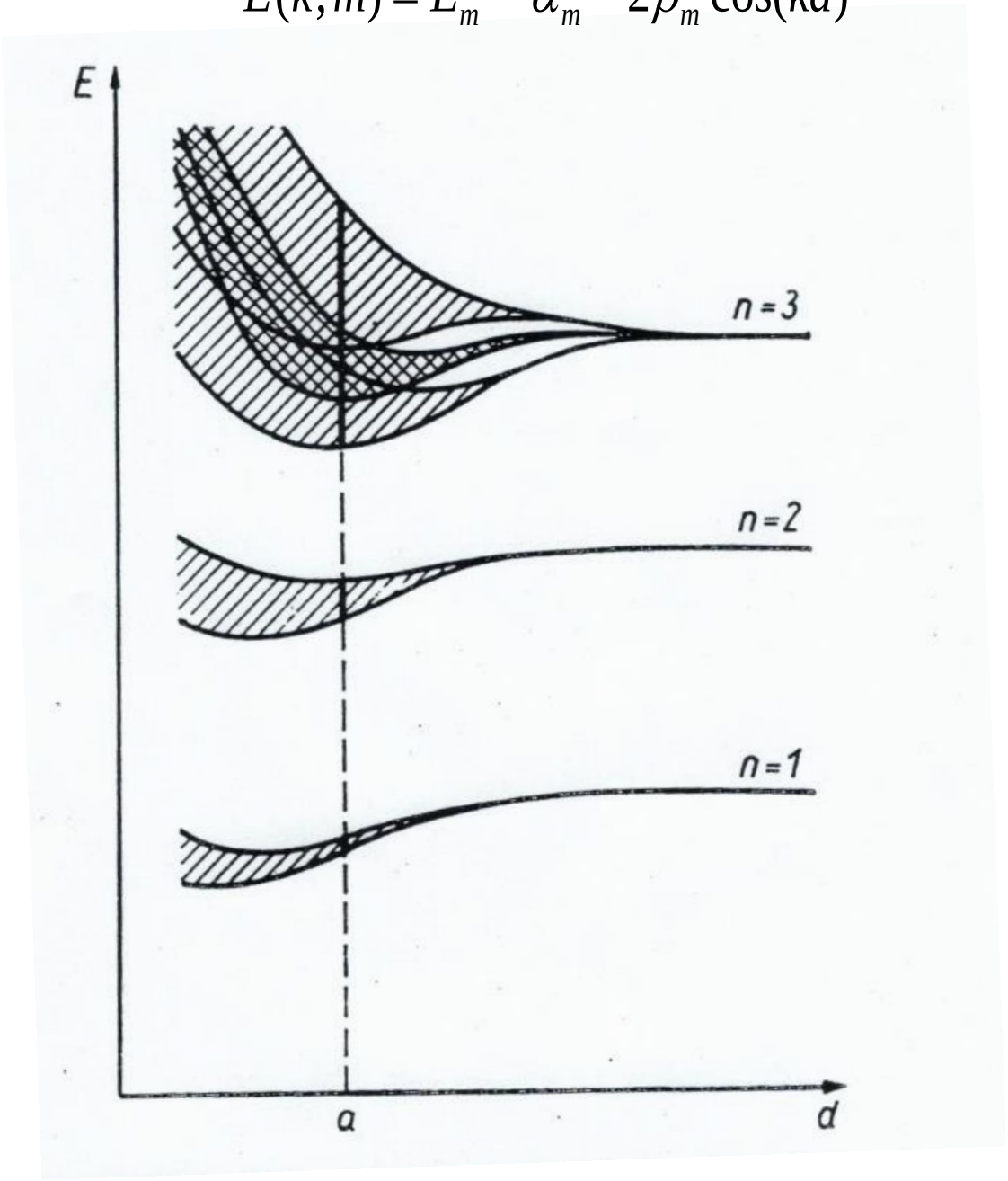
Solid state physics for Nano

Lecture 6: electronic band structure of solids

Prof. Dr. U. Pietsch

$$E(k,m) = E_m^{at} - \alpha_m - 2\beta_m \cos(ka)$$



Band of allowed states

Overlap between two neighboured atomic states results in 2 states : bonding and antibonding state. Bonding between 10^{23} atomic in solids results in 2 10^{23} solution, which are such as dense that they overlap and create „bands“ separated by „forbidden“ zones. Empirically described by

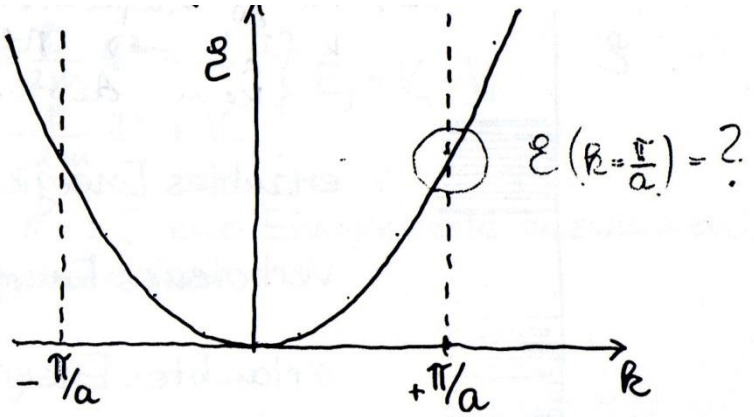
$$E(k,m) = E_m^{at} - \alpha_m - 2\beta_m \cos(ka)$$

α describes decrease of energy due to bonding, 4β measures the band width between k=0 and k=π/a. Many properties of solids can be described in terms of „electron gas“ (Sommerfeld) : electrons are moving as non-interacting particles with spin1/2

These „free electrons have kinetic energy $E = \frac{m}{2}v^2 = \frac{p^2}{2m}$

It describes a dispersion relation $\boxed{E = \frac{\hbar^2 k^2}{2m}}$ between energy E and momentum k

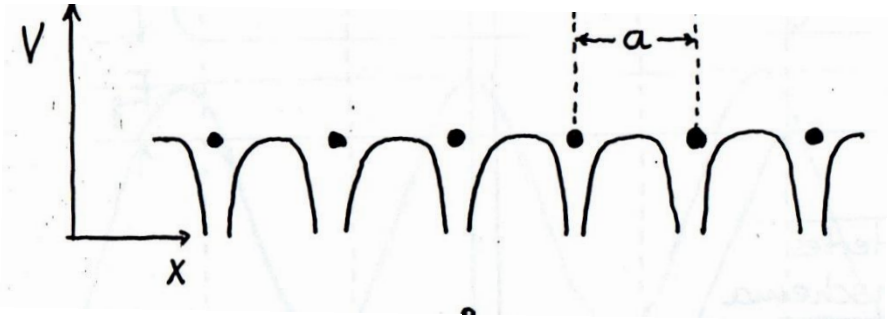
electron gas in solid



What happens, if k is approaching k=π/a ?

If k< π/a → λ>a → no interaction of electron wave with lattice
if k≈π/a → λ ≈ a → electron wave „reflected“ at lattice planes

Ansatz:



Electron wave propagates free as long as k< π/a

$$\psi_k = \psi_0 e^{ikx}$$

For k≈π/a =G/2 wave is Bragg reflected

$$\psi_{-k} = \psi_0 e^{-ikx}$$

$$\psi_+ = \psi_0 (e^{ikx} + e^{-ikx}) = 2\psi_0 \cos(kx)$$

$$\psi_- = \psi_0 (e^{ikx} - e^{-ikx}) = i2\psi_0 \sin(kx)$$

$$|\psi|^2 = e^{ikx}e^{-ikx} = 1$$

$$|\psi_+|^2 \approx \cos^2(kx)$$

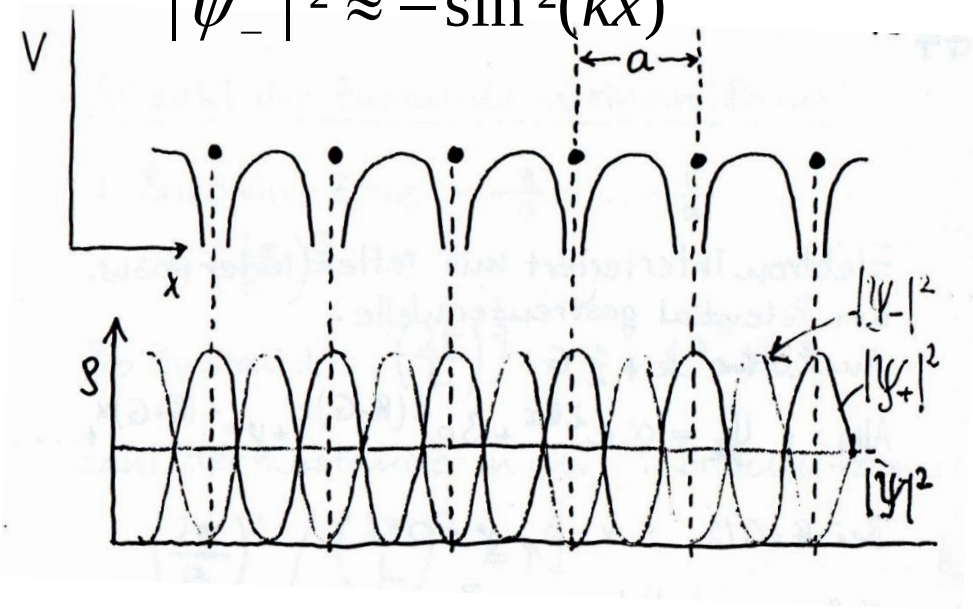
$$|\psi_-|^2 \approx -\sin^2(kx)$$

$|\psi_+|^2$

Largest probability between atoms

$|\psi_-|^2$

Largest probability at atoms

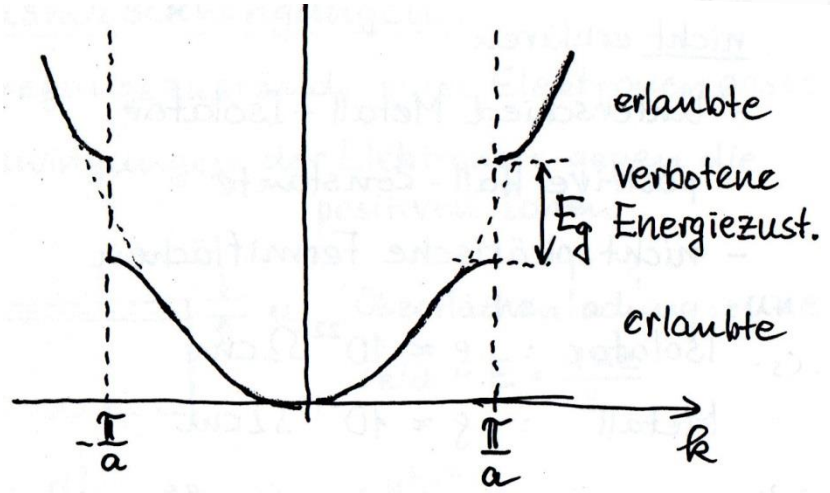


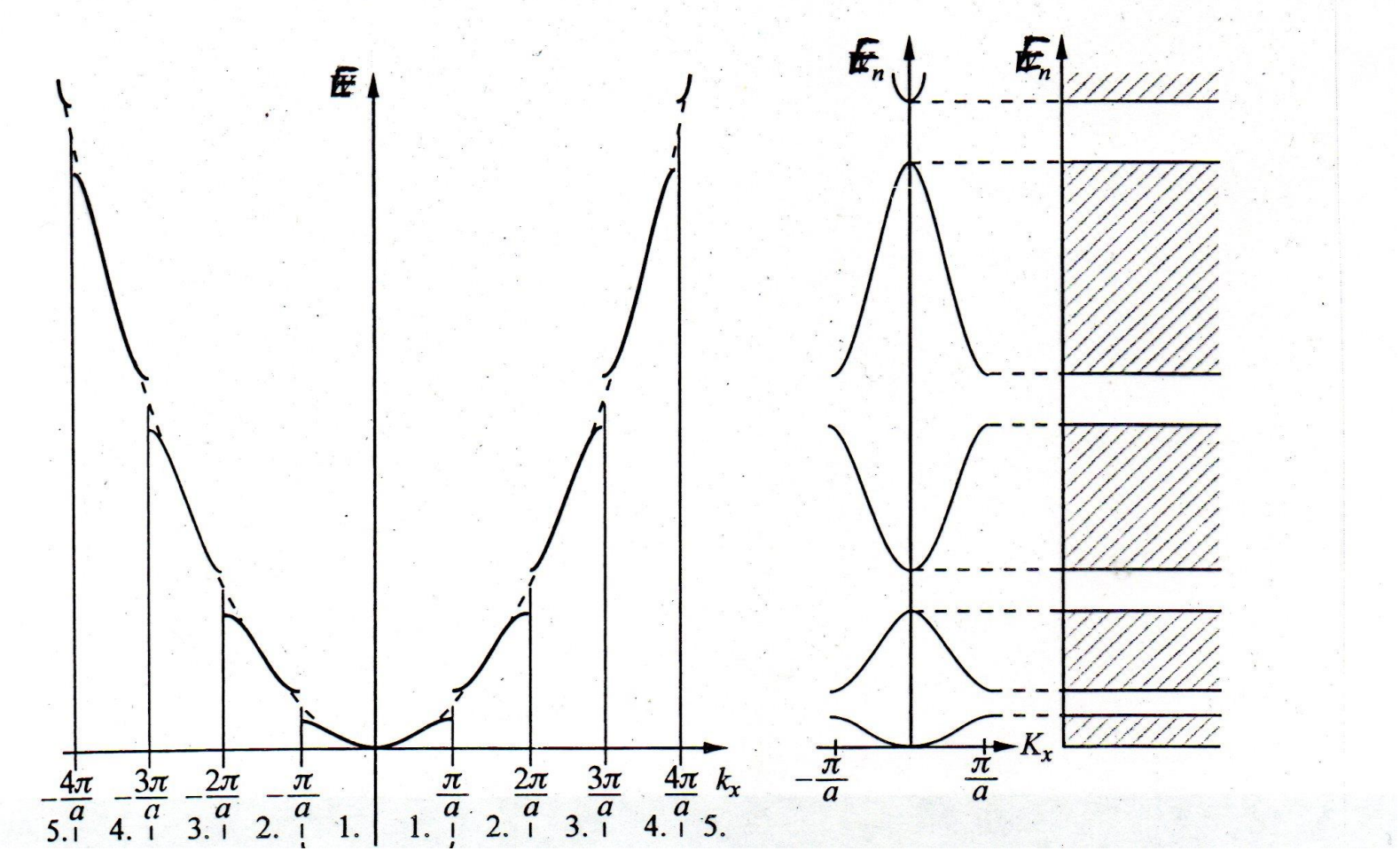
In terms of energy:

$$E(k)_+ = \frac{\hbar^2}{2m}k^2 - V_+$$

$$E(k)_- = \frac{\hbar^2}{2m}k^2 + V_-$$

$$V_+ - V_- = E_g$$ Energy gap





Valid also k=2π/a ; k=3π/a…..
→ Extended zone scheme

Parabel origin also at k=π/a ; k=2π/a…..
Overlap of peridodic zone scheme →
Folding into → -π/a < k < π/a
→ 1st Brillouin zone

→ Reduced zone scheme

“effective mass” of electrons in solid

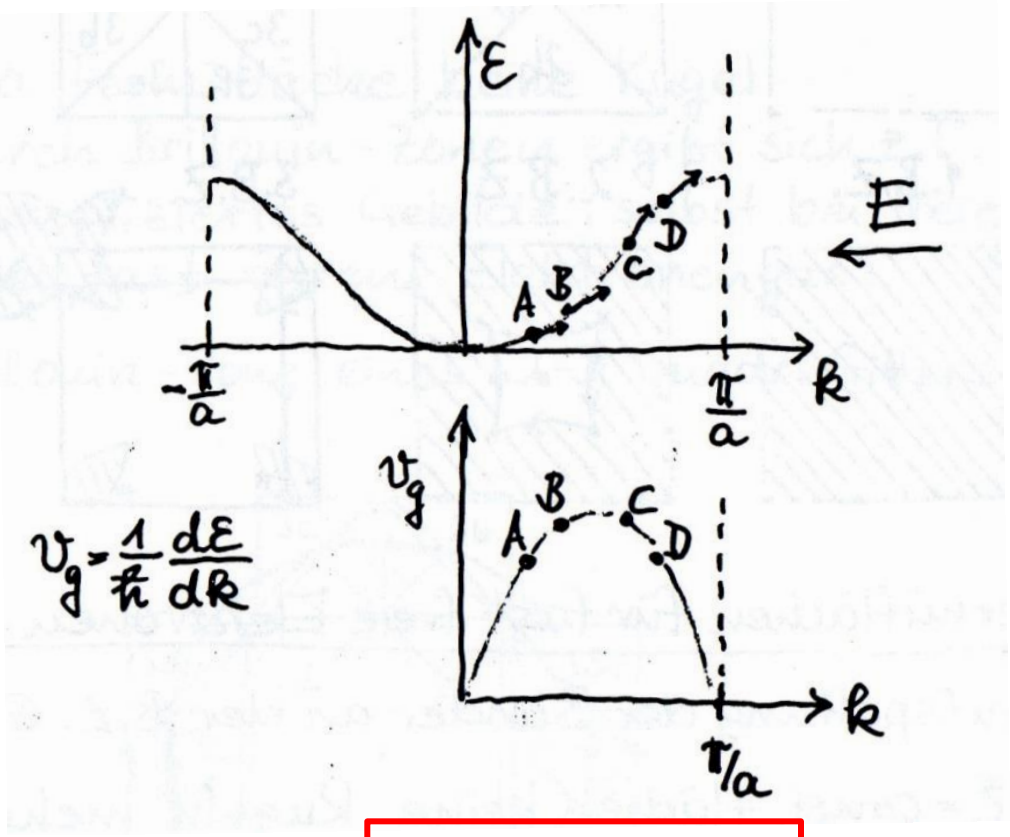
Due to specific badnd curvature

$$v = \frac{1}{\hbar}\frac{\partial E}{\partial k} \qquad \frac{dv}{dt} = \frac{1}{\hbar}\frac{\partial^2 E}{\partial k^2}\frac{dk}{dt}$$

$$\frac{dk}{dt} = \frac{F}{\hbar} = \frac{eE}{\hbar}$$

$$\frac{dv}{dt} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}F$$

$$F = \frac{\hbar^2}{\partial^2 E/\partial k^2}\frac{dv}{dt} = m^* a$$



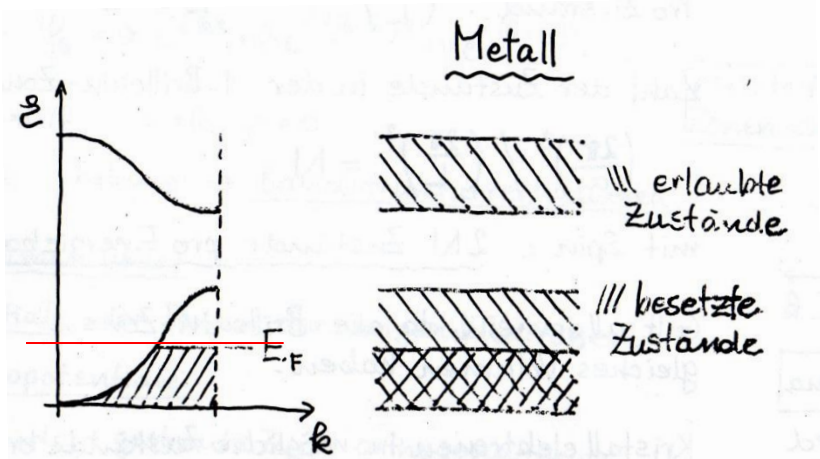
effective mass

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

Number of states per band in 1st BZ: $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$ $V = (\frac{2\pi}{a})^3$

$V = (\frac{2\pi}{L})^3$ $L^3 = Na^3$ $(\frac{2\pi}{a})^3 / (\frac{2\pi}{L})^3 = N$

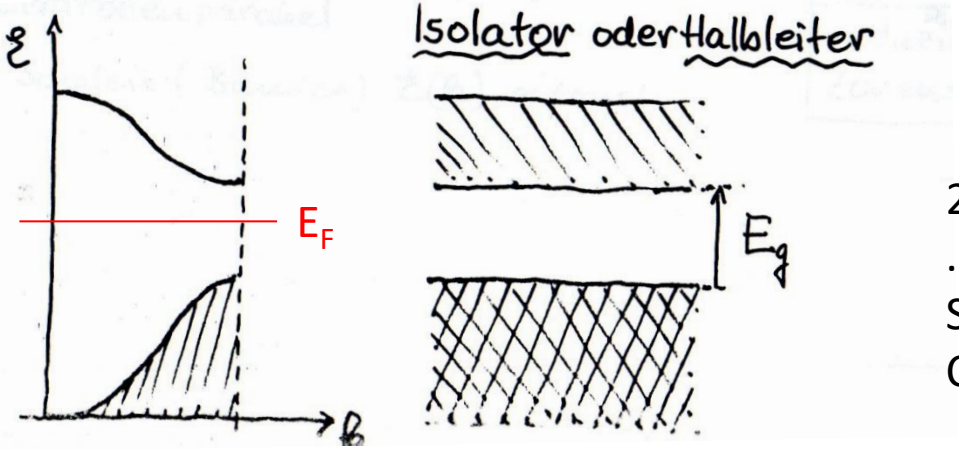
Because of spin → 2N states per energy band



1 or 3 electrons in upper band

Na: $1s^2 2s^2 2p^6, 3s^1$= Ne $3s^1$ upper band is filled with 1 electron only

Higherst populed energy – FERMI energy



2 or 4 electrons in upper band: Be, Mg, Ca, ……Sn T>18°C metal

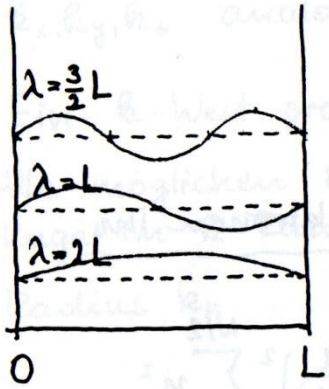
Si, Ge – typical semiconductors, E_g 0.1..2 eV

C, SiC … isolators E_g = 10eV

Density of states in 1D (DOS)

particle in box model, standing waves

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_n}{\partial x^2} = E_n\psi \qquad \psi_n(0) = \psi_n(L) = 0$$



$$\tfrac{1}{2}n\lambda_n = L$$

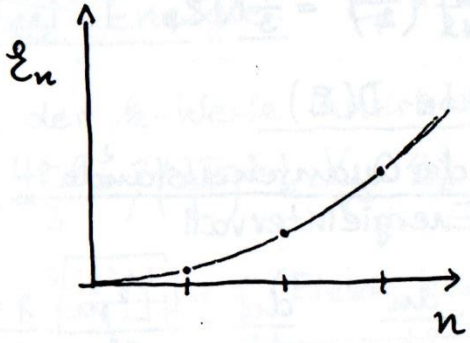
$$\psi_n = A\sin\left(\frac{n\pi}{L}x\right)$$

$$\frac{d\psi_n}{dx} = A\frac{n\pi}{L}\cos\left(\frac{n\pi}{L}x\right)$$

$$\frac{d^2\psi_n}{dx^2} = -A\left(\frac{n\pi}{L}\right)^2\sin\left(\frac{n\pi}{L}x\right)$$

$$\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{n}{2L}\right)^2$$

Energieniveaus



$$\varepsilon_n \sim n^2$$

N=2n due to spin

Total energy is:

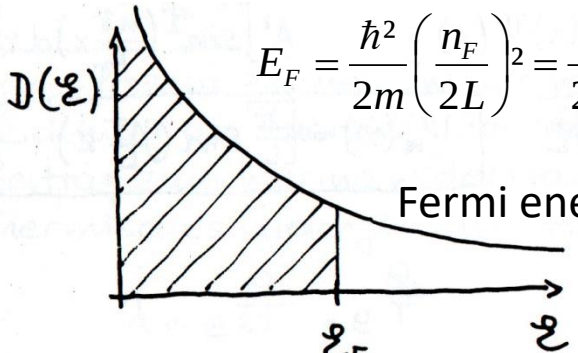
$$E = 2\sum_{n=1}^{n_F=N/2} E_n = 2\frac{\hbar^2}{2m}\left(\frac{1}{2L}\right)^2\sum_{n=1}^{N/2} n^2$$

$$E \approx \frac{\hbar^2}{2m}\left(\frac{1}{2L}\right)^2\left(\frac{N}{2}\right)^3 = \tfrac{1}{3}NE_F$$

$$D(E) = \frac{number\_of\_states}{energy\,\mathrm{int}\,ervall} = 2\frac{dn}{dE}$$

$$dE = \frac{h^2}{2m}\frac{n}{2L}\frac{dn}{2L} \qquad \frac{dn}{dE} = \frac{4L^2m}{h^2}\frac{1}{n}$$

$$D(E) = 2\frac{dn}{dE} = \frac{8L^2m}{\hbar^2}\frac{1}{n} = \frac{4L}{\hbar}\sqrt{\frac{m}{2E}} \approx \frac{1}{\sqrt{E}}$$



$$E_F = \frac{\hbar^2}{2m}\left(\frac{n_F}{2L}\right)^2 = \frac{\hbar^2}{2m}\frac{N^2}{(4L)^2}$$

Fermi energy

Fermi energy in 3D

Standing waves in 3D $\psi_n(\vec{r}) = \sqrt{\frac{8}{L^3}} \sin(\frac{n_x \pi}{L} x) \sin(\frac{n_y \pi}{L} y) \sin(\frac{n_z \pi}{L} z)$

Alternative $\psi_k(\vec{r}) = \sqrt{\frac{1}{V}} e^{i\vec{k}\vec{r}}$

Boundary conditions $\psi_k(x+L, y, z) = \psi_k(x, y+L, z) = \psi_k(x, y, z+L)$

$$k_x = 0, \pm\frac{2\pi}{L}; \pm\frac{4\pi}{L}; \ldots; \pm\frac{2n\pi}{L}; k_y = \ldots.; k_z = \ldots.$$

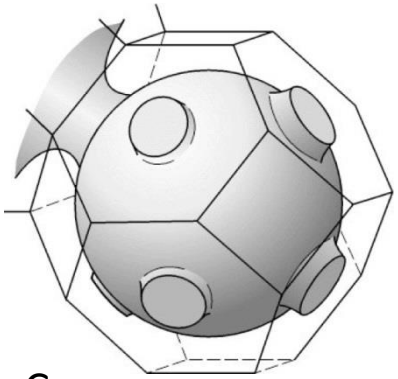
$$e^{ik_x(x+L)} = e^{i(2n\pi(x+L)/L)} = e^{i2\pi nx/L} e^{i2n\pi} = e^{i2\pi nL} = e^{ik_x x}$$

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

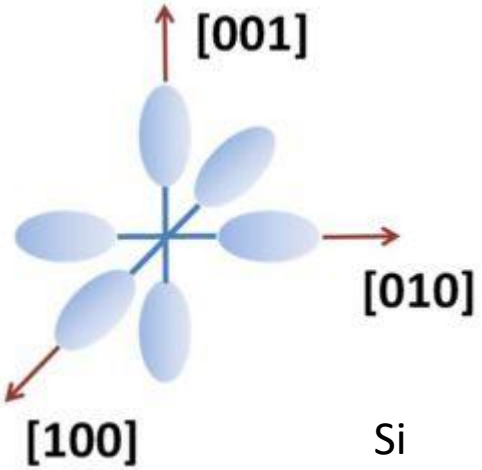
Dispersion relation for electrons

$$E(\vec{k}) == \frac{\hbar^2 k_F{}^2}{2m}$$

Fermi sphere with radius k_F



Cu



Si

Number of electrons in sphere with radius k_F

$$N = 2\frac{4\pi k_F^3}{3}/(\frac{2\pi}{L})^3 = \frac{V}{3\pi^2}k_F^3$$

$$k_F = \sqrt[3]{\frac{3\pi^2 N}{V}}$$

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

Fermi momentum $\hbar k_F = m v_F$ $\qquad m v_F = \hbar(\frac{3\pi^2 N}{V})^{1/3}$

Fermi velocity $v_F = \frac{\hbar}{m}(\frac{3\pi^2 N}{V})^{1/3}$

Fermi temperature $E_F = kT_F$

Example for Li: N/V= 4.6 10^{22} cm^{-3} =1 el/Li atom

k_F = 1.1 10^8 /cm = 1.1 /A
v_F = 1.3 10^8 cm/s = 1.3 10^3 km/s= 0.04% c
E_F = 4.7 eV → T_F = 55.000K

https://www.zahlen-kern.de/editor/

Density of states in 3D (DOS)

Analogous to phonons: Density of states

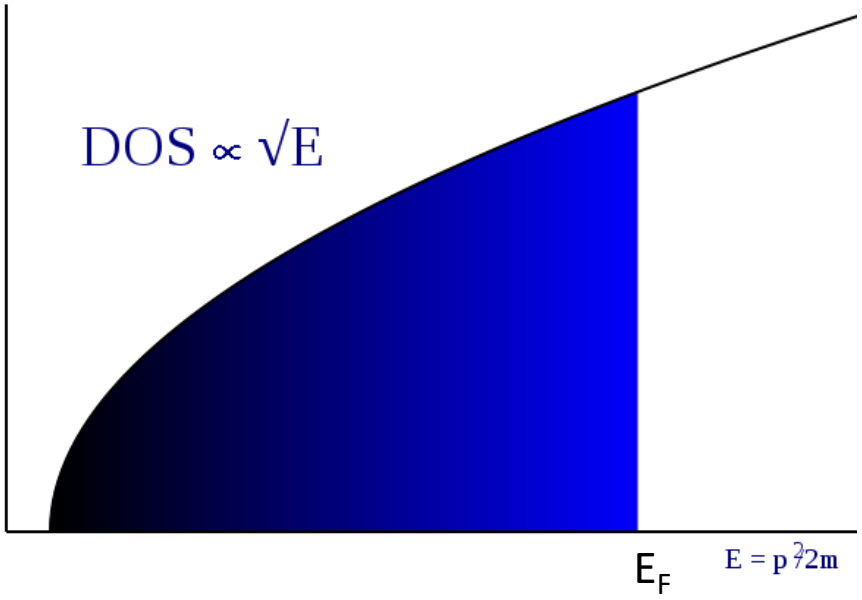
$$D(E) = 2\left(\frac{L}{2\pi}\right)^3 \iint \frac{dF}{|\, grad_k E\,|}$$

For perfect sphere:

$$|\, grad_k E\,| = \frac{\hbar^2 k}{m} \qquad dF = 4\pi k^2$$

$$D(E) = 2\left(\frac{L}{2\pi}\right)^3 \frac{4\pi k^2}{\hbar^2 k / m} = \frac{V}{\pi^2}\frac{mk}{\hbar^2}$$

$$D(E) = \frac{V}{\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$



Influence of Temperature on DOS

Bonding energy for lowest energy levels are large, all levels occupied

At T=0 probability of occupation

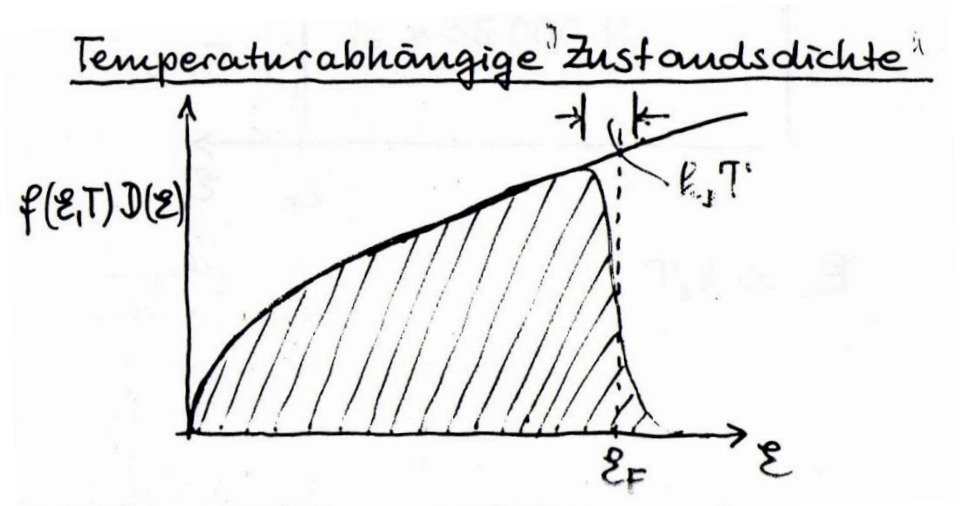
$$f(E) = \begin{cases} 1 \_ \ for \ \_ E \le E_F \\ 0 \_\_ \ for \ \_ E > E_F \end{cases}$$

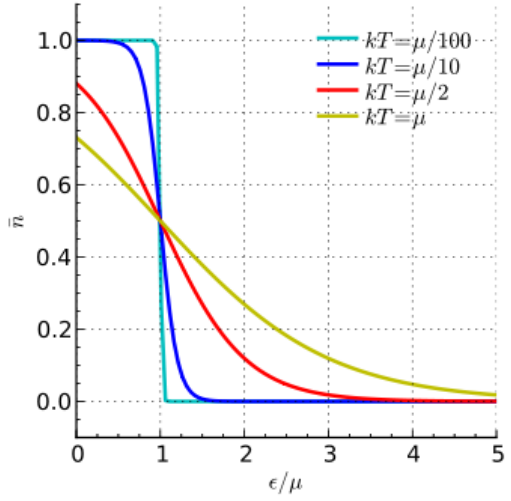
At T>0 , thermal energy kT, only levels close to E_F can be redistributed

$$f(E,T) = \frac{1}{\exp(\frac{E-\mu}{kT}) + 1}$$

$\mu \approx E_F$ chemical potential

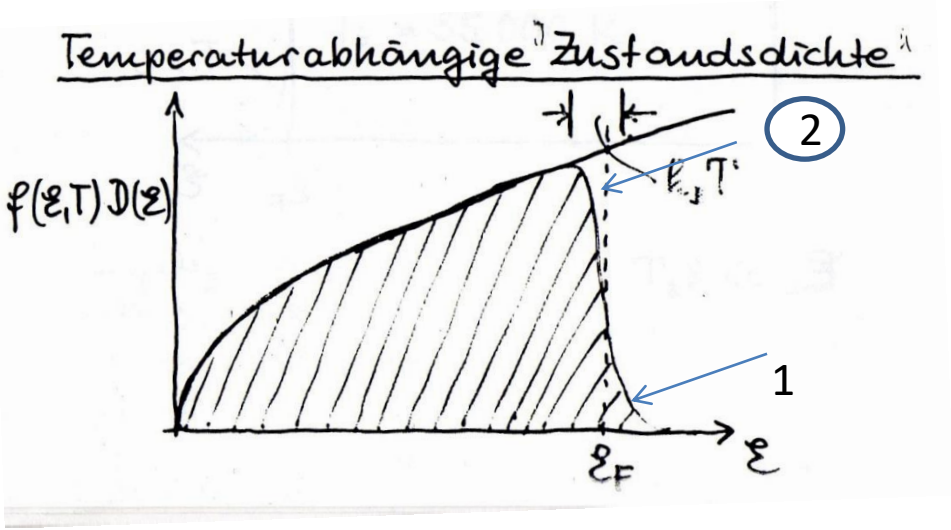
FERMI – DIRAC distribution





Impact of electrons to specific heat

Only electrons close to E_F can gain energy of about kT → this results in range E_F- ½ kT non occupied states (2) and in range E_F + ½ kT (1) and newly occopied states, all other electrons cannot contribute to specific heat

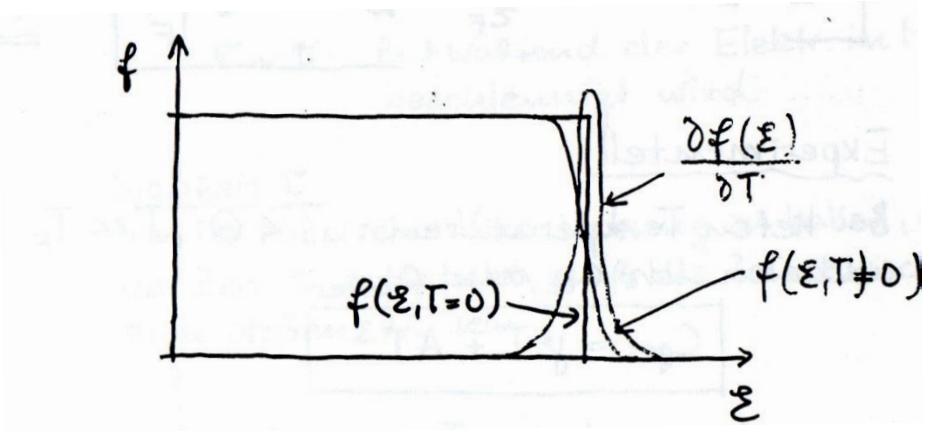


$$E_{el} == (1)\int_{E_F}^{\infty} dE(E-E_F)D(E)\,f(E,T)$$

$$+(2)\int_{0}^{E_F} dE(E-E_F)D(E)(1-f(E,T))$$

$$c_{el} = \frac{\partial E}{\partial T} = \int_0^{\infty} dE(E-E_F)D(E)\frac{\partial f}{\partial T}$$

Integral differs from zero only close to E_F



Impact of electrons to specific heat

$$\frac{\partial f}{\partial T} = \frac{E - E_F}{kT^2} \frac{\exp(\frac{E-E_F}{kT})}{[\exp(\frac{E-E_F}{kT}) + 1]^2}$$

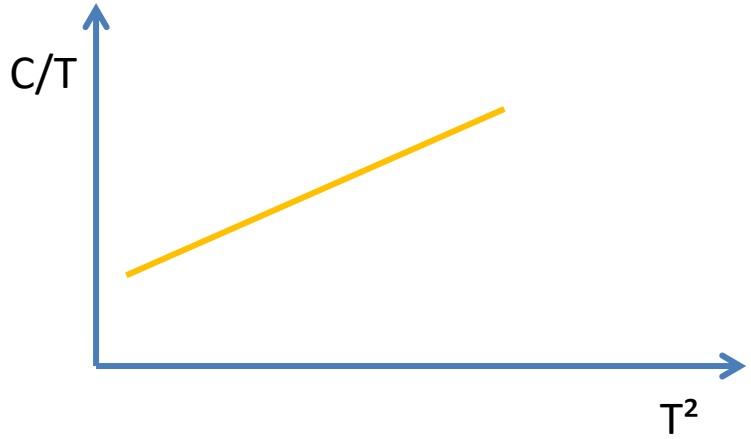
For $kT << E_F$: $D(E) = D(E_F)$ $$c_{el} = \frac{\partial E}{\partial T} = \int_0^\infty dE(E - E_F)D(E)\frac{\partial f}{\partial T} = \tfrac{1}{3}\pi^2 D(E_F)k^2 T$$

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

$$c_{el} = \tfrac{1}{2}\pi^2 Nk\frac{kT}{E_F} = \tfrac{1}{2}\pi^2 Nk\frac{T}{T_F} = \gamma T$$

Separation between electron and phonon contribution to specific heat

$$c_{total} = \gamma T + AT^3$$



Electrical charge transport

Electrons close to E_F contribute to charge transport only. Their characteristic velocity is → Fermi velocity,

$$v_F = \sqrt{\frac{2E_F}{m}}$$

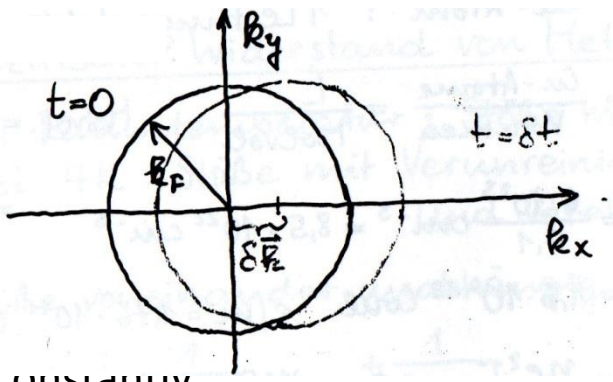
expressing the maximum velocity an electron can reach before scattering at another electron, defect, phonon aso. Is is much larger v_F >> drift velocity

$$v_D = \frac{j}{(N_e - N_p)e}$$

N_e, N_p – concentration of electrons and holes, v_D is the real velocity of signal transport .
Force, F, acting on an electron within electric field E

$$F == -eE = \frac{dp}{dt} = \hbar \frac{dk}{dt}$$

Means, Fermi sphere is constantly shifted



By collosion with defects, phonons etc. Fermi sphere is shifted constantly

$$dk = \frac{F}{m}\tau$$

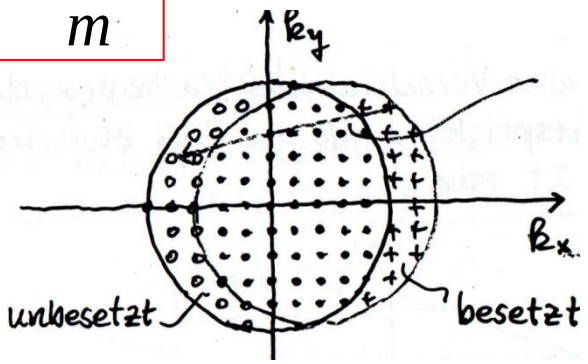
τ – is collision time

Electric transport

$$\hbar dk = 4mdv = F\tau \qquad dv = v_D = -\frac{eE\tau}{m}$$

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

$$j = \sigma E = nedv = -\frac{ne^2 E\tau}{m}$$ using



ne is transported amount of charge, τ – scattering time
Gained energy in field E is donated to lattice

$$\frac{\Delta Q}{\Delta t} = \frac{\frac{1}{2}m(2dv)^2}{2\tau} = \frac{ne^2E^2\tau}{m} = \sigma E^2$$ Joules heat

Temperature dependence

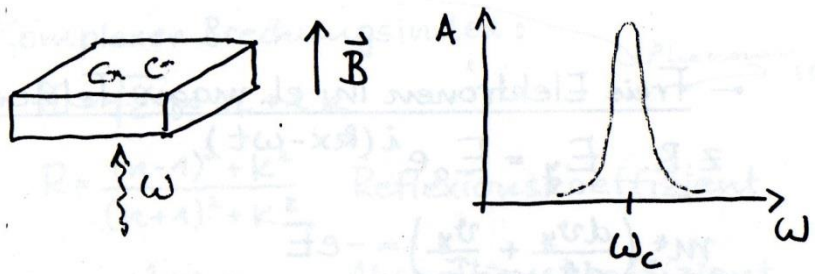
$$j(T) = \sigma(T)E = n(T)e\mu(T)E$$

μ - is the mobility (Beweglichkeit) [cm²/Vs], n – number of „free“ charge carrier.

In metals n is constant (and high) , μ and j increase with decreasing the temperature or decrease with increasing the temperature due to the increase of scattering at thermally excited phonons and defects.
Opposite for semiconductors, the μ and j increases for increasing temperature because more and more electrons are able to occupy states within the conduction band and can contribute to charge transport.

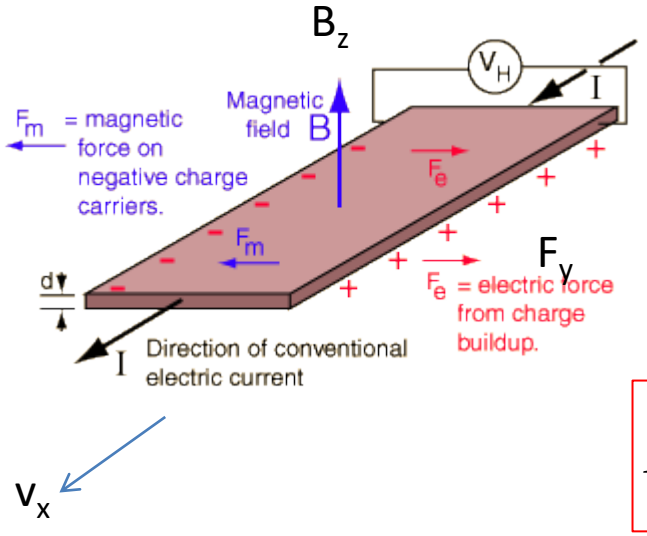
Cyclotron resonance spectroscopy

$$F = -ev \times B \qquad v = \omega r \qquad F = m\omega^2 r = e\omega r B \qquad \boxed{\omega_c = \frac{eB}{m}}$$



→ $\boxed{m^* = \frac{eB}{\omega_c}}$ m* from exp. ω_c

Hall effect



$$F = e[v \times B]$$

$$F_y = -ev_x B_z$$

creates Hall field E_H

$$-eE_H = -ev_x B_z$$

$$E_H = v_x B_z$$

$$j_x = -nev_x$$

$$\boxed{E_H = -\frac{1}{ne} j_x B_z = R_H j_x B_z}$$

R_H – Hall constant
Sign and concentration
Of charge carriers

Specific band structure of semiconductors

Generell insolator structure: with E_g >kT, 0.2…3 eV

$$j = \sigma \mathrm{E} \qquad \sigma = \sigma_0 \exp(-\frac{E_g}{kT})$$

Band structure in k-space:

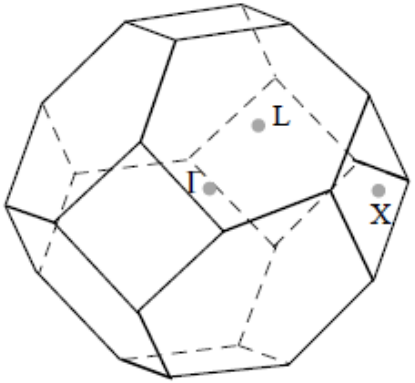
IMPORTANT HIGH SYMMETRY POINTS

Γ point: $k_x = 0 = k_y = k_z$

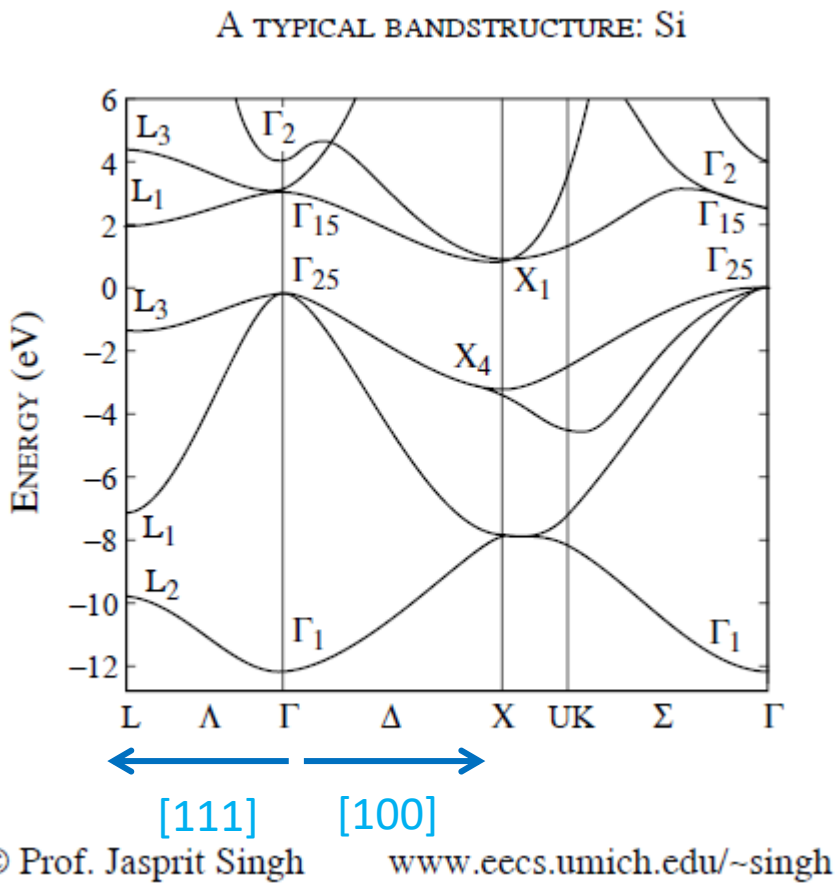
X point: $k_x = \frac{2\pi}{a}$; $k_y = k_z = 0$

L point: $k_x = k_y = k_z = \frac{\pi}{a}$

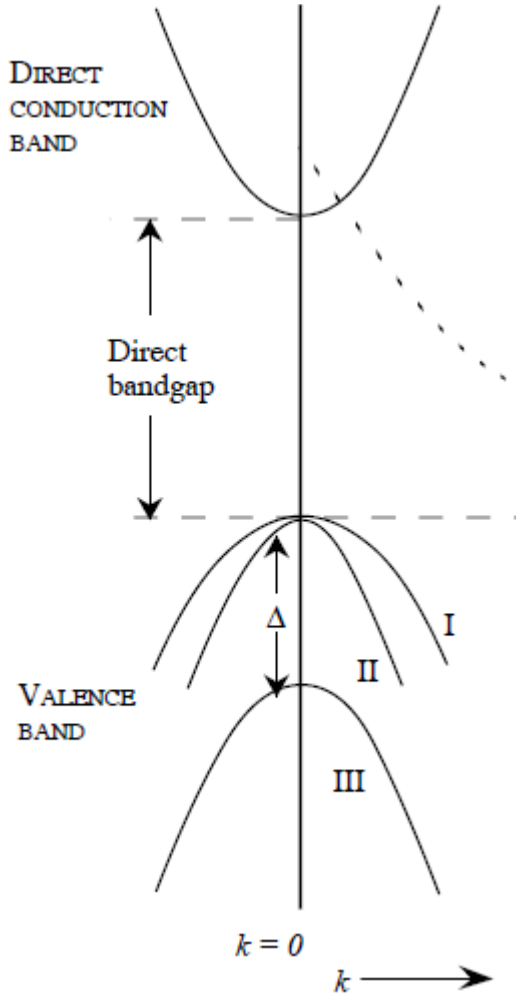
a = lattice constant (cube edge)

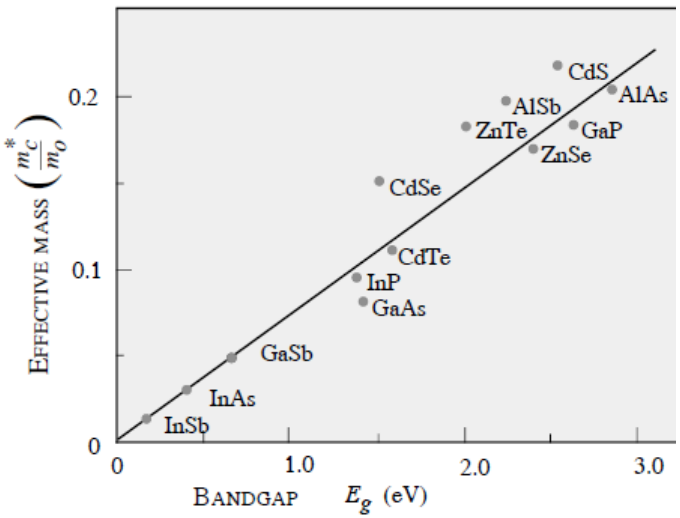


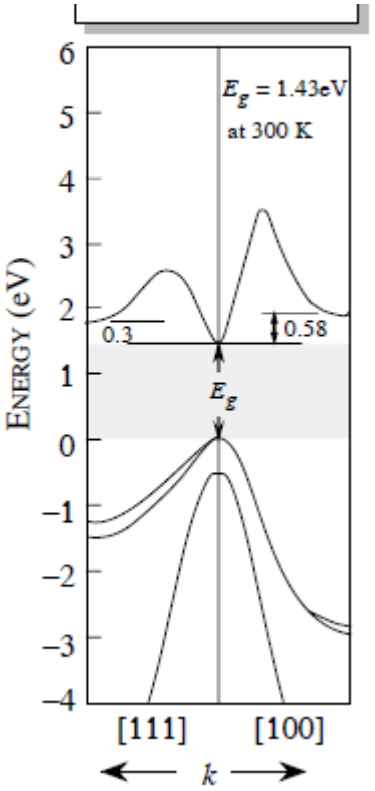
Γ – origin of Brillouin zone



Direct band semiconductor







I Heavy Hole Band

II Light Hole Band

III Split-Off Band

Δ = Split-Off Energy

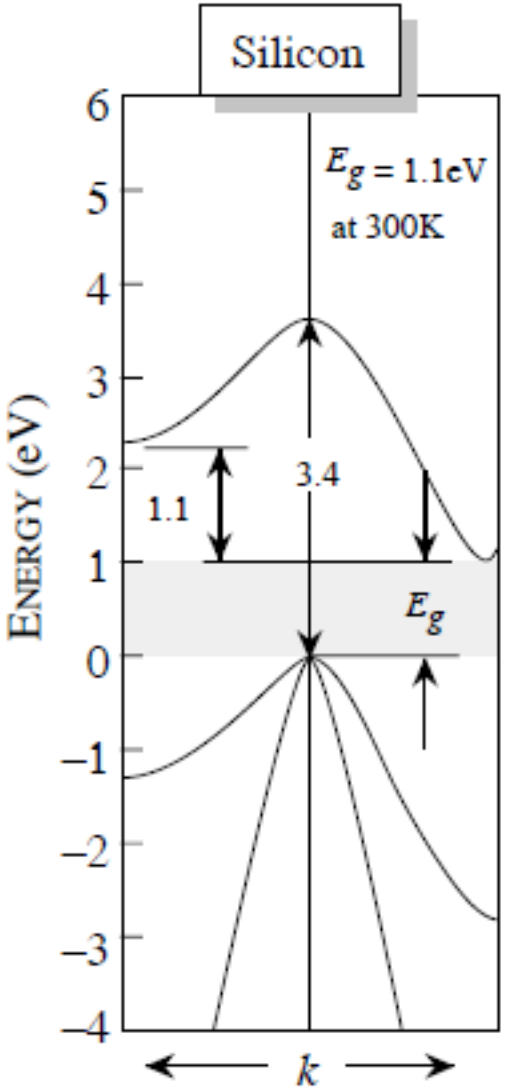
$$E_g = 1.519 - \frac{5.4 \times 10^{-4}\, T^2}{T + 204} \text{ (eV)}$$

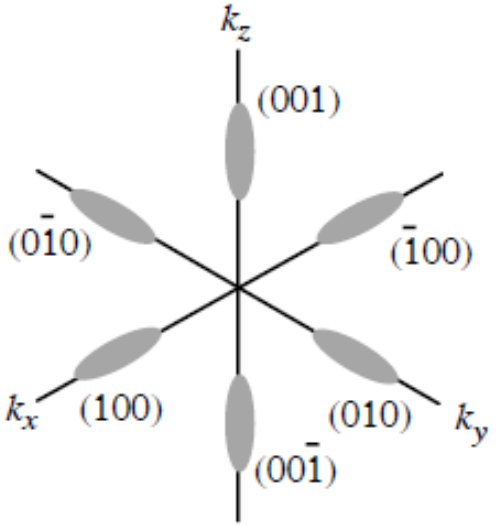
T = Temperature in K

Dispersion of electrons $$E_{CB}(\vec{k}) == E_{VB} + \frac{\hbar^2 k^2}{2m_e^*}$$

Dispersion of hole states $$E_{VB}(\vec{k}) == -\frac{\hbar^2 k^2}{2m_h^*}$$

Indirect band semiconductor





Six equivalent valleys at conduction bandedge

$$E_g = 1.17 - \frac{4.37 \times 10^{-4}\, T^2}{T - 636} \text{ (eV)} \qquad T = \text{Temperature in K}$$

Absorption vs direct gap = 3.4 eV
→ generation of electron hole-pairs

Recombination via indirect gap : 1.1 eV

$$E_{light} = E_g \pm \hbar\omega_{phonon}$$

Few band structure parameters

Material	Bandgap (eV)	Relative Dielectric Constant
C	5.5, I	5.57
Si	1.124, I	11.9
Ge	0.664, I	16.2
SiC	2.416, I	9.72
GaAs	1.424, D	13.18
AlAs	2.153, I	10.06
InAs	0.354, D	15.15
GaP	2.272, I	11.11
InP	1.344, D	12.56
InSb	0.230, D	16.8
CdTe	1.475, D	10.2
AlN	6.2, D	9.14
GaN	3.44, D	10.0
ZnSe	2.822, D	9.1
ZnTe	2.394, D	8.7

Material	Electron Mass (m_0)	Hole Mass (m_0)
AlAs	0.1	
AlSb	0.12	$m^*_{dos} = 0.98$
GaN	0.19	$m^*_{dos} = 0.60$
GaP	0.82	$m^*_{dos} = 0.60$
GaAs	0.067	$m^*_{lh} = 0.082$ $m^*_{hh} = 0.45$
GaSb	0.042	$m^*_{dos} = 0.40$
Ge	$m_l = 1.64$ $m_t = 0.082$ $m_{dos} = 0.56$	$m^*_{lh} = 0.044$ $m^*_{hh} = 0.28$
InP	0.073	$m^*_{dos} = 0.64$
InAs	0.027	$m^*_{dos} = 0.4$
InSb	0.13	$m^*_{dos} = 0.4$
Si	$m_l = 0.98$ $m_t = 0.19$ $m_{dos} = 1.08$	$m^*_{lh} = 0.16$ $m^*_{hh} = 0.49$

DOS of Semiconductors

$$f(E,T)=\frac{1}{\exp(\frac{E-\mu}{kT})+1}$$

E-μ >>kT; $E_F \approx \mu$ $$f(E,T)\approx \exp(-\frac{E-\mu}{kT})$$

Probability to occupy a state in CB:

$$E_{CB}(\vec{k}) == E_{VB}+\frac{\hbar^2 k^{\ 2}}{2m_e^*} \qquad D_e(E)=\frac{V}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{E-E_g}$$

$$n=\int_0^\infty D_e(E)\,f(E,T)dE=\frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)\int_0^\infty \sqrt{E-E_g}\,\exp(-\frac{E_g}{kT})$$

Number of electrons on CB:

$$n=2\left(\frac{2\pi m_e^* kT}{\hbar^2}\right)^{3/2}\exp(-\frac{E_g}{kT})$$

Probability to find holes $$f_h=1-f_e(E,T)\approx \exp(+\frac{E-\mu}{kT}) \qquad D_h(E)=\frac{V}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}\sqrt{-E}$$

Number of holes in VB:

$$p=2\left(\frac{2\pi m_h^* kT}{\hbar^2}\right)^{3/2}\exp(-\frac{\mu}{kT})$$

Carrier concentration in CB and VB

For intrinsic semiconductor yields : n=p $m_e^{3/2}\exp(-\frac{\mu - E_g}{kT} = m_h^{3/2}\exp(-\frac{\mu}{kt})$

$$\frac{3}{2}\ln\frac{m_e^*}{m_h^*} = -\frac{2\mu + E_g}{kT}$$

$$\mu = \frac{E_g}{2} - \frac{3}{4kT}\ln\frac{m_e^*}{m_h^*}$$

Because 2nd term is very small : $\mu = E_F = E_g/2$

Thermally excited charge carriers:

$$n = p = 2\left(\frac{2\pi kT}{\hbar^2}\right)^{3/2}(m_n^* m_h^*)^{3/4}\exp(-\frac{E_g}{2kT})$$

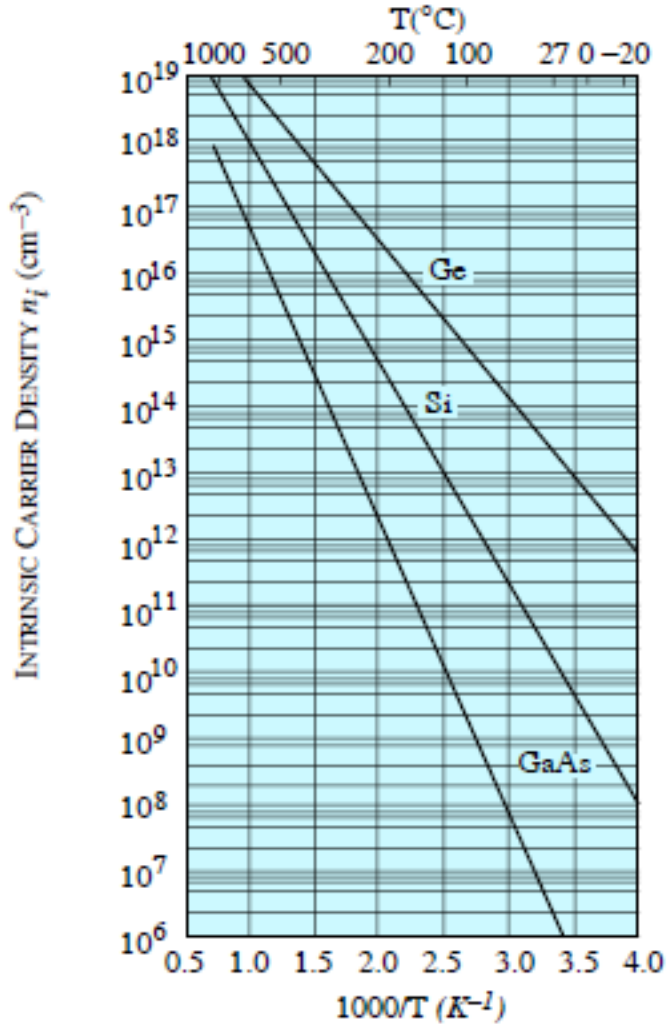
$$\sigma = \sigma_0\exp(-\frac{E_g}{2kT}) = n(T)e\mu_e + p(T)e\mu_p$$

$$n_i = p_i = 2.5*10^{13}cm^{-3}\_Ge\_E_g = 0.67eV$$

$$n_i = p_i = 1.4*10^{10}cm^{-3}\_Si\_E_g = 1.14eV$$

μ_e(Si) = 1300 Vs/cm²; μ_h(Si)=500Vs/cm²
μ_e(GaAs) = 8800 Vs/cm²; μ_h(GaAs)=400Vs/cm²

Temperature dependence of intrinsic charge carrier concentration



Temperature dependence of n_i, p_i in Si, Ge, GaAs

Material	Conduction band effective density (N_c)	Valence band effective density (N_v)	Intrinsic carrier concentration ($n_i = p_i$)
Si (300 K)	2.78×10^{19} cm^{-3}	9.84×10^{18} cm^{-3}	1.5×10^{10} cm^{-3}
Ge (300 K)	1.04×10^{19} cm^{-3}	6.0×10^{18} cm^{-3}	2.33×10^{13} cm^{-3}
GaAs (300 K)	4.45×10^{17} cm^{-3}	7.72×10^{18} cm^{-3}	1.84×10^{6} cm^{-3}

Doping of semiconductors

Effective number of charge carriers can be increased by DOPING:
replacement of very few Si atoms by P, As,…(donators) or by B, Al,…(acceptors).

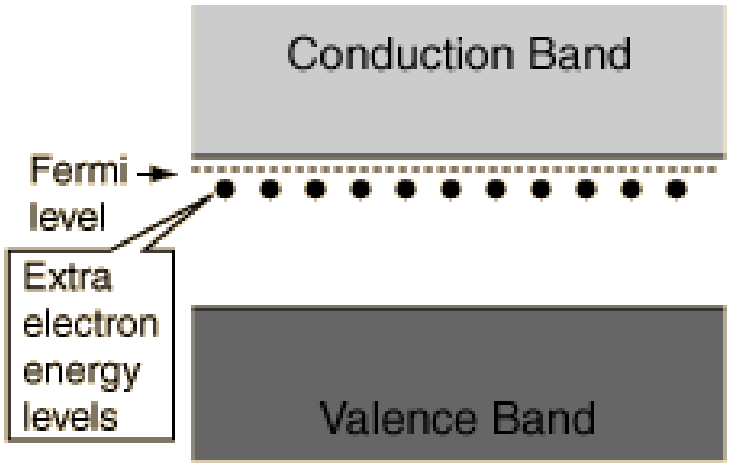
Energy states of dopands calculated by **effective mass theory:** (H-atom modell):
replacing $e^2 \rightarrow e^2/\varepsilon$ and $m \rightarrow m_{e,h}$. where **ε** is the statistic dielectric constant of host material.

$$E_H = -\frac{e^4 m}{2\hbar^2 n^2}$$

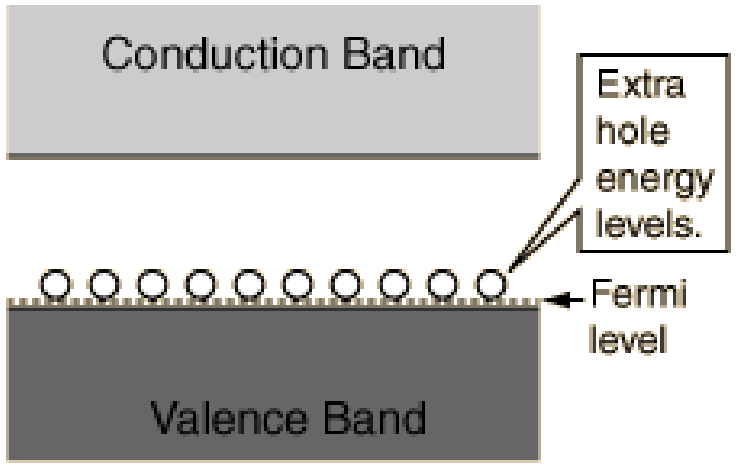
Donator energy $$E_{D,A} = 13.6eV \frac{m_{e,h}}{m\varepsilon^2} \frac{1}{n^2}$$ 6meV (Ge), 20meV (Si)

Radius of donator electron $$r_{D,A} = 0.0529nm \frac{\varepsilon m}{m_{e,h}} n^2$$ 8nm (Ge), 3nm(Si)

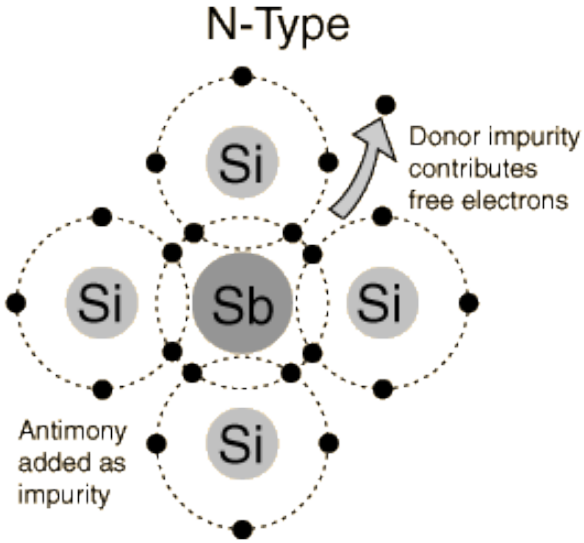
Donator doped semiconductors : → n- conductivity
Acceptor doped semicductor : → p - conductivity

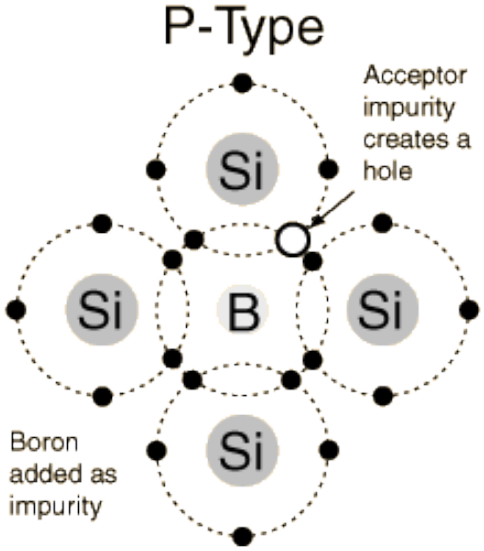

Conduction Band
Fermi level
Extra electron energy levels
Valence Band

N-Type


Conduction Band
Extra hole energy levels.
Fermi level
Valence Band

P-Type


N-Type
Si
Donor impurity contributes free electrons
Si
Sb
Si
Si
Antimony added as impurity


P-Type
Acceptor impurity creates a hole
Si
Si
B
Si
Si
Boron added as impurity

Temperature dependence of doped semiconductors

Low temperatures

$$n \propto \exp(-\frac{E_d}{kT})$$

$$p \propto \exp(-\frac{E_A}{kT})$$

high temperatures

$$n = p \propto \exp(-\frac{E_g}{2kT})$$