Welcome to

BYJU'S Classes

Chemistry

Solid State

A Deep Understanding of Voids in Solids

What you already know

- Packing fraction and Packing efficiency
- Packing efficiency in 1D lattice
- Calculating the packing fraction in a 2D lattice
- Calculating the packing fraction in a 3D lattice

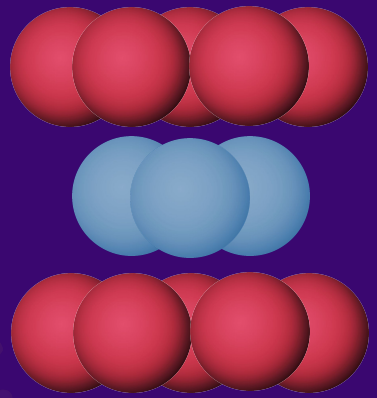
What you will learn

- Packing efficiency in three dimensional lattice (continued)
- Voids (Interstitial Voids)
- Voids in FCC or CCP Structure

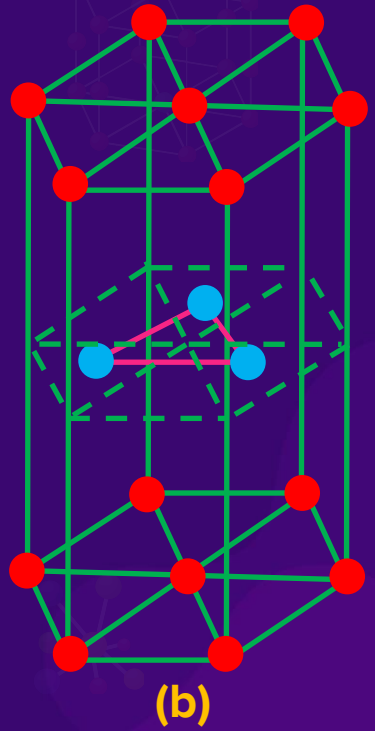
Packing Efficiency in Three Dimensional Lattice

Hexagonal close packing

When the tetrahedral voids of the second layer (i.e., B) are covered by the spheres of the third layer, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB. This structure is known as hexagonal close packed (hcp) structure. Three layers (ABA) are stacked one above the other as shown in **(a),** and the unit cell of the hexagonal close packing is shown in **(b)**.



(a)



(b)

Packing Efficiency in Three Dimensional Lattice

Number of particles in one hcp unit cell

A particle present at the corner of the hexagon in layer A is shared by six hcp unit cells. Half portion of the particle at the corner is shared by three hcp unit cells. Thus, each hcp unit cell has $\frac{1}{6}^{th}$ portion of the particle present at the corner. There are 12 particles at the corners (six particles in the corners of the hexagon at the top and the rest of the six in the corners of the hexagon at the bottom of an hcp unit cell) and each of these are shared by six other hcp unit cells. Hence, the contribution of the corner particles of the two hexagonal layers = 12 × (1/6) = 2

Packing Efficiency in Three Dimensional Lattice

Hexagonal close packing

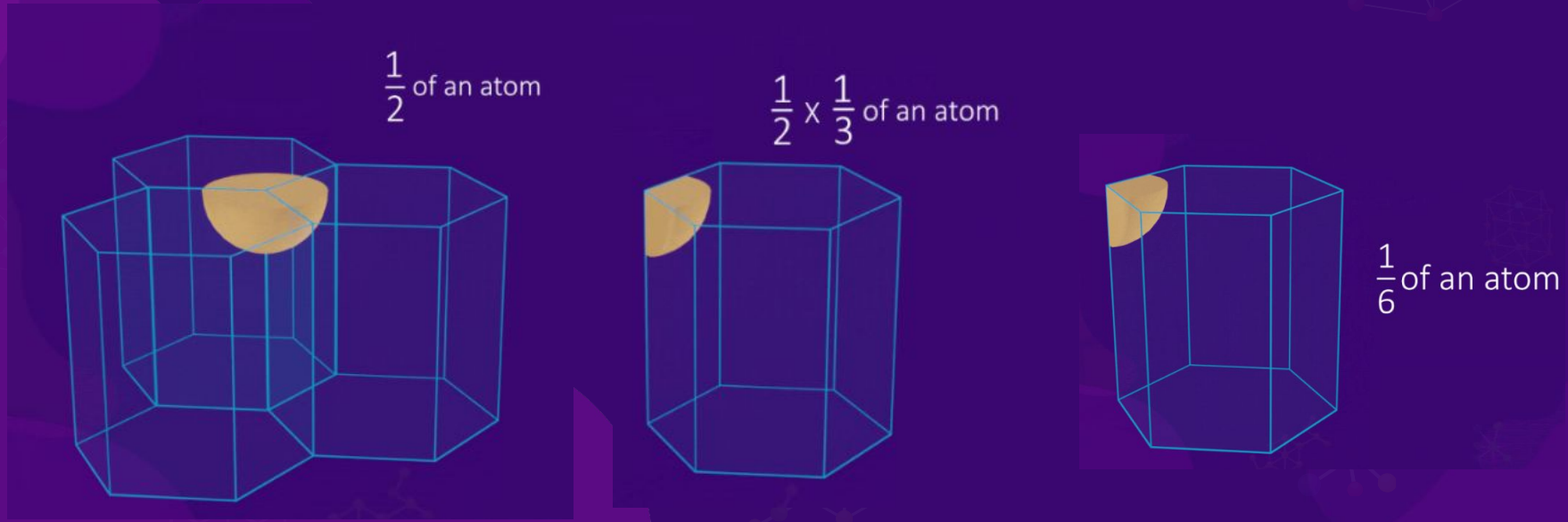
A particle present at the centre of the hexagon at the top and bottom faces of a hcp unit cell is shared by two unit cells. Hence, the contribution of the particle present in the centre of the hexagons at the top and bottom faces of hcp unit cell = $2 \times \frac{1}{2} = 1$

Also, three particles are present in the centre of the body of hcp unit cell which are not shared with any other unit cell. Hence, the contribution of particles present inside the unit cell = 3

Thus, the total number of particles in an hcp unit cell, $\mathbf{Z_{eff} = 2 + 1 + 3 = 6}$

Packing Efficiency in Three Dimensional Lattice

An illustration to understand the number of particles in a hcp unit cell is given below:



Packing Efficiency in Three Dimensional Lattice

Hexagonal close packing

$$\text{Packing efficiency (f)} = \frac{\text{No. of particles in one HCP unit cell} \times \text{Volume of each particle}}{\text{Total volume of the unit cell}}$$

The total number of particles in one hcp unit cell, $Z_{eff} = 6$

Packing Efficiency in Three Dimensional Lattice

Hexagonal close packing

Since the particles are assumed to be spheres, the volume of each particle is given as follows:

Volume of the hcp unit cell (hexagon)
= Base area × Height

Volume occupied by 1 particle $= \frac{4}{3}\pi r^3$

Volume occupied by 6 particles $= 6 \times \frac{4}{3}\pi r^3$

$= 8\pi r^3$

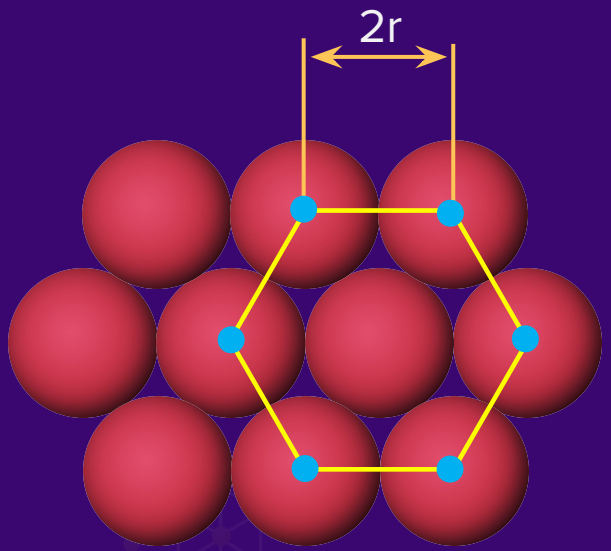
Packing Efficiency in Three Dimensional Lattice

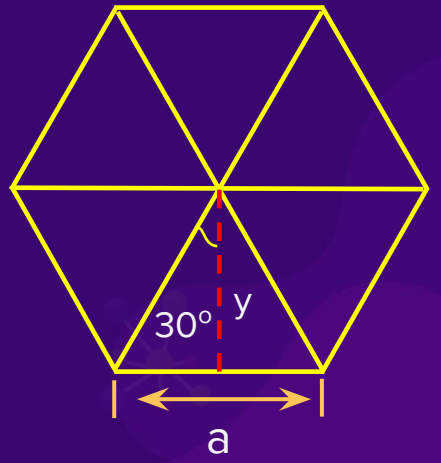
Calculating base area of hcp unit cell (Hexagon)

Consider layer A of hcp unit cell and spheres (particles) with radius r as shown. The edge length (a) of the hexagon is 2r.

$$a = 2r$$

$$\text{Area of an equilateral triangle} = \frac{\sqrt{3}}{4}a^2$$





Packing Efficiency in Three Dimensional Lattice

Since the hexagon has six equilateral triangles, its base area is given as follows:

$$\text{Base area of a regular hexagon} = 6 \times \frac{\sqrt{3}}{4}a^2 = \frac{3\sqrt{3}}{2}a^2 \quad \ldots (1)$$

We know that the relation between the edge length (a) and the radius of a sphere (particle or lattice point) in hcp is given by,

a = 2r

Thus, (1) becomes,

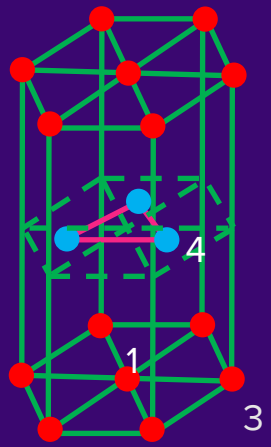
$$\text{Base area of a regular hexagon} = \frac{3\sqrt{3}}{2}(a)^2 = \frac{3\sqrt{3}}{2}(2r)^2 = 6\sqrt{3}\,r^2 \quad \ldots (2)$$

Packing Efficiency in Three Dimensional Lattice

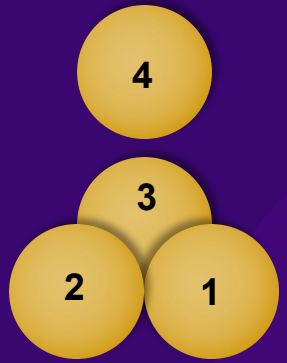
Calculating the height of a hexagon

hcp unit cell is given in **A.** The spheres (particles) labelled as 1, 2, 3, and 4 form a tetrahedral void as shown in **B**. Sphere 4 is in contact with spheres 1, 2, and 3. Similarly, spheres 1, 2, and 3 are in contact with each other. Spheres 1, 2, and 3 form an equilateral triangle with side **a = 2r.**

Since spheres 3 and 4 are in contact with each other, the distance between the centres of these spheres is 2r.



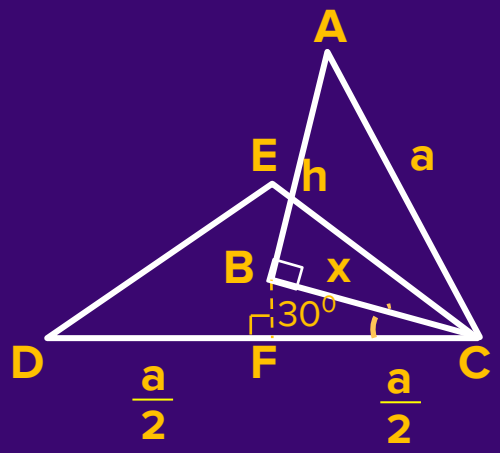
A

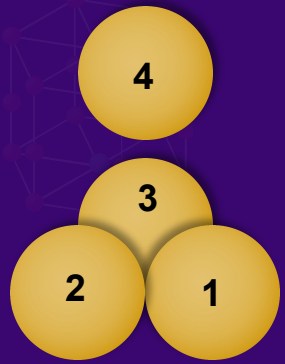


B

Packing Efficiency in Three Dimensional Lattice

For easy calculations, spheres 1, 2, 3, and 4 are arranged in such a way that they form triangles as shown (triangle ABC is a right-angled triangle and triangle CDE is an equilateral triangle). A perpendicular drawn from sphere 4 (point A) to the centre of the face below (point B) will give a right-angled triangle with a height (h) that is half of the height of the hexagon.





We know that the triangle formed by spheres 1, 2, and 3 is an equilateral triangle (for convenience, it is labelled as CDE). So, each angle will be 60°. When the line 'x' (CB) bisects this angle, we get the angle BCF as 30°.

$$\cos 30^\circ = \frac{a/2}{x} \Rightarrow x = \frac{a/2}{(\sqrt{3})/2} \Rightarrow x = \frac{a}{\sqrt{3}} \quad \ldots (3)$$

Packing Efficiency in Three Dimensional Lattice

By applying Pythagoras's theorem in the right-angled triangle ABC, we get,

$$AB^2 + BC^2 = AC^2$$
$$h^2 + x^2 = a^2$$
$$h^2 = a^2 - x^2$$

From (3), $x^2 = a^2/3$ and by substituting the value of x^2 in the expression for h^2, we get,

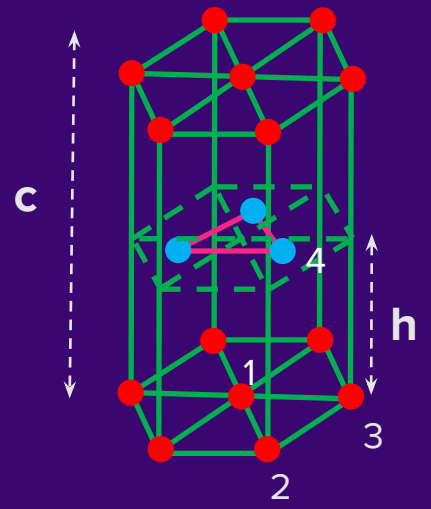
$$h^2 = a^2 - x^2$$

$$h^2 = a^2 - \frac{a^2}{3} = \frac{2a^2}{3}$$

Packing Efficiency in Three Dimensional Lattice

$$h = \frac{a\sqrt{2}}{\sqrt{3}}$$

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



h = Distance between two consecutive layers A – B

c = Height of hexagonal unit cell

Packing Efficiency in Three Dimensional Lattice

Base area of a regular hexagon $= 6 \times \frac{\sqrt{3}}{4} (a)^2 = 6 \times \sqrt{3} r^2$

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

Volume of hexagon (unit cell) $= 6 \times \sqrt{3} r^2 \times 4r \times \frac{\sqrt{2}}{\sqrt{3}}$

$= 24\sqrt{2} r^3$

Packing Efficiency in Three Dimensional Lattice

$$\text{Packing efficiency (f)} = \frac{\text{Volume occupied by particles}}{\text{Total volume of the unit cell}} \times 100$$

$$\text{Packing efficiency (f)} = \frac{6 \times (4/3)\pi r^3}{24\sqrt{2}r^3}$$

$$= \frac{\pi \times 100}{3\sqrt{2}} \approx 74\%$$

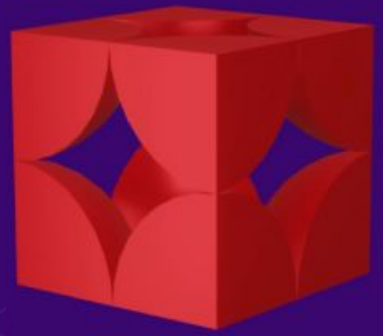
74% of the crystal space is filled in both fcc (ccp) and hcp crystals. Hence, both have a very efficient close packing.

Voids (Interstitial Voids)

The close-packed structures have the maximum packing efficiency, but there are some empty spaces left in the arrangement, which are known as voids.

For better understanding, an illustration for voids in a simple cubic unit cell is shown**. The** space of the unit cell filled by the constituent particles and the empty space inside the unit cell can be observed.

Voids are present in one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) arrangements of particles.



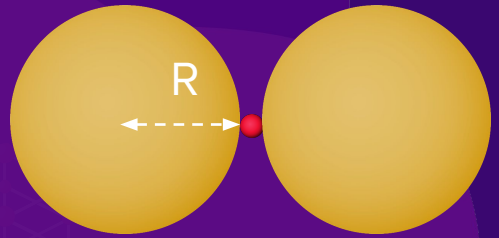
Filled space

Empty space

Voids (Interstitial Voids)

Voids in a one-dimensional arrangement

- Linear voids are observed in a one-dimensional packing.
- Linear voids are present in between two particles in a one-dimensional arrangement of particles.
- An illustration for a linear void is as shown. Consider the one-dimensional arrangement of two particles. The empty space (void) present between them is occupied by an unwanted particle/impurity (red particle).
- The coordination number of the linear void is two (this can also be interpreted that the coordination number of the particle in the void is two).

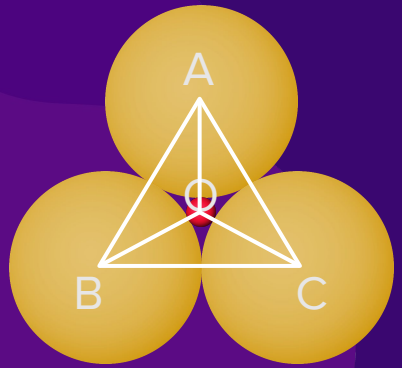


Coordination number = 2

Voids (Interstitial Voids)

Voids in a two-dimensional arrangement

- Triangular voids are present in a two-dimensional packing.
- It is found in a planar, close-packed structure (i.e., two-dimensional packing), where three spheres are in contact with each other.
- Consider a planar, close-packed structure as shown. The empty space (triangular void) present between them is occupied by an unwanted particle/impurity (red particle).
- The coordination number of the triangular void is three (this can also be interpreted that the coordination number of the particle in the void is three).

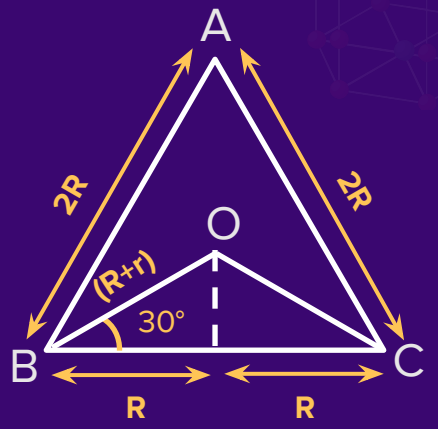


Coordination number = 3

Voids (Interstitial Voids)

Radius ratio (r/R) for a triangular void

The centre of masses of spheres (lattice points) are marked as A, B, and C. The centre of the triangular void is marked as O. The radius of the sphere (lattice point) is taken as ‘R’ and the radius of the void is taken as ‘r’ as shown. The radius of the triangular void (r) can be calculated in terms of the radius of the sphere/lattice point (R) as follows:



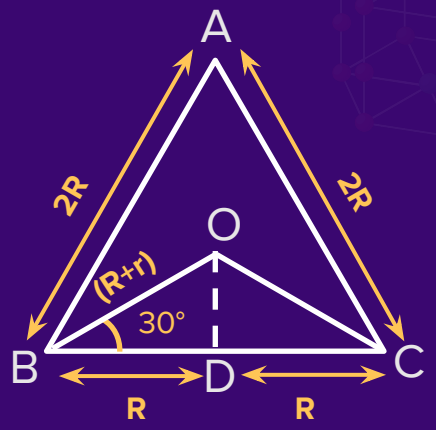
R → Radius of sphere (Lattice point)

r → Radius of void

Voids (Interstitial Voids)

From the geometry of the triangular void shown,

The triangle ABC is an equilateral triangle with the length of sides AB = BC = AC = 2R
OB and OC bisect the angles ABC and ACB, respectively. Also, OD bisects the side BC.
Hence,
Angle OBD = Angle OCD = 30°
And BD = CD = R
OB = OC = r + R



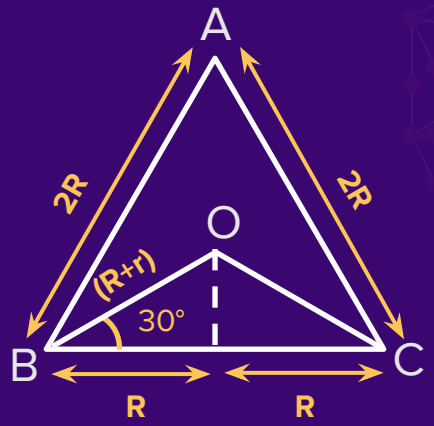
R → Radius of sphere (Lattice point)
r → Radius of void

Voids (Interstitial Voids)

$$\cos 30^\circ = \frac{R}{R + r}$$

$$\frac{R + r}{R} = \frac{1}{\cos 30^\circ}$$

$$\frac{r}{R} = 0.155$$



R → Radius of sphere (Lattice point)
r → Radius of void

i.e.,
Maximum radius of the triangular void = 0.155 × Radius of the sphere (Bigger atom or ion)

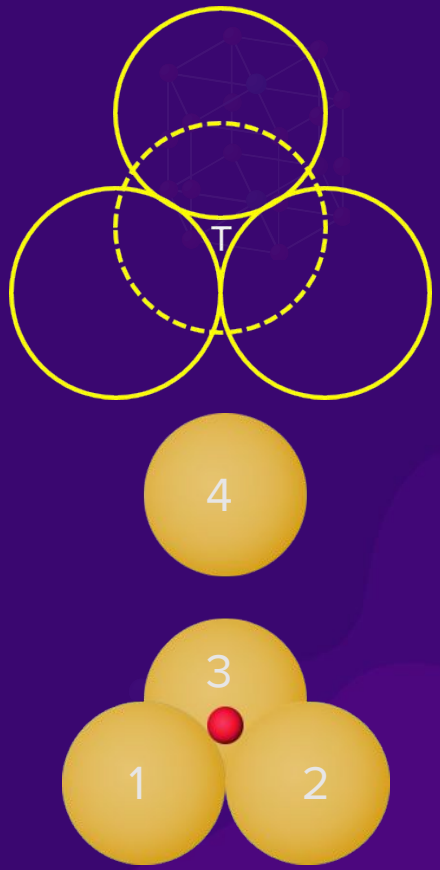
Voids (Interstitial Voids)

Voids in a three-dimensional arrangement

- Tetrahedral, octahedral, and cubical voids are present in a three-dimensional arrangement.

Tetrahedral voids

- When the sphere (lattice point) of the second layer is above the void of the first layer, it results in the formation of a tetrahedral void (T).
- The four spheres touch each other in a manner that a tetrahedron is formed when their centres are joined, and the space in the centre is known as a tetrahedral void.
- Sphere 4 is in contact with spheres 1, 2, and 3. Similarly, spheres 1, 2, and 3 are in contact with each other. The coordination number of a tetrahedral void is four (this can also be interpreted that the coordination number of the particle in the tetrahedral void is four).

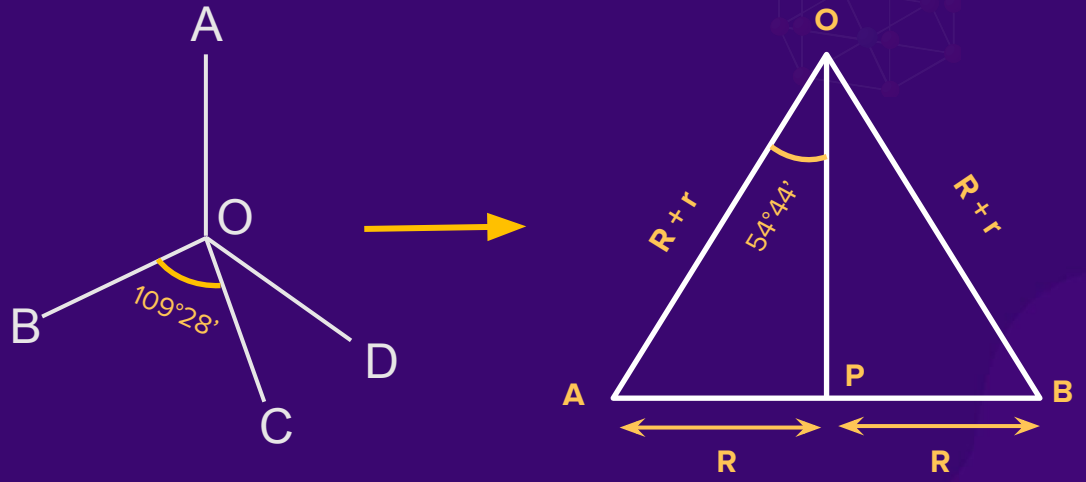


Voids (Interstitial Voids)

Radius ratio (r/R) of a tetrahedral void

Consider the radius of the sphere (lattice point) to be ‘R’ and the radius of the tetrahedral void to be ‘r’.

Consider the tetrahedron formed from the tetrahedral void as shown. On joining A and B, we get a triangle AOB as shown. Consider a perpendicular bisector (OP) from vertex O to the side AB. We know that the angle AOB is 109.48°. Since OP bisects the angle AOB,



Angle AOP = Angle BOP = 109.48°/2 = 54°44’
OA = OB = r + R
AP = PB = R and AB = 2R

Voids (Interstitial Voids)

$$\text{Sin } 54°44' = \frac{R}{r + R}$$

$$\frac{r}{R} = 0.225$$

Where,

R = Atomic radius

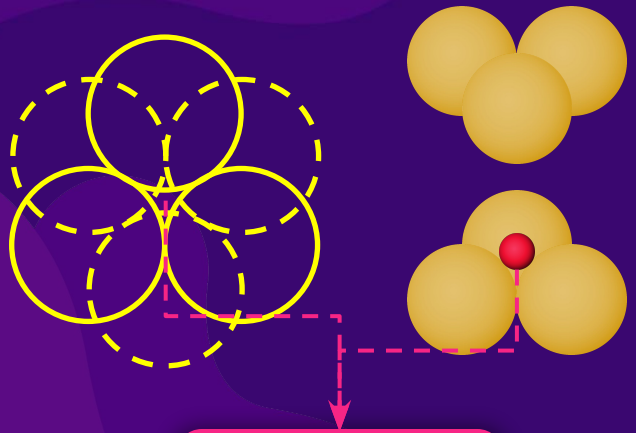
r = Radius of the tetrahedral void

Voids (Interstitial Voids)

Octahedral voids

- The triangular voids in the second layer are placed above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other has it pointing downwards.
- Such voids are surrounded by six spheres and are known as octahedral voids (O). An octahedral void is formed by six spheres, touching each other in the form of an octahedron. Hence, the coordination number of an octahedral void is six.
- In simple words, an octahedral void is formed when three ball arrangements are placed on top of each other.
- Octahedral voids are illustrated in next slide. The six spheres touch each other in a manner that an octahedron is formed when their centres are joined as shown.

Voids (Interstitial Voids)

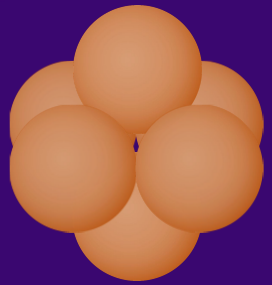


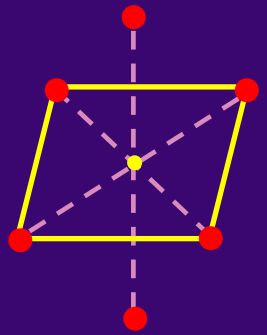
Octahedral void

Octahedron

- Octahedral voids can also be formed by placing two particles, one on the top and the other at the bottom of a square arrangement of spheres as shown in next slide. The coordination number of an octahedral void is six here as well.

Voids (Interstitial Voids)

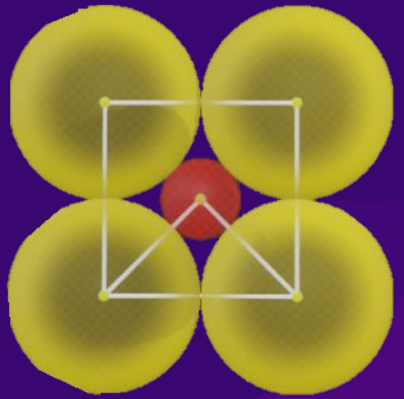




Octahedral void formed from the square arrangement of spheres

Radius ratio (r/R) of an octahedral void

For better understanding, an illustration for an octahedral void is shown. Consider the radius of the sphere (lattice point) to be ‘R’ and the radius of the octahedral void to be ‘r’.



Voids (Interstitial Voids)

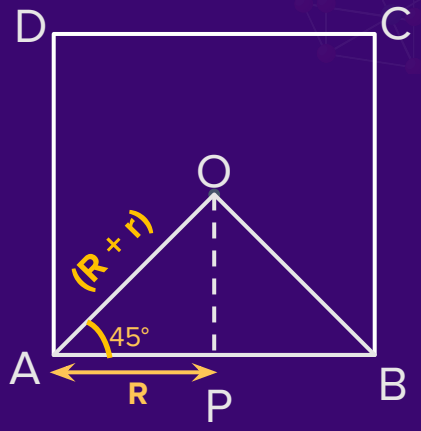
The geometrical representation of an octahedral void is given in **Fig.**

$$\cos 45^\circ = \frac{R}{R + r}$$

$$\frac{1}{\sqrt{2}} = \frac{R}{R + r}$$

$$\sqrt{2}R = R + r$$

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



R = Atomic radius

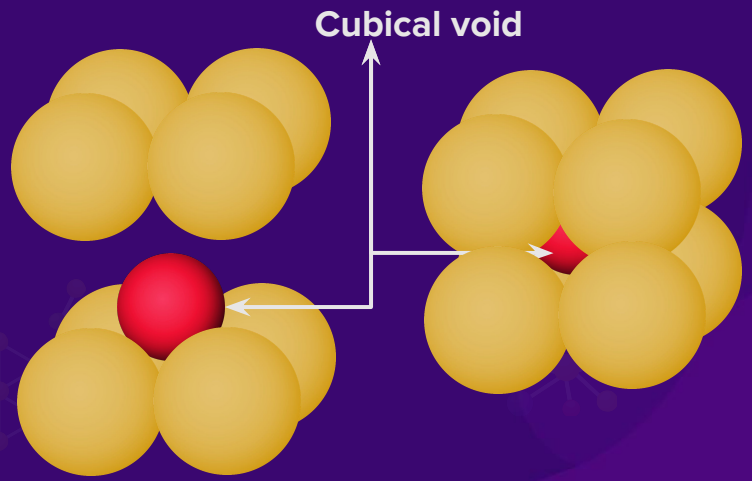
r = Radius of the octahedral void

Voids (Interstitial Voids)

Cubical void

- A cubical void is formed in a cubical arrangement of atoms.
- A cubical void is formed between eight closely spaced spheres, which occupies all the corners of the cube as shown. As these eight spheres touch each other, the coordination number of the cubical void is eight.

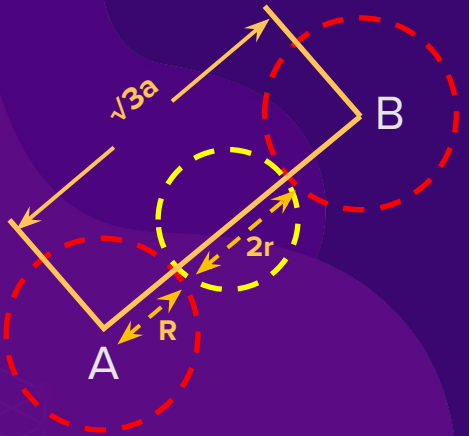
Coordination number = 8

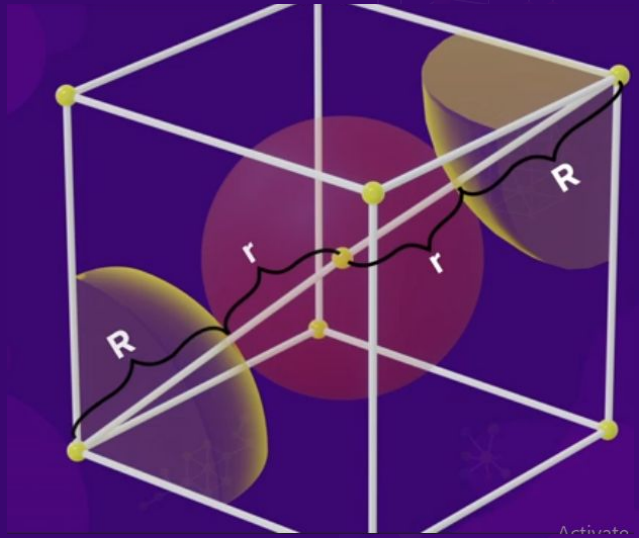


Voids (Interstitial Voids)

Radius ratio (r/R) of a cubical void

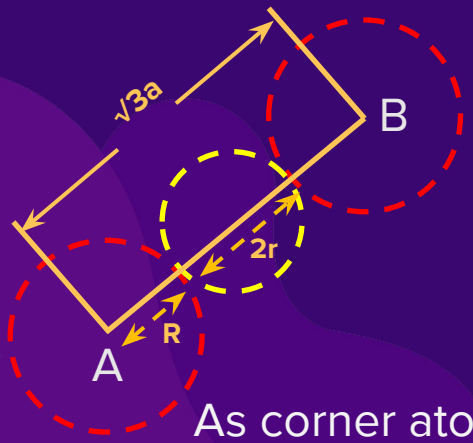
For better understanding, an illustration for a cubical void is shown. Here, we are considering the radius of the sphere (lattice point) as ‘R’ and the radius of the cubical void as ‘r’.





$$\text{Body diagonal} = \sqrt{3}\,a$$

Voids (Interstitial Voids)



As corner atoms are touching each other, a = 2R

$$\sqrt{3}a = 2[R + r]$$

$$2\sqrt{3}R = 2[R + r]$$

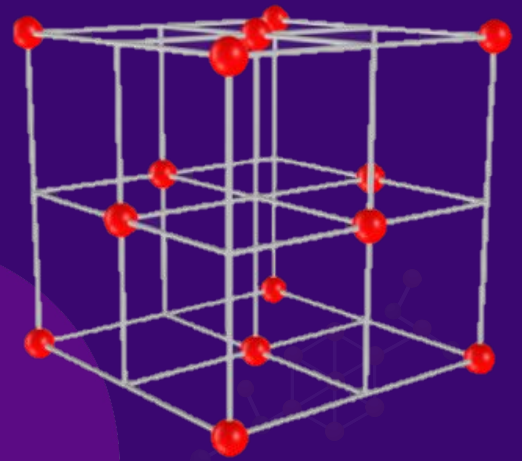
$$\frac{r}{R} = 0.732$$

Voids in FCC or CCP Structure

Tetrahedral and octahedral voids are present in fcc or ccp structure.

Tetrahedral voids in fcc or ccp structure

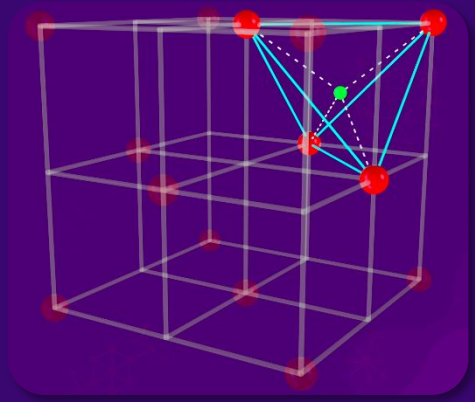
Consider a unit cell of fcc or ccp lattice as shown below. This unit cell is divided into eight small cubes.



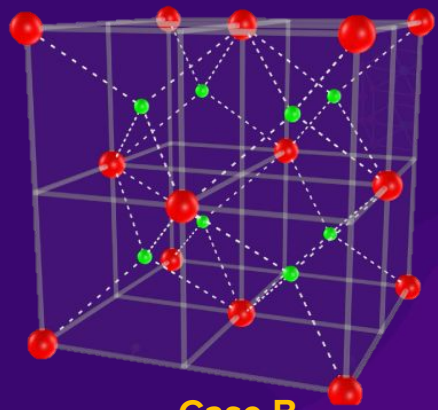
Voids in FCC or CCP Structure

Consider a single cube of the unit cell. The lattice points at the three face centres of a small cube are in contact with each other.

These three face centre lattice points are also in contact with an atom (lattice point) at the corner of the same cube. On joining the three face centre lattice points and the corner lattice points, it results in the formation of a tetrahedron as shown in **Case A**. Thus, there is one tetrahedral void in the centre of each small cube and a total of eight tetrahedral voids in the fcc/ccp unit cell as shown in **Case B**.



Case A

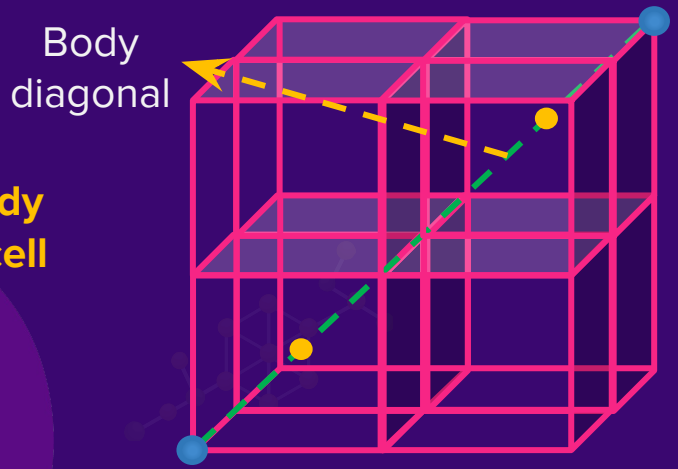


Case B

Voids in FCC or CCP Structure

Some important points for tetrahedral voids in fcc or ccp are given as follows:

- If a unit cell is divided into eight mini cubes, one tetrahedral void is present at the centre of each mini cube. Thus, a total of eight tetrahedral voids are present in the fcc/ccp unit cell.
- Each fcc/ccp unit cell has four body diagonals.
- Each body diagonal has two tetrahedral voids as shown below (the yellow-coloured sphere represents the tetrahedral void).



Tetrahedral voids in the body diagonal of fcc or ccp unit cell

Voids in FCC or CCP Structure

- Thus, an fcc or ccp unit cell has a total of eight tetrahedral voids.
- Each tetrahedral void is present entirely inside the unit cell. Each tetrahedral void contributes fully to the unit cell and is not shared with other unit cells.
- The distance between two tetrahedral voids and the distance of the tetrahedral void from the corner can be calculated as follows:

$$\sqrt{3}a = 4x$$

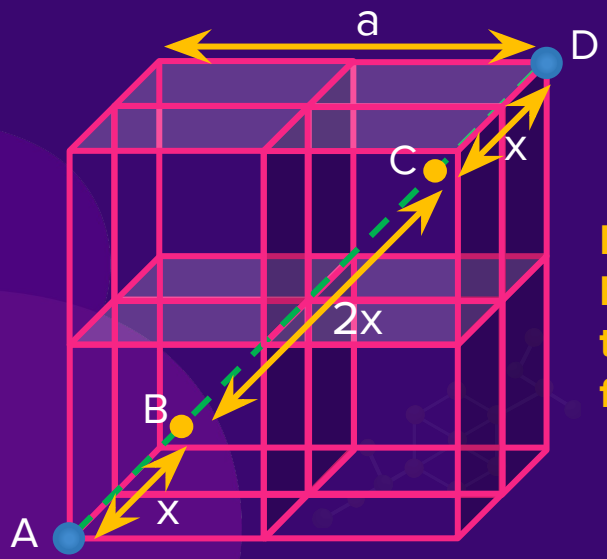


Illustration to determine the distance between two tetrahedral voids and the distance of the tetrahedral void from the corner

Voids in FCC or CCP Structure

In **Fig.**, the corner atoms are marked as A and D. The tetrahedral voids are marked as B and C. The distance between the corner atom and the tetrahedral void is assumed to be x. The distance between the two tetrahedral voids is assumed to be 2x.

Body diagonal AD = AB + BC + CD

$$\Rightarrow \sqrt{3}\,a = x + 2x + x = 4x$$

$$\text{Distance of tetrahedral void from the corner } (x) = \frac{\sqrt{3}\,a}{4}$$

$$\text{Distance between two tetrahedral voids } (2x) = \frac{\sqrt{3}\,a}{2}$$

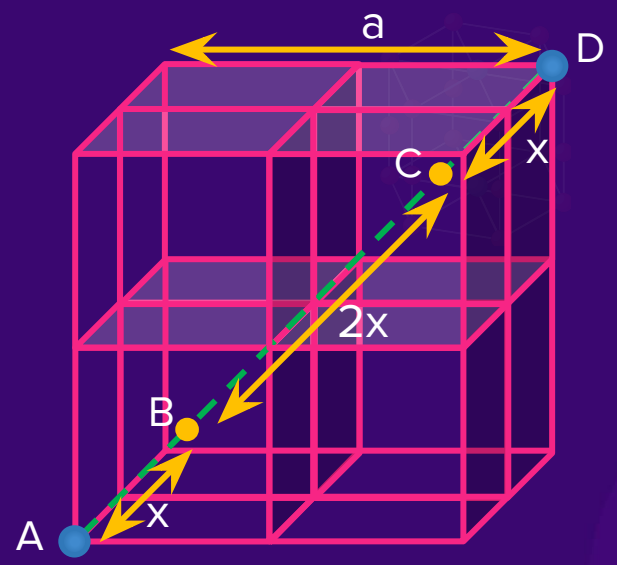


Illustration to determine the distance between two tetrahedral voids and the distance of the tetrahedral void from the corner