Electron and Hole Concentrations in an Intrinsic Semiconductor

Electrons:

density of states $$D_C(E) = 4\pi\left(2m_e^*/h^2\right)^{3/2} \cdot \sqrt{E - E_C}$$ with m_e^* effective DOS mass

electron density:
with <n>(E) using
Boltzmann's
approximation

$$n(E) \approx 4\pi\left(2m_e^*/h^2\right)^{3/2} \cdot \int_{E_C}^{\infty} \sqrt{E - E_C} \cdot \exp\left(-\frac{E - E_C + E_C - \mu_0}{kT}\right) dE$$

$$= 4\pi\left(2m_e^*/h^2\right)^{3/2} \exp\left(-\frac{E_C - \mu_0}{kT}\right) \cdot \int_{E_C}^{\infty} \sqrt{E - E_C} \cdot \exp\left(-\frac{E - E_C}{kT}\right) dE$$

$$= 4\pi\left(2m_e^*/h^2\right)^{3/2} \exp\left(-\frac{E_C - \mu_0}{kT}\right) \cdot (kT)^{3/2} \underbrace{\int_0^{\infty} \sqrt{\frac{E - E_C}{kT}} \cdot \exp\left(-\frac{E - E_C}{kT}\right) d\left(\frac{E - E_C}{kT}\right)}_{\Gamma\left(\frac{3}{4}\right) = \frac{\sqrt{\pi}}{2}}$$

$$= \underbrace{2\left(\frac{2\pi\, m_e^* kT}{h^2}\right)^{3/2}}_{} \exp\left(-\frac{E_C - \mu_0}{kT}\right)$$

$$n = N_C(T) \cdot \exp\left(-\frac{E_C - \mu_0}{kT}\right)$$ where μ_0 is the Fermi Energy E_F

→ **effective conduction band density of states**
(weakly temperature dependent!)

Holes: completely analogous!

The Effektive DOS Mass

Definition: $$D(E) = 4\pi\left(2m_e^*/h^2\right)^{3/2}\sqrt{\left|E-E_{C/V}\right|} = \sum_\alpha D_\alpha(E)$$

where the sum runs over all degenerate band extrema.

Case 1: Conduction bands (with g-fold effective valley degeneracy i.c.o. indirect)

$$D_\alpha(E) = 4\pi\left(2m_e^*/h^2\right)^{3/2}\sqrt{E-E_C} = g\cdot 4\pi\left(2\left(m_t{}^2 m_\ell\right)^{1/3}/h^2\right)^{3/2}\sqrt{E-E_C}$$

$$\longrightarrow \quad m_e^* = \left(g^2 m_t{}^2 m_\ell\right)^{1/3}$$

Examples

Si (indirect): $m_\ell = 0,92m, \quad m_t = 0,19m, \quad g = 6$

Ge (indirect): $m_\ell = 1,57m, \quad m_t = 0,082m, \quad g = 8/2 = 4$

GaAs (direct): $m_\ell = m_t = 0,07m, \quad g = 1$

Case 2: Valence bands

$$D_\alpha(E) = 4\pi\left(2m_\alpha/h^2\right)^{3/2}\sqrt{E_V - E} \qquad \text{with } \alpha = \text{lh, hh, so}$$

$$m_h^* = \left(m_{lh}{}^{3/2} + m_{hh}{}^{3/2} + e^{\frac{-\Delta_0}{kT}}\cdot m_{s.o.}{}^{3/2}\right)^{2/3}$$

Note: slightly temperature dependent if not $\Delta_0 \ll kT$ or $\Delta_0 \gg kT$!

Examples

Si: $\Delta_0 = 44\text{ meV}, m_{\ell h} = 0,15m, m_{hh} = 0,54m, m_{so} = 0,23m$

Ge: $\Delta_0 = 295\text{ meV}, m_{\ell h} = 0,043m, m_{hh} = 0,34m, m_{so} = 0,10m$

GaAs: $\Delta_0 = 341\text{ meV}, m_{\ell h} = 0,08m, m_{hh} = 0,53m, m_{so} = 0,15m$

Electrons and Holes in an Intrinsic Semiconductor

electron density:

$$n = N_C(T) \cdot \exp\left(-\frac{E_C - \mu_0}{kT}\right)$$

effective conduction band density of states

hole density:

$$p = N_V(T) \cdot \exp\left(\frac{E_V - \mu_0}{kT}\right)$$

effective valence band density of states

always: $$n \cdot p = n_i^2 = N_C N_V \cdot \exp\left(-\frac{E_C - E_V}{kT}\right)$$ independent of μ_0

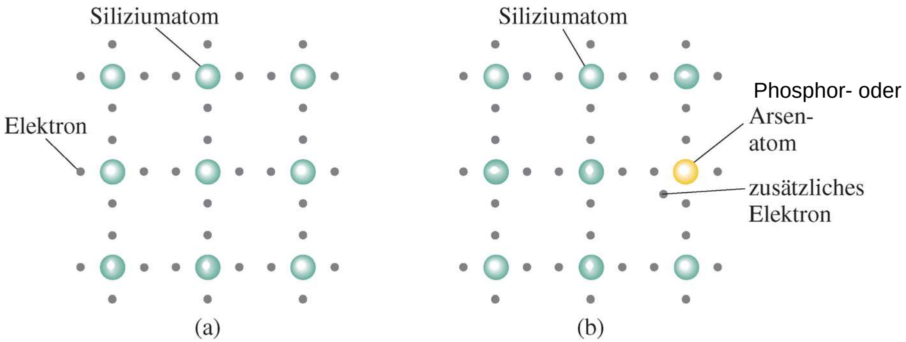
intrinsic: $$n = p = n_i = \sqrt{N_C N_V} \cdot \exp\left(-\frac{E_C - E_V}{2\,kT}\right)$$

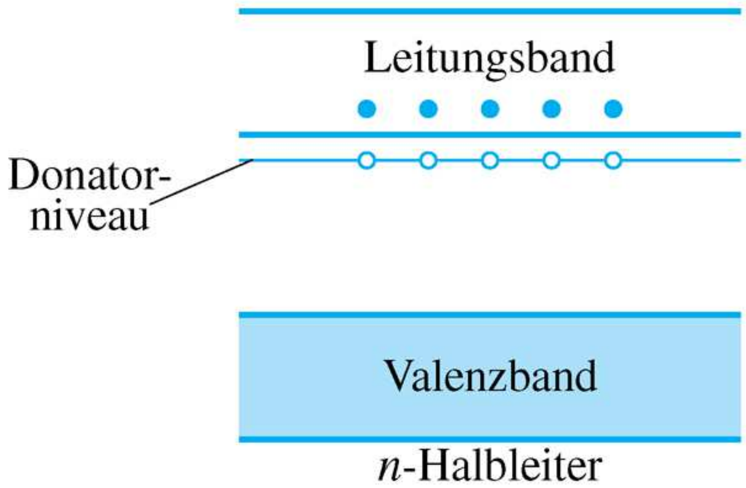
$$\rightarrow \quad \mu_0 = \frac{E_C + E_V}{2} - \frac{kT}{2} \cdot \ln\left(\frac{N_C}{N_V}\right)$$

Note: for low T is the Fermi level midway between the (essentially) occupied and unoccupied states; with increasing T it shifts logaritmically towards the reservoir of states with the lower DOS! This is a genaral behaviour!

Dotierung von Halbleitern

n-Dotierung:

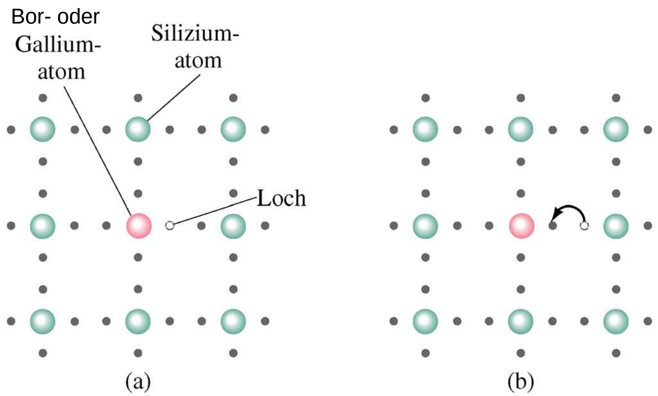


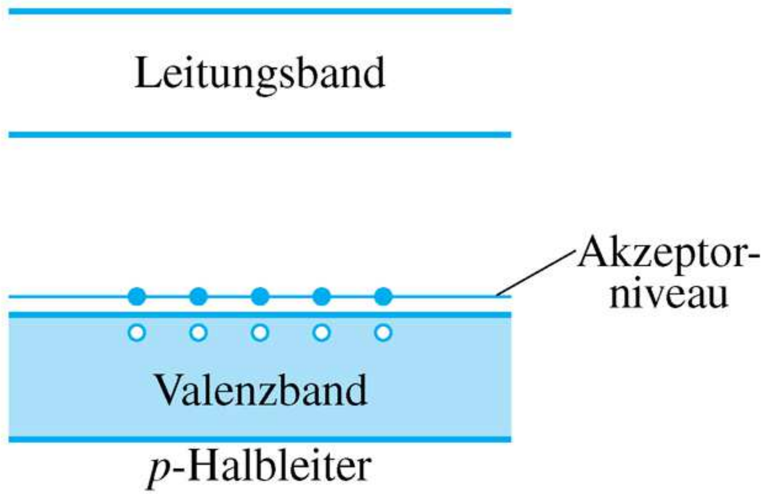


Zweidimensionale Darstellung eines Siliziumkristalls. (a) Vier (äußere) Elektronen umgeben jedes Siliziumatom. (b) Ein mit Arsenatomen oder Phosphoratomen dotierter Siliziumkristall: Die zusätzlichen Elektronen des ‘Donators’ werden für die chemische Bindung nicht benötigt. Es bleibt im wasserstoffähnlichen ‘Zusatzpotential’ des Donator-Atoms gebunden, aber in einem Zustand mit einer nur geringen ‘Bindungsenergie’ gegenüber den freien Bloch-Zuständen des Leitungsbandes. Im Termschema entsteht ein entsprechender ‘Donator-Zustand’.
Bei Raumtemperatur sorgt die Fermi-Statistik dafür, dass die von den Akzeptoren eingebrachten Elektronen die Donatorzustände verlassen und sich alle als freie Leitungsband-Blochelektronen bewegen können und zur Leitfähigkeit des Halbleiters beitragen.

Dotierung von Halbleitern

p-Dotierung:





Ein *p*-Halbleiter, Gallium- oder Bordotiertes Silizium. (a) Gallium oder Bor besitzen nur drei Außenelektronen, so dass es einen leeren Platz oder ein *Loch* innerhalb der Struktur gibt. (b) Elektronen des Siliziumatoms können in das Loch springen und es ausfüllen. Effektiv bewegt sich das Loch an eine andere Stelle (in der Abbildung nach rechts), an der sich vorher das Elektron befunden hat.
Im Termschema entsteht ein Zustand knapp oberhalb der Valenzbandkante (‘Akzeptorzustand’). Auch hier sorgt die Fermistatistik bei Raumtemperatur dafür, dass all diese Akzeptorzustände mit Elektronen besetzt (‘von Löchern entleert)’ sind, und es damit für jedes eingebrachte Akzeptor-Atom ein frei bewegliches Loch im Valenzband gibt.

Doping by Shallow Impurities

Electrons:

Essentially one excess electron + one more proton;

$\longrightarrow$ one electron around a screened positve space charge $\longrightarrow$ n-type

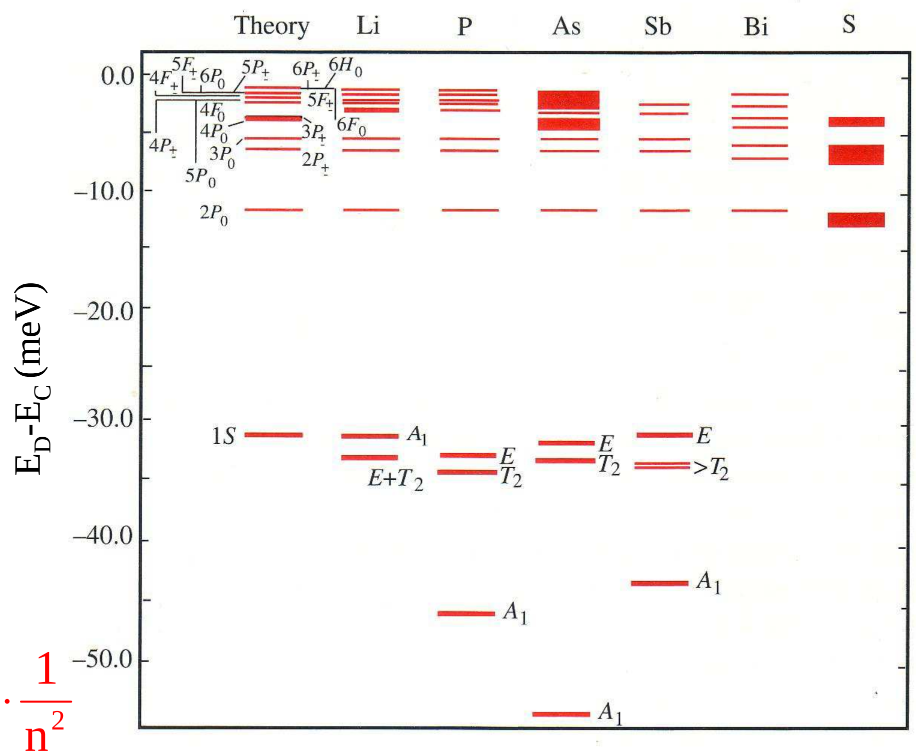
Hydrogen atom:

$$E_n = -\underbrace{\frac{m\,e^4}{8\varepsilon_0{}^2 h^2}}_{E_R} \cdot \frac{1}{n^2}$$

Hydrogen-like level scheme below the conduction band minimum; for the e-statistics, only the ground state at E_D is relevant!

$$E_n = E_C - E_R \cdot \frac{m^*}{m} \cdot \frac{1}{\left(\frac{\varepsilon\varepsilon_0}{\varepsilon_0}\right)^2} \cdot \frac{1}{n^2}$$

$$E_n = E_C - 13{,}6\,\text{eV} \cdot \frac{m^*/m}{\varepsilon^2} \cdot \frac{1}{n^2}$$



Estimate:

$m^*/m \approx 0{,}2$, $\qquad \varepsilon \approx 10$

$$\rightarrow\quad E_n \approx E_C - \frac{13{,}6 \cdot 0{,}2}{100}\,\text{eV} \cdot \frac{1}{n^2} = E_C - 28\,\text{meV} \cdot \frac{1}{n^2}$$

Holes:

Completely anaologous!

Charge Carrier Densities for Doped Semiconductorsn

n-tpye doping, electron density

Parameters:
donor density n_D,
compensating deep acceptor density n_A
fully occupied by electrons,
effectiv conduction band density of states N_C,
donor activation energy E_C-E_D.

Conduction band electron density n from charge balance:

$$n_A + N_C \cdot \exp\left(-\frac{E_C - E_F}{kT}\right) = n_D \cdot \left[\exp\left(-\frac{E_F - E_D}{kT}\right) + 1\right]^{-1}$$

yields

$$2x = \left(\frac{n_A}{N_C} + B\right) \cdot \left[\sqrt{1 + \frac{4\ (n_D - n_A)}{B\ N_C \cdot (1 + \frac{n_A}{BN_C})^2}} - 1\right]$$

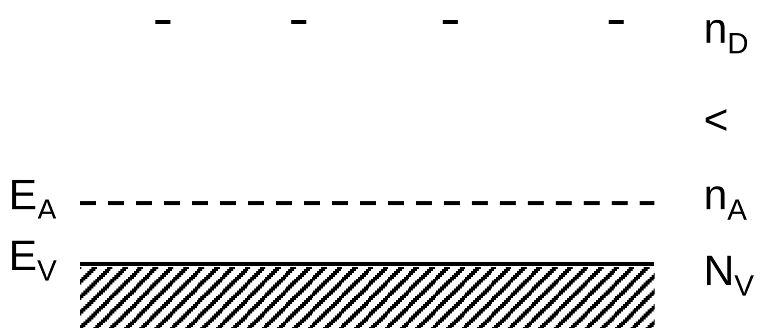
for the variable $x = \exp\left(-\frac{E_C - E_F}{kT}\right)$ with the abbreviation $B = \exp\left(-\frac{E_C - E_D}{kT}\right)$.

With that, $n = N_C\ x$ and $E_C - E_F = -kT \cdot \ln(x)$

Charge Carrier Densities for Doped Semiconductors

p-tpye doping, hole density

Parameters:
acceptor density n_A,
compensating deep donor density n_D
fully **un**occupied by electrons,
effective valence band density of states N_V,
donor activation energy E_A-E_V.



Valence band hole density p again from charge balance.

$$2x = \left(\frac{n_D}{N_V} + B\right) \cdot \left[\sqrt{1 + \frac{4(n_A - n_D)}{BN_V \cdot (1 + \frac{n_D}{BN_V})^2}} - 1\right]$$

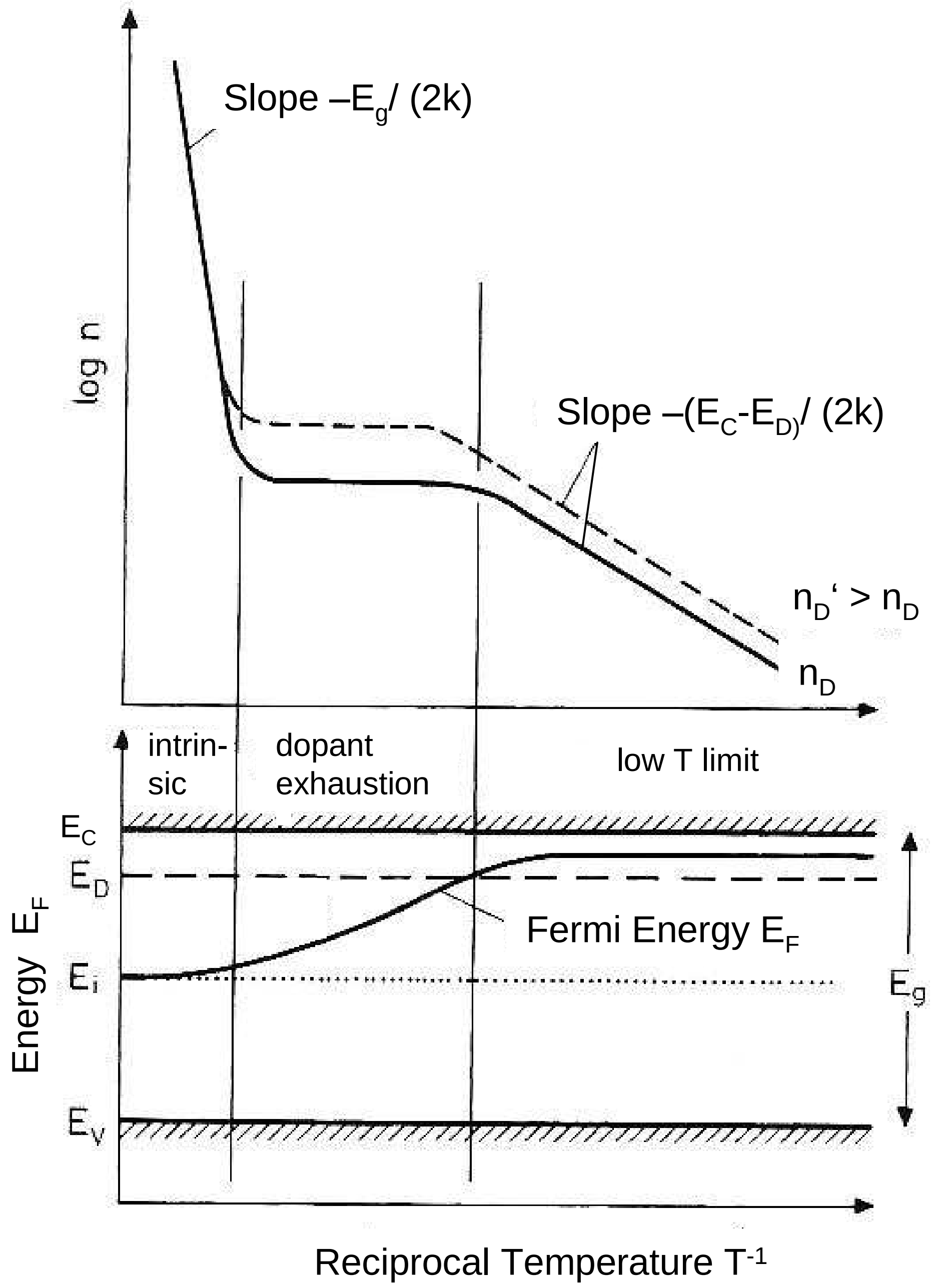
for the variable $x = \exp\left(-\frac{E_F - E_V}{kT}\right)$ with the abbreviation $B = \exp\left(-\frac{E_A - E_V}{kT}\right)$

With that, $p = N_V\ x$ and $E_F - E_V = -kT \cdot \ln(x)$

Combiniation Intrinsic + Extrinsic Charge Carrier Densities

Conduction band electron density n and Fermi Energy E_F

schematic for n_A=0



Special Case: Deep Dopants + Compensation

Example:
Hole density for Boron doped diamond
with $E_A - E_V = 350\ \mathrm{meV}$

$$2x = \left(\frac{n_D}{N_V} + B\right)\cdot\left[\sqrt{1+\frac{4(n_A-n_D)}{BN_V\cdot(1+\frac{n_D}{BN_V})^2}}-1\right]$$

for $\frac{n_D}{BN_V} \gg 1 \quad \Leftrightarrow \quad BN_V \ll n_D$

less holes than compensating defects!

$$2x \approx \frac{n_D}{N_V}\cdot\left[\sqrt{1+\frac{4(n_A-n_D)}{n_D^{\,2}}BN_V}-1\right]$$

and $BN_V \ll \frac{n_D^{\,2}}{4(n_A-n_D)} \approx \frac{n_D^{\,2}}{4n_A} = n_D\cdot\frac{n_D}{4n_A}$

even less holes that compensating defects times the (quarter of the) compensation ratio!

$$2x \approx \frac{n_D}{N_V}\cdot\frac{2(n_A-n_D)}{n_D^{\,2}}BN_V \;\Rightarrow\; p = N_V x = \frac{(n_A-n_D)}{n_D}N_V\cdot\exp\left(-\frac{E_A-E_V}{kT}\right)$$

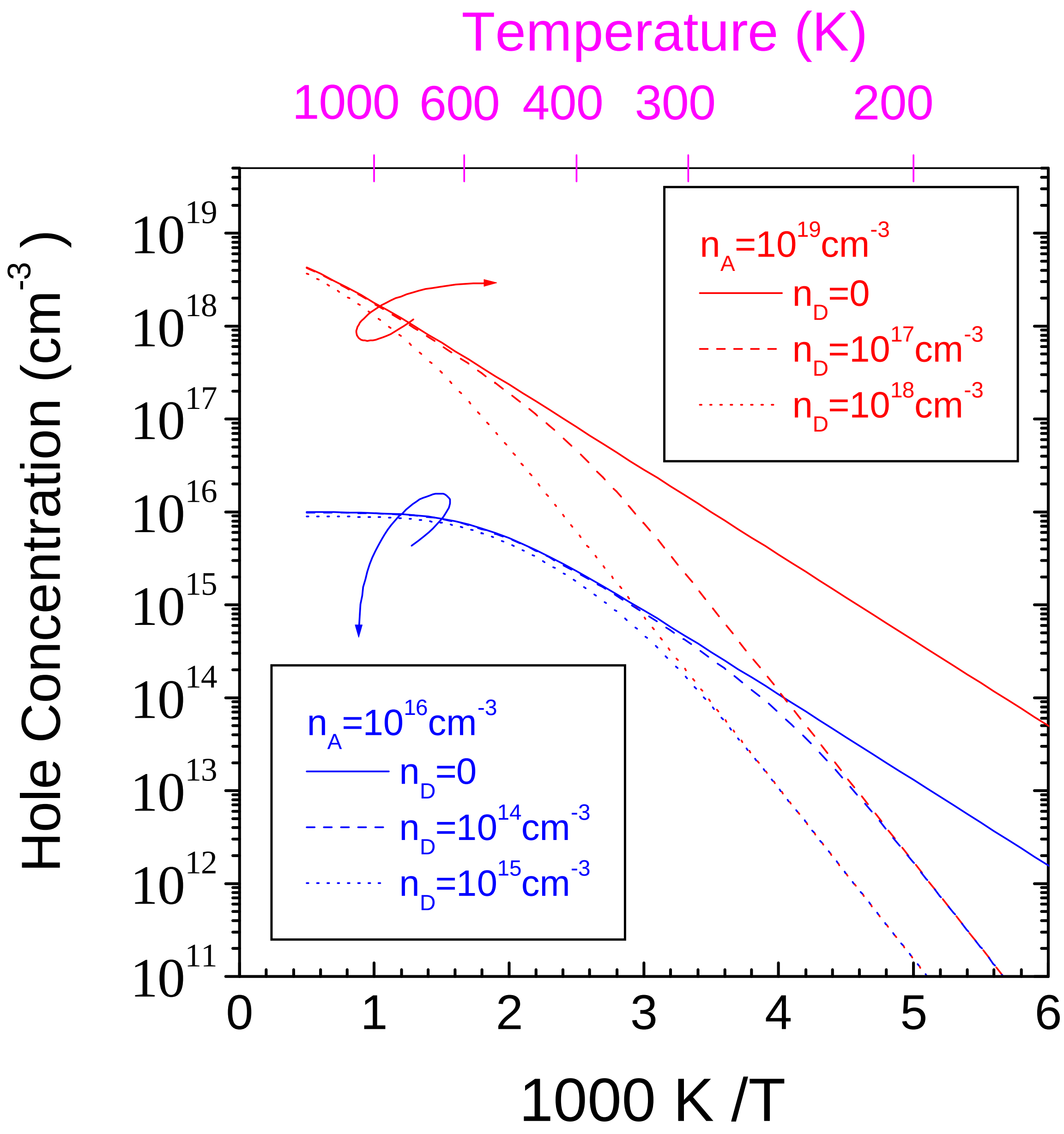
$$p(T) \sim \exp\left(-\frac{E_A-E_V}{kT}\right)$$

→ Activation energy of the hole concentration in the limit of low temperature is **identical with activation energy of the dopant itself**

Examlpe: p-type Doping of Diamond

Example:
Hole density for boron doped diamond

$$E_A - E_V = 350\ \mathrm{meV}$$



Note:
Compensation matters in case of large activation energy of dopants!