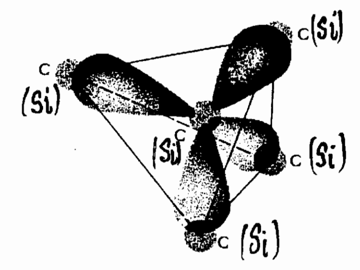
F. Doping and Extrinsic semiconductor

$E_g \sim 1\,eV$

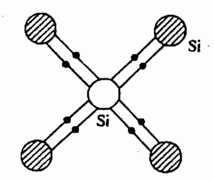
$\Rightarrow$ n_c and p_v are small by thermal excitations

- Use impurities ("doping") to put more electrons into CB or put more holes in VB.

Recall: pure semiconductors



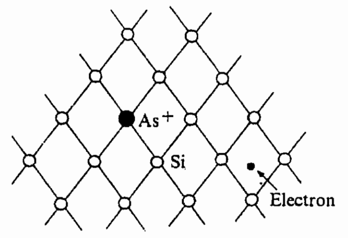
tetrahedrally bonded



Schematic figure showing each Si and its four neighbors ($\cdot$ = electron)

Impurity States : Donors

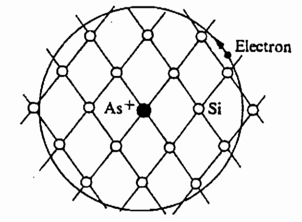
Si doped by As (Group V)



- As has 5 electrons
- Extra electron wanders around
- As^+

An As impurity in a Si crystal. The extra electron migrates through the crystal.

At T=0 or very low temperature, the extra electron and As^+ form a bound state similar to a hydrogen atom



Orbit of an electron around a donor.

Estimate binding energy of electron ↓ energy to free the electron from the As^+ attraction

For a hydrogen atom,

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r^2} \Rightarrow E_{binding} = \frac{e^4 m_0}{32\pi^2\varepsilon_0^2\hbar^2} = 13.6\,eV$$

$$a_B = \frac{4\pi\varepsilon_0\hbar^2}{m_0 e^2} = 0.53\,\text{Å} \quad \text{(Bohr radius)}$$

Requires 13.6eV to ionize H-atom and free the electron.

Now, for a single impurity,

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_r r^2}, \quad \varepsilon_r = \text{relative permittivity of Si} = 11.7 \quad (\sim 10 \text{ for semiconductors})$$

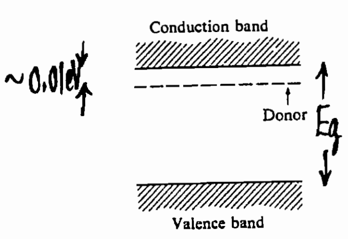
mass of electron $\neq m_0$, instead m_e^*

$$E_{binding}^{(impurity)} = \underbrace{\left(\frac{e^4 m_0}{32\pi^2\varepsilon_0^2\hbar^2}\right)}_{13.6eV} \cdot \underbrace{\frac{1}{\varepsilon_r^2}}_{\sim 0.01} \cdot \underbrace{\left(\frac{m_e^*}{m_0}\right)}_{\sim 0.1} \sim 0.01\,eV \text{ (typical)}$$

$$a_B^{(impurity)} = \varepsilon_r \cdot \left(\frac{m_0}{m_e^*}\right) \cdot a_B^{(hydrogen)} \sim (30\text{-}50)\ \text{Å} \quad \text{(typical)}$$

($\varepsilon_r \sim 10$, $\frac{m_0}{m_e^*} \sim 10$)

- If electron is in CB, it is free.
- Requires ~ 0.01 eV to set it free
  $\Rightarrow$ impurity state that is ~ 0.01 eV below the bottom of CB



} strictly speaking, altogether $2N$ electron states
$T=0$, these impurity states (donor states) are occupied by the extra electron from each donor impurity
(typically, $\sim 10^{15}$ cm^{-3} impurities)

$kT \sim 0.026$ eV ($T = 300$K) > 0.01eV

$\Rightarrow$ thermal energy is sufficient to put all the extra electrons from the donors to CB

$n_c \cdot p_v = n_i^2$ (holds for pure and doped cases)

$n_c \approx N_d$ = donor impurity concentration

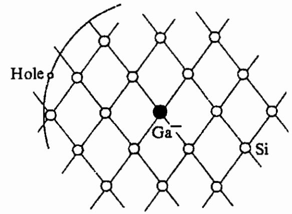
$p_v = \frac{n_i^2}{N_d} = N_d \left(\frac{n_i}{N_d}\right)^2$; but $n_i \ll N_d$

$\Rightarrow p_v \ll N_d = n_c$ or $n_c \gg p_v$

- carriers are <u>electrons</u> in CB : <u>n-type semiconductor</u>

<u>Impurity states</u> : <u>Acceptors</u>

Si doped by Ga (Group III)



A Ga impurity in a Si crystal. The extra hole migrates through the crystal.

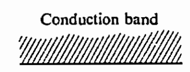
- Ga has 3 electrons
- one missing electron to saturate the bonds
- Ga^-

The hole (m_h^*) sees the attraction of Ga^-

$$E_{binding}^{(impurity)} = \left(\frac{e^4 m_0}{32\pi^2 \varepsilon_0^2 \hbar^2}\right) \cdot \frac{1}{\varepsilon_r^2} \cdot \left(\frac{m_h^*}{m_0}\right) \sim 0.01 \text{ eV (typical)}$$

- A hole is free when it is in VB
- Requires ~ 0.01eV to free the hole from binding

<u>Electron picture</u>



The acceptor level in a semiconductor.

$T=0$
- holes occupy acceptor states
- No holes in VB

$T \neq 0$
- Holes are excited to VB

} strictly speaking, $2N$ electron states
$T=0$, VB is filled by electrons
Acceptors are not occupied by electrons

kT can put electrons from VB to acceptor states $\Rightarrow$ missing electrons in VB
$\Rightarrow$ holes for conduction

N_a = acceptor number concentration

$p_v \simeq N_a \quad (\gg n_i)$

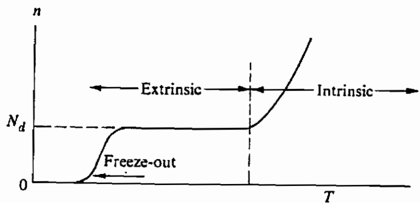
$n_e = \dfrac{n_i^2}{N_a} \ll p_v$

carriers are mainly holes ($+e$) : p-type semiconductors

Ionization Energies of Donors and Acceptors in Si and Ge (in Electron Volts)

Impurity	Si ($\epsilon_r = 11.7$)	Ge ($\epsilon_r = 16.0$)
Donors		
Li	0.033	—
P	0.044	0.012
AS	0.049	0.013
Sb	0.039	0.096
Bi	0.069	
Acceptors		
B	0.045	0.010
Al	0.057	0.010
Ga	0.065	0.011
In	0.16	0.011

Temperature-dependence of n_e for a n-type semiconductor



when kT can't free electrons from impurity bound states

When kT can excite electrons across gap

G. Conductivity and mobility

- Generally, electrons in CB and missing electrons in VB (holes) both contribute to conduction (Recall: Full bands don't contribute)

Recall: $\sigma = \dfrac{ne^2\tau}{m}$

$J = \sigma \mathcal{E}$ ← electric field

$= n\, e \left(\dfrac{e\tau}{m}\right) \mathcal{E}$

(n: number of carriers; e: charge)

The combination $\left(\dfrac{e\tau}{m}\right)$ is the mobility of electron μ.

- Semiconductor physicists use mobility of electron and hole to characterize a semiconductor
- Note that electrons and holes contribute hand-in-hand to conductor

$$J = \Big[n_e e \underbrace{\left(\frac{e\tau_e}{m_e^*}\right)}_{\mu_e} + p_v e \underbrace{\left(\frac{e\tau_h}{m_h^*}\right)}_{\mu_h} \Big] \mathcal{E}$$

$$\therefore \boxed{\sigma = n_e e \mu_e + p_v e \mu_h}$$

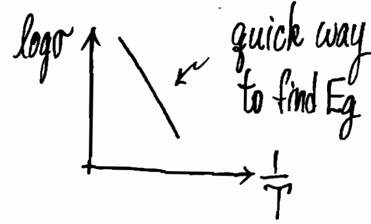
μ_e, μ_h give the response in speed of an electron and a hole to an applied $\mathcal{E}$

Mobilities for Various Semiconductors
(Room Temperature)

Crystal	μ, cm^2/volt-s	
	Electron μ_e	Hole μ_h
C	1800	1600
Si	1350	475
Ge	3900	1900
GaAs	8500	400
GaP	110	75
GaSb	4000	1400
InAs	33000	460
InP	4600	150
InSb	80000	750
CdS	340	18
CdSe	600	
CdTe	300	65
ZnS	120	5
ZnSe	530	16
ZnTe	530	900

$\mu_e, \mu_h \sim \tau_e, \tau_h$

$\therefore$ temperature dependence is related to different scattering mechanisms (e.g. phonons, impurity ions, etc.)



Intrinsic regime

$\sigma = n e \mu_e + p e \mu_h$

n, p dominate T-dependence ($e^{-E_g/2k_BT}$)

Extrinsic regime

$n_c \simeq N_d$ (in a range of temperatures, $n_c \simeq N_d$)

then T-dependence of σ is less drastic and comes from μ_e.

$\mu_e(T)$: scattering mechanisms (consider n-type)

$$\mu_e = \frac{e\tau_e}{m_e^*} = \frac{e}{m_e^*}\frac{l_e}{\bar{v}}$$

l_e = electron mean free path

$\bar{v}$ = some averaged speed of electrons in CB

Note: electrons in CB pick up only the tail of Fermi-Dirac distribution

$\Rightarrow$ ~ classical statistics (Maxwellian distribution in speed)

$$\frac{1}{2} m_e^* \bar{v}^2 \sim \frac{3}{2} k_B T$$

$\bar{v} \sim 10^4\ ms^{-1}$ in semiconductors

$$\mu_e = \frac{e}{\sqrt{m_e^*}} \frac{l_e}{\sqrt{3k_BT}}$$

[c.f. $v_F \sim 10^6\ ms^{-1}$ in metals]

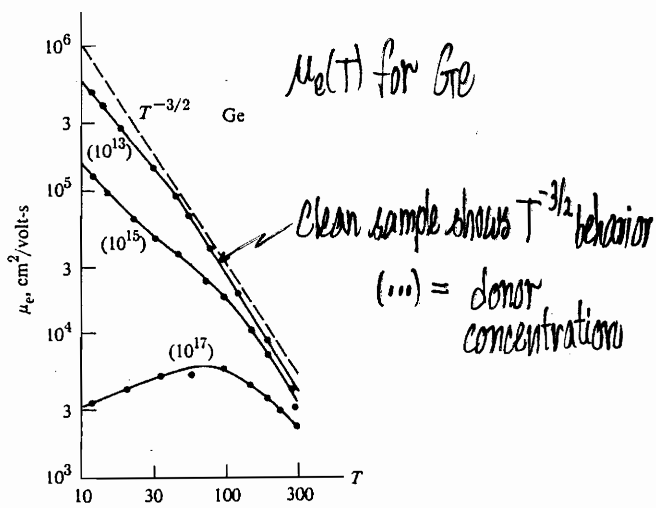
How about l_e?

At room temp., phonon scattering dominates $\Rightarrow l_e \sim \frac{1}{T}$

When temp. is lowered, impurity-scattering comes in.

$\Rightarrow \mu_e \sim \frac{l_e}{T^{1/2}} \sim T^{-3/2}$ for phonon-electron scattering

and impurity-electron scattering suppresses μ
(impurity = ionized impurities)



Electron mobility μ_e versus T in Ge. The dashed curve represents the pure phonon scattering; numbers in parentheses refer to donor concentrations.

- Electronic devices rely on high mobility of carriers
- An important research area is how to get at high electron mobility devices, e.g. HEMT (high electron mobility transistor)

H. Some Optical Properties

- Optical probes are important in semiconductor research

Generally[†], $\varepsilon_r(\omega)$ = frequency-dependent relative permittivity (complex) (or called dielectric constant)

$$\varepsilon_r(\omega) = (n + i\kappa)^2$$

n = refractive index; κ = extinction coefficient

$$\alpha = \frac{2\omega}{c}\kappa \quad ; \quad R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$$

α = absorption coefficient; R = reflectivity for normal incidence

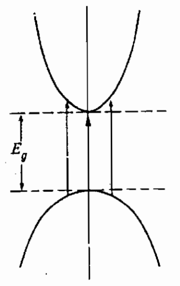
These are general relations (from EM).

Microscopic considerations come in through the evaluation of $\varepsilon_r(\omega)$ by quantum theory (needs band structure, phonon dispersion relation as inputs)

† For an elementary discussion, see Griffiths, "Introduction to Electrodynamics" (Ch.8). For more detailed discussions, see Mark Fox, "Optical Properties of Solids".

For semiconductors, we expect no absorption for $\hbar\omega < E_g$ (at least for clean samples).

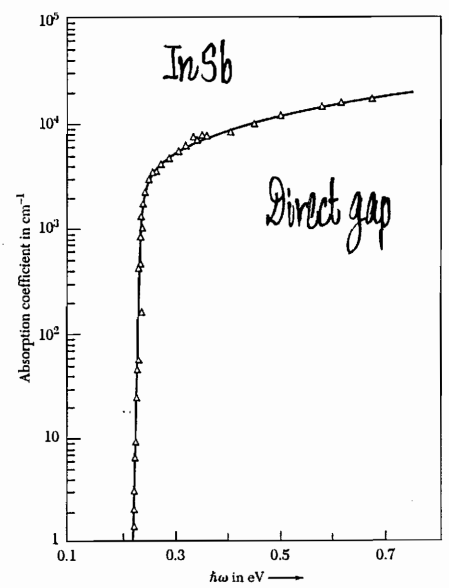
For direct gap semiconductors,



The fundamental absorption process in semiconductors.

⇒ expect to see a sharp absorption edge at $\hbar\omega = E_g$

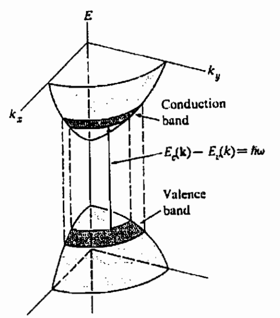
↑ from no absorption to significant absorption



This provides an efficient way to measure E_g.

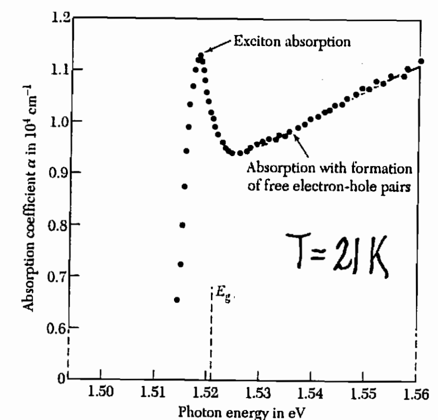
Closer inspection:

$\alpha \sim A\,(\hbar\omega - E_g)^{1/2}$ — due to DOS



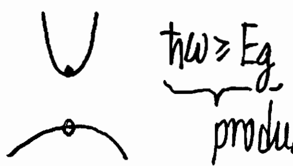
But even for very clean samples, there are structures in the absorption coefficient below E_g (at $\hbar\omega \lesssim E_g$) at low temperatures!

GaAs direct gap



Effect of an exciton level on the optical absorption of a semiconductor for photons of energy near the band gap E_g in gallium arsenide at 21 K. The vertical scale is the intensity absorption coefficient α, as in $I(x) = I_0 \exp(-\alpha x)$. The energy gap and exciton binding energy are deduced from the shape of the absorption curve: the gap E_g is 1.521 eV and the exciton binding energy is 0.0034 eV.

Why? Excitons: A many-body effect



$\hbar\omega \geq E_g$ produce free electrons and free holes

$(-e, m_e^*)$ $(+e, m_h^*)$

they may form a bound state — exciton

m_e^* and m_h^* are different but not by much

∴ need to use $\frac{1}{m_{reduced}} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$

Binding energy of exciton+

$$E_B^{(exciton)} = -\underbrace{\left(\frac{13.6}{n^2}\right)}_{\text{H-atom}} \underbrace{\frac{1}{\varepsilon_r^2}}_{\sim 0.01} \underbrace{\left(\frac{m_{reduced}}{m_0}\right)}_{\sim 0.01} \text{eV}, \quad n = 1, 2, \cdots$$

– few tens or few meV (milli-eV)

∴ Requires $|E_B^{(exciton)}|$ to break exciton into free electron and free hole

⇒ can create a bound electron-hole pair (exciton) at $E_g - |E_B|$

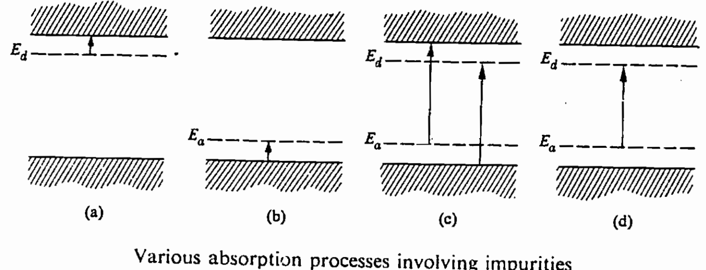
At room temperature, $kT > |E_B|$ ⇒ exciton is thermally broken

At low temperatures, possible to form exciton
⇒ structure in absorption

+ Kittel: Ch.15

Other optical processes for $\hbar\omega < E_g$:

for doped samples, there are impurity states



Various absorption processes involving impurities

And more... n-type (p-type) semiconductors, gas of electrons (holes) in CB (VB)

→ intra-band optical properties (treated like metals $\sigma(\omega) \Rightarrow \varepsilon_r(\omega)$)

Refs: Kittel: Ch.8, Ch.15

For further thorough treatment of semiconductor physics, see Yu and Cardona, "Fundamentals of semiconductors".