XI. After getting Energy Bands

$\mathcal{E}_n(\vec{k})$ $\quad \vec{k} \in 1^{st}$ BZ

N allowed $\vec{k}$'s × 2 (two spin states)

= 2N states for electrons in one band

A. Metals, Insulators, Semiconductors†

Every material ⇒ a number of electrons

Fill electrons into bands (Fermi-Dirac distribution)

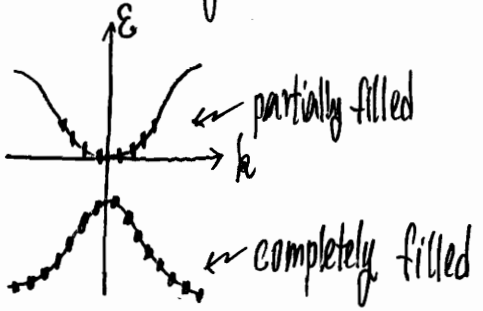
T=0 step function

⇒ different cases

- Completely filled bands separated with completely empty bands by a large gap ⇒ Insulator
- Highest occupied states are in a partially filled band ⇒ metal
- Completely filled bands separated with completely empty bands by a small gap ⇒ Semiconductor

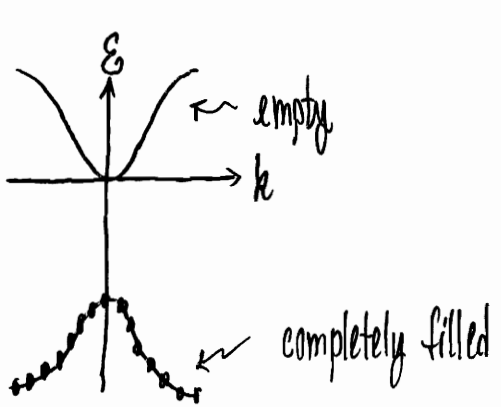
† See later discussion on electron dynamics.

Schematically,

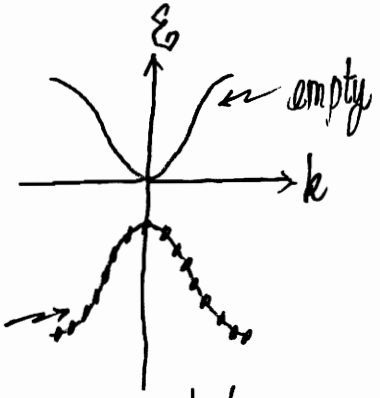


metal

"Valence Band" ≡ the topmost band occupied by electrons at T=0

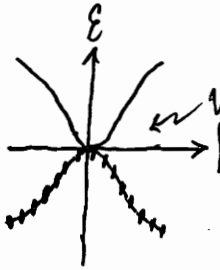


insulator

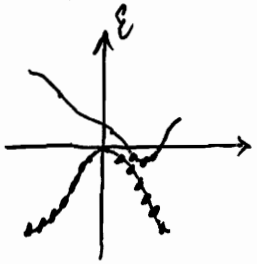


semiconductor

This classification is based on: A full band carries no electric current, even in the presence of an electric field.



or



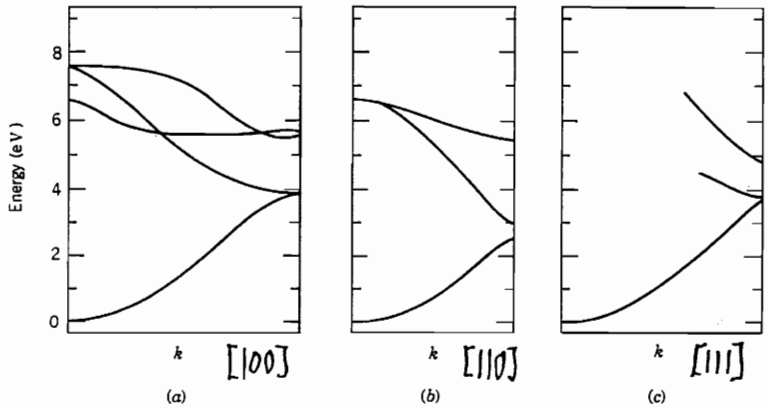
Semi-metals (e.g. Bi, Sb, As)

B. Some examples of Band Structure

Potassium

All the 1s, 2s, 2p, 3s, 3p bands are completely filled (not shown here).

These are the bands to fill the N 4s electrons.



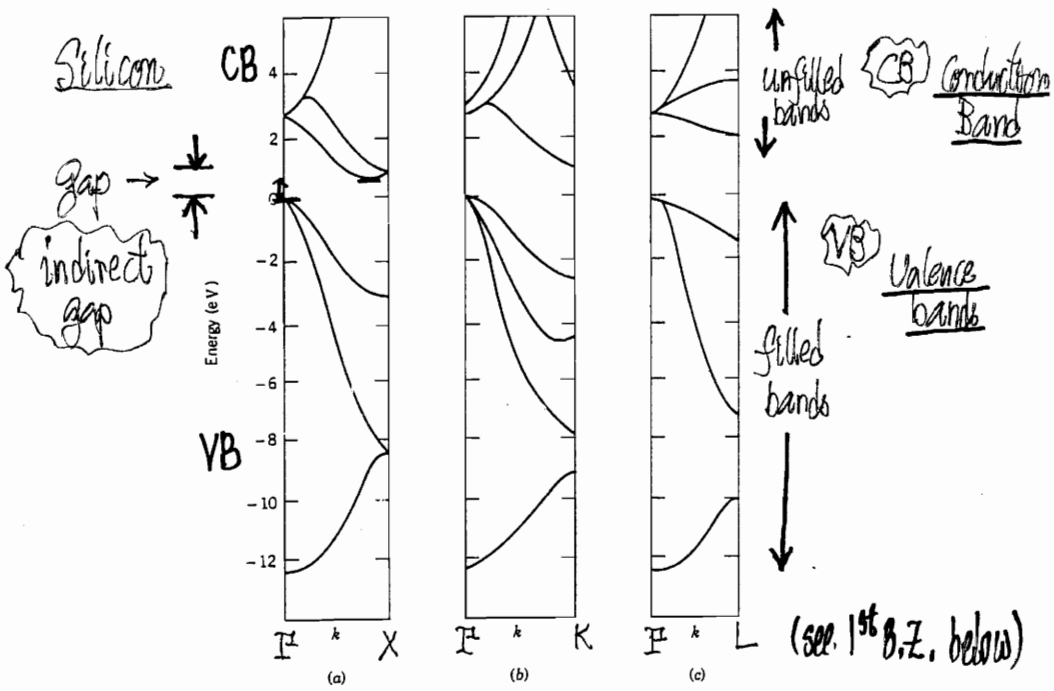
Electron band structure of potassium for energies near the 4s atomic level: (a) **k** in the [100] direction; (*b*) **k** in the [110] direction; and (c) **k** in the [111] direction. Some curves are incomplete. The bands shown are quite similar in form to those predicted by the nearly free electron model.

- Bands are similar to nearly free electron model
- Parabolic near bottom of band (and electrons will occupy)
  - ↳ $\mathcal{E} = \frac{\hbar^2 k^2}{2m^*}$ (can use free electron results!)

  m^* = effective mass (a simple way to include the effects of $V(\vec{r})$)
- Partially filled band ⇒ Metal

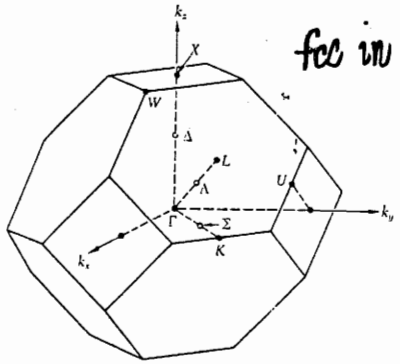
Semiconductors

Silicon



Electron band structure of crystalline silicon for energies near the 3s and 3*p* atomic levels: (a) **k** in the [100] direction; (*b*) **k** in the [110] direction; and (c) **k** in the [111] direction. Bands below $E = 0$ are valence bands and are associated with bonding. Higher bands are conduction bands and are important for the electrical properties of silicon. A gap exists between the valence and conduction bands.

B.Z. fcc in direct lattice

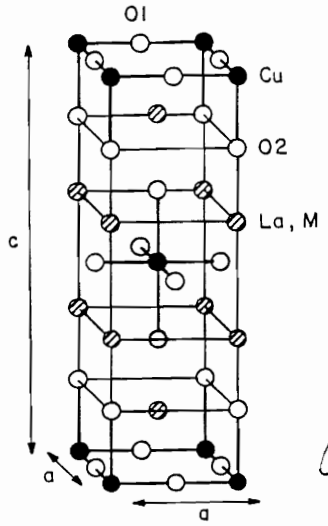


Note: See parabolic behavior near top of valence bands and bottom of conduction band.

High-Temperature Superconductors

$La_{2-x}M_xCuO_{4-y}$

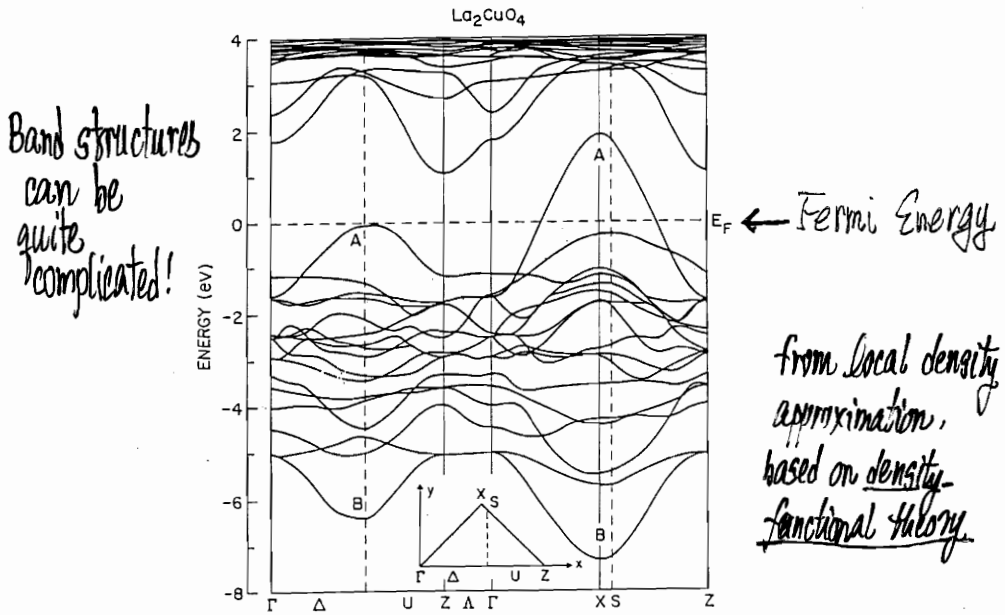
(M = Ba, Sr, Ca)



$T_c \lesssim 40K$

CuO_2 planes

Body-centered tetragonal structure of $La_{2-x}M_xCuO_{4-y}$ (M = Ba, Sr, Ca). Lattice vectors given by $(a, 0, 0)$, $(0, a, 0)$, and $(a/2, a/2, c/2)$. La and M atoms assumed to be randomly distributed over sites denoted by cross-hatched circles. Cu and O1 atoms form horizontal Cu-O_2 "planes."



Band structures can be quite complicated!

← Fermi Energy

from local density approximation, based on density-functional theory.

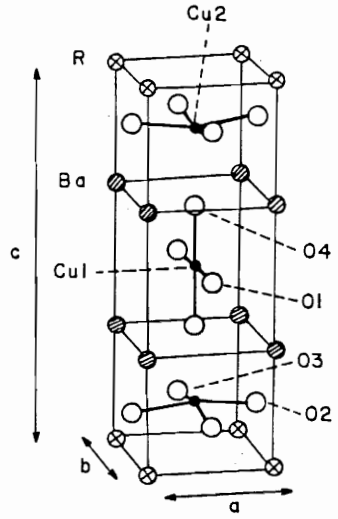
Calculated LDA energy bands for La_2CuO_4 along high symmetry directions in body-centered tetragonal Brillouin zone. Portion of x–y plane in extended zone scheme shown in inset.

YBCO

$RBa_2Cu_3O_7$

(R = Y, Eu, ...)

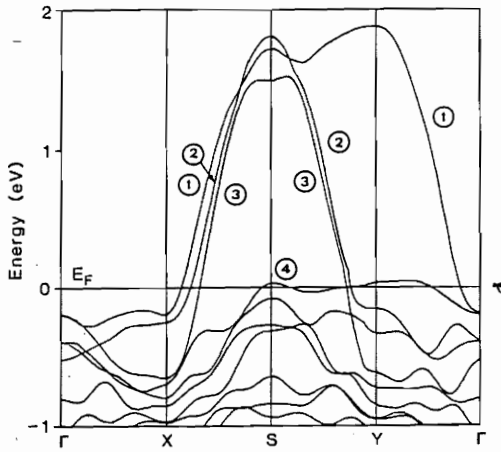
"123-Compounds"



$T_c \sim 90K$

CuO_2 planes

Unit cell of orthorhombic structure of $RBa_2Cu_3O_7$ (R = Y, Eu, . . .). Lattice vectors given by $(a, 0, 0)$, $(0, b, 0)$, and $(0, 0, c)$. Each set of Cu2, O2, and O3 atoms forms part of a slightly buckled Cu–O_2 "plane." Cu1 and O1 atoms form Cu–O "chains" along the b axis.



← Fermi Energy

Calculated LDA energy bands for $YBa_2Cu_3O_7$ at the top of the Cu–O complex in central plane of Brillouin zone.

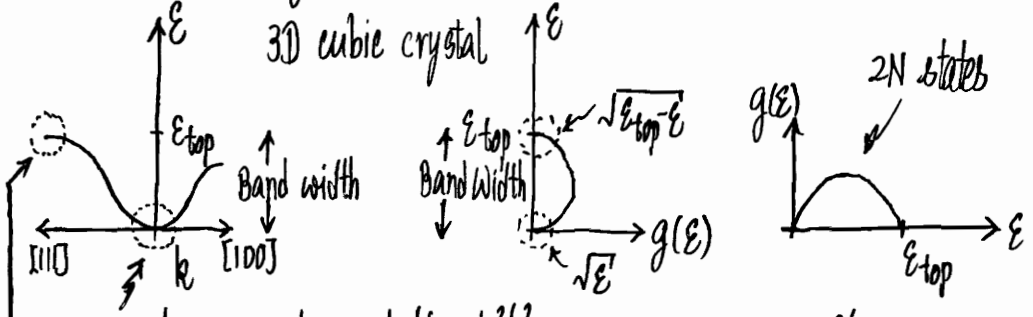
"Copy" from known results

3D Free electron: $\mathcal{E}(\vec{k}) = \frac{\hbar^2 k^2}{2m}$

$$g(\mathcal{E})\,d\mathcal{E} = 2 \cdot \frac{V}{(2\pi)^3}\, 4\pi k^2\, dk = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\mathcal{E}}\, d\mathcal{E}$$

$$\therefore\ g(\mathcal{E}) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\mathcal{E}} \sim \sqrt{\mathcal{E}}$$

- After including $V(\vec{r}) \Rightarrow$ Band structures

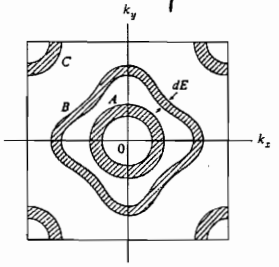


$\approx$ isotropic and parabolic $\frac{\hbar^2 k^2}{2m^*} \Rightarrow g(\mathcal{E}) = \frac{V}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \sqrt{\mathcal{E}}$ near bottom of band

(m^*: different from m)

More! near the zone corner (top of band), the band is also parabolic

$\Rightarrow g(\mathcal{E})$ goes to zero for $\mathcal{E} > \mathcal{E}_{top}$ as $\sqrt{\mathcal{E}_{top}-\mathcal{E}}$ for $\mathcal{E} \lesssim \mathcal{E}_{top}$



C. Electronic density of states $g(\mathcal{E})$

$g(\mathcal{E})\,d\mathcal{E}$ = number of electronic states with energy in the interval $\mathcal{E}$ to $\mathcal{E}+d\mathcal{E}$

$g(\mathcal{E})$ is the density of states (DOS)

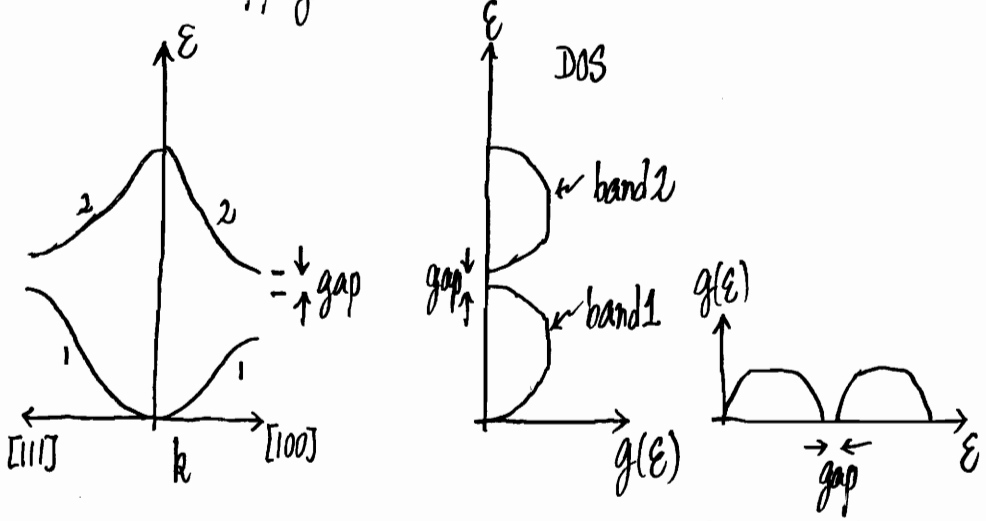
Following the same procedure as in phonons, we do the following for each band $\mathcal{E}_n(\vec{k})$:

- Make two cuts, one at $\mathcal{E}$ and another at $\mathcal{E}+d\mathcal{E}$
  $\Rightarrow$ two constant energy surfaces in $\vec{k}$-space
- # $\vec{k}$-values with energies in $\mathcal{E}$ to $\mathcal{E}+d\mathcal{E}$
  = (Volume between the two surfaces) $\times \frac{V}{(2\pi)^3}$ (3D)
- # states with energies in $\mathcal{E}$ to $\mathcal{E}+d\mathcal{E}$
  = 2 $\times$ (Volume between the two surfaces) $\times \frac{V}{(2\pi)^3}$
- sum up contributions from all bands

$$g(E) = 2 \cdot \frac{V}{(2\pi)^3} \oint_{S(E)} \frac{dS}{|\vec{\nabla}_{\vec{k}}\,\mathcal{E}(\vec{k})|}$$ for a band $\mathcal{E}(\vec{k})$

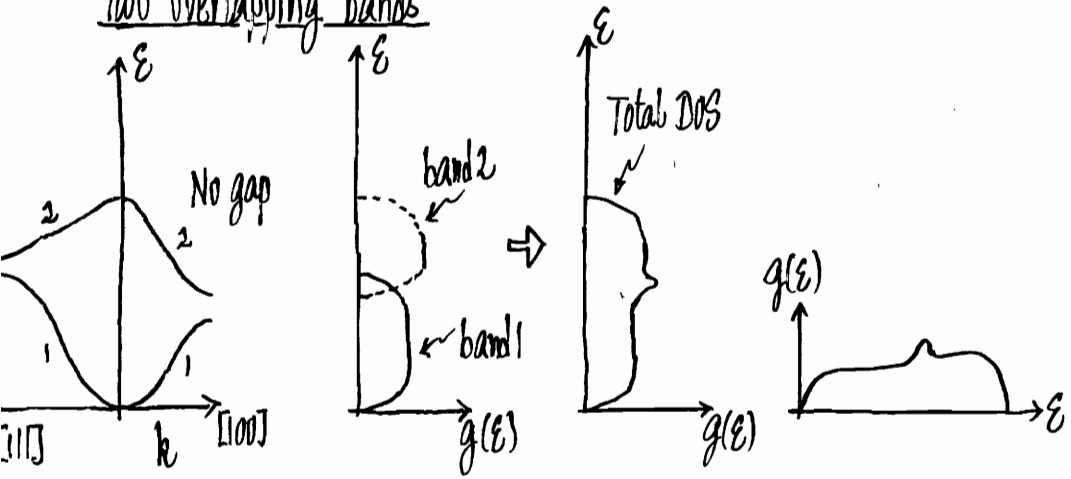
where the integral is over a constant-energy surface $S(E)$, and "2" comes from spin.

Two non-overlapping bands

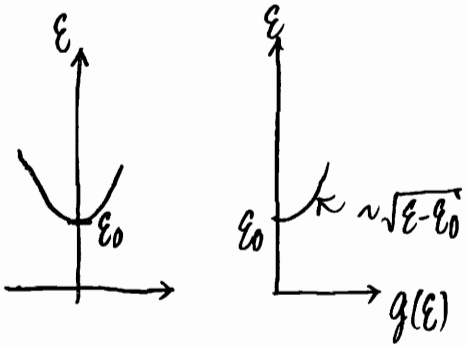


If there are 2N electrons, the lowest band will be filled and the upper band is empty ⇒ Non-conductor

Two overlapping bands



If there are 2N electrons, this will be a metal.
[This is why Mg, Ca, Be, Zn are metals.]



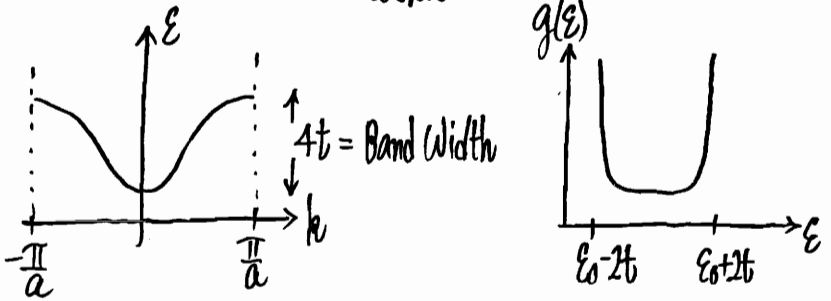
$$\varepsilon(k) = \varepsilon_0 + \frac{\hbar^2 k^2}{2m^*}$$

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon-\varepsilon_0}$$

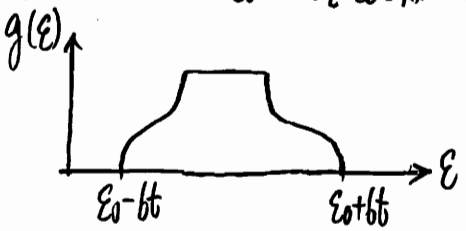
(useful in semiconductors)

DOS of tight-binding bands

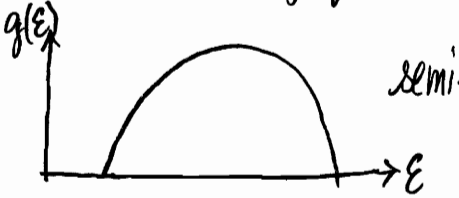
1D TBM $\varepsilon(k) = \varepsilon_0 - 2t\cos ka$



3D TBM $\varepsilon(\vec{k}) = \varepsilon_0 - 2t[\cos k_x a + \cos k_y a + \cos k_z a]$



A popular approximation of $g(\varepsilon)$ for a 3D band is



semi-circle.

- Flat band (narrow band width)

  ⇒ high DOS (e.g. bands related to d atomic orbitals)

  Physically, each band carries $2N$ electronic states

  Small band width ⇒ $2N$ states in a narrow range of energy

  ⇒ higher DOS

  Mathematically,

$$\oint \frac{dS}{|\vec{\nabla}_{\vec{k}} E(\vec{k})|}$$

  $|\vec{\nabla}\mathcal{E}(\vec{k})|$ is small for flat bands

- Wider band ⇒ smaller DOS

- Advantage of using DOS

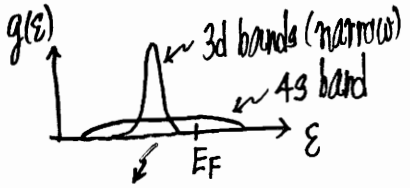
  Ordered systems (e.g. crystals)

  - $\mathcal{E}_n(\vec{k})$ and $g(\mathcal{E})$

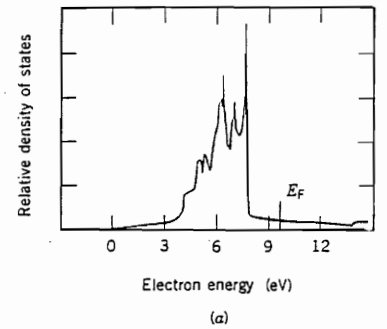
  Disordered systems (e.g. alloys, amorphous solids)

  - notion of $\mathcal{E}_n(\vec{k})$ is, strictly speaking, no longer valid
  - $g(\mathcal{E})$ is still a good physical quantity

e.g. DOS



Copper

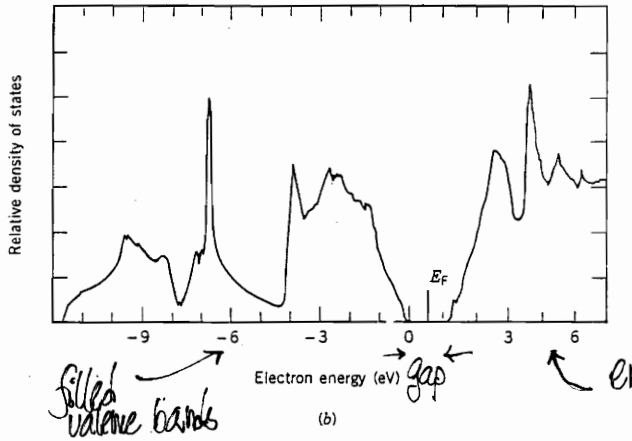


metal

E_F not in a gap!

[closely related to the colour of metals]

Silicon



E_F in a gap

filled valence bands

gap

empty conduction band

(a) Electron density of states for copper. The dotted line indicates the Fermi level. Many *d* states crowded into a small energy interval give rise to the peaks just below the Fermi energy. (*b*) Electron density of states for silicon. The gap between the valence and conduction bands is evident.

Gap between top of filled valence band and bottom of conduction band determines if the material is an insulator or semiconductor.

If gap $\gtrsim$ 3eV ⇒ Insulator

gap $\lesssim$ 3eV ⇒ semiconductor.

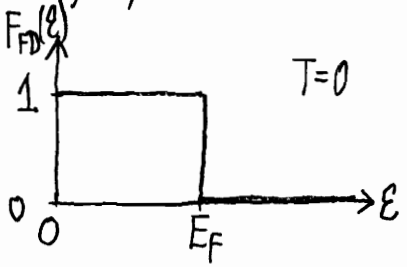
D. Electron Statistics

- Energy bands give the electronic states as allowed by Quantum Mechanics.
- To fill the electrons into these electronic states, we follow the Fermi-Dirac distribution, as electrons are fermions.

$$F_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT}+1}$$

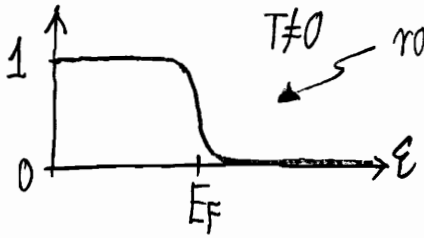
- gives the probability that a single-particle state of energy ε is occupied at temperature T.

$\mu = \mu(T)$ = chemical potential (shifts with T)



$T=0$

states with
$\varepsilon < E_F$: occupied
$\varepsilon > E_F$: unoccupied

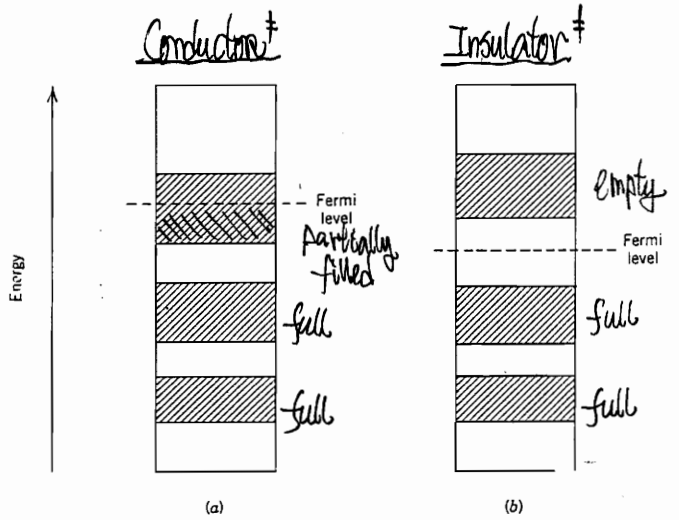


$T \neq 0$ — rounded off in the range of kT around E_F

$E_F/k \sim 10^4$ K for metals

T=0 (Putting back the electrons)

- Electrons fill the lowest energy states available upto an energy E_F.
- N_e = number of electrons† $= \int_{\varepsilon_0 \text{ (lowest energy)}}^{E_F} \underbrace{g(\varepsilon)}_{\text{density of states}} d\varepsilon$
- If E_F falls in a gap ⇒ insulator‡
  If E_F falls in a band ⇒ metal (conductor)‡



The relationship between the Fermi level and the energy spectrum for (a) a crystalline metal and (b) a crystalline insulator at $T = 0$ K. Allowed energies are indicated by shading. For a metal the Fermi level lies in a band, while for an insulator it is in a gap.

† The conduction electron number density $N_e/V \sim 10^{28}\ m^{-3}$ for metals.

‡ More on this in discussions on electron dynamics.

The Fermi Surface

- We have the energy bands $\mathcal{E}_n(\vec{k})$
- We have the Fermi-Dirac distribution (a step function at T=0) to fill the electrons into the bands.
- In metals, the states are filled up to E_F.

Fermi Surface:

- Make a cut at E_F on $\mathcal{E}_n(\vec{k})$
- Project on to the reciprocal space (k-space)
- the constant energy surface at energy E_F is the Fermi Surface

  i.e. the surface in k-space defined by

  $$\mathcal{E}_n(\vec{k}) = E_F$$

- The shape of the Fermi Surface could be quite complicated for real metals.

Simple example:

- a metal with model band structure (for the band that determines the physics)

$$\mathcal{E}(\vec{k}) = \mathcal{E}_0 + \frac{\hbar^2 k^2}{2m^*}$$

$\mathcal{E}(\vec{k})$: just like free electrons; $\mathcal{E}_0$: bottom of band; Effects of $V(\vec{r})$ are all put into m^* (parabolic, isotropic)

then we have all the standard results†

$$g(\mathcal{E}) = \frac{V}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{\mathcal{E}-\mathcal{E}_0}$$

$$E_F - \mathcal{E}_0 = \frac{\hbar^2}{2m^*}\underbrace{\left(3\pi^2\frac{Ne}{V}\right)^{2/3}}_{k_F^2} \propto \left(\frac{Ne}{V}\right)^{2/3}$$

↑ electron number density

$$k_F = \left(3\pi^2\frac{Ne}{V}\right)^{1/3}$$

Since $\mathcal{E}(\vec{k})$ is isotropic, a cut at E_F gives a spherical surface in k-space with radius k_F

↳ Fermi surface (Fermi sphere)

---

† See results of free electron model. When a metal has electrons filling the parabolic part of the bottom of a band, results from the free electron model are useful, after using m^* instead of m.

A way to show the Fermi surface:

If the Fermi surface is not entirely within the 1st B.Z., we translate the parts outside the 1st B.Z. by appropriate $\vec{G}$'s back into the 1st B.Z.

- Recall: in 3D, 2D - band overlap is common

  1st B.Z. ⇒ N allowed k-values

  (N = # states (not including spin) in one band)

  If at E_F, due to band overlap,

  { a lower band is nearly full
  { an upper band is nearly empty (but some states are occupied)

  → then we can represent this situation using two figures in the 1st B.Z.

- To illustrate the idea, let's consider free electron band in a 2D metal of square lattice in structure.

A = area of sample

$g(\mathcal{E}) = \frac{Am^*}{\pi\hbar^2}$ (2D DOS, free electron) $\mathcal{E} > \mathcal{E}_0$

$N_e = \int_{\mathcal{E}_0}^{E_F} g(\mathcal{E})\,d\mathcal{E} \Rightarrow E_F - \mathcal{E}_0 = \frac{\hbar^2}{2m^*}\underbrace{\left(2\pi\frac{N_e}{A}\right)}_{k_F^2} \propto \left(\frac{N_e}{A}\right)$

($\mathcal{E}_0$: bottom of band; $\frac{N_e}{A}$: areal density)

$k_F = \left(2\pi\frac{N_e}{A}\right)^{1/2}$

band is isotropic ⇒ a cut at E_F gives a circular surface of radius k_F

$k_F \sim \sqrt{\frac{N_e}{A}}$ if $\frac{N_e}{A}$ is small

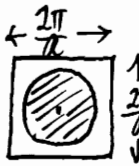
⇒ Fermi sphere lies inside 1st B.Z.

Fermi "sphere"

if $\frac{N_e}{A}$ is high, part of Fermi sphere lies outside 1st B.Z.

E.g. 1 electron per atom (1 atom/unit cell)

$\frac{N_e}{A} = \frac{1}{a^2} \Rightarrow k_F = \frac{\sqrt{2\pi}}{a}$; $k_F = \frac{\sqrt{2\pi}}{a} < \frac{\pi}{a}$



1st B.Z.

E.g. 2 electrons per atom

$\frac{N_e}{A} = \frac{2}{a^2} \Rightarrow k_F = \frac{2\sqrt{\pi}}{a} = \frac{2}{\sqrt{\pi}}\left(\frac{\pi}{a}\right) > \frac{\pi}{a} \Rightarrow$ Part of Fermi sphere lies outside 1st B.Z.

Empty-lattice

2D square lattice

One electron per atom

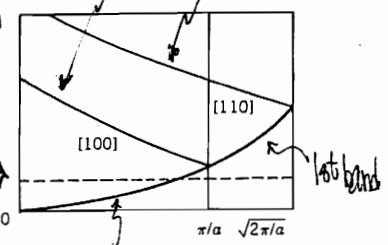
2nd band

2nd band

Free electron bands

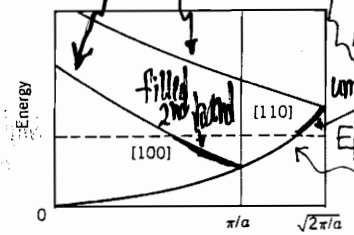
2nd band

Two electrons per atom



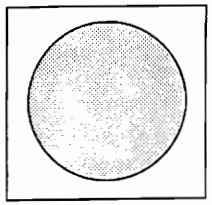
filled up to here in energy

1st band



unfilled part of 1st band

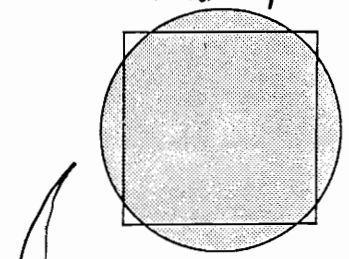
1st band



(a)

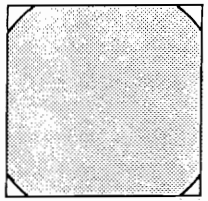
One electron per atom

Two electrons per atom

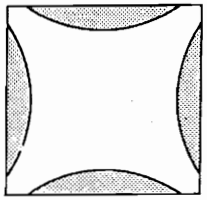


extended zone scheme

First-band Fermi surface



Second-band Fermi-surface

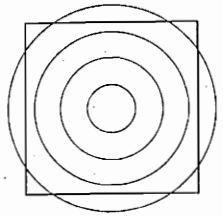


need two figures to show the Fermi surface

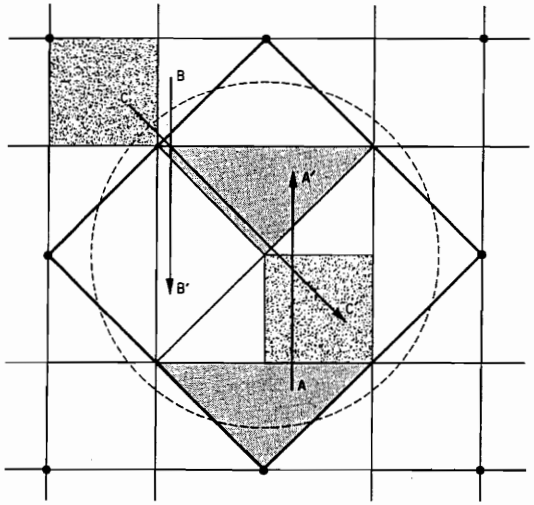
(b)

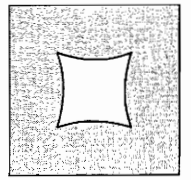
Free electron Fermi surfaces for a square crystal. Each diagram at the top shows free electron bands for k in [100] and [110] directions, drawn on the same graph. The Fermi level is shown as a dotted line. Lower diagrams show the Brillouin zone and Fermi surface. (*a*) One electron per primitive unit cell. The Fermi level is within the first band and the Fermi surface is within the Brillouin zone. (*b*) Two electrons per primitive unit cell. The Fermi level is in two bands. The second diagram from top shows the Fermi surface in the extended zone scheme, while the other diagrams show the first and second band surfaces, respectively, in the reduced zone scheme. The second-band surface is obtained from the extended zone surface by translating those parts that lie outside the zone by reciprocal lattice vectors. Occupied states are indicated by shading.

Thus, the Fermi surface is related to constant energy surface and electron number density.

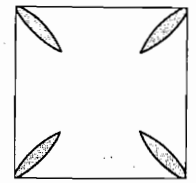


- empty-lattice approximation
- different constant energy surfaces
- higher electron number density
  ⇒ Fermi sphere of larger radius

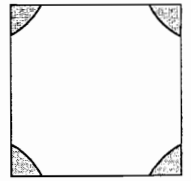




2nd Zone



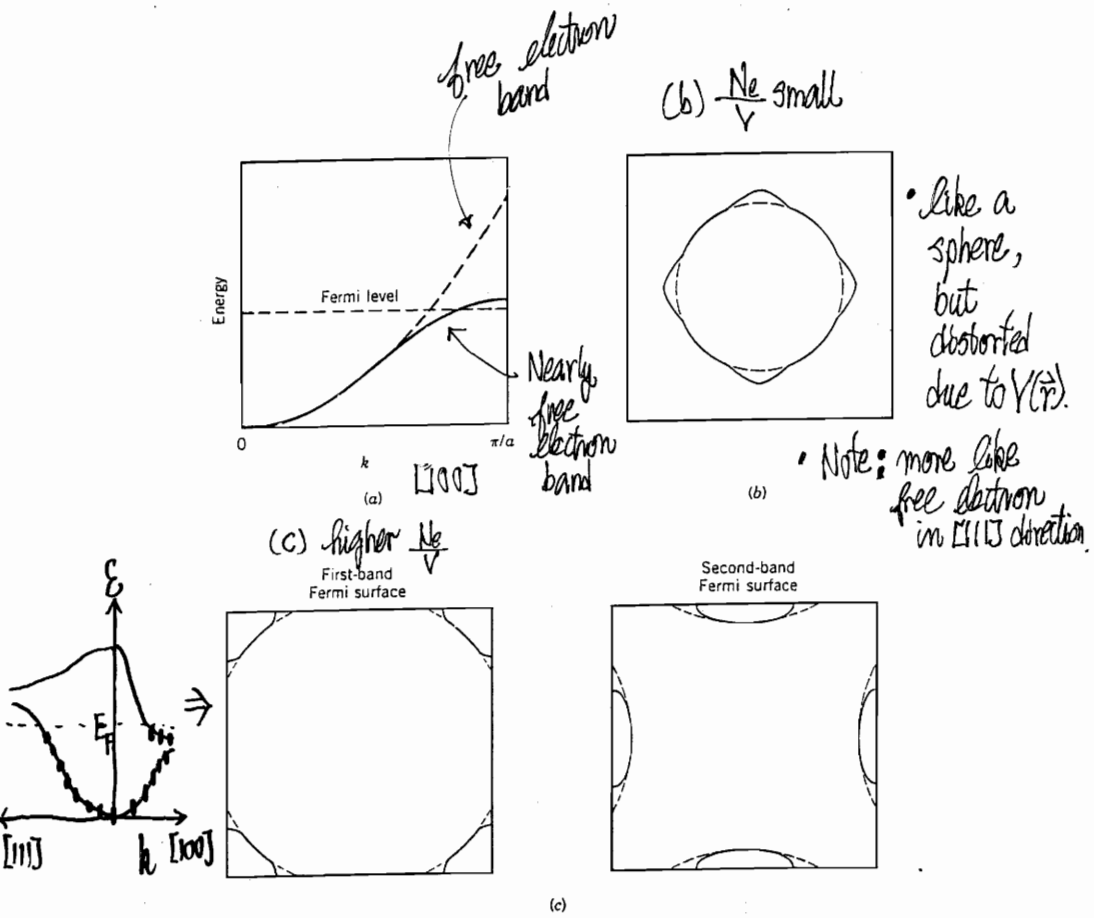
3rd Zone



4th Zone

- k-space of a square lattice
- circle shows the occupied states
- note that states up to the 4th zone are occupied (high number density)
- 1st zone is completely occupied (lowest band is full)

Nearly free electron bands

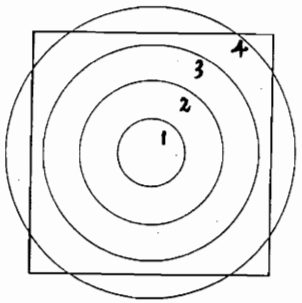


(a) Free (dotted curve) and nearly free (solid curve) electron bands, drawn on the same graph. (*b*) Fermi surfaces for free (dotted curve) and nearly free (solid curve) electrons. When electrons interact with atoms of the crystal, the Fermi surface bulges toward nearby zone boundaries. (c) The effect of a weak potential on a two-band Fermi surface. Each surface bends toward the zone boundary.

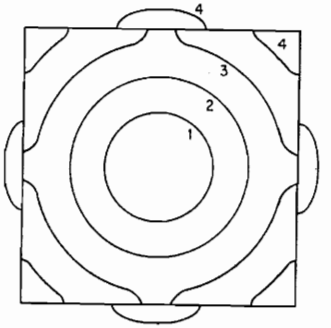
Fermi Temperature

$E_F = kT_F$ typically: $T_F \sim 10^4$ K for metals

	Li	Na	K	Rb	Cs	Cu	Ag
$T_F(K)$	5.48×10^4	3.75×10^4	2.46×10^4	2.15×10^4	1.55×10^4	8.12×10^4	6.36×10^4



4 constant energy surfaces of increasing energy in the empty lattice approximation



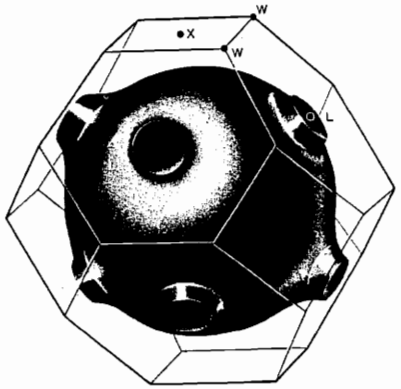
4 corresponding constant energy surfaces of increasing energy in the nearly free electron model

- For low electron number densities, only states near bottom of band are occupied
  - ⇒ Fermi surface in nearly free electron model is a Fermi sphere as in free electron model, but with m^* instead of m (band structure effect)
- This is why "Free electron model" works so well for many real metals!

For $T \ll T_F$, $C_v \sim \gamma T$ observed exp'tally,

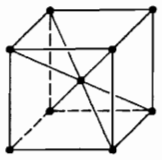
now $\gamma \sim g(E_F) \Rightarrow$ involves m^*

Example : Copper



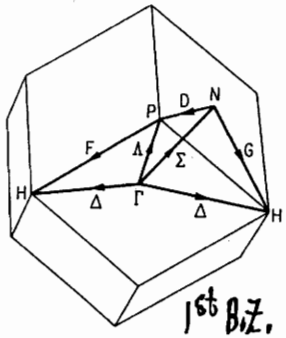
- Fermi surface of copper
- Filling the band that stems from 4s orbitals
- 3d bands are all-filled (not shown)

Example : sodium



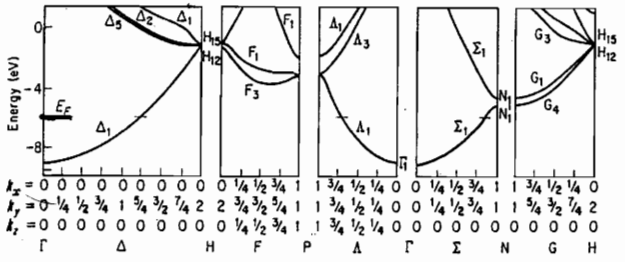
Body-centered cubic

(direct)



1st B.Z.

band structure of Na

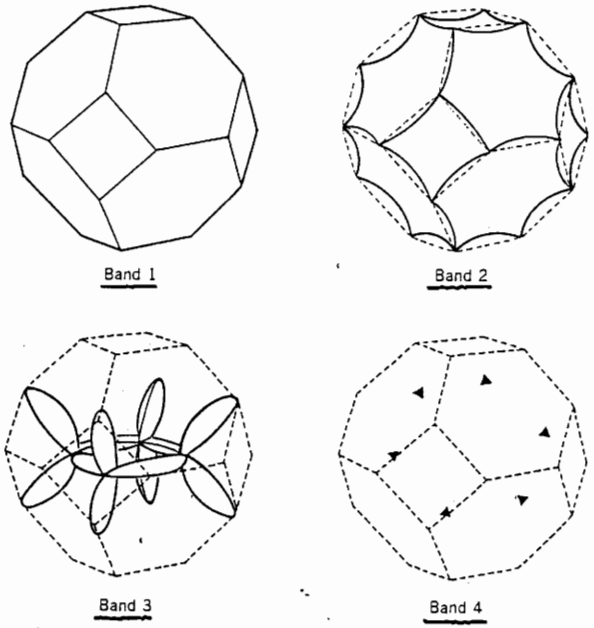


3s and 3p bands overlap

E_F in the rather parabolic band (3s band)
⇒ properties of Na ≈ free electron model

In general, many electrons per atom and the Fermi surface could be quite complicated (and form artistic shapes).

e.g. Aluminum



Band 1 Band 2 Band 3 Band 4

The Fermi surface of aluminum. The various branches can be constructed by translating portions of a sphere from outside the zone to inside. The first band is completely filled, while the second band surface encloses empty states; filled states are between the surface and the zone boundary. Filled states in the third band are enclosed by the surface shown. The fourth band has small pockets of filled states. Zones shown for the third and fourth bands have been shifted relative to zones used for the first and second bands; the zone center for the last two diagrams is at the center of a square face of the zone for the first two.

How about tight-binding bands?

$$\mathcal{E}(\vec{k}) = \mathcal{E}_0 - 2t(\cos k_x a + \cos k_y a + \cos k_z a) \quad \text{(3D cubic)}$$

- How do the constant energy surfaces look like?

(i) $\mathcal{E} \approx$ bottom of band ($\Rightarrow$ small $\vec{k}$)

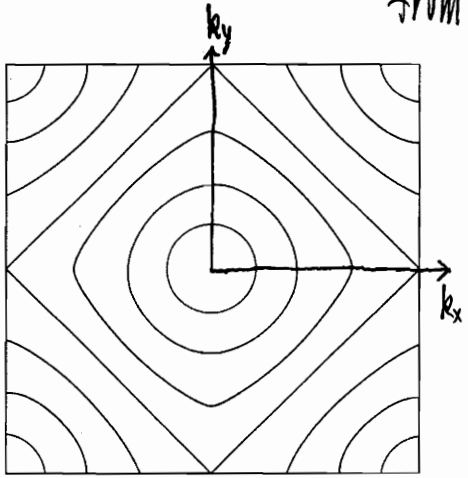
$$\mathcal{E}(\vec{k}) \approx \text{constant} + ta^2k^2 = \text{constant} + \frac{\hbar^2k^2}{2m^*}$$

$$m^* = \frac{\hbar^2}{2a^2t}$$ $\therefore$ parabolic near bottom of band

$\Rightarrow$ spheres for small energies

(ii) higher energy: deviate from parabolic band

$\Rightarrow$ constant energy surface deviates from a sphere



- constant energy surfaces for a 3D TBM (cubic) shown in the $k_z = 0$ plane
- these are also Fermi surfaces for different electron number densities filling into the TB band.

Summary

- $g(\mathcal{E})$ from bands
- why free-electron results are useful for simple metals
- constant-energy surfaces (empty-lattice, nearly free electron, tight-binding)
- Fermi surface (how to display Fermi surface) [for metals]

Questions to explore:

- Electron dynamics
- E_F and $\mu(T)$ for semiconductors
- What is effective mass?

References

Kittel: Ch.7, Ch.9
Christman: Ch.8
Omar: Ch.5