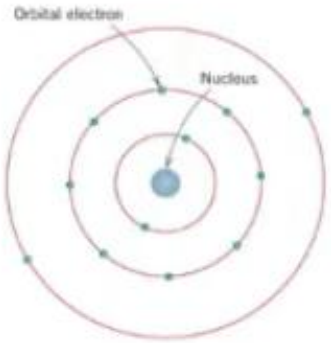
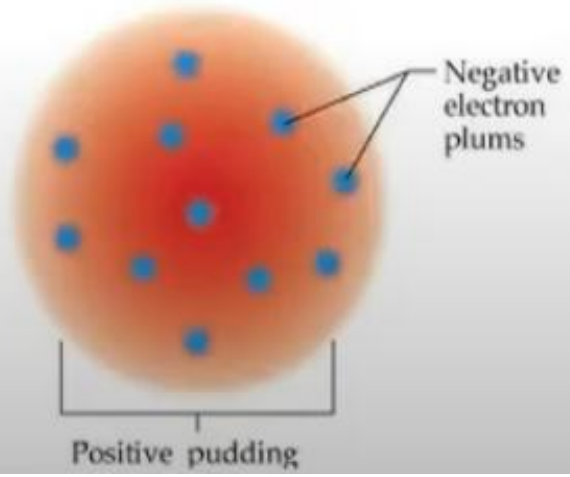
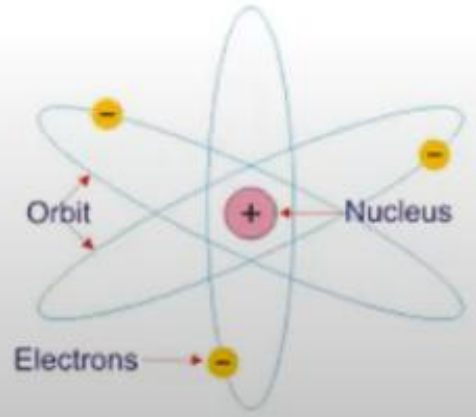
Atoms in crystals



Thomson's model of an atom



Rutherford's model of the atom



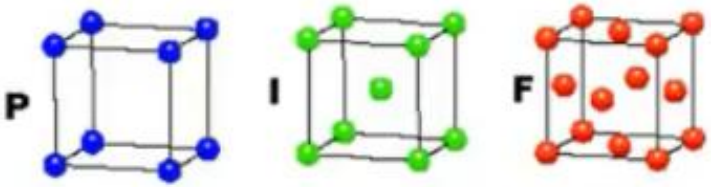
Rutherford's Atomic Model

Bohr's model of an atom

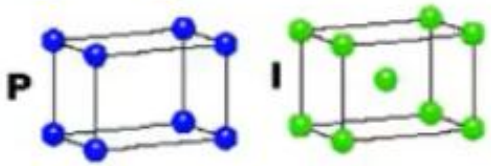
TYPICAL CRYSTAL STRUCTURES

3d – 14 Bravais lattices and seven crystal types

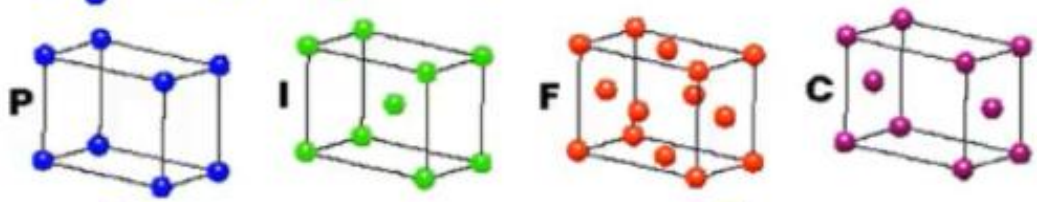
CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$



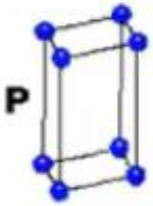
TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



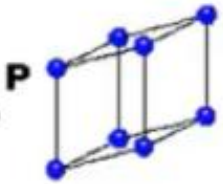
ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



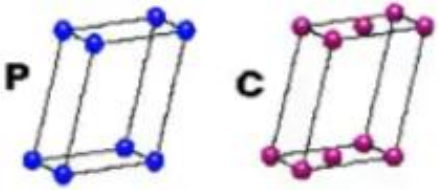
HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$



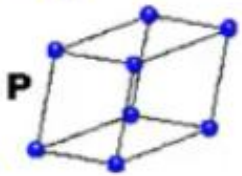
TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$



MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$



TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

INTERATOMIC FORCES

What kind of forces hold the atoms together in a solid?

- Energies of Interactions Between Atoms
- Ionic bonding
  - NaCl
- Covalent bonding
  - Comparison of ionic and covalent bonding
- Metallic bonding
- Van der waals bonding
- Hydrogen bonding

Energies of Interactions Between Atoms

- Energy of crystal is lower than that of free atoms by an amount equal to energy required to pull crystal apart into a set of free atoms called binding (cohesive) energy of the crystal.
  - NaCl is more stable than a collection of free Na and Cl.
  - Ge crystal is more stable than a collection of free Ge.

Types of Bonding Mechanisms

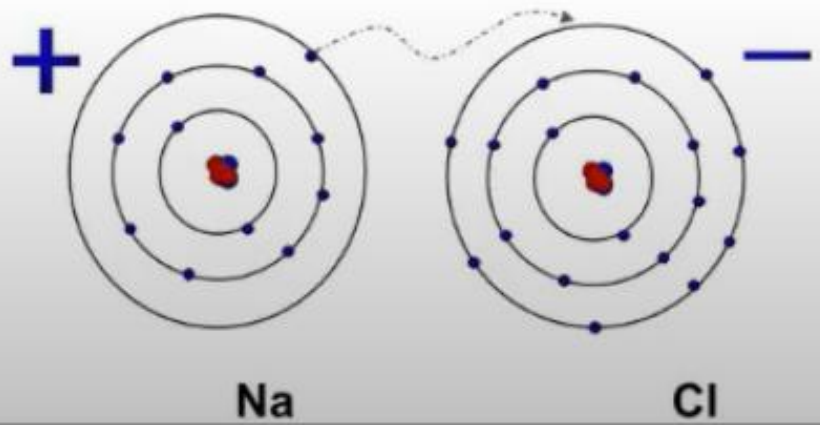
It is conventional to classify the bonds between atoms into different types as

- Ionic
- Covalent
- Metallic
- Van der Waals
- Hydrogen

All bonding is a consequence of the electrostatic interaction between the nuclei and electrons.

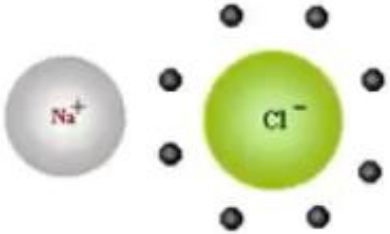
Ionic Bonding

- Electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals).
- All ionic compounds are crystalline solids at room temperature.
- NaCl is a typical example of ionic bonding.
- Metallic elements have only up to the valence electrons in their outer shell.
- When losing their electrons they become positive ions.
- Electronegative elements tend to acquire additional electrons to become negative ions or anions.



Ionic Bonding

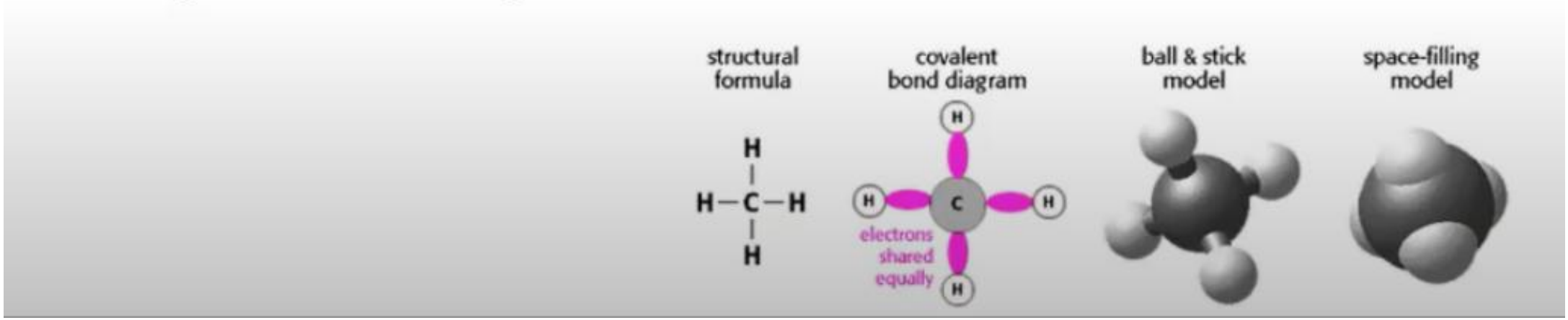
- Orbits of electron in ions begin to overlap with each other.
- Electron begins to repel each other by virtue of the repulsive electrostatic coulomb force. Ofcourse the closer together the ions are, the greater the repulsive force.



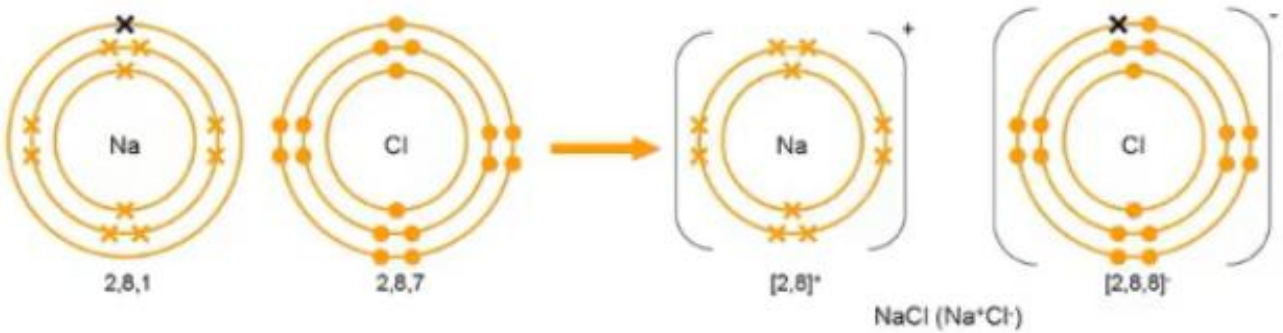
- Pauli exclusion principle has an important role in repulsive force.
- To prevent a violation of the exclusion principle, the potential energy of the system increases very rapidly.

Covalent Bonding

- Covalent bonding takes place between atoms with small differences in electronegativity, which are close to each other in the periodic table (*between non-metals and non-metals*).
- Covalent bonding is formed when the atoms share the outer shell electrons (i.e., s and p electrons) rather than by electron transfer.
- Noble gas electron configuration can be attained.

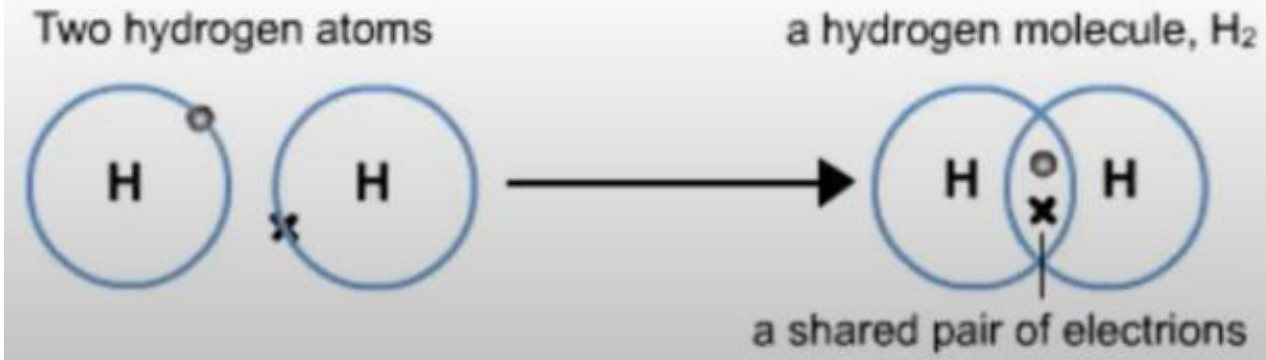


Ionic Bonding



- Ionic solids are rigid and crystalline in nature.
- High melting and boiling point
- Good electrical insulator in their solid state and good conductor of electricity in their molten state.
- Soluble in water and slightly soluble in organic solvent.

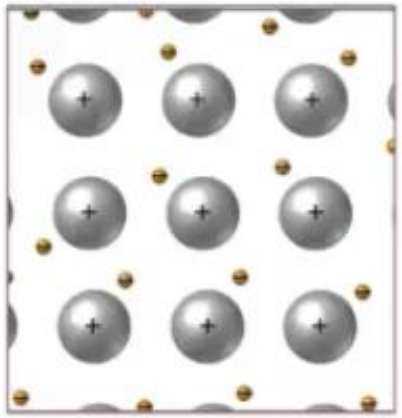
Covalent Bonding

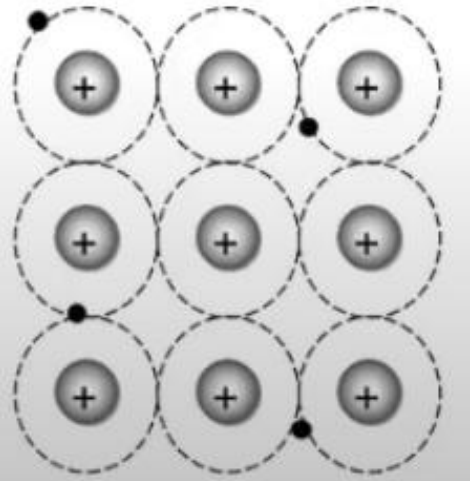


- Bad conductor of electricity.
- Low boiling and melting points.
- Insoluble in water
- Soluble in organic solvent like Benzene

Metallic Bonding

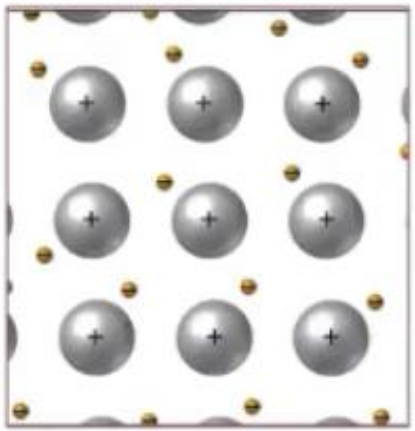
- Electrostatic force of attraction between positively charged ions and delocalized outer electrons.
- Metallic bond is weaker than ionic and covalent bonds.
- A metal may be described as a low-density cloud of free electrons.
- Metals have high electrical and thermal conductivity.
- Elements to left of fourth column in the periodic table exhibit metallic characteristics.
- Sharing of electrons between neighbouring atoms becomes delocalized as there are not enough electrons to produce inert gas configuration around each atom.

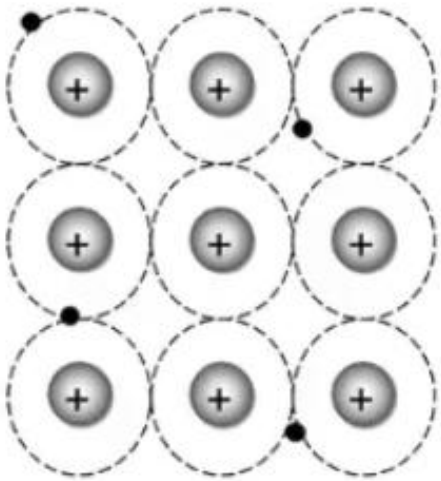




Metallic Bonding

- Metallic state can be visualized as an array of positive ions, with a common pool of electrons to which all the metal atoms have contributed their outer electrons.
- This common pool is called the free electron cloud or the free electron gas.



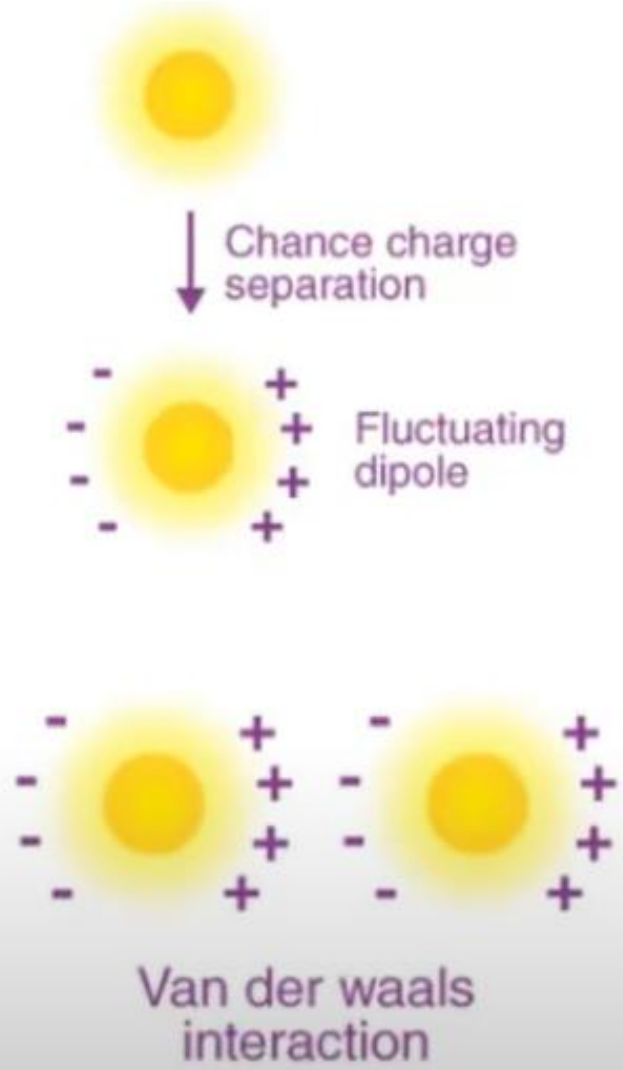


- High thermal and electrical conductivity
- Low melting and boiling point temperature.
- Have a bright lustre.
- They are malleable and ductile.

Secondary Bonding

Van der Waals Bond- weak, 0.4-4 kJ/mol

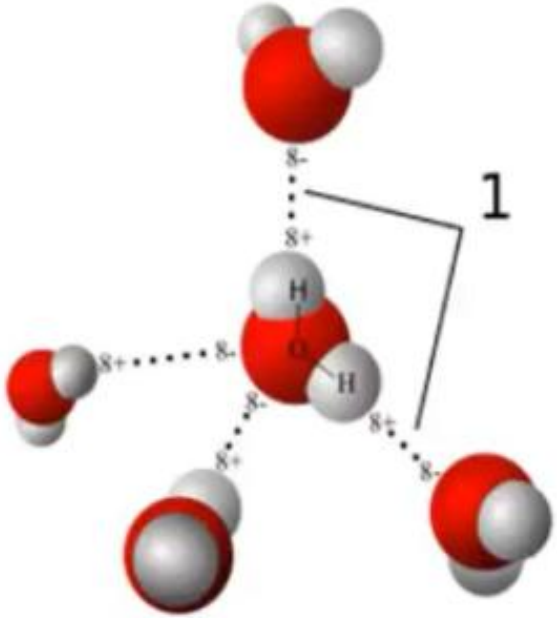
- Temporary bond between neutral atoms and molecules.
- Inert gases form solid crystals at sufficiently at low temperatures.
- Weak forces of attraction result from natural fluctuations in the electron density of all molecules that cause small temporary dipoles to appear within the molecules.
- Electric field of this imbalance can induce a dipole moment in a neighbouring atom, to attract it.
- Dipole in the second atom can in turn induce a dipole in a third atom in order to attract it.
- This dipole-induced-dipole attraction is non-directional in nature.



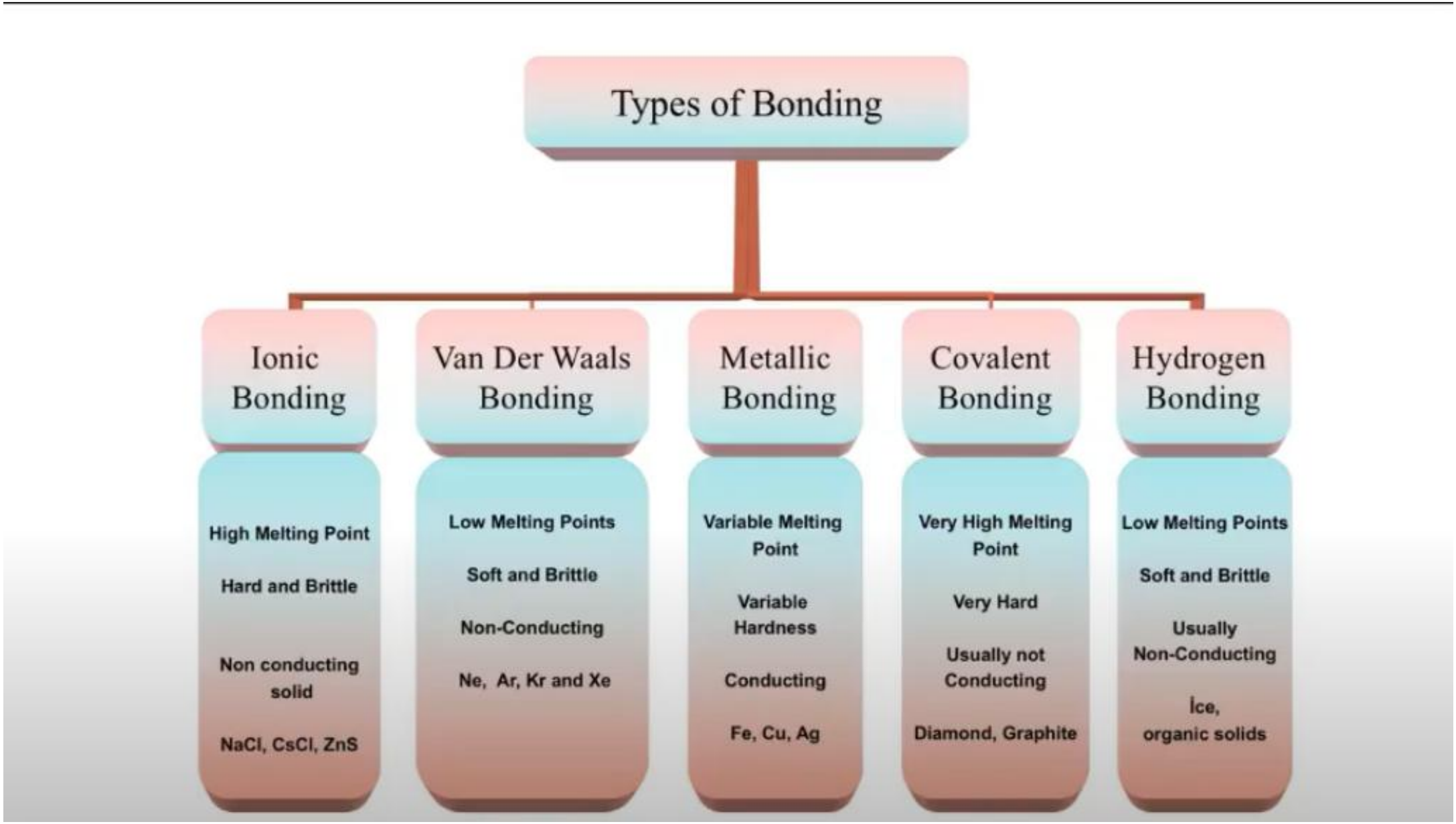
Secondary Bonding

Hydrogen Bonding- weaker, 5-30 kJ/mol

- Forms when charged part of molecule having polar covalent bonds forms electrostatic interaction with a substance of opposite charge.
- Exist in liquid and gaseous states.



- Low melting point.
- No valance electron hence good insulator.
- soluble in both polar and non-polar solvent.
- Transparent to light


Types of Bonding
Ionic Bonding
High Melting Point
Hard and Brittle
Non conducting solid
NaCl, CsCl, ZnS
Van Der Waals Bonding
Low Melting Points
Soft and Brittle
Non-Conducting
Ne, Ar, Kr and Xe
Metallic Bonding
Variable Melting Point
Variable Hardness
Conducting
Fe, Cu, Ag
Covalent Bonding
Very High Melting Point
Very Hard
Usually not Conducting
Diamond, Graphite
Hydrogen Bonding
Low Melting Points
Soft and Brittle
Usually Non-Conducting
İce, organic solids

Free electron theory

- The electron theory of metals explains structure and properties of solids through their electronic structure.
- Applicable to all solids i.e., both metals and non-metals.
- It explains electrical, thermal and magnetic properties of solids etc.
- The theory has been developed in three main stages.

1. The classical free electron theory

- Drude and Lorentz proposed this theory in 1900.
- According to this theory, metals containing free electrons obey the laws of classical mechanics.

2. The quantum free electron theory

- Somerfield developed this theory in 1928.
- Free electrons obey quantum laws.
- Free electrons are moving in a constant potential.

3. The zone theory

- Bloch stated this theory in 1928.
- According to this theory, the free electrons move in a periodic field provided by the lattice.
- Free electrons are moving in a constant potential.

- **Drift Velocity (v_d)**- Average velocity acquired by the free electrons of a metal in a particular direction by application of electric field.
- **Relaxation time (τ_r)**- Time taken by the free electrons to reach its equilibrium position from disturbed position in presence of electric field.
- **Collision time (τ)**- Average time taken by the free electrons between two successive collisions.
- **Current density (j)**- Magnitude of current passing through unit area.

$$J = \frac{I}{A} \qquad \text{or} \qquad I = \int J \bullet ds$$

The classical free electron theory of metals (Drude –Lorentz theory of metals)

The classical free electron theory is based on the following postulates.

1. Valence electrons of atoms are free to move about the whole volume of metal, like molecules of a perfect gas in a container.
2. Free electrons move in random direction and collide with either positive ions fixed to the lattice or other free electrons.
3. All the collisions are elastic in nature i.e., there is no loss of energy.
4. Momentum of free electrons obeys laws of classical kinetic theory of gases.
5. Electron velocities in a metal obey classical Maxwell-Boltzman distribution of velocities.

The classical free electron theory of metals (Drude –Lorentz theory of metals)

5. Free electrons are accelerated in the direction opposite to the direction of applied electric field on application of electric field.

6. Mutual repulsion among electrons is ignored, so that they move in all the directions with all possible velocities.

7. In the absence of field, energy associated with an electron at temperature *T* is given by $\frac{3}{2}kT$

8. Related to the kinetic energy equation $\frac{3}{2}kT = \frac{1}{2}mv_{th}^2$,

   v_{th} =thermal velocity.

Success of classical free electron theory

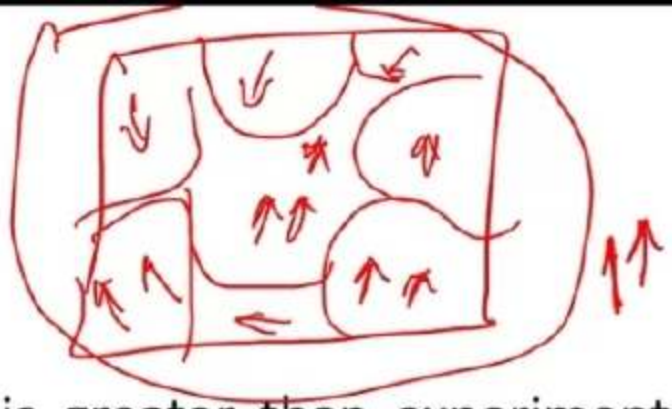
- It verifies ohm's law
- It explains electrical and thermal conductivity of metals.
- It derives Widemann – Franz law. (i.e. relation between electrical and thermal conductivity.

$\frac{\sigma}{K} = \text{const}$

Draw backs of classical free electron theory.

- Could not explain Photoelectric effect, Compton Effect and Black body radiation.
- Electrical conductivity of semiconductors and insulators could not be explained.
- Widemann – Franz law $\frac{K}{\sigma T} = constant$ is not applicable at lower temperatures.

Draw backs of classical free electron theory.



- Could not explain Ferromagnetism.
- Theoretical value of paramagnetic susceptibility is greater than experimental value.
- According to classical free electron theory the specific heat of metals is given by 4.5R whereas the experimental value is given by 3R
- According to classical free electron the electronic specific heat is equal to $\frac{3}{2}$R while the actual value is 0.01R

Merits of quantum free electron theory

- Successfully explains electrical and thermal conductivity of metals.
- Explains Thermionic phenomenon.
- Explains temperature dependence of conductivity of metals.
- It can explain the specific heat of metals.
- It explains magnetic susceptibility of metals.

Demerits of quantum free electron theory

- Unable to explain metallic properties of exhibited by only certain crystals.
- Unable to explain why the atomic arrays in metallic crystals should prefer certain structures only

Classical free electron theory –electrical conductivity

When an electric field E is applied between the two ends of a metal of area of cross section A

Force acting on the electron in the electric field $= eE$

From Newton's second law $F = ma$

The acceleration of electron $a = \frac{F}{m} = \frac{eE}{m}$

The average velocity acquired (i.e. drift velocity) by the electrons by the application of electric field is

$$v_d = a\tau = \frac{e\,E\,\tau}{m} \qquad (1)$$

$$v_d = a\tau = \frac{e\,E}{m} \cdot \frac{\lambda}{\bar{c}} \qquad (2)$$

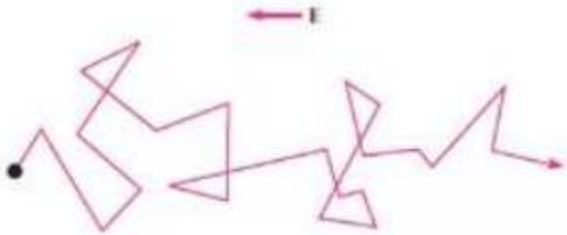
$$since\ \tau = \frac{\lambda}{\bar{c}}$$

Where $\bar{c}$ = RMS velocity.

Classical free electron theory –electrical conductivity

When an electric field E is applied between the two ends of a metal of area of cross section A

Force acting on the electron in the electric field $= eE$



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$$since\ \tau = \frac{\lambda}{\bar{c}}$$

Where $\bar{c}$ = RMS velocity.

Classical free electron theory –electrical conductivity

The relation between current and drift velocity is

$$i = neAv_d$$

$$j = nev_d \qquad (3)$$

Substituting the value of v_d in from equation (1) into equation (3), we get

$$j = \frac{ne^2 E\,\tau}{m}$$

Conductivity σ

$$\sigma = \frac{j}{E} = \frac{ne^2\,\tau}{m} = \frac{ne^2\,\lambda}{m\,\bar{c}}$$

Resistivity ρ

$$\rho = \frac{m}{ne^2\,\tau} = \frac{m\,\bar{c}}{ne^2\,\lambda}$$

According to kinetic theory of gasses $\bar{C} = \sqrt{\frac{3KT}{m}}$

$$\sigma = \frac{ne^2\,\lambda}{\sqrt{3m\,KT}}$$

Classical free electron theory –electrical conductivity

$$\rho = \frac{\sqrt{3m\,KT}}{ne^2\ \lambda}$$

Mobility μ

$$\mu = \frac{v_d}{E} = \frac{e\,\tau}{m}$$

$$\sigma = \frac{ne^2\,\tau}{m} = ne\mu$$

$$j = \frac{ne^2 E\,\tau}{m}$$

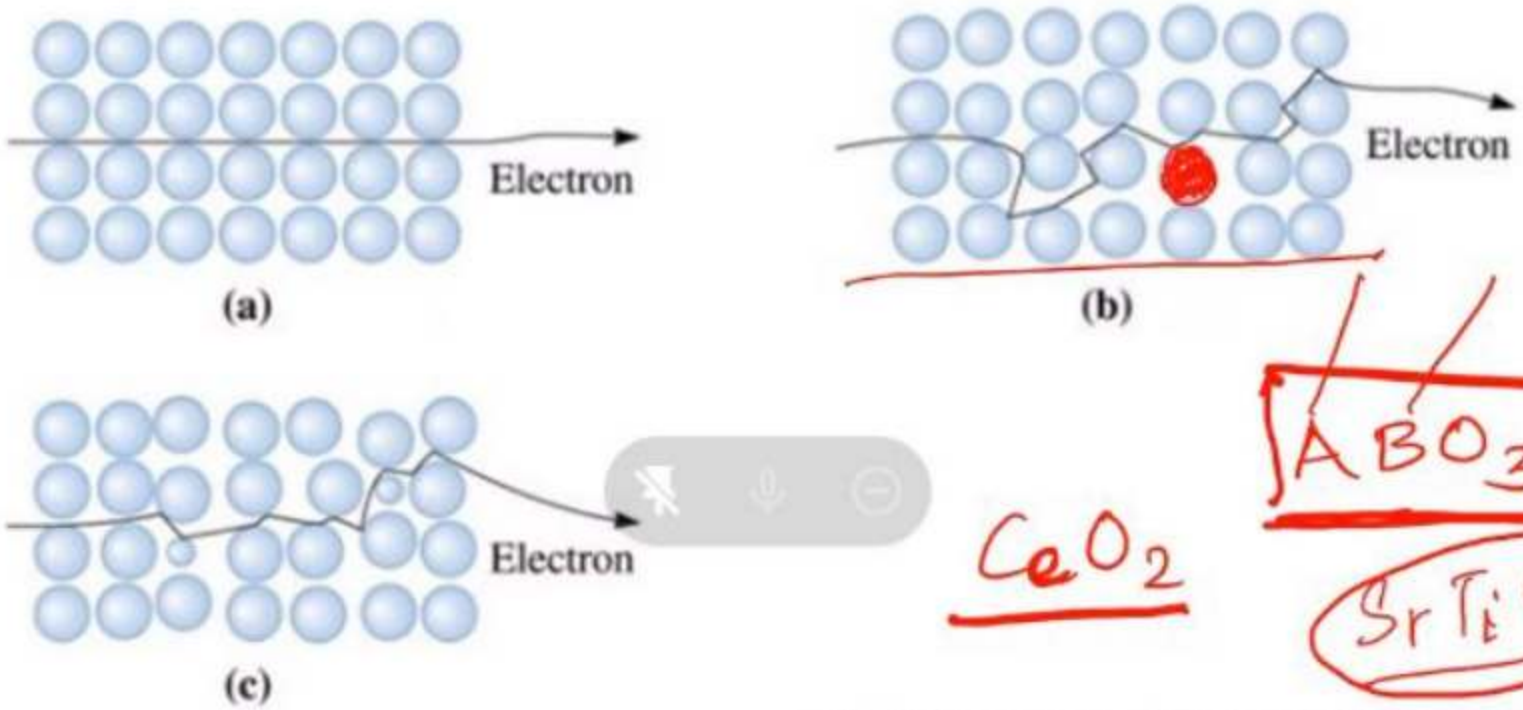
$$j = \sigma E$$

Sources of electrical resistance in metals

- According to quantum free electron theory, free electrons always collides with positive ions or electrons present in the metal.
- Scattering of conduction electrons are due to
  - Effect of temperature
  - Defect, e.g. impurities, imperfections, etc.

Conductivity of Metals and Alloys

- Mean free path - The average distance that electrons can move without being scattered by other atoms.
- Temperature Effect - When the temperature of a metal increases, thermal energy causes the atoms to vibrate
- Effect of Atomic Level Defects - Imperfections in crystal structures scatter electrons, reducing the mobility and conductivity of the metal
- Matthiessen's rule - The resistivity of a metallic material is given by the addition of a base resistivity that accounts for the effect of temperature (ρ_T), and a temperature independent term that reflects the effect of atomic level defects, including impurities forming solid solutions (ρ_d).
- Effect of Processing and Strengthening



ABO_3

CeO_2

$SrTiO_3$

Figure 18.8 Movement of an electron through (a) a perfect crystal, (b) a crystal heated to a high temperature, and (c) a crystal containing atomic level defects. Scattering of the electrons reduces the mobility and conductivity.

$SrTiO_{3-\delta}$

$SrTiO_{2.9}$

*Cristal with no defects is known as perfect Cristal

Temperature effect:

- Positive ions are always in oscillating state about their mean position.
- Vibrating amplitude is always depends on the temperature.
- Mean free path λ of electrons is inversely proportional to the mean square of amplitude of ionic vibrations A_0 .

$$\lambda \propto \frac{1}{A_0^2} \qquad (1)$$

The energy of lattice vibrations is proportional to A_0^2 and increases linearly with temperature T.

$$A_0^2 \propto T \qquad (2)$$

$$\lambda \propto \frac{1}{T} \qquad (3)$$

The resistivity ρ of the metal is inversely proportional to mean free path of electrons.

$$\rho \propto \frac{1}{\lambda} \qquad (4)$$

From equations (3) and (4)

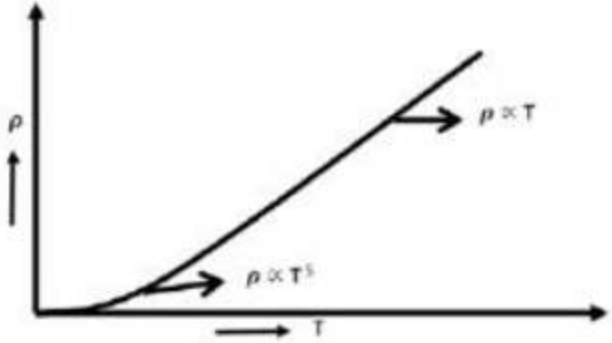
$$\rho \propto T \qquad (5)$$

From equation (5) we observe that the resistivity of metal is linearly increases with temperature.

The conductivity σ is defined as the reciprocal of resistance.

$$\sigma = \frac{1}{\rho} = \frac{1}{T} \qquad (6)$$

The conductivity of metal is inversely proportional to their temperature.



Defect dependence:

At a particular temperature the ideal resistivity of alloy can be written as

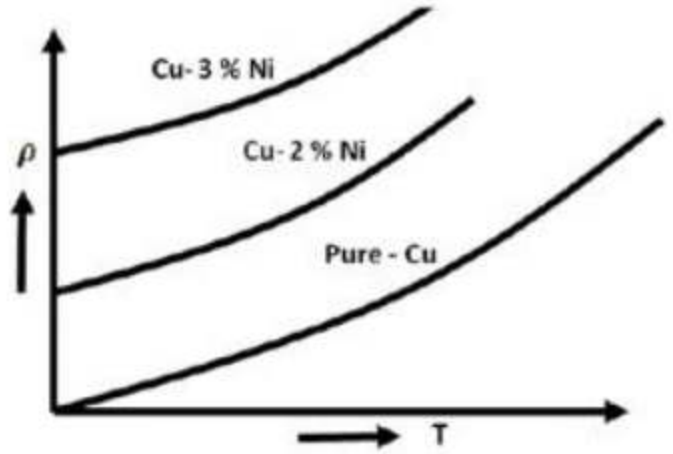
$\rho(x) = AX(1 - X)$

Where X is the concentration and A is a constant which depends upon the base metal and impurity.

The total resistivity change is generally given by the Matthiessen's rule

$\rho_{total} = \rho_{pure} + \rho_{impure}$

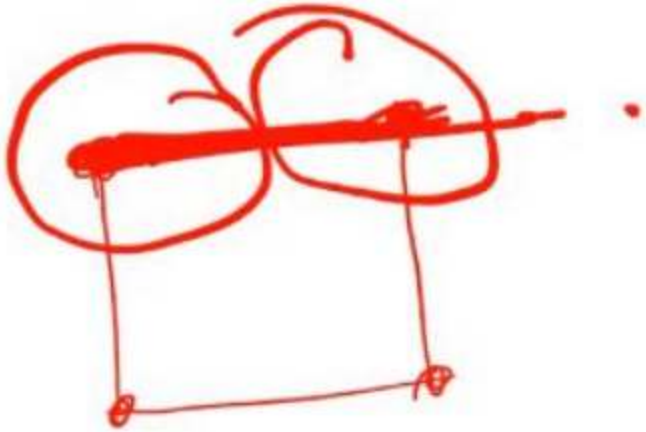
- ρ_{pure} - temperature dependent resistivity due to thermal vibrations of positive ions.
- ρ_{impure} - caused by scattering of electrons by impurity atoms.
- ρ_{pure} is dominant at higher temperature and ρ_{impure} is dominant at low temperature.



The variation of resistivity of copper- nickel alloys as a function of temperature

Thermal Conductivity (K)

- Thermal Conductivity- amount of heat energy (Q) conducted per unit area of cross section per second to temperature gradient $\frac{\Delta T}{\Delta x}$
- $\frac{\Delta Q}{\Delta t} = -KA\frac{\Delta T}{\Delta x}$ (K is the thermal conductivity.)
- $K = -\frac{\Delta Q}{\Delta t}/A\frac{\Delta T}{\Delta x}$
- $K_{total} = K_{electrons} + K_{Phonons}$



*Phonons is the lattice vibrations

Thermal Conductivity (K)

- Thermal Conductivity- amount of heat energy (Q) conducted per unit area of cross section per second to temperature gradient $\frac{\Delta T}{\Delta x}$
- $\frac{\Delta Q}{\Delta t} = -KA\frac{\Delta T}{\Delta x}$ (K is the thermal conductivity.)
- $K = -\frac{\Delta Q}{\Delta t} / A\frac{\Delta T}{\Delta x}$
- $K_{total} = K_{electrons} + K_{Phonons}$

$$K = -\frac{dQ/dt}{A \cdot \frac{dT}{dx}}$$

Metal –
Insulator –
Semicond- –

Weidemann-Franz Law

- Ratio K/σ (where $\sigma = 1/\rho$) between thermal and electric conductivities is the same for all metals and is a function only of temperature.
- If there is a temperature difference ΔT between the sides of a slab of material Δx thick whose cross-sectional area is A, the rate $\frac{\Delta Q}{\Delta t}$ at which heat passes through the slab is given by

$$\frac{\Delta Q}{\Delta t} = -KA\frac{\Delta T}{\Delta x}$$ (K is the thermal conductivity.)

$$K = \frac{knv_{\text{rms}}\lambda}{2}$$

According to the kinetic theory of a classical gas applied to the electron gas in Drude-Lorentz model,

$$\sigma = \frac{1}{\rho} = \frac{ne^2\lambda}{mv_{\text{rms}}}$$

$$\frac{K}{\sigma} = \left(\frac{knv_{\text{rms}}\lambda}{2}\right)\left(\frac{mv_{\text{rms}}}{ne^2\lambda}\right) = \frac{kmv_{\text{rms}}^2}{2e^2}$$

Ratio between thermal and electric resistivities of a metal

$v_{\text{rms}}^2 = 3kT/m$, which gives

$$\frac{K}{\sigma T} = \frac{3k^2}{2e^2} = 1.11 \times 10^{-8}\ \text{W} \cdot \Omega/\text{K}^2$$

Maxwell Boltzmann distribution

$$\frac{K}{\sigma T} = \frac{\pi^2 k^2}{3e^2} = 2.45 \times 10^{-8}\ \text{W} \cdot \Omega/\text{K}^2$$

Fermi Dirac distribution

Hall Effect

Maxwell Boltzmann distribution-

- Statistical description used for understanding how energy is held in the system.
- Applies to a collection of non-interacting particles such as atoms of an ideal gas.
- Estimates how many particles will occupy the energy level i.e how particles are distributed across energy levels.

Classical Mechanics

↓

Certainty

↓

Specific particle is at specific position

↓

Identical but distinguishable

Quantum Mechanics

↓

Probability

↓

There is high probability that a particle is at specific position

↓

Identical but indistinguishable

Distribution laws introduction

Three statistical distributions have been developed in explaining the distribution of atoms or molecules or electrons in energy levels.

1. Maxwell Boltzmann distribution
2. Bose Einstein distribution
3. Fermi Dirac distribution

Maxwell Boltzmann distribution

- In Maxwell Boltzmann distribution all the particles in the system are distinguishable and no more restrictions on filling the particles in the energy levels.
- This is mainly applicable particles with no spin. Ex. atoms and molecules.
- According to Maxwell Boltzmann distribution, the probability of occupying an energy level ε_i is

$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}}}$$

ε_i is the energy of ith level
ε_F is the energy of Fermi level,
k is a Boltzmann constant
T is the absolute temperature and
$f(\varepsilon_i)$ is the Fermi function

Bose Einstein distribution

- In Bose Einstein distribution all the particles in the system are indistinguishable and no more restrictions on filling the particles in the energy levels.
- This is mainly applicable for bosons. (Bosons are the particles with zero or integral spin. ex. photons).
- According to Bose Einstein distribution, the probability of occupying an energy level ε_i is

$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} - 1}$$

ε_i is the energy of ith level
ε_F is the energy of Fermi level,
k is a Boltzmann constant
T is the absolute temperature and
$f(\varepsilon_i)$ is the Fermi function

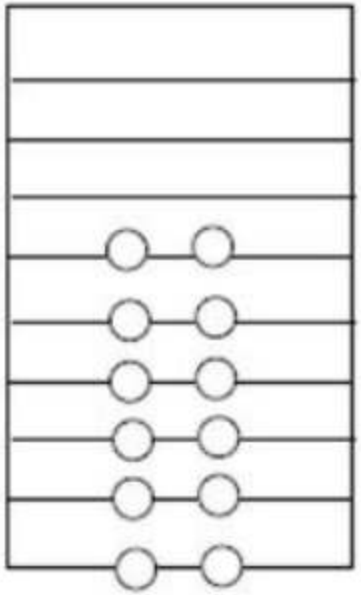
Fermi Dirac distribution

- In Fermi Dirac distribution all the particles in the system are indistinguishable and it obeys Pauli's exclusive principle (i.e., not more than two electrons can occupy the same energy level) on filling the particles in the energy levels.
- This is mainly applicable for fermions (Fermions are the particles with odd half integral spins $\left(0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\ldots\right)$ ex. Electrons.
- According to Fermi - Dirac distribution, probability of occupying an energy level ε_i is

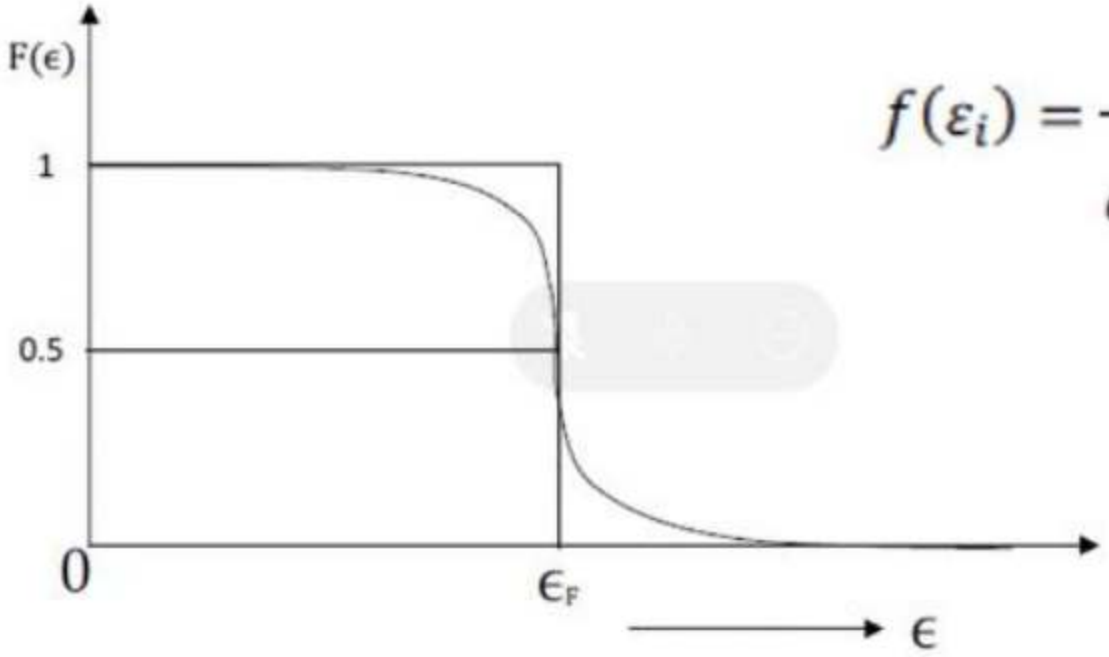
$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} + 1}$$

Fermi energy (E_F)

- It is the **energy** difference between highest and lowest occupied single-particle states in a quantum system of non-interacting fermions at absolute zero temperature.
- The energy level is referred as the Fermi level.
- The Fermi level is that energy level for which the probability of occupation is $\frac{1}{2}$ or 50% at any temperature.



Variation of Fermi function with temperature



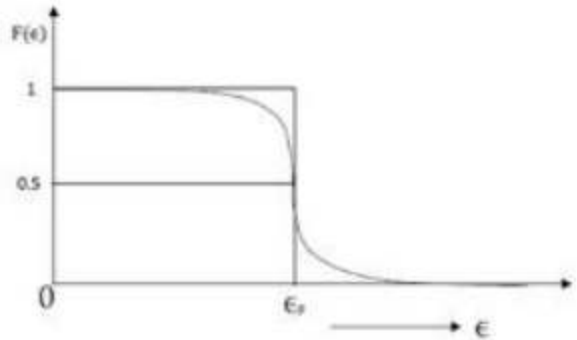
$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} + 1}$$

Probability of finding an electron at different temperatures.

Case I. At $T > 0k$ $if\ \varepsilon_i = \varepsilon_F,\ :\ f(\varepsilon_i) = \frac{1}{2}$

$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} + 1} = \frac{1}{e^{\left(\frac{0}{kT}\right)} + 1} = \frac{1}{e^0 + 1} = \frac{1}{1+1} = \frac{1}{2}$$

$$f(\varepsilon_i) = \frac{1}{2}$$



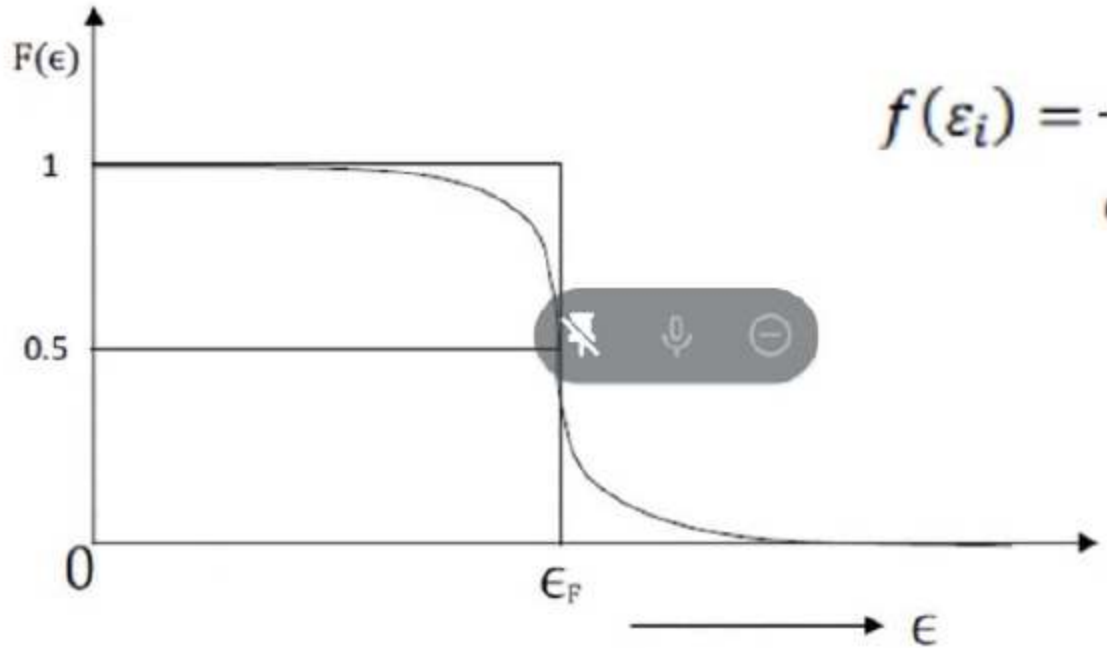
Case II. At $T = 0k$ $if\ \varepsilon_i > \varepsilon_F,\ :\ f(\varepsilon_i) = 0$

$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{0}} + 1} = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{0}} + 1} \qquad Science(\varepsilon_i - \varepsilon_F) = +ve\ valye$$

$$= \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = \frac{1}{\infty} = 0 \qquad since\ \frac{+ve\ value}{0} = \infty$$

$$f(\varepsilon_i) = 0$$

Variation of Fermi function with temperature



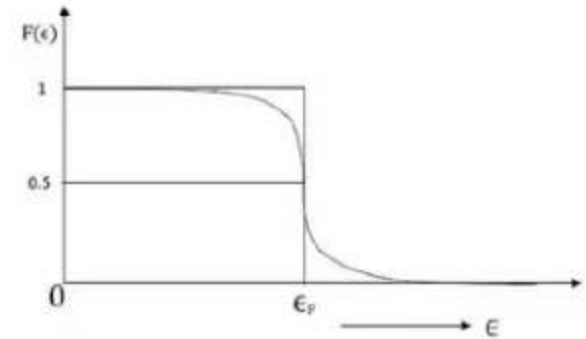
$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} + 1}$$

Probability of finding an electron at different temperatures.

Case I. At $T > 0k$ $if\ \varepsilon_i = \varepsilon_F$, : $f(\varepsilon_i) = \frac{1}{2}$

$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} + 1} = \frac{1}{e^{\left(\frac{0}{kT}\right)} + 1} = \frac{1}{e^0 + 1} = \frac{1}{1+1} = \frac{1}{2}$$

$$f(\varepsilon_i) = \frac{1}{2}$$



Case II. At $T = 0k$ $if\ \varepsilon_i > \varepsilon_F$, : $f(\varepsilon_i) = 0$

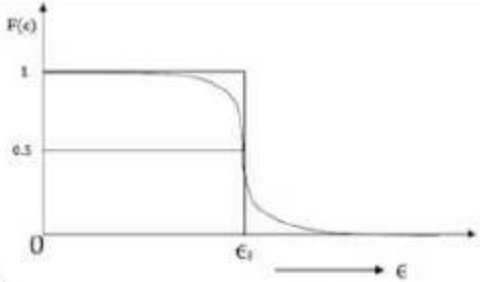
$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{0}} + 1} = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{0}} + 1}$$

~~Since~~ since $(\varepsilon_i - \varepsilon_F) = +ve$ ~~value~~ value

$$= \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = \frac{1}{\infty} = 0 \qquad since\ \frac{+ve\ value}{0} = \infty$$

$$f(\varepsilon_i) = 0$$

Probability of finding an electron at different temperatures.



Case III. At $T = 0k$ if $\varepsilon_i < \varepsilon_F$, : $f(\varepsilon_i) = 1$

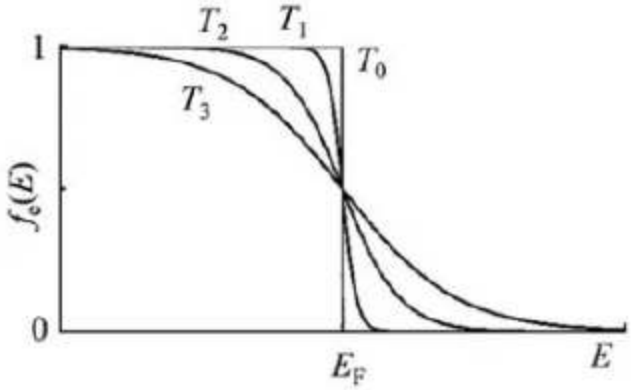
$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{0}} + 1} = \frac{1}{e^{\frac{-ve\ value}{0}} + 1} \qquad \because\ \varepsilon_i < \varepsilon_F \quad since\ (\varepsilon_i - \varepsilon_F)$$

$$= -ve\ value$$

$$= \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = \frac{1}{1} = 1 \qquad \because e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty} = 0$$

$$f(\varepsilon_i) = 1$$

From figure (1) we illustrate that



When $T > 0$ $f(\varepsilon_i) < 1$ $\left(but > \frac{1}{2}\right)$ for $\varepsilon_i < \varepsilon_F$

$$f(\varepsilon_i) > 0 \left(but < \frac{1}{2}\right) for\ \ \varepsilon_i > \varepsilon_F$$

When $T > 0k$ if $\varepsilon_i = \varepsilon_F$, : $f(\varepsilon_i) = \frac{1}{2}$

The energy level for which the probability of occupation is $\frac{1}{2}$ or 50% at any temperature.

Properties of Fermi function

1. It is applicable for all insulators, semiconductors and metals.

$$\text{At } T > 0k \;\; if \; \varepsilon_i = \varepsilon_F, \; : \; f(\varepsilon_i) = \frac{1}{2}$$
$$\text{At } T = 0k \;\; if \; \varepsilon_i > \varepsilon_F, \; : \; f(\varepsilon_i) = 0$$
$$\text{At } T = 0k \;\; if \; \varepsilon_i < \varepsilon_F, \; : \; f(\varepsilon_i) = 1$$

Fermi levels are totally fulfilled and above the levels are totally empty.

Significance of Fermi Energy

- Metal- Metal contacts
- Semiconductors
- Seebeck Effect
- Thermocouple

Band Theory

- Origin of an energy gap is explained by considering formation of energy bands in solids.
- Interaction between any two atoms in a gaseous substance is very weak, since interatomic distance is very large.
- In solid substance interatomic distance is very small, and hence there is an interaction between any two successive atoms.
- Due to this interaction energy levels of all atoms overlap with each other and hence bands are formed.

Band Theory

- Energy band structure of a solid determines whether it is a conductor, an insulator, or a semiconductor.
- In a solid, because the splitting is into as many levels as there are atoms present the levels are so close together that they form an energy band consisting of a virtually continuous spread of permitted energies.
- Energy bands of a solid, gaps between them, and extent to which they are filled by electrons not only govern the electrical behavior of the solid but also have important bearing on others of its properties.

Energy Band

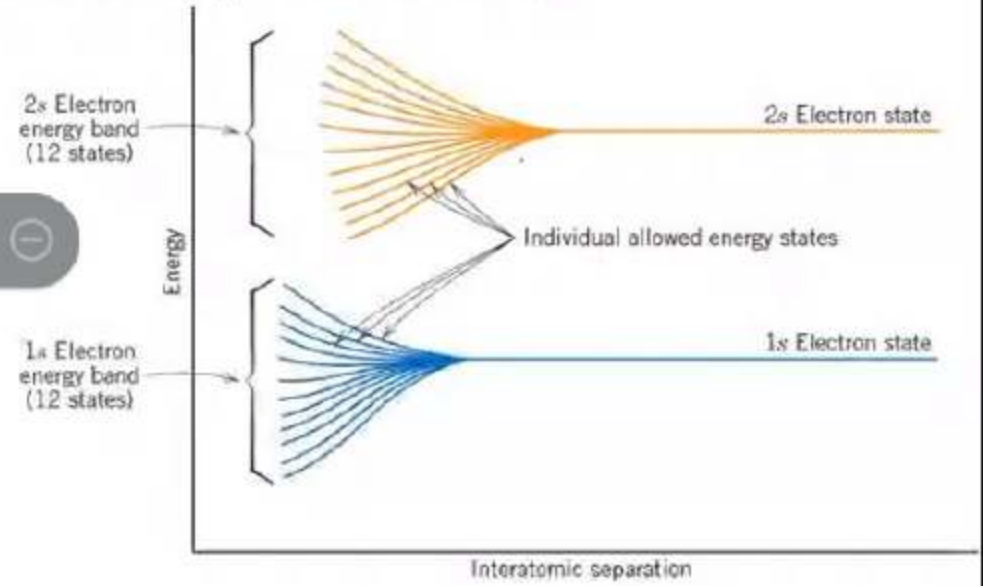
- Magnitude of electrical conductivity is strongly dependent on number of electrons available to participate in conduction process.
- Not all electrons will accelerate in an electric field.
- Number of electrons available for electrical conduction is based on arrangement of electron states.

Electron Arrangement

- In each atom, there are discrete energy levels that may be occupied by electrons, arranged into shells and subshells.
- Shells are designated by integers (1, 2, 3, etc.), and subshells by letters (*s*, *p*, *d*, and *f*).
- For each of *s*, *p*, *d*, and *f* subshells, there exist, respectively, one, three, five, and seven states.

Electron Arrangement

- As atoms come within proximity of one another, electrons are acted upon, or perturbed, by the nearby electrons and nuclei of adjacent atoms.
- This causes splitting of each distinct atomic states into a series of closely spaced electron states to form an electron energy band.
- Extent of splitting depends on interatomic separation and begins with outermost electron shells.



Schematic plot of electron energy versus interatomic separation for an aggregate of 12 atoms (N=12). Upon close approach, each of the 1*s* and 2*s* atomic states splits to form an electron energy band consisting of 12 states.

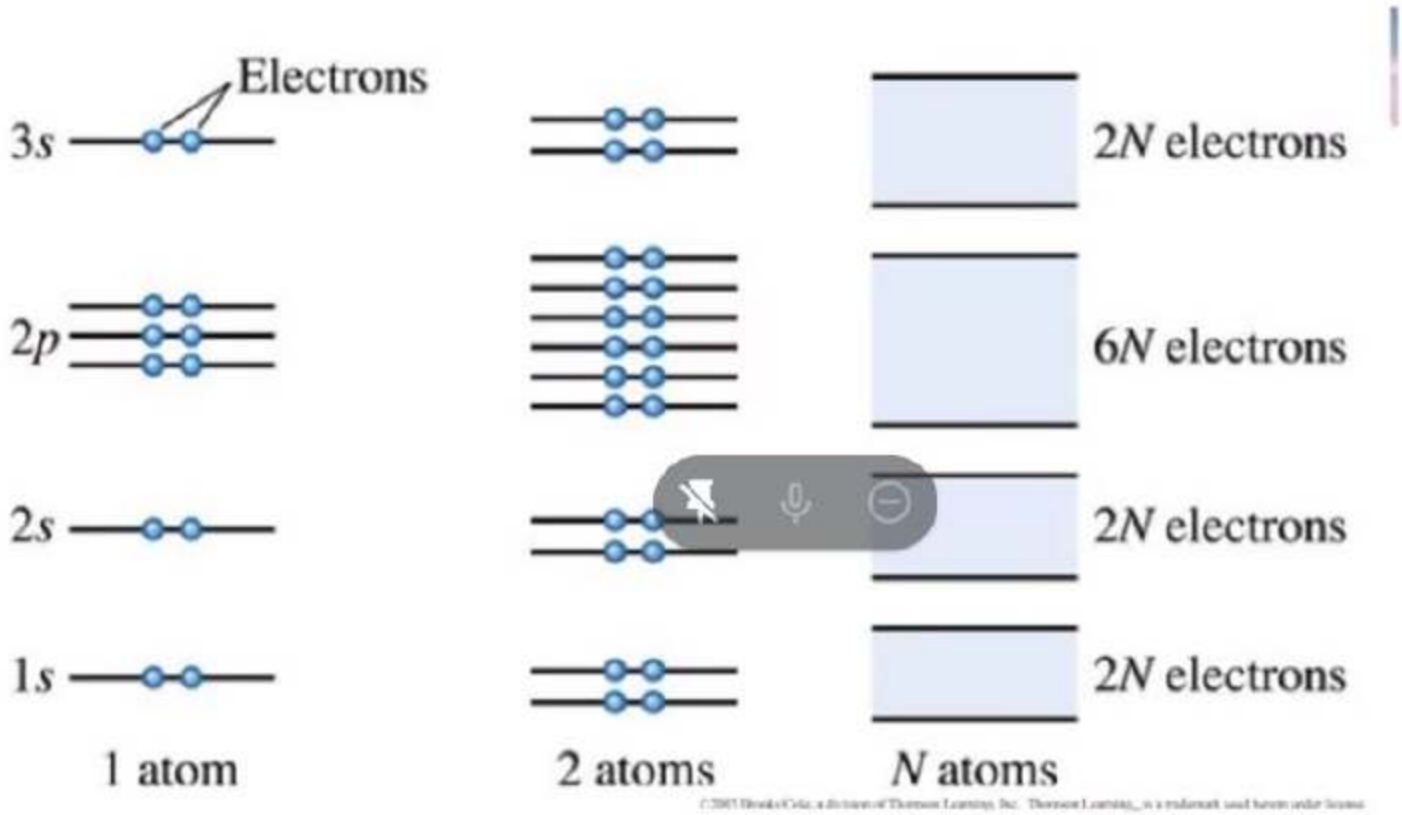
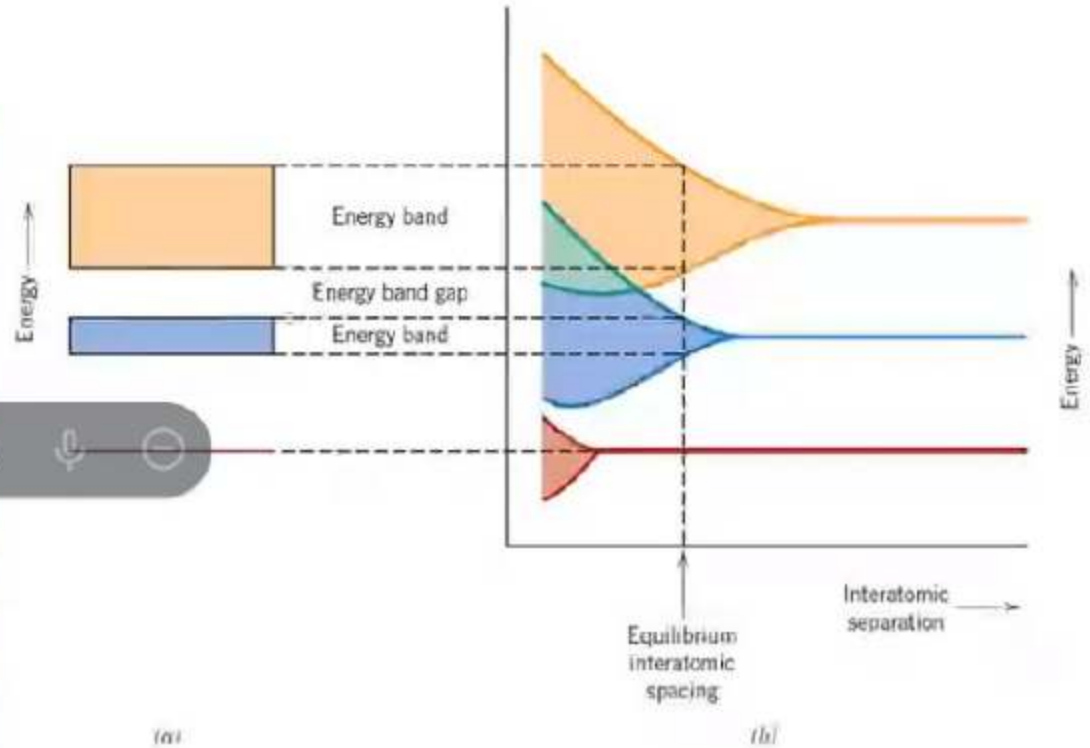


Figure 18.3 The energy levels broaden into bands as the number of electrons grouped together increases.

Electron Arrangement

Within each band, energy states are discrete, yet difference between adjacent states is exceedingly small.

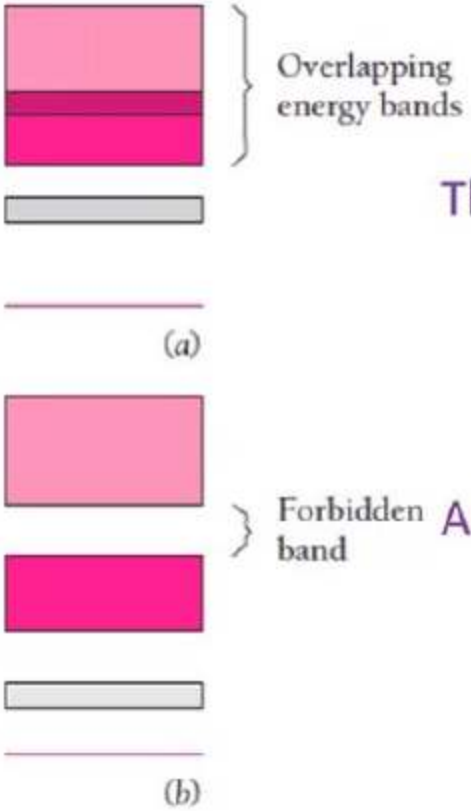
At equilibrium spacing, band formation may not occur for electron subshells nearest the nucleus.



(a) Electron energy band structure for a solid material at the equilibrium interatomic separation.
(b) Electron energy versus interatomic separation for an aggregate of atoms.

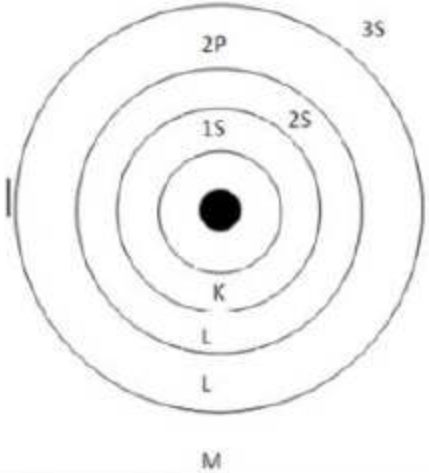
Electron Arrangement

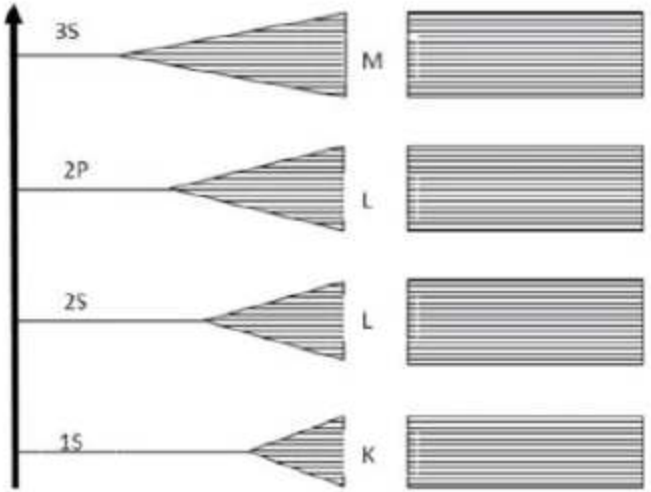
- Arrangement of outermost electron bands and the way in which they are filled with electrons determines electrical properties of a solid.
- Final two band structures are similar; one band is **valence band,** that is completely filled with electrons is separated from an empty **conduction band**, and an **energy band gap** lies between them.
- Greater the number of interacting atoms, greater the number of levels produced by mixing of their respective valence wave functions.



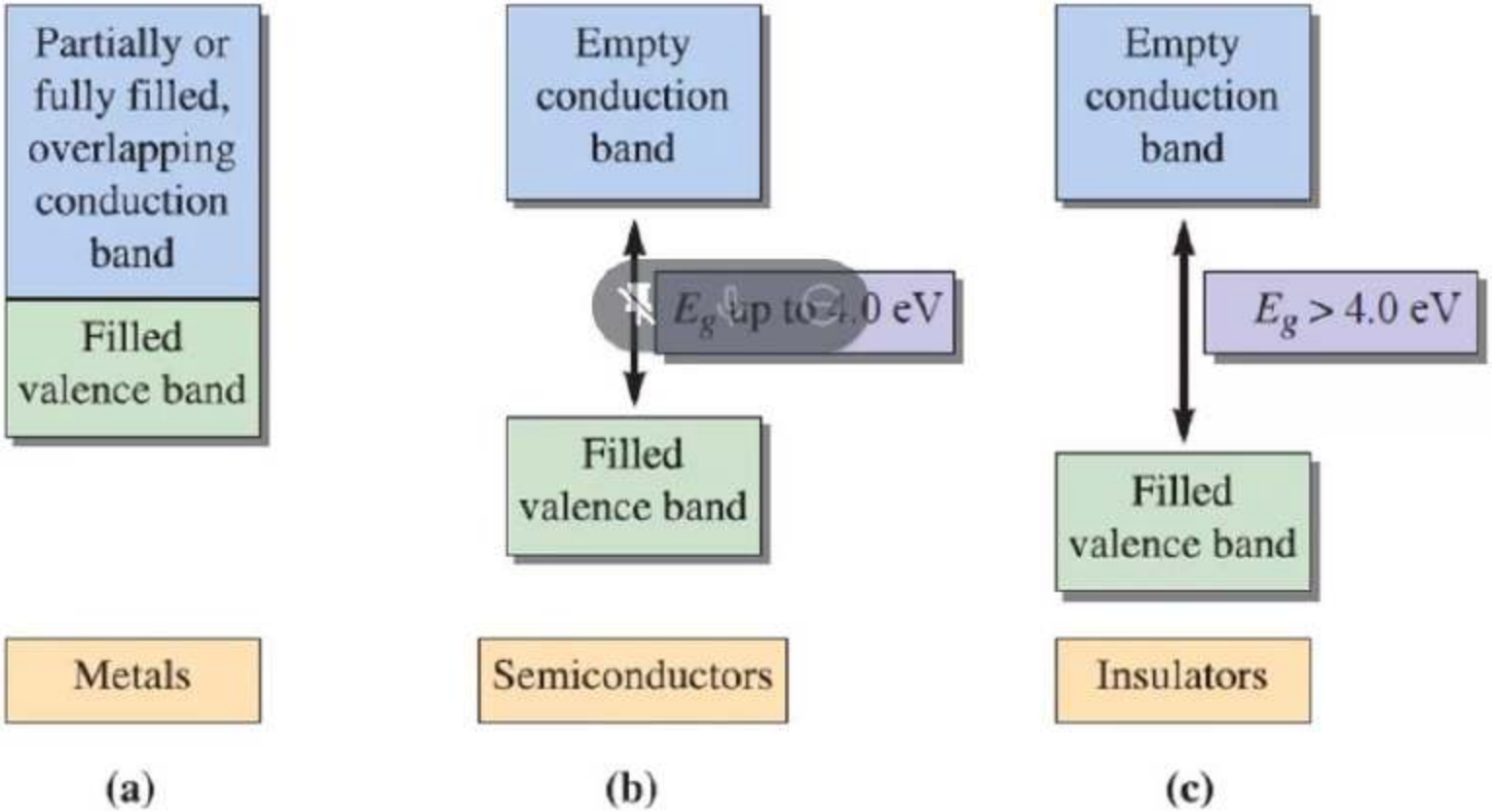
The energy bands in some solids may overlap to give a continuous band.

A forbidden band separate non-over-lapping energy bands in other solids.



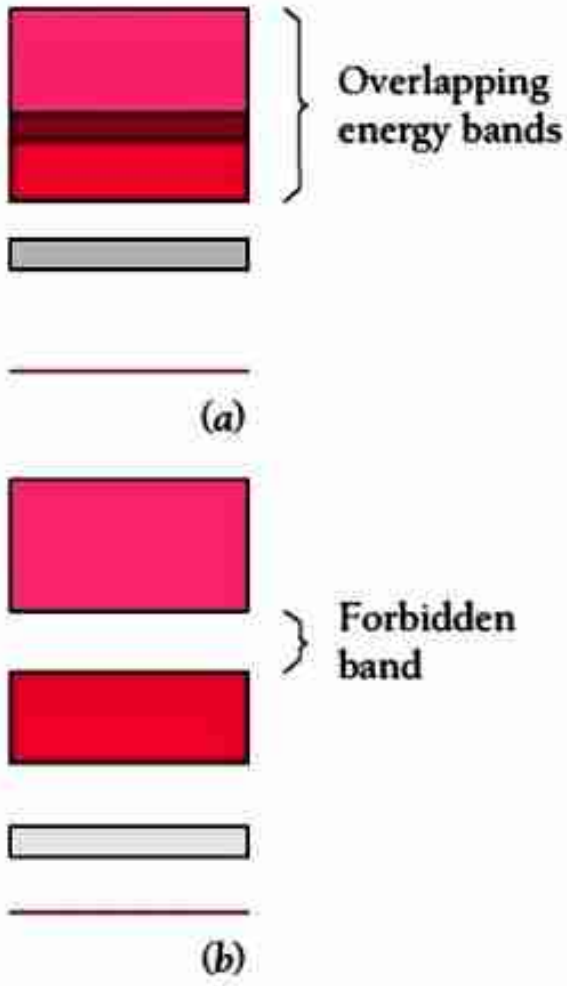


Conductors, Semiconductors and Insulators



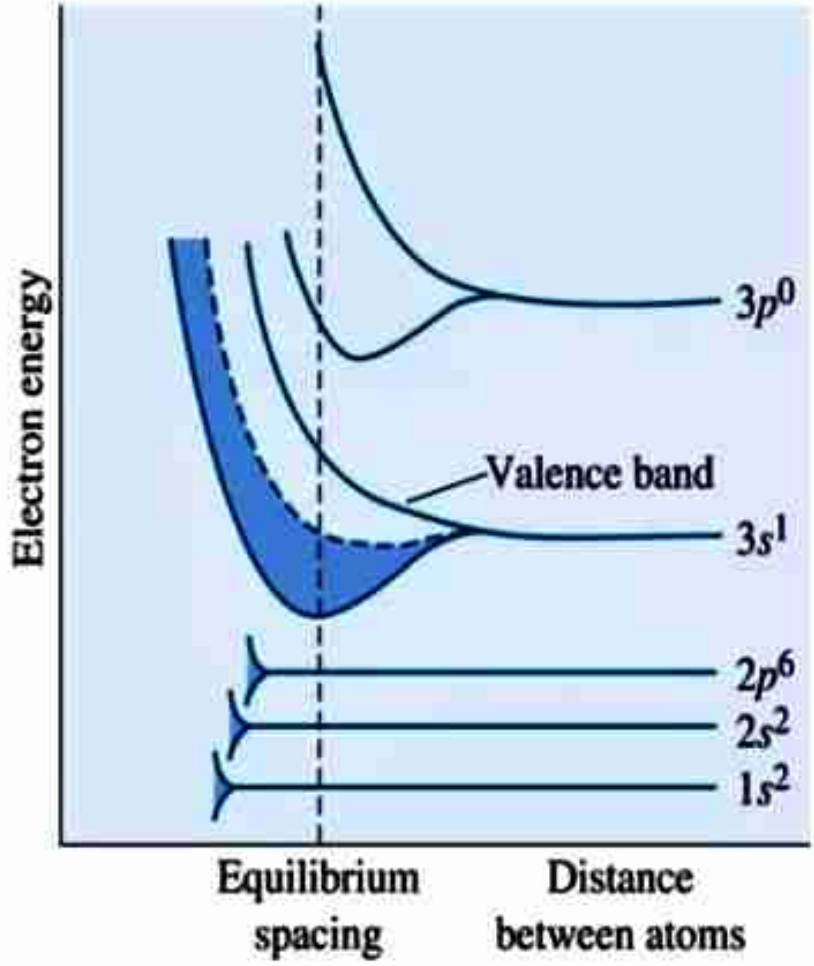
Conductors

- An electron in a solid can only have energies that fall within its energy bands.
- Various outer energy bands may overlap in which case its valence electrons have available a continuous distribution of permitted energies.
- In other solids bands may not overlap and the intervals between them represent energies their electrons cannot have.
- Such intervals are called **forbidden bands** or **band gaps.**



Conductors

- 3*s* level is first occupied level to broaden into a band.
- Lower 2*p* level does not begin to spread out until a much smaller internuclear distance because 2*p* wave functions are closer to nucleus than are 3*s* wave functions.
- Average energy in 3*s* band drops at first, which signifies attractive forces between atoms.
- Actual internuclear distance in solid sodium corresponds to minimum average 3*s* electron energy.



Semiconductors

- Intrinsic semiconductor - A semiconductor in which properties are controlled by the element or compound that makes the semiconductor and not by dopants or impurities.
- Extrinsic semiconductor - A semiconductor prepared by adding dopants, which determine the number and type of charge carriers.
- Doping - Deliberate addition of controlled amounts of other elements to increase the number of charge carriers in a semiconductor.
- Thermistor - A semiconductor device that is particularly sensitive to changes in temperature, permitting it to serve as an accurate measure of temperature.
- Radiative recombination - Recombination of holes and electrons that leads to emission of light; this occurs in direct bandgap materials.

Band Structure in Semiconductors

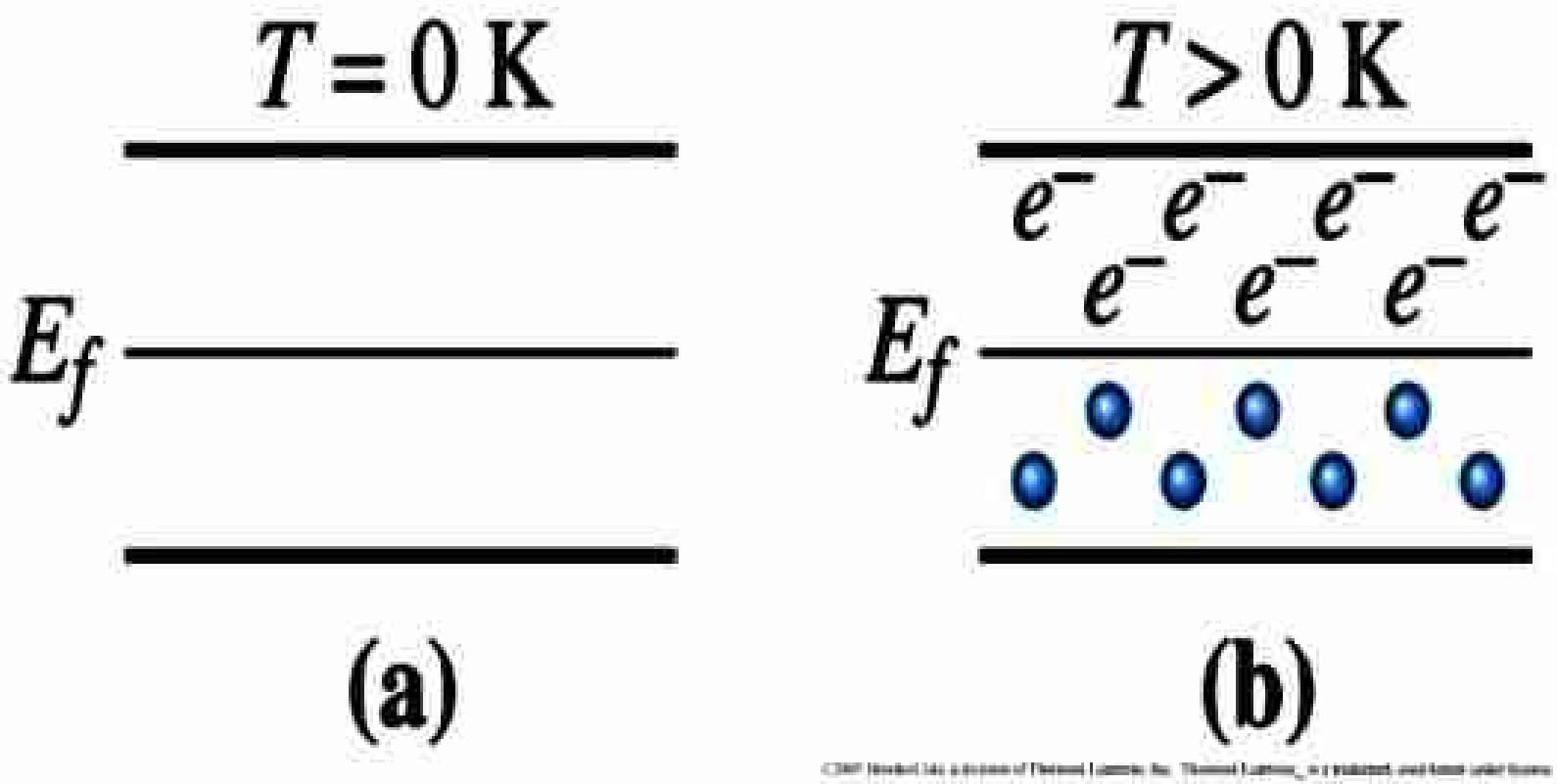
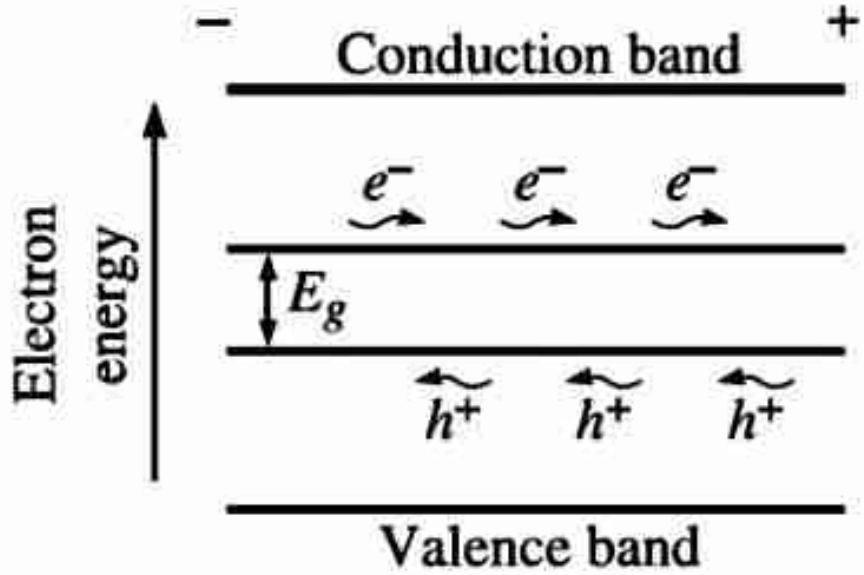


Figure 18.5 (a) At absolute zero, all of the electrons in the outer energy level have the lowest possible energy. (b) When the temperature is increased, some electrons are excited into unfilled levels. Note that the Fermi energy is unchanged.

Intrinsic Semiconductors



When a voltage is applied to a semiconductor, the electrons move through the conduction band, while the holes move through the valence band in the opposite direction.

Intrinsic Semiconductors

- Conductivity in semiconductor is determined by number of electrons and holes according to $\sigma = nq\mu_n + pq\mu_p$
- In intrinsic semiconductors, for every electron promoted to the conduction band, there is a hole left in the valence band $n_i = p_i$
- Conductivity of an intrinsic semiconductor is $\sigma = qn_i(\mu_n + \mu_p)$
- Number of electrons in conduction band, which is equal to the number of holes in valence band

$$n = n_i = p_i = n_0 \exp\left(\frac{-E_g}{2k_B T}\right)$$

$$\sigma = n_0 q(\mu_n + \mu_p) \exp\left(\frac{-E_g}{2k_B T}\right)$$

$C^6 =$

$1s^2 2s^2 2p^2$

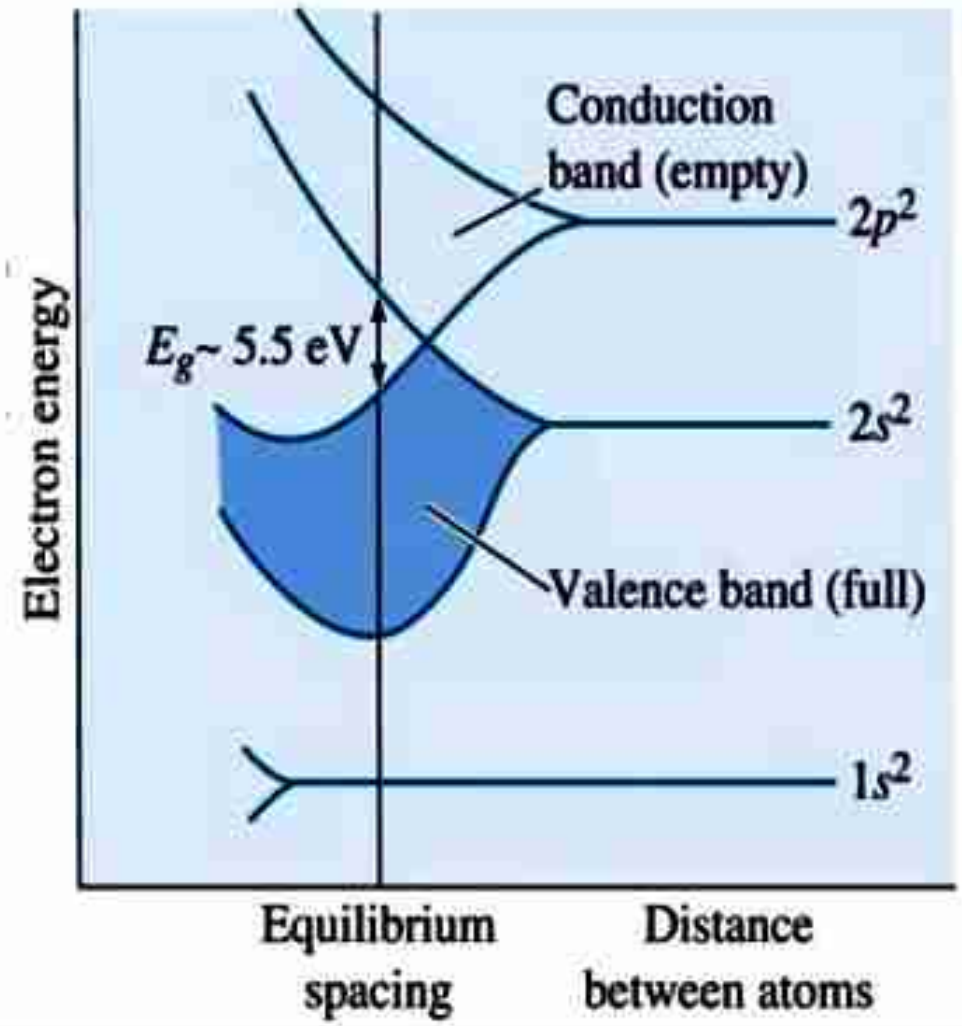
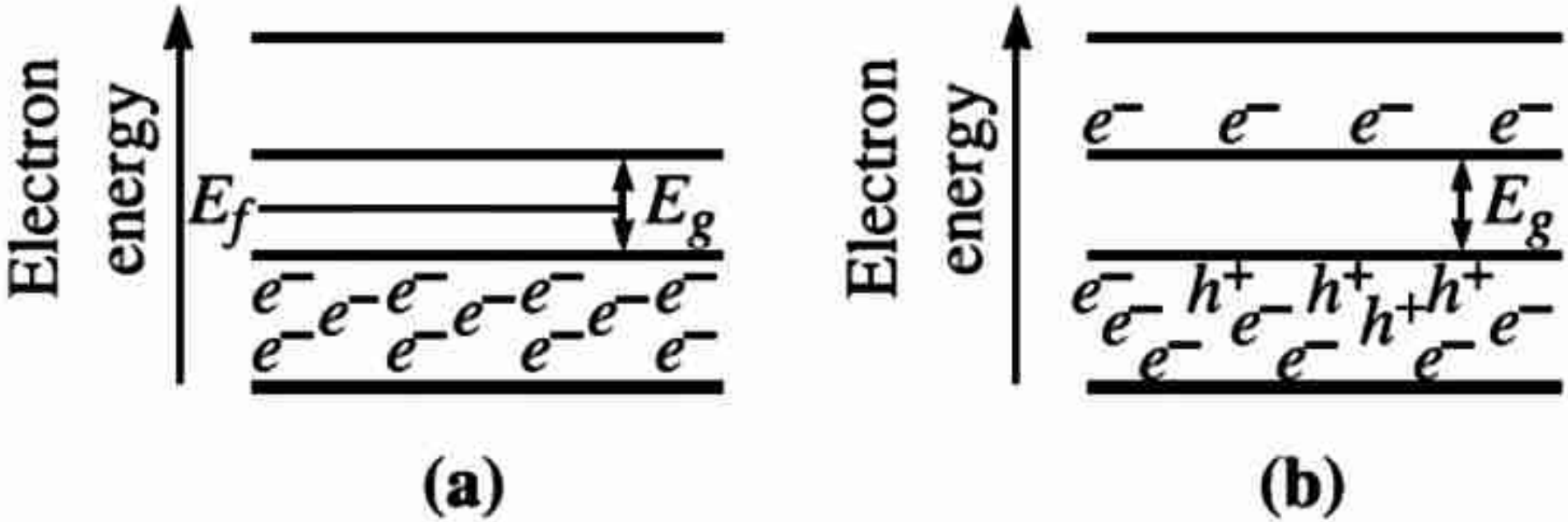


Figure 18.6 The band structure of carbon in the diamond form. The 2 *s* and 2 *p* levels combine to form two hybrid bands separated by an energy gap, E_g.

Semiconductors

Intrinsic Semiconductors



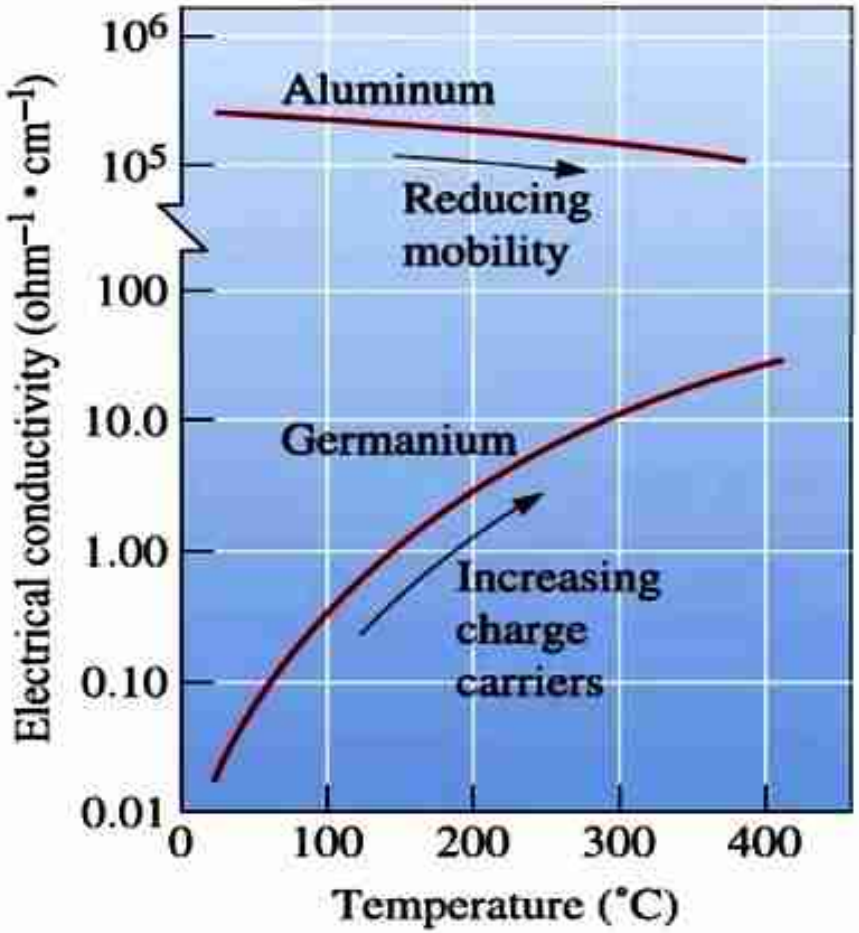
The distribution of electrons and holes in the valence and conduction bands (a) at absolute zero and (b) at an elevated temperature.

Temperature effect

- Conductivity of semiconductors increases with temperature, as more and more electrons are promoted to conduction band from valence band.
  - Increasing number of electrons from covalent bonds in a semiconductor is freed and becomes available for conduction.
- Conductivity of most metals, on the other hand, decreases with increasing temperature.
  - Number of electrons that are already available begin to scatter more (i.e., increasing temperature reduces mobility).

Temperature effect

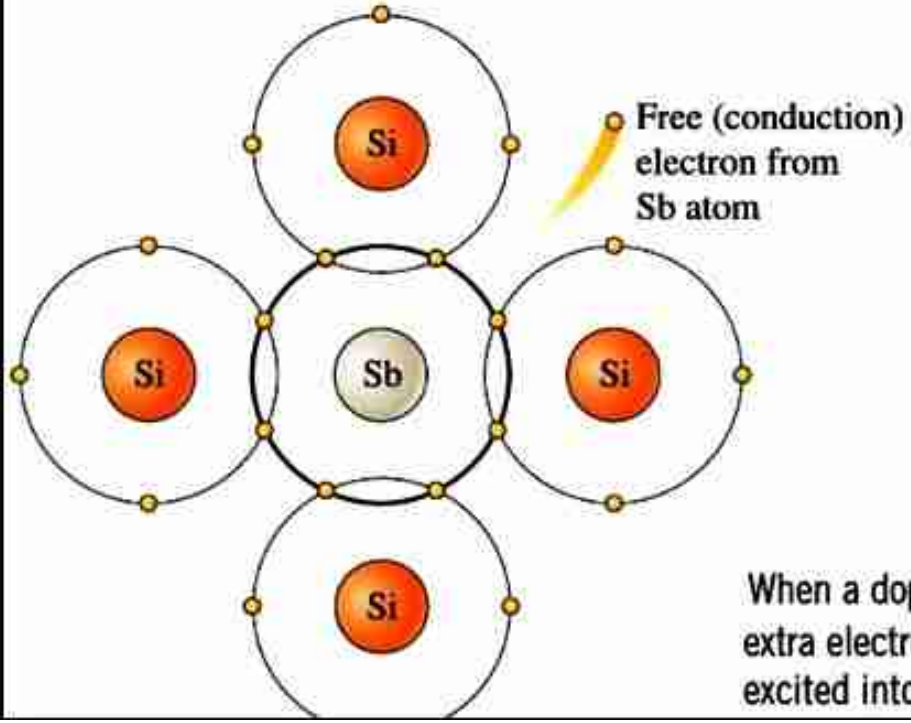
- Increase in conductivity with temperature in semiconductors sharply contrasts with decrease in conductivity of metals.
- Even at high temperatures, however, conductivity of a metal is orders of magnitudes higher than the conductivity of a semiconductor.

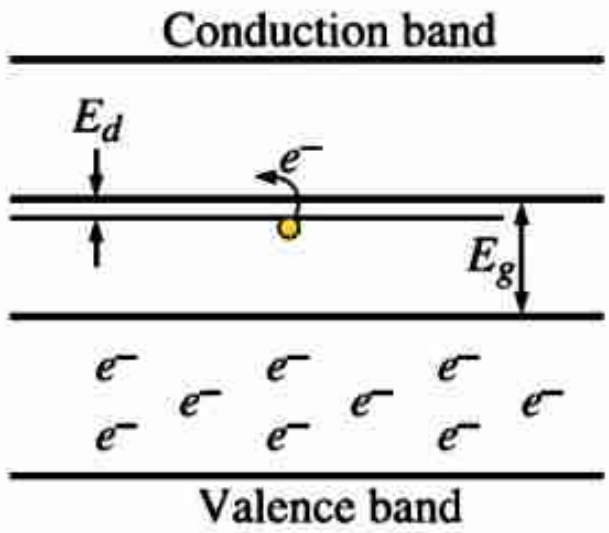


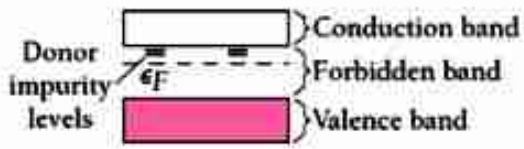
The electrical conductivity versus temperature for intrinsic semiconductors compared with metals. Note the break in the vertical axis scale.

Extrinsic Semiconductors

- Conductivity of extrinsic semiconductor depends primarily on number of impurity, or dopant, atoms and temperature.
- Presence of donor levels below conduction band raises Fermi energy above the middle of forbidden band between valence and conduction bands.

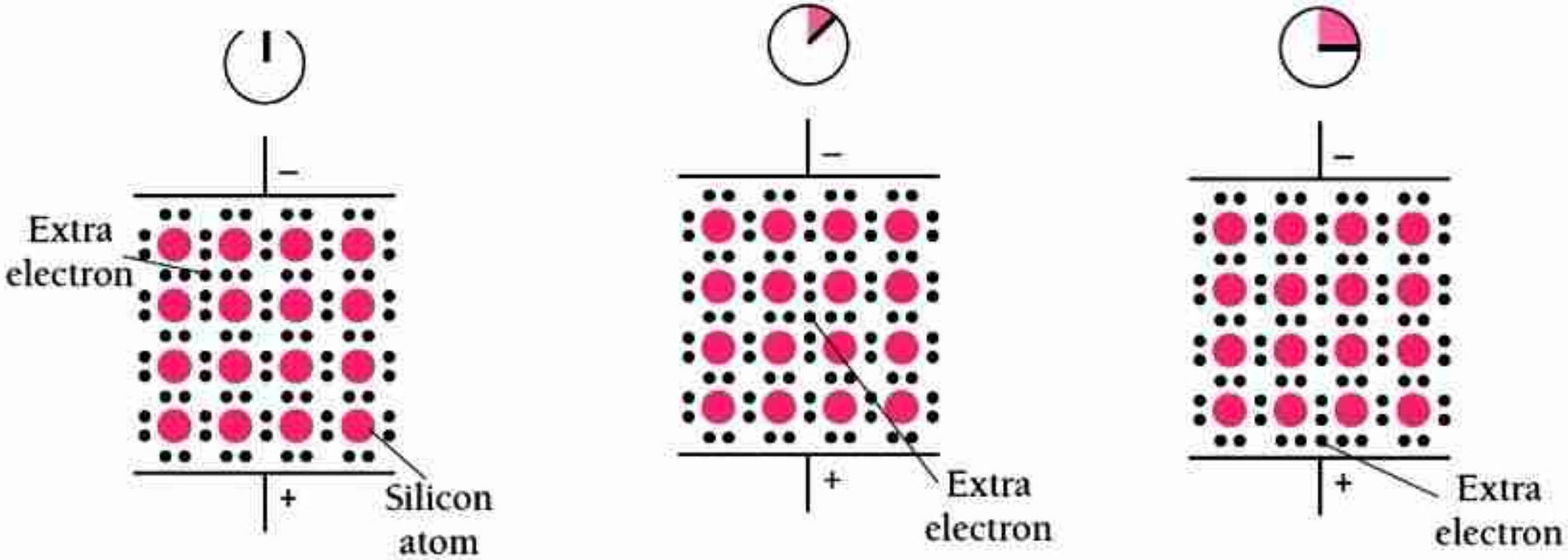






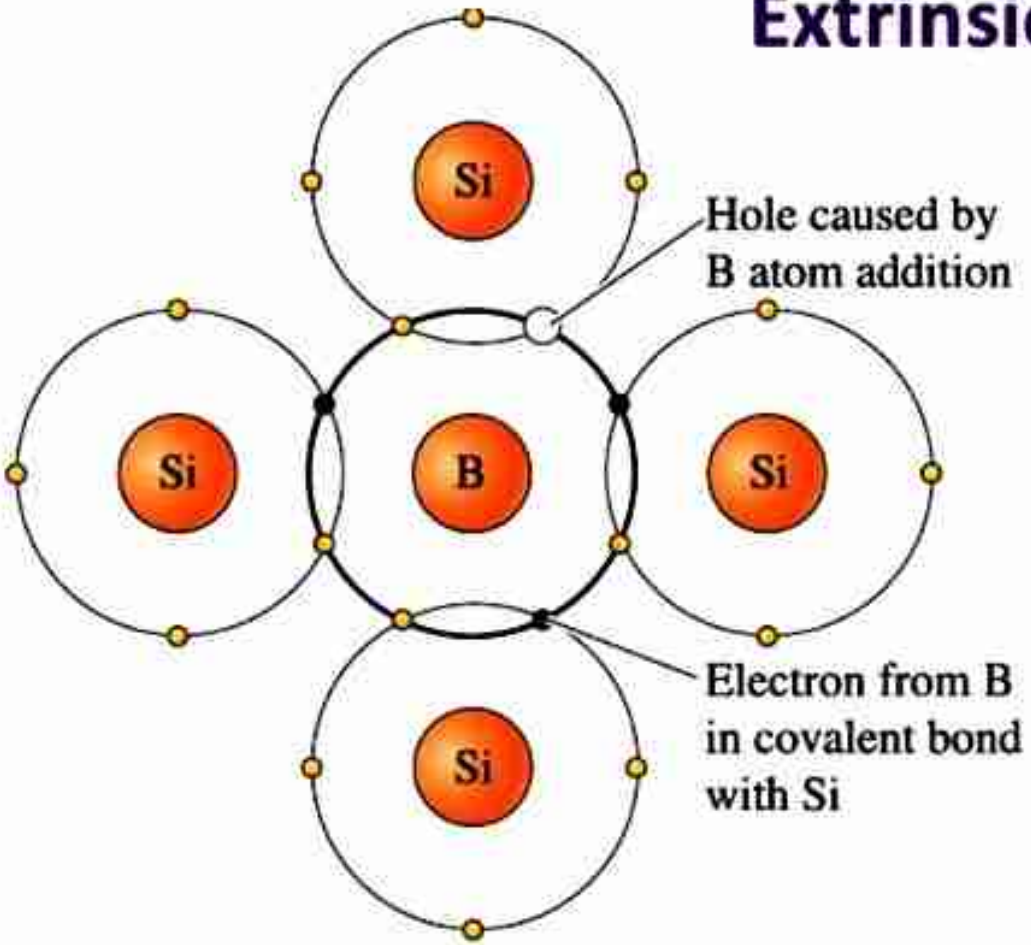
When a dopant atom with a valence greater than four is added to silicon, an extra electron is introduced and a donor energy state is created. Now electrons are more easily excited into the conduction band.

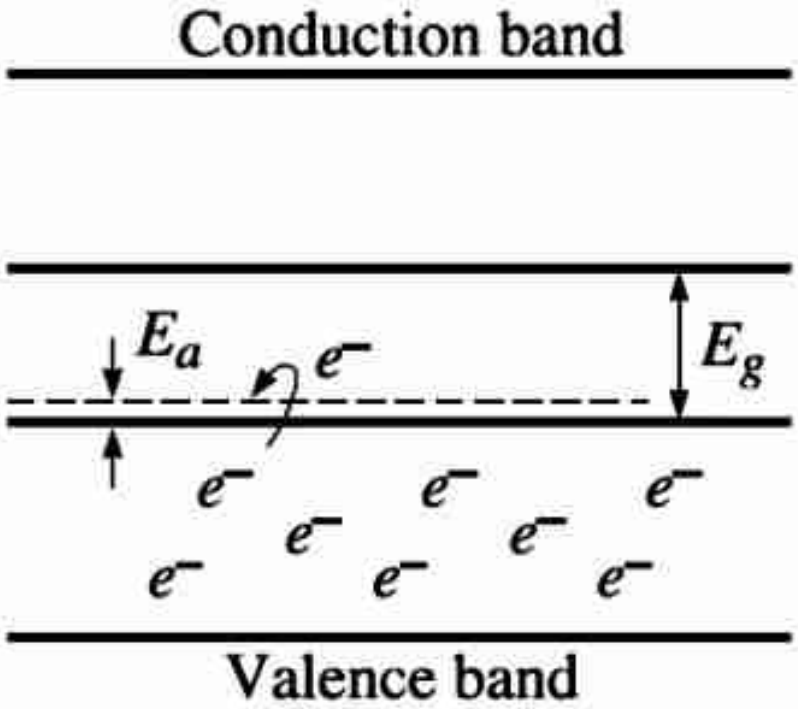
Extrinsic Semiconductors



Current in an n-type semiconductor is carried by surplus electrons that do not fit into the electron structure of a pure crystal.

Extrinsic Semiconductors

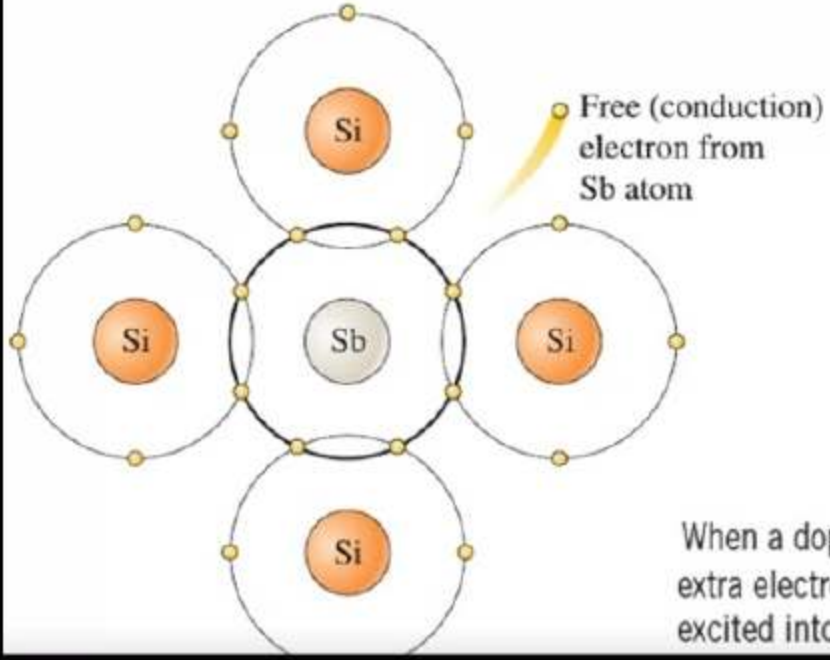


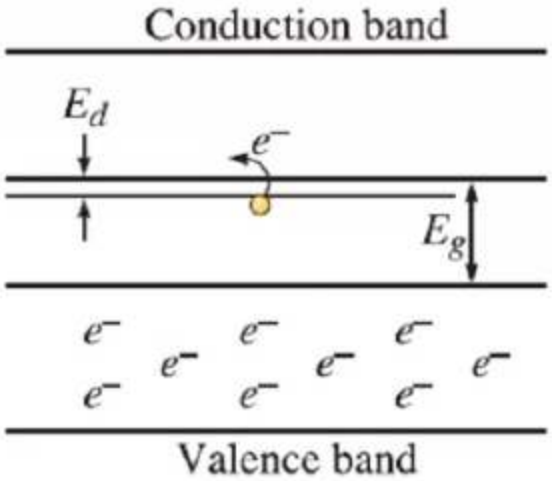


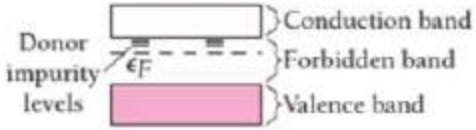
When a dopant atom with a valence of less than four is substituted into the silicon structure, a hole is introduced in the structure and an acceptor energy level is created just above the valence band.

Extrinsic Semiconductors

- Conductivity of extrinsic semiconductor depends on number of impurity, or dopant, atoms and temperature.
- Presence of donor levels below conduction band raises Fermi energy above middle of forbidden band between valence and conduction bands.

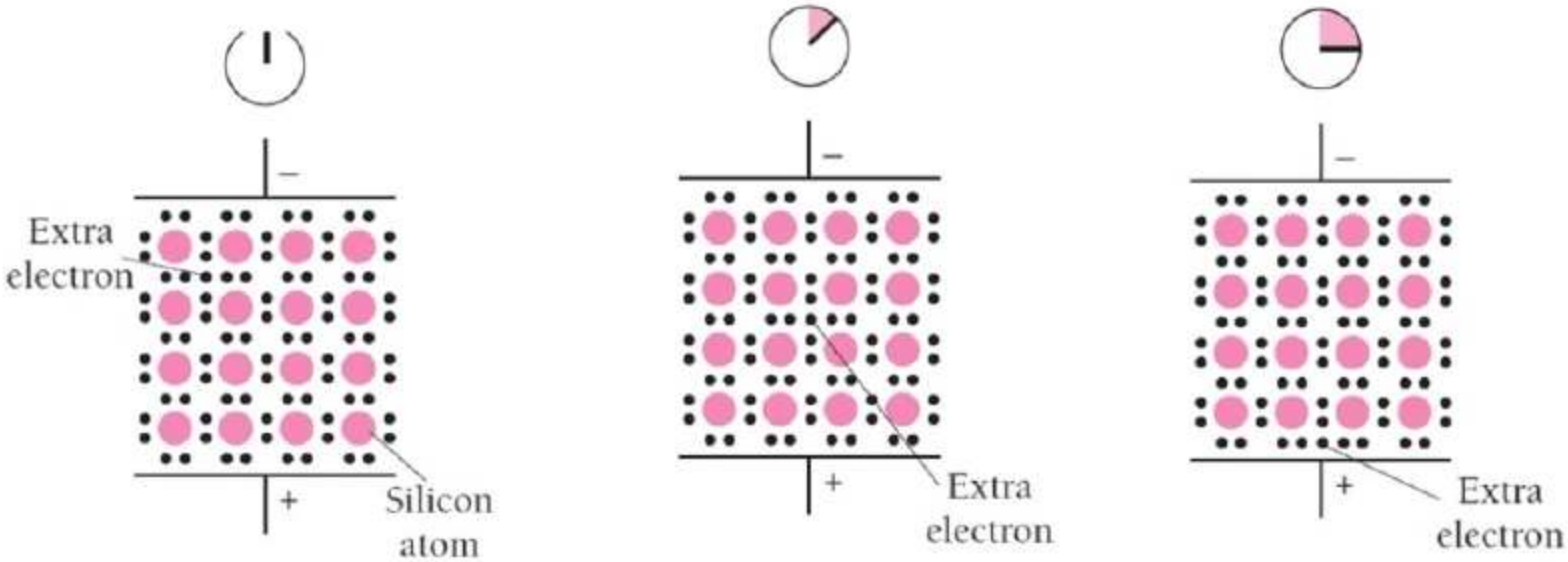






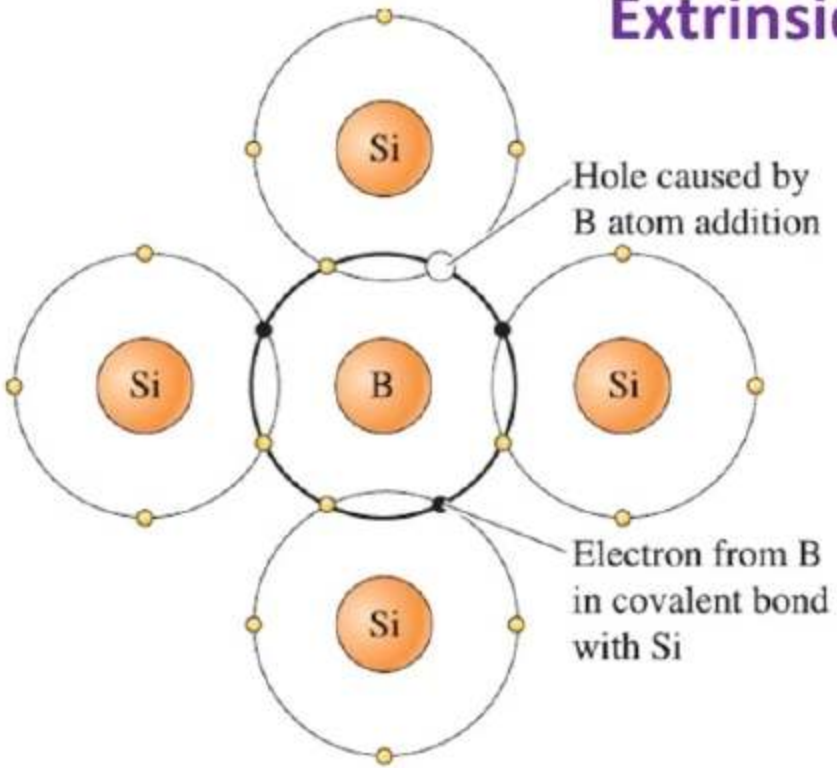
When a dopant atom with a valence greater than four is added to silicon, an extra electron is introduced and a donor energy state is created. Now electrons are more easily excited into the conduction band.

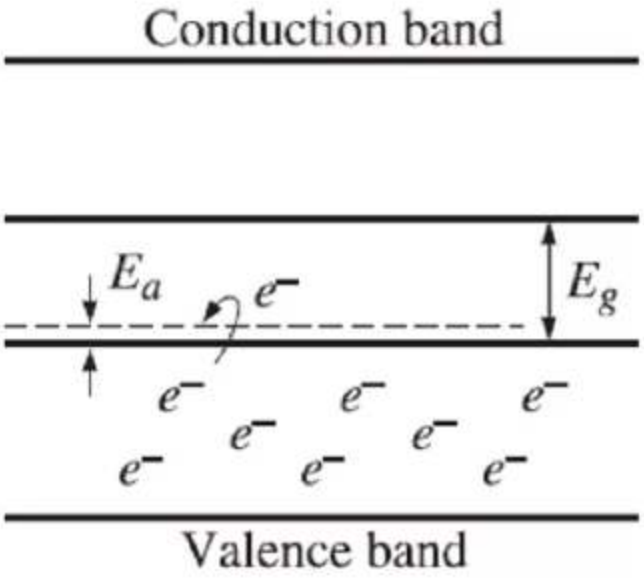
Extrinsic Semiconductors



Current in an n-type semiconductor is carried by surplus electrons that do not fit into the electron structure of a pure crystal.

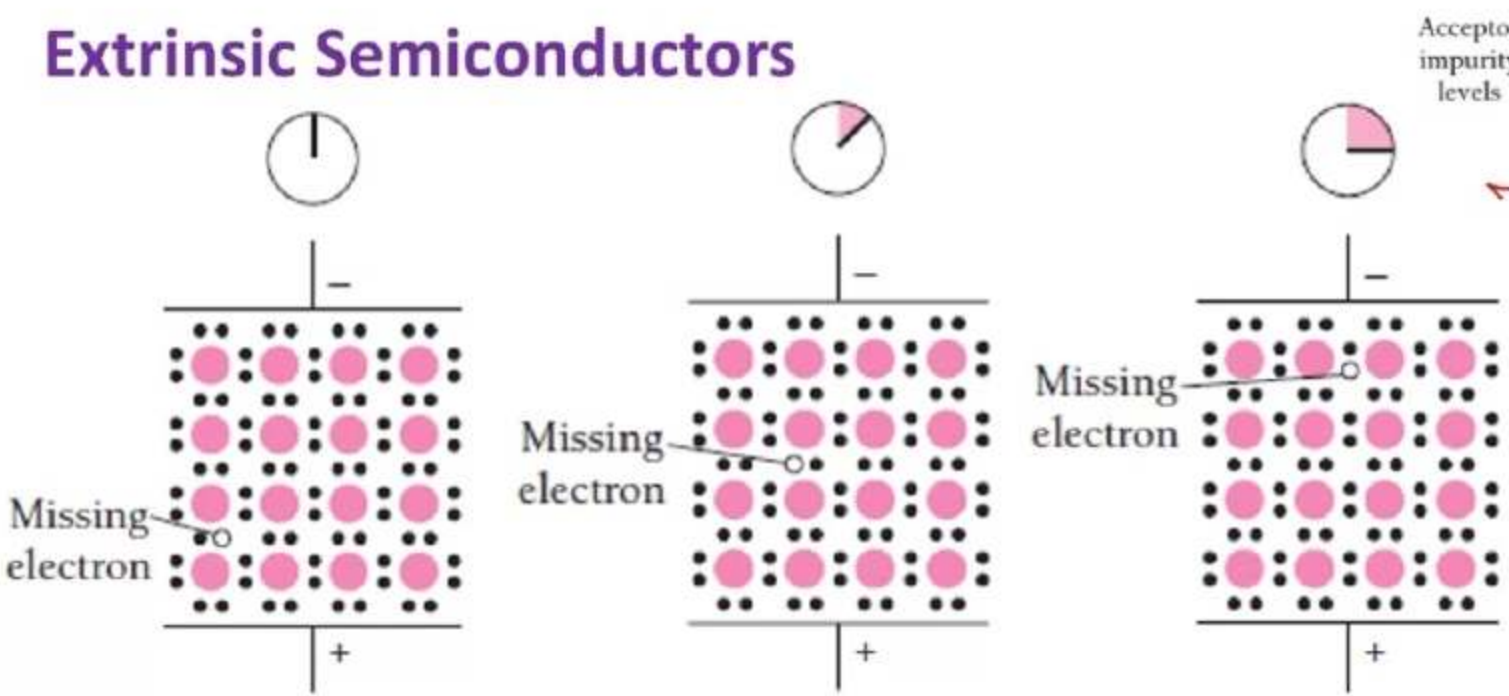
Extrinsic Semiconductors

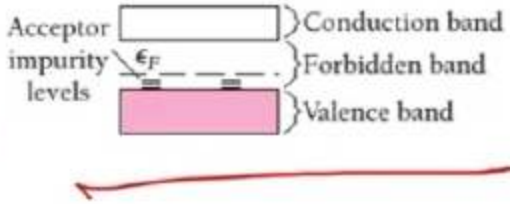




When a dopant atom with a valence of less than four is substituted into the silicon structure, a hole is introduced in the structure and an acceptor energy level is created just above the valence band.

Extrinsic Semiconductors





- Current in a p-type semiconductor is carried by the motion of "holes," which are sites of missing electrons.
- Holes move toward the negative electrode as a succession of electrons move into them.

Optical Properties of Solids

- Optical properties are related to energy-band structures.
- Photons of visible light have energies from about 1 to 3 eV.
- Metals are opaque: A free electron in a metal can readily absorb such an amount of energy without leaving its valence band.
- Characteristic luster of a metal is due to reradiation of light absorbed by its free electrons.
- If the metal surface is smooth, reradiated light appears as a reflection of original incident light.

Optical Properties of Solids

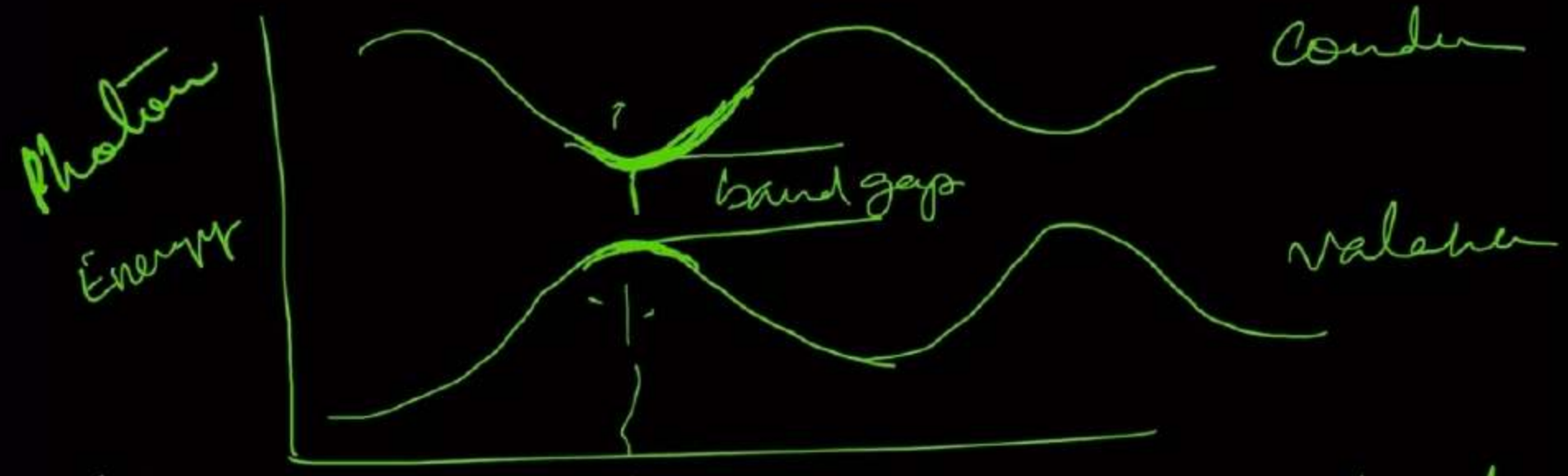
- Insulators cannot absorb photons of visible light (3 eV).
- For valence electron to absorb a photon, photon energy must be over 3 eV if electron is to jump across forbidden band to conduction band.
  - Insulators are transparent.
- Most samples of insulating materials do not appear transparent.
  - Scattering of light by irregularities in their structures.
- Insulators are opaque to ultraviolet light
  - Higher frequencies means high photon energies to allow electrons to cross forbidden band.

Optical Properties of Solids

- Forbidden bands in semiconductors are about same in width as photon energies of visible light
  - Semiconductors are usually opaque to visible light.
- Transparent to infrared light
  - Lower frequencies mean photon energies too low to be absorbed.
- For this reason infrared lenses can be made from the semiconductor germanium, whose appearance in visible light is that of an opaque solid.

Direct and Indirect Bandgap Semiconductors

- Direct bandgap semiconductor: an electron can be promoted from conduction band to valence band without changing the momentum of electron.
- When excited electron falls back into valence band, electrons and holes combine to produce light known as radiative recombination.
- Direct bandgap materials such as GaAs and solid solutions of these (e.g., GaAs-AlAs, etc.) are used to make light-emitting diodes (LEDs) of different colors.
- Direct bandgap materials are known as optoelectronic materials.


Photon
Energy
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band gap
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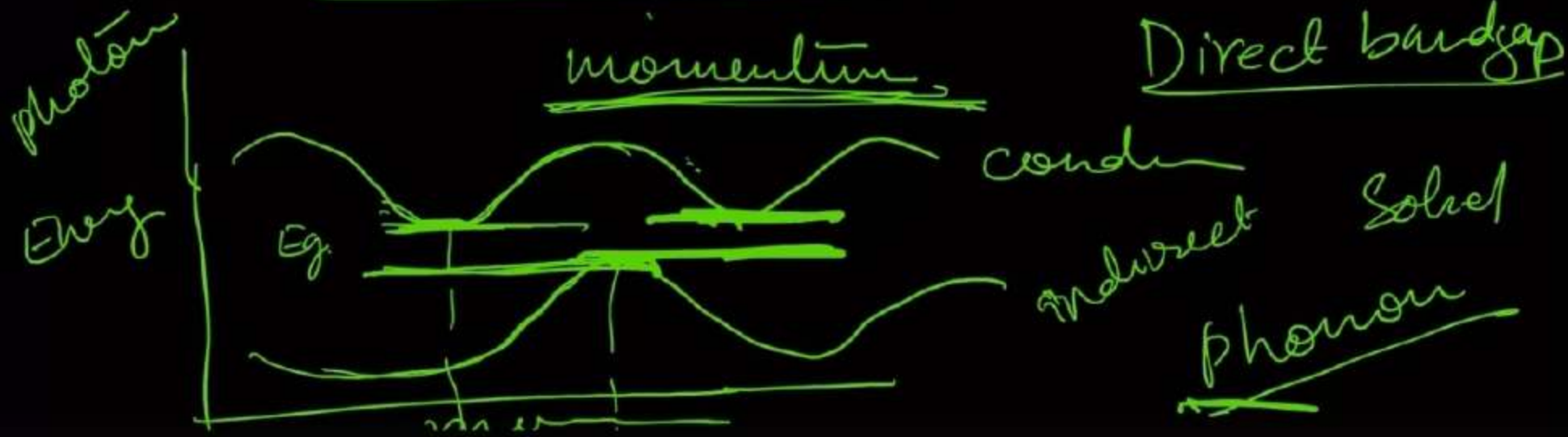
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Direct and Indirect Bandgap Semiconductors

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- Direct bandgap materials are known as optoelectronic materials.

Direct and Indirect Bandgap Semiconductors

- In an indirect bandgap semiconductor (e.g., Si, Ge, and GaP), electrons cannot be promoted to the valence band without a change in momentum.
- In materials that have an indirect bandgap (e.g., silicon), we cannot get light emission.
- Instead, electrons and holes combine to produce heat that is dissipated within material known as nonradiative recombination.
- Both direct and indirect bandgap materials can be doped to form n- or p-type semiconductors.

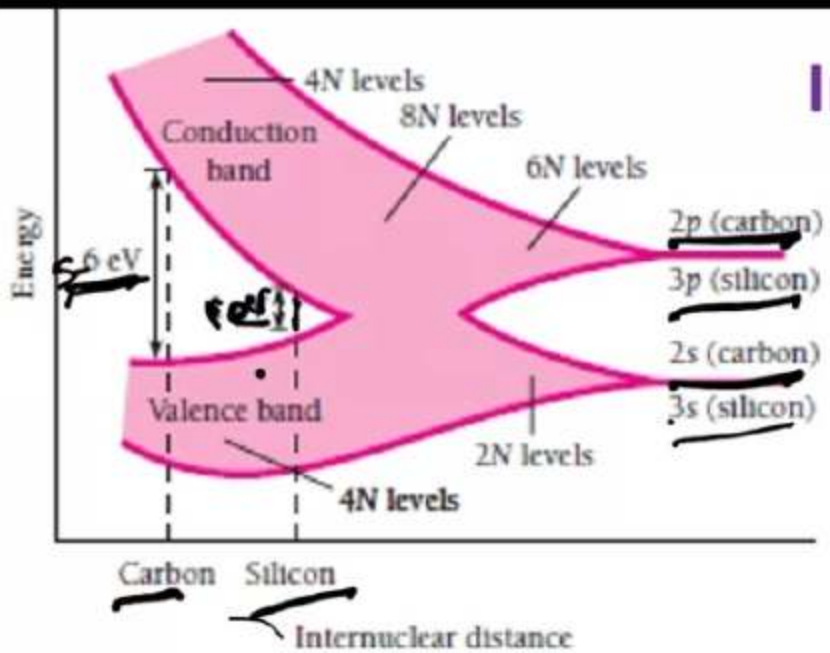
Applications of Semiconductors

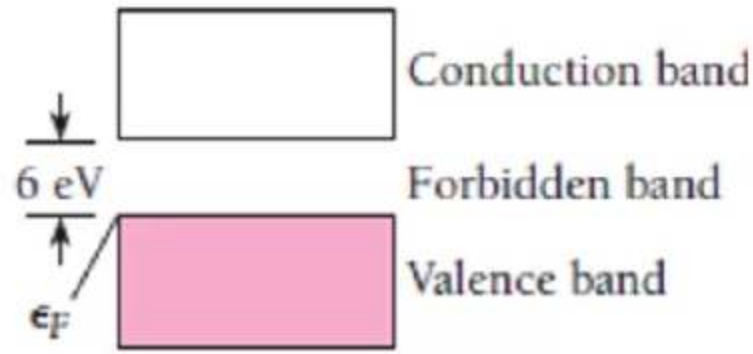
- Diodes, transistors, lasers, and LEDs are made using semiconductors. Silicon is the workhorse of very large scale integrated (VLSI) circuits.
- Forward bias - Connecting a *p-n* junction device so that the *p*-side is connected to positive. Enhanced diffusion occurs as the energy barrier is lowered, permitting a considerable amount of current can flow under forward bias.
- Reverse bias - Connecting a junction device so that the *p*-side is connected to a negative terminal; very little current flows through a *p-n* junction under reverse bias.
- Avalanche breakdown - The reverse-bias voltage that causes a large current flow in a lightly doped *p-n* junction.
- Transistor - A semiconductor device that can be used to amplify electrical signals.

Insulators and Dielectric Properties

- Materials used to insulate an electric field from its surroundings are required in a large number of electrical and electronic applications.
- Electrical insulators obviously must have a very low conductivity, or high resistivity, to prevent the flow of current.
- Porcelain, alumina, cordierite, mica, and some glasses and plastics are used as insulators.

Insulators





Fermi energy is at top of filled lower band.

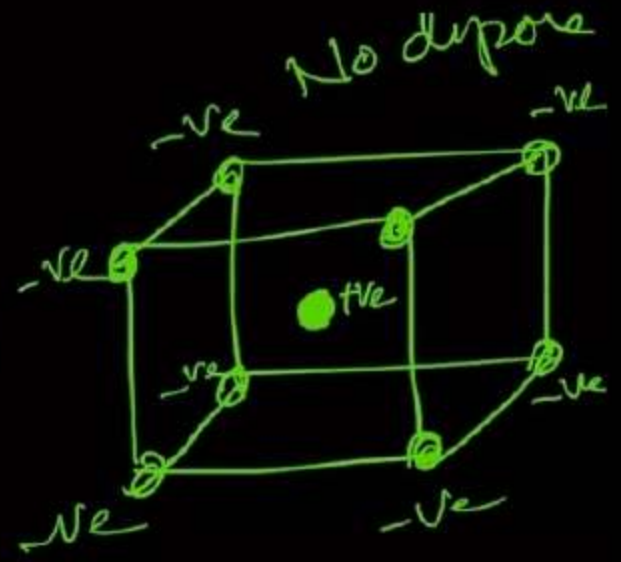
- 2s and 2p levels of carbon and 3s and 3p levels of silicon spread into bands that first overlap with decreasing atomic separation, Split into two diverging bands
- Lower band is occupied by valence electrons and upper conduction band is empty.
- Energy gap between bands depends on internuclear separation and is greater for carbon than for silicon.

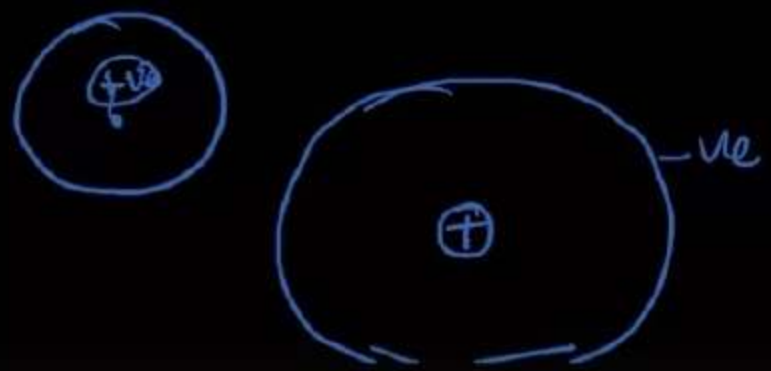
Polarization in Dielectrics

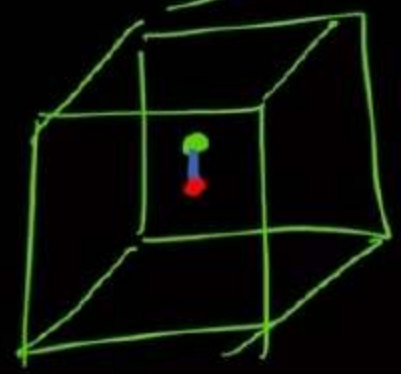
- Capacitor - A microelectronic device, constructed from alternating layers of a dielectric and a conductor, that is capable of storing a charge.These can be single layer or multi-layer devices.
- Permittivity - The ability of a material to polarize and store a charge within it.
- Linear dielectrics - Materials in which the dielectric polarization is linearly related to the electric field; the dielectric constant is not dependent on the electric field.
- Dielectric strength - The maximum electric field that can be maintained between two conductor plates without causing a breakdown.

Dielectric

1. electronic / atomic
2. ionic
3. orientational







Dielectric

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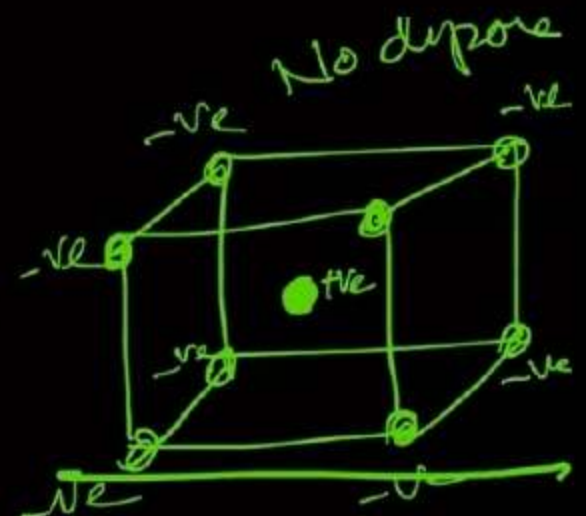

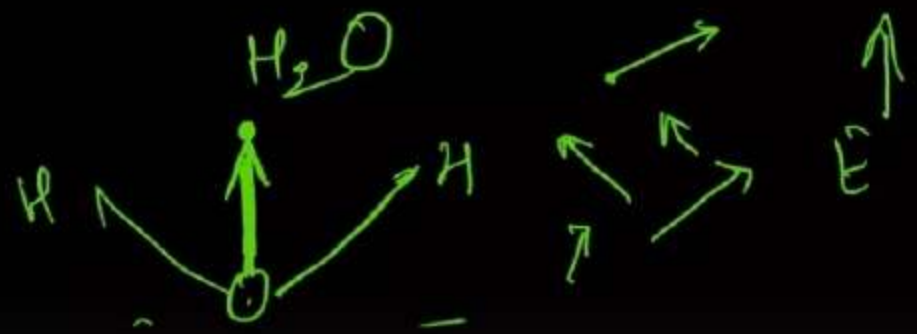

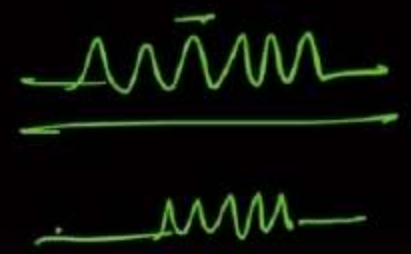

$BaTiO_3$

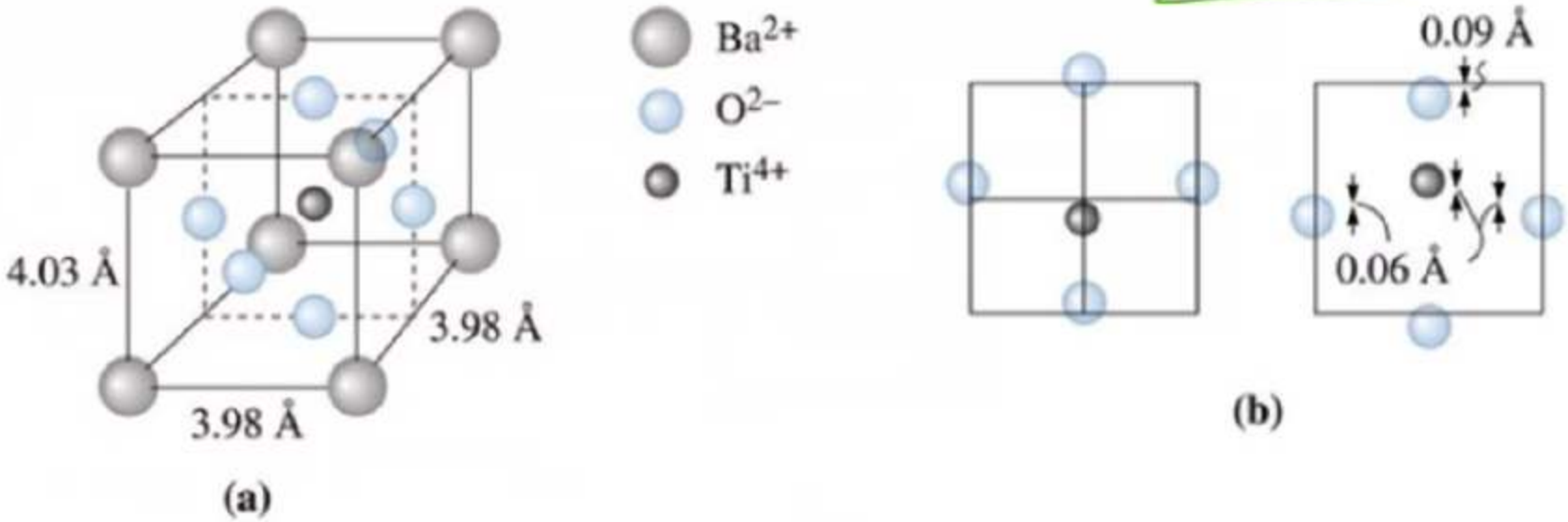

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Figure 18.28 (a) The oxygen ions are at face centers, Ba^{+2} ions are at cube corners and Ti^{+4} is at cube center in cubic $BaTiO_3$. (b) In tetragonal $BaTiO_3$, the Ti^{+4} is off-center and the unit cell has a net polarization.

Superconductivity

- Superconductivity - Flow of current through a material that has no resistance to that flow.
- Applications of Superconductors - Electronic circuits have also been built using superconductors and powerful superconducting electromagnets are used in magnetic resonance imaging (MRI). Also, very low electrical-loss components, known as filters, based on ceramic superconductors have been developed for wireless communications.

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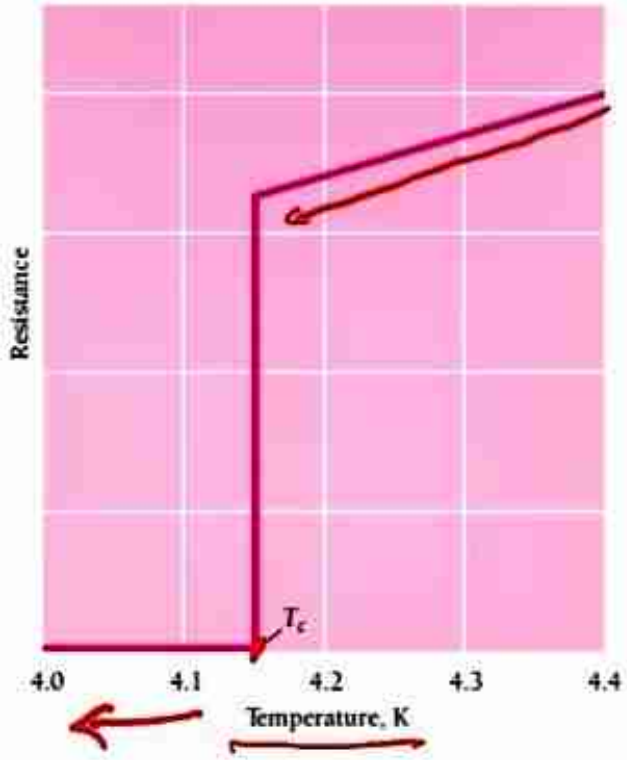
Superconductors

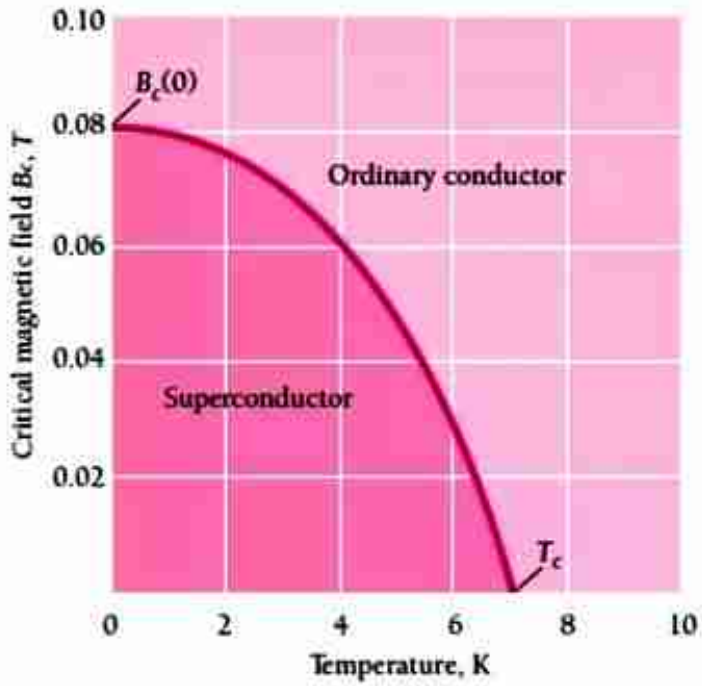
- At very low temperatures, most metals, many alloys, and some chemical compounds all allow current to pass freely through them. This phenomenon is called superconductivity.
- Elements which are ordinarily good conductors, such as copper and silver, do not become superconducting when cooled.



- Highest critical temperatures, as much as 134 K, are found in certain ceramic materials.
- Superconductors do have no resistance at all.

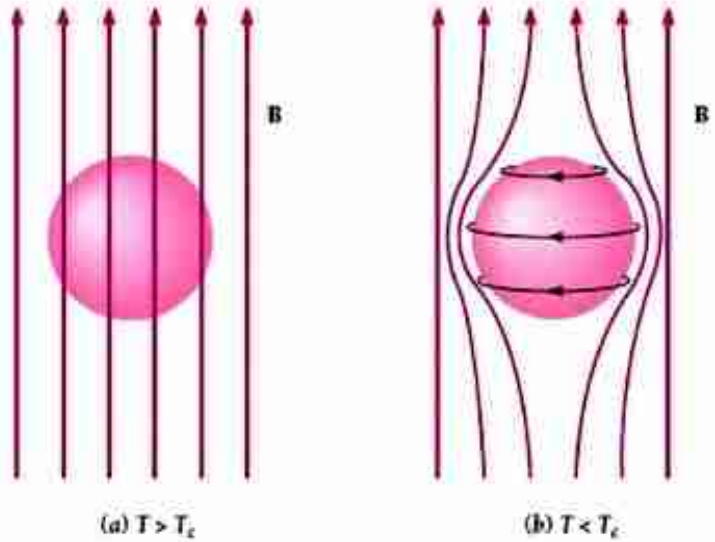
Superconductors

- Presence of a magnetic field causes critical temperature of type I superconductors to decrease.
- If magnetic field exceeds a certain critical value B_c, which depends on material and its temperature, its superconductivity disappears.



- Such materials are superconductors only for values of T and B below their respective curves and are normal conductors for values of T and B above these curves.
- Critical field B_c would be a maximum at 0 K.

Superconductors



- Superconductors are perfectly diamagnetic—no magnetic field can exist inside them under any circumstances.
- If we put a sample of a superconductor in a magnetic field weaker than critical field and then reduce temperature below Tc, field is expelled from the interior of the sample.
- Currents appear on surface of the sample whose magnetic fields exactly cancel the original field inside it.

Superconductors

$T > T_c$

rdinary conductor whose resistance

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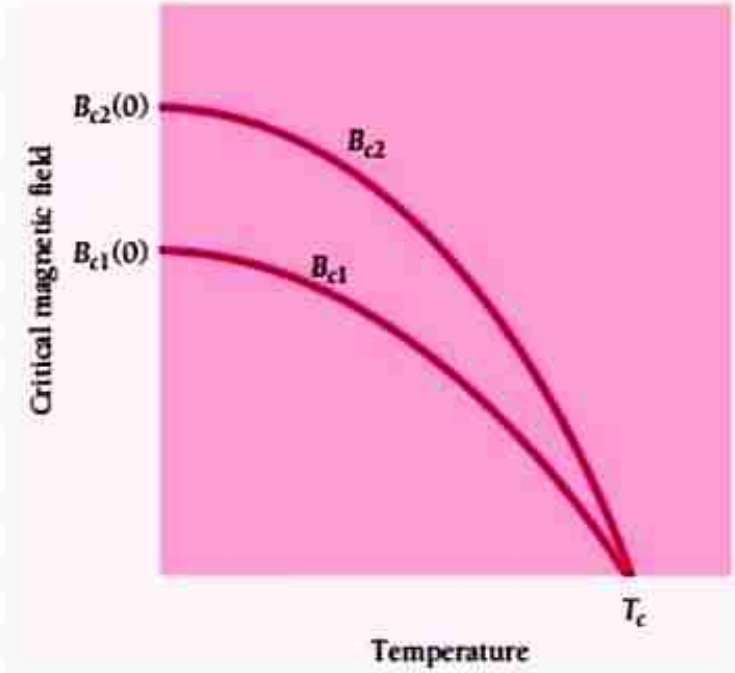

:ritical magnetic fields B_{c1} and B_{c2} with temperature for a type II su- ...lds between B_{c1} and B_{c2} the material is in a mixed state in which it is ıetic field can exist in its interior.

Superconductors

- For $B < B_{c1}$, type II superconductor behaves just like its type I counterpart : superconducting with no magnetic field in its interior.
- When $B > B_{c2}$, a type II superconductor exhibits normal behaviour, again like a type I superconductor.
- In applied fields between B_{c1} and B_{c2}, a type II superconductor is in a mixed state in which it contains some magnetic flux but is superconducting.
- Stronger the external field, the more flux penetrates the material, up to the higher critical field B_{c2}.

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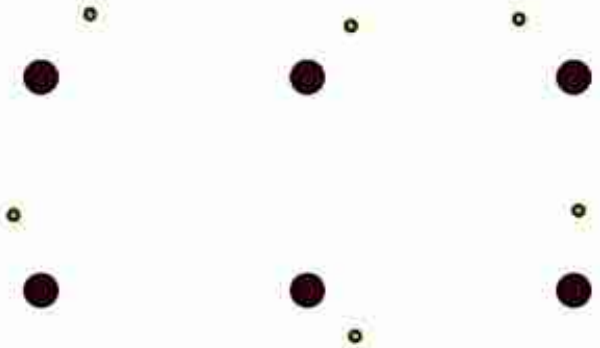
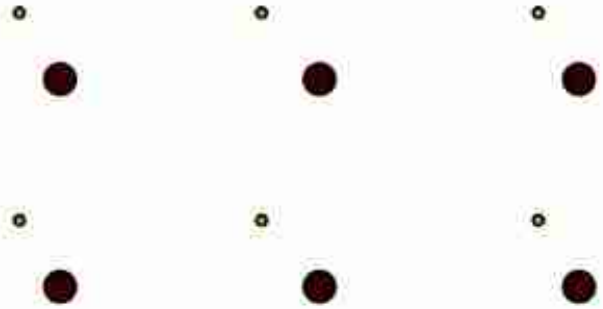
Superconductors

- A type II superconductor behaves as though it consists of filaments of normal and of superconducting matter mixed together.
- A magnetic field can exist in the normal filaments, while the superconducting filaments are diamagnetic and resistance less like type I superconductors.
- B_{c2} can be quite high
- Used to make high-field (up to 20 T) magnets for particle accelerators, fusion reactors, magnetic resonance imagery, and experimental **maglev** (magnetic levitation) trains in which magnetic forces provide both propulsion and frictionless support.

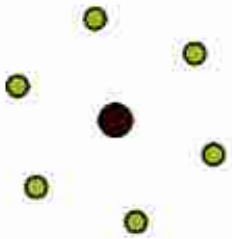
London Conjecture



In a normal state the electrons each have a separate wavefunction and move independently



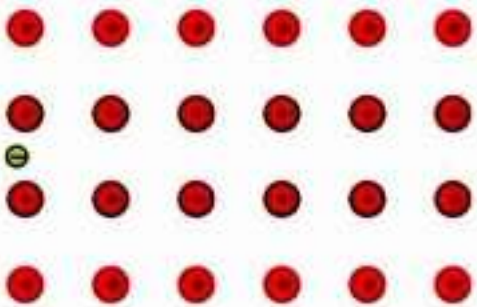
In a superconducting state some of the electrons act as though they have a single wavefunction. Thus they all move in phase and are said to be **coherent** - much like light is in a laser.



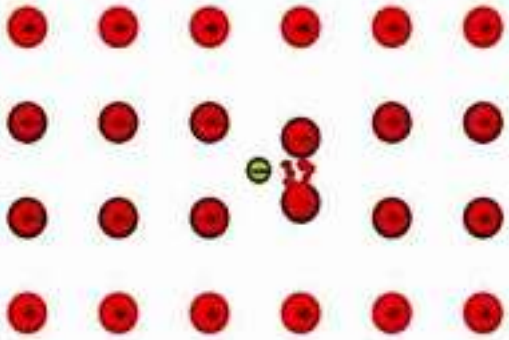
Therefore this state could be considered to be one giant atom with the electrons orbiting a single nucleus

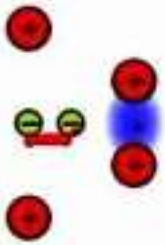
Cooper Pair Formation

In order to understand how an attraction between two electrons can occur, we must consider the interaction with the lattice.

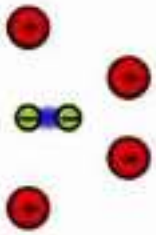


As an electron moves through the positively charged ion cores of the lattice, it attracts them and causes a distortion.





The area of positive charge can attract another electron towards the first



This attraction can overcome the repulsive Coulombic forces and create a binding between the two electrons.

moves through the positively charged ion
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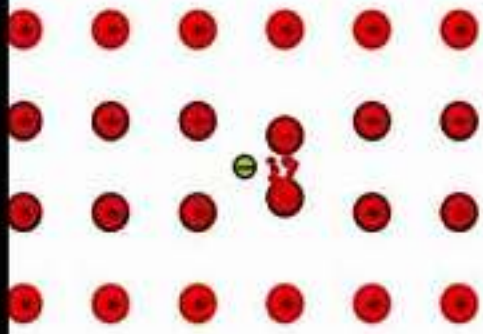
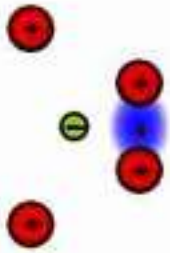
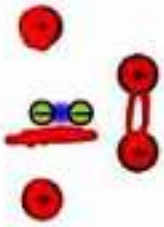
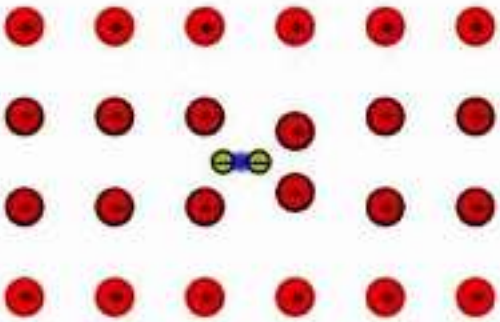




The distortion of the lattice causes the local area to gain a small net positive charge.





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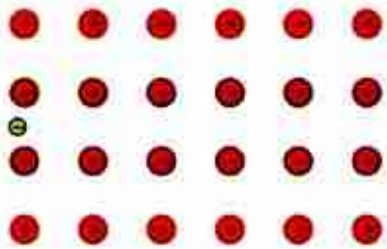
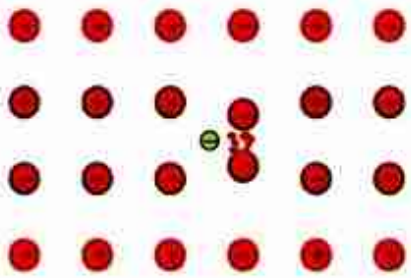
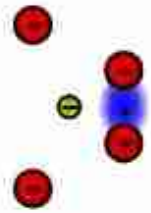
Cooper Pair Formation

In order to understand how an attraction between two electrons can occur, we must consider the interaction with the lattice.

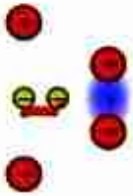


As an electron moves through the positively charged ion cores of the lattice, it attracts them and causes a distortion.

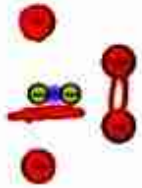




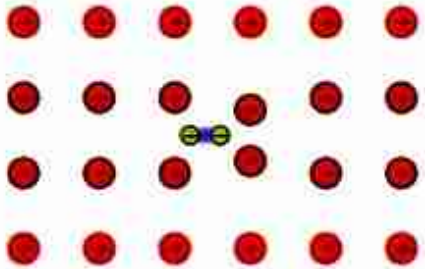
The distortion of the lattice causes the local area to gain a small net positive charge.



The area of positive charge can attract another electron towards the first



This attraction can overcome the repulsive Coulombic forces and create a binding between the two electrons.



This attraction can overcome the repulsive Coulombic forces and create a binding between the two electrons.

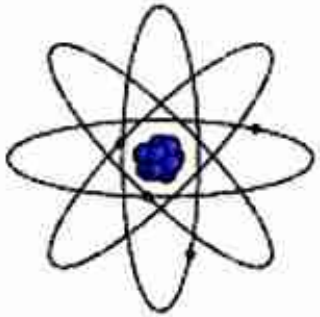
The electrons can then travel through the lattice as a single entity, known as a Cooper Pair.

Electrons vs Cooper Pairs

Quantum Statistics:
Occupying Energy Levels

Applying an Electric Field:
Metals vs Superconductors

Superconductors:
Origin of the Energy Gap

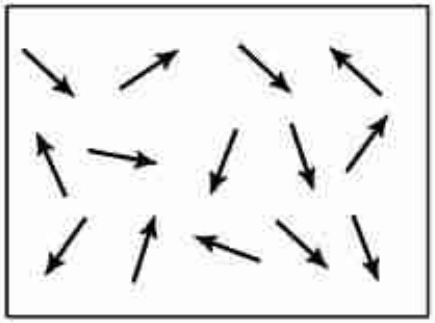


- Superconducting current is carried by Cooper pairs that have to be scattered as a single object without being broken apart.
- Cooper pair must be split apart to scatter individual electron to cause electrical resistance.
- This requires an energy at least equal to energy gap produced by binding energy of Cooper pairs.

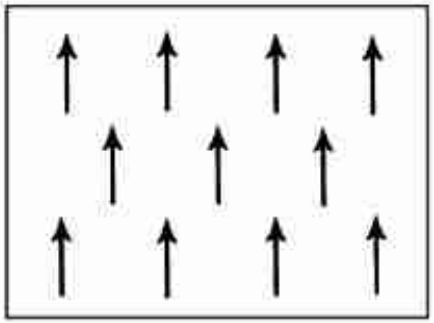
Electrons vs Cooper Pairs

- Due to random energy fluctuations, even at $T < T_c$, there will sometimes be enough energy to break the pair and alter the momentum of electrons.
- To stop current all of the pairs must be broken.
- With increase temperature above T_c more and more pairs are broken as electrons are excited above the energy gap.
- At T_c there are no Cooper pairs left.
- "free electrons" from broken Cooper Pair called as quasi-particles.
- At $T > 0$ K, there will be both bound pairs and quasi-particles present.

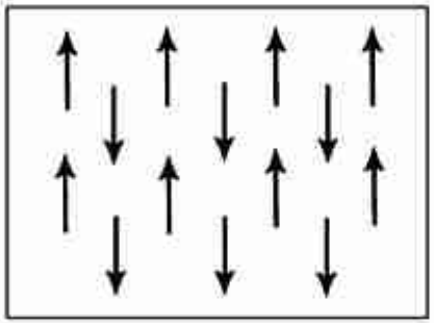
MAGNETIC MATERIALS



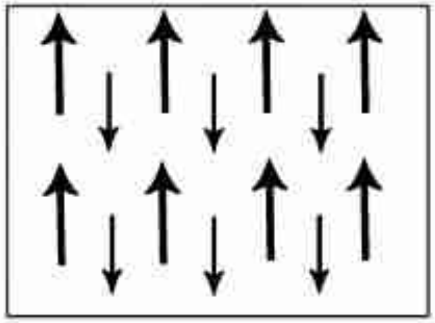
Paramagnetism



Ferromagnetism



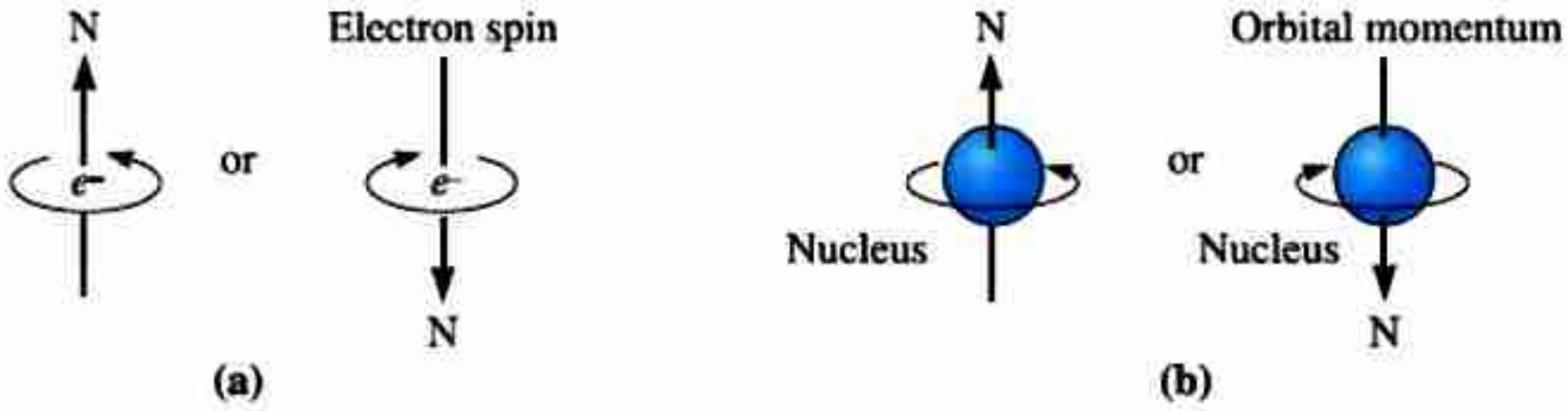
Antiferromagnetism



Ferrimagnetism

- Total magnetic moment of a free atom has two contributions from each electron:
  - **Orbital motion of electron around nucleus**
  - **Spin motion of electron itself**

Magnetic Dipoles and Magnetic Moments

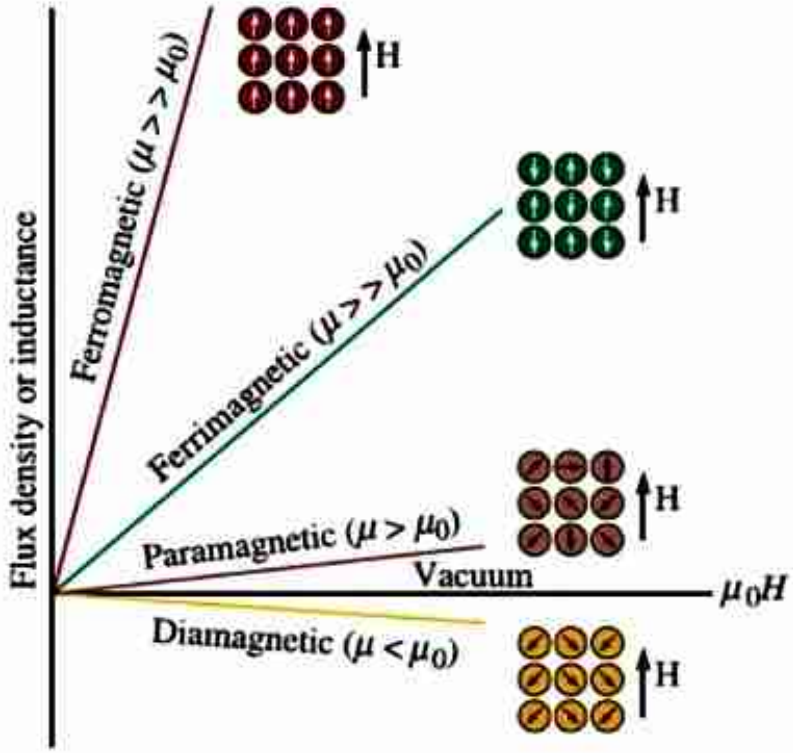


Magnetic moment of an electron due to its spin is known as Bohr magneton (μ_B).

$$\mu_B = \text{Bohr magneton} = \frac{qh}{4\pi m_e} = 9.274 \times 10^{-24} \text{A} \cdot \text{m}^2$$

Magnetic Dipoles and Magnetic Moments

- Magnetic moment opposes the field in diamagnetic materials.
- Progressively stronger moments are present in paramagnetic, ferrimagnetic, and ferromagnetic materials for same applied field.



Effect of core material on flux density.

Superparamagnetism

- When grain size of ferromagnetic and ferrimagnetic materials falls below certain critical size, materials behave as paramagnetic known as superparamagnetism.
- Magnetic dipole energy of each particle becomes comparable to thermal energy.
- This small magnetic moment changes its direction randomly (as a result of thermal energy). Thus, material behaves as if it has no net magnetic moment.
- Ex. Iron oxide (Fe_3O_4) in a 3 to 5 nm size, behave as superparamagnetic materials.
- Superparamagnetic particles of Fe_3O_4 are used to form dispersions in aqueous or organic carrier phases or to form "liquid magnets" or ferrofluids.

Superparamagnetism

- Particles in fluid move in response to a gradient in magnetic field.
- Since particles form a stable sol, entire dispersion moves and, hence, material behaves as a liquid magnet.
- Such materials are used as seals in computer hard drives and in loudspeakers as heat transfer (cooling) media.
- Permanent magnet used in loudspeaker holds liquid magnets in place.
- Superparamagnetic particles of Fe_3O_4 also can be coated with different chemicals and used to separate DNA molecules, proteins, and cells from other molecules.

Unit-III

Nanotechnology

A Frontier Field

Nanotechnology: Introduction

- Ultrafine microstructures of grain size of order nanometer (10^{-9}m) called nanostructured materials (NSMs).
- Currently, wider meaning,
  - Any material containing grains or clusters below 100 nm, or layers or filaments of that dimension, called as NSMs.
- Stimulated Interest in these materials owing to
  - Small size of building blocks (particle, grain, or phase)
  - High surface-to-volume ratio
- Expected to demonstrate unique
  - Mechanical
  - Optical
  - Electronic
  - Magnetic properties

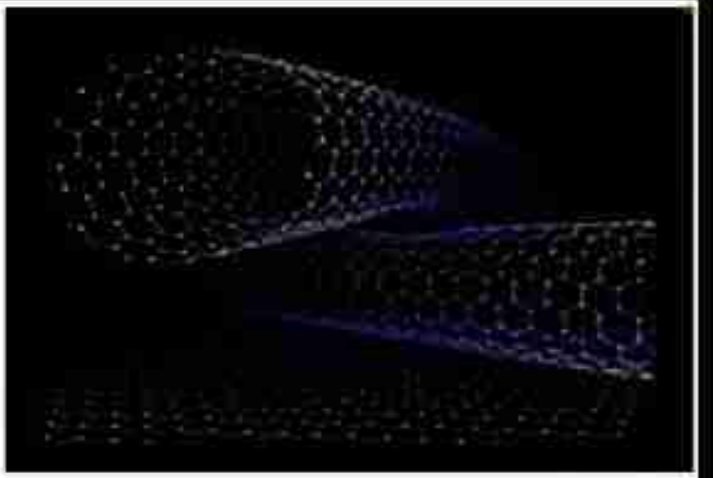
Nanotechnology: Introduction

- Properties of NSMs depend on
  - **Fine grain size and size distribution** (« 100 nm)
  - **Chemical composition of constituent phases**
  - **Presence of interfaces, more specifically**
    - Grain boundaries
    - Heterophase interfaces
    - Or free surface
  - **Interactions between constituent domains.**
- Presence and interplay of these four features largely determine unique properties of NSMs

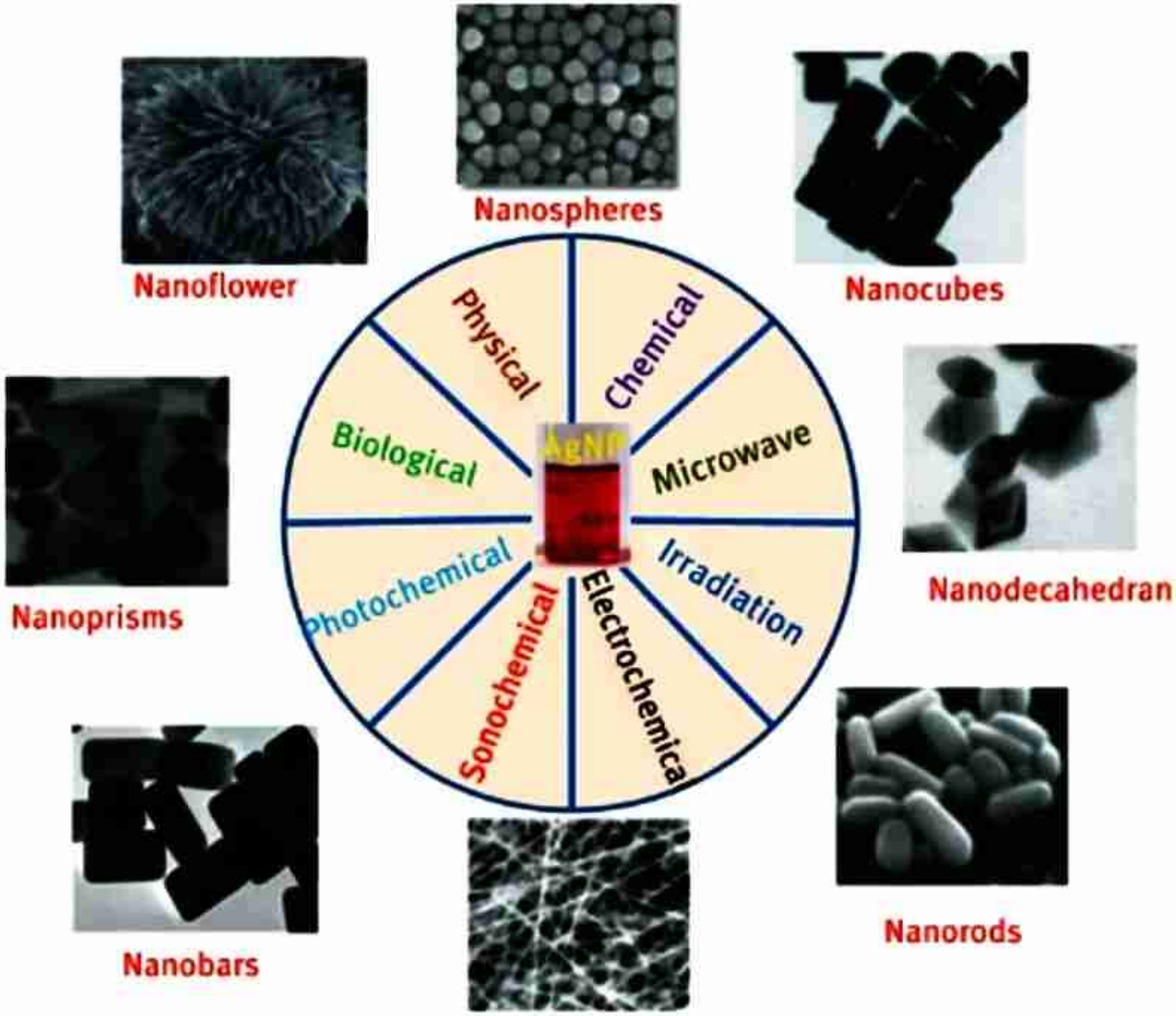
Types of Nanoparticles

- **Natural nanomaterials**—A nanomaterial made by nature through (bio)geochemical or mechanical processes, without direct or indirect connection to a human activity or anthropogenic process.
- **Incidental nanomaterials**—A nanomaterial unintentionally produced as a result of any form of direct or indirect human influence or anthropogenic process.
- **Engineered nanomaterials**—A nanomaterial conceived, designed, and intentionally produced by humans.
- **Anthropogenic nanomaterials**—Both incidental and engineered nanomaterials.

Shapes of Nanoparticles



- Nanosheets or nanofilms have one dimension in this size range; (e.g., clay minerals)
- Nanorods have two dimensions in this size range
- Nanoparticles have three dimensions in this size range
- Nanotubes are nanoscale materials that have a tube-like structure; e.g., carbon nanotubes in the accompanying figure.


Nanoflower
Nanospheres
Nanocubes
Nanoprisms
Nanodecahedran
Nanobars
Nanorods
Physical
Chemical
Biological
Microwave
Photochemical
Irradiation
Sonochemical
Electrochemical
AgNP

Size is a Material Property?

<u>The gold we know:</u>

Material properties don't change with size
- resistivity
- melting point
- optical absorption

<u>The gold we are discovering:</u>

Material properties (such as optical Absorption, shown here) change with the size of the gold nanoparticle.

Unique Characteristics of Nanoparticles

- Large surface to volume ratio
- High percentage of atoms/molecules on the surface
- Surface forces are very important, while bulk forces are not as important.
- Metal nanoparticles have unique light scattering properties and exhibit plasmon resonance.
- Semiconductor nanoparticles may exhibit confined energy states in their electronic band structure (e.g.quantum dots)
- Can have unique chemical and physical properties
- Same size scale as many biological structures

Examples of Unusual Properties

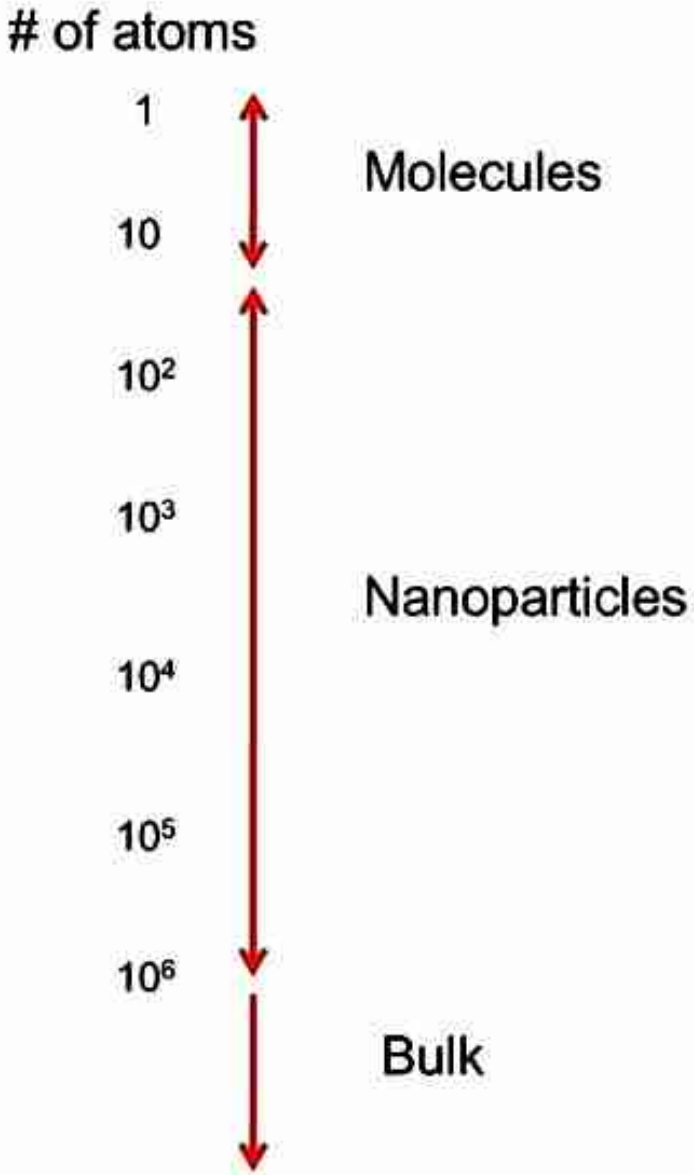
- Lowered phase transition temps
- Increased mechanical strength
- Different optical properties
- Altered electrical conductivity
- Magnetic properties
- Self-purification and self-perfection

Physical Properties of Nanoparticles

- Physical properties of nanoparticles are dependent on:
  - Size
  - Shape (spheres, rods, platelets, etc.)
  - Composition
  - Crystal Structure (FCC, BCC, etc.)
  - Surface ligands or capping agents
  - Medium in which they are dispersed

Size

- Molecules, nanoparticles, and bulk materials can be distinguished by the number of atoms comprising each type of material.
- *Note:* these are very approximate numbers!



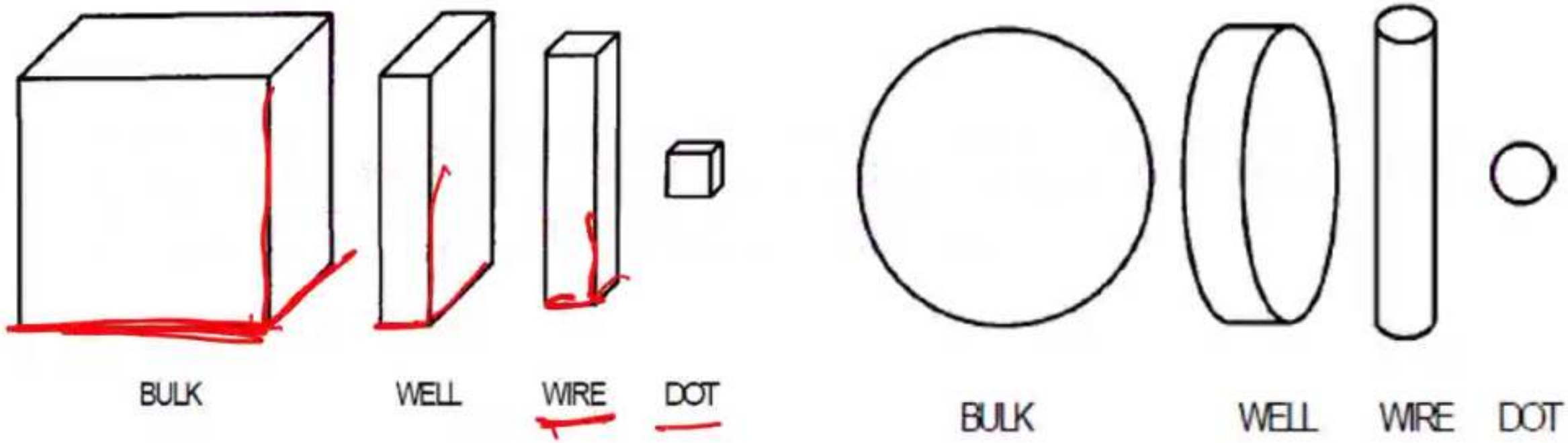
QUANTUM WELLS, WIRES, AND DOTS

- Word **quantum** is associated with three types of nanostructures
  - changes in properties arise from quantum-mechanical nature of physics in the domain of the ultrasmall.
- If one dimension is reduced to nano-range while other two dimensions remain large, then structure known as a **quantum well**.
- If two dimensions are so reduced and one remains large, structure is referred to as a **quantum wire**.
- Size reduction in all three dimensions is called **quantum dot**.

Electronic Structure

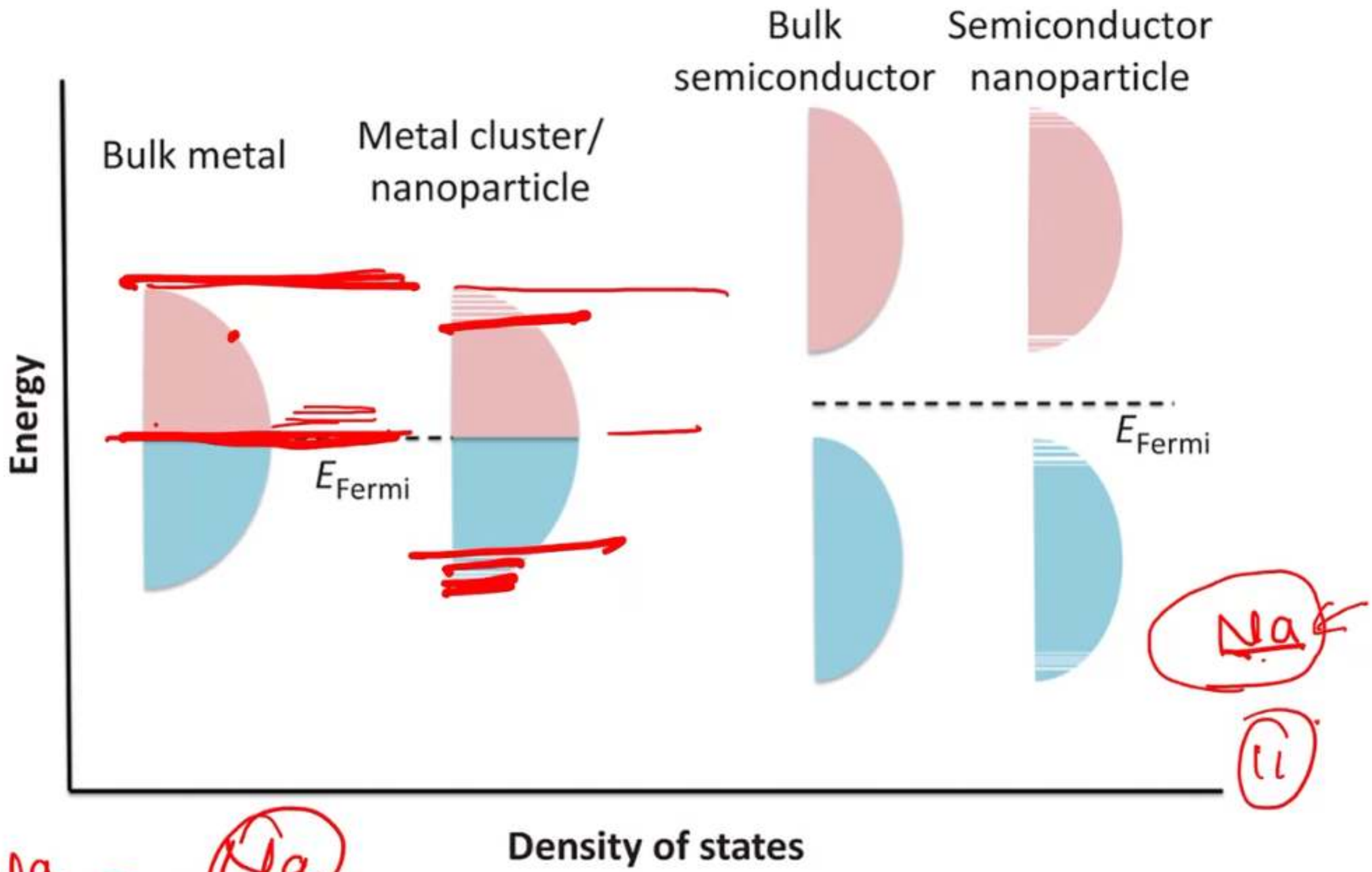
- Spacing of electronic levels and bandgap increases with decreasing particle size.
  - Because electron-hole pairs are now much closer together and Coulombic interaction between them can no longer be neglected giving an overall higher kinetic energy.
- Increase in bandgap can be observed experimentally by blue-shift in the absorption spectrum or sometimes even visually by colour of samples.
- A larger bandgap means more energy is required to excite an electron from valance band to conduction band.
  - hence light of a higher frequency and lower wavelength would be absorbed.

QUANTUM WELLS, WIRES, AND DOTS



- Dimensionality effects that occur when one, two, or all three dimensions becomes small.
- How electronic properties are altered by these changes?

Electronic Structure

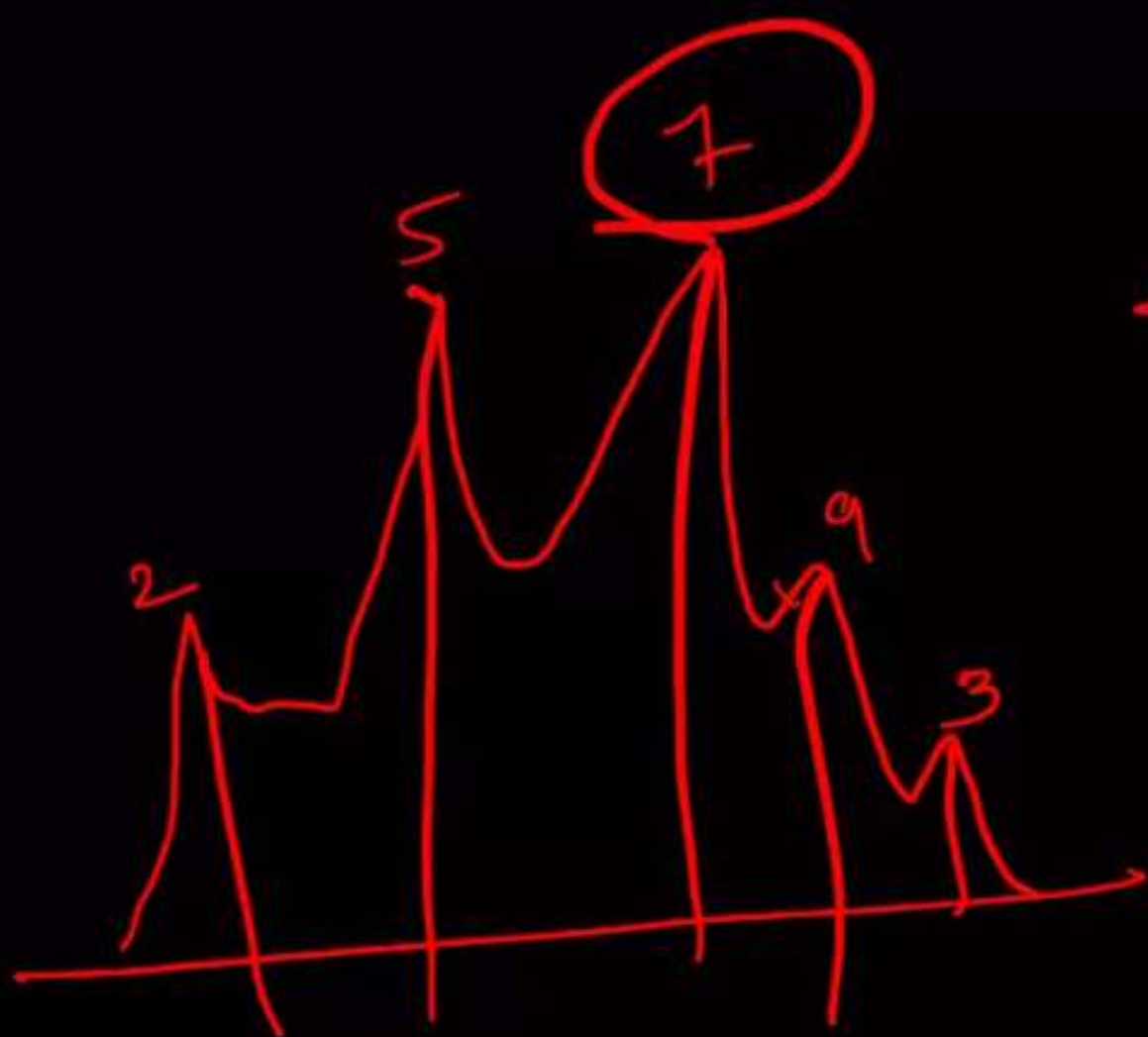


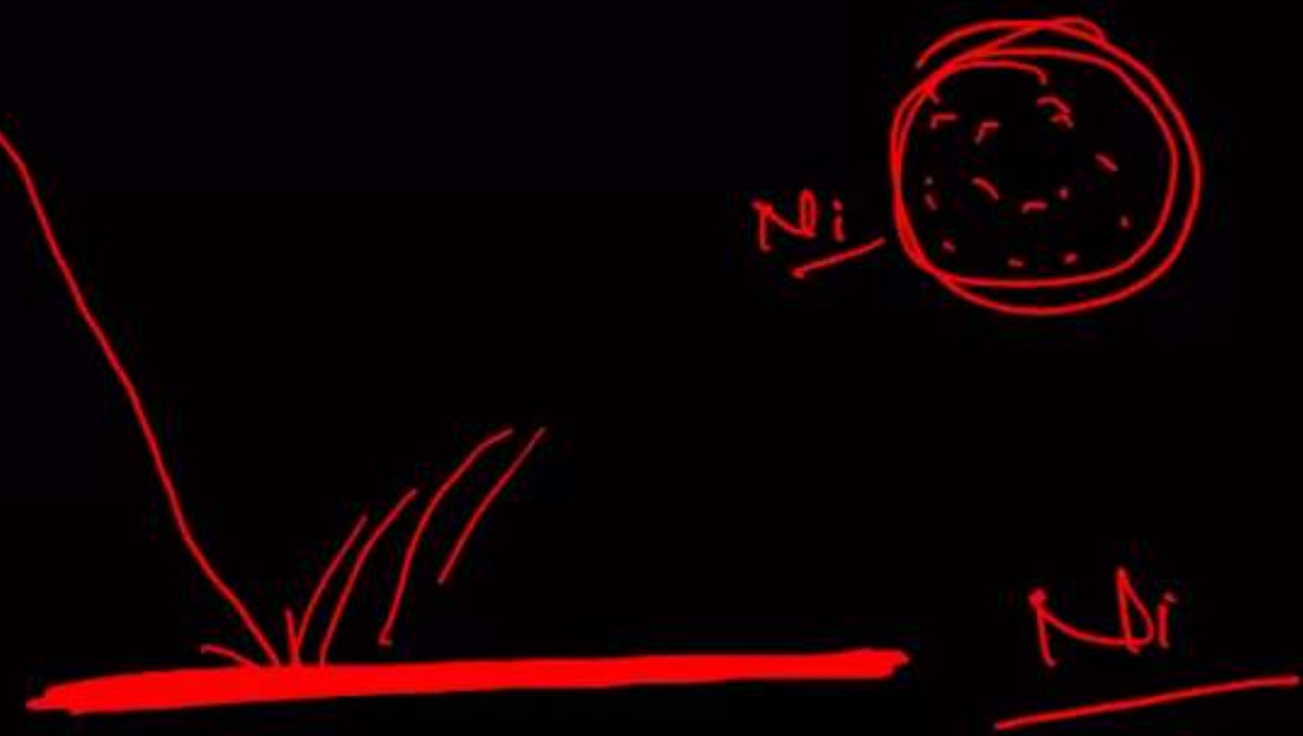
Na

(11)

Na

(11)





Ni 7 O2Ni

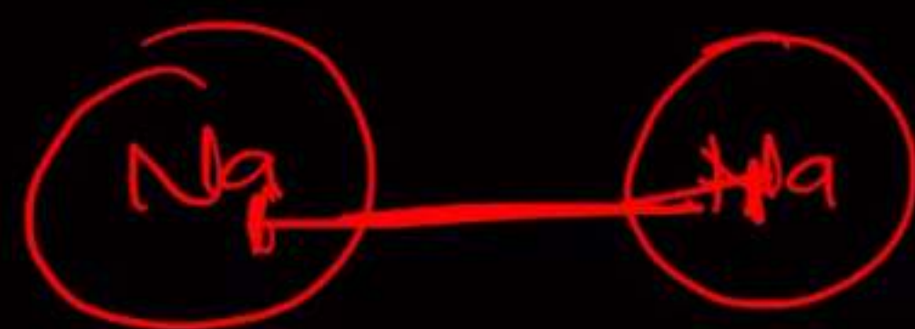
Cluster

O5

QUANTUM CONFINEMENT

- Particle behaves as if it was free when confining dimension is large compared to wavelength of particle.
- During this state, bandgap remains at its original energy due to a continuous energy state.
- As confining dimension decreases typically in nanoscale, energy spectrum becomes discrete.
- As a result, bandgap becomes size-dependent.
- As size of particles decreases, electrons and electron holes come closer, and energy required to activate them increases,
- Results in a blueshift in light emission.

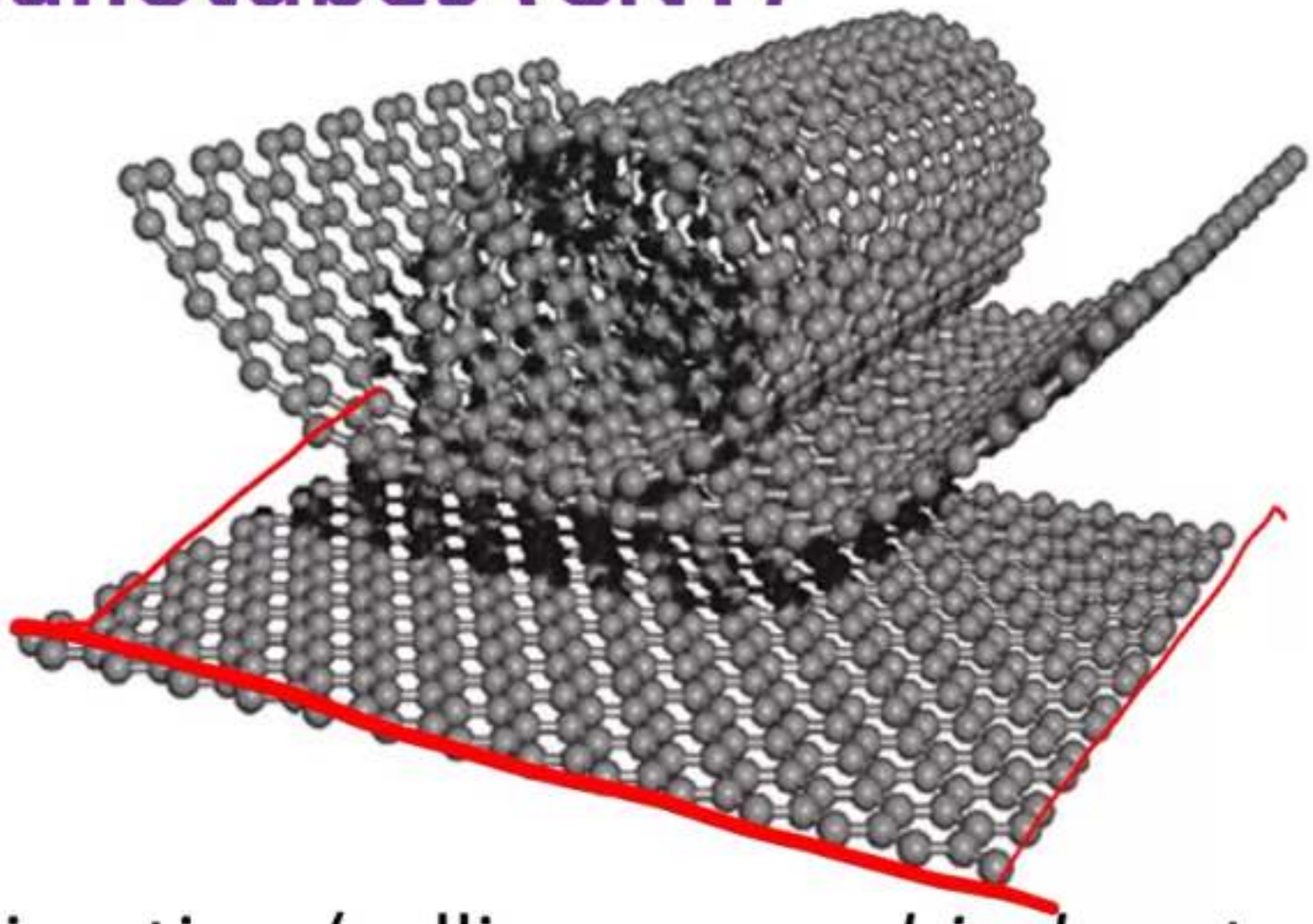
$Na^{11} = 1s^2\, 2s^2\, 2p^6\, 3s^1$



Carbon nanotubes (CNT)

- Cylindrical molecules consist of rolled-up sheets of single-layer carbon atoms (graphene).
- CNT can be
  - single-walled with a diameter of less than 1 nm or
  - multi-walled, consisting of several concentrically interlinked nanotubes, with diameters >100 nm.
- Their length can reach several μm or even mm.
- Ultra-high strength, low-weight materials that possess highly conductive electrical and thermal properties

Carbon nanotubes (CNT)



- Rolling-up direction (rolling-up or *chiral* vector) of graphene layers determines electrical properties of nanotubes.
- Chirality describes angle of nanotube's hexagonal carbon-atom lattice.

Carbon nanotubes (CNT)

- MWCNTs are always conducting and achieve at least same level of conductivity as metals.
- SWCNTs' conductivity depends on their chiral vector:
- They can behave like a metal and be electrically conducting; display the properties of a semi-conductor; or be non-conducting.
- Ex, a slight change in pitch of the helicity can transform the tube from a metal into a large-gap semiconductor.

Carbon nanotubes (CNT)- Properties

- High mechanical tensile strength 400 times that of steel.
- Light-weight –density is one sixth of that of steel.
- Thermal conductivity is better than that of diamond.
- Very high aspect ratio greater than 1000,
  - in relation to their length they are extremely thin;

Carbon nanotubes (CNT)- Properties

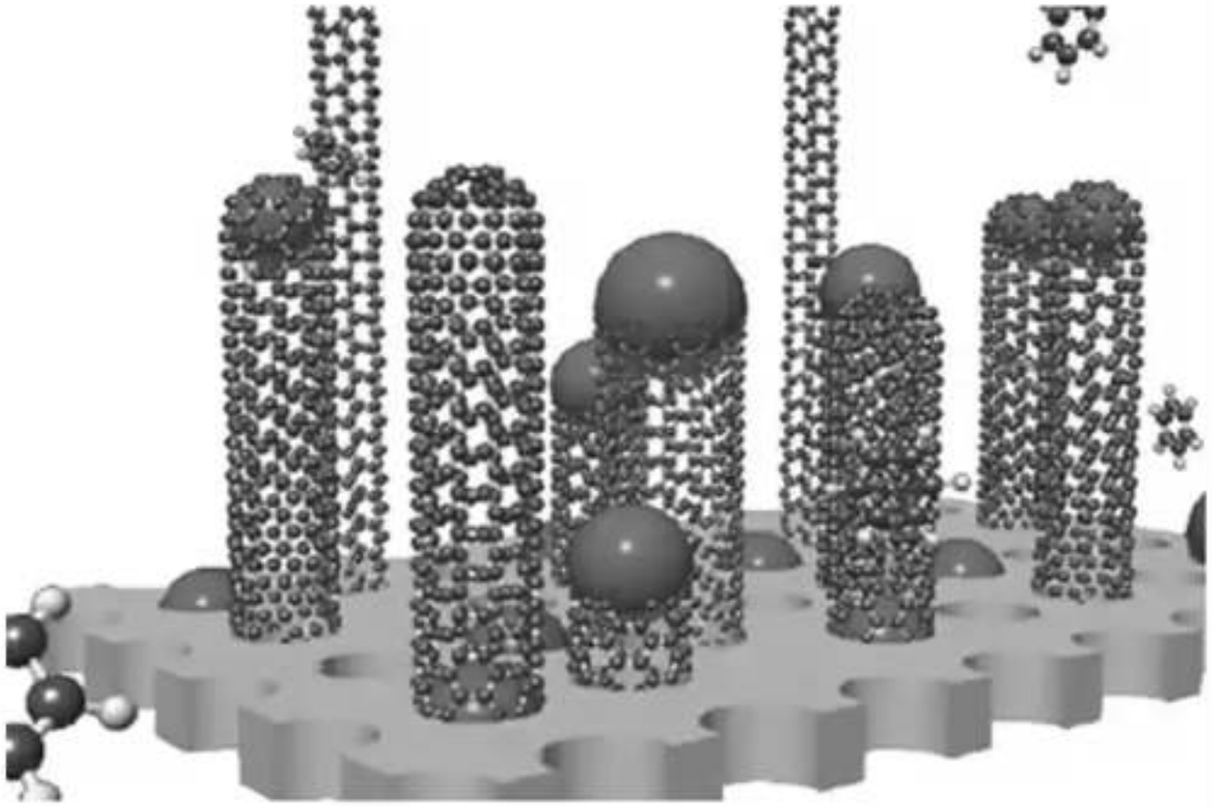
- Highly chemically stable and resist virtually any chemical impact unless they are simultaneously exposed to high temperatures and oxygen
  - Extremely resistant to corrosion;
- Hollow interior can be filled with various nanomaterials, separating and shielding them from the surrounding environment
  - Extremely useful for nanomedicine applications like drug delivery.

Carbon nanotubes (CNT)- Synthesis

- Three main methods currently available for the production of CNTs: Arc discharge, Laser ablation of graphite, and chemical vapor deposition (CVD).
- In first two processes, graphite is combusted electrically or by means of a laser, and CNTs developing in gaseous phase are separated.
- All three methods require use of metals (e.g. iron, cobalt, nickel) as catalysts.

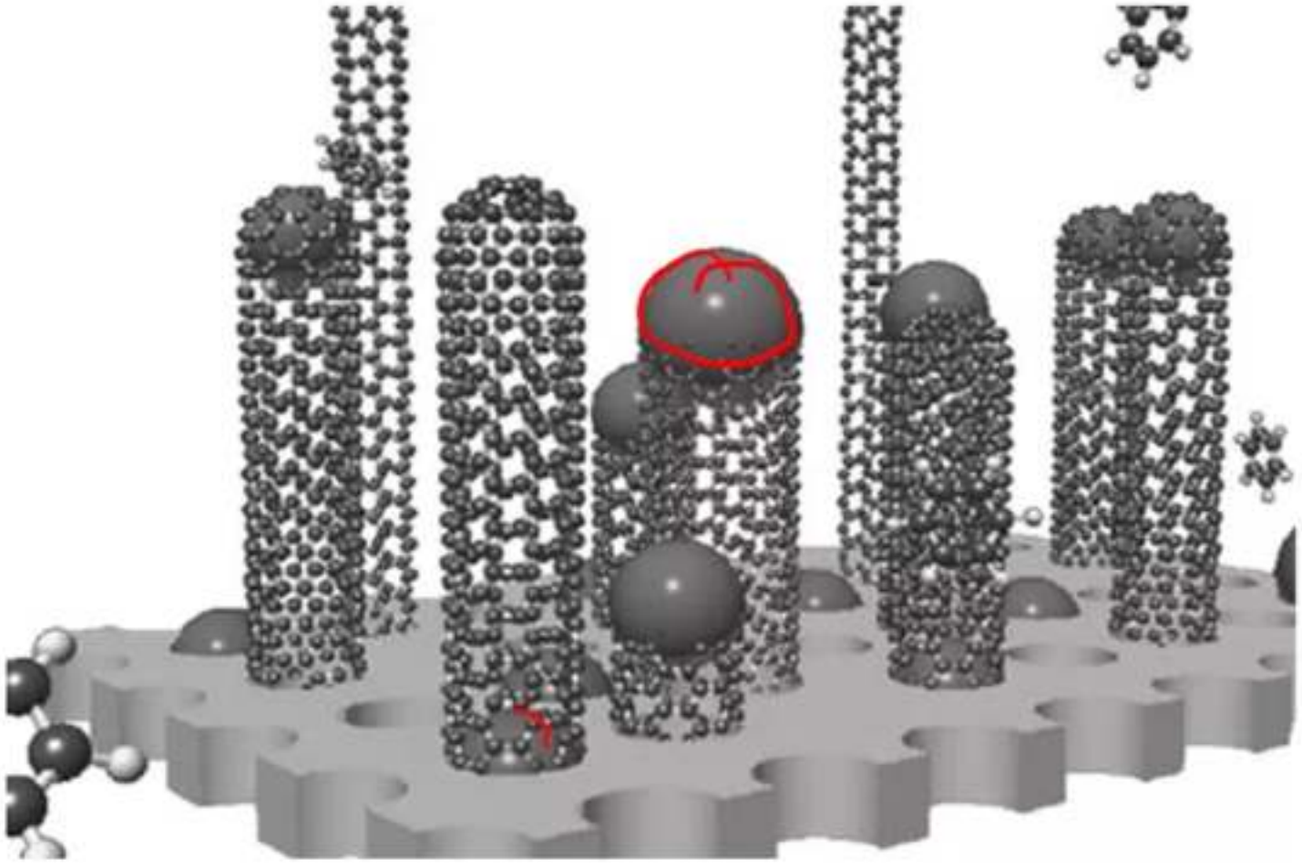
Carbon nanotubes (CNT)- Synthesis- CVD

- Production of larger quantities of CNTs under more easily controllable conditions and at lower cost.



- In CVD process, a metal catalyst (such as iron) combined with carbon-containing reaction gases (such as hydrogen or carbon monoxide) to form carbon nanotubes on catalyst inside a high-temperature furnace.

Synthesis- CVD



- First, small secondary catalyst particles of size of a CNT diameter develop on which nanotubes start growing.
- Catalyst particle is either at the top or at the bottom of emerging nanotube.
- Growth will stop if catalyst particle is deactivated through development of a carbon envelope.

Physics of Materials

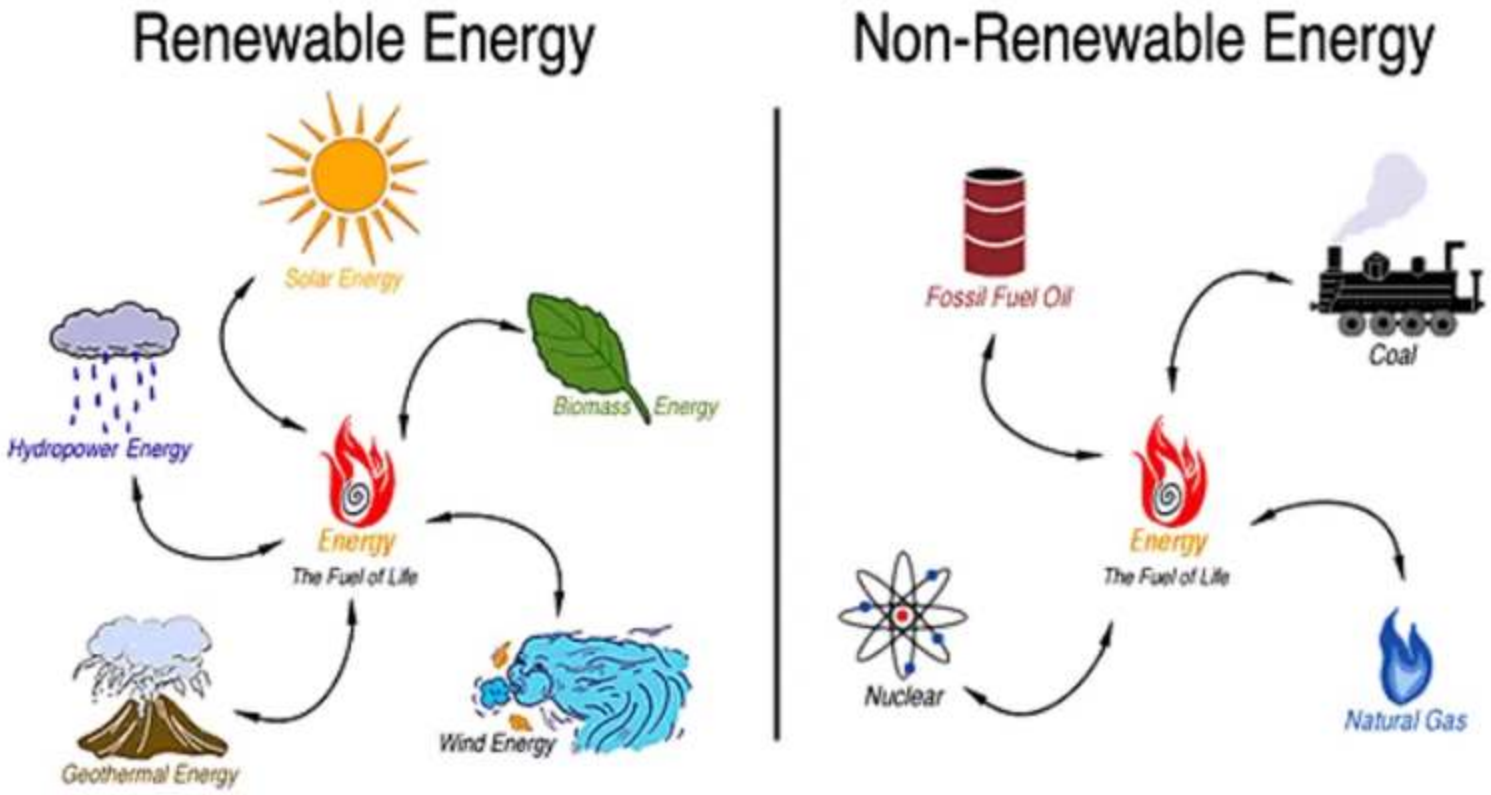
Unit III Physics of Energy

Sub Topics

- Introduction to energy sources
- Solar energy- Solar production and Radiation
- Photovoltaic solar cells
- Nuclear energy- Nuclear energy processes, Fission and Fusion
- Electrochemical energy- Storage and Conversion
- Bio-energy- Sources and Biomass

Classification of Energy Sources

Energy resources can be classified as conventional or non-renewable and non-conventional or renewable sources.



Conventional or non- renewable sources:

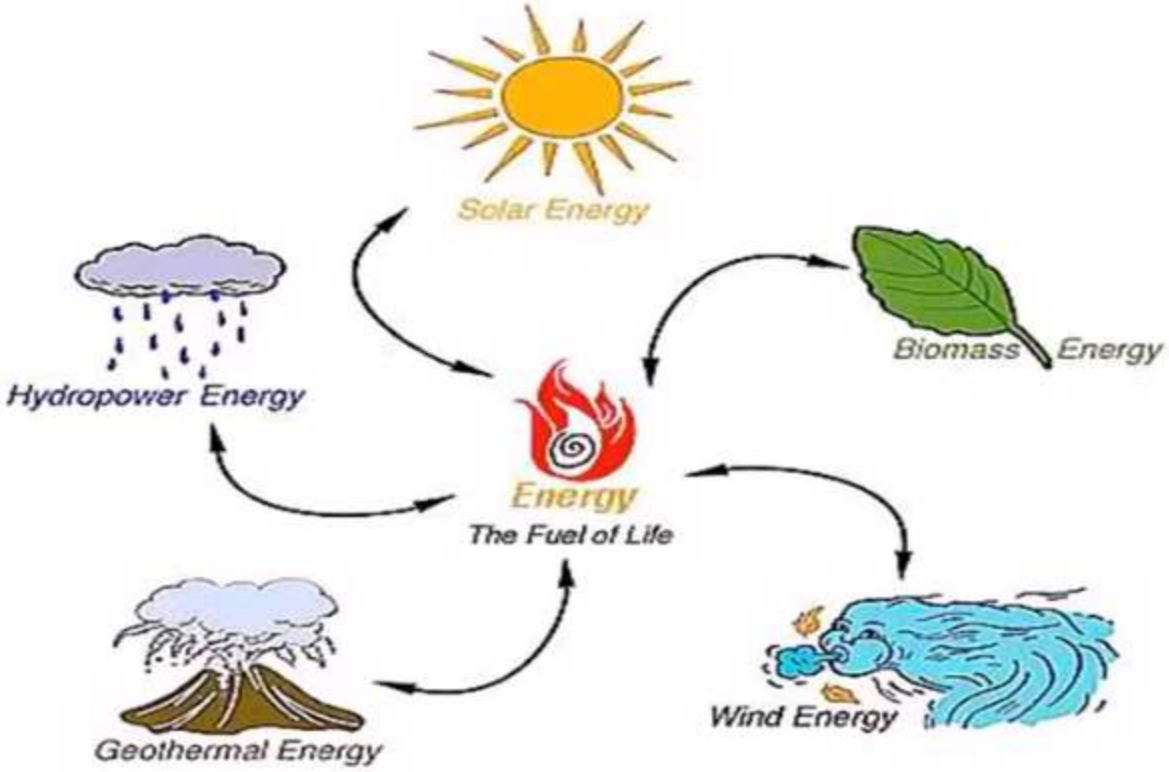
Resources that exist in limited supply and cannot be replaced if they are used up.

- firewood
- cattle dung cake
- Coal
- petroleum
- natural gas

Non-conventional or renewable sources

Resources that can be replenished naturally in the course of time are called *Renewable resources*

- Solar
- Wind
- Tidal
- Geothermal
- Biogas



Alternative Energy Sources

Solar	solar thermal [thermo] PV [quantum]	• Ultimate source of most E • Vast potential • Issues: efficiency, scaling, distribution
Nuclear	fission, fusion [quantum]	• Vast potential • Issues: safety, waste, security, technology
Other renewables	wind, waves, hydro, tides, [fluid mech] ocean, geothermal [thermo]	• Clean energy sources • Substantial potential in wind, geothermal; others more limited • Study physics of each

SOURCES	TRANS FORMATION AND STORAGE		USES
• Fossil fuels	• Batteries	Chemical$\leftrightarrow$ Electrical	• Heating & Cooling
• Biofuels	• Fuel Cells	Chemical$\leftrightarrow$ Electrical	• Transportation
• Wood, waste,	• Engines	$\left.\begin{array}{r}\text{Bio}\\ \text{Chemical}\end{array}\right\} \leftrightarrow$ Mechanical	• Manufacturing
	• Working fluids	Mechanical$\leftrightarrow$ Heat	• ...
	• Photosynthesis	Radiation$\leftrightarrow$ Biochemical	

Two Main Categories:

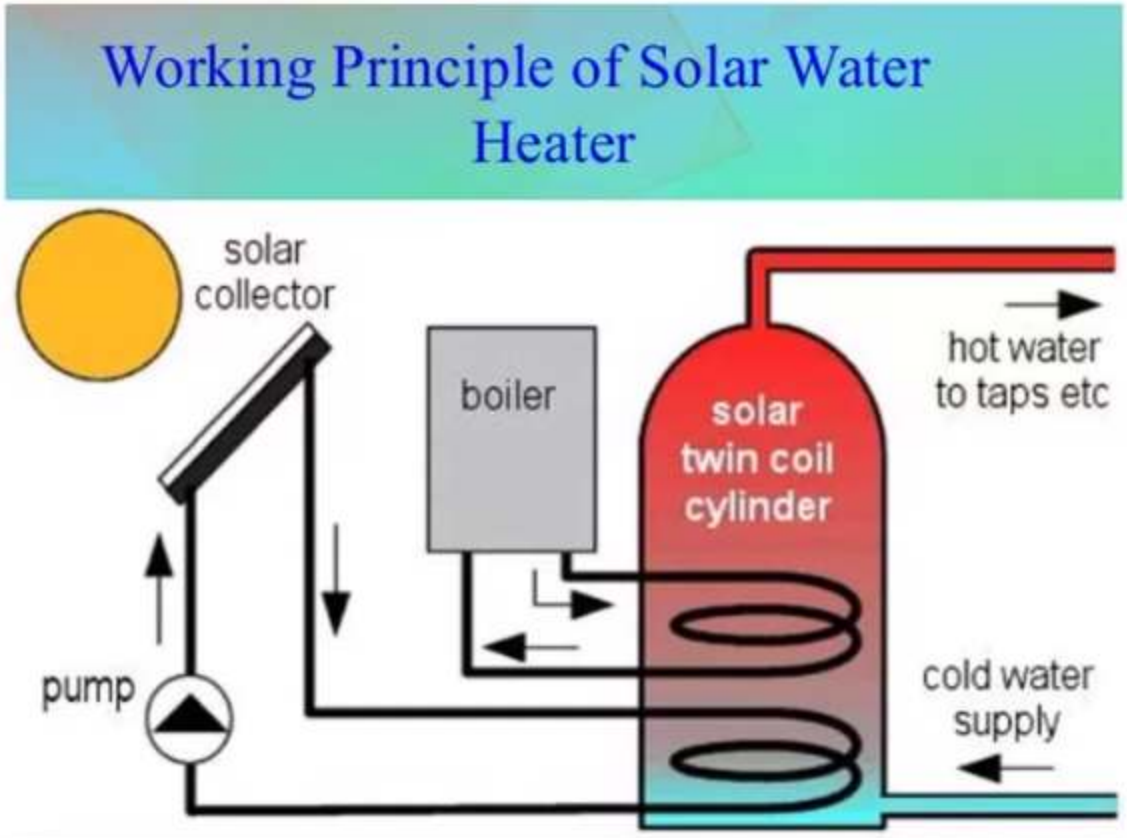
Solar Thermal

Water heating and cooking

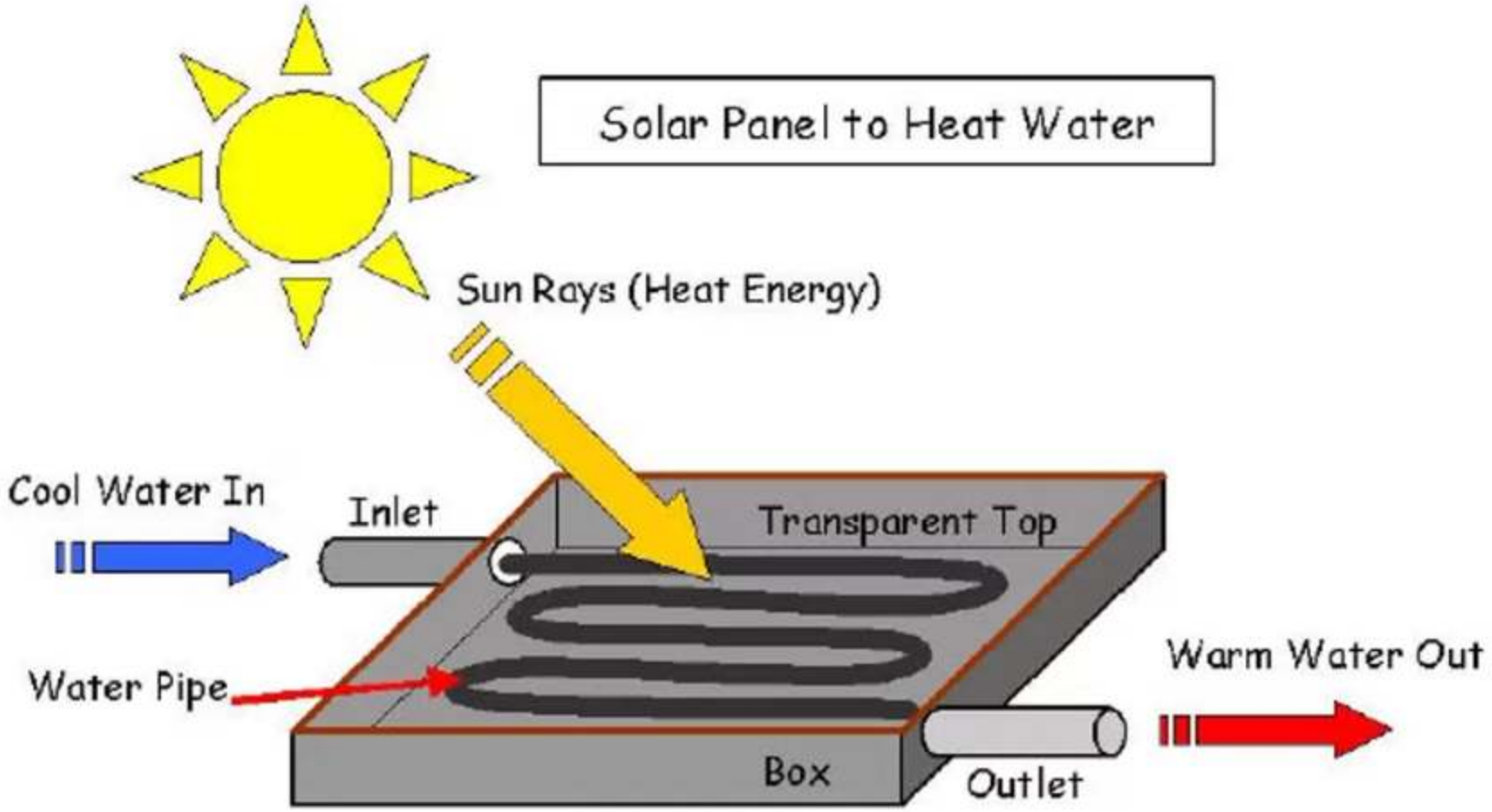
Solar Photovoltaic (PV)

Electricity production

Solar Water Heating



How Does it Work?



Benefits of Solar Cooking

- Consumes no fuels/wood

– No loss of trees & habitat

– Trees sequester carbon

- Generates no air pollution

- Generates no greenhouse gases

- Produces no smoke

– Cooking smoke kills over 1.6 million people each year, mostly women & children, according to a recent report

- Eliminates fire dangers

Energy from the sun is harnessed in two ways:

1. Active solar involves capturing and redistributing sunlight through the use of solar panels, pumps or solar fans to generate power usually on a large scale.
2. Passive solar works to reduce the amount of energy traditionally used to power allocation such as a building or house.

Solar Electric Systems

- Photovoltaic (PV) systems convert light energy directly into electricity.
- Commonly known as "solar cells."
- The simplest systems power the small calculators we use every day.
- More complicated systems will provide a large portion of the electricity in the near future.
- *PV represents one of the most promising means of maintaining our energy intensive standard of living while not contributing to global warming and pollution*.

Solid State Ionic Devices

- Solid State Batteries
  - Primary
  - Secondary/Rechargeable
- Fuel Cells
  - PEM based fuel cells (room temperature)
  - SOFC, IT-SOFC

Primary and Secondary Batteries

4 classes of electrochemical power sources

- Classified based on reactants stored within them used to obtain electrical energy.
  - Primary
  - Secondary
- Fuel cells

Secondary Batteries

- Important characteristics of secondary battery
  - Reversible charge and discharge
  - Energy efficient
  - Minimal physical changes that can limit cell's cycle life
  - Chemical reaction, may cause deterioration of cell's components, loss of life, or loss of energy (should be absent).

Batteries

Historical development of primary Batteries

Date	Battery type	Battery chemistry
1800	Volta pile	Zn/ salt / Ag
1836	Daniell cell	Zn / $ZnSO_4$ / $CuSO_4$ /Cu
1866	LeClanche cell	Zn / NH_4Cl /MnO_2
1878	Zinc air cell	Zn / NaOH /O_2
1945	Ruben cell	Zn / KOH / HgO
1955	Alkaline batteries	Zn / KOH / MnO_2
1950-1960	Silver solid electrolyte	Ag / AgI / V_2O_5
1960-1965	Silver solid electrolyte	Ag / Ag_3SI / I_2
1961	Silver zinc cell	Zn / KOH /AgO_2
1965-1970	Silver solid electrolyte	Ag / $RbAg_4I_5$ / Me_4NI_5

ee Khandale

Characteristics of Solid-State Batteries

Advantages

- Excellent Storage stability (Shelf life of 10 Yrs. or better)
- High energy Density
- No gassing or leakage
- Wide operating temperature range (up 200°C)
- Shock and vibration proof

Disadvantages

- High internal resistance (forbid to design high power battery)
- Low current drain
- Reduced power output at low temperatures
- Extra care to be exercised to prevent short circuiting cells (to avoid high current drain)

Present Demand : Long Operating Life, High Safety, High Power

Solid State Batteries

Basic constituents

Solid state anode

- Metals/Alloys
  Li, Na, Ag, Cu, Al-Li
- Intercalated compounds
- Composite
  (Mixed conductors)

Solid state cathode

- Mixed Conductors
  - Intercalated compounds
  - Bronzes
    M_xWO_3, $M_xV_2O_5$
  - Graphite complexes
    e.g. CF, $M_xCoM'_n$
  - Transition metal chalcogenides
    e.g. TiS_2, TaS_2
- Halogens
  (Primary batteries)

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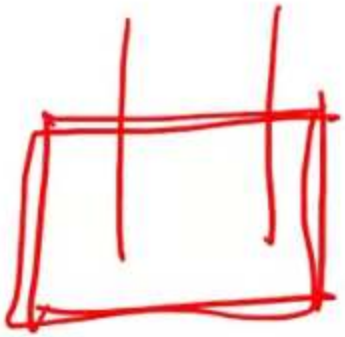
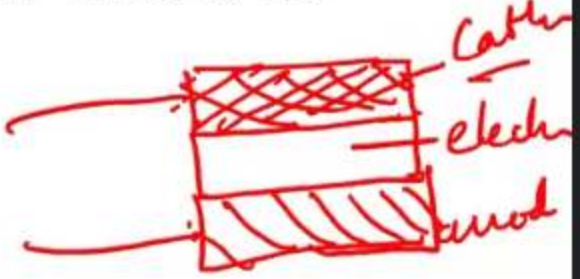
Requirement of Solid Electrolyte

- High ionic conductivity & negligible electronic
  - Minimize internal short circuiting
- Chemically stable with electrode
  - Avoid reaction with each other
- Good electrical contact with electrode
  - Ensures rapid equilibrium so minimum response time
  - Minimizes cell polarization so emf close to theoretical value





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Requirement of Solid Anode

- Efficiency as a reducing agent
- Light in weight
- Stable against thermal & chemical decomposition
- Chemically compatible with electrolyte
- Good electronic conductor
- Ease of fabrication
- Low cost

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Requirement of Solid Anode

- Metals are mainly used as anode
- Zinc predominant anode
- Lithium, lightest metal, is now becoming very attractive, but requires careful cell design to control its activity.

Advantages of Lithium Batteries

- High voltage:
  - Lithium cells have voltages as high as 3.9 V, depending on cathode material, compared with 1.5 V of most primary battery systems.
  - Higher cell voltage reduces number of cells in a battery pack by a factor of about 2.

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Advantages of Lithium Batteries

- High energy density:
  - Energy output (over 200 Wh/kg and 400 Wh/L) is 2 to 4 or more times better than conventional zinc anode batteries
- Operation over wide temperature range:
  - Many of lithium cells performs over temperature range from above 70 to – 4 ^{o}C or below.

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Advantages of Lithium Batteries

- Superior shelf life:
  - Cells can be stored for long periods even at elevated temperatures.
  - Storage of up to 10 yrs at room temperature is projected
  - Demonstrated storage of more than 5 yrs at 20 ^{o}C and 1 y at 70 ^{o}C.

Intercalation Compounds

- Intercalation denotes a process in which a molecule or ion (guest) is placed into host lattice.
- Structure of host remains unchanged or is only slightly altered in guest-host complex (intercalate).
- Insertion, inclusion or topotactic reaction are often used for intercalation reactions.

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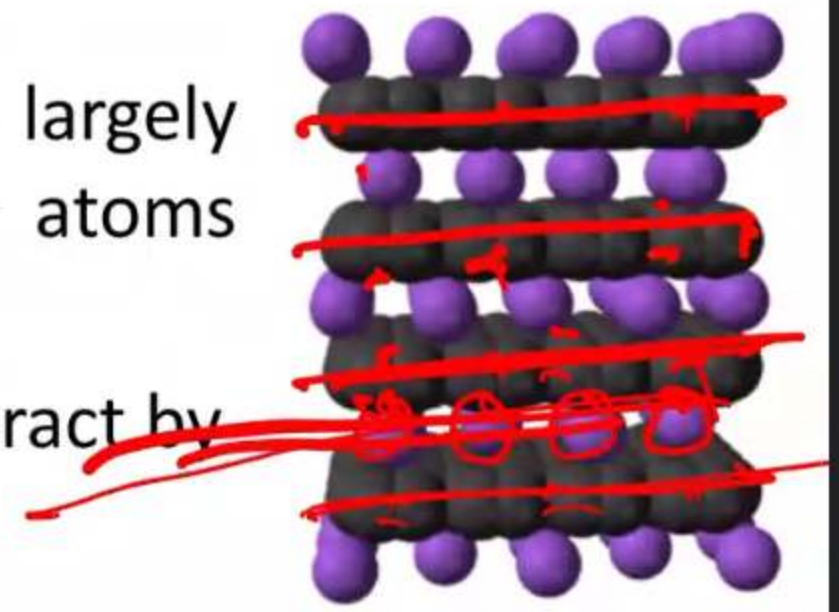
Intercalation Compounds

Graphite intercalation compounds

- Complex materials (formula *X*Cy) where element or molecule *X* is inserted (intercalated) between the graphite layers.
- Here, graphite layers remain largely intact and guest molecules or atoms are located in between
- Host (graphite) and guest X interact by charge transfer in-plane
- Electrical conductivity generally increases



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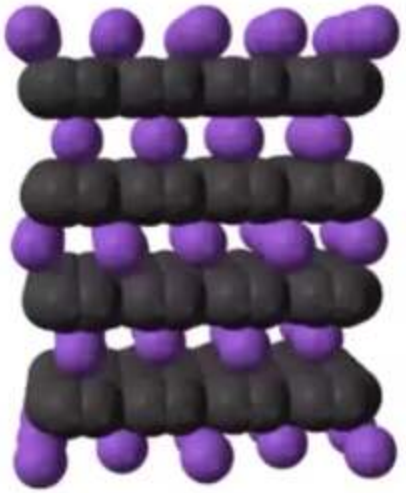
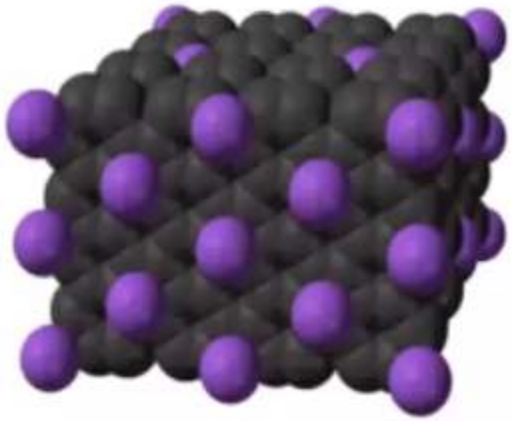
Intercalation Compounds

Graphite intercalation compounds

- Stage 1 compounds: graphite layers and intercalated layers alternate
- Stage 2 compounds: two graphite layers with no guest material in between alternate with an intercalated layer





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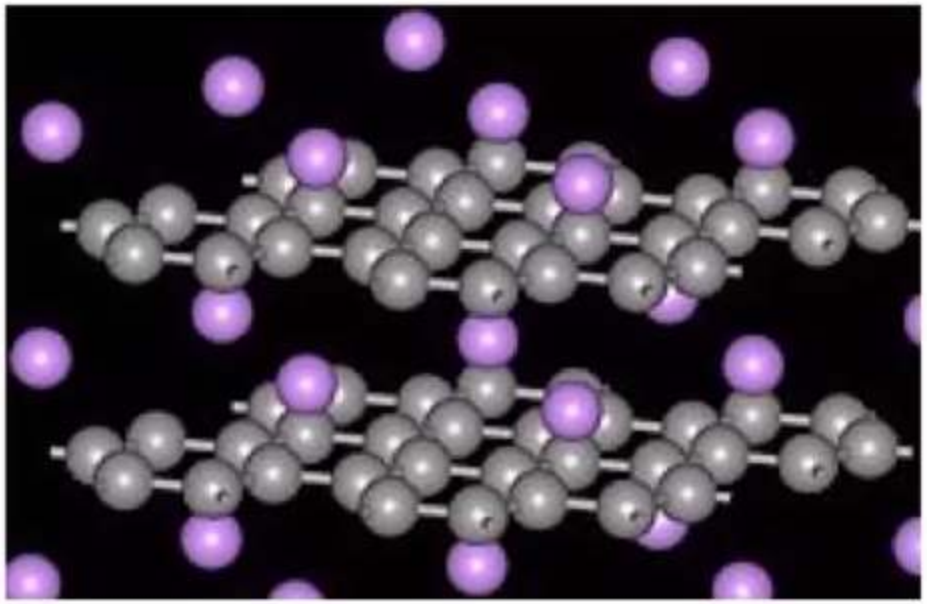
Intercalation Compounds

Graphite intercalation compounds

- CaC6 belongs to R-3m.
- Graphite interlayer distance increases
  - From 3.35 to 4.524 Å
- Carbon-carbon distance increases
  - From 1.42 to 1.444 Å



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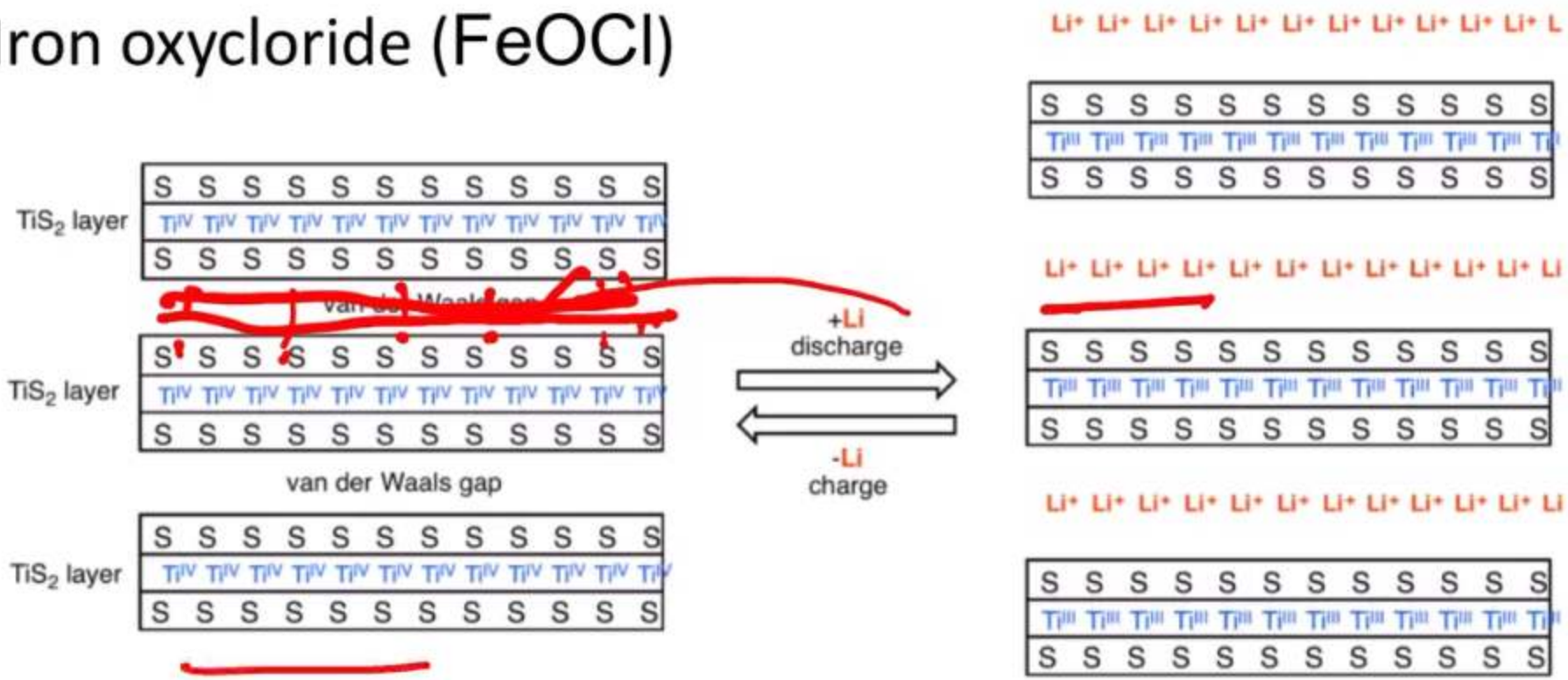
Intercalation Compounds

layered dichalcogenides

- Titanium/Tantalum disulphide (TiS_2/TaS_2)
- Iron oxycloride (FeOCl)



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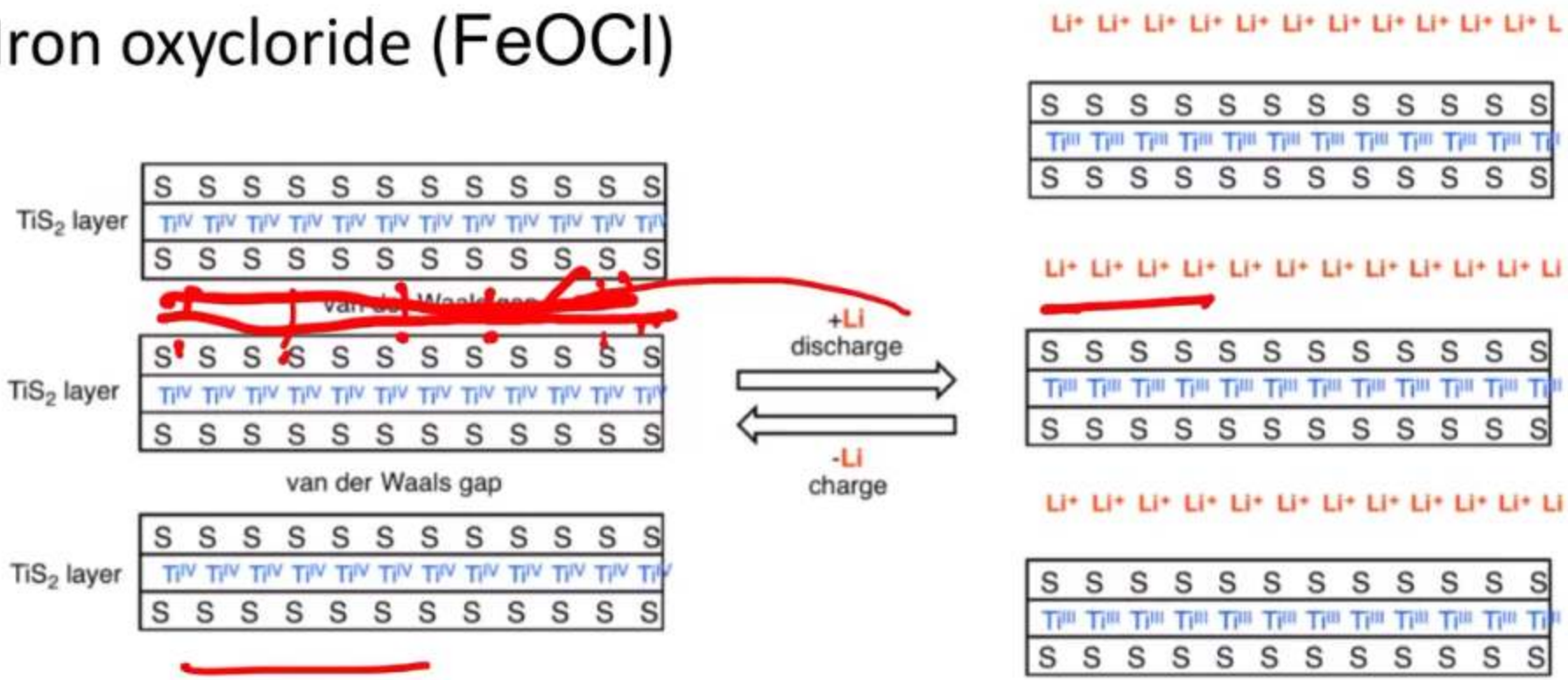


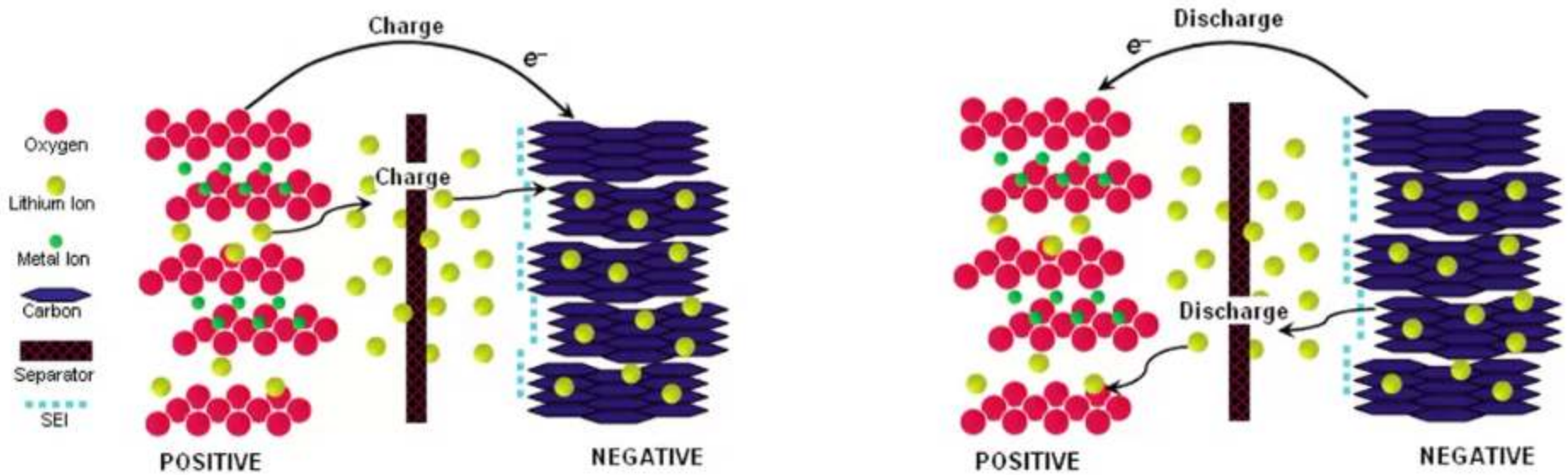
Intercalation Compounds

- Positive electrode half-reaction

$$LiCoO_2 \Leftrightarrow Li_{1-n}CoO_2 + nLi^+ + ne^-$$

- Negative electrode half-reaction

$$nLi^+ + ne^- + C \Leftrightarrow Li_nC$$



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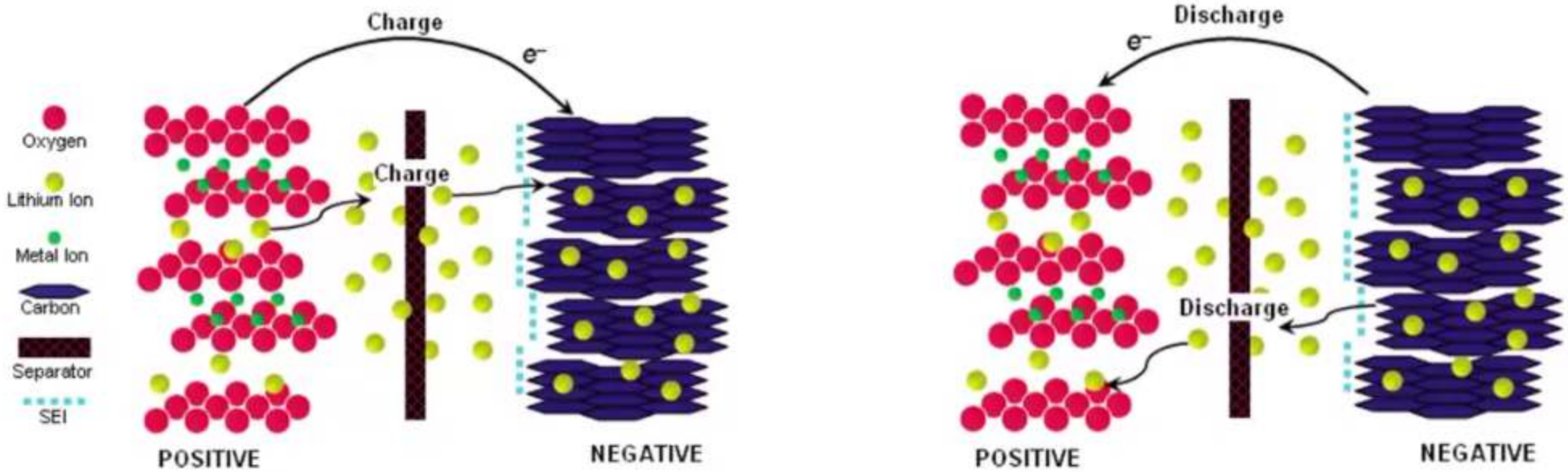

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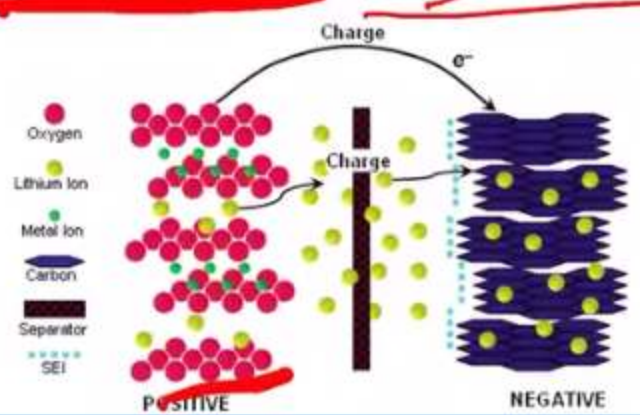
Intercalation Compounds

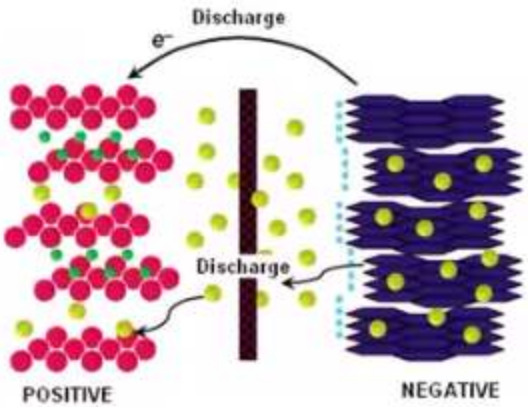
- Overall reaction has its limits
- Over-discharge supersaturates lithium cobalt oxide
  - Production of Li_2O possibly by irreversible reaction

$$Li^+ + e^- + LiCoO_2 \rightarrow Li_2O + CoO$$

- Overcharge up to 5.2 V leads to cobalt(IV) oxide formation (XRD)

$$LiCoO_2 \rightarrow Li^+ + e^- + CoO_2$$





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Intercalation Compounds

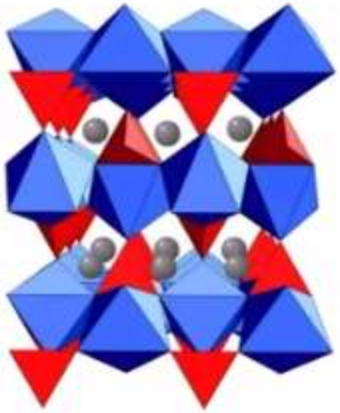
- Lithium ions are transported to and from cathode or anode through electrolyte
- During charging
  - Oxidize from Co^{3+} to Co^{4+}
- During discharge
  - Reduced from Co^{4+} to Co^{3+}.

Co in Li_xCoO_2

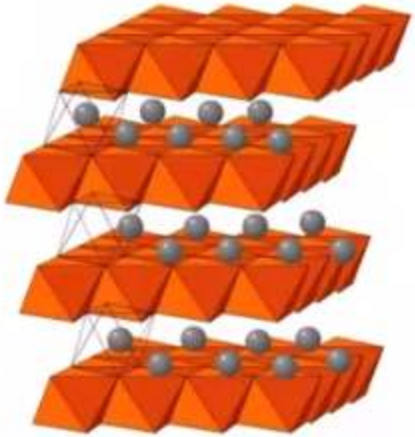
$$LiCoO_2 \Leftrightarrow Li_{1-n}CoO_2 + nLi^+ + ne^-$$

Intercalation Compounds

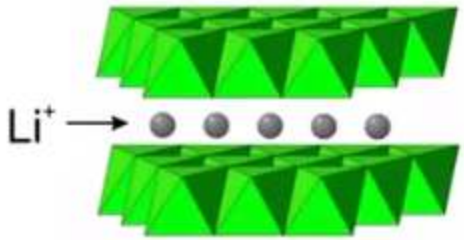
$LiFePO_4$



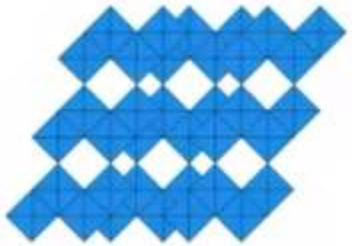
$LiCoO_2$



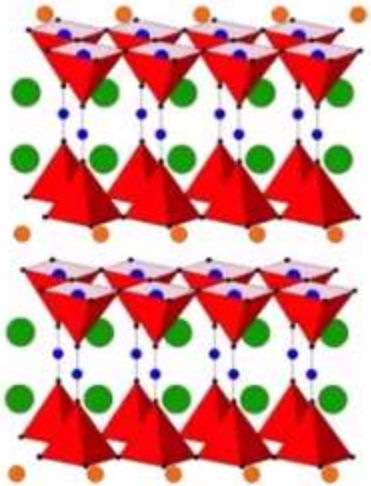
TiS_2



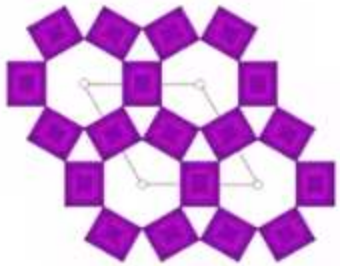
VO_2



$YBa_2Cu_3O_7$



WO_3



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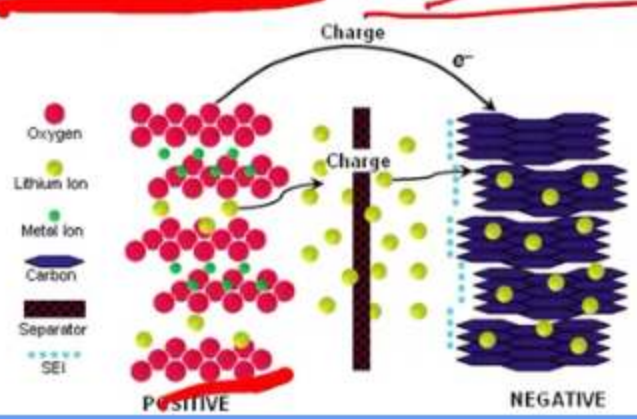

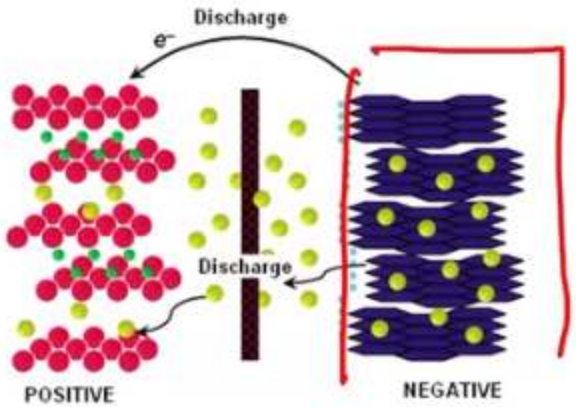

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Electrochemical reaction

- Cell connected to external load
  - Electron flow from anode, oxidized, through external load to cathode
  - At cathode electrons are accepted and cathode reduces.
- Chemical power source uses redox reaction, e.g.

$$\frac{Ag_2O}{reducer} \quad \frac{Zn}{oxidizer} \qquad 2Ag \quad Zn$$

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Electrochemical reaction

- O.C.V. causes electron to flow from negative to positive electrode.
- As per Faraday's law zinc oxidizes on negative electrode (anode) i.e. anodic reaction given by

$$Zn + 2OH^- \Leftrightarrow H_2O + ZnO + 2e^-$$

Electrochemical reaction

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- Chemical power source uses redox reaction, e.g.

$$\frac{Ag_2O}{reducer} \quad \frac{Zn}{oxidizer} \quad 2Ag \quad Zn$$

- Electrodes contact with electrolyte gives potential difference (V) called open circuit voltage (OCV)
- Potential of anode is more negative
  - It has stronger tendency to release electrons.
  - In silver-zinc cell V = 1.6 V (Zn electrode is negative).

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Open circuit and on load voltage

- OCV, V is potential difference between positive and negative electrodes with no current flowing in the external circuit

$$V\square = E_{(+)} - E_{(-)}$$

- It depends on nature of both, electrode and electrolyte but not on size or structure of cell.
- It is related to thermodynamic value e.m.f.
- OCV $\leq$ e.m.f.

Electrochemical reaction

- Ag_2O reduces on positive electrode (cathode) i.e. cathodic reaction as

$$Ag_2O + H_2O + 2e^- \Leftrightarrow 2Ag + 2OH^-$$

- Reactions called electrochemical or electrode reactions.
- Electric energy generated by chemical source is work of charge transfer in external circuit

Open circuit and on load voltage

- Potential difference between electrode changes
  - Galvanic cell delivers current.
  - It is called 'on load voltage' denoted by V_d.
  - Varies inversely with discharge current
- Under on load condition,
  - Ohmic potential difference $\varphi = IR_{ohm}$ changes voltage across cell
    - Determine by internal resistance R_{ohm}, and electrode polarization.
- Polarization accounts for
  - Change in potential caused by current flow, from initial (off load) value E to a new value $E^{(i)}$
- Polarization (over potential) is magnitude of shift in potential

$$\eta = \left| E^{(i)} - E \right|$$

Open circuit and on load voltage

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    - Determine by internal resistance R_{ohm},
    - Electrode polarization.

Open circuit and on load voltage

- Preferable to achieve high current drain by increasing surface area rather current density
  - Possible method to use thin electrode due to high surface to volume ratio.
- Porous electrodes often used for this purpose.
- Inner pores filled with electrolyte enlarge active surface of electrodes.

Open circuit and on load voltage

- Cathode current shifts potential towards more negative value, and anode more positive
  - So voltage across cell electrodes diminishes in discharge phase and it increases during charging.

Discharging- $V_d = E_{(+)} - E_{(-)} - I_d R_{ohm} = V + \eta_{(+)} - \eta_{(-)} - I_d R_{ohm}$

Charging- $V_c = E_{(+)} - E_{(-)} + I_d R_{ohm} = V + \eta_{(+)} - \eta_{(-)} + I_d R_{ohm}$

- Ohmic & polarization energy losses are related to
  - Discharge or charge
  - Electrode dimension: surface area in contact with electrolyte.
- Current density *J*, Polarization increases with increasing *J*

Open circuit and on load voltage

Theoretical Voltage

Anode (oxidation pot.) + cathode(reduction pot.)

= standard potential

$Zn + Cl_2 = ZnCl_2$ – over all cell reaction

$Zn \rightarrow Zn^{2+} + 2e^-$ = -(-0.76 V) (Anodic/oxidation)

$Cl_2 + 2e^- \rightarrow 2Cl^-$ = (1.36 V) (Cathodic/reduction)

2.12 V

$$E^o_{Cell} = E^o_{Red,Cathode} - E^o_{Red,Anode}$$

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Open circuit and on load voltage

Parameters that measure battery performance

- Voltage and capacity.
- Voltage force propelling electrons coming out of a battery
- Capacity is number of electrons that can be obtained from a battery.

Theoretical Capacity /Energy density

- Capacity of cell is number of electrons that can be obtained from it.
- Since current is number of electrons per unit time, cell capacity is current supplied by a cell over a time
  - Total quantity of electricity in electrochemical reaction and is defined in terms of coulombs or ampere-hours.

Theoretical Capacity /Energy density

- Cell capacity varies by quantity of active materials.
- Individual cells may range in capacity from fractions of ampere-hour to many thousands of ampere-hours.

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Theoretical Capacity /Energy density

- Capacity of batteries is also considered on an energy basis by taking voltage as well as quantity of electricity in to consideration:

  Watt-hour (Wh) = voltage (V) × ampere-hour (Ah)

$ZnCl_2$ example

Standard potential = 2.12 V
Capacity = 0.394Ah/g
then theoretical watt-hour capacity per gram of material
2.12 V × 0.394 Ah/g = 0.838 Wh/g

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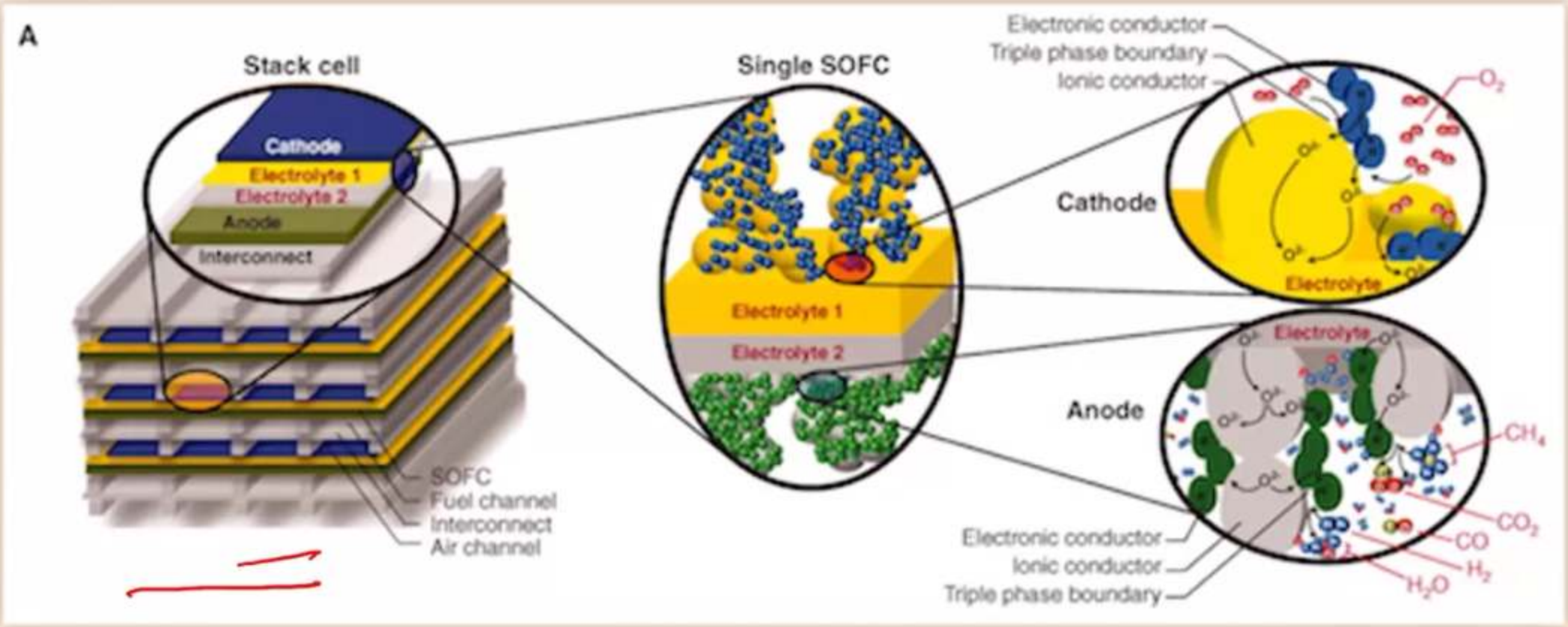
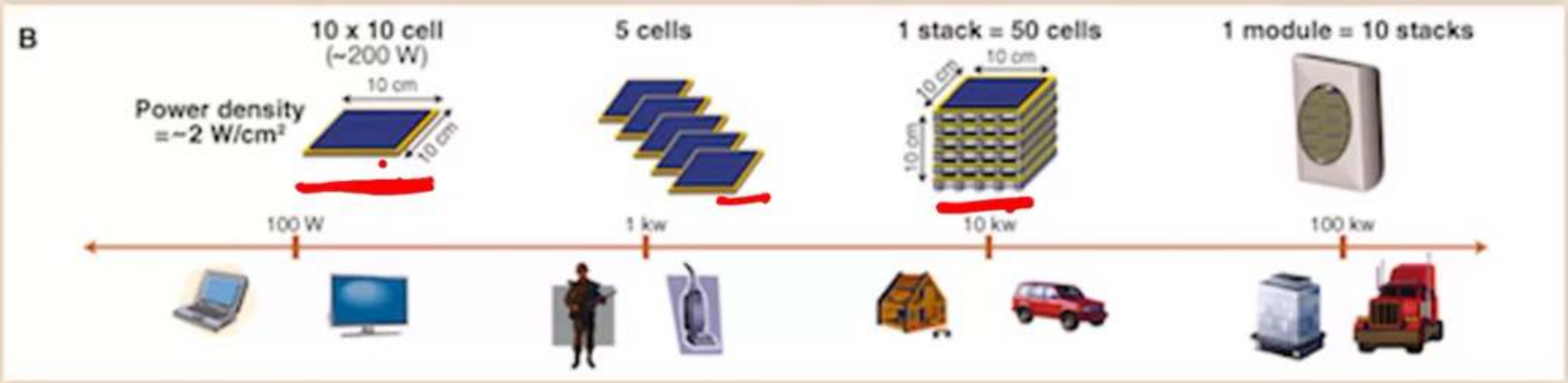
Theoretical Capacity /Energy density

- 1 g-equivalent weight of material is expected to deliver 96,487 C or 26.8 A-hour
  - a gram-equivalent weight is atomic or molecular weight of active material in grams divided by number of electrons involved in reaction

Introduction to Fuel Cell





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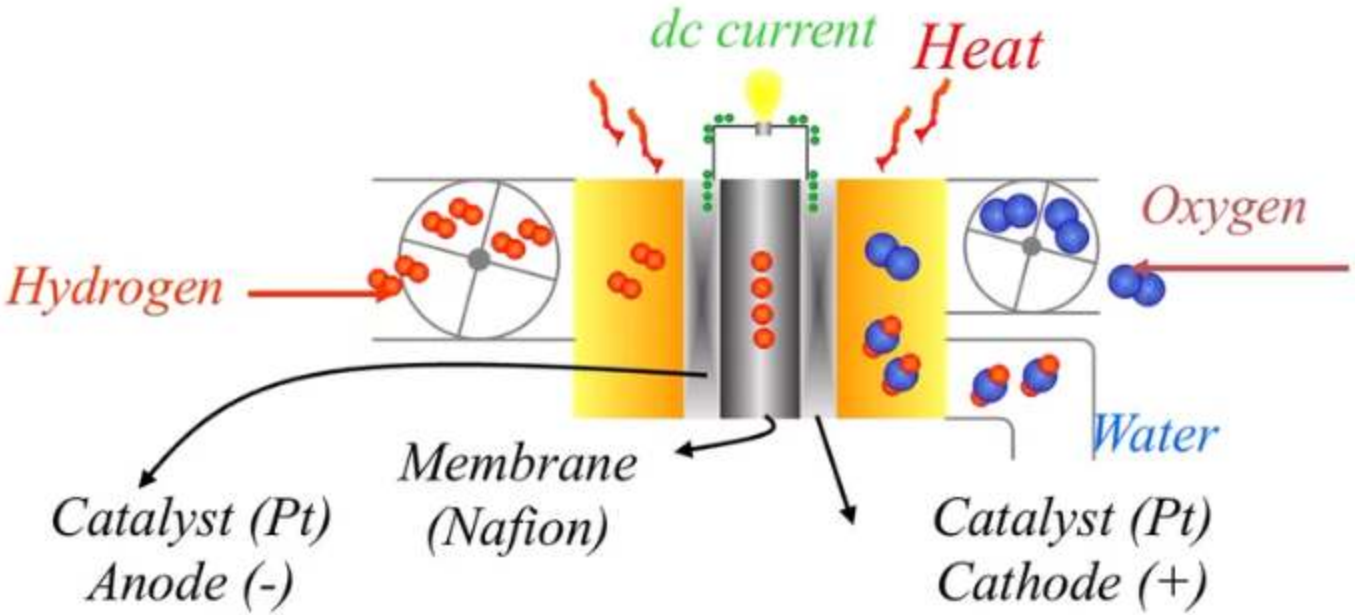
What is Fuel Cell?

- Difference with batteries: fuel cells require a fuel to flow in order to produce electricity.



$$O_2 + 2H_2 \rightarrow 2H_2O \qquad (E_r = 1.23\ V)$$

- Device consists
- Two electrodes and a Electrolyte
- Hydrogen (Fuel) & oxygen

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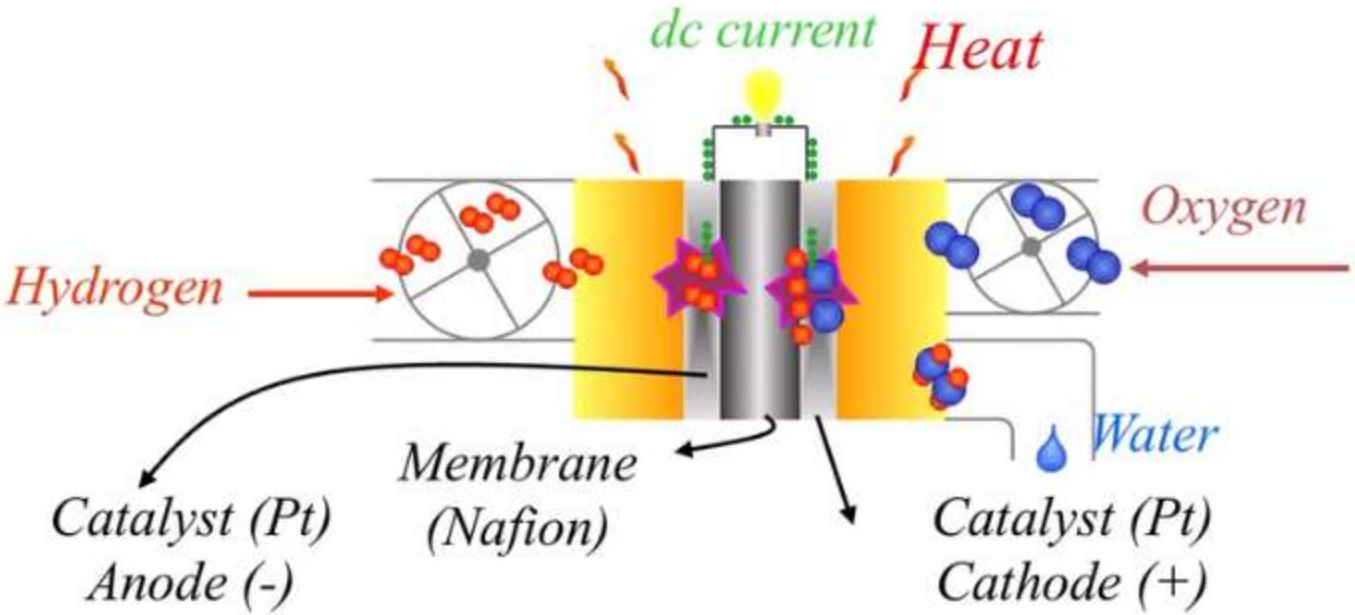

$$O_2 + 2H_2 \rightarrow 2H_2O \qquad (E_r = 1.23\ V)$$

- Device consists
- Two electrodes and a Electrolyte
- Hydrogen (Fuel) & oxygen

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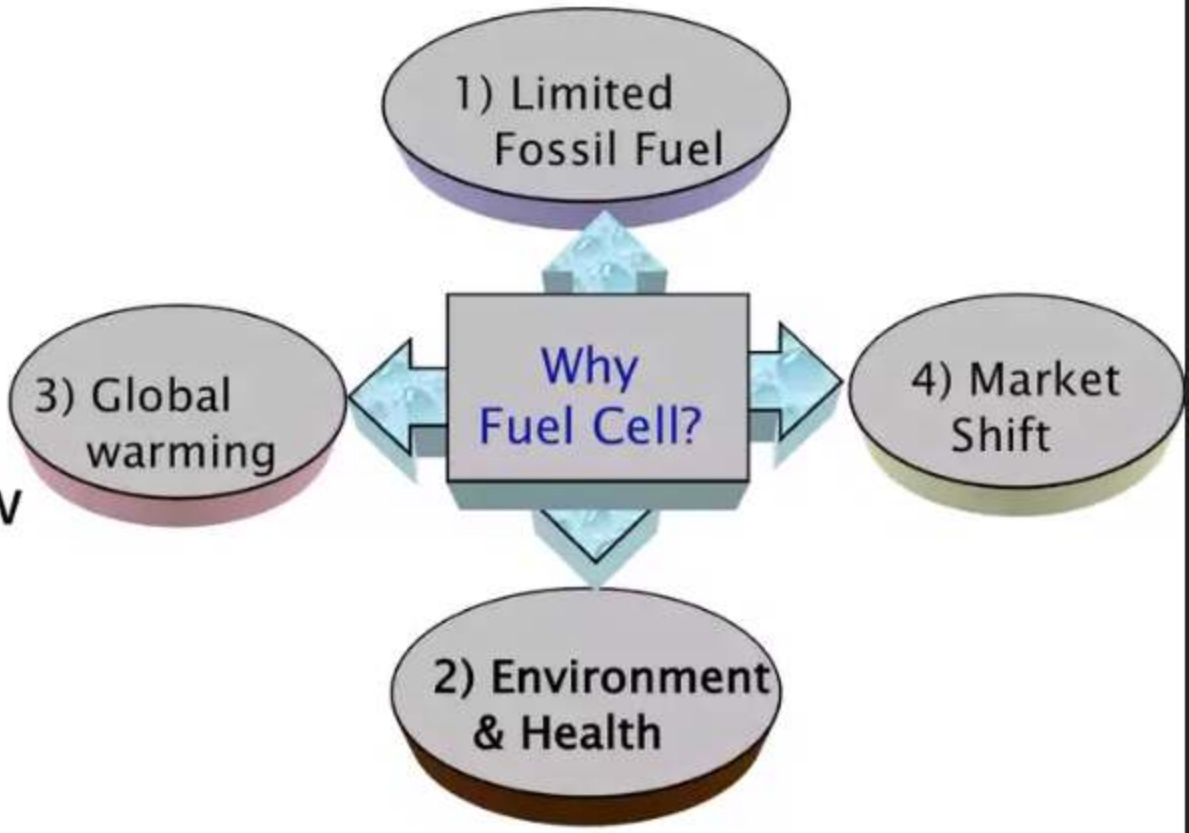
Why Fuel Cell?

- Fuel cells have captured imagination of people around world as next great energy alternative.

- Provides clean, cost-efficient and reliable electricity
- Fuel cells mark start of new power paradigm along path toward Hydrogen Economy.



Classification of Fuel Cell

- Fuel cells are classified primarily by the kind of electrolyte they employ.
- Classification determines
  - electro-chemical reactions that take place in the cell,
  - catalysts required,
  - temperature range in which cell operates,
  - fuel required, and other factors.
- These characteristics affect the applications for which cells are most suitable.
- There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications.

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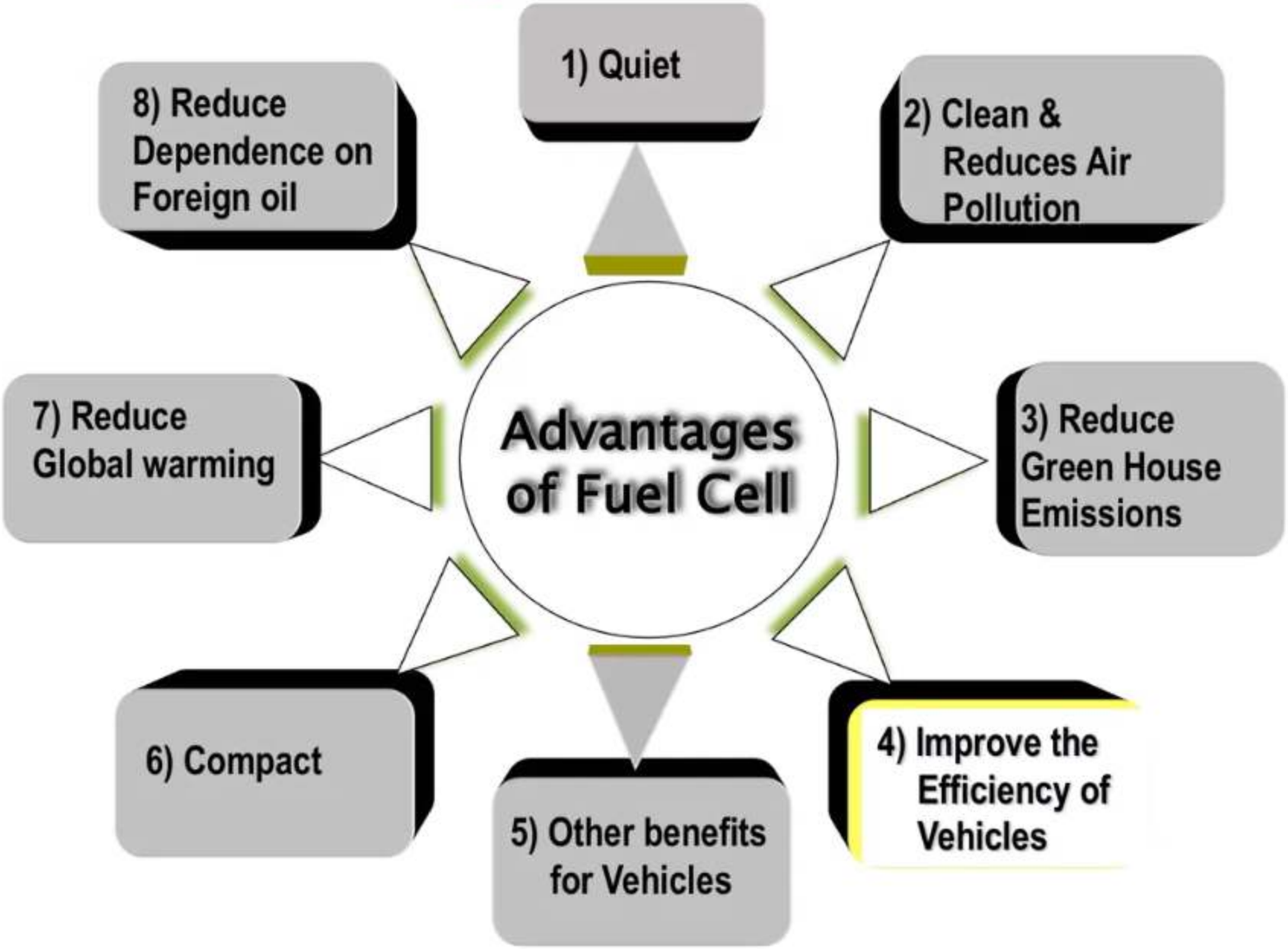
Advantages of Fuel Cells



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Fuel Cell: Types

Fuel cell type	Electrolyte	Anode gas	Cathode gas	Temp (°C)	Efficiency (%)
Proton exchange membrane (PEM)	Solid polymer membrane	Hydrogen	Pure atmospheric oxygen	75 °C	35 – 60
Alkaline (AFC)	Potassium hydroxide	Hydrogen	Pure oxygen	< 80	50 – 70
Direct methanol (DMFC)	Solid polymer membrane	Methanol solution in water	Atmospheric oxygen	75	35 – 40
Phosphoric acid (PAFC)	Phosphorous	Hydrogen	Atmospheric oxygen	210	35 – 50
Molten carbonate (MCFC)	Alkali carbonate	Hydrogen/ Methane	Atmospheric oxygen	650	40 – 55
Solid oxide (SOFC)	Ceramics	Hydrogen/ Methane	Atmospheric oxygen	800 – 1000	45 – 60

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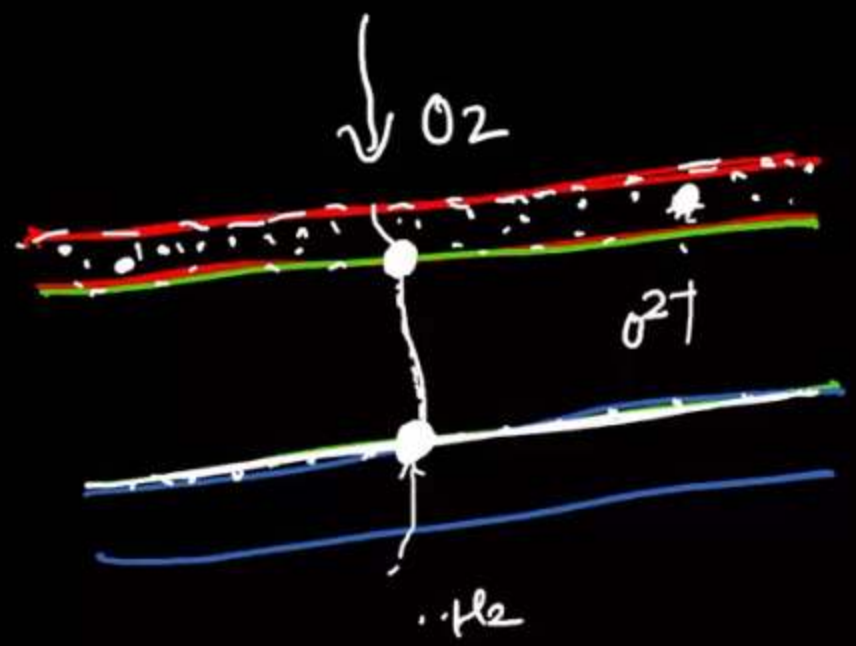
ORR

oxygen reduction reaction



— cathode

— electrolyte

— anode

$$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$$

cathode e^- —

O^{2-} —

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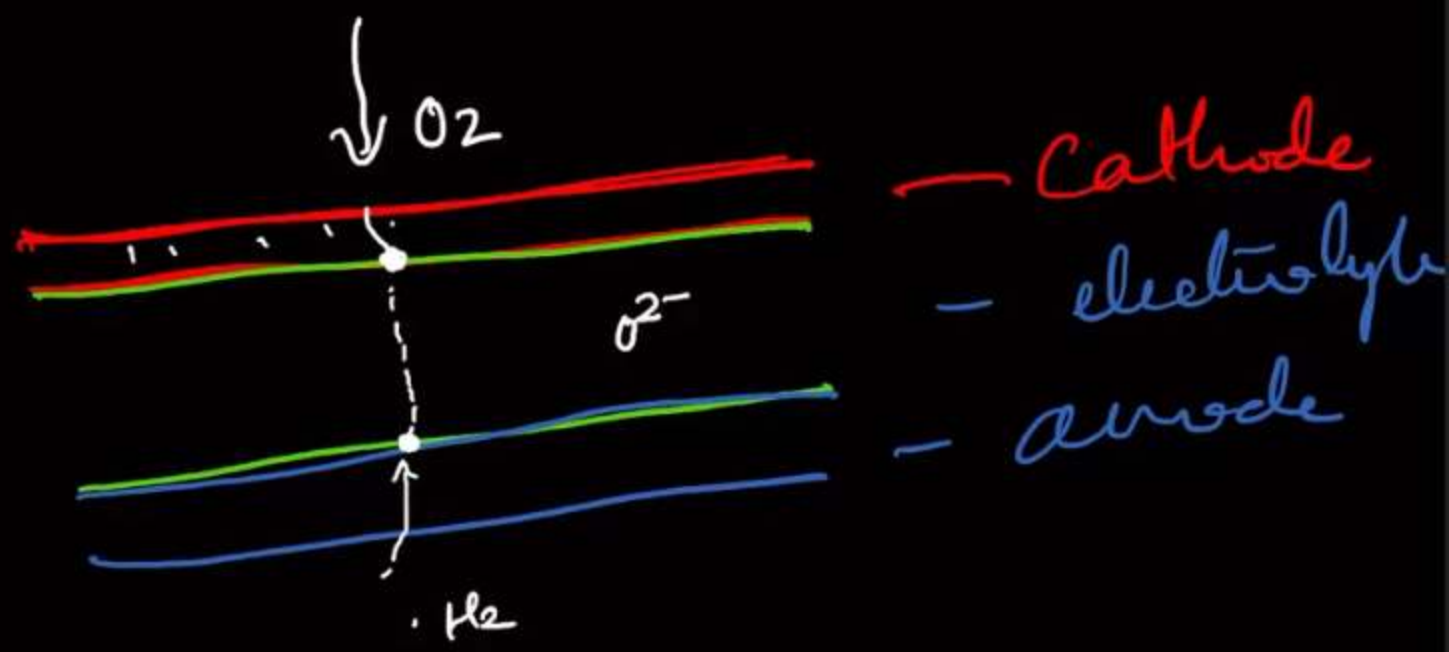


O_2 + cathode + electrolyte meet

TPB

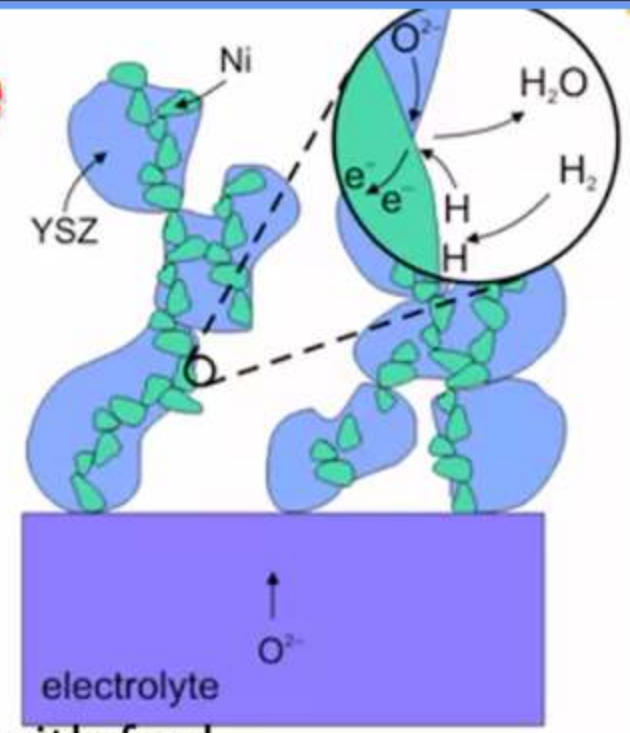
$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

H_2 + anode + electrolyte + PB

O_2

Considerations for Anode



- Nickel is used as anode
  - economical
  - exhibits high performance
- flakes off easily from electrolyte
  - Due to different expansion coefficients.
  - mixed with zirconia, creating a cermet.
- Ni-YSZ anode- allows a rapid and clean connection with fuel
  - good electronic conductor.
- Formation of carbon layer onto Ni when Carbon containing fuel is used.
- Certain additives to Ni+YSZ cermet, such as 5% ceria or 1% molybdena inhibit this process.
- Ni is also active in reforming of carbon containing fuels.
- Anodes, completely made of ceramics show good oxidation-reduction cyclability.

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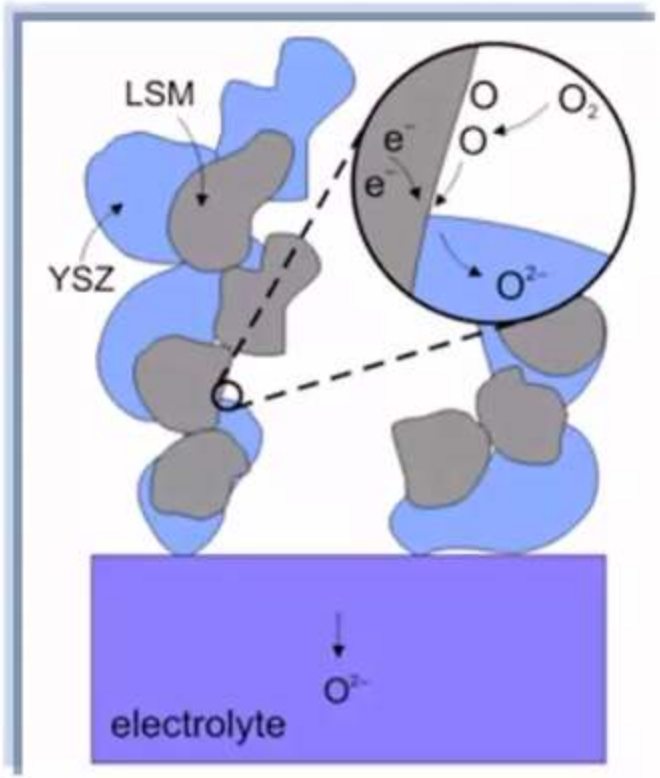
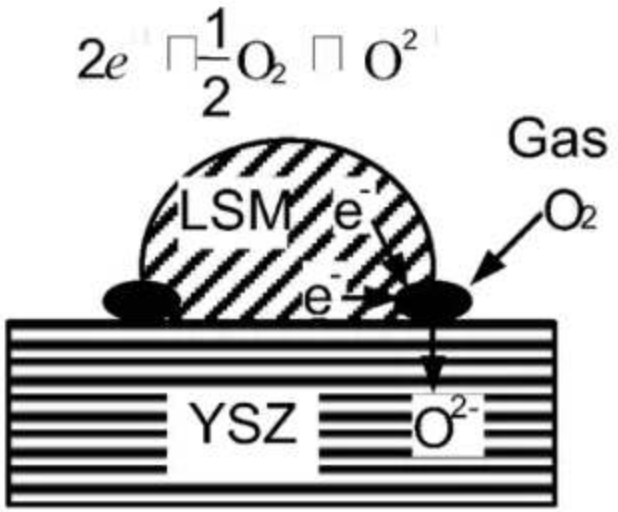
Considerations for Cathode

- Requirement
  - Good catalytic activity for ORR
  - Mixed conductivity
  - Thermally stable
- Selection Criteria
  - Electrolyte material used
    - TEC compatibility
    - Chemical stability with electrolyte
- Triple-phase boundary
  - Gas – electrode – electrolyte interface



Three Phase Boundary



Cell Fabrication

- Contact sides of electrolyte with fuel and oxidant are coated with electrode material.
- To form *porous* contact layers, partially sintered materials are used and to allow a gradient of properties, such as heat expansion coefficient several layers with different compositions are laid down.
- Three-phase boundary zone is required:
  - Gas phase (high porosity of electrolyte required for better access)
  - Electrolyte phase for ion transport
  - Metal phase for electron conduction
- Most common methods of applying electrode layer on electrolyte;
  - *plasma spraying,*
  - *vapor deposition,*
  - *solution coating* and
  - *colloidal ink* methods.
  - Inkjet printing
  - Screen printing

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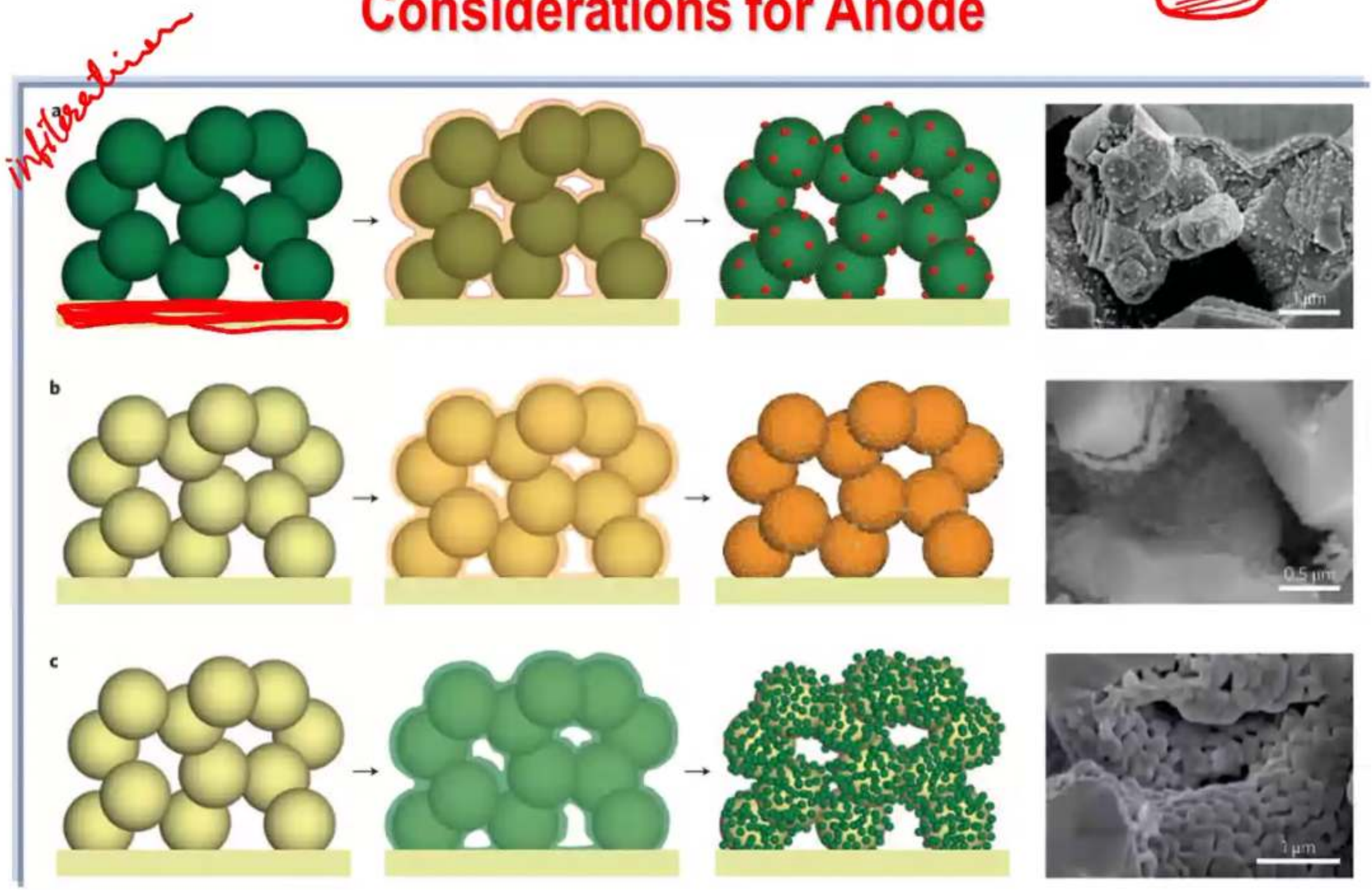
Considerations for Anode



Thermodynamics: EMF

- At the anode:

$$H_2 \rightarrow 2H^+ + 2e^-,$$

$$\Delta H = Q - W$$

- At the cathode:

$$1/2O_2 + 2H^+ + 2e^- \rightarrow 1H_2O,$$

- Hence, in a PEMFC
  - 285 kJ/mol is converted into heat (Q) and electricity (W).

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Demerits of SOFC and Merits of IT-SOFCs

- Demerits of SOFCs
  - Sealing problems
  - Degradation of cell components
  - Costly interconnects, etc.
- Merits of IT-SOFC
  - Stable cell components
  - Good compatibility within cell components
  - Ease of sealing
  - Low-cost interconnects, etc.

Thermodynamics: Cell Efficiency

- Efficiency of an actual fuel cell is often expressed in terms of ratio of operating cell voltage to the ideal cell voltage.
- Actual cell voltage is less than the ideal cell voltage because of losses associated with cell polarization and ohmic losses.
- Thermal efficiency of a hydrogen/oxygen fuel cell can be written in terms of the actual cell voltage:

$$\eta = \frac{\text{Useful Energy}}{\Delta H} = \frac{\text{Useful Power}}{(\Delta G/0.83)} = \frac{\text{Volts}_{actual} \times \text{Current}}{\text{Volts}_{ideal} \times \text{Current}/0.83} = \frac{(0.83)(V_{actual})}{E_{ideal}}$$

Thermodynamics: Cell Efficiency

- Maximum possible energy conversion efficiency is

$$\eta_{\max} = \frac{\Delta G}{\Delta H}$$

- Since ΔG = 237.2 kJ/mol and ΔH = 285.8 kJ/mol,

$$\eta_{\max} = \frac{\Delta G}{\Delta H} = \frac{237.2}{285.8} \cong 0.83$$

- Nevertheless, overall cell efficiency η is given by

$$\eta = \eta_g \eta_v \alpha$$

- η_g, η_v and a are Gibbs efficiency, voltage efficiency, fraction of fuel used

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Thermodynamics: Cell Efficiency

- Ideal voltage of a cell operating reversibly on pure hydrogen and oxygen at 1atm pressure and 25 °C is 1.229 V.
- Thus, thermal efficiency of an actual fuel cell operating at a voltage of V_{cell}, based on higher heating value of hydrogen,

$$\eta = 0.83 \times V_{cell} / E_{ideal} = 0.83 \times V_{cell} / 1.229 = 0.675 \times V_{cell}$$

$\eta = a$ → 400°C ↓ 750°C

IT-SOFC 600 – 750°C

SOFC < 600°C

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Thermodynamics: Cell Efficiency

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$\eta =$

IT-SOFC

600 – 750°C

SOFC

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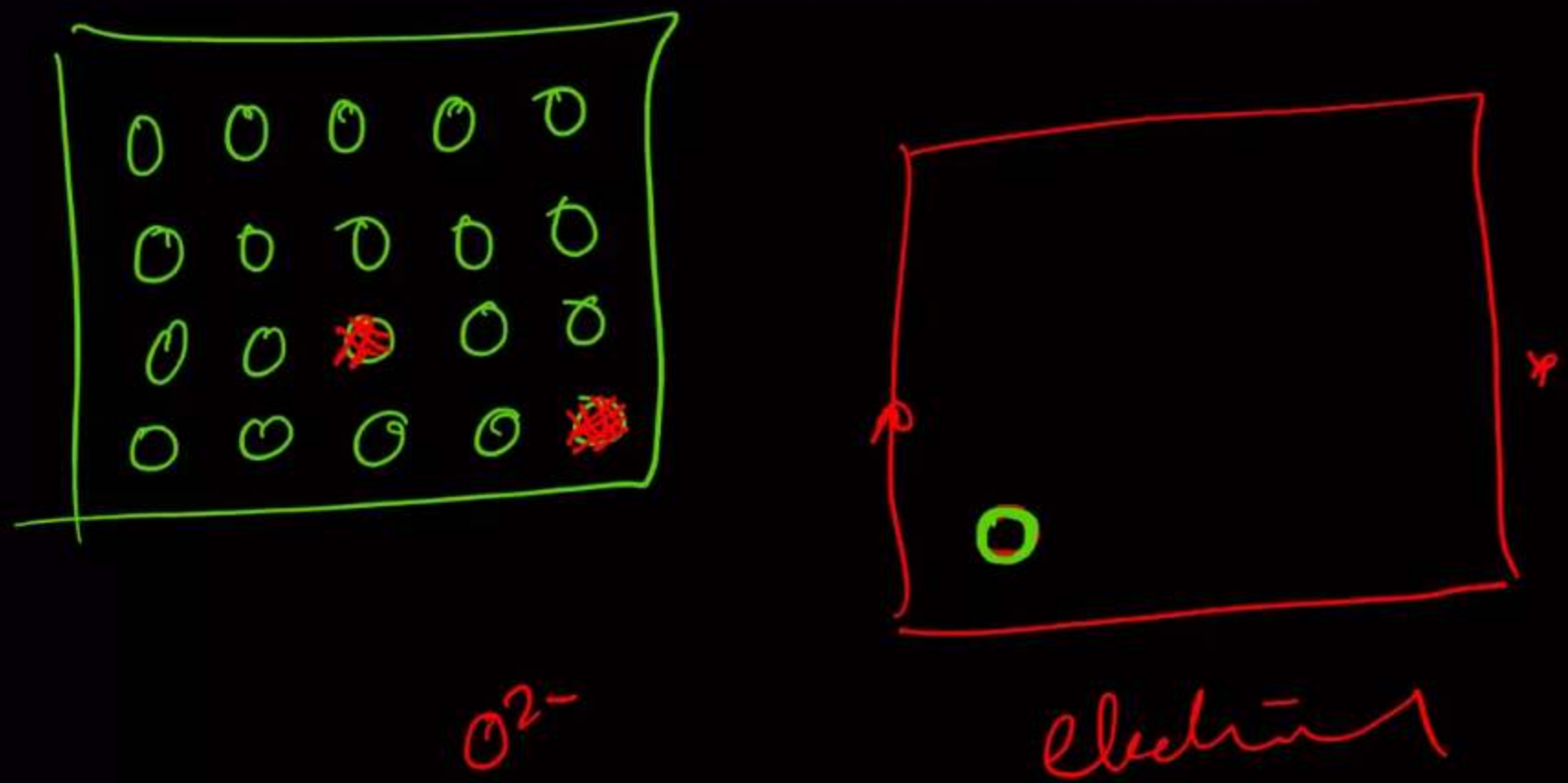
O^{2-}
electron

Nuclear Force

- Strong interactions – that holds nucleons together
- Three attractive forces in the nucleus
    - Neutron-neutron (n-n)
    - Neutron – Proton (n-p)
    - Proton- Proton (p-p)

Nuclear Binding Energy : the mass defect is based on the Einstein equation $E= mc^2$. Proton and neutron combined to form nucleus some of mass disappears (Δm). Which is converted into amount of energy $\Delta E = (\Delta m)\, c^2$

Nuclear Model

- **Liquid drop model** : proposed by Bohr, observed similarities between atomic nucleus and liquid drop
- **Shell model** : nucleus assume that the energy structure is similar to that of an electron cell in atom
- **Collective model** : combines the feature of liquid drop model and shell model.

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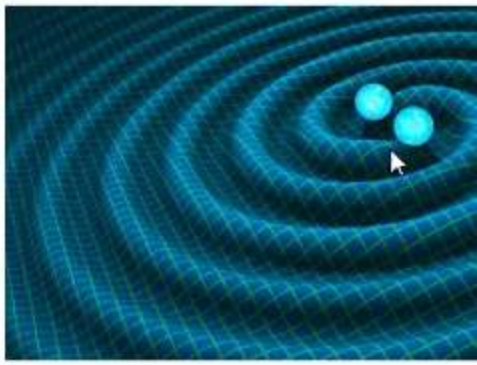
mental Forces in Nature

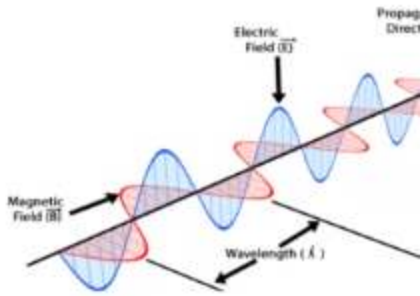
vitation

- Weak force interacting the object with mass
  Long range forces
  Graviton (hypothetical particle)



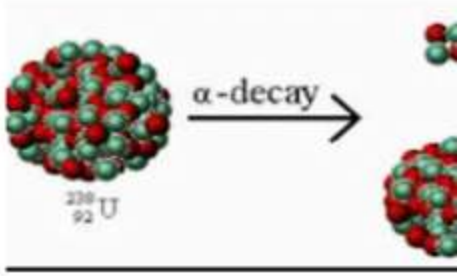
tromagnetism

- Interacting with electrically charged particles
  Long range forces
  Photons



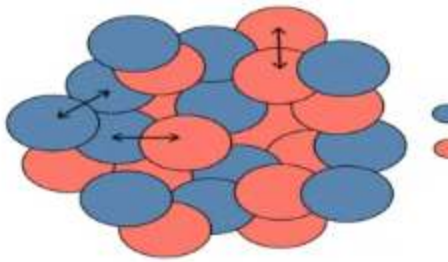
k Nuclear Force

- Particle Decay, Radioactive Decay
  Short range forces
  (W and Z particles)



ng Nuclear Force

- Force that hold Nuclear together
  Short range forces
  Gluons



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Otto Hahn

Germany – Nobel laureate

Discovery of Nuclear Fission

Fritz Strassman

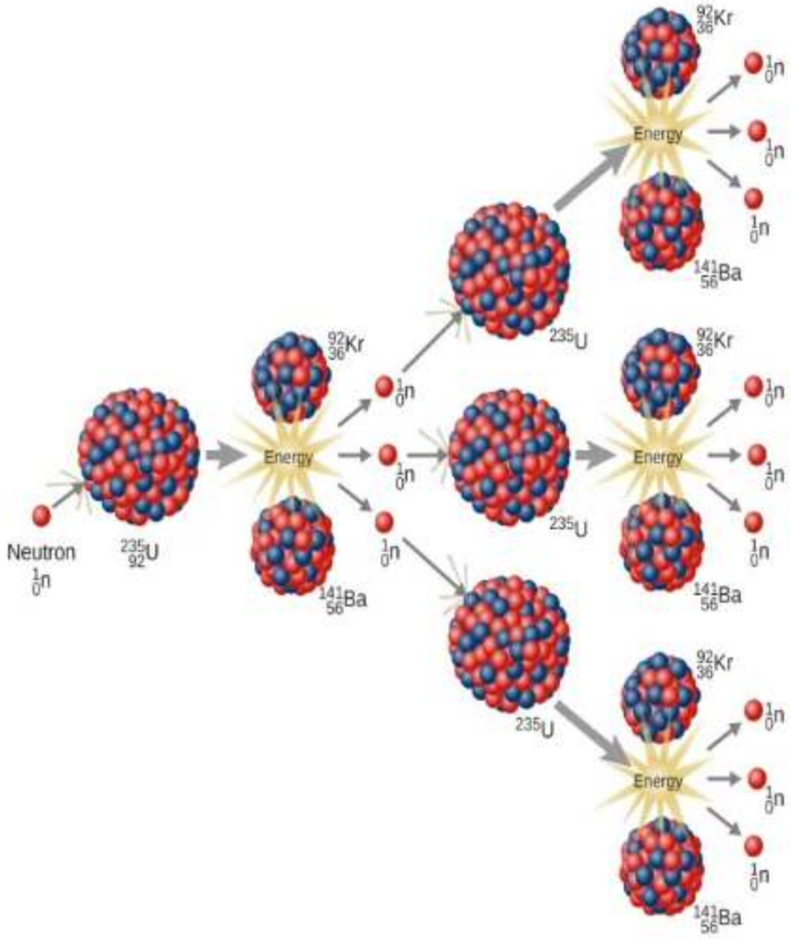
Germany – Nobel laureate
With Otto Hahn, Identifying Ba in the residue after bombarding uranium with neutrons

Enrico Fermi

Italy – Nobel laureate

Creation of world first nuclear chain reaction

Chain Reaction



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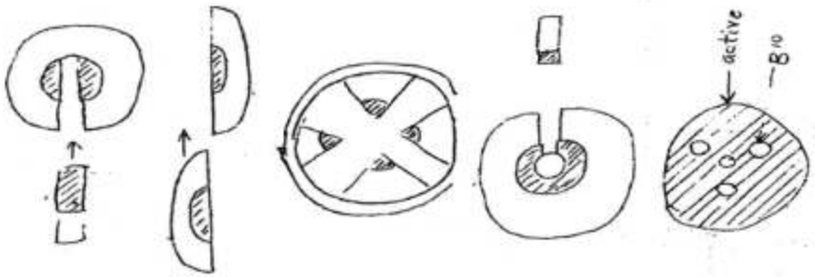
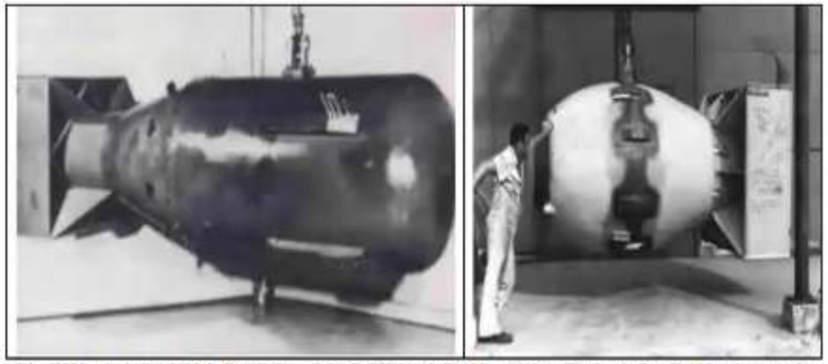
Atom bomb

- In chain reaction, the frequency of fission increases the energy released will be so rapid that an explosion will occur (atomic bomb)
- Essentially consists two pieces of U-235 or Pu-239 each smaller than critical size



Manhattan Project

- Research and development of nuclear energy during the world war II
- Little boy (U-235) – Hiroshima (Aug 6 -1945)
- Fat mam (Pu-239) – Nagasaki (Aug 9- 1945)



The U235 atomic bomb Little Boy (left) and the Pu239 bomb Fat Man (right). The imploding Fat Man became the prototype nuclear weapon after the Second World War, with all the plutonium being manufactured at Hanford, WA.

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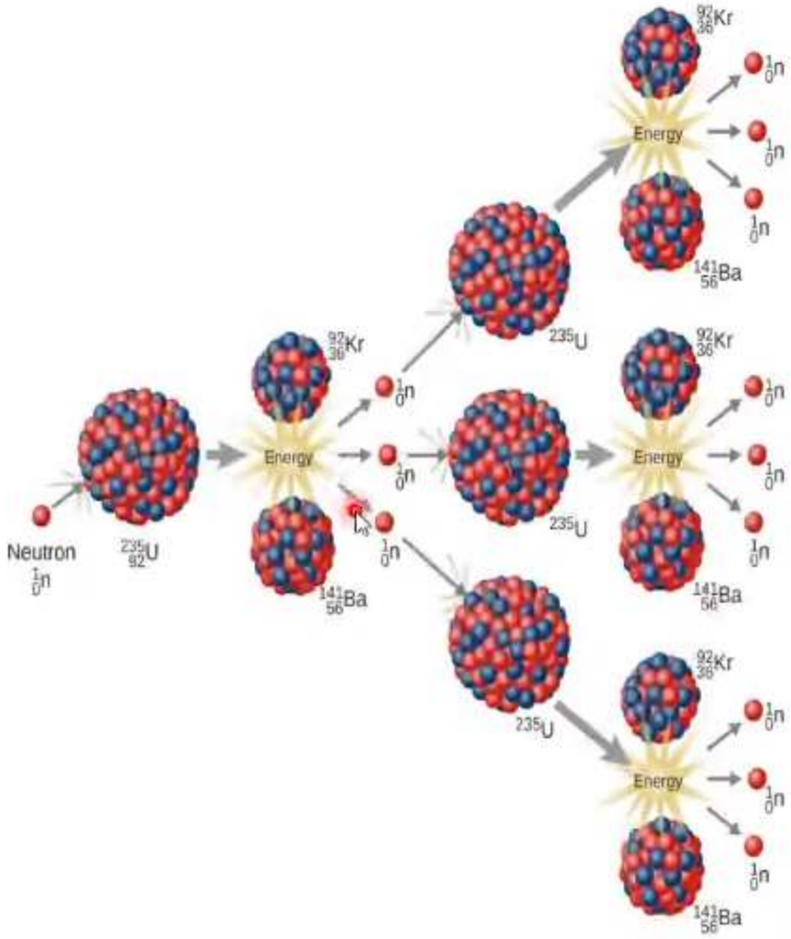

- Self propagating process in which number of neutrons goes on multiplying rapidly (3^n)
- ***Multiplication factor (k)*** – the ratio of secondary neutron produced by the original neutron
- Time taken by each fission 10^{-8} s
- Energy releases ≈ 5×10^{26} Mev in 0.6μs
- High temperature in the order of 10^7 K
- K = No. neutrons in one generation / No. neutrons in preceding generation

- K < 1 *Subcritical (Reaction does not develop)*
- K = 1 *Critical (Limit)*
- K [illegible] *in reaction occurs)*

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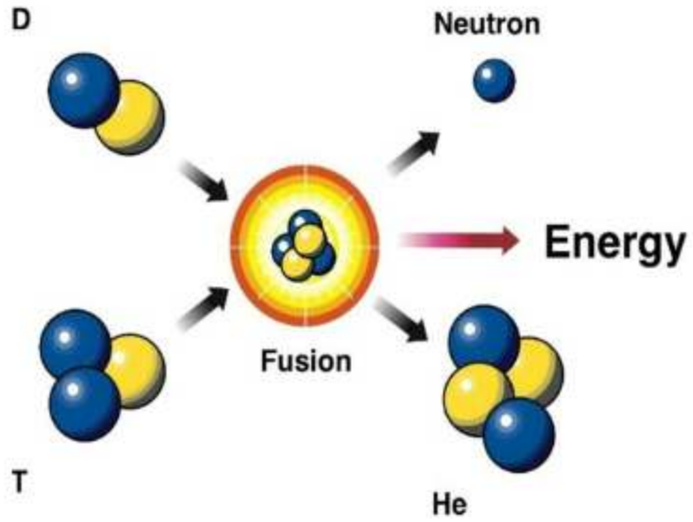
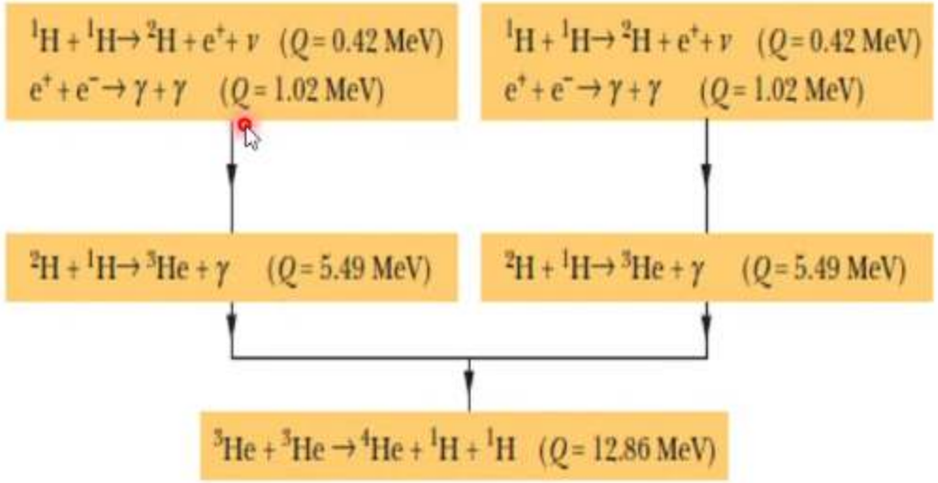
Nuclear Fusion – sources of suns energy

- Two lighter nuclei combined to form single larger nuclei
- Barrier – coulomb repulsive force
- Higher the energy of the nuclei , greater the probability tunnel through the barrier
- The energy of the nuclei comes from thermal motion
  Thermonuclear reaction
- Sun able to control thermonuclear fusion in its core because of its gravity
- multistep process in which hydrogen burned to form helium (p-p cycle). First proposed by Bethe



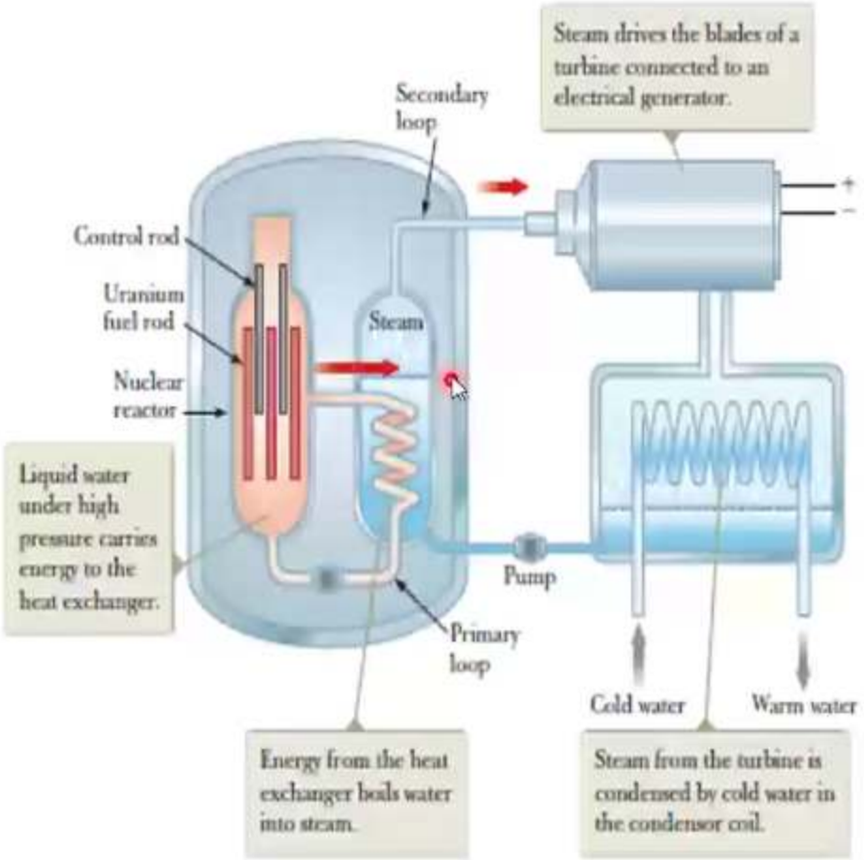


Nuclear Reactor

- The reaction is brought about under controlled.

- Due to fission reaction, the reactor core rise the temperature of the water contained primary loop, which maintain high pressure to keep boiling
- This water also served as the moderator to slow down the neutrons
- Hot water is pumped through the heat exchanger then hot water in the secondary loop converted into steam

- The main elements of the nuclear reactor
    - Fuel
    - Control rod
    - Moderator
    - Cooling system
    - Safety system



Fusion Reactor (controlled thermonuclear reaction)

- The large amount of energy released in the Hydrogen bomb
- The main problem is produce such a high temperature and container for the plasma which stand this temperature

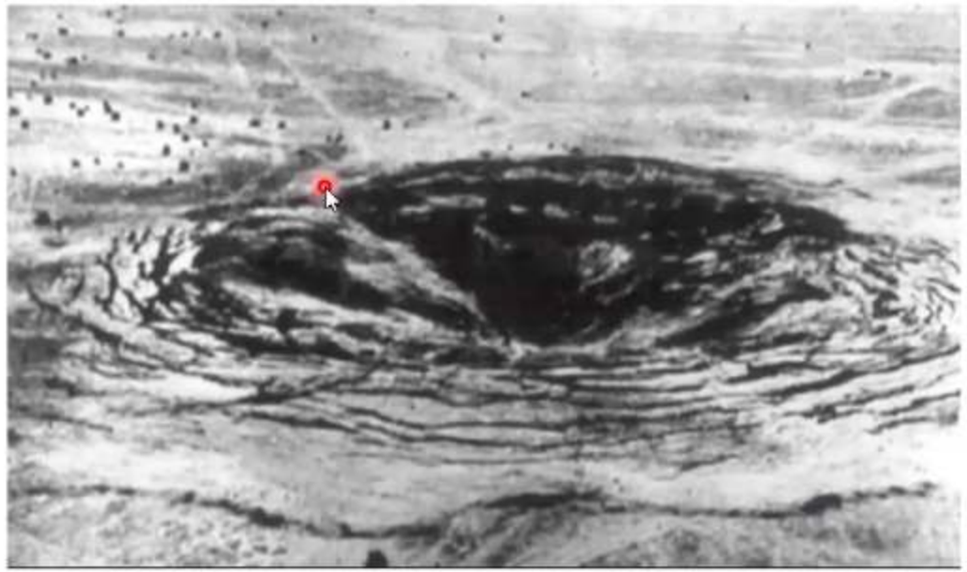
Three challenges for the successful thermonuclear reactor

- **High Particle density n**: the number of density of interacting particle must be great enough. High temperature required , the deuterium would be completely ionized forming an electrically neutral *plasma*
- **A High plasma temperature T** : plasma must be hot otherwise the colliding deuterons will not energetic enough to penetrate coulomb barrier
- **Long confinement time τ** : to contain the hot plasma long enough to maintains it at a density.
- The successful operation of thermonuclear reactor, to have

$$n\tau > 10^{20} s/m^3 \quad \text{- Lawson's criterion}$$

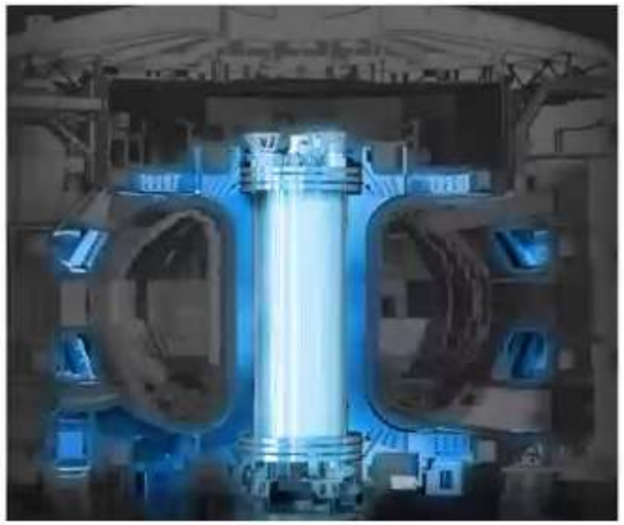
Hydrogen Bomb (uncontrolled thermonuclear reaction)

- Second generation nuclear weapon design
- Uncontrolled thermonuclear reaction
- Achieved by the detonation of atomic bomb
- Fission bomb produces the very high temperature at which thermonuclear reaction start
- Two stages
    - Primary explosive
    - Secondary explosive



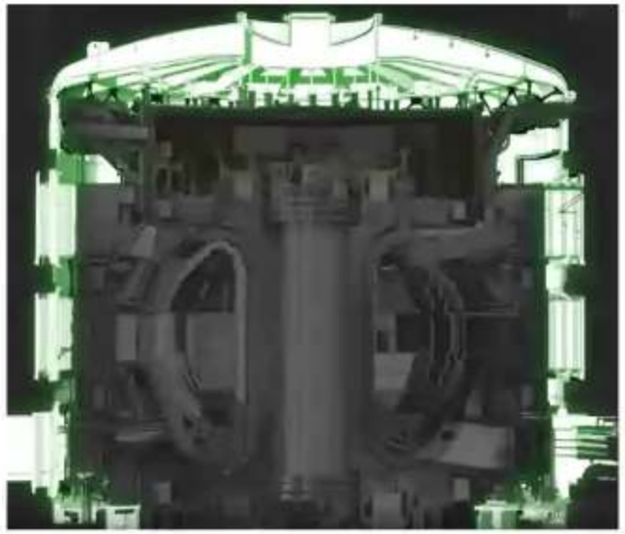
Pokhran nuclear test - 1998

ITER components



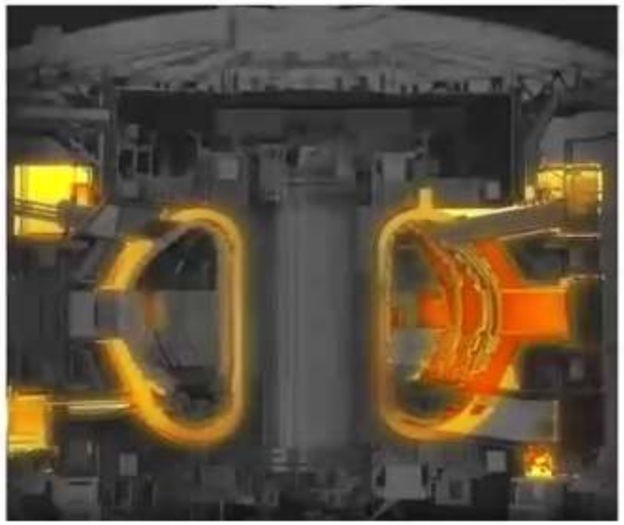
Magnets

- 10 thousand tonnes of superconducting magnet
- 51 KJ stored magnetic energy
- Magnetic temperature 4K (-269˚C) cooler than Pluto
- 100000km Nb3Sn superconducting stand



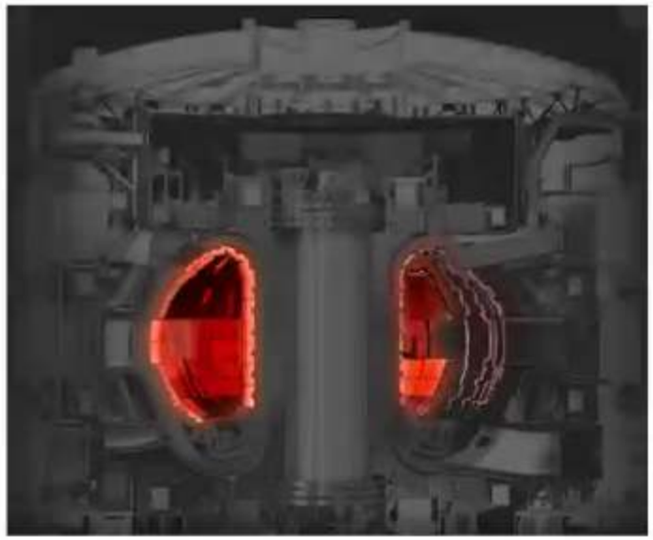
cryostat

- Stainless steel cryostat surrounded in a vacuum vessel and SC magnet
- 3800 T of steel
- 16000 m^3 total volume



Vacuum vessel

- Act as a first safety containment barrier
- 8000T steel plasma chamber
- 840 m^3 plasma volume
- 6m Plasma major radius



blanket

- The blanket shields the steel vacuum vessel and external machine components from high energy neutron produces

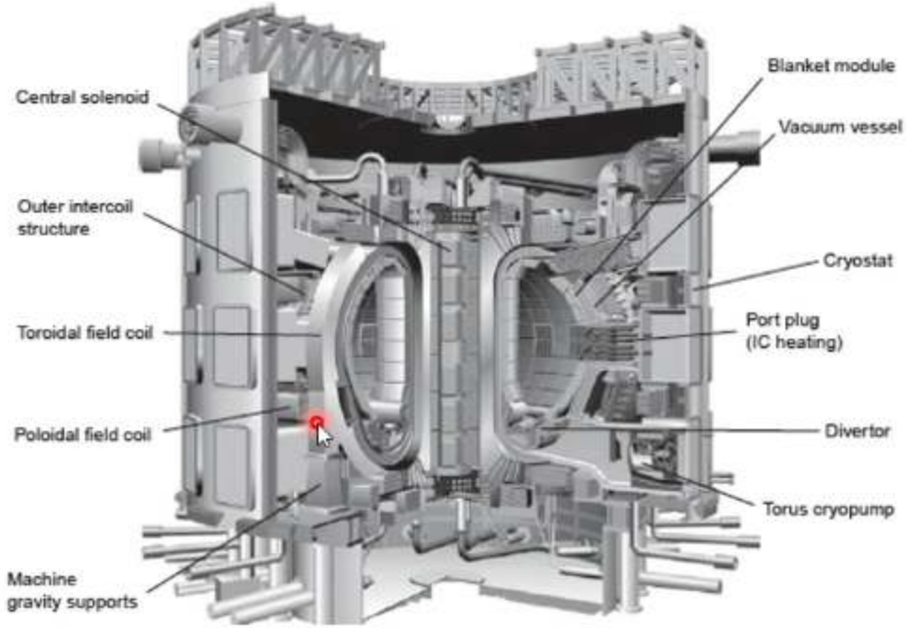
Two schemes for achieving Lawson's criterion :

Magnetic confinement

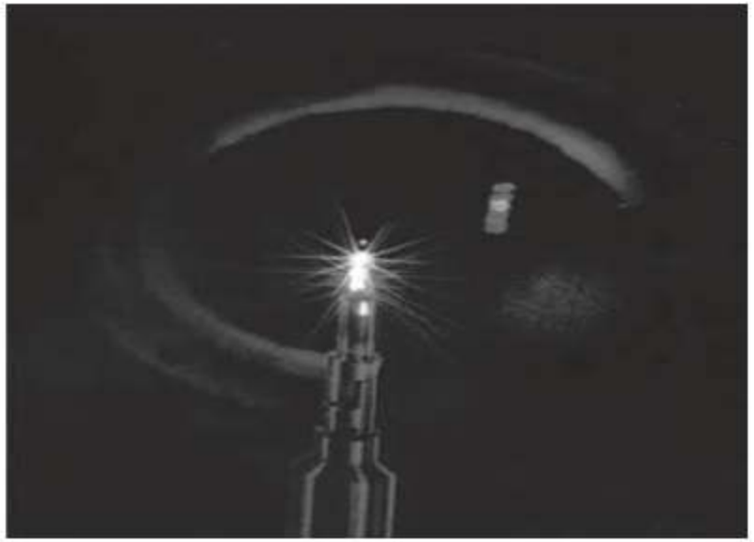
- the magnetic field used to confine the plasma
- Most common arrangement, first developed in Russia called *tokamak*
- The magnetic field is combination of doughnut-shaped magnetic field due to the current in the windings of the toroid
- The magnetic force acting on the charged particles that keep the plasma from touching the walls of the chamber

Inertial confinement

- The pellet of frozen –solid deuterium and tritium bombarded from all sides by pulsed laser beam
- Computer simulation indicate momentum absorbed by hydrogen nuclei from the beams
- It heat it to a temperature 10^8 K and produce 10^6 J of fusion energy in 10^{-10} s



Tokamak fusion reactor



Nova inertial confinement fusion reactor uses powerful laser beam focused on H containing pellet 0.5 mm in diameter to make fusion reaction