2. CRYSTALLOGRAPHY AND CRYSTAL STRUCTURES

CRYSTALLOGRAPHY

The branch of science which deals with the study of geometric form and other physical properties of the crystalline solids by using X-rays, electron beam, and neutron beams etc is called crystallography or crystal physics.

The solids are classified into two types crystalline and amorphous. A substance is said to be crystalline, when the arrangement of atoms, molecules or ions inside it is regular and periodic. Ex. NaCl, Quartz crystal. Though two crystals of same substance may look different in external appearance, the angles between the corresponding faces are always the same. In amorphous solids, there is no particular order in the arrangement of their constituent particles. Ex. Glass.

CRYSTALLINE SOLIDS	**AMORPHOUS SOLIDS**
1. Crystalline solids have regular periodic Arrangement of particles (atoms, ions, Or molecules).	1. Amorphous solids have no regularity in the arrangement Of particles.
2. They are un-isotropic i.e., they differ in Properties with direction.	2. They are usually isotropic i.e., They possess same properties in different directions.
3. They have well defined melting and Freezing points. Melting and freezing points occurs at different temperatures at different locations in the solids.	3. They do not posses well defined melting and freezing points.
4. Crystalline solids my be made up of materials are metallic crystals or non-metallic crystals. Some of the metallic crystals are Copper, silver, aluminum, tungsten, and manganese. Non-metallic crystals are crystalline carbon, crystallized polymers or plastics.	4. Most important amorphous glasses, plastics and rubber.
5. Metallic crystals have wide use in engineering because of their favorable Properties of strength, ductility, conductivity and reflection.	5. An amorphous structure does not generally posses elasticity but only plasticity.

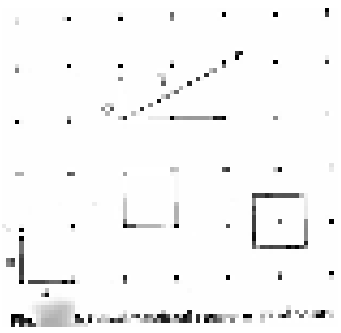
Lattice points: They are the imaginary points in space about which the atoms are located.

Lattice: The regular repetition of atomic, ionic or molecular units in 2-dimensional, 3-dimensional space is called lattice.

Space lattice or Crystal lattice: The totality of all the lattice point in space is called space lattice, the environment about any two points is same or An array of points in space such that the environment about each point is the same.

Consider the case of a 2-dimensional array of points.

Let O be any arbitrary point as origin, r1, r2 are position vectors of any two lattice points joining to O.



If T (translational vector) is the difference of two vectors r1, r2 and if it satisfies the condition

$$T= n_1a + n_2b \quad \text{where } n_1, n_2 \text{ are integers}$$

Then T represent 2-dimensional lattice.

For 3- dimensional lattice,

$$T= n_1a + n_2b + n_3c$$

Note: crystal lattice is the geometry of set of points in space where as the structure of the crystal is the actual ordering of the constituent ions, atoms, molecules in space

Basis and Crystal structure:

Basis or pattern is a group of atoms, molecule or ions identical in composition, arrangement and orientation. When the basis is repeated with correct periodicity in all directions, it gives the actual crystal structure.

Crystal structure = Lattice + Basis

FIG……..

The crystal structure is real while the lattice is imaginary.

In crystalline solids like Cu and Na, the basis is a single atom

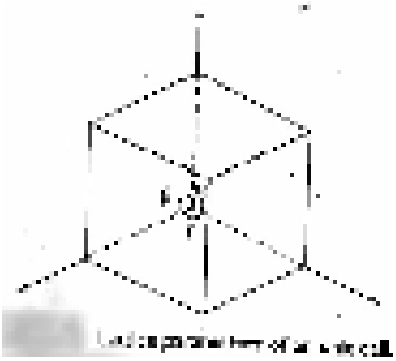
In NaCl and CsCl- basis is diatomic

In CaF_2 – basis is triatomic

Unit cell and Lattice parameters:

Unit cell is the smallest portion of the space lattice which can generate the complete crystal by repeating its own dimensions in varies directions. In describing the

crystal structure, it is convenient to subdivided the structure into small repetitive entities called unit cells. Unit cell is the parallelepiped or cubes having 3 sets of parallel faces. It is the basic structural unit or the building block of the crystal.



A unit cell can be described by 3 vectors or intercepts **a, b, c,** the lengths of the vectors and the interfacial angles **α, β, γ** between them. If the values of these intercepts and interfacial angles are known, then the form and actual size of the unit cell can be determined. They may or may not be equal. Based on these conditions, there are 7 different crystal systems.

Primitive Cell: A unit cell having only one lattice point at the corners is called the primitive cell. The unit cell differs from the primitive cell in that it is not restricted to being the equivalent of one lattice point. In some cases, the two coincide. Thus, unit cells may be primitive cells, but all the primitive cells need not be unit cells.

CRYSTAL SYSTEMS AND BRAVAIS LATTICES:

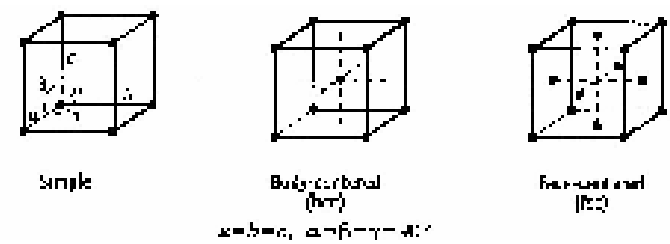
There are 7 basic crystal systems which are distinguished based on three vectors or the intercepts and the 3 interfacial angles between the 3 axes of the crystal. They are

1. Cubic
2. Tetragonal
3. Orthorhombic
4. Monoclinic
5. Triclinic
6. Trigonal (Rhombohedral)
7. Hexagonal

More space lattices can be constructed by atoms at the body centres of unit cells or at the centres of the faces. Based on this property, bravais classified the space lattices into 14.

1. Cubic crystal system

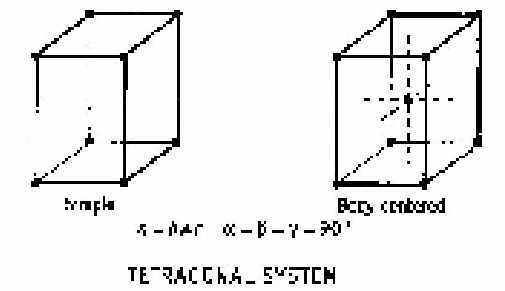
$a = b = c$, $\alpha = \beta = \gamma = 90^0$



The crystal axes are perpendicular to one another, and the repetitive interval in the same along all the three axes. Cubic lattices may be simple, body centered or face-centered.

2. Tetragonal crystal system

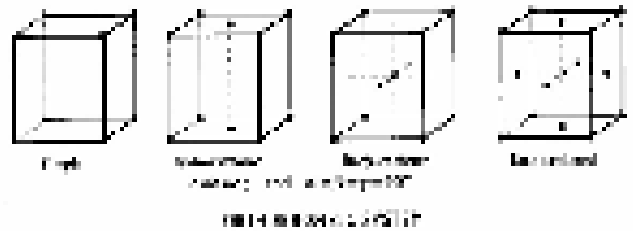
$a = b \neq c$, $\alpha = \beta = \gamma = 90^0$



The crystal axes are perpendicular to one another. The repetitive intervals along the two axes are the same, but the interval along the third axes is different. Tetragonal lattices may be simple or body-centered.

3. Orthorhombic crystal system.

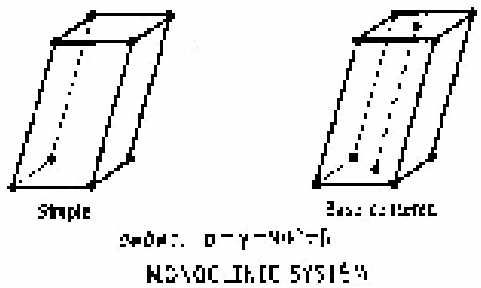
$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^0$



The crystal axes are perpendicular to one another but the repetitive intervals are different along the three axes. Orthorhombic lattices may be simple, base centered, body centered or face centered.

4. Monoclinic crystal system

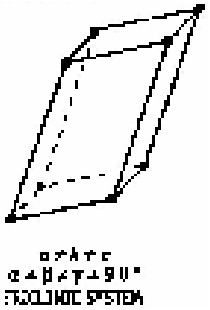
$a \neq b \neq c$, $\alpha = \beta = 90^0 \neq \gamma$



Two of the crystal axes are perpendicular to each other, but the third is obliquely inclined. The repetitive intervals are different along all the three axes. Monoclinic lattices may be simple or base centered.

5. Triclinic crystal system

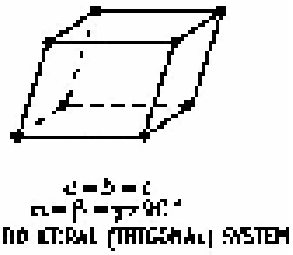
$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$



None of the crystal axes is perpendicular to any of the others, and the repetitive intervals are different along the three axes.

6. Trigonal(rhombohedral) crystal system

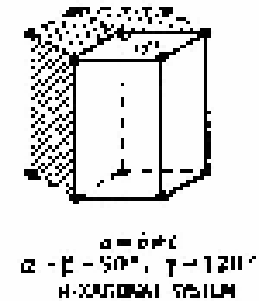
$a = b = c$, $\alpha = \beta = \gamma \neq 90^0$



The three axes are equal in length and are equally inclined to each other at an angle other than 90^0

7. Hexagonal crystal system.

$a = b \neq c$, $\alpha = \beta = \gamma = 90^0$, $\gamma = 120^0$



Two of the crystal axes are 60^0 apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60^0 apart, but the interval along the third axis is different.

Basic Crystal Structures:

The important fundamental quantities which are used to study the different arrangements of atoms to form different structure are

1. **Nearest neighbouring distance** (2r) : the distance between the centres of two nearest neighbouring atoms is called nearest neighbouring distance. If r is the radius of the atom, nearest neighbouring distance= 2r.
2. **Atomic radius** (r) : It is defined as of the distance between the nearest neighbouring atoms in a crystals.
3. **Coordination number** (N): It is defined as the number of equidistant nearest neighbours that an atom as in a given structure. More closely packed structure as greater coordination number.
4. **Atomic packing factor or fraction**: It is the ratio of the volume occupied by the atoms in unit cell(v) to the total volume of the unit cell (V).

   P.F. = v/ V

Simple cubic (SC) structure:

In the simple cubic lattice, there is one lattice point at each of the 8 corners of the unit cell. The atoms touch along cubic edges.

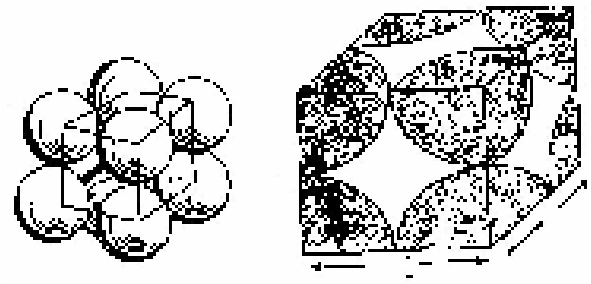


Fig. Simple Cubic Structure

Nearest neighbouring distance = 2r = a

Atomic radius = r = a / 2

Lattice constant = a = 2r

Coordination number = 6 (since each corner atom is surrounded by 6 equidistant nearest neighbours)

Effective number of atoms belonging to the unit cell or no. of atoms per unit cell = $\left(\frac{1}{8}\right)$x8 = 1 atom per unit cell.

Atomic packing factor = v/ V_ = volume of the all atoms in the unit cell
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volume of the unit cell.

$= 1 \times (4/3) \prod r^3 / a^3 = 4 \prod r^3 / 3(2r)^3$

$= \prod / 6 = 0.52 = 52\%$

This structure is loosely packed. Polonium is the only element which exhibits the simple cubic structure.

Body centered cube structure (BCC):

BCC structure has one atom at the centre of the cube and one atom at each corner. The centre atom touches all the 8 corner atoms.

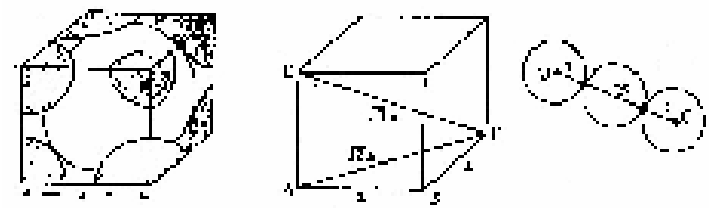


Fig. Body Centered Cubic Structure

Diagonal length = 4r

Body diagonal = $(\sqrt{3})a$

i.e. $4r = (\sqrt{3})a$

Nearest neighbouring distance = $2r = (\sqrt{3})a / 2$

Atomic radius = $r = (\sqrt{3})a / 4$

Lattice constant = $a = 4r / \sqrt{3}$

Coordination number = 8 (since the central atom touches all the corner 8 atoms)

Effective number of atoms belonging to the unit cell or no. of atoms per unit cell = $(1/8) \times 8 + 1 = 2$ atom per unit cell.

i.e. each corner atom contributes $1/8$th to the unit cell. In addition to it, there is a centre atom.

Atomic packing factor = v/ V_ = volume of the all atoms in the unit cell
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volume of the unit cell.

$= 2 \times (4/3) \prod r^3 / a^3 = 8 \prod r^3 / 3(4r/\sqrt{3})^3$

$= \sqrt{3} \prod / 8 = 0.68 = 68\%$

Tungsten, Na, Fe and Cr exhibits this type of structure.

Face centered cubic (FCC) structure:

In FCC structure, ther is one lattice point at each of the 8 corners of the unit cell and 1 centre atom on each of the 6 faces of the cube.

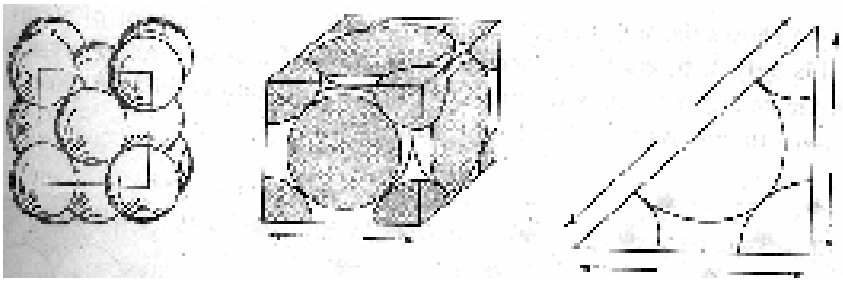


Fig. Face Centered Cubic Structure

Face diagonal length = $4r = (\sqrt{2})\, a$

Nearest neighbouring distance = $2r = (\sqrt{2})a / 2 = a / \sqrt{2}$

Atomic radius = $r = a / 2\sqrt{2}$

Lattice constant = $a = 2\sqrt{2}\, r$

Coordination number = 12 (the centre of each face has one atom. This centre atom touches 4 corner atoms in its plane, 4 face centered atoms in each of the 2 planes on either side of its plane)

Effective number of atoms belonging to the unit cell or no. of atoms per unit cell = $(1/8)$x8 + (1/2)x 6 = 1 + 3 = 4 atom per unit cell.

i.e. each corner atom contributes $1/8$th to the unit cell. In addition to it, there is a centre atom on each face of the cube.

Atomic packing factor = v/ V = $\dfrac{\text{volume of the all atoms in the unit cell}}{\text{Volume of the unit cell.}}$

$= 4 * (4/3) \prod r^3 / a^3 = 16 \prod r^3 / 3(2\sqrt{2}\, r)^3$

$= \prod / 3\sqrt{2} = 0.74 = 74\%$

Cu, Al, Pb and Ag have this structure. FCC has highest packing factor.