



Phys 570

Theory of Solids

Physics & Astronomy Dept.
College of Science
King Saud University

Lecture #1

Nasser S. Alzayed

nalzayed@ksu.edu.sa

Chapter 6: Free Electron Fermi Gas

Introduction

We can understand many physical properties of metals, and not only of the simple metals, in terms of the free electron model. **According** to this model, the valence electrons of the constituent atoms become conduction electrons and move about freely through the volume of the metal. The utility of the free electron model is greatest for properties that depend essentially on the kinetic properties of the conduction electrons.

The interpretation of metallic properties in terms of the motion of free electrons was developed long before the invention of quantum mechanics. **The classical theory** had several conspicuous successes, notably the derivation of the form of Ohm's law and the relation between the electrical and thermal conductivity.

The classical theory fails to explain the heat capacity and the magnetic susceptibility of the conduction electrons.

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Classical Vs. Quantum Mech. model

- **Classical Model:**

- Metal is an array of positive ions with electrons that are free to move through the ionic array
 - Electrons are treated as an ideal neutral gas, and their total energy depends on the temperature and applied field
 - In the absence of an electrical field, electrons move with randomly distributed thermal velocities
 - When an electric field is applied, electrons acquire a net drift velocity in the direction opposite to the field

- **Quantum Mech. Model:**

- Electrons are in a potential well with infinite barriers: They do not leave metal, but free to move inside
 - Electron energy levels are discrete (quantized) and well defined, so average energy of electron is not equal to $(3/2)k_B T$
 - Electrons occupy energy levels according to Pauli's exclusion principle
 - Electrons acquire additional energy when electric field is applied

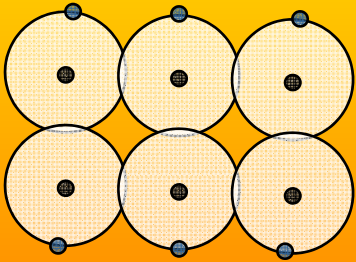
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The model in Brief

- This model explains lots of properties in metals.
 - It assumes free electrons in the so called conduction band:
 - Example: Na^{11} : We have 11 electrons distributed as follows:
 - $1s^2 2s^2 2p^6 3s^1$ ← Valance electron (loosely bound)
 - Hence, there is a free electron/atom in the 3S state
 - Or we have one electron/atom in the 3S conduction Band.
 - For a crystal of N atoms: we have N conduction electrons and N +tive Ions.
-
- Classical Theory fails to explain for C_v (heat capacity) and χ_p (magnetic Suc.) for the full range of Temperature.
 - What is Fermi Gas? : It is a collection of large No. of electrons that are free to move but subject to Pauli Exclusion Principle

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Conduction electrons in Sodium



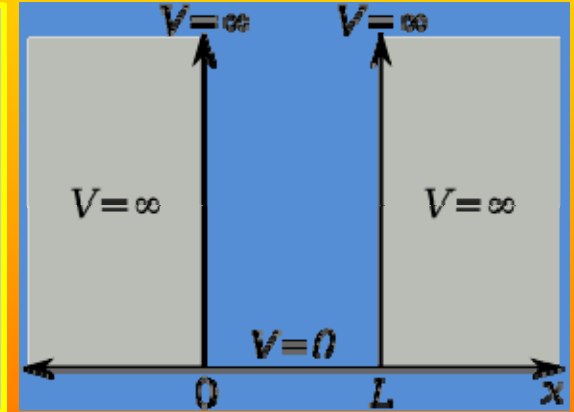
Na atoms in ***Na*** crystal overlap slightly. This leads to the fact that a valance electron is not attached to a particular ion, but belongs to all neighbouring ions at the same time.

- Accordingly; electrons can virtually move freely all over the crystal leading to conduction of electricity.

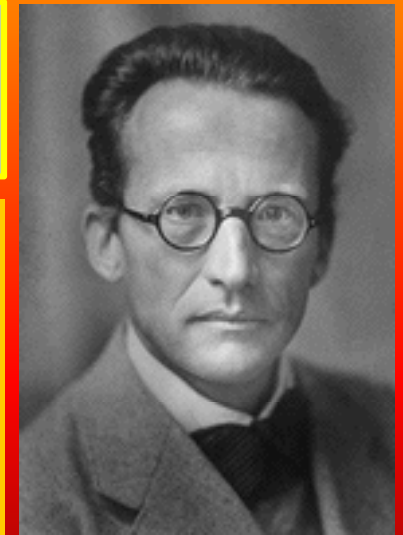
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Energy Levels in 1-D

- Consider a free electron gas in one dimension, taking account of quantum theory and of the Pauli principle. An electron of mass m is confined to a length L by infinite barriers.



- We will have to use Schrödinger Wave Equation to solve the problem and find out energy levels.



E. Schrödinger
(1887-1961)

$$H \psi_n = \varepsilon_n \psi_n$$

$$\text{with : } H = \frac{p^2}{2m} \quad \text{where : } p = -i \hbar \frac{d}{dx}$$

$$\therefore H \psi_n = -\frac{\hbar^2}{2m} \frac{d^2 \psi_n}{dx^2} = \varepsilon_n \psi_n \quad (1)$$

ε_n is the energy of the electron in the n th. state (orbit).

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Energy Levels in 1-D

- Applying Boundary Conditions for the wave function:

$$\left. \begin{aligned} \psi_n(0) &= 0 \\ \psi_n(L) &= 0 \end{aligned} \right\} \psi \text{ at borders} = 0$$

$$\left. \begin{aligned} \psi_n &= A \sin\left(\frac{2\pi}{\lambda_n} x\right) \\ \text{or } \psi_n &= A \sin\left(\frac{n\pi}{L} x\right) \end{aligned} \right\} \text{satisfies the wave function at boundary} \quad (2)$$

$$\Rightarrow \frac{d\psi_n}{dx} = A \frac{n\pi}{L} \cos\left(\frac{n\pi}{L} x\right) \text{ and } \Rightarrow \frac{d^2\psi_n}{dx^2} = -A \left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi}{L} x\right)$$

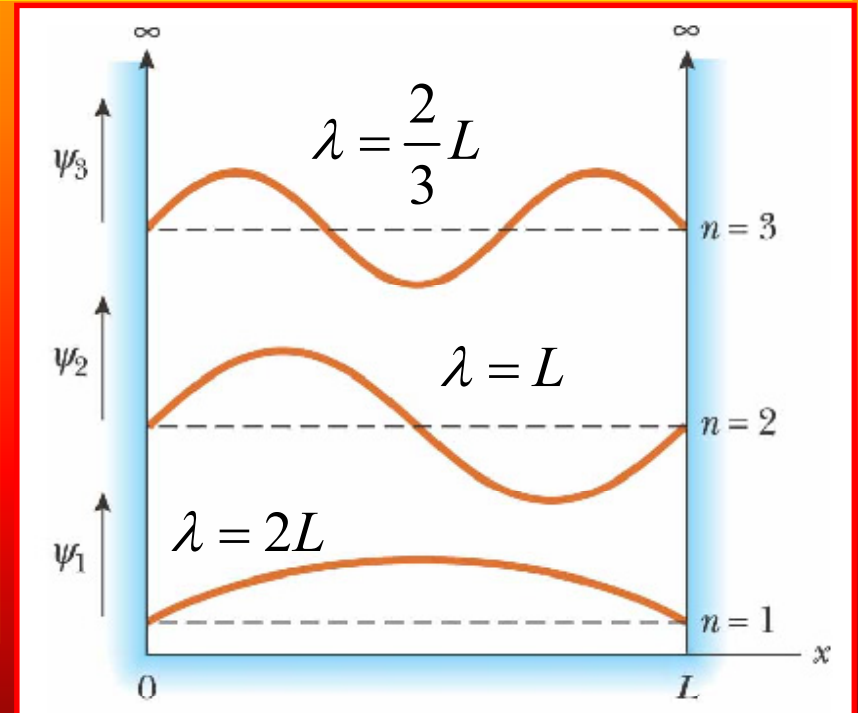
$$\therefore -\frac{\hbar^2}{2m} (-A) \left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi}{L} x\right) = \varepsilon_n A \sin\left(\frac{n\pi}{L} x\right)$$

$$\therefore \varepsilon_n = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{L^2} \quad (3)$$

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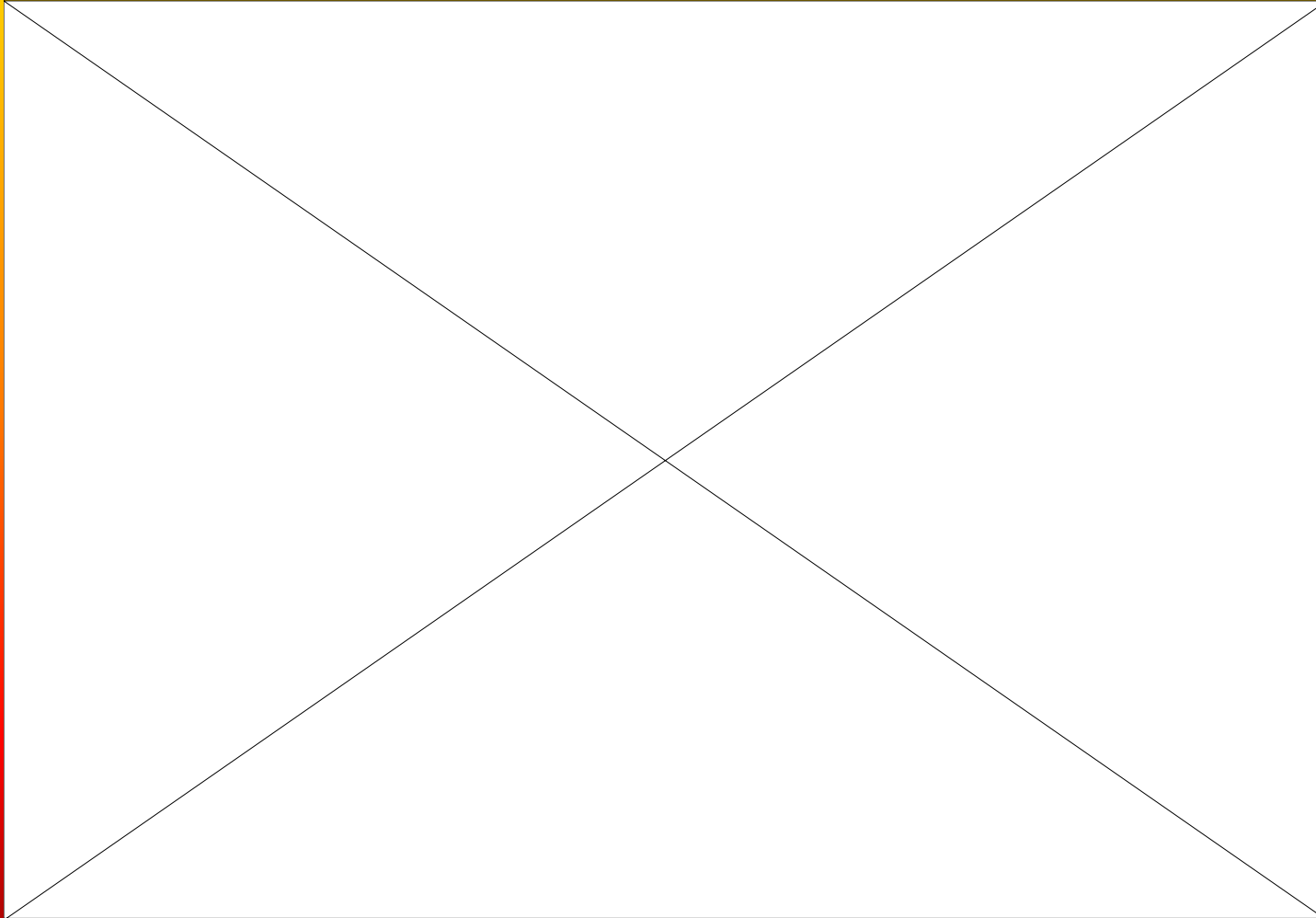
Energy Levels in 1-D

- Every state (n) can have two electrons; one at $m_s=+\frac{1}{2}$ and one at: $m_s=-\frac{1}{2}$.
- If state n has energy ε_n and a state m also has energy ε_n : We call this degeneracy.
- When we have many electrons, the energy levels are filled from the bottom to the top. The last filled level is the Fermi level and is denoted as: n_F
- Right: 1-D potential well. Energy of electron is shown for lowest 3 states ($n=1,2$, and 3)



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Energy Levels in 1-D



[Ref. Introductory Quantum Mechanics](#)

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Fermi Surface and Fermi Energy levels

- We can easily calculate the location of Fermi Level n_F for N-electron system (even No.): $2n_F = N$
- $\rightarrow n_F = N/2$
- Example: $N = 6$ electrons:
- $n = 1$ has 2 electrons
- $n = 2$ has 2 electrons
- $n = 3$ has 2 electrons (n_F)
- -----
- Total: 6 electrons $\rightarrow n_F = 6/2 = 3$

let ε_F = Fermi Energy

ε_F is the energy of the n_F level. in Ground State for N electrons:

$$(3) \Rightarrow \varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{n_F \pi}{L} \right)^2 = \frac{\hbar^2}{2m} \left(\frac{N \pi}{2L} \right)^2 \quad (4)$$

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Lecture #2



Lecture #2

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nalzayed@ksu.edu.sa

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EFFECT OF TEMPERATURE ON THE FERMI-DIRAC DISTRIBUTION

- *The ground state is the state of the N electron system at absolute zero.* What happens as the temperature is increased? The solution is given by the Fermi-Dirac distribution function.
- The kinetic energy of the electron gas increases as the temperature is increased: some energy levels are occupied which were vacant at absolute zero, and some levels are vacant which were occupied at absolute zero. The **Fermi-Dirac distribution gives the probability that an orbital at energy ϵ will be occupied in an ideal electron gas in thermal equilibrium.**

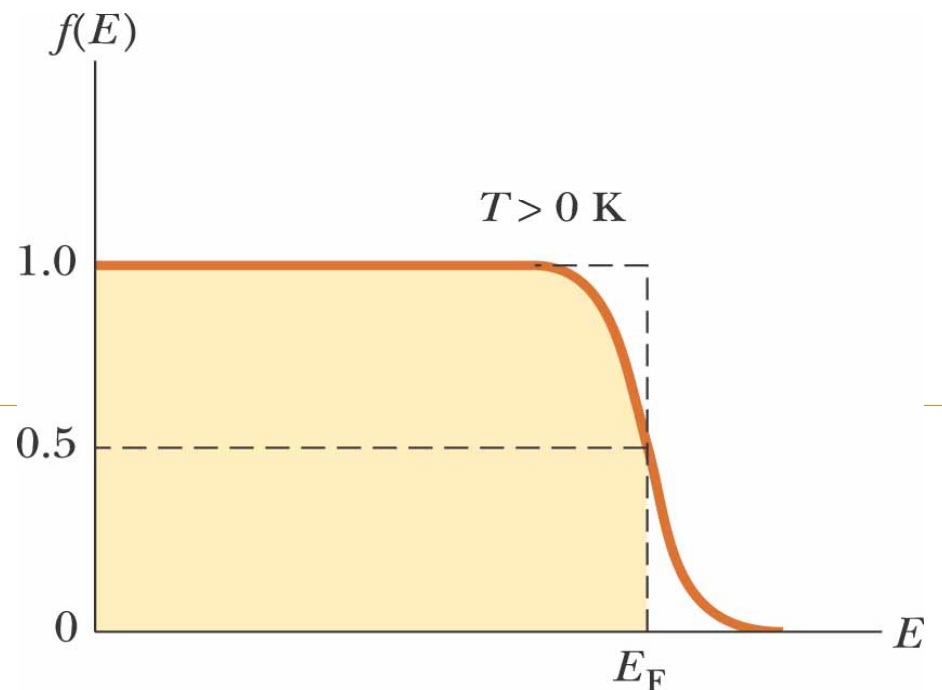
$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} \quad (5)$$

μ is a function of the temperature; it is to be chosen in such a way that the total number of particles = N . *At absolute zero $\mu = \epsilon_F$*

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EFFECT OF TEMPERATURE ON THE FERMI-DIRAC DISTRIBUTION

because in the limit $T \rightarrow 0$ the function $f(\epsilon)$ changes discontinuously from the value 1 (filled) to the value 0 (empty) at $\epsilon = \epsilon_F = \mu$. At all temperatures $f(\epsilon)$ is equal to $\frac{1}{2}$ when $\epsilon = \mu$, for then the denominator of (5) has the value 2.



$f(\epsilon) = 1$ (means full)

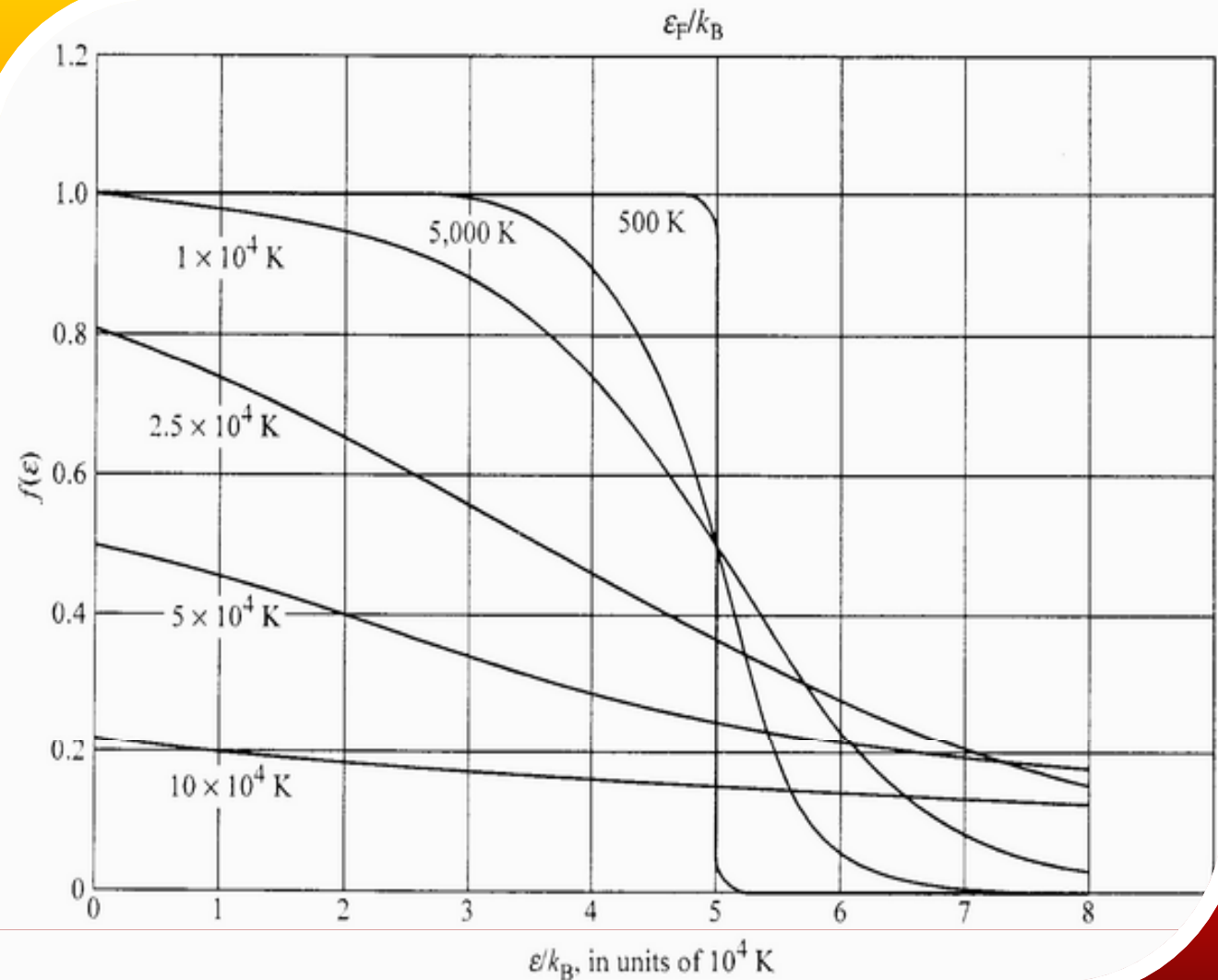
$f(\epsilon) = 0$ (means vacant)

At very low temp. $f(\epsilon)$ becomes similar to Boltzmann or Maxwell Distribution.

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EFFECT OF TEMPERATURE ON THE FERMI-DIRAC DISTRIBUTION

$f(\epsilon)$ at the various temperatures, for $T_\epsilon = \epsilon_F/k_B T = 50,000$ K. The total number of particles is constant, independent of temperature.

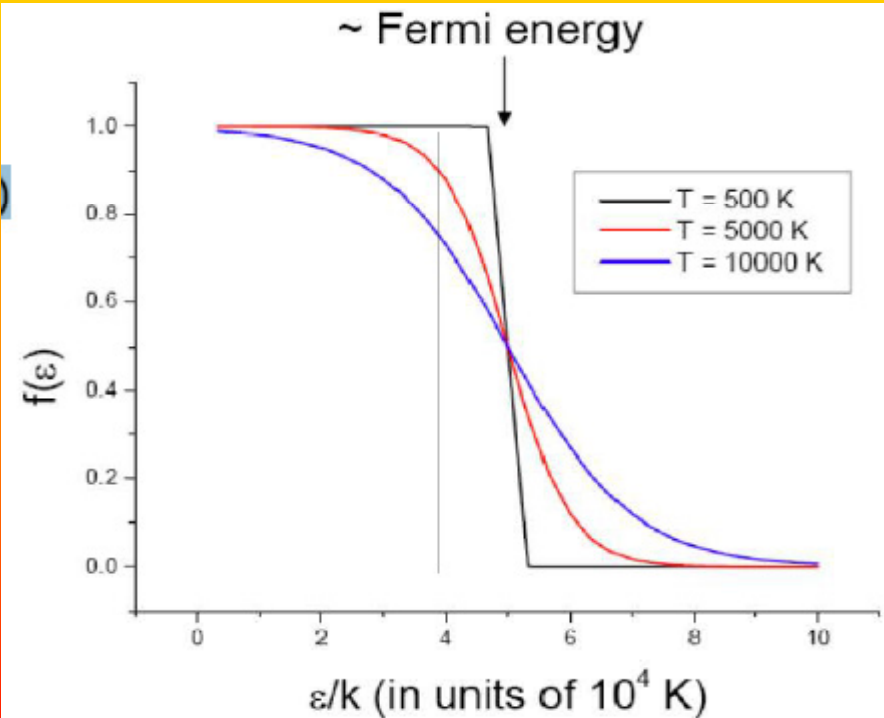


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FERMI-DIRAC DISTRIBUTION

This is what the $f(\epsilon)$ looks like at different Temperatures

- As $T \rightarrow 0$ K, it becomes a step function
- Note that the lower energy levels are usually filled first, and as temperature increases; no of electrons at higher energy levels increases.



Fermi energy changes as the temperature changes because it is defined as: $\mu = F_{n+1} - F_n$ (n = no. of particles, electrons)

Where F is the Helmholtz Free Energy: $F = U - TS$

U : System energy, S : Entropy (Increases as T increase)

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Different DISTRIBUTION Systems

Distribution System	Notes	
Maxwell-Boltzmann distribution	<ul style="list-style-type: none"> •identical particles •distinguishable •wave function : not overlap 	$f(\varepsilon) = Ae^{-\varepsilon/k_B T}$
Bose-Einstein distribution	<ul style="list-style-type: none"> •Identical particles •indistinguishable •wave function : overlap •spin quantum number = 0,1,2, ... 	$f(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/k_B T} - 1}$
Fermi-Dirac distribution	<ul style="list-style-type: none"> •Identical particles •indistinguishable •wave function: overlap •spin quantum number = 1/2,3/2,5/2 	$f(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/k_B T} + 1}$

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FREE ELECTRON GAS IN THREE DIMENSIONS

We just need to extend our results for 1-D.

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{dx^2} + \frac{\partial^2}{dy^2} + \frac{\partial^2}{dz^2} \right) \psi_k(r) = \varepsilon_k \psi_k(r) \quad (6)$$

for a cube of length L we have:

$$\psi_n(r) = A \sin\left(\frac{\pi n_x x}{L}\right) \sin\left(\frac{\pi n_y y}{L}\right) \sin\left(\frac{\pi n_z z}{L}\right) \quad (7)$$

n_x, n_y, n_z are all positive integers.

ψ is periodic in x, y, z with period L. Thus:

$$\psi(x + L, y, z) = \psi(x, y, z) \quad (8)$$

$$\psi(x, y + L, z) = \psi(x, y, z), \quad \psi(x, y, z + L) = \psi(x, y, z)$$

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FREE ELECTRON GAS IN THREE DIMENSIONS

Wave functions satisfying the free particle Schrodinger equation and the periodicity condition are of the form of a traveling plane

$$\psi_k(r) = e^{ik \cdot r} \quad (9)$$

$$\text{with: } k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots \quad (10)$$

Any component of k of the form $2n\pi/L$ will satisfy the periodicity condition over a length L , where n is a positive or negative integer. these values of k_x satisfy (8), for:

$$e^{ik_x(x+L)} = e^{i\frac{2n\pi}{L}(x+L)} = e^{i\frac{2n\pi}{L}x} \cdot e^{i2n\pi} = e^{i\frac{2n\pi}{L}x} = e^{ik_x x} \quad (11)$$

Differentiate (9) twice then put it back in Eq. (6):

$$\varepsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad (12)$$

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FREE ELECTRON GAS IN THREE DIMENSIONS

The energy at the surface of the sphere is the Fermi energy:

$$\varepsilon_F = \frac{\hbar^2}{2m} k_F^2 \quad (14)$$

We can calculate the total No. of states inside Fermi Sphere from dividing the total Fermi sphere volume on the volume of one state

$$\text{Volume of one state: } \left(\frac{2\pi}{L} \right)^3$$

$$\text{Total volume of Fermi Sphere: } \frac{4}{3} \pi k_F^3$$

$$\therefore N = 2 \cdot \frac{4}{3} \pi k_F^3 / \left(\frac{2\pi}{L} \right)^3 = \frac{V}{3\pi^2} k_F^3 \quad (\text{Total No. of states}) \quad (15)$$

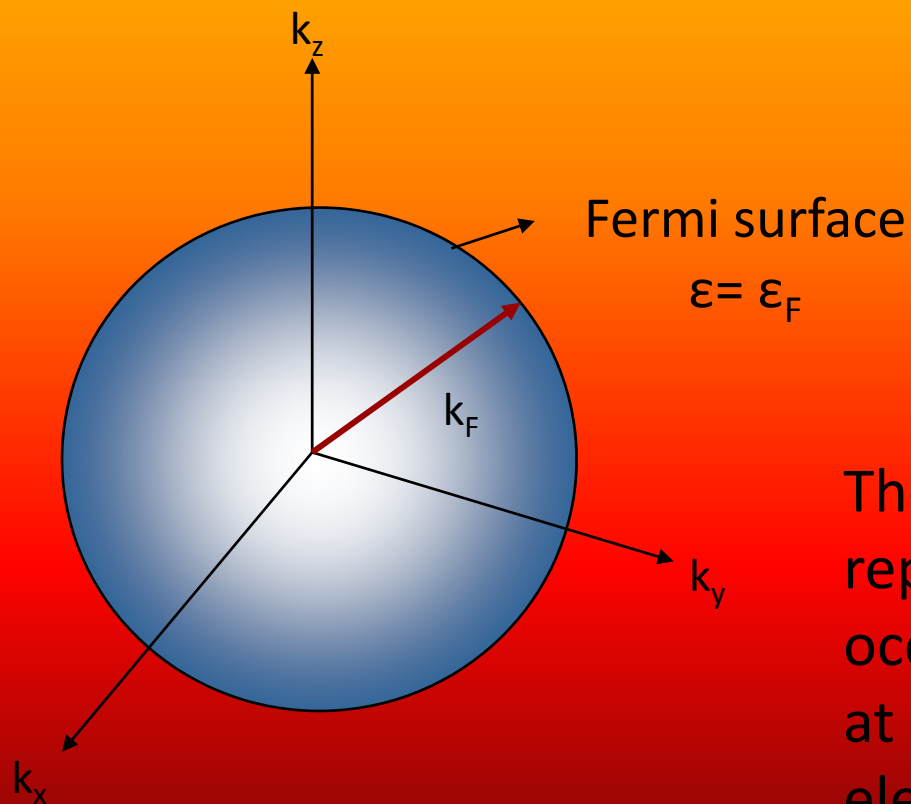
$$\Rightarrow k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} \quad (16)$$

Hence k_F depends only on particle concentration

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FREE ELECTRON GAS IN THREE DIMENSIONS – Fermi Sphere

The occupied states are inside the Fermi sphere in k -space as shown below; the radius is Fermi wave number k_F



$$\begin{aligned}\epsilon_F &= \frac{\hbar^2}{2m} k_F^2 \\ &= \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}\end{aligned}$$

The surface of the Fermi sphere represents the boundary between occupied & unoccupied k states at absolute zero for the free electron gas.

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FREE ELECTRON GAS IN THREE DIMENSIONS

Calculated values of k_F , v_F and E_F are given in Table 1 for selected metals.

Table 1 Calculated free electron Fermi surface parameters for metals at room temperature

(Except for Na, K, Rb, Cs at 5 K and Li at 78 K)

Valency	Metal	Electron concentration, in cm^{-3}	Radius* parameter r_s	Fermi wavevector, in cm^{-1}	Fermi velocity, in cm s^{-1}	Fermi energy, in eV	Fermi temperature $T_F = \epsilon_F/k_B$, in deg K
1	Li	4.70×10^{22}	3.25	1.11×10^8	1.29×10^8	4.72	5.48×10^4
	Na	2.65	3.93	0.92	1.07	3.23	3.75
	K	1.40	4.86	0.75	0.86	2.12	2.46
	Rb	1.15	5.20	0.70	0.81	1.85	2.15
	Cs	0.91	5.63	0.64	0.75	1.58	1.83
	Cu	8.45	2.67	1.36	1.57	7.00	8.12
	Ag	5.85	3.02	1.20	1.39	5.48	6.36
	Au	5.90	3.01	1.20	1.39	5.51	6.39
2	Be	24.2	1.88	1.93	2.23	14.14	16.41
	Mg	8.60	2.65	1.37	1.58	7.13	8.27
	Ca	4.60	3.27	1.11	1.28	4.68	5.43
	Sr	3.56	3.56	1.02	1.18	3.95	4.58
	Ba	3.20	3.69	0.98	1.13	3.65	4.24
	Zn	13.10	2.31	1.57	1.82	9.39	10.90
	Cd	9.28	2.59	1.40	1.62	7.46	8.66
3	Al	18.06	2.07	1.75	2.02	11.63	13.49
	Ga	15.30	2.19	1.65	1.91	10.35	12.01
	In	11.49	2.41	1.50	1.74	8.60	9.98
4	Pb	13.20	2.30	1.57	1.82	9.37	10.87
	Sn(w)	14.48	2.23	1.62	1.88	10.03	11.64

*The dimensionless radius parameter is defined as $r_s = r_0/a_H$, where a_H is the first Bohr radius and r_0 is the radius of a sphere that contains one electron.

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FREE ELECTRON GAS IN THREE DIMENSIONS – Fermi Sphere

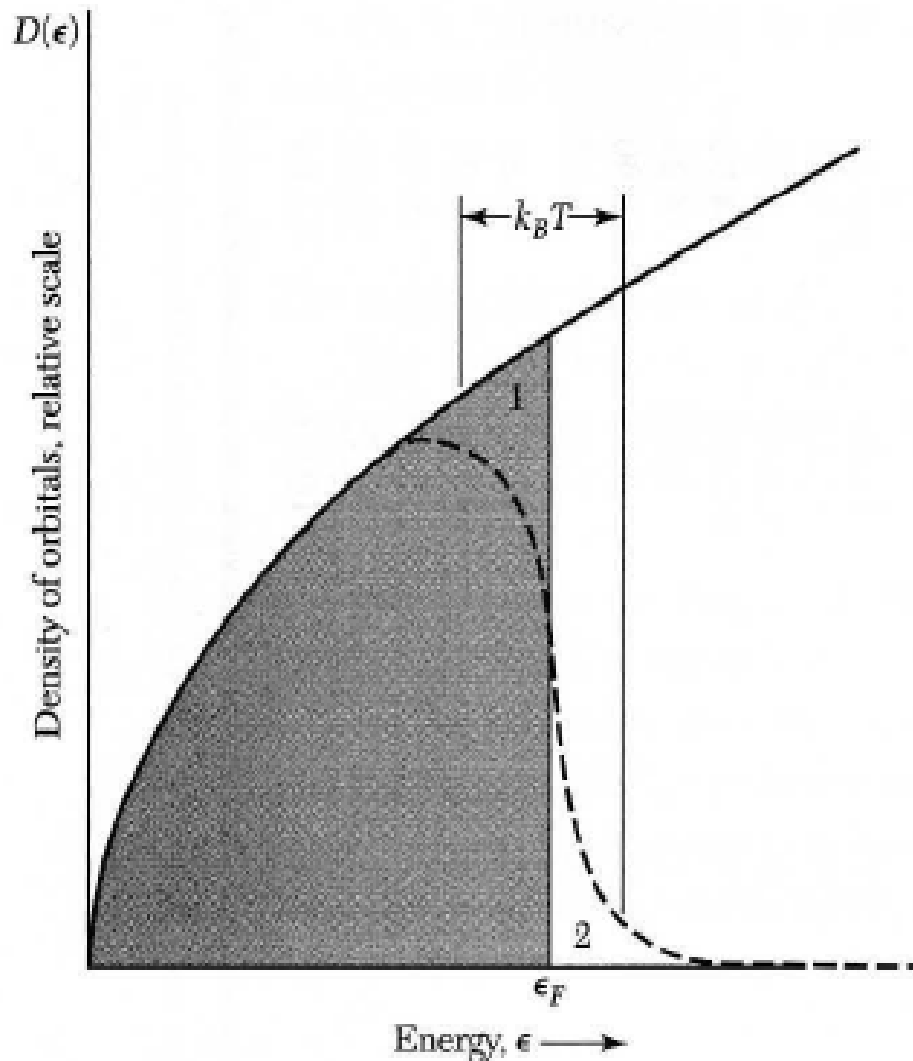


Figure 5 Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density $f(\epsilon, T)D(\epsilon)$ of filled orbitals at a finite temperature, but such that $k_B T$ is small in comparison with ϵ_F . The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to T , for electrons are thermally excited from region 1 to region 2.

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FREE ELECTRON GAS IN THREE DIMENSIONS – Fermi Sphere

The number of orbitals per unit energy range: $D(\epsilon)$ = density of states.

$$N = \frac{V}{3\pi^2} \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2} \quad (19)$$

This leads to:

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot \epsilon^{1/2} \quad (20)$$

Equation (19):

$$\ln N = \frac{3}{2} \ln \epsilon + \text{const.}$$

Hence:

$$\frac{dN}{N} = \frac{3}{2} \cdot \frac{d\epsilon}{\epsilon} \Rightarrow D(\epsilon) = \frac{dN}{d\epsilon} = \frac{3N}{2\epsilon} \quad (21)$$

Within a factor of the order of unity, the number of orbitals per unit energy range at the Fermi energy is the total number of conduction electrons divided by the Fermi energy.



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FREE ELECTRON GAS IN THREE DIMENSIONS – Fermi Sphere

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Within a factor of the order of unity, the number of orbitals per unit energy range at the Fermi energy is the total number of conduction electrons divided by the Fermi energy.

Chapter 6: Free Electron Fermi Gas

HEAT CAPACITY OF THE ELECTRON GAS

The question that caused the greatest difficulty in the early development of the electron theory of metals concerns the heat capacity of the conduction electrons. *Classical statistical mechanics predicts that a free particle should have a heat capacity of $\frac{2}{3}k_B$ where k_B is the Boltzmann constant.*

If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $\frac{2}{3}Nk_B$, just as for the atoms of a monatomic gas. But the observed electronic contribution at room temperature is usually less than 0.01 of this value.

When we heat the specimen from absolute zero, not every electron gains an energy $\sim k_B T$ as expected classically, *but only those electrons in orbitals within an energy range $k_B T$ of the Fermi level are excited thermally*

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HEAT CAPACITY OF THE ELECTRON GAS

If N is the total number of electrons, only a fraction of the order of T/T_F can be excited thermally at temperature T .

Each of these NT/T_F electrons has a thermal energy of the order of $k_B T$. The total electronic thermal kinetic energy U is of the order of:

$$U_{el} \approx N \frac{T}{T_F} k_B T \quad (22)$$

The electronic heat capacity is given by:

$$C_{el} = \frac{\partial U}{\partial T} \approx N k_B \frac{T}{T_F} \quad (23)$$

C_{el} is directly proportional to T , in agreement with the experiment.

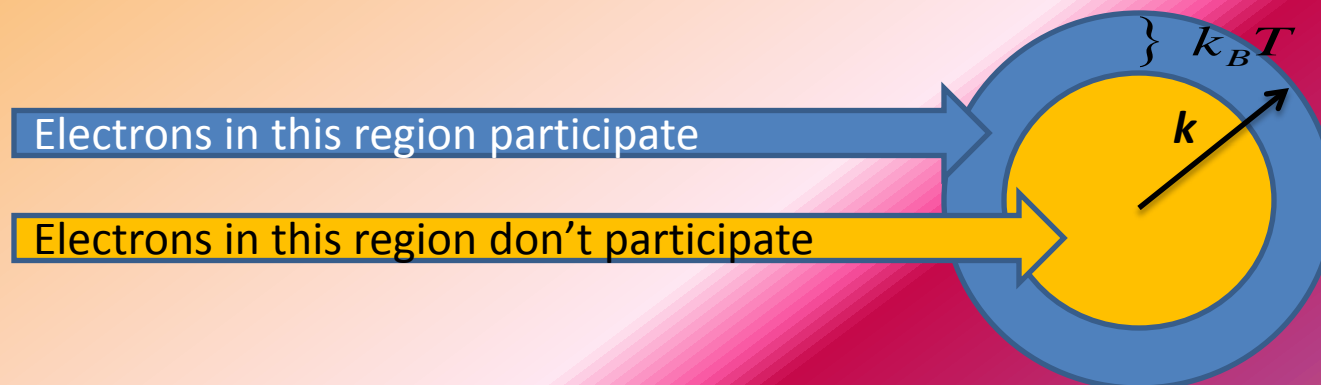
At room temperature C_{el} is smaller than the classical value $\frac{2}{3} N k_B$ by a factor of the order of 0.01 or less, for $T_F \sim 5 \times 10^4$ K.

Hence: Classical value does not agree with experiment

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HEAT CAPACITY OF THE ELECTRON GAS: *summary*

- Classical Statistical Physics heat capacity of one electron: $C = \frac{2}{3}k_B$
- Classical Statistical Physics heat capacity of N electrons: $C = \frac{2}{3}Nk_B$
- Experimental result of $C = 1\%$ of this value only
- Error in Classical theory was due to considering all electrons that participate in conductivity as *Free electrons*.
- Fermi solved this puzzle: Only electrons that have energies of $\sim k_B T$ below Fermi Surface or higher participate in Heat Capacity.
- Hence: only NT/T_F of electrons is important.
- All other electrons are not useful.



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HEAT CAPACITY OF THE ELECTRON GAS: *summary*

- \Rightarrow *All Free electrons participate in Electrical Conductivity*
- *But only T/T_F fraction participate in Heat Capacity*
- *This conclusion is a major indication of the success of the Fermi Free Electron Gas.*

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Deriving HEAT CAPACITY OF THE ELECTRON GAS

- We want to derive an expression for the *electronic heat capacity*:

The increase $\Delta U \equiv U(T) - U(0)$ in the total energy of a system of N electrons when heated from 0 to T is:

$$\Delta U \equiv \int_0^{\infty} \epsilon D(\epsilon) f(\epsilon) d\epsilon - \int_0^{\epsilon_F} \epsilon D(\epsilon) d\epsilon \quad (24)$$

Total No of electrons inside Fermi sphere (or including outside where no electrons):

$$N = \int_0^{\infty} D(\epsilon) f(\epsilon) d\epsilon = \int_0^{\epsilon_F} D(\epsilon) d\epsilon \quad (25)$$

we can write (then multiply both sides by ϵ_F :)

$$\begin{aligned} \int_0^{\infty} d\epsilon &= \int_0^{\epsilon_F} d\epsilon + \int_{\epsilon_F}^{\infty} d\epsilon \\ \left(\int_0^{\epsilon_F} + \int_{\epsilon_F}^{\infty} \right) D(\epsilon) f(\epsilon) \epsilon_F d\epsilon &= \int_0^{\epsilon_F} \epsilon_F D(\epsilon) d\epsilon \end{aligned} \quad (26)$$

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Deriving HEAT CAPACITY OF THE ELECTRON GAS

(26) & (24): 6 terms:

$$\Delta U = \int_{\varepsilon_F}^{\infty} (\varepsilon - \varepsilon_F) D(\varepsilon) f(\varepsilon) d\varepsilon + \int_0^{\varepsilon_F} (\varepsilon_F - \varepsilon) [1 - f(\varepsilon)] D(\varepsilon) d\varepsilon \quad (27)$$

The *first integral* on the right-hand side of (27) gives the energy needed to take electrons from ε_F to the orbitals of energy $\varepsilon > \varepsilon_F$, and the *second integral* gives the energy needed to bring the electrons to ε_F from orbitals below ε_F .

The product $f(\varepsilon)D(\varepsilon)d\varepsilon$ in the first integral of (27) is the number of electrons elevated to orbitals in the energy range $d\varepsilon$ at an energy ε . The factor $[1 - f(\varepsilon)]$ in the second integral is the probability that an electron has been removed from an orbital ε .

The heat capacity is found on differentiating ΔU with respect to T . The only temperature-dependent term in (27) is $f(\varepsilon)$

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Deriving HEAT CAPACITY OF THE ELECTRON GAS

The heat capacity of the electron gas is found on differentiating $8U$ with respect to T .

$$c_{el} = \frac{dU}{dT} = \int_0^{\infty} d\varepsilon [\varepsilon - \varepsilon_F] \frac{df}{dT} D(\varepsilon) \quad (28)$$

$$\text{Fermi Dirac: } f(\varepsilon) = \frac{1}{e^{\left(\frac{\varepsilon - \mu}{K_B T}\right)} + 1} \quad (x1)$$

Let $D(\varepsilon) \rightarrow D(\varepsilon_F)$ in (28) and $\mu \rightarrow \varepsilon_F$ in Fermi Dirac Function:

$$\therefore c_{el} \cong D(\varepsilon_F) \int_0^{\infty} d\varepsilon [\varepsilon - \varepsilon_F] \frac{df}{dT} \quad (29)$$

equation (x1) becomes:

$$f(\varepsilon) = \frac{1}{e^{\left(\frac{\varepsilon - \varepsilon_F}{K_B T}\right)} + 1} \quad (x2)$$

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Deriving HEAT CAPACITY OF THE ELECTRON GAS

let $k_B T \rightarrow \tau$:

$$f(\varepsilon) = \frac{1}{e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} + 1} \quad (x\ 3)$$

we then differentiate w.r.t τ :

$$\frac{df(\varepsilon)}{d\tau} = \frac{\left[-\left(\frac{\varepsilon - \varepsilon_F}{\tau^2}\right) e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} (-1) \right]}{\left[e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} + 1 \right]^2} = \left(\frac{\varepsilon - \varepsilon_F}{\tau^2}\right) \frac{e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)}}{\left[e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} + 1 \right]^2} \quad (x\ 4)$$

$$\because \tau = k_B T \Rightarrow d\tau = k_B dT$$

$$\frac{1}{dT} = k_B \frac{1}{d\tau}$$

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Deriving HEAT CAPACITY OF THE ELECTRON GAS

Rewriting Eq. (29):

$$c_{el} \cong k_B D(\varepsilon_F) \int_0^{\infty} d\varepsilon [\varepsilon - \varepsilon_F] \left(\frac{\varepsilon - \varepsilon_F}{\tau^2} \right) \frac{e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau} \right)}}{\left[e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau} \right)} + 1 \right]^2}$$

$$\Rightarrow c_{el} = k_B D(\varepsilon_F) \int_0^{\infty} d\varepsilon \left(\frac{\varepsilon - \varepsilon_F}{\tau} \right)^2 \frac{e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau} \right)}}{\left[e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau} \right)} + 1 \right]^2} \quad (30)$$

$$\text{let : } x = \left(\frac{\varepsilon - \varepsilon_F}{\tau} \right) \Rightarrow dx = \frac{d\varepsilon}{\tau} = \frac{d\varepsilon}{k_B T} \Rightarrow d\varepsilon = k_B T dx$$

→ we have $k_B T$ and k_B in (30) $\Rightarrow k_B^2 T$:

Chapter 6: Free Electron Fermi Gas

Deriving HEAT CAPACITY OF THE ELECTRON GAS

Hence, we have:

$$c_{el} = k_B^2 T D(\varepsilon_F) \int_{\frac{-\varepsilon_F}{\tau}}^{\infty} dx \, x^2 \frac{e^x}{[e^x + 1]^2} \quad (31)$$

for the lower limit of integral:

$$x = \left(\frac{\varepsilon - \varepsilon_F}{\tau} \right) \Rightarrow x = \frac{0 - \varepsilon_F}{\tau} = \frac{-\varepsilon_F}{\tau} \quad [\text{lower limit in (30)} = \varepsilon = 0]$$

as $T \rightarrow 0$, $x \rightarrow -\infty$

Using table of Integrals:

$$\int_{-\infty}^{\infty} dx \, x^2 \frac{e^x}{[e^x + 1]^2} = \frac{\pi^2}{3} \quad (32)$$

$$(32) \text{ in (31): } c_{el} = \frac{\pi^2}{3} k_B^2 T D(\varepsilon_F) \quad (33)$$

Chapter 6: Free Electron Fermi Gas

Electronic HEAT CAPACITY OF THE ELECTRON GAS

From eq. (21) above, we have:

$$D(\varepsilon_F) = \frac{3N}{2\varepsilon_F}$$

$$\therefore D(\varepsilon_F) = \frac{3}{2} \frac{N}{k_B T_F}$$

$$\text{with: } T_F = \frac{\varepsilon_F}{k_B}, (33) \rightarrow:$$

$$C_{el} = \frac{1}{2} \pi^2 k_B^2 \frac{T}{T_F} \quad (36)$$

$$T_F = \text{Const.}$$

Recall that although T_F is called the *Fermi temperature*, it is not the *electron temperature*, but only a convenient reference notation>
We shall compare this result with experimental data.

Chapter 6: Free Electron Fermi Gas

Experimental Heat Capacity of Metals:

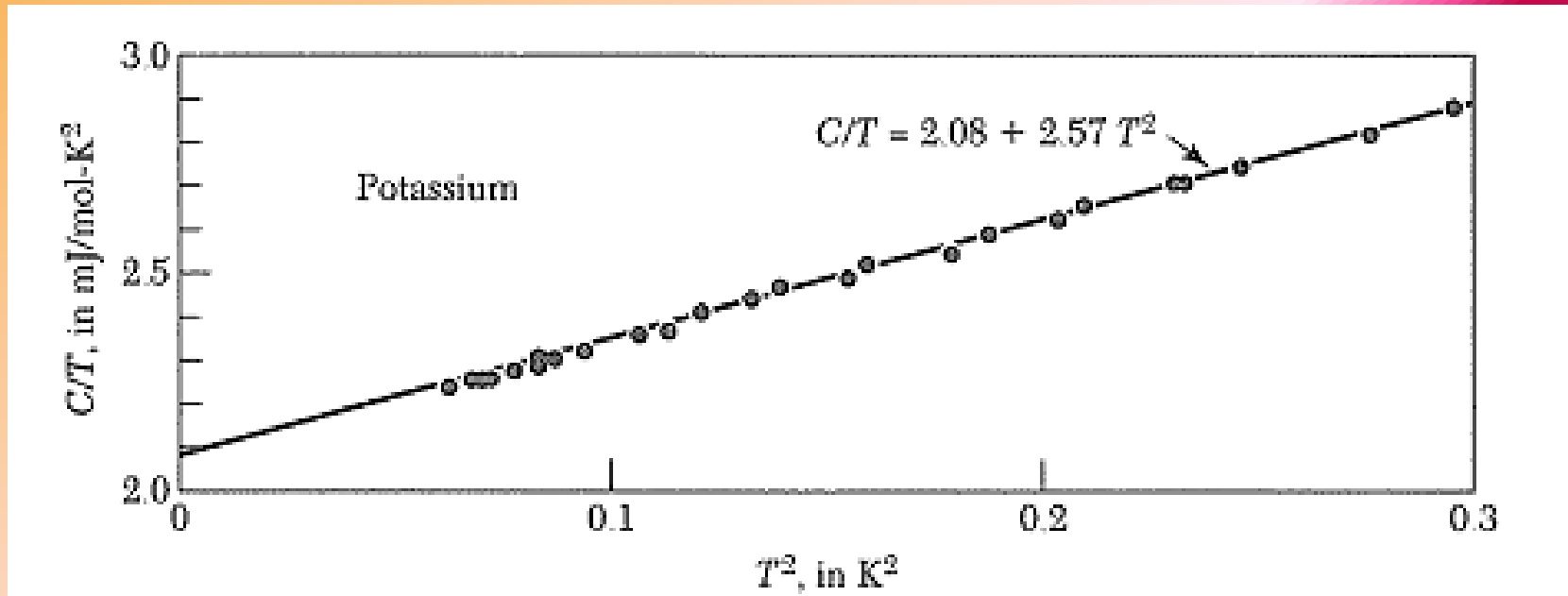
At temperatures much below both the Debye temperature and the Fermi temperature, the heat capacity of metals may be written as the sum of electron and phonon contributions:

$$C = \gamma T + AT^3$$

where γ and A are constants characteristic of the material.

\therefore Electronic part is Linear to T (Agree with Fermi Free Electron Model)

While Phononic part is $\propto T^3$ (Agree with Debye model)



Phys 570

Lecture #4

*Physics & Astronomy Dept.
College of Science
King Saud University*

Nasser S. Alzayed

nalzayed@ksu.edu.sa



Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

The momentum of a free electron is related to the wavevector by $m\mathbf{v} = \hbar\mathbf{k}$. In an electric field E and magnetic field B the force F on an electron of charge $-e$ can be written as:

$$F = m \frac{dv}{dt} = \hbar \frac{dk}{dt} = -e \left[E + \frac{1}{c} \mathbf{v} \times B \right] \quad (39)$$

This equation is the Newton's second law of motion for the electron of charge $-e$ and mass m_e in both of E and B . We want to find the Electrical Conductivity (From Ohm's Law). Hence, we set $B = 0$ (no magnetic Field):

$$\hbar \frac{dk}{dt} = -e [E] \Rightarrow dk = -eEdt / \hbar$$

by integrating both sides:

$$k(t) - k(0) = -eEt / \hbar \quad (40)$$

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

If the force $\mathbf{F} = -e\mathbf{E}$ is applied at time $t = 0$ to an electron gas that fills the Fermi sphere centered at the origin of k space, then at a later time t the sphere will be displaced to a new center at:

$$\delta k = -eEt / \hbar \quad (41)$$

Notice that the Fermi sphere is displaced as a whole because every electron is displaced by the same δk .

Because of collisions of electrons, the displaced sphere may be maintained in a steady state in an electric field. If the collision time is τ , the displacement of the sphere is given by (41) with $t = \tau$. The velocity is: $\mathbf{v} = \mathbf{P}/m = \hbar \mathbf{k} / m = -e\mathbf{E} \tau / m$.

If $\mathbf{E} = \text{constant}$; there are n electrons of charge $-e$ per unit volume, the electric current density is:

$$\mathbf{j} = nq\mathbf{v} = n(-e)\mathbf{v} = n(-e)(-e\mathbf{E} \tau / m) = ne^2 \tau \mathbf{E} / m \quad (42)$$

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

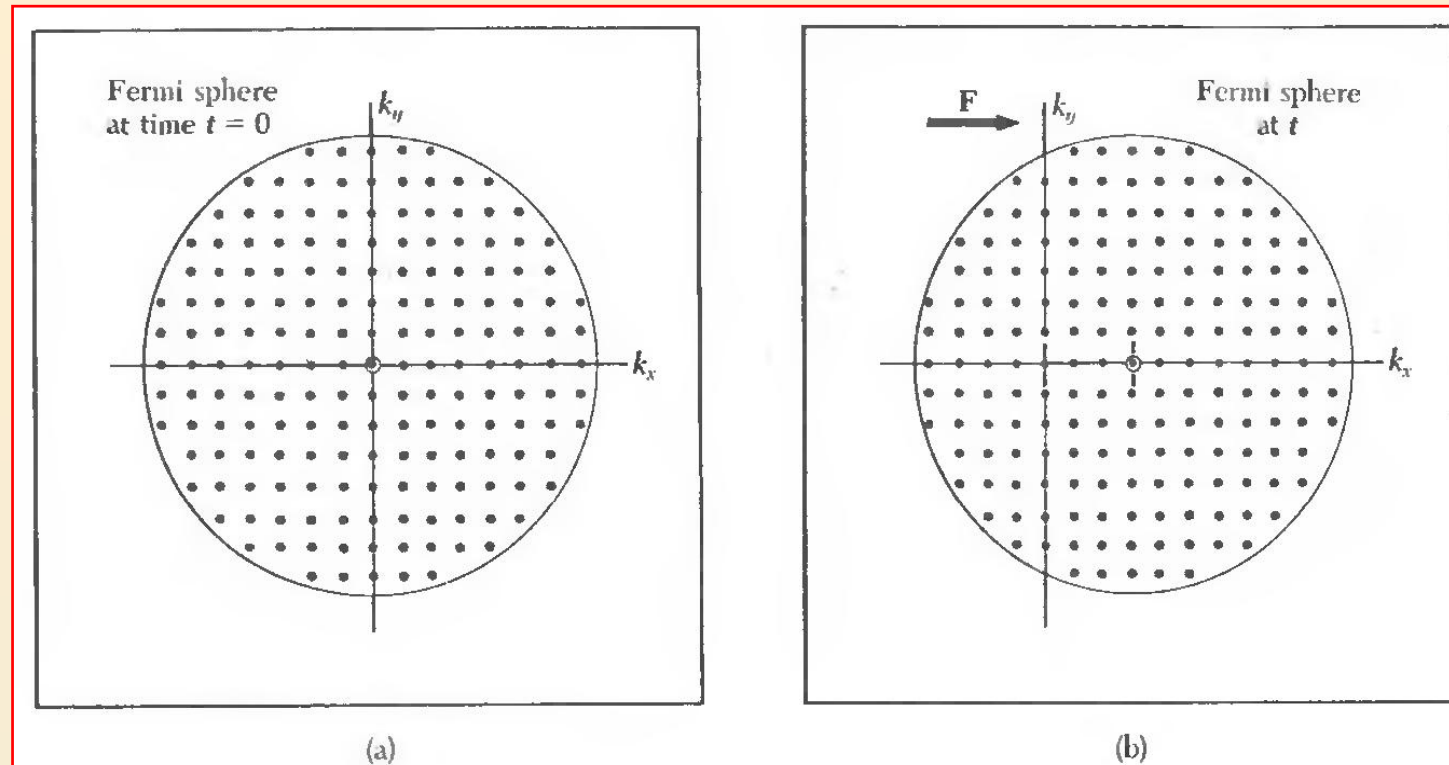


Figure 10 (a) The Fermi sphere encloses the occupied electron orbitals in k space in the ground state of the electron gas. The net momentum is zero, because for every orbital k there is an occupied orbital at $-k$. (b) Under the influence of a constant force F acting for a time interval t every orbital has its k vector increased by $\delta k = Ft/\hbar$. This is equivalent to a displacement of the whole Fermi sphere by δk . The total momentum is $N\hbar\delta k$, if there are N electrons present. The application of the force increases the energy of the system by $N(\hbar\delta k)^2/2m$.

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

Equation (42) is called Ohm's Law.

We can find the electrical conductivity σ defined by $\mathbf{j} = \sigma \mathbf{E}$, so by (42):

$$\sigma = \frac{ne^2\tau}{m} \quad (43)$$

The electrical resistivity ρ is defined as the reciprocal of the conductivity, so that: (see table 3)

$$\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} \quad (44)$$

It is easy to understand the result (43). Charge transported is proportional to the density ne ; e/m is because the acceleration is proportional to \mathbf{E} and inversely proportional to the mass m .

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

Li	Be
1.07 9.32	3.08 3.25
Na	Mg
2.11 4.75	2.33 4.30
K	Ca
1.39 7.19	2.78 3.6
Rb	Sr
0.80 12.5	0.47 21.5
Cs	Ba
0.50 20.0	0.26 39
Fr	Ra

Conductivity in units of 10^5 (ohm-cm) $^{-1}$.						
Resistivity in units of 10^{-6} ohm-cm.						
	Cr	Mn	Fe	Co	Ni	Cu
50	0.78	0.072	1.02	1.72	1.43	5.88
9.9	12.9	139.	9.8	5.8	7.0	1.70
b	Mo	Tc	Ru	Rh	Pd	Ag
69	1.89	~0.7	1.35	2.08	0.95	6.21
4.5	5.3	~14.	7.4	4.8	10.5	1.61
a	W	Re	Os	Ir	Pt	Au
76	1.89	0.54	1.10	1.96	0.96	4.55
3.1	5.3	18.6	9.1	5.1	10.4	2.20

O	F	Ne
S	Cl	Ar
Se	Br	Kr
Te	I	Xe
Po	At	Rn
6 0.22 46.		

Tm	Yb	Lu
0.16 62.	0.38 26.4	0.19 53.
Md	No	Lr

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

- According to Table 3, conductivity of copper could be: **$5.88 \times 10^5 \text{ } \Omega \cdot \text{cm}$** at room temp.
- This value could be as high as **10^5** times larger at low temperatures.
- Hence: copper crystals become more pure when cooled and vice versa. This applies to all crystals.
- This leads to large increase in relaxation time τ that can reach values: **$2 \times 10^{-9} \text{ s}$** at very low temp.
- We have a quantity that depends on τ which is ℓ (mean free path) which represents the mean distance between every two collisions.
- ℓ is expressed as: **$\ell = v_F \tau$**

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

if the electric field were switched off; the momentum distribution would relax back to its ground state with the net relaxation rate:

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i} \quad (45)$$

where τ_L and τ_i are the collision times for scattering by phonons and by imperfections, respectively.

Total resistance from phonons and impurities is:

$$\rho = \rho_L + \rho_i \quad (46)$$

First term is independent of impurities (when their concentration is small) .

and 2nd term is independent of temperature.

Chapter 6: Free Electron Fermi Gas

Resistance of Potassium

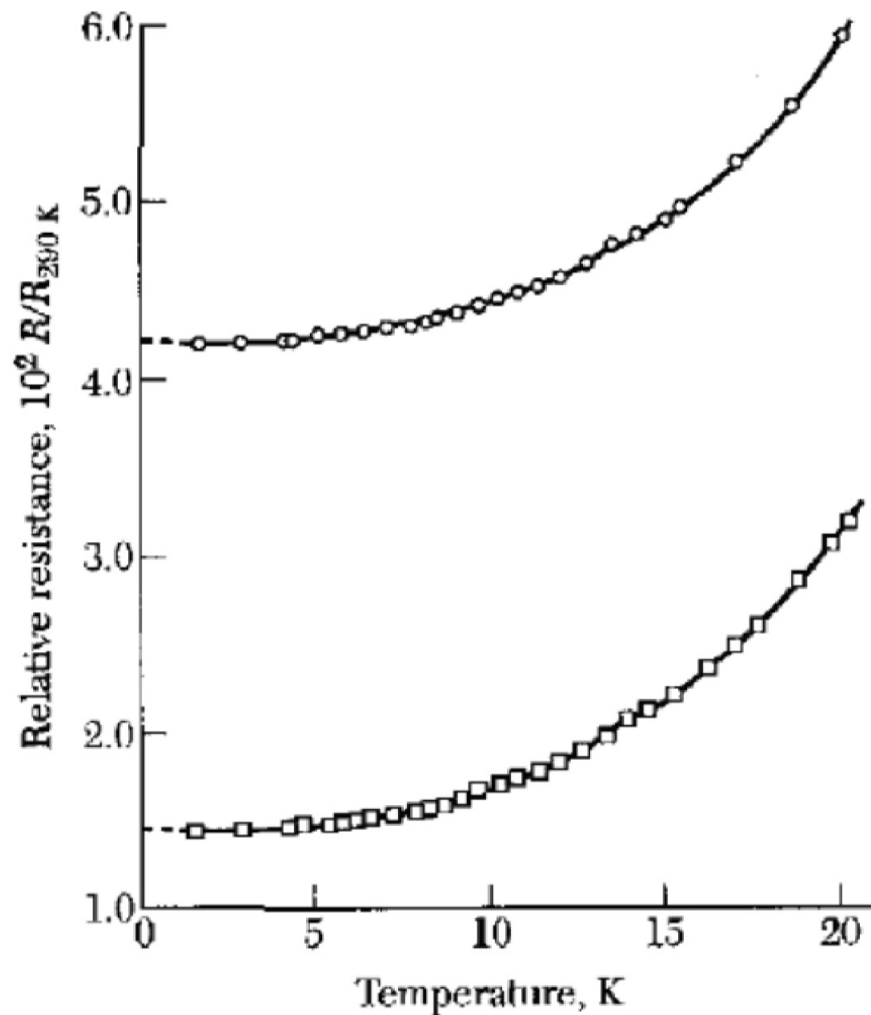


Figure 12 Resistance of potassium below 20 K, as measured on two specimens by D. MacDonald and K. Mendelssohn. The different intercepts at 0 K are attributed to different concentrations of impurities and static imperfections in the two specimens.

Chapter 6: Free Electron Fermi Gas

ELECTRICAL CONDUCTIVITY AND OHM'S LAW

The relation $\ell = v_F \tau$ shows clearly that Fermi velocity v_F is the same as the velocity of electrons in the conductor because all collisions involve only electrons near the Fermi surface.

From Table 1 we have $v_F = 1.57 \times 10^8 \text{ cm s}^{-1}$ for Cu, thus the mean free path is $\ell(4 \text{ K}) = 0.3 \text{ cm}$. *Mean free paths as long as 10 cm have been observed in very pure metals in the liquid helium temperature range.*

Since v_F is very high as we showed previously; and because ℓ is large (as large as 10 cm) then we expect that τ is very small. Usually this time is opposite to Fermi velocity.

Chapter 6: Free Electron Fermi Gas

MOTION of electrons IN MAGNETIC FIELDS

When electrons move under both of B and E:

$$\vec{F} = -e \left(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \quad (49)$$

1st term: eE is coulumbic force, 2nd term is Lorentz formce.

if $m\vec{v} = \hbar \delta \vec{k}$ then we have: $m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \vec{v} = -e \left(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \quad (50)$

if B lie along the z axis. Then the component equations of motion are:

$$\left. \begin{aligned} m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_x &= -e \left(E_x + \frac{B}{c} v_y \right) \\ m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_y &= -e \left(E_y + \frac{B}{c} v_x \right) \\ m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_z &= -e E_z \end{aligned} \right\} \quad (51)$$

Chapter 6: Free Electron Fermi Gas

MOTION of electrons IN MAGNETIC FIELDS

In the steady state in a static electric field the time derivatives are zero, so that the drift velocity is:

$$\left. \begin{aligned} v_x &= \frac{-e\tau E_x}{m} - \omega_c \tau v_y \\ v_y &= \frac{-e\tau E_y}{m} + \omega_c \tau v_x \\ v_z &= \frac{-e\tau E_z}{m} \end{aligned} \right\} \quad (52)$$

where $\omega_c = \frac{eB}{mc}$ is the cyclotron frequency

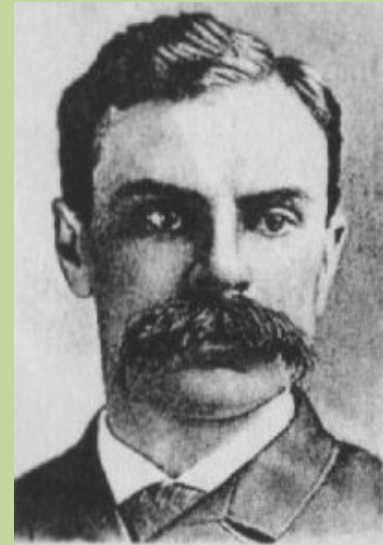
This means that when electron moves in the existence of magnetic field B, it will rotate with this frequency. We notice the linear dependence on B, when B increases w will increase.

Chapter 6: Free Electron Fermi Gas

Hall Effect

Since we are talking about motion of electrons under the effect of B , let us imagine that these electrons move inside a conductor. The Hall field is the electric field developed across two faces of a conductor, in the direction $j \times B$, when a current j flows across a magnetic field B .

** Let us consider a conductor in a form of *rectangular parallelepiped* with current flowing in x -direction. Hence we have: E_x .
We also have a B perpendicular on this conductor.
Current cannot move in y direction $\rightarrow v_y = 0$.
Hence, 2nd equation in (52) = 0.
Accordingly; we have:



Chapter 6: Free Electron Fermi Gas

Deriving Hall Effect

$$0 = -\frac{e\tau}{m}E_y + \omega_c \tau v_x = -\frac{e\tau}{m}E_y + \frac{eB\tau}{mc}v_x$$
$$\Rightarrow E_y = \frac{B}{c}v_x = \frac{B}{c} \left[-\frac{e\tau}{m}E_x \right] \Rightarrow E_y = -\frac{eB\tau}{mc}E_x \quad (53)$$

Hall coefficient is defined as:

$$R_H = \frac{E_y}{j_x B} \quad (54)$$

using: $j_x = \frac{ne^2\tau E_x}{m}$ we can get:

$$R_H = -\frac{eB\tau E_x / mc}{ne^2\tau E_x / m} = -\frac{1}{nec} \quad (55)$$

Hence; R_H is negative for free electron.

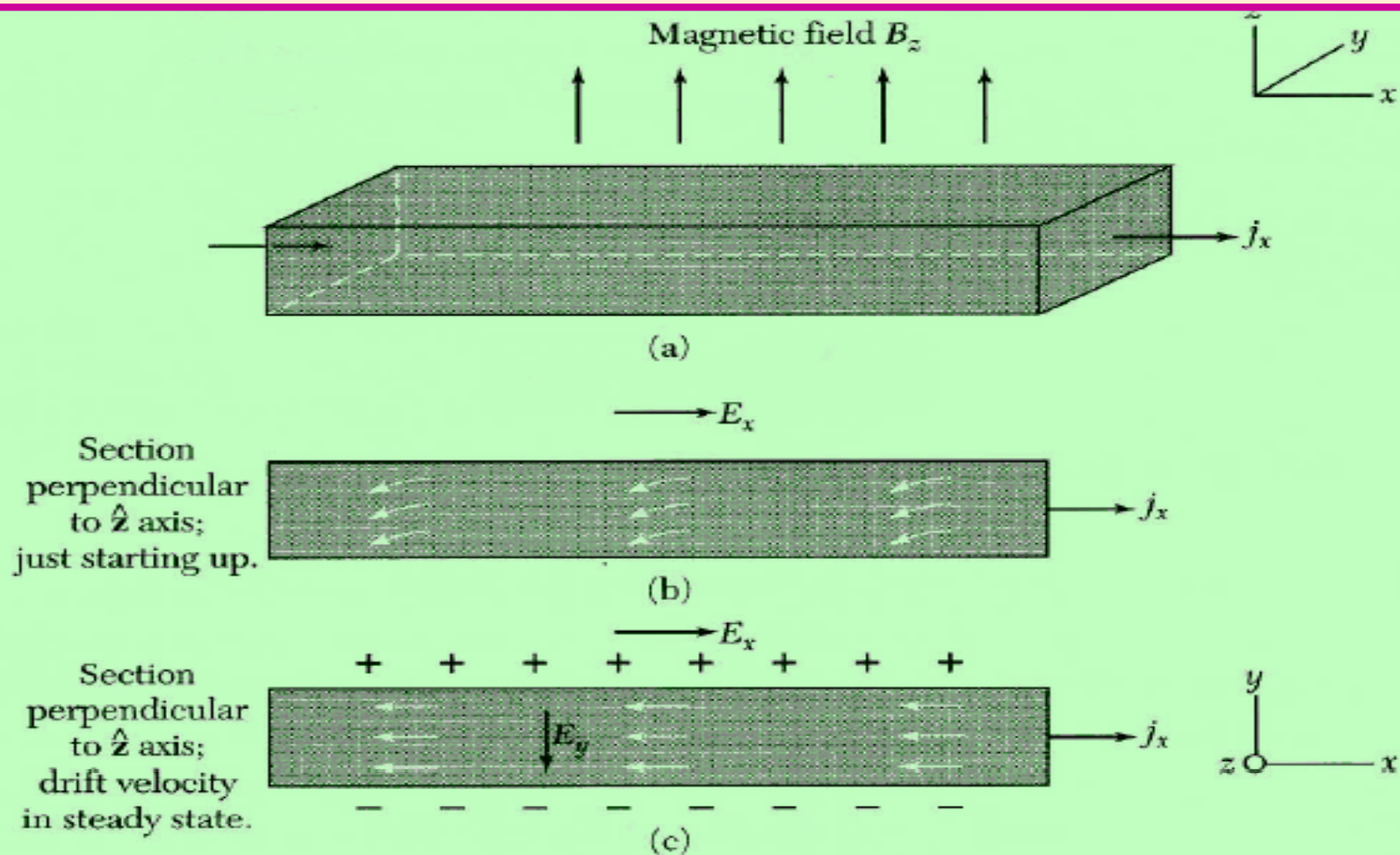


Figure 14 The standard geometry for the Hall effect: a rod-shaped specimen of rectangular cross-section is placed in a magnetic field B_z , as in (a). An electric field E_x applied across the end electrodes causes an electric current density j_x to flow down the rod. The drift velocity of the negatively-charged electrons immediately after the electric field is applied as shown in (b). The deflection in the $-y$ direction is caused by the magnetic field. Electrons accumulate on one face of the rod and a positive ion excess is established on the opposite face until, as in (c), the transverse electric field (Hall field) just cancels the Lorentz force due to the magnetic field.

Table 4 Comparison of observed Hall coefficients with free electron theory

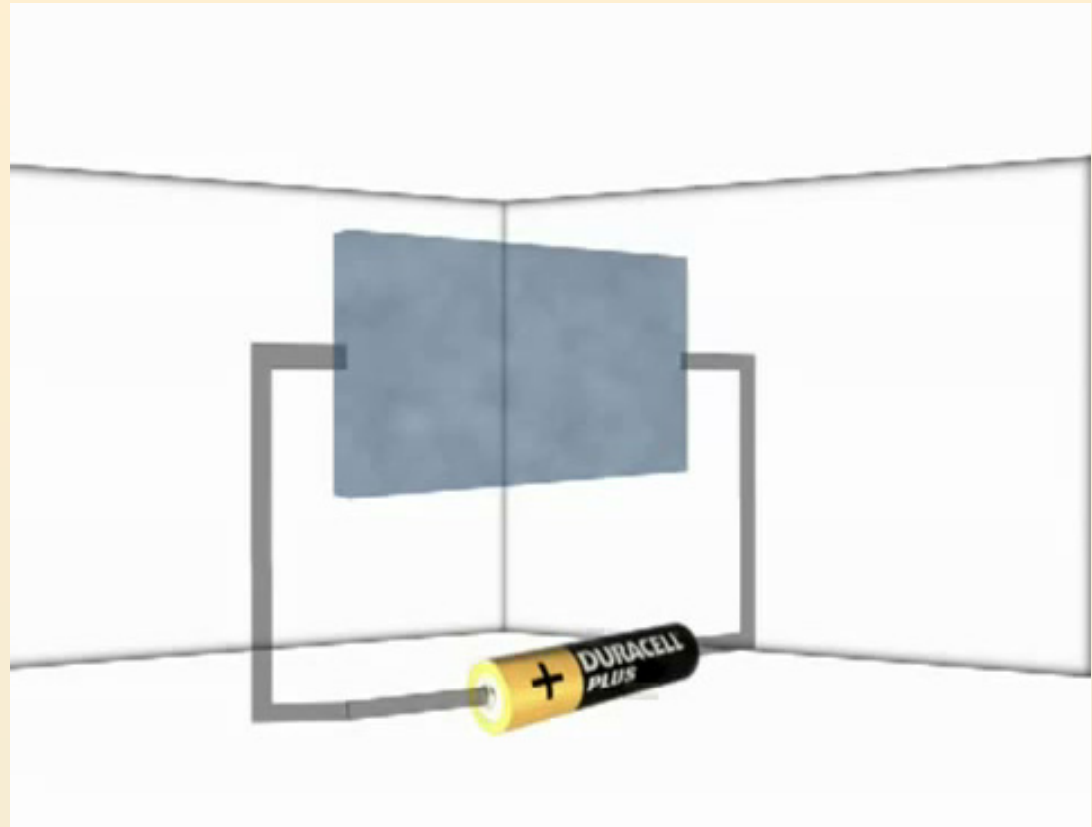
[The experimental values of R_H as obtained by conventional methods are summarized from data at room temperature presented in the Landolt-Bornstein tables. The values obtained by the helicon wave method at 4 K are by J. M. Goodman. The values of the carrier concentration n are from Table 1.4 except for Na, K, Al, In, where Goodman's values are used. To convert the value of R_H in CGS units to the value in volt-cm/amp-gauss, multiply by 9×10^{11} ; to convert R_H in CGS to $\text{m}^3/\text{coulomb}$, multiply by 9×10^{13} .]

Metal	Method	Experimental R_H , in 10^{-24} CGS units	Assumed carriers per atom	Calculated $-1/nec$, in 10^{-24} CGS units
Li	conv.	-1.89	1 electron	-1.48
Na	helicon	-2.619	1 electron	-2.603
	conv.	-2.3		
K	helicon	-4.946	1 electron	-4.944
	conv.	-4.7		
Rb	conv.	-5.6	1 electron	-6.04
Cu	conv.	-0.6	1 electron	-0.82
Ag	conv.	-1.0	1 electron	-1.19
Au	conv.	-0.8	1 electron	-1.18
Be	conv.	+2.7	—	—
Mg	conv.	-0.92	—	—
Al	helicon	+1.136	1 hole	+1.135
In	helicon	+1.774	1 hole	+1.780
As	conv.	+50.	—	—
Sb	conv.	-22.	—	—
Bi	conv.	-6000.	—	—

Chapter 6: Free Electron Fermi Gas

Hall Effect Animation

- ❑ From table we notice that: the lower the concentration, the greater R_H .
- ❑ Measuring R_H is important for measuring the carrier concentration.
- ❑ Eq. (55) follows from the assumption that τ for all electrons are equal, independent of the velocity of the electron.



Chapter 6: Free Electron Fermi Gas

THERMAL CONDUCTIVITY OF METALS

Thermal conductivity coefficient K is defined as:

$$j_u = -K \frac{dT}{dx}$$

J_u is the Thermal Energy Flux (Amount of thermal energy flown cross unit area in 1 sec. From previous lectures:

$$C_{el} = \frac{1}{2} \pi^2 N k_B \frac{T}{T_F} \quad \text{with } T_F = \frac{\varepsilon_F}{k_B} \quad \Rightarrow C_{el} = \frac{1}{2} \pi^2 N k_B \frac{T}{\varepsilon_F} k_B$$

from Chapt. 5: $K = \frac{1}{3} C v l$

$$\Rightarrow K_{el} = \frac{1}{3} \cdot \frac{1}{2} \pi^2 N k_B \frac{T}{\varepsilon_F} k_B v l = \frac{1}{3} \cdot \frac{1}{2} \pi^2 N k_B \frac{T}{m v_F^2} \cdot 2 k_B v_F l$$

$$\Rightarrow K_{el} = \frac{\pi^2 n k_B^2 T \tau}{3m} \quad (n \text{ for } N \text{ and } l = v_F \tau) \quad (56)$$

Chapter 6: Free Electron Fermi Gas

THERMAL CONDUCTIVITY OF METALS

- ☐ Do the electrons or the phonons carry the greater part of the heat current? in a metal?
- ☐ In pure metals the electronic contribution is dominant at all temperatures.
- ☐ In impure metals or in disordered alloys, the electron mean free
- ☐ path is reduced by collisions with impurities, and the phonon contribution may be comparable with the electronic contribution.



Phys 570

Lecture #5

Physics & Astronomy Dept.

College of Science

King Saud University

Nasser S. Alzayed

nalzayed@ksu.edu.sa

Chapter 7: Energy Bands

Introduction

- ❑ The free electron model of metals gives us good insight into the **heat capacity**, **thermal conductivity**, **electrical conductivity**, **magnetic susceptibility**, and **electrodynamics** of metals.
- ❑ But the model fails to help us with other large questions:
 - *the distinction between metals, semimetals, semiconductors, and Insulators*
 - *the occurrence of positive values of the Hall coefficient*
 - *the relation of conduction electrons in the metal to the valence electrons of free Atoms*
 - *many transport properties, particularly magnetotransport*
- ❑ Hence, we need to modify Fermi Electron Model to be able to answer these puzzles. We will see that little modification is just adequate.

Chapter 7: Energy Bands

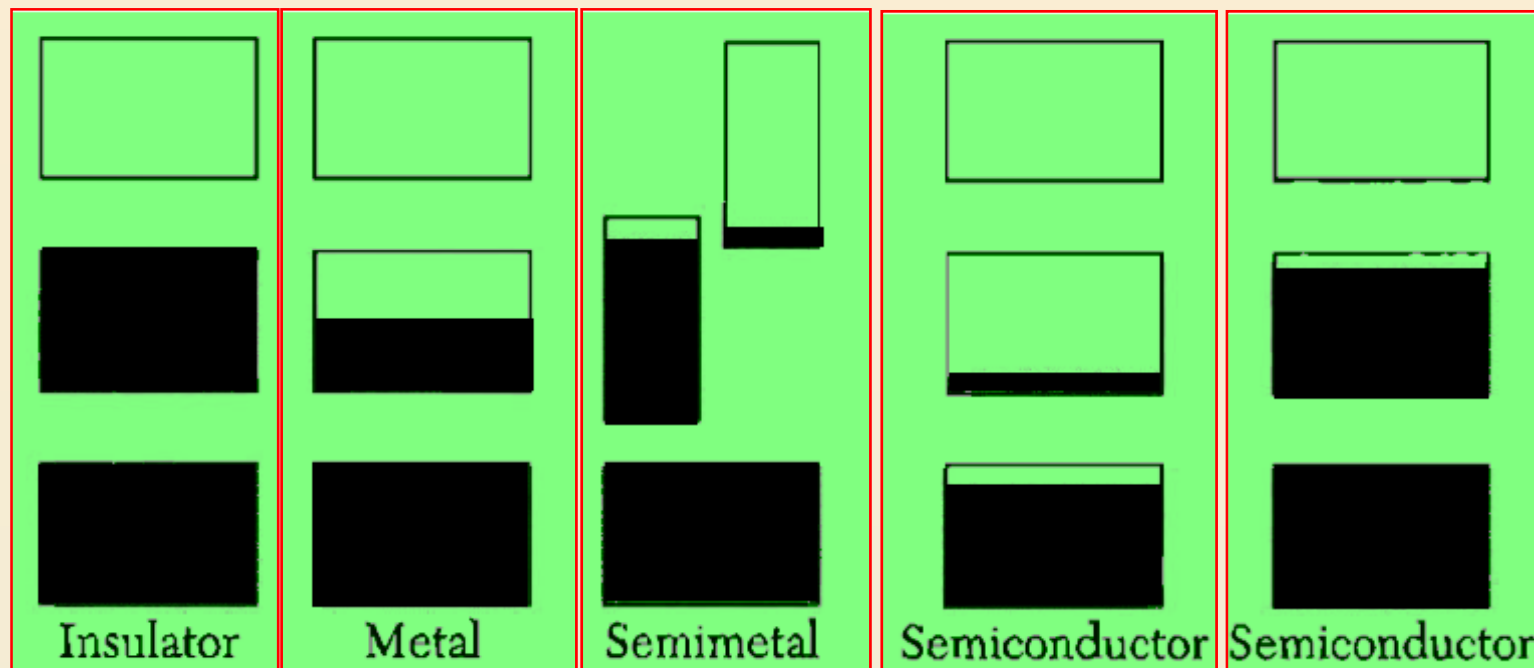
Introduction

- ☐ The difference between a good conductor and a good insulator is striking. The electrical resistivity of a pure metal may be as low as $10^{-10} \Omega \cdot \text{cm}$ at 1 K, apart from the possibility of superconductivity.
 - ☐ The resistivity of a good insulator may be as high as $10^{22} \Omega \cdot \text{cm}$.
 - ☐ This range of 10^{32} may be the widest of any common physical property of solids.
-
- ☐ Every solid contains electrons. The important question for electrical conductivity is how the electrons respond to an applied electric field.
 - ☐ electrons in crystals are arranged in energy bands.
 - ☐ Bands are separated by band gaps (Forbidden Regions)
 - ☐ Source of bands come from the interaction of the conduction electron waves with the ion cores of the crystal

Chapter 7: Energy Bands

Introduction

- ❑ Insulator: if the allowed energy bands are either filled or empty, for then no electrons can move in an electric field.
- ❑ Metal if one or more bands are partly filled.
- ❑ Semiconductor or a semimetal if one or two bands are slightly filled or slightly empty.



Chapter 7: Energy Bands

Introduction

- ❑ To modify the Free Electron Model; we will assume that electron is not totally free. It has to respect the periodicity of the crystal.
- ❑ This will directly lead to the important result: band gap.
- ❑ Also; we introduce the concept of effective mass of electron m^* *which may be larger or smaller* than the free electron mass, or may even be negative.
- ❑ Negative and Positive effective mass can directly explain for +tive Hall coefficient.



Phys 570

Lecture #6

Physics & Astronomy Dept.

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Nasser S. Alzayed

nalzayed@ksu.edu.sa

Chapter 7: Energy Bands

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Chapter 7: Energy Bands

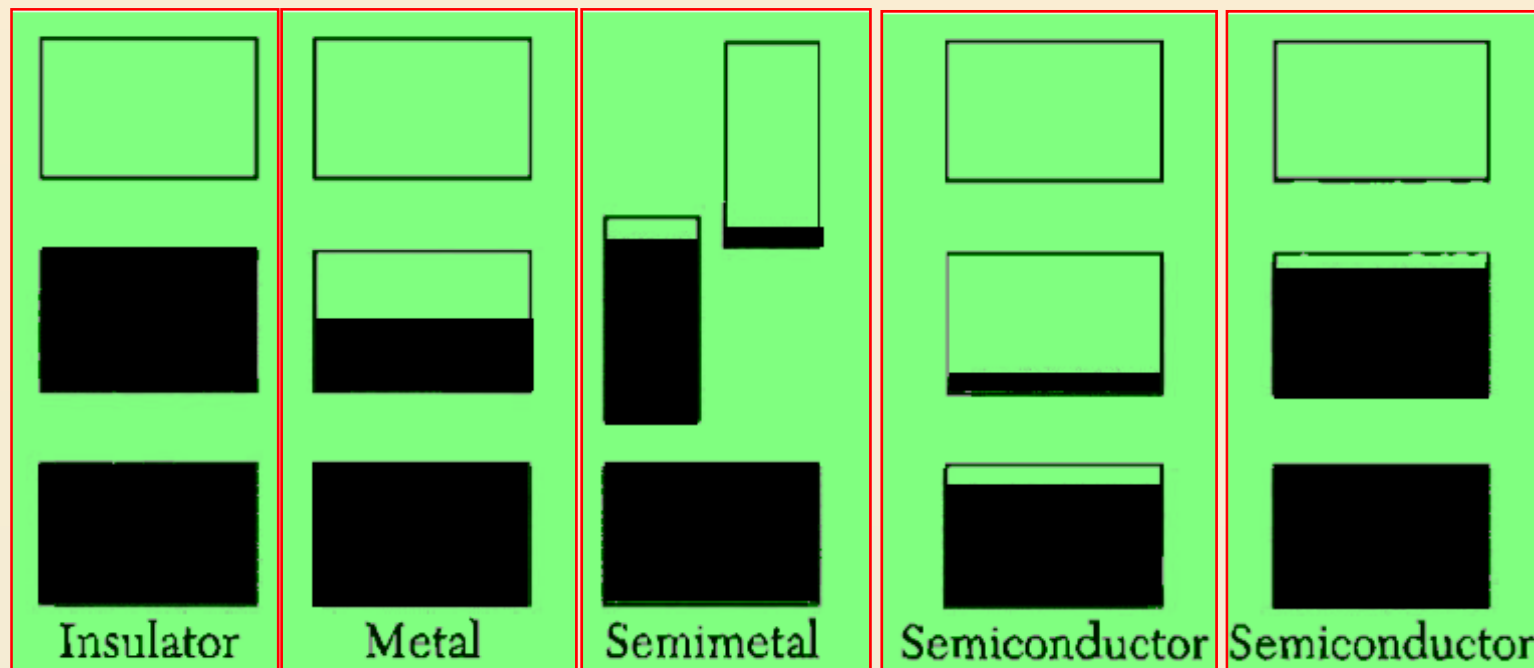
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Chapter 7: Energy Bands

Insulators, Metals and Semiconductors

- ❑ Insulator: if the allowed energy bands are either filled or empty, for then no electrons can move in an electric field.
- ❑ Metal if one or more bands are partly filled.
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Chapter 7: Energy Bands

Modifications needed for Free Electron Model

- ☐ To modify the Free Electron Model; we will assume that electron is not totally free. It has to respect the periodicity of the crystal.
- ☐ This will directly lead to the important result: band gap.
- ☐ Also; we introduce the concept of effective mass of electron m^* *which may be larger or smaller* than the free electron mass, or may even be negative.
- ☐ Negative and Positive effective mass can directly explain for +tive Hall coefficient.

Chapter 7: Energy Bands

NEARLY FREE ELECTRON MODEL (1-D)

❑ On the free electron model the allowed energy values are distributed essentially continuously from zero to infinity

$$\varepsilon_k = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad (1)$$

From boundary conditions over a cube of side L :

$$k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots \quad (2)$$

wavefunctions are of the form: $\psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}$ (3)

❑ The band structure of a crystal can often be explained by the nearly free electron model for which the band electrons are treated as perturbed only weakly by the periodic potential of the ion cores. This model answers almost all the qualitative questions about the behavior of electrons in metals.

Chapter 7: Energy Bands

Bragg Reflections

- ❑ Bragg reflection of electron waves in crystals is the cause of energy gaps. At Bragg reflection wavelike solutions of the Schrodinger equation do not exist, as in Fig. 2 (Forbidden Region)

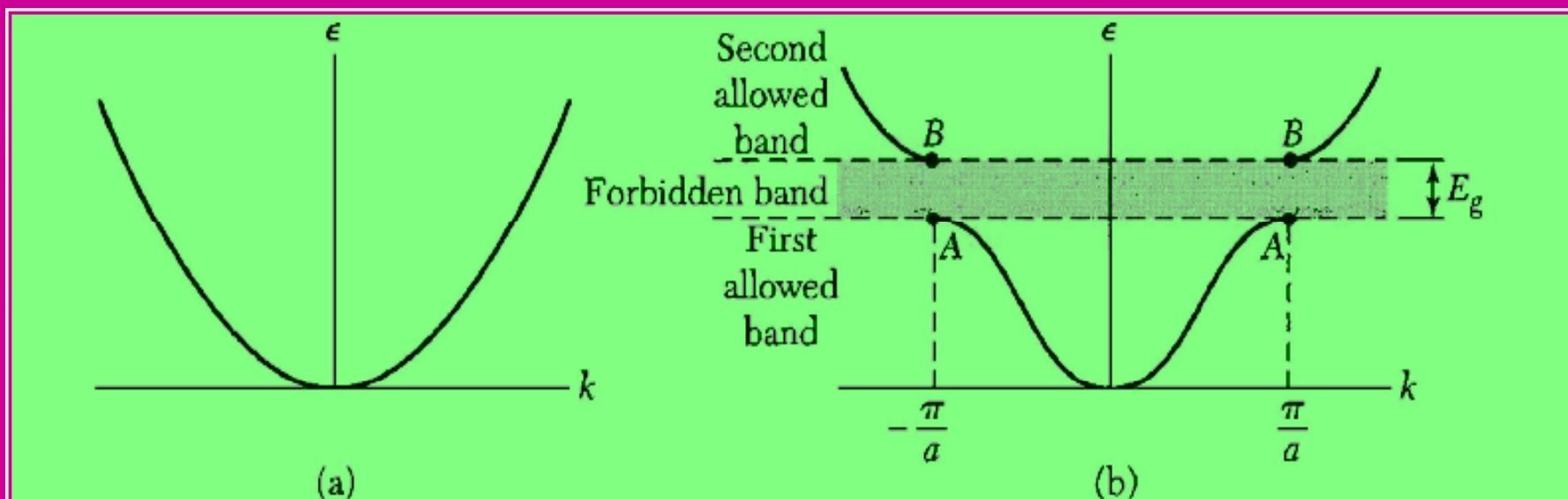


Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a . The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm \pi/a$; other gaps are found at higher energies at $\pm n\pi/a$, for integral values of n .

Chapter 7: Energy Bands

NEARLY FREE ELECTRON MODEL

□ Fig. 2, in (a) for entirely free electrons and in (b) for electrons that are nearly free, but with an energy gap at $k = \pm\pi/a$. The Bragg condition $(\mathbf{k} + \mathbf{G})^2 = \mathbf{k}^2$ for diffraction of a wave of wavevector \mathbf{k} becomes in one dimension:

$$k = \pm \frac{1}{2}G = \pm \frac{n\pi}{a} \quad (\text{in 1-D}) \quad (4)$$

□ where $G = 2\pi n/a$ is a reciprocal lattice vector and n is an integer. The first reflections and the first energy gap occur at $k = \pm\pi/a$. The region in k space between $-\pi/a$ and π/a is the first **Brillouin zone of this lattice**. Other energy gaps occur for other values of the integer n .

□ 2nd **Brillouin zone** is located between: $\pm 2\pi/a$ and so on.

Chapter 7: Energy Bands

Bragg Reflections lead to Band Gap

- ❑ Electron waves will move only inside the B.Z.
- ❑ All waves stop and Reflect at the borders of the B.Z. (From forbidden regions).
- ❑ we will have 3 different types of Waves:
 - Moving to the Right \rightarrow (will be reflected to the left from π/a)
 - Moving to the Left \leftarrow (will be reflected to the right from $-\pi/a$)
 - Standing waves (time independent. Do not move).
- ❑ Consequently: Standing waves can be used to describe the case.
- ❑ We can form two different standing waves from the two traveling waves:

$$e^{+i\pi x/a} = \cos(\pi x/a) + i \sin(\pi x/a) \quad \rightarrow$$

$$e^{-i\pi x/a} = \cos(\pi x/a) - i \sin(\pi x/a) \quad \leftarrow$$

$$\text{or: } e^{\pm i\pi x/a} = \cos(\pi x/a) \pm i \sin(\pi x/a)$$

Chapter 7: Energy Bands

NEARLY FREE ELECTRON MODEL

□ Hence; we have 2 standing waves: Even (+) and odd (-):

$$\left. \begin{aligned} \psi(+) &= e^{+i\pi x/a} + e^{-i\pi x/a} = 2\cos(\pi x/a) \\ \psi(-) &= e^{+i\pi x/a} - e^{-i\pi x/a} = 2i\sin(\pi x/a) \end{aligned} \right\} \quad (5)$$

□ In one dimension; solution to the Schrödinger equation at the boundaries of Brillouin Zone are standing waves.

Origin of the Energy Gap

- The two standing waves $\psi(+)$ and $\psi(-)$ pile up electrons at different regions, and therefore the two waves have different values of the potential energy in the field of the ions of the lattice. This is the origin of the energy gap.
- Waves traveling in different directions have different energies, leading to energy gap.

Chapter 7: Energy Bands

NEARLY FREE ELECTRON MODEL

- ❑ Let us consider the probability density ρ for both + and - (even and odd) functions.
- ❑ ρ is expressed as: $\rho = \psi^* \psi = |\psi|^2$
- ❑ For pure travelling wave: $\psi = e^{ikx} \rightarrow \rho = \psi^* \psi = |\psi|^2 = e^{-ikx} e^{ikx} = 1$
- ❑ This mean that probability of finding electron = 100% ($\rho = \text{const.}$)
- ❑ But in our case (Nearly Free Electron), ρ is not Const.

$$\rho(+)=|\psi(+)|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$$

$$\rho(-)=|\psi(-)|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$$

- ❑ Accordingly; for even functions (+): $\rho = 1$ only at specific values of x ; namely at: $x = 0, a, 2a, \dots$
- ❑ For odd functions (-): $\rho = 1$ only at: $x = 1/2 a, 3/2 a, 5/2 a, \dots$

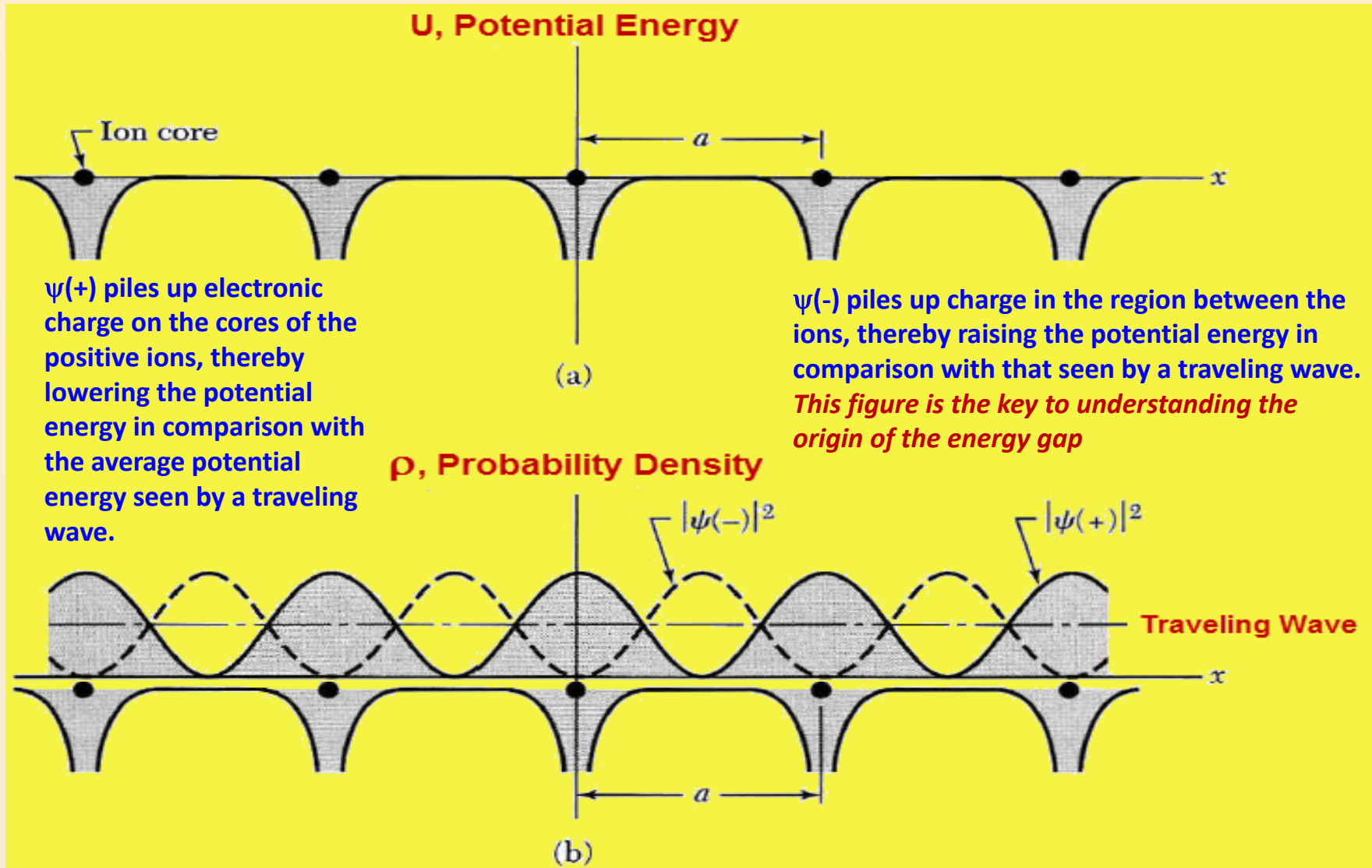
Chapter 7: Energy Bands

NEARLY FREE ELECTRON MODEL

- ☐ Hence; even function probability has its values max (=1) when the Pot. Energy is at lowest values (just at the Ions).
- ☐ On the other hand; odd function probability has its values max (=1) in the middle locations between the Ions.
- ☐ In other words: (+) function piles up electrons near the Ions while the (-) function piles up electrons in places mid-distance from two ions.
- ☐ This leads to an energy gap between the two pools of electrons.
- ☐ If we calculate the expectation values (average energy) in these three cases: + , - , and Free electron (travelling wave): we have:
 - ☐ that of $\rho(+)$ is lower than that of Free Electron
 - ☐ that of $\rho(-)$ is above that of Free Electron.
- ☐ Result is: E_g difference in energy between the $\rho(+)$ and $\rho(-)$
- ☐ This is the origin of the Band Gap.

Chapter 7: Energy Bands

NEARLY FREE ELECTRON MODEL



Chapter 7: Energy Bands

Magnitude of the Energy Gap

□ Let us suppose that the potential energy of an electron in the crystal at point x is:

$$U(x) = U \cos\left(\frac{2\pi}{a}x\right)$$

The first-order energy difference between the two standing wave states is :

$$\begin{aligned} E_g &= \int_0^1 U(x) \left[|\psi(+)|^2 - |\psi(-)|^2 \right] dx \\ &= \int U \cos\left(\frac{2\pi}{a}x\right) \left[\cos^2 \frac{\pi x}{a} - \sin^2 \frac{\pi x}{a} \right] dx \\ &= U \end{aligned} \tag{6}$$

□ We see that the gap is equal to the Fourier component of the crystal potential.

Chapter 7: Energy Bands

BLOCH FUNCTIONS

❑ F. Bloch proved the important theorem that the solutions of the Schrodinger equation for a periodic potential must be of a special form:

$$\psi_k(r) = u_k(r) e^{ik \cdot r} \quad (7)$$

❑ $u_k(r)$ has same periodicity of the crystal with $u_k(r) = u_k(r + T)$

❑ T is the translation vector of the lattice in normal space.

❑ Eq. (7) means that:

The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave $\exp(ik \cdot r)$ times a function $u_k(r)$ with the periodicity of the crystal lattice.

❑ Bloch functions can be assembled into wave packets to represent electrons that propagate freely through the potential field of the ion cores.

Chapter 7: Energy Bands

Proof of BLOCH FUNCTIONS

- We consider N identical lattice points on a ring of length Na . The potential energy is periodic in a , with $U(x) = U(x + sa)$, where s is an integer.
- symmetry of the ring leads to:

$$\psi(x + a) = C \psi(x) \quad (8)$$

where C is a constant. Then, on going once around the ring:

$$\psi(x + Na) = \psi(x) = C^N \psi(x)$$

because $\psi(x)$ must be single-valued.

It follows that C is one of the N roots of unity, or:

$$C = e^{i 2\pi s / N} \quad s = 0, 1, 2, \dots, N - 1 \quad (9)$$

satisfies (8), provided that $U_k(x)$ has the periodicity a , so that $U_k(x) = U_k(x + a)$.

This is the Bloch result (7).



Phys 570

Lecture #7

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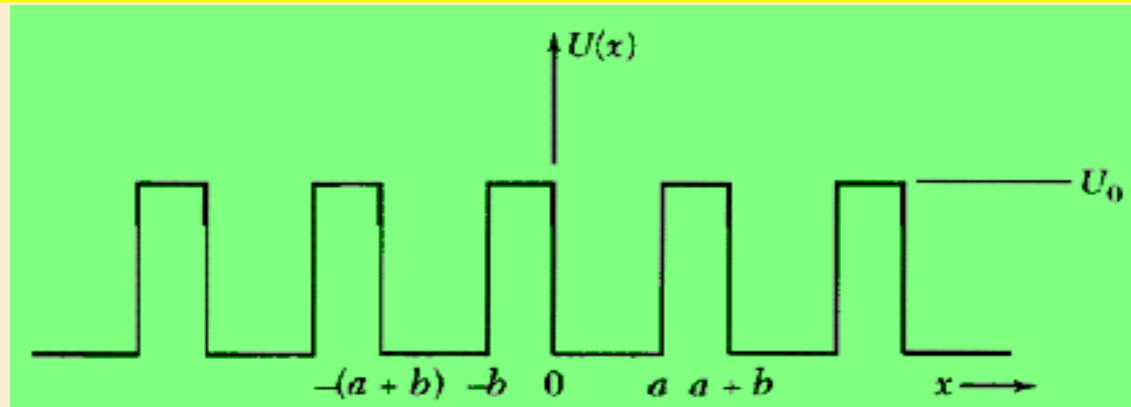
Nasser S. Alzayed

nalzayed@ksu.edu.sa

Chapter 7: Energy Bands

Kronig-Penny Model

- ❑ This model solves for periodic potential in a form of a square-well array:



- ❑ Schrodinger wave equation for this potential can take the form:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = \varepsilon\psi \quad (11)$$

where $U(x)$ is the potential energy and ε is the energy eigenvalue.
We have 2 regions: $0 < x < a$ ($U = 0$) and $-b < x < 0$ ($U \neq 0$)

Chapter 7: Energy Bands

Kronig-Penny Model

□ For the first region we have the wave function:

$$\psi = Ae^{iKx} + Be^{-iKx} \quad (12)$$

This is a combination of plane waves traveling to the right and to the left, with energy:

$$\varepsilon = \frac{\hbar^2 K^2}{2m} \quad (13)$$

□ In the 2nd region, wave function takes the form:

$$\psi = Ce^{Qx} + De^{-Qx} \quad (14)$$

with energy:

$$U_o - \varepsilon = \frac{\hbar^2 Q^2}{2m} \quad (15)$$

Chapter 7: Energy Bands

Kronig-Penny Model

- ❑ Solution of this equation shall be on the Bloch form (7) because it is a periodic potential.
- ❑ Thus the solution in the region $a < x < a+b$ must be related to the solution (14) in the region $-b < x < 0$ by the Bloch theorem:

$$\psi_k(r) = u_k(r) e^{ik \cdot r} \quad (7)$$

$$\psi(a < x < a+b) = \psi(-b < x < 0) e^{ik(a+b)} \quad (16)$$

- ❑ The constants A, B, C, D are chosen so that ψ and ψ' are continuous at $x=0$ and $x=a$. same as in square potential wells.
- ❑ At $x = 0$ we have (for both conditions): (12) + (14):

$$A + B = C + D \quad (17)$$

Derivatives of (12) and (14) at $x = 0$ provides:

$$iK(A - B) = Q(C - D) \quad (18)$$

Chapter 7: Energy Bands

Kronig-Penny Model

□ for the case of $x = a$; and applying continuity of ψ and ψ' we will get:

$$Ae^{iKa} + Be^{-iKa} = (Ce^{-Qb} + De^{Qb})e^{ik(a+b)} \quad (19)$$

$$iK(Ae^{iKa} - Be^{-iKa}) = Q(Ce^{-Qb} - De^{Qb})e^{ik(a+b)} \quad (20)$$

□ Solving equations from (17) to (20) can be done by putting all coefficients of A, B, C, D in a determinant. However, such solution is very difficult. We will only write down the final equation:

$$\left[\frac{Q^2 - K^2}{2QK} \right] \sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a+b) \quad (21a)$$

□ to simplify the solution; we represent the potential by a Delta Function. Let: $b \rightarrow 0$ and $U_0 \rightarrow \infty$

Chapter 7: Energy Bands

Kronig-Penny Model

□ We do some approximation:

$$Q \gg K \quad Qb \ll 1$$

$$\sinh Qb \rightarrow Qb$$

$$\cosh Qb \rightarrow 1$$

$$\cos k(a+b) \rightarrow \cos ka$$

notice that: $Q^2 \gg K^2$, hence: (21a) \Rightarrow

$$\frac{Q^2}{2QK} Qb \sin Ka + \cos Ka = \cos ka$$

$$\left[\frac{P}{Ka} \right] \sin Ka + \cos Ka = \cos ka \quad (21b)$$

$$\text{with } P = \frac{Q^2 ba}{2}$$

Chapter 7: Energy Bands

Kronig-Penny Model

- ❑ The ranges of K for which this equation has solutions are plotted in Fig. 5, for the case $P = 3\pi/2$. The corresponding values of the energy are plotted in Fig. 6. Note the energy gaps at the zone boundaries.

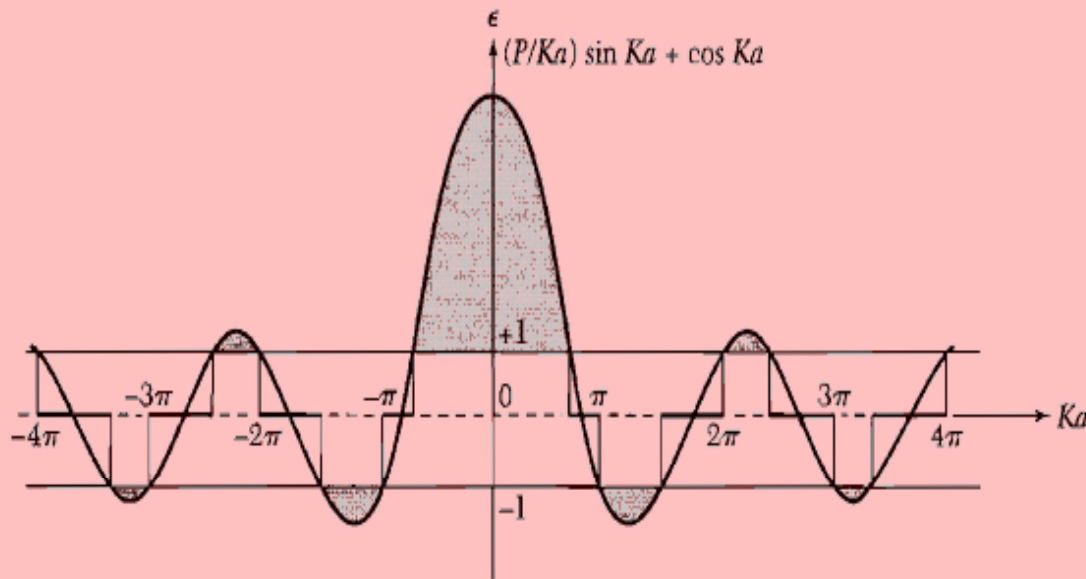
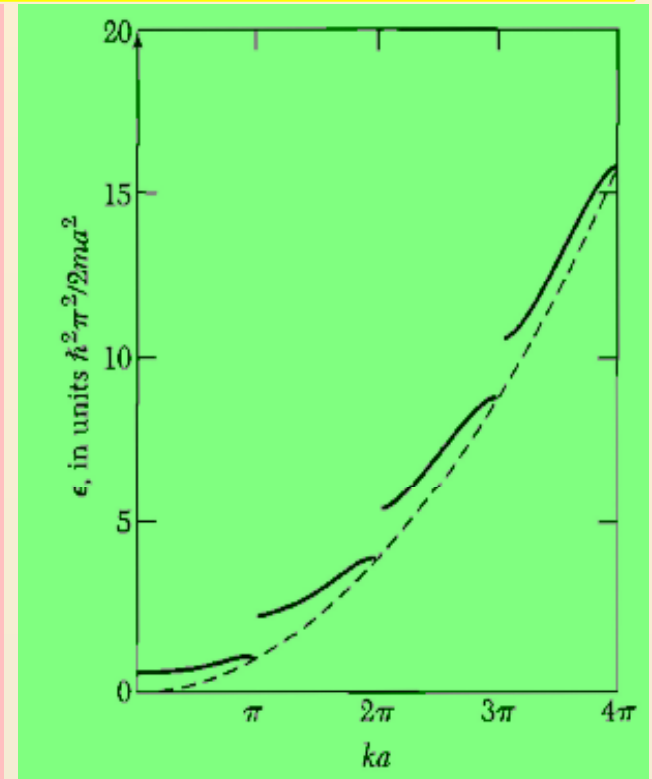


Figure 5 Plot of the function $(P/Ka) \sin Ka + \cos Ka$, for $P = 3\pi/2$. The allowed values of the energy e are given by those ranges of $Ka = (2m\epsilon/\hbar^2)^{1/2}a$ for which the function lies between ± 1 . For other values of the energy there are no traveling wave or Bloch-like solutions to the wave equation, so that forbidden gaps in the energy spectrum are formed.



Chapter 7: Energy Bands

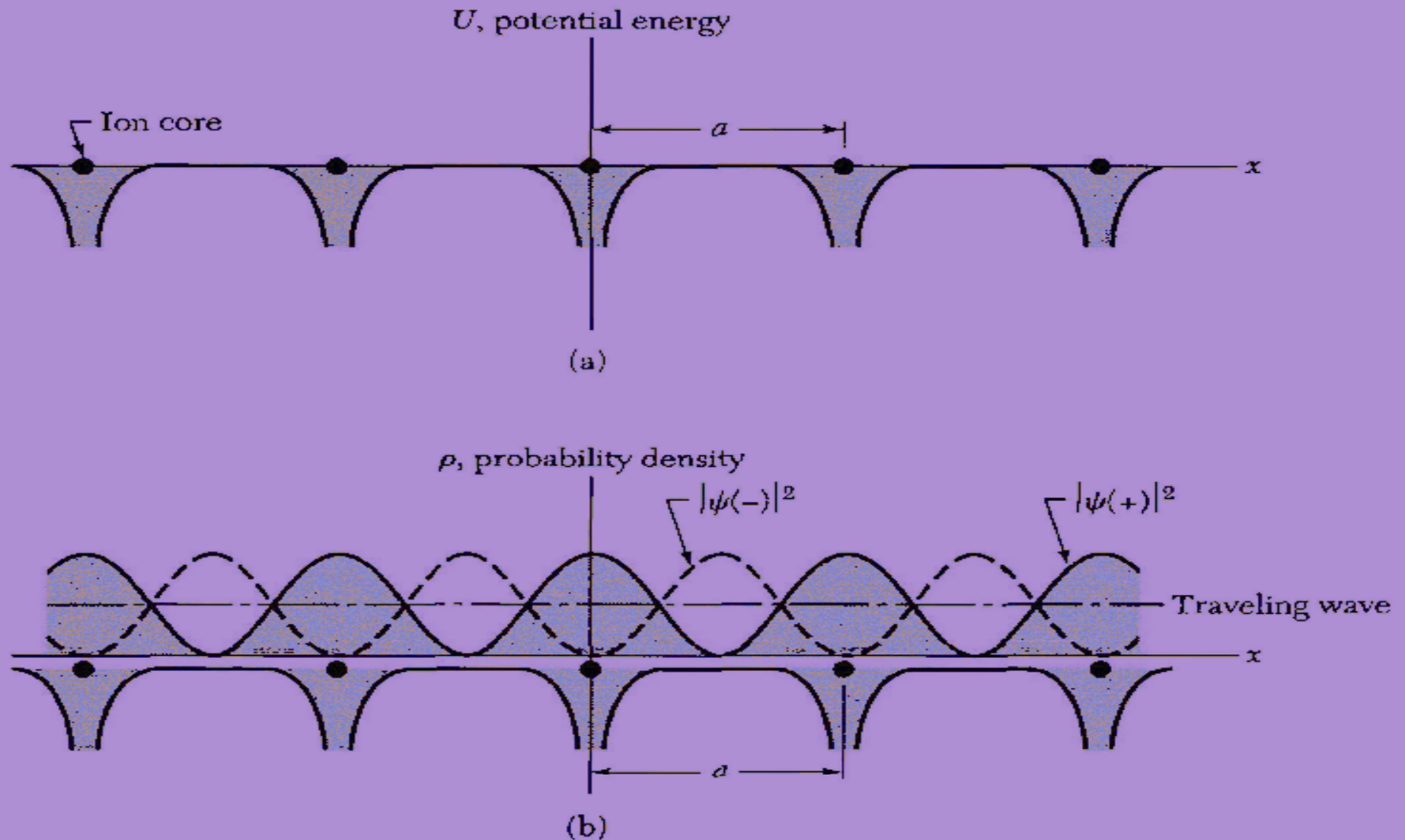
WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL

- ❑ We considered in Fig. 3 the approximate form we expect for the solution of the Schrödinger equation if the wave vector is at a zone boundary, as at $k = \pm\pi/a$.
- ❑ Here, we treat in detail the wave equation for a general potential, at general values of k .
- ❑ Let $U(x)$ denote the potential energy of an electron in a linear lattice of lattice constant a . Potential energy is invariant under the lattice translation. Hence: $U(x) = U(x + a)$.
- ❑ A function invariant under a crystal lattice translation may be expanded as a Fourier series in the reciprocal lattice vectors G .
- ❑ As a rule: **There is periodicity : There is Fourier Transform**
- ❑ We write the Fourier series for the potential energy as:

$$U(x) = \sum_G U_G e^{iGx} \quad (22)$$

Chapter 7: Energy Bands

WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL



Chapter 7: Energy Bands

WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL

- ❑ Please review Fourier Analysis.
- ❑ For actual crystal potentials; the values of the coefficients U_G tend to decrease rapidly with increasing magnitude of G . For a coulomb potential: U_G decreases as $1/G^2$
- ❑ In equation (22), we did not specify the x -values. We want to use only **real** values. Accordingly: (22) can be rewritten as:

$$U(x) = \sum_{G>0} U_G (e^{iGx} + e^{-iGx}) = 2 \sum_{G>0} U_G \cos Gx \quad (23)$$

- ❑ The wave equation of an electron in the crystal is $H\psi = \epsilon\psi$ where H is the Hamiltonian and ϵ is the energy eigenvalue.
- ❑ The full equation is then:

$$\left[\frac{p^2}{2m} + U(x) \right] \psi(x) = \left[\frac{p^2}{2m} + \sum_G U(x) e^{iGx} \right] \psi(x) = \epsilon \psi(x) \quad (24)$$

Chapter 7: Energy Bands

WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL

- ❑ Equation (24) is written in the one-electron approximation in which the orbital $\psi(x)$ describes the motion of one electron in the potential of the ion cores and in the average potential of the other conduction electrons.
- ❑ The wavefunction $\psi(x)$ may be expressed as a Fourier series summed over all values of the wavevector permitted by the boundary conditions, so that:

$$\psi = \sum_k C(k) e^{ikx} \quad (25)$$

- ❑ The set of values of k has the form $2\pi n/L$.
- ❑ To solve the wave equation, substitute (25) in (24) to obtain a set of linear algebraic equations for the Fourier coefficients.
- ❑ We will take the solution as term by term:

Chapter 7: Energy Bands

WAVE EQUATION OF ELECTRON IN A PERIODIC POTENTIAL

□ The kinetic energy term is:

$$\frac{p^2}{2m} \psi(x) = \frac{1}{2m} \left(-i \hbar \frac{d}{dx} \right)^2 \psi(x) = \frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = \frac{\hbar^2}{2m} \sum_k k^2 C(k) e^{ikx} \quad (i)$$

and the potential energy term is :

$$U(x) \psi(x) = \left(\sum_G U_G e^{iGx} \right) \psi(x) = \sum_G \sum_k U_G e^{iGx} C(k) e^{ikx} \quad (ii)$$

The full Schrodinger Eq. becomes:

$$\frac{\hbar^2}{2m} \sum_k k^2 C(k) e^{ikx} + \sum_G \sum_k U_G C(k) e^{i(k+G)x} = \varepsilon \sum_k C(k) e^{ikx} \quad (26)$$

For 1 K value, this equation becomes:

$$\frac{\hbar^2 k^2}{2m} C(k) + \sum_G U_G C(k - G) = \varepsilon \sum_k C(k) e^{ikx} \quad (26)$$

Chapter 7: Energy Bands

Solution of the Central Equation

□ Each Fourier component must have the same coefficient on both sides of the equation. Thus we have the **central equation**:

$$(\lambda_k - \varepsilon)C(k) + \sum_G U_G C(k - G) = 0 \quad (27)$$

with :

$$\lambda_k = \hbar^2 k^2 / 2m \quad (28)$$

- Eq. (27) is the Algebraic form of the well know Schrodinger equation in a periodic potential (24).
- It is not easy to solve it, but usually one can use only few terms.
- No. of solutions of this equation = no. of equations it has = No. of Fourier coefficients $C(K - G)$.

Chapter 7: Energy Bands

Solution of the Central Equation

- Eq. (27) represents a set of simultaneous linear equations that connect the coefficients $C(k - G)$ for all reciprocal lattice vectors G . It is a set because there are as many equations as there are coefficients C .
- To solve it, the determinant of the coefficients must vanish.
- As an application: for the case when $G = g$ (Shortest values of G):

$$\begin{bmatrix} \varepsilon_{k-2g} - \varepsilon & U_g & 0 & 0 & 0 \\ U_g & \varepsilon_{k-g} - \varepsilon & U_g & 0 & 0 \\ 0 & U_g & \varepsilon_k - \varepsilon & U_g & 0 \\ 0 & 0 & U_g & \varepsilon_{k+g} - \varepsilon & U_g \\ 0 & 0 & 0 & U_g & \varepsilon_{k+2g} - \varepsilon \end{bmatrix} \begin{bmatrix} C(k-2g) \\ C(k-g) \\ C(k) \\ C(k+g) \\ C(k+2g) \end{bmatrix} = 0 \quad (32)$$

- The solution of the determinant (32) gives a set of energy eigenvalues ε_{nk} .

Chapter 7: Energy Bands

Empty Lattice Approximation

- ❑ Band structures are usually plotted as energy versus wavevector in the first Brillouin zone. When wavevectors are outside this zone, they are carried back into the first zone by translation.
- ❑ We look for a G such that a k' in the first zone satisfies: $k' + G = k$
- ❑ where k is the free electron wavevector in the empty lattice.
- ❑ We can drop the ' from k since G can be - or + :

$$\varepsilon(k_x, k_y, k_z) = \frac{\hbar^2}{2m} (k + G)^2 = \frac{\hbar^2}{2m} \left[(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2 \right]$$

- ❑ We consider as an example free electron bands of a simple cubic lattice. Suppose we want to exhibit the energy as a function of k in the [100] direction. Let $\hbar^2 / 2m = 1$. We show several bands in this empty lattice approximation with their energies $\varepsilon(000)$ at $k = 0$ and $\varepsilon(k_x 00)$ along the k_x axis in the first zone:

Chapter 7: Energy Bands

Empty Lattice Approximation

Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x 00)$
1	000	0	k_x^2
2,3	100,100	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	010,0 $\bar{1}$ 0,001,00 $\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	$\bar{1}$ 10,101,1 $\bar{1}$ 0,10 $\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}$ 10, $\bar{1}$ 01, $\bar{1}$ 10, $\bar{1}$ 0 $\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
16,17,18,19	011,0 $\bar{1}$ 1,01 $\bar{1}$,0 $\bar{1}$ $\bar{1}$	$2(2\pi/a)^2$	$k_x^2 + 2(2\pi/a)^2$

Chapter 7: Energy Bands

Empty Lattice Approximation

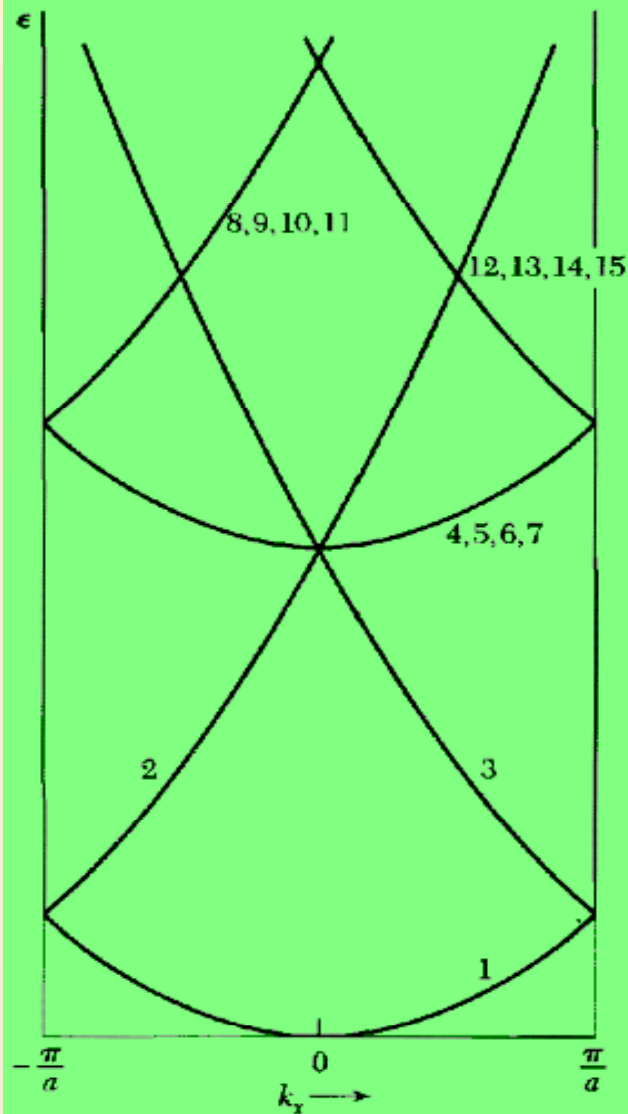


Figure 8 Low-lying free electron energy bands of the empty *sc* lattice, as transformed to the first Brillouin zone and plotted vs. $(k_x, 0)$. The free electron energy is $\hbar^2(\mathbf{k} + \mathbf{G})^2/2m$, where the \mathbf{G} 's are given in the second column of the table. The bold curves are in the first Brillouin zone, with $-\pi/a \leq k_x \leq \pi/a$. Energy bands drawn in this way are said to be in the reduced zone scheme.

Chapter 7: Energy Bands

Empty Lattice Approximation

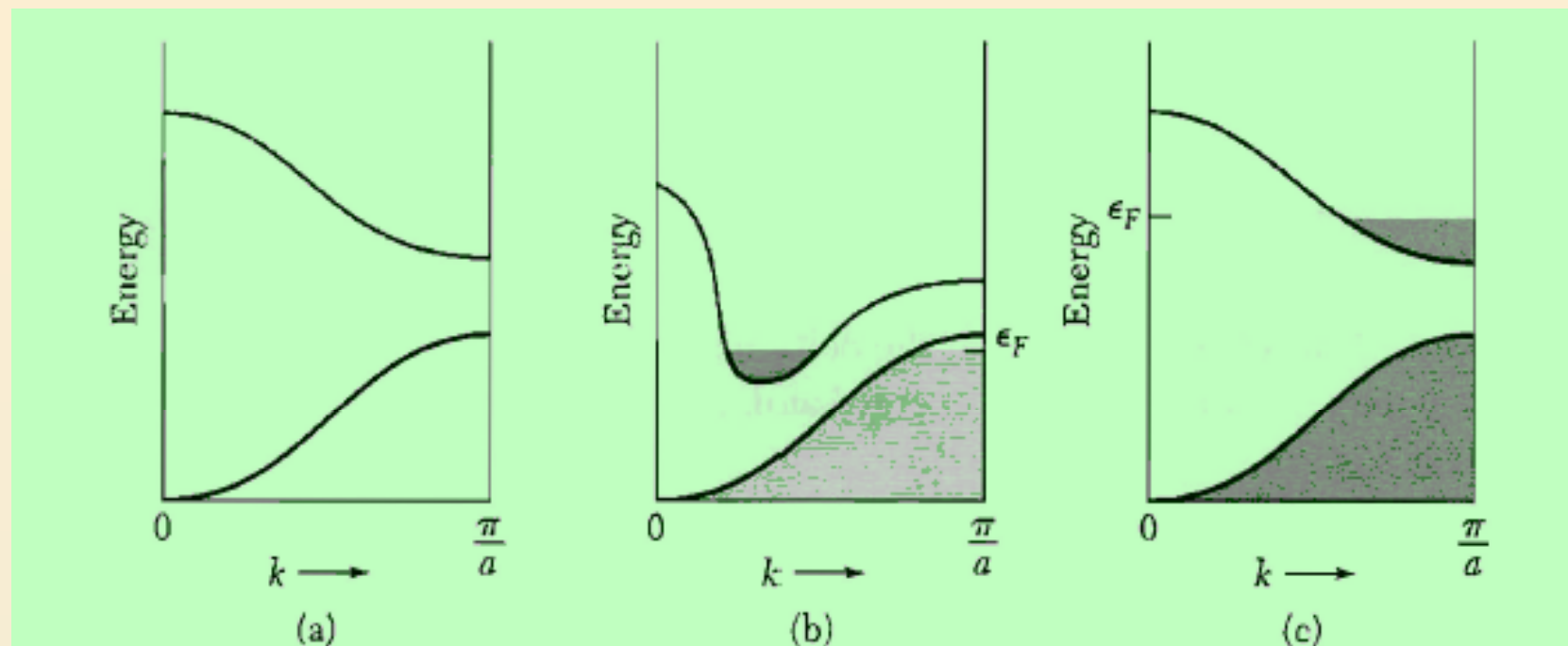


Figure 11 Occupied states and band structures giving (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration. In (b) the overlap need not occur along the same directions in the Brillouin zone. If the overlap is small, with relatively few states involved, we speak of a semimetal.



Phys 570

Lecture #8

Physics & Astronomy Dept.

College of Science

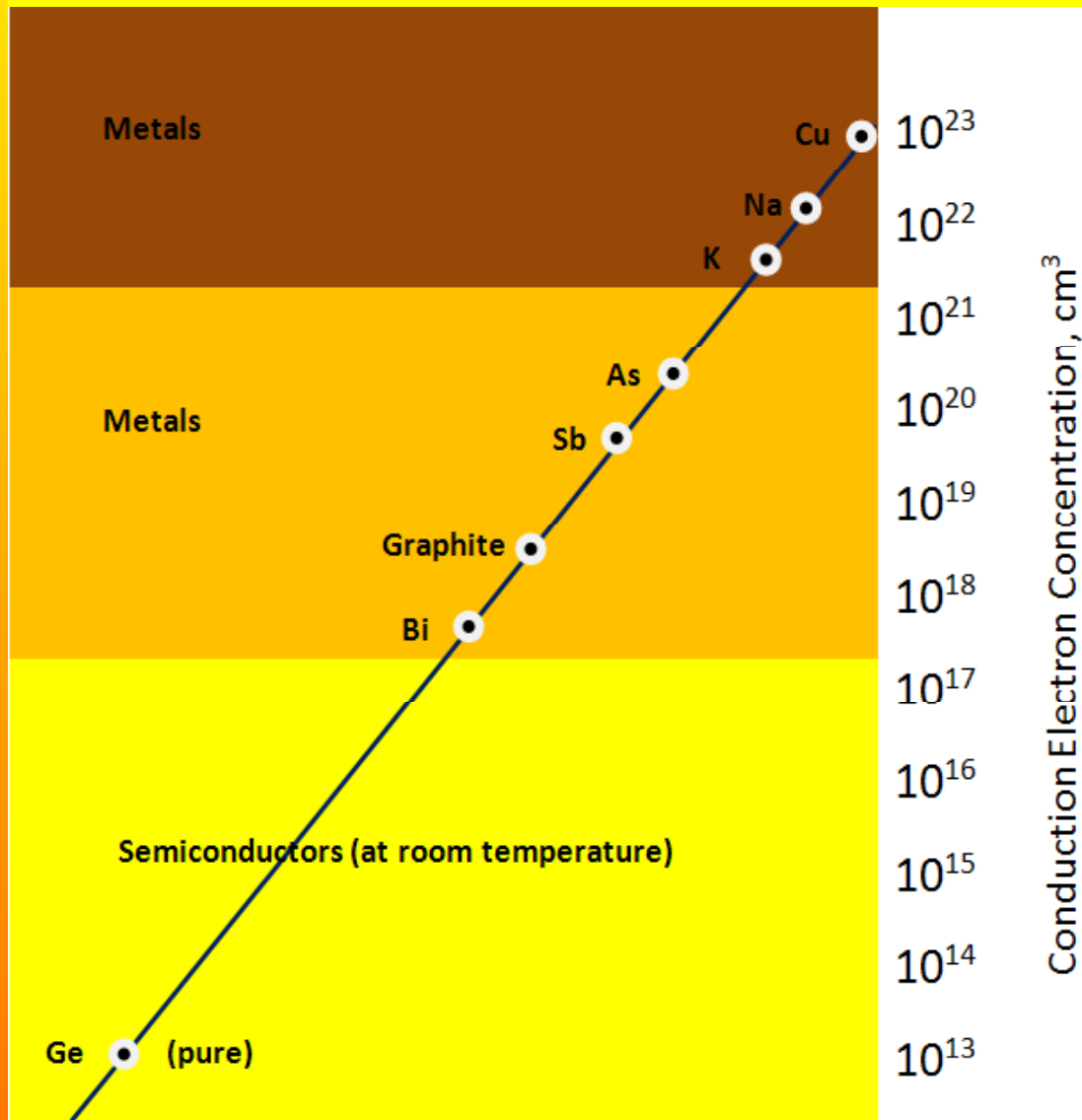
King Saud University

Nasser S. Alzayed

nalzayed@ksu.edu.sa

Chapter 8: SEMICONDUCTOR CRYSTALS

Introduction



Carrier concentrations for metals, semimetals, and semiconductors. The semiconductor range may be extended upward by increasing the impurity concentration, and the range can be extended downward to merge eventually with the insulator range.

Chapter 8: SEMICONDUCTOR CRYSTALS

Introduction

- ☐ Conductors are classified based on electron concentration.
- ☐ Semiconductors are generally classified by their electrical resistivity at room temperature, with values in the range of 10^{-2} to $10^9 \Omega\text{-cm}$, and strongly dependent on temperature.
- ☐ At 0 K, a pure, semiconductor will be an insulator.
- ☐ Devices based on semiconductors include:
 - ✓ transistors
 - ✓ Switches
 - ✓ Diodes
 - ✓ photovoltaic cells
 - ✓ Detectors
 - ✓ Thermistors
- ☐ Popular semiconductors are: **silicon**, **germanium**, and **gallium arsenide**.

Chapter 8: SEMICONDUCTOR CRYSTALS

Semiconductor Classes

Semiconductors are classified into 3 main types:

- ❑ III-V (three-five) compounds. Examples are indium antimonide and gallium arsenide.
- ❑ II -VI compound; examples are zinc sulfide and cadmium sulfide.
- ❑ IV-IV compound like: Silicon carbide SiC .

Semiconductors are also classified in different way:

- ❑ ***Intrinsic***: (pure semiconductor)
 - ✓ the electrical properties of a semiconductor are not essentially modified by impurities in the crystal.
 - ✓ An electronic band scheme leading to intrinsic conductivity is indicated in Fig. 2.
 - ✓ The conduction band is vacant at absolute zero and is separated by an energy gap E_g from the filled valence band.

Chapter 8: SEMICONDUCTOR CRYSTALS

Intrinsic Semiconductor

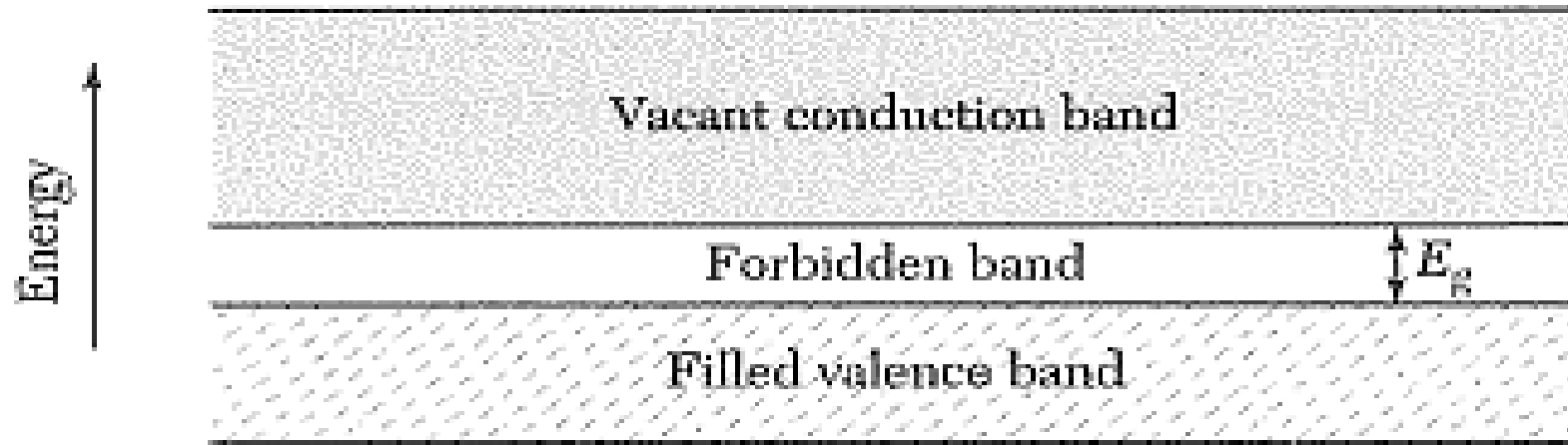


Figure 2 Band scheme for intrinsic conductivity in a semiconductor. At 0 K the conductivity is zero because all states in the valence band are filled and all states in the conduction band are vacant. As the temperature is increased, electrons are thermally excited from the valence band to the conduction band, where they become mobile. Such carriers are called "intrinsic."

Chapter 8: SEMICONDUCTOR CRYSTALS

Extrinsic Semiconductors

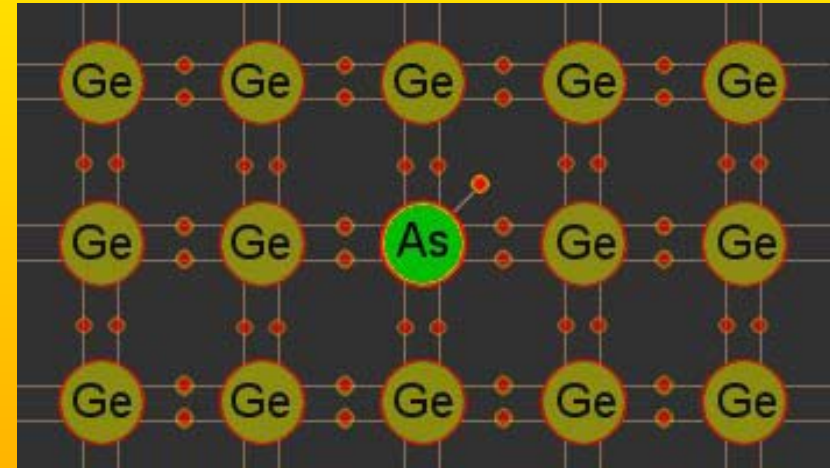
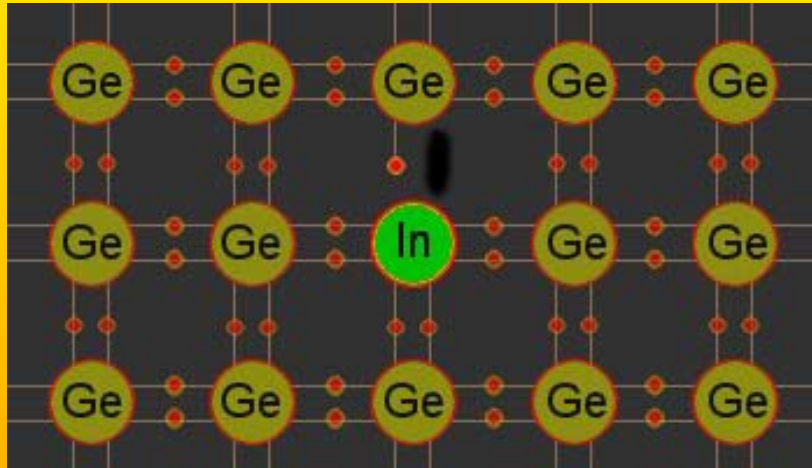
Extrinsic: (doped semiconductor)

- ❑ This type is not pure. Its conductivity depends on doping.
- ❑ An extrinsic semiconductor can be formed from an intrinsic semiconductor by adding impurity atoms to the crystal in a process known as doping.

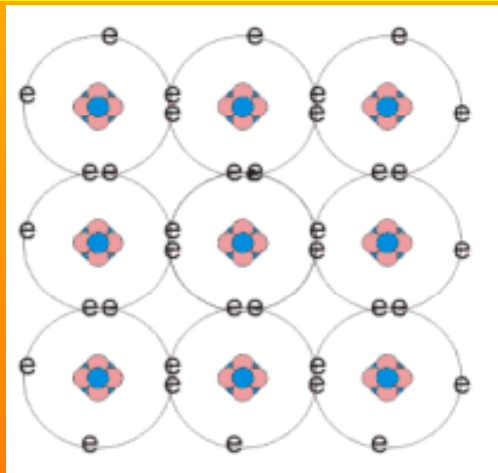
❑ For instance, Since Silicon belongs to group IV of the periodic table, it has 4 valence electrons. Each atom shares an electron with a neighboring atom. In this state it is an ***intrinsic*** semiconductor. B, Al, In, Ga all have three electrons in the valence band. When a small proportion of these atoms, (less than 1 in 10^6), is doped into the crystal the dopant atom has an insufficient number of bonds to share bonds with the surrounding Silicon atoms. One of the Silicon atoms has a vacancy for an electron. It creates a hole that contributes to the conduction process at all temperatures. Dopants that create holes in this manner are known as acceptors. This type of extrinsic semiconductor is known as ***p-type***. Elements that belong to group V of the periodic table such as As, P, Sb have an extra electron in the valence band. When added as a dopant to intrinsic Silicon, the dopant atom contributes an additional electron to the crystal. Dopants that add electrons to the crystal are known as donors and the semiconductor material is said to be ***n-type***.

Chapter 8: SEMICONDUCTOR CRYSTALS

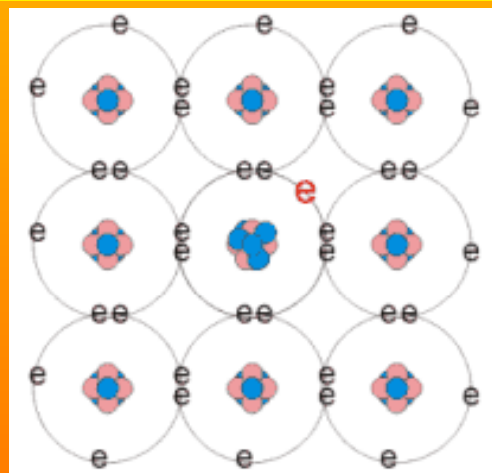
Intrinsic and Extrinsic Semiconductors



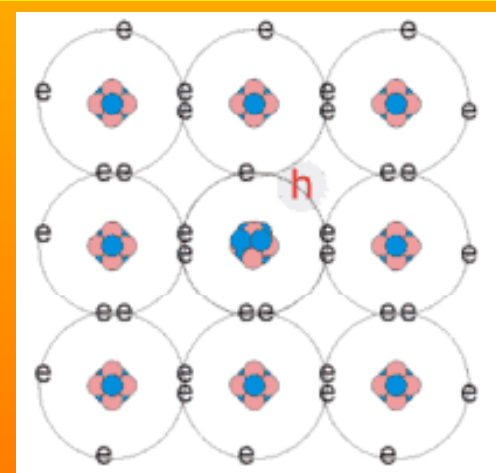
P-type (left) and n-type (right) of extrinsic semiconductors



Intrinsic



n-type



P-type

Chapter 8: SEMICONDUCTOR CRYSTALS

Definition of Band gap

- ❑ The band gap is the difference in energy between the lowest point of the conduction band and the highest point of the valence band.
- ❑ The lowest point in the conduction band is called the *conduction band edge*
- ❑ the highest point in the valence band is called the *valence band edge*.
- ❑ As the temperature is increased, electrons are thermally excited from the valence band to the conduction band (Fig. 3).
- ❑ Both the electrons in the conduction band and the vacant orbitals or holes left behind in the valence band contribute to the electrical conductivity.

Chapter 8: SEMICONDUCTOR CRYSTALS

Definition of Band gap

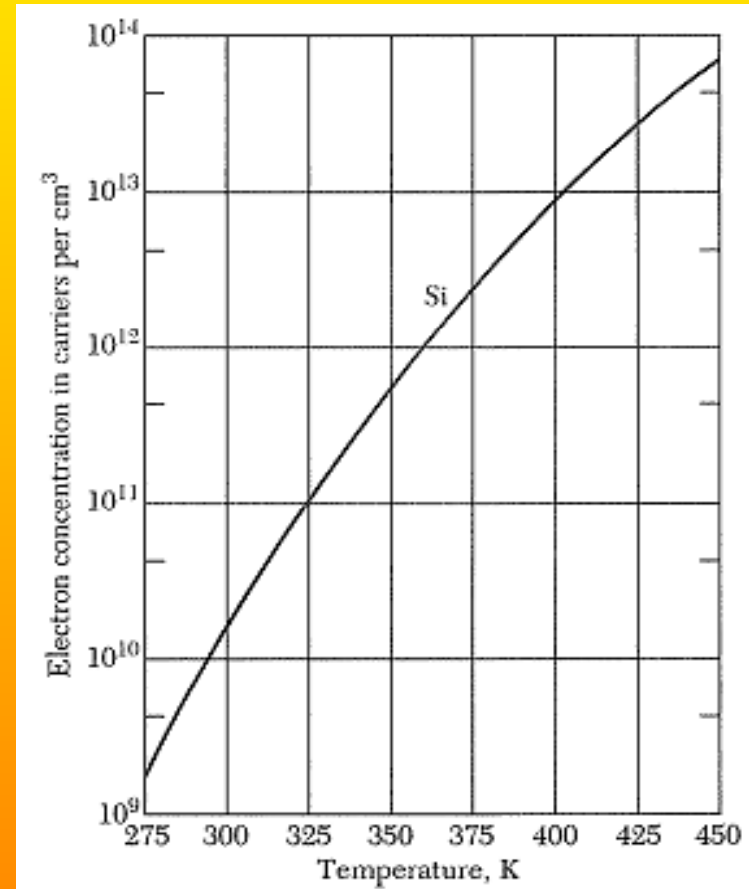
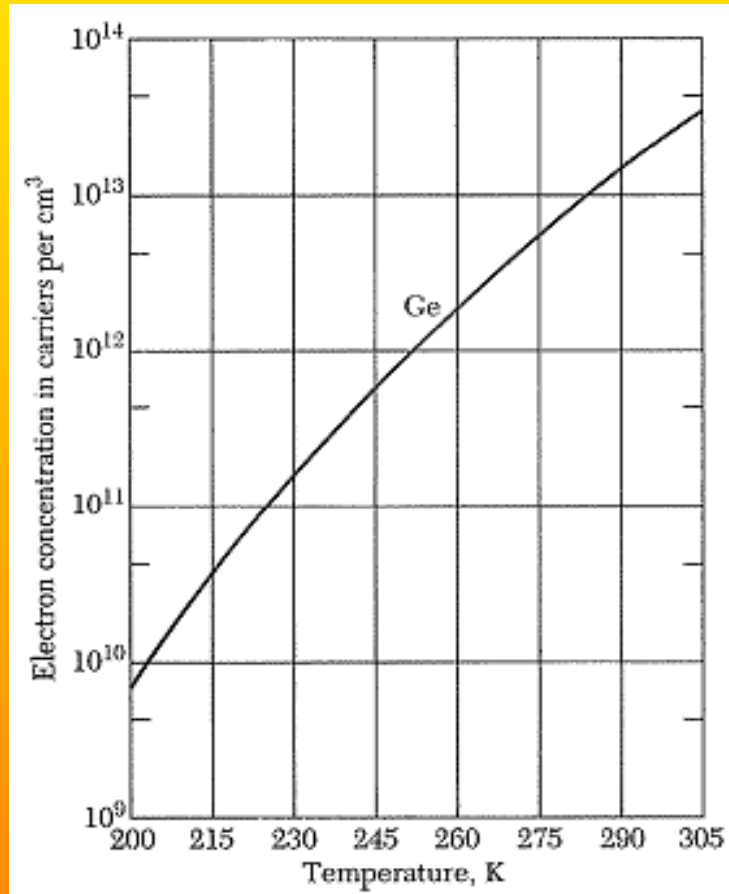


Figure 3: Intrinsic electron concentration as a function of temp. for (a) germanium and (b) silicon. Under intrinsic conditions the hole concentration is equal to the electron concentration.

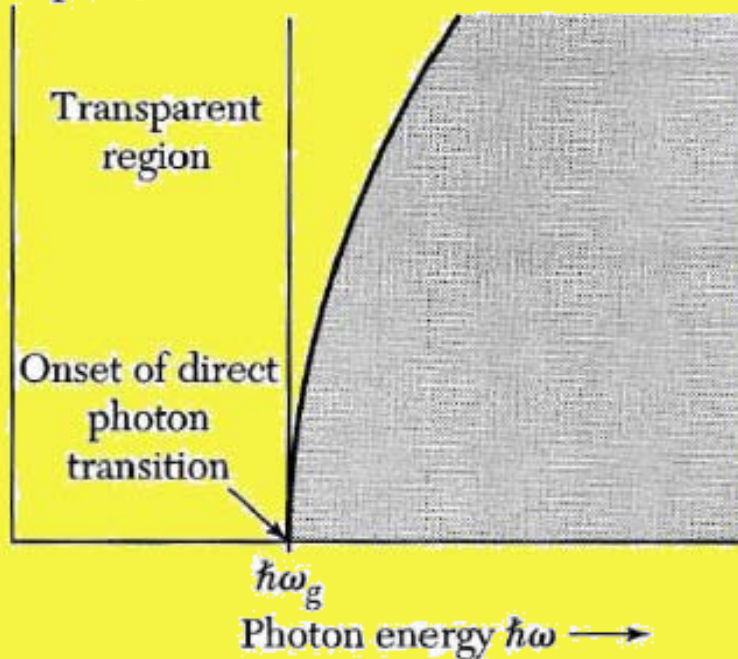
Chapter 8: SEMICONDUCTOR CRYSTALS

Direct and Indirect absorption

- ❑ The intrinsic conductivity and intrinsic carrier concentrations are largely controlled by $E_g/K_B T$
- ❑ When this ratio is large, the concentration of intrinsic carriers will be low and the conductivity will be low.
- ❑ The best values of the band gap are obtained by optical absorption. There are 2 different methods:
 - 1- direct absorption process**
 - 2- indirect absorption process**
- ❑ **For Direct absorption Process:**
the threshold of continuous optical absorption at frequency ω_g measures the band gap $E_g = \hbar \omega_g$ as shown in Figs. 4a and 5a. A photon is absorbed by the crystal with the creation of an electron and a hole.

CRYSTAL WITH DIRECT GAP

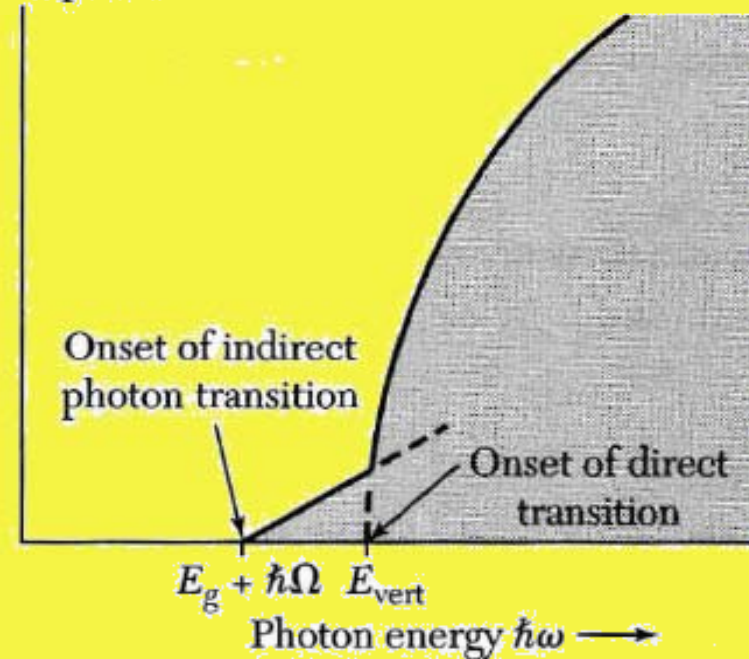
Absorption



(a)

CRYSTAL WITH INDIRECT GAP

Absorption



(b)

Figure 4 Optical absorption in pure insulators at absolute zero. In (a) the threshold determines the energy gap as $E_g = \hbar\omega_g$. In (b) the optical absorption is weaker near the threshold: at $\hbar\omega = E_g + \hbar\Omega$ a photon is absorbed with the creation of three particles: a free electron, a free hole, and a phonon of energy $\hbar\Omega$. In (b) the energy E_{vert} marks the threshold for the creation of a free electron and a free hole, with no phonon involved. Such a transition is called vertical; it is similar to the direct transition in (a). These plots do not show absorption lines that sometimes are seen lying just to the low energy side of the threshold. Such lines are due to the creation of a bound electron-hole pair, called an exciton.

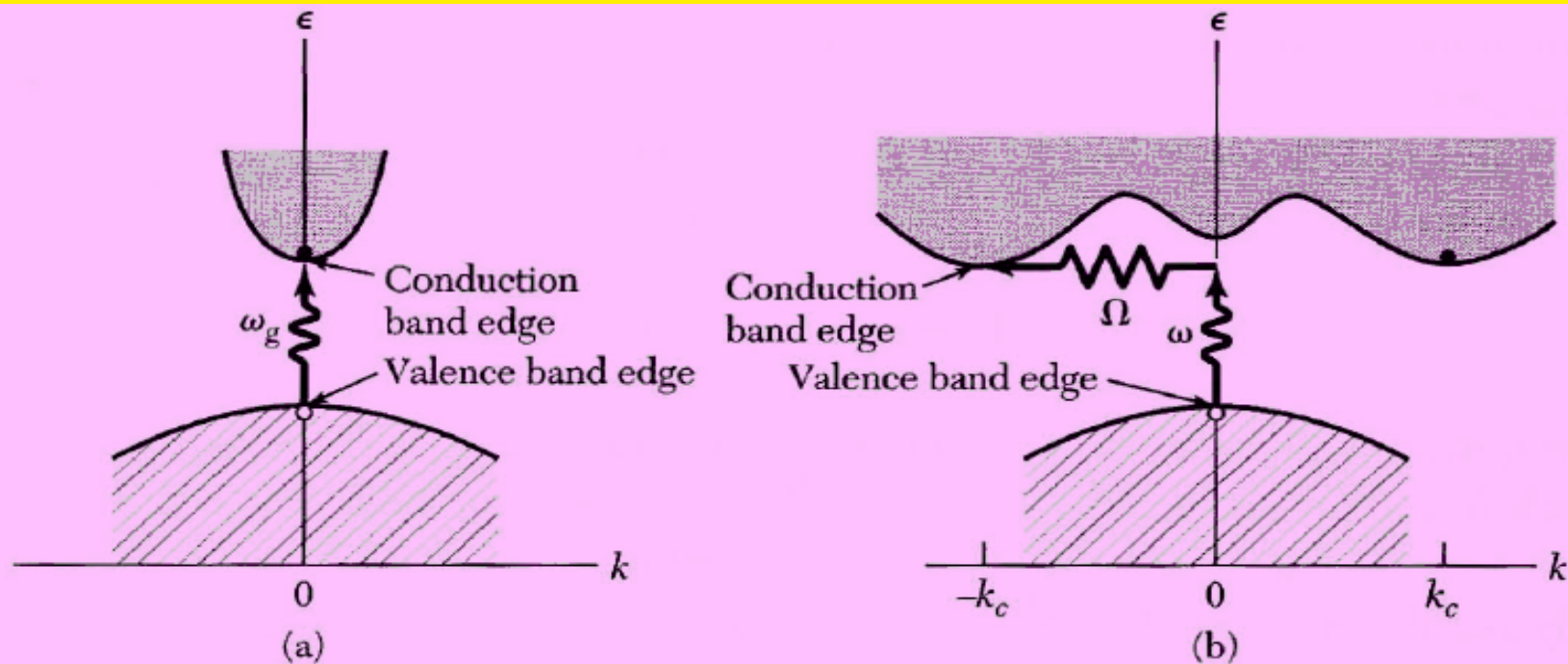


Figure 5 In (a) the lowest point of the conduction band occurs at the same value of k as the highest point of the valence band. A direct optical transition is drawn vertically with no significant change of k , because the absorbed photon has a very small wavevector. The threshold frequency ω_g for absorption by the direct transition determines the energy gap $E_g = \hbar\omega_g$. The indirect transition in (b) involves both a photon and a phonon because the band edges of the conduction and valence bands are widely separated in k space. The threshold energy for the indirect process in (b) is greater than the true band gap. The absorption threshold for the indirect transition between the band edges is at $\hbar\omega = E_g + \hbar\Omega$, where Ω is the frequency of an emitted *phonon* of wavevector $K \cong -k_g$. At higher temperatures phonons are already present; if a phonon is absorbed along with a photon, the threshold energy is $\hbar\omega = E_g - \hbar\Omega$. *Note:* The figure shows only the threshold transitions. Transitions occur generally between almost all points of the two bands for which the wavevectors and energy can be conserved.

Chapter 8: SEMICONDUCTOR CRYSTALS

Indirect Absorption Process

❑ For Indirect absorption Process:

- ✓ in Figs. 4b and Sb the minimum energy gap of the band structure involves electrons and holes separated by a substantial wavevector k_c .
- ✓ Here a direct photon transition at the energy of the minimum gap cannot satisfy the requirement of conservation of wavevector.
- ✓ But if a phonon of wave vector K and frequency Ω is created in the process, then we can have:

$$k(\text{photon}) = k_c + k \cong 0$$

$$\text{and } \hbar\omega = E_g + \hbar\Omega$$

as required by the conservation laws.

phonon energy $\hbar\Omega$ is usually much less than E_g

Chapter 8: SEMICONDUCTOR CRYSTALS

Energy Gap Experimental

Table 1 Energy gap between the valence and conduction bands
(*i* = indirect gap; *d* = direct gap)

Crystal	Cap	E_g , eV		Crystal	Cap	E_g , eV	
		0 K	300 K			0 K	300 K
Diamond	<i>i</i>	5.4		SiC(hex)	<i>i</i>	3.0	—
Si	<i>i</i>	1.17	1.11	Te	<i>d</i>	0.33	—
Ge	<i>i</i>	0.744	0.66	HgTe ^a	<i>d</i>	−0.30	
α Sn	<i>d</i>	0.00	0.00	PbS	<i>d</i>	0.286	0.34–0.37
InSb	<i>d</i>	0.23	0.17	PbSe	<i>i</i>	0.165	0.27
InAs	<i>d</i>	0.43	0.36	PbTe	<i>i</i>	0.190	0.29
InP	<i>d</i>	1.42	1.27	CdS	<i>d</i>	2.582	2.42
GaP	<i>i</i>	2.32	2.25	CdSe	<i>d</i>	1.840	1.74
GaAs	<i>d</i>	1.52	1.43	CdTe	<i>d</i>	1.607	1.44
GaSb	<i>d</i>	0.81	0.68	SnTe	<i>d</i>	0.3	0.18
AlSb	<i>i</i>	1.65	1.6	Cu ₂ O	<i>d</i>	2.172	—

^aHgTe is a semimetal; the bands overlap.

Chapter 8: SEMICONDUCTOR CRYSTALS

Direct and indirect Absorption schematically

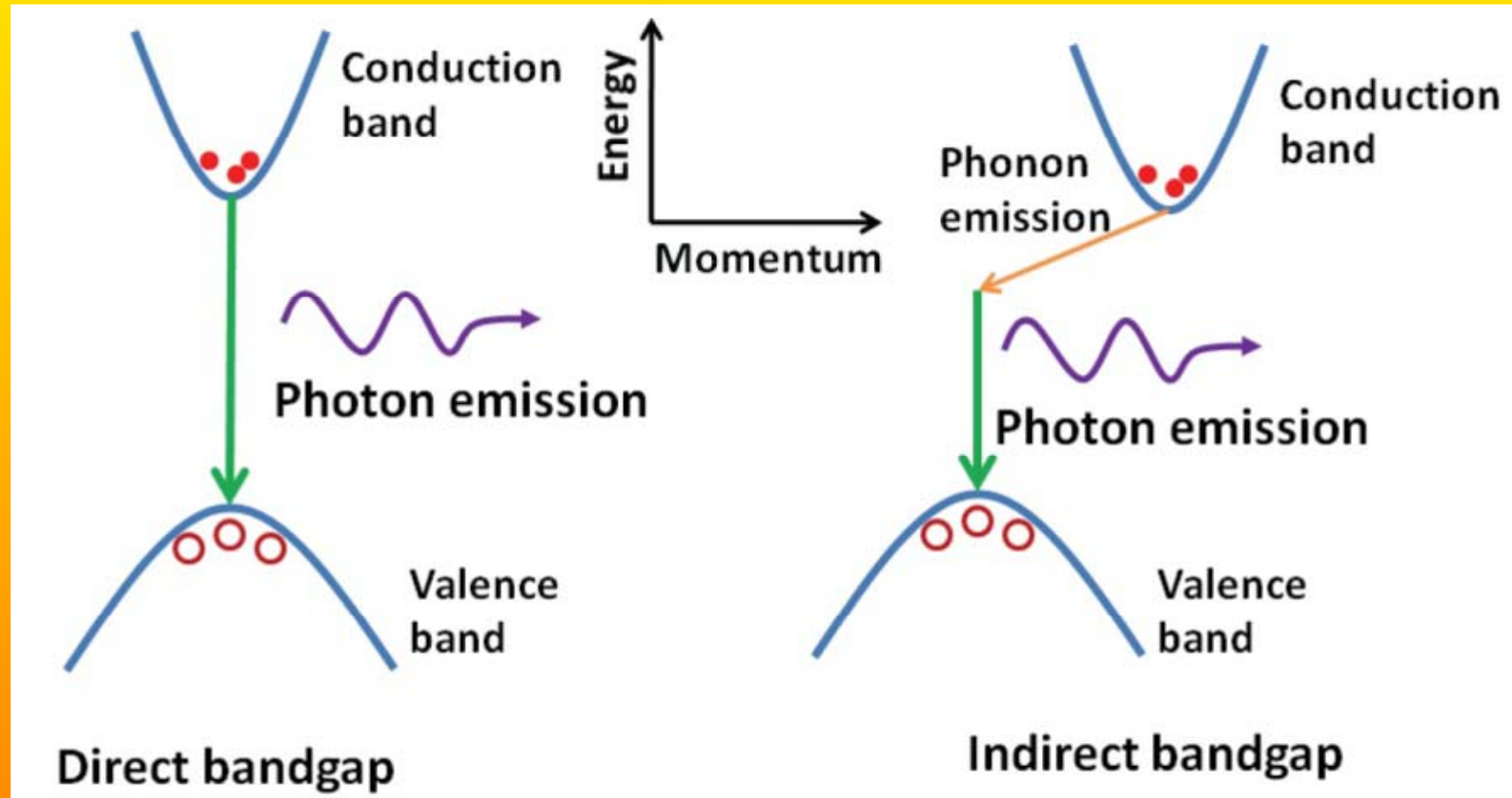


Illustration of a photon emission process in (a) the direct and (b) the indirect band gap semiconductors

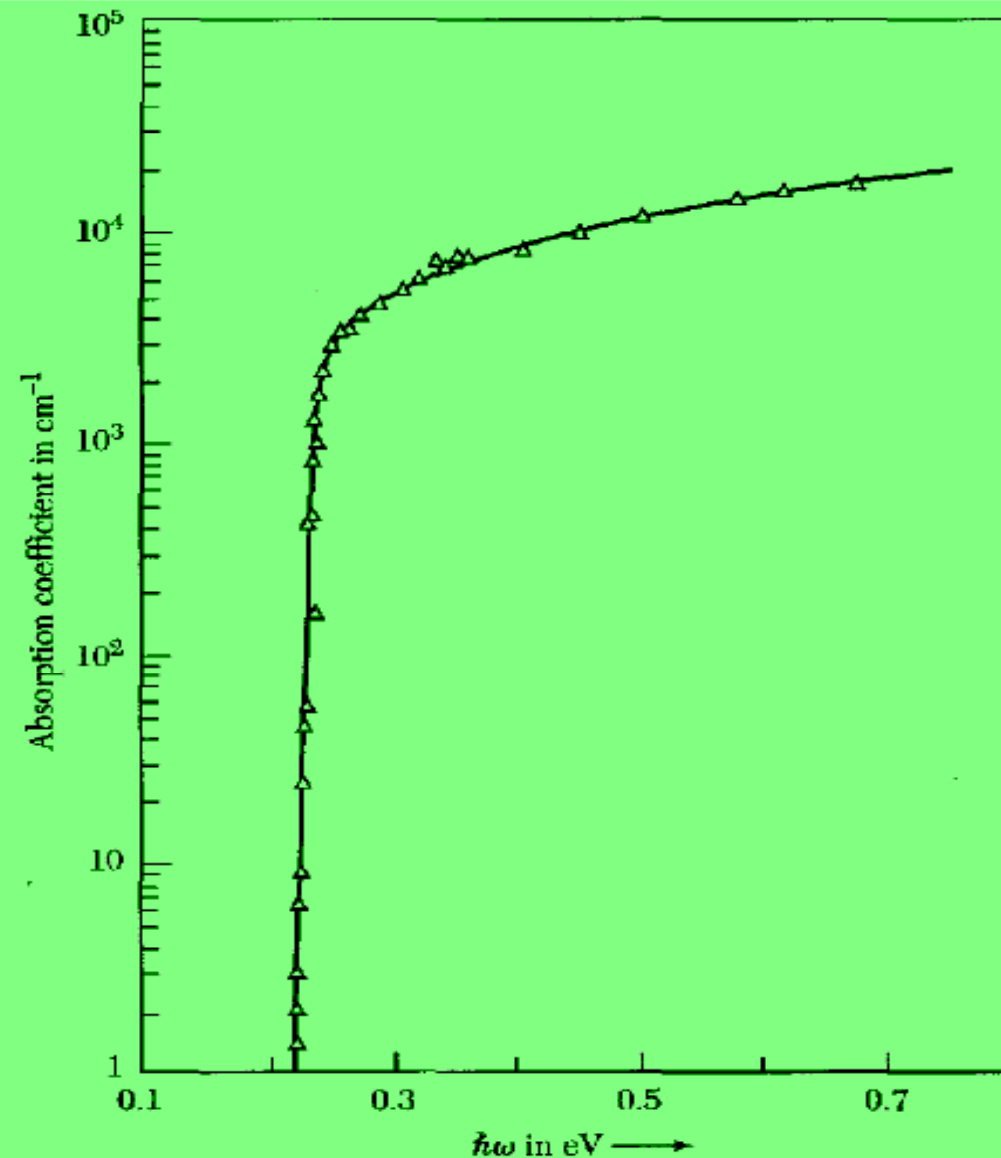


Figure 6 Optical absorption in pure indium antimonide, InSb. The transition is direct because both conduction and valence band edges are at the center of the Brillouin zone, $\mathbf{k} = 0$. Notice the sharp threshold. (After G. W. Gobeli and H. Y. Fan.)

Chapter 8: SEMICONDUCTOR CRYSTALS

Measuring Band gap

- ☐ The band gap may also be deduced from the temperature dependence of the conductivity or of the carrier concentration in the intrinsic range.
- ☐ The carrier concentration is obtained from measurements of the Hall voltage.
- ☐ Optical measurements determine whether the gap is direct or indirect.

Chapter 8: SEMICONDUCTOR CRYSTALS

EQUATIONS OF MOTION

□ We derive the equation of motion of an electron in an energy band. We look at the motion of a wave packet in an applied electric field .

Group velocity is defined as : $v_g = \frac{d\omega}{dk}$

$$\because \varepsilon = \hbar\omega \rightarrow \omega = \varepsilon / \hbar$$

$$\therefore v_g = \frac{1}{\hbar} \frac{d\varepsilon}{dk} \quad \text{or : } \vec{v} = \frac{1}{\hbar} \vec{\nabla}_k \varepsilon(\vec{k}) \quad (1)$$

The work $\delta\varepsilon$ done on the electron by the electric field E in the time interval δt is:

$$\delta\varepsilon = -eE v_g \delta t \quad (2)$$

We used the normal work eq. $-eE = \text{force}$, $v_b \delta t = \text{Displacement}$

Chapter 8: SEMICONDUCTOR CRYSTALS

EQUATIONS OF MOTION

From eq. (1) we notice that;

$$\delta\varepsilon = \frac{d\varepsilon}{d\kappa} \delta\kappa = \hbar v_g \delta\kappa \quad (3)$$

(2) and (3) give:

$$\delta\kappa = -(eE / \hbar) \delta t \quad (4)$$

$$\Rightarrow \hbar dk / dt = -eE$$

$$\Rightarrow \hbar \frac{dk}{dt} = F \quad (5)$$

- ☐ This is an important relation: in a crystal $\hbar dk/dt$ is equal to the external force on the electron.
- ☐ In free space $m dv/dt$ is equal to the force.
- ☐ the electron in the crystal is subject to forces from the crystal lattice as well as from external sources.

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EQUATIONS OF MOTION

- Eq. (5) Also includes forces from electric field (**E**) and from Lorentz force for a moving electron in Mag . Field (**B**).
- Hence, we can write the eq. of motion of the electron in the existence of **B** as:

$$\hbar \frac{d\mathbf{k}}{dt} = -e \vec{v} \times \vec{B} \quad (6)$$

using: $\vec{v} = \frac{1}{\hbar} \vec{\nabla}_k \varepsilon(\vec{k})$, we get:

$$\frac{d\mathbf{k}}{dt} = -\frac{e}{\hbar^2} \vec{\nabla}_k \varepsilon \times \vec{B} \quad (7)$$

Now LHS and RHS use **k** space.

- (7) means that in **B**, an electron moves in **k** space in a direction normal to the direction of the gradient of the energy ε , so that the electron moves on a surface of constant energy.



Phys 570

Lecture #9

Physics & Astronomy Dept.

College of Science

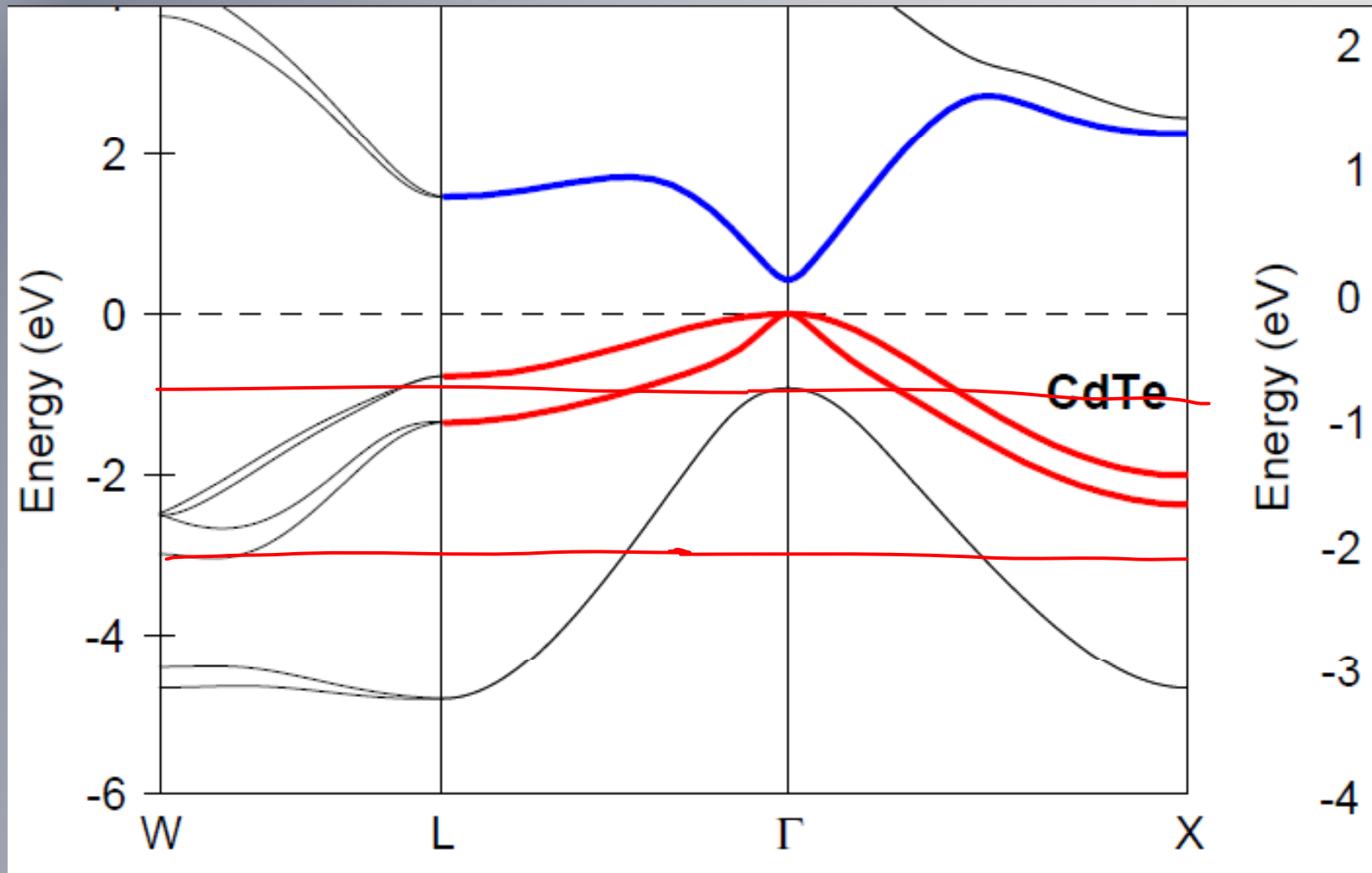
King Saud University

Nasser S. Alzayed

nalzayed@ksu.edu.sa

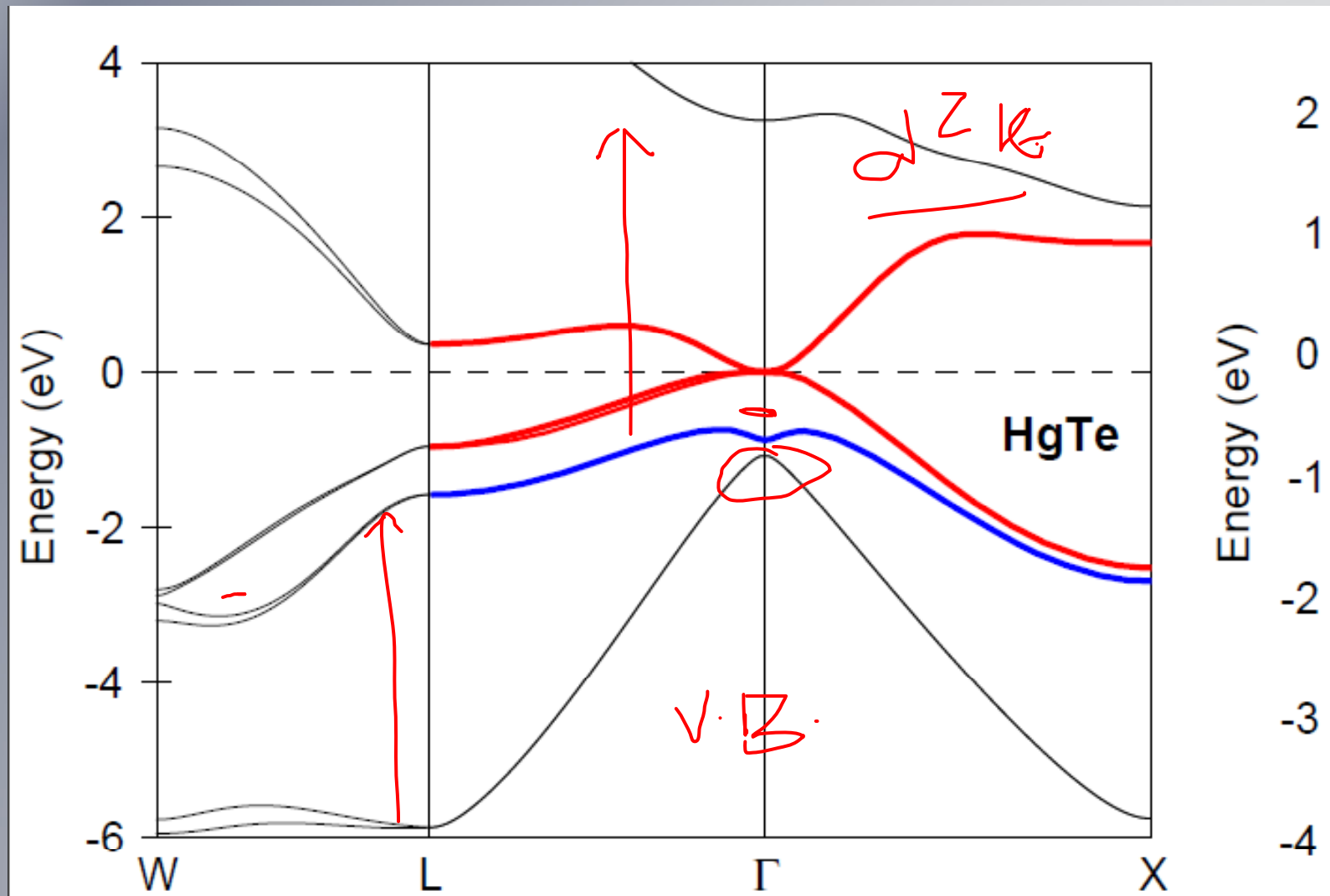
Chapter 8: SEMICONDUCTOR CRYSTALS

Band Structure in CdTe (negative band gap)



Chapter 8: SEMICONDUCTOR CRYSTALS

Band Structure in HgTe (negative band gap)



Chapter 8: SEMICONDUCTOR CRYSTALS

Holes

- ❑ The properties of vacant orbitals in an otherwise filled band are important in semiconductor physics and in solid state electronics. Vacant orbitals in a band are commonly called holes, and without holes there would be no transistors.
- ❑ A hole acts in applied electric and magnetic fields as if it has a positive charge $+e$. The reason is given in five steps:

1- $K_h = -k_e$ (17)

- ❑ The total wavevector of the electrons in a filled band is zero: $\Sigma \mathbf{k} = \mathbf{0}$, where the sum is over all states in a Brillouin zone.
- ❑ If the band is filled all pairs of orbitals \mathbf{k} and $-\mathbf{k}$ are filled, and the total wavevector is zero
- ❑ If an electron is missing from an orbital of wavevector \mathbf{k}_e , the total wavevector of the system is $-\mathbf{k}$, and is attributed to the hole
- ❑ ~~The hole is an alternate of a band with one missing electron.~~

Chapter 8: SEMICONDUCTOR CRYSTALS

Electron –Hole Conservation of Total Momentum

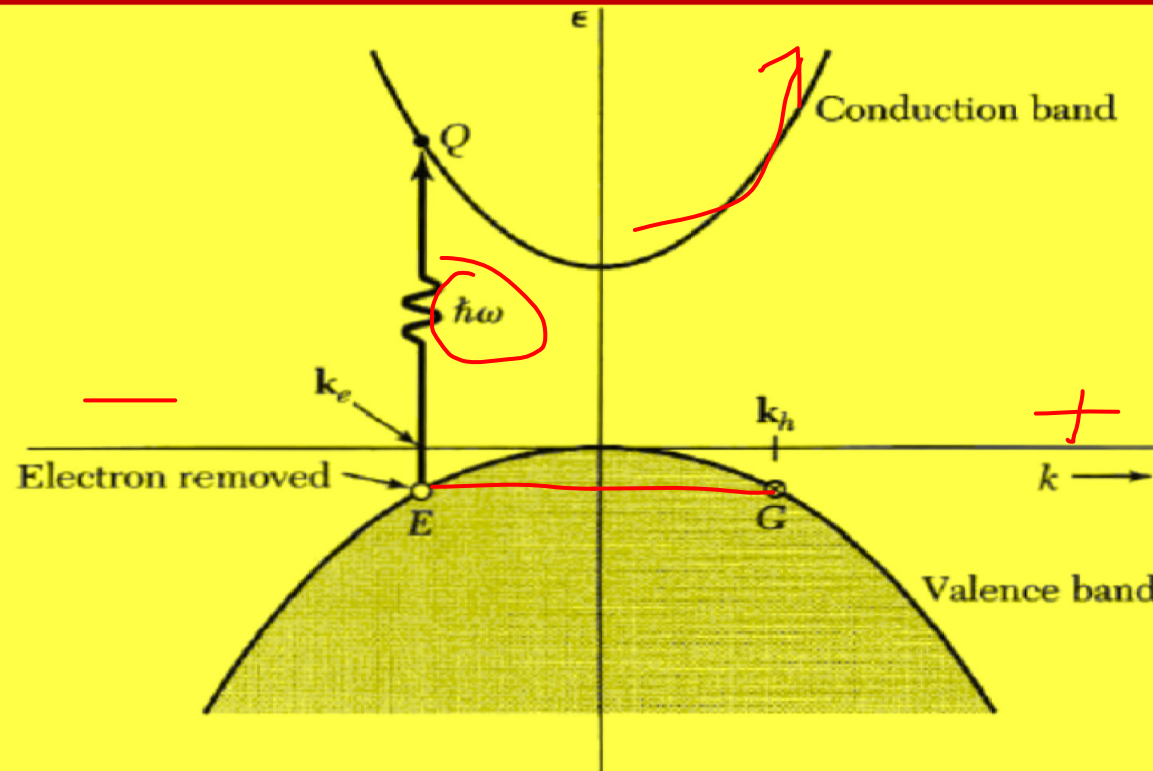


Figure 7 Absorption of a photon of energy $\hbar\omega$ and negligible wavevector takes an electron from E in the filled valence band to Q in the conduction band. If \mathbf{k}_e was the wavevector of the electron at E , it becomes the wavevector of the electron at Q . The total wavevector of the valence band after the absorption is $-\mathbf{k}_e$, and this is the wavevector we must ascribe to the hole if we describe the valence band as occupied by one hole. Thus $\mathbf{k}_h = -\mathbf{k}_e$; the wavevector of the hole is the same as the wavevector of the electron which remains at G . For the entire system the total wavevector after the absorption of the photon is $\mathbf{k}_e + \mathbf{k}_h = 0$, so that the total wavevector is unchanged by the absorption of the photon and the creation of a free electron and free hole.

Chapter 8: SEMICONDUCTOR CRYSTALS

Holes

$$2- \quad \varepsilon_h(K_h) = -\varepsilon_e(k_e) \quad (18)$$

- ☐ Here the zero of energy of the valence band is at the top of the band.
- ☐ The lower in the band the missing electron lies; the higher the energy of the system.
- ☐ The energy of the hole is opposite in sign to the energy of the missing electron, because it takes more work to remove an electron from a low orbital than from a high orbital
- ☐ Thus if the band is symmetric: $\varepsilon_e(k_e) = \varepsilon_e(-k_e) = -\varepsilon_h(-k_e) = -\varepsilon_h(k_h)$.

$$3- \quad V_h = V_e \quad (19)$$

- ☐ The velocity of the hole is equal to the velocity of the missing electron

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Electron –Hole Conservation of Total Momentum

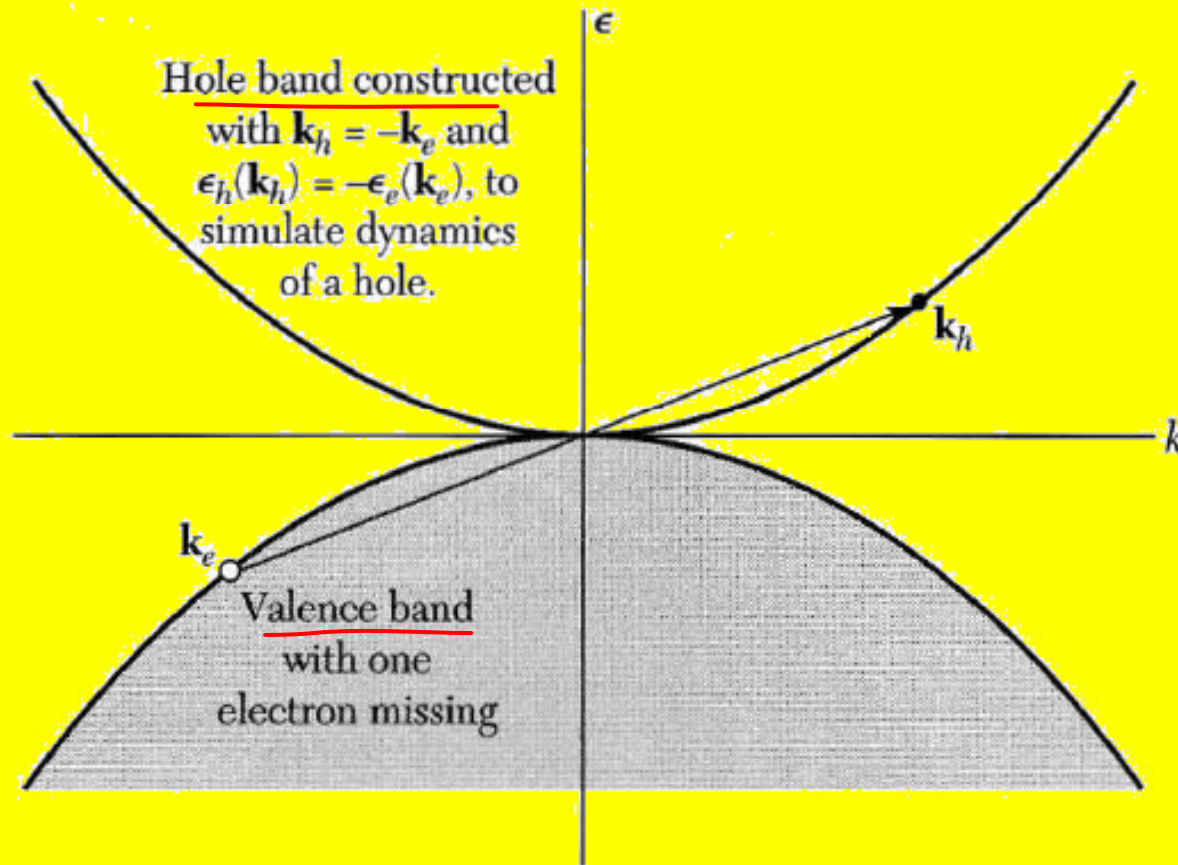


Figure 8 The upper half of the figure shows the hole band that simulates the dynamics of a hole, constructed by inversion of the valence band in the origin. The wavevector and energy of the hole are equal, but opposite in sign, to the wavevector and energy of the empty electron orbital in the valence band. We do not show the disposition of the electron removed from the valence band at k_e .

Chapter 8: SEMICONDUCTOR CRYSTALS

Holes

4- $m_h = -m_e$

(20)

- We show below that the effective mass is inversely proportional to the curvature $d^2\varepsilon/dk^2$ and for the hole band this has the opposite sign to that for an electron in the valence band. Near the top of the valence band m_e is negative, so that m_h is positive

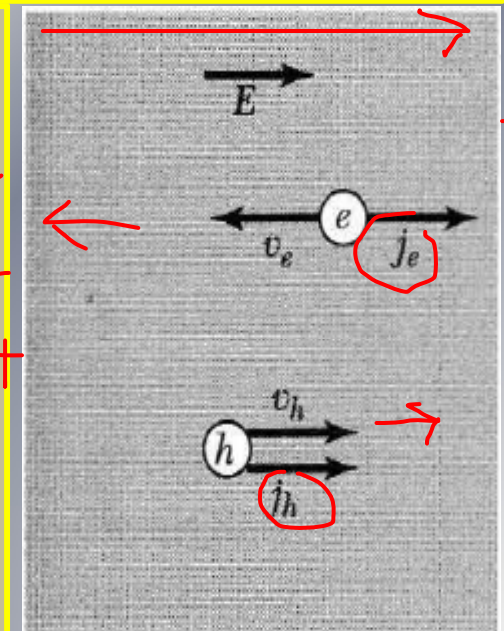
5-
$$\hbar \frac{d\mathbf{k}_h}{dt} = e(\mathbf{E} + \frac{1}{c} \mathbf{v}_h \times \mathbf{B})$$
 (21)

- The equation of motion for a hole is that of a particle of positive charge e .

- Current:

$$\mathbf{j} = (-e)\mathbf{v}(G) = (-e)[- \mathbf{v}(E)] = e\mathbf{v}(E) \quad (23)$$

- The hole and electron drift velocities are in opposite directions



Chapter 8: SEMICONDUCTOR CRYSTALS

Holes and Electrons (Comparison)

□ In the next table: We quickly compare between Holes & Electrons. Momentum, Energy, Velocity, mass and Eq. of motion



Hole	Electron	Quantity
$\mathbf{K}_h = -\mathbf{k}_e$	\mathbf{k}_e	Momentum
$\varepsilon_h(\mathbf{k}_h) = -\varepsilon_e(\mathbf{k}_e)$	$\varepsilon_e(\mathbf{k}_e)$	Energy
$\mathbf{V}_h = \mathbf{V}_e$	\mathbf{V}_e	Velocity
$\mathbf{m}_h = -\mathbf{m}_e$	\mathbf{m}_e	Mass
$\hbar \frac{d\mathbf{k}_h}{dt} = e(\mathbf{E} + \frac{1}{c} \mathbf{v}_h \times \mathbf{B})$	$\hbar \frac{d\mathbf{k}_e}{dt} = -e(\mathbf{E} + \frac{1}{c} \mathbf{v}_e \times \mathbf{B})$	Equation of Motion

Chapter 8: SEMICONDUCTOR CRYSTALS

*Effective Mass m^**

- ❑ When we look at the energy-wavevector relation $\varepsilon = (\hbar^2/2m)k^2$ for free electrons, we see that the coefficient of k^2 determines the curvature of ε versus k . Turned about, we can say that $1/m$, the reciprocal mass, determines the curvature.
- ❑ For electrons in a band there can be regions of unusually high curvature near the band gap at the zone boundary.
- ❑ In semiconductors the band width is of the order of 20 eV, while the band gap is of the order of 0.2 to 2 eV.
- ❑ Thus, the reciprocal mass is enhanced by a factor 10 to 100, and the effective mass is reduced to 0.1-0.01 of the free electron mass.
- ❑ These values apply near the band gap; as we go away from the gap the curvatures and the masses are likely to approach those of free electrons.

Chapter 8: SEMICONDUCTOR CRYSTALS

Electron –Hole Conservation of Total Momentum

Result: Bulk Central Bands

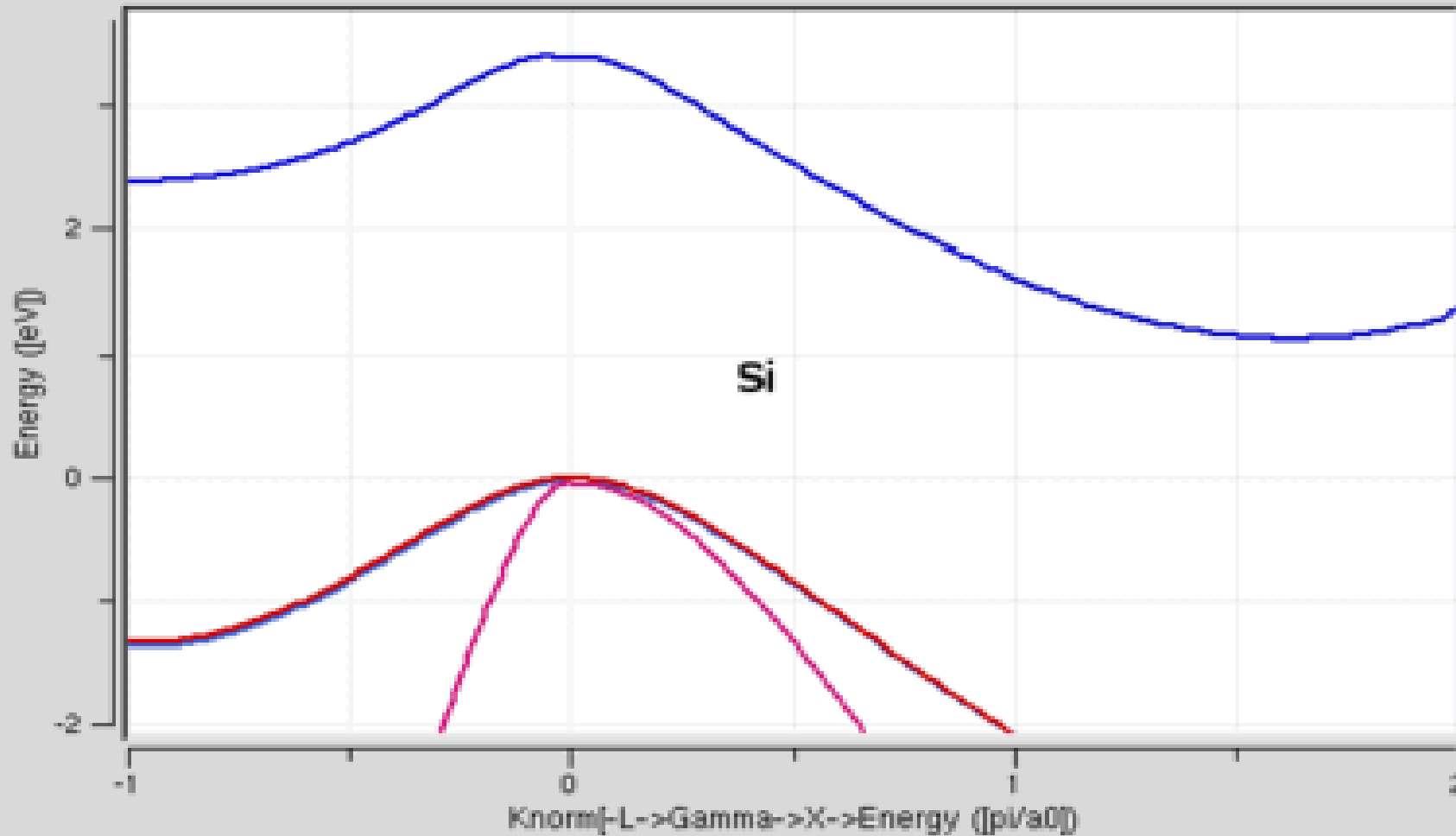


Image generated with Bandstructure Lab on nanoHUB.org

Chapter 8: SEMICONDUCTOR CRYSTALS

*Effective Mass m^**

□ Quotation from Arabic lectures:

□ وللتوضيح أكثر، فإن حركة الإلكترون داخل المادة تخضع لمؤثرات كثيرة بسبب وجود الأنوية بالقرب منه، مما يجعل حركته غير خاضعة لقوانين الحركة المعروفة (قوانين نيوتن). ومن هنا برزت فكرة الكتلة الفعالة كنوع من التعويض حتى يتمكن من الاستمرار في استخدام قوانين الحركة.

□ ربما نوضح الموضوع بشكل أفضل كما يلي: تصور شخصا مرتبه 1000 ريال في الشهر، ولكن بما أن الأسعار تتغير، مرات ترتفع و مرات تنخفض، إذن مرتبه (الفعال) قد يصبح 2000 أو 500 ريال. بمعنى قدرته الشرائية تعتمد على المؤثرات الخارجية وليس على مجرد الرقم الذي ينزل في البنك. إذن إذا كانت قيمة هذا الإنسان تعتمد فعليا على قيمة مرتبه الحقيقية، فقيمته تتذبذب بناءا على مؤشرات الأسعار. لو فرض أن الشركة التي تدفع له المرتب، تزيد من قيمته وتخفض بناءا على مؤشرات الأسعار، إذن يصبح مرتبه دائما هو 1000 ريال من حيث القيمة لا من حيث الرقم. فهذا العمل من الشركة مقابل تغير الأسعار مثل استخدام مفهوم الكتلة الفعالة مقابل تأثير الأنوية الأخرى على الإلكترون (تأثير موقعه من الشريحة).

Chapter 8: SEMICONDUCTOR CRYSTALS

Effective Mass Equation

First differentiate group velocity with time:

Wave function of a free electron is expressed as: $e^{ik \cdot x}$:

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{d\varepsilon}{dk}$$

Change of energy of electron by the work done by E is:

$$d\varepsilon = \frac{d\varepsilon}{dk} dk = -eE dx = -eE v dt = \frac{-eE}{\hbar} \frac{d\varepsilon}{dk} dt$$

$$\therefore \frac{dp}{dt} = \frac{d\hbar k}{dt} = \hbar \frac{dk}{dt} = m \frac{dv}{dt}$$

$$\therefore \frac{\hbar}{m} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d}{dt} \frac{d\varepsilon}{dk} = \frac{1}{\hbar} \frac{d^2\varepsilon}{dk^2} \frac{dk}{dt}$$

$$\Rightarrow \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2\varepsilon}{dk^2} \quad (28)$$

Chapter 8: SEMICONDUCTOR CRYSTALS

Effective Masses in Semiconductors

- ❑ In many semiconductors it has been possible to determine by cyclotron resonance the effective masses of carriers in the conduction and valence bands near the band edges.
- ❑ The determination of the energy surface is equivalent to a determination of the effective mass.
- ❑ Cyclotron resonance in a semiconductor is carried out so that the current carriers are accelerated in helical orbits about the axis of a static magnetic field.
- ❑ The angular rotation frequency ω_e is:

$$\omega_c = \frac{eB}{m^*} \quad \Rightarrow \quad m^* = \frac{eB}{\omega_c} \quad (30)$$

where m^* is the appropriate cyclotron effective mass

Chapter 8: SEMICONDUCTOR CRYSTALS

Effective Masses in Semiconductors

- Resonant absorption of energy from an rf electric field perpendicular to the static magnetic field occurs when the rf frequency is equal to the cyclotron frequency.
- Holes and electrons rotate in opposite directions.

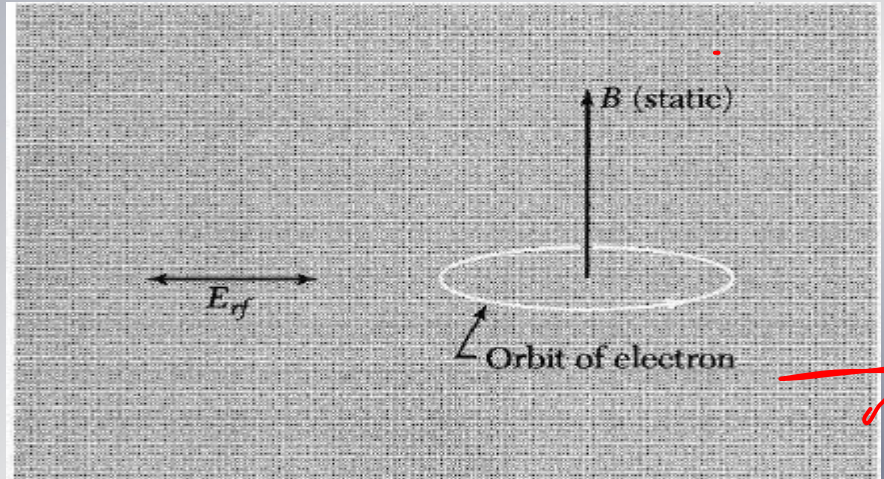


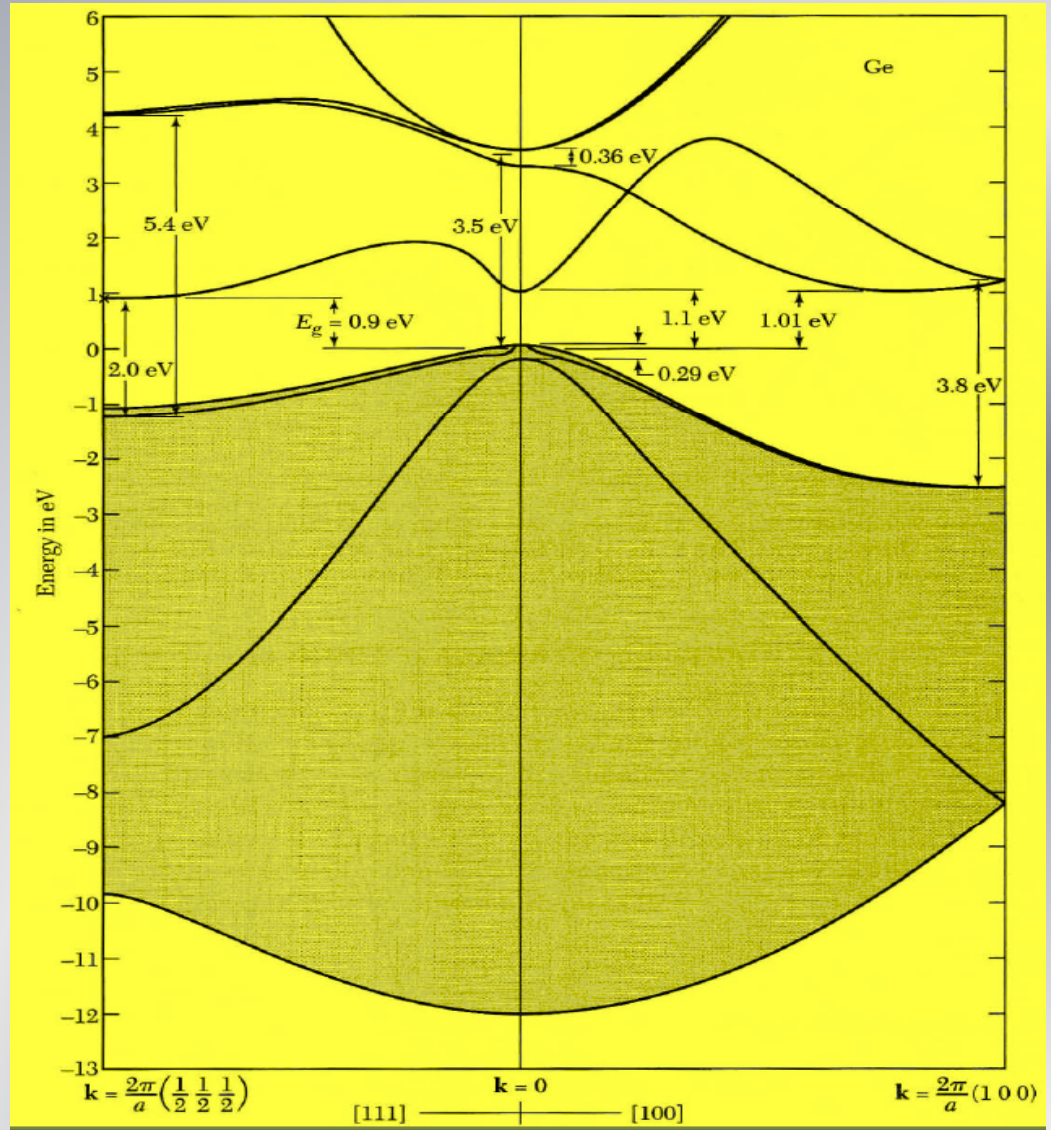
Table 2 Effective masses of electrons and holes in direct-gap semiconductors

Crystal	Electron m_e/m	Heavy hole m_{hh}/m	Light hole m_{lh}/m	Split-off hole m_{soh}/m	Spin-orbit Δ, eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34
Cu ₂ O	0.99	—	0.58	0.69	0.13

Chapter 8: SEMICONDUCTOR CRYSTALS

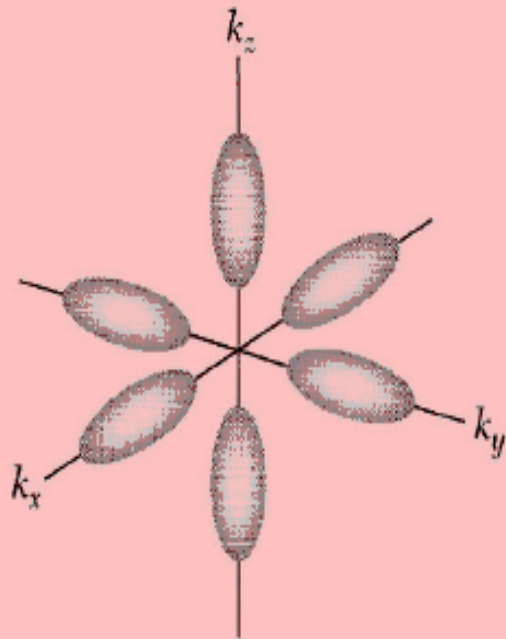
Electron –Hole Conservation of Total Momentum

Figure 14 Calculated band structure of germanium. The general features are in good agreement with experiment. The four valence bands are shown in gray. The fine structure of the valence band edge is caused by spin-orbit splitting. The energy gap is indirect; the conduction band edge is at the point $(2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.



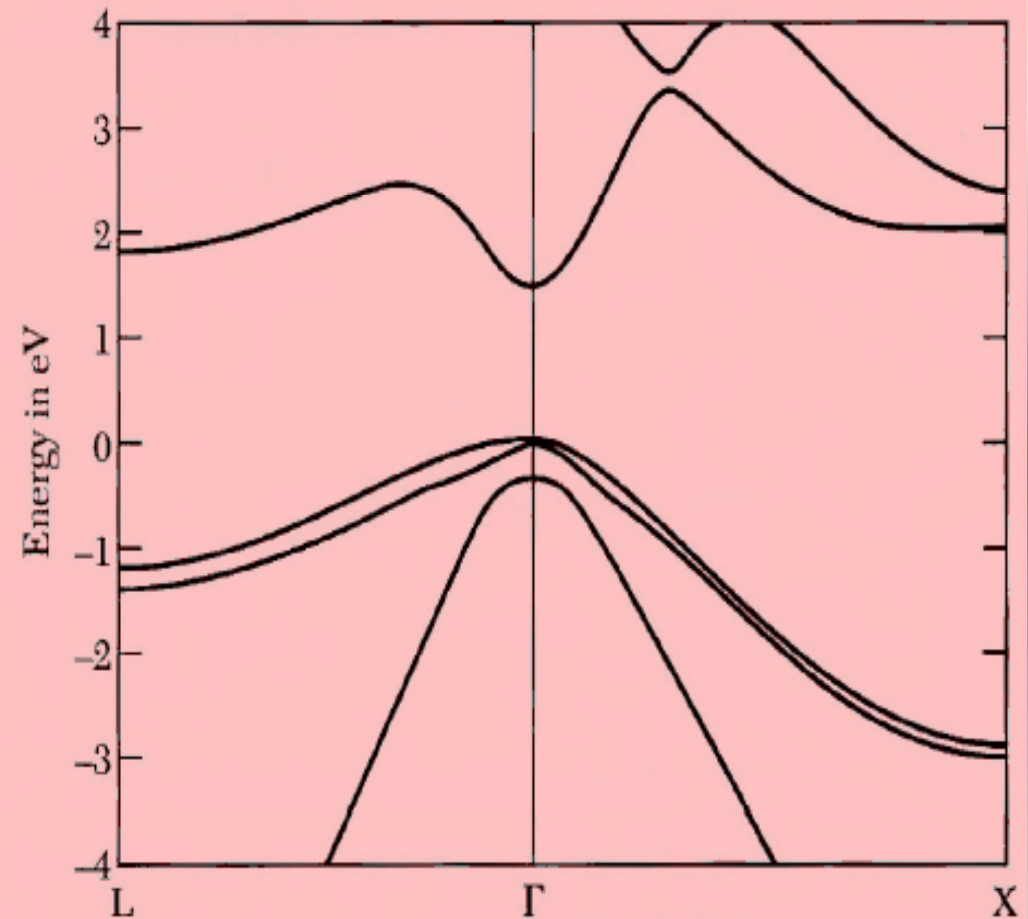
Chapter 8: SEMICONDUCTOR CRYSTALS

Electron –Hole Conservation of Total Momentum



(a)

Figure 17a Constant energy ellipsoids for electrons in silicon, drawn for $m_l/m_t = 5$.



(b)

Figure 17b Band structure of GaAs, after S. G. Louie.

Chapter 8: SEMICONDUCTOR CRYSTALS

INTRINSIC CARRIER CONCENTRATION

- ❑ We want the concentration of intrinsic carriers as a function of temperature, in terms of the band gap.
- ❑ we assume that $\epsilon - \mu \gg k_B T$, so that the Fermi-Dirac distribution function reduces to:

$$f_e \approx e^{\left[\frac{\mu - \epsilon}{k_B T} \right]} \quad (35)$$

- ❑ This is the probability that a conduction electron orbital is occupied, in an approximation valid when $f_e \ll 1$.
- ❑ The energy of an electron in the conduction band is:

$$\epsilon_k = E_c + \frac{\hbar^2 k^2}{2m_e^*} \quad (36)$$

- ❑ where E_c is the energy at the conduction band edge.

Chapter 8: SEMICONDUCTOR CRYSTALS

Electron –Hole Conservation of Total Momentum

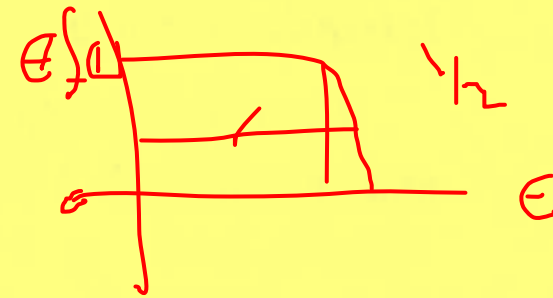
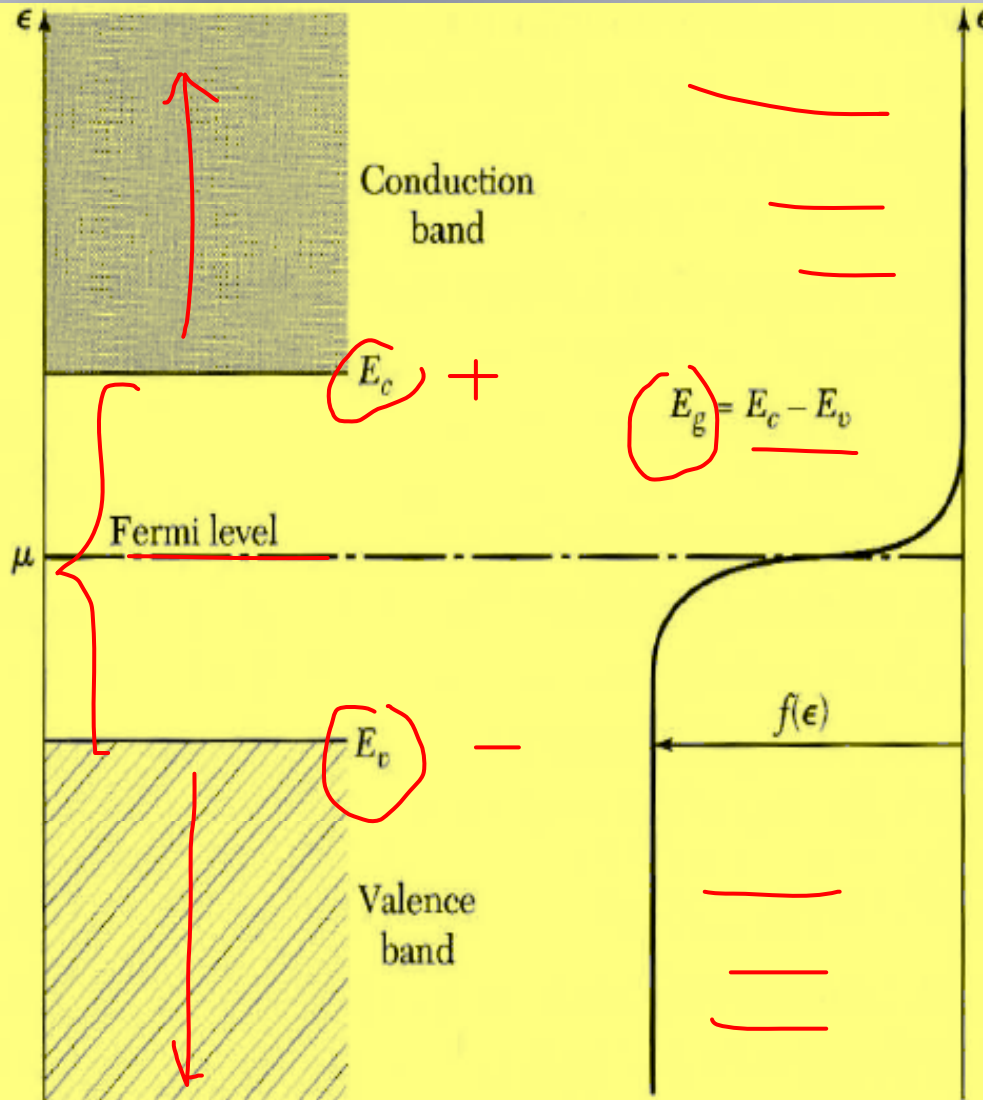


Figure 18 Energy scale for statistical calculations. The Fermi distribution function is shown on the same scale, for a temperature $k_B T \ll E_g$. The Fermi level μ is taken to lie well within the band gap, as for an intrinsic semiconductor. If $\epsilon = \mu$, then $f = \frac{1}{2}$.

Chapter 8: SEMICONDUCTOR CRYSTALS

INTRINSIC CARRIER CONCENTRATION

□ Thus from (6.20) the density of states at ε is:

$$D_e(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right) (\varepsilon - E_c)^{1/2} \quad (37)$$

The concentration of electrons in the conduction band is :

$$\begin{aligned} n &= \int_{E_c}^{\infty} D_e(\varepsilon) f_e(\varepsilon) d\varepsilon \\ &= \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right) e^{\mu/k_B T} \int_{E_c}^{\infty} (\varepsilon - E_c)^{1/2} e^{-\varepsilon/k_B T} d\varepsilon \end{aligned} \quad (38)$$

which integrates to give :

$$n = 2 \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(\mu - E_c)/k_B T} \quad (39)$$

Chapter 8: SEMICONDUCTOR CRYSTALS

INTRINSIC CARRIER CONCENTRATION

□ For the holes: $\mu - \varepsilon \gg K_B T$

$$f_h = 1 - \frac{1}{\exp(\varepsilon - \mu / k_B T) + 1} = \frac{1}{\exp(\mu - \varepsilon / k_B T) + 1} \quad (40)$$

$$\approx \exp[\varepsilon - \mu / k_B T]$$

we have:

$$D_h(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_h}{\hbar^2} \right)^{3/2} (E_v - \varepsilon)^{1/2} \quad (41)$$

$$\therefore p = 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(E_v - \mu)/k_B T} \quad (42)$$

From (39) and (42) we obtain the equilibrium relation:

$$np = 4 \left(\frac{k_B T}{2\pi \hbar^2} \right)^3 (m_e^* m_h^*) e^{-E_g/k_B T} \quad (43)$$