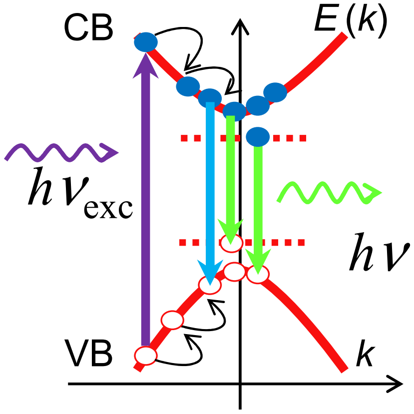
Lecture 14 – 17/12/2025

- Oscillator strength of excitons in semiconductors
- Electron-photon interaction beyond the semi-classical picture
- Spontaneous emission rate and bimolecular recombination coefficient
- Basic insights into near band edge photoluminescence transitions



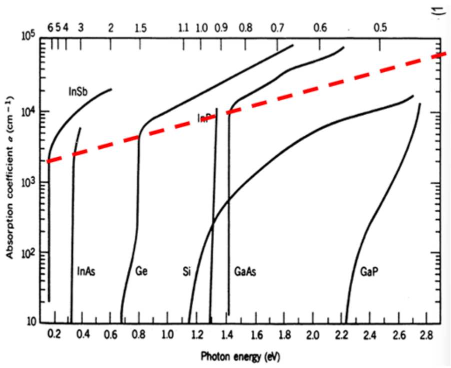
Summary Lecture 13

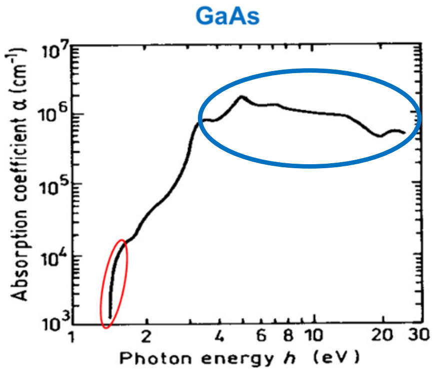
Absorption in Semiconductors

For direct bandgap SC, we use the JDOS to model α_0 with a square root law.

$$\boxed{\alpha_0(\omega) = \frac{q^2 x_{\mathrm{vc}}^2 \omega}{4\pi\varepsilon_0 \hbar n_{\mathrm{op}} c}\left(\frac{2m_r}{\hbar}\right)^{3/2}\sqrt{\omega - E_g/\hbar}}$$

Theory predicts $\alpha_0 \propto E_g^{1.5}$ in the vicinity of the band edge while experimental results are closer to $\alpha_0 \propto E_g^{1.3}$.





Refractive Index

The refractive index varies with ω (dispersive quantity).

Lorentz Model, Electrons = oscillating dipoles.

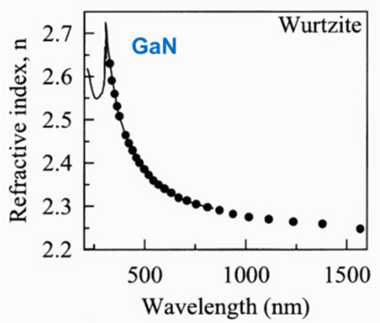
- At resonant frequency ω_0 the refractive index increases.

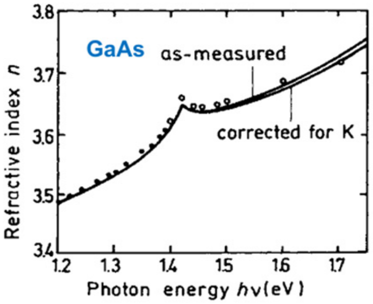
$$\boxed{n_{\mathrm{op}}^2(\omega) = 1 + \frac{q^2 N}{\varepsilon_0 m_0}\sum_j \frac{f_{0_j}}{\omega_{0_j}^2 - \omega^2 + i\gamma_j\omega}}$$

weight of resonance *j*

≡ ***oscillator strength***

Refractive index as a function of the wavelength/energy





Empirical formula: $\boxed{n_{\mathrm{op}}(\lambda) = \sqrt{a + \frac{b\lambda^2}{\lambda^2 - c^2}}}$ Sellmeier's law

a, *b* and *c* are material-dependent coefficients

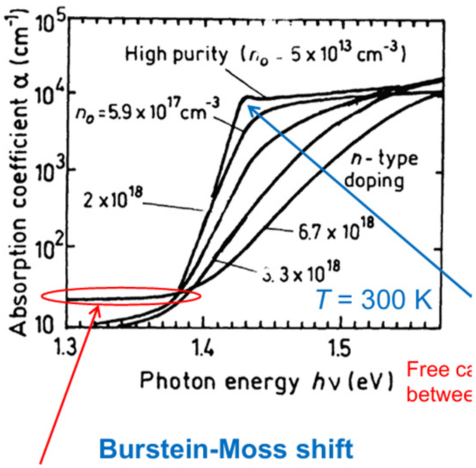
Summary Lecture 13

Absorption in Doped Semiconductors

Doping alters the absorption edge through two mechanisms:

- **Burstein-Moss Shift:** degenerate *n*-type, means the bottom of the conduction band is full and electrons promoted from the VB require more energy (blueshift) to find empty states.
- **Band Tailing (redshift):** tail states form inside the bandgap due to impurities, allowing absorption to occur at lower energies than the intrinsic bandgap.

***n*-doped GaAs**



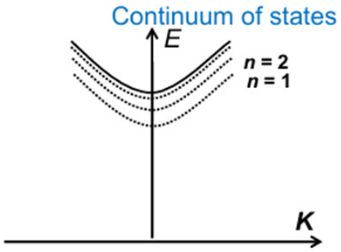
Burstein-Moss shift

Excitons

An electron and a hole bound together by Coulomb attraction.

Excitons are only stable if their binding energy R^* is greater than the thermal energy $k_B T$.

They appear as sharp absorption peaks below the bandgap energy.



Hydrogenic model

$$E_X = E_g + \frac{\hbar^2 K^2}{2M} - \frac{Ry^*}{n^2}$$

$$Ry^* = \frac{m_r}{m_0 \varepsilon_r^2} E_{H_I} = \frac{m_r e^4}{2\hbar^2 (4\pi\varepsilon_0\varepsilon_r)^2}$$

Same formula as that used for the binding energy of impurities (but ≠ m_r)

Ry^* = 4 meV for GaAs

Ry^* = 26 meV for GaN

Ry^* = 60-70 meV for ZnO

$$a_B = \frac{m_0}{m_r} \varepsilon_r a_0 = \frac{\hbar^2 4\pi\varepsilon_0\varepsilon_r}{m_r e^2}$$ **Bohr radius**

Excitons are huge! While a hydrogen atom is ~0.5 Å, an exciton in GaAs is ~100-200 Å wide.

Oscillator strength of excitons in semiconductors

Optical transition probability per unit time for converting a photon into an exciton, R_{exc}:[1]

$$\boxed{R_{\text{exc}} = \frac{2\pi}{\hbar}\sum_{f}\left|\langle f|H_{\text{xR}}|0\rangle\right|^{2}\delta\left(E_{f}(\mathbf{K})-E_{0}-\hbar\omega\right)}$$

Fermi's Golden Rule for excitons

Exciton-photon interaction

Wavefunction accounting for the relative motion of e-h pairs (cf. hydrogenic model)

$$\langle f|H_{\text{xR}}|0\rangle = \sum_{r,k}\left(1/\sqrt{N}\right)e^{i\mathbf{k}.\mathbf{r}}\phi_{nlm}(\mathbf{r})\langle\psi_{\mathbf{k}}(\mathbf{r}_{\text{e}})\psi_{-\mathbf{k}}(\mathbf{r}_{\text{h}})|H_{\text{xR}}|0\rangle = \sum_{r,k}\left(1/\sqrt{N}\right)e^{i\mathbf{k}.\mathbf{r}}\phi_{nlm}(\mathbf{r})\langle\psi_{\mathbf{k}}^{\text{c}}|H_{\text{eR}}|\psi_{\mathbf{k}}^{\text{v}}\rangle$$

Number of unit cells in the crystal

Independent of **k** (≡ vertical optical transitions)

with

$$\phi_{nlm}(\mathbf{r}) = R_{nl}(\mathbf{r})Y_{lm}(\theta,\phi) \quad \text{and} \quad H_{\text{eR}} = -e\mathbf{r}.\mathbf{E}$$

Electron-radiation interaction Hamiltonian in the electric dipole approximation

Associated Laguerre polynomials

Spherical harmonic

$$\sum_{\text{k}} e^{i\mathbf{k}.\mathbf{r}} = N\delta(\mathbf{r}) \Rightarrow \left|\langle f|H_{\text{xR}}|0\rangle\right|^{2} = N\left|\phi_{nlm}(0)\right|^{2}\left|\langle\psi_{\mathbf{k}}^{\text{c}}|H_{\text{eR}}|\psi_{\mathbf{k}}^{\text{v}}\rangle\right|^{2}$$

Probability of exciting an exciton optically is ∝ overlap of electron-hole wavefunctions

Non-zero only for $l = 0 \Rightarrow$ only excitons with an *s* symmetry can be optically excited

[1] Yu & Cardona, Chapter 6

Oscillator strength of excitons in semiconductors

Power loss of EM field due to absorption in a unit volume of a dielectric medium:[1]

$$\text{Power loss} = R_{\text{oep}}\hbar\omega$$

Transition rate in the one-electron picture (oep)

Energy lost per unit of time

$$I(z) = I_0 e^{-\alpha z} \text{ and } \tilde{n} = n_{\text{op}} + j\kappa$$

$$-\frac{dI}{dt} = -\left(\frac{dI}{dz}\right)\left(\frac{dz}{dt}\right)$$

Phase velocity

$$\Rightarrow \frac{dI}{dz} = -\alpha I_0 e^{-\alpha z} = -\alpha I \text{ and } \frac{dz}{dt} = \frac{c}{n_{\text{op}}} \Rightarrow -\frac{dI}{dt} = \frac{c}{n_{\text{op}}}\alpha I$$

$$\alpha = \frac{4\pi\kappa}{\lambda} \Rightarrow \alpha = \frac{\varepsilon_{\text{i,oep}}\omega}{c n_{\text{op}}} \Rightarrow -\frac{dI}{dt} = \frac{\varepsilon_{\text{i,oep}}\omega I}{n_{\text{op}}^2}$$

$$R_{\text{oep}}\hbar\omega = \frac{\varepsilon_{\text{i,oep}}\omega I}{n_{\text{op}}^2} \text{ and per definition } I = \frac{n_{\text{op}}^2}{8\pi}\left|E(\omega)\right|^2$$

$$\boxed{\Rightarrow \varepsilon_{\text{i,oep}} = \frac{8\pi R_{\text{oep}}\hbar}{\left|E(\omega)\right|^2}}$$

[1] Yu & Cardona, Chapter 6

Oscillator strength of excitons in semiconductors

$$R_{\text{oep}} = \frac{2\pi}{\hbar}\sum_{\mathbf{k}_c,\mathbf{k}_v}\left|\left\langle \psi_{\mathbf{k}}^{\text{c}}\middle|H_{\text{eR}}\middle|\psi_{\mathbf{k}}^{\text{v}}\right\rangle\right|^2\delta\left(E_{\text{c}}(\mathbf{k})-E_{\text{v}}(\mathbf{k})-\hbar\omega\right),$$

Use of the electron-radiation(photon) interaction Hamiltonian in the Coulomb gauge: $H_{\text{eR}} = -(e/m_0)\mathbf{A}\cdot\mathbf{p}$ with **A** the potential vector ($\propto E(\omega)/\omega$)

$$\Rightarrow R_{\text{oep}} = \frac{2\pi}{\hbar}\left(\frac{e}{m_0\omega}\right)^2\left|\frac{E(\omega)}{2}\right|^2\sum_{\mathbf{k}}|P|^2\delta\left(E_{\text{c}}(\mathbf{k})-E_{\text{v}}(\mathbf{k})-\hbar\omega\right)$$

Absorption transition rate per unit volume of the crystal (See Chap. 6 Yu&Cardona for technical details)

Two at the denominator because here we disregard stimulated emission processes

Electric dipole transition matrix element in the **p** representation

Imaginary part of the dielectric function for the continuum of states in the one-electron picture ($\varepsilon_{\text{i,oep}}$):[1]

$$\boxed{\varepsilon_{\text{i,oep}} = \frac{1}{4\pi\varepsilon_0}\left(\frac{2\pi e}{m_0\omega}\right)^2\sum_{\mathbf{k}}|P|^2\delta\left(E_{\text{c}}(\mathbf{k})-E_{\text{v}}(\mathbf{k})-\hbar\omega\right)}$$

Recommended homework:
Show using this expression of $\varepsilon_{\text{i,oep}}$ that you can recover the expression of $\alpha_0(\omega)$ obtained in slide 16 of Lecture 12

Imaginary part of the dielectric function for the exciton ($\varepsilon_{\text{i,exc}}$):[1]

$$\varepsilon_{\text{i,exc}} = \frac{2}{4\pi\varepsilon_0}\left(\frac{2\pi e}{m_0\omega}\right)^2\sum_{n=1}^{\infty}N\left|\phi_{nlm}(0)\right|^2|P|^2\delta\left(\hbar\omega-\hbar\omega_n\right)\ \text{and}\ \left|\phi_{n0m}(0)\right|^2 = \frac{(na_{\text{B}})^{-3}}{\pi}$$

Cf. slide 4

Spin degeneracy

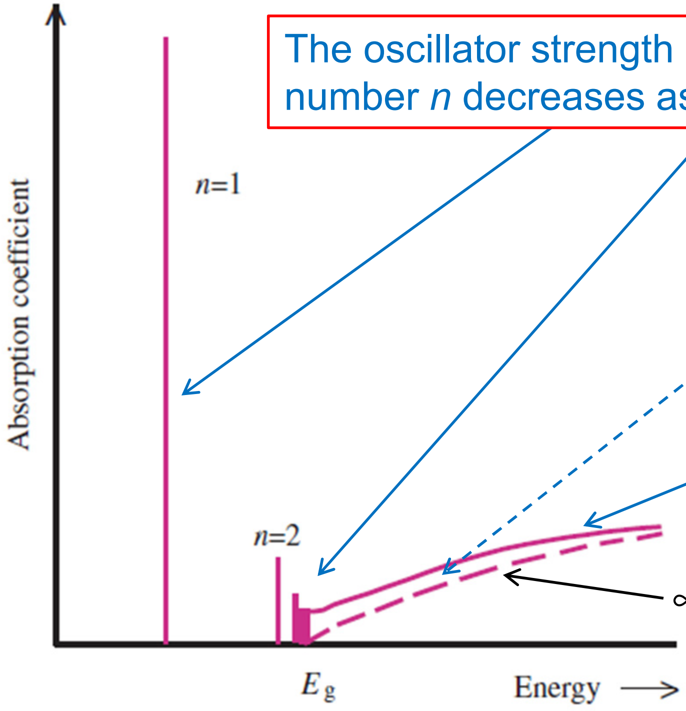
Cf. C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics*, (Wiley-VCH, Weinheim, 2020)

$$\boxed{\varepsilon_{\text{i,exc}}(\omega) = \frac{N}{32\pi^2}\frac{e^8}{(m_0\omega)^2}\frac{m_{\text{r}}^3}{\hbar^7\varepsilon_0^4\varepsilon_{\text{r}}^3}|P|^2\sum_{n=1}^{\infty}\frac{1}{n^3}\delta(\omega-\omega_n)}$$

[1] Yu & Cardona, Chapter 6

Oscillator strength of excitons in semiconductors

Absorption spectra of a direct gap semiconductor with (solid lines) and without (broken curve) exciton effects for the continuum states[1,2]



The oscillator strength of the excitonic bound states with principal quantum number n decreases as n^{-3} while their binding energy decreases as n^{-2}

$$E_X = E_g + \frac{\hbar^2 K^2}{2M} - \frac{Ry^*}{n^2}$$

$$Ry^* = \frac{m_r}{m_0 \varepsilon_r^2} E_{H_I} = \frac{m_r e^4}{2\hbar^2 (4\pi\varepsilon_0\varepsilon_r)^2}$$

Enhancement due to excitonic effects even in the continuum (cf. Ref. 1): Sommerfeld enhancement factor

$\propto \sqrt{(E - E_g)}$ Cf. expression of $\alpha_0(\omega)$

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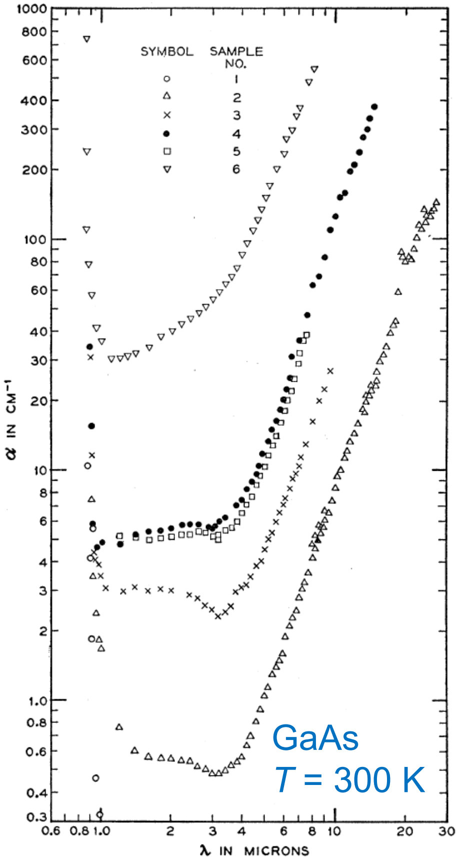
[1] R. J. Elliott, Phys. Rev. **108**, 1384 (1957) (> 2020 citations)

[2] Yu & Cardona, Chapter 6

Free carrier absorption in semiconductors



GaAs
T = 300 K

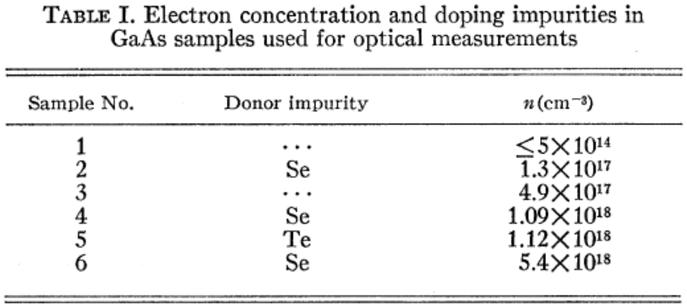


TABLE I. Electron concentration and doping impurities in GaAs samples used for optical measurements

Sample No.	Donor impurity	n (cm^{-3})
1	···	$\leq 5\times10^{14}$
2	Se	1.3×10^{17}
3	···	4.9×10^{17}
4	Se	1.09×10^{18}
5	Te	1.12×10^{18}
6	Se	5.4×10^{18}

$Z_0 \sim 377\ \Omega$ Impedance of free space

$$\alpha = \frac{\sqrt{\mu_0/\varepsilon_0}}{4\pi^2 c^2 n_{op}} \frac{nq^2\lambda^2}{m^*\tau}$$

n: doping level
λ: wavelength
τ: scattering rate (10^{-14} s)

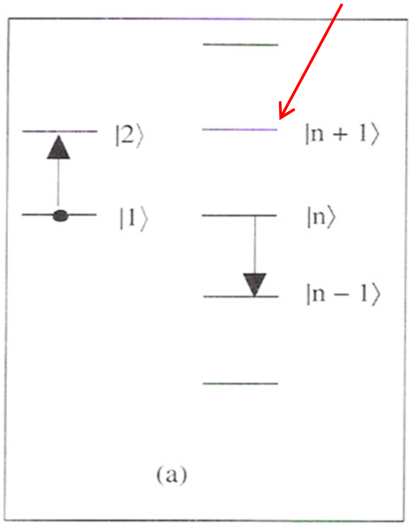
Example

Silicon doped at 10^{20} cm^{-3}
$\alpha \approx 2 \times 10^4$ cm^{-1} at 10 μm

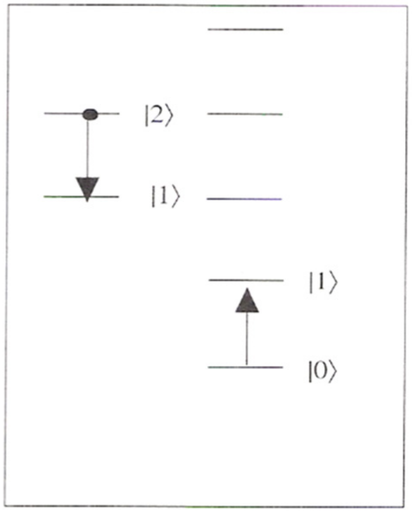
Electron-photon interaction

We consider a 2-level system with states $|i, n_l>$, where i is the charged particle state (= 1 or 2 for a 2-level system) and n_l is the number of photons in mode l.

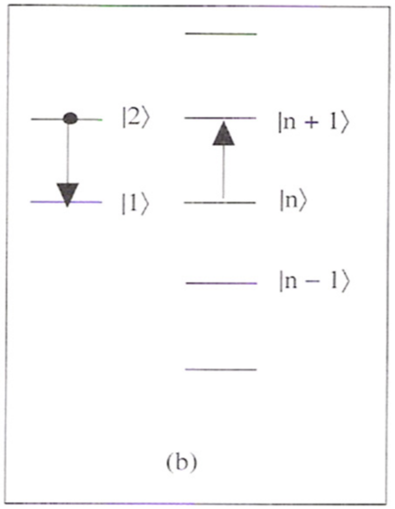
Ladder of photon number states (i.e., Fock states)



(a) Absorption



(b) Spontaneous emission



(c) Stimulated emission

Electron-photon interaction

Why does an electron on the excited state relax to the ground state? Or how does it release its energy?

$\Rightarrow$ **Stimulation by the vacuum field fluctuations F_l**

$$\boxed{F_l = \sqrt{\frac{\hbar\omega_l}{2\varepsilon_0 L^3}} \qquad (\textit{cavity } V = L^3)}$$

To be admitted
More information in Chaps. 2 & 3
Rosencher-Vinter

The Hamiltonian including the electric field quantization becomes

$$\boxed{\hat{W} = iqF_l(\hat{a}_l e^{i\mathbf{k}_l\mathbf{r}} - \hat{a}_l^+ e^{-i\mathbf{k}_l\mathbf{r}})\boldsymbol{\varepsilon}_\mathbf{l}\hat{r}}$$

F_l	*vacuum fluctuations in the mode* l
$\hat{a}_l^+, \hat{a}_l$	*creation and annihilation operators for photons in the mode* l
$\boldsymbol{\varepsilon}_\mathbf{l}$	*unit polarization vector of the electric field*

Electron-photon interaction

A few words on the vacuum field fluctuations

Photon number operator in mode *l*

- Hamiltonian of mode l of an EM wave $H_{\perp l} = \hbar\omega_l\left(\hat{a}_l^+\hat{a}_l + \frac{1}{2}\right)$

Normal component of the Hamiltonian, which is the only one to be of interest (Sec. 2.3 Rosencher-Vinter)

- Stationary state energy $E_{l,i} = \hbar\omega_l\left(i_l + \frac{1}{2}\right)$

Number of photons in mode *l*

- Vacuum energy of mode l (state $|0_l>$) $E_{vacuum,l} = \frac{1}{2}\hbar\omega_l$
  (inherited from Heisenberg uncertainty principle)

Mean value and variance of the electric field

$$\boxed{\begin{aligned}\overline{(\hat{\varepsilon}_{\perp l})} &= \langle i_l|\hat{\varepsilon}_{\perp l}|i_l\rangle = 0\\ \overline{(\hat{\varepsilon}_{\perp l})^2} &= \langle i_l|(\hat{\varepsilon}_{\perp l})^2|i_l\rangle = F_l^2(2i_l+1)\end{aligned}}$$

with $\hat{\varepsilon}_{\perp l} = iF_l(\hat{a}_l e^{i\mathbf{k}_l\mathbf{r}} - \hat{a}_l^+ e^{-i\mathbf{k}_l\mathbf{r}})\boldsymbol{\varepsilon}_\mathbf{l}$

See sections 2.5 and 2.6 in the book by Rosencher & Vinter

Even for an empty cavity (i_l= 0), the variance of the electric field is nonzero and proportional to the square of the *vacuum field fluctuations*

***Experimental signature:* Lamb shift** (degeneracy lift between $2s_{1/2}$ and $2p_{1/2}$ states in the hydrogen atom) signature of the coupling of H atoms with vacuum field fluctuations (full theory: *QED theory Feynman-Schwinger-Tomonaga, Nobel Prize in Physics 1965*)

Electron-photon interaction

Let us consider the absorption rate of a 2-level system experiencing an excitation with *n* photons within a mode *l*

The initial state is |1,*n*⟩ and the final state is |2,*n*-1⟩: *there is 1 photon less*

$$P_{1,2}=\frac{2\pi}{\hbar}\left|\langle 2,n-1|\hat{W}|1,n\rangle\right|^2\delta(\hbar\omega=E_2-E_1)$$

Fermi's Golden Rule

with the field quantization of the perturbation $\boxed{\hat{W}=iqF_l(\hat{a}_l e^{i\mathbf{k}_l\mathbf{r}}-\hat{a}_l^+e^{-i\mathbf{k}_l\mathbf{r}})\boldsymbol{\varepsilon}_l\hat{\mathbf{r}}}$ $\Rightarrow$

$$P_{1,2}=\frac{2\pi}{\hbar}q^2F_l^2\left|\langle 2,n-1|\left(\hat{a}_l e^{i\mathbf{k}_l\mathbf{r}}-\hat{a}_l^+e^{-i\mathbf{k}_l\mathbf{r}}\right)\boldsymbol{\varepsilon}_l\hat{\mathbf{r}}|1,n\rangle\right|^2\delta(\hbar\omega=E_2-E_1)$$

The electron state is independent of the photon state (i.e., we have two separable Hilbert spaces)

$$\Rightarrow\qquad P_{1,2}=\frac{2\pi}{\hbar}q^2F_l^2\underbrace{\left|\langle n-1|\left(\hat{a}_l e^{i\mathbf{k}_l\mathbf{r}}-\hat{a}_l^+e^{-i\mathbf{k}_l\mathbf{r}}\right)|n\rangle\right|^2}_{\langle n-1|\hat{a}_l|n\rangle=\sqrt{n}}\left|\langle 2|\boldsymbol{\varepsilon}_l\hat{\mathbf{r}}|1\rangle\right|^2\delta(\hbar\omega=E_2-E_1)$$

only non-zero related term

Electron-photon interaction

The absorption rate is then given by

$$P_{1,2}=\frac{2\pi}{\hbar}q^2F_l^2n\ \left|\langle 2|\boldsymbol{\varepsilon}_l\hat{\mathbf{r}}|1\rangle\right|^2\delta(\hbar\omega=E_2-E_1)$$

$$\boxed{F_l=\sqrt{\frac{\hbar\omega_l}{2\varepsilon_0L^3}}}$$

$$\boxed{P_{1,2}=\frac{2\pi}{\hbar}q^2\frac{\hbar\omega_l}{2\varepsilon_0L^3}n\ \left|\langle 2|\boldsymbol{\varepsilon}_l\hat{\mathbf{r}}|1\rangle\right|^2\delta(\hbar\omega=E_2-E_1)}$$

On the other hand, the amplitude of the classical electric field is such that $\boxed{E_0=\sqrt{\frac{2\hbar\omega_l}{\varepsilon_0L^3}n}}$

Thus, $\boxed{P_{1,2}=\frac{\pi}{2\hbar}q^2E_0^2\left|\langle 2|\boldsymbol{\varepsilon}_l\hat{\mathbf{r}}|1\rangle\right|^2\delta(\hbar\omega=E_2-E_1)}$ Cf. Lecture 12, slides 5-8

Absorption rate of a photon (with *n* photons in mode *l*) with an electron transitioning from state 1 to state 2

Electron-photon interaction

The recombination rate is calculated in the same way

The initial state is $|2,n\rangle$ and the final state is $|1,n+1\rangle$: *1 photon is created*

$$P_{2,1} = \frac{2\pi}{\hbar} q^2 F_l^2 \underbrace{\left|\langle n+1|\left(\hat{a}_l e^{i\mathbf{k}_l\mathbf{r}} - \hat{a}_l^+ e^{-i\mathbf{k}_l\mathbf{r}}\right)|n\rangle\right|}_{\langle n+1|\hat{a}_l^+|n\rangle = \sqrt{n+1}}{}^2 \left|\langle 2|\boldsymbol{\varepsilon}_{\mathbf{l}}\hat{\mathbf{r}}|1\rangle\right|^2 \delta\left(\hbar\omega = E_2 - E_1\right)$$

only non-zero related term

Thus, we have

$$\boxed{P_{2,1} = \frac{2\pi}{\hbar} q^2 \frac{\hbar\omega_l}{2\varepsilon_0 L^3}(n+1)\left|\langle 2|\boldsymbol{\varepsilon}_{\mathbf{l}}\hat{\mathbf{r}}|1\rangle\right|^2 \delta\left(\hbar\omega = E_2 - E_1\right)}$$

Recombination rate of an electron from state 2 to state 1 with 1 photon emitted in mode *l*

Electron-photon interaction

Recombination rate in a two-level system

$$P_{2,1} = \underbrace{q^2 \frac{\pi\omega_l}{\varepsilon_0 L^3} \boxed{n} \left|\langle 2|\boldsymbol{\varepsilon}_l \hat{\mathbf{r}}|1\rangle\right|^2 \delta(\hbar\omega = E_2 - E_1)}_{\text{Stimulated emission}} + \underbrace{q^2 \frac{\pi\omega_l}{\varepsilon_0 L^3} \left|\langle 2|\boldsymbol{\varepsilon}_l \hat{\mathbf{r}}|1\rangle\right|^2 \delta(\hbar\omega = E_2 - E_1)}_{\text{Spontaneous emission } (P_{sp})}$$

Stimulated emission ⇒ proportional to the photon number *n*

Spontaneous emission ⇒ due to vacuum fluctuations F_l

The **spontaneous emission rate** is calculated over all the cavity modes

Dipole element

Section 3.6 Rosencher-Vinter

$$\Gamma_{\mathrm{sp}} = \iiint P_{\mathrm{sp}} \mathrm{d}^3\mathbf{k}$$

+ substitute $\varepsilon_0 \rightarrow \varepsilon_r \varepsilon_0$

$$\Gamma_{\mathrm{sp}} = \frac{q^2 r_{12}^2 \omega^3 n_{\mathrm{op}}}{3\pi c^3 \hbar \varepsilon_0} = 1/\tau_{\mathrm{sp}}$$

τ_{sp} *radiative lifetime*

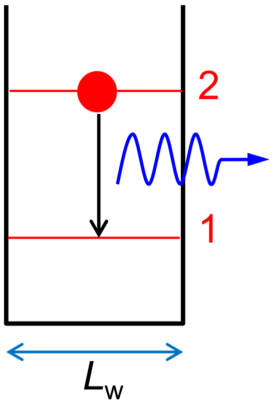
First derivation: Weisskopf-Wigner theory 1930

V. Weisskopf and E. Wigner, Z. Phys. **63**, 54 (1930) (> 1600 citations)

Spontaneous emission: case of discrete levels

Application:

Recombination lifetime in a quantum well with infinite barriers



1) Energy level

$$E_n = n^2 \frac{\hbar^2 \pi^2}{2m^* L_w^2}$$

Here, *n* is the principal quantum number of the quantized energy levels and not the photon number in the optical mode!

Then,

$$\hbar\omega_{12} = E_2 - E_1 = 3\frac{\hbar^2 \pi^2}{2m^* L_w^2}$$

2) Dipole element r_{12}

$$r_{12} = \langle \Psi_2(x) | x | \Psi_1(x) \rangle \quad \text{with} \quad \Psi_1(x) = \sqrt{\frac{2}{L_w}} \cos(\pi x / L_w) \quad \text{and} \quad \Psi_2(x) = \sqrt{\frac{2}{L_w}} \sin(2\pi x / L_w)$$

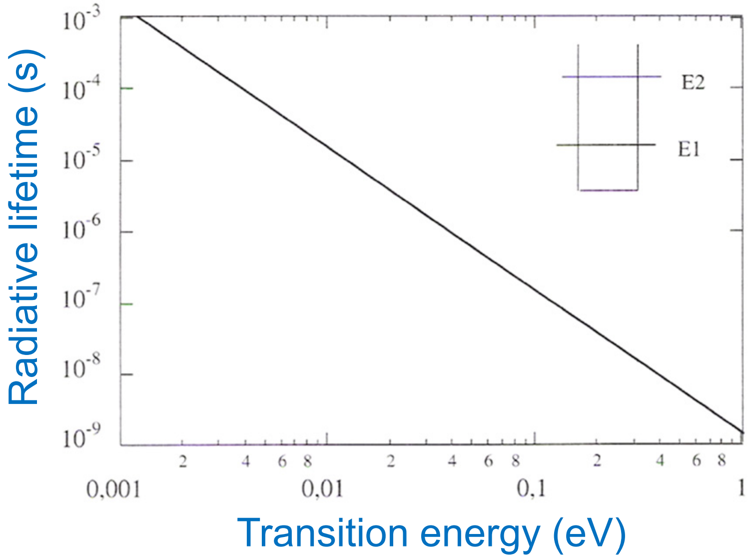
Finally, $r_{12} = \frac{2^4 L_w}{3^2 \pi^2}$ and $r_{12}^2 = \frac{2^7 m^*}{3^3 \pi^2 \hbar^2} 1 / E_{12}$

Spontaneous emission: case of discrete levels

Radiative lifetime:

$$1/\tau_{sp} = \frac{q^2 r_{12}^2 \omega^3 n_{op}}{3\pi c^3 \hbar \varepsilon_0}$$

$$\boxed{\tau_{sp} = \frac{3^4 \pi^3 m^* c^3 \hbar^2 \varepsilon_0}{2^7 q^2 n_{op}} \frac{1}{E_{12}^2}}$$



Transition energies > 1 eV
⇒ radiative lifetime ~1 ns

Values to be also compared to the optical phonon lifetime (slide #14 of Lecture 7) for a rough comparison !

Spontaneous emission in a bulk system

In an intrinsic bulk semiconductor:

The spontaneous recombination rate $r_{sp}(\mathbf{k})$ (s^{-1}) between the CB and the VB is given for a state with a wavevector **k**

$$\boxed{r_{sp}(\mathbf{k}) = A_{cv}\, f_c(E_c)\,(1-f_v(E_v))}$$

with $A_{CV} = 1/\tau_R$ *the spontaneous recombination rate*

and the radiative lifetime is given by

$$\boxed{\tau_R = \frac{\pi c^3 \hbar \varepsilon_0}{q^2 x_{vc}^2 n_{op} \omega_{vc}^3} = \frac{2\pi c^3 \hbar^2 \varepsilon_0 m_0}{q^2 n_{op} E_g E_p}}$$

$\tau_R \uparrow$ *when* $E_g \downarrow$ because, overall, the $n_{op}E_gE_p$ product decreases!

$\Rightarrow$ *It is more challenging to achieve a laser based on a wide bandgap SC!*

Spontaneous emission in a bulk system

In an intrinsic bulk semiconductor:

The spectral distribution of spontaneous recombination rate $R_{\mathrm{sp}}(h\nu)$ due to a quasi-equilibrium distribution of carriers is then given by

As usual two spin states are possible for a given wavevector **k**

$$R_{\mathrm{sp}}(h\nu) = \textcircled{2}\sum_{\mathbf{k}} r_{\mathrm{sp}}(\mathbf{k}) = 2\sum_{\mathbf{k}} \frac{1}{\tau_{\mathrm{R}}(\mathbf{k})} f_{\mathrm{c}}(\mathbf{k})\left(1 - f_{\mathrm{v}}(\mathbf{k})\right)\delta\left(E_{\mathrm{c}} - E_{\mathrm{v}} = h\nu\right)$$

The summation is performed over all the **k**-vectors verifying the energy conservation condition (hence the Dirac delta)

$$E_{\mathrm{c}}(\mathbf{k}) - E_{\mathrm{v}}(\mathbf{k}) = h\nu = E_{\mathrm{g}} + \frac{\hbar^2 k^2}{2m_{\mathrm{r}}}$$

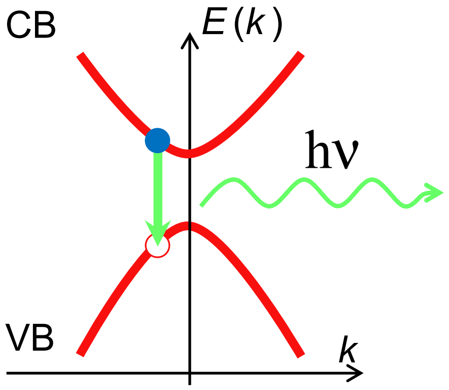
which leads to

$$R_{\mathrm{sp}}(h\nu) = \int_0^{\infty} r_{\mathrm{sp}}(E)\rho_{\mathrm{j}}(E)\delta(E = h\nu)\mathrm{d}E = r_{\mathrm{sp}}(h\nu)\rho_{\mathrm{j}}(h\nu) \quad \text{using the fact that } 2\sum_{\mathbf{k}} \leftrightarrow \int_{\mathbf{k}} \rho(\mathbf{k})d^3\mathbf{k} \leftrightarrow \int_E \rho(E)dE$$

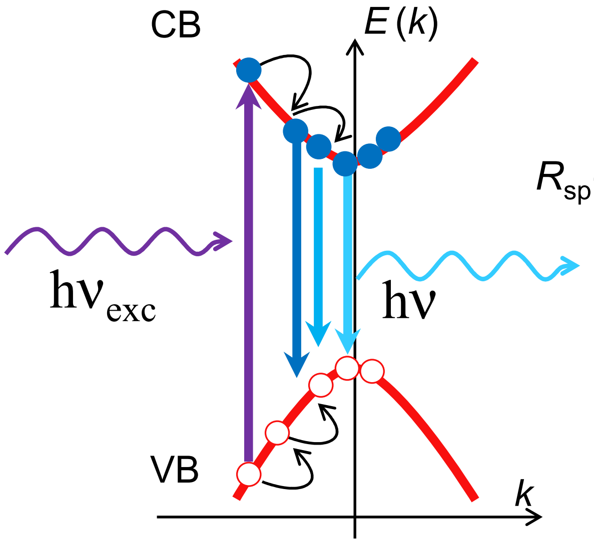
$$\boxed{R_{\mathrm{sp}}(h\nu) = \frac{1}{\tau_{\mathrm{R}}}\rho_{\mathrm{j}}(h\nu) f_{\mathrm{c}}\left(E_{\mathrm{c}}(h\nu)\right)\left(1 - f_{\mathrm{v}}\left(E_{\mathrm{v}}(h\nu)\right)\right)}$$

Spontaneous emission in a bulk system

Recombination and spontaneous emission

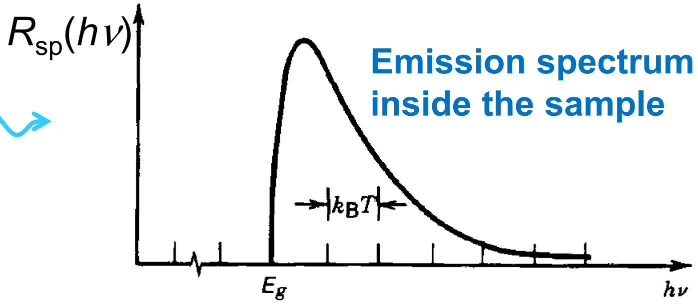


Spontaneous emission



Photoluminescence
(Electroluminescence)
(Cathodoluminescence)

van Roosbroeck-Shockley relation: link between emission rate and absorption at thermal (or quasi-thermal) equilibrium



Emission spectrum

$$R_{sp}(h\nu) = r_{sp}(h\nu)\rho_j(h\nu)$$

$$R_{sp}(h\nu) = \alpha(h\nu)\underbrace{\frac{8\pi n_{op}^2(h\nu)^2}{h^3c^2}\frac{1}{e^{\frac{h\nu}{k_BT}}-1}}_{\text{Planck radiation law}}$$

Spectral distribution of spontaneous recombination rate

W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954) (> 920 citations)

Bimolecular recombination coefficient

Total radiative recombination rate

$$R_{\mathrm{sp}} = \frac{1}{\tau_{\mathrm{R}}} \int_{E_{\mathrm{g}}}^{\infty} \rho_{\mathrm{j}}(h\nu) f_{\mathrm{c}}\left(E_{\mathrm{c}}(h\nu)\right)\left(1 - f_{\mathrm{v}}\left(E_{\mathrm{v}}(h\nu)\right)\right) \mathrm{d}h\nu$$

i.e., $R_{\mathrm{sp}} = \dfrac{e^{\left(E_{\mathrm{F_c}} - E_{\mathrm{F_v}}\right)/k_{\mathrm{B}}T}}{\tau_{\mathrm{R}}} \underbrace{\int_{E_{\mathrm{g}}}^{\infty} \rho_{\mathrm{j}}(h\nu) e^{-h\nu/k_{\mathrm{B}}T} \mathrm{d}h\nu}$

Expression valid within Boltzmann approximation!

Can be recast into a constant × the gamma function
(aka the *Euler integral of the 2nd kind*)!

which leads to

$$R_{\mathrm{sp}} = \frac{1}{\tau_{\mathrm{R}}} N_{\mathrm{j}} e^{\left(E_{\mathrm{F_c}} - E_{\mathrm{F_v}} - E_{\mathrm{g}}\right)/k_{\mathrm{B}}T}$$

with N_{j} the effective density of states with reduced mass m_{r}

Finally, we get: $R_{\mathrm{sp}} = \dfrac{1}{\tau_{\mathrm{R}}} \dfrac{N_{\mathrm{j}}}{N_{\mathrm{c}} N_{\mathrm{v}}} np$

$$\boxed{\begin{array}{l} R_{\mathrm{sp}} = Bnp \\ \text{with} \\ B = \dfrac{1}{\tau_{\mathrm{R}}} \dfrac{N_{\mathrm{j}}}{N_{\mathrm{c}} N_{\mathrm{v}}} = \dfrac{1}{\tau_{\mathrm{R}} N_{\mathrm{c}}} \left(\dfrac{m_{\mathrm{r}}}{m_{\mathrm{v}}}\right)^{3/2} \end{array}}$$

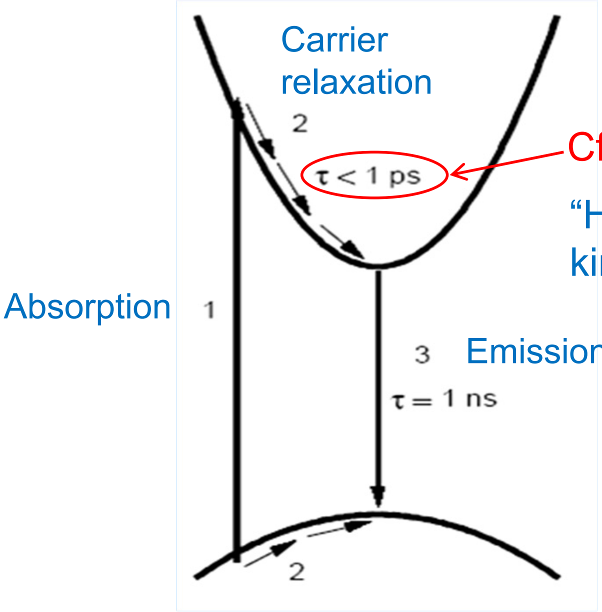
Cf. Lecture 7
Band-to-band recombinations
***Slides** 18-21*

Material	B (cm^3 s^{-1})
GaAs	7.2×10^{-10}
GaSb	2.4×10^{-10}
InP	1.3×10^{-9}
InAs	8.5×10^{-11}
InSb	4.6×10^{-11}

@ 300 K

Spontaneous emission

Photoluminescence

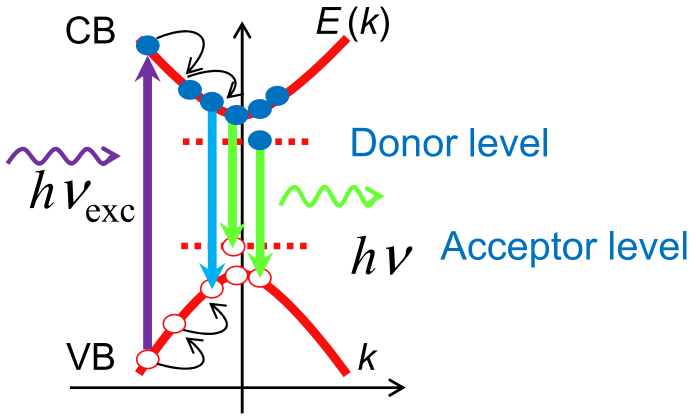


Cf. T_2 relaxation time in the expression of χ

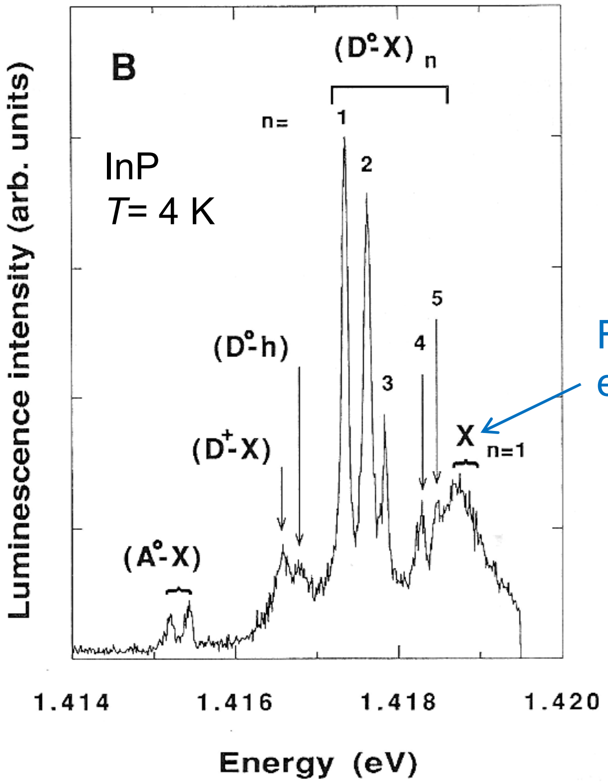
“Hot” carriers (electrons and holes) release their kinetic energy *via* LO and acoustic phonon emission

Spontaneous emission

Photoluminescence (case of bulk InP)



Bound state PL

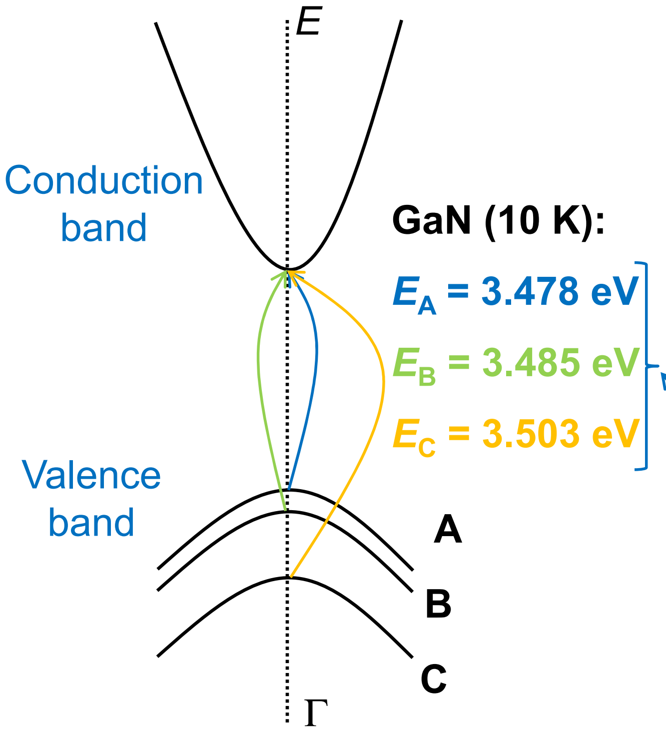


Free exciton PL

⇒ *How can we discriminate intrinsic PL from extrinsic one?*

Spontaneous emission

Photoluminescence and reflectivity (GaN)



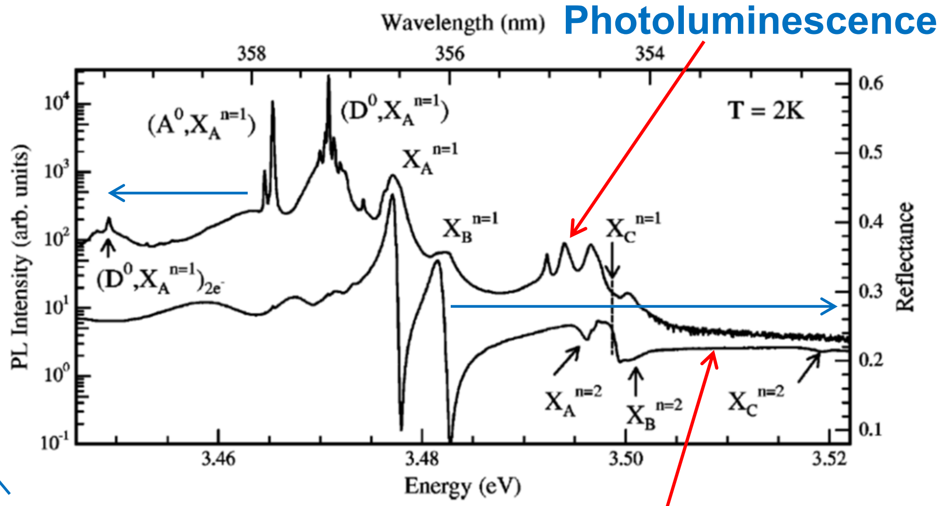
GaN (10 K):

E_A = 3.478 eV

E_B = 3.485 eV

E_C = 3.503 eV

Expected values in relaxed (strain-free) bulk GaN



Photoluminescence

Reflectivity (∝ JDOS, i.e., *A* or f_{osc})

$\boxed{R \cong 1\text{-}A}$

Exciton binding energy can also be determined from reflectivity spectra!

Examination protocol

Examination: 16/01/2026 from 9:15am until 12:15pm in room ELD 020

- The exam could cover any of the topics addressed during the 14 lectures of this semester and the corresponding series.
- The exam will be a mixture of problem solving (involving mathematical calculations) and analysis of figures/physical phenomena. Special care will be paid to the quality and the correctness of your explanations and/or arguments.
- The exam shall be written in *readable* English (**pay a special attention to your handwriting…**).
- Printed versions of the lectures with your personal notes as well as the exercises (+ solutions) are allowed (+ summary of the core concepts posted on Moodle) but you cannot bring anything else (no textbook, etc.)! **Any tool providing access to the Internet is strictly forbidden (no smartphone and smartwatch).**
- The reference for all the courses of this semester will be the version of the lectures posted on the Moodle repository, i.e., the files available from December 19, 2025!
- Do not forget to bring a scientific calculator for numerical applications. **There won't be any of them on loan!**
- You can reach out to me preferably by e-mail (from January 5, 2026): raphael.butte@epfl.ch (Samuele will always forward your requests to me so please use the shortest pathway!)