SIZES OF TETRAHEDRAL AND OCTAHEDRAL VOIDS

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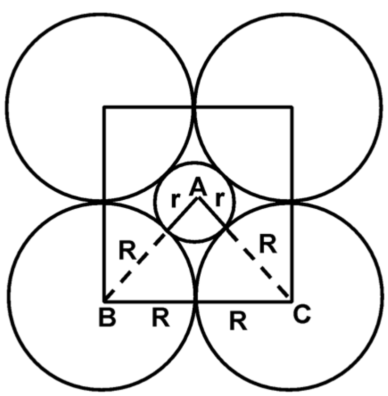
In close packing structures (hcp or ccp), there are two common types of voids: (i) octahedral voids (ii) tetrahedral voids. The radii of these voids in close packed structures are related to the sizes of the spheres present in the packing.

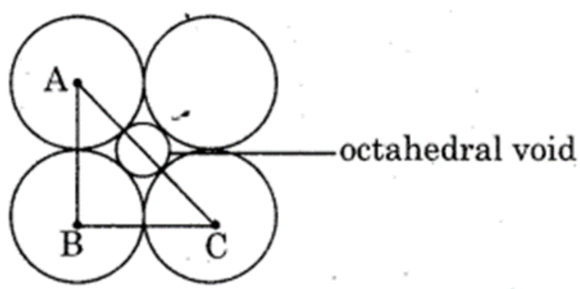
Let us calculate the radii of these voids in relation to the radii of the atoms in close packing.

Relationship between radius of octahedral void and radius of atoms in the close packing:

An octahedral void is shown in figure, though an octahedral void is surrounded by six spheres, only four are shown. The spheres present above and below the void are not shown

Let us assume that the length of the unit cell is 'a' cm and radius of octahedral void (shown by small sphere) is r and the radius of sphere is R.





If the length of the unit cell is a, then
in ⊥Δ ABC, AB =BC= a

The diagonal AC =$\sqrt{AB^2 + BC^2}$ =$\sqrt{a^2}$ +$\sqrt{a^2}$
AC = $\sqrt{2}$ a

also $\frac{AC}{AB} = \frac{\sqrt{2}a}{a}$ = $\sqrt{2}$

AB = 2R

AC = R +2r+R = 2R +2r

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

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

$\frac{r}{R} = \sqrt{2} - 1 = 0.414$

r= 0.414R thus, for an atom to occupy an octahedral void, its radius must be 0.414 times the radius of the sphere.

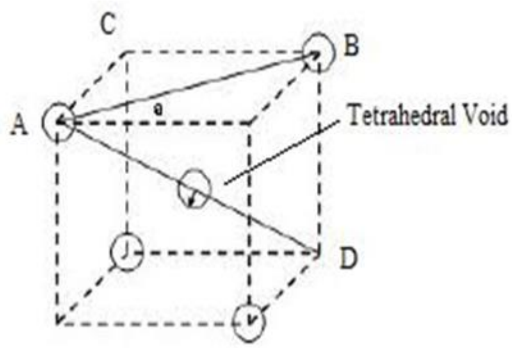
Relationship between radius of the tetrahedral void and radius of atoms in close packing:

A tetrahedral void may be represented by placing spheres at the alternate corner of a cube as shown in figure. It may be noted that a stable tetrahedral arrangement has four spheres at the corner touching each other. However, for simplicity, the spheres are shown by distant circles. All the spheres are touching one another. Let us assume that the length of each side of the cube is ‘a’ cm and the radius of tetrahedral void (shown by a sphere) is r and radius of the sphere is R.

In figure AC face diagonal in ΔABC

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

AB $= \sqrt{AC^2} + \sqrt{BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$



As spheres A and B at the face diagonal (though shown by distant circles) are actually touching each other so that

AC = R+R = 2R = √2a or R = $\frac{\sqrt{2}a}{2}$ ---------- (i)

Now in the ⊥Δ ABD, AD is body diagonal and $AD^2 = AB^2 + CD^2$

AD=$\sqrt{AB^2+CD^2}$ = $\sqrt{2a^2+a^2}$ = √3a

The tetrahedral void is present at the center of the body diagonal AD so that half the length of this diagonal is equal to the sum of the radii of R and r.

Thus, R+ r = $\frac{AD}{2} = \frac{\sqrt{3}a}{2}$ ------------- (ii)

dividing eq. (ii) by eq. (i), we get

$\frac{R+r}{R} = \frac{\sqrt{3}a}{2} \times \frac{2}{\sqrt{2}a} = \frac{\sqrt{3}}{\sqrt{2}}$

$1+\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$

r/R = (√3)/√2 - 1 = (√3− √2)/ (√2) = (1.732 −1.414)/(1.414) = 0.225

r = 0.225 R

Thus, for an atom to occupy a tetrahedral void, its radius must be 0.225 times the radius of the sphere. We observe that a tetrahedral void is much smaller than the octahedral void.

Stability of ionic solids and radius ratio of cations and anions:

In case of ionic solids, usually anions are present in the closed packed arrangement and cations occupy voids. Therefore, the relation between the size of the void and the sphere in the closed packed arrangement is expressed in terms of radius of cation to that of anion. The ratio of the radius of the cation to the radius of the anion is called radius ratio. Thus,

radius ratio = $\frac{radius\ of\ the\ cation}{radius\ of\ the\ anion} = \frac{r+}{r-}$

For cations occupying the tetrahedral voids, r+ = 0.225r- or $\frac{r+}{r-}$ = 0.225

For cations occupying the octahedral voids, r+ = 0.414 r- or $\frac{r+}{r-}$ = 0.414

The ratio of the radius of cation and the radius of anion i.e., radius ratio plays an important role in determining the structures of ionic solids and coordination number of ions. As it is clear, for the cations to occupy tetrahedral void the limiting lowest value of $(r+)/(r-)$ is 0.225 and to occupy octahedral void, it is 0.414. In other words, for tetrahedral coordination. the radius ratio should be in the range of 0.225 - 0.414. Similarly, it has been calculated that for stable arrangement of cations occupying octahedral voids (coordination number 6), the radius ratio should be more than 0.414 (in the range of 0.414- 0.732). If the radius ratio ($(r+)/(r-)$) is more than 0.732 (in the range 0.732-1.0), the cations occupy cubic void (coordination number 8). Similarly. below 0.225, the cations occupy simple trigonal voids. The possible coordination numbers and structure arrangement of anions around cations for different radius ratio values are given below:

Radius Ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular Planar	B_2O_3
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, NH_4Br
1	12	Close packing (ccp and hcp)	metals

Relationship between Radius Ratio and Coordination Number

Examples

Example 1: The radius of Na+ ion is 95 pm and that of Cl- ion is 181 pm. Predict whether the coordination number of sodium ion is 6 or 4.

Solution: Radius of Na+ = 95 pm, Radius of Cl- = 181 pm

Radius ratio, $(r+)/(r-)$= $(r(Na+))/(r(Cl-))$ =95/181 = 0.524

The radius ratio lies between 0.414- 0.732. hence, Na+ ions prefer to occupy octahedral holes having coordination number 6

Example 2: Bromide ions (Br-) form a close packed structure. If the radius of the Br- is 195pm, calculate the radius of the cation that just fits into the tetrahedral holes. Can a cation having a radius of 82 pm be slipped into the octahedral hole of the crystal A+Br-?

Solution: Radius of the cation just fitting into the tetrahedral hole
= radius of tetrahedral hole = 0.225 x r(Br-) = 0.225 x 195 = 43.875 pm

For the cation A+ with radius, 82 pm

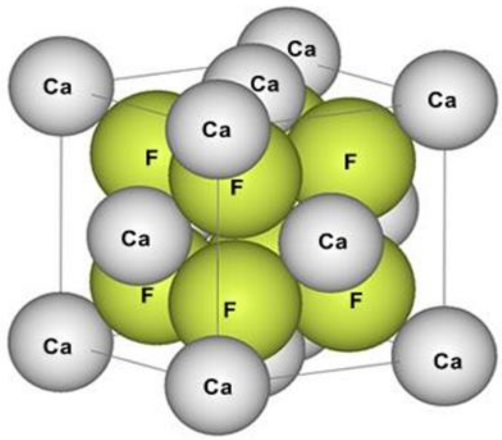
Radius ratio = $(r+)/(r-)$ = 82pm/ (195 pm) = 0.4105

Since the radius ratio lies in the range 0.414-0.732, hence the cation A+ can be slipped into octahedral hole of the crystal A+Br-.

Formula of a compound and number of voids filled:

- The Structures of metals can be easily described because all the lattice points are occupied by metal atoms. For example, copper has face centered cubic arrangement in which all the lattice points are occupied by copper atoms. However, if we describe the structures of simple ionic compounds, we will have to describe the relative arrangement of ions. In the case of simple ionic compounds, generally two types of arrangements are possible. These are ccp or fcc arrangement and hexagonal close packed arrangement. The larger ions (i.e., anions) adopt these arrangements. The other kinds of ions (cation) occupy different voids. There are two types of voids tetrahedral and octahedral, which are generally occupied. From the description of the close packed structures and types of voids occupied, we can easily draw inferences regarding the structures of simple ionic compounds. For example, consider a compound of general formula AB in which the B ions form a close packed lattice. There are two possibilities:
  - (i) Since there is only one octahedral void per atom in a closed packed lattice, all the octahedral voids will be occupied by A+ ions. In this case, the number of A+ ions and B- ions with be same. Sodium chloride has this type of structure in Cl- ions form a cubic close packed structure and Na+ ions occupy all the octahedral voids.
  - **(ii)** There are two tetrahedral voids per atom in close packed lattice. This means that there are two tetrahedral voids available for every B- ion. To form the compound AB, only one half of the tetrahedral voids will be occupied. Zinc blende (ZnS) has this type of structure, in which S^{-2} ions form cubic close packed structure zinc and Zn^{-2} ions occupy one-half of the tetrahedral voids.

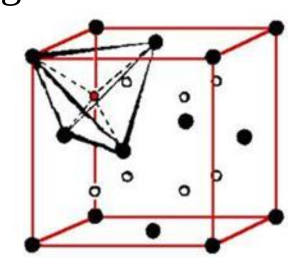
- If, on other hand, the formula of the compound is A_2B in which B- ions adopt cubic close packed lattice, then all the tetrahedral voids will be occupied by A^+ ions. Since there are two tetrahedral voids per atom, and all the voids are occupied, there will be two A+ ions for each B- ion. Sodium oxide adopts this type of structure. This structure is also known as antifluoride structure. Alternatively, if A^+ ions (though smaller in size than B^- ions) adopt cubic close packed structure and B^- ions occupy all the tetrahedral voids, then the formula of the compound is AB_2 . Calcium fluoride has similar type of structure. The structure is known as fluorite structure.



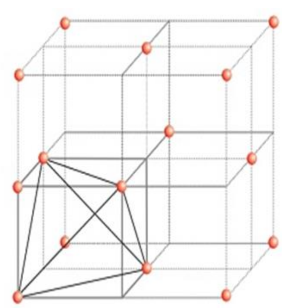
Locating tetrahedral and octahedral voids:

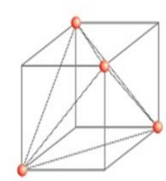
Close packed structures have both tetrahedral and octahedral voids. Let us visualize these voids in ccp or fcc structures.

Locating tetrahedral voids: let us consider a unit cell of ccp or fcc lattice. It has atoms at all the corners of the cube and at the centre of each face as shown in figure

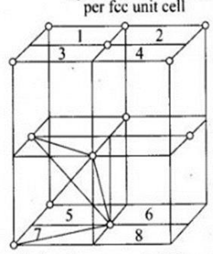


Tetrahedral Site

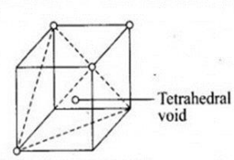




Eight tetrahedral voids per fcc unit cell

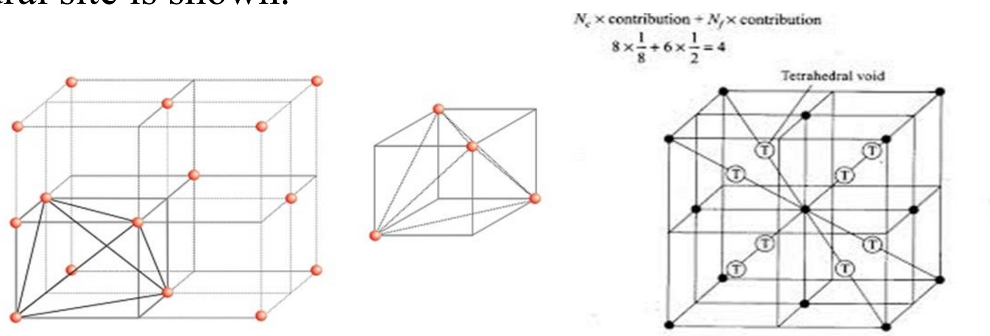


Each cube represented by numeric 1, 2, 3, 4, 5, 6, 7, 8 contains one tetrahedral void.

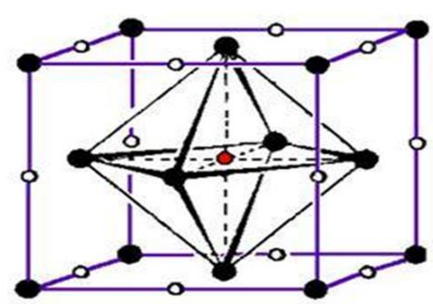


Each cube contains one tetrahedral void at its body centre as shown above

If we see carefully, we observed that the unit cell has eight small cubes. Each small cube has atoms at alternate corners. Therefore, each small cube has four atoms. When joined to each other they make a regular tetrahedron. The centre of the small cube become tetrahedral void. Thus, there is one tetrahedral void in each small cube. Since there are 8 small cubes and therefore there are 8 tetrahedral voids in ccp unit cell. We know that ccp structure has four atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms. In figure only one tetrahedral site is shown.

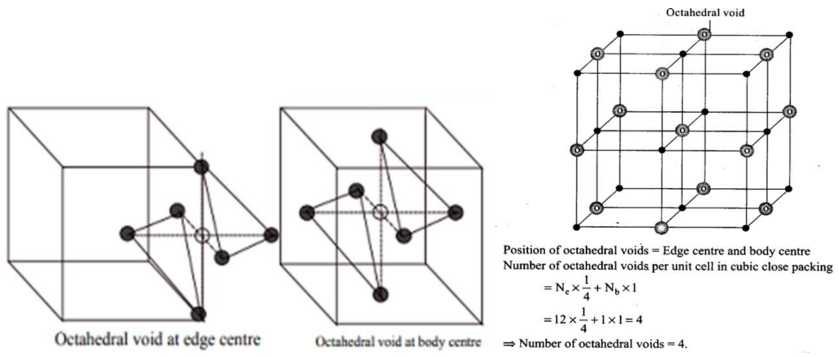


Locating octahedral voids: Let us consider the unit cell of ccp or fcc lattice. It has atoms at all the corners and at the centre of each face as shown in figure. If we carefully see, we observe that the body centre of the cube, O, is not occupied but it is surrounded by 6 atoms on centre of six faces. If these face centres are joined, they make an octahedron. Thus, the centre of this octahedron i.e., point O becomes octahedral void.



Octahedral Site

In addition to body centre, there is an octahedral void at the centre of each edge as shown in figure. It is also surrounded by 6 atoms as shown in figure. Thus in a ccp unit cell, there are 12 octahedral voids located on edges and one at the body centre of the cube. Now, each edge of the cube is shared between four adjacent unit cells, so is the octahedral void located on it. This means that 1/4th of each void belongs to a particular unit cell.



Thus, in ccp structure, the number of octahedral voids is:
Octahedral void at body centre of the cube =1
Octahedral void at the edges = 12 x1 /4 = 3
Total number of octahedral voids= 1 + 3 = 4
We know that in ccp structure, each unit cell has four atoms. Therefore, the number of octahedral voids is same as the number of atoms.

Examples

Example 1: A compound is formed by two elements M and N. The element N forms ccp and atoms of the element M occupy 1/3 of the tetrahedral voids. What is the formula of the compound?
***Solution*:** Let us suppose that,
The no. of atoms of N present in ccp = x
Since 1/3rd of the tetrahedral voids are occupied by the atoms of M, therefore,
The no. of tetrahedral voids occupied = 2x1/3
The ratio of atoms of N and M in the compound = x : 2x/3 or 3 : 2
∴ The formula of the compound = N_3M_2 or M_2N_3

Example 2: Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centered cubic and (iii) hexagonal close-packed lattice?
Solution: Packing efficiency of:
Simple cubic = 52.4% , bcc = 68% , hcp = 74%
hcp lattice has the highest packing efficiency.

Example 3: A compound forms hexagonal close-packed. structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Solution:

No. of atoms in 0.5 mol $= 0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

No. of octahedral voids = No. of atoms in packing $= 3.011 \times 10^{23}$

No. of tetrahedral voids = 2 x No. of atoms in packing

$$= 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$$

So, total no. of voids $= 3.011 \times 10^{23} + 6.022 \times 10^{23}$

$$= 9.033 \times 10^{23}$$

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