Fig. 13  Measured ionization energies for various impurities in Ge, Si, and GaAs. The levels below the gap centers are measured from the top of the valence band and are acceptor levels unless indicated by D for donor level. The levels above the gap centers are measured from the bottom of the conduction-band level and are donor levels unless indicated by A for acceptor level. The bandgaps at 300 K are 0.66, 1.12, and 1.42 eV for Ge, Si, and GaAs, respectively. (After Conwell, Ref. 27; Sze and Irvin, Ref. 28; Milnes, Ref. 24.)
Extrinsic Semiconductors

An extrinsic semiconductor is defined as a semiconductor in which controlled amounts of specific dopant or impurity atoms have been added so that the thermal-equilibrium electron and hole concentration are different from the intrinsic carrier concentration. One type of carrier will be predominant.

Adding impurities will change the distributions of electrons and holes in the material and since the Fermi level is related to the distribution function $E_F$ will also change.

In the figure: $E_F > E_g/2$, $n_o > p_o$, n-type

$$n_o = N_C \exp \left[ \frac{-(E_c - E_F)}{kT} \right]$$

$$p_o = N_V \exp \left[ \frac{-(E_F - E_v)}{kT} \right]$$

![Figure 4-8](image.png) Density of states functions, Fermi-Dirac probability function, and areas representing electron and hole concentrations for the case when $E_F$ is above the midgap energy.
Carrier distribution of a p-type semiconductor

\[ E_F < \frac{E_g}{2} \]

\[ p_0 > n_0 \quad \text{p-type semiconductor} \]
Extrinsic Semiconductors

The expressions previously derived for the thermal-equilibrium concentrations of electrons and holes are general:

\[ n_o = N_C \ exp\left(-\frac{(E_C - E_F)}{kT}\right) \quad p_o = N_v \ exp\left(-\frac{(E_F - E_V)}{kT}\right) \]

for n-type semiconductor electrons are majority carriers and holes minority
for p-type semiconductor holes are majority carriers and electrons minority

\[ n_o p_o \]

\[ n_o p_o = N_C N_v \ exp\left(-\frac{(E_C - E_F)}{kT}\right) \ exp\left(-\frac{(E_F - E_V)}{kT}\right) = N_C N_v \ exp\left(-\frac{E_G}{kT}\right) \]

\[ n_o p_o = n_i^2 \]

The product is always a constant for a given semiconductor at a given temperature (only when the Boltzmann approximation is valid).
Non validity of the Boltzmann approximation

If \((E_c - E_F) >> kT\) then \((E - E_F) >> kT\) the Fermi probability function reduces to the Boltzmann approximation

\[
f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \approx \exp\left[-\frac{(E - E_F)}{kT}\right]
\]

If the Boltzmann approximation does not hold \((E - E_F) \sim kT\) \((E_F\) very close to the conduction band) :

\[
n_o = \frac{4\pi(2m^*)^{3/2}}{h^3} \int_{E_c}^{\infty} \frac{\sqrt{E - E_c}}{1 + \exp\left[-\frac{(E - E_F)}{kT}\right]} dE
\]

If we again make a change of variable

\[
\eta = \frac{E - E_C}{kT}
\]

and also define

\[
\eta_F = \frac{E_F - E_C}{kT}
\]
Non validity of the Boltzmann approximation

\[ n_0 = \frac{4\pi(2m_n^*)^{3/2}}{h^3} \int_0^\infty \frac{\eta^{1/2}}{1 + \exp[(\eta - \eta_F)]} d\eta \]

The integral is defined as

\[ F_{1/2}(\eta_F) = \int_0^\infty \frac{\eta^{1/2}}{1 + \exp[(\eta - \eta_F)]} d\eta \]

This function is called Fermi-Dirac integral and is a tabulated function of the variable \( \eta_F \).

The same general method can be used to calculate the thermal equilibrium hole concentration

\[ p_0 = \frac{4\pi(2m_p^*)^{3/2}}{h^3} \int_0^\infty \frac{(\eta')^{1/2}}{1 + \exp[(\eta' - \eta_F')] d\eta'} \quad \eta' = \frac{E_V - E}{kT} \quad \text{and} \quad \eta_F' = \frac{E_V - E_F}{kT} \]
Example

Ex: Si at 300°K

\[ \eta_F = 2 \quad E_C - E_F = 52 \text{meV} \quad kT = 25 \text{meV} \quad E_C - E_F \approx KT \]

\[ n_0 = \frac{2}{\sqrt{\pi}} N_C F_{1/2}(\eta_F) \quad N_C = 2.8 \times 10^{19} \text{cm}^{-3} \quad \text{and} \quad F_{1/2}(2) = 2.3 \]

\[ n_0 = \frac{2}{\sqrt{\pi}} (2.8 \times 10^{19})(2.3) = 7.27 \times 10^{19} \text{cm}^{-3} \]

Note if we would used the Boltzmann approximation (not valid in this case)

\[ n_0 = 2.08 \times 10^{20} \text{cm}^{-3} \]
In the previous discussion of adding dopant atoms to a semiconductor we have implicitly assumed that the concentration of dopant atoms added is small when compared to the semiconductor atoms (~$10^{24} \text{ cm}^{-3}$). The impurity atoms are spread far enough apart so that there is not interactions between donor electrons. We have assumed that the impurities introduce discrete, noninteracting donor (acceptor) energy states in n-type (p-type) semiconductor (nondegenerate semiconductor).

If the impurity concentration increases the distance between the impurity atoms decreases and at one point the donor (acceptor) electrons will begin to interact with each other. When this occurs the single discrete donor (acceptor) energy state will split into a band of energies and may overlap the bottom of the conduction band. When the electron (hole) concentrations exceeds $N_c$ then $E_F$ lies within the conduction band (degenerate semiconductor).
Nondegenerate and Degenerate Energy-bands

Nondegenerate semiconductor

- Small $N_d$ or $N_a$ and $E_F$ in the gap

Degenerate semiconductor

- High $N_d$ or $N_a$
Statistics of donors and acceptors

The derivation of the Fermi-Dirac probability function was derived considering the Pauli exclusion principle. This principle also applies to the donor and acceptor states.

The statistics of filling band gap levels differs slightly from the statistics of filling energy band levels. A donor site can accommodate only one electron however the donor-site electron can have either spin-up and a spin-down (g=2 spin degeneracy). This fact increases the ways of arranging electrons on the donor-level sites.

The probability function of electrons occupying the donor state is:

\[
n_d = \frac{N_d}{1 + \frac{1}{g} \exp\left(\frac{E_d - E_F}{kT}\right)}
\]

where \(n_d\) is the electron density occupying the donor level and

\(E_d\) is the donor energy level

\(g = 2\)

\[
n_d = N_d - N_d^+
\]

\(N_d\) = density of the donor atoms
\(N_d^+\) = density of ionized donors
Statistics of acceptors

The same for acceptor atoms:

\[ p_a = \frac{N_a}{1 + \frac{1}{g} \exp\left(\frac{E_F - E_a}{kT}\right)} = N_a - N_a^- \]

where \( p_a \) is the hole density occupying the acceptor level and

\[ E_a \] is the acceptor energy level

\( g = 2 \times 2 = 4 \) for Si and GaAs due to two-fold (heavy and light-hole) degeneracy of the valence band

\[ N_a = \text{density of the acceptor atoms} \]
\[ N_a^- = \text{density of ionized acceptor atoms} \]
Number of electrons in the donor state

If we assumed \((E_d - E_F) \gg kT\)

\[
n_d \approx \frac{N_d}{1 + \exp \left( \frac{E_d - E_F}{kT} \right)} = 2N_d \exp \left[ -\frac{(E_d - E_F)}{kT} \right]
\]

In this condition the Boltzmann approximation is also valid then for the electron in the conduction band we have:

\[
n_o = N_C \exp \left[ -\frac{(E_C - E_F)}{kT} \right]
\]

We would like to determine the relative number of electrons in the donor state compared to the total number of electrons:

\[
\frac{n_d}{n_d + n_o} = \frac{2N_d \exp \left[ -\frac{(E_d - E_F)}{kT} \right]}{2N_d \exp \left[ -\frac{(E_d - E_F)}{kT} \right] + N_C \exp \left[ -\frac{(E_C - E_F)}{kT} \right]} = \frac{1}{1 + \frac{N_C}{2N_d} \exp \left[ -\frac{(E_C - E_d)}{kT} \right]}
\]
Complete Ionization

Ex: we want to determine the fraction of electrons are still in the donor state at $T=300^\circ K$
in the case of P donor atoms in Si ($N_d=10^{16}\text{cm}^{-3}$).

\[
\frac{n_d}{n_d + n_o} = \frac{1}{1 + \frac{2.8 \times 10^{19}}{2(10^{16})} \exp\left[\frac{-(0.045)}{0.0259}\right]} = 0.0041 = 0.4\%
\]

This example shows that at RT only few electrons are in the donor state compared with the conduction band. Only 0.4% of the donor states contain electrons: the donor states are said to be completely ionized. The same is valid for the acceptor states.

Therefore at RT all donor (acceptor) atoms have donated an electron to the conduction band.
The opposite occurs at $T=0^\circ K$. All electrons are in their lowest possible energy state

$$n_d = N_d \text{ or } N_d^+ = 0$$

$$n_d = \frac{N_d}{1 + \frac{1}{2} \exp\left(\frac{E_d - E_F}{kT}\right)} \Rightarrow$$

$$\exp\left(\frac{E_d - E_F}{kT}\right) = 0; \exp(-\infty) = 0$$

$$\Rightarrow E_F > E_d$$

Figure 4-13  Energy-band diagram at $T = 0^\circ K$ for (a) n-type and (b) p-type semiconductors.
Compensated semiconductors

In thermal equilibrium the semiconductor crystal is electrically neutral. This charge-neutrality condition is used to determine the thermal-equilibrium electron and hole concentrations as a function of the impurity doping concentration.

A compensated semiconductor is one that contains both donor and acceptor impurity atoms in the same region.

n-type compensated semiconductor occurs when \( N_d > N_a \)

p-type compensated semiconductor occurs when \( N_d < N_a \)

If \( N_d = N_a \) we have a completely compensated semiconductor (characteristics similar to intrinsic).
Compensated semiconductor

Figure 4-14  Energy-band diagram of a compensated semiconductor showing ionized and un-ionized donors and acceptors.
**n_o for compensated semiconductors**

In thermal equilibrium the semiconductor crystal is electrically neutral (the net charge density is zero).

\[
n_o + N^-_a = p_o + N^+_d \\
(n_o + (N_a - p_a)) = p_o + (N_d - n_d)
\]

If we assumed complete ionization (at RT)

\[
n_d = 0 \text{ and } p_a = 0
\]

\[
n_o + N_a = p_o + N_d = \frac{n_i^2}{n_o} + N_d =
\]

\[
n_o^2 - (N_d - N_a)n_o - n_i^2 = 0
\]

\[
n_o = \frac{(N_d - N_a)}{2} + \sqrt{\left(\frac{(N_d - N_a)}{2}\right)^2 + n_i^2}
\]

For an intrinsic semiconductor \(N_a = N_d = 0\)

\[
n_o = n_i
\]
Determination of \( n_o \) in compensated semiconductor

Ex: n-type Si at T=300°K with \( N_d = 10^{16} \text{ cm}^{-3} \) and \( N_a = 10^{12} \text{ cm}^{-3} \)
Assumed \( n_i = 1.5 \times 10^{10} \text{ cm}^{-3} \)

\[
n_o = \frac{(N_d - N_a)}{2} + \sqrt{\left(\frac{(N_d - N_a)}{2}\right)^2 + n_i^2} = \]

\[
= \frac{10^{16}}{2} + \sqrt{\left(\frac{10^{16}}{2}\right) + \left(1.5 \times 10^{10}\right)^2} \approx 10^{16} \text{ cm}^{-3}
\]

majority carrier concentration

\[
p_o = \frac{n_i^2}{n_o} = \frac{\left(1.5 \times 10^{10}\right)^2}{1 \times 10^{16}} = 2.25 \times 10^4 \text{ cm}^{-3}
\]

minority carrier concentration

NOTE:

<table>
<thead>
<tr>
<th>Table 4–2</th>
<th>Commonly accepted values of ( n_i ) at ( T = 300°K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>( n_i = 1.5 \times 10^{10} \text{ cm}^{-3} )</td>
</tr>
<tr>
<td>Gallium arsenide</td>
<td>( n_i = 1.8 \times 10^6 \text{ cm}^{-3} )</td>
</tr>
<tr>
<td>Germanium</td>
<td>( n_i = 2.4 \times 10^{13} \text{ cm}^{-3} )</td>
</tr>
</tbody>
</table>

\( n_o > n_i \)  
\( p_o < n_i \)

electron redistribution along the available energy states =>
The electron concentration in the conduction band increases above $n_i$ as we add donor atoms and the minority carrier hole concentration will decrease.
Between $T=0^\circ K$ (freeze-out) and $T=300^\circ K$ (complete ionization), we have partial ionization of donor and acceptor atoms ($n=N_d$).

$$n_d = N_d \text{ or } N_d^+ = 0$$

High T the semiconductor shows an intrinsic behaviour
$n_i$ strongly depends on T. By increasing T, electron and hole pairs are thermally generated and then the $n_i^2$ term starts to dominate. The semiconductor will lose its extrinsic characteristics.

\[ n_o = \left( \frac{N_d - N_a}{2} \right) + \sqrt{\left( \frac{N_d - N_a}{2} \right)^2 + n_i^2} \]

**Figure 4-16** Electron concentration versus temperature showing the three regions: partial ionization, extrinsic, and intrinsic.
Position of the Fermi energy level for n-type

Determination of the position of the Fermi level as a function of doping concentration and as a function of temperature.

We assume that the Boltzmann approximation is valid.

\[ n_o = N_c \exp\left[-\frac{(E_C - E_F)}{kT}\right] \Rightarrow E_C - E_F = kT \ln\left(\frac{N_c}{n_o}\right) \]

If we consider an n-type semiconductor \( n_o \approx N_D \) all donor atoms are ionized

\[ E_C - E_F = kT \ln\left(\frac{N_c}{N_d}\right) \]

\( E_F \) moves to \( E_c \) if the donor concentration \( (N_d) \) increases. For a compensated semiconductor \( N_d \) term is replaced with \( N_d - N_a \).
If we assumed complete ionization

\[ n_d = 0 \text{ and } p_a = 0 \quad N_a^- = N_a \text{ and } N_d^+ = N_d \]

\[ n_o + N_a = \frac{n_i^2}{p_o} + N_d = p_o + N_d = \]

\[ p_o^2 - (N_d - N_a)p_o - p_i^2 = 0 \]

\[ p_o = \frac{(N_a - N_d)}{2} + \sqrt{\left(\frac{(N_a - N_d)}{2}\right)^2 + n_i^2} \quad N_a > N_d \]

Thermal-equilibrium majority carrier hole concentration in a p-type semiconductor or when \( N_a > N_d \).

Minority carrier concentration:

\[ n_o = \frac{n_i^2}{p_o} = \frac{n_i^2}{N_a - N_d} \]
Position of the Fermi energy level for n-type

EX: Si T=300°K \( N_d = 10^{16} \text{ cm}^{-3} \) \( N_a = 0 \) \( n_i = 1.5 \times 10^{10} \text{ cm}^{-3} \) n-type semiconductor

\[
E_C - E_F = kT \ln \left( \frac{N_c}{N_d} \right) = 0.0259 \ln \left( \frac{2.8 \times 10^{19}}{10^{16}} \right) = 0.206eV \gg kT \text{ (valid the Boltzmann appr.)}
\]

We develop a different expression for \( E_F \) for n-type semiconductor

\[
n_o = n_i \exp\left[ \frac{(E_F - E_{Fi})}{kT} \right] \Rightarrow E_F - E_{Fi} = kT \ln \left( \frac{n_o}{n_i} \right) \text{ with}
\]

\[
n_o = \frac{(N_d - N_a)}{2} + \sqrt{\left( \frac{(N_d - N_a)}{2} \right)^2 + n_i^2}
\]

For a semiconductor with \( N_d - N_a = 0 \) (completely compensated) then \( n_o = n_i \) and \( E_F = E_{Fi} \Rightarrow \text{same characteristics of an intrinsic semiconductor.} \)
For a p-type semiconductor

\[ p_o = N_v \exp \left[ \frac{-(E_F - E_V)}{kT} \right] \Rightarrow E_F - E_V = kT \ln \left( \frac{N_v}{p_o} \right) \]

If we consider an p-type semiconductor \( p_o \equiv N_A \)

\[ E_F - E_V = kT \ln \left( \frac{N_v}{N_a} \right) \]

as the \( N_a \) increases \( E_F \) moves closer to the valence band

or

\[ p_o = n_i \exp \left[ - \frac{(E_F - E_{Fi})}{kT} \right] \]

\[ \Rightarrow E_{Fi} - E_F = kT \ln \left( \frac{p_o}{n_i} \right) \]
$E_F$ vs $E_{Fi}$

For n-type $n_o > n_i$
$E_F > E_{Fi}$

For p-type $p_o > n_i$
$E_{Fi} > E_F$
\[ E_F - E_{Fi} = kT \ln \left( \frac{n_o}{n_i} \right) \]

\[ E_{Fi} - E_F = kT \ln \left( \frac{p_o}{n_i} \right) \]

\[ n_i^2 = N_C N_V \exp \left[ -\frac{E_g}{kT} \right] \]

\( n_i \) strongly depends from \( T \)
\( E_F \) is a function of \( T \) also.
As \( T \) increases \( n_i \) increases too an
\( E_F => E_{Fi} \)

At high \( T \) the semiconductor loses the extrinsic characteristics and behaves as intrinsic.

At low \( T \) freeze-out occurs, Boltzmann approximation is not longer valid. The equations we derived the Fermi level position no longer apply. \( E_F => E_d \) for n-type and \( E_F => E_a \) for p-type.
$E_F$ vs doping

**Figure 4–18** Position of Fermi level as a function of donor concentration (n-type) and acceptor concentration (p-type).

\[
E_C - E_F = kT \ln \left( \frac{N_c}{N_d} \right) \quad \text{n-type semiconductor}
\]

\[
E_F - E_V = kT \ln \left( \frac{N_V}{N_a} \right) \quad \text{p-type semiconductor}
\]
Relevance of $E_F$

$E_F$ and his relations are significant in p-n junctions or other semiconductor devices. In thermal-equilibrium $E_F$ is constant throughout a system.