"Complementi di Fisica"
Lecture 2

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Trieste, 22-09-2006, 02-10-2006

Course Outline - Reminder

- **The physics of semiconductor devices: an introduction**
  - Basic properties; energy bands, density of states
  - Equilibrium carrier concentration ("intrinsic", "extrinsic")
  - Carrier transport phenomena
    - Drift and Diffusion
    - Generation and Recombination
    - Continuity equations
- **Quantum Mechanics: an introduction**
- **Advanced semiconductor fundamentals**

Broken bonds: electrons and holes

Basic bond model of "intrinsic" (= "pure") Silicon
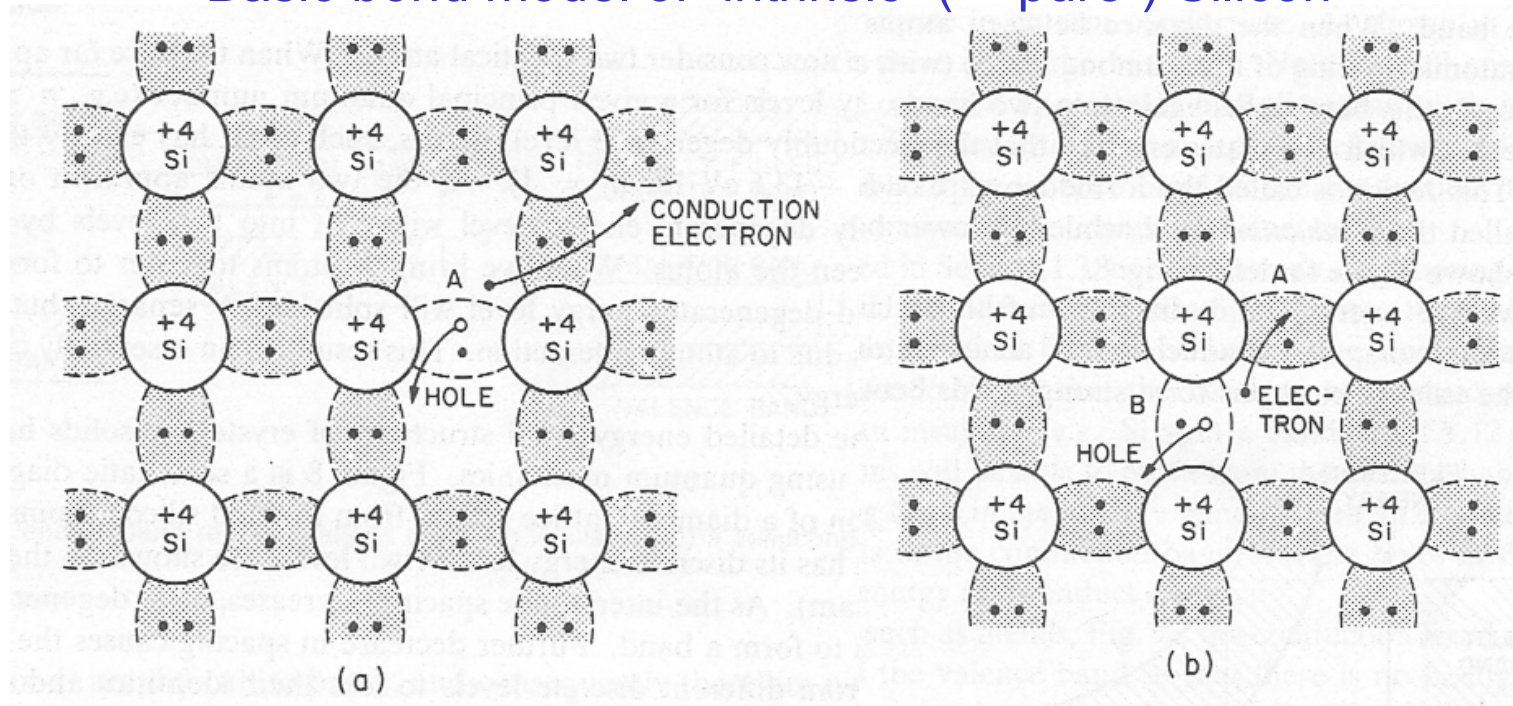
a broken bond at position A, resulting in a conduction electron and a "hole"

deficiency filled by one of the neighboring electrons (in B), resulting in a shift of the "hole" from A to B
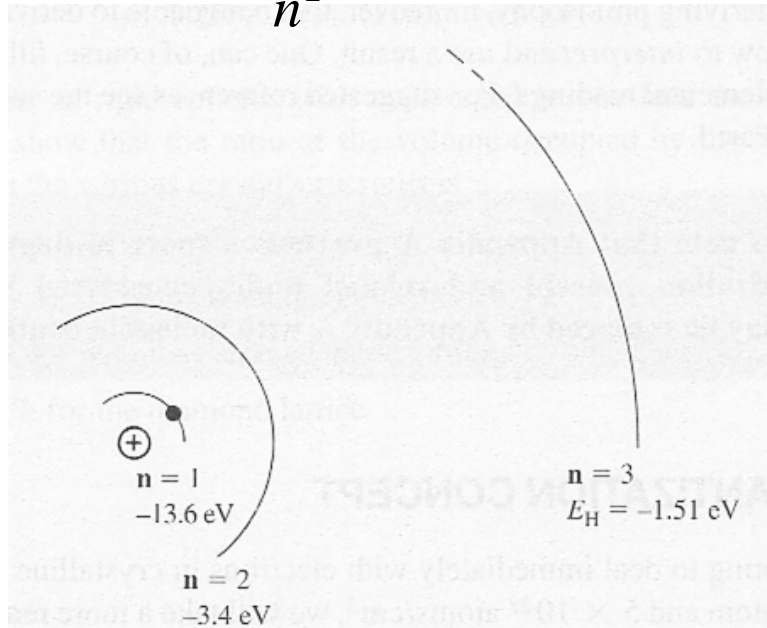
Both "freed" electrons and "left-over" holes contribute to conduction!

Isolated atoms: energy levels
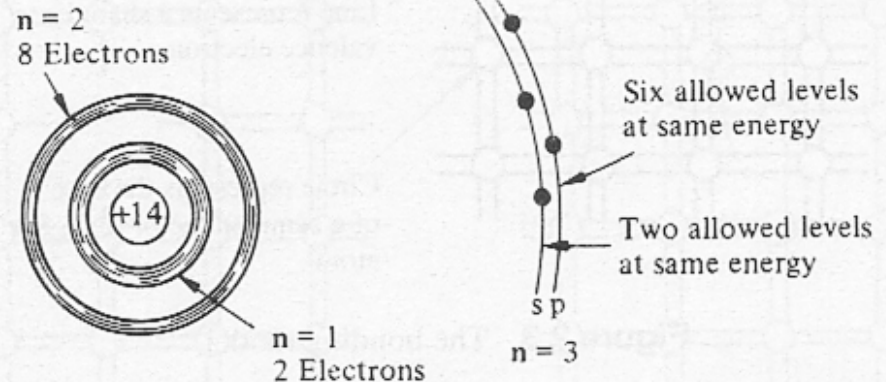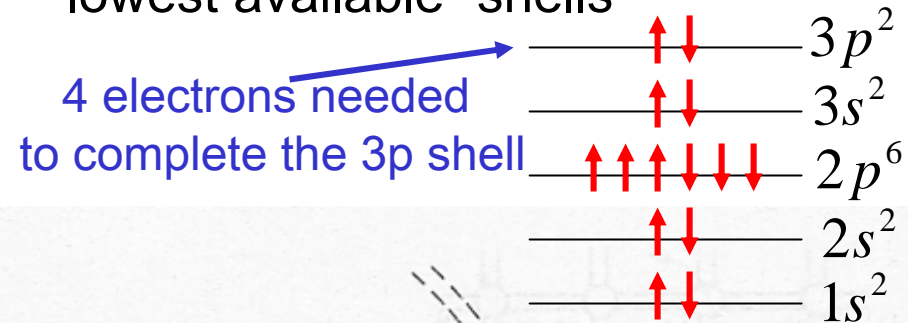
Hydrogen atom (Z=1)

Idealized representation of the first three allowed "Bohr orbits" and their quantized energy levels

$$E_n = -\frac{13.6\,\text{eV}}{n^2}$$

Silicon atom (Z=14)

Schematic representation of how the 14 electrons fill the lowest available "shells"

4 electrons needed to complete the 3p shell

$$3p^2$$
$$3s^2$$
$$2p^6$$
$$2s^2$$
$$1s^2$$

n = 1
−13.6 eV

n = 3
E_H = −1.51 eV

n = 2
−3.4 eV

n = 2
8 Electrons

+14

n = 1
2 Electrons

Six allowed levels at same energy

Two allowed levels at same energy

s p

n = 3

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From energy levels to energy bands
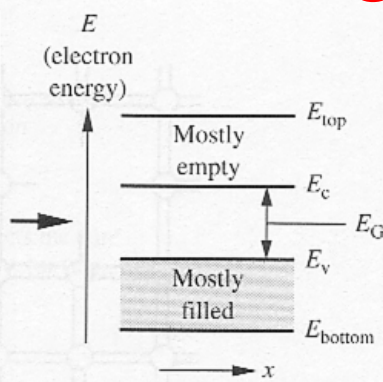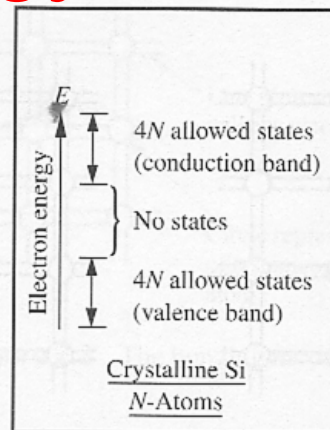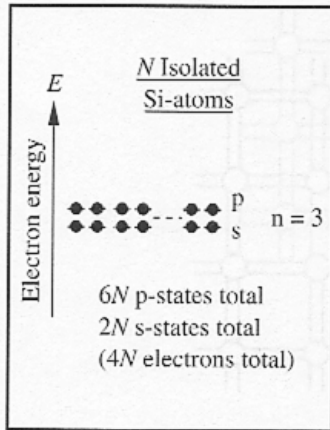
"Conduction Band"

"Gap"

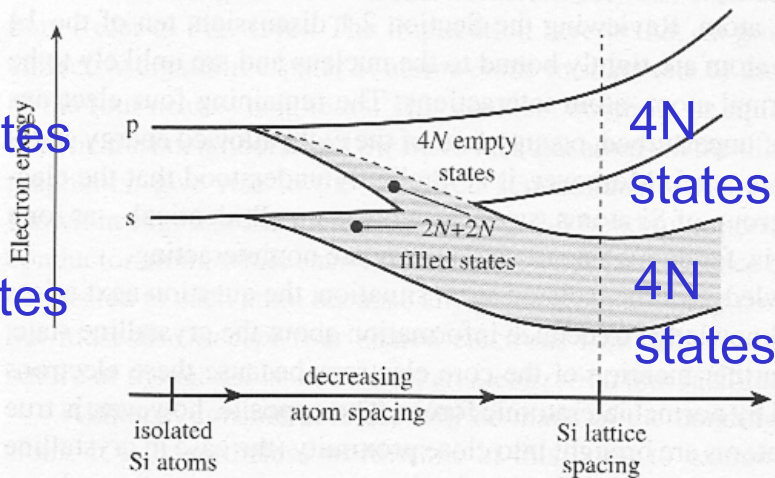"Valence Band"

N isolated
Si atoms

N bound
Si atoms

Somehow (quantum mechanics !),
when many atoms get close together
their quantized energy levels split
and turn into many states grouped in
"energy bands", see diagrams

6N
p-states

2N
s-states

4N
states

4N
states

Conduction only happens if electrons
have empty "states" available at
nearby energy !

Energy levels and energy bands diagrams

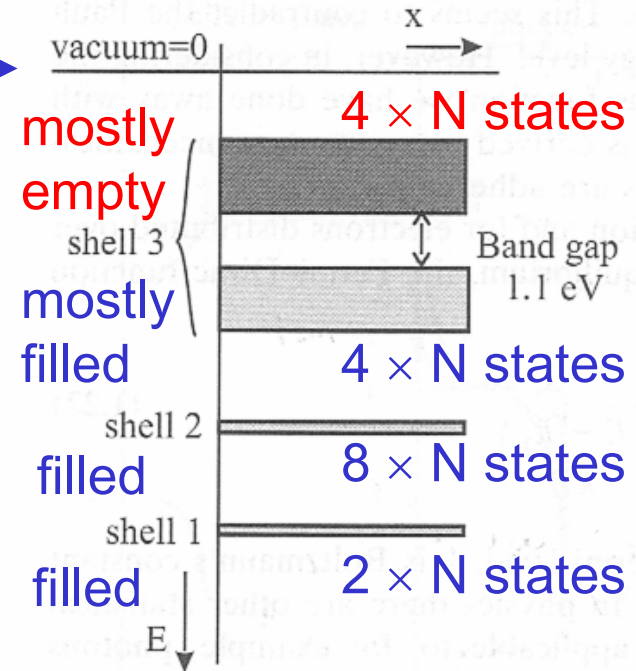$$E = E_{pot} + E_{kin} < 0 \quad \text{for bound electrons}$$

$$E_{pot} < 0, \quad E_{kin} > 0$$

N Silicon atoms,
$14 \times$ N electrons:
allowed states grouped
in *energy bands*, filled
according to Pauli Principle

Isolated hydrogen atom,
only one electron:
allowed *energy levels* E_n

$$E_{pot} \to 0 \quad \text{for} \quad r \to \infty$$

Balmer Series

$$E_5 = -\frac{13.6}{25} = -.54 \quad \text{eV}$$

$$E_4 = -\frac{13.6}{16} = -.85 \quad \text{eV}$$

$$E_3 = -\frac{13.6}{9} = -1.51 \quad \text{eV}$$

$$E_2 = -\frac{13.6}{4} = -3.40 \quad \text{eV}$$

$$E_1 = -\frac{13.6}{1} = -13.6 \quad \text{eV}$$

vacuum=0

mostly empty — $4 \times$ N states

shell 3

Band gap 1.1 eV

mostly filled — $4 \times$ N states

shell 2 — filled — $8 \times$ N states

shell 1 — filled — $2 \times$ N states

Outline – Lecture 2

- **Something more on the energy band model**
  - Electron and holes: energy, momentum, mass
  - Density of states

- **"Intrinsic" (= pure) semiconductor** *at equilibrium*
  - Population of states: Fermi-Dirac distribution function
  - "intrinsic" carrier concentration and Fermi level

  Next:

- **"Extrinsic" (= doped) semiconductor** *at equilibrium*
  - Bond model: "donors" and "acceptors"
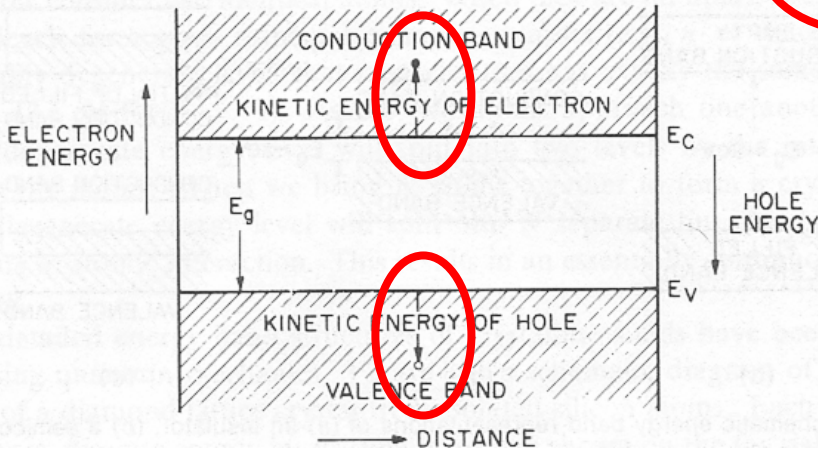 - Energy band model: band diagrams, density of states, carriers concentration, Fermi level

Energy band model

Electron and holes:

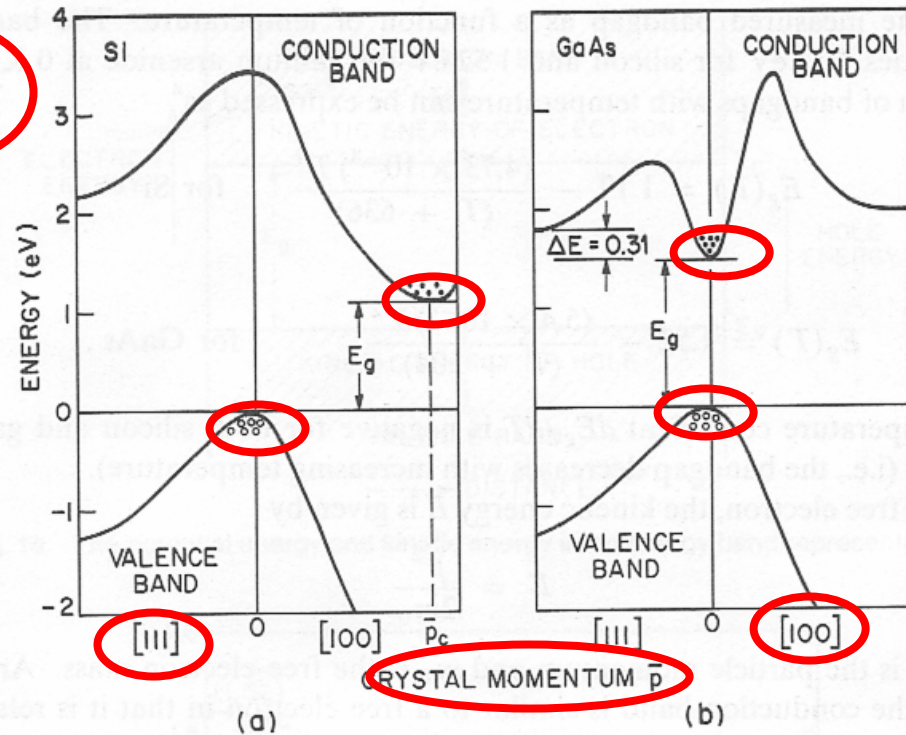*energy, momentum, mass*

Density of states

Band diagrams: what do they mean?

$$E = E_c + \frac{\overline{p}^2}{2m_n^*} \qquad \overline{p} = m_n^* v$$

???

$$E_{hole} = \frac{\overline{p}^2}{2m_p^*} \qquad \overline{p} = m_p^* v$$
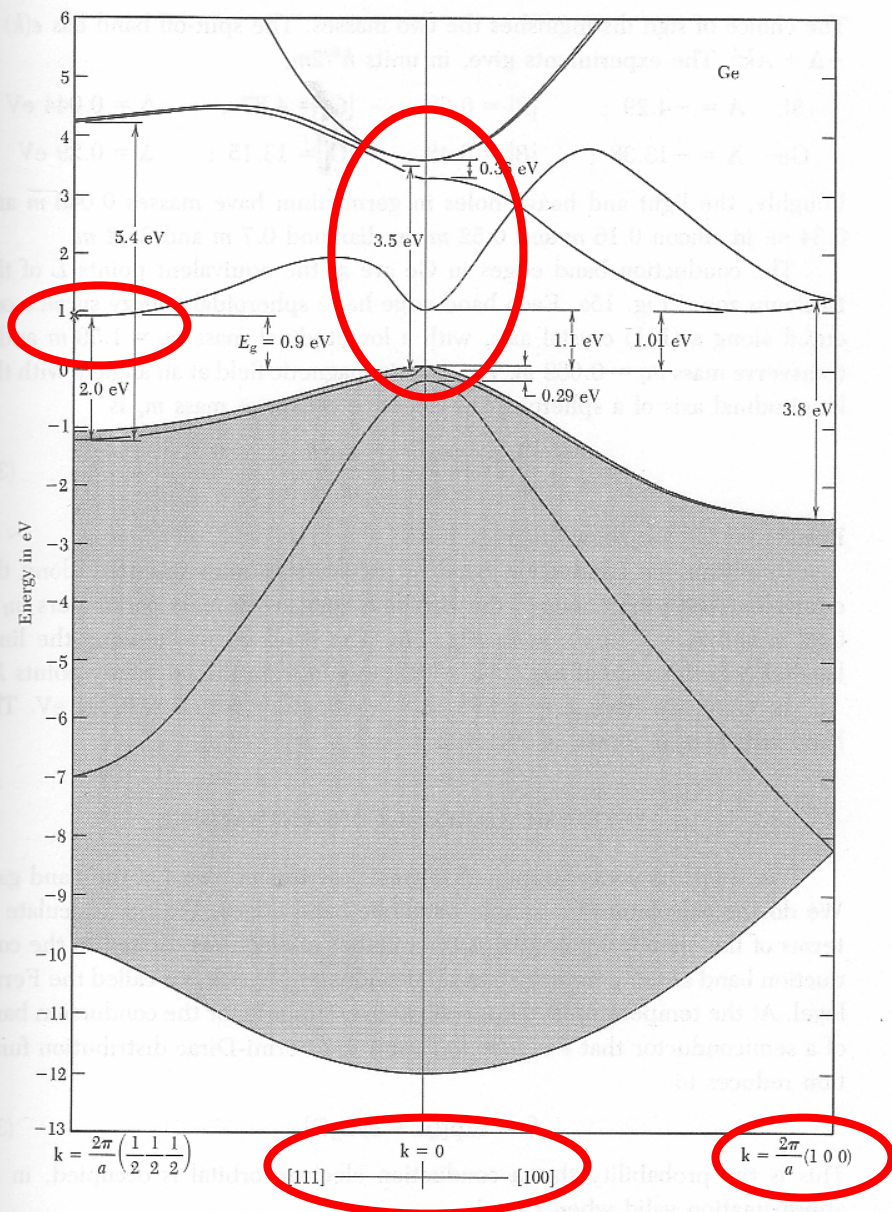

1. "Mass" = ? "Effective mass" = ?
2. "Momentum" = ? "Crystal momentum" = ?
3. "1st Brillouin zone" = ? ("Bragg condition", "reciprocal lattice", …)
4. "Energy" – "crystal momentum" functions ("band structure") = ?
5. Little dots/circles = ? States?

A "real life" example (Ge)

Figure 14 Calculated band structure of germanium, after C. Y. Fong. The general features are in good agreement with experiment. The four valence bands are shown in gray. The fine structure of the valence band edge is caused by spin-orbit splitting. The energy gap is indirect; the conduction band edge is at the point $(2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The constant energy surfaces around this point are ellipsoidal.
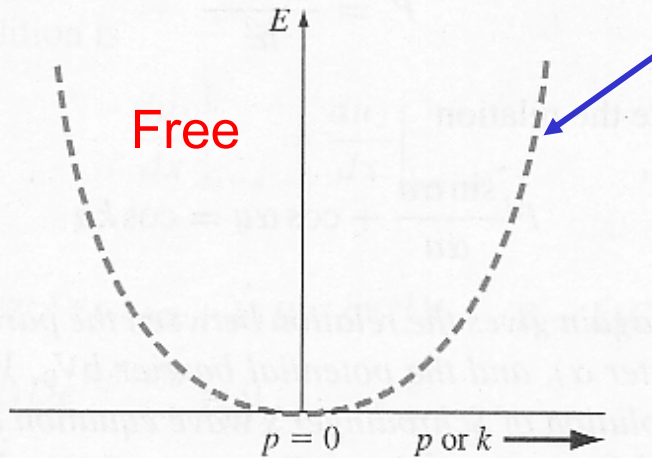
Theoretical computation of the "band structure of Ge", in good agreement with experimental data (not shown)

From:
C.Kittel,
Introduction to Solid State Physics

1. "mass", "effective mass" from *E(p)*

Free

Energy vs. momentum

In a crystal

$m < 0$

Parabolic fit

$m > 0$

E_{edge}

k_{edge}

p

Free electron: energy and momentum

$$E = \frac{p^2}{2m_0}, \quad p = m_0 v$$

Free electron: "mass"

$$\frac{dE}{dp} = \frac{2p}{2m_0} = \frac{p}{m_0} \qquad \frac{d^2E}{dp^2} = \frac{1}{m_0}$$

$$\Rightarrow m_0 = \frac{1}{\dfrac{d^2E}{dp^2}} = \text{const.}$$

m_0 allows us to predict the effect of an "external" force (example: el.field):
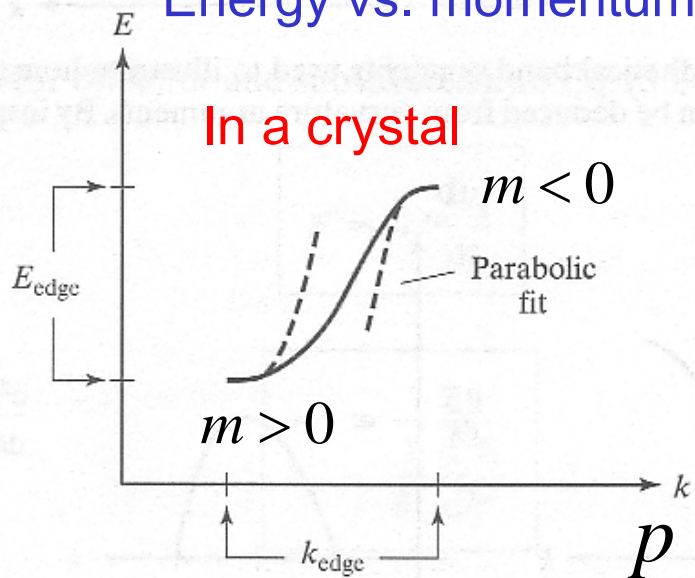
Electron in a crystal: "effective mass"

$$m \equiv \frac{1}{\dfrac{d^2E}{dp^2}} \neq \text{const.}$$

m allows us to predict the effect of an "external" force; interactions with the crystal are "hidden" in m (that can be < 0)!

E(p): more complicated

Effective mass: comments

- The quantum mechanical behaviour of electrons (and holes) propagating in a periodic crystal lattice can be approximated as those of classical particles with "effective masses" m^*_n and m^*_p

- Near the minimum of the conduction band or the maximum of the valence band, the E-p relationship is approximately quadratic, so that one can obtain:

$$m^* = \left(\frac{d^2 E}{dp^2} \right)^{-1} \approx \text{const.}$$

This makes it useful!

- The narrower the parabola, the smaller the effective mass; in general, m* depends on the crystal direction

- The (E-p) energy band structure can be both computed by theory and measured by experiment (more on this later)

2. wave number, crystal momentum

Plane waves
(for instance: e.m.)

$$e^{i(kx-\omega t)} = e^{ik(x-vt)}; \qquad k = \frac{2\pi}{\lambda}, \qquad \omega = \frac{2\pi}{T}$$

$$v_f = \frac{\omega}{k}$$

Phase velocity   Wavelength   Period

Wave number

DeBroglie:
particles → waves

$$p = \frac{h}{\lambda} = \hbar \frac{2\pi}{\lambda} = \hbar k \qquad E = \hbar \omega$$

⇒ "matter waves"

$$e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}$$

associated with
the propagation
of particles
in space and time

In crystals, wave number
and momentum include
(somehow) the interactions
with the crystal
⇒ "crystal momentum"

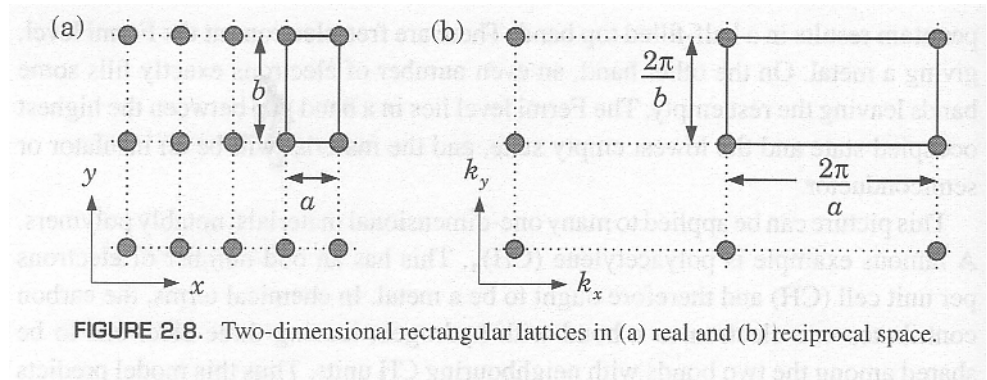# 3. Bragg, "reciprocal lattice", Brillouin
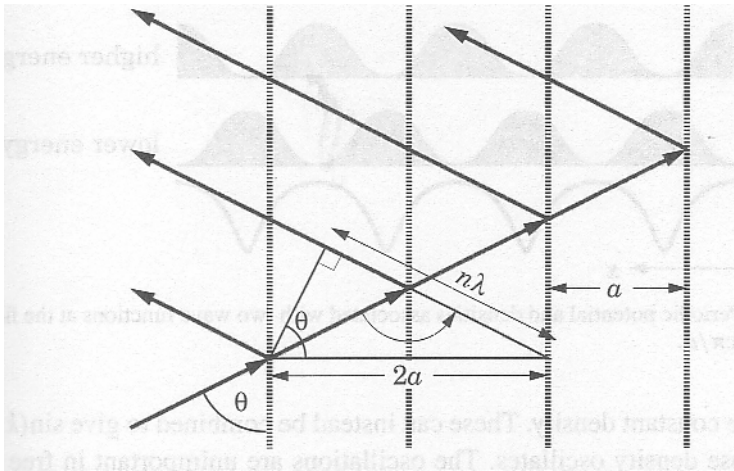
FIGURE 2.8. Two-dimensional rectangular lattices in (a) real and (b) reciprocal space.

"real" space
(x, y, z)

"reciprocal" space
(k_x, k_y, k_z)

Constructive interference (Bragg) if:

$$n\lambda = 2a \sin\theta \qquad \left(\lambda = 2\pi/k\right)$$

One-dimensional lattice reflections:

$$\theta = \pi/2 \quad \Rightarrow \quad \sin\theta = 1 \quad \Rightarrow \quad n\frac{2\pi}{k} = 2a \quad \Rightarrow \quad k = \frac{n\pi}{a}$$

$$-\pi/a \qquad 0 \qquad \pi/a$$

$$k_x \left(\text{m}^{-1}\right)$$
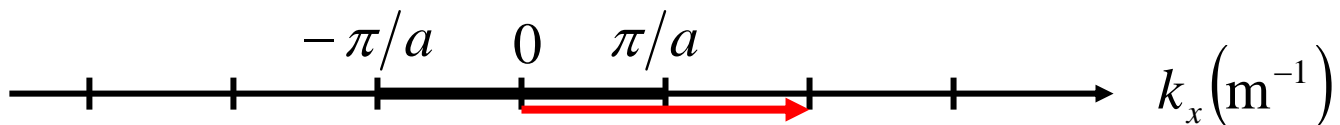
One-dimensional "reciprocal lattice": "first Brillouin zone" and "basis vector"

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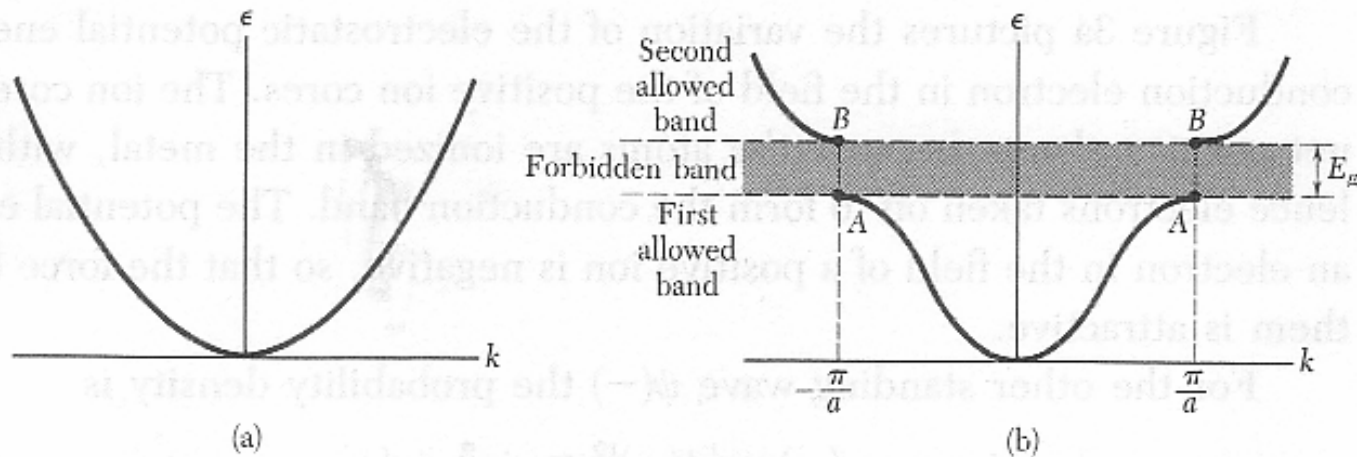
Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm \pi/a$; other gaps are found at $\pm n\pi/a$,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

Band structure, 1-d crystal

Figure 2.2. Band structure of a one-dimensional crystal in the (a) extended, (b) reduced, and (c) repeated zone schemes, and (d) the density of states as a function of energy. The thick lines show $\varepsilon(k)$ in a weak periodic potential, with bands labelled by n, while the thin parabola is $\varepsilon_0(k)$ for free electrons. The grey lines are periodic repeats.

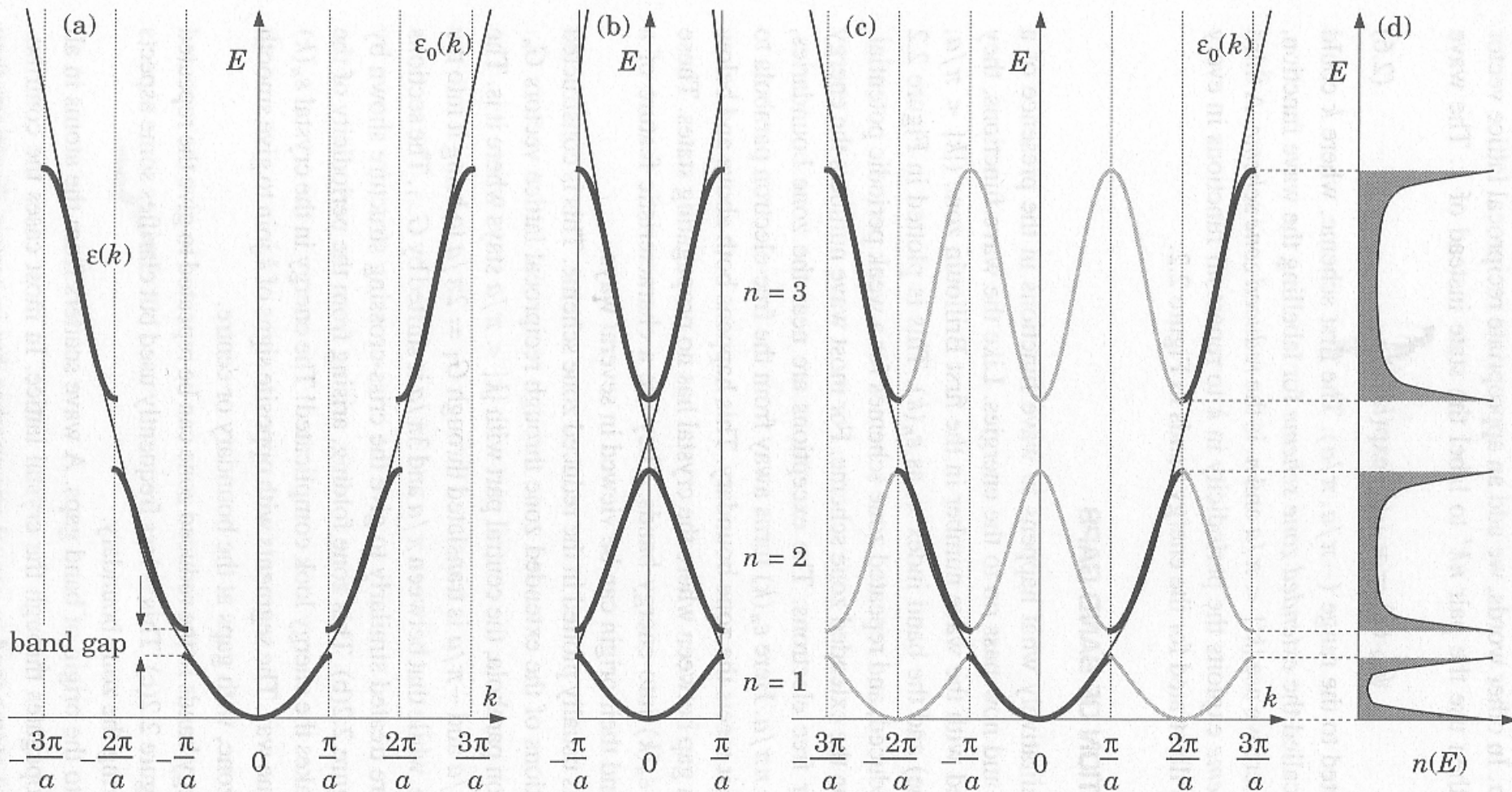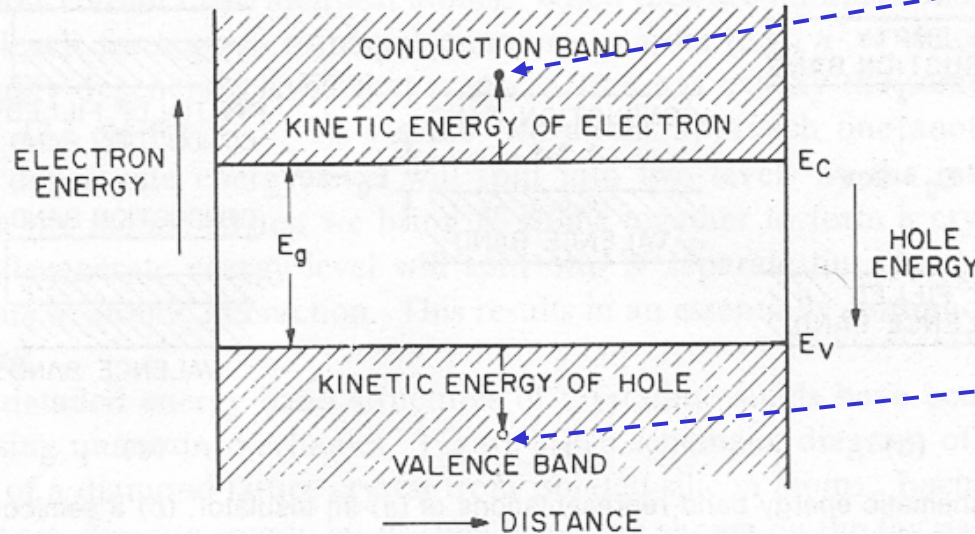# crystal momentum and effective mass

From the practical point of view:
treat electrons and holes in a crystal
as classical particles characterized by
"effective mass", kinetic energy, and
"crystal momentum":

Free electron:

$$E = \frac{p^2}{2m_0} \qquad p = m_0 v$$

**Electrons close to the bottom
of the conduction band (E>E_c):**

$$E = E_c + \frac{\overline{p}^2}{2m_n^*} \qquad \overline{p} = m_n^* v$$

ELECTRON ENERGY

CONDUCTION BAND

KINETIC ENERGY OF ELECTRON

E_c

E_g

HOLE ENERGY

E_v

KINETIC ENERGY OF HOLE

VALENCE BAND

DISTANCE

**Holes close to the top
of the valence band:**

$$E_{hole} = \frac{\overline{p}^2}{2m_p^*} \qquad \overline{p} = m_p^* v$$

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Energy-momentum in three dimensions

Si crystals: **GaAs crystals:**

$m_n^* \sim 0.19 m_0$

$m_n^* \sim 0.07 m_0$
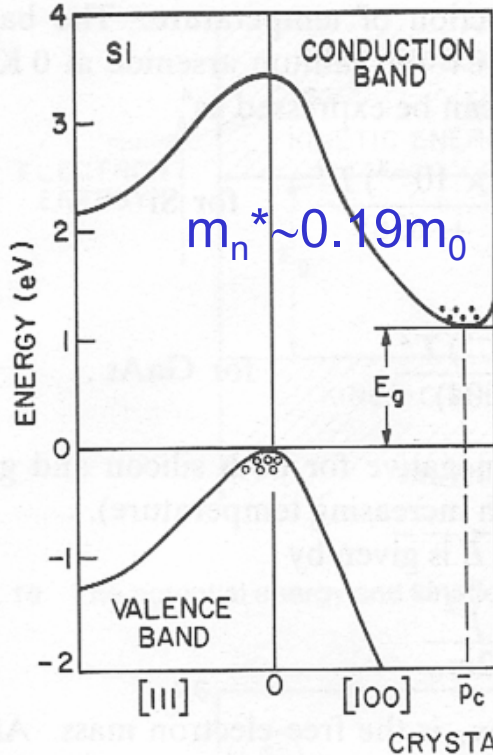
"indirect"
semiconductor
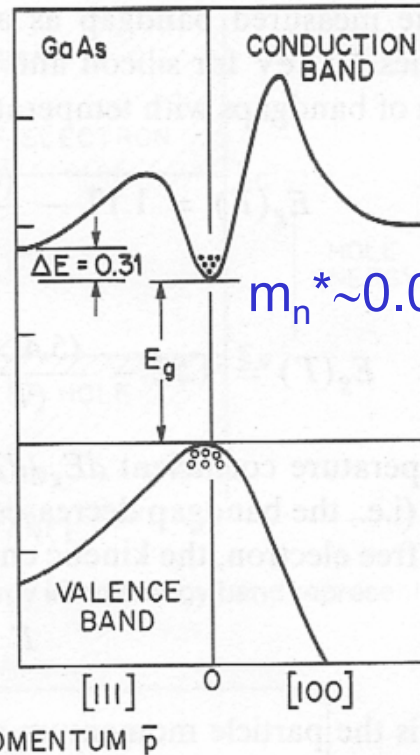
"direct"
semiconductor

- **More complications:**
  - Different E-p relations in different space directions
  - Usually only [111] and [100] are shown
  - Minimum E in conduction band and maximum E in valence band may occur for different crystal momenta ! ("indirect" semiconductors)
  - Practical consequences, see later (for instance: optoelectronic devices)

Band gap: temperature dependence
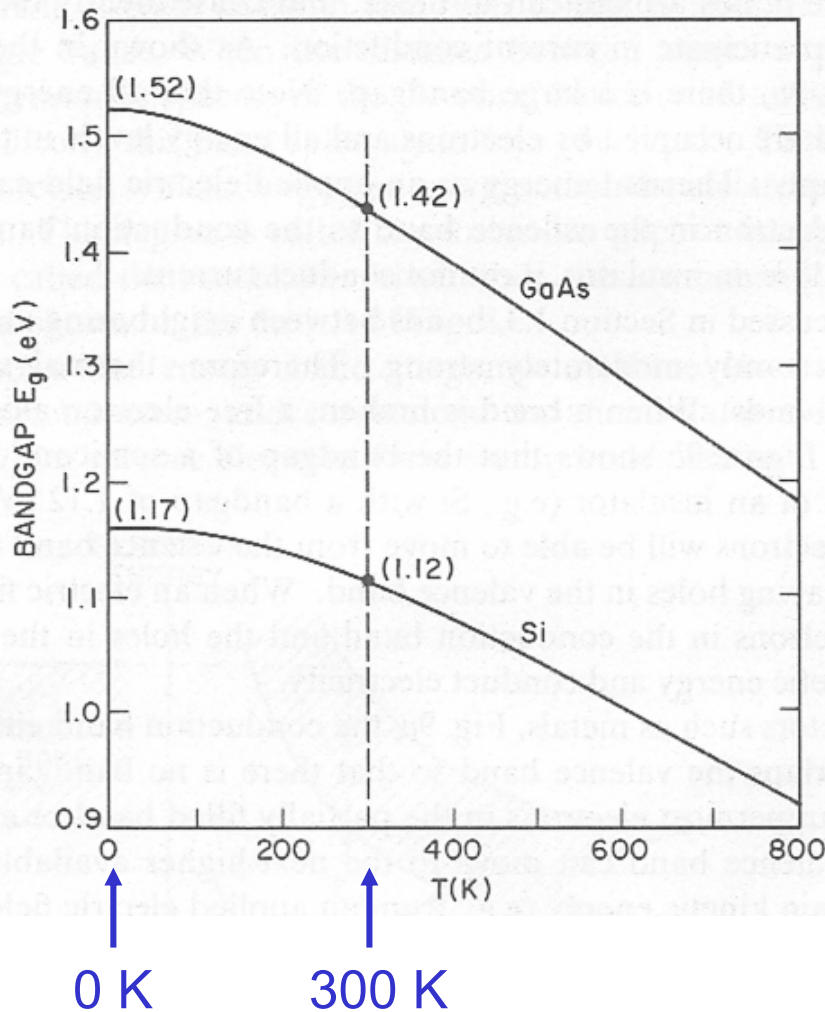
Empirical, from fit to data:

GaAs:

$$E_g(T) = 1.17 - \frac{\left(4.73 \times 10^{-4}\right)T^2}{T + 636}$$

Si:

$$E_g(T) = 1.52 - \frac{\left(5.4 \times 10^{-4}\right)T^2}{T + 204}$$

0 K   300 K

Density of states

- How many states are available for electrons per unit volume, close to the band edges, as a function of E?

    – Essential ingredient for computing the concentration of carriers and then the conduction properties!

    – Treating electrons as "standing waves" with wavelength given by the DeBroglie relation, we will find (see second part of the course) that:

$$N(E) = 4\pi \left(\frac{2m_e^*}{h^2} \right)^{3/2} E^{1/2}$$

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3} \quad , \quad E \geq E_c$$

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3} \quad , \quad E \leq E_V$$

SZE notation

PIER notation

Intrinsic semiconductors

Fermi-Dirac distribution function
Intrinsic carriers concentration, Fermi level

Fermi probability distribution function

- Electrons fill up available states following the Pauli principle (two electrons with opposite spin for each level)

- Probability distribution function (Fermi-Dirac, more details in the second part of the course):

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

$$E = E_F \Rightarrow F(E) = 1/2$$

$$E \to \infty \Rightarrow F(E) \to 0$$

$$E \to -\infty \Rightarrow F(E) \to 1$$

$$k = 8.617 \times 10^{-5} \; eV/K \quad \text{Boltzmann constant,} \quad T \;\; \text{temperature} \left(K\right)$$

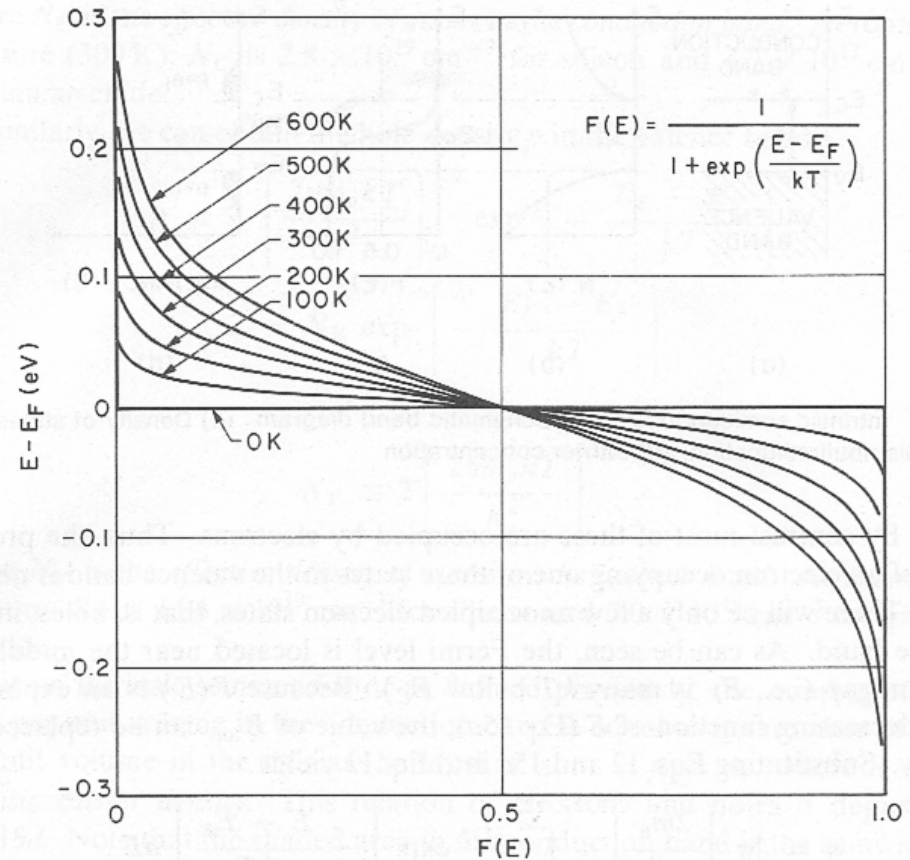$$F(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_F}{kT}\right)}$$

Fig. 14 Fermi distribution function $F(E)$ versus $(E - E_F)$ for various temperatures.

Fermi pdf: approximate expressions

- Simpler expressions for energies far enough from E_F:

$$F(E) \cong e^{-(E-E_F)/kT} \quad \text{for} \quad E - E_F > 3kT$$

$$F(E) \cong 1 - e^{-(E_F-E)/kT} \quad \text{for} \quad E - E_F < -3kT$$

Intrinsic carrier concentrations

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3}$$

$$F(E) \cong e^{-(E - E_F)/kT}$$

**Effective density of states
In the conduction band**

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

E ↑
CONDUCTION BAND
E_C
E_g
E_V
VALENCE BAND

N (E)

F(E)
0   0.5   1.0

E_C n=n_i
E_F
E_V
p=n_i

n(E) AND p(E)
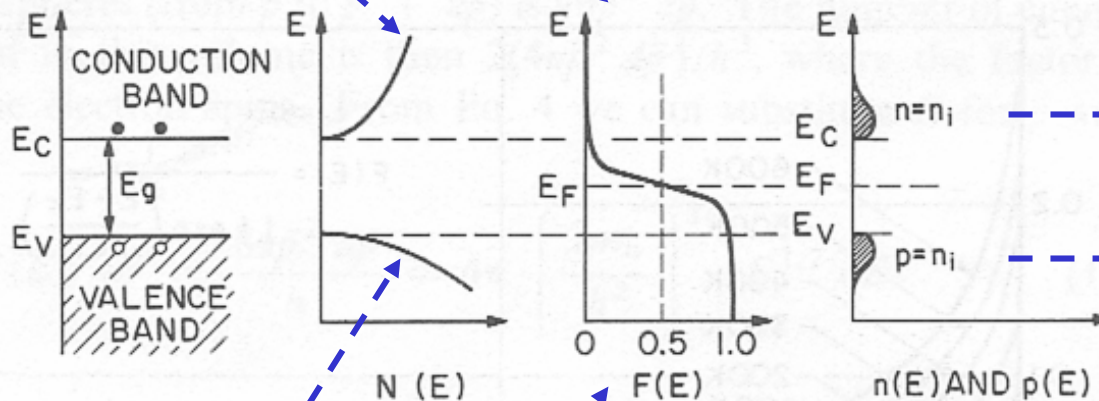
$$n \cong N_C e^{-(E_F - E_C)/kT}$$

$$p \cong N_V e^{-(E_V - E_F)/kT}$$

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

**Effective density of states
In the valence band**

$$1 - F(E) \cong e^{-(E_F - E)/kT}$$

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3}$$

Exercise 2.1 Integrate g(E)F(E) to obtain n and p

Intrinsic Fermi level and carrier density

Effective density of states
In the conduction band

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

$$\cong 2.8 \times 10^{19}\, cm^{-3}\ (Si),\ \ 4.7 \times 10^{17}\, cm^{-3}\ (GaAs)$$

Effective density of states
In the valence band

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

@ T~300K

$$\cong 1.04 \times 10^{19}\, cm^{-3}\ (Si),\ \ 7.0 \times 10^{18}\, cm^{-3}\ (GaAs)$$

$$n \cong N_C e^{-(E_F - E_C)/kT}$$
$$p \cong N_V e^{-(E_V - E_F)/kT}$$

For an intrinsic
semiconductor:

$$n = p = n_i$$

Intrinsic
carrier
density

$$n = p \Rightarrow E_i = E_F = \frac{E_C + E_V}{2} + \frac{kT}{2}\ln\left(\frac{N_V}{N_C}\right) = \frac{E_C + E_V}{2} + \frac{3kT}{4}\ln\left(\frac{m_p}{m_n}\right) \Rightarrow E_i \cong \frac{E_C + E_V}{2}$$

Intrinsic
Fermi
level

"mass action law": at thermal equilibrium:

$$np = n_i^2 = N_C N_V e^{-E_g/kT} \qquad n_i = \sqrt{N_C N_V}\, e^{-E_g/2kT}$$

Intrinsic carrier densities

- ## Temperature dependence
  - Increase with temperature; smaller with larger Eg
- ## Caveats:
  - Pure Si: very low conductivity: $\sigma \approx 10^{-6} (\Omega\ cm)^{-1}$ at $T \approx 300K$
  - However, in practice dominated by defects (Kowalski method: typically $10^{11}/cm^2$) $\Rightarrow \sigma \approx 10^{-5} (\Omega\ cm)^{-1}$
  - Doping is needed in practice, to control conductivity!
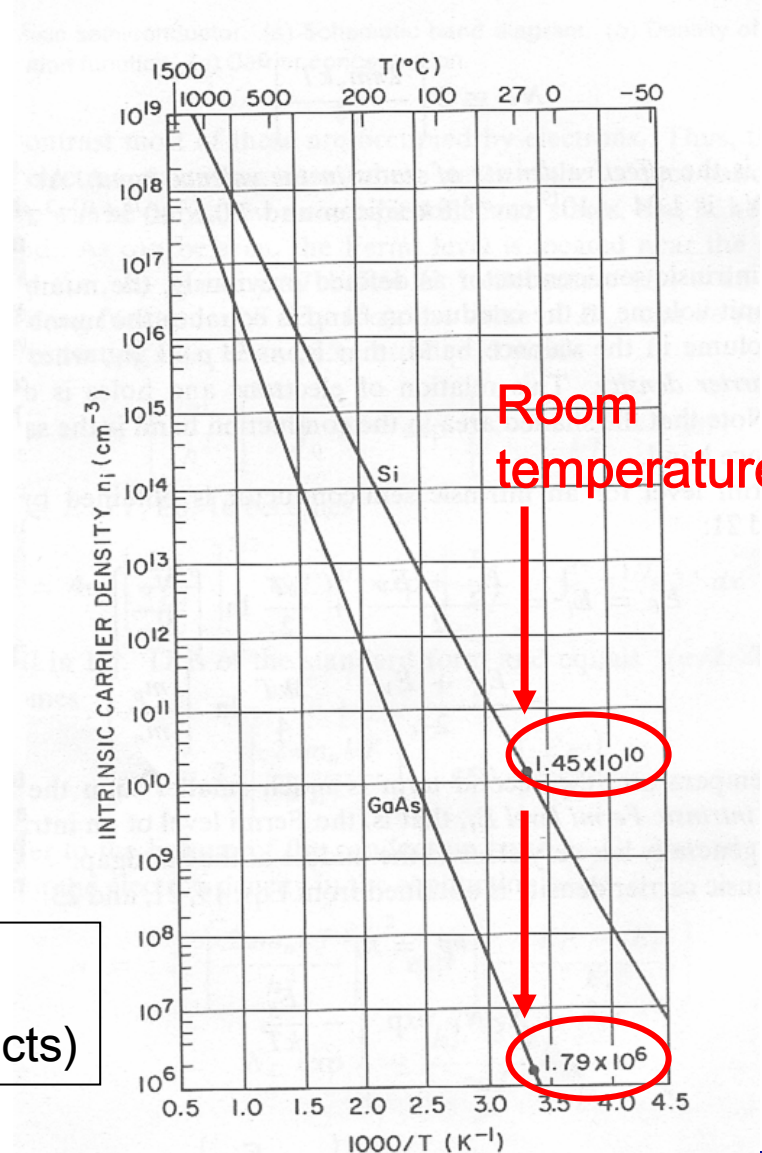
Exercise 2.2 Estimate orders of magnitude for the conductivity of Si (pure and with realistic defects)

Room temperature

1.45x10^{10}

1.79x10^6

Lecture 2 - summary

- ## Something more on the energy band model
  - Electron and holes: energy, momentum, mass
  - Density of states

- ## "Intrinsic" (= pure) semiconductor *at equilibrium*
  - Population of states: Fermi-Dirac distribution function
  - "intrinsic" carrier concentration and Fermi level

  Next:

- ## "Extrinsic" (= doped) semiconductor *at equilibrium*
  - Bond model: "donors" and "acceptors"
  - Energy band model: band diagrams, density of states, carriers concentration, Fermi level

- ## Semiconductors off-equilibrium: transport phenomena

Lecture 2 – Items to be understood…

- Some items that require a deeper explanation:
    - Bohr orbits, orbitals, shells, bands
    - Dispersion relations for electrons in crystals; computations and results in 1-d and 3-d
    - Effective mass, crystal momentum
    - Direct and indirect semiconductors
    - Density function and Fermi functions
    - Etc… (add your own questions: "perche`…?" !)

Lecture 2 - Glossary

wave number	numero d'onda	
effective mass	massa efficace	
crystal momentum	impulso reticolare?	

Lecture 2 - exercises

- **Exercise 2.1:** Integrate the product of the density function and Fermi function g(E)F(E) to obtain the carrier concentrations n and p.

- **Exercise 2.2:** Estimate orders of magnitude for the conductivity of Si (pure and with realistic defects)

- **Exercise 2.3:** At room temperature (300K) the effective density of states in the valence band is 1.04×10^{19} cm^{-3} for silicon and 7×10^{19} cm^{-3} for gallium arsenide; find the corresponding effective masses of holes. Compare these masses with the free-electron mass.

- **Exercise 2.4:** Calculate the location of the intrinsic Fermi level E_i in silicon at liquid nitrogen temperature (77K), at room temperature (300K), and at 100°C (let $m_p=0.5m_0$ and $m_n=0.3\ m_0$). Is it reasonable to assume that E_i is at the center of the forbidden gap?

- (the use of MATLAB or similar programs to perform computations, plot functions etc. is encouraged; for instance: plot the Fermi function for different values of the temperature T).

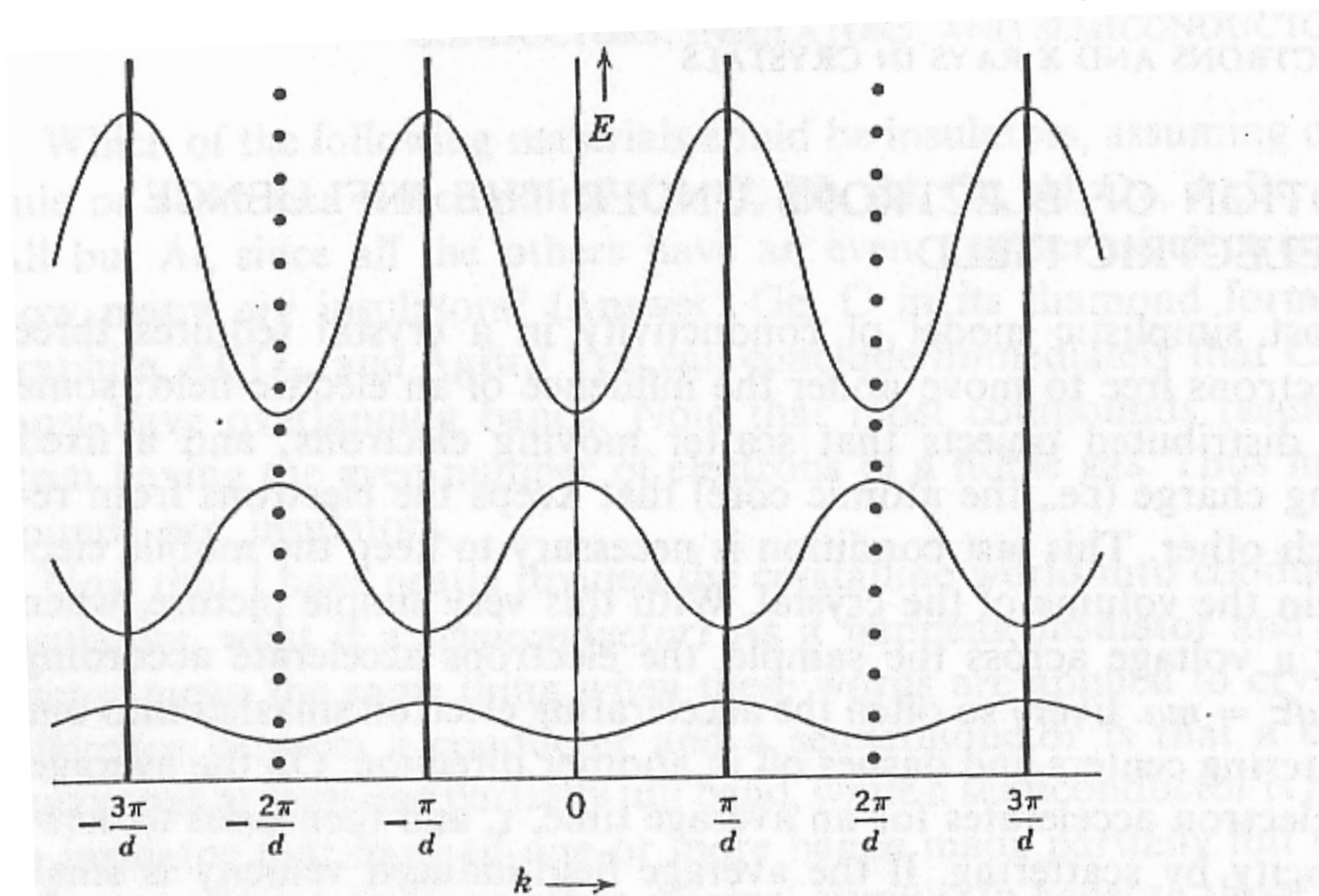# Back-up slides

Unreduced Bloch E-k diagram

Figure 2.18 Complete unreduced Bloch diagram. Any interval of $2\pi/d$ along the k axis (a *zone*) contains a complete set of solutions. The usual set of zones is indicated by the bold vertical lines.

Energy E, momentum p, mass m

E-k (~*E-p*) diagrams ("dispersion relations"):
quantum mechanical propagation of electrons as "waves" in periodic crystals!!!
Important result of a one-dimensional simplified model (Kronig-Penney):

Free electron:

$$E = \frac{p^2}{2m_0}, \quad p = m_0 v$$

Electron in periodic potential,
close to the bottom of the
allowed conduction band:

$$E = \frac{\overline{p}^2}{2m_n^*} \quad , \quad \overline{p} = m_n^* v$$

"effective mass"
"crystal momentum"

E

allowed

forbidden

allowed

forbidden

U_0

Free particle

"wave number"

$$\frac{-4\pi}{a+b} \quad \frac{-3\pi}{a+b} \quad \frac{-2\pi}{a+b} \quad \frac{-\pi}{a+b} \quad 0 \quad \frac{\pi}{a+b} \quad \frac{2\pi}{a+b} \quad \frac{3\pi}{a+b} \quad \frac{4\pi}{a+b}$$

Zone 2 | Zone 1 | Zone 2

$$k = p/\hbar$$