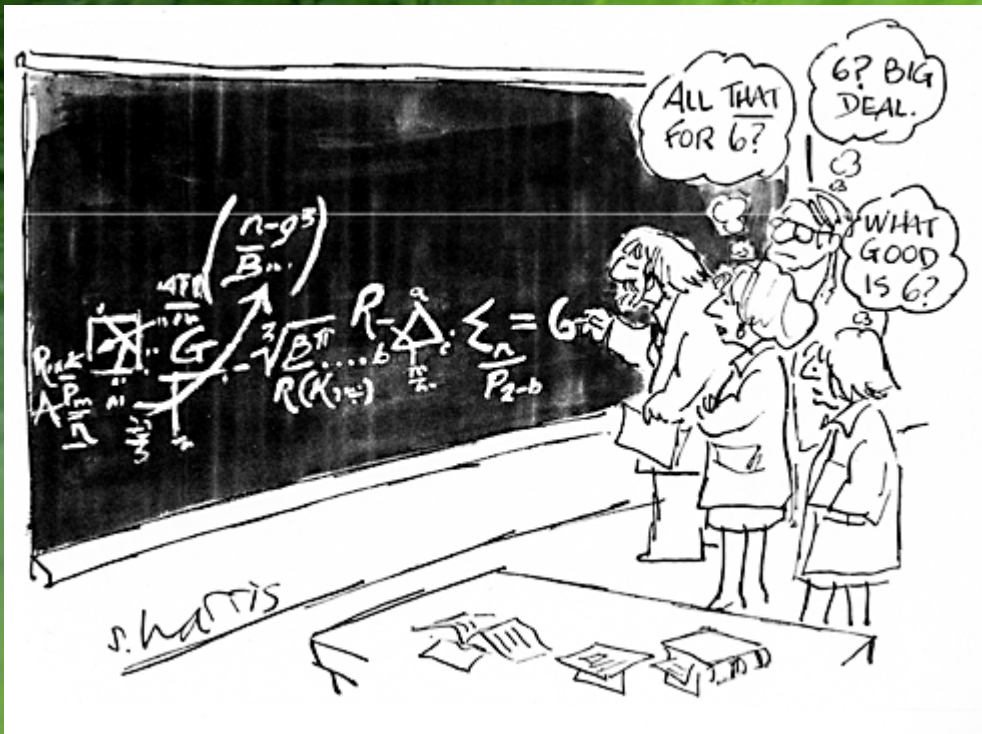# Nanostructures – density of states
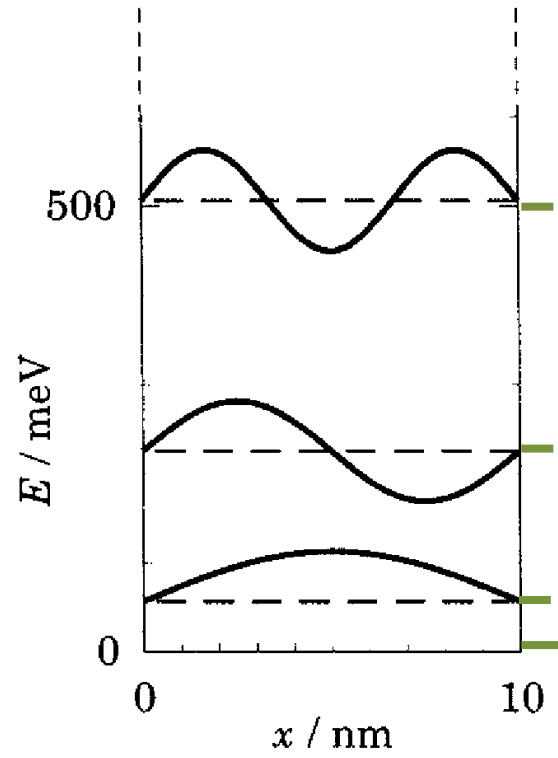

Faculty of Physics UW

Jacek.Szczytko@fuw.edu.pl

Density of states

What is the difference between 2D, 1D i 0D nanostructures?

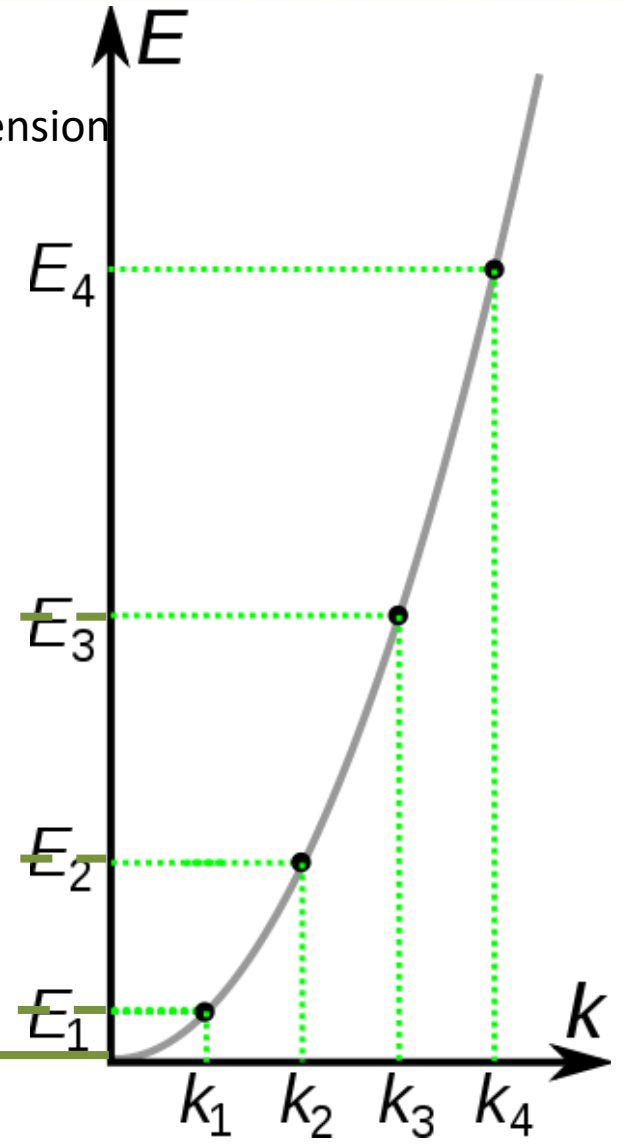Number of states per unit energy $\rho^{nD}(E)$ depends on the dimension

$$\varepsilon_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

$$\varepsilon_3 = E_c + \frac{9\hbar^2 \pi^2}{2m_0 m^* L^2}$$

$$\varepsilon_2 = E_c + \frac{2\hbar^2 \pi^2}{m_0 m^* L^2}$$

$$\varepsilon_1 = E_g + \frac{\hbar^2 \pi^2}{2m_0 m^* L^2}$$

Density of states

Density of states Number of states per unit energy $\rho^{nD}(E)$ depends on the dimension

If our crystal has a finite size the set of $k-$vectors is finite (though enormous!).
For example: we can assume periodic boundary conditions and then:
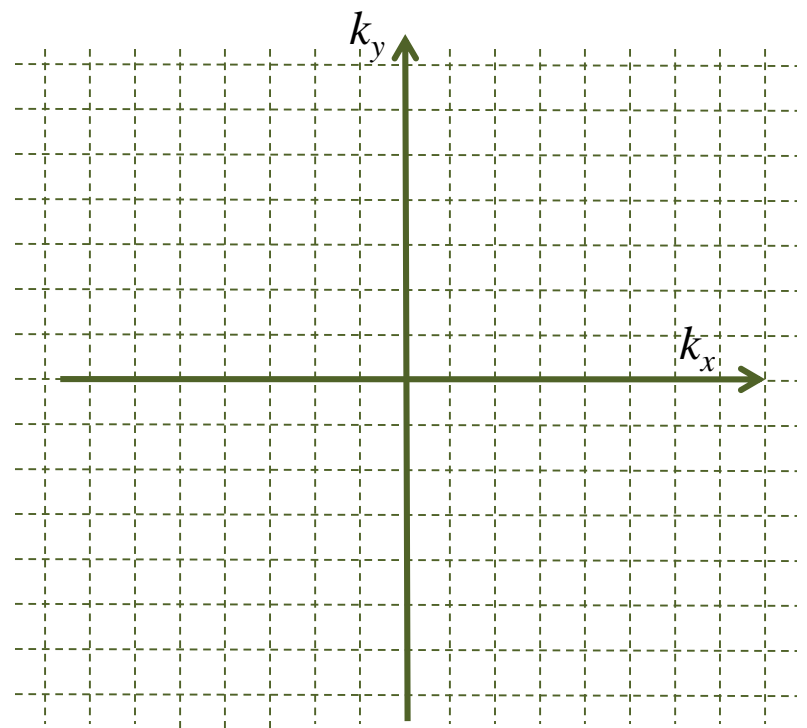
Born- von Karman boundary conditions

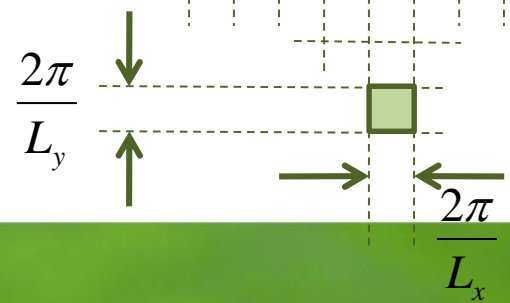Finite size of the crystal L_x, L_y, L_z

$\Psi -$ the Bloch function

$\Psi(x + L_x, y, z) = \Psi(x, y + L_y, z) = \Psi(x, y, z + L_z)$

$$e^{ik_x L_x} = 1$$
$$e^{ik_y L_y} = 1$$
$$e^{ik_z L_z} = 1$$

$$\vec{k}_i = 0, \pm \frac{2\pi}{L_i}, \pm \frac{4\pi}{L_i}, ..., \pm \frac{2\pi n_i}{L_i}$$

Number of states in the volume V $= \dfrac{2}{\dfrac{2\pi}{L_x} \times \dfrac{2\pi}{L_y} \times \dfrac{2\pi}{L_z}} = \dfrac{2V}{(2\pi)^3}$

k_y

k_x

$\dfrac{2\pi}{L_y}$

$\dfrac{2\pi}{L_x}$

Density of states

Density of states Number of states per unit energy $\rho^{nD}(E)$ depends on the dimension

The density of states in k-space of n dimension (and the unite volume)
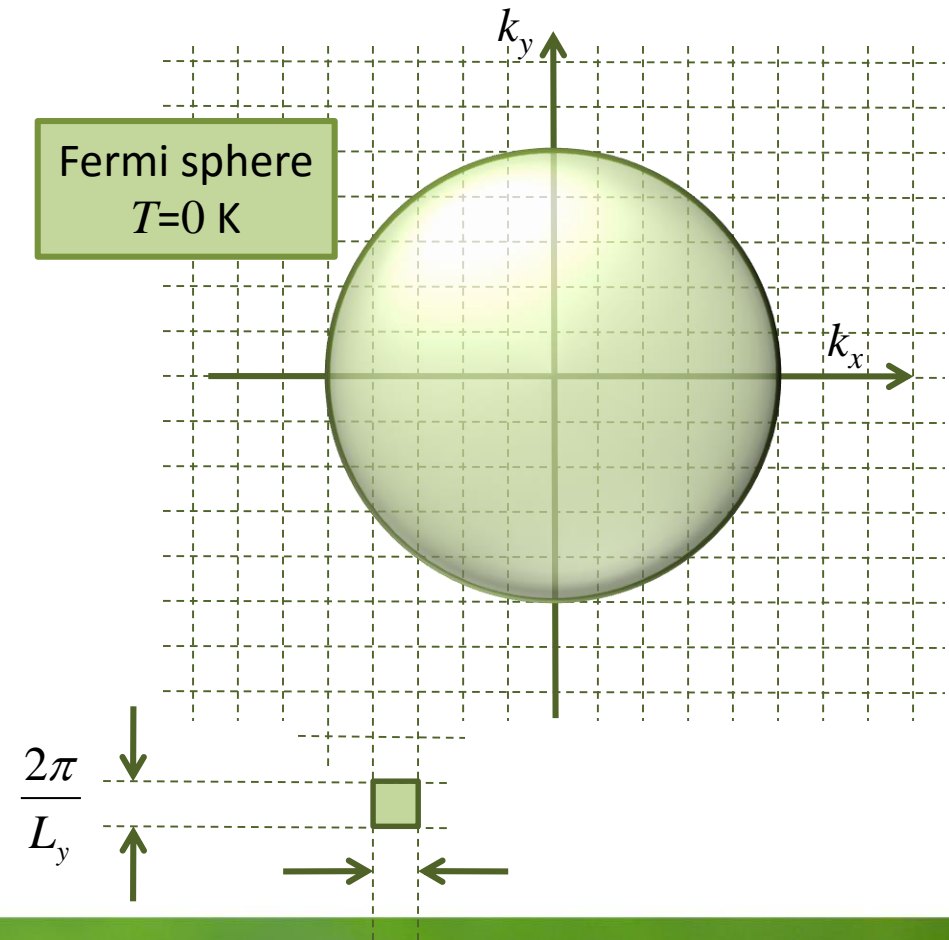
$$\rho_k^{nD} = 2\left(\frac{1}{2\pi}\right)^n$$

3D case

$$\rho^{3D}(E)dE = \rho_k^{3D}d\vec{k} = 2\left(\frac{1}{2\pi}\right)^3 4\pi k^2 dk$$

For a spherical and parabolic band:

$$\rho_c^{3D}(E) = \frac{1}{2\pi^2}\left(\frac{2m_0 m_c^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_c}$$

$$\rho_v^{3D}(E) = \frac{1}{2\pi^2}\left(\frac{2m_0 m_h^*}{\hbar^2}\right)^{3/2}\sqrt{E_v - E}$$

Fermi sphere
T=0 K

k_y

k_x

$\dfrac{2\pi}{L_y}$

Density of states

Density of states Number of states per unit energy $\rho^{nD}(E)$ depends on the dimension

The density of states in k-space of n dimension (and the unite volume)
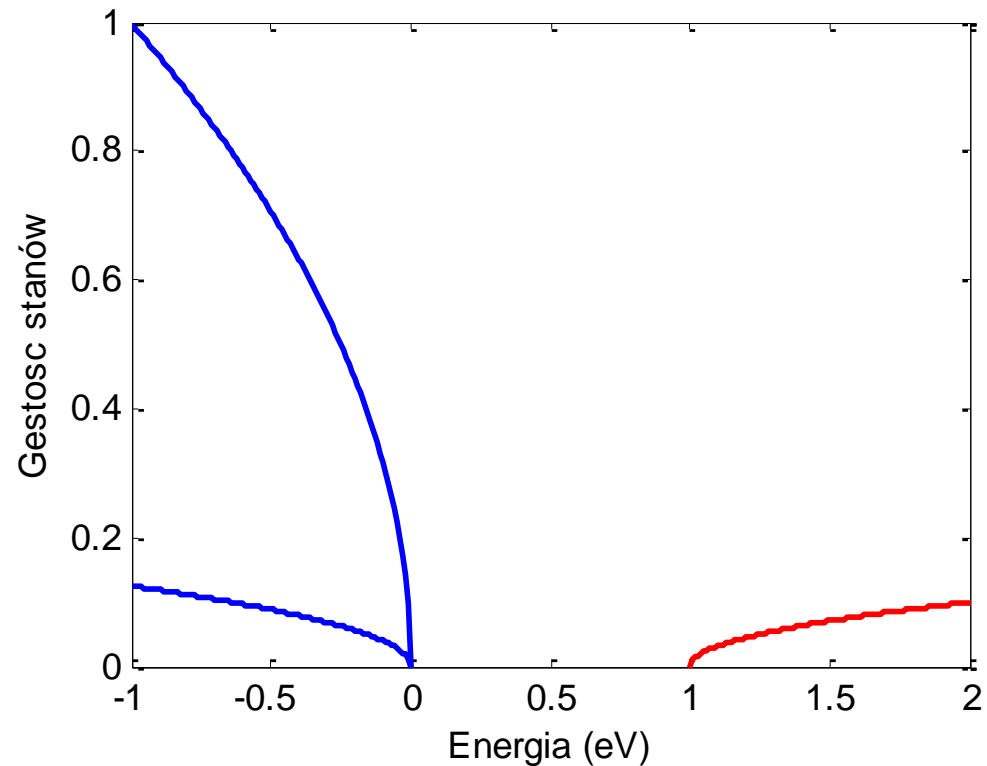
$$\rho_k^{nD} = 2\left(\frac{1}{2\pi}\right)^n$$

3D case

$$\rho^{3D}(E)dE = \rho_k^{3D}d\vec{k} = 2\left(\frac{1}{2\pi}\right)^3 4\pi k^2 dk$$

For a spherical and parabolic band:

$$\rho_c^{3D}(E) = \frac{1}{2\pi^2}\left(\frac{2m_0 m_c^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_c}$$

$$\rho_v^{3D}(E) = \frac{1}{2\pi^2}\left(\frac{2m_0 m_h^*}{\hbar^2}\right)^{3/2}\sqrt{E_v - E}$$

Density of states

Inside the well:

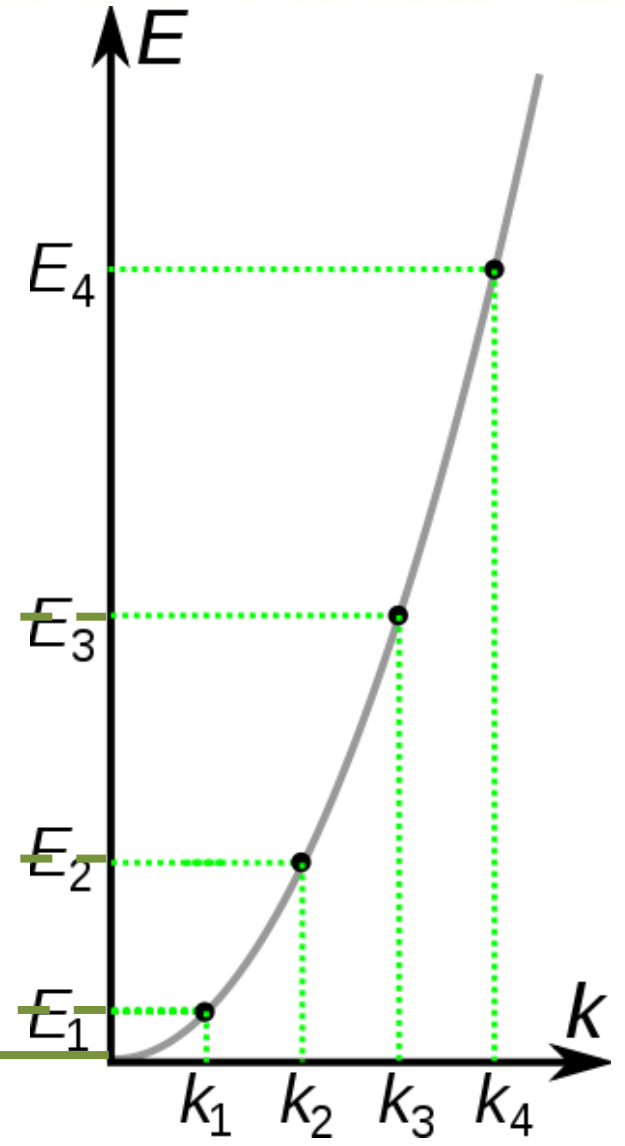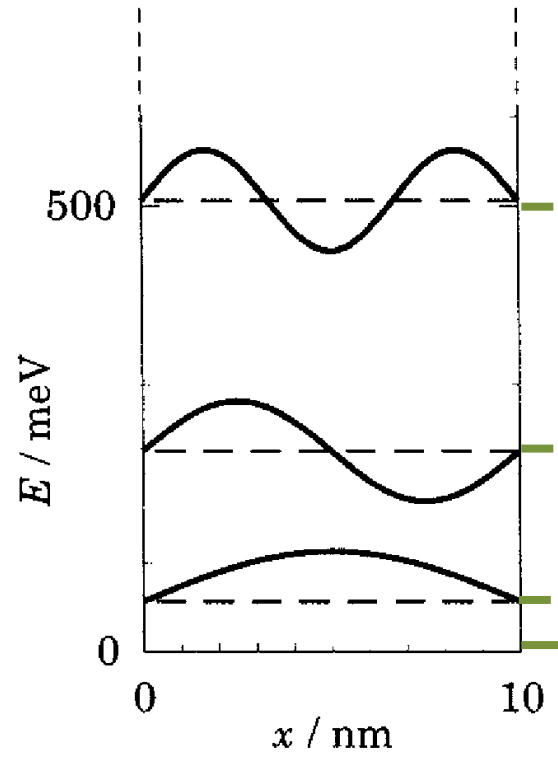$$\psi(x,t) = \sqrt{\frac{2}{L}} \sin(k_n x)\, e^{-i\omega t} \qquad k_n = \frac{n\pi}{L}$$

$$\varepsilon_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

$$\varepsilon_3 = E_c + \frac{9\hbar^2 \pi^2}{2m_0 m^* L^2}$$

$$\varepsilon_2 = E_c + \frac{2\hbar^2 \pi^2}{m_0 m^* L^2}$$

$$\varepsilon_1 = E_g + \frac{\hbar^2 \pi^2}{2m_0 m^* L^2}$$

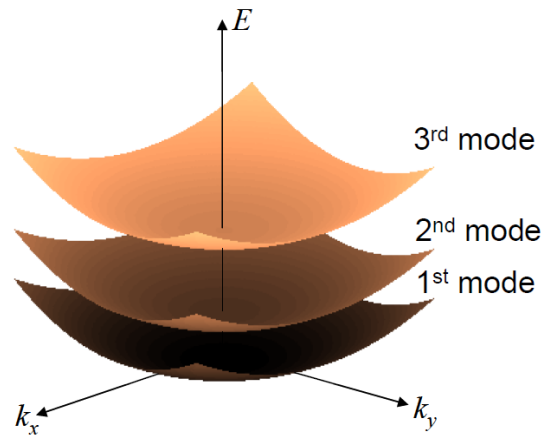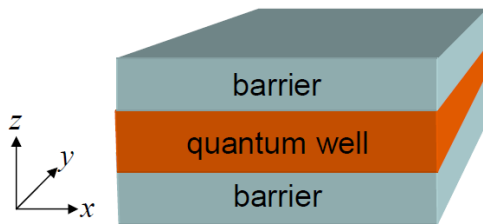## 2D density of states — for a spherical and parabolic band:

$$\rho^{2D}(E)dE = \rho_k^{2D}d\vec{k} = 2\left(\frac{1}{2\pi}\right)^2 2\pi k \, dk$$

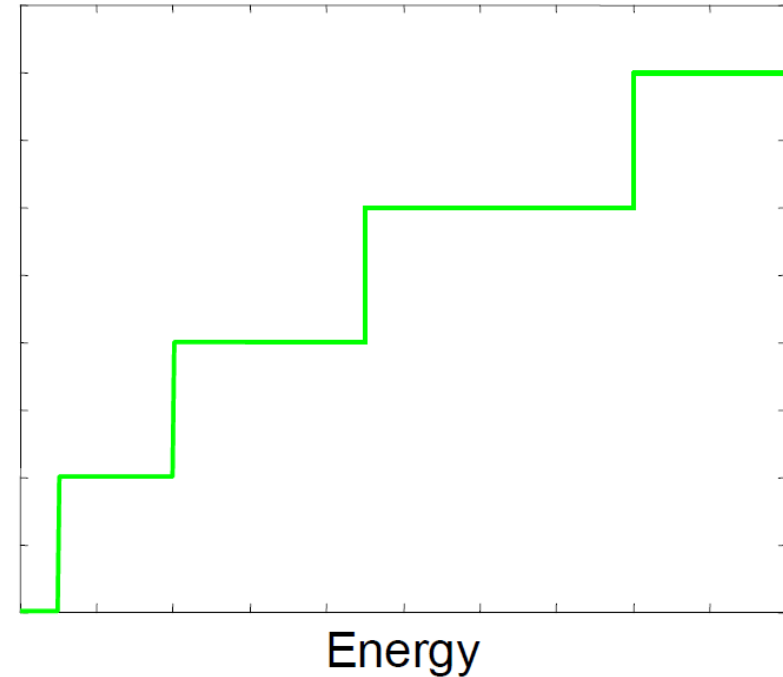$$\rho_a^{2D}(E)dE = \frac{m_0 m^*}{\pi\hbar^2}\theta(E - E_a) \, dE$$

Step-like θ Heaviside function

$$\rho^{2D}(E)dE = \frac{m_0 m^*}{\pi\hbar^2}\sum_a \theta(E - E_a) \, dE$$

barrier

quantum well

barrier

3rd mode

2nd mode

1st mode

Density of states – 2D

$$\psi_{k_x,k_y,n}(x,y,z) = \exp(ik_x x)\exp(ik_y y)\,u_n(z) = \psi_{k,n}(r,z) = \exp(ik \cdot r)\,u_n(z)$$

$$E_n(k_x,k_y) = \varepsilon_n + \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} \qquad\qquad E_n(k) = \varepsilon_n + \frac{\hbar^2 k^2}{2m}$$
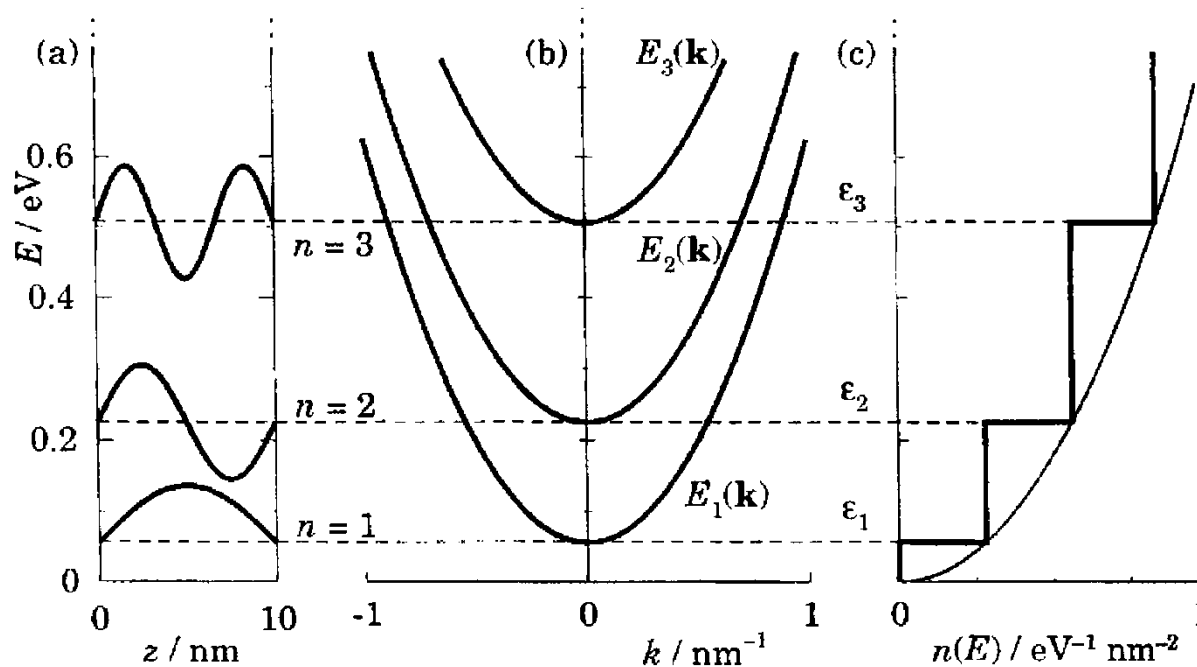

FIGURE 4.7. (a) Potential well with energy levels, (b) total energy including the transverse kinetic energy for each subband, and (c) steplike density of states of a quasi-two-dimensional system. The example is an infinitely deep square well in GaAs of width 10 nm. The thin curve in (c) is the parabolic density of states for unconfined three-dimensional electrons.

Density of states – 2D
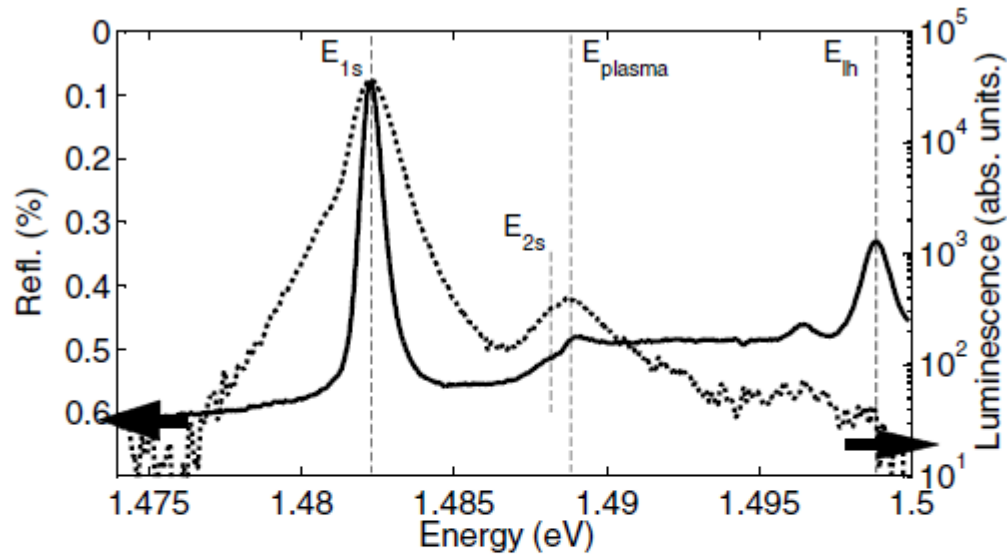
FIG. 1. cw absorption (i.e., $1 - $ reflectivity; bold line, left axis) and the TR-PL integrated over 1300 ps (logarithmic scale, right) results. $E_{1s} = 1.4823$ eV ($E_{2s} = 1.4882$ eV) is the $1s$ ($2s$) heavy-hole exciton, $E_{plasma} = 1.4888$ eV, light-hole exciton $E_{lh} = 1.4988$ eV (vertical lines). The low energy exponential tail of the excitonic transition originates from the trion at 1.4807 eV (discussed in [18]).

J. Szczytko, et al. Phys. Rev. Lett. 93, 137401 (2004)

Density of states – 1D

1D density of states for a spherical and parabolic band:

$$\rho^{1D}(E)dE = \rho_k^{1D}d\vec{k} = 2\left(\frac{1}{2\pi}\right)^1 2\,dk$$

$$\rho^{1D}(E)dE = \frac{2}{\pi}\sqrt{\frac{m_0 m^*}{2\hbar^2}} \sum_{a_x,a_y} \frac{\theta\left(E - E_{a_x,a_y}\right)}{\sqrt{E - E_{a_x,a_y}}}\,dE$$
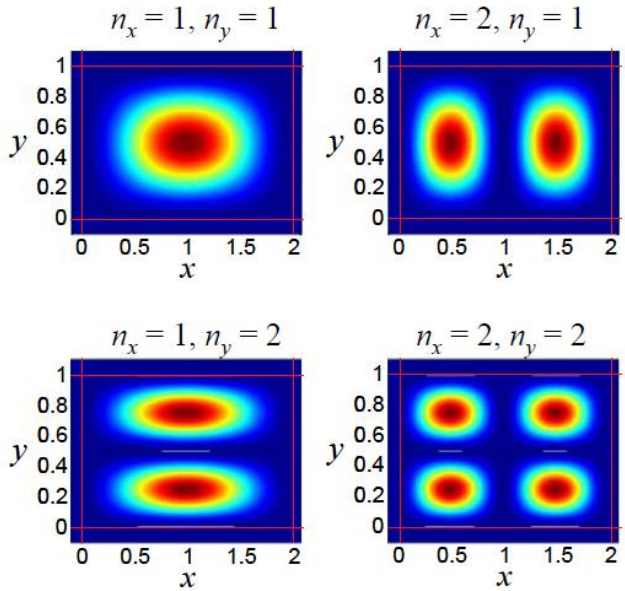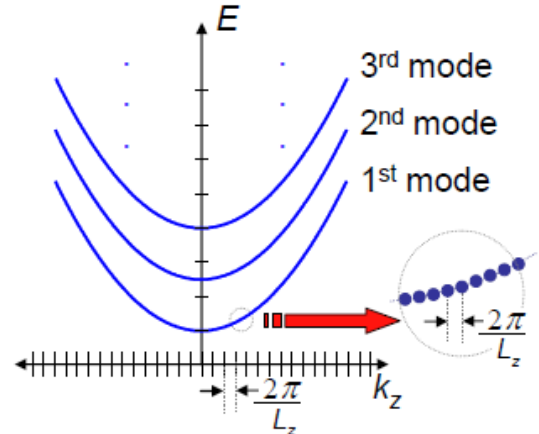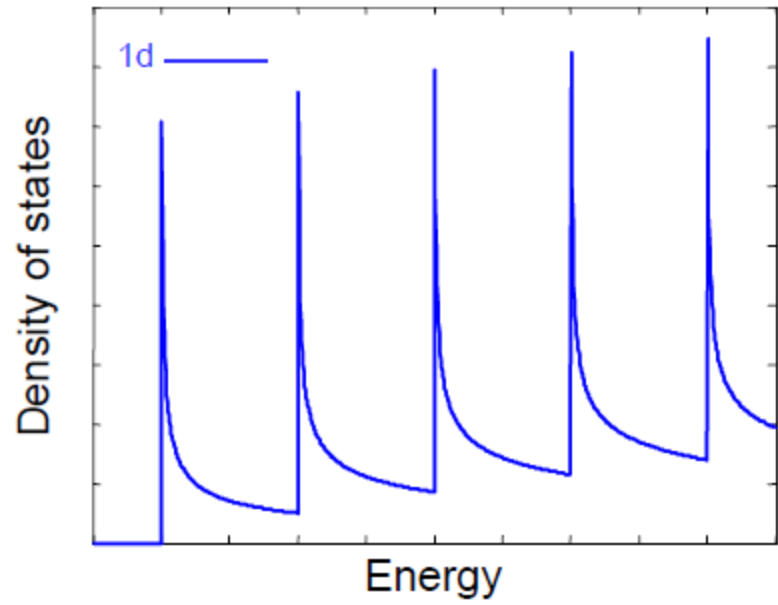
Fig. 2.13. The first four modes of the quantum wire. Since in this example, $L_x > L_y$ the $n_x = 2$, $n_y = 1$ mode has lower energy than the $n_x = 1$, $n_y = 2$ mode.

Density of states – 1D

0D density of states

For the ISOLATED QD: $\Delta E \to 0, \Delta t \to \infty$ $\rho^{0D}(E)dE = g_n \delta(E - E_n)dE$

Suppose that the lifetime of the state energy E is equal to τ, we assume an exponential decay

$$|\psi(t)|^2 = |A|^2 \exp\left(-\frac{t}{\tau}\right), \qquad t > 0$$

$$\psi(t) = A \exp\left(-i\frac{E_0 t}{\hbar} - \frac{t}{2\tau}\right), \qquad t > 0$$

Fourrier transform

$$\psi(\omega) = \frac{A}{\frac{1}{2\tau} + i\left(\frac{E_0}{\hbar} - \omega\right)}$$

Lorentz profile

$$\rho^{0D}(E)dE = \frac{1}{2\pi}|\psi(\omega)|^2 \frac{d\omega}{dE} = \frac{2}{\pi} \frac{\frac{\hbar}{2\tau}}{(E - E_0)^2 + \left(\frac{\hbar}{2\tau}\right)^2}$$
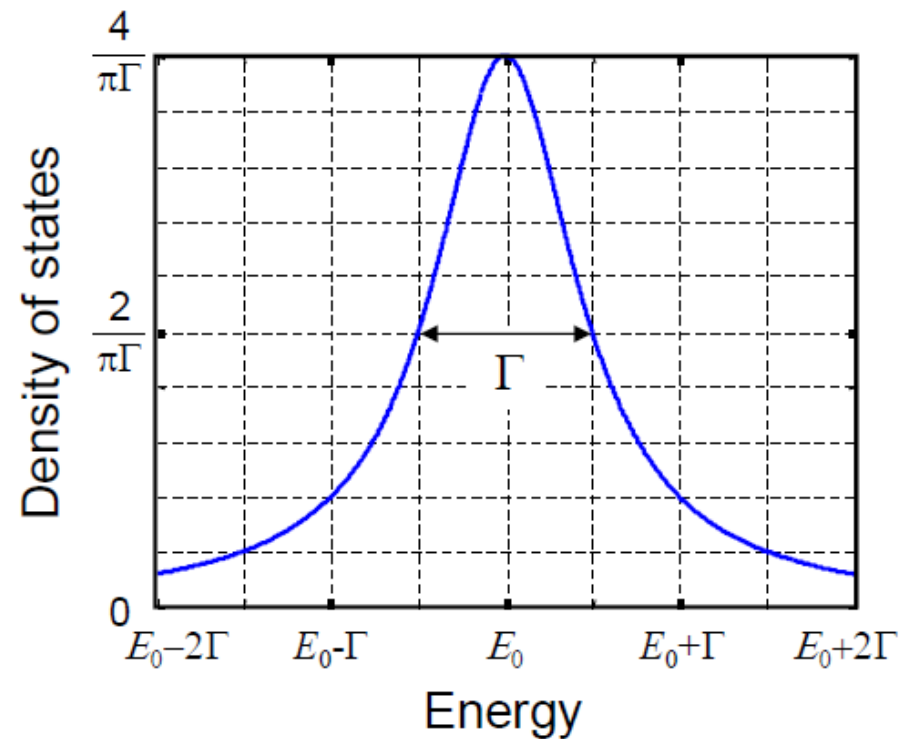
Density of states – the summary

Density of states

(a) Partly filled = metal

electrons

Density of States (DOS)
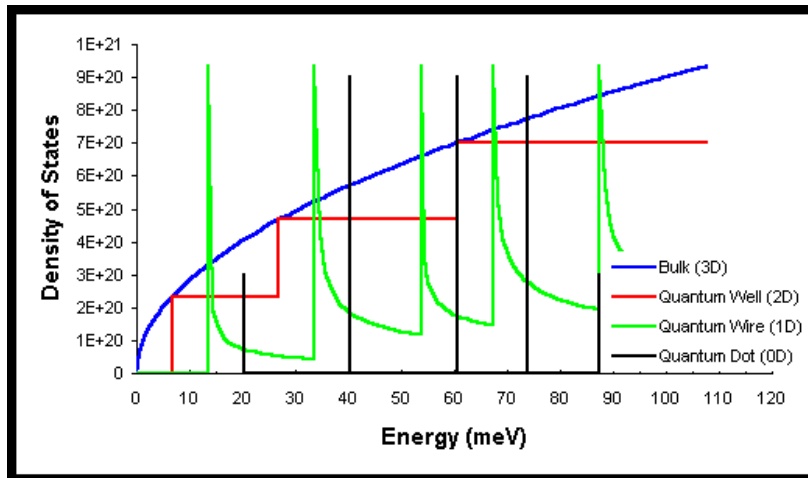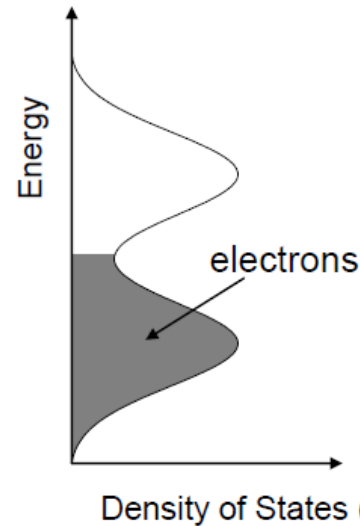
(b) Completely filled or empty = insulator or semiconductor

Density of States (DOS)

Marc Baldo MIT OpenCourseWare Publication May 2011
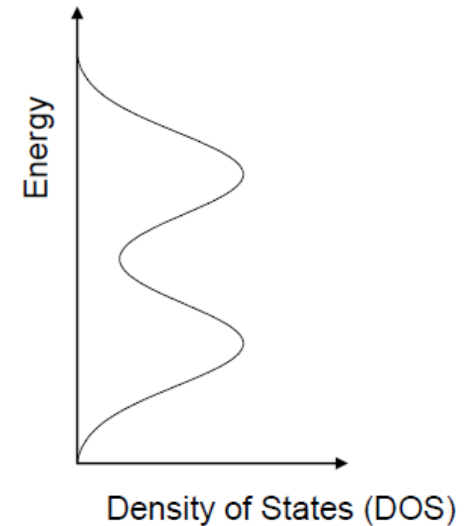
Harmonic potential 2D

CB

VB
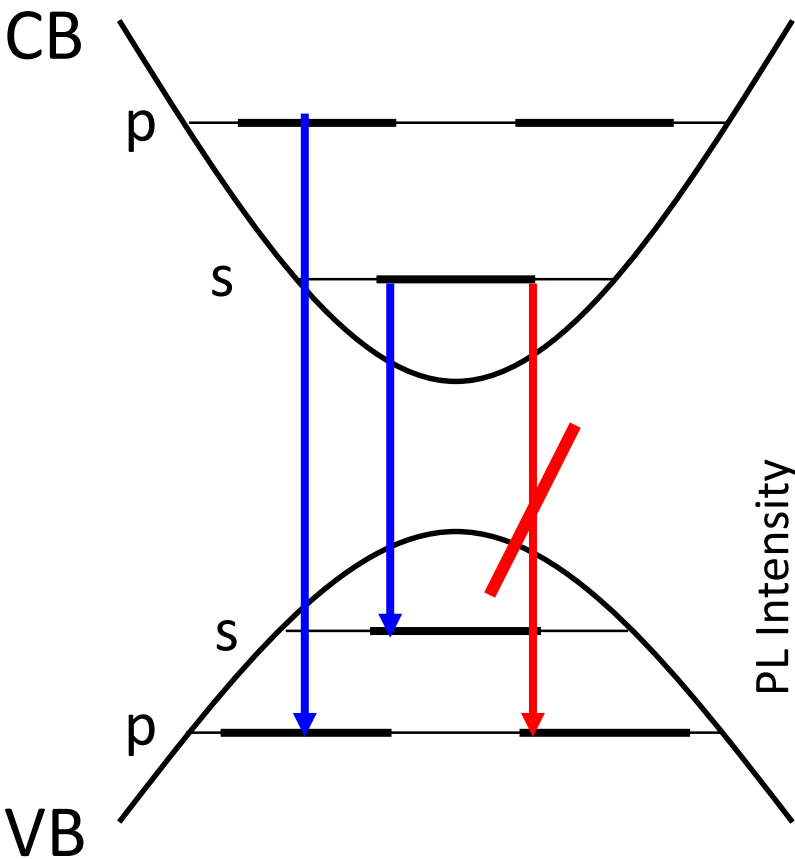
Harmonic oscillator model:

- s-, p-, d-,… shells

- Allowed interband transition
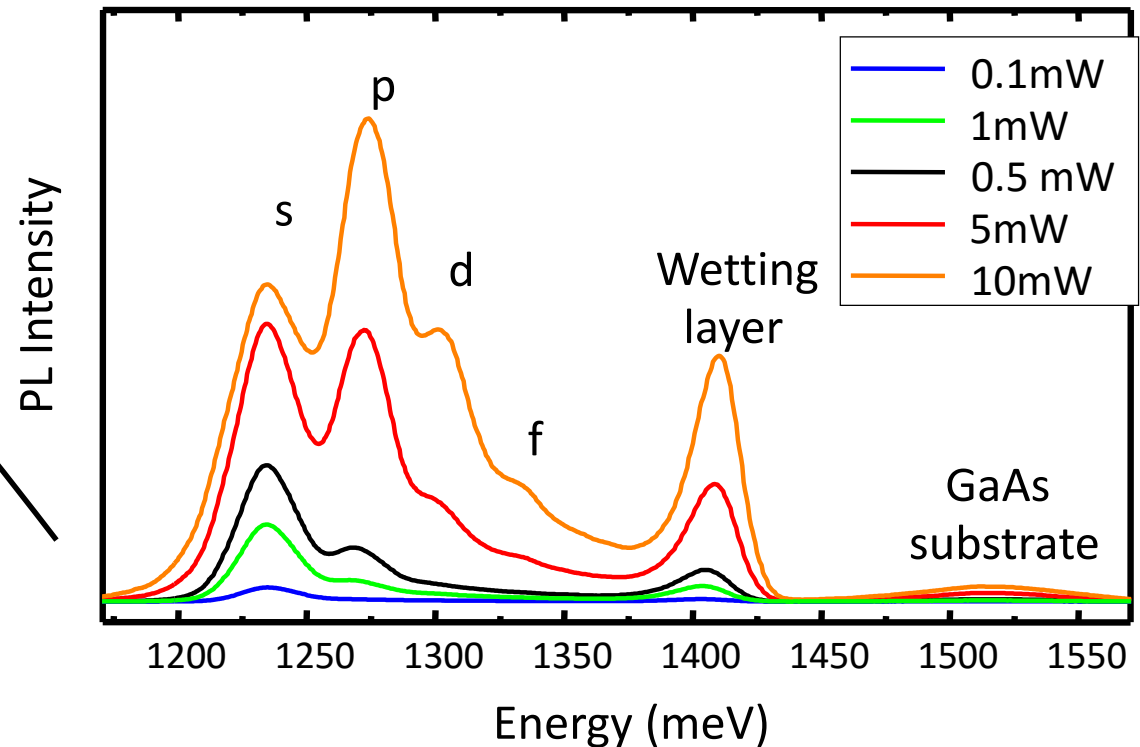
Summary – Fermi golden rule

The probability of transition per unit time:

$$W(t) = W$$
$$0 \leq t \leq \tau$$

$$P_{mn} = \frac{w_{mn}}{\tau} = \frac{2\pi}{\hbar} |\langle m|W|n\rangle|^2 \delta(E_m - E_n)$$

Transitions are possible only for states, for which $\quad E_m = E_n$

$$W(t) = w^{\pm} e^{\pm i\omega t}$$
$$0 \leq t \leq \tau$$

$$P_{nm} = \frac{w_{nm}}{\tau} = \frac{2\pi}{\hbar} \left|\langle n|w^{\pm}|m\rangle\right|^2 \delta(E_n - E_m \pm \hbar\omega)$$

Transitions are possible only for states, for which $\quad E_m = E_n \pm \hbar\omega$

The perturbation in a form of an electromagnetic wave:

$$A_{nm} = \frac{\omega_{nm}{}^3 e^2}{3\pi\varepsilon_0 \hbar c^3} |\langle m|\vec{r}|n\rangle|^2 = \frac{4\alpha}{3} \frac{\omega_{nm}{}^3}{c^2} |\langle m|\vec{r}|n\rangle|^2$$

$$P_{nm} = A_{nm} \delta(E_n - E_m \pm \hbar\omega)$$

Summary –Fermi golden rule

The transition rate – the probability of transition per unit time – from the initial state $|i\rangle$ to final $|f\rangle$ is given by:

Szybkość zmian – czyli prawdopodobieństwo przejścia na jednostkę czasu – ze stanu początkowego $|i\rangle$ do końcowego $|f\rangle$ dane jest wzorem:

$$P_{mn} = \frac{2\pi}{\hbar} |\langle f|W|i\rangle|^2 \rho(E_f)$$

W - interaction with the field

$\rho(E_f)$ - the density of final states

Perturbation W does not have to be in the form of an electromagnetic wave.

Density of states – the summary

a

b

HOMO

LUMO
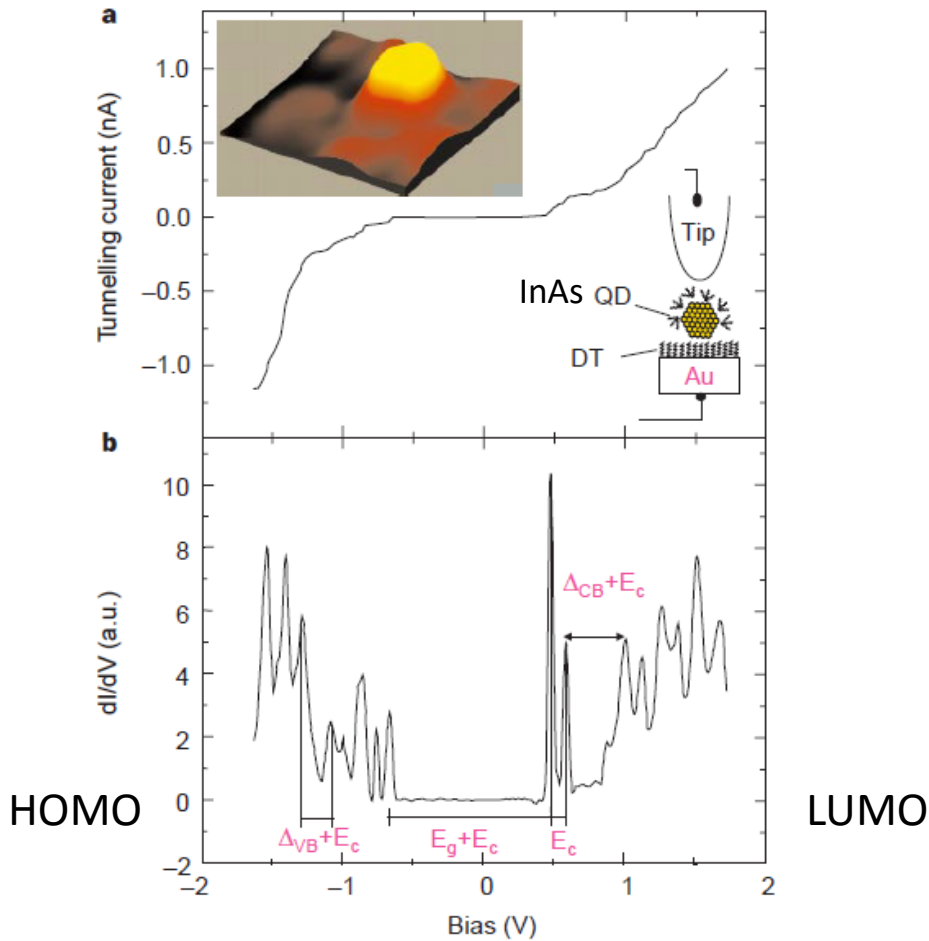
NATURE | VOL 400 | 5 AUGUST 1999 |
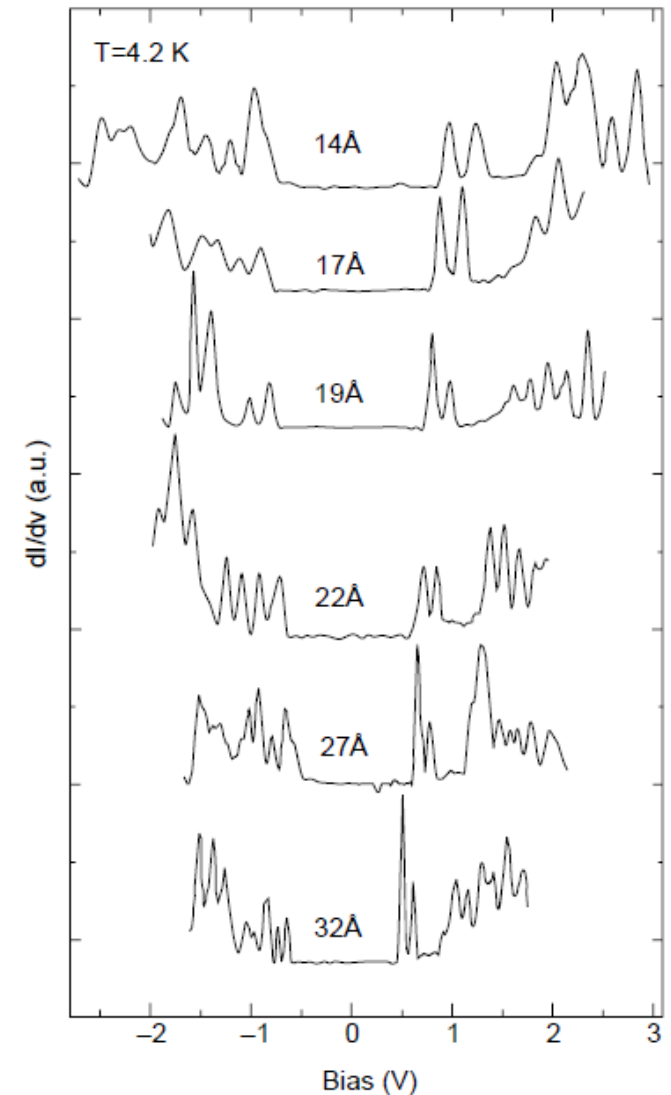
The Fermi-Dirac distribution

The probability that a state of the energy E will be occupied

E_F – chemical potential

Fermions:

$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

Electrons
Holes
Trions (charged excitons)

Bosons:

$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} - 1}$$

Polaritons
Phonons
Magnons
Excitons, biexcitons
Plasmons

Boltzman distribution:

$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} \pm 1} \approx e^{-\frac{E-E_F}{k_B T}}$$

$$E_F = \frac{\partial F}{\partial n}$$

$$F = U - TS$$

Anyons – eg. composite fermions $\quad |\Psi_1 \Psi_2\rangle = e^{i\theta} |\Psi_2 \Psi_1\rangle$

Slave fermions (chargon, holon, spinon) = fermion+bozon with the charge-spin separation

The Fermi-Dirac distribution
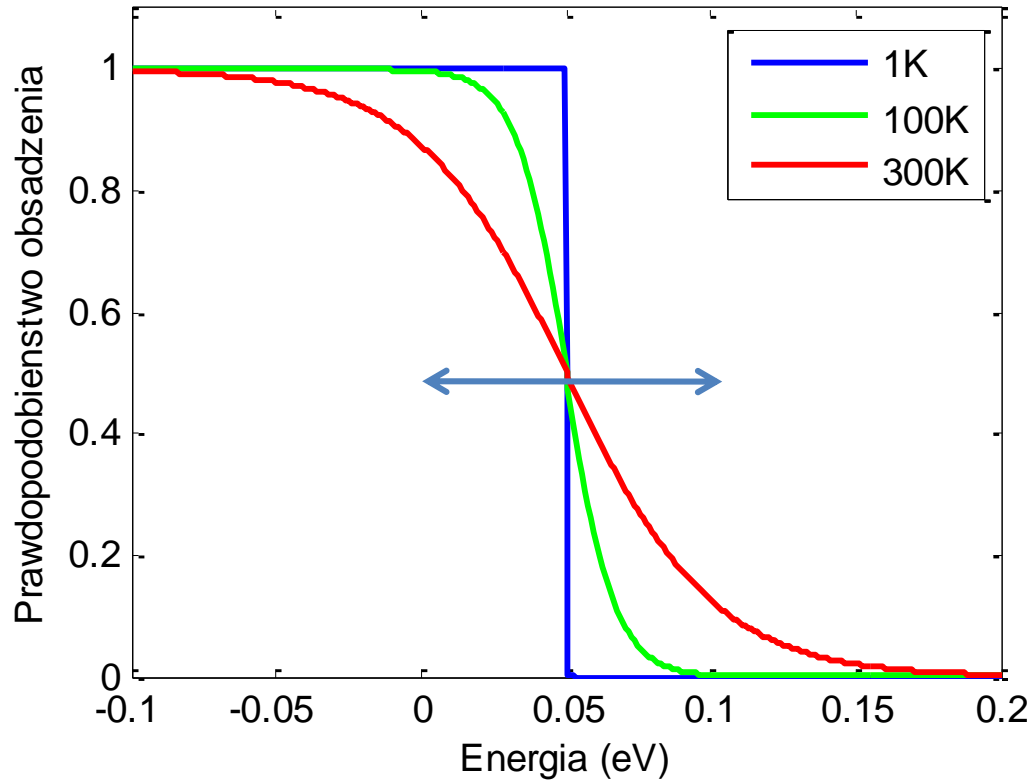
$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

Enrico Fermi
1901 − 1954

Paul Adrian
Maurice Dirac
1902 − 1984
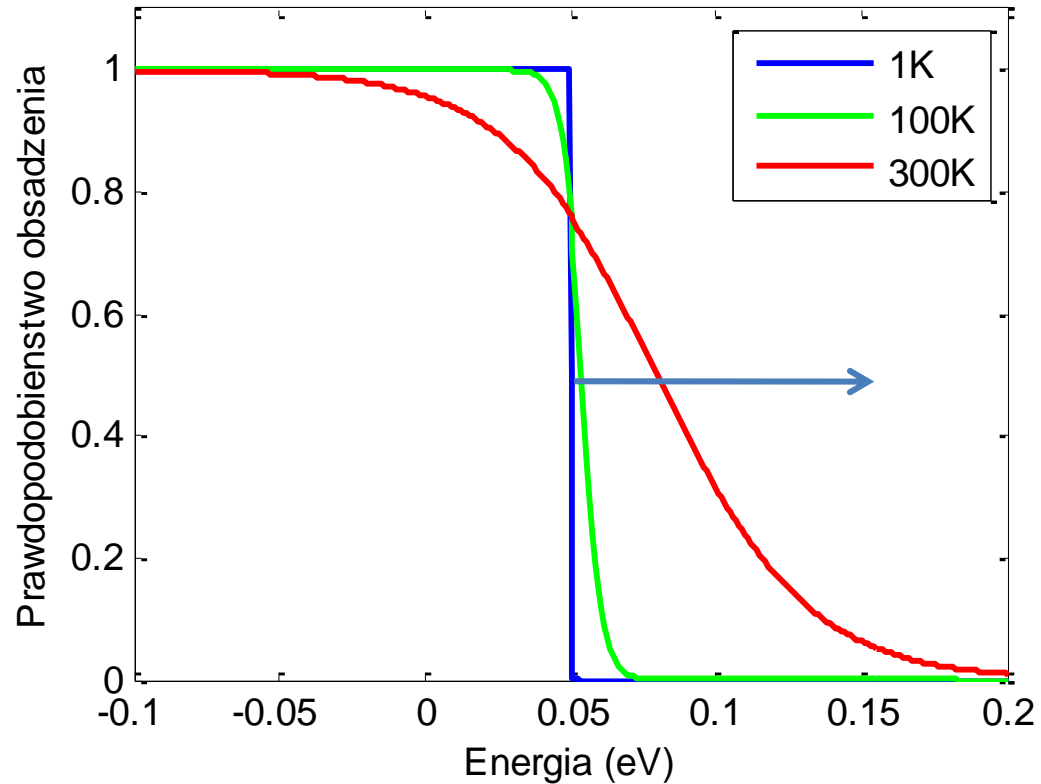
Prawdopodobienstwo obsadzenia

Energia (eV)

1K
100K
300K

The Fermi-Dirac distribution

$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

The Fermi-Dirac distribution
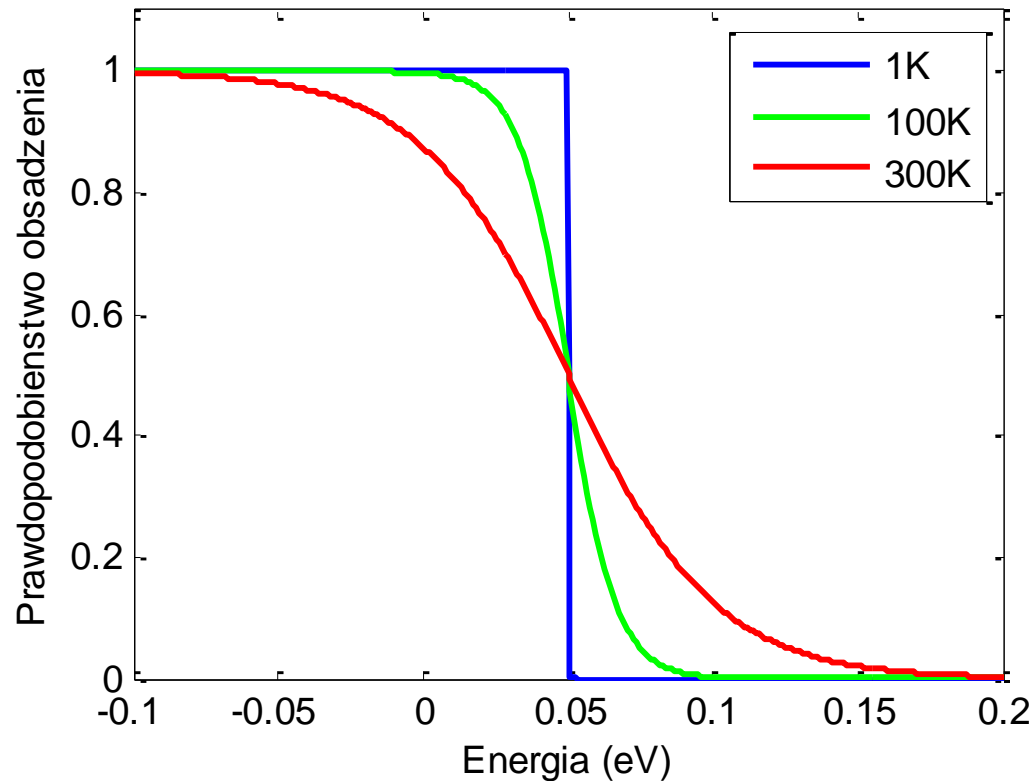
$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

The Fermi-Dirac distribution

The probability that a state of the energy E will be occupied

E_F – chemical potential
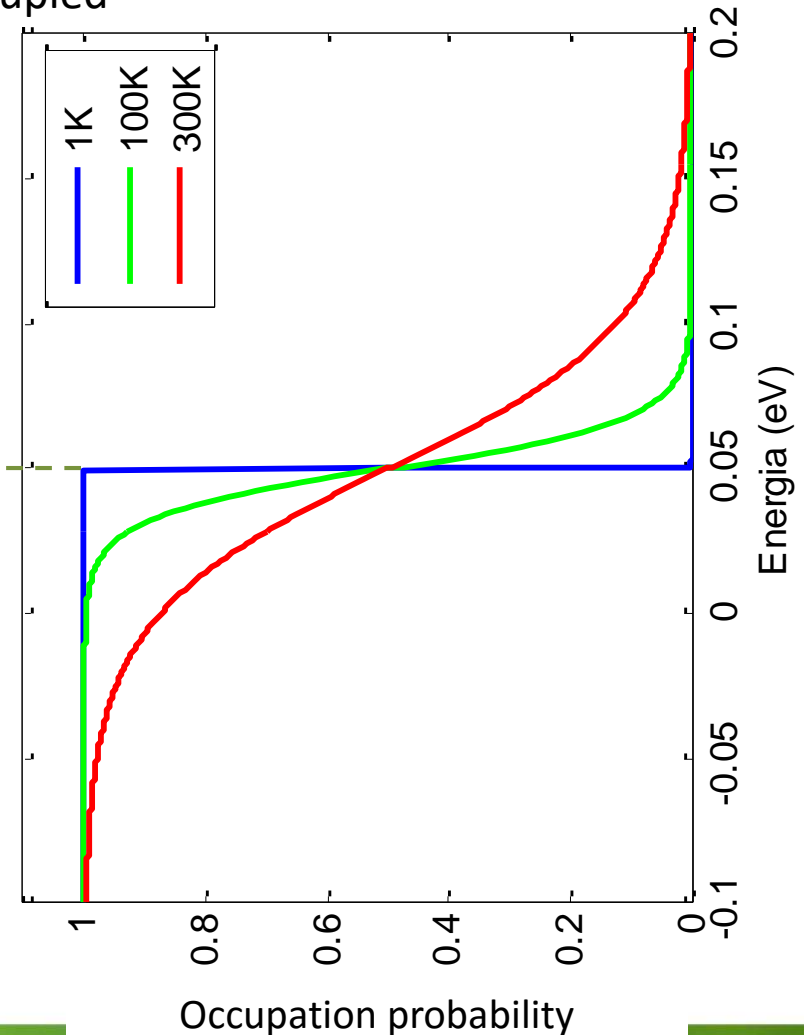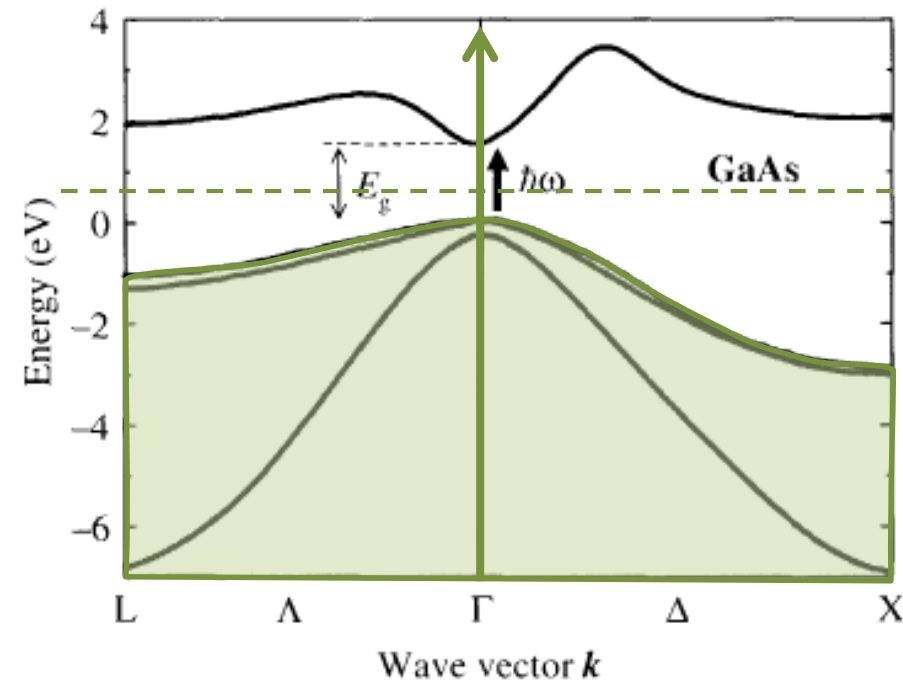
$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

The Fermi-Dirac distribution

The probability that a state of the energy E will be occupied

E_F – chemical potential

$$f_0 = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$
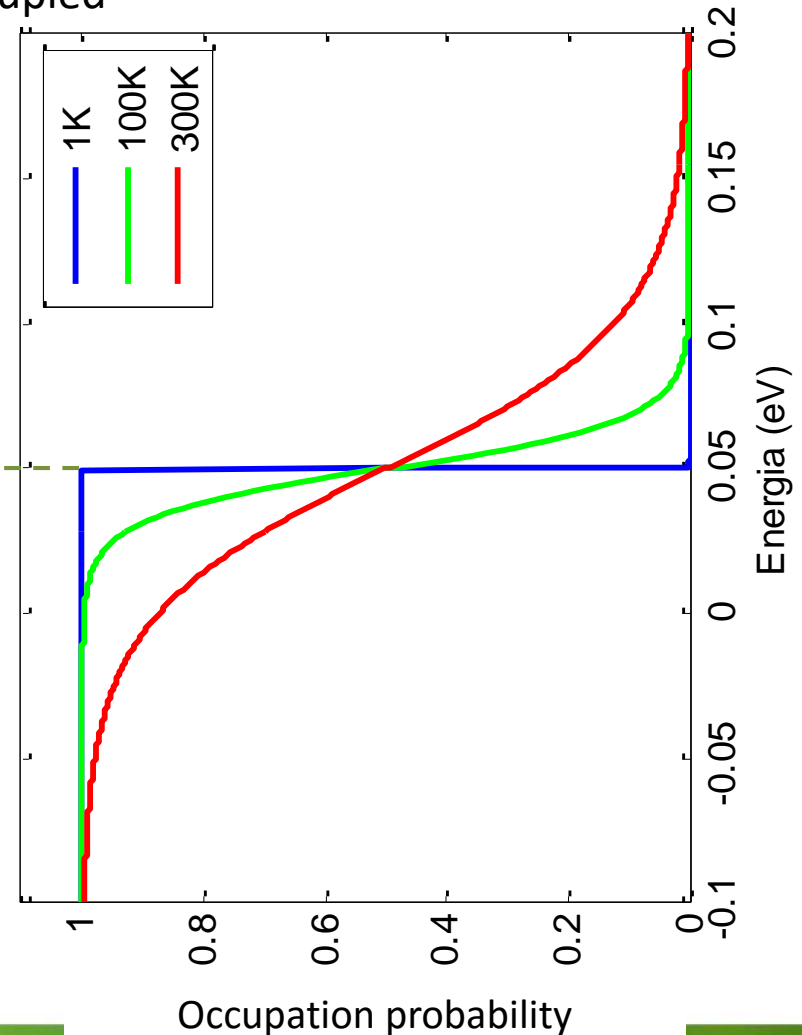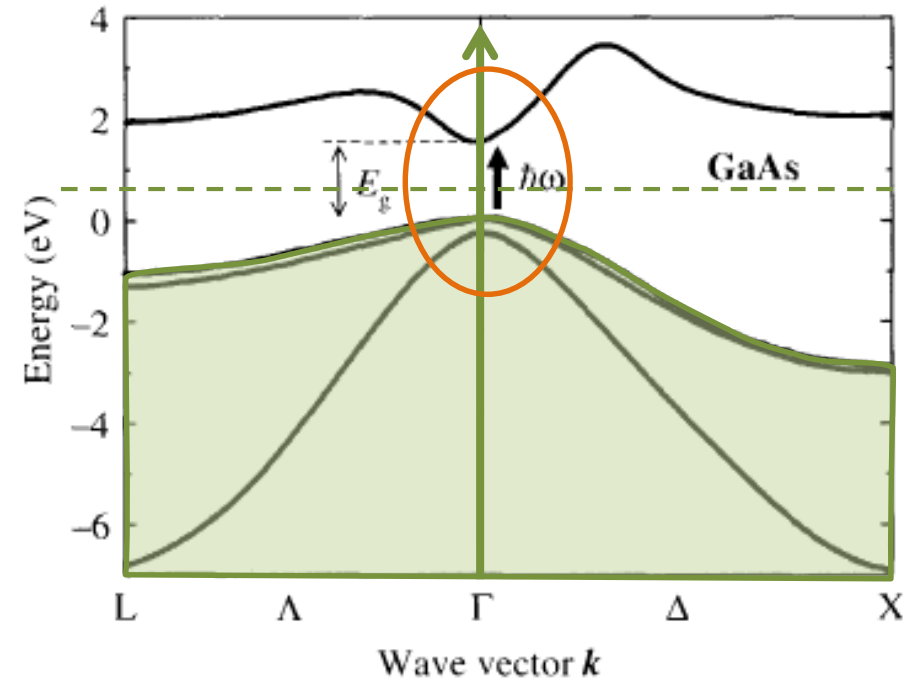
The Fermi-Dirac distribution

Electrons statistics in crystals

The case of a semiconductor, in which both the electron gas and hole gas are far from the degeneracy:

$$\frac{E_c - \xi}{k_B T} \gg 1$$

$$\frac{\xi - E_v}{k_B T} \gg 1$$

$$\frac{E_c - E_v}{k_B T} = \frac{E_g}{k_B T} \gg 1$$

The probability of filling of the electronic states:

$$f_e = \frac{1}{e^{\frac{E - \xi}{k_B T}} + 1} = \frac{1}{e^{\frac{E_G}{2k_B T} + \frac{E_e}{k_B T} - \frac{\xi}{k_B T}} + 1}$$

and of holes: $f_h = 1 - f_e$
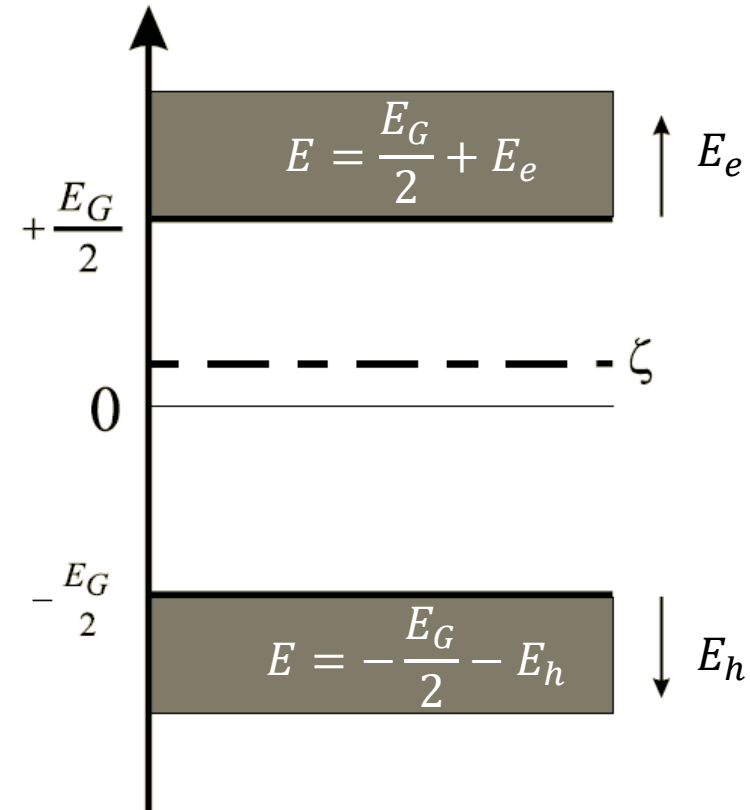
$$f_h = \frac{1}{e^{\frac{-E + \xi}{k_B T}} + 1} = \frac{1}{e^{\frac{E_G}{2k_B T} + \frac{E_h}{k_B T} + \frac{\xi}{k_B T}} + 1}$$

Electrons statistics in crystals

The case of a semiconductor, in which both the electron gas and hole gas are far from the degeneracy:

$$\frac{E_c - \xi}{k_B T} \gg 1$$

$$\frac{\xi - E_v}{k_B T} \gg 1$$

$$\frac{E_c - E_v}{k_B T} = \frac{E_g}{k_B T} \gg 1$$

The probability of filling of the electronic states:

$$f_e = \frac{1}{e^{\frac{E-\xi}{k_B T}} + 1} = \frac{1}{e^{\frac{E_G}{2k_B T} + \frac{E_e}{k_B T} - \frac{\xi}{k_B T}} + 1} \approx e^{-\frac{E_G}{2k_B T} - \frac{E_e}{k_B T} + \frac{\xi}{k_B T}}$$

and of holes: $f_h = 1 - f_e$

$$f_h = \frac{1}{e^{\frac{-E+\xi}{k_B T}} + 1} = \frac{1}{e^{\frac{E_G}{2k_B T} + \frac{E_h}{k_B T} + \frac{\xi}{k_B T}} + 1} \approx e^{-\frac{E_G}{2k_B T} - \frac{E_h}{k_B T} - \frac{\xi}{k_B T}}$$
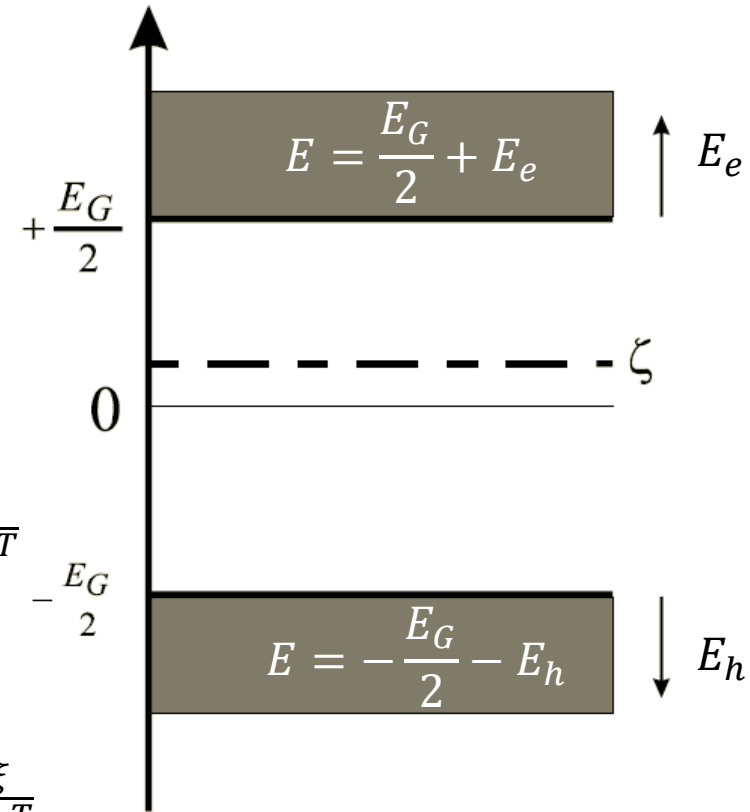
$E = \frac{E_G}{2} + E_e$

E_e

$+\frac{E_G}{2}$

0

ζ

$-\frac{E_G}{2}$

$E = -\frac{E_G}{2} - E_h$

E_h

Electrons statistics in crystals

The case of a semiconductor, in which both the electron gas and hole gas are far from the degeneracy:

the probability of filling of the electronic states:

$$f_e \approx e^{-\frac{E_G}{2k_B T} - \frac{E_e}{k_B T} + \frac{\xi}{k_B T}}$$

and of holes $f_h = 1 - f_e$

$$f_h \approx e^{-\frac{E_G}{2k_B T} - \frac{E_h}{k_B T} - \frac{\xi}{k_B T}}$$

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

Thus:

$$n(\xi) = 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_G}{2k_B T}} \cdot e^{\frac{\xi}{k_B T}} = N_c(T) \, e^{\frac{-(E_c - \xi)}{k_B T}}$$

$$p(\xi) = 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_G}{2k_B T}} \cdot e^{-\frac{\xi}{k_B T}} = N_v(T) \, e^{\frac{-(\xi - E_v)}{k_B T}}$$
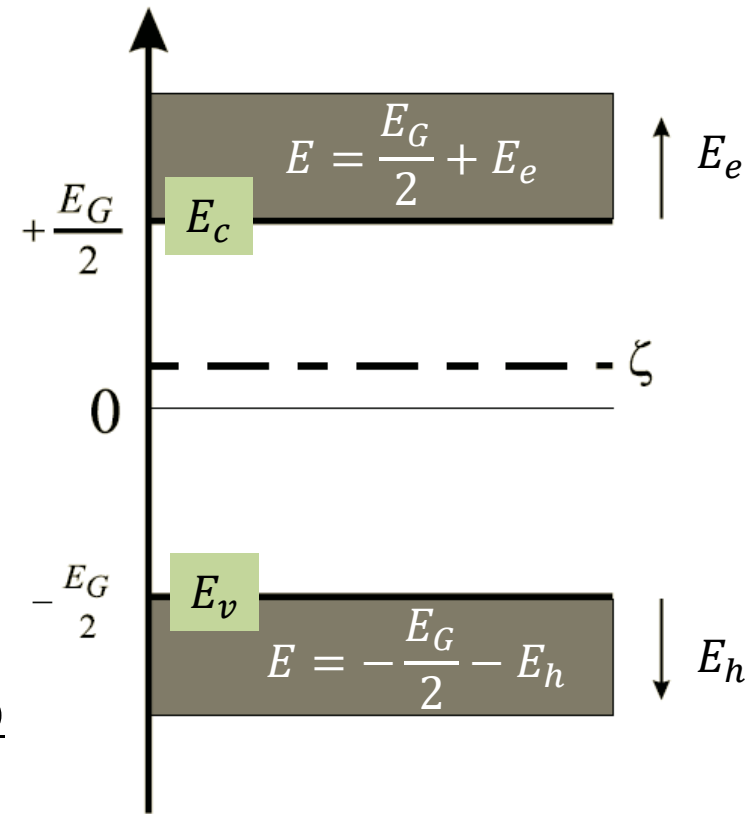
Electrons statistics in crystals

What is the concentration of carriers for T>0?

In the thermodynamic equilibrium for an intrinsic semiconductors (*półprzewodniki samoistne*), the concentration of electrons in the conduction band is equal to the concnetration of holes in the valence band (because they appear only as a result of excitation from the valence band).

$n = p = n_i$ (an intrinsic case)

$$n \cdot p = n_i^2 = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{\frac{3}{2}} e^{-\frac{E_g}{k_B T}} = N_c N_v e^{-\frac{E_g}{k_B T}}$$

$$n = p = n_i = 2 \left(\frac{k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} e^{-\frac{E_g}{2k_B T}} = \sqrt{N_c N_v} e^{-\frac{E_g}{2k_B T}}$$
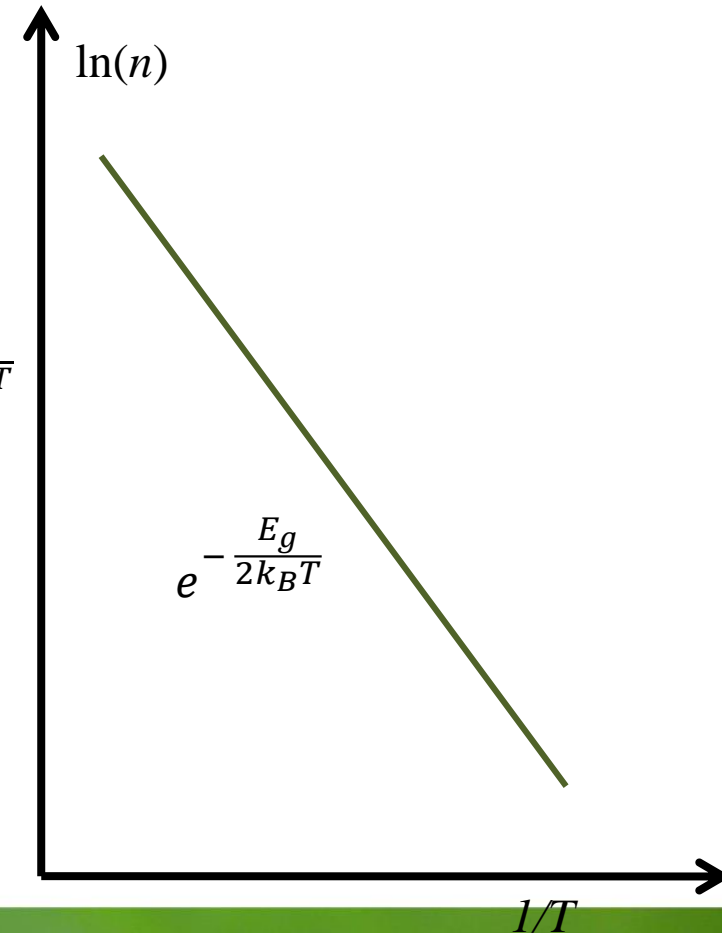
$\ln(n)$

$e^{-\frac{E_g}{2k_B T}}$

$1/T$

Intrinsic carrier concentration

What is the concentration of carriers for T>0?

In the thermodynamic equilibrium for an intrinsic semiconductors (*półprzewodniki samoistne*), the concentration of electrons in the conduction band is equal to the concnetration of holes in the valence band (because they appear only as a result of excitation from the valence band).

$$n \cdot p = n_i^2 = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{\frac{3}{2}} e^{-\frac{E_g}{k_B T}} = N_c N_v e^{-\frac{E_g}{k_B T}}$$

(general formula)

$n = p = n_i$ (an intrinsic case)

$$n = p = n_i = 2 \left(\frac{k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} e^{-\frac{E_g}{2k_B T}} = \sqrt{N_c N_v} e^{-\frac{E_g}{2k_B T}}$$

$$\frac{N_c}{N_v} = e^{\frac{2\xi - E_g}{k_B T}} \Rightarrow \xi = \frac{1}{2}(E_c + E_v) + \frac{3}{4} k_B T \ln\left(\frac{m_h^*}{m_e^*} \right)$$

in our notation the middle of the band is 0

empty band

E_g

T

filled band
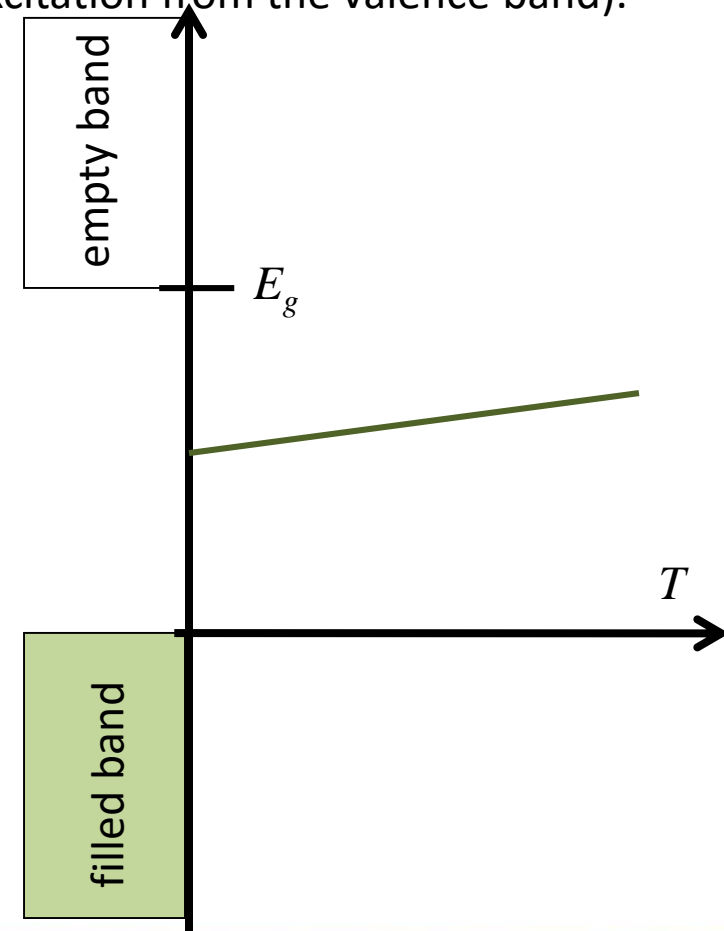
Intrinsic carrier concentration

What is the concentration of carriers for T>0?

The intrinsic semiconductors (*półprzewodniki samoistne*) in thermal equilibrium, the concentration of electrons in the conduction band is equal to the concnetration of holes in the valence band.

Koncentracja samoistna typowych półprzewodników

Eg \ T	77K	300K	1200K	materiał
0,25eV	10^9 cm^{-3}	10^{16} cm^{-3}	10^{18} cm^{-3}	InSb PbSe
1eV	-	10^{10} cm^{-3}	10^{17} cm^{-3}	Ge, Si, GaAs
4eV	-	-	10^{11} cm^{-3}	ZnS, SiC, GaN, ZnO, C (diament)

The concentration values less than 10^{10} cm^{-3} do not make sense because the concentration of impurities, and thus the concentration resulting from unintentional doping, is greater

$$n = p = \sqrt{N_c N_v}\, e^{-\frac{Eg}{2k_B T}}$$

$$n = N_c\, e^{\frac{E_F - E_c}{k_B T}}$$

$$p = N_v\, e^{-\frac{E_F - E_v}{k_B T}}$$

Domieszkowanie półprzewodników

Semiconductors
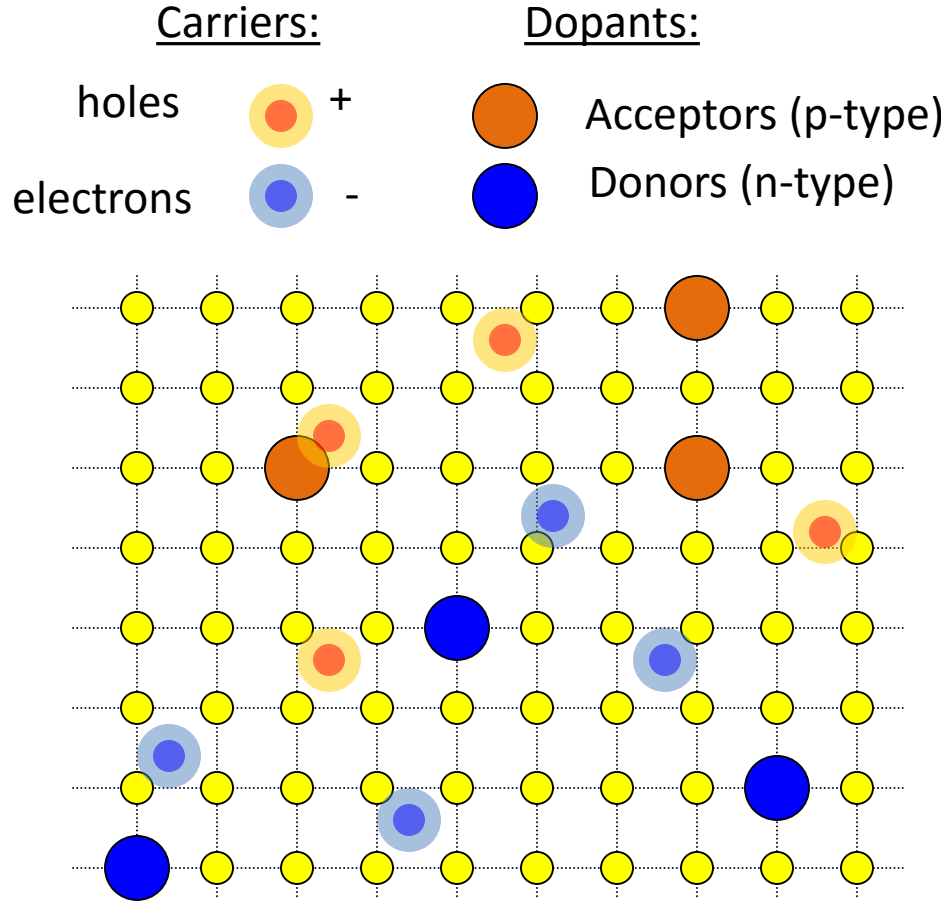
Carriers:

holes   +

electrons   −

Dopants:

Acceptors (p-type)

Donors (n-type)

II	III	IV	V	VI
Be	B	C	N	O
Mg	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

Group IV: diamond, Si, Ge
Group III-V: GaAs, AlAs, InSb, InAs...
Group II-VI: ZnSe, CdTe, ZnO, SdS...

Dopants, impurities and defects

How to control the concentration of carriers?

In semiconductors we can find several deviations from the ideal crystal structure:
· Defects of the crystal structure, vacancies, the atoms in interstitial positions, dislocations created eg. during the growth process.
· Foreign atoms (dopants) introduced intentionally or by adding impurities

As a result of their presence:
· allowed states in the forbidden gap due to deviations from the ideal crystalline potential
· space charges in insulators
· screening by free carriers

Dopant states can be classified into:
· Deep - the short-range potential located mainly in the area of one unit cell - eg. a vacancy, izoelectronics dopant (the same valency as atom of the base material e.g. N InP).
· Shallow - mainly long-range Coulomb potential

Dopants, impurities and defects

Hydrogen-like model

Atom of a valency higher than the base material atom becomes a source of Coulomb potential (modified by the dielectric constant of the crystal ε_r) caused by an extra proton in the nucleus. Extra electron in the conduction band feels this potential. The states are described by the effective mass equation:

$$T = -\frac{\hbar^2}{2m^*}\Delta \qquad U = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\varepsilon_r r}$$

$$[T + U]\phi(\vec{r}) = E\phi(\vec{r})$$

II	III	IV	V	VI
Be	B	C	N	O
Mg	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

Group IV: diamond, Si, Ge
Group III-V: GaAs, AlAs, InSb, InAs...
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Dopants, impurities and defects

Hydrogen-like model

Finally, the problem reduces to the problem of hydrogen atpom with a free carrier of mass m^* in the medium of dielectric constant ε and with a small "perturbation" potential.

$$E_n = -\left(\frac{m^*}{m_0}\right)\frac{1}{\varepsilon_r^2}Ry\frac{1}{n^2}$$

For typical semiconductors $m_e^* \approx 0.1 m_e$ $\varepsilon_s \approx 10$

$$a_B^* = \frac{4\pi\varepsilon_r\varepsilon_0\hbar^2}{m_0 e^2}\left(\frac{m_0}{m^*}\right) = a_B\varepsilon_r\left(\frac{m_0}{m^*}\right)$$

For Hydrogen
$Ry = 13.6$ eV and $a_B = 0.053$ nm

For GaAs semiconductor
$Ry^* \approx 5$ meV and $a_B^* \approx 10$ nm

II	III	IV	V	VI
Be	B	C	N	O
Mg	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

Group IV: diamond, Si, Ge
Group III-V: GaAs, AlAs, InSb, InAs...
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Far infrared spectroscopy

D^0

Silicon
$R_y = 30.28(5)$ meV

D^0
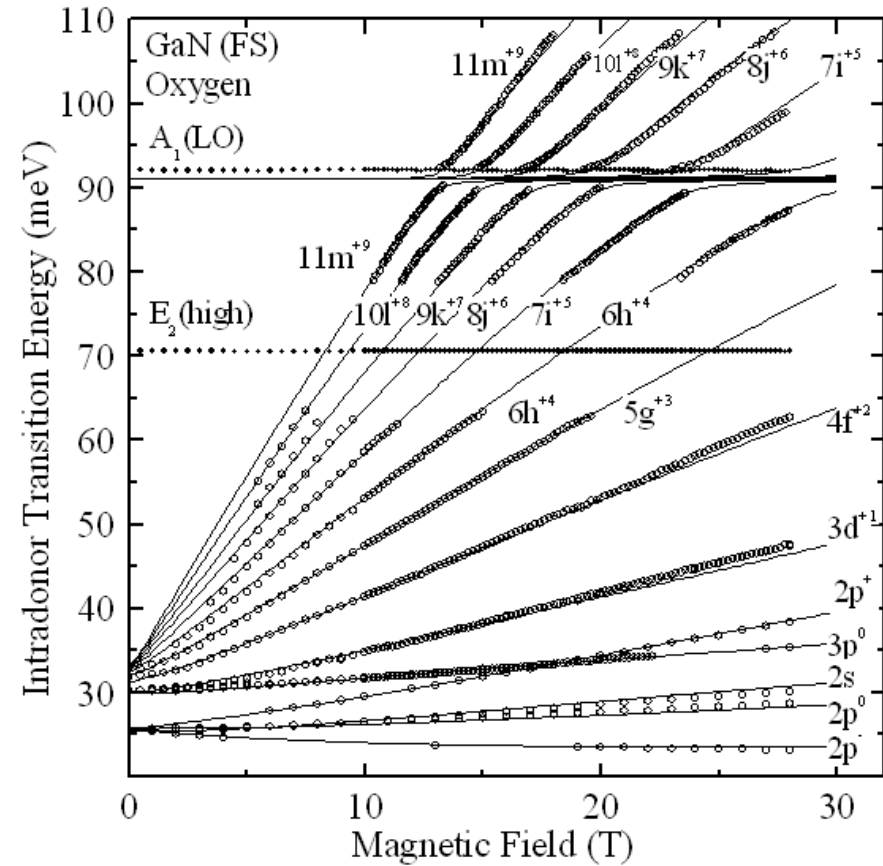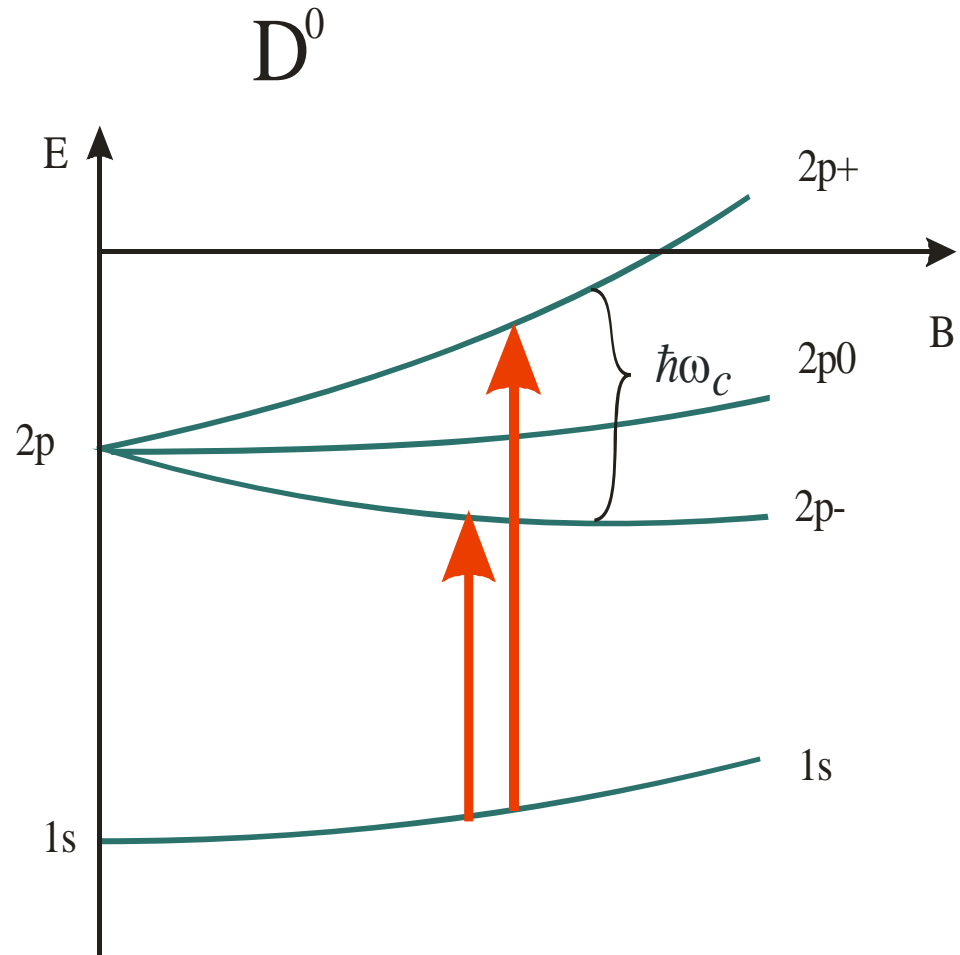
Oxygen
R_y=30.28(5) meV

Dopants, impurities and defects

Hydrogen-like model – ionization of the dopant

Doping

(diagram) Electron energy vs. x:
conduction band, donor level, acceptor level, vallence band, with levels E_D, $E_g/2$, E_F, 0, E_A, $-E_g/2$

The carrier concentration in extrinsic semiconductor (*niesamoistny*)

Consider a semiconductor, in which:

N_A – concentration of acceptors

N_D – concentration of donors

p_A – concentration of neutral acceptors

n_D – concentration of neutral donors

n_c – concentration of electrons in conduction band

p_v – concentration of holes in valence band

From the charge neutrality of the crystal:

Blackboard!

Dopants, impurities and defects

Doping

The carrier concentration in extrinsic semiconductor (*niesamoistny*)

Consider a semiconductor, in which:

N_A – concentration of acceptors

N_D – concentration of donors

p_A – concentration of neutral acceptors

n_D – concentration of neutral donors

n_c – concentration of electrons in conduction band

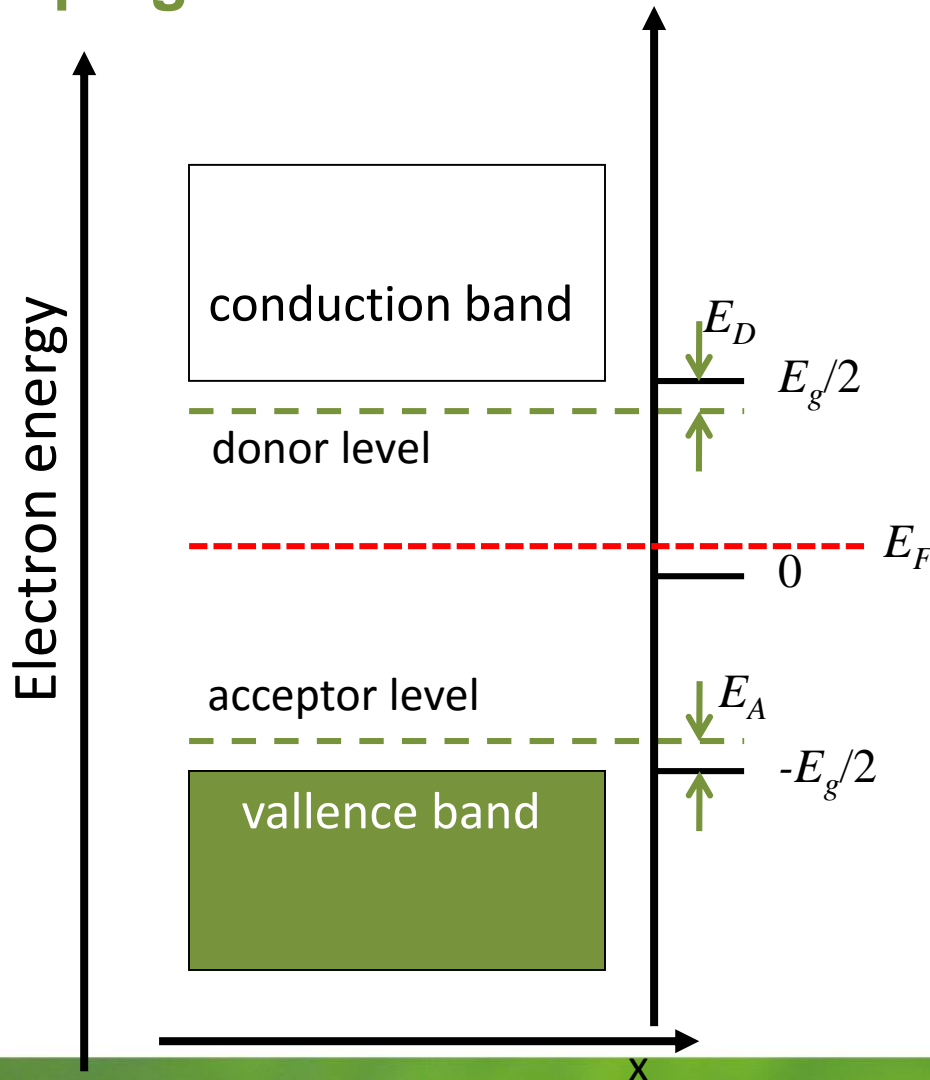p_v – concentration of holes in valence band

From the charge neutrality of the crystal:

$$n_c + (N_A - p_A) = p_v + (N_D - n_D)$$
$$n_c + n_D = (N_D - N_A) + p_v + p_A$$

The occupation of impurity levels

Occupation of impurity / defect levels in the thermodynamic equilibrium

„Occupation" of localized or band states means the exchange of particles (electrons) between the reservoir and considered subsystem (microstate).

The grand canonical ensemble (subsystem exchange particles and energy with the environment)

Thermodynamic probability (unnormalized) of finding subsystem in a state j, in which there are n_j particles (electrons) and which subsystem energy is E_j (the total energy of all n_j particles):

$$P_j = e^{-\beta(E_j - n_j \xi)}, \qquad \beta = \frac{1}{k_B T}$$

ξ - chemical potential.

Statistical sum:

$$Z = \sum_j P_j = \sum_j e^{-\beta(E_j - n_j \xi)}$$

TUTAJ 2015.11.12

The occupation of impurity levels

Statistical sum :

$$Z = \sum_j P_j = \sum_j e^{-\beta(E_j - n_j \xi)}$$

Statistical means:

$$\langle A \rangle = \frac{\sum_j A_j \cdot e^{-\beta(E_j - n_j \xi)}}{\sum_j e^{-\beta(E_j - n_j \xi)}}$$

Examples:

free electron occupying (or not) the quantum state of the $\vec{k}$-vector and spin:

2 possible states of the subsystem (microstate):

$n_0 = 0; E_0 = 0$

$n_1 = 1; E_1 = E$ (the occupation only for one spin state)

the average number of particles of the subsystem:

$$\langle n \rangle = \frac{0 \cdot e^0 + 1 \cdot e^{-\beta(E - \xi)}}{1 + e^{-\beta(E - \xi)}} = \frac{1}{e^{\beta(E - \xi)} + 1} = f(E, T)$$

(Fermi-Dirac distribution)

The occupation of impurity levels

Examples :

free electron occupying (or not) the quantum state of the $\vec{k}$-vector and ANY spin:
4 possible states of the subsystem (microstate):

$n_0 = 0; E_0 = 0$
$n_1 = 1; E_1 = E$ (spin ↑)
$n_2 = 1; E_2 = E$ (spin ↓)
$n_3 = 2; E_3 = 2E$ (spin ↑↓)

the average number of particles of the subsystem:

$$\langle n \rangle = \frac{0 \cdot e^0 + 1 \cdot e^{-\beta(E-\xi)} + 1 \cdot e^{-\beta(E-\xi)} + 2 \cdot e^{-\beta(2E-2\xi)}}{1 + e^{-\beta(E-\xi)} + e^{-\beta(E-\xi)} + e^{-\beta(2E-2\xi)}} = 2 \frac{e^{-\beta(E-\xi)}\left(1 + e^{-\beta(E-\xi)}\right)}{(e^{-\beta(E-\xi)} + 1)^2} =$$
$$= 2f(E,T)$$

(Fermi-Dirac distribution x2)

The occupation of impurity levels

The ratio of the probability of finding dopant / defect of $n + 1$ electrons and of n electrons:

$$\frac{p_{n+1}}{p_n} = \frac{N_{n+1}/N_{total}}{N_n/N_{total}} = \frac{\sum_{j:n_j=n+1} e^{-\beta[E_j-(n+1)\xi]}}{\sum_{k;n_k=n} e^{-\beta[E_k-n\xi]}} = \frac{g_{n+1}}{g_n} \cdot e^{-\beta[(E_{n+1}-E_n)-\xi]}$$
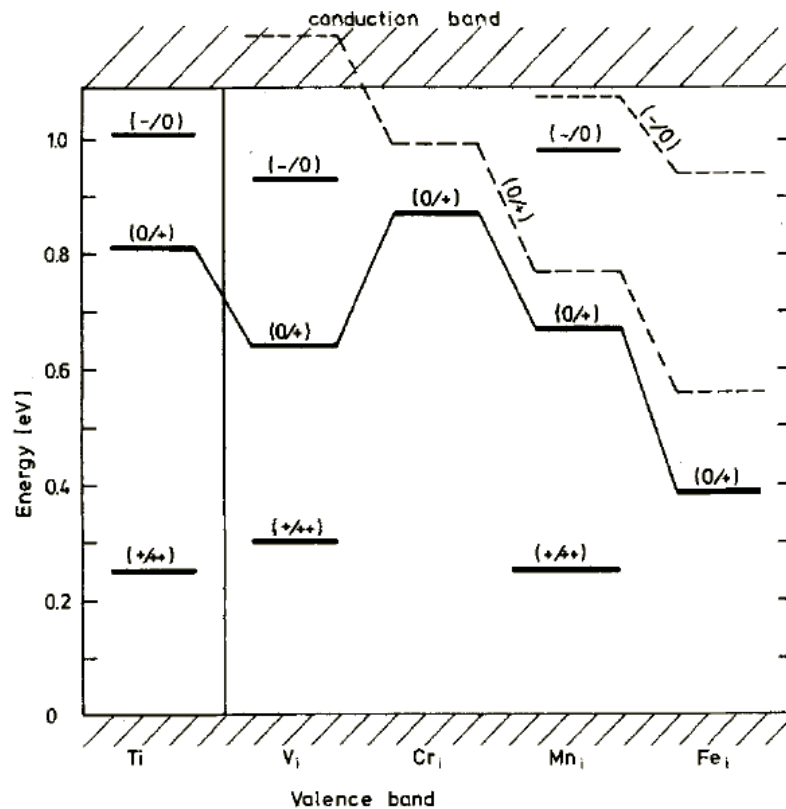

Fig. 15. Energy levels of interstitial 3d metals in silicon (full lines), see Table 3, compared with the results of X_α calculations of DeLeo et al. [15] (broken lines)

$\sum_n N_n = N$ – impurity (dopants) concentration

E_{n+1} i E_n – the lowest of all subsystem energies E_j with $n + 1$ and n electrons respectively

Successive impurity energy levels are filled with the increase of the Fermi level.

$E^{n+1/n}$ – so-called *energy level* of the impurity/ defect „numbered" by charge states $n + 1$ and n

g_{n+1}, g_n – so-called degeneration of states of subsystem of $n + 1$ and n electrons

The occupation of impurity levels

g_{n+1}, g_n – so-called degeneration of states of subsystem of $n + 1$ and n electrons.

The degeneracy g_{n+1} and g_n takes into account the possibility of the existence of different subsystem states corresponding to a same number of particles (including the excited states):

Fig. 15. Energy levels of interstitial 3*d* metals in silicon (full lines), see Table 3, compared with the results of X_α calculations of DeLeo et al. [15] (broken lines)

$$g_n = \alpha_{n,0} + \sum_{i=1,2,\ldots} \alpha_{n,i} e^{-\beta \varepsilon_{n,i}}$$

$\alpha_{n,0}$ i $\alpha_{n,i}$ they are respectively: the degeneracies of the n-electronic ground state and its excited states of energies higher than the ground state by $\varepsilon_{n,i}$ (excitation energies)

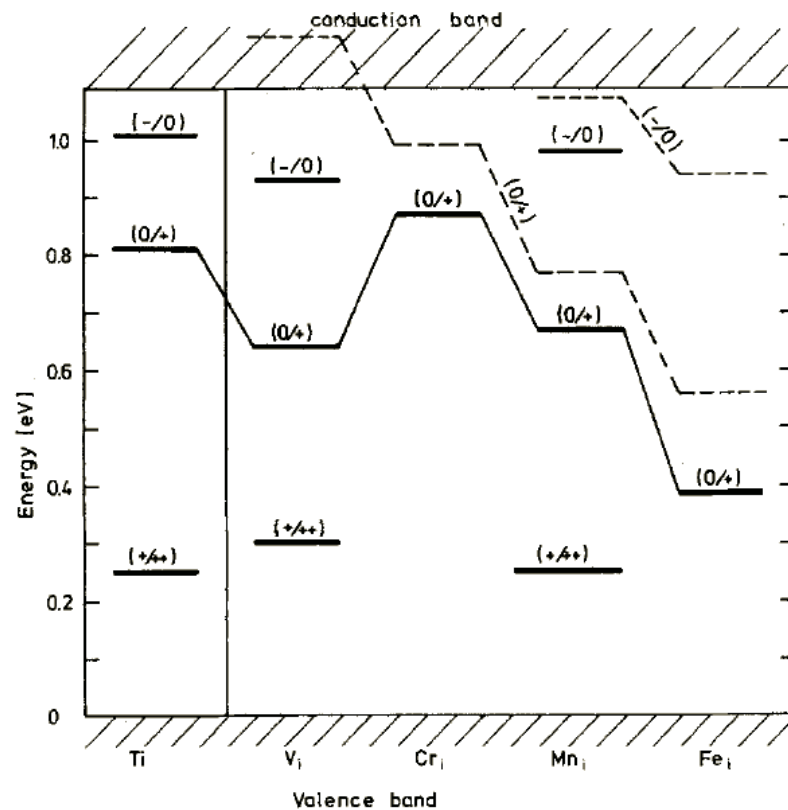**Such defined degeneration g_n generally depends on temperature**

The occupation of impurity levels

Example – donor (we omit the excited states)

charge state $(+)$ implemented in 1 way : $g_+ = 1$
charge state (0) implemented in 2 ways (spin $\uparrow$ or $\downarrow$): $g_0 = 2$
the energy of the donor state $\mathrm{E}^{0/+} = E_D$
Doping concentration of donors N_D

$$\frac{p_{n+1}}{p_n} = \frac{p_0}{p_+} = \frac{g_0}{g_+} \cdot e^{-\beta[E_D-\xi]}, \qquad p_+ + p_0 = 1$$

The occupation probability of the donor state:

$$p_0 = \langle n \rangle = \frac{1}{1 + \dfrac{g_+}{g_0} \cdot e^{\beta[E_D-\xi]}} = \frac{1}{1 + \dfrac{1}{2} \cdot e^{\beta[E_D-\xi]}}$$

The concentration of occupied donor states (neutral donors are N_D^0)

$$N_D^0 = \frac{N_D}{1 + \dfrac{1}{2} \cdot e^{\beta[E_D-\xi]}}$$