Chapter 3 Free electrons in solids

3.1 Free electron model

3.1.1 Drude Model

- Classical Free Electron Model

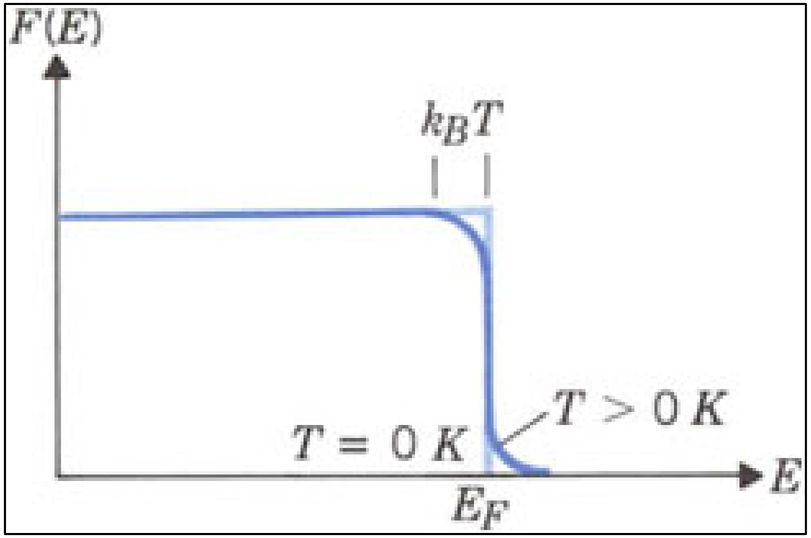
3.1.2 Sommerfeld Model

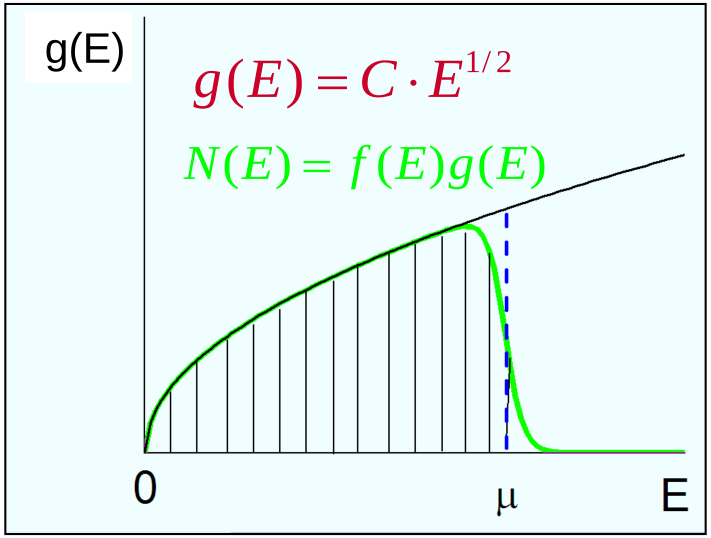
- Quantum Mechanical Free Electron Model

3.2 Heat capacity of free electron gas

3.3 Transport properties of conductive electrons

3.4 Electron emission and contacting voltage





At T=0K, the average energy of free electrons is 60% of the E_F.

Calculation of Heat Capacity of free Electrons

At T>0K， the total energy of free electrons is:

$$E=\int E\mathrm{d}N=\int Eg(E)f(E)\mathrm{d}E=C\int_0^\infty E^{3/2}\frac{1}{e^{(E-E_F)/k_BT}+1}\mathrm{d}E$$

$$=\frac{3}{5}N_eE_F^0[1+\frac{5}{12}\pi^2(\frac{k_BT}{E_F^0})^2]$$

$$C_V^e=\frac{\partial E}{\partial T}=\frac{\pi^2N_ek_B^2T}{2E_F^0}=\frac{\pi^2N_ek_B}{2}(\frac{T}{T_F})=\gamma T$$

$$\gamma=\frac{\pi^2N_ek_B^2}{2E_F^0}$$

$$N_e=NZ$$

N_e: the total number of free electrons

N: the number of atoms

Z: the number of free electrons provided by one atom

e.g. $$C_V^e=\frac{\pi^2k_B}{2E_F^0}RT=\frac{\pi^2\times1.38\times10^{-23}}{2\times5\times1.6\times10^{-19}}RT\approx10^{-4}RT$$

in agreement with the experimental results

Comparison of C_V^e and C_V^l

The total heat capacity of a metal includes electron contribution and phonon contribution:

$$C_V = C_V^e + C_V^L$$

At high temperature (T > Θ_D)

$$\left.\begin{aligned} C_V^e &= \frac{\pi^2 NZk_B{}^2 T}{2E_F^o} \\ C_V^L &= 3Nk_B \end{aligned}\right\} \longrightarrow \frac{C_e}{C_L} \approx \frac{\pi^2 Z}{6}\left(\frac{T}{T_F}\right) \longrightarrow C_V \approx C_V^L$$

At low temperature (T << Θ_D)

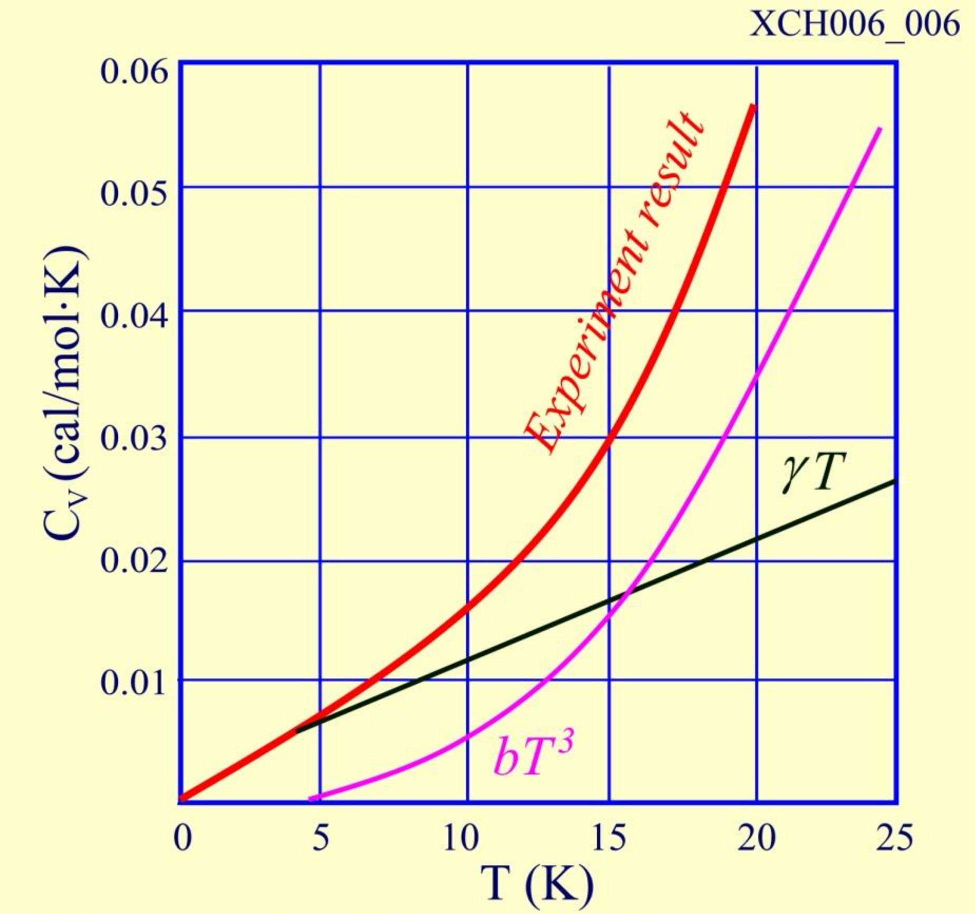
$$C_V = C_V^e + C_V^L = \gamma T + bT^3$$

$$\left.\begin{aligned} C_V^e &= \frac{\pi^2 NZk_B^2 T}{2E_F^0} \\ C_V^L &= \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_D}\right)^3 \end{aligned}\right\} \longrightarrow \frac{C_e}{C_L} = \frac{5Z\Theta_D^3}{24\pi^2 T_F}\cdot\frac{1}{T^2} \longrightarrow C_V = \gamma T + bT^3$$

Heat Capacity of Iron

$$C_V^{Metal} = \begin{cases} C_V^{Phonon} = bT^3 \\ C_V^{Electron} = \gamma T \end{cases}$$

At low temperature, the electronic contribution may be comparable with the phonon's contribution



Heat capacity of Iron under low temperature

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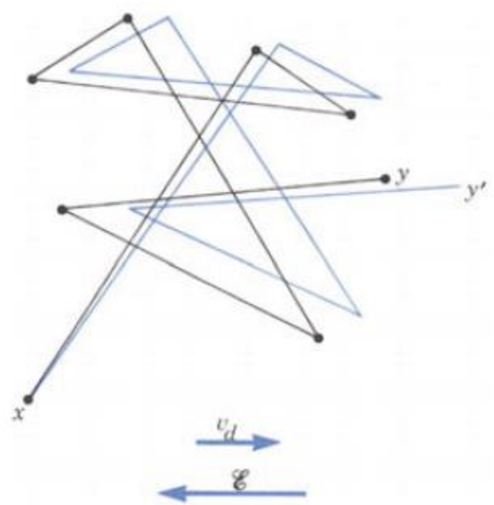
Electrical conductivity vs Temperature

$$\begin{cases} \text{CFE model predicts} \rightarrow \sigma \propto T^{-1/2} \\ \text{experiments show} \rightarrow \sigma \propto T^{-1} \end{cases}$$

From Drude Model: $\sigma = \dfrac{ne^2}{m}\tau$ **τ is temperature dependent**



Experimentally: $\sigma \propto T^{-1}$

Quantum Mechanical FEM: $\sigma = \dfrac{n_e e^2}{m}\tau$ The τ ?

Mattheisen's Rule

The electrons scattering includes two parts:

$$\frac{1}{\tau} = \frac{1}{\tau_{ph}(T)} + \frac{1}{\tau_0}$$

- **By phonons**
- **Temperature dependent**

- **By imperfections**
- **Temperature independent, Sample dependent**

$$\rho = \frac{m_e}{ne^2\tau} = \frac{m_e}{ne^2\tau_{ph}(T)} + \frac{m_e}{ne^2\tau_0} = \rho_I(T) + \rho_0$$

- **ideal resistivity**
- **residual resistivity**

What is the key factor affecting the theoretical electrical conductivity of metals?

Electrical conductivity depends on the DOS at E_F and the size of the Fermi surface. ---Related to its crystal structure and its valent electrons!

Electrical Conductivity of Metals at 295K

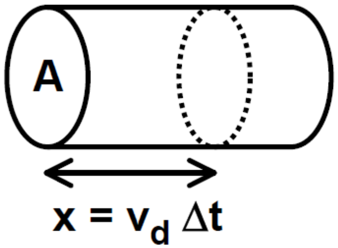
in units of $10^5(\text{ohm.cm})^{-1}$

Li	Na	K	Mg
1.07	2.11	1.39	2.33
Fe	**Ni**	**Cu**	**Zn**
1.02	1.43	5.88	1.69
Al	**Ag**	**Au**	**Ga**
3.65	6.21	4.55	0.67

Electrons' Heat Transport

$$J_{thermal} = -K \mathrm{d}T / \mathrm{d}x$$

If an electron moves from one region with *T* to another region with (*T-ΔT*), it supplies excess energy : *$\Delta Q = C_V \Delta T$*, c_V --- heat capacity per electron



$$J^{electrical} = \frac{n(-e)(\mathbf{v_d}\Delta t)\cdot A}{\Delta t \cdot A} = -ne\mathbf{v_d}$$

$$J_x^{themal} = -n_e \cdot v_x \cdot \Delta Q$$

$$= -n_e \cdot v_x \cdot C_V \cdot v_x \tau \, \mathrm{d}T/\mathrm{d}x \qquad \Delta T = (\mathrm{d}T/\mathrm{d}x) v_x \tau$$

$$= -\frac{1}{3} C_V \cdot v \cdot l \, \mathrm{d}T/\mathrm{d}x \qquad v_x = (1/3)v$$

$$K^{electron} = (1/3) C_V^e \cdot v \cdot l = (1/3) C_V^e \cdot v_F^2 \cdot \tau \qquad K^{\mathrm{phonon}} = \frac{1}{3} C_V^p v_0 \lambda$$

Q: $\mathrm{K^{electron}}$ vs $\mathrm{K^{phonon}}$, metal vs ceramic

Thermal Conductivity K

$$K^{electron} = (1/3)C_V \cdot v \cdot l = (1/3)C_v \cdot v_F^2 \cdot \tau$$

$$E_F = \frac{1}{2}mv_F^2 \qquad C_V^e = \frac{\pi^2 N_e k_B}{2}\left(\frac{T}{T_F}\right)$$

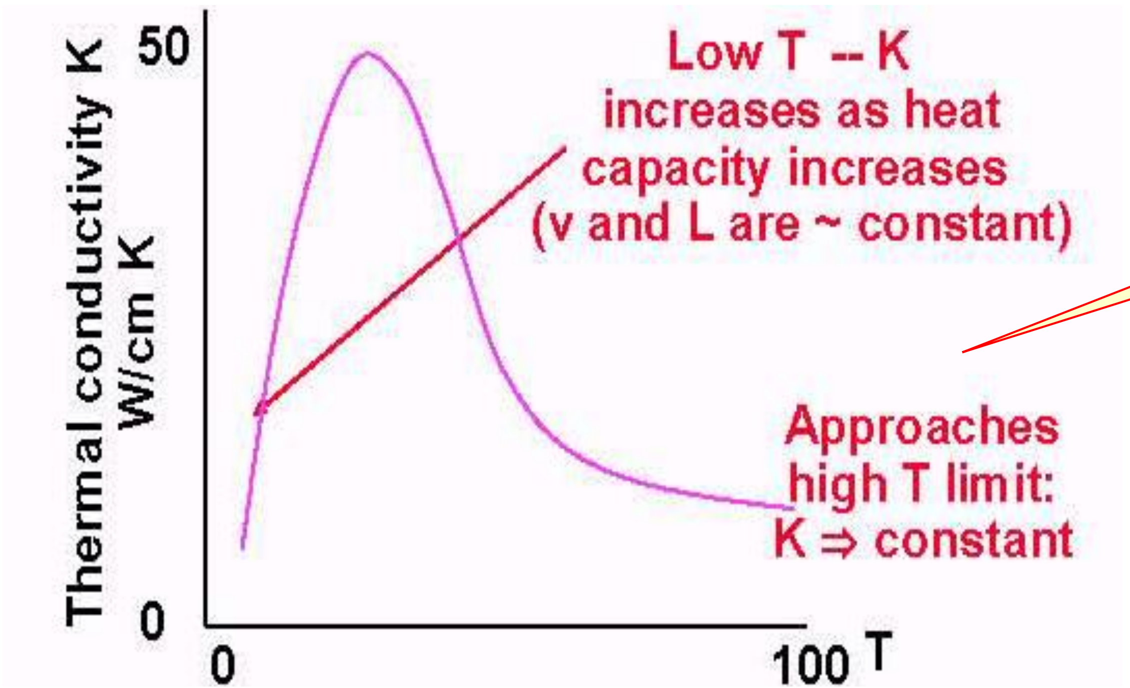
$$K^{electron} = \frac{1}{3}C_V v_F^2 \tau = \ldots = \frac{\pi^2 n k_B^2 T \tau}{3m_e}$$

The speed of conductive electrons are in the Fermi velocity , which is much higher than that of phonons.

$$\boxed{K_{metals} >> K_{non-metals}}$$

Dependence of Electron's Heat Transport on T

$$K^{electron} = \frac{1}{3} C_V v_F^2 \tau = \frac{\pi^2 n k_B^2 T \tau}{3m_e}$$



Compared with phonons?

In pure metals, the electronic contribution is dominant at all temperatures. In impure metals or in disordered alloys, phonon contribution may be comparable with the electronic contribution. Phonons dominate in non-metals.

Wiedemann—Franz Law

In physics, the Wiedemann–Franz law states that the ratio of the electronic contribution to the thermal conductivity (κ) and the electrical conductivity (σ) of a metal is proportional to the temperature (T).

$$\frac{K}{\sigma} = LT$$

The proportioality constant *L* is known as the Lorentz number

On the assumption that the mean free paths of thermal and electrical conductivities of free electrons are the same, then

$$\begin{cases} \sigma = \dfrac{ne^2\tau}{m} \\ K_e = \dfrac{1}{3} C_V^e v_F^2 \tau \\ v_F^2 = \dfrac{2E_F}{m} \\ C_v^e = \pi^2 n k_B^2 T / 2E_F^0 \end{cases}$$

$$\frac{K_e}{\sigma} = \frac{2}{3}\frac{C_V^e E_F}{ne^2} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

Metals with a high electric conductivity usually have a high thermal conductivity.

Lorentz Constant

$$\begin{cases} \sigma = \dfrac{ne^2\tau}{m} \\ K_e = \dfrac{1}{3} C_V^e v_F^2 \tau \Rightarrow \dfrac{K_e}{\sigma} = \dfrac{2}{3}\dfrac{C_V^e E_F}{ne^2} \xrightarrow{C_V^e = \pi^2 n k_B^2 T / 2E_F^0} \dfrac{K_e}{\sigma} = \dfrac{\pi^2}{3}\left(\dfrac{k_B}{e}\right)^2 T \\ v_F^2 = \dfrac{2E_F}{m} \end{cases}$$

$$\frac{K}{\sigma} = LT$$

$$L = \frac{K_e}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 5.87\times10^{-9}\,\mathrm{cal}\cdot\Omega/s\cdot K^2 = 2.45\times10^{-8}\,(V/K)^2$$

Some experimental data of Lorenz number[$10^{-8}(V/K)^2$]

T(°C)	Ag	Au	Cu	Cd	Ir	Zn	Pb	Pt	Sn
0	2.31	2.35	2.23	2.42	2.49	2.31	2.47	2.51	2.52
100	2.37	2.40	2.33	2.43	2.49	2.33	2.56	2.60	2.49

Hall Effect: In a conductor, an associated electric field (Hall field) is build in the direction J×B when a current J flows across a magnetic field B

Nature：Lorentz force causes the deflection of electrons and then accumulate electrons on one face of the conductor. At stable state, the electrostatic force of Hall field just cancels the Lorentz force duo to magnetic field.

The force on a positive charge q is：

$$\boldsymbol{F} = q\left(\boldsymbol{E}_H + \boldsymbol{v}\times\boldsymbol{B}\right)$$

v: drift velocity of charges

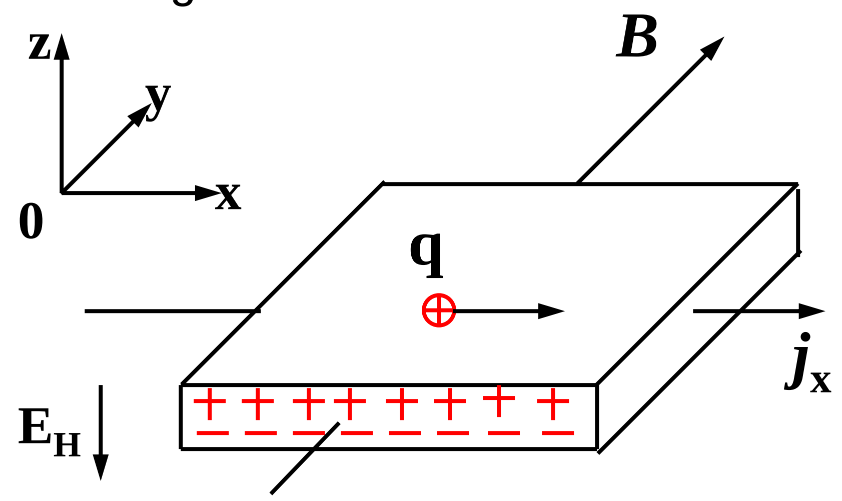
In stable state, F=0

$$q\left(-E_H + vB\right) = 0$$

$$E_H = vB = \left(\frac{1}{nq}\right) j_x B = R_H B j_x$$

$$J = -ne\mathbf{v}_{\mathbf{d}} \qquad j_x = nqv$$

Hall coefficient $R_H = \dfrac{1}{nq}$ For e^-, q=-e; For holes, q=+e



The lower the carrier concentration, the bigger the Hall coefficient is.

Q: Can you find out the applications of Hall effect? Compare the Hall coefficients of metals and semiconductors.

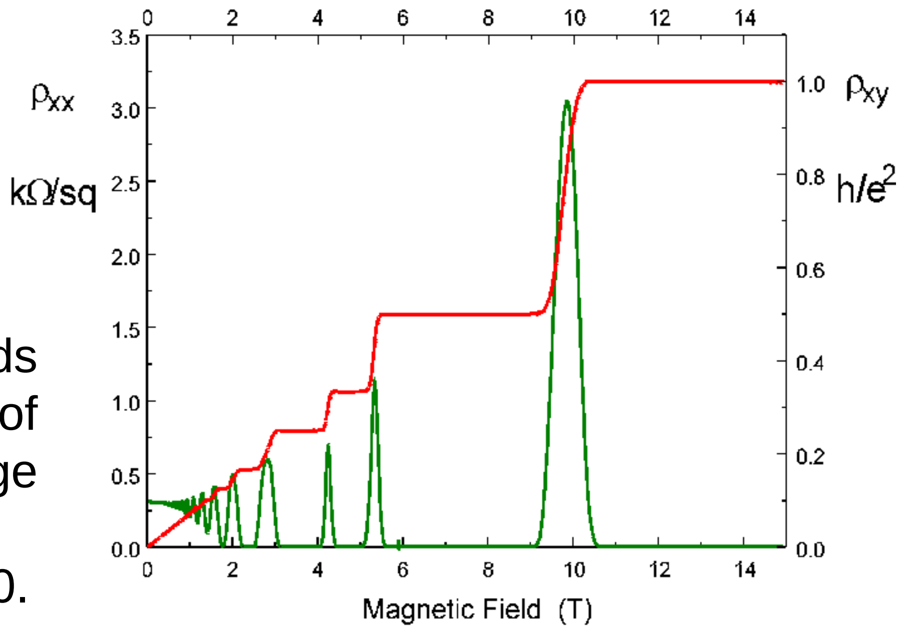
Quantum Hall Effect

In 1985 Klaus von Klitzing won the Nobel Prize for discovery of the quantised Hall effect. In a two-dimensional metal or semiconductor the Hall effect is also observed, but at low temperatures a series of steps appear in the Hall resistance as a function of magnetic field instead of the monotonic increase. What is more, these steps occur at incredibly precise values of resistance which are the same no matter what sample is investigated. The resistance is quantised in units of h/e^2 divided by an integer. This is the QUANTUM HALL EFFECT.

$$\sigma = \frac{I_{\mathrm{channel}}}{V_{\mathrm{Hall}}} = \nu \frac{e^2}{h},$$

Important points to note are:

- The value of resistance only depends on the fundamental constants of physics: *e* the electric charge and *h* Plank's constant.
- It is accurate to 1 part in 100,000,000.



The figure shows the integer quantum Hall effect in a GaAs-GaAlAs heterojunction, recorded at 30mK

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Emission of electrons: the phenomenon that electrons in a material overcome the restriction to become free electrons.

Two main situations of electron emission:

Cold electron emission: low pressure , high voltage.

Thermal electron emission: high temperature.

Work function: the amount of energy per electron is required to emit (i.e. removing from a material). (analogous to ionization potential)

Richardson Law

The current density caused by thermal electron emission is a function of T and work function:

$$j = AT^2 \exp\left(-\frac{W}{k_B T}\right)$$

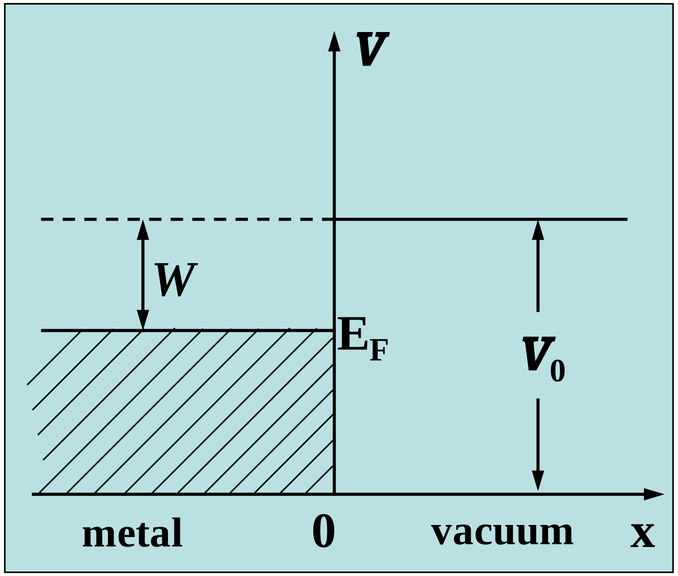
A: constant;

W: work function

$$W = V_0 - E_F$$

W ~ several eV

V_0: free electron energy



Work Function of Some Metals

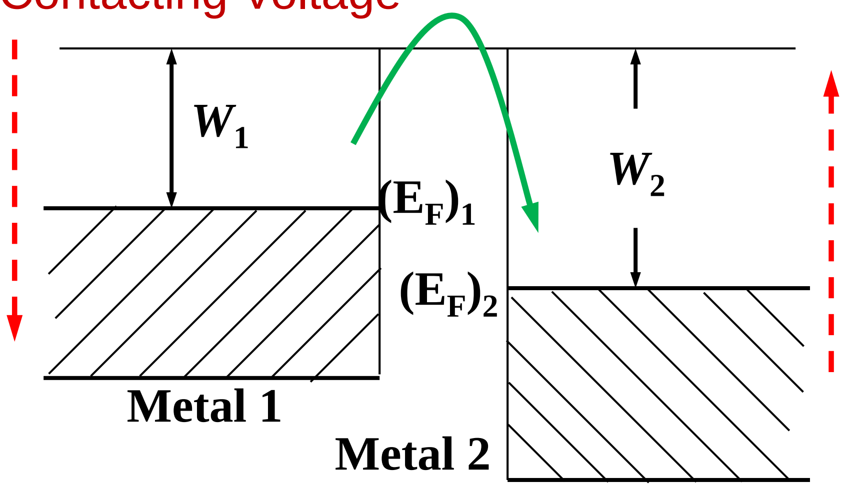
The average work functions of some metals (eV)

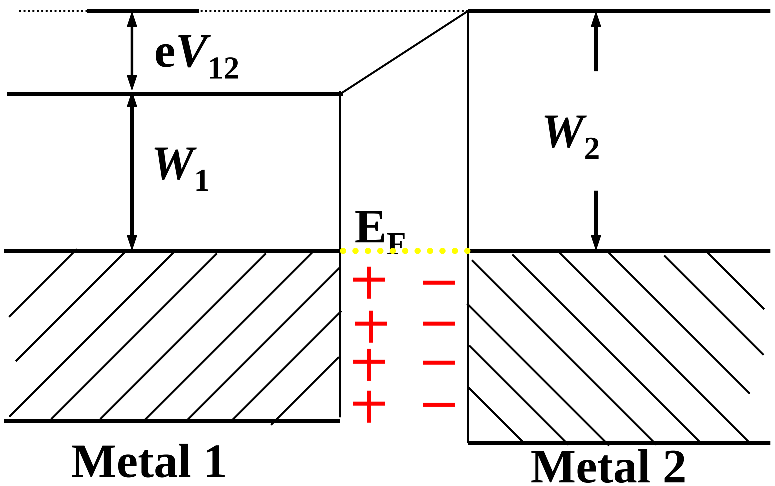
Li	Na	K	Mg	Al	Cu	Ag	Au	Pt
2.48	2.28	2.22	3.67	4.20	4.45	4.46	4.89	5.36

Note: The work functions of metals change with the temperature.

Q: How to choose a metal for thermal electron emission?

Contacting Voltage





Metal 1: positive charge, contact potential > 0

Metal 2: negative charge, contact potential < 0

contact voltage: $V_{12} = \frac{1}{e}(W_2 - W_1) = \frac{1}{e}(E_{1F} - E_{2F})$

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