BASIC SOLID
STATE PHYSICS

17 Sep 2009
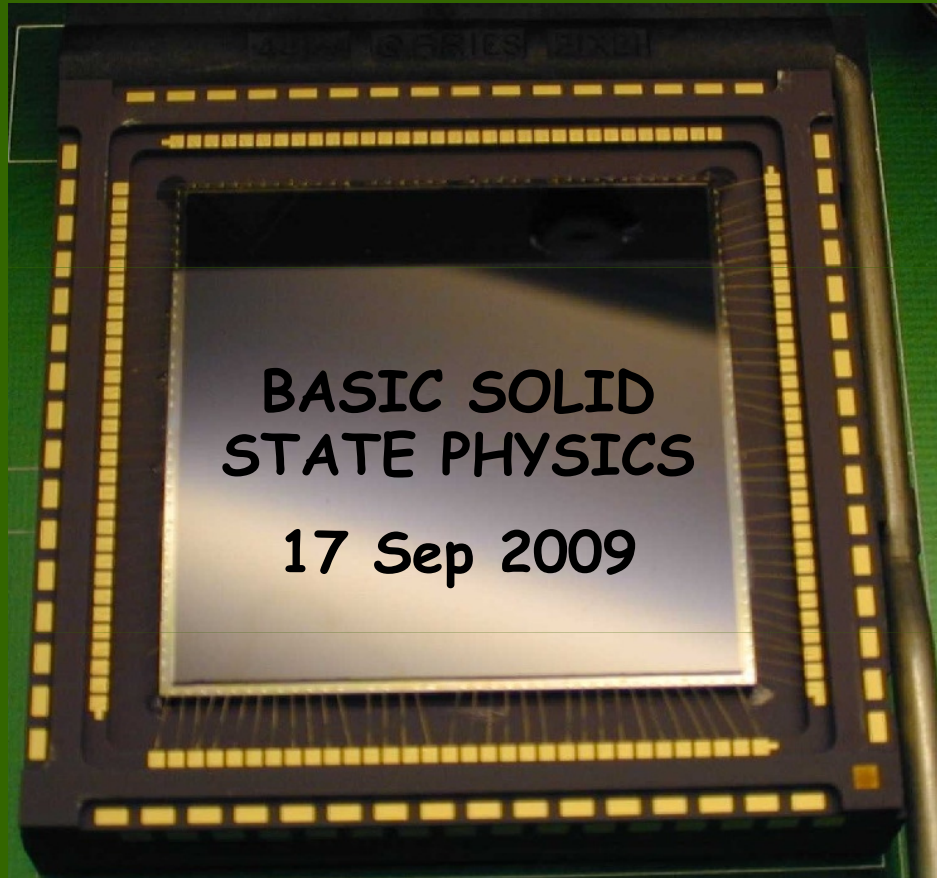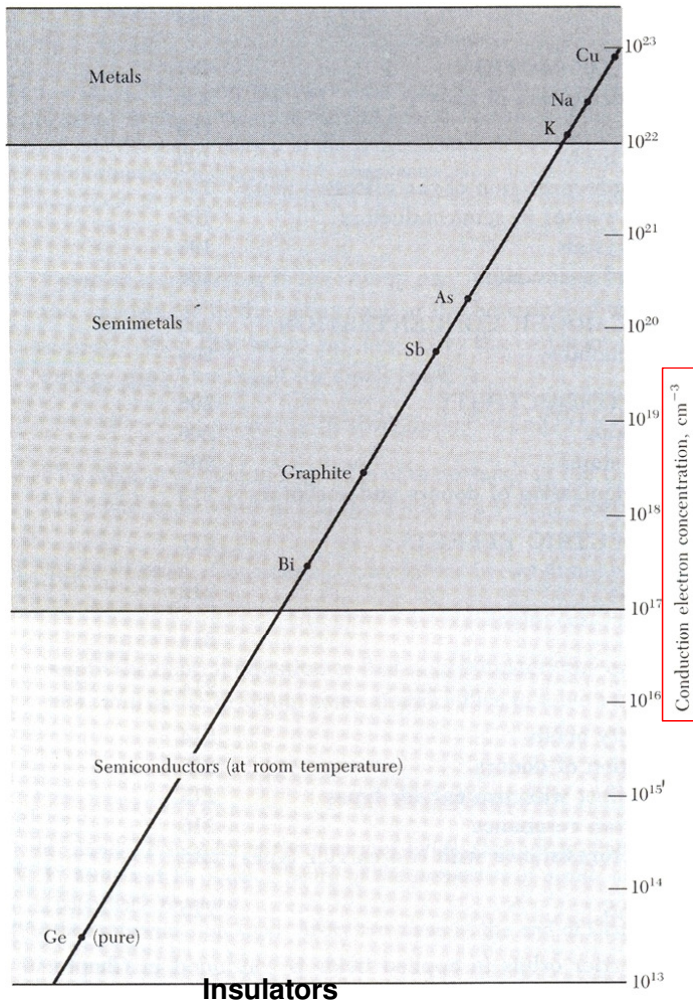
See http://www.strw.leidenuniv.nl/~brandl/DOL/Detection_of_Light.html
for more info

Metals, Semiconductors, Insulators

Metals, Semiconductors and Insulators

from Wikipedia:

- **Metals** are characterized by high electrical conductivity and consist of positive ions in a crystal lattice, surrounded by a cloud of delocalized electrons.

- An **insulator**, also called a dielectric, is a material that resists the flow of electric current. (Semiconductors at T=0K are insulators.)

- A **semiconductor** is a material that has an electrical resistivity between that of a conductor and an insulator.

The Periodic System of the Elements

"Classical" semiconductors: 4 e$^-$ in valence state (outer shell) form a diamond lattice structure (each atom bonds to 4 n)

"New" semiconductors are 3-5 compounds (e.g., GaAs)

Metals are to the left of the green line.

Semiconductors

(a)	II	III	IV	V	VI
		B	C	N	
		Al	Si	P	S
	Zn	Ga	Ge	As	Se
	Cd	In		Sb	Te

(b) Elemental	IV compounds	Binary III–V compounds	Binary II–VI compounds
Si	SiC	AlP	ZnS
Ge	SiGe	AlAs	ZnSe
		AlSb	ZnTe
		GaN	CdS
		GaP	CdSe
		GaAs	CdTe
		GaSb	
		InP	
		InAs	
		InSb	

Electronic Bands

Electronic States ... and Bands

Single atomic system

Example: H atom
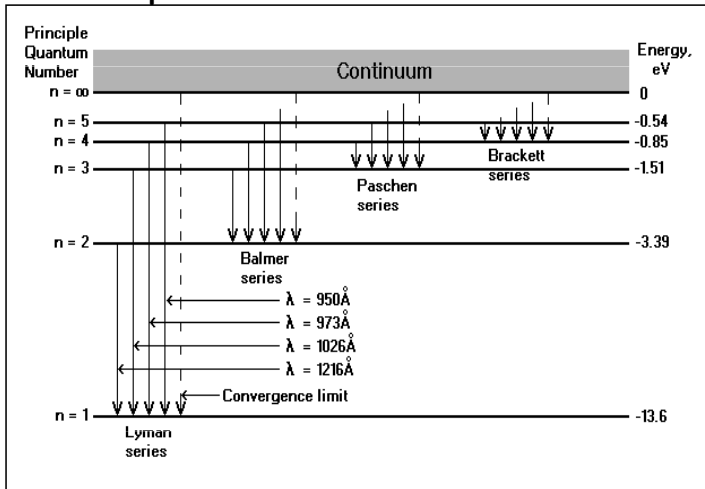
e⁻ can be in the:

   ground state ⟷ valence band

   excited state ⟷ conduction band

Atomic crystal

Wavefunctions Ψ overlap

→ Energy levels of individual atoms split due to Pauli principle (avoiding the same quantum states)

→ Multiple splitting ➔ "bands"

e⁻ can be in the:

   valence band

   conduction band

Electronic States and Bands (2)

Single atomic system
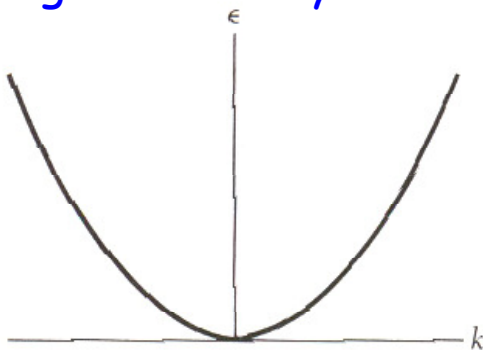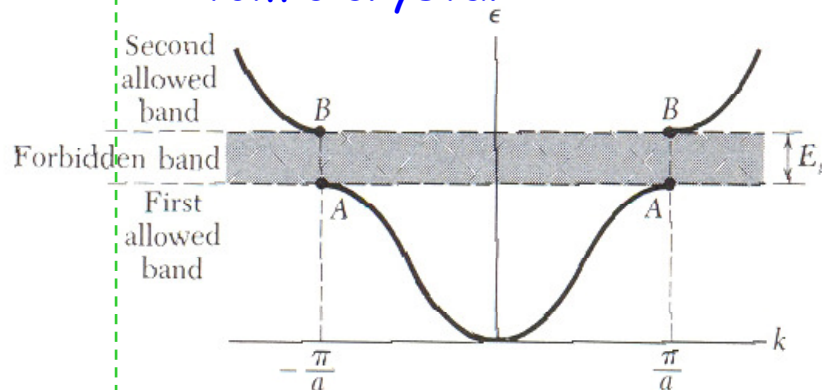
There are more than just two bands:

Atomic crystal
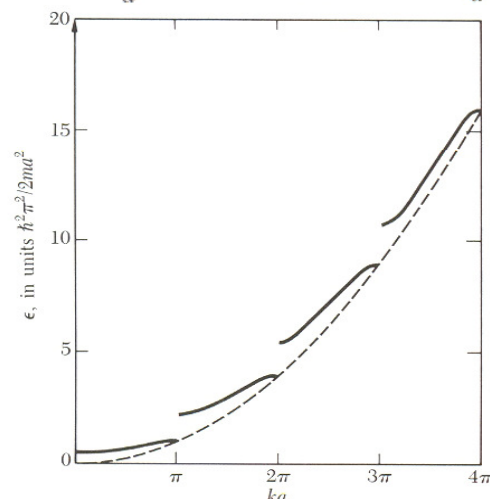
Side Note: The Wavevector k

Consider a crystal lattice with base vectors a, b, c. There are 14 Bravais lattices with 7 lattices systems (triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, **cubic**.)

The wavefunction of a free electron is: $\Psi_k(r) = e^{ik \cdot r} 1$

It is most convenient to work with the reciprocal lattice, which is the set of all wave vectors k such that: $e^{ik \cdot r} = 1$
for all lattice point position vectors r.

For a periodic Bragg crystal: $k = \pm \dfrac{n\pi}{a}$

Δk is a momentum difference. It can be directly measured from X-ray scattering → reciprocal vectors of the lattice.

In Reality: more Complex Band Structure
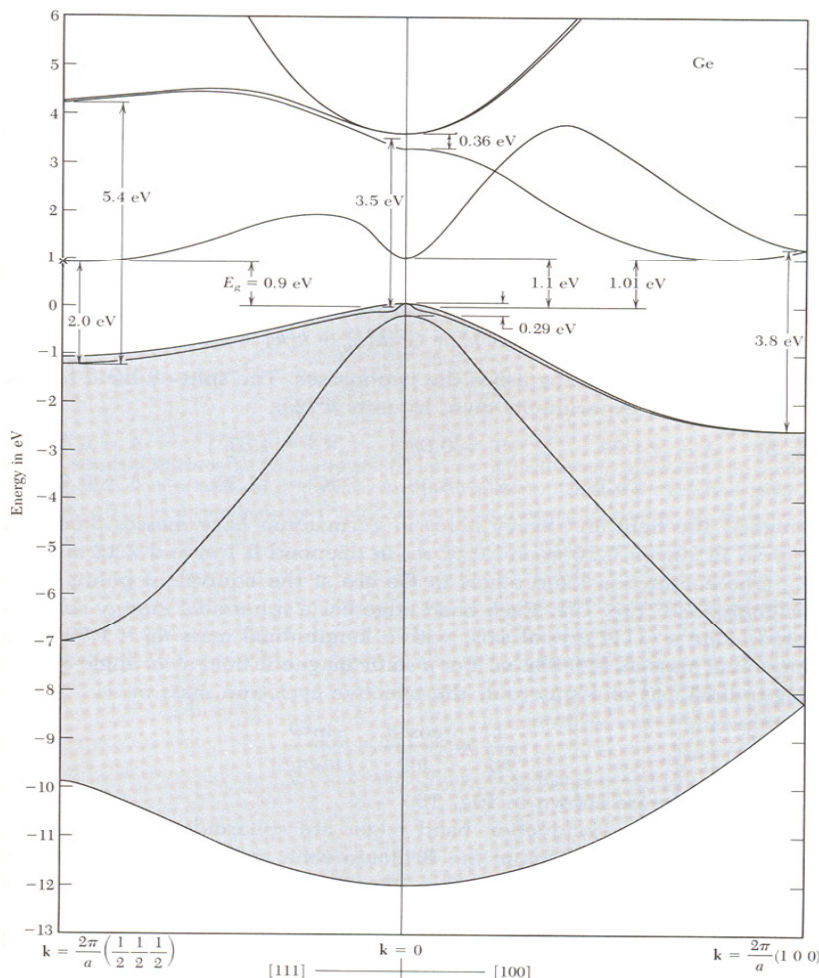
The band gap E_g depends also on the location within the periodic crystal lattice!

←Germanium

↓ Silicon
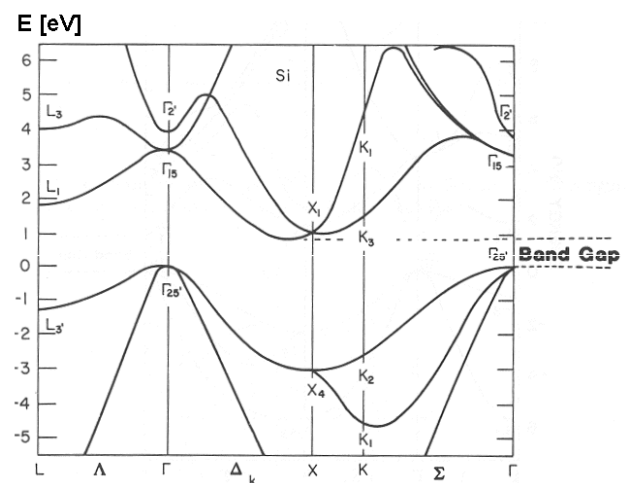
Band Gaps

The Size of Bandgaps

- E_g is the band gap energy (difference between the lowest level in the conduction band and the highest level in the valence band).

- For semiconductors, typically: $0 < E_g < 3.6$ eV

Table 1 Energy gap between the valence and conduction bands

(i = indirect gap; d = direct gap)

Crystal	Gap	E_g, eV 0 K	E_g, eV 300 K	Crystal	Gap	E_g, eV 0 K	E_g, eV 300 K
Diamond	i	5.4		HgTe[a]	d	−0.30	
Si	i	1.17	1.11	PbS	d	0.286	0.34–0.37
Ge	i	0.744	0.66	PbSe	i	0.165	0.27
αSn	d	0.00	0.00	PbTe	i	0.190	0.29
InSb	d	0.23	0.17	CdS	d	2.582	2.42
InAs	d	0.43	0.36	CdSe	d	1.840	1.74
InP	d	1.42	1.27	CdTe	d	1.607	1.44
GaP	i	2.32	2.25	ZnO		3.436	3.2
GaAs	d	1.52	1.43	ZnS		3.91	3.6
GaSb	d	0.81	0.68	SnTe	d	0.3	0.18
AlSb	i	1.65	1.6	AgCl		—	3.2
SiC(hex)	i	3.0	—	AgI		—	2.8
Te	d	0.33	—	Cu$_2$O	d	2.172	—
ZnSb		0.56	0.56	TiO$_2$		3.03	—

Bandgaps and Lattice Struture

Direct and Indirect Band Gaps

source: Wikipedia

Minimum in the conduction band and maximum in the valence band are characterized by the wavevector k

If the k-vectors for minimum and maximum are the same, it is called a "direct gap".
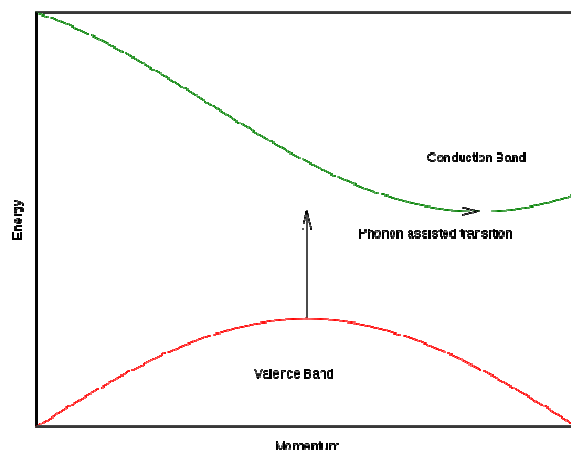
If the k-vectors for minimum and maximum are different it is called an "indirect gap", and a transition must involve the absorption or emission of a phonon to conserve momentum.

Direct and Indirect Band Gaps (2)

Indirect gaps make electronic transitions less likely → light-emitting and laser diodes are almost always made of direct band gap materials (e.g., GaAs), and not indirect ones (e.g. Si)

Consider a compound material like:

$$\left(Al_x Ga_{1-x}\right)_{0.5} In_{0.5} P$$
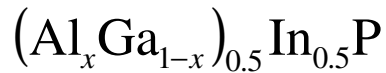
Al and Ga have ~ same atomic size within the lattice ⇔ exchangeable

• If $x \leq 0.7$ → bandgap is direct

• If $x > 0.7$ → bandgap is indirect.

(Fletcher et al. 1993)

1A									noble
H[1] $1s^1$	2A				3A	4A	5A	6A	7A	He[2] $1s^2$

Abridged Periodic Table of the Elements
4/17/96 ghw

Li[3] $1s^2 2s^1$	Be[4] $1s^2 2s^2$			B[5] $2s^2 2p^1$	C[6] $2s^2 2p^2$	N[7] $2s^2 2p^3$	O[8] $2s^2 2p^4$	F[9] $2s^2 2p^5$	Ne[10] $2s^2 2p^6$
Na[11] [Ne]$3s^1$	Mg[12] [Ne]$3s^2$	1B	2B	Al[13] $3s^2 3p^1$	Si[14] $3s^2 3p^2$	P[15] $3s^2 3p^3$	S[16] $3s^2 3p^4$	Cl[17] $3s^2 3p^5$	Ar[18] $3s^2 3p^6$
K[19] [Ar]$4s^1$		Cu[29] $4s^1$	Zn[30] $4s^2$	Ga[31] $4s^2 4p^1$	Ge[32] $4s^2 4p^2$	As[33] $4s^2 4p^3$	Se[34] $4s^2 4p^4$	Br[35] $4s^2 4p^5$	Kr[36] $4s^2 4p^6$
Rb[37] [Kr]$5s^1$		Ag[47] $5s^1$	Cd[48] $5s^2$	In[49] $5s^2 5p^1$	Sn[50] $5s^2 5p^2$	Sb[51] $5s^2 5p^3$	Te[52] $5s^2 5p^4$	I[53] $5s^2 5p^5$	Xe[54] $5s^2 5p^6$
Cs[55] [Xe]$6s^1$		Au[79] $6s^1$	Hg[80] $6s^2$	Tl[81] $6s^2 6p^1$	Pb[82] $6s^2 6p^2$	Bi[83] $6s^2 6p^3$	Po[84] $6s^2 6p^4$	At[85] $6s^2 6p^5$	Rn[86] $6s^2 6p^6$

Electrical Conductivity

Requirement for Electric Conductivity

Needed: charge carriers in the conduction band
→ to provide conductivity one must provide E_g

$$\lambda_c = \frac{hc}{E_g} = \frac{1.24\,\mu m}{E_g\,[eV]}$$

Excitation lifts an e^- into the conduction band _and_ leaves a hole in the valence band; both e^- and hole contribute to electric current.

Possibilities for excitation:

1. external excitation, e.g. via a photon ← detector

2. internal excitation due to thermal energy

(3. impurities)

Conductivity ~ # Electrons in Conduction Band
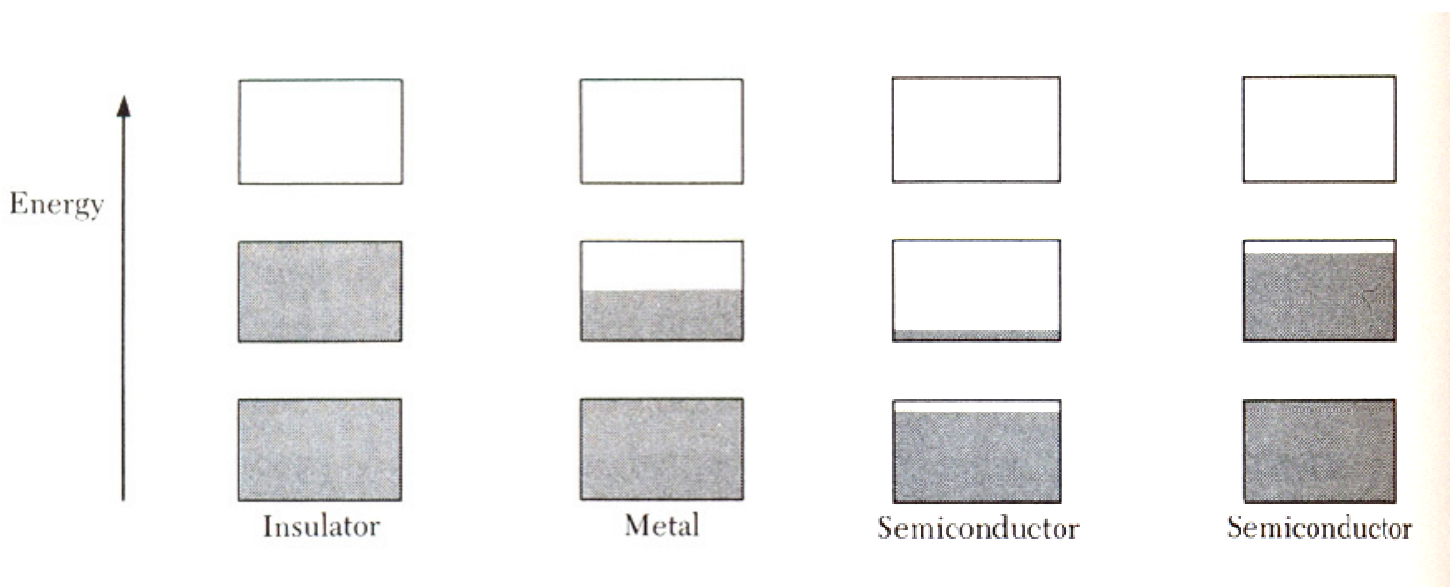
- Semiconductors at T=0K are insulators
- The left of the two semiconductors is at T>0K with thermally excited electron.
- The right of the two semiconductors is electron-deficient because of impurities.

Thermal Excitation and the Fermi Energy
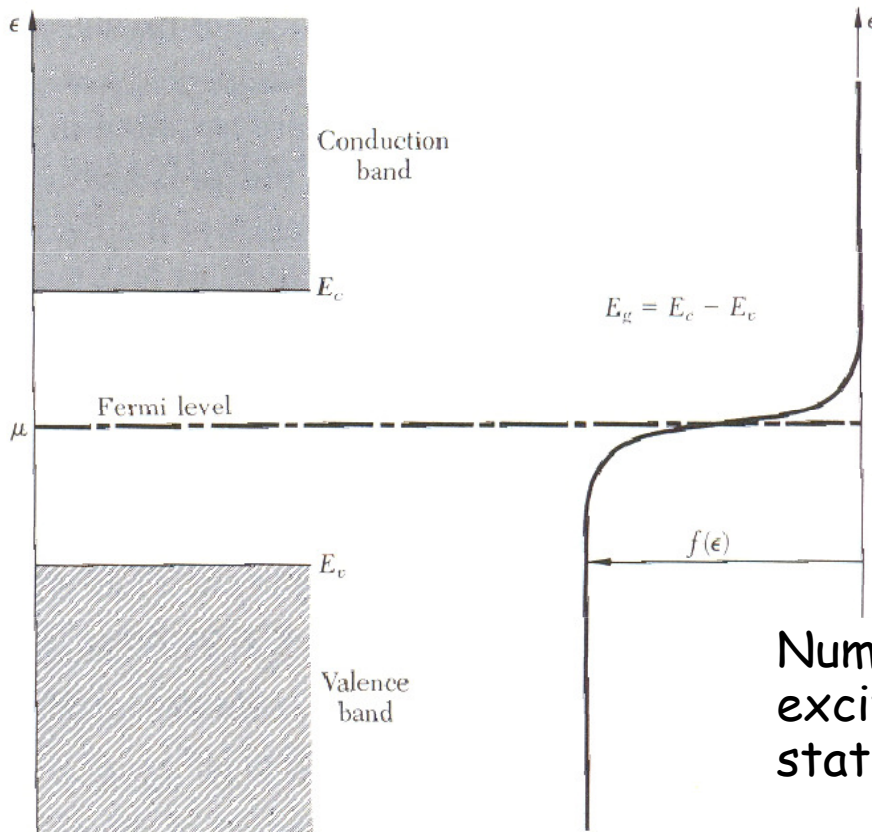
Number of thermally excited charge carriers = statistical process

→Fermi statistics $f(\epsilon)$, depends on Fermi energy E_F

The Energy Distribution of Electrons (1)

In the classical picture the energetic distribution of electrons would be given by the Maxwell-Boltzmann statistics:

$$\frac{n_2}{n_1} = e^{-(E_2 - E_1)/kT} = e^{-E_g/kT}$$

In the QM picture the concentration of electrons in the conduction band is given by:

$$n_0 = \int_{E_c}^{\infty} f(E)N(E)dE$$

where $N(E)dE$ is the density of states and $f(E)$ the Fermi distribution (Fermi-Dirac statistics):

$$f(E) = \frac{1}{1 + e^{\frac{E - E_F}{kT}}}$$

The Energy Distribution of Electrons (2)

f(E) vs E curves showing T = 0, T > 0, T >> 0 with axes labeled E_v, E_F, E_c, E

At T = 0 $\rightarrow$ $f(E < E_F) = 1$

$f(E > E_F) = 0$
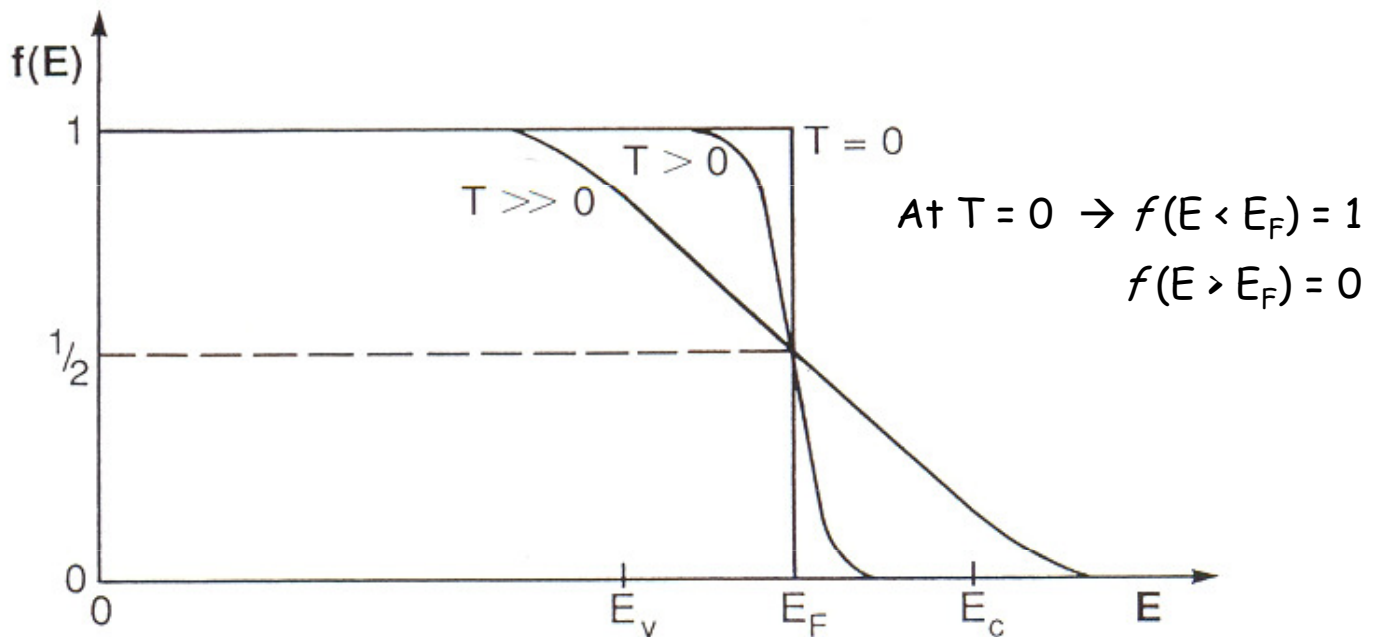
For intrinsic semiconductors: $E_c - E_F = E_F - E_v = E_g/2$

The Energy Distribution of Electrons (3)

Note: Even at $T \sim T_{room}$ the conduction electrons occupy only the lowest states in the conduction band

If $f(E)N(E)$ is close to zero at $E > E_c$, it can be described by an average "effective density** of states N_c" near $E \sim E_c$:

$$n_0 = N_c f(E_c) \quad \text{where} \quad N_c = 2\left(\frac{2\pi m_{eff} kT}{h^2}\right)^{3/2}$$

Hence the Fermi-Dirac statistics becomes:

$$f(E_c) = \frac{1}{1+e^{\frac{E_c-E_F}{kT}}} \overset{E_c-E_F \gg kT}{\approx} e^{-\frac{E_c-E_F}{kT}}$$

And we get:

$$\boxed{n_0 = N_c f(E_c) = 2\left(\frac{2\pi m_{eff} kT}{h^2}\right)^{3/2} e^{-(E_c-E_F)/kT}}$$

** see, e.g., Streetman & Banerjee, Appendix IV for a derivation

Intrinsic and Extrinsic Semiconductors

Limitations of Intrinsic Semiconductors

- Wavelength coverage: $\lambda_c = \dfrac{hc}{E_g} = \dfrac{1.24\,\mu m}{E_g\,[eV]}$

  → Germanium: $\lambda_c \sim 1.8\mu m$

  → Silicon: $\lambda_c \sim 1.1\mu m$

  → GaAs: $\lambda_c \sim 0.87\mu m$

- Low impedances ⇔ high Johnson (reset) noise

- Poor stability of material → non-uniformity

- Problems to make good electrical contacts

Doping

Pure semiconductors are termed "intrinsic".

Semiconductors with added impurities (doped) are termed "extrinsic".

The deliberate** addition of impurities to a semiconductor is called doping.

Example: addition of boron to silicon in the ratio 1:100,000 increases its conductivity by a factor 1000!

** most materials are impure; however, Ge can be produced with 1 impurity in 10^{11} Ge atoms

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Donors and Acceptors

Imagine silicon or germanium ← diamond structure, each atom has covalent bonds to each of its four neighbors.
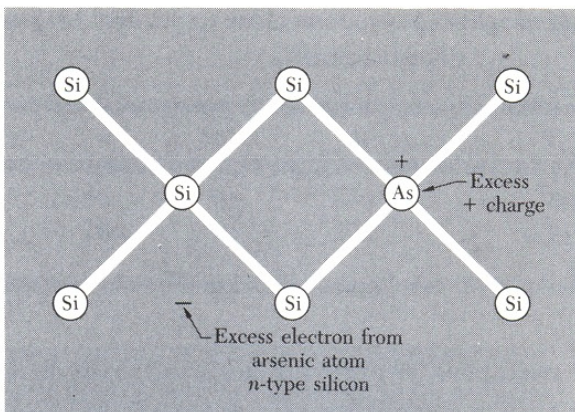
Replacing one Si or Ge against one atom with 5 valence electrons leaves one electron "left over" ➔ Donors, n-type semiconductors
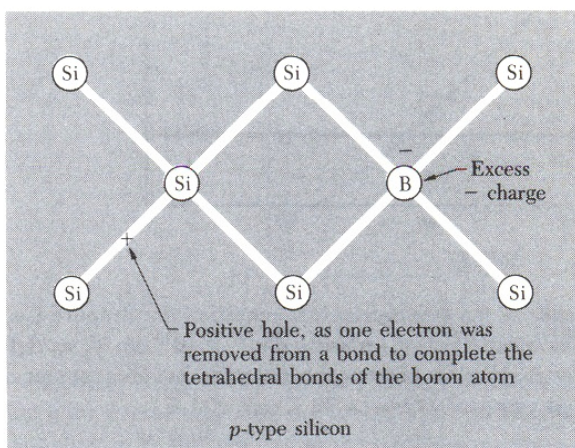
Replacing one Si or Ge against one atom with 3 valence electrons leaves one electron "missing" ➔ Acceptors, p-type semiconductors

The Fermi Energy in Extrinsic Materials

(a) Intrinsic
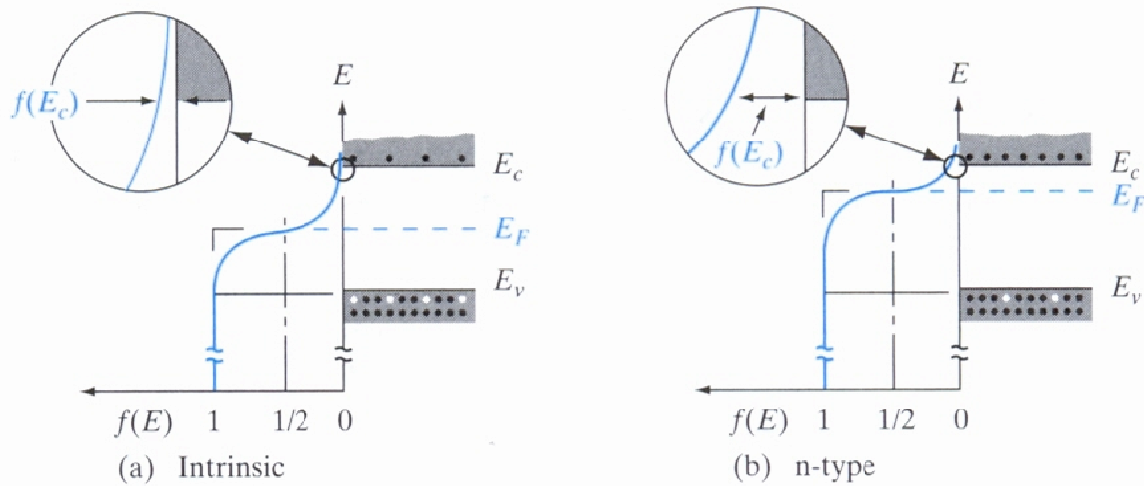
(b) n-type

(c) p-type

(a) intrinsic material
(b) n-type material
(c) p-type material
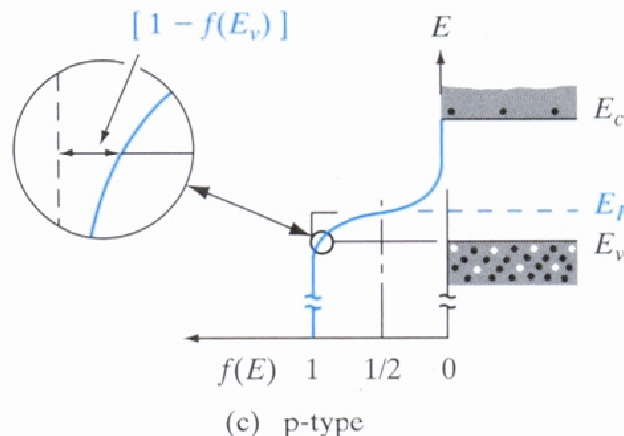
Thermal Excitation in Extrinsic Materials
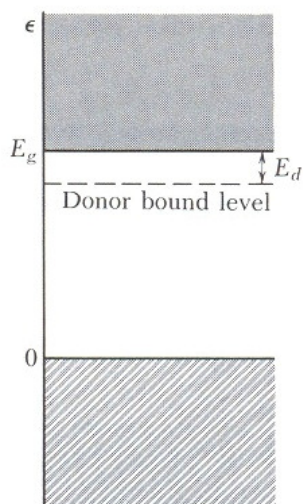
The doping with impurities shifts the level of E_F toward (n-type) or away from (p-type) the conduction band.

Concentration of neutral + ionized donors:

$$N_D = N_D^n + N_D^i$$

Ideally: $N_D^n = 0$, $N_D^i = N_D$ and the number of electrons is $n = N_D - N_A$

However, in reality $n \ll N_D$ since $N_A > 0$

Donor and Acceptor Energies

Observed donor E_d and acceptor E_a ionization energies:

Donor	Si [meV]	Ge [meV]
P	45	12
As	49	13
Sb	39	10
B	45	10
Ga	65	11
In	157	11

Note:

- at room temperature: kT ≈ 26 meV ⇔ thermal excitation

- ⇔ intrinsic band gaps of ~1100 meV (Si), ~700 meV (Ge)

Another Way to look at it …

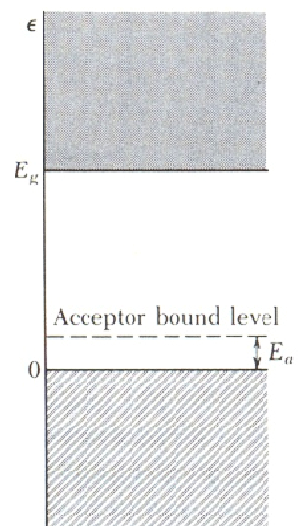Consider Bohr's hydrogen atom: $$r = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$

In a semiconductor the electron moves in the Coulomb potential e/εr, where ε is the static dielectric constant. (1/ε accounts for the reduction of the Coulomb force between charges).

Now replace $e^2 \rightarrow e^2/\varepsilon$ and $m \rightarrow m_{eff}$

to get the "Bohr radius" of the donor: $$a_d = \frac{4\pi\varepsilon\varepsilon_0 \hbar^2}{m_{eff}e^2}$$

which is *typically* ~100 times larger than for the hydrogen atom.

Reference Properties of Semiconductor Materials

		E_g (eV)	μ_n (cm^2/V-s)	μ_p (cm^2/V-s)	m_n^*/m_o (m_l, m_t)	m_p^*/m_o (m_{lh}, m_{hh})	a (Å)	ϵ_r	Density (g/cm^3)	Melting point (°C)
Si	(i/D)	1.11	1350	480	0.98, 0.19	0.16, 0.49	5.43	11.8	2.33	1415
Ge	(i/D)	0.67	3900	1900	1.64, 0.082	0.04, 0.28	5.65	16	5.32	936
SiC (α)	(i/W)	2.86	500	—	0.6	1.0	3.08	10.2	3.21	2830
AlP	(i/Z)	2.45	80	—	—	0.2, 0.63	5.46	9.8	2.40	2000
AlAs	(i/Z)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(i/Z)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(i/Z)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
GaAs	(d/Z)	1.43	8500	400	0.067	0.074, 0.50	5.65	13.2	5.31	1238
GaN	(d/Z, W)	3.4	380	—	0.19	0.60	4.5	12.2	6.1	2530
GaSb	(d/Z)	0.7	5000	1000	0.042	0.06, 0.23	6.09	15.7	5.61	712
InP	(d/Z)	1.35	4000	100	0.077	0.089, 0.85	5.87	12.4	4.79	1070
InAs	(d/Z)	0.36	22600	200	0.023	0.025, 0.41	6.06	14.6	5.67	943
InSb	(d/Z)	0.18	10^5	1700	0.014	0.015, 0.40	6.48	17.7	5.78	525
ZnS	(d/Z, W)	3.6	180	10	0.28	—	5.409	8.9	4.09	1650*
ZnSe	(d/Z)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
ZnTe	(d/Z)	2.25	530	100	0.18	0.65	6.101	10.4	5.51	1238*
CdS	(d/W, Z)	2.42	250	15	0.21	0.80	4.137	8.9	4.82	1475
CdSe	(d/W)	1.73	800	—	0.13	0.45	4.30	10.2	5.81	1258
CdTe	(d/Z)	1.58	1050	100	0.10	0.37	6.482	10.2	6.20	1098
PbS	(i/H)	0.37	575	200	0.22	0.29	5.936	17.0	7.6	1119
PbSe	(i/H)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(i/H)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

All values at 300 K.   *Vaporizes

second column: i=indirect, d=direct, D=diamond, Z=zinc blende, W=wurtzite, H=NaCl; source: Streetman & Banerjee, Appendix III