

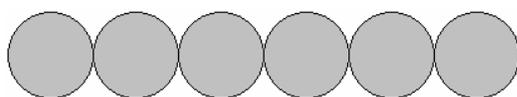
THE SOLID STATE

Substances in their lowest energy states are in the solid state. When liquids are allowed to cool very slowly, their particles (ions, atoms or molecules) take up a very ordered arrangement known as the **crystalline state**. The driving force behind this may be the attraction between oppositely charged ions or dipoles, or the weak van der Waal's forces acting between neutral atoms or molecules. *The energy decrease when 1 mole of the particles which are far away from each other (as if in a gas) fall into position in the crystal lattice is known as the **lattice energy**.* If the liquid is cooled very rapidly, the motion of the particles may be arrested before they get a chance to become properly ordered. This is called an **amorphous solid** (also known as a **glass** or a **super-cooled liquid**). Since most of the solids are in the crystalline state, it is important to study the structure of crystals in order to get a proper understanding of the properties of matter in the solid state.

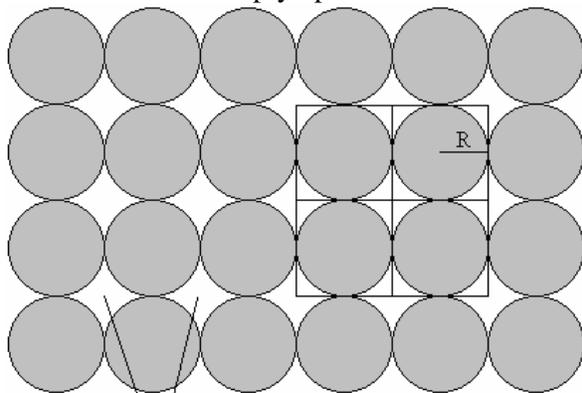
A **lattice** means an orderly arrangement in which something is placed regularly at constant intervals. Examples are soldiers standing in a line, or lamp posts along a street. For purpose of study, we shall imagine a lattice to be made up of points called *lattice points*. In an actual crystal, we have atoms, ions or molecules instead of these points. Since there is much evidence indicating that atoms and ions have an approximately spherical shape, we shall discuss the properties of lattices made up of identical spheres. Since the attractive forces between atoms or ions tend to force the particles as close to each other as possible, we will assume that the spheres are touching each other. This is called **close packing** of the spheres. Then the following conditions have to be satisfied:

- (1) The number and kind of ions in the structure must be such that the total structure is electrically neutral.
- (2) The particles must be arranged in such a way that they are as tightly packed as possible.

An arrangement satisfying condition (2) is sometimes called the *closest packing*. A *one-dimensional* close-packed lattice of identical **circles** is shown below:



This type of a linear array of spheres is usually found at the edges of a crystal. If other linear arrays similar to this are stacked exactly one above the other, the following *two-dimensional lattice* results. Since each circle occupies a total space in the form of a square, this is known as a *square close packing* in two dimensions. The empty spaces in between the circles (or spheres in three dimensions) are called



voids (square shape)
Square close packing in two dimensions

voids. *The economy in the utilization of space by the particles is called **packing efficiency** or **packing fraction**.* The packing efficiency of square close packing can be calculated as follows:

$$\text{Actual area of one circle} = \pi R^2$$

$$\text{Total area used up by the circle} = \text{area of square with side } 2R = (2R)^2 = 4R^2.$$

$$\text{Packing efficiency} =$$

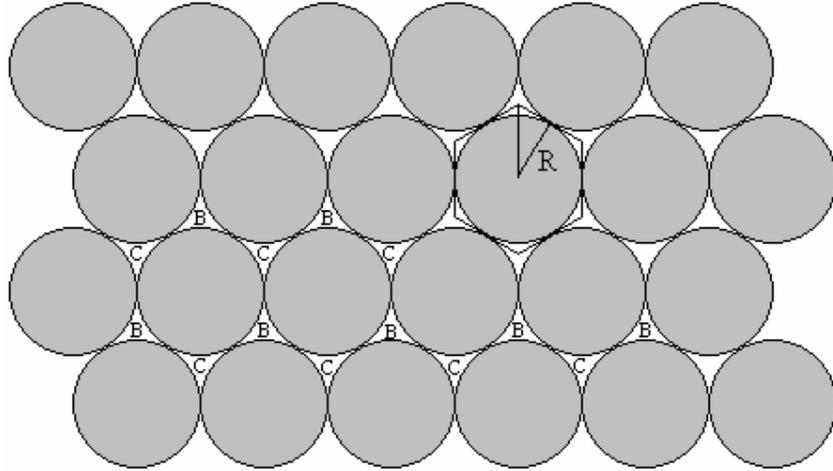
$$\frac{\text{Actual area of circle}}{\text{Area apparently used up}} = \frac{\pi R^2}{4R^2} =$$

$$\pi/4 = 0.785 \text{ or } 78.5\%$$

The number of other circles (or spheres) touching a particular circle (or sphere) is known as its **coordination number**. Thus the coordination number of a circle in this arrangement is 4.

But a more efficient use of space can be made if each row of circles is slightly displaced laterally so that they sit in the voids created by the rows above and below them. Some authors refer to such packing as the “**closest packing**”. Then we get a new arrangement called *hexagonal close packing in two dimensions*. Each circle apparently takes up a hexagonal area in the whole structure.

The packing efficiency (in 2D) is obtained by dividing the area of the circle by the area of the hexagon. The hexagon can be assumed to be made up of 12 right-angled triangles as indicated. Area of each triangle = $\frac{1}{2}bh$, where $h = R$, the radius of the circle.



Hexagonal close packing in two dimensions

Note two kinds of triangular voids, one marked 'B' and the other 'C'

$$\tan 30^\circ = b/R$$

$$\therefore b = \tan 30^\circ \times R =$$

$$= \frac{1}{\sqrt{3}} R = 0.577 R$$

$$\therefore \text{Area of one triangle} =$$

$$\frac{1}{2} \times 0.577 R \times R$$

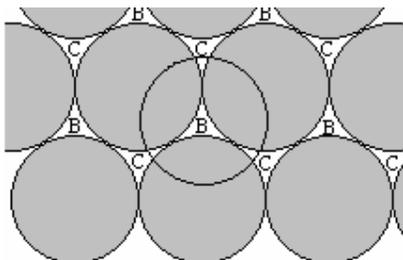
$$\text{Area of the hexagon} = \text{area of 12 triangles} = 12 \times \frac{1}{2} \times 0.577 R^2 = 3.462 R^2$$

$$\text{Area of circle} = \pi R^2 = 3.142 R^2 \quad \therefore \text{Packing efficiency} = 3.142 R^2 / 3.462 R^2 = 0.908 \text{ or } 90.8\%$$

Therefore it can be seen that hexagonal close packing is more efficient than square close packing in two dimensions. Further, note that the voids are all triangular. Also note that there are two types of triangular voids, one marked 'B' (with corner pointing upwards) and the other 'C' (with corner pointing downwards) in the diagram (names given are arbitrary). Other special features of the structure are noted below:

- (1) Each circle (or sphere) is surrounded by six circles (or spheres) touching it; therefore coordination number of each circle (or sphere) is 6.
- (2) Each circle (or sphere) is surrounded by six voids, out of which three are B-type and three are C-type. These are placed alternately.
- (3) Each void is surrounded by three circles (or spheres); therefore coordination number of each void is 3.

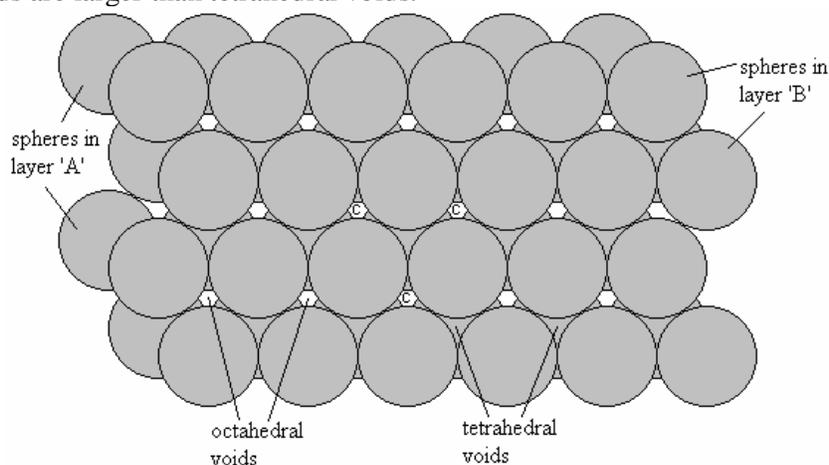
From (3) we find that one-third of a void belongs to a sphere, and there are six such voids around it. Therefore there are $6 \times \frac{1}{3} = 2$ voids for each sphere. Also, from (2) we find that one-sixth of a sphere belongs to each void, and since there are 3 spheres around each of them. Therefore there are $3 \times \frac{1}{6} = \frac{1}{2}$ sphere per void in this arrangement.



Since hexagonal close packing is more efficient (than square close packing) in two dimensions, we will adopt this scheme when extending the lattice in three dimensions. For this, let us call the first (2D) layer of spheres the 'A' layer. Now we place a second layer similar to layer 'A' over it in such a way that the spheres of this second layer sit in the voids created by the first layer. But note that if we place a sphere in a B-type void, it will

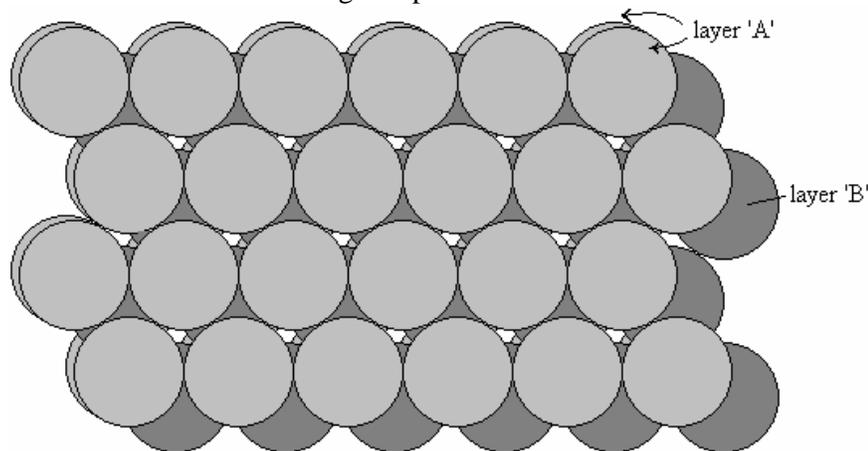
partially cover all the C-type voids around it; therefore other spheres cannot be placed over C-type voids. Similarly, if we choose to place spheres over C-type voids, no spheres can be placed over B-type voids. Thus the second layer can be placed either over B-type voids or over C-type voids only.

Let us place the second layer over the B-type voids. Then the spheres in this second layer will not be directly over the spheres in the 'A' layer. Therefore this is a new arrangement and we shall call this the 'B' layer. Note that the C-type voids are still not covered fully. These have now become **octahedral voids** surrounded by six spheres (three in layer 'A' and three in layer 'B'). There are also **tetrahedral voids**, surrounded by four spheres (one in layer 'A' and three in layer 'B'). Octahedral voids are larger than tetrahedral voids.

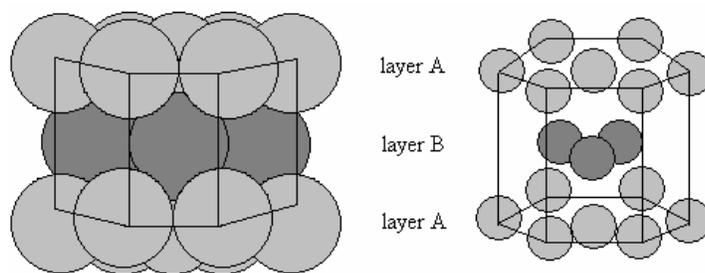


Extending the argument further, we shall now attempt to place a third layer of spheres over the second. This can be done in two ways. The third layer can be placed in such a way that all spheres in it are over the *tetrahedral* voids of the second layer, or in such a way that all spheres in it are over the *octahedral* voids of the second layer.

If the spheres are placed over the *tetrahedral* voids, they will be directly over the spheres in layer 'A', and the third layer will then be similar to layer 'A'. On repeating the process, the pattern 'ABABAB ...' will be repeated in the three dimensional lattice. This is represented in abbreviated form using the repeating unit AB as ' $\dots AB \dots$ ', where the *ellipsis* (...) indicates repetition. This type of close packing is known as **hexagonal close packing** or '*hcp*' (in three dimensions). The octahedral voids are aligned one behind the other in this arrangement, and so are the tetrahedral voids. This arrangement is called **hexagonal close packing** because the unit cells in this arrangement are in the form of a hexagonal prism.



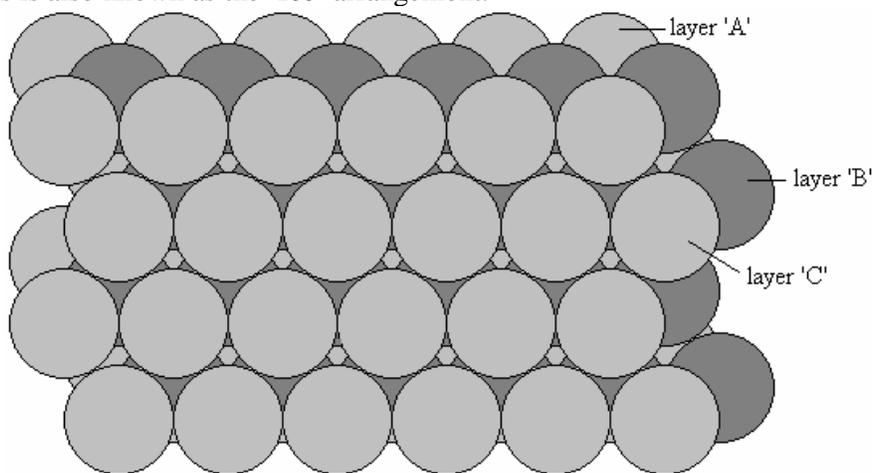
Hexagonal close packing. Note that the octahedral voids are never covered in this arrangement



The hexagonal unit cell in hcp

Side-view of hcp

If the spheres of the third layer are placed over the *octahedral* voids in the second layer, they will not be directly over any spheres either in layer 'A' or in layer 'B'. The third layer will then be a new arrangement which we shall call layer 'C'. On repeating the process, the pattern 'ABCABCABC ...' will be repeated in the three dimensional lattice. This is represented in abbreviated form using the repeating unit ABC as '... ABC ...'. This type of close packing is known as **cubic close packing** or '*ccp*' (in three dimensions). Tetrahedral and octahedral voids appear in alternate positions in this arrangement. Visualisation of the unit cell is not as easy as in the case of hcp, but the **unit cell in cubic closest packing is in the form of a face-centered cube**. Therefore this is also known as the '**fcc**' arrangement.



Cubic close packing in three dimensions. The octahedral holes between layers 'A' and 'B' are closed by spheres in layer 'C'

Coordination number of any sphere in the hcp or ccp arrangements: Any sphere is surrounded by six other spheres touching it in the same layer. It is also touching three spheres in the layer below (since it is sitting in a depression) and three spheres in the layer above. Thus any given sphere is touching $6+3+3 = 12$ other spheres. Therefore the coordination number or C.N. = 12.

Also note that other arrangements like '...ABAC...' or '...ABACBC...' etc are also possible, and the packing fraction in all these arrangements will be the same. In fact, an infinite number of such arrangements are possible. Also understand that '...AB...' is the same as '...BA...' and '...ABC...' is the same as '...BCA...' or '...CAB...' etc, but the number of layers to be mentioned in the repeating unit cannot be arbitrary. For example, although '...AB...' may also be written as '...ABAB...', it cannot be written as '...ABA...' (since on repeating, the pattern obtained will be 'ABAABA' etc and not 'ABABAB'). These abbreviated representations are also known as the **stacking formulae**. The minimum number of layers '*n*' that must be written in the stacking formula to correctly represent the repeating pattern is called the **identity period**. For example,

$$\begin{array}{ll} \text{'...ABAC...'} & n = 4 \\ \text{'...ABACBC...'} & n = 6 \end{array}$$

What are the identity periods for the *hcp* and *ccp* structures?

Note that as the identity period increases, the number of different arrangements possible also increases.

The Pauling notation

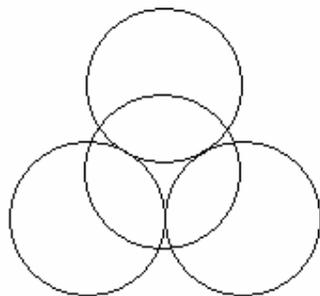
Pauling suggested another method for representing the stacking formula, based on the following rules:

- (1) Any layer having identical layers on both sides is represented by the letter 'h'.
- (2) Any layer having different layers on both sides is represented by the letter 'c'.

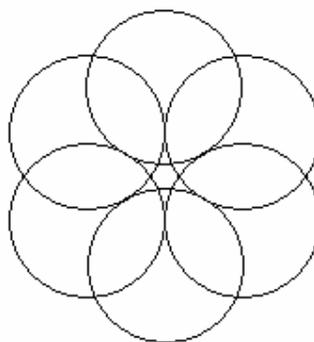
In '...AB...' arrangement, layer 'A' has identical layers 'B' on both sides and therefore is 'h'. Layer 'B' has identical layers 'A' on both sides and therefore is also 'h'. Thus the '...AB...' arrangement is represented as '...hh...' in Pauling notation. In the '...ABC...' arrangement, layer A has C on the left and B on the right, and is therefore represented by 'c'. Layer B has A on the left and C on the right, and is therefore represented by 'c'. Thus the '...ABC...' arrangement is represented as '...ccc...' in Pauling notation. You will note that for the '...hcc...' arrangement, three letters are not sufficient to represent the identity period in the ABC notation. Thus *one defect of the Pauling notation is that the identity period is not clear without converting to the ABC notation.*

Voids in closest packings

Significance of voids: Although an infinite number of closest packings are theoretically possible, only a few arrangements like *hcp* and *ccp* actually occur in nature. Further, in most inorganic compounds, the cations are much smaller than the anions. Therefore the large anions touch each other in closest packing and the cations are found in the voids formed in them. The size of the voids determines the size of the cations that can be accommodated in them. Metals like platinum, palladium and nickel (which are common catalysts in hydrogenation reactions) have the ability of absorbing large amounts of hydrogen gas. This process is known as **occlusion**. The small hydrogen molecules are accommodated in the voids of the metal structure. In crystal defects like the Frenkel defect, small cations are dislodged from the lattice positions into suitable voids. Foreign atoms or ions (impurities) present in the crystal voids give rise to formation of alloys, solid solutions and modify the properties of semiconductors. The presence of such interstitial ions can be studied using recent techniques like paramagnetic resonance, and requires a knowledge of the environment in which they are present.



Tetrahedral void



Octahedral void

Classification of voids: Only two types of voids are seen in the hcp and ccp (or fcc) arrangement. As already discussed, these are the tetrahedral and octahedral voids. Cubic voids occur in more open packings such as an extension of the square packing in three dimensions. The names come from the coordination number of a particle placed within the void. A particle within a tetrahedral void will be touching four other particles (C.N. = 4), the one within an octahedral void touches six other particles (C.N. = 6), and the one within a cubic void touches eight other particles (C.N. = 8; e.g. that of the central particle in a body-centered cube or *bcc*). Other less common voids are the triangular void (C.N. = 3) and the cuboctahedral void (C.N. = 12).

Relationship between the numbers of particles and voids: If you examine the hcp or ccp structure closely, you can see that any sphere in the 'A' layer is surrounded by six triangular voids. When a sphere is placed over any of them in the second layer, three of these become tetrahedral voids and three of them become octahedral voids. Similar is the case with the (3rd) layer above it also. Thus any sphere is surrounded by 6 octahedral voids (3 in the lower layer and 3 in the upper layer). Since each octahedral void is surrounded by 6 spheres, only $\frac{1}{6}$ of a void belongs to each sphere. Thus

$$\text{Number of octahedral voids per sphere} = 6 \times \frac{1}{6} = 1.$$

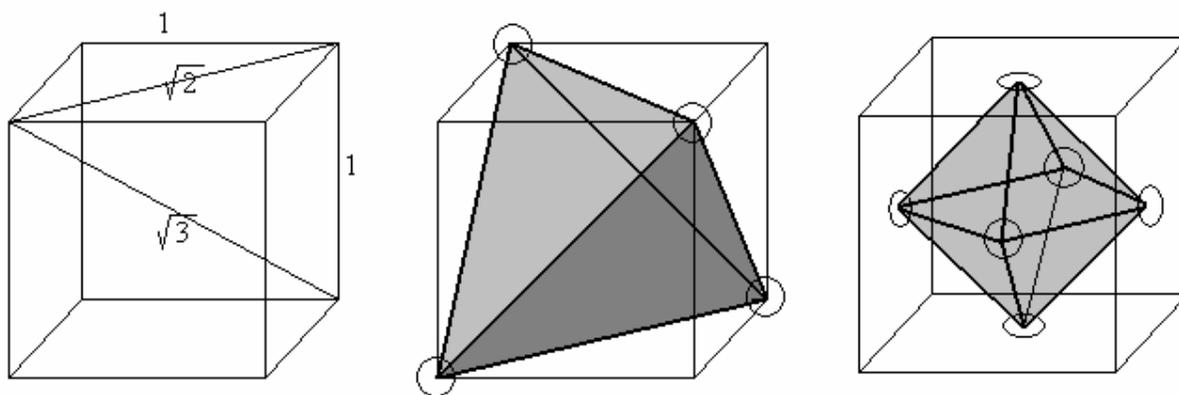
Similarly, there are 6 tetrahedral voids (3 in the lower layer and 3 in the upper layer) around any sphere. In addition, the sphere being considered is itself sitting in a tetrahedral void in the layer below and above. Thus there are $6+2 = 8$ tetrahedral voids around a sphere. Each void is shared by 4 spheres. Therefore

$$\text{Number of tetrahedral voids per sphere} = 8 \times \frac{1}{4} = 2.$$

In other words, the number of octahedral voids is equal to the number of spheres.

The number of tetrahedral voids is double the number of spheres.

The number of tetrahedral voids is double the number of octahedral voids.



Some facts about a cube will help further discussion.

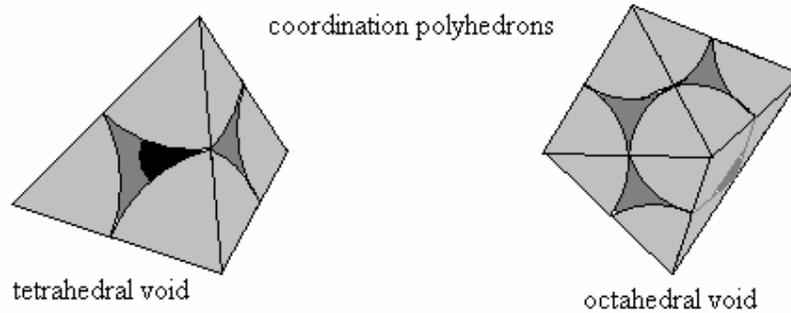
The diagonal in a square of side 1 unit is $\sqrt{2}$. The face of a cube is a square. Therefore in a cube of side 1, the face diagonal is $\sqrt{2}$. The body diagonal then will be $\sqrt{3}$.

A tetrahedron can be inscribed in a cube by joining the alternate corners.

An octahedron can be inscribed in a cube by joining the face centres.

Coordination of voids: The number of spheres surrounding a void is called the coordination number of that void.

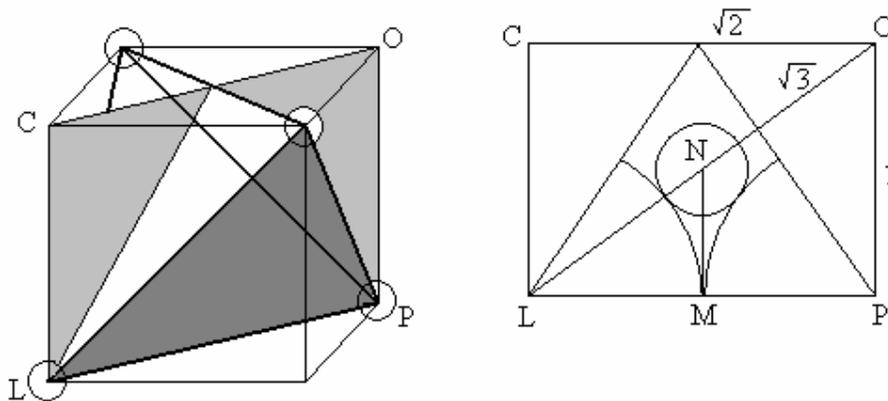
Coordination polyhedron: If the centres of the spheres surrounding a void are joined by straight lines, we get the coordination polyhedron of that void. This will clearly indicate all the spheres which are in contact with a sphere occupying that void.



Radius ratios: If a tightly fitting sphere is placed inside a void, it will just touch all the spheres in the coordination polyhedron of the void. Then *the ratio of the radius of the sphere inside the void (usually a cation) to the radius of the spheres surrounding it (usually anions) is called the radius ratio of that void.*

Example: Calculate the radius ratio for a tetrahedral void.

Imagine the coordination polyhedron to be inscribed in a cube as shown. Consider the cross section along the diagonal plane indicated.



If the radius of the sphere inside the void is 'r' and the radius of the larger sphere is 'R', then

$$LN = R + r \qquad LM = \frac{\sqrt{2}}{2} \quad \text{and} \quad LN = \frac{\sqrt{3}}{2}$$

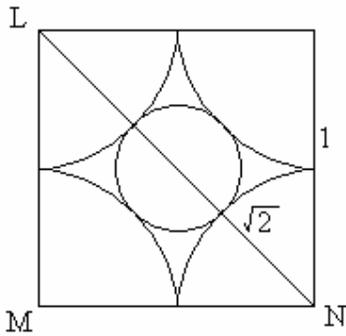
$$\frac{LM}{LN} = \frac{R}{R + r} = \frac{\sqrt{2}}{\sqrt{3}}$$

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

$$(\sqrt{3} - \sqrt{2}) R = \sqrt{2} r$$

$$\frac{r}{R} = \frac{(\sqrt{3} - \sqrt{2})}{\sqrt{2}} = 0.225$$

Example: Calculate the radius ratio for an octahedral void.



$$LM = 2R \text{ and } LN = 2(R + r)$$

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

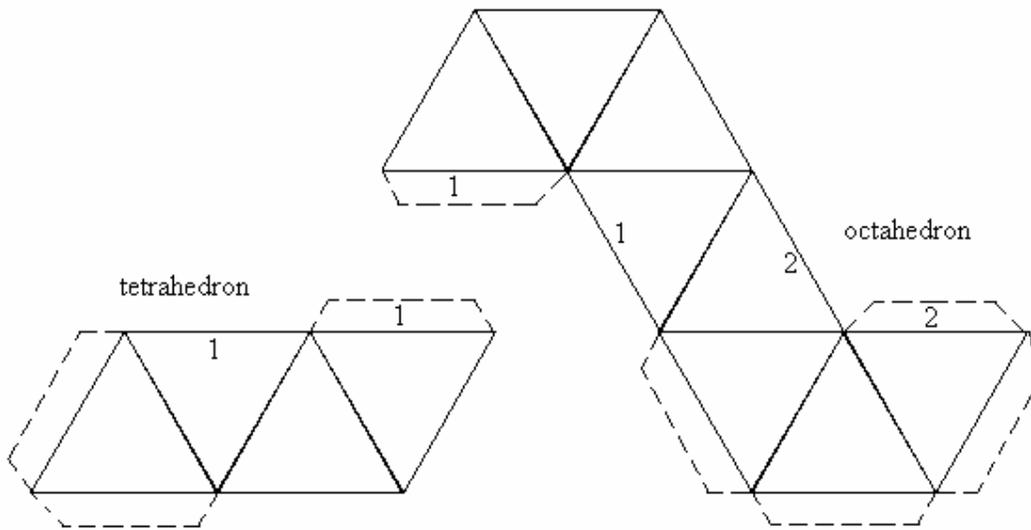
$$\sqrt{2} R = R + r$$

$$(\sqrt{2} - 1)R = r$$

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

Assignment:

On a suitable piece of thick paper (use chart paper or old wedding cards), draw figures having all triangles of equal sides as given below. Cut out the figures including the dotted part, fold and paste along the dotted area such that 1 and 1 are joined together etc. to make models of a tetrahedron and an octahedron. Study their shapes and properties.



The radius ratio rule (What is the importance of radius ratio?):

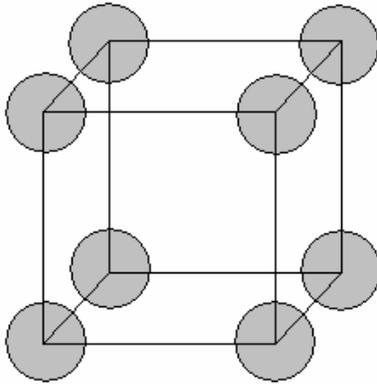
The calculated radius ratios are for exact fit, and this is sometimes called the **critical radius ratio**. If the sphere inside the void is smaller than the critical radius ratio, then it will not touch all the spheres in the coordination polyhedron. On the other hand, if the sphere inside the void is larger, it will not only touch all the spheres in the coordination polyhedron, but will push them out slightly so that the closest packing of the larger spheres is not possible. Since an octahedral void is larger than a tetrahedral void, a sphere with exact fit for an octahedral void cannot be accommodated in a tetrahedral void. Thus the structure and type of close packing is determined by the ratio of the radii of cations to anions when both are present in the solid. When the cations become larger and larger, higher coordination numbers become possible (it can touch more spheres). But note that there are no radius restrictions for coordination numbers 1 and 2.

Coordination number as a function of radius ratio

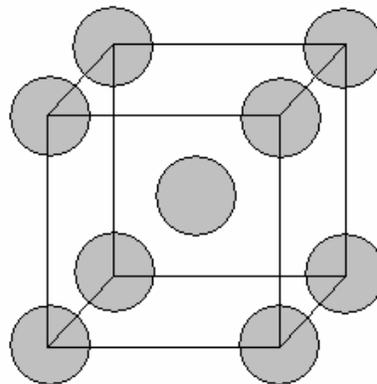
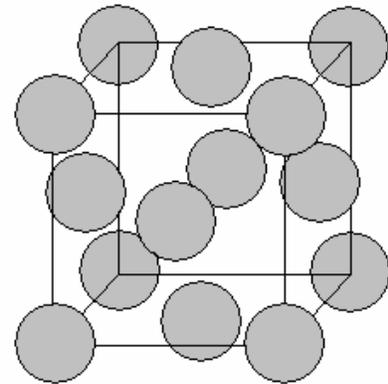
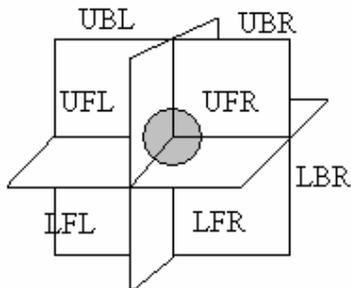
| Radius ratio for stable coordination | Packing | Coordination No. |
|--------------------------------------|----------------------|------------------|
| 0.0 – 0.155 | linear | 2 |
| 0.155 – 0.225 | triangular | 3 |
| 0.225 – 0.414 | tetrahedral | 4 |
| 0.414 – 0.732 | Octahedral or square | 6 or 4 |
| 0.732 – 1.0 | cubic | 8 |
| 1.0 | hcp | 12 |
| 1.0 | fcc (ccp) | 12 |

Other types of packings

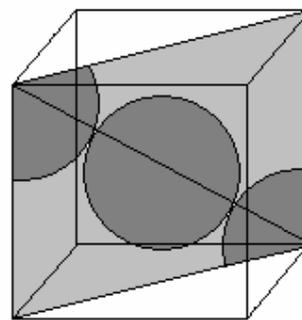
With spheres of unequal sizes (eg. anions and cations), other types of packing are also possible. Examples are the simple cubic and body-centred cubic packings.



simple cubic

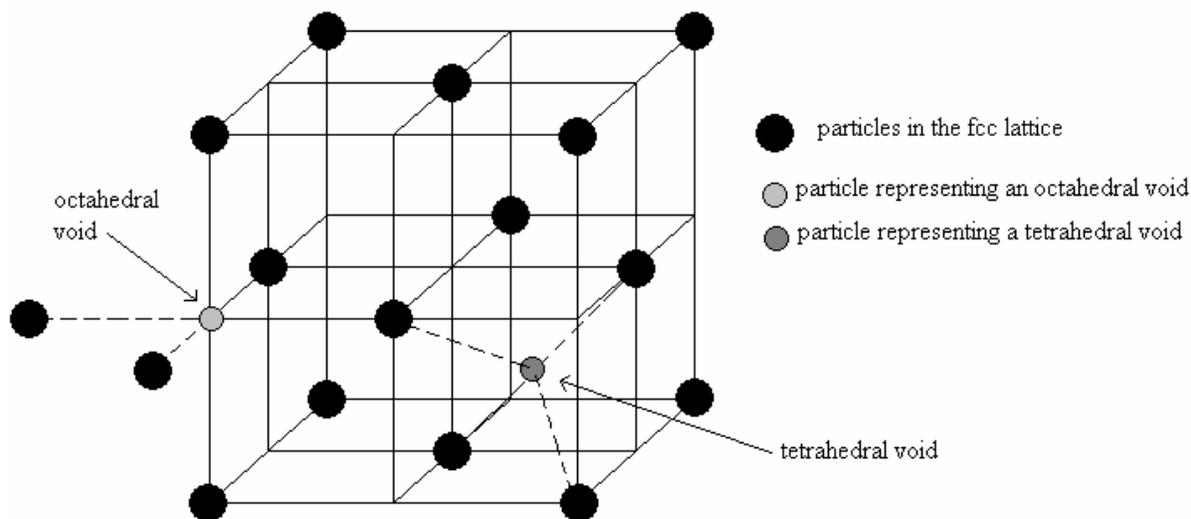
body-centred cubic
(bcc)face-centred cubic
(fcc = hcp)

A particle at the corner of a cube is shared by 8 cubes



bcc

Where are the octahedral and tetrahedral voids in a face-centred cubic unit cell?



Note that the black spheres in the large cube shown above make a face-centred cubic unit cell. (In reality, the spheres will be touching each other, and there will be no lines in the crystal structure. The spheres are drawn far apart with lines connecting them only to make the relationships clear). These spheres are joined by lines to form eight smaller cubes, representing corner positions of the unit cell.

Now, imagine another particle to be placed at the centre of the large cubic unit cell (body-centre position). Then note that it will have six black spheres around it (left, right, above, below, front, back). In other words, the new particle is in an octahedral void! Similarly, imagine a ‘foreign’ particle placed at the centre of one edge of the cube (shown in the figure). This particle is also surrounded by six black spheres (the ones on the left and front belong to other unit cells). This means that this new particle is also in an octahedral void.

The octahedral voids are at the edge-centres and at the body-centre of the fcc unit cell.

Imagine a ‘foreign’ particle placed at the centre of one of the smaller cubes (shown in the figure). It has four black spheres as its nearest neighbours (at alternate corners of the small cube). That is, the new particle is now sitting in a tetrahedral void.

The tetrahedral voids are at the centres of the eight corner-cubes of the fcc unit cell.

The total number of particles belonging to a unit cell in the fcc arrangement is four. It is easily seen that there are **eight tetrahedral voids in the unit cell**. Each of them lies entirely within the unit cell and belongs to it completely. The octahedral void at the centre of the unit cell is not shared and belongs completely to the unit cell. Each edge of the unit cell is shared by four other unit cells. Therefore only one-fourth of each octahedral void at the edge belongs to the unit cell, but there are twelve such edges in a cube. Thus the total number of octahedral voids belonging to the unit cell is $1 + 12 \times \frac{1}{4} = 1 + 3 = 4$. There are **four octahedral voids in a unit cell**. Thus the number of octahedral voids is the same as the number of particles and the number of tetrahedral voids is double the number of particles in fcc arrangement. This result is the same as that obtained earlier using another method.

Since we have now understood the basic principles of crystal geometry, we shall now have a look at the crystal structures of some of the common inorganic compounds which are predominantly ionic in character. Such structures must conform to the following rules:

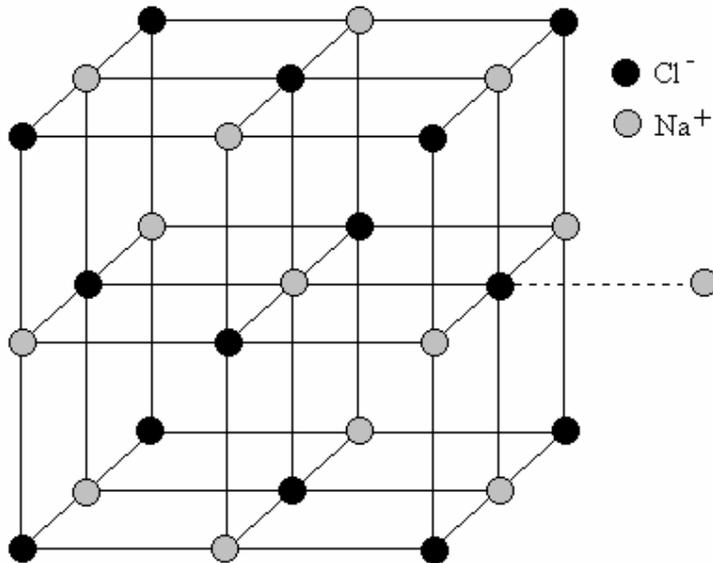
- (1) Radius ratio rules
- (2) Overall neutrality of total charge
- (3) Stoichiometry. ie. number of cations and anions must agree with the molecular formula for the compound.

THE 'AX' TYPE CRYSTAL STRUCTURES

(These have equal number of anions and cations).

The rock salt structure:(Sodium chloride structure)

Crystalline sodium chloride deposits are found in some places on land in the form of rocks. Hence the name.



A unit cell of NaCl is shown in the figure (The smaller cubes cannot be considered as unit cells because if the first cube is repeated on the right, a sodium ion appears in the place of a chloride ion). One may think of it as a face-centred cubic lattice (ccp) of chloride ions with Na⁺ ions in all the octahedral voids (edge-centres and body centre). Or one can equally well imagine a face-centred cubic lattice (ccp) of sodium ions with Cl⁻ ions in all the octahedral voids. Both are equally valid. It is also sometimes described as two interpenetrating hcp lattices of sodium and chloride

ions, but some authors disagree with such description. Since Cl⁻ ions are almost double the size of Na⁺ ions, the first description is better.

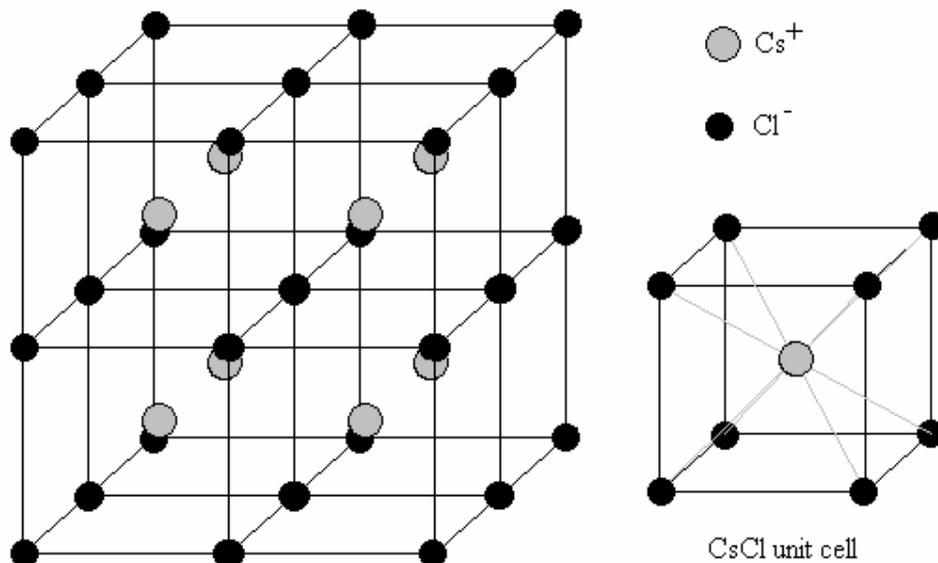
The coordination numbers of both chloride ions and sodium ions is six (6:6 coordination). For precise fitting in an octahedral void, the radius ratio must be 0.414, but the actual radius ratio of Na⁺/Cl⁻ is 0.525. Therefore the chloride ions in the lattice have to move apart slightly to accommodate the sodium ions. There are four sodium ions and four chloride ions (equal numbers) in a unit cell; therefore the ratio of cation to anion is 1:1, and the formula is NaCl.

*If two different substances have the same crystal structure, then the substances are said to be **isomorphous**. The phenomenon is called **isomorphism**. The phenomenon by which the same compound exists in more than one crystal structures is called **polymorphism**.*

Some other compounds having the rock salt structure are halides and hydrides of Li, Na, K, and Rb, cesium fluoride (CsF), AgCl, AgBr and NH₄Cl; oxides of alkaline earth metals (MgO, CaO, SrO, BaO) and FeO. In FeO, the oxide ions (O²⁻) are arranged in ccp, and Fe²⁺ ions occupy the octahedral voids. But FeO is a **non-stoichiometric compound** having the composition Fe_{0.95}O. This can be explained by assuming that some of the Fe²⁺ ions are missing and a few other Fe²⁺ ions change to Fe³⁺ ions in order to maintain charge neutrality.

Cesium chloride structure:

In the cesium chloride unit cell, the chloride ions are at the corners of a cube (they are in 3D square close packing arrangement) with the cesium ions at the centre of the cube. Since the cesium ions are large, they occupy cubic voids in a 3D square close packing arrangement. The unit cell is thus a body-centered cube. There are 8 chloride ions around each cesium ion and 8 cesium ions around each chloride ion (see the chloride ion at the center of the larger cube). Thus the coordination number of each ion is eight (8:8 coordination). There is one ($8 \times \frac{1}{8} = 1$) chloride ion and one cesium ion (body center) in a unit cell. The ratio of ions is thus 1:1; therefore formula is CsCl.

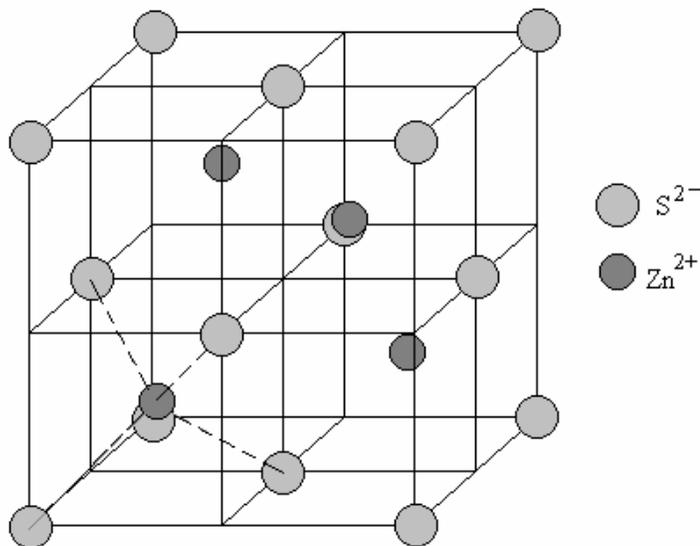


The cesium chloride structure is also exhibited by CsBr and CsI (CsF has the rock salt structure). Thallium chloride and bromide also have this structure. NH_4Cl has this structure at low temperature.

The zinc blende structure:

This structure is also known as the **sphalerite structure** or the **cubic zinc sulphide structure**.

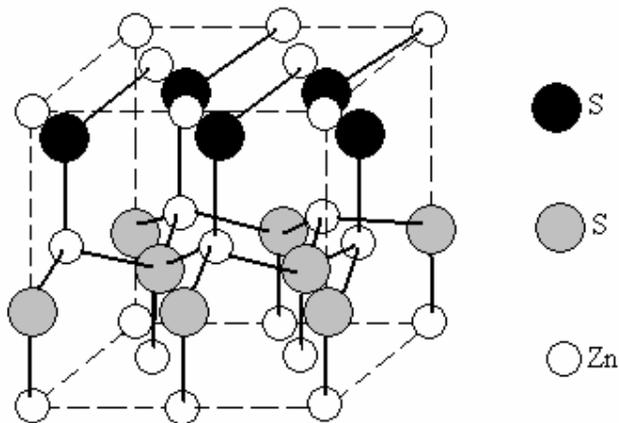
A unit cell is shown in the figure. In this structure, the sulphide ions (S^{2-}) are in a face-centered cubic close packing (ccp) with the Zn^{2+} ions occupying only half of the available tetrahedral voids (they are at the centers of the four alternate smaller cubes). For correct fit, the radius ratio of $\text{Zn}^{2+}/\text{S}^{2-}$ should be 0.225, but the actual ratio is 0.4. Therefore the sulfide ions are forced apart and do not actually touch each other. Each Zn^{2+} ion is tetrahedrally surrounded by four S^{2-} ions, and each S^{2-} ion is tetrahedrally surrounded by four Zn^{2+} ions (4:4 coordination). There are four Zn^{2+} ions and four S^{2-} ions in a unit cell. The ratio of the ions is thus 1:1; therefore formula is ZnS .



Cuprous chloride, bromide and iodide (CuCl , CuBr and CuI) also have this structure.

The wurtzite structure

This is another type of structure in which zinc sulphide naturally occurs. This structure is also known as **hexagonal zinc sulphide structure**, or the **zinc oxide structure**. The phenomenon in



Wurtzite

which a single compound (having same molecular formula) exists in different crystal forms is called **polymorphism**. The different varieties of the same compound are then known as *polymorphs* or *polymorphic modifications*. Thus zinc sulphide exhibits polymorphism, sphalerite and wurtzite being the polymorphic modifications.

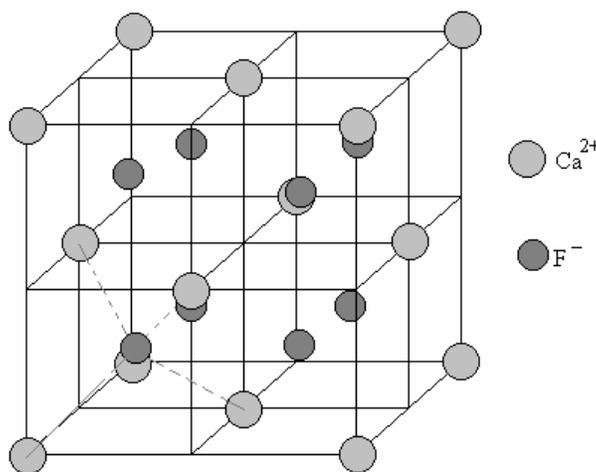
While the sulphide ions are in ccp (...ABC...) arrangement in sphalerite, they are in hcp (...AB...) arrangement in wurtzite (hence the name "hexagonal" zinc sulphide structure). In the figure, the grey layer represents the

'A' layer of sulphide ions and the black layer represents the 'B' layer of sulphide ions. In both cases, the zinc ions are occupying tetrahedral voids. Both Zn^{2+} and S^{2-} ions have tetrahedral (4:4) coordination. Since only half of all the tetrahedral voids are occupied, there are equal numbers of Zn^{2+} and S^{2-} ions. The structure resembles the structure of diamond. Hexagonal rings in the chair form with alternate positions occupied by Zn^{2+} and S^{2-} ions can be easily found in the structure (very clear in the grey layer in the figure). In diamond, all the six positions in the ring are occupied by carbon atoms. In diamond, the atoms are covalently bonded, but in wurtzite, there are only ionic bonds. AgI, ZnO and aluminium nitride (AlN), NH_4F , SiC, BeS, MnS, CdS and HgS are some other compounds having the wurtzite type of crystal structure.

THE 'AX₂' TYPE CRYSTAL STRUCTURES

1. Fluorite (CaF₂) structure

In CaF_2 , the Ca^{2+} ions have a *fcc* arrangement similar to that of S^{2-} ions in zinc blende (sphalerite). All the eight tetrahedral voids are occupied by fluoride ions. [Note that the **large cations** are in *ccp* and the **small anion** F^- is in voids]. The F^- ions are at the centers of each of the eight smaller cubes in the following figure, which represents a unit cell of fluorite. Each Ca^{2+} ion is surrounded by eight F^- ions, and each F^- ion is surrounded by four Ca^{2+} ions. The coordination is thus 8:4.



Fluorite

The number of Ca^{2+} ions in the unit cell (*fcc* arrangement) = 4. Number of F^- ions in the unit cell (all within the cube) = 8. Thus cation : anion = 4:8 or 1:2. The formula is thus CaF_2 . There are four CaF_2 units in the unit cell.

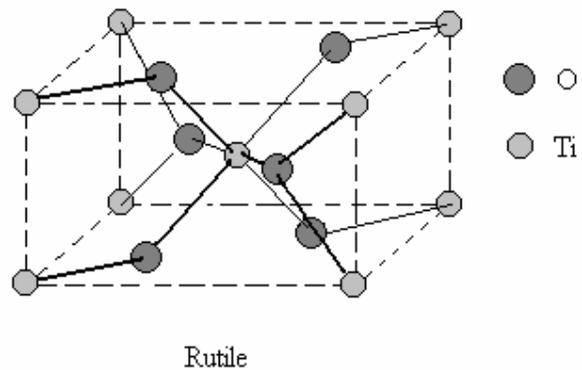
Other compounds which have the fluorite structure are alkaline earth metal fluorides (SrF_2 , BaF_2), BaCl_2 , fluorides of cadmium, mercury and lead (CdF_2 , HgF_2 and PbF_2) and dioxides of cerium, thorium, uranium, zirconium and hafnium (CeO_2 , ThO_2 , UO_2 , ZrO_2 and HfO_2).

2. The antifluorite structure

If the positions of anions and cations in the fluorite structure are reversed, we get the antifluorite structure (A_2X type). The anions make up the *fcc* arrangement with cations occupying all the tetrahedral voids. The coordination will be 4:8. There will be eight cations and four anions in every unit cell (4 formula units). Examples are the alkalimetal oxides and sulphides (Li_2O , Li_2S , Na_2O , Na_2S etc. upto Rb). Alloys like Mg_2Si and Mg_2Sn also have this structure.

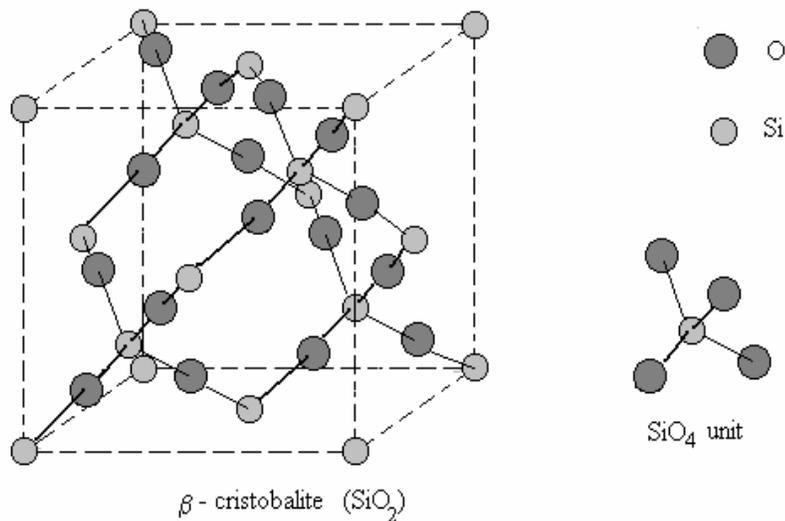
3. The rutile (titanium dioxide, TiO_2) structure

TiO_2 crystallises in three different forms, anatase, brookite and rutile. Rutile has the tetragonal symmetry ($a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$). The coordination number of Ti^{4+} is six (octahedral) and the coordination number of O^{2-} is three (equilateral triangle) i.e. 6:3. The number of Ti^{4+} ions in a unit cell is $8 \times \frac{1}{8} + 1 = 2$ and that of O^{2-} is $4 \times \frac{1}{2} + 2 = 4$. Thus there are two TiO_2 units per unit cell. This structure is also found in the dioxides of Cr, Mn, Ge, Ru, Rh, Sn, Os, Ir, Pt and Pb.



4. The β -cristobalite structure (SiO_2 structure)

Silicon dioxide crystallizes in several forms, of which one is the β -cristobalite structure. One may think of this as the zinc blende structure in which all positions occupied by zinc and sulphur together are occupied by silicon atoms, with oxygen atoms between every two silicon atoms. This structure has cubic symmetry for the unit cell. 14 Si^{4+} ions (8 corners + 6 face centers) make a *fcc* lattice. Four tetrahedral SiO_4 units are placed towards the alternate corners of this cube. One O^{2-} ion in each SiO_4 unit points towards a Si^{4+} ion at the corner of the cube. The remaining three O^{2-} ions point towards the nearest Si^{4+} ions at the face centers. The coordination number of each Si^{4+} ion is 4

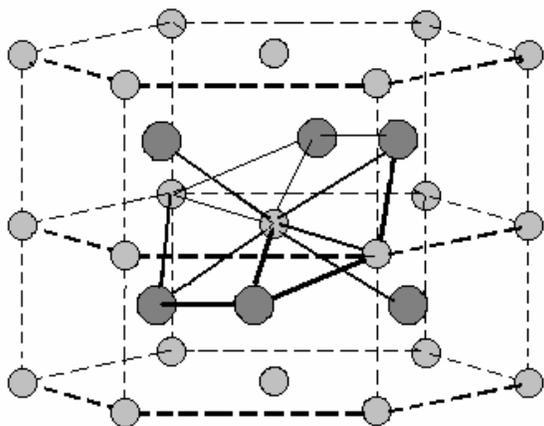


(tetrahedrally surrounded by O^{2-} ions). The coordination number of each O^{2-} ion is 2. The Si-O-Si bond angle is less than 180° . The total number of Si^{4+} ions is $(8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4)$ eight. All the O^{2-} ions are fully within the cube, thus 16. Therefore there are eight SiO_2 units in the unit cell. BeF_2 , $ZnCl_2$, $Be(OH)_2$, $Zn(OH)_2$ and GeO_2 also have the β -cristobalite structure.

Another form of SiO_2 , **tridymite**, is related to wurtzite in the same way as the β -cristobalite structure is related to sphalerite.

THE ' A_mX_2 ' TYPE CRYSTAL STRUCTURES

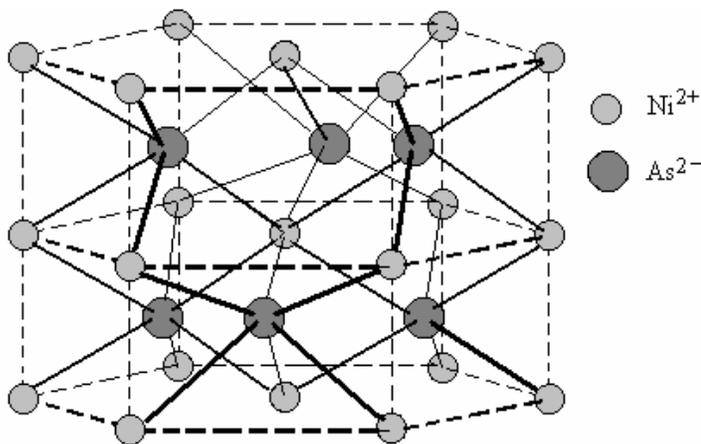
The nickel arsenide structure



Some of the lines removed to bring out the 8-fold coordination of the Ni ion

In this structure, the Ni^{2+} ions are in *hcp* arrangement, with As^{2-} ions occupying all the octahedral holes (the effect will be the same even if we assume that the As^{2-} ions are in *hcp* arrangement, with Ni^{2+} ions occupying all the octahedral holes). The unit cell is hexagonal, with alternate layers of Ni^{2+} ions and As^{2-} ions. Each As^{2-} ion is surrounded by six Ni^{2+} ions (three above and three below, in the form of a trigonal prism); therefore coordination number of arsenic is 6. The Ni^{2+} ion is surrounded hexagonally by four As^{2-} ions and two Ni^{2+} ions. In addition it has one As^{2-} ion above and one below it. This can be clearly seen from the following figure in which the connecting lines have been removed for clarity. Thus the coordination number of

nickel is eight (8:6 type coordination). Arsenic is a metalloid, and the electronegativities are small. The sizes of Ni^{2+} ions and As^{2-} ions are not very different. Therefore such crystals show many of the characters of a true metal rather than that of a compound. In addition, there can be some covalent character in the bonds, and the coordination numbers are also fairly large. Therefore the structure will be fairly stable even if some of the ions are missing, or replaced by ions of opposite charge. Therefore this kind of a crystal structure is exhibited by compounds having widely varying formulae like FeS_2 , Sb_2S_3 , Co_3S_4 , Cr_6S_7 , CuS , Co_9S_8 , Cu_9S_5 , Ni_3S_2 , Cu_2S etc. (Hence defined as the ' A_mX_2 ' type).

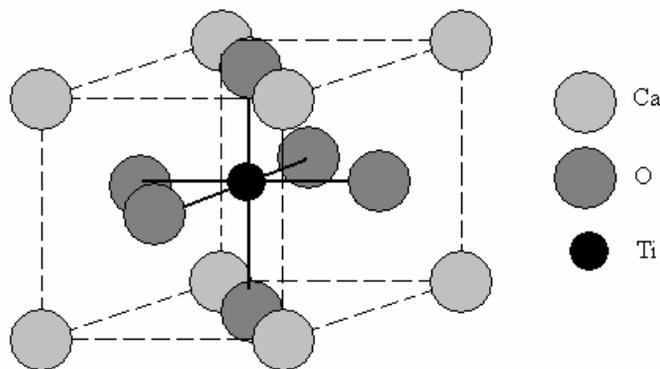


Hexagonal structure of Nickel arsenide

THE 'AXO₃' TYPE CRYSTAL STRUCTURES

1. The perovskite structure

Perovskite is the mineral name of calcium titanate, CaTiO₃, and therefore its structure is representative of mixed oxides of two metals 'A' and 'X', in the ratio A:X:O = 1:1:3. 'A' is in the +2 oxidation state and 'X' is in the +4 oxidation state. Note that all particles at the corners of a cubic unit cell together amount to 1 particle. Similarly, a particle at the body centre of a cube counts as 1 particle,



The perovskite structure

while all the particles at the face centers of a cube amount to 3 particles. Thus if metal atoms of type 'A' are present at the corners of a cube, with a metal atom of type 'X' at the body centre and the oxygen atoms at the face centres, then the ratio required by the chemical formula can be satisfied. Such a situation is seen in the perovskite structure. This structure is adopted when the two different metal ions involved (eg. Ca²⁺ and Ti⁴⁺) differ appreciably in their sizes. A large number of oxides like SrTiO₃, BaZrO₃, and BaTiO₃ have this structure and also fluorides like KMgF₃.

2. The Ilmenite structure

Ilmenite is iron titanate, FeTiO₃, which is the largest source of titanium. Both metal atoms belong to the transition series and are similar in size. This structure is found when both metal ions are about the same size. Ilmenite structure consists of a lattice of oxygen atoms in hexagonal close packing. Ti⁴⁺ ions occupy one-third of the octahedral voids and Fe²⁺ ions occupy another one-third of the octahedral voids. If both metal ions in ilmenite are replaced by Fe³⁺ ions, we get the **hematite** (Fe₂O₃). If both metal ions are replaced by Al³⁺ ions, we get the **corundum** (Al₂O₃).

NORMAL SPINELS AND INVERSE SPINELS

Spinels are compounds (mixed metal oxides) having the general formula AB₂O₄, where 'A' is a metal in the +2 oxidation state (usually an alkaline earth metal) and 'B' is a metal in the +3 oxidation state (usually a transition metal or Al). Eg. MgAl₂O₄. In the spinel structure, the oxide ions are arranged in the form of a face-centered cubic lattice. [From the formula, we see that the number of 'A' atoms is one-fourth the number of oxygen atoms and the number of 'B' atoms is half the number of oxygen atoms. Further, remember that the number of particles in an *fcc* unit cell is 4. Then there are the same number of octahedral voids and double that number of tetrahedral voids]. The 'A' atoms occupy one-eighth of all the tetrahedral voids and the 'B' atoms occupy half of all the octahedral voids in the oxygen lattice. Thus the formula becomes AB₂O₄. This type of an arrangement is called the **normal spinel structure**. ZnFe₂O₄, FeCr₂O₄ and NiAl₂O₄ are other examples of normal spinels.

Since many of the voids are not occupied, the repeating unit (unit cell) in the spinel structure is quite large. One can imagine it to be a supercube consisting of 8 units of zinc blende type, where the sulphide ions are replaced by oxide ions. Thus there are 4 × 8 = 32 oxide ions in the unit cell. Then there should be 32 octahedral voids and 64 tetrahedral voids in it. Of these, only 8 tetrahedral voids are occupied by 'A' type metal atoms and 16 octahedral voids by 'B' type metal atoms. Thus there are **eight formula units in a unit cell**. The coordination number of 'A' atoms is 4 and that of

'B' atoms is 6. In the rock salt structure, the sodium ions are in the octahedral voids in a chloride lattice, and in the zinc blende structure, the zinc ions are in the tetrahedral voids in a sulphide lattice. The spinel structure can therefore be considered as a mixture of rock salt and zinc blende structures.

Classification of spinels: The spinel structure is adopted by a large number of crystals having a variety of atoms present in different ratios. These are classified according to their composition, mainly depending on the 'B' type metal atoms. For example, those conforming to the formula MA_2O_4 are called **aluminates**, MFe_2O_4 are called **ferrites**, M_2TiO_4 are called **titanates** etc. According to the compositional formula AB_2O_4 , the total positive charge of the two cations must total to +8. It is possible to satisfy this condition by combinations of +2 and +3 ions (eg. MA_2O_4), or +2 and +4 ions (eg. M_2TiO_4) etc. They are then classified as **2-3 spinels**, **2-4 spinels** and so forth.

The type of voids occupied by the metal ions may be explained on the basis of the number of electrons in the d-orbitals and the resultant CSFE, and the preferred coordination numbers of the metal ions. It is usually observed that divalent ions such as M^{2+} usually prefer a coordination number of 4 (eg. $[Be(H_2O)_4]^{2+}$, $[Ni(CN)_4]^{2-}$ etc.) and trivalent ions prefer a coordination number of 6 (eg. $[Al(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.). Therefore the divalent metal ions prefer the tetrahedral voids, and the trivalent ions prefer octahedral voids.

Inverse spinels or inverted spinels: It is very interesting to note that *there are many spinels in which the positions of 'A' and 'B' are reversed! These are known as inverse spinels.* In such spinels, the 'B' atoms occupy one-eighth of all the tetrahedral voids. Equal numbers of 'A' and 'B' atoms occupy half of the octahedral voids. The net effect is that half of the 'B' atoms in a normal spinel have exchanged places with 'A' atoms. Therefore the formula of such spinels may be more aptly written as $B(AB)O_4$ instead of AB_2O_4 . Most spinels of the 'ferrite' type (MFe_2O_4) are found to be inverse spinels. This is probably because the CSFE of Fe^{3+} (high-spin d^5 system) is zero for both tetrahedral and octahedral coordination; it thus has no site preference. Then the voids occupied are determined by the divalent metal ion. $NiFe_2O_4$ and $MgFe_2O_4$ are examples. **The structure of magnetite** ($Fe_3O_4 = FeFe_2O_4$) **is also that of an inverse spinel.** Here the divalent ion and the trivalent ion are both of the same atom. The composition may be represented as $Fe^{2+}(Fe^{3+}Fe^{2+})O_4$ [compare with $B(AB)O_4$]. *But Mn_3O_4 has a normal spinel structure.*

Many spinels are also known in which the structure is intermediate between that of a normal spinel and an inverse spinel. In such cases, an arbitrary fraction of 'B' ions go into the tetrahedral voids. This fraction is usually designated as λ , with the value of λ varying from 0 (in normal spinels) to 0.5 (in inverse spinels). Since many of the voids are not occupied, defects caused by the presence of foreign ions in these voids, presence of Frenkel type defects etc. are very common in spinels. Migration of ions through the voids or interstitial positions give rise to interesting electrical conductivity in such crystals. They also have interesting magnetic properties.

DISORDER IN CRYSTALS

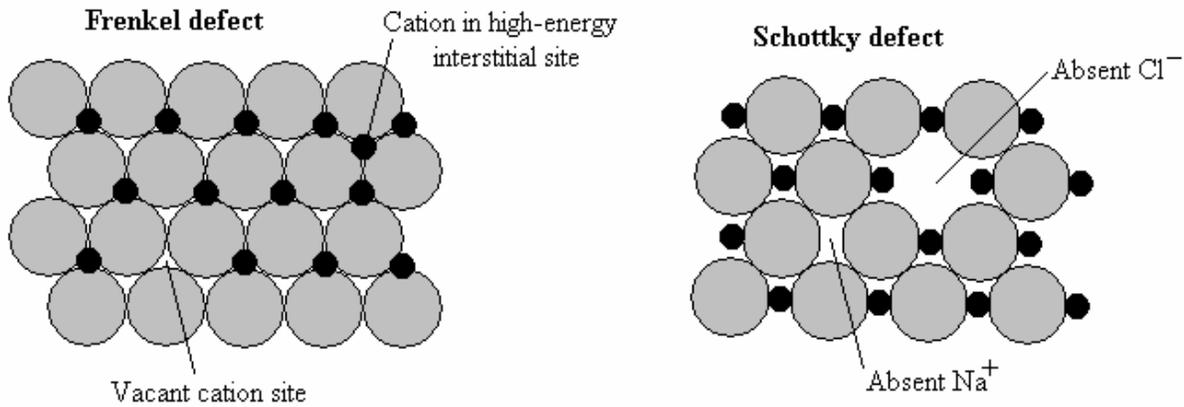
The perfectly ordered arrangement of particles in the crystal structures are found only at the lowest energy state of the crystal. Thus the atoms, ions or molecules are expected to be at their equilibrium lattice points only at or near a temperature of absolute zero. At any higher temperature, entropy effects may offset enthalpy effects, and many of the particles may deviate from their ideal positions in the lattice and the structure of the crystal tends to become more disordered. At temperatures above absolute zero, the particles have thermal energy leading to vibrations that may cause dislocations or imperfections. Such changes are called **order-disorder transitions**. *During such changes, the voids or spaces between particles may become temporarily larger, permitting the ions*

to be displaced and may even allow them to migrate through the crystal structure. The phenomenon thus gives rise to crystal defects, electrical conductivity by the migrating ions and solid-state reactions. At very high temperatures, increasing disorder leads to melting of the crystal, and to vapourisation at still higher temperatures. But even in the solid state itself, several order-disorder processes are possible, such as **electronic** (insulator to semiconductor or conductor), **magnetic** (ferro to antiferromagnetic or ferrimagnetic to paramagnetic etc.) or **structural** (one crystal structure to another). Generally, the most commonly observed order-disorder processes are structural changes or defects involving lattice positions. Since energy is required for an order-disorder process (the particle migrating from one void to another must push apart particles in the lattice points on its way), **such processes are endothermic** and often accompanied by changes in heat capacity of the material.

Mechanisms of order-disorder transitions

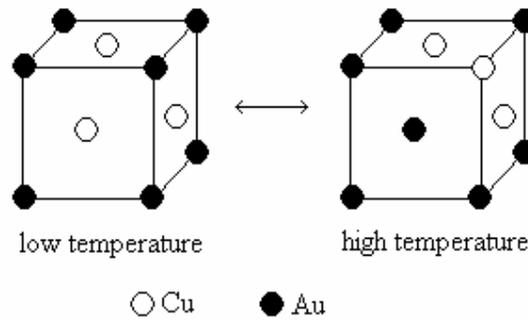
Five basically different mechanisms have been identified for such transitions in a stoichiometrically pure 'AB' type compound (where 'A' is the cation and 'B' is the anion).

- (1) Displacement of some of the 'A' atoms to interstitial sites, producing an equal number of A-type vacancies. This is commonly known as **Frenkel defect**.
- (2) Displacement of some of the 'B' atoms to interstitial sites, producing an equal number of B-type vacancies. This is also Frenkel defect, *but not very common as the large anions cannot be easily accommodated in the interstitial positions*. But it becomes possible when cations and anions are of similar size.



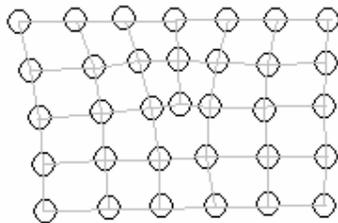
- (3) Missing 'A' and 'B' atoms. This is also explained as creation of equal number of A- and B-type vacancies (so that electrical neutrality is preserved) by the migration of atoms to the crystal surface. This is the most commonly observed defect called **Schottky defect** or sometimes **Schottky-Wagner defect**.
- (4) Creation of equal numbers of interstitial A and B atoms and A- and B-type vacancies. This defect probably never occurs as such, but may appear in combination with other defects.
- (5) Interchange of A and B atoms in the structure so that some of the A atoms occupy B sites and an equal number B atoms occupy A sites. The name '**antistructure disorder**' has been suggested for this mechanism. This type of disorder is rare in ionic crystals because this would bring ions of like charge next to each other. But it occurs quite frequently in alloys at elevated temperatures.

An example for (5) is provided by an alloy of copper and gold Cu_3Au . It has a cubic unit cell in which the gold atoms are at the corners and copper atoms at the face-centers. But on heating, some of the copper and gold atoms interchange positions leading to a random arrangement of Cu and Au atoms. The probability of any particular lattice site to be occupied by copper atom is 75% and for gold atom is 25%.

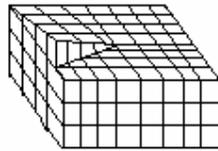


Defects in crystals belong to two broad classes, namely **stoichiometric defects** and **non-stoichiometric defects**. Defects in which the ratio of anion to cation remains unchanged are termed *stoichiometric defects*. The commonly observed stoichiometric defects fall in the following categories:

- (1) Simple vacancies (Schottky defect)
- (2) Unexpected occupation of interstitial sites (Frenkel defect)
- (3) Various lattice imperfections, for example **edge dislocations, screw dislocations, stacking faults** etc.



Edge dislocation
(only one layer shown)



Screw dislocation

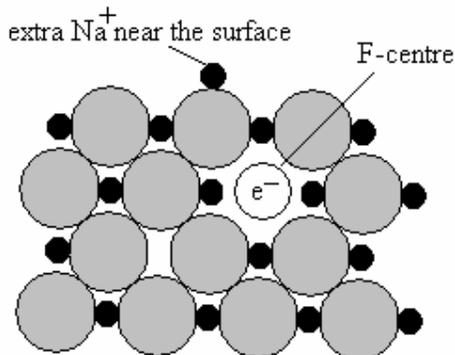
Stacking faults: These are departures from ideal layer in close-packed structures. For example, in the crystal lattice of graphite, the layers are usually stacked in the 'ABCABC' pattern. But sometimes graphite exhibits the 'ABAB' type of stacking, or a mixture of the two types.

Non-stoichiometric defects: Those defects leading to a change in the anion to cation ratio are called *non-stoichiometric defects*. This may be due to an excess of one kind of atoms present in the compound, or incorporation of ions or atoms other than those present in the compound. Atoms or molecules with sizes similar to those in the crystal may replace them leading to impure crystals. (This sometimes results in precious minerals such as rubies and emeralds, imparts rare and beautiful colours to diamonds etc). Let us consider the situation in which a slight excess of B is present in the ideal crystal structure of composition AB. This can happen in three ways.

- (1) **Substitutional incorporation**, in which a few extra B atoms occupy positions normally occupied by A atoms. This is usually shown by alloys in which the A and B type atoms have comparable sizes.
- (2) **Interstitial incorporation**, in which a few excess B atoms occupy interstitial positions. For example, when ZnO is heated, a little oxygen is lost and the Zn atoms so formed occupy interstitial positions. The composition of the resulting phase at 800°C is $Zn_{1.00007}O$, and the colour changes from white to yellow. This type of defect is similar to Frenkel defect except that there is no vacant position to compensate for the interstitial atom.
- (3) **Subtractive incorporation**, in which the B atoms are all in their correct positions but some of the A atoms are missing. This is analogous to the Schottky defect with loss of one type of atom only. Density measurements have shown that FeO and FeS are deficient in iron. Their composition is better represented as $Fe_{0.84-0.94}O$ and $Fe_{0.88-1.00}S$. CdO loses oxygen on heating, but the resulting structure is found to be deficient in oxygen, with a composition of $CdO_{0.9995}$ at 650°C.

Crystal defects can again be classified into **point defects**, **line defects**, **plane defects** and **electronic imperfections**. Schottky and Frenkel defects are examples of point defects. Edge dislocation and screw dislocation are examples of line defects. Stacking fault is an example of plane defect. Doping with extraneous material may cause the presence of excess electrons or holes in the structure as in semiconductors. These are electronic imperfections.

F-centres: An anion vacancy may not be a true vacancy, but may contain a “trapped” electron to maintain electrical balance. For example, if a small amount of sodium metal is doped into a sodium chloride crystal, the crystal energy causes the sodium to ionize to $\text{Na}^+ + e^-$ and the electron occupies a site normally occupied by a chloride ion. The resulting “trapped” electron can absorb light in the visible region and the compound becomes coloured. Such trapped electron locations are sometimes called F-centers (F stands for *farbe*, which means *colour* in German).

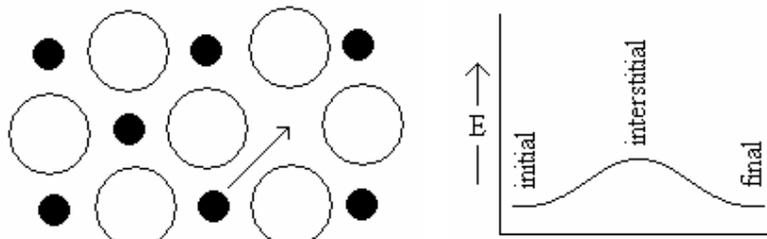


Finally, *defects in which foreign ions are not involved are called intrinsic defects*, such as missing ions in the crystal (Schottky defect) or ions of the crystal occupying interstitial positions (intrinsic Frenkel defect) or line defects, plane defects etc. Defects in which foreign ions are incorporated, such as substitutional incorporation to produce coloured gems, doping to produce semiconductors etc. are called **extrinsic defects**.

SOLID STATE REACTIONS

Since the motion of particles in the solid state is very much restricted, reactions in the solid state are extremely slow and can take place only along the boundary of contact. For the same reason, pure ionic solids are usually insulators. If reactions or conductivity to any extent exists, it must be due to the diffusion of ions through the lattice. Such migration of ions is difficult in the case of perfect crystals, but may be facilitated by the presence of crystal defects giving rise to vacancies. The conductivity of most ionic crystals is low and rises only near the melting point. Because the number of defects is quite small, the conductivities are low, of the order of $10^{-6} \Omega^{-1} \text{cm}^{-1}$. In addition, **extrinsic vacancies** will be induced by ions of different charge. (For example, if a crystal of AgCl is doped with a minute amount of CdCl_2 , the size of the Cd^{2+} ion is such that it fits easily into the AgCl lattice. But the dipositive charge of the ion makes the absence of an Ag^+ from the lattice so that the charge is balanced.) The **mechanism of migration of the ions** through the solid may be classified into three types:

- (1) **Vacancy mechanism:** If there is a vacancy in a lattice, it may be possible for another ion of the missing type, usually a cation, to migrate into the vacant position. This in turn creates another vacancy, and the process can continue. But the ion has to pass through an interstitial position on its way to the stable vacancy position. This will disturb the lattice and will be a high energy position. The energy profile of the movement will be as in the figure. The cycle is repeated.



The vacancy mechanism

The energy profile of the movement will be as in the figure. The cycle is repeated.

- (2) **Interstitial mechanism:** A small ion, initially occupying an interstitial site, may move to another interstitial site.
- (3) **Interstitialcy mechanism:** This is a concerted mechanism, in which an interstitial ion moves into a vacancy created by another ion moving from its normal position into an interstitial position.

Solid electrolytes: (Ref. 6, 9) A few ionic compounds in the solid state have conductivities much higher than that described above at room temperature. This is because they permit the diffusion of ions (generally cations) without the need for defects. The general requirements for a good solid electrolyte are:

- (1) The presence of a large number of mobile ions
- (2) The presence of many empty sites that the mobile ions can jump into.
- (3) The empty sites should be of similar or the same energy as the filled ones, with only a small energy barrier between them.
- (4) There should be an anionic framework within which there are either open channels, or else the framework should be soft, polarizable and deformable.

An example for a solid electrolyte with a rigid structure in which the vacant sites are arranged in channels down which the ions can easily move is **sodium β -alumina**. It has a composition close to $\text{Na}_2\text{Al}_{22}\text{O}_{34}$, but there is always an excess of sodium. α -alumina and γ -alumina are two polymorphic forms of pure alumina. The name β -alumina is a misnomer, given at a time when it was believed to be another polymorphic form of pure alumina. In reality, β -alumina contains a nonstoichiometric amount of sodium and may be formulated as $\text{Na}_{1+x}\text{Al}_{11}\text{O}_{17+x/2}$. It has a structure closely related to that of spinels. It consists of sheets of hard, rigid γ -alumina held together by thin layers of Na^+ and O^{2-} ions. Since many of the voids in spinel structures are unoccupied, the excess sodium ions can migrate through these voids. The possible use of β -alumina in Na/S batteries has made it an object of detailed study.

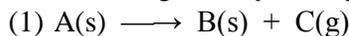
Another well-established solid ionic conductor is a material called **NASICON** (an acronym for sodium superionic conductor). The formula is $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$. It consists of a framework built up of ZrO_6 octahedra sharing corners with PO_4 or SiO_4 tetrahedra. In this framework there is a network of tunnels through which the Na^+ ions can comfortably migrate.

Examples of “soft” solid electrolytes are provided by silver iodide, and ternary silver iodides like HgAg_2I_4 and RbAg_4I_5 . In all of these, the Ag^+ ions can move fairly easily even though there are no large channels, because of the low lattice energies of these substances. **Rubidium silver iodide, RbAg_4I_5** , has a room temperature conductivity of $0.27 \Omega^{-1} \text{cm}^{-1}$. This conductivity is comparable to that of a 35% aqueous solution of sulfuric acid. Its structure consists of a complex arrangement (not closest packed) of iodide ions with Rb^+ ions in octahedral holes and Ag^+ ions in tetrahedral holes. Of the 56 tetrahedral holes, only 16 are occupied, leaving many vacancies. The relatively small size of the silver ion (114 pm) compared to rubidium (166 pm) and iodide (206 pm) makes it easy for them to move through the lattice.

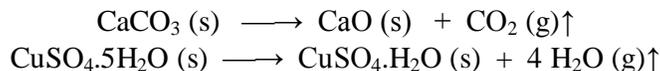
There are many potential applications for solid electrolytes, mainly in batteries delivering very high power but having small volumes and low weight.

THERMAL DECOMPOSITION OF SOLIDS

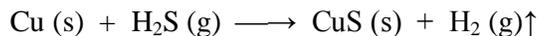
These reactions generally belong to two categories:



Decomposition of metal carbonates on heating to give the oxide with liberation of carbon dioxide, and decomposition of hydrated salts on heating into the anhydrous salt and water vapour are examples of the first type of reaction. Such a reaction in the solid state can proceed to a large extent only if the gaseous product can migrate to the surface of the crystal through the lattice and escape into the atmosphere.



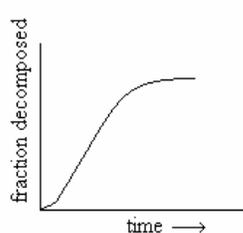
Diffusion of hydrogen sulphide into the crystal lattices of metals and formation of the solid sulphide with liberation of hydrogen is an example of the second type of reaction. Such reactions can proceed appreciably only if the hydrogen sulphide gas can diffuse into the crystal lattice from outside and the hydrogen produced must migrate to the surface.



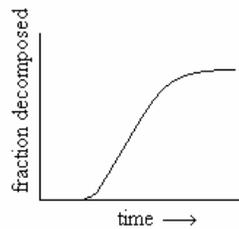
Decomposition of solid A on heating to give solid B may or may not have an induction period. At some stage of heating, nuclei of B will be formed, which are embedded in a matrix of A. The solid product may or may not have a crystal structure similar to the initial solid material. If it has a different structure, local imperfections due to formation of the new type of lattice may create strain in the structure, making diffusion of gases easy. The strain energy may then provide the activation energy needed for further reaction, thus leading to an increased reaction rate. There exists a critical size of B at which thermodynamic stability of B will overcome the strain energy. If the source of heat is removed before attaining the critical size of B, it reverts back to A. Otherwise the transformation of A to B will continue.

Such decompositions of solids are usually studied by Differential Thermal Analysis (DTA) or Thermo Gravimetric Analysis (TGA). Thermal decomposition may follow any of the following kinetics.

If the formation of nuclei is followed by rapid growth, it will be autocatalytic in nature. If the activation energy for the reaction is less than that for formation of nuclei, the reaction will proceed only at a few nuclei leading to large crystals of B. This is the case with many dehydration reactions.

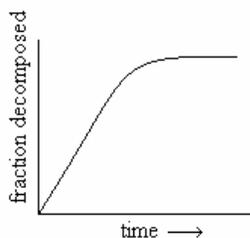


(a) self catalysed

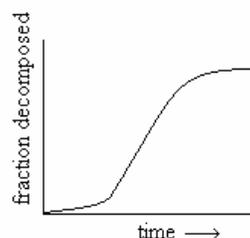


(b) short induction period followed by rapid decomposition

If the activation energies for the reaction and formation of nuclei are comparable, there will be practically no induction period. A large number of nuclei are formed initially followed by rapid growth all over, leading to the formation of a large number of very small crystals. If a gas is evolved, nucleation usually occurs only at the surface of the crystals so that the gaseous product can escape.

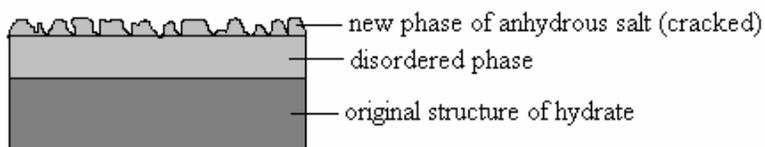


(c) no induction period



(d) initial slow gas evolution followed by rapid decomposition

The decomposition reactions may be either endothermic or exothermic. The most commonly studied endothermic reactions are dehydration of metal salt hydrates and the decomposition of metal carbonates. The decomposition products of some metal hydrates have crystal lattices identical with that of the parent solid. In some cases the product may not have any well defined crystal structure (glass). In the third case, the product may have a distinctly different crystal structure, forming a new phase.



The process of dehydration may be imagined as follows: The heating initially produces a highly disordered structure. This rearranges to a new crystalline form accompanied

by a change in volume (shrinkage or expansion), producing minute cracks through which the steam will have to escape. Since the surface is covered with anhydrous salt, water can escape only by diffusion through the cracks. Hence the rate of dehydration slows down.

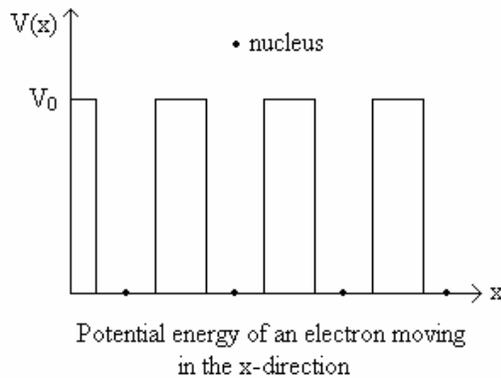
Decomposition of some metal azides, metal oxalates and metal hydrides are exothermic reactions. Metal azides of alkali metals are stable, but other metal azides are highly sensitive explosives. They decompose giving the metal and nitrogen, and are studied by plotting pressure – time curves.

ELECTRICAL, MAGNETIC AND OPTICAL PROPERTIES OF SOLIDS

The Free Electron Theory of metals (Drude-Lorentz theory of metals): This is the classical theory of bonding in metals. In 1900, even before the lattice structure of crystals were established, Drude suggested that metals are composed of positively charged ions and an *electron gas* consisting of free mobile electrons. Lorentz modified the theory and therefore it has come to be known as Drude-Lorentz theory of metals. The atoms in the metal are held together by *electrostatic attraction* between the cations and the mobile electrons. The same electrostatic attraction prevents the free electrons from leaving the metal surface. (*One may also say that there is an energy barrier or that there is a large potential difference across the boundary; it all means the same thing.*) When an external electric field is applied, it accelerates the flow of electrons towards the positive plate in the direction of the field. This constitutes the electric current and explains the **electrical conductivity** of metals. During this flow, metallic ions in the lattice deflect them, offering **resistance** to the flow. When temperature increases, the oscillations of the cations in the lattice also increase, thus increasing the resistance to electron flow. At equilibrium, electrons move with a constant average **drift velocity**. The mean free path between two collisions is assumed to be of interatomic distances. Since the free electrons can absorb light of all frequencies, metals appear to be opaque (i.e. they do not transmit light). When the absorbed light is re-emitted, only those coming from atoms close to the surface can escape. This explains the **metallic lustre**. When a temperature gradient is applied, the freely moving electrons quickly carry away the heat to the other end, which explains the good **thermal conductivity** of metals.

Drawbacks of the free electron theory: (1) It does not explain why only some crystals are metallic. (2) It does not explain why metals prefer only certain structures. (3) The actual observed heat capacity of metals is only about 1% of that calculated on the basis of free electron theory. (4) The observed electronic contribution to magnetic susceptibility is only about 1% of the calculated value. (5) It does not explain the temperature dependence of conductivity in metals and semiconductors. (6) It cannot explain why some metals are very good conductors while others are not.

Zone theory (the Kronig-Penny model): In the free electron theory, the electrons in a metal are supposed to move in a uniform electric field within the crystal (i.e. the influence of the cations is not considered). But because of the presence of nuclei, the electrons are subjected to a periodically varying potential. In 1930, Kronig and Penny proposed a one-dimensional model to describe the behaviour of electrons moving under a periodically varying potential. The potential energy of the electrons reduces to zero when they reach the nuclei and increases to a maximum value V_0 midway between two nuclei. Thus the electron faces rectangular potential barriers as indicated in the figure.

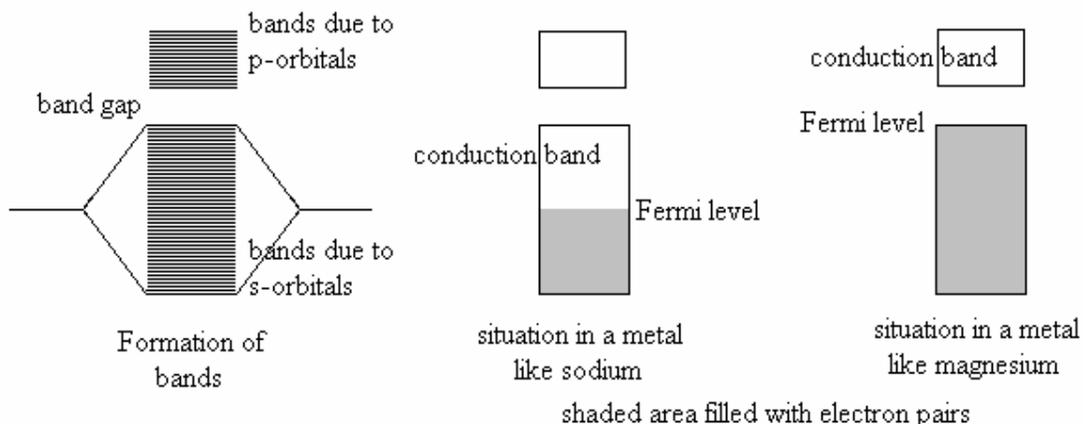


The mathematical treatment of this theory finds that the permissible values of electron energies are governed by the relation:

$$P\left(\frac{\sin \alpha a}{\alpha a}\right) + \cos \alpha a = \cos ka$$

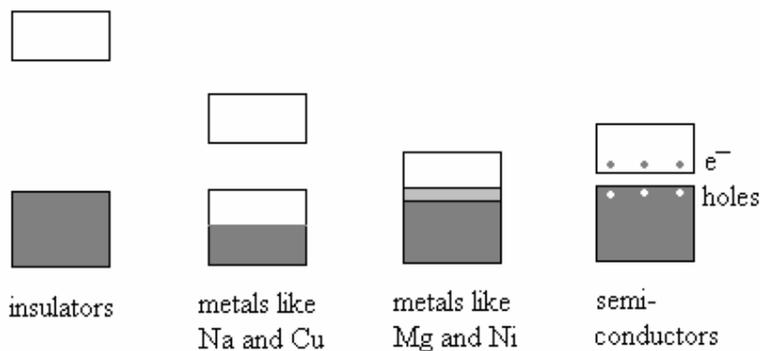
where 'a' is the internuclear distance. The right side of the equation indicates that the possible values of the left side must lie between -1 and +1. Thus the energies of the electron lie only in certain allowed zones; other energies are forbidden.

Molecular orbital theory of solids (band theory): According to this theory, the entire metallic crystal is considered as one giant molecule consisting of N atoms, where N is of the order of the Avogadro number. According to molecular orbital theory, when N atoms come close enough to each other, each energy level in the atoms splits into N energy levels (half of which are considered bonding orbitals and the other half as antibonding orbitals). Since there is an Avogadro number of atoms, these levels are very closely spaced and therefore appear like bands. When N atoms are brought together to form a solid, the outermost levels split first and the inner levels do so only at very small interatomic distances. The levels corresponding to valence electrons form the **valence band**; the adjacent empty band above the valence band is called the **conduction band**. Fermi-Dirac statistics is used for the computation of these orbitals.



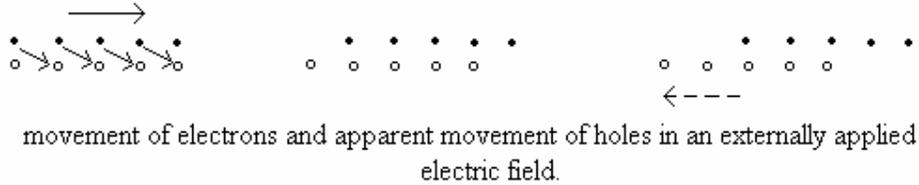
The highest band having electrons in them at 0 K is the valence band. The uppermost level filled with electrons at 0 K is called the **Fermi level**, and the energy corresponding to this level is **Fermi energy**. *The band lying immediately above the Fermi level is known as the conduction band.* For an alkali metal like sodium, with ns^1 configuration, the electrons pair up and occupy half of the orbitals in the valence band (the bonding orbitals only) at 0 K. For alkaline earth metals like magnesium, with ns^2 configuration, the electrons occupy the complete valence band (bonding as well as antibonding) at 0 K. The bands formed by overlap of the p -orbitals lie above the s -band, and are empty.

Insulators, conductors and semiconductors: The extent of separation or overlap between the valence band and the conduction band determines whether a material is an insulator, conductor or semiconductor. In principle, each energy band corresponds to one quantum energy level, and the gaps or forbidden regions correspond to the quantum jump from one energy level to another. Then four situations can be imagined, depending on the band width and the band gap.



- (1) In the case of insulators, each occupied band is completely filled. The energy gap to the next higher level (conduction band) is very large. Therefore the higher level is empty. Application of low potential differences or temperature differences is not sufficient to excite electrons into the conduction band. Thus electrical insulators are also poor thermal conductors. Examples are alkali metal halides, for which $\Delta E = 670$ to 1170 kJmol^{-1} . But in extremely high applied fields, electrons can be excited into the conduction band; thus all insulators break down at some point.
- (2) In metals like sodium and copper, the energy gap between the occupied band and conduction band is small. But the valence band is only half-filled. Therefore the electrons can almost freely move into higher levels within the valence band itself without any excitation and move in a small applied potential field applied externally. They are therefore good conductors of heat also.
- (3) In metals like magnesium and nickel, the valence band is completely filled. Since the energy of the uppermost filled orbital in the valence band is more than that of the lowermost unfilled orbital in the conduction band, the bands overlap. Therefore the electrons can almost freely move into higher levels in the conduction band without any excitation and move in a small applied potential field applied externally. They are therefore good conductors of heat also. As temperature increases, the nuclei start vibrating faster and disrupt the electron bands. Therefore conductivity decreases when temperature increases.
- (4) For semiconductors, the energy difference between the completely filled band and the conduction band is small. But since the conduction bands are unoccupied at low temperatures, they behave like insulators. With increasing temperature, a few electrons can be promoted to

the conduction band, leaving 'holes' in their original locations in the valence band. The electrons in the conduction band and the holes in the valence band move in an externally applied electric field (the holes behave like positive charges and move in a direction opposite to that of electrons). Thus they become weakly conducting and the conductivity increases with

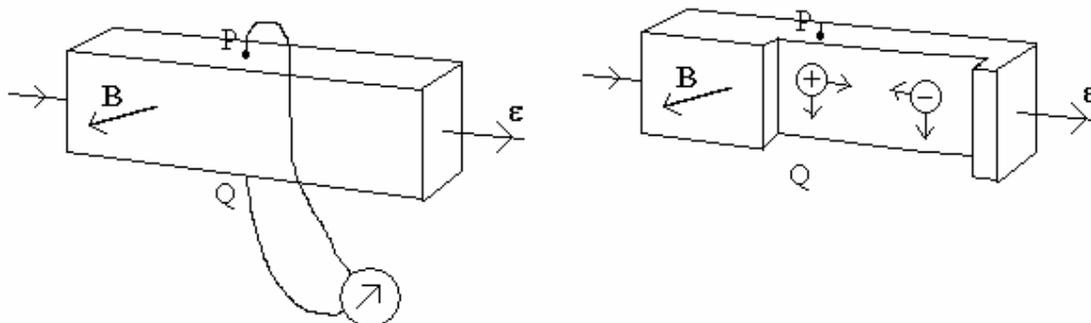


increasing temperature. Such materials are called **intrinsic semiconductors**. Silicon and Germanium are examples. Even exposure to light can excite electrons into the conduction band, making them better conductors in the presence of light than when kept in darkness. This type of conductivity is called **photoconductivity**. Excess electrons in the conduction band can also be created by doping silicon or germanium with phosphorus or arsenic having five valence electrons. (Example: gallium arsenide). Holes (electron deficiency) can be created by doping with boron having only three valence electrons. These doped materials also behave as semiconductors and they are known as **extrinsic semiconductors**.

As we move towards the upper right of the periodic table, the atoms become smaller and the valence electrons are under the influence of greater nuclear charge. This increases the energy difference between the valence band and conduction band, and the elements become insulators. In the opposite direction towards the lower left of the periodic table, the atoms are larger and the outer electrons experience decreased nuclear charge due to screening. The valence bands therefore have high energies and merge with the conduction band. The metals are thus good conductors. Detailed studies of the properties of nickel lead to the conclusion that in the metal, the average electronic distribution is not $3d^8 4s^2$ as in the gas, but is $3d^{9.5} 4s^{0.5}$. In the absence of thermal motion, a perfect metallic crystal should have no resistance.

According to the MO theory, the electronic contribution to heat capacity and magnetic susceptibility comes only from electrons having energies close to the Fermi energy. This satisfactorily explains the discrepancy shown by the free electron theory.

The mobility of charge carriers – The Hall effect: When a magnetic field is applied perpendicular to a current-carrying conductor, a potential difference is developed in the direction which is perpendicular to both the electric current and the magnetic field. This causes a momentary drop in the original current flow.



A current of strength ϵ is flowing in a metal bar in the direction indicated. If the points P and Q in a perpendicular direction are connected to a galvanometer, no current will flow indicating that P and

Q are at the same potential. If a magnetic field B is now applied in the direction indicated, the galvanometer is deflected indicating a current flow in the direction P to Q. This is the Hall effect. The potential difference between P and Q is called the **Hall potential difference**. *The sign of the Hall potential difference enables us to decide whether the current ϵ is due to the flow of electrons to the left or due to the movement of positive ions to the right.* In the situation given in the diagram, the magnetic field produces a force vector acting downward according to the left hand rule, irrespective of whether the current is due to movement of positive ions or electrons. If it is due to the flow of electrons, the electrons migrate downwards and collect at the surface, making the point Q negative. If it is due to positive ions, they migrate downwards making the point Q positive. However, this new potential difference induces a current in the opposite direction and the two opposing forces will cancel off in a short time.

Applications of Hall effect: [Ref: West AR. Solid State Chemistry and its Applications. John Wiley. (2003)]. Measurement of the Hall effect gives an important source of information about conduction mechanisms, especially in semiconductors. Conductivity of a metal, σ , is given by the equation

$$\sigma = ne\mu$$

where n is the number of current carriers, e is the charge on each carrier and μ is their mobility. Measurement of conductivity alone can give only the combined effect of the number of current carriers and their mobility. Measurement of Hall potential along with conductivity enables the separate determination of n and μ .

The Hall coefficient R , for a particular material, is the potential gradient produced when I and H are both unity. The sign of R depends on the sign of the current carriers and is therefore different for positive holes and electrons.

$$R = \frac{1}{ne}$$

Therefore n can be calculated by measuring the Hall potential for known values of I and H . Then μ can be calculated by measuring the conductivity.

Most metals have negative Hall coefficients, which indicate that electrons are the current carriers. Some metals like Zn and Cd have positive R values. The qualitative explanation given by band theory is that conduction in Zn and Cd is primarily by positive holes, or vacancies, at levels just below the Fermi level. The sign and temperature dependence of R are different for n-type and p-type semiconductors. Hall voltages are usually too small to be detected in ionically conducting materials because n and μ are both small. But the effect is noticeable in some solid electrolytes like RbAg_4I_5 which has high Ag^+ ion conductivity.

Piezoelectricity: This is a phenomenon associated with induction of polarization under the influence of mechanical stress. It is exhibited by twenty out of the twenty-one noncentrosymmetric crystal classes (crystal structures having no centre of symmetry). When the arrangement of anions and cations are not in a symmetric manner, application of a stress will change the orientation of the electrical dipoles in the crystal. It does not matter whether the stress is compression, dilation or shear. Conversely, when an electric field is applied to such crystals, a mechanical strain is produced in the crystal. This is known as **inverse piezoelectric effect**. *In piezoelectric effect, the strain is proportional to the applied field* so that it changes sign (compression changes to expansion) when the electric field is reversed. If an alternating field is applied, the displacement of the electric dipoles and the mechanical strain due to it also varies periodically. This generates a mechanical vibration of some particular frequency in the crystal. Generally the displacement of the electric

dipole lags behind the applied frequency and the two are out of phase. At some frequency of the applied field, the oscillation of the crystal will exactly match that of the applied field. This frequency is known as the **resonance frequency**. This phenomenon is used in the manufacture of electronic oscillators used to keep time in electronic clocks, control the clockspeeds in computers and so on. The presence or absence of piezoelectric effect is used to determine whether a crystal is centrosymmetric or not. There is another phenomenon called **electrostriction**, in which the *mechanical strain is proportional to the square of the applied electric field*. Therefore the direction does not change in an alternating field.

Ferroelectricity: [Charles Kittel, “Introduction to solid state physics”, 7th edn., John Wiley (2004); p. 393.] A ferroelectric crystal exhibits an electric dipole moment even in the absence of an external electric field. In the ferroelectric state, the centre of positive charge of the crystal does not coincide with the centre of negative charge. The structures of some piezoelectric materials are asymmetric in such a way that they are spontaneously polarized even in the absence of an external field. The polarization is due to the presence of permanent dipoles and is temperature dependent. If it is possible to reverse the polarization direction by the application of a sufficiently large external field, then the crystal is said to be ferroelectric and the phenomenon of reversing the polarity is called ferroelectric effect.

The plot of polarization versus electric field for the ferroelectric state shows a hysteresis loop. A crystal in a normal dielectric state usually does not show significant hysteresis when the electric field is increased and then reversed, both slowly. The term *ferroelectric* comes from its similarity to ferromagnetism. Many ferroelectric crystals undergo a transformation at a certain temperature, often called the **Curie point** T_c , above which they are no longer polar. Then they are said to have become **paraelectric** (similar to paramagnetic). The term paraelectric suggests an analogy with paramagnetism; similarly, there is usually a rapid drop in the dielectric constant as temperature increases. Polarised domains similar to ferromagnetic domains exist in ferroelectric materials also.

Classification of ferroelectric crystals: The following table lists some ferroelectric crystals along with their transition temperature or Curie point T_c at which the crystal changes from the low temperature polarized state to the high temperature unpolarised state.

| | | T_c (K) | P_s ($\mu\text{C cm}^{-2}$ at T K)* |
|-------------|---------------------------|-----------|--|
| KDP type | KH_2PO_4 | 123 | 4.75 |
| | KD_2PO_4 | 213 | 4.83 |
| | RbH_2PO_4 | 147 | 5.60 |
| | KH_2AsO_4 | 97 | 5.00 |
| | GeTe | 670 | - |
| TGS type | Triglycine sulphate | 322 | 2.80 |
| | Triglycine selenate | 295 | 3.2 |
| Perovskites | BaTiO_3 | 408 | 26.0 |
| | KNbO_3 | 708 | 30.0 |
| | PbTiO_3 | 765 | > 50 |
| | LiTaO_3 | 938 | 50.0 |
| | LiNbO_3 | 1480 | 71.0 |

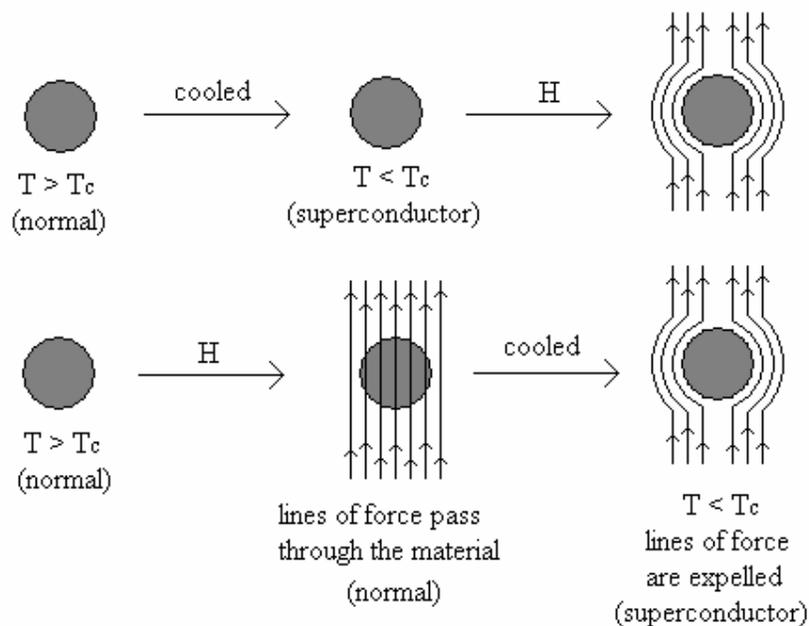
*To obtain P_s in the cgs unit of esu cm^{-2} , multiply given value with 3×10^3 .

Pyroelectricity: In some crystals, the ferroelectric dipole moment is not changed by an electric field of the maximum intensity which it is possible to apply before causing electrical breakdown. In these crystals, we are often able to observe a change in the spontaneous moment when the temperature is changed. If a change in temperature produces a change in the polarization and generates an electric field, this is called the **pyroelectric effect**, and is useful in the manufacture of devices like thermometers. Ten out of the twenty types of piezoelectric crystals exhibit pyroelectric effect.

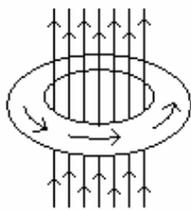
Lithium niobate, LiNbO_3 , is pyroelectric at room temperature. It has a high transition temperature ($T_c = 1480\text{K}$) and a high saturation polarization ($50 \mu\text{C cm}^{-2}$). It can be “poled” which means given a remnant polarization, by an electric field over 1400K .

Superconductivity: In 1911, Kammerlingh Onnes discovered that when highly purified mercury was cooled below 3.7 K , it lost all traces of electrical resistance. Since then, a large number of materials have been found to exhibit zero resistivity below a temperature called *critical temperature*, T_c , of the substance. This phenomenon is called superconductivity. Measurements show that the resistance of superconductors are less than that of metals by a factor of at least 10^{17} , and therefore very close to zero. It has been noted that a current induced in a closed circuit of superconducting material underwent no perceptible reduction in more than a year’s time. Superconducting wires can be used for the transport of electricity without transmission loss and in very powerful electromagnets with low power consumption.

Meissner effect: Superconducting materials have very interesting magnetic properties. They will not permit a magnetic flux to pass through them, and are therefore *perfectly diamagnetic*. This is called Meissner effect. Not only that, any magnetic flux which might already have been present in the material before it was cooled below the critical temperature will be expelled completely when it became a superconductor. The Meissner effect is a more characteristic and important property of a superconductor than the lack of resistance.



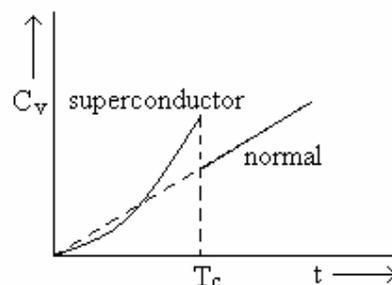
Critical field strength: The Meissner effect is observed only when magnetic fields below a critical field strength H_c are used. At higher field strengths, the lines of force start penetrating the material, and then the superconductivity will be lost.



Persistent current: If the superconductor has a doughnut shape, a circular flow of electric current is induced in it when it is placed in a magnetic field. But the current does not stop even after the field is removed, since there is no resistance. The circular current induces a magnetic field passing inside the toroid. This field is sustained by the un-ending ring current, and the magnetic field can be sustained indefinitely without consuming any electrical energy. This is perhaps the most important application of superconductivity.

Levitation: Since a superconductor repels a magnetic field, a magnet placed over a superconducting surface is raised against gravity. This is called levitation, and is expected to be used in the development of superfast trains which do not touch the rails and therefore has no friction.

Specific heat of superconductors: The specific heat of a normal substance decreases linearly with decreasing temperature. But in the case of a superconductor, there is a sharp break at T_c in the curve as the material is cooled, where specific heat is higher than expected. Below T_c , the specific heat decreases exponentially within the superconducting material. Although there is a discontinuity, there is no latent heat associated with this transition.



High temperature superconductors (HTSCs):

[Ref: (1) Ramakrishnan T.V. and Rao C.N.R., *Superconductivity Today*, 2nd edn, Universities Press, 1999. (2) Kettle S.F.A., *Physical Inorganic Chemistry – A Coordination Chemistry Approach*, Spektrum Academic Publishers, 1996] The technological difficulty involved in exploiting the phenomenon of superconductivity is the prohibitive cost involved in maintaining the material at such low temperatures. The breakthrough came when compounds of the general formula $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-\delta}$ were synthesized and found to exhibit superconductivity below 35 K.

Conventional superconductors show superconducting behaviour below 4 K (or $T_c < 4$ K, bp of liquid helium). Over a period of time, research has led to the development of new materials exhibiting superconducting behaviour above 77 K (or $T_c > 77$ K, bp of liquid nitrogen). Such substances are called high temperature superconductors. The advantages of using liquid nitrogen as coolant are (1) low cost (2) it has a larger heat capacity than helium and is therefore a better coolant (3) the design of the container for liquid nitrogen is much simpler than that of liquid helium.

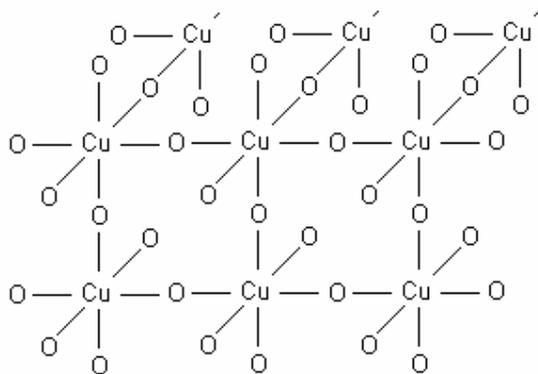
Applications of high temperature superconductors: Technology has not developed to the point where superconductors can be used instead of normal conductors in electric bulbs, fans or motors. Most of the applications of superconductors are in the production of very high magnetic fields. Construction of highly powerful magnets using ordinary metallic conductors are difficult because of the large bulk of winding needed, and loss of energy in the form of heat due to electrical resistance. With HTSCs, there can be great improvement in efficiency, and a ten-fold increase in field strength. The disadvantage is the need for refrigeration to maintain nitrogen in the liquid state, and the cost involved.

Areas in which HTSCs may find application are:

- (1) In huge motors consuming very large quantities of electricity, the improvement in efficiency can lead to considerable savings and offset the cost of maintaining liquid nitrogen.
- (2) In nuclear fusion, where containing the reacting plasma requires powerful magnetic fields.
- (3) In the field of magnetically levitated (Maglev) transportation.

- (4) In magnetic ship propulsion. Here there are no moving parts. The water behind the ship is electrically charged from an electric current supplied from the ship, and generates a magnetic field which repels a superconducting magnet kept on-board. This can, at least theoretically, lead to lighter and faster ships. Use of conventional propellers has inherent limitations of speed due to churning and development of vacuum or air-pockets at high speeds. This also leads to faster corrosion of the propellers.
- (5) In huge transformers for electrical transmission and industrial applications.
- (6) In the manufacture of powerful lasers.
- (7) A superconducting quantum interference device (SQUID) is capable of detecting extremely weak magnetic fields generated by the brain or the heart. This property is used in biomedical applications such as MRI scanners.
- (8) In electronics. Computing and storage devices can be made extremely small and highly powerful by the application of superconducting materials.
- (9) In producing very high magnetic fields required for the magnetic separation of ores.

High temperature superconducting materials: At the present time, several different classes of HTSCs are known. One of these is a family of compounds discovered by Bednorz and Müller in 1986, with general formula $\text{La}_{2-x}\text{M}_x\text{CuO}_4$, (where $\text{M} = \text{Ba}$ or Sr), based on the parent compound

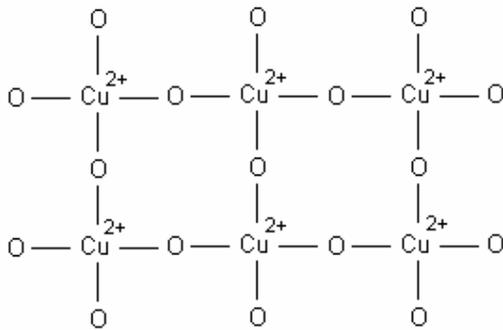


La_2CuO_4 . This compound has a structure consisting of planes of Cu and O atoms, with oxygen atoms arranged octahedrally around the copper atoms. The La^{3+} ions are sandwiched between these layers. The system becomes superconducting when Sr^{2+} ions are substituted for La^{3+} . To maintain overall charge neutrality, one Cu^{2+} has to become Cu^{3+} for every substituted Sr^{2+} ion. It seems that superconductivity is due to the presence of Cu^{3+} ions in the Cu-O planes. It also appears that superconductivity is localized in these planes. The highest temperature superconductor

reported to date belongs to this class. It contains Sr, Ca and Bi as well as Cu and O. It is reported to be superconducting at 250 K (-23°C).

The second class of HTSCs have an approximate formula $\text{YBa}_2\text{Cu}_3\text{O}_7$ (and therefore sometimes called **1,2,3 superconductors**). The oxygen content in both classes is slightly variable. Since Y^{3+} and Ba^{2+} do not exhibit variable valency, there are two Cu^{2+} and one Cu^{3+} ions in this system. The Cu^{2+} ions are at five-coordinate square pyramidal sites and the Cu^{3+} ions are at square planar sites. Therefore the structure is more complicated than the La_2CuO_4 type. Here also, the superconductivity is attributed to the presence of Cu^{3+} ions. Since both the above types of HTSCs are not metals, but mixed oxides of metals, they are also known as **ceramic superconductors**. Both are **cuprates**. These had layered structure similar to perovskite and the critical temperature increased with pressure. This suggested that T_c depends on lattice distances. Therefore strontium ($r_+ = 132$ pm) was substituted for barium ($r_+ = 149$ pm) with some increase in T_c . But dramatic improvement occurred when yttrium ($r_+ = 104$ pm) was substituted for La ($r_+ = 117$ pm), giving a new type of compound with formula $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This is the so-called **1-2-3 superconductor** (from the ratio of Y-Ba-Cu). The current maximum critical temperature is 125 K for $\text{Ti}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$.

Theories of superconductivity: By the early 1950s, it became clear that lattice vibrations are somehow important in superconductivity. For instance, the superconducting T_c of different isotopes of mercury are different. T_c is found to be inversely proportional to the square root of atomic mass. Fröhlich demonstrated that two electrons in a metal can effectively attract each other, the attraction being mediated by lattice vibrations. In 1957, Bardeen, Cooper and Schrieffer developed a complete theory (known as the **BCS theory**) of superconductivity based such pairs of electrons which can move through metal lattices without any resistance. Such mutually-assisting pairs of electrons are known as **Cooper pairs**. The two electrons are said to be coherent and are in a single quantum state. Bardeen, Cooper and Schrieffer were awarded the Nobel prize in 1972 for this work. An oversimplified explanation of the model, avoiding all mathematics and derivations, is given below:



A copper-oxygen plane in La_2CuO_4 is shown in figure 1. There are additional oxygen atoms above and below the Cu^{2+} ions which are omitted for simplicity. Superconductivity is believed to occur along these planes. Each Cu(II) ion has a single unpaired electron, and these are antiferromagnetically coupled, giving the arrangement shown in figure 2. It is known that La_2CuO_4 is an antiferromagnetic insulator.

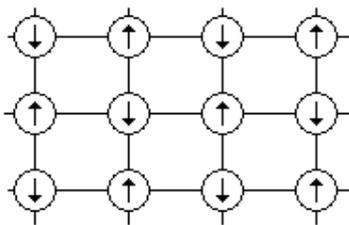


Figure 2

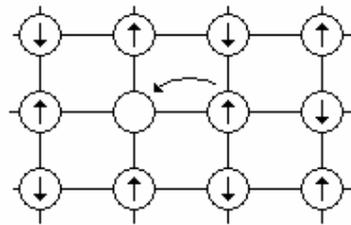


Figure 3

When a Sr(II) ion substitutes for a La(III) ion between these layers, an electron is lost from a Cu(II) ion and becomes a Cu(III) ion. Thus a hole appears in the structure, as shown in figure 3. For conduction to occur, electrons have to move from site to site. If movement occurs from any of the nearby positions as indicated by the curved arrow (diagonal positions are too far for orbital overlap to occur), the result will be as given in figure 4. This will not be identical with the original situation since nearby positions now have parallel spins. Energy will be required to reverse the spin of the electron. This is not suitable for superconduction to occur.

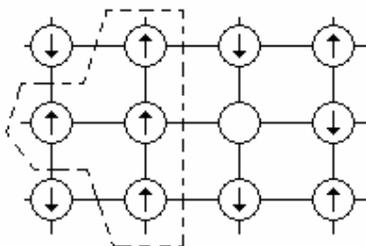


Figure 4

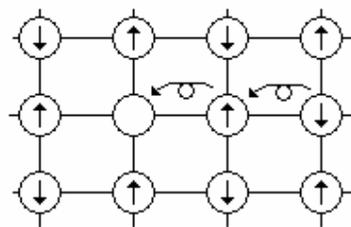


Figure 5

But if two electrons nearby move simultaneously, also exchanging their spins in the process, the crystal can retain in its initial state without need for extra energy, as shown in figure 5. Exchange of spins between two electrons in the same quantum state does not require energy, and the pair of electrons can shift without any resistance. This is the simple meaning of saying that the Cooper pair

is coherent and in a single quantum state. The simultaneous movement and exchange of spins between the Cooper pair is assisted by small lattice vibrations prevailing at low temperatures.

Magnetic properties: When a substance is placed in an external magnetic field of strength H , the magnetic induction or the density of lines of force B within the substance is given by:

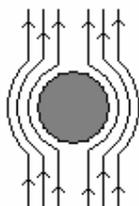
$$B = H + 4\pi I$$

where I is the intensity of magnetization or magnetic moment per unit volume. Dividing both sides by H , the equation may be written in the form:

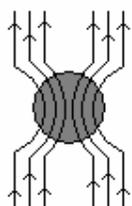
$$P = 1 + 4\pi\kappa$$

Where P is called permeability and κ is the susceptibility per unit volume. In practice, susceptibility is expressed per unit mass and is given the symbol χ . The molar susceptibility χ_m is the product of gram susceptibility and molar mass.

If P is less than unity, the substance causes a reduction in the intensity of the applied magnetic field inside the substance, and moves towards the region of lowest field strength when kept in an inhomogeneous magnetic field. Such a substance is called diamagnetic. Values of χ for diamagnetic substances are very small (about -1×10^{-6}) and are usually independent of field strength and temperature. All substances have diamagnetic susceptibility, which arises from induction of a small magnetic moment opposing the external field. It is necessary to apply a correction for this diamagnetism when determining paramagnetic susceptibility.



diamagnetism



paramagnetism

Paramagnetism: If the value of P is greater than unity (i.e. κ is positive), the substance is said to be paramagnetic. It causes an increase in the intensity of the field inside the substance, and the substance moves to the region of highest field strength when kept in a heterogeneous magnetic field. Paramagnetic susceptibilities are usually much higher than diamagnetic

susceptibilities (χ is about 1 to 100×10^{-6}). They are usually independent of field strength, but are inversely proportional to temperature. This is because thermal motion resists the ordering of magnetic moments.

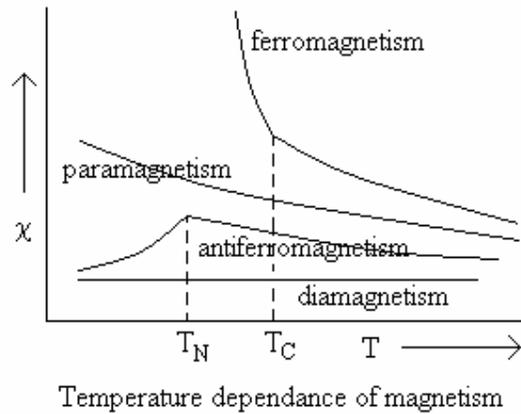
$$\chi_m \propto \frac{1}{T} \quad \text{or} \quad \chi_m = \frac{C}{T}$$

This is known as **Curie's law** (Pierre Curie, Mary Curie's husband and winner of Nobel prize in physics, did much of the work related to magnetism of materials) and C is called the **Curie constant** and T is the absolute temperature. For some paramagnetic substances, molar susceptibility is inversely proportional to $(T + \theta)$ or $(T - \theta)$, where θ is called the **Curie temperature**.

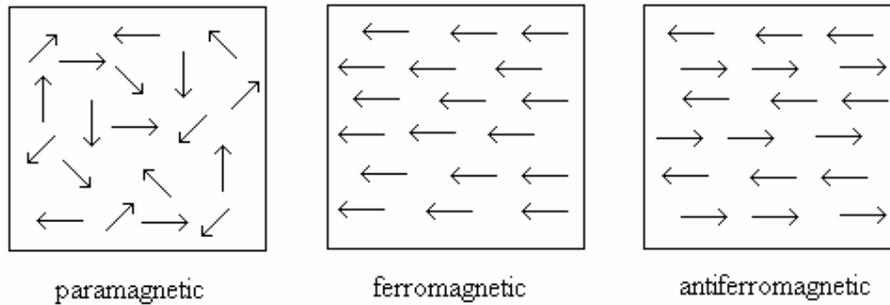
$$\chi_m \propto \frac{1}{T + \theta} \quad \text{or} \quad \chi_m = \frac{C}{T + \theta}$$

This is known as the **Curie – Weiss law**.

There are five types of magnetic behaviour, namely diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism.



Arrangement of magnetic dipoles (domains) in various materials



(1) **Diamagnetism:** In this case, there is no increase in magnetic flux within the substance on application of a strong external magnetic field. This is the behaviour of solids in which the constituent atoms, ions or molecules do not have any unpaired electrons in them.

(2) **Paramagnetism:** This is exhibited by magnetically dilute materials and crystals in which the resultant magnetic moments of individual unit cells are randomly oriented. Therefore the crystal shows no overall magnetic moment in the absence of an external magnetic field. But in the presence of a strong magnetic field applied externally, the magnetic moments of individual unit cells try to align themselves parallel to the external field; therefore there is a slight increase in the magnetic flux within the substance in the presence of an external magnetic field.

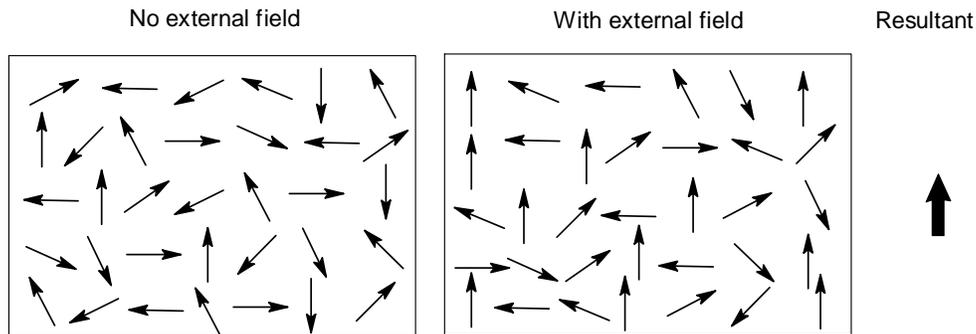


Figure (a) Magnetism of unit cells in paramagnetic crystals

(3) Ferromagnetism: There are materials that retain the magnetization even when the external magnetic field is removed (this phenomenon is called '**hysteresis**'). Such materials are called 'ferromagnetic' and can be made into permanent magnets. Very small magnetic fields applied externally are capable of producing intense magnetic fields within such substances. Examples are Fe, Co, Ni, gadolinium, dysprosium and their alloys, some compounds like CrBr_3 , EuO , EuS etc. The phenomenon of hysteresis is exhibited only upto a certain temperature T_c called **Curie point**. After that they exhibit normal paramagnetism.

Weiss explains ferromagnetism as follows:

When paramagnetic species are close together, such substances are called 'magnetically concentrated' substances. Examples are metals, salts in which there are large metal ions and very small anions. 'Magnetically dilute' materials are paramagnetic substances, dilute solutions of ferromagnetic substances etc.

In magnetically concentrated substances in which the magnetic species are close together, the magnetic field is exchanged or transmitted through cooperative effects over an entire unit cell. The total magnetic field of the unit cell may be directed perpendicular to any of the six faces of the unit cell. Over short distances, a few of the unit cells have their fields aligned parallel to each other. These regions are known as **domains**. But overall, the domains are randomly arranged so that the fields cancel out. A small external magnetic field is capable of aligning all these domains in a parallel orientation. On heating, domains are present upto a certain temperature T_c called Curie point. Above this temperature, thermal agitation destroys the domains and the material exhibits normal paramagnetic properties. Hysteresis occurs because thermal energy is not always able to randomize the alignment of the domains.

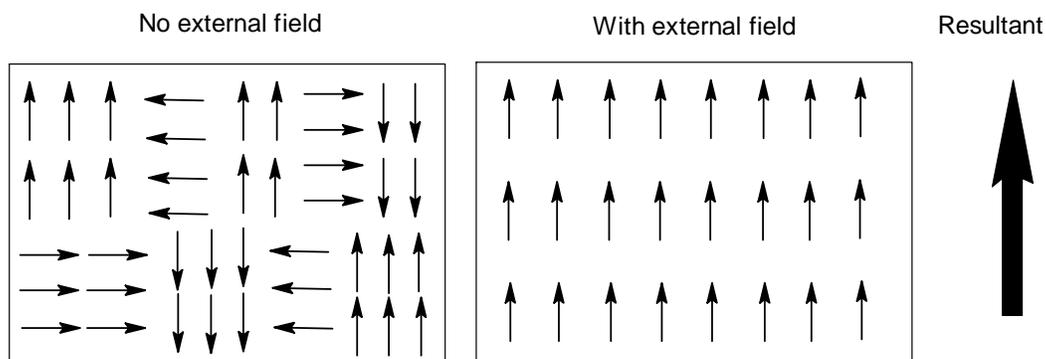


Figure (b) Magnetic alignment of unit cells in ferromagnetic crystals

Antiferromagnetism: This type of substances have strong coupling of antiparallel magnetic dipoles. Neel suggested the presence of sublattices to explain antiferromagnetism. The spins of all atoms within a sublattice are parallel, but two nearby sublattices have their atomic spins in opposite directions. *The resultant magnetic moment of the material is zero.* Increase in temperature tends to make spins in nearby sublattices parallel, upto a point called **Neel temperature** T_N . Beyond that temperature, they exhibit normal paramagnetism. MnO , KNiF_3 and K_2OsCl_6 are examples of antiferromagnetic materials. In such crystals, the distance between metal atoms is such that direct coupling of magnetic moments are improbable. The coupling is expected to take place through the ligands (oxide, fluoride or chloride ions).

In antiferromagnetic materials, transition metal ions are separated by small ligands. Thus many oxides and halides of transition metals show antiferromagnetic behaviour. In such compounds,

adjacent metal ions couple with their spins antiparallel so that there is no resultant magnetization in the absence of an external magnetic field.

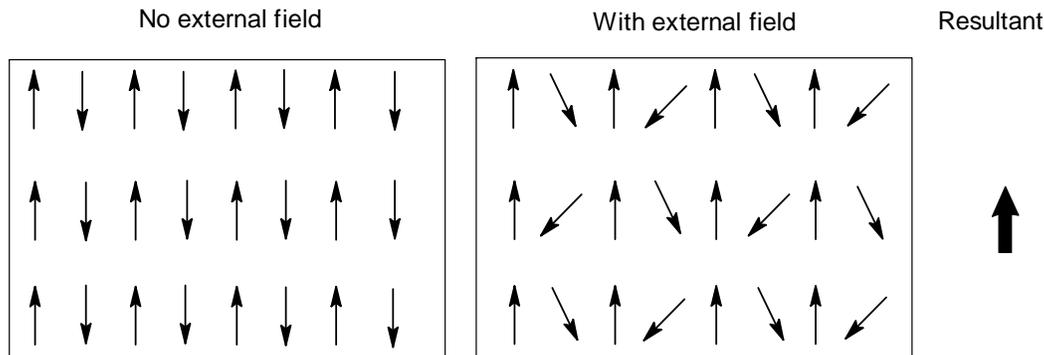
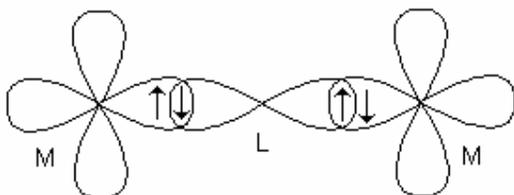


Figure (c) Antiferromagnetically coupled domains

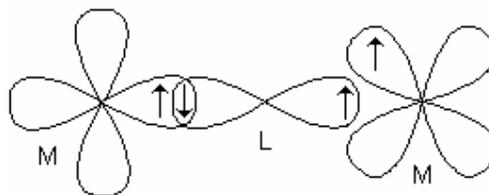
Ligand-mediated antiferromagnetic coupling: Molecular antiferromagnetism occurs when two transition metal ions, both having unpaired electrons, are bonded together by bridging ligands. In such cases the magnetic property of the complex is not simply the sum those of the two individual metal ions. There is a magnetic interaction between them. Such a situation is shown in the following figure.



Consider a case in which there is bonding between the metal orbital containing unpaired electron and a pure p -orbital of the ligand. The ligand bridges to metal atoms. The metal ion on the left-side has up spin. Although there are formally two electrons in the ligand p -orbital, still they are capable of bonding. These two electrons will have opposite

spins. Thus we can see that the two metal ions bonded to them must have electron spins in opposite directions. That is, the two metal ions are antiferromagnetically linked by the ligand. In this example, the two metal ions were considered to be identical. What if they are different?

Consider two metal ions, one of which has its unpaired electron in an e_g orbital and the other has its unpaired electron in an t_{2g} orbital. The t_{2g} orbital is orthogonal to the ligand p -orbital (ie. they have zero overlap integral). Electrons in orthogonal orbitals tend to align themselves with parallel spins. The two metal ions are then ferromagnetically linked by the ligand.



Molecular antiferromagnetism is of great interest at present because of the possibility of developing devices for information storage at the molecular level.

Ferrimagnetism: This is similar to antiferromagnetism, except that the magnetic moment of the material is *not zero* even at low temperatures. This is explained by assuming that the opposing magnetic moments in the sublattices do not cancel each other exactly, producing a resultant residual magnetic moment inside the substance. This unequal magnetic moments may be due to the following reasons:

- (1) All atoms have identical spins, but the number of atoms in the sublattices are not equal.
- (2) The number of atoms in the sublattices are equal, but their spins are not equal.

Just as in the case of antiferromagnetic materials, ferrimagnetic materials have ions on two sets of lattice sites. These have opposed spin arrangements, but their magnitudes are not the same and do not cancel out. Therefore there is a resultant permanent magnetic moment. The best known example is the magnetic oxide of iron, Fe_3O_4 . In this, one site contains Fe(III) while the other site contains equal number of Fe(II) and Fe(III) ions.

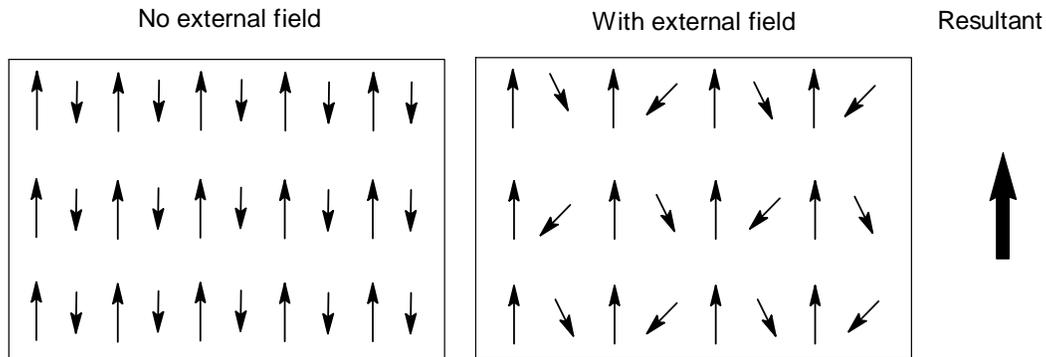
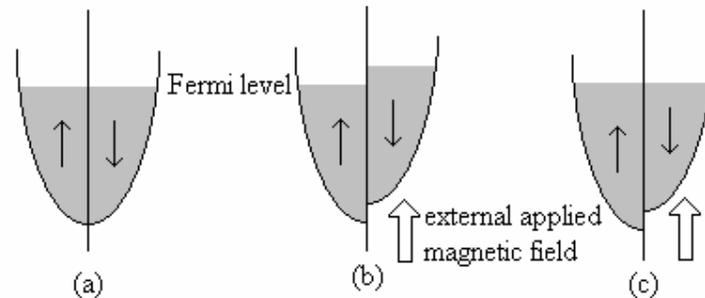


Figure (d) Ferrimagnetism. Note that the opposing moment is weaker in one direction

Temperature independent paramagnetism: According to the free electron theory, the magnetism exhibited by materials is because of the valence electrons which are free. Calculations based on the assumption that *all valence electrons contribute* predict that such paramagnetism should vary greatly with temperature, and the calculated susceptibilities much higher than those really observed.

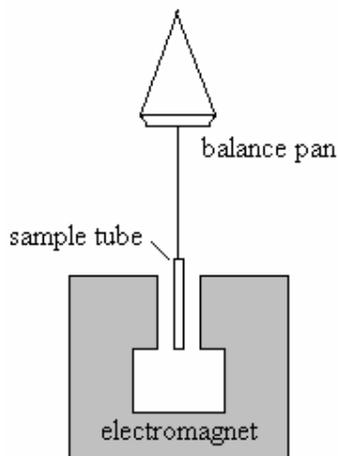


According to MO theory or band theory, the phenomenon is explained as follows: In the absence of an external magnetic field, the valence band is populated by equal number of electrons having + and – spins upto the Fermi level, as shown in (a). In presence of an external magnetic field, the energy of the electrons with a spin parallel to the applied field is lowered, while that of the electrons with opposing spin is raised, as shown in (b). Therefore a few electrons with opposing spin change their spin value and migrate to the lower energy level to reach equilibrium, as shown in (c). *Only these small number of excess electrons in the lower energy state contribute to paramagnetism* while the field due to other electrons are cancelled by the electrons with opposite spin. Therefore the paramagnetism and temperature dependence are much less than what is predicted by the free electron theory.

The *magnetic properties of a crystal are anisotropic*. A ferromagnetic crystal is easily magnetized in a certain direction called the easy direction while it may be difficult in other directions. This is due to the presence of magnetic domains aligned in certain directions. The electrons in a domain may exert an influence on nearby domains and align them parallel to it. This is called **cooperative magnetism**.

Experimental measurement of magnetic susceptibilities – the Guoy method:

Two very common methods used for the measurement of magnetic susceptibilities are the Guoy and the Faraday methods. They are very similar to each other and the Faraday method is a refinement overcoming the defects of the Guoy method. (1) While the Guoy method requires approximately 1 gram of substance, the Faraday method requires only a few milligrams of the substance. (2) Guoy method gives only the volume susceptibility which can be converted to specific susceptibility only if density is known; this may vary depending on how the substance, usually in powder form, is packed. The Faraday method gives the specific susceptibility directly. Both methods make use of determining the weight of a small quantity of the substance with and without an externally applied magnetic field.



The setup for measurement is known as a **Guoy balance**, and is given schematically in the diagram. The powdered sample is packed tightly in a uniform sample tube and suspended from the pan of a sensitive balance between the poles of a strong electromagnet with non-uniform field. The weight of the sample is first determined in the absence of the magnetic field, and then again after switching on the magnetic field. The excess weight in the latter case is due to the force exerted on the sample by the magnetic field gradient. If 'm' is the mass of the sample, ' χ ' is the specific susceptibility, 'H' is the field strength and $(\delta H/\delta x)$ is the field gradient, the force 'f' exerted by it on the substance is given by:

$$f = m \chi H (\delta H/\delta x)$$

Usually the experiment is simplified by measuring the force ' f_s ' exerted on a standard of known susceptibility such as $\text{Hg}[\text{Co}(\text{SCN})_4]$ for which $\chi = 16.44 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ on the same machine under identical conditions. Then for the standard,

$$f_s = m_s \chi_s H (\delta H/\delta x)$$

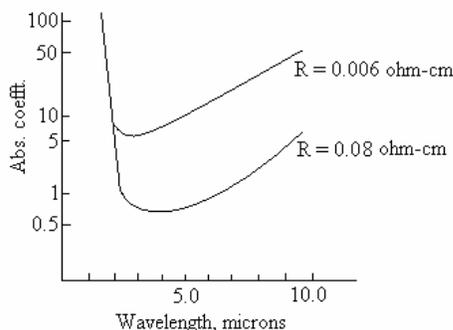
and for the sample,

$$f = m \chi H (\delta H/\delta x)$$

Then,

$$\frac{f_s}{m_s \chi_s} = \frac{f}{m \chi}$$

from which ' χ ' can be calculated since the other quantities are known. Multiplying χ with the molar mass of the substance gives the molar susceptibility.

OPTICAL PROPERTIES

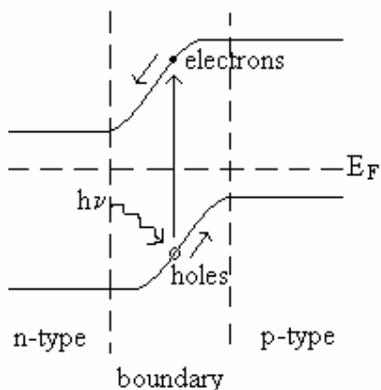
Many semiconductors such as Si, Ge and InSb exhibit typical metallic luster when viewed with ordinary light. But when examined under monochromatic radiation in the infrared region, the absorption is found to depend on the wavelength. The figure shows the variation of the linear absorption coefficient with wavelength for two germanium crystals of different resistances. On moving from higher wavelength to shorter wavelength (right to left) in the diagram, it is seen that the absorption initially decreases, indicating that the crystals become more

transparent. This is because photons of lower wavelength have more energy and penetrate deeper into the crystal. But the striking feature is that at about 1.7μ , the absorption becomes extremely high. The reason for this becomes clear when the band model for germanium is considered. The energy of the radiation corresponding to 1.7μ is 0.72 eV , which is the width of the energy gap in germanium. Thus a photon having this energy is capable of exciting an electron a quantum state at the top of the valence band into a quantum state at the bottom of the conduction band. Radiation of shorter wavelength can also excite electrons from lower energy quantum states into other states in the conduction band. The increased number of free electrons produced accounts for the metallic luster because these electrons reradiate the energy when they fall back to lower energy levels. Note that the lower resistivity germanium has greater absorption at all wavelengths. Lower resistivity means that there are more electrons in the conduction band. Thus, absorption measurements can be used to determine the nature of the band model of semiconductors. The measurements have to be made at very low temperatures in order to minimize the thermal excitation of the electrons.

Photoconductivity: When an electric field is applied to a semiconducting crystal and radiation of appropriate wavelength is allowed to fall on it, an increase in its conductivity is observed. This property of photoconductivity is utilized in a large number of applications. One of the simplest application is that the crystal can be used as a detector for that radiation. Depending on the gap width of the material, detectors for various wavelengths such as visible light, X-rays or nuclear radiations can be designed. Although the general nature of photoconductivity has been extensively studied, the exact theory for the process is not yet developed (as in 1960). This is mainly because there is a possibility for the excited electrons in the conduction band to recombine with the holes generated. Direct combination is forbidden and has to take place through electron-phonon interactions (see diagram under photovoltaic effect).

Photoelectromagnetic effect: It is possible to combine photoconductivity with Hall effect. The conduction electrons and holes produced on the surface of a suitably irradiated semiconductor tend to diffuse into the bulk of the specimen. When such a crystal is then placed in a transverse magnetic field, the electrons and holes are deflected through the Hall angle to opposite sides of the crystal. This produces a current which can be measured, and the phenomenon is called photoelectromagnetic effect, or abbreviated as **PEM effect**.

Photovoltaic effect: It is possible to grow a single crystal containing both n-type and p-type regions. The boundary between two such regions is called a p-n junction and has some very interesting properties. Consider a crystal containing two such regions and a transition zone between



them. At the transition zone, there is a bend (energy barrier) in the energy level diagram, as indicated in the figure. When light is incident on the crystal, electron-hole pairs are produced and the electrons diffuse into the n-region (“rolls down to lower energy region”) while the holes diffuse into the p-region. This diffusion is called **photocurrent**. Thus the p-region becomes progressively positively charged and the n-region negatively charged. This is called photovoltaic effect. Such a crystal obviously can be used as a *battery* whose energy is derived from light, and is used in **solar cells**. The maxima in the solar radiation curve corresponds to about 1 eV , and therefore Si, Ge and GaAs with band gaps of 1.12 eV , 0.66 eV and 1.42 eV are suitable. GaAs is a **direct gap semiconductor** while the other two are indirect gap semiconductors (semiconductors having

the same wave vector for the maximum of the valence band and minimum of the conduction band are called direct gap semiconductors. Transitions are easier in such cases). Incident radiation is absorbed rapidly on the surface of a direct gap semiconductor and hence GaAs is the most widely

used. For very large light intensities, it is found that the voltage generated varies logarithmically with the photocurrent. This is why photovoltaic cells are very useful in ordinary light meters used by photographers.

Luminescence: An electron that has been photo-excited to the conduction band can return to a lower-lying allowed state provided that such transition is accompanied by emission of an appropriate quantum of energy. The number of different transitions possible is determined by the number and kinds of allowed states lying in the forbidden energy band. Consequently, these phenomena are rather complicated. *The term **luminescence** is used to describe phenomenon whereby a crystal absorbs energy, usually in the form of radiation, and reemits in the form of visible light. If the crystal emits light immediately after (less than 10^{-7} seconds) excitation, it is called **fluorescence**. If emission takes place some time after excitation, it is called **phosphorescence**, and such a crystal is called a **phosphor**.*

There are two distinct processes for luminescence, both of which require the presence of impurity atoms called **activators** in them. In the first one, the incident radiation is absorbed by the activator atom and then reemitted. Since the transitions are characteristic of the energy levels in the activator atoms, this process is called **characteristic luminescence**. The second process is more complicated. Consider a divalent sulphide in which many of the normal metal atoms have been substituted by monovalent cations. Other ions called **coactivators** are necessary to maintain electrical neutrality. When an electron-hole pair is created by irradiation, the extra electron on the monovalent cation combines with the hole, emitting a photon. The colour of the emitted light depends on the imperfections introduced.

When luminescence is produced by incident X-rays, UV or visible light, IR etc, it is called **photoluminescence**. When a phosphor is irradiated by high energy electrons, the electrons lose part of their energy by electron-electron collision in the crystal. The secondary electrons combine with holes in the crystal, producing luminescence. This is called **cathodoluminescence**. Electrical energy is absorbed and reemitted as visible light of a suitable colour in light-emitting diodes or LEDs. This is called electroluminescence. If a phosphor excited by any of the above methods is cooled, the reduced energy of the electrons retard luminescence till the temperature is raised. This is called **thermoluminescence**.

Magnetic properties of metal complexes

As already discussed, paramagnetism is produced by unpaired electrons in a sample. The spins and orbital motions of these electrons give rise to a permanent molecular magnetic moment. Once the macroscopic magnetic susceptibility of a substance is measured, the next step is to connect this data to the number of unpaired electrons present in the sample. Susceptibility measurements can be used to determine whether a complex is high spin or low spin. [For discussions on L, S and J values of atoms and ions, refer to notes on Term Symbols].

The molar susceptibility is related to the permanent paramagnetic moment of a molecule, μ , by:

$$\chi_M = \frac{N^2 \mu^2}{3RT}$$

where N is the Avogadro number, R is the gas constant, T is the absolute temperature and μ is expressed in Bohr magnetons (BM). [1 BM = $eh/4\pi m$]. Solving for μ and substituting the values of N and R in the equation,

$$\mu = 2.84 \sqrt{\chi_M T}$$

There are three modes of coupling between spin and orbital contributions to magnetic moment. These are spin-spin, orbital-orbital and spin-orbital. For some complexes, particularly those of the

lanthanides, all these couplings have to be taken into consideration, and then the theoretical magnetic moment is given by:

$$\mu = g \sqrt{J(J+1)}$$

where 'g' is known as the gyromagnetic ratio or the Landé splitting factor and its value is about 2.0 and 'J' is the total angular momentum quantum number. For complexes in which spin-orbit coupling is negligible but both spin and orbital contributions are significant, the expression for μ is:

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

This is usually not applicable to complex compounds since the orbital contribution of the metal ion is reduced by the presence of ligands. In the extreme case where $L = 0$ or negligible, the equation becomes:

$$\mu = 2 \sqrt{S(S+1)}$$

which is known as the spin-only formula for magnetic moment. This is the case with first-row transition elements. Further, since the number of unpaired electrons $n = 2S$, the expression may be simplified to:

$$\mu = \sqrt{n(n+2)}$$

The experimental and calculated magnetic moments are in good agreement as indicated by a few values for high-spin complexes of ions given below:

| Metal ion | Ti ³⁺ | V ³⁺ | Cr ³⁺ | Cr ²⁺ | Fe ³⁺ | Ni ²⁺ |
|---------------------------|------------------|-----------------|------------------|------------------|------------------|------------------|
| No. of unpaired electrons | 1 | 2 | 3 | 4 | 5 | 2 |
| Calculated BM | 1.73 | 2.83 | 3.88 | 4.90 | 5.92 | 2.83 |
| Experimental BM | 1.73 | 2.75-2.85 | 3.80-3.90 | 4.75-4.90 | 5.70-6.0 | 2.80-3.50 |

The theoretical magnetic moment for a metal complex can be calculated using all the above equations separately, and the equation which fits the experimental value most can be determined. This then gives the type of coupling present in that complex. The numbers of unpaired electrons in low-spin and high-spin complexes of the same ion are different. The number of unpaired electrons present can be determined by measuring the magnetic moment. These will then lead to a proper understanding of the structure of the complex.