

PHYS-E0421 Solid-State Physics (5cr), Spring 2019

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Today's topics

- Intrinsic (undoped) semiconductors
 - Electronic structure of semiconductors
 - Carrier statistics
 - Chemical potential position
 - Extrinsic (doped) semiconductors
 - Dopants and their electronic structure
 - Effective mass theory
 - Carrier statistics
 - Chemical potential position
 - Conductivity and mobility
-

Additional reading

<http://britneyspears.ac/lasers.htm>

<http://www.halbleiter.org/en>

Motivation

Why semiconductors?:

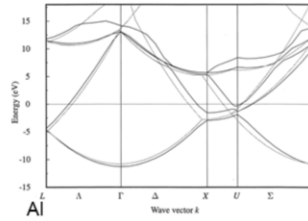
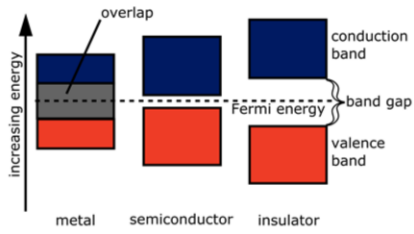
- Semiconductor electronics: transistors, diodes, ...
- Miniaturization: integrated circuits, microprocessors
- Optoelectronics: LEDs, lasers, solar cells

- Properties can be altered via impurities = doping
 - Control of charge carrier concentrations (Fermi-level), conductivity
- Band gaps in the visible light range

Ask students.

- Behavior can be changed either more metallic or more insulating material
- Ability to do electronics coupled with optical properties

Metals, semiconductors and insulators

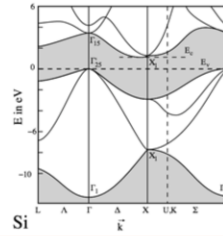


Al

Resistivity ρ ($T = 300\text{K}$)

Insulators	$\sim 10^{10} - 10^{22} \Omega\text{cm}$	(\rightarrow quarz)
Semiconductors	$\sim 10^{-3} - 10^9 \Omega\text{cm}$	
Metals	$\sim 10^{-6} - 10^{-4} \Omega\text{cm}$	(\leftarrow Cu)

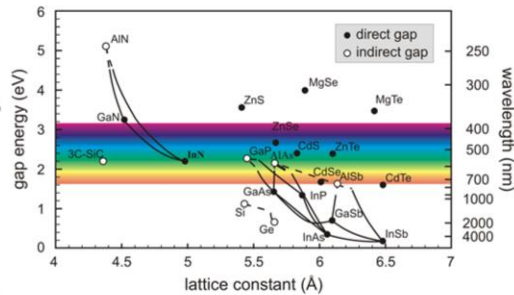
Conductivity $\sigma(T) = 1/\rho(T)$



Si

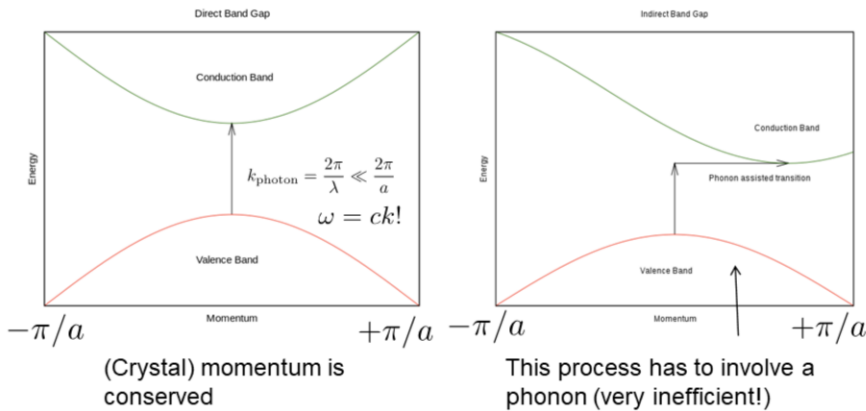
Elemental vs. compound semiconductors

- Group IV: Si, Ge, $\text{Si}_x\text{Ge}_{1-x}$ alloy (high mobility)
- III-V compounds: GaAs, $\text{Ga}_x\text{Al}_{1-x}\text{As}$ (heterostructures, lasers) GaN, InN (optoelectronics, LED's, power el.)
- II—VI compounds: CdTe, HgTe (IR detectors), ZnS (Electroluminescence) ZnSe
- And many others: CuInSe_2 , MoS_2 , carbon nanotubes, transp. conducting oxides



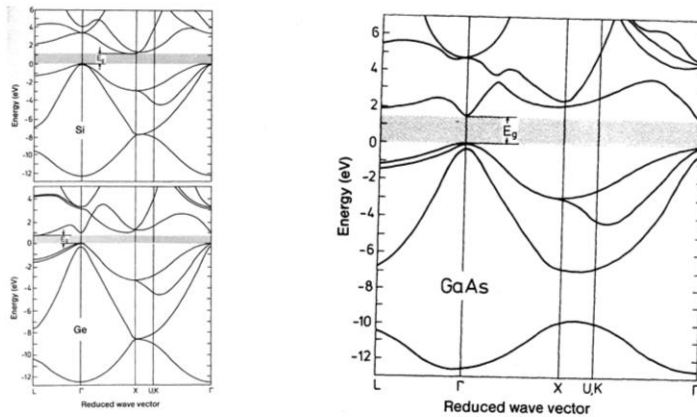
- Visible light: red 1.65 eV – violet 3.26 eV, silicon 1.1 eV, GaAs 1.4, GaN, 3.4 eV, band gap tends to decrease with increasing principal quantum number (going down the column in periodic table)
- CuInSe_2 is used in thin-film solar cells.
- MoS_2 is 2D material with band gap ~2 eV.
- Carbon nanotubes are metallic or semiconducting depending on the chirality of the tube.
- Many oxides tend to be easy to n-dope, but difficult to p-dope. Band gaps 2-3 eV. TCOs (ZnO , SnO_2 , In_2O_3) used e.g. in touch screens.

Indirect vs. direct energy gap: optical absorption and emission



- Wave vector conservation $k+q=k'$, where k is the state in the valence band, k' in the conduction band, and q for the photon. Also energy conservation.
- Indirect process, goes through virtual state or virtual transitions: off-resonance transition to intermediate state and then immediately another transition to final state.
- Total probability is the product of the probabilities of the two processes (and scaled by the amount of off-resonance), and thus unlikely
- Numbers: $q = 2\pi/\lambda = 2\pi c/f = c/\omega = c\hbar/E$, for $E = 1 \text{ eV} \Rightarrow \lambda = 1.24 \text{ } \mu\text{m} \Rightarrow q = 5 \times 10^6 \text{ 1/m}$. For $a = 3.14 \text{ \AA}$, Brillouin zone boundary is at $\pi/a = 1 \times 10^{10} \text{ 1/m}$

Indirect vs. direct energy gap



- Absorption of all photons with energy $>$ gap. Thermalization/relaxation of electrons to lowest unoccupied states. Can't get to valence band via single scattering events. Needs to emit photon with energy \sim gap.
- Direct gap is good if light emission is wanted.
- Indirect gap can be good in solar cells to avoid recombination (de-excitation), or perhaps also in transistors.
- Parabolic shape of band structure at valence band maximum and conduction band minimum.

Homework question 1

Why are direct wide band gap materials useful?

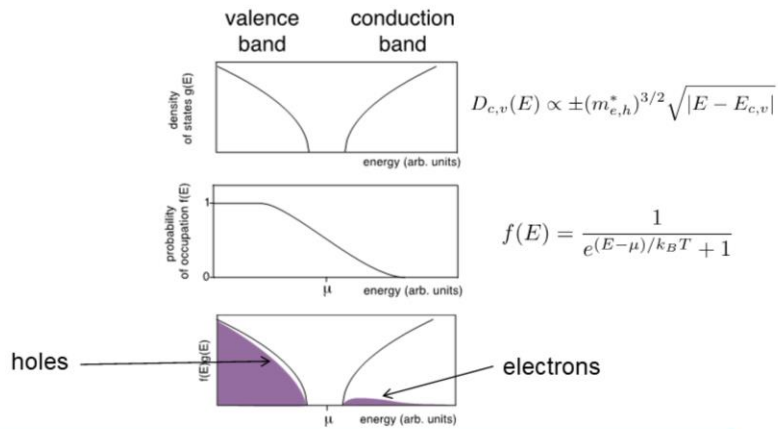
See, for example, [the background of the Nobel Prize in Physics 2014](#)

(awarded "*for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources*")

[2014 Nobel Lectures in Physics in Reviews of Modern Physics](#)

- Growth is difficult (requires high T_p), but also difficult to achieve p-type doping

Intrinsic conductivity: Can a material with Fermi-level in band gap conduct?



- Density of states of parabolic band, Elliott eq. (6.193)
- In semiconductor physics Fermi-level and chemical potential are used interchangeably
- Thermal excitations over the gap

The effective mass

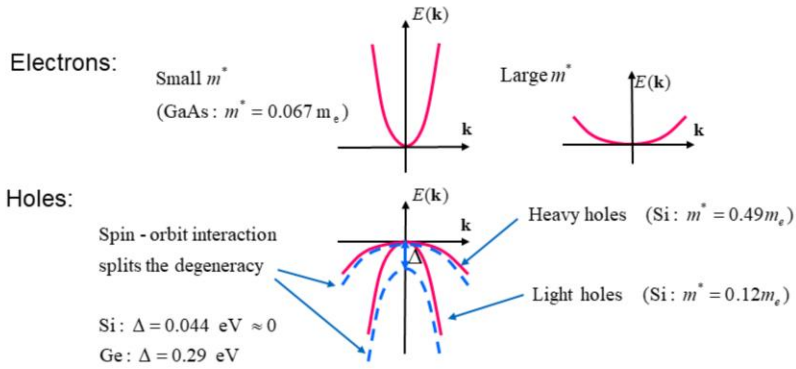
- A concept in the semiclassical theory of electron dynamics characterizing electrons near the bottom of the conduction band and holes near the top of the valence band

Definition: $m^* = \pm \hbar^2 \left(\frac{d^2 E(k)}{dk^2} \right)^{-1}$ ($\rightarrow E(k) = \frac{\hbar^2 k^2}{2m^*}$ as for free el.)

Note: In the original image, a blue arrow labeled 'e-' points to the '+' sign, and another blue arrow labeled 'hole' points to the '-' sign.

- Description appropriate when considering distance (much) larger than interatomic spacing.
- Effect of atomic scale details on the electron dynamics are built into the effective mass.

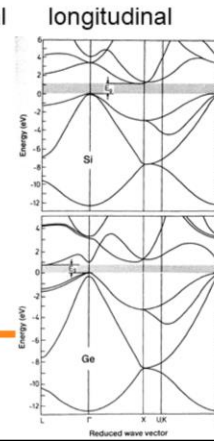
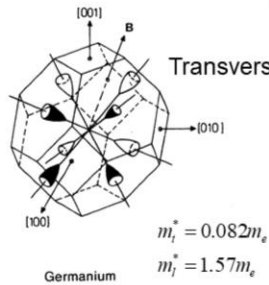
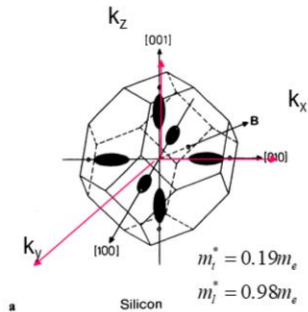
The effective mass (2)



In addition to affecting the dynamics of electrons and holes the effective masses also determine the densities of states of the band edges, $D(E) \propto (m^*)^{3/2}$

Longitudinal and transverse effective masses

$$E(\mathbf{k}) = \hbar^2 \left(\frac{k_x^2 + k_y^2}{2m_t^*} + \frac{k_z^2}{2m_l^*} \right)$$



"Electron pockets" in the conduction band minima of Si and Ge.

Electron and hole densities

Fermi-Dirac statistics \Rightarrow

$$e^- \text{'s in conduction band: } n(T) = \int_{E_c}^{\infty} dE D_c(E) \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

$$h^+ \text{'s in valence band: } p(T) = \int_{-\infty}^{E_v} dE D_v(E) \left(1 - \frac{1}{\exp[(E - E_F)/k_B T] + 1} \right)$$

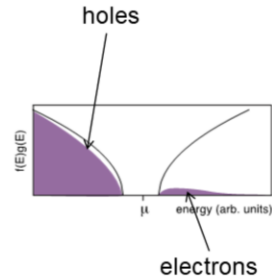
E_F = chemical potential (Fermi level)

Non-degenerate (low density) e^- and h^+ gases

$$E_c - E_F \gg k_B T ; \quad E_F - E_v \gg k_B T \Rightarrow$$

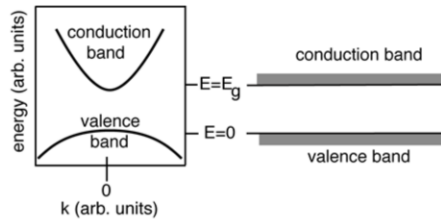
$$n(T) = \int_{E_c}^{\infty} dE D_c(E) \exp[-(E - E_F)/k_B T]$$

$$p(T) = \int_{-\infty}^{E_v} dE D_v(E) \exp[-(E_F - E)/k_B T]$$



- Non-degenerate: not metallic, occupation of states much smaller than one (determined by the "Boltzmann tail"), \sim independent particles
- $|E - E_F| > 2kT$ or $3kT$ is usually enough for non-degeneracy
- I don't like the hole-band formalism used in Elliott sometimes (it's also never used in semiconductor physics books)
- Use $\exp(-(E - E_F)/kT) = \exp(-(E - E_c)/kT) * \exp(-(E_c - E_F)/kT)$ to get to the result in next slide

Effective concentrations of electron levels



$$n(T) \approx N_{eff}^c(T) \exp[-(E_c - E_F) / k_B T]$$

$$p(T) \approx N_{eff}^v(T) \exp[-(E_F - E_v) / k_B T]$$

Maxwell - Boltzmann statistics for effective levels at E_c and E_v

with effective degeneracies/ volume $N_{eff}^c(T) = \int_{E_c}^{\infty} dE D_c(E) \exp[-(E - E_c) / k_B T]$

$$N_{eff}^v(T) = \int_{-\infty}^{E_v} dE D_v(E) \exp[-(E_v - E) / k_B T]$$

- We are usually interested in calculating n, p as a function of Fermi-energy
- One interpretation: replaces the band by a delta-function distribution at VBM/CBM with an effective density of states
- n, p depend exponentially on Fermi-energy

Effective concentrations of electron levels (2)

$$\text{For parabolic bands } D_{c,v}(E) = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} (|E - E_{c,v}|)^{1/2}$$

$$\Rightarrow$$

$$N_{eff}^{c,v} = 2 \left(\frac{2\pi m_{n,p}^* k_B T}{\hbar^2} \right)^{3/2} \approx 2.5 \left(\frac{m_{n,p}^*}{m_e} \right)^{3/2} \left(\frac{T}{300 \text{ K}} \right)^{3/2} \cdot 10^{19} \text{ 1/cm}^3$$

weak T dependence order of magnitude

$\exp[-(\dots)/k_B T] \Rightarrow n, p \ll 10^{18} \dots 10^{19} \text{ 1/cm}^3$, i.e. nondegenerate gases

The above formulas are used, with shifted E_F also for doped semiconductors



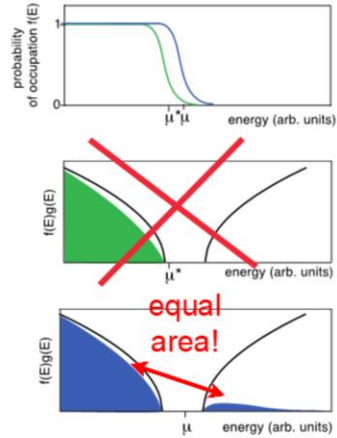
- Naturally depends on the curvature of the band (m^*) = ok
- Depends on temperature = not so nice
- Does not depend on Fermi-level = nice!
- Compare, number of atoms or number of unit cells per volume is 10^{22} - 10^{23} 1/cm^3 , that is, there is less than one electron per 1000 unit cells.

Where is the chemical potential?

The chemical potential must be roughly in the middle of the gap. Otherwise one would get incorrect number of electrons, or an imbalance between the number of conduction electrons and vacant valence states (holes).

Homework question 2

How do the curvatures of bands affect the chemical potential position?



- Always charge neutrality holds, the macroscopic sample is neutral, number of electrons = number of protons.
- Starting from 0K and then adding excitations, electrons and holes are always created as pairs, thus their numbers also need to match $n=p=n_i$ (intrinsic carrier concentration)
- HW2: similar to how chemical potential depends on T...

The law of mass action / chemical potential position

$$np = N_{\text{eff}}^c N_{\text{eff}}^v \exp[-(E_c - E_v) / k_B T] = n_i^2 \quad \leftarrow \text{Holds also with doping!}$$

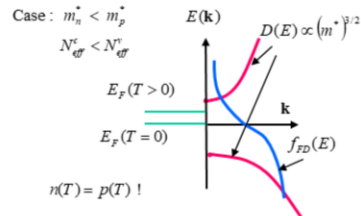
Intrinsic semiconductors i.e. no doping

$$n(T) = p(T) = n_i(T) = [N_{\text{eff}}^c N_{\text{eff}}^v]^{1/2} \exp[-E_g / 2k_B T]$$

	$n_i(T = 300\text{K})$
Si	$1.5 \times 10^{10} \text{ 1/cm}^3$
Ge	$2.4 \times 10^{13} \text{ 1/cm}^3$

$$n = N_{\text{eff}}^c(T) \exp[-(E_c - E_F) / k_B T] \Rightarrow E_F = E_c - E_g / 2 + \frac{k_B T}{2} \ln \frac{N_{\text{eff}}^v(T)}{N_{\text{eff}}^c(T)}$$

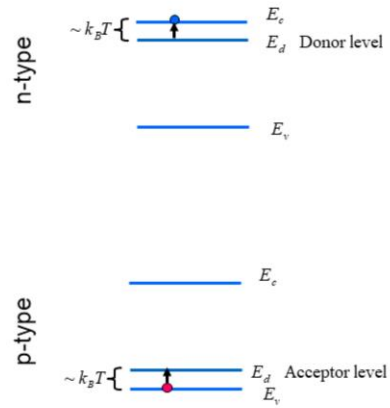
$$\text{If } N_{\text{eff}}^v = N_{\text{eff}}^c \text{ or } T \rightarrow 0 \Rightarrow E_F = E_v + E_g / 2$$



- Balance in generation (electrons in VB and holes in CB are the "reactants" and E_g is the activation energy) and recombination (free electrons in CB and holes in VB are the "products" and no activation energy).
- n^*p is independent of Fermi-level, and $n^*p = n_i^2$ holds also for doped (non-degenerate) systems
- n_i confirmed to be much less than N_{eff}
- The shift is usually fairly small, i.e., the Fermi-level remains quite close to midgap in intrinsic semiconductors
- Note, E_g is energy difference. E_F , E_c , and E_v are energies with respect to arbitrary (unknown) reference, thus only their difference has a "meaning", not their absolute values.

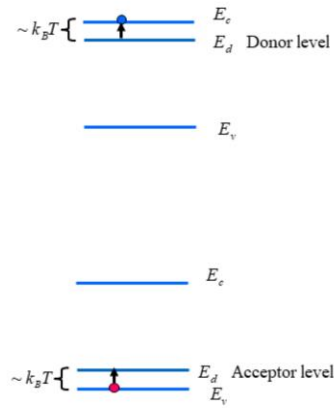
Extrinsic (doped) semiconductors, n- and p-type

- Fermi-level position controlled by introducing impurities, also called "doping"
 - $n \neq p$
- If larger number of electrons than holes: "negative" material = n-type
- If larger number of holes: "positive" material = p-type



n- and p-type doping

- Both n- and p-type conductors needed for electronic devices.
- Donors → n-type conductors e.g. P ($3s^23p^3$) in Si ($3s^23p^2$). Extra ionic charge → a weakly bound state below E_c → electrons to conduction band by thermal excitation
- Acceptors → p-type conductors e.g. Al ($3s^23p^1$) in Si ($3s^23p^2$). Lack of ionic charge → a weakly bound state above E_v → holes to valence band by thermal excitation



- P- \rightarrow Si, one extra proton and one extra electron. The positive potential perturbs the VB and CB states. In CB, one state drops down from CBM which then holds the extra electron. It is localized due to being inside the gap. In VB, these "defect states" are within VB states and uninteresting. States are also "resonant", i.e., poorly localized due to mixing with host states.
- Electron going to acceptor = hole going to VBM
- Even fairly small concentration of dopants is enough to move Fermi-level close to VBM/CBM, e.g. in parts-per-million

Doping

Hydrogen 1 H 1.00794																	Helium 2 He 4.002602	
Lithium 3 Li 6.941	Beryllium 4 Be 9.012182											Boron 5 B 10.811	Carbon 6 C 12.011	Nitrogen 7 N 14.00644	Oxygen 8 O 15.999	Fluorine 9 F 18.9984032	Neon 10 Ne 20.1797	
Sodium 11 Na 22.98976928	Magnesium 12 Mg 24.304											Aluminum 13 Al 26.9815386	Silicon 14 Si 28.0855	Phosphorus 15 P 30.973762	Sulfur 16 S 32.06	Chlorine 17 Cl 35.453	Argon 18 Ar 39.948	
Potassium 19 K 39.0983	Calcium 20 Ca 40.078	Scandium 21 Sc 44.955912	Titanium 22 Ti 47.88	Vanadium 23 V 50.9415	Chromium 24 Cr 51.9961	Manganese 25 Mn 54.938045	Iron 26 Fe 55.845	Cobalt 27 Co 58.933195	Nickel 28 Ni 58.6934	Copper 29 Cu 63.546	Zinc 30 Zn 65.38	Gallium 31 Ga 69.723	Germanium 32 Ge 72.64	Arsenic 33 As 74.9216	Selenium 34 Se 78.96	Bromine 35 Br 79.904	Krypton 36 Kr 83.80	
Rubidium 37 Rb 85.4678	Sr 87.62	Yttrium 39 Y 88.905848	Zirconium 40 Zr 91.224	Niobium 41 Nb 92.90638	Molybdenum 42 Mo 95.94	Technetium 43 Tc 98.906250	Ruthenium 44 Ru 101.07	Rhodium 45 Rh 101.07	Palladium 46 Pd 106.36	Silver 47 Ag 107.8682	Cadmium 48 Cd 112.411	Indium 49 In 114.818	Tin 50 Sn 118.710	Antimony 51 Sb 121.757	Tellurium 52 Te 127.60	Iodine 53 I 126.905	Xenon 54 Xe 131.29	
Cesium 55 Cs 132.90545196	Ba 137.327	* 57-70	Lanthanum 57 La 138.90547	Hafnium 72 Hf 178.49	Tantalum 73 Ta 180.94788	Tungsten 74 W 183.84	Rhenium 75 Re 186.207	Osmium 76 Os 190.23	Iridium 77 Ir 192.222	Platinum 78 Pt 195.084	Gold 79 Au 196.966569	Mercury 80 Hg 200.59	Thallium 81 Tl 204.38	Lead 82 Pb 207.2	Bismuth 83 Bi 208.9804	Po 209	Astatine 84 At 210	Rn 222
Francium 87 Fr 223	Radium 88 Ra 226	** ** 89-102	Lr 260	Rf 261	Db 262	Sg 263	Bh 264	Hs 265	Mt 266	Uun 267	Uub 268	Uuq 269						

* Lanthanide series

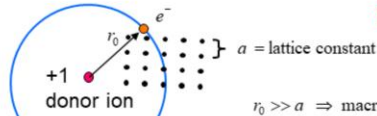
** Actinide series

57 La 138.905	58 Ce 140.12	59 Pr 140.90765	60 Nd 144.242	61 Pm 144.9126	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.5001	67 Ho 164.93032	68 Er 167.259	69 Tm 168.93032	70 Yb 173.045
89 Ac 227	90 Th 232.0377	91 Pa 231.036889	92 U 238.02891	93 Np 237.048173	94 Pu 244.06422	95 Am 243.061381	96 Cm 247.07647	97 Bk 247.0703	98 Cf 251.079589	99 Es 252.083	100 Fm 257.103	101 Md 258.103	102 No 259.103



Effective mass theory

Consider, e.g.,
a donor level



Exercise 1

$r_0 \gg a \Rightarrow$ macroscopic ϵ (\leftarrow screening), m^* OK!

H-atom levels

$$E_n = -\frac{m^* e^4}{8(\epsilon\epsilon_0)^2 n^2 \hbar^2} + E_c \leftarrow \text{energy zero}$$

$$-13.6 \text{ eV} \left(\frac{m^*}{m_e} \right) \frac{1}{\epsilon^2 n^2}$$

$$\epsilon \approx 10 \dots 20 ; m^* \approx 0.1 m_e \Rightarrow$$

Electron binding energy :

$$E_c(n=1) - E_d \sim \frac{1}{1000} 13.6 \text{ eV} \sim 10 \text{ meV} \sim k_B T \ll E_g$$

Effective electron radius :

$$r_0 \approx a_0 \epsilon \frac{m_e}{m^*} n^2 \sim 100 \text{ \AA} \gg a$$

A consistent picture

- Extra electron would go to conduction band, but it is then attracted by the extra proton
- Semiclassical dynamics and effective mass valid when distances larger than lattice constant
- Coulomb potential $1/r \rightarrow 1/(\epsilon\epsilon_0 r)$

Donor and acceptor states

- Sometimes works very well

Table 6.7 Theoretical (hydrogenic) and experimental donor binding energies ϵ_d for shallow donors in III-V and II-VI semiconductors

Semiconductor	ϵ_d^{th} (meV)	ϵ_d^{exp} (meV)
GaAs	5.72	5.84 (Si _{Ga}); 5.88 (Ge _{Ga}); 5.87 (S _{As}); 5.79 (Se _{As})
InSb	0.6	0.6 (Te _{Sb})
CdTe	11.6	14 (In _{Cd}); 14 (Al _{Cd})
ZnSe	25.7	26.3 (Al _{Zn}); 27.9 (Ga _{Zn}); 29.3 (F _{Se}); 26.9 (Cl _{Se})

After Yu and Cardona (1996), *Fundamentals of Semiconductors*, p. 159, Table 4.1, © Springer-Verlag GmbH & Co. KG.

										Helium 2 4.0026
					Boron 5 10.811	Carbon 6 12.011	Nitrogen 7 14.007	Oxygen 8 15.999	Fluorine 9 18.998	Neon 10 20.180
					Aluminum 13 26.982	Silicon 14 28.086	Phosphorus 15 30.974	Sulfur 16 32.065	Chlorine 17 35.453	Argon 18 39.948
					Zinc 30 65.38	Gallium 31 69.723	Germanium 32 72.61	Selenium 34 78.96	Bromine 35 79.904	Krypton 36 83.905
					Cadmium 48 112.41	Indium 49 114.82	Tin 50 118.71	Antimony 51 121.76	Tellurium 52 127.60	Xenon 54 131.29
					Mercury 80 200.59	Thallium 81 204.38	Lead 82 207.2	Bismuth 83 208.98	Poison 84 209	Radium 86 226
					Uub 112	Uuq 114				

Donor and acceptor states

Effective mass theory
 $m^* = 0.2 m_e$; $\epsilon = 11.9$ (Si), 16 (Ge)

Table 12.5. Ionization energies E_d for a few donor species in silicon and germanium

	P [meV]	As [meV]	Sb [meV]	
Si	45	54	43	20
Ge	13	14	10	11

Table 12.6. Ionization energies E_a for a few acceptor species in silicon and germanium

	B [meV]	Al [meV]	Ga [meV]	In [meV]
Si	45	67	74	153
Ge	11	11	11	12

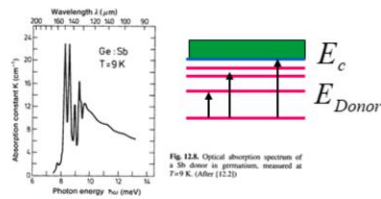


Fig. 12.8. Optical absorption spectrum of a Sb donor in germanium, measured at $T=9$ K. (After [12.2])

The figure on the left:

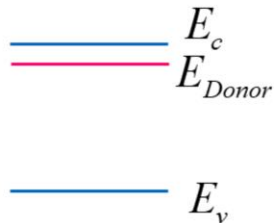
Optical absorption spectrum of a Sb donor in germanium ($T = 9$ K)

- Shallow levels in band gap
- Absorption to conduction band starts at ~ 10 meV
- Below that absorption to several (higher-n) Rydberg states (split in the crystal symmetry)

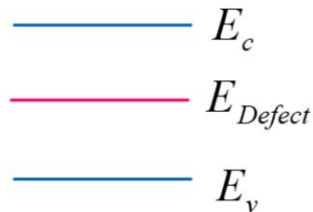
- Works less well when the band edges are located outside the Gamma-point, VBM (or CBM) are degenerate, and/or effective mass is anisotropic

Shallow vs. deep dopant levels

A "shallow" donor level



A "deep" level



- Shallow means that it is easy to excite electron from defect to band edge. Easy means "by thermal excitation".
- Shallow \approx hydrogenic solution and effective mass description applies
- Hydrogenic impurities in large band gap semiconductors can become deep when mass increases and dielectric constant decreases. Effective mass description not valid any more. Level positions more dependent on electronegativity.
- \Rightarrow ZnO, O-2p derived VBM states so deep in energy that there is no hydrogenic acceptor (e.g. N leads to deep state), p-doping so far impossible. Growth of p-type Mg-doped GaN, Nobel prize

Shallow vs. deep dopant levels

Shallow dopant levels in the band gap

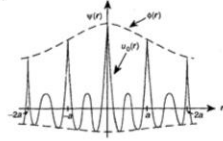


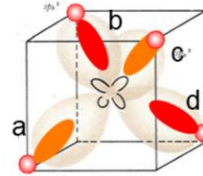
Fig. 6.52 Schematic illustration of a shallow hydrogenic donor-electron wavefunction in real space, being the product of a periodic function $u_0(r)$ and an envelope function $v(r)$ that is the solution of the Schrödinger equation for the orbital motion of an electron, bound to a donor. The lattice separation is a .

Extended wave function!

Deep defect levels in the band gap

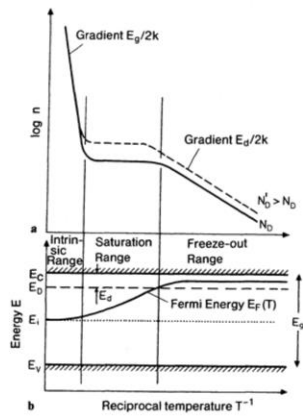
e.g. a vacancy in Si

Localized wavefunction!



- Shallow state, being perturbation on the host, can be written as the periodic part of the CBM/VBM Bloch wave functions times the hydrogenic envelope

Charge carrier density in doped semiconductors



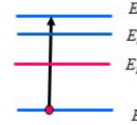
Low temperature $|E_c - E_d| \gg k_B T$
(freeze out)



High temperature (intrinsic)

$$n_i > N_d$$

$$|E_c - E_d| \ll k_B T$$



Intermediate temperature (saturation) $n = N_d$

- Only the number of free electrons/holes matter for conductivity.
- Intrinsic when $n_i > N_d$
- The $T \rightarrow 0$ limit is the same independent of the defect concentration... as is $T \rightarrow \infty$

Charge carrier density in doped semiconductors

Ionization of dopant atoms :

$$N_d^0 + N_d^+ = N_d \quad \text{donor ion density}$$

$$N_a^0 + N_a^- = N_a \quad \text{acceptor ion density}$$

Charge neutrality :

$$n + N_a^- = p + N_d^+$$

n : all electrons in CB

p : all holes in VB

- Donor can donate away the electron to CB and leave behind a positively charged ion
- Acceptor can accept an electron from VB and become a negatively charged ion

Charge carrier density in doped semiconductors

$$k_B T \ll |E_c - E_d| \Rightarrow \text{freeze out } n < N_d$$

$$k_B T \approx |E_c - E_d| \Rightarrow \text{saturation } N_d^+ \approx N_d \approx n$$

$$k_B T \gg |E_c - E_d| \Rightarrow \text{intrinsic } n_i \approx n \gg N_d$$

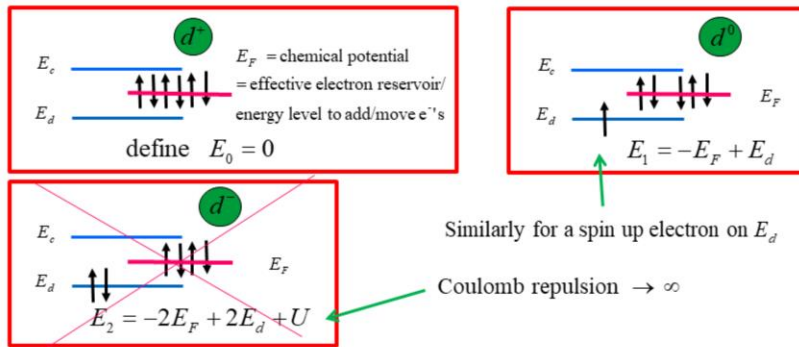
Freeze out

Assume: $N_d \gg n_i$

$$d \leftrightarrow d^+ + e^- \Rightarrow n = N_d^+ = N_d \langle d^+ \rangle ; \langle d^+ \rangle = \text{ionization probability}$$

Charge carrier density in doped semiconductors

Different states for a donor



- d-: defect cannot bind another electron. Alternatively, consider just that the energy is much higher than E_0 or E_1

Charge carrier density in doped semiconductors

$$\langle d^+ \rangle = \frac{e^{-E_d/k_B T}}{\sum_i e^{-E_i/k_B T}} = \frac{1}{1 + 2e^{(E_d - E_i)/k_B T} + 0} \Rightarrow n = N_d \langle d^+ \rangle$$

$$e^{(E_d - E_i)/k_B T} = e^{-(E_d - E_i)/k_B T} \underbrace{e^{-(E_i - E_d)/k_B T}}_{n/N_{eff}^c} \Leftarrow n(T) \approx N_{eff}^c(T) e^{-(E_d - E_i)/k_B T}$$

$$\Rightarrow n = N_d / [1 + 2e^{-(E_d - E_i)/k_B T} n/N_{eff}^c]$$

$$2n^2 + nN_{eff}^c e^{-(E_d - E_i)/k_B T} = N_{eff}^c N_d e^{-(E_d - E_i)/k_B T}$$

Exercises 3 and 4

Freeze out : $n < N_d \Rightarrow n = \left[\frac{N_d N_{eff}^c}{2} \right]^{1/2} e^{-(E_d - E_i)/2k_B T}$

Saturation : $n \rightarrow N_d = \text{constant}$

Intrinsic : $n = n_i = (N_{eff}^v N_{eff}^c)^{1/2} e^{-E_g/2k_B T}$

- To see why the first term is larger than the second term, plug in $n = N_{eff}^c \exp(\dots)$ to both

Fermi level position in doped semiconductors

Fermi - level position $E_F(T) = ?$

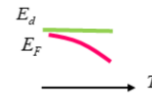
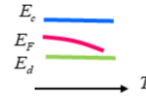
Freeze out : $n = N_{\text{eff}}^c(T) e^{-(E_c - E_F)/k_B T} = \left[\frac{N_d N_{\text{eff}}^c}{2} \right]^{1/2} e^{-(E_c - E_d)/2k_B T}$

$$\Rightarrow E_F = E_c - (E_c - E_d) / 2 - \frac{k_B T}{2} \ln \frac{2 N_{\text{eff}}^c}{N_d}$$

Saturation : $n = N_{\text{eff}}^c(T) e^{-(E_c - E_F)/k_B T} = N_d$

$$\Rightarrow E_F = E_c - k_B T \ln \frac{N_{\text{eff}}^c}{N_d}$$

Intrinsic : $E_F = E_g / 2 + \frac{k_B T}{2} \ln \frac{N_{\text{eff}}^v}{N_{\text{eff}}^c}$



Homework question 2

- Saturation: only valid when Fermi-level is below defect level. To keep defect level occupation (and n) low upon increasing width of the FD distribution, Fermi-level needs to move further down.
- Can all be obtained from charge neutrality

Full solution

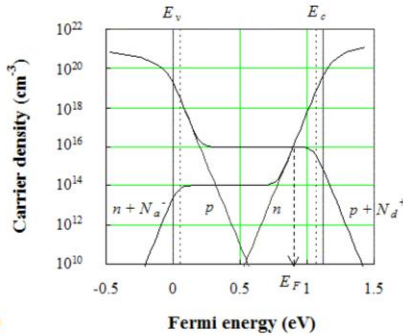
- Usually, Fermi-level can not be solved analytically from

$$n + N_a^- = p + N_d^+$$

→

$$N_{eff}^c(T) \exp[-(E_c - E_F)/k_B T] + \frac{N_a}{1 + g_a e^{(E_F - E_d)/k_B T}} =$$

$$N_{eff}^v(T) \exp[-(E_F - E_v)/k_B T] + \frac{N_d}{1 + g_d e^{(E_F - E_d)/k_B T}}$$



- I.e., where will Fermi-level lie so that the total system remains charge neutral (number of electrons is conserved)
- Degeneracy factors depend on the defect and on the band edge (i.e. Material)

Charge carrier density

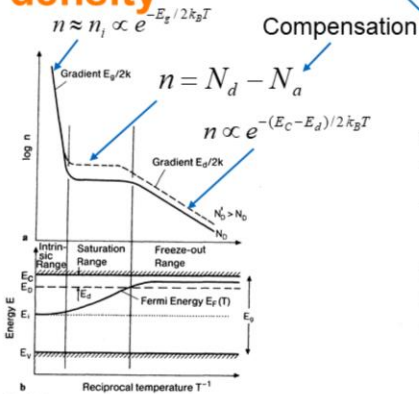
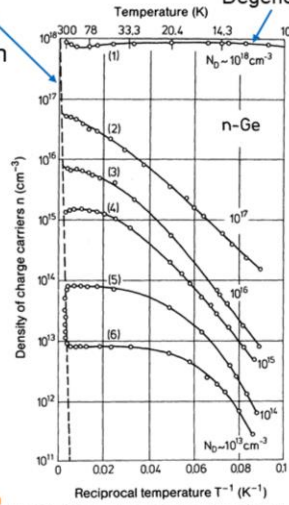


Fig. 12.10. (a) Qualitative temperature dependence of the concentration n of electrons in the conduction band of an n -type semiconductor for two different donor concentrations $N_d > N_a$. The width of the forbidden band is E_g and E_d is the ionization energy of the donors; (b) qualitative temperature dependence of the Fermi energy $E_f(T)$ in the same semiconductor. E_c and E_v are the lower edge of the conduction band and the upper edge of the valence band, respectively. E_d is the position of the donor levels and E_i is the Fermi level of an intrinsic semiconductor

Intrinsic

Compensation

Very high N_D : Impurity band, Degenerate el. gas



High N_D :
 -narrow saturation region
 -intrinsic region not seen

Fig. 12.11. The concentration n of free electrons in n -type germanium, measured using the Hall effect (Panel XIV). For the samples (1) to (6), the donor concentration N_D varies between 10^{18} and 10^{13} cm^{-3} . The temperature dependence of the electron concentration in the intrinsic region is shown by the dashed line. (After [12.3])

Scattering mechanisms for electrons and holes in semiconductors

The carrier concentrations alone do not determine the conductivity but the mobility affects as well. The main scattering mechanisms are,

$$\mathbf{j} = e(n\mu_n + p\mu_p)\mathbf{E}$$

1. Phonon scattering
2. Ionized impurity scattering (doped semiconductors)

$$\mu_{n,p} = \frac{e\tau_{n,p}}{m_{n,p}^*}$$

- We saw in last exercise that for free electron gas we get Drude-like expression. Here we have quite similar case with parabolic bands near band extrema.
- Scattering mechanisms go into mobility. Expression for mobility looks exactly like in Drude model.
- Electron-electron scattering ignored (also) due to low concentration of electrons

Conductivity of semiconductors – mobility of charge carriers

$$\mathbf{j} = \sigma \mathbf{E} = e(n\mu_n + p\mu_p)\mathbf{E} \quad \begin{array}{l} \mu_n = \text{electron mobility} \quad \sigma = \text{conductivity} \\ \mu_p = \text{hole mobility} \end{array}$$

$$\mu = \frac{\sigma}{en} \quad (\text{carrier-specific quantity})$$

Semiconductors: $E_F = \text{chemical potential}$; $\tau = \text{time between scattering events} \Rightarrow \tau = \frac{\Lambda}{\langle v \rangle}$

$$\mu = \frac{e\Lambda}{m \langle v \rangle_{av}} \quad ; \quad \Lambda = \text{mean free path} \quad ; \quad \langle v \rangle_{av} = \langle v(T) \rangle_{av} \neq v_F$$

Maxwell-Boltzmann: $\langle v \rangle_{av} \propto \sqrt{T}$

$T \sim 300\text{K} \sim \Theta_{\text{Debye}}$: acoustic longitudinal phonons $\Rightarrow \Lambda \propto 1/(\# \text{ of scattering events in the sample})$
 $\Rightarrow \Lambda \propto 1/n_{ph}$ (Here Λ is a property of the host material only)

Bose-Einstein: $n_{ph} \propto \frac{1}{\exp(\hbar\omega/k_B T) - 1} \approx \frac{1}{1 + \hbar\omega/k_B T - 1} \propto T$

Homework question 3

- Assuming relaxation time is same as scattering time, as they should roughly be for phonon- and defect-scattering.
- We could just take $\tau \sim 1/T$ from the previous lecture...
- MB statistics: independent particles with MB energy distribution and parabolic energy dispersion
- Many semiconductors have Debye temperature close to RT, after which quantum effects can be ignored = each degree of freedom has energy of kT

$$\mu_{ph} \propto \frac{1}{\sqrt{T}} \frac{1}{T} = T^{-3/2}$$

$$T \approx \Theta_{Debye}$$

Doped semiconductors, $T \ll \Theta_{Debye}$, impurity scattering

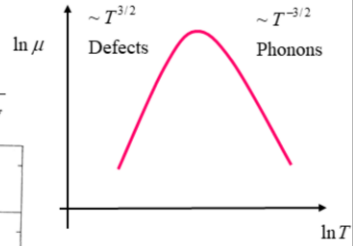
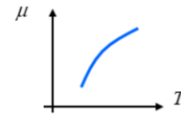
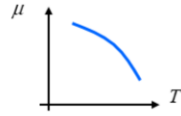
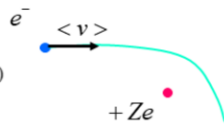
(Classical) Rutherford scattering:

$$\text{Cross section } \Sigma_{def} \propto \langle v \rangle^{-4} \propto T^{-2} \propto 1/\Lambda$$

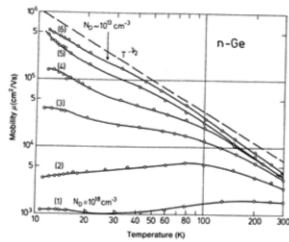
(Here Λ is a property of the charge carrier, too)

$$\mu_{def} \propto \frac{\Lambda}{\langle v \rangle} \propto \frac{1}{\langle v \rangle \Sigma_{def}} \propto T^{3/2}$$

Phonons and impurities: $\left(\frac{1}{\tau_{tot}} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{def}} \right) \Rightarrow \frac{1}{\mu} = \frac{1}{\mu_{ph}} + \frac{1}{\mu_{def}}$



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- Rutherford, Elliott eqn. 6.40
- Lecture 3: $R_{def} = 1/\tau_{def} = N_{def} \cdot \Sigma_{def} \cdot v$

Charge carrier mobility and conductivity in doped semiconductors

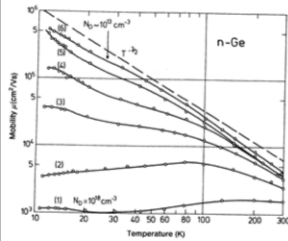


Fig. 12.13. Experimentally determined temperature dependence of the mobility μ of free electrons. For the samples (1) to (6), the donor concentration N_D varies between 10^{18} and 10^{13} cm^{-3} . The samples are the same as those used for the measurements in Fig. 12.11. (After [12.3])

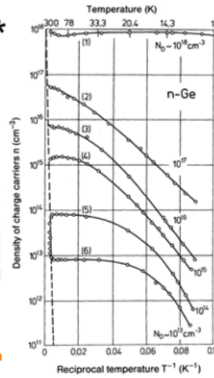


Fig. 12.11. The concentration n of free electrons in n -type germanium, measured using the Hall effect (Panel XIV). For the samples (1) to (6), the donor concentration N_D varies between 10^{18} and 10^{13} cm^{-3} . The temperature dependence of the electron concentration in the intrinsic region is shown by the dashed line. (After [12.3])

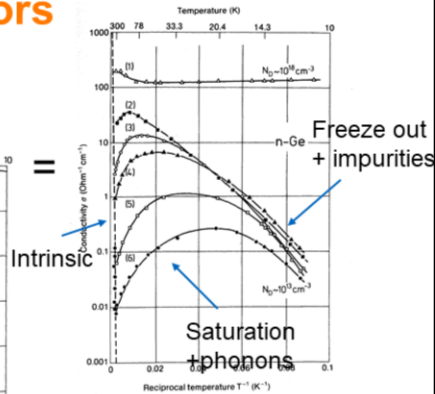
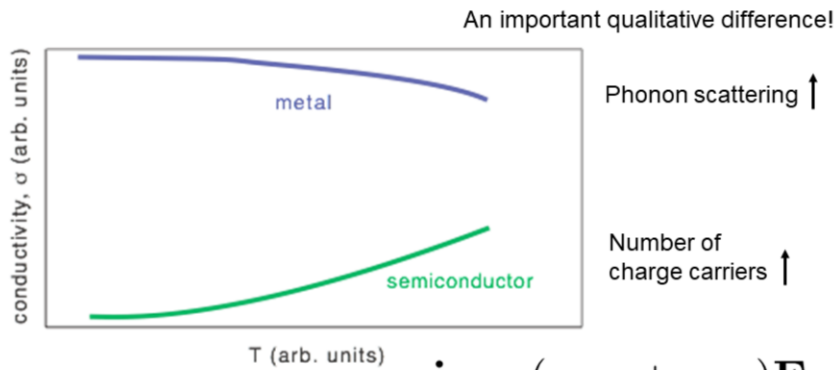


Fig. 12.14. Experimentally measured conductivity σ of n -type germanium as a function of temperature. For the samples (1) to (6), which were also used for the measurements in Figs. 12.11 and 12.13, the donor concentration N_D varies between 10^{18} and 10^{13} cm^{-3} . (After [12.3])



- Notice T vs $1/T$
- Total temperature dependence comes from both carrier concentration and mobility: with different regimes in both

Metals vs. semiconductors



$$\mathbf{j} = e(n\mu_n + p\mu_p)\mathbf{E}$$

Near future program

- Friday, exercise session 3
(deadline for session 2 problems)
- Monday: lecture and homework on "Semiconductor devices", Elliott 8.4-8.5