

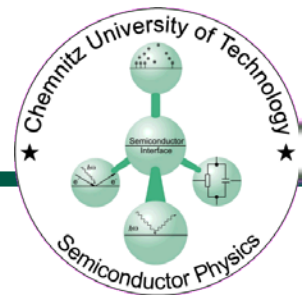
# Electronic properties of semiconductors

Bond model

**The Band (theory) Model**

**... remember the first lecture ?!**

**The chapter about the History of semiconductors?**



## Alan Wilson in 1931

Proposes the **Band Theory of Semiconductors** soon after the basis of quantum mechanics was established.

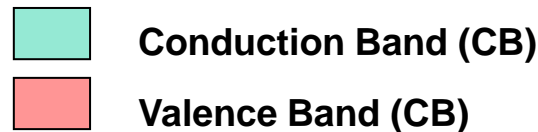
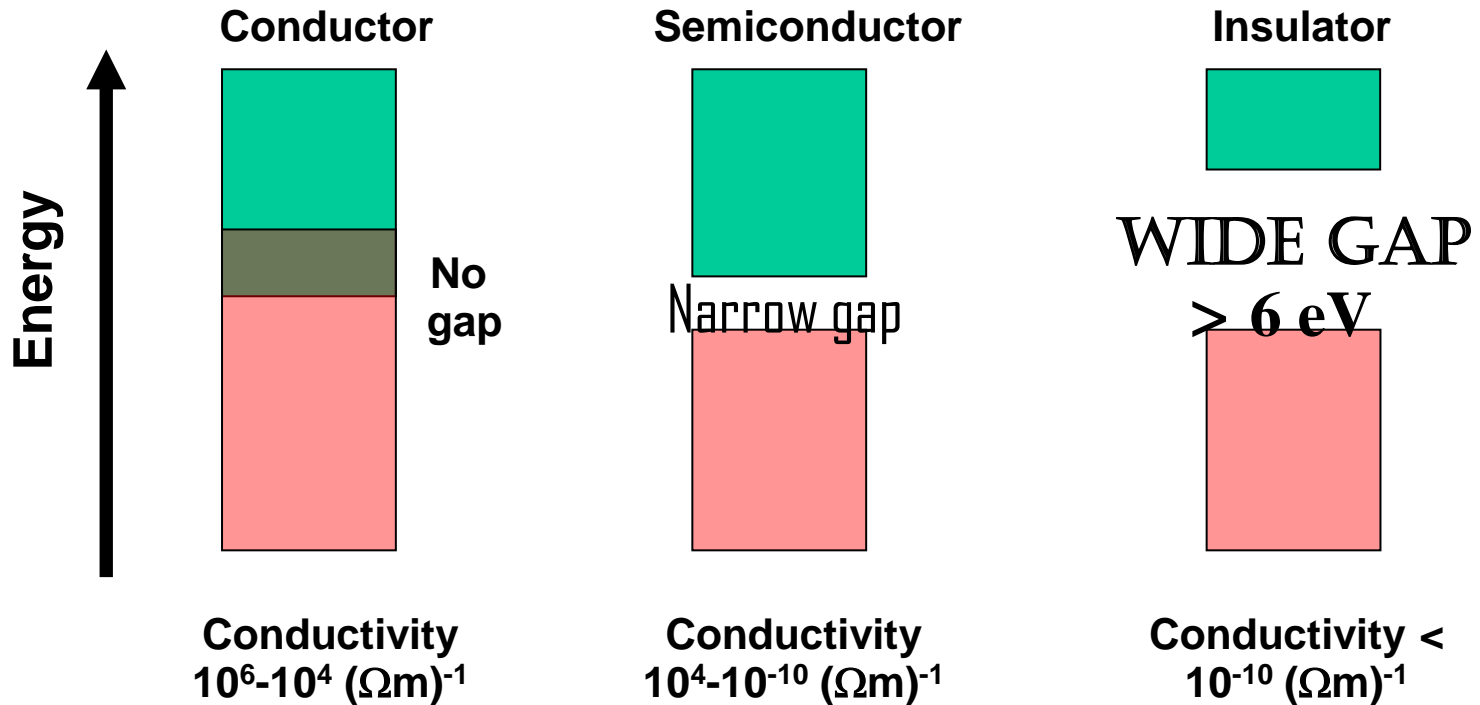
- He draws the picture of energy bands and energy gaps in between, giving like this physical meaning to the Koenigsberger's dissociation energy:
- The gap between the upper band, completely occupied by electrons ('valence band'), and the next empty one ('conduction band').

**Werner Heisenberg in 1931** comes up with the concepts of :

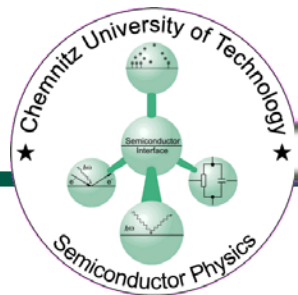
“holes” - carriers with positive charge, presenting unoccupied positions in the mainly occupied valence band.

# 1. General Properties of Semiconductors

## 1.1. Qualitative Properties



...

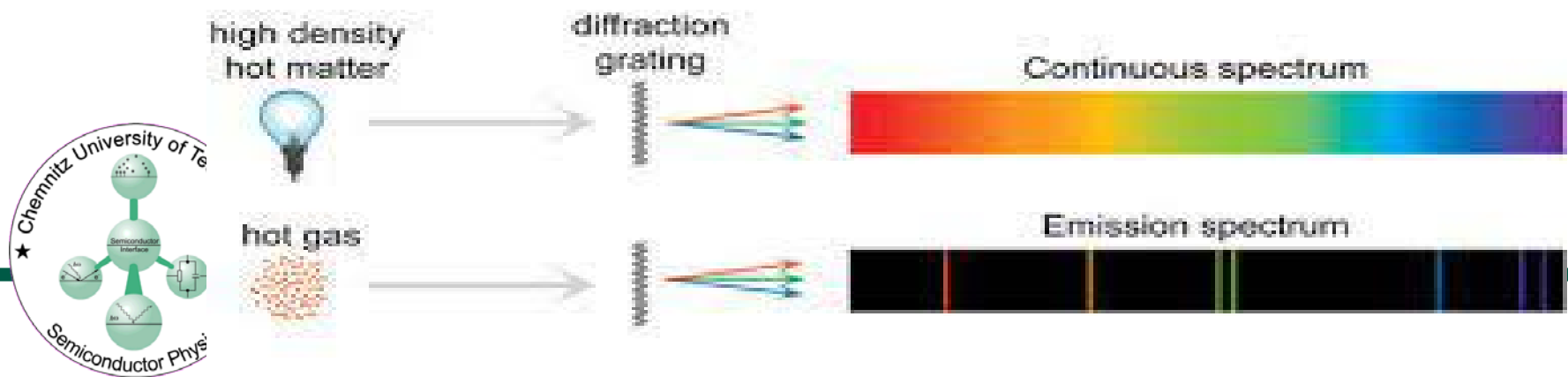


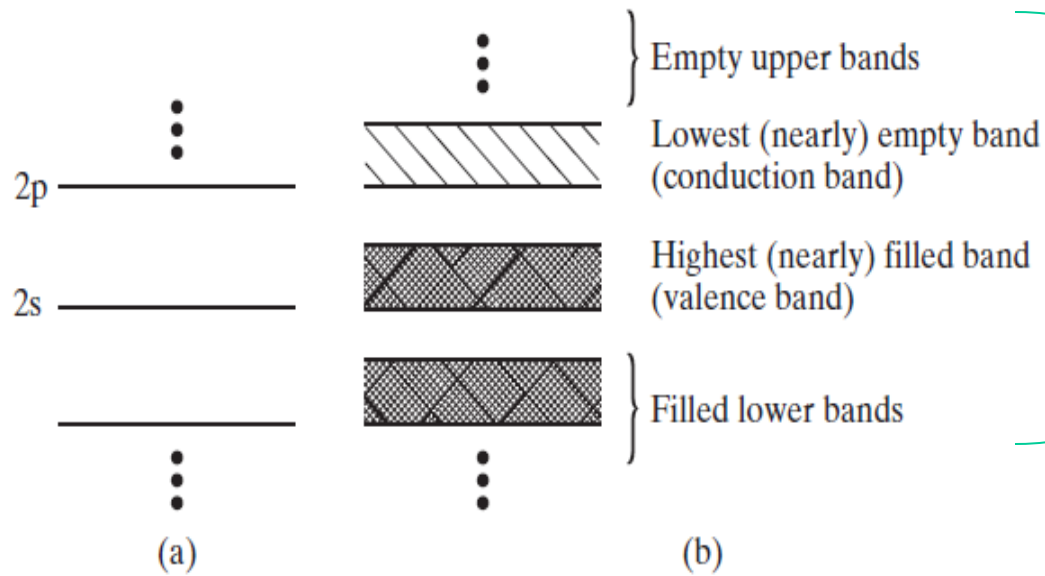


# The Band (theory) Model

8th lecture

- ✓ electrons in an atom occupy discrete energy levels;
- ✓ two atoms are in close proximity, each energy level will split into 2 due to the Pauli exclusion principle that states that each quantum state can be occupied by no more than one electron in an electron system such as an atom molecule, or crystal;
- ✓ When many atoms are brought into close proximity as in a crystal, the discrete energy levels are replaced with *bands* of a **semicontinuum** of a very large energy states separated by gaps between the bands.

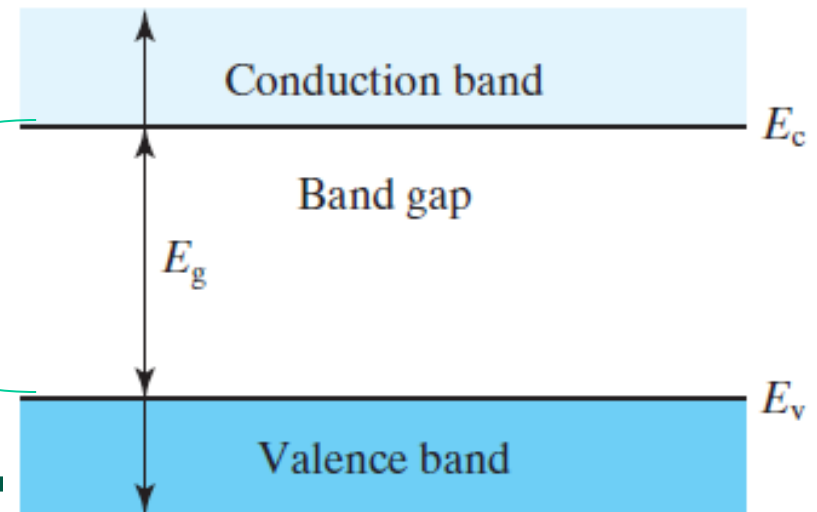






The discrete energy states of a Si atom (a) convert or transform into energy bands in a Si crystal (b).

The difference between  $E_c$  and  $E_v$  is the **bandgap energy** or **energy gap**,  $E_g$ :

$$E_g = E_c - E_v$$



- 
- the electrons tend to fill up the low energy bands first.
  - the lower the energy, the more completely a band is filled.
  - In a semiconductor, most of the lower energy bands will be totally filled; the higher energy bands are totally empty. Between them lie two bands that are only nearly filled and nearly empty:
    - the **valence band** – **top** nearly filled
    - the **conduction band** – *low nearly filled*
    - The gap between them is called the **band gap**.
  - The electrons in a totally filled band do not have a net velocity and do not conduct current.
  - A totally empty band cannot contribute to current conduction.



The **valence band** and the **conduction band** are the only energy bands that contribute to current flows in a semiconductor.



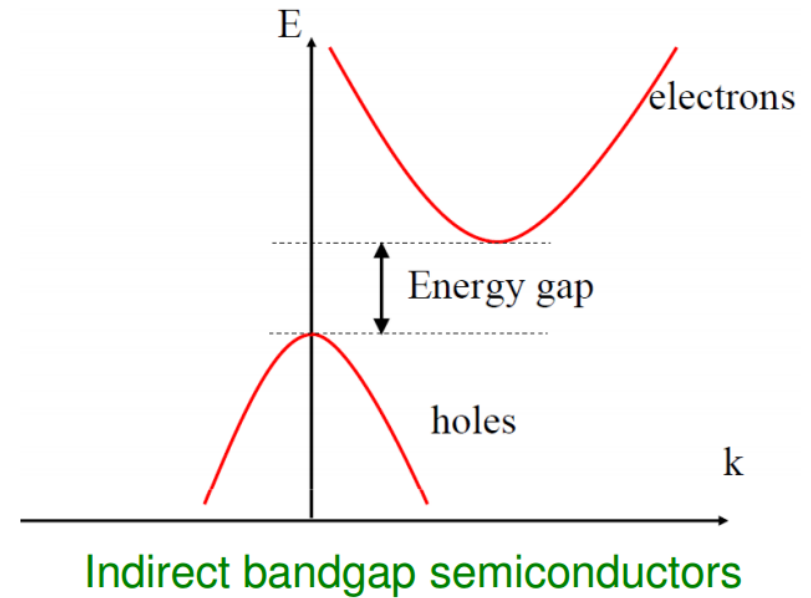
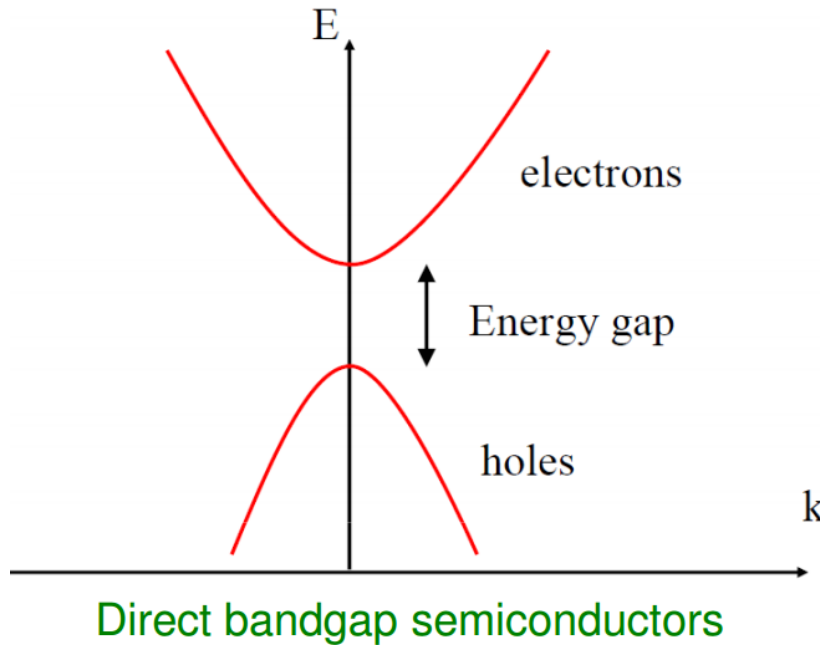
- ❑ Conduction electrons can move around in a crystal and therefore can carry electrical currents. For this reason, the **conduction electrons are of more interest to the operation of devices** than valence electrons.
- ❑ When an electron breaks loose and becomes free leaves behind a void, or a **hole**. The hole can readily accept a new electron, which provides another means for electrons to move and conduct currents.
- ❑ An alternative way to think of this process is that **the hole moves** to a new location in such case we speak of **current conduction as the motion of a positive hole**.
- ❑ In semiconductors, **current conduction by holes is as important as electron conduction** in general. It is important to become familiar with thinking of the **holes as mobile particles carrying positive charge**, just as real as conduction **electrons are mobile particles carrying negative charge**.
- ❑ The densities of thermally generated electrons and holes in semiconductors are generally very small at room temperature given that the thermal energy,  $kT$ , is 26 meV at room temperature.

The band gap of a semiconductor is always one of two types:

**direct** band gap

or

**indirect** band gap



The **band-gap energy** can be determined by measuring the **absorption of light** by the semiconductor as a function of the **photon energy,  $h\nu$** .



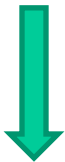
- Light is strongly absorbed only when  **$h\nu$  is larger than  $E_g$** .
- The absorbed photon energy is consumed to create an **electron–hole** pair.



A much larger number of conduction electrons can be introduced if desired by introducing suitable impurity atoms—a process called **doping**.

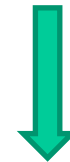
**Dopants**: atoms or impurities deliberately added to the semiconductors crystal structure with specific purpose to manipulate its conduction properties.

Electron **Donors**



**N (negative) -type semiconductors**

Electron **Acceptors**



**P (positive) -type semiconductors**

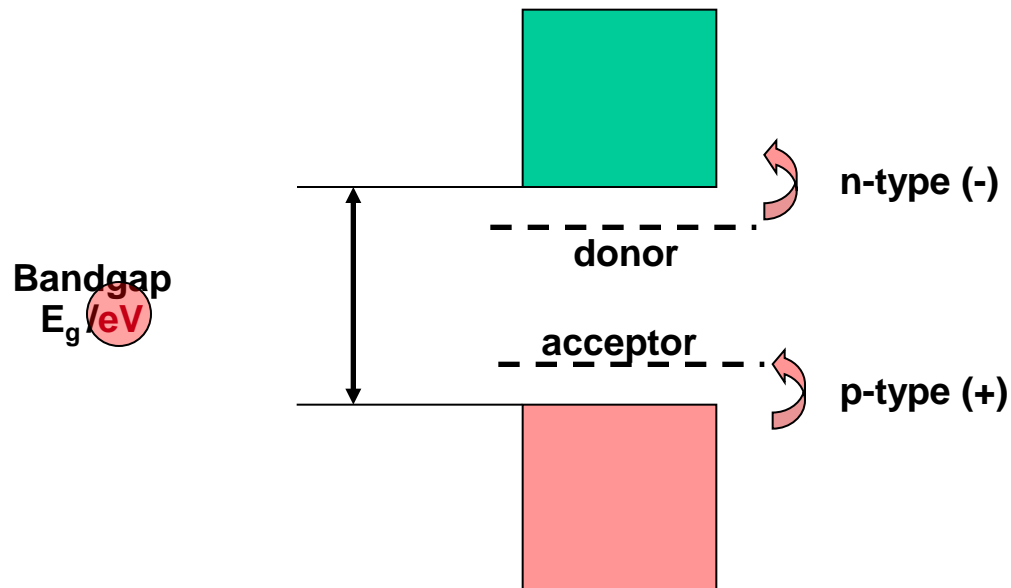
- Dopants introduce or create additional energy levels in the semiconductors band structure.

Which goes back to Koenigsburg observation:  
semiconductors properties vary with impurity and defects

**Intrinsic semiconductors**

**Extrinsic semiconductor**

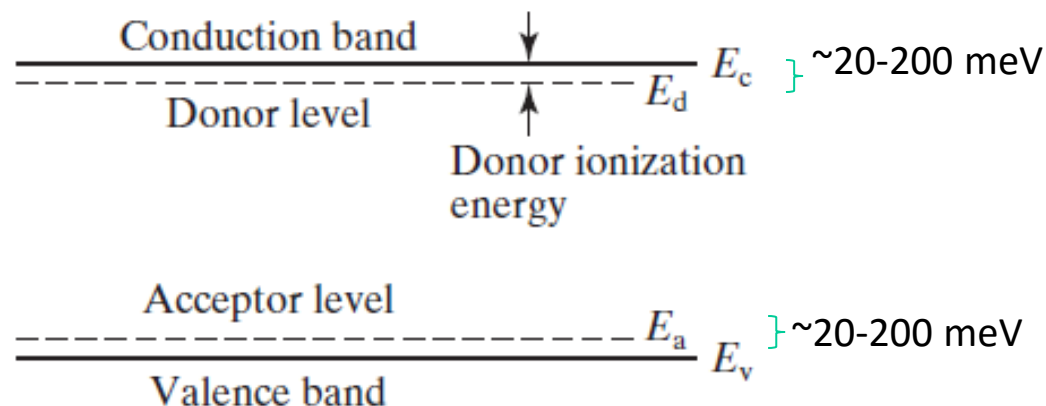
- dopants (impurities)





Although less important than  $E_c$  and  $E_v$ , two other energy levels are present in the energy band diagram:

**Donor** energy level -  $E_d$  & **Acceptor** energy level -  $E_a$



**$E_c - E_d$**  = donor ionization energy

**$E_a - E_v$**  = acceptor ionization energy

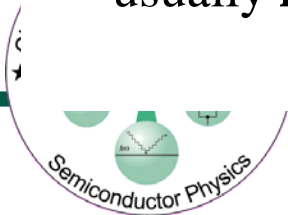
The energy required to ionize a donor atom (i.e., to free the extra electron and leave a positive ion behind) may be estimated by modifying the theory of the ionization energy of a hydrogen atom:

$$E_{\text{ion}} = \frac{m_0 q^4}{8 \epsilon_0^2 h^2} = 13.6 \text{ eV}$$

$m_0$  = free electron mass  
 $\epsilon_0$  = permittivity of free space  
 $h$  = Planck's constant.  
 $q$  = electron charge

The modification involves replacing  $\epsilon_0$  with the relative permittivity of the material and replacing  $m_0$  with the charge carrier effective mass,  $m_{\text{eff}}$ , which is a few times smaller than  $m_0$

- Because **donors and acceptors** have very small ionization energies, they are usually **fully ionized at room temperature**.



## Typical Band gap values for some relevant semiconductors

Semiconductor	InSb	Ge	Si	GaAs	GaP	ZnSe	Diamond
$E_g$ (eV)	0.18	0.67	1.12	1.42	2.25	2.7	6.0

## Typical Donors and Acceptors Energy values in Silicon

	Donors			Acceptors		
Dopant	Sb	P	As	B	Al	In
Ionization energy, $E_c - E_d$ or $E_a - E_v$ (meV)	39	44	54	45	57	160





# Description of motion of electrons and holes

## Dispersion relation & DOS

8th lecture

### Assumption 1

The crystal is understood as a periodic coulombic field.

### Assumption 2

- a) To describe the motion of electrons and holes with the laws of motion of the classical particles, we must assign **effective masses** ( $m_n$  and  $m_p$ ) to them because they will be different from the masses of the free particles.

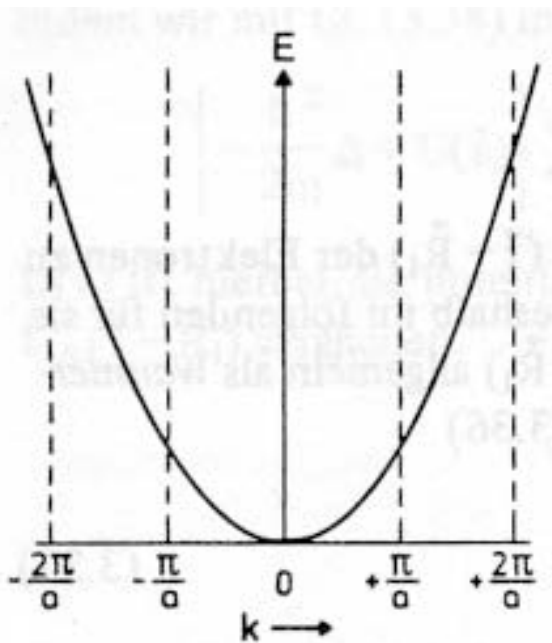
### Measured effective masses for different semiconductor materials

	Si	Ge	GaAs	InAs	AlAs
$m_n/m_0$	0.26	0.12	0.068	0.023	2.0
$m_p/m_0$	0.39	0.30	0.50	0.30	0.3

### Assumption 2b)

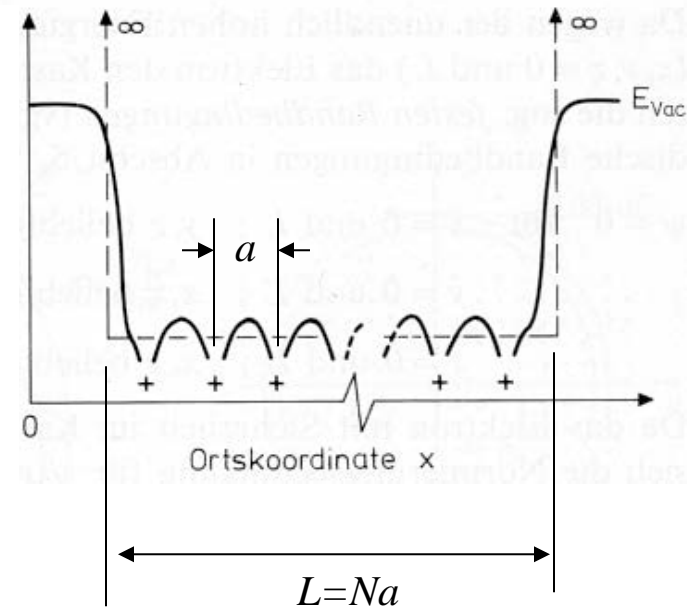
The movement of electrons and holes in a crystal will be conditioned by the crystal periodic coulombic field:

#### 1. Introduce periodicity



**Fig. 6.1.** Qualitative form of the potential for an electron in a periodic lattice of positive cores (+). The vacuum level  $E_{vac}$  is the level to which the electron must be promoted in order for it to leave the crystal and escape to infinity. The simplest approximation to describe this system is that of the square well potential (---) with infinitely high walls at the surfaces of the crystal

#### 2. Introduce periodic potential



### Assumption 3

Charged particles move when magnetic, electric fields or both are applied, then the particles are accelerated:

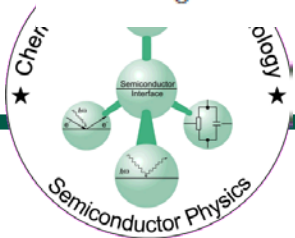
$$\text{Acceleration} = \frac{-q\mathcal{E}}{m_n} \quad \text{electrons}$$

$$\text{Acceleration} = \frac{q\mathcal{E}}{m_p} \quad \text{holes}$$

### Assumption 4

A complete description of the electrons in a crystal must be based on their wave characteristics, not just the particle characteristics. The electron wave function is the solution of the three-dimensional Schrödinger wave equation:

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi + V(\mathbf{r})\psi = E\psi$$



$\hbar = h/2\pi$  = reduced Planck constant,  
 $m_0$  = is the free electron mass,  
 $V(\mathbf{r})$  = potential energy field in the 3D space  
 $E$  = energy of the electron.

$$\mathcal{H}\psi(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{r}_n); \quad \mathbf{r}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Solution: Bloch wavefunction

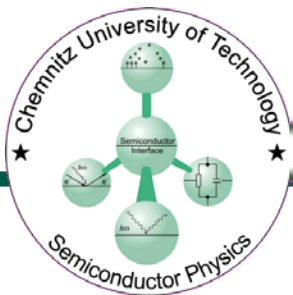
$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}$$

With the periodicity of the lattice

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{r}_n)$$

Group velocity of  
the electron wave

$$v_{n,k} = \frac{\partial \omega_n(k)}{\partial k} = \frac{1}{\hbar} \frac{\partial E_n(k)}{\partial k}$$

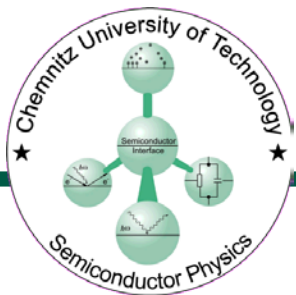


## Resolution Method

- Born-Oppenheimer or adiabatic approximation  $\rightarrow$  electrons motion independent from nucleus.
- Electrons do not interact with each other  $\rightarrow$  free electrons
- Electrons in a square box with dimensions  $L_x = L_y = L_z = L$
- $V(x, y, z) = \begin{cases} V_0 = \text{const} & \text{for } 0 \leq x, y, z \leq L \\ \infty & \text{otherwise} \end{cases}$ , fixed boundary conditions

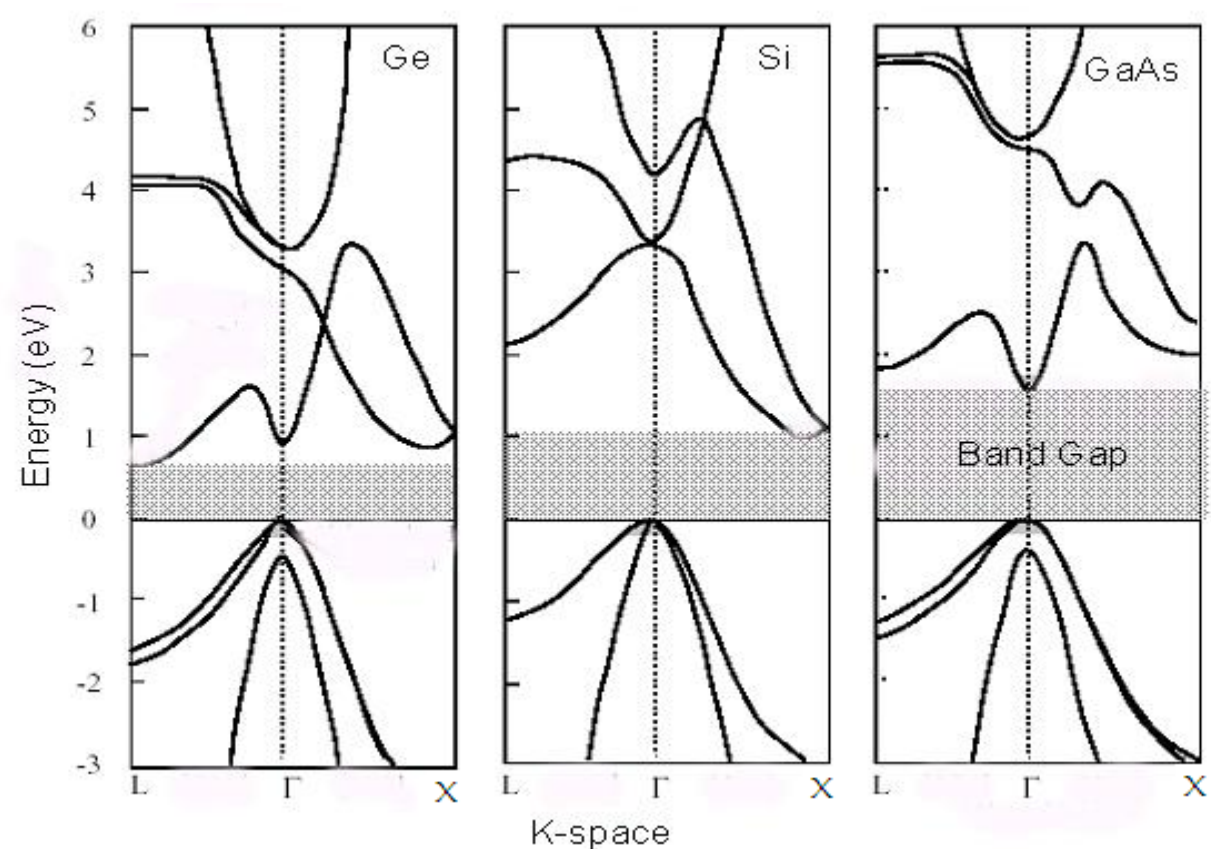
$$\Psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \longrightarrow \psi(r) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin k_x x \cdot \sin k_y y \cdot \sin k_z z$$

$$\text{with } k_x = \frac{\pi}{L} n_x \quad \text{and} \quad n_x = 1, 2, \dots$$



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

- Each semiconductor material has a unique  $E-k$  relationship (due to the unique  $V(\mathbf{r})$ ) for its conduction band and another unique  $E-k$  relationship for its valence band.



Energy band diagram of Germanium (Ge), Silicon (SI) and Gallium Arsenide (GaAs)

- Therefore, each semiconductor material has its unique  $m_n$  and  $m_p$ .

## Density of states

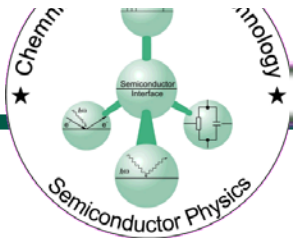
It is useful to think of an energy band as a collection of discrete energy states.

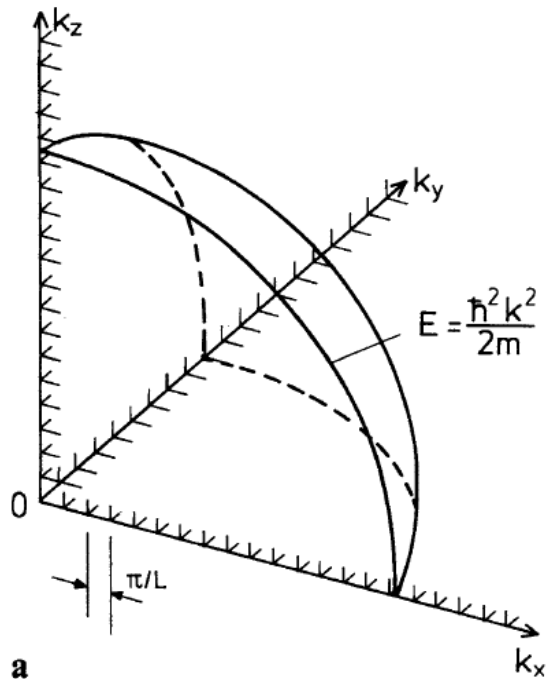
In quantum mechanics terms, each state represents a unique spin (up and down) and unique solution to the Schrodinger's wave equation for the periodic electric potential function of the semiconductor.

Each state can hold either one electron or none. If we count the number of states in a small range of energy,  $\Delta E$ , in the conduction band, we can find the **density of states**:

$$D_c(E) \equiv \frac{\text{number of states in } \Delta E}{\Delta E \times \text{volume}}$$

Similarly, there is a valence-band density of states,  $D_v(E)$  defined in the same way.





- Volume of an electronic state in the k-space

$$V_k = \left(\frac{\pi}{L}\right)^3$$

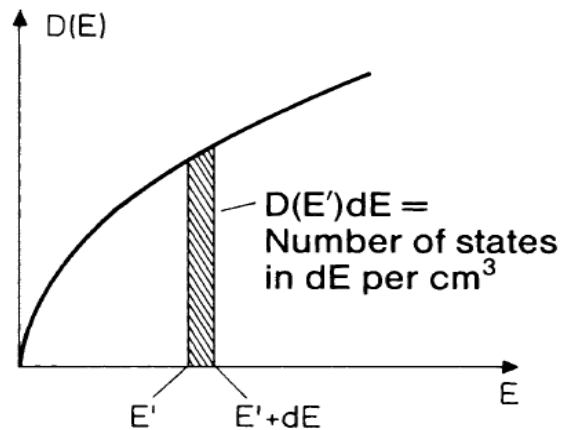
- Nr. Of states in  $dE/\text{cm}^3$

$$dZ' = \frac{1}{8} 4\pi k^2 dk / (\pi/L)^3$$

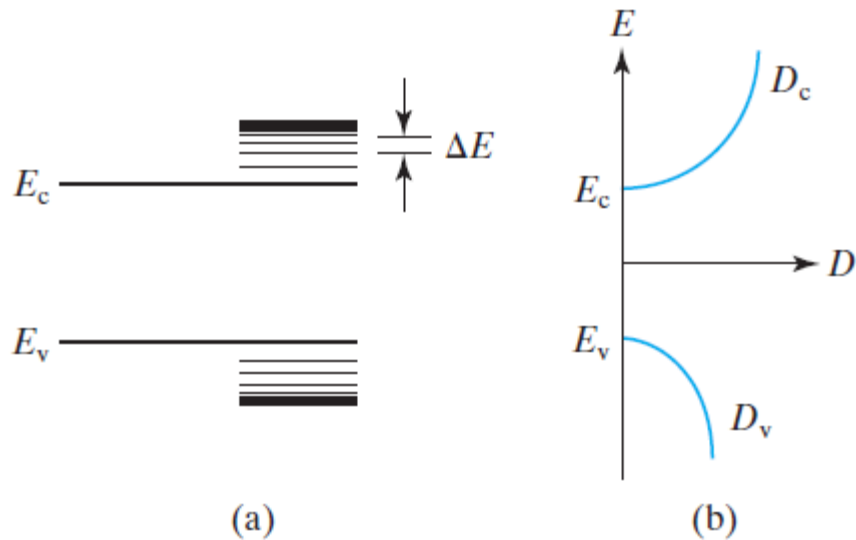
- $\Delta E \rightarrow dE = (\hbar^2 k/m) dk$

## Density of states

$$D(E) = dZ/dE$$

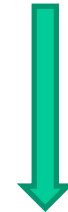






$$D_c(E) = \frac{8\pi m_n \sqrt{2m_n(E - E_c)}}{h^3}, \quad E \geq E_c$$

$$D_v(E) = \frac{8\pi m_p \sqrt{2m_p(E_v - E)}}{h^3}, \quad E \leq E_v$$



(a) Energy band as a collection of discrete energy states.

(b)  $D$  is the density of the energy states.

$D_c(E)$  and  $D_v(E)$  have the dimensions of number per cubic centimeter per electronvolt.

The product  $D_c(E) dE$  and  $D_v(E) dE$  are the numbers of energy states located in the energy range between  $E$  and  $E + dE$  per cubic centimeter of the semiconductor volume.



# The Fermi Function

8th lecture

**Thermal agitation** gives each energy state a certain **probability of being occupied** by an electron. That probability is expressed by the **Fermi function**.

\*The **Fermi function  $f(E)$**  gives the **probability that a given available electron energy state will be occupied at a given temperature**. The Fermi function comes from Fermi-Dirac statistics and has the form:

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

At ordinary temperatures, most of the levels up to the Fermi level  $E_F$  are filled, and relatively few electrons have energies above the Fermi level.

The **Fermi level** is on the order of a few **electron volts**, whereas the **thermal energy  $kT$**  is only about **0.026 eV at 300 K**.

# Fermi Function:

the Probability of an Energy State Being Occupied by an Electron  
Or  
the probability of finding an electron at a certain energy.

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

For large E  $\rightarrow E - E_F \gg kT$

$$f(E) \approx e^{-(E - E_F)/kT}$$

Boltzmann Approximation

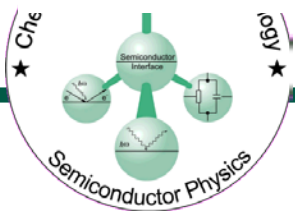
For small E  $\rightarrow E - E_F \ll -kT$

occupation probability  $\sim 1$

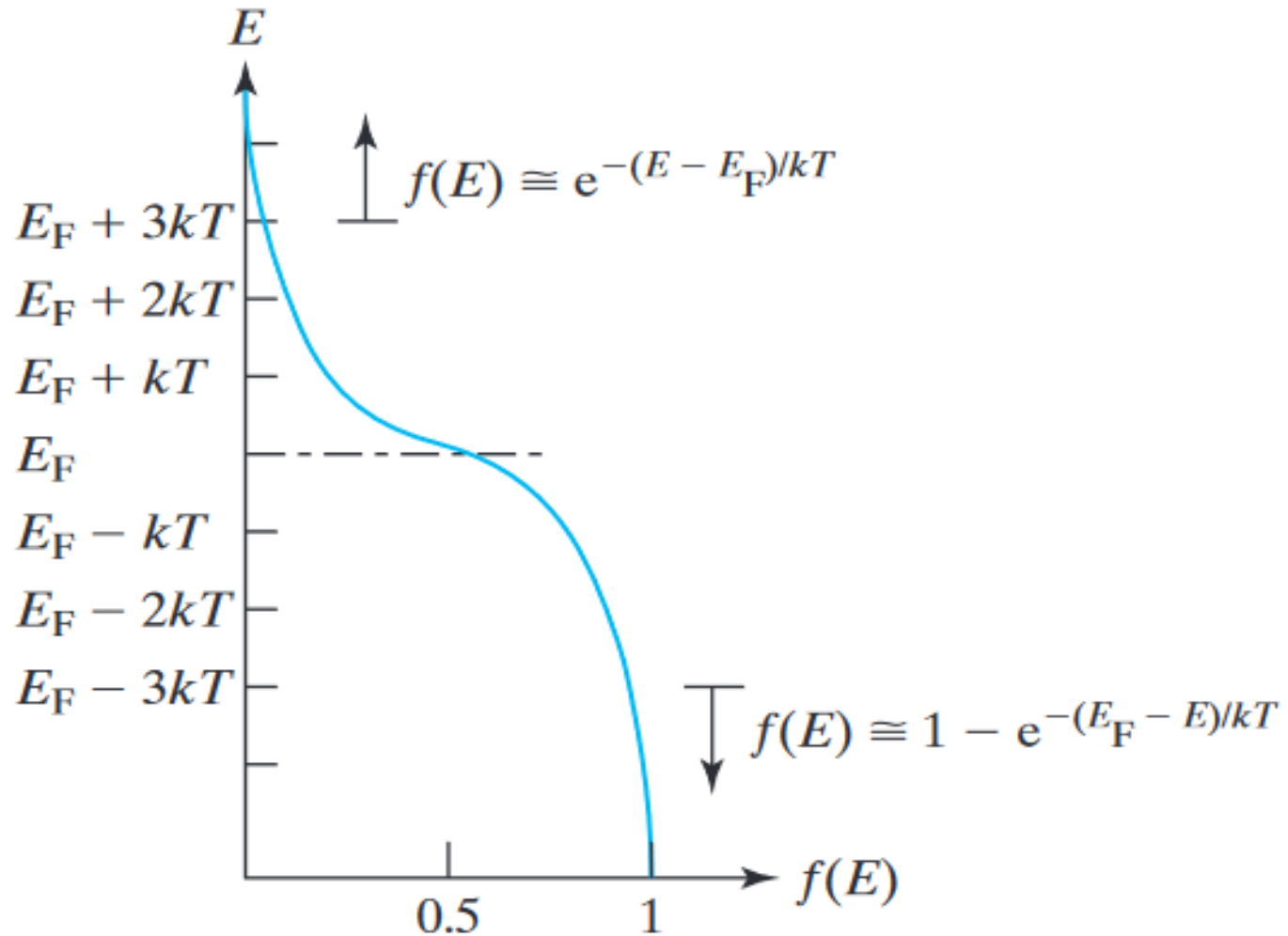


the low energy states tend to be fully occupied

$$f(E) \approx 1 - e^{-(E_F - E)/kT}$$

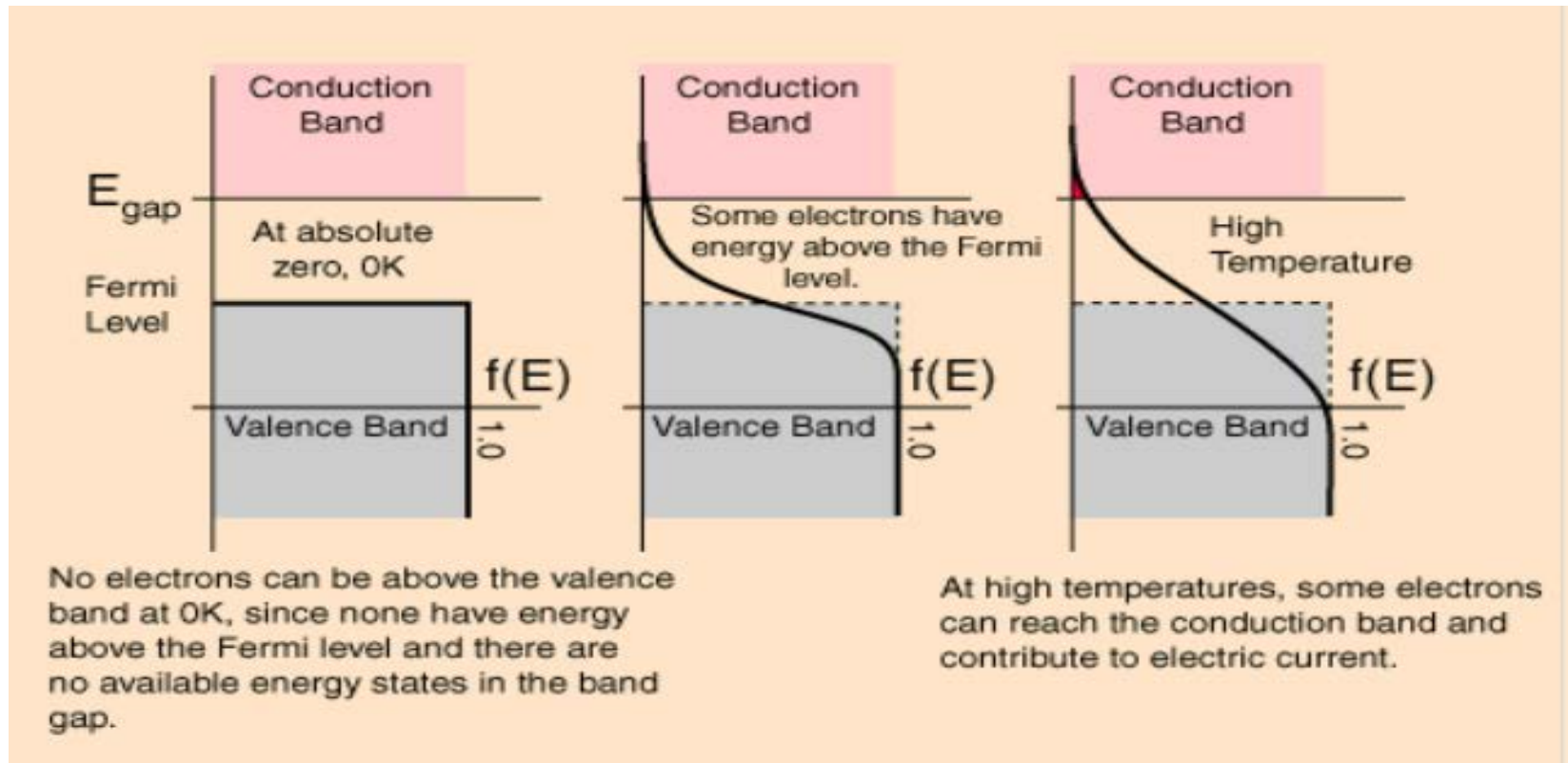


# The Fermi function diagram



## Implications of the Fermi function for the electrical conductivity of a semiconductor

The band theory of solids gives the picture that there is a sizable gap between the Fermi level and the conduction band of the semiconductor.



At higher temperatures, a larger fraction of the electrons can bridge this gap and participate in electrical conduction.



## SUMMARY

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Although the Fermi function has a finite value in the gap, there is no electron population at those energies (that's what you mean by a gap).

The population depends upon the product of the Fermi function and the **electron density of states**.

So in the gap there are no electrons because the density of states is zero.

In the conduction band **at 0 K, there are no electrons** even though **there are plenty of available states**, but the **Fermi function is zero**.

At high temperatures, the density of states and the Fermi function have finite values in the conduction band, so there is a finite **conducting population**.



## Note that:

- $E_F$  is called the Fermi energy or the Fermi level
- the Fermi level  $E_F$  is determined by the available electrons and states in the system.
- the probability of occupation at  $E_F$  is  $Eg/2$
- The probability approaches unity if  $E$  is much lower than  $E_F$
- The probability approaches zero at  $E$  much higher than  $E_F$
- A very important fact to remember about  $E_F$  is that **there is only one Fermi level in a system at thermal equilibrium**
- In doped semiconductors, **p-type** and **n-type**, the Fermi level is shifted by the impurities, illustrated by their **band gaps**.

**Fermi level:** Is the term used to describe the top of the collection of electron energy levels at absolute zero temperature.

OR

Is the highest **energy** state occupied by electrons in a material at absolute zero temperature. As the temperature is increased, electrons start to exist in higher **energy** states too.

This concept comes from **Fermi-Dirac statistics**. Electrons are **fermions** and by the **Pauli exclusion principle** cannot exist in identical energy states. So at absolute zero they pack into the lowest available energy states and build up a "Fermi sea" of electron energy states.

The Fermi level is the surface of that sea at absolute zero where no electrons will have enough energy to rise above the surface.

- The concept of the Fermi energy is a crucially important concept for the understanding of the **electrical** and **thermal** properties of solids.
- The Fermi level is referred to as the **electron chemical potential** in other contexts.



In metals, the Fermi energy gives information about the velocities of the electrons which participate in ordinary electrical conduction.

The amount of energy which can be given to an electron in such conduction processes is on the order of micro-electron volts so only those electrons very close to the Fermi energy can participate.

The **Fermi velocity** of these conduction electrons can be calculated from the Fermi energy.

$$v_F = \sqrt{\frac{2E_F}{m}}$$

This speed is a part of the **microscopic Ohm's Law** for electrical conduction. For a metal, the density of conduction electrons can be implied from the Fermi energy.




The **position of the Fermi level** with respect to valence and or conduction bands depends on various parameters.

temperature  
effective masses of electrons and holes  
number of free electrons and holes.

This variation of the Fermi level obeys two conservation conditions :

mass & charge

- the "**mass action law**" which states that the number of particles of each type as well as the overall number of the particles must conserve whatever is their distribution on the available energy levels.
  - the **neutrality equation** which states that the electrical neutrality has to be fulfilled, i.e. the number of negative charges must be counter balanced exactly by the same number of positive charges.
- 

## The Fermi Level & Intrinsic semiconductors

In an **intrinsic semiconductor** (with no doping at all), the Fermi level is **lying exactly at the middle of the energy bandgap** at  $T=0$  Kelvin.

- With **increasing/decreasing temperature  $T>0$  Kelvin** the Fermi energy **remains at this midgap position** if conduction and valence bands have exactly the same dispersion energy or more simply the **same effective masses** for electrons and holes.

Or it will move towards the band with the **smaller/higher effective mass**, in case they are different.

## The Fermi Level & Extrinsic/Doped semiconductors

In an **extrinsic semiconductors** (with added doping), in order to conserve the number of particles (mass action law) and to fulfill the overall electrical charge neutrality (neutrality equation), the Fermi level has to move away from the midgap position.

- It shifts towards **conduction band in an n-type semiconductor** (extrinsic semiconductors with added doping impurities which are donors i.e. impurities which give additional electrons to the system) where the number of electrons  $n$  is higher than the number of holes ( $n > p$ ).
- It shifts towards **valence band in a p-type semiconductor** (extrinsic semiconductors with added doping impurities which are acceptors i.e. impurities which trap electrons from the system giving rise to a deficit of electrons or an excess of holes ) where the number of electrons  $n$  is lower than the number of holes ( $n < p$ ).

## In reality:

The electron and hole concentrations in a semiconductor are usually very different.

+

There are four types of charged species in a semiconductor: electrons, holes, positive donor ions, and negative acceptor ions. Their densities are represented by the symbols  $n$ ,  $p$ ,  $N_d$ , and  $N_a$ .

+

In an N-type semiconductor, the abundant electrons are called the **majority carriers** and the almost nonexistent holes are the **minority carriers**.

+

In P-type semiconductors, the **holes are the majority carriers** and the electrons are the minority carriers.

+

The shallow donor and acceptor levels ( $E_d$  and  $E_a$ ) are **energy states** and their occupancy by electrons is **governed by the Fermi function**.

+

$E_F$  cannot be close to both  $E_c$  and  $E_v$

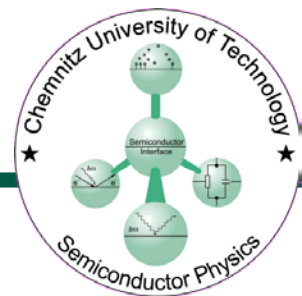
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$n$  and  $p$  cannot both be large numbers at the same time

## ELECTRON AND HOLE CONCENTRATIONS

What are the carrier concentrations in undoped & doped semiconductors? The  $np$  product.

These questions will be answered by relating the **Fermi level** and the **carrier concentrations**.



Next Lecture

## Electronic properties of semiconductors (cont.)

