Crystal struct = lattice + basis (decor) → identical assembly of atoms when each lattice point

det by translational syms points in space
def primitive vectors $\vec{a}, \vec{b}, \ldots$
lattice vector $\vec{R} = n_1\vec{a} + n_2\vec{b} + \ldots$

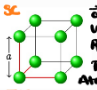
2D Area: $|\vec{a} \times \vec{b}|$
3D Vol: $|\vec{a} \cdot (\vec{b} \times \vec{c})|$

unit c: repeated, primitive - 1

Bravais lattices

oblique $a \neq b$, $\gamma \neq 90°$ — rectangular $a \neq b$, $\gamma = 90°$ — centered rectang $a \neq b$, $\gamma = 90°$ — square $a = b$, $\gamma = 90°$ — hexagonal $a = b$, $\gamma = 60°$

SC

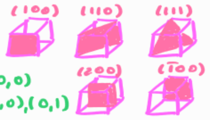


$\vec{a} = a\hat{i}$, $\vec{b} = a\hat{j}$, $\vec{c} = a\hat{k}$
Vol = a^3
$R_{nn} = a$
PF = 0.52
Atomic rad: $R_{nn}/2$

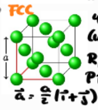
Direct's: OP: [001], OR: [110], OQ: [010], TS: [2 1 1]
Plane (h k l) { }
< > symmetrically equiv

centered rect lattice
3 atom basis: $s(0,0)$, $(1,0),(0,1)$

(100) (110) (111) (200) (100)

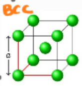


FCC



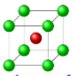
4 atom basis $= 8 \times \frac{1}{8}$(corner) $+ 6 \times \frac{1}{2}$(face)
$(u,v,w) = (0,0,0), (\frac{1}{2},\frac{1}{2},0), (\frac{1}{2},0,\frac{1}{2}), (0,\frac{1}{2},\frac{1}{2})$
$R_{nn} = a/\sqrt{2}$
PF: 0.74
$\vec{a} = \frac{a}{2}(\hat{i}+\hat{j})$, $\vec{b} = \frac{a}{2}(\hat{j}+\hat{k})$, $\vec{c} = \frac{a}{2}(\hat{i}+\hat{k})$
Vol = $a^3/4$

BCC



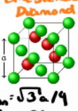
2 atoms $= 8 \times \frac{1}{8} + 1 \times 1$(inside)
$(u,v,w) = (0,0,0), (\frac{1}{2},\frac{1}{2},\frac{1}{2})$
$R_{nn} = \sqrt{3}a/2$
PF: 0.32
$\vec{a} = \frac{a}{2}(\hat{i}+\hat{j}-\hat{k})$, $\vec{b} = \frac{a}{2}(-\hat{i}+\hat{j}+\hat{k})$, $\vec{c} = \frac{a}{2}(\hat{i}-\hat{j}+\hat{k})$
$V = a^3/2$

Cesium Chloride



$(0,0,0)$
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

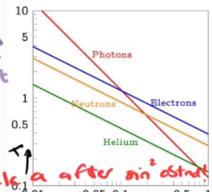
Zincblende Diamond



$(0,0,0), (\frac{1}{2},\frac{1}{2},0), (\frac{1}{2},0,\frac{1}{2}), (0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{4},\frac{1}{4},\frac{1}{4}), (\frac{3}{4},\frac{3}{4},\frac{1}{4}), (\frac{3}{4},\frac{1}{4},\frac{3}{4}), (\frac{1}{4},\frac{3}{4},\frac{3}{4})$
8 atoms: $8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 \times 1$
$R_{nn} = \sqrt{3}a/4$
PF: 0.34
$(0,0,0)$
$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$

Photons: $E = pc$, $\lambda = \frac{hc}{E}$
TRIG! $p = h/\lambda$
$E = hc/\lambda$
$\ln\lambda = \ln hc - \ln t$

m = massive particles
~ low energy neutrons
$t = p^2/2m$ (non-relat)
$= \frac{h^2}{2m}\frac{1}{\lambda^2}$
$\lambda = \sqrt{\frac{h^2}{2m}}\frac{1}{\sqrt{t}}$



Photons in 100 keV
Electrons in keV
Neutrons/He in eV

Crystal structure determinat°
- scatter radiat°/particles of sample
- crystal ~ 3D diffract° grating
- scattering intensity pattern analysis det: structure — lattice param, composit°, orientat°

recall a after sin abstr

$\sin^2\theta = \frac{\lambda^2}{4a^2} \times (h^2+k^2+l^2)$

(sc) 1:2:3:4:5:6:8
(bcc) has 7
(fcc) 1 : $\frac{4}{3}$: $\frac{8}{3}$

Bragg's Law — Scattering angle 2θ

$n\lambda = 2d\sin\theta$

n - diffract° order, d - spacing lattice plans, λ - wavelength radiat°, θ - Bragg angle diffract°

AB:CD, θ = φ (reflect°)
ABC = $2d\sin\theta$ = $n\lambda$

$n\lambda = 2\sin(\theta)$
$\sin(\theta) = n\lambda/2d$

Diffract° crystal - ATOMIC PERSPECTIVE — tell U diff things ↓
incident radiat°, $\vec{k}$, $\vec{k}'$
$\lambda = 2\pi/|\vec{k}|$
coherent scattering, energy conserved
$|\vec{k}'| = |\vec{k}|$

	energy E	wavelength λ	scattered by	penetration depth
X-rays	10^4 eV	1.2 Å	electrons	~ cm
neutrons — massive particles	10^{-2} eV	2.8 Å	nuclei	~ cm
electrons	10-100 eV LEED (surface struct) / 10^5 eV TEM (bulk probe)	~ 1 Å / ~ 0.04 Å (E verylig high necessary)	electrons & nuclei	~ nm / ~ µm

1_{100} $\frac{1}{110}$ $\frac{1}{111}$ ... Bragg angle

α probe: charged, easy to contron

Neutrons → f within factor 3-4
→ neighbouring elements often different
→ varies with isotope
→ can be negative
→ sensitive to unpaired spins

Total Amplitude
$A = c\sum_i f_i e^{\ldots}$
$\vec{Q} = \vec{k}' - \vec{k}$
$|\vec{Q}| = 2k\sin\theta$
$\sum_i e^{-in\vec{Q}\cdot\vec{r}_i}$ = $S(h,k,l)$, 0 otherwise
Bragg angle

Laue condit°s
$A(\vec{Q}) = S_{cell}F_{cell}$
$\vec{Q} \cdot \vec{a} = 2\pi h$, $\vec{Q} \cdot \vec{b} = 2\pi k$, $\vec{Q} \cdot \vec{c} = 2\pi \ell$
sc: $\vec{a} = a\hat{i}$, $\vec{b} = a\hat{j}$ ...
Let $\vec{Q} = Q_x\hat{i} + Q_y\hat{j} + Q_z\hat{k}$
$\vec{Q} \cdot \vec{a} = 2\pi h \Rightarrow Q_x a = 2\pi h$, $Q_y a = 2\pi k$, $Q_z a = 2\pi l$
$Q = \frac{2\pi}{a}(h\,k\,l)$
→ Q sits at an sc lattice with lattice const $2\pi/a$

monatomic cryst
$\vec{r}_i = \vec{g}$ & $\vec{r}_j = n\vec{a} + m\vec{b} + l\vec{c}$
$A(\vec{Q}) = Cg(\sum_n e^{-in\vec{Q}\cdot\vec{a}})(\sum_m e^{-im\vec{Q}\cdot\vec{b}})(\sum_\ell e^{\ldots})$

Reciprocal lattice
dimens° length^{-1} [$Å^{-1}$]
measured in diffract° experiments
$\vec{G}_{hkl} = h\vec{A} + k\vec{B} + \ell\vec{C}$
* lattice in reciprocal space ~ also called momentum wave vecter

$\vec{A} = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}\cdot(\vec{b}\times\vec{c})}$
$\vec{B} = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{a}\cdot(\vec{b}\times\vec{c})}$
$\vec{C} = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{a}\cdot(\vec{b}\times\vec{c})}$

incoming, scattering angle, out, spots Laue cond
X-ray → Angular positi°s
reciprocal lattice — crystal struct

	Probe
Elemental solid	X-rays
Uranium Oxide	X-rays
Sucrose	Neutrons (H atoms locat°s undetectable by X-rays)
β-brass	Neutrons
Platinum	Electrons ← surface segregat°

form factors = atomic scattering amplitude
X-rays → $f \propto Z$: atomic n°
cheap & easy to produce → hard to observe light elements when heavy ones present → hard to distingui elemnts with similar Z

Square lattice:
$d: \{a, \frac{a}{\sqrt{2}}, \ldots\}$ ratio $1 : \frac{1}{\sqrt{2}} : \ldots$
unlikely rise diffract° d small
$d = a$

Hexagonal lattice
$d = \{\frac{\sqrt{3}a}{2}, \frac{a}{2}, \ldots\}$
ratio $\frac{\sqrt{3}}{2}, \frac{1}{2}, \ldots$

Electrons in solids
e-e interact°: $\frac{e^2}{4\pi\varepsilon_0 a} \approx$ a few eV
$r_s \approx (\frac{V}{N})^{1/3}$ electron separat°, 1-5 Å
kinetic energy $\frac{1}{2}mv^2 = \frac{3}{2}k_BT \approx 40$ meV
Cu $z = 1$
fcc $a = 3.695$ Å
cond electron density $\frac{n_0}{vol} = \frac{4\times1}{3.615 Å} = 8.47\times10^{22}$ cm^{-3}

n - conduct° e density
$n = z(N/V)$

DRUDE
① Btw collis's electron interact° with other electrons are neglected ✗ ions
② Collis's are instantaneous, abruptly changing velocity ✗
③ E collide with % $\frac{1}{\tau}$ — τ: Relaxat° Collis° Scattering Mean free
④ E are in thermal eq with their surroundings
$\langle\frac{1}{2}mv^2\rangle_{inst} = \frac{3}{2}k_BT_{local}$

DEOM → Free space: $\frac{d\vec{p}}{dt} = \vec{F} - \frac{\vec{p}}{\tau}$ external force, scattering damping
$\delta\vec{v} = \frac{\vec{F}}{m}\delta t$
TIME τ: relaxat° rate
Solid: frac° $\frac{\delta t}{\tau}$ of e scatter in time after which their velocity is 0 avg
$\delta\vec{v} = \frac{\vec{F}}{m}\delta t - \vec{v}\frac{\delta t}{\tau} \Leftrightarrow \frac{d\vec{p}}{dt} = F - \frac{\vec{p}}{\tau}$

Ohm's law $V = IR$, resistivity: ρ [Ωm]
DC conductivity $\mathcal{E} = \rho\vec{J}$ or $\vec{J} = \sigma\vec{\mathcal{E}}$
Origin: electrons undergo collisions that randomise their velocity in terms of dt factor or/τ scatter
collis°s introduce frictional damping
conductivity [S/m]
$\sigma = \frac{ne^2\tau}{m}$, $\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau}$

deriv: $\vec{F} = -e\vec{\mathcal{E}}$ ss $\frac{d}{dt} = 0$ ∴ $0 = -e\vec{\mathcal{E}} - \vec{p}/\tau$
$\vec{p} = -e\tau\vec{\mathcal{E}} = m\vec{v}_d$
$\vec{J} = -en\vec{u} = -en(-e\vec{\mathcal{E}}/m)$
$\rho = \frac{m}{ne^2\tau}$ → T-indep sample dependent, T-dep sample indep

Scattering event
mean free path $l = v\tau$ distance btw collis's

DEOM steady state $\frac{d}{dt} \to 0$
$\vec{p} = -e\tau\vec{\mathcal{E}}$
Wire
$V = \mathcal{E}L$, $J = \frac{I}{A}$
$R = \rho L/A$
average e velocity = drift velocity
$\vec{v}_d = \frac{\vec{p}}{m} = -\frac{e\tau}{m}\vec{\mathcal{E}}$
corresponding current density
$\vec{J} = -ne\vec{v}_d = \frac{ne^2\tau}{m}\vec{\mathcal{E}}$
D model predicts V ∝ I ✓

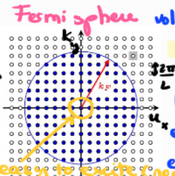
SOMMERFELD
% occupat° Fermi-Dirac distribut°

E in units of $\frac{\hbar^2}{2m}(\frac{\pi}{L})^2$; n = 3, n = 2, n = 1

$g(\epsilon)$
$E - \mu \gg k_BT$
$f(\epsilon) \propto e^{-(\epsilon-\mu)/k_BT}$ - Boltzmann distribut°
$\sim k_BT$

3D E free e: $\hbar^2k^2/2m$
Schröd eq°: $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_n(\vec{r}) = \epsilon_n\psi_n(\vec{r})$
Periodic BC: $\psi(x+L,y,z) = \psi(x,y,z)$
$\psi(x,y+L,z) = \psi(x,y,z)$
$\psi(x,y,z+L) = \psi(x,y,z)$
sols
$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}$
Electron momentum $\vec{p} = \hbar\vec{k}$
Electron energy $\epsilon_k = \frac{\hbar^2k^2}{2m}$
$\vec{p} = m\vec{v} \Rightarrow \epsilon = \frac{p^2}{2m} = \frac{1}{2}mv^2$

Fermi sphere



vol: $\Omega = \frac{4\pi}{3}k_F^3$
N° points $= \frac{\Omega}{8\pi^3/V} = \frac{k_F^3}{6\pi^2}V$
$\frac{2\pi}{L} = \Delta k$
N° electrons $= 2 \times$ n° points
e density $n = \frac{N}{V} = k_F^3/3\pi^2$
e wavelength $\lambda_F = 2\pi/k_F$
not energy to excite (need a lot of E)
Vol per point: $(\frac{2\pi}{L})^3 = \frac{8\pi^3}{V}$
allowed k vals: $\Delta k = \frac{2\pi}{L}$

$\boxed{k_F = (3\pi^2n)^{1/3} \quad \epsilon_F = \frac{\hbar^2k_F^2}{2m} \quad T_F = \epsilon_F/k_B \quad v_F = \hbar k_F/m}$

n° free e states with energies up to $\epsilon = \hbar^2k^2/2m$
$N(\epsilon) = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}$

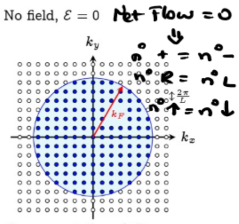
Quantum gas in reciprocal space
- N (n°e in syst): $N = \sum_{occ} ① \to \int g(\epsilon)f(\epsilon)d\epsilon$
- u (int E of the e gas) $\xrightarrow{T=0} \int_0^{\epsilon_F} \alpha\sqrt{\epsilon}\, d\epsilon$
$u = \sum_{occup} \epsilon_k = \int \epsilon g(\epsilon)f(\epsilon)d\epsilon \xrightarrow{T=0} \int_0^{\epsilon_F} \epsilon\alpha\sqrt{\epsilon}\,d\epsilon$
$= \alpha\int_0^{\epsilon_F}\epsilon^{1/2} = \frac{2}{3}\alpha\epsilon^{3/2}$
$\epsilon_k = \frac{\hbar^2k^2}{2m}$
$= \alpha\int_0^{\epsilon_F}\epsilon^{3/2}d\epsilon = \alpha\frac{2}{5}\epsilon_F^{5/2}$
$\langle u\rangle = \frac{K}{N} = \frac{\frac{2}{5}\alpha\epsilon_F^{5/2}}{\frac{2}{3}\alpha\epsilon_F^{3/2}} = \frac{3}{5}\epsilon_F$

density 3D electron gas $g(\epsilon) = \alpha\epsilon^{1/2}$
$g(\epsilon)f(\epsilon)$, T=0, filled, empty, T>0
area = $\int_0^\infty g(\epsilon)f(\epsilon)d\epsilon$

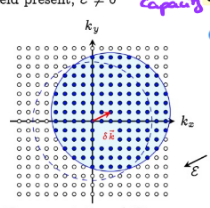
Total energy of e gas at T=0
$U_0 = \int_0^{\epsilon_F}\epsilon g(\epsilon)d\epsilon = \frac{2}{5}\alpha\epsilon_F^{5/2}$
$= \frac{3}{5}N\epsilon_F$
average kinetic energy = kinetic energy per electron
$\langle k.e.\rangle = \frac{U_0}{N} = \frac{3}{5}\epsilon_F$

Electrical conduct° scattering
$\vec{F} = \frac{d\vec{p}}{dt} = \frac{d}{dt}(\hbar\vec{k}) = -e\vec{\mathcal{E}}$: Lorentz force
$\frac{d\vec{k}}{dt} = \frac{-e\vec{\mathcal{E}}}{\hbar}$
$\vec{u}(t) - \vec{u}(0) = \frac{-e}{\hbar}\vec{\mathcal{E}}t = \delta\vec{k}$

Heat capacity $C_v = \left(\frac{\partial U(T)}{\partial T}\right)_V \sim 2Nk_B(T/T_F)$
$U(T) - U(0) \sim N\times(\frac{T}{T_F})\times k_BT = \frac{Nk_BT^2}{T_F}$
Qntum c_v smaller than classic ($\frac{3}{2}Nk_B$) by factor ~ $\frac{T}{T_F}$
~1% room tmp



No field, $\mathcal{E} = 0$ — Net Flow = 0
n°→ + n°← = n°→ — n°R = n°L, n°↑ = n°↓
2D representation of 3D space
average $\langle\vec{k}\rangle = 0$, no current



Field present, $\mathcal{E} \neq 0$
2D representation of 3D space
average $\langle\vec{k}\rangle \neq 0$, current flows

Classic v^2 Qntm
$v^2 \sim \frac{k_BT}{m}$ — $v_F^2 = \frac{2\epsilon_F}{m}$
$v_Q \sim \frac{\epsilon_F}{k_BT}v_c \approx 100\,v_c$

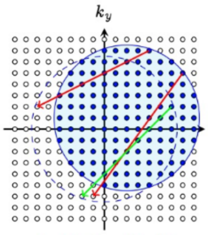
Classic	E SPEED Qntum
$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$	$\langle\frac{1}{2}mv^2\rangle = \frac{3}{5}\times\frac{1}{2}mv_F^2$, $\langle v\rangle = \sqrt{\frac{3}{5}}v_F$

At T=0K: $V_{Qnt} = 10\times V_{class}$

Hall effect: voltage applied to drive current along a wire in presence B
Lorentz force: $\vec{F} = -e(\vec{\mathcal{E}} + \vec{v}_d \times \vec{B})$
$B = 0$, e flow opp current; $B > 0$ initially; $B > 0$ steady state
SS: $0 = e(\mathcal{E}_y + v_d B)$ → $\mathcal{E}_y = v_d B$
Hall coeff $R_H = \frac{\mathcal{E}_y}{J_x B} = -\frac{1}{ne}$, $R_H = \frac{V_H d}{IB}$
Hall voltage $V_H = \mathcal{E}_y w$
N atoms, Z vol V
$-\frac{1}{R_H}\frac{1}{N}\frac{1}{e} = \frac{n}{N/V} = Z$ ← valence
charge carriers are holes (+), e flows up either side wire creating E field across with charges left

N states in a band = $\frac{\text{range}}{\text{spacing}} = \frac{2\pi/a}{2\pi/L} = \frac{L}{a}$ = n° unit cells
Brillouin zone $2\pi/a$, $-\pi/a$ … π/a, $\Delta k = \frac{2\pi}{L}$
Each band can hold 2 electrons from each unit cell

$v_d = \frac{j}{ne} \sim 1$ cm/s
minuscule % Fermi velocity $v_F \sim 10^8$ cm/s
Scattering btw states on Fermi surface is the important one



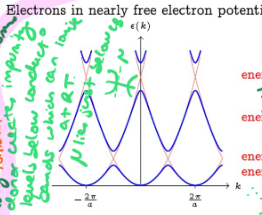
inelastic - $\delta\epsilon \neq 0$
elastic - $\delta\epsilon = 0$

Resistivity
$\rho = \rho_i + \rho_{ph}(T)$
or $\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_{ph}}$
$= \frac{1}{\tau_1} + \frac{1}{\tau_2} + \ldots$ Matthiessen's rule

relative resistance $10^3 R/R_{300K}$, Temp K

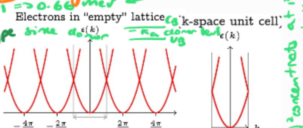
Bloch's Thm
$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$
Bloch wave = plane wave × lattice period f°
$\psi(x+L) = \psi(x) = e^{ik(x+L)}u_k(x+L) = e^{ikx}u_k(x)$
$u_k(x+L) = u_k(x+a) = u(x) \Rightarrow e^{ikL} = 1$, $k = \frac{2\pi}{L}\times$int

Electrons in nearly free electron potential

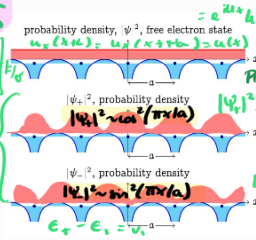


energy gap, Free e, energy band, energy gap, energy band
Prob densities indicate $E_+ < E_-$
heavily ionised donor atom; donor levels just below conduct° band ...

ionis energy $E_n \approx \frac{m^*}{m}\frac{1}{\epsilon_r^2}\ldots = -0.66$ meV
+IONS (charge)
Ionised, n-type since $\ldots$
real ground state of donor imp $a_0^* = \frac{\epsilon_r}{m^*}a_0$
$\epsilon = \hbar^2k^2/2m$
donor concentrat° overlaps $n_c = 1/(a_0^*)^3$ [$/m^3$]

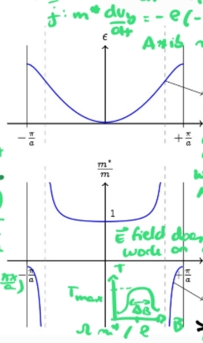


Electrons in "empty" lattice — k-space unit cell



probability density, ψ^2, free electron state
$u_k(x+L) = u_k(x+a) = u(x) \Rightarrow e^{ikL} = 1$
$|\psi_+|^2$, probability density
$|\psi_+|^2 \propto \cos^2(\pi x/a)$
$|\psi_-|^2$, probability density
$|\psi_-|^2 \propto \sin^2(\pi x/a)$
Prob densities
$E_+ - E_- = \ldots$

Drift velocity $2\langle u.\epsilon\rangle = T = \frac{1}{2}m^*|\vec{v}|^2$
EOM no field: if $\vec{\mathcal{E}} = 0$, $\vec{B} = 0$ & steady state $\frac{d}{dt} = 0$
$0 = -m^*\vec{v}/\tau \Rightarrow \vec{v} = 0$, $T = 0$
EOM fields: $\vec{v}\times\vec{B} = \begin{vmatrix}\hat{i} & \hat{j} & \hat{k} \\ v_x & v_y & v_z \\ 0 & 0 & B\end{vmatrix} = \hat{i}v_yB + \hat{j}(v_xB)$
$\hat{i}$: $m^*dv_x/dt = -e(\mathcal{E}e^{\ldots} + v_yB) - m^*v_x/\tau$ (A)
$\hat{j}$: $m^*dv_y/dt = -e(-v_xB) - m^*v_y/\tau$ (B)
A + iB: $m^*\frac{d}{dt}(v_x + iv_y) = -e\mathcal{E}e^{i\omega t} - eB(v_y - iv_x)$
$m^*\frac{du}{dt} = -e\mathcal{E}e^{i\omega t} - eB(-iu) - m^*u/\tau$
$\frac{du}{dt} = \ldots - i\omega u - \ldots$
$\omega = eB/m^*$
$A = -e\mathcal{E}/m^*$



$\frac{d^2\epsilon}{dk^2}$
EOM: $\hbar\frac{d\vec{k}}{dt} = -e(\vec{\mathcal{E}} + \vec{v}(\vec{k})\times\vec{B})$
$\vec{v}(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\epsilon(\vec{k})$
$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\epsilon}{dk^2}$
semi-conductor: small ← Gap → BIG: insulator
mass
E field does not work on electrons
negative mass!
Only partially occupied bands contribute to conduct°
momentum transfer with lattice (diffract°) is > momentum from the applied field → forward mom
def effective mass

SEMI-CONDUCTORS

Energy conserv: $\hbar\omega \simeq E_G$
Momentum conserv: $\hbar\Delta k = \hbar\omega/c$

DIRECT GAP / INDIRECT GAP
: indirect absorption process, phonon, lattice vibration
inert, no effect

CB: $\epsilon(\vec{k}) = E_G + \frac{\hbar^2 k^2}{2m_c^*}$, $m_c^* > 0$

VB: $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m_v^*}$, $m_v^* < 0$ — electron concentration, hole conc.

METAL — filled band

Holes: band of $N - n$ e ≡ full band N e + n holes
charge $q_h = +e$
wave vector $\vec{k}_h = -\vec{k}_e$
velocity $\vec{v}_h = \vec{v}_e$
positive effective mass $m_h^* > 0$
positive energy $\frac{\hbar^2 k_h^2}{2m_h^*} > 0$

EOM: $\hbar\frac{d\vec{k}}{dt} = -e(\vec{\mathcal{E}} + \vec{v}(\vec{k})\times\vec{B})$, $\quad \vec{v}(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\,\epsilon(\vec{k})$
For parabolic bands $\epsilon(\vec{k}) = \epsilon(0) + \hbar^2k^2/2m^*$, group v: $\vec{v} = \frac{\hbar\vec{k}}{m^*}$
$\Rightarrow m_e^* \, d\vec{v}_e/dt = -e(\vec{\mathcal{E}} + \vec{v}_e\times\vec{B}) - m_e^*\vec{v}_e/\tau_e$
$\Rightarrow m_h^* \, d\vec{v}_h/dt = +e(\vec{\mathcal{E}} + \vec{v}_h\times\vec{B}) - m_h^*\vec{v}_h/\tau_h$, $\quad m_h^* = -m_v^*$

$\Delta E: E_2 - E_1$

$\left[E_G + \frac{\hbar^2 k_e^2}{2m_c}\right] - \left[\frac{\hbar^2 k_h^2}{2m_v}\right]$

Current density: $\vec{J}_{tot} = \vec{J}_e + \vec{J}_h \rightarrow I = j_{tot}A$
$\vec{J}_e = n(-e)\vec{v}_e$, $\quad \vec{J}_h = p(+e)\vec{v}_h$

E conductivity: $\sigma = \frac{ne^2\tau_e}{m_e^*} + \frac{pe^2\tau_h}{m_h^*}$

electrons, heavy hole, light hole, split-off hole

Intrinsic = pure
$n = p = n_i = p_i$
band intrinsic found $\ln\left(\frac{n_i}{T^{3/2}}\right)$ vs $1/T$
$n = N_c e^{-(E_G-\mu)/(k_BT)}$, $p = N_v e^{-\mu/(k_BT)}$
intrinsic: $n = p = n_i$
$n_i = BT^{3/2} e^{-E_G/2k_BT}$ $\iff$ $\ln(n_i/T^{3/2}) = -\frac{E_G}{2k_B}\frac{1}{T} + \ln B$
→ Fermi-Dirac occupation $f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1} \simeq e^{-(\epsilon-\mu)/k_BT}$
$E_G = 2$ gradient

n^o conduct^n e: $N_c = \int_{E_G}^{\infty} g_c(\epsilon) f_e(\epsilon)\, d\epsilon$
concentration: $n = \frac{N_c}{V}$
$= N_c e^{-(E_G-\mu)/k_BT}$, $E_G = 1\,\text{eV}$, $T = 300\text{K}$

effective density of states $N_c = 2\left(\frac{m_e^* k_BT}{2\pi\hbar^2}\right)^{3/2}$ of CB

n^o holes $N_h = \int g_h f_h\, d\epsilon$, VB
concentration holes: $p = N_v e^{-\mu/k_BT}$
$f_h = 1 - \frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$ approx $f_h(\epsilon) \simeq e^{(\epsilon-\mu)/k_BT}$
effective density VB: $N_v = 2\left(\frac{m_h^* k_BT}{2\pi\hbar^2}\right)^{3/2}$
$n = p \Rightarrow N_c e^{-(E_G-\mu)/k_BT} = N_v e^{-\mu/k_BT}$ — substitute, solve

energy, free e: $\epsilon = \hbar^2k^2/2m$
density of states: $g(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\epsilon}$
cond^n e: $\epsilon - E_G = \hbar^2k^2/2m_e^*$; holes: $\epsilon = -\hbar^2k^2/2m_h^*$
$g_c(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{\epsilon - E_G}$
$g_h(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}\sqrt{-\epsilon}$

Carrier concentrations
$n = N_c e^{-(E_G-\mu)/k_BT}$
$p = N_v e^{-\mu/k_BT}$
$N_c = 2(m_e^* k_BT/2\pi\hbar^2)^{3/2}$
$N_v = 2(m_h^* k_BT/2\pi\hbar^2)^{3/2}$
$n \times p = n_i^2 = N_c N_v e^{-E_G/k_BT}$
$n = p = n_i = \sqrt{N_c N_v}\, e^{-E_G/2k_BT}$

Determining gaps
recall $N_c = 2\left(\frac{m_e^* k_BT}{2\pi\hbar^2}\right)^{3/2}$
$N_v = 2(m_h^* k_BT/2\pi\hbar^2)^{3/2}$
$n_i = \sqrt{N_c N_v}\, e^{-E_G/2k_BT}$
$\ln(n_i/T^{3/2}) = \ln A e^{-E_G/2k_BT} = \ln A - \frac{E_G}{2k_B}\frac{1}{T}$
form straight line: $y = c - mx$
Plotting $n_i/T^{3/2}$ v.s $1/T$ yields a straight line with slope $-E_G/2k_B$ allowing E_G to be det

Extrinsic - impurities / dopants
(n) e donors: ↑ n^o negative charged carriers
(IV) replace Si, Ge by P, As (V) — Ga → IV Si
extra e weakly bound to the donor
easy thermally excite
V → IV semicond adds extra e & proton to a periodic crystal

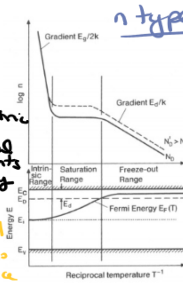
Show chemical potential — superconductor eqt
reminders: Energy levels
$\epsilon_n^H = \frac{-me^4}{2(4\pi\epsilon_0)^2\hbar^2}\times\frac{1}{n^2} = \frac{-13.6}{n^2}$ eV
Bohr rad $a_0 = \frac{(4\pi\epsilon_0)\hbar^2}{me^2} = 0.529$ Å

H-model dopants: $m \to m_e^*$, $\epsilon_0 \to \epsilon_r\epsilon_0$
energy levels $\epsilon_n^D = -\frac{1}{\epsilon_r^2}\left(\frac{m_e^*}{m}\right)\times\frac{13.6}{n^2}$ eV $\sim$ 6-8 [meV]
donor Bohr: $a_D = \epsilon_r(m/m_e^*)\times 0.529$ Å $\sim$ 5 [nm] $\gg a_0$
continuum (e free); ionisation energy; $\Phi_{1s}(r)$: ground state wave fn
Electron orbits the donor atom; donor = neutral
Electron is removed, donor is ionised (charge +e)
ionisation energy $\epsilon^D = \epsilon_1^D \sim 10$ [meV]

(IV) Si, Ge → III B, Al
(P) e acceptors: ↑ n^o + charged particles
hole energy increases
CB, $\epsilon_e \sim 10$ meV, VB, $E_G \sim 1$ eV $(\gg \epsilon^D)$
$\epsilon_n^A = \frac{-1}{\epsilon_r^2}\left(\frac{m_h^*}{m}\right)\times\frac{13.6}{n^2}$ eV
$a_A = \epsilon_r(m/m_h^*)a_0$
note: $n = \infty \Rightarrow$ hole escapes from acceptor i.e. to VB

p type: $p \sim N_A e^{-\epsilon^A/k_BT}$, $p \simeq N_A$, $p_i \simeq \sqrt{N_c N_v}\, e^{-E_G/2k_BT}$

n type:



For Si, plateau at $N_D \sim 10^{15}/\text{cm}^3$ extends between $150K < T < 500K$.

From previous lecture $n = N_C e^{-(E_G-\mu)/k_BT}$.

At low T: $k_BT < \epsilon^D$ electrons occupy the bound states of the donor atoms – carrier freeze out. The Fermi level lies at the donor level, $\mu = E_G - \epsilon^D$:

$n \simeq N_D e^{-\epsilon^D/k_BT} \quad k_BT \ll \epsilon^D$

Around room T: $k_BT \simeq 25$ meV, which is $> \epsilon^D \sim 10$ meV. The donors will be ionised. The effective conduction band density of states $N_C \sim 10^{19}/\text{cm}^3 \gg N_D \sim 10^{14-18}/\text{cm}^3$. The probability of excitation will be large:

$n \simeq N_D$ - saturation

At high T: donor atoms will be ionised, donating their electrons to the CB. Direct excitation across the gap also possible, and dominates – intrinsic behaviour.

$n \simeq n_i \propto T^{3/2}e^{-E_G/2k_BT}$

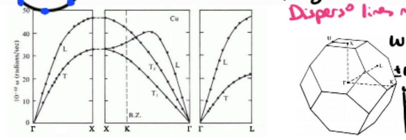
Heat capacity C_V
Electrons within k_BT of E_F/μ are excited when heated $T{:}0 \to T$
Excited e: fract^n T/T_F when $kT_F = E_F$
Tot gain E $\sim k_BT \times \frac{T}{T_F}\times N$ $= RT^2/T_F$ per mole
$C_V = \frac{\partial E}{\partial T} = \frac{2RT}{T_F}$ per mole
Classic: N indep atoms each with 6 deg freedom (3 kinetic, 3 potential) $C_V = 3R$/mole at all T
Einstein: 3N identical oscillators with quantised E_s $C_V \to 3R$ at high T, & drops to 0 exp as $T \to 0$
Debye: 3N quantised oscill with freq satisf $\omega = ck$ of long wavelength acoustic vibrations $C_V \to 3R$ at high T & goes like $C_V T^3$ as low T
$\frac{C_V}{T} = \alpha + \beta T^2$ at low T; $\alpha = 0$ for insulator

Fermi level
intrinsic semi-conductor
$\mu = \frac{E_G}{2} + \frac{k_BT}{2}\ln\left(\frac{N_v}{N_c}\right) = \frac{E_G}{2} + \frac{3k_BT}{4}\ln\left(\frac{m_h^*}{m_e^*}\right)$
Prob occupation $f_e(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$
$\epsilon = \mu$ & $f_e(\epsilon) = \frac{1}{2}$
Fermi level occ is $\frac{1}{2}$
CB $f_e(\epsilon, T) \simeq 0$; $\mu \simeq \frac{1}{2}E_G$ — $f_e(\epsilon, T) = \frac{1}{2}$; VB $f_e(\epsilon, T) \simeq 1$

CRYSTAL DYNAMICS
No dispersion (continuum): $\frac{\partial^2 u}{\partial t^2} = \frac{E}{\rho}\frac{\partial^2 u}{\partial x^2}$
solution: $u(x,t) = u_0\cos(kx - \omega t + \phi)$
$\omega = \sqrt{E/\rho}\,k$; phase $v_p = \omega/k$; group $v_g = \sqrt{E/\rho}$

Dispersion relation deriv
Hooke's law: forces on atoms are
• $K(u_s - u_{s-1})$ to the left
• $K(u_{s+1} - u_s)$ to the right
EOM atom: $M\frac{d^2u_s}{dt^2} = K(u_{s+1} + u_{s-1} - 2u_s)$
wavelike sol: $u_s = ue^{i(ksa - \omega t)}$
substit: $-M\omega^2 = 2K(\cos ka - 1)$
two possible sol → $u = 0$ (no waves) ; $\omega^2 = \frac{2K}{M}(1 - \cos ka) = \frac{4K}{M}\sin^2(ka/2)$
$\omega(k) = \sqrt{\frac{4K}{M}}\,|\sin\frac{ka}{2}|$

$\omega > \omega_{max}$; cut off freq $\omega_{max} = \sqrt{4K/M}$
$\omega^2 = \frac{4K}{M}\sin^2(ka/2)$
range k = Brillouin zone; dimension = π/a
$v = \sqrt{\frac{K}{M}}a = \sqrt{\frac{E}{\rho}}$, $\quad v_g = \sqrt{\frac{Ka^2}{M}}\cos\frac{ka}{2}$
$u_s = ue^{i(ksa - \omega t)}$; $\Delta k = 2\pi/Na$; Tot n^o different modes
$k = \pm\pi/a$ & $v_g = 0$ = standing wave
$\frac{\text{length Brillouin zone}}{\text{spacing btw points}} = \frac{2\pi/a}{2\pi/Na} = N$
Dispersion lines real solid - Cu (fcc)
$\omega^2 = K\left(\frac{1}{m} + \frac{1}{M}\right) \pm K\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4}{mM}\sin^2\frac{ka}{2}}$
Brillouin zone



It is not easy to plot ω versus (k_x, k_y, k_z). Therefore dispersion plots for real materials are normally displayed with ω plotted against k for wavevectors in a small number of special directions within the Brillouin zone.

The end points are labelled using special letters. For fcc materials, $\Gamma = \frac{2\pi}{a}(0,0,0)$, $X = \frac{2\pi}{a}(1,0,0)$, $L = \frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $K = \frac{2\pi}{a}(\frac{3}{4},\frac{3}{4},0)$.

optical, acoustic, LO, TO, LA, TA, 2 atom basis; $\sqrt{2K/M}$, $\sqrt{2K/m}$

MAGNETISM
origins → moving electric charges → fundamental mag moments of elementary particles
Magnetisation $\vec{M} = \frac{1}{V}\sum_i \vec{\mu}_i$
$\vec{B}_M = \mu_0\vec{M}$; $\vec{M} = \chi\frac{\vec{B}_0}{\mu_0}$; $= \chi B_0$
measures tendency of a solid to exhibit magnetisation in presence mag field — magnetic susceptibility
$\chi > 0$ Paramagnetic; $\chi < 0$ Diamagnetic; Ferromagnetic
mag field: Heat vector, cancels; directed field; solid under mag field, create magnetisation and orient

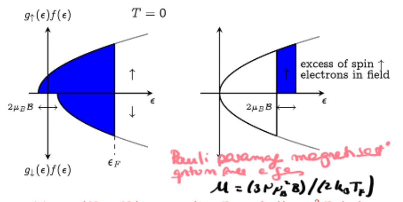
PARAMAGNETISM
arise from preferred alignment of randomly and oriented mag moments under applied field
solid containing atoms with permanent dipoles
applied $\vec{B}_0$ ⇒ torque $\vec{\tau} = \vec{\mu}\times\vec{B}$ ⇒ $\vec{\mu}$ to randomly aligned $\vec{\mu} = 0$
non-vanishing $\vec{\mu} \parallel \vec{B}_0$, thermal disorder ↓ M
atomic moments $\vec{\mu} = -g\mu_B\vec{J}$
Reminders:
• tot ang momentum $\hbar\vec{J} = \hbar\vec{L} + \hbar\vec{S}$
• Bohr magneton: μ_B
• Landé g factor $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$
• J_z quantised: $m_J = -J, -J+1, \dots, J-1, J$

Atomic moments
current: $i = \frac{\text{charge}}{\text{time}} = \frac{-e}{2\pi/\omega} = \frac{-e\omega}{2\pi}$
enclosing area: $A = \pi r^2$
resulting magnetic dipole moment: $\vec{\mu} = i\vec{A} = -\frac{e\hbar}{2m}\vec{L}$
$|\hbar\vec{L}|$: orbital angular momentum of e $= m\omega r^2$ ← direct^n $\vec{\mu}$: clockwise looking along $\vec{\mu}$
Bohr magneton $\mu_B = \frac{e\hbar}{2m} = 9.27\times10^{-24}\text{JT}^{-1} = 5.79\times10^{-5}\text{eVT}^{-1}$
Total orbital momentum $\vec{\mu} = -\mu_B\vec{L}$
when $\hbar\vec{L} = \hbar\sum\vec{\ell}$ = tot orbital angular momentum
$\vec{\mu} = -g_0\mu_B\vec{S}$ where $g_0 = 2$ = electron spin g factor
note: close shell e: $\sum\vec{\ell}$ & $\vec{S} = 0$ ∴ no permanent magnetic moment
Add mag field: $U = -\vec{\mu}\cdot\vec{B}_0 = m_J g\mu_B B$, $m_J = -J, -J+1, \dots, J-1, J$

(ex) no orbital momentum ($L = 0$), single spin ($S = 1/2$)
$J = 1/2$, $m_J = \pm 1/2$, $g = 2$, $U = \pm\mu_B B$
$\vec{B}_0 = 0$, $\vec{B}_0 \neq 0$: $m_J = +\frac{1}{2}$, $\mu_z = -\mu_B$, $\epsilon_2 = +\mu_B B$; $m_J = -\frac{1}{2}$, $\mu_z = +\mu_B$, $\epsilon_1 = -\mu_B B$; $2\mu_B B$
p = probability to occupy level
$P_1 = \frac{1}{Z}e^{+\mu_B B/k_BT}$, $\quad P_2 = \frac{1}{Z}e^{-\mu_B B/k_BT}$
$\langle\mu_z\rangle = (+\mu_B)P_1 + (-\mu_B)P_2 = \mu_B\tanh\left(\frac{\mu_B B}{k_BT}\right)$
For N indep atoms: $M = N\langle\mu\rangle = N\mu_B\tanh\left(\frac{\mu_B B}{k_BT}\right)$
$M \propto B$ for weak fields; M saturates for strong fields
$\tanh x \simeq x$, x small; $\Rightarrow M \simeq \frac{N\mu_B^2 B}{k_BT} = \chi\frac{B}{\mu_0}$, B small
$\Rightarrow \chi = C/T$ Curie's Law

DIAMAGNETISM
arise from induced change in orbital motion of e in mag field
~ applied field changes e motion
• $\vec{B} = 0 \Rightarrow \frac{Ze^2}{4\pi\epsilon_0 r^2} = m\omega_0^2 r \Rightarrow \omega_0^2 = \frac{Ze^2}{4\pi\epsilon_0 mr^3}$ (electrostatic = centripetal)
• $\vec{B} \neq 0 \Rightarrow \frac{Ze^2}{4\pi\epsilon_0 r^2} + e\omega rB = m\omega^2 r$
$\omega^2 - \frac{eB}{m}\omega - \omega_0^2 = 0$
∴ $\omega \simeq \omega_0 + eB/2m$
B field induces additional angular freq $\omega_{ind} = \frac{eB}{2m}$
induced current clockwise
$i_{ind} = \frac{\text{charge}}{\text{time}} = -e^2B/4\pi m$
$|\mu| = i_{ind}A = -e^2Br^2/4m$ ∴ $\mu = -\frac{Ze^2B}{4m}\langle\rho^2\rangle$
$\langle\rho^2\rangle = \langle x^2\rangle + \langle y^2\rangle = \frac{2}{3}\langle r^2\rangle$
$\vec{M} = N\vec{\mu} \Rightarrow \chi = \frac{\mu_0 M}{B} = -\frac{\mu_0 NZe^2}{6m}\langle r^2\rangle$
Superconductor: Classical Langevin diamagnetic susceptibility $\chi = -1$ perfect diamagnet; $\sim 10^{-5}$ weak, only evident no paramagnetism

States with spin ↑ lowered in energy by $\mu_B B$, states with spin ↓ raised in energy by $\mu_B B$. Let the density of states of spin up (down) electrons be $g_\uparrow(\epsilon)$ $(g_\downarrow(\epsilon))$, and fill the lowest N states with electrons.

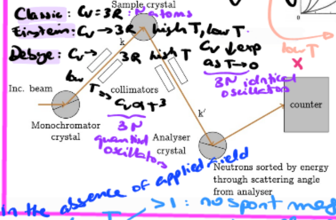


Pauli paramag magnetisation: quantum free e gas
$M = (3N\mu_B^2 B)/(2k_BT_F)$
$M = \mu_B(N_\uparrow - N_\downarrow) \simeq \mu_B\times(2\mu_B B\times g_\uparrow(\epsilon_F)) = \mu_B^2 Bg(\epsilon_F)$.

Levitat^n mag force: $\vec{F} = \nabla(\vec{\mu}\cdot\vec{B}) = (\chi/\mu_0)\nabla B^2$
diamag attracted field minima

Low Dulong & Petit: $C_V = \frac{\partial}{\partial T}\left(\frac{\langle E\rangle}{n}\right)_V$, solids high T: $= 3R = 25\,[\text{Jmol}^{-1}\text{K}^{-1}]$
Speed sound mat; $C = \frac{\partial\omega}{\partial k}$
oscillators quantised energies: $E_n = n\hbar\omega$, $n = 0, 1, 2, \dots$
Einstein model: $P_i = \frac{e^{-E_i/k_BT}}{\sum_{i=0}^{\infty} e^{-E_i/k_BT}}$, $\langle E_n\rangle = \sum_{i=0}^{\infty}E_iP_i$
~ fits data well until low T - exp (assumes 1 freq vibrat^n)
Debye model: 2 transverse, 1 acoustic modes; $C_V \propto T^3$ at low temp ✓

Phonons ~ inelastic neutron scattering probe
$\hbar\omega = \hbar\omega_0 \pm \hbar\omega$
$\hbar\vec{k}' = \hbar\vec{k} \pm \hbar\vec{q} + \hbar\vec{G}$
Classic: $C_V = 3R$, N atoms
Einstein: $C_V \to 3R$ high T, low T
Debye: $C_V \to 3R$ high T, C_V drop as $T \to 0$, $C_V \propto T^3$
3N identical oscillators; 3N quantised oscillators



in the absence of applied field: no spont mag

FERROMAGNETISM
spontaneous mag order in which quantum mech exchange field favours the alignment of mag moments
low T → spont mag: dipole tend alignments
Ferromagnetic order: all moments contribute ↑↑↑ or ↗↗
Ferrimag: some cancelled; overall finite M ↑↓↑↓
Antiferromag: no spont magnet, but mag order ↑↓↑↓
Exchange interaction: T ~ 1000K magnetic ordering require another origin: $-2\vec{J}\vec{S}_1\cdot\vec{S}_2$
energy diff btw ∥ & anti-∥ alignment of moments
Exchange E: Heisenberg Hamiltonian
$\mathcal{H} = -\sum_i\sum_{j\neq i} J_{ij}\vec{S}_i\cdot\vec{S}_j = \sum_i \vec{\mu}_i\cdot(\lambda\mu_0\vec{M})$ where $\lambda = \frac{\sum_{j\neq i}J_{ij}}{\mu_0 g^2\mu_B^2(N/V)}$
exchange int acts like extra mag field: $\vec{B}_E = \lambda\mu_0\vec{M}$
Curie-Weiss law: $\chi = \mu_0\frac{M}{B} = \frac{C}{T - T_c}$
$C = N\mu_B^2\mu_0/k_B$, $T_c = \lambda C$
$t = \frac{T}{T_c} < 1$: spont mag sets; $M = N\mu_B\tanh\left(\frac{\mu_B\lambda M}{k_BT}\right)$ when $T > T_c$
$m = \tanh\left(\frac{m}{t}\right)$; reduced magnetisation: $m = \frac{M}{N\mu_B}$; reduced temp $t = T/T_c$
curie temp: susceptibility $\chi \to \infty$ since $M = \frac{\chi B}{\mu_0}$ finite M can occur even if B = 0