

6.0 Electronic Properties Overview.

Divide materials into metals & insulators.

Resistivity	10^{-8} to 10^{-5} Ωm	metal
	10^{-5} to 10 Ωm	semiconductor
	10 to ∞ Ωm	insulator.

Striking difference in T -dependence.

Metals ρ increases with T (usually $\propto T$)

S'cond ρ decrease with T .

Alloys have higher resistivity than constituents.

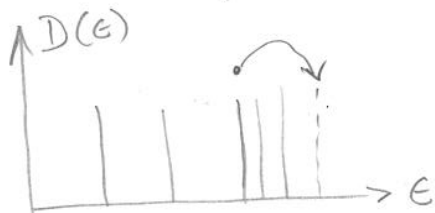
- no law of mixing
- suggests 'impurity' mechanism.

Optical properties.

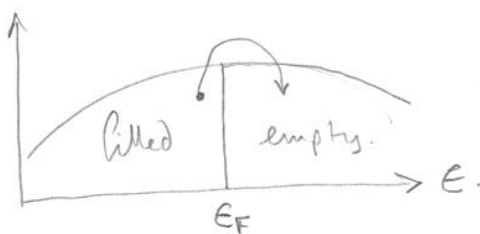
Metals are silvery / opaque

Insulators are often transparent. or coloured.

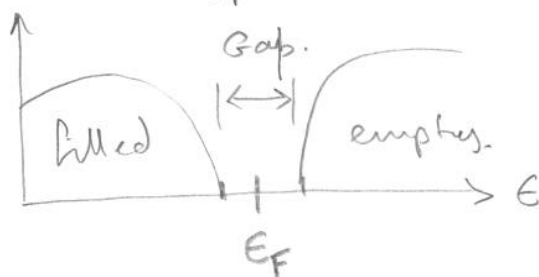
General explanation: density of electron states



atom, optical transition
single energy / wavelength.



metal, E_F = Fermi energy
transitions possible
at all wavelengths.



semiconductor $\Delta E \sim k_B T$
insulator $\Delta E \gg k_B T$

ΔE relates to colour.

(51a)

General features of metals.

Extra thermal energy, specific heat.

Associated with free electrons.

Drude model as classical gas

- ✓ i) electrical conduction, limited by collisions
- X ii) too much specific heat.
- ✓ iii) optical properties.

Needs Quantum picture to explain C_v .

$C_v \sim 1\% k_B$ due to electrons.

Drude "free electron gas" (1900)

fills space outside atom cores (+ve charge)

- i) no collisions with cores. (Bloch, later)
- ii) allows collisions with impurities / phonons.
- iii) no electron-electron collisions

= requires QM (Pauli E.P.) to rationalise

$\rho \propto T$ known but not explained by Drude.
also needs (quantum picture, or) phonons.

6.1 Free Electron Gas

Simplest model of a metal due to Fermi. Idea is to carry over ideas of electron orbitals in atoms to a macroscopic object. Fundamental behaviour always Pauli Exclusion Principle.

- For now, we will ignore the crystal lattice and return to it next week. We assume:
- fixed background of N +ve charged ^{cores} nuclei 15% vol.
 - N electrons moving freely inside metal without seeing the nuclei (monatomic case)
 - Coulomb interactions ignored because system is neutral overall.

This model works quite well for alkali metals Na K Rb Cs, so we should try to understand why.

⇒ Justification will come later: why are electrons not scattered strongly by nuclei as they migrate through metal? Once again, the answer is a property of a crystal.

'Electron in a Box' paradigm. { need to explain why all electrons not allowed in ground state

12.02.07 I $\nabla^2 \psi = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi$ 1D Schrödinger equation

There is no potential energy (inside the box) for free electrons, only boundary conditions: $V \rightarrow \infty$ at walls, so $\psi(x) = 0$ at $x = 0, L$

$\psi_n(x) = A \sin\left(\frac{2\pi}{\lambda_n} x\right)$ $\frac{2\pi}{\lambda_n} L = n\pi \Rightarrow \lambda_n = \frac{2L}{n}$

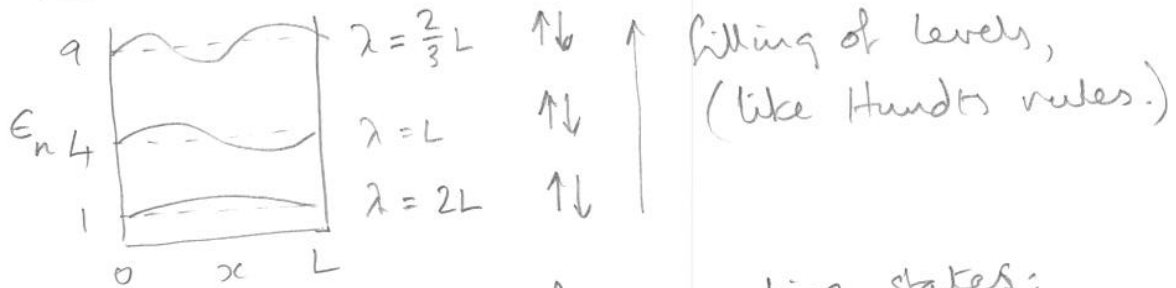
$+\frac{\hbar^2}{2m} \left(\frac{2\pi}{\lambda_n}\right)^2 = E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2$ quadratically spaced energy levels.

Or $\psi_n = A \sin kx$, $kL = n\pi \Rightarrow k = (\pi/L)n$.
 $E_n = k^2 \frac{\hbar^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2$

6.2 Filling of levels "orbitals"

Unlike the phonon case, where all the phonon modes were independently excited by thermal activation, electrons interact strongly via

Pauli Exclusion Principle \Rightarrow two electron / state



Quantum numbers for counting states:

n = principal Q.N. $n > 0$

m_s = 'magnetic' Q.N. $m_s = \pm 1/2$, degenerate here.

Topmost level $n = n_{\text{Fermi}}$ $2n_F = N$, number of electrons

13.02.06 I Fermi Energy = $E_F = \frac{\hbar^2}{2m} \left(\frac{n_F \pi}{L} \right)^2 = \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L} \right)^2$

This is defined as the highest energy filled level of the N -electron system.

$E_F \propto (\text{electron density, } N/L)^2$

6.3 3D case.

3D Schrödinger equation in a cube, $L^3 = V$

$$\Psi_n(\vec{r}) = A \sin\left(\frac{\pi n_x x}{L}\right) \sin\left(\frac{\pi n_y y}{L}\right) \sin\left(\frac{\pi n_z z}{L}\right)$$

As with phonons, it is convenient to use periodic

boundary conditions $\Psi(x, y, z) = \Psi(x+L, y, z)$ etc.

$$\Psi_{\vec{k}}(\vec{r}) = A e^{i\vec{k} \cdot \vec{r}} \quad \vec{k} = \frac{2\pi}{L} (n_x, n_y, n_z)$$

$$E_{\vec{k}} = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

\vec{k} label can be identified in quantum mechanics with the momentum of the electron.

Momentum operator $\vec{P} = -i\hbar \vec{\nabla}$ $\vec{\nabla} = \left(\frac{d}{dx} \frac{d}{dy} \frac{d}{dz} \right)$

$\vec{P} \psi = -i\hbar \vec{k} A e^{i\vec{k} \cdot \vec{r}} = \hbar \vec{k} \psi$

(eigen) value of momentum.

Filling of levels, as before. Since energy is proportional to k^2 , they fill in shells from the origin, up to a maximum radius k_{Fermi} .

$$2 \cdot \underbrace{\frac{4}{3} \pi k_F^3}_{\text{vol. Sphere}} / \underbrace{\left(\frac{2\pi}{L} \right)^3}_{\text{vol of one state}} = N = \frac{V}{3\pi^2} k_F^3$$

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

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

Don't forget the degeneracy! 2x phonon result.

Nice result that k_F depends only on $\frac{N}{V}$ = density of atoms
Typical numbers, derived from density. ($SI \times 10^6$)

(Valency=1)	Sodium	Copper
Electron density	$2.65 \times 10^{28} \text{ m}^{-3}$	$8.45 \times 10^{28} \text{ m}^{-3}$
k_F wavevector	$9.2 \times 10^9 \text{ m}^{-1}$	$13.6 \times 10^9 \text{ m}^{-1}$
'u' wavelength	0.68 nm	0.46 nm
Fermi velocity	$1.07 \times 10^6 \text{ m/s}$	$1.57 \times 10^6 \text{ m/s}$
Fermi energy	3.23 eV	7.0 eV

So we see the first-principles consideration, assuming only $m = \text{mass of electron}$, yields outer electron states with $\left\{ \begin{array}{l} \text{wavelength} \approx \text{spacing} \\ \text{energy} \approx \text{binding energy} \end{array} \right.$

- Big contribution to binding energy $E_F \approx \text{ionisation energy}$.
- Energy increases with density: this is the Pauli repulsion we discussed before.

6.4 Thermal excitation.

Thermal energy 0.025 eV cannot affect the deepest electrons, only those near E_F .

Deepest states, all filled, are inaccessible - just like "core" electrons of atoms.

Electrons are 'Fermions', which obey the statistical law of the Fermi-Dirac distribution:

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}$$

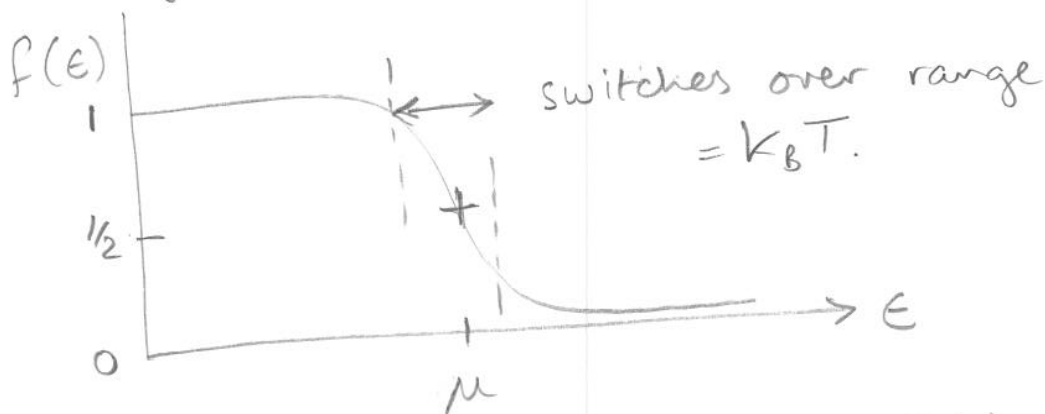
[was a "-" sign in the Planck dist. for bosons]

There is a new parameter in this function,

16.02.09 II $\mu = \text{Chemical potential.}$

Bosons could be created and destroyed, but fermions are conserved particles, so they are supplied by a "reservoir" at energy μ .

μ can be thought of as a normalization parameter to adjust the "zero" of the Schrödinger equation that sets baseline energy.

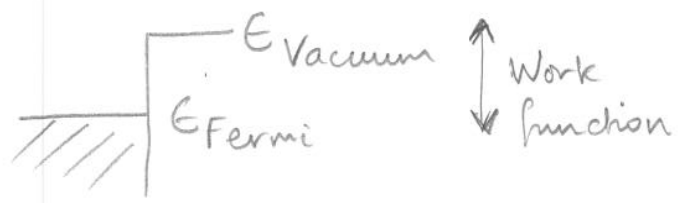
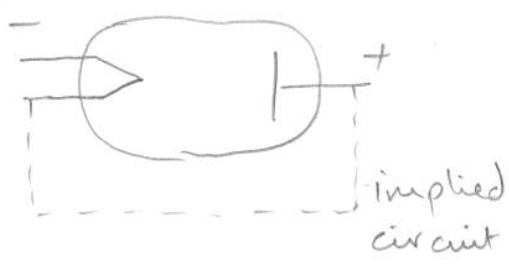


At finite $T > 0$, $f(\epsilon)$ will determine which energy levels are filled and which are empty.

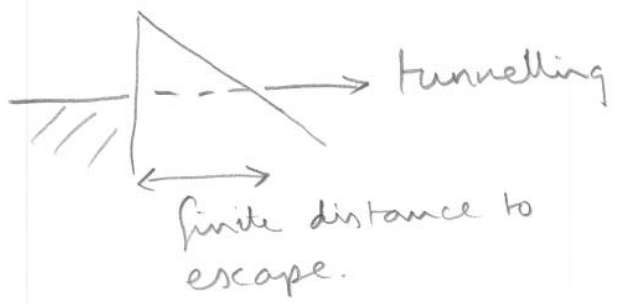
We can see $\mu \approx E_F$ is the cutoff, but the exact relation that sets μ will need to consider "density of states," as with phonons.

6.5 Work Function

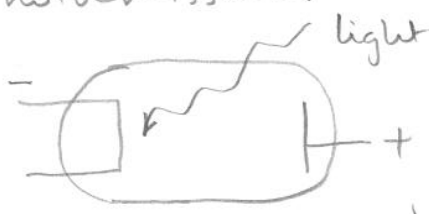
i) Field emission from a sharp tip.



With large applied field gradient (eg at a tip):



ii) Photoemission.



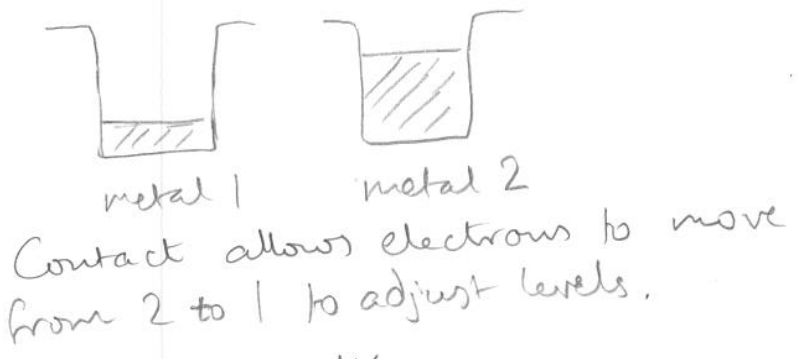
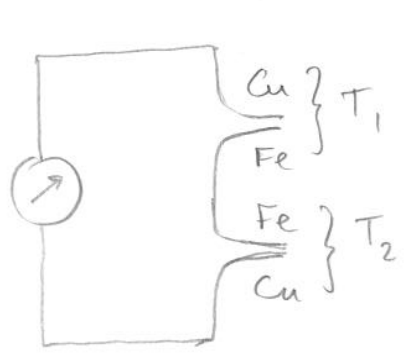
Small voltage applied to collect current (and to analyse energy distribution of emitted electrons)

Best cathode material is Cs with WorkFunction $\sim 1\text{eV}$.

Quantum efficient process: 1 electron for 1 photon
So makes very sensitive photodetector.

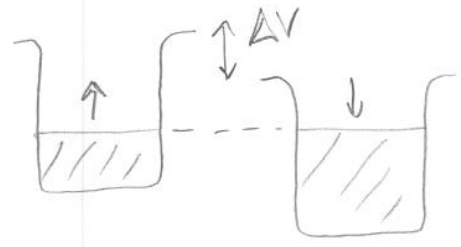
Interpretation by Einstein in 1905 (Nobel prize)

iii) Contact potential when 2 metals are joined to make a thermocouple



Contact allows electrons to move from 2 to 1 to adjust levels.

ΔV is offset after charge redistribution.



$\Delta V(T)$ gives measured thermo-voltage.

Answer EVERY question from section A and TWO questions from section B.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

Mass of the electron	m_e	=	9.11×10^{-31}	kg
Charge on the electron	e	=	-1.602×10^{-19}	C
Permittivity of free space	ϵ_0	=	8.854×10^{-12}	F m ⁻¹
Bohr magneton	μ_B	=	9.273×10^{-24}	J T ⁻¹
Boltzmann's constant	k_B	=	1.38×10^{-23}	J K ⁻¹
Planck's constant/ 2π	\hbar	=	1.05×10^{-34}	J s

SECTION A

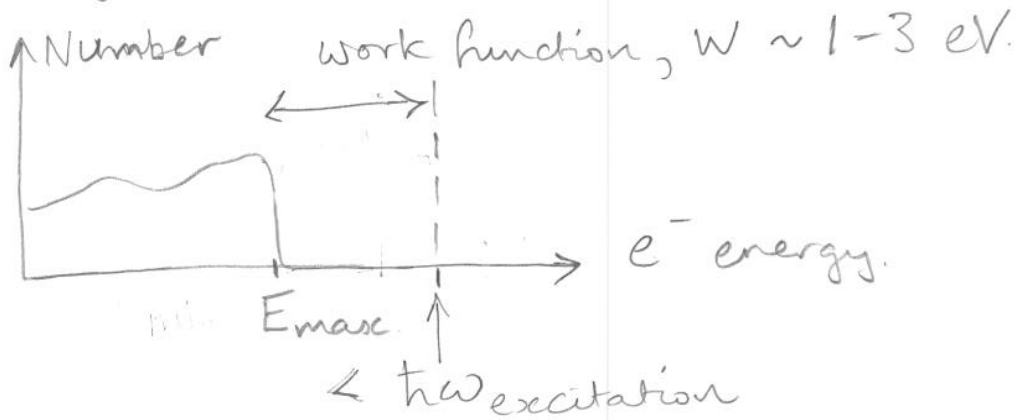
[Part marks]

1. For an ionic solid, give an equation describing the interaction between any two ions at long range. Define any symbols you use. [3]
If the crystal structure is held fixed, but the lattice constant is increased by 1%, does the strength of the interaction increase or decrease? By how much? [4]
2. With the aid of a sketch, show that packing of spheres with the minimum of empty space between them can form a crystal lattice which obeys the definition of the hexagonal crystal system. [4]
For this "hexagonal close-packed" lattice, determine the ratio of the a and c lattice constants. [3]
3. In a free electron metal, why is it not possible for all the electrons to have the same energy? [4]
Imagine shining light on a piece of this metal. Suppose the wavelength of the light is varied, starting from a large value and gradually becoming smaller. At a certain value electrons begin to be emitted from the metal. Sketch the variation of the maximum kinetic energy of emitted electrons against the wavelength of the incident light. [3]

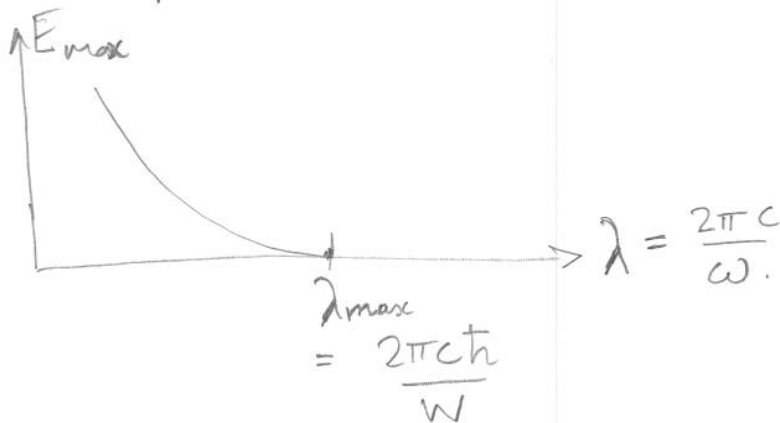
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Photoemission notes:

Energy distribution seen:



Vary excitation energy:



6.6 Electron Heat Capacity.

A major success of this formalism of Fermi was that it could explain the excess (over phonons) heat capacity of metals. $C_V \ll k_B N_{\text{electrons}}$ however. as for a classical gas.

Ingredients of theory of free-electron gas:

i) Fermi-Dirac distribution (temperature)

ii) $\epsilon = \frac{\hbar^2}{2m} k^2$ free electrons.

iii) $N = (V/3\pi^2) k^3$ total number of electrons.

The total number of electrons inside a (variable) radius of k is:

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

$$D(\epsilon) = \frac{dN}{d\epsilon} = \left(\frac{V}{3\pi^2}\right) \frac{3}{2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} = \frac{3N}{2\epsilon}$$

The density of states increases slowly as $\epsilon^{1/2}$.
Total electron energy:

$$U = \int_0^\infty \epsilon D(\epsilon) f(\epsilon) d\epsilon$$

We don't know μ , but that defines ϵ_F :

$$N \equiv \int_0^\infty D(\epsilon) f(\epsilon) d\epsilon = \int_0^{\epsilon_F} D(\epsilon) d\epsilon \quad \leftarrow T=0 \text{ case}$$

We need a few approximations. Mostly $T \ll T_F$ meaning $k_B T \ll \epsilon_F$ which is very safe $T_F \sim 10^4 \text{K}$

Then $\mu \approx \epsilon_F = \text{constant}$.

$$f(\epsilon) \approx \frac{1}{e^{(\epsilon - \epsilon_F)/k_B T} + 1} \quad \text{contains the } T\text{-dependence of } U, \text{ which gives } C_V.$$

Want to write as a standard integral:

$$f(\epsilon) = \frac{1}{e^x + 1} \quad \text{where } x = (\epsilon - \epsilon_F)/k_B T.$$

$$U = N\epsilon_F = \int_0^\infty (\epsilon - \epsilon_F) D(\epsilon) f(\epsilon) d\epsilon$$

$$C_V = \frac{\partial U}{\partial T} = \int_0^\infty (\epsilon - \epsilon_F) D(\epsilon) \frac{\partial f}{\partial T} d\epsilon$$

$$\frac{\partial f}{\partial T} = \frac{e^x}{(e^x + 1)^2} \frac{(\epsilon - \epsilon_F)}{k_B T^2} \quad \text{mixing variations} \quad \left[\frac{\partial f}{\partial T} = \frac{\partial f}{\partial x} \frac{\partial x}{\partial T} \right]$$

this is only large near $\epsilon = \epsilon_F$ or $-1 < x < 1$,
 so we can approximate $D(\epsilon) \approx D(\epsilon_F) = \text{const}$

$$C_V = D(\epsilon_F) \int_0^\infty \frac{e^x}{(e^x + 1)^2} \frac{(\epsilon - \epsilon_F)^2}{k_B T^2} d\epsilon \quad \leftarrow dx = \frac{d\epsilon}{k_B T}$$

$$= k_B^2 T D(\epsilon_F) \int_{-\frac{\epsilon_F}{k_B T}}^\infty \frac{e^x}{(e^x + 1)^2} x^2 dx$$

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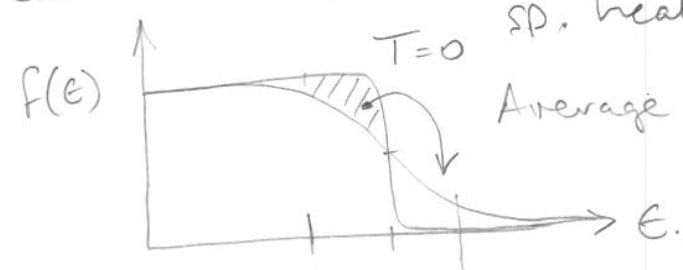
The standard integral is $\pi^2/3$, so we are done.
 $\frac{-\epsilon_F}{k_B T} \leftarrow$ same as $-\infty$ since $\epsilon_F \gg k_B T$

13.02.07

$$C_V = \frac{\pi^2}{3} k_B^2 T D(\epsilon_F) = \frac{\pi^2}{3} k_B^2 T \frac{3N}{2\epsilon_F} = \frac{\pi^2}{2} k_B^2 T \frac{N}{\epsilon_F}$$

The important result is $C_V \propto T$ for electrons. $\sim \frac{k_B T}{\epsilon_F} N k_B$

i) Qualitative picture of electronic sp. heat: Small fraction of $N k_B$.



Average energy of these electrons is higher due to T .

No. of promoted electrons $\sim \text{area} \sim k_B T$
 Average increase of energy $\sim k_B T$
 $\Delta U \sim (k_B T)^2$

If $U \sim (k_B T)^2$, then $\partial U / \partial T \sim k_B^2 T$ as found.

ii) Experimental result. electrons phonons (Debye)

$$C_V = \gamma T + AT^3 \Rightarrow \frac{C_V}{T} = \gamma + AT^2$$

see by plotting C_V/T vs T^2 and look for intercept.
 Linear coef $\gamma \sim 1/\epsilon_F$ of m_e no other unknowns.

Define "thermal effective mass" m_{th} .

$$\frac{m_{th}}{m_e} = \frac{\gamma(\text{observed})}{\gamma(\text{free electron})} = 1.26, 1.4, 1.4, 2.0$$

(Na) (Cs) (Cu) (Pb)

"Heavy Fermion" metals have $m_{th} \sim 10^3 m_e$.
 indicates breakdown of free-electron picture.

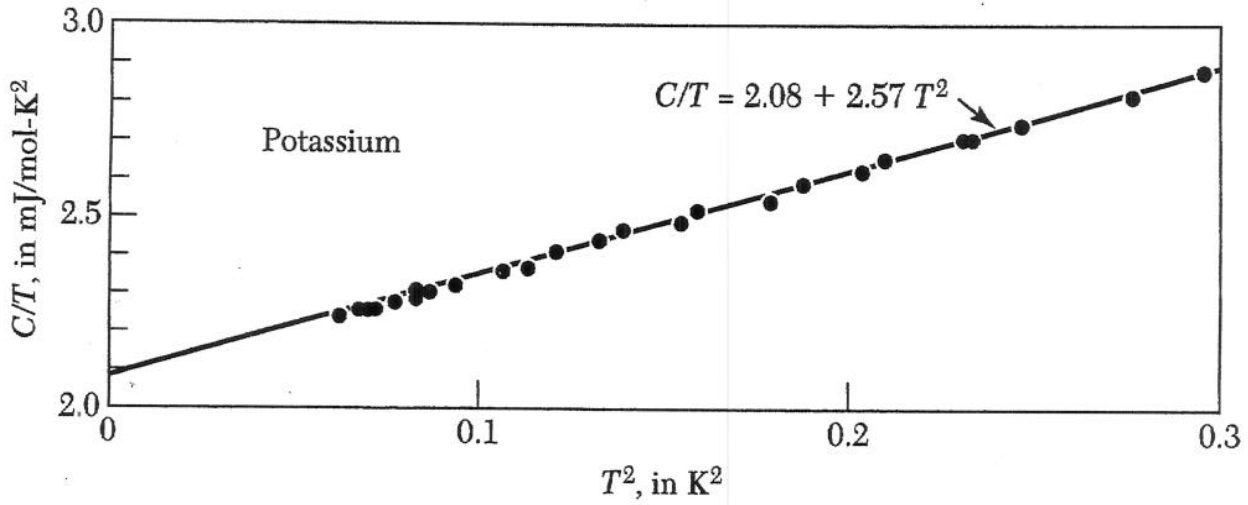


Figure 9 Experimental heat capacity values for potassium, plotted as C/T versus T^2 . (After W. H. Lien and N. E. Phillips.)

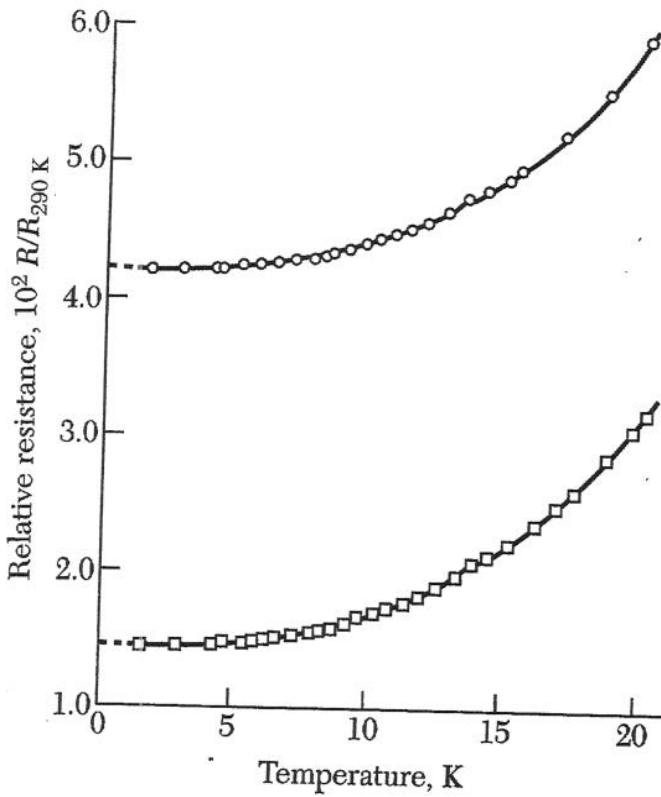


Figure 12 Resistance of potassium below 20 K, as measured on two specimens by D. MacDonald and K. Mendelssohn. The different intercepts at 0 K are attributed to different concentrations of impurities and static imperfections in the two specimens.

Table 5 Experimental Lorenz numbers

$L \times 10^8$ watt-ohm/deg ²			$L \times 10^8$ watt-ohm/deg ²		
Metal	0°C	100°C	Metal	0°C	100°C
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Su	2.52	2.49
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

6.7 Electrical Conduction

Apply an electromagnetic field:

$$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B}) \quad \text{Lorentz force.}$$

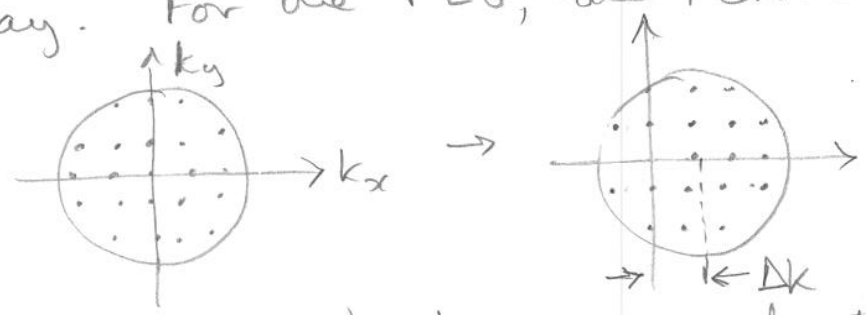
ignore magnetic part for now.

$$= m \frac{d\vec{v}}{dt} = \hbar \frac{d\vec{k}}{dt} \quad \text{Newton's law.}$$

Integrating for a time t :

$$\Delta \vec{k} = -\frac{e\vec{E}}{\hbar} t \quad \text{or} \quad \Delta \vec{v} = \frac{-e\vec{E}}{m} t$$

All electrons are affected in exactly the same way. For the FEG, the Fermi sphere shifts



field along x direction.

We have raised the energy of the system by depopulating on left and adding on right. Reset by collisions (inelastic) that allow electrons to repopulate lower-lying orbitals:

- i) impurities or defects.
- ii) phonons eg umklapp.

rate = $1/\tau$

Characteristic lifetime $t = \tau$, after which the Fermi sphere is reset, on average. Net displacement of all states gives current density

$$\vec{J} = n \quad q \quad \langle \vec{v}_x \rangle$$

(A/m²) (m⁻³) (-e) average velocity (m/s).

$$= -ne \left(\frac{-e\vec{E}}{m} \tau \right) = \frac{ne^2 \tau}{m} \vec{E}$$

This is Ohm's Law. Conductivity $\sigma = \frac{ne^2 \tau}{m}$

$$\vec{J} = \sigma \vec{E}$$

14.02.06

(60)

The dissipation is due to the inelastic collisions which release heat at rate $1/\tau$.

Fermi sphere remains shifted, with a continuous flow of electrons being scattered.

$$\text{Resistivity: } \rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} = \frac{m}{ne^2} \left(\frac{1}{\tau_i} + \frac{1}{\tau_p} \right)$$

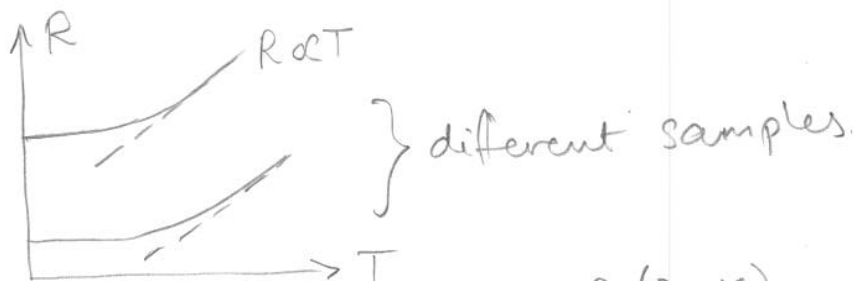
$$\rho = \rho_i + \rho_p \text{ Matthiesen's rule}$$

Matthiesen's rule assumes impurity and phonon scattering rates are independent.

Useful for interpretation of experimental data:

ρ_i = "residual resistivity" sample dependent

ρ_p = T-dependent part, goes away at $T=0$



$$\text{"Resistivity Ratio"} = \frac{R(300K)}{R(0K)} = \frac{\rho_i + \rho_p}{\rho_i}$$

Ratio ~ 1000 for pure samples
 < 10 for certain alloys.

18.02.08 II

can be as high as 10^6 , when size-dependent effects kick in.

Electron-phonon interaction responsible for τ_p :
 (\vec{k}) (\vec{q}) conserves momentum, not energy.

$$\vec{k}' = \vec{k} + \vec{q}$$

$$\vec{k}' = \vec{k} + \vec{q} + \vec{G}$$

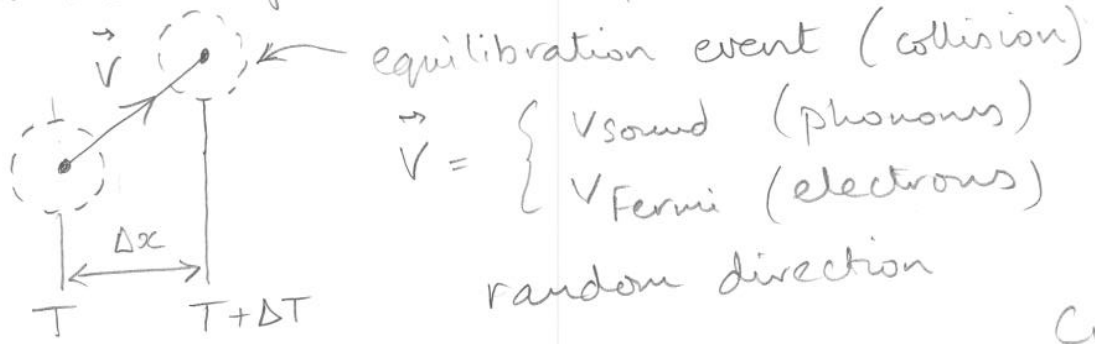
e-p scattering, rate $\propto T$ (Debye)
unklapp. faster rate

Difficult to calculate, requires lattice not FEG.

(61)

6.8 Thermal Conductivity of Metals.

Identical argument for phonons or electrons.



Particle carries energy $c \Delta T$ where $c = \frac{C_V}{n}$

$$\Delta T = \frac{dT}{dx} \Delta x = \frac{dT}{dx} v_x \tau$$

τ ← x-component (e/volume)

Heat Flow per unit area:

$$j_V = n \quad c \Delta T \quad \langle v_x \rangle = n c \langle v_x \rangle^2 \tau \frac{dT}{dx}$$

(density) (heat) (velocity)

This is the definition of therm. cond: κ

$$\kappa = n c \langle v_x \rangle^2 \tau = C_V \frac{1}{3} v^2 \tau = \frac{1}{3} C_V v l$$

19.02.07 I

where $l = v \tau$ is mean free path travelled between collisions.

Substituting our earlier result for C_V :

$$C_V = \frac{\pi^2}{2} k_B^2 T \frac{n}{E_F} \quad E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{(mv_F)^2}{2m} = \frac{1}{2} m v_F^2$$

$$\kappa = \frac{1}{3} \frac{\pi^2}{2} k_B^2 T \frac{n}{\frac{1}{2} m v_F^2} v_F^2 \tau = \frac{\pi^2}{3} \frac{k_B^2 T \tau}{m} n$$

In metals, this is much larger than the phonon contribution, which can be neglected.

$\kappa_{\text{metals}} \gg \kappa_{\text{insulators}}$ generally

Exception: disordered / amorphous metals which are more like insulators.

6.9 Wiedemann-Franz Law. (1853)

Experimental observation that the ratio of thermal to electrical conductivity is same for all metals.

+ proportional to temperature. (Lorenz, 1872).

This follows from our theory if we assume:

i) carriers of heat and electricity are electrons

ii) scattering rate is the same $1/\tau = 1/\tau_i + 1/\tau_p$

$$\frac{\kappa}{\sigma} = \frac{\frac{\pi^2}{3} k_B^2 T \cdot \frac{\tau n}{m}}{e^2 \frac{\tau n}{m}} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 T = LT$$

L is called the Lorenz number (1872).

$$= 2.45 \times 10^{-8} \text{ Watt-Ohm/deg}^2$$

2.31	Ag
2.23	Cu
2.61	Mo
2.47	Pb
3.04	W (worst case)

hardly any change with temperature (2%/100K)

This proves the common origin of the electrical and thermal conductivities of metals.

→ Application: Thermoelectric effect
Peltier cooler.

20.02.06 I.

Deviations From Wiedemann-Franz:

23.02.09 I

$$\tau_{\text{heat}} \neq \tau_{\text{elect}}$$

Energy relaxation \neq Momentum relaxation