# Band filling and relaxation effects in the transient dielectric function of Ge

Stefan Zollner

New Mexico State University, Las Cruces, NM 88003

**Ph.D. thesis of Carlos Armenta (2025)**
**To be continued by Beata Hroncova**

In collaboration with:
Martin Zahradník, Mateusz Rebarz, Carola Emminger, Shirly Espinoza, Saul Vazquez-Miranda, Jakob Andreasson
ELI Beamlines Facility, The Extreme Light Infrastructure ERIC, Za Radnicí 835, 25241 Dolní Brežany, Czech Republic

- AFOSR (Grant No. FA9550-24-1-0061, Lt. Col. Wooddy S. Miller Ph.D.)
- AFRL (Grant No. FA9453-23-2-0001)

# New Mexico State University, Las Cruces

**Land grant institution, Carnegie R1**
Comprehensive: Arts and Sciences, Education, Business, Agriculture
Ph.D. programs in sciences, engineering, agriculture; Ag extension;
**Chile Pepper Institute**

**12,700 students** (11,000 UG, 1,700 GR), 1000 faculty

**Minority-serving**, Hispanic-serving (60% Hispanic/NA, 26% White)
Small-town setting (111,000)

**Military-friendly** institution (Army and Air Force ROTC programs)

**Nearby federal labs:** WSMR, NASA, Holloman AFB, Ft. Bliss, Sandia, LANL, AFRL.

**Community engagement** classification
(first-generation students, Pell grant recipients)

**Physics: BS/BA, MS, PhD degrees**. 67 UG and 39 GR students.
**12 faculty** (HE Nuclear and Materials Physics), **2.4 M$ research expenditures.**
**ABET-accredited BS in Physics** and **BS in Engineering Physics**

# DOD SCALE: Clearable Semiconductor Workforce

**PhD. students (10):**
Lina S. Abdallah, Nalin Fernando, Nuwanjula S. Samarasingha, Farzin Abadizaman, Carola Emminger, **Rigo A. Carrasco**, **Carlos A. Armenta**, *Yoshitha D. Hettige, Sonam Yadav, Beata Hroncova.*

**MS students (5):**
**Travis I. Willett-Gies**, Cesar A. Rodriguez**, Jaden R. Love**, ***Haley B. Woolf***, *Aaron Lopez Gonzalez*.

**Undergraduate students (22):**
**Amber A. Medina**, Maria Spies, **Cayla M. Nelson**, **Eric DeLong**, **Christian J. Zollner**, **Khadijih Mitchell**, Ayana Ghosh, **T. Nathan Nunley**, **Laura G. Pineda**, **Luis A. Barrera**, **Dennis P. Trujillo**, **Jaime M. Moya**, **Jacqueline A. Cooke**, **Alexandra P. Hartmann**, **Cesy M. Zamarripa**, **Zachary Yoder**, **Pablo P. Paradis**, Melissa Rivero Arias, **Atlantis K. Moses**, **Danissa P. Ortega**, ***Gabriel Ruiz, Meghan Worrell, Jesus Marquez***.

US citizens in **bold**. Current students in *italics*.
Most work in semiconductor wafer manufacturing, electronics and photonics, aerospace R&D, STEM education.

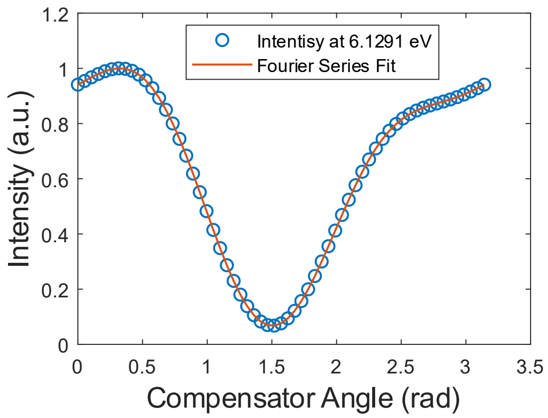
# Current Projects and Interests

- Improve the fundamental understanding of photonic devices and components (AFOSR).
- Explore or re-examine fundamental principles underlying **light propagation** and **light-matter interaction** (ONR EO/IO Sensors).
- **Materials characterization** (ellipsometry, photoluminescence, XRD) for IR detectors and lasers.

- Fundamental principles of photon absorption at the **direct band gap** (Emminger, Hroncova).
- Explore photon absorption by **optical interband transitions** above the lowest gap (Armenta).
- Explore photon absorption in **highly excited semiconductors** (Armenta).

- *Defects in Ge-Sn alloys by IR photoluminescence under hydrostatic pressure (Yadav, Worrell).*
- *Thermal oxidation of Ge and Ge-Sn alloys (Woolf, MS thesis).*
- *Direct gap absorption in $\alpha$-tin to measure hole concentration (Love, MS thesis).*
- *Characterization of insulating TaN for superconducting Q-bits (Lopez-Gonzalez, MS thesis)*

# Spectroscopic ellipsometry




Fundamental equation of ellipsometry:

$$\rho = \tan\Psi e^{i\Delta} = \frac{r_\mathrm{p}}{r_\mathrm{s}}$$

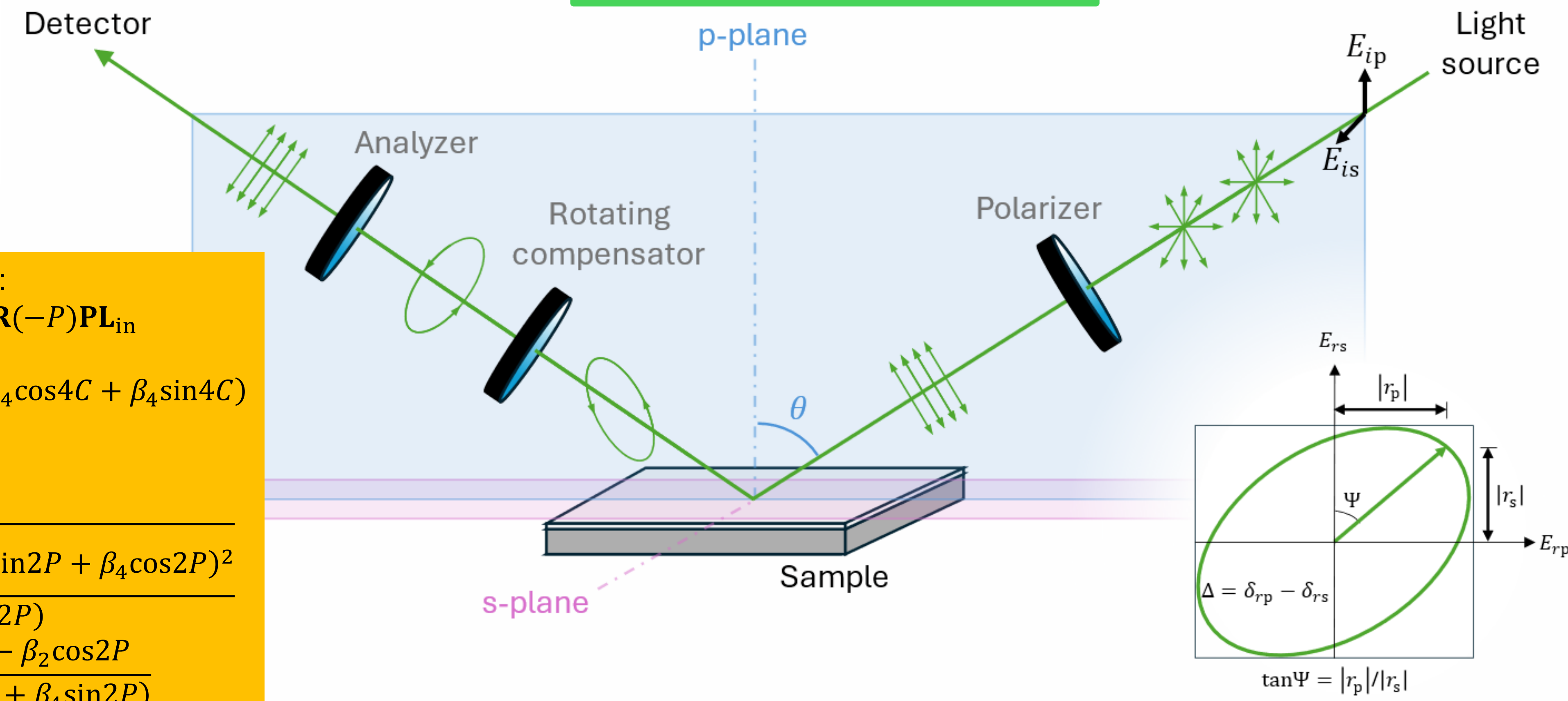
Complex pseudo-dielectric function:

$$\langle\varepsilon\rangle = \sin^2\theta\left[1 + \tan^2\theta\left(\frac{1-\rho}{1+\rho}\right)\right]$$

Fresnel equations:

$$r_\mathrm{p} = \frac{\varepsilon\cos\theta - (\varepsilon - \sin^2\theta)^{1/2}}{\varepsilon\cos\theta + (\varepsilon - \sin^2\theta)^{1/2}}$$

$$r_\mathrm{s} = \frac{\cos\theta - (\varepsilon - \sin^2\theta)^{1/2}}{\cos\theta + (\varepsilon - \sin^2\theta)^{1/2}}$$




RCE in Jones matrix/vector formalism:

$$\mathbf{L}_\mathrm{out} = \mathbf{A}\mathbf{R}(-A)\mathbf{R}(C)\mathbf{C}\mathbf{R}(-C)\mathbf{S}\mathbf{R}(-P)\mathbf{P}\mathbf{L}_\mathrm{in}$$

$$I(C) = I_0(\alpha_0 + \alpha_2\cos2C + \beta_2\sin2C + \alpha_4\cos4C + \beta_4\sin4C)$$

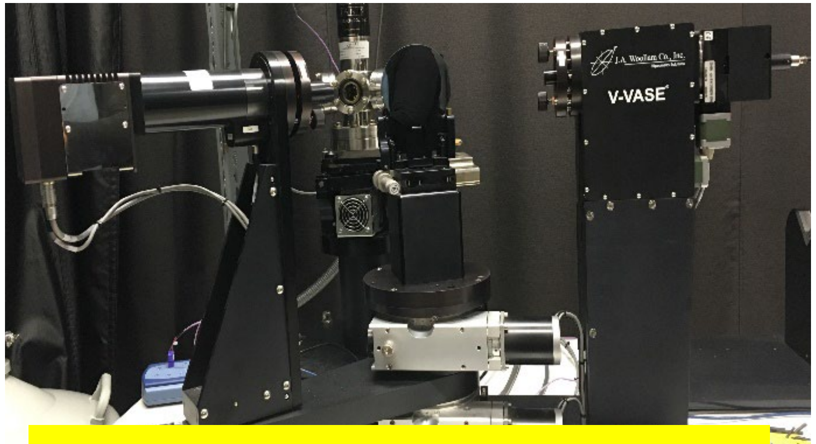
Ellipsometric angles:

$$\tan2\Psi = -\frac{\sqrt{\dfrac{(\alpha_2^2+\beta_2^2)(1-\cos\delta)^2}{\sin^2\delta} + 4(-\alpha_4\sin2P + \beta_4\cos2P)^2}}{2(\alpha_4\cos2P + \beta_4\sin2P)}$$

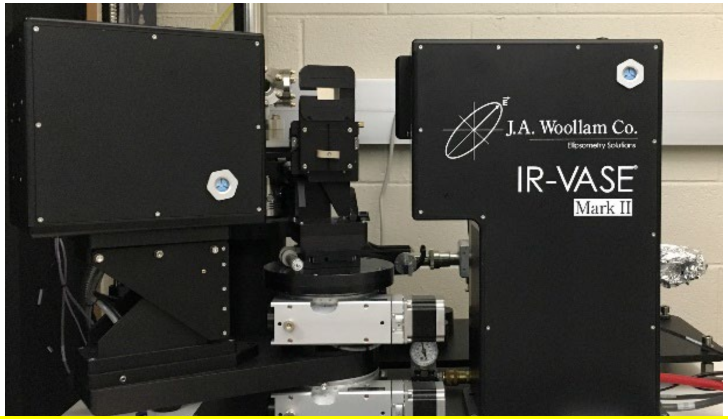
$$\tan2\Delta = \left(\frac{1-\cos\delta}{2\sin\delta}\right)\frac{\alpha_2\sin2P - \beta_2\cos2P}{2(\alpha_4\cos2P + \beta_4\sin2P)}$$


H. Fujiwara, *Spectroscopic Ellipsometry* (Wiley, 2007).
R. Kleim *et al.*, J. Opt. Soc. Am. A **11**, 2550 (1994).

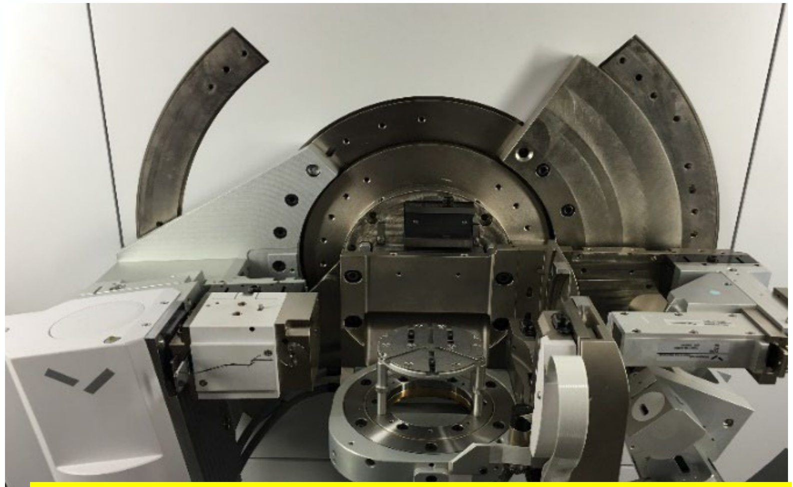
# Ellipsometry and X-Ray Instrumentation




**Spectroscopic Ellipsometer**
**190 to 2500 nm (0.5 to 6.5 eV)**



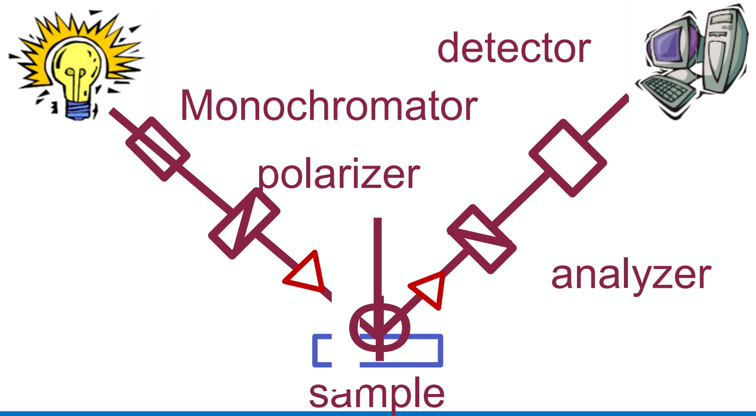

**Mid-Infrared Ellipsometer**
**1.25 to 40 μm (250 to 8000 cm$^{-1}$)**



**X-ray diffraction & reflectance**

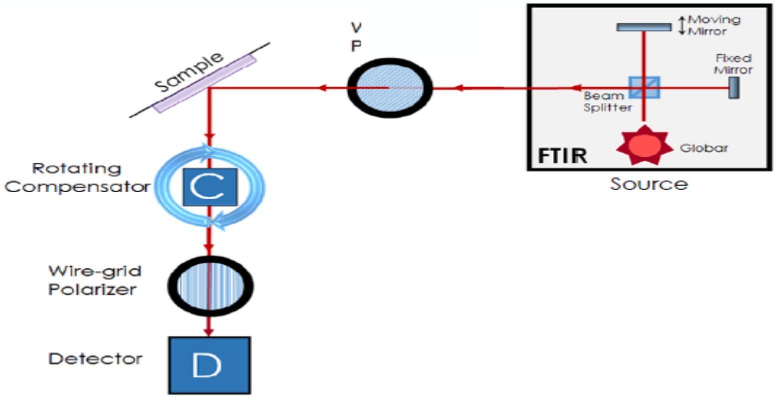
## Spectroscopic Ellipsometry:

- **Thickness (100 to 10000 Å)**
- **Absorption, band gap**
- **Refractive index**



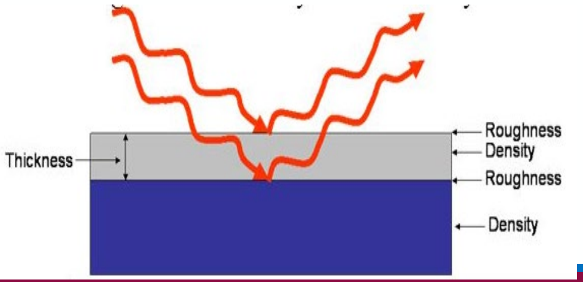

## FTIR ellipsometry:

- **Very thick films (> 5000 Å)**
- **Phonon absorption**
- **Optical Constants**




## XRD/XRR:

- **Crystal structure**
- **Lattice spacings** (strain)
- **Thickness** (5 Å to 1000 Å)
- **Surface, roughness** layer
- **Density**



# Tools for Temperature-Dependent Ellipsometry

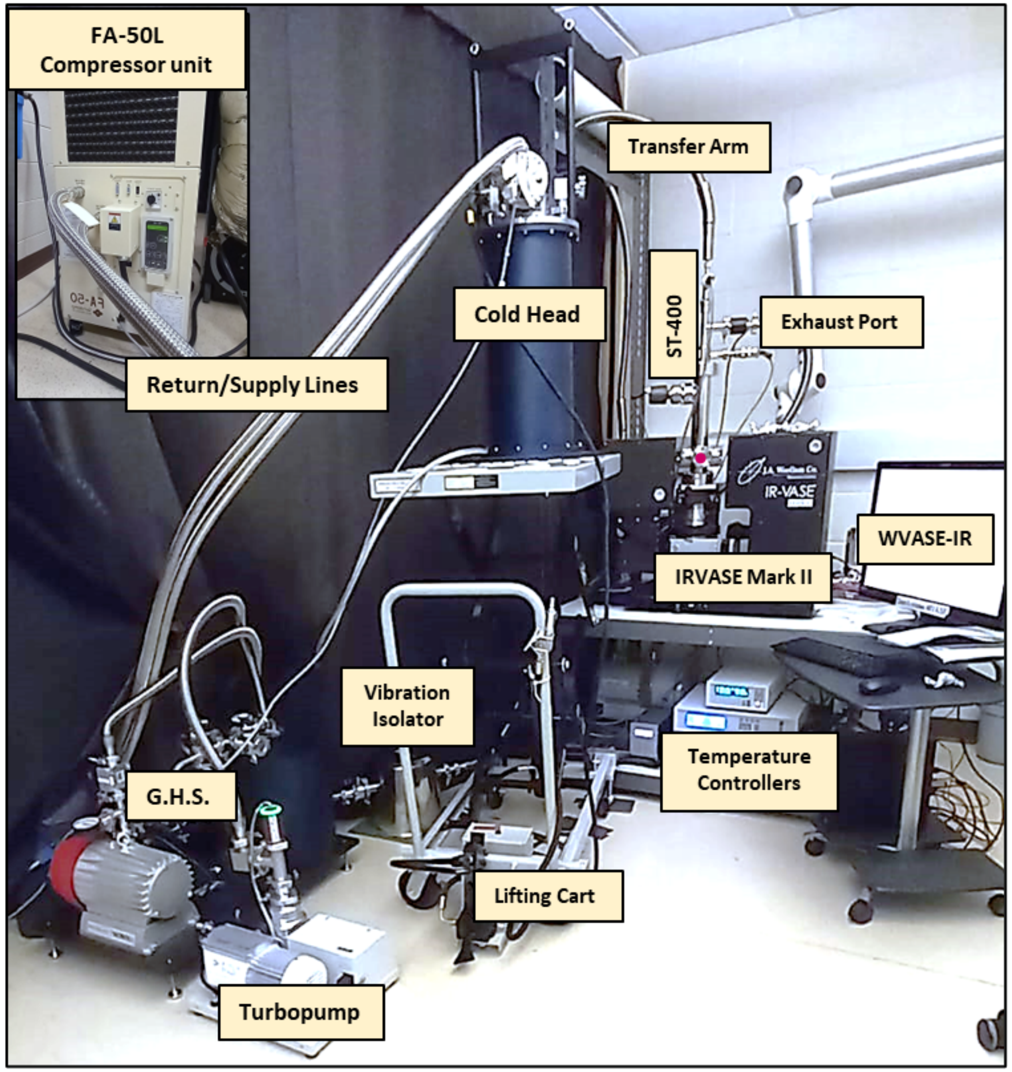
| Combined System for Temperature Dependent SE | |
|---|---|
| FA-50L Helium Compressor Unit | Sumitomo Heavy Industries, Ltd. |
| RGC4 Cryogen Free Recirculating Gas Cooler | Lake Shore Cryotronics, Inc. |
| ST-400 Cryostat | Lake Shore Cryotronics, Inc. |
| IR-VASE Mark II | J.A. Woollam Co. |

**Sample preparation:**

- Samples were mounted using Ag conductive paint.
- Light pressure was applied to maximize contact with the cryostat sample stage.
- The Ag paint cured overnight at room temperature.

**Measurement procedure:**

- 300 K scans were taken outside of the cryostat.
- The sample was then aligned inside the cryostat.
- Programed an automated temperature series in WVASE-IR.
- Collected data from 300 K to 10 K in 25 K steps with 64 $cm^{-1}$ resolution.




Closed-cycle system works well.

Vibrations do not seem to be a problem.

Ongoing issue: Thin ice layer forms on sample (even in UHV).

Window calibration is important.

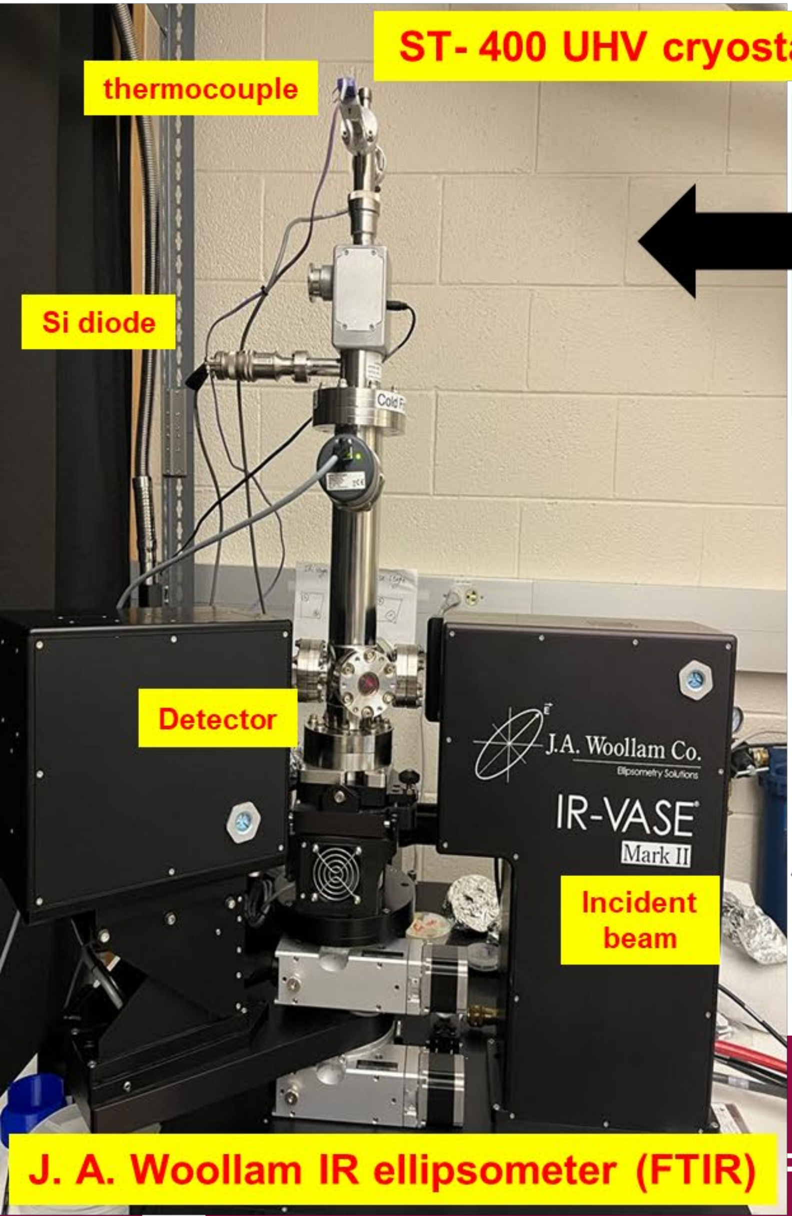
<u>Custom feature:</u> **Diamond windows** for cryostat.


NM STATE

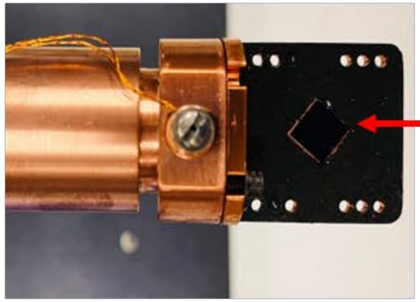
ARO (W911NF-22-2-0130)

Jaden Love, Atlantis Moses
SZ, Adv. Opt. Techn. **11**, 117 (2022)

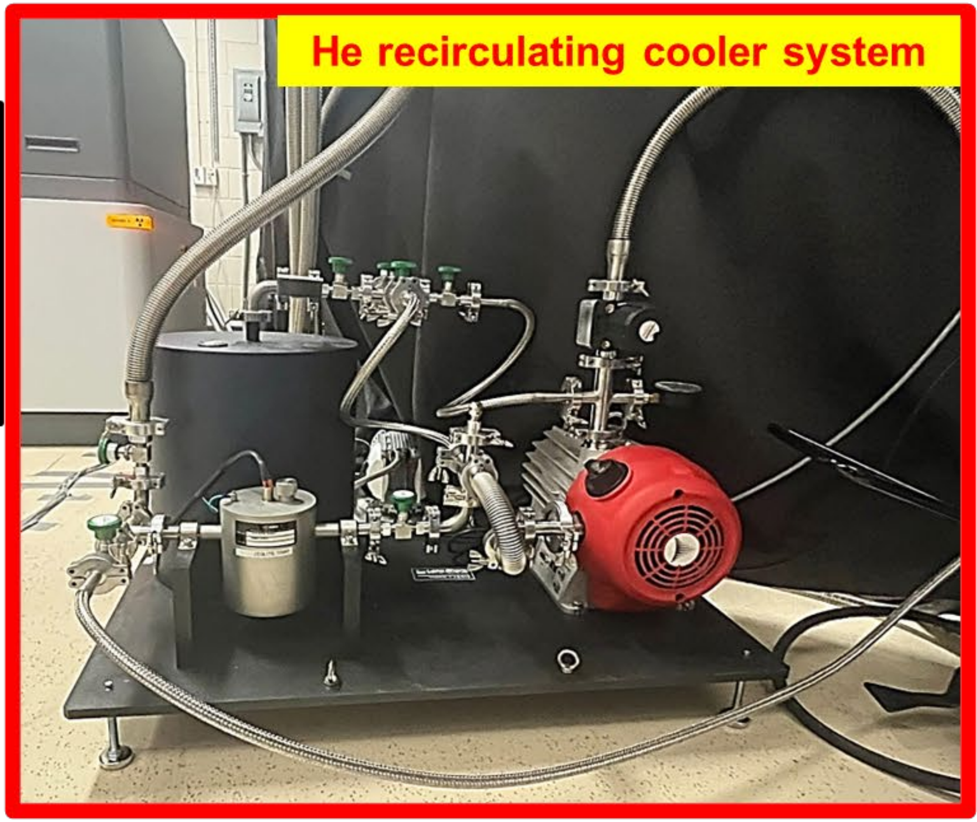
# Tools for Temperature-Dependent Ellipsometry



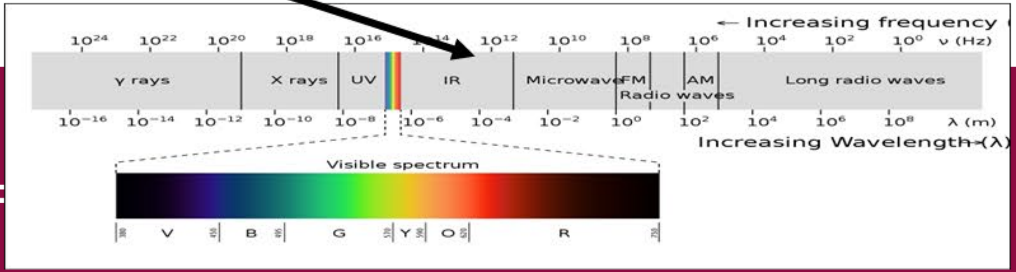

- Temperature range : **25 K to 500 K** (He recirculating cooler).
- Pressure : **$10^{-8}$ Torr**.
- Resolution : **8 $cm^{-1}$**




Lake Shore model RGC 4 cryogen free closed cycle refrigerated system




Measured the ellipsometric angles $\Psi$ and $\Delta$ of NiO from 250-8000 $cm^{-1}$ at 8 $cm^{-1}$ resolution from 25 to 500 K.





Jaden Love
Atlantis Moses

# Direct Gap Absorption in Germanium

**Fundamental interaction:**

- k.p band structure theory.
- Elliot-Tanguy theory for excitonic absorption.

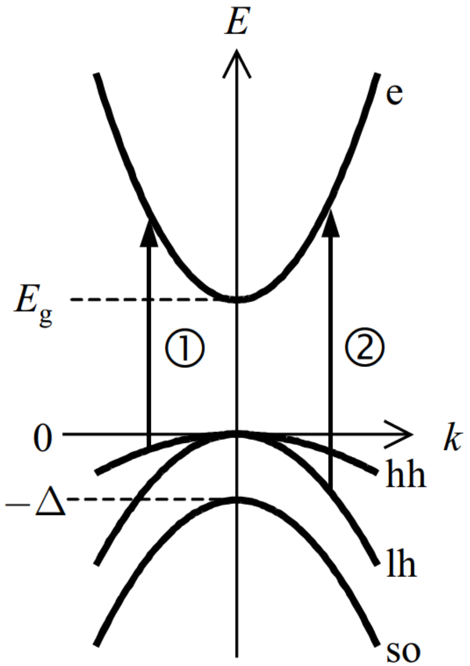
**Fixed parameters:**

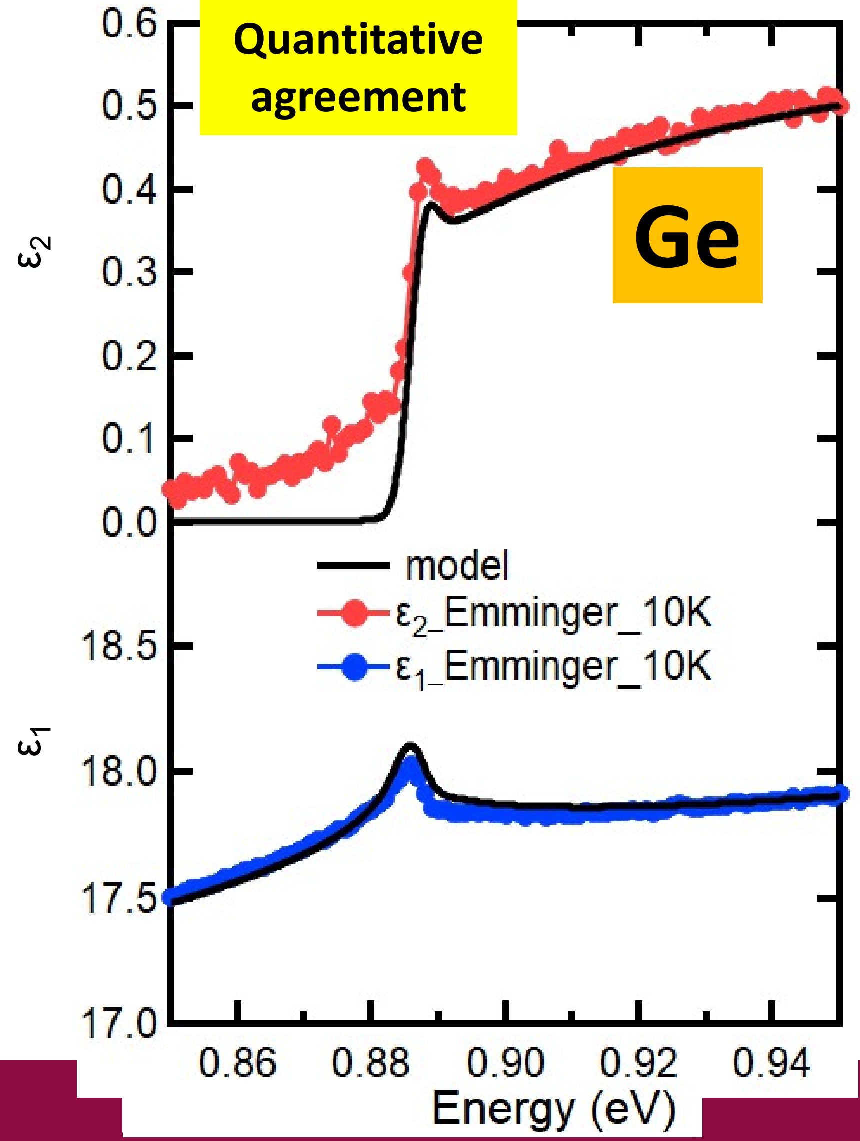
- Electron and hole masses (temperature dependent).
- Excitonic binding energy R.
- **Amplitude A (derived from k.p matrix element P).**

**Adjustable parameters:**

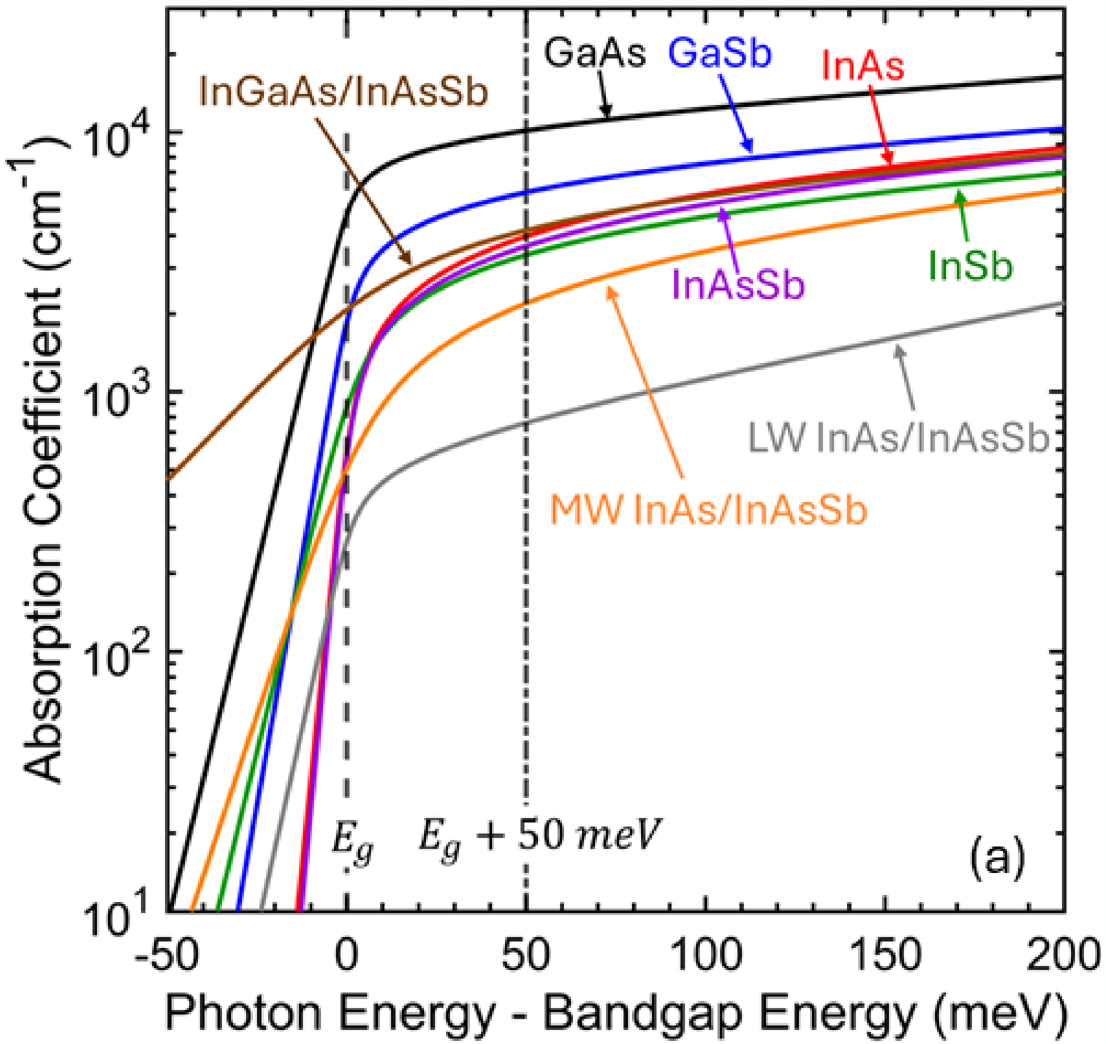
- Broadening Γ: 2.3 meV
- Band gap $E_0$
- Linear background $A_1$ and $B_1$ (contribution from $E_1$ to real part of ε)

**To be continued** for other materials (Ge-Sn alloys) and higher temperatures.



# Can k.p Theory Predict Absorption for Other Materials?




Experimental data suggests that there should be a **universal scaling law** for the direct gap absorption.

Need low-temperature ellipsometry measurements for InAs, GaSb, GaAs, InP, GaP, etc.

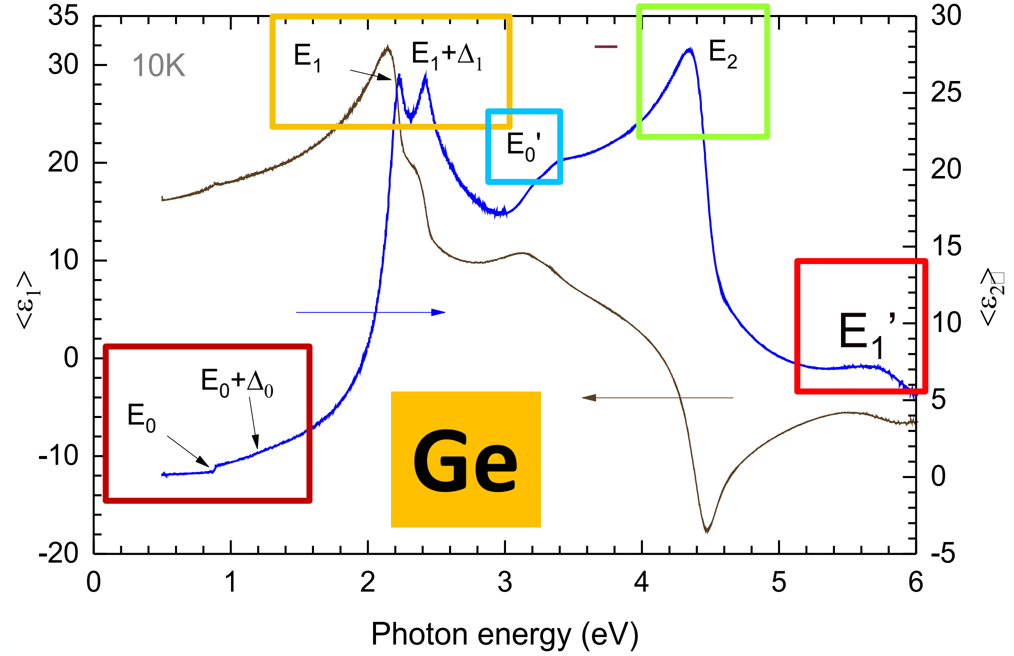
Need to verify with calculations for **binary compounds** and **semiconductor alloys**.

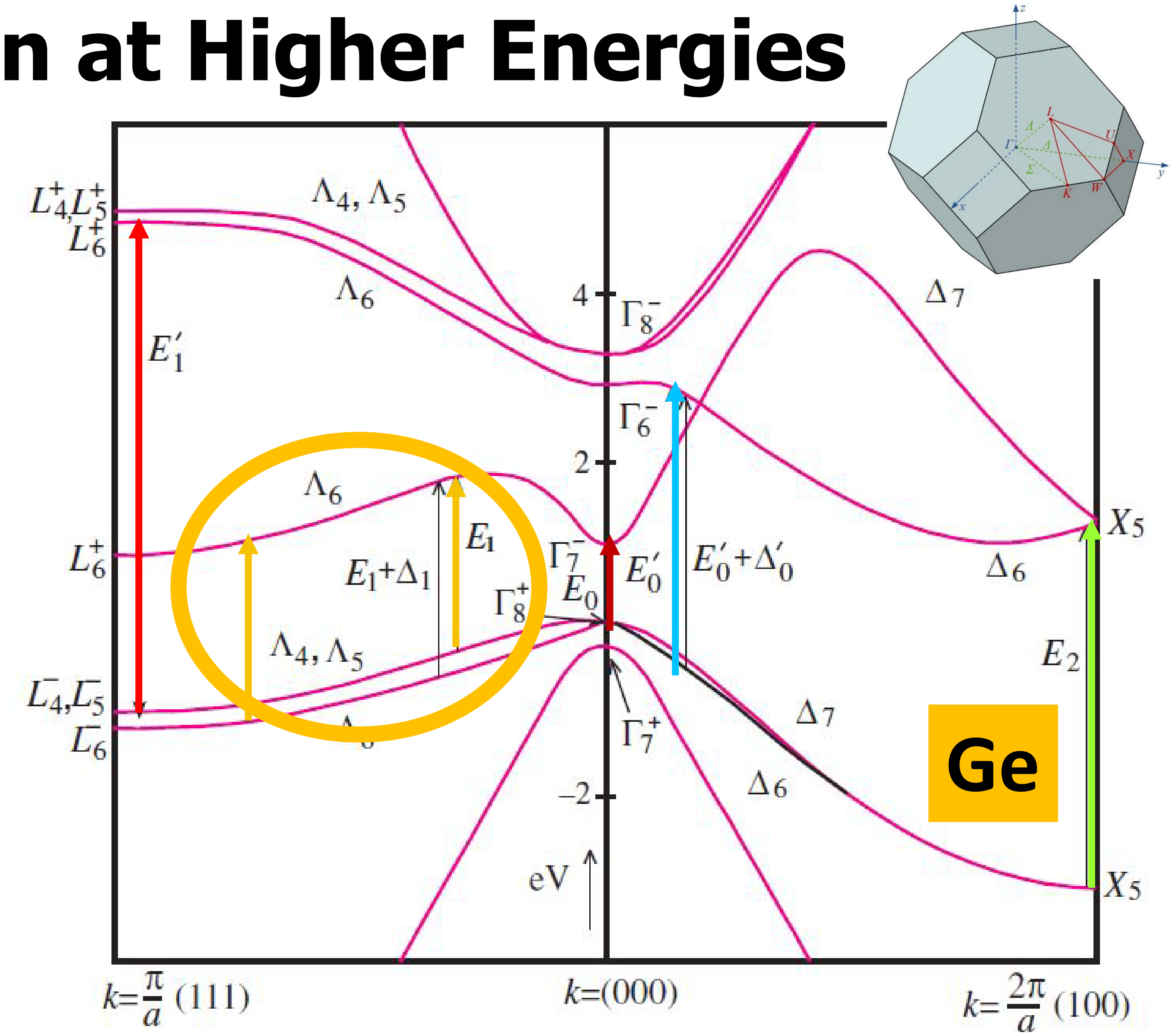
Can this theory be generalized for **superlattices** (Kronig-Penney model)?

# Direct Absorption at Higher Energies

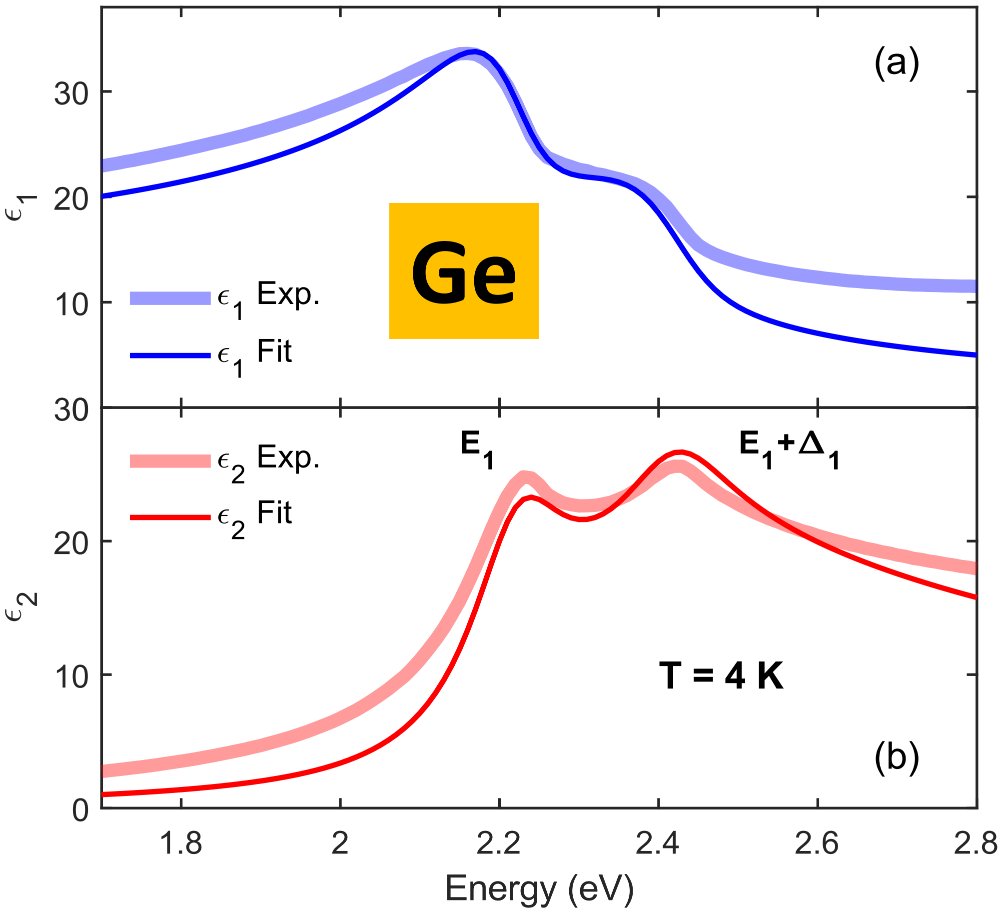
- Structures in $\varepsilon$ due to interband transitions
- Joint density of states
- Van Hove singularities

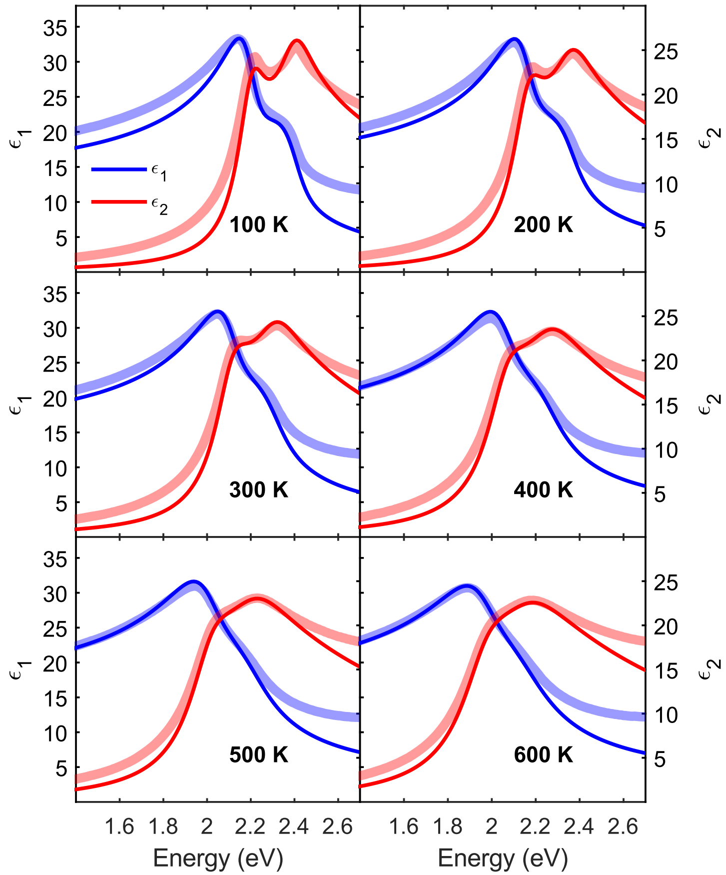
$$D_j(E_{CV}) = \frac{1}{4\pi^3}\int \frac{dS_k}{|\nabla_k(E_{CV})|}$$



# Direct Absorption at Higher Energies



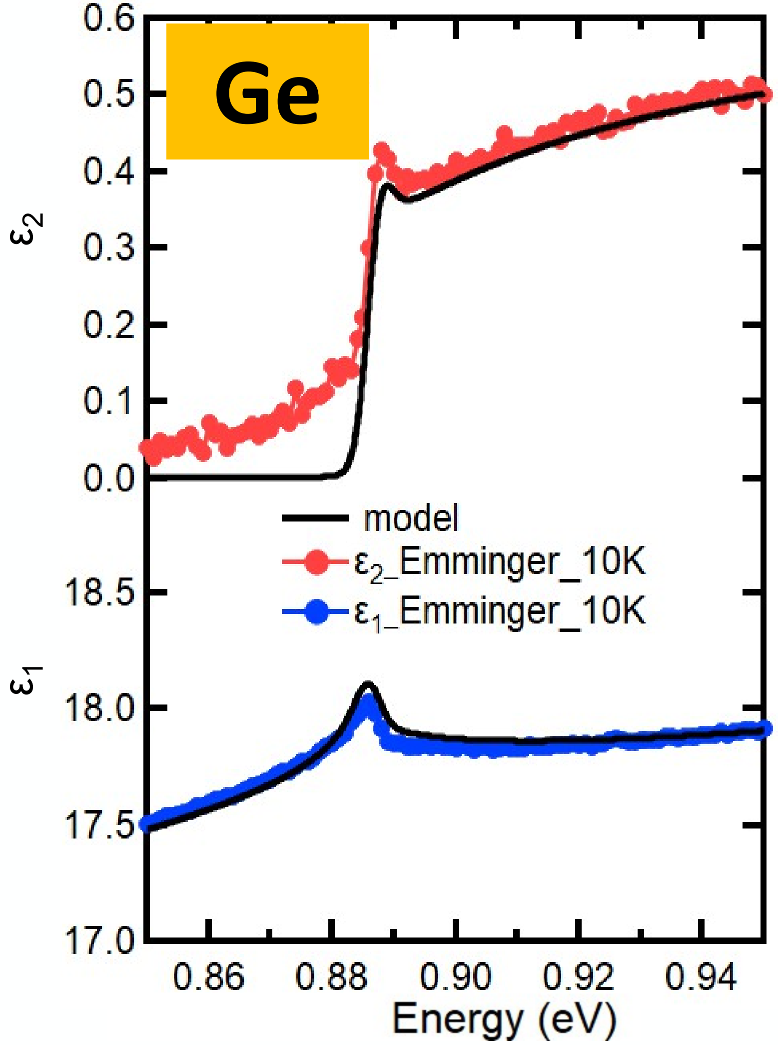

k.p theory works very well for $E_1$ and $E_1+\Delta_1$ transitions.

Effective masses and dipole matrix element from k.p theory.

**Two-dimensional excitons (Tanguy).**

**No parameter for amplitude of absorption peaks.**

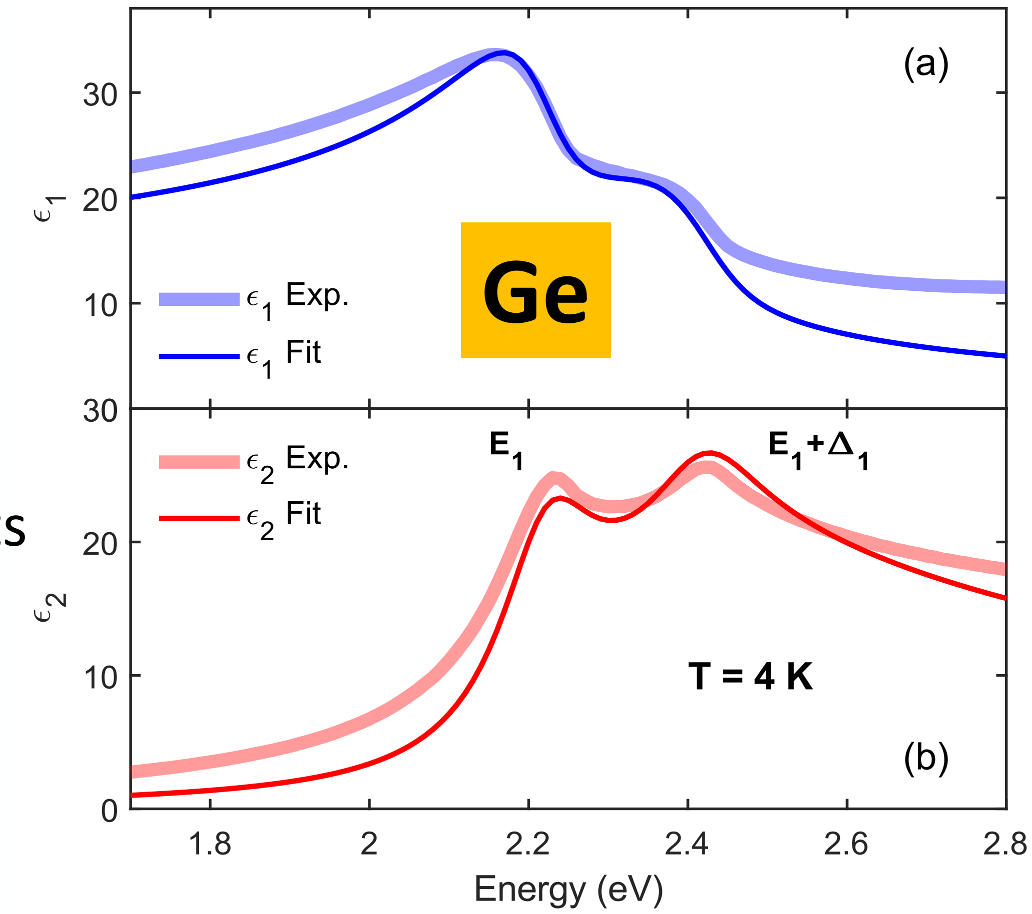
# Can we connect the two spectral regions?




Maybe ???

Conduction band nonparabolicity

k-dependent optical transition matrix elements



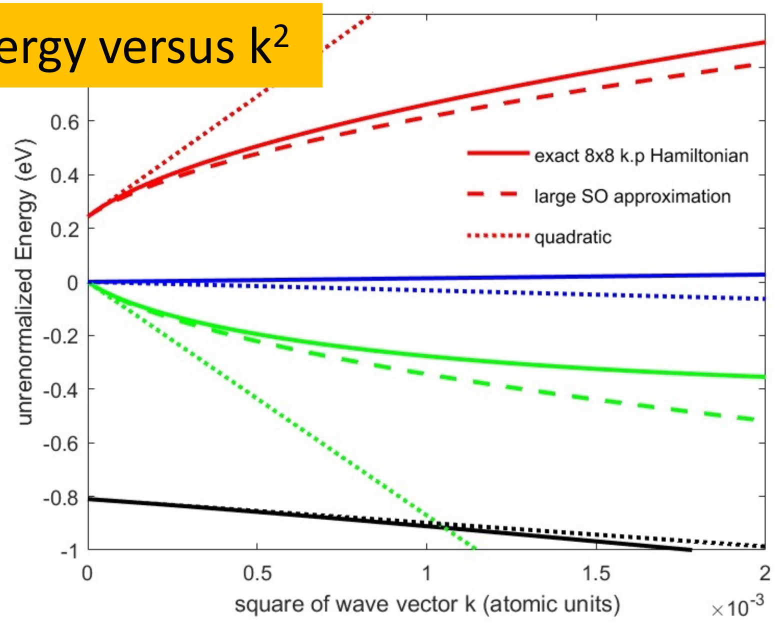


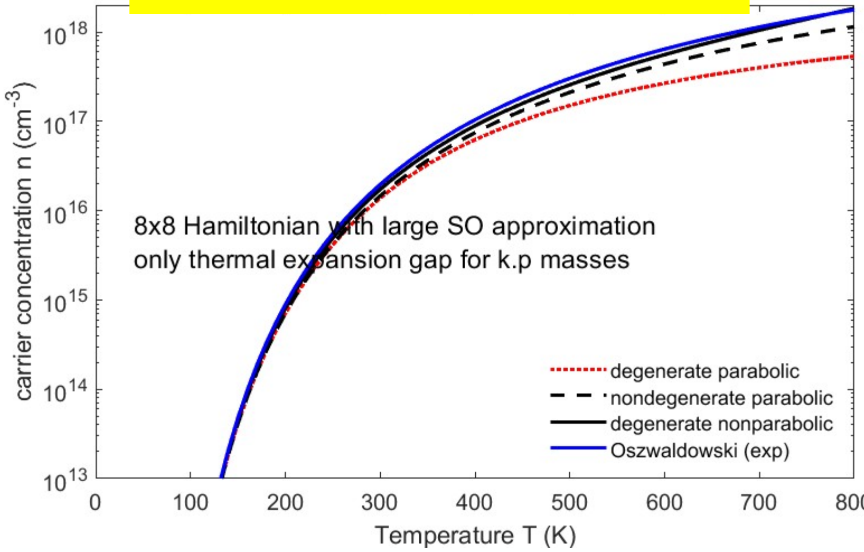

Kane, J. Phys. Chem. Solids **1**, 249 (1957)

# Nonparabolicity of InSb conduction band from k.p theory

Kane 8x8 k·p Hamiltonian:

$$\widetilde{H}_{\vec{k}} = \begin{pmatrix} E_0 & 0 & -\frac{\hbar\vec{k}}{m_0}iP & 0 \\ 0 & -\frac{2\Delta_0}{3} & \frac{\sqrt{2}\Delta_0}{3} & 0 \\ \frac{\hbar\vec{k}}{m_0}iP & \frac{\sqrt{2}\Delta_0}{3} & -\frac{\Delta_0}{3} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$



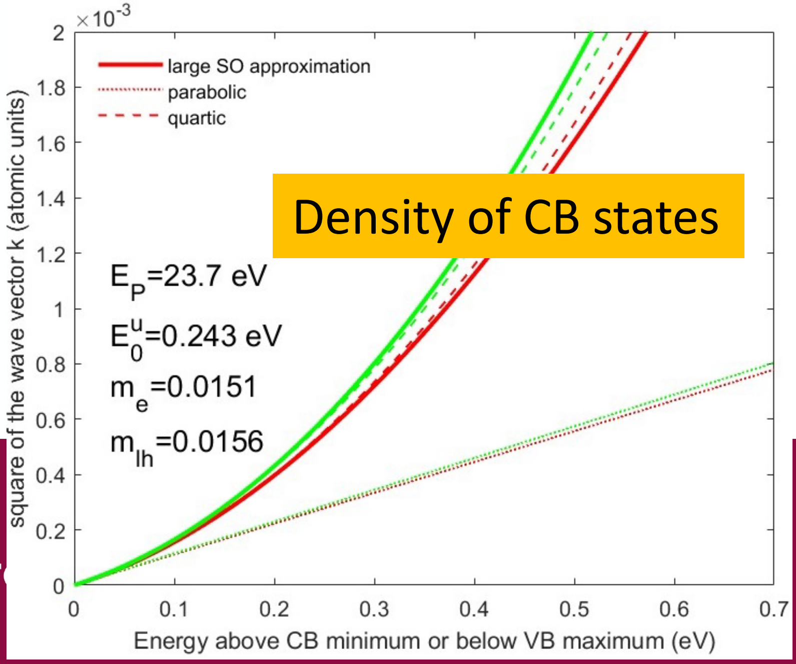




Cubic characteristic equation (solid):

$$\tilde{E}\left(\tilde{E}-E_0\right)\left(\tilde{E}+\Delta_0\right)-\frac{\hbar^2k^2E_P}{2m_0}\left(\tilde{E}+\frac{2\Delta_0}{3}\right)=0$$

Large spin-orbit approximation (dashed):

$$E_{3,4}=\frac{\hbar^2k^2}{2m_0}+\frac{E_0}{2}\left(1\pm\sqrt{1+\frac{\hbar^2k^2}{2m_0}\frac{2}{\mu_{lh}E_0}}\right)$$



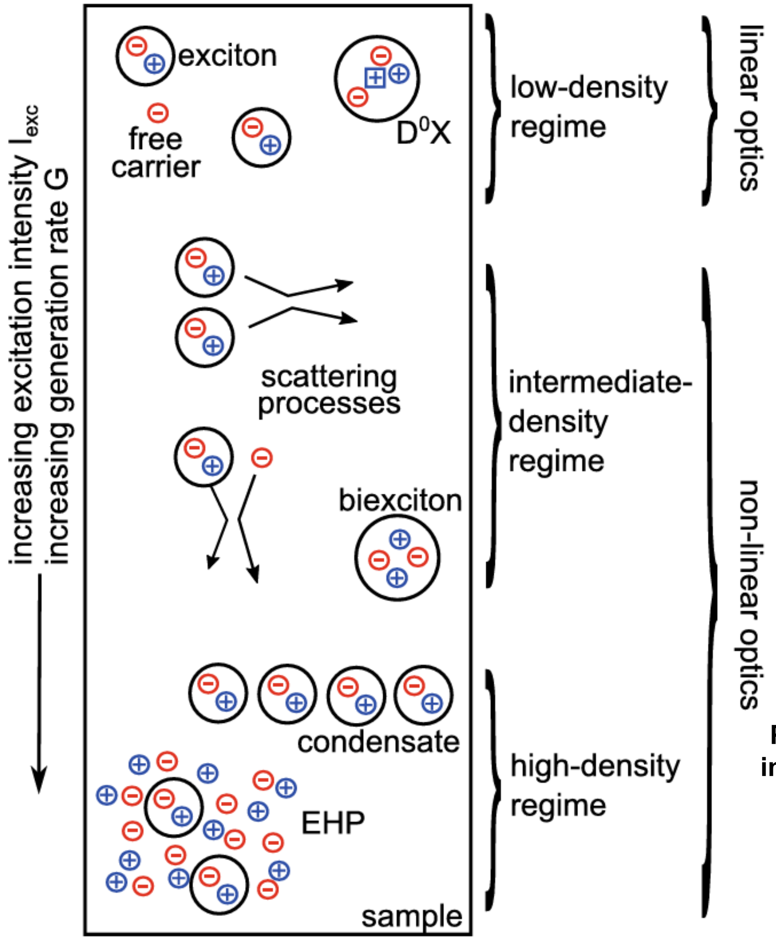

$$\frac{\hbar^2k^2}{2m_0m^*}=\varepsilon\left(1+\alpha\varepsilon+\beta\epsilon^2\right)$$

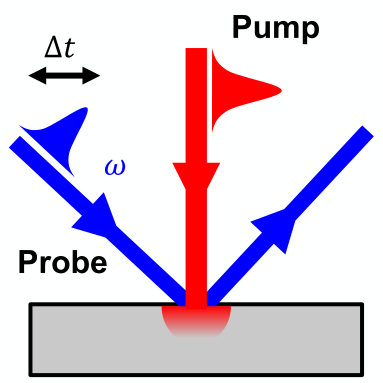
$$\alpha=\frac{(1-m^*)^2}{E_0}$$

Kane, J. Phys. Chem. Solids **1**, 249 (1957).

S. Zollner, JVST A **43**, 012801 (2025)

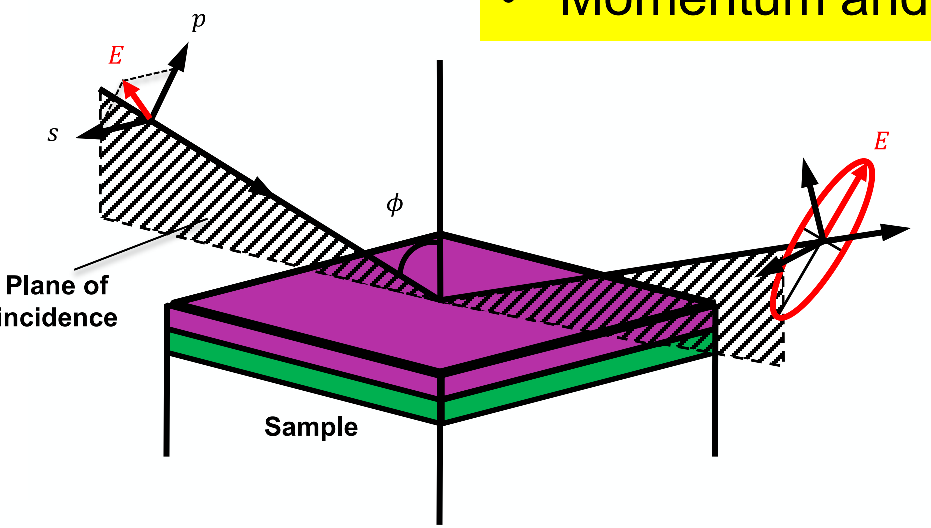
# Absorption in Highly Excited Semiconductors

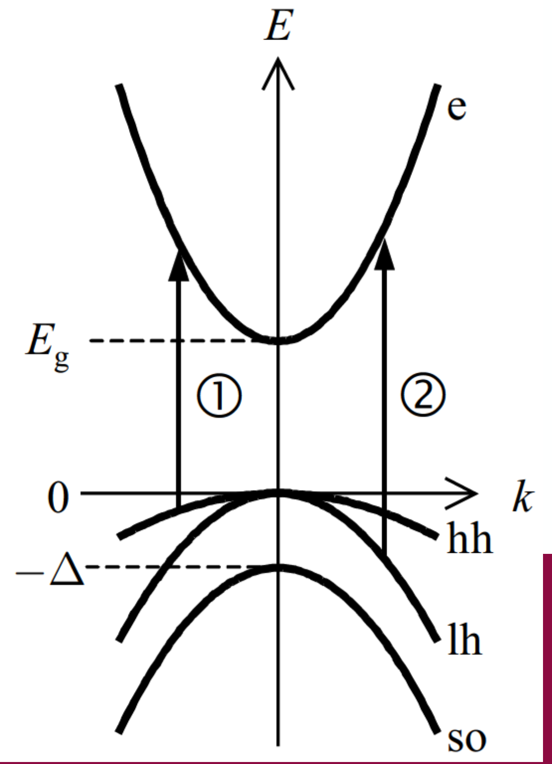



The study of non-linear effects in germanium induced by photoexcited carriers by using time resolved ellipsometry:

- Carrier-carrier scattering.
- **Carrier-phonon scattering.**
- **Intervalley scattering.**
- Momentum and energy relaxation of hot carriers.

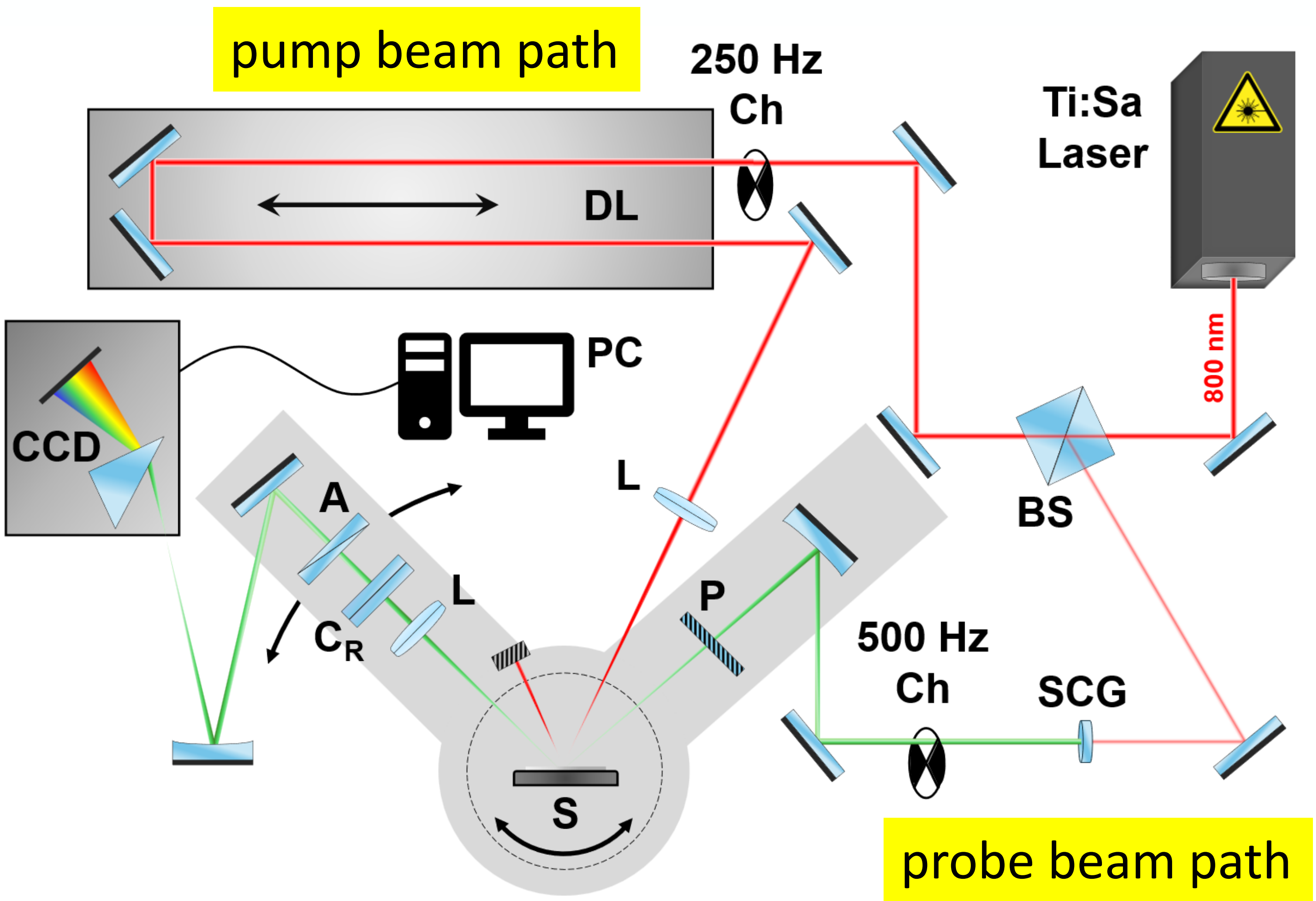





Kalt, Klingshirn, *Semiconductor Optics 2* (Springer, 2024)

# Experiment: Pump-Probe Ellipsometry




Ch: Chopper (500 Hz, 250 Hz)

A: Analyzer

P: Polarizer

$C_R$: Rotating Compensator

L: Lens

S: Sample

DL: Delay Line
(~6.67 ns pump-probe delay, 3 fs resolution)

BS: Beam Splitter

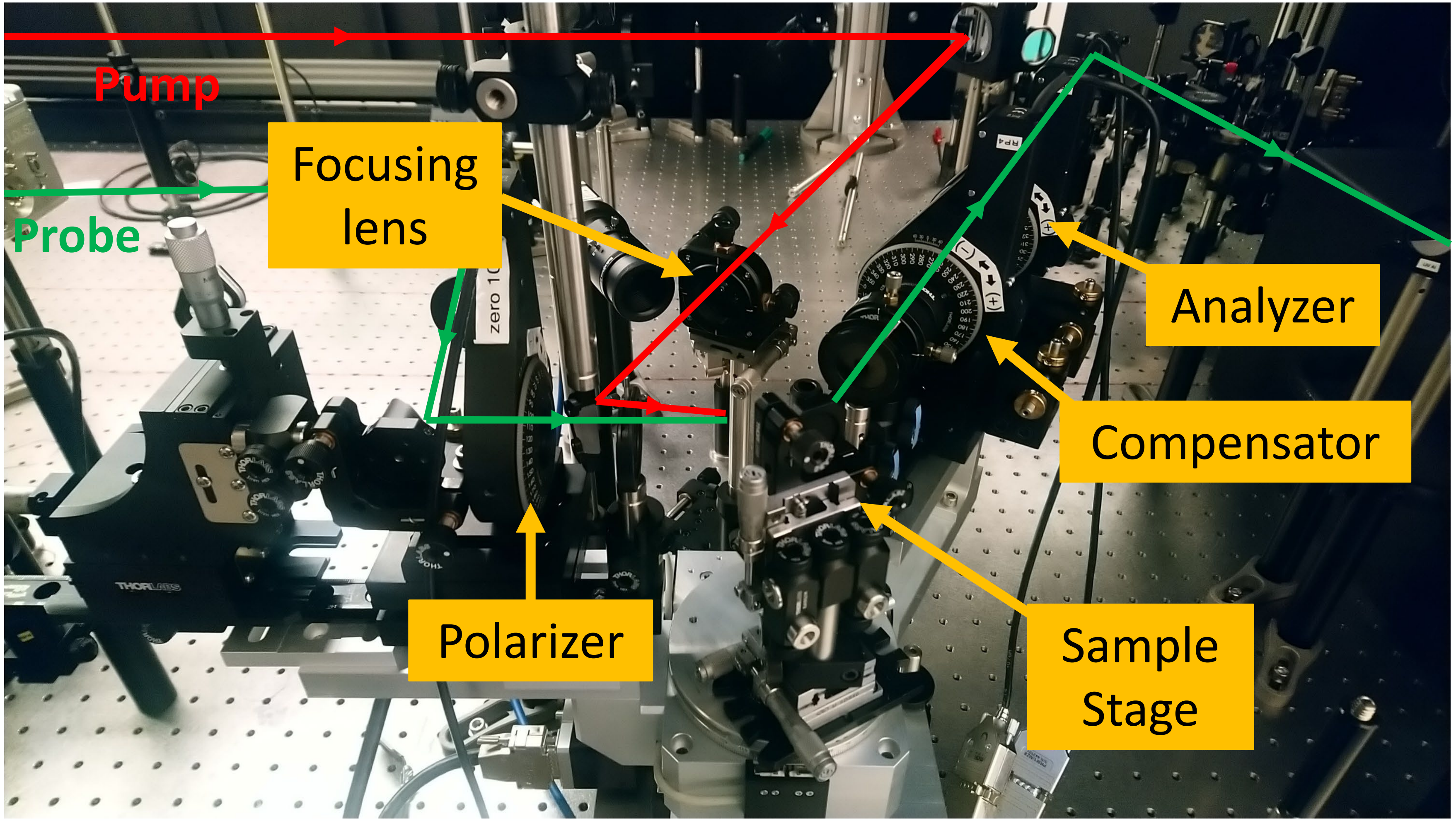
SCG: **Super-continuum Generation**

CCD: Charge-coupled device detector



S. Richter, Rev. Sci. Instrum. **92**, 033104 (2021).
S. Espinoza, Appl. Phys. Lett. **115**, 052105 (2019)
ELI Beamlines, Dolni Bezany, Czech Republic

# Set-up: Femtosecond pump-probe ellipsometry




**Rotating compensator ellipsometer:**

Compensator was rotated in steps of 10$^{o}$ for a total of 55-65 angles.

Probe beam of 350-750 nm at 60$^{o}$ incidence angle.

P-polarized pump beam: 35 fs pulses of 800 nm wavelength at 1 kHz repetition rate.

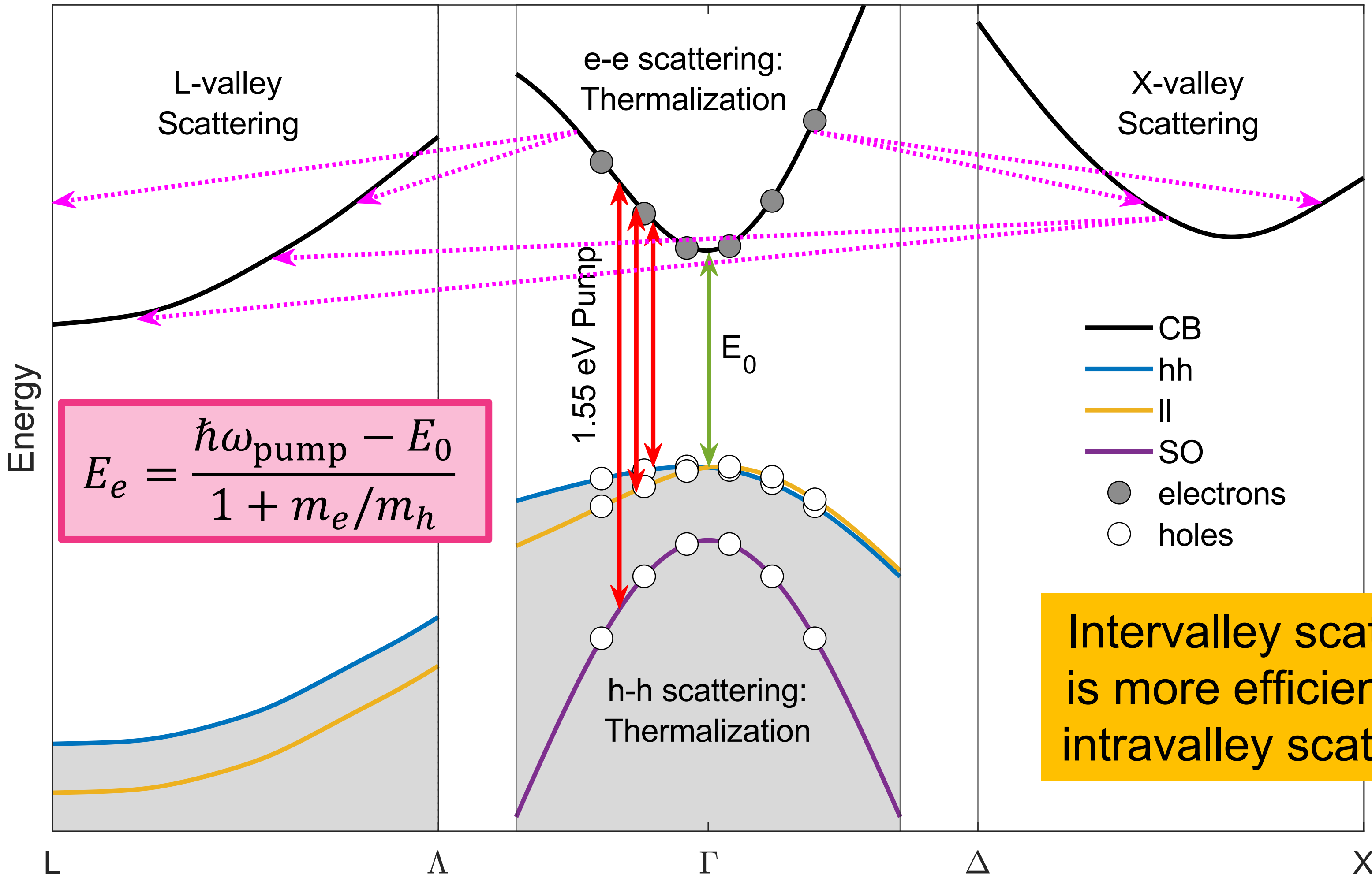
Delay time from -10 to 50 ps.

Time resolution of about 500 fs.



Espinoza et al., APL **115**, 052105 (2019)
ELI Beamlines, Dolni Bezany, Czech Republic

# First 100s of femtoseconds




$$E_e = \frac{\hbar\omega_{\mathrm{pump}} - E_0}{1 + m_e/m_h}$$

Plasma temperature:

$$T_c \approx \frac{E_e}{3k_B}$$

2600 K

$10^{20}$ cm$^{-3}$

Intervalley scattering is more efficient than intravalley scattering.



H. Kalt, C. F. Klingshirn, *Semiconductor Optics 2* (Springer, 2024).
R. R. Alfano, *Semiconductors Probed by Ultrafast Laser Spectroscopy I* (Academic, 1984).

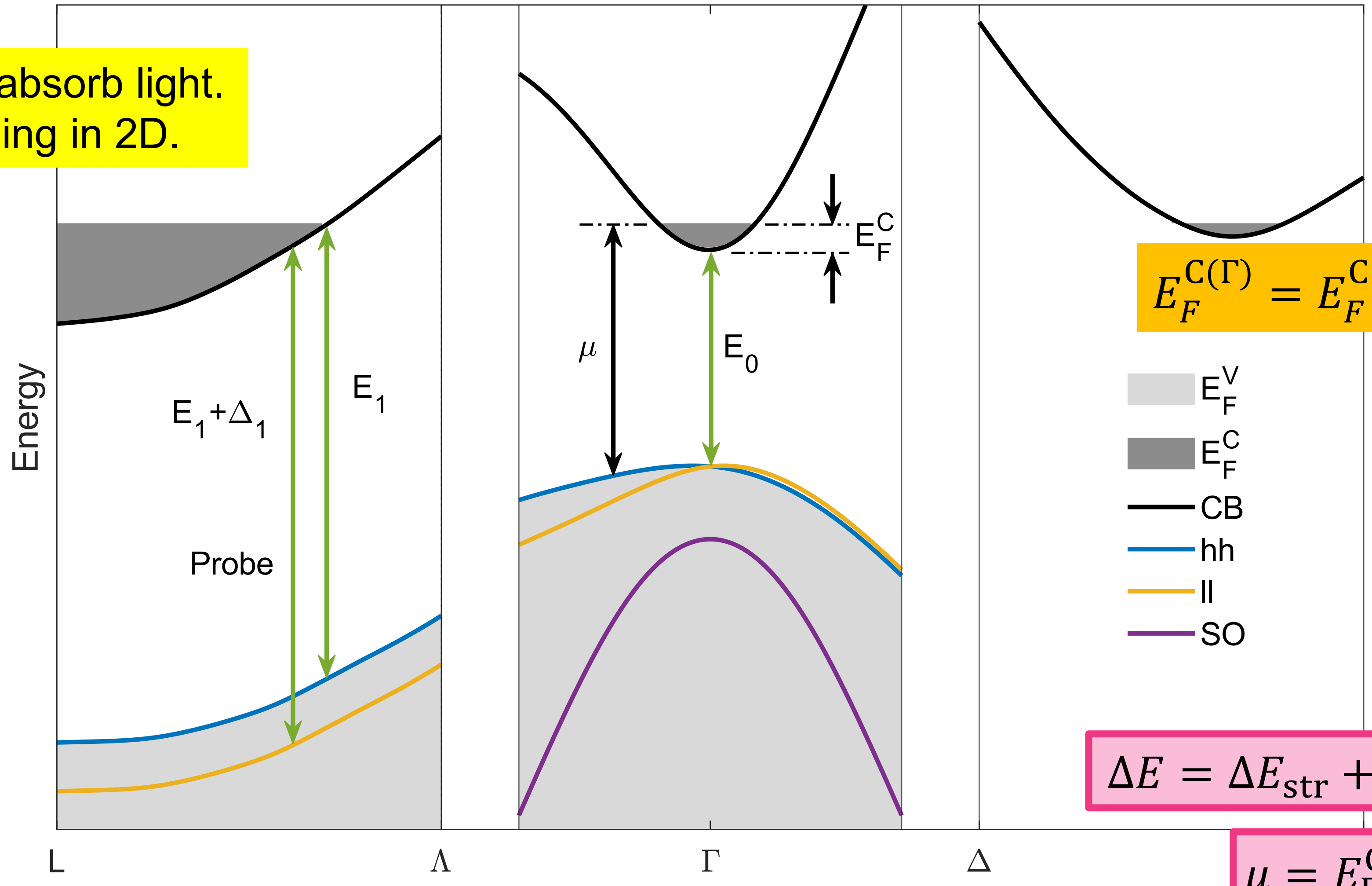
# First few Picoseconds: Thermal Equilibrium

Filled states cannot absorb light.
No theory for screening in 2D.

Plasma temperature:

$$T_c \approx \frac{E_e}{3k_B}$$

2600 K
$10^{20}$ cm$^{-3}$




$$E_F^{C(\Gamma)} = E_F^{C(L)} = E_F^{C(X)}$$

$$\Delta E = \Delta E_{str} + \Delta E_{BGR} + \Delta E_{BM}$$

$$\mu = E_F^C + E_g$$




H. Kalt, C. F. Klingshirn, *Semiconductor Optics 2* (Springer, 2024).
P. Vashishta, Appl. Phys. Rev. B. **25**, 6492 (1982).

# Charge Carrier Statistics from Device Physics

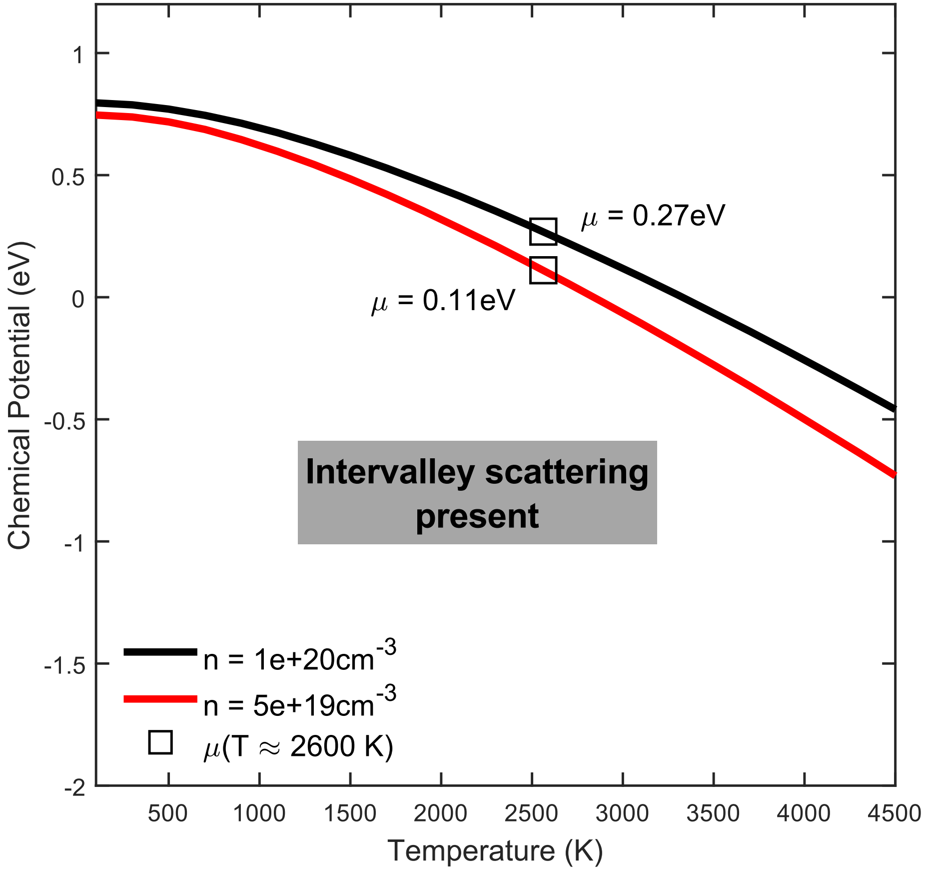
Plasma temperature:

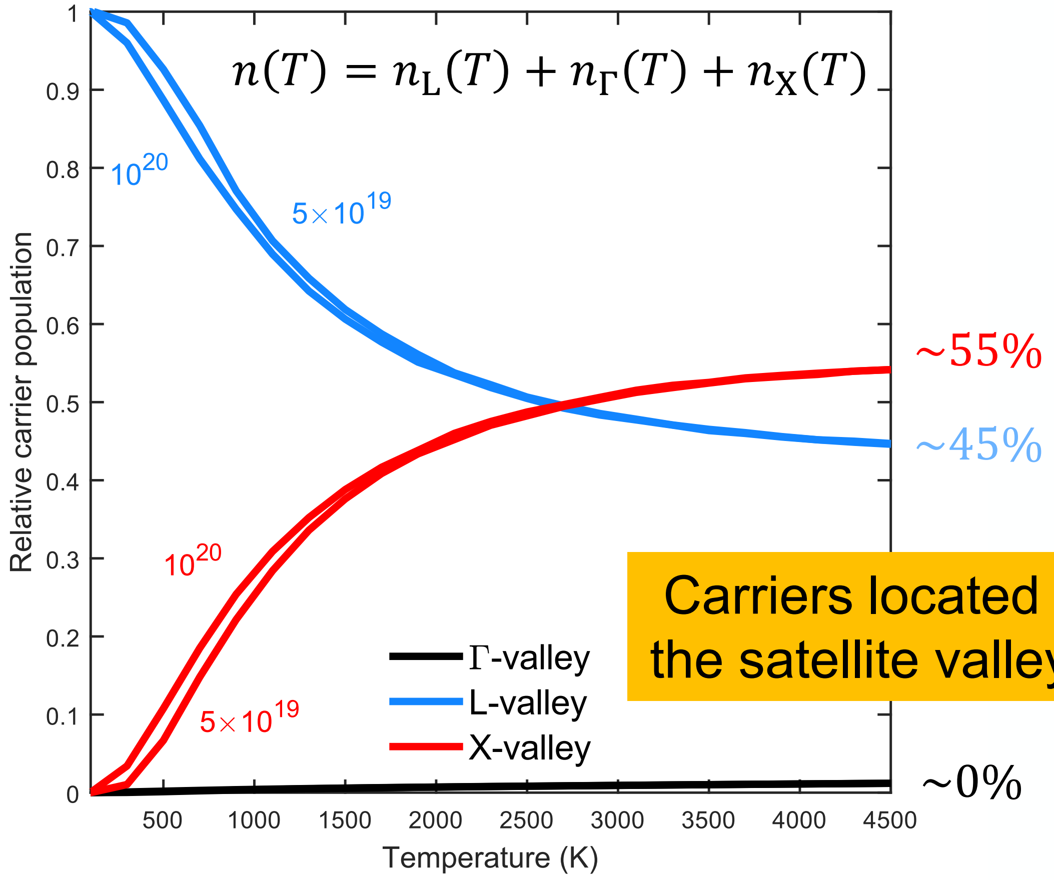
$$T_c \approx \frac{E_e}{3k_B}$$

2600 K

$10^{20}$ cm$^{-3}$

μ=0.27 eV




Carriers located at the satellite valleys.

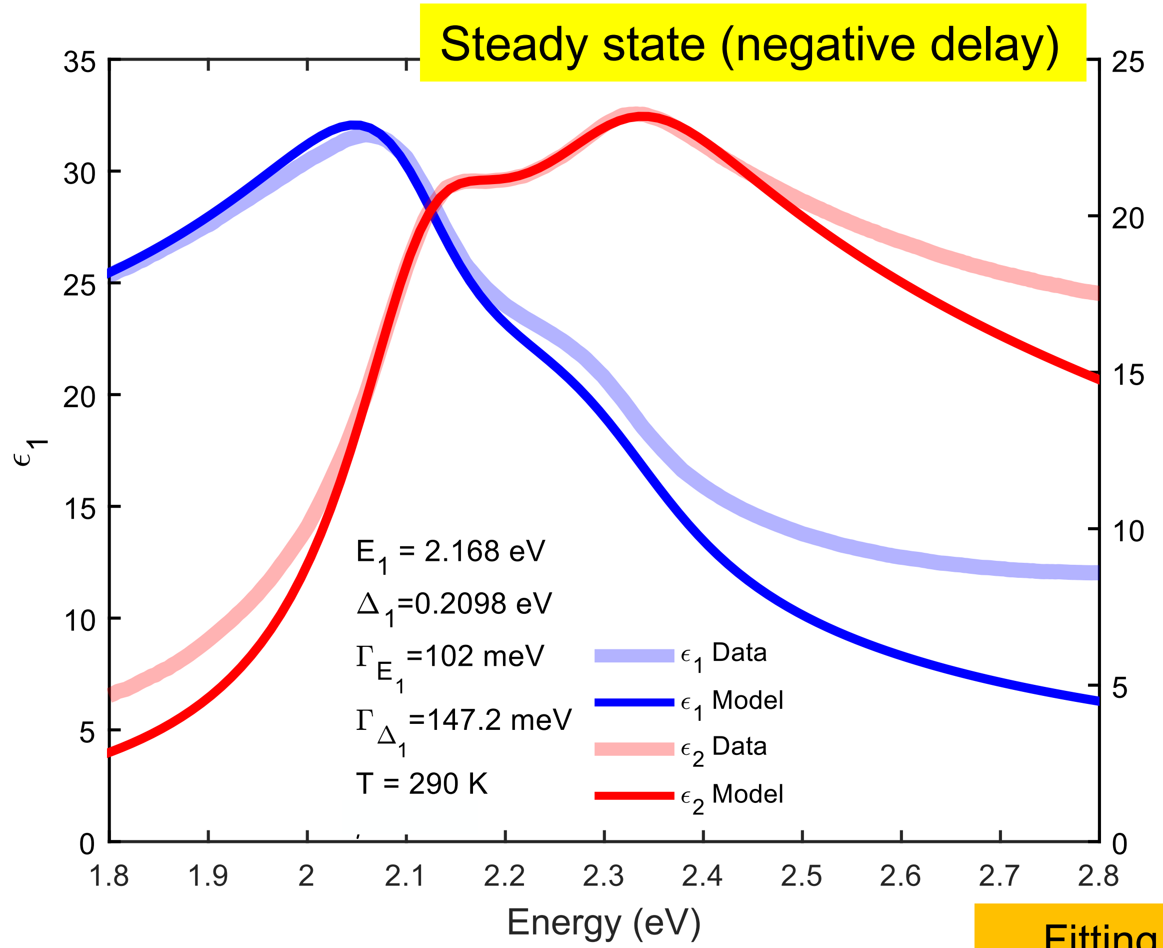
NM STATE BE BOLD. Shape the Future.®

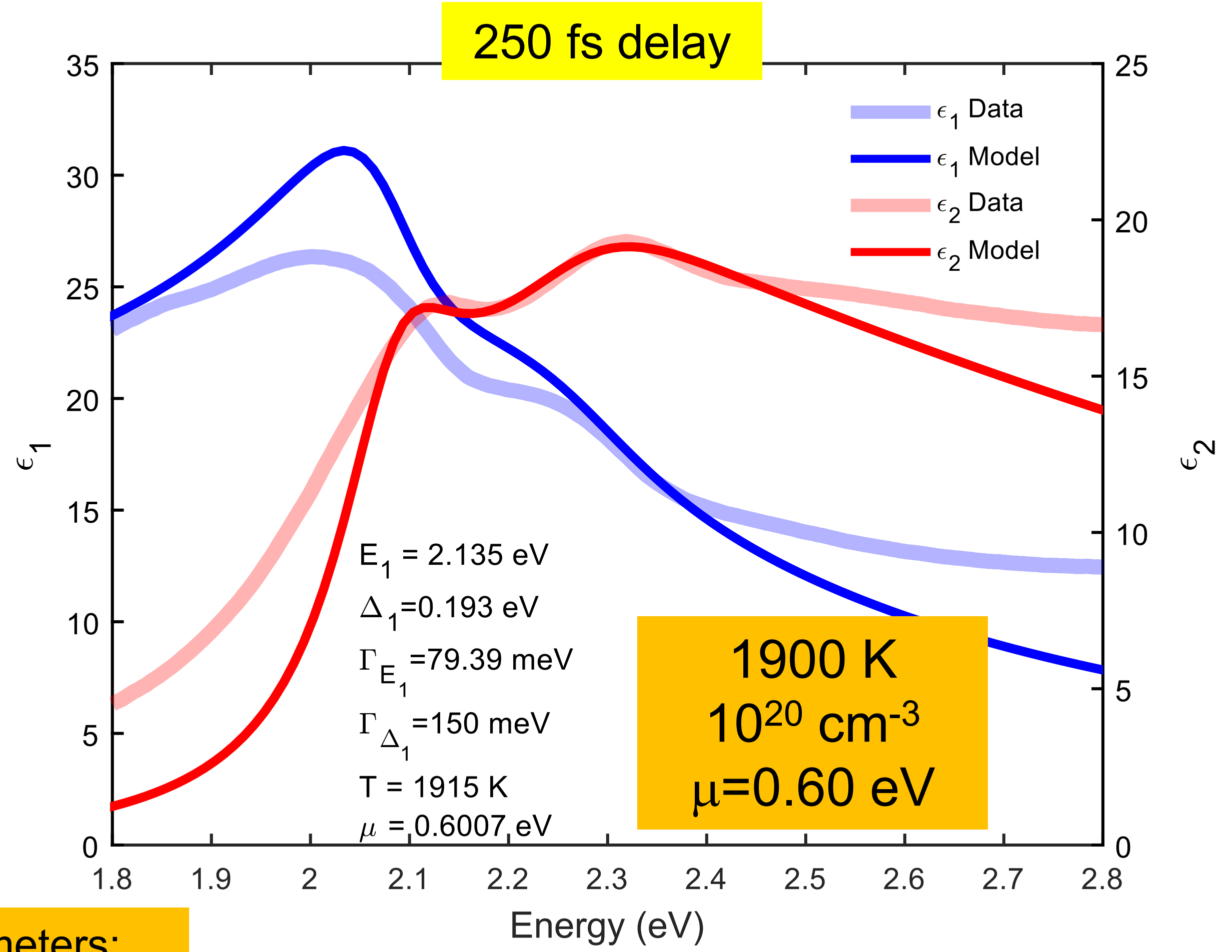
A. L. Smirl, in *Physics of Nonlinear Transport in Semiconductors*, ed. by Kerry, Barker, and Jacoboni (Plenum, 1980).
J. Menéndez *et al.*, Phys. Rev. B. **101**, 195204 (2020).

# Band Filling Model

2D exciton model with band filling effects:

$$\varepsilon_2(E) = \frac{2e^2\mu_\perp^{(E_g)}\bar{P}^2}{3\varepsilon_0 m^2\pi}\,\mathrm{Im}\left\{\frac{g_a[\xi(E+i\Gamma)]+g_a[\xi(-E-i\Gamma)]-2g_a[\xi(0)]}{(E+i\Gamma)^2}\right\}\int_{-k_{\mathrm{max}}}^{k_{\mathrm{max}}}\{1-f[E_c(E,k_z^2)]\}dk_z$$



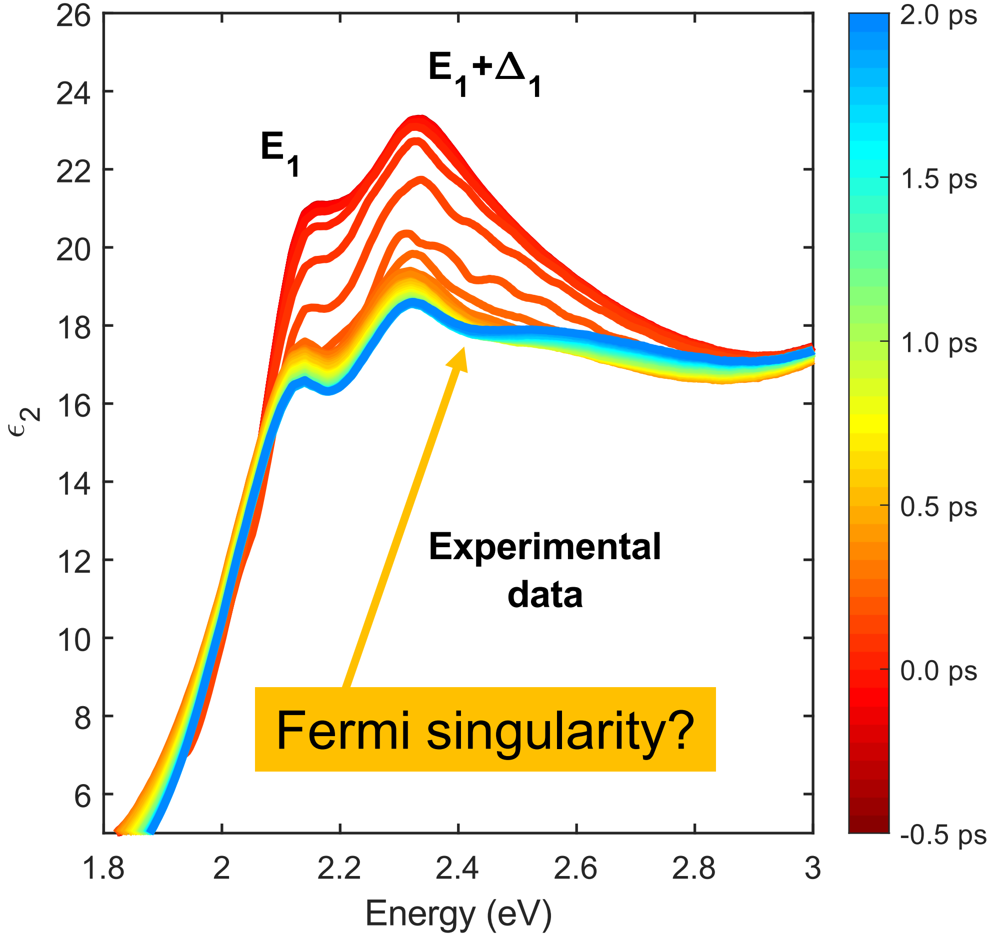



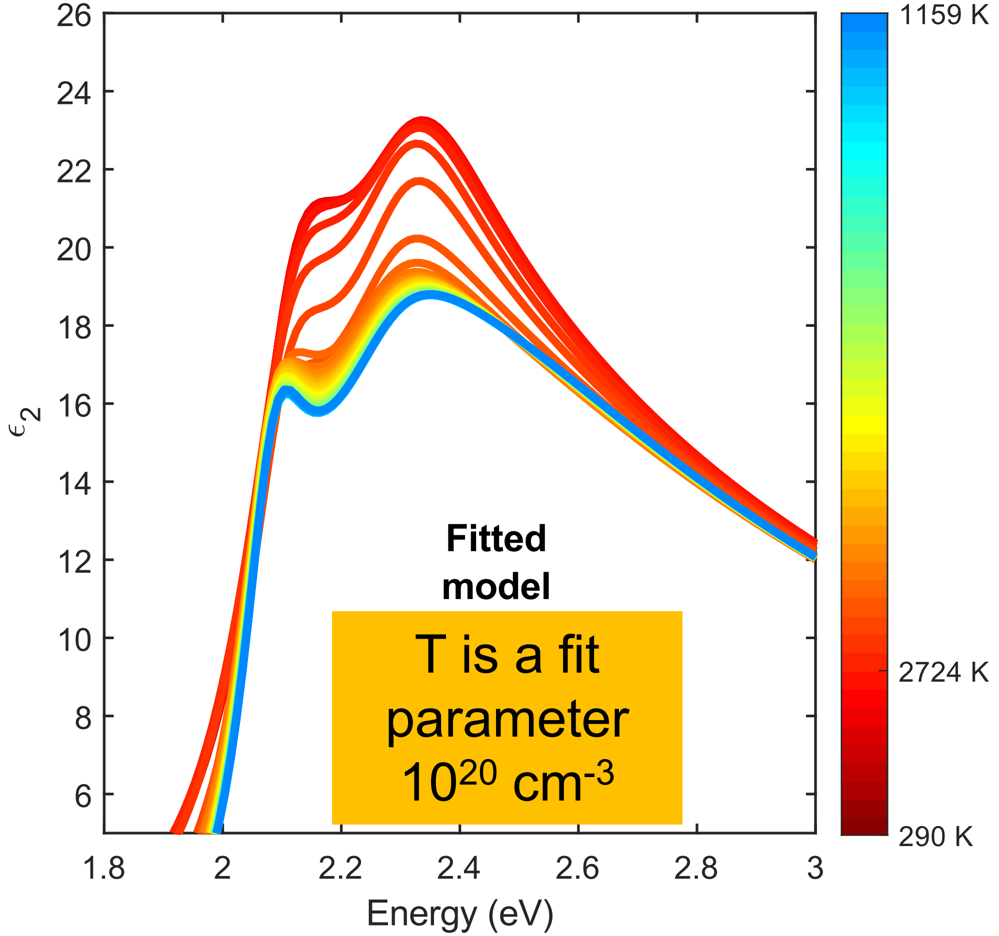

Fitting parameters:
$E_1, \Delta_1, \Gamma^{(E_1)}, \Gamma^{(E_1+\Delta_1)}, T_c, \mu$

# Band Filling Model

2D exciton model with band filling effects:

$$\varepsilon_2(E) = \frac{2e^2 \mu_\perp^{(E_g)} \bar{P}^2}{3\varepsilon_0 m^2 \pi} \mathrm{Im}\left\{\frac{g_a[\xi(E+i\Gamma)] + g_a[\xi(-E-i\Gamma)] - 2g_a[\xi(0)]}{(E+i\Gamma)^2}\right\} \int_{-k_{\max}}^{k_{\max}} \{1 - f[E_c(E, k_z^2)]\} dk_z$$



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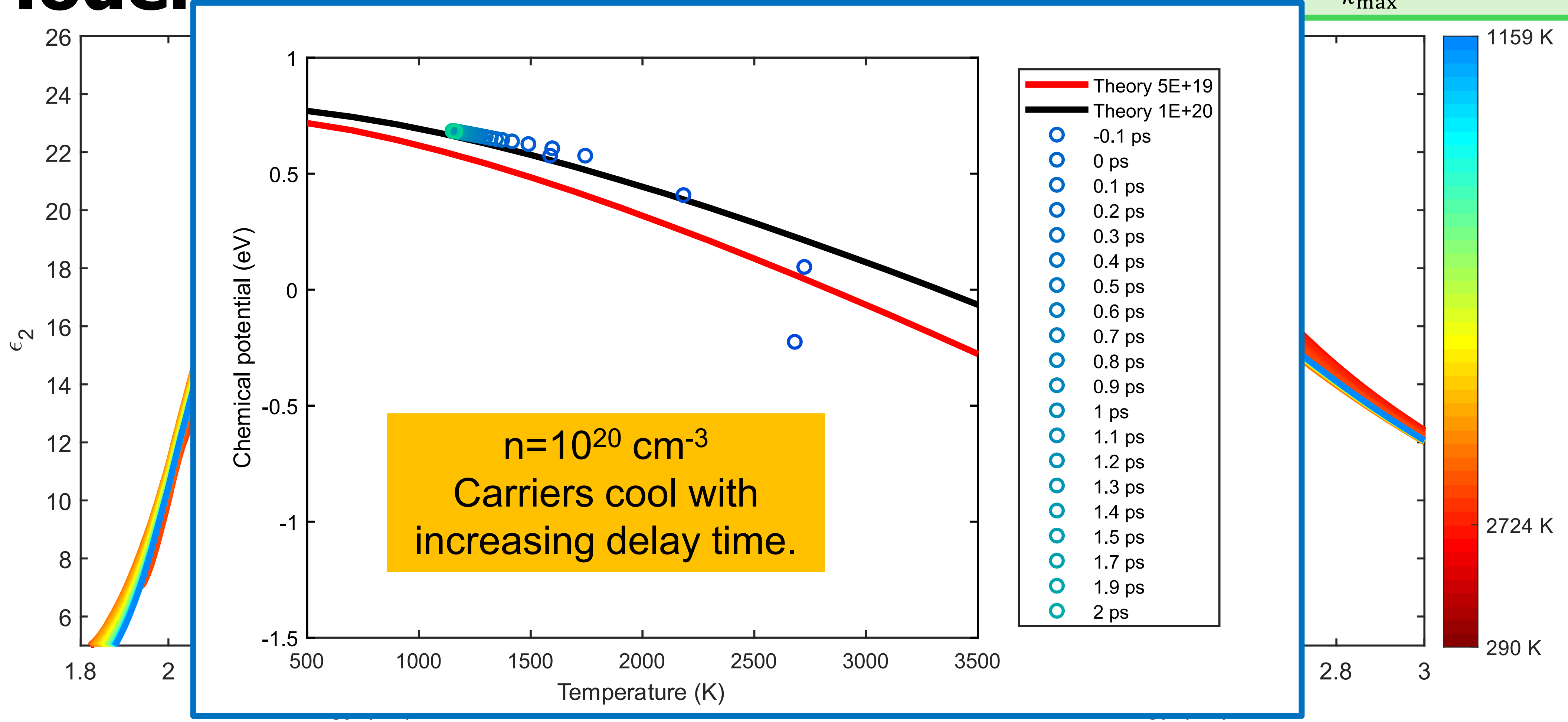

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2D exciton model with band filling effects:

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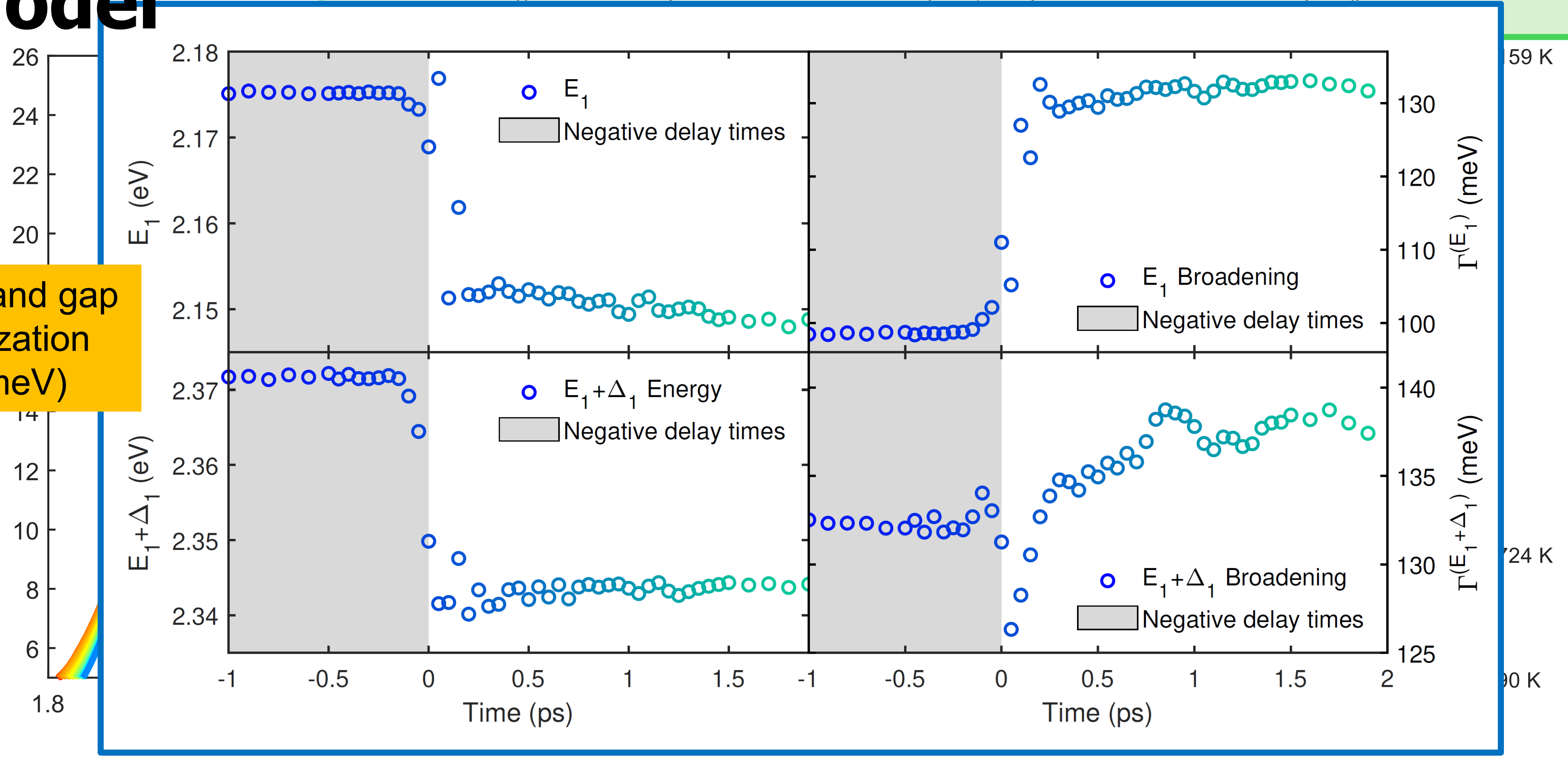
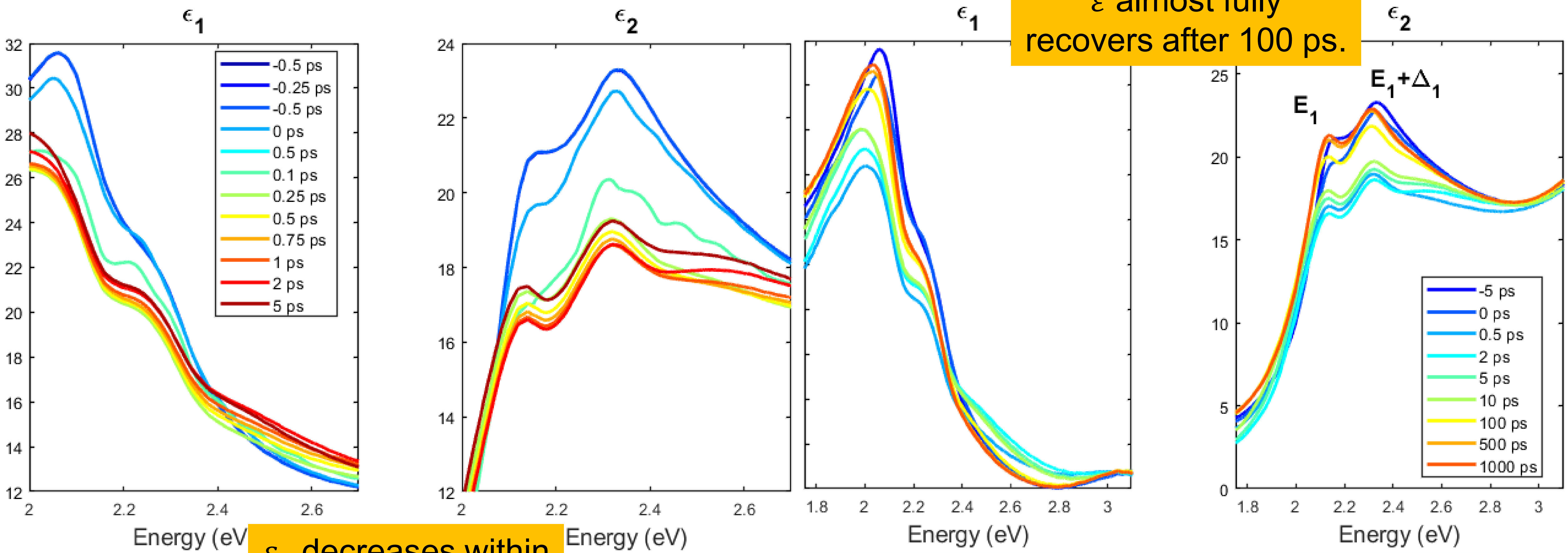



Redshift: band gap renormalization (25-30 meV)

Carlos Armenta, Ph.D. thesis (NMSU, 2025)

# Dielectric Function at Longer Delay Times




$\varepsilon$ almost fully recovers after 100 ps.

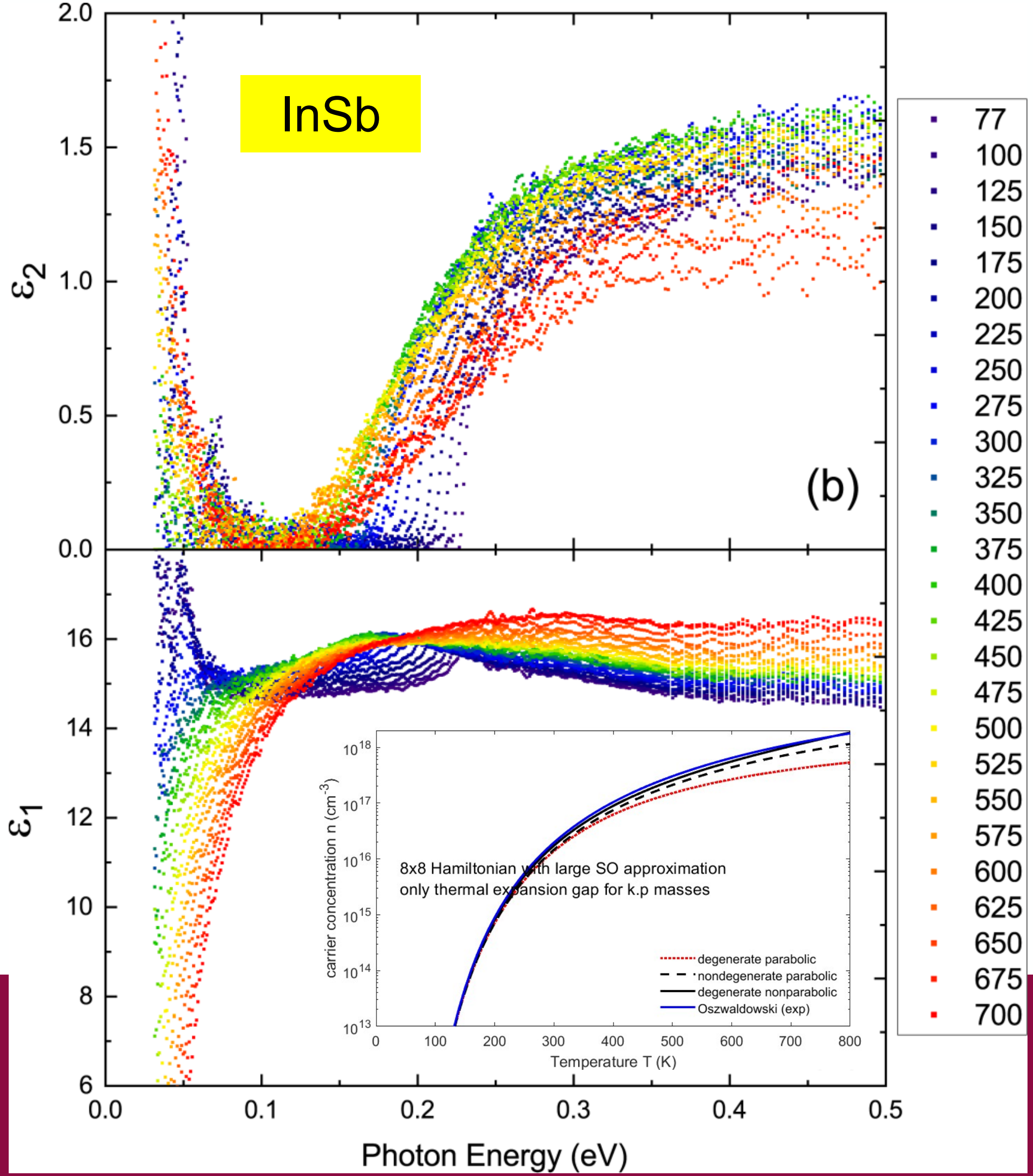
$\varepsilon_2$ decreases within the first 2 ps.

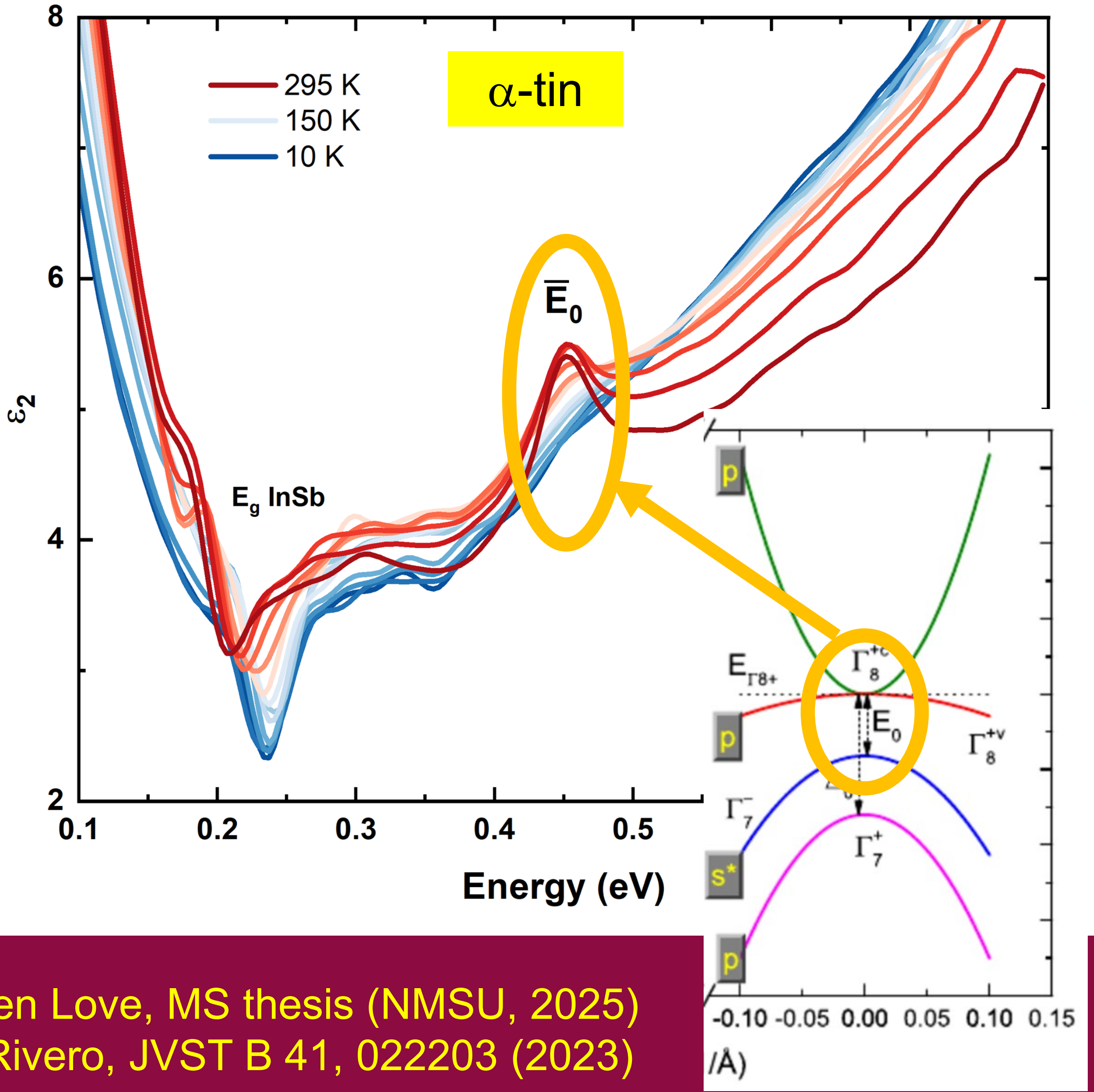
Model diffusion and recombination.

BE BOLD. Shape the Future.®

Carlos Armenta, Ph.D. thesis (NMSU, 2025)

# Thermal Excitation of Electron-Hole Pairs




Jaden Love, MS thesis (NMSU, 2025)
M. Rivero, JVST B 41, 022203 (2023)

# Conclusions

- Precision measurements of optical absorption from mid-IR to near-UV with temperature-dependent spectroscopic ellipsometry.
- It is possible to predict direct gap IR absorption in Ge from k.p theory.
- A similar theory describes the UV absorption in Ge near $E_1$ and $E_1+\Delta_1$.
- Can we close the gap in our theory between IR and UV?
  (conduction band nonparabolicity, k-dependent optical dipole matrix element)
- Does this theory work for other materials? Is there a universal scaling law?
  (Need measurements on binary compounds and thick Ge-Sn and III/V alloy layers.)
- Femtosecond pump-probe ellipsometry measurements of transient absorption in Ge at high carrier concentration.
- Good agreement with band filling model based on Fermi-Dirac carrier statistics.
- No model for screening of excitonic absorption in two dimensions.
- Test band filling model to describe temperature-dependent dielectric function of InSb.