their linear dimensions a, b and c, and angular dimensions α, β and γ.
- Dimensions a, b and c are along the x, y and z axes respectively; and angles α, β and γ between *xy*, *yz* and *zx* axes respectively.
- These are shown in Fig. 2.9.
- Bravais has classified 14 space lattices into 7 crystal systems.
- These are displayed in Table 2.2.
- Crystals have inherent symmetry of different types.
- Different crystals exhibit vivid varieties of symmetry.
- The cubic crystal is most symmetric while the triclinic is least symmetric. Symmetry decreases as we move from cubic crystal system towards triclinic crystal system in Table 2.2.

Crystal Structures

- **Bravais Crystal System:**

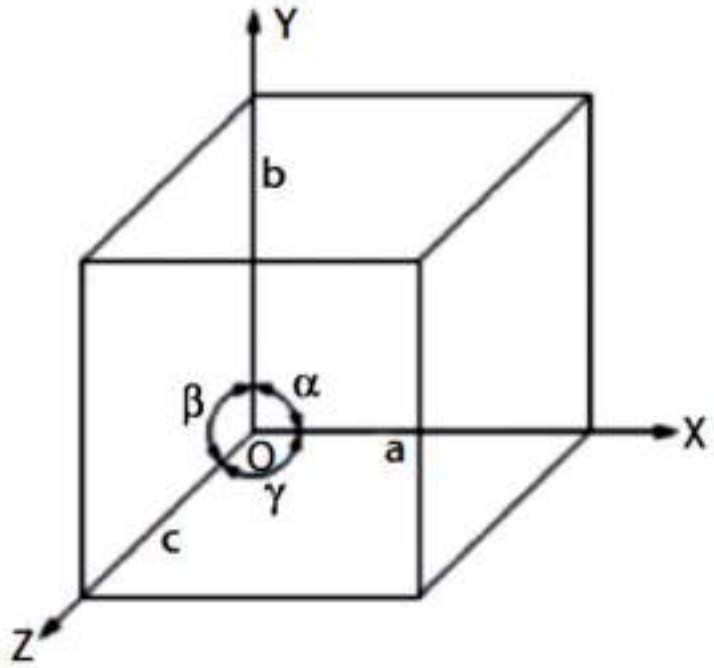
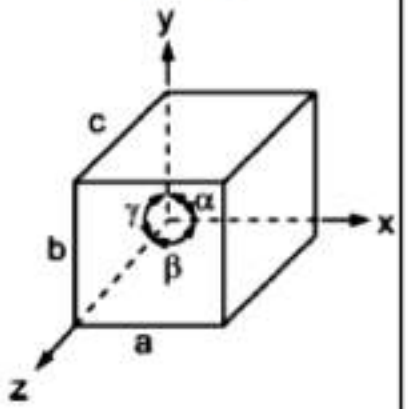


Figure 2.9 Geometry of unit cell

Crystal Structures

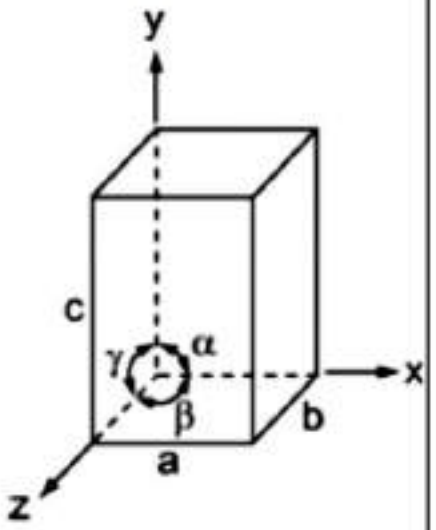
- **Bravais Crystal System:**

Table 2.2 Bravais crystal system

Unit cell (geometry)	Space lattice	Abbreviation	Example
1. Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^{o}$  	1. Simple (Points at the eight corners of the unit cell)	SC	Po
	2. Body Centred (Points at the eight corners and at the body centre)	BCC	Li, Na, V, Ta, Cr, Mo, W, Fe, CsCl
	3. Face Centred (Points at the eight corners and at the six face centres)	FCC*	Ni, Pt, Cu, Ag, Au, Al, Pb, Ne, Ar, Kr, Xe, NaCl

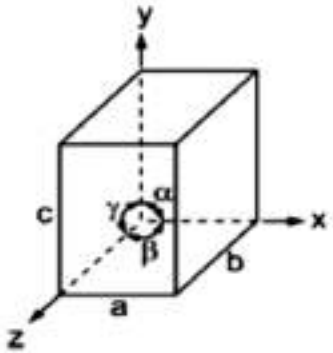
Crystal Structures

- **Bravais Crystal System:**

2. Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^{o}$ 	4. Simple (Points at the eight corners of the unit cell)	ST	Pa, In
	5. Body Centered (Points at the eight corners and at the body centre)	BCT	White Sn, KH_2PO_4, U between 668 °C–774 °C

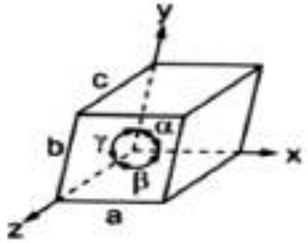
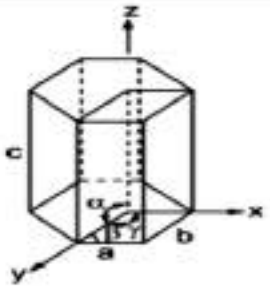
Crystal Structures

➢ Bravais Crystal System:

Unit cell (geometry)	Space lattice	Abbreviation	Example
3. Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$ 	6. Simple (Points at the eight corners of the unit cell)	SO	As, Sb, Bi
	7. End Centred. (Also called side Centred or base Centred) (Points at the eight corners and at the face centres opposite to each other)	ECO	$BaSO_4$, KNO_3, $MgSO_4$
	8. Body Centred (Points at the eight corners and at the body centre)	BCO	–
	9. Face Centred (Points at the eight corners and at the six face centres)	FCO	S, Ga

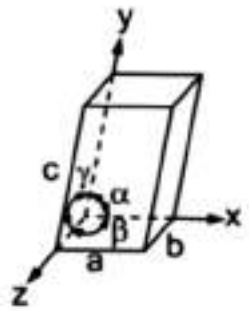
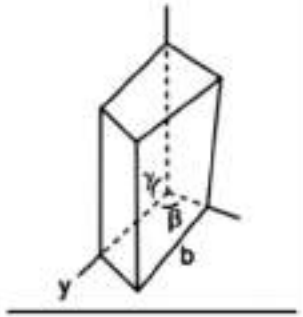
Crystal Structures

- **Bravais Crystal System:**

4. Rhombohedral (or trigonal) $a = b = c$ $\alpha = \beta = \gamma \neq 90°$ 	10. Simple (Points at the eight corners of the unit cell)	SR	B, SiO_2 $CaCO_3$, Lithium niobate ($LiNbO_3$), Lithium tantalate ($LiTaO_3$)
5. Hexagonal $a = b \neq c$ $\alpha = \beta = 90°$, $\gamma = 120°$	11. Simple [(*i*) Points at the eight corners of the unit cell outlined by thick lines OR	SH	La, Pr, Nd, Am, Se, Te, graphite, AgCl
	(*ii*) Points at the twelve corners of the hexagonal prism and at the centres of the two hexagonal faces]		

Crystal Structures

➢ Bravais Crystal System:

6. Monoclinic $a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$ 	12. Simple (Points at the eight corners of the unit cell) 13. End Centred (Points at the eight corners and at two face centres opposite to each other)	SM ECM	$NaSO_4$, Li_2SO_4, $CaSO_4$, Rochelle salt, $FeSO_4$ S
7. Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$ 	14. Simple (Points at the eight corners of the unit cell)	STC	$K_2Cr_2O_7$, $CuSO_4$

* FCC is also known as CCP (Cubic Closed Packed)

Crystal Structures

- **Primitive and Non-Primitive Unit Cells:**
- Primitive cells are those unit cells which contain atoms at corner lattice points only.
- So these cells have least number of total atoms and the least volume of atoms per unit cell.
- All unit cells of Table 2.2 namely simple cube (SC), simple tetragon (ST), simple orthorhombic (SO), simple rhombohedral (SR) etc. are primitive cells.
- All those unit cells which do not fall under this category are nonprimitive cells.

Crystal Structures

- **Primitive and Non-Primitive Unit Cells:**

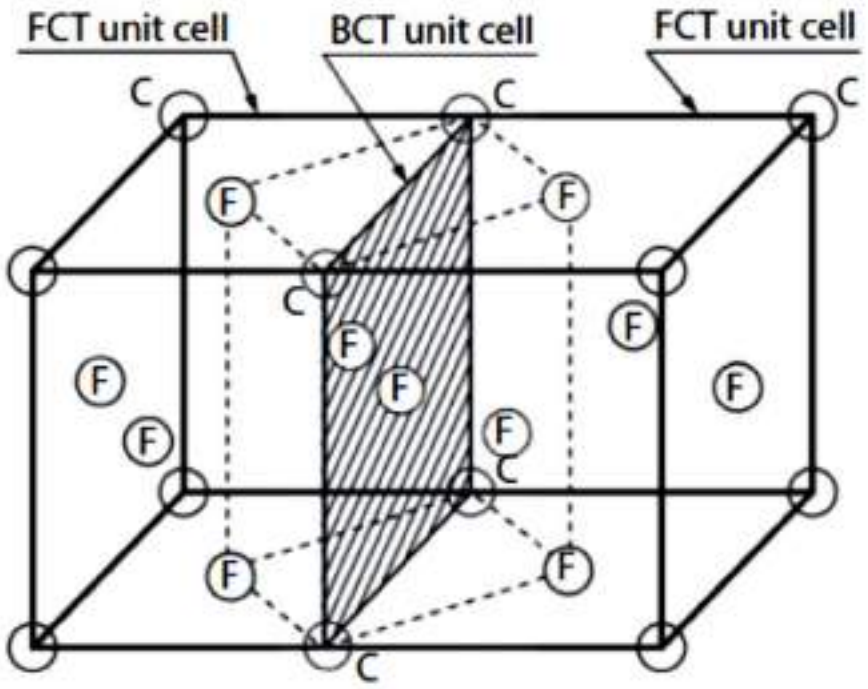


Figure 2.10 A BCT unit cell shown by dotted lines within two FCT unit cells. C and F indicate corner and face atoms respectively.

Crystal Structures

- **Coordination Number**
- **Definition:**
- Each atom in a crystal is surrounded by a number of atoms.
- The surrounding atoms are located at different distances.
- *"The coordination number is defined as the number of nearest and equidistant atoms with respect to any other atom in a unit cell."*
- Effective number of atoms per unit cell N_e is different from total number of atoms per unit cell.
- The atom at the corner of a cubical unit cell has only 1/8 of it inside the boundary of that unit cell.
- The remaining 7/8 of it lies in the surrounding unit cells of the crystal.
- Similarly the atom at the face in FCC is shared 1/2 by that atom and 1/2 by the neighbouring atom.
- In BCC, the atom at the centroid is wholly occupied by that unit cell in which it lies.
- Thus the effective number of atoms are 1, 2 and 4 in SC, BCC and FCC respectively. Figures 2.11 a-b-c explain these details.
- Effective number of atoms for different unit cells are summarized in Table 2.3.

Crystal Structures

➢ Coordination Number:

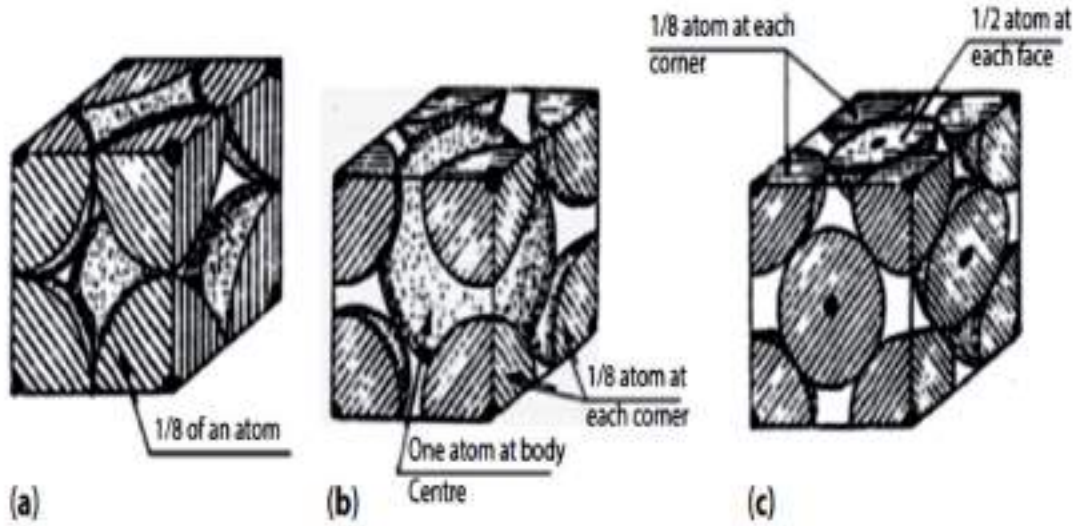


Figure 2.11 Effective number of atoms in (a) SC, (b) BCC, and (c) FCC

Table 2.3 Details of crystal geometry

Types of crystal	Effective number of atoms	Coordination number	APF	Relation between 'a' and 'r'
SC	1	6	0.52	$2r = a$
FCC	4	12	0.74	$2r = \frac{a}{\sqrt{2}}$
BCC	2	8	0.68	$2r = \frac{a\sqrt{3}}{2}$
ST	1	4	$\pi a/6c$	$2r = a = b < c$
BCT	2	8	$\frac{\pi(2a^2 + c^2)^{3/2}}{24a^2c}$	$r = \sqrt{(2a^2 + c^2)/4}$
SO	1	2	$\pi a^2/6bc$	$2r = a$ for $a < b, a < c$
ECO	2	2	$\pi(b^2 + c^2)/24abc$	$r = \sqrt{(b^2 + c^2)/4}$
BCO	2	8	$\pi\left(\frac{a^2 + b^2 + c^2}{24abc}\right)^{3/2}$	$4r = \sqrt{a^2 + b^2 + c^2}$
FCO	4	2	—	—
SH	3	—	$\pi a/3\sqrt{3c}$	$2r = a$