

## 8. Electrons and holes in equilibrium

In a semiconductor crystal, there is usually a small concentration of freely moving charges, electrons and holes, formed by the wavefunctions from small ranges of  $k$ -vectors around the bottom of the conduction band and the top of the valence band. The gas of free quasiparticles is in a thermal contact with “the rest” of the crystal, in particular with the vibrational movement of the lattice; we treat the latter as the thermal reservoir having a given temperature  $T$ . The free carrier concentration can vary due to changes of temperature or in an external electromagnetic field. Consequently, the change of internal energy  $U$  of the gas is composed of the acquired heat, thermodynamic work  $A$  performed by the gas, and the work needed to change the number  $N$  of the carriers:

$$dU = TdS - \delta A + \mu dN , \quad (8.1)$$

where  $S$  is entropy and a  $\mu$  chemical potential. Statistical equilibrium of the gas in contact with the thermal reservoir is described by the grandcanonical distribution of the probability  $w$  of finding the gas in a state with the energy  $E_a$  and the number of particles  $N_a$  (this probability is proportional to the number of possibilities of achieving this state),

$$w(E_a, N_a) = \frac{1}{Z} \exp\left(-\frac{E_a - \mu N_a}{kT}\right), \quad Z = \sum_a \sum_{N_a} g_a \exp\left(-\frac{E_a - \mu N_a}{kT}\right). \quad (8.2)$$

The normalizing factor  $Z$  is called statistical sum, or partition function;  $g_a$  is the degree of degeneracy of the state with the energy  $E_a$ . The grandcanonical potential is related to the partition function by

$$\Omega = -kT \ln(Z) . \quad (8.3)$$

## Fermion gas

The gas consisting of  $N$  (identical, non-interacting) fermions is subject of Pauli exclusion principle. Its Hamiltonian is the sum of single-particle terms,

$$\hat{H} = \sum_{i=1}^N \hat{H}_i, \hat{H}_i |\psi_i\rangle = E_i |\psi_i\rangle. \quad (8.4)$$

The state vector of the fermi gas is antisymmetric with respect to exchange of particles. The energy levels  $E_i$  can be degenerate; we have therefore add an index to denote the corresponding states,  $\alpha_i$ . The probability

$$w_{i,\alpha_i} = \frac{1}{Z_{i,\alpha_i}} \exp\left(-\frac{E_i - \mu}{kT} n_{i,\alpha_i}\right),$$
$$Z_{i,\alpha_i} = \sum_{n_{i,\alpha_i}} \exp\left(-\frac{E_i - \mu}{kT} n_{i,\alpha_i}\right) \quad (8.5)$$

depends on the number  $n_{i,\alpha_i}$  of occupied states  $\alpha_i$  with the energy  $E_i$ . In the model of gas, the occupation of various states is independent of each other and the corresponding probabilities are multiplied, as well as the corresponding factors in the partition function. The allowed number of occupied single-particle function for fermions is restricted to either 0 or 1; the mean (expectation) value of the number is therefore

$$\langle n_{i,\alpha_i} \rangle = \sum_{n_{i,\alpha_i}} n_{i,\alpha_i} w_{i,\alpha_i} = -\frac{\partial \Omega_{i,\alpha_i}}{\partial \mu} = \frac{1}{\exp\left(\frac{E_i - \mu}{kT}\right) + 1} = f_{FD}\left(\frac{E_i - \mu}{kT}\right), \quad (8.6)$$

since

$$\Omega_{i,\alpha_i} = -kT \ln \left[ 1 + \exp \left( \frac{E_i - \mu}{kT} \right) \right]. \quad (8.7)$$

The mean value of Eq. (8.6) has also the meaning of the probability of the occupation of the state  $i, \alpha_i$ ; it is usually called Fermi-Dirac statistics,

$$f_{FD}(x) = \frac{1}{\exp(x) + 1}. \quad (8.8)$$

The mean number of particles with the energy  $E_i$  ( $\alpha_i = 1, \dots, g_i$ ) is

$$\langle n_i \rangle = g_i f_{FD} \left( \frac{E_i - \mu}{kT} \right). \quad (8.9)$$

Approximating the actual energies by a continuous spectrum, the number of particles having the energies between  $E$  and  $E + dE$  is

$$f_{FD} \left( \frac{E - \mu}{kT} \right) D(E) dE, \quad (8.10)$$

where  $D$  is the density of states. The mean value of the number of particles becomes

$$\langle N \rangle = \int_{-\infty}^{\infty} f_{FD} \left( \frac{E - \mu}{kT} \right) D(E) dE, \quad (8.11)$$

and the mean value of energy is

$$\langle E \rangle = \int_{-\infty}^{\infty} E f_{FD} \left( \frac{E - \mu}{kT} \right) D(E) dE . \quad (8.12)$$

### Parabolic minimum of band energies

The quadratic dispersion

$$E(\vec{k}) = \frac{\hbar^2}{2} \left( \frac{k_x^2}{m_x} + \frac{k_y^2}{m_y} + \frac{k_z^2}{m_z} \right) \quad (8.13)$$

results in the density of states within the volume  $V$  (in practical terms, in the close neighborhood the minimum)

$$D(E) = V \frac{\sqrt{2}}{\pi^2} \frac{\sqrt{m_x m_y m_z}}{\hbar^3} \sqrt{E} . \quad (8.14)$$

This density includes the double (spin) degeneracy. Denoting

$$m^* = (m_x m_y m_z)^{1/3} , \quad (8.15)$$

equation (8.11) results in the concentration of electrons in the gas equal to

$$\begin{aligned}
n &= \frac{\langle N \rangle}{V} = \frac{\sqrt{2}}{\pi^2} \frac{(m^*)^{3/2}}{\hbar^3} \int_0^\infty f_{FD} \left( \frac{E - \mu}{kT} \right) \sqrt{E} dE \\
&= \frac{\sqrt{2}}{\pi^2} \frac{(m^* kT)^{3/2}}{\hbar^3} \int_0^\infty \frac{t^{1/2} dt}{\exp(t - z) + 1}, \quad z = \frac{\mu}{kT}.
\end{aligned} \tag{8.16}$$

The integral in (8.16) cannot be expressed using elementary functions. It belongs to a class of Fermi-Dirac integrals (for  $j = 1/2$ )

$$F_j(z) = \int_0^\infty \frac{t^j dt}{\exp(t - z) + 1}, \quad j > -1, \tag{8.17}$$

obeying the recurrent relation

$$\frac{d}{dz} F_j(z) = j F_{j-1}(z). \tag{8.18}$$

Of special importance is the limit

$$F_j(z) \rightarrow \exp(z) \int_0^\infty t^j \exp(-t) dt = \exp(z) \Gamma(j+1) \quad \text{for } z \rightarrow -\infty, \tag{8.19}$$

where  $\Gamma$  is the Euler function (generalized factorial),  $\Gamma(j+1) = j \Gamma(j)$ ,  $\Gamma(1/2) = \sqrt{\pi}$ ,  $\Gamma(3/2) = \sqrt{\pi}/2$ .

### Nondegenerate gas (classical limit)

In the limit of Eq. (8.19), the chemical potential lies deep below the lowest band energy and the gas is denoted as non-degenerate. The requirement for fulfilling this condition is evidently the possibility to consider the unity in the denominator in the fraction of Fermi-Dirac statistics of Eq. (8.8) negligible in comparison with the large values of the exponential function. Resulting statistics is the classic (Boltzmann)  $f_B$ :

$$f_{FD}\left(\frac{E-\mu}{kT}\right) \approx f_B\left(\frac{E-\mu}{kT}\right) = \exp\left(\frac{\mu}{kT}\right) \exp\left(-\frac{E}{kT}\right). \quad (8.20)$$

Equation (8.16) for the concentration is reduced to

$$n = 2 \frac{(2\pi m^* kT)^{3/2}}{8\pi^3 \hbar^3} \exp\left(\frac{\mu}{kT}\right). \quad (8.21)$$

The condition for the validity of Boltzmann statistics can be interpreted in a simple way. Equation (8.21) can be rewritten in the following form,

$$\exp\left(\frac{\mu}{kT}\right) = n \frac{1}{2} \frac{8\pi^3 \hbar^3}{(2\pi m^* kT)^{3/2}} = \frac{\langle N \rangle}{V} \frac{1}{2} \lambda_T^3, \quad \lambda_T^3 = \frac{h^3}{\sqrt{2\pi m^* kT}}; \quad (8.22)$$

the quantity  $\lambda_T$  is de Broglie wavelength of the quasiparticle having the effective mass  $m^*$  and energy  $kT$ . For reaching the classical limit, the volume per a single particle,  $V/\langle N \rangle$ , is required to be much larger than the volume of the cube with the edge equal to the de Broglie wavelength corresponding the the thermal energy of  $kT$ . This means the negligibility of the quantum effects related to the symmetry particle exchange, and the gas follows the classical physics. Of course, the pronounced quantum effects remain in the presence of effective masses.

At a prescribed concentration (achieved, e.g., by the level of doping, with the temperature small to prevent the excitation "over the gap"), equation (8.21) provides the following explicit dependence of chemical potential on temperature:

$$\mu = kT \ln \frac{4\pi^3 \hbar^3 n}{(2\pi m^* kT)^{3/2}}. \quad (8.23)$$

Reaching the limit of classical statistics is supported by large temperature, large effective mass, and small concentration. At the temperature of 300 K and effective mass of  $9.1E-28$  g (this is the rest mass of free electron), the value of the exponential function in the classical statistics is

$$\exp\left(\frac{\mu}{kT}\right) = \frac{4\pi^3 \hbar^3}{(2\pi m^* kT)^{3/2}} n = \frac{n}{2.51 \times 10^{19} \text{ cm}^{-3}}; \quad (8.24)$$

at the concentration of  $1E18 \text{ cm}^{-3}$ , the chemical potential has the value of  $-0.107$  eV, and the values of Boltzmann and Fermi-Dirac statistics for the energy  $E = 0$  are 0.0159 and 0.0157, respectively. Using the classical statistics is evidently allowed in this situation.

### Strongly degenerate gas

Another simplification occurs for large concentrations, low temperatures, and small effective masses. For chemical potential much larger than  $kT$ , the Fermi-Dirac statistics is close to the step function, assuming the value of 1 for  $E < \mu_0$  and 0 for  $E > \mu_0$  ( $\mu_0$  is the limit value for the chemical potential at vanishing temperature). In this approximation, the concentration of Eq. (8.16) is

$$n = \frac{\sqrt{2}}{\pi^2} \frac{(m^* kT)^{3/2}}{\hbar^3} \int_0^{\frac{\mu_0}{kT}} t^{1/2} dt = \frac{(2m^*)^{3/2}}{3\pi^2 \hbar^3} \mu_0^{3/2}. \quad (8.25)$$

Inversely, the chemical potential at zero temperature is

$$\mu_0 = \frac{(3\pi^2)^{2/3} \hbar^2}{2m^*} n^{2/3} = \left(\frac{3}{8\pi}\right)^{2/3} \frac{\hbar^2}{2m^*} n^{2/3}. \quad (8.26)$$

The mean value of energy in a unit volume is then

$$\frac{\langle E \rangle}{V} = \frac{\sqrt{2}}{\pi^2} \frac{(m^*)^{3/2}}{\hbar^3} \int_0^{\mu_0} E^{3/2} dE = \frac{3}{5} \frac{(2m^*)^{3/2}}{3\pi^2 \hbar^3} \mu_0^{5/2} = \frac{3}{5} n \mu_0 . \quad (8.27)$$

Note the difference from the classical result, where the volume density of energy is  $3nkT/2$ .  $\mu_0$  is usually called Fermi energy; for metals, it is the largest single-electron energy in the limit of zero temperature.

Quantitative orientation can use the free electron mass and the electron density of  $1E22$  (typical metal); equation (8.26) leads to the Fermi energy of 7.8 eV. For a heavily doped semiconductor, the typical concentration can be about  $1E19 \text{ cm}^{-3}$ ; with the effective mass  $0.1m_0$ , the Fermi energy is 0.78 eV. V takové hloubce vodivostního pásu ovšem nemůžeme očekávat platnost předpokládané kvadratické disperze pásových energií.

### Intrinsic semiconductor

In an ideal semiconducting crystal at nonzero temperature, thermal excitation of valence states leads to the occupation of conduction band states, leaving mobile holes in the valence bands. The thermal movement always excites electron-hole pairs. Their concentration is determined by the ratio  $E_g/kT$  and effective masses of electrons and holes,  $E_g$  is width of the forbidden gap. We will retain the zero of the energy scale at the bottom of the conduction band, Eq. (8.13); consequently, the top of the valence band is located at the energy  $-E_g$ . We will limit ourselves to isotropic bands around the Brillouin zone center, with the dispersions ( $E'$  is the energy of valence band)

$$E(\vec{k}) = \frac{\hbar^2}{2} \frac{|\vec{k}|^2}{m_n} , E'(\vec{k}) = -E_g - \frac{\hbar^2}{2} \frac{|\vec{k}|^2}{m_p} , \quad (8.28)$$

where  $m_n$  and  $m_p$  are the effective masses of the negatively and positively charged carriers (elektrons and holes, respectively). The probability of the state with the energy  $E'$  being unoccupied by an electron, i.e., it represents a hole, results from Eq. (8.6) as



$$f'_{FD}(E') = 1 - f_{FD}(E') = 1 - \frac{1}{\exp\left(\frac{E' - \mu}{kT}\right) + 1} = \frac{1}{\exp\left(\frac{\mu - E'}{kT}\right) + 1} . \quad (8.29)$$

According to the assumption of the thermal excitation of the pairs, the concentrations of electrons ( $n$ ) and holes ( $p$ ) are equal; they are given by the following formulas:

$$\begin{aligned} n &= \frac{\sqrt{2}}{\pi^2} \frac{(m_n)^{3/2}}{\hbar^3} \int_0^\infty f_{FD}\left(\frac{E - \mu}{kT}\right) \sqrt{E} dE, \\ p &= \frac{\sqrt{2}}{\pi^2} \frac{(m_p)^{3/2}}{\hbar^3} \int_{-\infty}^{-E_g} f_{FD}\left(\frac{\mu - E'}{kT}\right) \sqrt{-E_g - E'} dE' = \frac{\sqrt{2}}{\pi^2} \frac{(m_p)^{3/2}}{\hbar^3} \int_0^\infty f_{FD}\left(\frac{\mu + E_g + E}{kT}\right) \sqrt{E} dE . \end{aligned} \quad (8.30)$$

In the classical limit (small concentrations, large temperatures and effective masses), the Fermi-Dirac functions may be replaced by the Boltzmann statistics; using (8.20) and (8.21), the concentrations have the simplified form:

$$\begin{aligned} n &= 2 \frac{(2\pi m_n kT)^{3/2}}{8\pi^3 \hbar^3} \exp\left(\frac{\mu}{kT}\right), \\ p &= 2 \frac{(2\pi m_p kT)^{3/2}}{8\pi^3 \hbar^3} \exp\left(-\frac{E_g + \mu}{kT}\right). \end{aligned} \quad (8.31)$$

The condition of neutrality ( $n=p$ ) leads to

$$\exp\left(\frac{\mu}{kT}\right) = \left(\frac{m_p}{m_n}\right)^{3/4} \exp\left(-\frac{E_g}{2kT}\right),$$

$$\mu = -\frac{E_g}{2} + \frac{3}{4}kT \ln\left(\frac{m_p}{m_n}\right).$$
(8.32)

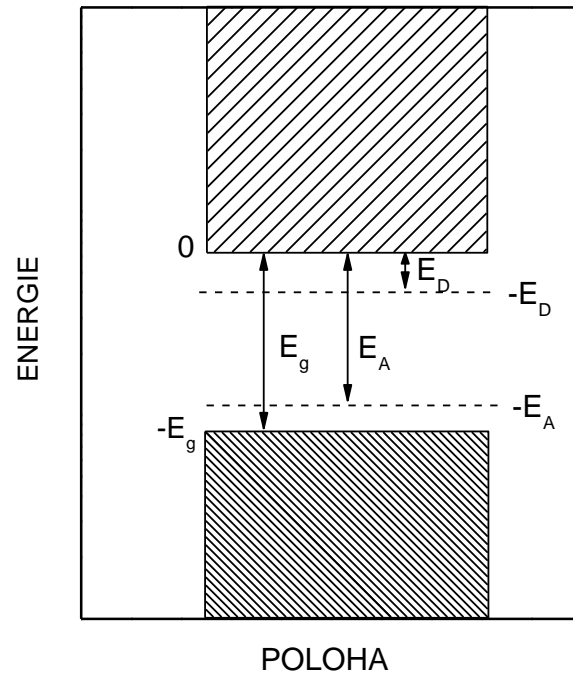
The chemical potential at zero temperature (Fermi energy) is located in the middle of the forbidden gap. The hole effective masses are typically multiples of those of electrons, the chemical potential at finite temperatures is located above the mid-gap, with the values of the order of  $kT$ . The concentration of electrons and holes (called *intrinsic*) is

$$n_i = n = p = 2 \frac{(2\pi\sqrt{m_n m_p} kT)^{3/2}}{8\pi^3 \hbar^3} \exp\left(-\frac{E_g}{2kT}\right) = n_{0T} \exp\left(-\frac{E_g}{2kT}\right).$$
(8.33)

The value of the factor  $n_{0T}$  in front of the exponential (the latter is typically rather small) in Eq. (8.33) corresponds to a single electron-hole pair in the volume of the cube with the edge equal to de Broglie wavelength of a particle, having the mass  $\sqrt{m_n m_p}$  and energy  $kT$ , see Eq. (8.22). At the temperature of 300 K and effective masses of both electrons and holes of  $9.1\text{E-}28$  g (i.e., the rest mass of free electrons), this concentration amounts to  $2.5\text{E}19$   $\text{cm}^{-3}$ , de Broglie wavelength is 4.3 nm; The intrinsic concentration  $n_i$  with the gap  $E_g$  of 1 and 0.1 eV is  $1\text{E}11$  and  $3.6\text{E}18$   $\text{cm}^{-3}$ , respectively.

## Doped semiconductors

The presence of donor and acceptor levels is schematically shown in the following figure:



Energies in a doped semiconductor.

At finite temperatures, the conduction-band states are occupied via the thermal excitation of (localized) impurity states, and also via the excitation of valence states. The charge neutrality requires the equality (the number of electrons in the conduction band) + (the number of electrons in the acceptor states) = (the number of holes in the valence band) + (the number of holes in the donor states), i.e.,

$$\begin{aligned} & \frac{\sqrt{2}}{\pi^2} \frac{(m_n)^{3/2}}{\hbar^3} \int_0^\infty f_{FD} \left( \frac{E - \mu}{kT} \right) \sqrt{E} dE + n_A f_{FD} \left( \frac{-E_A - \mu}{kT} \right) \\ &= \frac{\sqrt{2}}{\pi^2} \frac{(m_p)^{3/2}}{\hbar^3} \int_0^\infty f_{FD} \left( \frac{\mu + E_g + E}{kT} \right) \sqrt{E} dE + n_D f_{FD} \left( \frac{E_D + \mu}{kT} \right). \end{aligned} \quad (8.34)$$

The consequences of the occupation of different states can be assessed relatively easily in the following situation. Let us assume the chemical potential within the forbidden band, far from its edges; in addition, we will assume the temperature and effective masses large enough for the approximation of the Fermi-Dirac statistics in Eq. (8.34) by the Boltzmann exponential. This assumption requires the following inequality to be satisfied,

$$X \equiv \exp \left( \frac{\mu}{kT} \right) \ll 1, \quad (8.35)$$

and Eq. (8.34) reduces to

$$\begin{aligned} & 2 \frac{(2\pi m_n kT)^{3/2}}{8\pi^3 \hbar^3} X + \frac{n_A}{(1/X) \exp \left( \frac{-E_A - \mu}{kT} \right) + 1} \\ &= 2 \frac{(2\pi m_p kT)^{3/2}}{8\pi^3 \hbar^3} \exp \left( \frac{-E_g}{kT} \right) \frac{1}{X} + \frac{n_D}{X \exp \left( \frac{E_D}{kT} \right) + 1}. \end{aligned} \quad (8.36)$$

This is an algebraic equation of the order of 4 for the root  $X$ , which specifies the chemical potential.

Further simplification occurs for a single type of dopants, let us select donors (meaning no acceptors,  $n_A = 0$ ), and a small ionization energy compared with the gap ( $E_D \ll E_g$ ):

$$2 \frac{(2\pi m_n kT)^{3/2}}{8\pi^3 \hbar^3} X = \frac{n_D}{X \exp\left(\frac{E_D}{kT}\right) + 1} . \quad (8.37)$$

For low temperatures ( $kT \ll E_D$ ), the value of 1 in the numerator of Eq. (8.37) is negligible, leading to

$$X = \frac{(2\pi \hbar)^{3/2}}{\sqrt{2}(2\pi m_n kT)^{3/4}} \sqrt{n_D} \exp\left(-\frac{E_D}{2kT}\right) , \quad (8.38)$$

and the chemical potential

$$\mu = -\frac{E_D}{2} + \frac{kT}{2} \ln \frac{(2\pi \hbar)^3 n_D}{2(2\pi m_n kT)^{3/2}} \quad (8.39)$$

and the concentration of conduction electrons

$$n = \frac{\sqrt{2}(2\pi m_n kT)^{3/4}}{(2\pi \hbar)^{3/2}} \sqrt{n_D} \exp\left(-\frac{E_D}{2kT}\right) . \quad (8.40)$$

Conversely, for high temperatures ( $E_D \ll kT$ ), the value of the exponential in the numerator of Eq. (8.37) is negligible, leading to

$$X = \frac{(2\pi \hbar)^3}{2(2\pi m_n kT)^{3/2}} n_D , \quad (8.41)$$

chemical potential

$$\mu = kT \ln \frac{(2\pi\hbar)^3 n_D}{2(2\pi m_n kT)^{3/2}} \quad (8.42)$$

and the concentration of conduction electrons

$$n = n_D . \quad (8.43)$$

This is expected, as the thermal energy ionizes all of the donors.

Relations (8.37-43) can be used for the acceptor doping (setting  $n_D = 0$ ), via the substitution of  $n_D, E_D, n_n$  by  $n_A, E_A, n_p$ , setting the zero energy at the valence band maximum, and the direction of increasing energies inside the valence band.

Let us note a consequence of Eqs. (8.31) and (8.33). The product of the electron and hole concentrations is

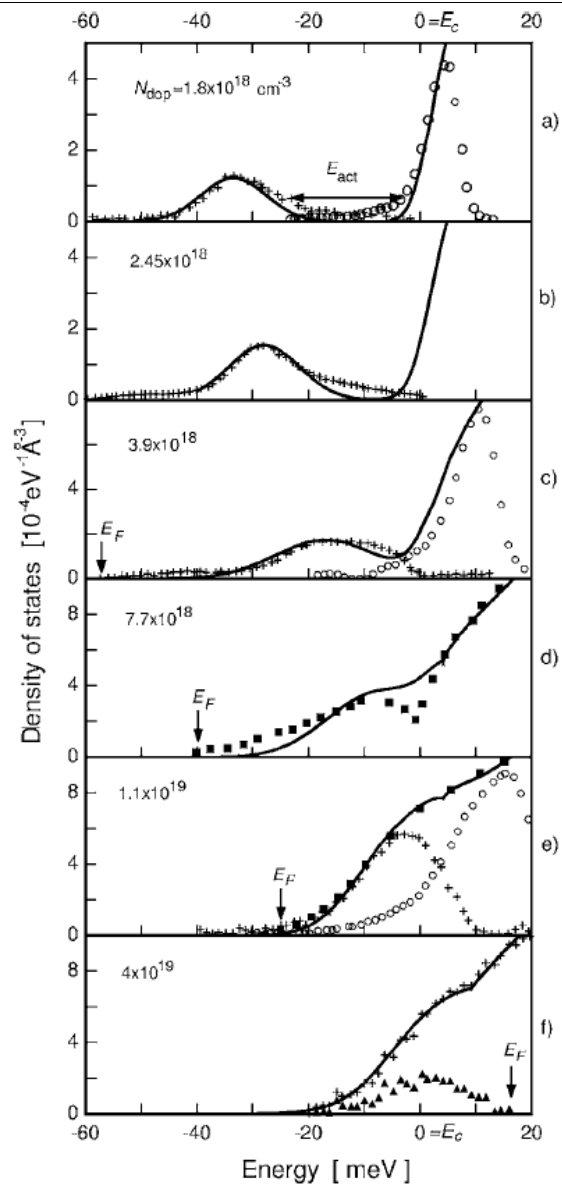
$$np = 2 \frac{(2\pi\sqrt{m_n m_p} kT)^3}{(8\pi^3 \hbar^3)^2} \exp\left(-\frac{E_g}{kT}\right) = n_i^2, \quad (8.44)$$

which is the square of the intrinsic concentration (on the absence of doping). The free electrons or holes from impurity states reduces the concentration of the carriers of the opposite sign; this effect becomes more pronounced for smaller intrinsic concentrations.

Semiconductor crystals containing both donor and acceptor levels are called (usually only partly) *compensated*.

The statistical equilibrium in crystals with anisotropic and degenerate bottom of the conduction band requires the density of states to be modified (planned for exercises). Similar problems occur for non-quadratic dispersion of valence bands.

The density of states is well known from measurements on many doped semiconductors. Shown below are examples, in particular for Si:P in the neighborhood of the metal-insulator (MI) transition, occurring at  $\sim 3.5 \times 10^{18} \text{ cm}^{-3}$ .



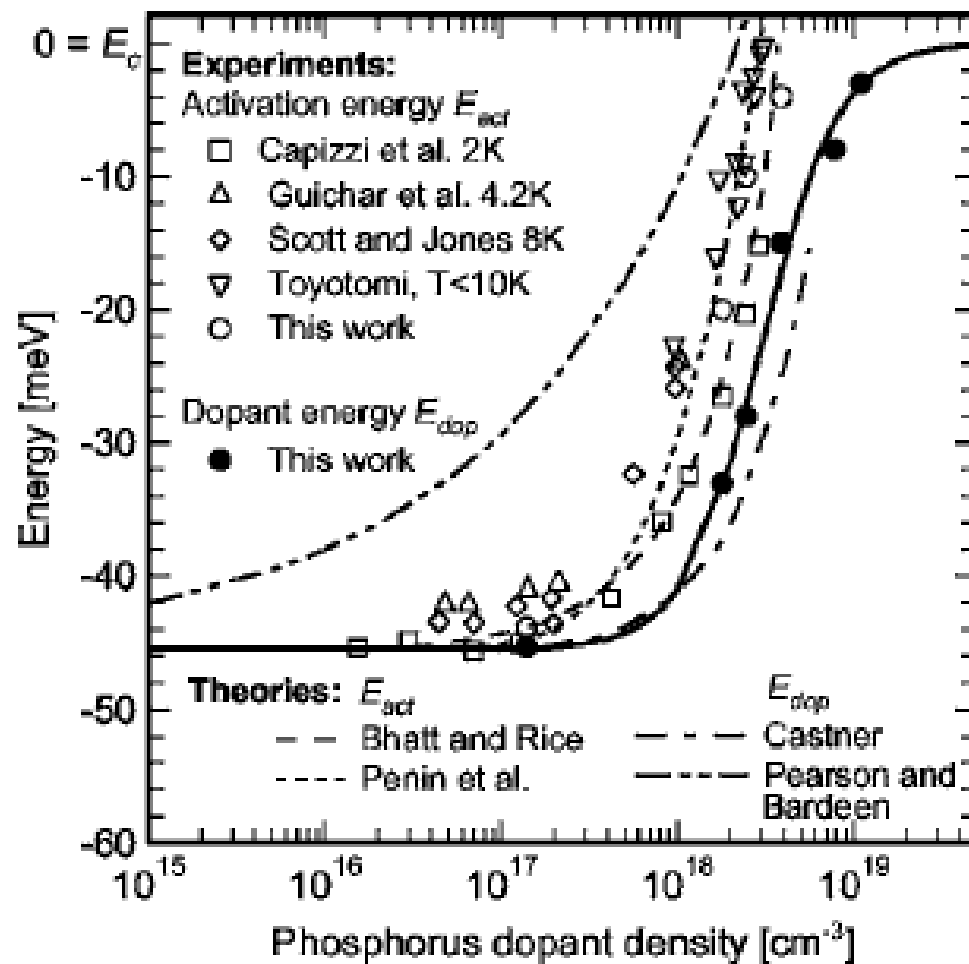
Photoluminescence spectra of Si:P at weak (crosses) and strong (circles) injection, and density of states from transport measurements (full squares), at 4.2 K.

Different levels of phosphorus doping.

Parametrized density of states (solid lines).

From Altermatt et al., JAP 2006.



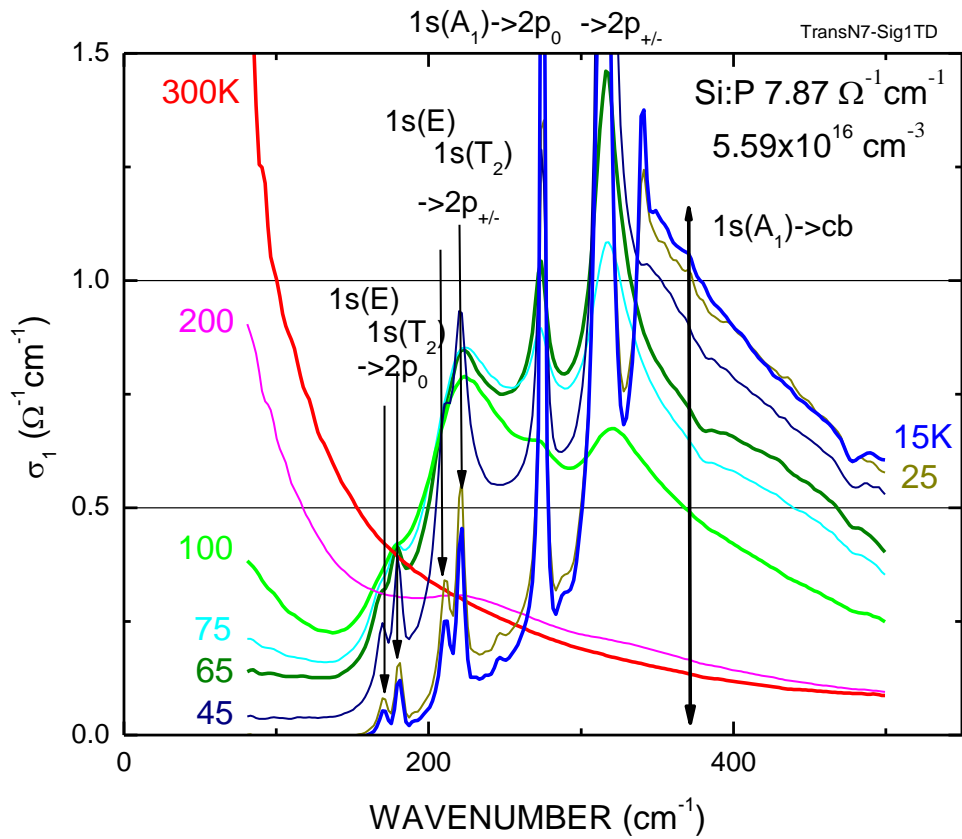


Energy of the maxima of impurity band (full circles) and activation energies (empty symbols) in phosphorus doped Si.

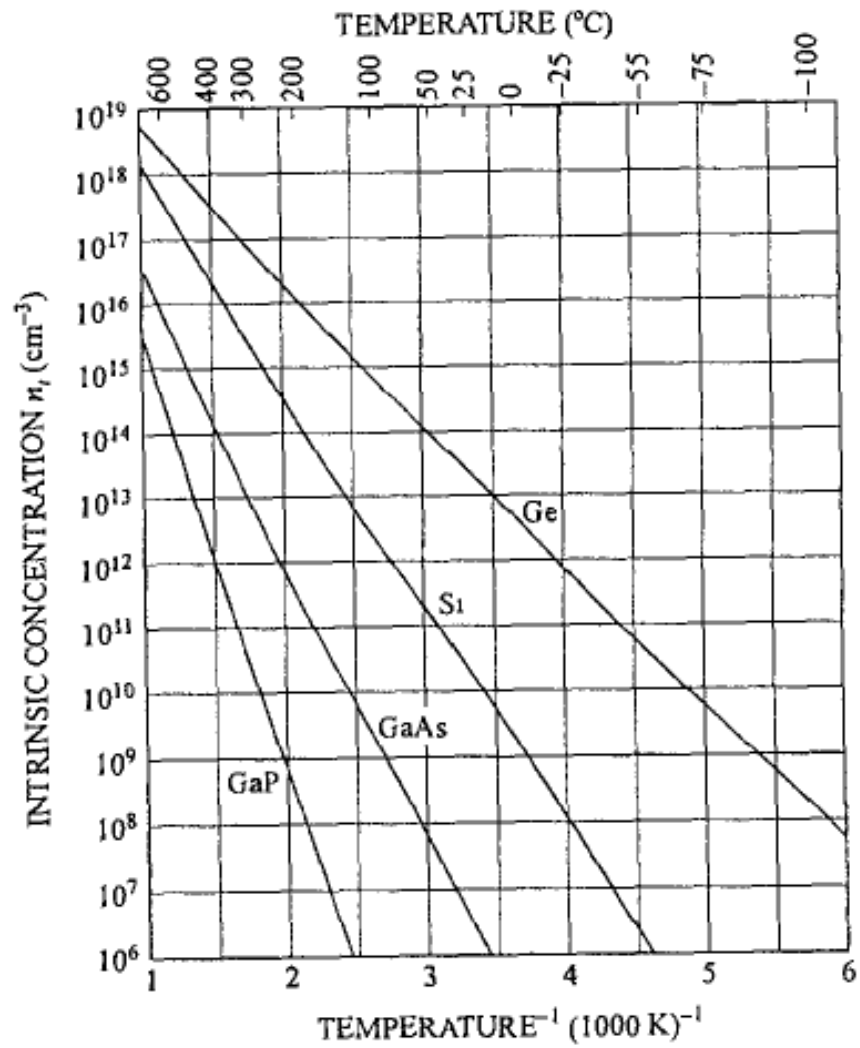
Solid line: parametrized position of the band maximum.

Dashed/dotted lines: results of several theoretical treatments.

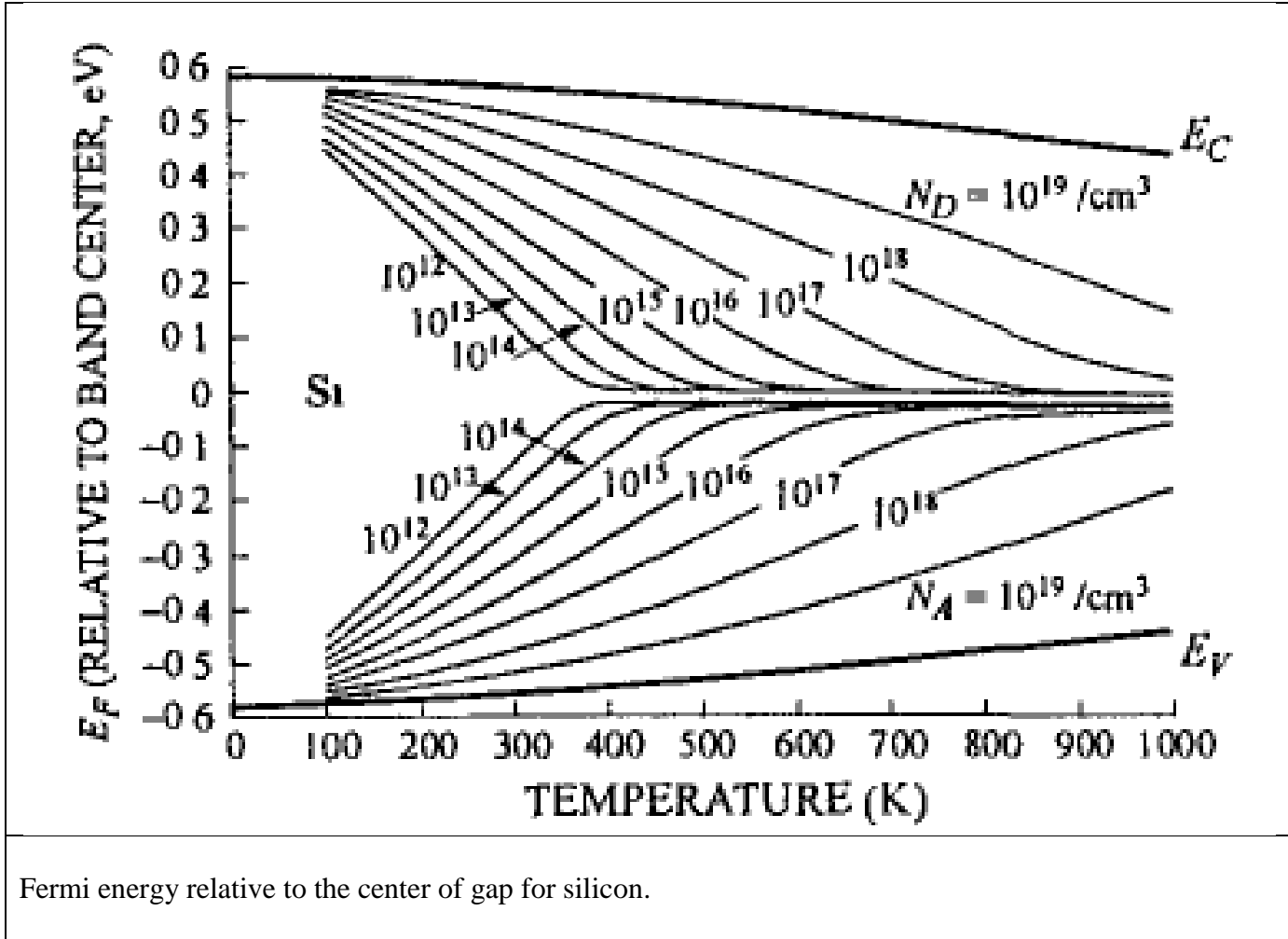
From Altermatt et al., JAP 2006.



Real part of conductivity derived from transmission spectra of Si:P ( $5.59 \times 10^{16} \text{ cm}^{-3}$ ) at different temperatures. The wavenumber of  $363 \text{ cm}^{-1}$  corresponds to the ionization energy of 45 meV.



Intrinsic concentration for several semiconductors.



Fermi energy relative to the center of gap for silicon.