5/02/24

Unit:- 1 Electronic Materials:

Free Electron Theory

Step 1:- 1900 Drude and Lawrentz are study about the classical free electron theory.

- In which free electrons obey the law of classical mechanics.
- Good initiating, but can't explain all properties.

Step 2:-

- In 1928 sumer field explained the quantum free electron theory.
- Freee electrons obey the quantum mechanics.
- Explain all properties of metal but approximately

Step 3:-

- In 1928 Bloch explain the Zone theory or the band theory in solids.
- Free e⁻ obey the law of quantum mechanics
- Free $\bar{e}$ moving in a periodic potential field

Assumptions of classical free electron theory.

- Every material is composed with atoms
- when there is no potential across the ends of metals then
- Free electrons moves randomly so net current is zero.
- Since free e^- move randomly Just like gas molecules that why they are called as free e gas.
- Drude and Lorentz assumed that these free electron gas perform its randomly motion when potential across the end of the metal is zero
- Here on free E gas we can apply the kinetic gas theory as free e^-s perform like motion Just like a gas molecule inside a container. $K.E = \frac{3}{2}KT = \frac{1}{2}mv^2 = \frac{3}{2}KT$
- These free e^- collide with each other also collide with positive ion also with the wall of metal All the collisions are elastic in which there is no loss of energy.

Advantages

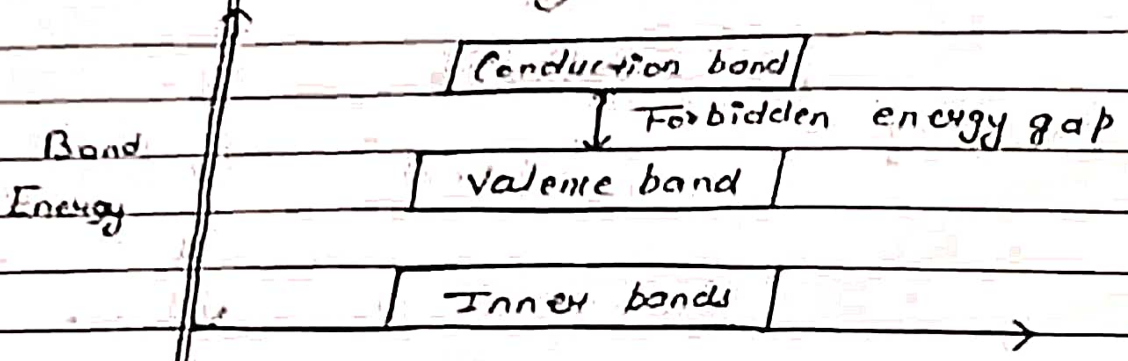
(1) Electrical conductivity or thermal conductivity of metal are explained.
(2) Verified ohm's law
(3) Optical properties of metal are explained.

Drawbacks

(1) Failed to explain specific heat capacity of metals.
(2) Superconductivity property of metal.
(3) Explained photoelectric effect.
(4) According to this theory conductivity directly proportional to resistivity which is wrong.
(5) Failed to explained ferromagnetism
(6) Determines greater values than experimental values.

Energy bands and diagram.

According to the theory of Bohr, each shell from an atom include a separate quantity of energy at diverse levels. This theory mainly gives details about the communication of es among the inside shell and outside shell. As to the theory of energy band, the energy bands are classified into three types which include the following.



Energy- band- theory

There are three types of band

- ### Valance band

The Flow of electrons within the atoms in fixed energy levels however the energy of electron in inner shell is superior to the outer shell of electrons. The electrons which are present within the outer shell are named as valence electrons.

These es include a sequences of energy levels which forman energy band named as valence band. This band include max occupied energy.

- ### Conduction band

The Valence es are attached loosely toward the nucleus at room temp. some of the electrons from valence electrons will leave the band freely. so these are called free eS because they flow toward the neighboring atoms. These free eS will conduct the flow of current within a conductor which is known as conduction electrons. The band which includes eS is named as conduction band and occupied energy of this will be the less.

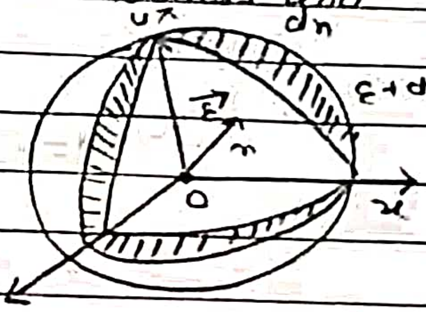
Forbidden gap

The forbidden gap is the gap b/w the conduction band and the valence band. This band is forbidden one without energy. Therefore there is no electron flow in this band. The flow of electron from the valence to conduction will pass through this gap. If this gap is greater, then the electrons in valence band are strongly bound toward the nucleus.

Based on the gap size, the semiconductors, conductors and Insulators are formed.

Density of Energy States

$$\frac{\text{No. of energy level (states)}}{\text{Volume}}$$



By the term density of available electron states $Z(E)$, we mean the total number of available electron states per unit energy range at E.

we know that the number of energy states with a particular value of E depends on how many combinations of quantum number result in the same value of n as $n^2 = n_x^2 + n_y^2 + n_z^2$.

we construct a space of points represented by the values of nx, ny and nz. Then each point with Integer values of co-ordinates represents an energy state.

All points of the sphere of radius n will have the same energy

The Volume of the sphere of radius n is given by

$$n = \left(\frac{4}{3}\pi n^3\right)$$

$$Z(E)dE = N(E)dE$$

$$(n^2 = nx^2 + ny^2 + nz^2)$$

$$n = \frac{4}{3}\pi n^3 \qquad (n = \text{radius})$$

$$V = \frac{4}{3}\pi n^3$$

$$n = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

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

$$Z(E)dE = \frac{1}{8_2}\left(\frac{4}{3}\pi(n+dn)^3 - \frac{1}{8_2}\left(\frac{4}{3}\pi n^3\right)\right.$$

$$= \frac{\pi}{6}\left((n^3 + dn^3 + 3n^2dn + 3n^2dn^2) - n^3\right.$$

$$Z(E)dE = \frac{\pi}{6}(dn^3 + 3n^2dn + 3ndn^2)$$

$$\approx \frac{\pi}{6}3n^2dn = \frac{\pi}{2}n^2dn \quad -(1)$$

$$E = \frac{1}{8}\frac{h^2}{mL^2}(nx^2 + ny^2 + nz^2)$$

$$E = \frac{h^2n^2}{8mL^2} \Rightarrow n^2 = \frac{8mL^2}{h^2} \times E \quad - ②$$

$$n = \left(\frac{8mL^2}{h^2}\right)^{1/2} (E)^{1/2} \quad \text{— (3)}$$

diff. eq^n (3)

$$2n\,dn = \left(\frac{8mL^2}{h^2}\right) dE$$

$$dn = \frac{1}{2n}\left(\frac{8mL^2}{h^2}\right) dE \quad \text{— ④}$$

$$Z(E)\,dE = n\,\frac{\pi}{2}\,(n\,dn)$$

$$= \frac{\pi}{2}\left(\frac{8mL^2}{h^2}\right)^{1/2}.(E)^{1/2}\left(n.\frac{1}{2n}\left(\frac{8mL^2}{h^2}\right) dE\right)$$

$$= Z(E)\,dE = \frac{\pi}{4}\left(\frac{8mL^2}{h^2}\right)^{3/2} E^{1/2}\,dE$$

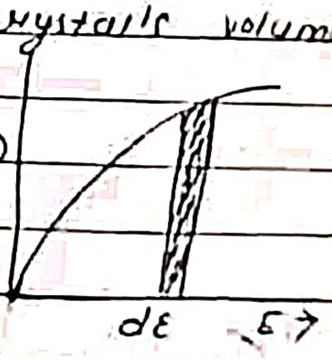
Acc. to pauli exclusion principle

$$Z(E)\,dE = 2\times\frac{\pi}{4_2}\left(\frac{8mL^2}{h^2}\right)^{3/2}(E)^{1/2}\,dE$$

$$\boxed{Z(E)\,dE = \frac{\pi}{2}\left(\frac{8mL^2}{h^2}\right)^{3/2}(E)^{1/2}\,dE}$$

This expression show that Z(E) is parabolic function of energy E is shown. Z(E) inc with inc. in crystal's volume

The number of energy states present Z(E) in unit volume having energy values lying b/w E and E+dE) can be obtained by putting $V = L^3 = 1$

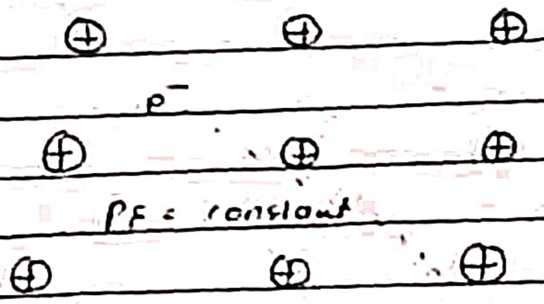


Density of es state versus energy

$$Z(E)\,dE = \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{3/2} E^{1/2}\,dE$$

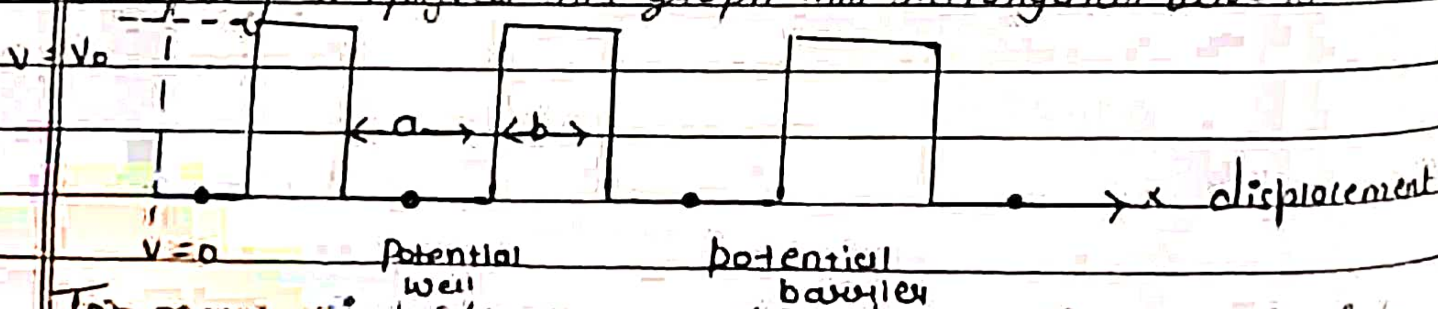
KRONIG- PENNEY MODEL

Let us consider a crystal. suppose, PE = constant
Here PE is change periodically

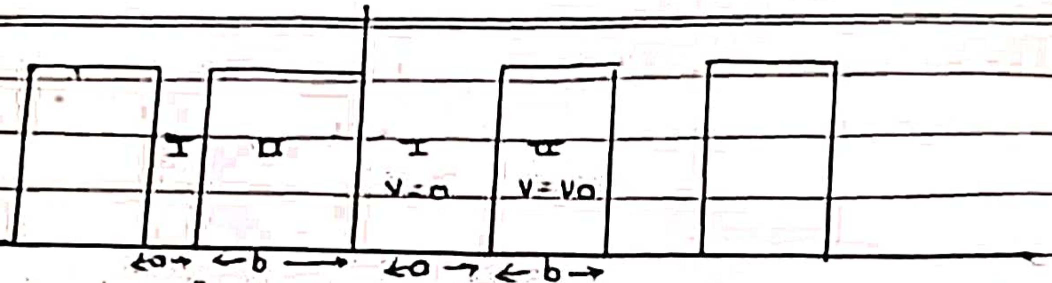


In Kronig - penny model, potential of e^- varies periodically and PE of e^- is zero near nucleus and max. (V_0) b/w two nuclei which are separated by interatomic spacing a

with the help of this graph, the study of motion of e^- or periodic potential is a difficult so for simplification Kroning and penny simplified this graph into rectangular wave form



For more simplification we can change this graph into this/that form.



This graph gives two reasons (1) Region (1) $0<x<a$ $\boxed{V=0}$
(2) Region (2) $-b<x<0$ $\boxed{V=V_0}$

Acc to Schrodinger wave eqn

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m(E-V)\psi}{h^2} = 0$$

ψ = wave function
x = displacement of e^-
m = mass of charge e^-

$\hbar$ - plank's constant
E : Energy / electric field of crystal
V : potential.

Region - (I)

$(0<x<a)$ $V=0$ (potential well)

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2mE}{h^2}\psi = 0 \quad -(1)$$

Region - (II)

$(-b<x<0)$ $V=V_0$ (potential barrier)

$$\frac{\partial^2\psi}{dx^2} + 2m(E-V_0)\psi = 0 \quad -(2)$$

Let us consider $\frac{2mE}{h^2} = \alpha^2$

and $2m\frac{(V_0 - E)}{h^2} = \beta^2$

So, eqn (1) and (2) becomes

$$\frac{\partial^2\psi}{dx^2} + \alpha^2\psi - \quad (3)$$

$$\frac{\partial^2\psi}{\partial x^2} - \beta^2\psi = 0 \quad -(4)$$

Now general eqn of this sol (3) and (4) is

$$\psi = e^{ikx} u(x) \quad -(5)$$

Now diff. eq(5) twicely w.r.t. x

$$\frac{d\psi}{dx} = e^{ik} \frac{d\,u(x)}{dx} + u(x)\, ik\, e^{ikx} \quad -(6)$$

$$\frac{d^2\psi}{dx^2} = e^{ikx} \frac{d^2u}{dx^2} + \frac{du}{dx}\, ik e^{ikx} + ux\, ik \cdot ik\, e^{ikx} + ik e^{ikx} \frac{du}{dx}$$

$$\frac{d^2\psi}{dx^2} = e^{ikx} \frac{d^2u}{dx^2} + \frac{du}{dx}\, ik e^{ikx} - ux k^2 e^{ikx} + ik e^{ikx} \frac{du}{dx} \quad -(7)$$

$(i^2 = -1)$

Put eqn (7) in (3) and (4),

$$e^{ikx} \frac{d^2u}{dx^2} + \frac{du}{dx}\, ik e^{ikx} - u(x) k^2 e^{ikx} + ik e^{ikx} \frac{du}{dx} + \alpha^2 e^{ikx} u(x) = 0$$

Then, divide above eqn by e^{ikx}

$$\frac{d^2u}{dx^2} + ik \frac{du}{dx} - k^2 u(x) + ik \frac{du}{dx} + \alpha^2 (x) u = 0$$

$$\frac{d^2u}{dx^2} + 2ik \frac{du}{dx} + (\alpha^2 - k^2)(kx) = 0 \quad - ⑧$$

Similarly

Put eqn (7) in eqn (4),

$$\frac{d^2u}{dx^2} + 2ik \frac{du}{dx} - (\beta^2 + k^2)\, u(x) = 0 \quad - ⑨$$

By Solving eqⁿ (8) and eqⁿ (9) with help of matrix method-

we get, $P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$

Above eqⁿ is called Kronig Pening eqⁿ for 1-D motion of an e⁻ above eqⁿ, we will apply for 2 cases and will find energy of electron.

Case I- $P \to 0$ (Potential well)

Case II- $P \to \infty$ (Potential barrier)

Case I - $P \to 0$

$$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$$

$$\cos\alpha a = \cos ka$$

$$\alpha a = ka$$

$$\alpha = k$$

$$\frac{2mE}{\hbar^2} = \frac{4\pi^2}{\lambda^2}$$

$$E = \frac{2\pi^2}{\lambda^2} \times \frac{\hbar^2}{m} \qquad \hbar = \frac{h}{2\pi}$$

$$E = \frac{2\pi^2}{\lambda^2} \times \frac{h^2}{4\pi^2 m} \qquad \hbar = \frac{h^2}{4\pi^2} \qquad \lambda = \frac{h}{mv}$$

$$E = \frac{h^2}{2\lambda^2 m}$$

$$E = \frac{h^2}{2} \cdot \frac{m^2v^2}{h^2\, m}$$

$$E = \frac{m^2v^2}{2m}$$

$$\boxed{p = mv}$$

Case II - $P \to \infty$

$$P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

$$\sin \alpha a = \frac{\cos ka - \cos \alpha a}{P}$$

$$\sin \alpha a = 0 \Rightarrow \alpha a \Rightarrow \sin^{-1}(0)$$

$$\alpha a = 0, \pi, 2\pi, 3\pi$$

$$\alpha a = n\pi \quad (n = 0, 1, 2, 3, 4 \ldots)$$

$$\alpha = \frac{n\pi}{a}$$

$$\alpha^2 = \frac{n^2\pi^2}{a^2} \Rightarrow \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{a^2}$$

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2\pi^2}{2ma^2} \times \frac{h^2}{4\pi^2}$$

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

Energy for potential (∞)

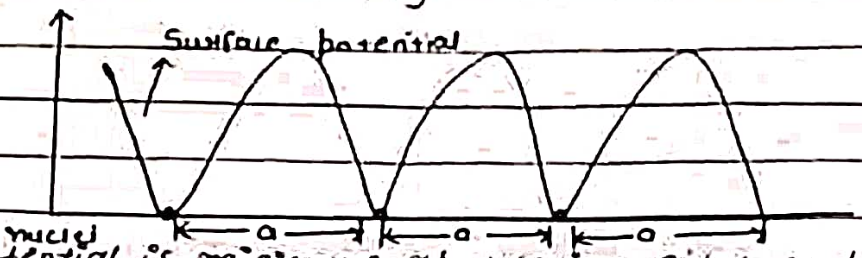
Application

- Case I - used in finding E-K curve
- case II - used in density of state.

Question:- Explain Bloch theorem or electron in periodic potential

A crystalline solid consists of a lattice, which is composed of a large no of ion cores at regular intervals and conduction electron that can move freely throughout the lattice. The

The conduction e^- move inside periodic positive ion cores. Hence, instead of considering uniform constant potential as we have done in e^- theory, we have to consider variation of potential inside metallic crystal with periodicity of lattice as shown in fig.



The potential is minimum at +ve ion sites and max b/w two ions. The one-dimensional Schrodinger eqn corresponding to this can be written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \quad \text{where } \hbar = h/2\pi$$

$$\frac{d^2\psi}{dx^2} + \frac{8m\pi^2}{h^2}(E-V(x))\psi = 0 \quad -(1)$$

The periodic potential V(x) may be defined by means of lattice constant 'a' as

$$V(x) = V(x+a) \quad - (2)$$

Bloch has shown that one dimensional solution of Schrodinger eqn is of the form

$$\psi(x) = e^{ikx}.\, U_k(x) \quad - (3)$$

In above eqn $U_k(x)$ is called "modulating function", because free e^- wave is modulated by $U_k(x)$ is periodic with periodicity of crystal lattice. Let us now consider a linear chain of atoms of length L in 1D case with "N" number of atoms in the chain. Then,

$$U_k(x) = U_k(x+Na) \quad - (4)$$

where 'a' is a lattice distance.

From eqn (3) and (4)

$$\psi(x+Na) = e^{ik(x+Na)}.\, U_k(x+Na)$$

$$= e^{ikNa}.\, U_k(x)\, e^{ikx}$$

$$\psi(x+Na) = \psi(x).\, e^{ikNa} \quad - (5)$$

This is referred to as bloch condition. Similarly, complex conjugate of eqn (5) can be written as

$$\psi^*(x+Na) = \psi^*(x)\, e^{-ikNa} \quad -(6)$$

From eqn (5) and eqn (6),

$$\psi(x+Na)\cdot\psi^*(x+Na) = \psi(x)\cdot\psi^*(x)$$

$$|\psi(x+Na)|^2 = |\psi(x)|^2 \quad -(7)$$

→ This means that electron is not localised around one particular atom and the prob. of finding e^- is same throughout crystal.

Hence in eq(5),

$$e^{ikNa} = 1$$

$kNa = 2\pi n$, where n is an integer

$k = (2\pi n)/Na$

$k = (2\pi n)/L$

where L is length of chain of atoms.

and $n = \pm 1, \pm 2, \pm 3, \pm 4 \ldots$

when $n = N/2$, we have $k = \pi/a$

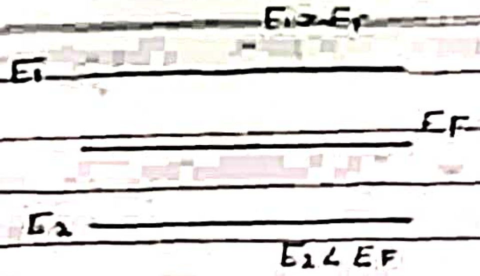
This is edge of First Brillouin zone.

✱ Fermi Function

When energy level are occupied by electrons in material This called as distribution of electron

Fermi function is that the energy level which has 50% probability of occupation of electrons at absolute 0K temperature.

$$F(E) = \frac{1}{1+e^{(E-E_F)/kT}}$$



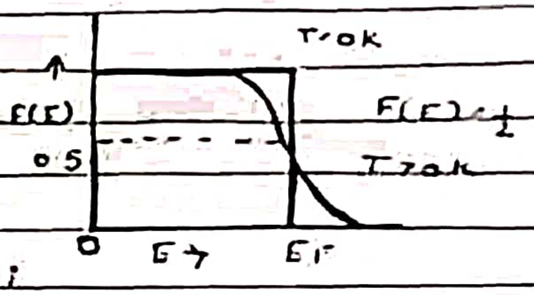
(1) Prob. of occupation

for $E_1 > E_F$ at $T = 0K$

$$F(E_1) = \frac{1}{1+e^{(E_1-E_F)/kT}}$$

$$= \frac{1}{1+e^{+ve/k(0)}} = \frac{1}{1+e^{\infty}} = \frac{1}{1+\infty} = \frac{1}{\infty}$$

$$= 0$$



at T = 0, all energy levell above fermi level are unoccupied.

(2) Prob. of occupation

$E_2 < E_F$

$$F(E_2) = \frac{1}{1+e^{(E_2-E_F)/kT}} = \frac{1}{1+e^{-ive/k(0)}} = \frac{1}{1+e^{\infty}} = \frac{1}{1+\frac{1}{e^{\infty}}}$$

$$= \frac{1}{1+0} = \frac{1}{1} = 100\%$$

Here F(E) = 1 means that energy levels are certainly occupied. Therefore, all energy level below are occupied.

(3) Prob. of occup. at ordinary temp.

E_F

$$F(E_F) = \frac{1}{1+e^{(E_F-E_F)/kT}} = \frac{1}{1+e^{0/k(0)}}$$

$$= \frac{1}{1+1} = \frac{1}{2} = 0.5 \Rightarrow 50\%$$

it is level of maximum energy of filled state at 0K.

Ek diagram :-

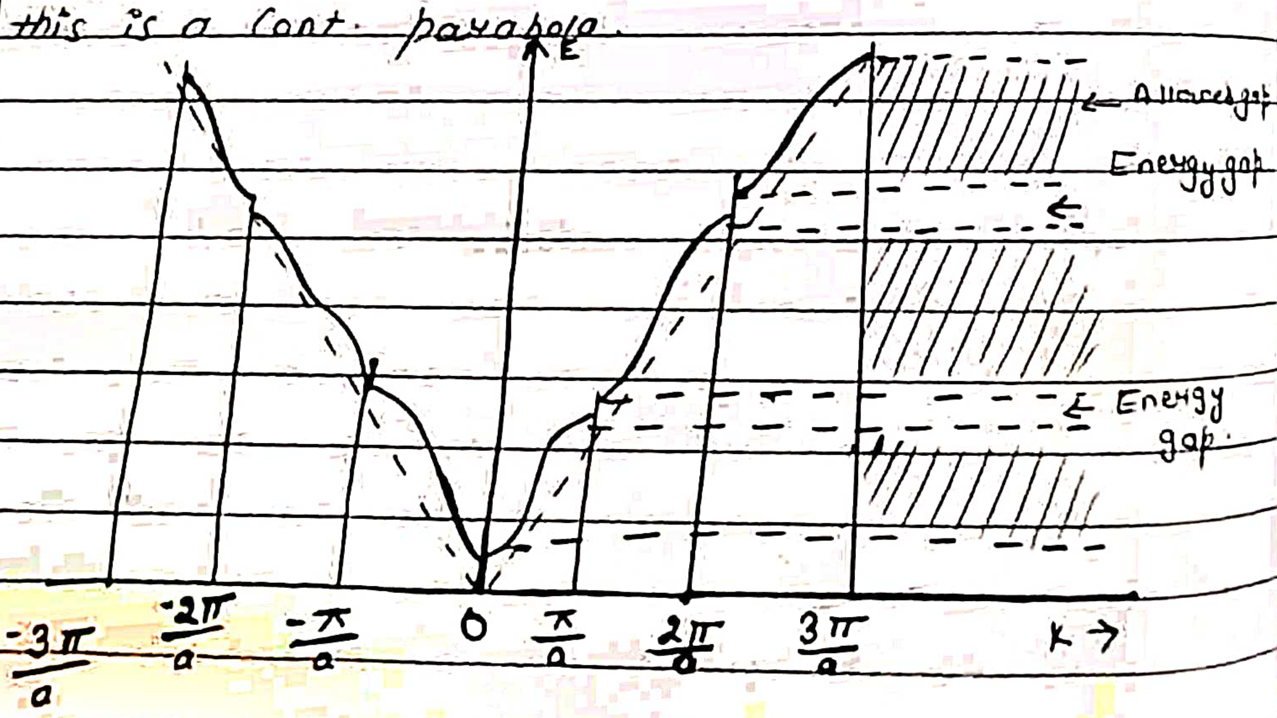
- In kronig-penney model an equation was obtained for energy eigen values of an electron moving in a peri potential. It was observed that electrons have energy values only b/w allowed energy band. The allowed energy ban are separated by forbidden energy bands. The allowed energy values arise at point $\alpha a = \pm n\pi (n \neq 0)$

- The allowed eigen values are

$$E = \frac{\hbar^2 k^2}{2m} \quad -(1)$$

where k is wave number, $k + (n\pi/a)$
n takes the values $n = \pm 1, \pm 2, \pm 3 \ldots\ldots$
a = atomic periodicity.

$Eq^n(1)$ gives the E-k curve. It is clear that E-k curve is a parabola. Due to discontinuities in the energy values the parabola is discont. while in case of free e^-, this is a cont. parabola.



* E-k Curve for an electron in periodic potential

At $K = \pm\frac{\pi}{a}$, E has two values The lower belonging to region $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ and higher b/w $\frac{\pi}{a}$ to $\frac{2\pi}{a}$ (or $-\frac{\pi}{a}$ to $-\frac{2\pi}{a}$) There is a definite gap in energy at the boundary of these two regions similarly. the gaps exists for higher k values These discon in energy.

Follow from the fact that k values, the electronic waves are Bragg reflected (acc. to formula $2a\sin\theta = n\lambda$) back and forth.

Therefore, instead of a travelling wave, a standing wave solution exists.

Effective mass :-

An electron has a well-defined mass m when it is placed in an external field. it obeys Newtonian mechanics The acceleration is given by $\alpha = \frac{\text{Force}}{\text{Mass}} = \frac{e\xi}{m}$ (ξ = Electric Field)

The electron in crystal interacts with crystal lattice As result its behaviour toward external forces is diff. from that of free electrons.

The deviation in the behaviour of electron in crystal lattice from the free e⁻ behaviour can be taken into account simply by considering the electron to have an effective mass m* rather than the free mass m. m* depend on the nature of crystal lattice

13/02/24

* Effective mass

- The mass exhibited by an electron when inside the semiconductor.
- Electron moving in the semiconductor is moving under the influence of atom and other electron due to that the is an electrostatic field at one e^- known as crystal field this is called internal electric field.

- on applying an external electric field as shown in the fig.

- F = force of external + force of internal field is the total force of an electron.

- If we define the mass of an electron as effective mass then the e^- can be treated as free electron it is represented by (M^*)

- So you need not to consider the internal electric field

- when effective mass is smaller than electron mobility is higher.
- when effective mass is higher than holes mobility is smaller

$M_e^* < M_h^*$

$\mu_e > \mu_h$

- We know that de-broglie eqn explain when electron moves than a group of wave associate with it now group velocity

$$V_g = \frac{d\omega}{dk} \quad -①$$

we know that $E = h\nu \Rightarrow \frac{h\omega}{2\pi} = \hbar\omega$ - ②

$\left[\because \nu = \frac{\omega}{2\pi}\right]$

From eqn (2)

$$\omega = \frac{E}{\hbar}$$

on putting this in eqn (1)

$$V_g = \frac{1}{\hbar}\frac{dE}{dk}$$

on diff. with respect to t

$$a = \frac{dV_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} \quad -(3)$$

we know that,

by de-broglie-

$$p = \frac{h}{\lambda} \times \frac{2\pi}{2\pi} = \hbar k.$$

Force acting on $\bar{e}$,

$$F = \frac{dp}{dt} = \hbar\frac{dk}{dt} \quad -(4)$$

Now we know that

$$F = m^* a \Rightarrow m^* = \frac{F}{a}$$

on putting the value of eqn (3) and (4)

$$m^* = \frac{F}{a}$$

$$= \frac{\hbar\frac{dk}{dt}}{\frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}} = \frac{\hbar^2 dk^2}{d^2E}$$

$$\boxed{m^* = \frac{\hbar^2 dk^2}{d^2E}}$$

* Phonons :-

- Phonons are partial representation of vibration in a crystal.
- It is called a vibration of the atomic lattice
- In normal condition, atoms vibrates as a result of their thermal energy.
- The higher the thermal energy the greater is the vibrational energy.
- In a solid lattice, individual vibration is not possible, vibration passes from atom to atom
- Such vibration pass through the whole lattice, which can vibrate as a wave at a single frequency. when this happen vibration is called as phonons.
- This single frequency wave has fixed energy and momentum and known as packets of mechanical vibrations energy just as photons is known a packets of EMW energy.
- Phonons can lost / loss or accept the energy according to planck's relation. $\Delta E = \frac{h}{F}$.
- phonons can carry heat and sound through the solids and liquids. • It play an imp. role in determing heat capacity of solids and liquids.