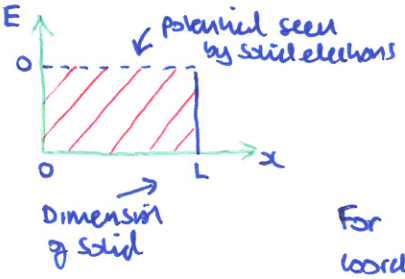
SOLID STATE PHYSICS

1) The free electron model

* Solid made up of many atoms bound together by their mutual interactions. Electrons in a solid can be divided into two types (i) CORE electrons – tightly bound to the nucleus (ii) VALENCE electrons – not tightly bound to nucleus and participate in electrostatic interactions which lead to the bonding of solid atoms. In the free electron model we assume VALENCE electrons to behave as a fermi gas and ignore $e^- - e^-$ and e^- – nucleus interactions. The reason this works for simple metals is that we model these interactions via a constant electrostatic potential.



– Schrödinger equation (Time independent) for ith free electron is $-\frac{\hbar^2}{2m_e}\nabla^2\Phi_i = E_i\Phi$ (we set potential to zero) – arbitrary choice since constant

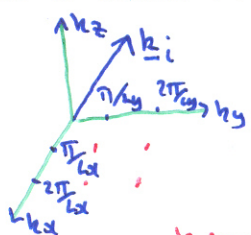
Solutions are travelling waves $\Phi_i = \frac{1}{\sqrt{V}} e^{i\underline{k}\cdot\underline{r}}$ V = solid volume.

$\Rightarrow E_i = \frac{\hbar^2 k_i^2}{2m_e}$ Momentum of electrons is $\langle\Phi_i|\frac{\hbar}{i}\nabla|\Phi_i\rangle = \hbar\underline{k}$

For a cuboid solid of dimensions L_x, L_y, L_z: $\Phi_i = \Phi(x,y,z) = A\sin\left(\frac{l\pi x}{L_x}\right)\sin\left(\frac{m\pi y}{L_y}\right)\sin\left(\frac{n\pi z}{L_z}\right)$ for each coordinate i. $\Rightarrow$

where $n,l,m \in \mathbb{Z}^+$. (Structure of S.E $\Rightarrow$ solution is product of sines of x,y,z respectively. Specific bcs give the quantisation). Allowed values of $k_i = \sqrt{\left(\frac{l\pi}{L_x}\right)^2 + \left(\frac{m\pi}{L_y}\right)^2 + \left(\frac{n\pi}{L_z}\right)^2}$ (k_x^2, k_y^2, k_z^2)

form a lattice in k space with volume / point $= \frac{\pi^3}{L_xL_yL_z} = \frac{\pi^3}{V}$

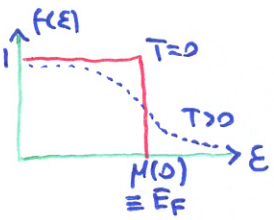


$\therefore$ # states / unit volume of k space is V/π^3

× spin degeneracy $\sigma = 2S+1$ ($=2$ for electron $S=\frac{1}{2}$).

$\therefore$ # electrons $= \frac{\sigma V}{8\pi^3}\int_0^\infty 4\pi k^2 f(E_k)\,dk$ ← occupation # of state k; ← shell of k space; only +ve octant of k space allowed

Now since free electrons are a Fermi gas $f(E_k) = \frac{1}{e^{\frac{E_i-\mu}{k_BT}}+1}$



At T=0, the # electrons in the solid N

$= \frac{\sigma V}{2\pi^2}\int_0^{E_F} k^2\,dk = \frac{\sigma V}{2\pi^2}\int_0^{E_F}\frac{2m_eE}{\hbar^2}\frac{1}{2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{1}{2}}E^{-\frac{1}{2}}dE$

($k = \left(\frac{2m_e}{\hbar^2}\right)^{\frac{1}{2}}E^{\frac{1}{2}}$ $\therefore dk = \frac{1}{2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{1}{2}}E^{-\frac{1}{2}}dE$)

$\Rightarrow N = \frac{\sigma V}{4\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}\int_0^{E_F}E^{\frac{1}{2}}dE$ → This allows us to define DENSITY OF STATES $D(E) = \frac{\sigma V}{4\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}$ s.t. $N = \int_0^\infty f(E)D(E)dE$

$\Rightarrow \frac{4\pi^2N}{\sigma V}\left(\frac{\hbar^2}{2m_e}\right)^{\frac{3}{2}} = \frac{2}{3}E_F^{\frac{3}{2}}$

So FERMI ENERGY $E_F = \frac{\hbar^2}{2m_e}\left(\frac{6\pi^2N}{\sigma V}\right)^{\frac{2}{3}}$

Can also define FERMI WAVEVECTOR $k_F = \left(\frac{2m_e}{\hbar^2}\right)^{\frac{1}{2}}E_F^{\frac{1}{2}} = \left(\frac{6\pi^2N}{\sigma V}\right)^{\frac{1}{3}}$

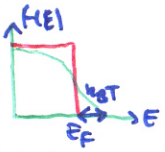
and FERMI TEMPERATURE $T_F = E_F/k_B$

Total energy of solid (well free electrons in solid) $= \int_0^\infty E f(E) D(E)\,dE \equiv U$

At T=0 $f(E) = \begin{cases}1 & E<E_F\\ 0 & E>E_F\end{cases}$ So $U(T=0) = \frac{\sigma V}{4\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}\int_0^{E_F}E^{\frac{3}{2}}dE$

$= \frac{2}{5}\frac{\sigma V}{4\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}E_F^{\frac{5}{2}} = \frac{3}{5}NE_F$ (using N integral above).

Now at finite T $\propto D(E_F)k_BT$ electrons get their energy changed by $\propto k_BT$.

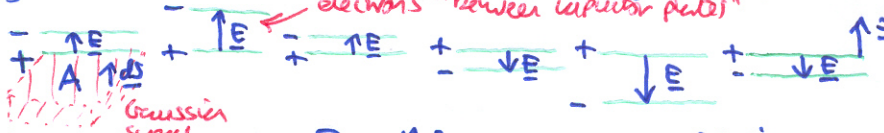


So $U(T) - U(0) \propto D(E_F)k_B^2T^2$ $\Rightarrow$ Heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$\approx \textcircled{2}D(E_F)k_B^2T$ $\Rightarrow C_V \propto \frac{\sigma V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{\frac{3}{2}}E_F^{\frac{1}{2}}k_B^2T$

This is correct in limit $T \ll T_F$ but with ② incorrect not quite right. (See TASP 13 → should be $\frac{\pi^2}{3}$). For metals phonons also contribute to heat capacity but with $\propto T^3$ dependence. So overall $C_V = \gamma T + \alpha T^3$ can find electronic, phonon coefficients by plotting $\frac{C_V}{T}$ vs T^2.

* Plasmons are quantised longitudinal oscillations of the electron gas. Long wavelength plasmon consists of electron gas vibrating as a whole with uniform +ve charge density fixed. - react as an 'oscillating capacitor'



Apply Gauss $\nabla \cdot \underline{E} = \rho_f/\varepsilon_0$ ← no free charges

$\Rightarrow \int_A \underline{E}\cdot d\underline{s} = \frac{ne}{\varepsilon_0} A\underline{x} \Rightarrow EA = \frac{neA\underline{x}}{\varepsilon_0} \Rightarrow \underline{E} = \frac{ne}{\varepsilon_0}\underline{x}$ n = density of electrons.

Now using Lorentz force write down Newton's 2nd law for electron in plasmon:

$-e\underline{E} = m\ddot{\underline{x}} \Rightarrow \ddot{\underline{x}} + \frac{e^2 n}{m\varepsilon_0}\underline{x} = 0$ SHM with frequency $\omega_p^2 = \frac{ne^2}{m\varepsilon_0}$

→ system actually a quantum S.H.O. i.e. energy levels $E_n = (n+\frac{1}{2})\hbar\omega_p$ where $n \in \mathbb{Z}^+$.

* Susceptibility of metals $\chi_M = \frac{M}{H} = \frac{\mu_0 M}{B}$ where M = magnetic moment / unit volume.

DIAMAGNETIC if χ_M -ve

PARAMAGNETIC if χ_M +ve.

Now for PAULI PARAMAGNETISM $M = -\frac{\mu_B}{V}(N_\uparrow - N_\downarrow)$

Bohr magneton $\frac{e\hbar}{2m_e}$ $N_{\uparrow,\downarrow}$ = # electrons with ↑, ↓ spins. Magnetic moment of electron $= \frac{ge}{2m_e} m_s$, $g = 2$, $m_s = \pm\frac{1}{2}$

Now ↑ spins ($\parallel \underline{B}$) lower energy by $\mu_B B$, ↓ spins raise energy by $\mu_B B$.

$\therefore N_\uparrow = \frac{1}{2}\int_{\mu_B B}^{E_F} D(E-\mu_B B)\,dE$ $N_\downarrow = \frac{1}{2}\int_{-\mu_B B}^{E_F} D(E+\mu_B B)\,dE$ ½ for averaging between ↑, ↓

At $T \approx 0$ K

Now consider substitution $x = E - \mu_B B$ for $N_\uparrow$: $N_\uparrow = \frac{1}{2}\int_0^{E_F-\mu_B B} D(x)\,dx$

$\int_0^{E_F-\mu_B B} = \int_0^{E_F} - \int_{E_F-\mu_B B}^{E_F}$ $D(E) \approx D(E_F)$

in limit $\mu_B B \ll E_F \Rightarrow N_\uparrow \approx \frac{1}{2}\int_0^{E_F} D(x)\,dx - \frac{1}{2}\mu_B B D(E_F)$

Similarly for $N_\downarrow \Rightarrow N_\downarrow \approx \frac{1}{2}\int_0^{E_F} D(x)\,dx + \frac{1}{2}\mu_B B D(E_F)$

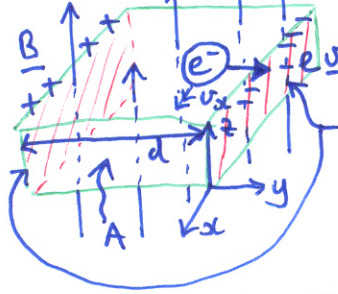
$\therefore M = +\frac{\mu_B^2}{V} B D(E_F)$ so $\chi_M = \frac{\mu_0 \mu_B^2 D(E_F)}{V}$ Note useful result $D(E_F) = \frac{3N}{2E_F}$

for free electrons. Prog: $D(E_F) = \frac{\sigma V}{4\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E_F^{1/2}$ $E_F = \frac{\hbar^2}{2m_e}\left(\frac{6\pi^2 N}{\sigma V}\right)^{2/3}$

Now $E_F^{-3/2} = \left(\frac{2m_e}{\hbar^2}\right)^{3/2}\frac{\sigma V}{6\pi^2 N}$ so $\frac{3}{2}N E_F^{-3/2} = \left(\frac{2m_e}{\hbar^2}\right)^{3/2}\frac{\sigma V}{4\pi^2}$ $\therefore D(E_F) = \frac{3}{2}N E_F^{-1}$ QED.

Note: χ_M above is not quite right – doesn't take into account motion due to magnetic fields (in general a precession about).

* Hall Effect



Lorentz force on electron moving in uniform magnetic field $\underline{B} = B_z\hat{\underline{z}}$ with velocity $v_x\hat{\underline{x}}$ is $-e\underline{v}\times\underline{B} = ev_x B_z\hat{\underline{y}}$ → results in pile up of charge on surfaces which creates an $\underline{E}$ field $\underline{E} = E_y\hat{\underline{y}}$. So net force $\parallel \hat{\underline{y}}$ is reduced by eE_y until eq is reached ($F_y = 0$) when $E_y = v_x B_z$

Now current density $\underline{j}_x = -nev_x\hat{\underline{x}} = j_x\hat{\underline{x}}$ and current I is Aj_x. Now HALL VOLTAGE $= E_y d = V_H$

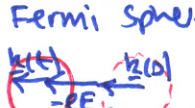
$\therefore -ne = j_x/v_x = \frac{j_x B_z}{E_y} = j_x B_z d/V_H$ Define Hall coefficient $R_H = \frac{1}{-ne}$

So $V_H = j_x B_z d R_H$

* D.C. Electrical conductivity Electrons can be described as wavepackets of solutions to S.E. centered on a well defined mean $\underline{k}$ vector $\underline{k}$ at location in real space $\underline{r}$. Now subject to an electric field $\underline{E}$ $-e\underline{E} = m_e\frac{d^2\underline{r}}{dt^2} = m_e\frac{d\underline{v}}{dt}$

Now $m_e\underline{v} = \hbar\underline{k}$ so $-e\underline{E} = \hbar\frac{d\underline{k}}{dt} \Rightarrow \underline{k}(t) = \underline{k}(0) - e\underline{E}t/\hbar$

i.e. Fermi sphere of each electron moves in k space with velocity $-e\underline{E}/\hbar$

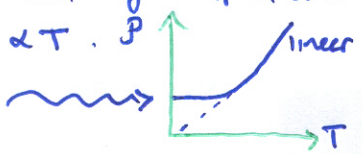


After time τ (average) assume phonon / lattice impurity / imperfection scattering event occurs $\Rightarrow$ eq. $\Delta\underline{k} \approx -\frac{e\underline{E}\tau}{\hbar}$

This corresponds to real space velocity change $\Delta v = \frac{\hbar}{m_e}\Delta k = -\frac{eE\tau}{m_e}$
which gives rise to current density $j = -en\Delta v = \frac{e^2 n E \tau}{m_e}$ Now $j = \sigma E$
$\Rightarrow$ conductivity $\sigma = ne^2\tau/m_e$

*Temperature dependence of σ e^--phonon and e^--defect collision rates $(1/\tau)$ are $\approx$ independent so $\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_d}$. Now since resistivity $\rho = \frac{1}{\sigma}$ and $\sigma \propto \tau$ from above $\Rightarrow \rho = \rho_{ph} + \rho_d$ MATTHEISSEN'S RULE

Now $\tau_d \approx$ independent of temperature whereas at high T # phonons / unit volume $\approx \propto T$ so $\rho_{ph} \propto T$.



*Wiedmann Franz ratio and Lorentz number

Kinetic Theory $\Rightarrow$ Thermal conductivity $\kappa = \frac{1}{3}\lambda C_V v_F / V$
λ = mean free path $= v_F\tau$
$v_F = \sqrt{2E_F/m}$ "Typical electron velocity"

Now derived above, $C_V = \frac{\pi^2}{3} D(E_F) k_B^2 T/V$
$= \frac{\pi^2}{2} k_B^2 n \frac{T}{E_F}/V$ using $D(E_F) = \frac{3N}{2E_F}$

Now since $\sigma = \frac{ne^2}{m_e}\frac{\lambda}{v_F} \Rightarrow \frac{\kappa}{\sigma} = \frac{1}{3}\lambda\frac{\pi^2}{2}k_B^2\frac{n}{E_F}T\,\frac{v_F}{1}\,\frac{m_e}{ne^2\lambda}\,\frac{v_F}{1}\,E_F$

WIEDMANN FRANZ LAW $\frac{\kappa}{\sigma} \propto T$

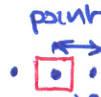
$\Rightarrow \frac{\kappa}{\sigma} = \frac{\pi^2 k_B^2}{3e^2} T$ Define LORENTZ # $L = \frac{\kappa}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2}$ $(= 2.44 \times 10^{-8}\,J\,s^{-1}\,K^{-2})$

2) Electrons in a periodic potential - "nearly free electron theory"
Instead of $V(x)$ being constant - let it be periodic to reflect periodicity of lattice of solid. [use lattice parameter a for primitive cubic lattice]. - consider 1D case to yield insight.



Let $V(x) = -2V\cos\left(\frac{2\pi x}{a}\right)$ i.e. when $x = Na$ $(N \in \mathbb{Z})$ - minimum in potential
$\therefore$ S.E becomes $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Phi(x) - V\left(e^{i\frac{2\pi x}{a}} + e^{-i\frac{2\pi x}{a}}\right)\Phi(x) = E\Phi(x)$ $q = k - \frac{\pi}{a}$

Let $\Phi_q(x) = Ae^{i(\frac{\pi}{a}-q)x} + Be^{-i(\frac{\pi}{a}+q)x}$ where q is a parameter measuring the deviation from the BRILLOUIN ZONE (1st primitive constructed by drawing $\perp$ bisectors between at lattice point chosen to be the origin of RECIPROCAL SPACE and all surrounding lattice points)

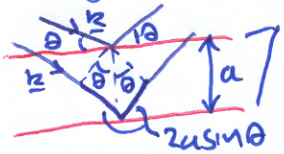


Note when $k = \frac{\pi}{a} \Rightarrow$ condition for 'Bragg reflection.

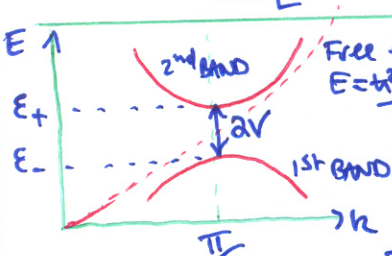
Solution for $E(k)$ and $E(q)$ are:

$$E(q) = \frac{\hbar^2}{4m_e}\left[\left(\frac{\pi}{a}-q\right)^2 + \left(\frac{\pi}{a}+q\right)^2\right] \pm \frac{1}{2}\sqrt{\frac{\hbar^4}{4m_e^2}\left[\left(\frac{\pi}{a}-q\right)^2 - \left(\frac{\pi}{a}+q\right)^2\right]^2 + 4V^2}$$

$$E(k) = \frac{\hbar^2}{4m_e}\left[\left(\frac{2\pi}{a}-k\right)^2 + k^2\right] \pm \frac{1}{2}\sqrt{\frac{\hbar^4}{4m_e^2}\left[\left(\frac{2\pi}{a}-k\right)^2 - k^2\right]^2 + 4V^2}$$

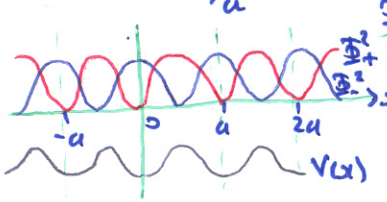


constructive interference if $N\lambda = 2a\sin\theta$ $N \in \mathbb{Z}$
$\Rightarrow \frac{2\pi N}{k} = 2a\sin\theta$
$\Rightarrow \frac{\pi N}{ka} = \sin\theta$
if $k = N\pi/a \Rightarrow \sin\theta = 1$
i.e. reflection.



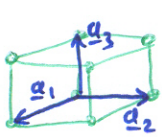
when $q = 0$, or $k = \pi/a$
$\varepsilon_+ = \frac{\hbar^2\pi^2}{2ma^2} + V$ $\varepsilon_- = \frac{\hbar^2\pi^2}{2ma^2} - V$

Eigenstates corresponding to these energies (well the two roots of $E(k)$) are $\Phi_+(x) = \sin\left(\frac{\pi x}{a}\right)$ $\Phi_-(x) = \cos\left(\frac{\pi x}{a}\right)$ charge density $\propto \Phi_\pm\Phi_\pm^*$ plotted below.



$\rightarrow \Phi_+^2$, peaks match peaks of $V(x) \Rightarrow$ higher P.E.
$\rightarrow$ MAJOR feature to note is BAND GAP between energy levels.

3) The Reciprocal Lattice, Bloch's Theorem



-Translation vectors of the crystal lattice $\underline{R} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$ $n_i \in \mathbb{Z}$
-Crystal potential has lattice periodicity $V(\underline{r}+\underline{R}) = V(\underline{r})$
$\Rightarrow$ write $V(\underline{r})$ as a fourier series $V(\underline{r}) = \sum_{\underline{G}} V(\underline{G})e^{i\underline{G}\cdot\underline{r}}$

SS ③

what is G? well $\sum_G v(G) e^{iG\cdot(r+R)} = \sum_G v(G) e^{iG\cdot r}$ by periodicity.

$\Rightarrow G\cdot R = 2\pi N \quad \forall R$ where $N \in \mathbb{Z}$. can show if $G = m_1 b_1 + m_2 b_2 + m_3 b_3$

where $b_1 = \frac{2\pi a_2 \times a_3}{a_1 \cdot a_2 \times a_3}$ $b_2 = \frac{2\pi a_3 \times a_1}{[a_1, a_2, a_3]}$ $b_3 = \frac{2\pi a_1 \times a_2}{[a_1, a_2, a_3]}$ and $m_1, m_2, m_3 \in \mathbb{Z}$ this is satisfied.

Same

G is a 'reciprocal lattice vector' when m_1 or m_2 or $m_3 = 1$ and the others 0 marks out 1st Brillouin zone.

* Bloch's Theorem - charge density must be the same in each unit cell of a crystal lattice i.e. $|\Phi(r+R)|^2 = |\Phi(r)|^2 \Rightarrow \Phi(r+R) = e^{if(R)}\Phi(r)$ $f(R)$ phase factor.

Bloch's theorem states that if $f(R)$ is linear in R it must $= k.R$ where k is wavevector of eigenstate Φ. So $\Phi(r+R) = e^{ik.R}\Phi(r)$

* Volume of a Brillouin zone volume of reciprocal space bounded by B.Z

is $|b_1 \cdot (b_2 \times b_3)| = \frac{(2\pi)^3}{|a_1 \cdot (a_2 \times a_3)|^3} |(a_2 \times a_3) \cdot [(a_1 \times a_3) \times (a_1 \times a_2)]|$

$\Rightarrow |b_1 \cdot (b_2 \times b_3)| = \frac{(2\pi)^3}{|a_1 \cdot (a_2 \times a_3)|} = \frac{(2\pi)^3}{\text{volume of unit cell.}}$

Now $(a_2 \times a_3) \times (a_1 \times a_2)$
$= [(a_1 \times a_2) \cdot a_1] a_3 = 0$
$- [(a_1 \times a_2) \cdot a_3] a_2$
$= -a_1 [a_1 \cdot (a_2 \times a_3)]$

* Allowed values of k consider crystal made up of $N = N_1 N_2 N_3$ unit cells.

i.e N_i in a_i direction. - B.C.'s on Φ at surface are $\Phi(r + N_i a_i) = \Phi(r)$ $i = 1,2,3$

Must also obey Bloch condition: $\Phi(r + N a_i) = e^{ik.N_i a_i}\Phi(r)$

$\Rightarrow k.N_i a_i = 2\pi m_i$ where $m_i \in \mathbb{Z}$ similar to condition for G

i.e $k_i = G_i / N_i$ or $k = \frac{m_1}{N_1} b_1 + \frac{m_2}{N_2} b_2 + \frac{m_3}{N_3} b_3$

Volume / k vector is $\frac{b_1}{N_1} \cdot \frac{(b_2 \times b_3)}{N_2 N_3} = \frac{(2\pi)^3}{\#\text{ unit cells} \times \text{volume of unit cell}}$

$= \frac{(2\pi)^3}{\text{volume of crystal}}$ $\Rightarrow$ # k vectors / BZ = # unit cells.

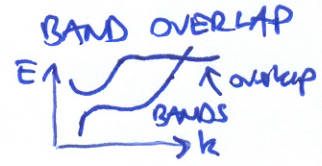
Each state can have at most two electrons $(\uparrow, \downarrow)$ so Full BZ

(All k states occupied) $\Rightarrow$ 2 e^- / unit cell.

So..... Full bands $\Rightarrow$ no free states $\Rightarrow$ insulator unless (Higher E bands are lower in E than bp of lower E bands

NOT FULL (i.e # e^- / unit cell = 1) $\Rightarrow$ METAL.

BAND OVERLAP



4) Conservation of energy and crystal momentum

In phonon interactions and scattering processes energy is conserved

i.e $\sum_i \hbar\omega_i = \sum_f \hbar\omega_f$ and so is CRYSTAL MOMENTUM (to the nearest of a reciprocal lattice vector)

i.e $\sum_i \hbar k_i = \sum_f \hbar k_f + \hbar G$ Note crystal momentum differs from linear 'normal' momentum in the sense that any state where Bloch's theorem applies is not an eigenstate of $\frac{\hbar}{i}\nabla$ like solutions to S.E for a constant potential. ($\hbar k$ is not the expectation value).

Note: Electronic transitions between energy bands occur via PHOTON OR PHONON events.

→ PHOTONS appear vertical (high E, small Δk)
PHONONS appear horizontal (small E, high Δk)



5) Electron Dynamics - Think of electron as a wave packet with mean wavevector $\underline{k}$ and position $\underline{r}$. Assume $\underline{E}$ and $\underline{B}$ fields vary slowly over size of wave packet ⇒ dynamics of electron can be described by classical equations of motion.

For free electron $\underline{p} = \hbar\underline{k} \Rightarrow \underline{v} = \hbar\underline{k}/m$ For Bloch electron of energy $E(k)$

$\underline{v}(k) = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k}\hat{k}$ (Quoted result). $\therefore \frac{d\underline{v}}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{\partial E(k)}{\partial k}\right)\hat{k} = \frac{1}{\hbar}\frac{\partial^2 E}{\partial k^2}\frac{dk}{dt}\hat{k}$

$= \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}\hbar\frac{d\underline{k}}{dt}$ Now Lorentz force is still valid but 'Force = rate of change of crystal momentum $\hbar\underline{k}$ i.e. $\hbar\frac{d\underline{k}}{dt} = -e(\underline{E} + \underline{v}\times\underline{B})$

So by Newton's 2nd law $\underline{F} = m^*\underline{a}$ ($\hbar\frac{d\underline{k}}{dt}$ = effective mass, $\frac{d\underline{v}}{dt}$) $\Rightarrow m^* = \hbar^2/\frac{\partial^2 E}{\partial k^2}$ Effective mass of Bloch electron.

→ So Bloch electrons behave like free electrons but with mass m^*. (can use all results of free electron theory (v, σ etc....) (often $\gg m_e$). → Though $\underline{k}$ vectors constrained to Brillouin zone.

6) Holes A singly electron deficient band responds to $\underline{E}$ and $\underline{B}$ fields as if it was a single hole. If properties of the electron used to fill the band are characterised by $-e$, ε_e, $\underline{k}_e$, $\underline{v}_e$, m_e^* Turns out:

Electron	Hole
$-e$	e
ε_e	$-\varepsilon_e$
$\underline{k}_e$	$-\underline{k}_e$
$\underline{v}_e$	$\underline{v}_e$
m_e^*	$-m_e^*$

Proof

Total charge $Q = \sum_{f.b}(-e) - (-e) = \sum_{f.b}(-e) + q_h \Rightarrow q_h = e$

Total energy $E = \sum_{full\,band} \varepsilon_i - \varepsilon_e = \sum_{f.b}\varepsilon_i + \varepsilon_h \Rightarrow \varepsilon_h = -\varepsilon_e$

$\underline{K} = \sum_{f.b}\underline{k}_i - \underline{k}_e = \sum_{f.b}\underline{k}_i + \underline{k}_h \Rightarrow \underline{k}_h = -\underline{k}_e$

Total current $\underline{I} = -e\sum_{f.b}\underline{v}_i - (-e)\underline{v}_e = -e\sum_{f.b}\underline{v}_i + (+e)\underline{v}_h \Rightarrow \underline{v}_h = \underline{v}_e$

$\frac{d\underline{I}}{dt} = -e\sum_{f.b}\frac{d\underline{v}_i}{dt} - (-e)\frac{d\underline{v}_e}{dt} = -e\sum_{f.b}\frac{d\underline{v}_i}{dt} - (-e)\frac{1}{m_e^*}\hbar\frac{d\underline{k}_e}{dt}$

$= -e\sum_{f.b}\frac{d\underline{v}_i}{dt} + (+e)\frac{1}{m_h^*}\hbar\frac{d\underline{k}_h}{dt}$ so since $\frac{d\underline{k}_h}{dt} = -\frac{d\underline{k}}{dt}$

$\Rightarrow m_e^* = -m_h^*$

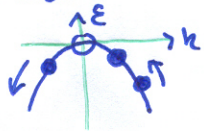
Note can't just make these substitutions for Lorentz force for holes.

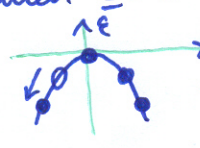
i.e. $\hbar\frac{d\underline{k}_e}{dt} = -e[\underline{E} + \underline{v}_e\times\underline{B}]$ ✓

$\hbar\frac{d\underline{k}_h}{dt} = e[\underline{E} + \underline{v}_h\times\underline{B}]$ ✓

Justification? → consider case when $\underline{B} = 0$.

$\Delta\underline{k}_e = -e\underline{E}\Delta t/\hbar$





Hole moves to left as well. So $|\Delta\underline{k}_e| = |\Delta\underline{k}_h|$

But since $\underline{k}_h = -\underline{k}_e \Rightarrow \Delta\underline{k}_e = -\Delta\underline{k}_h$

$\Rightarrow \Delta\underline{k}_h = e\Delta t\underline{E}/\hbar$ → yields correct Lorentz force.

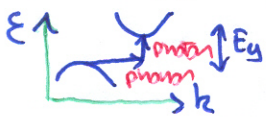
7) Semiconductors

→ Two main types

DIRECT BANDGAP (e.g. GaAs)



INDIRECT BAND GAP (e.g. Si)



- Simultaneous photon, phonon absorption for indirect band gap transitions make them much less probable than direct band gap transitions.

* Thermal excitations

Let n = # electrons/unit volume excited to conduction band ⇒ p(= # holes in valence band) = n by charge conservation

Now $n = \int_{-\infty}^{\infty}\frac{D_c(E)f(E)}{V}dE$ $D(E) = \frac{\sigma V}{4\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}E^{\frac{1}{2}} \Rightarrow D_c(E) = \frac{\sqrt{2}}{\pi^2}\frac{m_e^{3/2}}{\hbar^3}(E - \varepsilon_c)^{\frac{1}{2}}$ (conduction band energy)

for $E > \varepsilon_c$, 0 for $E < \varepsilon_c$.

Now if $E - E_F \gg k_BT$ ($\mu \times E_F$) $f(E) = \frac{1}{e^{(E-\mu)/kT}+1} \approx e^{-(E-E_F)/kT}$ → cont....

$\therefore n = \frac{\sqrt{2}}{\pi^2}\frac{m_e^{3/2}}{\hbar^3}\int_{E_c}^{\infty}(E-E_c)^{\frac{1}{2}} e^{-(E-E_F)/k_BT}\,dE \Rightarrow n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{(E_F-E_c)/k_BT}$

Substitute $x = \frac{E-E_c}{k_BT}$ use $\frac{\sqrt{\pi}}{2} = \int_0^\infty \sqrt{x}\, e^{-x}\,dx$

Similarly for holes:

$p = \int_{-\infty}^{\infty} \frac{D_v(E)}{V} f_h(E)\,dE$ where $f_h(E) = 1 - f(E) = 1 - \frac{1}{e^{E-E_F/kT}+1} = \frac{e^{E-E_F/kT}}{e^{E-E_F/kT}+1}$

Now here $E < E_F$ and $E - E_F \gg k_BT$

So $e^{E-E_F/kT} \ll 1 \Rightarrow f_h(E) \approx e^{E-E_F/kT}$ Now $\frac{D_v(E)}{V} = \frac{\sqrt{2}}{\pi^2}\frac{m_h^{3/2}}{\hbar^3}(E_v - E)^{\frac{1}{2}}$

for $E < E_v$, 0 for $E > E_v$.

$\Rightarrow p = \int_{-\infty}^{E_v}(E_v-E)^{\frac{1}{2}} e^{E-E_F/kT}\,dE \cdot \frac{\sqrt{2}}{\pi^2}\frac{m_h^{3/2}}{\hbar^3}$

$\Rightarrow p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\frac{E_v - E_F}{k_BT}}$ Now since $n = p \Rightarrow E_F = \frac{E_v + E_c}{2} + \frac{3}{4}k_BT \ln\left(\frac{m_h}{m_e}\right)$

Substituting this in p results: $p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}\cdot\left(\frac{m_h}{m_e}\right)^{-\frac{3}{4}} e^{\left[E_v - \left(\frac{E_v+E_c}{2}\right)\right]/k_BT}$

$= 2\left(\frac{k_BT}{2\pi\hbar^2}\right)^{3/2}(m_h m_e)^{3/4} e^{-(E_c-E_v)/2k_BT}$ ↙ Bandgap.

So carrier concentration $n_i = n = p = 2\left(\frac{k_BT}{2\pi\hbar^2}\right)^{3/2}(m_h m_e)^{3/4} e^{-E_g/2k_BT}$

This is ok for NON DEGENERATE semiconductors, i.e E_F is well away from E_c and E_v.

* Doped semiconductors – Add impurities to increase p or n. when impurity adds an electron (increasing n) → DONOR, when adds a hole → ACCEPTOR.
(i.e add Group V impurities → DONOR, n type semiconductor).

S.E. for DONOR electron is $\left[\frac{-\hbar^2}{2m_e^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right]\Phi(r) = \theta E_d \Phi(r)$ bound so -ve but want E_d +ve.

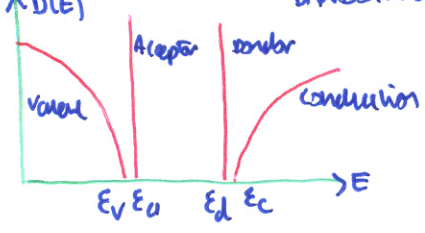
m_e^* periodic cubic potential; ε_r in dielectric medium of semiconductor

{ Analogous results for Acceptors }

i.e Hydrogenic orbitals and energy states.

Ionization energy $E_d = \frac{e^2}{8\pi\varepsilon_0\varepsilon_r a_d}$ where a_d (c.f Bohr radius) $= \frac{4\pi\varepsilon_0\varepsilon_r\hbar^2}{m_e e^2}$ ~ 5meV for GaAs.

BANDSTRUCTURE



Occupation # of donor / acceptor levels is found using the Gibbs Distribution.

$f_d = \frac{\sum_i N_i e^{-(E_i - N_i E_F)/k_BT}}{\sum_i e^{-(E_i - N_i E_F)/k_BT}}$

i	N_i	E_i	
0	0	0	degeneracy 2 due to spin + none.
1	g_d	E_d	
2	≈0	$2E_d$ + repulsion	↑ double occupancy

$\approx \frac{1}{\frac{1}{g_d}e^{(E_d - E_F)/k_BT}+1}$ If double occupancy is deemed impossibly unlikely (i.e ↑↓ configuration).

{ Note $\varepsilon_{hole} = \varepsilon_{electron}$ so use $e^{+(E_i - N_i E_F)}$ with $E_i = \begin{cases} 0 & i=0 \\ \varepsilon_a & i=1 \end{cases}$ }.

Similarly $f_a \approx \frac{1}{\frac{1}{g_a}e^{(E_F - E_a)/k_BT}+1}$

Now $f_d = \frac{N_d - N_d^+}{N_d}$ ← ionized donors and $f_a = \frac{N_a - N_a^-}{N_a}$ ionized acceptors

N_d = # donor atoms / unit volume N_a = ...

$\therefore$ Find E_F using 5 Equations

D(E) not altered much by impurities so still valid

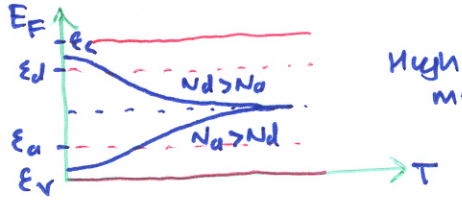
① $\frac{N_d - N_d^+}{N_d} = \frac{1}{\frac{1}{g_d}e^{(E_F - E_d)/k_BT}+1}$ ② $\frac{N_a - N_a^-}{N_a} = \frac{1}{\frac{1}{g_a}e^{(E_F - E_a)/k_BT}+1}$ ③ $n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{(E_F - E_c)/k_BT}$

④ $p = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left[\frac{E_v - E_F}{k_BT}\right]$ ⑤ $N_d^+ + p = N_a^- + n$ SS 6

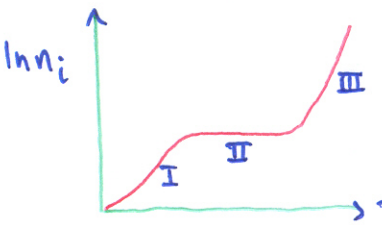
Hence carrier concentration above is NOT valid now since $n \neq p$ in general. However np is independent of E_F so $n_i^2 = 4\left(\frac{k_B T}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2} e^{-E_g/kT}$ is valid. (∴ if one knows n_i and p → calculate n).

Variation of E_F with $N_d - N_a$ @ fixed T





High T → E_F moves to middle of band gap.



I - Low T EXTRINSIC regime. As T > donors, acceptors gradually ionized — increases n_i. Fermi level close to majority carrier level.

II - All donors, acceptors ionized - EXHAUSTION REGIME. $E_F \sim$ middle of band gap.

III - Thermal excitation across bandgap now likely. $n = p$ now - behaves like undoped semiconductor.

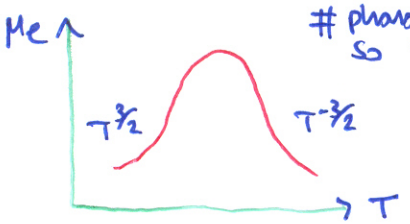
Note in exhaustion regime: if donor, acceptor levels ionized then $n = N_d - N_a \approx N_d$, $p = N_a - N_d \approx N_a$ respectively (two cases). Allows n, p to be calculated from N_d, N_a (p, n) and n_i. Can also calculate position of Fermi level in limits $N_d \gg N_a$ and $N_a \gg N_d$ using $n = N_d$ and $p = N_a$ respectively and n, p formulae.

8) Dynamics of carriers in semiconductors

Define MOBILITY $\mu = \frac{|v|}{|E|}$ v is drift velocity of particle in electric field E

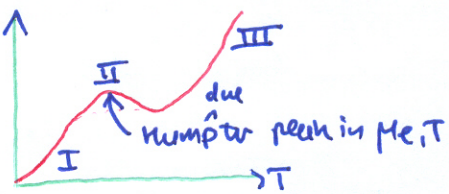
∴ write $\sigma = n e \mu_e + p e \mu_h$ ⇒ $\mu_e = \frac{e\tau_e}{m_e}$ $\mu_h = \frac{e\tau_h}{m_h}$ from page ③

Now $\tau_{phonons} \propto T^{-3/2}$ $\tau_{ionized\ impurities} \propto T^{3/2}$ (c $\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_i}$ MATTHIESSEN'S RULE)



phonons increases linearly with T / unit volume. So $T^{-3/2}$ dominates at high T.

So sketching $\ln n_i, T$ curve above ⇒ (n type sample $n \gg p$).



*Einstein Relations when n and p are not uniform in space get diffusion as well as E stimulated drift.

$j_e(r) = e\mu_e n(r) E(r) + eD_n \nabla n(r)$
$j_h(r) = e\mu_h p(r) E(r) - eD_p \nabla p(r)$

→ At eq $j_e(r) = j_h(r) = 0$

⇒ $e\mu_e n(r) E(r) = -eD_n \nabla n(r)$ (1)
$e\mu_h p(r) E(r) = eD_p \nabla p(r)$ (2)

Assuming E_F constant and non degeneracy $n(r) = N_c e^{\frac{E_F - E_c(r)}{kT}}$ (3) $p(r) = N_v e^{\frac{E_v(r) - E_F}{kT}}$ (4)

where $N_c = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}$ $N_v = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}$

$E_c(r) = E_c - eV(r)$
$E_v(r) = E_v - eV(r)$
$-\nabla V(r) = E(r)$

⇒ $\mu_e = \frac{eD_n}{k_B T}$ $\mu_h = \frac{eD_p}{k_B T}$ EINSTEIN RELATIONS

* Carrier generation and recombination. Consider an injection of electrons into a p type region where current flow is dominated by carrier diffusion. Let Ω be bounded by surface S.



$\frac{\partial}{\partial t}\int_\Omega n\,d\Omega = \frac{1}{e}\int_S j_e \cdot dS - \int_\Omega \frac{(n-n_0)}{\tau_n} d\Omega$ → Model recombination rate = $\frac{n-n_0}{\tau_n}$ ← e.g. value encountered typical.

using $j_e = eD_n \nabla n$ and divergent Theorem: $\int_S j_e \cdot dS = \int_\Omega \nabla^2 n\, d\Omega\, eD_n$ ⇒ $\frac{\partial n}{\partial t} = D_n \nabla^2 n - \frac{(n-n_0)}{\tau_n}$ Diffusion Equation.

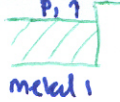
If $\frac{\partial n}{\partial t} = 0$ and $n - n_0|_{x=0} = c$ (1D example) SS

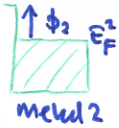
$n - n_0 = ce^{-\frac{x}{L_n}}$ Diffusion length $L_n = \sqrt{D_n \tau_n}$

Devices

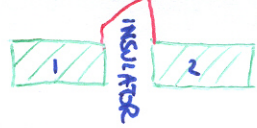
* metal rectifier

- Bring two metals together. Join with insulating layer of oxide.





At eq. →



Apply bias V →

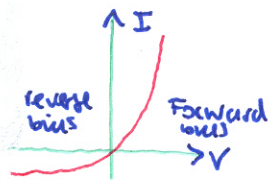


E_F lines up. $I_{\rightarrow} = I_{\leftarrow} = I_0$ in e.g. (so no net current)

$I_{\rightarrow} = I_0 e^{eV/kT}$ (-ve energy) and $I_{\leftarrow}$ unchanged.

$\therefore$ Assuming no QM tunnelling

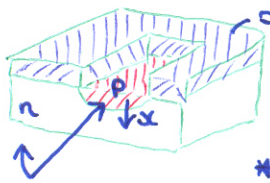
$$I = I_{\rightarrow} - I_{\leftarrow} = I_0\left(e^{eV/kT} - 1\right)$$



RECTIFIER or DIODE

→ Rectifier difficult to make reliable – oxide layer thickness + purity etc.

* Semiconductor p-n junction



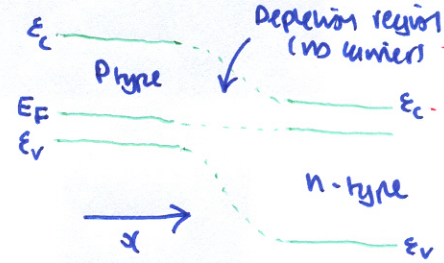
n, p doped semiconductor e.g. GaAs or Si;

- planar structure → high level integration
- dopants introduced by DIFFUSION, ION IMPLANTATION or EPITAXIAL GROWTH.

Add layers in vacuo ↓

* unbiased p-n junction

- E_F equalises on p, n sides.
- contact potential eV_i set up.



Now in p type region (pure, undoped material) $E_F = \mathcal{E}_v + kT\ln\left(\frac{p_v}{N_a}\right)$ (p dominant, $N_a \approx p$) and for n type $E_F = \mathcal{E}_c - kT\ln\left(\frac{N_c}{N_d}\right)$

$\therefore$ noting $E_g = \mathcal{E}_c - \mathcal{E}_v$ and $eV_i = E_F(n) - E_F(p)$

$$\Rightarrow eV_i = E_g - k_B T \ln\left(\frac{N_c P_v}{N_d N_a}\right)$$

dropped almost exclusively across it.

* P-n junction with applied bias V.

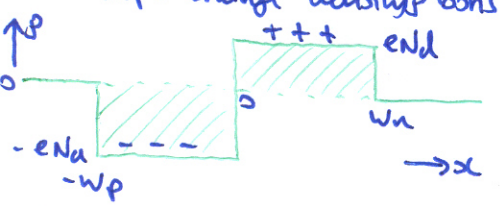
- Depletion region has no conductivity $\Rightarrow$ potential V_T

$$V_T = \phi(+\infty) - \phi(-\infty) = V_i - V$$

↑ junction potential

V -ve FORWARD BIAS
V +ve REVERSE BIAS

Now assuming edges of depletion region are sharp: charge density looks like this. (charge flowing from electron rich donor band to hole rich acceptor band)



- Find potential by solving Poisson's equation $-\varepsilon\varepsilon_0 \nabla^2\phi = \rho(x)$

$$\Rightarrow \phi(x) = \begin{cases} \phi(-\infty) & x < -w_p \\ \phi(-\infty) + \frac{eN_a}{2\varepsilon\varepsilon_0}(x+w_p)^2 & -w_p < x < 0 \\ \phi(+\infty) - \frac{eN_d}{2\varepsilon\varepsilon_0}(x-w_n)^2 & 0 < x < w_n \\ \phi(+\infty) & x > w_n \end{cases}$$

- continuity at $x=0$ yields

$$\phi(-\infty) + \frac{eN_a w_p^2}{2\varepsilon\varepsilon_0} = \phi(+\infty) - \frac{eN_d w_n^2}{2\varepsilon\varepsilon_0} \Rightarrow V_T = \frac{e}{2\varepsilon\varepsilon_0}\left[N_a w_p^2 + N_d w_n^2\right]$$

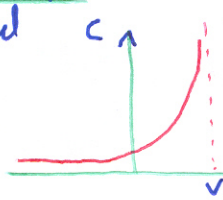
- Now charge neutrality $\Rightarrow N_d w_n = N_a w_p \Rightarrow$

$$w_n = \left[\frac{2\varepsilon\varepsilon_0 V_T}{e}\left(\frac{N_a}{N_d(N_d+N_a)}\right)\right]^{1/2}$$

$$w_p = \left[\frac{2\varepsilon\varepsilon_0 V_T}{e}\left(\frac{N_d}{N_a(N_a+N_d)}\right)\right]^{1/2}$$

$\Rightarrow$ depletion region acts like a charged capacitor $Q = eN_d w_n \; (= eN_a w_p)$

$$\Rightarrow C = \frac{dQ}{dV_T} = \left[\frac{\varepsilon\varepsilon_0 e}{2V_T}\left(\frac{N_a N_d}{N_a + N_d}\right)\right]^{1/2}$$



→ TV tuning ckt..... VARACTORS....

* current flow in biased p-n junction

In non degenerate regime ($kT \ll E_g$) and with no applied bias $n(x) = N_c e^{(E_F - \mathcal{E}_c + e\phi(x))/kT}$ and $p(x) = P_v e^{(\mathcal{E}_v - e\phi(x) - E_F)/kT}$. With applied bias drift and diffusion terms in $\downarrow$ $\approx$ cancel each other in depletion region so we can use the above to work out n and p at it's edges.

$$\frac{n(-w_p)}{n(w_n)} = e^{-e(V_i - V)/kT} \qquad \frac{p(-w_p)}{p(w_n)} = e^{e(V_i - V)/kT}$$

Now $\frac{n(\infty)}{n(-\infty)} = e^{eV_i/kT}$ ← Not affected by bias voltage

$\frac{p(-\infty)}{p(\infty)} = e^{eV_i/kT}$

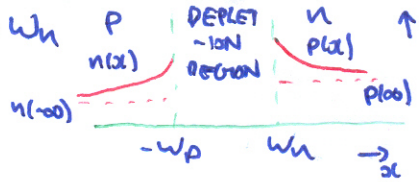
and assume $\frac{n(w_n) \times n(\infty)}{p(-w_p) \times p(-\infty)}$

Hence: $n(-w_p) - n(-\infty) = n(-\infty)\left(e^{eV/kT} - 1\right)$

and $p(w_n) - p(\infty) = p(\infty)\left(e^{eV_i/kT} - 1\right)$

Now use result $n(x) - n_0 = C_0 e^{-x/L_n}$ except 0 is shifted to $-w_p$ and a measured (same for p) backwards $\Rightarrow \Delta n = n(x) - n(-\infty) = n(-\infty)\left(e^{eV/kT} - 1\right) e^{(x + w_p)/L_n}$ $x < -w_p$

and $\Delta p = p(x) - p(\infty) = p(\infty)\left(e^{eV/kT}-1\right)e^{-(x-w_n)/L_p}$ $x > w_n$



Now drift current are not affected by bias

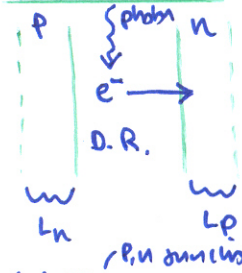
So only diffusion terms contribute to $j_e(x)$ and $j_n(x)$

Total $j = j_e(-w_p) + j_n(w_n)$ (must be independent of x)

$$= eD_n \frac{d\Delta n}{dx}\bigg|_{-w_p} - eD_p \frac{d\Delta p}{dx}\bigg|_{w_n} = \underbrace{\left(\frac{eD_n}{L_n} n(-\infty) + e\frac{D_p}{L_p} p(\infty)\right)}_{j_0}\left(e^{eV/kT}-1\right)$$

P,n junction — i.e. RECTIFIER

* Solar cell / P,n junction



Photons can excite electrons across bandgap if of sufficient energy. Electrons generated in the depletion region are rapidly swept into the n-type region (and opposite for holes) creating a "PROMPT PHOTOCURRENT" (& FAST. (note reverse direction to diode). GaAs cells better matched to solar spectrum but more expensive than less efficient Si ones.

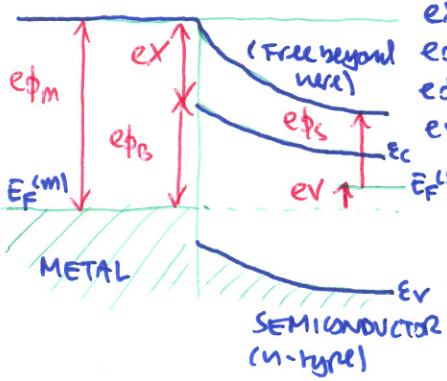
* LED reverse process of above: electron in conduction band can recombine with a hole in valence band to produce a photon or heat emission. (Radiative and non radiative recombination). Radiative processes more efficient in DIRECT GAP materials like GaAs.

→ LED is P,n junction under forward bias. → inject electrons and holes as minority carriers from both sides of depletion region → Radiative recombination generates light.

→ Add phosphorus (same group and telluric type as As) to increase E_g and alter colour.

* Metal - Semiconductor junctions - Schottky diode. (can be ohmic as well i.e. $V \propto I$)

- consider Schottky case first with metal - n type junction.



$e\chi$ = electron affinity of semiconductor
$e\phi_m$ = work function of metal
$e\phi_B$ = Schottky barrier height
eV = Applied (Forward) bias
$e\phi_s$ = work function of semi.

SCHOTTKY DIODE WHEN $\phi_m > \phi_s$ (OHMIC OTHERWISE

Now $n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\frac{E_F - E_c}{kT}}$ at barrier and $E_F - E_c = eV - e\phi_B$ here.

Flow of +ve charge over barrier (⇐) due to electrons flowing over barrier (→) results in current $I_{\leftarrow} = neA\frac{\langle v\rangle}{4}$ (eA = flux of electrons).

Find $\langle v\rangle$ from Maxwell - Boltzmann speed distribution

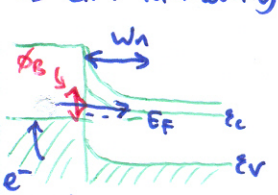
$$\langle v\rangle = \left(\frac{8k_BT}{\pi m_e}\right)^{\frac{1}{2}} \quad \therefore I_{\leftarrow} = \frac{1}{4}eA\left(\frac{8k_BT}{\pi m_e}\right)^{\frac{1}{2}} \cdot 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\frac{eV - e\phi_B}{kT}}$$

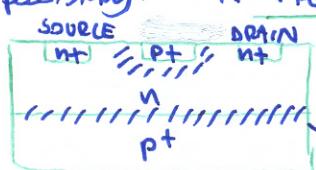
At $V=0$ this is balanced by V independent $I_{\rightarrow}$ to yield $I = I_{\leftarrow} - I_{\rightarrow} = 0$

$$\Rightarrow I(V) = A\left(\frac{m_e e k_B^2}{2\pi^2\hbar^3}\right)T^2 e^{-(e\phi_B/kT)}\left(e^{eV/kT}-1\right) \qquad \frac{m_e k_B^2}{2\pi^2\hbar^3} \equiv R^* \text{ RICHARDSON CONSTANT}$$

Schottky diode switching time not dependent of minority carrier lifetime as in pn. ∴ much faster.

* ohmic contacts - either find semiconductor where $\phi_s > \phi_m$ (ie no barrier presented and $V \propto I$) OR heavily dope semiconductor ⇒ depletion region v. narrow (see w_n formula) ⇒ QM tunnelling a possibility. * Field Effect Transistors (FET's) - 3 terminal device.





Voltage at gate determines width of depletion region. Now current same - drain ⇒ bias drain - source since n channel resistive. ⇒ Asymmetric depletion region, larger at source, thinner at drain region. Eventually they merge ⇒ no current flows regardless V_{DS}

+ ⇒ heavily doped.



b) Magnetism. Magnetic moments of free atoms can arise from (i) electron spin (ii) orbital A.M of electrons (iii) orbital A.M induced by applied magnetic fields.

* Dia magnetism (classical derivation - see QM (II) for quantum derivation)

-Arises from Larmor precession of electron about lines of $\underline{B}$ - consider classical orbit of nucleus (charge Ze) by single electron.



e^- with no $\underline{B}$ current $I = \frac{-e\omega_0}{2\pi}$ $\therefore$ dipole moment $m = I\pi r_0^2 = -\frac{e\omega_0}{2} r_0^2$ ⊙

Now $m_e r_0 \omega_0^2 = \frac{Ze^2}{4\pi\varepsilon_0 r_0^2}$. When $\underline{B}$ is applied ⊙ extra $-e\underline{v}\times\underline{B}$ pre in same direction as electrostatic (centripetal attraction). Assume new circular orbit at $r_0+\Delta r$ at frequency $\omega_0+\Delta\omega$. $\therefore$ $m_e(r_0+\Delta r)(\omega_0+\Delta\omega)^2 = \frac{Ze^2}{4\pi\varepsilon_0(r_0+\Delta r)^2} + eB(\omega_0+\Delta\omega)(r_0+\Delta r)$

Now assume $\frac{\Delta r}{r_0} \ll \frac{\Delta\omega}{\omega_0}$ (Quantum result) $\Rightarrow$ A.M not affected much by $\underline{B}$. since quantised.

$\Rightarrow \Delta\omega \propto \frac{eB}{2m_e}$

$\Rightarrow (\omega_0+\Delta\omega)^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e (r_0+\Delta r)^3} + \frac{eB}{m_e}(\omega_0+\Delta\omega)$

$\Rightarrow \omega_0^2\left(1+\frac{2\Delta\omega}{\omega_0}\right) \approx \frac{Ze^2}{4\pi\varepsilon_0 m_e r_0^3}\left(1-\frac{3\Delta r}{r_0}\right) + \frac{eB}{m_e}(\omega_0+\Delta\omega)$ ($\frac{Ze^2}{4\pi\varepsilon_0 m_e r_0^3} = \omega_0^2$)

$\Rightarrow 1+\frac{2\Delta\omega}{\omega_0} \approx 1-\frac{3\Delta r}{r_0} + \frac{eB}{m_e\omega_0}$ ($\frac{eB}{m_e\omega_0^2}\Delta\omega$ negligible)

$\Rightarrow \frac{2\Delta\omega}{\omega_0} + \frac{3\Delta r}{r_0} \approx \frac{eB}{m_e\omega_0}$

$\therefore \Delta I = -e\Delta\omega/2\pi = \frac{e^2B}{4\pi m_e}$

$\therefore \Delta m = +\Delta I \pi r_0^2$ (Again $\frac{\Delta\omega}{\omega_0} \gg \frac{\Delta r}{r_0}$)

$\Rightarrow \Delta m = -\frac{e^2B}{4m_e} r_0^2$

$\langle r^2\rangle = 3\langle x^2\rangle = 3\langle y^2\rangle = 3\langle z^2\rangle$

$\langle r_0^2\rangle = 2\langle x^2\rangle \therefore \langle r_0^2\rangle = \frac{2}{3}\langle r^2\rangle$

Now $\langle m\rangle_{tot} = \langle m\rangle + \langle\Delta m\rangle$ interested in $\langle\Delta m\rangle = \frac{e^2B}{4m_e}\langle r_0^2\rangle = -\frac{e^2B}{6m_e}\langle r^2\rangle$

So $\chi_m = \frac{-e^2}{6m_e}\langle r^2\rangle \frac{NZ}{V}$ ($\frac{ZN}{V}$ electrons per unit volume i.e. Z per atom).

↑ Diamagnetic susceptibility.

* Spin paramagnetism from QM course

$\underline{\mu} = -g\mu_B m_S$

g - Lande g factor
m_S - A.M. projected in z direction (//B)
μ_B is Bohr magneton $\frac{e\hbar}{2m_e}$

Energy is $-\underline{B}.\underline{\mu} = m_S g\mu_B B$

→ Boltzmann distribution $\therefore$ Partition function

$Z = \sum_{m_S=-S}^{S} e^{-m_S g\mu_B B/k_BT}$ G.S $\rightarrow Z = \frac{\sinh(g\mu_B B(S+\frac{1}{2})/k_BT)}{\sinh(g\mu_B B/2k_BT)}$

Now $F = -k_BT\ln Z$

$F = U - TS \Rightarrow dF = dU - TS$

$dU = TdS - pdV + \mu dN - m dB$

$(dV = dN = 0) \Rightarrow dF = -SdT - m dB$

$\therefore m = -\left(\frac{\partial F}{\partial B}\right)_T$ $M = \frac{mN}{V}$

$\Rightarrow m = g\mu_B J B_J(g\mu_B JB/k_BT)$ B_J = Brillouin Function

$B_J = \frac{2S+1}{2S}\coth\left[\frac{(2S+1)}{2S}x\right] - \frac{1}{2S}\coth\left[\frac{x}{2S}\right]$

$T\to 0$ $B_J \to 1$ i.e. Spins all aligned

$T\to\infty$ $B_J \to 0$ i.e. spins all disordered.

$\Rightarrow B_J(x) \approx \left(\frac{S+1}{3S}\right)x + O(x^3)$ if $x \ll 1$.

$\Rightarrow \chi_M = \frac{M}{B} = \frac{\mu_0 N(g\mu_B)^2}{3}\frac{S(S+1)}{k_BT}$ Curie's law - applies $k_BT \gg g\mu_B JB$

* Ferromagnetism - Spontaneous magnetism below a critical temperature, paramagnetism above. Results from magnetic domains within ferromagnet where regions of spin alignment occur on macroscopic (cish) scales. Spin Alignment at low T due to EXCHANGE INTERACTIONS. (unstable)

Le to minimise total spin $\Rightarrow$ lowering of energy (since electrons must have antisymmetric wf under particle exchange, spin w.f sym $\Rightarrow$ spatial antisym which lowers coulomb repulsion)

4 types of exchange interaction: (1) Direct exchange - electrons in same atomic orbital

(2) Superexchange - non magnetic ion mediates interaction between two magnetic ions

↑ ↑ (3) Indirect exchange (rare earth metals) partially filled f orbitals heavily overlap but CAN couple with conduction electrons (4) Itinerant exchange - exchange interaction between delocalised electrons - i.e in iron

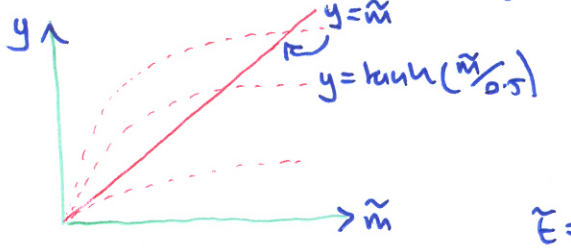
* Weiss Theory is quite a good model for spontaneous magnetisation in ferromagnetic materials. In absence of applied $\underline{B}$ model internal magnetic moments interact via "applied" field $B_i = \frac{\lambda M N}{V}$ (λ = Weiss parameter). For electrons $J = \frac{1}{2}$ (assume $L = 0$)

$$\Rightarrow \quad m = \frac{g\mu_B}{2} \tanh\left(\frac{g\mu_B \lambda M N}{2 k_B T V}\right)$$

Write $\tilde{m} = \frac{M}{\left(\frac{g\mu_B}{2}\right)}$ DIMENSIONLESS VARIABLES

$$\Rightarrow \quad \tilde{m} = \tanh\left(\frac{\tilde{m}}{\tilde{t}}\right)$$

$$\tilde{t} = \frac{k_B T V}{\left(\frac{g\mu_B}{2}\right)^2 \lambda N}$$



For $\tilde{t} > 1$ only solution is $\tilde{m} = 0$

For $\tilde{t} \leq 1$ non zero magnetisation appears.

$\tilde{t} = 1 \Rightarrow$ critical temperature $= T_c = \frac{\lambda \left(\frac{g\mu_B}{2}\right)^2 N}{k_B V}$

Now for applied field replace B_i by $B + \frac{\lambda M N}{V}$

Using curie limit ($k_B T \gg g\mu_B J B$) $\tanh(x) \approx x$

$$\Rightarrow \quad m = \frac{1}{k_B T}\left(\frac{g\mu_B}{2}\right)^2 \left(B + \frac{\lambda m N}{V}\right) \quad \Rightarrow \quad \frac{\partial m}{\partial B} = \frac{1}{k_B T}\left(\frac{g\mu_B}{2}\right)^2 \left(1 + \frac{\lambda N}{V}\frac{\partial m}{\partial B}\right)$$

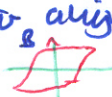
$$\Rightarrow \quad \frac{\partial m}{\partial B} = \frac{1}{k_B T}\left(\frac{g\mu_B}{2}\right)^2 \left(1 - \left(\frac{\lambda N}{V}\right)\left(\frac{g\mu_B}{2}\right)^2 \frac{1}{k_B T}\right)^{-1} = \frac{V}{\lambda N T} T_c \left[1 - \frac{T_c}{T}\right]^{-1}$$

$$= \frac{V}{\lambda N}\frac{T_c}{T - T_c} \quad \therefore \quad \chi_m = \frac{\mu_0 N}{V}\frac{\partial m}{\partial B} = \frac{\mu_0 T_c}{\lambda}\frac{1}{T - T_c}$$ CURIE WEISS LAW

→ OK for $T \gg T_c$ but diverges more like $(T - T_c)^{-3/2}$ near T_c.

(EXPERIMENTAL OBSERVATIONS)

* Magnetic domains tend to align with an applied field to lower magnetic energy $E = \frac{1}{2}\int \underline{B} \cdot \underline{H}\, d\tau$ If the field is strong enough → rotation of domain magnetisation to align with field. This is IRREVERSIBLE and ∴ leads to Hysteresis.



* Antiferromagnetism → In an antiferromagnet ∥ spin alignment but pairs are mutually anti ∥ ∴ no net magnetisation.



e.g. MnO → Arises from superexchange interaction since Mn^{2+}, O^{2-} far apart.

* Ferrimagnetism

As antiferromagnetism but moments are of different magnitude so don't cancel.

↑ net $\underline{M}$

e.g. Fe_3O_4 which contains Fe^{2+} and Fe^{3+} ions – different magnetic moments. FERRITES. (High ρ, μ which makes them useful).