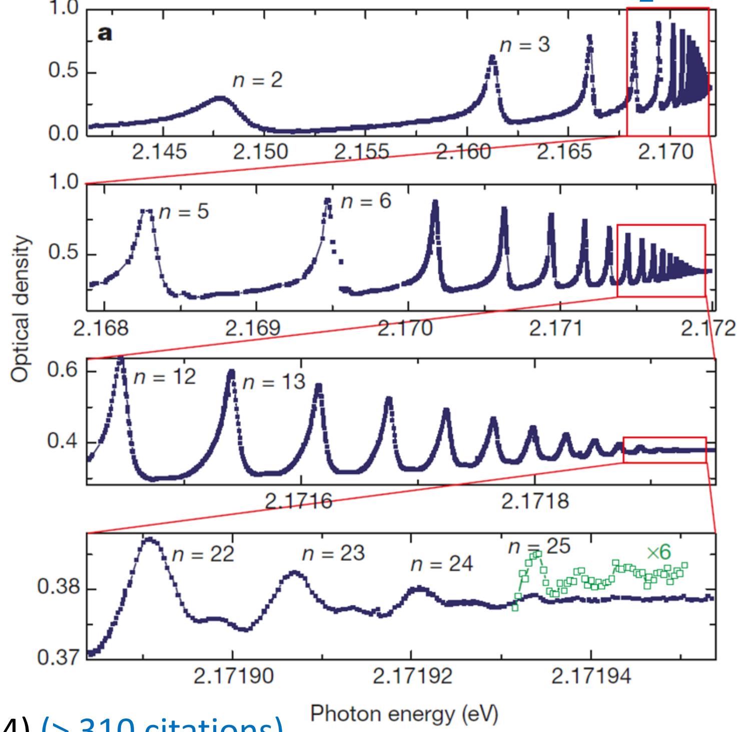
Lecture 13 – 10/12/2025

- Absorption
  - Refractive index
  - Absorption in doped semiconductors
  - Excitonic features in bulk semiconductors

Excitonic absorption in Cu_2O



T. Kazimierczuk *et al.*, Nature **514**, 343 (2014) (> 310 citations)

Summary Lecture 5

Optical transitions and Fermi's Golden Rule

Fermi's Golden Rule

$$\boxed{P_{n,\mathbf{k},n',\mathbf{k}'} = \frac{\pi}{2\hbar}\left|\langle \Psi_{n',\mathbf{k}'}|\hat{\mathrm{W}}|\Psi_{n,\mathbf{k}}\rangle\right|^2 \delta\left(E_{n',\mathbf{k}'} - E_{n,\mathbf{k}} - \hbar\omega\right)} \longrightarrow [\delta(\Delta E)] = \text{Joule}^{-1}$$

$$E_{n',\mathbf{k}'} - E_{n,\mathbf{k}} = \hbar\omega \quad \Rightarrow \textit{energy conservation}$$

Where:

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{u_{n,\mathbf{k}}(\mathbf{r})}{\sqrt{V_s}} e^{-i\mathbf{k}.\mathbf{r}} \qquad \langle \Psi_{c,\mathbf{k}'}|\hat{\mathrm{W}}|\Psi_{v,\mathbf{k}}\rangle = -qE\delta(\mathbf{k}' - \mathbf{k}_{\mathbf{op}} - \mathbf{k}) \times r_{vc}$$

Unitless Kronecker delta

Outcomes:

- The momentum is conserved $\mathbf{k}' = \mathbf{k} + \mathbf{k}_{\mathbf{op}}$
- (Quasi) verticality of optical transition $\mathbf{k}' \approx \mathbf{k}$

$$\boxed{r_{vc} = \frac{\hbar}{E_g}\sqrt{\frac{E_p}{2m_0}}}$$

Absorption and susceptibility

Optical susceptibility: $\chi(\omega) = \chi_{\Re}(\omega) + i\chi_{\Im}(\omega)$

Refractive index absorption

From Maxwell's eq: Dispersion relation:

$$\boxed{k = |\mathbf{k}| = \frac{n_{op}\omega}{c}\left|1 + \frac{\varepsilon_0}{\varepsilon}\chi(\omega)\right|^{1/2}} \uparrow$$

$$n_{op} = \sqrt{\frac{\varepsilon}{\varepsilon_0}} \quad \text{and} \quad \mu_0\varepsilon_0 c^2 = 1$$

⚠ k is a **complex number**

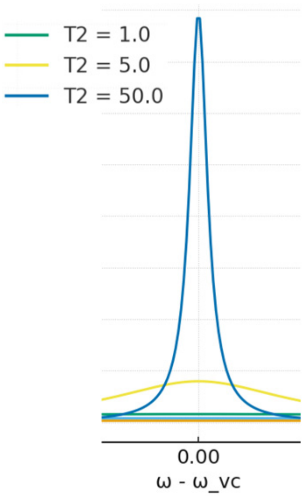
$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{k_{\Im} r}\,\Re[e^{-i(k_{\Re} r - \omega t)}]$$
$$= \mathbf{E}_0 e^{-\frac{\alpha}{2} r}\,\Re[e^{-i(k_{\Re} r - \omega t)}]$$

$$\boxed{\alpha(\omega) = -2k_{\Im} = -\frac{\omega}{c n_{op}}\chi_{\Im} \quad (\chi_{\Im} < 0)}$$

Main mathematical simplification:

$$\frac{1/\pi T_2}{(\omega - \omega_{vc})^2 + (1/T_2)^2} \Leftrightarrow \delta(\omega - \omega_{vc})$$

Dirac function



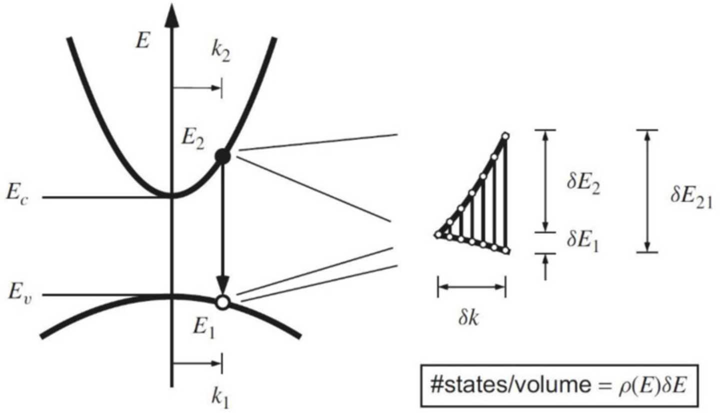
$$\boxed{\chi_{\Im}(\omega) = -\frac{q^2 x_{vc}^2 \pi}{2\varepsilon_0\hbar}\rho_j(\omega)\left[f_v(E_v(\mathbf{k})) - f_c(E_c(\mathbf{k}))\right]}$$

Joint density of states (3D case):

$$\boxed{\rho_j(\omega) = \frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar}\right)^{3/2}(\omega - E_g/\hbar)^{1/2}} \quad \text{with} \quad \frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h}$$

Summary Lecture 5

$$\boxed{\rho_j(\omega) = \frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar}\right)^{3/2}(\omega - E_g/\hbar)^{1/2}} \quad \text{with } \frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h}$$



$$\boxed{\alpha(\omega) = \alpha_0(\omega)\left[f_v(\hbar\omega) - f_c(\hbar\omega)\right]}$$

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

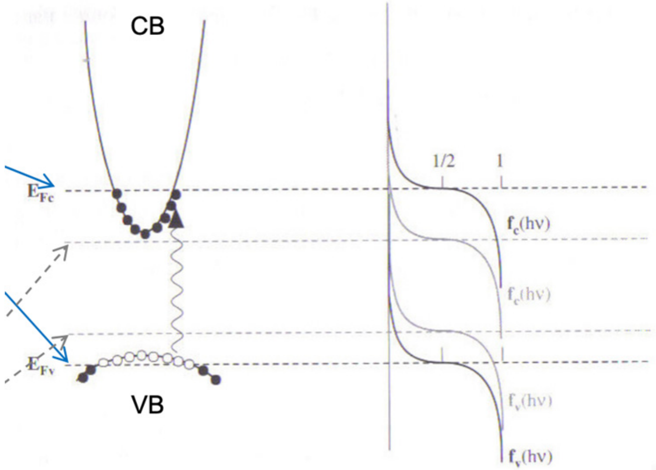
See exercice 12

Bernard-Duraffourg condition

$$\boxed{E_{Fc} - E_{Fv} > \hbar\omega > E_g}$$

Light gets **amplified** only once the Bernard-Duraffourg condition is fulfilled, i.e., when the semiconducting medium exhibits optical gain!

Out of equilibrium



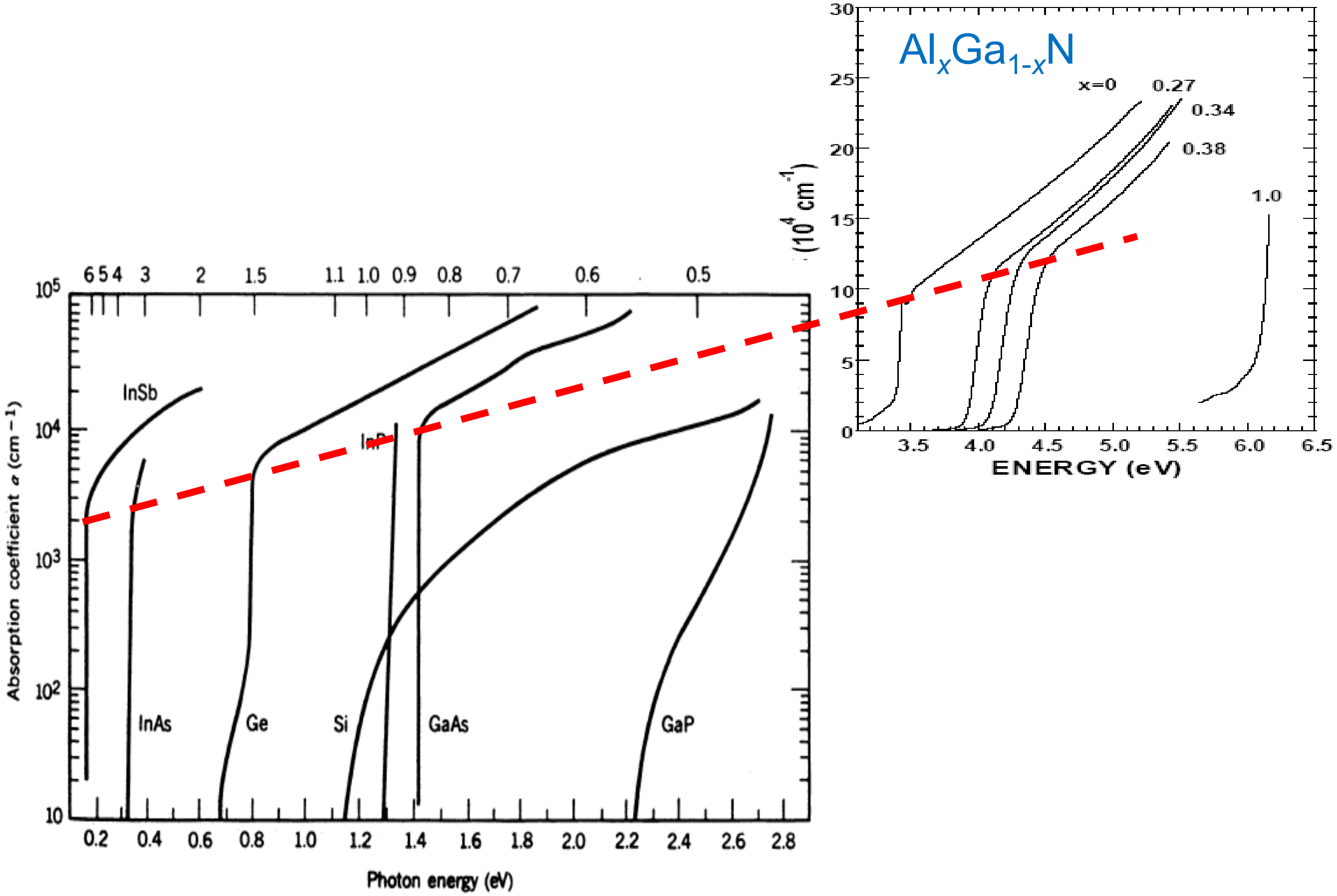
Strong excitation

- ✓ At least one of the two bands is degenerate
- ✓ All the states satisfying the *B-D* inequality are “fully occupied”, i.e., the SC is transparent for those λ!

Weak or moderate excitation

- ✓ None of the bands are degenerate, i.e., $n < N_C$ and $p < N_V \Rightarrow$ use of Boltzmann approximation
- ✓ $\Rightarrow$ photon absorption is still at play since there are available states in the CB where e^- from the VB can be promoted

Experimental account of absorption in semiconductors



Absorption in semiconductors

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

How does α_0 vary with the bandgap at $\omega \approx E_{\mathrm{g}}/\hbar$?

$$x_{\mathrm{vc}}^2 \propto E_{\mathrm{g}}^{-2}$$

$$m_{\mathrm{r}}^{3/2} \propto E_{\mathrm{g}}^{3/2}$$

cf. nearly-free electron model and **k.p** method

$$\omega \propto E_{\mathrm{g}}$$

$$n_{\mathrm{op}} \text{ vs } \omega?$$

Refractive index in semiconductors

Refractive index:

A semiconductor is a dispersive medium ⇒ the refractive index varies with ω

Refractive index modeling:

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon\mathbf{E}$$

where $\varepsilon = \mathbf{D}/\mathbf{E} = \varepsilon_0 + \mathbf{P}/\mathbf{E}$ and $n_{\mathrm{op}} = \sqrt{\dfrac{\varepsilon}{\varepsilon_0}}$

Determination of the polarization P of the medium when the latter experiences an electric field perturbation (⇒ modification of the charge distribution in the crystal)

Refractive index in semiconductors

Let us simplify the medium by considering a dipole experiencing an electric field perturbation

If one considers the analogy between a dipole and a spring, then we get:

$F = -kx$ and the angular frequency is given by: $\omega_0{}^2 = k/m_0$

restoring force

This dipole undergoes an external force, which is given by: $F_{\text{ext}} = qE(t) \ = qE_0 \cos(\omega t)$

The equation of motion is given by:

$$qE_0 \cos(\omega t) - m_0 \omega_0^2 x = m_0 \frac{\mathrm{d}^2 x}{\mathrm{d}t^2}$$

of solution equal to:

$$x(t) = x_0 \cos(\omega t) = \frac{qE(t)}{\left[m_0\left(\omega_0^2 - \omega^2\right)\right]}$$

Refractive index in semiconductors

The polarization can be written as:

$P(t) = qx(t)N$

q	charge
x	displacement
N	electron density

The displacement $x(t)$ is equal to $\dfrac{qE(t)}{\left[m_0\left(\omega_0^2-\omega^2\right)\right]}$

Thus, $P(t)=\dfrac{q^2NE(t)}{\left[m_0\left(\omega_0^2-\omega^2\right)\right]}$

One recalls that $\varepsilon = \mathbf{D}/\mathbf{E} = \varepsilon_0 + \mathbf{P}/\mathbf{E}$

$$\varepsilon = \varepsilon_0 + q^2N/[m_0(\omega_0^2-\omega^2)]$$

$$\boxed{n_{\mathrm{op}}^2(\omega)=1+\frac{q^2N}{\varepsilon_0 m_0\left(\omega_0^2-\omega^2\right)}}$$

Refractive index in semiconductors

Note that in solids (e.g., in semiconductors), atomic interactions lead to a damping of the oscillations (losses). This effect is accounted for by introducing a friction force $m_0\gamma\, \mathrm{d}x/\mathrm{d}t$.

$$n_{\mathrm{op}}^2(\omega) = 1 + \frac{q^2 N}{\varepsilon_0 m_0\left(\omega_0^2 - \omega^2 + i\gamma\omega\right)}$$

We must also consider multiple resonances, then it comes*:

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

weight of resonance j
$\equiv$ ***oscillator strength***

$$\boxed{f_{0_j} = 2\frac{\left|\langle f_j|\boldsymbol{\eta}\cdot\mathbf{p}|i\rangle\right|^2}{m_0\hbar\omega_{0_j}} = \frac{2m_0\omega_{0_j}}{\hbar}\left|\langle f_j|\boldsymbol{\eta}\cdot\mathbf{r}|i\rangle\right|^2}$$

η is the unit polarization vector of the EM wave

$$\boxed{\sum_j f_{0_j} = 1}$$

Thomas-Reiche-Kuhn sum rule

Generalization necessary, e.g., to account for the degeneracy or the near degeneracy of optical transitions

Far from resonances ($\omega \ll \omega_{0j}$), the refractive index slowly varies and depends on ω_{0j}. On the other hand, it rapidly increases close to the bandgap.

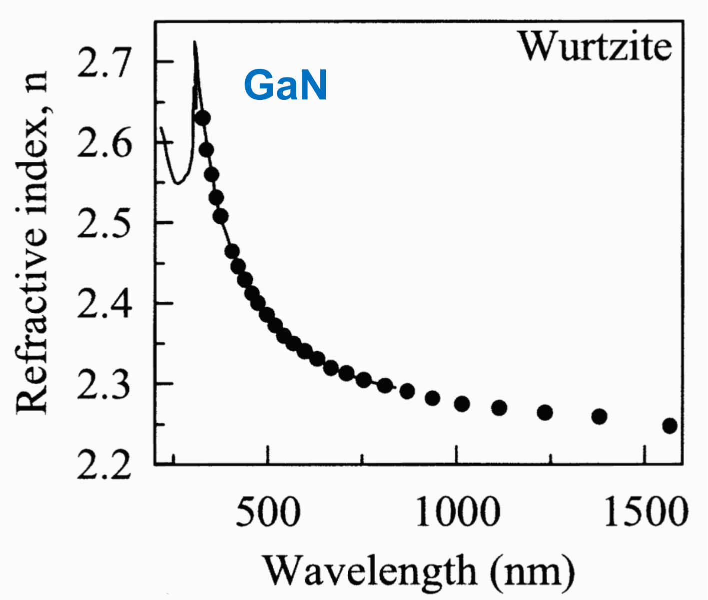
Examples:

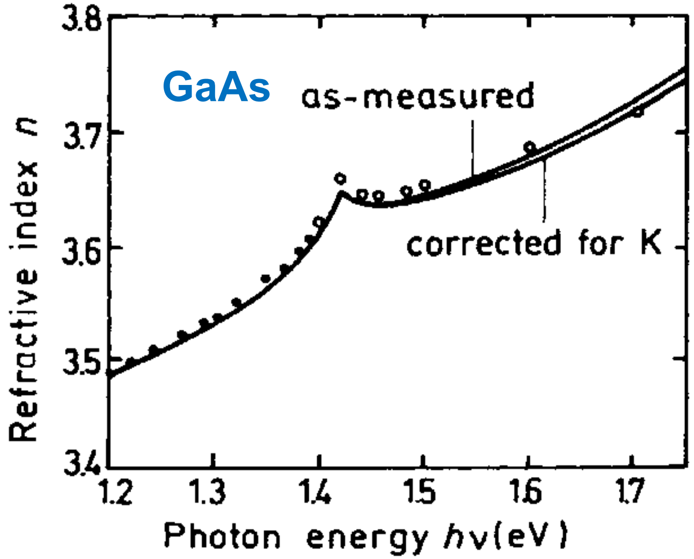
GaAs $n_{\mathrm{op}} \approx 3.6$ with bandgap of 1.42 eV
GaN $n_{\mathrm{op}} \approx 2.6$ with bandgap of 3.42 eV

* The full expression is much more complicated due to long-distance interactions

Refractive index in semiconductors

Refractive index as a function of the wavelength/energy





Empirical formula:

$$\boxed{n_{op}(\lambda) = \sqrt{a + \frac{b\lambda^2}{\lambda^2 - c^2}}}$$

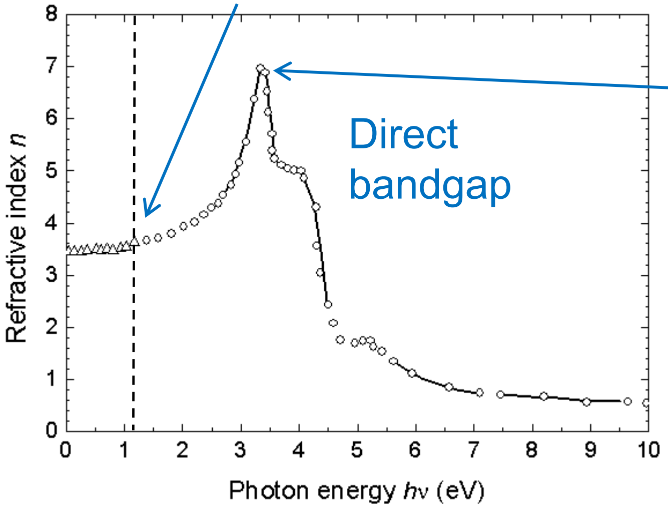
Sellmeier's law

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

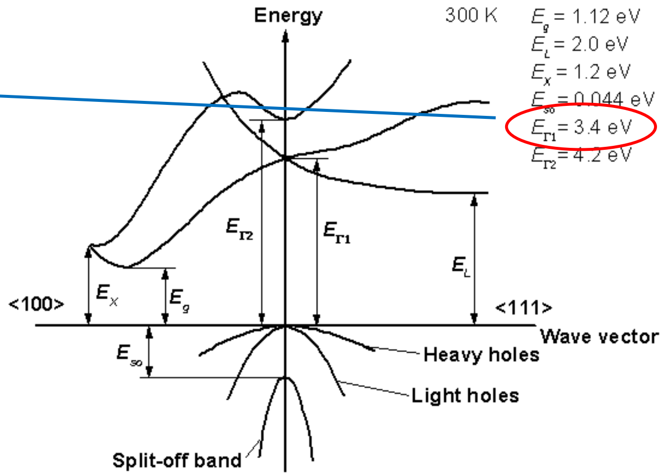
Refractive index in semiconductors

Indirect bandgap semiconductor: the case of silicon

Indirect bandgap



Direct bandgap



Absorption in semiconductors

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

How does α_0 vary with the bandgap at $\omega \approx E_{\mathrm{g}} / \hbar$?

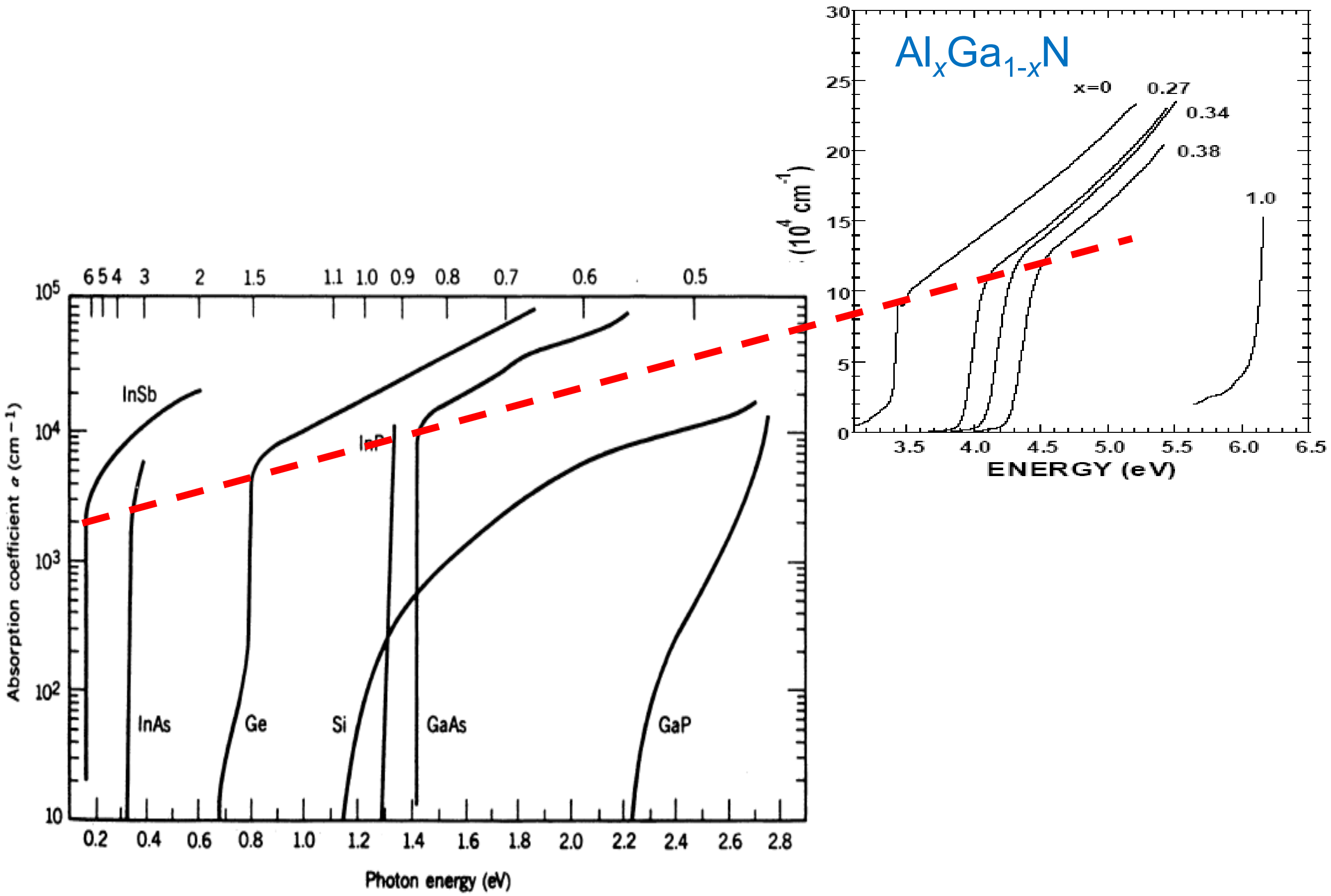
$$x_{\mathrm{vc}}^2 \propto E_{\mathrm{g}}^{-2}$$

$$m_{\mathrm{r}}^{3/2} \propto E_{\mathrm{g}}^{3/2}$$

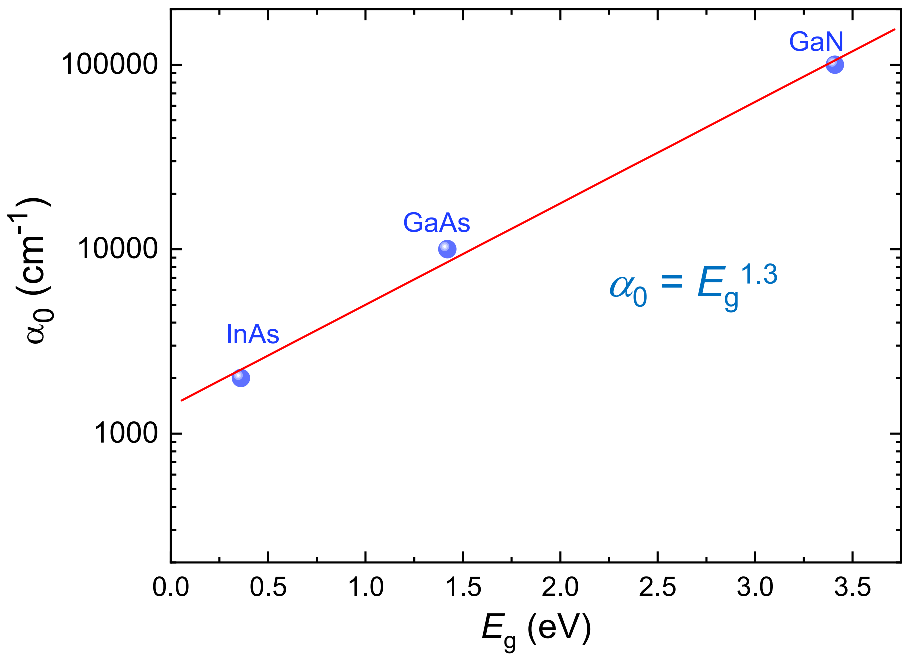
$$\omega \propto E_{\mathrm{g}}$$

$$\boxed{n_{\mathrm{op}}^{-1} \propto E_{\mathrm{g}}}$$

Experimental observations



Absorption in semiconductors



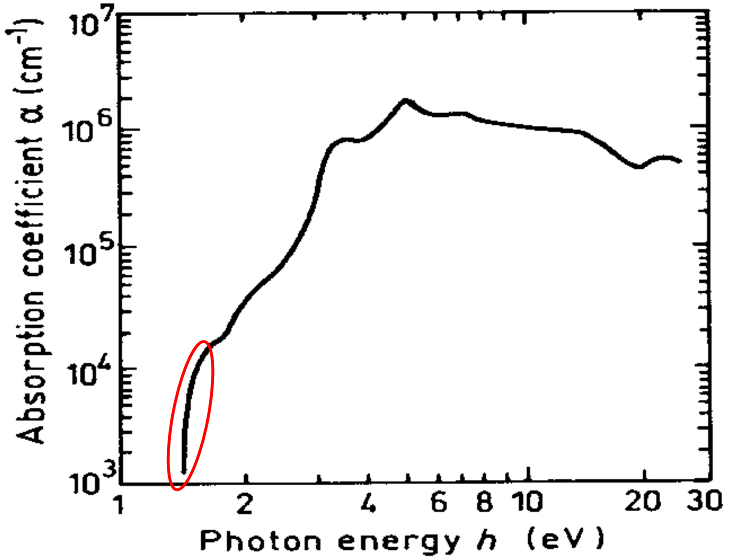
To be compared with theoretical prediction:

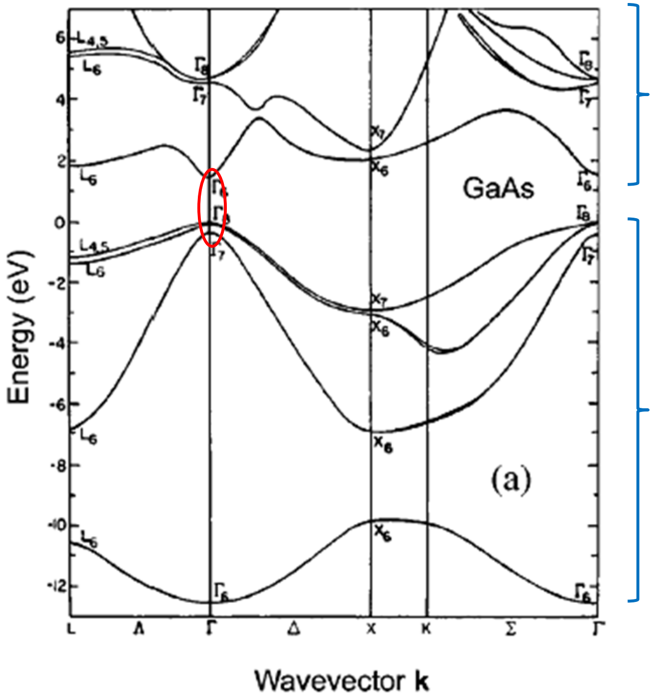
$\alpha_0 \propto E_g^{1.5}$

Absorption in semiconductors

Absorption coefficient far above the bandgap

GaAs





Empty states

Filled states

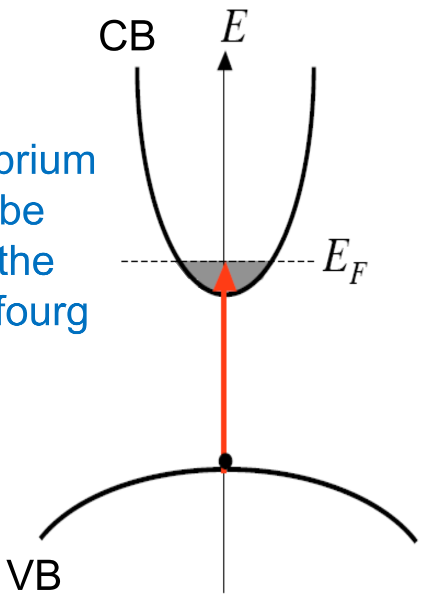
The joint-DOS is getting larger with increasing photon energy and hence $\alpha_0(\omega)$ until reaching a plateau-like region!

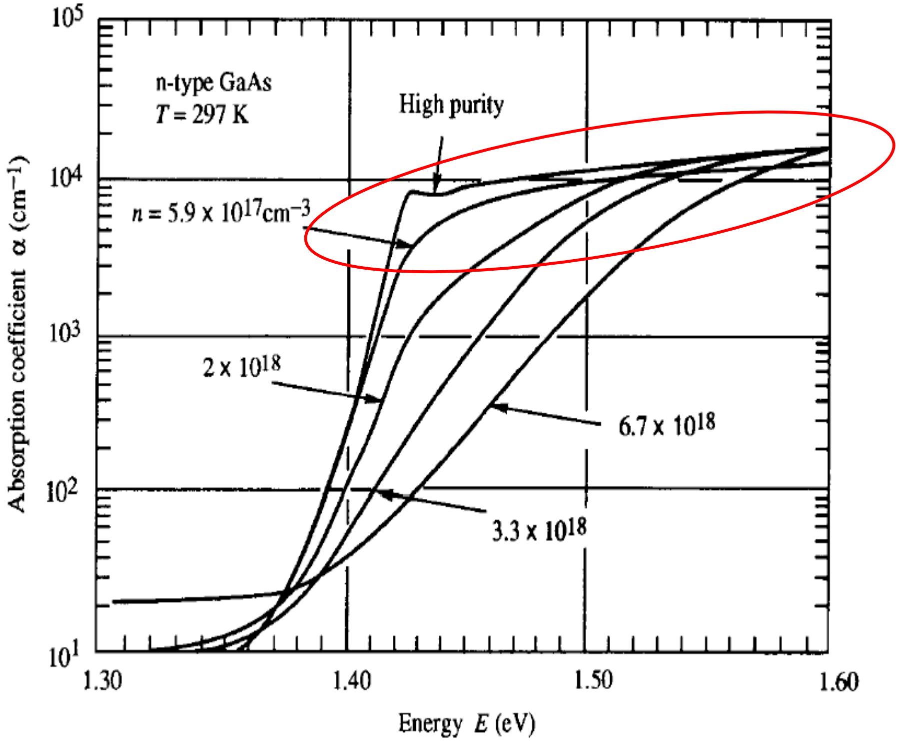
Absorption in doped semiconductors

Doping effect: e.g., degenerate *n*-type semiconductor ($E_{Fn} \geq E_C$)

Burstein-Moss shift[1,2] → blueshift of the absorption edge due to band filling

Thermal equilibrium case ⇒ not to be confused with the Bernard-Duraffourg condition!





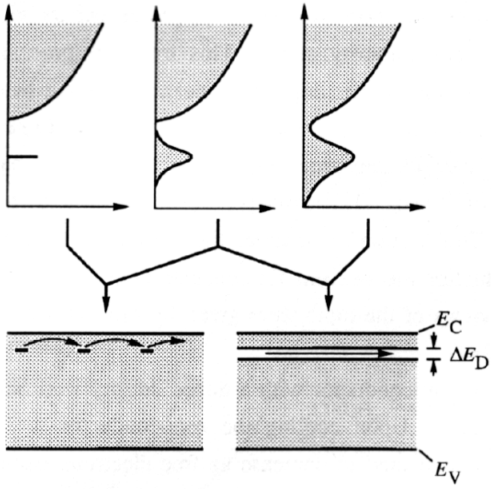
[1] E. Burstein, Phys. Rev. **93**, 632 (1954) (> 3700 citations)

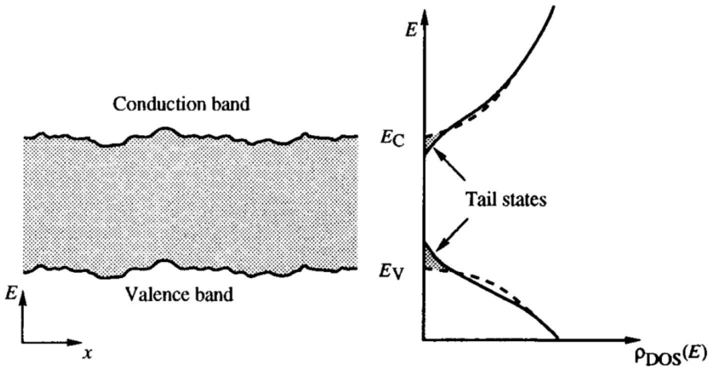
[2] T. S. Moss, Proc. Phys. Soc. (London) **B76**, 775 (1954) (> 1800 citations)

Absorption in doped semiconductors

High doping level: tail states in the bandgap are observed and bandgap narrowing

“Band tailing” due to an impurity band and/or to bandgap potential fluctuations

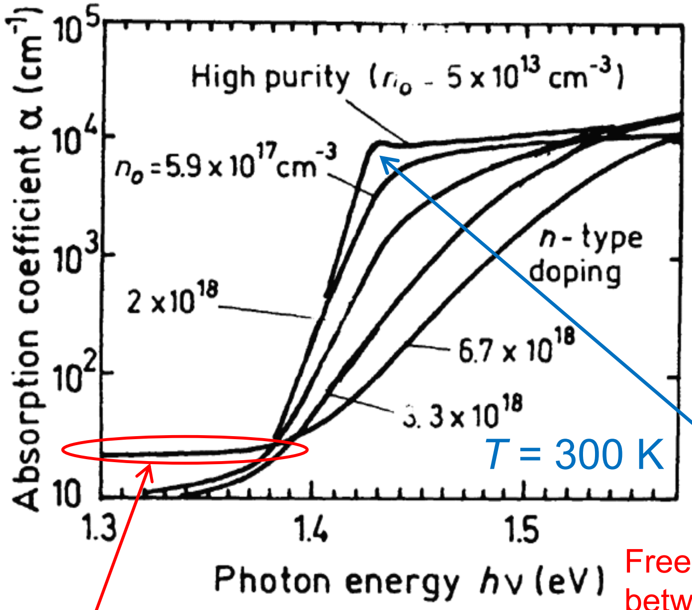




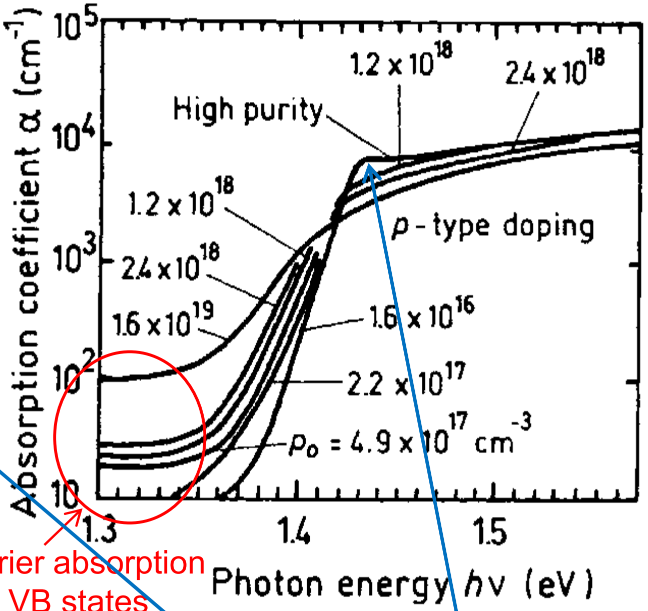
- Random distribution of impurities
- Ionized donors exert an attractive force on conduction electrons and a repulsive force on valence holes (reverse for acceptors)
- Local energy gap constant but DOS distribution is position dependent (number of states at each energy over whole volume) $\Rightarrow$ hence the presence of tail states

Absorption in doped semiconductors

n-doped GaAs



p-doped GaAs



Free carrier absorption between VB states

Non-degenerate p-type doped GaAs, because $m_h >> m_e$ (almost one order of magnitude difference)

Burstein-Moss shift

Free carrier absorption between CB state minima

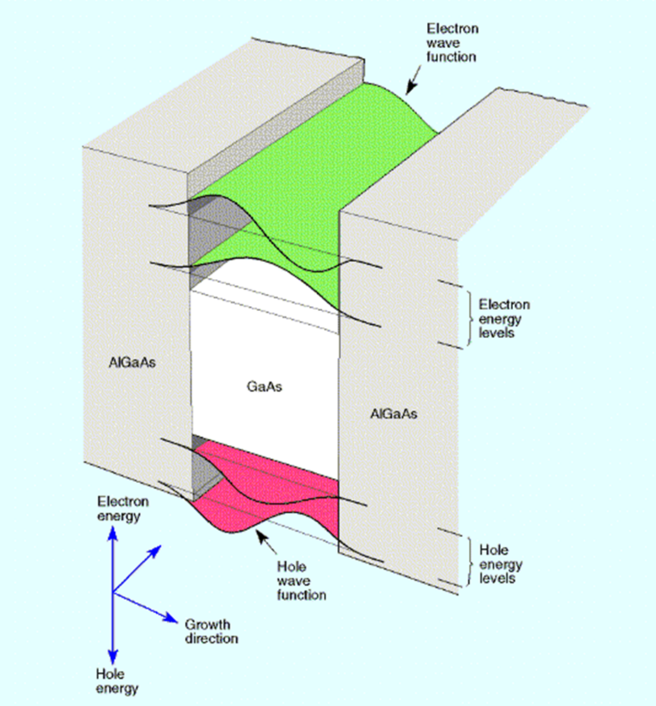
Band tailing

Absorption process promotes e⁻ from filled states near or above the parabolic VB edge to the CB tail ⇒ absorption edge shifts to lower E as band tails increase

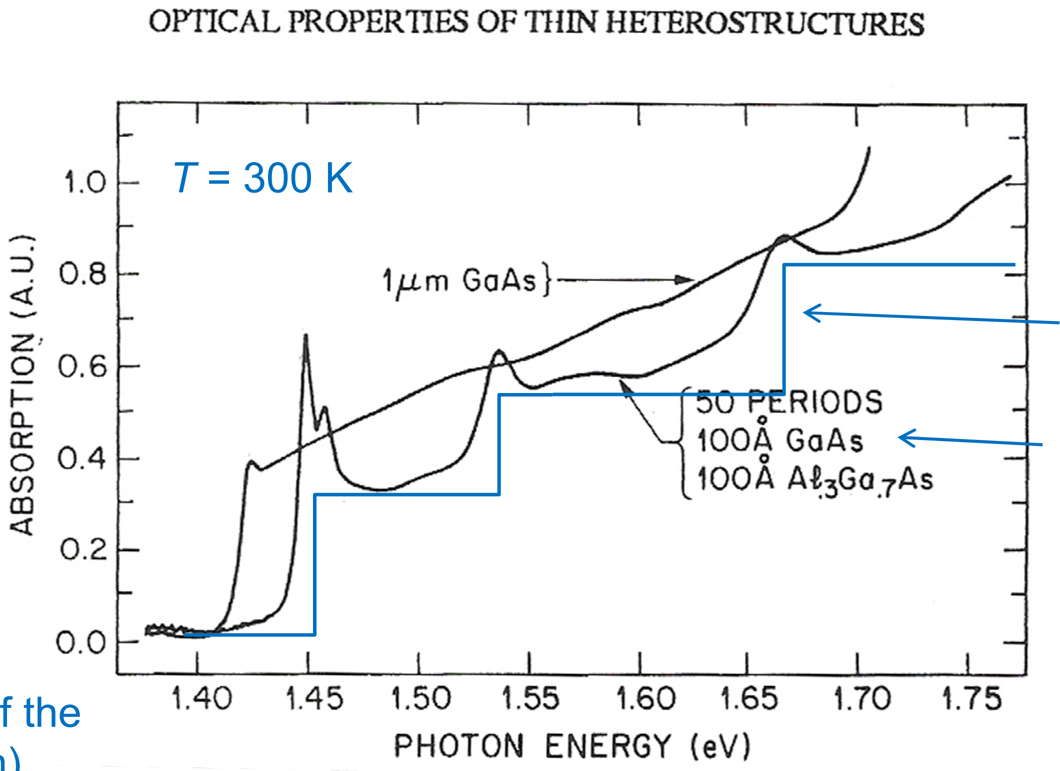
Decrease of α near the undoped E_g value due to the quenching of excitonic features

Absorption and excitons in semiconductors

Exciton: electron-hole pair bound via Coulomb interaction



- The shape of $\alpha(\omega)$ is a function of the joint-DOS (e.g., 3D vs 2D system)
- The stability of excitons is reinforced when decreasing the dimensionality of the system



T = 300 K

Staircase profile

≡ 2D multiple quantum well system

Absorption in quantum wells

Absorption and excitons in semiconductors

Temperature effect

Bulk GaAs

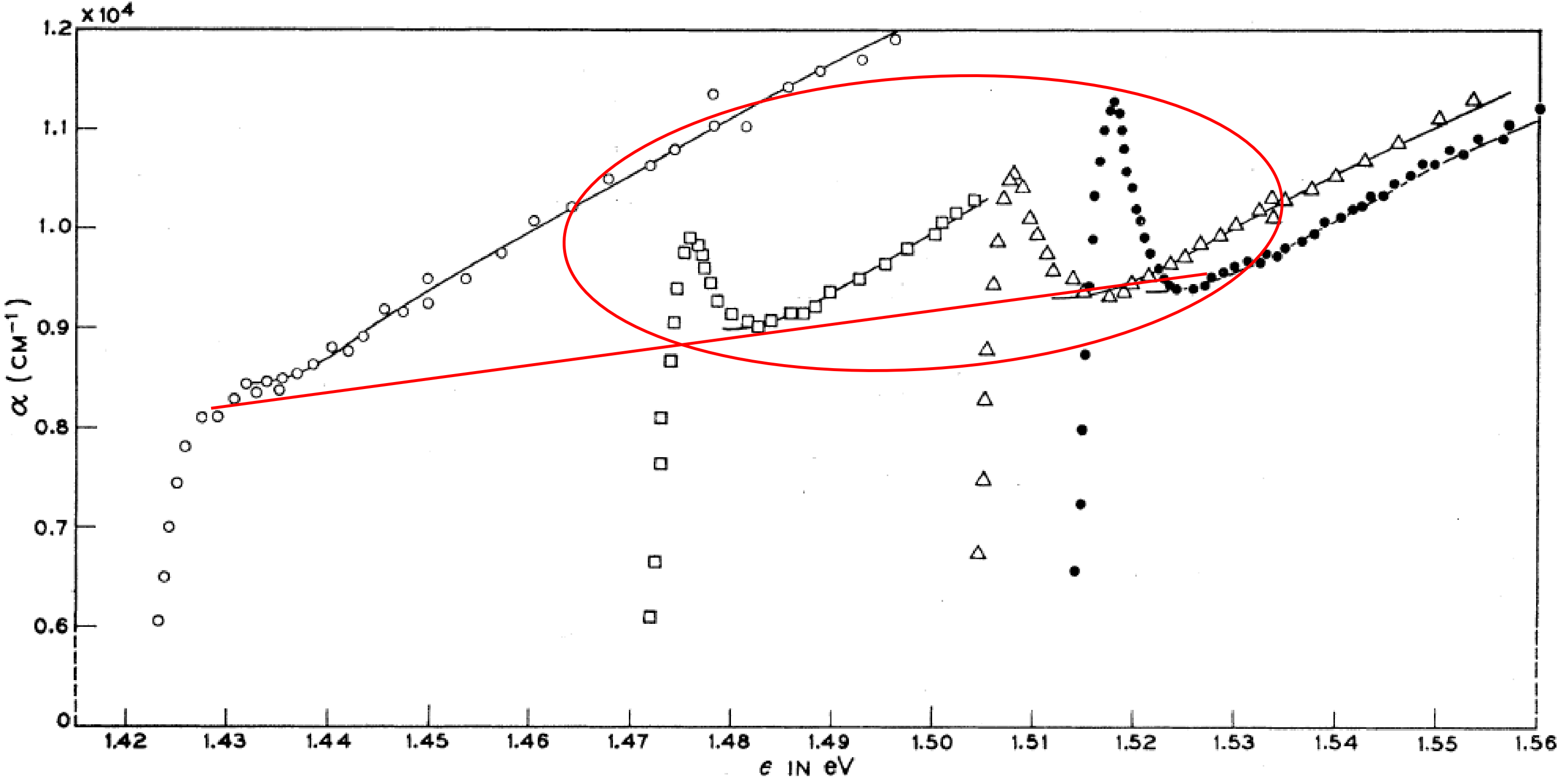


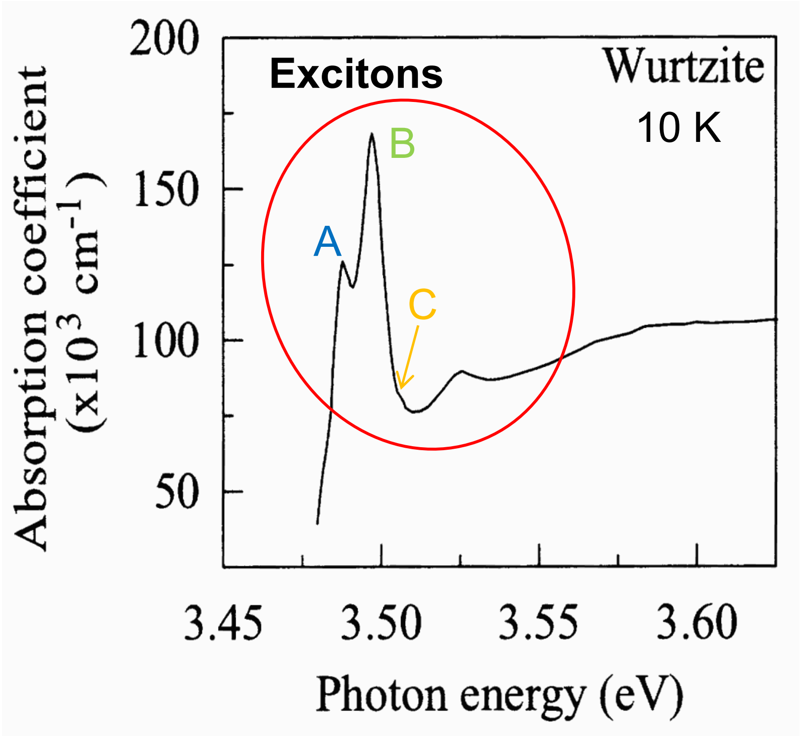
FIG 3 Exciton absorption in GaAs; ○ 294°K, □ 186°K, Δ90°K, ● 21°K.

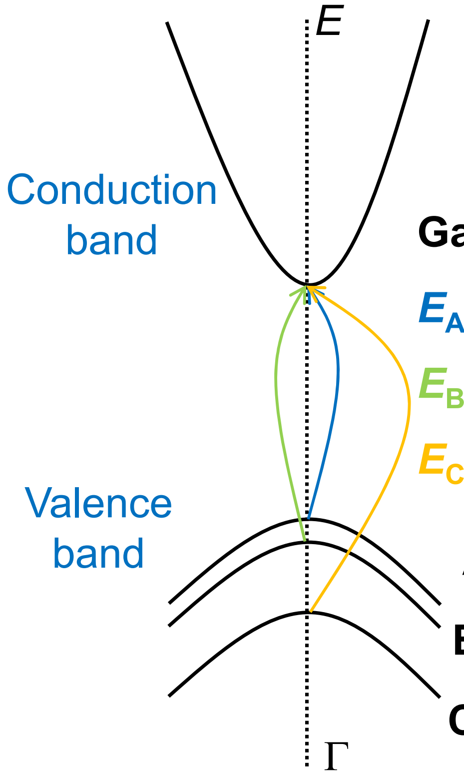
With increasing *T*(K):

- Redshift of the absorption edge due to the anharmonic potential
- Decrease in the magnitude of excitonic absorption features
- Decrease in $\alpha_0(\omega)$

Absorption and excitons in semiconductors

GaN





GaN (10 K):

E_A = 3.478 eV
E_B = 3.485 eV
E_C = 3.503 eV

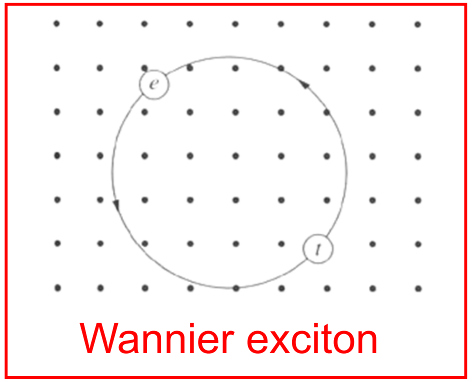
Expected values in relaxed (strain-free) bulk GaN

The magnitude of excitonic features in absorption spectra is a function of their oscillator strength!

The exact transition energy of excitons is related to their binding energy!

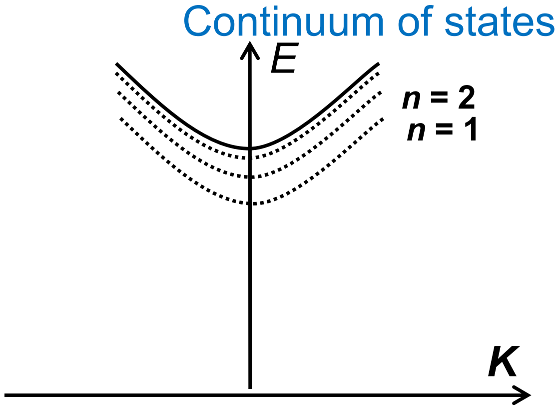
Excitons in semiconductors

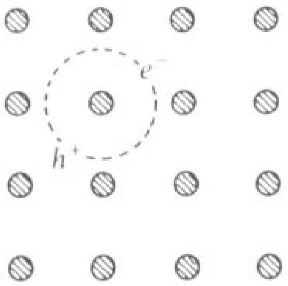
Exciton: electron-hole pair bound via Coulomb interaction



Wannier exciton

⇒ III-V and II-VI semiconductors (but also TMDCs)





Frenkel exciton

⇒ organic semiconductors

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

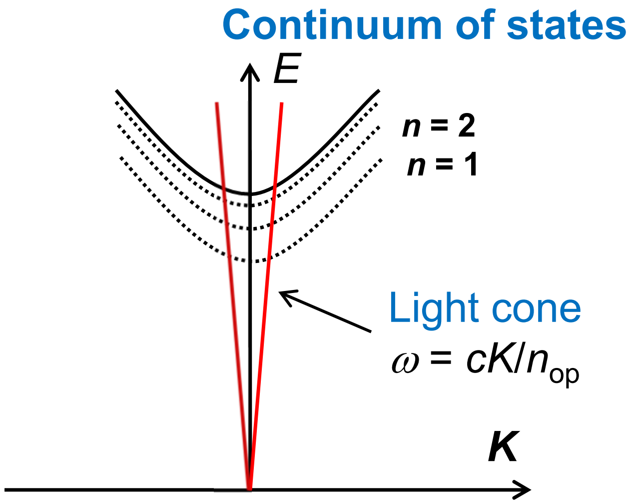
Ry^* = 26 meV for GaN

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 in semiconductors



Continuum of states

Light cone

$\omega = cK/n_{op}$

Optical transitions imply energy and momentum conservation $\Rightarrow$ radiative recombinations of excitons only allowed for excitons of wavevector K such that $E_{exc}(K)$ lies within the light cone!

[1]

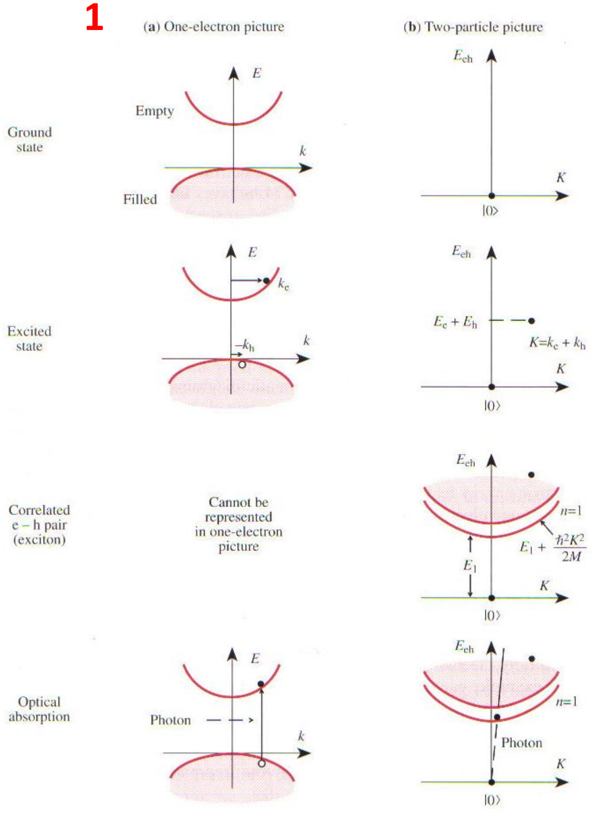


Fig. 6.20. Comparison between the energy levels of the ground state and excited states of a semiconductor in a one-electron band picture (**a**) and in a two-particle picture (**b**). Also, schematic diagrams showing processes in which a photon is absorbed while producing an electron-hole pair

[1] Yu & Cardona, Chapter 6

Some important features of excitons in bulk semiconductors

- Excitons are the fundamental electronic excitation in semiconductors, i.e., they form the lowest intrinsic energy state above the ground state ($\equiv$ no electron-hole pair).

- As a first approximation, their main features can be determined by solving Schrödinger's equation in the context of the hydrogenic model. The exciton center of mass behaves like a free particle of total mass $M = m_e + m_h$.

- The wavevectors $\mathbf{k_e}$ and $\mathbf{k_h}$ are not suitable quantum numbers anymore. One should consider the total wavevector $\mathbf{K}$ (= $\mathbf{k_e} + \mathbf{k_h}$) instead to depict the exciton that is a bosonic quasiparticle, i.e., a particle of integer spin inherited from the half-integer spin of its constituents.

- Excitons will remain stable until they get ionized. Hence, their stability is essentially governed by the magnitude of their binding energy vs. the thermal energy $k_B T$.