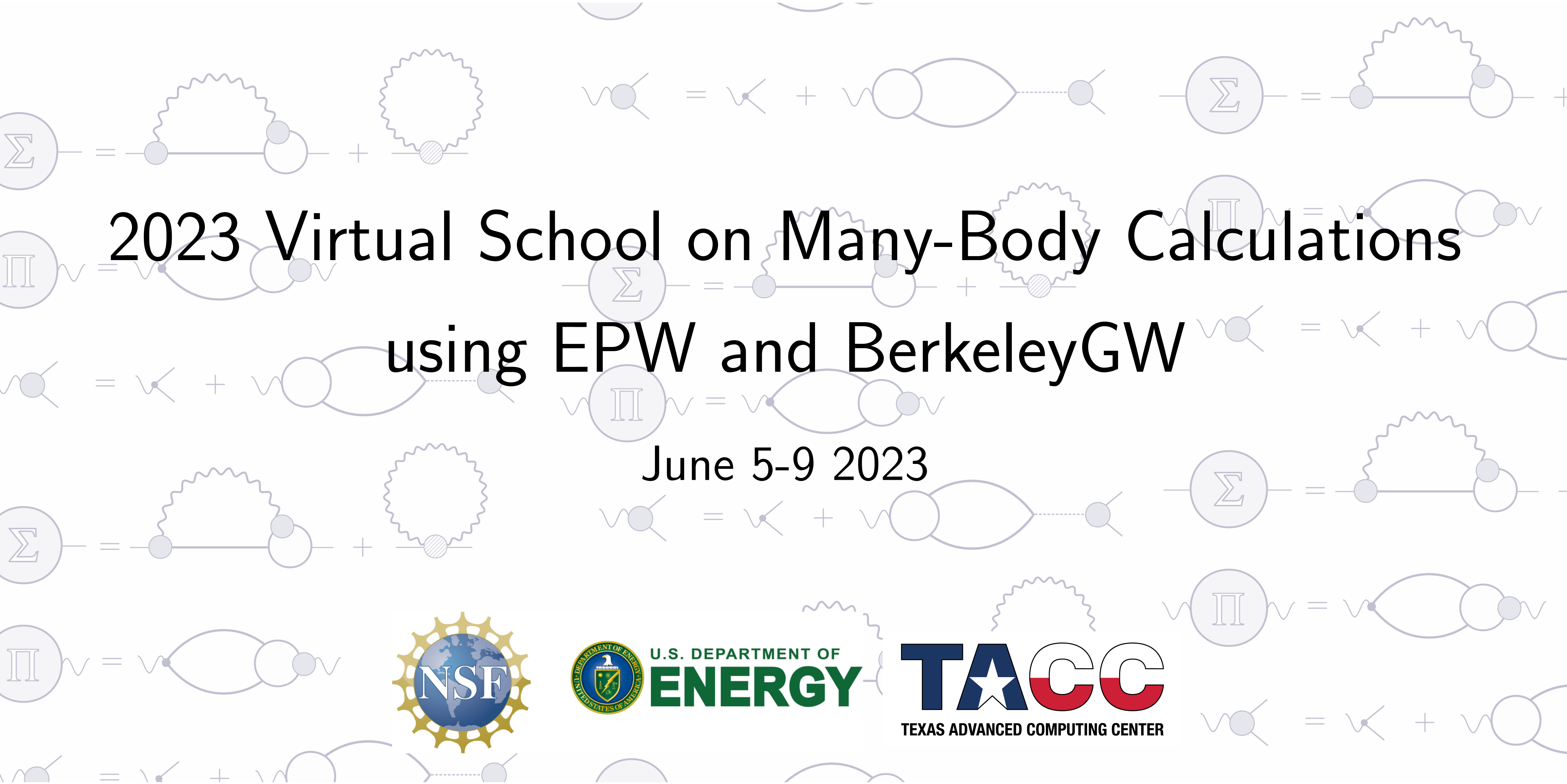

2023 Virtual School on Many-Body Calculations using EPW and BerkeleyGW

June 5-9 2023

NSF

U.S. DEPARTMENT OF
ENERGY

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TEXAS ADVANCED COMPUTING CENTER

Lecture Tue.2

Phonon-assisted optical processes

Emmanouil (Manos) Kioupakis

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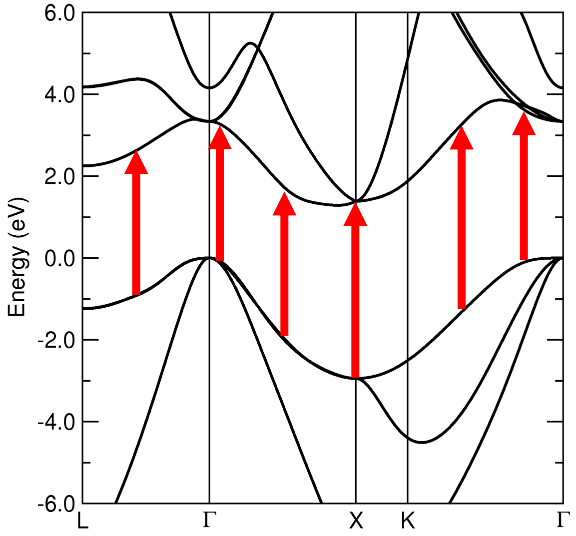
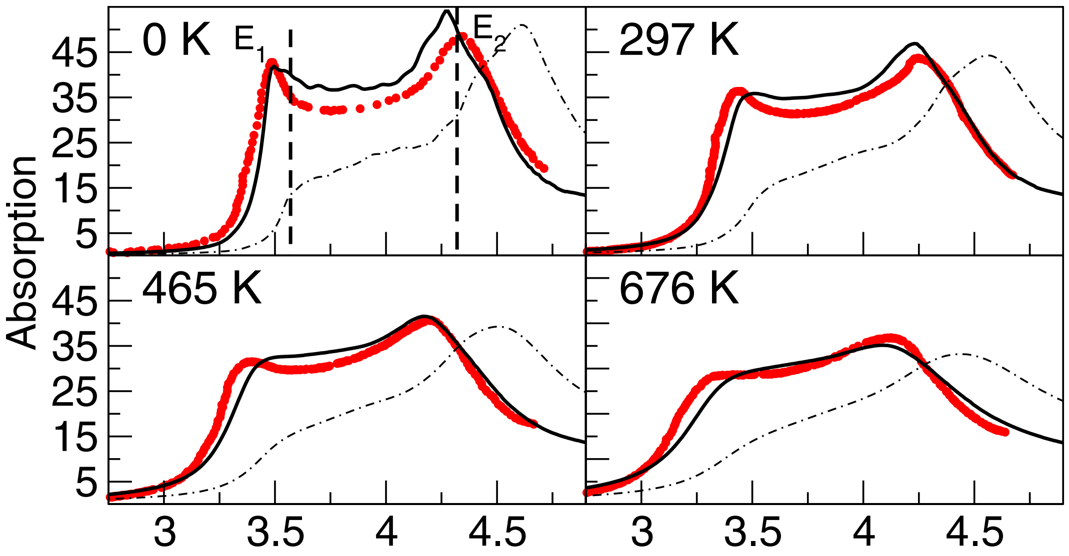
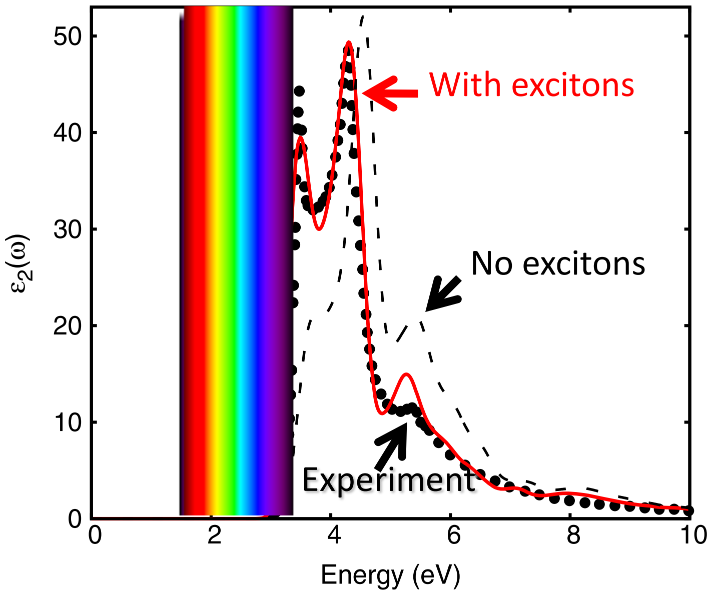
https://kioupakisgroup.engin.umich.edu/

Motivation: optical absorption in Si



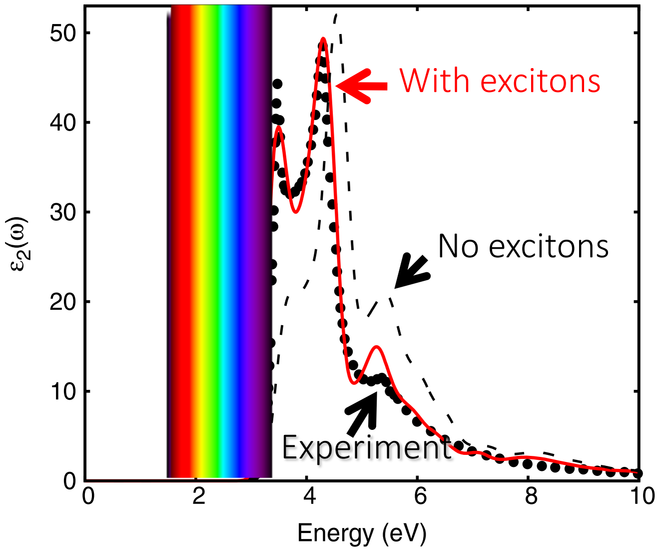




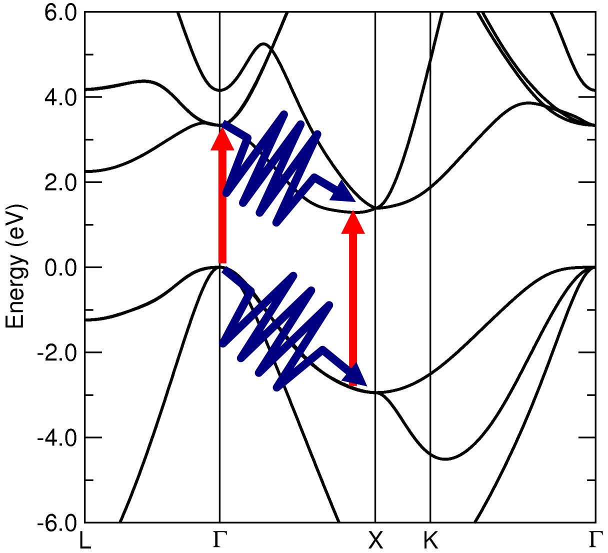
Direct absorption well understood, including excitons and temperature

Albrecht, Reining, Del Sole, Onida, *Phys. Rev. Lett*. **80**, 4510 (1998)
Rohlfing and Louie, *Phys. Rev. B* **62**, 4927(2000)
Marini, *Phys. Rev. Lett*. **101**, 106405 (2008)
Deslippe et al., *Comput. Phys. Commun*. **183**, 1269 (2012)

Motivation: silicon solar cells



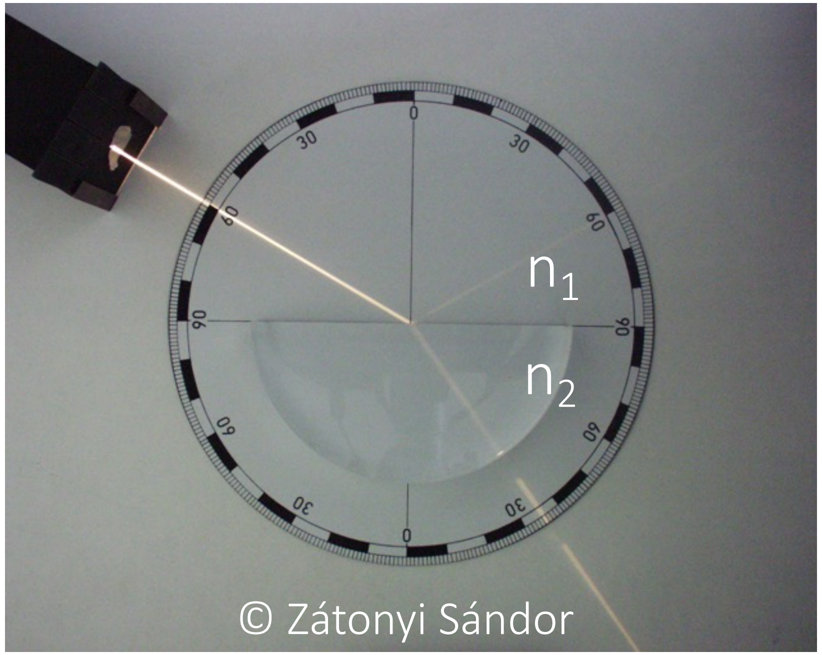
Deslippe et al. *Comput. Phys. Commun.* **183**, 1269 (2012)



Gap of silicon is indirect (1.2 eV), minimum direct gap is 3.4 eV.
Direct optical absorption impossible in the visible.
Absorption in the visible is phonon-assisted, enables silicon solar cells.

Linear optics

Refraction: Snell's law



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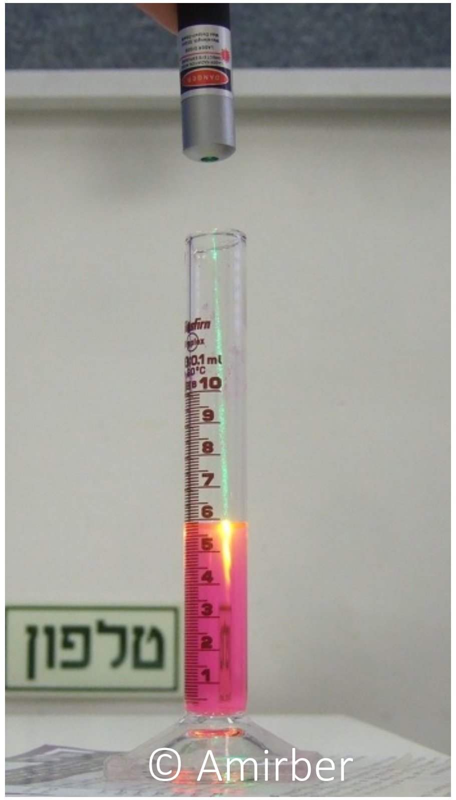
Absorption: Beer-Lambert law



© Amirber

$$I(x) = I_0 e^{-\alpha x}$$

α = absorption coefficient [cm^{-1}]
$1/\alpha$ = penetration depth

Strong absorbers:
$\alpha \sim 10^5 – 10^6\ \text{cm}^{-1}$

Optical parameters of materials

Complex refractive index: $\tilde{n} = n + i\kappa$

Complex dielectric function: $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$

Their connection:

$$n = \frac{1}{\sqrt{2}}\left(\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{\frac{1}{2}}\right)^{\frac{1}{2}}$$

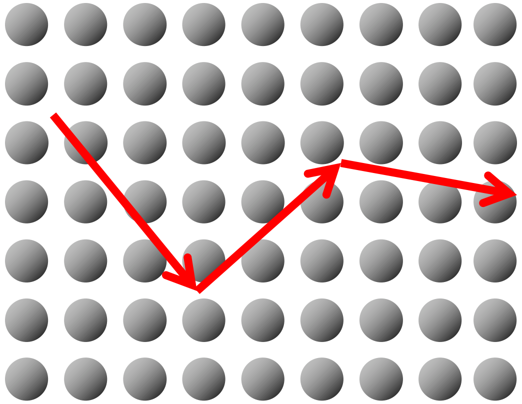
$$\kappa = \frac{1}{\sqrt{2}}\left(-\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{\frac{1}{2}}\right)^{\frac{1}{2}}$$

Absorption coefficient: $\alpha = \frac{2\kappa\omega}{c} = \frac{4\pi\kappa}{\lambda}$

Classical theory of light absorption

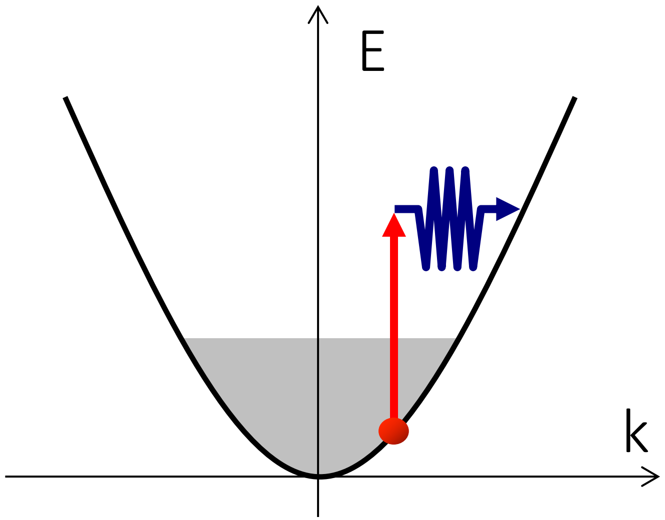
Semiclassical Drude model: $m^*\frac{d\vec{v}}{dt} = -e\vec{E} - \frac{m^*\vec{v}}{\tau}$

e.g., DC conductivity: $\sigma = \frac{ne^2\tau}{m^*}$



AC field: Absorption coefficient in metals

$$\alpha(\omega) = \frac{4\pi ne^2}{m^* n_r c\tau}\frac{1}{\omega^2}$$



But: τ : Phenomenological

Quantum theory of optical absorption

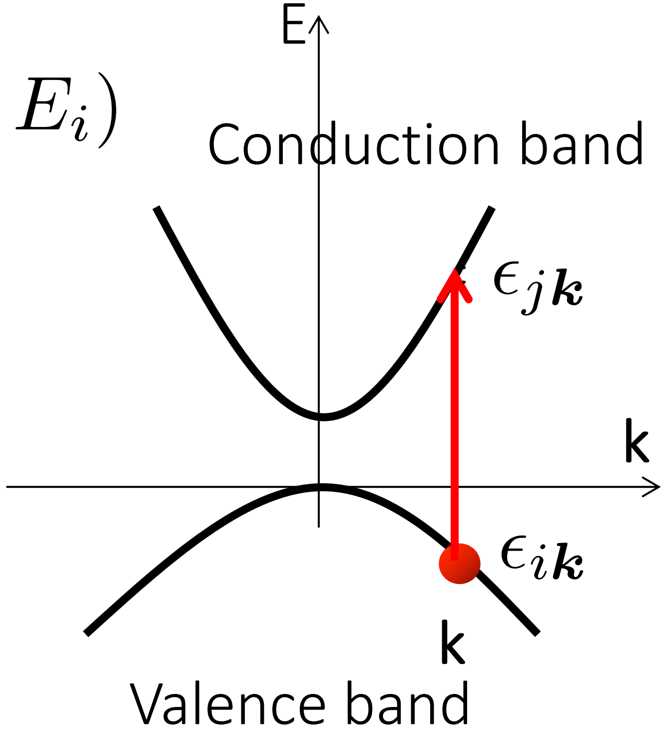
Treat with first-order perturbation theory

Unperturbed state = DFT or GW wave functions and eigenvalues.
Perturbation: electron-photon Hamiltonian
A = vector potential, p = momentum, v = velocity.

$$H_{\text{el-phot}} = \frac{e}{m_e c}\vec{A}\cdot\vec{p} = \frac{e}{c}\vec{A}\cdot\vec{v}$$

Recombination probability per unit time:

$$P_{i\to f} = \frac{2\pi}{\hbar}\left|\langle f|H_{\text{el-phot}}|i\rangle\right|^2 \delta(E_f - E_i)$$



Initial and final states: $E_i = \epsilon_{i\boldsymbol{k}} + \hbar\omega, E_f = \epsilon_{j\boldsymbol{k}}$

Absorbed power: $\hbar\omega \sum_{i,f}(f_i - f_f)P_{i\to f}$

Incident power: $\dfrac{n_r^2 A^2 \omega^2}{2\pi c^2}$

Quantum theory of optical absorption

Absorption coefficient = energy absorbed per unit volume divided by energy flux

v = velocity matrix elements

λ = light polarization vector

$$\alpha(\omega) = \frac{\hbar\omega \sum_{i,j}(f_i - f_j)P_{i\to j}}{\frac{n_r^2 A^2 \omega^2}{2\pi c^2}\frac{c}{n_r}}$$

$$= 2\frac{4\pi^2 e^2}{n_r c\omega}\frac{1}{N_{\boldsymbol{k}}}\sum_{i,j,\boldsymbol{k}}(f_{i,\boldsymbol{k}} - f_{j,\boldsymbol{k}})\left|\boldsymbol{\lambda}\cdot\boldsymbol{v}_{ij}(\boldsymbol{k})\right|^2 \delta(\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega)$$

Dielectric function, imaginary part:

$$\varepsilon_2(\omega) = \frac{\alpha n_r c}{\omega} = 2\frac{4\pi^2 e^2}{\omega^2}\frac{1}{N_{\boldsymbol{k}}}\sum_{i,j,\boldsymbol{k}}(f_{i,\boldsymbol{k}} - f_{j,\boldsymbol{k}})\left|\boldsymbol{\lambda}\cdot\boldsymbol{v}_{ij}(\boldsymbol{k})\right|^2 \delta(\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega)$$

Real part: from Kramers-Kronig relation:

$$\varepsilon_1(\omega) = 1 + 16\pi^2 e^2\frac{1}{N_{\boldsymbol{k}}}\sum_{i,j,\boldsymbol{k}}(f_{i,\boldsymbol{k}} - f_{j,\boldsymbol{k}})\frac{\left|\boldsymbol{\lambda}\cdot\boldsymbol{v}_{ij}(\boldsymbol{k})\right|^2}{\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}}}\frac{1}{(\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}})^2/\hbar^2 - \omega^2}$$

Phonon-assisted optical absorption

Treat with second-order perturbation theory.
Perturbation: electron-photon + electron-phonon Hamiltonian

$$P_{i\to f} = \frac{2\pi}{\hbar}\left|\sum_m \frac{\langle f|H|m\rangle\langle m|H|i\rangle}{E_m - E_i}\right|^2 \delta(E_f - E_i)$$

Keeping cross terms only (the other two terms correspond to two-photon and two-phonon absorption/emission:

$$P_{i\to f} = \frac{2\pi}{\hbar}\left|\sum_m \frac{\langle f|H_{\text{el-phot}}|m\rangle\langle m|H_{\text{el-phon}}|i\rangle}{E_m - E_i} + \right.$$

$$\left.\sum_{m'} \frac{\langle f|H_{\text{el-phon}}|m'\rangle\langle m'|H_{\text{el-phot}}|i\rangle}{E_{m'} - E_i}\right|^2 \delta(E_f - E_i)$$

Phonon-assisted optical absorption

Imaginary part of dielectric function:

$$\mathrm{Im}[\epsilon(\omega)] = 2\frac{\pi e^2}{\epsilon_0 \Omega}\frac{1}{\omega^2}\sum_{mn\nu,\beta=\pm1}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}}\int\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}\left|\mathbf{e}\cdot[\mathbf{S}_{1,mn\nu}(\mathbf{k},\mathbf{q})+\mathbf{S}_{2,mn\nu\beta}(\mathbf{k},\mathbf{q})]\right|^2$$
$$\times P_{mn\nu\beta}(\mathbf{k},\mathbf{q})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega+\beta\hbar\omega_{\mathbf{q}\nu}),$$

v = velocity matrix elements
g = electron-phonon coupling
λ = light polarization

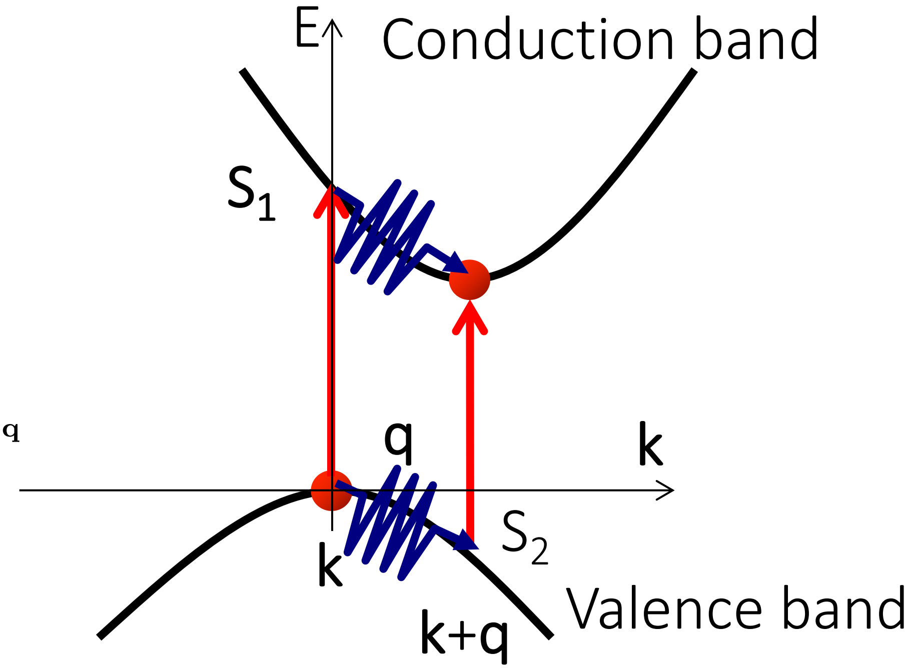
Two paths:

$$\mathbf{S}_{1,mn\nu}(\mathbf{k},\mathbf{q}) = \sum_j \frac{g_{mj\nu}(\mathbf{k},\mathbf{q})\mathbf{v}_{jn}(\mathbf{k})}{\varepsilon_{j\mathbf{k}}-\varepsilon_{n\mathbf{k}}-\hbar\omega+i\eta},$$
$$\mathbf{S}_{2,mn\nu\beta}(\mathbf{k},\mathbf{q}) = \sum_j \frac{\mathbf{v}_{mj}(\mathbf{k}+\mathbf{q})g_{jn\nu}(\mathbf{k},\mathbf{q})}{\varepsilon_{j\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\beta\hbar\omega_{\mathbf{q}\nu}+i\eta},$$

Occupations:

$$P_{mn\nu\beta}(\mathbf{k},\mathbf{q}) = \left(n_{\mathbf{q}\nu}+\frac{1+\beta}{2}\right)f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})-\left(n_{\mathbf{q}\nu}+\frac{1-\beta}{2}\right)(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}$$

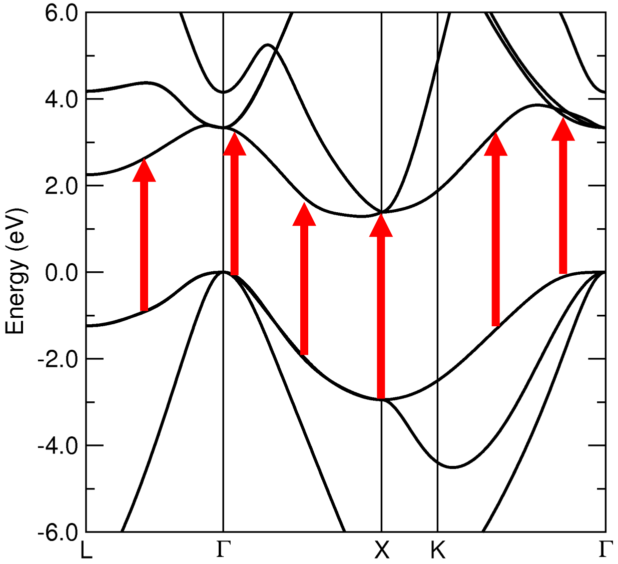
β = +1 (phonon emission) or –1 (phonon absorption)

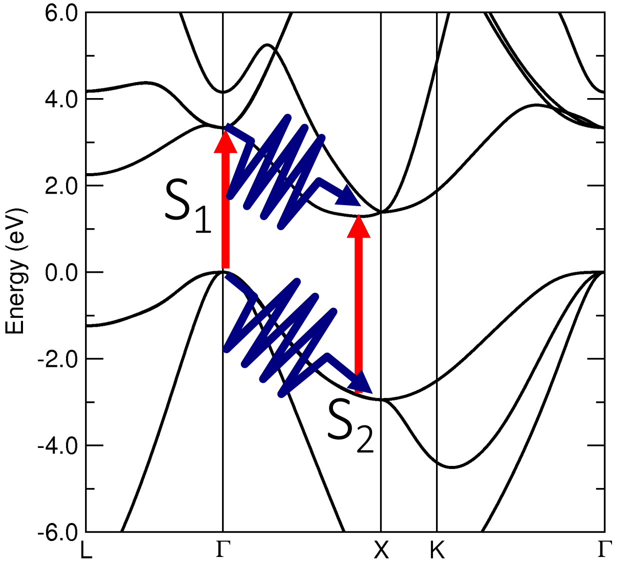


Absorption coefficient: $\alpha(\omega) = \dfrac{\omega\,\mathrm{Im}[\epsilon(\omega)]}{c\,n(\omega)}$

Computational challenge with phonon-assisted absorption

Direct absorption: **single sum** vs. *Phonon-assisted absorption*: **double sum**





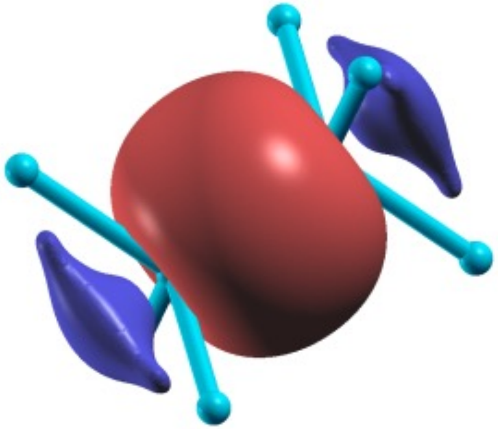
$$\alpha(\omega) \propto \sum_{\boxed{i,j},\nu} P|\boldsymbol{S}_1 + \boldsymbol{S}_2|^2 \delta(\epsilon_j - \epsilon_i - \hbar\omega \pm \hbar\omega_\nu)$$

Double sum over all initial and final states is **expensive**:

For energy resolution of 0.03 eV → need 24 × 24 × 24 k-grid and q-grid, ~200M combinations of initial and final wave vectors

Solution: Wannier interpolation

Max. localized Wannier functions
From Bloch to Wannier basis

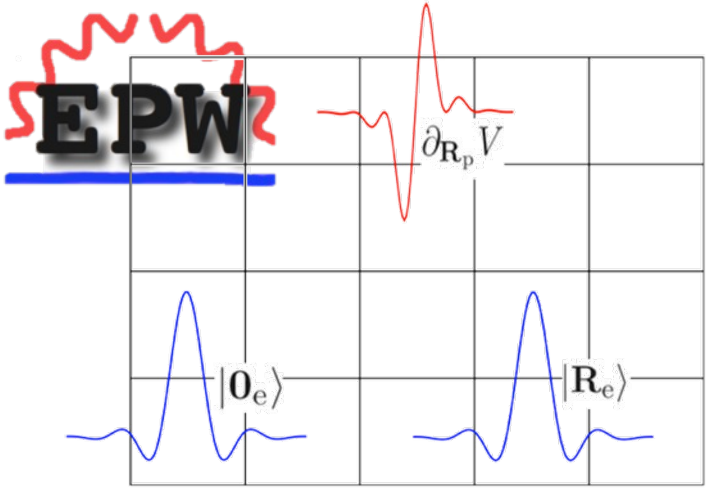


Interpolate quasiparticle energies, optical matrix elements.

Mostofi, Yates, Pizzi, Lee, Souza, Vanderbilt, Marzari, Comput. Phys. Commun. 185, 2309 (2014).
http://www.wannier.org/

Fourier

$$\langle \boldsymbol{k}|\partial_{\boldsymbol{q}}V|\boldsymbol{k}+\boldsymbol{q}\rangle \to \langle \mathbf{0}_e|\partial_{\boldsymbol{R}_p}|\boldsymbol{R}_e\rangle$$



Interpolate electron-phonon and optical (velocity) matrix elements

H. Lee et al, arXiv:2302.08085 (2023)
http://epw-code.org

Measuring direct and indirect band gaps

How does experiment determine whether a measured gap in optical absorption is direct or indirect? Answer: Tauc plot

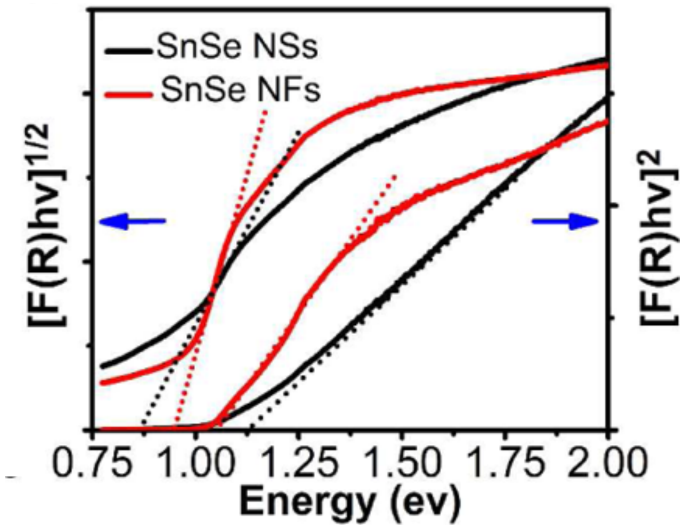
For direct absorption:

$$\alpha \propto \frac{(\hbar\omega - E_g^d)^{1/2}}{\omega} \Rightarrow (\alpha\omega)^2 \propto \hbar\omega - E_g^d$$

For indirect absorption:

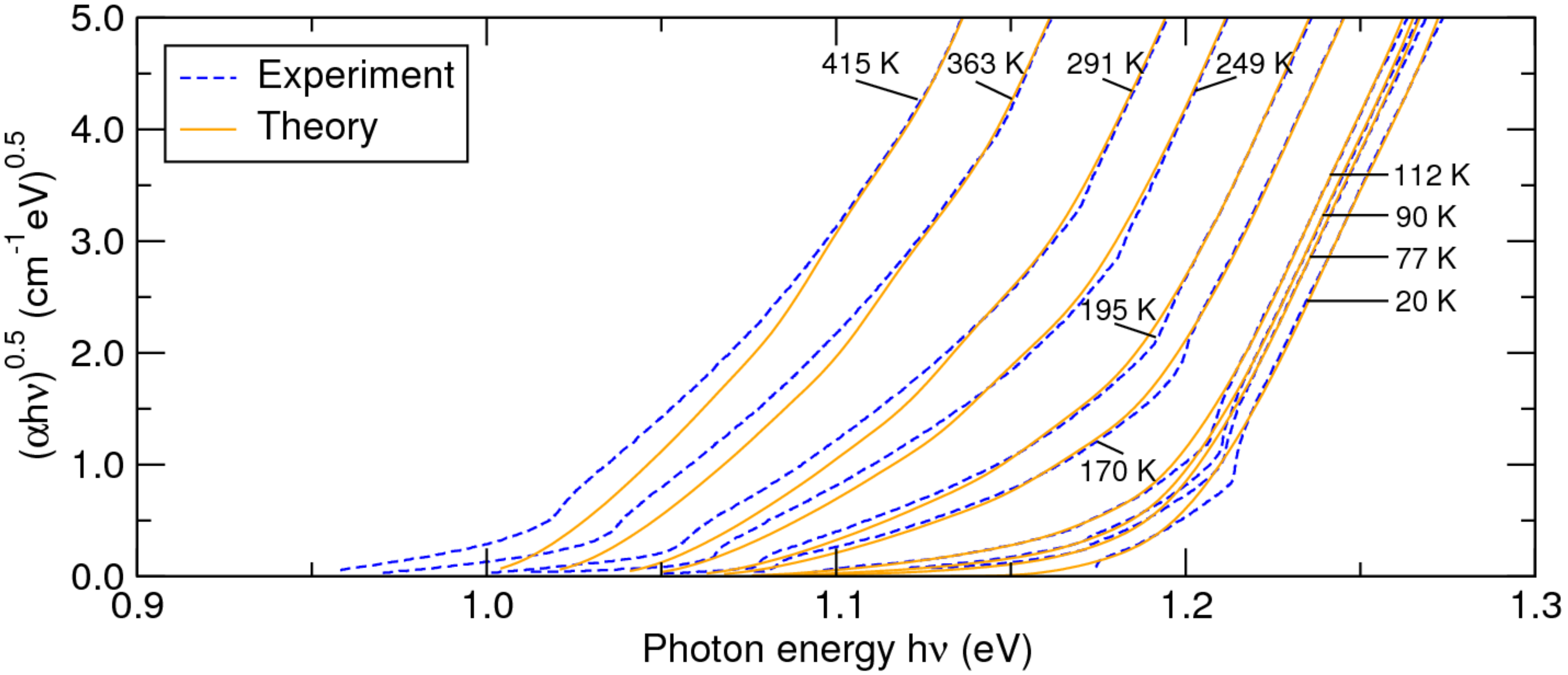
$$\alpha \propto \frac{(\hbar\omega - E_g^i \pm \hbar\omega_{\text{phonon}})^2}{\omega} \Rightarrow (\alpha\omega)^{1/2} \propto \hbar\omega - E_g^i \pm \hbar\omega_{\text{phonon}}$$

Exponent determines type and value of gap.
Two indirect terms for emission/absorption.



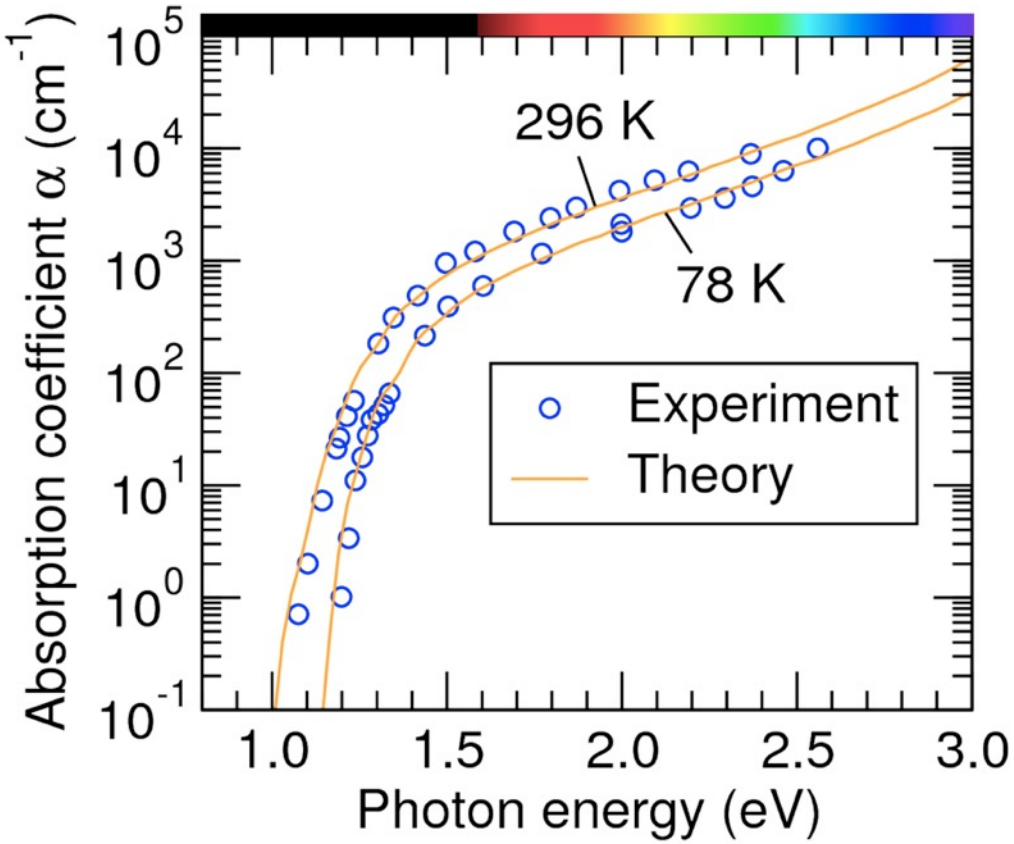
J. Am. Chem. Soc. 2013, 135, 1213

Indirect absorption edge for silicon



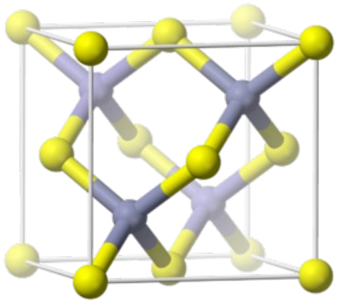
Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)
* Shifted the energy of onset by 0.15-0.23 eV to match experiment

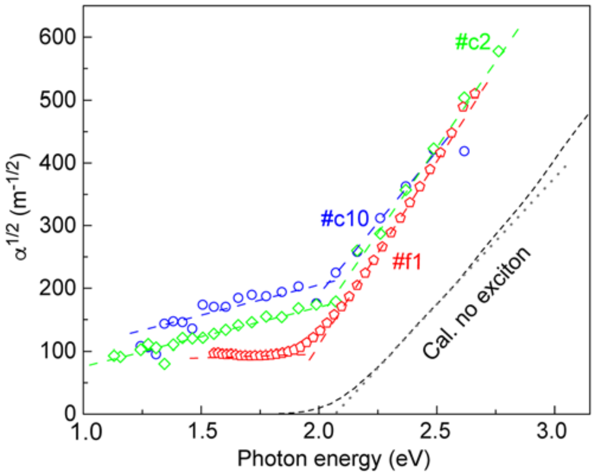
Si absorption in the visible

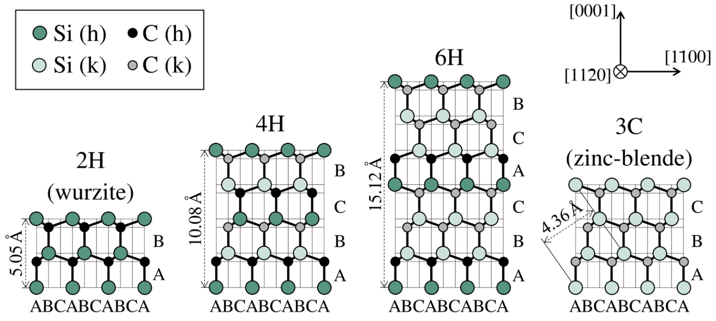


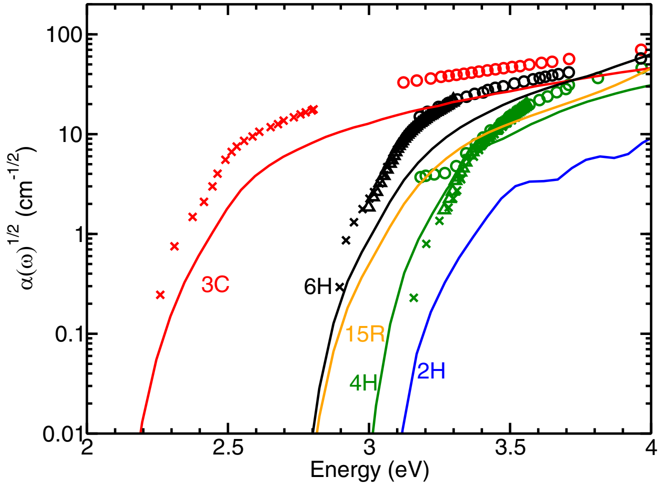
Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)
* Shifted the energy of onset to match experiment

Other materials





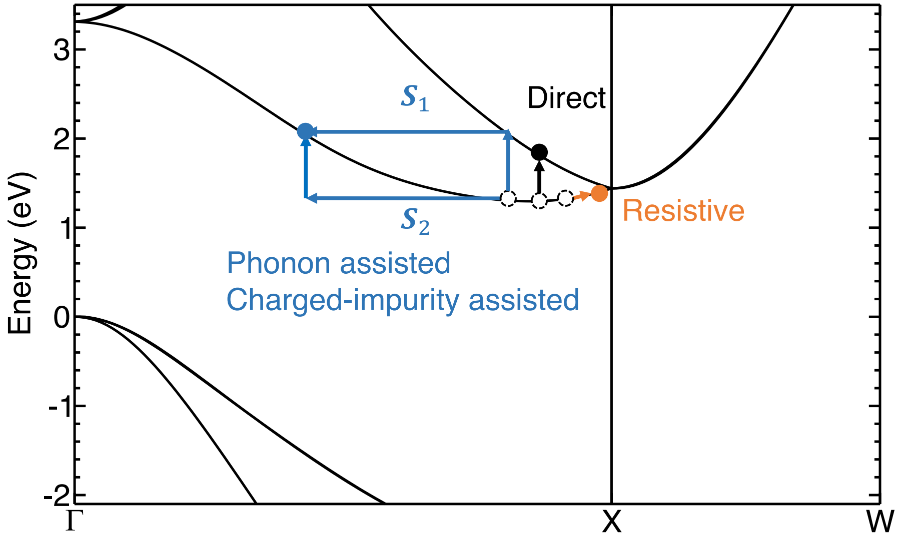


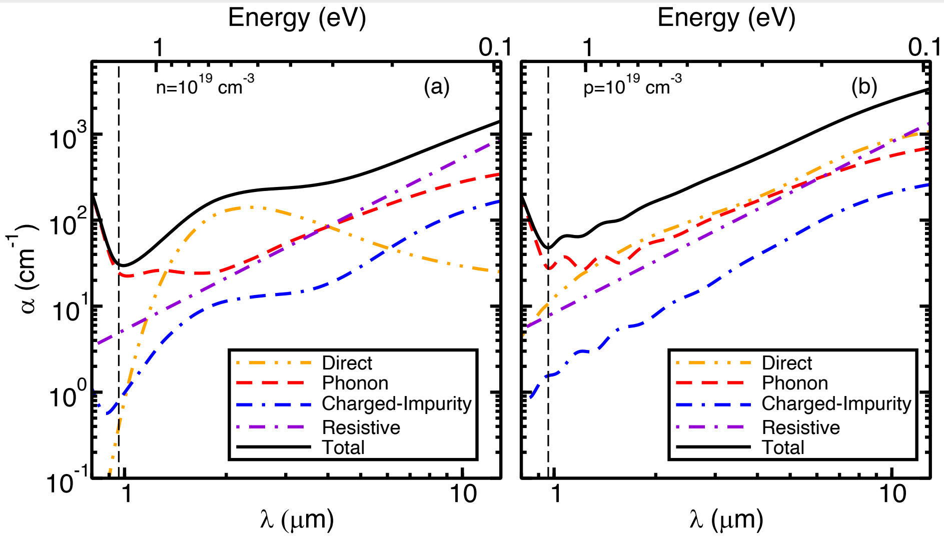


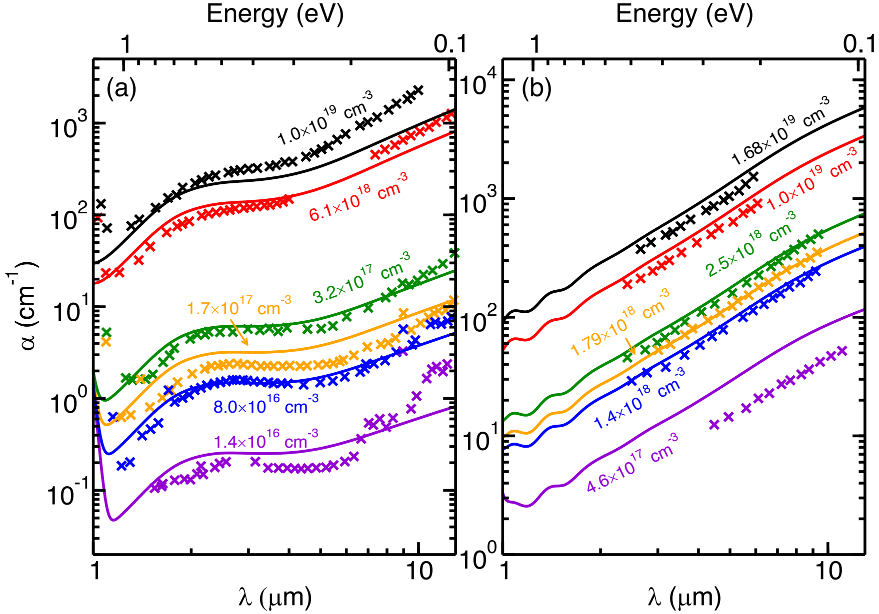
- BAs: a new compound semiconductor with ultrahigh thermal conductivity [1]. Our GW calculations predict an indirect band gap of 2.05 eV [2]. Calculated phonon-assisted absorption spectra agree with experiment [3].
- SiC polytypes with indirect gaps: the calculated spectra also agree with experiment [4]

1. F. Tian, et al., *Science* **361**, 582 (2018).
2. **Kyle Bushick**, K. Mengle, N. Sanders, and E. Kioupakis, *Applied Physics Letters* **114**, 022101 (2019)
3. B. Song, K. Chen, **Kyle Bushick**, K. A. Mengle, F. Tian, G. A. G. U. Gamage, Z. Ren, E. Kioupakis, and G. Chen, *Applied Physics Letters* **116**, 141903 (2020).
4. **Xiao Zhang** and Emmanouil Kioupakis, Phys. Rev. B 107, 115207 (2023)

Free-carrier absorption in doped silicon





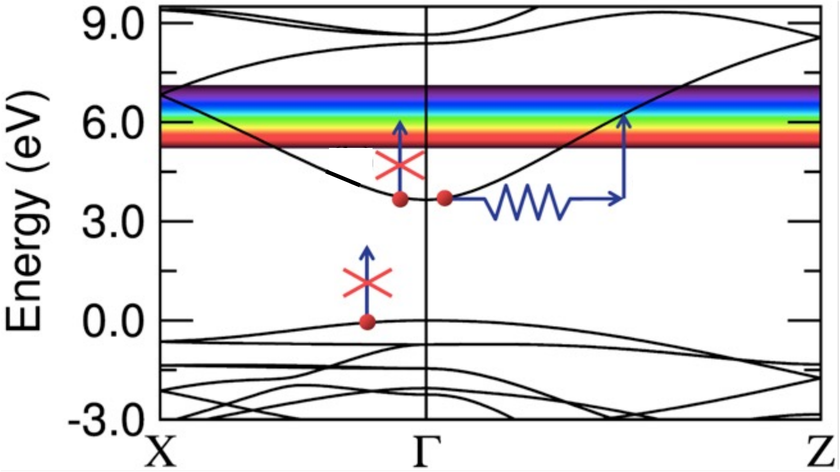


- Absorption of light in doped silicon competes with interband absorption.
- Also: absorption for photon energy below gap
- Direct + indirect absorption possible.
- Results for α vs. doping in agreement with experiment.

Xiao Zhang, G. Shi, J. A. Leveillee, F. Giustino, and E. Kioupakis, Ab-initio theory of free-carrier absorption in semiconductors, *Phys. Rev. B* **106**, 205203

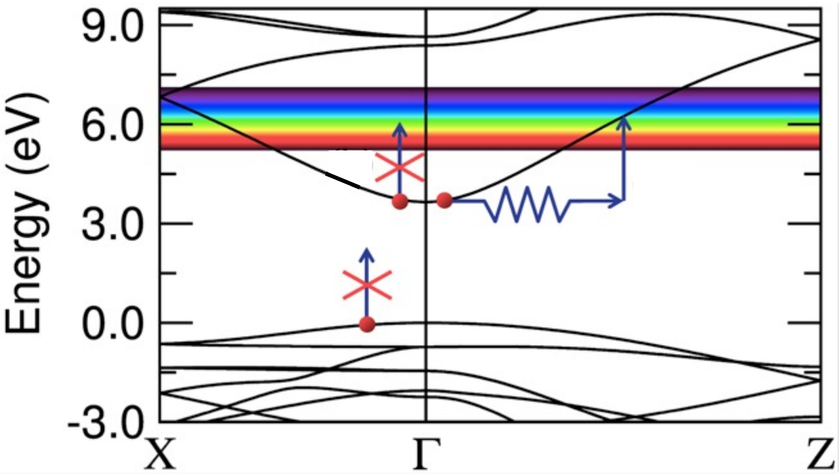
Absorption in transparent conducting oxides

Conducting oxides (e.g., SnO_2) used for transparent electrical contacts



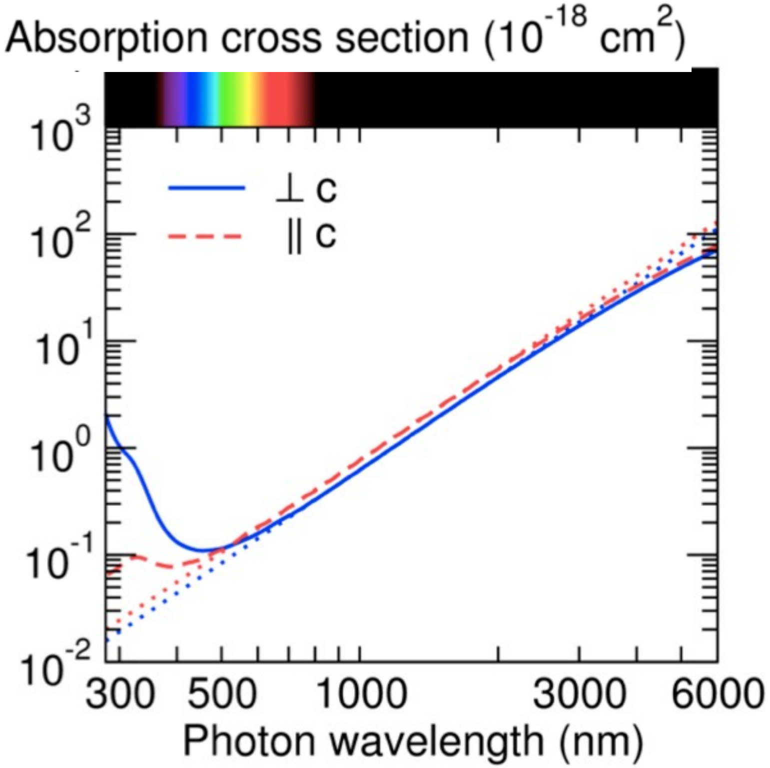
Fundamental transparency limit due to free-carrier absorption

Free-carrier absorption in n-type SnO_2 and In_2O_3



$$\alpha = \sigma n$$

σ = absorption cross section



Fundamental limits on optical transparency of transparent conducting oxides: free-carrier absorption in SnO_2 and In_2O_3

H. Peelaers, E. Kioupakis, and C. G. Van de Walle

- *Appl. Phys. Lett*. **100**, 011914 (2012); https://doi.org/10.1063/1.3671162
- *Phys. Rev. B* **92**, 235201 (2015); https://doi.org/10.1103/PhysRevB.92.235201
- *Appl. Phys. Lett*. **115**, 082105 (2019); https://doi.org/10.1063/1.5109569

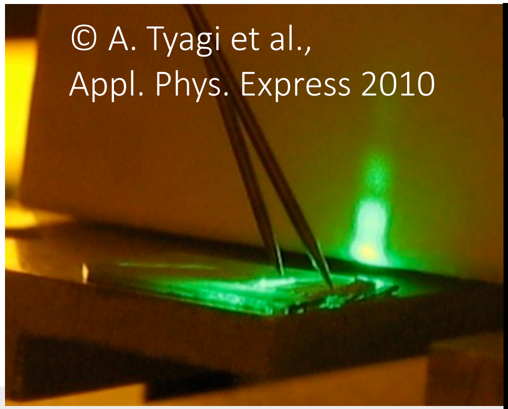
Laser diodes

Blu-ray laser diodes (405 nm , violet) based on GaN

Applications:

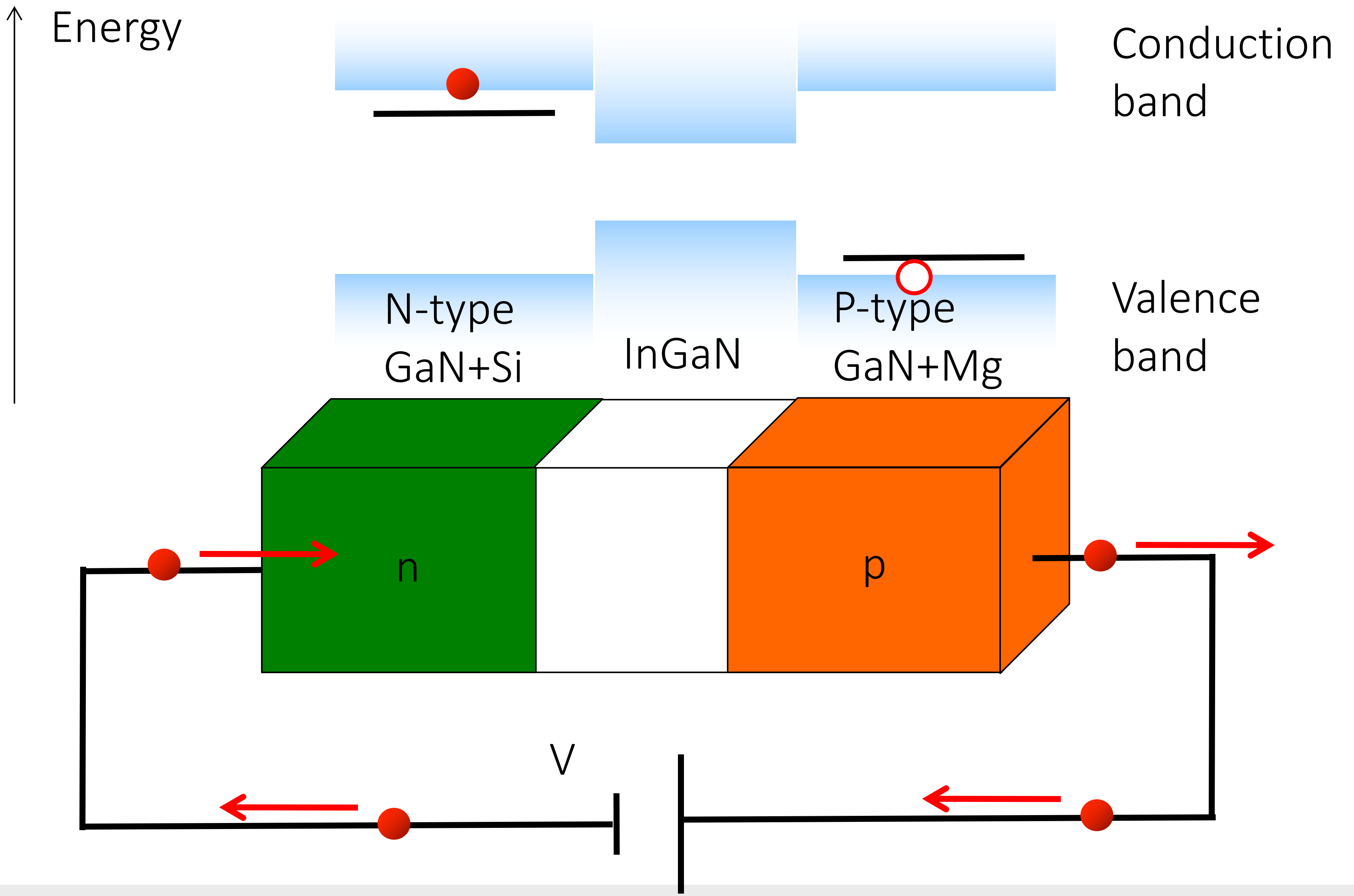
- Optical storage
- Laser projectors

Aim: high-power nitride green lasers.



© A. Tyagi et al., Appl. Phys. Express 2010

How nitride LEDs/lasers work



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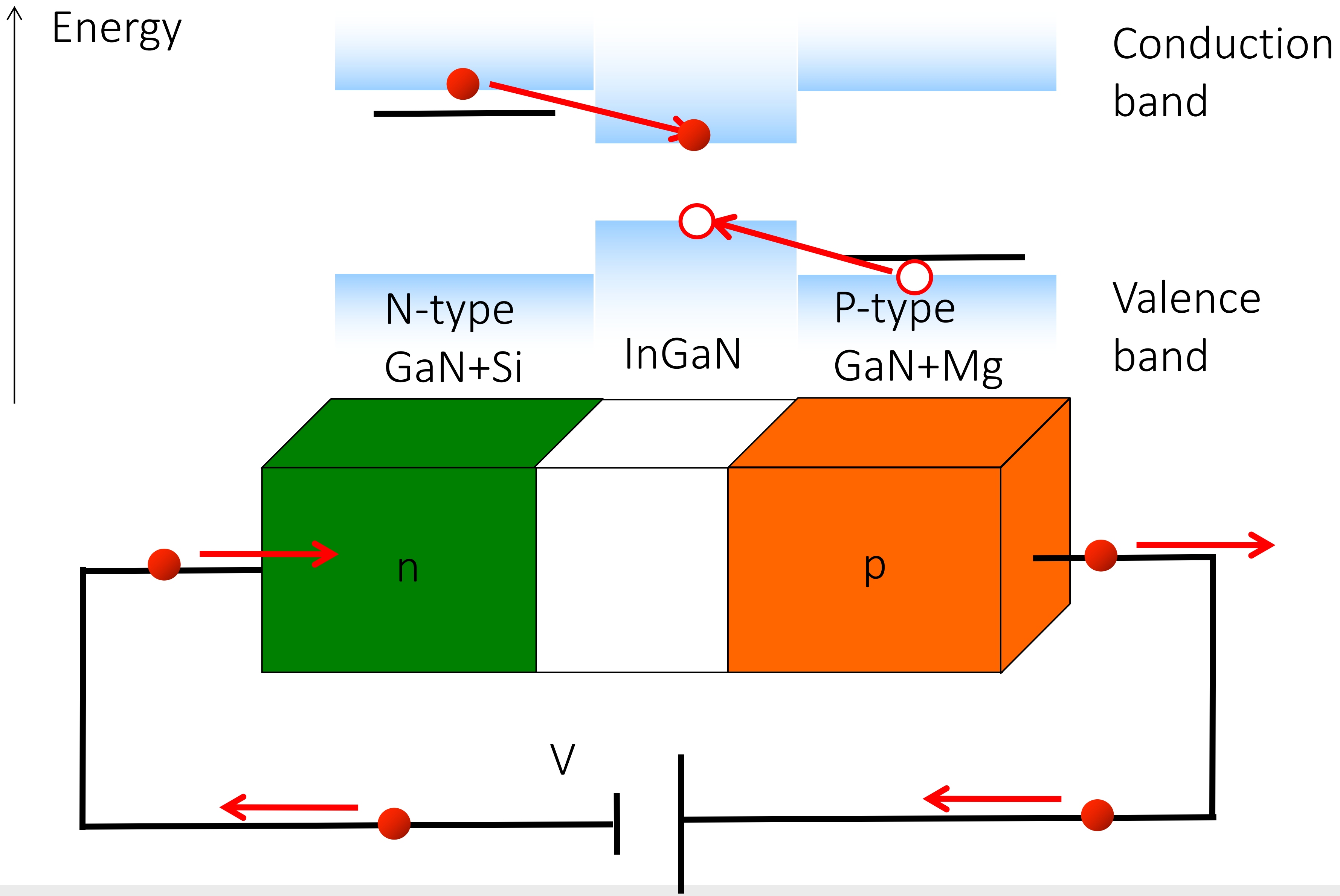
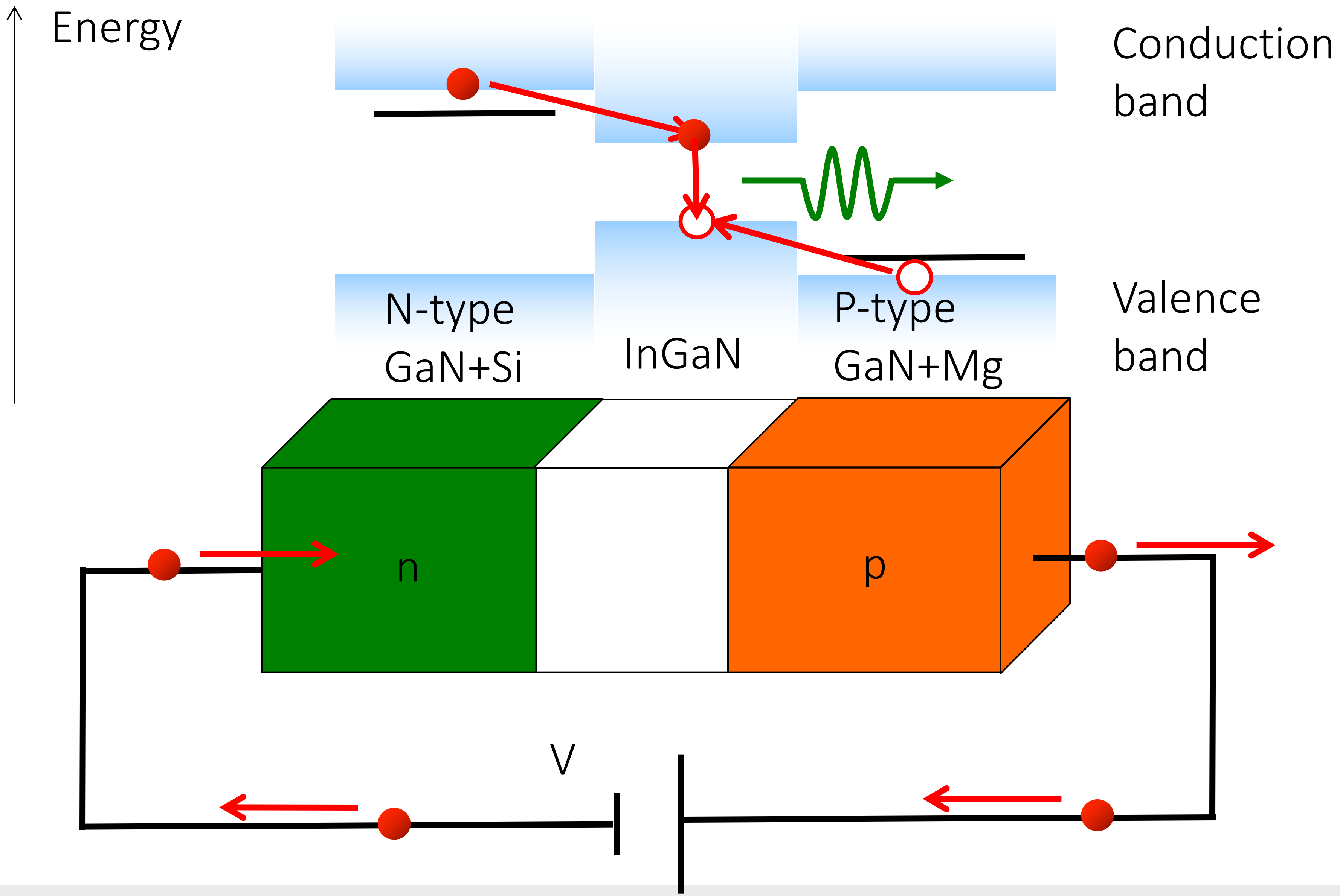
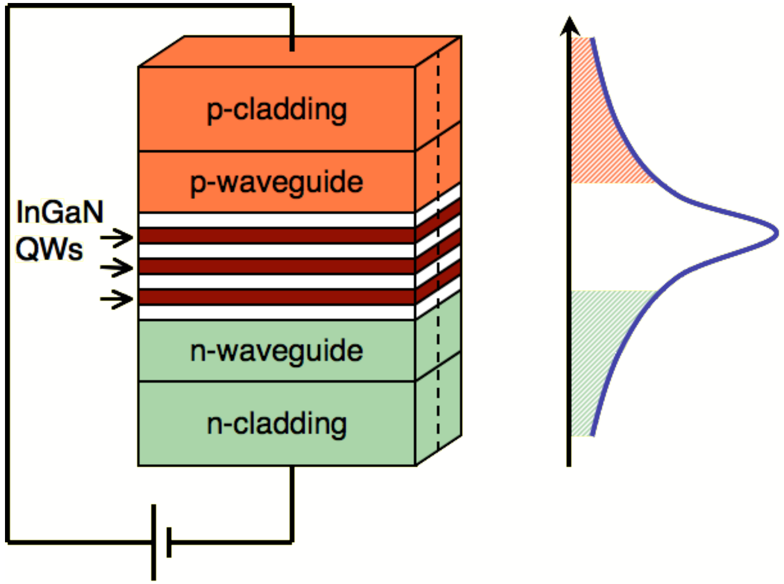


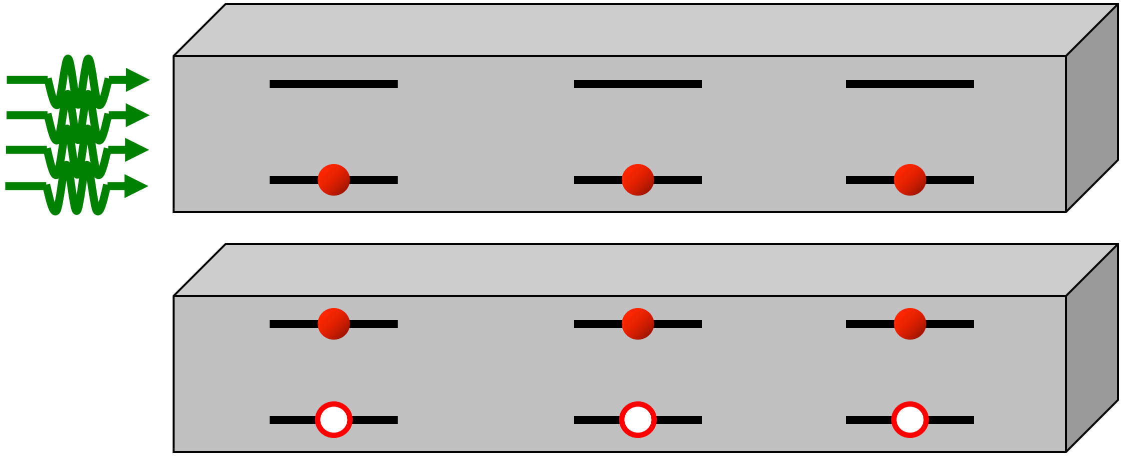
How nitride LEDs/lasers work



Absorption and gain



Optical mode profile
(photon density)



Absorption:

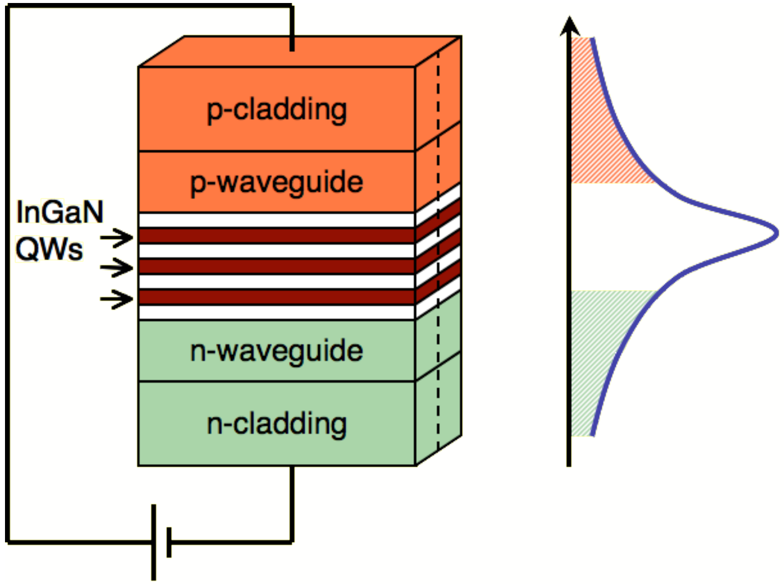
$$I(x) = I_0 e^{-\alpha x}$$

Gain in the QWs:

$$I(x) = I_0 e^{+gx}$$

Output = Gain – Absorption

Absorption and gain



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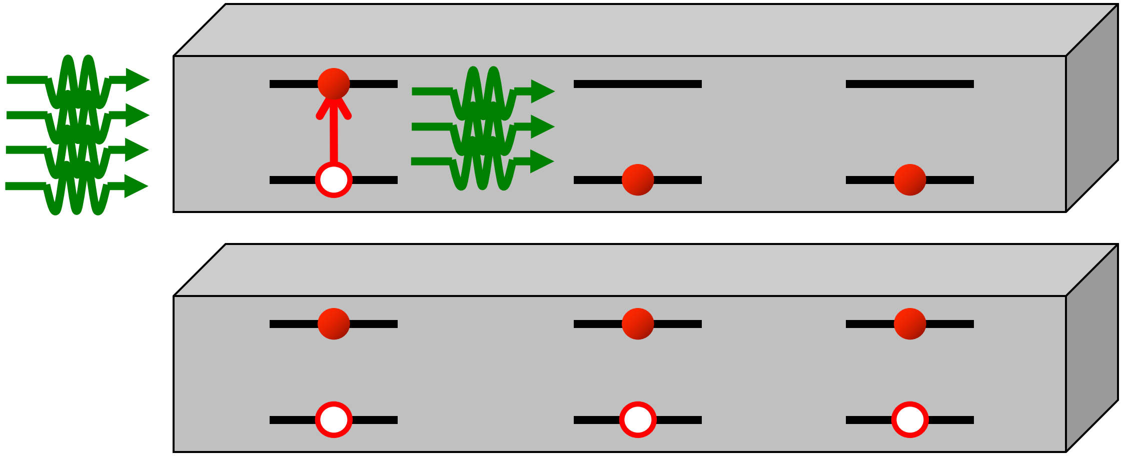

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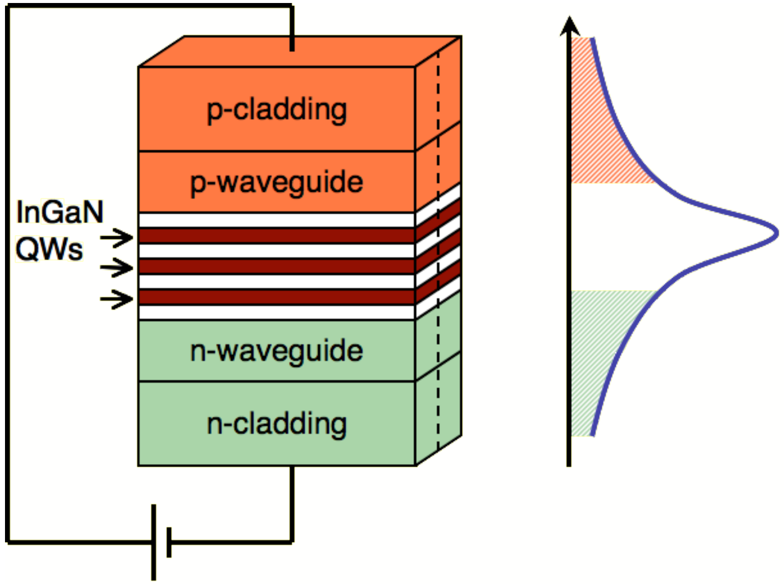

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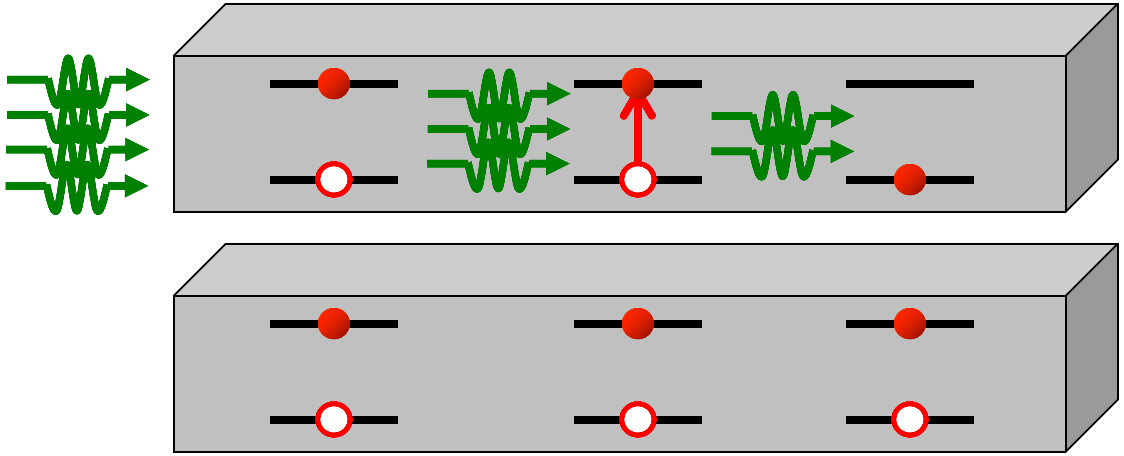

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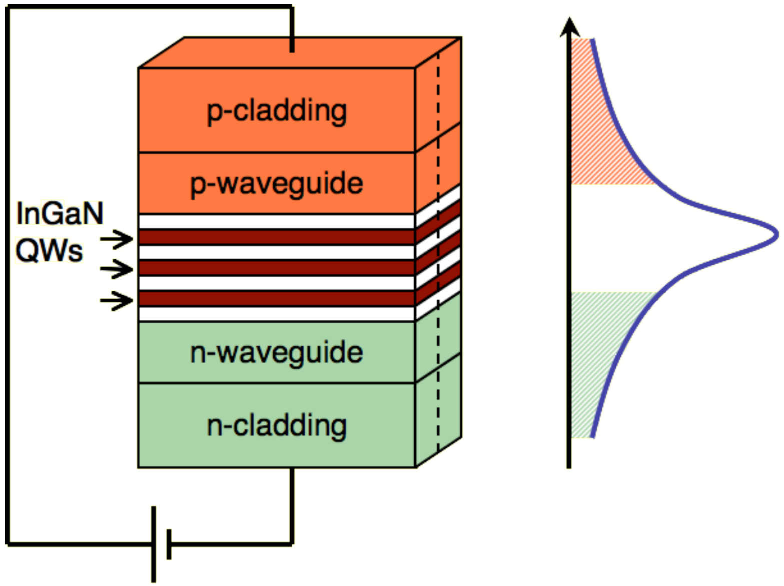
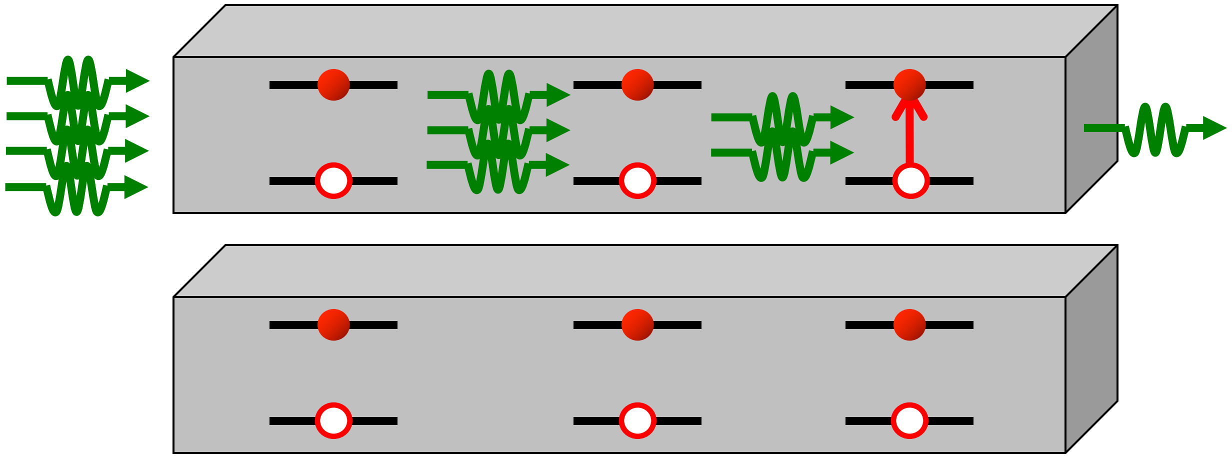


Optical mode profile (photon density)



Absorption:

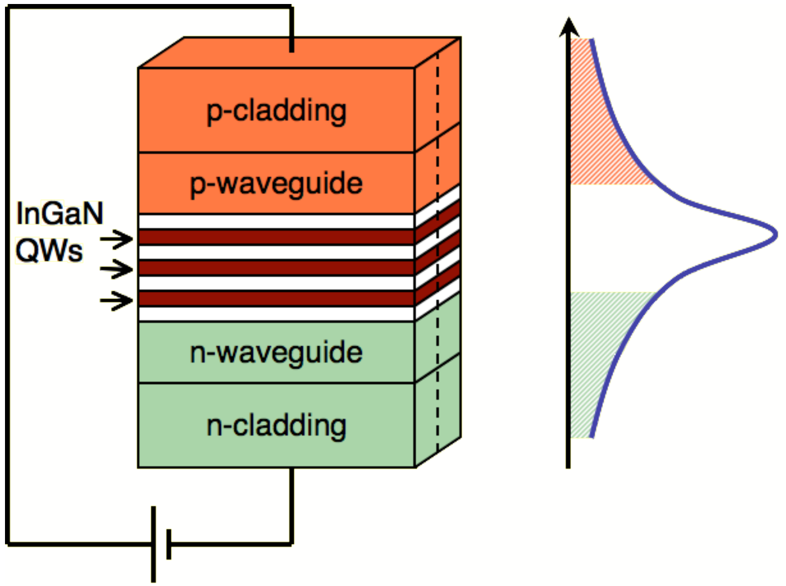
$$I(x) = I_0 e^{-\alpha x}$$

Gain in the QWs:

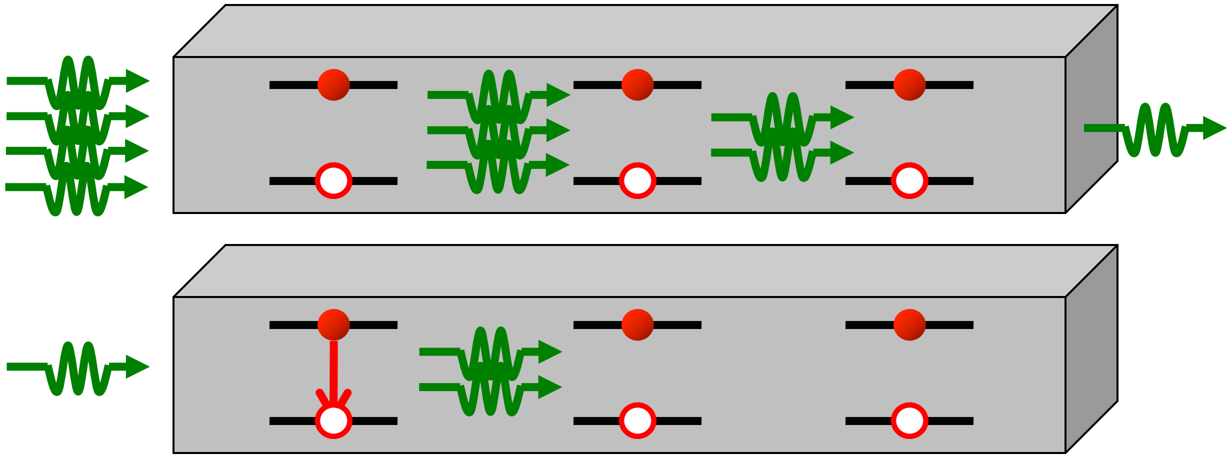
$$I(x) = I_0 e^{+gx}$$

Output = Gain – Absorption

Absorption and gain



Optical mode profile
(photon density)



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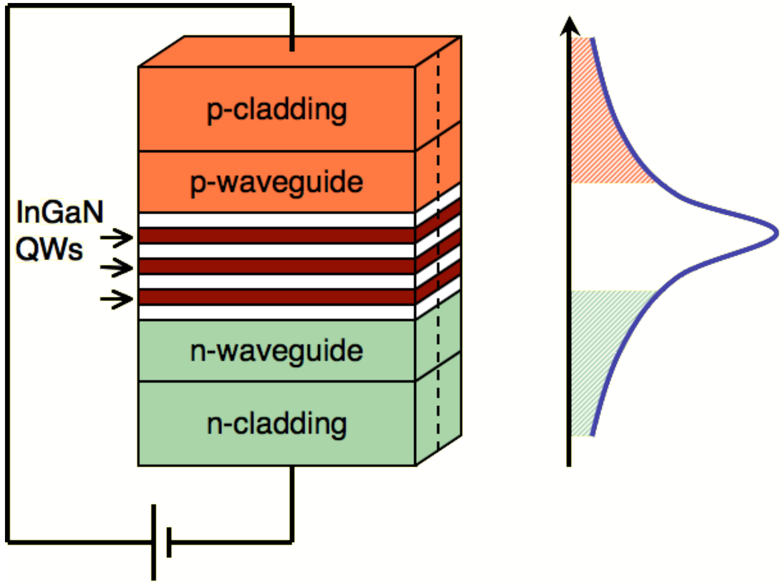
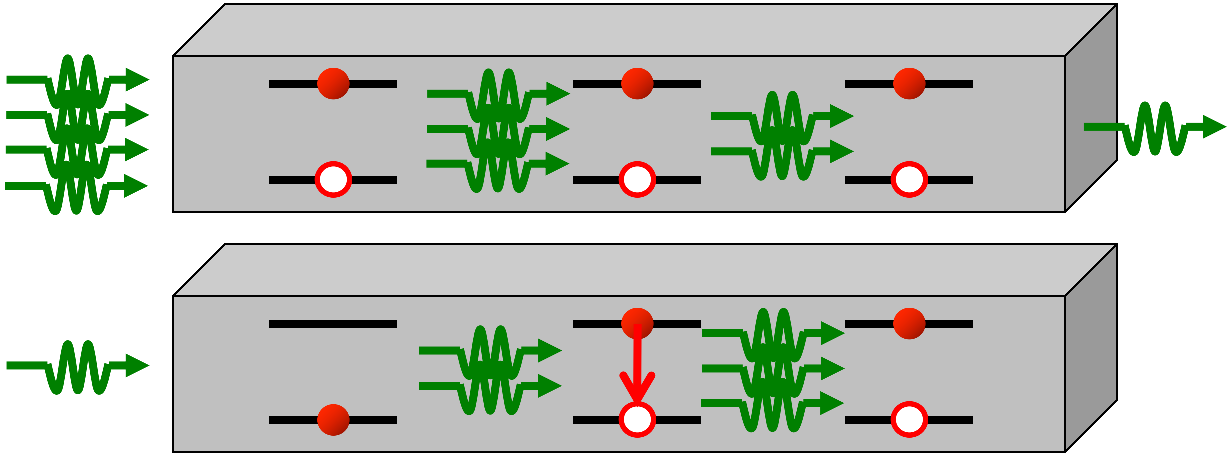
Absorption and gain



Optical mode profile
(photon density)



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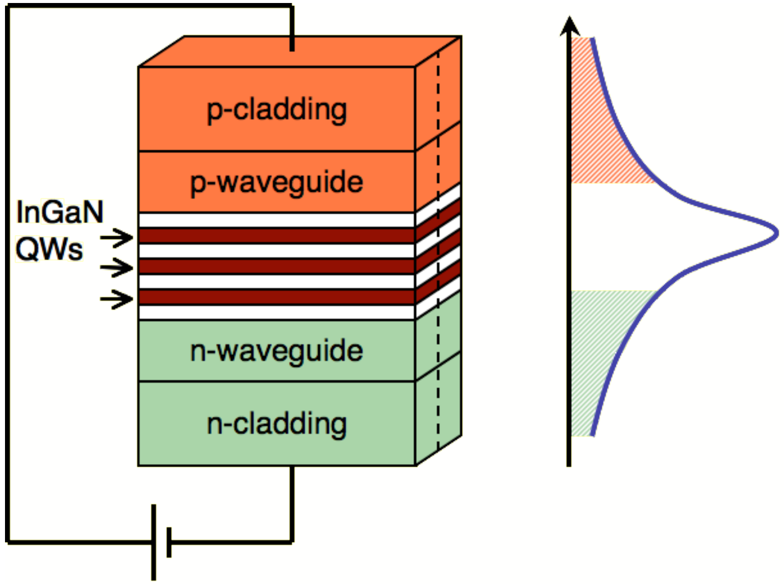
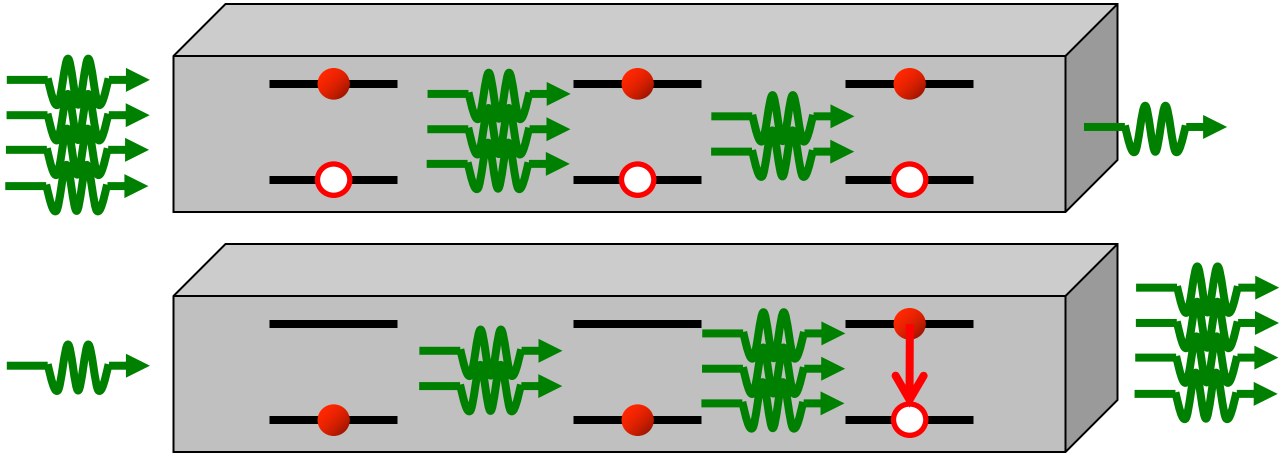
Absorption and gain



Optical mode profile
(photon density)



Absorption:

$$I(x) = I_0 e^{-\alpha x}$$

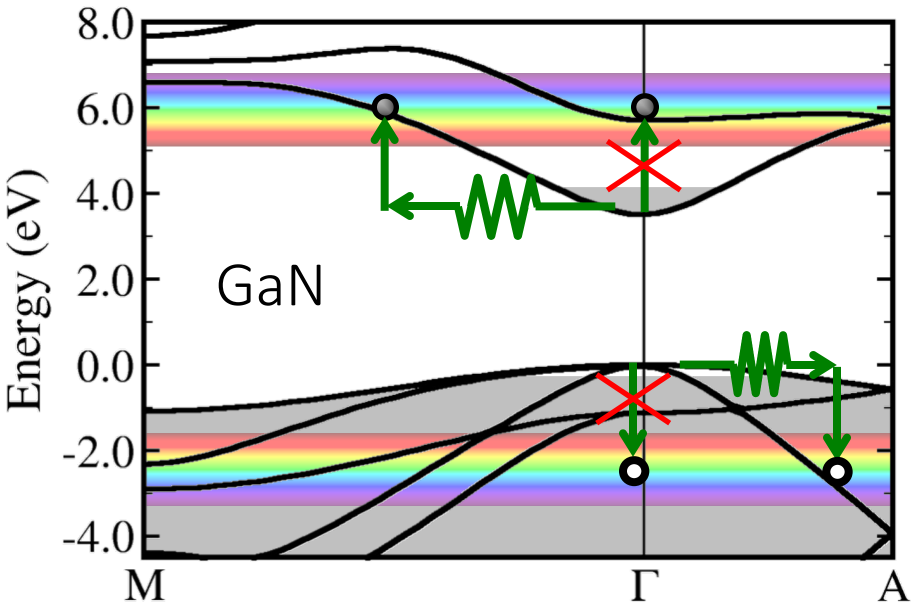
Gain in the QWs:

$$I(x) = I_0 e^{+gx}$$

Output = Gain – Absorption

Free-carrier absorption

Band gap wider than photon energy, no absorption across gap
High concentration of free carriers in lasers,
free-carrier absorption a potential source of loss

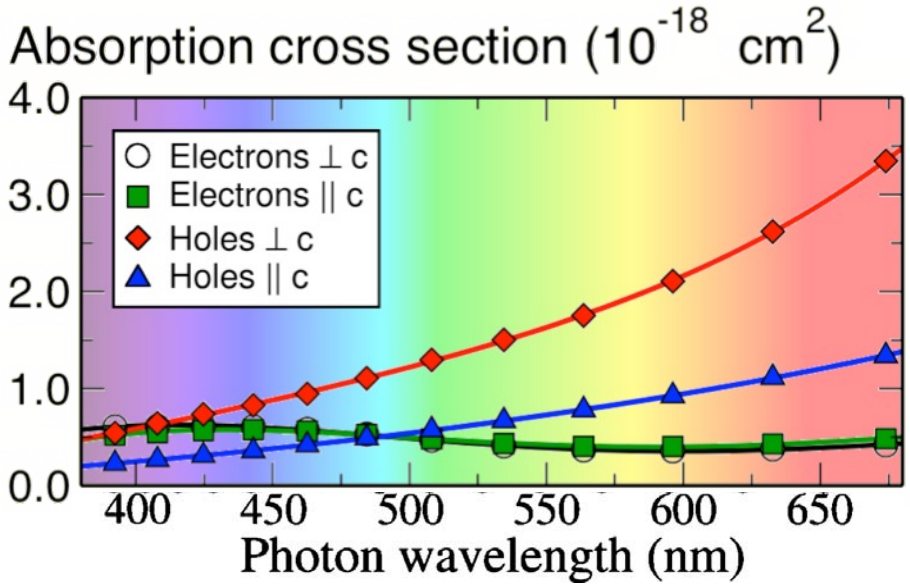


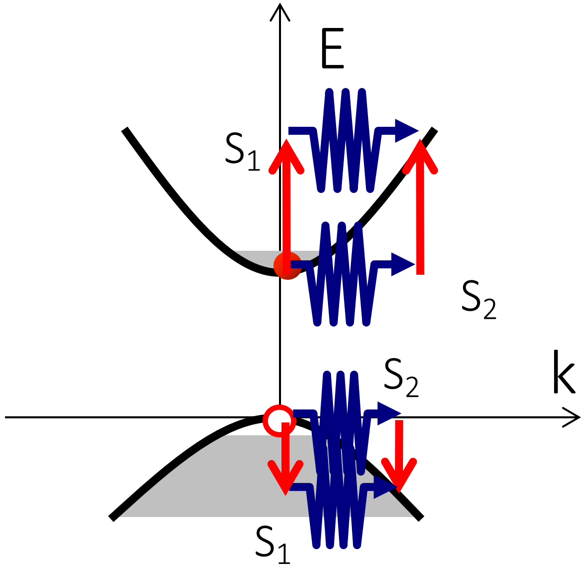
- Direct absorption is weak:
- Holes: impossible
- Electrons: dipole-forbidden

- Phonon-assisted absorption:

Possible for every photon energy

Phonon-assisted free-carrier absorption





Absorption cross section σ:

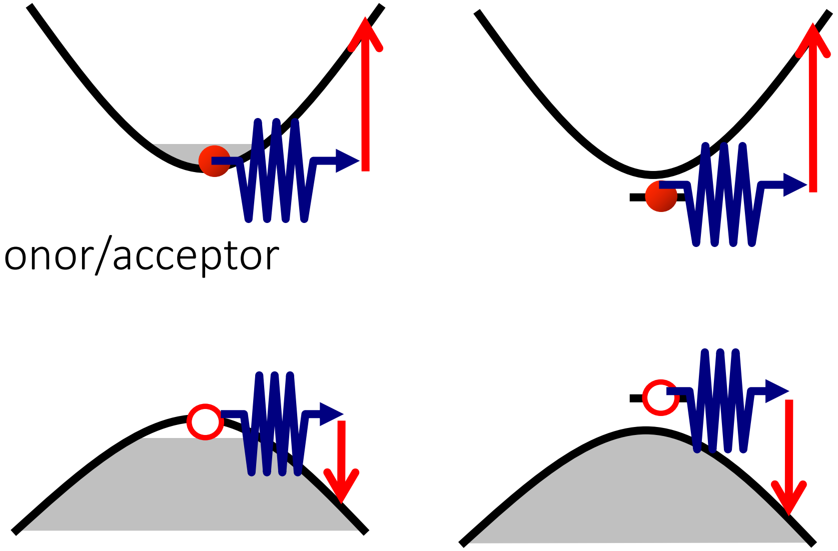
$$\alpha = n\sigma$$

For n = 10^{19} cm^{-3} (lasers under operating conditions): α = 10 cm^{-1}
Contrast with direct gap materials: α = 10^5–10^6 cm^{-1}

Absorption by non-ionized Mg in p-GaN

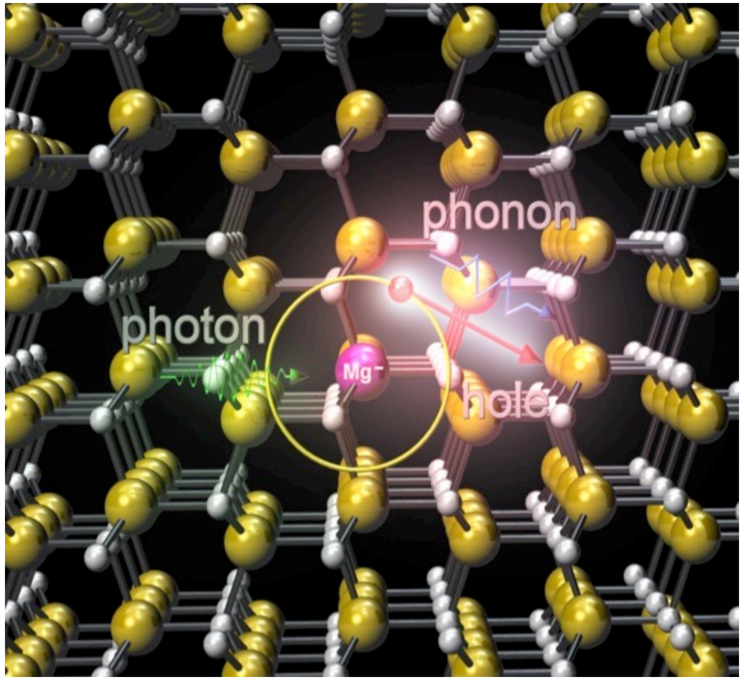
Absorption by carriers bound to dopants

Free carriers vs. donor/acceptor bound



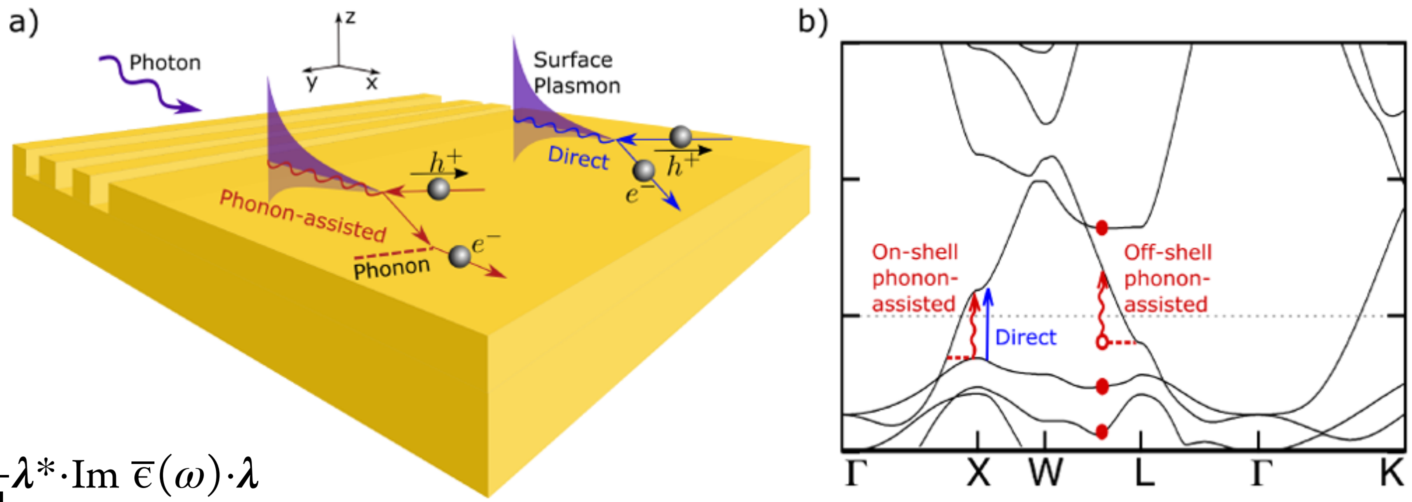
Activation energies:
GaN:Si : 50 meV
GaN:Mg : 200 meV

Large concentration (10^{19} cm^{-3}) of non-ionized Mg in p-GaN, causes internal absorption loss, more important at longer wavelengths



1.) Kioupakis, Rinke, Schleife, Bechstedt, & Van de Walle, *Phys. Rev. B* **81**, 241201 (2010); doi:10.1103/PhysRevB.81.241201
2.) Kioupakis, Rinke, & Van de Walle, *Appl. Phys. Express* **3**, 082101 (2010); doi:10.1143/APEX.3.082101

Plasmon decay in metals



$$\Gamma = \frac{\omega}{2L(\omega)|\gamma(z<0)|}\boldsymbol{\lambda}^{*}\cdot \mathrm{Im}\,\overline{\epsilon}(\omega)\cdot\boldsymbol{\lambda}$$

Imaginary part of dielectric function also describes plasmon energy loss in metals

Strong contribution from phonon-assisted terms

Brown et al., ACS Nano 10, 957–966 (2016)

$$\boldsymbol{\lambda}^{*}\cdot \mathrm{Im}\,\overline{\epsilon}_{\mathrm{phonon}}(\omega)\cdot\boldsymbol{\lambda} = \frac{4\pi^2 e^2}{m_e^2\omega^2}\int_{\mathrm{BZ}}\frac{\mathrm{d}\mathbf{q}'\mathrm{d}\mathbf{q}}{(2\pi)^6}$$

$$\sum_{n'n\alpha\pm}(f_{\mathbf{q}n}-f_{\mathbf{q}'n'})\left(n_{\mathbf{q}'-\mathbf{q},\alpha}+\frac{1}{2}\mp\frac{1}{2}\right)$$

$$\delta(\varepsilon_{\mathbf{q}'n'}-\varepsilon_{\mathbf{q}n}-\hbar\omega\mp\hbar\omega_{\mathbf{q}'-\mathbf{q},\alpha})\times$$

$$\left|\boldsymbol{\lambda}\cdot\sum_{n_1}\left(\frac{g^{\mathbf{q}'-\mathbf{q},\alpha}_{\mathbf{q}'n',\mathbf{q}n_1}\langle\mathbf{p}\rangle^{\mathbf{q}}_{n_1 n}}{\varepsilon_{\mathbf{q}n_1}-\varepsilon_{\mathbf{q}n}-\hbar\omega+i\eta}\right.\right.$$

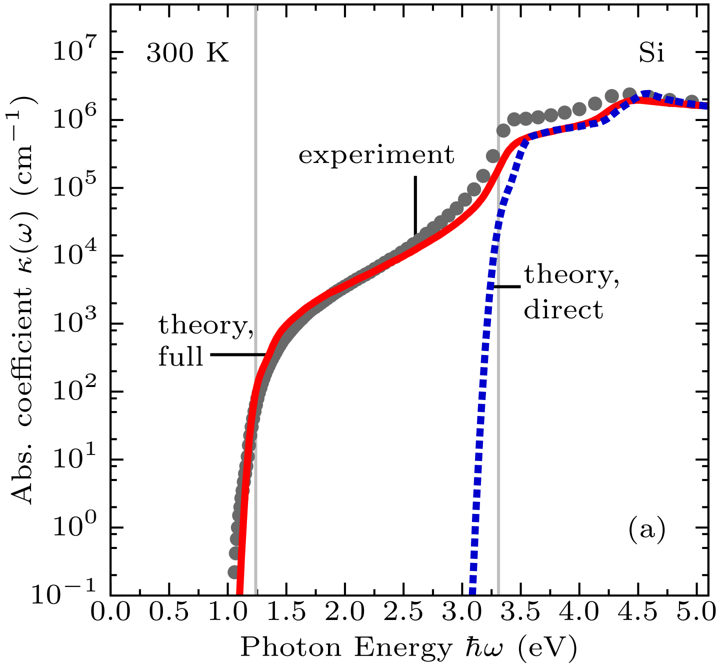
$$\left.\left.+\frac{\langle\mathbf{p}\rangle^{\mathbf{q}'}_{n'n_1}g^{\mathbf{q}'-\mathbf{q},\alpha}_{\mathbf{q}'n_1,\mathbf{q}n}}{\varepsilon_{\mathbf{q}'n_1}-\varepsilon_{\mathbf{q}n}\mp\hbar\omega_{\mathbf{q}'-\mathbf{q},\alpha}+i\eta}\right)\right|^2$$

Alternative method: Zacharias and Giustino

Calculate direct optical absorption in a single optimal supercell with atoms displaced according to a linear combination of the phonon modes (**Special Displacement Method**)

Advantages:
-Avoids divergence
-No need for Wannier interpolation
-T-dependence of eigenvalues, band gap, and Urbach tail.
-Can be generalized for other functionals, excitons, …

See **Marios Zacharias**' talk on **Wednesday** and [Phys. Rev. Research 2, 013357 (2020)]



Zacharias and Giustino
Physical Review B 94, 075125 (2016)

$$\Delta\tau_{\kappa\alpha} = (M_\mathrm{p}/M_\kappa)^{\frac{1}{2}} \sum_\nu (-1)^{\nu-1} e_{\kappa\alpha,\nu}\, \sigma_{\nu,T}$$

$$\sigma^2_{\nu,T} = (2n_{\nu,T} + 1)\, l^2_\nu,$$

$$n_{\nu,T} = [\exp(\hbar\omega_\nu/k_\mathrm{B}T) - 1]^{-1}$$

$$l_\nu = (\hbar/2M_\mathrm{p}\Omega_\nu)^{1/2}$$

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- Giustino, *Rev. Mod. Phys*. **89**, 015003 (2017)
- Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett.* **108**, 167402 (2012)
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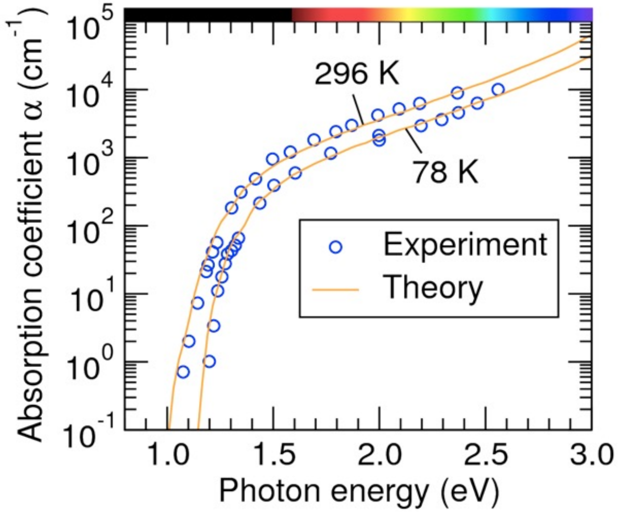
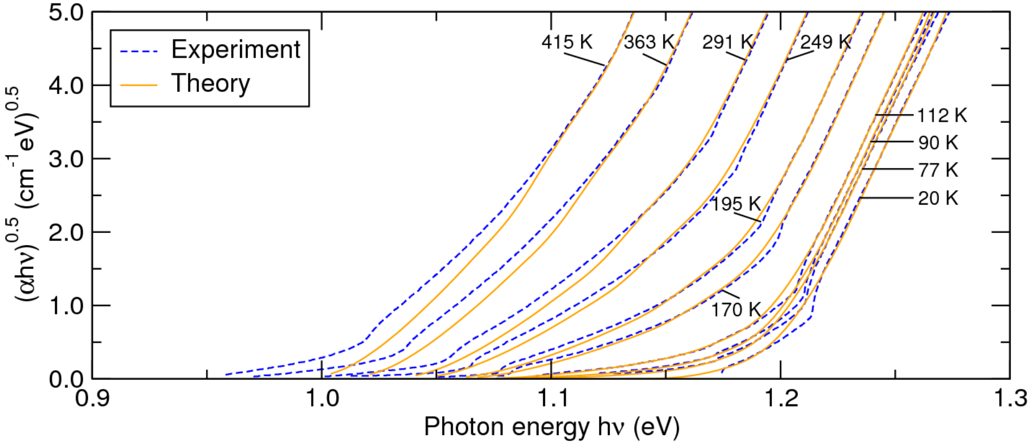
- H. Lee et al, arXiv:2302.08085 (2023) http://epw-code.org





Acknowledgements

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Thank you for your attention