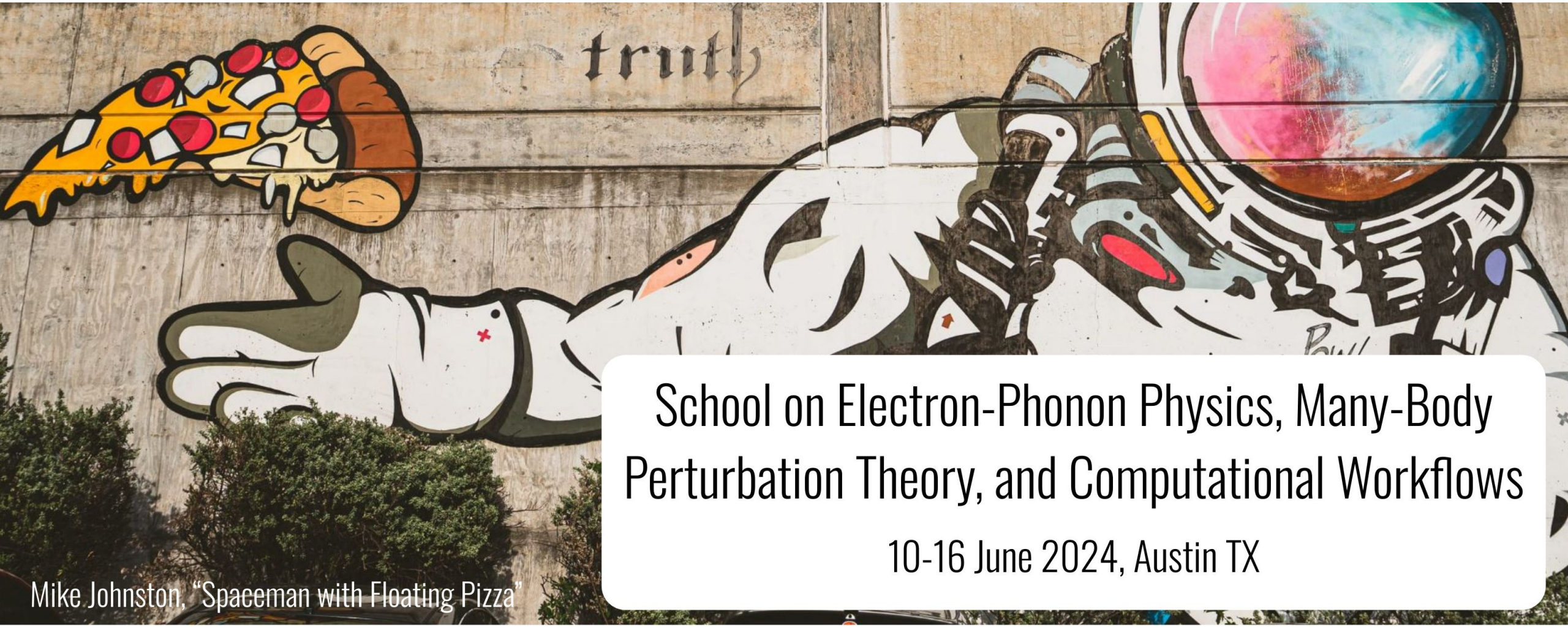

Mike Johnston, “Spaceman with Floating Pizza”

School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows

10-16 June 2024, Austin TX

U.S. DEPARTMENT OF ENERGY

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Lecture Wed.3

Phonon-assisted optical processes

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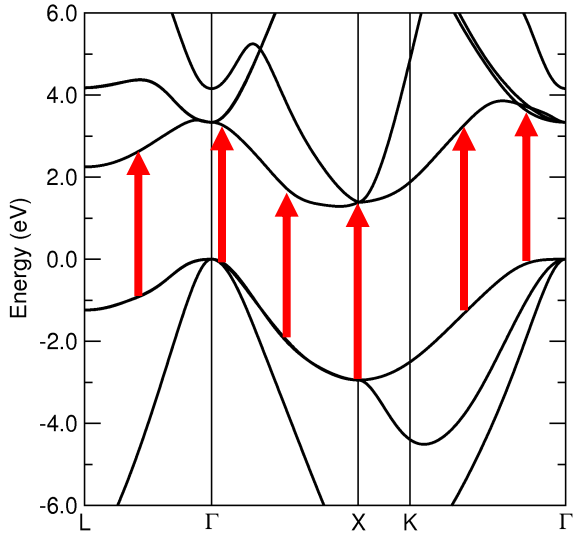
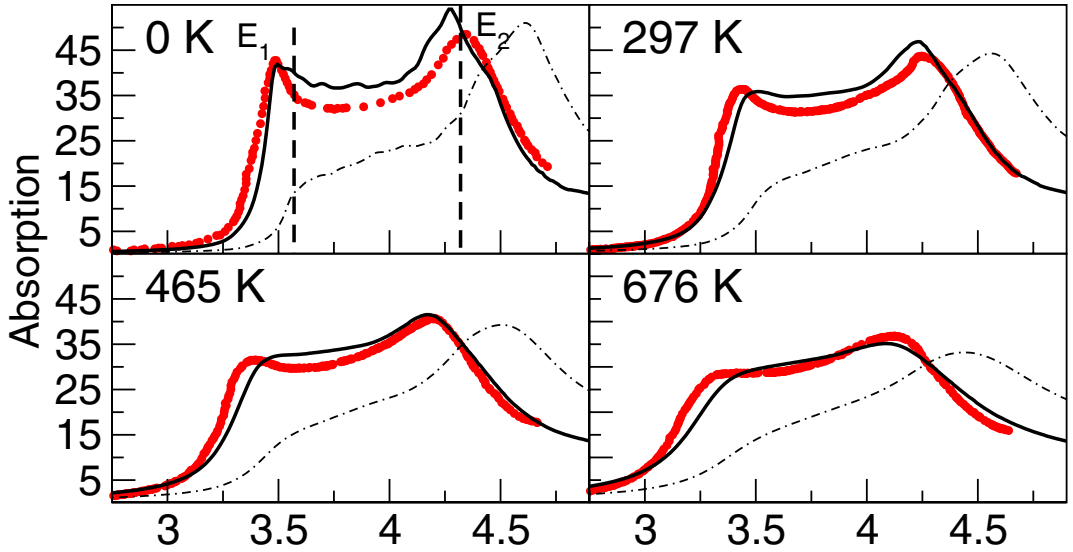
Materials Science and Engineering
University of Michigan

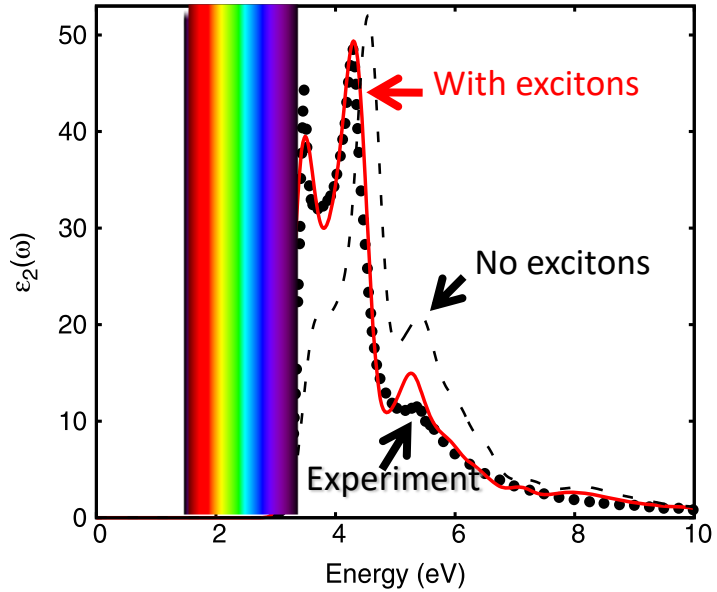
Overview

- The need for phonon-assisted optics
- Optical properties of materials
- Classical theory of photon absorption
- Quantum theory of direct optical absorption
- Quantum theory of phonon-assisted optical absorption
- Applications for silicon, indirect-gap semiconductors, metals, doped semiconductors, transparent conductors.
- Alternative methods:
  - Special Displacement Method (Zacharias Fri.1)
  - Quasi-Degenerate Perturbation Theory (Tiwari Sat.6)
- References

Motivation: optical absorption in Si



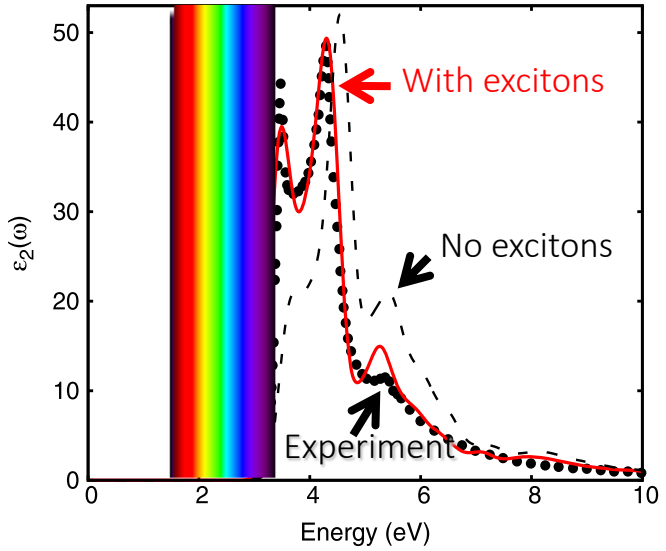


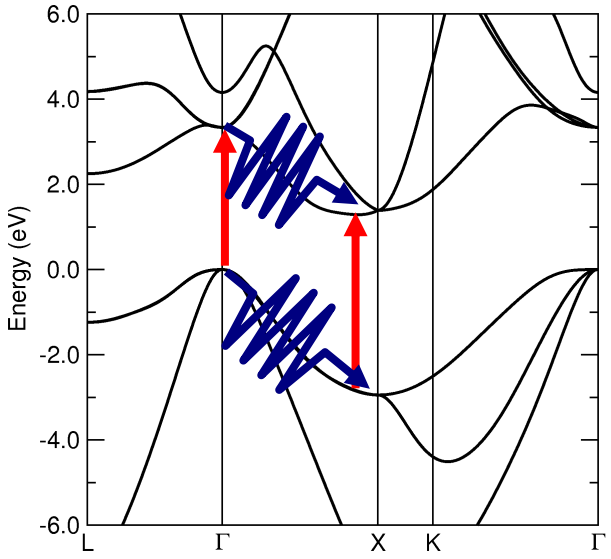


The direct absorption of photons in materials is well understood, including the effects of excitons and temperature broadening

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





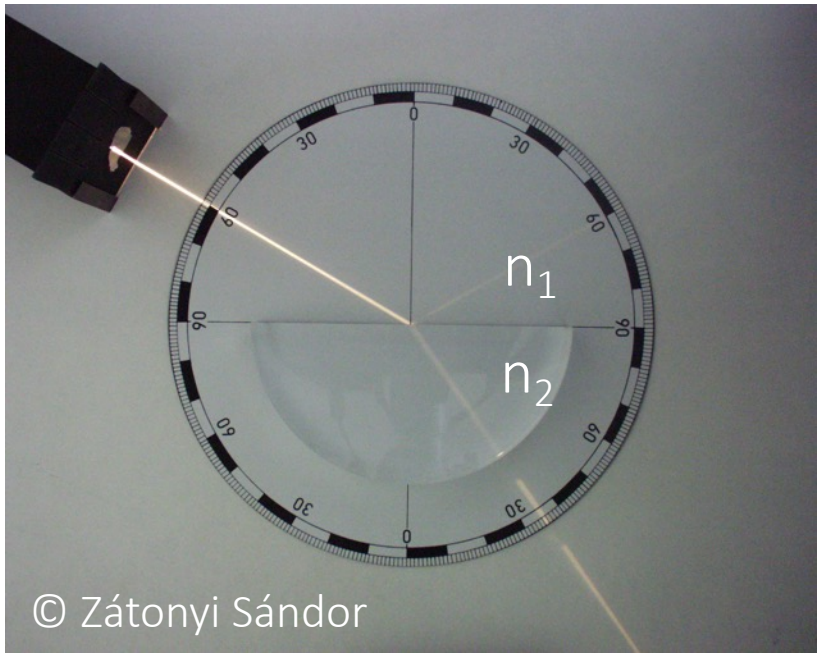
Deslippe et al. Comput. Phys. Commun. 183, 1269 (2012)

However, the band gap of silicon (1.2 eV) is indirect (minimum direct gap is 3.4 eV).
The direct absorption of visible photons is ***impossible*** in silicon.

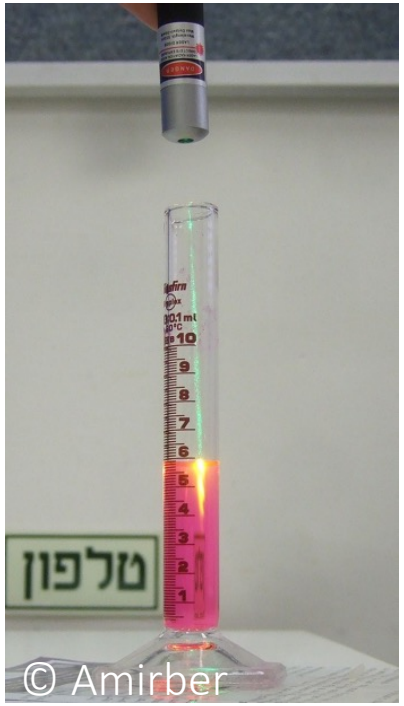
→ Atomic vibrations provide the additional momentum to enable **phonon-assisted optical transitions** across the indirect band gap of silicon, and enable the operation of silicon solar cells.

Linear optics

Refraction: Snell's law



Absorption: Beer-Lambert law



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

α = absorption coefficient [cm^{-1}]
Strong absorbers: α ~ 10^5 –10^6 cm^{-1}

Optical parameters of materials

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

Real part: propagation/refraction
Imaginary part: absorption/dissipation

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

Their connection:

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

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

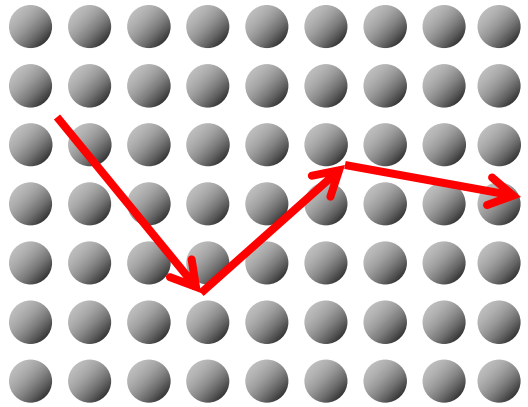
Absorption coefficient:

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

Classical theory of light absorption in metals

Semiclassical Drude model:

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

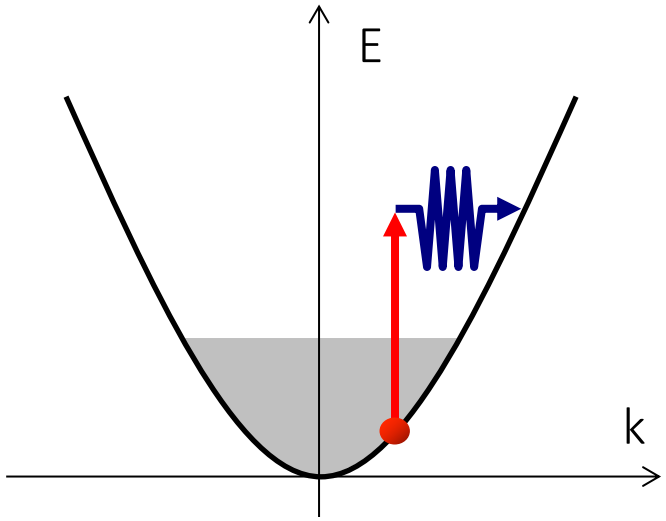


e.g., DC conductivity:

$$\sigma = \frac{ne^2\tau}{m^*}$$

AC field: Absorption coefficient in metals

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



But: τ : Phenomenological

Also: classical theory cannot describe light absorption in materials with a band gap

Quantum theory of optical absorption

Treat with first-order perturbation theory

Unperturbed state = DFT of GW wave functions and eigenvalues

Perturbation: electron-photon Hamiltonian $H_{\text{el-phot}} = \frac{e}{m_e c}\vec{A}\cdot\vec{p} = \frac{e}{c}\vec{A}\cdot\vec{v}$

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: $\frac{n_r^2 A^2 \omega^2}{2\pi c^2}$

Quantum theory of optical absorption

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

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

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

v = velocity matrix elements
λ = light polarization vector

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: $\varepsilon_1(\omega) = 1 + \frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{\varepsilon_2(\omega')}{\omega' - \omega}d\omega'$

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

Phonon-assisted optical absorption

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 (other terms are two-photon and two-phonon absorption/emission:

$$P_{i\to f} = \frac{2\pi}{\hbar}\left|\sum_m \frac{\langle f|H_{\text{el-phot}}|m\rangle\langle m|H_{\text{el-phon}}|i\rangle}{E_m - E_i} + \sum_{m'} \frac{\langle f|H_{\text{el-phon}}|m'\rangle\langle m'|H_{\text{el-phot}}|i\rangle}{E_{m'} - E_i}\right|^2 \delta(E_f - E_i)$$

Phonon-assisted optical absorption

Absorption coefficient:

$$\alpha(\omega) = 2\frac{4\pi^2 e^2}{n_r c\omega}\frac{1}{N_{\boldsymbol{k}}N_{\boldsymbol{q}}}\sum_{i,j,\boldsymbol{k},\boldsymbol{q},\nu} P\,|\boldsymbol{\lambda}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2)|^2$$

$$\times\,\delta(\epsilon_{j,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega \pm \hbar\omega_{\nu,\boldsymbol{q}})$$

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

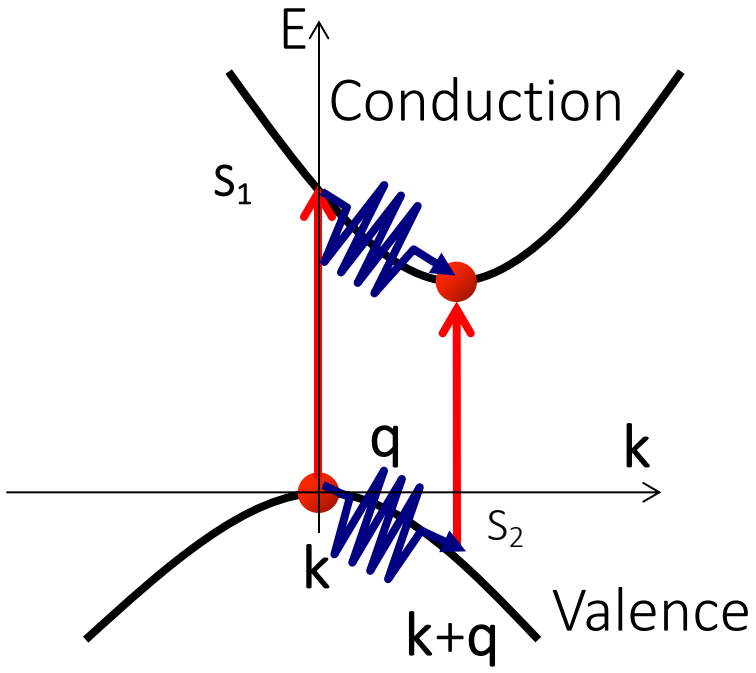
Two paths:

$$\boldsymbol{S}_1(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{\boldsymbol{v}_{im}(\boldsymbol{k})\,g_{mj,\nu}(\boldsymbol{k},\boldsymbol{q})}{\epsilon_{m\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega}$$

$$\boldsymbol{S}_2(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{g_{im,\nu}(\boldsymbol{k},\boldsymbol{q})\,\boldsymbol{v}_{mj}(\boldsymbol{k}+\boldsymbol{q})}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} \pm \hbar\omega_{\nu\boldsymbol{q}}}$$

Occupations:

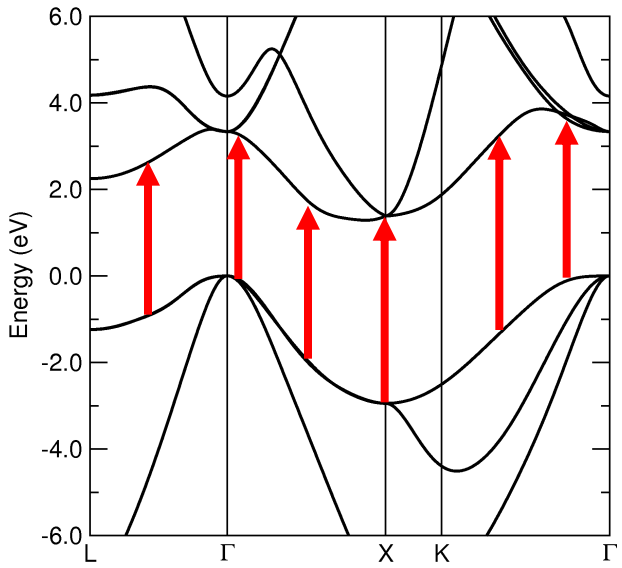
$$P = \left(n_{\nu\boldsymbol{q}} + \frac{1}{2} \pm \frac{1}{2}\right)(f_{i\boldsymbol{k}} - f_{j,\boldsymbol{k}+\boldsymbol{q}})$$

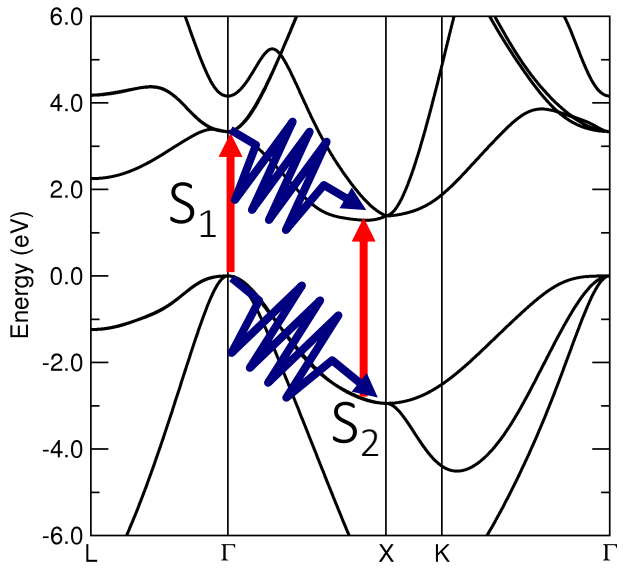


Upper sign: phonon emission
Lower sign: phonon absorption
Sum over intermediate states *m*: both occupied + empty states

Computational challenge with phonon-assisted absorption

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

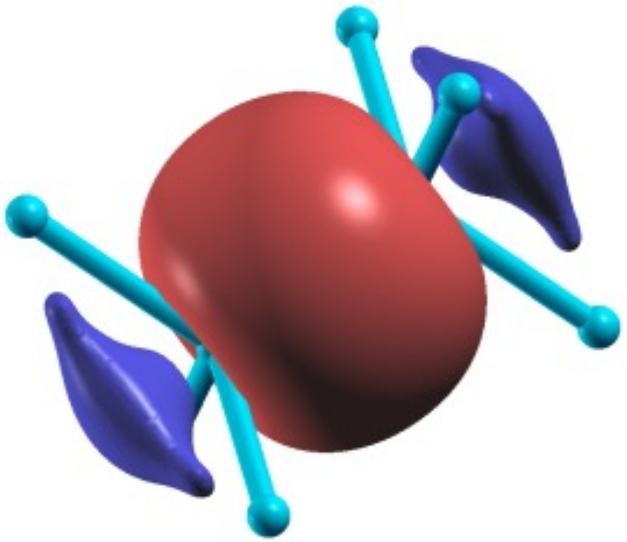




$$\alpha(\omega) \propto \sum_{i,j,\nu} P|\boldsymbol{S}_1 + \boldsymbol{S}_2|^2 \delta(\epsilon_j - \epsilon_i - \hbar\omega \pm \hbar\omega_\nu)$$

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

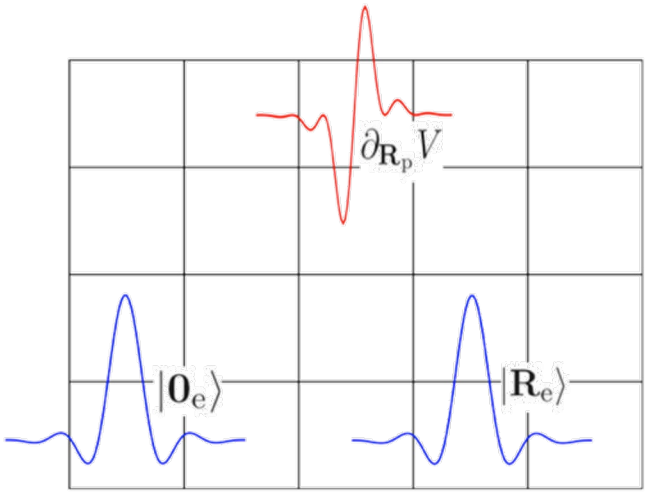
Solution: interpolation with Maximally Localized Wannier Functions



Interpolate quasiparticle energies and optical (velocity) matrix elements.
(Marzari Mon.3)

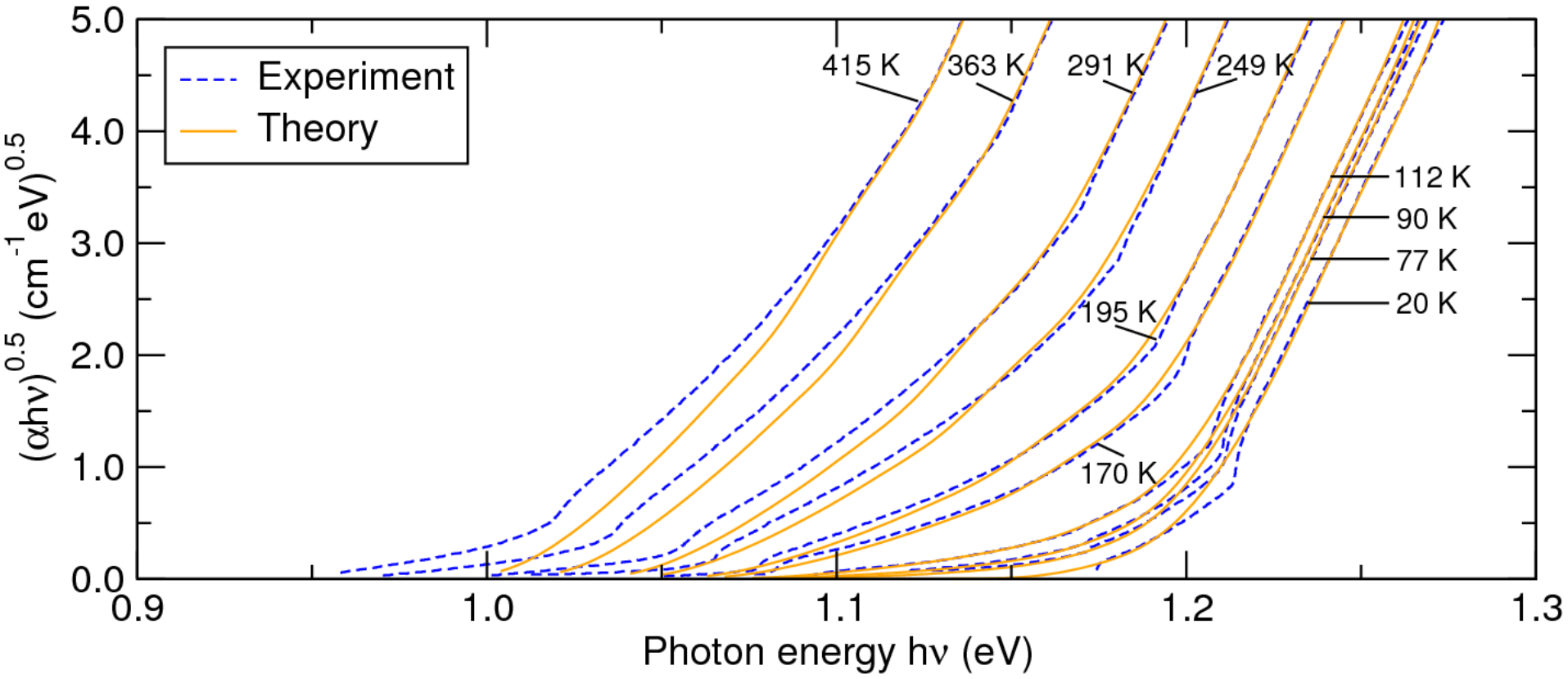
Fourier

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



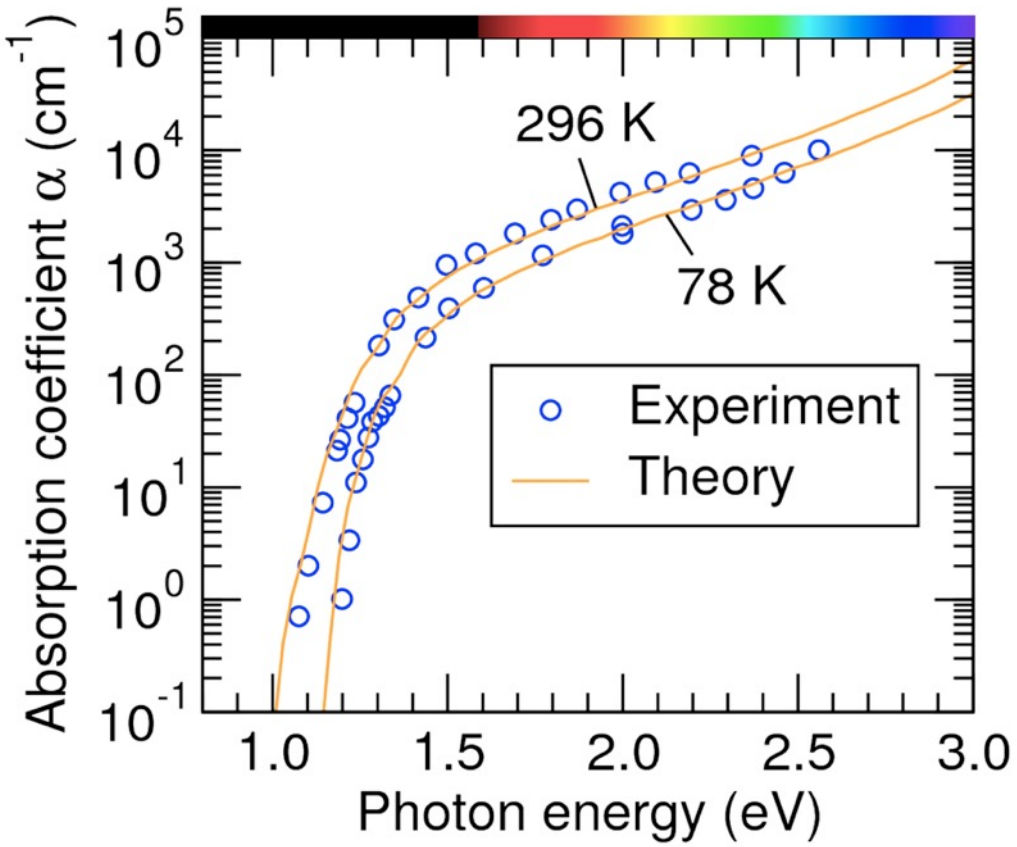
Interpolate electron-phonon matrix elements
(Giustino Mon.1)

Indirect absorption edge for silicon



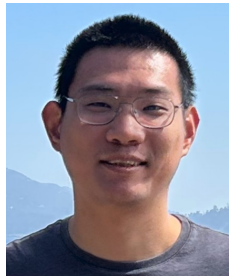
Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)
* Shifted the energy of onset by 0.15-0.23 eV to match experiment

Si absorption in the visible

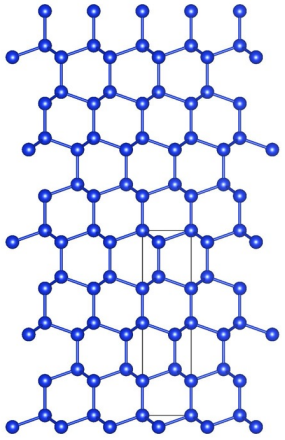


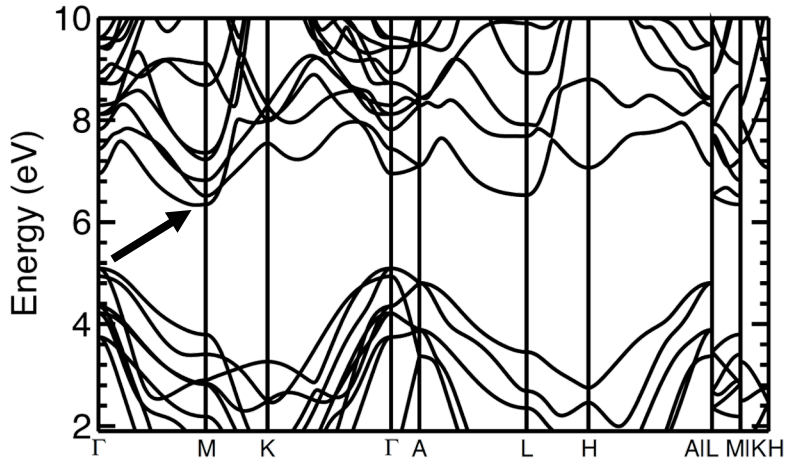
Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)
* Shifted the energy of onset to match experiment

Intrinsic semiconductors: 4H silicon



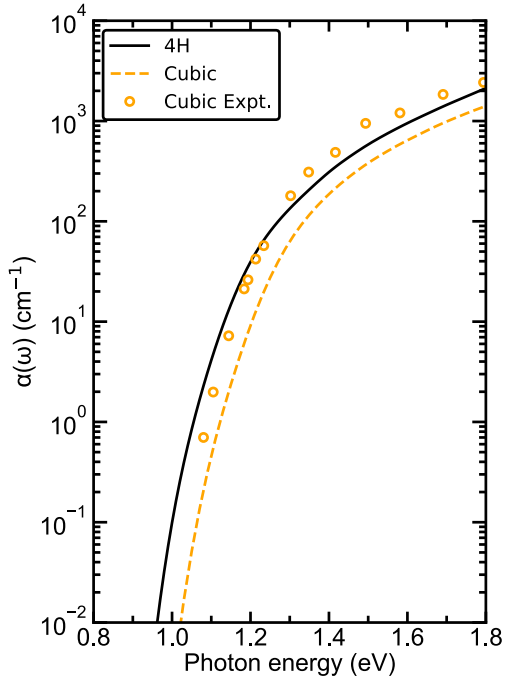
- Cubic silicon: well-studied[1,2]
- 4H silicon: Recently synthesized in bulk[3]
- $\mathbf{ABCB}$ stacking along [001]
- Indirect band gap

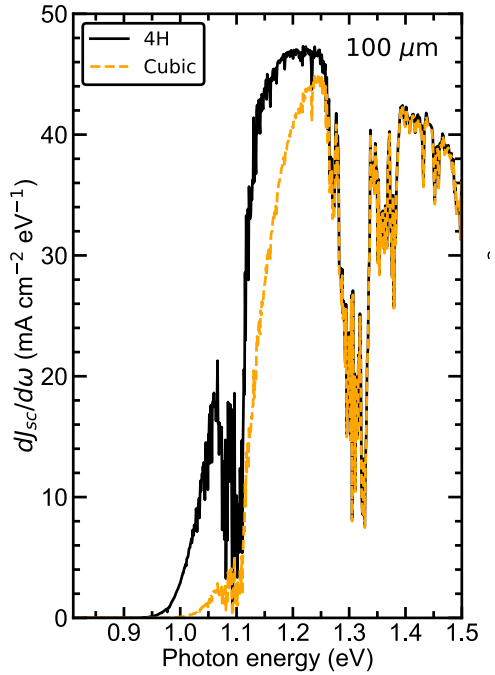




X. Zhang and E. Kioupakis, *AIP Adv.* 14 (3): 035149. (2024)

- Significantly higher absorption coefficient of 4H silicon
  - ~ 0.05 eV smaller gap
  - Stronger electron-phonon coupling
- Absorption coefficient can be used to evaluate solar efficiency[4]

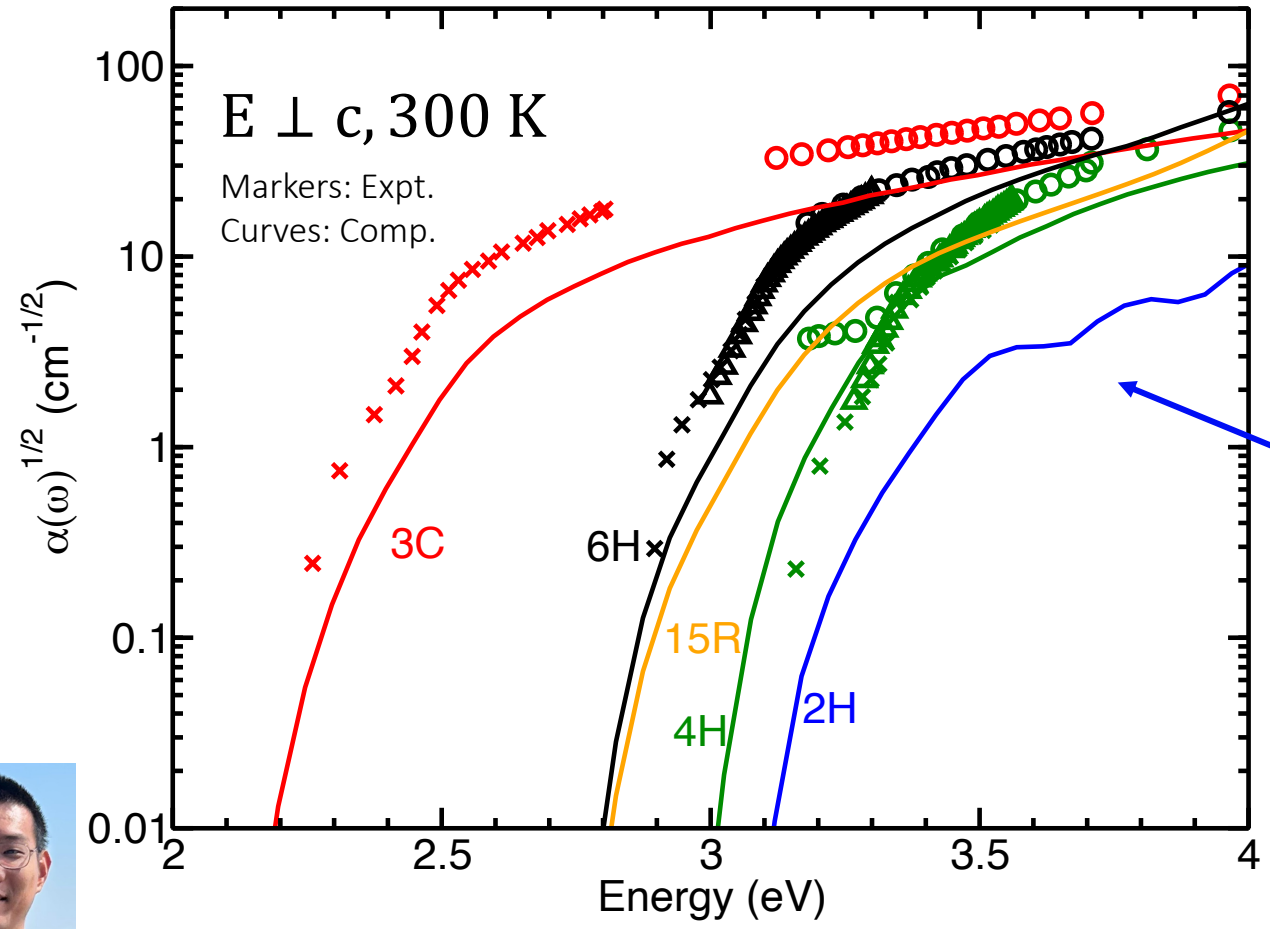




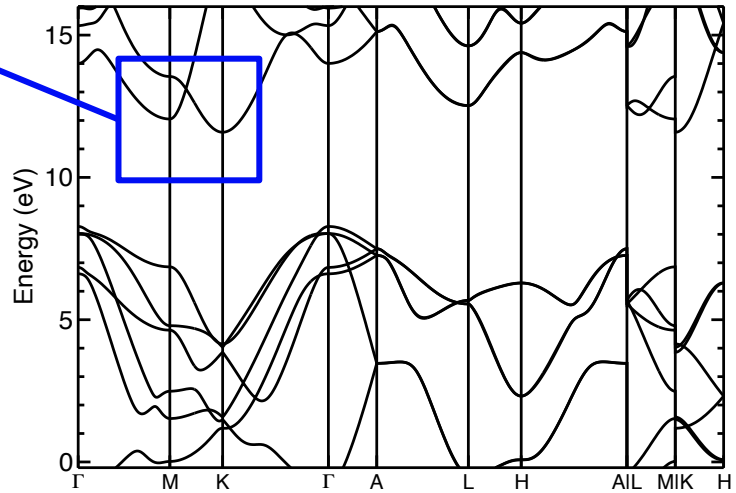
[1] J. Noffsinger, et al., Phys. Rev. Lett. 108, 167402 (2012).
[2] H. Lee, et al., npj Comput. Mater. 9, 156 (2023).
[3] T. B. Shiell, et al., Phys. Rev. Lett., 126.21, 215701. (2021)

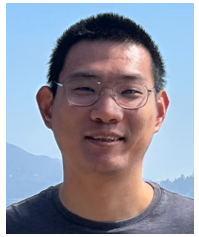
Cubic Expt.: R. Braunstein, A.R. Moore, and F. Herman, Phys. Rev. 109, 695 (1958).
[4] T. O. M. Tiedje, et al. IEEE Trans. Electron Devices 31.5, 711-716. (1984)

SiC phonon-assisted optical properties



- Rigid shifts to match experimental band gap
- Good agreement with experiments
- Step-like feature in 2H structure
- Match the feature in the band structure





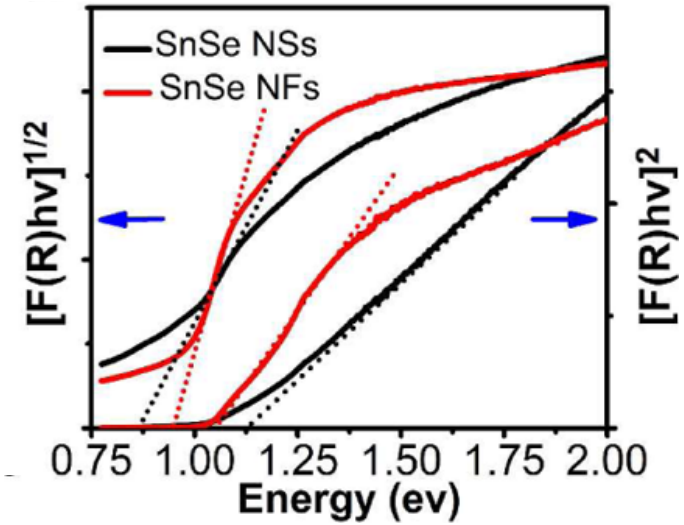
X. Zhang and E. Kioupakis, *Phys. Rev. B* 107, 115207, (2023)

Measuring direct and indirect band gaps

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

For direct absorption:

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



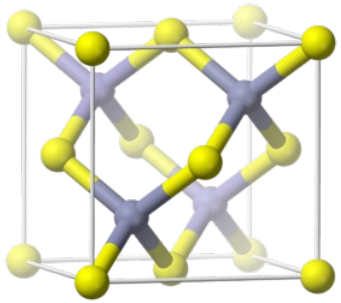
J. Am. Chem. Soc. 2013, 135, 1213

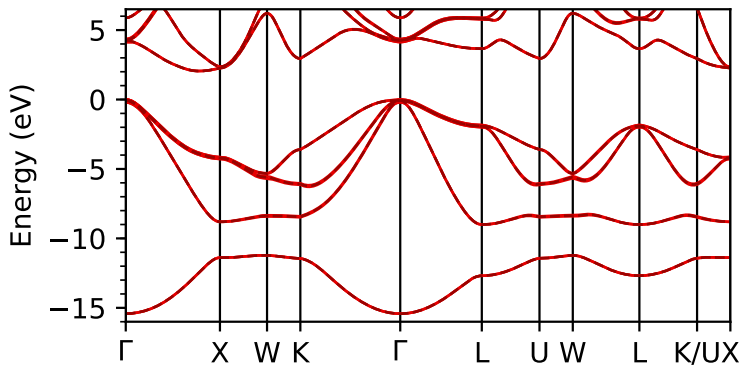
For indirect absorption:

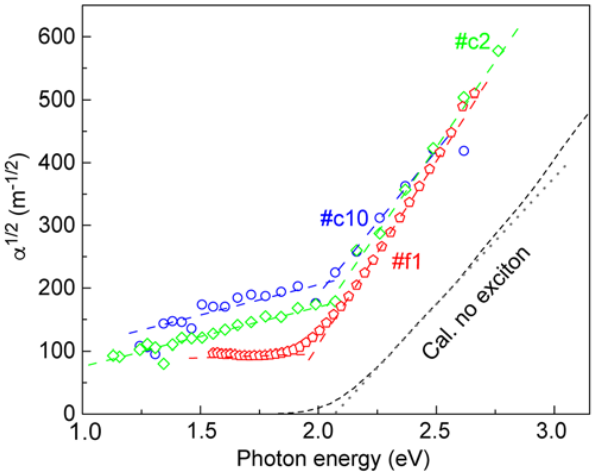
$$\alpha \propto \frac{(\hbar\omega - E_g^i \pm \hbar\omega_{\text{phonon}})^2}{\omega} \Rightarrow (\alpha\omega)^{1/2} \propto \hbar\omega - E_g^i \pm \hbar\omega_{\text{phonon}}$$

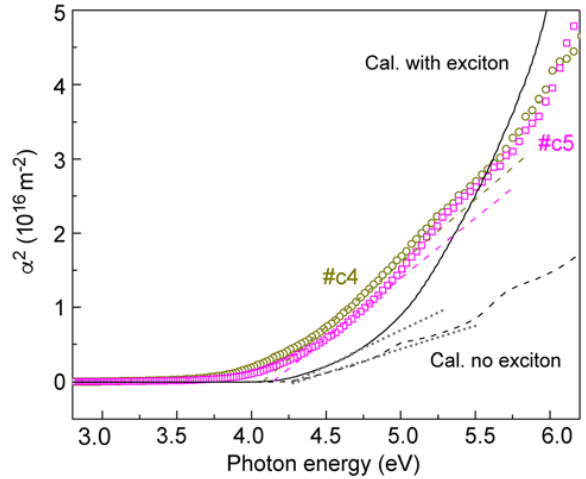
Exponent determines type and value of gap.
Two terms (emission/absorption) for phonon-assisted optics.

Phonon-assisted optical absorption in BAs









- BAs: a new compound semiconductor with ultrahigh thermal conductivity. [1]
- Our GW calculations predicted an indirect band gap of 2.05 eV and a direct gap of 4.14 eV [2], subsequently verified experimentally [3].
- Calculated phonon-assisted absorption coefficient in good agreement with experiment [3].

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).

Optical properties: noble metals

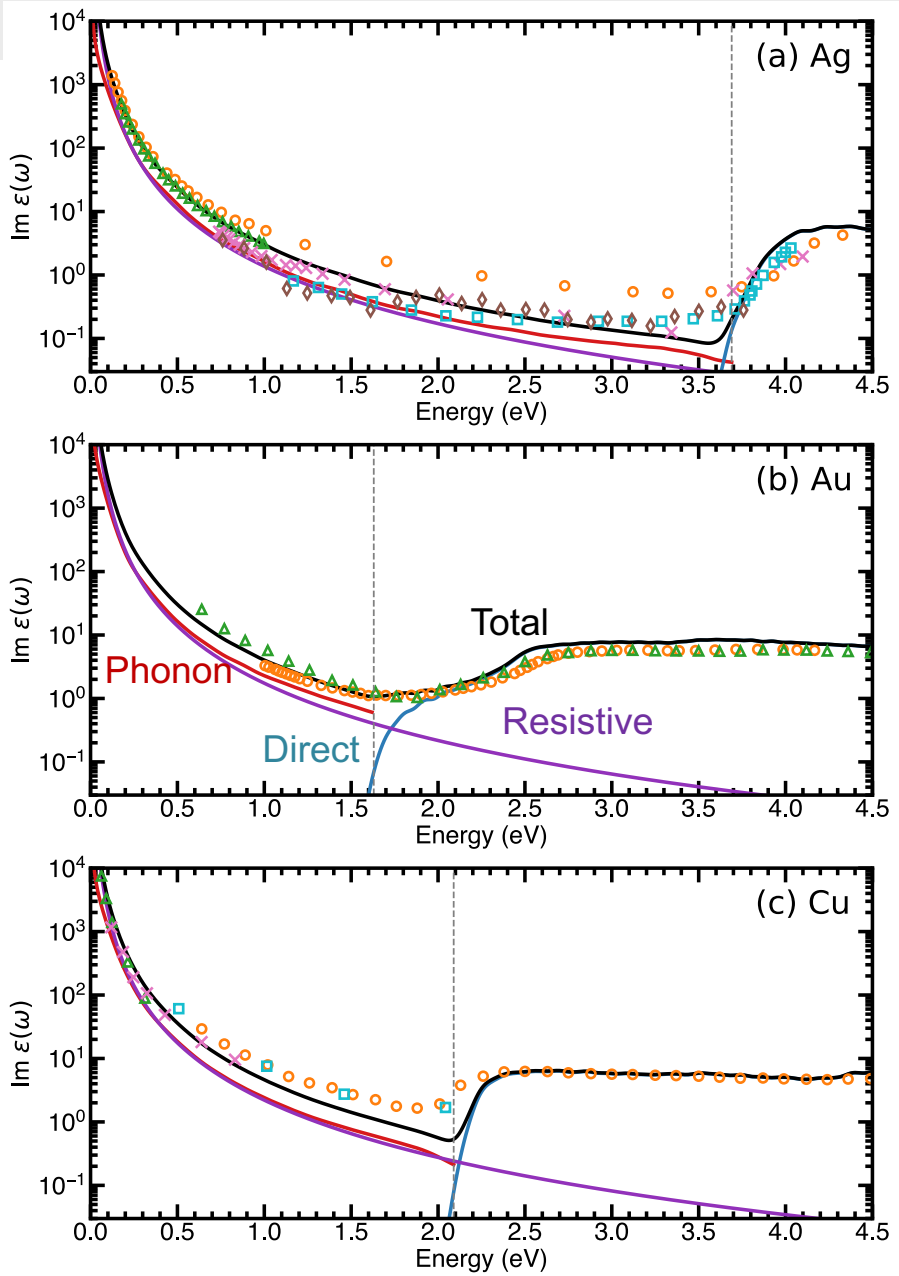
Metals: additional absorption term (Drude) due to dynamical response of free electrons:

$$\mathrm{Im}\,\varepsilon^{\mathrm{resis}}(\omega) = \frac{4\pi\sigma}{\omega(1+\omega^2\tau^2)}$$

σ = DC conductivity

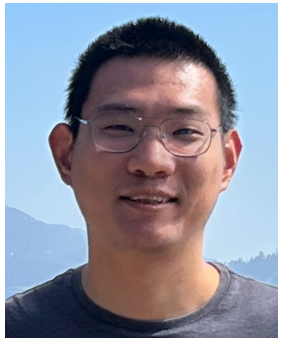
τ = scattering time

- Overall, good agreement with experimental measurements for Ag, Au, Cu
- Low energy: Drude (resistive) contribution and phonon-assisted contribution equally important
- Beyond direct gap: direct contribution
- **Single particle** contributions and **resistive contributions** are equally important in metallic systems

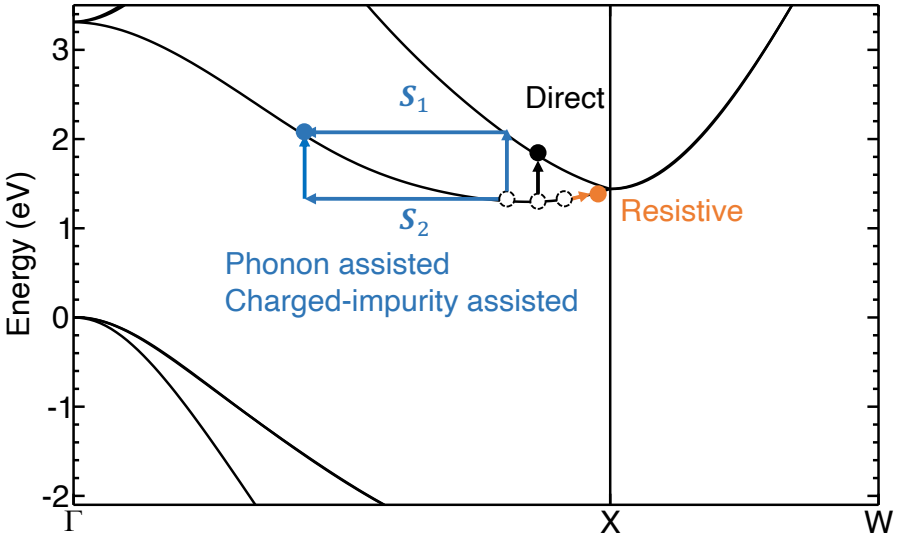


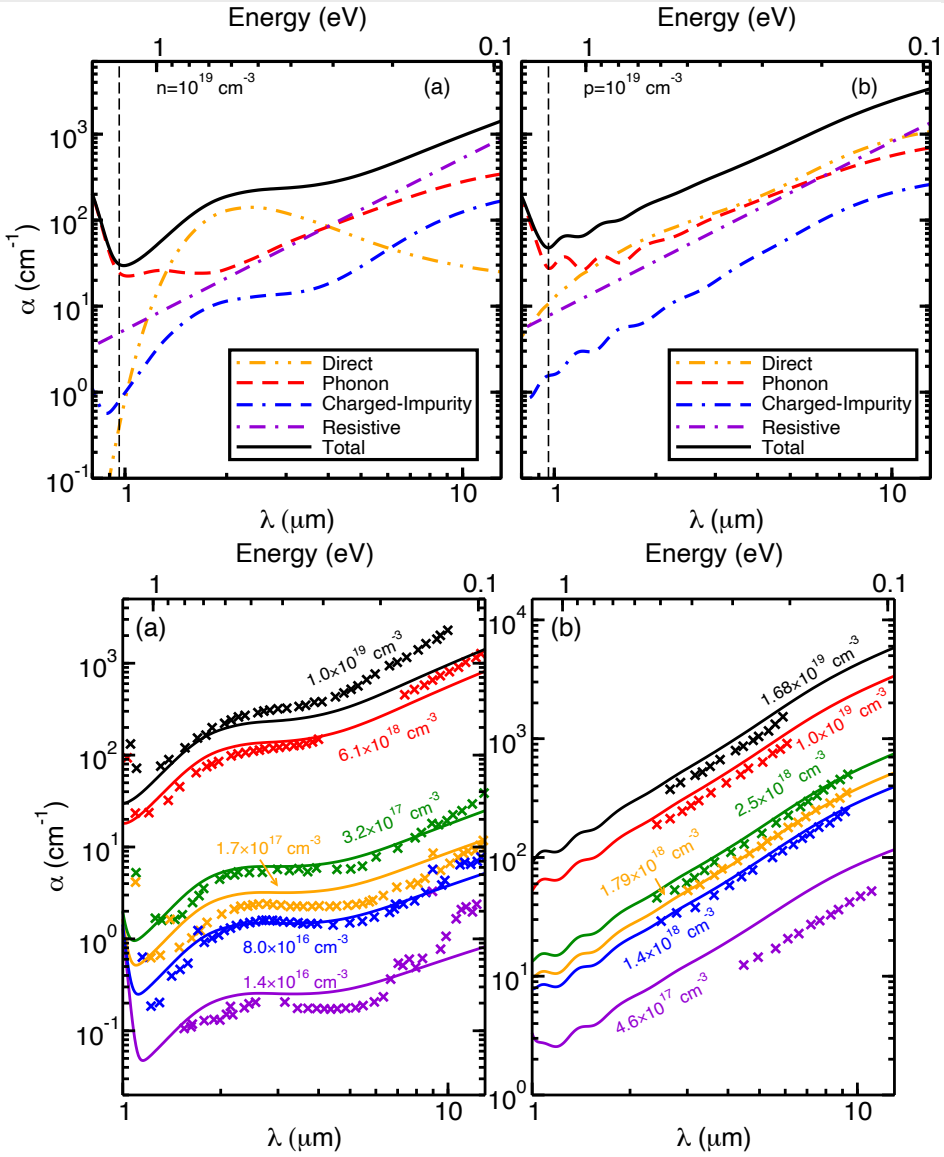
Expt.: Appl. Opt. 1998, 37 (22), 5271–5283; Opt. Mater. Express 2020, 10 (2), 693–703; ACS photonics 2015, 2 (3), 326–333; Adv. Mater. 2014, 26 (35), 6106–6110; Phys, Rev. B 1972, 6 (12), 4370; Phys, Rev. B 2012, 86 (23), 235147; JOSA 1966, 56 (5), 683–685; Optik 1965, 22 (6), 435; JOSA 1975, 65 (6), 742–744

Free-carrier absorption in doped silicon



Xiao Zhang



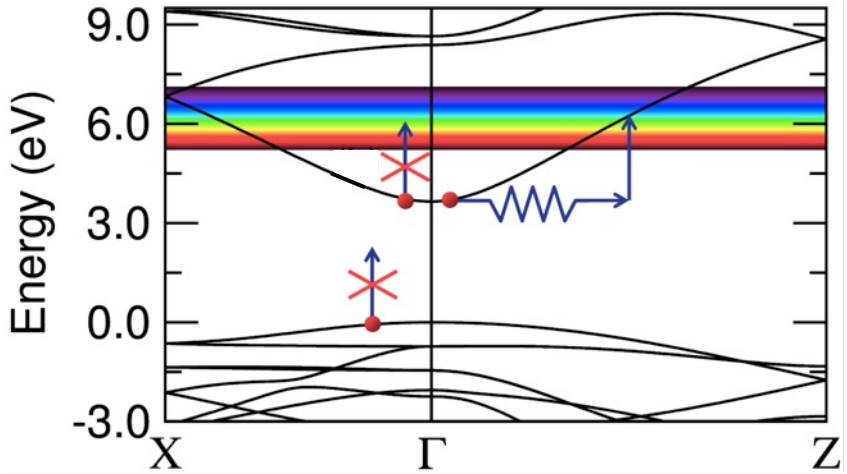


- Absorption of light in doped silicon competes with interband absorption.
- Also: absorption in the infrared (photon energy below gap)
- Direct + indirect absorption possible. Also, resistive loss term.
- Results for α vs. doping in good agreement with experiment.

Xiao Zhang, G. Shi, J. A. Leveillee, F. Giustino, E. Kioupakis, *Ab initio* theory of free-carrier absorption in semiconductors, *Phys. Rev. B* **106**, 205203 (2022); https://doi.org/10.1103/PhysRevB.106.205203

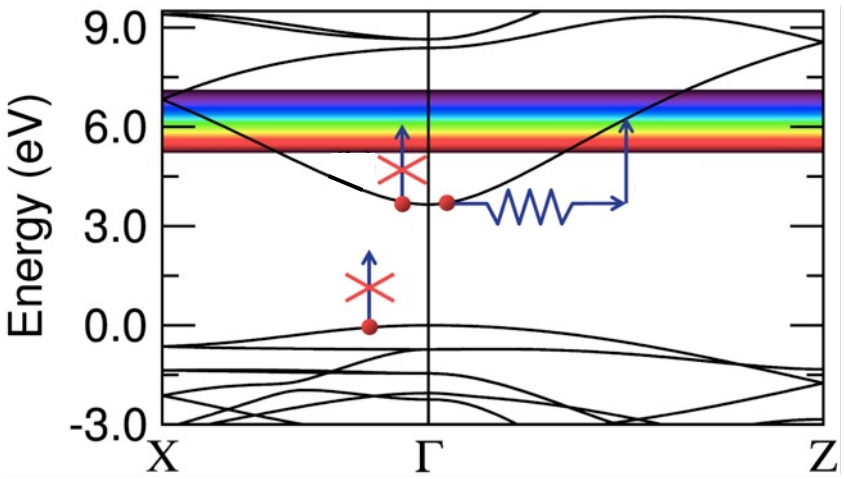
Absorption in transparent conducting oxides

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



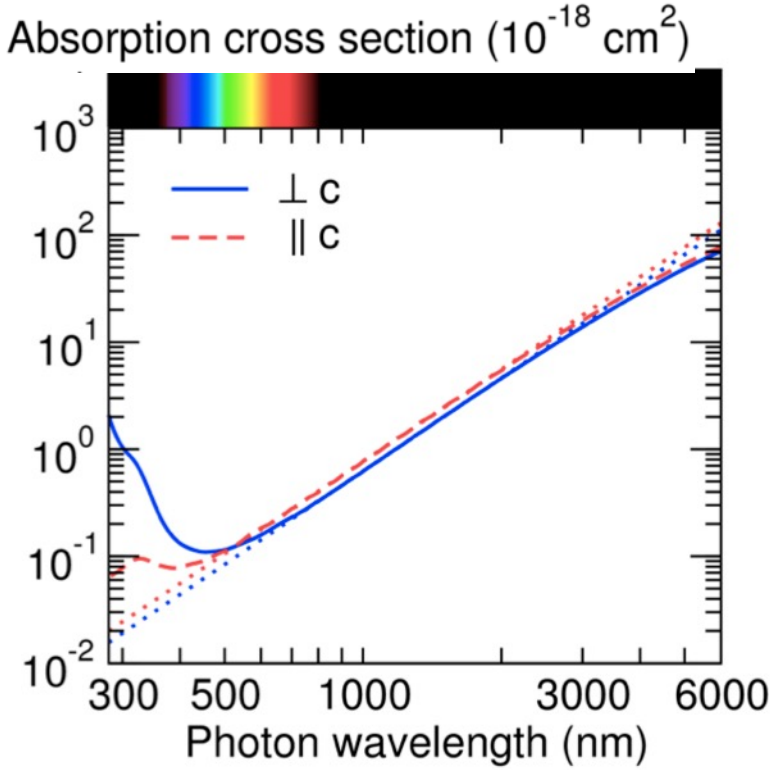
Fundamental transparency limit due to free-carrier absorption

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

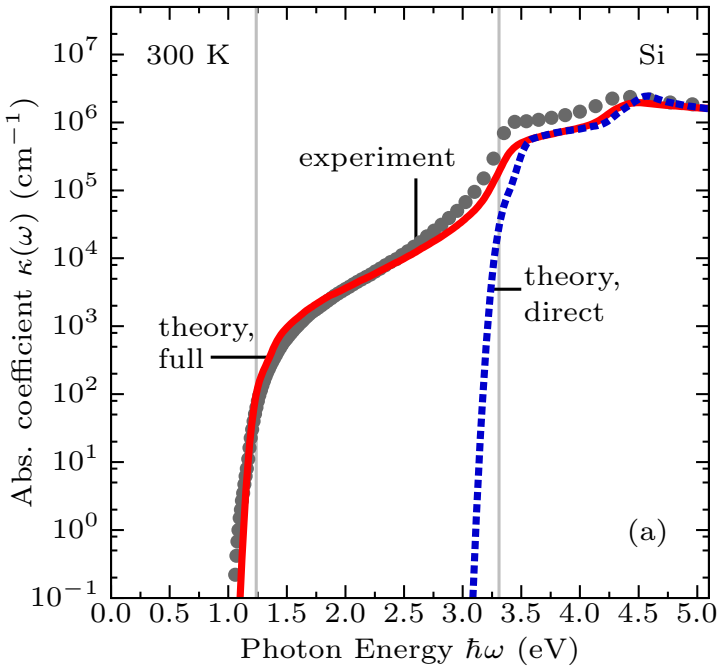
- *Appl. Phys. Lett*. **100**, 011914 (2012); https://doi.org/10.1063/1.3671162
- *Phys. Rev. B* **92**, 235201 (2015); https://doi.org/10.1103/PhysRevB.92.235201
- *Appl. Phys. Lett*. **115**, 082105 (2019); https://doi.org/10.1063/1.5109569

Alternative method (1): Special Displacement Method

Calculate direct optical absorption in a single optimal supercell with atoms displaced according to a linear combination of the phonon modes.

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

See lecture on special displacement method (Zacharias Fri.1) and Phys. Rev. Research 2, 013357 (2020)



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

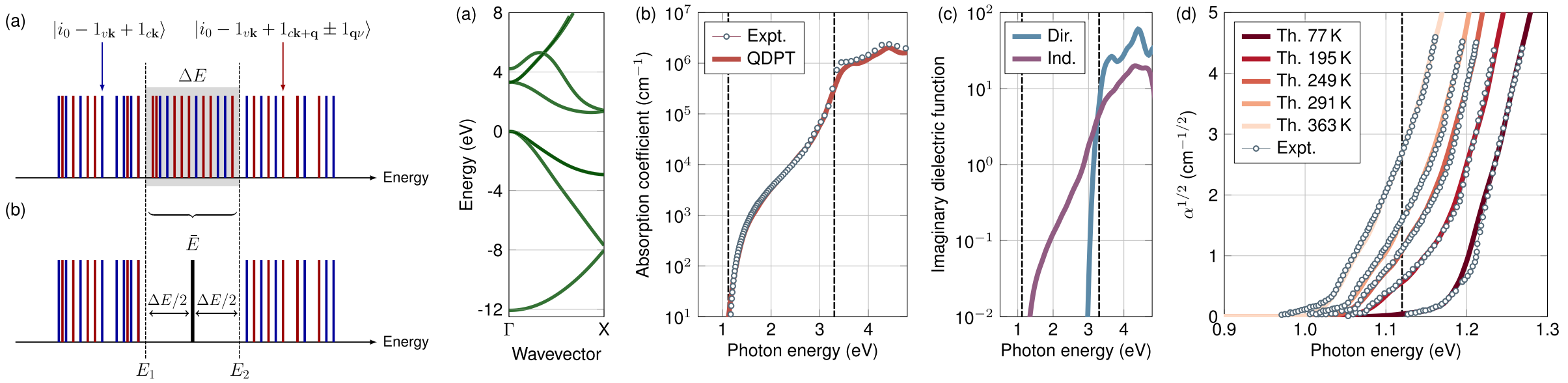
$$\Delta\tau_{\kappa\alpha} = (M_{\rm p}/M_\kappa)^{\frac{1}{2}} \sum_\nu (-1)^{\nu-1} e_{\kappa\alpha,\nu}\, \sigma_{\nu,T}.$$

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

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

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

Alternative method (2): Quasi-Degenerate Perturbation Theory

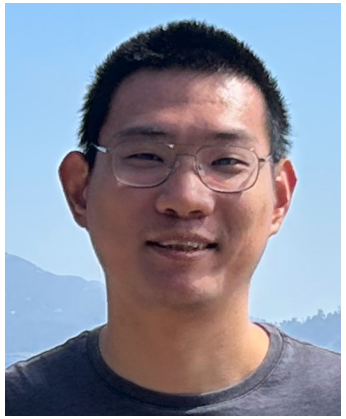


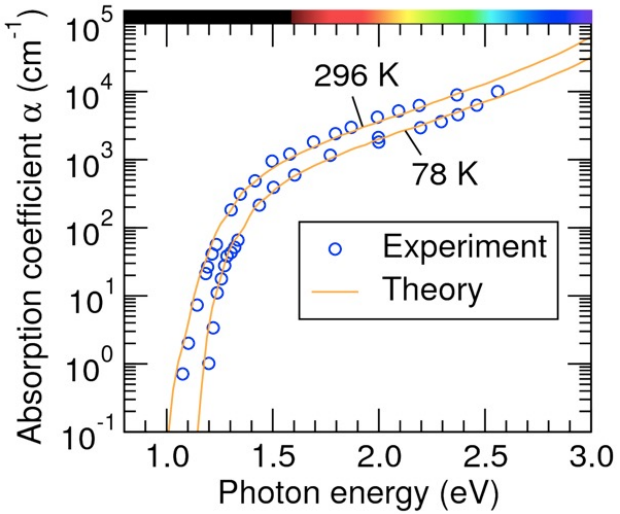
The electron-phonon interaction mixes states within a quasi-degenerate window, the resulting states incorporate the effect of phonons on the wave functions. Optics is then calculated using first-order perturbation theory. Good agreement with experiment for direct and indirect regime simultaneously.

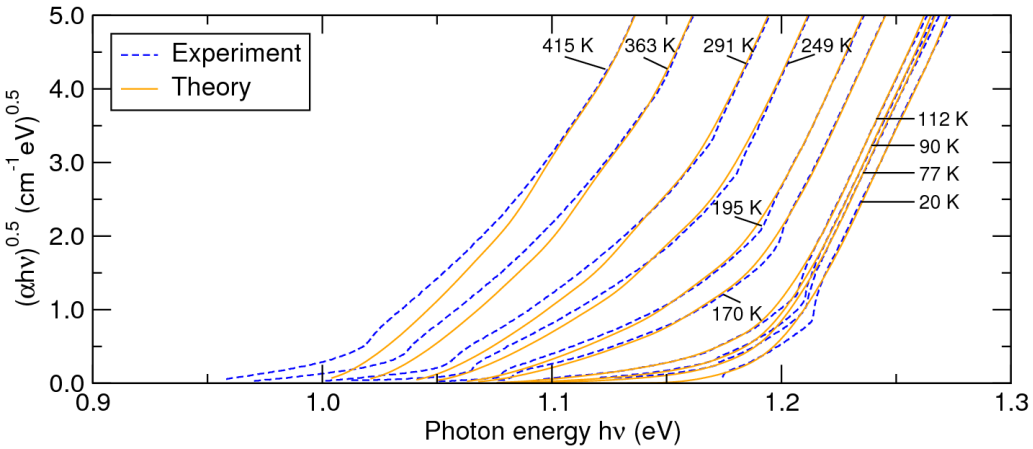
See (Tiwari Sat.6) and *Phys. Rev. B* **109**, 195127 (2024), https://doi.org/10.1103/PhysRevB.109.195127

References

- Mark Fox, *Optical Properties of Solids*, Oxford Master Series in Condensed Matter Physics
- Bassani and Pastori Parravicini, *Electronic States and Optical Transitions in Solids*, Oxford, New York, Pergamon Press, Chapter 5.
- Rondinelli and Kioupakis, *Annu. Rev. Mater. Res.* **45**, 491 (2015)
- Giustino, *Rev. Mod. Phys*. **89**, 015003 (2017)
- Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett.* **108**, 167402 (2012)
- Lee et al., *npj Computational Materials* **9**, 156 (2023)
- Zhang, Shi, Leveillee, Giustino, Kioupakis, *Phys. Rev. B* **106**, 205203 (2022)







Acknowledgements

Developers: **Xiao Zhang** (Thu.4), Kyle Bushick (LLNL), Joshua Leveillee (LANL), Feliciano Giustino (U Texas Austin), Samuel Poncé (Université catholique de Louvain), Roxana Margine (Binghamton), Marios Zacharias (Rennes), Sabyasachi Tiwari (UT Austin)

Collaborators: Chris Van de Walle (UCSB), Hartwin Peelaers (U Kansas), Steven Louie, Marvin Cohen, (Berkeley), Andre Schleife (Illinois) and Friedhelm Bechstedt (Jena)

Thank you for your attention