

Electronic Properties of Solids

R.J. Nicholas

Electronic Properties:

- Metals
- Semiconductors
- Insulators
- Paramagnets
- Diamagnets
- Ferromagnets
- Superconductors

Combination of :

Crystal Structure
Atomic Structure

Free electron theory of metals

- Metals are good conductors (both electrical and thermal)
- Electronic heat capacity has an additional (temperature dependent) contribution from the electrons.
- Why are some materials metals and others not?

Simple approximation: treat electrons as free to move within the crystal

Free electron theory of metals

- Alkali metals (K, Na, Rb) and Noble metals (Cu, Ag, Au) have filled shell + 1 outer s-electron.
- Atomic s-electrons are *delocalised* due to overlap of outer orbits.
- Crystal looks like positive ion cores of charge $+e$ embedded in a sea of conduction electrons
- Conduction electrons can interact with each other and ion cores but these interactions are weak because:

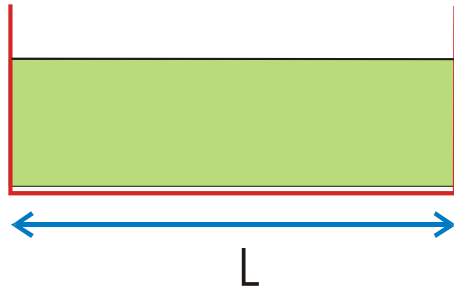
(1) Periodic crystal potential (ion cores) is orthogonal to conduction electrons - they are eigenstates of total Hamiltonian e.g. for Na conduction electrons are 3s states, but cores are n=1 and n=2 atomic orbitals.

(2) Electron-electron scattering is suppressed by Pauli exclusion principle.

Assumptions:

- (i) ions are static - adiabatic approx.
- (ii) electrons are independent - do not interact.
- (iii) model interactions with ion cores by using an “effective mass” m^*
- (iv) free electrons so we usually put $m^* = m_e$

Free Electron Model



Put free electrons into a very wide potential well the same size as the crystal i.e. they are 'de-localised'

Free electron properties

Free electron Hamiltonian has only kinetic energy operator:

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

Free electrons are plane waves

$$\psi = A e^{\pm ikx}$$

with:

Momentum:

$$i\hbar \frac{\partial \psi}{\partial x} = \pm \hbar k \psi$$

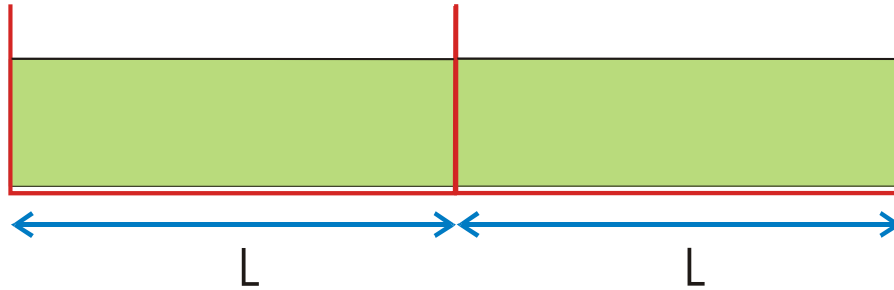
Energy:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{\hbar^2 k^2}{2m} \psi$$

Group velocity:

$$\frac{\partial \omega}{\partial k} = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \frac{\hbar k}{m}$$

Free Electron Model – Periodic boundary conditions



Add a second piece of crystal the same size:
The properties must be the same.

Density of states

Calculate allowed values of k.	$\psi(x) = \psi(x + L)$
Use periodic (Born-von Karman) boundary conditions:	$\therefore e^{ikx} = e^{ik(x+L)}$
	$\therefore e^{ikL} = 1$

L = size of crystal	$\therefore k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}$
	$\therefore \delta k = \frac{2\pi}{L}$

Density of allowed states in reciprocal (k-) space is:

$$\frac{\Delta K}{\delta k} \text{ in } 1-D \quad \text{or} \quad \frac{\Delta V_K}{\delta k^3} \text{ in } 3-D \quad \text{x 2 for spin states}$$

Density of states (2)

States have energies
 ε to $\varepsilon + d\varepsilon$

$$g(\varepsilon)d\varepsilon = g(k)dk = 4\pi k^2 dk \times \frac{2}{\delta k^3}$$

$$\therefore g(\varepsilon)d\varepsilon = g(k) \frac{dk}{d\varepsilon} d\varepsilon$$

$$\begin{aligned} \varepsilon &= \frac{\hbar^2 k^2}{2m} \\ k &= \left(\frac{2m\varepsilon}{\hbar^2} \right)^{1/2} \\ \frac{dk}{d\varepsilon} &= \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{2\varepsilon^{1/2}} \end{aligned}$$

$$\begin{aligned} &= \frac{8\pi}{\left(\frac{2\pi}{L}\right)^3} k^2 \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{2\varepsilon^{1/2}} d\varepsilon \\ &= \frac{4\pi}{\left(\frac{2\pi}{L}\right)^3} \frac{2m\varepsilon}{\hbar^2} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{\varepsilon^{1/2}} d\varepsilon \end{aligned}$$

$$= 4\pi \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon \times V$$

Fermi Energy

Electrons are Fermions $N = \int_0^{\infty} g(\varepsilon) f_{F-D}(\varepsilon) d\varepsilon$

at $T = 0$ $N = \int_0^{\mu} g(\varepsilon) d\varepsilon$

$$n = \frac{N}{V} = \frac{8\pi}{3} \left(\frac{2mE_F}{\hbar^2} \right)^{3/2}$$

μ at $T = 0$ is known as the
 Fermi Energy, E_F

$$E_F = \left(\frac{3N}{8\pi V} \right)^{2/3} \frac{\hbar^2}{2m}$$

Previously

we have $n = AE_F^{3/2}$

$$\therefore \ln n = \frac{3}{2} \ln E + \text{const.}$$

$$\therefore \frac{dn}{n} = \frac{3}{2} \frac{dE}{E}$$

$$\frac{dn}{dE} = \frac{3}{2} \frac{n}{E_F} = g(E_F)$$

$$\therefore C_v = 3nk_B \frac{k_B T}{E_F} = 3nk_B \frac{T}{T_F}$$


\therefore Heat Capacity is:

- (i) less than classical value by factor $\sim k_B T / E_F$
- (ii) proportional to $g(E_F)$


Is this significant?

	Lattice	Electrons
Room Temperature	$3n_{\text{at.}} k_B$	$\pi^2/2 nk_B (k_B T / E_F)$
Low Temperature	$12\pi^4/5 n_{\text{at.}} k_B (T/\Theta_D)^3$	$\pi^2/2 nk_B (k_B T / E_F)$

$$C/T = \beta T^2 + \gamma$$



Debye term



free electron term

Rigorous derivation

$$\begin{aligned}
 U &= \int_0^{\infty} \varepsilon g(\varepsilon) f_{F-D}(\varepsilon) d\varepsilon \\
 \therefore \frac{\partial U}{\partial T} &= \int_0^{\infty} \varepsilon g(\varepsilon) \frac{\partial f}{\partial T} d\varepsilon \\
 &= g(E_F) k_B^2 T \int_{\frac{-E_F}{k_B T}}^{\infty} \frac{x^2 e^x dx}{(e^x + 1)^2} + \delta \\
 &= \frac{\pi^2}{3} g(E_F) k_B^2 T \approx -\infty
 \end{aligned}$$

$$\begin{aligned}
 &\frac{\partial f_{F-D}}{\partial T} ? \\
 &f = \frac{1}{e^x + 1}, \quad x = \frac{\varepsilon - \mu}{kT} \\
 &\frac{\partial f}{\partial T} = \frac{-e^x}{(e^x + 1)^2} \times \frac{\partial x}{\partial T}
 \end{aligned}$$

$$\begin{aligned}
 \delta &\propto \int_{\frac{-E_F}{k_B T}}^{\infty} \frac{x e^x dx}{(e^x + 1)^2} \\
 &= 0 \text{ (why?) }
 \end{aligned}$$

Magnetic susceptibility

- Susceptibility for a spin $\frac{1}{2}$ particle is:

$$\chi = \frac{\mu_B^2 \mu_0}{kT} / \text{electron}$$

- This is much bigger than is found experimentally
- Why?

Pauli paramagnetism

Separate density of states for spin up and spin down,
shifted in energy by $\pm \frac{1}{2}g\mu_B B$ ($g=2$)

Imbalance of electron moments Δn

$$\Delta n = \frac{1}{2} g(\epsilon_F) \times 2\mu_B B$$

giving a magnetization M

$$M = \mu_B \Delta n = \mu_B^2 g(\epsilon_F) B$$

and a susceptibility

$$\chi = M/H = \mu_0 \mu_B^2 g(\epsilon_F) = 3n\mu_0 \mu_B^2 / 2\epsilon_F$$

k-space picture and the Fermi Surface

T=0 states filled up to E_F $\therefore \frac{\hbar^2 k^2}{2m} = E_F$

Map of filled states in k-space
= Fermi surface $\therefore k_F = \sqrt{\frac{2mE_F}{\hbar^2}}$

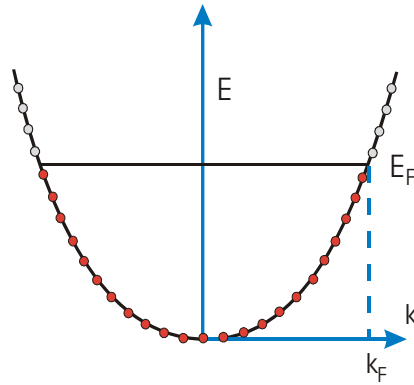
or we can write: $N = 2 \times \frac{4\pi}{3} \frac{k_F^3}{\left(\frac{2\pi}{L}\right)^3}$

$$\therefore k_F^3 = \frac{3\pi^2 N}{V}$$

k-space picture and the Fermi Surface

T=0 states filled up to E_F

$$\therefore \frac{\hbar^2 k^2}{2m} = E_F$$



$$\therefore k_F = \sqrt{\frac{2mE_F}{\hbar^2}}$$

How big is Fermi surface/sphere compared to Brillouin Zone?

Simple cubic structure

$$\text{volume of Brillouin Zone} = (2\pi/a)^3$$

$$\text{electron density } n = 1/a^3$$

$$\text{volume of Fermi sphere} = 4\pi k_F^3/3 = 4\pi^3/a^3$$

$$= \text{half of one B.Z.}$$

Electron Transport - Electrical Conductivity

Equation of motion: Force = rate of change of momentum

$$\hbar \frac{\partial k}{\partial t} = -e(\mathbf{E} + \mathbf{B} \times \mathbf{v})$$

Apply electric field - electrons are accelerated to a steady state with a drift velocity v_d - momentum is lost by scattering with an average momentum relaxation time τ

$$\therefore \text{momentum loss} = \frac{mv_d}{\tau} = -eE$$

$$\therefore \text{current } j = nev_d = \frac{ne^2\tau}{m} E$$

$$\therefore \text{conductivity } \sigma = \frac{ne^2\tau}{m} = ne\mu$$

μ is mobility with:

$$v_d = \mu E$$

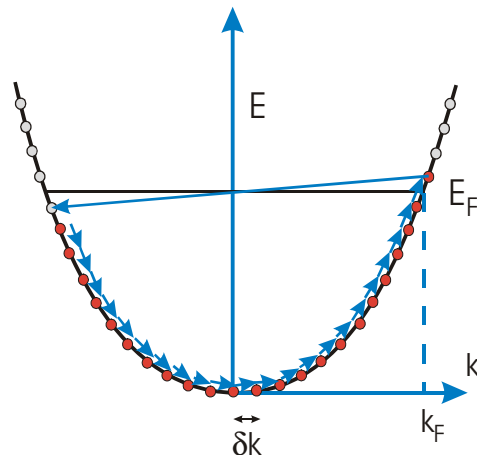
What happens in k-space?

All electrons in k-space are

accelerated by electric field: $\hbar \delta k = F \delta t = -eE \delta t$

On average all electrons

shifted by: $\delta k = -\frac{eE\tau}{\hbar}$



What happens in k-space?

All electrons in k-space are accelerated by electric field: $\hbar \delta k = F \delta t = -eE \delta t$

On average all electrons shifted by: $\delta k = -\frac{eE\tau}{\hbar}$

Fermi sphere is shifted in k-space by $\delta k \ll k_F$

\therefore To relax electron momentum k must be changed by $\sim k_F$

Scattering occurs at E_F

\therefore we need phonons with large value of k. But phonon energy is small so only a small fraction of electrons $k_B T / \epsilon_F$ can be scattered

Scattering processes

Basic Principle: Scattering occurs because of deviations from perfect crystal arrangement

Electron scattering mechanisms:

- (i) thermal vibrations i.e. phonons (vibrations of the atoms are a deviation from perfect crystal structure)
- (ii) presence of impurities - charged impurities are very important - scattering is by Coulomb force i.e. Rutherford scattering.

Matthiessen's rule: Scattering rates ($1/\tau$) add

$$\therefore \rho = \frac{m}{ne^2} \sum 1/\tau = \rho_T + \rho_i$$

Mean free path (λ):

electrons are moving with Fermi velocity v_F

$$\therefore \lambda = v_F \tau \text{ (NOT } v_d \tau \text{)}$$

Low temperature mean free paths can be very long as electrons are only scattered by impurities

Hall Effect

In a magnetic field \mathbf{B} the electron experiences a force perpendicular to its velocity.

A current \mathbf{j} causes a build up of charge at the edges which generates an Electric field \mathbf{E} which balances the Lorentz force

$$(-e) (\mathbf{E} + \mathbf{v}_d \times \mathbf{B})_y = 0; \quad E_y = (v_d)_x B_z$$

Hall Effect

In a magnetic Field \mathbf{B} the electron experiences a force perpendicular to its velocity.

A current \mathbf{j} causes a build up of charge at the edges which generates an Electric field \mathbf{E} which balances the Lorentz force

Balance of forces:

$$(-e)(\mathbf{E} + \mathbf{v}_d \times \mathbf{B})_y = 0; \quad E_y = (v_d)_x B_z$$

The Hall coefficient R_H is:

$$R_H = \frac{E_y}{j_x B_z}$$

$$j_x = n(-e)v_d \Rightarrow R_H = -\frac{1}{ne}$$

Negative sign is sign of the charge on the electron

Metal	Charge/Atom (units of electron charge e)		Group
	Hall Expt.	FE Theory	
Lithium	-0.79	-1	I
Sodium	-1.13	-1	I
Potassium	-1.05	-1	I
Copper	-1.36	-1	IB
Silver	-1.18	-1	IB
Gold	-1.47	-1	IB
Beryllium	+0.1	-2	II
Magnesium	-0.88	-2	II
Calcium	-0.76	-2	II
Zinc	+0.75	-2	IIB
Cadmium	+1.2	-2	IIB
Aluminium	+1.0	-3	III
Indium	+1.0	-3	III

Thermal conductivity

In metals heat is mainly carried by the electrons

Simple kinetic theory formula for thermal conductivity K :

$$\begin{aligned} K &= \frac{1}{3} C \lambda v_F & [C &= \pi^2/3 k_B^2 T g(E_F) = \pi^2/2 n k_B k_B T/E_F] \\ &= \pi^2/6 \lambda v_F n k_B k_B T/E_F & [\lambda &= v_F \tau ; \quad E_F = \frac{1}{2} m v_F^2] \\ &= \pi^2/3 m n k_B^2 \tau T \end{aligned}$$

Scattering processes

- Low temperatures: defects, τ independent of T
- Intermediate temp. : Low Temp phonons - Debye model $\tau \propto T^{-3}$
- High temperatures: 'classical' phonons $\tau \propto T^{-1}$

Wiedeman-Franz ratio

Electrical and Thermal conductivities of electrons are both proportional to the relaxation time τ

Taking the ratio of the two should make this cancel so if we define the Lorenz number as $L = K/(\sigma T)$ we have the

$$\text{Wiedeman-Franz Law: } L = \frac{K}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2}$$

Predicted value is absolute and the same for all metals.

Works well at high and low temps, - breaks down in 'Debye' region where energy and charge scattering are different

Successes and Failures of Free Electron Model

Successes:

- Temperature dependence of Heat Capacity
- paramagnetic (Pauli) susceptibility
- Ratio of thermal and electrical conductivities (Lorentz number)
- Magnitudes of heat capacities and Hall effect in simple metals

Failures:

- Heat capacities and Hall effect of many metals are wrong
- Hall effect can be **positive**
- Does not explain why mean free paths can be so long
- Does not explain why some materials are metals, some insulators and some are semiconductors

Nearly Free Electron Approximation

Use a travelling wavefunction for an electron, e^{ikx} , with kinetic energy $\hbar^2 k^2 / 2m$

Assume that this is Bragg scattered by the wavevector $G=2\pi/a$ to give a second wave $e^{i(k-G)x}$ with energy $\hbar^2(k-G)^2/2m$

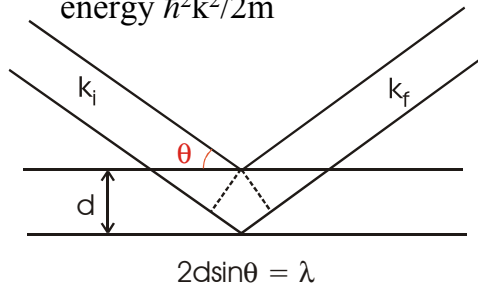
Crystal potential is periodic in real space. Therefore we can Fourier Transform the potential so that:

$$V(x) = \sum_G V_G \exp(iGx)$$

For a schematic solution we calculate what happens for a single Fourier component V_G so $V(x) = V_G(e^{iGx} + e^{-iGx})$

Nearly Free Electron Approximation

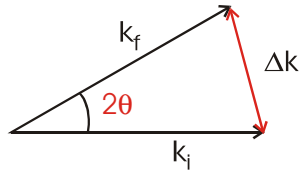
Use a travelling wavefunction for an electron, e^{ikx} , with kinetic energy $\hbar^2 k^2 / 2m$



Bragg scattering

$$\begin{aligned} \Delta \mathbf{k} &= 2|k| \sin \theta \\ &= 4\pi / \lambda \sin \theta = 2\pi / d \end{aligned}$$

$$\Delta \mathbf{k} = \mathbf{G} = \mathbf{h}\mathbf{a}^* + \mathbf{k}\mathbf{b}^* + \mathbf{l}\mathbf{c}^*$$



$$\text{With } d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Formally what we are doing is to solve the Hamiltonian form of Schrödinger equation

$$\mathbf{H} \psi = E \psi$$

where ψ are the two travelling wave solutions. Expanding gives:

$$\begin{pmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{pmatrix} \begin{pmatrix} e^{ikx} \\ e^{i(k-G)x} \end{pmatrix} = (E - \lambda) \begin{pmatrix} e^{ikx} \\ e^{i(k-G)x} \end{pmatrix}$$

$$H_{11} = \left\langle \psi_1^* \left| -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right| \psi_1 \right\rangle = \frac{\hbar^2 k^2}{2m}, \quad H_{22} = \frac{\hbar^2 (k-G)^2}{2m}$$

$$H_{12} = \left\langle \psi_1^* \left| V(x) \right| \psi_2 \right\rangle = V_G$$