Course 411Ch: Inorganic Chemistry: Part (III): Inorganic Structure

Inorganic Structure

N.B.: The source of this course is the references and books mentioned at the end.

Attainment of a Stable Configuration

How do atoms combine together to form molecules and why do atoms form bonds?

The molecule formed must be more stable than the individual atoms, or molecules would not be formed, i.e. the process must be energetically favorable and lead to a minimum energy.

Atoms of the noble gases do not normally react with any other atoms and their molecules are monoatomic – that is, they contain only one atom. The lack of reactivity indicates that these atoms are extremely stable, their energy being so favorable that it cannot be improved by compound formation.

The inert gases all have a complete outer shell of electrons, so that we can conclude that this is a very stable arrangement.

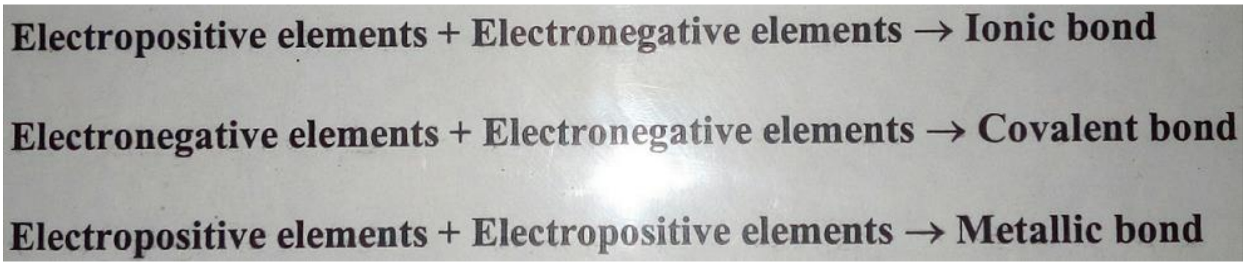
Accordingly, the atoms combine together to reach the electronic configuration of the next inert gas.

Types of Bonds

There are several ways in which atoms may obtain a stable electronic configuration: by losing, gaining or sharing electrons.

(a) Electropositive elements, whose atoms give up one or more electron fairly readily,
(b) Electronegative elements which take up electrons, and
(c) Elements which neither tend to loss nor gain electrons.

Accordingly, the following three main types of bonds are formed:

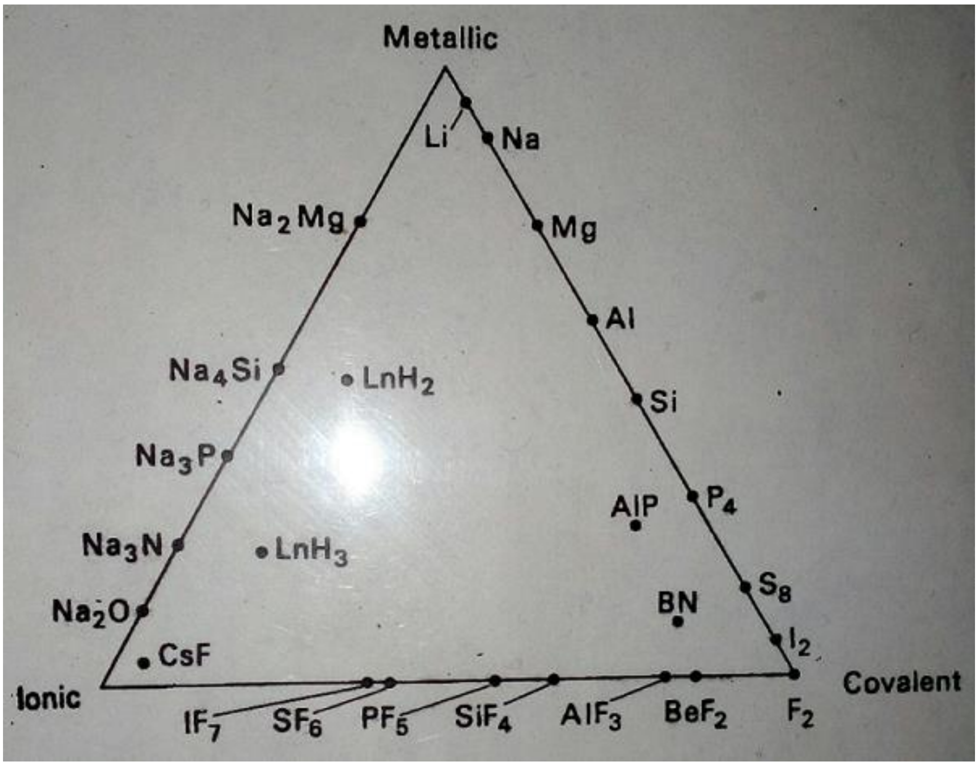


Electropositive elements + Electronegative elements → Ionic bond

Electronegative elements + Electronegative elements → Covalent bond

Electropositive elements + Electropositive elements → Metallic bond

The types of bonds are idealized or extreme representation, and in most substances the bond type is somewhere in between these extreme forms, though generally one of these types predominates.



For example, lithium chloride is considered to be an ionic compound, but it is soluble in alcohol, which suggests that it also possesses a small amount of covalent character.

General Properties of Ionically and Covalently Bonded Compounds:

Compounds containing ionic linkages are made up of positive and negative ions arranged together in a regular way in a lattice. Compounds with covalent bonds are usually made up of discrete molecules.

In ionic compounds, the attraction between ions is electrostatic and non-directional, and extends equally in all directions. In covalent compounds, the bonds are directional, and strong covalent bonding forces exist between the atoms in a molecule.

Ionic compounds are very hard solids and they have high melting and boiling point, because a considerable high energy is necessary to break the lattice and to melt the compounds. Covalently bonded compounds are often gases, liquids or soft solids with low melting points (in covalent solid compounds, the only forces between one molecule and another are weak van der Waals forces).

Ionic compounds conduct electricity because ions migrate towards the electrodes when the compound is melted or in solution. In an ionic crystal, the ions are trapped in fixed places in the crystal lattice; hence they cannot migrate and therefore cannot conduct electricity. If the crystal is not perfect (most crystals have defects) and a lattice site is left vacant, that is an ion is missing, some very slight conduction may occur by migration of an ion from its lattice site to the vacant site. In contrast, covalent compounds are insulators. They have no electric charges and carry no current in either the solid, liquid or gaseous state.

Ionic compounds are usually soluble in polar solvents: that is solvents of high dielectric constant such as water. Covalent compounds are not normally soluble in these solvents but are soluble in non-polar (organic) solvents: that is, solvents of low dielectric constant such as benzene and carbon tetrachloride.

Ionic reactions are usually rapid, since the reacting species have only to collide. Covalent compounds usually react slowly since the reaction usually involves breaking a bond and substituting or adding another group. Thus, collisions between the reactant molecules will only cause reaction if they have sufficient energy.

It is important to realize that bonds are not necessarily 100% covalent or 100% ionic and that bonds of intermediate character exist. In a molecule made up of two identical atoms, both atoms have an equal tendency to gain electrons, so that the electron pair forming the bond is equally shared by both atoms. This constitutes a 100% covalent bond. In molecules formed between different atoms, the tendency to gain electrons differs – hence the bond pair electrons is unequally shared by the two atoms, one atom having a very small negative charge $\boldsymbol{\delta}$- and the other a small positive charge $\boldsymbol{\delta}$+

$$^{\delta+}\mathrm{A}—\mathrm{B}^{\delta-}$$

This covalent bond is therefore partially ionic in character.

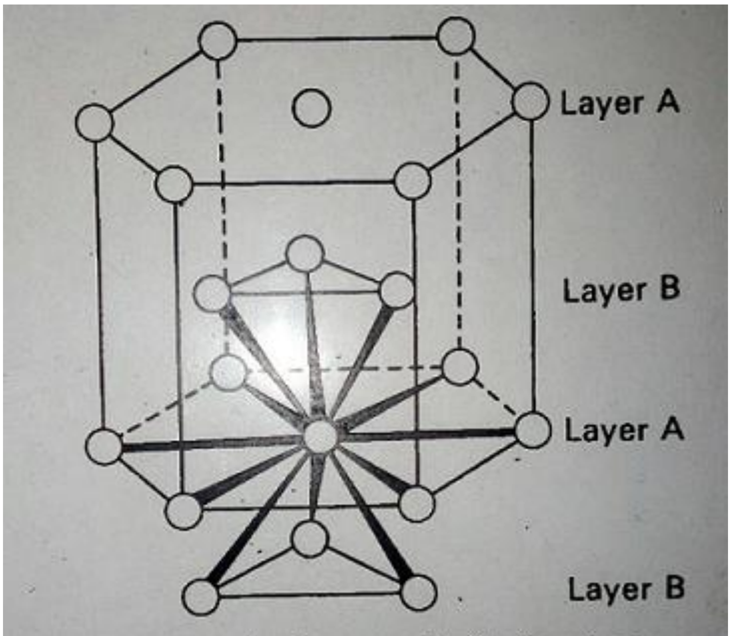
Metallic Bonds and Metallic Structures

Metals are made up of positive ions packed together, usually in one of the three following geometrical arrangements:

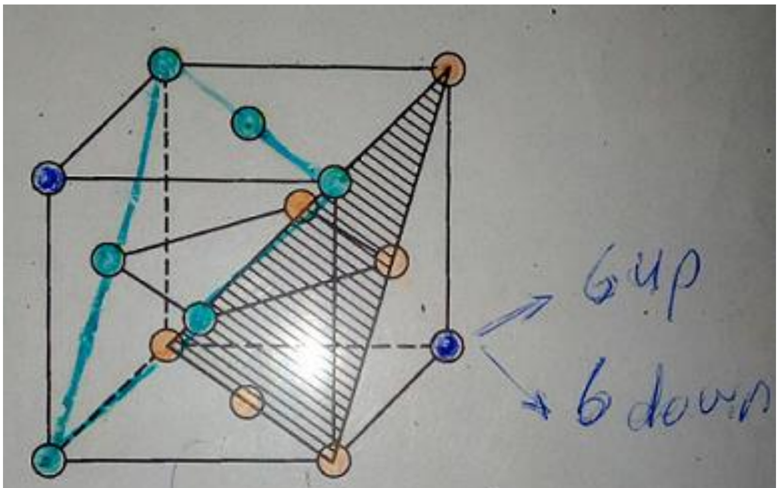
1. Hexagonal close-packed
2. Cubic close-packed (Face-centered cubic)
3. Body-centered cubic

Negatively charged electrons hold the ions together, and the positive and negative charges are balanced, since the electron originated from the neutral metal atoms.

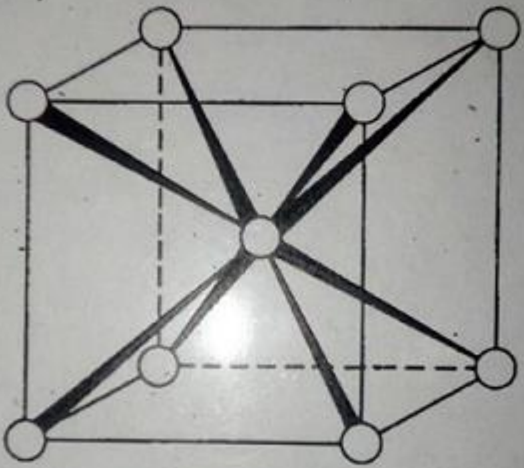
The outstanding feature of metals is their very high electrical conductivity, which is due to mobility of these electrons through the lattice.



(a) Hexagonal close packed structure showing the repeat pattern of layers ABABAB … and the 12 neighbours surrounding each sphere.



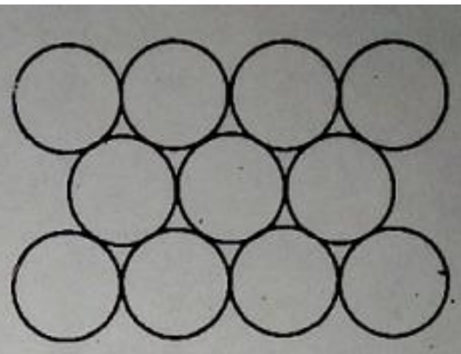
Cubic close-packed structure (coordination number is also 12).



(c) Body-centred cubic structure showing the 8 neighbours surrounding each sphere.

Two of these arrangements (cubic close-packed and hexagonal close-packed) are based on the closest packing of spheres.

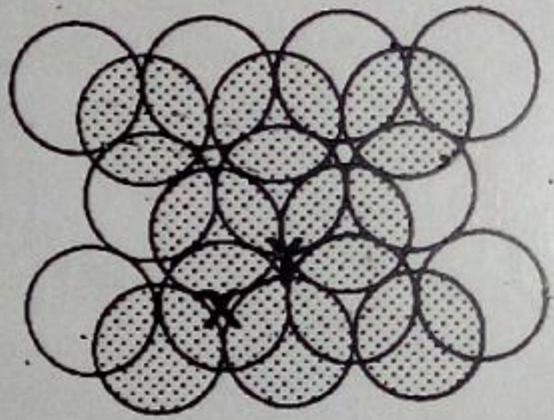
The metal ions are assumed to be spherical, and are packed together to fill the space most effectively as shown below:



(d) A single layer of close-packed spheres.

Each sphere touches six other spheres within this one layer.

A second layer of spheres is arranged on top of the first layer, the protruding parts of the second layer fitting into the hollows in the first layer:



(e) Two layers of close-packed spheres (second layer is shaded).

A sphere in the first layer touches three spheres in the layer above it, and similarly it touches three spheres in the layer bellow it, plus six spheres in its own layer, making a total of twelve. The coordination number, or the number of atoms or ions in contact with a given atom, is therefore 12 for a close-packed arrangement.

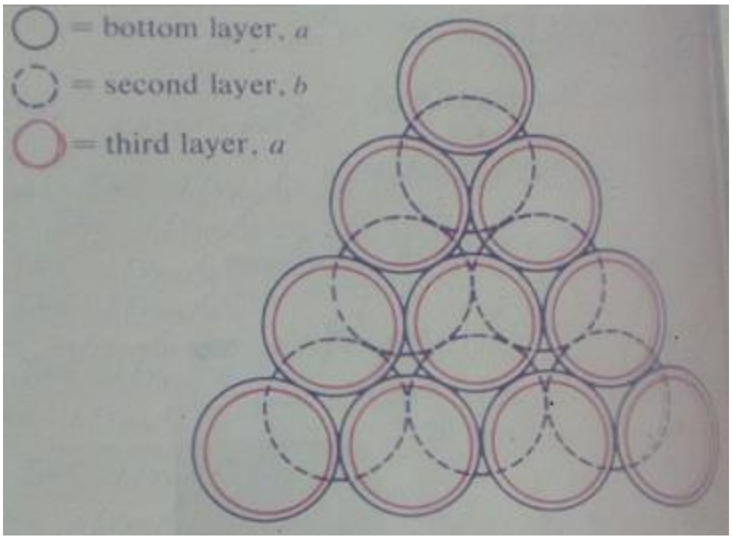
With a close-packed arrangement, the spheres occupy 74% of the total space, whereas and the remaining 26% of the total are holes.

When adding a third layer of spheres, two different arrangements are possible, each preserving the close-packed arrangement:

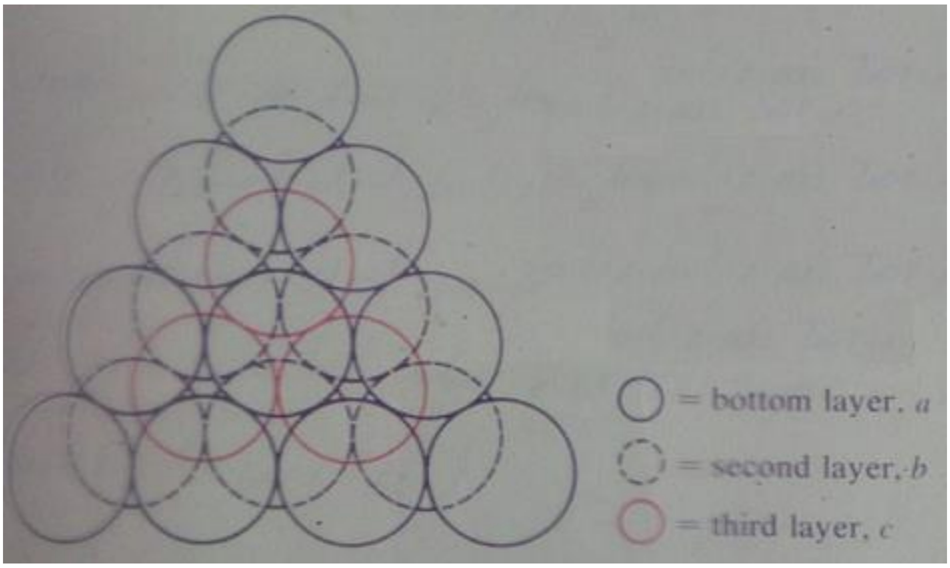
If the first sphere of the third layer is placed in the depression X shown in the previous figure.

It can be seen that this sphere is exactly above a sphere in the first layer.

It follows that every sphere in the third layer is exactly above one of the first layer. If the first sheet is represented by A, and the second sheet by B, the repeating pattern of the close-packed sheets is ABABAB….., and such a structure is said to be hexagonal close-packed.

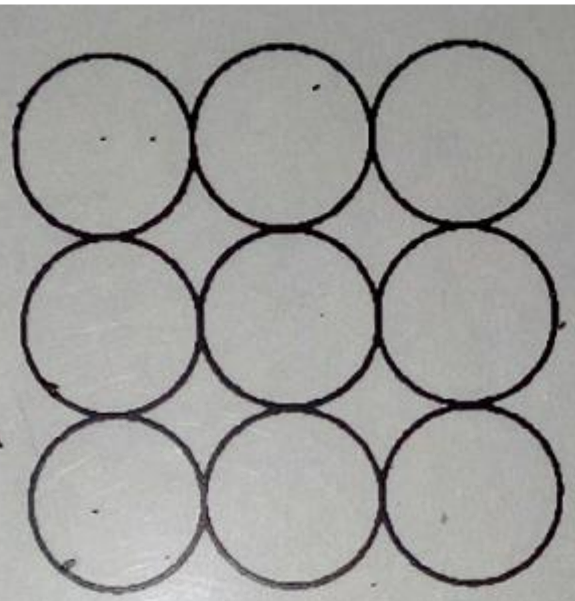


Alternatively, the first sphere of the third layer may be placed in a depression such as Y in the figure. The sphere is not exactly above a sphere in the first layer, and it follows that all the spheres in the third layer are not exactly above spheres in the first layer. If the three layers are represented A, B and C, the repeating pattern of sheets is ABCABCABC…., and such a structure is said to be cubic-close packed. An alternative name for this structure is face-centered cubic.



The third common metallic structure is called body-centred cubic.

The spheres are packed in sheets as shown below:



(g) Packing of spheres a body-centred cubic a rangement.

This form of packing is rather less efficient at filling the space than the closest packing, and the spheres occupy 68% of the total space, and 32% of the total space are holes.

The coordination number of the body-centred arrangement is then 8.

Structures of Ionic Solids

The coordination number

In an ionic solid, positive ions are surrounded by negative ions, and vice versa.

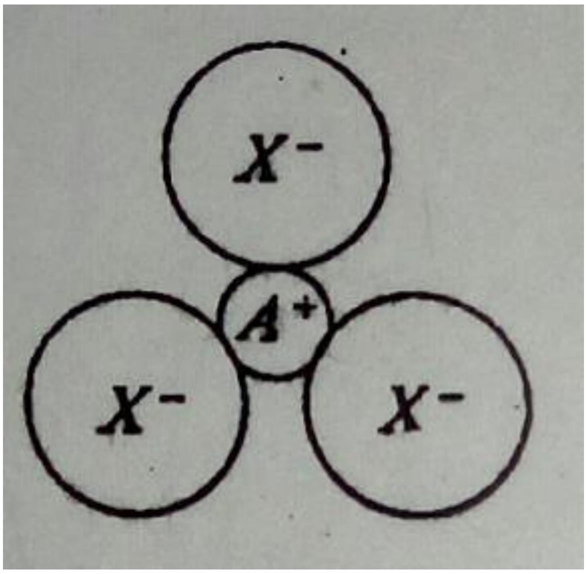
Normally each ion is surrounded by the greatest possible number of oppositely charged ions and this number is called the coordination number.

The coordination numbers of positive and negative ions are the same if there are equal numbers of both ions, as in NaCl, and are different when there are different numbers of both ions, as in $CaCl_2$.

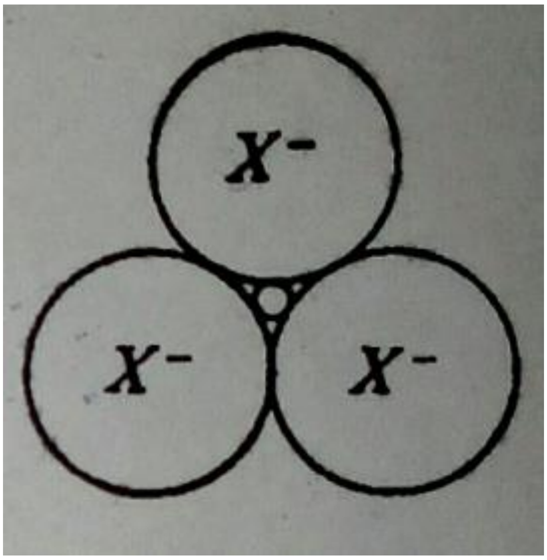
The coordination number is related to the relative sizes of the ions.

Radius Ratios and Limiting Radius Ratios

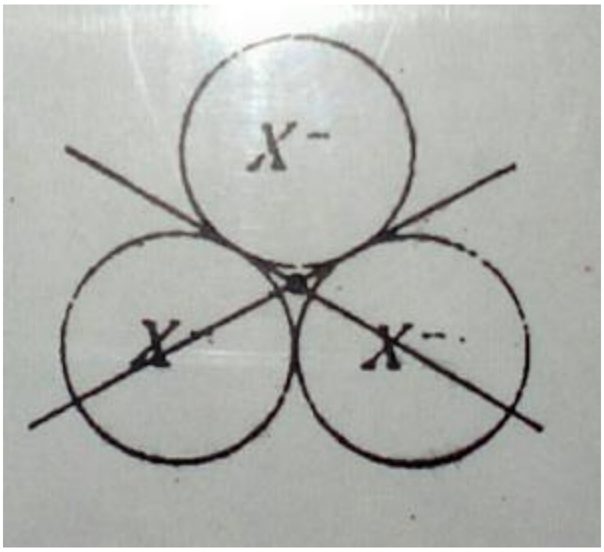
When the coordination number is three in an ionic compound AX, three X^- ions are in contact with one A^+ ion:



A limiting case arises when the X^- ions are also in contact with one another:

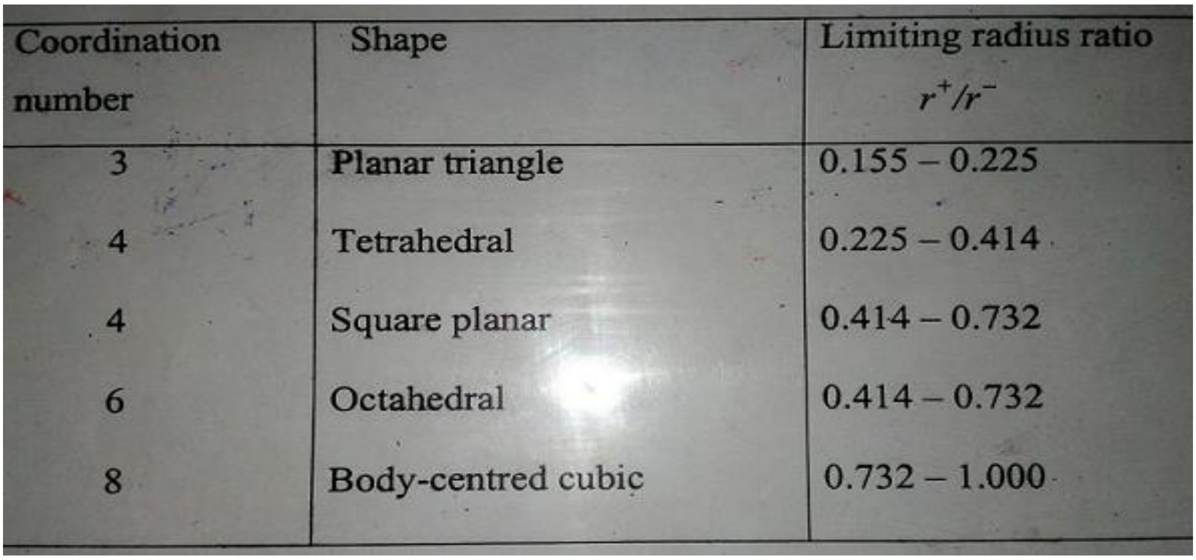


By simple geometry this gives the ratio: radius A^+/radius X^- = 0.155. If the ratio falls below this value then the structure is unstable:



Coordination numbers 3, 4, 6 and 8 are common, and the appropriate limiting radius ratios can be worked out.

Thus, if the ionic radii are known, the radius ratio can be calculated and hence the coordination number and shape may be predicted. Some of coordination numbers, their limiting radius ratios and the predicted corresponding shapes are given in the following table.



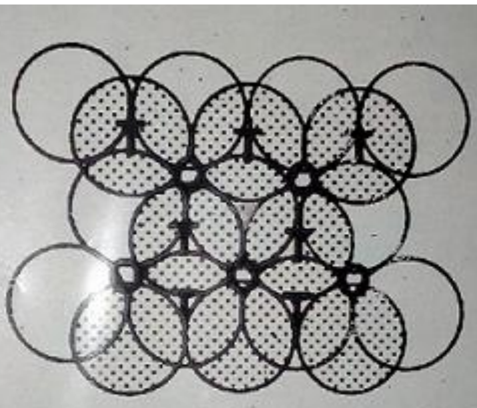
Coordination number	Shape	Limiting radius ratio r^+/r^-
3	Planar triangle	0.155 – 0.225
4	Tetrahedral	0.225 – 0.414
4	Square planar	0.414 – 0.732
6	Octahedral	0.414 – 0.732
8	Body-centred cubic	0.732 – 1.000

Close Packing

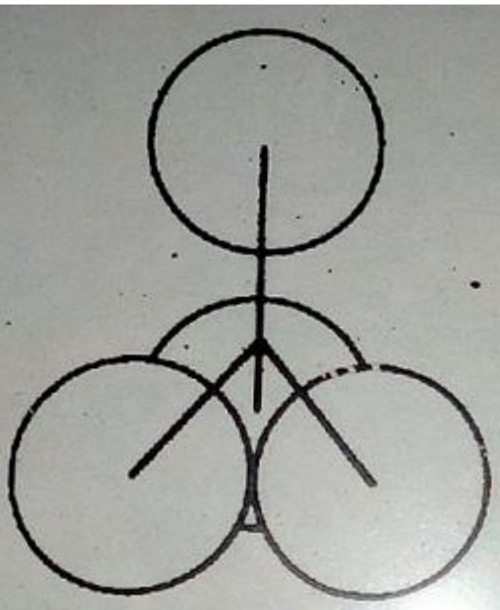
Many common crystal structures are related to, and may be described in terms of, hexagonal or cubic close-packed arrangements.

In a close-packed arrangement of spheres, 26% of the space is unoccupied, and may be regarded as holes in the crystal lattice.

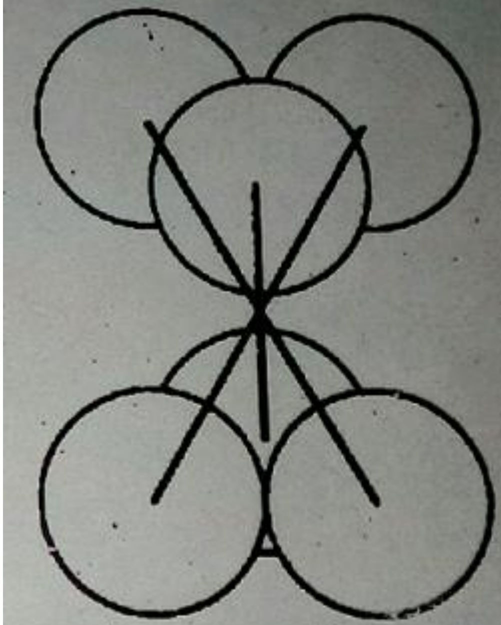
Two different types of hole occur. Those marked T (in the Fig. below) are bounded by four spheres and are called tetrahedral holes, and those marked O (in this Fig.) are bounded by six spheres are called hexagonal holes.



Tetrahedral and octahedral sites in a close packed lattice.



Tetrahedral site.



Octahedral site.

For every sphere in the close-packed arrangement there will be one octahedral hole and two tetrahedral holes. The octahedral holes are larger than the tetrahedral holes.

An ionic structure is composed of oppositely charged ions. If the larger ions are close-packed, then the smaller ions may occupy either the octahedral holes or the tetrahedral holes depending on their size. Normally the type of hole occupied can be obtained from the radius ratio. Thus an ion occupying a tetrahedral hole has a coordination number of four, whilst one occupying an octahedral hole has a coordination number of six.

In some compounds the relative sizes of the ions are such that the smaller ions are too large to fit in the holes, and they force the larger ions out of contact with each other so that they are no longer close packed. Despite this, the relative positions of the ions remains unchanged, and it is convenient to retain the description in terms of lose packing.

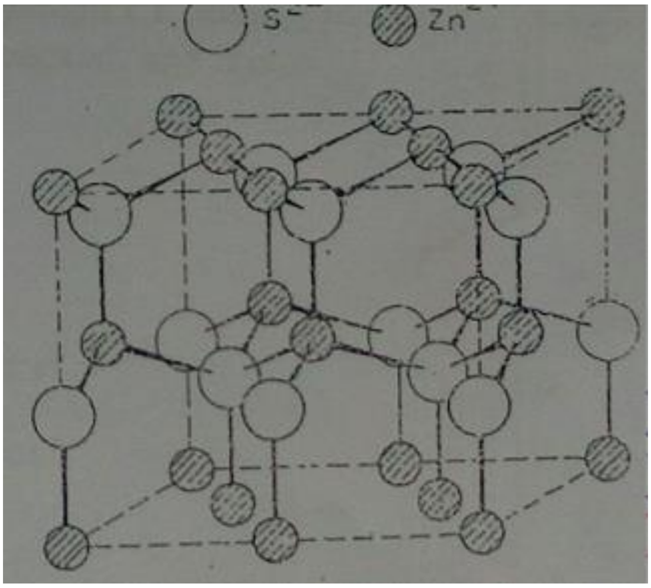
Ionic Compounds of the Type AX (ZnS, NaCl, CsCl)

Three structural arrangements commonly found are zinc sulphide, sodium chloride and cesium chloride structures.

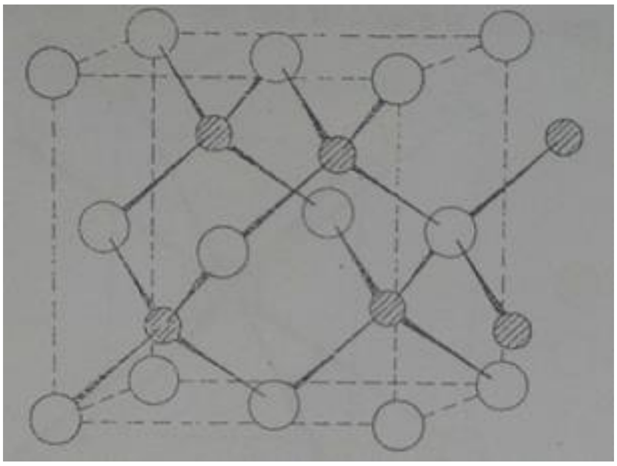
Zinc Sulphide Structure

In zinc sulphide, ZnS, the radius ratio of 0.40 suggests a tetrahedral arrangement. Each Zn^{2+} ion is tetrahedrally surrounded by four S^{2-} and each S^{2-} is tetrahedrally surrounded by four Zn^{2+} ions. This is therefore a 4:4 arrangement since the coordination number of both ions is four.

Actually two different forms of zinc sulphide exist, both 4 : 4 arrangements, one being called zinc blende and the other wurtzite.



Wurtzite (ZnS) structure



Zinc blende (ZnS) structure

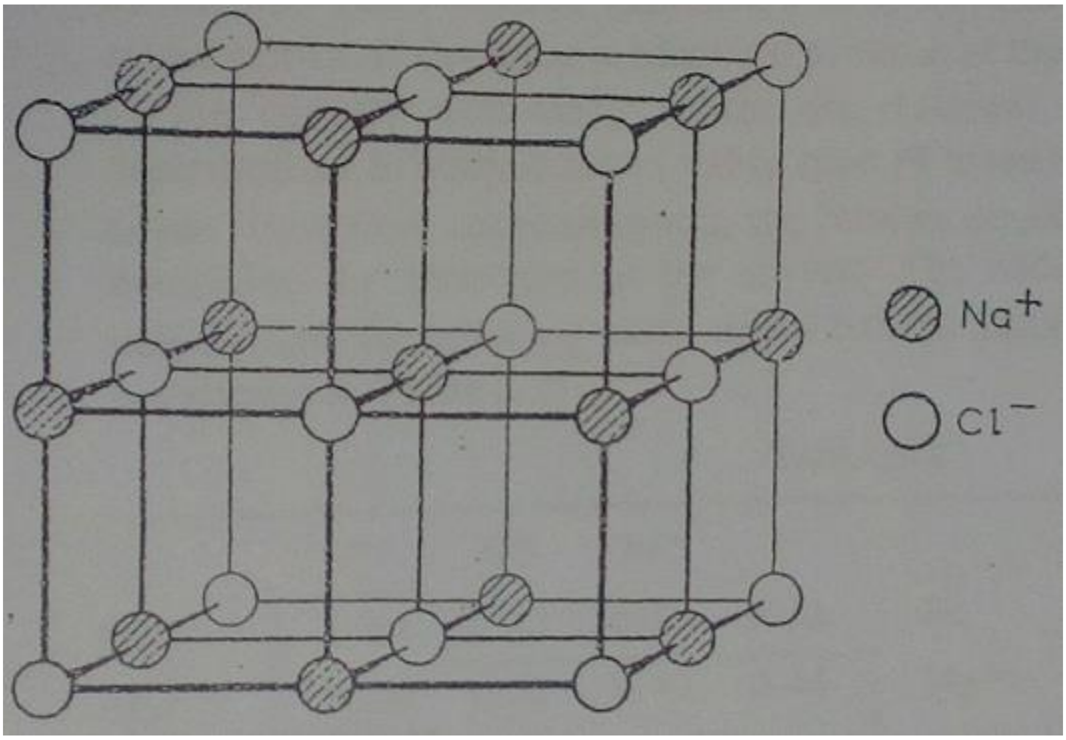
They may be considered as close-packed arrangements of S^{2-} ions with Zn^{2+} ions occupying tetrahedral holes in the lattice. Since there are twice as many tetrahedral holes as there are S^{2-} spheres, it follows that to obtain a formula ZnS only half of the tetrahedral holes are occupied by Zn^{2+} ions (that is every alternate tetrahedral site is unoccupied).

The difference between the two forms of ZnS is that zinc blende is related to a cubic close-packed structure whilst wurtzite is related to a hexagonal close-packed structure.

Sodium Chloride Structure

The radius ratio of sodium chloride, NaCl, is 0.52 and suggests an octahedral arrangement. Each Na^+ ion is surrounded by six Cl^- ions at the corners of a regular octahedron and similarly each Cl^- ion is surrounded by six Na^+ ions.

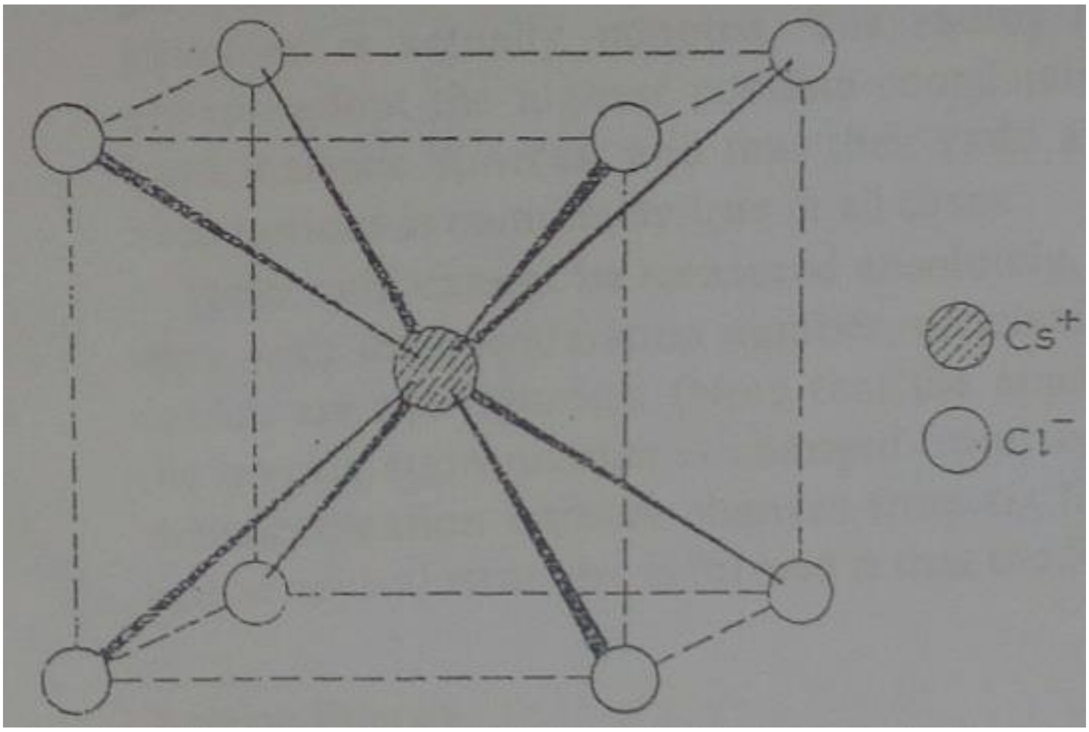
This structure may be regarded as having Cl^- ions occupying cubic close-packed positions, with Na^+ ions in all the octahedral holes.



NaCl Structure

Cesium Chloride Structure

In cesium chloride, CsCl, the radius ratio is 0.93, indicating a body-centred cubic type of arrangement, where each Cs^+ ion is surrounded by eight Cl^- ions, and vice versa.

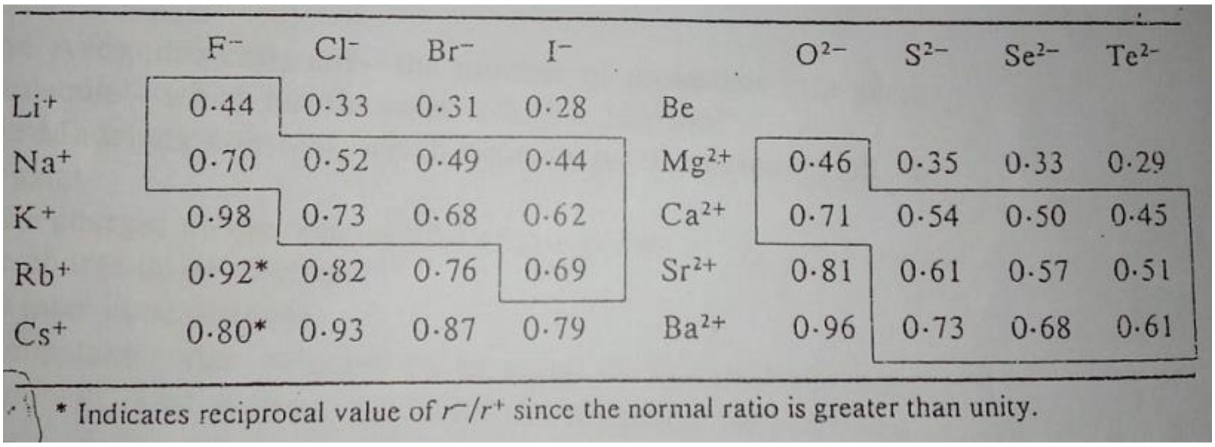


CsCl Structure

Note that this structure is not close packed, and it is not strictly body-centred cubic. In a body-centred cubic arrangement, the atom at the centre of the cube is identical to those at the corners. In this case the ions at the corners and body centre are different, and the structure must be described as a body-centred cubic type of arrangement and not body-centred cubic.

Radius Ratio and Structure

The following table shows radius ratios of some of the alkali metal halides and the alkaline earth metal oxides, sulphides, selenides and tellurides.



	F^-	Cl^-	Br^-	I^-		O^{2-}	S^{2-}	Se^{2-}	Te^{2-}
Li^+	0·44	0·33	0·31	0·28	Be				
Na^+	0·70	0·52	0·49	0·44	Mg^{2+}	0·46	0·35	0·33	0·29
K^+	0·98	0·73	0·68	0·62	Ca^{2+}	0·71	0·54	0·50	0·45
Rb^+	0·92*	0·82	0·76	0·69	Sr^{2+}	0·81	0·61	0·57	0·51
Cs^+	0·80*	0·93	0·87	0·79	Ba^{2+}	0·96	0·73	0·68	0·61

* Indicates reciprocal value of r^-/r^+ since the normal ratio is greater than unity.

It has been shown from the table that, except for CsCl, CsBr and CsI, which have a cesium chloride structure, and MgTe, which has a zinc sulphide structure, all the above compounds have a sodium chloride lattice at normal temperature.

Only those crystals with a radius ratio between 0.41 and 0.73 (enclosed by full line in the above table) would be expected to have the sodium chloride structure.

The difference in stability and lattice energy between coordination numbers six and eight for RbCl and RbBr is small since they have a coordination number of six at normal temperatures and pressures, but adopt the higher coordination number if crystallized at high pressures or temperatures.

Thus, radius ratios provide a useful guide to what is possible on geometrical grounds, but do not necessarily provide a reliable method for predicting which structure is actually adopted. The radius ratio concept assumes that ions always adopt the highest possible coordination number, they behave as hard inelastic spheres, and that their radii are known exactly. None of these assumptions is completely true in all cases.

Ionic radii cannot be measured absolutely, but are estimated, and since they vary with the coordination number, conclusions based on them, though often useful, are not rigorous. (Note that the apparent ionic radius increases 3% if the coordination number is changed from six to eight and decreases 6% when the coordination number changes from six to four.

The reason why any particular crystal structure is formed is that the lattice energy is favorable.

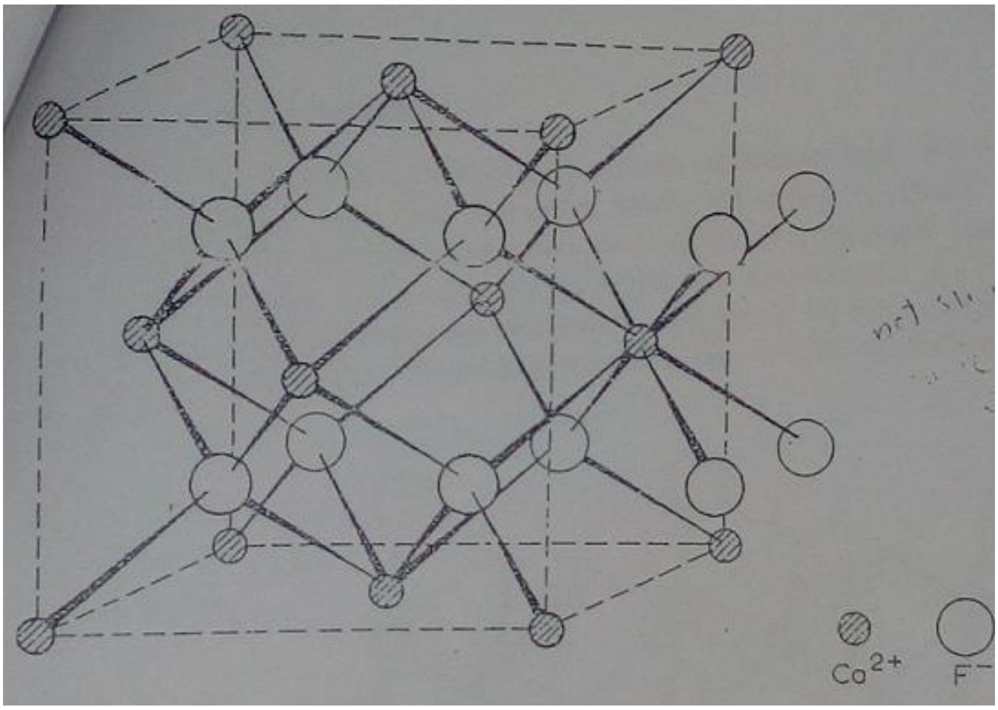
Meanwhile, lattice energy depends on: ionic charges, crystal structure and distance between ions.

Ionic Compounds of the Type AX_2 (CaF_2, TiO_2)

There are two very common structures: fluorite, CaF_2, and rutile, TiO_2. Many difluorides and dioxides have one of these structures.

Fluorite Structure

In fluorite, CaF_2, each Ca^{2+} ion is surrounded by eight F^- ions in a body-centred cubic arrangement. Since there are twice a many F^- ions as Ca^{2+} ions, the coordination number of both ions is not the same, and four Ca^{2+} ions are tetrahedrally arranged round each F^- ion. The coordination numbers are eight and four and this is called an 8 : 4 arrangement.



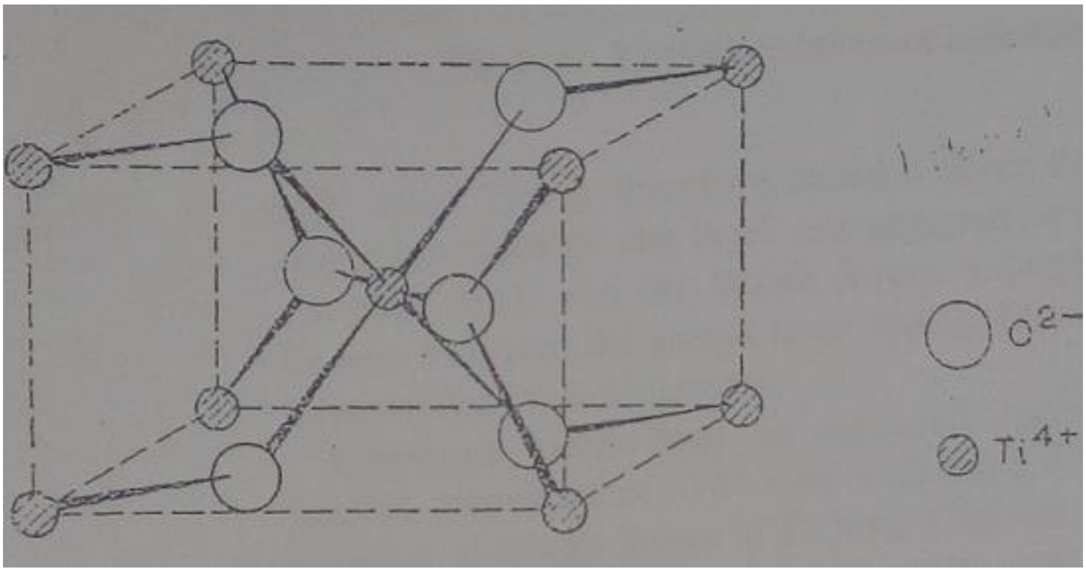
Fluorite (CaF_2) structure

The fluorite structure is found when the radius ratio is 0.73 or above. It may be related to the close-packed structures. Though the Ca^{2+} ions are too small to touch each other (so the structure is not strictly close packed), their relative positions are like those in a cubic close-packed structure, and the F^- ions occupy all of the tetrahedral holes.

Rutile Structure

The rutile structure is found where the radius ratio is between 0.73 and 0.41.

The coordination numbers are six and three, each Ti^{4+} ion being octahedrally surrounded by six O^{2-} ions and each O^{2-} ion having three Ti^{4+} ions round it in a plane triangular arrangement.



Rutile (TiO_4) structure

The rutile structure is not close packed, but the Ti4+ ions may be considered as forming a considerably distorted body-centred cubic lattice.

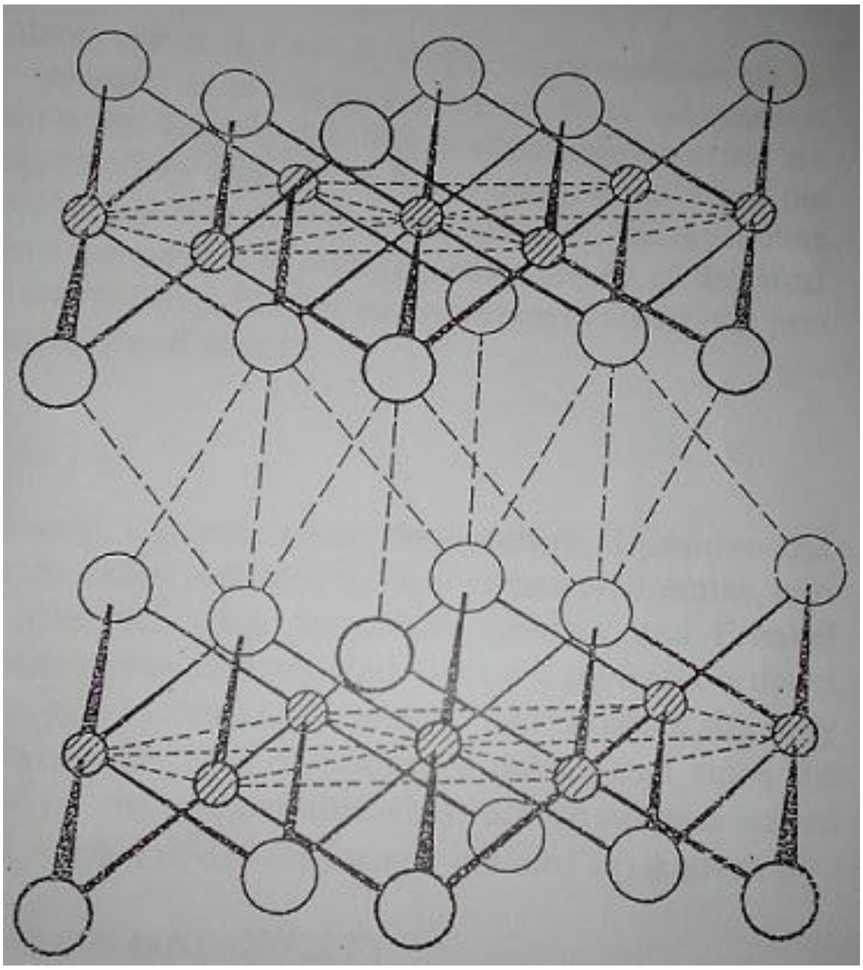
There are only a few cases where the radius ratio is below 0.41, examples being silica SiO_2, and beryllium fluoride BeF_2. These have coordination numbers of four and two, but radius ratio predictions are uncertain, as they are appreciably covalent.

Layer Structures

Many AX_2 compounds are not sufficiently ionic to form the perfect regular ionic structures described.

Many chlorides, bromides, iodides and suphides crystallize into structures very different from those described.

Thus cadmium iodide, CdI_2, does not form the fluorite structure like CdF_2. the radius ratio 0.45 indicates a coordination number of six for cadmium, but the structure is made up of electrically neutral layers of Cd^{2+} ions sandwiched between layers of I^- ions.



Layer structure, (CdI_2)

This is therefore called a layer structure, and since the negatively charged I^- ions of one layer are adjacent to those of the next layer, and there are only weak van der Waals forces holding the sheets together, the crystal cleaves into parallel sheets quit easily. Most hydroxides of formula $M(OH)_2$ have similar layer structure.

Cadmium iodide may be regarded approximately as a hexagonal close-packed arrangement of I^- ions with the Cd^{2+} ions occupying octahedral sites between alternate layers of I^- ions.

Cadmium chloride forms a closely related layer structure but with the chloride ions approximately in a cubic close-packed arrangement.

The CdI_2 structure is related to the nickel arsenide NiAs structure, where the arsenic atoms form a hexagonal close-packed type of lattice with nickel atoms occupying octahedral sites between all of the layers of arsenic atoms.

Layer structures are intermediate inn type between the extreme cases: (1) a totally ionic crystal with a regular arrangement of ions and strong electrostatic forces in all directions, and (2) a crystal in which small discrete molecules are held together by weak residual forces such as van der Waals forces and hydrogen bonds.

Defects in Ionic Compounds

The essential feature about crystalline solids is that the constituent molecules, atoms or ions are arranged in a completely regular three-dimensional pattern.

Models built to show the detailed structure of crystalline materials are usually grossly misleading, for they imply a perfect, static pattern. Since the atoms or ions have a considerable degree of thermal vibration, the crystalline state is far from static, and the pattern is seldom perfect.

Many of the most useful properties of solids are related to the thermal vibration of atoms, the presence of impurities or the existence of defects.

Stoichiometric Defects

In stoichiometric compounds, i.e. ones where the numbers of positive and negative ones are exactly in the ratios indicated by their chemical formulae, two types of defects may be observed. They are called Schottky and Frenkel defects.

At absolute zero, crystals tend to have a perfectly ordered arrangement. As the temperature increases, the chance that a lattice site may be unoccupied by an ion increases. This constitutes a defect, and since the number of defects depends on the temperature they are sometimes called thermodynamic defects.

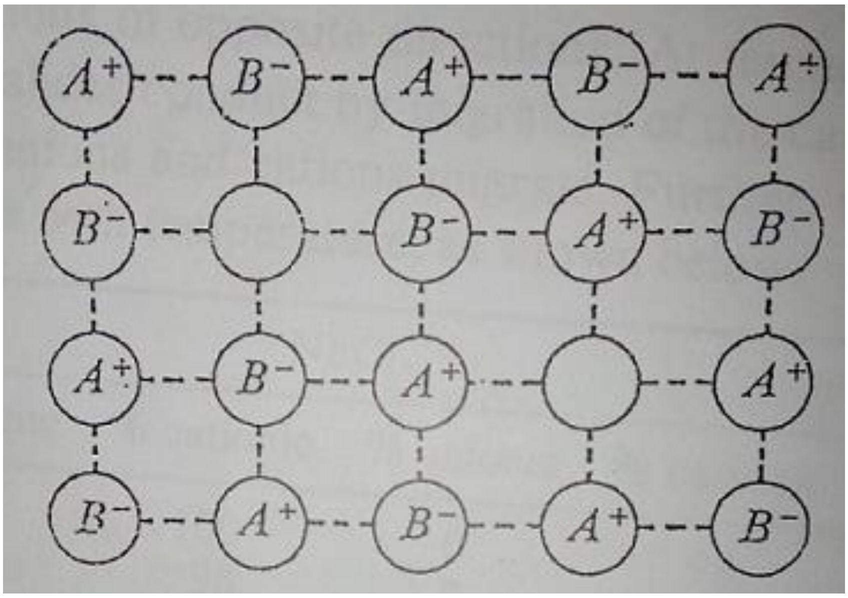
The number of defects formed per cm^3 (n) is given by:

$$n = N \exp(-W/2kT)$$

where N is the number of sites per cm^3 that could be left vacant, W is the work necessary to form a defect, k is the gas constant and T the absolute temperature.

Schottky Defects

A pair of 'holes' exist in the crystal lattice due to one positive ion and one negative ion being absent from the crystal lattice.

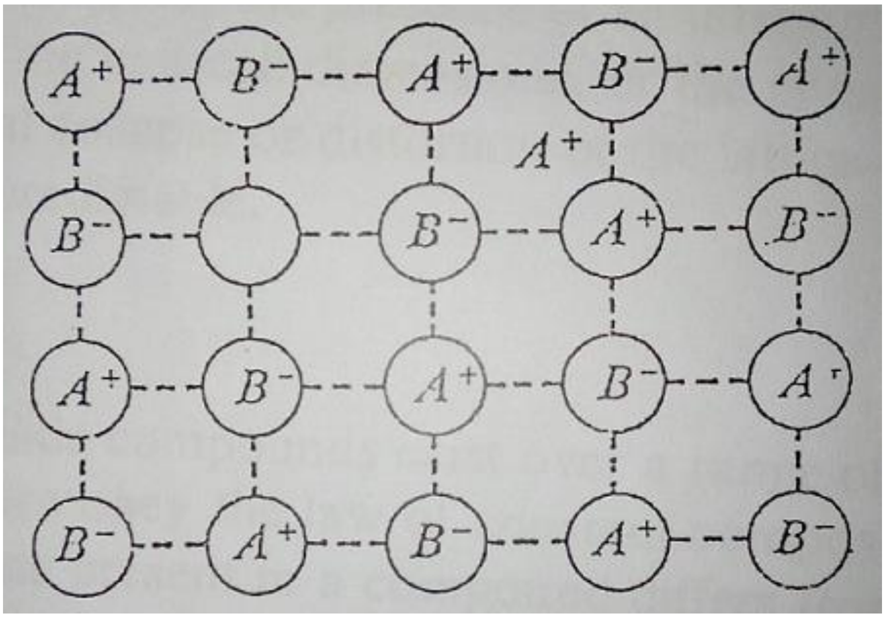


Schottky Defects

This sort of defect tends to be formed in highly ionic compounds with high coordination numbers and where the positive and negative ions are of similar size, e.g. NaCl, CsCl, KCl and KBr.

Frenkel Defects

A 'hole' may exist in the lattice because an ion occupies an interstitial position rather than its correct lattice site.



Frenkel Defects

This type of defect is fovoured by a large difference in size between the positive and negative ions.

Since positive ions are generally smaller than negative ions, it is more common to find the positive ions occupying interstitial positions. Small positive ions are highly polarizing and large negative ions are readily polarized; hence these compounds have some covalent character. This distortion of ions, and the proximity of like charges leads to a high dielectric constant. It is easier to form Frenkel defects in compounds that have a low coordination number, since fewer attractive forces to be broken. Examples of this type of defect are ZnS, AgCl, AgBr and AgI.

The energy needed to form a Schottky defect is usually less than to form a Frenkel defect, and in a given compound one type generally predominates.

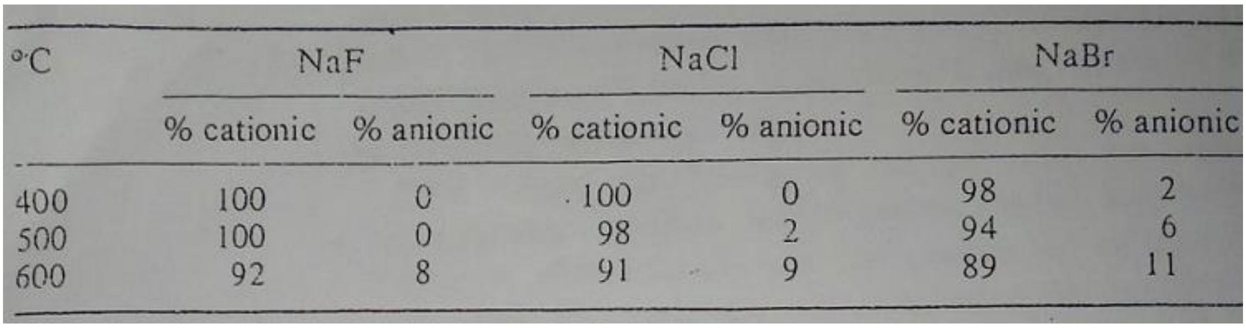
In NaCl, the energy to form a Schottky defect is about 200 kJ mol^{-1} compared with a lattice energy of approx. 750 kJ mol^{-1}. It is therefore much easier to form a defect than to break the lattice.

The number of defects is relatively small, and at room temperature NaCl has only one defect in 10^{15} lattice sites, this value rising to one in 10^{6} sites at 500 °C and one in 10^{4} sites at 800 °C.

A consequence of these defects is that a crystalline solid that has defects may conduct electricity to a small extent, by an ionic mechanism. If an ion moves from its lattice site to occupy a 'hole', it creates a new 'hole', and in this way a 'hole' may migrate across a crystal, which is effectively moving a charge in the opposite direction.

In the case of Schottky defects, conduction may arise either from migration of the smaller ion only (usually the positive ion) or from migration of both type of ions in opposite directions.

At temperature bellow 400 °C most of the alkali halides conduct by migration of the cations only, but at high temperatures both anions and cations migrate. Further, the amount of anionic conduction increases with temperature, as hown in the below:



°C	NaF		NaCl		NaBr	
	% cationic	% anionic	% cationic	% anionic	% cationic	% anionic
400	100	0	100	0	98	2
500	100	0	98	2	94	6
600	92	8	91	9	89	11

Frenkel defect may also give rise to ionic conduction, if the thermal vibration is sufficient to allow the interstitial ion to move to another interstitial site.

Defects and Densities

The density of a defect lattice should be lower than for a perfect lattice, because of the 'holes' present.

However, the presence of an interstitial ion may expand the lattice and increase the unit cell dimension, or the presence of too many 'holes' may allow a partial collapse or distortion of the lattice—in which case the change in density is unpredictable.

Nonstoichiometric Defects

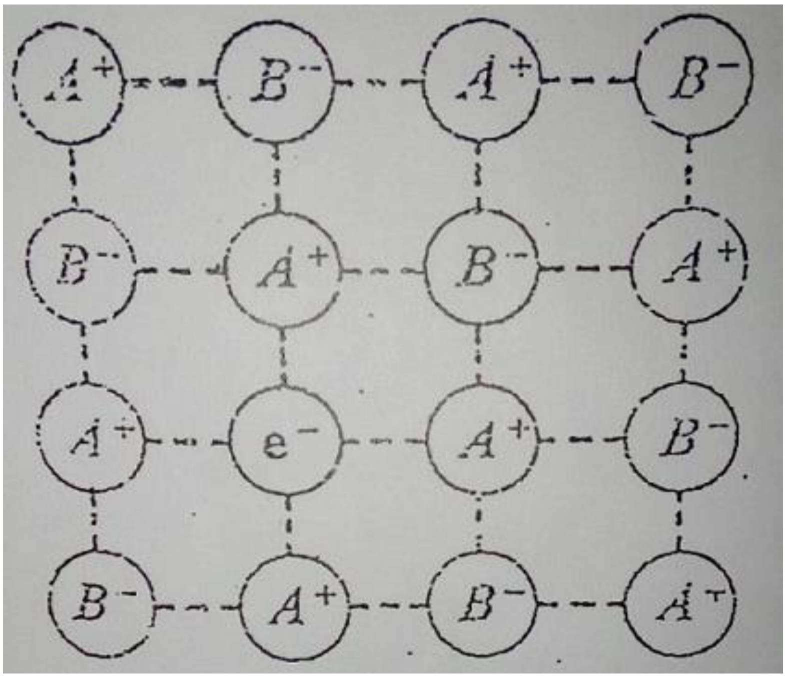
Nonstoichiometric or Berthollide compounds exist over a range of chemical composition, and do not therefore obey the law of constant composition.

The ratio of positive and negative ions present in a compound differs from that indicated by the ideal chemical formula, and the balance of + and – charges is maintained by having either extra electrons or extra positive charges present.

This makes the structure irregular in some way, i.e. it contains defects, which are in addition to the normal thermodynamic defects already disussed. Nonstoichiometry implies that either the metal or the nonmetal atoms are present in excess.

Metal Excess

This may occur in either of two ways. In the first, a negative ion may be absent from its lattice site, having a 'hole' which is occupied by an electron, thereby maintaining the electrical balance.



Metal excess (Type A)

This is rather similar to a Schottky defect in that there are 'holes' and not interstitial ions, but only one 'hole' is formed rather than a pair.

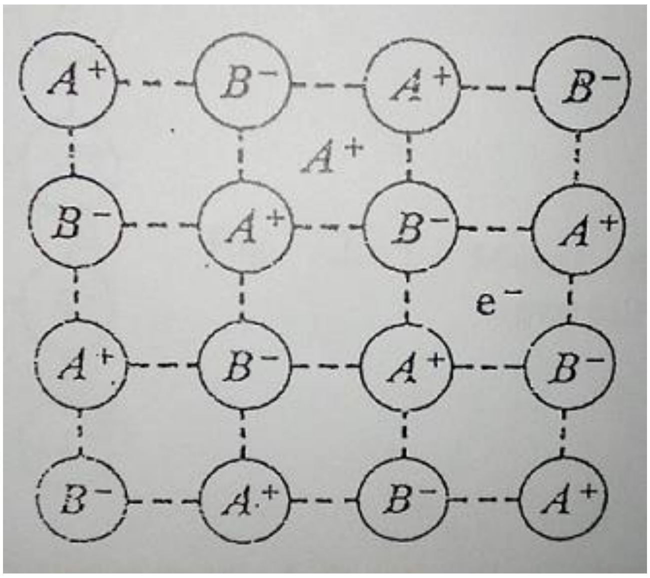
This type of defect is formed by crystals which would be expected to form Schottky defects. Examples are uncommon, but if NaCl is treated with Na vapour, a yellow nonstoichiometric form of NaCl is obtained, and a blue-coloured nonstoichiometric form of KCl may be prepared by analogous means.

The vacant sites occupied by electrons are called F-centers (or colour centers), and it is these which are associated with the colour of the compound. The more F-centers present, the greater the intensity of the colouration.

Solids containing F-centers are paramagnetic, because the electrons occupying the vacant sites are unpaired.

If materials with F-centers are irradiated with light they become photocoductors. It is though that the electrons in the F-centers absorb the light energy and become promoted into a conduction band, rather similar to the conduction bands present in metals.

A second way in which metal excess defects may occur is if an extra positive ion occupies an interstitial position in the lattice. Electrical neutrality is maintained by an electron, also in an interstitial position.



Metal excess (Type B)

This type of defect is rather like a Frenkel defect in that ions occupy interstitial positions, but there are no 'holes', and there are also interstitial electrons.

This second kind of metal excess defect is much more common than the first, and is formed in crystals which would be expected to form Frenkel defects, e.g. ZnO.

Crystals with either type of metal excess defect contain free electrons, and if these migrate they conduct an electric current.

Since there are relatively few defects and hence few free electrons that can conduct electricity, the amount of current carried is very small compared with that in metals, fused salts or salts in aqueous solutions, and these materials are called semiconductors.

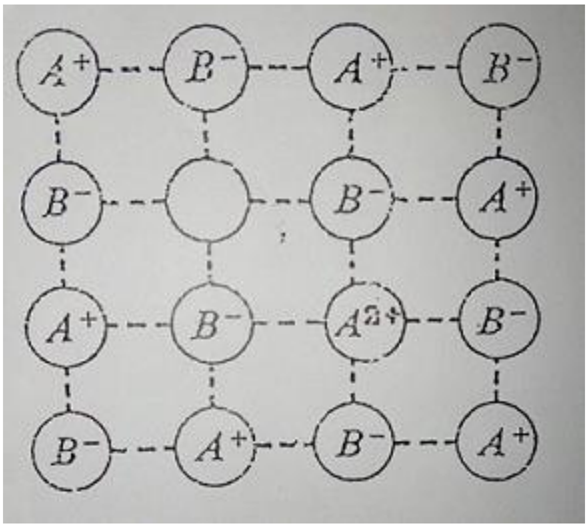
Since the mechanism is normal electron conduction, these are called n-type semiconductors.

These free electrons may be excited to higher energy levels giving absorption spectra, and in consequence their compounds are often coloured, e.g. nonstoichiometric NaCl is yellow, nonstoichiometric KCl lilac, and ZnO is white when cold but yellow when hot.

Metal Deficiency

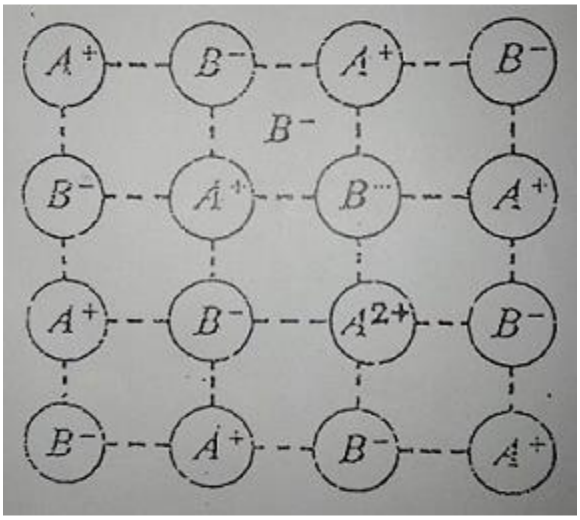
Theoretically metal deficiency can occur in two ways. Both require variable valency of metal, and might therefore be expected with the transition metals.

In the first way, a positive ion is absent from its lattice site, and the charges are balanced by an adjacent metal ion having two charges instead of one. Examples of this are FeO_2, FeS and NiO.



Metal Deficiency (Type A)

The second possibility is to have an extra negative ion in an interstitial position and to balance the charges by means of an extra charge on an adjacent metal ion. Negative ions are usually large, and it would be expected to be difficult to fit them into interstitial positions. In fact no examples of crystals containing such negative interstitial ions are known at present.



Metal Deficiency (Type B)

Crystals with metal deficiency defects are semiconductors because of the moving of an electron from an A^+ ion to an A^{2+} ion, i.e. an apparent movement of A^{2+} . This is called positive hole, or p-type semiconduction.

References:

1- J.D. LEE; A New Concise Inorganic Chemistry, 3rd Edition, Chapman and Hall, London, 1977

2- William W. Porterfield; Concepts of Chemistry, 1st Edition, W. W. Norton & Company Inc., New York, 1972