4. Metals

4.1 The Free Electron Model

It is surprising to suggest a free-electron model at all. Charged particles at high densities must interact strongly with each other. But we know metals are good conductors of electricity and heat, so let's suppose there are electrons free to carry charge and energy around inside a metal.

4.1.1 Assumptions

- 1. There are electrons free to move in the crystal. The number of electrons per atom is equal to the chemical valency (the number of electrons in the outermost shell of the atom).
- 2. These electrons must undergo collisions, with some mean time τ between collisions.
- 3. Between collisions, there are no interactions with other electrons or with the ion cores.
- 4. The electrons are governed by Fermi-Dirac statistics.

4.1.2 One-electron States

Assume a crystal of cubic volume V, side L. Between collisions, the potential is zero. Solutions of Schrödinger's equation are

$$\psi(\underline{r}) = V^{-\frac{1}{2}} e^{i\underline{k}\cdot\underline{r}}$$

Boundary conditions are that ψ is zero on the faces. This implies that

$$\underline{k}_{x,y,z} = \frac{\pi}{L} n_{x,y,z},$$

where $n_{x,y,z}$ are integers. We must allow for two electron spin states for each translational state, so the density of states is

$$\rho(\underline{k})d\underline{k}=2\frac{V}{\pi^3}\underline{dk}\,.$$

In terms of k, it is

$$\rho(k)dk = \frac{1}{8} \times 4\pi k^2 dk \times \frac{2V}{\pi^3} = \frac{Vk^2}{\pi^2} dk.$$

For a classical particle,

$$\varepsilon = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$
$$k = \frac{(2m\varepsilon)^{\frac{1}{2}}}{\hbar}.$$

And

$$\frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m}$$
$$d\varepsilon = \frac{\hbar^2 k}{m} dk$$

So looking at the density of states again, we have

$$\rho(\varepsilon)d\varepsilon = \frac{V}{\pi^2}(k)(kdk) = \frac{V}{\pi^2} \frac{(2m\varepsilon)^{\frac{1}{2}}}{\hbar} \frac{m}{\hbar^2} dk$$
$$= \frac{V}{\pi^2 \hbar^3} (2m^3)^{\frac{1}{2}} (\varepsilon)^{\frac{1}{2}} d\varepsilon$$

The occupancy of the states is given by the Fermi function

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)\beta} + 1}$$

where μ is the chemical potential.

The total number of electrons (or in general, particles), N, is given by $N = \int_0^\infty f(\varepsilon) \rho(\varepsilon) d\varepsilon$

At T = 0,

$$f(\varepsilon) = \begin{cases} 1 & \varepsilon < \mu \\ 0 & \varepsilon > \mu \end{cases}$$

so we can write

$$N = \int_{0}^{\mu} \frac{V(2m^{3})^{\frac{1}{2}}}{\pi^{2}\hbar^{3}} \varepsilon^{\frac{1}{2}} d\varepsilon = \frac{V(2m^{3})^{\frac{1}{2}}}{\pi^{2}\hbar^{3}} \left[\frac{2}{3}\varepsilon^{\frac{3}{2}}\right]_{0}^{\mu}$$

If we have n = N / V, then

$$\mu = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{2/3}$$

The highest occupied energy at T = 0 is called the Fermi energy ε_f .

$$\varepsilon_f = \mu(T=0) = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3},$$

and the corresponding wavevector, which is the largest occupied wavevector, is called the Fermi wavevector k_f .

$$k_{f}^{2} = (3\pi^{2}n)^{\frac{2}{3}}$$
$$k_{f} = (3\pi^{2}n)^{\frac{1}{3}}$$

Also define a Fermi temperature $k_B T_f = \varepsilon_f$ (the temperature equivalent of the highest Fermi electron), and a Fermi velocity $mv_f = \hbar k_f$, which is the fastest velocity of the Fermi electrons.

Note that we are still using a k-space, or reciprocal space, representation. The sphere whose surface is defined by the wavevectors of magnitude k_f is called the Fermi sphere.

For example: for sodium (monatomic bcc, a = 4.23 Å) (Valence 1);

$$k_f = 0.92 \overset{\circ}{A}^{-1}$$

$$\varepsilon_f = 3.2 eV$$

$$T_f = 3.7 \times 10^4 k$$

$$v_f = 1.1 \times 10^6 m s^{-1}$$

The fact that $v_f \ll c$ justifies the use of the classical dispersion relation.

Compare ε_f with the Coulomb energy of two electrons separated by inter-atomic distances, which is 3.9eV.

Compare the melting point of Sodium 371k, which is around 1% of the Fermi temperature.

4.1.3 Results of Free-electron model

1. Specific heat

$$C_{v} = \frac{1}{V} \frac{\partial \varepsilon_{total}}{\partial T}$$
$$\varepsilon_{total} = \int_{0}^{\infty} f(\varepsilon) \rho(\varepsilon) \varepsilon d\varepsilon$$
$$C_{v} = \frac{1}{V} \int_{0}^{\infty} \varepsilon \rho(\varepsilon) \frac{\partial f(\varepsilon)}{\partial T} d\varepsilon$$

All of the changes in $f(\varepsilon)$ happen near ε_f , so $\rho(\varepsilon) \rightarrow \rho(\varepsilon_f)$, and we can replace the lower limit by $-\infty$. Also substitute $x = (\varepsilon - \mu)\beta$.

$$C_{v} = \frac{\rho(\varepsilon_{f})k_{B}^{2}T}{V} \int_{-\infty}^{\infty} \frac{x^{2}e^{x}}{\left(e^{x}+1\right)^{2}} dx$$

The integral is $\pi^2/3$, so

$$C_v = \frac{\pi^2 \rho(\varepsilon_f) k_B^2 T}{3V}$$

Note that so far, this is a more general than the free electron model. Any density of states at the Fermi energy can be used. In the Free Electron model,

$$\varepsilon_{f} = \frac{\hbar^{2}}{2m} (3\pi^{2}n)^{\frac{2}{3}}$$

$$T_{f} = \frac{\varepsilon_{f}}{k_{B}}$$

$$\rho(\varepsilon_{f}) = \frac{V(2m^{3})^{\frac{1}{2}}}{\pi^{2}\hbar^{3}} \varepsilon_{f}^{\frac{1}{2}}$$

$$\Rightarrow C_{v} = \frac{3}{2} \frac{N}{V} k_{B} \left(\frac{\pi^{2}}{3} \frac{T}{T_{f}}\right)$$

This is the classical result for free particles reduced by a term of order T/T_f . Only electrons within an energy of $k_B T$ of ε_f contribute.

For any real metal, there is also the lattice term.

$$C_V = \gamma T + \alpha T^3$$

Plotting $\frac{C_v}{T}$ vs T^2 should give a linear relation, with an intercept of γ and a slope of α .

Metal	$\gamma_{FE} \left[mJ mol^{-1} k^{-2} \right]$	$\gamma_{\rm exp} \left[mJ mol^{-1} k^{-2} \right]$
Sodium Na	1.09	1.38
Gold Au	0.64	0.73
Iron Fe	0.64	5.02
Bismuth <i>Bi</i>	1.80	0.08

There is enough agreement in the form (linear in T), and in the approximate size of the coefficients, to say that the idea is right. The details are wrong in Fe (transition or d-band metal) and Bi (which is a semi-metal).

2. Electrical Conductivity

We need to assume that after a collision, each electron travels in a random direction. Under the influence of an electric field \underline{E} , each electron acquires a drift velocity after time t of

$$-\frac{e\underline{E}t}{m}$$

If the average time since the last collision in au , then the drift velocity

$$\underline{v}_{drift} = -\frac{e\underline{Et}}{m}$$

The current density j is given by

$$j = -e \underline{v}_{drift} n$$

where n is the number density of the electrons.

The electrical conductivity, σ , is given by

$$\underline{E}\sigma = j$$

(Ohm's law in "fancy form"). So

$$\sigma = \frac{ne^2\tau}{m}$$

Metal	Mean collision time $\begin{bmatrix} 10^{-15} s \end{bmatrix}$	
	T = 77k	T = 293k
Na	170	32
An	120	30
Fe	32	2.4
Bi	0.72	0.23

So the electrons are moving freely throughout the metals.

3. Thermal Conductivity

If Q is the heat flow for a temperature gradient in the z-direction, $\frac{dT}{dz}$, then the thermal conductivity κ is given by

$$Q = \kappa \frac{dT}{dz}$$

For any quantity P, the flux of P in the z-direction given a gradient $\frac{dP}{dz}$ is given by kinetic theory,

Flux of
$$P = \frac{1}{3}\lambda \overline{v} \frac{dP}{dz}$$

Where the 1/3 arises from angular averaging, λ is the mean free path, and \overline{v} is the mean speed.

$$Q = \frac{1}{3} \frac{\lambda \overline{v}}{V} \frac{d\varepsilon}{dz}$$

i.e. the energy gradient drives the heat flow.

$$\frac{d\varepsilon}{dz} = \frac{d\varepsilon}{dT}\frac{dT}{dz}$$

Since $\frac{1}{V} \frac{d\varepsilon}{dT}$ is C_v ,

$$Q = \frac{1}{3}\lambda \overline{v}C_v \frac{dT}{dz}$$

so we can write

$$\kappa = \frac{1}{3}\lambda \overline{v}C_v$$

Since $\lambda = \overline{v}\tau$,

$$\kappa = \frac{1}{3}\overline{v}^2 \tau C_v$$

At low temperatures, all the velocities are close to the Fermi velocity v_f . So,

$$\kappa = \frac{nk_B^2 \tau}{m} \left(\frac{\pi^2 T}{3}\right)$$

The ratio $\frac{\kappa}{\sigma T}$, which is known as the Lorentz ratio, should be constant.

$$\frac{\kappa}{\sigma T} = \left(\frac{k_B}{e}\right)^2 \frac{\pi^2}{3} = 2.44 \times 10^{-8} W \Omega k^{-2}$$

This relation is known as the Wiedemann-Franz law. It is frequently observed to hold, and the constant is about right.

A purely classical theory gives $\frac{9}{2\pi^2}$ times this constant.



Metal	273k	373k
Li	2.22	2.43
Cu	2.20	2.29
Au	2.32	2.36
Fe	2.61	2.88
Bi	3.53	3.35

4.2 Hall Effect

A current density j flowing in a magnetic field \underline{B} generates a transverse electric field E_H . The Hall Coefficient R_H is called the Hall Resistance.

$$\underline{E}_{H} = R_{H} \underline{B} \times \underline{j}$$

What is the effect of collisions on the current? They provide an effective force equal to the rate of change of momentum.

The probability of a collision in time dt is $\frac{dt}{\tau}$. In this time, the change of momentum

is

$$d\left(mv_{drift}\right) = -\frac{dt}{\tau}mv_{drift}$$

The force from the collisions plus the force from the electromagnetic field must be 0 in steady state.

$$\frac{d\left(\underline{m}\underline{v}_{drift}\right)}{dt} = -e\left(\underline{E} + \underline{v}_{drift} \times \underline{B}\right) - \frac{\underline{m}\underline{v}_{drift}}{\tau} = 0$$

Split this up into the x and y directions.

x:
$$0 = -eE_x - eBv_{drift,y} - \frac{mv_{drift,x}}{\tau}$$

y: $0 = -eE_y - eBv_{drift,x} - \frac{mv_{drift,y}}{\tau}$
multiply by $\frac{ne\tau}{m}$, and substitute $\sigma = \frac{ne^2\tau}{m}$
x: $\sigma E_x = -\frac{ne^2\tau}{m}Bv_{drift,y} - nev_{drift,x}$
y: $\sigma E_y = \frac{ne^2\tau}{m}Bv_{drift,x} - nev_{drift,y}$
Substitute $\underline{j} = -e\underline{v}_{drift}n$
x: $\sigma E_x = \frac{e\tau}{m}Bj_y + j_x$
y: $\sigma E_y = -\frac{e\tau}{m}Bj_x + j_y$
But $j_y = 0$, so

$$\sigma E_x = j_x$$

$$\sigma E_y = -\frac{eB\tau}{m} j_x$$

$$\frac{E_y}{j_x B} = -\frac{1}{ne} = R_H$$

Metal	$-\frac{1}{R_{H}ne}$
Na	1.2
Au	1.5
Mg	-0.4
Al	-0.3

So there is some measure of agreement, but for some metals we even have the sign wrong.

4.1.4 Review of Free-Electron Model

Successes:

- Form of low-T specific heat (linear in T) correct.
- Quantitative agreement on specific heat (within 20%) for some, but not all, metals.
- Good quantitative agreement for Lorentz ratio at high T for most metals.
- Hall effect agreement (within 50% or so) for some metals, but not all metals.

Failures:

- Doesn't explain strong temperature dependence of the electrical or thermal conductivity.
- Specific heat coefficient is not always correct.
- Wiedemann- Franz law fails at intermediate temperatures.
- Doesn't explain the positive Hall coefficient in some metals.

Puzzles:

- What causes the collisions?
- Why are there no (other) interactions in between collisions?

4.2 Wavefunction in a periodic potential

Translational symmetry means that the potential provided by the nuclei in the crystal is periodic. Assume that the effect of all the other electrons is to provide an additional potential which is also periodic.

Consider a wavefunction in a one-dimensional periodic potential with time dependence $e^{-i\omega t}$.

$$\Psi(x,t) = \Psi(x)e^{-i\omega t}$$

If the wavefunction varies by a factor A when x increases by a, the lattice parameter, then the magnitude of A must be 1, otherwise the wavefunction is not well-behaved. So we can write,

 $A = e^{i\theta}$

For any θ , we can find k such that $ka = \theta$. If we take the wavefunction at the origin to be ψ_0 , then

$$\Psi(\ell a,t) = \psi_0 e^{i(k\ell a - \omega t)}$$

So far, this is like the development of the phonon states, but in that case the function is defined only for the atomic positions. This is not the case – we need to have the wavefunction defined everywhere.

Now the wavefunction at other positions in the unit cell will be different from the wavefunction at the origin, but the same relationship will apply to all points related by a specific lattice vector.

So

$$\Psi(x,t) = u(x)e^{i(kx-\omega t)}$$

where u(x) is a function with the same periodicity as the crystal.

The total wavefunction is this periodic function multiplied by a traveling wave function which is characterised by a wavevector k.

Applying the usual boundary conditions will restrict the values of k to integer multiples of $\frac{2\pi}{Na}$.

k can always be chosen to be within the Brillouin zone, but sometimes it will be illuminating to look at k values in other zones.

(Block's theorem)

Focusing on the spatial part of the wavefunction, and generalising to 3D,

 $\psi(\underline{r}) = u(\underline{r})e^{i\underline{k}\cdot\underline{r}}$

4.3 Free-Electron States in 1D K-space

Energy of classical non-relativistic particle is quadratic in k. But k values are related by \pm a reciprocal lattice vector are equivalent.



This is the case of a Repeated Zone Scheme, where there is more than 1 curve is represented.

Therefore we can represent all energies of the free particle in one Brillouin zone, that

between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$. This is called the reduced zone scheme.

Each k value corresponds to an infinite number of energies, but we can represent all of the free electron dispersion relation in one Brillouin zone.

Note that all of the points where energies are degenerate are at zone boundaries or zone centre.

4.4 Bragg Scattering of electrons

If we think of the "free electron" as interacting with the potential provided by the crystal, it might undergo Bragg diffraction. The condition that it does so is

$$\underline{Q} = \underline{G} = \underline{k_I} - \underline{k_F} \; .$$

For Bragg diffraction in 1D, this implies a reversal of k, which can happen only when

$$2|\underline{k}| = |\underline{G}|$$

This implies that Bragg diffraction may occur whenever the k value is at any integer multiple of π / a , i.e. at any zone boundary or any zone center which coincides exactly with the condition for two states to be degenerate. One of these states is the incident wave, and the other is the scattered wave.

We might expect the net result to be a standing wave. There are two possible standing waves, which differ by their phase. They are $\sin\left(\frac{\pi x}{a}\right)$ and $\cos\left(\frac{\pi x}{a}\right)$.



 $\cos\left(\frac{\pi x}{a}\right)$ has antinodes near the nuclear positions, where the potential is attractive

(negative), whereas $\sin\left(\frac{\pi x}{a}\right)$ has antinodes in between the nuclear positions, where the potential is positive. Therefore the energy of the former is lower than the energy of the latter.



Even small changes in the energies change the picture completely. There are now energies for which there are no states, which is not the case for free electrons. Also, we have created bands of energies which have states which are adjacent in energy.

4.4.1 What is the meaning of k?

 $\psi(\underline{r}) = u(\underline{r})e^{i\underline{k}\cdot\underline{r}}$

For a free electron, we know $\hbar \underline{k} = \underline{p}$, but $\underline{p} = -i\hbar \nabla$. So $\psi(r)$ is not an eigenstate of $\underline{p} \cdot \underline{p}\psi(r) = \hbar \underline{k}\psi(r) - i\hbar e^{i\underline{k}\cdot\underline{r}}\nabla u(\underline{r})$. So \underline{k} is related to momentum, and reduces to it when $u(\underline{r})$ is constant. We call \underline{k} the crystal momentum.

4.4.2 What is the electron velocity?

In 3D, we are looking at the group velocity.

$$\underline{v} = \frac{1}{\hbar} \nabla_k \varepsilon(\underline{k})$$

So the velocity of electrons affected by the periodic potential is similar to the free electron value for most states, but near the zone boundary and the zone centre, the group velocity is reduced to 0. This is true however small the energy gap is. This is consistent with the picture of the Bragg scattering causing standing waves.

Thu main conclusion is that electrons are still free to travel with non-zero velocity through the crystal in the presence of a periodic potential. These are eigenstates of the energy which involve electrons with non-zero velocities. The nuclei and the other electrons may affect the velocity, but they do not reduce it to zero, except for very specific states.

We say we have "nearly free" electrons. This is the "Nearly Free Electron Model".

4.5 Effective Mass

Near the zone boundary and zone centre, the change in the group velocity from the free electron value is equivalent to altering the mass. The new value is called the *effective mass*. Sometimes it can be negative.

4.6 What are the collisions?

Collisions with what? Take Na at 77k. The collision time is around $1.7 \times 10^{-13} s$. The Fermi velocity is around $10^6 m s^{-1}$. So the mean free path is around $1.7 \times 10^3 Angstroms$, and the nearest neighbour distance is around 3.7 Angstrom.

Therefore the collisions are not due to the ion cores. The atoms in a perfect structure, and indeed the average effect of the other electrons, do not give rise to collisions. It is the differences from the perfect structure which cause collisions.

Defects

Such as impurities, vacancies, dislocations (imperfections in the atomic layers) can cause collisions, but they are not temperature dependent, and they are generally elastic as there is no change in the electron energy.

Phonons

These can cause scattering of the electrons, which depends on the number of phonons (which changes with temperature), and is inelastic (phonon creation or absorption).

Why does Wiedeman-Franz Law fail? Low temperatures No phonons thermally excited, so dominant scattering process is defect scattering. Degrades the heat current by reversing the direction on scattering of electrons with higher energy than average, and with lower energy. Degrades the electrical conductivity by randomizing the direction after acquiring a drift velocity. Processes are similar but different in detail, so Lorentz ratio is constant, but not exactly the free electron value.

High temperatures

 $T > T_D$ the Debye temperature.

Many phonons thermally excited. Inelastic scattering can change both energy and randomize the direction of the electrons, so mean collision time is really the same for both electrical and thermal currents.

In between, only low energy phonons are populated, which have small wavevectors (acoustic modes near zone centre). Therefore complex behaviour. See Hook and Hall, pages 90-97.

4.7 Nearly-Free Electron Model

Free electron model failures:

- Does not explain why the conductivity is strongly temperature dependent.
- Although the free electron model got the form of the specific heat about right, the coefficient was not always correct.
- W-F law fails at intermediate temperatures.
- Does not explain positive Hall coefficients.

Nearly-free electron model:

- Collisions are with predominantly with phonons at high temperature, and the number of phonons are strongly temperature dependent.
- An effective mass change will change the specific heat coefficient.
- At intermediate temperatures, we get a complex interplay between the collision mechanisms.
- Effective mass may be negative, which would explain the positive Hall coefficients.

4.8 Energy Bands



Energies with states are called bands. Energies without states are called band gaps.

$$\Delta k = \frac{2\pi}{Na}$$
$$\Delta \varepsilon = \frac{2\pi}{Na} \frac{\partial \varepsilon}{\partial k}$$

These states are eigenstates, so small perturbations (e.g. applied electric or magnetic field) can change the electrons from one state to a neighbouring one in energy. Band gaps prevent a change of state, without some substantial and appropriate perturbation (e.g. photon absorption).



Fermi energy is determined by

$$N = \int_0^{\varepsilon_f} \rho(\varepsilon) f(\varepsilon) d\varepsilon$$

The Fermi level lies either within a band, or within a band gap.

4.8.1 Full Bands

All states occupied at T = 0k. Consider a 1D slice:



For any state the x-component of the velocity v_x is given by

$$v_x = \frac{1}{\hbar} \frac{\partial}{\partial k_x} \varepsilon(k_x)$$

The mean total velocity is found by integrating over all states.

$$\overline{v}_{x} = \int_{-k_{ZB}}^{k_{ZB}} \frac{1}{\hbar} \frac{\partial}{\partial k_{x}} \varepsilon(k_{x}) dk_{x} = \frac{1}{\hbar} \left(\varepsilon(k_{ZB}) - \varepsilon(-k_{ZB}) \right) = 0$$

Since k_{ZB} and $-k_{ZB}$ are related by a reciprocal lattice vector, they represent the same wavevector k, so \overline{v}_x is always zero. The same result follows in 3D. Both the

mathematics, and the symmetry, shows that the mean velocity must be zero. Therefore a full band does not contribute to conduction.

4.8.2 Metals, Insulators and Semiconductors

If the Fermi level does not lie within a band, all of the bands are either full or empty at T = 0. This is an insulator.

If the Fermi level lies within a band, then small perturbations (e.g. E field) can cause an imbalance in velocities, so electrons may then contribute to conduction. This is a metal.

If an insulator has the Fermi energy within a small band gap (small cf. k_BT), then at non-zero temperature, electrons can be thermally excited from the full to the empty band. Both bands may then contribute to conduction. This is called a semiconductor.

The nearly free electron model has done away with assumption 1 of the free electron model. It provides a basis for dealing with insulators as well as metals, and even semiconductors. It treats all bonding on the same level. The difference arises as a result of the position of the Fermi level.

Bands in Two-Dimensions – Overlapping Bands

Consider a crystal with a square lattice.

(4)

The energies of the bands may overlap. The first band is not full at the second band contour, but the second band has some occupied states. Thus the Fermi energy can lie in more than one band at once, if the bands are overlapping.

Number of Conduction Electrons

Each band has a state for each k-value in the BZ, which is equal to the number of primitive unit cells, N. So 2N electrons may be accommodated in each band, where the 2 is due to the two possible spins of the electrons.

The band (or bands if overlap) in which the Fermi level lies has a number of electrons, which are the conduction electrons.

For the Fermi level to lie between bands, the total number of electrons must be a multiple of 2N. So a primitive unit cell must contain an even number of electrons. Conversely, a primitive unit cell with an odd number of electrons must give rise to a metal.

However, if there are overlapping bands, an even number of electrons in each primitive unit cell may also give rise to a metal.

Material	Structure	Basis	Number of	Туре
			electrons in	
			basis	
Na	Monatomic	Na	11	Metal
	bcc			
Al	Monatomic fcc	Al	13	Metal
Au	Monatomic fcc	Au	79	Metal

V	Monatomic	V	23	Metal
	bcc			
NaCl	Rocksalt	Na^+Cl^-	28	Insulator
Diamond	Diamond	2C	12	Insulator
Ca	Monatomic fcc	Ca	20	Metal
Mg	Нср	2Mg	24	Metal
Fe	Monatomic	Fe	26	Metal
	bcc			
Si	Diamond	2Si	28	Semiconductor
GaAs	Zincblende	GaAs	64	Semiconductor

4.9 Application of Nearly-Free Electron Model to Metals

The existence of extended states with non-zero velocity depends only on having a periodic potential. What happens to the "core electrons", e.g. 1s electrons in Na $(1s^22s^22p^63s^1)$



Tend to become less dispersive, and the curvature goes to 0, i.e. zero velocity. For core states, all energies are well below Fermi level there is no contribution to conduction to specific heat. So the fact that the approximation is poor for these states does not matter.

What about the "valence electrons", e.g. $3s^1$ in Na? There are two factors which conspire.

Firstly the potential is strongest near to the ion cores (nuclei), but the Pauli principle

tends to exclude conduction electrons as there are already many core electrons states there.

Secondly, "other electrons" which are free to move tend to "screen" the potential. The net effect is that, for the s-electrons at least, the nearly free electron theory is rather good. Less so for p and d electrons.

4.10 Fermi Surfaces

The set of wavevectors $\left\{\underline{k_f}\right\}$ which describe the states whose energy is the Fermi energy is a sphere for free particles.

In the presence of the periodic potential, this set of wavevectors is no longer a sphere; it can be a more complicated surface. It may even be multiply-connected. This set of wavevectors is called the Fermi surface.

Alkali metals (Na, K, etc)

Monatomic bcc. One electron per atom. Free electron Fermi sphere has magnitude

$$0.62\left(\frac{2\pi}{a}\right)$$
. The shortest distance to the BZ boundary is $\frac{1}{\sqrt{2}}\left(\frac{2\pi}{a}\right)$. Then the

occupied states are not affected much at all by the periodic potential. So Fermi surface is in fact almost spherical. We therefore expect these metals to behave like freeelectron metals.

Noble metals (Cold, silver, copper)

Full d-shell and one s-electron. Monatomic fcc, so nearest zone boundary is in [111]



In this case the energy changes are large enough to change the slope of the Fermi surface, and create a "neck" on the surface.

For the most part, this still looks like a free-electron Fermi surface but the necks create new possibilities for the behaviour of electrons at the Fermi level.

The free electron values are still mostly quite good for the noble metals.

4.11 The Semi-Classical Model

Given the band structure (the dispersion relation $\varepsilon_n(k)$).

Assume that electrons undergo collisions without making inter-band transitions. Continue to assume that we have Fermi-Dirac statistics.

How far can we get by treating the electrons as classical particles? Velocity of the particle:

$$\frac{d\underline{r}}{dt} = \underline{v}(\underline{k}) = \frac{1}{\hbar} \nabla_k \varepsilon_n(\underline{k})$$

Rate of change of momentum:

$$\hbar \frac{d\underline{k}}{dt} = -e \left[\underline{E} + \underline{v}(\underline{k}) \times \underline{B} \right]$$

using the classical Lorentz force.

This model is called the Semi-Classical because it treats the dynamics classically. It can be justified in detail, provided (from a full quantum mechanical approach):

- 1. The mean free path is not too small
- 2. The fields (*E* and *B*) are not too rapidly varying either in time or in space.

DC E-Field

Take the second equation, and integrate it.



Without collisions, k would increase continuously. As it approaches k_{ZB} , the velocity reduces to 0, then it reverses. The effect of collisions is to prevent the continual increase of k, but to balance the external force by a small shift in all of the states. This is equivalent to adding a drift velocity to all of the electrons.

The acceleration of the particles is (switching to a 1D model)

$$\underline{a} = \frac{d\underline{v}(\underline{k})}{dt} = \frac{1}{\hbar} \frac{\partial^2 \varepsilon(\underline{k})}{\partial \underline{k}^2} \frac{\partial \underline{k}}{\partial t}$$

Note that if the Fermi energy falls in a region where the second derivative is negative, the drift velocity is in the opposite direction from what you would expect.

Effective mass: Holes

For a free electron, the energy and acceleration depend on the difference of k from the minimum Δk .

$$\varepsilon(\underline{k}) = \frac{\hbar^2}{2m} (\Delta k)^2$$
$$\underline{v}(\underline{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} = \frac{\hbar}{m} \Delta k$$
$$\underline{a} = \frac{\hbar}{m} \frac{d(\Delta k)}{dt}$$

Near to a local maximum of the energy,

$$\varepsilon(\underline{k}) = \varepsilon_{\max} - \alpha (\Delta k)^2$$

i.e. a maximum, then some dependence on $(\Delta k)^2$ through a Taylor expansion. We can put in $\alpha = \frac{\hbar^2}{2m^*}$.

$$\varepsilon(\underline{k}) = \varepsilon_{\max} - \frac{\hbar^2}{2m^*} (\Delta k)^2$$

$$\underline{v}(\underline{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} = -\frac{\hbar}{m^*} \Delta k$$
$$\underline{a} = -\frac{\hbar}{m^*} \frac{d(\Delta k)}{dt}$$

Therefore the response is as if it were a free particle, but with a negative mass. We could treat it as a free particle if the force were in the opposite direction and it had a positive mass. This would be so if it had a positive charge (+e) and a positive mass

 $(+m^*)$. This is a hole.

Near any turning point in the dispersion relation, ε_{tp}

$$\varepsilon(\underline{k}) = \varepsilon_{tp} + \frac{1}{2} \frac{\partial^2 \varepsilon}{\partial k^2} (\Delta k)^2,$$

and the effective mass in general is then

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial k^2}$$

Under certain circumstances, when $\frac{\partial^2 \varepsilon}{\partial k^2}$ is negative at the Fermi level, it may be

advantageous to think of the charge carriers not as negative electrons with negative mass, but as positive holes with a positive mass.

Another picture from holes

The current density is the mean velocity times the charge.

$$j = -e \int_{\substack{\text{occupied}\\\text{states}}} v(\underline{k}) \frac{dk}{4\pi^3}$$

where the $4\pi^3$ is from the density of states. We can alternatively write this as

$$j = -e\left(\int_{\substack{all \\ states}} v(k) \frac{dk}{4\pi^3} - \int_{\substack{unoccupied \\ states}} v(k) \frac{dk}{4\pi^3}\right)$$

As the integral of the velocity over all of the states is 0, we can write

$$j = +e \int_{\substack{\text{unoccupied}\\\text{states}}} v(k) \frac{dk}{4\pi^3}$$

This means that the current can be considered to be carried by positively charged particles which are in the states unoccupied by electrons. Note that these may have positive or negative mass; there is no reason to choose one or the other.

Under certain circumstances, particularly when the second derivative is negative at the Fermi level, it may be advantageous to think of the charge carriers as positive holes with positive mass, occupying the states which are in fact unoccupied by electrons in a band.

DC B Field

The force is the cross-product of the velocity and B. The velocity is the gradient of the energy with respect to k, so the force acts to move the electrons on energy contours orthogonal to the velocity and <u>B</u>.



i.e. electron orbits in the opposite sense. The sense is that which would be followed by a positively charged free particle. Can now have

- Free-electron-like orbits
- Hole orbits (positive charge)
- Open orbits particles oscillate.

4.12 Metal Properties in the Semi-classical Model

1. Specific Heat

$$c_{v} = \frac{\pi^{2} \rho(\varepsilon_{f}) k_{B}^{2} T}{3V}$$

But now we have no simple expression for the density of states at the Fermi level, $\rho(\varepsilon_f)$. For example, d-band metal (Fe)



For Fe, γ is 8 times the free electron value. In some materials (so-called "heavy fermion"), γ may be up to 1000 times the free electron value.

2. Electrical Conductivity

The electrons respond like free particles, but with the mass replaced by the effective mass m^* .

$$\sigma = \frac{ne^2\tau}{m^*}$$

3. Thermal Conductivity

$$\kappa = \frac{nk_B^2 \tau}{m^*} \left(\frac{\pi^2 T}{3}\right)$$

Note that the Lorentz ratio

$$\frac{\kappa}{\sigma T} = \left(\frac{k_B}{e}\right)^2 \frac{\pi^2}{3} = 2.44 \times 10^{-8} W \Omega k^{-2}$$

remains the same, as the effective mass does not appear in it.

4. Hall Effect

The electron orbits in \underline{B} fields may look like positive or negatively charged particles. For complicated Fermi surfaces, both electrons and holes.

$$R_{H} = -\frac{1}{n_{e}e} \text{ (electrons)}$$

$$R_{H} = +\frac{1}{n_{h}e} \text{ (holes)}$$

$$R_{H} = \frac{1}{n_{eff}e} \text{ (combination of both)}$$

4.13 Summary of Metals

We can explain a great many properties of metals if we assume there are nearly free electrons, where the effect of the nuclei and the other electrons can be considered as a periodic potential. This affects the dispersion relation, and may form complicated Fermi surfaces. The curvature of the bands may change the effective mass of the

electrons. Collisions are with things which cause deviations from the periodicity of the crystal – defects and phonons.