Lecture 01: Crystalline and Non-crystalline solids

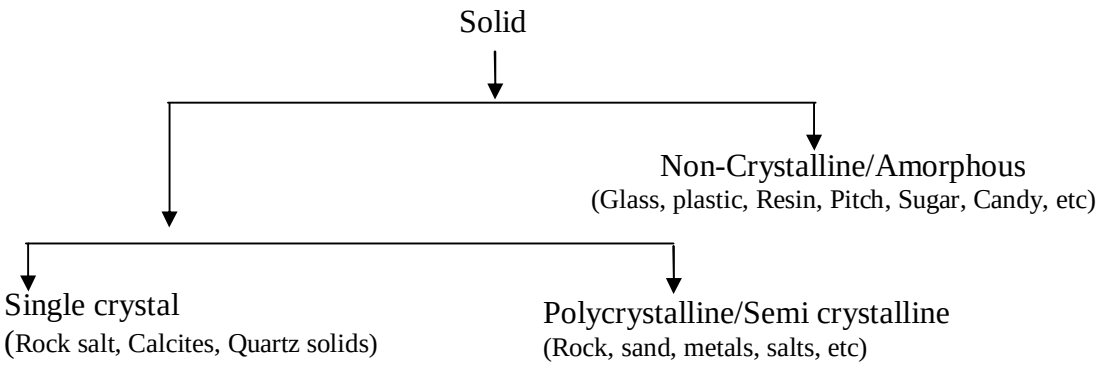
Introduction

Matter can be subdivided into two states-solid and fluid, of which the later is subdivided into liquid and gaseous state. Matter can also be subdivided into condensed stated and gaseous state where condensed state is subdivided into the solid and liquid state.

Although very little of the matter in the universe is in the solid state, solids constitute much of the physical world around us and a large part of the modern technology is based on the special characteristics of the various solid materials.

Crystalline and non-crystalline (Amorphous Solids)

Nature favors the crystalline state of the solids, because the energy of the ordered atomic arrangement is lower than that of an irregular packing of atoms.



Crystalline Solids

A solid in general is said to be a crystal if the constituent particles (atoms, ions or molecules) are arranged in a three dimensional periodic manner or simply it has a reticular structure. In crystalline solids the atoms are stacked in a regular manner, forming a 3-D pattern which may be obtained by a 3-D repetition of a certain pattern unit. It has long-range orderness and thus has definite properties such a sharp melting point. Thus we can say, crystal is a three dimensional periodic array of atoms. When the crystal grows under constant environment, the external geometrical shape of the crystal often remains unchanged. Thus, the shape is a consequence of the internal arrangement of constituent particles. The ideal crystal has an infinite 3D repetition of identical units, which may be atoms or molecules. All ionic solids and most covalent solids are crystalline. All solid metals, under normal circumstances, are crystalline.

Single crystal

When the periodicity in crystal pattern extends throughout a certain piece of materials, one speaks of a single crystal or unit crystal or mono-crystal. Rock salt, calcites, quartz, etc. are examples of common single crystal.

Polycrystalline solids (Polymorphism)

When the periodicity in the crystal structure is interrupted at so-called grain boundaries, the crystal is said to be polycrystalline. In this case the size of the grains or crytallites is smaller than the size of the pattern unit which forms the periodicity. The size of the grain in which the structure is periodic may vary from macroscopic dimensions to several angstroms. In general, the grains in such a solid are not related in shape to the crystal structure, the surface being random in shape rather than well defined crystal planes. Rock, sand, metals, salts, etc. are some examples of polycrystalline solids.

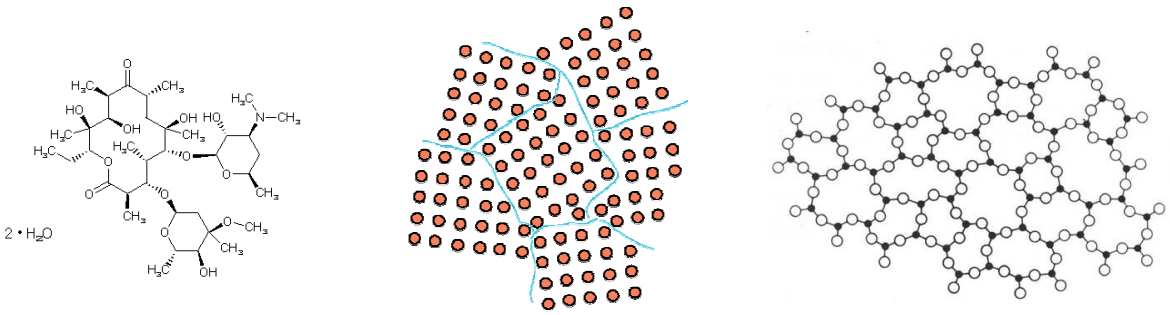
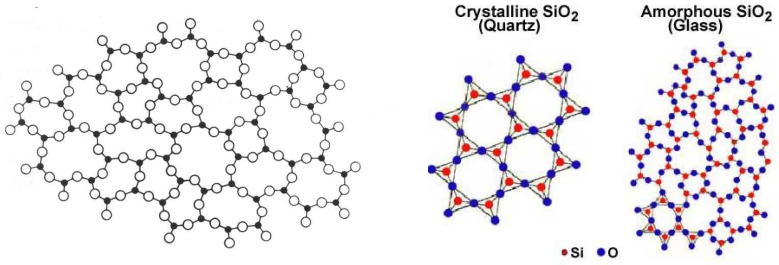


Fig. Single crystal, polycrystalline, amorphous

Noncrystalline solids

It is the opposite extreme of a single crystal. These types of solids have neither reticular nor granular structure. At most causes exhibit short range orderness in their structure. Glass and plastic are common example of this class. When the size of the grains or crystallites becomes comparable to the size of the pattern unit, we speak of amorphous substances. A typical feature of these substances is that they have no definite melting points. As their temperature is increased, they gradually become soft; their viscosity drops, and begins to behave like ordinary viscous liquids.

Amorphous solids have no long-range order. The atoms or molecules in these solids are not periodically located over large distances. An amorphous structure is shown below.



Many amorphous materials have internal structures similar to liquids. In fact, the only obvious distinction between amorphous materials, such as glass, and liquids is the high viscosity (resistance to flow) of the amorphous solids.

All solids tend to exist in the crystalline state rather than the amorphous state because the crystalline structure always has a larger binding energy. However, in numerous instances amorphous solids are formed when liquids are cooled below the melting temperature. This occurs for two reasons:

1) the structure of the molecules is so complex that they cannot easily rearrange themselves to form a crystalline structure, and/or
2) the solid forms so rapidly that the atoms or molecules do not have time enough to rearrange themselves in a crystalline structure.

Generally, amorphous solids have one of two distinct atomic arrangements: either a tangled mass of long-chained molecules or a 3-dimentional network of atoms with no long-range order.

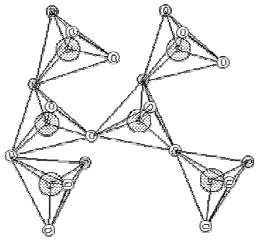
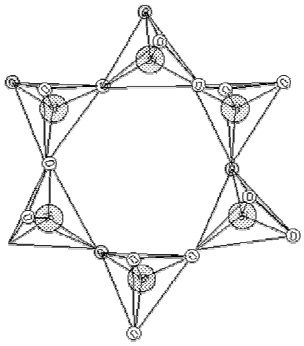
Amorphous materials with long-chained molecules (e.g. polymers) have a structure similar to that shown below.

Each segment in above figure represents one of the repeating units of the polymer chain. The arrangement of the molecules is fairly random, resulting in a loosely packed structure. Network amorphous solids are usually Oxides, the most common being Silica (SiO_2). The amorphous SiO_2 structure is also shown above. Only oxygen atoms are shown (corners of tetrahedral) in this amorphous SiO_2 structure. There is a Silicon atom at the center of each tetrahedral which is not shown here. This structure has short-range order but none of the long-range order found in crystalline Silica. Thus, in both amorphous and crystalline Silica, each Silicon atom and each

Oxygen atom have essentially the same local surroundings, even though there is no long-range periodicity in the amorphous structure.

Solids that do not have long range atomic order are called amorphous solids. They often have subunits that have consistent form, but their long-range order is disturbed because the sub-units pack randomly. Amorphous solids are formed when liquids are cooled too quickly from the molten state to allow the sub-units to arrange themselves in the low energy, crystalline state.

Solids with pure ionic bonds do not form amorphous solids but all the other bond types can produce amorphous solids. Silica (SiO2) can form either covalent amorphous solids, usually called glasses or regular crystal structrures (Quartz).

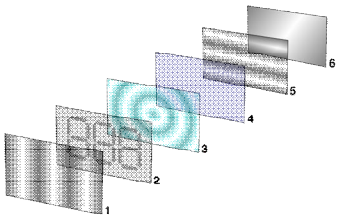
In glasses, the tetrahedral SiO_2 structure forms the sub-unit, and it is the flexibility of corner to corner links that accounts for the ability of SiO_2 to form the random structures shown below. 	If the molten Silica is cooled very slowly, the sub-units fall into the regular crystal structure of Quartz, shown below. 
Impurities in SiO_2 hinder crystallisation. Common window glass (soda lime glass) has Na_20 and CaO added. Ovenware glass (borosilicate glass) has B_20_3 added.	

Liquid crystals (LCs) are a state of matter that have properties between those of a conventional liquid and those of a solid crystal.[1] For instance, an LC may flow like a liquid, but its molecules may be oriented in a crystal-like way. There are many different types of LC phase, which can be distinguished by their different optical properties (such as birefringence). When viewed under a microscope using a polarized light source, different liquid crystal phases will appear to have distinct textures.

Examples of liquid crystals can be found both in the natural world and in technological applications. Most modern electronic displays are liquid crystal based. Lyotropic liquid-crystalline phases are abundant in living systems. For example, many proteins and cell membranes are LCs. Other well-

known LC examples are solutions of soap and various related detergents, as well as tobacco mosaic virus.

Liquid crystal display



Structure of liquid crystal display:
1 – vertical polarization filter,
2,4 – glass with electrodes,
3 – liquid crystals,
5 – horizontal polarization filter,
6 – reflector

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field. In a typical device, a liquid crystal layer (typically 10 μm thick) sits between two polarizers that are crossed (oriented at 90° to one another). The liquid crystal alignment is chosen so that its relaxed phase is a twisted one (see Twisted nematic field effect). This twisted phase reorients light that has passed through the first polarizer, allowing its transmission through the second polarizer (and reflected back to the observer if a reflector is provided). The device thus appears transparent. When an electric field is applied to the LC layer, the long molecular axes tend to align parallel to the electric field thus gradually untwisting in the center of the liquid crystal layer. In this state, the LC molecules do not reorient light, so the light polarized at the first polarizer is absorbed at the second polarizer, and the device loses transparency with increasing voltage. In this way, the electric field can be used to make a pixel switch between transparent or opaque on command. Color LCD systems use the same technique, with color filters used to generate red, green, and blue pixels. Similar principles can be used to make other liquid crystal based optical devices.

They are used in a wide range of applications, including computer monitors, television, instrument panels, aircraft cockpit displays, signage, etc. They are common in consumer devices such as video players, gaming devices, clocks, watches, calculators, and telephones.

Polymorphism

Polymorphism refers to the ability of a solid to exist in more than one crystalline form or structure. According to Gibbs' rules of phase equilibria, these unique crystalline phases will be dependent on such intensive variables as pressure, temperature and volume. Polymorphism can potentially be found in many crystalline materials including polymers, minerals, and metals, and is related to

allotropy, which refers to elemental solids. The complete morphology of a material is described by polymorphism and other variables such as crystal habit, amorphous fraction or crystallographic defects. Polymorphs have different stabilities and may spontaneously convert from a metastable form (or thermodynamically unstable form) to the stable form at a particular temperature. They also exhibit different melting points, solubilities, and X-ray diffraction patterns.

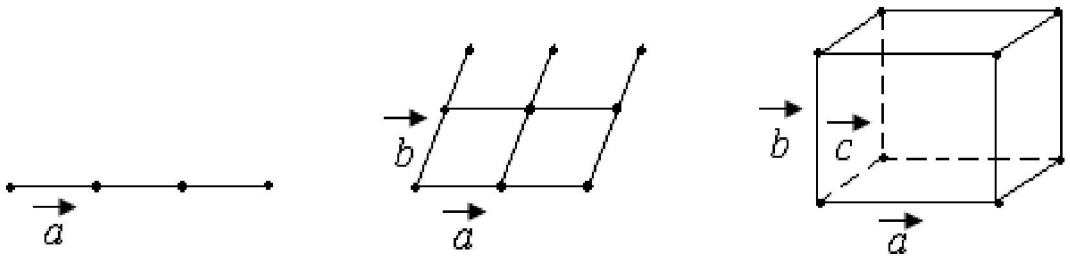
One good example of this is the quartz form of silicon dioxide, or SiO2. Quartz is one of the several thermodynamically stable crystalline forms of silica, SiO2. The most important forms of silica include: α-quartz, β-quartz, tridymite, cristobalite, coesite, and stishovite. In the vast majority of silicates, the Si atom shows tetrahedral coordination by 4 oxygens. All but one of the crystalline forms involve tetrahedral SiO4 units linked together by shared vertices in different arrangements. In different minerals the tetrahedra show different degrees of networking and polymerization. For example, they occur singly, joined together in pairs, in larger finite clusters including rings, in chains, double chains, sheets, and three-dimensional frameworks. The minerals are classified into groups based on these structures. In each of its 7 thermodynamically stable crystalline forms or polymorphs of crystalline quartz, only 2 out of 4 of each the edges of the SiO4 tetrahedra are shared with others, yielding the net chemical formula for silica: SiO2.

Another example is elemental tin (Sn), which is malleable near ambient temperatures but is brittle when cooled. This change in mechanical properties due to existence of its two major allotropes, α- and β-tin. The two allotropes that are encountered at normal pressure and temperature, α-tin and β-tin, are more commonly known as gray tin and white tin respectively. Two more allotropes, γ and σ, exist at temperatures above 161 °C and pressures above several GPa.[12] White tin is metallic, and is the stable crystalline form at or above room temperature. Below 13.2 °C, tin exists in the gray form, which has a diamond cubic crystal structure, similar to diamond, silicon or germanium. Gray tin has no metallic properties at all, is a dull-gray powdery material, and has few uses, other than a few specialized semiconductor applications.[13] Although the α-β transformation temperature of tin is nominally 13.2 °C, impurities (e.g. Al, Zn, etc.) lower the transition temperature well below 0 °C, and upon addition of Sb or Bi the transformation may not occur at al.

Lecture 02: Space lattice and Translation vectors

The property that distinguishes crystals from other solids is that the constituent particles in crystals are arranged in a three dimensional periodic manner. In 1848 Bravais introduced the concept of space lattice.

Lattice: A lattice is a regular periodic array of points in space where objects are replaced by points-imaginary points. It may consider as removal of the atom but the centre remains there.



Lattice arrangement in 1-D is the line of Lattice, in 2-D is the Lattice plane, in 3-D is the space Lattice.

Thus the three dimensional lattice arrangements with translation vectors is the space lattice. Let us consider the translation of an object to a finite distance and then repeated systematically along 3-D crystallographic directions x, y, z to obtain 3-D space lattice.

Lattice is a mathematical abstraction which is defined by 3 fundamental translation vectors $\vec{a}, \vec{b}, \vec{c},$ such that the atomic arrangement looks the same in every respect when viewed from the point r as when viewed from the point

$$\bar{r}' = \bar{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \quad \text{..... (1)}$$

Where n_1, n_2, n_3 are arbitrary integers and the set of points r' defined by (1) for all n_1, n_2, n_3 defines a lattice.

Lattice point can thus be defined by 3-fundmental basis vectors called primitive translation vector in x, y, z crystallographic direction as

$$\vec{\tau} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

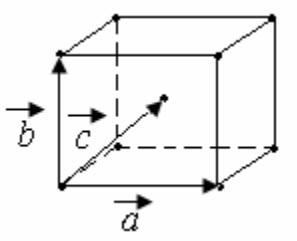
So that

$$\bar{r}' = \bar{r} + \vec{\tau}$$

For example: If the 3-D fundamental basis vectors of a crystal are $\vec{a}=3\hat{i}$, $\vec{b}=3\hat{j}$ and $\vec{c}=1.5(\hat{i}+\hat{j}+\hat{k})$, the primitive translation operation

$$\vec{\tau} = n_1(3\hat{i}) + n_2(3\hat{j}) + n_3 \times 1.5(\hat{i}+\hat{j}+\hat{k})$$

gives the body centered cubic structure.



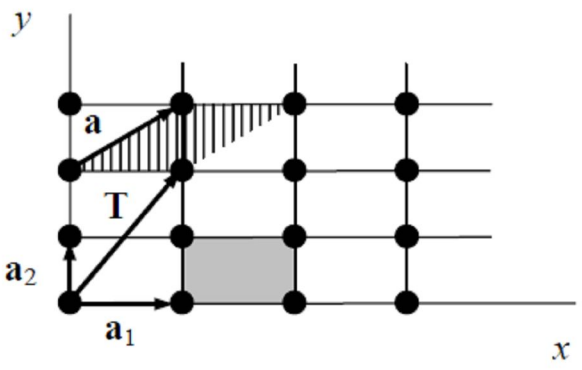
Bravais and Non-Bravais lattice

There are two classes of lattices: the *Bravais* and the *non-Bravais*. In a Bravais lattice all lattice points are equivalent and hence by necessity all atoms in the crystal are of the same kind. On the other hand, in a non-Bravais lattice, some of the lattice points are non-equivalent. Non-Bravais lattices are often referred to as a *lattice with a basis*. The basis is a set of atoms which is located near each site of a Bravais lattice.

The lattice is defined by fundamental translation vectors. For example, the position vector of any lattice site of the two dimensional lattice in figure can be written as

$$\mathbf{T}=n_1\mathbf{a}_1+n_2\mathbf{a}_2$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the two vectors shown in figure, and n_1, n_2 is a pair of integers whose values depend on the lattice site. So, the two non-collinear vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be used to obtain the positions of all lattice points which are expressed by the equation. The set of all vectors **T** expressed by this equation is called the *lattice vectors*. Therefore, the lattice has a translational symmetry under displacements specified by the lattice vectors **T**. In this sense the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be called *the primitive translation vectors*. The choice of the primitive translations vectors is not unique. One could equally well take the vectors $\mathbf{a}_1$ and $\mathbf{a} = \mathbf{a}_1+\mathbf{a}_2$ as primitive translation vectors. This choice is usually dictated by convenience.



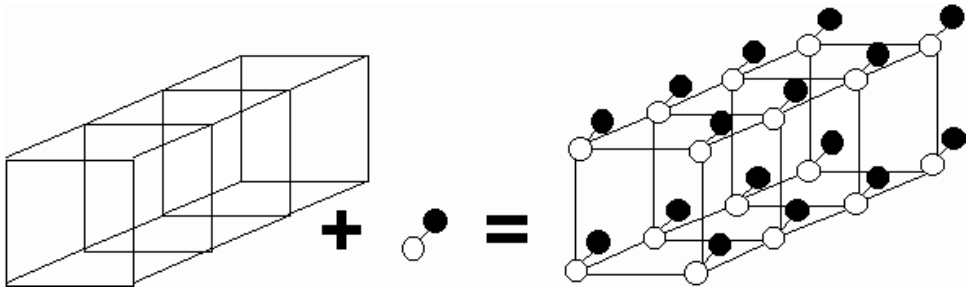
Crystal structure

A crystal structure is formed when a group of atoms or molecules are attached identically to each lattice point. This group of atoms or molecules are called basis.

Basis is identical – in composition,
in arrangement,
in orientation .

and repeated periodically in space to form the crystal structure which can be represented by the logical formula:

Lattice + Basis = crystal structure



Lattice + Basis crystal structure

2-D noncollinear translation define a plane lattice

3-D non-coplanar translation defined a space lattice

Primitive unit cell & Non-primitive unit cell

All solids are composed of discrete basic units which are the atoms. These atoms are not distributed randomly, but are arranged in a highly ordered manner relative to each other. Such a group of ordered atoms is referred to as a crystal.

In 3-D, the simplest parallelepiped formed by the primitive translation operation *T* is called unit cell.

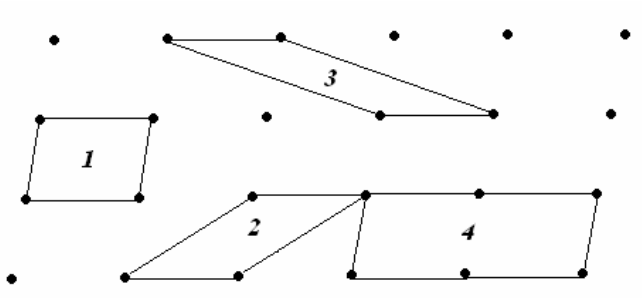
The parallelepiped defined by primitive axes a, b, c is called primitive cell. The number of atoms in a **primitive cell** or primitive basis is always the same for a given crystal structure.

It is the minimum volume cell.

It is the building block element.

It has always only one lattice point per cell.

Volume of the unit cell $V_c = \left|\bar{a}.\bar{b}\times\bar{c}\right|$ *or* $\left|\bar{a}\times\bar{b}.\bar{c}\right|$



Here parallelogram 1, 2, 3 are equal in area and any one of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell and thus a compound cell. **The compound cell**

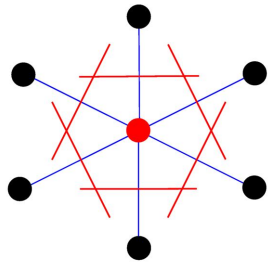
is also a non-primitive cell. There is more than one lattice point and the area is constant multiple of primitive cell.

Example of primitive cell – Simple cubic; Non-primitive cell – Body centered cubic, Face centered cubic; Base centered orthorhombic, Hexagonal structure, etc.

Wigner-Seitz cell

It was first suggested by E. P Wigner and F. Seitz. A primitive cell can also be chosen as:

- Firstly, draw lines to connect a given lattice point to all nearby lattice points.
- Secondly, at the midpoint and normal to these lines draw new lines or planes.

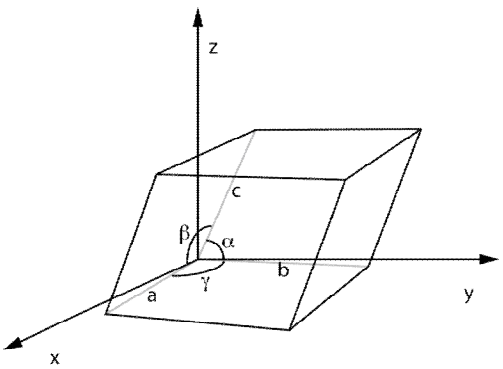


The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All the space of the crystal may be filled by these primitive cells, by translating the unit cell by the lattice vectors.

Lattice parameters and lattice constant

The lattice constant [or lattice parameter] refers to the constant distance between unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as *a*, *b*, and *c*. However, in the special case of cubic crystal structures, all of the constants are equal and we only refer to *a*. Similarly, in hexagonal crystal structures, the *a* and *b* constants are equal, and we only refer to the *a* and *c* constants. A group of lattice constants could be referred to as lattice parameters. However, the full set of lattice parameters consist of the three lattice constants and the three angles between them.

For example the lattice constant for a common carbon diamond is $a = 3.57$Å at 300 K. The structure is equilateral although its actual shape can not be determined from only the lattice constant. Furthermore, in real applications, typically the average lattice constant is given. As lattice constants have the dimension of length, their SI unit is the meter. Lattice constants are typically of the order of several angstroms (i.e. tenths of a nanometre). Lattice constants can be determined using techniques such as X-ray diffraction or with an atomic force microscope (AFM).



Thus, the tree fundamental translation vectors $\bar{a}, \bar{b}, \bar{c}$ along with opposite angles α, β, γ, each of between two crystallographic axis as shown in figure are the lattice parameters and the distance between two identical atoms or molecules is the lattice constant.

Co-ordination number

The points in a Bravais lattice that are closest to a given point are called its nearest neighbors. Because of the periodic nature of a Bravais lattice, each point has the same number of nearest neighbors. This number is thus a property of the lattice and is referred to as the co-ordination number of the lattice.

In solid-state structures of crystals are defined by a simpler model in which the atoms are represented by touching spheres. In this model the coordination number of an atom is the number of other atoms which it touches. For an atom in the interior of a crystal lattice the number of atoms touching the given atom is the **bulk coordination number**; for an atom at a surface of a crystal, this is the **surface coordination number**.

A simple cubic lattice has co-ordination no. 6, Body centered cubic lattice has co-ordination no. 8 and face centered cubic lattice has co-ordination no. 12.

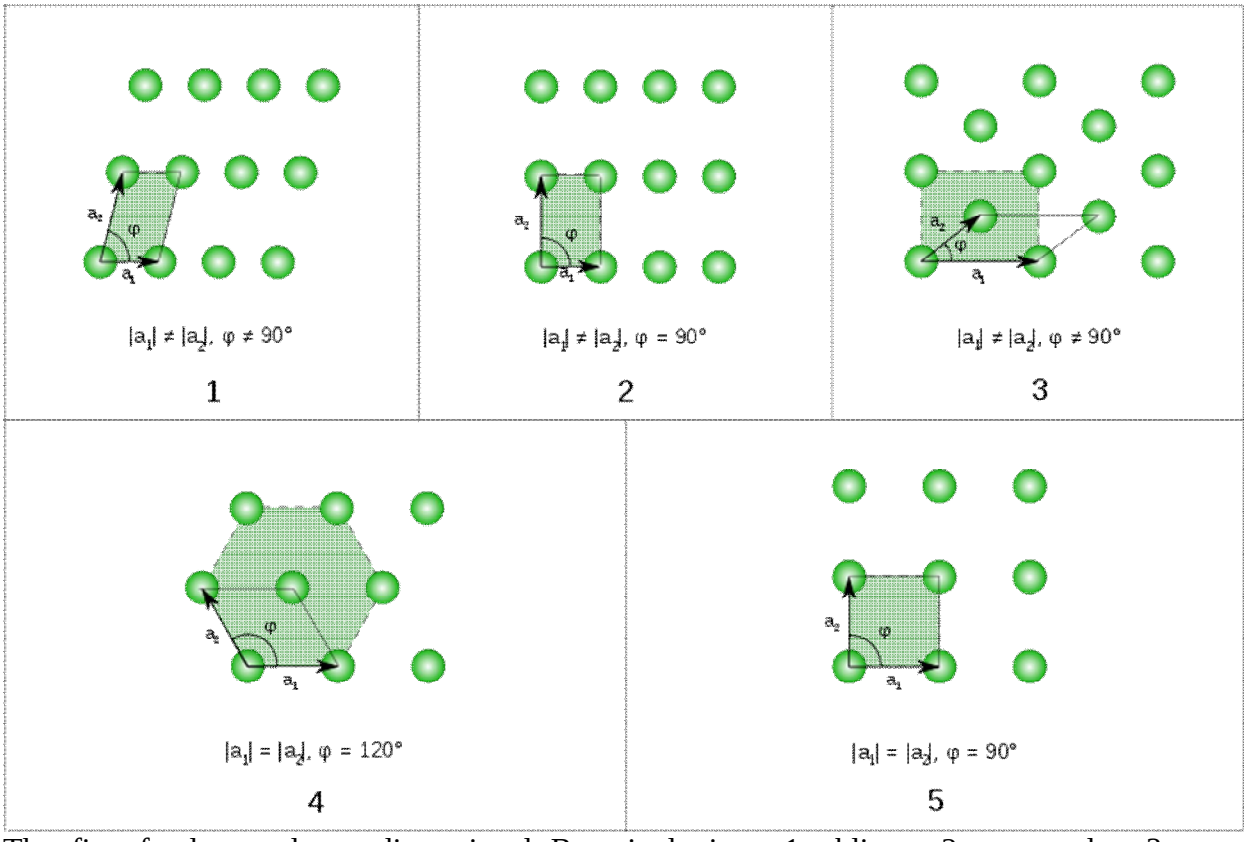
Lecture 03: Crystal Systems

Two dimensional lattice symmetry:

There are unlimited number of possible lattices because there is no natural limitation on the lengths of the lattice translation vectors or no the angle of between them.

Bravais lattice is a common phrase for a distinct lattice type. In a Bravais lattice, all lattice points are equivalent and hence by necessity all atoms in the crystal are of the same kind.

There are five distinct types (Bravais) of lattice symmetry in two dimensions such as:
(i) Oblique (a ≠b, $\phi \neq 90^0$) (ii) Square (a = b, $\phi = 90^0$), (iii) Hexagonal (a = b, $\phi = 120^0$) (iv) Rectangular (a ≠b, $\phi = 90^0$) (v) Centered rectangular (a ≠b, $\phi = 90^0$). Of these (i) $\rightarrow$ general, (ii) to (v) $\rightarrow$ special types.



The five fundamental two-dimensional Bravais lattices: 1 oblique, 2 rectangular, 3 centered rectangular, 4 hexagonal, and 5 square

Three dimensional lattice symmetry:

The point symmetry groups in 3-D requires the 14 different lattice types listed in Table-1,. The general lattice is triclinic, and there are 13 special lattices. These are grouped for convenience into systems classified according to seven types of cells which are

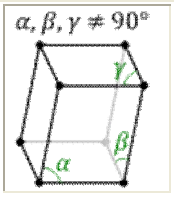
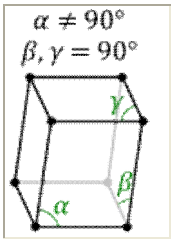
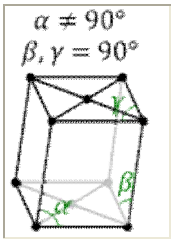
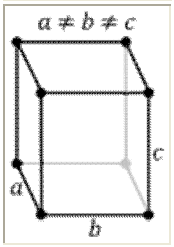
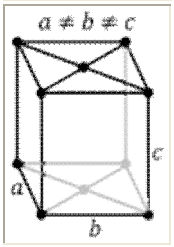
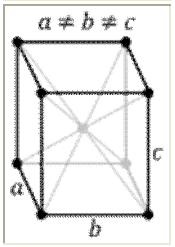
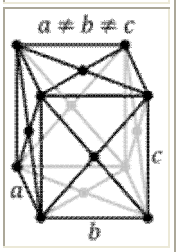
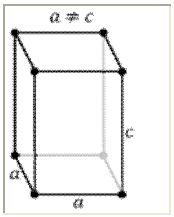
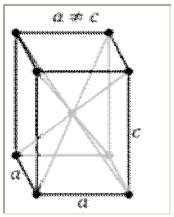
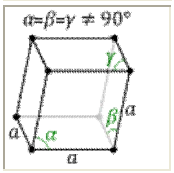
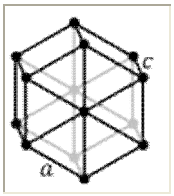
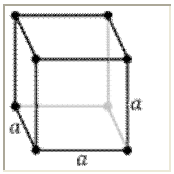
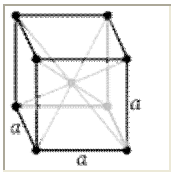
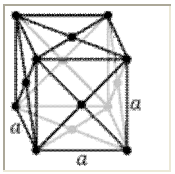
1. Triclinic (General Types – $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$)
2. Monoclinic
3. Orthorhombic (Rhombic)
4. Tetragonal
5. Cubic
6. Trigonal (Rhombohedral)
7. Hexagonal

Table: 1 The seven crystal systems divided into 14 Bravais lattices.

Sl. No	Crystal system	Bravais lattice (Number & symbol)	Unit cell characteristics (axes and angles)	Lattice parameters	Examples
1	Triclinic	1, simple (P)	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$	a, b, c / α, β, γ | 6	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3
2	Monoclinic	2, simple (P) Base-centred (C)	$a \neq b \neq c$, $\alpha \neq \beta \neq 90^0 \neq \gamma$	a, b, c / γ | 4	Monoclinic Sulpher, $Na_2SO_4.10H_2O$
3	Orthorhombic	4, simple (P) Base-centred (C) Body-centred (I) Face-centred (F)	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^0$	$a \quad b \quad c$ | 3	Rhombic sulphur, KNO_3 $CaCO_3$,, Ba_2SO_4
4	Tetragonal	2, simple (P) Body-centred (1)	$a = b \neq c$, $\alpha = \beta = \gamma = 90^0$	$a \quad c$ | 2	SnO_2, White tin, TiO_2, Ca_2SO_4
5	Cubic	3, simple (P) Body-centred (I) Face-Centred (F)	$a = b = c$, $\alpha = \beta = \gamma = 90^0$	a | 1	Copper, KCl, NaCl, Zinc blend, Diamond
6	Trigonal	1, simple (P)	$a = b = c$, $\alpha = \beta = \gamma \neq 90^0$, $< 120^0$	a / α | 2	Ca_2CO_3 (Calcite), HgS (Cinnaber)
7.	Hexagonal	1, simple (P)	$a = b \neq c$, $\alpha = \beta = 90^0$, $\gamma = 120^0$	$a \quad c$ | 2	Graphite, Mg, ZnO, CdS,

P → Primitive (it has atoms only at the corners of the parallelepiped)
C → Base-centered (it has extra atom at the centre of the base)
I → Body centered (From German word Innenzentriete)
F → Face-centered

triclinic	P

				
monoclinic	P 	C 		
orthorhombic	P 	C 	I 	F 
tetragonal	P 	I 		
rhombohedral	P 			
hexagonal	P 			
cubic	P (pcc) 	I (bcc) 	F (fcc) 	

The volume of the unit cell can be calculated by evaluating $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ where **a**, **b**, and **c** are the lattice vectors. The volumes of the Bravais lattices are given below:

Lattice system	Volume
Triclinic	$abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$
Monoclinic	$abc\ \sin\alpha$
Orthorhombic	abc
Tetragonal	a^2c
rhombohedral	$a^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha}$
Hexagonal	$\frac{\sqrt{3}\ a^2c}{2}$
Cubic	a^3

Bravais lattices in 4 dimensions

In four dimensions, there are 52 Bravais lattices. Of these, 21 are primitive and 31 are centered.

Lattice points per unit cell

In primitive cell, lattice points are located only at corners, while each corners of the cell is common to eight neighboring unit cells and the contribution towards the unit cell per corner is only one-eight. Since there are eight corners, therefore the number of lattice point per unit cell is only one.

Primitive cell contains one lattice point.

Cubic cell contains one lattice point.

Body centered cubic contains 2 lattice points

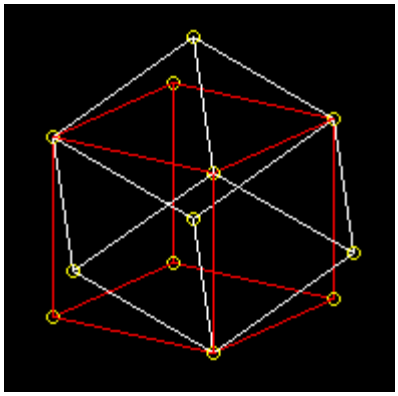
and conventional face centered cubic (fcc) cell contains four lattice points.

Characteristics of cubic lattices:

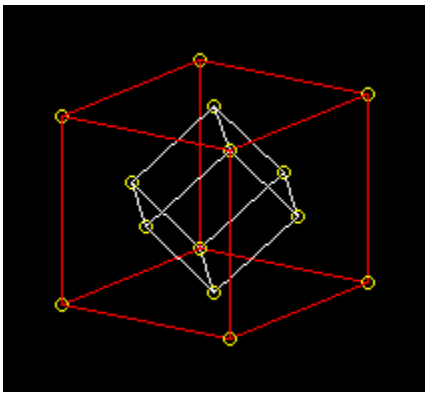
Volume, conventional cell	Simple a^3	Body-Centred a^3	Face Centred a^3
Lattice points per unit cell	1	2	4
Volume of primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Number of nearest neighbors	6	8	12
Packing fraction or efficiency	0.524 or 52%	0.680 or 68%	0.740 or 74%

Hexagonal close packed $\rightarrow$ 74%, c/a = 1.633

Primitive cell of bcc and fcc structure



Body centered cubic, showing a primitive cell which is a rhombohedron of edge $\frac{\sqrt{3}}{2}a$ and angle between adjacent edges is $109^0 28'$ and Translation vector $\vec{a}$



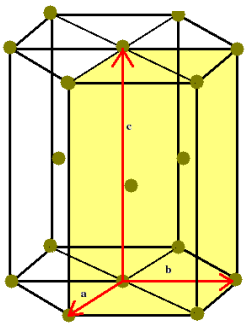
The rhombohedral primitive cell of the face centered cubic crystal with translation vectors

$\vec{a} = \frac{1}{2}a(\hat{x} + \hat{y})$

$\vec{b} = \frac{1}{2}b(\hat{y} + \hat{z})$

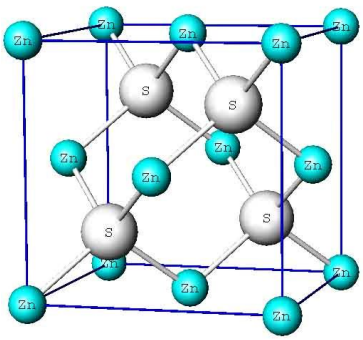
$\vec{c} = \frac{1}{2}c(\hat{z} + \hat{x})$

and the angles between the axes are 60^0



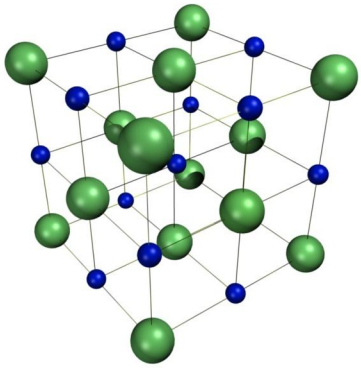
Hexagonal close packed structure (hcp)

Diamond Structure

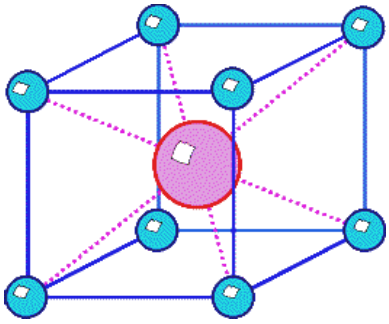


Zinc blend (ZnS) Structure

The NaCl and CsCl structure:



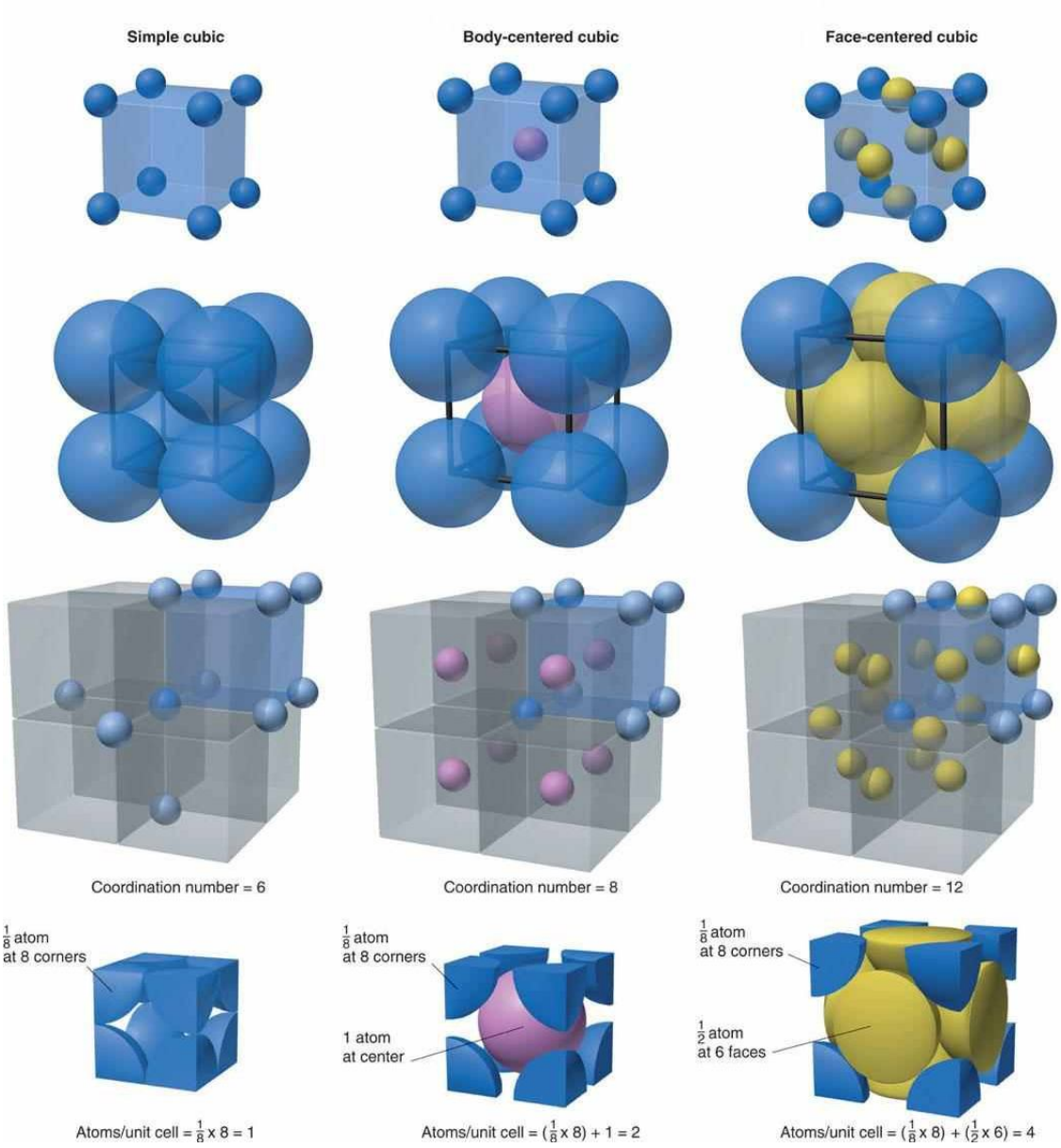
NaCl



CsCl

The sodium chloride crystal structure can be (is) construct by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six (6) nearest neighbors of the opposite charge. The space lattice is fcc and the basis has one cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Figure shows conventional cubic cell. Variation in ion diameters is due to clarify the spatial arrangement. Example: LiH, NaCl, KBr, KCl, PbS, NH_4I, AgBr, Mgo, MnO, BaO, etc.

In the cesium chloride crystal structure, space lattice is simple cubic and the basis has one Cs^+ ion at 000 and one Cl^- at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. There is one molecule per primitive cell, with atoms at the corners 000 and body centered positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic space lattice. Each atom may be viewed as at the center of a cube of atoms of the opposite kind. So the number of nearest neighbors or co-ordination number is eight (8). Example: CsCl, NH_4Cl, etc.


Simple cubic
Body-centered cubic
Face-centered cubic
Coordination number = 6
Coordination number = 8
Coordination number = 12
1/8 atom at 8 corners
1/8 atom at 8 corners
1 atom at center
1/8 atom at 8 corners
1/2 atom at 6 faces
Atoms/unit cell = 1/8 x 8 = 1
Atoms/unit cell = (1/8 x 8) + 1 = 2
Atoms/unit cell = (1/8 x 8) + (1/2 x 6) = 4

Lecture 04: Density and Packing fraction

Density: Let us consider a cubic cell of lattice constant `*a*' contains `*n*' atoms per unit cell, then density of the crystal material is defined as

$$\rho = \frac{Mass\ of\ unit\ cell}{Volume\ of\ the\ unit\ cell} = \frac{Mn}{NV} = \frac{Mn}{Na^3}$$

Where M = atomic weight and N ≡Avogadro's number and $\frac{M}{N}$ = Mass of each atom or molecule. N = 6.023×10^{23} mol^{-1} = 6.023×10^{26} $kmol^{-1}$.

The number of lattice points can be determined if we know the volume, density and molecular weight of the constituent atom of the cell.

Problem 1: Calculate the lattice constant for rock salt crystal of density 2180 kg/m^3 assuming that it has *fcc* lattice. Molecular weight of NaCl is 58.5.

Solution: For *fcc* lattice, $n = 4$ and here $V = a^3$.

Therefore, $$a^3 = \frac{Mn}{\rho N} = \frac{58.5\times4}{2180\times6.023\times10^{26}} = 178.22\times10^{-30}\ m^3$$

$$a = 5.63\times10^{-10}\ m = 5.63\ \text{Å}$$

Problem 2: Calculate the number of atoms per unit cell for an *fcc* lattice of copper (Cu) crystal. It is given that a = 3.6 Å, atomic weight of Cu = 63.6, ρ_{cu} = 8960 kg/m^3 and N = 6.023×10^{26} per kmole.

Ans: $3.959 \approx 4$

Exercise: The lattice parameter and atomic mass of a dimond crystal are 3.57Å and 12 respectively. Calculate the density of dimond.

Solution: $a^3 = \left(3.57\times10^{-10}\right)^3$, $M = 12$, No of atoms $\left(\frac{1}{8}\times8\right)+\left(\frac{1}{2}\times6\right)+1\times4=8$

$$\rho = \frac{Mn}{Na^3} = 3540\ kg/m^3$$

Exercise: Aluminium has fcc structure. If the density of Al is 2.7×10^3 kg/m^3. Calculate the unit cell dimensions and the atomic diameter. (At wt. of al; = 26.98, Avogadro No. = 6.023×10^{26} kg mole).

Solution: $V = a^3 = \frac{Mn}{\rho N} = \frac{26.98 \times 4}{2.7 \times 10^3 \times 6.023 \times 10^{26}} = 66.34 \times 10^{26}\, m^3$, This gives, a = 4.05 $\overset{o}{A}$

Now for fcc crystal, we know that $\sqrt{2}a$ = 4D = 2D , $\therefore$ D = $\frac{a}{\sqrt{2}}$ = 2.86 $\overset{o}{A}$

Atomic packing factor

In crystallography, atomic packing factor (APF) or packing fraction is the fraction of volume in a crystal structure that is occupied by atoms. It is dimensionless and always less than unity. For practical purposes, the APF of a crystal structure is determined by assuming that atoms are rigid spheres. The radius of the spheres is taken to be the maximal value such that the atoms do not overlap. It is defined as the ratio of the actual volume occupied by the spherical atoms to the total available of the structure. It is also known as relative pacing density, efficiency or packing fraction. For one-component crystals (those that contain only one type of atom), the APF is represented mathematically by

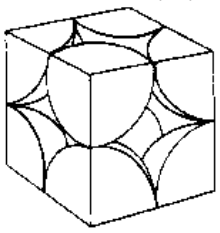
$$APF = \frac{Volume\ occupied\ by\ the\ sphere\ in\ unit\ cell}{Volume\ of\ the\ unit\ cell}$$

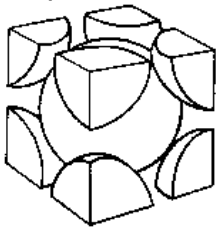
i.e., $APF = \frac{N_{atoms} V_{atom}}{V_{unitcell}}$

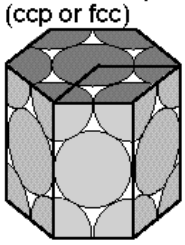
and Effeciency, $\eta = \frac{N_{atoms} V_{atom}}{V_{unitcell}} \times 100\%$

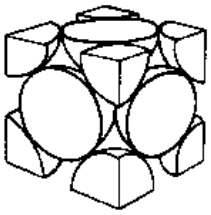
where N_{atoms} is the number of atoms in the unit cell, V_{atom} is the volume of an atom, and $V_{unit\ cell}$ is the volume occupied by the unit cell. It can be proven mathematically that for one-component structures, the most dense arrangement of atoms has an APF of about 0.74. In reality, this number can be higher due to specific intermolecular factors. For multiple-component structures, the APF can exceed 0.74.

Type of Packing	Packing Efficiency	Coordination Number
Simple cubic (sc)	52%	6
Body-centered cubic (bcc)	68%	8
Hexagonal close-packed (hcp)	74%	12
Cubic close-packed (ccp or fcc)	74%	12









APF for simple cubic:

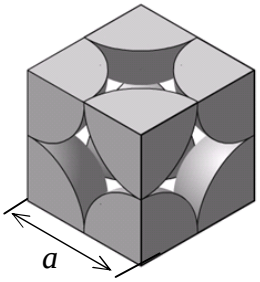
In this case, the side of the cube 'a' must be equal to 2R, where R is the atomic radius. i.e., $R = \frac{a}{2}$

and number of atoms in simple cubic $= \frac{1}{8} \times 8 = 1$

$\therefore$ Volume of atoms within the unit cell is $V_a = 1 \times \frac{4}{3}\pi R^3 = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$

and volume of the unit cell, $V_c = a^3$.

Therefore, packing factor = $\frac{V_a}{V_c} \times 100\% = \frac{\pi}{6} = 0.52$



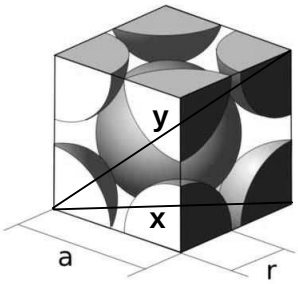
APF for body-centered cubic (bcc) structure:

In this case the diagonal of the cube y = 4R, where is the atomic radius.

From figure, we can write, $x^2 = a^2 + a^2 = 2a^2 \Rightarrow x = \sqrt{2}a$

$y^2 = x^2 + a^2 = 2a^2 + a^2 = 3a^2 \Rightarrow a = \sqrt{3}a$

$\therefore 4R = \sqrt{3}a$ or $R = \frac{\sqrt{3}}{4}a$



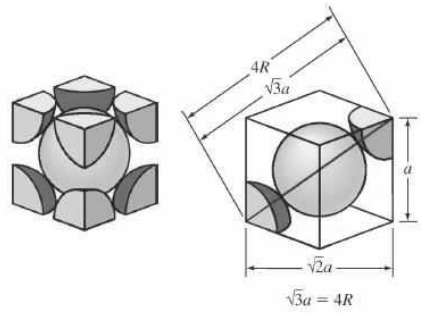
Now, total number of atoms in bcc structure = $(\frac{1}{8} \times 8 + 1) = 1 + 1 = 2$

$\therefore$ The volume of atoms in the unit cell

$V_a = 2 \times \frac{4}{3}\pi R^3 = \frac{8}{3}\pi(\frac{\sqrt{3}}{4}a)^3 = \frac{\sqrt{3}}{8}\pi a^3$

and volume of the unit cell, $V_c = a^3$

Therefore, efficiency, $\eta = \frac{V_a}{V_c} \times 100\% = \frac{\sqrt{3}}{8}\pi = 68\%$



The primitive unit cell for the body-centered cubic (BCC) crystal structure contains nine atoms: one on each corner of the cube and one atom in the center. Because the volume of each corner atom is shared between adjacent cells, each BCC cell contains two atoms.

Each corner atom touches the center atom. A line that is drawn from one corner of the cube through the center and to the other corner passes through 4*r*, where *r* is the radius of an atom. By geometry, the length of the diagonal is $a\sqrt{3}$. Therefore, the length of each side of the BCC structure can be related to the radius of the atom by

$$a = \frac{4r}{\sqrt{3}}.$$

Knowing this and the formula for the volume of a sphere $\frac{4}{3}\pi r^3$, it becomes possible to calculate the APF as follows:

$$\text{APF} = \frac{N_{\text{atoms}} V_{\text{atom}}}{V_{\text{crystal}}} = \frac{2(4/3)\pi r^3}{(4r/\sqrt{3})^3} = \frac{\pi\sqrt{3}}{8} \approx 0.68.$$

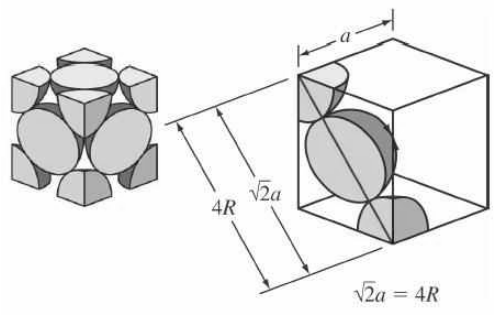
Face centered cubic lattice:

In this case the face diagonal y = 4R.

From figure we get, $y^2 = a^2 + a^2 = 2a^2$

or $y = \sqrt{2}\, a$

$\therefore$ $4R = \sqrt{2}\, a$ or, $R = \frac{\sqrt{2}}{4}a$



Total number of atoms in *fcc* structure is $= (\frac{1}{8} \times 8) + (\frac{1}{2} \times 6) = 1 + 3 = 4$

$\therefore$ Volume of atoms within the unit cell is $V_a = 4 \times \frac{4}{3}\pi R^3 = 4 \times \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3 = \frac{\sqrt{2}\pi a^3}{6}$

and volume of unit cell, $V_c = a^3$.

Therefore, packing density, $\eta = \frac{V_a}{V_c} \times 100\,\% = \frac{\sqrt{2}}{6}\pi = 74\%$

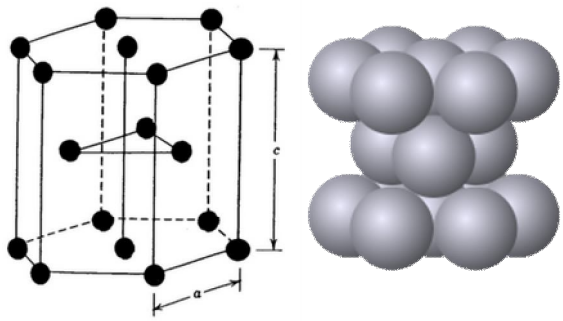
Hexagonal close-packed (hcp) structure

For the hexagonal close-packed (HCP) structure the derivation is similar. The side length of the hexagon will be denoted as *a* while the height of the hexagon will be denoted as *c*. Then:

In hexagonal close packed structure we can write A = 2 R, where r is the atomic radius, $R = \frac{a}{2}$

Total no. of atoms in hc-p structure

$$\left(\frac{1}{6} \times 6\right) \times 2 + \left(\frac{1}{2} \times 2\right) + 3 = 2 + 1 + 3 = 6$$



Volume of the unit cell $= 3 \times c\ ab \sin 60^0$

$$= 3\left|\vec{c}.\left(\vec{a}\times\vec{b}\right)\right|$$

$$= 3\left|\vec{c}.ab\sin\theta^0\, c\right|$$

$$= 3\times abc\sin\theta$$

$$= 3\times a^2c\sin 60^0 \qquad \left[\because a=b,\theta=60^0\right]$$

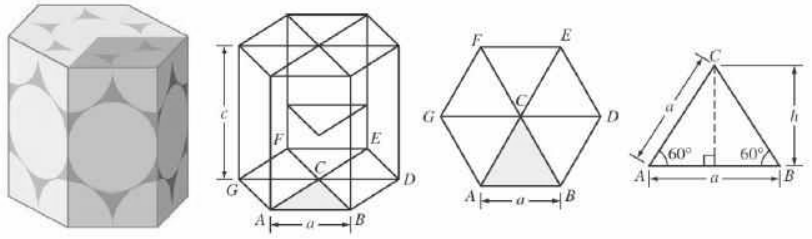
$$= \frac{3\sqrt{3}}{2}\ a^2c$$

$\therefore$ packing factor for h.c.p structure,

$$\eta = \frac{Va}{Vc} = \frac{\pi a^3\times 2}{3\sqrt{3}\,a^2c} = \frac{2\pi}{3\sqrt{3}}\left(\frac{a}{c}\right) = \frac{2\pi}{3\sqrt{3}\times 1.633} = 74\%$$

Here, $c/a = 1.633$

$$a = 2r$$
$$c = \sqrt{\frac{2}{3}}(4r).$$



It is then possible to calculate the APF as follows:

$$\text{APF} = \frac{N_{\text{atoms}}V_{\text{atom}}}{V_{\text{crystal}}} = \frac{6(4/3)\pi r^3}{[(3\sqrt{3})/2](a^2)(c)} = \frac{6(4/3)\pi r^3}{[(3\sqrt{3})/2](2r)^2(\sqrt{\frac{2}{3}})(4r)} = \frac{6(4/3)\pi r^3}{[(3\sqrt{3})/2](\sqrt{\frac{2}{3}})(16r^3)}$$
$$= \frac{\pi}{\sqrt{18}} \approx 0.74.$$

By similar procedures, the ideal atomic packing factors of all crystal structures can be found. The common ones are collected here as reference, rounded to the nearest hundredth.

- Simple cubic: 0.52
- Body-centered cubic: 0.68
- Hexagonal close-packed: 0.74
- Face-centered cubic: 0.74
- Diamond cubic: 0.34

Hexagonal close-packed crystals: the axial ratio

From figure we can easily write

$$x^2 = a^2 - \left(\frac{a}{2}\right)^2 = \frac{3a^2}{4}, \quad \therefore x = \frac{\sqrt{3}}{2}a$$

where a is the centre to centre distance of the atom.

and $$h = \frac{2}{3}x = \frac{2}{3}\times\frac{\sqrt{3}}{2}a = \frac{a}{\sqrt{3}}$$

From Δ ABC, we can write,

$(AC)^2 = (AB)^2 + (BC)^2$

$$\Rightarrow a^2 = \left(\frac{c}{2}\right)^2 + (h)^2$$

$$\Rightarrow a^2 = \frac{c^2}{4} + \frac{a^2}{3}$$

$$\Rightarrow a^2 - \frac{c^2}{3} = \frac{c^2}{4}$$

$$\Rightarrow \frac{2a^2}{3} = \frac{c^2}{4}$$

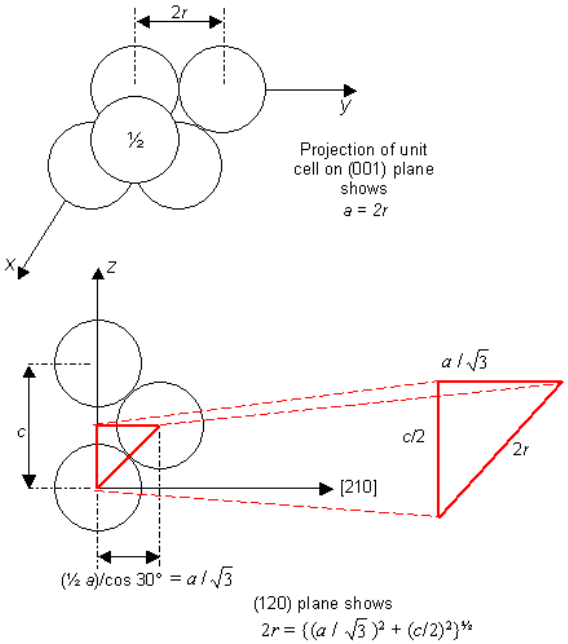
$$\Rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

The ideal axial ratio (c/a) for a hexagonal close-packed crystal structure can be calculated by considering non-interacting hard spheres packed in an h.c.p. lattice.

If the sphere radius is r, then the lattice parameters a (= b) and c can be written in terms of r:

These two relationships can be solved for the ideal axial ratio c/a:

$$2r = a = \left(\frac{a^2}{3} + \frac{c^2}{4}\right)^{\frac{1}{2}}$$



$a^2 = a^2/3 + c^2/4$

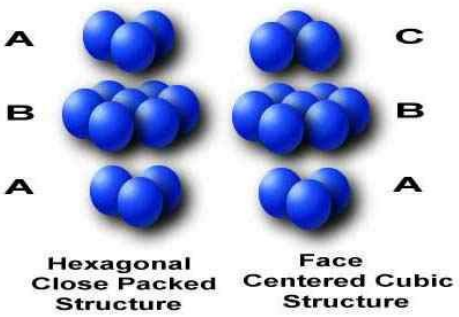
$4 = 4/3 + c^2/a^2$

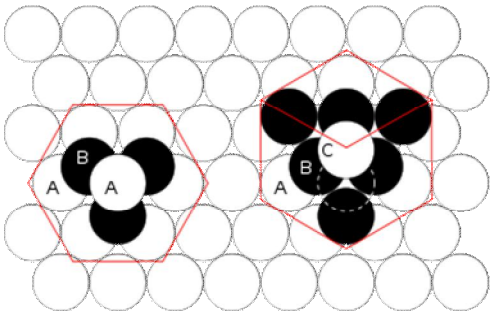
$c/a = 1.633$

Many materials have the hexagonal P crystal system, but the axial ratio is rarely ideal. Cadmium, for example, has an axial ratio of c/a = 1.886. This non-ideal structure has implications for the behaviour of the material, for example in slip.

Similarities and Difference between the FCC and HCP Structure

The face centered cubic and hexagonal close packed structures both have a packing factor of 0.74, consist of closely packed planes of atoms, and have a coordination number of 12. The difference between the fcc and hcp is the stacking sequence. The hcp layers cycle among the two equivalent shifted positions whereas the fcc layers cycle between three positions. As can be seen in the image, the hcp structure contains only two types of planes with an alternating ABAB arrangement. Notice how the atoms of the third plane are in exactly the same position as the atoms in the first plane. However, the fcc structure contains three types of planes with a ABCABC arrangement. Notice how the atoms in rows A and C are no longer aligned. Remember that cubic lattice structures allow slippage to occur more easily than non-cubic lattices, so hcp metals are not as ductile as the fcc metals.





HCP lattice (left) and the fcc lattice (right)

The table below shows the stable room temperature crystal structures for several elemental metals.

Metal	Crystal Structure	Atomic Radius (nm)
Aluminum	FCC	0.1431
Cadmium	HCP	0.1490
Chromium	BCC	0.1249
Cobalt	HCP	0.1253
Copper	FCC	0.1278
Gold	FCC	0.1442
Iron (Alpha)	BCC	0.1241
Lead	FCC	0.1750
Magnesium	HCP	0.1599
Molybdenum	BCC	0.1363
Nickel	FCC	0.1246
Platinum	FCC	0.1387
Silver	FCC	0.1445
Tantalum	BCC	0.1430
Titanium (Alpha)	HCP	0.1445
Tungsten	BCC	0.1371
Zinc	HCP	0.1332