Chapter 8

Semiconductor Crystals

PHYS 432

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- Band Gap
- Equations of Motion
- Holes
- Effective Mass
- Silicon and Germanium
- Intrinsic Carrier Concentration
- Intrinsic Mobility
- Impurity Conductivity
- Donor States
- Acceptor States
- Thermal Ionization of Donors and Acceptors
- Thermoelectric Effects
- Semimetals
- Superlattices
- Bloch Oscillator
- Zener Tunneling

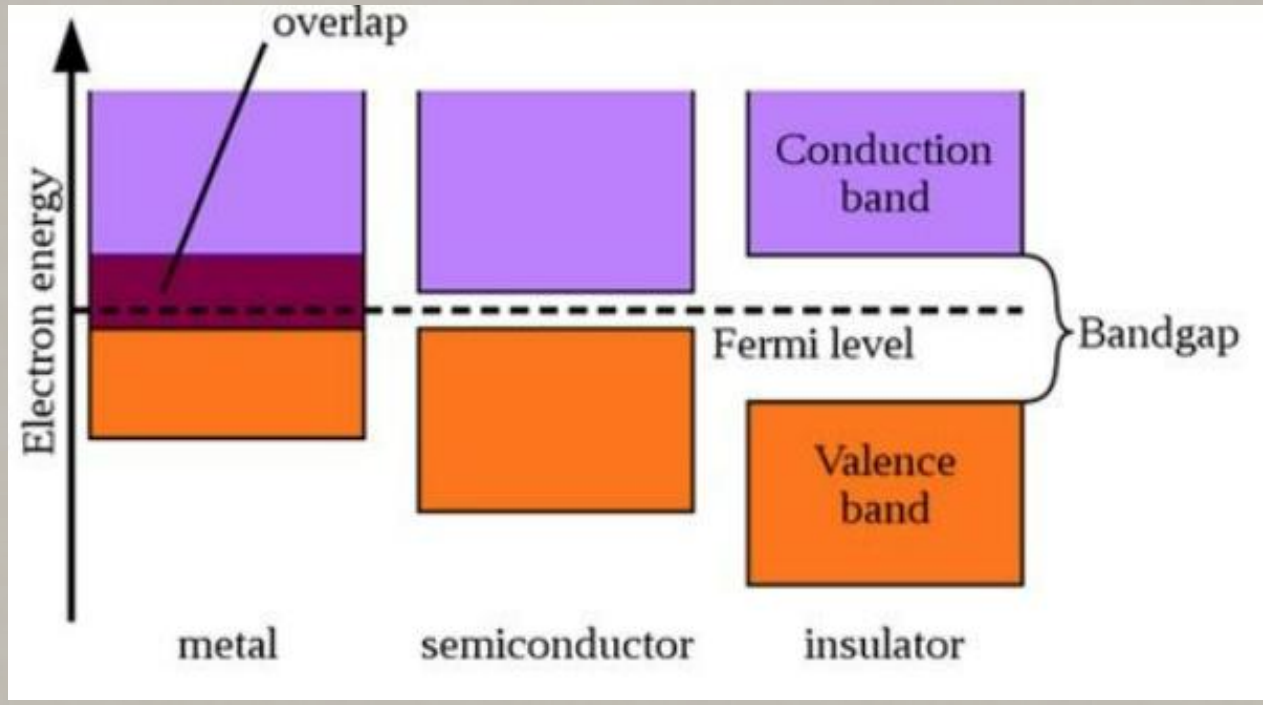
Conductors, Semiconductors, and Insulator

In Chapter 6 we had derived an equation for the Fermi energy

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

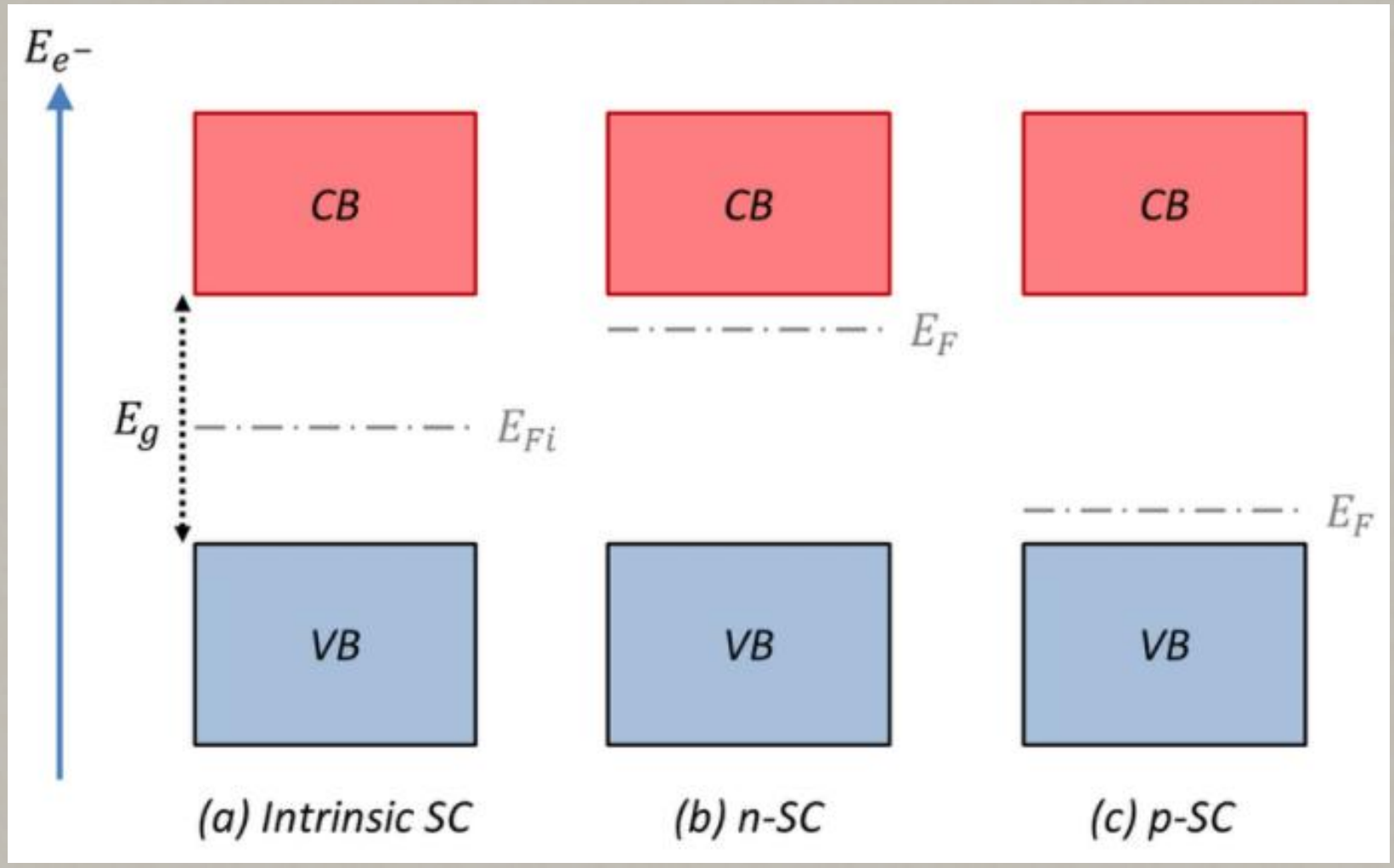
The N/V is the concentration of electrons.

The Fermi energy is one of the main parameters for determining whether a material is metal or insulator.



Metals have no bandgap.
Semiconductors and insulators have bandgap.
Wide band gap semiconductors have bandgap from 2 to 4 eV.
Insulators have bandgap greater than 4 eV.

P- and N-Type Semiconductors



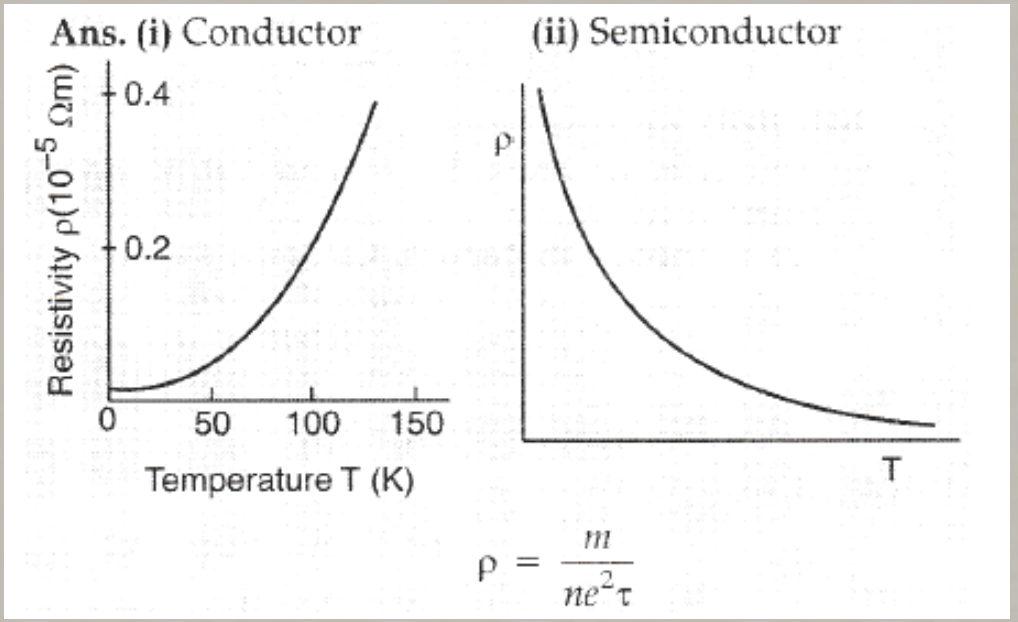
Conductors vs. Semiconductors

- In metals the charge is carried by only electrons. The electrical resistance increases with an increase in the sample temperature.

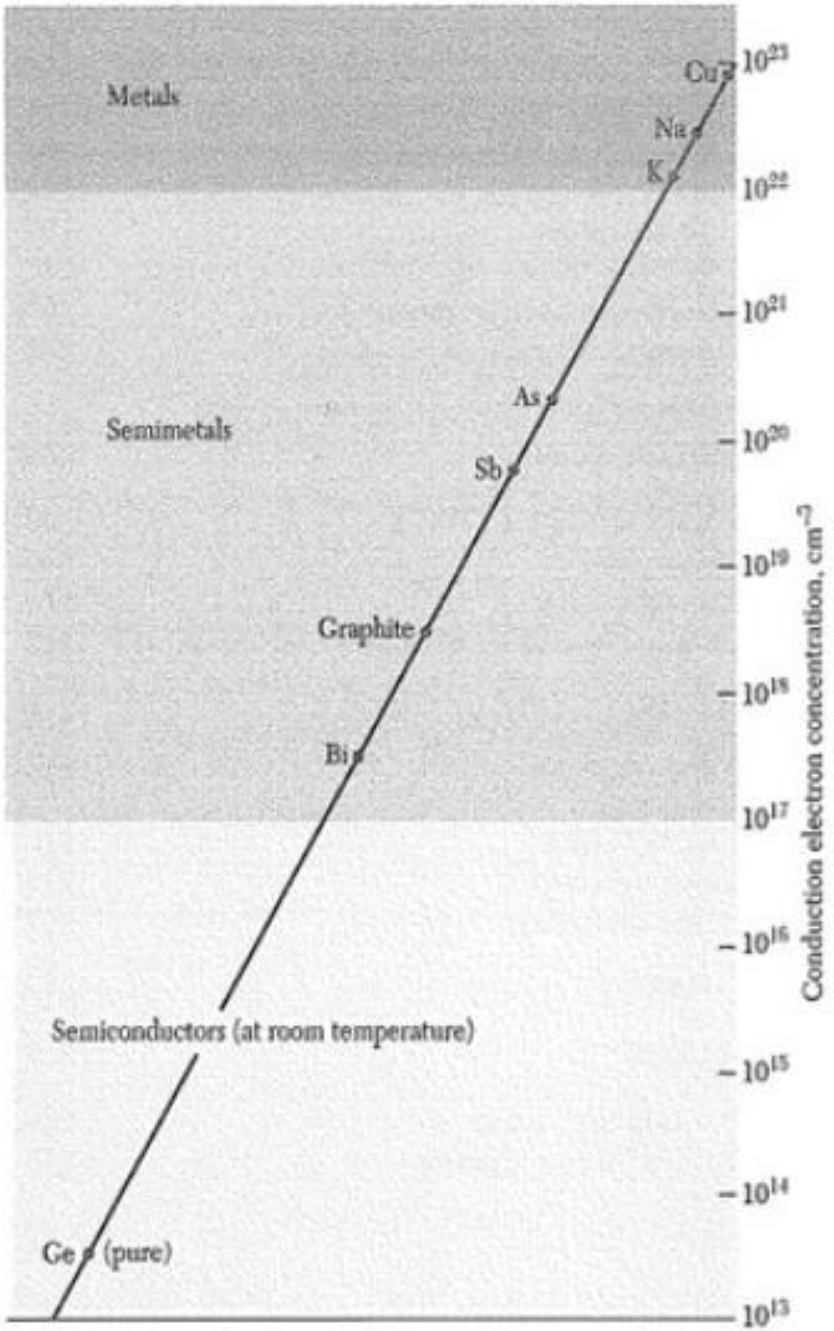
- In semiconductors, both the electrons in the conduction band and the vacant orbitals (holes) left behind in the valence band contribute to the electrical conductivity.

- In conductors, average relaxation time decreases with increase in temperature, resulting in an increase in resistivity.

- In semiconductors, the increase in number density (with increase in temperature) is more than the decrease in relaxation time; the net result is, therefore, a decrease in resistivity.



Carrier density of metals and semiconductors

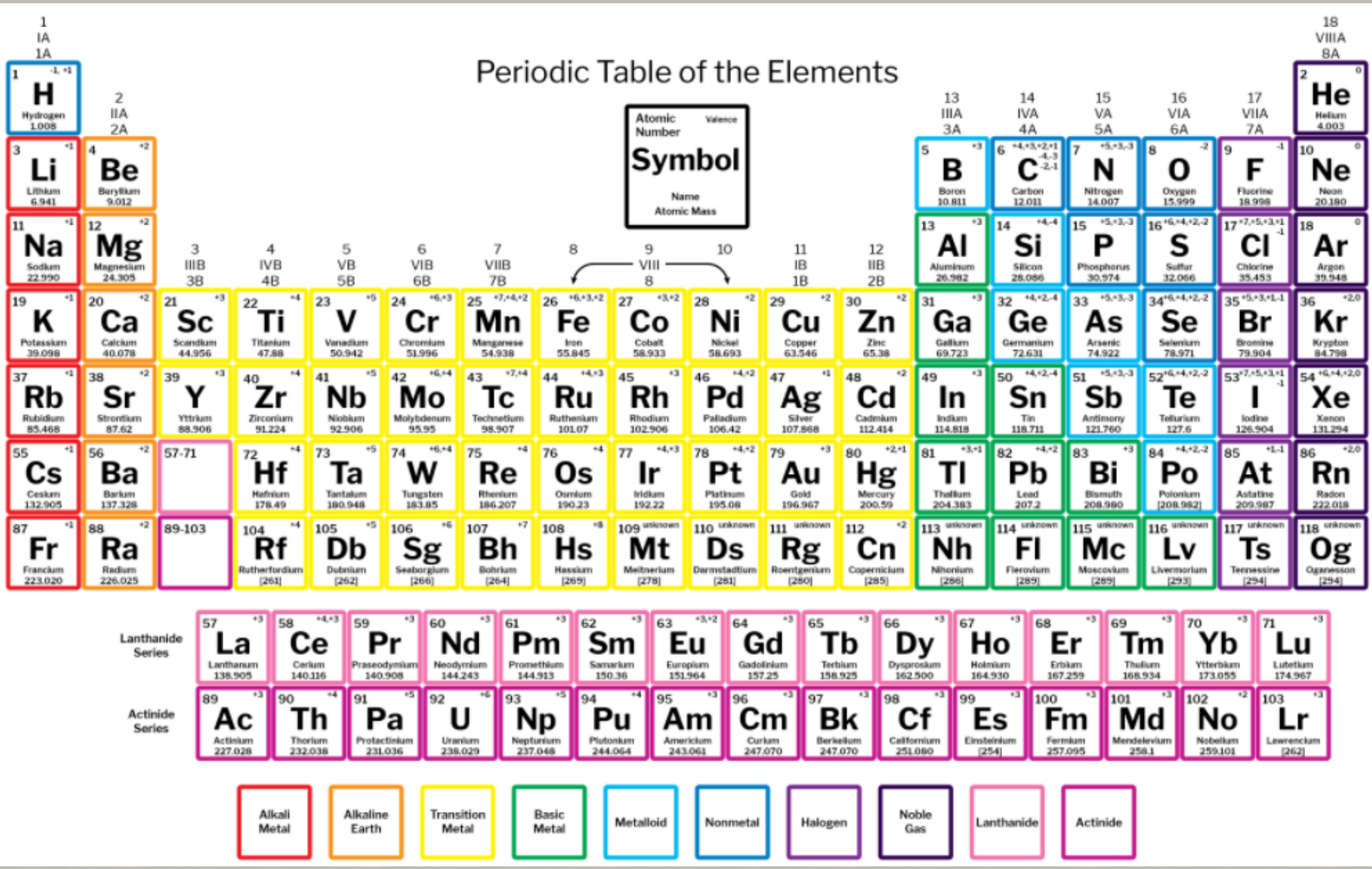


Insulator: $\rho > 10^{14}\ \Omega$ cm

SemiC: $10^{9} > \rho > 10^{-2}\ \Omega$ cm

Strong T dependence

Transistors, switches, diodes, photovoltaic cells, detectors, thermistors, …


Periodic Table of the Elements
Atomic Number
Valence
Symbol
Name
Atomic Mass
1 IA 1A
2 IIA 2A
3 IIIB 3B
4 IVB 4B
5 VB 5B
6 VIB 6B
7 VIIB 7B
8 9 VIII 8 10
11 IB 1B
12 IIB 2B
13 IIIA 3A
14 IVA 4A
15 VA 5A
16 VIA 6A
17 VIIA 7A
18 VIIIA 8A
1 H Hydrogen 1.008
2 He Helium 4.003
3 Li Lithium 6.941
4 Be Beryllium 9.012
5 B Boron 10.811
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998
10 Ne Neon 20.180
11 Na Sodium 22.990
12 Mg Magnesium 24.305
13 Al Aluminum 26.982
14 Si Silicon 28.086
15 P Phosphorus 30.974
16 S Sulfur 32.066
17 Cl Chlorine 35.453
18 Ar Argon 39.948
19 K Potassium 39.098
20 Ca Calcium 40.078
21 Sc Scandium 44.956
22 Ti Titanium 47.88
23 V Vanadium 50.942
24 Cr Chromium 51.996
25 Mn Manganese 54.938
26 Fe Iron 55.845
27 Co Cobalt 58.933
28 Ni Nickel 58.693
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.631
33 As Arsenic 74.922
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 84.798
37 Rb Rubidium 85.468
38 Sr Strontium 87.62
39 Y Yttrium 88.906
40 Zr Zirconium 91.224
41 Nb Niobium 92.906
42 Mo Molybdenum 95.95
43 Tc Technetium 98.907
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.906
46 Pd Palladium 106.42
47 Ag Silver 107.868
48 Cd Cadmium 112.414
49 In Indium 114.818
50 Sn Tin 118.711
51 Sb Antimony 121.760
52 Te Tellurium 127.6
53 I Iodine 126.904
54 Xe Xenon 131.294
55 Cs Cesium 132.905
56 Ba Barium 137.328
57-71
72 Hf Hafnium 178.49
73 Ta Tantalum 180.948
74 W Tungsten 183.85
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.22
78 Pt Platinum 195.08
79 Au Gold 196.967
80 Hg Mercury 200.59
81 Tl Thallium 204.383
82 Pb Lead 207.2
83 Bi Bismuth 208.980
84 Po Polonium [208.982]
85 At Astatine 209.987
86 Rn Radon 222.018
87 Fr Francium 223.020
88 Ra Radium 226.025
89-103
104 Rf Rutherfordium [261]
105 Db Dubnium [262]
106 Sg Seaborgium [266]
107 Bh Bohrium [264]
108 Hs Hassium [269]
109 Mt Meitnerium [278]
110 Ds Darmstadtium [281]
111 Rg Roentgenium [280]
112 Cn Copernicium [285]
113 Nh Nihonium [286]
114 Fl Flerovium [289]
115 Mc Moscovium [289]
116 Lv Livermorium [293]
117 Ts Tennessine [294]
118 Og Ogaresson [294]
Lanthanide Series
57 La Lanthanum 138.905
58 Ce Cerium 140.116
59 Pr Praseodymium 140.908
60 Nd Neodymium 144.243
61 Pm Promethium 144.913
62 Sm Samarium 150.36
63 Eu Europium 151.964
64 Gd Gadolinium 157.25
65 Tb Terbium 158.925
66 Dy Dysprosium 162.500
67 Ho Holmium 164.930
68 Er Erbium 167.259
69 Tm Thulium 168.934
70 Yb Ytterbium 173.055
71 Lu Lutetium 174.967
Actinide Series
89 Ac Actinium 227.028
90 Th Thorium 232.038
91 Pa Protactinium 231.036
92 U Uranium 238.029
93 Np Neptunium 237.048
94 Pu Plutonium 244.064
95 Am Americium 243.061
96 Cm Curium 247.070
97 Bk Berkelium 247.070
98 Cf Californium 251.080
99 Es Einsteinium [254]
100 Fm Fermium 257.095
101 Md Mendelevium 258.1
102 No Nobelium 259.101
103 Lr Lawrencium [262]
Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Metalloid
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide

Conductors vs. Semiconductors

Semiconductors include a large number of substances of different chemical and physical properties. Main types of semiconductors:

•Group IV semiconductors - Si, Ge.

- Crystallize in the diamond structure (fcc lattice with a basis composed of two identical atoms)
- covalent crystals, i.e., the atoms are held together by covalent bonds
- the covalent electrons forming the bonds are hybrid sp3 atomic orbitals

•III-V (GaN, GaAs, InP, etc.), II-VI (ZnSe, ZnS) semiconductors and alloys

- zinc blende structure (same as diamond but with two different atoms) or hexagonal wurtzite structure (GaN)
- also covalent bonds, but polar - the distribution of the electrons along the bond is not symmetric.

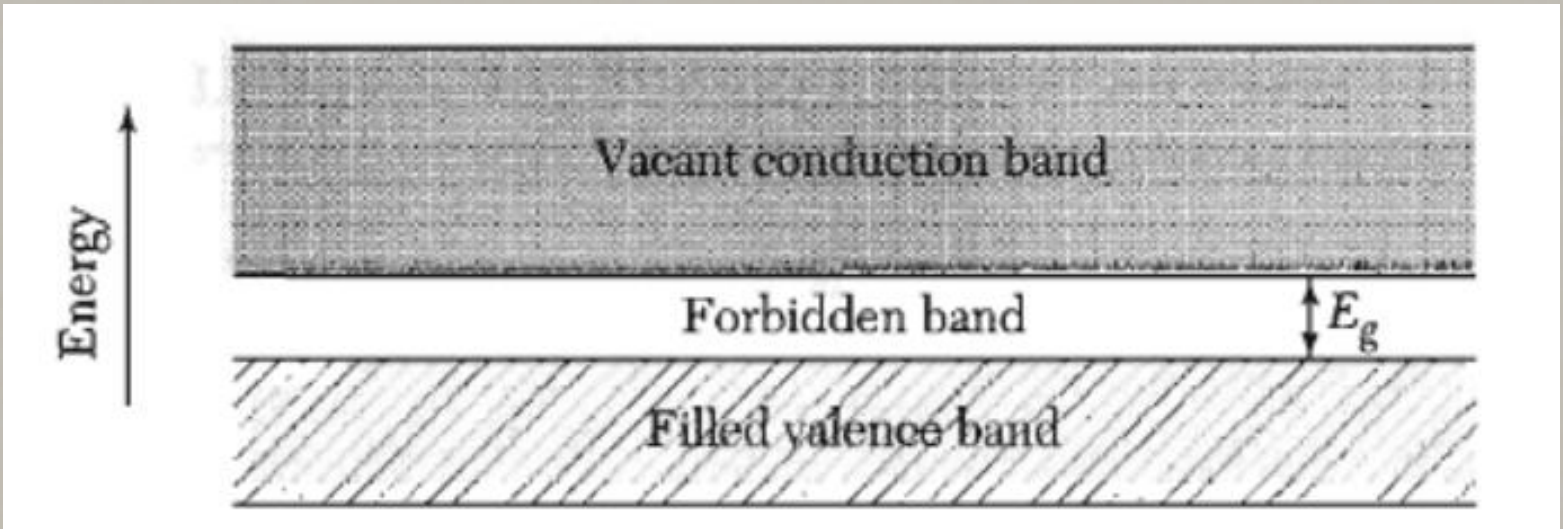
•Some other compounds (I-VII, various oxides, halogenides, organic semiconductors...)

Band Gap

- The band gap is the difference in energy between the lowest point of the conduction band and the highest point of the valence band.

- The lowest point in the conduction band is called the conduction band edge; the highest point in the valence band is called the valence band edge.

- At 0 K the conductivity is zero because all states in the valence band are filled and all states in the conduction band are vacant. As the temperature is increased, electrons are thermally excited from the valence band to the conduction band, where they become mobile. Such carriers are called 'intrinsic."



Band Gap

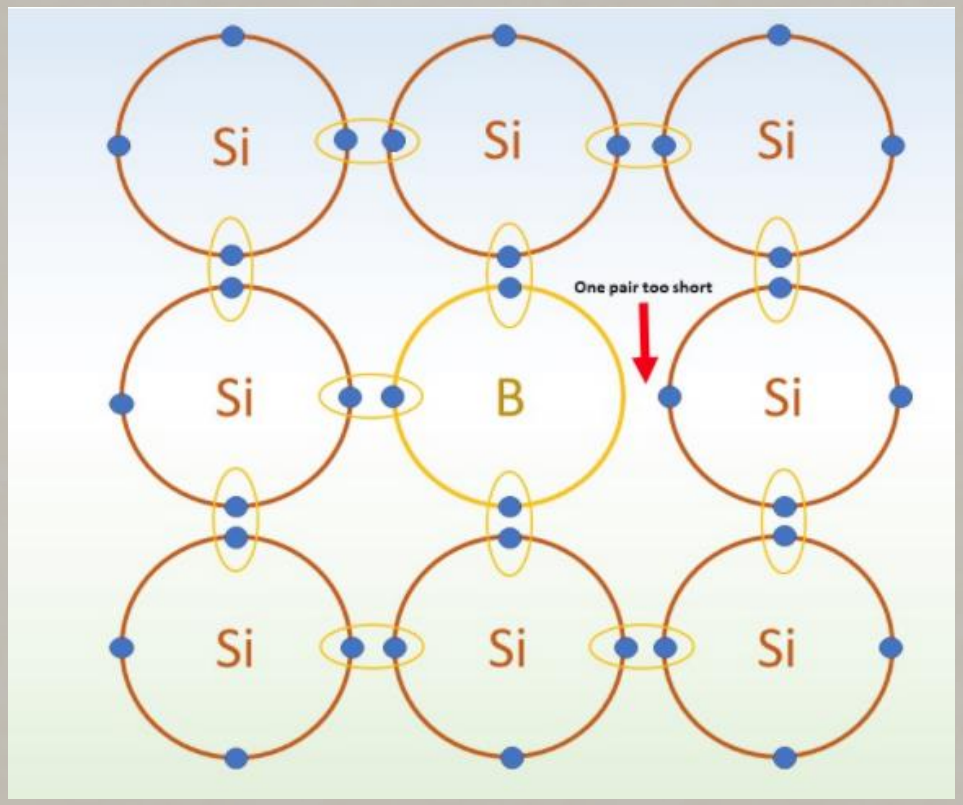
- A highly purified semiconductor exhibits **intrinsic conductivity**, as distinguished from the **impurity conductivity** of less pure semiconductors. In the intrinsic temperature range the electrical properties of a semiconductor are not essentially modified by impurities in the crystal.

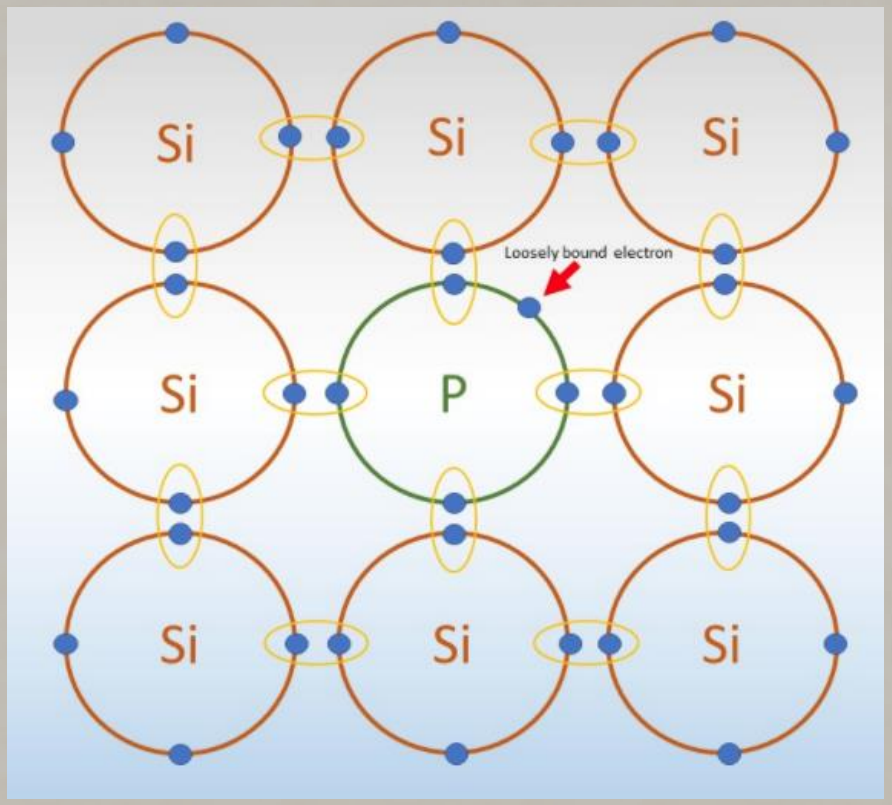
- Under intrinsic conditions the hole concentration is equal to the electron concentration.

- The intrinsic conductivity and intrinsic carrier concentrations are largely controlled by $\frac{E_g}{k_B T}$, the ratio of the band gap to the sample thermal energy. When this ratio is large, the concentration of intrinsic carriers will be low and the hence electrical conductivity will be low.

Basis of Comparison	Intrinsic Semiconductor	Extrinsic Semiconductor
Impurity present in the material	Intrinsic semiconductors are pure forms of semiconductors, hence they do not have a significant amount of impurity.	Extrinsic semiconductors are made by adding some impurity to the pure form of semiconductors.
Electrical conductivity	They exhibit poor electrical conductivity.	Electrical conductivity in the case of extrinsic semiconductors is significantly high as compared to intrinsic semiconductors.
The density of charge carriers	In intrinsic semiconductors, the number of free electrons in the conduction band is equal to the number of holes in the valence band.	The number of electrons and holes are not equal in extrinsic semiconductors and depends on the type of extrinsic semiconductor.
Dependency of electrical conductivity	The electrical conductivity of intrinsic semiconductors depends only on the temperature.	The electrical conductivity of extrinsic semiconductors depends on the temperature as well as the amount of doped impurity.
Position of Fermi level	In intrinsic semiconductors, the Fermi energy levels lie in the middle of the valence and conduction band.	In extrinsic semiconductors, the Fermi level shifts towards the valence or conduction band.
Examples	Examples include the crystalline forms of pure silicon or germanium.	Examples include Silicon (Si) and germanium (Ge) crystals with impurity atoms of As, Sb, P, etc., or In, B, Al, etc.

P type and N type Semiconductor





Difference between P type and N type Semiconductor – Table

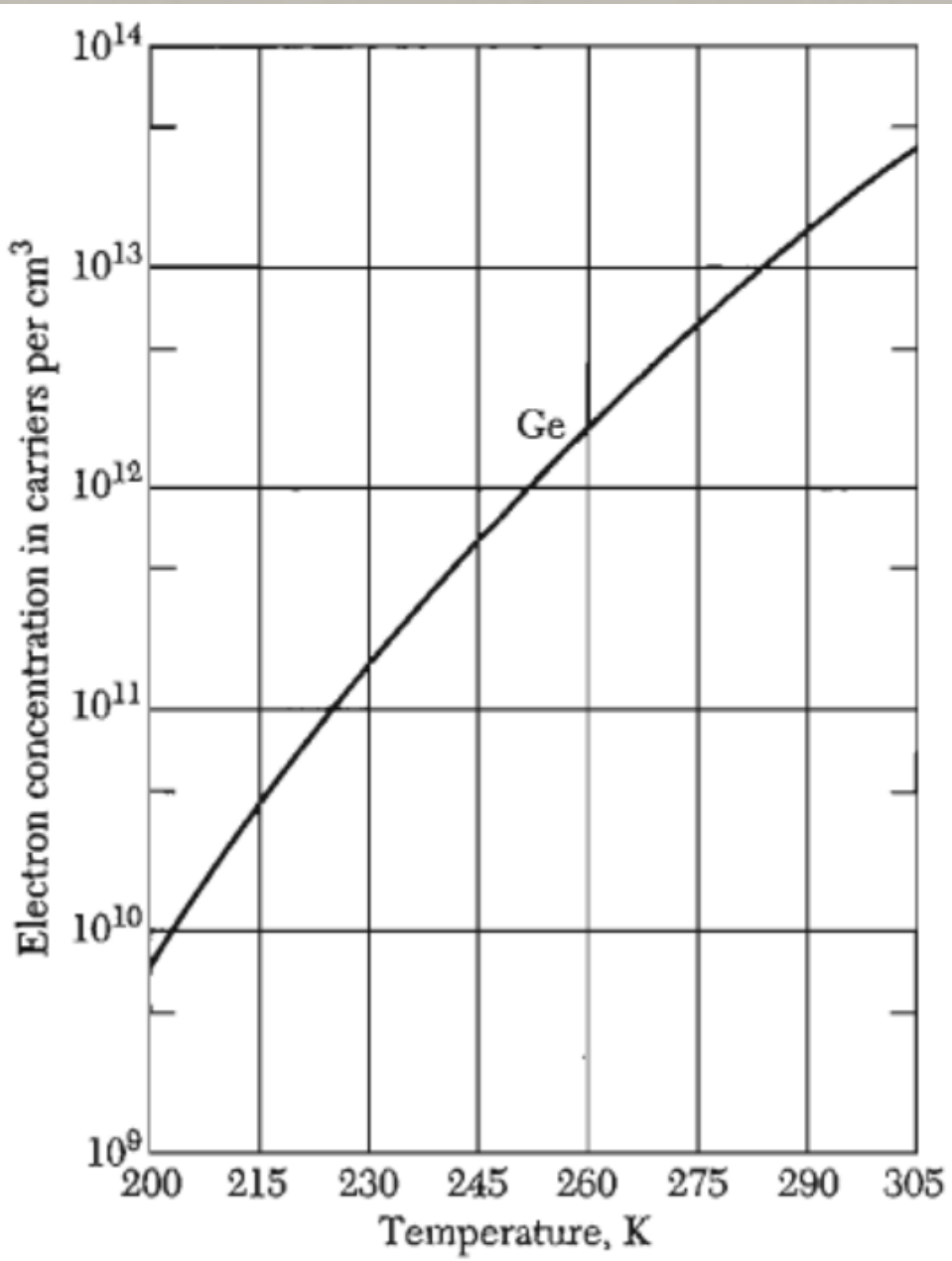
Now let's see the difference between p-type and n-type semiconductor with the help of a table.

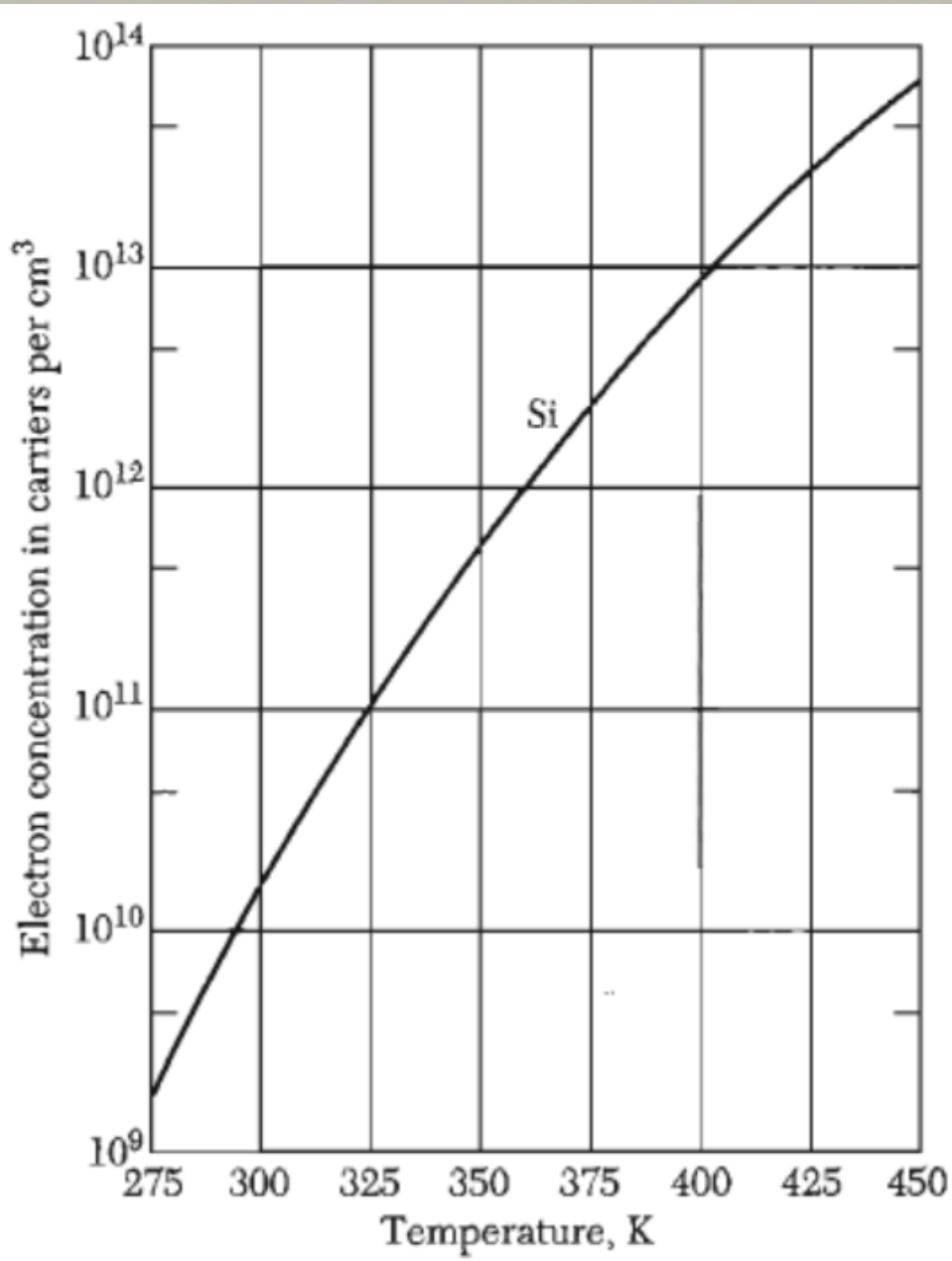
P-type semiconductor	N-type semiconductor
P-type semiconductors are formed due to doping of elements of group III i.e. Boron, Aluminium, Thallium, etc.	N-type semiconductors are formed due to doping of elements of group V i.e. Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth, etc.
Holes are the majority carriers in P-type semiconductors.	Electrons are the majority carriers in n-type semiconductors.
Electrons are the minority carriers in P-type semiconductors.	Holes are minority carriers in N-type semiconductors.
The fermi energy levels of these materials lie between the impurity energy level and the valence band.	The Fermi levels of these materials lie between the impurity energy level and the conduction band.
The movement of majority carriers is from higher potential to lower potential.	The movement of majority carriers is from lower potential to higher potential.
In P-type semiconductors, hole density is greater than the electron density. $N_h > N_e$	Electron density is much greater than the hole density for the n-type semiconductors. $N_e > N_h$

- **Electron Concentration Versus Temperature**
- **Direct and Indirect Band Gaps**
- **Equations of Motion**

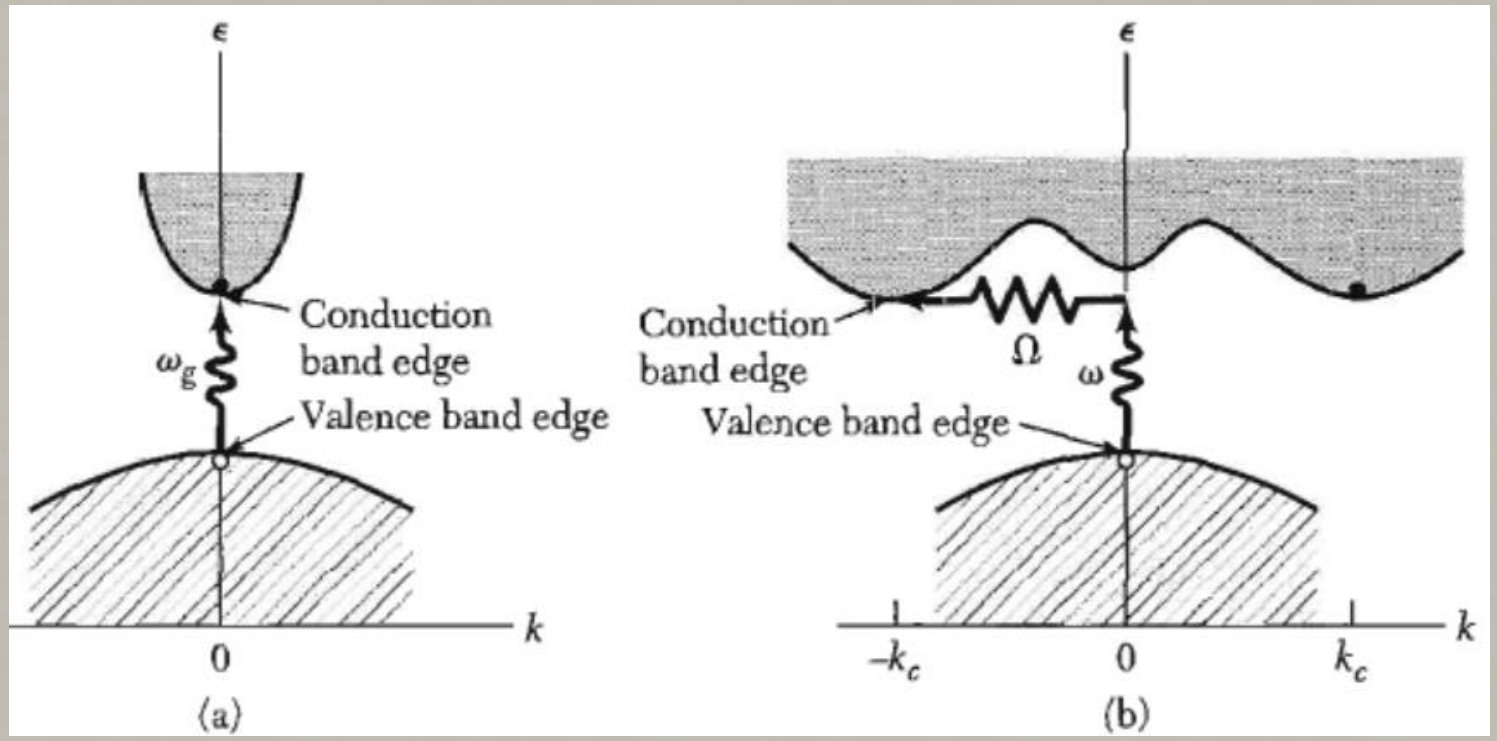
Electron concentration versus temperature

- The intrinsic concentration at a given temperature is higher in Ge than in Si because the energy gap is narrower in Ge (0.66 eV) than in Si (1.11 eV)





Direct and Indirect Band Gaps

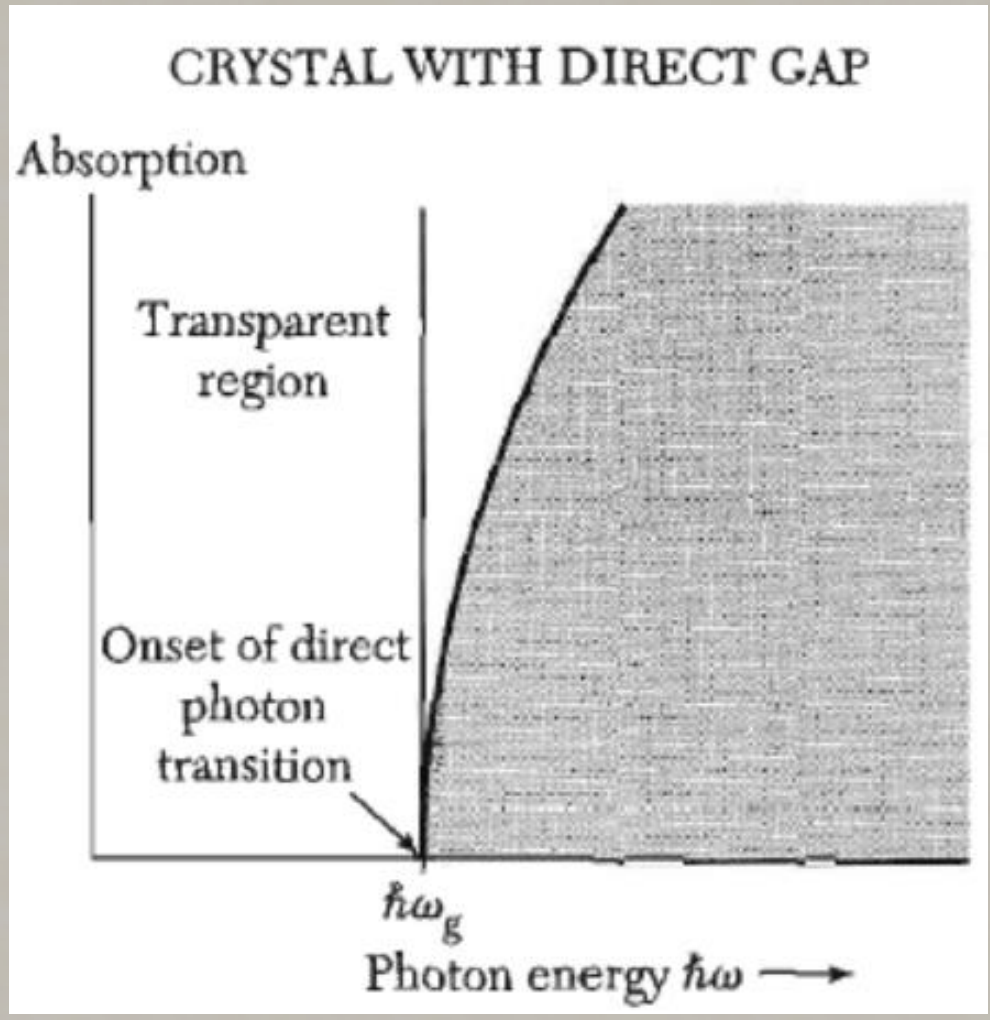


In (a) the lowest point of the conduction band occurs at the same value of k as the highest point of the valence band. A direct optical transition is drawn vertically with no change in k.

The indirect transition in (b) involves both a photon and a phonon because the band edges of the conduction and valence bands are widely separated in k space**. The threshold energy for the indirect process in (b) is greater than the true band gap.** The absorption threshold for the indirect transition between the hand edges is at $\hbar\omega = E_g + \hbar\Omega$, where Ω is the frequency of an emitted phonon of wavevector K $= -k_c$.

Direct and Indirect Band Gaps

Optical absorption in pure insulators at absolute zero temperature. In the, direct band gap semiconductor the threshold determines the energy gap as $E_g = \hbar\omega_g$.

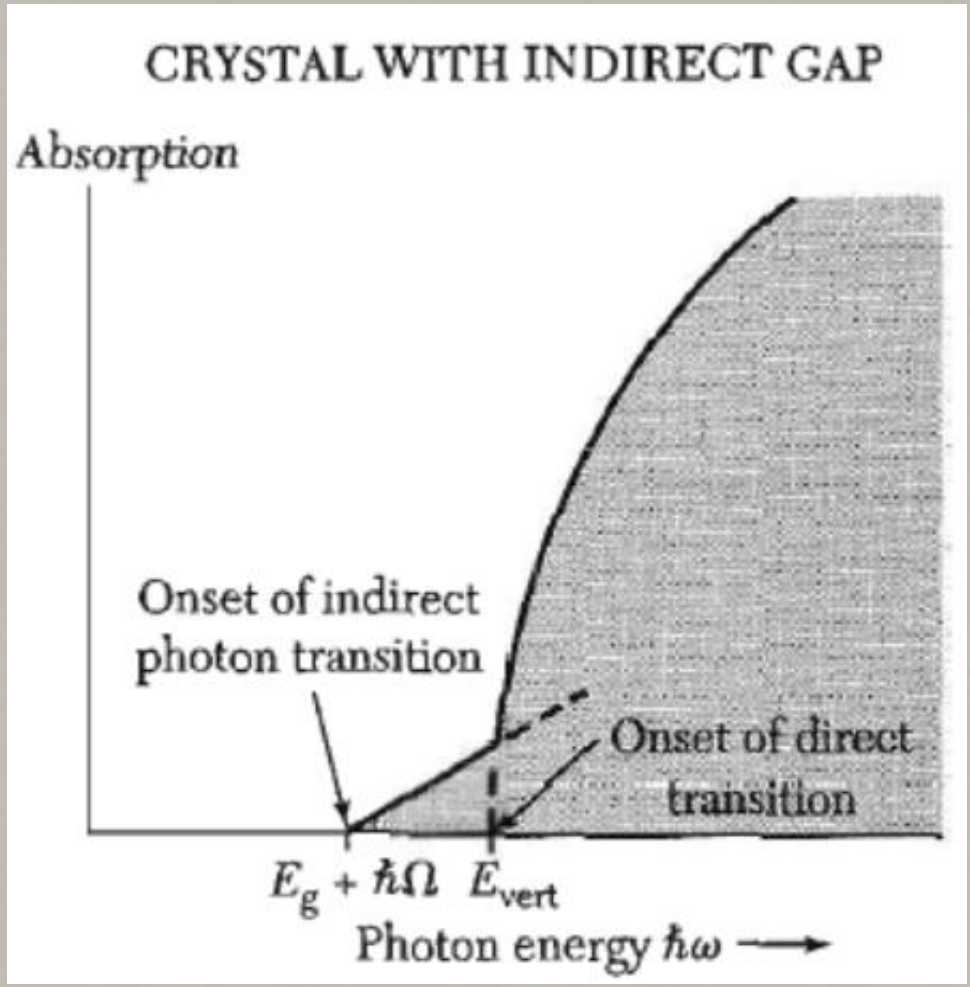


Direct and Indirect Band Gaps

In the indirect band gap semiconductor, the optical absorption is weaker near the threshold.

A photon of energy $\hbar\omega$ is absorbed with the creation of three particles: a free electron, a free hole, and a phonon of energy $\hbar\Omega$. Thus $\hbar\omega = E_g + \hbar\Omega$.

The energy $\boldsymbol{E_{vert}}$ marks the threshold for the creation of a free electron and a free hole, with no phonon involved. Such a transition is called **vertical**; it is similar to the direct transition in (a).



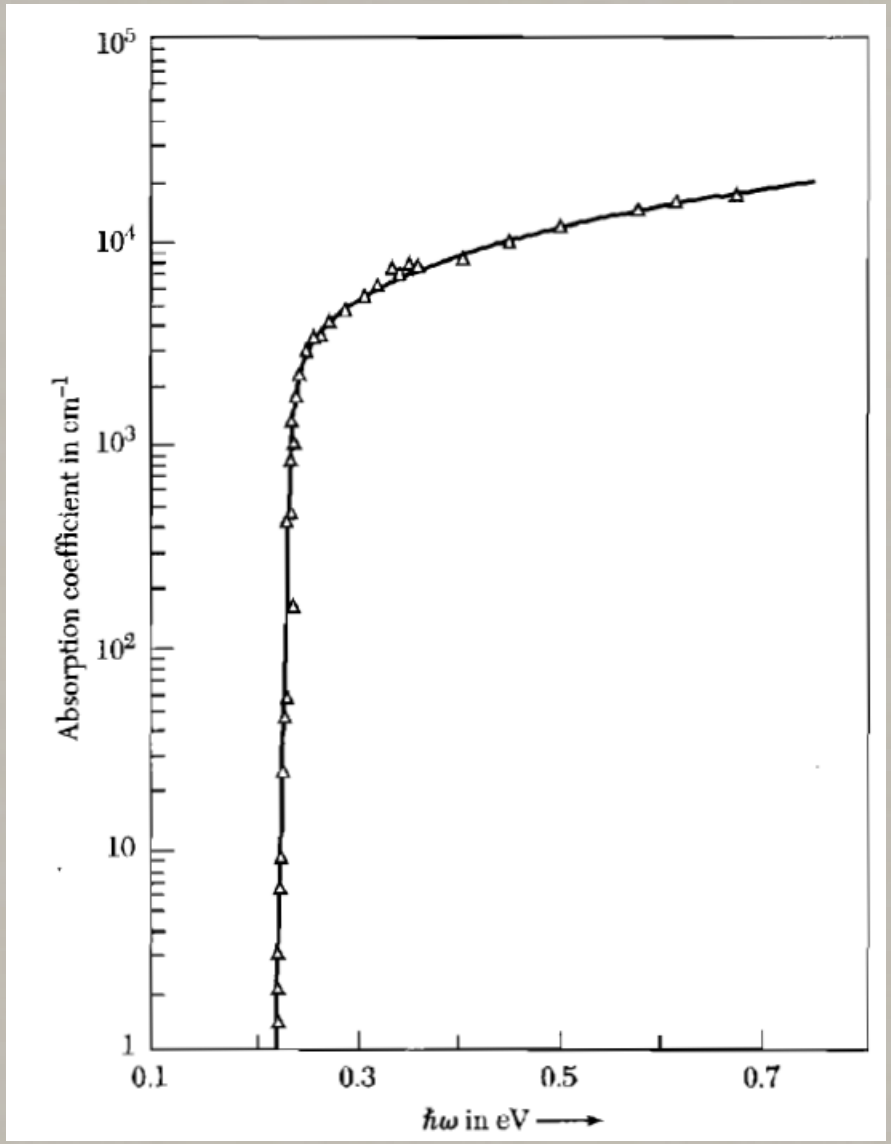
Direct and Indirect Band Gaps

The band gap may also be deduced from the temperature dependence of the conductivity or of the carrier concentration in the intrinsic range.

The carrier concentration is obtained from measurements of the Hall voltage, sometimes supplemented by conductivity measurements.

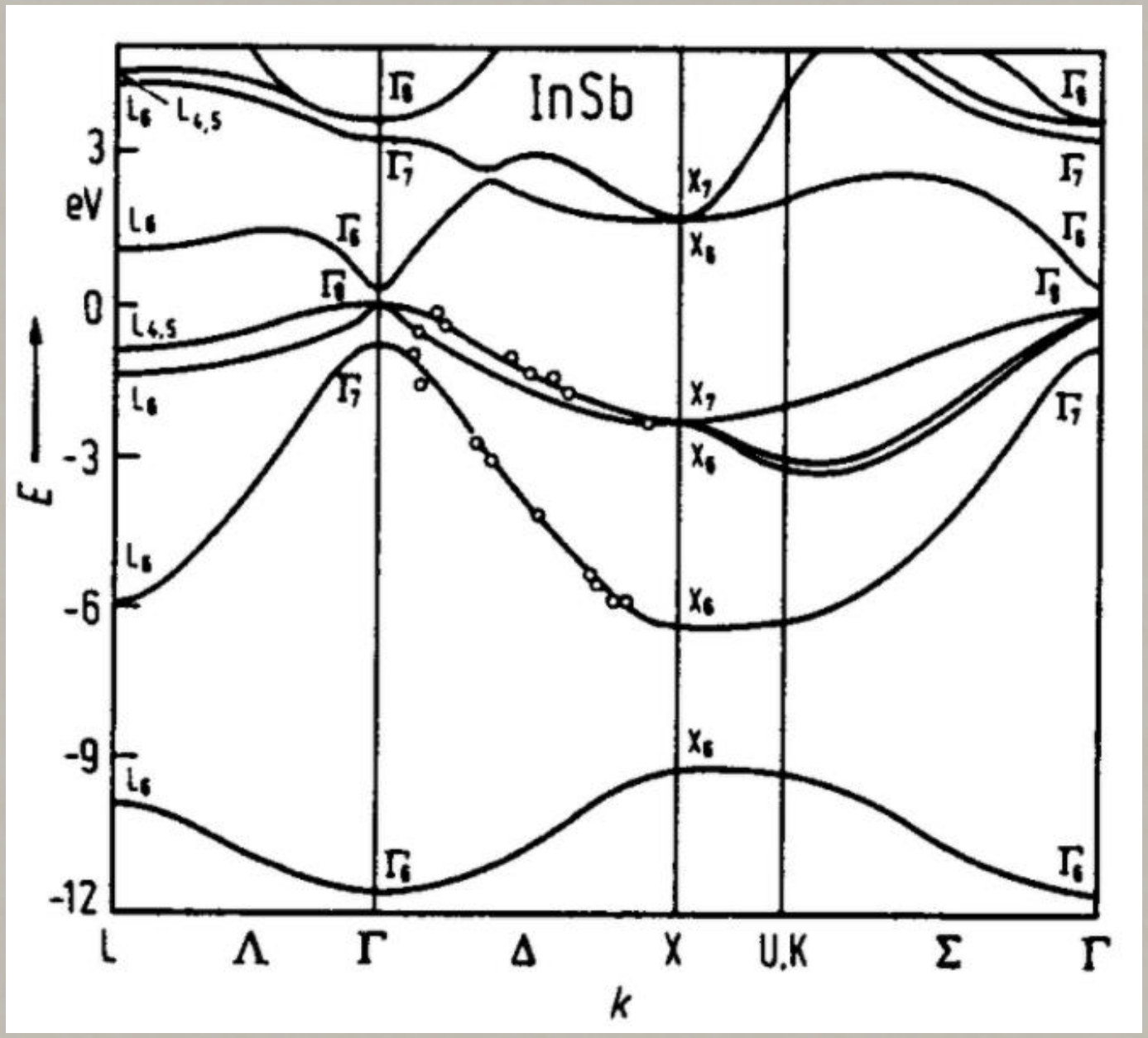
Optical measurements determine whether the gap is direct or indirect.

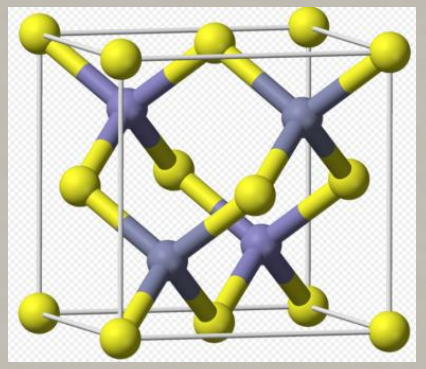
Optical absorption in pure indium antimonide, InSb. Notice the sharp threshold.

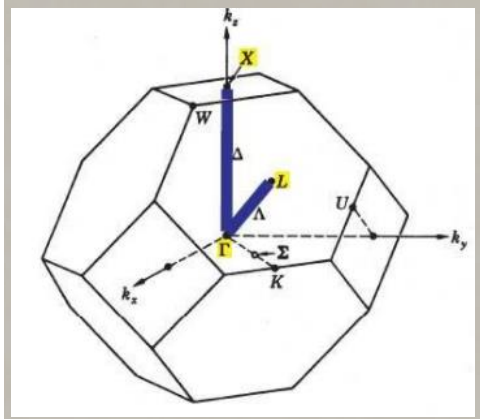


Direct and Indirect Band Gaps

In InSb, the transition is direct because both conduction and valence band edges are at the center of the Brillouin zone (Γ), k = 0.







Direct and Indirect Band Gaps

Table 1 Energy gap between the valence and conduction bands

(i = indirect gap; d = direct gap)

		E_g, eV				E_g, eV	
Crystal	Gap	0 K	300 K	Crystal	Gap	0 K	300 K
Diamond	i	5.4		SiC(hex)	i	3.0	—
Si	i	1.17	1.11	Tc	d	0.33	—
Ge	i	0.744	0.66	HgTe[a]	d	−0.30	
αSn	d	0.00	0.00	PbS	d	0.286	0.34–0.37
InSb	d	0.23	0.17	PbSe	i	0.165	0.27
InAs	d	0.43	0.36	PbTe	i	0.190	0.29
InP	d	1.42	1.27	CdS	d	2.582	2.42
GaP	i	2.32	2.25	CdSe	d	1.840	1.74
GaAs	d	1.52	1.43	CdTe	d	1.607	1.44
GaSb	d	0.81	0.68	SnTe	d	0.3	0.18
AlSb	i	1.65	1.6	Cu_2O	d	2.172	—

[a]HgTe is a semimetal; the bands overlap.

	Free electron model (Sommerfeld)	Nearly free electron model (Bloch theorem)
	k ($\hbar$k is the momentum)	n , k (n is the band index, $\hbar$k is the crystal momentum)
Energy	$\varepsilon(\mathrm{k}) = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}$	For a given band n, no simple explicit form. General property : $\varepsilon_n(\vec{k}+\vec{G}) = \varepsilon_n(\vec{k})$
Velocity	$\vec{v}(\mathrm{k}) = \frac{\hbar\vec{k}}{\mathrm{m}} = \frac{1}{\hbar}\nabla_{\vec{k}}\varepsilon(\vec{k})$	The mean velocity for e in band n with k $\vec{v}_n(\mathrm{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\varepsilon_n(\vec{k})$
Wave function	$\psi_{\vec{k}}(\mathrm{r}) = \frac{e^{i\vec{k}\bullet\vec{r}}}{\sqrt{V}}$	$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})e^{i\vec{k}\bullet\vec{r}}$ $u_{n\vec{k}}(\vec{r}+\vec{T}) = u_{n\vec{k}}(\vec{r})$

Equations of Motion

We derive the equation of motion of an electron in an energy band. We look at the notion of a wave packet in an applied electric field. Suppose that the wave packet is made up of wavefunctions assembled near a particular wavevector k. The group velocity by definition

$$v_g = \frac{d\omega}{dk} = \hbar^{-1}\frac{d\epsilon}{dk} \qquad \text{or} \qquad v_g = \hbar^{-1}\nabla_k \epsilon(k).$$

The work ($\delta\epsilon$) done on the electron by the electric field E in the time interval (δt).

$$\delta\epsilon = -eEv_g\delta t$$

and

$$\delta\epsilon = \hbar\delta\omega = \hbar v_g\,\delta k$$

$$\delta k = -\left(\frac{eE}{\hbar}\right)\delta t$$

When electron is in an electric field E, the force on the electron is

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

Equations of Motion

The Lorentz force on an electron in a magnetic field, under ordinary conditions where the magnetic field is not so strong to break down the band structure.

For $E = 0$, the equation of motion of an electron of group velocity v_g in a constant magnetic field B is

$$F = \hbar \frac{dk}{dt} = -e\,(v_g \times B).$$

$$\hbar \frac{dk}{dt} = -\frac{e}{\hbar}\,(\nabla_k \epsilon(k) \times B)$$

In the presence of both electric and magnetic fields, the equation will become

$$\hbar \frac{\boldsymbol{dk}}{\boldsymbol{dt}} = -\left(\boldsymbol{eE} + \frac{\boldsymbol{e}}{\hbar}\boldsymbol{\nabla_k \epsilon(k)} \times \boldsymbol{B}\right).$$

Physical Derivation of $\frac{\hbar dk}{dt} = F$

The Bloch eigenfunction ψ_k belonging to the energy eigenvalue ϵ_k and wavevector k:

$$\psi_k = \sum_G C_{k+G} \exp[i(k+G).r] .$$

The expectation value of the momentum of an electron in the Bloch state k is

$$< P_{el} > = < \psi_k | -i\hbar\nabla | \psi_k >$$

$$< P_{el} > = \sum_G \hbar\,(k+G) |C_{k+G}|^2$$

Using $\sum_G |C_{k+G}|^2 = 1$, in the first term, we write.

$$< P_{el} > = \hbar k + \hbar \sum_G G |C_{k+G}|^2$$

Physical Derivation of $\frac{\hbar dk}{dt} = F$

We suppose that a weak external force is applied for a time interval such that the total impulse given to the entire crystal system is $J = \int F\, dt$.

If the conduction electron is free, the total momentum imparted to the crystal system by the impulse would appear in the change of momentum of the conduction electron.

$$J = \Delta P_{tot} = \Delta P_{el} = \hbar \Delta k$$

If the conduction electron interacts with the periodic potential of the crystal lattice, we must have.

$$J = \Delta P_{tot} = \Delta P_{el} + \Delta P_{lat} = \hbar \Delta k$$

On the previous slide, we note that

$$\Delta P_{el} = \hbar \Delta k + \sum_G \hbar\, G\, [\nabla_k\, |C_{k+G}|^2 \,.\, \Delta k]$$

So

$$\Delta P_{lat} = -\sum_G \hbar\, G\, [\nabla_k\, |C_{k+G}|^2 \,.\, \Delta k]$$

Physical Derivation of $\frac{\hbar dk}{dt} = F$

Thus external force on applied on electron can be determined by the rate of change of impulse:

$$F = \frac{dJ}{dt} = \frac{\hbar dk}{dt}.$$

- **Holes**
- **Effective Mass**
- **Silicon and Germanium**

Holes

The properties of vacant orbitals in an otherwise filled band are important in semiconductor physics and in solid state electronics. Vacant orbitals in a band are commonly called holes, and without holes there would be no transistors.

The empty states in the valence band are called “holes”. It acts under external forces s if it has a positive charge $+e$.

In a completely filled band, no current can flow because no states are available for electrons to move to. The electrons can “move” in the valence band if there is an empty state i.e a hole available.

Further elaboration of the hole is given in the following five steps.

1. The total wavevector of the electrons in a filled band is zero: $\sum k = 0$, where the sum is over all states in a Brillouin zone. Due to the inversion symmetry of the Brillouin zone, if the band is filled all pairs of orbitals k and $-k$ are filled, and the total wavevector is zero.

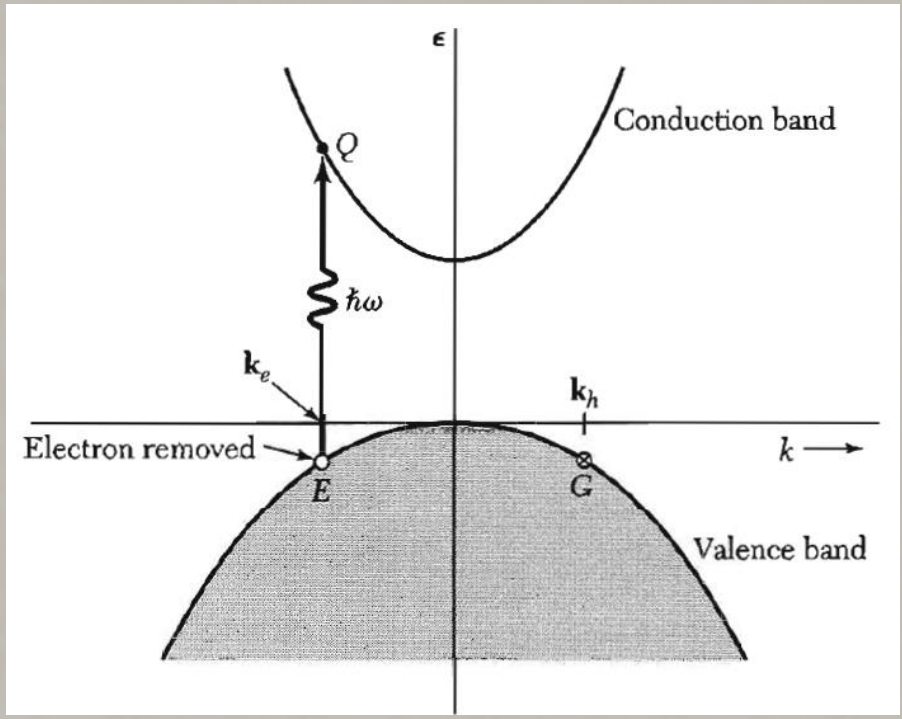
Holes

If we choose that the total wavevector of the system after the absorption of the photon is $k_h + k_e = 0$. Then when an electron of wavevector k_e is excited to the conduction band a hole of wavevector $k_h = -k_e$ is created in the valance band, thus

$$k_h = -k_e$$

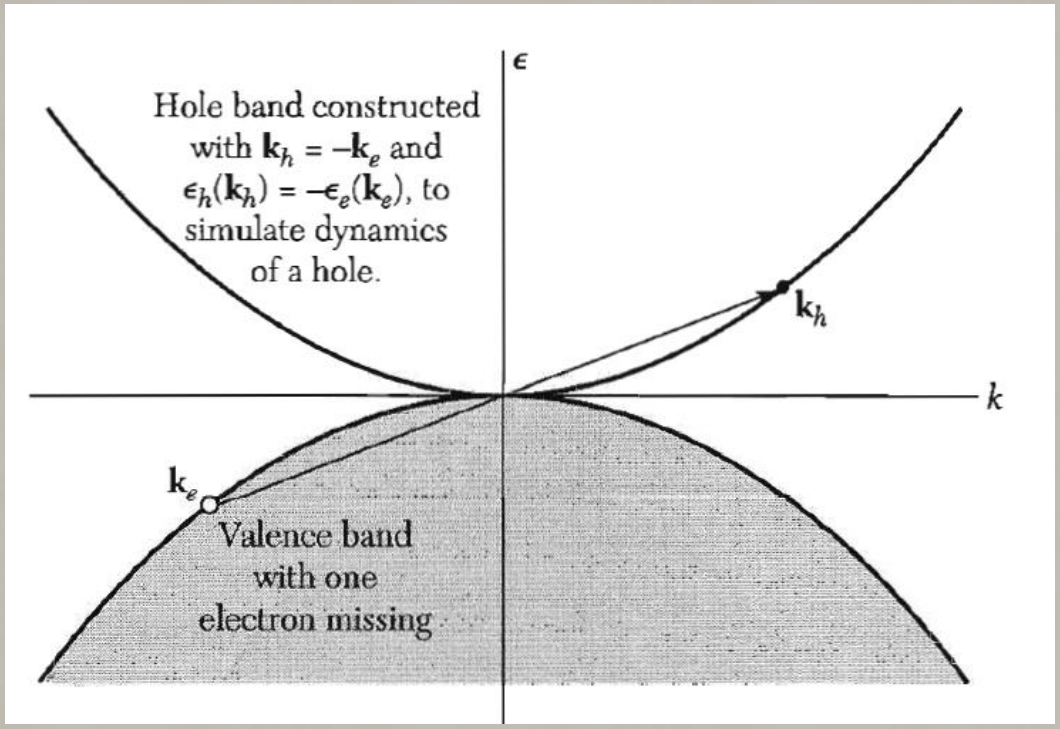
The wavevector $-k_e$, enters into selection rules for photon absorption.

$$k + k_e = k_h + k_e$$



2. The wavevector and energy of the hole are equal, but opposite in sign, to the wavevector and energy of the empty electron orbital in the valence band. It takes more work to remove an electron from a low orbital than from a high orbital.

$$\epsilon_e(k_e) = \epsilon_e(-k_e) = -\epsilon_h(-k_e) = -\epsilon_h(k_h)$$



The upper half of the figure shows the hole band that simulates the dynamics of a hole, constructed by inversion of the valence band in the origin. We do not show the disposition of the electron removed from the valence band at k_e.

3. The velocity of the hole is equal to the velocity of the missing electron.

$$v_h = v_e$$

From the figure on the last slide, we see that

$$\nabla_{k_h} \epsilon_h(k_h) = \nabla_{k_e} \epsilon_e(k_e)$$

4. We show below that the effective mass is inversely proportional to the curvature $d^2\epsilon/dk^2$, and for the hole band this has the opposite sign to that for an electron in the valence band. Near the top of the valence band m_e is negative, so that m_h is positive.

$$m_h = -m_e$$

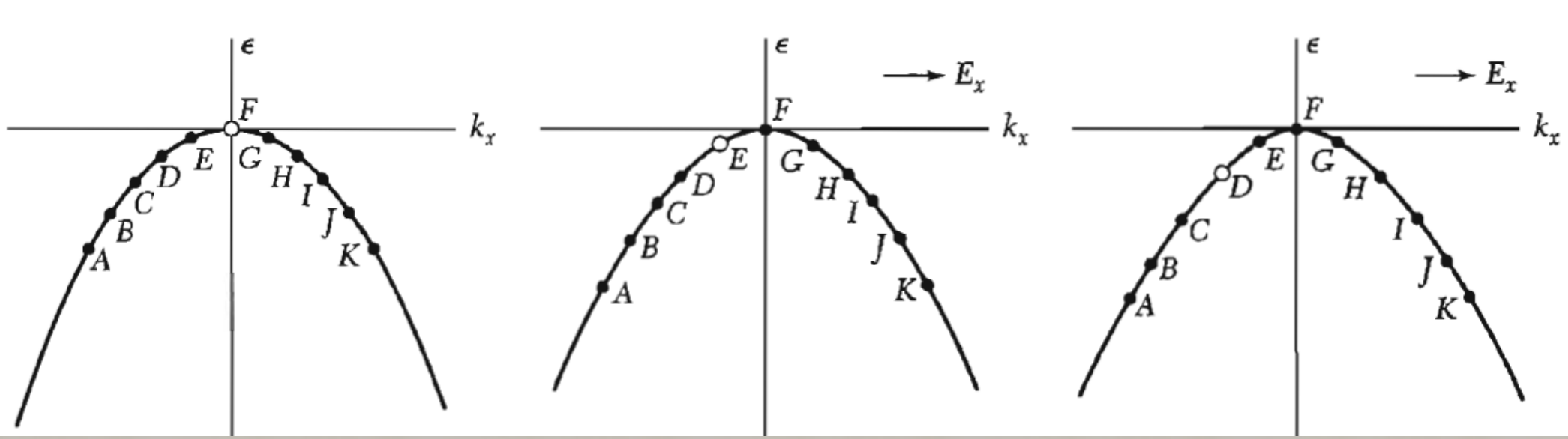
5. Equation of motion for hole is:

$$\hbar \frac{dk_h}{dt} = e\left(E + \frac{1}{c} v_h \times B\right).$$

This comes from equation of motion of electron for $k_h = -k_e$ and $v_h = v_e$.

$$\hbar \frac{dk_e}{dt} = -e\left(E + \frac{1}{c} v_e \times B\right).$$

The equation of motion for a hole is that of a particle of positive charge $+e$.

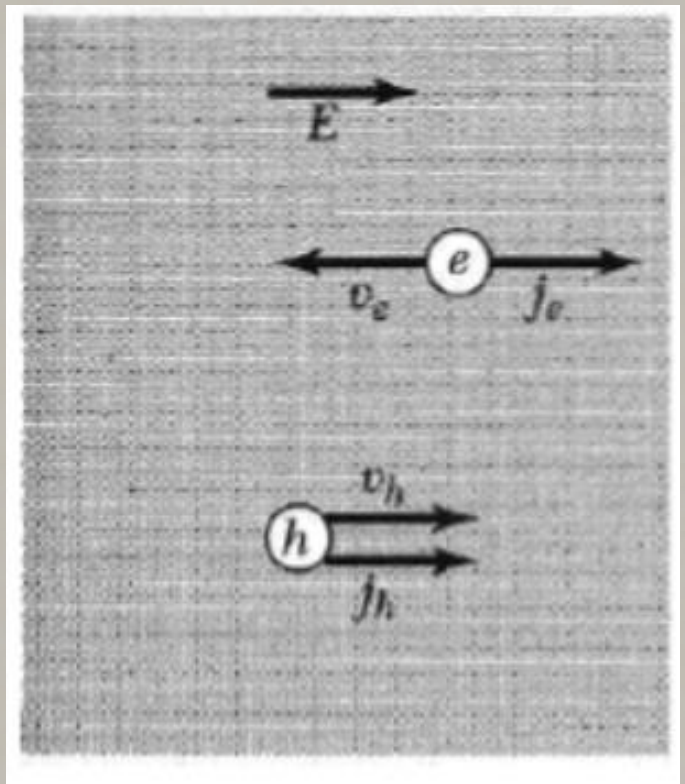


Hole

Motion of electrons in the conduction band and holes in the valence band in the electric field *E*. The hole and electron drift velocities are in opposite directions, but their electric currents are in the same direction, the direction of the electric field.

$$j_e = -ev_e \text{ and } j_h = +ev_h$$

$$j_{tot} = j_e + j_h$$



Effective Mass

When we look at the energy-wavevector relation $\epsilon = \frac{\hbar^2 k^2}{2m}$ for free electrons, we see that the coefficient of k^2 determines the curvature of ϵ versus k. Turned about, we can say that $1/m$, the reciprocal mass, determines the curvature. For free electron $m^* = m = 9.1 \times 10^{-31} kg$.

For electrons in a band there can be regions of unusually high curvature near the band gap at the zone boundary, as we see from the solutions in Chapter 7 of the wave equation near the zone boundary.

If the energy gap is small in comparison with the free electron energy λ at the boundary, the curvature is enhanced by the factor λ/E_g.

In semiconductors the band width, which is like the free electron energy, is of the order of 20 eV, while the band gap is of the order of 0.2 to 2 eV. Thus the reciprocal mass $(1/m)$ is enhanced by a factor 10 to 100, and the effective mass is reduced to 0.1-0.01 of the free electron mass.

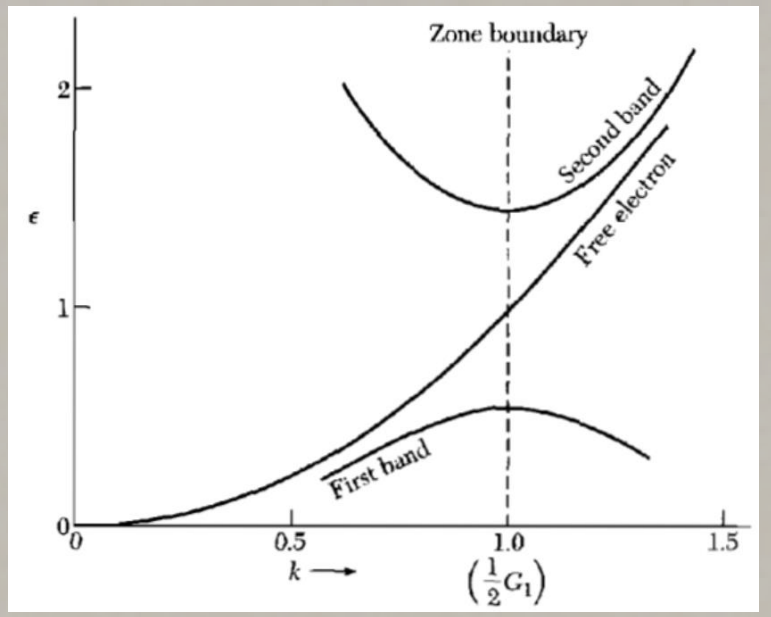
These values apply near the band gap; as we go away from the gap the curvatures and the masses are likely to approach those of free electrons.

Effective Mass

For electrons in a band, their masses depend on the band curvature.

$$\epsilon_{\tilde{K}}(\pm) = \epsilon(\pm) + \frac{\hbar^2 \tilde{K}^2}{2m}\left(1 \pm \frac{2\lambda}{U}\right).$$

The electron energy at the zone boundary at G/2.



Effective Mass

For U positive, the solution $\epsilon\,(+)$ correspond to the upper of the two bands, and $\epsilon\,(-)$ to the lower of the two bands.

$$\epsilon_{\tilde{K}}(\pm) = (\lambda \pm U) + \frac{\hbar^2 \tilde{K}^2}{2m}\left(1 \pm \frac{2\lambda}{U}\right).$$

$$\tilde{K} = k - G/2$$

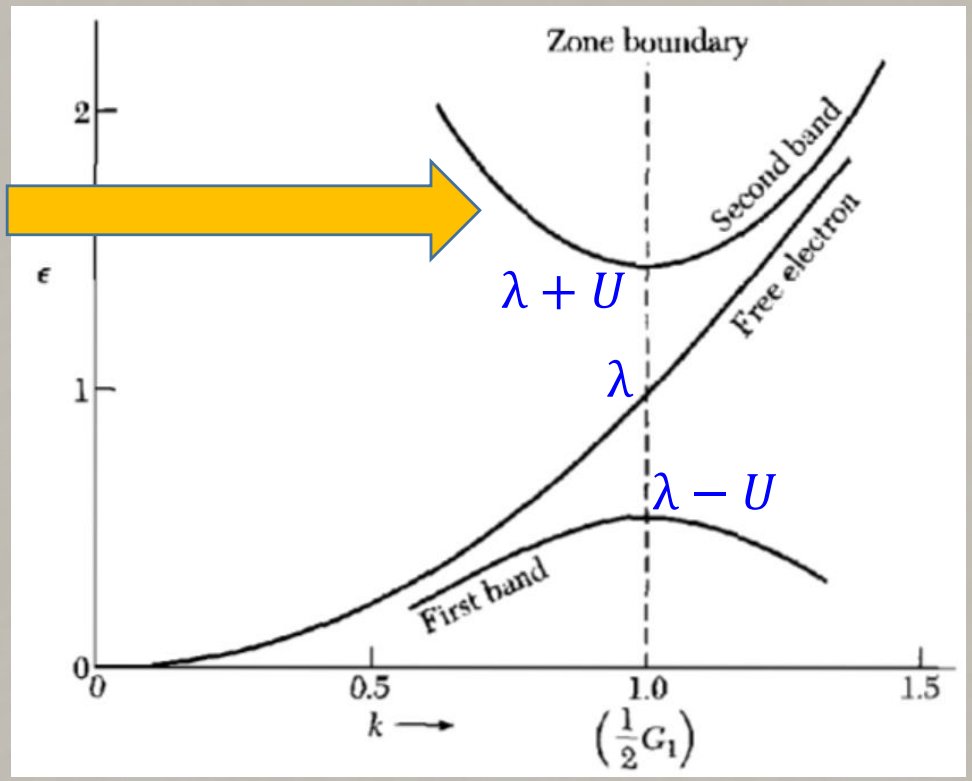
The $\epsilon_{\tilde{K}}(+)$ is

$$\epsilon_{\tilde{K}}(+) \approx (\lambda + U) + \frac{\hbar^2 \tilde{K}^2}{2m}\left(1 + \frac{2\lambda}{U}\right).$$

With the effective mass of the electron

$$\frac{1}{m_e} = \frac{1}{m}\left(1 + \frac{2\lambda}{U}\right), , \epsilon_c = \lambda + U$$

$$\epsilon_{\tilde{K}}(+) \approx \epsilon_c + \frac{\hbar^2 \tilde{K}^2}{2m_e}.$$



Effective Mass

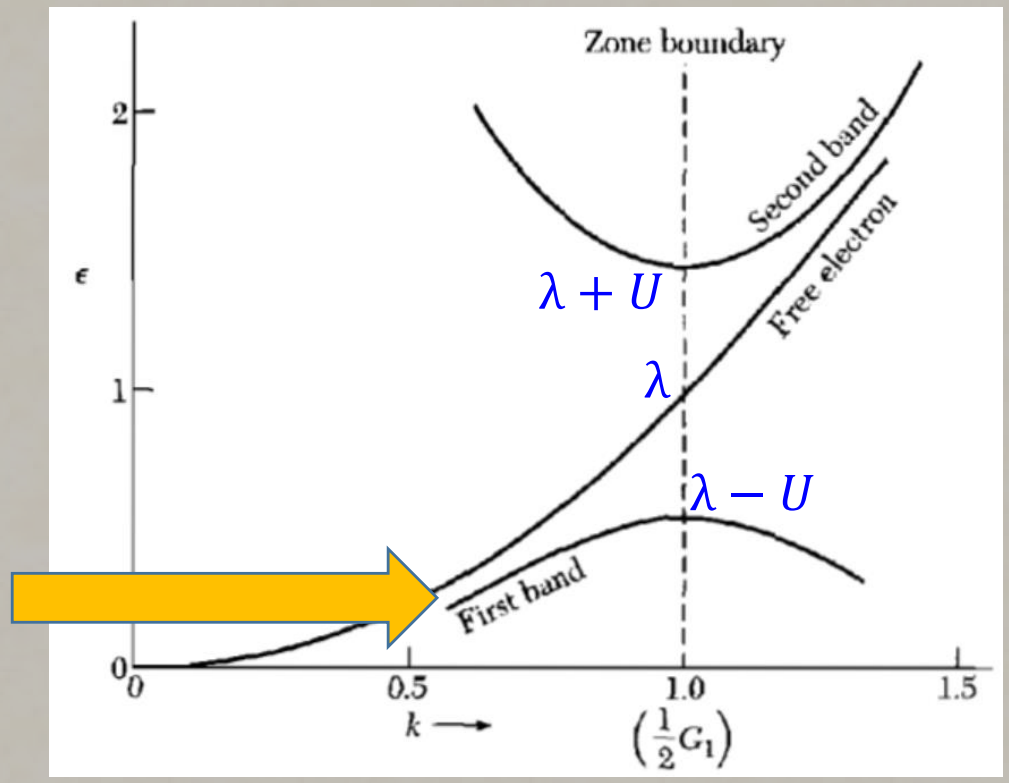
The $\epsilon_{\widetilde{K}}(-)$ is

$$\epsilon_{\widetilde{K}}(-) \approx (\lambda - U) + \frac{\hbar^2 \widetilde{K}^2}{2m}\left(1 - \frac{2\lambda}{U}\right)$$

With the effective mass of the electron

$$\frac{1}{m_h} = \frac{1}{m}\left(\frac{2\lambda}{U} - 1\right), \epsilon_v = \lambda - U$$

$$\epsilon_{\widetilde{K}}(-) \approx \epsilon_v - \frac{\hbar^2 \widetilde{K}^2}{2m_h}.$$



Effective Mass

The important point is that an electron in a periodic potential is accelerated relative to the lattice in an applied electric or magnetic field as if the mass of the electron were equal to an effective mass which we now define.

$$\vec{v}(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}}\varepsilon(\vec{k})$$

$$\frac{d\vec{v}(k)}{dt} = \frac{1}{\hbar}\frac{d\nabla_k\varepsilon(\vec{k})}{dt} = \frac{1}{\hbar}\frac{d^2\varepsilon(k)}{dk^2}\frac{d\vec{k}}{dt} = \frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk^2}\left(\hbar\frac{d\vec{k}}{dt}\right)$$

$\vec{F}$

$$\frac{dv}{dt} = \frac{1}{m^*}F$$

From Newton's 2nd law →

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

Definition of the effective mass

Considering an anisotropic energy surface

$$\left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk_\mu dk_\nu}$$

where μ and ν are Cartesian coordinates.

reciprocal effective mass tensor (3x3)

Effective Mass

In three (two) dimensions, constant energy surfaces (lines) are not necessarily spherical (circular), and the effective mass is a tensor:

$$\left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk_\mu dk_\nu}$$

In two dimensions, free electrons $\varepsilon(k_x, k_y) = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2\right)$

$$\because \left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2}\frac{d^2\varepsilon(k)}{dk_\mu dk_\nu}$$

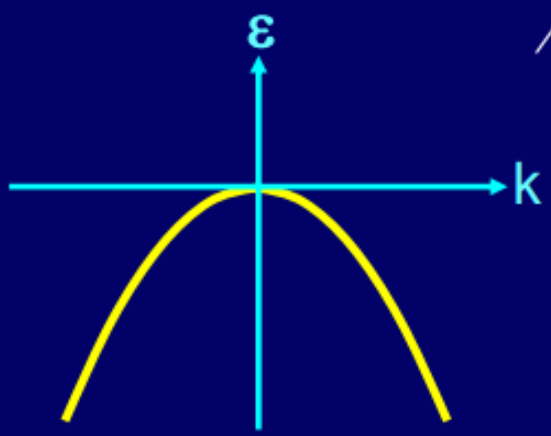
The effective mass depends on the ***curvature*** of the bands;

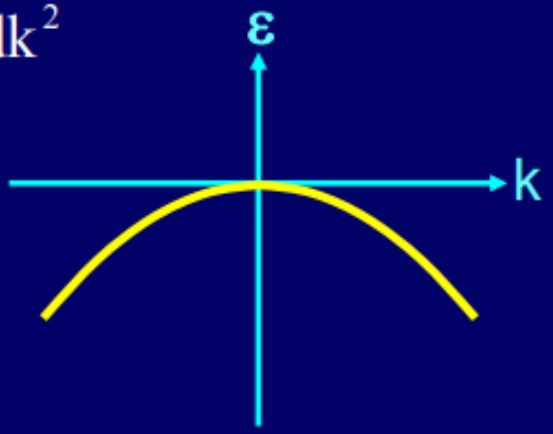
- The flat bands have large effective masses
  The curved bands have small effective masses
- Near the bottom of a band, m^* is *positive*
  Near the top of a band, m* is *negative*

Effective Mass

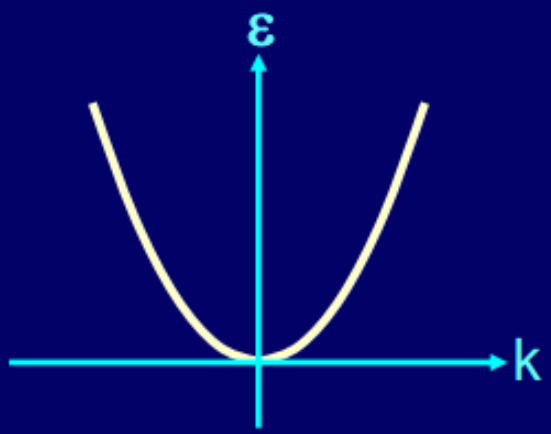
$$m^* = \frac{\hbar^2}{\frac{d^2\varepsilon(k)}{dk^2}}$$

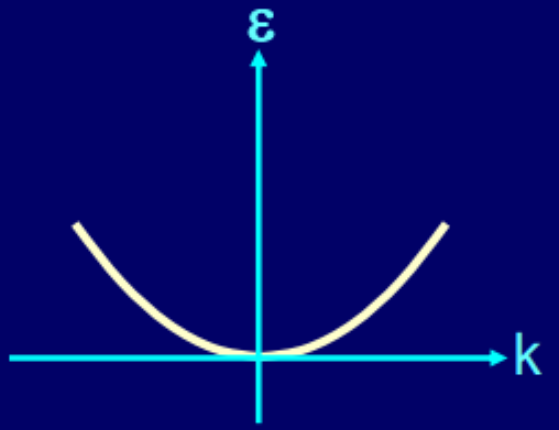
$m^* < 0$





$m^* > 0$





m^* can be determined by cyclotron resonance measurements.

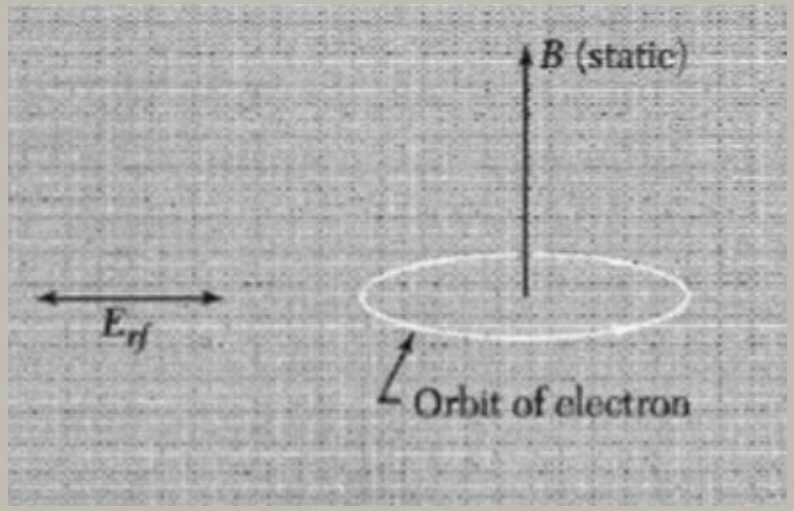
- **Effective Mass**
- **Silicon and Germanium**
- **Intrinsic Carrier Concentration**
- **Intrinsic Mobility**

Effective Mass in Semiconductors

In many semiconductors it has been possible to determine by cyclotron resonance the effective masses m^* of carriers in the conduction and valence bands near the band edges by using cyclotron resonance. The current carriers are accelerated in helical orbits about the axis of a static magnetic field. The angular rotation frequency ω_c, is

$$\frac{mv^2}{r} = evB \quad \Rightarrow \quad \omega_c = \frac{eB}{m^*}$$

Resonant absorption of energy from an radio frequency (rf) electric field E_{rf} perpendicular to the static magnetic field occurs when the rf frequency is equal to the cyclotron frequency. Holes and electrons rotate in opposite senses in a magnetic field.



Effective Mass in Semiconductors

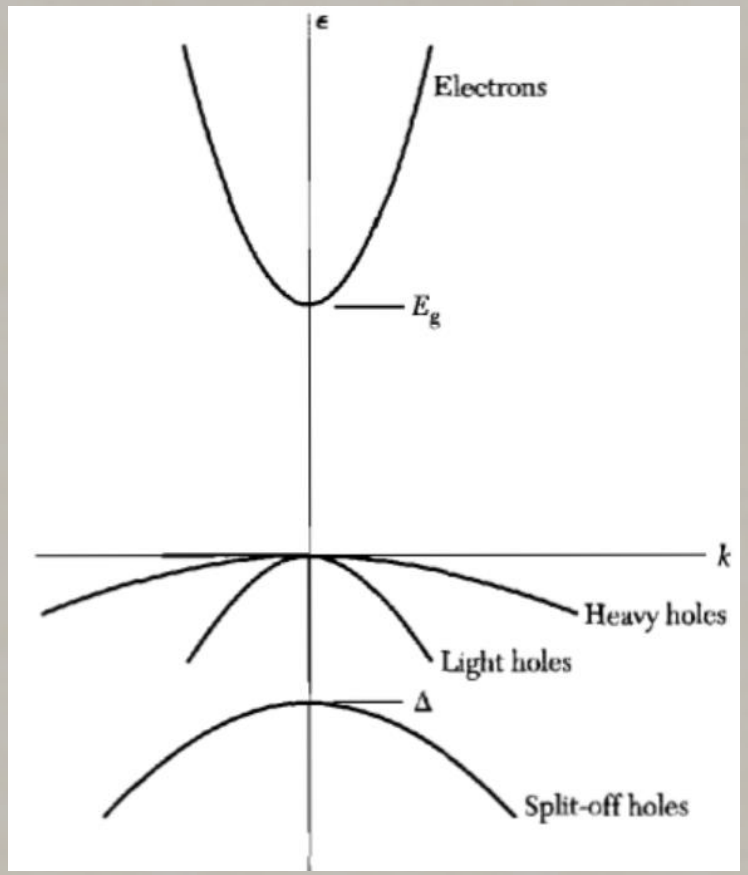
In direct-gap semiconductors with band edges at the center of the Brillouin zone, the bands have the structure shown in Figure. The conduction band edge is spherical with the effective mass m_o:

$$\epsilon_c = E_g + \frac{\hbar^2 k^2}{2m_e},$$

The valence bands are characteristically threefold near the edge, with the heavy hole ***hh*** and light hole ***lh*** bands degenerate at the center, and a band **soh** split off holes by the spin-orbit splitting Δ:

$$\epsilon_v(hh) \cong -\frac{\hbar^2 k^2}{2m_{hh}}, \epsilon_v(lh) \cong -\frac{\hbar^2 k^2}{2m_{lh}},$$

$$\epsilon_v(soh) \cong -\Delta - \frac{\hbar^2 k^2}{2m_{soh}}.$$



Effective Mass in Semiconductors

The so called "Split off holes" band appears when we consider spin orbit interaction.

The spin orbit interaction (J = L+S) is the superposition of the hole spin momentum (S) and its orbital angular momentum (L). The energy difference Δ is a measure of the spin-orbit interaction.

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

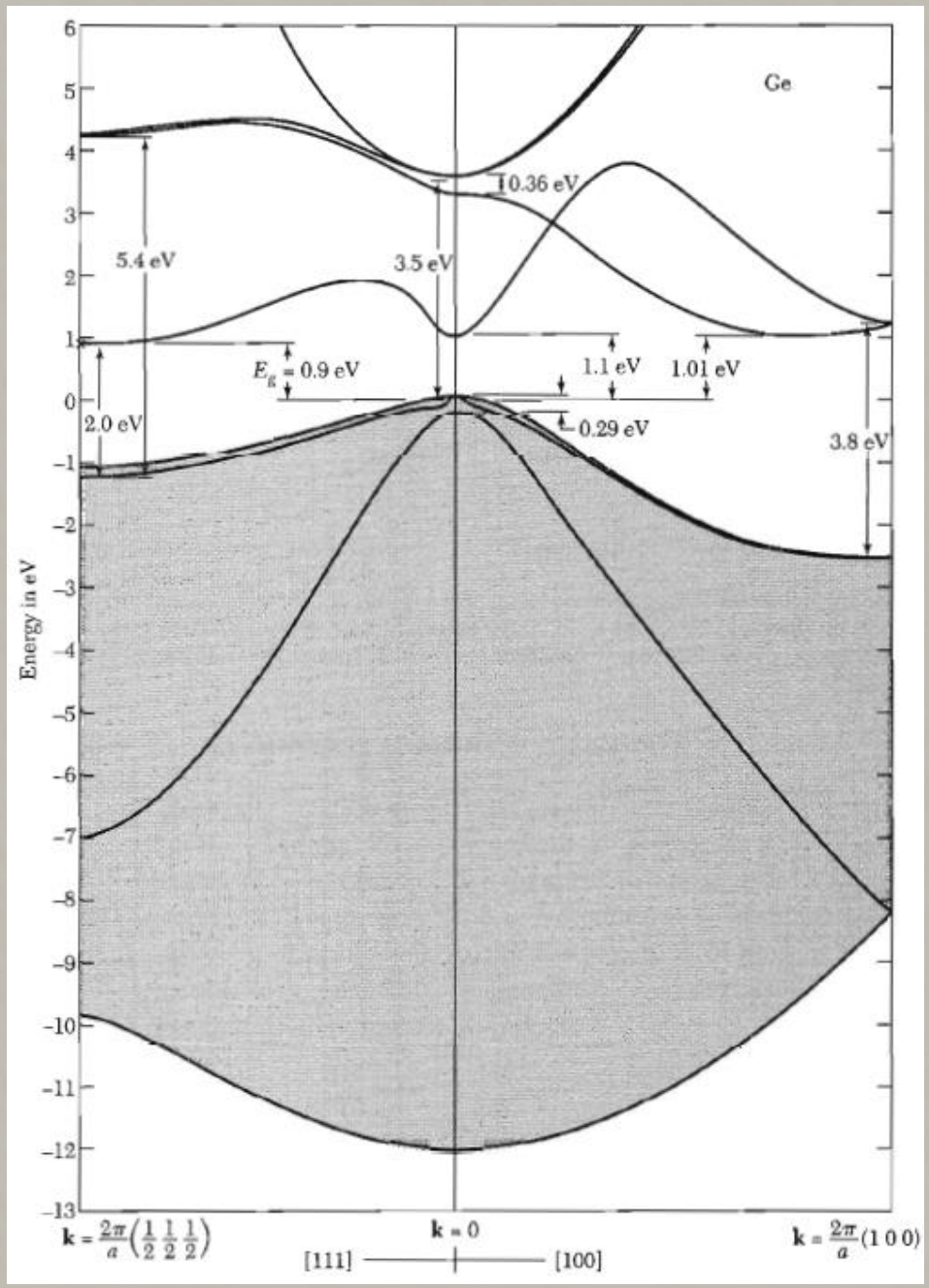
Silicon and Germanium

The conduction and valence band of germanium are shown in the figure. The valence band edge in both Si and Ge is at $k = 0$ and is derived from $p_{1/2}$ and $p_{3/2}$ states of the free atoms (Read Chapter 9).

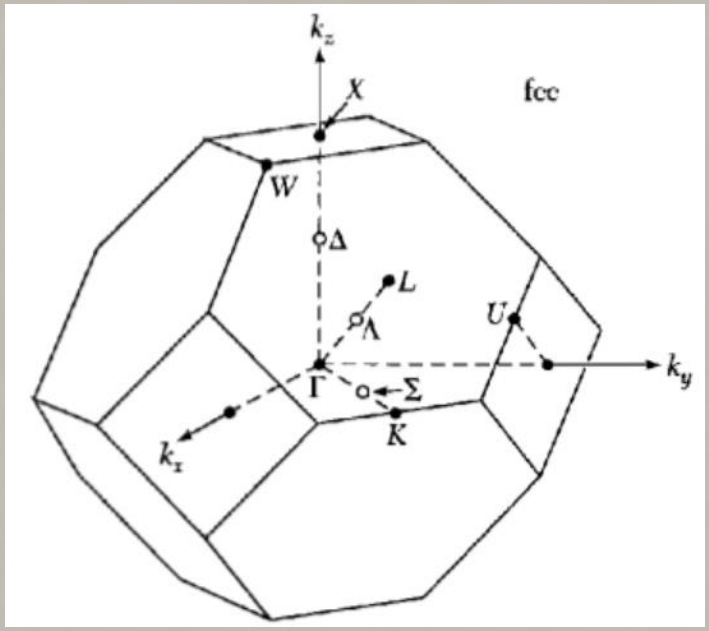
The $p_{3/2}$ level is fourfold degenerate as in the atom; the four states correspond to J (=L±S), values $\pm 3/2$ and $\pm 1/2$. The $p_{1/2}$ level is doubly degenerate, with $m_J = \pm 1/2$. The $p_{3/2}$ states are higher in energy than the $p_{1/2}$ states.

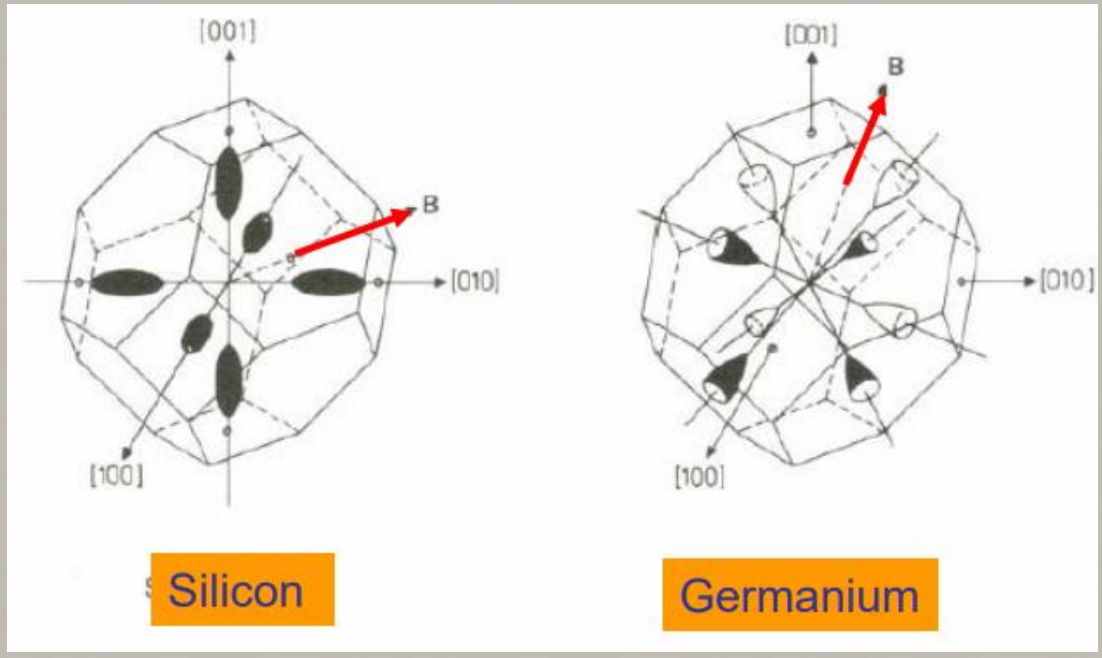
The energy surfaces are not spherical, but warped and can be determine using the following equation.

$$\epsilon(k) = Ak^2 \pm \left[B^2k^4 + C^2\left(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2\right)\right]^{1/2}$$



Silicon and Germanium





The conduction band edges in Ge are at the equivalent points L of the Brillouin zone. Each band edge has a spheroidal energy surface oriented along a <111> crystal axis, with a longitudinal mass $m_l = 1.59$ m and a transverse mass $m_t = 0.082$ m.

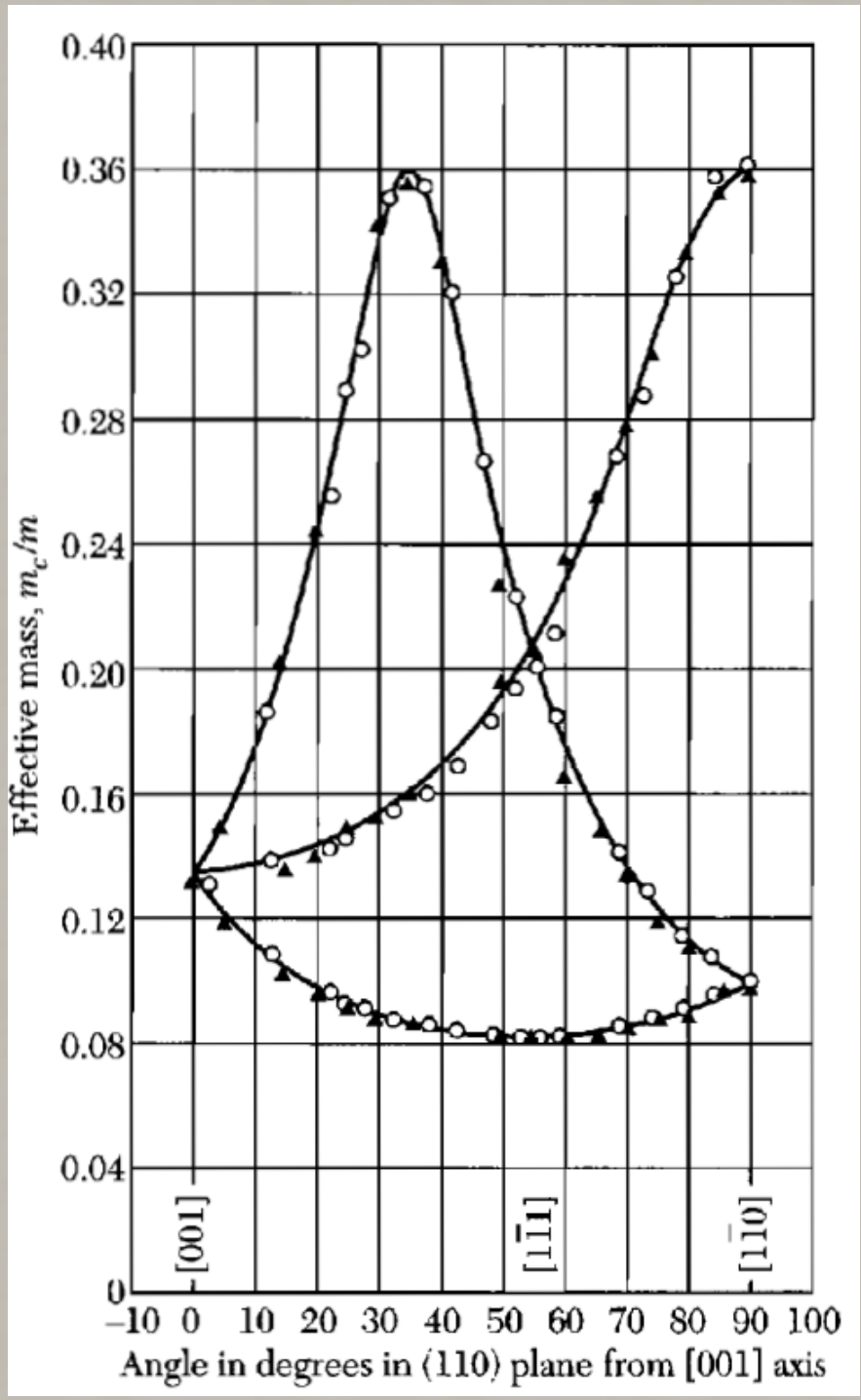
In silicon the conduction band edges are spheroids oriented along the equivalent <100> directions in the Brillouin zone, with mass parameters $m_l = 0.92$ m and $m_t = 0.19$ m, as shown in the figure.

Silicon and Germanium

For a static magnetic field at an angle θ with the longitudinal axis of a spheroid, the effective cyclotron mass m_c, is

$$\frac{1}{m_c^2} = \frac{\cos^2\theta}{m_t^2} + \frac{\sin^2\theta}{m_t m_l}$$

Effective cyclotron mass of electrons in germanium at 4 K for magnetic field directions in a (110) plane. There are four independent mas spheroids in Ge, one along each [I l l] axis, but viewed in the (110) plane two spheroids always appear equivalent.



Silicon and Germanium

Derivation of

$$\frac{1}{m_c^2} = \frac{\cos^2\theta}{m_t^2} + \frac{\sin^2\theta}{m_t m_l}.$$

Suppose a variable magnetic field applied along x and z axes; $B_y = 0$. The particle moves in a helical orbit.

$$\vec{F} = q\left(\vec{v} \times \vec{B}\right) = m\frac{d\vec{v}}{dt} \quad \text{----(1)}$$

$$\vec{F}_x = qv_yB_z = m_t^*\frac{d\vec{v}_x}{dt} \quad \text{----(2)}$$

$$\vec{F}_y = q(v_zB_x - v_xB_z) = m_t^*\frac{d\vec{v}_y}{dt} \quad \text{----(3)}$$

$$\vec{F}_z = -qv_yB_x = m_l^*\frac{d\vec{v}_z}{dt} \quad \text{----(4)}$$

Silicon and Germanium

Take derivative of Eq. 3 with respect to t.

$$m_t^* \frac{d^2\vec{v}_y}{dt^2} = q\left(\frac{dv_z}{dt}B_x - \frac{dv_x}{dt}B_z\right)$$

Eliminate $\frac{dv_z}{dt}$ and $\frac{dv_x}{dt}$, by putting its values from Eqs. 2 and 5.

$$m_t^* \frac{d^2\vec{v}_y}{dt^2} = q\left(\left(\frac{-qv_yB_x}{m_l^*}\right)B_x - \left(\frac{qv_yB_z}{m_t^*}\right)B_z\right)$$

$$\frac{d^2\vec{v}_y}{dt^2} = -v_y\left(\left(\frac{q^2B_x^2}{m_l^*m_t^*}\right) + \left(\frac{q^2B_z^2}{m_t^{*\,2}}\right)\right)$$

$$B_x = B_o \sin\theta\,, B_z = B_o \cos\theta\,, B_y = 0$$

And

$$\omega_l = \frac{qB_0}{m_l^*}, \omega_t = \frac{qB_0}{m_t^*}$$

Silicon and Germanium

$$\frac{d^2\vec{v}_y}{dt^2} = -v_y(\omega_l\omega_t \sin^2\theta + \omega_t^2 \cos^2\theta)$$

$$\frac{d^2\vec{v}_y}{dt^2} + \omega^2 v_y = 0$$

$$\omega^2 = \left(\frac{qB_0}{m_c^*}\right)^2 \equiv (\omega_l\omega_t \sin^2\theta + \omega_t^2 \cos^2\theta)$$

$$\left(\frac{qB_0}{m_c^*}\right)^2 \equiv \frac{qB_0}{m_l^*}\frac{qB_0}{m_t^*}\sin^2\theta + \left(\frac{qB_0}{m_t^*}\right)^2 \cos^2\theta$$

$$\frac{1}{m_c^{*2}} = \frac{\sin^2\theta}{m_l^* m_t^*} + \frac{\cos^2\theta}{m_t^{*2}}$$

Intrinsic Carrier Concentration

Semiconductor are called “intrinsic”, when concentration of free electrons in the conduction band and holes in the valence bands are equal.

Both n and p type charge concentration are temperature dependent

$n = \frac{1}{V}\int_{E_c}^{\infty} D_e(\epsilon) f_e(\epsilon) d\epsilon$, Electron concentration in the conduction band

$p = \frac{1}{V}\int_{-\infty}^{E_v} D_h(\epsilon) f_h(\epsilon) d\epsilon$, Hole concentration in the conduction band

At the temperatures of interest we may suppose for the conduction band of a semiconductor that $\epsilon - \mu \gg k_B T$.

Fermi Dirac Distribution $f_e(\epsilon) = \frac{1}{\exp\left[\frac{\epsilon-\mu}{k_B T}\right]+1} \approx \exp\left[-\frac{\epsilon-\mu}{k_B T}\right]$

Fermi Dirac Distribution $f_h(\epsilon) = 1 - f_e(\epsilon) = \frac{1}{\exp\left[-\frac{\epsilon-\mu}{k_B T}\right]+1} \approx \exp\left[+\frac{\epsilon-\mu}{k_B T}\right]$

Intrinsic Carrier Concentration

We want the concentration of intrinsic carriers as a function of temperature, in terms of the band gap. For semiconductors, μ is replaced by Fermi level ϵ_F.

For simplicity, we do the calculation for parabolic band edges $\epsilon \propto k^2$.

Energy of electron in conduction band

$$\epsilon_k = E_c + \frac{\hbar^2 k^2}{2m_e}$$

Density of states, $D_e(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\epsilon - E_c}$

Energy of hole in valence band,

$$\epsilon_k = E_v - \frac{\hbar^2 k^2}{2m_h}$$

Density of states, $D_h(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}\sqrt{E_v - \epsilon}$

Intrinsic Carrier Concentration

The concentration of electrons in the conduction band at $k_B T$ is:

$$n = \frac{1}{V}\int_{E_c}^{\infty} D_e(\epsilon) f_e(\epsilon) d\epsilon$$

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

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

Let $x = \frac{(\epsilon - E_c)}{k_B T}$ $\quad \Rightarrow \frac{\epsilon}{k_B T} = x + \frac{E_c}{k_B T}$, $\quad d\epsilon = k_B T dx$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e k_B T}{\hbar^2}\right)^{3/2} e^{\frac{\mu - E_c}{k_B T}} \int_0^{\infty} x^{1/2} e^{-x}\, dx$$

Intrinsic Carrier Concentration

The integral is a gamma function.

$$\int_0^\infty x^{1/2} e^{-x}\, dx = \frac{\sqrt{\pi}}{2}$$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e k_B T}{\hbar^2}\right)^{3/2} e^{\frac{\mu - E_c}{k_B T}}\, \frac{\sqrt{\pi}}{2}$$

The concentration of electrons in the conduction band is

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

The concentration of electrons is temperature dependent. The problem is solved for n when μ is known.

- **Intrinsic Carrier Concentration**
- **Intrinsic Mobility**
- **Impurity conductivity**
- **Thermal Ionization of Donors and Acceptors**

Intrinsic Carrier Concentration

It is useful to calculate the equilibrium concentration of holes p. The distribution function f_h for holes is related to the electron distribution function by $f_h = 1 - f_e$, because a hole is the absence of an electron.

$$p = \frac{1}{V}\int_{-\infty}^{E_v} D_h(\epsilon) f_h(\epsilon) d\epsilon$$

$$p = \frac{1}{V}\int_{-\infty}^{E_v} \frac{V}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} (E_v - \epsilon)^{1/2} e^{\frac{(\epsilon-\mu)}{k_B T}}\, d\epsilon$$

$$p = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} e^{-\frac{\mu}{k_B T}} \int_{-\infty}^{E_v} (E_v - \epsilon)^{1/2} e^{\frac{\epsilon}{k_B T}}\, d\epsilon$$

Let $x = \frac{(E_v-\epsilon)}{k_B T}$ $\quad \Rightarrow \frac{\epsilon}{k_B T} = -x + \frac{E_v}{k_B T}$, $\quad d\epsilon = -k_B T dx$

$$p = -\frac{1}{2\pi^2}\left(\frac{2m_h k_B T}{\hbar^2}\right)^{3/2} e^{\frac{E_v-\mu}{k_B T}} \int_{\infty}^{0} x^{1/2} e^{-x}\, dx$$

Intrinsic Carrier Concentration

This integral is also a gamma function.

$$\int_{\infty}^{0} x^{1/2} e^{-x}\, dx = -\int_{0}^{\infty} x^{\frac{3}{2}-1} e^{-x}\, dx = \Gamma(3/2) = -\frac{\sqrt{\pi}}{2}$$

$$p = +\frac{1}{2\pi^2}\left(\frac{2m_h k_B T}{\hbar^2}\right)^{\frac{3}{2}} e^{\frac{E_v-\mu}{k_B T}} \frac{\sqrt{\pi}}{2}$$

The concentration of holes in the valence band is

$$p = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\frac{E_v-\mu}{k_B T}}.$$

Similar to the concentration of electrons, the concentration of holes is also temperature dependent.

Intrinsic Carrier Concentration

We multiply together the expressions for n and p to obtain the equilibrium relation, with the energy gap $E_g = E_c - E_v$ and eliminate the Fermi energy μ.

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

This product of the electron and hole concentrations is a constant and is independent of impurity concentration at a given temperature.

If one carrier concentration was desired more than the other then introduction of a small proportion of a suitable impurity can increase n (or p) and decrease p (or n). Such semiconductors are called **extrinsic semiconductors.**

This result is important in practice-we can reduce the total carrier concentration $n + p$ in an impure crystal, sometimes enormously, by the controlled introduction of suitable impurities. Such a reduction is called **compensation**.

Intrinsic Carrier Concentration

For an intrinsic semiconductor $n = p$

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

The dependence of Fermi level on temperature and its location inside the band gap is obtained by setting $n = p$.

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

$$e^{\frac{2\mu}{k_B T}} = \left(\frac{m_h}{m_e}\right)^{3/2} e^{\frac{E_c + E_v}{k_B T}}$$

$$\frac{2\mu}{k_B T} = \frac{3}{2} \ln\left(\frac{m_h}{m_e}\right) + \frac{E_c + E_v}{k_B T}$$

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

Intrinsic Carrier Concentration

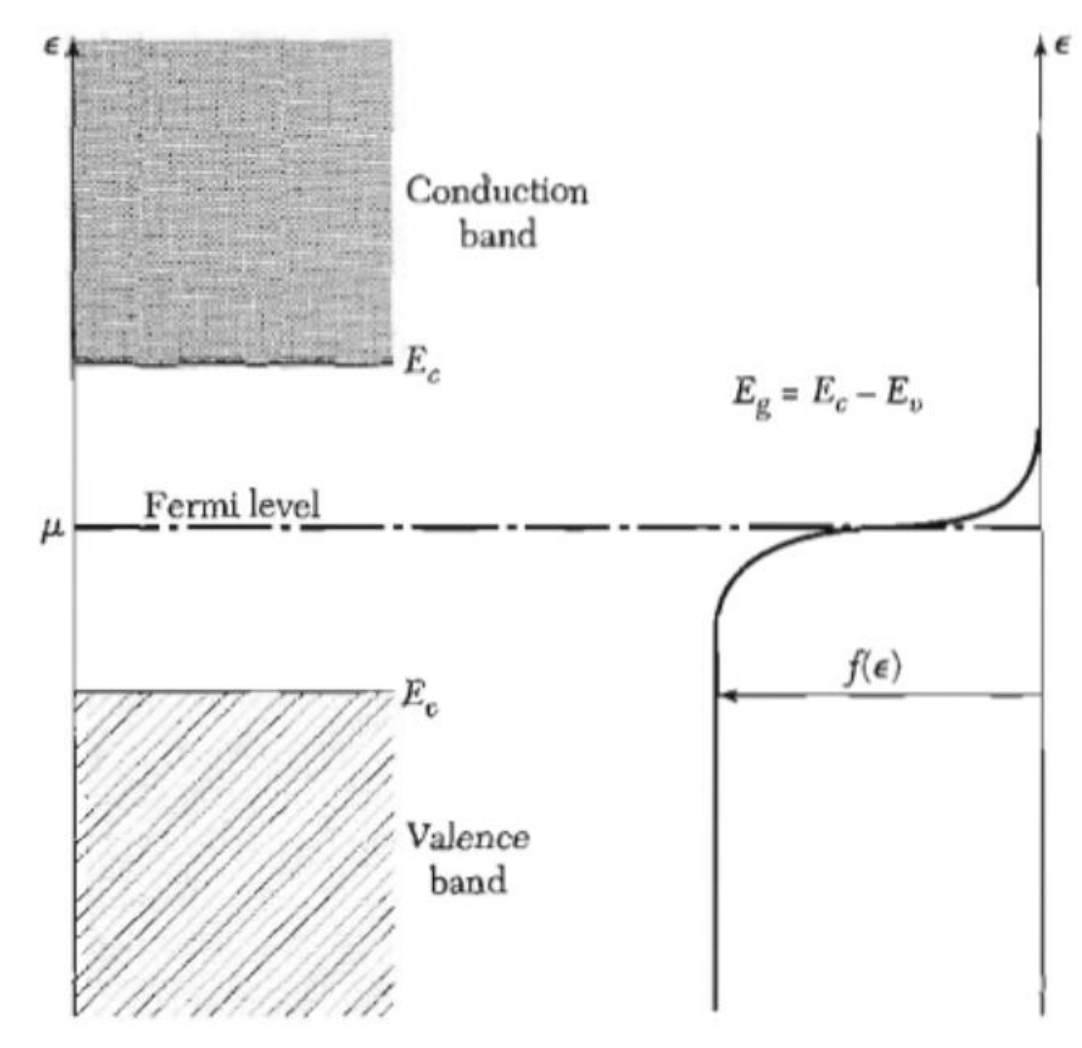
Fermi level $\mu = \frac{1}{2} E_g + \frac{3}{4} k_B T \, \ell n \left(\frac{m_h}{m_e} \right)$

At T=0, μ lies half-way between the conduction and valence bands.

As T increases, μ moves toward the band with smaller effective mass

μ does not go far from mid-gap when $m_h \approx m_e$

Intrinsic Carrier Concentration



Energy scale for statistical calculations. The Fermi distribution function is shown on the same scale, for a temperature $k_BT < E_g$. The Fermi level μ is taken to lie well within the band gap, as for an intrinsic semiconductor. If $\epsilon = \mu$, then $f = 1/2$.

Intrinsic Mobility

For semiconductors, Ohm law for current density $j = e(pv_h - nv_e)$ and electric field E is written as

$$j = \sigma E.$$

$$\sigma = e\left(\frac{pv_h}{E} - \frac{nv_e}{E}\right)$$

The electron and hole velocities are

$$v_h = \frac{eE\tau}{m_h}, \qquad v_e = -\frac{eE\tau}{m_e}$$

The conductivity becomes

$$\sigma = \frac{pe^2\tau}{m_h} + \frac{ne^2\tau}{m_e}$$

The electron mobility is $\mu_e = \frac{e\tau}{m_e}$ and hole mobility is $\mu_h = \frac{e\tau}{m_h}$.

Intrinsic Mobility

The electrical conductivity is therefore,

$$\sigma = ne\mu_e + pe\mu_h.$$

Since n, p, and τ all depends on temperature, but the temperature dependence of the carrier concentration is dominated by the exponential dependence $e^{-\frac{E_g}{2k_BT}}$. Therefore, with an increase in temperature of semiconducting sample its conductivity will increase.

Intrinsic Mobility

crystal	$\mu_e(cm^2/Vs)$	$\mu_h(cm^2/Vs)$
GaAs	8000	300
InAs	30000	450
Diamond	1800	1200
Si	1350	480
Ge	3600	1800
PbS	550	600

T=300K

The hole mobilities are typically smaller than the electron mobilities because of the occurrence of band degeneracy at the valence band edge at the zone center, thereby making possible interband scattering processes that reduce the mobility.

Impurity Conductivity

Si and Ge are group IV elements. Doping it with proper impurities can increase electrons or holes concentration.

(1) Donors – Group of V such as P, As, Sb

N-type

substitutional impurity for semiconductor

each dopant atom contribute an electron

(2) Acceptors – Group of III such as Al, Ga, In

P-type

attract electrons from valence band of semiconductor

create a hole per atom

Where do electrons / holes of the dopants go? free or bound

Low T : bound

High T : free $k_B T > E_d$ (electron), E_a (hole)

Donor activated energy

Acceptor activated energy

Activated energy – From Bohr model

Hydrogen atom

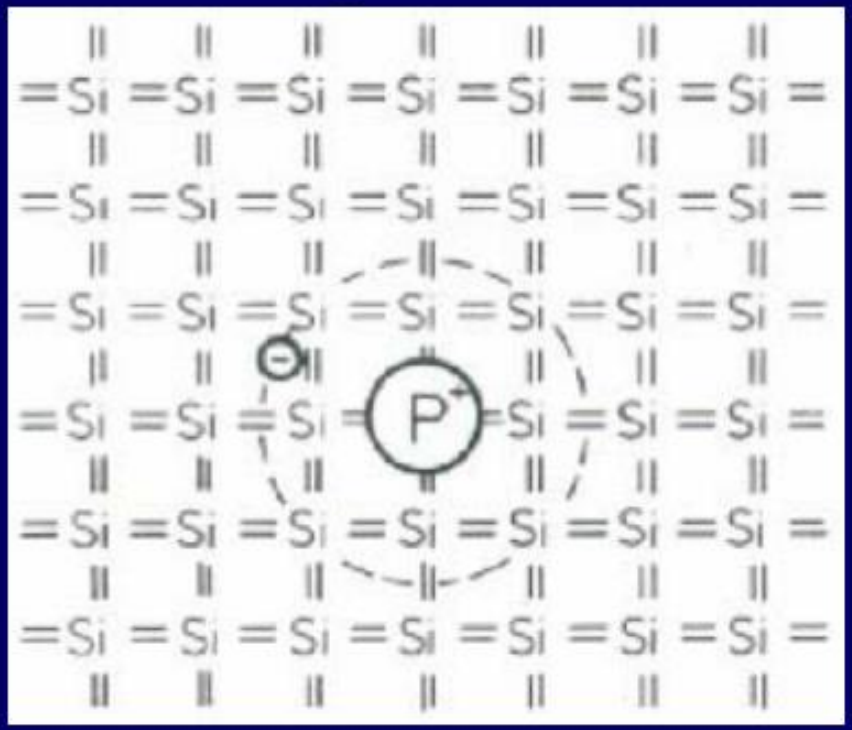
$$F = \frac{e^2}{4\pi\varepsilon_o r^2} = \frac{mv^2}{r}$$

$$r_n = \frac{4\pi\varepsilon_o \hbar^2}{me^2} n^2 = a_o n^2$$

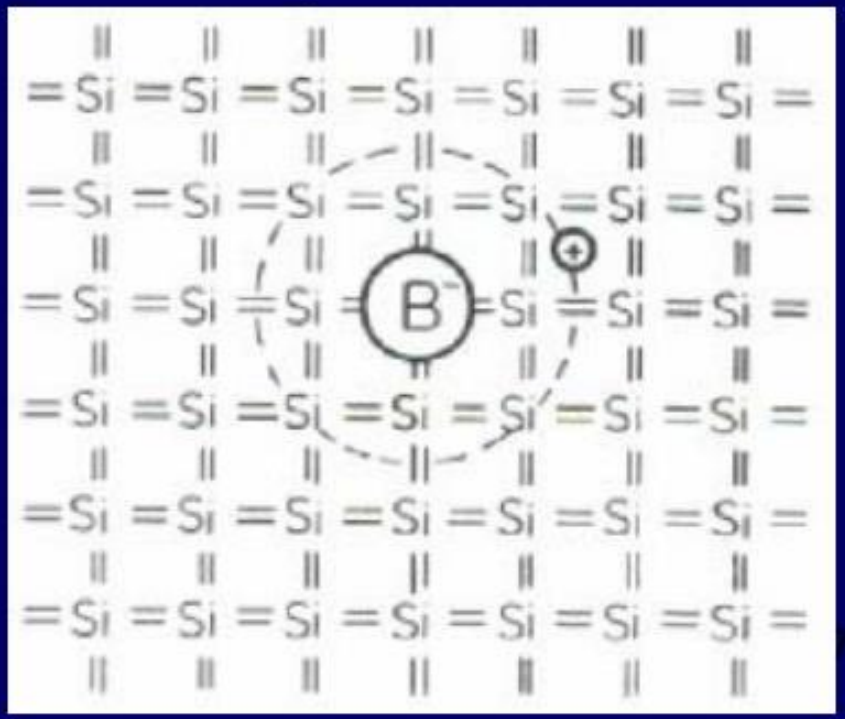
$$E_n = -\frac{e^4 m}{32\pi^2\varepsilon_o^2\hbar^2}\frac{1}{n^2} = -\frac{13.6\text{eV}}{n^2}$$

Ionization energy
13.6eV

N-doped Silicon



P-doped Silicon



Impurity Conductivity

In n-doped silicon, the 5th valence electron of P does not make bonds with neighbor atoms and thus only weakly bound with P atoms.

Its radius and binding energy can be estimated by treating the system as a hydrogen atoms embedded in a dielectric of dielectric constant $\kappa = \epsilon/\epsilon_o$ and effective mass of electron m_e.

$$a_d = \frac{4\pi\kappa\epsilon_o\hbar^2}{m_e e^2} n^2$$

For the ground state $n = 1$.

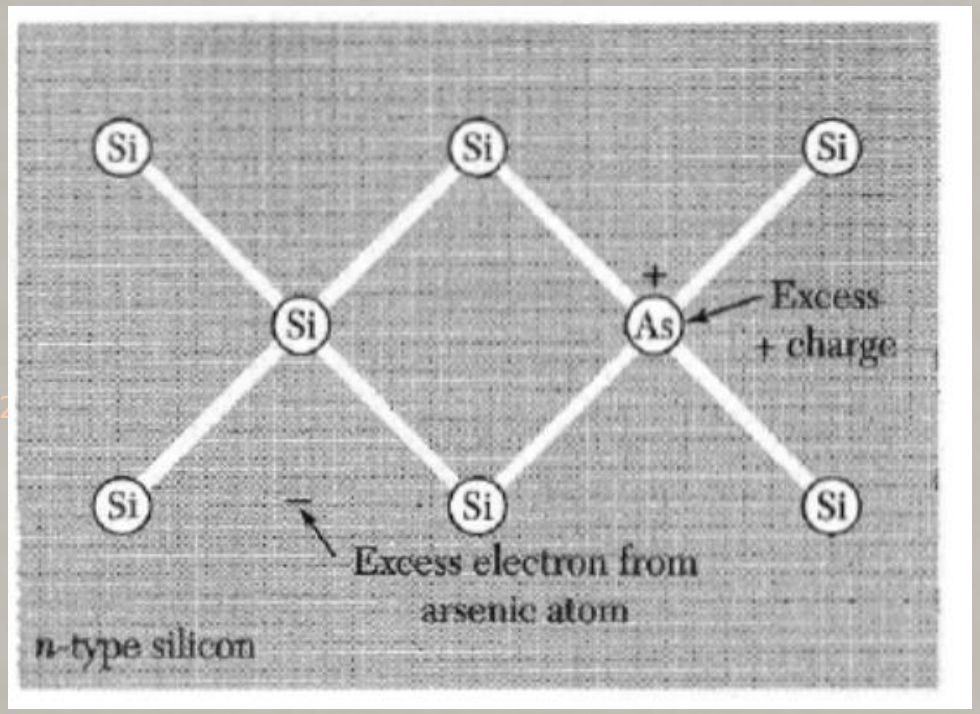
$$a_d = \frac{4\pi\epsilon_o\hbar^2}{me^2} \frac{\kappa\, m}{\mathrm{m_e}} = a_\mathrm{o} \left(\kappa \frac{m}{\mathrm{m_e}}\right),$$

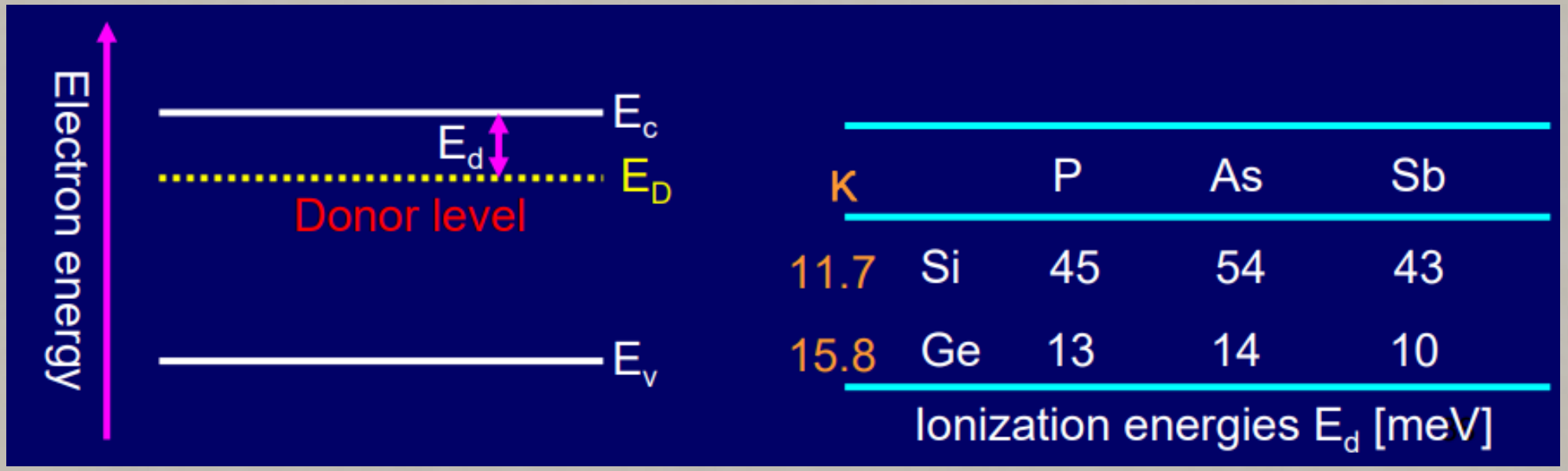
where a_o is the Bohr radius. Binding energy of the donor state electron is

$$E_d = -\frac{e^4 m_e}{32\pi^2\kappa^2\epsilon_o^2\hbar^2} \frac{1}{n^2} = \frac{-13.6\ eV}{\kappa^2} \left(\frac{m_e}{m}\right)$$

For semiconductor with $\kappa = 10$ and $\frac{m}{m_e} = 10, \Rightarrow a_d = 52.9$ Å and $E_d = -13.6\ meV$

Impurity Conductivity





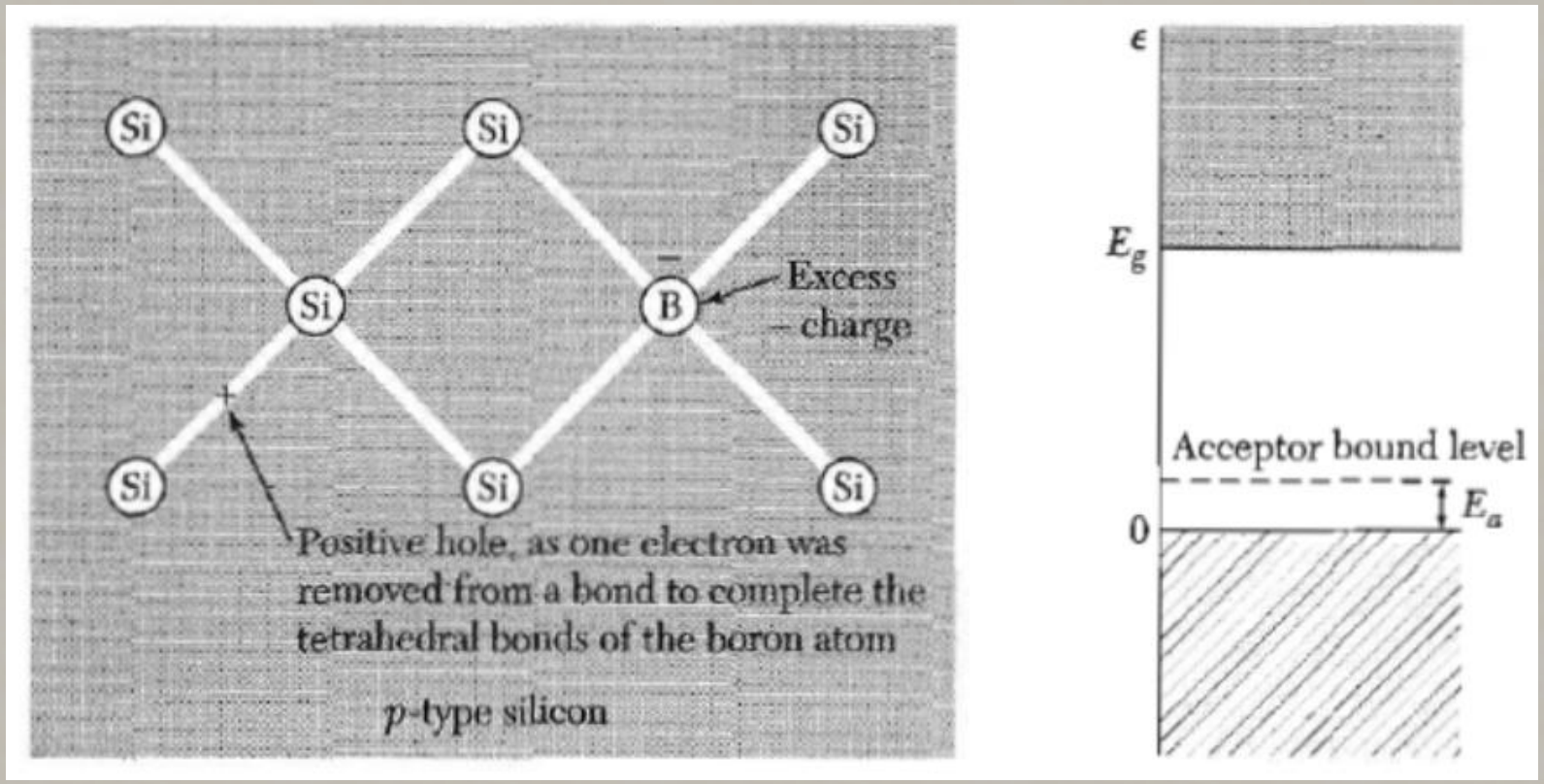
K		P	As	Sb
11.7	Si	45	54	43
15.8	Ge	13	14	10

Ionization energies E_d [meV]

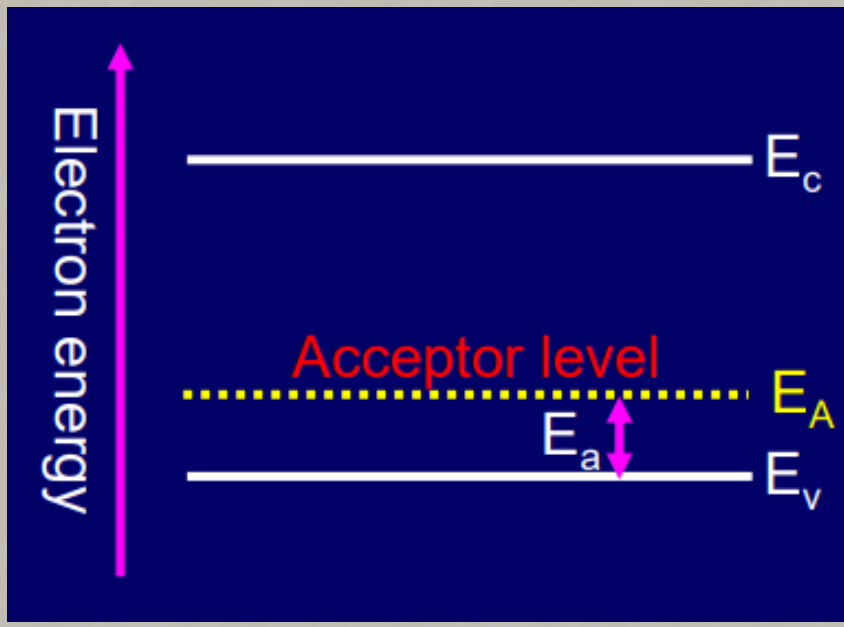
Impurity Conductivity

In p-doped silicon, the dopant has less number of valence electrons than Si. For example, B has 3 electrons, therefore, each B atom creates one hole, which orbits around it in the valence band.

The Bohr model applies qualitatively for the holes just as for the electrons, but due to degeneracies at the top of valence band complicates the effective mass problem.



Impurity Conductivity



	B	Al	Ga	In
Si	45	57	65	157
Ge	10.4	10.2	10.8	11.2

Ionization energies E_a [meV]

Thermal Ionization of Donors and Acceptors

The calculation of the equilibrium concentration of conduction electrons from ionized donors is identical with the standard calculation in statistical mechanics of the thermal ionization of hydrogen atoms.

For n-type semiconductor, the Fermi level lies between donor level and conduction band.

$$\epsilon_{Fn} = \frac{E_d + E_c}{2} + \frac{1}{2} k_B T \ln\left(\frac{N_d}{N_c}\right) --- (1)$$

For p-type semiconductor, the Fermi level lies between accepter level and valence band.

$$\epsilon_{Fp} = \frac{E_a + E_v}{2} + \frac{1}{2} k_B T \ln\left(\frac{N_a}{N_v}\right) --- (2)$$

In the above energies, N_d and N_a are the densities of donors and acceptors.

Thermal Ionization of Donors and Acceptors

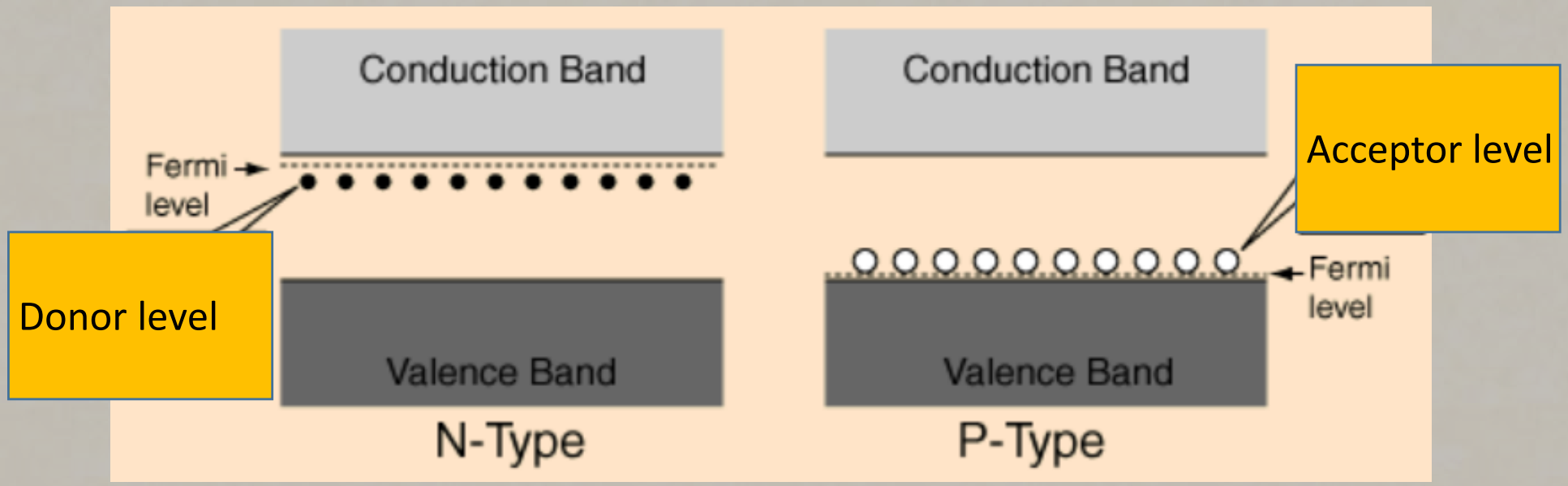
The electron concentration in n-type semiconductor is

$$n = (2N_d)^{1/2}\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-\frac{E_d}{2\,k_B T}}.$$

The hole concentration in p-type semiconductor is

$$p = (2N_a)^{1/2}\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-\frac{E_a}{2\,k_B T}}.$$

The electron and hole concentrations are temperature dependent. With an increase in the sample temperature, the concentration of electrons in the conduction and holes in the valence bands will increase.



Thermal Ionization of Donors and Acceptors

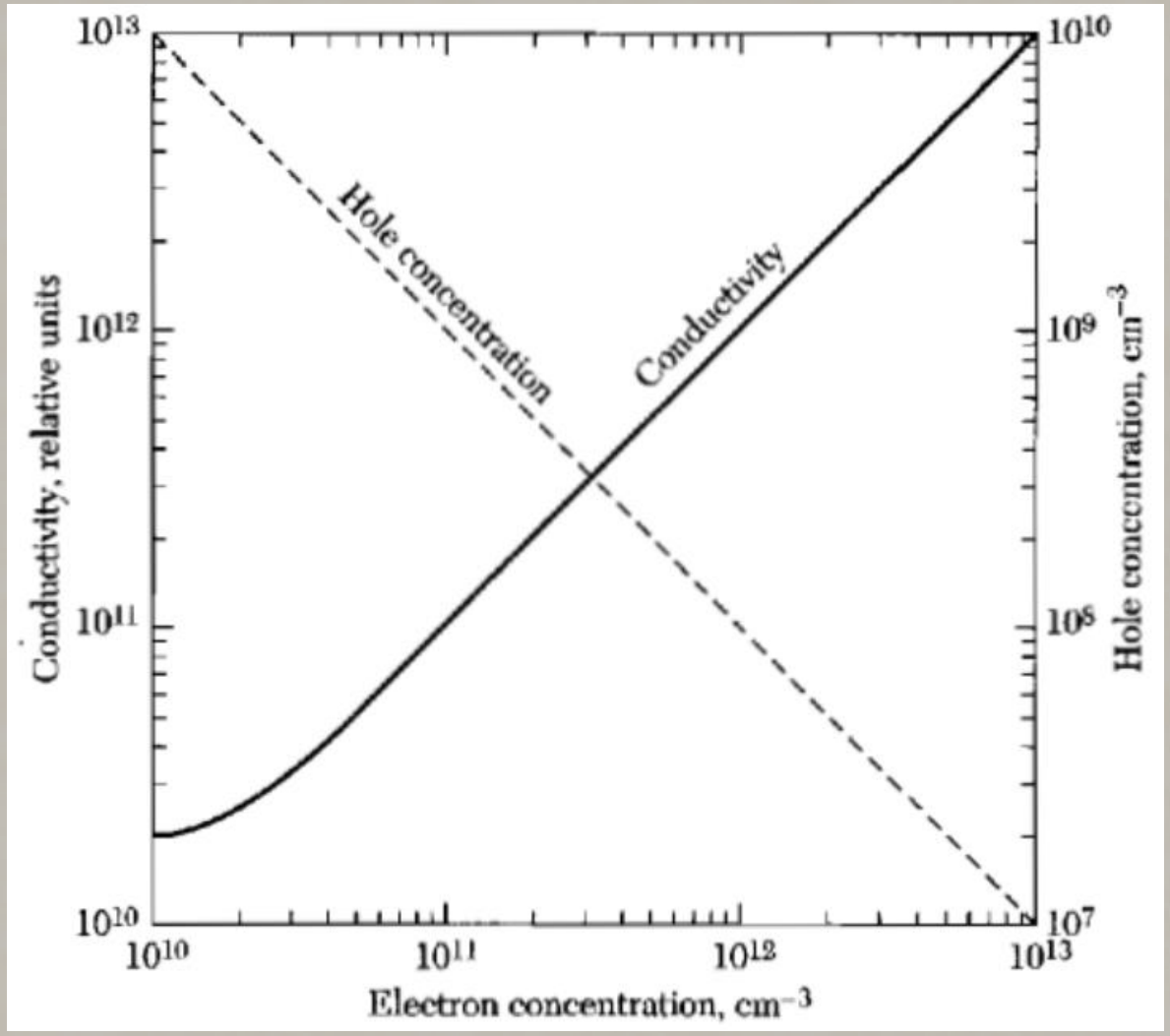


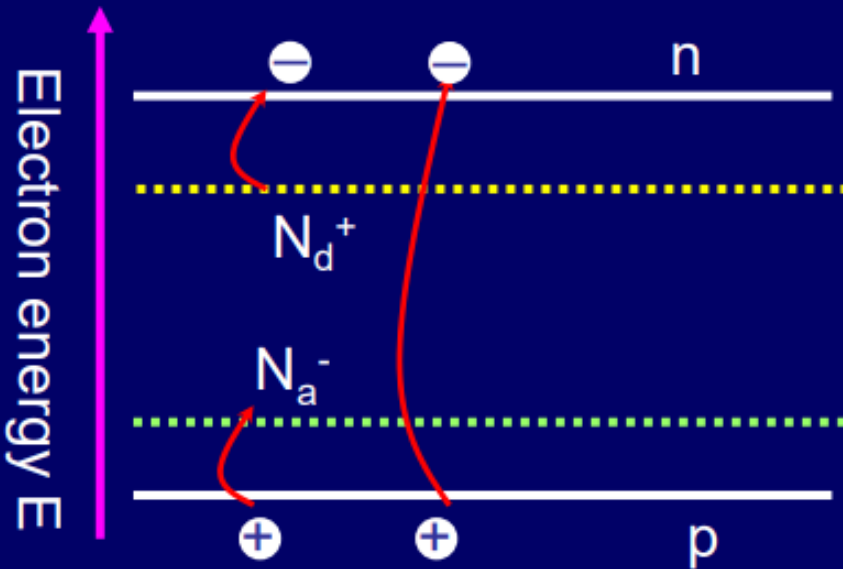
Figure 22 Electrical conductivity and hole concentration p calculated as a function of electron concentration n for a semiconductor at a temperature such that $np = 10^{20}$ cm^{-6}. The conductivity is symmetrical about $n = 10^{10}$ cm^{-3}. For $n > 10^{10}$, the specimen is n type; for $n < 10^{10}$, it is p type. We have taken $\mu_e = \mu_h$, for the mobilities.

Derivation of the electron and hole concentrations

In a doped semiconductor,

an electron in the conduction band can originate either from the valence band or from the ionization of a donor;

a hoe in a valence band may correspond either to the electron in the conduction band or to the negatively charged acceptor.



(neutral)
Density of doped donor $N_d = N_d^o + N_d^+$
(ionized) donor

(neutral)
Density of doped acceptor $N_a = N_a^o + N_a^-$
(ionized) acceptor

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

$$N_d^o = N_d \frac{1}{\exp[(E_D - E_F)/k_B T] + 1}$$

$$N_a^o = N_a \frac{1}{\exp[(E_F - E_A)/k_B T] + 1}$$

For pure N-type semiconductor : only donors are available

$$n = n_o \exp\left(\frac{E_F - E_c}{k_B T}\right) \quad \text{where} \quad n_o = 2\left(\frac{k_B T m_e}{2\pi\hbar^2}\right)^{3/2} \quad \text{and} \quad p_o = 2\left(\frac{k_B T m_h}{2\pi\hbar^2}\right)^{3/2}$$

$$N_d = N_d^o + N_d^+$$

And $n = N_d^+ + p$

For the simple case $N_d^+ >> n_i$ $k_B T << E_g$ therefore, $n \sim N_d^+ = N_d - N_d^o$

$$n \approx N_d - N_d^o = N_d\left(1 - \frac{1}{\exp[(E_D - E_F)/k_B T] + 1}\right) = N_d\left(\frac{1}{1 + \exp[-(E_D - E_F)/k_B T]}\right)$$

$$\frac{n}{n_o}\exp\left(\frac{E_c}{k_B T}\right) = \exp\left(\frac{E_F}{k_B T}\right)$$

$$n \approx N_d\left(\frac{1}{1 + \frac{n}{n_o}\exp[E_c/k_B T]\exp[-E_D/k_B T]}\right)$$

$$n\left(1 + \frac{n}{n_o}\exp\left[\frac{E_d}{k_B T}\right]\right) \approx N_d \rightarrow \frac{1}{n_o}\exp\left[\frac{E_d}{k_B T}\right]n^2 + n - N_d = 0$$

solution $$n = \frac{n_o}{2}\exp\left(-\frac{E_d}{k_B T}\right)\left[-1+\sqrt{1+4\frac{N_d}{n_o}\exp\left(\frac{E_d}{k_B T}\right)}\right]$$

At low temperatures, such that $$4\frac{N_d}{n_o}\exp\left(\frac{E_d}{k_B T}\right) >> 1$$

$$n \approx \sqrt{n_o N_d}\exp\left[-\frac{E_d}{2k_B T}\right]$$

Freeze-out range

A sufficiently large number of donors still retain their valence electrons, i.e. are not ionized.

At the intermediate temperatures, such that $$4\frac{N_d}{n_o}\exp\left(\frac{E_d}{k_B T}\right) << 1$$

$$n \approx N_d = \text{constant}$$

Saturation range

The concentration of donor electrons in the conduction band has reached the maximum possible value, equal to the concentration of donor.
All donors are ionized.

- **Intrinsic Mobility**
- **Impurity conductivity**

  Thermal Ionization of Donors and Acceptors
- **Thermoelectric Effects**
- **Semimetals**
- **Superlattices**

  Bloch Oscillator

  Zener Tunneling

Thermoelectric Effects

Consider a semiconductor maintained at a constant temperature while an electric field drives through it an electric current density j_d. If the current is carried only by electrons, the charge flux is

$$j_d = n(-e)(-\mu_e)E \quad --(1)$$

If the average energy transported by an electron is referred to the Fermi level μ is,

$$< \epsilon_e > = (E_c - \mu) + \frac{3}{2} k_B T \quad --(2)$$

then the energy flux that accompanied the charge flux is

$$j_U = n\left[(E_c - \mu) + \frac{3}{2} k_B T\right](-\mu_e)E \quad --(3)$$

The Peltier coefficient Π is defined by $j_U = \Pi\, j_e$; or the energy carried per unit charge.

Thermoelectric Effects

The Peltier coefficient Π for electrons is

$$\Pi_e = -\frac{\left[(E_c - \mu) + \frac{3}{2}k_B T\right]}{e}$$

and is negative because the energy flux is opposite to the conventional charge flux.

Similarly, the Peltier coefficient Π for holes is

$$\Pi_h = +\frac{\left[(\mu - E_v) + \frac{3}{2}k_B T\right]}{e}.$$

The absolute thermoelectric power Q (seebeck coefficient) is defined from the open circuit electric field created by a temperature gradient

$$E = Q\nabla T$$

The Peltier coefficient Π is related to the thermoelectric power Q by

$$\Pi = QT,$$

which is the famous Kelvin relation of irreversible thermodynamics.

Thermoelectric Effects

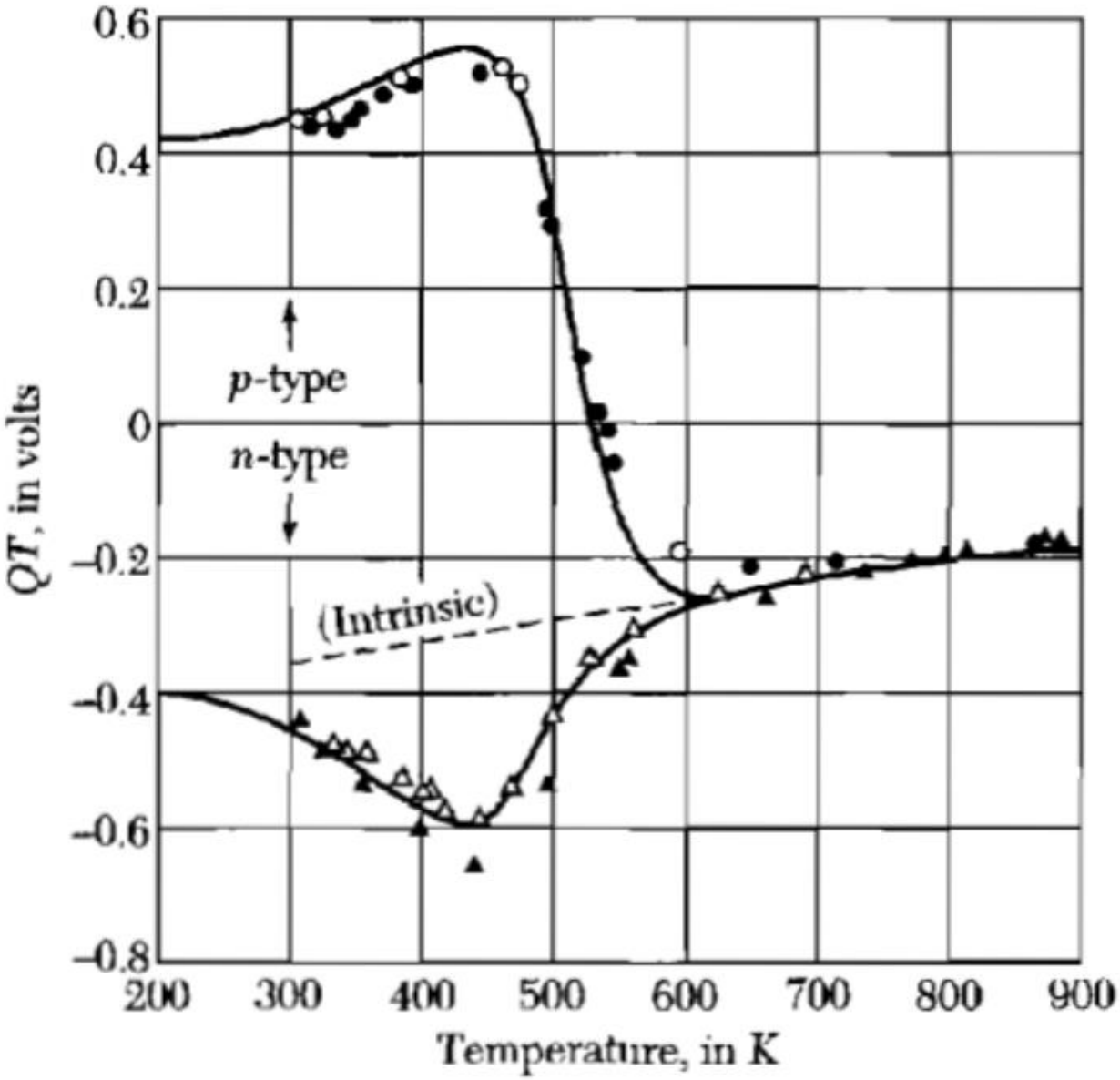


Figure 23 Peltier coefficient of n and p silicon as a function of temperature. Above 600 K the specimens act as intrinsic semiconductors. The curves are calculated and the points are experimental. (After T. H. Geballe and G. W. Hull.)

Semimetals

- In semimetals the conduction band edge is very slightly lower in energy than the valence band edge. A small overlap in energy of the conduction and valence bands leads to small concentration of holes in the valence band and of electrons in the conduction band. Three of the semimetals, arsenic, antimony, and bismuth, are in group V of the periodic table.

- Their atoms associate in pairs in the crystal lattice, with two ions and ten valence electrons per primitive cell. The even number of valence electrons could allow these elements to be insulators.

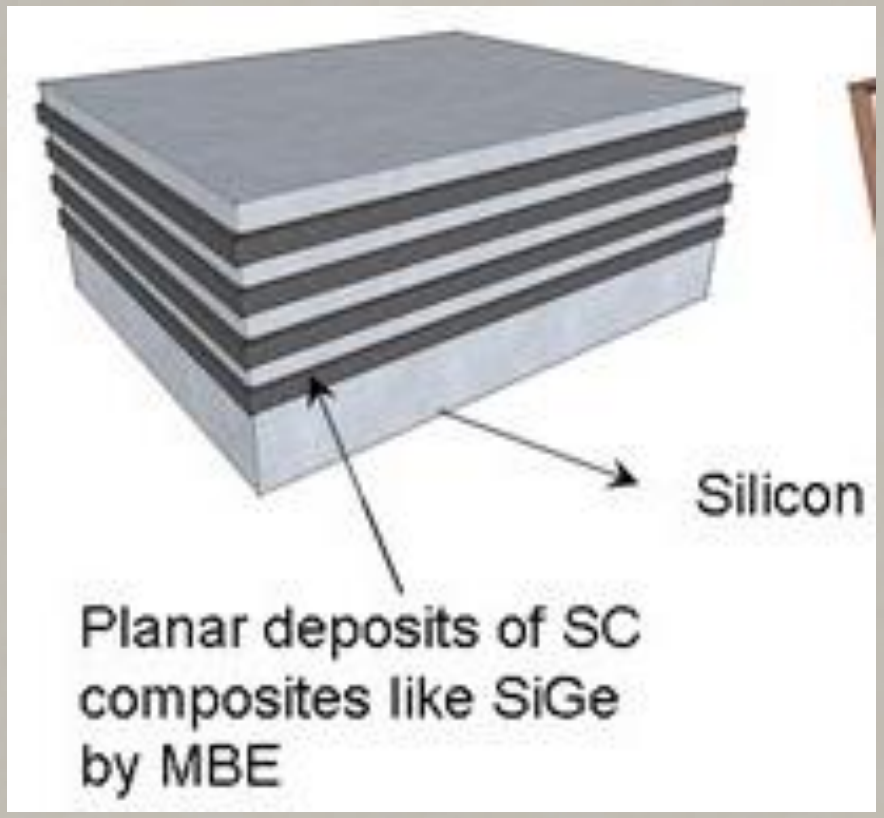
- Like semiconductors, the semimetals may be doped with suitable impurities to vary the relative numbers of holes and electrons. Their concentrations may also be varied with pressure, for the band edge overlap varies with pressure.

Table 7 Electron and hole concentrations in semimetals

Semimetal	n_e, in cm^{-3}	n_h, in cm^{-3}
Arsenic	$(2.12 \pm 0.01) \times 10^{20}$	$(2.12 \pm 0.01) \times 10^{20}$
Antimony	$(5.54 \pm 0.05) \times 10^{19}$	$(5.49 \pm 0.03) \times 10^{19}$
Bismuth	2.88×10^{17}	3.00×10^{17}
Graphite	2.72×10^{18}	2.04×10^{18}

Superlattices

Coherent layers on a nanometer thickness scale may be deposited by molecular-beam epitaxy, metal-organic vapor deposition, or RF/DC sputtering thus building up a superperiodic structure on a large scale.



Bloch Oscillator

Consider a collisionless electron in a periodic lattice in one dimension, with motion normal to the planes of the superlattice.

We consider the motion in a model system in real space. We suppose that the electron lies in a simple energy band of width ϵ_0 and layer thickness of A.

$$\epsilon = \epsilon_0(1 - coskA).$$

The velocity in k-space (momentum space) is

$$v = \frac{1}{\hbar}\frac{d\epsilon}{dk} = \frac{A\epsilon_0}{\hbar}\, sinkA$$

and the position or the electron in real space, with the initial condition z = 0 at t = 0, is given by

$$z = \int_0^t v\, dt = \int_0^k \frac{A\epsilon_0}{\hbar}\, sinkA\, \frac{dt}{dk} dk = \int_0^k \frac{A\epsilon_0}{\hbar}\, sinkA \left(-\frac{\hbar}{eE}\right) dk$$

Using relation $\frac{dk}{dt} = -\frac{eE}{\hbar}$

Bloch Oscillator

$$z = \frac{A\epsilon_0}{\hbar}\left(-\frac{\hbar}{eE}\right)\frac{1}{A}(\cos kA - 1) = -\frac{\epsilon_0}{eE}(\cos kA - 1)$$

For $k = -\frac{\mathrm{eEt}}{\hbar}$

$$z = -\frac{\epsilon_0}{eE}\left[\cos\left(-\frac{\mathrm{eEt}}{\hbar}A\right) - 1\right]$$

With the Bloch oscillation frequency in real space $\omega_B = \frac{\mathrm{eEt}}{\hbar}A$.

Zener Tunneling

Under a high reverse-bias voltage, the depletion of pn-junction region widens which leads to a high-strength electric field across the junction. At sufficiently strong electric fields the tunneling of electrons across the depletion region of a semiconductor increase free charge carriers. This sudden generation of carriers rapidly increases the reverse current and gives rise to the high slope conductance of the Zener diode.