Close Packing of Spheres

It has been observed that the structures of most of the crystals studied in inorganic chemistry is obtained by the most efficient packing of the units of which these crystals are composed. These units may be either atoms, ions or molecules which are of approximately spherical shape, having equal size. It is, therefore, essential to study the ways in which these units are packed together in three dimensions.

Place some solid spheres of equal size in one row on the table. Place another row of the spheres in such a manner that the spheres of the second row rest between the depressions of every two spheres of the first now. In this way place some rows of the spheres as shown in Fig. 9.14(a) in which three rows of spheres have been shown. The spheres of this layer have been represented by full line circles.

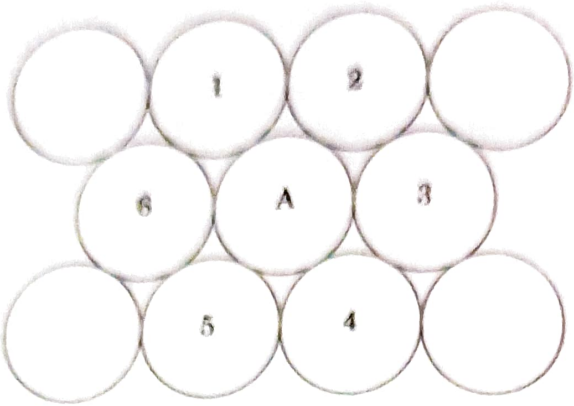
The following points may be noted from Fig. 9.14(a).

(i) Every sphere is surrounded by six other similar spheres. For example the sphere marked with A is surrounded by six other similar spheres marked as 1, 2, 3, 4, 5 and 6. Thus we see that every sphere has 6 nearest neighbours. The number of nearest neighbours is called the **coordination number (C. N.).** Thus the C. N. of each of the spheres arranged in this manner is six. It has been shown by calculation that in this arrangement only 60.4% of the space is occupied by the spheres while the remaining 39.6% of the space remains unoccupied (vacant). This vacant space is called **void volume.**

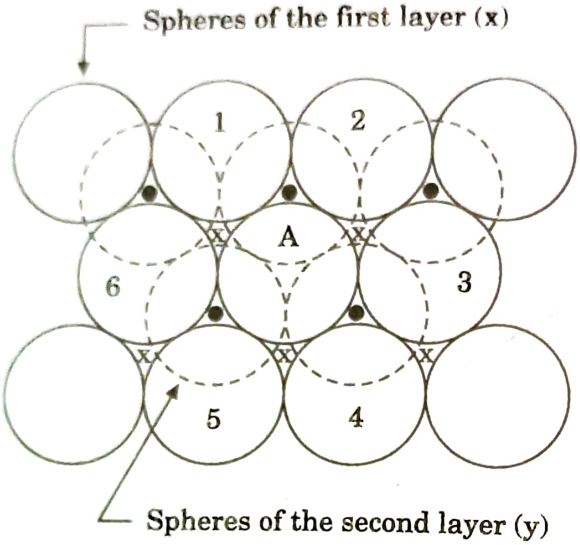
(ii) There is an opening between each set of three touching spheres. These openings have been represented as • and ×.

Now place a second layer of spheres (shown by dotted line spheres) on the spheres of the first layer so that the openings shown as • are covered by them while those shown as × remain uncovered [Fig. 9.14 (b)].

Now suppose we have to build up a third layer of spheres over the second layer. It can be done in any of the following two ways :



(*a*)



(*b*)

Fig. 9.14. Close packing of spheres. (*a*) Close packing of spheres in one layer. (*b*) Close packing of spheres in two layers.

First way. In this way, the spheres of 3*rd* layer (not shown in the Figure) are placed so that the centres of the spheres of the 3rd layer are directly above the centres of the spheres of the first layer. Thus in this arrangement the spheres of the first layer and those of the third layer are exactly identical. This arrangement of close-packing of spheres is referred to as X Y X arrangement of spheres where X, Y and X represent the 1*st*, 2*nd* and 3*rd* layers of spheres. Quite obviously 1*st* and 3*rd* layers are identical.

When X Y X Y X Y ... arrangement of packing of spheres is continued indefinitely, the system obtained is found to possess *hexagonal symmetry* (This system should not be confused with the hexagonal pattern of spheres), *i.e.* this system possesses *one 6-fold axis of symmetry* which is perpendicular to the planes of the close- packed spheres. Such as arrangement of three dimensional packing of spheres is shown in Fig. 9.15. Because of its hexagonal symmetry this arrangement is called **hexagonal close-packing** of spheres and is abbreviated as **hcp.**

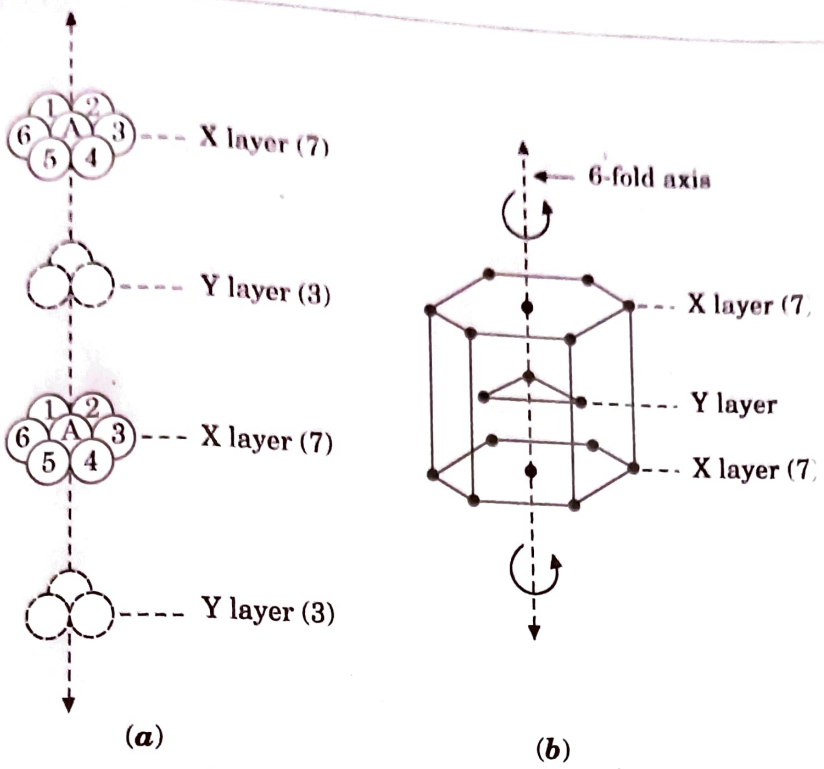


Fig. 9.15. Hexagonal close-packing of spheres
(*a*) Exploded view (*b*) Composite view.

In the hexagonal close-packing of spheres the spheres in the two X-layers occupy the sites of the unit cell of the hexagonal lattice while the three spheres of Y-layer are situated within the unit cell and do not occupy the lattice sites. It can be seen from the figure that when the hexagonal structure is rotated about the axis perpendicular to the layers and passing through one sphere, it presents identical view thrice in one rotation.

Second way. In this way the spheres of the third layer are placed on the spheres of the 2*nd* layer so that the openings marked as × in the first layer are covered. Note that these openings were left uncovered in arranging the second layer of spheres. It may also be noted that in this arrangement the spheres of the third layer do not come over those of the first layer. This arrangement of close- packing of spheres is referred to as X Y Z arrangement of spheres where X, Y and Z represent the three layers. When X Y Z X Y Z...arrangement of packing of spheres is continued indefinitely, the system obtained is found to possess *cubic symmetry*, *i.e.* this system has *four 3-fold axes of symmetry* which pass through the diagonals of the cube. Such an arrangement of three dimensional packing of spheres is shown in Fig. 9.16. Because of its cubic symmetry this arrangement is called *cubic close-packing* of spheres and is abbreviated as **ccp.** The unit cell of this structure is a cube which contains 14 spheres. An examination of the arrangement of 14 spheres in the unit cell of ccp structure reveals that this structure has one sphere at the centre of each of the six faces of the unit cell. It is for this reason that ccp structure is also sometimes called **face-centred cubic (fcc) structure.**

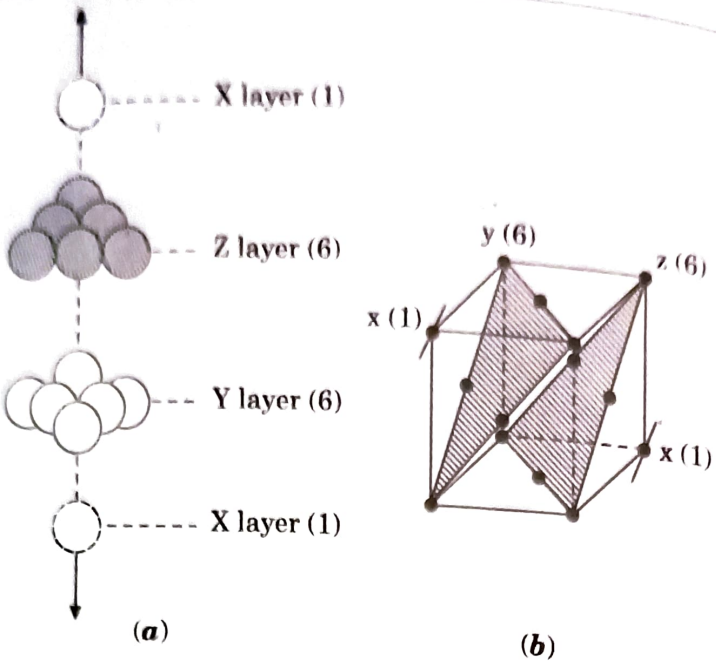


Fig. 9.16. Cubic close-packing (or face-centred cubic packing) of spheres. (*a*) Exploded view (*b*) Composite view.

Although the two closest packing of spheres (*hcp* and *ccp*) described above differ in the mode of arranging the spheres, yet they have the following common characteristics :

(*i*) In both the packings of spheres, each sphere is surrounded by 12 other equidistant spheres, *i.e.* coordination number of each sphere in both the packings of spheres is 12. This fact has been illustrated in Fig. 9.17 (*a*) and (*b*).

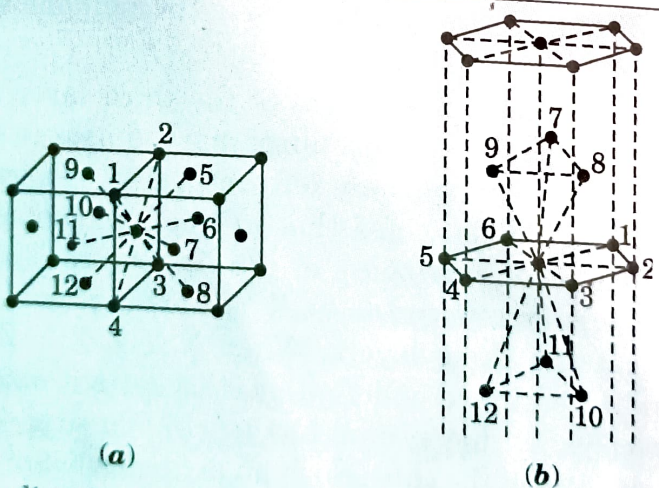


Fig. 9.17. Coordination number of each sphere in (*a*) cubic close-packing and (*b*) hexagonal close-packing of spheres is 12.

(*ii*) In cubic close-packing of spheres [Fig. 9.17 (*a*)] the sphere lying at the centre of the middle face has four nearest neighbours marked as 1, 2, 3 and 4 lying at the corners of that face and eight more marked as 5, 6, 7, 8, 9, 10, 11 and 12 at the same distance at the centres of four faces of adjoining cubes.

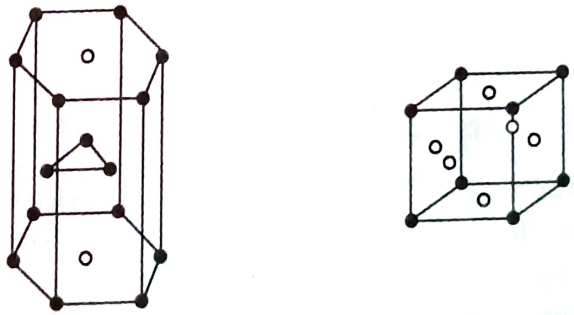
(iii) In hexagonal close-packing of spheres [Fig. 9.17 (*b*)] the sphere lying at the centre of the hexagon has six nearest neighbours marked as 1, 2, 3, 4, 5 and 6 lying at the corners of the hexagon and six more marked as 7, 8, 9, 10, 11 and 12 at the same distance at the corners of the two adjascent triangular planes, one above and the other below the hexagonal plane. All the three planes are parallel to each other.

Structure of Metallic Crystals

Most of the metals belonging to *s*- and *d*-block elements of the long form of periodic table have any of the following structures.

1. Hexagonal close-packed (hcp) structure. In this structure the atoms are located at the corners and centres of two hexagons which are placed parallel to each other and three more atoms are placed in a parallel triangular plane lying mid way in between the two hexagonal planes [Fig. 9.18 (*a*)]. This structure is obtained by A B A B A... type of close-packing of atoms. Each atom in this structure has 12 nearest neighbours, *i.e.* the coordination number of each of the atoms in *hcp* structure is 12. Examples of metals having *hcp* structure are Cr, Mo, V, Mg, Zn etc.

2. Cubic close-packed (ccp) or face-centred cubic (fcc) structure. In this structure the atoms are located at the corners and at the centres of all the six faces of a cube (Fig. 9.18 (*b*)). This structure is obtained by ABC ABC type of close-packing of atoms. Each atom in this structure has 12 nearest neighbours, *i.e.* coordination number of each atom in this structure is 12 as already discussed. Examples of metals having *ccp* or *fcc* structure are Cu, Ag, Au, Ni, Pt etc.



(*a*) (*b*)

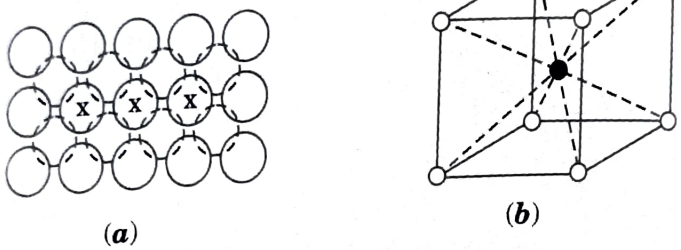
Fig. 9.18 (*a*) Hexagonal close-packed (hcp) structure (*b*) Cubic close-packed (ccp) or face-centred cubic (fcc) structure. The white circles indicate the atoms placed at the centre of the face of the cube or hexagon while the black circles indicate the atoms lying at the corners of hexagon or cube.

3. Body-centred cubic (bcc) structure. In this structure the atoms are not closely packed as in the above two structures. This structure is obtained by the following two steps :

(*i*) Place some spheres (represented by full line circles) side by side so that *they are slightly opened up*. By doing so none of the spheres touches each other [See Fig. 9.19 (*a*)].

(*ii*) Place the second layer of spheres (represented by clotted line) on the openings between the spheres of the first layer so that each sphere of the 2nd layer is in contact with four spheres of the first layer.

(*iii*) Now place a third layer of spheres so that the openings in the second layer (marked as ×) are covered by them. Thus we see that third layer is exactly identical to first layer. This type of arrangement of spheres gives *body-centred cubic* (*bcc*) *structure* in which each of the spheres (or atoms) is attached with eight nearest spheres (four spheres in the layer just above and four spheres in the layer just below) and so the *coordination number in body-centred cubic structure is only eight*. It is for this reason that the atoms in this structure are *not closely packed*, and only 68% of the total volume is actually occupied by the atoms. However, the atoms are in *close contact along body diagonals*. The unit cell of this structure has one atom at each corner and one atom at the centre of the cube [Fig. 9.19 (*b*)]. Alkali metals have body centred cubic structure.



(*a*) (*b*)

Fig. 9.19. Body-centred cubic structure (*a*) Arrangement of spheres in three layers to get body-centred cubic structure (*b*) Unit cell of body-centred cubic structure.

Malleability and Ductility of Metals

Malleability and ductility of metals are related with the deformation in the crystals of the metals. Deformation in crystals means that one layer of atoms slides over the other layer. Now since the cubic close-packed structure contains *four* sets of parallel close-packed layers of atoms, the chances of slipping of one layer of atoms over the other layer are more in case of the metals having cubic close-packed structure (*e.g.* Cu, Ag, Au, Ni, Pt etc.) On the other hand, since the hexagonal close-packed structure contains only *one* set of parallel close-packed layer of atoms, the chances of slipping of one layer of atoms over the other layer are very little in case of metals having hexagonal structure (*e.g.* Cr, Mo, V, Mg, Zn etc.). From the above discussion it can be concluded that the metals like Cu, Ag, Au, Ni, Pt etc which have cubic close-packed structure are more malleable (*i.e.* can be beaten into sheets) and ductila (*i.e.* can be drawn into wires) than the metals like Cr, Mo, V, Mg, Zn etc which have hexagonal close-packed structure.

Since Fe can adopt both these structures depending on temperature, this metal shows a wide variety of properties.

Characteristics of hcp, ccp and bcc Structures

The characteristics of *hcp*, *ccp* and *bcc* structures mentioned above have been summarised in Table 9.4.

Table 9.4. Characteristics of hexagonal close-packed (hcp), cubic close-packed (ccp) and body centred-cubic (bcc) structures.

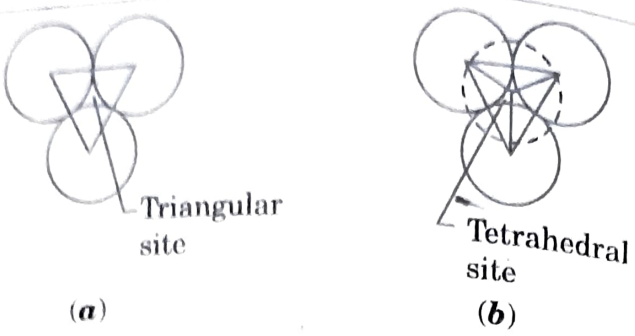
Characteristics	Structure		
	Hexagonal close-packed (hcp)	Cubic close packed (ccp)	Body centred cubic (bcc)
1. Nature of packing of atoms	Close-packed	Close-packed	Not close-packed
2. Volume occupied by atoms	74% of the total volume	74% of the total volume	68% of the total volume
3. Type of packing of atoms	ABABABA.....	ABCABC.....	...
4. Coordination number	12	12	8
5. Malleability and ductility	Less malleable and ductile	More malleable and ductile	Malleable and ductile
6. Examples of metals	Cr, Mo, V, Mg, Zn etc.	Cu, Ag, Au, Ni, Pt etc.	Alkali metals.

Interstitial Sites in Closely-packed Arrangement of Atoms

The interstitial sites formed in between the closely-packed atoms of a given crystal are of the following types :

1. Triangular or trigonal site. When the spheres are placed at the vertices of an equilateral triangle, a triangular arrangement of close-packed spheres is obtained and some empty space (hole or void) is left between the three touching spheres. This empty space is called *triangular or trigonal site*. The corners of the triangle are occupied by the spheres [Fig. 9.20 (*a*)]. It has been shown by calculations that the radius of the sphere which can fit into the trigonal site without disturbing the close-packed arrangement of the surrounding large spheres should not be greater than 0.155 times that of the surrounding large close-packed spheres.

2. Tetrahedral site. When a sphere is placed on the three spheres placed at the vertices of an equilateral triangle and touching each other, a tetrahedral arrangement of close-packed spheres is obtained. In this arragement the centres of the four spheres lie at the apices of a regular tetrahedron [Fig. 9.20 (*b*)]. The empty space left at the centre of this tetrahedron is called *tetrahedral site*. It may be mentioned here that it is not the shape of the void which is tetrahedral but it is the arrangement of the spheres which is tetrahedral. In a close-packed arrangement of spheres, each sphere is in contact with three spheres in the layer above it and other spheres in the layer below it. Thus there are two tetrahedral sites associated with each sphere. The size of the tetrahedral site is much smaller than the size of the sphere. With the increase of the size of the spheres, the size of the tetrahedral site also increases. Calculations have shown that a tetrahedral site can accomodate a sphere whose radius should not be greater than 0.225 times that of the spheres forming the tetrahedral site.



(*a*) (*b*)

Fig. 9.20. Formation of (*a*) triangular or trigonal site by close-packed arrangement of three spheres (*b*) tetrahedral site by close-packed of arrangement four spheres.

3. Octahedral site. This interstitial site is formed by joining six spheres whose centres lie at the apices of a regular octahedron as shown in Fig. 9.21. This site is found in both *hcp* and *ccp* systems. Fig. 9.21 shows that an octahedral site is generated by two equilateral triangles whose apices point in opposite directions. One of these triangles joins the centres of three spheres in one plane while the other triangle (shown by dotted lines) joins the centres of the three spheres (shown by dotted lines) in the second plane. The octahedral site marked as × is formed where two triangles of spheres belonging to different layers are super-imposed on each other. It may also be noted that there is only one octahedral site for each sphere. Thus the number of octahedral sites is half the number of tetrahedral sites. The sizes of different sites studied so far are related as :

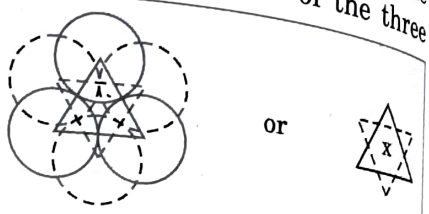


Fig. 9.21. Formation of octahedral site by close-packing of six spheres.

octahedral site > tetrahedral site < trigonal site.

Calculations have shown that an octahedral site can accomodate a sphere whose radius should not be greater than 0.414 times that of the spheres forming octahedral site.

Radius Ratio Rule and its Effect on the Shape of Ionic Crystals.

The ratio of the radii of the positive and negative ions is called the radius ratio. Thus :

$$\textbf{\textit{Radius ratio}} = \frac{\textbf{\textit{Radius of positive ion (cation)}}}{\textbf{\textit{Radius of negative ion (anion)}}}$$

The effect of radius ratio in determining the coordination number and the shape of the ionic crystals is known as *radius ratio effect*. The radius ratio can be used in determining the most stable form of arrangement of ions in the crystal lattice of an ionic solid.

In order to understand the application of radius ratio concept, let us suppose that the coordination number of a cation C^+, in an ionic crystal, C^+A^- is 3. Thus three A^- anions are in contact with one C^+ ion [Fig. 9.22 (*a*)].

In the structure shown in Fig. 9.22(*a*), since the cation (C^+) is in close contact with the anions (A^-), the force of attraction between C^+ and A^- ions is quite strong. At the same time, since the anions are not at all in contact with each other, the force of repulsion between them is quite small. Thus this structure is quite stable.

In the structure shown in Fig. 9.22(*b*), since the cation is touching the anions, the force of attraction between C^+ and A^- ions is quite strong. At the same time, since the anions are also touching one another, the force of repulsion between them is also quite strong. Thus this structure is a limiting case of stable structure of C^+A^- ionic crystal. It can be shown by simple calculation that in this structure the radius ratio, $r(C^+)/r(A^-) = 0.155$. If the value of radius ratio, $r(C^+)/r(A^-)$ falls below this value (*i.e.* if C^+ cation becomes still smaller in size), the structure of C^+A^- ionic crystal will become unstable and will be as shown in Fig. 9.22 (*c*). In the structure shown at (*c*), since the cation is not touching the anions, the force of attraction between C^+ and A^- is weak. At the same time, since the anions are still touching each other, the force of repulsion between them is strong. Thus this structure is unstable and cannot exist. The above discussion makes it evident that for coordination number of 3, the limiting radius ratio value $r(C^+)/r(A^-) = 0.155$.

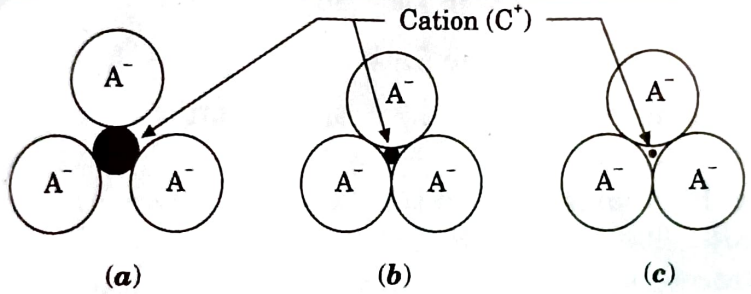


Fig. 9.22. Stability of C^+A^- ionic crystal in which the cation C^+ has coordination number equal to 3. (*a*) stable structure of C^+A^- ionic crystal. (*b*) Limiting case of stable structure of C^+A^- ionic crystal with $r(C^+)/r(A^-) = 0.155$. (*c*) Unstable structure of C^+A^- ionic crystal.

By applying simple geometry in the same way, the limiting radius ratio values for various maximum coordination numbers of the cation can be calculated. These values and the shapes of the ionic crystals resulted from various coordination numbers are given in Table 9.5.

Table 9.5. Radius ratio values for different coordination numbers of a cation.

Radius ratio, $[r(C^+)/r(A^-)]$ value	Maximum coordination number of cation	Arrangement of anions round the cation	Examples
0 to 0.155	2	Linear	—
0.155 to 0.225	3	Trigonal planar	B_2O_3
0.225 to 0.414	4	Tetrahedral	ZnS
0.414 to 0.732	6	Octahedral	NaCl
0.732 to 1.000	8	Body-centered cubic	CsCl