



**RAJARAM COLLEGE, KOLHAPUR**

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**WELCOME TO**  
**DEPARTMENT OF CHEMISTRY**



# 1. COURSE

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- B.Sc.Part – III
  
  - Title of paper
  
  - 1 Paper - V : Physical Chemistry
  - 2 Paper - VI: Inorganic Chemistry
  - 3 Paper- VII: Organic Chemistry
  - 4 Paper – VIII: Analytical &Industrial Chemistry
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## 2. NATURE OF PAPER:

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### **Paper V to VII (Marks 40)**

Question No.		Marks	Options
1	Multiple choose questions	08	--
2	Long answer type questions (2 out of 3)	20	10
3	Short answer type questions (3 out of 5)	12	08
	<b>Total</b>	<b>40</b>	<b>18</b>

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### 3. General Structure (Practical Exam)

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#### **Practical examination :**

Practical examination will be of 200 marks. The distribution is as follows :

Physical Section 2 Practicals + Journal + Oral : 60

Inorganic Section 3 Practicals + Journal + Oral : 65

Organic Section 3 Practicals + Journal + Oral : 60

Project : 15

**Total : 200**

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## 5. INORGANIC CHEMISTRY: Syllabus

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- Unit 1. Hard and Soft Acids and Bases (HSAB).
  - Unit 2. Metal ligand bonding in Transition metal complexes
  - Unit 3. Inorganic Polymers
  - Unit 4. Metals, Semiconductors and Superconductors
  - Unit 5. Organometallic Chemistry
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## 6. Reference Books:

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1. Concise Inorganic Chemistry (ELBS, 5th Edition) – J. D. Lee.
2. Inorganic Chemistry (ELBS, 3rd Edition) D. F. Shriver, P. W. Atkins, C.
3. Basic Inorganic Chemistry : Cotton and Wilkinson.
4. Advanced Inorganic Chemistry (4th Edn.) Cotton and Wilkinson.
5. Concepts and Models of Inorganic Chemistry : Douglas and Mc. Daniel.
6. Fundamental concepts of Inorganic Chemistry by E. S. Gilreath.
7. Structural principles in inorganic compounds. W. E. Addison.
8. T. B. of Inorganic analysis – A. I. Vogel.
9. Theoretical principles of Inorganic Chemistry – G. S. Manku.
10. Theoretical Inorganic Chemistry by Day and Selbine.
11. Co-ordination compounds SFA Kettle.
12. Essentials of Nuclear Chemistry by H. J. Arnikar.
13. Organometallic Chemistry by R. C. Mahrotra A. Sing,
14. Progress in inorganic polymer by Laport and Leigh.
15. Organometallic Chemistry by P. L. Pauson.

## 7. Laboratory Course

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### Laboratory Course

- (i) Use of Digital/Analytical/Chainometric/Single pan balance is allowed.
  - (ii) Use of Scientific calculator (without memory) is allowed.
  - (iii) Use of Chart/Text book/Hand book of practical is allowed.
  - (iv) There will be a project having weightage of **15** marks.
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## 7. Laboratory Course contd...

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### **Project (15 Marks)**

On following areas but focused on applications of Chemistry.

- a) Society oriented
- b) Daily use
- c) Industrial based
- d) Analytical based
- e) Technology based

**The project will be assessed by 3 examiners at the time of practical examinations.**

**One copy of the project to be submitted during examination.**

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## 7. Laboratory Course contd...

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### **Nature of Practical Examination**

- 1) **200** marks.
  - 2) The duration : **three days – 6 & 1/2h / day.**
  - 3) Questions related to the practical exercise will be asked in viva.
  - 4) Use of scientific calculator is allowed.
  - 5) S.I. units should be used w
  - 6) Use of Chart / Hand book / Text book of practical is allowed.
  - 7) A journal certified by the Head of the Department is **REQUIRED**
  - 8) **NO LOST CERTIFICATES WILL BE GIVEN.**
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<input type="checkbox"/>	The distribution of marks for practical examination:	
<input type="checkbox"/>	<b>A) Physical Chemistry (60 marks)</b>	
<input type="checkbox"/>	i) Non-instrumental experiment	25 marks
<input type="checkbox"/>	ii) Instrumental experiment	25 marks
<input type="checkbox"/>	iii) Viva	05 marks
<input type="checkbox"/>	iv) Journal	05 marks
<input type="checkbox"/>	<b>B) Inorganic Chemistry (65 marks)</b>	
<input type="checkbox"/>	i) Gravimetric analysis	25 marks
<input type="checkbox"/>	ii) Preparation	15 marks
<input type="checkbox"/>	iii) Volumetric estimation	15 marks
<input type="checkbox"/>	iv) Viva	05 marks
<input type="checkbox"/>	v) Journal	05 marks
<input type="checkbox"/>	<b>C) Organic Chemistry (60 marks)</b>	
<input type="checkbox"/>	i) Mixture separation and identification of compounds	25 marks
<input type="checkbox"/>	ii) Estimation/Preparation	20 marks
<input type="checkbox"/>	iii) Derivative	05 marks
<input type="checkbox"/>	iv) Viva	05 marks
<input type="checkbox"/>	v) Journal	05 marks
<input type="checkbox"/>	<b>D) Project</b>	<b>15 marks</b>
<input type="checkbox"/>	<b>Total:-</b>	<b>200 marks</b>

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# UNIT 4

## Metals, Semiconductors and Superconductors

STATES OF  
**MATTER**

	<u>SOLID</u>	<u>LIQUID</u>	<u>GAS</u>	(PLASMA)	(BOSON)
<b>Examples:</b>	(Stone)	(Water)	(Air)	Ionic solid at high temp.	Nano- materials particle group
<b>Bonding present:</b>	Covalent /Metallic /ionic	Covalent/ Ionic with vanderwaal bondings	No	Ionic	All

# Solid State Materials

## □ Characteristics:

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- ❖ Rigid
  - ❖ Incompressible
  - ❖ Inflowable
  - ❖ Have definite shape, Volume and size
  - ❖ Particles are bonded by relatively strong bonding
  - ❖ May be Crystalline or Amorphous
  - ❖ Crystalline- **Particles (atoms/Ions/Molecules) are arranged in definite manner**, have sharp melting point and has a break in cooling curve, eg. Plastic, salt, sugar
  - ❖ Amorphous (non crystalline)- **Particles are arranged randomly**. Do not have sharp melting point, has no break in cooling curve e.g. rubber, glass etc.
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# Classification of Solids

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Solids are classified on the basis of attraction that holds particles in solid materials

*Types-(Four)*

- 1. Ionic Solids - Has ionic bonding in it-e.g. salts
  - 2. covalent Solids -Has covalent bonding in it- e.g. Diamond
  - 3. Molecular Solids -Has molecular bonding in it- (vanderwaal) among the particles
  - 4. Metallic solids - (Metals) has metallic bonding in it-among particles e.g. Metals
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# METALS

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- What would be bonding in metals?
  - Ionic?
  - Covalent?
  - Coordinate?
  - If yes, why?
  - If not why?
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# Metals

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- **About 2/3<sup>rd</sup> elements are metals.**
  - **It is a solid having following properties:**
    - **Luster**
    - **Crystalline Structure**
    - **Emissivity**
    - **Electrical & thermal conductivity**
    - **Higher M.P.,B.P.,Density**
    - **Malleability**
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# Theory of Metallic Bonding

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- Metals do not have sufficient electrons to form ionic or covalent bonding . That is ionic / covalent bonding is ABSENT
  - Metallic Bonding:
  - DEFINATION:
  - The attraction that holds metal atoms together strongly is called **metallic bond.**
  - This type of bonding is explained on the basis 2 different theories:
  - A) Free Electron (Electron sea/gas/pool) or Drude Lorentz Theory:
  - B) Band or Molecular Orbital Theory:
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# A) Free Electron or Drude Lorentz Theory: (Electron sea/gas/pool)

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## Assumptions:

1. There is no mutual repulsion among like charges

2. The field created by +ve ions is uniform

As per this theory the metallic bond is said to be formed after completion of the following steps;

a) Ionization of Metals into metal ions and free electrons.

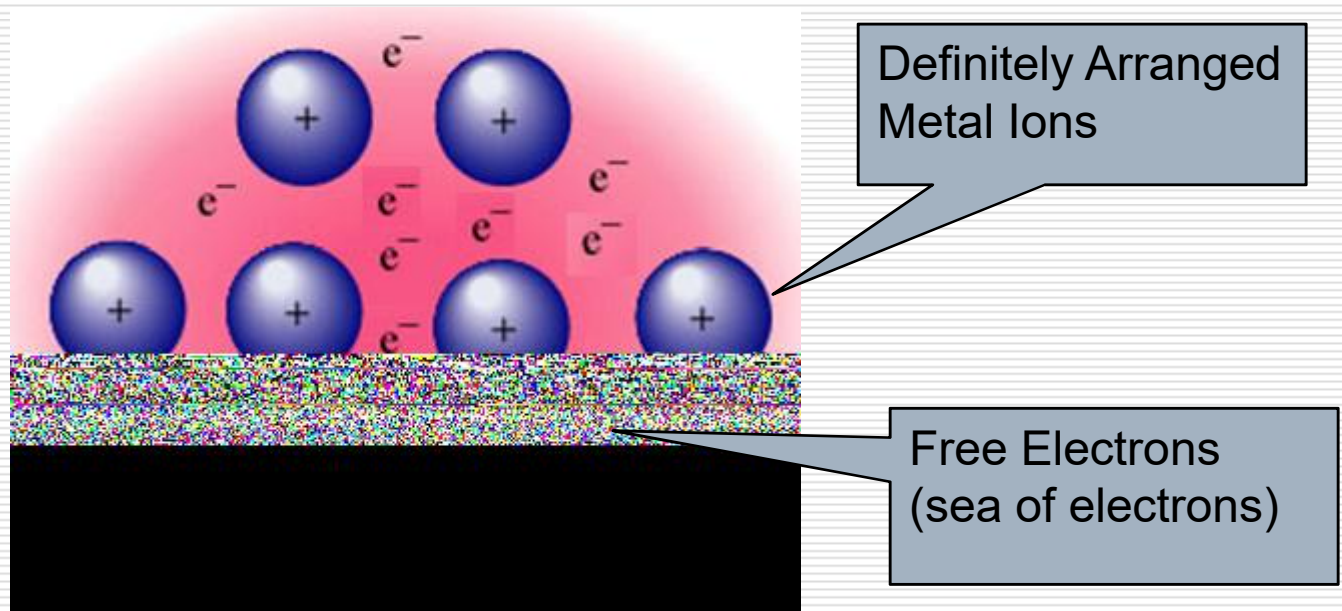
b) Arrangements of all ions in to definite crystal structure.

c) Delocalization of all free electrons over metallic array.

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# Electron Sea Model

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## LIMITATIONS OF ELECTRON SEA MODEL

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- ❑ IT CANNOT EXPLAIN CONDUCTIVITY OF Silicon(Si) AND Germanium (Ge)
  - ❑ CONDUCTIVITY DATA CANNOT BE QUANTITATIVELY EXPLAINED
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- Thus we must switch over to another theory that can explain conductivities of Si and Ge
  - THAT IS,
  - ANOTHER THEORY IS NEEDED
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**This theory uses the concept of**  
**Molecular orbital Theory**

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# Molecular orbital Theory

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# Comparison of AO & MO

AO	MO
Monocentric	Bi/polycentric
Under influence of one nuclei	Under influence of more than one nuclei
e.g. are S, $P_x, P_y, P_z, d_{xy}, d_{yx}, d_{xz},$ $dx^2-y^2, dz^2$	Bonding MO, antibonding MO, nonbonding MO,

**BMO****ABMO**

Addition overlap

Subtraction overlap

viewed as constructive interference of waves

viewed as destructive interference of waves

$$\Psi = \Psi_A + \Psi_B$$

$$\Psi = \Psi_A - \Psi_B$$

Lower in energy

Higher in energy

Electron in bMO shield nuclear charge between two nuclei i.e. binds two nuclei, so called bonding MO.

Electron in abMO cannot shield nuclear charge between two nuclei (i.e cannot bind), so called bonding MO.

Nuclear density concentrated between internuclear line joining two nuclei.

Nuclear density concentrated outside of nuclear line.

Electron in BMO increases bond order

Electron in ABMO decreases bond order



# Types of Overlap: 1.s-s

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2.  $p_x - p_x$

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### 3. py-py/pz-pz ( 'side-on' overlap )

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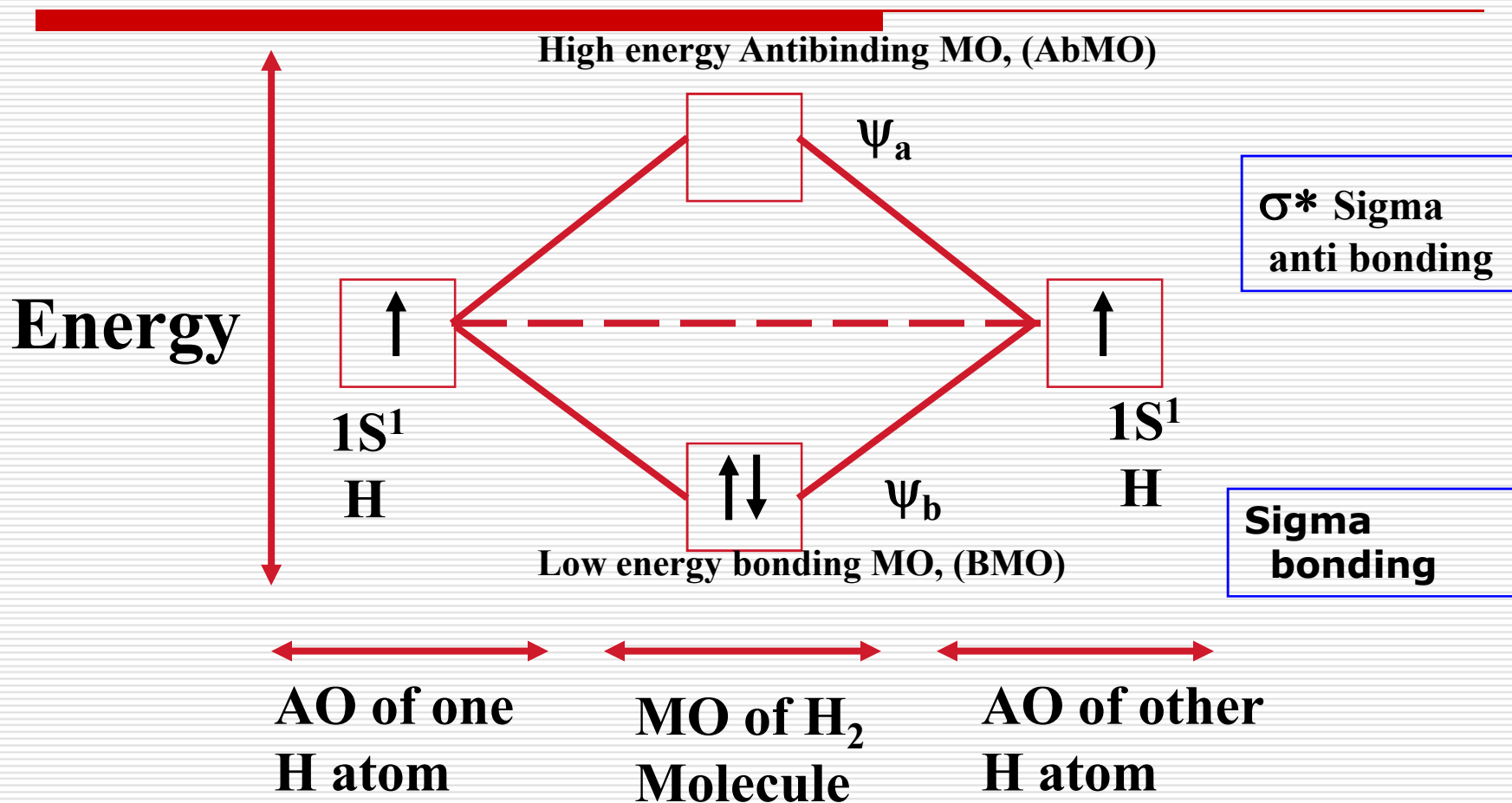
# H<sub>2</sub> Molecule:

(2 nuclei and 2 electron)

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- 2H are written as  $\Psi_A$  &  $\Psi_B$ .
  - AO overlaps means  $\Psi_A$  and  $\Psi_B$  overlap
  - As per LCAO
  - $\Psi = \Psi_A + \Psi_B$  (Addition) gives BMO
  - $\Psi = \Psi_A - \Psi_B$  (Subtraction) gives AbMO.
  - BMO is low in energy
  - AbMO is high energy
-

# How to draw MO Diagram?



a) Homonuclear Diatomic Molecules  
1. H<sub>2</sub> molecule (n=1, K shell)

**Bond order: 1**  
**Diamagnetic**

two electrons go es to BMO and none in the ABMO.

The bond order is =  $\frac{1}{2} (2 - 0) = 1$

**Orbital energy sequence:  $\sigma < \sigma^*$**

## 2. He<sub>2</sub> Molecule (n=1, K shell)

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□ He(2): 1s<sup>2</sup>

□  $BO = \frac{1}{2} (2 - 2) = 0$

- BO=0.
  - That is no bond between two He atom.
  - Therefore, He<sub>2</sub> does not exist.
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## Basics

**\*When AO of 2 atoms combined, 1 BMO's & 1 ABMO's are formed.**

**\*When AO of 3 atoms are combined, 1 BMO's , 1 ABMO's and 1 nbMO's are formed.**

**\*When AO of 4 atoms combined, 2 BMO's & 2 ABMO's are formed.**



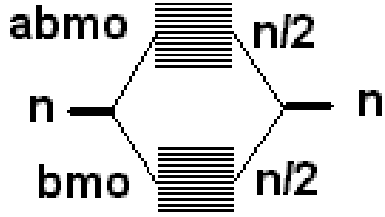
**SO ON.....**

**\*When AO of n atoms combined, n/2 BMO's & n/2 ABMO's are formed.**

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# Construction of MO

<u>No of atoms</u>	<u>bmo</u>	<u>abmo</u>	<u>Picture</u>
<u>2</u>	1	1	
<u>4</u>	2	2	
<u>n</u>	n/2	n/2	

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**So for n number of atoms,  $n/2$  are BMO's &  $n/2$  are ABMO's.**

**The orbitals are so closely spaced in energy that it appears just like a band.**

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# Formation of Li Metal.

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Li(3) – 1S<sup>2</sup>, 2S<sup>1</sup> 2P<sup>0</sup>

Lithium Metal = Li<sub>n</sub>

n 1S<sup>2</sup> from n Li combines to produce a band, which is filled called *Nonconducting band*.

n 2S<sup>1</sup> from n Li combines to produce a band, which is half-filled called *Valence band*.

n 2P<sup>0</sup> from n Li combines to produce a band, which is empty called *Conduction band*.

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# Band Theory:

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- Two bands are separated by energy gap called ***Band gap***
  - The levels upto which electron can move is called permitted zone or ***Brillouin zone***.
  - The levels, below which all levels are filled is called ***Fermi level***
  - *The conduction of electricity is nothing but the jumping of electrons from valence band to conduction band.*
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# Classification of Solids as Conductor, Semiconductor, Insulator.

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## □ DEFINITIONS:

### □ Conductor

□ Can conduct electricity through it.

### □ Insulator

□ Cannot conduct electricity through it.

### □ Semiconductor

□ Insulator at absolute zero but shows increase in conductivity with the rise in temperature.

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# Classification of Solids as Conductor, Semiconductor, Insulator.

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- **Conductor**
  - A conductor is a substance having overlapped VB & CB, or separated by very small energy gap or partially filled V.B.
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# Classification of Solids as Conductor, Semiconductor, Insulator.

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- **Insulator**
  - An insulator has a large energy gap between V.B. & C.B.
-



# Classification of Solids as Conductor, Semiconductor, Insulator.

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## □ Semiconductor

- Have a small energy gap between V.B. & C.B,
  - At absolute zero, electron cannot jump to VB so it behaves like insulator.
  - But as temperature increases, the electrons in VB acquires sufficient kinetic energy and jumps to CB, where they are free to move anywhere thereby making the material conductor.
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# SEMICONDUCTOR TYPES

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- Semiconductors are of two types
  - **1. Intrinsic &**
  - **2. Extrinsic**
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# **1. Intrinsic semiconductors**

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- ❑ Pure semiconductors are Intrinsic semiconductors
  - ❑ Examples Silicon (Si), Germanium (Ge)
  - ❑ The conductivity of intrinsic semiconductors increases to certain extent with rise in temperature. e.g. Si-( 1.1 eV), Ge-(0.72 eV.)
  - ❑ At low temperature, conductivity is zero or very low
-

# **Semiconducting action of Intrinsic semiconductors**

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## **1. ☹️ (Classical approach)**

Si(14):  $1S^2, 2S^2, 2P^6, 3S^2, 3P^2$  (GS) : Si(14):  $1S^2, 2S^2, 2P^6, 3S^1, 3P^3$  (ES)

Hybridization:  $SP^3$ : Geometry: Tetrahedral

A Tetrahedral network of Si atoms.  
Each Si is linked with other tetrahedrally.

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# Semiconducting action: Classical Approach

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- With increase of temp., some covalent bonds are partially broken to form a vacancy (hole) and free electrons.
  - Free electrons and hole which behave like positive charge conduct electricity under applied potential
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## **2. 😊 Semiconducting action** **(Band theory approach)**

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- According to Band theory, at low temp. a gap exist between VB & CB which do not permit passage of electron from CB to VB. But as temp. is increased, the electrons in VB acquire sufficient kinetic energy to cross the barrier, thus entering it into CB, where they are available for conduction purpose.
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# Pictorially



## **Extrinsic Semiconductors:**

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- SC's obtained by mixing extrinsic semiconductors with either trivalent (Ga, In, Tl) or pentavalent (P, As, Sb) are called extrinsic semiconductors.
  - The concentration of impurities is upto  $10^{20}$  atoms /  $m^3$  of SC.
  - They show greater conductivity than pure SC.
  - **2 Types** -
  - 1. **n-type** & 2. **p-type**
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# 1. n -type

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- ❑ Preparation:
- ❑ Pure SC(Intrinsic)+Pentavalent Impurity → n-type
- ❑  $\text{Si} + \text{P} \xrightarrow{(\text{Doping})} \text{Si:P}$
- ❑ P atoms added in Si forms a mixed network.
- ❑ P being pentavalent (having  $5e^-$ ) uses  $4e^-$  for bonding with adjacent  $4\text{Si}$ , leaving behind loosely attached fifth  $e^-$ .
- ❑ This fifth  $e^-$  can be easily detached for use in conduction along with conductivity due to partial breaking of a bond.
- ❑ ~~The extrinsic SC shows enhanced conductivity.~~

# 1. n -type conducting action

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***Classical***

***Band***

*In general, n-type semiconductor has more number of  $e^-$  than holes so called*

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## 2. p-type

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- ❑ Preparation:
  - ❑ Pure SC(Intrinsic)+Trivalent Impurity → p-type
  - ❑ In atoms in Si forms a mixed network. 'In' being trivalent (having  $3e^-$ ) uses only  $3e^-$  for bonding with adjacent 4 Si. Thus one of the bond is electron deficient.
  - ❑ The deficiency of  $e^-$  is considered as presence of a hole which behaves like a positive charge in conduction, so extrinsic SC shows enhanced conductivity.
  - ❑ The conductivity due to partial breaking of a bond is also dominant.
  - ❑ The charge carriers are MAJOR- holes; MINOR-electrons
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# 1. p -type conducting action

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***Classical***

***Band***

*In general, p type SC has more number of holes than electrons*

Majority carriers- holes

Minority carriers-electrons

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# Superconductors

1972 – John Bardeen and two others won a Nobel Prize for their development of a theory of superconductivity at low temperatures.

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- ❑ Metal show increase in resistivity with increase in temperature  
OR
- ❑ Metal show decrease in resistivity with decrease in temperature.
- ❑ At some low temperature, resistivity becomes zero! ( $R=0$ )  
As  $C = 1/R = 1/0 = \infty$
- ❑ i.e.  $C = \infty$ ; Means metal can conduct infinite amount of energy through it.

That is it becomes superconductor!

Example: Hg at 4K temp is superconductor!

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The temp at which material show superconductivity is called Critical Temperature.

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<b>Material</b>	<b>Critical Temperature (<math>T_c</math>)</b>
<b>Titanium</b>	<b>0.39 Kelvin</b>
<b>Aluminum</b>	<b>1.20 Kelvin</b>
<b>Mercury</b>	<b>4.16 Kelvin</b>
<b>Lead</b>	<b>7.20 Kelvin</b>

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- **1986 - Discovery of a ceramic-like material that became a superconductor at “higher” temperatures – 30 K or -243°C. This was a miracle , because normally ceramics are insulator!**
  - **1987 – Discovery of a new ceramic that becomes a superconductor at even higher temperatures (95 K). It can be cooled with cheap liquid nitrogen. (which is at the *high temp of 77 K or -196 °C or -321 °F!*)**
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# Ceramic / Mixed oxide/ Oxide Superconductors

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- Mixed oxide materials (ceramic) can show superconductivity at high temperature than metals. They are called high temperature superconductors.
  - A ceramic is burnt earth (potters clay). It is non-molecular, inorganic crystalline / amorphous material
  - e.g. Y-Ca-Cu oxide i.e.  $[\text{YBa}_2\text{Cu}_3\text{O}_{7-x}]$ ;  $x = 0.0-0.5$  show superconductivity at 93K
  - This is called **1-2-3 superconductor.**
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# 1-2-3 Superconductor: Structure

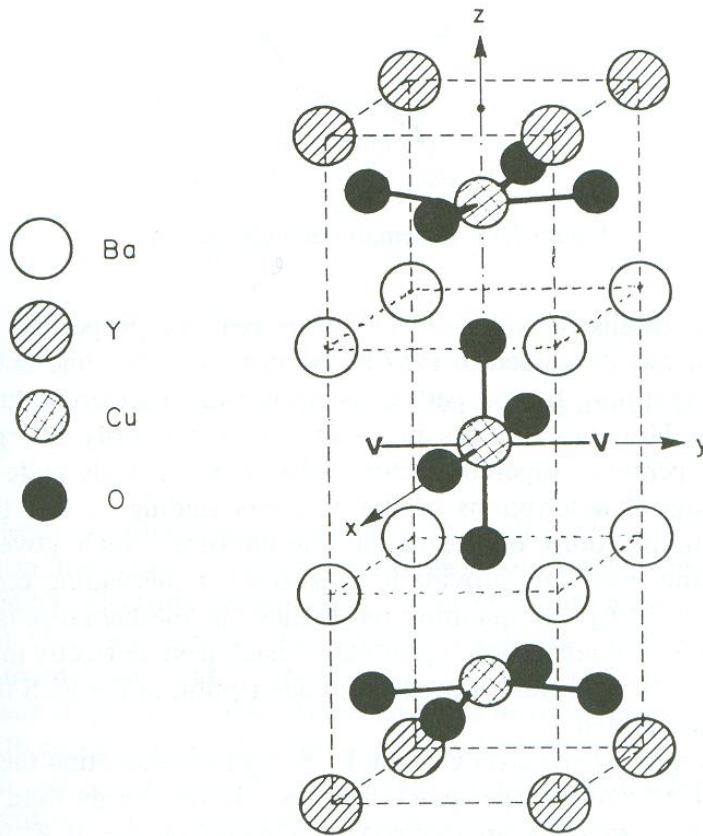


Figure 7.14. Room-temperature unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . The structure is an orthorhombic layered perovskite ( $\text{BaTiO}_3$ ) containing periodic oxygen vacancies. Two examples for oxygen vacancies are indicated by a "V." Adapted from M. Stavola, *Phys. Rev. B*, **36**, 850 (1987).

# Preparation

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## □ 1. Bulk Method:

- The constituents  $\text{BaCO}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$ , taken in proper proportion are fused in an open alumina / sealed gold tube at  $800\text{-}900^\circ\text{C}$  for 1-3 days in air. Finally mass is cooled (annealed) slowly in  $\text{O}_2$  to produce non-stoichiometric, amorphous  **$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$**
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## **2. Chemical vapour deposition method (sputtering).**

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The volatile complexes of Y, Ba, Cu held at  $T_1$ ,  $T_2$ ,  $T_3$ , temp. are brought into reaction chamber through a carrier gas. They are sprayed on wedge shaped block heated by an IR lamp to a high temp. Carrier gas is a mixture of oxygen, water vapour and Helium. When conditions are set, an amorphous film is formed which can be converted into crystalline form after annealing.

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# A schematic of CVD



# The Meissner Effect

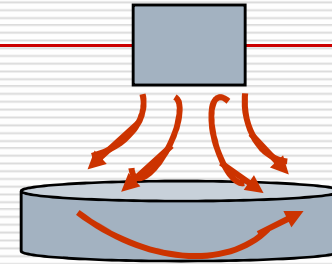
It was discovered in 1933 that a super-conductor has a second property. It will REPEL a magnet regardless of its North/South orientation!!

A super conductor is NEVER ATTRACT to a magnet.

This effect gives rise magnetic levitation (floating in air). This effect can be used to drive magnetically levitated trains.

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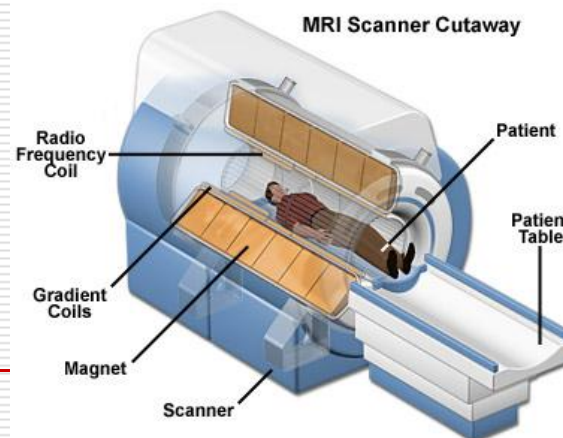
# Maglev (magnetically levitated) Trains



• Maglev Train in Japan

## • Medical MRI's (Magnetic Resonance Imaging)

use superconducting magnets to generate the strong magnetic fields required.



# **Applications**

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- ❑ 1. Ceramic SC shows zero resistance to electrical conductance, so huge amount of energy can be transported through wire of it, which can reduce the conduction loss to 0%.
  - ❑ 2. A huge transportation tower system will be replaced by a compact, easily accessible system.
  - ❑ 3. They can be used for manufacture of powerful magnet
  - ❑ 4. SC can be used in electronic devices, computers, and satellites.
  - ❑ 5. Surface of SC can acts as magnetic mirror, so it can be used in MRI scan, electron microscope, cavity resonators, bearings etc.
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