# PHYS 342/555
# Introduction to solid state physics

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Chapter 7: Energy Bands

Lecture in pdf format will be available at:

http://www.phys.utk.edu

# Bloch's theorem

The eigenstates $\psi$ of the one-electron Hamiltonian

$$H = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right), \text{ where } U(\vec{r} + \vec{R}) = U(\vec{r}) \text{ for all } \vec{R} \text{ in}$$

a Bravias lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravias lattice:

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}), \text{ where } u_{n\vec{k}}(\vec{r} + \vec{R}) = u_{n\vec{k}}(\vec{r})$$
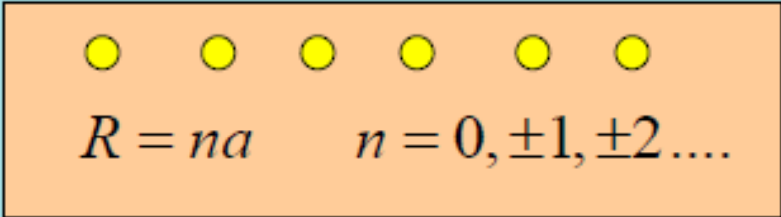
for all $\vec{R}$ in the Bravias lattice. or

$$\boxed{\psi(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi(\vec{r})}$$

**Proof: Bloch theorem in 1 D**

if  $V(x + R) = V(x)$

then  $\psi(x + R) = \exp(ikR)\psi(x)$



$R = na \qquad n = 0, \pm1, \pm2 \ldots$

Define  $T_R$  (translation operation)

$$T_R[H(x)\psi(x)] = H(x+R)\psi(x+R) = H(x)\psi(x+R) = H(x)T_R\psi(x)$$

$$\therefore [T_R, H] = 0 \quad \Longrightarrow \quad \begin{cases} H\psi_n = E_n\psi_n \\ \\ T_R\psi_n = C(R)\psi_n \end{cases}$$

$$\therefore T_R\psi(x) = \psi(x+R) = C(R)\psi(x)$$

$$\int |\psi(x+R)|^2 \, dx = \int |C(R)|^2 |\psi(x)|^2 \, dx = \int |\psi(x)|^2 dx$$

$$|C(R)|^2 = 1 \qquad \Rightarrow C(R) = e^{i\theta(R)}$$

$$T_a T_a\psi(x) = \psi(x+2a) = T_{2a}\psi(x) \qquad \Rightarrow C(a)C(a) = C(2a)$$

$$C(a) = e^{ika} ; \qquad C(2a) = C(a)C(a) = e^{i2ka} \qquad C(R) = e^{ikR}$$

# Another form of the Bloch function

$$\psi_k(\bar{r}) = e^{i\bar{k}\cdot\bar{r}}u(\bar{r}) \qquad where \quad u(\bar{r}+\bar{R}) = u(\bar{r})$$

Proof:

$$\psi_k(\bar{r}+\bar{R}) = \exp[i\bar{k}\cdot(\bar{r}+\bar{R})]u(\bar{r}+\bar{R})$$

$$= \exp(i\bar{k}\cdot\bar{R})\exp(i\bar{k}\cdot\bar{r})u(\bar{r})$$

$$= \exp(i\bar{k}\cdot\bar{R})\psi(\bar{r})$$

## General remarks about Bloch's Theorem

(1) $\psi_{nk}$ is not a momentum eigenstate, $\hbar\bar{k}$ is crystal momentum

$$\bar{p}\psi_{nk} = \frac{\hbar}{i}\bar{\nabla}\psi_{nk} = \frac{\hbar}{i}\bar{\nabla}[e^{i\bar{k}\cdot\bar{r}}u_{nk}(\bar{r})]$$

$$= \hbar\bar{k}\psi_{nk} + e^{i\bar{k}\cdot\bar{r}}\frac{\hbar}{i}\bar{\nabla}u_{nk}(\bar{r})$$

(2) $\bar{k}$ can always be confined to the first B.Z.

let $\bar{k}' = \bar{k} + \bar{G}$

$$\because \exp(i\bar{k}'\cdot\bar{R}) = \exp[i(\bar{k}+\bar{G})\cdot\bar{R}] = \exp(i\bar{k}\cdot\bar{R})$$

$$\therefore \psi_{n\bar{k}'}(\bar{r}+\bar{R}) = \exp(i\bar{k}'\cdot\bar{R})\psi_{n\bar{k}'}(\bar{r}) = \exp(i\bar{k}\cdot\bar{R})\psi_{n\bar{k}'}(\bar{r})$$

$$\psi_{n,\bar{k}+\bar{G}}(\bar{r}) = \psi_{n,\bar{k}}(\bar{r})$$
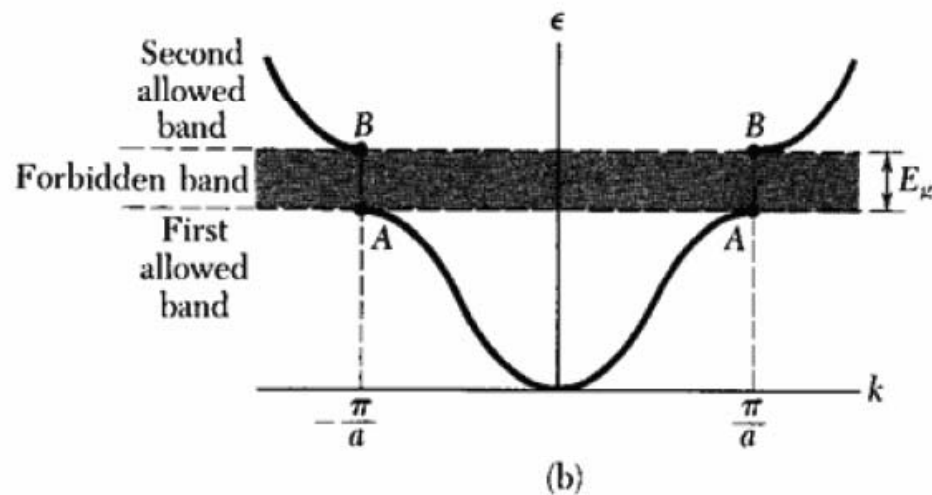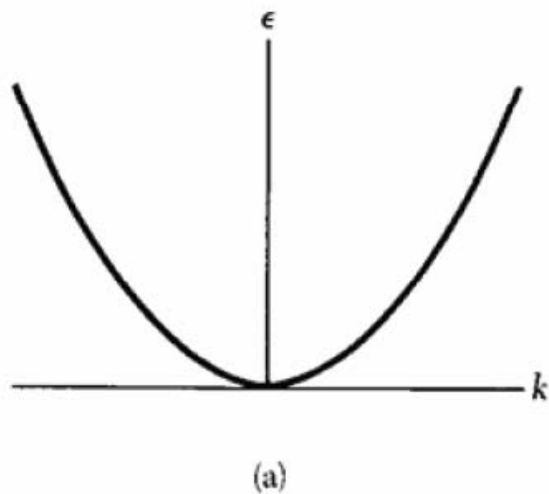
$$E_{n,\bar{k}+\bar{G}} = E_{n,\bar{k}}$$

# The effect of a periodic potential

The periodic potential has form:

$$U = U_0 + U_1 \cos\frac{2\pi x}{a}, \text{ where } a \text{ is lattice parameter}$$

and $U_1 \ll U_0$. If $U_1 = 0$ then we have the free

electron gas case where $\varepsilon = \dfrac{\hbar^2 k^2}{2m}$

Also, for small $\vec{k}$, $U_1$ effectively averages to zero so it still looks like the free electron case where

$\psi(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}}$ and $\varepsilon = \hbar^2 k^2 / 2m$

As $\vec{k}$ approaches $\pi/a$ ($k = 2\pi / \lambda = \pi / a$), we expect a Bragg reflection or a standing wave. We can form two different standing waves from the two traveling waves $\exp(\pm i\pi x / a)$, or

$\psi(+) = \exp(+i\pi x / a) + \exp(-i\pi x / a) = 2\cos(\pi x / a);$

$\psi(-) = \exp(+i\pi x / a) - \exp(-i\pi x / a) = 2i\sin(\pi x / a)$

Both standing waves are composed of equal parts of right- and left-directed traveling 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. This is the origin of the energy gap. The probability density $\rho$ of a particle is $\psi^*\psi = |\psi|^2$. For a standing wave $\psi(+)$,
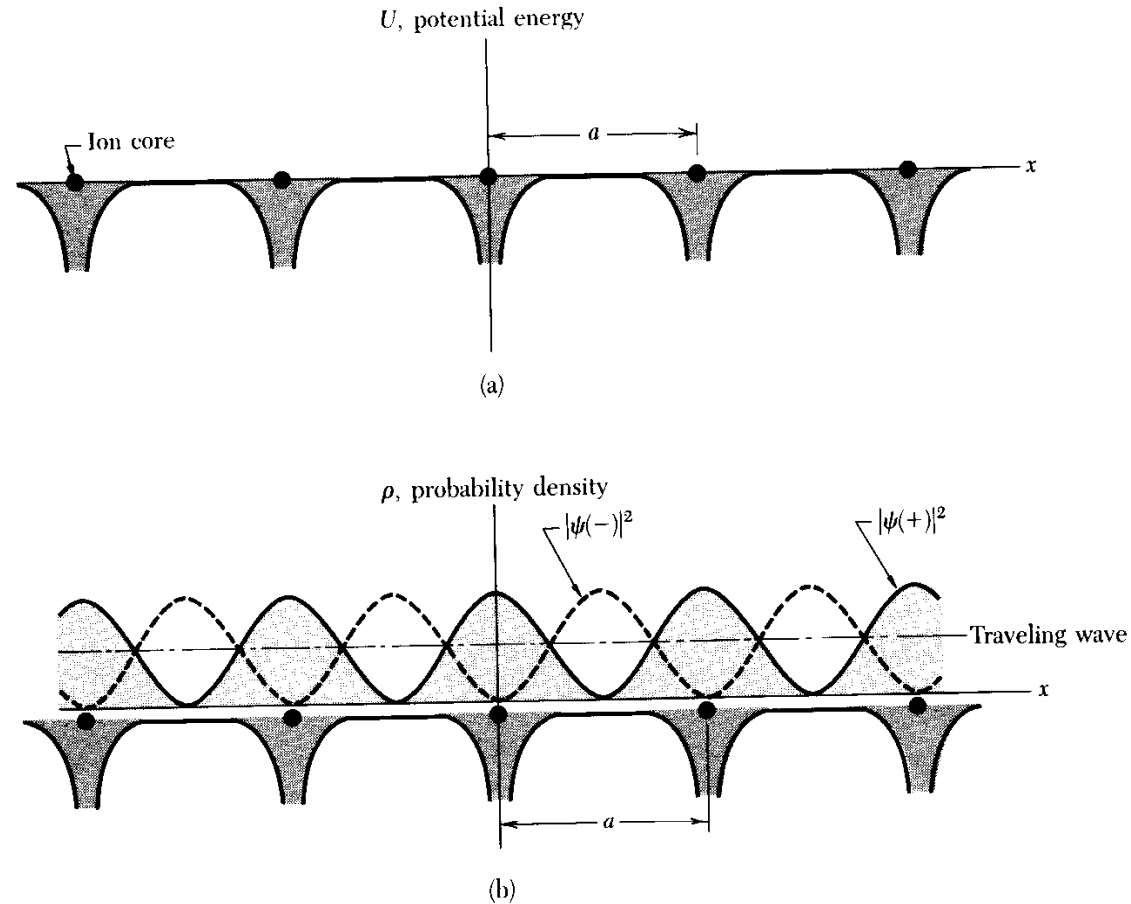
$$\rho(+) = |\psi(+)|^2 \propto \cos^2 \pi x / a.$$

This function piles up electrons (negative charge) on the positive ions centered at $x = 0, a, 2a, ...$ where the potential energy is lowest.

For the other standing wave $\psi(-)$ the probability density is

$$\rho(-) = |\psi(-)|^2 \propto \sin^2 \pi x / a.$$

U, potential energy

Ion core

a

(a)

ρ, probability density

$|\psi(-)|^2$     $|\psi(+)|^2$

Traveling wave

a

(b)

The potential energy of $\rho(+)$ is lower than that of the traveling wave, and that of $\rho(-)$ is higher than the traveling wave. The difference is the energy gap.

# Magnitude of the energy gap

The wavefunction at the Brillouin zone boundary $k = \pi / a$ are $\sqrt{2} \cos \pi x / a$ and $\sqrt{2} \sin \pi x / a$, normalized over unit length of line. If the potential energy of an electron in the crystal at point $x$ is
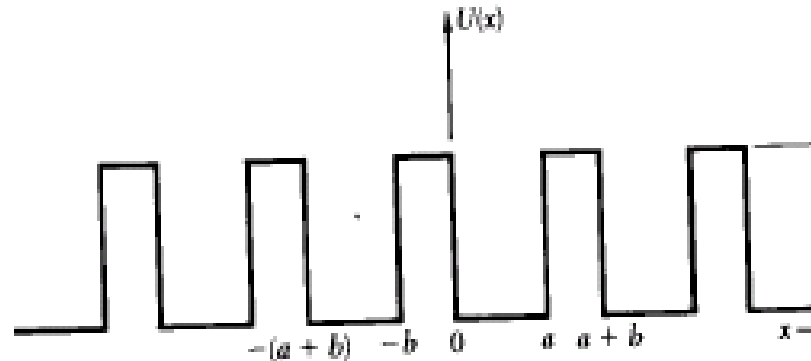
$$U(x) = U \cos 2\pi x / a$$

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

$$E_g = \int_0^1 dx U(x)[|\psi(+)|^2 - |\psi(-)|^2]$$

$$= 2\int dx U \cos(2\pi x / a)(\cos^2 \pi x / a - \sin^2 \pi x / a) = U$$
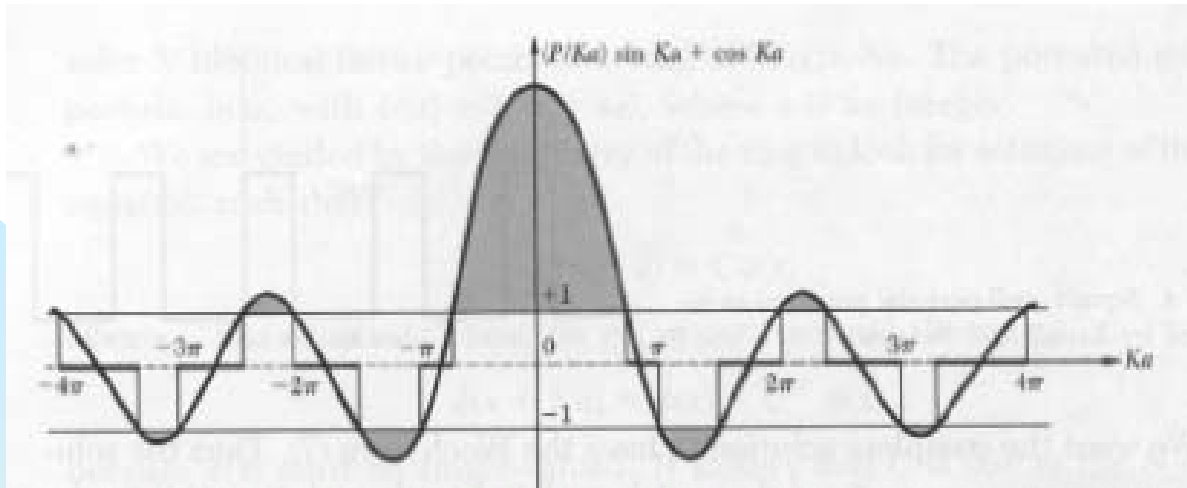
# Kronig-Penney Model



The wave equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = \varepsilon\psi, \text{ where } U(x) \text{ is the potential energy}$$

and $\varepsilon$ is the energy eigenvalue.

In region $0 < x < a$, $\psi = Ae^{ikx} + Be^{-ikx}$, $\varepsilon = \hbar^2 k^2 / 2m$.

In region $-b < x < 0$, $\psi = Ce^{Qx} + De^{-Qx}$, $U_0 - \varepsilon = \hbar^2 Q^2 / 2m$.

Block theorem: $\psi(a < x < a+b) = \psi(-b < x < 0)e^{ik(a+b)}$

$(P/Ka)\sin Ka + \cos Ka$



$\epsilon$, in units $\hbar^2\pi^2/2ma^2$
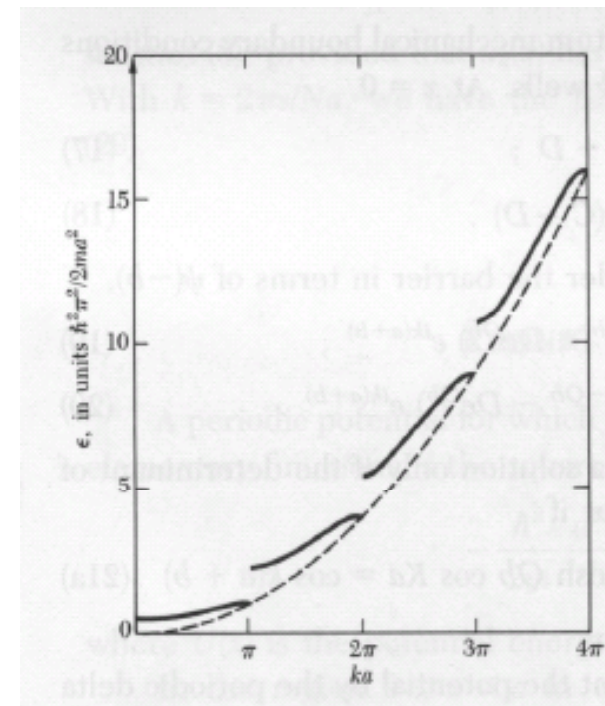
At $x = 0$, $A + B = C + D$;

$iK(A - B) = Q(C - D)$.

At $x = a$, $Ae^{ika} + Be^{-ika} = (Ce^{-Qb} + De^{Qb})e^{ik(a+b)}$;

$iK(Ae^{ika} - Be^{-ika}) = Q(Ce^{-Qb} - De^{Qb})e^{ik(a+b)}$.

In the limit $b = 0$ and $U_0 = \infty$:

$(P/ka)\sin ka + \cos ka = \cos ka$, where

$P = Q^2ba/2$.

# Wave equation of electron in periodic potential

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

$$H\psi = \varepsilon\psi = (\frac{1}{2m}p^2 + \sum_G U_G e^{iGx})\psi(x) = \varepsilon\psi(x)$$

$$\psi(x) = \sum_k C(k)e^{ikx}, k = 2\pi n / L.$$

$$\frac{1}{2m}p^2\psi(x) = \frac{\hbar^2}{2m}\sum_k k^2 C(k)e^{ikx},$$

$$(\sum_G U_G e^{iGx})\psi(x) = \sum_G \sum_k U_G e^{iGx} C(k)e^{ikx},$$

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

$$(\frac{\hbar^2 k^2}{2m} - \varepsilon)C(k) + \sum_G U_G C(k-G) = 0. \quad \lambda_k = \hbar^2 k^2 / 2m.$$

# Crystal momentum of an electron
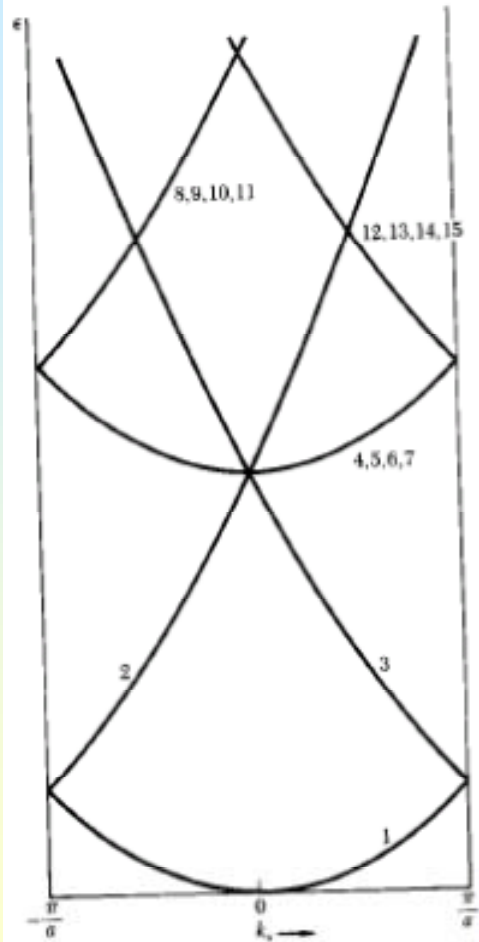
Under a crystal lattice translation we have

$$\psi_k(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}} e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}} \psi_k(\vec{r}).$$

If the lattice potential vanishes, the result recovers to that of free electron gas.

$\hbar\vec{k}$ is called the crystal momentum of an electron. If an electron $\vec{k}$ absorbs in a collision a phonon of wavevector $\vec{q}$, the selection rule is $\vec{k} + \vec{q} = \vec{k}' + \vec{G}$.
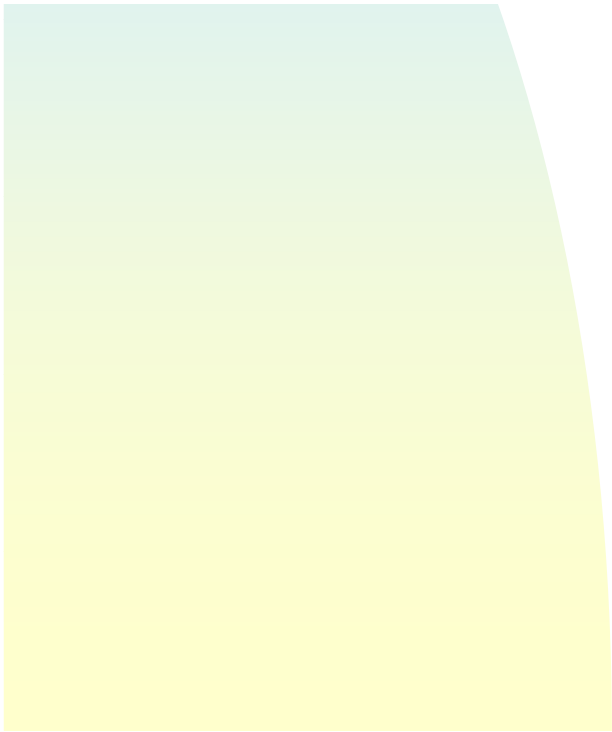
# Empty lattice approximation



The free electron energy can be written as

$$\varepsilon(k_x, k_y, k_z) = (\hbar^2 / 2m)(\vec{k} + \vec{G})^2$$

$$= (\hbar^2 / 2m)\left[ (k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2 \right]$$

*Square lattice, free electron energies.* (a) Show for a simple square lattice (two dimensions) that the kinetic energy of a free electron at a corner of the first zone is higher than that of an electron at midpoint of a side face of the zone by a factor of 2. (b) What is the corresponding factor for a simple cubic lattice (three dimensions)? (c) What bearing might the result of (b) have on the conductivity of divalent metals?
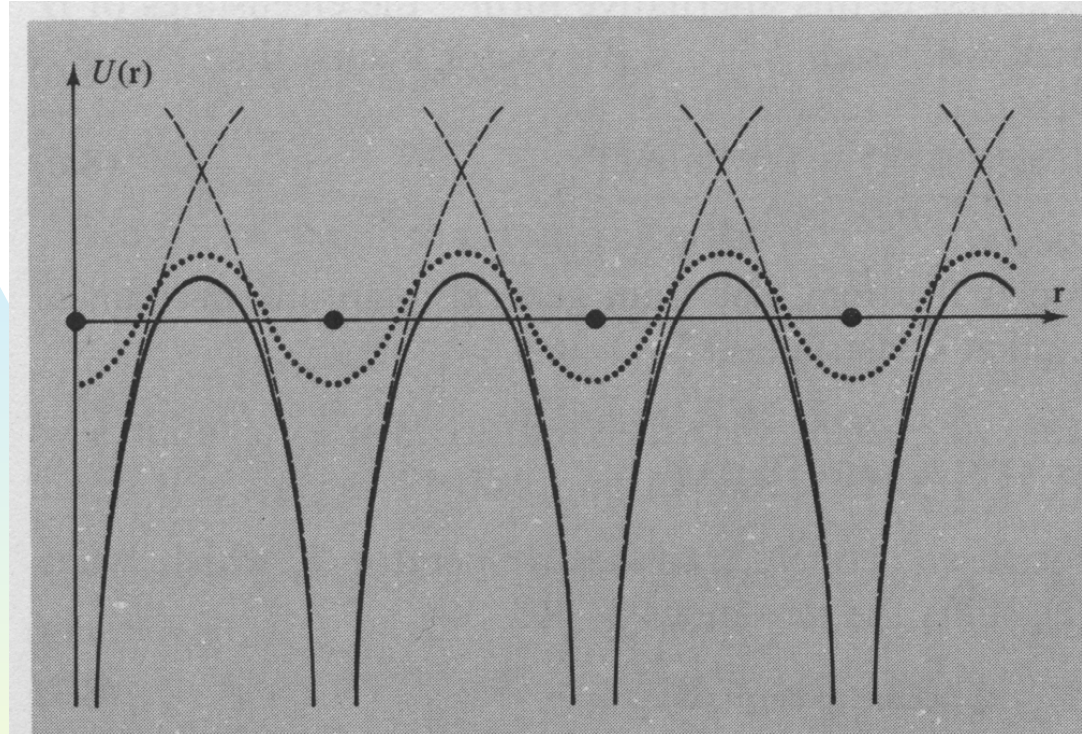
# Chapter 7: Energy Bands
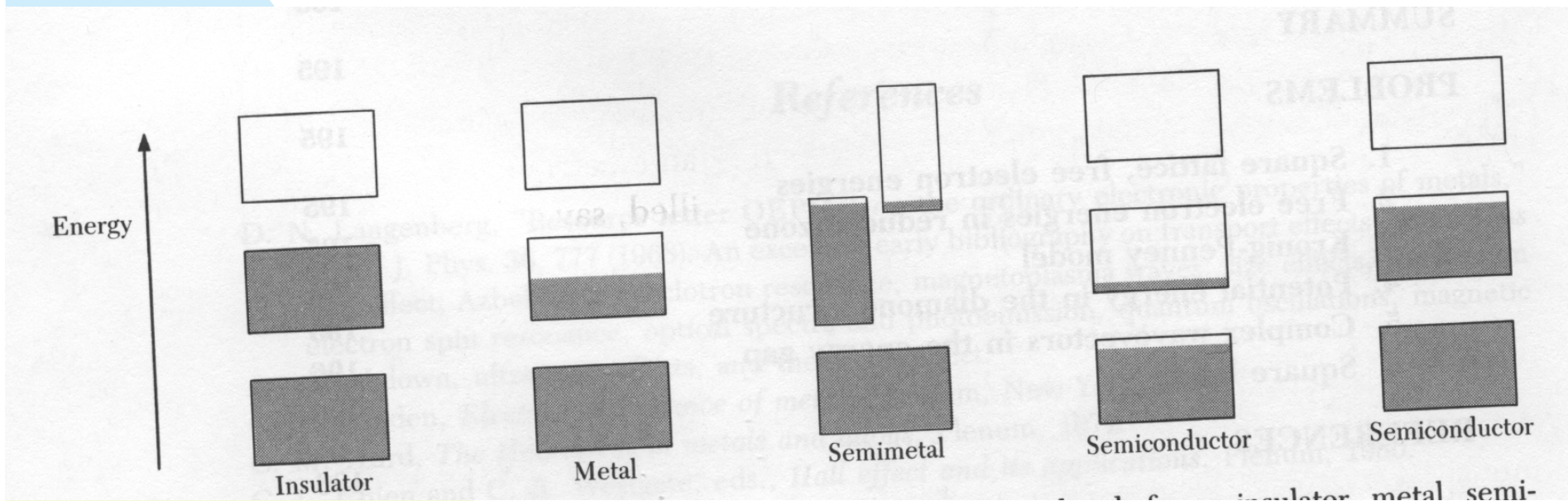
# The periodic potential



$$H\psi = \left( -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r}) \right)\psi = \varepsilon\psi$$

## Approximate solution near a zone boundary

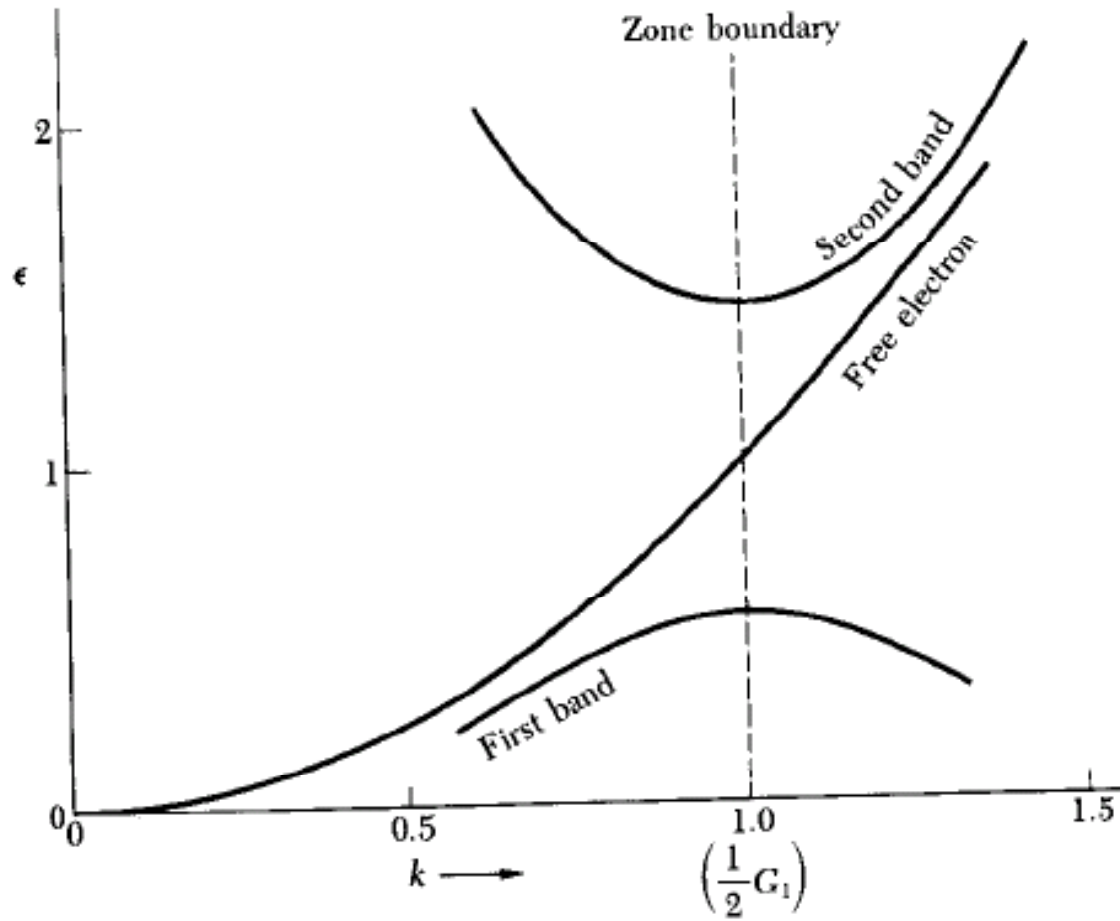At the zone boundary the kinetic energy of the waves

$k = \pm \dfrac{1}{2} G$ are equal. $(\lambda - \varepsilon)C(k) + \sum_G U_G C(k-G) = 0.$
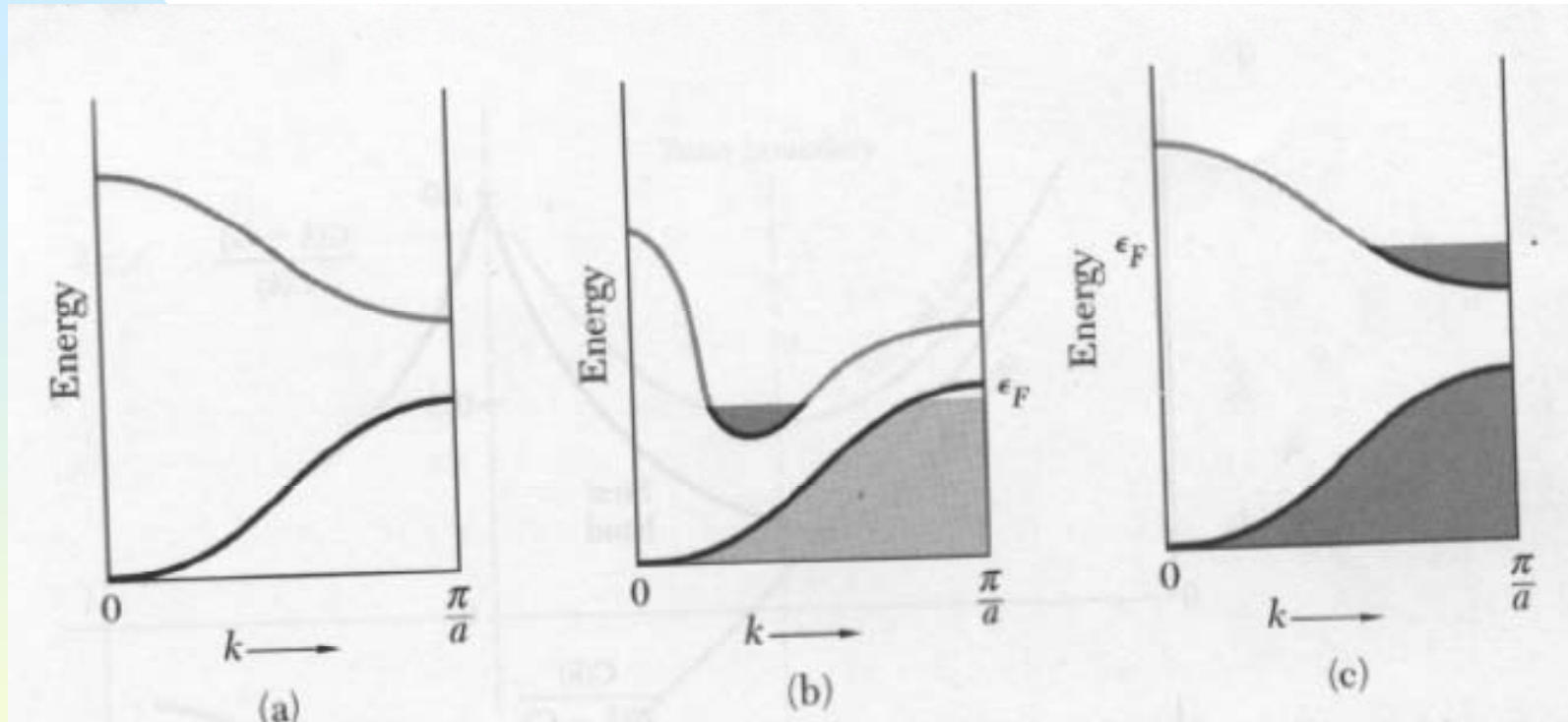
$(\lambda - \varepsilon)C(G/2) + UC(-G/2) = 0$

$(\lambda - \varepsilon)C(-G/2) + UC(G/2) = 0$

$(\lambda - \varepsilon)^2 = U^2; \quad \varepsilon = \lambda \pm U = \dfrac{\hbar^2}{2m}(\dfrac{1}{2}G)^2 \pm U.$

Thus the potential energy has created an energy gap $2U$ at the zone boundary.

# Metals and insulators
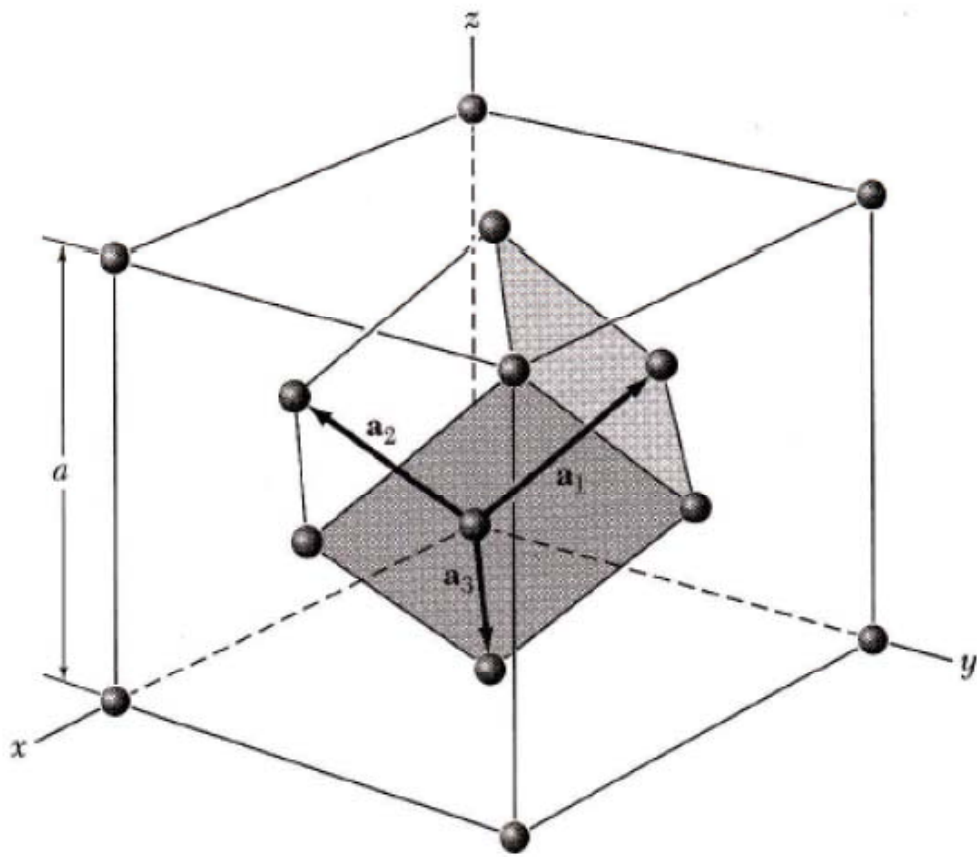
Consider the free electron energy bands of an fcc crystal lattice in the approximation of an empty lattice, but in the reduced zone scheme in which all $k$'s are transformed to lie in the first Brillouin zone. Plot roughly in the [111] direction the energies of all bands up to six times the lowest band at the zone boundary at

$$k = (2\pi / a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).$$

**Figure 14** Primitive basis vectors of the face-centered cubic lattice.

### Reciprocal Lattice to fcc Lattice

The primitive translation vectors of the fcc lattice of Fig. 14 are

$$\mathbf{a_1} = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ; \quad \mathbf{a_2} = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \; ; \quad \mathbf{a_3} = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \; .$$
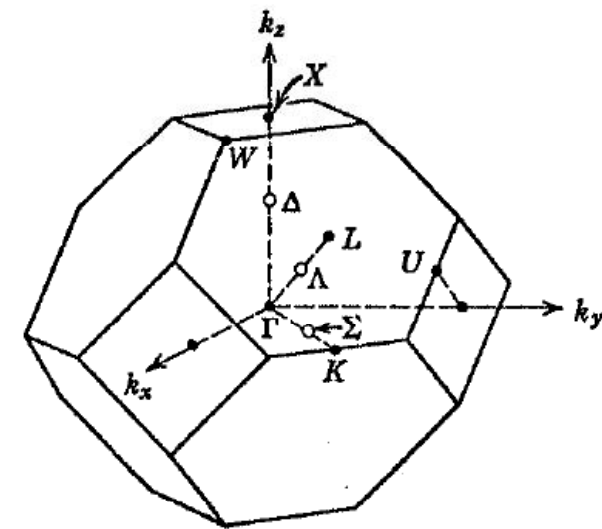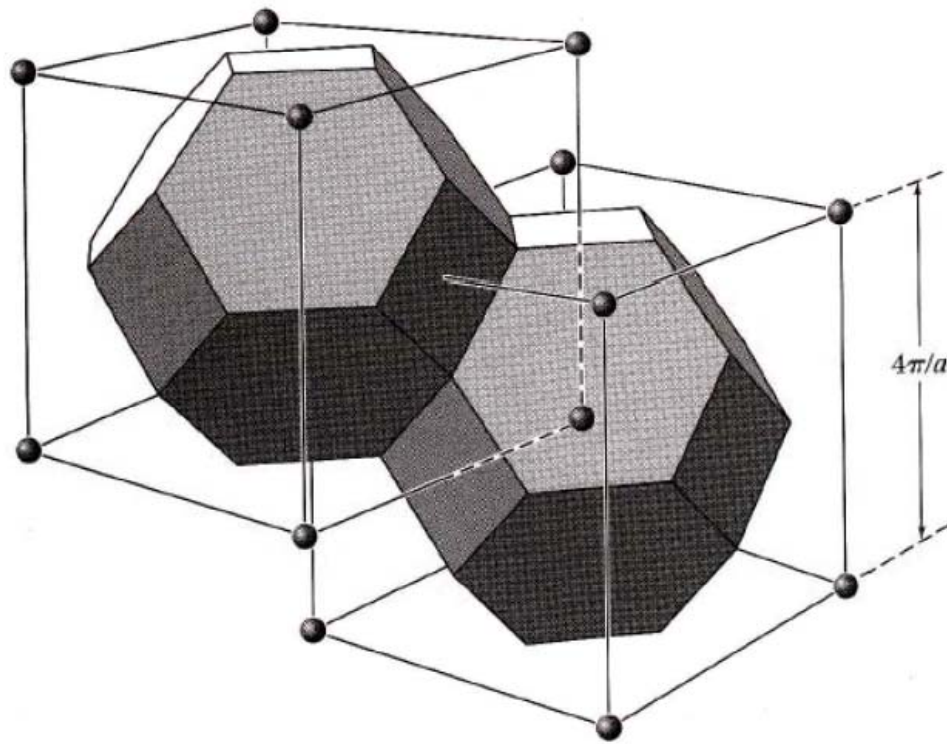
The volume of the primitive cell is

$$V = |\mathbf{a_1} \cdot \mathbf{a_2} \times \mathbf{a_3}| = \frac{1}{4}a^3 \; .$$

The primitive translation vectors of the lattice reciprocal to the fcc lattice are

$$\mathbf{b_1} = (2\pi/a)(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ; \qquad \mathbf{b_2} = (2\pi/a)(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ;$$
$$\mathbf{b_3} = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \; . \tag{36}$$

These are primitive translation vectors of a bcc lattice, so that the bcc lattice is reciprocal to the fcc lattice. The volume of the primitive cell of the reciprocal lattice is $4(2\pi/a)^3$.

$4\pi/a$

## Intrinsic Electrical Conductivity

In a very pure sample the conductivity of a semiconductor is due to the excitation of electrons from the valence to the conduction band by thermal fluctuations. For a semiconductor at room temperature the resistivity is between $10^{-2}\,\Omega$-cm and $10^9\,\Omega$-cm depending on the band gap of the material. In contrast, a typical metal has a resistivity of $10^{-6}\,\Omega$-cm and a typical insulator satisfies $10^{14}\,\Omega$-cm $\leq \rho \leq 10^{22}\,\Omega$-cm. A plot of carrier concentration versus temperature and a plot of conductivity versus temperature is shown in Figure 7.1(a) and (b).
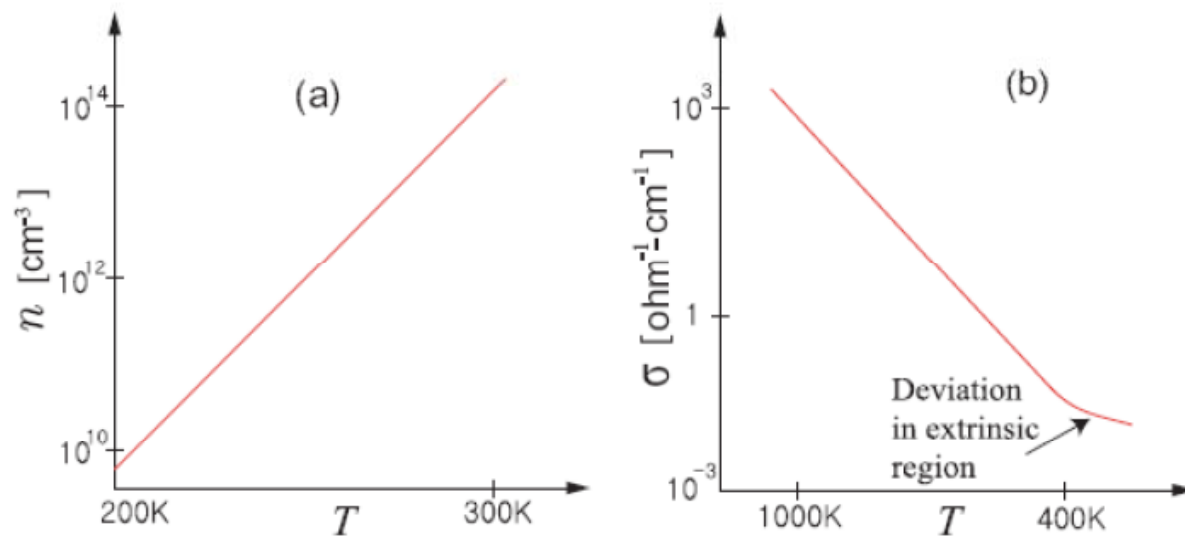


Fig. 7.1. Temperature dependence of carrier concentration (a) and electrical conductivity (b) of a typical semiconductor

# Semiconductor crystals

A solid with an energy gap will be nonconducting at $T = 0$ unless electric breakdown occurs or unless the AC field is of such high frequency that $\hbar\omega$ exceeds the energy gap. However, when $T \neq 0$ some electrons will be thermally excited to unoccupied bands (conduction bands).

If the enegy gap $E_g \approx 0.25$ eV, the fraction of electrons across the gap is of order $e^{-E_g / 2k_B T} \approx 10^{-2}$, and observable conductivity will occur. These materials are semiconductors.

**Table 7.1.** Comparison of energy gaps of Si, Ge, and various III-V compound semiconductors

| Crystal | Type of Energy Gap | $E_G$ [eV] at 0K |
|---------|--------------------|------------------|
| Si | indirect | 1.2 |
| Ge | indirect | 0.8 |
| InSb | direct | 0.2 |
| InAs | direct | 0.4 |
| InP | direct | 1.3 |
| GaP | indirect | 2.3 |
| GaAs | direct | 1.5 |
| GaSb | direct | 1.8 |
| GaN | direct | 3.5 |
| ZnO | direct | 3.4 |
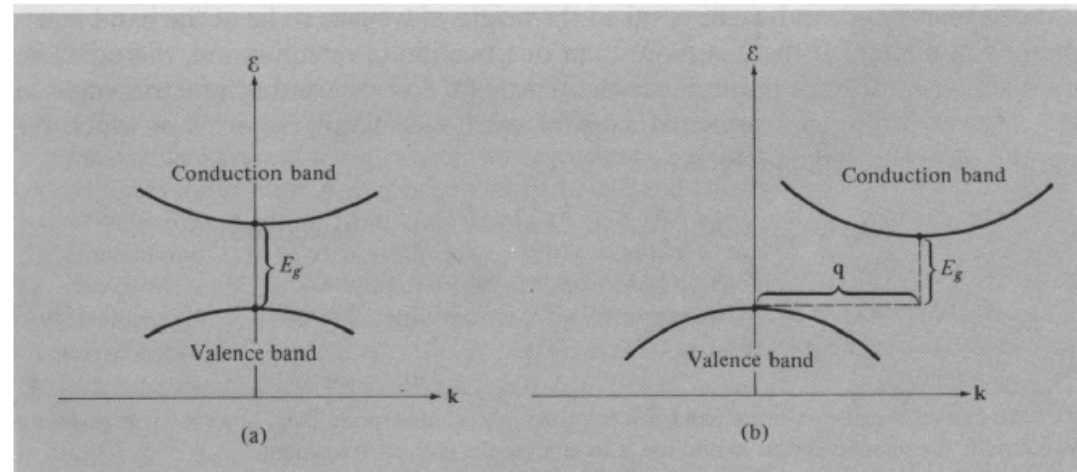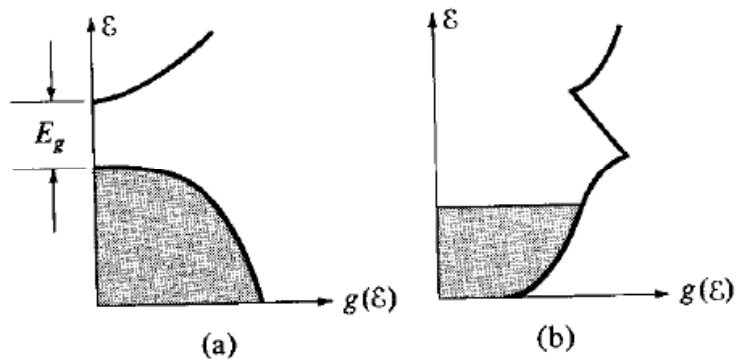
The energy gap can be measured by optical absorption. If the conduction band minimum occurs at the same point in $k$-space as the valence band maximum, the energy gap can be directly determined from the optical threshold. If the minima and maxima occur at different points in $k$-space, then for phonon must also participate in the process.

The energy can may also be deduced from the temperature dependence of the intrinsic conductivity, varying as $e^{-E_g/2k_BT}$.

# Equations of motion

The group velocity $v_g = d\omega/dk$, $\omega = \varepsilon/\hbar$, so $v_g = \hbar^{-1} d\varepsilon/dk$.

The work $\delta\varepsilon$ in interval $\delta t$ is $\delta\varepsilon = -eEv_g \delta t$.

Note $\delta\varepsilon = (d\varepsilon/dk)\delta k = \hbar v_g \delta k$.

$$\hbar\delta k = -eE\delta t, \text{ Hence } \hbar\frac{d\vec{k}}{dt} = -e\vec{E} = \vec{F}.$$

The electron in the crystal is subject to forces from the crystal lattice as well as from external sources.

$$\vec{F} = -eE - \frac{e}{c}v \times \vec{B}.$$

# Holes



Conduction band

$\hbar\omega$

Electron removed

Valence band

Hole band constructed with $k_h = -k_e$ and $\epsilon_h(k_h) = -\epsilon_e(k_e)$, to simulate dynamics of a hole.

Valence band with one electron missing.
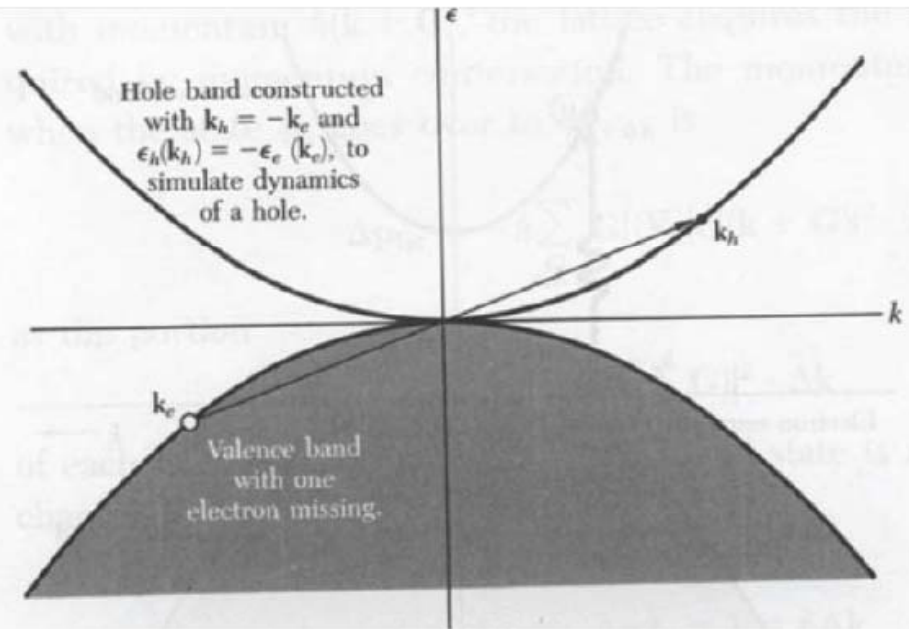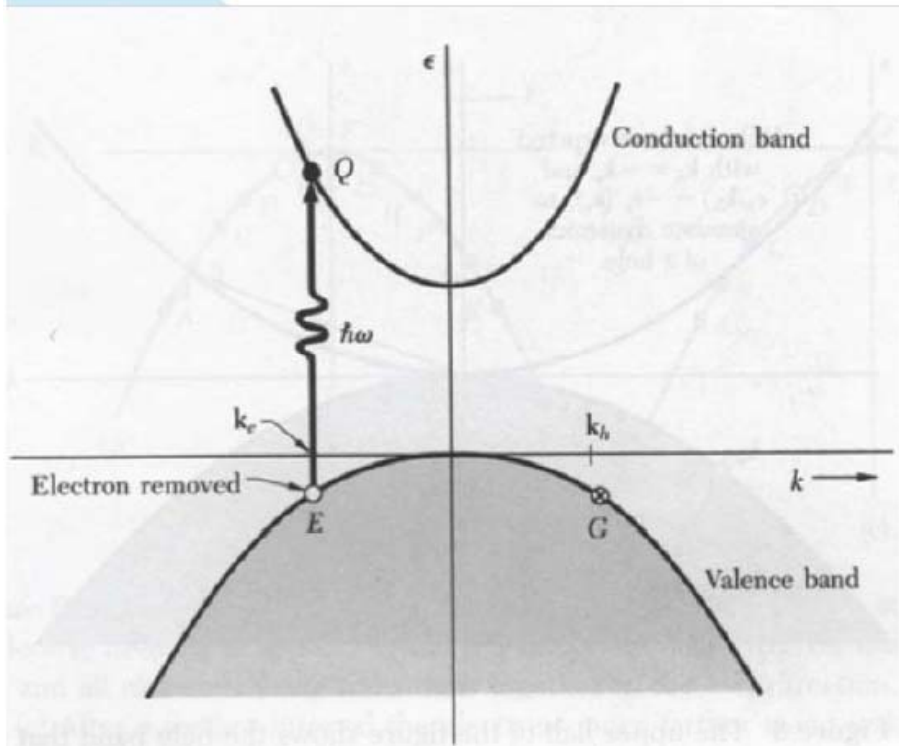
1. The total wavevector of the electrons in a filled band is zero: $\sum \vec{k} = 0$ or $\vec{k}_h = -\vec{k}_e$.

2. 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.
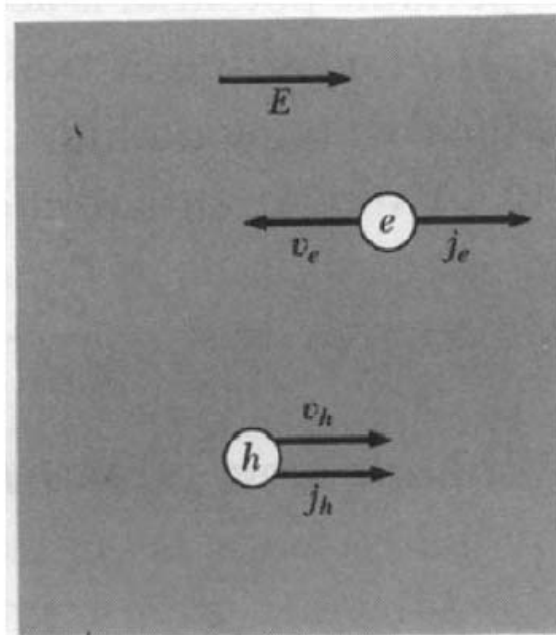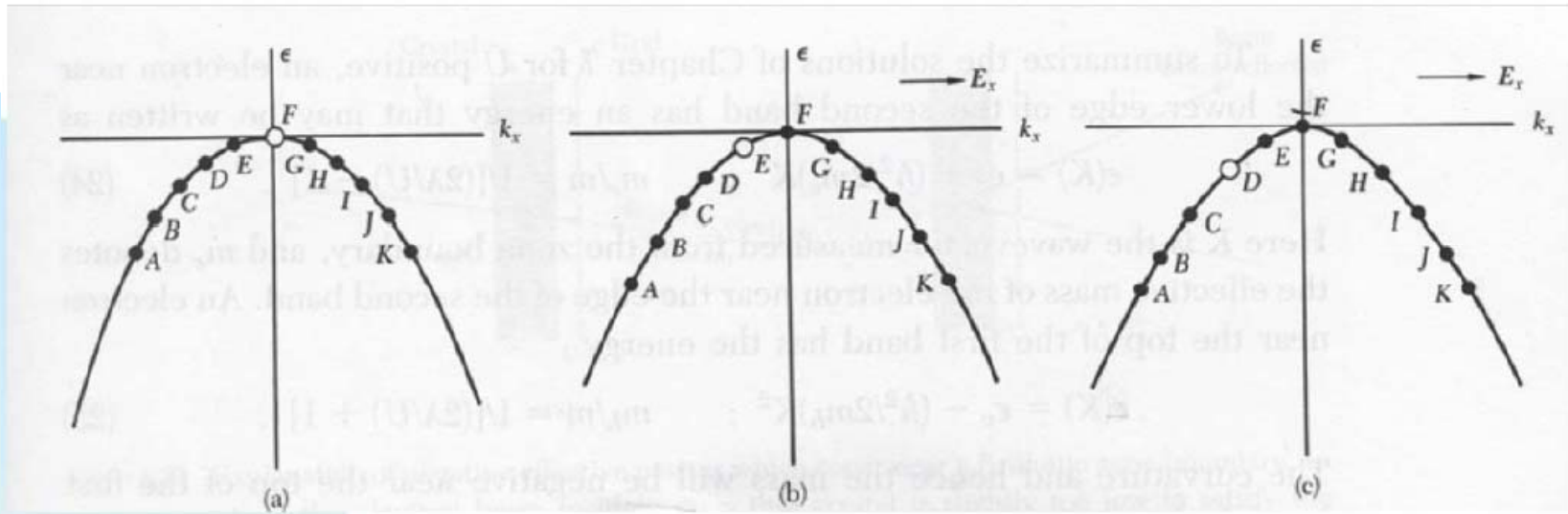
$$\varepsilon_h(\vec{k}_h) = -\varepsilon_e(\vec{k}_e).$$

3. $\vec{v}_h = \vec{v}_e$. The velocity of the hole is equal to the velocity of the missing electron.

4. $m_h = -m_e$.

5. $\hbar \dfrac{d\vec{k}_h}{dt} = (e\vec{E} + \dfrac{1}{c}\vec{v}_h \times \vec{B})$

# Effective Mass

For $U$ positive, an electron near the lower edge of the second band has an energy: $\varepsilon(k) = \varepsilon_c + (\hbar k)^2 / (2m_e)$

Here $k$ is the wavevector measured from the zone boundary, and $m_e$ denotes the effective mass of the electron near the second band.

The group velocity $v_g = d\omega/dk$, $\omega = \varepsilon/\hbar$, so $v_g = \hbar^{-1} d\varepsilon/dk$.

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2\varepsilon}{dkdt} = \frac{1}{\hbar}\left(\frac{d^2\varepsilon}{dk^2}\frac{dk}{dt}\right) = \frac{1}{\hbar}\left(\frac{d^2\varepsilon}{dk^2}\right)\left(\frac{dk}{dt}\right) = \frac{1}{\hbar}\left(\frac{d^2\varepsilon}{dk^2}\right)\left(\frac{F}{\hbar}\right)$$

$F = ma$, then we have $\dfrac{1}{m^*} = \dfrac{1}{\hbar^2}\left(\dfrac{d^2\varepsilon}{dk^2}\right)$.

# Physical interpretation of Effective Mass
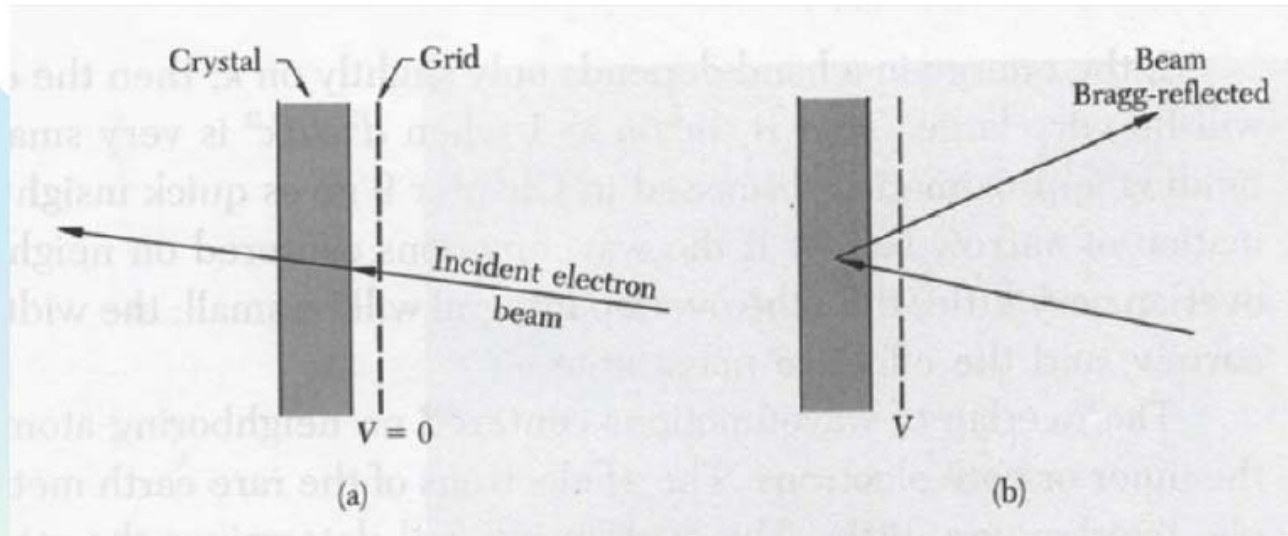


Near the bottom of the lower band, $\psi = e^{ikx}$ with momentum $\hbar k$; $m^* \approx m$. Positive $m^*$ means that the band has upward curvature $(d^2 \varepsilon / dk^2 > 0)$. A negative effective mass means that on going from state $k$ to state $k + \Delta k$, the momentum transfer to the lattice from the electron is larger than the momentum transfer from the applied force to the electron.
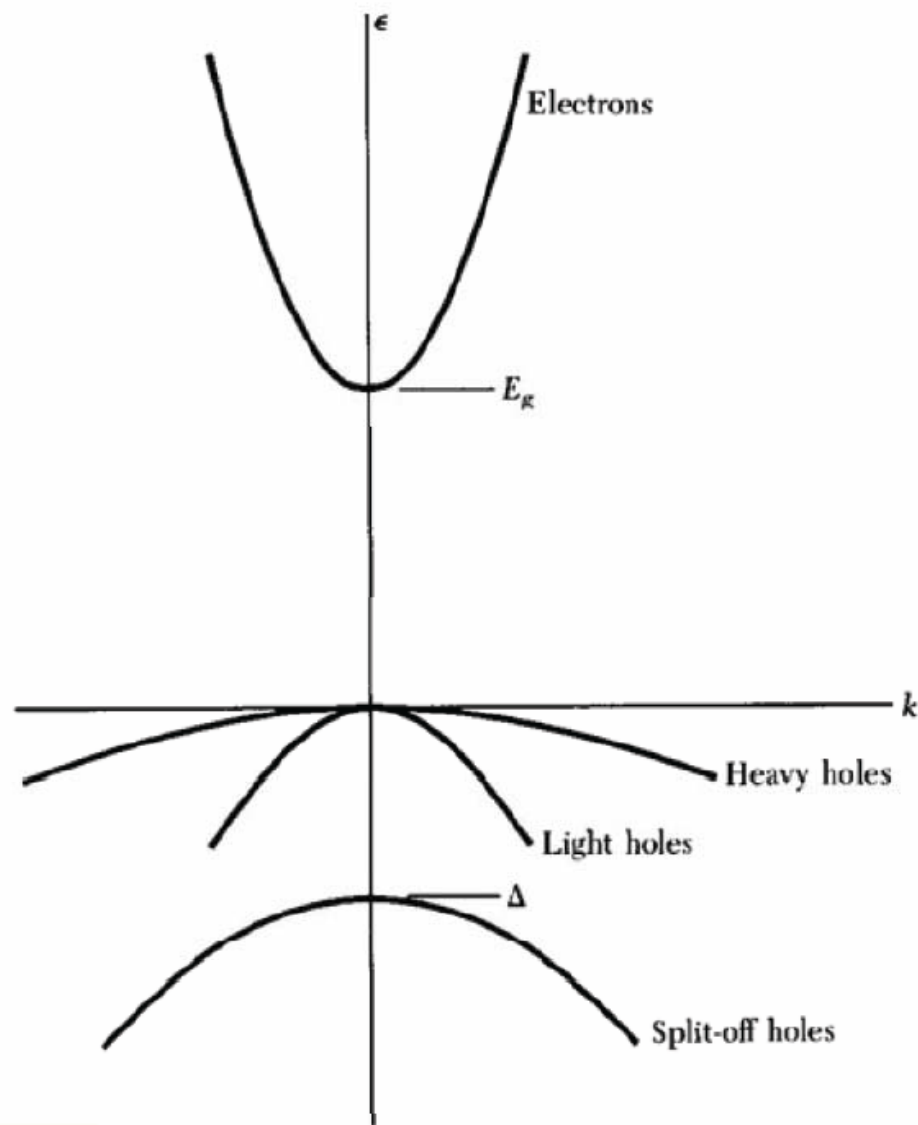
# Effective Mass in Semiconductors

The angular rotation frequency $\omega_c$ of the current carriers

is: $\omega_c = \dfrac{eB}{m^* c}$, where $m^*$ is the effective mass.

**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 $\Delta$, 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 |

ε

Electrons

$E_g$

k

Heavy holes

Light holes

Δ

Split-off holes

# Effect of temperature on the Fermi-Dirac distribution
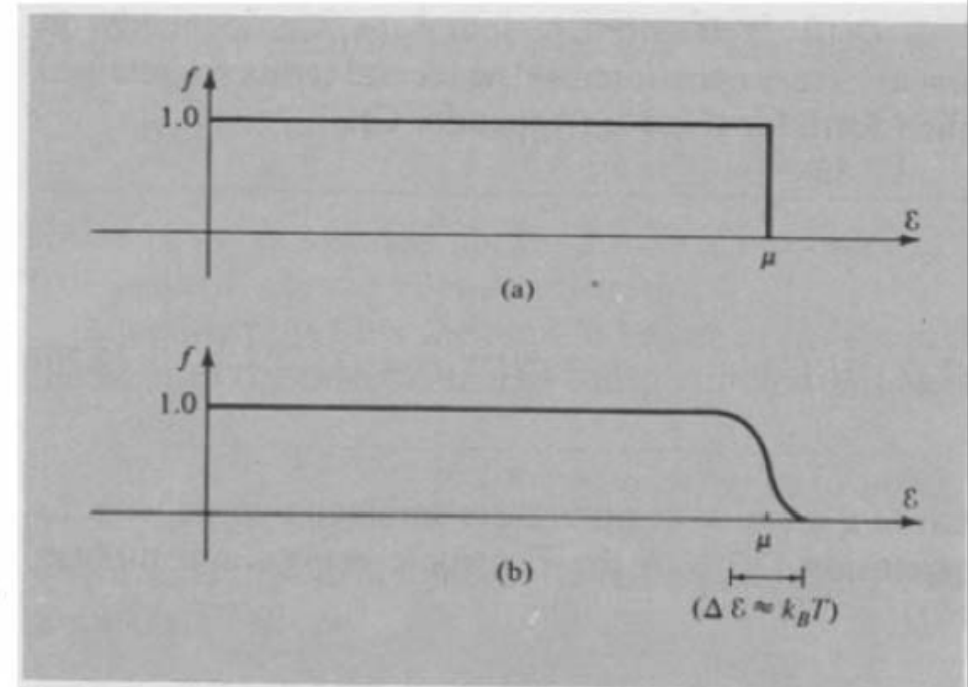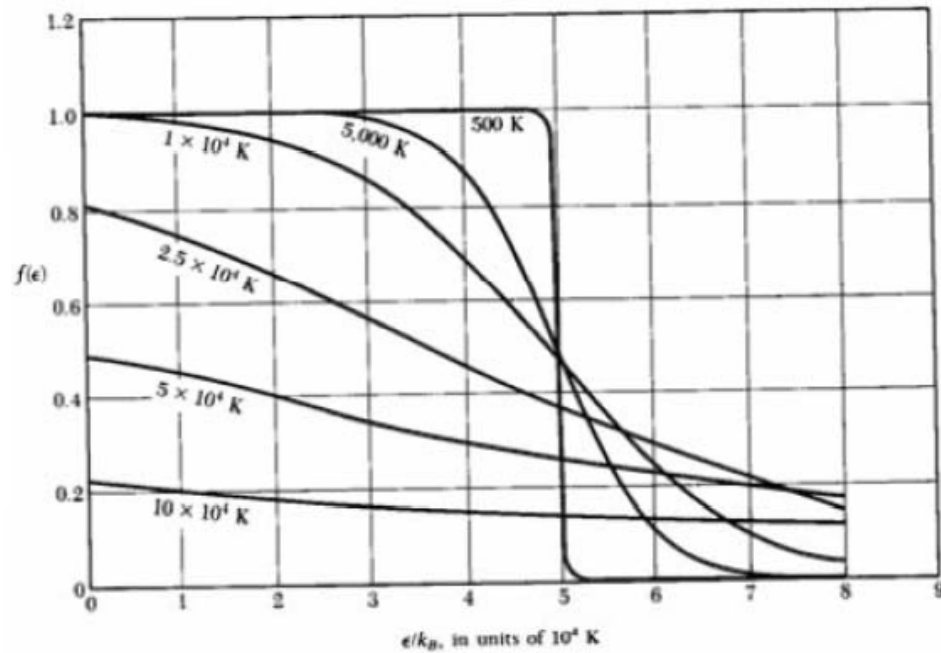


$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1}. \quad \mu \text{ is chemical potential,}$$

$$f(\varepsilon) = 1/2 \text{ when } \varepsilon = \mu.$$

# Intrinsic carrier concentration

In semiconductor physics $\mu$ is called Fermi level.
If $\varepsilon - \mu \gg k_B T$, the Fermi-Dirac distribution function
reduces to $f_e \simeq \exp[(\mu - \varepsilon)/k_B T]$. The energy of an
electron in the conduction band is $\varepsilon_k = E_c + \hbar^2 k^2 / 2m_e$.
Note the total number of electrons $N$:

$$N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}, D(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}(\varepsilon - E_c)^{1/2}.$$

The concentration of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} D_e(\varepsilon)f_e(\varepsilon)d\varepsilon = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}\exp[(\mu - E_c)/k_B T].$$

The distribution function $f_h$ for holes is $f_h = 1 - f_e$.

We have $f_h = 1 - \dfrac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1} \cong \exp[(\varepsilon - \mu)/k_B T]$.

If the holes near the top of the valence band behave as particles with effective mass $m_h$, the density of hole states is given

$$D_h(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} (E_v - \varepsilon)^{1/2}.$$

The concentration of holes in the valence band is

$$p = \int_{-\infty}^{E_v} D_h(\varepsilon) f_h(\varepsilon) d\varepsilon = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(E_v - \mu)/k_B T].$$

The energy gap $E_g = E_c - E_v$,

$$np = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2} \exp(-E_g/k_B T).$$
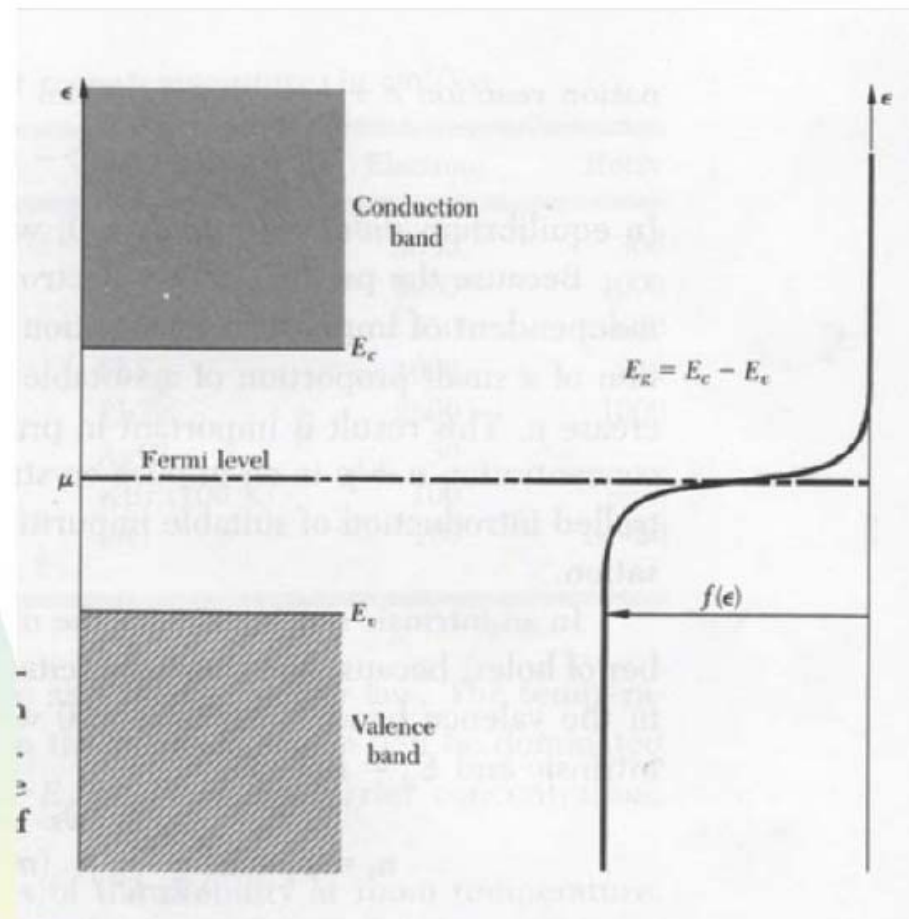
In an intrinsic semiconductor, $n = p$, $E_g = E_c - E_v$,

$$n = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} \exp[(E_g / 2k_B T].$$

# Intrinsic carrier mobility

The mobility is the magnitude of the drift velocity per unit electric field: $\mu = |v|/E$

The electric conductivity is the sum of the electron and hole contributions. $\sigma = (ne\mu_e + pe\mu_h)$

**Table 3** Carrier mobilities at room temperature, in cm²/V-s

| Crystal | Electrons | Holes | Crystal | Electrons | Holes |
|---------|-----------|-------|---------|-----------|-------|
| Diamond | 1800 | 1200 | GaAs | 8000 | 300 |
| Si | 1350 | 480 | GaSb | 5000 | 1000 |
| Ge | 3600 | 1800 | PbS | 550 | 600 |
| InSb | 800 | 450 | PbSe | 1020 | 930 |
| InAs | 30000 | 450 | PbTe | 2500 | 1000 |
| InP | 4500 | 100 | AgCl | 50 | — |
| AlAs | 280 | — | KBr (100 K) | 100 | — |
| AlSb | 900 | 400 | SiC | 100 | 10–20 |

# Impurity conductivity

Impurities that contribute to the carrier density of a semiconductor are called *donors* if they supply additional electrons to the conduction band, and *acceptors* if they supply additional holes to (*i.e.*, capture electrons from) the valence band.

The impurities are at $N_D$ fixed attractive centers of charge $+e$, per unit volume, along with the same # of additional electrons. If the impurity were not embedded in the semiconductor, but in empty space, the binding energy of the electron would just be the first ionization potential of the impurity ion, 9.81 eV for arsenic. However, since the impurity is embedded in the medium of the pure semiconductor, this binding energy is enormously reduced (to 0.013 eV for arsenic in Ge).

1. The field of the charge representing the impurity must be reduced by the static dielectric constant $\varepsilon$ (16 for Ge) of the semiconductor.

2. A electron moving in the medium of the semiconductor should be described by the semiclassical relation, where $\hbar\vec{k}$ is the electron crystal momentum. The additional electron introduced by impurity should be thought of as being in a superposition of conduction band levels of the pure host material. The electron can minimize its energy by using only levels near the bottom of the conduction band.

We have a particle of charge $-e$ and mass $m^*$, moving in free space in the presence of an attractive center of charge $e/\varepsilon$.

The radius of the first Bohr orbit, $a_0 = \hbar^2 / me^2$, becomes

$r_0 = \dfrac{m}{m^*} \varepsilon a_0$, and the ground-state binding energy, $me^4 / \hbar^2 = 13.6$ eV

becomes $\varepsilon = \dfrac{m^*}{m} \dfrac{1}{\varepsilon^2} \times 13.6$ eV. $r_0 = 100$ angstrom.



$\bigcirc$ = Ge

(a)          (b)          (c)
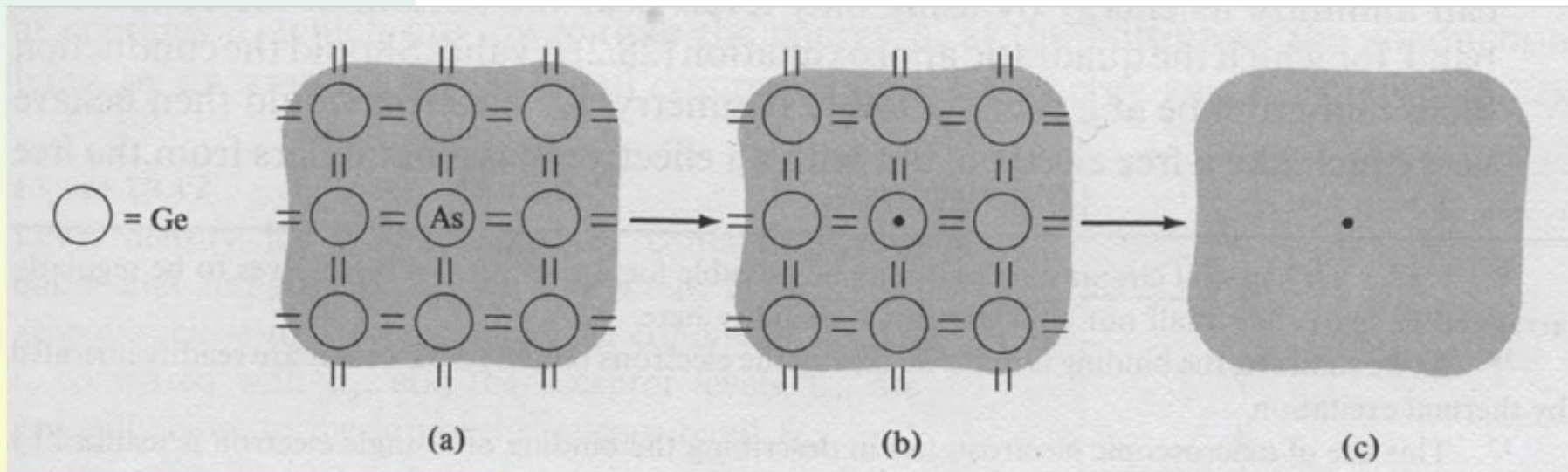
## 7.4 Donor and Acceptor Impurities

Si and Ge have four valence electrons. If a small concentration of a column V element replaces some of the host atoms, then there is one electron more than necessary for the formation of the covalent bonds. The extra electron must be placed in the conduction band, and such atoms like As, Sb, and P are known as **donors**. For column III elements (Al, Ga, In, etc.) there is a shortage of one electron, thus the valence band is not full and a hole exists for every **acceptor** atom.

Let us consider the case of donors (for acceptors, the same picture applies if electrons in the conduction band are replaced by holes in the valence band and, as an example, $As^+$ ions are replaced by $Al^-$ ions). To a first approximation the extra electron of the As atom will go into the conduction band of the host material. This would give one conduction electron for each impurity from the column V. However, these conduction electron leaves behind an $As^+$ ion, and the $As^+$ ion acts as a center of attraction which can bind the conduction electron similar to the binding of an electron by a proton to form a hydrogen atom.

For a hydrogen atom, the Hamiltonian for an electron moving in the presence of a proton located at $r = 0$ is

$$H = \frac{p^2}{2m} - \frac{e^2}{r}. \tag{7.22}$$

The Schrödinger equation has, for its ground state eigenfunction and eigenvalue,

$$\Psi_0 = N_0 e^{-r/a_B} \quad \text{and} \quad E_0 = -\frac{e^2}{2a_B}, \tag{7.23}$$

where $a_B = \frac{\hbar^2}{me^2}$ is the Bohr radius ($a_B \sim 0.5\text{Å}$).

For a conduction electron in the presence of a donor ion, we have

$$H = \frac{p^2}{2m_c^*} - \frac{e^2}{\epsilon_s r}. \tag{7.24}$$

Here $m_c^*$ is the conduction band effective mass and $\epsilon_s$ is the background dielectric constant of the semiconductor. The ground state will have

$$\Psi_0 = N_0 e^{-r/a_B^*} \quad \text{and} \quad E_0 = -\frac{e^2}{2\epsilon_s a_B^*}. \tag{7.25}$$

The effective Bohr radius $a_B^*$ is given by $a_B^* = \frac{\hbar^2 \epsilon_s}{m_c^* e^2}$. For a typical semiconductor $m_c^* \simeq 0.1m$ and $\epsilon_s \simeq 10$. This gives $a_B^* \approx 10^2 a_B \simeq 50\text{Å}$ and $E_0 \approx -10^{-3} \frac{e^2}{2a_B} \simeq -13\text{meV}$.

When donors are present, the chemical potential $\zeta$ will move from its intrinsic value $\zeta_i$ to a value near the conduction band edge. We know that $n_c(T) = N_c(T)e^{-\frac{\varepsilon_c - \zeta}{\Theta}}$; we can define the intrinsic carrier concentration $n_i(T)$ by $n_i(T) = N_c(T)e^{-\frac{\varepsilon_c - \zeta_i}{\Theta}}$. Then we can write for the general case

$$n_c(T) = n_i(T)e^{\frac{\zeta - \zeta_i}{\Theta}} \quad \text{and} \quad p_v(T) = n_i(T)e^{-\frac{\zeta - \zeta_i}{\Theta}}. \tag{7.26}$$
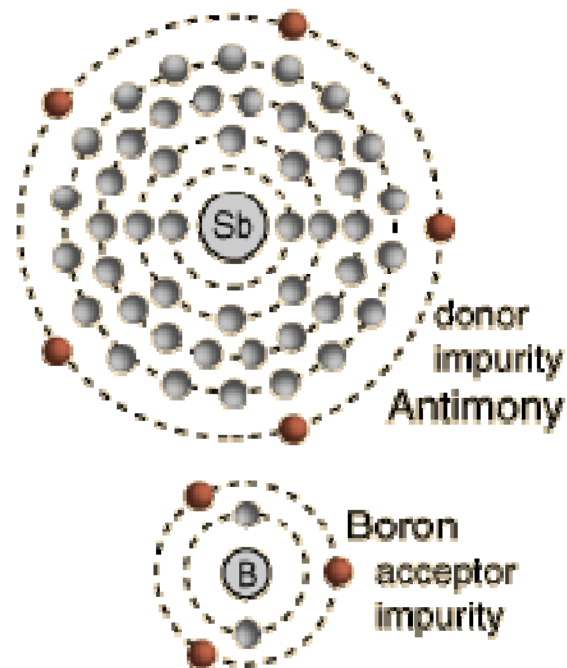
Pentavalent impurities
Impurity atom with 5 valence electrons produce n-type semiconductors
by contributing extra electrons.

Trivalent impurities
Impurity atoms with 3 valence electrons produce p-type semiconductors
by producing a "hole" or electron deficiency.

Antimony
Arsenic
Phosphorous

Boron
Aluminum
Gallium

donor
impurity
Antimony

Boron
acceptor
impurity

The addition of pentavalent impurities such as antimony, arsenic or phosphorous contributes free electrons, greatly increasing the conductivity of the intrinsic semiconductor. Phosphorous may be added by diffusion of phosphine gas (PH3).
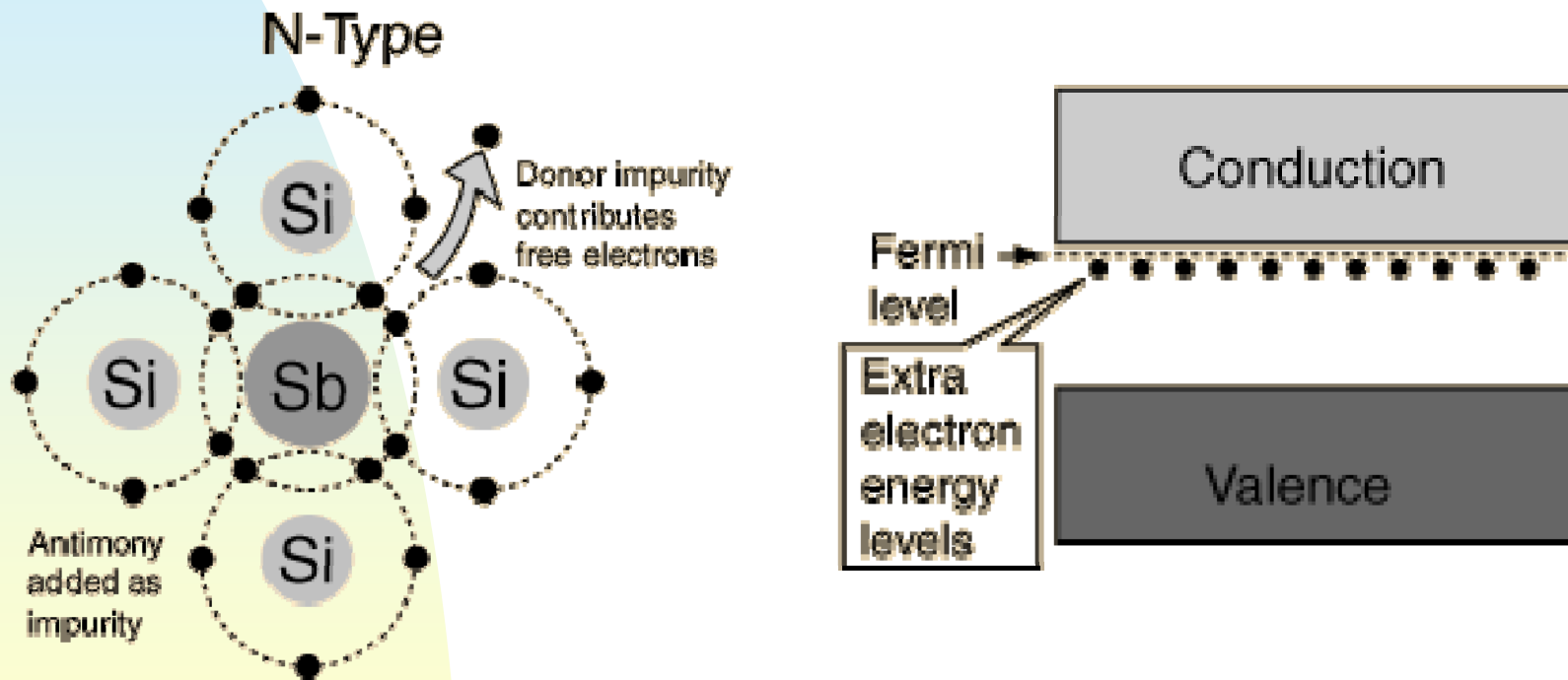
The addition of trivalent impurities such as boron, aluminum or gallium to an intrinsic semiconductor creates deficiencies of valence electrons, called "holes". It is typical to use $B_2H_6$ diborane gas to diffuse boron into the silicon material.
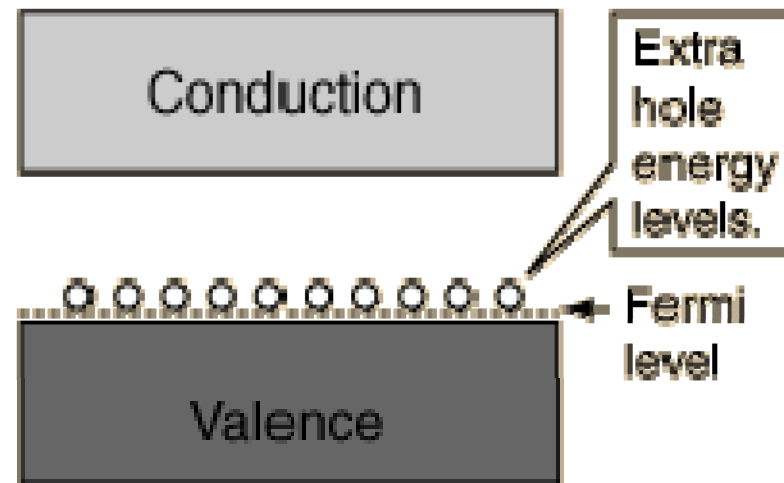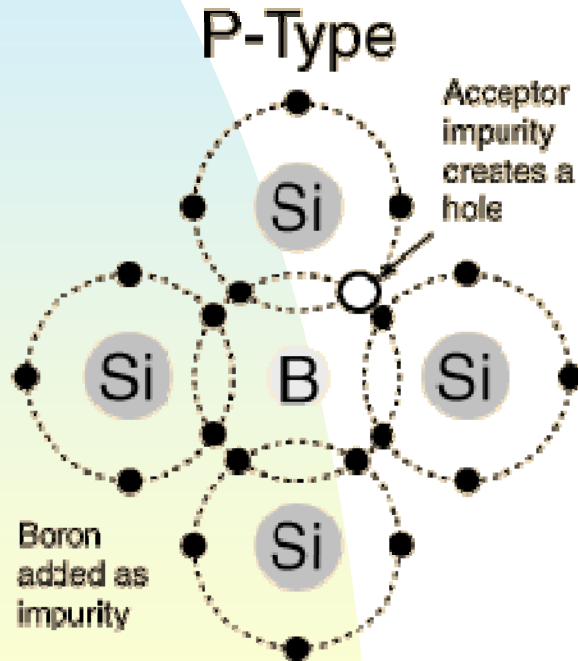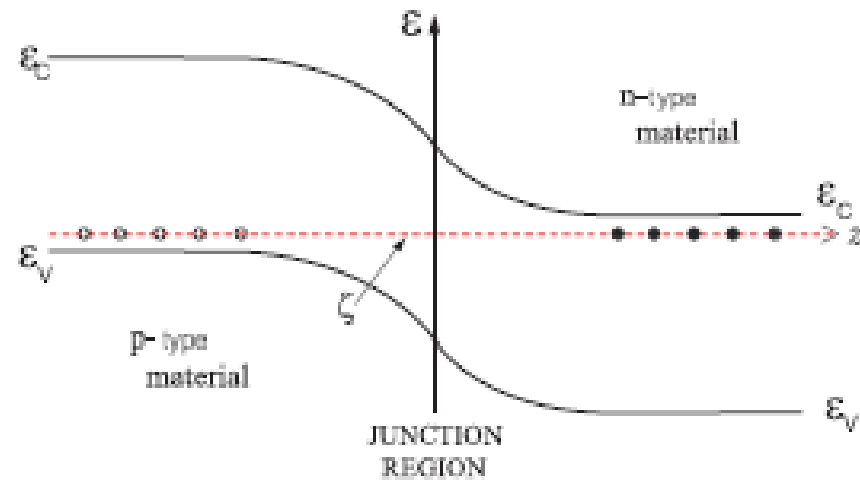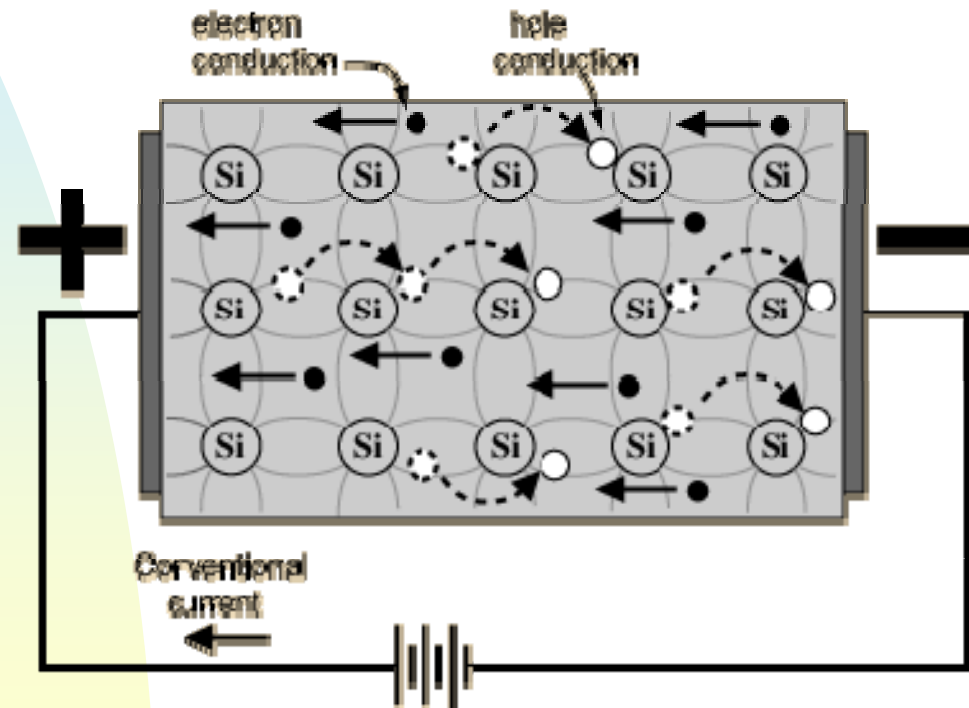
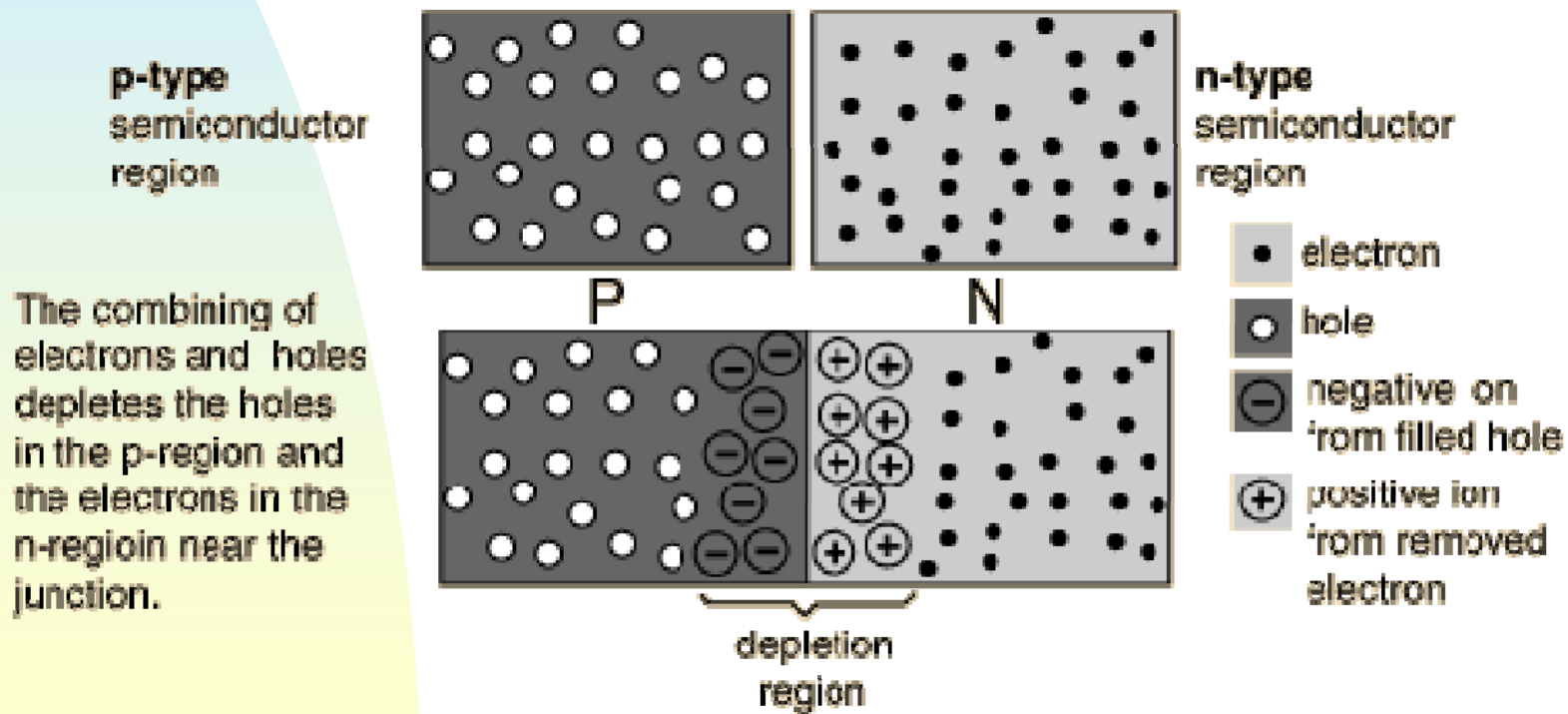Fig. 7.4. Impurity levels and chemical potential across the p–n junction

# Semiconductor Current

Both electrons and holes contribute to current flow in an intrinsic semiconductor.

# Depletion Region

When a p-n junction is formed, some of the free electrons in the n-region diffuse across the junction and combine with holes to form negative ions. In so doing they leave behind positive ions at the donor impurity sites.

p-type
semiconductor
region

The combining of electrons and holes depletes the holes in the p-region and the electrons in the n-regioin near the junction.

P          N

n-type
semiconductor
region

• electron

○ hole

⊖ negative on from filled hole

⊕ positive ion from removed electron

depletion region

# P-N Energy Bands

For a p-n junction at equilibrium, the fermi levels match on the two sides of the junctions. Electrons and holes reach an equilibrium at the junction and form a depletion region. The upward direction in the diagram represents increasing electron energy. That implies that you would have to supply enery to get an electron to go up on the diagram, and supply energy to get a hole to go down.



Depletion Region

N

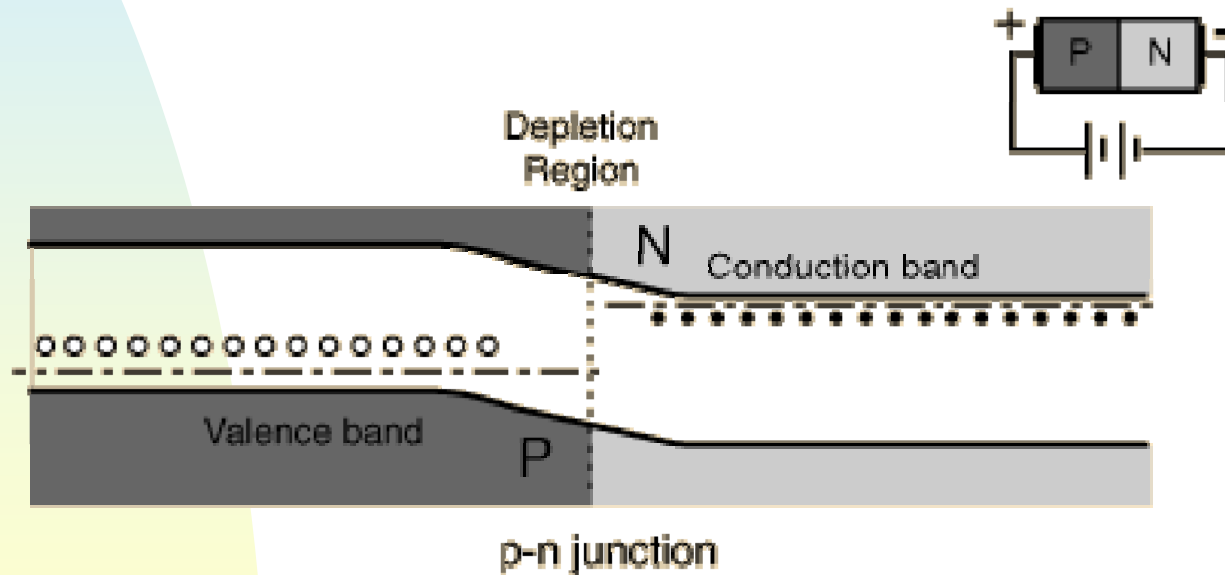Conduction band

Fermi Level

P

Valence band
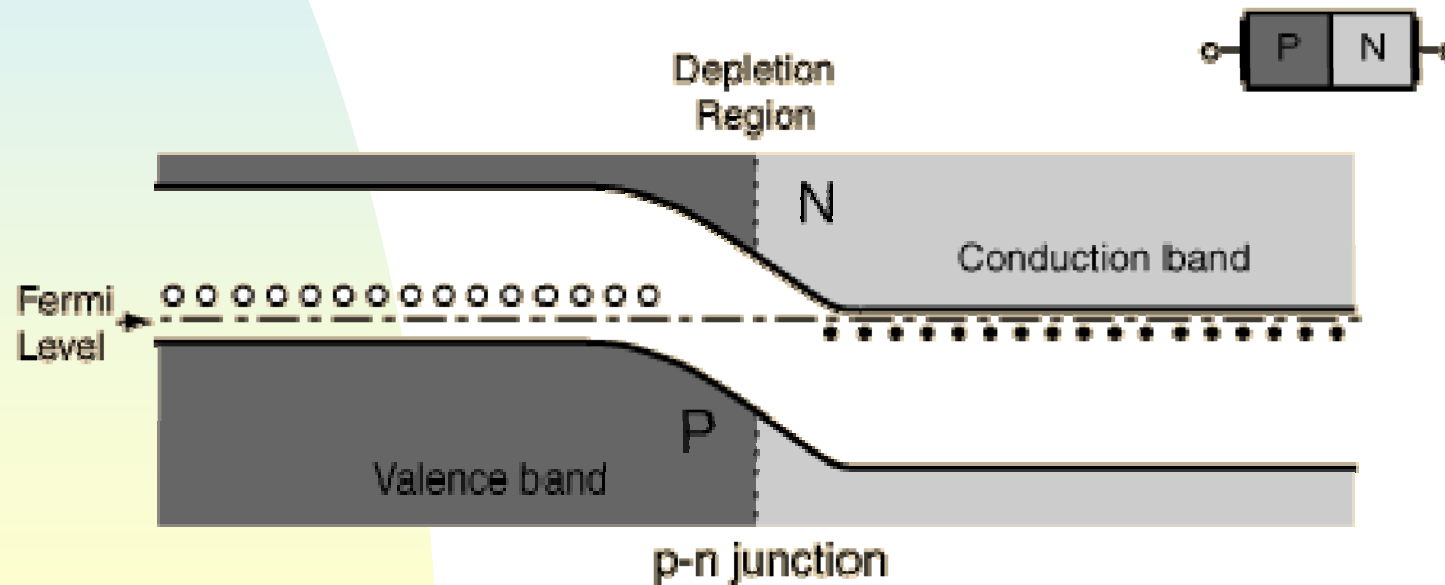
p-n junction

# P-N Energy Bands

To reverse-bias the p-n junction, the p side is made more negative, making it "uphill" for electrons moving across the junction. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.
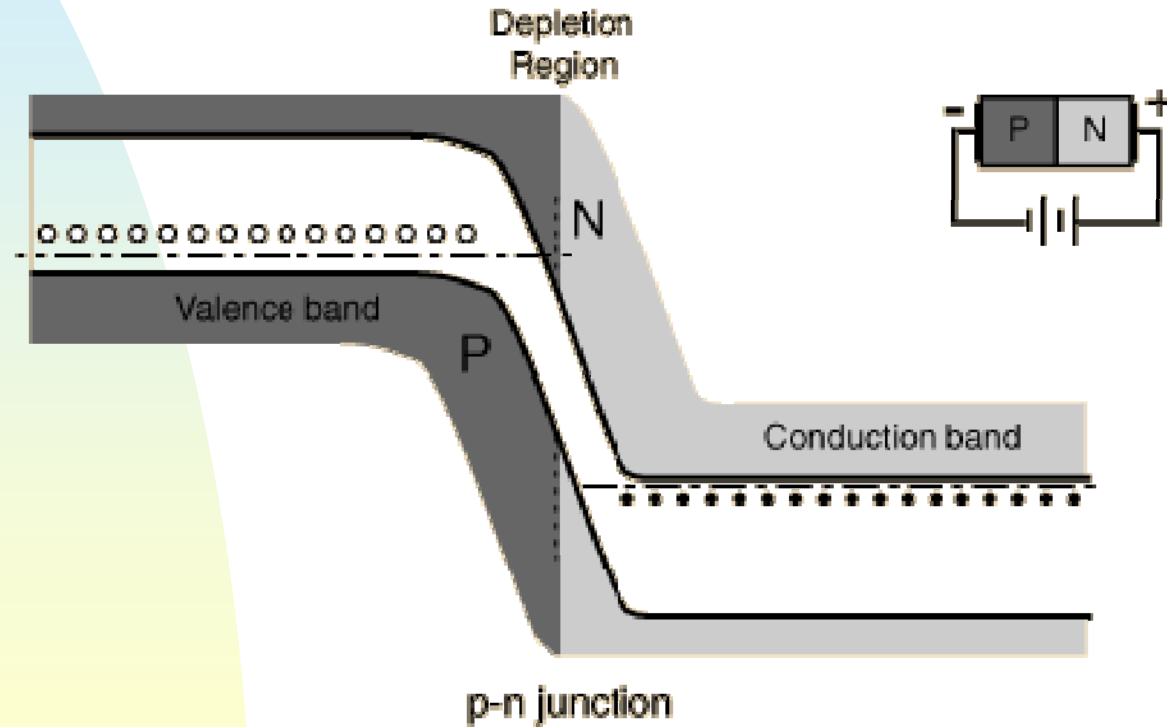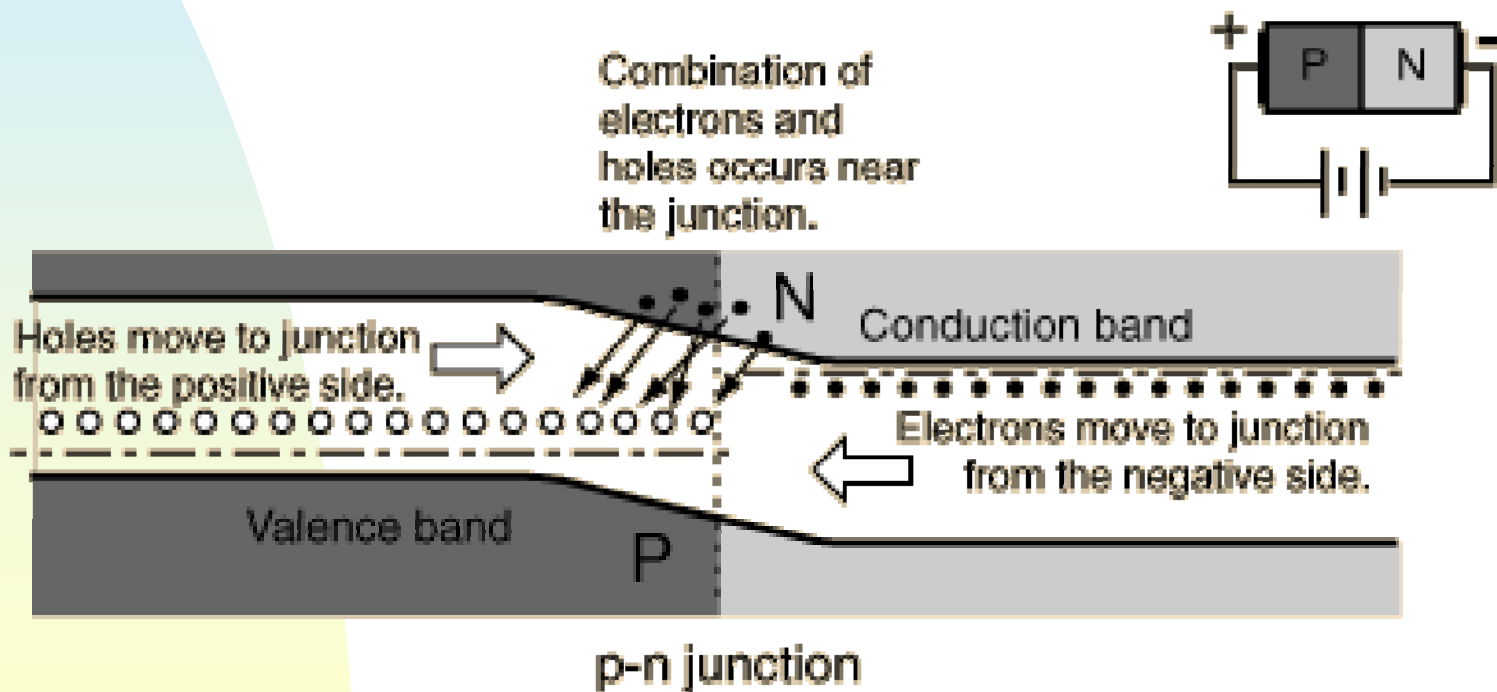
## -N Energy Bands

To forward bias the p-n junction, the p side is made more positive, so that it is "downhill" for electron motion across the junction. An electron can move across the junction and fill a vacancy or "hole" near the junction. It can then move from vacancy to vacancy leftward toward the positive terminal, which could be described as the hole moving right. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.

Depletion
Region

N

Conduction band

Valence band

P

p-n junction

When the p-n junction is forward biased, the electrons in the n-type material which have been elevated to the conduction band and which have diffused across the junction find themselves at a higher energy than the holes in the p-type material. They readily combine with those holes, making possible a continuous forward current through the junction.

Combination of
electrons and
holes occurs near
the junction.

Holes move to junction
from the positive side.

N

Conduction band

Electrons move to junction
from the negative side.

Valence band

P

p-n junction

# Forward Biased Conduction

The forward current in a p-n junction when it is forward-biased (illustrated below) involves electrons from the n-type material moving leftward across the junction and combining with holes in the p-type material. Electrons can then proceed further leftward by jumping from hole to hole, so the holes can be said to be moving to the right in this process.
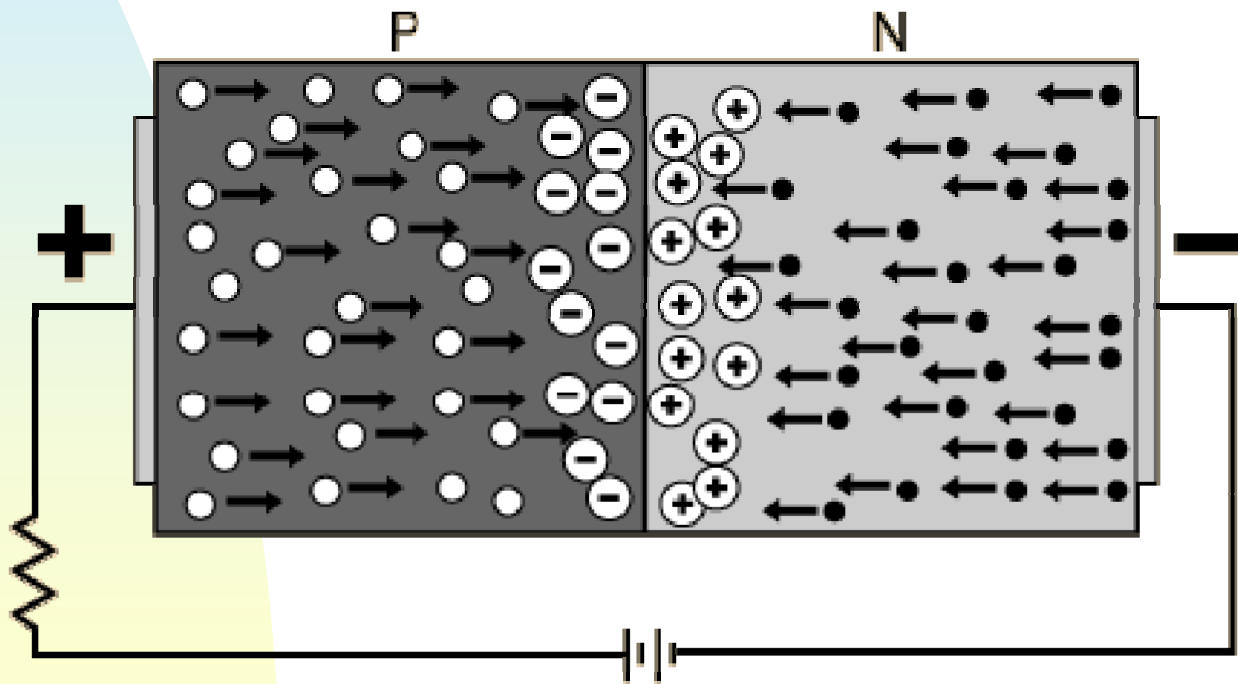
Consider the energy surface

$$\varepsilon(k)=\hbar^2\left(\frac{k_x^2+k_y^2}{2m_t}+\frac{k_z^2}{2m_l}\right), \text{ where } m_t \text{ and } m_l \text{ are transvers and longitudinal}$$

mass parameter. Use equation of motion to show that

$$\omega_c = eB/(m_l m_t)^{1/2}c \text{ when the static magnetic field } B \text{ lies in the}$$

$x, y$ plane.