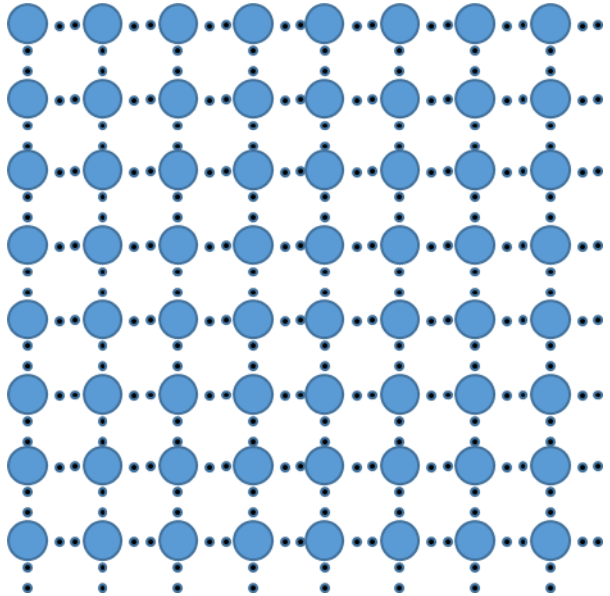
Class 05
Doping in semiconductors

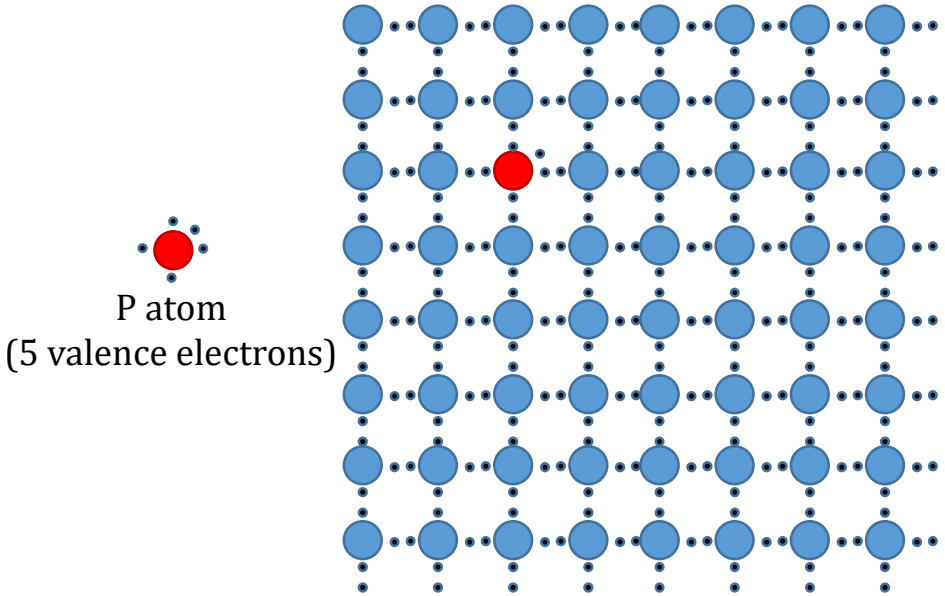
10.03.2025

- ❑ Adding impurities: dopants
- ❑ Ionization energy
  - Bohr's model
  - Dopants in real materials
- ❑ Carrier statistics in doped semiconductors
  - Impact of T
  - Degenerate semiconductors

Intrinsic and n-doped semiconductors



Pure Silicon (100% Si)



Almost pure silicon (99.99999% Si + 0.00001% P)

Lattice constant: 0.54 nm
10^{22} atoms/cm^3

ni = 10^{10} cm^{-3} at room temperature

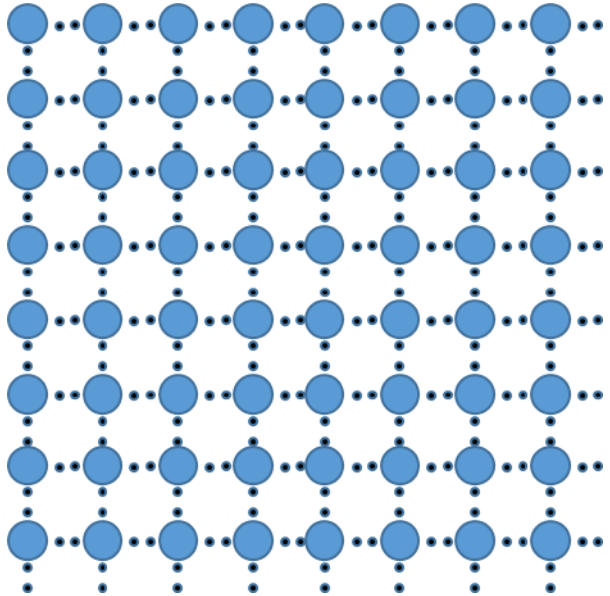
One atom every 10^{12} contributes to the electrons in the conduction band

0.00001% P = 1 P atom every 10^7 Si atoms.
10^{15} P atoms/cm^3

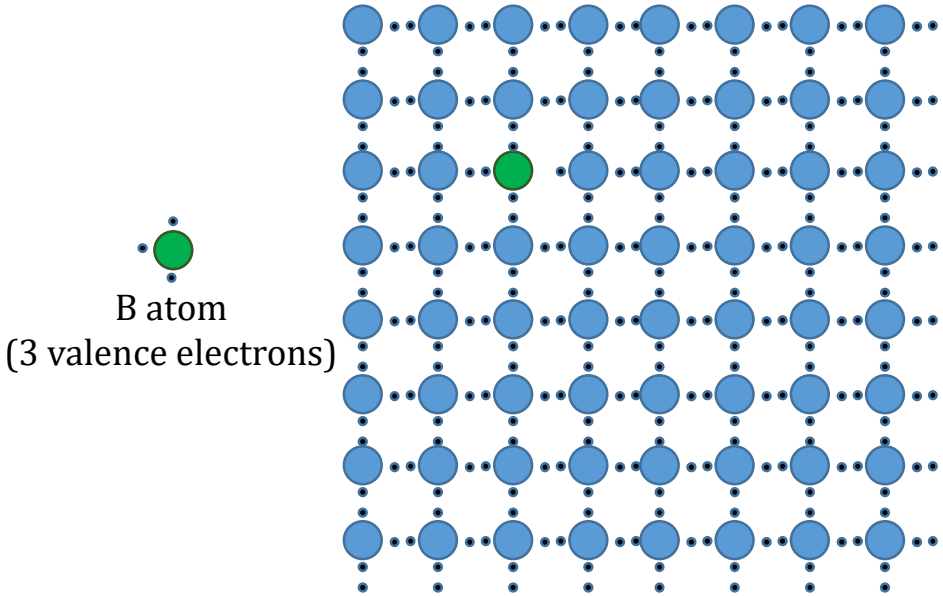
As the P has an extra valence electron, the conduction band can gain 1 e- per P atom (donor).

n = 10^{15} cm^{-3} at room temperature
(100'000 times higher than intrinsic)

Intrinsic and p-doped semiconductors



Pure Silicon (100% Si)



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Lattice constant: 0.54 nm
10^{22} atoms/cm^3

ni = 10^{10} cm^{-3} at room temperature

One atom every 10^{12} contributes to the electrons in the conduction band

0.00001% B = 1 B atom every 10^7 Si atoms.
10^{15} B atoms/cm^3

As the B has one valence electron less, the valence band can gain 1 h+ per B atom (acceptor).

p = 10^{15} cm^{-3} at room temperature
(100'000 times higher than intrinsic)

Modified Bohr's model

The simplified atomistic picture assumes that the extra charge of dopants act as a free charge in the lattice.

The correct description instead must consider the charge unrelated to the molecular bonds of the lattice but binded to the dopant nucleus. In the case of monovalent dopant, we can use a modified Bohr model to describe the system.

Modified Bohr model

P atom with
one unbound valence electron

The equilibrium is reached when the Coulomb attraction equals the centripetal force.

$$\frac{e^2}{4\pi\varepsilon r_n^2} = \frac{m_e^* v^2}{r_n}$$

v is the velocity of the electron in a circular orbit which defines the quantized angular momentum L

$$L = m_e^* * v * r_n = n\hbar$$

$$v^2 = \frac{e^2}{4\pi\varepsilon r_n m_e^*}$$

$$v^2 = \frac{n^2\hbar^2}{r_n^2 m_e^{*2}}$$

$$r_n = n^2 \frac{\hbar^2 4\pi\varepsilon}{m_e^* e^2}$$

Radius of the extra charge rotating around its P atom embedded in a Si lattice

$$a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2}$$

Radius of electron in the hydrogen atom (original Bohr's model)

$$\frac{r_n}{a_0} = n^2 \varepsilon_r \left(\frac{m_e}{m_e^*}\right) = 45$$

Ionization energy

Modified Bohr model

P atom with
one unbound valence electron

$$\frac{r_n}{a_0} = n^2 \varepsilon_r \left(\frac{m_e}{m_e^*}\right) = 45$$

The electron in P:Si orbits far from the nucleus (with respect to the analogous case of H atom). It is expected a lower binding energy.

$$E_n = -\frac{m_e^* e^4}{2\pi\ (4\pi\varepsilon\ * n\hbar)^2}$$

The binding energy is associated to the orbit radius and can therefore be calculated.

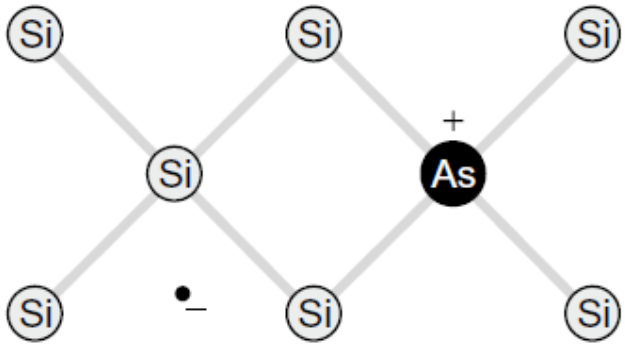
$E_n = -13.6\ eV$ for H atom

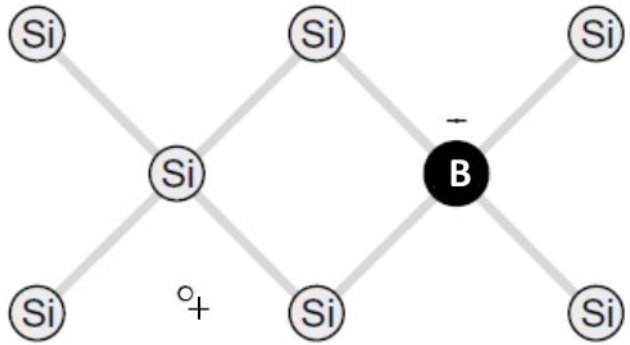
$E_n = -26\ meV$ For P atom in Si lattice

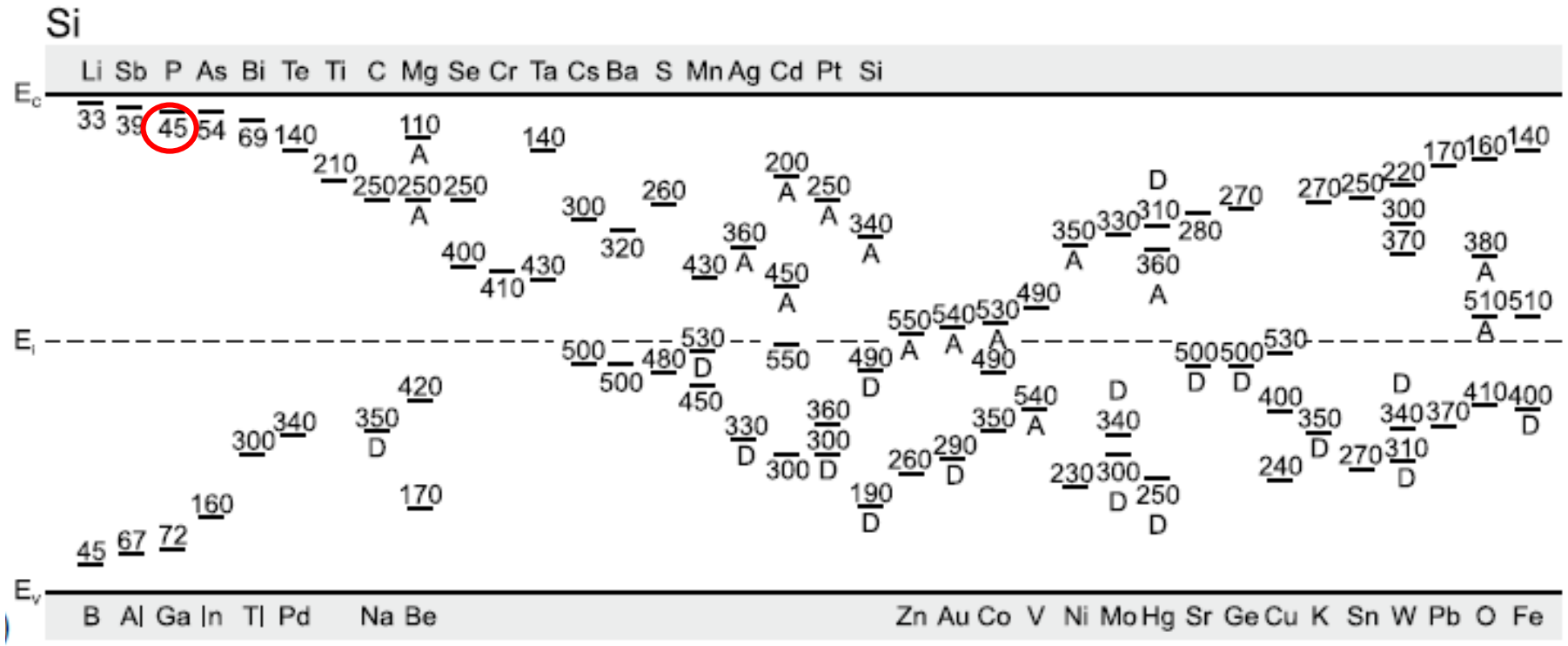
Energy required to separate the «extra» charge from its nucleus,i.e. IONIZATION ENERGY (E_D)

The modified Bohr's model offers a simple estimation of the ionization energy (correct order of magnitude). This result shows that the energy required for the dopants to provide free charges to the material is in the order of kT.

Dopants and ionization energies for Si





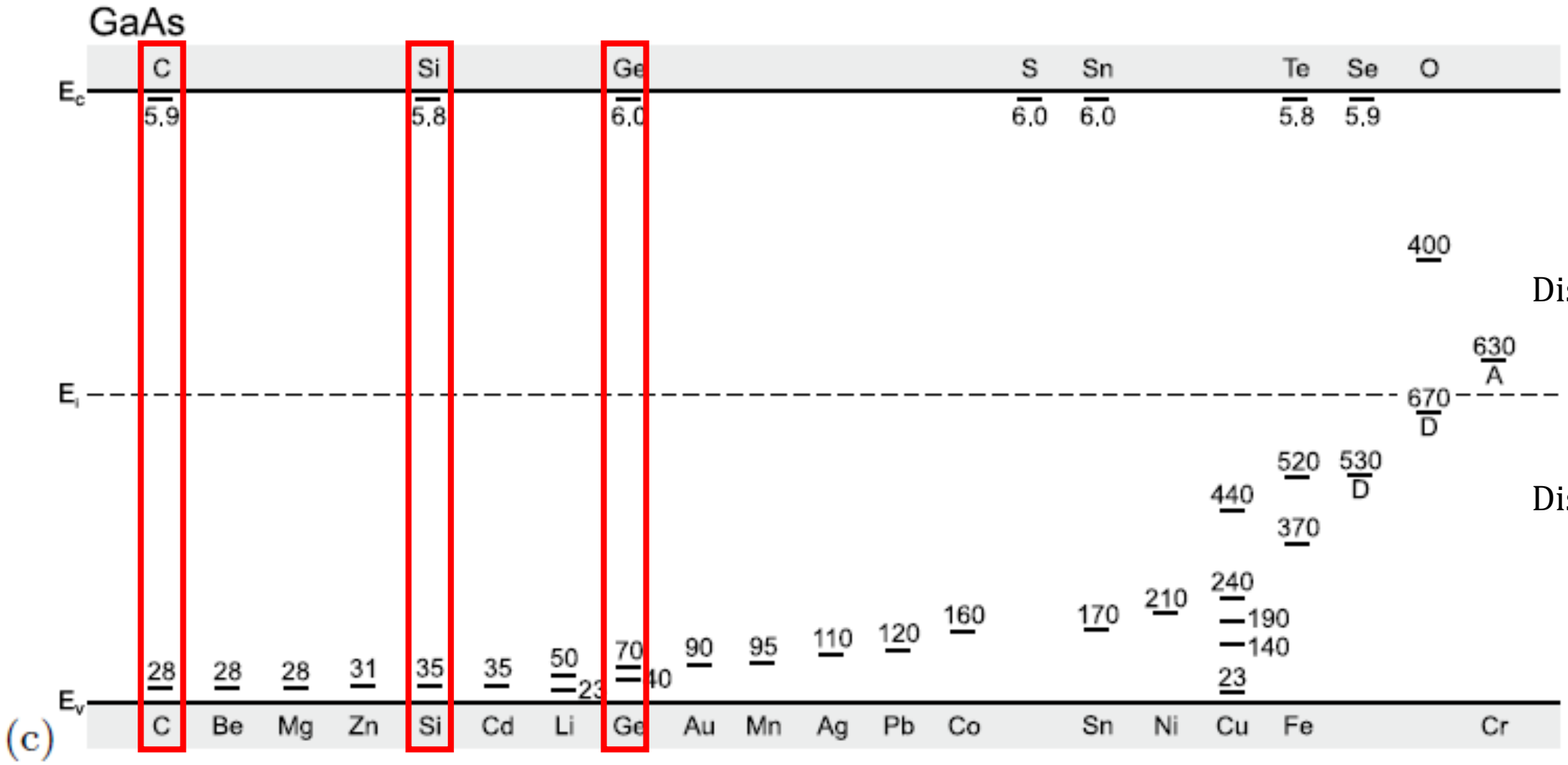


Distance from E_C (meV)

Distance from E_V (meV)

Grundmann, Ch 7

Dopants and ionization energies for GaAs



Distance from E_C (meV)

Distance from E_V (meV)

Grundmann, Ch 7

Carrier statistics in doped semiconductors

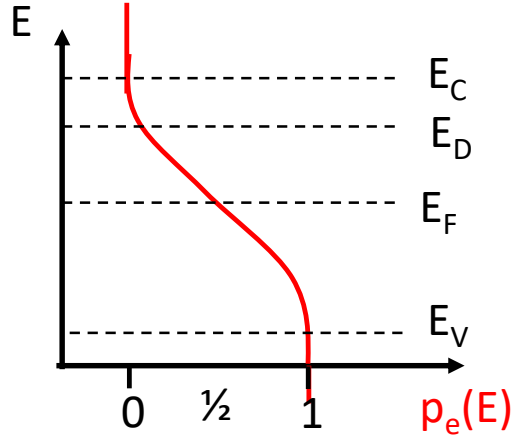
When adding dopants, the carrier density will depend on:

- Dopant density (N_D)
- Ionized (empty) dopant density (N_D^+)
- Non-ionized (populated) dopant density (N_D^0)

where $N_D = N_D^+ + N_D^0$

Assuming that $N_D^+ >> n_i$, then $n = N_D^+$

The ionization of atoms will follow a distribution depending on the ionizaion energy and the temperature.



$$f_e(E) = \frac{1}{\exp\left(\frac{E-E_F}{kT}\right)+1}$$

$$N_D^0 = N_D\, f_e(E_D)$$

$$N_D^+ = N_D\,(1 - f_e(E_D))$$

If we consider the ratio empty and populated donor, it is clear that a degeneracy factor $\hat{g}_D$ (usually equal to 2) must be taken into account.

$$\frac{N_D^0}{N_D^+} = \hat{g}_D \exp\left(\frac{E_F - E_D}{kT}\right)$$

The charged donor has one e- (either spin up or down, deg. 2)

The neutral donor has two e- (spin up and down, deg. 1)

$$f^0 = \frac{N_D^+}{N_D} = \frac{1}{\hat{g}_D \exp\left(-\frac{E_D-E_F}{kT}\right)+1}$$

$$n = f^0\, N_D = N_D^+ = \frac{N_D}{1 + \hat{g}_D \exp\left(\frac{E_F-E_D}{kT}\right)}$$

E_F for doped semiconductors

$$n = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(\frac{E_F - E_C}{kT}\right) = N_C \exp\left(\frac{E_F - E_C}{kT}\right).$$

$$p = 2\left(\frac{m_h kT}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{E_F - E_V}{kT}\right) = N_V \exp\left(-\frac{E_F - E_V}{kT}\right).$$

where: $N_C = 2\left(\frac{m_e\, kT}{2\pi\,\hbar^2}\right)^{3/2}$ $N_V = 2\left(\frac{m_h\, kT}{2\pi\,\hbar^2}\right)^{3/2}$,

+

ELECTRONEUTRALITY CONDITION

$-n + N_D^+ = 0$ (for doped semiconductors , ass. $N_D^+ >> n_i$)

$n = N_D^+$

$$N_C\, exp\left(\frac{E_F - E_C}{kT}\right) = \frac{N_D}{1 + \hat{g}_D exp\left(\frac{E_F - E_D}{kT}\right)}$$

Approx. solution for low T

Approx. solution for high T

$$E_F \cong E_C - \frac{1}{2}E_D + \frac{1}{2}kT * ln\left(\frac{N_D}{\hat{g}_D N_C}\right)$$

$$E_F \cong E_C + kT * ln\left(\frac{N_D}{N_C}\right)$$

Fermi energy vs T in doped semiconductors

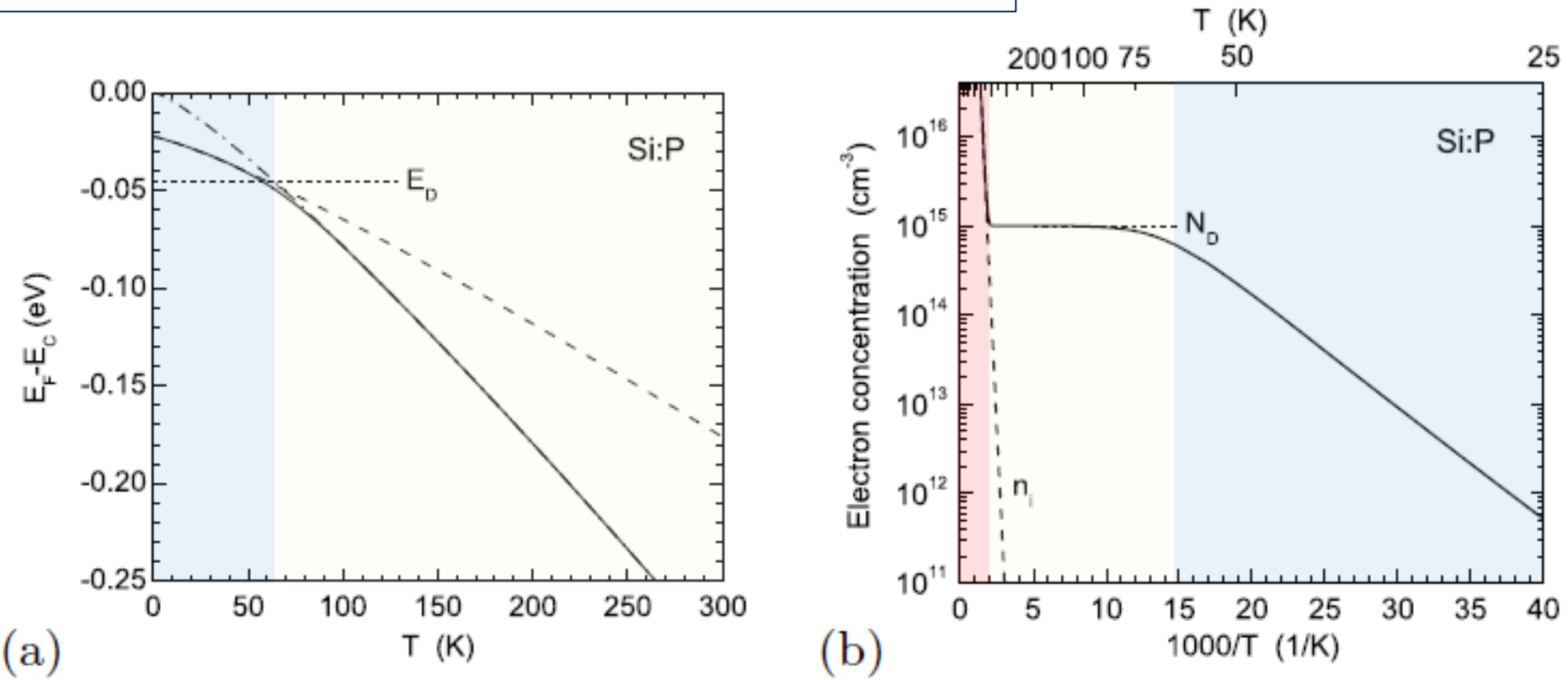


Fig. 7.9 **a** Position of the Fermi level in Si:P ($N_D = 10^{15}\,\mathrm{cm}^{-3}$, $E_D^b = 45\,\mathrm{meV}$, no acceptors) as a function of temperature *without* consideration of intrinsic carriers. Zero energy refers to the (temperature-dependent, Table 6.4) conduction-band edge E_C with approximative solutions for low (*dashed line*, (7.31)) and high (*dash-dotted line*, (7.32)) temperatures. **b** Corresponding density of conduction-band electrons as a function of temperature

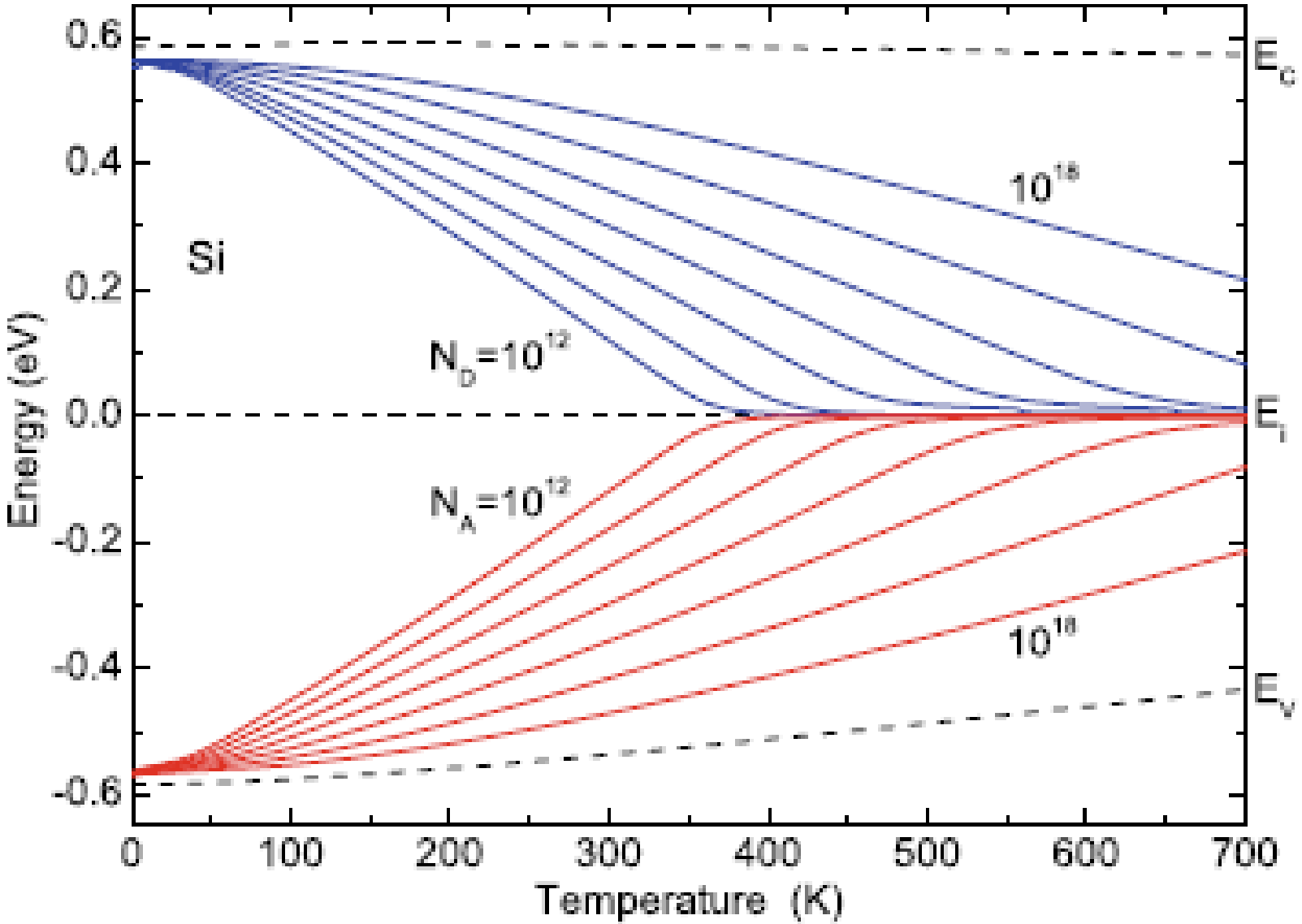
High T: Intrinsic regime

Intermediate T: Saturation regime ⟶ $E_F \cong E_C + kT \ln\left(\frac{N_D}{N_C}\right)$

Low T: Freeze out regime

Fermi energy vs T in doped Si

Fig. 7.12 Fermi level in silicon as a function of temperature for various doping levels (n-type (*blue lines*) and p-type (*red lines*)) of $10^{12}, 10^{13}, \ldots, 10^{18}\,\mathrm{cm}^{-3}$. The intrinsic Fermi level is chosen as zero energy for all temperatures. The (temperature-dependent) conduction and valence band edges are shown as *dashed lines*



Degenerate semiconductors

Homogeneously distributed

Cluster

Degenerate semiconductor

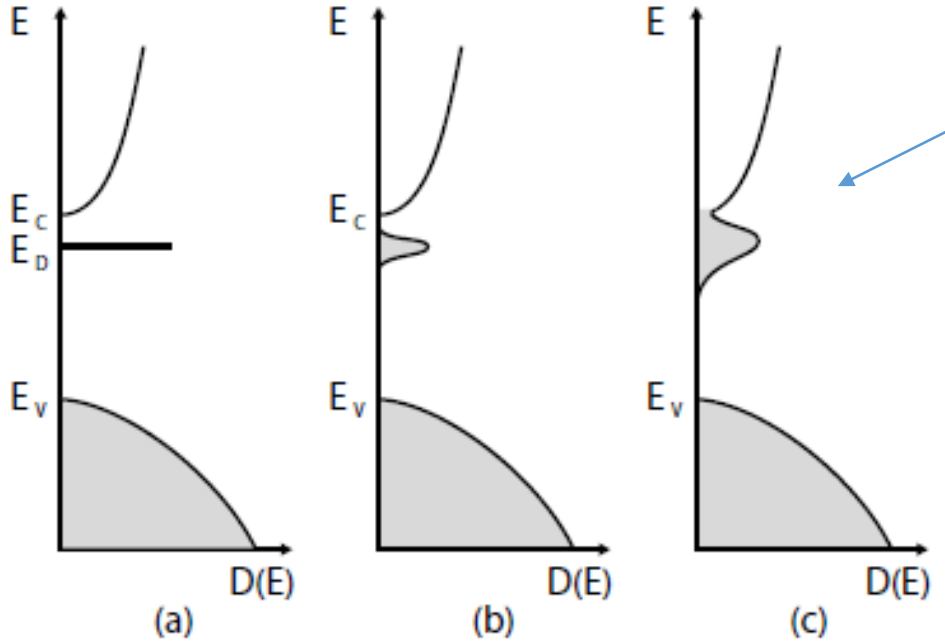


Fig. 7.25 Principle of the formation of a (donor) impurity band. **a** Small doping concentration and sharply defined impurity state at E_D, **b** increasing doping and development of an impurity band that **c** widens further and eventually overlaps with the conduction band for high impurity concentration. The *shaded areas* indicate populated states at $T = 0\,K$