Semiconductor statistics

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Here we discuss the ststistics of semiconductor. The semiconducstors consists of three types semiconductor; intrinsic semiconductor, *N*-type semiconductor, and *P*-type semiconductor.

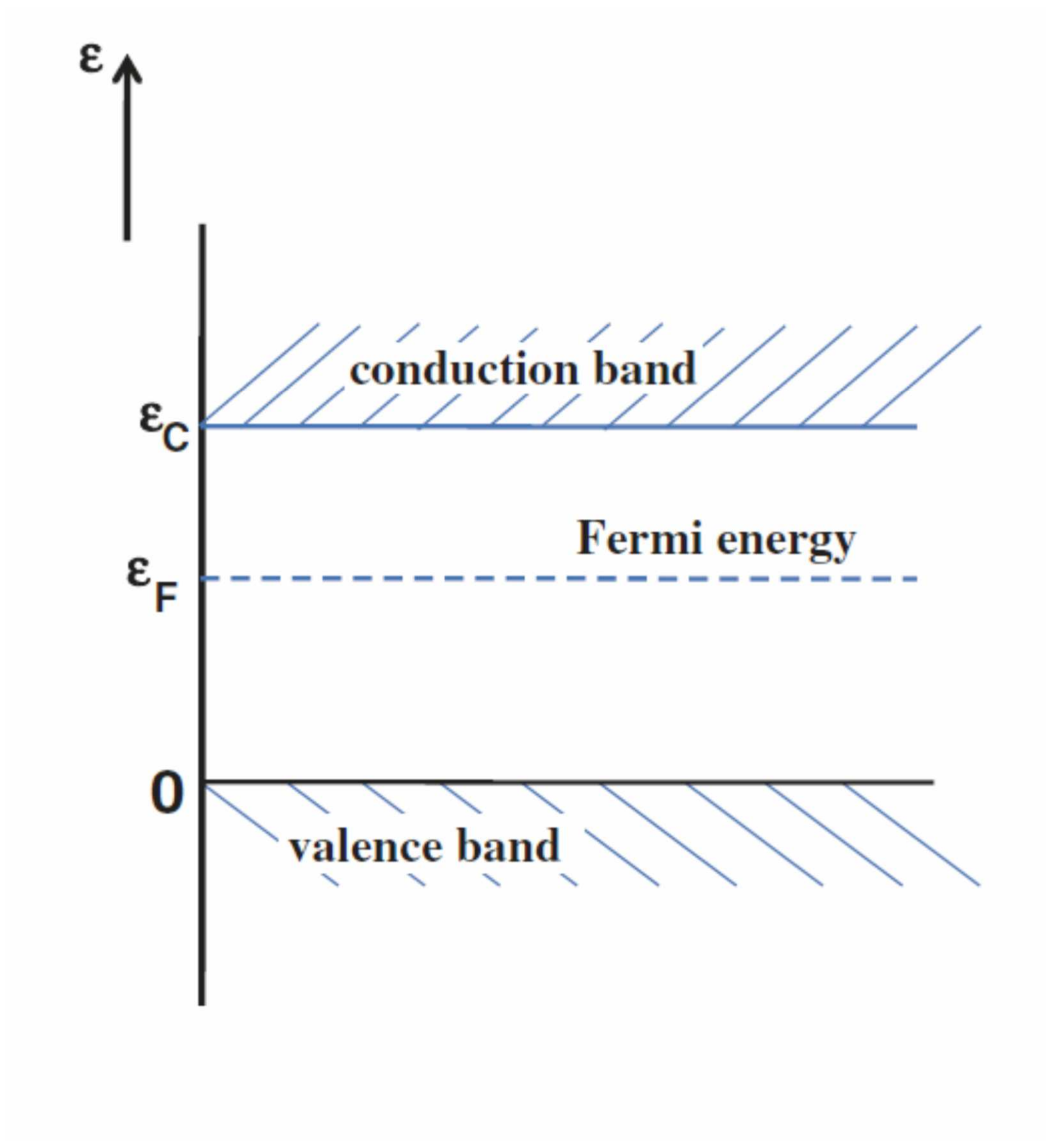


Fig. Intrinsic semiconductor

The energy gap:

$$\varepsilon_g = \varepsilon_c - \varepsilon_v$$

In Si, $\varepsilon_g = 1.1$ eV.

The number of conduction electrons is given by

$$N_e = \sum_{CB} f_e(\varepsilon) .$$

The number of holes is given by

$$N_h = \sum_{VB} [1 - f_e(\varepsilon)] = \sum_{VB} f_h(\varepsilon)$$

where

$$f_e(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = 1 - f_h(\varepsilon)$$

Classical regime

$$e^{\beta(\mu-\varepsilon_c)} << 1 , \qquad e^{\beta(\varepsilon_v-\mu)} << 1$$

Such a semiconductor is called nondegenerate.

Then we have

$$f_e(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \approx e^{-\beta(\varepsilon-\mu)}$$

$$f_h(\varepsilon) = 1 - \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = \frac{e^{\beta(\varepsilon-\mu)}}{e^{\beta(\varepsilon-\mu)} + 1} = \frac{1}{e^{-\beta(\varepsilon-\mu)} + 1} = e^{\beta(\varepsilon-\mu)}$$

The total number of conduction electrons is

$$N_e = \sum_{CB} e^{-\beta(\varepsilon-\mu)} = e^{-\beta(\varepsilon_c-\mu)} \sum_{CB} e^{-\beta(\varepsilon-\varepsilon_c)}$$

or

$$N_e = N_c e^{-\beta(\varepsilon_c - \mu)}$$

where

$$N_C = \sum_{CB} e^{-\beta(\varepsilon - \varepsilon_c)}$$
$$= 2\left(\frac{m_e{}^* k_B T}{2\pi\hbar^2}\right)^{3/2} V$$

where $m_e{}^*$ is the effective mass.

((**Calculation**))

$$N_c = 2\frac{V}{(2\pi)^3}\int 4\pi k^2 dk\, e^{-\beta(\varepsilon - \varepsilon_c)}$$

$$\varepsilon - \varepsilon_c = \frac{\hbar^2 k^2}{2m_e{}^*}, \qquad k = \left(\frac{2m_e{}^*}{\hbar^2}\right)^{1/2}\sqrt{\varepsilon - \varepsilon_c}$$

$$dk = \left(\frac{2m_e{}^*}{\hbar^2}\right)^{1/2}\frac{1}{2\sqrt{\varepsilon - \varepsilon_c}}d\varepsilon$$

Then we get

$$N_c = 2\frac{V}{(2\pi)^3}\int 4\pi k^2 dk\, e^{-\beta(\varepsilon - \varepsilon_c)}$$
$$= \frac{V}{2\pi^2}\left(\frac{2m_e{}^*}{\hbar^2}\right)^{3/2}\int_{\varepsilon_c}^{\infty}\sqrt{\varepsilon - \varepsilon_c}\, e^{-\beta(\varepsilon - \varepsilon_c)} d\varepsilon$$

We put $x = \beta(\varepsilon - \varepsilon_c)$. Since $dx = \beta d\varepsilon$, we have

$$N_c == \frac{V}{2\pi^2}\left(\frac{2m_e^* k_B T}{\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{x}e^{-x}dx$$

$$= \frac{V}{2\pi^2}\left(\frac{2m_e^* k_B T}{\hbar^2}\right)^{3/2}\frac{\sqrt{\pi}}{2}$$

$$= 2V\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2}$$

Note that

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

Similarly, for holes, we have

$$N_h = \sum_{VB} e^{\beta(\varepsilon-\mu)} = \sum_{VB} e^{\beta(\varepsilon-\varepsilon_v+\varepsilon_v-\mu)} = e^{-\beta(\mu-\varepsilon_v)}\sum_{VB} e^{-\beta(\varepsilon_v-\varepsilon)}$$

or

$$N_h = N_v e^{-\beta(\mu-\varepsilon_v)}$$

where

$$N_v = 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} V .$$

((**Calculation**))

$$N_v = 2\frac{V}{(2\pi)^3}\int 4\pi k^2 dk\, e^{-\beta(\varepsilon_v-\varepsilon)}$$

$$\varepsilon_v - \varepsilon = \frac{\hbar^2 k^2}{2m_h^*}, \qquad k = \left(\frac{2m_h^*}{\hbar^2}\right)^{1/2}\sqrt{\varepsilon_v - \varepsilon}$$

$$dk = \left(\frac{2m_h^*}{\hbar^2}\right)^{1/2} \frac{1}{2\sqrt{\varepsilon_v - \varepsilon}} d\varepsilon$$

Then we get

$$\begin{aligned} N_v &= 2\frac{V}{(2\pi)^3}\int 4\pi k^2 dk\, e^{\beta(\varepsilon-\varepsilon_v)} \\ &= \frac{V}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} \int_{-\infty}^{\varepsilon_c} \sqrt{\varepsilon_v - \varepsilon}\, e^{-\beta(\varepsilon_v-\varepsilon)} d\varepsilon \end{aligned}$$

We put $x = \beta(\varepsilon_v - \varepsilon)$. Since $dx = -\beta d\varepsilon$, we have

$$\begin{aligned} N_C &= \frac{V}{2\pi^2}\left(\frac{2m_h^* k_B T}{\hbar^2}\right)^{3/2} \int_0^{\infty} \sqrt{x} e^{-x} dx \\ &= \frac{V}{2\pi^2}\left(\frac{2m_h^* k_B T}{\hbar^2}\right)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= 2V\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} \end{aligned}$$

We define the number density n_c and n_v as

$$n_e = \frac{N_e}{V} = n_c e^{-\beta(\varepsilon_c - \mu)},$$

$$n_h = \frac{N_h}{V} = n_v e^{-\beta(\mu - \varepsilon_v)}$$

where

$$n_c = 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2} = 2n_Q(e).$$

$$n_v = 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} = 2n_Q(h)$$

Note that the factor 2 is from the spin degeneracy of spin 1/2 fermion.

2. Law of mass action

We note that

$$n_e n_h = n_c n_v e^{-\beta(\varepsilon_c-\mu)} e^{-\beta(\mu-\varepsilon_v)} = n_c n_v e^{-\beta(\varepsilon_c-\varepsilon_v)} = n_c n_v e^{-\beta\varepsilon_g}$$

which is independent of the chemical potential.

In a pure semiconductor, $n_e = n_h = n_i$. Then we have the intrinsic carrier concentration

$$n_i^2 = n_c n_v e^{-\beta\varepsilon_g}$$

or

$$n_i = \sqrt{n_c n_v} e^{-\frac{\beta\varepsilon_g}{2}}$$

3. Intrinsic Fermi level

In general we have the relation

$$n_e n_h = n_i^2$$

For the intrinsic semiconductor, $n_e = n_h = n_i$, leading to

$$n_e = n_c e^{-\beta(\varepsilon_c-\mu)} = n_i = \sqrt{n_c n_v} e^{-\frac{\beta\varepsilon_g}{2}}$$

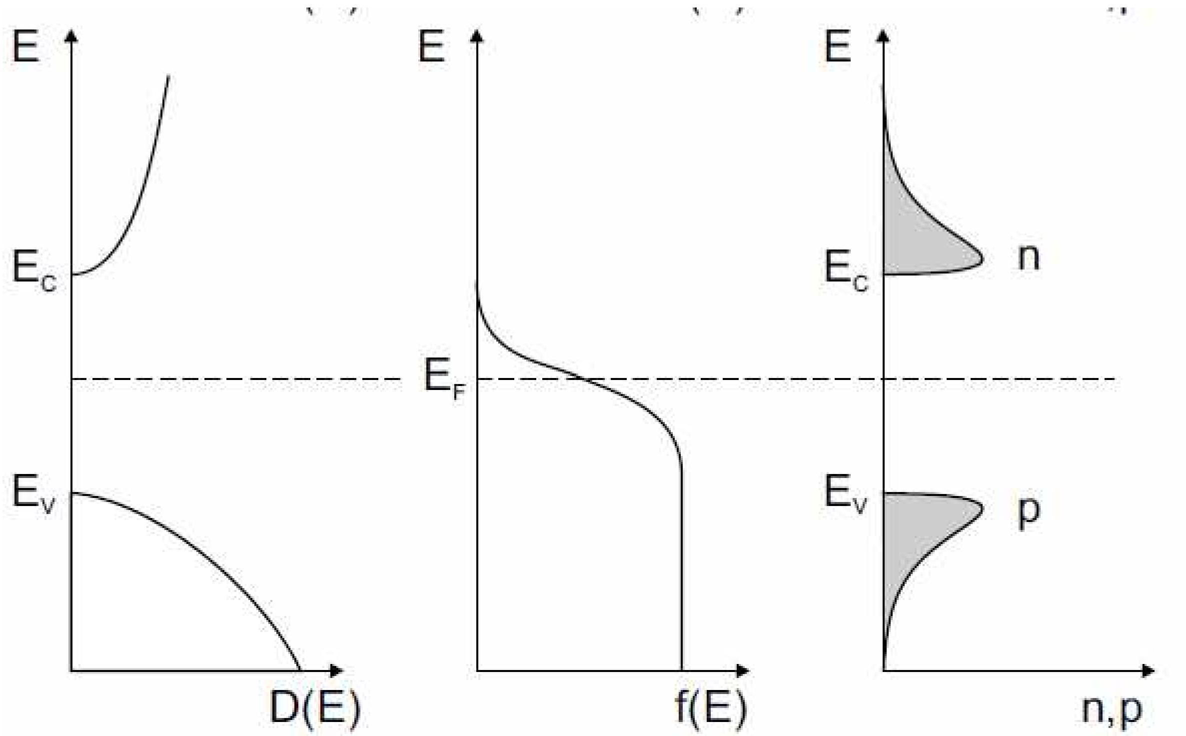
The chemical potential is

$$\mu = \frac{\varepsilon_c+\varepsilon_v}{2} + \frac{k_B T}{2}\ln\left(\frac{n_v}{n_c}\right) = \frac{\varepsilon_c+\varepsilon_v}{2} + \frac{3k_B T}{4}\ln\left(\frac{m_h^*}{m_e^*}\right)$$

where

$$\frac{n_v}{n_c} = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

The Fermi level for an intrinsic semiconductor lies near the middle of the forbidden gap.



4. The n-type and p-type semiconductor

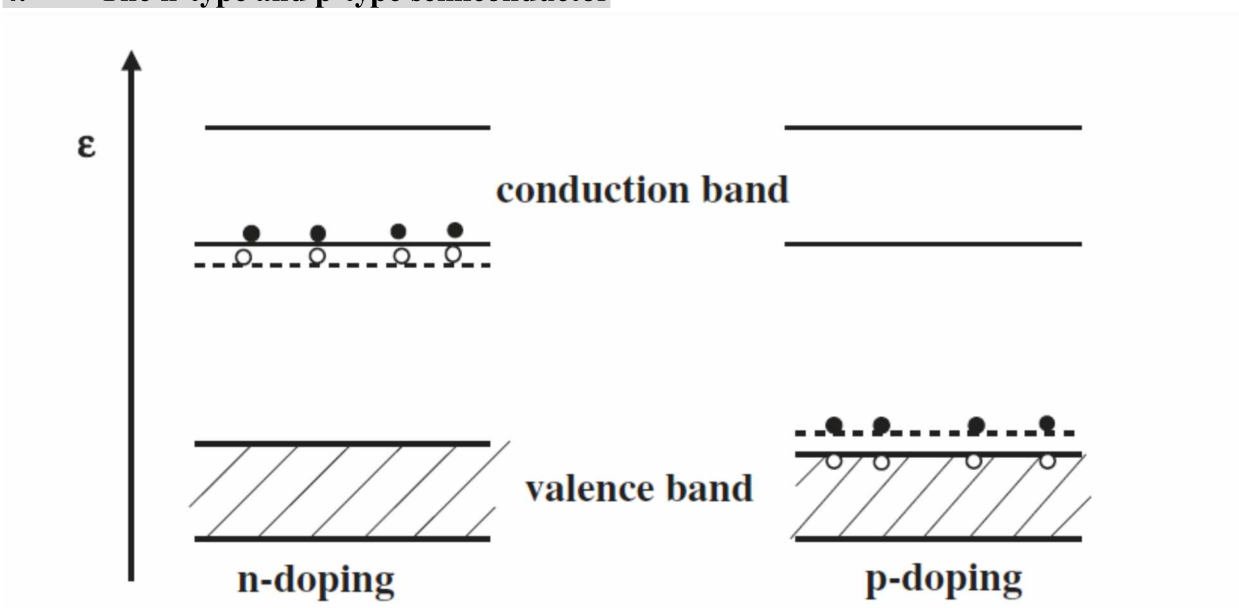


Fig. Energy diagram for *N*-type and *P*-type semiconductors. The acceptor level for the *P*-type semiconductor and donor level for the *N*-type semiconductor.

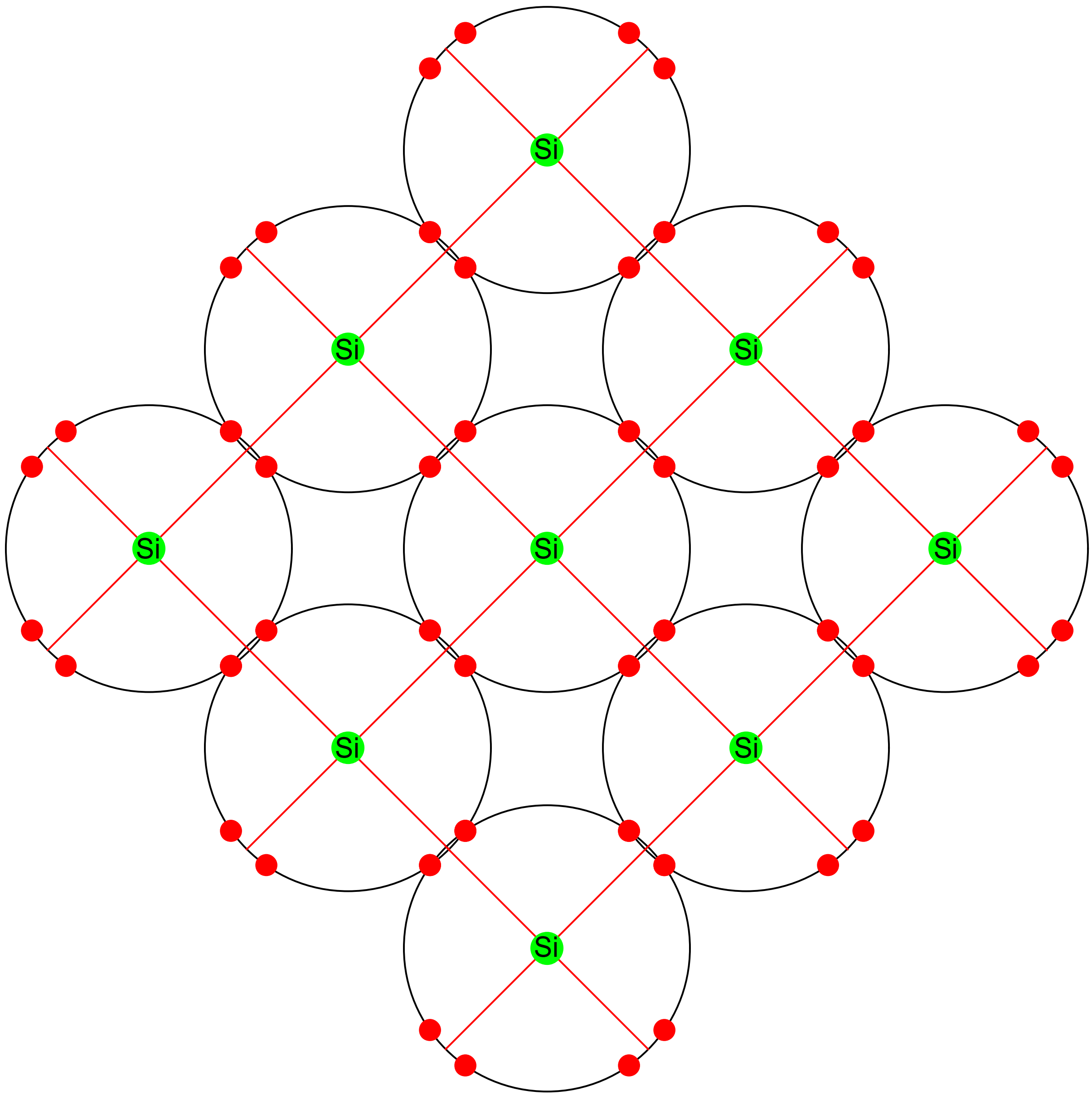


Fig. Intrinsic semiconductor Si. Si has four electrons

((*N*-type semiconductor))

Si has for electrons, while Sb (antimony) has five electrons. Each Sb has exactly one electron more than Si it replaces. Sb behaves like a donor; $Sb = Sb^{+} + e^{-}$

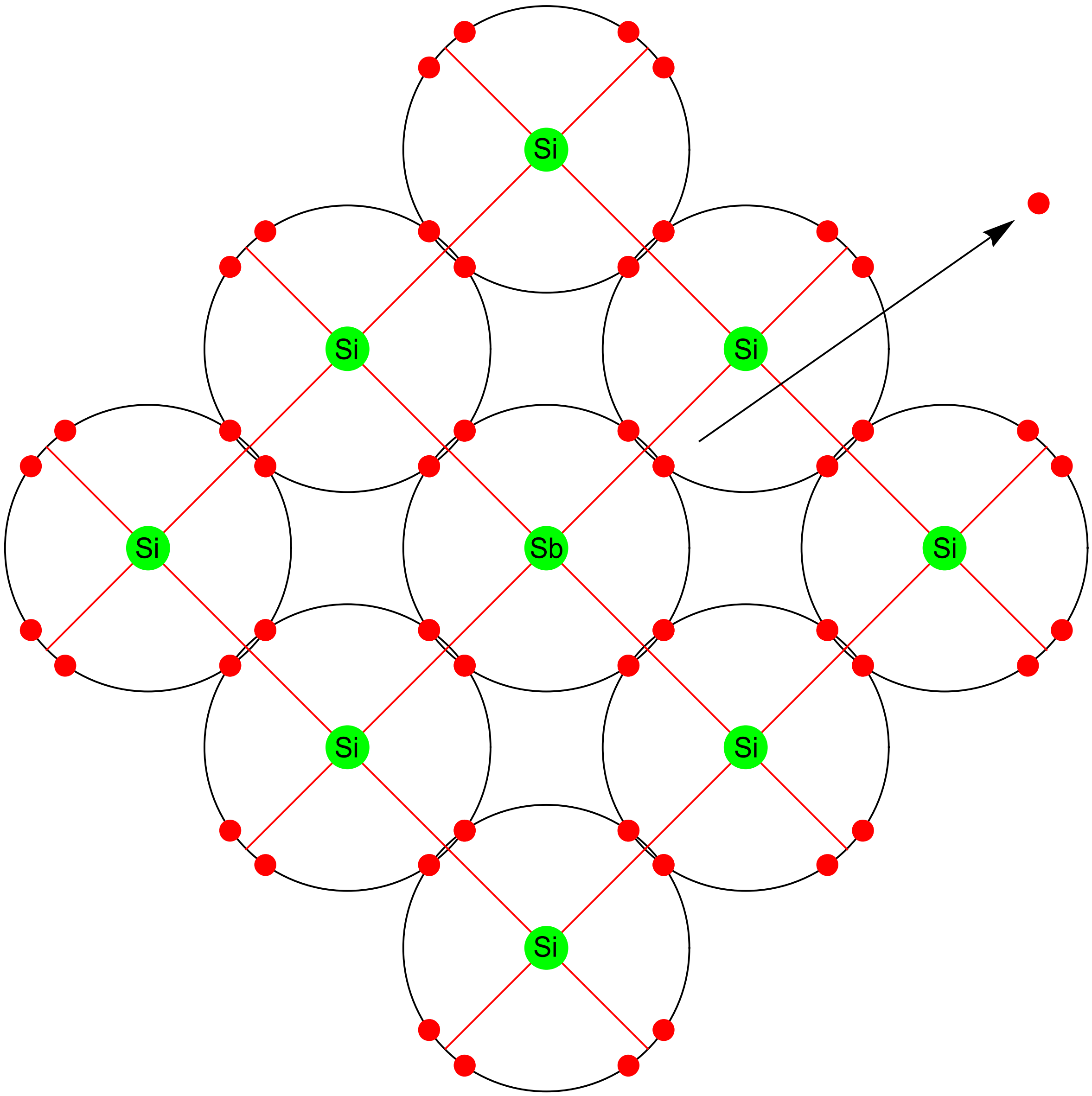


Fig. N-type semiconductor. Sb (donors) is added as impurity. A part of Si is replaced by Sb. Acceptor impurity creates a electron. Sb has five electrons. Notre that P, As, Sb, are donors.

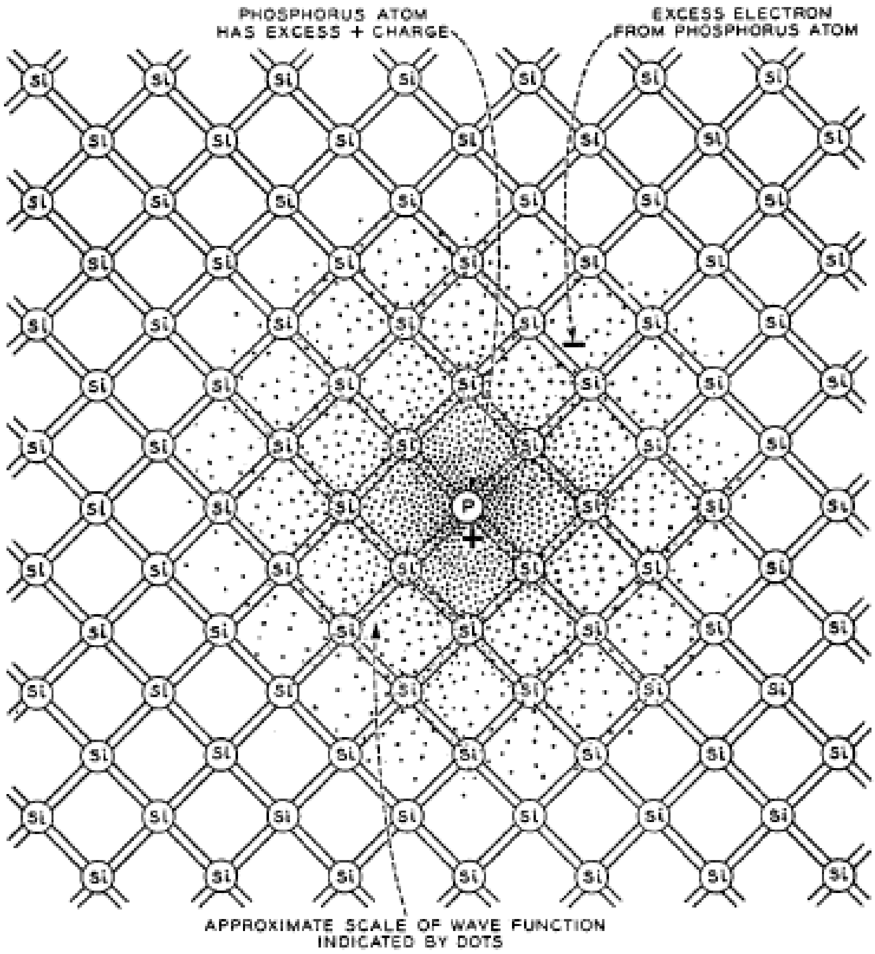
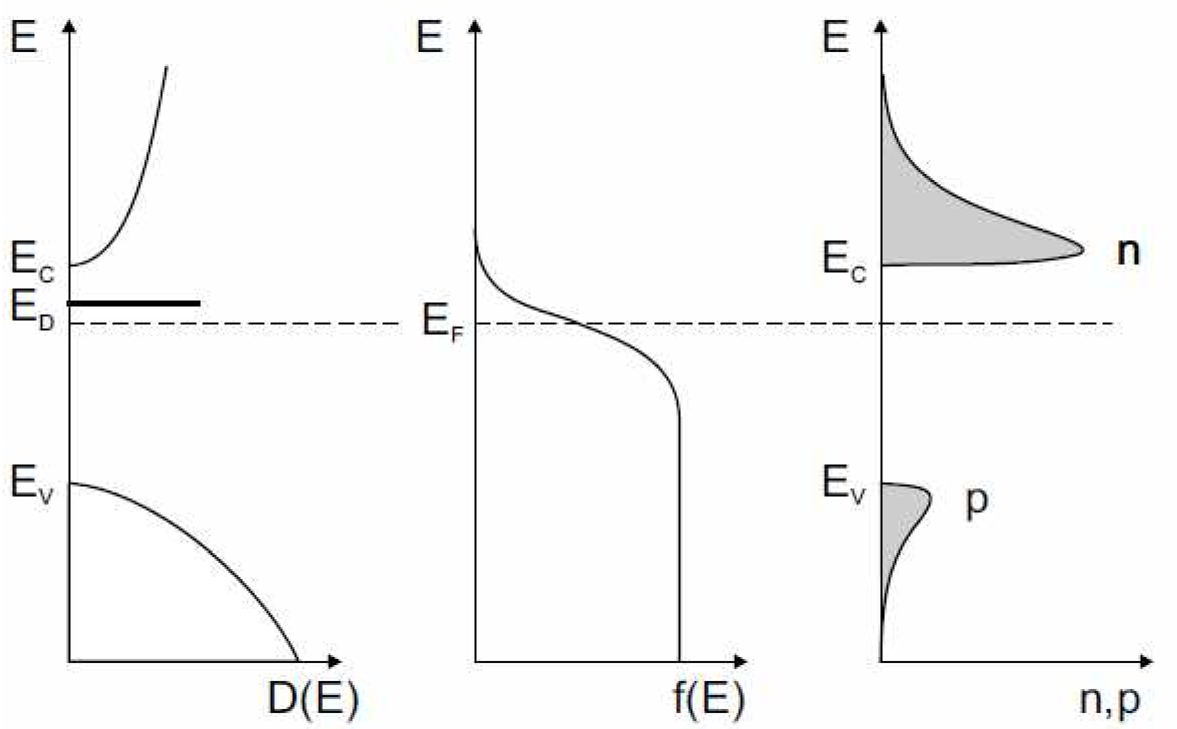


Fig. Wave function of electron bound to P atoms in Si (W. Shockley, Electrons and Holes in Semiconductors, D. van Nostrand, 1950).



((*P*-type semiconductor))

Si has for electrons, while B (boron) has three electrons. Each B has exactly one electron less than Si it replaces

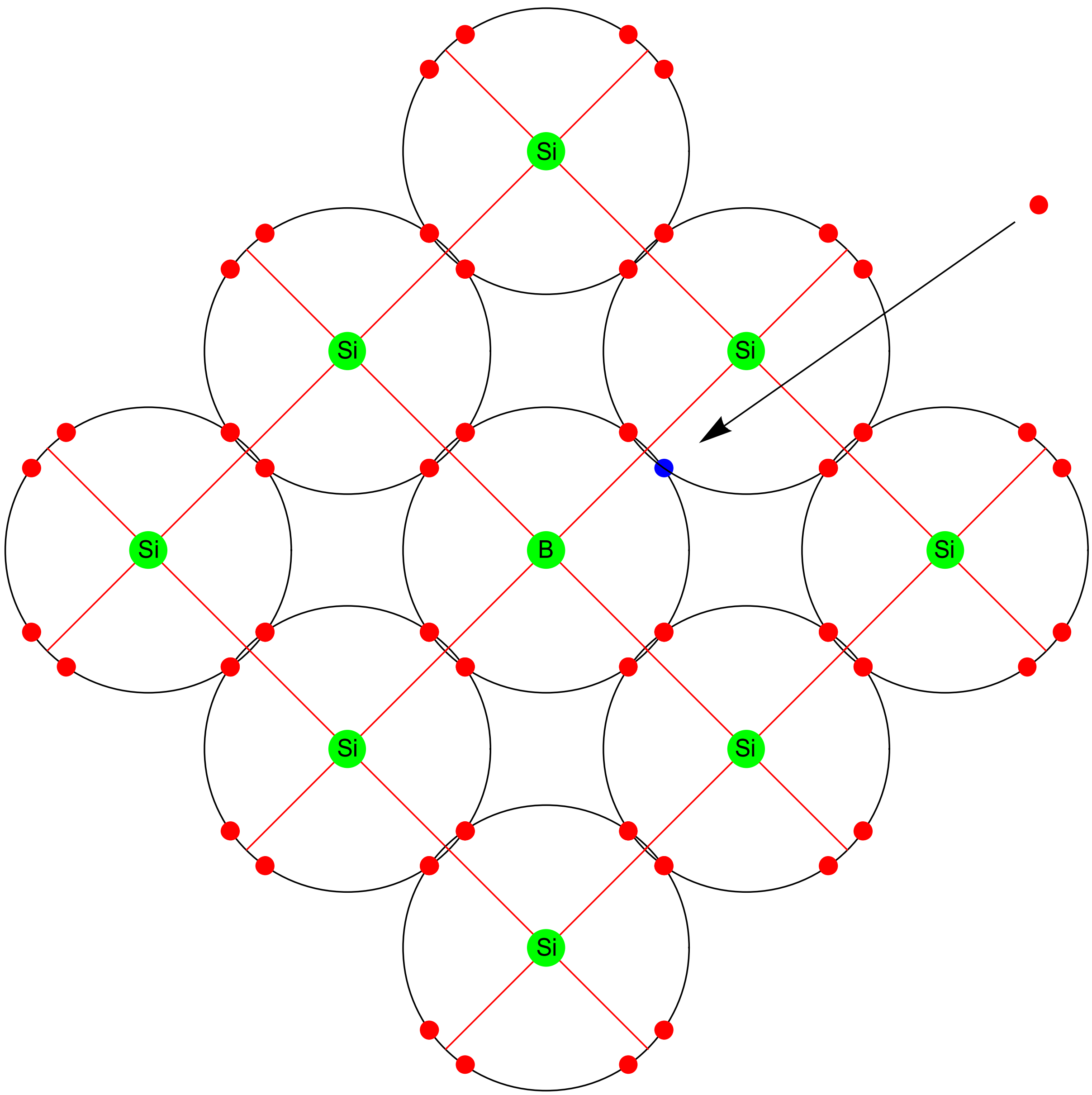
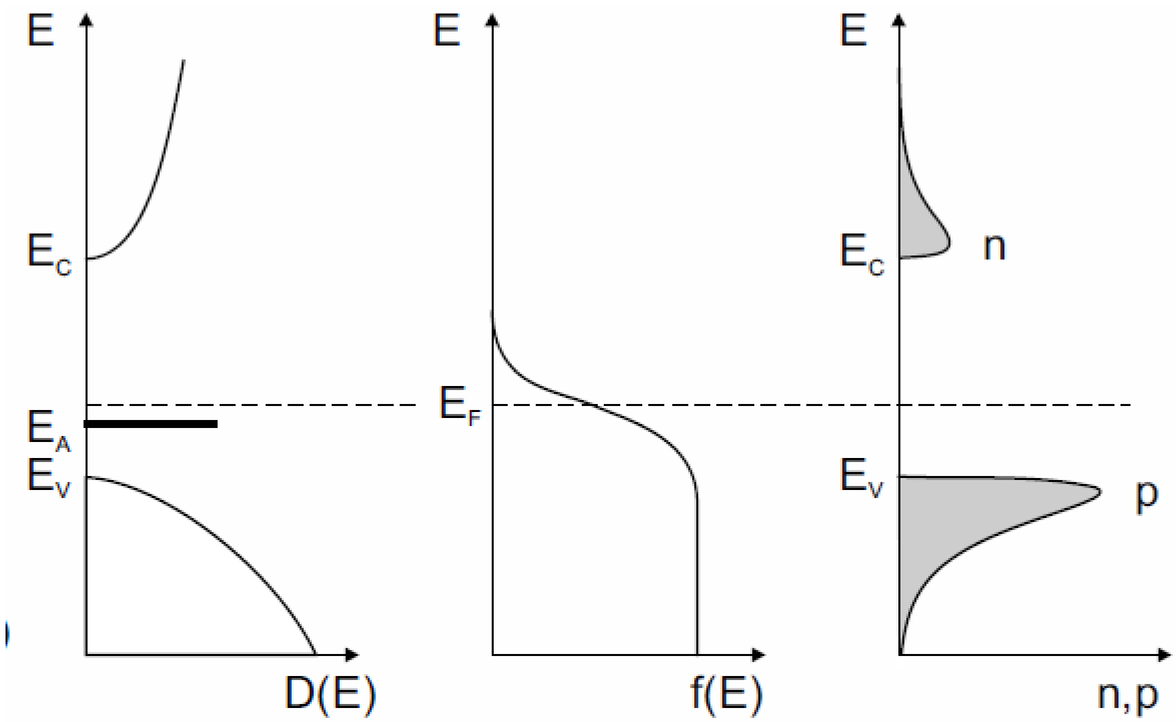


Fig. *P*-type semiconductor. Boron (acceptor) is added as impurity to Si. A part of Si is replaced by B. Acceptor impurity creates a hole. Boron has three electrons. Co-valent bonds are incomplete. Note that B, Al, Ga, In, and so on are acceptors.


E
E
E
E_C
E_C
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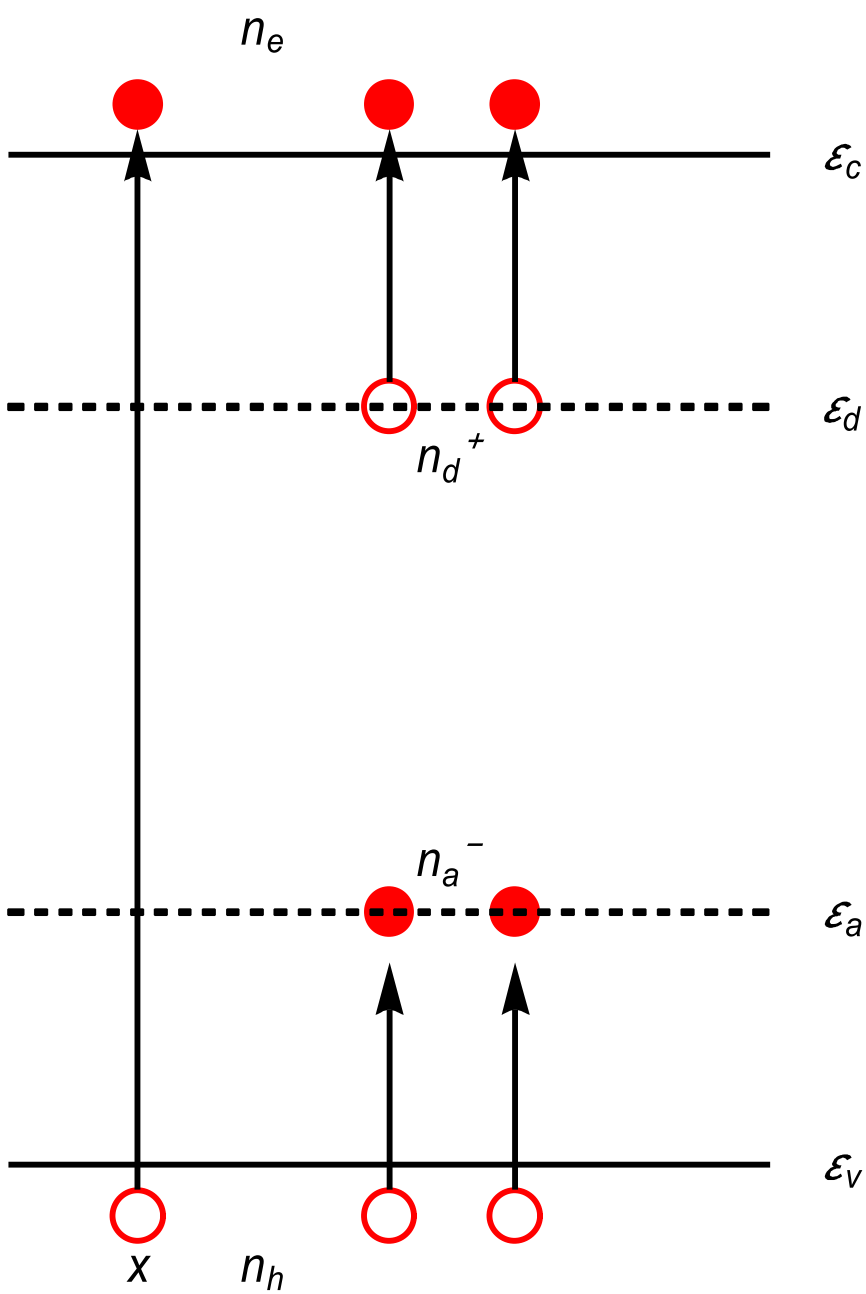


In the above figure, we have the relation

$$n_h = x + n_a^-$$

$$n_e = x + n_d^+$$

Then we have

$$n_h - n_a^- = x = n_e - n_d^+$$

or

$$n_e - n_h = n_d^+ - n_a^-$$

((Neutral (electrical) condition))

$$n_e + n_a^- = n_h + n_d^+ .$$

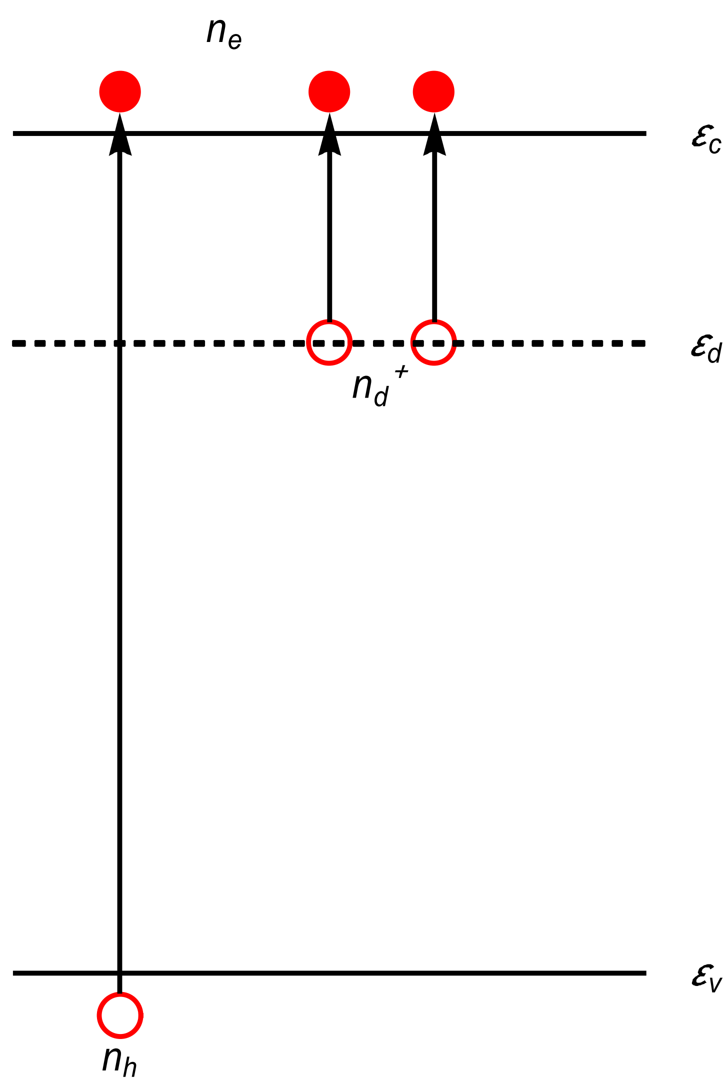
n_d^+ : concentration of positively charged donors.

n_a^- : concentration of negatively charged acceptors.

(a) *N*-type semiconductor

N-type semiconductors have impurity levels which are filled by electrons at 0 K. At finite temperatures, electrons are excited from these levels to the conduction band, thus producing conduction electrons in the conduction band. These impurities are called donors.

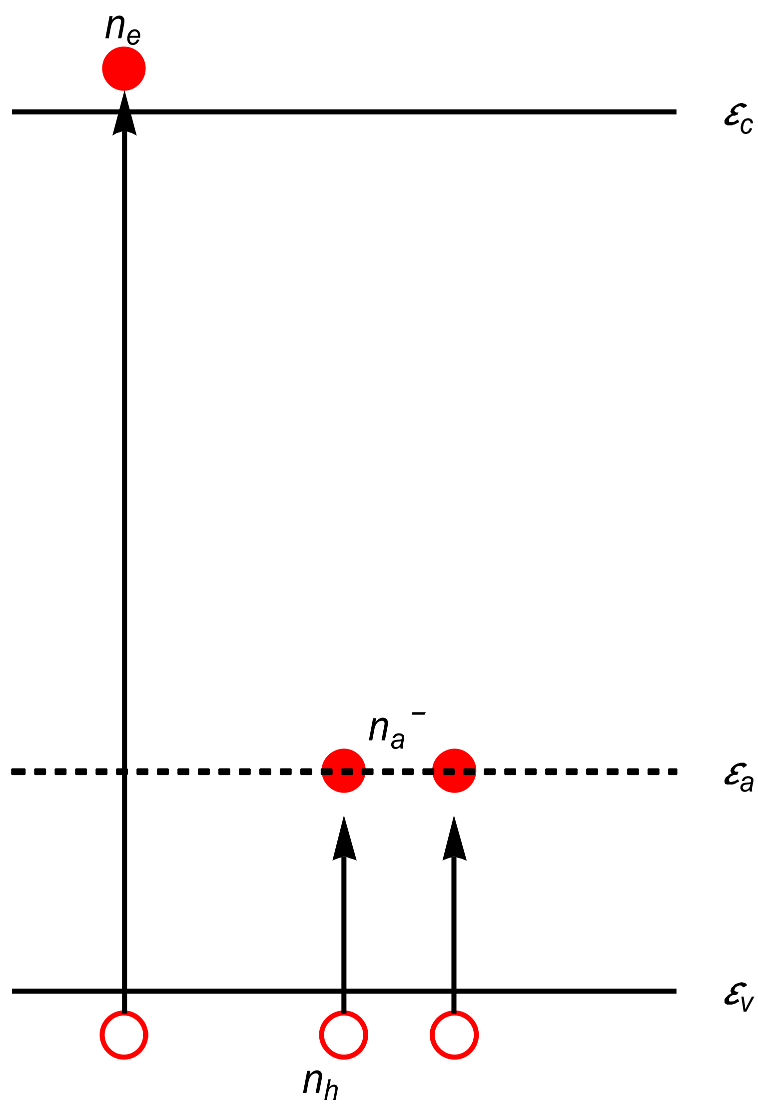
$$n_e = n_h + n_d^+$$



(b) *P*-type semiconductor

P-type semiconductors have impurity levels which are not occupied by electrons at 0 K. At finite temperatures, electrons are excited from the valence band to these levels, thus producing holes in the valence band. These impurities are called acceptors.

$$n_e = n_h - n_a^-$$



5. Determination of Fermi levels

The neutrality (in electric charges) condition leads to

$$n^- = n_e + n_a{}^- = n_h + n_d{}^+ = n^+$$

where n^- is the number of electrons in the system and n^+ is the number of holes in the system

$$n_e = n_c e^{-\beta(\varepsilon_c - \mu)}, \qquad n_h = n_v e^{-\beta(\mu - \varepsilon_v)}$$

and

$$n_a{}^- = \frac{n_a}{1+2e^{\beta(\varepsilon_a-\mu)}},$$ (the number of electrons occupied in the acceptor sites)

$$n_d{}^+ = \frac{n_d}{1+2e^{\beta(\mu-\varepsilon_d)}}.$$ (the number of holes occupied in the donor sites, or the number)

The chemical potential can be determined from the equation

$$n_c e^{-\beta(\varepsilon_c-\mu)} + \frac{n_a}{1+2e^{\beta(\varepsilon_a-\mu)}} = n_v e^{-\beta(\mu-\varepsilon_v)} + \frac{n_d}{1+2e^{\beta(\mu-\varepsilon_d)}}$$

((Occupancy of donor))

A donor level can be occupied by an electron with either spin up or spin down. Once the level is occupied by one electron, the donor cannot bind a second electron with opposite spin. We suppose that one, but only one, electron can be bound to an impurity atom, either orientation ↑ or ↓ of the electron spin is accessible. The possible microscopic states for a donor level are the empty state, the state occupied by an electron of spin up and that of spin down.

1. electron detached (energy 0)
2. 1 electron attached: $|+z\rangle$ (energy ε_d)
3. 1 electron attached: $|-z\rangle$ (energy ε_d)

The Gibbs sum is given by

$$Z_G = 1 + ze^{-\beta\varepsilon_d} + ze^{-\beta\varepsilon_d} = 1 + 2ze^{-\beta\varepsilon_d}$$

$f(D^+)$: probability that the donor orbit is vacant

$$f(D^+) = \frac{1}{1+2ze^{-\beta\varepsilon_d}}$$

$f(D)$: probability that the donor orbit is occupied by one electron

$$f(D) = \frac{2ze^{-\beta\varepsilon_d}}{1+2ze^{-\beta\varepsilon_d}} = \frac{1}{1+\frac{1}{2}e^{\beta(\varepsilon_d-\mu)}} = 1 - f(D^+)$$

The factor 2 is the spin degeneracy.

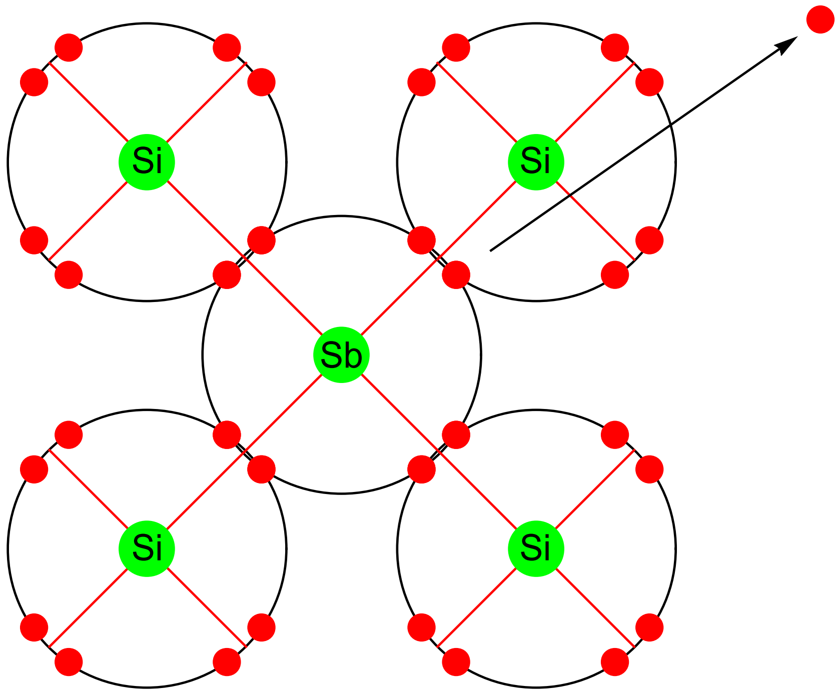


Fig. *N*-type semiconductor with donor level.

((Occupancy of acceptor))

In the ionized condition A^- of the acceptor, each of the chemical bonds between the acceptor atom and the surrounding semiconductor Si atoms, contains a pair of electrons with antiparallel spins. There is only one such state.

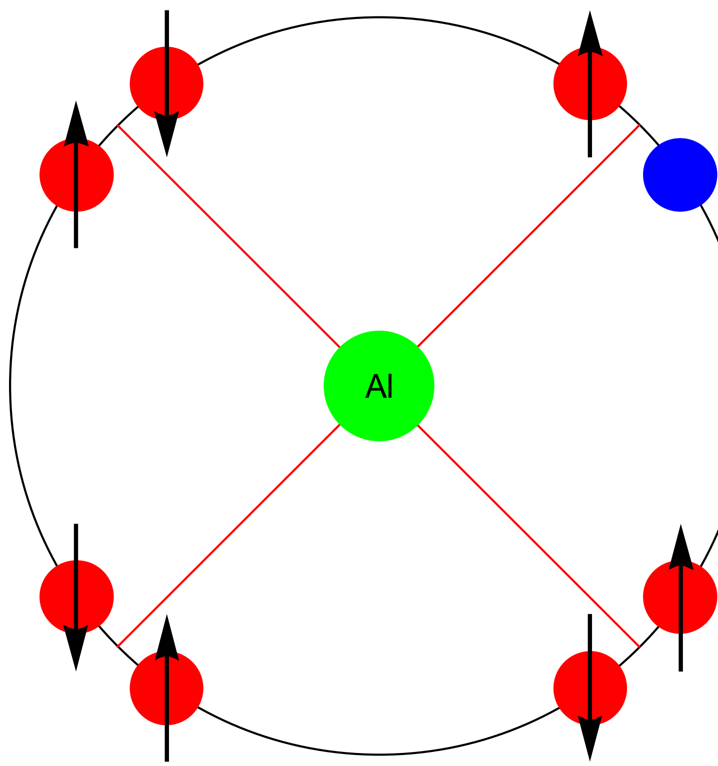


Fig. The spin direction is fixed.

In the above figure, the electron in the spin down state.

1. $1\, ze^{-\beta\varepsilon_a}$: one electron with spin down

In the neutral condition A of the acceptor, one electron is missing from the surrounding bonds. The missing electron may have either spin up or spin down.

2. one $\uparrow$ electron missing ($N = 0$, zero energy)
3. one $\downarrow$ electron missing ($N = 0$, zero energy)

Thus we have the partition function

$$Z_G = 2 + ze^{-\beta\varepsilon_a}.$$

$$f(A^-) = \frac{ze^{-\beta\varepsilon_a}}{2 + ze^{-\beta\varepsilon_a}} = \frac{1}{1 + ze^{\beta(\varepsilon_a - \mu)}}$$ (the acceptor orbital occupied)

$$f(A) = \frac{2}{2 + ze^{-\beta\varepsilon_a}} = \frac{1}{1 + \frac{1}{2}e^{\beta(\mu - \varepsilon_a)}}$$ (the acceptor orbital unoccupied)

The concentration

$$n_d^{\ +} = n_d f(D^+) = \frac{n_d}{1 + 2e^{\beta(\mu - \varepsilon_d)}}$$ (donor orbital unoccupied)

$$n_a^{\ -} = n_a f(A^-) = \frac{n_a}{1 + 2e^{\beta(\varepsilon_a - \mu)}}$$ (donor orbital unoccupied)

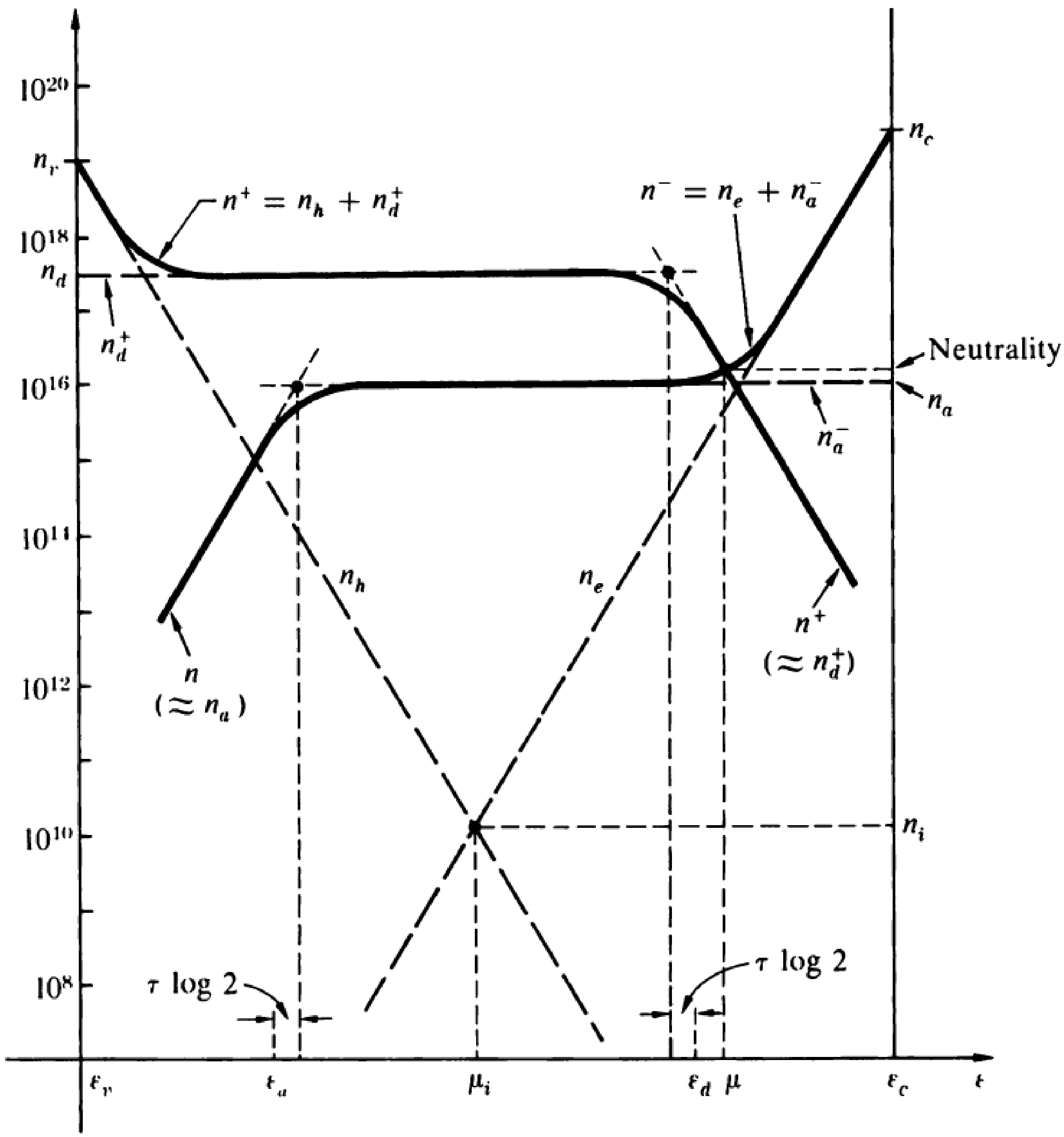


Fig. Graphical determination of the Fermi level and electron concentration in an n-type semiconductor containing both donors and acceptors. (Kittel and Kromer, Thermal Physics)

6. *N*-type semiconductor

For *N*-type semiconductor, we have

$$n_c e^{-\beta(\varepsilon_c-\mu)} = n_v e^{-\beta(\mu-\varepsilon_v)} + \frac{n_d}{1+2e^{\beta(\mu-\varepsilon_d)}}$$

In the limit of $T \to 0$, we can neglect the term $n_v e^{-\beta(\mu-\varepsilon_v)}$ (the excitation of electrons from the valence band). So we get

$$e^{-\beta(\varepsilon_c-\mu)}[1+2e^{\beta(\mu-\varepsilon_d)}] = \frac{n_d}{n_c}$$

When $\mu \approx \varepsilon_c$,

$$e^{-\beta(\varepsilon_c-\mu)} + 2e^{\beta(2\mu-\varepsilon_d-\varepsilon_c)} = \frac{n_d}{n_c}$$

or

$$2e^{\beta(2\mu-\varepsilon_d-\varepsilon_c)} = \frac{n_d}{n_c}$$ (the first term of the left-hand side is neglected).

$$\mu = \frac{\varepsilon_d+\varepsilon_c}{2} + \frac{k_B T}{2}\ln(\frac{n_d}{2n_c})$$

The chemical potential is $\mu \approx \frac{\varepsilon_d+\varepsilon_c}{2}$. Then the number density

$$n_e = n_c e^{-\beta(\varepsilon_c-\mu)} = \frac{1}{\sqrt{2}}\sqrt{n_c n_d}\, e^{\frac{1}{2}\beta(\varepsilon_d-\varepsilon_c)}$$

7. *P*-type semicondictor

For *P*-type semiconductor, we have

$$n_c e^{-\beta(\varepsilon_c-\mu)} + \frac{n_a}{1+2e^{\beta(\varepsilon_a-\mu)}} = n_v e^{-\beta(\mu-\varepsilon_v)}$$

In the limit of $T \to 0$, we can neglect the term $n_c e^{-\beta(\varepsilon_c-\mu)}$ (the excitation of electrons from the conduction band). So we get

$$\frac{n_a}{1+2e^{\beta(\varepsilon_a-\mu)}} = n_v e^{-\beta(\mu-\varepsilon_v)}$$

When $\mu \approx \varepsilon_v$,

$$e^{-\beta(\mu-\varepsilon_v)} + 2e^{\beta(\varepsilon_a+\varepsilon_v-2\mu)} = \frac{n_a}{n_v}$$

or

$$2e^{\beta(\varepsilon_a+\varepsilon_v-2\mu)} = \frac{n_a}{n_v}$$ (the first term of the left-hand side is neglected).

$$\mu = \frac{\varepsilon_a+\varepsilon_v}{2} - \frac{k_B T}{2}\ln(\frac{n_a}{2n_v})$$

The chemical potential is $\mu \approx \frac{\varepsilon_a+\varepsilon_v}{2}$. Then the number density

$$n_h = n_v e^{-\beta(\mu-\varepsilon_v)} = \frac{1}{\sqrt{2}}\sqrt{n_v n_a}\, e^{\frac{1}{2}\beta(\varepsilon_v-\varepsilon_a)}$$

REFERENCES

C. Kittel and H. Kromer, Thermal Physics, second edition (W.H. Freeman and Company, 1980).
W. Shockley, Electrons and Holes in Semiconductors, D. van Nostrand, 1950).

APPENDIX

Free electron with

$$\varepsilon = \frac{\hbar^2}{2m}k^2, \qquad k = \sqrt{\frac{2m}{\hbar^2}}\sqrt{\varepsilon}$$

$$
\begin{aligned}
N_e &= 2\frac{V}{(2\pi)^3}\int 4\pi k^2 dk \frac{1}{e^{\beta(\varepsilon-\mu)}+1} \\
&= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} \\
&= \frac{V(4\pi)^{3/2}}{2\pi^2}\left(\frac{2mk_BT}{4\pi\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{x}dx}{\lambda e^{-x}+1} \\
&= V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\frac{4}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{x}dx}{\lambda e^{-x}+1}
\end{aligned}
$$