

In 1911 Lord Rutherford gave atomic model after the famous gold leaf experiment conducted by a group of researchers who saw anomalous deflection of beam of α -particles when bombarded towards a gold foil. It has many flaws. Later, Bohr and then Sommerfeld gave atomic model using quantum mechanical approach.

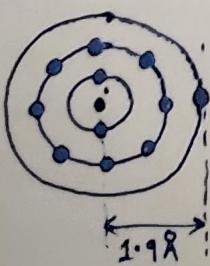
There are interatomic forces acting and hence bonds are formed between atoms of a molecule. Chemical bonds are forces that hold the atoms together in a molecule. They are a result of strong intermolecular interactions among the atoms of a molecule. The outermost electrons of the atoms participate in chemical bonds though electrons repel each other. Bonds are mainly five types – Ionic, Covalent, metallic, hydrogen and van der wall. A bond between two atoms depends upon the electronegativity difference between the atoms. If the electronegativity difference is significantly high, the atoms transfer electrons to form ions and thereby form an ionic bond. If the electronegativity difference is zero or small, then the atoms combine to form covalent bonds.

Solid are aggregates of atoms. The arrangements of atoms in any solid material is determined by the character, strength and directionality of the binding forces. Ionic bonding involves the transfer of electrons and is usually observed when a metal bonds to a nonmetal. Covalent bonding involves the sharing of electrons and is usually observed when a nonmetal bonds to a nonmetal. Metallic bonding involves electron pooling and occurs when a metal bonds to another metal. In hydrogen bonding, interaction involving a hydrogen atom located between a pair of other atoms having a high affinity for electrons (having lone pair). Van der Waals forces include attraction and repulsions between atoms, molecules, and surfaces, as well as other intermolecular forces unlike ionic and covalent bond. Almost two third of elements are metals. Metals are perhaps the most versatile materials from the point of view of utility. Metals are ideal materials for making machines, industrial equipment, household goods, automobiles etc. Some metals are good conductors.

So it was thought that valence electrons in the metals are responsible for conduction.

Na^+ example : valence electrons

In Na metal atom, 11 e^- s revolve around the nucleus in various orbits : $1s^2, 2s^2, 2p^6, 3s^1$. The electron in the outermost orbit is responsible for most of the chemical properties of Na and called valence e^- . The radius of the outermost orbit is nearly 1.9 \AA .



Introduction:

In solids, electrons in outer most orbits of atoms determine its electrical properties. Electron theory is applicable to all solids, both metals and non-metals. In addition, it explains the electrical, thermal and magnetic properties of solids. The structure and properties of solids are explained employing their electronic structure by the electron theory of solids. It has been developed in three main stages.

1. Classical free electron theory
2. Quantum Free Electron Theory.
3. Zone Theory.

1. Classical free electron theory: The first theory was developed by Drude and later it was developed by Lorentz in 1900. According to this theory, metal contains free electrons which are responsible for the electrical conductivity and electrons obey the laws of classical mechanics.
2. Quantum Free Electron Theory: In 1928 Sommerfeld developed the quantum free electron theory. According to Sommerfeld, the free electrons move with a constant potential. This theory obeys quantum laws.
3. Zone Theory: Bloch introduced the band theory in 1928. According to this theory, free electrons move in a periodic potential provided by the lattice. This theory is also called "Band Theory of Solids". It gives complete informational study of electrons.

Assumptions (or) Salient features in classical free electron theory

1. In metals there are a large number of free electrons moving freely in all possible directions.
2. These free electrons behave like gas molecules in a container obeying the laws of kinetic theory of gases.
3. In the absence of field the energy associated with each electron at a temperature T is given by $\frac{3}{2}kT$. It is related to kinetic energy as $\frac{3}{2}kT = \frac{1}{2}mv_{th}^2$. Where v_{th} is the thermal velocity and k is Boltzmann constant.
4. In metals, the positive ion cores are at fixed positions and the free electrons move randomly and collide either with positive ion cores or with other free

electrons or with boundaries. Hence these collisions are elastic. Therefore the electric conduction is due to free electrons only.

5. Electron velocities in a metal obey Maxwell-Boltzmann distribution of velocities.
6. The free electrons move in a constant potential field. Hence the potential energy of the electrons is constant.
7. When an electric field is applied to a metal, free electrons are accelerated in the direction opposite to the direction of applied electric field with a velocity called drift velocity represented as v_d .

Definitions and relations

Drift velocity (v_d)

It is defined as the average velocity acquired by the free electrons of a metal in a particular direction by the application of electric field.

Relaxation time (τ_r)

It is defined as the time taken by the free electrons to reach its equilibrium position from the disturbed position in the presence of electric field.

Collision time (τ)

It is defined as the average time taken by the free electrons between two successive collisions.

Current density (j)

It is defined as the magnitude of current passing through unit area.

$$J = \frac{I}{A} \quad \text{or} \quad I = J \cdot A$$

Mean free path

The average distance travelled by a free electron between two successive collisions is called mean free path.

Electrical conductivity.

Electrical conductivity σ is defined as the rate of charge flow across unit area in a conductor per unit potential (voltage) gradient.

$$\sigma = \frac{J}{E}. \text{ Its unit is } \Omega^{-1}m^{-1} \text{ or } Sm^{-1}.$$

Mobility

It is defined as the drift velocity of the charge carrier per unit applied electric field.

Expression for Relaxation time (τ_r)

When the metal is subjected to an external electric field, the electrons move opposite to the applied field. After removal of electric field the drift velocity decays exponentially as

$$v_d = v_o e^{-t/\tau_r}$$

Where v_o is the initial velocity of an electron, before application of electric field and τ_r is the relaxation time.

$$\text{If } t = \tau_r \text{ then } v_d = v_o e^{-1} \text{ or } v_d = \frac{v_o}{e}$$

Thus the relaxation time may be stated as the time taken for the drift velocity to decay to $\frac{1}{e}$ of its original initial value.

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 distance traveled by the electron between two successive collisions is called as free path and their mean is called the mean free path.

The average distance traveled by the electron between two successive collisions is called mean free path.

Or

The mean free path is the average distance traveled by an electron between two successive collisions with other free electrons.

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

Where \bar{c} is the mean square velocity of electron.

$$\bar{c} = \sqrt{\frac{3K_B T}{m}}$$

Expression for 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.
If 'v' be the total velocity of electron i.e. thermal and drift velocity, then the mean collision time is given by

$$\tau = \frac{\lambda}{v}$$

$$v = v_d + v_{th}$$

If $v_d \ll v_{th}$ then $v = v_{th}$

$$\therefore \tau = \frac{\lambda}{v_{th}}$$

Expression for drift velocity

When electric field is applied on an electric charge 'e', then it moves in opposite direction to the field with a velocity v_d . This velocity is known as drift velocity.

The Lorentz force acting on the electron is $F_L = -eE$

The resistance force acting on the electron is $F_r = \frac{mv_d}{\tau_r}$

When the system is in steady state $F_r = -F_L$

$$\frac{mv_d}{\tau_r} = -(-eE)$$

$$v_d = \frac{eE\tau_r}{m}$$

Mobility of electrons

The mobility of electrons is defined as the magnitude of drift velocity acquired by the electron in a unit field.

$$\mu = \frac{v_d}{E}$$

$$\text{We know } \sigma = \frac{J}{E} = \frac{I}{AE} = \frac{neAv_d}{AE} = \frac{nev_d}{E} = ne\mu \quad \therefore I = neAv_d$$

$$\therefore \mu = \frac{\sigma}{ne} = \frac{ne^2\tau}{mne} = \frac{e\tau}{m} \quad \therefore \sigma = \frac{ne^2\tau}{m}$$

According to Drude, the metal must have two type of particles. They are negatively charged electron and positively charged entities.

1. Electron-electron and electron ion interactions are neglected.
2. Under the action of an external electric field, electrons move opposite to the field direction and make collision with immobile and impenetrable ion cores.

3. All electrons move with RMS speed of a Maxwell-Boltzmann distribution, representing the random or thermal velocity of electrons. The average electron velocity immediately after the collision is zero.

$$\text{drift velocity } V_d = \left(-\frac{eE}{m} \right) t$$

sign of charge of electron
m is mass of an electron

A large influence of electric field is reflected in a long mean free time or relaxation time t . The probability of collision per unit time is $1/t$. If there are n electrons per unit volume, dar is the amount of charge passing through cross sectional area A in time dt , then amount of charge passing through the cross-sectional area A in time dt is $-nArV_d A dt$.

$$\text{current density } J = I/A \quad \text{and} \quad I = \frac{dar}{dt}$$

$$J = \frac{dar}{dt}/A$$

$$= -narV_d$$

$$= -nar \left(-\frac{eE}{m} \right) t$$

$$= \frac{nare^2}{m} \cdot E$$

$$= \sigma E$$

$$\text{dc electrical conductivity } \sigma = \frac{nare^2}{m} t$$

$$V = IR$$

$$EL = J/A \cdot R$$

$$J = E (L/R) (1/R)$$

$$\text{resistivity } (\rho) = R(R/L)$$

$$J = E / \rho = \sigma E$$

$$\sigma = 1/\rho$$

$$V_d = \left(-\frac{ar}{m} E \right) t$$

for a given electric field, the drift velocity of an electron continuously increases with time.

σ is not universally scalar since some complicated situations become nonlinear w.r.t E making σ to behave as a tensor.

$$\sigma = \frac{ne\mu}{W} = \frac{nV_d}{t}$$

V_{th} is thermal velocity.

$$T = \frac{V_{th}^2}{2\mu}$$

$$\text{av. K.E of electron} \frac{3}{2} k_B T = \frac{1}{2} m V_{thms}^2 = \frac{1}{2} m V_{th}^2$$

$$\sigma = \frac{nare^2 \lambda}{(3mkB)^{1/2}} \quad \lambda \text{ is electron mean free path.}$$

so electrical conductivity increases with decrease in temperature.

Electronic Properties

We can express Ohm's law in terms of parameters independent of physical dimensions of the specimen by replacing I with current density J and potential difference V by electric field ϵ . Current density J is defined as electric current flowing through unit cross-sectional area, i.e., $J = I/A$ where A is the area of cross-section of the specimen.

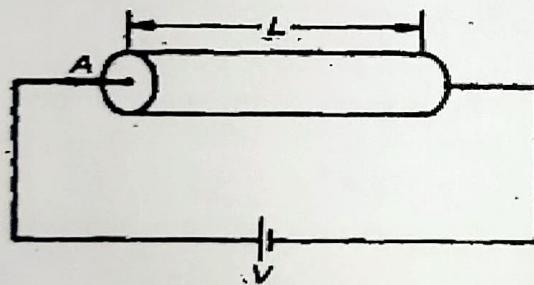


Fig.9.3: An electric field ϵ applied to a metal specimen of length L and cross-sectional area A

Also, we may write the potential difference V as

$$V = \epsilon L = \text{Electric field strength} \times \text{Length of the specimen}$$

On substituting for I and V in the relation $V = IR$ and rearranging terms we obtain,

$$J = \epsilon (L/A) (1/R)$$

If we define a parameter, called **resistivity**, as

$$\rho = R (A/L)$$

we can write

$$J = \epsilon / \rho = \sigma \epsilon$$

where $\sigma (= 1/\rho)$ is called the **electrical conductivity**.

Current density, J is defined as $J = I/A$ and, current is defined as $I = dq/dt$ where dq is the amount of charge passing through unit cross-sectional area. The amount of charge (electron) passing through the cross-sectional area A in time dt is

$$-n e v_d A dt$$

where, n is the number of electrons per unit volume and v_d is the drift velocity of the electrons. Thus

$$J = \frac{dq}{dt} \cdot \frac{1}{A}$$

In vector form, we can write

$$\mathbf{J} = -n e \mathbf{v}_d$$

~~Debye Temperature~~ : The temp^r of the crystal's highest

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Ohm's law

$$V = IR \quad (9.1)$$

where R is electrical resistance offered by the material.

Note that Ohm's law is an empirical law; that is, it is a generalisation based on experimental results. You may also note that Ohm's law as expressed by Eq. (9.1) is easier to verify experimentally. For theoretical analysis however we express Ohm's law in terms of current density J and electric field \mathcal{E} (see margin remark) as

$$J = \sigma \mathcal{E} \quad (9.2)$$

where σ is electrical conductivity of the material. Electrical conductivity is one of the important parameters that enable us to differentiate a metal from an insulator. The value of σ is very large ($\sim 10^7 (\Omega m)^{-1}$) for metals and very small ($\sim 10^{-10} (\Omega m)^{-1}$) for insulators.

Now, two things are desirable: a) to explain Ohm's law from atomic point of view; and b) to obtain an expression for σ on the basis of Drude-Lorentz theory. In other words, we wish to know how Drude-Lorentz theory provides physical basis of Ohm's law.

To this end let us consider a metal specimen. In thermal equilibrium at temperature T , free electrons move randomly inside the specimen (refer Fig. 9.2b) just like the molecules of an ideal gas in a container. In the absence of an electric field, there is no net flow of electrons along any direction due to their random motion. Thus, the average thermal velocity along any direction in the bulk of the specimen is zero.

When an electric field (\mathcal{E}) is applied, (randomly moving) electrons experience a net force in the direction opposite to the electric field due to negative charge on the electron and get accelerated. That is, electrons gain a net drift velocity (v_d) due to the presence of an electric field. You must note that drift velocity is over and above the random thermal velocity, v_t and is responsible for flow of electric current.

Under the influence of applied electric field, electron experiences acceleration and gets drifted with velocity v_d . Thus, we may write, using Newton's second law of motion

$$\left(\frac{\partial v_d}{\partial t} \right)_{\text{field}} = \frac{\text{Force}}{m} = -\frac{e}{m} \epsilon \quad (9.3)$$

where m is mass and e is charge of electron.

Eq. (9.3) shows that for a given electric field, the drift velocity of an electron continuously increases with time. This inference, however, is not in agreement with experimental observations (expressed as Ohm's law). At a given temperature, electrical conductivity of a metal is constant. Thus, from Eq. (9.2) we may conclude that for a given electric field, the current density should be constant suggesting that drift velocity of the electron cannot increase infinitely (see lower margin remark) and must obtain a steady value.

You may ask: How does Drude-Lorentz theory overcome this problem? In other words, what makes the accelerating electron acquire a steady drift velocity? It was suggested that accelerating electrons collide with the ions (or the impurity atoms) within the specimen. As a result, on collision, an electron loses drift velocity completely and it is left only with random thermal velocity. After emerging from the collision, an electron begins to accelerate in the electric field afresh and acquires drift velocity. At the next collision, the drift velocity is again lost completely and this process goes on.

- electrons acquire a drift velocity v_d due to the applied electric field, and
- accelerating electrons suffer collisions with ions (and impurities) and lose their drift velocity and are left only with the thermal velocity, v_t .

We have already discussed the first process (Eq. (9.3)). To visualise the second process, we seek analogy with a mechanical system. You may recall from elementary mechanics that when a body falls through a viscous medium, its accelerated motion becomes uniform with a constant limiting velocity. Here, an accelerating electron suffers collisions with ions (and impurities) and attains a steady drift velocity. Thus, the effect of collisions is analogous to a viscous (or frictional) force, F which is proportional to mass and drift velocity of electrons:

$$F \propto m v_d$$

$$= \frac{m v_d}{\tau} \quad (9.4)$$

where, $1/\tau$ is the proportionality constant. τ is known as **collision time** or **relaxation time** for collision between electron and ions.

Relaxation time is assumed to be independent of energy and direction of motion of electrons. It refers to the average time interval between two successive collisions. You may now ask: Is there some experimental evidence in favour of the existence of such a viscous force in a metal? Well, so far as Drude-Lorentz theory is concerned, it was simply assumed that such a force does exist and can be represented in terms of relaxation time. They did not elaborate upon the nature of such processes. Let us see how does this assumption influences electrical conductivity. The change in drift velocity due to collisions can be expressed, using Newton's second law of motion, as

$$\left(\frac{\partial v_d}{\partial t} \right)_{\text{collision}} = \frac{F}{m} = - \frac{v_d}{\tau} \quad (9.5)$$

The negative sign indicates that drift velocity decreases due to collisions.

Under the influence of two competing processes, a steady state is obtained and electrons move with a constant drift velocity. That is, in the steady state, we must have

$$\frac{d v_d}{dt} = 0.$$

This may be expressed as a sum of two terms:

$$\left(\frac{\partial v_d}{\partial t} \right)_{\text{field}} + \left(\frac{\partial v_d}{\partial t} \right)_{\text{collision}} = 0$$

Using Eqs. (9.3) and (9.5), we obtain

$$v_d = -\frac{e\tau}{m} \epsilon \quad (9.6)$$

This expression shows that drift velocity of electrons is linearly proportional to the electric field. To see whether or not this conclusion about v_d is consistent with Ohm's law, let us substitute $\mathbf{J} = -n e v_d$ in Eq. (9.2);

$$\mathbf{J} = -n e v_d = \sigma \epsilon$$

$$v_d = -\frac{\sigma}{ne} \epsilon \quad (9.7)$$

Thus, Ohm's law also predicts linear dependence of drift velocity on the applied electric field, and is consistent with Drude-Lorentz theory. Further, on comparing Eqs. (9.6) and (9.7), we get

$$\sigma = \frac{n e^2 \tau}{m} \quad (9.8)$$

Relaxation Time

From Eq. (9.4) you know that relaxation time is closely related to collisions between electrons and ions in a specimen. Further, drift velocity gained by electrons is completely lost in any such collision. In other words, due to collisions, velocity of electrons varies between v_t and $v_t + v_d$; as shown in Fig. 9.4. The time elapsed between two consecutive minimum values of the velocity of electron is called the relaxation time. This is shown as the time between points A and B in Fig. 9.4.

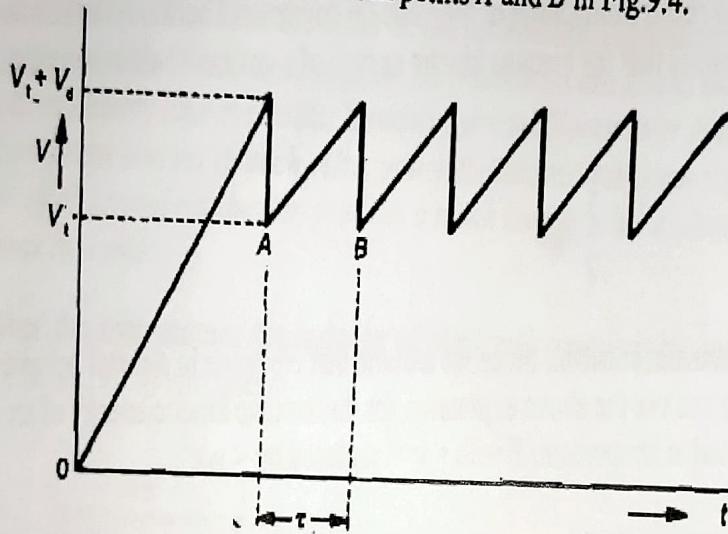


Fig. 9.4: Plot of velocity of electrons vs. time showing the relaxation time

Solving SAQ 2, you know that for a typical metal, relaxation time is very small ($\sim 10^{-14}$ s). To obtain an expression for relaxation time, Drude used concepts of elementary kinetic theory. He argued that if the average distance travelled by an electron between two successive collisions is denoted by λ , the mean free path of an electron, the mean free time between these collisions is given by

$$\tau = \langle t \rangle = \frac{\lambda}{\langle |v_t + v_d| \rangle}$$

where $\langle |v_t + v_d| \rangle$ is the average speed between two successive collisions. From SAQ 1 you know that v_d is very small compared to v_t . Therefore, for all practical purposes, we can express above result as

$$\tau = \frac{\lambda}{\langle |v_t| \rangle}. \quad (9.9)$$

Further, you may recall from Unit 9 of the PHE-06 course on Thermodynamics and Statistical Mechanics that the average kinetic energy of a gas molecule at temperature T is given by

$$\frac{1}{2}m\langle v \rangle^2 = \frac{3}{2}k_B T$$

where k_B is Boltzmann constant. Since we assume that electrons in a metal behave as an ideal gas, we can use the above expression for the average kinetic energy of an electron in a metal at temperature T with $\langle v \rangle^2$ replaced by $\langle v_t \rangle^2$:

$$\frac{1}{2}m\langle v_t \rangle^2 = \frac{3}{2}k_B T$$

$$\langle v_t \rangle = \sqrt{\frac{3k_B T}{m}} \quad (9.10)$$

On substituting for $\langle v_t \rangle$ from Eq. (9.10) in Eq. (9.9), we get

$$\tau = \frac{\lambda}{\sqrt{\frac{3k_B T}{m}}} = \lambda \sqrt{\frac{m}{3k_B T}} . \quad (9.11)$$

Since relaxation time is of the order of 10^{-14} s, the mean free path of electrons in a metal is about 10 \AA . This is of the order of the interatomic separation in a metal. It seems, therefore, that Drude's assumption that collisions are due to electrons bumping into larger and heavy ions is correct. However, you will learn later in this unit that this assumption is not correct as such. Also, you will discover that quantum mechanical treatment of electrical conduction predicts a much larger value of the mean free path of electrons in a metal.

To discover the temperature dependence of electrical conductivity, we substitute the value of τ in Eq. (9.8) and obtain

$$\sigma = \frac{n e^2 \lambda}{\sqrt{3k_B m}} \frac{1}{\sqrt{T}} \quad (9.12)$$

Eq. (9.12) shows that σ is inversely proportional to half power of temperature. Since $\sigma = \frac{1}{\rho}$, electrical resistivity (ρ) varies as \sqrt{T} . But this prediction is at variance with experimentally observed temperature variation of resistivity. In addition, Drude-Lorentz theory was also unable to explain some other experimental observations pertaining to electrical conduction in metals. You will learn them now.

5. The de-Broglie wavelengths of the e⁻s with some thermal energy are on the nanometer or Angstrom scale. This means that e⁻s can't be treated as classical particles (since they have substantial wave character) under the conditions of the Drude model.

Success or Advantages or Merits classical free electron theory

- 1) It verifies ohm's law.
- 2) It explains electrical and thermal conductivities of metals.
- 3) It derives Widemann-Franz law.
- 4) It explains optical properties of metals.

Limitations or drawbacks or Demerits classical free electron theory

- 1) It fails to explain the electrical conductivity of semiconductors and insulators.
- 2) It fails to explain the temperature variation of electrical conductivity at low temperature.
- 3) It fails to explain the concept of specific heat of metals.
- 4) It fails to explain the mean free path of the electrons.
- 5) The phenomenon like photo electric effect, Compton effect and black body radiation could not be explained by classical free electron theory.
- 6) It fails to explain temperature dependence of paramagnetic susceptibility and ferromagnetism.

Limitations of the Drude-Lorentz theory

Some of the experimentally observed behaviour of metals with respect to electrical conduction which could not be explained by Drude-Lorentz theory are listed below:

1. You have seen above (Eq. 9.12) that according to Drude-Lorentz theory, resistivity of a metal is proportional to the square root of temperature. However, experiments show that above the Debye temperature, resistivity varies linearly with temperature, as shown in Fig. 9.5.
2. For an impure metallic specimen or a specimen with imperfections in its crystal, the resistivity is given by the relation

$$\rho = \rho_0 + \rho(T) \quad (9.13)$$

where ρ_0 , a constant, is called *residual resistivity* and is independent of temperature. However, ρ_0 increases with increasing impurity concentration in a specimen. Eq. (9.13) is known as Matthiessen's rule.

3. The resistivity of some metals almost vanishes at low temperatures, i.e. they become superconductors.

Some of the unexplained features of electrical conduction were overcome by Sommerfeld model. You will learn about it later in this unit. Now, before we proceed to discuss the thermal properties of metals in the light of Drude-Lorentz theory, you should answer the following SAQ.

4. The Drude Model does n't take part into account collisions between e⁻s themselves & also doesn't consider electrostatic interactions between the e⁻s and the lattice ions.

(*) Debye Temperature : The temp^r of the crystal's highest normal mode of vibrations, i.e., the highest temperature that can be achieved due to single normal vibration

$$\Rightarrow \Theta_D = \frac{h v_m}{k_B} \quad [k_B \rightarrow \text{Boltz Const.}]$$

Electronic Heat Capacity

From your elementary physics classes, you may recall that heat capacity is defined as the amount of thermal energy absorbed by a substance to increase its temperature by one degree. As mentioned above, in metals, the absorbed thermal energy can induce following two processes:

- increase the vibrations of lattice atoms about their respective equilibrium positions, and
- increase the kinetic energy of electrons.

In view of above, we may express the heat capacity of a metal (per mole) as a sum of heat capacities due to lattice vibrations and due to electrons:

$$C = C_{\text{lat}} + C_{\text{el}} \quad (9.14)$$

You have already studied about C_{lat} in Unit 8. You may recall that at a given temperature T , it is given by

$$C_{\text{lat}} = \begin{cases} 3R & ; \text{ for } T \gg T_D \\ BT^3 & ; \text{ for } T < T_D \end{cases} \quad (9.15a)$$

Debye
Temperature

$$(9.15b)$$

where, $R (=N_A k_B)$ is universal gas constant, B is constant of proportionality, N_A is the Avogadro's number and T_D is the Debye temperature.

Refer to Fig. 9.6 which depicts the temperature variation of heat capacity of a typical solid and that of a metal (silver). You should note that in both the plots, the heat

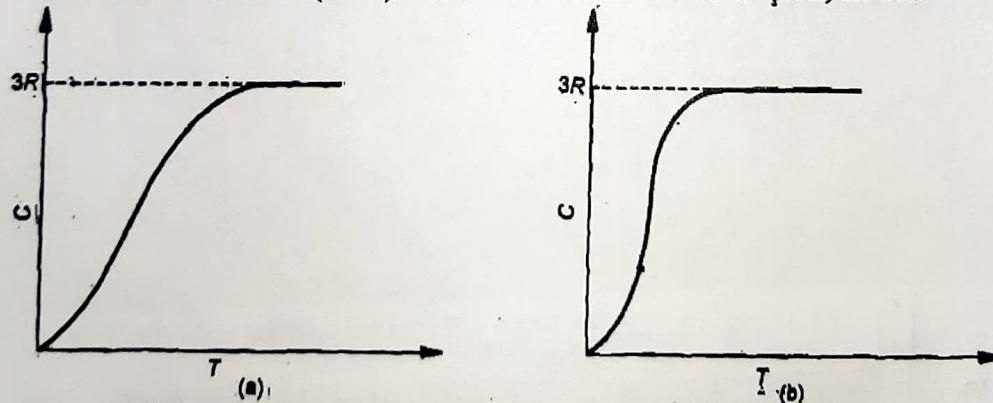


Fig. 9.6: Heat capacity vs. temperature plot for a) a typical solid; and b) for silver

Thermal properties

The explanation of thermal properties lies in the fact that

thermal energy supplied to a solid is absorbed by its atoms resulting in the increase of their internal energy. While in case of heat capacity, thermal energy increases vibrations of atoms /ions at lattice sites, in case of thermal conduction, transfer of thermal energy across the solid specimen takes place via elastic waves. However, these explanations are valid only for insulators which have no free electrons. In metals, thermal energy can also be absorbed by free electrons. Therefore, it is only logical for us to expect an electronic contribution to heat capacity as well as thermal conductivity of metals. Let us discuss these contributions.

Dulong Petit's Law

heat capacity of a mole of many solid element is $3R$, regardless of the nature of the substance

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk_B$$

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

N is total number of atoms.

$$T_D = \frac{h\nu_p}{k_B}$$

\rightarrow Planck's constant

ν_p is maximum frequency of the vibrations

of a solid's atoms.

Dulong Petit Law :-

Sp. ht. of a substance \rightarrow heat required to rise temp of 1gm of substance by 1°C

This ht. capacity/gm \rightarrow multiplied by Atm. wt, i.e., Atm. heat = $A \times S$ $A \rightarrow \text{Atm. wt}$ $S \rightarrow \text{Sp. ht.}$

② Dulong-Petit Law states that :-

Atomic heat of almost all solid elements is nearly constant, i.e. 6.4 cal.

- The constancy of atm. ht of an element in the solid state can be shown by the application of equipartition principle. [In solid, translation and rotation are not possible but there will be 3 vibration degree of freedom which each contributes energy of ' $k_B T$ '. The Energy of 1 particle = $3 k_B T$]

$$\begin{aligned} \text{For } N_A \text{ atoms, } E &= 3 N_A k_B T \\ &= 3 R T \quad [R = N_A k_B] \end{aligned}$$

↓
Equipartition
of Energy Principle

capacity saturates at $3R$ at high temperatures. In other words, at high temperatures, metals obey Dulong-Petit's law like any other solid.

If electrons behave as molecules of an ideal gas obeying elementary kinetic theory, their average energy at temperature T will be $(3/2)k_B T$. Therefore, energy of electrons in one mole of a monovalent metal, $\langle E \rangle = (3/2)N_A k_B T = (3/2)RT$. Thus, the electronic heat capacity is given by

$$C_{el} = \frac{\partial \langle E \rangle}{\partial T} = (3/2)R \quad (9.16)$$

Combining Eqs. (9.15a) and (9.16), we find that total heat capacity of a monovalent metal at high temperature ($T \gg T_D$) should be

$$C = C_{lat} + C_{el} = 4.5 R. \quad (9.17)$$

This value of heat capacity obtained on the basis of Drude-Lorentz theory is much higher than the experimental value (Fig. 9.6b). You will naturally like to know: What is the way out? The correct explanation was provided by Sommerfeld. Before you learn about it in the next section, let us obtain the expression for thermal conductivity of a metal.

Dulong Petit Law
composition of energy

Electronic Thermal Conductivity

You may recall that thermal conduction refers to the net transfer of energy from hot end to cold end of a specimen. Thermal conductivity K is numerically equal to amount of thermal energy crossing a unit area per unit time (Q) when unit temperature gradient exists across a specimen:

$$Q = -K \frac{dT}{dx}.$$

As you studied in Unit 7, the thermal energy is transported from one point to another by lattice waves or phonons. However, in a metal free electrons can also act as carriers of thermal energy. Thus, the thermal conductivity of metals should be expressed as

$$K = K_{\text{lattice}} + K_{\text{el.}}$$

From Unit 10 of PHE-06 course you may recall that according to the kinetic theory, thermal conductivity of an ideal gas is given by

$$K = \frac{1}{3} c \langle v \rangle \lambda$$

where c , $\langle v \rangle$ and λ are respectively the heat capacity per unit volume, average speed and mean free path of gas molecules.

Thus, according to Drude-Lorentz theory, thermal conductivity of a metal due to electron gas can be written as,

$$K_{\text{el.}} = \frac{1}{3} c_{\text{el.}} \langle v_t \rangle \lambda \quad (9.18)$$

where $c_{\text{el.}}$ is the electronic heat capacity per unit volume, and $\langle v_t \rangle$ and λ is average thermal speed and mean free path of electrons, respectively.

If we substitute $c_{el} = \frac{3}{2} nk_B$, $\langle v_t \rangle = \sqrt{\frac{3k_B T}{m}}$ (Eqs. 9.16 and 9.10) and $\lambda \sim 10 \text{ \AA}$ in

Eq. (9.18), we find that $K_{el} \sim 100 \text{ W m}^{-1} \text{ K}^{-1}$ which is much higher than the experimental value of K for a typical metal. We will discuss this discrepancy and its resolution in the next section.

Till now, you have studied Drude-Lorentz theory in which free electrons in a metal are treated as classical particles obeying the laws of kinetic theory. While this theory qualitatively explained Ohm's law, it could not account for many other experimental observations pertaining to electrical conduction; failed to explain why, like other solids, the heat capacity of metals saturates at $3R$ at high temperatures; and could not account for the experimental values of thermal conductivity of metals. To overcome these limitations of Drude-Lorentz theory, Sommerfeld proposed that electrons are quantum particles and should be treated as such. You will now learn Sommerfeld model.

The calculation of C_{el} is made by taking the thermal energy per electron at temperature T is $\frac{3}{2} k_B T$, in accordance with the law of equipartition energy.

$$C_{el} = \frac{3}{2} \left(\frac{N_A k_B^2 \tau}{m} \right) T$$

Relation between electrical conductivity and thermal conductivity

$$\frac{K}{\sigma} = \frac{3}{2} \left(\frac{k_B}{m} \right)^2 T$$

Lorenz number (L) $\frac{K}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{m} \right)^2$

dc electrical conductivity using Lorentz model

$$\sigma_L = \left(\frac{8}{3\pi} \right)^{1/2} \frac{m\tau^2 \lambda}{(3mk_B T)^{1/2}}$$

Lorentz modifications provide neither any noteworthy change.

5. Sources of electrical resistance in metals

According to quantum free electron theory, the free electrons always collides with the positive ions or electrons present in the metal. The scattering of conduction electrons are due to

1. Effect of temperature
2. Defect, e.g. impurities, imperfections, etc.

Temperature effect:

The positive ions are always in oscillating (or vibrating) state about their mean position; even the substance is present at 0K temperature. The vibrating amplitude of ions is always depends the temperature. The mean free path λ of the 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 .

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

From equations (1) and (2)

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

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)

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

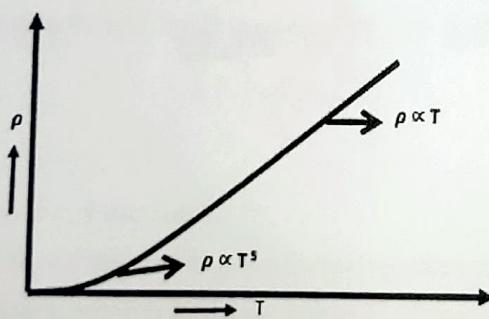
From equation (5) we observe that the resistivity of metal is linearly increases with temperature.

The conductivity σ is defined as the reciprocal of resistance.

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

From equation (6) we observe that the conductivity of metal is inversely proportional to their temperature.

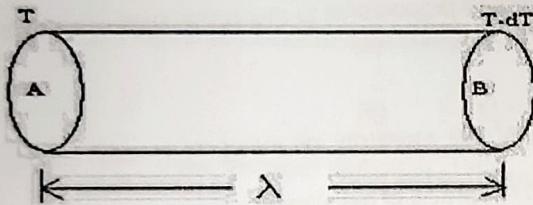
The variation of resistivity of metal with temperature is shown in figure.



Thermal conductivity K is defined as the amount of heat flowing per unit time through the material having unit area of cross-section per unit temperature gradient. $Q = K \frac{dT}{dx}$.

Expression for Thermal Conductivity of a Metal

Consider two cross-sections A and B in a uniform metallic rod AB separated by a distance λ . Let A at a high temperature (T) and B at low temperature ($T-dT$). Now heat conduction takes place from A and B by the electrons. The conduction electron per unit volume is n and average velocity of these electrons is v . During the movement of electrons in the rod, collision takes place. Hence, the electrons near A lose their kinetic energy while electrons near B gain kinetic energy.



$$\text{At A, average kinetic energy of an electron} = \frac{3}{2} kT \dots (1)$$

$$\text{At B, average kinetic energy of the electron} = \frac{3}{2} k(T-dT) \dots (2)$$

The excess of kinetic energy carried by the electron from A to B is,

$$\frac{3}{2} k dT \dots\dots(3)$$

Number of electrons crossing per unit area per time from A and B is,

$$\frac{1}{6} n v$$

The excess of energy carried form (A to B) per unit area in unit time is = $\frac{1}{4} n v k d T \dots\dots(4)$

Similarly, the deficient of energy carried from B to A per unit area per unit time is

$$= -\frac{1}{4} n v k d T \dots\dots(5)$$

Hence, the net amount of energy transferred from A to B per unit area per unit time is,

$$Q = \frac{1}{2} n v k d T \dots\dots(6)$$

But from the basic definition of thermal conductivity, the amount of heat conducted per unit area per unit time is,

$$Q = K \frac{dT}{\lambda} \text{ i.e., } \frac{1}{2} n v k d T = K \frac{dT}{\lambda}; \therefore K = \frac{1}{2} n v k \lambda \dots\dots(7)$$

We know that for the metals i.e. $\tau = \tau_c = \frac{\lambda}{v} = \tau v = \lambda \dots\dots(8)$

Substituting the equation (8) in equation (7), we have

$$K = \frac{1}{2} n v^2 k \tau \dots\dots(9)$$

Wiedemann – Franz law:

The law states that the ratio of thermal comnductivity to electrical conductivity of the metal is directly proportional to the absolute temperature of the metal.

We know that,

$$\sigma = \frac{n e^2 \tau}{m} \dots\dots(1) \quad \text{and}$$

$$K = \frac{1}{2} n v^2 k \tau \dots\dots(2)$$

$$\frac{\text{Thermal conductivity}}{\text{Electrical conductivity}} = \frac{K}{\sigma} = \frac{\frac{1}{2} n v^2 k \tau}{\frac{n e^2 r}{m}}; \frac{k}{\sigma} = \frac{1}{2} \frac{m v^2 k}{e^2} \dots\dots(3)$$

We know that the kinetic energy of an electron,

$$\frac{1}{2} m v^2 = \frac{3}{2} k T \dots\dots(4)$$

Substituting the equation (4) in the equation (3). We have

$$\frac{k}{\sigma} = \frac{3}{2} \frac{k T \times k}{e^2} = \frac{3 k^2 T}{2 e^2}, \text{ or } \frac{K}{\sigma} = \frac{3}{2} \left[\frac{k}{e} \right]^2 T, \text{ or } \frac{K}{\sigma} = L T \dots\dots(5)$$

Where $L = \frac{3}{2} \left[\frac{k}{e} \right]^2$ is a constant and it is known as Lorentz number.

$$\frac{K}{\sigma} \propto T \quad \dots\dots(6)$$

Hence, it is proved that the ratio of thermal conductivity of a metal is directly proportional to the absolute temperature of the metal.

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 for atoms and molecules. According to Maxwell Boltzmann distribution, the probability of occupying an energy level ϵ_i is

$$f(\epsilon_i) = \frac{1}{e^{\frac{(\epsilon_i - \epsilon_F)}{k T}}}$$

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). According to Bose Einstein distribution, the probability of occupying an energy level ε_i is

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

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

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

pictures

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 applicable for fermions (Fermions (e.g. electrons, protons, neutrons, etc.) are the particles with odd half integral spins ($0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$)).

According to Fermi - Dirac distribution, the probability of electron occupying an energy level ϵ_i is

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

ϵ_i is the energy of i^{th} level

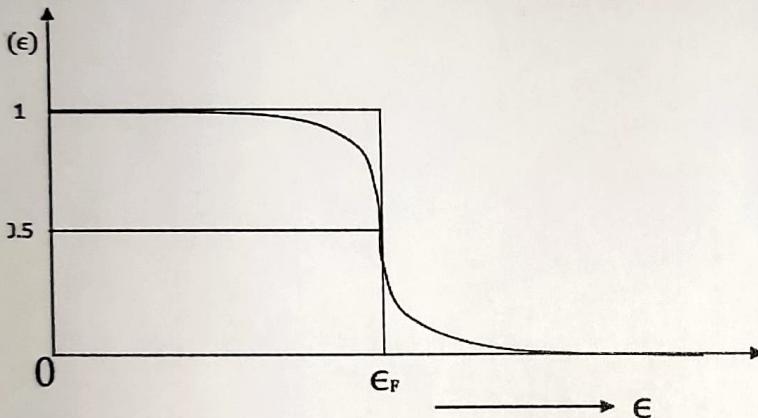
ϵ_F is the energy of Fermi level,

k is a Boltzmann constant

T is the absolute temperature and

$f(\epsilon_i)$ is the Fermi function

The variation of Fermi function with temperature is shown in figure.



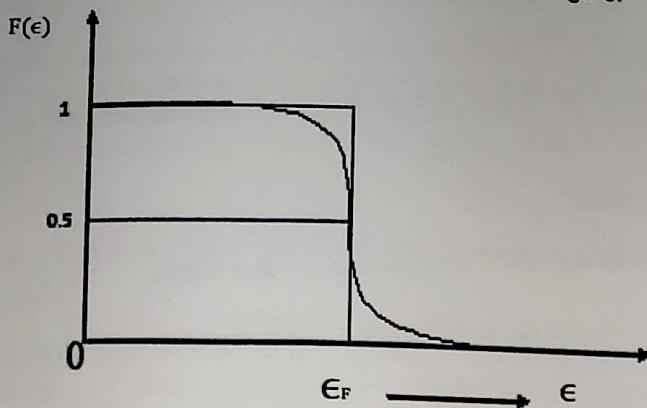
Effect of temperature on Fermi Dirac distribution

When the material is at a temperature 'T' 0K, below the Fermi energy levels are totally fulfilled and above the energy levels are empty. When it receives thermal energy from surroundings, the electrons are thermally excited into higher energy levels. The occupation of electrons in energy levels obeys a Fermi Dirac statistical distribution law.

According to Fermi - Dirac distribution, the probability of electron occupying an energy level ϵ_i is

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

15
The variation of Fermi function with temperature is shown in figure.



From this curve we can observe the probability of finding an electron at different temperatures.

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

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

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

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

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

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

$$f(\varepsilon_i) = 0$$

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

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

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

$$f(\varepsilon_i) = 1$$

From figure (1) we illustrate that

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

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

When $T > 0k$ if $\varepsilon_l = \varepsilon_F$, : $f(\varepsilon_l) = \frac{1}{2}$
So the Fermi level can be defined as

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.
2. In semiconductor the probability of electron occupying an energy level ε_l is

$$f_e(\varepsilon_l) = \frac{1}{e^{\frac{(\varepsilon_l - \varepsilon_F)}{kT}} + 1}$$

3. In semiconductor the probability of hole occupying an energy level ε_l is

$$f_h(\varepsilon_l) = 1 - f_e(\varepsilon_l) = 1 - \frac{1}{e^{\frac{(\varepsilon_l - \varepsilon_F)}{kT}} + 1} = \frac{1}{e^{\frac{(\varepsilon_l - \varepsilon_F)}{kT}} + 1}$$

4. At $T > 0k$ if $\varepsilon_l = \varepsilon_F$, : $f(\varepsilon_l) = \frac{1}{2}$
5. At $T = 0k$ if $\varepsilon_l > \varepsilon_F$, : $f(\varepsilon_l) = 0$
6. At $T = 0k$ if $\varepsilon_l < \varepsilon_F$, : $f(\varepsilon_l) = 1$

From the Fermi Dirac distribution we understood that, below the Fermi levels are totally fulfilled and above the levels are totally empty

UNIT-III

QUANTUM MECHANICS AND ELECTRON THEORY

Basic terms and definitions

| | |
|--|---|
| Matter waves | Wave associated with the motion of a particle (or) Matter waves are nothing but waves and are usually associated with a moving quantum particle. |
| de Broglie hypothesis | Matter waves are a central part of the theory of quantum mechanics, being an example of wave–particle duality. All matter can exhibit wave-like behaviour. The concept that matter behaves like a wave was proposed by Louis de Broglie in 1924. It is also referred to as the de Broglie hypothesis. |
| Mobility | In steady state the drift velocity per unit electric field is called Mobility. |
| Relaxation Time | The time taken for the drift velocity of an electron to decay $1/e$ times of its initial value is called Relaxation Time |
| Mean collision time | The duration between two successive collisions when electron is in random motion is called Mean collision time |
| Mean free path | The average distance travelled by an electron between two successive collisions during their random motions is called mean free path |
| Drift Velocity | When an electric field (E) is applied to the metal electrons experience force (F) in opposite direction to the applied field. this force is called Drift Velocity |
| Merits of Classical free electron | 1. It verifies ohm's law 2. It explains the electrical and thermal conductivities of metals. 3. It derives Wiedemann-franz law. 4. It explains optical properties of metal. |
| Postulates of Classical free electron theory | 1. In metals there are large number of free electrons moving freely in all possible directions 2. free electrons in the metals are assumed to behave like gas molecules obeying the kinetic theory of gases 3. In metals electrons move randomly and collide with either +ve ions or with free electrons all the collisions are elastic (i.e., no loss of energy) 4. When electron field is applied to the metal the free electrons accelerated in the opposite direction to the applied field |
| Drawbacks of Classical free electron | 1. Classical free electron fails to explain the temperature dependence of electrical conductivity 2. fails to explain specific heat of a solid. 3. fails to explain Wiedemann-franz law that is at lower temperatures, the ratio of thermal conductivity to electrical conductivity is proportional to temperature. 4. Electrical conductivity for semiconductors and insulators are not explained. |

| | |
|--|---|
| Postulates of quantum free electron theory | <ol style="list-style-type: none"> 1 .In a metal the available free electrons are fully responsible for electrical conduction. 2. The electrons move in a constant potential inside the metal.. 3. Electrons have wave nature, the velocity and energy distribution of the electron is given by Fermi-Dirac distribution function. 4. The loss of energy due to interaction of the free electron with the other free electron. 5.Electron's distributed in various energy levels according to Pauli Exclusion Principle. |
| Advantages of Quantum free electron theory | <ol style="list-style-type: none"> 1.This theory explains the specific heat capacity of materials. 2.This theory explains photo electric effect, Compton Effect and black body radiation. etc. 3.This theory gives the correct mathematical expression for the thermal conductivity of metals. |
| Drawbacks of Quantum free electron theory | <ol style="list-style-type: none"> 1.This theory fails to distinguish between metal, semiconductor and Insulator. 2.It also fails to explain the positive value of Hall Co-efficient. 3.According to this theory, only two electrons are present in the Fermi level and they are responsible for conduction which is not true. |
| Fermi Level | The Fermi Level is the highest energy level which an electron can occupy at the absolute zero temperature. |
| Fermi energy | The Fermi energy is the energy of the highest level of quantum state which is occupied by the fermions (like electrons, protons or neutrons) at the absolute zero temperature. |
| Sources of electrical resistances | <ol style="list-style-type: none"> 1.Lattice vibration 2.Impurities 3.Structural imperfection |
| Energy band | Energy bands consisting of a large number of closely spaced energy levels exist |
| Energy Gap | <p>The gap between conduction band and valence band. It is denoted by E_g. Energy gap value is different for different solids.</p> <p>Energy gap in Metals-0 ev</p> <p>Energy gap in semiconductors $\approx 1\text{ev}$</p> <p>Energy gap in Insulators - $>5\text{ev}$</p> |

Concepts:

Quantum Mechanics:

Dual nature of matter (de-Broglie Hypothesis)

Light exhibits the phenomenon of interference, diffraction, photoelectric effect and Compton Effect. The phenomenon of interference, diffraction can only be explained with the concept that light travels in the form of waves. The phenomenon of photoelectric effect and Compton Effect can only be explained with the concept of *Quantum theory of light*. It means to say that light possess particle nature. Hence it is concluded that light exhibits dual nature namely wave nature as well as particle nature.

de-Broglie's Wavelength:

A particle of mass 'm' moving with velocity 'c' possess energy given by

$$E = mc^2 \quad \rightarrow \text{(Einstein's Equation) (1)}$$

According to Planck's quantum theory the energy of quantum of frequency

'v' is

$$E = hv \rightarrow (2)$$

From (1) & (2)

$$mc^2 = hv = hc / \lambda \text{ since } v = c/\lambda$$

$$\lambda = hc / mc^2 = h/mc$$

$$\lambda = h/mv \quad \text{since } v \approx c$$

Relation between de-Broglie wavelength and kinetic energy

Consider an electron in an electric potential V , the energy acquired is given by

$$E = eV = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Where 'm' is the mass, 'v' is the velocity and 'p' is the momentum of the particle. 'e' is charge of an electron.

$$p = \sqrt{2meV} = \sqrt{2mE}$$

The expression for de-Broglie wavelength is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2mE}}$$

de-Broglie Wavelength of an Accelerated Electron:

An electron accelerated with potential difference ' V ' has energy ' eV '. If 'm' is the mass and 'v' is the velocity of the electron.

$$\text{Then } eV = 1/2(mv^2) \rightarrow (1)$$

If 'p' is the momentum of the electron, then $p=mv$

Squaring on both sides, we have

$$p^2 = m^2v^2$$

$$mv^2 = p^2/m$$

Using in equation (1) we have

$$eV = p^2/(2m) \text{ or } p = \sqrt{(2meV)}$$

According to de-Broglie $\lambda = h/p$

$$\text{Therefore } \lambda = \left[\frac{h}{\sqrt{2meV}} \right] = \frac{1}{\sqrt{V}} \left[\frac{h}{\sqrt{2me}} \right]$$

$$\lambda = \frac{1}{\sqrt{V}} \left[\frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.11 \times 10^{-31} \times 1.602 \times 10^{-19}}} \right]$$

$$= \frac{1.226 \times 10^{-9}}{\sqrt{V}} \text{ m} \quad \text{or} \quad \lambda = \frac{1.226}{\sqrt{V}} \text{ nm}$$

Matter wave Properties:

1. Waves associated with moving particles are called matter waves. The wavelength ' λ ' of a de-Broglie wave associated with particle of mass 'm' moving with velocity 'v' is
$$\lambda = h/(mv)$$
2. Matter waves are not electromagnetic waves because the de Broglie wavelength is independent of charge of the moving particle.
3. The velocity of matter waves (v_p) is not constant. The wavelength is inversely proportional to the velocity of the moving particle.
4. Lighter the particle, longer will be the wavelength of the matter waves, velocity being constant.
5. For a particle at rest the wavelength associated with it becomes infinite. This shows that only moving particle produces the matter waves.

- 1) The time dependent Schrodinger equation: It takes care of both the position and time variations of the wave function. It involves imaginary quantity i .

The equation is:
$$-\frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} + V\psi = -\frac{ih}{2\pi} \frac{d\psi}{dt}$$

- 2) The time independent Schrodinger equation: It takes care of only position variation of the wave function.

The equation is:
$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

Time independent Schrodinger wave equation

Consider a particle of mass ‘m’ moving with velocity ‘v’. The de-Broglie wavelength ‘λ’ is

$$\lambda = \frac{h}{mv} = \frac{h}{P} \rightarrow (1)$$

Where ‘mv’ is the momentum of the particle.

The wave eqn is

$$\psi = A e^{i(kx - \omega t)} \rightarrow (2)$$

Where ‘A’ is a constant and ‘ω’ is the angular frequency of the wave.

Differentiating equation (2) with respect to ‘t’ twice

$$\frac{d^2\psi}{dt^2} = -A\omega^2 e^{i(kx-\omega t)} = -\omega^2 \psi \quad \rightarrow (3)$$

The equation of a travelling wave is

$$\frac{d^2y}{dx^2} = \frac{1}{v^2} \frac{d^2y}{dt^2}$$

Where 'y' is the displacement and 'v' is the velocity.

Similarly for the de-Broglie wave associated with the particle

$$\frac{d^2\psi}{dx^2} = \frac{1}{v^2} \frac{d^2\psi}{dt^2} \rightarrow (4)$$

where 'ψ' is the displacement at time 't'.

From eqns (3) & (4)

$$\frac{d^2\psi}{dx^2} = -\frac{\omega^2}{v^2} \psi$$

But $\omega = 2\pi v$ and $v = \lambda$ where 'v' is the frequency and 'λ' is the wavelength.

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \text{ or } \frac{1}{\lambda^2} = -\frac{1}{4\pi^2 \psi} \frac{d^2\psi}{dx^2} \rightarrow (5)$$

$$K.E = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{P^2}{2m} \rightarrow (6)$$

$$= \frac{h^2}{2m\lambda^2} \rightarrow (7)$$

Using eqn (5)

$$K.E = \frac{h^2}{2m} \left(-\frac{1}{4\pi^2 \psi} \right) \frac{d^2 \psi}{dx^2} = -\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2} \rightarrow (8)$$

Total Energy E = K.E + P.E

$$E = -\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2} + V$$

$$E - V = -\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2}$$

$$\frac{d^2 \psi}{dx^2} = -\frac{8\pi^2 m}{h^2} (E - V) \psi$$

$$\boxed{\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0}$$

This is the time independent Schrodinger wave equation.

Physical significance of ψ :

- The wave function ψ enables all possible information about the particle. ψ is a complex quantity and has no direct physical meaning. It is only a mathematical tool in order to represent the variable physical quantities in quantum mechanics.
- 2. Born suggested that, the value of wave function associated with a moving particle at the position co-ordinates (x,y,z) in space, and at the time instant 't' is related in finding the particle at certain location and certain period of time 't'.
- 3. If ψ represents the probability of finding the particle, then it can have two cases.
Case 1: certainty of its Presence: +ve probability
Case 2: certainty of its absence: - ve probability, but -ve probability is meaningless,
Hence the wave function ψ is complex number and is of the form $a+ib$
- 4. Even though ψ has no physical meaning, the square of its absolute magnitude $|\psi|^2$ gives a definite meaning and is obtained by multiplying the complex number with its complex conjugate then $|\psi|^2$ represents the probability density 'p' of locating the particle at a place at a given instant of time. And has real and positive solutions.

$$\psi(x,y,z,t)=a+ib$$

$$\psi^*(x,y,z,t)=a-ib \quad p = |\psi\psi^*| = |\psi|^2 = |a^2 + b^2| \text{ as } i^2 = -1$$

Where 'P' is called the probability density of the wave function

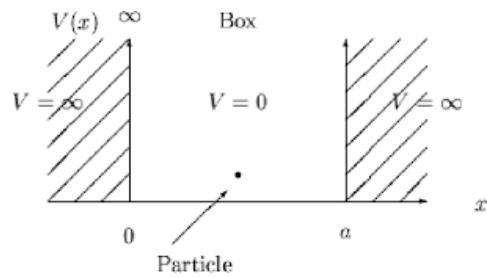
- 5. If the particle is moving in a volume 'V', then the probability of finding the particle in a volume element dv , surrounding the point x,y,z and at instant 't' is Pdv

$$\int |\psi|^2 dv = 1 \text{ if particle is present}$$

$$\int |\psi|^2 dv = 0 \text{ if particle does not exist}$$

This is called normalization condition

Particle in one dimensional Potential Box:



- The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely i.e when a particle bounces back and forth between the walls of a box.
- The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely i.e when a particle bounces back and forth between the walls of a box.
- The Schrodinger wave equation will be applied to study the motion of a particle in 1-D box to show how quantum numbers, discrete values of energy and zero point energy arise.
- From a wave point of view, a particle trapped in a box is like a standing wave in a string stretched between the box's walls.
- Consider a particle of mass 'm' moving freely along x- axis and is confined between x=0 and x=a by infinitely two hard walls, so that the particle has no chance of penetrating them and bouncing back and forth between the walls of a 1-D box.
- If the particle does not lose energy when it collides with such walls, then the total energy remains constant.
- This box can be represented by a potential well of width 'a', where V is uniform inside the box throughout the length 'a' i.e $V=0$ inside the box or convenience and with potential walls of infinite height at $x=0$ and $x=a$, so that the PE 'V' of a particle is infinitely high $V=\infty$ on both sides of the box.

The boundary condition are

$$v(x)=0, \psi(x)=1 \text{ when } 0 < x < a \dots \quad (1)$$

$$v(x)=\infty, \psi(x)=0 \text{ when } 0 \geq x \geq a \dots \quad (2)$$

Where $\psi(x)$ is the probability of finding the particle.

The Schrodinger wave equation for the particle in the potential well can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E \psi = 0, \text{ as } V = 0 \text{ for a free particle... (3)}$$

- In the simplest form eqn (3) can be written as

$$\frac{d^2\psi}{dx^2} + k^2 \psi = 0 \dots \text{(4)} \text{ Where } k = \text{propagation constant and is given by } k = \sqrt{\frac{8\pi^2 m E}{h^2}} \dots \text{(5)}$$

- The general solution of equation (4) is $\psi(x) = A \sin(kx) + B \cos(kx) \dots \text{(6)}$
- Where A and B are arbitrary constants, and the value of these constant can be obtained by applying the boundary conditions.
- Substitute eqn(1) in (6)

$$0 = A \sin(k(0)) + B \cos(k(0)) \rightarrow B=0 \text{ in eqn (6)}$$

$$\psi(x) = A \sin(kx) \dots \text{(7)}$$

Substituting eqn (2) in (7)

$$0 = A \sin(k(a))$$

$\rightarrow A = 0 \text{ or } \sin(ka) = 0$, But ' A ' $\neq 0$ as already $B=0$ & if $A=0$, there is no solution at all.

- Therefore $\sin(ka)=0$ (if $\sin\theta=0$, then general solution is $\theta=n\pi$), i.e $ka=n\pi$

$k = \frac{n\pi}{a} \dots \text{(8)}$, Where $n = 1, 2, 3, 4, \dots$ and $n \neq 0$, because if $n=0, k=0, E=0$ everywhere inside the box and the moving particle cannot have zero energy.

$$\text{From (8)} \quad k^2 = \left(\frac{n\pi}{a}\right)^2$$

$$\text{From (5)} \quad \frac{8\pi^2 m E}{h^2} = \frac{n^2 \pi^2}{a^2}$$

$$E = \frac{n^2 h^2}{8ma^2}$$

$$E_n = \frac{n^2 h^2}{8ma^2} = \text{the discrete energy level... (9)}$$

The lowest energy of a particle is given by putting $n=1$ in the eqn (9), $E_1 = \frac{h^2}{8ma^2} = \text{lowest energy, minimum energy, ground state energy or zero point energy of the system.}$

$$E_n = n^2 E_1$$

From eqn(10), $\int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1$

$$A^2 \int_0^a \frac{1}{2} \left[1 - \cos \frac{2n\pi x}{a} \right] dx = 1$$

$$\left(\frac{A}{2}\right)^2 \left[x - \frac{a}{2n\pi} \sin \frac{2n\pi x}{a} \right]_0^a = 1$$

The second term of the integrand expression becomes zero at both the limits.

$$\frac{A^2}{2} = 1$$

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

The normalized wave function is $\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$

The wave functions ψ_n corresponding to E_n are called Eigen functions of the particle, the integer 'n' corresponding to the energy E_n is called the quantum number of the energy level E_n .

Substituting (8) in (7), $\psi_n = A \sin \frac{n\pi x}{a} ..(10)$

Normalization of wave function: The wave functions for the motion of the particle are

$$\psi_n = A \sin \frac{n\pi x}{a}, \text{ for } 0 < x < a$$

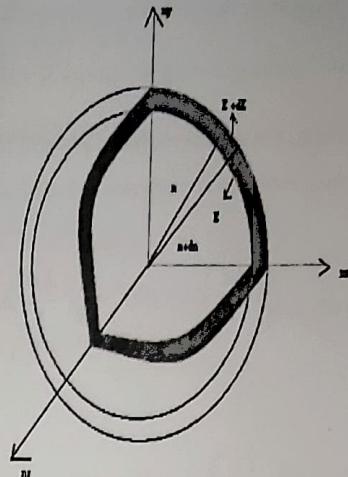
$$\psi_n = 0, \text{ for } 0 \geq x \geq a$$

According to normalization condition, the total probability that the particle is somewhere in the box must be unity.

$$\int_0^a p_x dx = \int_0^a |\psi_n|^2 dx = 1$$

Density of energy states.

Definition: It is defined as the number of available electron states per unit volume in an Energy interval E and $E + dE$. It is denoted by $Z(E)dE$.



Expression for density of energy states.

Let us consider a cubical sample with side 'a'. A sphere is constructed with three quantum numbers n_x, n_y, n_z as coordinate axes in three-dimensional space as shown.

A radius vector n is drawn from origin 'O' to a point with co-ordinates n_x, n_y, n_z in this space. All the points on the surface of that sphere will have the same energy E . Thus, $n^2 = n_x^2 + n_y^2 + n_z^2$ denotes the radius of the sphere with energy E . This sphere can be further divided into many shells. Each shell represents a particular combination of quantum numbers (n_x, n_y, n_z) . Therefore, it denotes a particular energy value with a particular radius. In this space, unit volume represents one energy state.

$$\text{Number of energy states within a sphere of radius } 'n' = \frac{4}{3}\pi n^3 \dots (1)$$

Since the quantum numbers n_x, n_y, n_z can have only positive integer values, we have to take

only one octant of the sphere, i.e., $\frac{1}{8}$ th of the spherical volume.

Therefore, the number of available energy states within one octant of the sphere of radius ' n '

corresponding to energy E is $= \frac{1}{8} \left[\frac{4}{3}\pi n^3 \right] \dots (2)$

Similarly, the number of available energy states within one octant of the sphere of radius 'n + dn' corresponding to energy E + dE

$$= \frac{1}{8} \left[\frac{4}{3} \pi (n + dn)^3 \right] \dots (3)$$

Now, the number of available energy states between the shell of radius n and n + dn i.e., between the energy values E and E + dE,

$$N(E) dE = \frac{1}{8} \left(\frac{4\pi}{3} \right) (n + dn)^3 - \frac{1}{8} \left(\frac{4\pi}{3} \right) n^3 = \frac{1}{8} \left(\frac{4\pi}{3} \right) [(n + dn)^3 - n^3]$$

$$N(E) dE = \left(\frac{\pi}{6} \right) [n^3 + dn^3 + 3n^2 dn + 3ndn^2 - n^3]$$

Since dn is very small, higher powers of dn terms dn^2 and dn^3 can be neglected.

$$N(E) dE = \frac{\pi}{6} 3n^2 dn = N(E) dE = \frac{\pi}{2} n^2 dn = N(E) dE = \frac{\pi}{2} n(ndn) \dots (4)$$

We know that the energy of an electron in a cubical metal piece of sides 'a' is given by

$$E = \frac{n^2 h^2}{8ma^2} \dots (5) \text{ or; } n^2 = \frac{8ma^2 E}{h^2} \dots (6) \text{ or; } n = \left[\frac{8ma^2 E}{h^2} \right]^{1/2} \dots (7)$$

Differentiating the equation (6), we get

$$2ndn = \frac{8ma^2 dE}{h^2} \text{ or; } ndn = \frac{8ma^2 dE}{h^2} \dots (8)$$

Substituting equations (7) and (8) in equation (4), we have

$$\begin{aligned} N(E) dE &= \frac{\pi}{2} \left(\frac{8ma^2 E}{h^2} \right)^{1/2} \left[\frac{8ma^2 dE}{2h^2} \right] = \frac{1}{2} \frac{\pi}{2} \left(\frac{8ma^2 E}{2h^2} \right)^{1/2} \left[\frac{8ma^2 dE}{h^2} \right] \\ &= \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{1/2} E^{1/2} \left(\frac{8ma^2}{h^2} \right) dE = N(E) dE = \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE \dots (10) \end{aligned}$$

Pauli's exclusion principle states that two electrons of opposite spins can occupy each state and hence the number of energy states available for electron occupancy is given by

$$\begin{aligned}
 N(E)dE &= 2 \times \frac{\pi}{4} \left[\frac{8ma^2}{h^2} \right]^{1/2} E^{1/2} dE = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{1/2} a^3 E^{1/2} dE \\
 &= \frac{\pi}{2} (8m)^{3/2} \left(\frac{a^3}{h^3} \right) E^{1/2} dE = N(E)dE = \frac{\pi}{2} \left(\frac{a}{h} \right)^3 (8m)^{3/2} E^{1/2} dE \\
 N(E)dE &= \frac{\pi}{2} \left(\frac{a}{h} \right)^3 8(2m)^{3/2} E^{1/2} dE = \frac{4\pi}{h^3} (2m)^{3/2} a^3 E^{1/2} dE
 \end{aligned}$$

Density of states is given by the number of energy states per unit volume,

$$Z(E)dE = \frac{N(E)dE}{V}$$

$$\text{i.e., Density of states } Z(E)dE = \frac{4\pi}{h^3} \frac{(2m)^{3/2} a^3 E^{1/2} dE}{a^3}; ; [\because \text{Volume } V = a^3]$$

$$Z(E)dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \dots \dots (11)$$

This is the expression for the density of charge carriers in the energy interval E and $E + dE$.