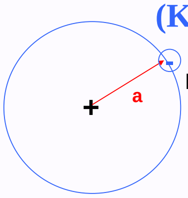
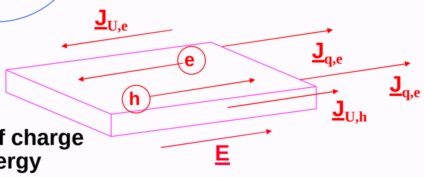
Lecture 18 - Semiconductors - continued

Lecture 18: Semiconductors - continued (Kittel Ch. 8)



Donors and acceptors



Transport of charge and energy

Outline

- **More on concentrations of electrons and holes in Semiconductors**
  Control of conductivity by doping (impurities)
- **Mobility and conductivity**
- **Thermoelectric effects**
- **Carriers in a magnetic field**
  Cyclotron resonance
  Hall effect
  (Read Kittel Ch 8)

Law of Mass Action (from last time)

- Product
  $n\, p = 4\, (k_B T / 2\, \pi^2)^3\, (m_c\, m_v)^{3/2} \exp(-(E_c - E_v)/k_B T)$
  is independent of the Fermi energy
- Even though n and p vary by huge amounts, the product np is constant!
- Why?
  There is an equilibrium between electrons and holes! Like a chemical reaction, the reaction rate for an electron to fill a hole is proportional to the product of their densities. If one creates more electrons by some process, they will tend to fill more of the holes leaving fewer holes, etc.

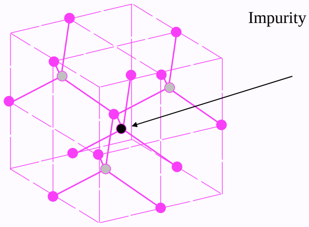
Control of carriers by "doping"

- Impure crystals may have added electrons or holes that change the balance from an intrinsic ideal crystal.
- If an impurity atom adds an electron, it is called a "donor"
- If an impurity atom subtracts an electron, it is called a "acceptor" (it adds a hole)
- The Fermi energy changes (n and p change)
- But (Law of mass action) the product
  $n\, p = 4\, (k_B T / 2\, \pi^2)^3\, (m_c\, m_v)^{3/2} \exp(-(E_c - E_v)/k_B T)$
  does not change!
- Even though n and p vary by huge amounts, the product np is constant!

What does it mean to say an impurity atom adds or subtracts an electron?

- Consider replacing an atom with one the that has one more electron (and one more proton), e.g., P in Si, As in Ge, Zn replacing As in GaAs, ….
- Question:
  Is that electron bound to the impurity site?
  Or is it free to move and count as an electron charge carrier?
- The probability that it escapes depends on the crystal and the impurity --- But if it escapes from the impurity, then it acts as an added electron independent of the nature of the impurity
- Similar argument for holes

Substitution Impurities in Diamond or Zinc-blende crystals



Impurity substituting for host atom, e.g.,
Donors: P in Si
Se on As site in GaAs

Acceptors: B in Si
Zn on Ga site in GaAs

Zinc-blende structure crystal (e.g., GaAs)
Diamond (e.g., Si) if pink and grey atoms are the same

Lecture 18 - Semiconductors - continued

Binding of electron to impurity

- Simplest approximation – accurate in many cases - qualitatively correct in others (Kittel p 210)
- Electron around impurity is exactly like a hydrogen atom -- except that the electron has effective mass m* and the Coulomb interaction is reduced by the dielectric constant ε

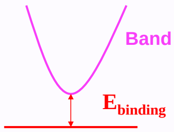
  $m \rightarrow m^*; \quad e^2 \rightarrow e^2/\varepsilon$
- The binding is (see back inside cover of Kittel)

  $E_{binding} = (e^4 m^*/ 2\, \varepsilon^2 \hbar^2)$

  $= (1/\varepsilon^2)(m^*/m)\ 13.6\ \text{eV}$
- The radius is:

  $a_{binding} = (\varepsilon \hbar^2 / m^* e^2) = \varepsilon\, (m/m^*)\, a_{Bohr}$

  $= \varepsilon\, (m/m^*)\ .053\ \text{nm}$



Binding of electron to impurity

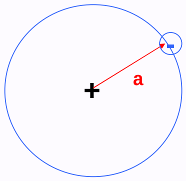
- Typical values in semiconductors

  $m^* \sim 0.01 - 1\ m$;

  $\varepsilon \sim 5 - 20$
- Thus binding energies are

  $E_{binding} \sim 0.0005 - 0.5$ eV

  ~ 5 K - 5,000 K
- Sizes $a \sim$ 2.5 - 50 nm



- In many cases the binding can be very weak and the size much greater than atomic sizes
- Holes are similar (but often m* is larger)

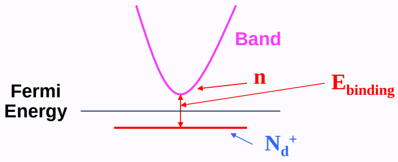
Thermal ionization of donors and acceptors

- Suppose we have donors with binding energy much less than the band gap (the usual case).
- The fraction of ionized donors can be worked out simply if the density of donor atoms N_d is much greater than the density of acceptors and intrinsic density of holes and electrons (otherwise it is messy)
- Then the density of ionized donors N_d^+ equals the density n of electrons that escape, which can be found by the same approach as the density of electrons and holes for an intrinsic crystal.

Thermal ionization of donors and acceptors

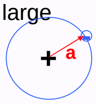
- Assuming $k_B T \ll E_{binding}$ the result is (Kittel p 213)

$$n = 2(m_c k_B T/ 2\, \pi^2)^{3/2} N_d^{1/2} \exp(-E_{binding}/k_B T)$$

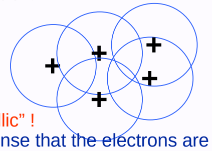


When is a doped semiconductor a metal?

- If the density of donors (or acceptors) is large then each impurity is not isolated
- The picture of an isolated hydrogen-like bound statedoes not apply



- What happens if the states overlap?

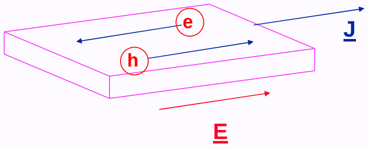


- The system becomes “metallic” !
- Similar to Na metal in the sense that the electrons are delocalized and conduct electricity even at T=0
- This is a metal if the distance between the impurity atoms is comparable to or less than the radius a
- There are also special cases – see later

Conductivity with electrons and holes

- Both electrons and holes contribute to conductivity
- Current density j = density x charge x velocity

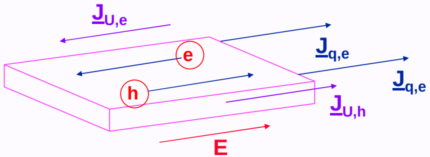
  $J = n\, q_e\, v_e + p\, q_h\, v_h = -\, n\, e\, v_e + p\, e\, v_h$
- Note: e = |charge of electron| >0



Lecture 18 - Semiconductors - continued

Thermopower and Peltier Effect

- Both electrons and holes contribute to conductivity **and conduct heat**
- **The Peltier effect** is the generation of a heat current J_u due to an electric current J_q **in the absence of a thermal gradient**
- Electrons and holes tend to cancel - can give either sign - one way to determine whether electrons or holes dominate the transport!

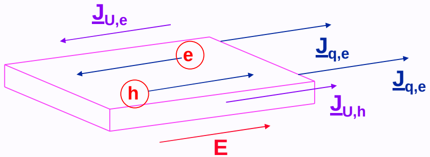


Thermopower and Peltier Effect

- Quantitative definition: **Peltier coefficient is the ratio of energy to charge transported for each carrier**

Surprising?

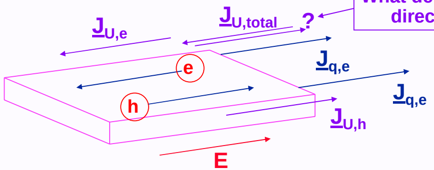
- The energy for an electron is $E_c - \mu + (3/2) K_BT$; and for a hole is $\mu - E_v + (3/2) K_BT$
- $\Pi_e = (E_c - \mu + (3/2) K_BT) / q_e = - (E_c - \mu + (3/2) K_BT) /e$
  $\Pi_h = (\mu - E_v + (3/2) K_BT) / q_h = + (\mu - E_v + (3/2) K_BT) /e$



How a solid state refrigerator works

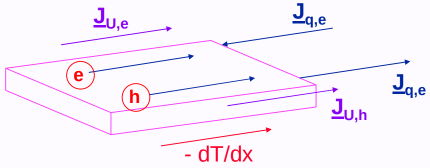
- **The Peltier effect** is the generation of a heat current J_u due to an electric current J_q **in the absence of a thermal gradient**
- Why semiconductors? Because Π is so large due to the large value of the energy per carrier ($E_c - \mu + (3/2) K_BT$) or ($\mu - E_v + (3/2) K_BT$)
- Demonstration

What determines direction?



Thermopower and Peltier Effect

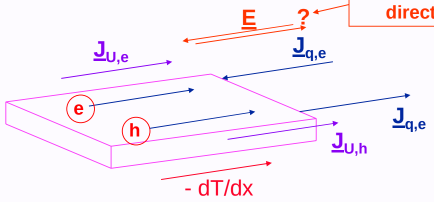
- Recall: Both electrons and holes contribute to conductivity and conduct heat
- **The thermoelectric effect** is the generation of an electrical voltage by a heat current J_u **in the absence of an electric current.**
- Just as in Peltier effect, electrons and holes tend to cancel - can give either sign



Thermopower

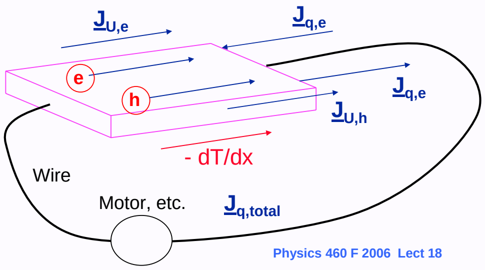
- If there is a thermal gradient but no electrical current, there must be an electric field to prevent the current
- The logic is very similar to the Hall effect and leads to the expression for the electric field needed to prevent electrical current

What determines direction?



Thermopower

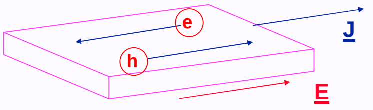
- This leads to thermopower: generation of power from heat flow (by allowing the current to flow through a curcuit)



Lecture 18 - Semiconductors - continued

Mobility

- Characterizes the quality of a semiconductor for electron and hole conduction separately
- Recall: Current density j = density x charge x velocity
  $J = n\, q_e\, v_e + p\, q_h\, v_h = -\, n\, e\, v_e + p\, e\, v_h$
- Define **mobility** μ = speed per unit field = v/E
  $J = = (n\, \mu_e + p\, \mu_h)\, e\, E$



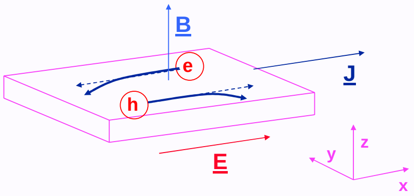
Note: the symbols μ_e and μ_h denote mobility
(Do not confuse with the chemical potential μ)

Experiments:
How do we know holes are positive?
How do we know that electrons act like they have effective masses?

- **Experiments in magnetic fields**
  - **Hall Effect**
  - **Cyclotron resonance**

Hall Effect I

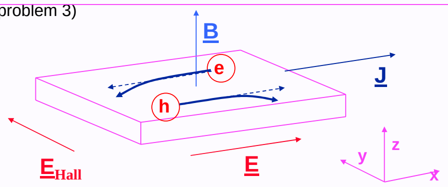
- From our analysis before
  Adding a perpendicular magnetic field causes the electrons and holes to be pushed the same direction with force -- but since their charges are opposite, the current in the y direction tends to cancel



Hall Effect II

- In order to have no current in the y direction, we must have electric field in the y direction, i.e.,
  $j_y = (n\, \mu_e + p\, \mu_h)\, e\, E_y + (-\, n\, \mu_e\, |v_e| + p\, \mu_h\, |v_h|)\, e\, B_z = 0$
- Thus $E_y = B_z\, (-\, n\, \mu_e\, |v_e| + p\, \mu_h\, |v_h|) / (n\, \mu_e + p\, \mu_h)$
- $R_{Hall} = E_{Hall} / j\, B = (1/e)\, (-\, n\, \mu_e^2 + p\, \mu_h^2) / (n\, \mu_e + p\, \mu_h)^2$

(Kittel problem 3)

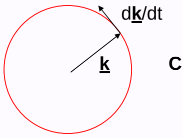


Cyclotron resonance

- **Measures effective mass directly**
- **Subtle points**
- **THIS IS EXTRA MATERIAL – NOT REQUIRED FOR HOMEWORK OR THE EXAM**

Motion of carrier in Magnetic field

- Force: $q\, (\underline{\mathbf{v}} \times \underline{\mathbf{B}}) = \hbar\, d\underline{\mathbf{k}}/dt$
- Electron moves on constant energy surface, with only change in direction of **k**
- Thus $dk/dt = -\, e\, |\, \underline{\mathbf{v}} \times \underline{\mathbf{B}}| / \hbar = -\, (e/m^*)\, k\, B$
- Isotropic bands (same in all directions like for free electrons): period of revolution in k space is $2\pi k/(dk/dt) = 2\pi/\omega_c$ and $\omega_c = qB/m^*$

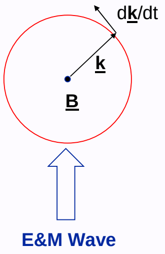


Cyclotron Resonance

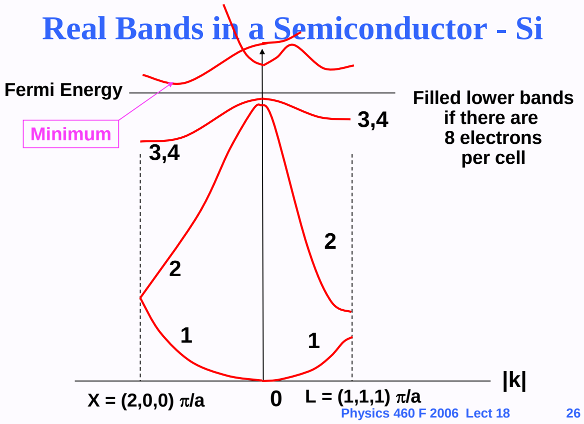
Lecture 18 - Semiconductors - continued

Cyclotron Resonance

- Experimental way to measure effective masses
- Magnetic field **B** defines particular direct in space
- Electron rotate in plane perpendicular to **B** with a period of revolution $\omega_c = qB/m^*$
- Observed experimentally by the absorption of electromagnetic waves at frequency ω_c
- Interpretation: wave causes electron bunches to move in circle - resonance occurs when electrons are wave are in phase at frequency ω_c

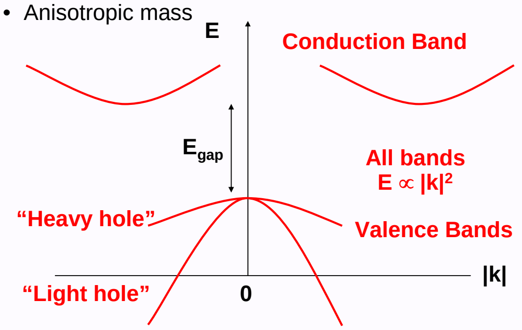


Real Bands in a Semiconductor - Si



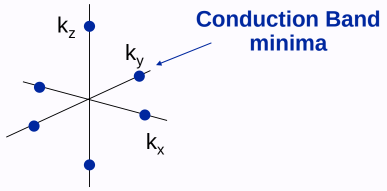
What if minimum is not at k = 0?

- Multiple equivalent minima
- Anisotropic mass



Multiple minima

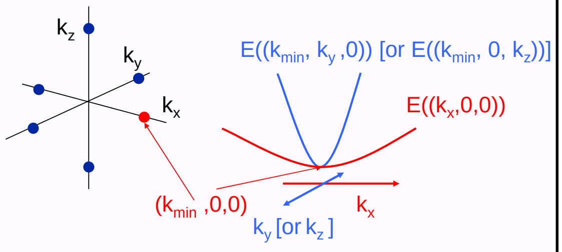
- Conduction band of Si - 6 minima along $(k_x,0,0)$, $(0,k_y,0)$, $(0, 0, k_z)$ directions



- In Ge, 8 minima along directions with $|k_x| = |k_y| = k_z|$

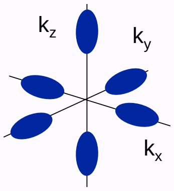
Anisotropic Mass

- Consider only one minimum at **k** $= (k_{min}, 0,0)$
- Anisotropic mass: $\frac{d^2E}{d^2k_x} \neq \frac{d^2E}{d^2k_y} = \frac{d^2E}{d^2k_z}$



Constant energy surfaces

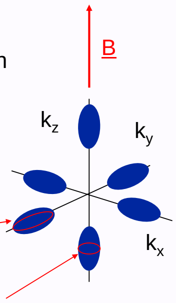
- Around each of the the minima, the surfaces of constant energy in k space are circles or ellipses
- Example of Si



Lecture 18 - Semiconductors - continued

Cyclotron Resonance

- Dependence upon direction of magnetic field **B** shows the anisotropy of the mass
- Example: In Si all along **B** any cubic axis is the same. In each direction there are two resonance frequencies $\omega_c = qB/m^*$ corresponding two different masses for motion perpendicular to **B**



Large orbit, large mass

Small orbit, small mass

Summary for Today

- **Control of conductivity by doping (impurities)**
  - **Donors and acceptors**
  - **Hydrogenic equations for binding**
  - **Important that binding be weak for carrier to escape and be able to move**
- **Conductivity and Mobility**
- **Thermoelectric effects**
  - **Peltier Effect**
  - **Thermopower**
  - **Sign of carrier important**
- **Carriers in a magnetic field**
  - **Hall effect**
  - **Cyclotron resonance (extra – not required)**

(Read Kittel Ch 8)

Summary of Semiconductors I

- **Typical bands - understanding from nearly free electron picture**
- **Optical properties - (direct vs indirect gap)**
- **Motion of wave packets** $\mathbf{F} = \hbar \, d\mathbf{k}/dt$
- **Group velocity**
- **Effective mass m*:** $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2E}{d\mathbf{k}^2}$
- **m* tends to be small if the gap is small**
- **Negative electrons; positive holes**
- **Law of mass action: np = "constant"**
- **Doping and concentrations of electrons, holes**
  Donors, acceptors
  Binding of carrier to impurity site

Summary of Semiconductors II

- **Thermoelectric effects: Peltier; Thermopower**
  - **Sign of carrier important**
- **Carriers in a magnetic field**
  - **Hall effect**
  - **Cyclotron resonance (extra – not required)**

  Sign of carrier important
- **(Read Kittel Ch 8)**
- **LATER: Inhomgeneous Semiconductors - e.g., variations in dopin in space, p-n junctions,**

Next time

- **Semiconductor devices**
- **Created by inhomogeneous material or doping**
  - **Variation in concentrations of electrons and holes by controlled doping profiles**
- **p-n junctions - rectification- forward - reverse bias**
- **Metal-semiconductor junctions**
  - **Schottky barriers - rectification**
- **Solar Cells**
- **Light emitting diodes**
- **Bipolar transistor n-p-n p- n-p**
- **(Kittel Ch. 17, p. 503 - 512 + extra class notes)**