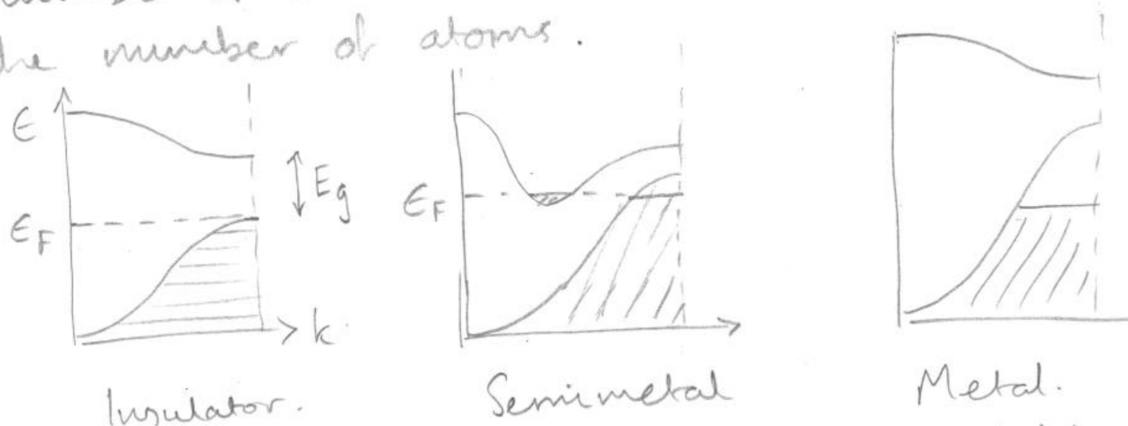
8.1 Semiconductors.

We have seen the origin of electron bands from both sides: free electrons + Pauli repulsion
bound electrons in atoms + overlap.

Either way we find discrete bands with the number of available states exactly equal to the number of atoms.



Insulator. Semimetal Metal.

Semimetal has only a few states available at the Fermi level for excitation. Sometimes, as in the example shown, phonons can help with the excitation.

Semiconductor is an insulator with a small value of E_g such that $k_B T$ is a reasonable fraction of the gap. Electrons can be thermally excited across the gap.

To fill the band exactly is only possible for even valency in an element. All elemental semiconductors are group IV: Si and Ge. C has too large E_g, Sn has too small

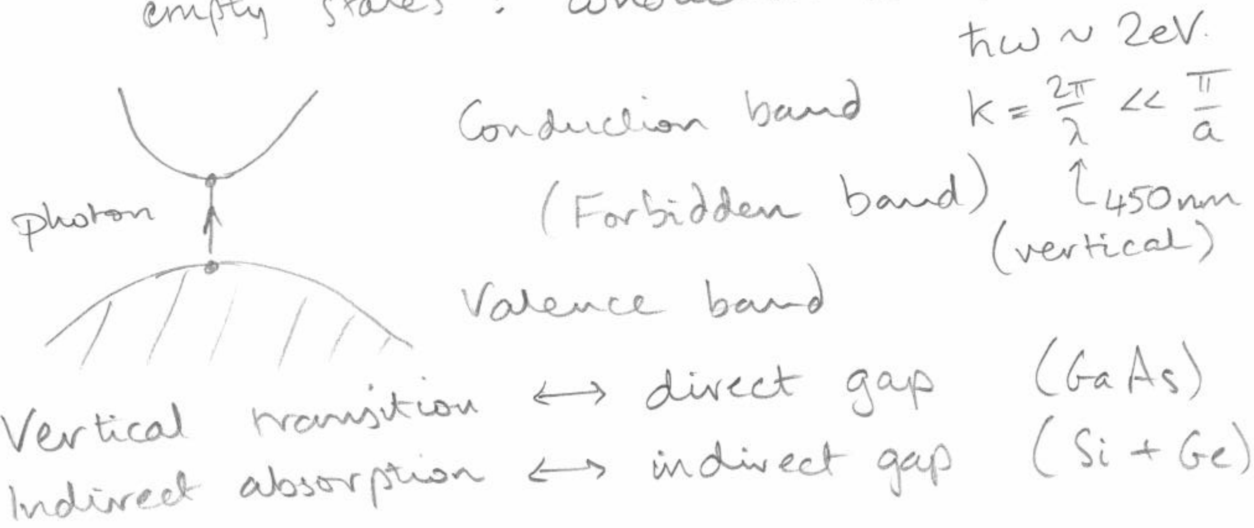
Si : $E_g = 1.11$ eV C : 5.4 eV
Ge $E_g = 0.66$ eV Sn : 0.0 eV

III - V and II - VI compounds also suitable:

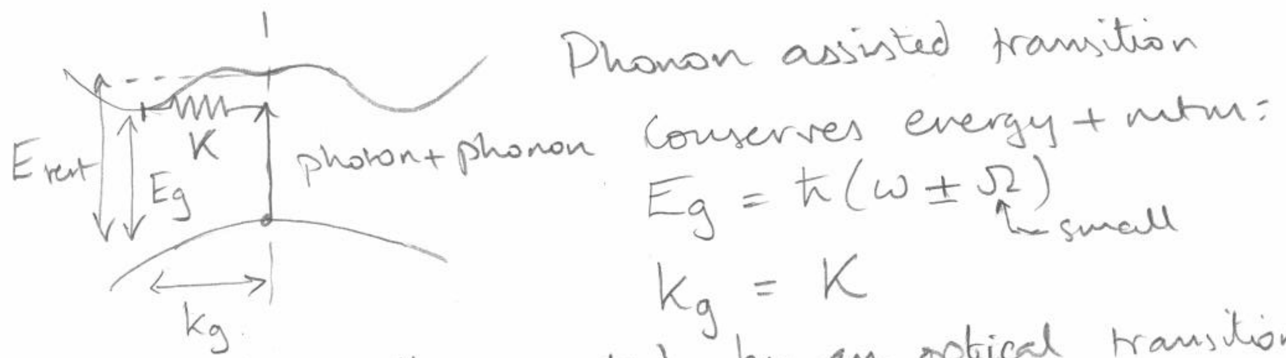
GaAs $E_g = 1.43$ eV CdS 2.42
InSb $E_g = 0.17$ CdSe 1.74

8.2 Direct / Indirect gap.

In a 3D reciprocal space there are many locations (directions) in which a gap can form, not necessarily in the same place for the filled states : "valence" band
empty states : "conduction" band:



Vertical transition ⟷ direct gap (GaAs)
Indirect absorption ⟷ indirect gap (Si + Ge)



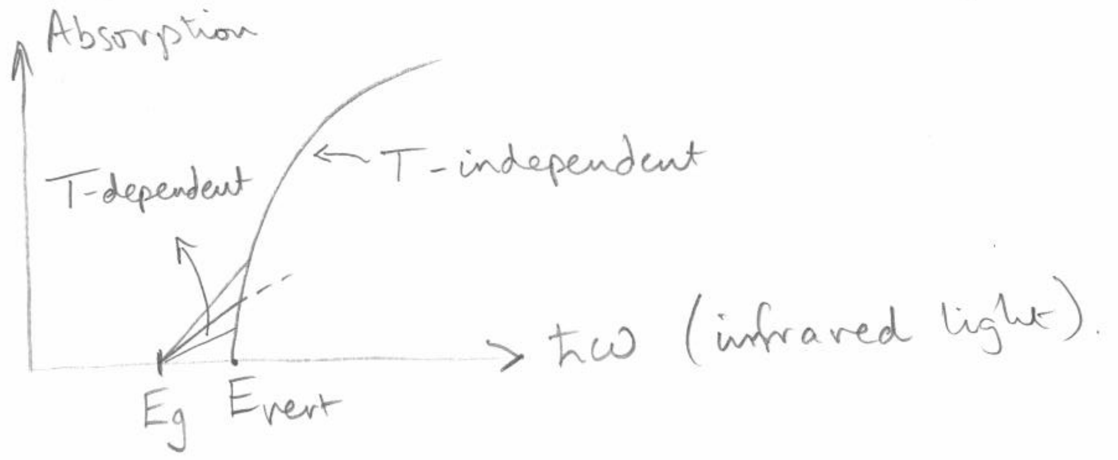
Phonon assisted transition conserves energy + mtm:

$$E_g = \hbar(\omega \pm \Omega)$$ (Ω small)

$$k_g = K$$

Phonon is usually created by an optical transition but can also be destroyed.

See by optical absorption spectrum.



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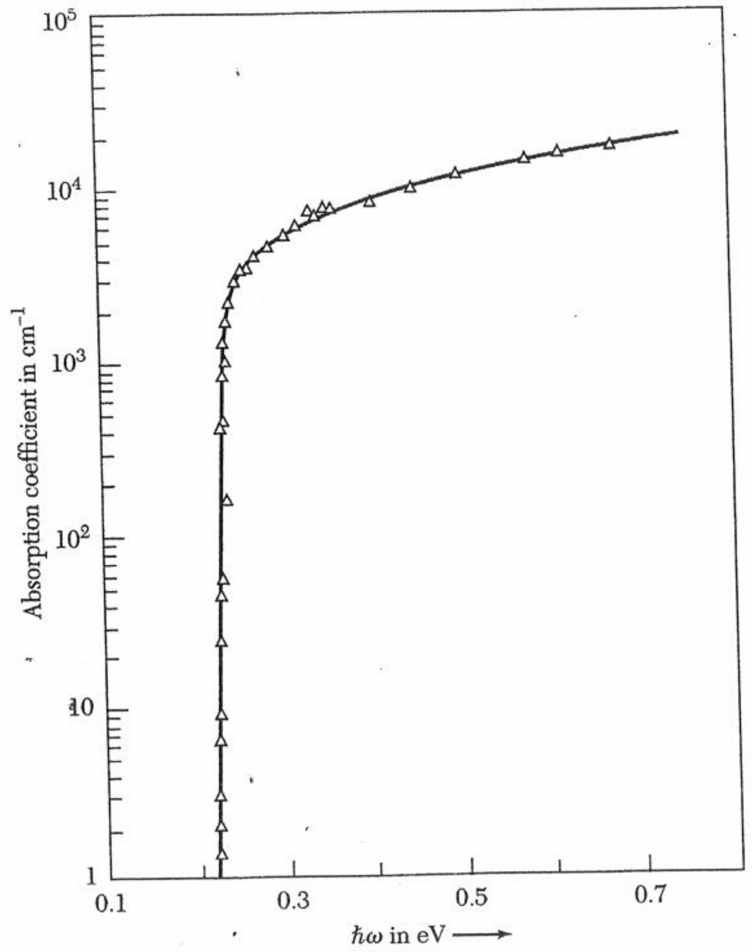


Figure 6 Optical absorption in pure indium antimonide, InSb. The transition is direct beca both conduction and valence band edges are at the center of the Brillouin zone, $\mathbf{k} = 0$. Notice sharp threshold. (After G. W. Gobeli and H. Y. Fan.)

Figure 14 Calculated band structure of germanium, after C. Y. Fong. The general features are in good agreement with experiment. The four valence bands are shown in gray. The fine structure of

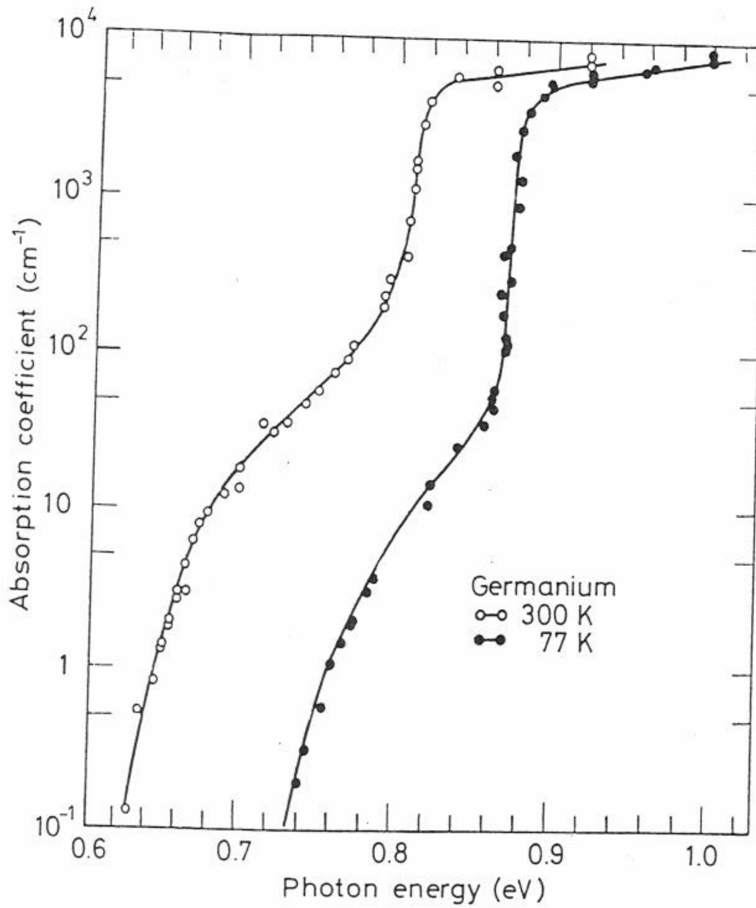


Fig. 5.7 Absorption coefficient for electromagnetic radiation of germanium versus photon energy at temperatures of 77 and 300 K. (Reproduced with permission from W. C. Dash and R. Newman, *Phys. Rev.* **99**, 1151 (1955))

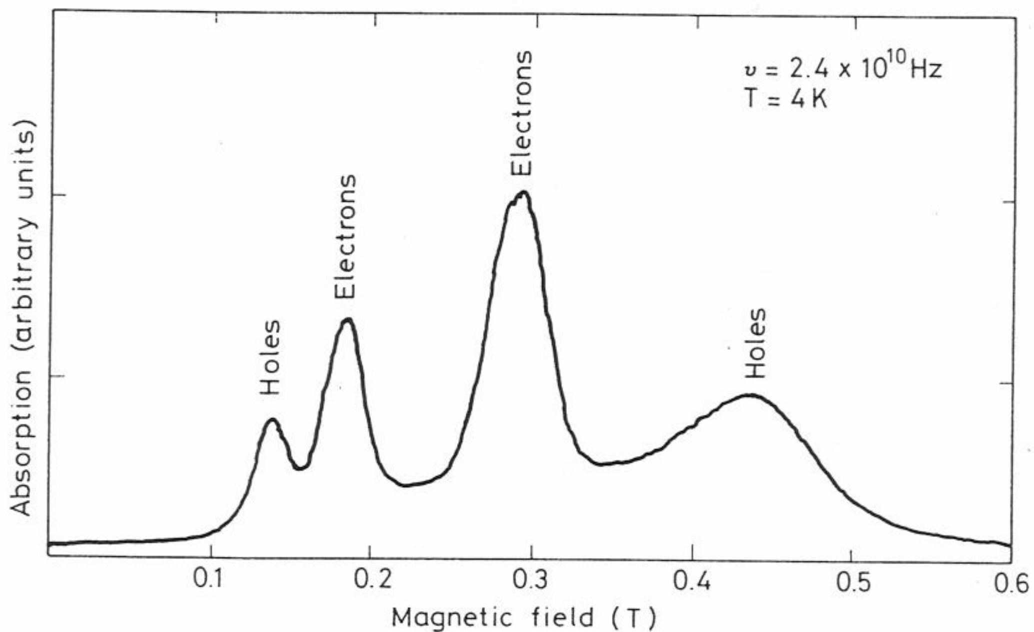


Fig. 5.12 Typical cyclotron resonance signal from silicon. The field lies in the (1 1 0) plane and is at 30° to the [0 0 1] axis. (Reproduced with permission from G. Dresselhaus, A. F. Kip and C. Kittel, *Phys. Rev.* **98**, 368 (1955))

8.3 Electrons and Holes

The spectrum shows the density of states, but all the applications depend on the electrical conduction of a semiconductor.:

i) neither a filled nor an empty band can carry <u>any</u> current. Filled states merely precess in an electric field $\hbar \frac{d\vec{k}}{dt} = -e\vec{E}$

ii) current is carried by:
- electron, promoted to conduction band.
- hole, left behind in valence band.

Matching of states to no. of electrons means these two mechanisms occur together, often giving similar contributions to current.

Current is carried by wave <u>packet</u>.
Velocity is given by <u>group</u> velocity:

$v_g = \frac{1}{\hbar}\frac{d\epsilon}{dk}$, just as with phonons, but $\epsilon = \hbar\omega$.
Band structure determines v_g everywhere.
Band structure determines v_g everywhere.
In δt, Lorenz force acts on packet moving at v_g

$\delta\epsilon$ = force × distance = $F \cdot v_g \delta t$
$\delta\epsilon = \hbar v_g \delta k$ from above
$\Big\}$ $F = \hbar \frac{dk}{dt}$

Classically $F = \frac{d}{dt}(mv)$
So we identify $\hbar\vec{k}$ as the crystal momentum.
eg in a magnetic field:

$$F = \hbar \frac{d\vec{k}}{dt} = e\vec{v} \times B.$$

$$\vec{v} \to v_g = \frac{1}{\hbar}\frac{d\epsilon}{dk} \to \frac{1}{\hbar}\vec{\nabla}_k \epsilon \text{ in 3D.}$$

8.03.10
9.03.09 I

electrons move perpendicular to energy gradient making <u>orbits</u> on constant energy surfaces.

W. Shockley (1950)

conductivity.[4] In Figure 1.5(a) we represent a photon delivering its energy to an electron which is ejected from one of the bonds.[5] This ejected electron constitutes a localized negative charge in the crystal as shown in (c), since before it arrived in that part of the crystal the electron-pair bond structure was electrically neutral. Such an electron, which represents an excess over and above that required to complete the bond structure in its

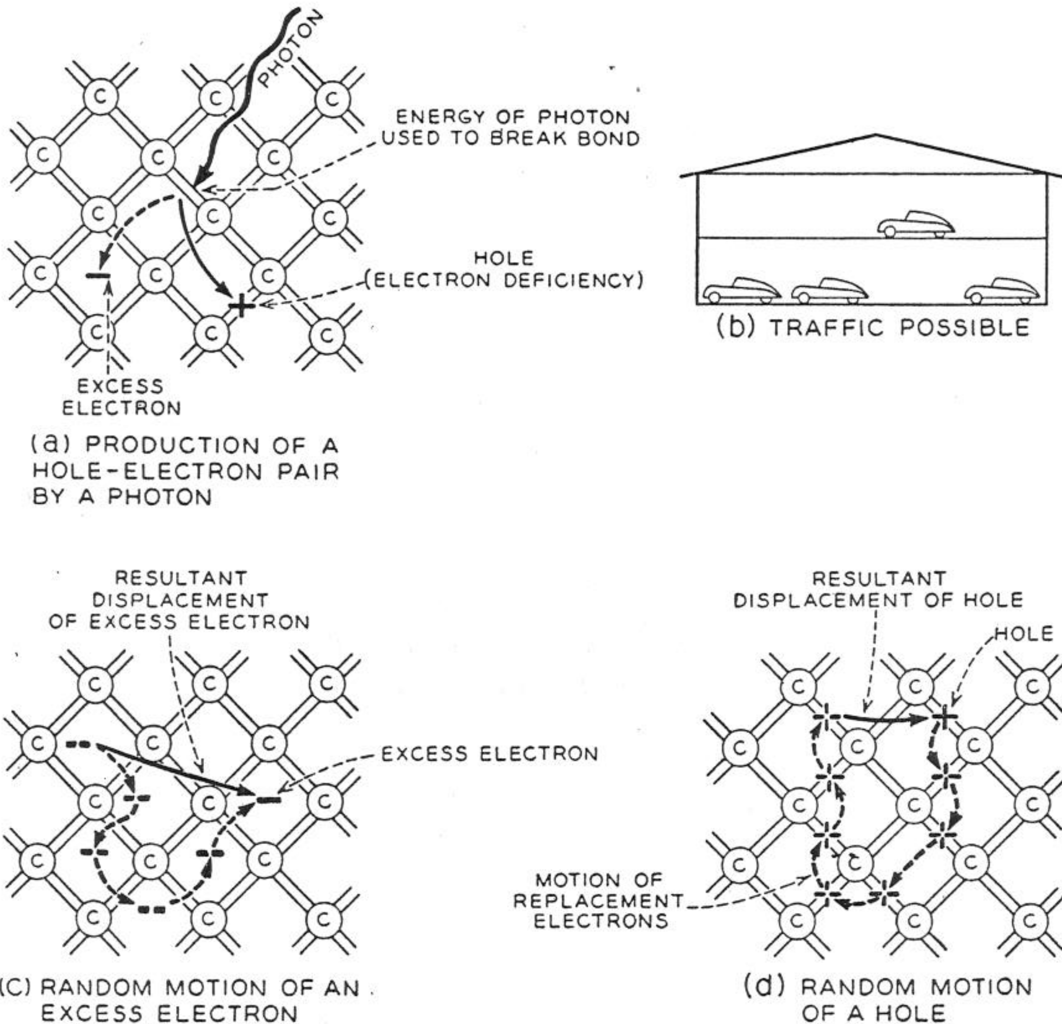


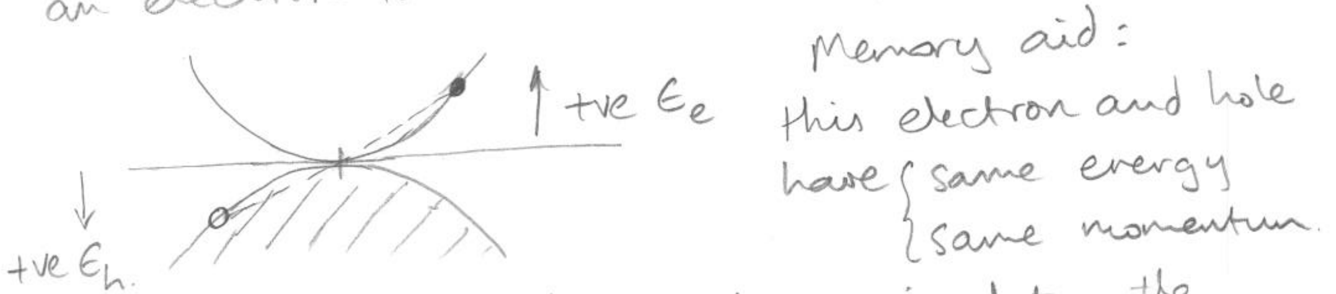
Fig. 1–5—Excess Electrons and Holes in a Diamond Crystal.

8.4 Hole dynamics.

A hole is a missing electron in an otherwise filled electron band. Symmetry says that:

i) $\vec{k}_h = -\vec{k}_e$. The total $\vec{k}$ for a filled band is zero, so the missing electron has negative $\vec{k}_e$.

ii) $\epsilon(k_h) = -\epsilon(k_e)$. Assuming the top of the band is the zero of energy, the deeper states have lower energy for electrons, but higher for holes, since these require promotion of an electron to the Fermi Level / band edge



Memory aid: this electron and hole have { same energy, same momentum.

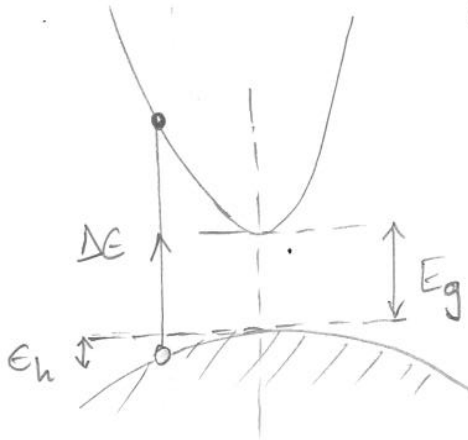
The upper band of this picture simulates the properties of holes in the lower picture.

Creation of electron-hole pair (eg in absorption) requires two contributions to energy:

3.03.08 I

$$\Delta\epsilon = E_g + \epsilon_h + \epsilon_e$$

$k_e + k_h = 0$ for vertical transition even far away from $k = 0$.



iii) $V_e = V_h = \frac{1}{\hbar}\frac{d\epsilon}{dk}$ follows from i) and ii)

iv) $m_e = -m_h$ see below.

v) equation of motion:

$$\hbar \frac{d\vec{k}_e}{dt} = -e\left(\vec{E} + \vec{v}_e \times \vec{B}\right) \qquad \hbar \frac{d\vec{k}_h}{dt} = +e\left(\vec{E} + \vec{v}_h \times \vec{B}\right)$$

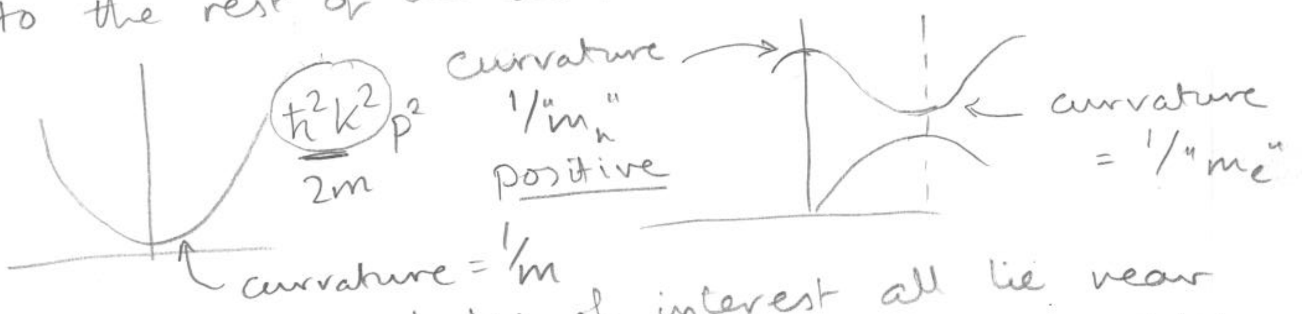
reverse sign   same sign.

So the hole is a positively charged carrier.
Carries current in a wire in the opposite direction.

8.5 Effective Mass

Free electron has $\epsilon = \frac{\hbar^2}{2m}k^2$ } $\epsilon = \frac{p^2}{2m}$ Classical result.
Crystal momentum $= \hbar k$ }

The concept of "mass" as the coefficient coupling the energy and $(\text{momentum})^2$ can be extended to the rest of the band structure:



The electrons & holes of interest all lie near the turning points of the band structure, which are parabolic to second order.

Definition $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\epsilon(k)}{dk^2}$

verify for free electron: $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2}{dk^2}\left(\frac{\hbar^2}{2m}k^2\right) = \frac{1}{m}$

Effective mass can be anisotropic

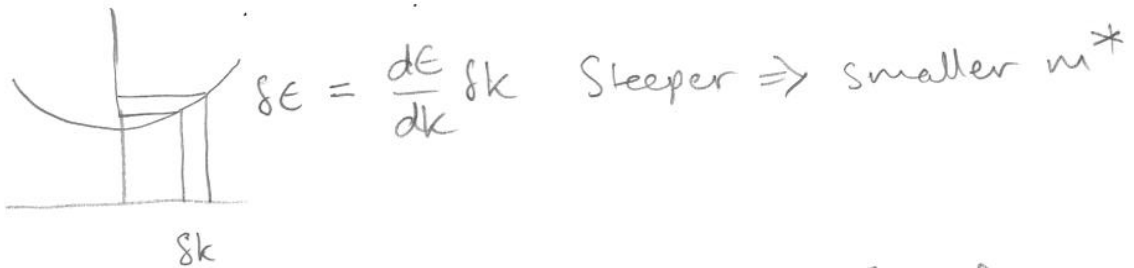
$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\frac{d^2\epsilon(\vec{k})}{dk_i\,dk_j}$ tensor form, directions $i\,j$

8.6 Physical Interpretation.

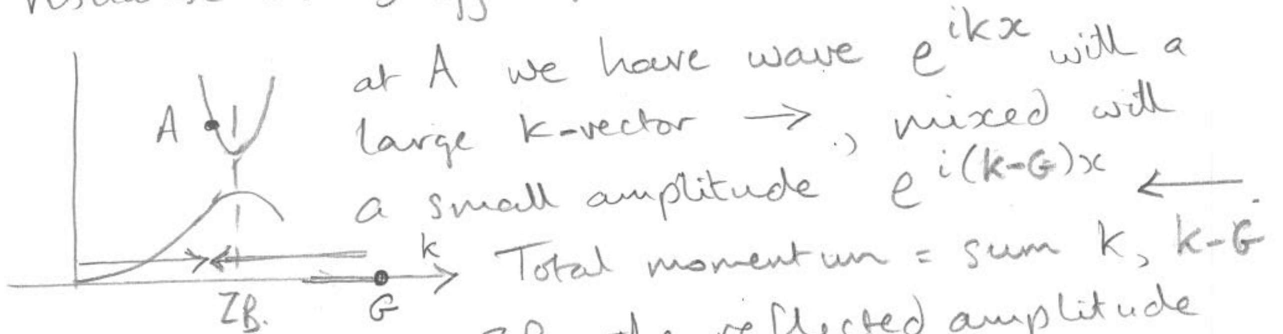
Mass quantifies "inertia" = resistance to acceleration

Forces acting on electrons in a crystal will change the crystal momentum: $\hbar \frac{dk}{dt}$ = Force.

The rate at which the energy rises is given by the shape of the band structure:



Visualise as Bragg reflection near Zone Boundary:



at A we have wave e^{ikx} with a large k-vector →, mixed with a small amplitude $e^{i(k-G)x}$ ←

Total momentum = sum k, k−G

energy↑ mtm↓ ⇒ −ve m.

As we approach ZB, the reflected amplitude increases, reducing the total momentum, until it reaches zero at the ZB. ⇒ negative m^* at top of band

Tight-binding picture: small overlaps (γ) ⇒ shallow bands with Large m^*.

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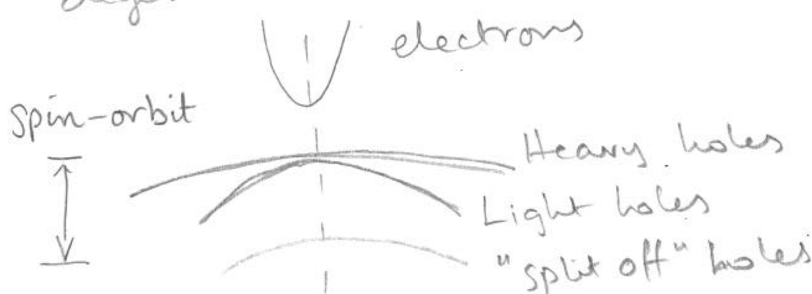
Eg. III-V semiconductors have direct gap. In 3D there are 3 bands, 3 eigenstates for each k. They have different curvature; two are degenerate at zone centre.

Ga As.



$m^* = 0.066\, m_e$

$m^* = 0.5\, m_e$

$m^* = 0.082\, m_e$

$m^* = 0.17\, m_e$ $\Delta = 0.34\,eV$

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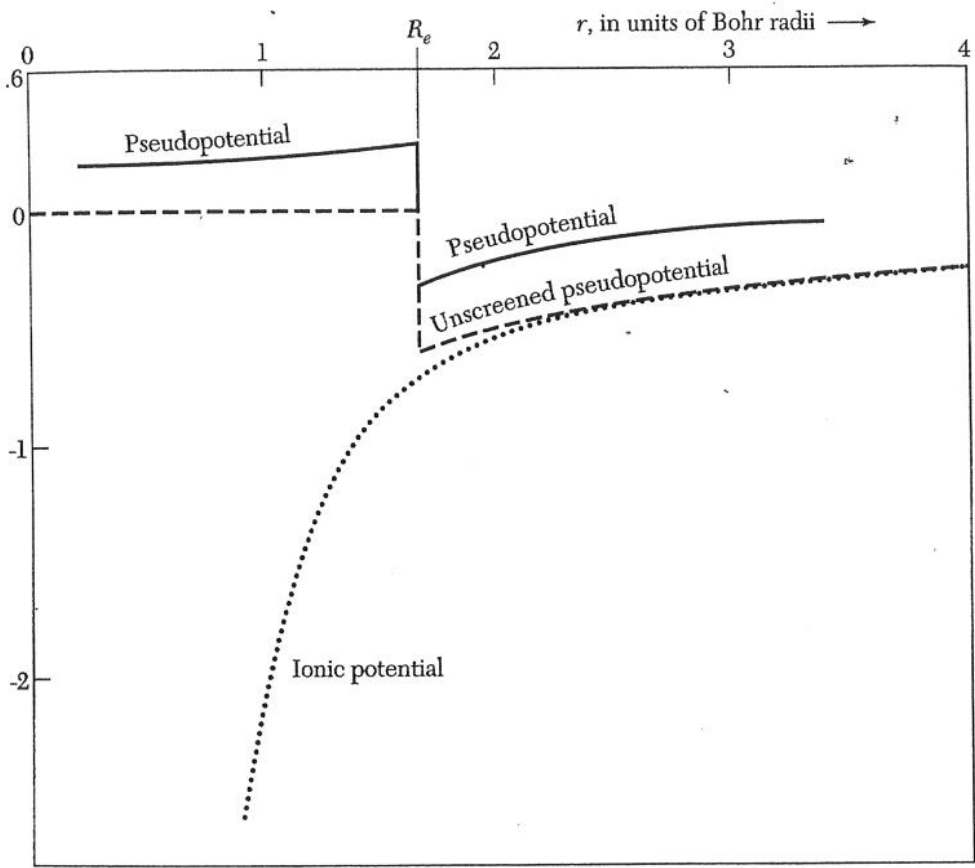


ıre 22a Pseudopotential for metallic sodium, based on the empty core model and screened ıe Thomas-Fermi dielectric function. The calculations were made for an empty core radius 1.66a_0, where a_0 is the Bohr radius, and for a screening parameter $k_s a_0 = 0.79$. The dashed e shows the assumed unscreened potential, as from (21). The dotted curve is the actual ntial of the ion core; other values of $U(r)$ are -50.4, -11.6, and -4.6, for $r = 0.15$, 0.4, and respectively. Thus the actual potential of the ion (chosen to fit the energy levels of the free ı) is very much larger than the pseudopotential, over 200 times larger at $r = 0.15$.

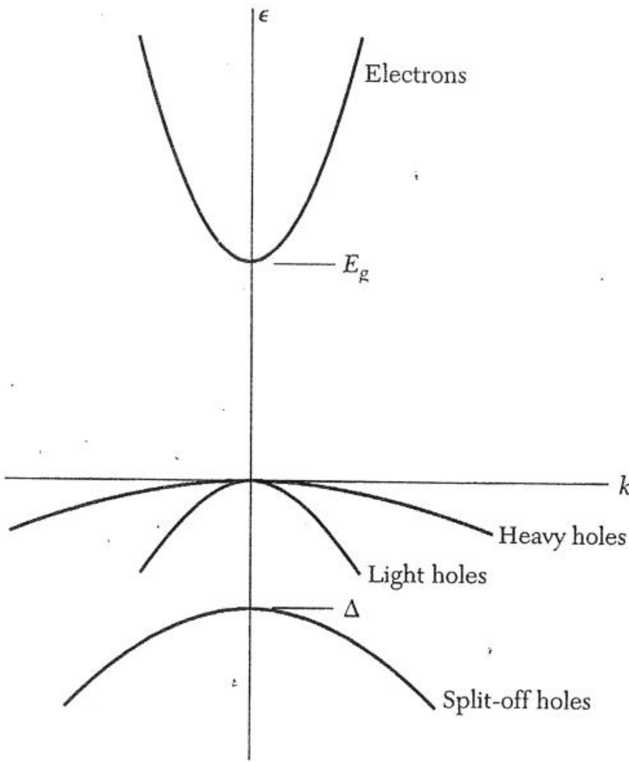


Figure 13 Simplified view of the band edge structure of a direct-gap semiconductor.

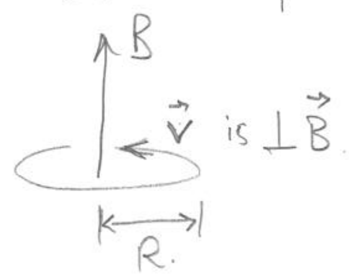
Table 2 Effective masses of electrons and holes in direct-gap semiconductors

Crystal	Electron m_e/m	Heavy hole m_{hh}/m	Light hole m_{lh}/m	Split-off hole m_{soh}/m	Spin-orbit Δ, eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34
Cu_2O	0.99	—	0.58	0.69	0.13

8.7 Measurement of m^*

Cyclotron resonance detects the characteristic frequencies of motion of free carriers in an applied magnetic field:

Lorentz force $e\vec{v} \times \vec{B} = m\frac{v^2}{R}$ centripetal accel.



$eB = m\omega_c$ ← cyclotron resonance frequency.

(needs m^* effective mass)

Typical setup $\frac{\omega_c}{2\pi} \sim 20$ GHz (millimeter wave)

$B \sim 1000$ G (0.1 T); $T \sim 1$ K so $\tau \approx \frac{1}{\omega_c}$

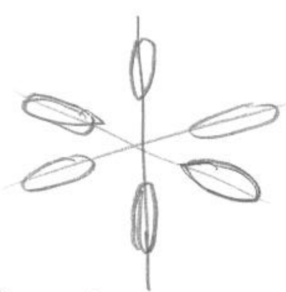
All electrons (and holes) near the band edge contribute, but only free carriers.

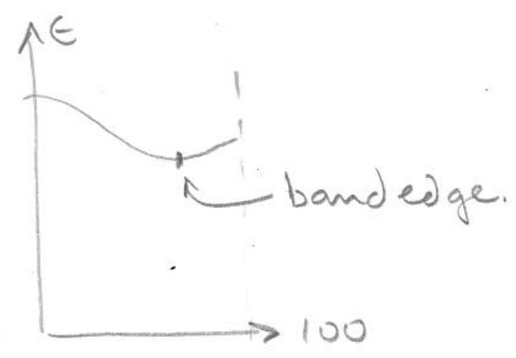
Example of valence band edge in Ge:

$P_{3/2}$ two degenerate bands
$P_{1/2}$ split off by 0.29 eV } tight binding.

Conduction band edge is not in zone centre, but shifted along 111 to the zone boundary.

Si is similar, but lowest point of conduction band is shifted along 100:





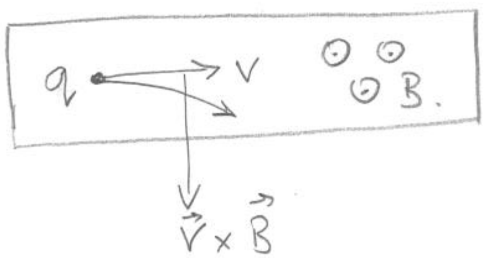
"Cigars" with anisotropic m^*

$m^* = 0.92m$ along cigar
$0.19m$ across cigar.

9.03.09 II

Hall effect (Kittel p164) Prof. M. Pepper LCN.

Transverse conductivity in presence of magnetic field



$$\vec{F} = q\vec{v} \times \vec{B}$$

Sideways force depends on sign of q:

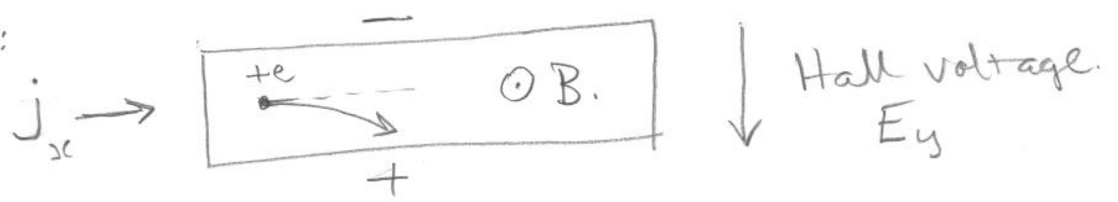
hole: $q = +e$ as shown

electron $q = -e$ reverse.

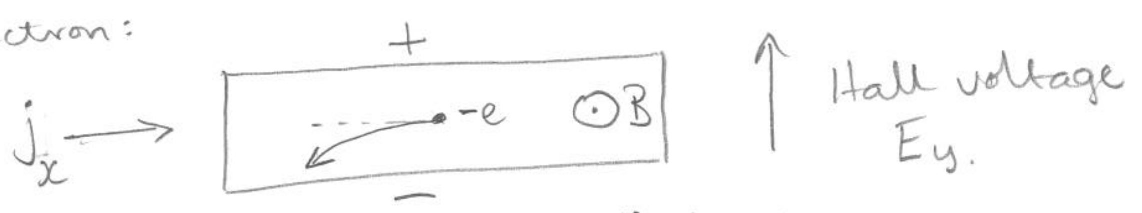
But direction of current also depends on sign

And polarity of voltage generated " " "

Hole:



Electron:



B × Hall Resistance = Hall Coefficient

$$R_H = \frac{E_y}{j_x B_Z} = +\frac{1}{nq}$$ changes sign with q.

n = carrier density, electrons / holes per m^3

Electrons and holes together

$$R_H = \frac{-1}{e}\left(\frac{1}{n_{holes}} - \frac{1}{n_{electrons}}\right)$$

i) intrinsic: $n_{holes} \simeq n_{electrons}$ $R_H = 0$.

ii) doped: $n_{holes} \neq n_{electrons}$. $R_H \neq 0$

sign identifies "majority" carrier

8.8 Intrinsic carrier concentration.

At finite temperature, carriers are excited by the Fermi-Dirac distribution:

$$\frac{1}{e^{(\epsilon-\mu)/kT}+1} \simeq e^{(\mu-\epsilon)/kT}$$ [$\mu = \epsilon_F$ definition

for $(\epsilon-\mu) \gg kT$ in the conduction band.

$$\epsilon_k = E_c + \frac{\hbar^2}{2m_e}k^2 \qquad m_e = m^* \text{ (electrons)}$$

↑ band edge (E_c)

For $\epsilon > E_c$, density of states is given by the usual argument:

N/L = total electron dens.

NB. $\rightarrow 2 \cdot \frac{4}{3}\pi k^3 = N\left(\frac{2\pi}{L}\right)^3 = (2\pi)^3 n_0$

$$D(\epsilon) = \frac{dn_0}{d\epsilon} = \frac{2}{(2\pi)^3}\frac{4}{3}\pi \frac{d}{d\epsilon}\left(\left(\epsilon - E_c\right)\frac{2m_e}{\hbar^2}\right)^{3/2}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}(\epsilon - E_c)^{1/2}$$

So the concentration of electrons in the cond. band is

new use of n

$$n = \int_{E_c}^{\infty} D(\epsilon)\, e^{(\mu-\epsilon)/kT}\, d\epsilon$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} e^{\mu/kT}\int_{E_c}^{\infty}(\epsilon - E_c)^{1/2} e^{-\epsilon/kT}\, d\epsilon$$

Change variables, integrate by parts, standard integral

$$n = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{(\mu - E_c)/k_B T}$$

← see $(k_B T)^{3/2}$ $\int_0^\infty x^{1/2} e^{-x} dx = \frac{1}{2}\pi^{1/2}$

The only unknown is μ, the Fermi level, which could be anywhere.

☆ The constraint is the carrier concentrations of electrons and holes are linked, so we can determine μ.

8.9 Concentration of holes.

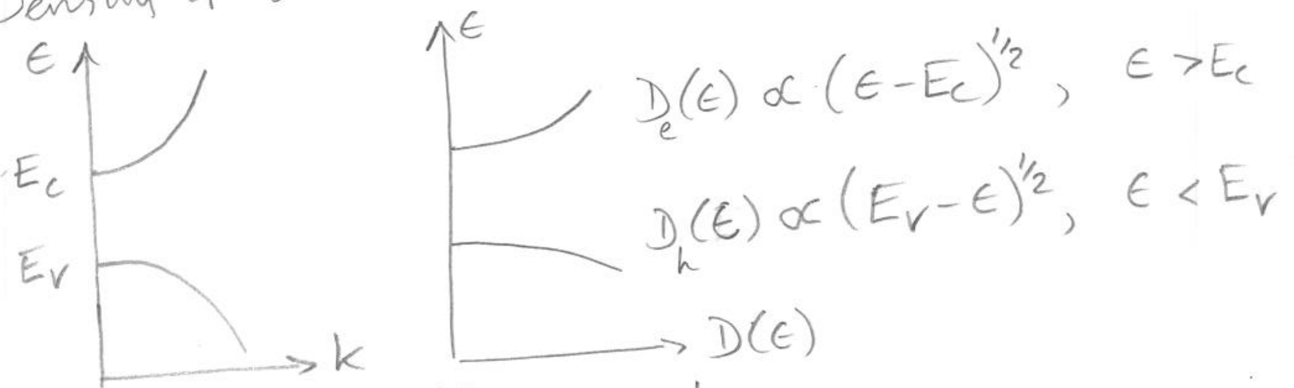
Everything is up-side down: conc(holes) = 1 − conc(electrons), since they are missing:

$$f_h = 1 - f_e = 1 - \frac{1}{e^{(\epsilon-\mu)/kT}+1} = \frac{1}{1+e^{-(\epsilon-\mu)/kT}}$$

We now assume $(\mu-\epsilon) \gg kT$, or that the energy of the states we consider is $\ll \mu$. (Opposite)

$$f_h \simeq e^{(\epsilon-\mu)/kT} \quad \text{ignoring the "1"}$$

Density of states is upside down also



$D_e(\epsilon) \propto (\epsilon - E_C)^{1/2}$, $\epsilon > E_C$

$D_h(\epsilon) \propto (E_V - \epsilon)^{1/2}$, $\epsilon < E_V$

$$D_h(\epsilon) = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}(E_V-\epsilon)^{1/2} \quad \text{by analogy.}$$

So concentration of holes:

$$p = \int_{-\infty}^{E_V} D_h(\epsilon)\, e^{(\epsilon-\mu)/kT}\, d\epsilon \qquad p = \text{"positive" } n$$

$$= 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} e^{(E_V-\mu)/k_BT} \quad \text{exact analogy.}$$

But this lets us fix μ, which cancels out:

$$np = 4\left(\frac{k_BT}{2\pi\hbar^2}\right)^3 (m_e m_h)^{3/2}\, e^{-\overbrace{(E_C-E_V)}^{E_g}/k_BT}$$

Called the "law of mass action." (as in chemistry)

We did not require material to be intrinsic (pure)

This result holds for "doped" semiconductors too.

Only assumption is that the Fermi level is <u>far</u> from both band edges, relative to k_BT.

6.03.06 I

8.10 Law of Mass Action (Intrinsic)

We know all the numbers, so can determine the expected concentrations. At 300K

Si	$np = 2.10 \times 10^{19}\,/cm^6$	$E_g = 1.1\,eV$
Ge	$np = 2.89 \times 10^{26}\,/cm^6$	$E_g = 0.7\,eV$
GaAs	$np = 6.55 \times 10^{12}\,/cm^6$	$E_g = 1.4\,eV$

Intrinsic case (no doping): every electron in the conduction band leaves a hole in the valence band.

$$n = p = n_i = \sqrt{np} = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2}(m_e m_h)^{3/4} e^{-E_g/2k_BT}$$

Numbers are $\sqrt{np}$ values above.

Ge has $10^{13}/cm^3$; atom density $\sim 10^{22}/cm^3$ (N_A) so only 1 in 10^9 electrons is in conduction band.

Si and GaAs are much less.

Intrinsic semiconductors do not conduct very well!

exam_2007.pdf 11.03.10

We also get μ_i since $n = p$:

$$m_e^{3/2} e^{(\mu - E_c)/kT} = m_h^{3/2} e^{(E_v - \mu)/kT} \quad \text{rest cancels}$$

$$e^{2\mu/kT} = (m_h/m_e)^{3/2} e^{(E_v + E_c)/kT}$$

mid-gap level

$$\frac{2\mu}{kT} = \frac{3}{2}\ln\left(\frac{m_h}{m_e}\right) + \frac{2E_v + E_g}{kT}$$

$$\mu_i = \frac{3}{4} k_B T \ln\left(\frac{m_h}{m_e}\right) + \frac{1}{2}E_g + E_v$$

So if $m_h = m_e$, the Fermi level $\mu = \frac{1}{2}E_g + E_v$ is right in the middle of the gap. This justifies all our assumptions.

The correction for effective mass is extremely small, amounting to a fraction of $k_BT = 25\,meV$.

4.03.08.

8.11 Intuitive derivation of Mass Action:

$np = \text{const}(T)$ $n, p = [\text{electrons}], [\text{holes}]$.

Considerations: Kittel ch 8.

i) rate of <u>creation</u> of e-h pairs depends only on temperature and the (fixed) band structure. rate $= A(T)$

ii) rate of <u>destruction</u> of electrons and holes depends on concentration of <u>both</u>.

$$\text{rate} = B(T)\,np$$

iii) in steady state, rates are equal

$$A(T) = np\,B(T)$$

$$\Rightarrow np = A(T)/B(T)$$