

Physics of Materials

Physics of Matter: Atoms in crystals, Atomic bonding, Free electron theory, Band theory, Fermi Level, Energy bands, Conductors, Insulators, Semiconductors, Superconductors, Dielectrics, Magnetic and Plasmonic materials .

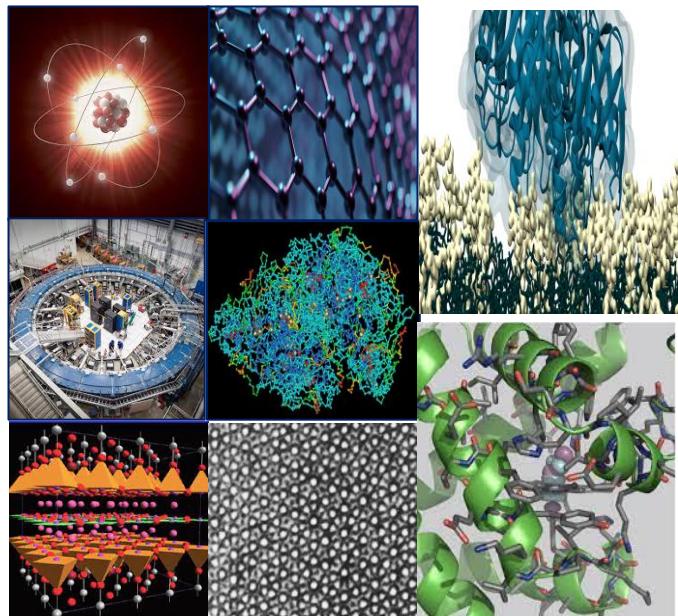
Physics of Nano: Introduction to nanomaterials, Properties of nanomaterials, Types of nanomaterials, Synthesis of Nanomaterials- Top-down and Bottom-up approaches, Quantum confinement, Quantum well, Wire and Dot, Carbon Nano tubes (CNTs), Nanotechnology for medical and industrial applications.

Physics of Energy: 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; Thermal Energy- Conduction, Convection and Radiation; Wind Energy- Turbines and Utility scale wind; Bio energy- Sources and Biomass.

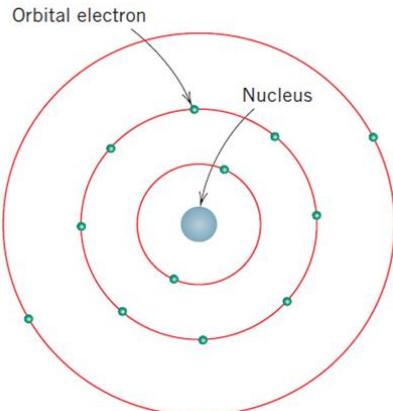
- 1. Arthur Beiser**, Shobhit Mahajan, S. Rai Choudhury, **Concepts of Modern Physics**, 7th Edition, 2017.
- 2. Charles P. Poole**, Jr. Frank J. Owens, **Introduction to Nanotechnology**, A John Wiley-Interscience publication, 2003.
- 3. Robert L. Jaffe**, Washington Taylor, **The Physics of Energy**, Cambridge University Press, 2018. (or)

Physics of Matter

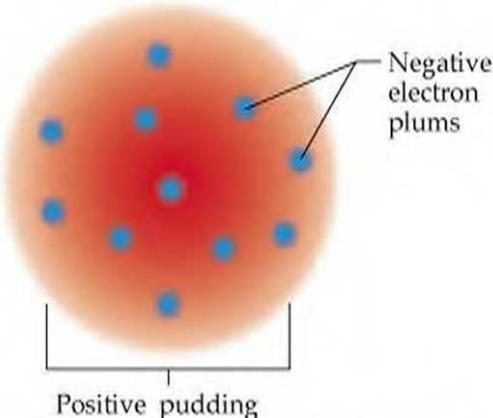
- Atoms in crystals, Atomic bonding.
- Free Electron Theory, Band Theory.
- Fermi Level, Energy Bands.
- Conductors, Insulators, Semiconductors.
- Dielectrics and Magnetic Materials.



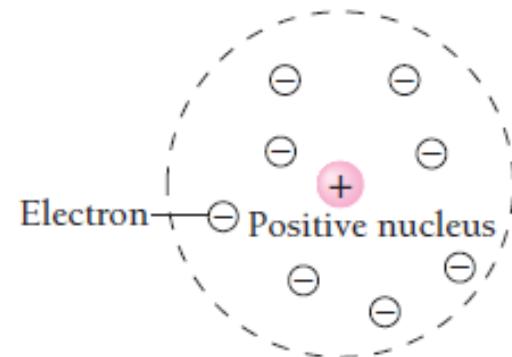
Atoms in crystals



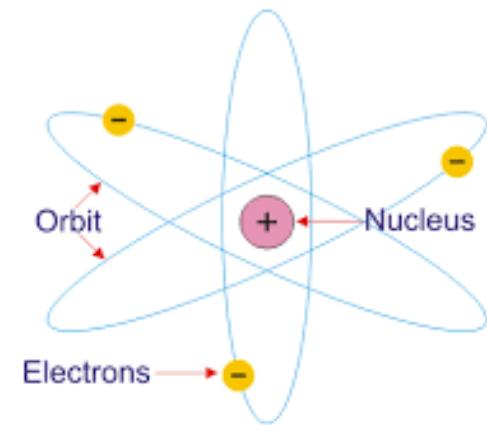
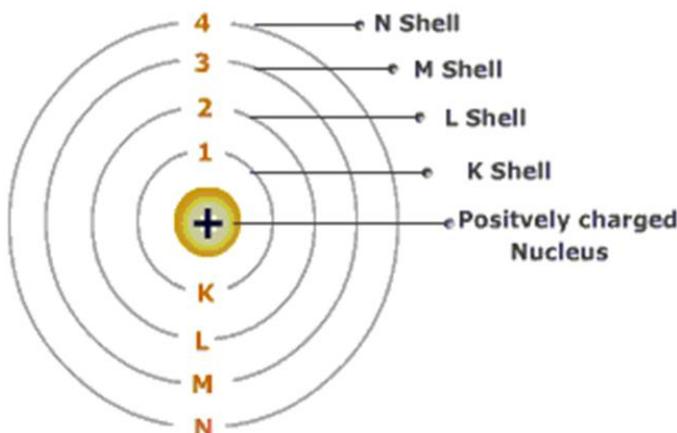
Thomson's model of an atom



Rutherford's model of the atom



Bohr's model of an atom

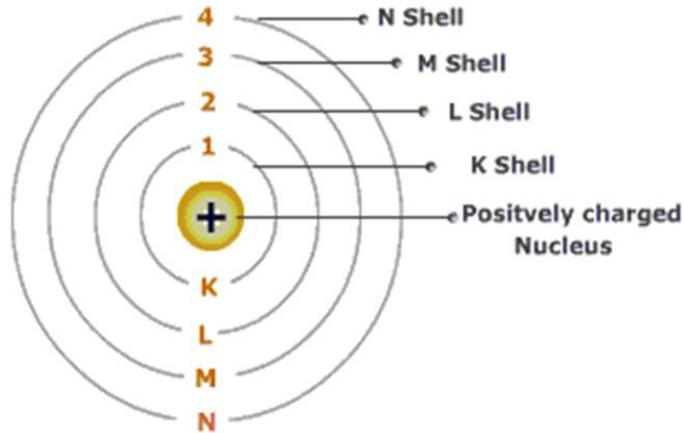


Rutherford's Atomic Model

An electron can circle a nucleus only if its orbit contains an integral number of de Broglie wavelengths

Atoms in crystals

Bohr's model of an atom



An electron can circle a nucleus only if its orbit contains an integral number of de Broglie wavelengths

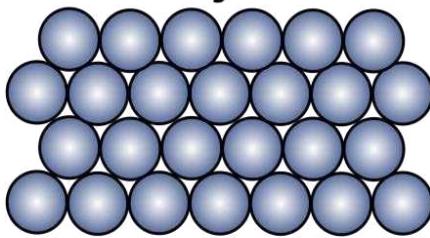
- Combines both the particle and wave characters of the electron since the electron wavelength depends upon the orbital velocity needed to balance the pull of the nucleus.

Atoms in crystals

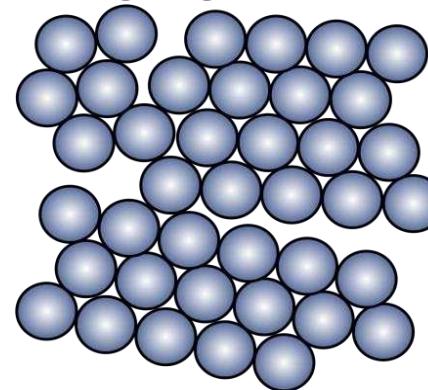
Solids

- *Crystalline* and *Amorphous*
- In a **Crystalline solid**, atoms are arranged in an orderly manner.
- The atoms are having long range order.

Monocrystalline

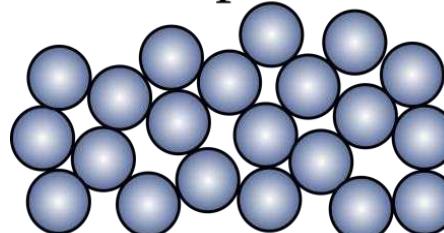


Polycrystalline



- In an **Amorphous solid**, atoms are not present in an orderly manner.
- They are haphazardly arranged.

Amorphous



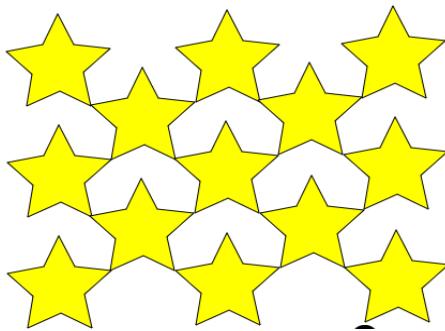
Atoms in crystals

- A crystal or crystalline solid is a solid material whose parts of atoms, molecules, or ions are arranged in a highly ordered microscopic structure to form a **crystal lattice**.

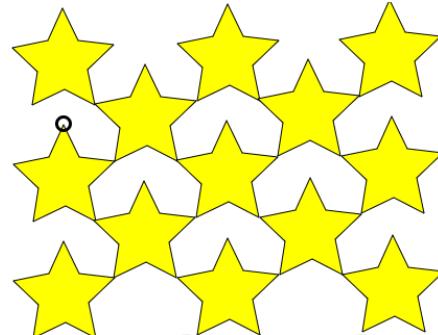
Crystal structure = **Lattice + Basis**

- A crystal structure can be formed with a combination of **Lattice** and **Basis**.

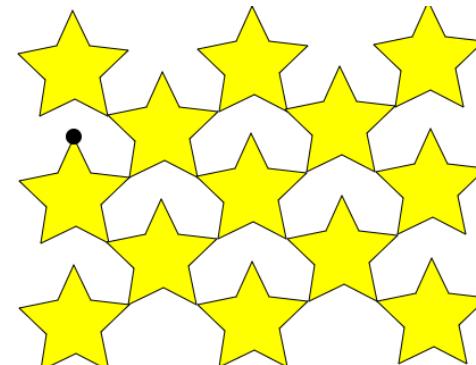
Atoms in crystals



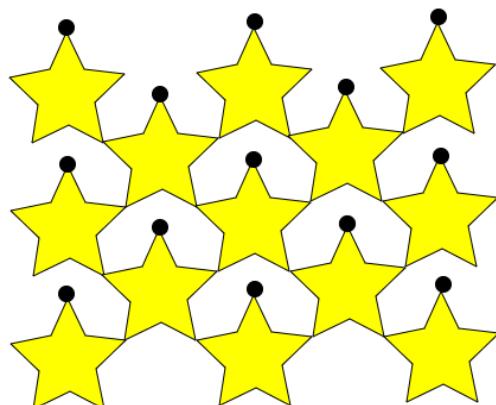
Consider a pattern as such which displays translational periodicity



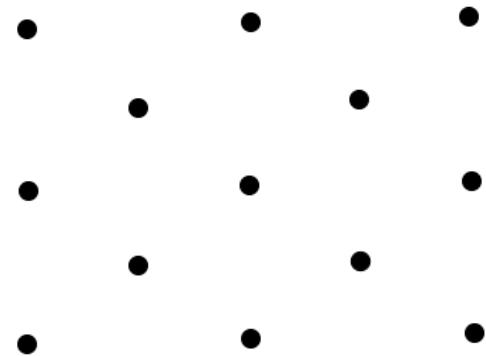
Choose any point on the pattern. Say the tip of the star for example



Mark this point



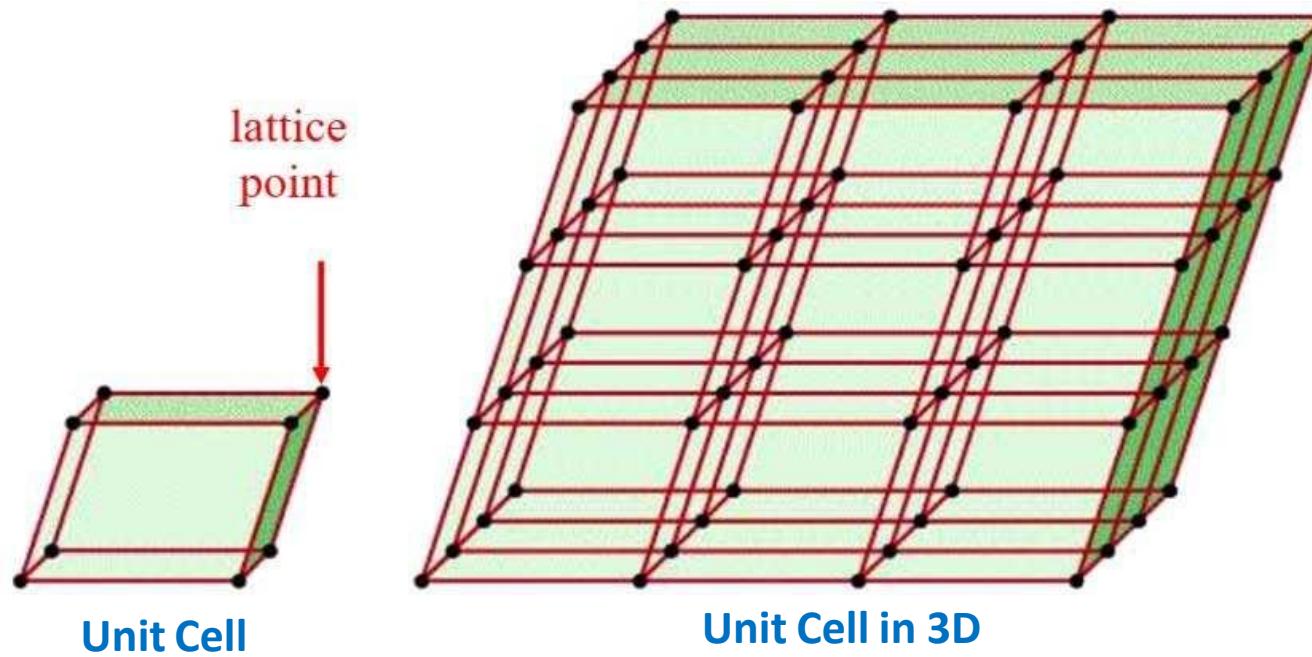
Now mark all identical points in a similar manner



Now remove the background to produce the lattice. This is the lattice

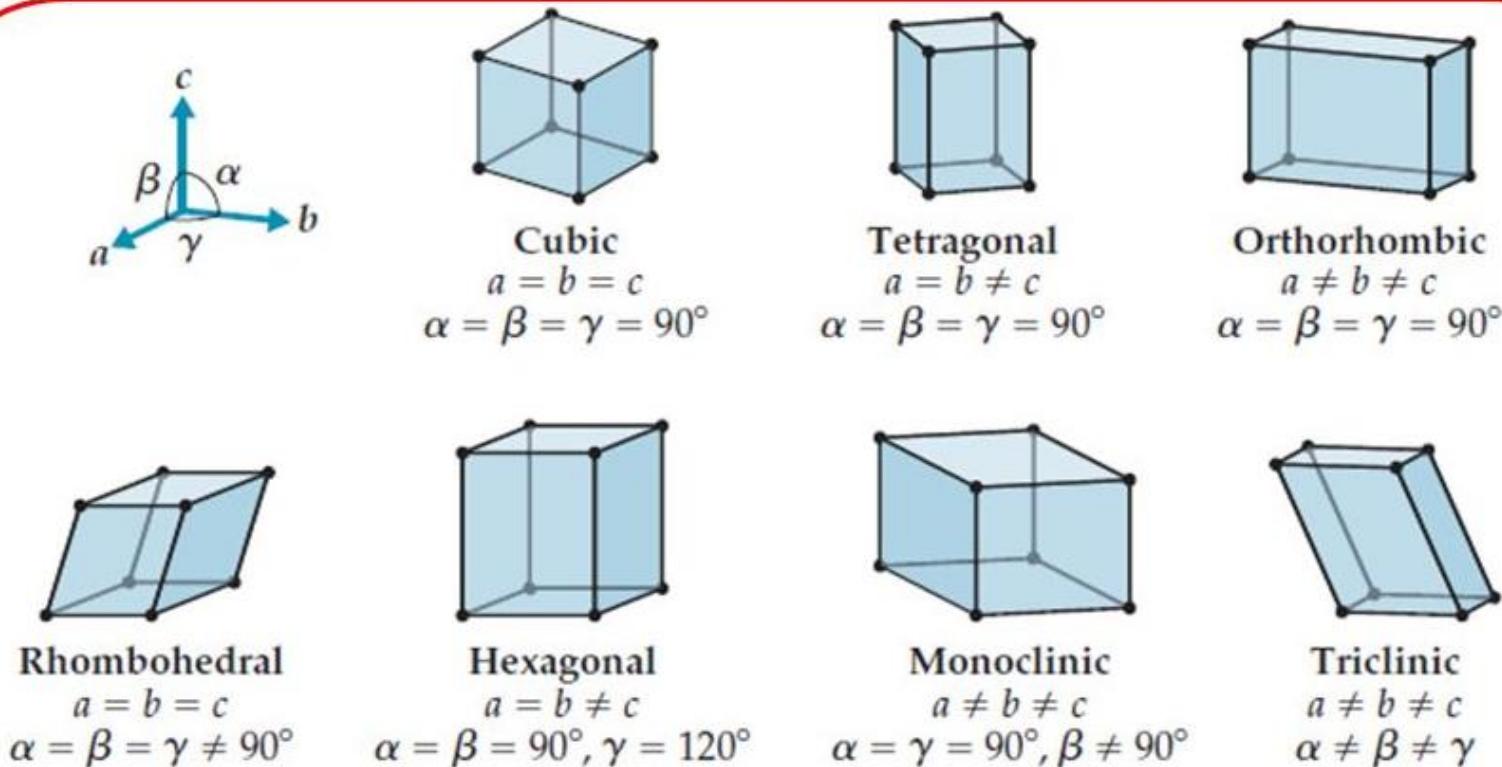
Unit Cell

- Atoms or group of atoms forming a building block of smallest acceptable size of the whole volume of a crystal is defined as a **unit cell**.



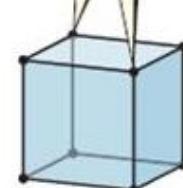
- By stacking identical unit cells, entire lattice can be constructed.
- Lattice points are located at the *corner of the unit cell* and in some cases, at either *faces* or the *center of the unit cell*.

Crystal System



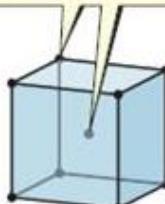
▲ FIGURE 12.6 The seven three-dimensional primitive lattices.

Lattice points only at corners



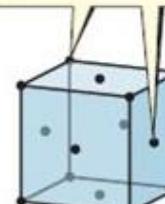
Primitive cubic lattice

Lattice points at corners plus one lattice point in center of unit cell



Body-centered cubic lattice

Lattice points at corners plus one lattice point at the center of each face

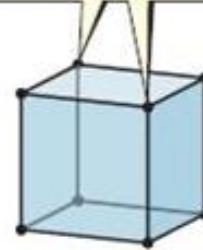


Face-centered cubic lattice

Crystal System

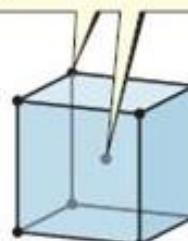
- *The unit cell is chosen such that it is the smallest unit cell that reflects the symmetry of the structure.*

Lattice points only at corners



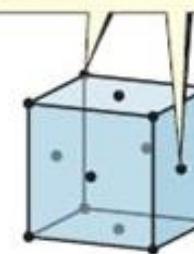
Primitive cubic lattice

Lattice points at corners plus one lattice point in center of unit cell



Body-centered cubic lattice

Lattice points at corners plus one lattice point at the center of each face



Face-centered cubic lattice

Primitive and Non-primitive Unit Cells:

- Primitive unit cells contain only one lattice point, which is made up from the lattice points at each of the corners.
- Non-primitive unit cells contain additional lattice points, either on a face of the unit cell or within the unit cell, and so have more than one lattice point per unit cell.

Atomic Bonding

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

There are four important mechanisms by which atoms are bonded in materials.

1. Metallic bonds
2. Covalent bonds
3. Ionic bonds
4. Van der Waals bonds
5. Hydrogen Bonds

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

Atomic Bonding

Distance between two atoms and nature of atoms determines type of bonding and amount of interaction.

Primary Bonding- Interatomic bonding (Stronger and high energy (1-5 eV)

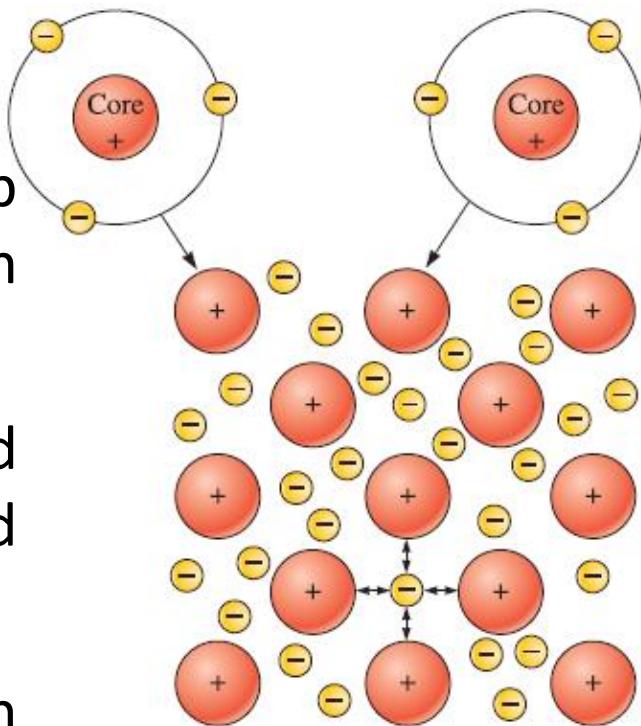
1. Ionic Bonding- bond between metals and non-metals (NaCl)
2. Covalent Bonding- bond between non-metals (CO₂)
3. Metallic Bonding- bond between metallic elements

Secondary Bonding- Intermolecular bonding (Weaker, 0.02-0.5 eV)

1. Van Der Waal's Bonding
2. Hydrogen Bonding

Metallic Bonding

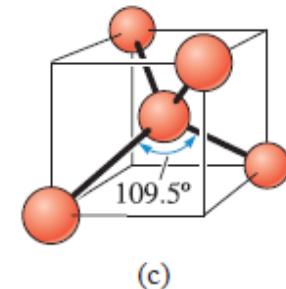
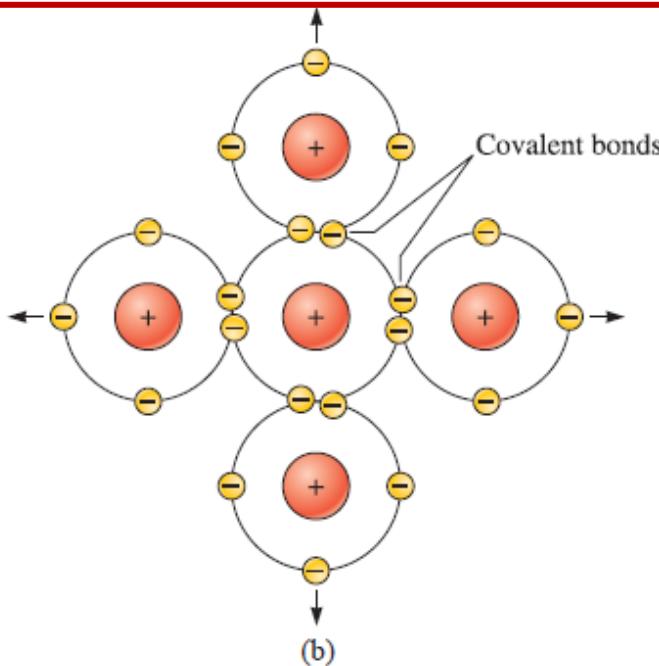
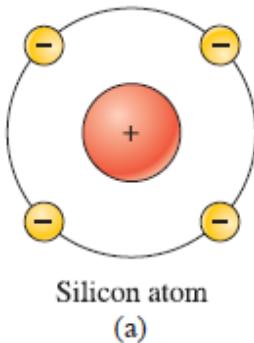
- Metallic bond forms when atoms give up their valence electrons, which form an electron sea.
- Positively charged atom cores are bonded by mutual attraction to negatively charged electrons.
- Electrostatic force of attraction between positively charged ions and delocalized outer electrons.
- As valence electrons are not fixed in any one position, most pure metals are good electrical conductors of electricity at relatively low temperatures.
- Metallic bonds are non-directional- provides ductility to metals.



cont.....

- 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 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.*

The Covalent Bond

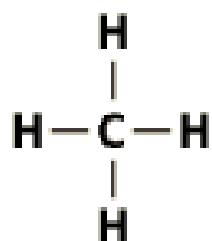


- Covalent bonding requires electrons be shared between atoms so that each atom has its outer sp orbitals filled.
- In silicon, with valence of four, four covalent bonds must be formed.
- Covalent bonds are directional.
- In silicon, a tetrahedral structure is formed with angles of 109.5° required between each covalent bond.

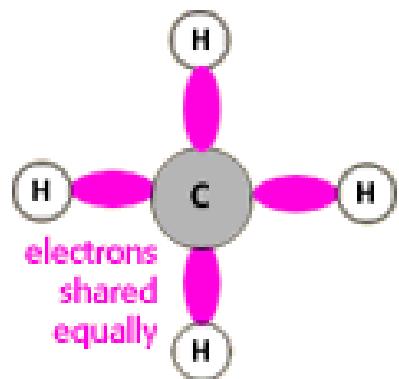
The Covalent Bond

- 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.

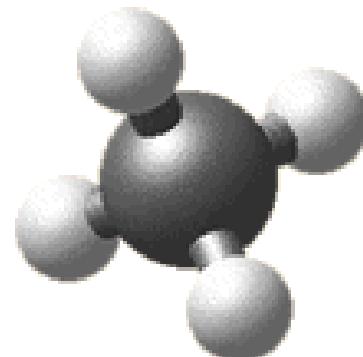
structural formula



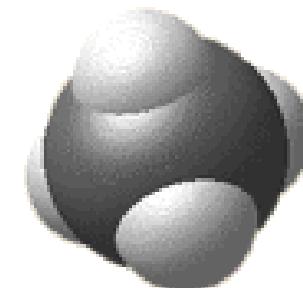
covalent bond diagram



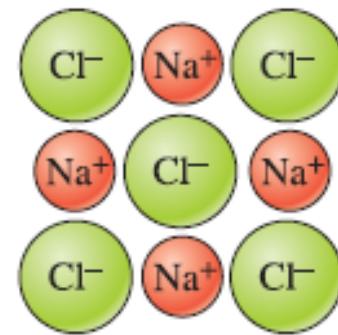
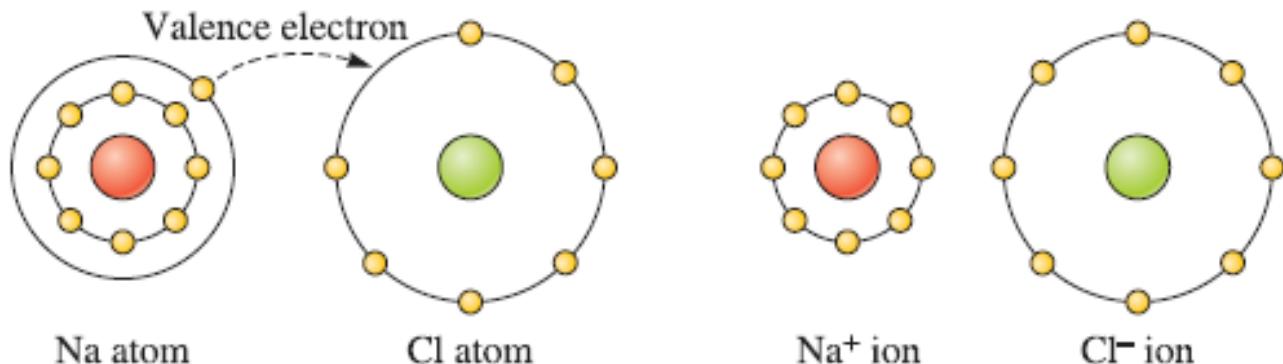
ball & stick model



space-filling model



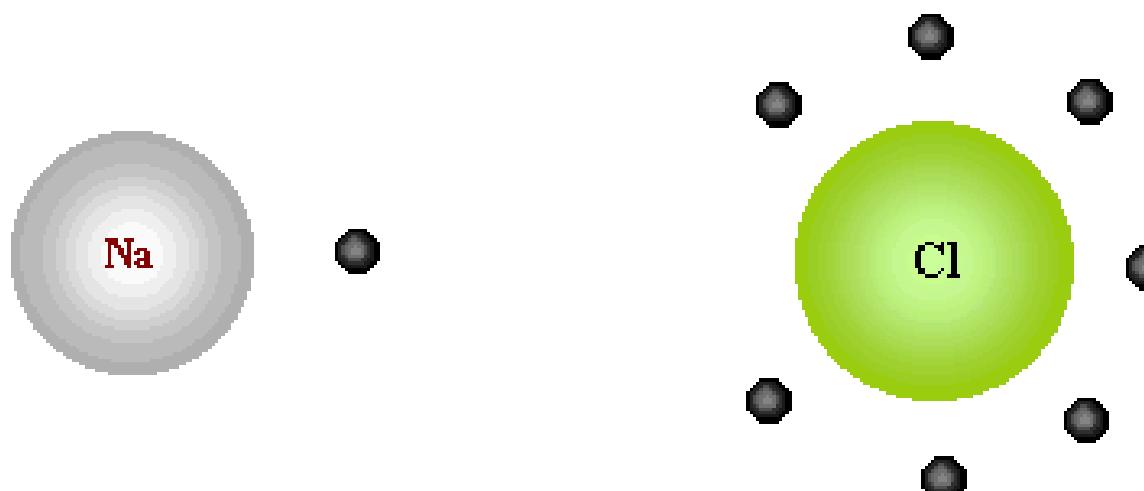
The Ionic Bond



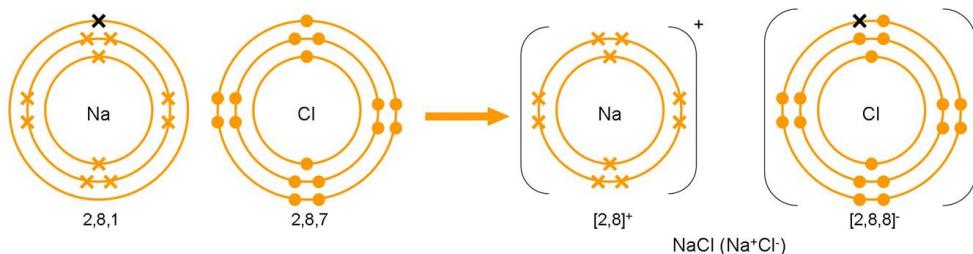
- Electrostatic force of attraction between positively and negatively charged ions (**between non-metals and metals**).
- All ionic compounds are crystalline solids at room temperature.
- An ionic bond is created between two unlike atoms with different electronegativities.
- When sodium donates its valence electron to chlorine, each becomes an ion, attraction occurs, and the ionic bond is formed.

The Ionic Bond

- Orbita of electron in ions begin to overlap with each other.
- Electron begins to repel each other by virtue of the repulsive electrostatic coulomb force.
- Of course, closer together the ions are, 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 system increases very rapidly.

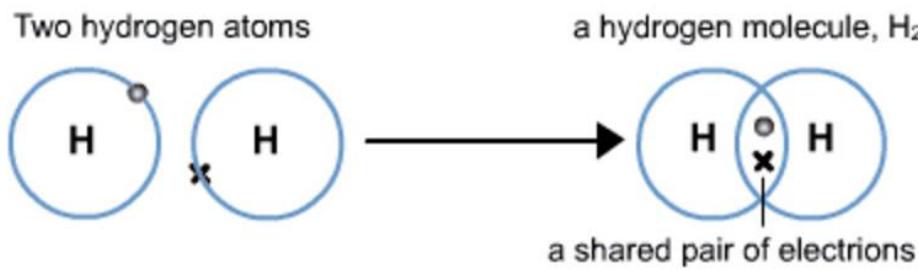


Ionic Bonding



- 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

Van der Waals Bonding

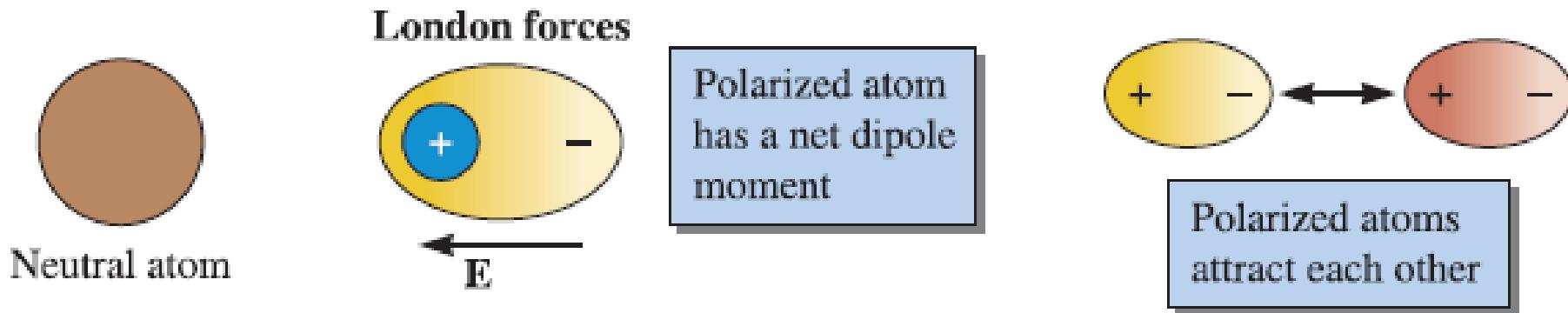
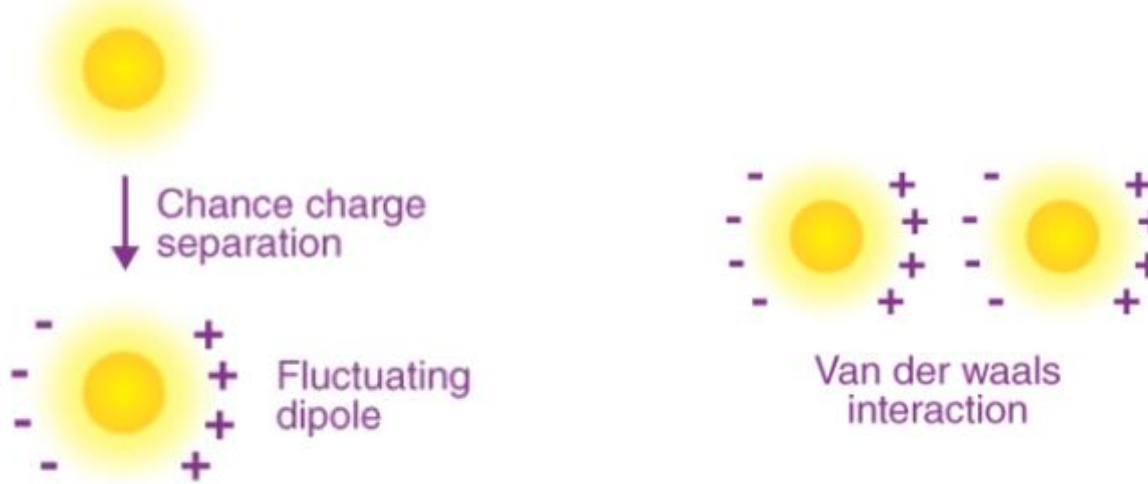


Illustration of London forces, a type of a van der Waals force, between atoms.

- Temporary bond between neutral atoms and molecules.
- Inert gases form solid crystals at sufficiently low temperatures.

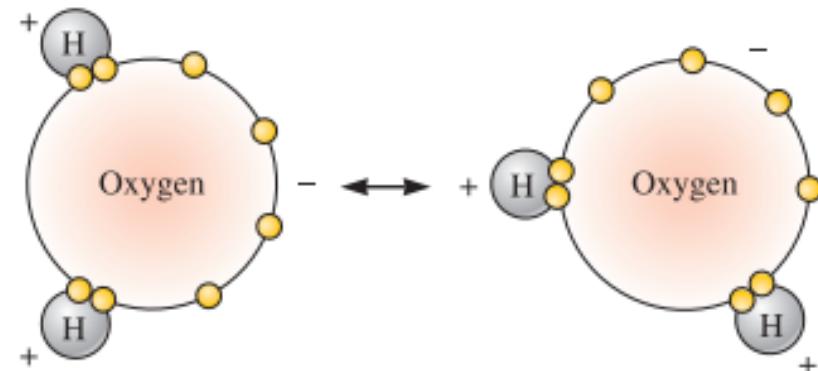
Van der Waals Bond



- Weak forces of attraction result from natural fluctuations in the electron density of all molecules causes small temporary dipoles within the molecules.
- Electric field of this imbalance can induce a dipole moment in a neighbouring atom, to attract it.
- Dipole in 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.

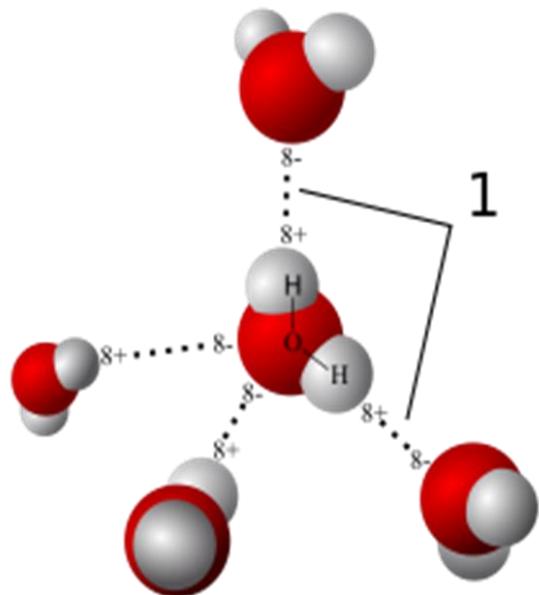
Hydrogen Bond

- Bonding between molecules that have permanent dipole moment, known as Keesom force.
- Referred as **hydrogen bond**, where hydrogen atoms represent one of the polarized regions.
- Hydrogen bonding is essentially Keesom force and is type of **van der Waals force**.
- Keesom interactions are formed as a result of polarization of molecules or groups of atoms.
- In water, electrons in oxygen tend to concentrate away from hydrogen.
- Resulting charge difference permits molecule to be weakly bonded to other water molecules.



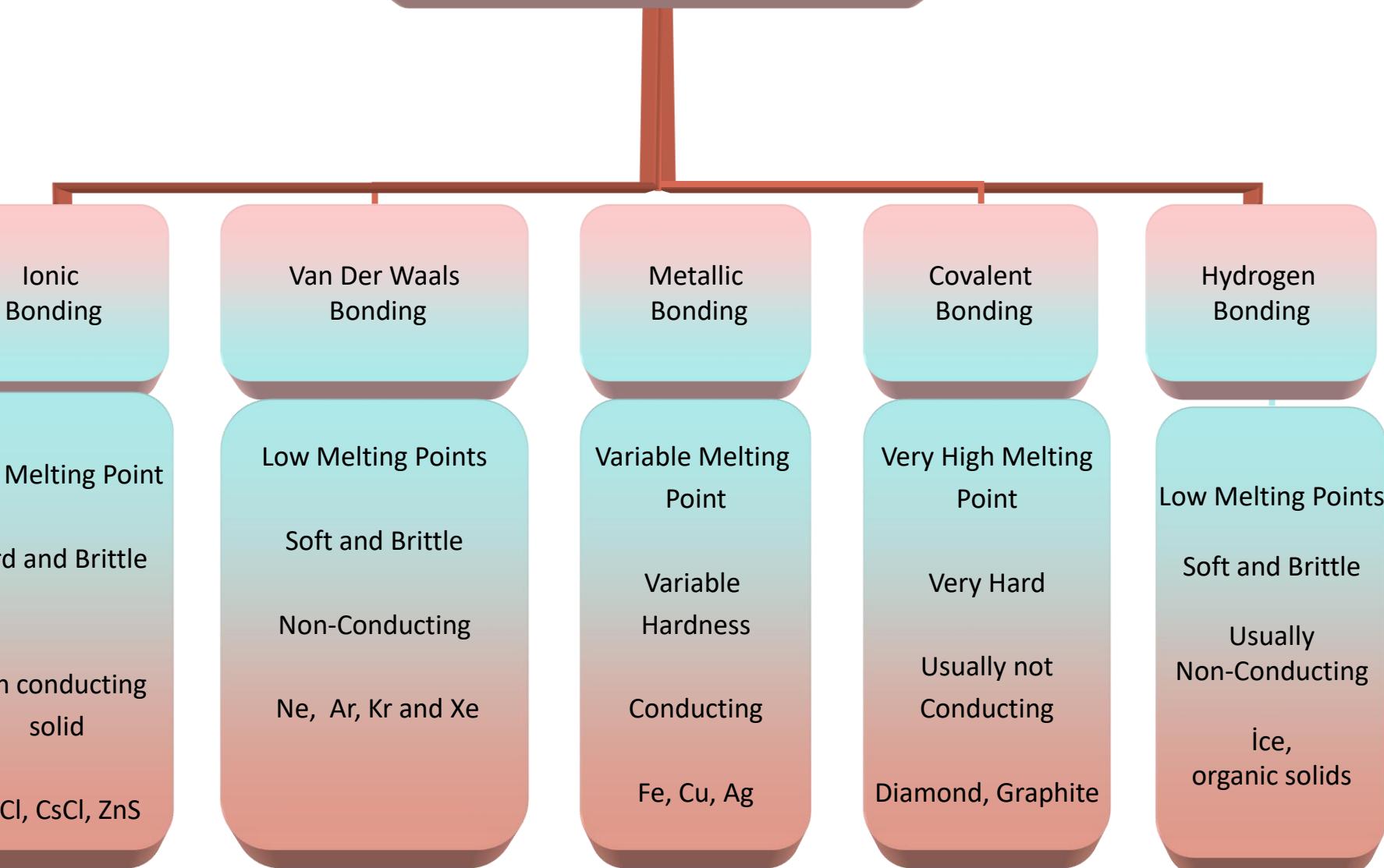
Hydrogen Bond

- 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



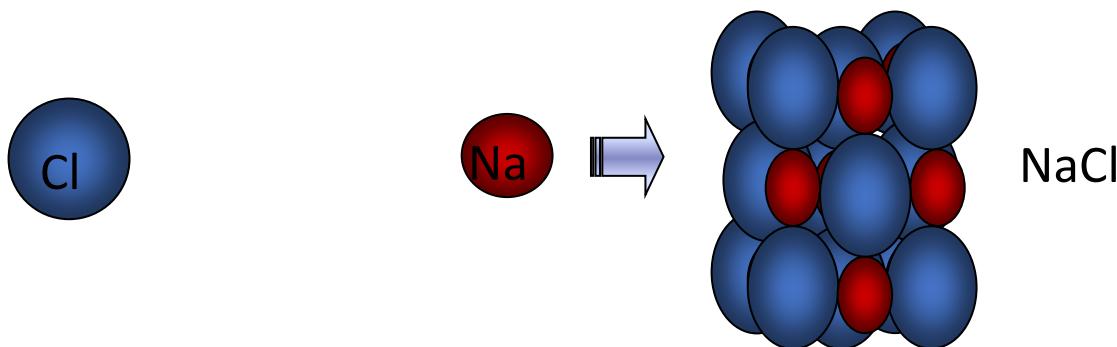
Summary

Types of Bonding

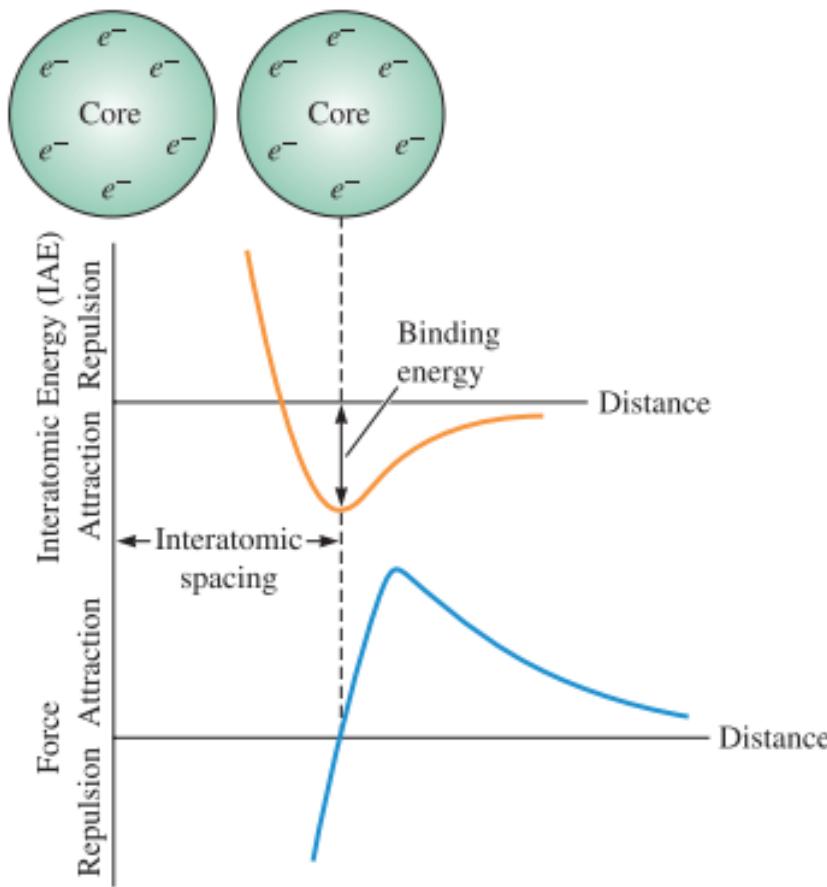


Energies of Interactions Between Atoms

- 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.



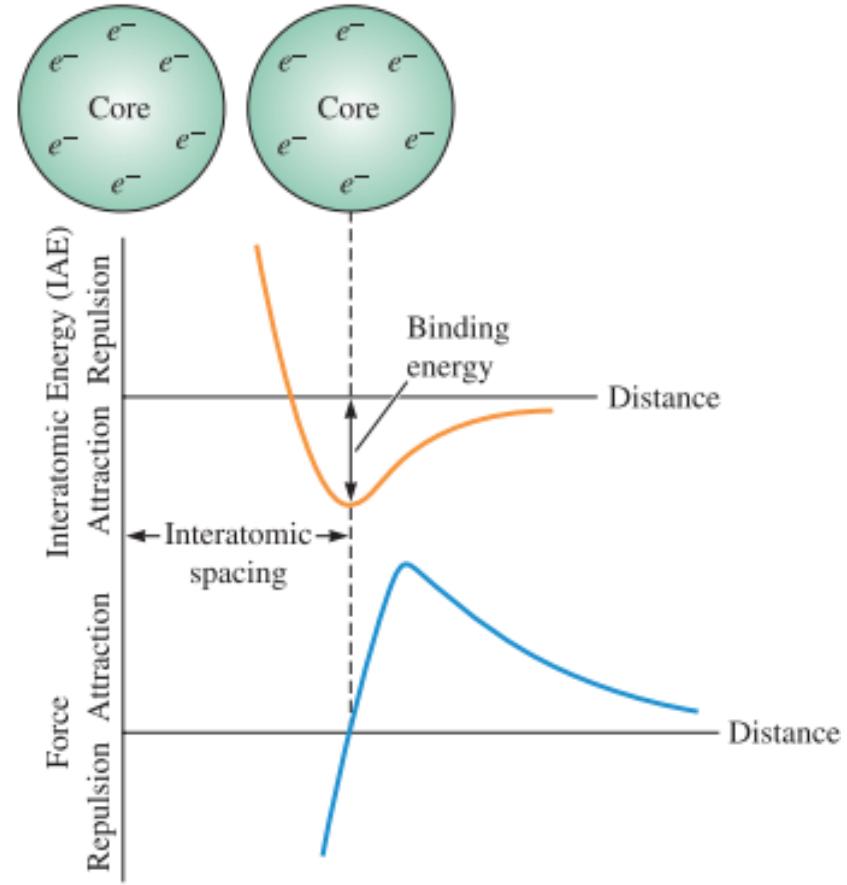
Interatomic spacing



Atoms or ions are separated by an equilibrium spacing that corresponds to the minimum interatomic energy for a pair of atoms or ions (or when zero force is acting to repel or attract the atoms or ions)

Interatomic Spacing: Equilibrium distance between atoms is caused by a balance between repulsive and attractive forces.

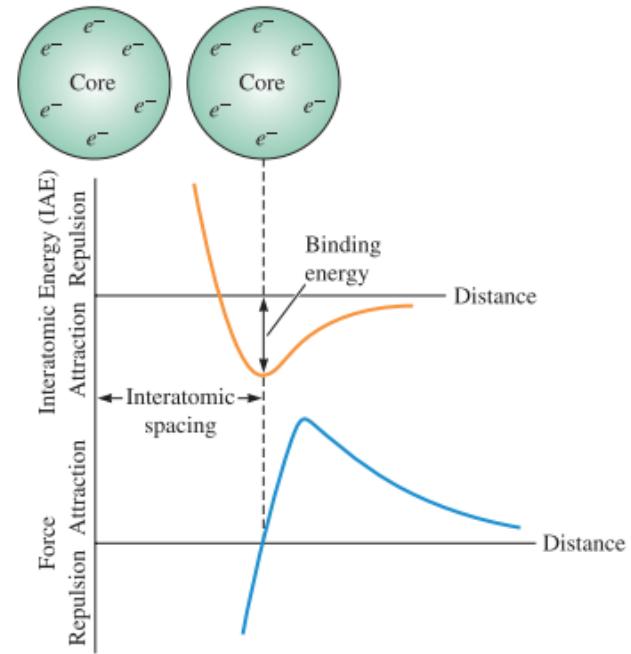
Interatomic spacing



- In metallic bond, attraction between electrons and ion cores is balanced by the repulsion between ion cores.
- Equilibrium separation occurs when total interatomic energy (IAE) of the pair of atoms is at a **minimum**, or when no net force is acting to either attract or repel the atoms

Binding Energy

- Minimum energy or energy required to create or break the bond is **binding energy**.
- Materials having a high binding energy also have a high strength and a high melting temperature.
- Ionically bonded materials have a particularly large binding energy because of the large difference in electronegativities between the ions.
- Metals have lower binding energies because electronegativities of atoms are similar.



Bond	Binding Energy (kcal/mol)
Ionic	150–370
Covalent	125–300
Metallic	25–200
Van der Waals	<10

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.

Free electron theory

Important Terminologies

- **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.

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

Free electron theory

Cont.....

- **Mean free path (λ):**
- Free electrons in a metal are continuously moving in all directions and with various speeds.
- They frequently collide with one another.
- Therefore, they move in straight line with constant speeds between two successive collisions.
- The mean free path is the average distance traveled by an electron between two successive collisions with other free electrons.
- **Mean collision time:**
- The average time taken by the electrons between two consecutive collisions of electron with the lattice points is called mean collision time.

Free electron theory

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.

Free electron theory

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

6. Free electrons are accelerated in the opposite direction of applied electric field on application of electric field.
7. Mutual repulsion among electrons is ignored, so that they move in all the directions with all possible velocities.
8. In the absence of field, energy associated with an electron at temperature T is given by $\frac{3}{2} kT$
9. Related to the kinetic energy equation $\frac{3}{2} kT = \frac{1}{2} m v_{th}^2$,
 v_{th} = thermal velocity.

Free electron theory

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.)

Drawbacks 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 $\frac{K}{\sigma T} = \text{constant}$ is not applicable at lower temperatures.

Free electron theory

Drawbacks 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 theory the electronic specific heat is equal to $\frac{3}{2}R$ while the actual value is $0.01R$

Free electron theory

Quantum free electron theory-electrical conductivity

- Electron as a quantum particle and follows quantum laws.
- Fermi level electrons have maximum velocity and are known as Fermi velocity and is represented by the Fermi sphere.

Free electron theory

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

Free electron theory

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 $F = ma$

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

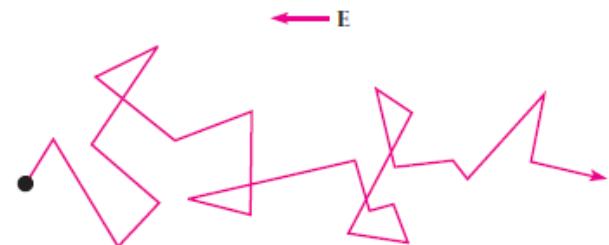
The average velocity acquired (i.e. drift velocity) by the electrons by the application of electric field is

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

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

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

Where \bar{c} = RMS velocity.



Free electron theory

Classical free electron theory –electrical conductivity

The relation between current and drift velocity is

$$i = neAv_d$$
$$j = nev_d \quad (3)$$

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 $\bar{c} = \sqrt{\frac{3KT}{m}}$

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

Free electron theory

Classical free electron theory –electrical conductivity

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

Mobility μ

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

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

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

$$j = \sigma E$$

Free electron theory

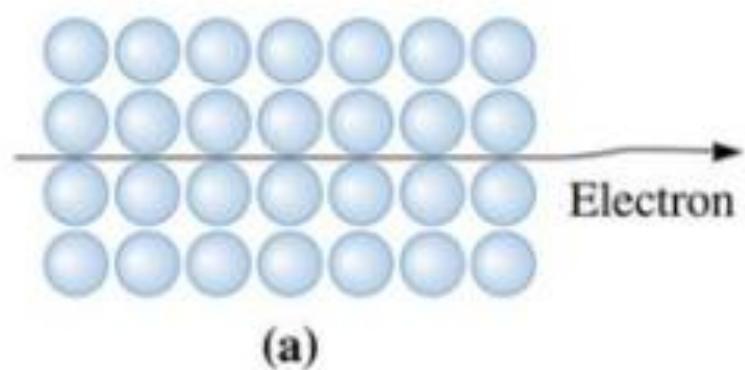
Sources of electrical resistance in metals

- 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.

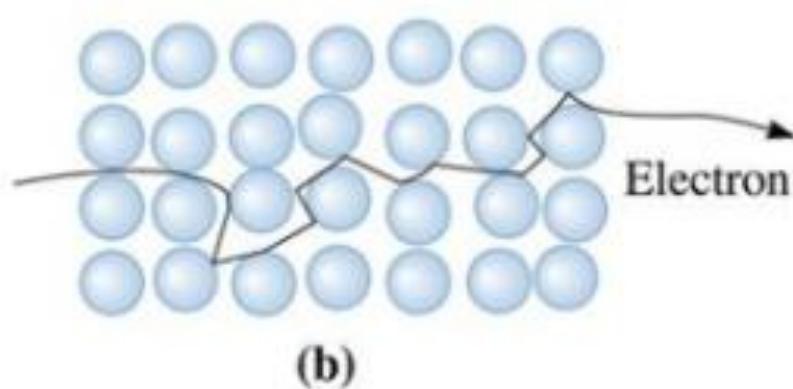
Conductivity of Metals and Alloys

- 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

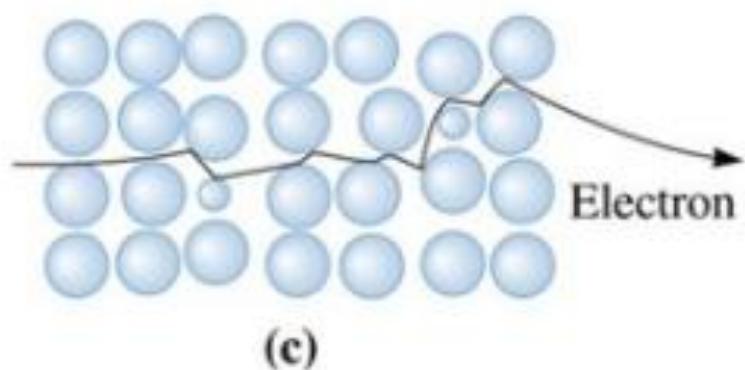
Conductivity of metals



(a)



(b)



(c)

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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.

Conductivity of metals

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 .

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

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

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

Conductivity of metals

Temperature effect:

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

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

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

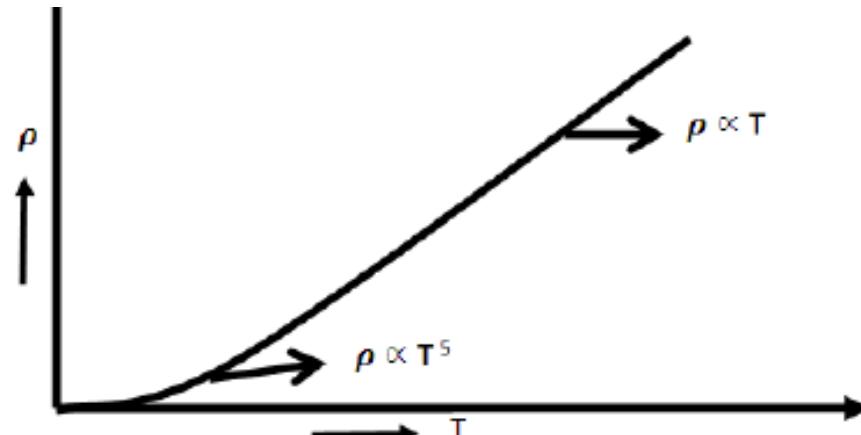
From equations (3) and (4)

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

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.

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



The conductivity of metal is inversely proportional to their temperature.

Conductivity of metals

Defect dependence:

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

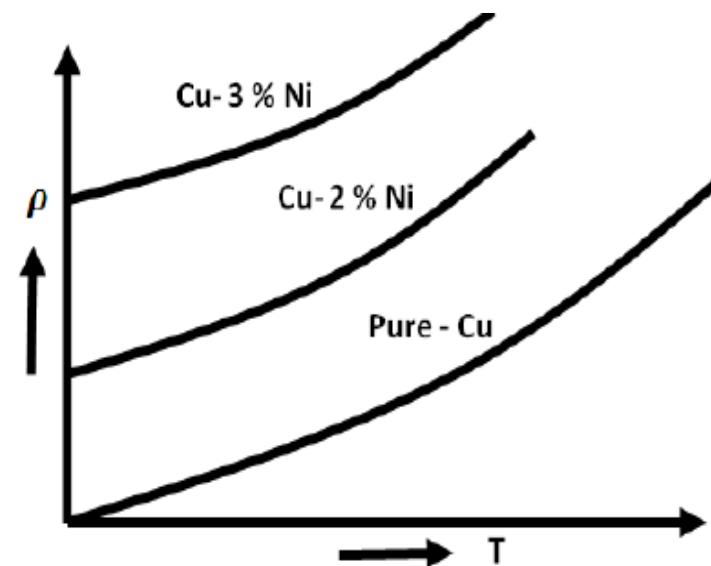
$$\rho(x) = AX(1 - X)$$

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

Conductivity of metals

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.)
- $K = -\frac{\Delta Q}{\Delta t} / A \frac{\Delta T}{\Delta x}$
- $K_{\text{total}} = K_{\text{electrons}} + K_{\text{Phonons}}$

Conductivity of metals

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

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

$$K = \frac{k n v_{\text{rms}} \lambda}{2}$$

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

Cont.....

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

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

Ratio between thermal and electric conductivities of a metal

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

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

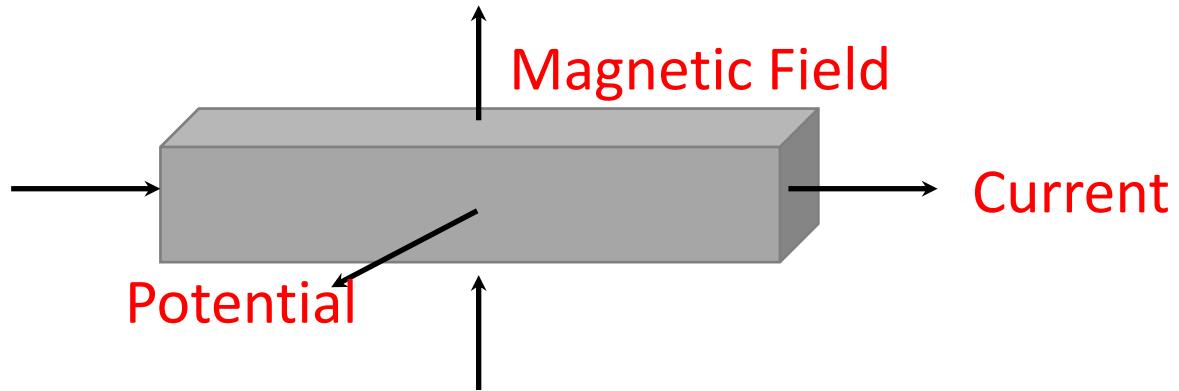
$$\frac{K}{\sigma T} = \frac{\pi^2 k^2}{3e^2} = 2.45 \times 10^{-8} \text{ W} \cdot \Omega / \text{K}^2$$

Maxwell Boltzmann distribution

Fermi Dirac distribution

Hall Effect

If a conductor carrying current is subjected to magnetic field perpendicular to the current, a potential is developed, which is perpendicular to both current and magnetic field



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 Drude Model



Certainty



Specific particle is at
specific position



Identical but
distinguishable



Pauli Exclusion Principle
does not apply

Quantum Drude-Sommerfeld Model



Probability



There is high probability that a
particle is at specific position



Identical but
indistinguishable



Pauli Exclusion Principle
applies

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 i^{th} 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 i^{th} 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

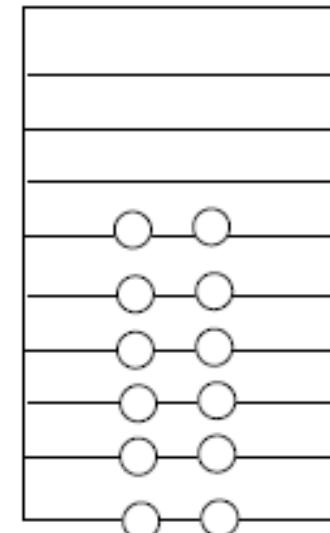
Fermi Dirac distribution

- 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** $\left(0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \dots \right)$ ex. Electrons.
- According to Fermi - Dirac distribution, probability of occupying an energy level ε_i is

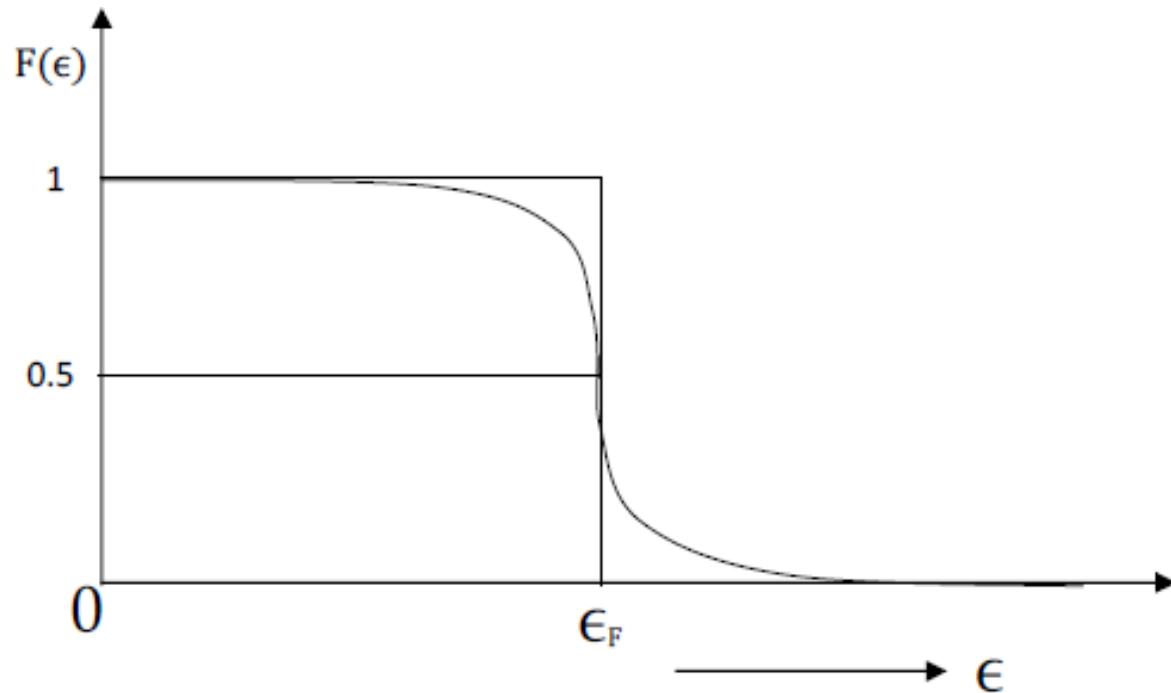
$$f(\varepsilon_i) = \frac{1}{e^{\frac{(\varepsilon_i - \varepsilon_F)}{kT}} + 1}$$

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.*

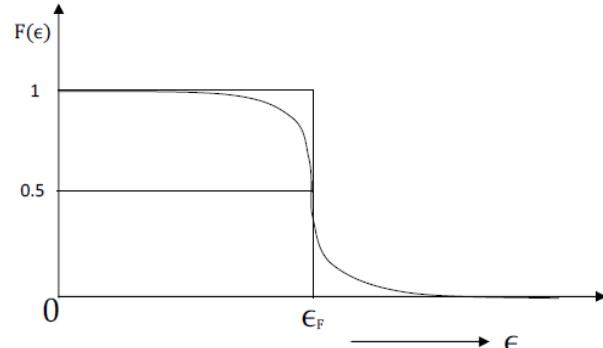


Variation of Fermi function with temperature



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

Probability of finding an electron at different temperatures.



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

$$f(\epsilon_i) = \frac{1}{e^{\frac{(\epsilon_i - \epsilon_F)}{kT}} + 1} = \frac{1}{e^{\frac{(0 - \epsilon_F)}{kT}} + 1} = \frac{1}{e^0 + 1} = \frac{1}{1 + 1} = \frac{1}{2}$$

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

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

$$\begin{aligned} f(\epsilon_i) &= \frac{1}{e^{\frac{(\epsilon_i - \epsilon_F)}{0} + 1}} = \frac{1}{e^{\frac{(\epsilon_i - \epsilon_F)}{0} + 1}} && \text{Science } (\epsilon_i - \epsilon_F) = +ve \text{ value} \\ &= \frac{1}{e^\infty + 1} = \frac{1}{\infty + 1} = \frac{1}{\infty} = 0 && \text{since } \frac{+ve \text{ value}}{0} = \infty \end{aligned}$$

$$f(\epsilon_i) = 0$$

Probability of finding an electron at different temperatures.

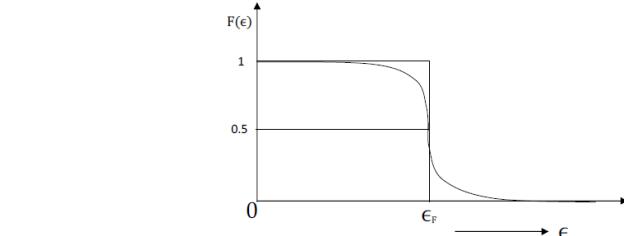
Case III. At $T = 0k$ if $\varepsilon_i < \varepsilon_F$, : $f(\varepsilon_i) = 1$

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

$= -ve\ value$

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

$f(\varepsilon_i) = 1$



$\because \varepsilon_i < \varepsilon_F$ since $(\varepsilon_i - \varepsilon_F)$

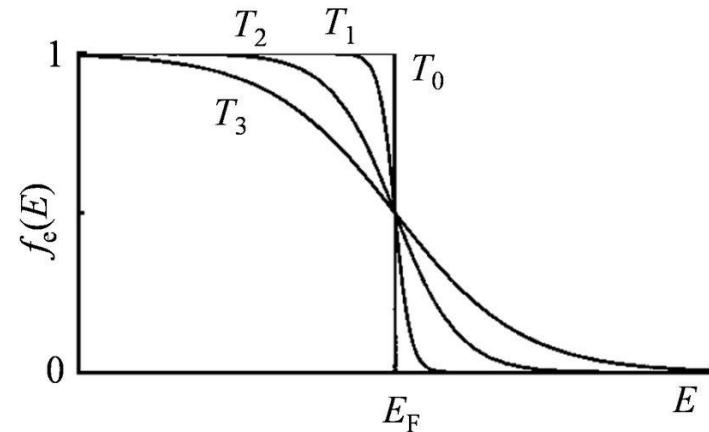
$$\because e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty} = 0$$

From figure (1) we illustrate that

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

$f(\varepsilon_i) > 0$ (but $< \frac{1}{2}$) 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.

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

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

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

Fermi levels are totally fulfilled and above 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.

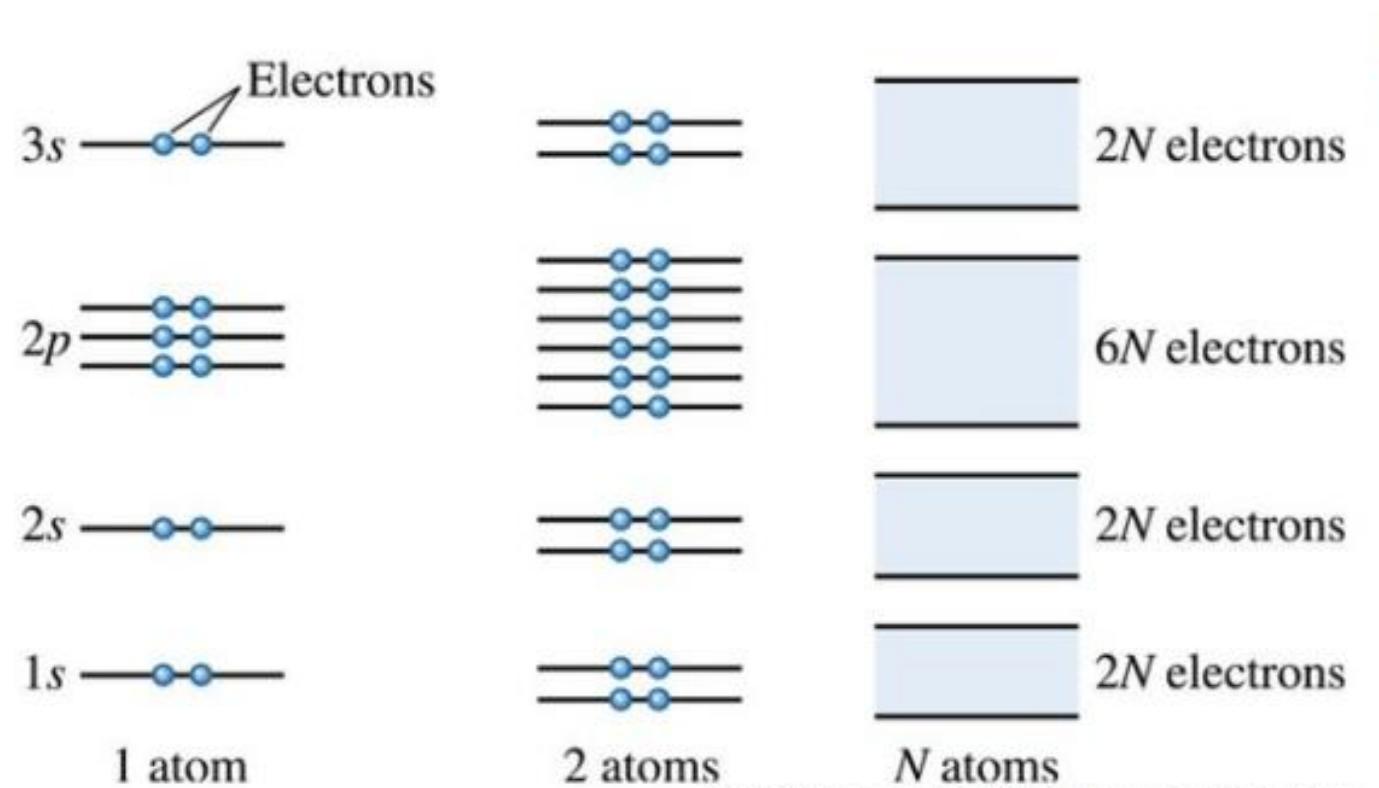
Band Theory

- Energy band structure of a solid determines whether it is a conductor, an insulator, or a semiconductor.
- In a solid, because the splitting 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



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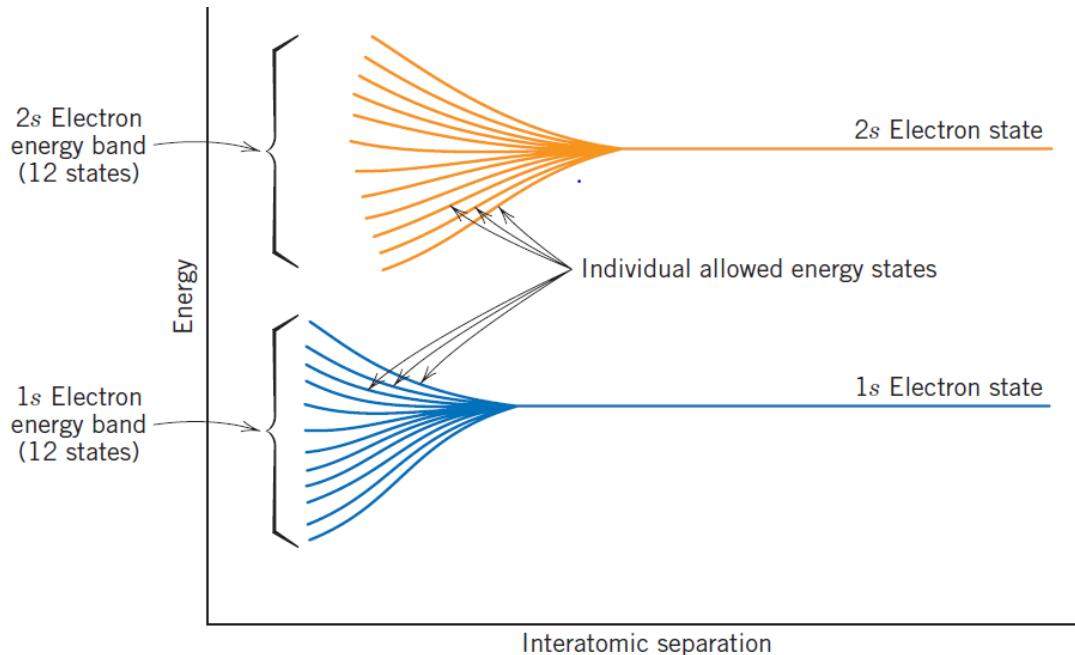
Figure 18.3 The energy levels broaden into bands as the number of electrons grouped together increases.

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.
- As atoms come within proximity of one another, electrons are acted upon, or perturbed, by the nearby electrons and nuclei of adjacent atoms.

Cont.....

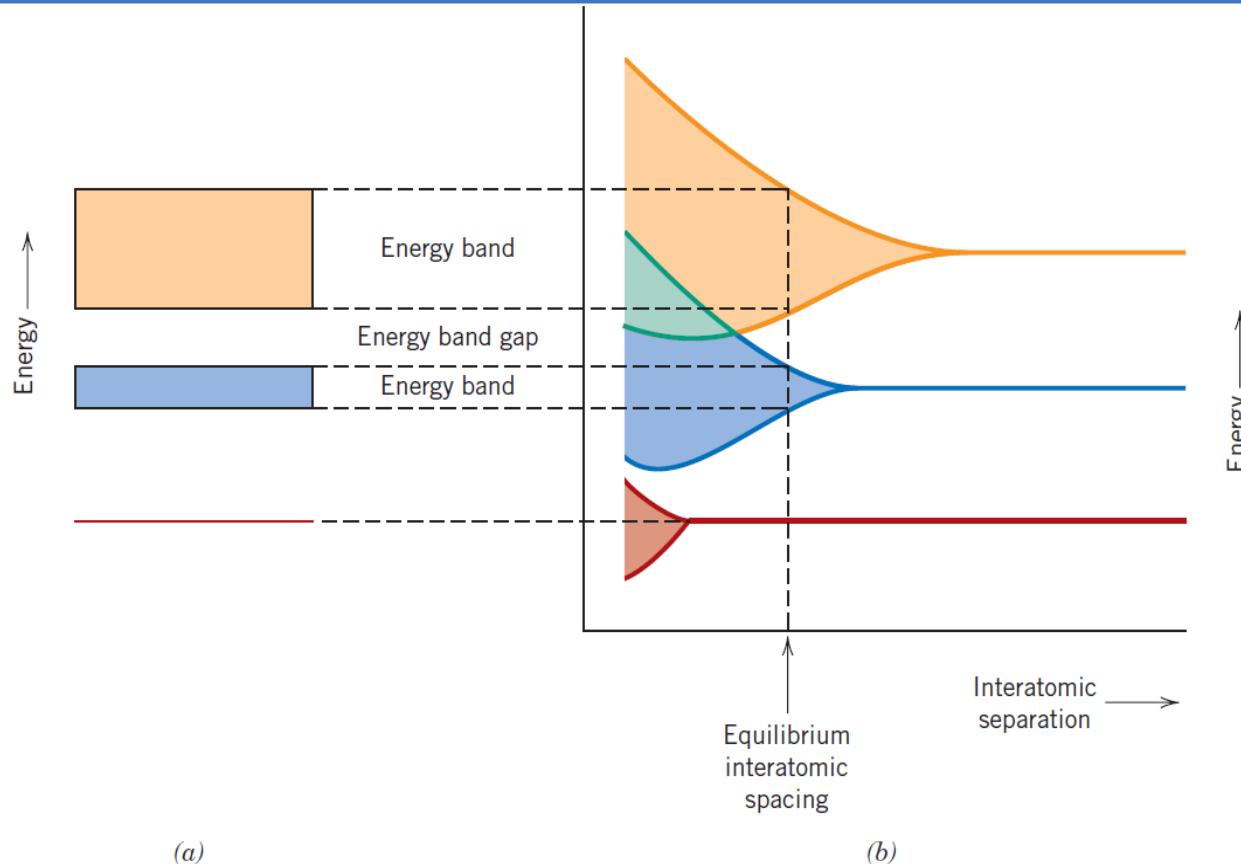
- This causes splitting of each distinct atomic states into a series of closely spaced electron states to form **an electron energy band**.
- Extent of splitting depends on interatomic separation and begins with outermost electron shells.



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

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.

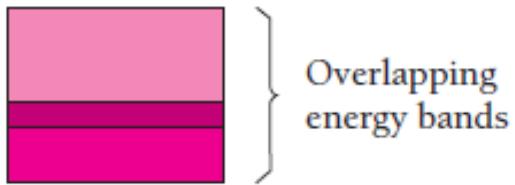


(a) Electron energy band structure for a solid material at the equilibrium interatomic separation. (b) Electron energy versus interatomic separation for an aggregate of atoms.

Electron Arrangement

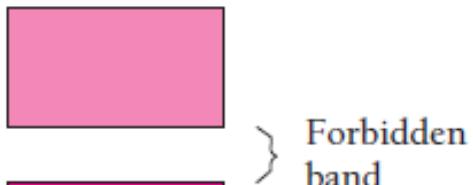
- Arrangement of outermost electron bands and the way in which they are filled with electrons determines electrical properties of a solid.
- Final two band structures are similar; one band is **valence band**, that is completely filled with electrons is separated from an empty **conduction band**, and 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.

Electron Arrangement



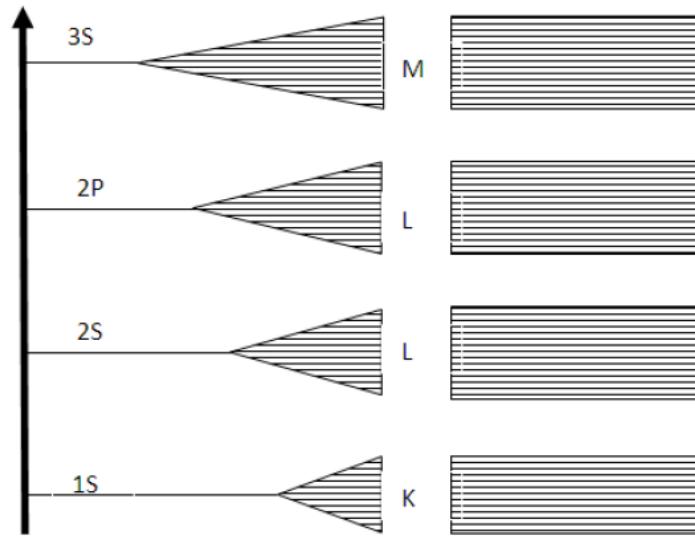
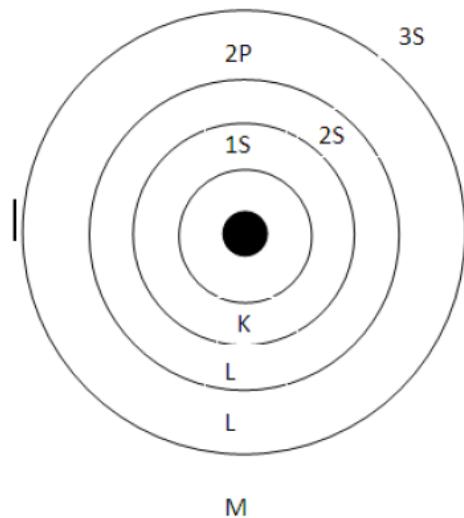
The energy bands in some solids may overlap to give a continuous band.

(a)

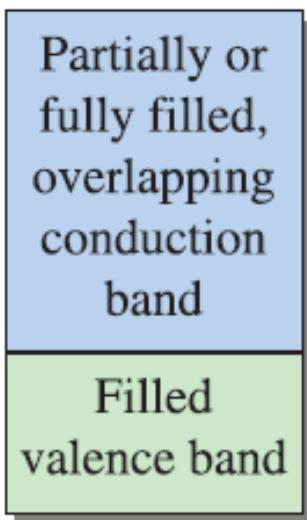


A forbidden band separate non-over-lapping energy bands in other solids.

(b)

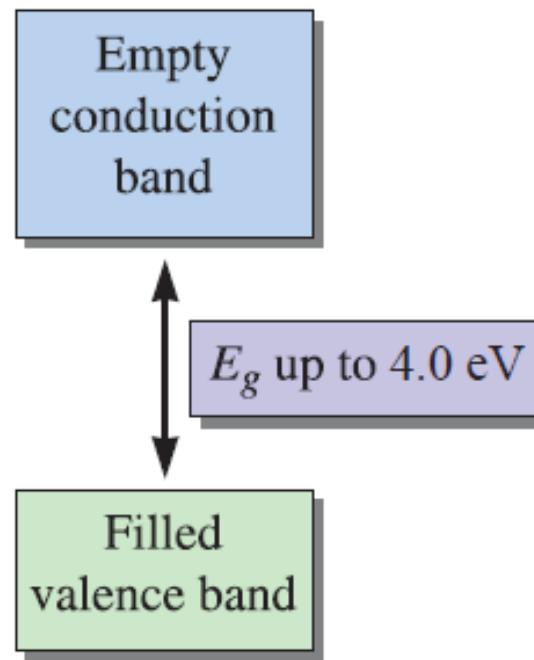


Conductors, Semiconductors and Insulators



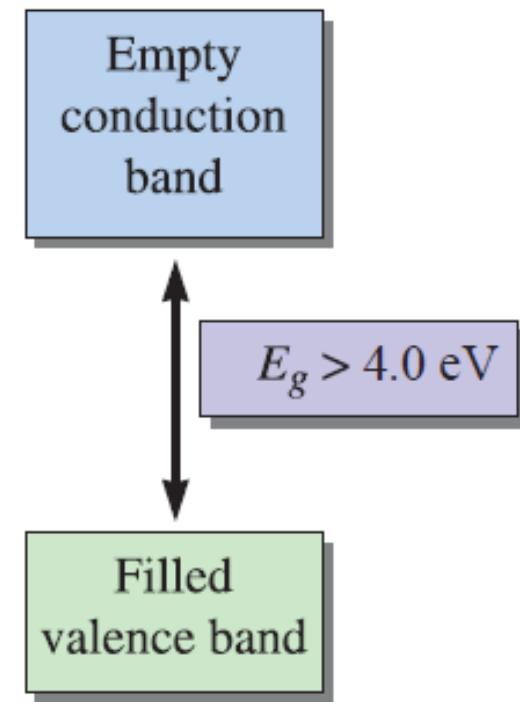
Metals

(a)



Semiconductors

(b)

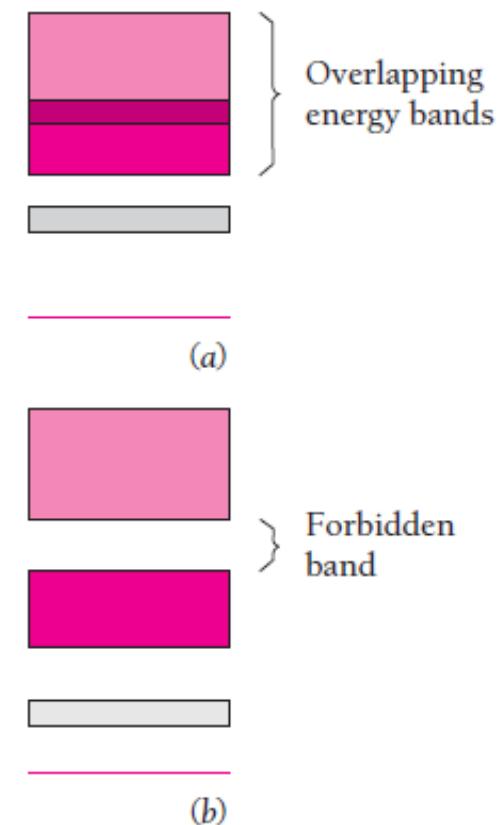


Insulators

(c)

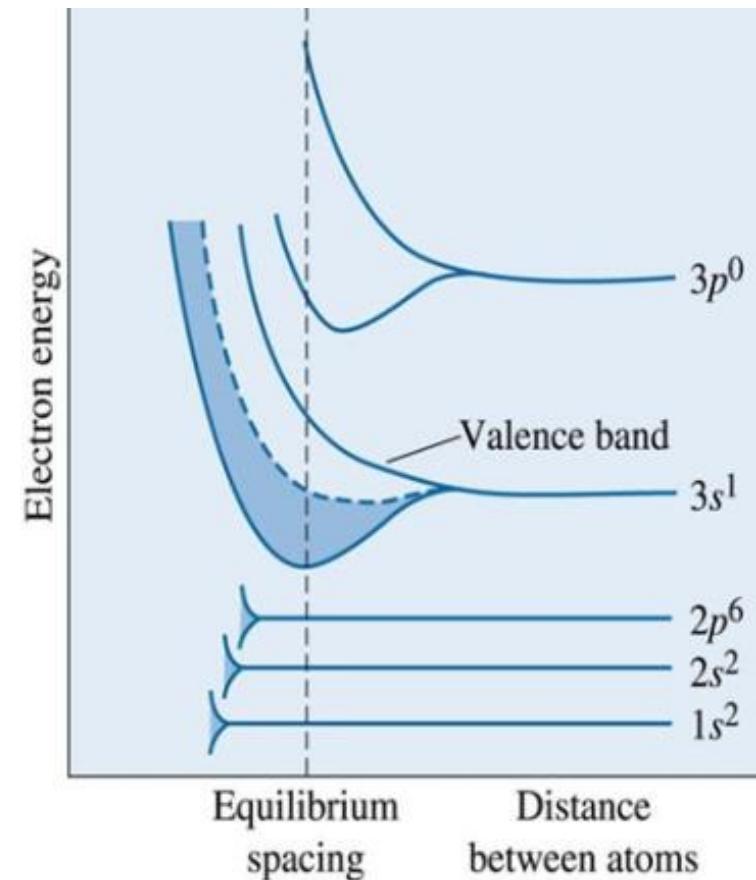
Conductors

- 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

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



Conductors

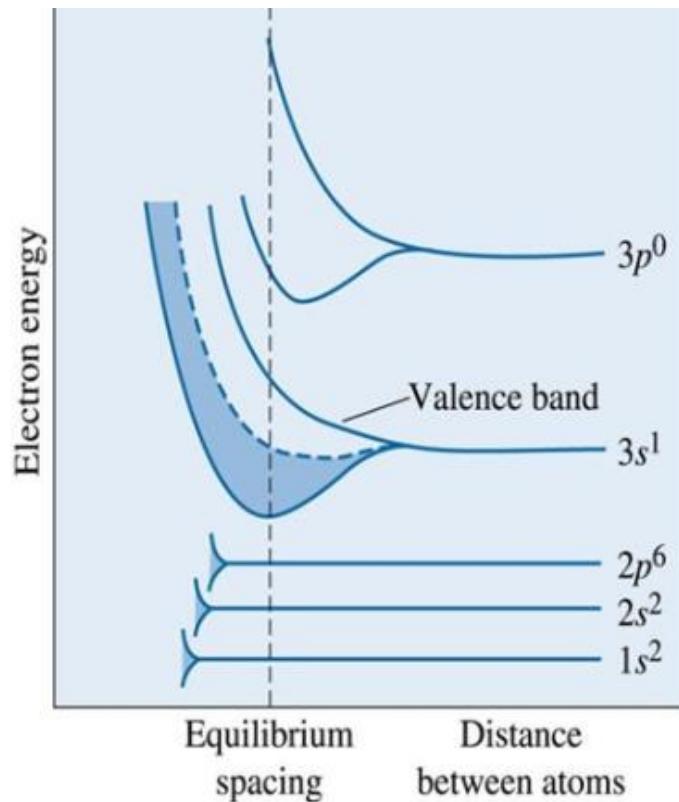
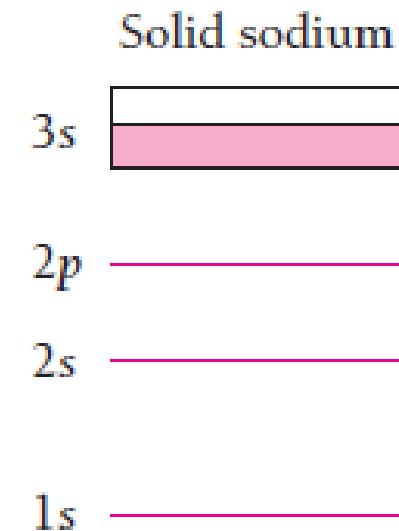


Figure 18.4 The simplified band structure for sodium. The energy levels broaden into bands. The 3 s band, which is only half filled with electrons, is responsible for conduction in sodium.



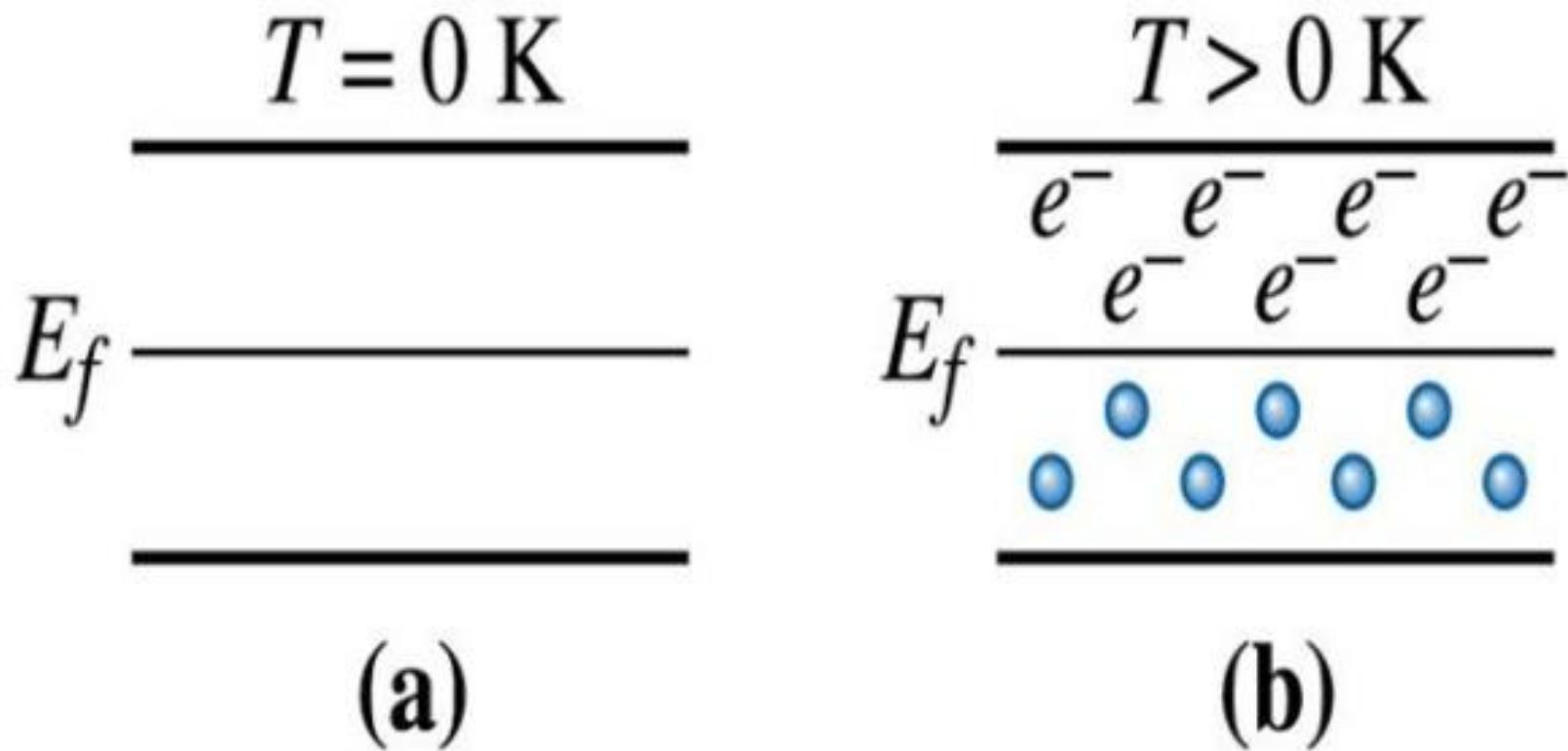
- When a potential difference is applied across a piece of solid sodium, 3s electrons can pick up additional energy while remaining in their original band.
- The additional energy is in the form of KE, and the drift of electrons constitutes an electric current.
- Sodium is therefore a good conductor, as are other solids with partly filled energy bands.

Q1. Considering the energy band structure, explain how Magnesium is a conductor.

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.

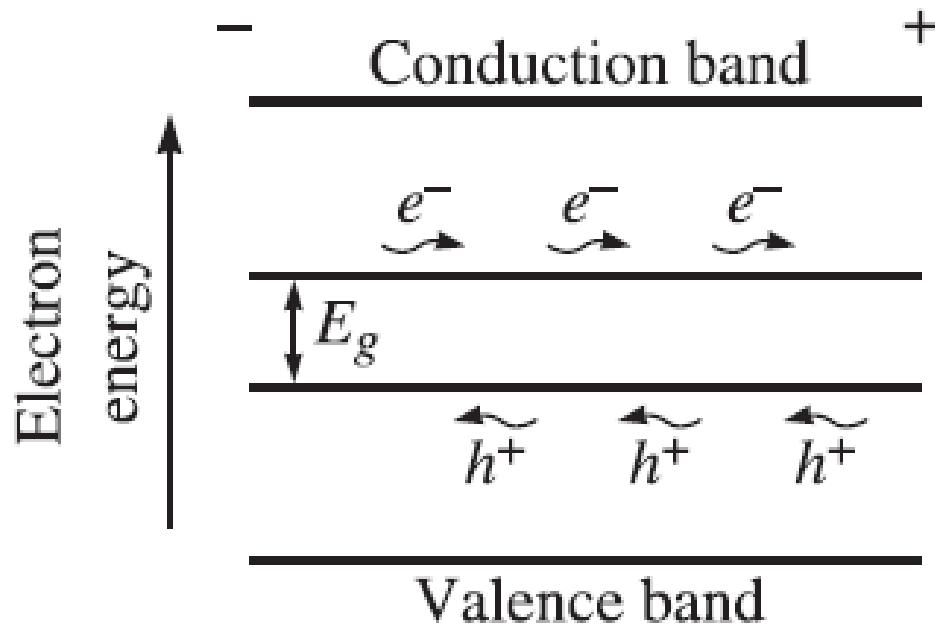
Band Structure in Semiconductors



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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

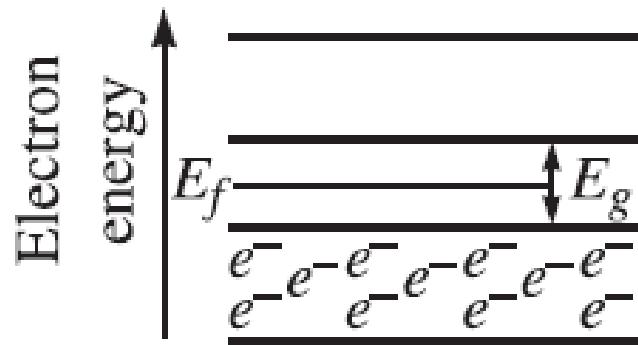
- Conductivity in semiconductor is determined by number of electrons and holes according to $\sigma = nq\mu_n + pq\mu_p$
- In intrinsic semiconductors, for every electron promoted to the conduction band, there is a hole left in the valence band $n_i = p_i$
- Conductivity of an intrinsic semiconductor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

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

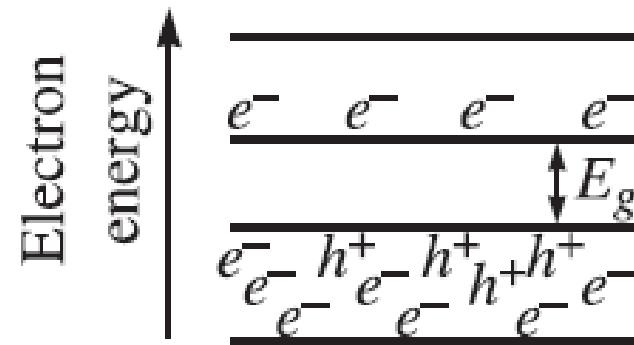
$$\sigma = n_0 q(\mu_n + \mu_p) \exp\left(\frac{-E_g}{2k_B T}\right)$$

Semiconductors

Intrinsic Semiconductors



(a)



(b)

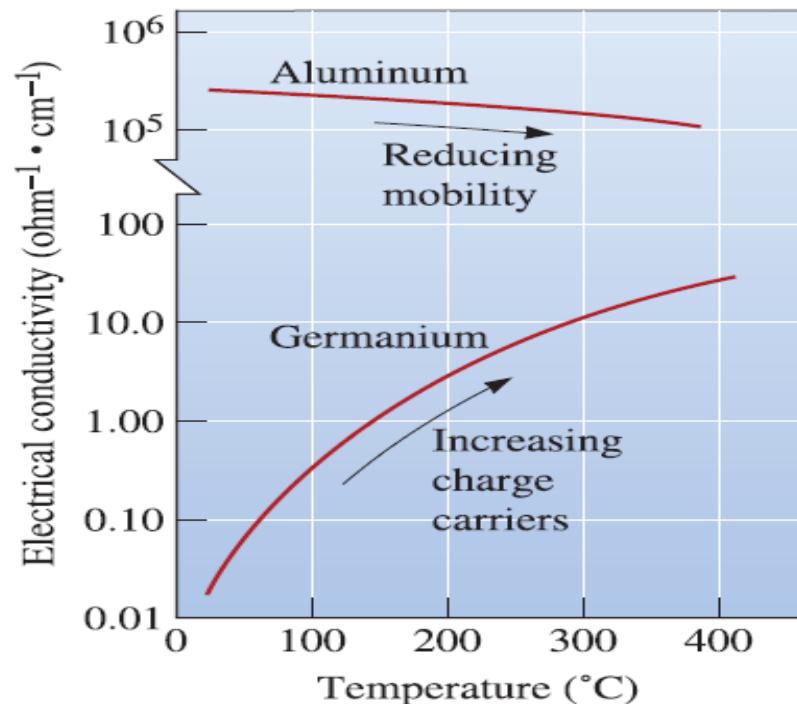
The distribution of electrons and holes
in the valence and conduction bands
(a) at absolute zero and (b) at an
elevated temperature.

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

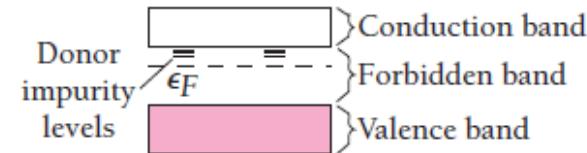
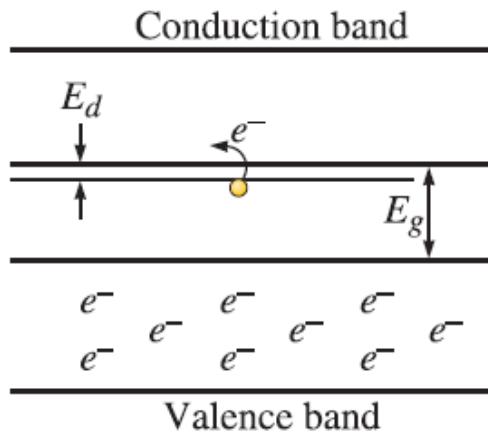
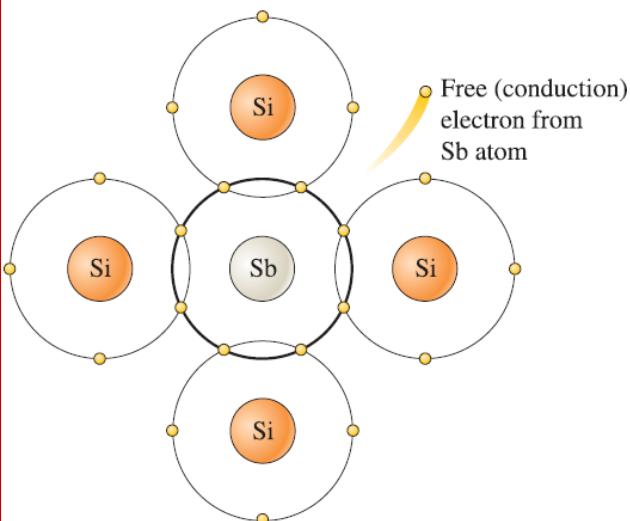
- Increase in conductivity with temperature in semiconductors sharply contrasts with decrease in conductivity of metals.
- Even at high temperatures, however, conductivity of a metal is orders of magnitudes higher than the conductivity of a semiconductor.



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

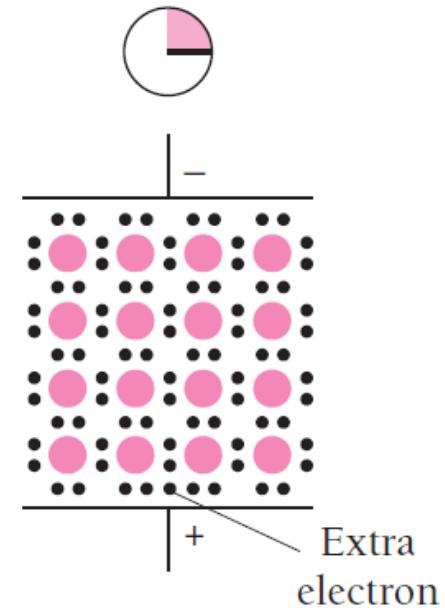
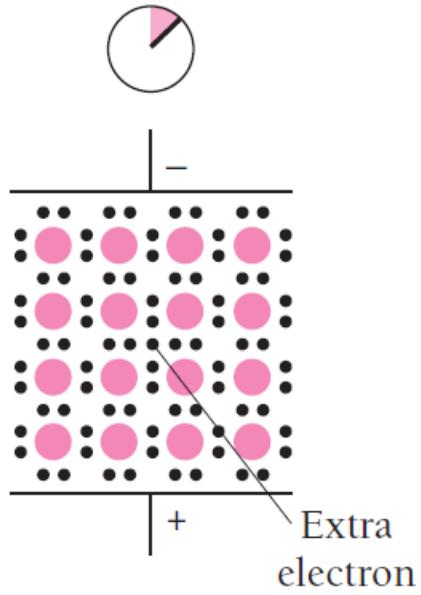
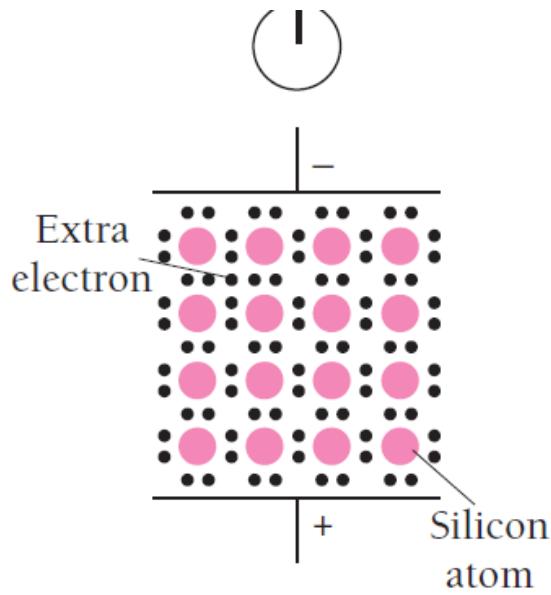
Extrinsic Semiconductors

- Conductivity of extrinsic semiconductor depends 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.



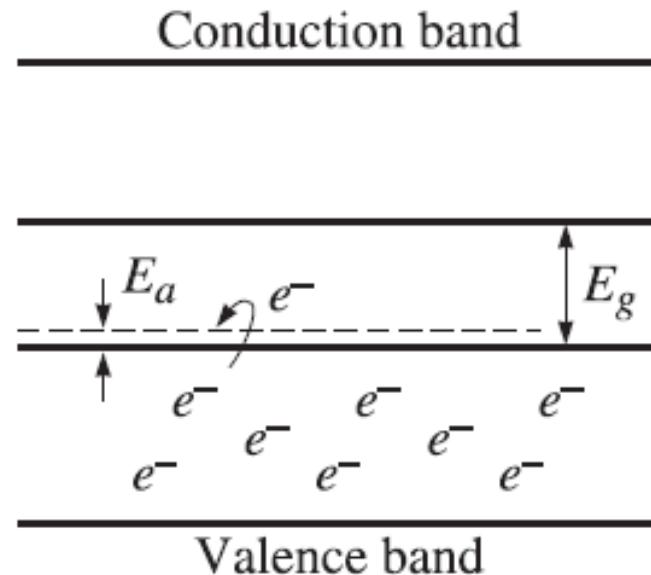
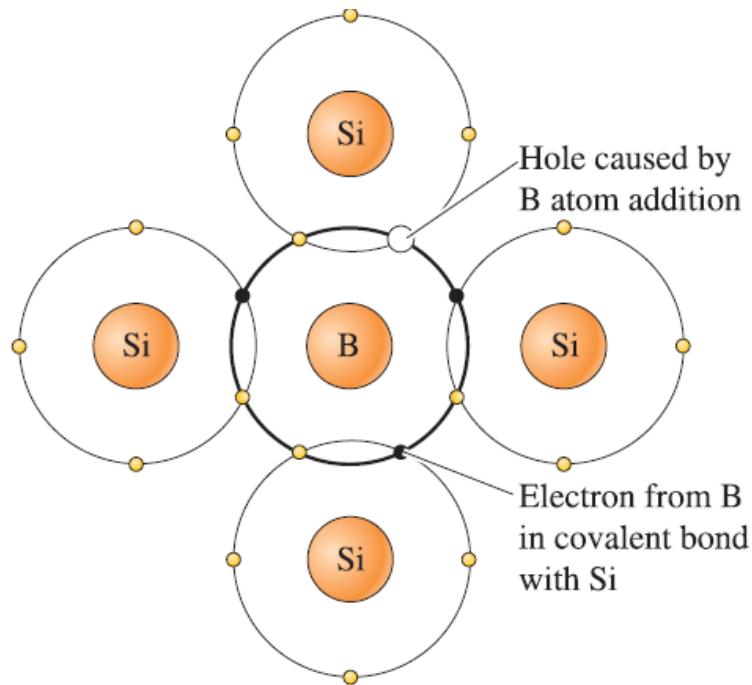
- When a dopant atom with a valence greater than four is added to silicon, an extra electron is introduced, and a donor energy state is created.
- Now electrons are more easily excited into the conduction band.

Extrinsic Semiconductors



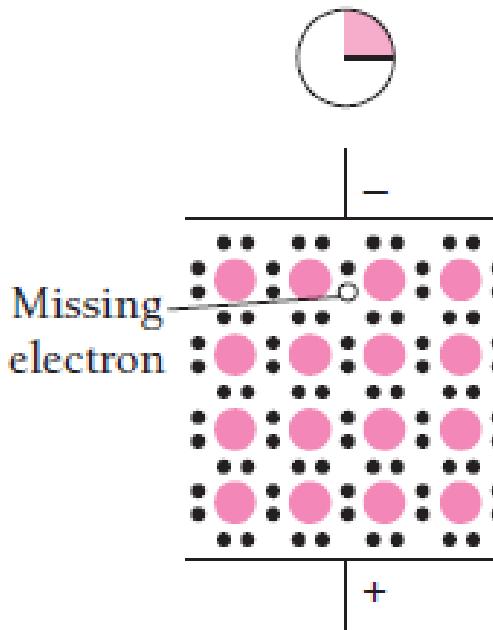
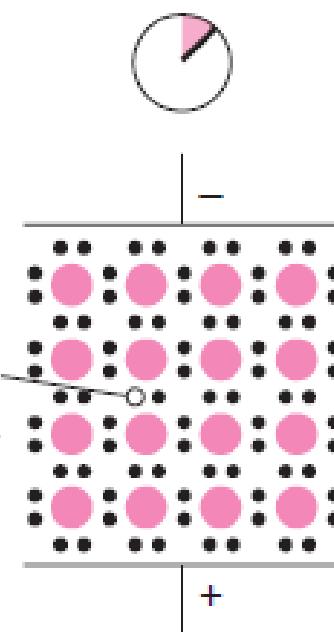
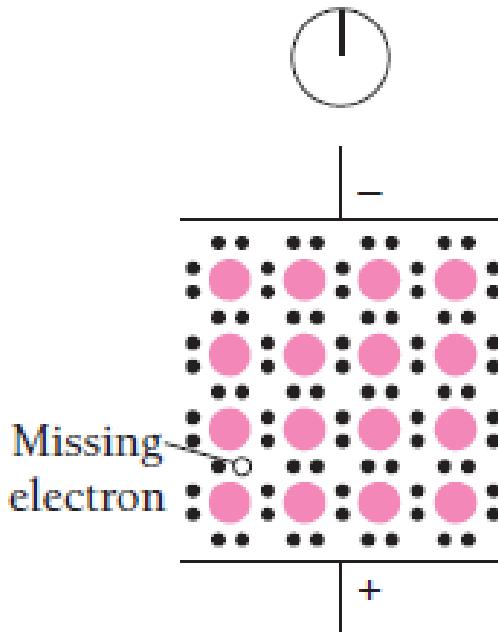
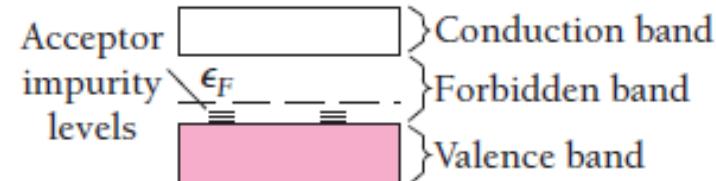
Current in an n-type semiconductor is carried by surplus electrons that do not fit into the electron structure of a pure crystal.

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.

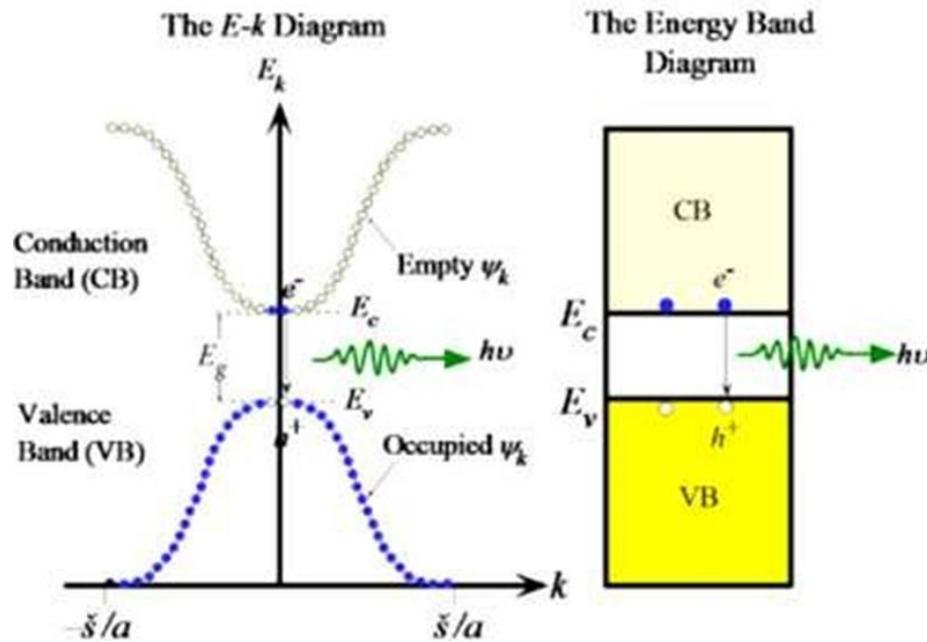
Optical Properties of Solids

- 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

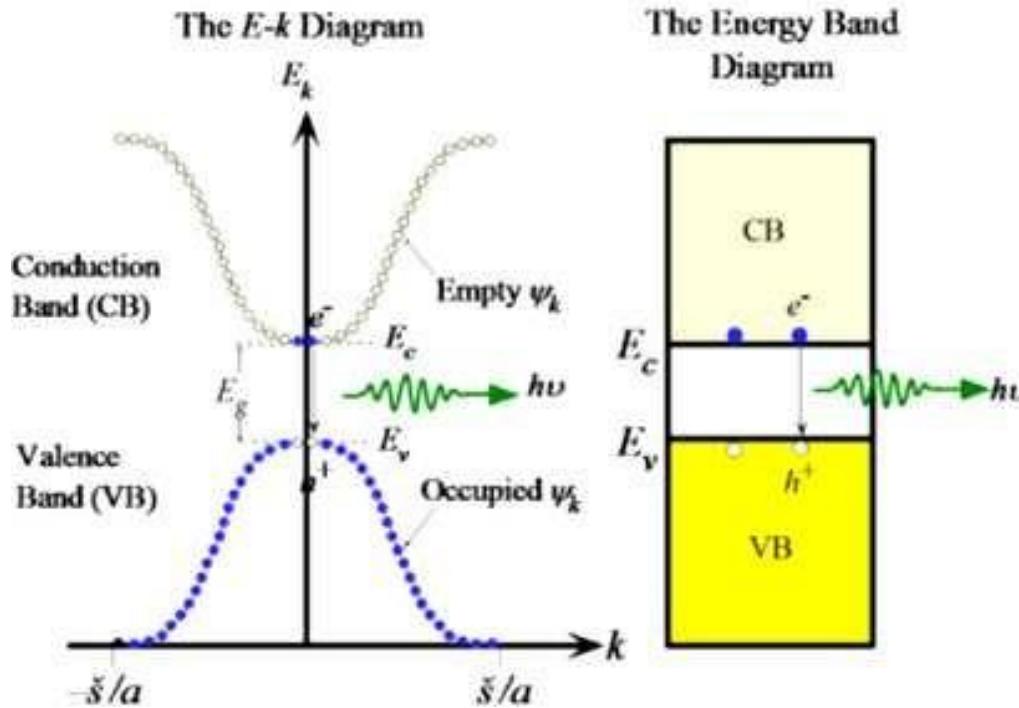
- Forbidden bands in semiconductors are about same in width as photon energies of visible light
 - Semiconductors are usually opaque to visible light.
- Transparent to infrared light
 - Lower frequencies mean photon energies too low to be absorbed.
- For this reason infrared lenses can be made from the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

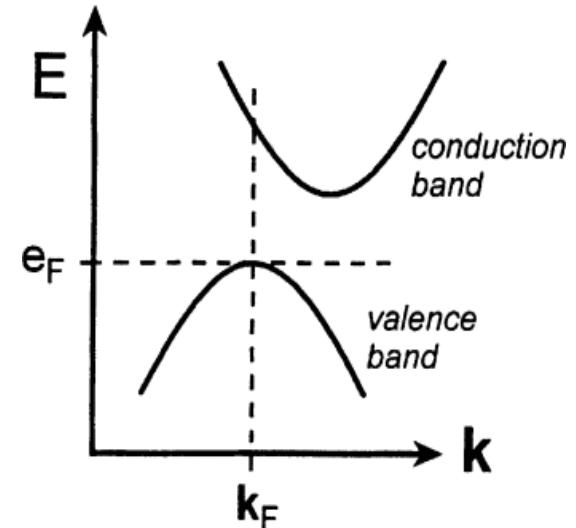
Direct and Indirect Bandgap Semiconductors



- 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.

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

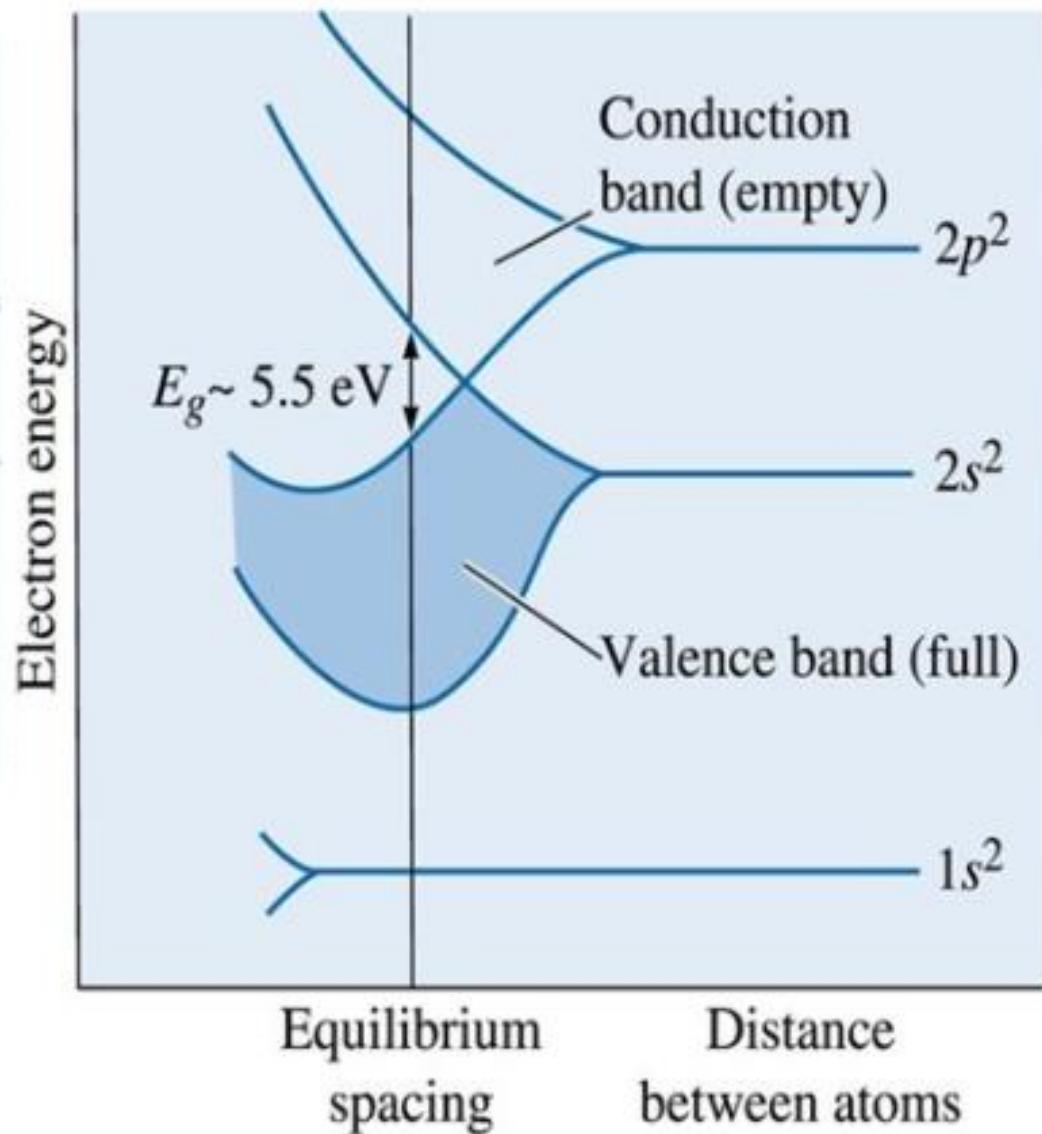
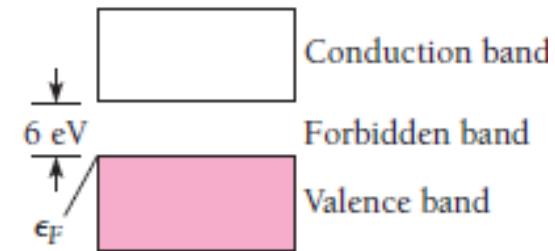
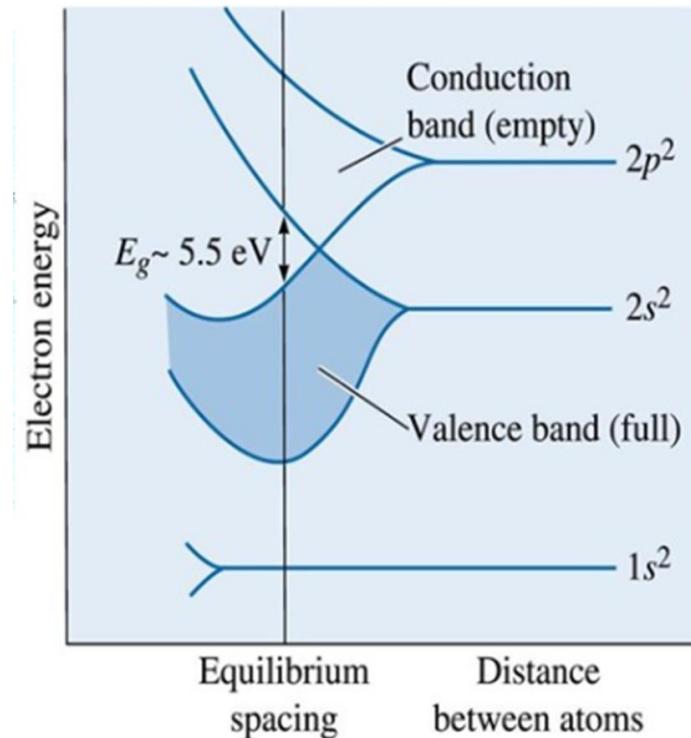


Figure 18.6 The band structure of carbon in the diamond form. The $2s$ and $2p$ levels combine to form two hybrid bands separated by an energy gap, E_g .

Insulators

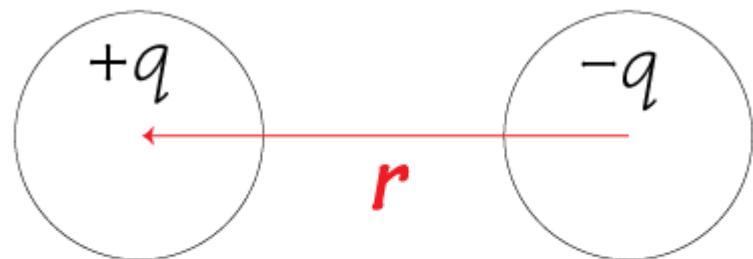


Fermi energy is at top of filled lower band.

- 2s and 2p levels of carbon 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.

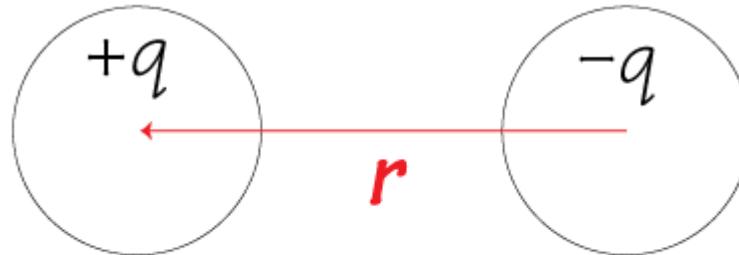
Dielectrics

- A dielectric material is any material that supports charge without conducting it to a significant degree.
- In principle all insulators are dielectric, although the capacity to support charge varies greatly between different insulators.
- Dielectric materials are used in many applications, from simple electrical insulation to sensors and circuit components.

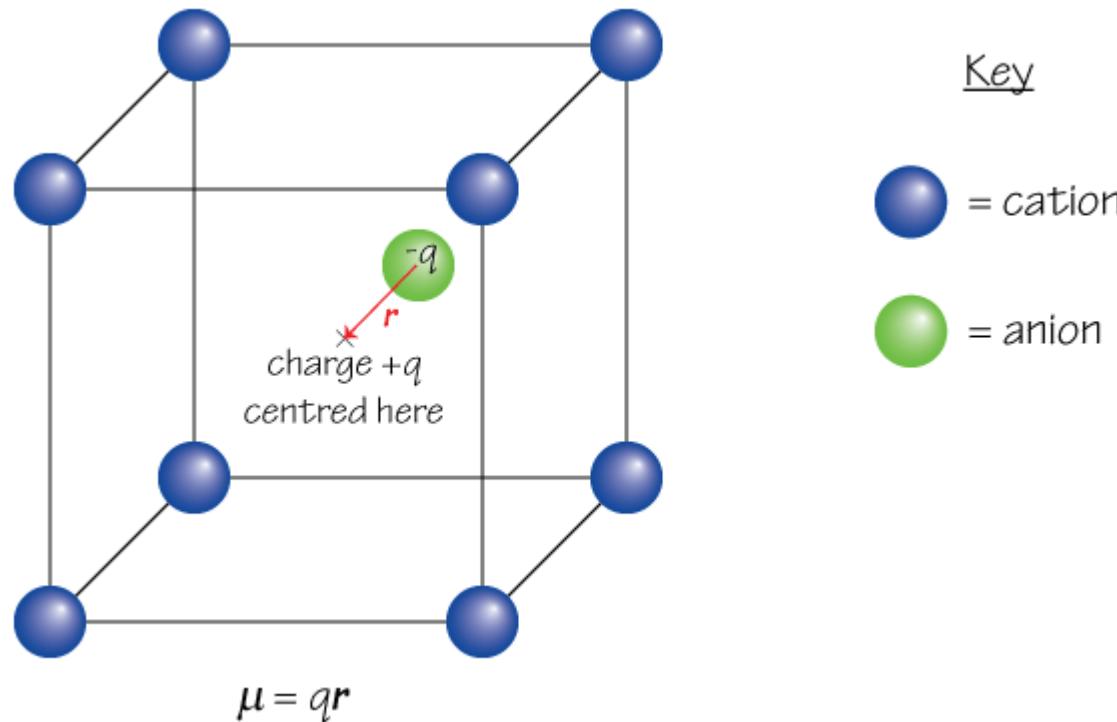


$$\mu = qr$$

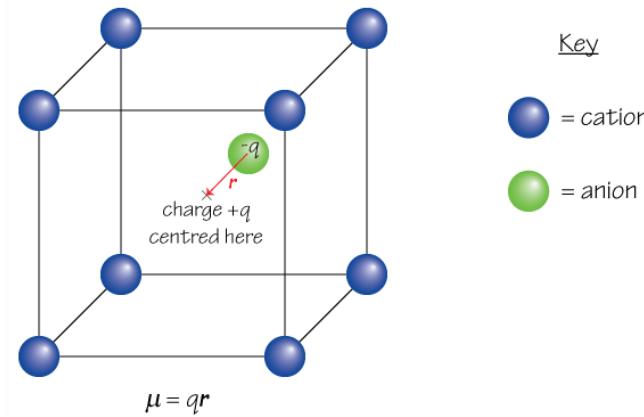
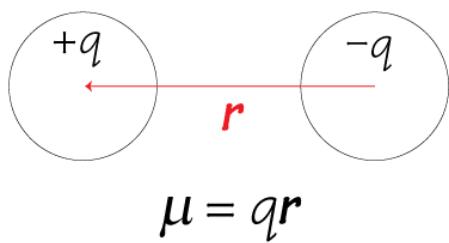
Electric dipoles



$$\mu = qr$$



Electric Polarization



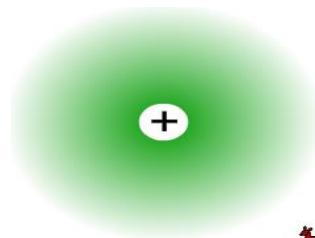
- The polarization of a material is simply the total dipole moment for a unit volume.

$$P = \frac{\sum \mu}{V}$$

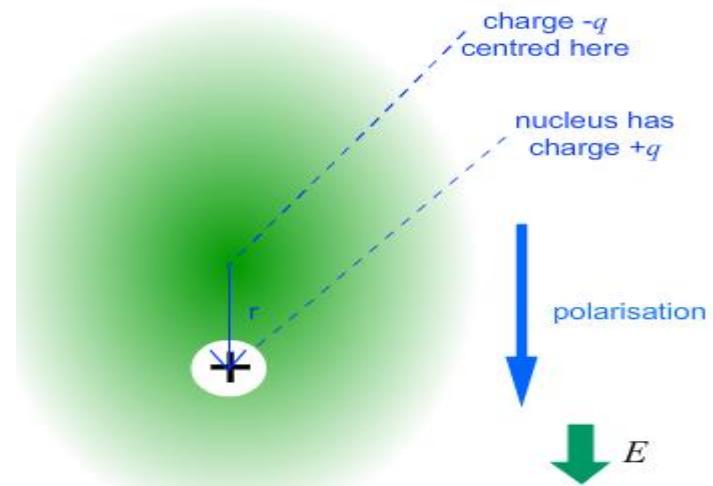
where V is the overall volume of the sample.

Polarization

- Three main polarisation mechanisms occur within a dielectric material: electronic polarisation, ionic polarisation (atomic polarisation) and orientational polarisation.



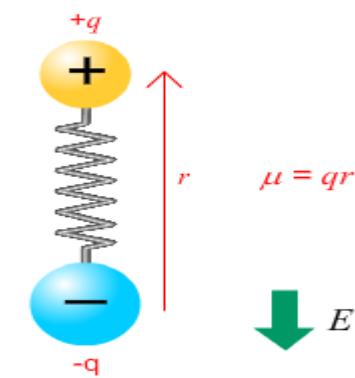
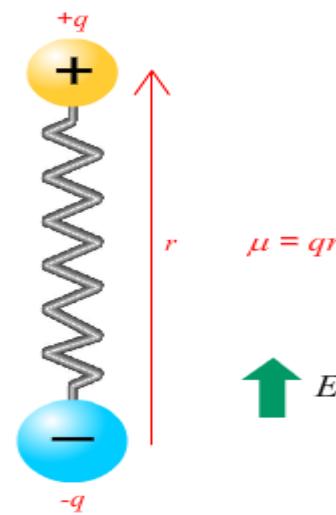
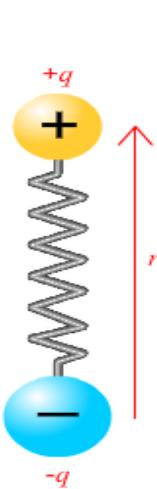
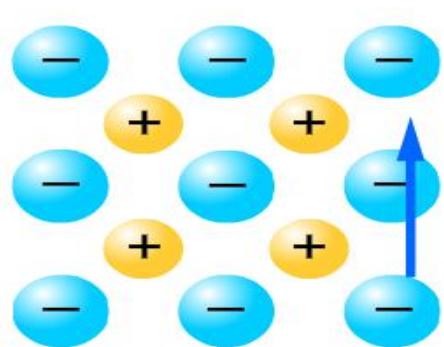
Electronic polarisation



$$\mathbf{p} = \alpha \mathbf{E}$$

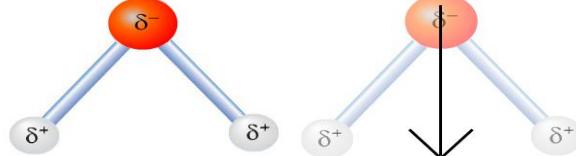
- Atom develops dipole moment \mathbf{p} , which points in the same direction as \mathbf{E} .
- α atomic polarizability depends on the structure of atom

Ionic polarisation

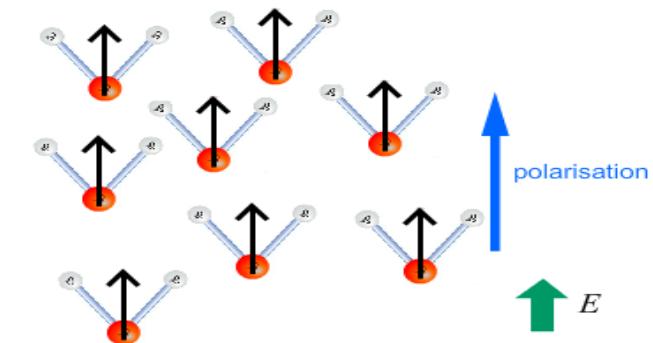
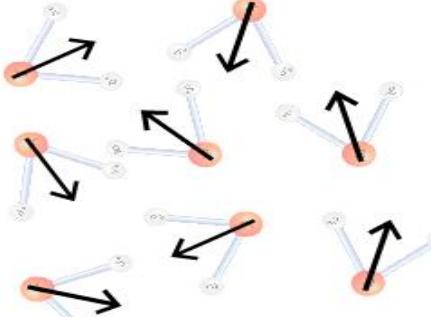


Orientational polarisation

- All non-conducting materials are capable of electronic polarisation, which is why all insulators are dielectric to some degree.
- In contrast, ionic and orientational modes are only available to materials possessing ions and permanent dipoles respectively.



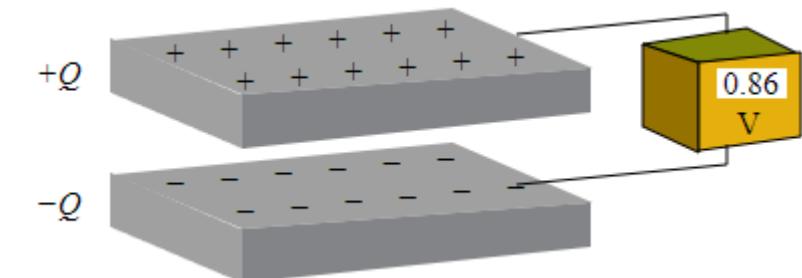
Permanent dipoles



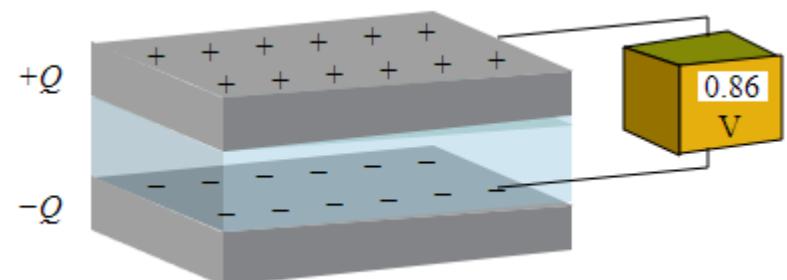
Polarization in Dielectrics

- **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.

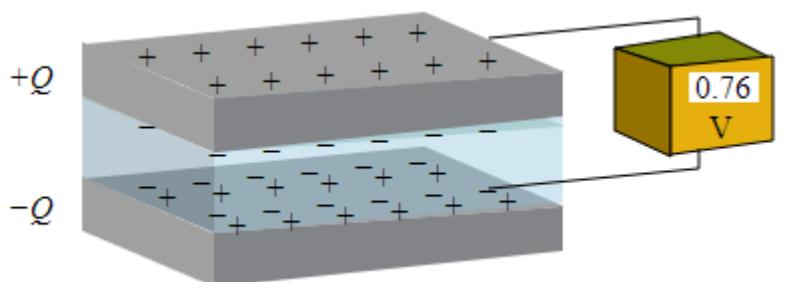
Polarization in Dielectrics



- An empty parallel plate capacitor, with capacitance $C = Q/V$



- Since, two capacitor plates have opposite charges, there is an electric field between them. The dielectric will develop a polarization in response to this field.



- Polarization of dielectric leads to a net buildup of charge on the surfaces that are in contact with the capacitor plates.
- This partially counteracts the electric field between the plates, leading to a decrease in field strength.
- This is observed as a fall in voltage.

- Since the voltage between the capacitor plates has decreased without any change to the charge on the plates, ***inserting the dielectric has led to an increase in capacitance.***

Polarization in Dielectrics

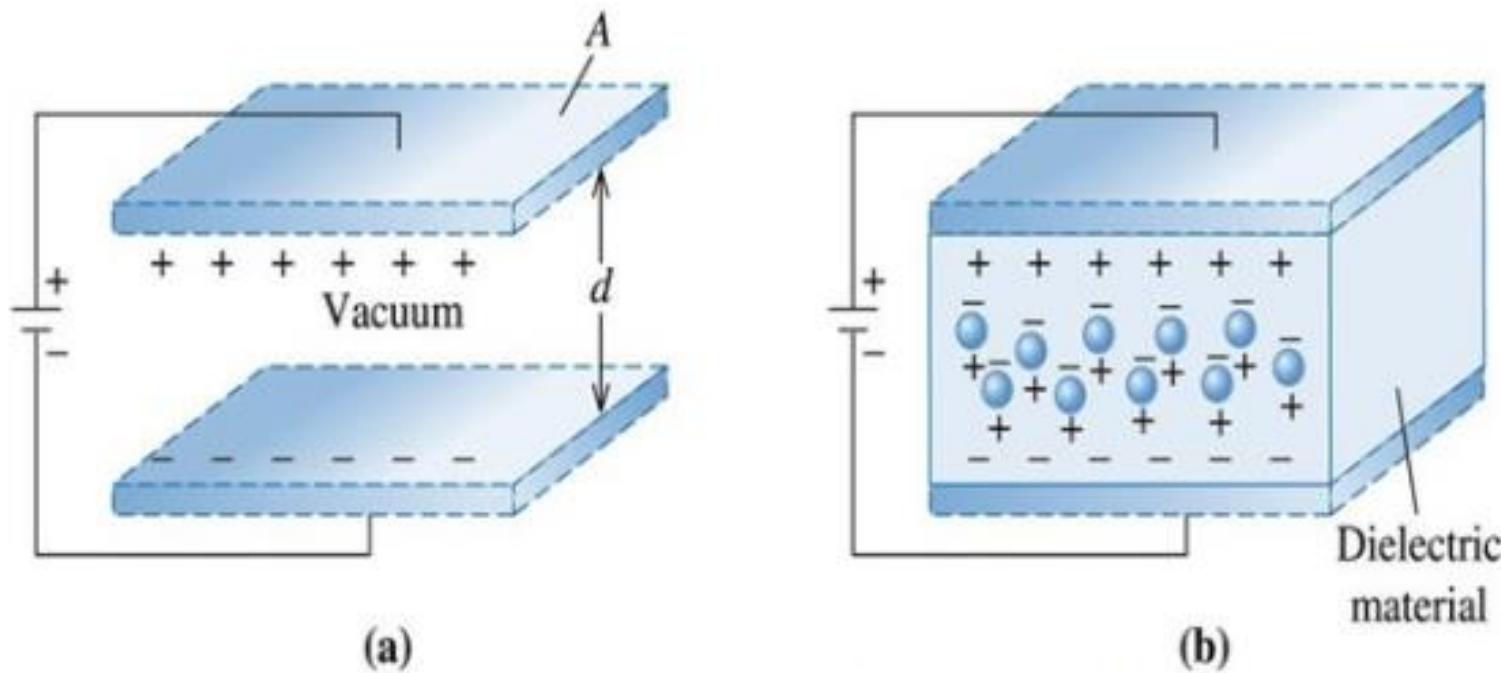


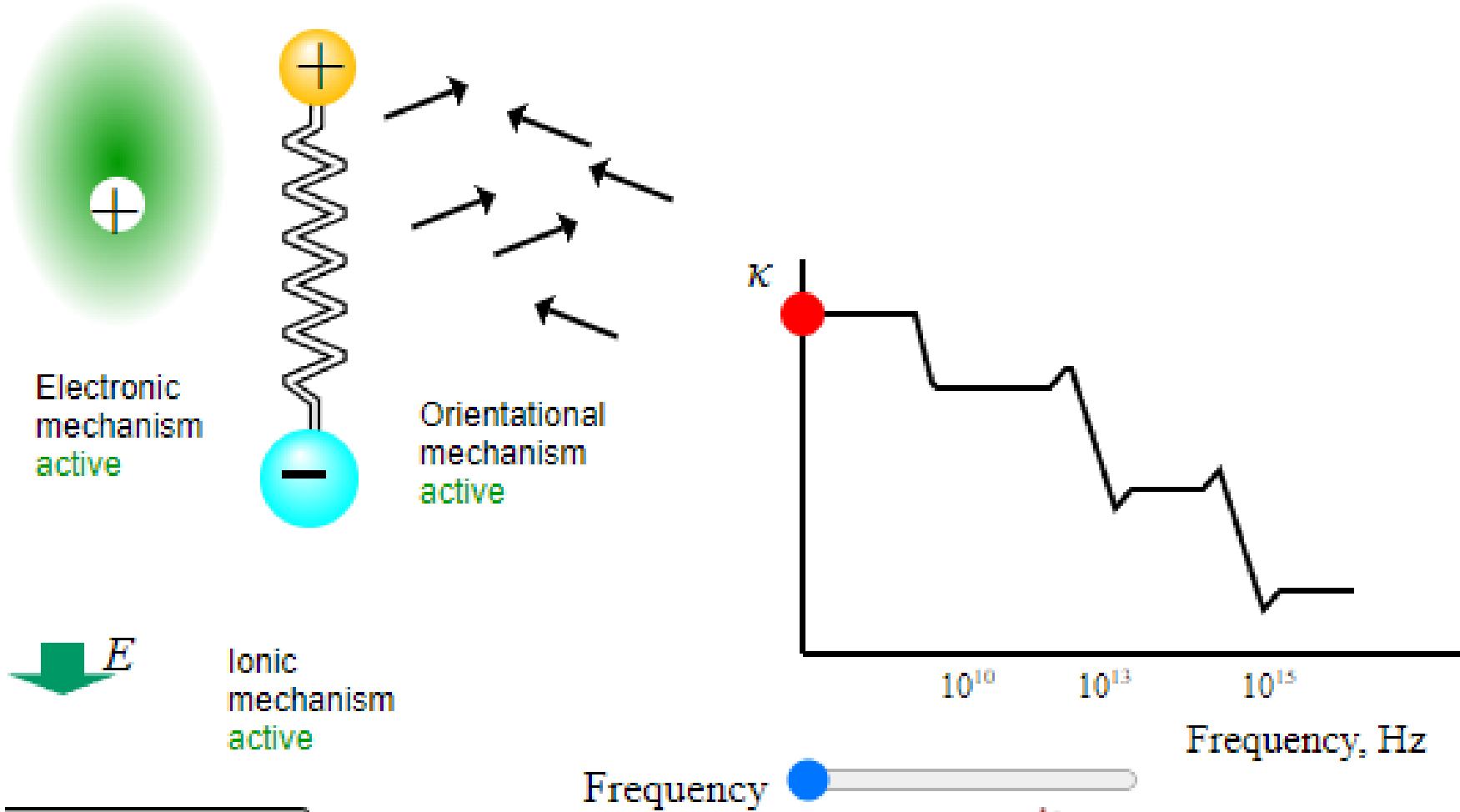
Figure 18.29 A charge can be stored at the conductor plates in a vacuum (a). However, when a dielectric is placed between the plates (b), the dielectric polarizes and additional charge is stored.

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The dielectric constant

- The dielectric constant of a material provides a measure of its effect on a capacitor.
- It is the ratio of the capacitance of a capacitor containing the dielectric to that of an identical but empty capacitor.

Variation of the dielectric constant in alternating fields



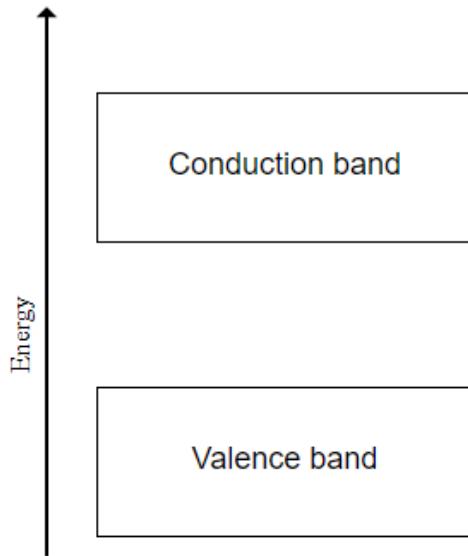
Effect of temperature on the dielectric constant

- For materials that possess permanent dipoles, there is a significant variation of the dielectric constant with temperature. This is due to the effect of heat on orientational polarization.
- The molecules in a structure always possess some energy and this causes random motion.
- For a system at equilibrium, there is as much random motion in any one direction as in the opposite direction, therefore the average positions of the molecules remain constant.
- As the temperature is increased, the dielectric constant will.
- As the temperature increases, the molecules have more thermal energy and therefore the amplitude of random thermal motion is greater.
- This means that the range of deviation from a perfect alignment with the field is greater, therefore the molecules are less closely aligned with each other, therefore the orientational polarization of the material - and hence the dielectric constant is less.

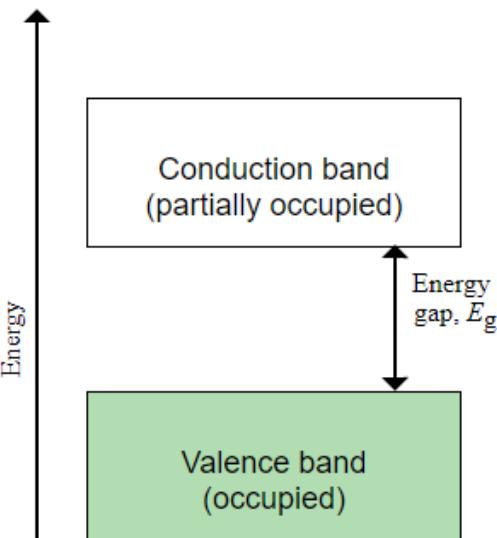
Dielectric Loss and Dielectric Breakdown

- An efficient dielectric supports a varying charge with minimal dissipation of energy in the form of heat.
- There are two main forms of loss that may dissipate energy within a dielectric.
- In conduction loss, a flow of charge through the material causes energy dissipation.
- Dielectric loss is the dissipation of energy through the movement of charges in an alternating electromagnetic field as polarization switches direction.
- At high electric fields, a material that is normally an electrical insulator may begin to conduct electricity – i.e. it ceases to act as a dielectric. This phenomenon is known as dielectric breakdown.

Dielectric Loss and Dielectric Breakdown

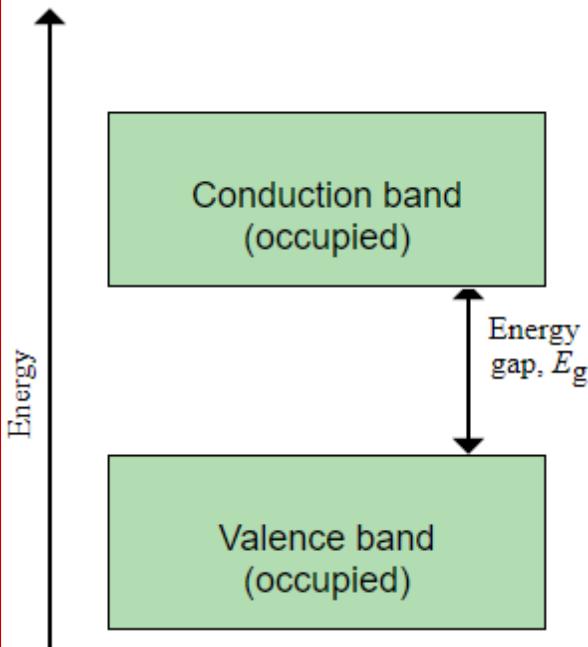


- In dielectrics the two bands are separated by a certain energy gap E_g , corresponding to energies that are forbidden to the electrons.
- Since the valence band is lower in energy, electrons will preferentially occupy this band. Therefore, in a dielectric under normal conditions, **the conduction band will be empty**.



- If an electron in the valence band is supplied with energy greater than or equal to E_g , for example from a high-energy photon, it may be promoted to the conduction band.

Dielectric Loss and Dielectric Breakdown



- An electric field of sufficient strength can supply enough energy to promote many electrons to the conduction band at once.
- Since electrons in the conduction band act as charge carriers, the material now conducts charge rather than storing it.

Applications of dielectrics

- A major use of dielectrics is in fabricating capacitors.
- These have many uses including storage of energy in the electric field between the plates, filtering out noise from signals as part of a resonant circuit, and supplying a burst of power to another component.

Superconductor

- **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.

Superconductor

Properties

- **Electrical resistivity:** It is less than $10^{-26} \Omega \text{ m}$ for superconductors.
- This is ~ 18 orders of magnitude smaller than the resistivity of copper at room temperature ($10^{-8} \Omega \text{ m}$).
- **Effects of impurities:** When impurities are added to superconducting element, its *superconducting property is not lost*, but the value is lowered.
- **Effect of Pressure and Stress:** Certain metals are found to exhibit superconductivity phenomenon on *increasing the pressure over them*.
- Ex. Cesium is found to exhibit superconductivity phenomenon at $T_c = 1.5 \text{ K}$ on applying a pressure of 110 Kbar.

Cont.....

- **Isotope effects:** The critical temperature (T_c) value of a superconductor is found to vary with its isotopic mass.
- The *transition temperature* is inversely proportional to the *square root of isotopic mass* of single superconductors.

$$T_c \propto \frac{1}{\sqrt{M}}$$

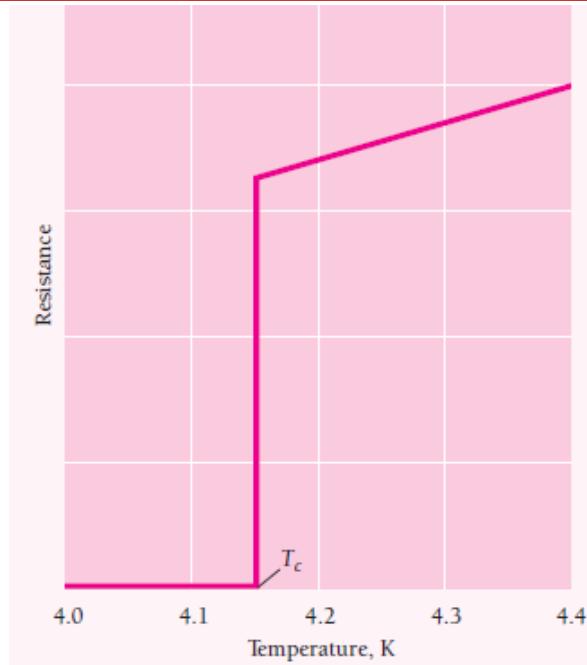
- **Magnetic field effect:** If a sufficiently strong magnetic field is applied to a superconductor at any temperature below its critical temperature T_c , the superconductor is found to undergo a *transition from the superconducting state to the normal state*.

Cont.....

- **Critical current density:** It can be defined as the *maximum current* that can be permitted in a superconducting material without destroying its superconductivity state.

$$J_c = \frac{I_c}{A}$$

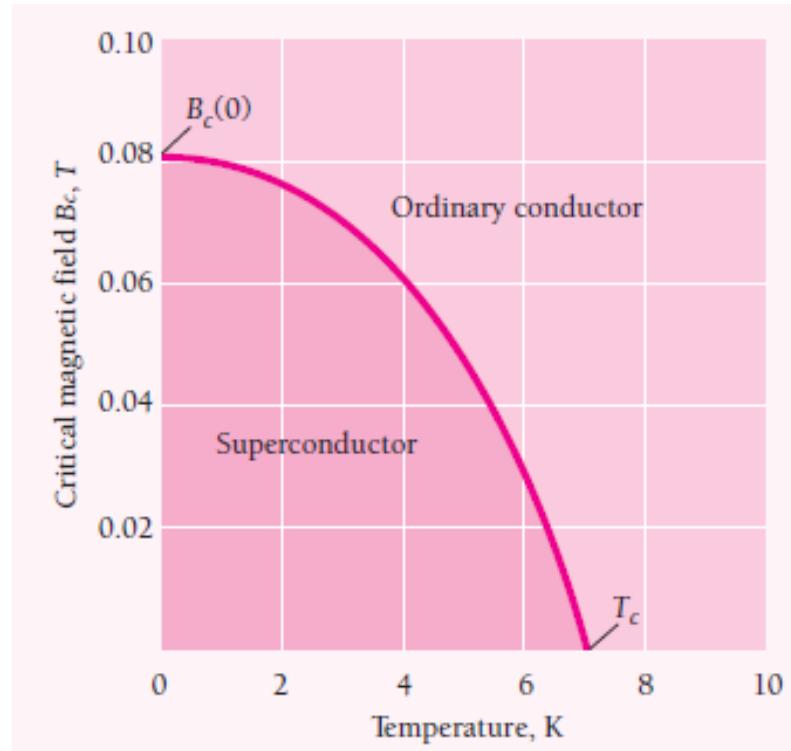
Superconductors



- 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.

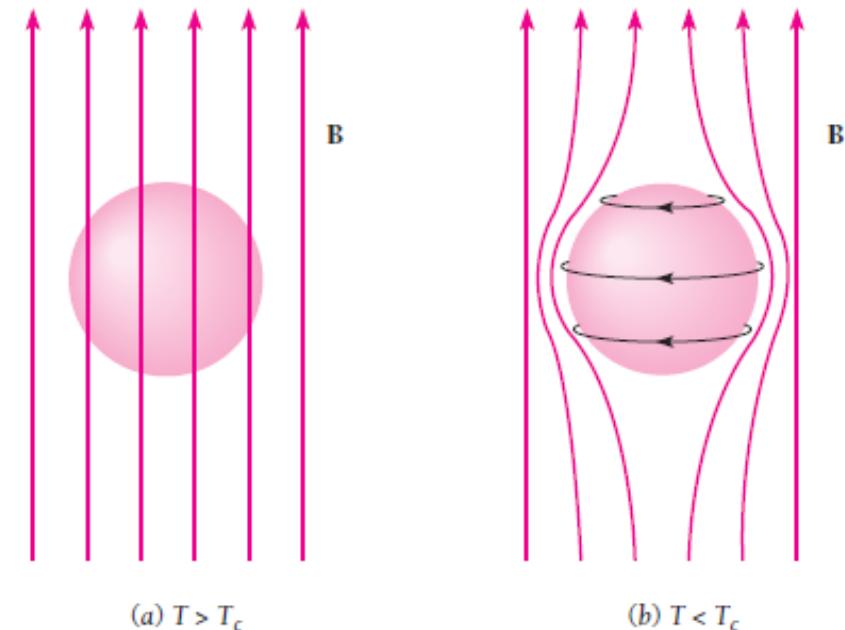
Superconductors

- 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 T_c , 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.



(a) $T > T_c$

(b) $T < T_c$

Superconductors

- This **Meissner effect** would not occur in an ordinary conductor whose resistance reduced to zero.
- Type I superconductors exist only in two states, normal and superconducting.
- Type II superconductors, are usually alloys, have an intermediate state as well.
- Such materials have two critical magnetic fields, B_{c1} and B_{c2} .

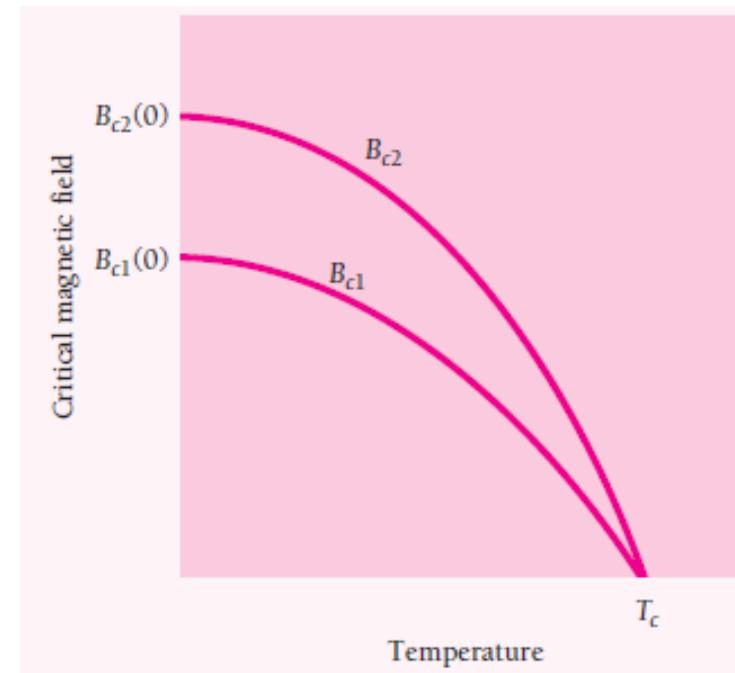


Figure 10.52 Variation of the critical magnetic fields B_{c1} and B_{c2} with temperature for a type II superconductor. For magnetic fields between B_{c1} and B_{c2} the material is in a mixed state in which it is superconducting but a magnetic field can exist in its interior.

Superconductors

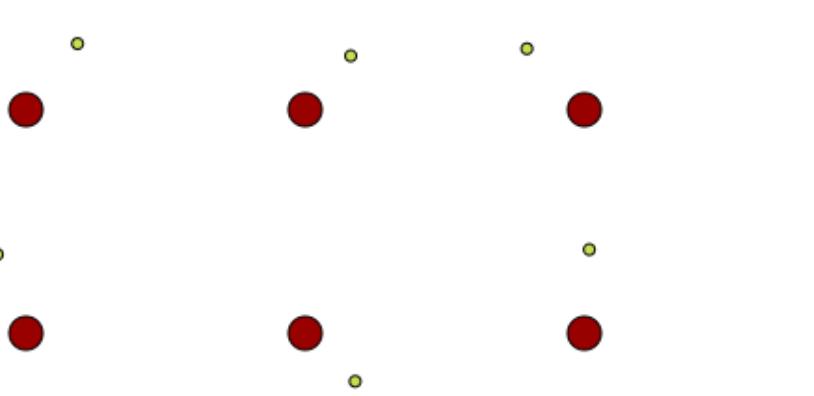
- For $B < B_{c1}$, type II superconductor behaves just like its type I counterpart : superconducting with no magnetic field in its interior.
- When $B > B_{c2}$, a type II superconductor exhibits normal behaviour, again like a type I superconductor.
- In applied fields between B_{c1} and B_{c2} , a 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} .

Superconductors

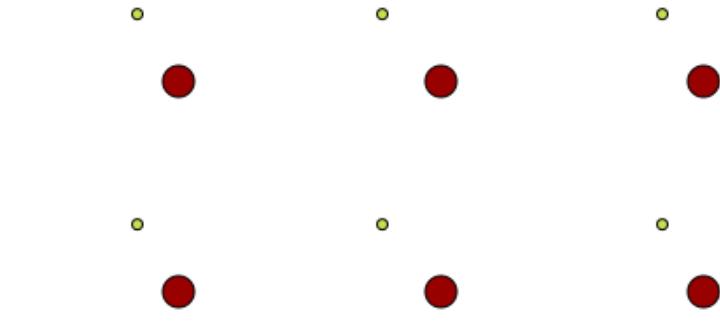
- A type II superconductor behaves as though it consists of filaments of normal and of superconducting matter mixed together.
- A magnetic field can exist in the normal filaments, while the superconducting filaments are diamagnetic and resistance less like type I superconductors.
- B_{c2} can be quite 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.

Superconductivity

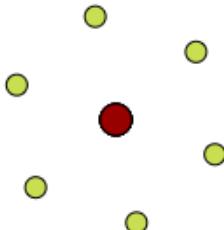
London Conjecture



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.



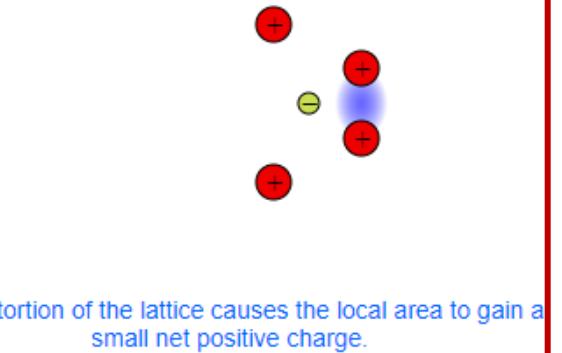
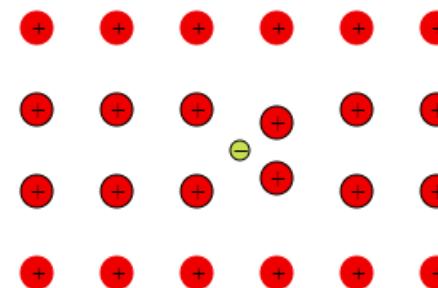
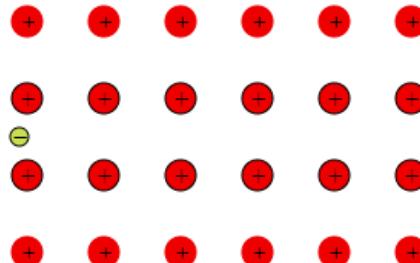
Therefore this state could be considered to be one giant atom
with the electrons orbiting a single nucleus

Superconductivity

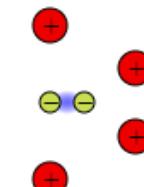
Cooper Pair Formation

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

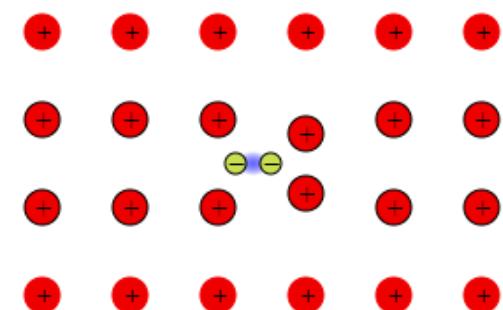
As an electron moves through the positively charged ion cores of the lattice, it attracts them and causes a distortion.



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.



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.

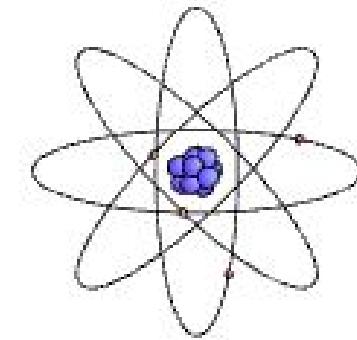
Superconductivity

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.

Superconductivity

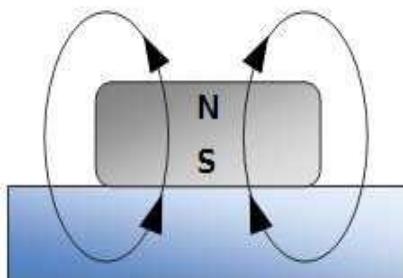
Electrons vs Cooper Pairs

- 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.

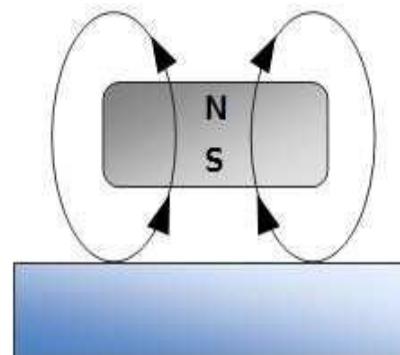
Applications of Superconductors:

Magnetic Levitation (Maglev):

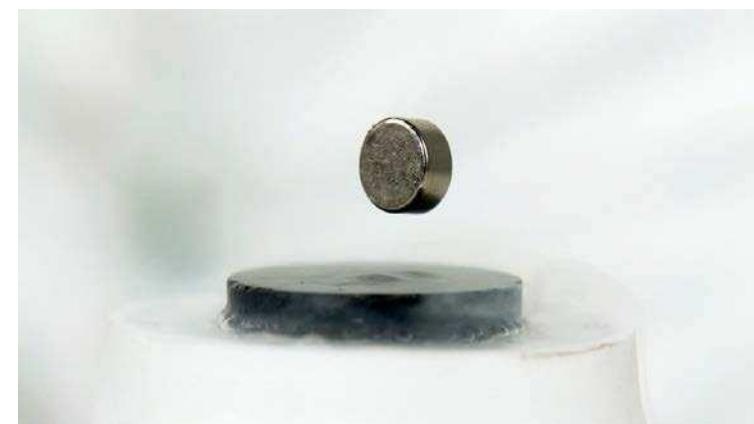
- ✓ Magnetic Levitation or Maglev is the process by which an object is suspended above another object with no other support but magnetic fields.
- ✓ The phenomenon of magnetic levitation is based on Meissner effect.
- ✓ The magnetic levitation is brought about by enormous repulsion between two highly powerful magnetic fields.



Superconductor:
Above Critical Temp.



Superconductor:
Below Critical Temp.



- ✓ **Maglev Train:** The levitation is based on two techniques: (i) Electromagnetic suspension (EMS) and (ii) Electrodynamic suspension (EDS).
- ✓ The basic idea of maglev train is to levitate it with magnetic fields so that there is no physical contact between the train and the rails.
- ✓ Consequently, the maglev train can travel at very high speed.
- ✓ These trains travel at a speed of about 500 km/h.

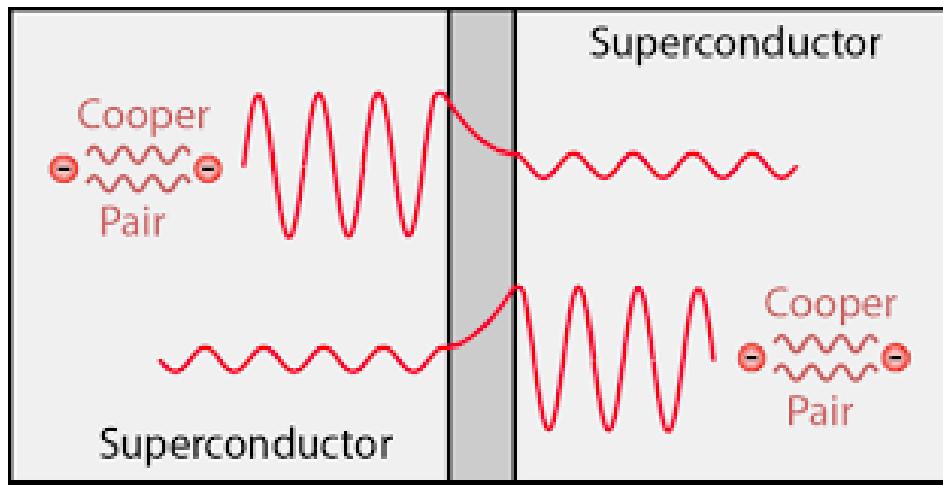


Applications of Superconductors:

- ✓ RF and microwave filters (e.g., for mobile phone base stations, as well as military ultrasensitive/selective receivers)
- ✓ High sensitivity particle detectors, including the transition edge sensor, the superconducting bolometer, the superconducting tunnel junction detector, the kinetic inductance detector, and the superconducting nano wire single- photon detector.
- ✓ Rail gun and coil gun magnets.
- ✓ Electric motors and generators.
- ✓ Very strong magnetic fields can be generated with coils made of high T_c superconducting materials.
- ✓ Ore separation can be done efficiently using superconducting magnets.

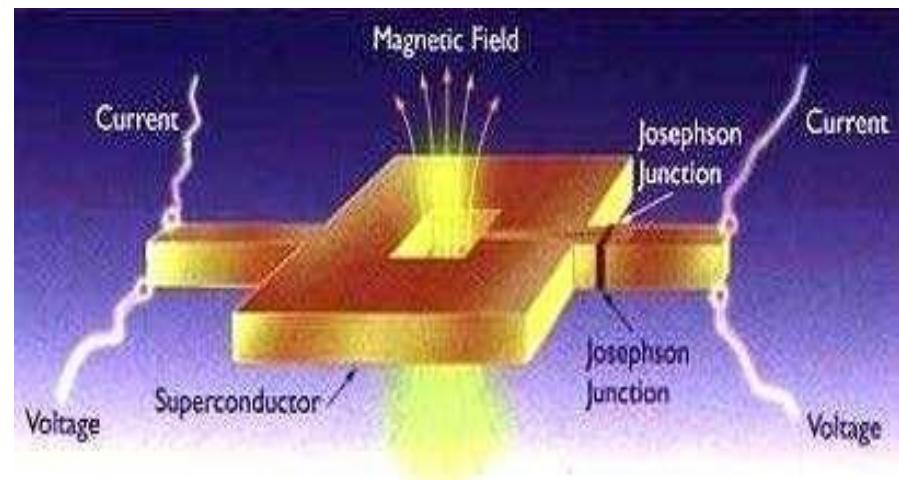
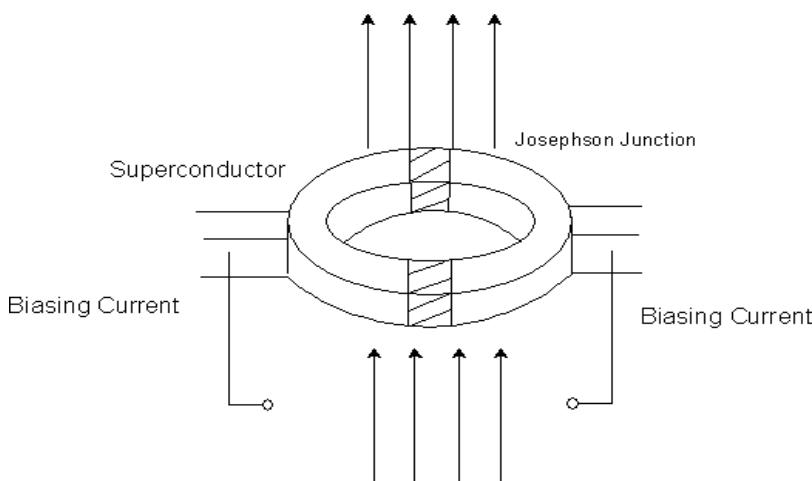
Josephson Effect:

- Josephson effect, **flow of electric current between two pieces of superconducting material separated by a thin layer of insulating material.**
- The Josephson effect produces a current, known as a supercurrent, that flows continuously without any voltage applied, across a device known as a Josephson junction.



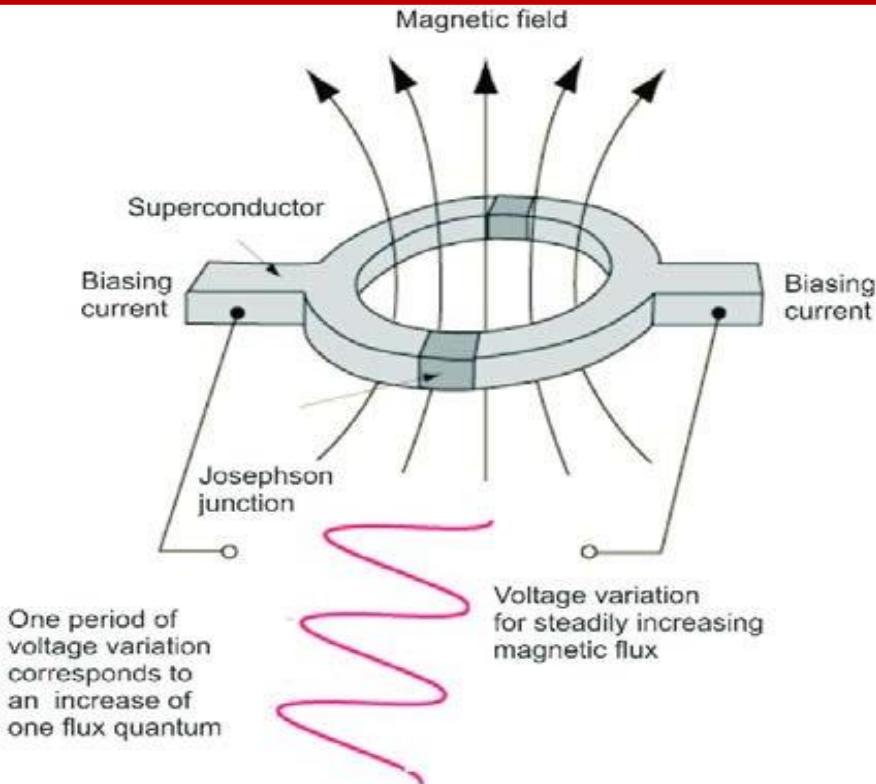
Application of Josephson junction:

- A SQUID (superconducting quantum interference device) is a very sensitive magnetometer used to measure extremely subtle magnetic fields, based on superconducting loops containing Josephson junctions.



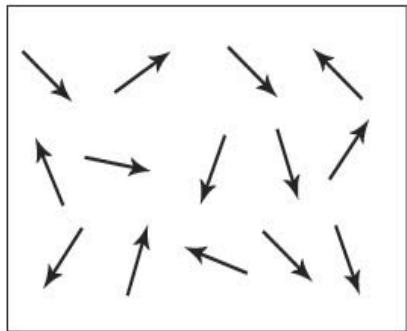
SQUID Schematics

SQUID:

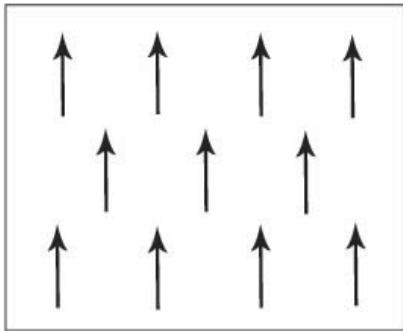


- When current is passed into this arrangement, it splits flowing across the two opposite arc.
- The current through the circuit will have a periodicity, which is very sensitive to the magnetic flux passing normally through the closed circuit.
- As a result, extremely small magnetic flux can be detected with this device.
- This device can also be used to detect voltage as small as 10^{-15} V.
- Magnetic field changes as small as 10^{-21} T can be detected.

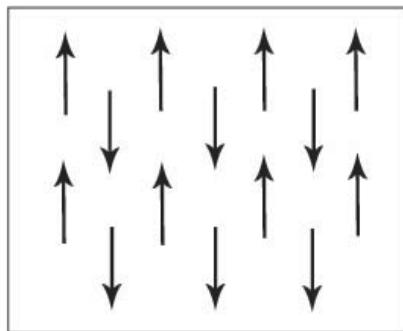
Magnetic Materials



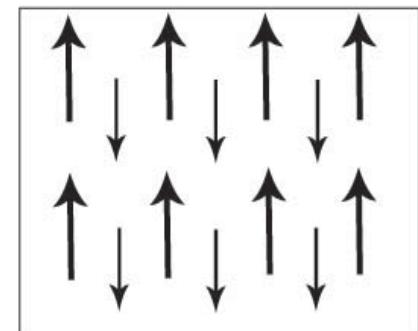
Paramagnetism



Ferromagnetism



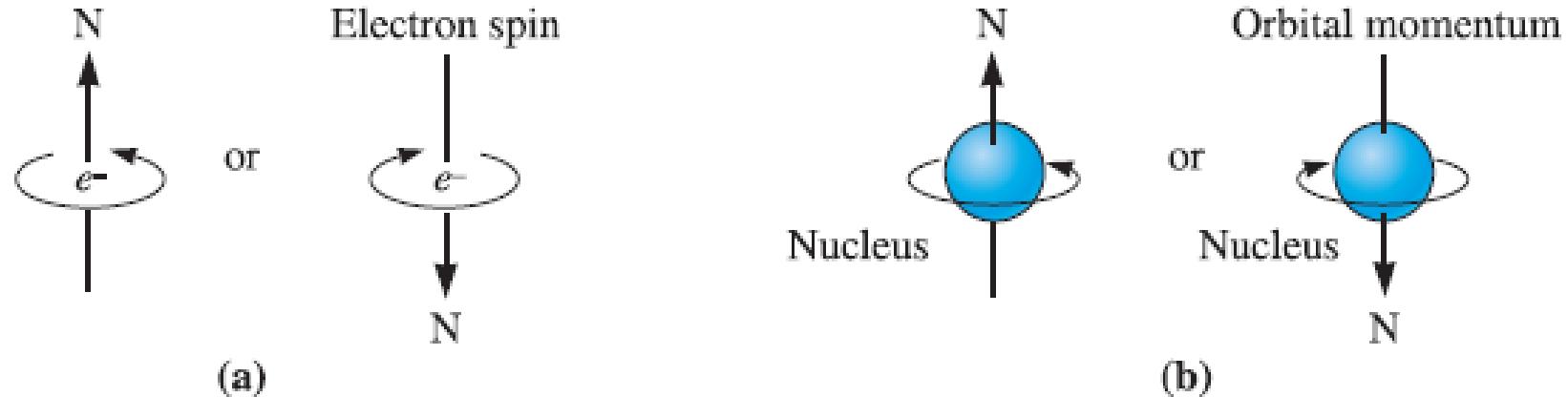
Antiferromagnetism



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

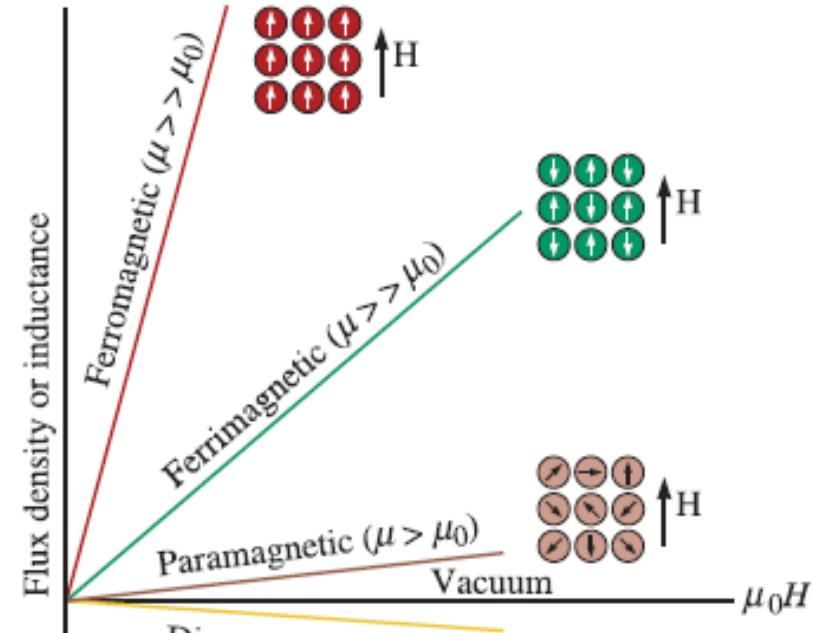


Magnetic moment of an electron due to its spin is known as Bohr magneton (μ_B).

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

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.

Superparamagnetism

- Superparamagnetic particles of Fe_3O_4 are used to form dispersions in aqueous or organic carrier phases or to form “liquid magnets” or ferrofluids.
- 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.

Plasmonic materials

- A **plasmonic material** is a **material** that exploits *surface plasmon resonance* effects to achieve optical properties not seen in nature.
- Surface plasmon resonance originates from *interaction of light with metal-dielectric materials*, through a collective oscillation of free electrons.
- Ability to harvest and manipulate light at the nanoscale.
- Plasmonic materials are metals or metal-like materials that exhibit *negative real permittivity*.
- Most common plasmonic metals are *gold* and *silver*.
- However, many other materials show metal-like optical properties in specific wavelength ranges.
- Plasmonic materials that exhibit *lower losses and tunable optical properties*-current research

Plasmonic materials

- Applications based on plasmonic materials are being developed at a high pace in various fields, including medical, sensors, photovoltaics and plasmon-mediated photocatalysis.

Particle synthesis

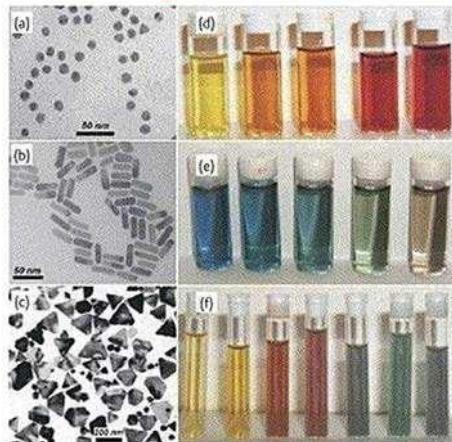


Image: Jain et al, Nano Today, 2(1) 2007, 18–29

Sensing

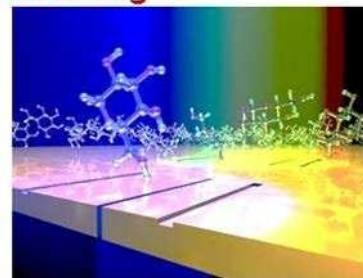


Image: D. Pacifici, Brown University

Theragnostics



Spectroscopy

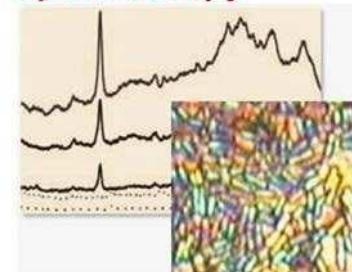
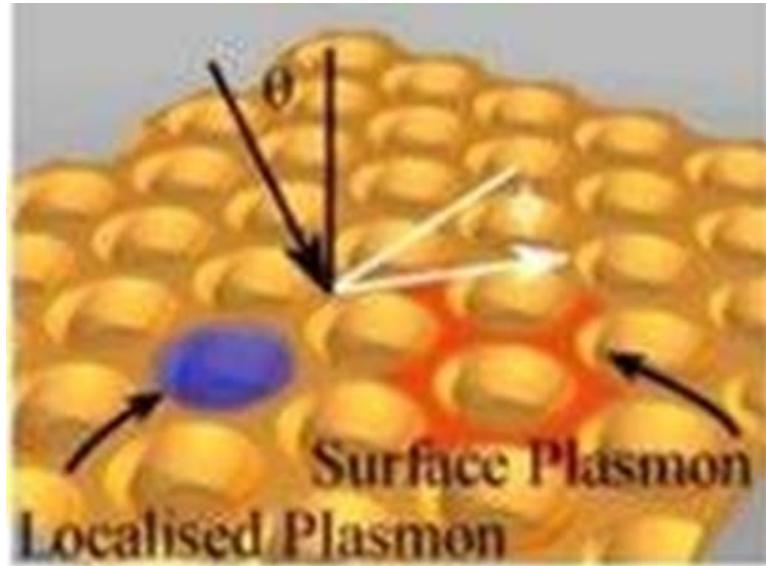


Image: Reinhard group, Boston University

What is Plasmonics?

- Current communication systems are based on either electronics or photonics.
- However, for transporting huge amounts of data at a high speed along with miniaturization, both these technologies are facing limitations.
- Plasmonics is the *study of the interaction of light and metal under precise circumstances*.
- Plasmonics is thought to embody the strongest points of *both optical and electronic data transfer*, allowing the fast transmission of information over very small wires.

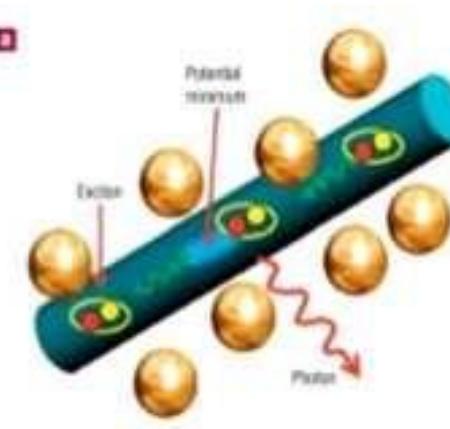
Plasmons:



- Plasmons are *density waves of electrons*, created when *light hits the surface of metal under precise circumstances*.
- These density waves are generated at *optical frequencies*, and are very small and rapid.
- They can theoretically encode a lot of information, more than what's possible for conventional electronics.
- Plasmons are the nanostructured metals.

What is Plasmons?

- When the light incidents on the metal surface, under ideal conditions, it emit the waves which have certain density, known as Plasmons.
- A Plasmon is a collective oscillation of the conduction electrons.
- Surface plasmon resonance (SPR)** is the manifestation of a resonance effect due to the interaction of conduction electrons of metal **nanoparticles** with incident photons.
- Localized Surface plasmon resonance (LSPR)** is an attractive characteristic of metal nanoparticles SPR and is a collective oscillation of conduction band electrons in metal nanoparticles excited by the electromagnetic of incident light.



Necessity of Plasmonics:

- Optical fibers now span the entire globe, guiding light signals that convey voluminous streams of voice command vast amount of data.
 - ✓ Photonic devices
 - ✓ Electronic circuits
 - ✓ Photons & Electronics
 - ✓ Mismatched capacities and sizes

Communication with Plasmonics:

- Huge control over EM waves at nano-scale.
- Surface Plasmons generated at the metal-dielectric interface cloud allow Plasmons to travel along nano-scale wires.
- In order to fabricate effective plasmonic devices, nanostructure materials must be used.

Quantum dot Plasmonics:

- These are the semiconductor nano-crystals.
- It couples strongly both photonics and electronic property.
- These are used for making *superfast computers* that can transfer data up-to 10 Gbps.
- Used in optical applications such as imaging, quantum dot plasmonics are required.

Future directions:

- To develop new *optical components and systems* that are of same size using as today smallest integrated chips.
- Plasmon sources, detectors, switches and wires as well as splitters can be developed.
- Molecular switches &
- All frequencies of the visible light must be covered.

Challenges

- The dream of making all-Plasmonic devices requires further research.
- In order to realize advanced active circuits, there is a need for active modulator and components operating at ultra-high bandwidth and low power utilization.

Conclusion:

- Plasmonics will drive us to a work of high speed communication network, where we can convey voluminous stream of voice and vast amount of data.
- Plasmonics are the *great boon of nanotechnology*.

Metal plasmonic particles importance

- Metals are unique in their physical and chemical properties compared to other compound materials such as metal oxides, sulphides and nitrides.
- When a *nanoparticle is much smaller than the wavelength of light, coherent oscillation of the conduction band electrons induced by interaction with an electromagnetic field- SPR.*
- Nanoparticles of noble metals have attracted immense interest incurring applications in catalysis, electronics, optics, environmental and biomedical applications due to their quantum confinement effects and their large reactive surfaces.

Advantages

- ✓ Strong plasma absorption
- ✓ Enhance Rayleigh scattering
- ✓ Surface enhanced Raman scattering
- ✓ Biological system imaging
- ✓ Determine chemical information on metallic nanoscale substrate

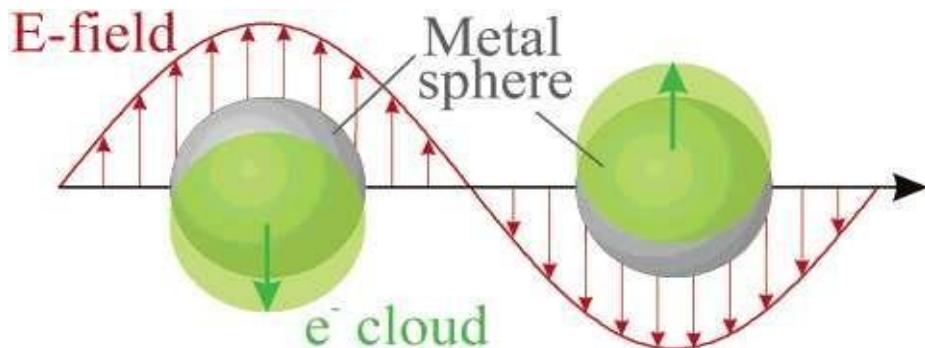
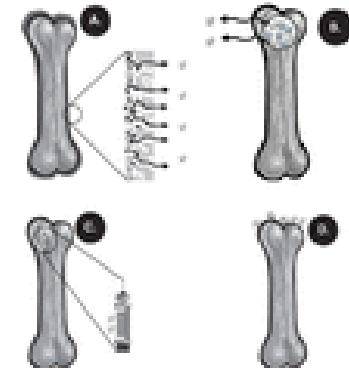


Fig: Surface Plasmon Resonance (SPR)

Silver plasmonic particles significance

- In particular, “silver nanoparticles” have expunged a considerable attention in present tremendous research due to their exquisite fascinating spectrum of physical properties such as catalytic, optical, electrical and antimicrobial applications.
- Silver had gained a privilege position promising vast biomedical applications not only due to their high surface to volume ratio but also due to their *biomedical activities*.
- Nevertheless, this precious metal was originally used as an effective anti-microbial agent and as a disinfectant as it was relatively free of adverse effects.

Bone Cement



Applications

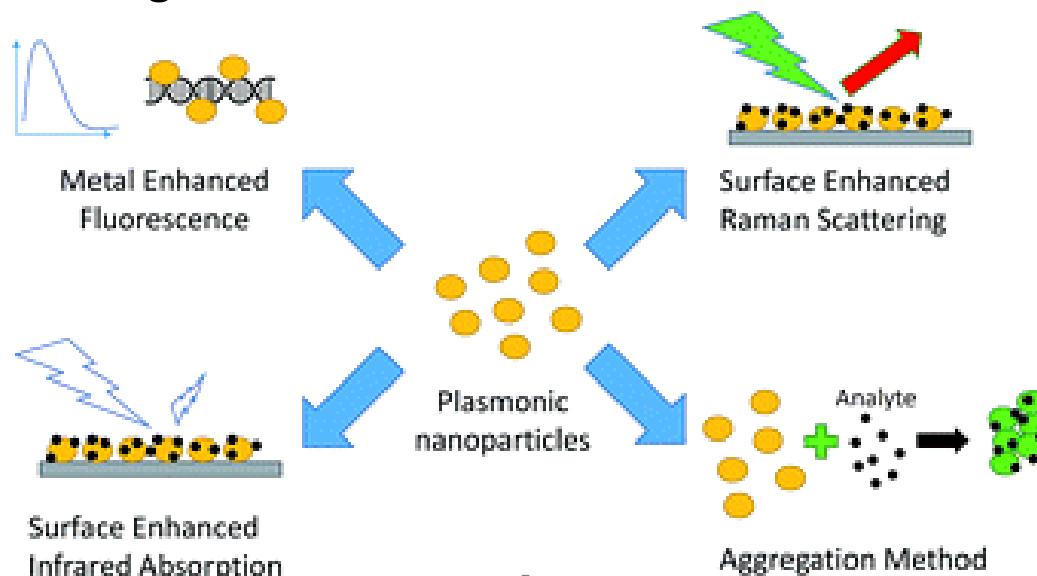
- ✓ Conductive inks
- ✓ Textile engineering
- ✓ Water treatment and Silver-based consumer products
- ✓ Antibacterial/antifungal agents in biotechnology
- ✓ Biological tags and biosensors in diagnostic applications
- ✓ In apparels, footwear, wound dressings, paints and cosmetics
- ✓ Optical applications in metal enhanced fluorescence (MEF) and surface enhanced Raman scattering (SERS)



Fig: Applications of AgNPs

Metal plasmonic nanorods significance

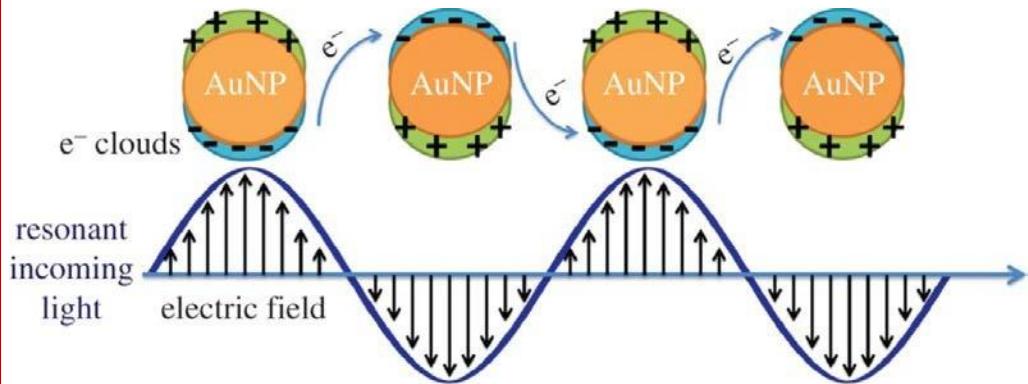
- ✓ Noble metal nanorods and nanowires are known to exhibit unique optoelectronic, mechanical, electronic, and chemical properties due to their anisotropy and tunability of size and shape.
- ✓ The advances seen in the fabrication of MNPs have led to considerable progress in the development of a range of LSPR biosensors in the past decade.
- ✓ Shape-dependent optical properties make anisotropic nanoparticles attractive for applications ranging from sensing to imaging and photo-thermal therapy.
- ✓ Changing nanorods surface chemistry improves cell uptake, reduces toxicity, nanorods can be imaged in cells.



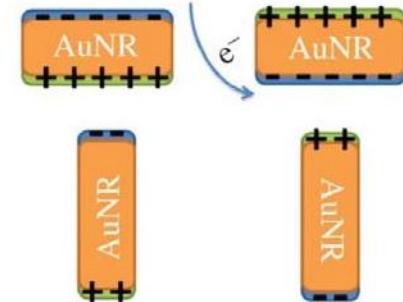
Gold plasmonic nanorods significance

- Gold nanorods are of particular interest due to their stability under ambient conditions relative to other metals, such as *silver* and *copper*.
- Colloidal suspensions of gold nanoparticles display intense extinction in the visible region of the electromagnetic spectrum due to the coherent oscillation of free electrons with the electric field of the incident light, called a *localized surface plasmon resonance*.
- Gold nanospheres exhibit only a single LSPR, but the anisotropy of gold nanorods causes them to exhibit two

Gold plasmonic nanorods significance



longitudinal direction

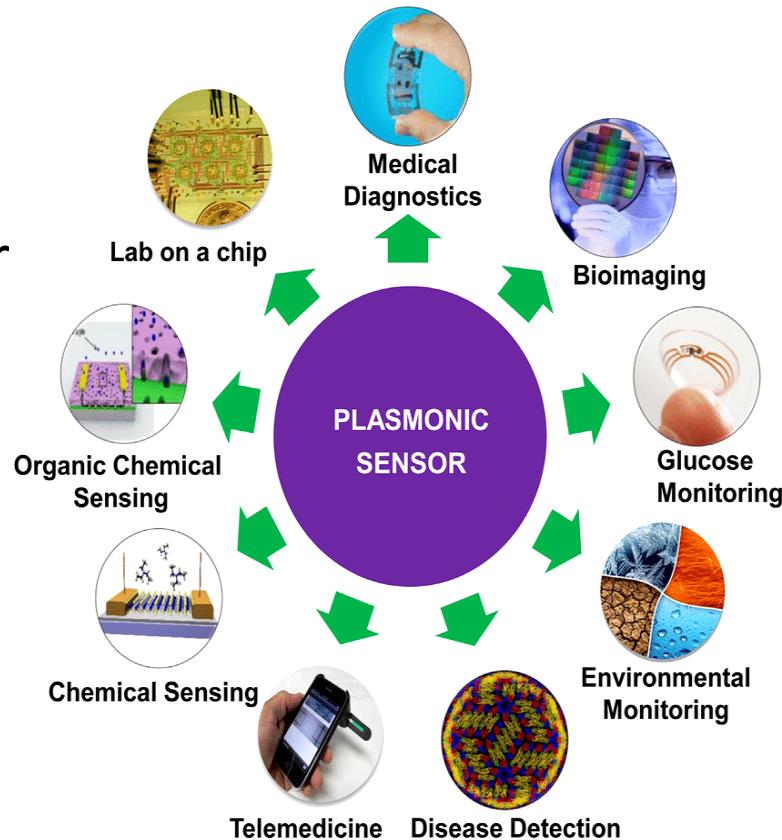


transverse direction

- LSPRs, one corresponding to the transverse axes of the nanorod and the other to the longitudinal axis.
- By changing the aspect ratio “**the ratio of length to diameter**” of the nanorod, with greater aspect ratios causing the longitudinal LSPR to shift to longer wavelengths.
- In addition to LSPR sensing, GNRs have also been applied in many other fields such as **SERS** sensing, chemical imaging and **cancer therapy**.

Applications:

- ✓ Plasmonic solar cells
- ✓ Plasmonsters - A faster chip Graphene structure
- ✓ Plasmonic LED
- ✓ Invisibility cloak
- ✓ Plasmonic Therapy – Cure for cancer
- ✓ Quantum dot Plasmonics
- ✓ Plasmon printing



Applications:

Microscopy:

- ✓ Gradient index plasmonics were used to produce Luneburg and Eaton lenses that interact with surface plasmon polaritons rather than photons.
- ✓ The sub-wavelength domain could be optical switches, modulators, photodetectors and directional light emitters.

Biological and chemical sensing:

- ✓ Other proof-of-concept applications under review involve high sensitivity biological and chemical sensing.
- ✓ They may enable the development of optical sensors that exploit the confinement of surface Plasmons within a certain type of Fabry-Perot nano-resonator.

Applications:

Optical computing:

- ✓ Optical computing replaces electronic signals with light processing devices.
- ✓ The optical switch is made of a metamaterial consisting of nanoscale particles of VO_2 , a crystal that switches between an opaque, metallic phase and a transparent, semiconducting phase.
- ✓ Femto-second laser pulses free electrons in the gold particles that jump into the VO_2 and cause a sub-pico-second phase change.

Photovoltaics:

- ✓ Gold group metals (Au, Ag and Cu) have been used as direct active materials in photovoltaics and solar cells.
- ✓ The materials act simultaneously as electron and hole donor, and thus can be sandwiched between electron and hole transport layers to make a photovoltaic cell.
- ✓ At present these photovoltaic cells allow powering smart sensors for the Internet of Things (IoT) platform.

Applications:

Biomedical applications:

- ✓ The conversion of light to thermal energy, known as the photo-thermal effect, by plasmonic nanomaterials has been extensively used for photo-thermal therapy applications.
- ✓ Since, the discrete size and unique shape of nanoparticles are directly correlated with their plasmonic properties, particularly with localized surface plasmon resonance (LSPR), and the converted heat energy (photo-thermal effect).
- ✓ Thus, application of plasmonic photo-thermal nanomaterials has been extended to various biomedical applications, including bio-sensing, bio-imaging, drug delivery, and therapy.
- ✓ In addition for non-biomedical applications, such as energy, chemical separation, nano-fluidics, nano-catalysis, steam generation, and even synthesis, which all require and utilize specific and localized heat energy.