DIRECTORATE OF DISTANCE & CONTINUING EDUCATION

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI- 627 012

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

M. Sc. Chemistry

Course material

Core II - STRUCTURE AND BONDING IN INORGANIC COMPOUNDS

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Tirunelveli - 12

Semester - I

Course: CORE - II **Course Code** SCHM12

STRUCTURE AND BONDING IN INORGANIC COMPOUNDS

UNIT-I: Structure of main group compounds and clusters: VB theory – Effect of lone pair and electronegativity of atoms (Bent's rule) on the geometry of the molecules; Structure of silicates - applications of Paulings rule of electrovalence - isomorphous replacements in silicates – ortho, meta and pyro silicates – one dimensional, two dimensional and three-dimensional silicates. Structure of silicones, Structural and bonding features of B-N, S-N and P-N compounds; Poly acids – types, examples and structures; Borane cluster: Structural features of closo, nido, arachano and klado; carboranes, hetero and metalloboranes; Wade's rule to predict the structure of borane cluster; main group clusters –zintl ions and mno rule.

UNIT-II: Solid state chemistry – I: Ionic crystals: Packing of ions in simple, hexagonal and cubic close packing, voids in crystal lattice, Radius ratio, Crystal systems and Bravis lattices, Symmetry operations in crystals, glide planes and screw axis; point group and space group; Solid state energetics: Lattice energy – Born-Lande equation - Kapustinski equation, Madelung constant.

UNIT-III: Solid state chemistry – II: Structural features of the crystal systems: Rock salt, zinc blende & wurtzite, fluorite and anti-fluorite, rutile and anatase, cadmium iodide and nickel arsenide; Spinels -normal and inverse types and perovskite structures. Crystal Growth methods: From melt and solution (hydrothermal, sol-gel methods) – principles and examples.

UNIT-IV: Techniques in solid state chemistry: X-ray diffraction technique: Bragg's law, Powder diffraction method – Principle and Instrumentation; Interpretation of XRD data – JCPDS files, Phase purity, Scherrer formula, lattice constants calculation; Systematic absence of reflections; Electron diffraction technique – principle, instrumentation and application. Electron microscopy – difference between optical and electron microscopy, theory, principle, instrumentation, sampling methods and applications of SEM and TEM.

UNIT-V: Band theory and defects in solids

Band theory – features and its application of conductors, insulators and semiconductors, Intrinsic and extrinsic semiconductors; Defects in crystals – point defects (Schottky, Frenkel, metal excess and metal deficient) and their effect on the electrical and optical property, laser and phosphors; Linear defects and its effects due to dislocations.

Recommended Text

1. A R West, Solid state Chemistry and its applications, 2ndEdition (Students Edition), John Wiley & Sons Ltd., 2014.
2. A K Bhagi and G R Chatwal, A textbook of inorganic polymers, Himalaya Publishing House, 2001.
3. L Smart, E Moore, Solid State Chemistry – An Introduction, 4th Edition, CRC Press, 2012.
4. K. F. Purcell and J. C. Kotz, Inorganic Chemistry; W.B. Saunders company: Philadelphia, 1977.
5. J. E. Huheey, E. A. Keiter and R. L. Keiter, Inorganic Chemistry; 4th ed.; Harper and Row: NewYork, 1983.

Reference Books

1. D. E. Douglas, D.H. McDaniel and J. J. Alexander, Concepts and Models in Inorganic Chemistry, 3rd Ed, 1994.
2. R J D Tilley, Understanding Solids - The Science of Materials, 2nd edition, Wiley Publication, 2013.
3. C N R Rao and J Gopalakrishnan, New Directions in Solid State Chemistry, 2nd Edition, Cambridge University Press, 199.
4. T. Moeller, Inorganic Chemistry, A Modern Introduction; John Wiley: New York, 1982.
5. D. F. Shriver, P. W. Atkins and C.H. Langford; Inorganic Chemistry; 3rd ed.; Oxford University Press: London, 2001.

STRUCTURE AND BONDING IN INORGANIC COMPOUNDS

Unit-I Structural and Bonding Features of Boranes

Valence Bond Theory (VBT)

Introduction

We have already said that Werner was the first to explain the nature of bonding in complex compounds. However, with the advancement of theories of valence, modern theories have been proposed to explain the nature of metal-ligand bonding in complexes. These theories can also explain the colour, geometry and magnetic properties of the complex compounds. These mode theories are:

(i) Valence Bond Theory: VBT (due to L. Pauling and JL Slater, 1935)

(ii) Crystal Field Theory: CFT (due to H. Bethe. 1929 and Van Vleck, 1932) (iii) Ligand Field Theory LFT or Molecular Orbital Theory, MOT (due to J. Van Vleck, 1935). Here we shall discuss only valence bond theory.

Valence Bond Theory (VBT)

This theory is mainly due to Pauling. It deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

Assumptions of valence bond theory :

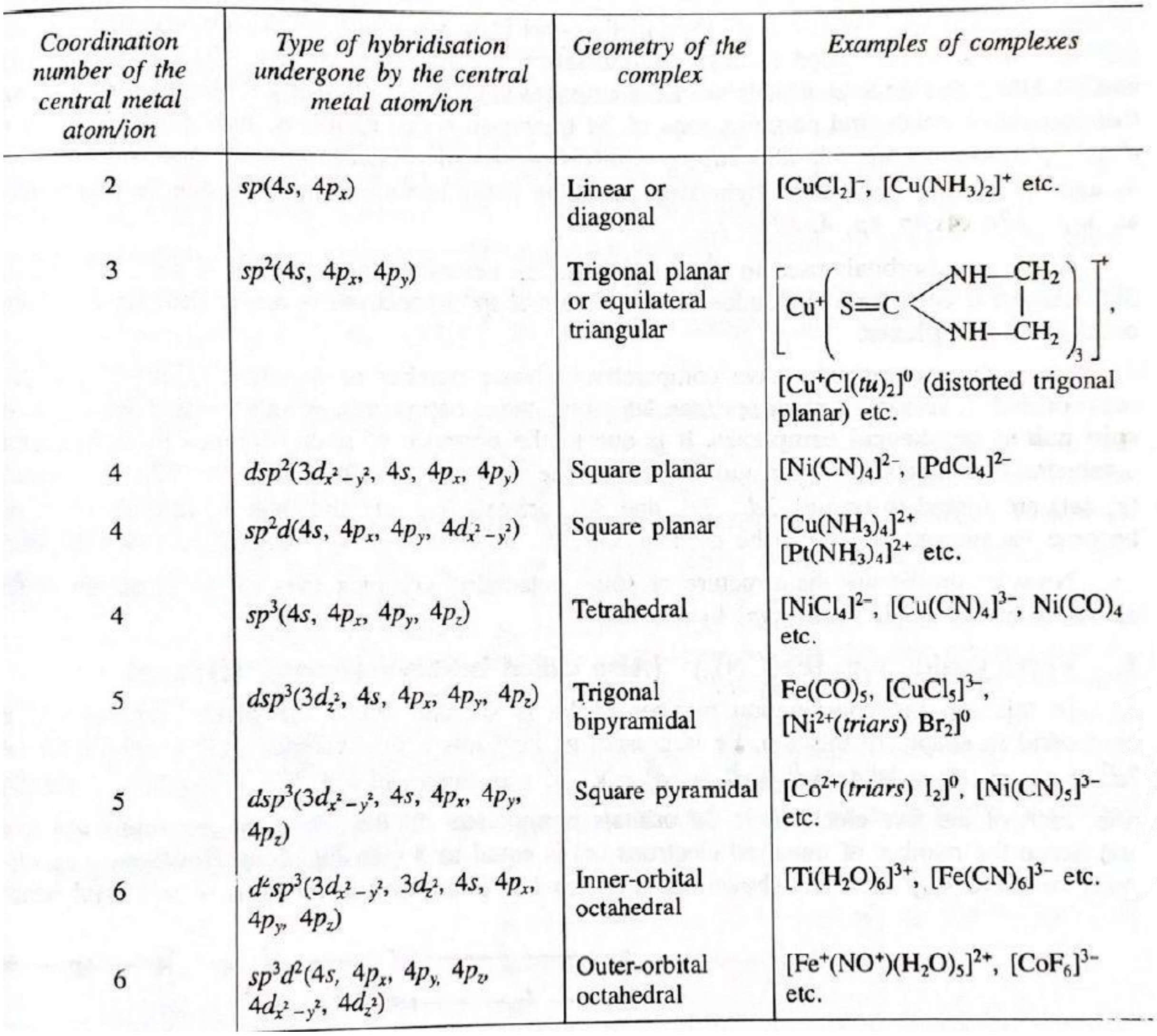
1. The central metal atom or ion makes available a number empty s, p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridized together to form hybrid orbitals which are the same in number as the atomic orbitals hybridized together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry: Important types of hybridisation occuring in the first row transition metal (3d) complexes and the geometry of the complex are given in Table.

2. The ligands have at least one -orbital containing a lone pair of electrons.

3. Vacant hybrid orbitals of the metal atom or ion overlap with the filled (containing lone pair of electrons) -orbitals of the ligands to form ligand→ metal -bond. This bond is known as coordinate bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation

4. The non-bonding electrons of the metal atom or ion are rearranged in the metal orbitals (viz. pure d, s or p orbitals as the case may be) which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's rule.

Table: Important types of hybridisation found in the first row transition metal complexes and the geometry of the complexes



Coordination number of the central metal atom/ion	*Type of hybridisation undergone by the central metal atom/ion*	*Geometry of the complex*	*Examples of complexes*
2	$sp(4s, 4p_x)$	Linear or diagonal	$[CuCl_2]^-$, $[Cu(NH_3)_2]^+$ etc.
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar or equilateral triangular	$\left[Cu^{+}\left(S{=}C\begin{smallmatrix}NH{-}CH_2\\ \vert\\ NH{-}CH_2\end{smallmatrix}\right)_3\right]^{+}$, $[Cu^+Cl(tu)_2]^0$ (distorted trigonal planar) etc.
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$
4	$sp^2d(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$	Square planar	$[Cu(NH_3)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$ etc.
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $Ni(CO)_4$ etc.
5	$dsp^3(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$, $[Ni^{2+}(triars)\ Br_2]^0$
5	$dsp^3(3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$	Square pyramidal	$[Co^{2+}(triars)\ I_2]^0$, $[Ni(CN)_5]^{3-}$ etc.
6	$d^2sp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2})$	Outer-orbital octahedral	$[Fe^+(NO^+)(H_2O)_5]^{2+}$, $[CoF_6]^{3-}$ etc.

Geometry of 6-coordinated complex ions:

In all the complex ions the coordination number of the central metal atom or ion is six the complex ions have octahedral geometry.

This octahedral geometry arises due to d^2sp^3 or sp^3d^2 hybridisation of the central metal atom or ion. What type of hybridisation will occur depends on the number of unpaired or paired electrons present in the complex ion. d^2sp^3 or sp^3d^2 hybridisation is also called octahedral hybridisation.

Octahedral complexes in which the central atom is d^2sp^3 hybridised are called inner-orbital octahedral complexes while the octahedral complexes in which the central atom is sp^3d^2 hybridised are called outer-orbital octahedral complexes.

d^2sp^3 Hybridisation in Inner Orbital Octahedral Complexes:

This type of hybridisation takes place in those octahedral complexes which contain strong ligands. On the basis of the orientation of the lobes of d-orbitals in space, these orbitals have been classified into two sets viz. t_{2g} (d_{xy}, d_{yz} and d_{xz}) and e_g ($d_{z2}$and d_{x2-y2}) orbitals. In the formation of six d^2sp^3 hybrid orbitals, two (n-1) d-orbitals of e_g set, one ns and three np (np_x, np_y, and np_z) orbitals combine together and form six d^2sp^3 hybrid orbitals.

Thus we see that the two d-orbitals used in d^2sp^3 hybridisation are from penultimate shells [ie. (n-1)th shell] while s and three p-orbitals are from ultimate shell (ie. nth shell). This discussion shows that in case of octahedral complex ions of 3d transition series elements, two d-orbitals used in d^2sp^3 hybridisation are $3d_{z2}$ and $3d_{x2-y2}$ orbitals while s- and p-orbitals are 4s and 4p orbitals. Thus d^2sp^3 hybridization taking place in such complexes can be represented as: $d_{x2-y2}.d_{z2}.4s.4p_x.4p_y.4p_z(d^2sp^3)$.

Since two d-orbitals used in d^2sp^3 hybridisation belong to the inner shell [i.e. (n-1)th shell], the octahedral complex compounds resulting from d^2sp^3 hybridisation are called **inner orbital octahedral complexes**.

Ferrocyanide ion OR hexacyanoferrate (II) ion $[Fe(CN)_6]^{4-}$:

In this ion, since the coordination number of Fe is six, the given complex ion has octahedral geometry. In this ion, Fe is present as Fe^{2+} ion whose valence-shell configuration is $3d^6\ 4s^0\ 4p^0$ or , $t_{2g}\ ^4\ e_g\ ^24s^0\ 4p^0$ which shows that Fe^{2+} ion has 4 unpaired electrons. Magnetic studies have, however, shown that the given complex ion is diamagnetic and hence it has no unpaired electrons ($n = 0$). Hence in order to get all the electrons in the paired state, two electrons of e_g orbitals are sent to t_{2g} orbitals so that n becomes equal to zero.

Since CN^- ions (ligands) are strong ligands, they are capable of forcing the two electrons of e_g orbitals to occupy t_{2g} orbitals and thus make all the electrons paired. Now for the formation of $[Fe(CN)_6]^{4-}$ ion, two 3d orbitals of e_g set, 4s orbital (one orbital) and three 4p orbitals (all these six orbitals are vacant orbitals) undergo d^2sp^3 hybridisation (see Figure). It is due to d^2sp^3 hybridisation that $[Fe(CN)_6]^{4-}$ ion is an inner orbital octahedral complex ion. The electron pair donated by CN^- ion (ligand) is accommodated in each of the six d^2sp^3 hybrid orbitals as shown in Figure 5.2.

sp^3d^2 Hybridisation in Outer Orbital Octahedral Complexes

This type of hybridisation takes place in those octahedral complex ions which contain weak ligands. Weak ligands are those which cannot force the electrons of d_{z2} and d_{x2-y2} orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{xz} orbitals of the same shell. Thus in this hybridisation. $(n-1)d_{z2}$ and $(n-1)d_{x2-y2}$ orbitals are not available for hybridisation. In place of these orbitals, we use nd_{z2} and nd_{x2-y2} orbitals (These d-orbitals belong to the outer shell) and hence sp^3d^2 hybridisation can be represented as ns, np_x, np_y, np_z, nd^2, nd_{x2-y2} .

This hybridisation shows that all the six orbitals involved in hybridisation belong to the higher energy level (outer shell). This discussion shows that in the case of octahedral ions of 3d transition series, d-orbitals used in hybridisation are $4d_{z2}$ and $4d_{x2-y2}$ orbitals. Since two d-orbitals are from the outer shell (i.e., nth shell), the octahedral complexes resulting from sp^3d^2

hybridisation are called **outer orbital octahedral complexes**. Since these complexes have a comparatively greater number of unpaired electrons than the inner orbital octahedral complexes, these are also called **high spin or spin free octahedral** complexes. Now let us discuss the structure of some octahedral complex ions of 3d transition series elements which are formed by sp^3d^2 hybridisation.

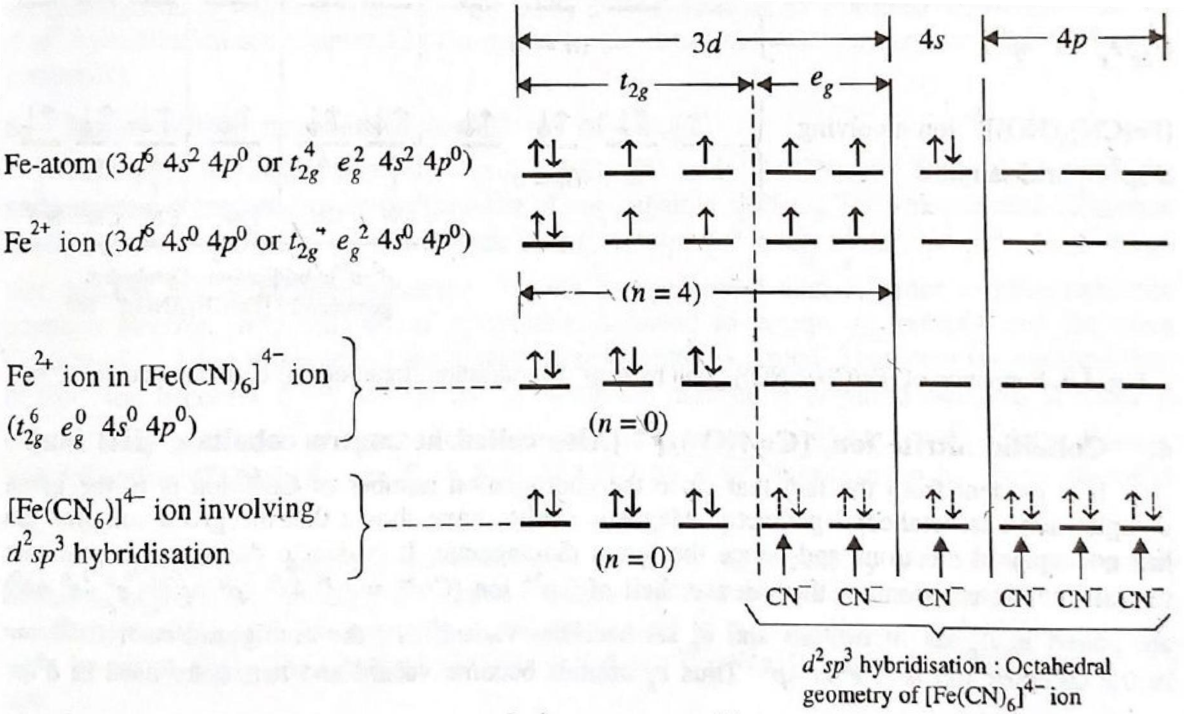


Fig. 5.2. Formation of $[Fe(CN)6]^{4-}$ ion by d^2sp^3 hybridisation. ↑↓ indicates electron pair donated by each CN^- ion (ligand) (Inner-orbital octahedral complex ion).

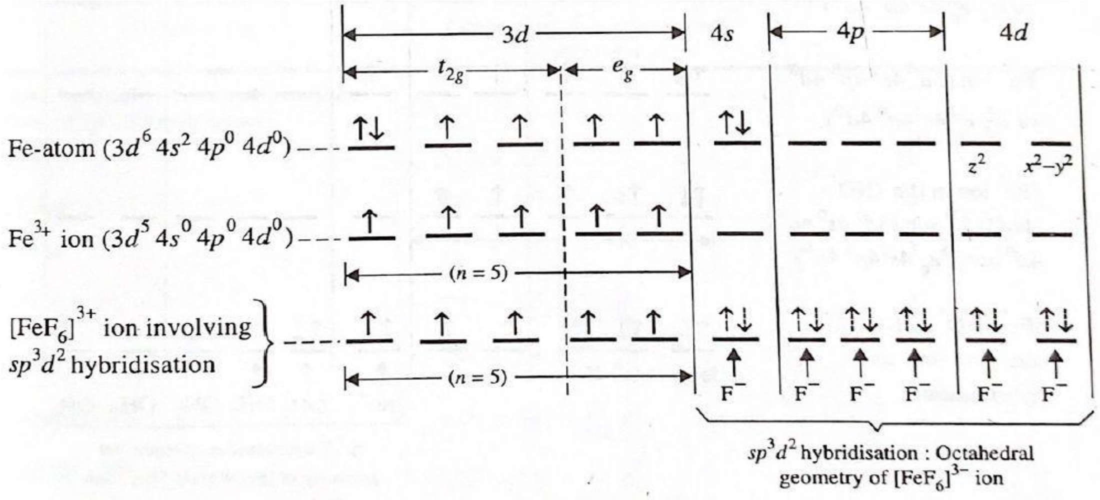


Fig. 5.7. Formation of $[FeF_6]^{3-}$ ion by sp^3d^2 hybridisation. (Outer-orbital octahedral complex ion).

Hexafluroferrate (III) ion $[FeF_6]^{3-}$:

In this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry. Here iron is present as Fe^{3+} whose valence shell electronic configuration is $3d^5\ 4s^0\ 4p^0$ or $t_{2g}^{3}\ e_g^{2}$. Each of the five electrons is unpaired and hence n = 5. Magnetic properties of the given ion have also shown that the ion has five unpaired electrons and hence is paramagnetic corresponding to the presence of five unpaired electrons. Thus two electrons residing in orbitals cannot be forced to occupy t_{2g} orbitals as we have done in case of $[Fe(CN)_6]^{3-}$ ion, otherwise the number of electrons would become equal to one.

Thus we find that in case of the given ion, the two d-orbitals used in hybridisation are $4d_{z2}$ and $4d_{x2-y2}$, (and not $3d_{z2}$ and $3d_{x2-y2}$ as in case of $[Fe(CN)_6]^{3-}$ ion) and s and p orbitals are 4s and 4p. Thus the given ion results from $(4s)\ (4p^3)\ (4d_{z2})\ (4d_{x2-y2})$ hybridisation as shown in Figure. This discussion shows that in the formation of $[FeF_6]^{3-}$ in the original valence-shell configuration of Fe^{3+} ion is not disturbed.

Differences between inner orbital and outer orbital octahedral complexes

Inner orbital octahedral complexes	**Outer orbital octahedral complexes**
(i) These are formed by d^2sp^3 hybridisation i.e.in the formation of six d^2sp^3 hybrid orbitals, two (n-1)d orbitals of e_g set, one ns and three np orbitals are used. (n-1)d orbitals belong to the inner (penultimate) shell while ns and np orbitals belongto the outer (ultimate) shell.	(i) These are formed by sp^3d^2 hybridisation i.e.in the formation of six sp^3d^2 hybrid orbitals, two nd orbitals of e_g set, one ns and three np orbitals are used. Thus all the orbitals belong to the outer (ultimate) shell.
(ii) These complexes have comparatively lesser number of unpaired electrons and hence are also called low spin or spin paired complexes.	(ii) These complexes have a comparatively greater number of unpaired electrons and hence are also called high spin or spin free complexes.
(iii) These are given by strong ligands.	(iii) These are given by weak ligands.

Geometry of 4-coordinate complex ion:

Examples of 4-coordinated complex ions formed by some transition metals. In these complex ions the coordination number of the central metal atom or ion is four. Such complex ions may have either square planar or tetrahedral geometry, depending on whether the central atom or ion is dsp^2 or sp^3 hybridised. What type of hybridisation (ie.. whether dsp^2 or sp^3) the central metal atom or ion of a 4-coordinated complex ion undergoes depends on the number of unpaired or paired electrons present in the complex ion.

Square Planar geometry (dsp^2) $[Ni(CN)_4]^{2-}$ Tetracyanonickelate(II) :

When $[NI(CN)_4]^{2-}$ion is square planar geometry, Ni^{2+} ion should be dsp^2 hybridised. In this hybridisation, due to the energy made available by the approach of four CN^- ions (ligands), the two unpaired 3d-electrons are paired up, thereby, making one of the 3d orbitals empty. This empty 3d orbital (which is $3d_{x2-y2}$ orbital) is used in dsp^2 hybridisation. This hybridisation makes all the electrons paired (n = 0) and hence is diamagnetic, as shown in Figure.

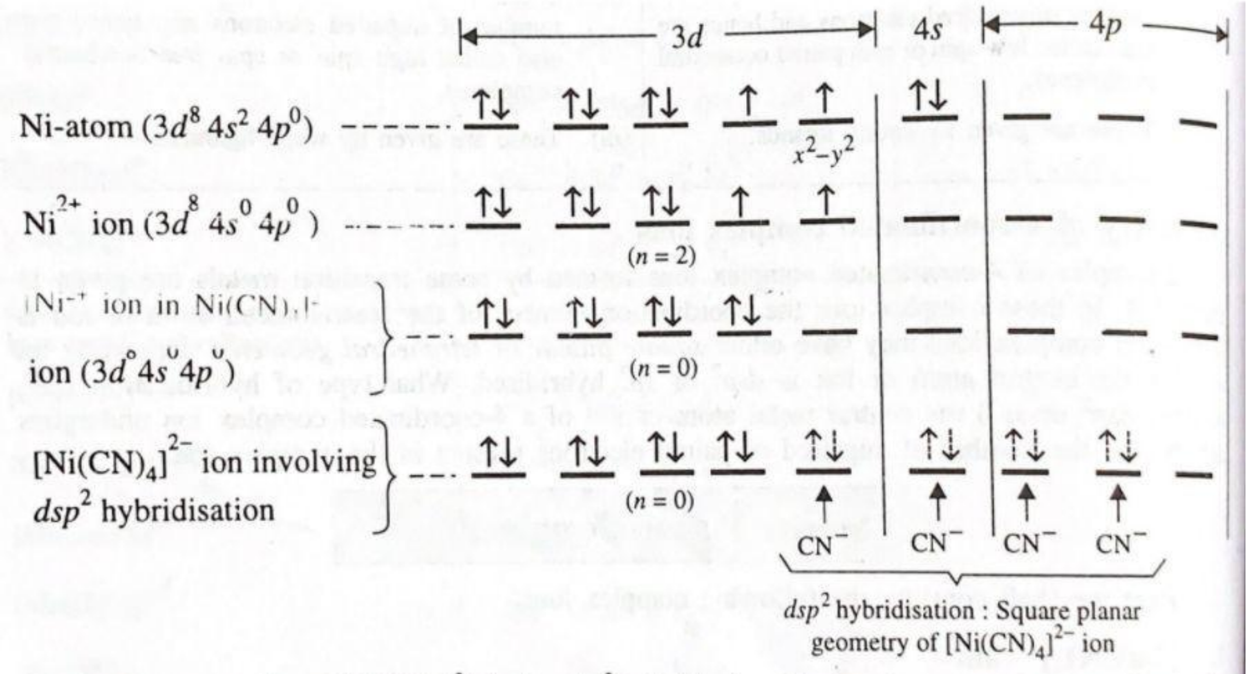


Fig. 5.11. Formation of $[Ni(CN)_4]^{2-}$ ion by dsp^2 hybridisation (Square planar complex ion with $n = 0$)

Tetrahedral geometry (sp^3)

$[Ni(CO)_4]$ molecule (Tetracarbonylnickel):

In this complex compound Ni is in zero oxidation state and has its valence-shell configuration as $3d^8 4s^2$. This compound has tetrahedral geometry which arises due to sp hybridisation of Ni atom.

The magnetic studies of $[Ni(CO)_4]$ have indicated that this molecule is diamagnetic (n = 0), showing that the two 4s electrons are forced to pair up with 3d orbitals. This results in sp^3 hybridisation and the $[Ni(CO)_4]$ molecule has a tetrahedral structure in the figure.

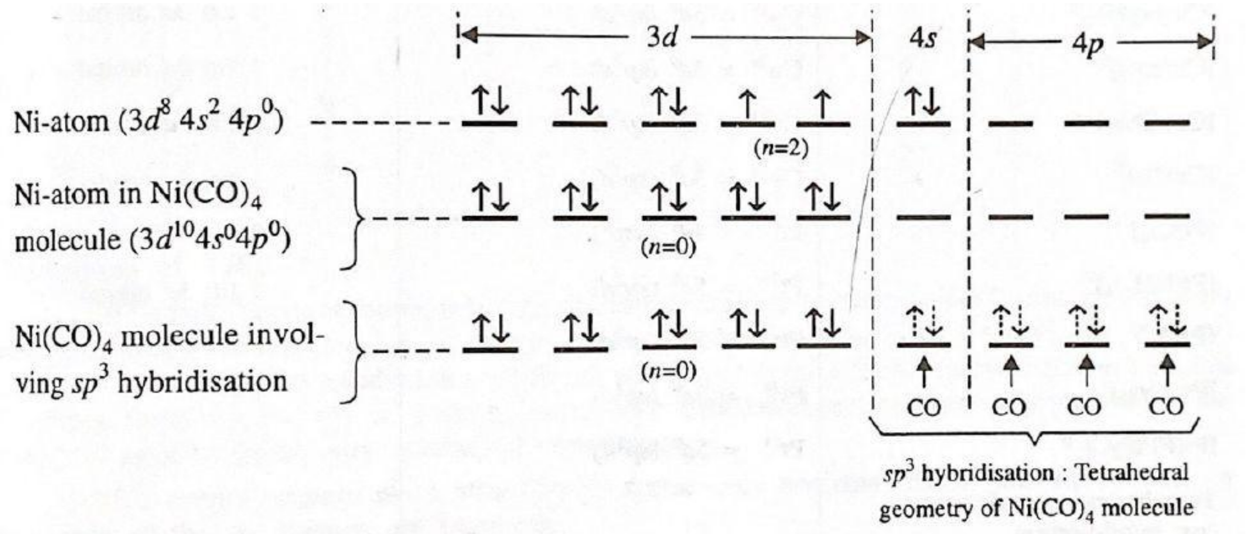
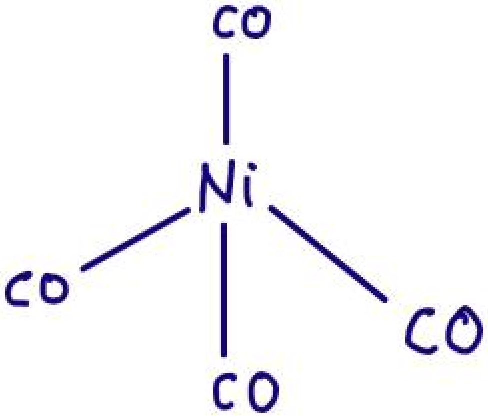
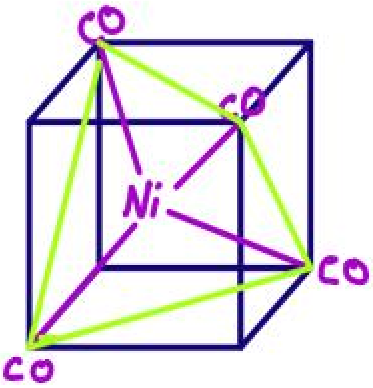


Fig. 5.16. sp^3 hybridisation of Ni-atom in $Ni(CO)_4$ molecule which has tetrahedral shape.





$[NICl_4]^{2-}$ ion (Tetrachloronickelate(II)) :

This complex ion has Ni^{2+} ion whose valence-shell configuration is $3d^8 4s^0$. Magnetic measurements reveal that the given ion is paramagnetic and has two unpaired electrons (n = 2). This is possible only when this ion is formed by sp^3 hybridisation and has tetrahedral geometry in the figure.

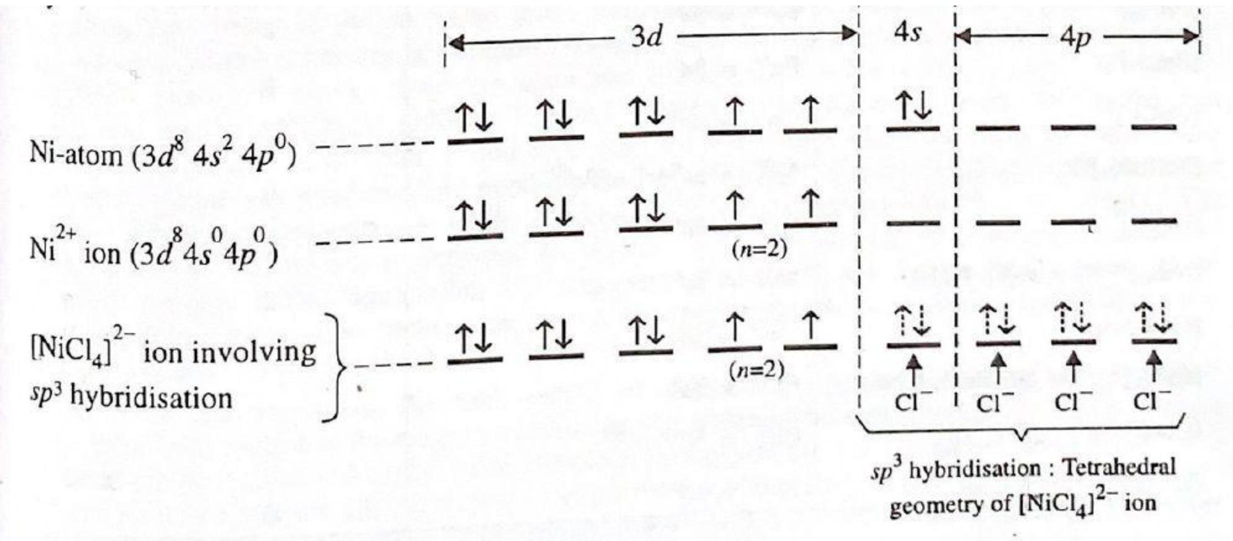


Fig. 5.17. sp^3 hybridisation of Ni^{2+} ion in $[NiCl_4]^{2-}$ ion which has tetrahedral geometry.

Limitations of Valence bond theory :

1. VBT cannot account for the relative stabilities of different shapes and different coordination numbers in metal complexes, e.g., it cannot explain satisfactorily as to why Co(+2) (d^8 system) forms both octahedral and tetrahedral complexes while Ni(+2) (d^7 system) rarely forms tetrahedral complexes.

2. VBT cannot explain as to why Cu(+2) forms only one distorted octahedral complex even when all the six ligands are identical.

3. This theory cannot account for the relative rates of reactions of analogous metal complexes. e.g. $[Mn(phen)_3]^{2+}$ dissociates instantaneously in acidic aqueous solution while $[Fe(phen)_3]^{2+}$dissociates at a slow rate.

(1) The classification of metal complexes on the basis of their magnetic behaviour into covalent (inner-orbital) and ionic (outer-orbital) complexes is not satisfactory and is often misleading.

(2) VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments, i.e. although both tetrahedral (sp^3 hybridisation) and outer-orbital octahedral (sp^{2}d^2 hybridisation) complexes of Co(+2) (d^7 system) have three unpaired electrons and are, therefore, expected to have value equal to 3.87 B.M.; the tetrahedral complexes generally have value in the range of 4.4 - 4.8 B.M., while the octahedral complexes have still higher value of in the range of 4.7 - 5.2 B.M. The increase in the value of is due to the orbital contribution. Similar is the case with tetrahedral and octahedral complexes of Ni(+2) (d^8 system). VBT cannot explain the increase in the value of .

(3) VBT cannot interpret the spectra (colour) of the complexes.

(4) This theory does not predict or explain the magnetic behaviours of complexes. This theory only predicts the number of unpaired electrons. Its prediction even for the number of unpaired electrons and their correlation with stereochemistry is misleading. VBT cannot explain the temperature dependent paramagnetism of the complexes.

(5) VBT cannot give any explanation for the order of reactivities of inner-orbital inert complexes of d^3, d^4, d^5 and d^6 ions of the observed differences in the energies of activation in a series of similar complexes.

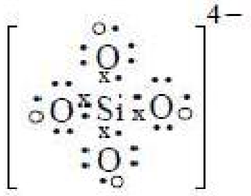
(6) The magnetic moment values of the complexes of certain ions (e.g., Co^{2+}, Ni^{2+} etc.) are much higher than those expected by spin-only formula. VBT cannot explain the enhanced values of magnetic moments.

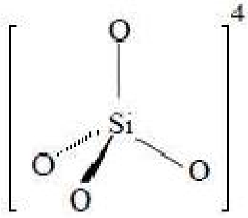
SILICATES

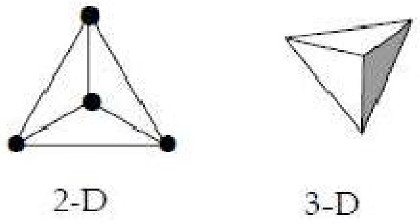
Silicates are salts containing anions of silicon (Si) and oxygen. There are many types of silicates, because the silicon-to-oxygen ratio can vary widely. In all silicates, however, silicon atoms are found at the centres of tetrahedrons with oxygen atoms at the corners. The silicon is always tetravalent (i.e., has an oxidation state of +4). The variation in the silicon-to-oxygen ratio occurs because the silicon-oxygen tetrahedrons may exist as discrete, independent units or may share oxygen atoms at corners, edges, or in rarer instances faces in several ways. Thus, the silicon-to- oxygen ratio varies according to the extent to which the oxygen atoms are shared by silicon atoms as the tetrahedrons are linked together. The linkage of these tetrahedrons provides a rather convenient way of classifying silicates. Seven different classifications are commonly recognized.

The building block of the silicate minerals

All silicate minerals are built up from the basic unit of silicate(IV) ion, SiO_4^{4-}, which has the following structural representations:







“Dot-and-cross” 3-dimensionalrepresentation Simplified representation

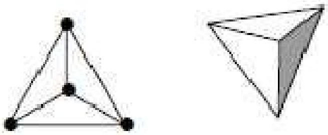
The Si atom is covalently bonded to 4 oxygen atoms. Each oxygen atom possesses a formal negative charge. Hence each tetrahedral unit has a formal charge of –4. When linked together, the extended units are also negatively charged. Presence of other metallic ions such as Ca2+or Mg2+ are necessary for electrical neutrality. The covalent Si-O bond, having a bond enthalpy of 466 kJ mol-1, is particularly strong compared with the C-C bond which has a bond enthalpy of 347 kJ mol-1. The linkage -Si-O-Si-O- is very stable and instead of existing as discrete units of SiO44- ions, the silicates tend to form chains, sheets or networks.

Classification of silicate

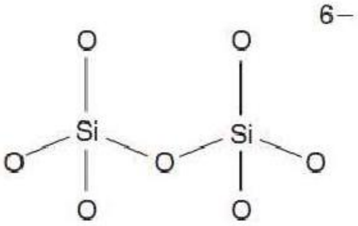
- Orthosilicate
- Pyrosilicate
- Cyclic silicate
- Chain silicate
- Sheet silicate
- 3D silicate

(i) Orthosilicate: If the corner oxygens are not shared with other SiO_4^{4-} tetrahedrons, each tetrahedron will be isolated. Thus, this group is often referred to as the island silicate group.

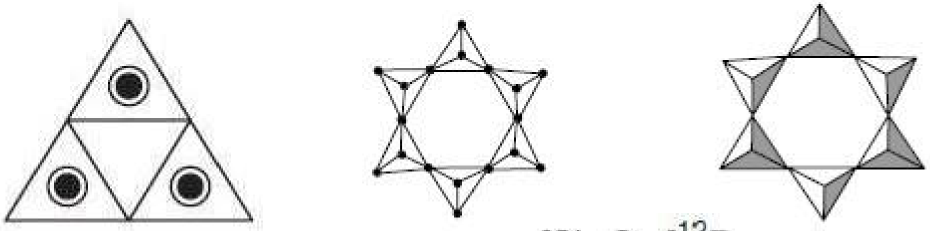
The basic structural unit is then SiO_4^{4-}. In this group the oxygens are shared with octahedral groups that contain other cations like Mg^{+2}, Zr^{+2}, or Ca+2. Simple silicate containing discrete SiO_4^{4-} tetrahedral. Silicates of magnesium (Mg_2SiO_4) and zirconium ($ZrSiO_4$) are examples.



(ii) Pyrosilicate: one of the corner oxygens is shared with another tetrahedron, this gives rise tothisn group. It is often referred to as the double island group because there are two linkedtetrahedrons isolated from all other tetrahedrons. Two SiO_4 tetrahedrons share one corner oxygenatom to form discrete $Si_2O_7^{6-}$ ions. Two compounds with this type of linkage are $Ca_2ZnSi_2O_7$ and $Zn_4(OH)_2Si_2O_7 \cdot H_2O$.



(iii) Cyclic silicate (ring silicate): If two of the oxygens are shared and the structure is arranged in a ring, such as that shown here, we get the basic structural unit of the cyclosilcates or ring silicates. Shown here is a six membered ring forming the structural group $Si_6O_{18}^{-12}$. Three membered rings, $Si_3O_9^{-6}$, four membered rings,$Si_4O_{12}^{-8}$, and five membered rings $Si_5O_{15}^{-10}$ are also possible. In $BaTiSi_3O_9$, three SiO_4 tetrahedrons share corners, whereas in $Be_3Al_2Si_6O_{18}$ (beryl), six tetrahedrons share corners to form a closed ring.

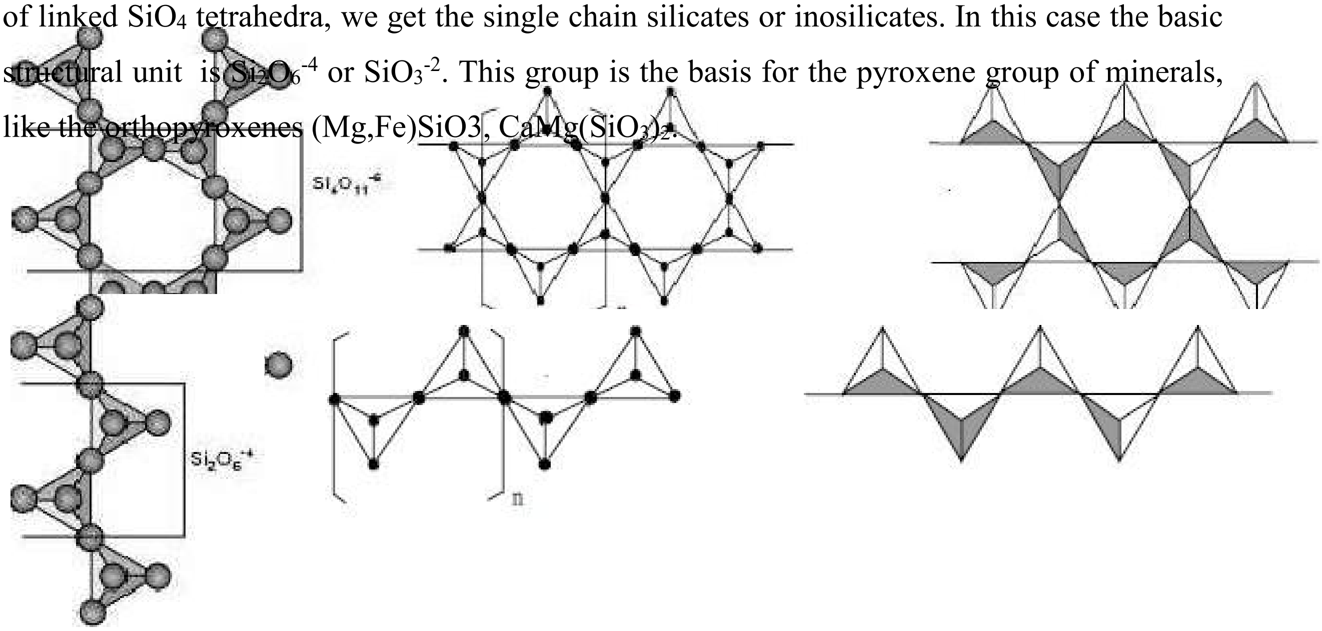


$[Si_6O_{18}]^{12-}$

$Si_3O_9^{6-}$

(iv) Chain silicate:

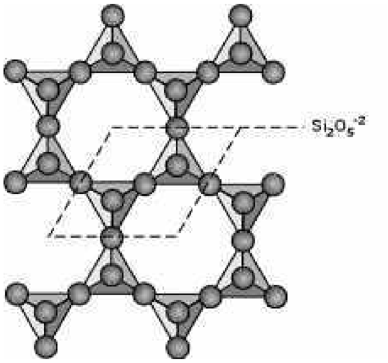
Single Chain Silicates: If two of the oxygens are shared in a way to make long single chains of linked SiO_4 tetrahedra, we get the single chain silicates or inosilicates. In this case the basic structural unit is $Si_2O_6^{-4}$ or SiO_3^{-2}. This group is the basis for the pyroxene group of minerals, like the orthopyroxenes (Mg,Fe)SiO3, $CaMg(SiO_3)_2$.

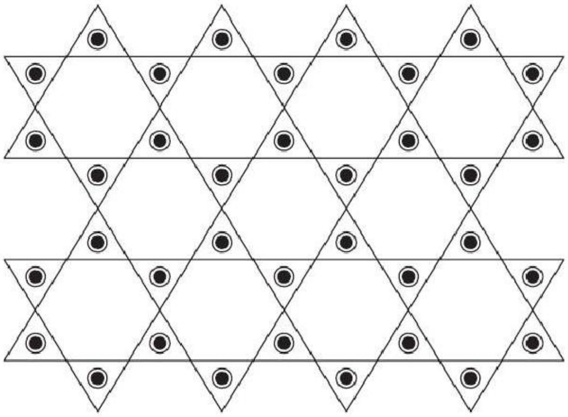


Double Chain Silicates: If two chains are linked together so that each tetrahedral group shares 3 of its oxygens, we can from double chains, with the basic structural group being $Si_4O_{11}^{-6}$.When SiO_4 tetrahedrons in single chains share oxygen atoms, double silicon-oxygen chains form. Metal cations link the parallel chains together. Many of these silicates are fibrous in nature, because the ionic bonds between the metal cations and the silicate anions are not as strong as the silicon- oxygen bonds within the chains. A class of fibrous silicate minerals that belong to this group is collectively called asbestos. The amphibole group of minerals are double chain silicates, for example the tremolite – ferroactinolite series - $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$.

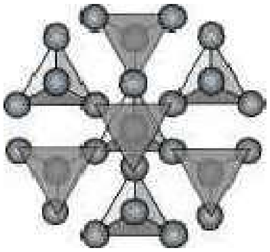
(v) Sheet silicate: If 3 of the oxygens from each tetrahedral group are shared such that an infinite sheet of SiO_4 tetrahedra are shared we get the basis for the phyllosilicates or sheet silicates. In this case the basic structural group is $Si_2O_5^{-2}$. The micas, clay minerals, chlorite, talc, and serpentine minerals are all based on this structure. A good example is biotite - $K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$.

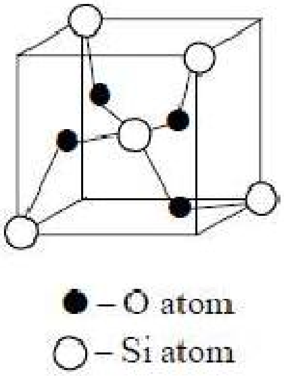
Talc**,** Mg3(Si4O10)(OH)2**,** has a structure consisting of layers and parallel sheets. All of the strong bonding interactions among the atoms occur within the layers. Two parallel sheets have the unshared oxygen atoms of the tetrahedra pointing toward each other. In the middle of this sandwich are the magnesium and hydroxide ions, which serve to bind the two silicate sheets together. Only weak van der Waals forces hold the sandwiches (layers) together. Thus layers can slip easily across one another and accounts for the ease for it to be pulverized to make talcum powder, a soft and fine powder to make one's skin feel smooth and dry.





(vi) 3D silicate: If all of the corner oxygens are shared with another SiO_4 tetrahedron, then a framework structure develops. The basic structural group then becomes SiO_2. The minerals quartz, cristobalite, and tridymite all are based on this structure. If some of the Si^{+4} ions are replaced by Al^{+3} then this produces a charge imbalance and allows for other ions to be found coordinated indifferent arrangements within the framework structure. Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.





Quartz:: The mineral Quartz is one form of silica. In quartz, all the four vertices of each tetrahedron are linked to other tetrahedra. The quartz network carries no charge and there are no cations in its structure. The three-dimensional network silicates such as quartz are much harder than their linear or layer counterparts. As the silica structure consists of a giant network of strongcovalent bonds. Melting points of quartz and silica (sand) are very high.

Zeolite: A most interesting class of silicates consists of the zeolites. These compounds are three- dimensional silicon-oxygen networks with some of the tetravalent silicon ions replaced bytrivalent aluminum (Al^{3+}) ions. The negative charge that results—because each Al^{3+} ion has one fewer positive charge than the Si^{4+} ion it replaces—is neutralized by a distribution of positive ions throughout the network. An example of a zeolite is $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$. Zeolites are characterized by the presence of tunnels and systems of interconnected cavities in their structures. Zeolites are used as molecular sieves to remove water and other small molecules frommixtures, and they can also be employed to separate molecules for which the molecular masses are the same or similar but the molecular structures are different. In addition, they are used as solid supports for highly dispersed catalysts and to promote specific size-dependent chemical reactions.

The aluminosilicates

Very often the silicon atoms are replaced by aluminium atoms to form the silicate analogue, the aluminosilicates. When an aluminium atom replaces a silicon atom, it contributes only three electrons to the bonding framework in place of the four electrons of silicon atoms. The remainingelectron is supplied by the ionization of a metal atom such as sodium or potassium.

a) Sheets

Mica belongs to a family in which one of the four silicon atoms in the structural unit of talc is replaced by an aluminium atom and inserting a potassium atom to supply the fourth electron needed for electrical neutrality. Mica has a composition of $KMg_3(AlSi_3O_{10})(OH)_2$. Micas are harder than talc and their layers slide less readily over one another. Like talc, crystals of mica cleave easily into sheets. The cations occupy sites between the sheets. The van der Waals attraction between sheets is increased by the presence of extra ionic charge and accounts for the overall hardness of mica over talc.

(b) Three-dimensional network

The feldspars, in which albite $NaAlSi_3O_8$ is an example, are the most abundant aluminosilicate minerals in the Earth surface. The silicon atoms and aluminum atoms occupy the centers of interlinked tetrahedra of SiO_4^{4-} and AlO_4^{5-}. These tetrahedra connect at each corner to other tetrahedra forming an intricate, three-dimensional, negatively charged framework. The sodium cations sit within the voids in this structure.

Daily life importance of some of the silicate minerals

(a) Silicates

(i) Asbestos (double chains or sheets): Asbestos is an excellent thermal insulator that is non-combustible, acid-resistant, and strong. In the past, it was used extensively in construction work to make cement floor tiles, roof covers and ducts. It can also be woven into fabric to make fire- resistant blankets. Its use has been decreased greatly in recent years because inhalation of small asbestos fibres during mining and manufacturing or during the removal of frayed and crumbled building materials can cause the lung disease called **asbestosis**.

(ii) Talc (sheets): The common use of talc crystals is to make talcum powder which is a soft and fine powder to make one's skin feel smooth and dry . Its resistance to heat and electricity makes it ideal for surfacing benches and switchboards. It is also an important filler for paint and rubber

(iii) Quartz (three-dimensional network): The hardness of quartz is widely made use of in construction work as sandstones. Quartz/silica tubing are used for high temperature heating.

Quartz possesses piezoelectric property which enables it to make crystal oscillators used in watches and electronic circuits and also as pressure sensor in electronic balances. Quartz is also widely used in jewelry and ornamental decorations.

(b) Aluminosilicates

(i) Feldspar (three-dimensional network): In glassmaking, feldspar provides alumina for improving hardness, durability, and resistance to chemical corrosion. In ceramics, feldspar is used as a flux, lowering the vitrifying temperature of a ceramic body during firing and forming a glassy phase.

(ii) Mica (sheets): Mica possesses excellent electrical insulation and is widely used in electronic products such as capacitors, washers for transistors and radar high tension coils. It also has excellent heat insulation and is used in soldering irons and jet engines.

Silicones

General introduction

Originally this word was coined by F. S. Kipping to mean a silicon atom substituting carbon in a ketone (>C=O). But it was soon found that even the first such compound Ph_2SiO was a polymer and it had no chemical resemblance with ketones. Today silicones are well known polymers having extensive Si-O-Si linkages similar to those in silicates. Silicon is sp^3 hybridized and the tetrahedra undergo permutations and combinations to give large variety of polymeric structures. But unlike silicates, in which there are terminal oxygens, silicones contain organic moieties (e. g. CH_3, C_6H_5) attached to silicon and hence Si-C bonds. For this reason they are also called organosilicon polymers. Such polymeric structures are formed in many ways *viz*., linear and cyclic; chains and cross-linked. Depending upon the degree of polymerization the polymer formed may be a liquid (oils), semisolid (greases), rubber like solid (elastomers) or hard solid (resins). They are often classified on the basis of physical state as

(a) Linear silicones (silicone oils)
(b) Silicone elastomers
(c) Silicone resins

Some are also called silicone greases.

Structural features and synthesis

Silicones contain Si–O–Si linkages and Si–C bonds. Naturally, the synthetic routes involve formation of one or both of the two. Formation of Si–O–Si linkage is simple and is achieved through condensation of two Si–OH bonds (as in the case of formation of silicates from hydrolysis product of $SiCl_4$). The first step in synthesis of silicones naturally, involves putting 'R' groups (R = – CH_3, –C_6H_5) on the tetrahedral Si atom. Care is taken to have at least one 'X' (X = Cl) on this atom so that it could be substituted by hydrolysis. Subsequent condensation through Si–OH bonds generate Si–O–Si linkage.

Step 1 - Introduction of Si–C bonds: Preparation of alkyl (or aryl) substituted chlorosilanes:

i) Treating $SiCl_4$ with a Grignard reagent in laboratory gives organosilanes:

$$SiCl_4 + CH_3MgCl \longrightarrow CH_3SiCl_3 + MgCl_2$$

Further alkylation will depend upon the molar ratio of the two reactants:

$$CH_3SiCl_3 + CH_3MgCl \longrightarrow (CH_3)_2SiCl_2 + MgCl_2$$

$$(CH_3)_2SiCl_2 + CH_3MgCl \longrightarrow (CH_3)_3SiCl + MgCl_2$$

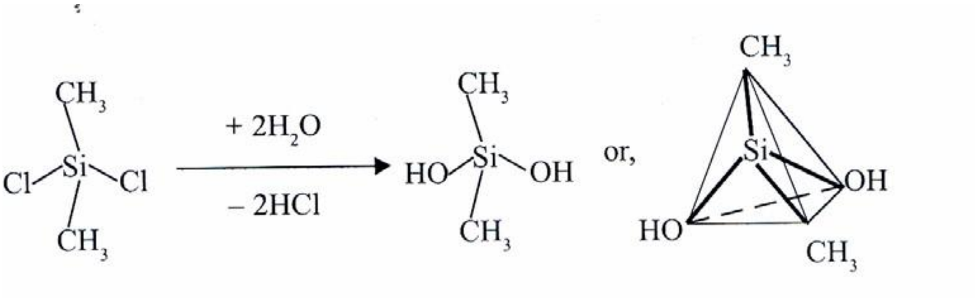
ii) Industrially, such organosilanes are prepared by direct reaction of alkyl or aryl halides with Si. A fluidized silicon bed is used in presence of copper catalyst (90% Si ; 10% Cu metal by weight) :

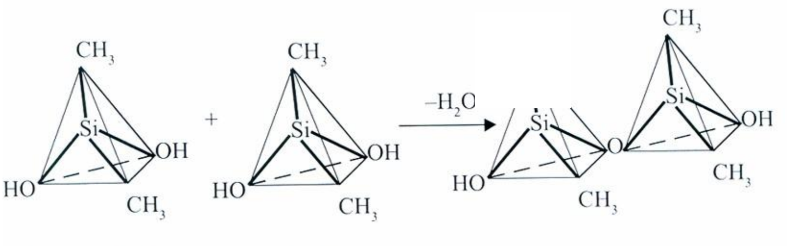
$$2CH_3Cl + Si \xrightarrow[300^0C]{Cu\ powder} (CH_3)_2\,SiCl_2$$

The reaction proceeds via free radical mechanism and the role of Cu is to form free radical intermediates such as {CuCl} and {$CuCH_3$}. CuCl halogenates Si and $CuCH_3$ dissociates to give $CH_3 \cdot$ radical. Some mono and trimethyl derivatives are also formed. Adding HCl increases the yield of the monoderivative and reduces that of the dimethlyl derivative. The reactions in both the cases are exothermic. Naturally, the heat generated has to be removed. The product is always a mixture which has to be fractionated to bring desired perfection in polymerization ahead.

Step 2 – Hydrolysis of alkyl / aryl halosilanes :

The substituted halosilanes undergo hydrolysis to corresponding substituted silanols, which on condensation produce silicones. The properties of these silicones depend upon the degree of polymerization and stereochemistry. More – OH groups in the silanols naturally, lead to condensations in more directions. The silanol is usually acidic so it is easily converted to its sodium salt using a 12 M solution of NaOH:

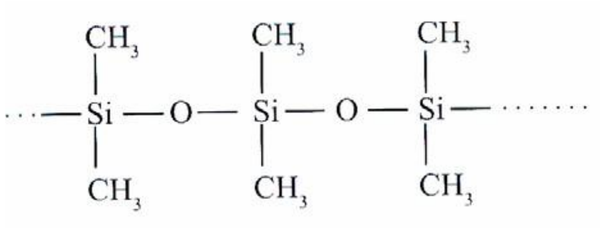




Similar condensations may go on.

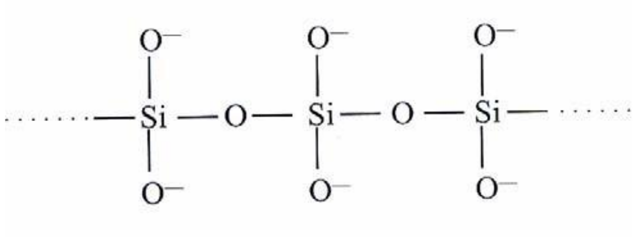
In place of $-CH_3$, there could be a $-C_6H_5$. Further condensations lead to higher polymers.

As we have seen, the reaction represented by equation (1) gives linear silicones:

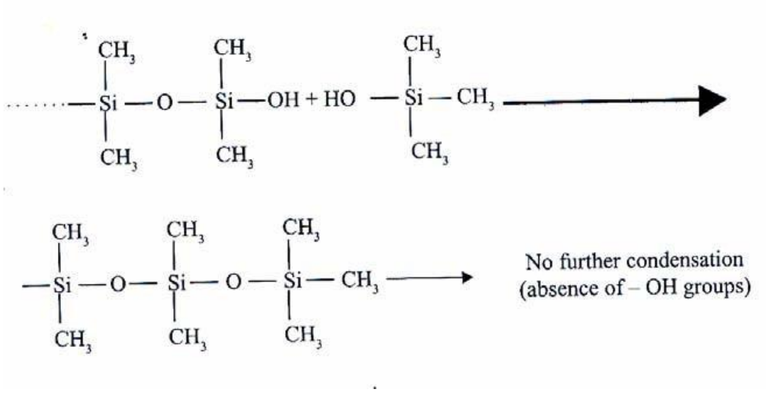


(Polydimethylsiloxane)

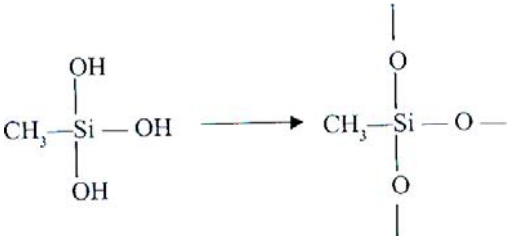
It has structural resemblance with silicates:



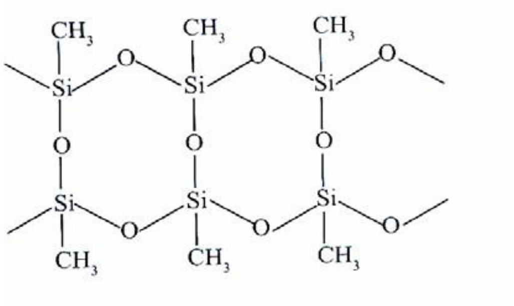
To terminate the process of polymerization, appropriate amounts of trimethyl silanols are used:



Monoalkyl silanols are used to incorporate in order to achieve desired branching and bridging groups,



These may give siloxenes (silicone resins)



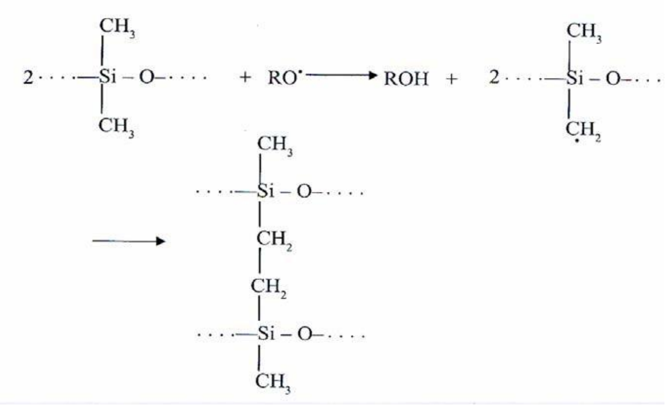
Thus, for getting a desired variety of silicone, calculated amounts of the mono -, di- and trihalosubstituted versions of alkyl silanes are used. The following examples may be given as illustration:

Silicone oils: These are prepared by stirring hexamethyl disiloxane and the cyclo tetramer, tetrakis*cyclo*-dimethyl siloxane in suitable ratio with a little of conc. H_2SO_4. The Si–O bonds are broken to form esters with H_2SO_4 :

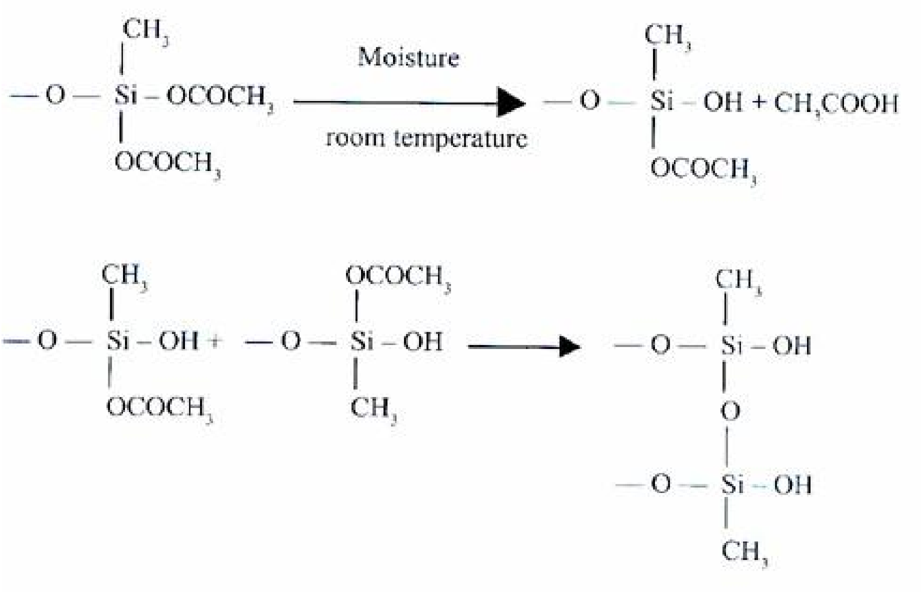
$$>Si-O-Si< \xrightarrow{H_2SO_4} >Si-O-SO_3H+HO-Si<$$

Thereafter, hydrolysis gives new Si – O bonds and this brings randomness in the Si–O–Si linkages. The molecular weight, viscosity etc. depend on the initial ratio.

Silicone elastomers: These are prepared by taking the dihaloderivatives only. The dimethyl polysiloxanes thus obtained are reinforced using fumed silica. The chain blocking precursors [monohalo derivative which gives $(CH_3)_3Si–O–$] and the precursors causing cross-linking are totally avoided. KOH is used and the linear polymer thus produced is in form of a viscous gum. For effective use, vulcanization is carried out using benzoyl peroxide etc. This brings about cross-linking in the polymer:



Using catalytic techniques, vulcanization is also effected by introducing acetoxy groups in the side chain:



Simultaneous condensation through hydroxyl group brings out desired, cross-linking. This controlled cross-linking (1 in every 100-1000 Si units) brings about unusual flexibility, elasticity, strength and capacity to bear temperature as high as 250^0C and as low as -100^0C.

Silicone resins: These are prepared by hydrolyzing methyl and phenyl substituted dichloro and trichloro silanes in toluene. Introduction of phenyl groups in place of methyl brings about further heat stability and flexibility. Extensive cross-linking makes them look like bakelite but with better dielectric properties suitable for use as insulators.

The nature of the polymer is determined by the extent of cross-linking and the nature of the alkyl/aryl substituent.

Interesting properties and uses

All silicones are excellent water repellent, thermally and electrically insulating and chemically inert. They exhibit antistick, antifoam and flame resistance properties. As such, they have brought out technological revolutions in all walks of life. A few of their applications are given below:

(i) Silicone oils: They have extremely high viscosity (*ca.* 50,000 to 3,00,000 times that of water depending upon the chain length) which does not change appreciably with temperature. Their surface tension is low. Chemical inertness and presence non-polar groups make them non-toxic. They are used:

- As dielectric insulating media e.g. in transformer oils.
- As hydraulic oils
- As compressible fluids for liquid springs
- As antifoaming agents in sewage disposal plants, textile dyeing, cooking oil etc. (ppm quantities do wonder!)
- As an additive in cosmetics (lipsticks, sun tan lotion, hair oil etc.)

(ii) Silicone greases: Silicone oils are thickened to make silicone greases for use in heavy-duty steel gears and shafts. For this purpose, methyl phenyl silicone oils are thickened by Li-soaps.

(iii) Silicone rubber: Silicon rubbers are used in making

- Cable insulation
- Static and rotary seals
- Gaskets
- Diaphragms
- Electric tape insulation
- Industrial sealants and adhesives
- Heart valves
- Space suits
- Accurate impressions for dentures
- Masks in cinema.

(iv) Silicone resins: Silicone resins are used in making

- Insulations in electrical equipments
- Laminates and printed circuit boards for electronic equipments
- High temperature paints and coatings on cooking utensils.

Phosphazenes

General introduction

Phosphazenes were initially termed phosphonitrilic polymers. Later on, the new term was used to represent **phosph**orus, nitrogen (=**az**o) and P = N double bonds (=**ene**) which are always present in these polymers. They are thus 'unsaturated PN compounds' containing phosphorus, mostly in +V state. As is usual with polymers, they may have cyclic or chain structure. The nitrogen in groups is in 2-coordination and phosphorus in 4-coordination. They contain
the group

groups of silicones. Their polymers differ in substitution on phosphorus and on the nature of those substitutents besides the way and the extent, to which polymerization has taken place. Their water repellent, solvent resistant and flame resistant properties have found new applications and these have led to many technological innovations during the last few decades. They are usually classified on the basis of number of phosphazene units that are incorporated in the structure:

Monophosphazenes: Monophosphazenes are compounds of the type $X_3P = NR$, (X and R = Cl, OR, NR_2, Ar etc.). These are unsaturated compounds and can be prepared as follows:

(a) Reacting an azide ($R - N_3$) with PR_3 (R = Ar, OR, Cl, NR_2) :

$$P(C_6H_5)_3 \quad + \quad C_6H_5{-}N_3 \xrightarrow[-N_2]{} (C_6H_5)_3 - P = N - C_6H_5$$

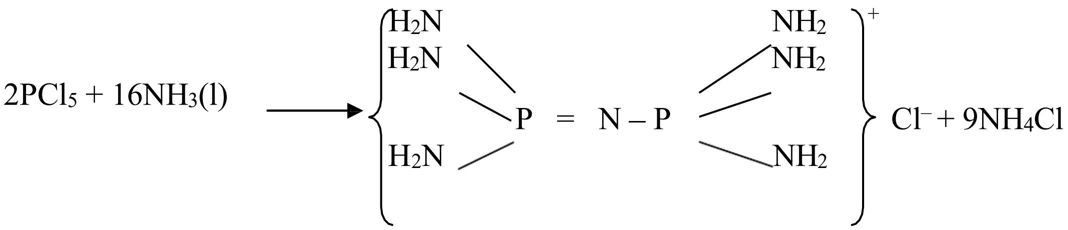
(b) Reacting dihalotriphenylphosphenes with aromatic amines :-

$$(C_6H_5)_3PCl_2 \quad + \quad C_6H_5{-}NH_2 \xrightarrow[-2HCl]{} (C_6H_5)_3 - P = N - C_6H_5$$

Diphosphazenes: These contain two $>P = N -$ groups and the P = N and the P – N bonds are equivalent. These are usually prepared by reacting PCl_5 with NH_4Cl under mild conditions:

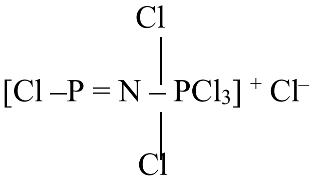
$$PCl_5 + NH_4Cl \xrightarrow{\text{Chlorohydrocarbon solvents}} [Cl_3P = N - PCl_2 = N - PCl3]^+Cl^-$$

However, PCl_5 undergoes ammonolysis in liq. NH_3 :



The disphosphazenes exist both in covalent and ionic forms . Thus

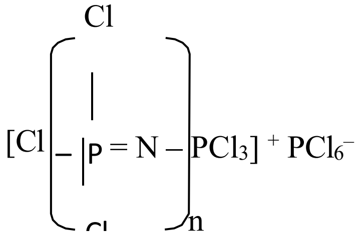
the halo form can be represented as



$$[Cl - \underset{Cl}{\overset{Cl}{P}} = N - PCl_3]^+ Cl^-$$

Polyphosphazenes:

These contain more than two $>P = N -$ groups. Polymeric phosphazene dichlorides are formed when further halogen or halophosphorus substitutions of $- NH_2$ groups in P takes place. The polymeric phosphazene dichlorides can be represented as



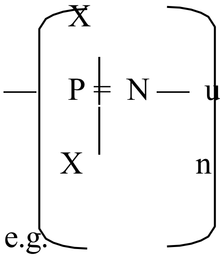
$$[Cl - \left(\begin{array}{c} Cl \\ | \\ P \\ | \\ Cl \end{array} = N - \right)_n PCl_3]^+ PCl_6^-$$

These form chains and cyclic structures having ‘n’ value upto 10^4. The simple representation of polyphosphazene dichlorides is made as $(NPCl_2)_n$. These are prepared as follows:

$$nPCl_5 + nNH_4Cl \xrightarrow[120 - 150^0C]{\text{Solvent (a halo hydrocarbon)}} [NPCl_2)_n] + 4n\ HCl$$

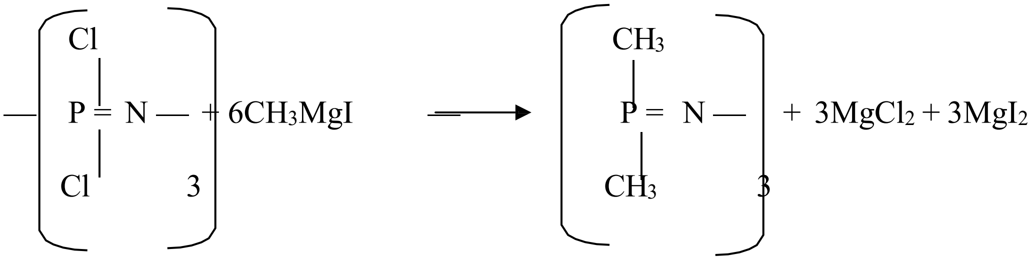
Cyclic trimer, tetramer etc. are prepared by using different conditions. Separation is done through fractionation. The cyclic trimer, *cyclo* – $[NPCl_2]_3$ on heating at 150 – 300^{0}C furnishes polymeric products. But heating at a higher temperature (350 – 360^{0}C) causes cleavage and depolymerization.

The chlorines in the product may be substituted by nucleophiles and varieties of substituted polyphosphazenes are obtained having



$-\left[\overset{X}{\underset{X}{P}} = N - \right]_n$ units in which X = OCH_3,OC_6H_5, NHPh, $N(CH_3)_2$, R,Ar etc.:

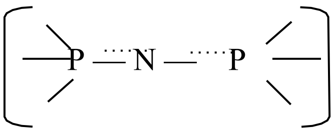
e.g.



$$-\left[\overset{Cl}{\underset{Cl}{P}} = N - \right]_3 + 6CH_3MgI \longrightarrow \left[\overset{CH_3}{\underset{CH_3}{P}} = N - \right]_3 + 3MgCl_2 + 3MgI_2$$

Nature of bonding in triphosphazenes

Bonding in phosphazenes is quite interesting. Diphosphazene contains one P = N and one P – N bonds both of which are equivalent and the bond length is shorter than single bond. This is easily explained by resonance

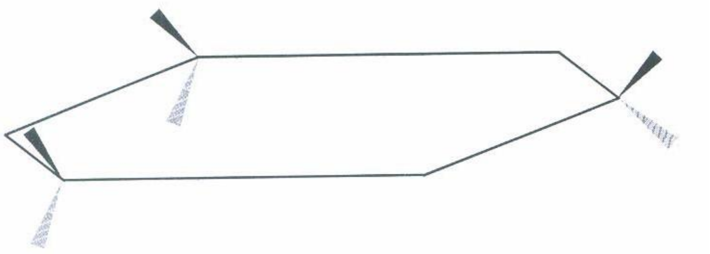


In case of trimer and higher phosphazenes however, things are complex. At first sight, there seems to be alternate single and double bond conjugate systems through out P – N – P skeleton. Such conjugate systems are expected to lead to delocalization of the sort of benzene. The cyclic trimer has an accurately planar 6-membered ring structure but, unlike aromatic systems, it is difficult to reduce it electrochemically. Also, the spectral evidence of delocalized system (bathochromic ultraviolet shift) is not found. This is explained by the unique and interesting structure that triphosphazenes possess.

As in other phosphazenes, triphosphazenes have

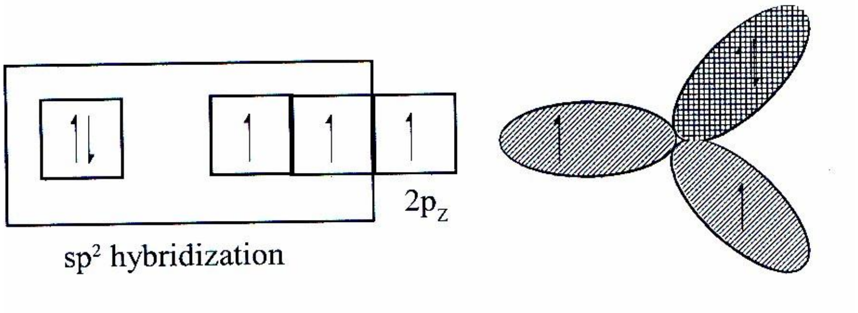
(i) Very stable ring
(ii) All the skeletal interatomic distances are equal if all the six substituent groups on phosphorus are identical.
(iii) A shorter P – N bond length (~ 158 pm) than single bond (~177 pm)
(iv) All the nitrogen atoms weakly basic hence protonable (more so if substituents on P are electron releasing).

The symmetry of the molecule is like that of benzene. It has planar structure with three nitrogen and three phosphorus atoms situated on alternate corners of the hexagon. The substitutents (X) on P are placed above and below the plane. If all the substituents are identical then three of them form together one plane above and three form one plane below the molecular plane.



Some more features are mentioned below:

- Nitrogen atoms are sp^2 hybridized:

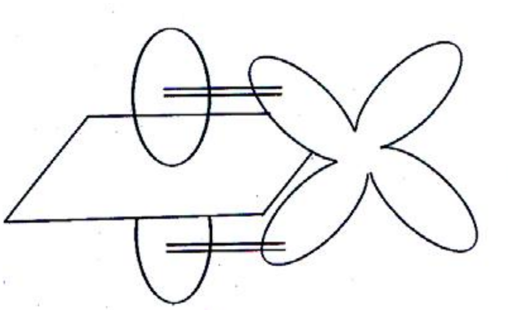


Two such hybrid orbitals are involved in σ -. .bonding

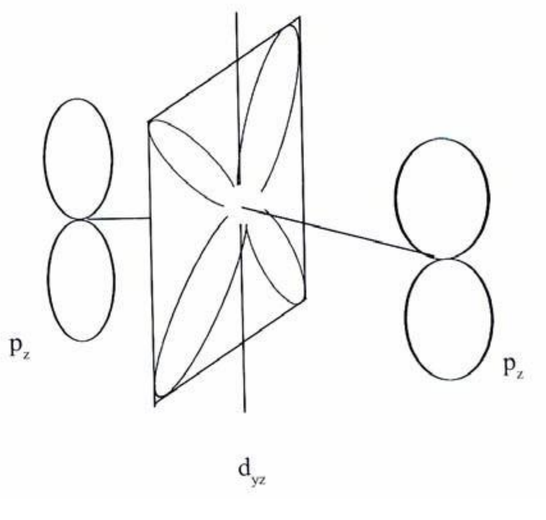
- Similarly, each phosphorus is sp^3 hybridized

Three such hybrid orbitals are involved in σ.- bonding.

- There is then one 'in plane' π-bonding involving the lone pair of N (sp^2 orbital) in xy plane and the vacant d_{xy} or $d_{x^2-y^2}$ orbital of the P — atom.
- There are two 'out of plane' interactions:
  (i) Heteromorphic interactions: The singly occupied p_z^1 orbital on the nitrogen overlaps with the d_{xz}^o or d_{yz}^o orbital of phosphorus (pπ – dπ bonding).



  (ii) Homomorphic interactions: There is a pπ – pπ interaction of p_z orbitals of two nitrogens through the d_{yz} orbital of the phosphorus in between.



- It is believed that the two contributions *viz.* heteromorphic and homomorphic are equal. This results in separation of the .π .orbitals into localized 3-centre orbital islands. There are 3 such islands with interruptions at the three phosphorus atoms. These interruptions in the M. O's. prevent the systems from exhibiting delocalization of the π-electron.

Uses

Both the cyclic and non-cyclic polyphosphazenes have great oxidative, thermal & radiative stabilities. Substituents such as $–NH_2$, $–OR$, $–OC_6H_5$ or fluorinated derivatives bring about further stabilities. Their water repellency, solvent resistance, flame resistance, retention of flexibility at low temperatures and their dielectric properties make them very useful for a variety of modern technological purposes. These are used for making:

i) rigid plastics, plastic films, expanded foams
ii) fuel hoses, gaskets
iii) O-ring seals for use in extremely cold climate (e.g. in high flying aircrafts or in vehicles for Arctic type climate)
iv) metal coatings & wire insulation
v) composite materials together with asbestos, glass or with ordinary phenolic resins.

Boranes:

Preparation: Diborane can also be obtained in small quantities by the reaction of iodine with sodium borohydride in diglyme.

$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

On heating magnesium boride with HCl a mixture of volatile boranes are obtained.

$2Mg_3B_2 + 12HCl \rightarrow 6MgCl_2 + B_4H_{10} + H_2B_4H_{10} + H_2 \rightarrow 2B_2H_6$

PHYSICAL PROPERTIES

- Colourless and highly inflammable gas at room temperature.
- At high concentrations, it ignites rapidly in the presence of moist air at room temperature.
- It smells sweet.
- It has boiling point of about 180 K

- It is toxic gas

- It releases huge amount of energy when burnt in the presence of O2.

- It readily hydrolysed in the water to give hydrogen gas and boric acid.

Chemical Properties:

i) Diboranes reacts with water and alkali to give boric acid and metaborates respectively.

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2B_2H_6 + 2NaOH + 2H_2O \rightarrow 2NaBO_2 + 6H_2$

ii) Action of air: At room temperature pure diborane does not react with air or oxygen but in impure form it gives B_2O_3 along with large amount of heat.

iii) Diborane reacts with methyl alcohol to give trimethyl Borate.

$B_2H_6 + 6CH_3OH \rightarrow 2B(OCH_3)_3 + 6H_2$

iv) Hydroboration: Diborane adds on to alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration and is highly used in synthetic organic chemistry, especially for anti-Markovnikov addition.

$B_2H_6 + 6RCH{=}CHR \rightarrow 2B(RCH\text{-}CH_2R)_3$

v) Reaction with ionic hydrides When treated with metal hydrides it forms metal borohydrides

vi) Reaction with ammonia: When treated with excess ammonia at low temperatures diborane gives diboranediammonate. On heating at higher temperatures, it gives borazole.

Structure and Bonding in diborane:

In diborane two BH_2 units are linked by two bridged hydrogens. Therefore, it has eight B-H bonds. However, diborane has only 12 valance electrons and are not sufficient to form normal covalent bonds. The four terminal B-H bonds are normal covalent bonds (two centre - two electron bond or 2c-2e bond). The remaining four electrons have to be used for the bridged bonds. i.e. two three centred B-H-B bonds utilise two electrons each. Hence, these bonds are three centre- two electron bonds (3c-2e). The bridging hydrogen atoms are in a plane as shown. In diborane, the boron is sp^3 hybridised. Bonding in diborane Three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty. Two of the half-filled hybridised orbitals of each boron overlap with the two hydrogens to form four terminal 2c-2e bonds, leaving one empty and one half-filled hybridised orbitals on each boron. The Three centre - two-electron bonds), B-H-B bond formation involves overlapping the half-filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half-filled 1s orbital of hydrogen. Uses of diborane:

i) Diborane is used as a high energy fuel for propellant

ii) It is used as a reducing agent in organic chemist

iii) It is used in welding torches

2. Borazine:

- Borazine, also known as borazole.
- It is a polar inorganic compound with the chemical formula $B_3H_6N_3$.
- In this cyclic compound, three BH units and three NH units alternate.
- The compound is isoelectronic and isostructural with benzene.
- Borazine has polar hexagonal structure containing 6 membered ring, in which B and N atoms are arranged alternately.
- Because the similarity between the structures of borazine and benzene that borazine is called inorganic benzene.
- In borazine, both Boron and Nitrogen are sp^2 hybridized.

- Each N-atom has an empty p-orbital.
- B-N bond in borazine is dative bond, while arises from the sidewise overlap between the filled porbitals of N-atom and empty p-orbitals of B-atom.
- Since borazine is isoelectronic with benzene, both the compounds have aromatic electron cloud.
- Due to greater difference in electronegativity values of B and N - atoms, the electron cloud in B_3N_3 ring of the borazine molecule is partially delocalized. While in the case of benzene ring, the electron cloud is completely delocalized.
- MO calculations have indicated that electron drift from N to B is less than the electron drift from B to N due to the greater electronegativity of the N-atom.
- In benzene molecules, C=C bonds are non-polar, while in case of B3H6N3, due to difference in electronegativities between B and N atoms, the B-N bond is polar.
- It is due to the partial delocalization of electron clouds that bonding in the B_3N_3 ring is weakened.
- N-atoms retain its basicity and B-atoms retain its acidity.
- In borazine, B-N bond length is equal to 1.44 Ao, which is between calculated single B-N bonds (1.54 A o).
- B=N bond length is 1.36 Ao .
- The angles are equal to 120o.

Preparation: $3B_2H_6 + 6NH_3$ —-> $3[BH_2(NH_3)_2][BH_4]$ —heat—> $2B_3N_3H_6 + 12H_2$ NH_4Cl BCl_3 ——>$Cl_3B_3N_3H_9$—$NaBH_4$—>$B_3N_3H_6$ $NH_4Cl + NaBH_4$ ——> $B_3N_3H_6 + H_2 + NaCl$

PROPERTIES

- Colorless liquid
- Volatile liquid
- boiling point 84.5℃
- Melting point -58 ℃
- decomposes at -80 ℃

Structure:

Chemical properties

$2B_3N_3H_6 + 6HCl \longrightarrow 2Cl_3B_3N_3H_9 \xrightarrow{6NaBH_4} 2B_3N_3H_{12} + 3B_2H_6 + 6NaCl$

- Borazines are also starting materials for other potential ceramics such as boron carbonides.
- Borazine can also be used as a precursor to growing boron nitride thin films on surfaces, such as nanomesh structure which is formed on rhodium 3. BORON HETEROCYCLES If one or more CH group in Benzene and cyclopentadienyl are replaced by BH group then it is called Boron heterocycles.

PREPARATION

When stanno-hydration of diethynyl methane with dibutyl tin hydride gives 1,4-dihydro - 1,4-dibutyl stanno benzene . It reacts with renal Boron Bromide to give 1-phenyl-1,4-dihydroxy-bromobenzene. When compound is converted to its anion by dipronatio with 3 0 -butyl / lithium which on reaction with $FeCl_2$, which gives bis(1-phenyl borate benzene) iron.

Introduction

Solid-state chemistry deals with the synthesis, structure, properties and applications of solid materials. There is great diversity in the range of properties and applications of solids. With the advent of structure-property relations, it is becoming possible to design new materials, which have specific structures and properties.

Properties of solid

- They are incompressible, inflexible and Mechanical strength.

- They have specific mass, volume and shape.
- Intermolecular force is physically powerful.
- Intermolecular distance is minute.

These properties indicate that the molecules, atoms or ions that make up a solid are closely packed i.e., they are held together by strong forces and cannot move at random.

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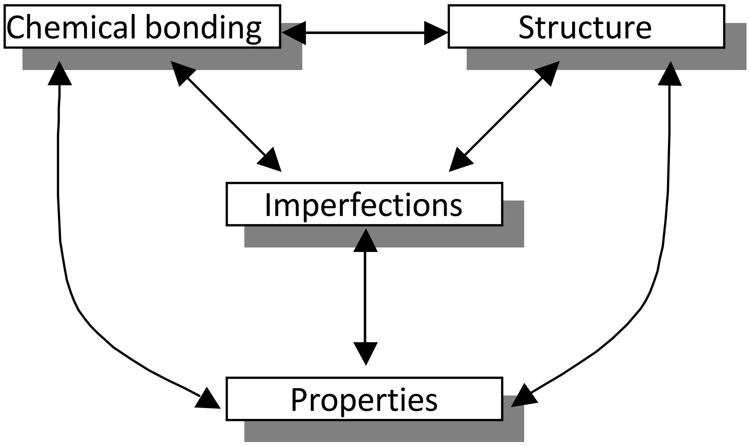
Interrelations of chemical bonding, structure, imperfections and properties due to electronic arrangements present a bird's eye-view of the applications of solids in various spheres.



Classification of Solids

Solids can be classified into three categories based on their structural features:

1. Crystalline solids
2. Amorphous solids (non-crystalline)
3. Polycrystalline solids

Solids

- **Non – Crystalline**
  The constituents are not arranged regularly.
  Amorphous
- **Crystalline**
  “A substance whose constituents are arranged in an orderly manner in a definite geometric form” (-have sharp melting points)
  - **Dielectric** eg. Ultrasonic Generators
  - **Electrical** eg. Diodes, Solar Cells
  - **Magnetic** eg. Telephones, Tapes
  - **Thermal** eg. Thermistores
  - **Optical** eg. Lasers
- **Poly Crystalline**
  Occur as powder resembles amorphous, but properties are just like crystalline solids

Crystalline Solids

The solids that have their atoms, ions, or molecules which are arranged in a definite three-dimensional pattern are called crystalline solids.

They have the following characteristics

- Crystalline Solids have a characteristic geometrical shape.
- Crystalline solids have sharp melting points, indicating the presence of a long-range order arrangement in them
- Crystalline solids are anisotropic by nature i.e., their mechanical, electrical and optical properties depend upon the direction along which they are measured.
- When cut or hammered gently they show a clean fracture along a smooth surface.

Some of the examples of crystalline solids are

Sodium chloride, Cesium Chloride etc.

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Some of the examples of crystalline solids are

Sodium chloride, Cesium Chloride etc.

Amorphous Solids

Substances whose constituent's atoms, ions, or molecules do not possess a regular orderly arrangement are called amorphous solids. They are different from crystalline solids in many respects.

They have the following characteristics

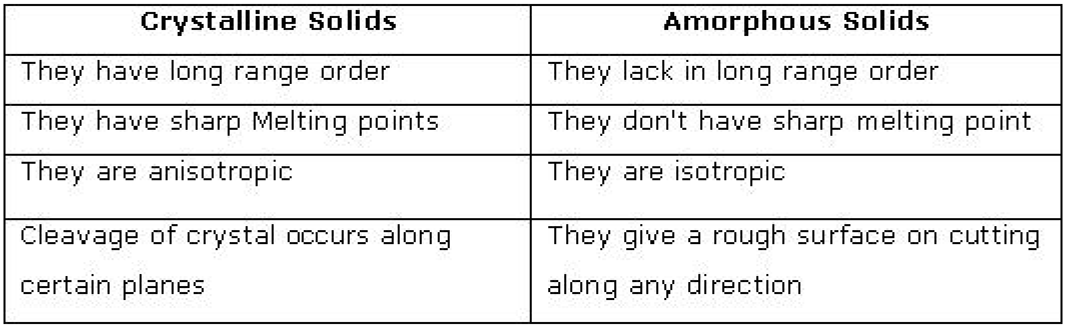
- These Solids do not have a definite geometrical shape.
- Amorphous solids do not have a fixed melting point. They melt over a wide range of temperatures.
- Amorphous solids are isotropic in nature.
- Amorphous solids do not break at a fixed cleavage plane.

The common examples of amorphous solids are

Glass, Rubber, Cotton candy, Fused silica, Ceramic, Plastics, Glue.

The above properties suggest that the properties of the solids not only depend upon the nature of the constituents but also on their arrangements.

Difference between amorphous and crystalline solids



Crystalline Solids	Amorphous Solids
They have long range order	They lack in long range order
They have sharp Melting points	They don't have sharp melting point
They are anisotropic	They are isotropic
Cleavage of crystal occurs along certain planes	They give a rough surface on cutting along any direction

Types of Crystalline Solid

Crystalline solids may be classified into four types depending on the nature of bonds present in them. Crystalline solids can be further classified depending on the nature of the bonding:

1. ***Ionic*** *(Nature of force:* Strong electrostatic forces of attraction) Eg: NaCl, LiF, MgO, etc.
2. ***Molecular,*** contains discrete molecular units held by relatively weak intermolecular forces *(*VanderWaal's forces, Dipole interaction, Hydrogen bonding). Eg: Solid Ar, Kr and etc.
3. ***Covalent*** *(*Covalent bonds). Lattice points are atoms. Eg: Diamond, graphite, Si, Ge and etc.
4. ***Metallic*** *(*Metallic bonds). Eg: Al, Cu, etc.

Symmetry elements and Symmetry operations

Symmetry operations

It is an action that leaves an object looking the same after it has been carried out. It includes rotation, reflection, and inversion.

Symmetry elements

For each symmetry operation, there is a corresponding symmetry element which is the point, line, or plane with respect to which the symmetry operation is performed. Symmetry based on simple rotation is often called symmetry of the first kind and symmetry based on reflection (or) rotation/reflection is known as symmetry of the second kind.

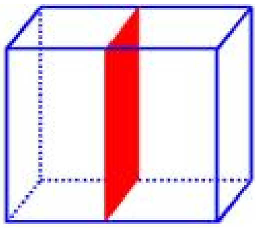
Symmetry Elements	**Symmetry Operation**
1. Plane (σ)	Reflection in the plane
2. Proper axis (Cn)	One or more rotations about the axis
3. Improper axis (Sn)	One or more repetitions of the sequence: rotation followed by reflection in a plane perpendicular to the rotation axis.
4. Center of symmetry (or) Center of Inversion	Inversion of all atoms through the center.

Symmetry elements present in Cubic Crystal
The elements of symmetry present in a cube are represented below.

Plane of symmetry
Two types of planes of symmetry are possessed by the cubic system.

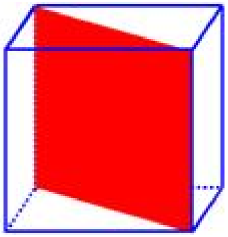
1. **Rectangular plane of symmetry**

This is shown in the fig- There will be two more such planes hence there are three rectangular plane of symmetry in all.



2. **Diagonal plane of symmetry**

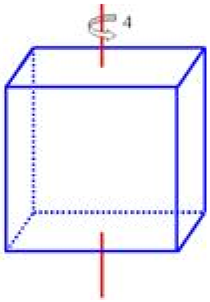
There are the planes passing diagonally through the cube as shown in the fig There are total of 6 such planes passing diagonally through the cube.



Axis of symmetry

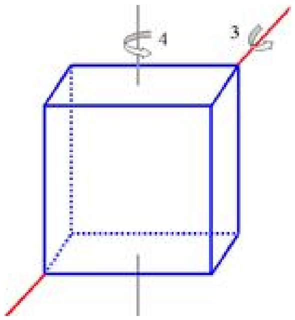
1. **Four-fold axis of symmetry**

One of the four-fold axes is shown in the fig. evidently there can be a total of 3 such four-fold axes are possible passing through pairs of opposite face centres, parallel to cell axes.



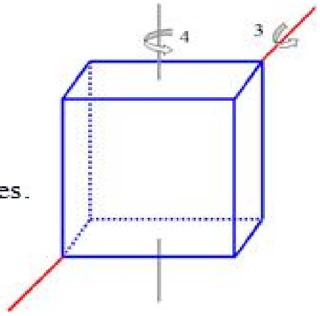
2. Three-fold axis of symmetry

One of the three-fold axes is shown in the fig.
Evidently there can be a total of 4 such three-fold
axes are possible passing through cube body diagonals.



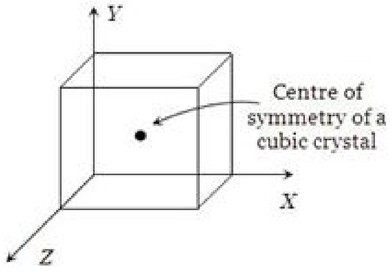
3. Two-fold axis of symmetry.

One of the two-fold axes is shown in the fig.
Evidently there can be a total of 6 such two-fold
axes are possible, passing through diagonal edge centres.



Centre of symmetry

Only simple cubic system has one centre
of symmetry. Other system do not have
centre of symmetry. it is shown in the figure

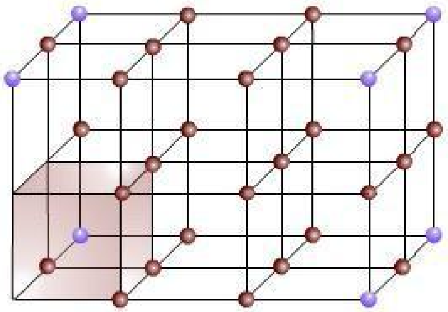


Hence, a cubic crystal possesses a total of 23 elements of symmetry.

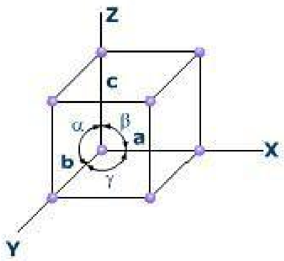
Plane of symmetry (3 + 6) = 9
Axes of symmetry (3 + 4 + 6) = 13
Centre of symmetry (1) = 1
Total symmetry = 23

Space lattice or crystal lattice

A space lattice is an array of points showing how atoms, molecules or ions are arranged at different sites in a 3D space. The points are known as lattice points.



Representation of space lattice and unit cell



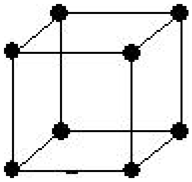
Representation of dimensions of a unit cell

Unit Cell

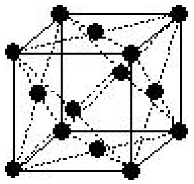
- *The unit cell is the smallest repeating unit in the space lattice when repeated again and again, it results in the crystal of the substance.*
- The crystal may be considered to consist of an infinite number of unit cells.
- Thus, the unit cell may be considered as the brick of the wall (where the wall represents the crystal).
- Just as the shape of the wall depends on the shape of the brick, the shape of the crystal also depends on the shape of the unit cell. The size and shape of a unit cell are determined by the lengths of the edges of the unit cell (a, b, and c) and by the angles alpha, beta and gamma.
- Therefore, a unit cell is the fundamental pattern of a crystalline solid and it is characterized by the distance *a, b and c* and the interfacial angles alpha, beta, and gamma.

Types of unit cells: ***There are four different types of unit cells.***

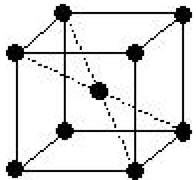
Simple or primitive or basic unit cell (P): The unit cell having lattice points only at the corners is called Simple or primitive or basic unit cell.



Face-centered unit cell (FC). The unit cell having lattice points at the center of each face in addition to the lattice points at the corners is called Face centered unit cell. Fig1b

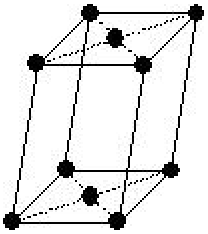


Body-centered **unit cell (BC)**. The unit cell having lattice points at the center of the body in



addition to the lattice points at the corners is called Face centered unit cell.

End face centered unit cell or Base centred unit cell (I). The unit cell having lattice points at the two opposite faces in addition to the lattice points at the corners is called Face centred unit cell.

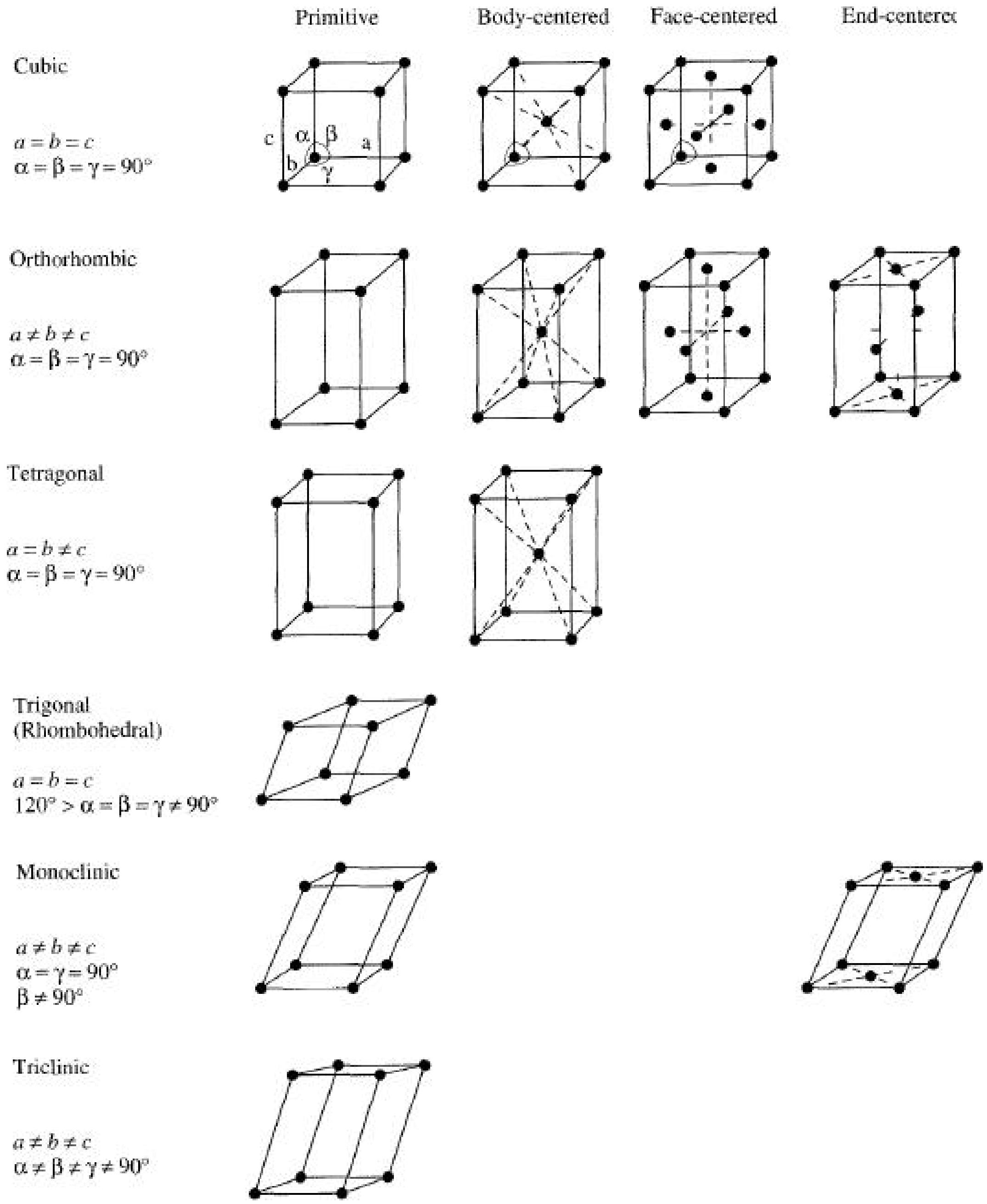


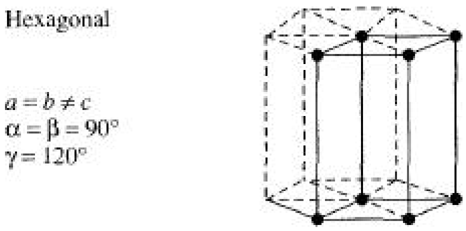
Seven Crystal System

Crystal system	Examples
1. Cubic	NaCl, Diamond, ZnS, CaF_2
2.Ortho Rhombic	$PbCO_3$, $BaSO_4$, K_2SO_4
3. Tetragonal	TiO_2, PO_4, SnO_2
4.Rhombohedral	Calcite, Magnacite, Quartz.
5. Monoclinic	$CaSO_4.2H_2O$, $K_2MgSO_4.6H_2O$
6. Triclinic	$CuSO_4.5H_2O$, $K_2Cr_2O_7$
7. Hexagonal	Graphite, Zn, Cd, MgS.

There are 14 Bravais Lattices

Bravais in 1848 showed that there are only 14 different ways by which atoms, ions and molecules can be arranged in three dimensions. Of these 7 are primitive systems and others may be body-centered, face-centered, or end-centered. These 14 different types of arrangement are called Bravais lattices.





Cubic crystal system

The cubic crystal system is the simplest system analysed mathematically (although other systems can also be analysed accordingly).

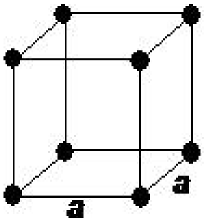
The analysis reflects the following characteristics

1. Atomic radius
2. Number of atoms per unit cell
3. Coordination number
4. Density of lattice crystal
5. Packing fraction (efficiency of packing or % efficiency or density of packing)

Atomic radius

It is defined as ‘Half the distance between nearest neighboring atoms’ in a crystal. The atomic radius is represented in terms of length of edge ‘a’ in the unit cell.

Simple cubic structure (SC)

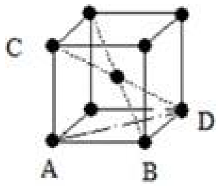


The distance between the nearest neighbour (d) = a

Radius is , $r = d/2$

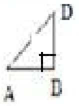
$r = a/2$

Body-centered cubic structure (BCC)



The distance between the nearest neighbour (d) = 1/2 CD

In the right angled triangle ABD,



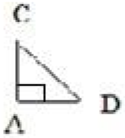
$$AD = \sqrt{AB^2 + BD^2}$$

$$= \sqrt{a^2 + a^2}$$

$$= \sqrt{2a}$$

$$AD^2 = 2a^2$$

Now, trianglee, ACD



$$CD = \sqrt{AC^2 + AD^2}$$

$$= \sqrt{a^2 + 2a^2}$$

$$= \sqrt{3a^2}$$

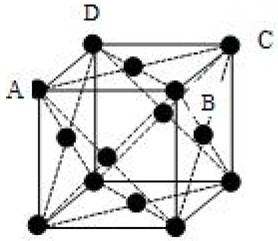
$$= \sqrt{3}\ a$$

Therefore

$$d = ½\ CD = \frac{\sqrt{3}\ a}{2}$$

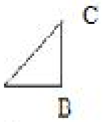
$$r = d/2 = \frac{\sqrt{3}\ a}{4}$$

Face-centered cubic structure (FCC).



The distance between nearest neighbours (d) = 1/2 AC

In the right angled triangle ABD,



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

$$= \sqrt{a^2 + a^2}$$

$$= \sqrt{2}\ a$$

Therefore

$$d = \tfrac{1}{2}\ AC = \frac{\sqrt{2}\ a}{2}$$

$$r = d/2 = \frac{\sqrt{2}\ a}{4}$$

$$r = \frac{a}{2\sqrt{2}}$$

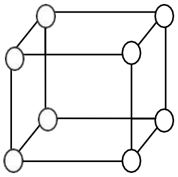
Number of atoms per unit cell

Keeping the following points in mind, we can calculate the number of atoms in a unit cell.

- An atom at the corner is shared by eight unit cells.
  Hence an atom at the corner contributes 1/8 to the unit cell
- An atom at the face is a shared by two unit cells, hence, Contribution of each atom on the face is 1/2 to the unit cell.
- An atom within the body of the unit cell is shared by no other unit cell, hence, Contribution of each atom within the body is 1 to the unit cell.
- An atom present on the edge is shared by four unit cells, hence, Contribution of each atom on the edge is 1/4 to the unit cell.
- By applying these rules, we can calculate the number of atoms in the different cubic unit cells of monatomic substances.

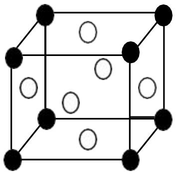
Simple cubic

Simple Cubic Lattice (Primitive-P): In which there are points only at the corners of each unit.



Total number of atoms per unit cell of P = (1/8) x 8 = 1

Face Centered Cubic Lattice (F C): In which there are points at the corners as well as at the center of each of the six faces of the cube.



Total number of atoms per unit cell = 8 x (1/8) = 1

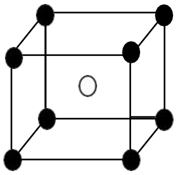
(since 8 corners occupied 1/8 atoms)

6 faces shared by ½ atoms each

6 x ½ = 3

Total = 1 + 3 = 4

Body Centered Cubic Lattice (BC): In which there are points at the corners as well as in the center of each cube.

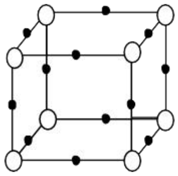


Total number of atoms = 8 x (1/8) = 1

At the center 1 atom

Total = 1 + 1 = 2

Base Centered Cubic Lattice (C): In which there are points at the corners as well as in the edges of each cube



At the corners 8 x (1/8) = 1

At the edges 12 x (1/4) = 3

Total = 1 + 3 = 4

Number of atoms per unit cell in cubic lattice

Types of Lattice	***Location of atoms***	**Portion in the unit cell**	**Number of atoms in the unit cell**
Primitive (P)	Corner	1/8	1
FC	Face + Corner	1/2	3+1 = 4
BC	Body + Corner	1+1	2
Edge or base centered	Edge + Corner	1/4	3+1 = 4

Coordination number

It is defined as the number of nearest neighbors that an atom has in a unit cell. In an ionic crystal, the number of oppositely charged ions surrounding each ion is called its coordination number. Thus, the coordination number of a crystal depends upon the structure. *For any system, the number of atoms touching the particular atom is called coordination number.*

Simple cubic structure has coordination number = 6
Body centered cubic structure has coordination number = 8
Face centered cubic structure has coordination number = 12

Density of lattice crystal

Calculation of Density of a Cubic Crystal from its Edge Length ‘a’ (The edge length should be in cm)

The edge length of a cubic crystal can be obtained from X-ray studies and knowing the crystal structure possessed by it so that the number of particles per unit cell are known, the density of the crystal can be calculated.

$$m = \text{mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

Therefore,

$$\text{Density} = \frac{n \times \text{atomic mass}}{\text{Avogadro number} \times \text{vol.of uint cell}}$$

Where, n is the number of atoms per unit cell. The volume of unit cell is to be calculated for the given crystal system

For cubic crystal, volume of unit cell is a^3.

For simple cubic, the density is given by

$$\rho = \frac{1 \times M}{N_A \times a^3}$$

For body centered cubic the density is given by

$$\rho = \frac{2 \times M}{N_A \times a^3}$$

For body centered cubic the density is given by

$$\rho = \frac{4 \times M}{N_A \times a^3}$$

Density of the substance is same as the density of the unit cell.

For the density equation it is also possible to calculate the edge length (a) of the unit cell.

Packing fraction (efficiency of packing or % efficiency or density of packing) and Void (or) Empty Space in Cubic Lattices

It is defined as ratio of volumes occupied by atom in unit cell (u) to the total volume of the unit cell (V).

It suggests that how closely the atoms are packed (stacked) together in the unit cell. For three cubic cells, these are illustrated.

Efficiency of packing in simple cubic structure

Let ‘a’ be the edge length og unit cell and ‘r’ be the atomic radius. In Simple Cubic system, the total number of atoms per unit cell is ONE. Thus the volume of atoms in the unit cell is given by

$$u = 1\times 4/3\ \pi\ r^3$$

$$= 4/3 \times \pi \times (a/2)^3 \qquad \text{Since, } r = a/2 \text{ for Simple cubic system}$$

$$= \frac{\pi \times a^3}{6}$$

Since the total volume of the unit cell is V= a^3

Therefore, Packing fraction of simple cubic system is given by $= \frac{u}{V} = \frac{\pi \times a^3}{6\times\ a^3}$

$$= \frac{\pi}{6}$$

$$= \frac{22.6}{6\times 2}$$

$$= 0.52$$

This reveals that 52% of the unit cell is occupied by atoms and remaining 48% is empty.

Efficiency of packing in Body centered cubic structure

We know, for a bcc structure

$$r = \frac{\sqrt{3}}{4}a$$

In bcc structure, the total number of atoms per unit cell is 2.

$$\text{Volume of two spheres} = 2\times\frac{4}{3}\pi r^3$$

Volume of the cube = a^3

$$= \left(\frac{4}{\sqrt{3}}r\right)^3$$

Therefore, Percentage efficiency

$$= \frac{\text{Volume occupied by two spheres in the unit all}}{\text{Total volume of the unit cell}}$$

$$= \frac{2\times(4/3)\pi r^3 \times 100}{\left(\frac{4}{3}r\right)^3}\%$$

$$= \frac{(8/3)\pi r^3 \times 100}{\left(\frac{64}{3\sqrt{3}}\right)r^3}$$

$= 68\%$

This reveals that 68% of the unit cell is occupied by atoms and 32% is empty.

Efficiency of packing in Face centered cubic structure

We have found that for a ccp arrangement

$$r = \frac{a}{2\sqrt{2}}$$

We also know that, per unit cell in ccp arrangement has effectively 4 spheres.

$$\text{Volume of four spheres} = 4 \times \frac{4}{3}\pi r^3$$

$$\text{Volume of the cube is} = a^3 = (2\sqrt{2}r)^3$$

Therefore, Percentage efficiency

$$= \frac{\text{volume occupied by four spheres} \times 100}{\text{Total volume of the unit cell}}$$

$$= \frac{4\times(4/3)\,\pi r^3 \times 100}{(2\sqrt{2}r)^3}$$

$$= \frac{(16/3)\pi r^3 \times 100}{16\sqrt{2}r^3} = 74\%$$

This reveals that 74% of the unit cell is occupied by atoms and 26% is empty.

Thus, the % efficiency of packing in SC, BCC and FCC are 52%, 68% and 74% respectively.
The packing density data; FCC > BCC > SC
That is, FCC is more closely packed and more stable.

Volume of unit cell = V = a^3

Hence, we notice that in the cubic closest packed structure only 74% of the space is actually occupied by spheres.

Summary:

Characters of the unit cell	SC	BCC	FCC
Atomic radius	$r = a/2$	$r = \frac{\sqrt{3}\,a}{4}$	$r = \frac{a}{2\sqrt{2}}$

Number of atoms per unit cell	1	2	4
Coordination number	6	8	12
Density of lattice crystal.	$\rho = \dfrac{1\times M}{N_A \times a^3}$	$\rho = \dfrac{2\times M}{N_A \times a^3}$	$\rho = \dfrac{4\times M}{N_A \times a^3}$
Packing fraction	52%	68%	74%

The structure of a typical ionic solid - sodium chloride:

How the ions are arranged in sodium chloride:

Sodium chloride is taken as a typical ionic compound. Compounds like this consist of a giant (endlessly repeating) lattice of ions. So sodium chloride (and any other ionic compound) is described as having a giant ionic structure.

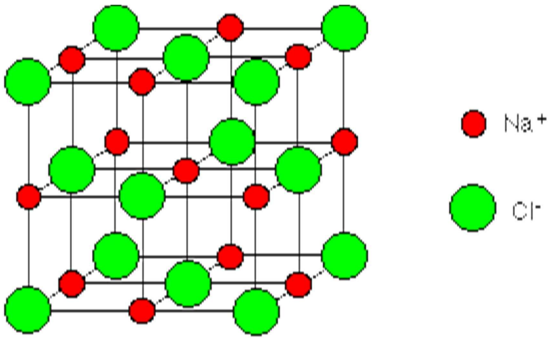
You should be clear that giant in this context doesn't just mean very large. It means that you can't state exactly how many ions there are.

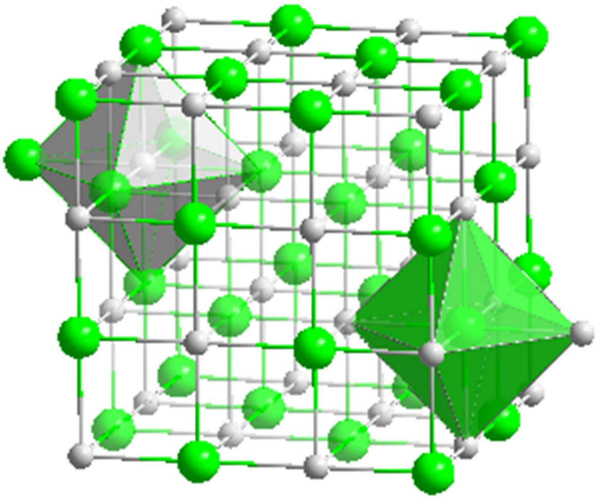
There could be billions of sodium ions and chloride ions packed together, or trillions, or whatever - it simply depends how big the crystal is. That is different from, say, a water molecule which always contains exactly 2 hydrogen atoms and one oxygen atom - never more and never less.

A small representative bit of a sodium chloride lattice looks like this:

If you look at the diagram carefully, you will see that the sodium ions and chloride ions alternate with each other in each of the three dimensions.

This diagram is easy enough to draw with a computer, but extremely difficult to draw convincingly by hand. We normally draw an "exploded" version which looks like this:


Na^+
Cl^-



Only those ions joined by lines are actually touching each other. The sodium ion in the center is being touched by 6 chloride ions. By chance we might just as well have centered the diagram around a chloride ion - that, of course, would be touched by 6 sodium ions. Sodium chloride is described as being 6:6- co-ordinated.

You must remember that this diagram represents only a tiny part of the whole sodium chloride crystal. The pattern repeats in this way over countless ions.

Why is sodium chloride 6:6-co-ordinated?

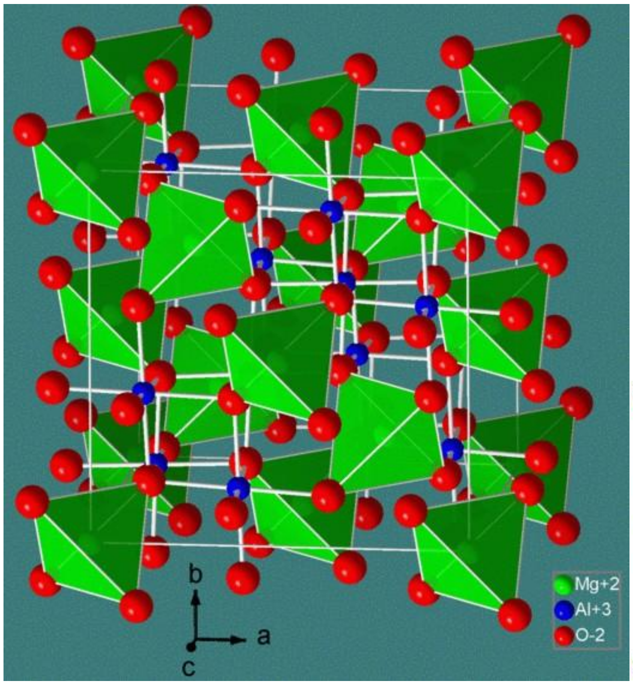
The more attraction there is between the positive and negative ions, the more energy is released. The more energy that is released, the more energetically stable the structure becomes.

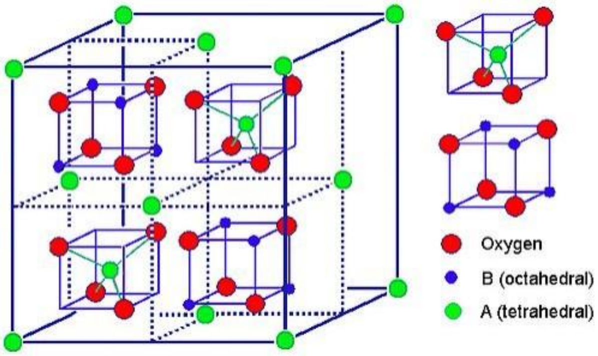
That means that to gain maximum stability, you need the maximum number of attractions. So why does each ion surround itself with 6 ions of the opposite charge?

That represents the maximum number of chloride ions that you can fit around a central sodium ion before the chloride ions start touching each other. If they start touching, you introduce repulsions into the crystal which makes it less stable.

Spinel, Perovskite, and Rutile Structures

There are three more structures, which are derived from close-packed lattices, that are particularly important because of the material properties of their compounds. These are the **spinel** structure, on which ferrites and other magnetic oxides are based, the **perovskite** structure, which is adopted by ferroelectric and superconducting oxides, and the **rutile** structure, which is a common binary 6:3 structure adopted by oxides and fluorides.





The **spinel structure** is formulated MM'_2X_4, where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula AB_2O_4.

In the **normal spinel** structure, there is a close-packed array of anions. The A-site cations fill 1/8 of the tetrahedral holes and the B- site cations fill 1/2 of the octahedral holes. A polyhedral view of the normal spinel unit cell is shown at the left, and a simplified view (with the contents of the back half of the cell removed for clarity) is shown above. Each unit cell contains eight formula units and has a composition $A_8B_{16}O_{32}$.

Inverse spinels have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places. Inverse spinels are thus formulated $B(AB)O_4$, where the AB ions in parentheses occupy octahedral sites, and the other B ions are on tetrahedral sites. There are also mixed spinels, which are intermediate between the **normal** and **inverse** spinel structure.

Some spinel and inverse spinel AB

combinations are: $A^{2+}B^{3+}$, e.g.,

$MgAl_2O_4$ (normal spinel)

$A^{4+}B^{2+}$, e.g., $Pb_3O_4 = Pb^{II}(Pb^{II}Pb^{IV})O_4$

(inverse spinel) $A^{6+}B^{+}$, e.g., Na_2WO_4

(normal spinel)

Many magnetic oxides, such as Fe_3O_4 and $CoFe_2O_4$, are spinels.

Normal vs. inverse spinel structure

For transition metal oxide spinels, the choice of the normal vs. inverse spinel structure is driven primarily by the **crystal field stabilization energy** (CFSE) of ions in the tetrahedral and octahedral sites. For spinels that contain 3d elements such as Cr, Mn, Fe, Co, and Ni, the electron configuration is typically **high spin** because O^{2-} is a **weak field ligand**.

Ferrites are compounds of general formula $\mathbf{M^{II}Fe_2O_4}$. We can see that magnetite is one example of a ferrite (with M = Fe). Other divalent metals (M = Mg, Mn, Co, Ni, Zn) also form ferrites. Ferrites can be normal or inverse spinels, or mixed spinels, depending on the CFSE of the M^{II} ion. Based on their CFSE, Fe^{2+}, Co^{2+}, and Ni^{2+} all have a strong preference for the octahedral site, so those compounds are all inverse spinels. $ZnFe_2O_4$ is a normal spinel because the small Zn^{2+} ion (d^{10}) fits more easily into the tetrahedral site than Fe^{3+} (d^5), and both ions have zero CFSE. $MgFe_2O_4$ and $MnFe_2O_4$, in which all ions have zero CFSE and no sitepreference, are mixed spinels. **Chromite** spinels, $\mathbf{M^{II}Cr_2O_4}$, are always **normal spinels** because the d^3 Cr^{3+} ion has a strong preference for the octahedral site.

Examples of normal and inverse spinel structures:

$\mathbf{MgAl_2O_4}$ is a **normal spinel** since both Mg^{2+} and Al^{3+} are non-transition metal ions and thus CFSE = 0. The more highly charged Al^{3+} ion prefers the octahedral site, where it is surrounded by six negatively charged oxygen atoms.

$\mathbf{Mn_3O_4}$ is a **normal spinel** since the Mn^{2+} ion is a high spin d^5 system with zero CFSE. The two Mn^{3+} ions are high spin d^4 with higher CFSE on the octahedral sites ($3/5\ \Delta_O$) than on the tetrahedral site (2/5 $\Delta_t \sim 1/5\ \Delta_O$).

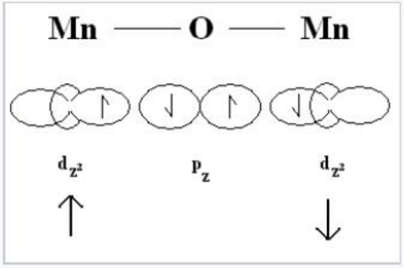
Fe_3O_4 is an **inverse spinel** since the Fe^{3+} ion is a high spin d^5 system with zero CFSE. Fe^{2+} is a high spin d^6 system with more CFSE on an octahedral site than on a tetrahedral one.

$NiFe_2O_4$ is again an **inverse spinel** since Ni^{2+} (a d^8 ion) prefers the octahedral site and the CFSE of Fe^{3+} (a d^5 ion) is zero.

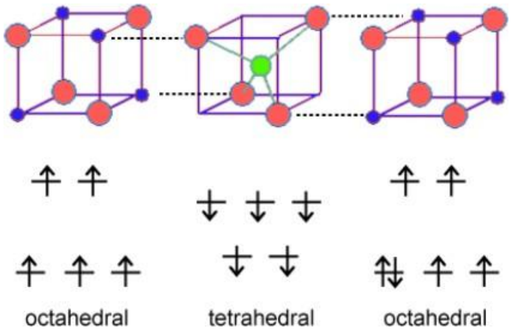
Co_3O_4 is a **normal spinel**. Even in the presence of weak field oxo ligands, Co^{3+} is a low spin d^6 ion with very high CFSE on the octahedral sites, because of the high charge and small size of the Co^{3+} ion. Hence the Co^{3+} ions occupy both octahedral sites, and Co^{2+} occupies the tetrahedral site.

Magnetism of ferrite spinels

Ferrite spinels are of technological interest because of their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure (normal or inverse) and the nature of the metal ions. Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$ are all inverse spinels and are ferrimagnets. The latter two compounds are used in magnetic recording media and as deflection magnets, respectively.



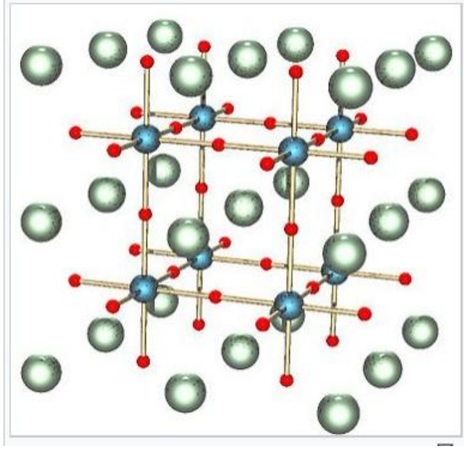
In order to understand the magnetism of ferrites, we need to think about how the unpaired spins of metal ions are coupled in oxides. If an oxide ion is shared by two metal ions, it can mediate the coupling of spins by superexchange as shown at the right. The coupling can be antiferromagnetic, as shown, or ferromagnetic, depending on the orbital filling and the symmetry of the orbitals involved. The **Goodenough-Kanamori rules** predict the local magnetic ordering (ferromagnetic vs. antiferromagnetic) that results from superexchange coupling of the electron spins of transition metal ions. For ferrites, the strongest coupling is between ions on neighboring **tetrahedral and octahedral sites**, and the ordering of spins between these two sites is reliably **antiferromagnetic**.



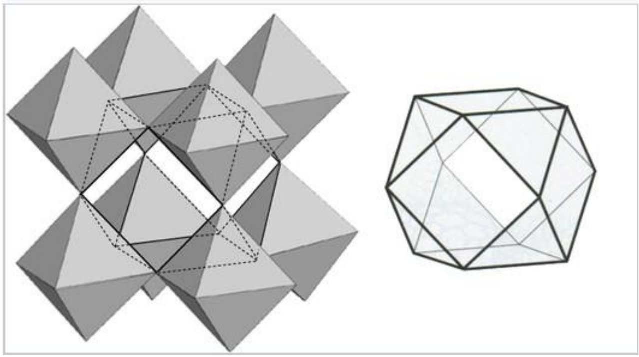
Because all the tetrahedral and octahedral sites in a spinel or inverse spinel crystal are coupled together identically, it works out that ions on the tetrahedral sites will all have one orientation (e.g., spin down) and ions on all the octahedral sites will have the opposite orientation (e.g., spin up). If the number of spins on the two sites is the same, then the solid will be antiferromagnetic. However, if the **number of spins is unequal** (as in the case of Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$) then the solid will be **ferrimagnetic**. This is illustrated above for Fe_3O_4. The spins on the Fe^{3+} sites cancel, because half of them are up and half are down. However, the four unpaired electrons on the Fe^{2+} ions are all aligned the same way in the crystal, so the compound is ferrimagnetic.

Perovskites are **ternary oxides** of general formula **ABO_3**. More generally, the perovskite formula is ABX_3, where the anion X can be **O, N, or halogen**. The A ions are typically large ions such as Sr^{2+}, Ba^{2+}, Rb^{+}, or a lanthanide 3+ ion, and the B ions are smaller transition metal ions such as Ti^{4+}, Nb^{5+}, Ru^{4+}, etc. The mineral after which the structure is named has the formula $CaTiO_3$.

The perovskite structure has simple cubic symmetry, but is related to the fcc lattice in the sense that the A site cations and the three O atoms comprise a fcc lattice. The B-site cations fill 1/4 of the octahedral holes and are surrounded by six oxide anions.



The coordination of the A ions in perovsite and the arrangement of BO_6 octahedra is best understood by looking at the ReO_3 structure, which is the same structure but with the A-site cations removed. In the polyhedral representation of the structure shown at the right, it can be seen that the octahedra share all their vertices but do not share any octahedral edges. This makes the ReO_3 and perovskite structures flexible, like three-dimensional wine racks, in that the octahedra can **rotate and tilt cooperatively**. Eight such octahedra surround a large **cuboctahedral cavity**, which is the site of the A ions in the perovskite structure. Cations in these sites are coordinated by 12 oxide ions, as expected from the relationship between the perovskite and fcc lattices.



Because the A-site is empty in the ReO_3 structure, compounds with that structure can be reversibly **intercalated** by small ions such as **Li^+ or H^+**, which then occupy sites in the cuboctahedral cavity. For example, smart windows that darken in bright sunlight contain the **electrochromic** material WO_3, which has the ReO_3 structure. In the sunlight, a photovoltaic cell drives the reductive intercalation of WO_3.

WO_3 is a light yellow compound containing d^0 W(VI). In contrast, H_xWO_3, which is mixed-valent W(V)-W(VI) = d^1-d^0, has a deep blue color. Such coloration is typical of mixed-valence transition metal complexes because their d-electrons can be excited to delocalized conduction band levels by red light. Because the electrochemical intercalation-deintercalation process is powered by a solar cell, the tint of the windows can adjust automatically to the level of sunlight.

Ferroelectric perovskites

The flexibility of the network of corner-sharing BO_6 octahedra is also very important in ferroelectric oxides that have the perovskite structure. In some perovsites with small B-site cations, such as Ti^{4+} and Nb^{5+}, the cation is too small to fit symmetrically in the BO_6 octahedron. The octahedron distorts, allowing the cation to move off-center. These distortions can be **tetragonal** (as in the example shown at the right), **rhombohedral**, or **orthorhombic**, depending on whether the cation moves towards a vertex, face, or edge of the BO_6 octahedron. Moving the cation off-center in the octahedron creates an **electric dipole**. In ferroelectrics, these dipoles align in neighboring unit cells through cooperative rotation and tilting of octahedra. The crystal thus acquires a net electrical polarization.

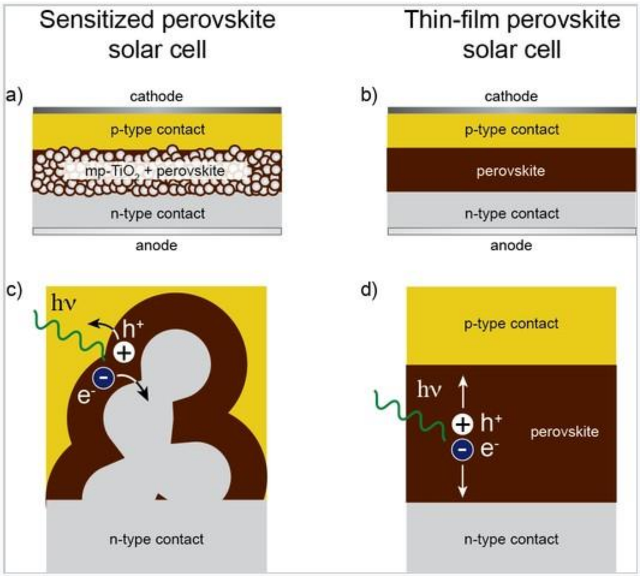
Ferroelectricity behaves analogously to **ferromagnetism**, except that the polarization is electrical rather than magnetic. In both cases, there is a **critical temperature (T_c)** above which the **spontaneous polarization** of the crystal disappears. Below T_c, the electric polarization of a ferroelectric can be switched with a coercive field, and hysteresis loop of polarization vs. field resembles that of a ferromagnet. Above T_c, the crystal is **paraelectric** and has a high dielectric permittivity.

Ferroelectric and paraelectric oxides (along with piezoelectrics and pyroelectrics) have a wide variety of applications as switches, actuators, transducers, and dielectrics for capacitors. **Ferroelectric capacitors** are important in memory devices (FRAM) and in the tuning circuits of cellular telephones. **Multiferroics**, which are materials that are simultaneously ferroelectric and ferromagnetic, are rare and are being now intensively researched because of their potential applications in electrically adressable magnetic memory.

Halide perovskites (ABX_3, X = Cl, Br, I) can be made by combining salts of monovalent A ions ($A^+ = Cs^+$, NH_4^+, RNH_3^+) and divalent metal salts such as $PbCl_2$ or PbI_2. These compounds have sparked recent interest as light absorbers for **thin film solar cells** that produce electricity from sunlight. Lead and tin halide perovskites can be grown as thin films from solution precursors or by thermal evaporation at relatively low temperatures. In some lead halide perovskites, the mobility of electrons and holes is very high, comparable to that of more expensive III-V semiconductors such as GaAs, which must be grown as very pure single crystals at high temperatures for use in solar cells. Because of their high carrier mobility, some lead halide perovskites are also electroluminescent and are of interest as inexpensive materials for light-emitting diodes (LEDs).

Tin and lead halide perovskites were first studied in the 1990s as materials for thin film electronics,[4] and more recently as light absorbers in dye-sensitized solar cells. Soon after the results on dye-sensitized perovskite cells were reported, it was discovered that halide perovskites could also be used in thin film solid state solar cells. The structures of these solar cells are shown schematically at the right. The highest reported solar power conversion efficiencies of perovskite solar cells have jumped from 3.8% in 2009 [5] to 10.2% in 2012[6] and a certified 20.1% in 2014.[7]. The highest performing cells to date contain divalent lead in the perovskite B cation site and a mixture of methylammonium and formamidinium ions in the perovskite A cation site.

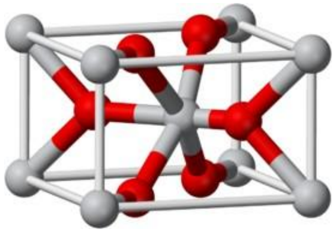
Despite their very impressive efficiency, perovskite solar cells are stable for relatively short periods of time and are sensitive to air and moisture. Current research is focused on understanding the degradation mechanisms of these solar cells and improving their stability under operating conditions.

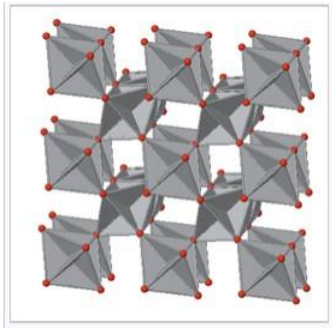


The **rutile structure** is an important MX_2 (X = O, F) structure. It is a 6:3 structure, in which the cations are octahedrally coordinated by anions, and as such is intermediate in polarity between the CaF_2 (8:4) and SiO_2 (4:2) structures. The mineral rutile is one of the polymorphs of TiO_2, the others (anatase and brookite) also being 6:3 structures.

The rutile structure can be described as a distorted version of the NiAs structure with half the cations removed. Recall that compounds with the NiAs structure were typically metallic because the metal ions are eclipsed along the stacking axis and thus are in relatively close contact. In rutile, the MO_6 **octahedra share edges** along the tetragonal c-axis, and so some rutile oxides, such as **NbO_2, RuO_2 and IrO_2,** are also **metallic** because of **d-orbital overlap** along that axis. These compounds are important as electrolyzer catalysts and catalyst supports because they combine high catalytic activity with good electronic conductivity.

Rutile TiO_2, because of its high refractive index, is the base pigment for white paint. It is a wide bandgap semiconductor that has also been extensively researched as an electrode for water splitting solar cells and as a photocatalyst (primarily as the anatase polymorph) for degradation of pollutants in air and water. Self-cleaning glass exploits the photocatalytic properties of a thin film of TiO_2 to remove oily substances from the glass surface and improve the wetting properties of the glass.





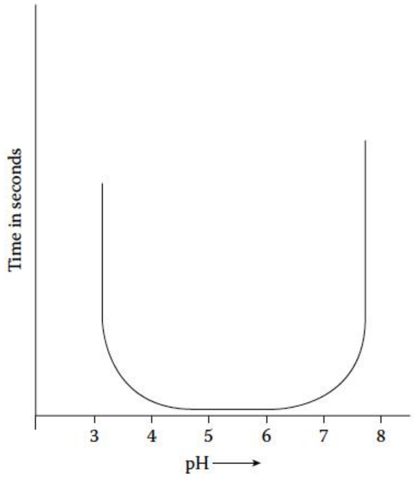
What Are Crystals? Matter exists in three states—gaseous, liquid, and solid—ignoring the fourth state called the plasma state, which consists of equal number of positive ions and electrons. These three general states of matter represent very different degrees of atomic or molecular mobility. In the gaseous state, the molecules are in constant, vigorous, and random motion. A gas let into an evacuated container takes the shape of the container, is readily compressible, and exhibits very low viscosity. In the liquid state, the random molecular motion is much more restricted. Unlike a gas, the volume occupied by a liquid is limited. The liquid only takes the shape of the occupied part of its container, and its free surface is flat except in regions where it comes into contact with the container walls. A liquid exhibits a much higher viscosity than a gas and is less easily compressed. In the solid state, however, molecular motion is confined to an oscillation about a fixed position, and the structure is elastically deformable only to a small extent. In fact, it will often fracture when subjected to a large deforming force. Solids may be crystalline or amorphous, and the crystalline state differs from the amorphous state in the regular arrangement of constituent molecules, atoms, or ions into some fixed and rigid pattern known as a lattice. The term "crystalline" is very frequently used to indicate the high degree of internal regularity resulting in the development of definite external faces. Hence, crystals grown without space constraints are polyhedral, bounded by flat faces meeting at straight edges. These flat faces, which are highly polished in good crystals, are inclined to each other at angles that are characteristic of a particular material irrespective of the external shape. The interfacial angles display certain symmetries and are in accordance with the structural symmetries possessed by the crystal. In fact, accurate measurement of the inter-facial angles has shown that often there exists a small variation in interfacial angles from one crystal to another of the same substance, and these variations were discovered even between the faces giving sharp light signals in the optical goniometer.

Why Single Crystals? Single crystals find important uses in research and development. In fact, according to one classification, all true solids are crystals. Thus, for an understanding of the physics and chemistry of the solid state, single crystals are a prerequisite. One may use polycrystalline samples rather than single crystals for many studies, but often single crystals are preferred. As we know, poly- crystals contain grain boundaries. If we desire to know some bulk property of a material and we measure that property on a polycrystalline specimen, it will in many cases include the effect of grain boundaries. A notable example of a property where single crystals are essential is electrical conductivity, which is particularly impurity sensitive. Impurities tend to segregate at grain bound- aries, thereby obstructing the passage of current. Hence, single crystals are almost always required for determining any conductivity-dependent property. Another common effect of grain boundaries and associated voids is light scattering and, hence, single crystals are required in optical studies as well. Many properties of crystals depend on the crystallographic direction in which the measurement is carried out, because the spatial arrangement of the constituent atoms is not in general the same in all directions. Consequently, if we determine a directionally dependent property in a polycrystalline specimen, where the crystallites are randomly oriented, we will obtain only an aver- age value of the property in which the directional dependence gets masked. Single crystals have important practical applications in technology. For example, in quartz oscillators, much better frequency stability can be achieved in single-crystal quartz than polycrystalline samples. In nonlinear optical conversion processes, one invariably uses oriented single crystals. One can give many such examples where single crystals are always required.

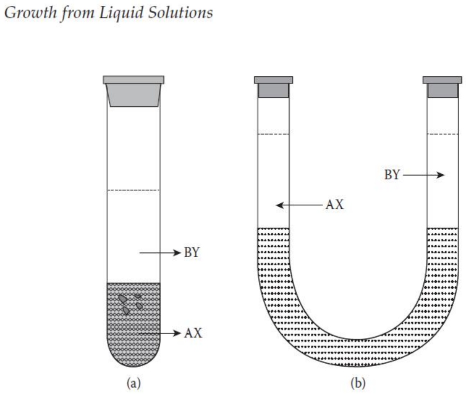
Growth from Silica Gel: Growing crystals in gels has been known since the end of the nineteenth century, but the method went into a state of hibernation until the interest in it was revived afresh by Henisch and his coworkers through their extensive work in the 1960s. The method was initially used to grow only those crystals that had very low solubility in water. Since then, various modifications have been introduced to the basic gel method, and different types of crystals, including the ones soluble in water, have been grown with a high degree of perfection. Although the size of the crystals that could be grown by the gel method is limited, its ability to grow practically insoluble materials (in water) at room temperatures with exceedingly simple and inexpensive equipment makes the technique attractive. Also, since the gel medium is almost transparent, the growing crystals can be viewed during the entire growth period. Further, since the growth occurs at room temperature, one can expect them to contain a lower con- centration of equilibrium defects than those grown by high-temperature techniques.

Gel Preparation The first step in crystal growth from gels is the preparation of the gel. A gel has been defined as a two-component system of a semisolid nature rich in liquid. Closest to gel in structures are sols from which they are usually pre- pared. Sols, which are likewise two-component systems, resemble liquids more than solids. Further, because gels are formed by the process of gelling of sols, it is essentially the preparation of sols that needs to be carried out first. In fact, the preparation of sols is more difficult than the preparation of gels. To produce sols that are stable at a reasonably high concentration, it is necessary to grow the clusters of molecules to a certain size under alkaline conditions (clusters are negatively charged in alkaline conditions) so that they will not flocculate or gel. Gels can be prepared from a variety of materials. The most commonly used ones for growing crystals are those prepared from agar, gelatin, silica, tetramethoxysilane (TMOS), and polyacrylamide. The procedure to form gel from these materials varies. For example, to form agar gel, 1%–2% by weight of agar-agar is dissolved in water. The clear solution is boiled and cooled down slowly. The gelation takes place during cooling. Gelatin gel is prepared by dissolving gelatin in water and stirring it at a constant temperature of 50°C for an hour or so and then cooling it down to room temperature. A small quantity of formaldehyde, if added, strengthens the gel. Silica gel is prepared by neutralizing the aqueous solution of sodium metasilicate with mineral or organic acids. Silica gels can also be pre- pared by adding water to silanes, such as TMOS or tetraethoxysilane , and the references therein]. Polyacrylamide gel is prepared by dissolving ~4% by weight of acrylamide and 0.02% by weight of a cross-linking agent in water. The solution is bubbled with nitrogen gas and then degassed by reducing the pressure. This gives a rigid transparent gel [27]. Other gels used in crystal growth are polyethylene oxide and polyvinyl alcohol. In physical gels such as agar and gelatin the sol-to-gel transition is reversible. However, in chemi- cal gels like silica and polyacrylamide, the transition is irreversible. Among the various gels that can be used for growing crystals, silica gel seems to be the most widely used. Many processes have been employed for producing colloidal silica from low-cost sodium silicate solution. Dialysis, electrodialysis, ion exchange, peptization of gel, hydrolysis of silicon com- pounds, and neutralization of soluble silicate with acids are some of the processes used for gelation. Of these, the one that is generally employed by crystal growers is the method of neutralizing soluble silicates with acids; hence, we deal with this method in greater detail. When a dilute solution of sodium silicate (which is alkaline) is partially neutralized with acid to a pH in the range of 8–0, a silica sol rather than a gel is obtained, provided the concentration of the resulting sodium salt is less than about 0.3 N. While making a sol by neutralizing with acids, the mixing by stirring should be carried out so rapidly that no part of the solu- tion remains in the pH range of 5–6 for an appreciable time. This is because silicic acid would transform into gel almost instantaneously at these pH values. Silica sol thus prepared changes into gel in due course at times that can vary widely from minutes to many days, depending on the material, its tem- perature, pH, and history. Initially, there is only a slow increase in viscosity. Then, the viscosity begins to increase rapidly and solidification occurs at the gel point. The gel point can easily be determined by tilting the container in which it is being set. If the gel is set, the meniscus will no longer remain horizontal when tilted. Now, depending on the density and precise condi- tions during gelling, the hardness of fully developed gels can vary widely from being very soft to hard. However, in most of the crystal growth studies, it is the soft gel that is used. One of the most important factors affecting the hardness of the gel medium is the density of the sodium metasilicate solution. In almost all cases, dense and hard gels have produced poor-quality crystals. On the other hand, if the gel density is too low, it will take a very long time to set, and the resulting gel will be mechanically fragile and hence unstable. Experimenters have realized that solutions with densities in the range of 1.03–1.06 g/cc yield satisfactory results. Silica gel can be set by adding either acid to sodium metasilicate or sodium metasilicate to the acid. The two routes are not the same because in one case the gelation pH is approached from the acid side (pH 0.5–4.0) and in the other it is from the alkaline side (pH ~12). These are sometimes called acid and alkali set gels, respectively. Gelling Mechanism and Structure When sodium metasilicate is dissolved in water, the following reaction would take place to produce orthosilicic acid. $Na2SiO3 + 3H2O \equiv H4SiO4 + 2NaOH$ It is generally accepted that orthosilicic acid can polymerize with the liberation of water. As mentioned earlier, the rate of polymerization depends on the pH value of the solution.

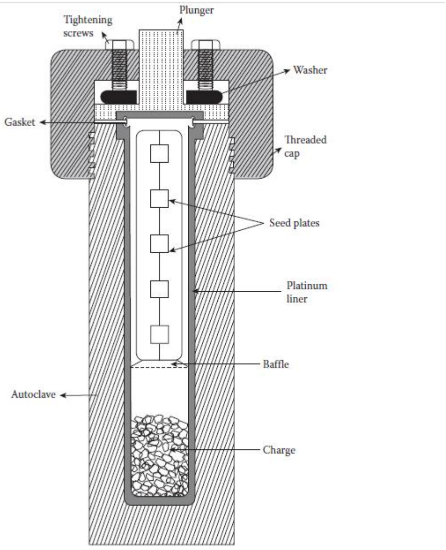
Expulsion of water would also occur due to gel shrinkage. Such a phenomenon is known as syneresis. It is important to realize that the gelation time is extremely sensitive to solution pH. Figure 9.8 schematically shows the relationship between the time required for gelation and pH of the solution. During polymerization, in addition to the formation of H2SiO4 – shown by the earlier reaction, H3SiO4 – ions are also produced, the relative amounts of which depend on the pH value. The formation of more reactive H2SiO4 – is favored at high pH values. Because of the higher charge of this species, there is a greater degree of repulsion between them, thus slowing down the gelation process. H3SiO4 – is favored by moderately low pH values and is believed to be responsible for initial formation of long chains due to polymerization. Subsequently, cross-linkages are formed between these chains, leading to sharp increase in viscosity that signals the onset of gelation. At very low pH values, however, the tendency toward polymerization itself is diminished, thus slowing down the process of polymerization. This qualitatively explains the gelation time versus pH curve shown in Figure.



Some efforts have been made to study the structure of these gels by direct visualization. Transmission electron microscope study of the frozen gels gives information about the maximum size of macropores, where the nucleation and growth of the crystals occur [28]. Pore-to-pore distance has also been deduced from light-scattering experiments performed on these gels [29]. From the scanning electron microscopy study of frozen gel, it has been realized that gel actually consists of sheet-like structure of varying degrees of surface roughness and porosity, the pore sizes varying widely from 0.1 to 5 µm. Apparatus and Techniques One of the overriding features of the gel method is the simplicity of the growth apparatus used. In fact, the gel may be allowed to set in a simple test tube with one of the reactants already added to it. Once the gel is set, the other reactant may be poured over the gel without damaging its surface. Alternatively, a U tube may be used with the gel set at the bottom and the reactants added to the two arms of the U tube. These two basic growth apparatus are shown in Figure 9.9. The reaction that would take place may be represented as AX + BY → AY↓ + BX in which the desired product is insoluble and the by-product is usually highly soluble in water. This technique is termed “growth by chemical reaction.” The main drawback of the test tube method is the limited range of reagents and concentration which may be added to the gel without interfering with its setting characteristics. Also, since the quantity of the reagent that can be added is limited, the size of the crystals that can be obtained would also be limited. Although this disadvantage is overcome with the U tube method, the awkward shape of the U tube requires special support to keep it vertical. It is also more difficult to clean U tubes compared to a test tube.



Hydrothermal Growth The growth of single crystals from aqueous solution is usually performed by a careful control of supersaturation of the solution in the presence of a seed crystal. The process is generally carried out at atmospheric pressure. However, if the normal solution growth is unsuccessful because of low solubility, one can still try solution growth by suitably modifying the growth conditions, thereby increasing the solvent action, or using other solvents with greater solvent powers. One way of increasing the solvent action is to use a mineralizer, which forms additional species (complexes) that increase the overall solubility. The addition of mineralizers can be used only when the complexes formed with them are not stable solids under the prevailing growth conditions. One can also increase the solubility by conducting the growth at elevated temperatures. However, in the hydrothermal growth, an aqueous solution is held not only at high temperature but also at high pressure so that the nutrient that is otherwise insoluble at ambient conditions dissolves appreciably. Additionally, a mineralizer is also used to enhance the solubility. Some of the mineralizers used in hydrothermal growth are NaOH, KOH, NH4Cl, NaCl, KCl, KF, CsF, Na2CO3, and so on. Hydrothermal growth is normally carried out in a sealed vertical autoclave with a temperature gradient established between the top and bottom of the vessel. Usually, the nutrient is placed in the lower, hotter part of the autoclave, and the seeds are mounted in the cooler, upper part. The seeds are single crystal plates properly oriented and mounted on a suitable wire frame. A perforated metal disc called the baffle is often placed to separate the dissolution and growth regions so that the temperature gradient is localized. A schematic of the arrangement is shown. Transport of hot solution from the dissolution region to the growth region containing the seeds is by convection. Once the solution reaches the growth region, it becomes supersaturated with respect to the temperature of that region and the material is deposited on the seeds. The cooler depleted solution then returns to the hotter zone by convection and dissolves more nutrients, and the cycle repeats. Because hydrothermal growth is quite involved in terms of both equipment and procedure, not many laboratories practice this technique. However, in recent years, low-pressure and moderate-temperature hydrothermal synthesis has gained prominence particularly in the preparation of nanoparticles. Excellent reviews on these aspects are available in the literature. Here, we discuss only the conventional hydrothermal growth. In writing this section on hydrothermal growth, we have relied on the classic review written by Laudise and Nielsen. Autoclaves The success of the hydrothermal crystal growth experiments depends mainly on the quality of the autoclaves, which contain corrosive aqueous solution at high temperature and pressure. Therefore, the first consideration in the fabrication of an autoclave is the material of construction. For temperature in the range of 250°C–300°C, sealed glass or vitreous silica tubes have been used fairly successfully up to 6 atm. The use of glass in hydrothermal growth has not been explored fully because early works were mainly on the growth of materials that could not be dissolved readily in the pressure–temperature (P–T) range attainable in glass autoclaves. However, it has been realized that there is a wide range of materials that can be crystallized in the range of temperature and pressure attainable in glass. Further, glass is not corroded by neutral and acidic solutions (except hydro fluoric acid (HF)). Being transparent, it allows constant observation and measurement during growth. For pressures above 6 atm, it is necessary to use steel or its alloys. Many designs have been developed for the fabrication of autoclaves. Different designs have different pressure-holding capabilities. Proper selection of the autoclave is necessary to prevent failures. The autoclave failures may either be catastrophic or noncatastrophic. The catastrophic failure is usually associated with brittle fracture and the noncatastrophic to the failure of the pressure seal.



Semiconductor: Types and Band structure

What are Semiconductors?

Semiconductors are the materials which have a **conductivity and resistivity in between conductors** (generally metals) and non-conductors or **insulators** (such ceramics). Semiconductors can be compounds such as gallium arsenide or pure elements, such as germanium or silicon.

Properties of Semiconductors

Semiconductors can conduct electricity under preferable conditions or circumstances. This unique property makes it an excellent material to conduct electricity in a controlled manner as required.
Unlike conductors, the charge carriers in semiconductors arise only because of external energy (thermal agitation). It causes a certain number of valence electrons to cross the energy gap and jump into the conduction band, leaving an equal amount of unoccupied energy states, i.e. holes. Conduction due to electrons and holes are equally important.

- **Resistivity:** 10^{-5} to 10^{6} Ωm
- **Conductivity:** 10^{5} to 10^{-6} mho/m
- Temperature coefficient of resistance: Negative
- **Current Flow:** Due to electrons and holes
- Semiconductor acts like an insulator at Zero Kelvin. On increasing the temperature, it works as a conductor.
- Due to their exceptional electrical properties, semiconductors can be modified by doping to make semiconductor devices suitable for energy conversion, switches, and amplifiers.
- Lesser power losses.
- Semiconductors are smaller in size and possess less weight.
- Their resistivity is higher than conductors but lesser than insulators.
- The resistance of semiconductor materials decreases with the increase in temperature and vice-versa.

Examples of Semiconductors:

Gallium arsenide, germanium, and silicon are some of the most **commonly used semiconductors**. Silicon is used in electronic circuit fabrication and gallium arsenide is used in solar cells, laser diodes, etc.

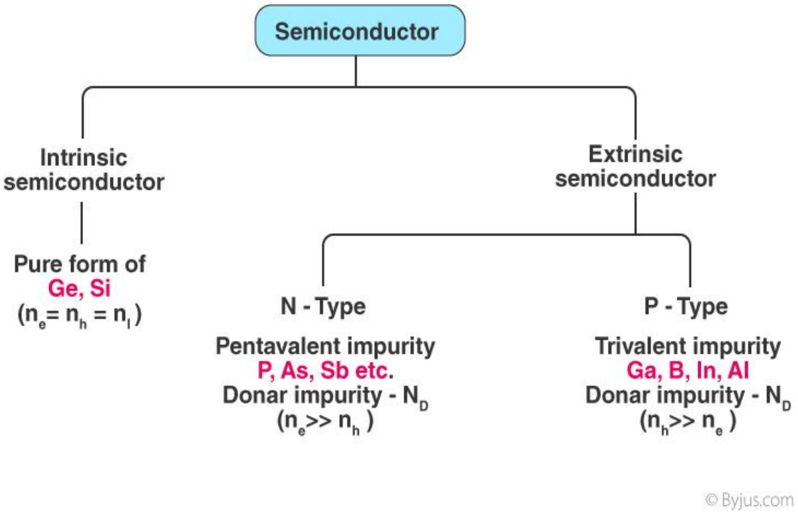
Types of Semiconductors

Semiconductors can be classified as:

- Intrinsic Semiconductor
- **Extrinsic Semiconductor**

Intrinsic Semiconductor

An **intrinsic type of semiconductor material** is made to be very pure chemically. It is made up of only a single type of element. Germanium (Ge) and Silicon (Si) are the most common type of intrinsic semiconductor elements. They have four valence electrons (tetravalent). They are bound to the atom by



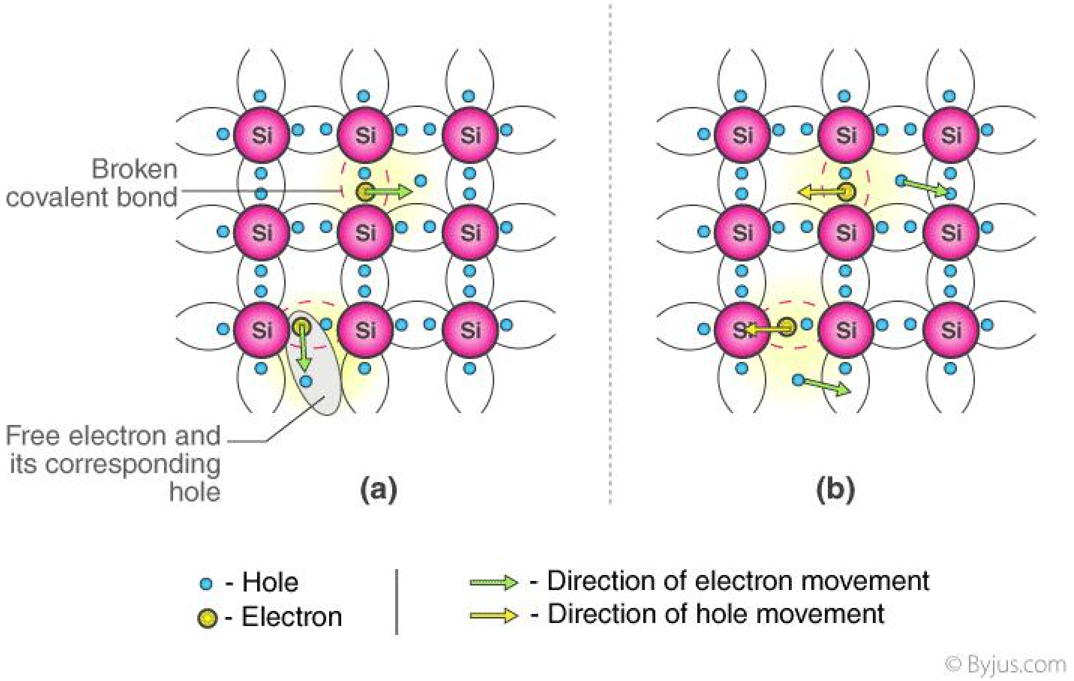
covalent bond at absolute zero temperature.

When the temperature rises, due to collisions, few electrons are unbounded and become free to move through the lattice, thus creating an absence in its original position (hole). These free electrons and holes contribute to the conduction of electricity in the semiconductor. The negative and positive charge carriers are equal in number.

The thermal energy is capable of ionizing a few atoms in the lattice, and hence their conductivity is less.

Lattice of Pure Silicon Semiconductor at Different Temperatures

- **At absolute zero kelvin temperature:** At this temperature, the covalent bonds are very strong and there are no free electrons and the semiconductor behaves as a perfect insulator.
- **Above absolute temperature:** With the increase in temperature few valence electrons jump into the conduction band and hence it behaves like a poor conductor.

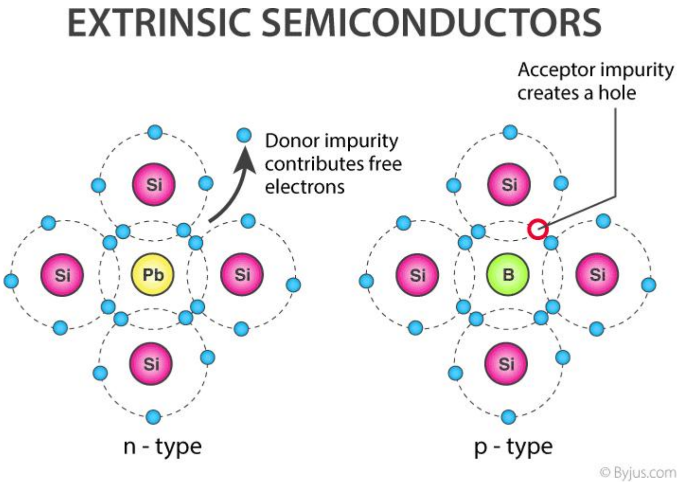


Conduction Mechanism in Case of Intrinsic Semiconductors (a) In absence of electric field **(b) In presence of electric Field**

Extrinsic Semiconductor

The conductivity of semiconductors can be greatly improved by introducing a small number of suitable replacement atoms called IMPURITIES. The process of adding impurity atoms to the pure semiconductor is called DOPING. Usually, only 1 atom in 10^7 is replaced by a dopant atom in the doped semiconductor. An extrinsic semiconductor can be further classified into:

- **N-type Semiconductor**
- **P-type Semiconductor**



Classification of Extrinsic Semiconductor

N-Type Semiconductor

- Mainly due to electrons
- Entirely neutral
- $I = I_h$ and $n_h >> n_e$
- Majority – Electrons and Minority – Holes

When a pure semiconductor (Silicon or Germanium) is doped by pentavalent impurity (P, As, Sb, Bi) then, four electrons out of five valence electrons bonds with the four electrons of Ge or Si.

The fifth electron of the dopant is set free. Thus the impurity atom donates a free electron for conduction in the lattice and is called "**Donar**".

Since the number of free electron increases by the addition of an impurity, the negative charge carriers increase. Hence it is called n-type semiconductor.

Crystal as a whole is neutral, but the donor atom becomes an immobile positive ion. As conduction is due to a large number of free electrons, the electrons in the n-type semiconductor are the MAJORITY CARRIERS and holes are the MINORITY CARRIERS.

P-Type Semiconductor

- Mainly due to holes
- Entirely neutral
- $I = I_h$ and $n_h >> n_e$
- Majority – Holes and Minority – Electrons

When a pure semiconductor is doped with a trivalent impurity (B, Al, In, Ga) then, the three valence electrons of the impurity bonds with three of the four valence electrons of the semiconductor.

This leaves an absence of electron (hole) in the impurity. These impurity atoms which are ready to accept bonded electrons are called "**Acceptors**".

With the increase in the number of impurities, holes (the positive charge carriers) are increased. Hence, it is called p-type semiconductor.

Crystal as a whole is neutral, but the acceptors become an immobile negative ion. As conduction is due to a large number of holes, the holes in the p-type semiconductor are MAJORITY CARRIERS and electrons are MINORITY CARRIERS.

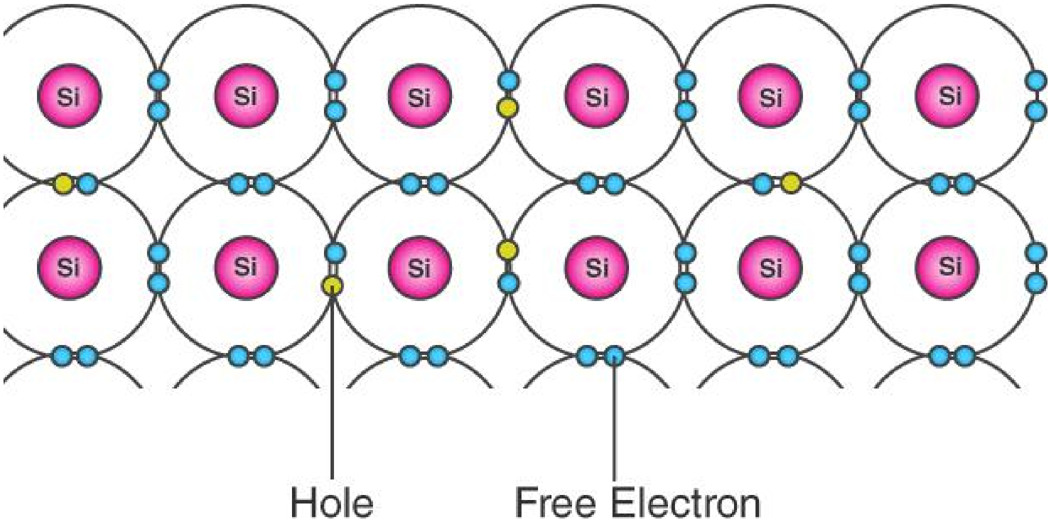
Difference between Intrinsic and Extrinsic Semiconductors

Intrinsic Semiconductor	**Extrinsic Semiconductor**
Pure semiconductor	Impure semiconductor
Density of electrons is equal to the density of holes	Density of electrons is not equal to the density of holes
Electrical conductivity is low	Electrical conductivity is high
Dependence on temperature only	Dependence on temperature as well as on the amount of impurity
No impurities	Trivalent impurity, pentavalent impurity

Holes and Electrons in Semiconductors

Holes and electrons are the types of charge carriers accountable for the flow of current in semiconductors. **Holes** (valence electrons) are the positively charged electric charge carrier whereas **electrons** are the negatively charged particles. Both electrons and holes are equal in magnitude but opposite in polarity.

The **bond model** of electrons in silicon of valency 4 is shown below. Here, when one of the free electrons (blue dots) leaves the lattice position, it creates a hole (grey dots). This hole thus created takes the opposite charge of the electron and can be imagined as positive charge carriers moving in the lattice.



Concept of Electrons and Holes in Semiconductors

Band Formation in crystals

We know that the electrons in an atom are present in different energy level. When we try to assemble a lattice of a solid with N atoms, then each level of an atom must split up into N levels in the solid. This splitting up of sharp and tightly packed energy levels forms **Energy Bands**. The gap between adjacent bands representing a range of energies that possess no electron is called a **Forbidden gap**.

Banding of Discrete states and the Simplified Model

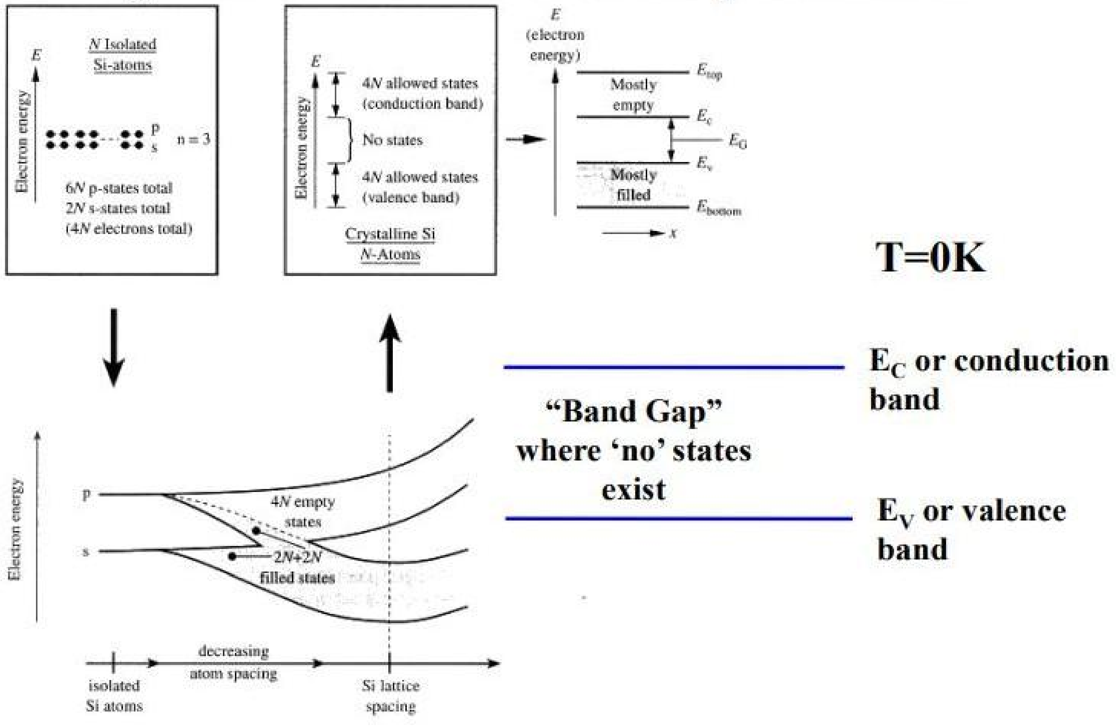
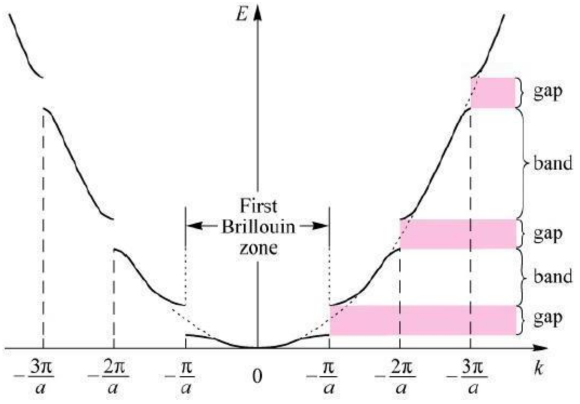


Figure 2.5 Conceptual development of the energy band model starting with N isolated Si atoms on the top left and concluding with a "dressed-up" version of the energy band model on the top right.

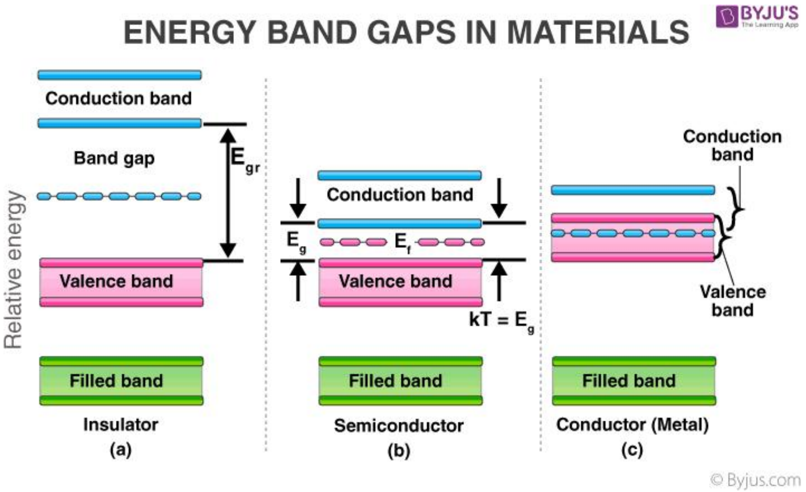
Since the electron energy levels are determined by the quantum numbers and, in a conglomeration of atoms of same type, the electron energy levels will separate into bands of energy levels. Such bands have energy widths typical of a given solid; however, the number of levels within the band is determined only by the number of atoms present. Recalling the Kronig- Penney model for a free electron in a solid, which resulted in an energy distribution as a function of *k*, the wave number, given by Fig. below

E-*k* plot from Kronig Penney Model

The allowed electronic energy states thus fall into bands, separated by regions known forbidden gaps. The number of available states in the band depends upon the number of atoms N present, and due to spin (± 1/2) of electrons, 2N electrons will be required to fill the first band, the two bands of importance for semiconductor terminology are the valance band and conduction band.



The lowest completely filled band is called the valence band the lowest partially filled band is called conduction band. In silicon and certain other diamond structures, for example, there is a quantum-mechanically forbidden zone between the valence and conduction bands. Metals have overlapping of band and therefore no forbidden zone exists at these higher energy levels. With reference to silicon, this forbidden gap occurs between 3S and 3P shells and has an energy span of 1.11 ev. In case of germanium, the gap is 0.72 ev and occurs between 4S and 4P shells. On the other hand, diamond is known to have a gap of 6 eV, located between 2S and 2P shells. With these ideas in mind, one can distinguish between insulators, semiconductors and metals (good conductors) pictorially shown below. In a metal, the uppermost energy band containing electrons is only partially filled, or a filled band overlaps an empty band (this is what allows some divalent metals to be good conductors, even though divalence is normally associated with good insulation). In semiconductors conductions happens as a result of thermally exciting electrons in the valence band of a crystal are able to jump the forbidden gap and enter the conduction band. This simultaneously creates an electron and hole called "pair". If an electric field were now applied, a net current would be observed. If a thermally excited electron gives up its energy and jumps back to the valence band, it will reunite with a hole in a process known as recombination.



Energy Band Diagram for Semiconductors, Conductors, and Insulators

Conduction Band (CB) and Valence Band (VB) in Semiconductors

Valence Band:

The energy band involving the energy levels of valence electrons is known as the valence band. It is the highest occupied energy band. When compared with insulators, the bandgap in semiconductors is smaller. It allows the electrons in the valence band to jump into the conduction band on receiving any external energy.

Conduction Band:

It is the lowest unoccupied band that includes the energy levels of positive (holes) or negative (free electrons) charge carriers. It has conducting electrons resulting in the flow of current. The conduction band possess high energy level and are generally empty. The conduction band in semiconductors accepts the electrons from the valence band.

What is Fermi Level in Semiconductors?

Fermi level (denoted by EF) is present between the valence and conduction bands. It is the highest occupied molecular orbital at absolute zero. The charge carriers in this state have their own quantum states and generally do not interact with each other. When the temperature rises above absolute zero, these charge carriers will begin to occupy states above Fermi level.

Typical Band Structure of Semiconductors

A semiconductor was defined as defined above as a solid in which the highest occupied energy band, the valence band, is completely full at T = 0K, but in which the gap above this band is also small, so that electrons may be excited thermally at room temperature from the valence band to the next-higher band, which is known as the conduction band. Generally speaking, the number of excited electrons is appreciable (at room temperature) whenever the energy gap E, is less than 3.5 eV. The substance may then be classified as a semiconductor. When the gap is larger, the number of electrons is negligible, and the substance is an insulator. When electrons are excited across the gap, the bottom of the conduction band (CB) is populated by electrons, and the top of the valence band (VB) by holes. As a result, both bands are now only partially full, and would carry a current if an electric field were applied. The conductivity of the semiconductor is small compared with the conductivities of metals of the small number of electrons and holes involved, but this conductivity is nonetheless sufficiently large for practical purposes. Only the CB and VB are of interest to us here, because only these two bands contribute to the current. Bands lower than the VB are completely full, and those higher than the CB completely empty, so that neither of these groups of bands contribute to the current; hence they may be ignored so far as semiconducting properties are concerned. In characterizing a semiconductor, therefore, we need describe only the CB and VB. The simplest band structure of a semiconductor is indicated in figure below. The energy of the CB has the form

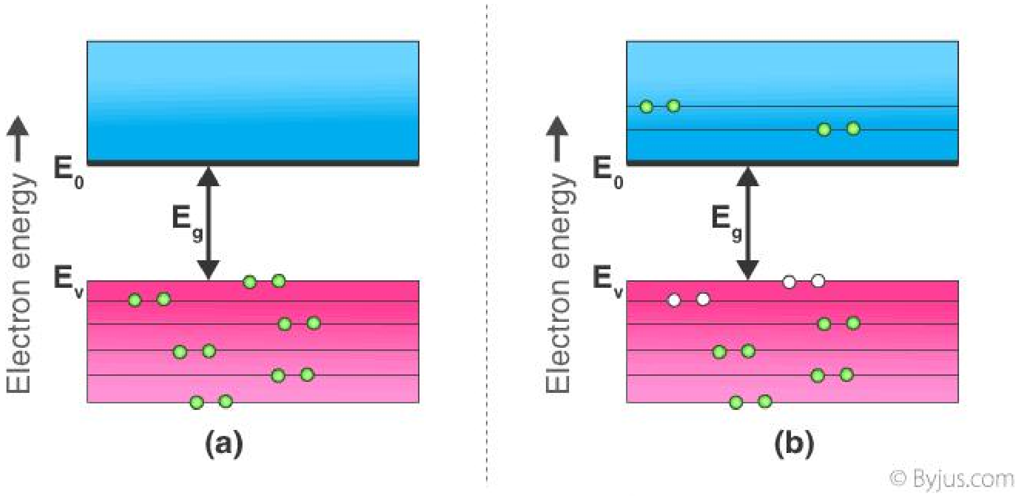
$$E_c(\mathbf{k}) = E_g + \frac{\hbar^2 k^2}{2m_e^*}$$

where k is the wave vector and m_e* the effective mass of the electron. The energy E_g represents the energy gap. The zero-energy level is chosen to lie at the top of the VB. We have used the standard band form to describe the CB, because we are primarily interested in the energy range close to the bottom of the band, since it is this range which contains most of the electrons. The energy of the VB may be written as

$$E_v(\mathbf{k}) = -\frac{\hbar^2 k^2}{2m_h^*}$$

where m_h* is the effective mass of the hole. The VB is again represented by the standard inverted form because we are interested only in the region close to the top of the band, where most of the holes lie. The primary band-structure parameters are thus the electron and hole masses m_e and m_h (the asterisks have been dropped for convenience), and the band gap Ec. Note that the masses differ considerably from-and are often much smaller than-the freeelectron mass, and that the energy gaps range from 0.18 eV in InSb to 3.7 eV in ZnS.

The energy gap for a semiconductor varies with temperature, but the variation is usually slight. That a variation with temperature should exist at all can be appreciated from the fact that the crystal, when it is heated, experiences a volume expansion, and hence a change in its lattice constant. This, in turn, affects the band structure, whichis a sensitive function of the lattice constant. It also follows that the gap may be varied by applying pressure, as this too induces a change in the lattice constant. Studies of semiconductors under high pressure have, in fact, proved very helpful in elucidating some of their properties. The conduction and valence bands in semiconductors are related to the atomic states. When two hydrogen atoms are brought together to form a molecule, the atomic l*s* state splits into two states: a low-energy bonding state and a high-energy antibonding state. In solid hydrogen, these states broaden into bonding and antibonding energy bands, respectively. In like fashion, the valence and conduction bands in semiconductors are, respectively, the bonding and antibonding bands of the corresponding atomic valence states. Thus the VB and CB in Si, for example, result from the bonding and antibonding states of the hybrid $3s^1 3p^3$. Similar remarks apply to the bands in Ge, C, and other semiconductors.



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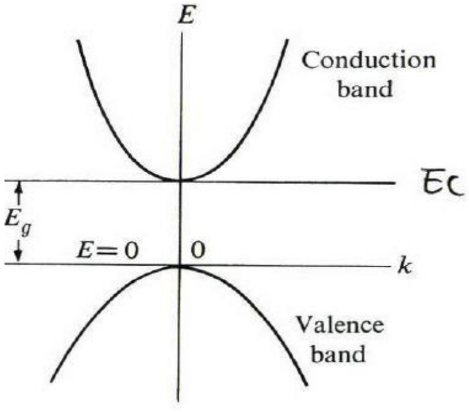


Band structure in a semiconductor.

(a) Intrinsic Semiconductor at T = 0 Kelvin, behaves like an insulator (b) At t>0, four thermally generated electron pairs

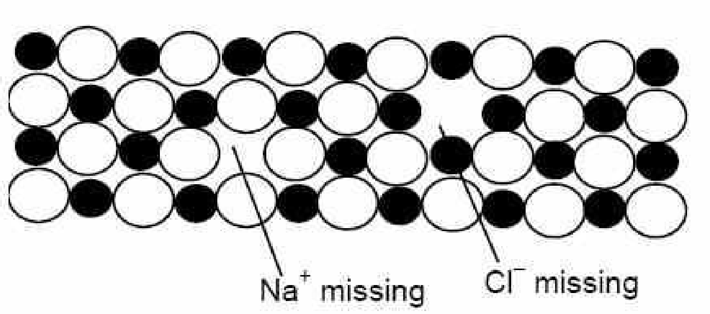
Imperfections in a Crystals:

The discovery of imperfections in an otherwise ideally perfect crystal is one of the most fascinating aspects of solid-state science. An ideally perfect crystal has the same unit cell and contains the same lattice points throughout the crystal. The term ***imperfection*** or ***defect*** is generally used to describe *any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.*

Stoichiometric Defects:

Stoichiometric compounds are those where the numbers of the different types of atoms or ions present are exactly in the ratios indicated by their chemical formulae. They obey the law of constant composition that “the same chemical compound always contains the same elements in the same composition by weight”. Previously these were called Daltonide compounds.

Two types of defects may be observed in stoichiometric compounds, called Schottky and Frenkel defects respectively. At absolute zero, crystals tend to have a perfectly ordered arrangement. As the temperature increases the amount of thermal vibration of ions in their lattice sites increases and if the vibration of a particular ion becomes large enough, it may jumpout of its lattice site. The higher the temperature, the greater the chance that lattice sites may be unoccupied. Since the number of defects depends on the temperature, these are sometimescalled thermodynamic effect.

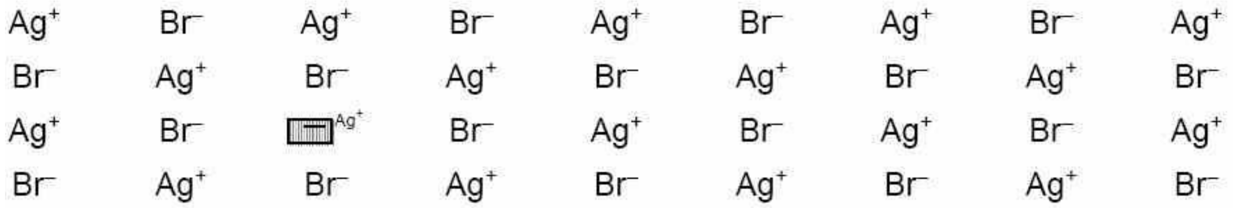


Schottky Defects: The defects rise if *some of the lattice points in a crystal are unoccupied*. The points which are unoccupied are called *lattice vacancies*. The existence of two vacancies, one due to a missing Na^+ ion and the other due to a missing Cl^- ion in a crystal of NaCl, is shown in figure 16. The crystal, as a whole remains neutral because the number of missing positive and negative ions is the same. Thus a Schottky defects consists of a pair of holes in the crystal lattice.

Schottky defects appear generally in highly ionic crystals in which *the positive and the negative ions do not differ much in size.* Sodium chloride and cesium chloride furnish good examples of ionic crystals in which Schottky defects occurs.

Frenkel Defects:

These defects arise when *an ion occupies an interstitial position between the lattice points.* This is shown in figure for the crystal of AgBr.



Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-
Ag^+	Br^-	▨ $^{Ag^+}$	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+
Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-	Ag^+	Br^-

As can be seen, one of the Ag+ ions occupies a position in the interstitial space rather than its own appropriate site in the lattice. A vacancy is thus created in the lattice as shown. It may be noted again that the crystal remains neutral since the number of positive ions is the same as the number of negative ions. The presence of Ag+ ions in the interstitial space of AgBr crystal isresponsible for the formation of a photographic image on exposure of AgBr crystals (i.e., photographic plate) to light. ZnS is another crystal in which Frenkel defects appear. Zn^{2+} ions are entrapped in the interstitial space leaving vacancies in the lattice.

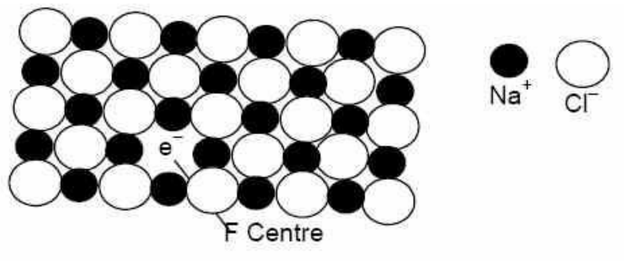
Frenkel defects appear in crystals in which the negative ions are much larger than the positive ions. Like Schottky defects, the Frenkel defects are also responsible for the conduction of electricity in crystals and also for the phenomenon of diffusion in solids.

Non-Stoichiometric Defects:

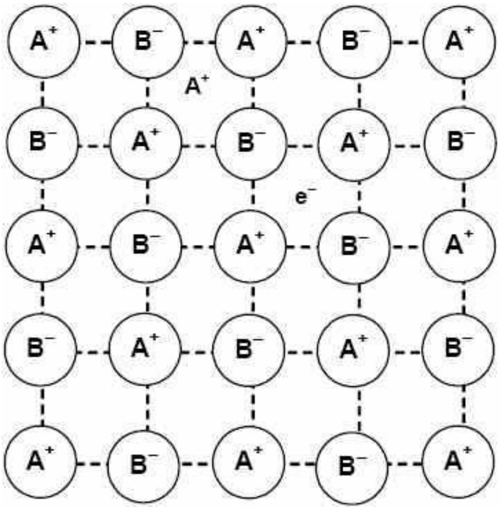
In non-stoichiometric or Berthollide compounds the ratio of the number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula. Such compounds do not obey the law of constant composition. There are many examples of these compounds particularly in the oxides and sulphides of the transition elements. Thus in FeO, FeS or CuS the ratio of Fe : O, Fe : S or Cu : S differs from that indicated by the ideal chemical formula. If the ratio of atoms is not exactly 1 : 1 in the above cases, there must be either an excess of metal ions or a deficiency of metal ions. Electrical neutrality is maintained either by having extra electrons in the structure or changing the charge on some of the metal ions. This makes the structure irregular in some way i.e., it contains defects.

Metal Excess Defect: This may occur in two different ways

F-Centres: A negative ion may be absent from its lattice site leaving a hole which is occupied by an electron, thereby maintaining the electrical balance. This type of defect is formed by crystals which would be expected to form Schottky defects. When compounds such as NaCl, KCl, are heated with excess of their constituent metal vapours, or treated with high energy radiation, they become deficient in the negative ions and their formulae may be represented by $AX_{1-\beta}$, where β is a small fraction. The crystal lattice has vacant anion sites which are occupied by electrons. Anion sites occupied by electrons in this way are called F centres (F is an abbreviation Farbe, the German word for colour).



Interstitial ions and electrons: Metal excess defects also occur when an extra positive ion occupies an interstitial position in the lattice and electrical neutrality is maintained by the inclusion of an interstitial electron. Their composition may be represented by general formula $A_{1+\beta}X$. This kind of metal excess defect is much more common than the first and is formed in crystals which would be expected to form Frenkel defects. Examples include ZnO, CdO, Fe_2O_3.



Crystals with either type of metal excess defect contain free electrons, and if these migrate they conduct an electric current. These free electrons may be excited to higher energy levels, giving absorption spectra and in consequence their compounds are often coloured e.g. non-stoichiometric NaCl is yellow, nonstoichiometric KCl is lilac.

Metal Deficiency Defects: In certain cases, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one. There is evidently, a deficiency of the metal ions although the crystal as a whole

Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}
O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}
Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	▨	O^{2-}	Fe^{2+}	O^{2-}
O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{+3}	O^{2-}	Fe^{+3}	O^{2-}	Fe^{2+}
Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}	Fe^{2+}	O^{2-}

is neutral. This type of defect is generally found amongst the compounds of transition metals which can exhibit variable valency. Crystals of FeO, FeS and NiO show this type of defects. The existence of metal deficiency defects in the crystal of FeO is illustrated.

It is evident from the above discussion that all types of point defects result in the creation of vacancies or 'holes' in the lattice of the crystals. The presence of holes lowers the density as well as the lattice energy or the stability of the crystals. The presence of too many holes may cause apartial collapse of the lattice.

DEFECTS IN CRYSTALS AND DISLOCATIONS

POINT AND LINE DEFECTS

All real crystals contain imperfections which may be point, line, surfaceor volume defects, and which disturb locally the regular arrangement of the atoms. Their presence can significantly modify the properties of crystalline solids. Furthermore, for each material there can be a specific defect which has a particular influence on the material properties. Inthis work are presented point and line defects.

Point defects

All the atoms in a perfect lattice are at specific atomic site, if the thermal vibration is ignored. In a pure metal two types of point defects are possible, namely a "vacant atomic site" or "vacancy", and a "self- interstitial atom".

The vacancy has been formed by the removal of a single atom from its lattice site in the perfect crystal. The interstitial has been formed by the introduction of an extra atom into an interstice between perfect lattice sites. Vacancies and interstitial can be produced in materials by plastic deformation and high-energy particle irradiation. Furthermore, intrinsic point defects are introduced into crystals simply by virtue of temperature, for at all temperatures above 0 K there is a thermodynamically stable condition. The equilibrium concentration of defects, given by the ratio of the number of defects to the number of atomic sites, corresponding to the condition of minimum free energy.

For the vacancy, the formation energy Ef, is that required to remove oneatom from its lattice site to a place on the surface of the crystal. The self-interstitial is created by removing one atom from the surface and inserting it into an interstitial site, and the formation energy is tipically two to four times the formation energy for vacancies. Thus, the concentration given by equation (2.1) is many orders of magnitude smaller for interstitials, and so in metals in thermal equilibrium the concentration of interstitials may be neglected in comparison with that of vacancies.

As atoms vibrate randomly due to thermal fluctuations, these pointdefects can occasionally jump from one lattice site or interstice toanother. For large numbers of atoms under equilibrium conditions, theserandom jumps produce no net effect, as there are as many jumps in one direction as in any other. However, under any driving force, such as an applied stress or temperature gradient, more of these jumps will occur in a preferred direction. For example, interstitials may move preferentially from regions of high stress to region of law stress.

Impurity atoms in a crystal can be considered as extrinsic point defects and they play a very important role in the physical and mechanical properties of all materials. Impurity atoms can take up two different types of site, as illustrated.

- Substitutional impurity atom, in which an atom of the parent lattice lying in a lattice site is replaced by the impurity atom.
- Interstitial impurity atom, in which the impurity atom is at a non-lattice site similar to the self-interstitial atoms referred to above.

All the point defects mentioned produce a local distortion in the otherwise perfect lattice. The amount of distortion and hence the amount of additional energy in the lattice due to the defects depends on the amount of "*space*" between the atoms in the lattice and the "*size*" of the atoms introduced.

The interstice sites between atoms generally have volumes of less than one atomic volume, and the interstitial atoms therefore tend to produce large distortions among the surrounding atoms. That's why the formation energy for interstitial atoms takes large volumes, and can result in crystal volume increases as large as several atomic volumes perinterstitial atom.

Additional effects are important when the removal of addition of atoms changes the local electric charge in the lattice.

Experimental evidence of existence of dislocations.

From the perspective of mechanical properties, the dislocation is perhaps the most important crystalline defect. These are essentially lines through a crystal along which there is a systematic error in the way the atoms are arranged. Although there are many techniques now available for the direct observation of dislocations, the existence of these line defects was deduced by inference in the early stages of dislocation study. Strong evidence arose from attempts to reconcile theoretical and experimental values of the applied shear stress required to plastically deform a single crystal. This deformation occurs by atomic planes sliding over each other. In a perfect crystal, in the absence of dislocations, the sliding of one plane past and adjacent plane would have to be a rigid co-operative movement of all the atoms from one position of perfect registry to another. The shear stress required for this process was first calculated by Frenkel in 1926. The situation illustrated in the following scheme. :

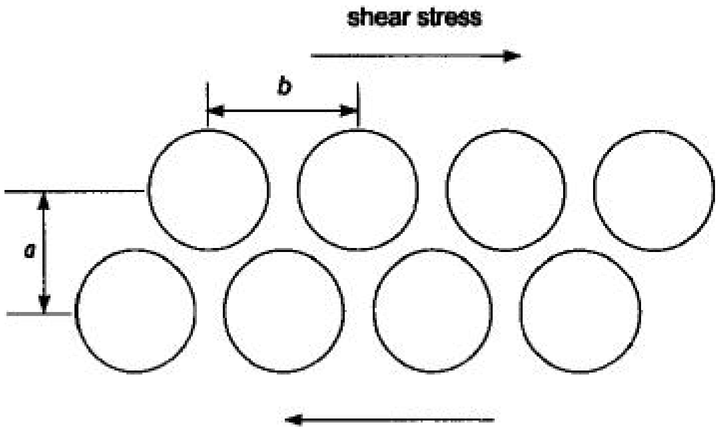


Figure - *Representation of atom position used to estimate the theoretical shear stress for slip*

It is assumed that there is a periodic shearing force required to move thetop row of atoms across the bottom row which is given by the sinusoidal relation:

$$\tau = \frac{Gb}{2\pi a}\sin\frac{2\pi x}{b}$$

Where τ is the applied shear stress, *G* is the shear modulus, *b* the spacing between atoms in the direction of the shear stress, *a* the spacingof the rows of atoms and x is the shear translation of the two rows awayfrom the low-energy equilibrium position.

The maximum value of τ is then the theoretical critical shear stress and is:

$$\tau_{th} = \frac{b}{a}\frac{G}{2\pi}$$

Since b ≈ a, the theoretical shear strength is a sizeable fraction of the shear modulus. Using more realistic expressions for the force as a function of shear displacement, values of $\tau_{th} \approx G/30$ have been obtained. Although these are approximate calculations, they show that τ_{th} is many orders of magnitude greater than observed values (10^{-4} to 10^{-8} G) of the resolved shear stress for slip measured in real, well-annealed crystals. This striking difference between prediction and experiment was accounted for by the presence of dislocations independently by Orowan,Polanyi and Taylor in 1934.

Dislocations are now recognized as the primary carriers of plastic deformation in crystalline solids, giving rise to the ductility that makes metals workable and, through their manipulation and entanglement, to the work hardening that makes those same metals strong.

GEOMETRY OF DISLOCATION.

The basic geometries of dislocations are the edge and screw dislocation.

Edge dislocation

An edge dislocation is a defect where an extra half-plane of atoms is introduced mid way through the crystal, distorting nearby planes of atoms. When enough force is applied from one side of the crystal structure, this extra plane passes through planes of atoms breaking and joining bonds with them until it reaches the grain boundary.

A schematic example of an edge dislocation is shown.

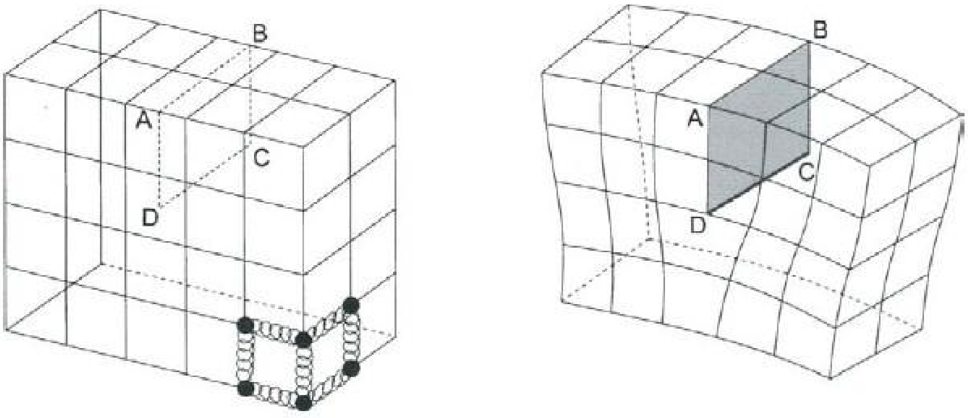


Figure - *Model of a simple cubic lattice and representation of an edge dislocation*

The arrangement of atoms around an edge dislocation can be simulated by the following sequence of operations. Suppose that all the bonds across the surface *ABCD* are broken and the faces of the crystal are separated so that an extra half-plane of atoms can be inserted in the slot, as illustrated in figure. The faces of the slot will be displaced by one atom spacing, but the only large disturbance of the atoms from their normal position relative to their neighbors is close to the line *DC*. The deflection and distortion of the interatomic bonds decrease with increasing distance from the line. This line *DC* is called a *positive edge dislocation*. A *negative edge dislocation* would be obtained by inserting the extra plane of atoms below plane *ABCD*.

Screw dislocation

A screw dislocation is much more harder to visulaize.

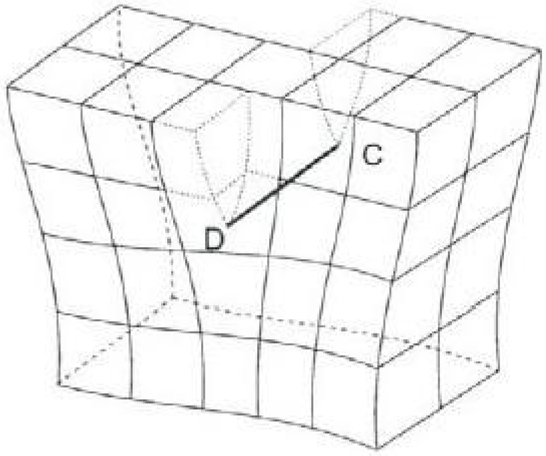


Figure *Left-handed screw dislocation*

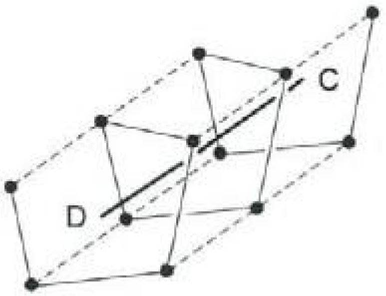


Figure *Spiral of atoms adjacent to the line DC*

The arrangement of atoms round a screw dislocation can be simulated by displacing the crystal on one side of ABCD relative to the other side in the direction AB as in figure 2.6. The set of parallel planes initially perpendicular to *DC* have been transformed into a single surface, and the spiral nature is clearly demonstrated by the atom position shown in Figure. In this figure DC is a screw dislocation. Looking down the dislocation line, if the helix advances one plane when a clockwise circuit is made around it, it is referred to as a right-handed screw dislocation, and if the reverse is true it is left-handed.

Actually, edge and screw dislocations are just extreme forms of the possible dislocation structures that can occur. Most dislocations are a hybrid of the edge and screw forms.

BURGUERS VECTOR AND BURGERS CIRCUIT

The most useful definition of a dislocation is given in terms of the Burgers circuit. A burgers circuit is any atom-to-atom path taken in a crystal containing dislocations which forms a closed loop. Such a path, *MNOPQ*, is illustrated in the following figure:

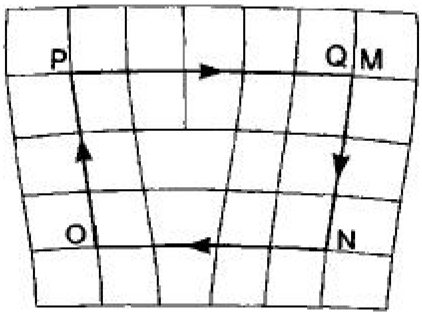


Figure - *Burger circuit round an edge dislocation*

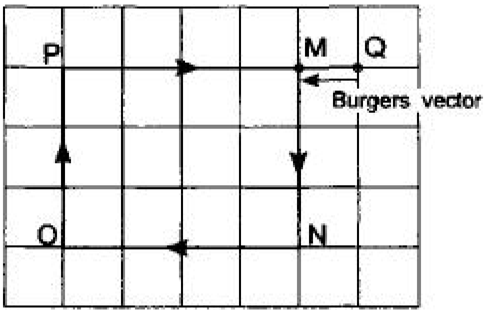


Figure - *The same circuit of figure 2.7 in a perfect crystal*

If the same atom-to-atom sequence is made in a dislocation-free crystal,as in figure, and the circuit does not close, then the first circuit, the one showed in figure, must enclose one or more dislocations. The vector required to complete the circuit is called the Burgers vector.

- The Burgers vector of an edge dislocation is normal to the line of the dislocation.
- The Burgers vector of a screw dislocation is parallel to the line of the dislocation.

In the most general case the dislocation line lies at an arbitrary angle to its Burgers vector and the dislocation line has a mixed edge and screw character. However, the Burgers vector of a single dislocation has fixed length and direction, and is independent of the position and orientation of the dislocation line.

Burgers circuit taken around other defects, such as vacancies and interstitials, do not lead to closure failures. Two roles are used defining Burgers vectors and Burger circuits.

First, when looking along the dislocation line, which defines the positive line sense or direction of the dislocation, the circuit is taken in a clockwise fashion. Second, the Burgers vector is taken to run from the finish to the star point of the reference circuit in the perfect crystal. This defines the right-hand/finish-start (RH/FS) convention. Reversing the line sense reverses the direction of the Burgers vector for a given dislocation.

Furthermore, dislocations with the same line sense but oppositeBurgers vectors (or alternatively with opposite line senses and the same Burgers vector) are physical opposites. Dislocations which are physical opposites of each other annihilate and restore perfect crystalif brought together. The Burgers vector b is conveniently described using Miller's indices.

Dislocations lines can end at the surface of a crystal and at grain boundaries, but never inside a crystal. Thus, dislocations must either form closed loops or branch into other dislocations. When three or more dislocations meet at a point, or node, it is a necessary conditionthat the Burgers vector is conserved.

A schematic example of this condition is shown

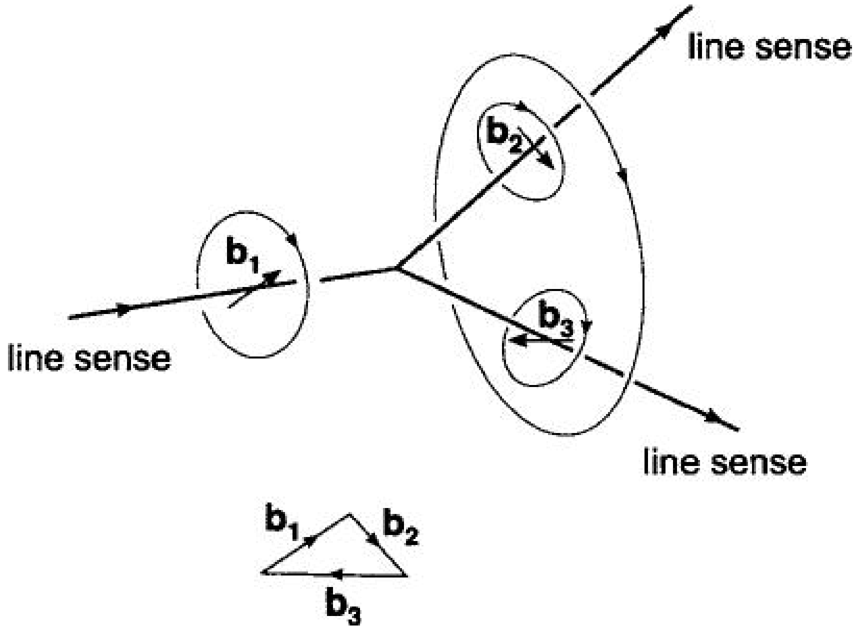


Figure *Three dislocations forming a node and Burgers' conservation condition*

The mathematical expression of this condition can be expressed :

$$b_1 = b_2 + b_3$$

The dislocation density ρ is defined as the total length of dislocation line per unit volume of crystal. An alternative definition, which is sometimes more convenient to use, is the number of dislocations intersecting a unit area, again measured in units of m^{-2}. If all the dislocations are parallel, the two density values are the same, but for a completely random arrangement the volume density is twice the surface density.

The average distance between dislocations in a network of density ρ is of the order of 1/√ρ.

MOVEMENT OF DISLOCATIONS

There are two basic types of dislocation movement. Glide or conservative motion occurs when the dislocation moves in the surface which contains both its line and Burgers vector. Climb or non- conservative motion occurs when the dislocation moves out of the glidesurface, and thus normal to the Burgers vector.

Concept of slip

Glide of many dislocations results in slip, which is the most common manifestation of plastic deformation in crystalline solids. It can be envisaged as sliding or successive displacement of one plane of atoms over another on so-called slip planes. This is uniquely defined as the plane which contains both the line and the Burgers vector of the dislocation.

Further deformation occurs either by more movement on existing slip planes or by the formation of new slip planes.

The slip planes are normally the planes with the highest density of atoms, and the direction of slip is the shortest lattice translation vectors.Often, this direction is one in which the atoms are most closely spaced.

A slip plane and a slip direction in the plane constitute a slip system.

Slip results in the formation of steps on the surface of the crystal. The slip direction is necessarily always parallel to the Burgers vector of the dislocation responsible for slip. The movement of one dislocation across the slip plane to the surface of the crystal produces a surface slip step equal to the Burgers vector.

A characteristic shear stress is required for slip. It can be schematically shown:

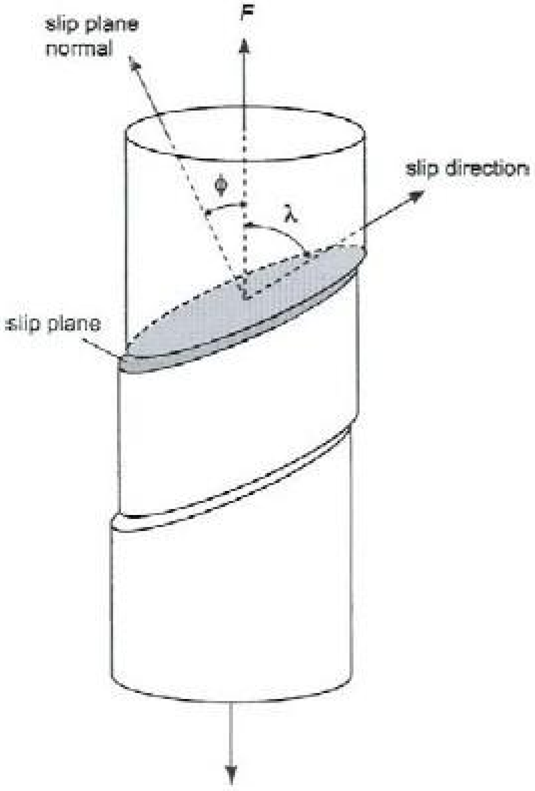


Figure *Illustration of the geometry of slip in crystalline materials*

The illustrated crystal is being deformed in tension by an applied force$F$ along the axis of the cylindrical crystal. The cross sectional Area is A and so the tensile stress parallel to F is :

$$\sigma = \frac{F}{A}$$

The force has a component $F\cos\lambda$ in the slip direction, where λ is theangle between F and the slip direction. This force acts over the slip surface which has an area $A/\cos\phi$, where ϕ is the angle between F and the normal to the slip plane. Thus the *shear stress* τ, resolved on the slipplane in the slip direction, is :

$$\tau = \frac{F}{A}\cos\phi\cos\lambda$$

If F_c is the tensile force required to start slip, the corresponding value ofthe shear stress τ_c is called the critical resolved shear stress for slip. It has been found in some crystals which deform on a single slip system that τ_c is independent of the orientation of the crystal.

DISLOCATIONS AND SLIP.

With the concept of slip just introduced, dislocation can be defined as the boundary between the slipped and unslipped parts of the crystal. As showed in chapter. the theoretical shear stress for slip was many times greater than the experimentally observed stress. The low value can be accounted for by the movement of dislocations.

Only a relatively small applied stress is required to move the dislocationalong the slip plane, as it is demonstrated in the following scheme foran edge dislocation:

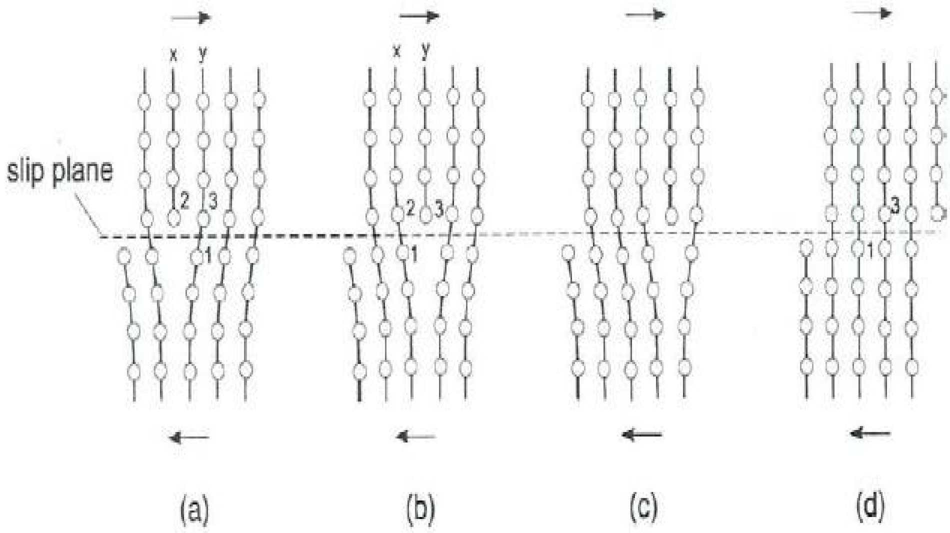


Figure *Movement of an edge dislocation*

where the arrow indicate the applied shear stress.

Well away from the dislocation, the atom spacing are close to the perfect crystal values, and a shear stress as high as the theoretical value would be required to slide them all past each other. Near the dislocation line itself, some atom spacing are far away from the ideal values, and small relative changes in position of only a few of atoms are required for the dislocation to move. Thus the applied stress required to overcome the lattice resistance to the movement of the dislocation is much more smaller than the theoretical shear stress of a perfect lattice, due to the successive glide of the extra half-plane.

It is also possible to see that two neighbouring atoms on sites adjacent across the slip plane, like the atoms "1" and "3" in figure, are displaced relative to each other by the Burgers vector when the dislocation glides past. The global effect of many thousands of such dislocations is a surface step on the material:

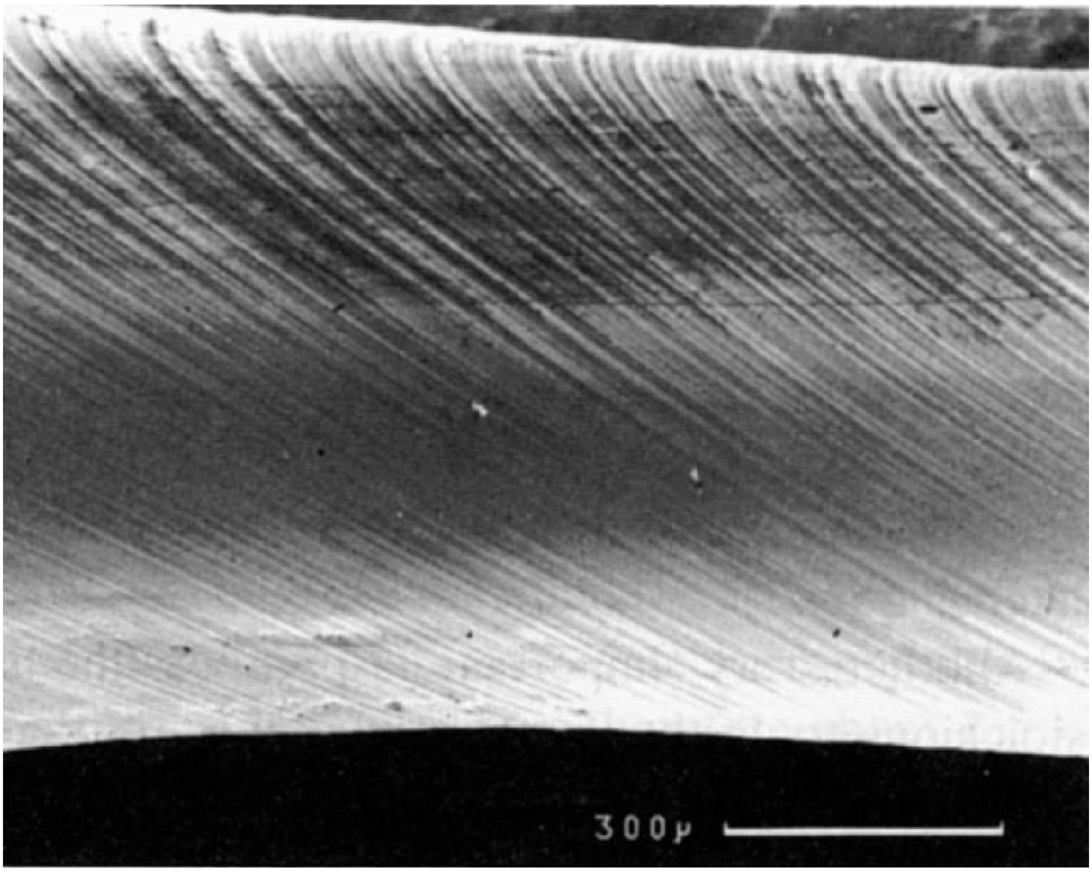


Figure *Single crystal of cadmium deforming by dislocation slip, forming steps on the surface*

It is important to remark two particular rule for dislocation glide :

- dislocations of opposite sign glide in opposite directions under the same stress

- for dislocation glide a shear stress must act on the slip plane in the direction of the Burgers vector, irrespective of the direction of the dislocation line

Those properties are schematically shown for an edge and screw dislocation:

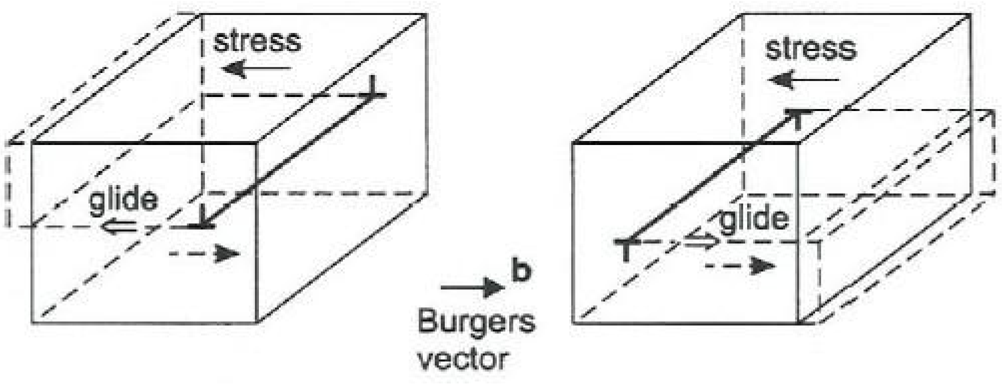


Figure *Plastic deformation by glide of edge dislocation under the applied shear stress*

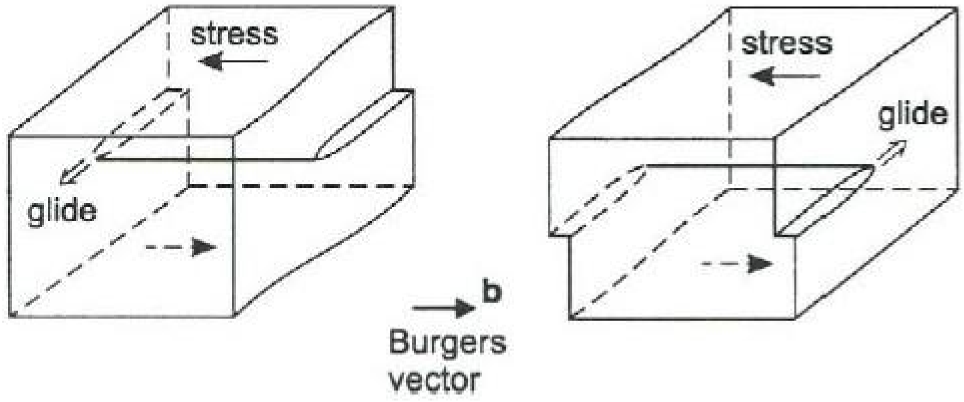


Figure *Plastic deformation by glide of screw dislocation underthe applied shear stress*

CLIMB

At low temperatures where diffusion is difficult, and in the absence of a non-equilibrium concentration of point defects, the movement of dislocations is restricted almost entirely to glide. However, at higher temperatures and edge dislocation can move out of its slip plane by a process called climb:

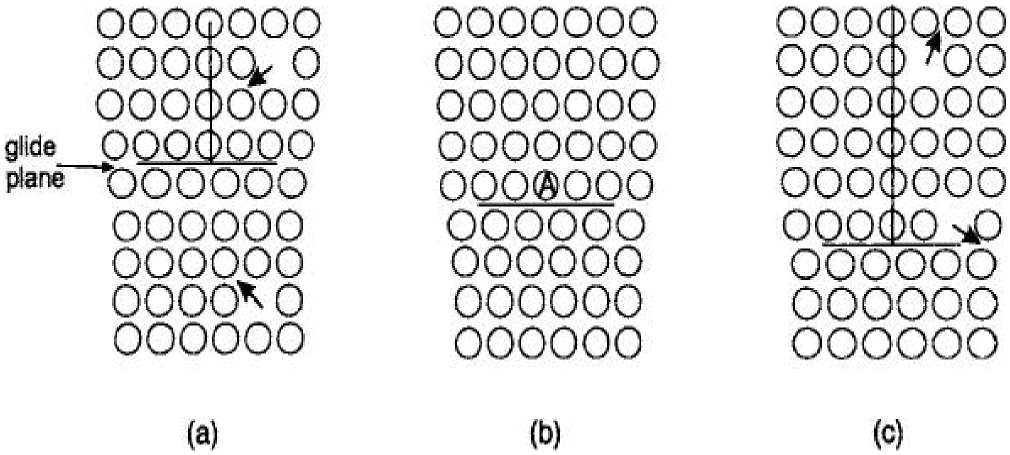


Figure *Positive and negative climb of an edge dislocation*

The row of atoms *A* normal to the plane of the diagram is removed, the dislocation line moves up one atom spacing out of its original slip plane: this is called positive climb. Similarly, if a row of atoms is introduced below the extra half-plane the dislocation line moves down one atom spacing, negative climb. For this kind of movements, volumes are not conserved. The mass transport involved occurs by diffusion and therefore climb requires thermal activation.

It has been implied above that a complete row of atoms is removed simultaneously, whereas in practice individual vacancies or small clusters of vacancies diffuse to the dislocation. The effect of this is that the climb of a short section of a dislocation line results in the formation of two steps called jogs :

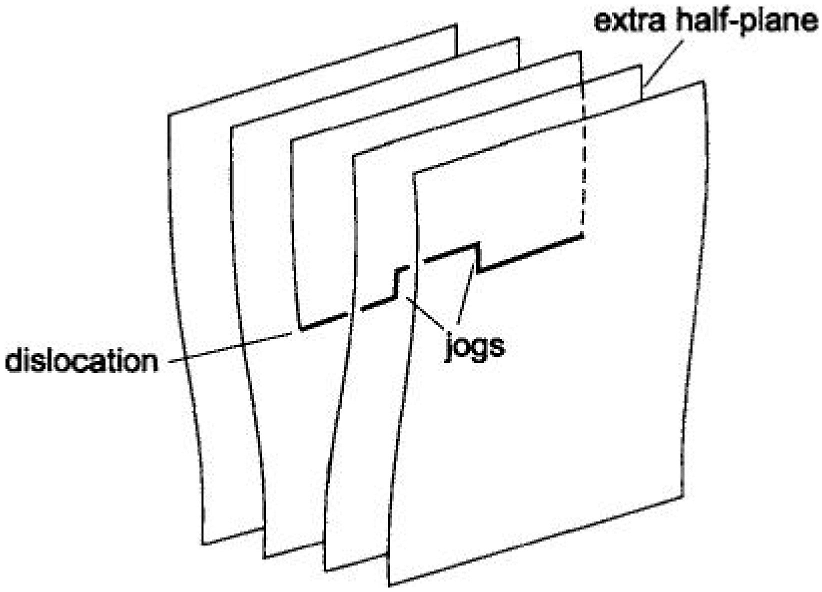


Figure *Single jogs on an edge dislocation*

Both positive and negative climb proceeds by the nucleation and motionof jogs. Conversely, jogs are sources and sinks for vacancies.

Jogs are steps on the dislocation which move it from one atomic slipplane to another. Steps which displace it on the same slip plane are called kinks. The two are distinguished below for and edge and screwdislocation:

Jogs and kinks are short elements of dislocation with the same Burgers vector as the line on which they lie, and the usual rules apply for their conservative and non-conservative movements.

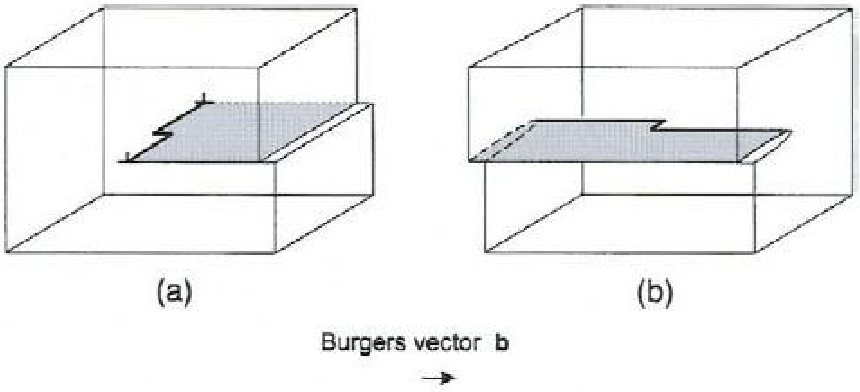


Figure *Kinks in edge (a) and screw(b) dislocation*

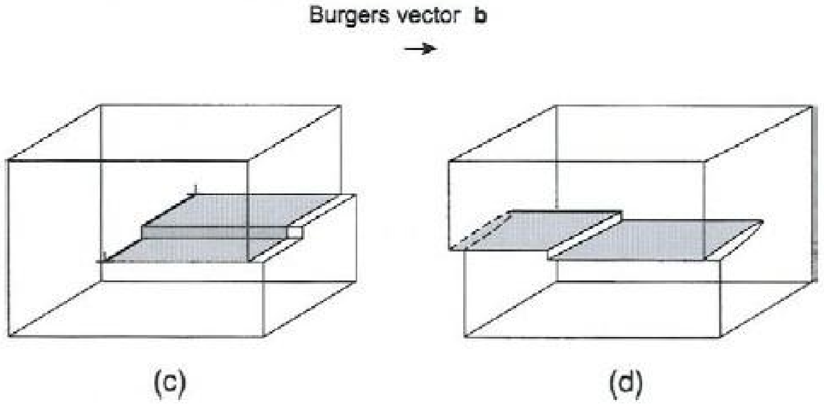


Figure *Jogs in edge (c) and screw (d) dislocation*