Packing constituents in Crystals.

(1) Close packing in crystalline solids: In the formation of crystals, the constituent particles (atoms, ions or molecules) get closely packed together. The closely packed arrangement is that in which maximum available space is occupied. This corresponds to a state of maximum density. The closer the packing, the greater is the stability of the packed system. It is of two types:

(i) Close packing in two dimensions: The two possible arrangement of close packing in two dimensions.

(a) Square close packing: In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. Each sphere in this arrangement is in contact with four spheres.

(b) Hexagonal close packing: In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with spheres in first row. The similar pattern is noticed throughout the crystal structure. Each sphere in this arrangement is in contact with six other spheres.

4 2 4 3 Square close packing



Note: Hexagonal close packing is denser than square close packing.

In hexagonal close packing about 60.4% of available space is occupied by spheres. Whereas, square close packing occupies only 52.4% of the space by spheres.

In square close packing the vacant spaces (voids) are between four touching spheres, whose centers lie at the corners of a square are called square voids. While in hexagonal close packing the vacant spaces (voids) are between three touching spheres, whose centers lie at the corners of an equilateral triangle are called triangular voids.

(ii) Close packing in three dimensions: In order to develop three dimensional close packing, let

us retain the hexagonal close packing in the first layer. For close packing each spheres in the second layer rests in the hollow at the center of three touching spheres in the layer as shown in figure. The spheres in the first layer are shown by solid lines while those in second layer are shown by broken lines. It may be noted that only half the triangular voids in the first layer are occupied by spheres in the second layer (i.e., either b or c). The unoccupied hollows or voids in the first layer are indicated by (c) in figure.



There are two alternative ways in which species in third layer can be arranged over the second layer,

(a) Hexagonal close packing: The third layer lies vertically above the first and the spheres in third layer rest in one set of hollows on the top of the second layer. This arrangement is called ABAB Type and 74% of the available space is occupied by spheres.

(b) Cubic close packing: The third layer is different from the first and the spheres in the third layer lie on the other set of hollows marked 'C' in the first layer. This arrangement is called ABCABC..... Type and in this also 74% of the available space is occupied by spheres. The cubic close packing has face centered cubic (fcc) unit cell.



This arrangement is found in Be, Mg, Zn, Cd, Sc, Y, Ti, Zr.



This arrangement is found in Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr.

(c) Body centered cubic (bcc): This arrangement of spheres (or atoms) is not exactly close

packed. This structure can be obtained if spheres in the first layer (A) of close packing are slightly opened up. As a result none of these spheres are in contact with each other. The second layer of spheres (B) can be placed on top of the first layer so that each sphere of the second layer is in contact with four spheres of the layer below it. Successive building of the third will be exactly like the first layer. If this pattern of building layers is



repeated infinitely we get an arrangement as shown in figure. This arrangement is found in Li, Na, K, Rb, Ba, Cs, V, Nb, Cr, Mo, Fe.

Property	Hexagonal close packed (hcp)	Cubic close packed (ccp)	Body centered cubic (bcc)
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	AB AB AB A	ABC ABC A	AB AB AB A
Available space occupied	74%	74%	68%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard and brittle	Malleable and ductile	

(2) Comparison of hcp, ccp and bcc

(3) Interstitial sites in close packed structures: Even in the close packing of spheres, there is left some empty space between the spheres. This empty space in the crystal lattice is called site or void or hole. Voids are of following types

(i) Trigonal void: This site is formed when three spheres lie at the vertices of an equilateral triangle. Size of the trigonal site is given by the following relation.



Where, r = Radius of the spherical trigonal site

R = Radius of closely packed spheres



(ii) Tetrahedral void: A tetrahedral void is developed when triangular voids (made by three spheres in one layer touching each other) have contact with one sphere either in the upper layer or in the lower

layer. This type of void is surrounded by four spheres and the centers of these spheres lie at the apices of a regular tetrahedron, hence the name tetrahedral site for this void.

In a close packed structure, there are two tetrahedral voids associated with each sphere because every void has four spheres around it and there are eight voids around each sphere. So the number of

tetrahedral voids is double the number of spheres in the crystal structure. The maximum radius of the atoms which can fit in the tetrahedral voids relative to the radius of the sphere is calculated to be 0.225: 1, i.e.,

where *r* is the radius of the tetrahedral void or atom $\frac{r}{R} = ($ occupying tetrahedral void and *R* is the radius of spheres $\frac{r}{R} =$ forming tetrahedral void.

(a) Octahedral void: This type of void is surrounded by six closely packed spheres, i.e. it is formed by six spheres. Out of six spheres, four are placed in the same plane touching each other, one sphere is placed from above and the other from below the plane of these spheres. These six spheres surrounding the octahedral void are present at the vertices of regular octahedron. Therefore, the number of octahedral voids is equal to the number of spheres. The ratio of the radius (r) of the atom or ion which can exactly fit in the octahedral void formed by spheres of radius R has been calculated to be 0.414, i.e.



Cubic void Cubic void

_____ Thus, the decreasing order of the size of the various voids is Cubic > Octahedral > Tetrahedral > Trigonal

(b) Cubic void: This type of void is formed between 8 closely packed spheres which occupy all the eight corner of cube i.e. this site is surrounded by eight

Important Tips

At the limiting value of radius ratio r^+/r^- , the forces of attraction & repulsion are equal.

The most malleable metals (Cu, Ag, and Au) have cubic close packing.

Cubic close packing has FCC (face centered cubic) unit cell

Number of octahedral voids = Number of atoms present in the closed packed arrangement.

Number of tetrahedral voids = 2 × Number of octahedral voids = 2 × Number of atoms.







 $\frac{r}{R} = 0.414$