Lecture contents

- Density of states
- Statistics
- Metals: transport

Density of states

How to fill the states in almost free electron band structure ?

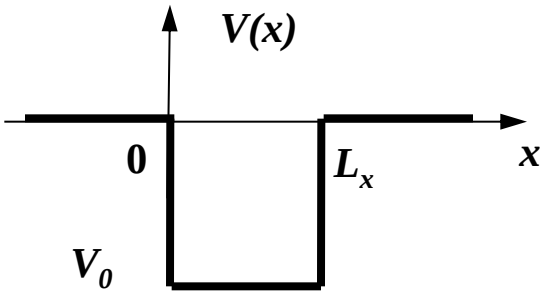
1. Calculate number of states per unit energy per unit volume
2. Use Pauli exclusion principle and distribution function to fill the bands

- Electrons are waves !

- Large 3D box (L is large, n is large) with Born-von Karman boundary Conditions:

$$\psi(x+L_x, y, z) = \psi(x, y, z)$$

same for y and z



- Free electron approximation:

$$\psi = Ae^{\pm ikr}$$

$$k_x = \frac{2\pi}{L_x} n_x$$

$$k_y = \frac{2\pi}{L_y} n_y$$

$$k_z = \frac{2\pi}{L_z} n_z$$

$$\Omega = \Delta k_x \Delta k_y \Delta k_z = \frac{(2\pi)^3}{L_x L_y L_z} \Delta n_x \Delta n_y \Delta n_z$$

- Number of states:

1D : $N = \frac{\Delta k L}{2\pi}$

2D : $N = \frac{\Sigma S}{(2\pi)^2}$

3D : $N = \frac{\Omega V}{(2\pi)^3}$

Density of states

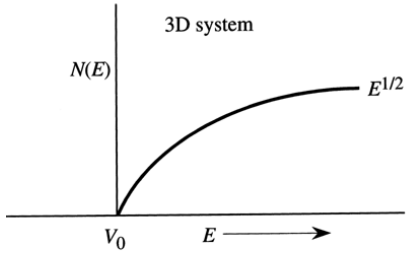
$$N = \frac{\Omega V}{(2\pi)^3} \qquad E = V_0 + \frac{\hbar^2 k^2}{2m} \qquad k = \frac{1}{\hbar}\left[(2m)(E - V_0)\right]^{1/2} \qquad \Delta E = \frac{\hbar^2 k \Delta k}{m}$$

$$N(E) = \frac{1}{V}\frac{\Delta N}{\Delta E}$$

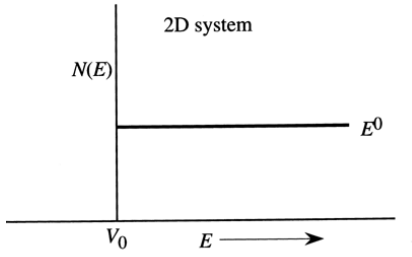
In the interval k to $k+\Delta k$ number of states :

In the interval E to $E+dE$ number of states per unit "volume" (spin included):

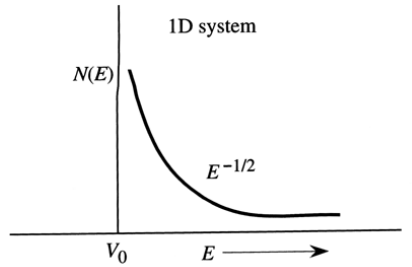
3D : $\Delta N = \dfrac{4\pi k^2 \Delta k L^3}{(2\pi)^3}$ $\qquad N(E) = \dfrac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}(E - V_0)^{1/2}$



2D : $\Delta N = \dfrac{2\pi k \Delta k L^2}{(2\pi)^2}$ $\qquad N(E) = \dfrac{m}{\pi\hbar^2}$



1D : $\Delta N = \dfrac{\Delta k L}{2\pi}$ $\qquad N(E) = \dfrac{\sqrt{2}m^{1/2}}{\pi\hbar}(E - V_0)^{-1/2}$



Density of states and dimensionality

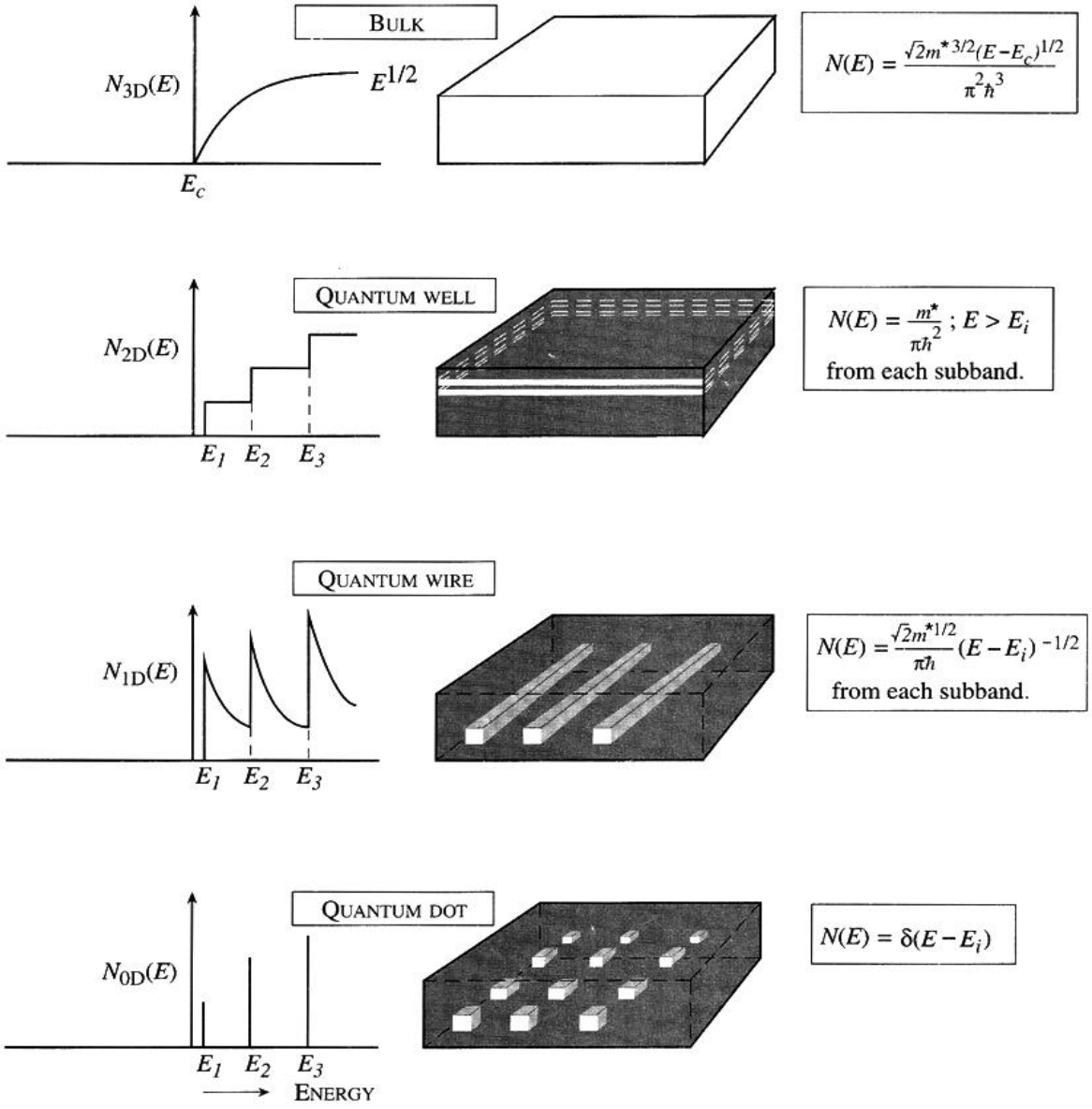
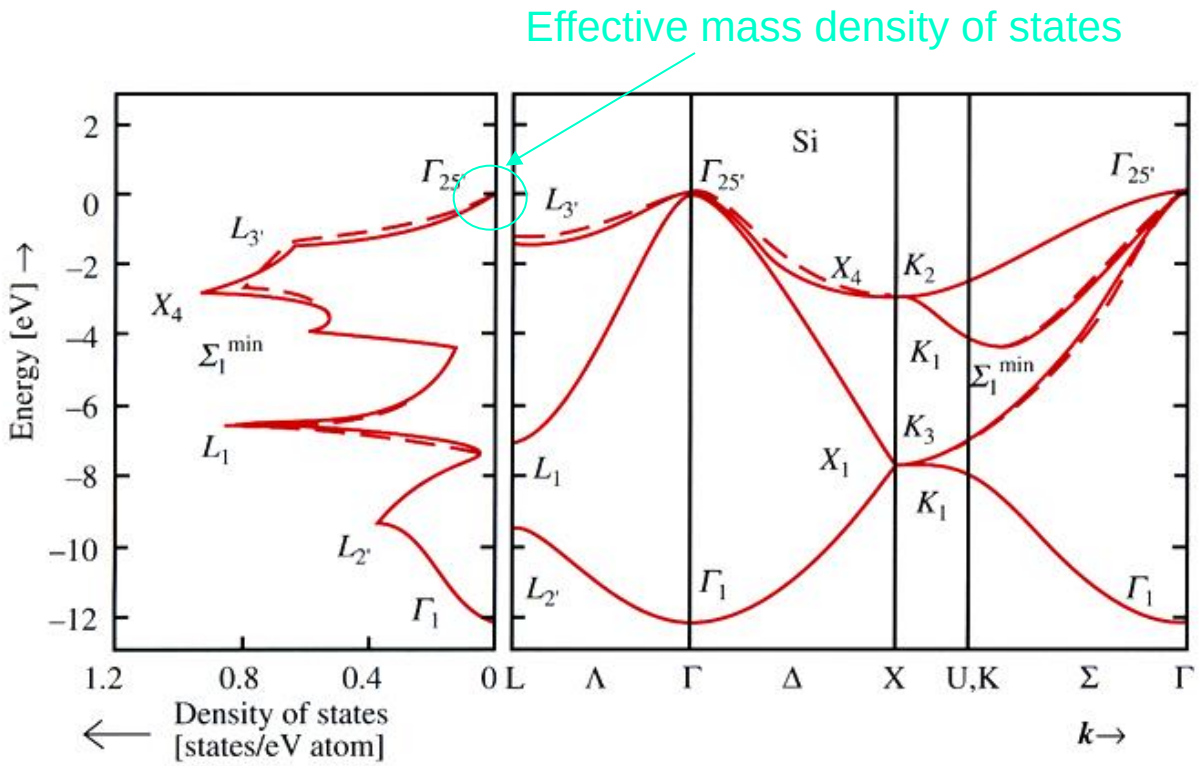


Figure 3.13: A schematic of how the density of states change as a function of dimensionality.

From Singh, 2003

Density of states in 3D and DOS effective mass

Valence band density of states for Si (calculations)



3D density of states

$$N(E) = \frac{\sqrt{2}m^{*3/2}}{\pi^2\hbar^3}\left(E - V_0\right)^{1/2}$$

Conduction band DOS mass in Γ point:

$$m_{dos}^{*} = m_c^{*}$$

Conduction band DOS mass in indirect gap semiconductors:

$$m_{dos}^{*} = \eta_c^{\,2/3}\left(m_1^{*} m_2^{*} m_3^{*}\right)^{1/3}$$

Valence band DOS mass :

$$m_{dos}^{*} = \left(m_{hh}^{*\,3/2} + m_{lh}^{*\,3/2}\right)^{2/3}$$

Filling the empty bands: Distribution function

- Electron concentration at the energy *E* (Density of states) x (distribution function):

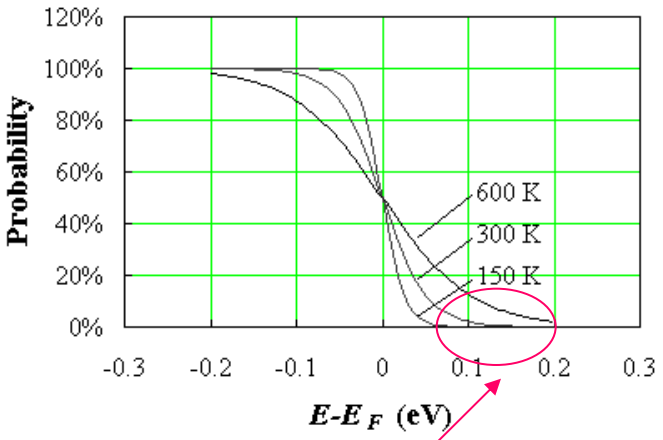
$$n(E) = N(E)\, f(E)$$

- Pauli Exclusion Principle: No two electrons (fermions) can have identical quantum numbers.

- Electrons follow Fermi-Dirac statistics.

- Fermi-Dirac distribution function:

$$f_{FD}(E) = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$



In the non-degenerate case (electron energies are far from E_F):
Boltzmann distribution function may be used:

$$E - E_F >> k_B T$$

$$f_B(E) = e^{-(E-E_F)/k_B T}$$

Filling parabolic empty bands: Fermi energy

- Fermi energy is obtained by solving: $$n = \int_{V_o}^{\infty} N(E)\, f(E)\, dE \approx \int_{V_o}^{E_F} N(E)\, dE$$

If DOS changes slowly at E_F

- if n is concentration of electrons in the band:

$$n = \frac{\sqrt{2}m^{*3/2}}{\pi^2\hbar^3}\int_{V_0}^{E_F}(E - V_0)^{1/2}\, dE = \frac{2\sqrt{2}m^{*3/2}}{3\pi^2\hbar^3}(E_F - V_0)^{3/2}$$

- The Fermi energy is found: $$E_F = V_0 + \frac{\hbar^2}{2m^*}(3\pi^2 n)^{3/2}$$

- And Fermi surface (sphere in this case) $$k_F = \frac{\hbar^2}{2m^*}(3\pi^2 n)^3$$ since $$E_F = V_0 + \frac{\hbar^2 k_F^2}{2m}$$

for Na with $n = 2.65\text{x}10^{22}$ cm^{-3}

$$E_F = V_0 + 3.22eV$$
$$k_F = 0.92A^{-1}$$
$$v_F = 1\cdot 10^8 \text{ cm/s}$$

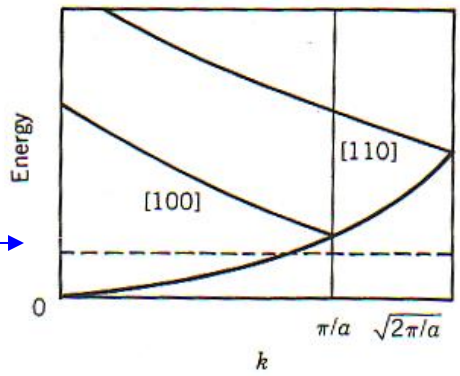
- What is happening if the Fermi surface is not entirely within the Brillouin zone?

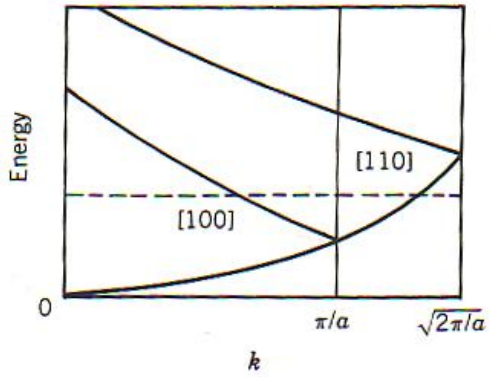
Nearly free electrons: Fermi surfaces in 2D (square crystal)

One electron per unit cell

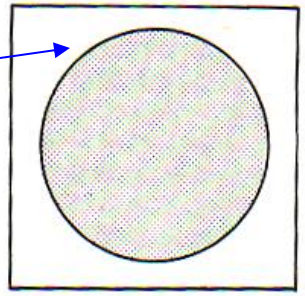
Two electron per unit cell

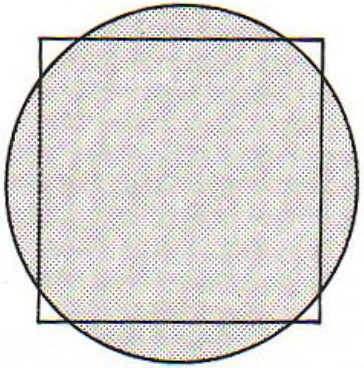
Fermi level

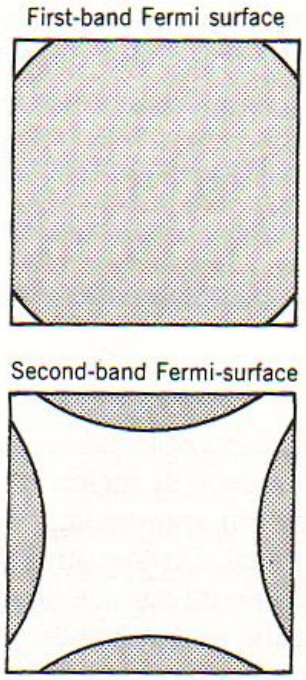




Fermi surface







- Fermi level is within the first band

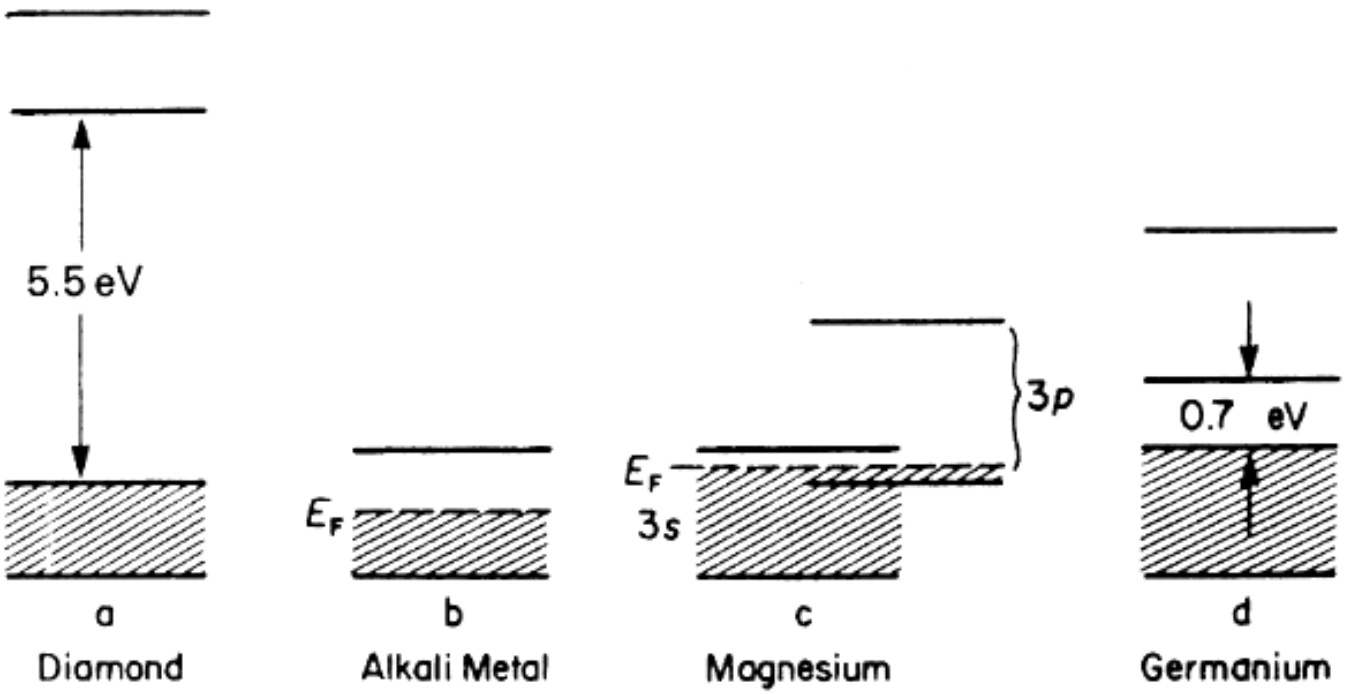
- Fermi level is in two bands

From Hummel, 2000

Consequences of band model: Metals, dielectrics and semiconductors

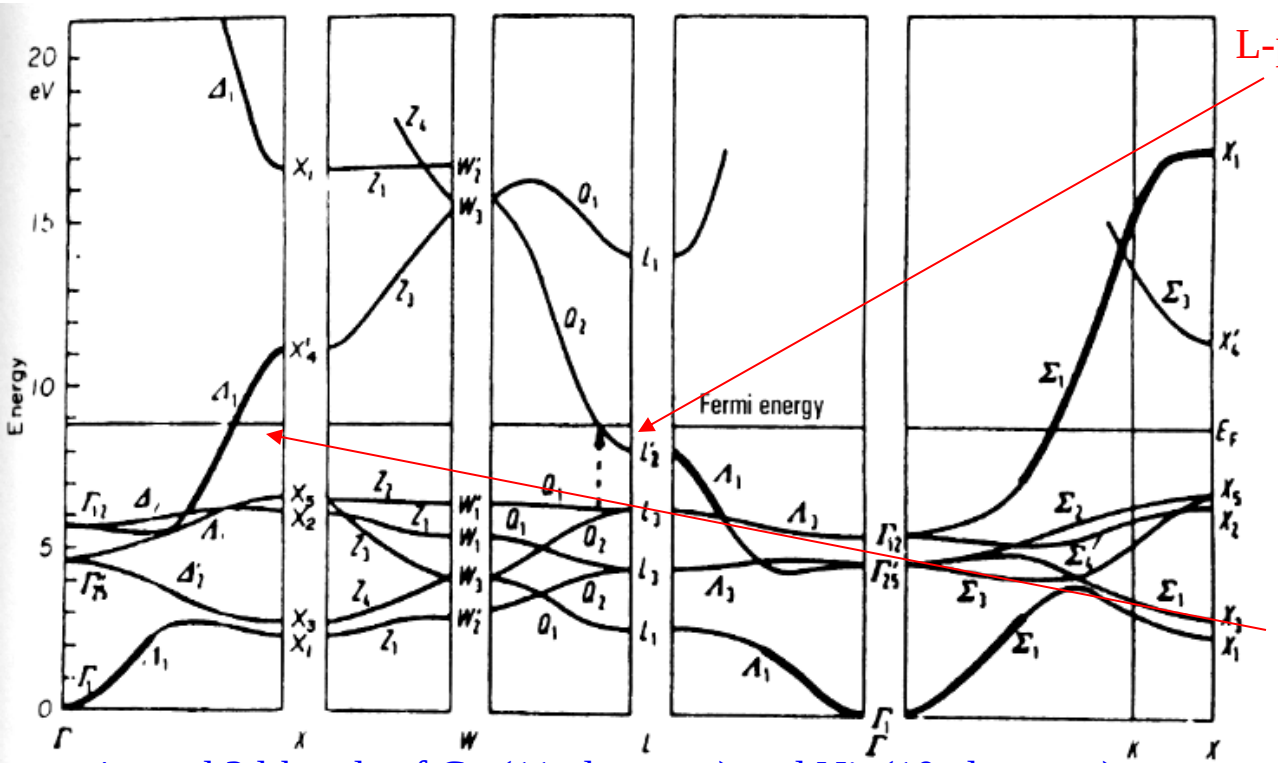
Pauli Exclusion Principle controls filling of the band structure

- Insulators – highest filled band is completely occupied.
- Metals with one valence electron – half band occupied
- Bivalent metals – have s-p overlap – bands partially occupied
- Semiconductors – most common has intermixed s-p states with completely occupied one of the sp sub-bands

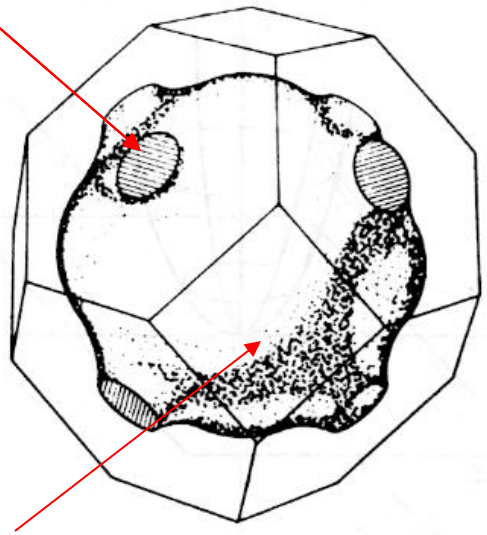


Nearly free electrons: band structure of Cu

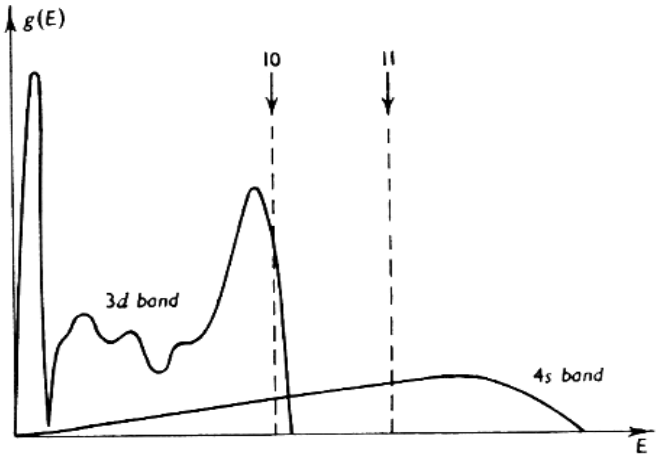
Band structure of Copper (fcc) (from Segal, 1962)

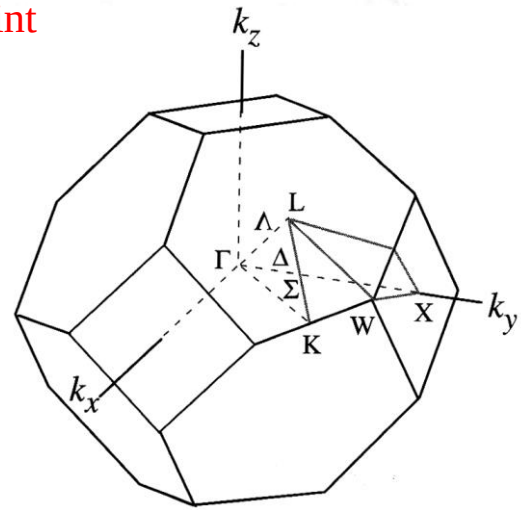


Fermi-surface for Cu



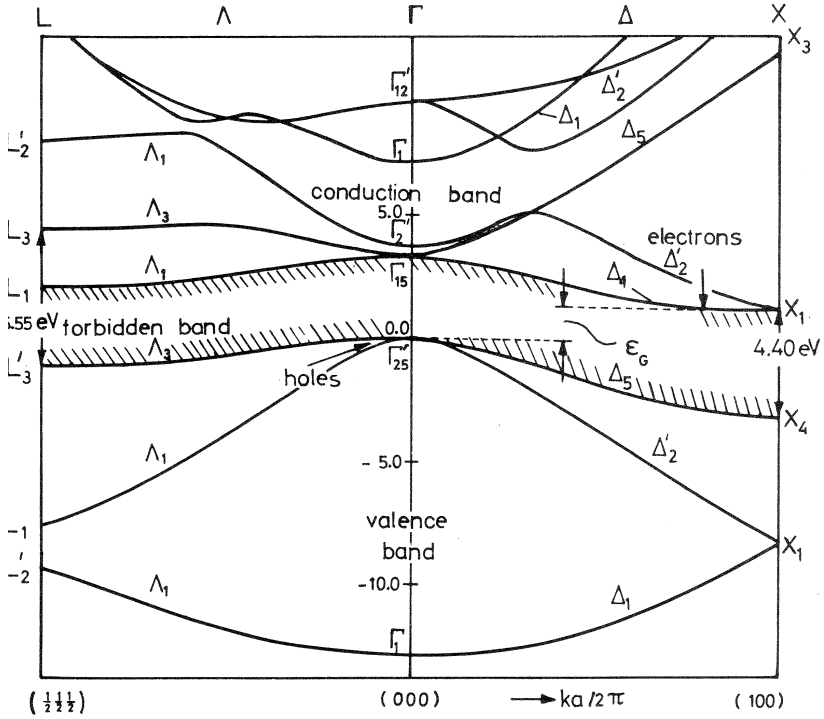
4s- and 3d-bands of Cu (11 electrons) and Ni (10 electrons)

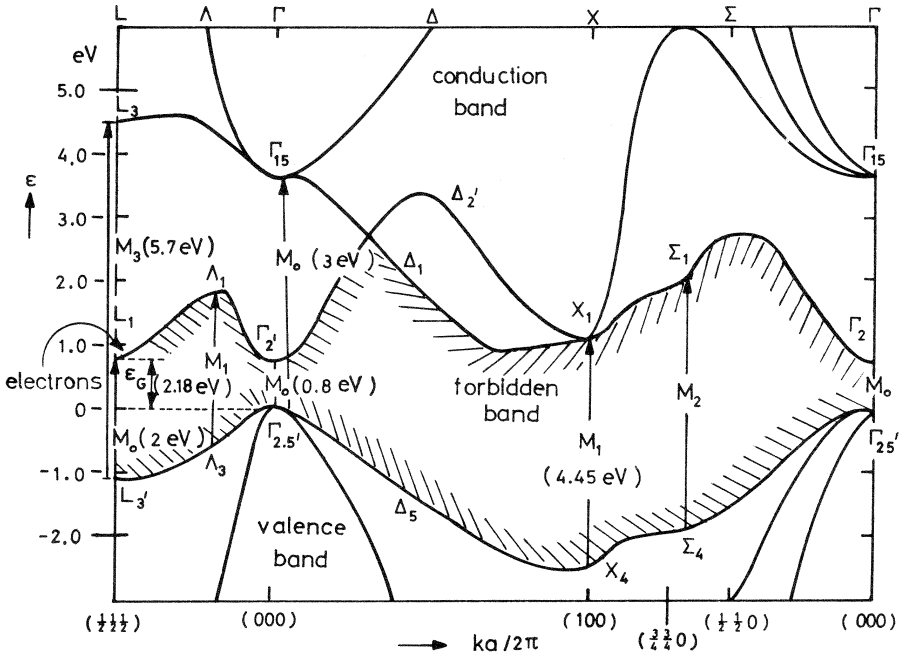




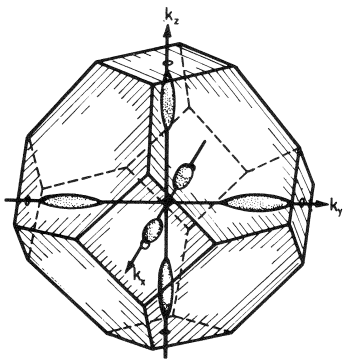
From Hummel, 2000

Band-structures of Si and Ge: Fermi level is in the bandgap ! (in pure materials)

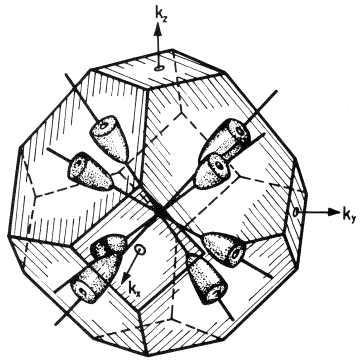




Energy band structure of germanium.



Surfaces of constant energy in $\vec{k}$-space for the conduction band edge of silicon.



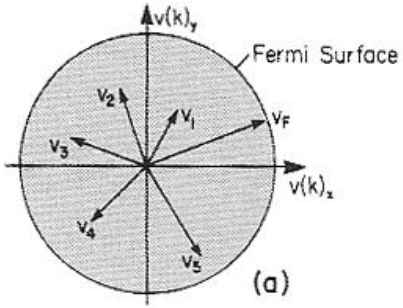
Surfaces of constant energy in $\vec{k}$-space for the conduction band edge of germanium: 8 half-ellipsoids of revolution centered at L points on the zone boundary

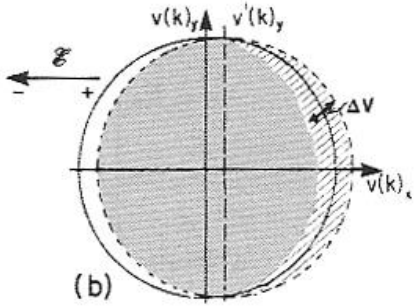
	m_ℓ^*	m_t^*	$\bar{m}_{\ell h}^*$	$\bar{m}_{hh}^*$
Si	0.92	0.19	0.16	0.52
Ge	1.59	0.082	0.043	0.34

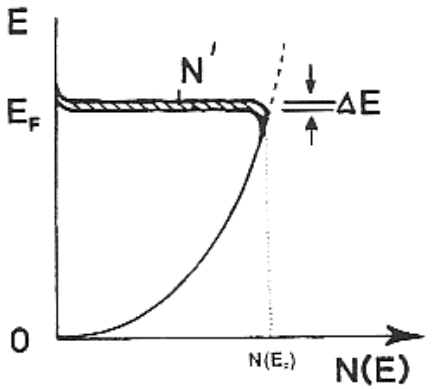
From Seeger, 1973

Conductivity of metals – Quantum mechanical considerations

- Let's consider parabolic band with minimum in the center of Brillouin zone.
- In metals the conduction band is filled up to Fermi energy (within kT):
- If electric field is applied, the distribution of velocities is displaced by drift velocity Δv.
- Only electrons close to Fermi surface participate in current transport.







- In one dimension: $J = qv_F N(E_F)\Delta E$ ⟹
- compare with classical form: $J_{class} = qnv_d$
- From definition of velocity $\Delta E = \hbar v_F \Delta k$
- And "drift" momentum $\Delta k = \frac{e\mathcal{E}}{\hbar}\tau$ ⟹ $J = q^2 v_F^2 N(E_F)\tau\mathcal{E}$
- If accurate 3D averaging is applied: $J = \frac{1}{3} q^2 v_F^2 N(E_F)\tau\mathcal{E}$
- Conductivity: $\boxed{\sigma = \frac{1}{3} q^2 v_F^2 N(E_F)\tau}$

compare with classical form:

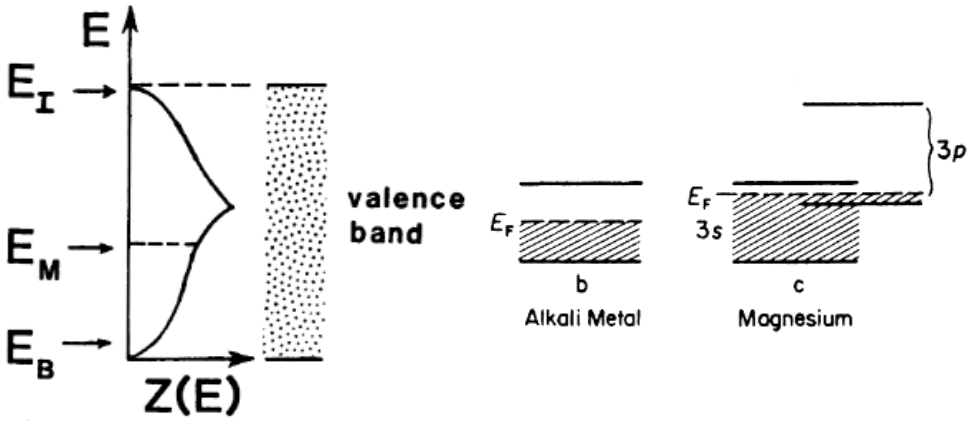
$$\sigma = \frac{q^2\tau}{m} n$$

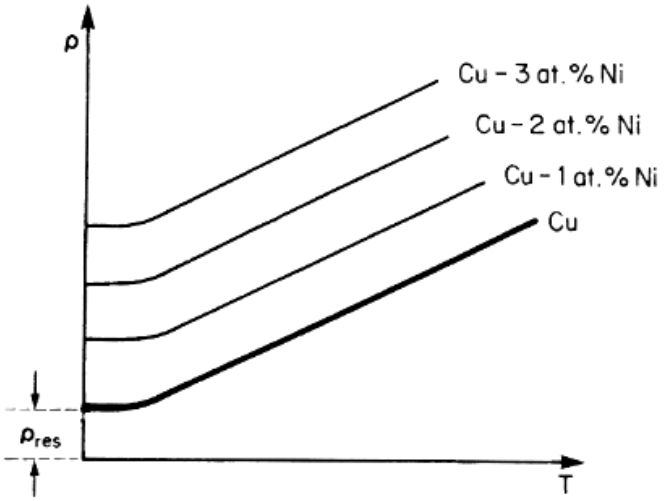
From Hummel, 2000

Conductivity of metals – examples

- Conductivity of metals depends mainly on scattering (quite expected) and density of states at Fermi level
- Conductivity is high in monovalent metals: Cu, Ag, Au
- Conductivity is lower in bivalent metals
- Conductivity can be controlled in semiconductors by filling the bands with doping
- In metals, temperature dependence of resistivity is linear (phonon scattering), reaching residual value at low temperatures (imperfections scattering).

$$\sigma = \frac{1}{3} q^2 v_F^2 N(E_F) \tau$$



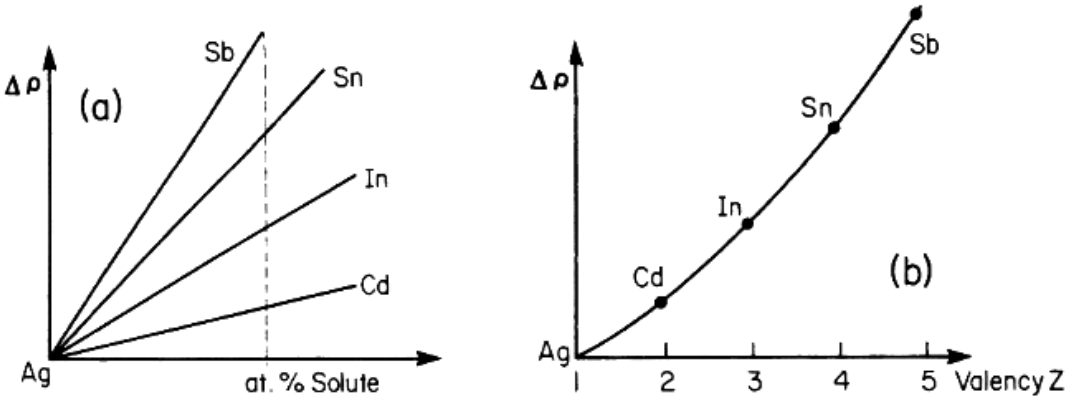


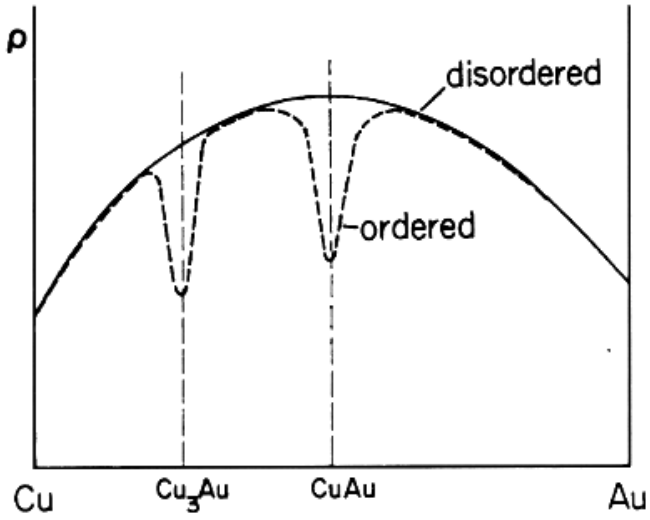
From Hummel, 2000

Conductivity of alloys – examples

$$\sigma = \frac{1}{3} q^2 v_F^2 N(E_F) \tau$$

- Resistivity of dilute single-phase alloys increases with the square of the valence difference (Linde's rule)
  - Scattering on local lattice imperfections and local charge differences
  - Shift of Fermi level position
- Usually resistivity has maximum at 50% solute content
- If ordered phase forms, the resistivity drops

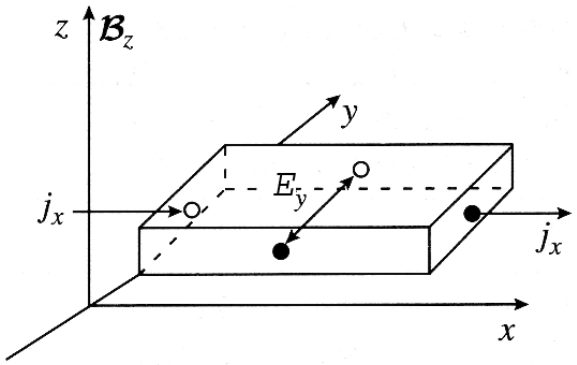




From Hummel, 2000

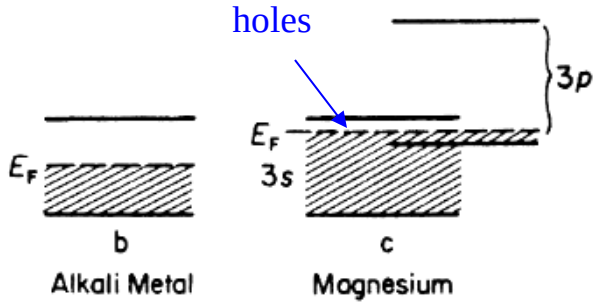
Hall effect: carrier charge

Hall coefficient: $$R_H = \frac{E_y}{J_x B_z} = \begin{cases} -\frac{1}{ne} & for \quad n-type \\ \frac{1}{pe} & for \quad p-type \end{cases}$$



Dimensionless Hall coefficient for metals: $$= -\frac{R_H}{\left(e\frac{N}{V}\right)^{-1}}$$
(= 1 in Drude theory)

Li	0.78	Cu	1.4	Be	−0.1
Na	1.1	Ag	1.2	Mg	0.88
K	1.1	Au	1.5	Ca	0.76
Rb	0.92			Zn	−0.75
				Cd	−1.2



Materials with >1 electrons per unit cell can have:

- Complex Fermi surface
- Fermi energies close to discontinuities in the E vs. k
- Almost full bands where the carriers behave as positively charged (holes)