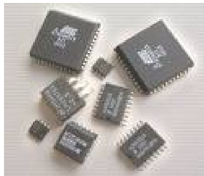
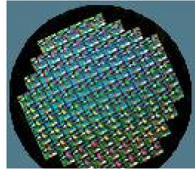


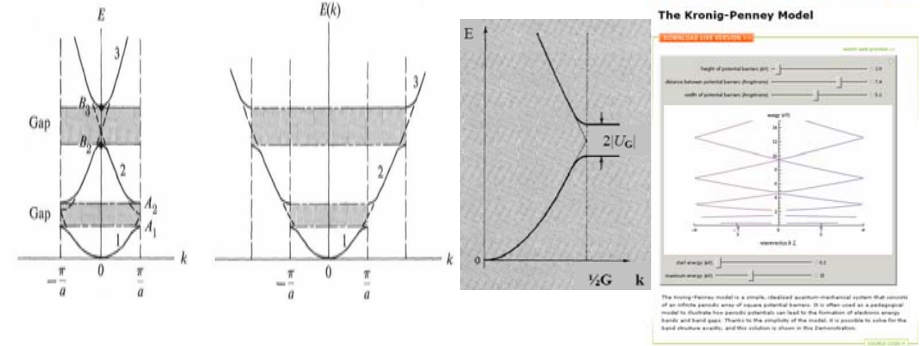
Phys 446 Solid State Physics
Lecture 9 Nov 9, 2007
(Ch. 6.1-6.5)



Last time: Finished with the band theory of metals

Today: Semiconductors

Origin of the energy gaps



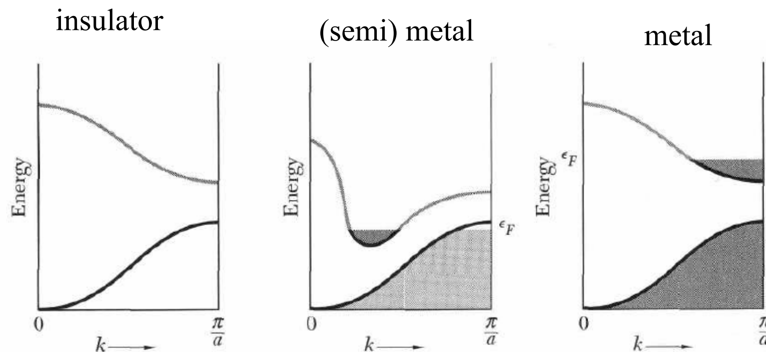
We focused on the energy values

got $$E(\mathbf{k}) = E^0(\mathbf{k}) + \sum_{\mathbf{G}\neq 0} \frac{|U_\mathbf{G}|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})}$$ away from the zone edges

and $$E = \frac{1}{2}\left(E^0(\mathbf{k}) + E^0(\mathbf{k}-\mathbf{G})\right) \pm \left[\frac{1}{4}\left(E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})\right)^2 + |U_\mathbf{G}|^2\right]^{1/2}$$

near the zone edges. $E^0(\mathbf{k}) = E^0(\mathbf{k}-\mathbf{G})$ $\qquad E = E^0(\mathbf{k}) \pm |U_\mathbf{G}|$

Metals, Insulators, semimetals, semiconductors



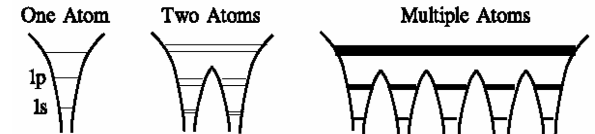
Tight binding model

Assumptions:

– atomic potential is strong, electrons are tightly bound to the ions

– the problem for isolated atoms is solved: know wave functions ϕ_n and energies E_n of atomic orbitals

– weak overlapping of atomic orbitals



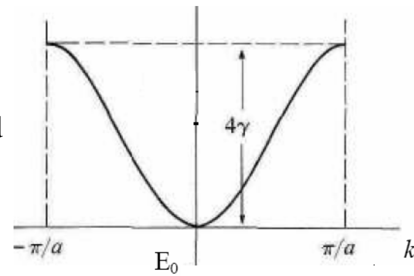
Start with 1D case

Bloch function in the form: $$\psi(k,x) = \frac{1}{N^{1/2}} \sum_{j=1}^{N} e^{ikX_j} \phi_n(x - X_j)$$

where $X_j = ja$ – position of the jth atom, a – lattice constant;
$\psi_n(x - X_j)$ – atomic orbital centered around the jth atom – large near X_j, but decays rapidly away from it.
Small overlap exists only between the neighboring atoms

$$E(k) = E_0 + 4\gamma \sin^2\left(\frac{ka}{2}\right)$$

Original energy level E_n has broadened into an *energy band*.



The bottom of the band is E_0
- located at $k = 0$

The band width = 4γ – proportional to the overlap integral

For small k, $ka/2 << 1$ (near the zone center)

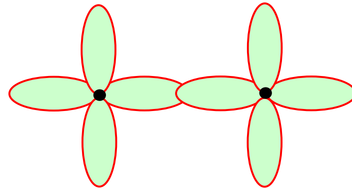
$E(k) - E_0 = \gamma a^2 k^2$ - quadratic dispersion, same as for free electron

$$E(k) - E_0 = \frac{\hbar^2 k^2}{2m^*} \quad \text{where} \quad m^* = \frac{\hbar^2}{2a^2}\frac{1}{\gamma}$$ - *effective mass*

For $k = \pi/2$, you will find that

$$m^* = -\frac{\hbar^2}{2a^2}\frac{1}{\gamma}$$

Generally: $$m^* = \hbar^2 \left(\frac{d^2E}{dk^2}\right)^{-1}$$

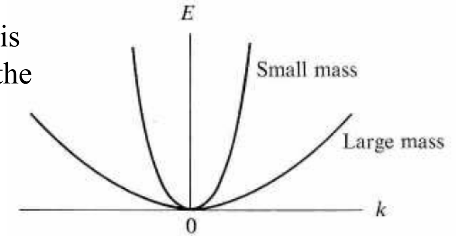


The results obtained can be extended to 3D case.

For simple cubic lattice, get

$$E(k) = E_0 + 4\gamma\left[\sin^2\left(\frac{k_x a}{2}\right) + \sin^2\left(\frac{k_y a}{2}\right) + \sin^2\left(\frac{k_z a}{2}\right)\right]$$

$$m^* = \hbar^2 \left(\frac{d^2E}{dk^2}\right)^{-1}$$ Effective mass is determined by the curvature of dispersion



Generally, anisotropic:

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j} \quad i,j = x,y,z$$ - *inverse effective mass tensor*

Velocity of the Bloch electron: $v = \frac{1}{\hbar}\frac{\partial E}{\partial k}$ 3D: $v = \frac{1}{\hbar}\nabla_{\mathbf{k}} E(\mathbf{k})$

Summary

- Tight binding model – strong crystal potential, weak overlap. The band width increases and electrons become more mobile (smaller effective mass) as the overlap between atomic wave functions increases
- Concept of effective mass: in a periodic potential electron moves as in free space, but with different mass:
$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j} \quad i,j = x,y,z$$
- Metals: partially filled bands; insulators – at 0 K the valence band is full, conductance band is empty. Semiconductors and semimetals.
- Velocity of the Bloch electron: $v = \frac{1}{\hbar}\nabla_{\mathbf{k}} E(\mathbf{k})$
  remains constant in perfectly periodic lattice
- Density of states. Simple case: $D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}$

Summary

- Velocity of the Bloch electron: $\mathbf{v} = \frac{1}{\hbar}\nabla_{\mathbf{k}} E(\mathbf{k})$
- In the presence of an electric field the electron moves in k-space according to the relation: $\hbar\frac{d\mathbf{k}}{dt} = \mathbf{F}(\mathbf{r},t) = -e\mathbf{E}(\mathbf{r},t)$

  This is equivalent to the Newton's second law if we assume that the electron momentum is equal to $\hbar\mathbf{k}$
- Dynamical effective mass: $m^* = \hbar^2 \left(\frac{d^2E}{dk^2}\right)^{-1}$

  m^* is inversely proportional to the curvature of the dispersion.

  In a general case the effective mass is a tensor: $\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j} \quad i,j = x,y,z$
- $\mathbf{p}_c = \hbar\mathbf{k}$ is called the *crystal momentum or quasi-momentum.*

  The actual momentum is given by $\langle \psi_{\mathbf{k}} | -i\hbar\nabla | \psi_{\mathbf{k}} \rangle$

  Can show that $\mathbf{p} = m_0\mathbf{v}$, where m_0 is the free electron mass, $\mathbf{v}$ is given by the above expression

Physical origin of the effective mass

Since $\mathbf{p} = m_0\mathbf{v}$ - true momentum, one can write: $$m_0 \frac{d\mathbf{v}}{dt} = \mathbf{F}_{tot} = \mathbf{F}_{ext} + \mathbf{F}_L$$

The total force is the sum of the external and lattice forces.

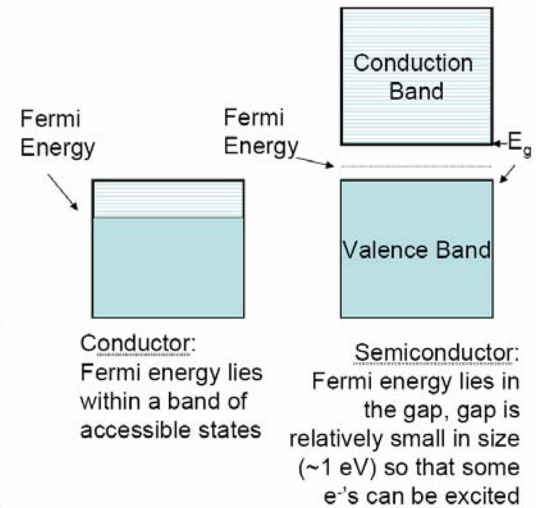
But $$m_0 \frac{d\mathbf{v}}{dt} = m_0 \frac{\mathbf{F}_{ext}}{m^*}$$

So, we can write
$$m^* = m_0 \frac{\mathbf{F}_{ext}}{\mathbf{F}_{ext} + \mathbf{F}_L}$$

The difference between m^* and m_0 lies in the presence of the lattice force $\mathbf{F}_L$

Conductors vs. Semiconductors

- Remember, where the Fermi level is is largely determined by the density: $k_F = (3\pi^2 N/V)^{1/3}$
- It is also determined by how many electrons are free, and how many are tied up in chemical bonds
- The lower the density of carriers, the higher the Fermi Energy
- When the Fermi Energy is so high that it appears in the gap, then we have a semiconductor
- If the gap is large enough, we will have an insulator (you need a large amount of energy to make the electrons mobile)

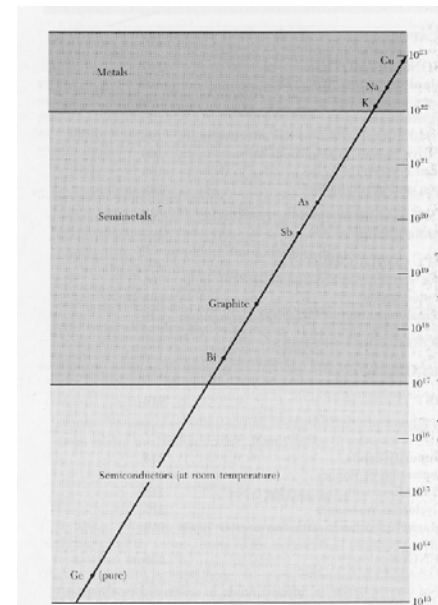


Crystal structure and bonding

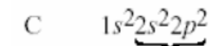
Semiconductors include a large number of substances of different chemical and physical properties. Main types of semiconductors:

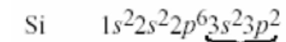
- Group IV semiconductors - Si, Ge.
  - Crystallize in the diamond structure (fcc lattice with a basis composed of two identical atoms)
  - covalent crystals, i.e., the atoms are held together by covalent bonds
  - the covalent electrons forming the bonds are hybrid sp^3 atomic orbitals
- III-V (GaAs, InP, etc.), II-VI (ZnSe, ZnS) semiconductors and alloys
  - zinc blende structure (same as diamond but with two different atoms) or hexagonal wurtzite structure (GaN)
  - also covalent bonds, but polar - the distribution of the electrons along the bond is not symmetric
- Some other compounds (I-VII, various oxides, halogenides, organic semiconductors...)

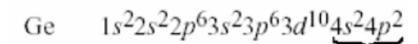
Carrier density of metals and semiconductors



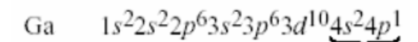
IV Semiconductors

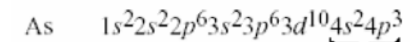
C 

Si 

Ge 

III-V Semiconductors

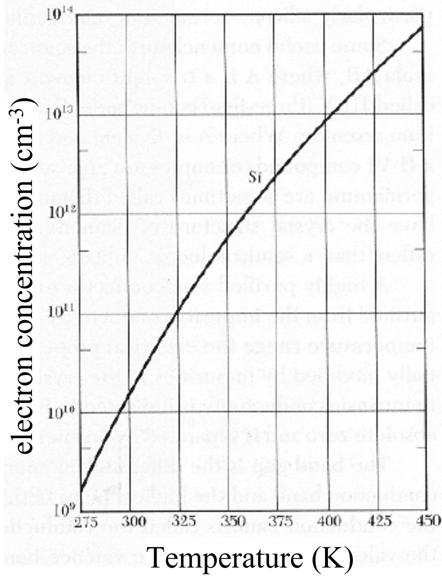
Ga 

As 

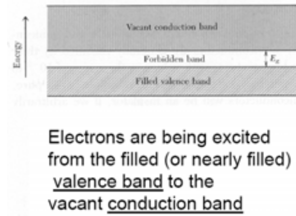
Semiconductors have higher resistance than metals (~ 10^{-2} to 10^9 Ohm·cm)

Typical metals: 10^{-6} Ohm·cm

Temperature dependence of conductivity



- Semiconductors have the property that the resistance increases with decreasing temperature – opposite to metal behavior
- This is because the number of conduction electrons changes dramatically as a function of temperature



Electrons are being excited from the filled (or nearly filled) valence band to the vacant conduction band

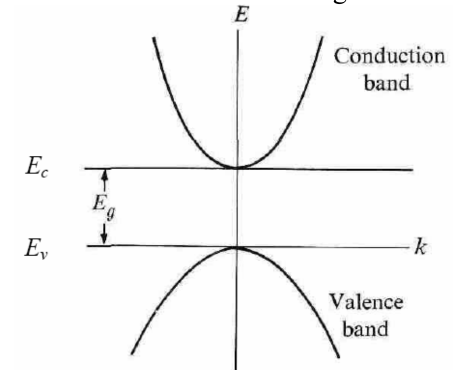
Band structure

Semiconductor - a solid in which the highest occupied energy band, the *valence band* (VB), is completely full at $T = 0°K$

However, the gap above this band is small, so that electrons may be excited thermally at room temperature from the valence band to the next-higher band – the *conduction band* (VB).

Electrons are excited across the gap → the bottom of the conduction band is populated by electrons, and the top of the valence band - by holes.

As a result, both bands are now only partially full → can carry a current if an electric field were applied



The energy of the CB has the form:

$$E_c(k) = E_c + \frac{\hbar^2 k^2}{2m_e}$$

The energy of the VB may be written as

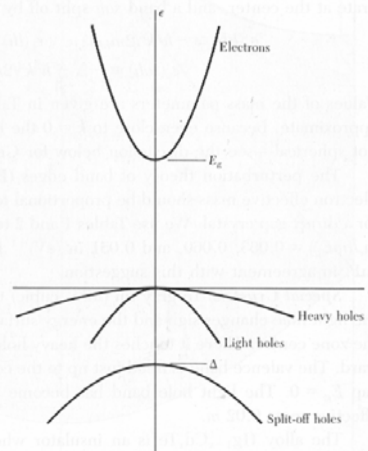
$$E_v(k) = E_v - \frac{\hbar^2 k^2}{2m_h}$$

Meaning of curvature

- A small curvature – small effective mass
- A large curvature – large effective mass
- Examples of band masses:

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

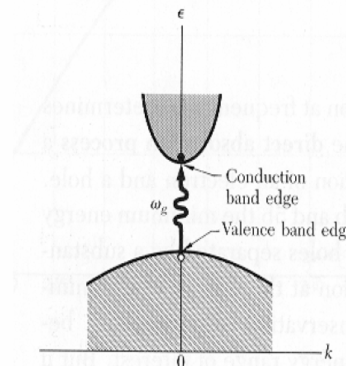
Crystal	Electron m_e/m	Heavy hole m_{hh}/m	Light hole m_{lh}/m	Split-off hole m_{soh}/m	Spin-orbit Δ, eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34
Cu_2O	0.99	—	0.58	0.69	0.13

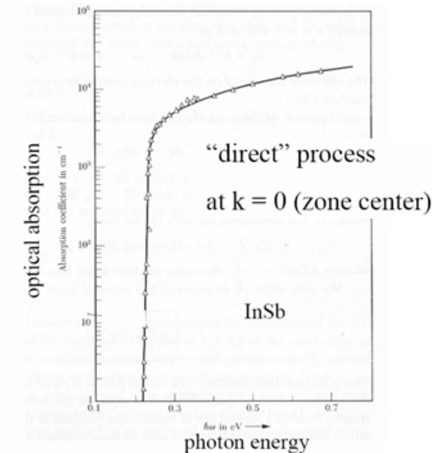


(see assignment for an example of m* for Ge)

Spectroscopy

- Electrons can absorb light, and when it is of the right energy (frequency), you get absorption





powerful method to determine the energy gap E_g

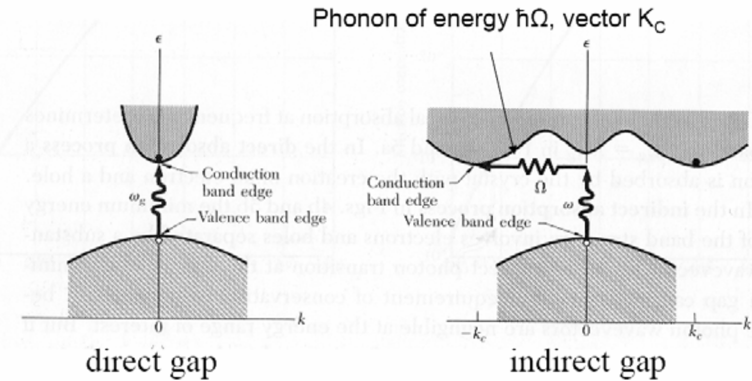
Band structure parameters of some semiconductors (room temperature)

Group	Crystal	E_g, eV	Effective mass, m/m_0 Electrons	Holes
IV	C	5.3		
	Si	1.1	$m_l = 0.97, m_t = 0.19$	0.5, 0.16
	Ge	0.7	$m_l = 1.6, m_t = 0.08$	0.3, 0.04
	α Sn	0.08		
III–V	GaAs	1.4	0.07	0.09
	GaP	2.3	0.12	0.50
	GaSb	0.7	0.20	0.39
	InAs	0.4	0.03	0.02
	InP	1.3	0.07	0.69
	InSb	0.2	0.01	0.18
II–VI	CdS	2.6	0.21	0.80
	CdSe	1.7	0.13	0.45
	CdTe	1.5	0.14	0.37
	ZnS	3.6	0.40	5.41
	ZnSe	2.7	0.10	0.60
	ZnTe	2.3	0.10	0.60
IV–VI	PbS	0.4	0.25	0.25
	PbSe	0.3	0.33	0.34
	PbTe	0.3	0.22	0.29

The energy gap varies with temperature – due to a change in lattice constant. This affects the band structure, which is sensitive to the lattice constant.

Direct and Indirect Gaps

- A direct gap is when you can excite an electron to the conduction band (leaving a hole behind) without assistance from phonons
- An indirect gap is when the electron cannot be excited to a higher level without the aid of a phonon (the electron has to change it's momentum to get to the next band. For a direct gap, the change in momentum is very small)



Band structure parameters of some semiconductors (room temperature)

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

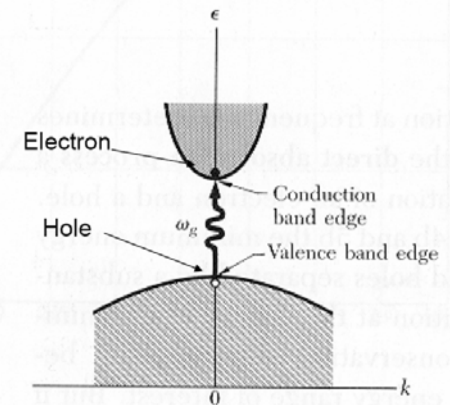
Crystal	Gap	E_g, eV 0 K	E_g, eV 300 K	Crystal	Gap	E_g, eV 0 K	E_g, eV 300 K
Diamond	i	5.4		HgTe[a]	d	−0.30	
Si	i	1.17	1.11	PbS	d	0.286	0.34–0.37
Ge	i	0.744	0.66	PbSe	i	0.165	0.27
αSn	d	0.00	0.00	PbTe	i	0.190	0.29
InSb	d	0.23	0.17	CdS	d	2.582	2.42
InAs	d	0.43	0.36	CdSe	d	1.840	1.74
InP	d	1.42	1.27	CdTe	d	1.607	1.44
GaP	i	2.32	2.25	ZnO		3.436	3.2
GaAs	d	1.52	1.43	ZnS		3.91	3.6
GaSb	d	0.81	0.68	SnTe	d	0.3	0.18
AlSb	i	1.65	1.6	AgCl		—	3.2
SiC(hex)	i	3.0	—	AgI		—	2.8
Te	d	0.33	—	Cu_2O	d	2.172	—
ZnSb		0.56	0.56	TiO_2		3.03	—

The energy gap varies with temperature – due to a change in lattice constant. This affects the band structure, which is sensitive to the lattice constant.

Electrons and holes

- When an electron is excited to a higher band, it leaves hole behind in the valence band
- What are the properties of holes?

1. $\vec{K}_h = -\vec{K}_{el}$ (this is because the total momentum must be zero for the electron being excited to a higher state – if it has momentum $\vec{K}_{el}$, then the hole has to have momentum $-\vec{K}_{el}$)
2. $Energy_h$ = - $Energy_{el}$ (again, for the same reason as the momentum: this is the energy needed to create a hole, which isn't a spontaneous process, so it is negative)
3. $Mass_h$ = $-Mass_{el}$ (this is harder to prove. You can think of it as missing mass, but that isn't quite right)



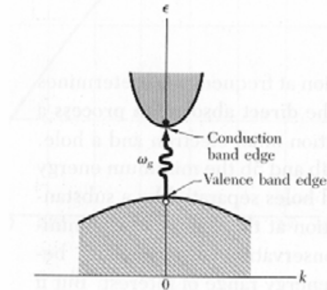
Holes having negative mass

$$\varepsilon = \frac{(\hbar k)^2}{2m} \rightarrow \frac{d^2\varepsilon}{dk^2} = \frac{\hbar^2}{m}$$

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

This is sometimes called an effective mass (we have seen this before – thermal mass of free electrons)

- This derivative is the curvature of the E vs K graph
- Concave up: positive, with a positive mass
- Concave down: negative, with a negative mass

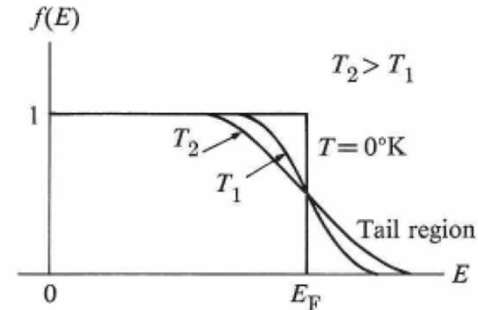


Carrier concentration: intrinsic semiconductors

In order to determine the number of carriers, recall the Fermi-Dirac distribution function:

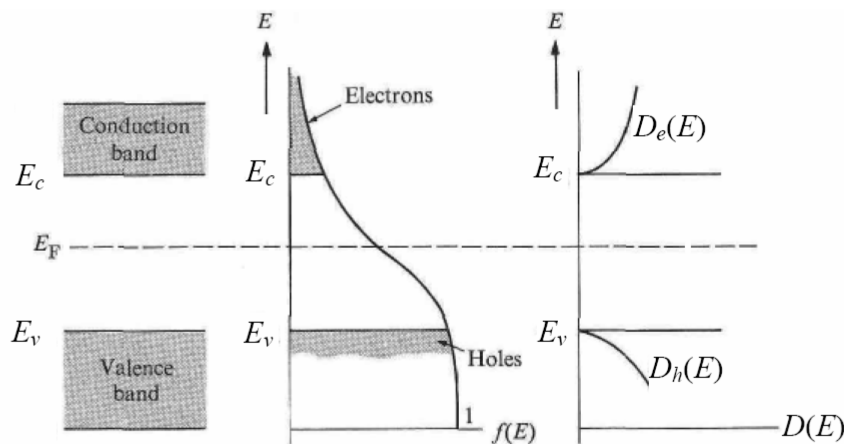
$$f(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1}$$

- probability that an energy level E is occupied by an electron at T



Fermi level in intrinsic semiconductors lies close to the middle of the band gap.

The distribution function and the conduction and valence bands of a semiconductor:



The distribution function

Density of states for electrons and holes

First, calculate the concentration of electrons in the CB.

The number of states in the energy range (E, $E + dE$) is equal to $D_e(E)dE$, where $De(E)$ - the density of electron states.

Each of these states has an occupation probability $f(E) \Rightarrow$ the number of electrons in this energy range is equal to $f(E)D_e(E)dE$.

The concentration of electrons throughout the CB is thus given by the integral over the conduction band:

$$n = \int_{E_c}^{\infty} f_e(E)D_e(E)dE$$

$E_g \sim 1\text{eV} >> kT \Rightarrow$ can neglect the unity term in the denominator $F_e(E)$

$$f(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1} \quad \rightarrow \quad f_e(E) \approx e^{-(E-\mu)/k_BT}$$

The density of states for the conduction band is given by

$$D_e(E) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}(E - E_c)^{1/2}$$

substitute expressions for $f_e(E)$ and $D_e(E)$ into the integral, obtain

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} e^{\mu/kT} \int_{E_c}^{\infty} \left(E - E_c\right)^{1/2} e^{-E/k_BT} dE$$

change the variable and use the result $\int_0^\infty x^{1/2} e^{-x} dE = \frac{\sqrt{\pi}}{2}$

get $n = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} e^{(\mu - E_c)/k_BT}$

Apply the same ideas to evaluate the number of holes in the VB.

The probability that a hole occupies a level E in this band is equal to $1-f_e(E)$, since $f_e(E)$ is the probability of electron occupation

Assuming that the Fermi level lies close to the middle of the band gap, i.e. $(\mu - E) >> k_BT$ we find for the distribution function of holes:

$$f_h(E) = 1 - \frac{1}{e^{(E-\mu)/k_BT} + 1} = \frac{1}{e^{(\mu - E)/k_BT} + 1} \approx e^{-(\mu - E)/k_BT}$$

The density of states for the holes is

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

where E_v is the energy of the valence band edge.

Similarly to the way we did for electrons, can find for the concentration of holes in the valence band:

$$p = \int_{-\infty}^{E_v} f_h(E) D_h(E) dE = 2\left(\frac{m_h kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - \mu)/k_BT}$$

For intrinsic semiconductors $n = p$

and $\left(m_e\right)^{3/2} e^{(\mu - E_c)/k_BT} = \left(m_h\right)^{3/2} e^{(E_v - \mu)/k_BT}$

Solve this for the Fermi energy: $\mu = \frac{E_v + E_c}{2} + \frac{3}{4} k_B T \ln \frac{m_h}{m_e}$

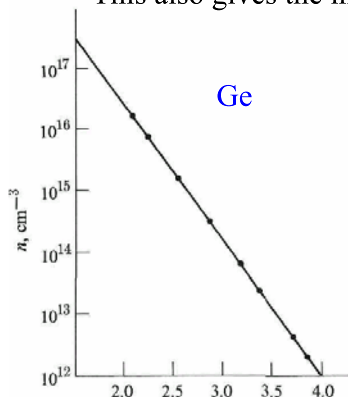
The second term is very small compared with the first → the Fermi level is close to the middle of the energy gap.

Substituting μ into the formula for n gives $n = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} e^{(\mu - E_c)/k_BT}$

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

where $E_g = E_c - E_v$ is the band gap.

This also gives the intrinsic hole concentration, since $n = p$.



n increases very rapidly - exponentially - with temperature

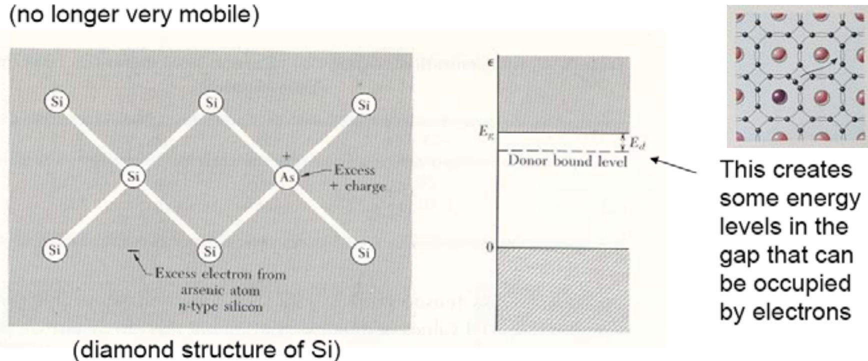
For Ge at room temperature $n \sim 10^{14}$ cm^{-3} - typical for intrinsic carrier concentration in semiconductors.

Intrinsic vs Extrinsic Semiconductors

- Intrinisic semiconductors: the Fermi energy lies within the energy gap without altering the materials (valence band is completely filled at T = 0 K, for temperatures higher than this, electrons can be excited to the conduction band).
- Extrinsic semiconductors: we can add impurities to make a material semiconducting (or to change the properties of the gap)
- There are 2 types of extrinsic semiconductors: p-type and n-type (you many have heard of p-n junctions in electronics courses – these are based upon interfaces of p and n-type materials)
- These are materials which have mostly hole carriers (p) or electron carriers (n)
- These give you ways of modifying the band gap energies (important for electronics, detectors, etc)

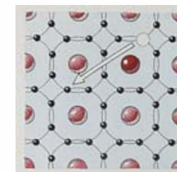
Extrinsic semiconductors: n-type

- To see how this works, lets add a small amount of Arsenic (As: $4s^2 4p^3$) to Silicon (Si:$3s^2 3p^2$) (generally, a group V element to a group IV host)
- As replaces a Si atom, but it donates an electron to the conduction band (As is called the donor atom)
- This is an n-type semiconductor – more electrons around that can be mobile, and the Fermi energy is usually near the Conduction band
- At low temperatures, these extra electrons get trapped at the donor sites (no longer very mobile)



This creates some energy levels in the gap that can be occupied by electrons

(diamond structure of Si)

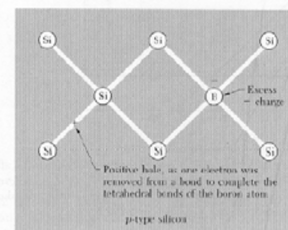


Extrinsic semiconductors: p-type

- The p-type semiconductors rely on a similar principle: now we are doping the lattice with ions that want to take electrons away (these are called acceptors), leaving mobile holes in the lattice
- An example: Doping Boron (B: $2s^2 2p$) into Si (Si: $3s^2 3p^2$). The Boron takes an extra electron so that it has the same bonding as Si, and leaves a hole in the lattice

Table 6 Acceptor ionization energies E_a of trivalent impurities in germanium and silicon, in meV

	B	Al	Ga	In
Si	45.	57.	65.	16.
Ge	10.4	10.2	10.8	11.2



Acceptor bound level

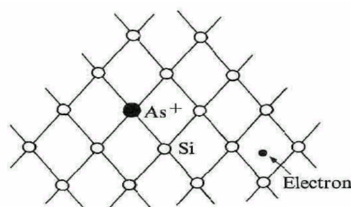
This creates holes in the lattice, which are these states near the valence band

Impurity states

Consider, for instance, a sample of Si, which has been *doped* by As

The As atom has five electrons while Si has valence 4.

4 of As electrons form the tetrahedral bonds with Si. The fifth electron cannot enter the bond, which is now saturated, and hence this electron detaches from the impurity.



Impurities that contribute electrons to the CB of the semiconductors are called *donors.*

Note that electrons have been created without the generation of holes.

We can calculate the binding energy by using the familiar Bohr model.

Must take into account the dielectric constant of the medium. Thus the coulomb potential is now given by

$$V(r) = -\frac{e^2}{\varepsilon r}$$

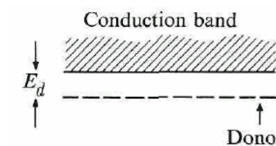
$\varepsilon = 11.7$ in Si

in the Bohr model, the binding energy is

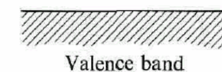
$$E_d = -\frac{e^4 m_e}{2\varepsilon^2 \hbar^2}$$

(if $m_e = m_0$ and $\varepsilon = 1$, get $R_y = 13.6$ eV)

The binding energy of the donor is reduced by the factor $1/\varepsilon^2$ (usually ~0.01), and also by the mass factor m_e/m_0 (usually < 1).



The binding energy of these *shallow* donors is about 10^{-3} of R_y – agrees with experiment.



Bohr radius of the donor electron: $r_d = \varepsilon \frac{m}{m_e} a_0$

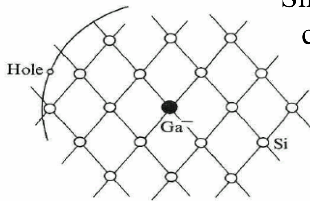
where a_0 is the Bohr radius for hydrogen atom, equal to 0.53 Å.

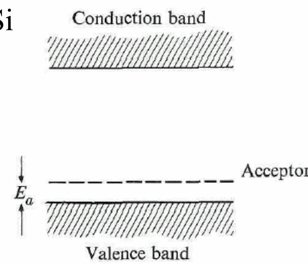
The radius of the orbit >> a_0, by a factor of ~100, typically ~50 Å → much greater than the interatomic spacing.

At room T almost all the donors are ionized → the concentration of electrons is nearly equal to that of the donors.

Acceptors

Similarly, consider the Si crystal doped with Ga atoms.





Intermediate Summary

- Semiconductors are mostly covalent crystals with moderate energy gap (~0.5 – 2.5 eV)
- Intrinsic carrier concentration

$$n = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2k_B T} = p = n_i$$

- Fermi level position in intrinsic semiconductor:

$$\mu = \frac{E_v + E_c}{2} + \frac{3}{4} k_B T \ln \frac{m_h}{m_e}$$

- In a doped semiconductor, many impurities form shallow hydrogen-like levels close to the conductive band (donors) or valence band (acceptors), which are completely ionized at room T:

$n = N_d$ or $p = N_a$

Statistics of charge carriers in semiconductors.
Electrical conductivity. Mobility.

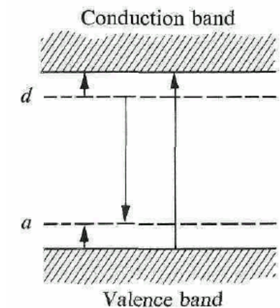
Semiconductor statistics

Semiconductors usually contain both donors and acceptors

Electrons in the CB can be created either by thermal interband excitation or by thermal ionization of the donors.

Holes in the VB may be generated by interband excitation, or by thermal excitation of electrons from the VB into the acceptor level.

In addition, electrons may fall from the donor levels to the acceptor level.



Finding the concentrations of carriers, both electrons and holes, taking all these processes into account, is quite complicated.

We shall treat a few special cases, which are often encountered in practice.

Intrinsic region:

Carrier concentration is determined primarily by thermally induced interband transitions. In this region $n = p$.

The intrinsic region: the impurity doping is small.

If the concentrations of donors and acceptors are N_d and N_a, the requirement for the validity of the intrinsic condition is: $n >> N_d - N_a$

n increases rapidly with temperature $\Rightarrow$ the intrinsic condition becomes more favorable at higher temperatures. In fact, all semiconductors become intrinsic at sufficiently high temperatures (unless the doping is unusually high).

In this case, the carrier concentration is:

$$n = p = n_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/2k_B T}$$

Extrinsic region:

For the common doping levels, about 10^{15} cm^{-3}, the number of carriers supplied by the impurities is large enough to change the intrinsic concentration appreciably at room temperature.

Two different types of extrinsic regions may be distinguished.

1) $N_d >> N_a$.

In this case, to a good approximation, $n = N_d$

Hole concentration p is small. To calculate it, note that

$$n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{(E_F - E_g)/k_B T} \quad \text{and} \quad p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-E_F/k_B T}$$

are still valid even for doped sample (here $E_v = 0 \rightarrow E_c = E_g$)

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

$p << N_d = n$ *n-type* semiconductor

2) $N_a >> N_d$

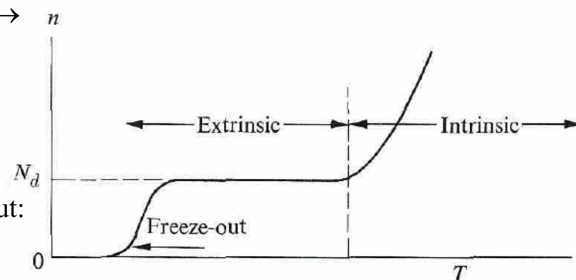
In this case, $p = N_a$ n is small

Similarly get $n = \dfrac{n_i^2}{N_a}$ $n << N_a = p$ *p-type* semiconductor

Assumed temperature to be high enough so that all impurities are ionized - True at room temperature.

If the temperature is lowered, a point is reached at which the thermal energy becomes too small to cause electron excitation - electrons fall from the CB into the donor level $\rightarrow$ the conductivity diminishes dramatically - *freeze-out* – electrons are now "frozen" at their impurity sites.

The temperature of freeze-out: $E_d \sim k_B T \rightarrow T \sim 100$ K.



Electrical conductivity. Mobility

Both electrons and holes contribute to electric current.

Assume first that a sample is strongly *n*-type.

Conductivity in the free electron model: $\sigma_e = \dfrac{ne^2\tau_e}{m_e}$

Estimate the value for σ_e: $n = 10^{14}$ cm^{-3} (~10^{-8} of that in metals); $m_e = 0.1\ m_0$

$\rightarrow \sigma_e \sim 10^{-7}$ (μohm·cm)$^{-1}$ Typically, in metals $\sigma \sim 1$ (μohm·cm)$^{-1}$

σ in a semiconductor is still sufficiently large for practical applications

In semiconductor physics another transport coefficient is often used: *mobility* μ_e *- proportionality coefficient between the electron drift velocity and the applied electric field*: $|\mathrm{v}_e| = \mu_e E$

Taking into account that $\mathbf{j}_e = -en_e\mathbf{v}_e$ and $\mathbf{j}_e = \sigma_e\mathbf{E}$, we find that

$$\boxed{\mu_e = \frac{e\tau_e}{m_e}}$$

- mobility is a measure of the rapidity of the electron motion in the field.

express electrical conductivity in terms of mobility: $\sigma_e = ne\mu_e$

A typical value for μ_e: $\sigma_e = 10^{-7}$ (μohm·cm)$^{-1}$ and $n = 10^{14}$ cm^{-3}

$\rightarrow \mu_e \sim 10^3 cm^2V^{-1}s^{-1}$

Apply the above considerations to the case of holes in a strongly p-type substance. The conductivity of the holes is given by

$$\sigma_h = \frac{pe^2\tau_h}{m_h} = pe\mu_h$$ where μ_h is the hole mobility

General case (both electrons and holes are present):

When a field is applied, electrons drift opposite to the field and holes drift in the same direction as the field.

The currents of the two carriers are additive $\Rightarrow \sigma = \sigma_e + \sigma_h$

In terms of the mobilities: $\sigma = ne\mu_e + pe\mu_h$

is in the intrinsic region, $n = p$, $\Rightarrow \sigma = ne(\mu_e + \mu_h)$ where n is the intrinsic concentration

Dependence of conductivity on temperature

Consider a semiconductor in the intrinsic region. In this situation the concentration n increases exponentially with temperature:

$$n = 2\left(\frac{k_BT}{2\pi\hbar^2}\right)^{3/2}(m_em_h)^{3/4}e^{-E_g/2k_BT}$$

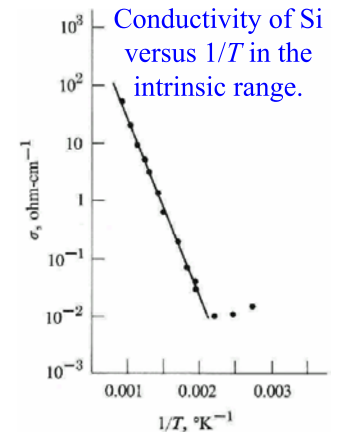
We may write the conductivity as

$$\sigma = F(T)e^{-E_g/2kT}$$

where $F(T)$ is a function which depends only weakly on the temperature.

When the substance is not in the intrinsic region, its conductivity is given by the general expression

$$\sigma = ne\mu_e + pe\mu_h$$



Conductivity of Si versus $1/T$ in the intrinsic range.

Mobility versus temperature: scattering mechanisms

In n-type semiconductor: $$\mu_e = \frac{e\tau_e}{m_e} = \frac{el_e}{m_e v_e}$$

collision time l_e varies with temperature $\Rightarrow$ mobility also varies.

Normally, both l_e and mobility μ_e diminish as the temperature rises.

Evaluate the conductivity by assuming that v_e is the average velocity.

Electrons at the bottom of the conduction band in a semiconductor obey the classical statistics, not the highly degenerate Fermi statistics, as in metals.

The average velocity can be estimated using the procedure of the kinetic theory of gases:

$$\frac{1}{2}m_ev_e^2 = \frac{3}{2}kT \quad \Rightarrow \quad \mu_e = \frac{el_e}{m_e^{1/2}(3kT)^{1/2}}$$

l_e also depends on the temperature - much the same way as it does in metals.

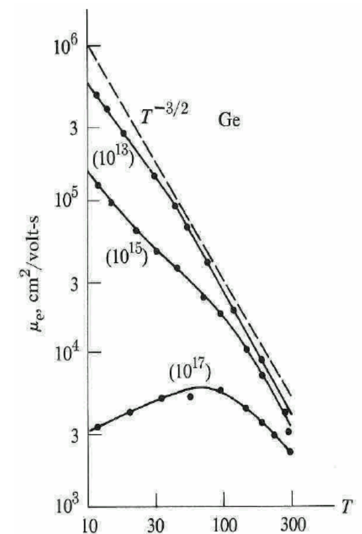
l_e is determined by the various collision mechanisms acting on the electrons.

These scattering mechanisms are:

- collisions of electrons with thermally excited phonons
- collisions with impurities.

At high temperatures, at which collisions with phonons is the dominant factor, $l^e \sim T^{-1}$. In that case, mobility varies as $\mu_e \sim T^{-3/2}$.

Scattering by *ionized* impurities dominates at low temperatures when the phonon scattering mechanism becomes weak



Electron mobility versus T in Ge.

Band structure of real semiconductors

GaAs,
along the [100] and [111] directions

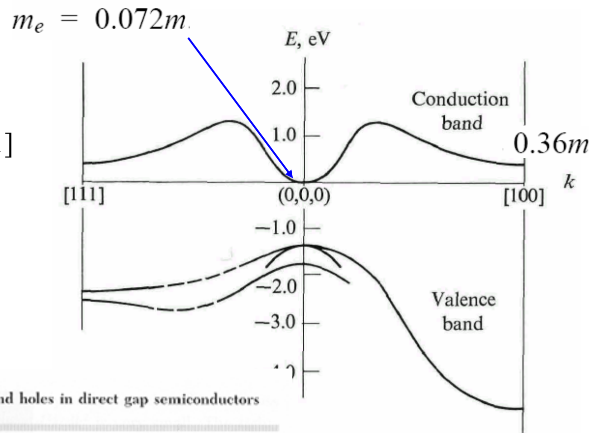
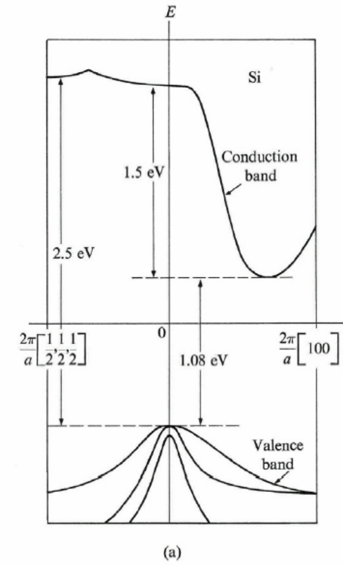


Table 2 Effective masses of electrons and holes in direct gap semiconductors

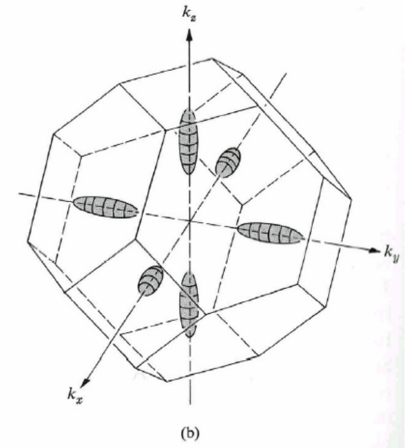
Crystal	Electron m_e/m	Heavy hole m_{hh}/m	Light hole m_{lh}/m	Split-off hole m_{soh}/m	Spin-orbit Δ, eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34
Cu_2O	0.99	—	0.58	0.69	0.13

Band structure of Si plotted along the [100] and [111] directions



(a)

Ellipsoidal energy surfaces corresponding to primary valleys along the [100] directions.



(b)