

Spectroscopic Ellipsometry Studies of Optical Constants in Highly Excited Semiconductors

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Ask me about MS/Ph.D. student positions at NMSU.



AVS 2022, Pittsburgh, PA

Biography

Regensburg/Stuttgart
Germany



Motorola (Mesa, Tempe)
Arizona, 1997-2005



Freescale, IBM
New York, 91-92;07-10

Las Cruces, NM
Since 2010

Motorola, Freescale
Texas, 2005-2007



Where is Las Cruces, NM ???



White Sands NP



Problem Statement

- **(1)** Achieve a quantitative understanding of **absorption** and **emission** processes.
- Our qualitative understanding of such processes is 50-100 years old,
- But insufficient for modeling of detectors and emitters.
- **(2)** How are optical processes affected by high carrier concentrations (screening)?
- High carrier densities can be achieved with
 - **In situ doping** or
 - **ultrafast lasers** or
 - **high temperatures.**
- **Goal:** CMOS-integrated mid-infrared camera (thermal imaging with a phone).
- Future: How are optical processes affected by an electric field (pin diode or thin layer)?

Intensity of Optical Absorption by Excitons

R. J. Elliott

Phys. Rev. **108**, 1384 – Published 15 December 1957

Article

References

Citing Articles (1,780)

PDF

Export Citation

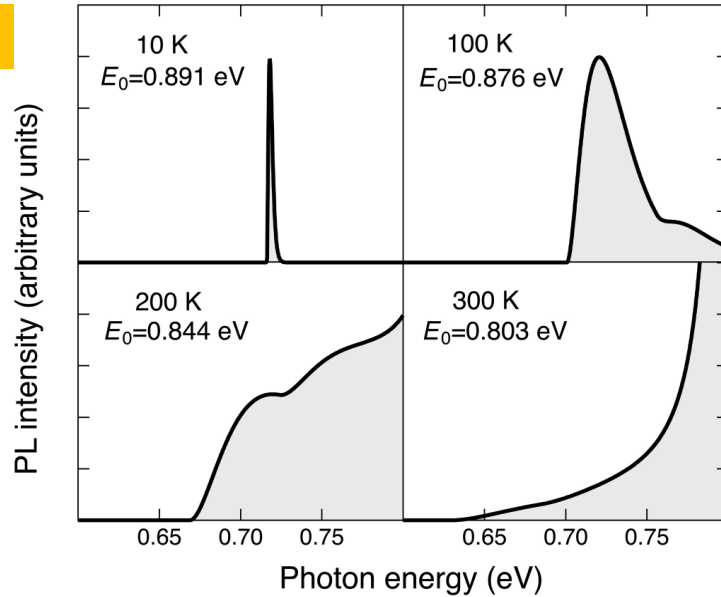
ABSTRACT

The intensity of optical absorption close to the edge in semiconductors is examined using band theory together with the effective-mass approximation for the excitons. Direct transitions which occur when the band extrema on either side of the forbidden gap are at the same \mathbf{K} , give a line spectrum and a continuous absorption of characteristically different form and intensity, according as transitions between band states at the extrema are allowed or forbidden. If the extrema are at different \mathbf{K} values, indirect transitions involving phonons occur, giving absorption proportional to $(\Delta E)^{\frac{1}{2}}$ for each exciton band, and to $(\Delta E)^2$ for the continuum. The experimental results on Cu_2O and Ge are in good qualitative agreement with direct forbidden and indirect transitions, respectively.

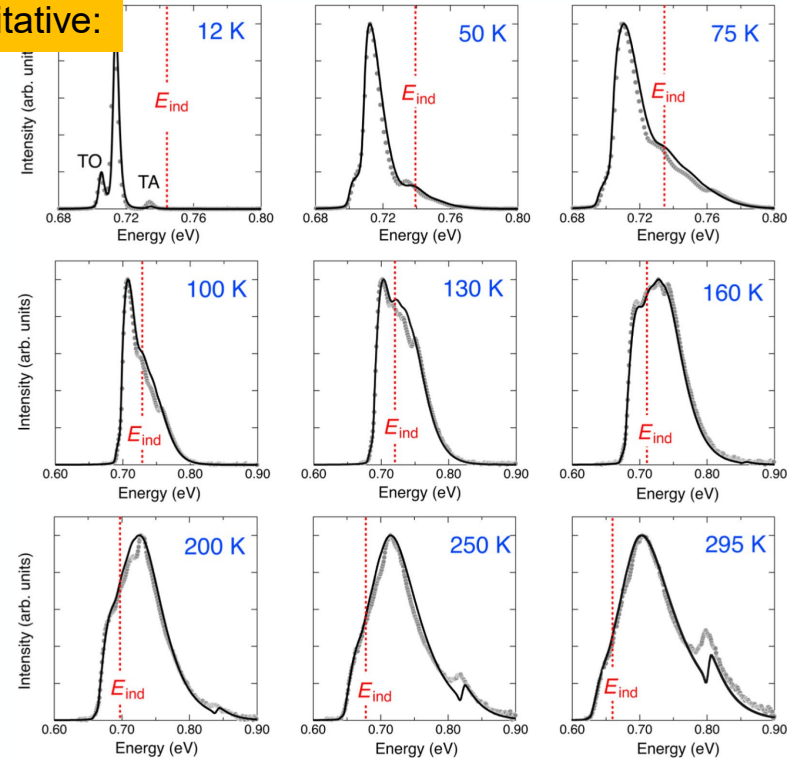
Received 9 April 1957

Example 1: Photoluminescence in Germanium

Qualitative:



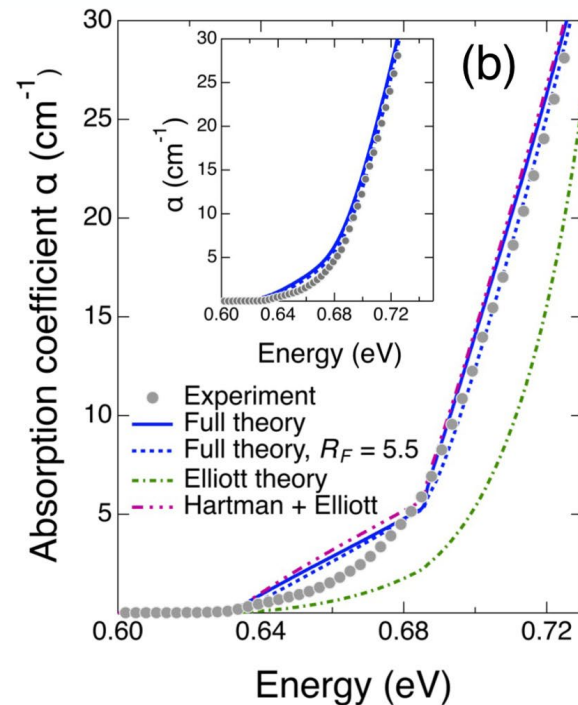
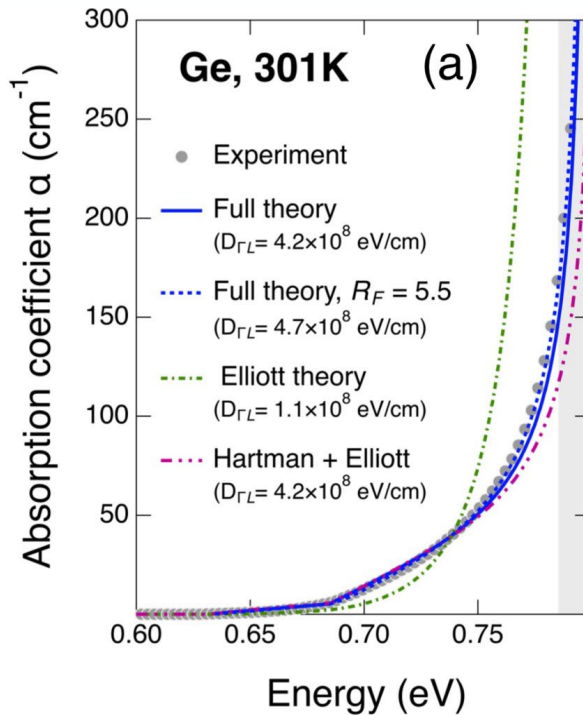
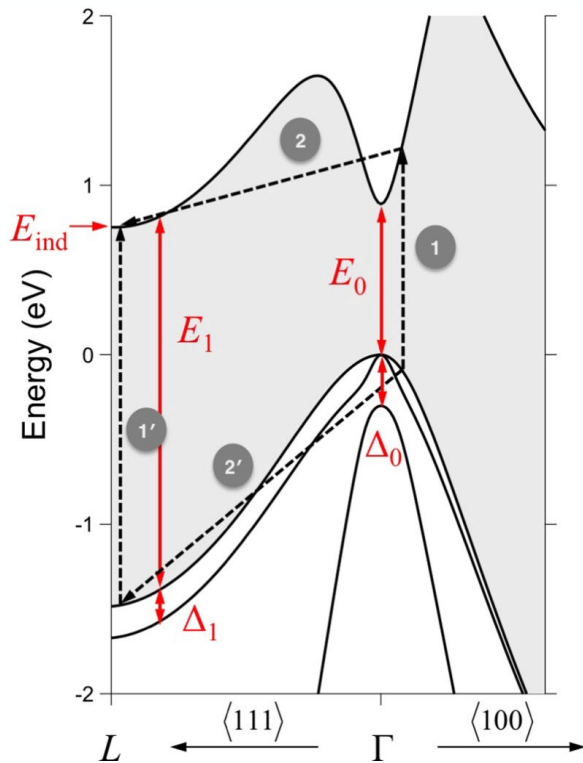
Quantitative:



Rosbroeck-Shockley equation (PR **94**, 1558, 1954).

Complete failure above 200 K and at RT.

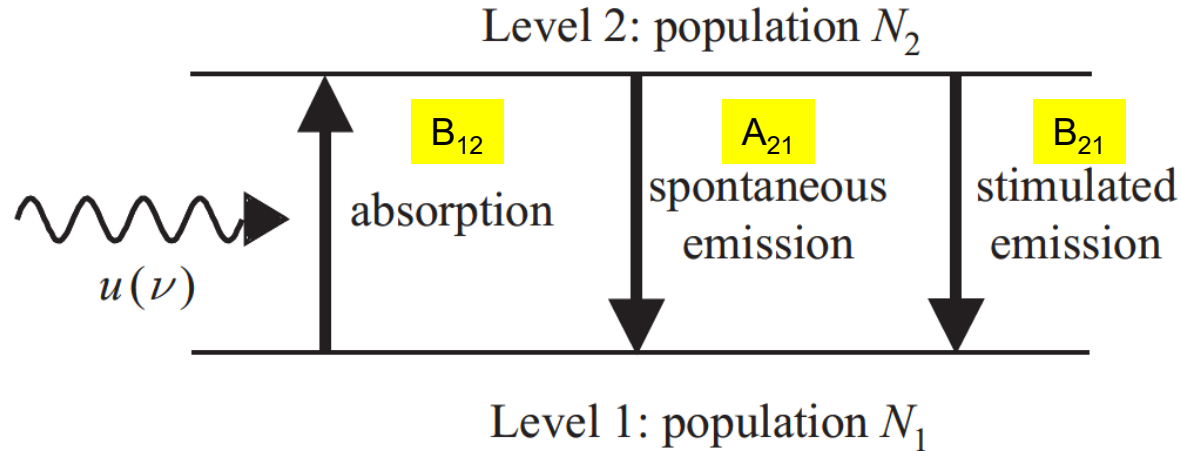
Example 2: Indirect Absorption in Germanium



Optical Constants of Highly Excited Semiconductors

- Einstein coefficients, Fermi's Golden Rule, Elliott-Tanguy excitons
- Direct gap absorption in **germanium** from 10 to 800 K
- Optical constants of highly excited semiconductors
 - Direct gap absorption in **InSb** from 10 to 800 K
 - Optical constants of **highly excited germanium**
(femtosecond ellipsometry at ELI Beamlines in Prague)
- Conclusion and Outlook

Einstein Coefficients



One coefficient is sufficient:

$$g_1 B_{12} = g_2 B_{21}$$

$$A_{21} = \frac{2\hbar\omega^3}{\pi c^3} B_{21}$$

Use Fermi's Golden Rule
to calculate B_{12}

In equilibrium: N_1, N_2 constant.
Absorption and emission balance.
Black-body radiation $u(\hbar\omega)$

$$B_{12}N_1u(\hbar\omega) = A_{21}N_2 + B_{21}N_2u(\hbar\omega)$$

Fermi's Golden Rule: Tauc Plot

Direct band gap absorption

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \int_{i,f} |\langle f | H_{eR} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) = \frac{2\pi}{\hbar} |\langle f | H_{eR} | i \rangle|^2 g_{fi}(\hbar\omega)$$

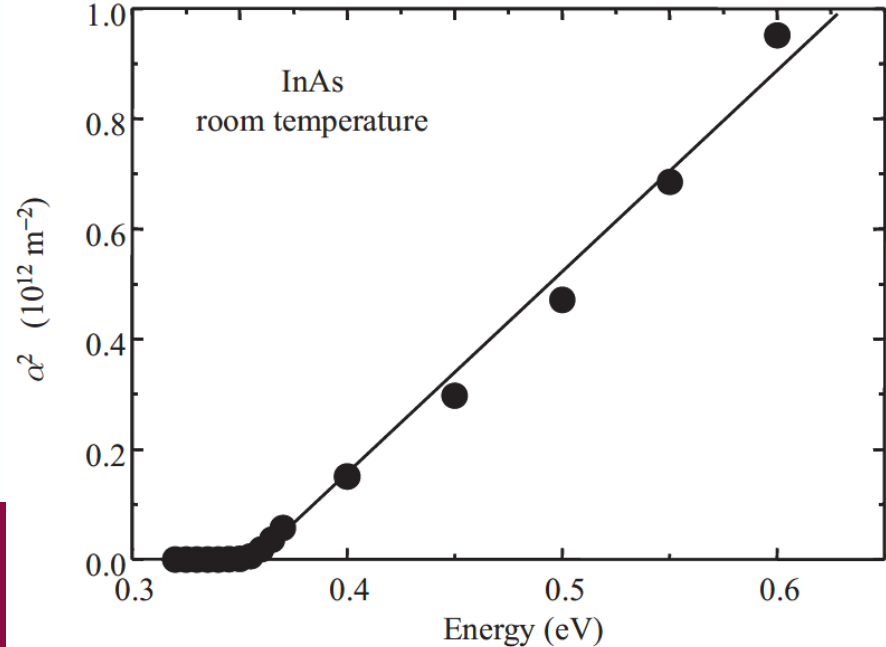
constant $\mathbf{k} \cdot \mathbf{p}$ matrix element

Joint DOS

$$\langle f | H_{eR} | i \rangle = \frac{e}{m_0} \langle f | \vec{p} | i \rangle \cdot \vec{A}_0$$

Use $\mathbf{k} \cdot \mathbf{p}$ matrix element P : $E_P = 2P^2/m_0$

$$\varepsilon_2(\hbar\omega) = \frac{e^2 \sqrt{m_0} \mu^{\frac{3}{2}} E_P \sqrt{E_0}}{3\pi \sqrt{2} \varepsilon_0 \hbar (\hbar\omega)^2} \sqrt{\frac{\hbar\omega}{E_0} - 1}$$



Fermi's Golden Rule: Tauc Plot



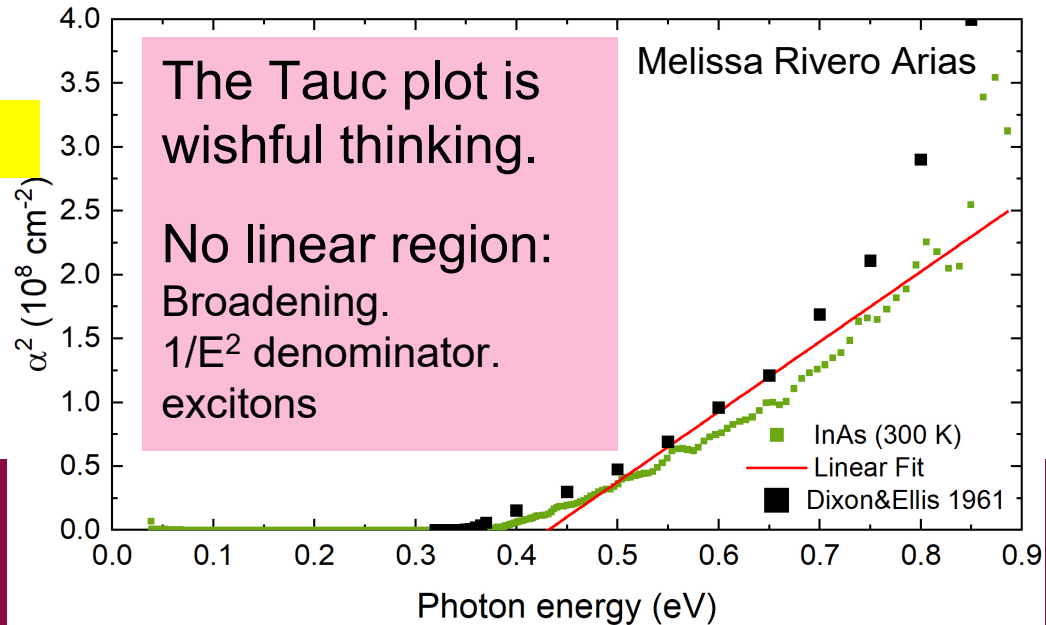
Direct band gap absorption

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \int_{i,f} |\langle f | H_{eR} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) = \frac{2\pi}{\hbar} |\langle f | H_{eR} | i \rangle|^2 g_{fi}(\hbar\omega)$$

$$\langle f | H_{eR} | i \rangle = \frac{e}{m_0} \langle f | \vec{p} | i \rangle \cdot \vec{A}_0$$

Use $\mathbf{k} \cdot \mathbf{p}$ matrix element P : $E_p = 2P^2/m_0$

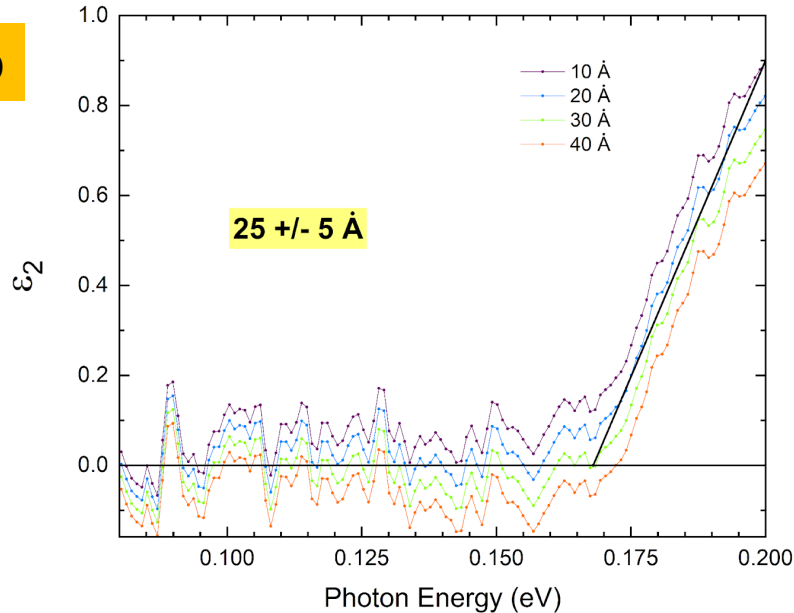
$$\varepsilon_2(\hbar\omega) = \frac{e^2 \sqrt{m_0} \mu^{\frac{3}{2}} E_p \sqrt{E_0}}{3\pi \sqrt{2} \varepsilon_0 \hbar (\hbar\omega)^2} \sqrt{\frac{\hbar\omega}{E_0} - 1}$$



BE BOLD. Shape the Future.

Practical Tip: Oxide or Surface Correction

InSb



**Jellison-Sales Method for Transparent Glasses:
How thick is the surface region?**

Optical constants for anodic oxide of InSb:

$$\epsilon_{\infty} \approx 3.8$$

Mattausch, PRB **23**, 1896 (1981).

Zollner, APL **63**, 2523 (1993).

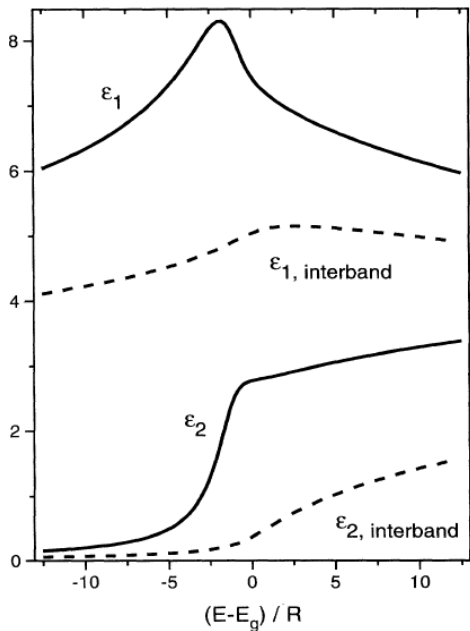
Below the band gap, ϵ_2 must be **exactly** zero for a bulk insulator (not positive, not negative). This method requires a compensator to measure Δ exactly near 0 or 180 degrees. (Also change JAW software settings to allow negative ϵ_2 values.)

Elliott-Tanguy Exciton Absorption

Direct band gap absorption

Excitonic binding energy: $R=R_H \times \mu_h / \epsilon_s^2$

$$\epsilon_2(\hbar\omega) = \frac{e^2 \sqrt{m_0} \mu^{\frac{3}{2}} E_P \sqrt{R}}{3\pi \sqrt{2} \epsilon_0 \hbar (\hbar\omega)^2} \left[\sum_{n=1}^{\infty} \frac{4\pi R}{n^3} \delta\left(\hbar\omega - E_0 + \frac{R}{n^2}\right) + \frac{2\pi H(\hbar\omega - E_0)}{1 - \exp\left(-2\pi \sqrt{R/\hbar\omega - E_0}\right)} \right]$$

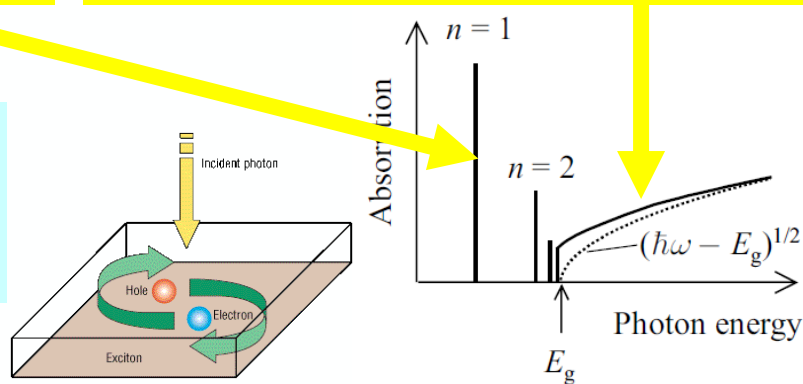


bound excitons

exciton continuum enhancement

Tanguy's contributions:

- Add Lorentzian broadening
- Kramers-Kronig transform to get the real part.



R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

Christian Tanguy, Phys. Rev. Lett. **75**, 4090 (1995) + (E)

... the Future.

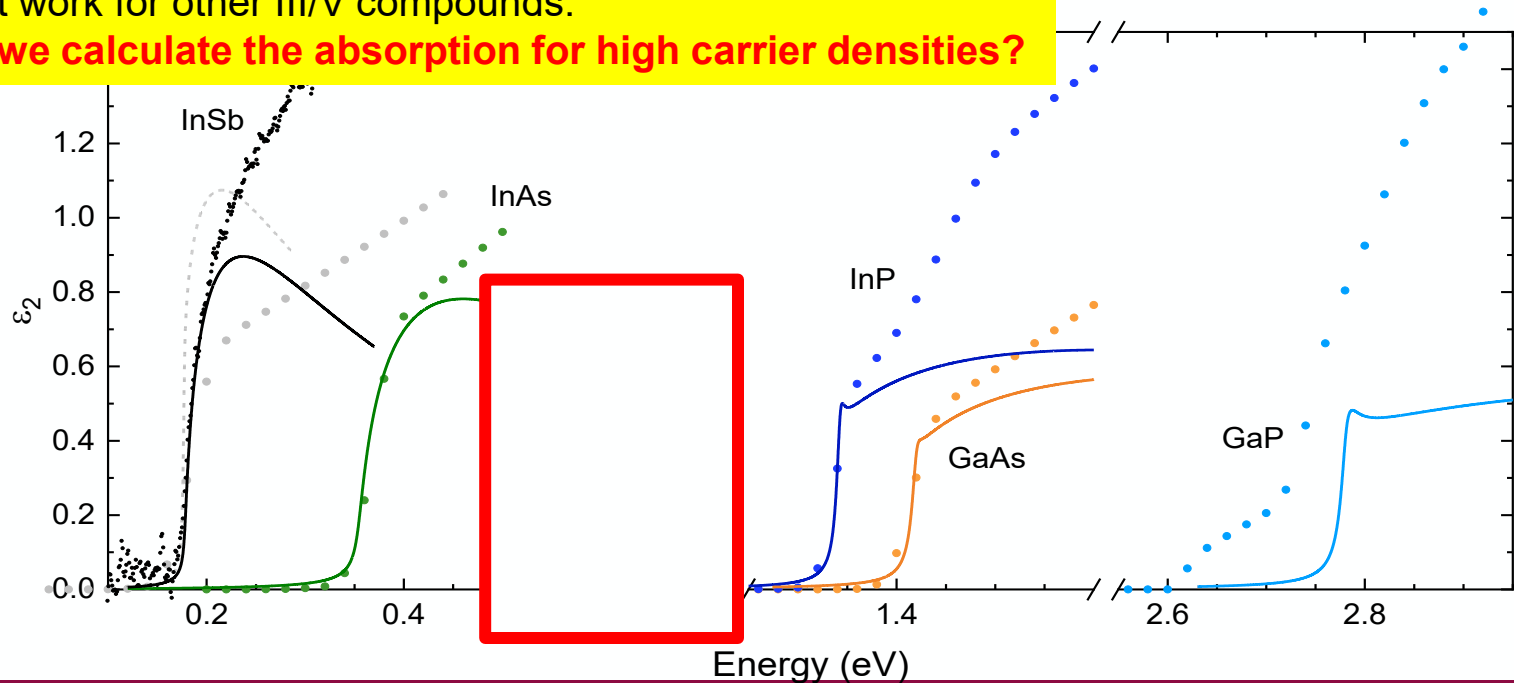
Calculation of Absorption Spectrum from k.p Theory

Can we calculate the absorption spectrum?

Yes, we can for Ge in the low carrier density limit.

It does not work for other III/V compounds.

How can we calculate the absorption for high carrier densities?



Elliott-Tanguy theory applied to Ge

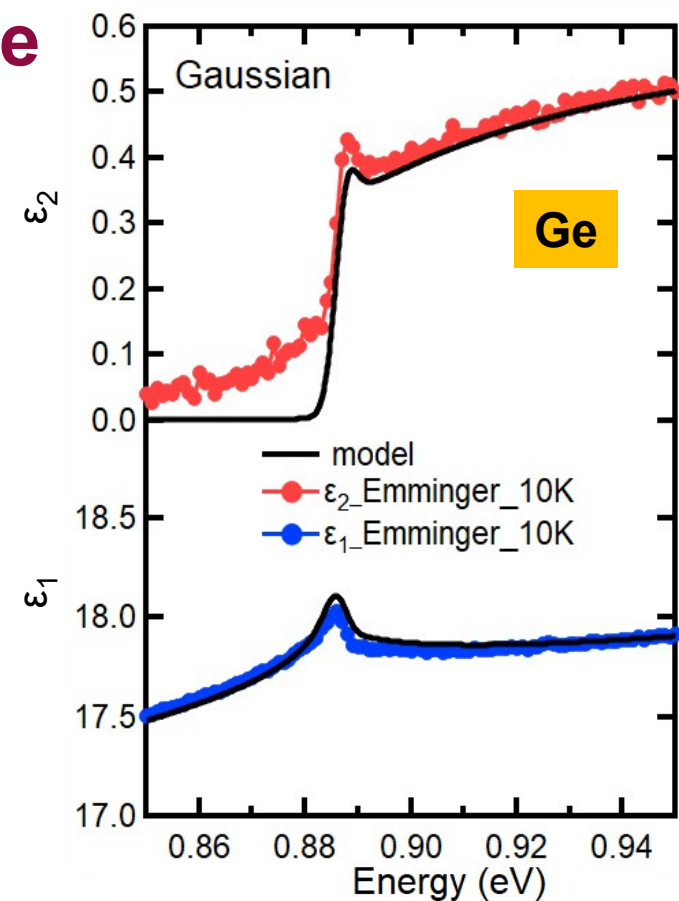
• Fixed parameters:

- Electron and hole masses (temperature dependent)
- Excitonic binding energy R
- Amplitude A (derived from 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)

Quantitative agreement



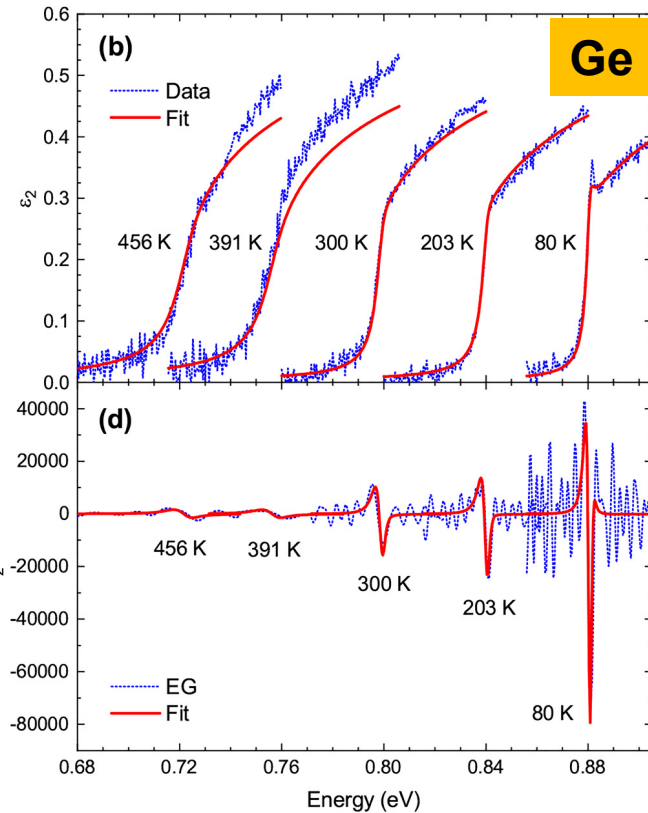
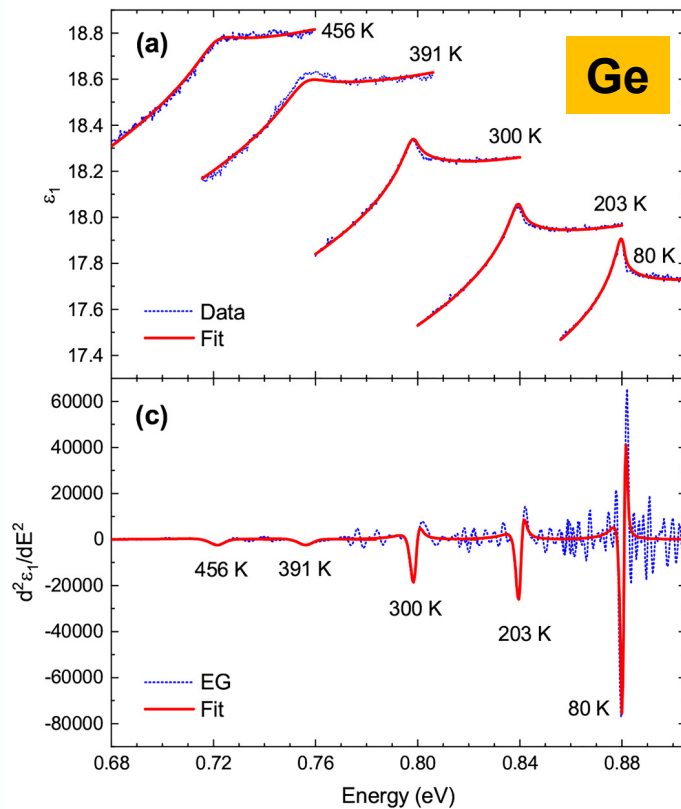
Elliott-Tanguy theory applied to Ge

Good agreement at low temperatures.

Model also describes second derivatives.

Potential problems:

- Matrix element k -dependent
- Nonparabolicity
- Resonant indirect absorption
- ??? at high T.



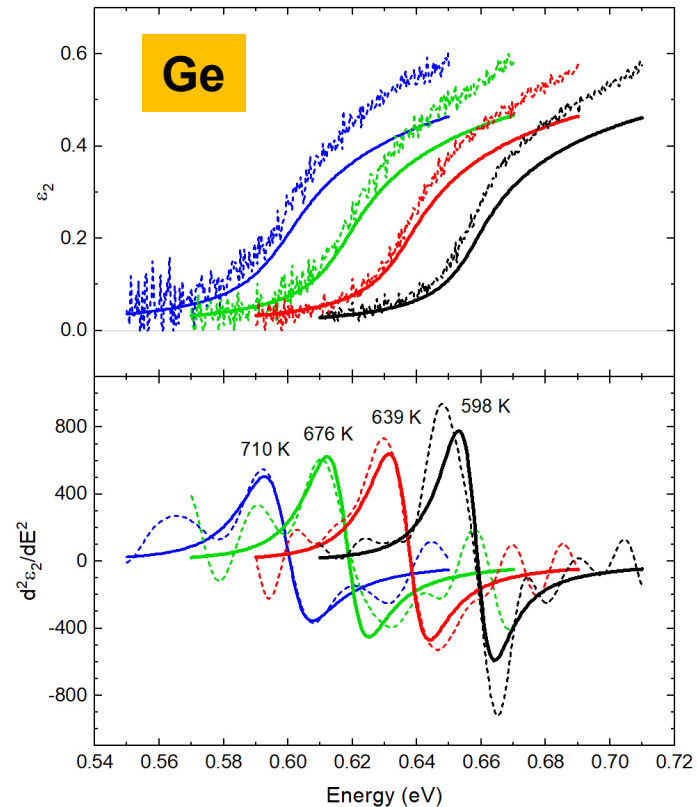
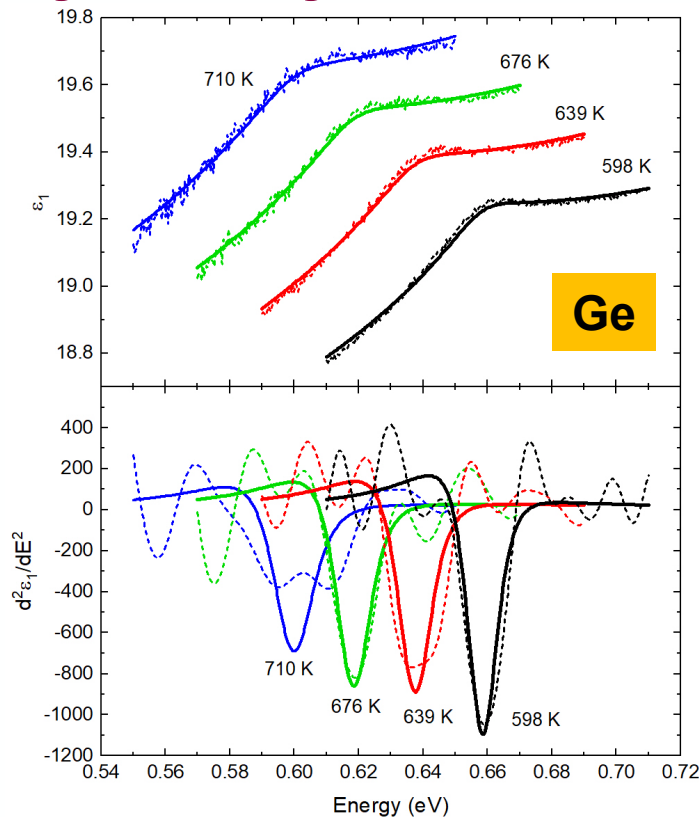
Elliott-Tanguy theory: Problems for Ge at high T

Good agreement at low temperatures.

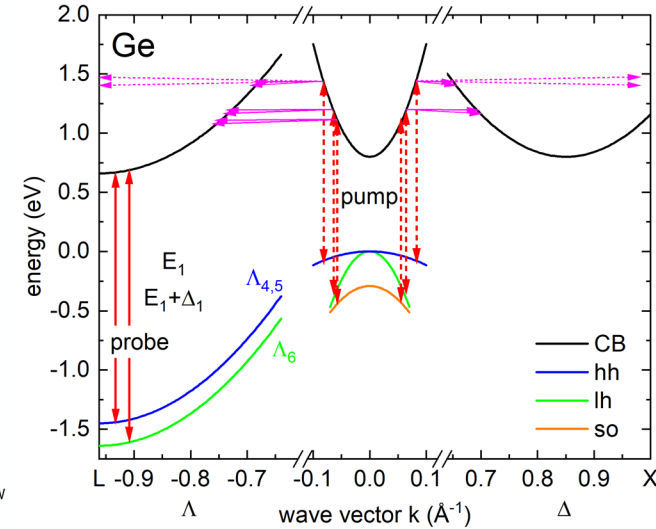
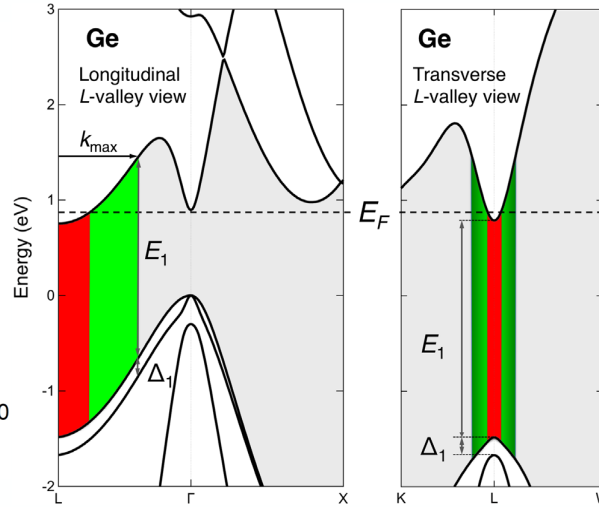
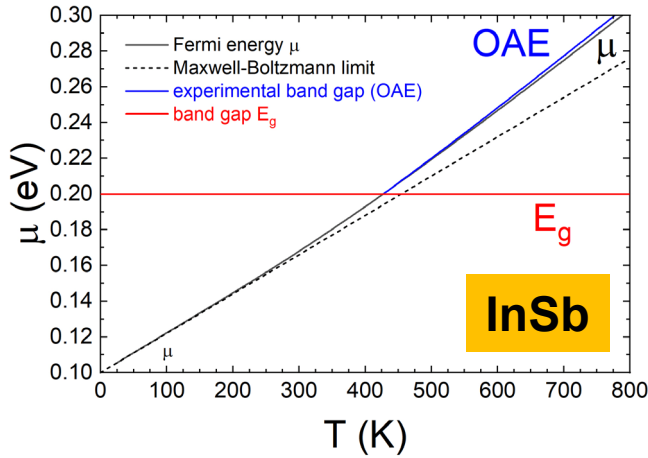
Model also describes second derivatives.

Potential problems:

- Matrix element k -dependent
- Nonparabolicity
- Resonant indirect absorption
- ??? at high T.
- Measurement error ??



Optical Absorption at High Carrier Densities



High temperature
(thermal excitation of e-h pairs)
constant m and E_g

High n-doping of Ge with P
(free electrons pile up at L-point)

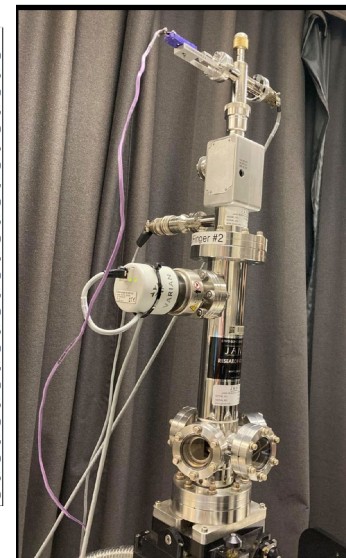
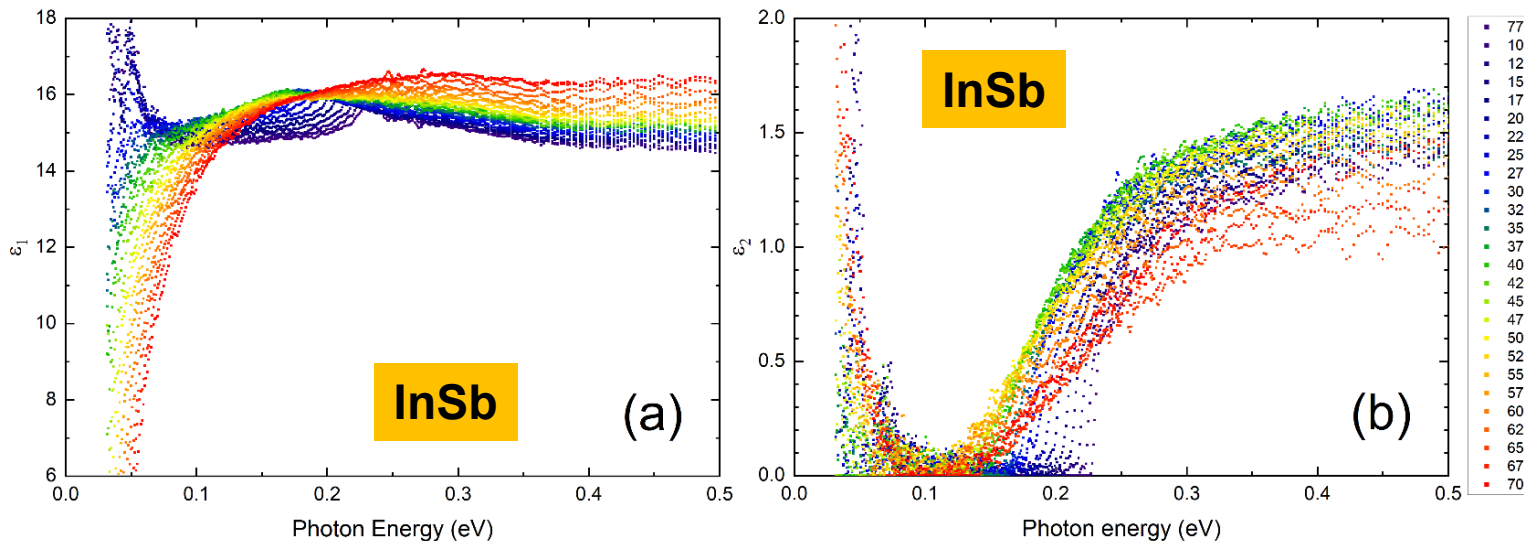
Intense femtosecond laser excitation (ELI Beamlines)
(electrons pile at L-point)

Rivero, JVSTB **41**, 022203 (2023)

Xu et al., PRL **118**, 267402 (2017)

Espinoza, APL **115**, 052105 (2019)

(1) Dielectric function of InSb from 80 to 800 K

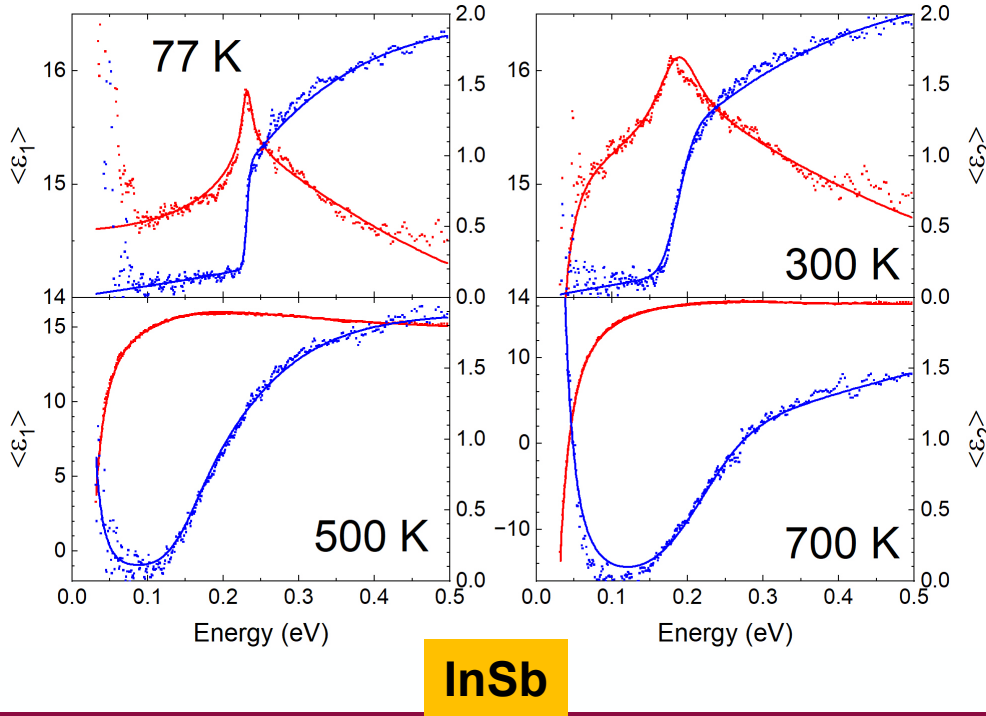


Woollam FTIR-VASE cryostat with CVD diamond windows

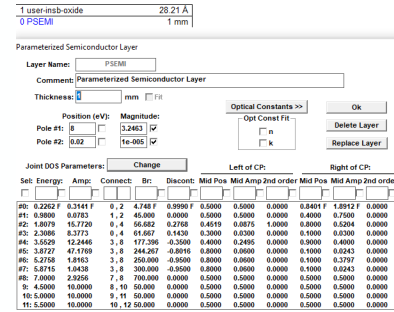
- **Band gap** changes with temperature (but only below 500 K).
- **Amplitude reduction at high temperatures (Pauli blocking, bleaching)**
- **Drude response** at high temperatures (thermally excited carriers).
- Depolarization artifacts at long wavelengths (below 300 K).

Band gap analysis for InSb

How does the band gap of InSb change with temperature?



Parametric-Semiconductor Model:



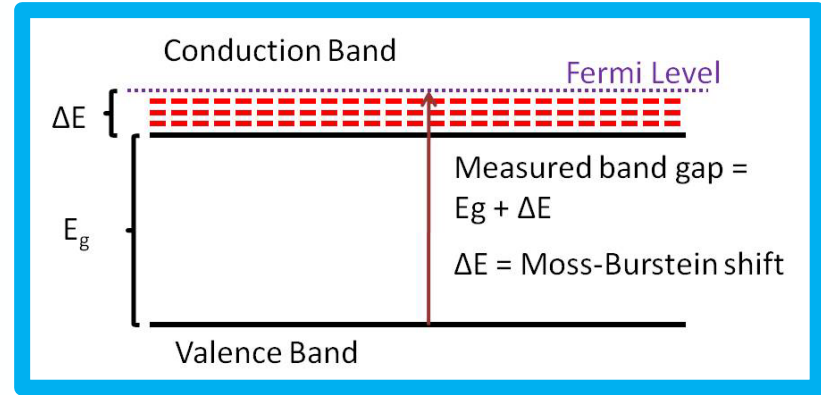
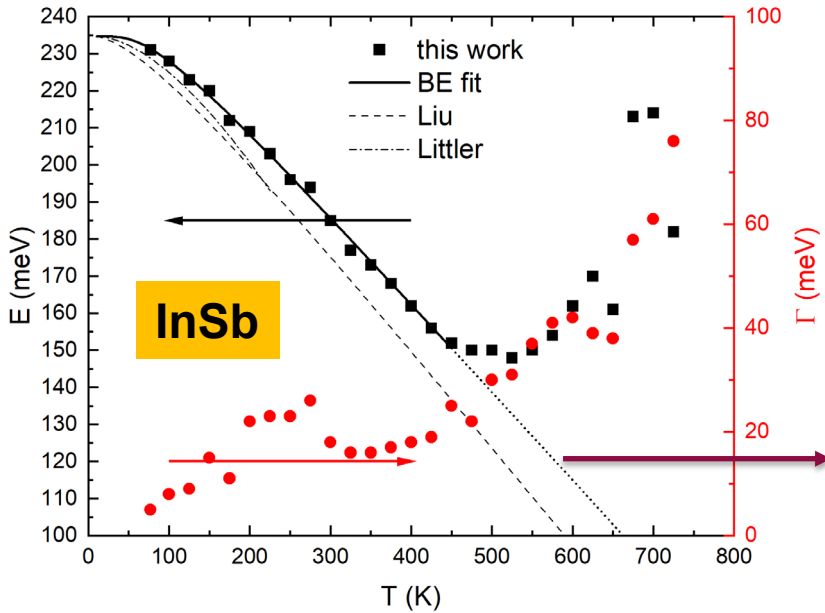
Also vary "shape parameters".

Asymmetric peak shape poorly described.

Try Tanguy oscillator for excitonic line shape.

Fit	
	Final
MSE	0.2958
En0.0	0.22615 ± 0.000889
Br0.0	4.7478 ± 1.32
Am0.0	0.31415 ± 124
Disc0.0	0.999 ± 788
RPos0.0	0.84009 ± 0.0264
RAmp0.0	1.8912 ± 0.191
PoleMag.0	3.2469 ± 6.56
PoleMag2.0	1e-005 ± 0.000568

Band gap of InSb from 80 to 800 K

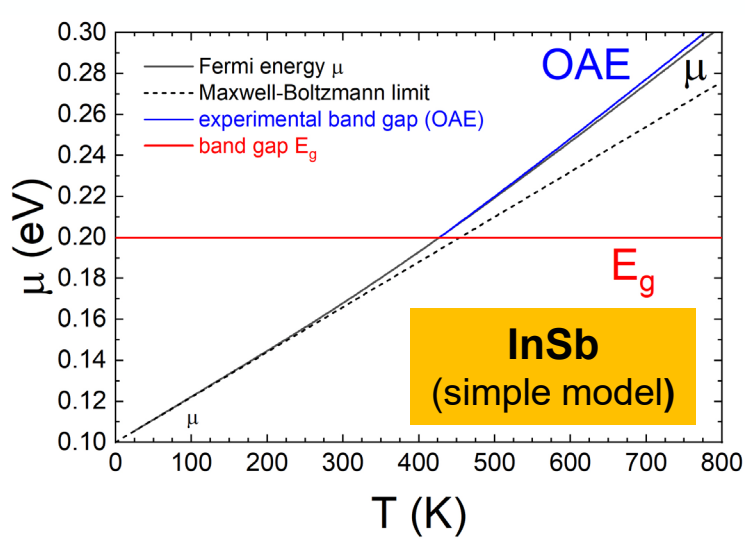


Bose-Einstein Model

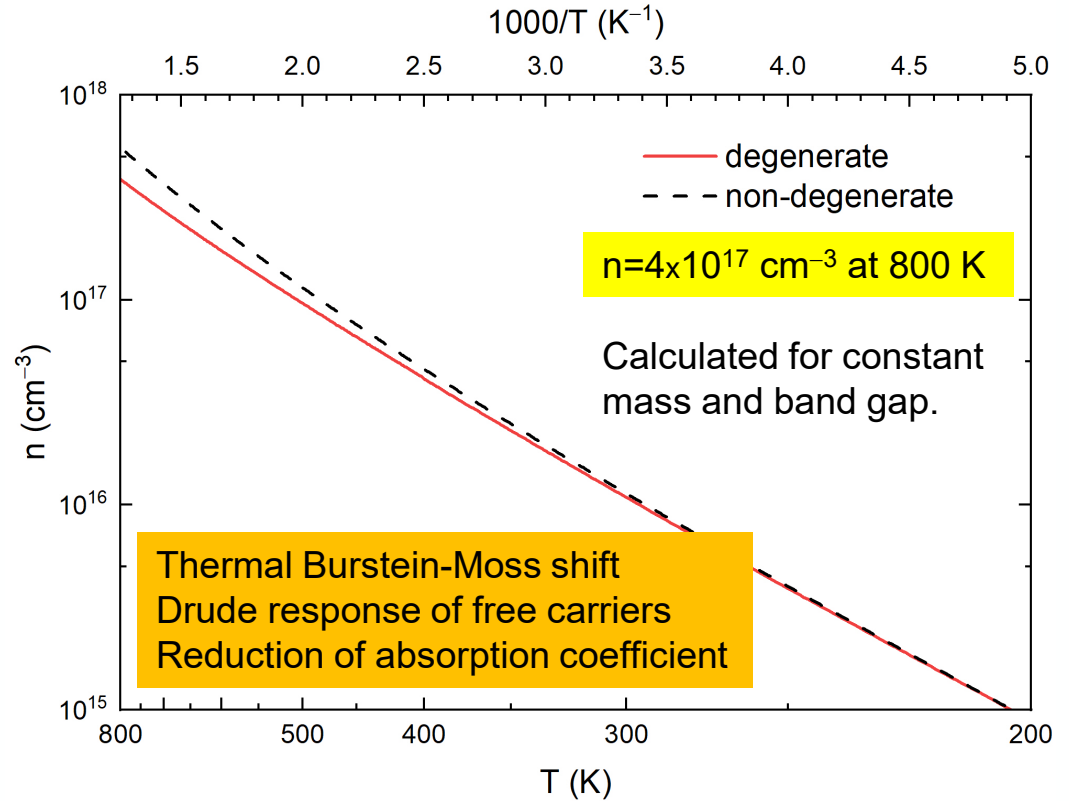
$$E_g(T) = a - b \left[1 + \frac{2}{e^{\frac{T}{\theta}} - 1} \right]$$

- Band gap changes with temperature (but only below 500 K)
- Described by Bose-Einstein model below 500 K: Logothetidis, PRB **31**, 947 (1985).
- No redshift above 500 K: **Thermal Burstein-Moss shift**

Thermal excitations of electron-hole pairs in InSb



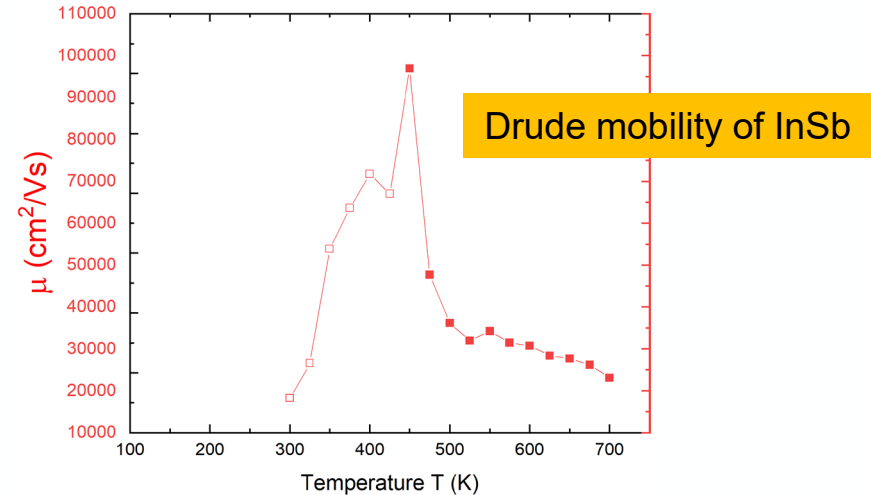
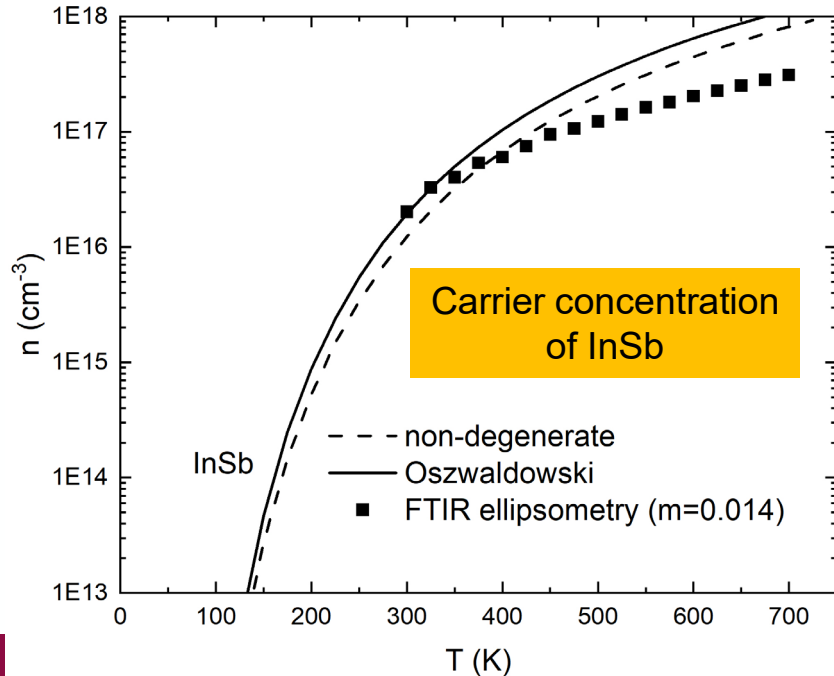
$k_B T = E_g / 4$ at 600 K
 Fermi level above the conduction band edge above 450 K.
 (Calculated for constant m and E_g)



Carrier concentration and mobility from 80 to 800 K

To model the **Drude response**, we make some really simple assumptions:

- Parabolic bands (ignore non-parabolicity)
- Effective mass constant $m_e=0.014$ (independent of temperature)



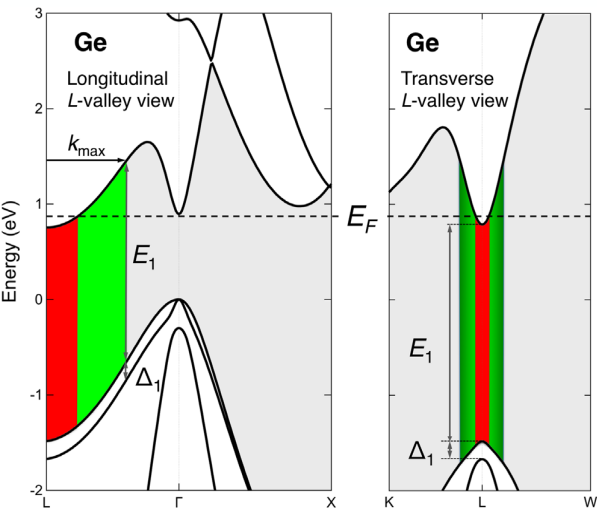
Reasonable agreement with Hall measurements.
Large errors below 400 K (depolarization).

Required model improvements: Screened Excitons

$$\varepsilon_2(E) = \frac{2\pi A\sqrt{R}}{E^2} \left\{ \sum_{n=1}^{\sqrt{g}} \frac{2R}{n} \left(\frac{1}{n^2} - \frac{n^2}{g^2} \right) \delta \left[E - E_0 + \frac{R}{n^2} \left(1 - \frac{n^2}{g} \right)^2 \right] + \frac{\sinh(\pi g k) H(E - E_0)}{\cosh(\pi g k) - \cosh \left(\pi g \sqrt{k^2 - \frac{4}{g}} \right)} \right\} [f_h(E) - f_e(E)]$$

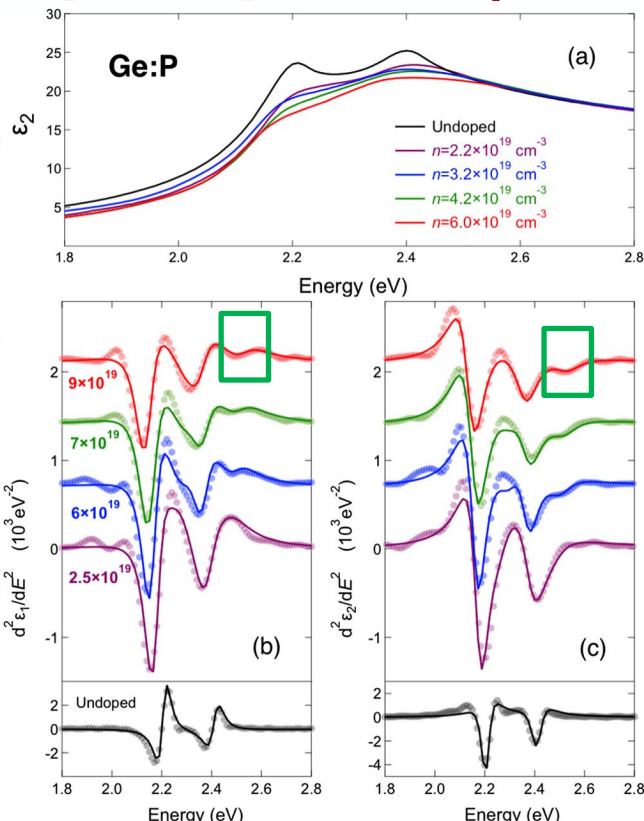
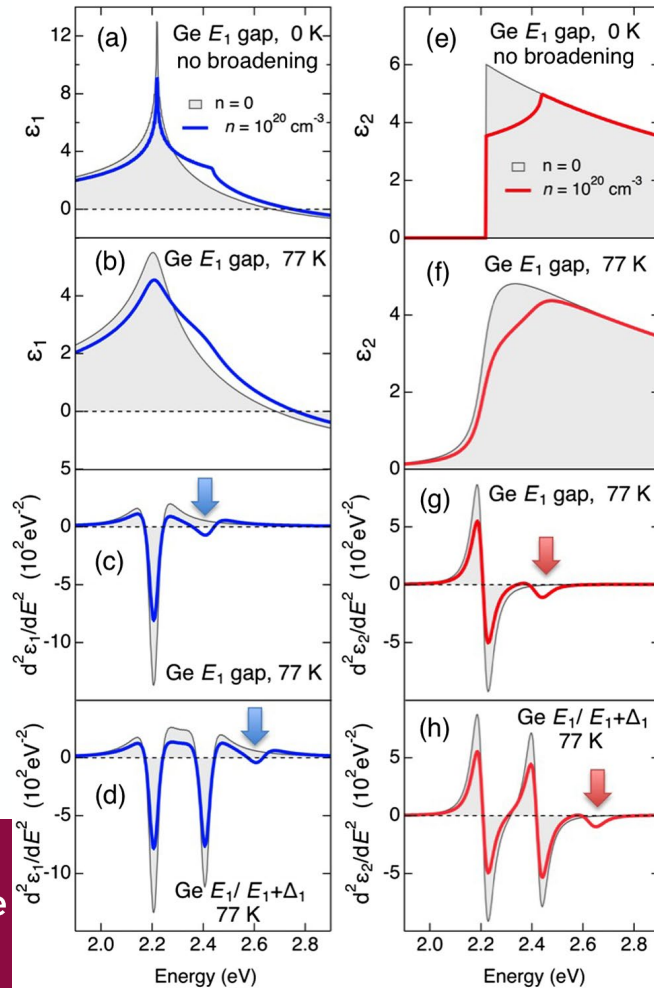
- **Absorption by screened excitons** (Hulthen potential)
- Kramers-Kronig transform following Tanguy (includes broadening Γ)
- **Degenerate Fermi-Dirac statistics** to calculate f_h and f_e .
- Two terms for light and heavy excitons
- **Non-parabolicity and temperature-dependent mass** included from k.p theory
- **k-dependent matrix element P .**
- Screening parameter $g=12/\pi^2 a_R k_{TF}$ (large: no screening)
- **Only two free parameters: Band gap E_0 and broadening Γ**
- Amplitude A and exciton binding energy R from k.p theory and effective masses

(2) Highly doped Ge (n-type, with phosphorus)



Electrons pile up at the L-point.
Transitions in red region blocked.

Phase filling singularity



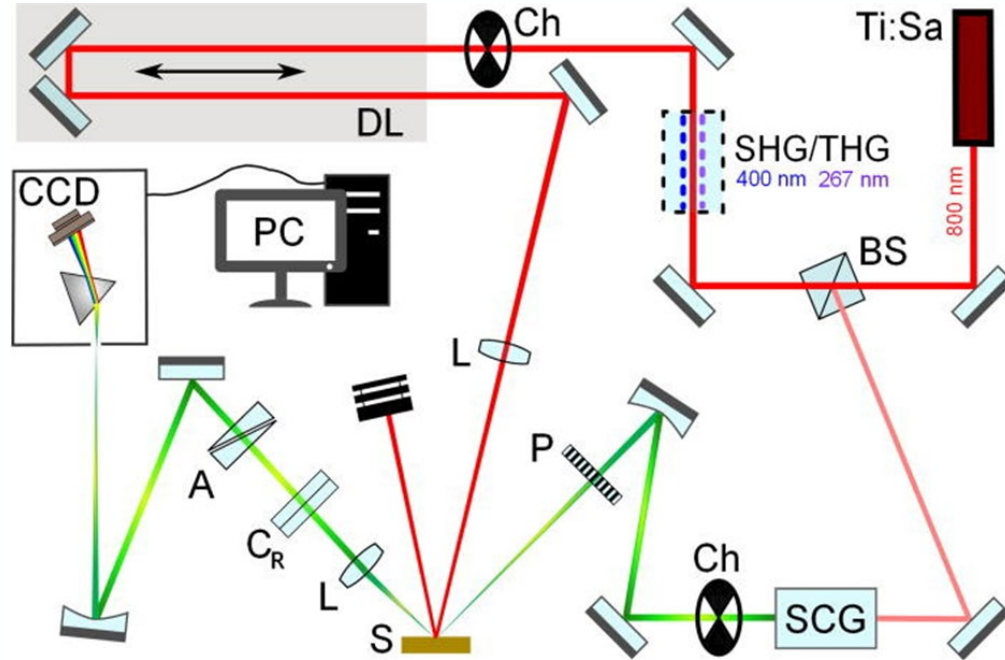
Phase shift



BE BOLD. Shape the

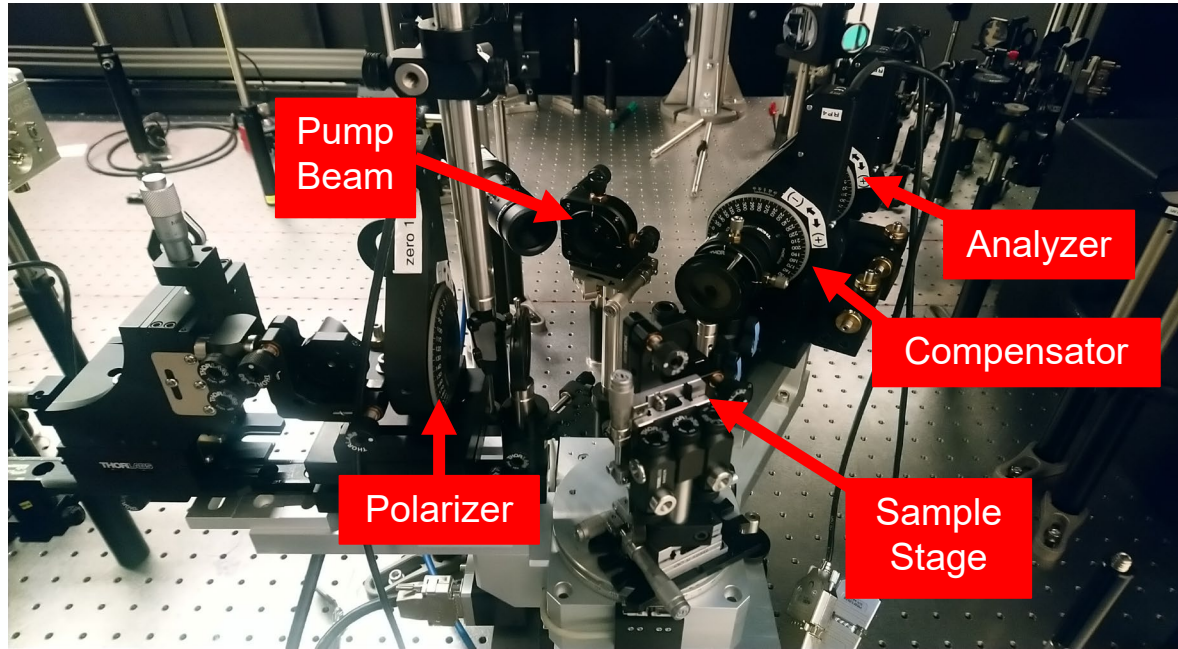
Xu et al., PRL 118, 267402 (2017)
Xu et al., JAP 125, 085704 (2019)

(3) Set-up: Femtosecond 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 and 3 fs resolution)
- BS: Beam splitter
- SHG/THG: 2nd/3rd harmonic generation
- SCG: Super-continuum generation
- CCD: Charge-coupled device detector

Set-up: Femtosecond pump-probe ellipsometry



Rotating compensator ellipsometer:

Compensator was rotated in steps of 10° for a total of 55-65 angles.

Probe beam of 350-750 nm at 60° 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.

ELI Beamlines: ELI ERIC. Dolní Břežany (near Prague)

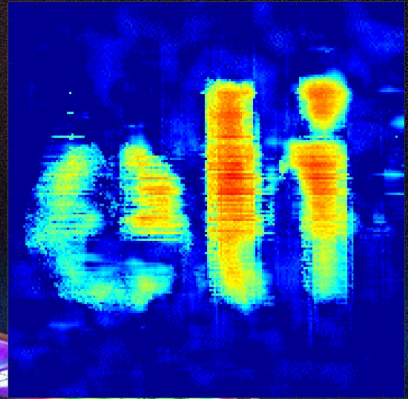
Second user call due **April 25th, 2023**: <https://up.eli-laser.eu/>
Contact Shirly Espinoza: shirly.espinoza@eli-beams.eu

Semiconductors

Metal oxides

Bulk and thin films

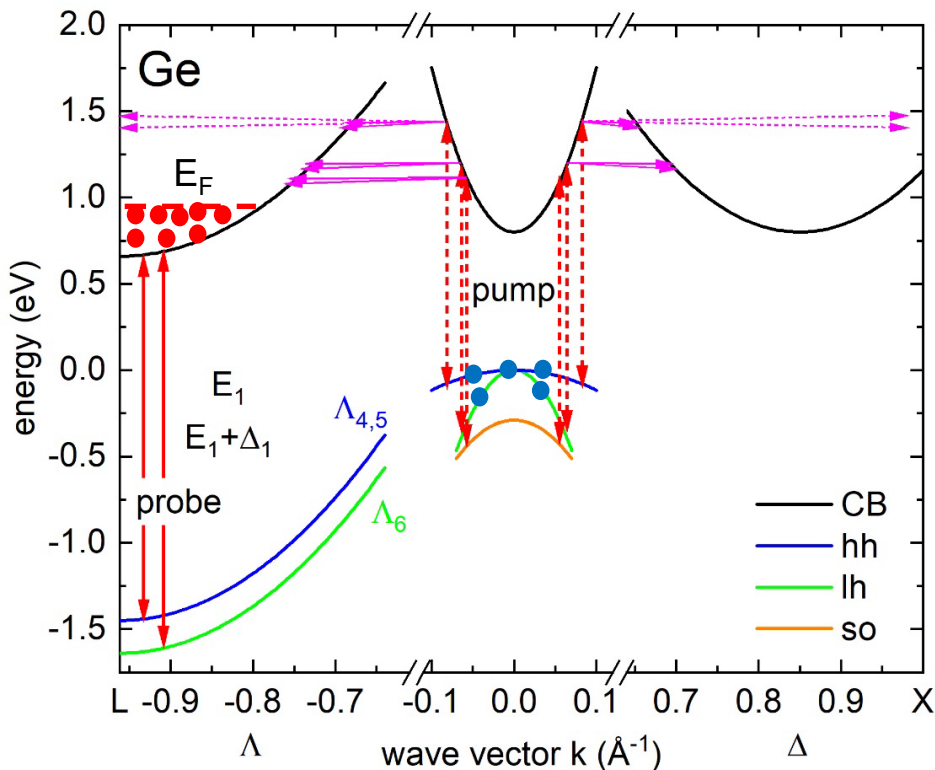
Etc.



eli

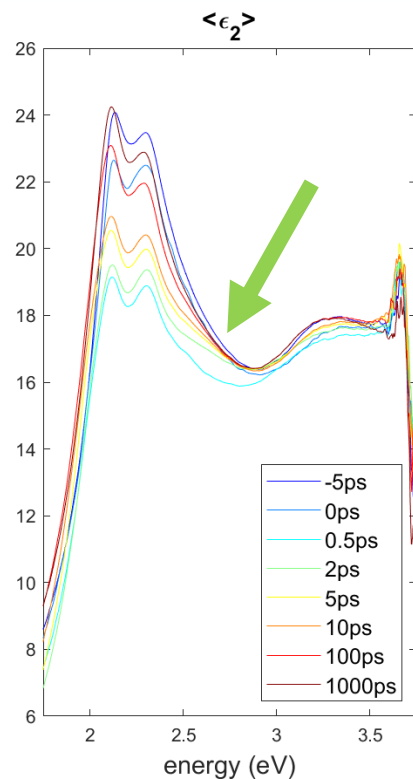
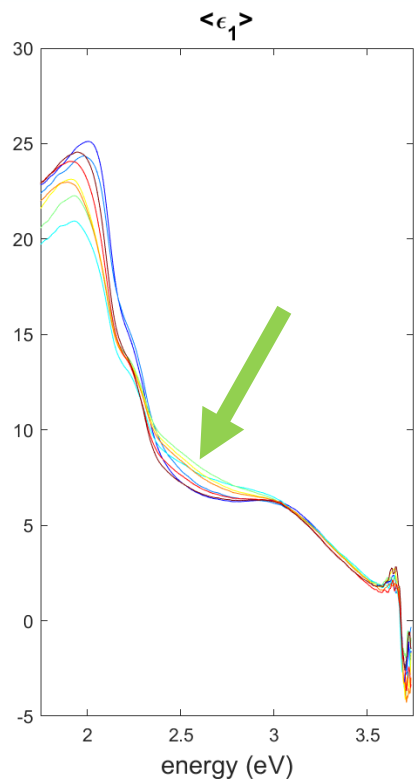
beamlines

Ultrafast processes in photoexcited Germanium



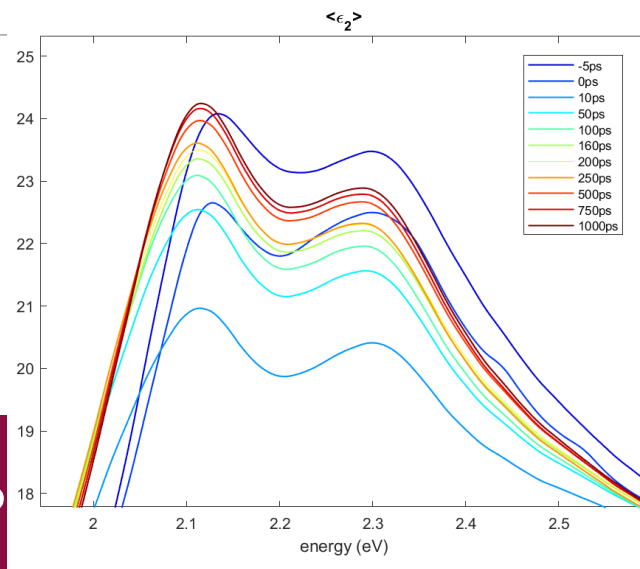
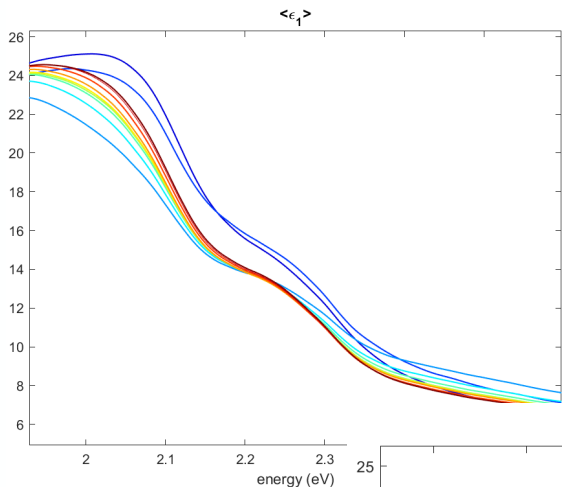
- 1.55 eV pump beam creates $N=10^{21} \text{ cm}^{-3}$ electron-hole pairs near Γ -point. 9 mW power.
- Heavy, light, split-off bands.
- Ignore diffusion (for 1.55 eV pump).
- Ignore Auger recombination.
- Thermalization: Fermi-Dirac distribution
- **Intervalley scattering: $\Gamma \rightarrow X \rightarrow L$**
- Electrons accumulate at L.
- Holes remain near Γ .
- Electrons at L block E_1 and $E_1 + \Delta_1$ transitions (**Fermi-level singularity**)
- **Bandgap renormalization: redshift expected**
- Lattice heating (25 K): redshift
- **Exciton screening**

Ultrafast processes in photoexcited Germanium



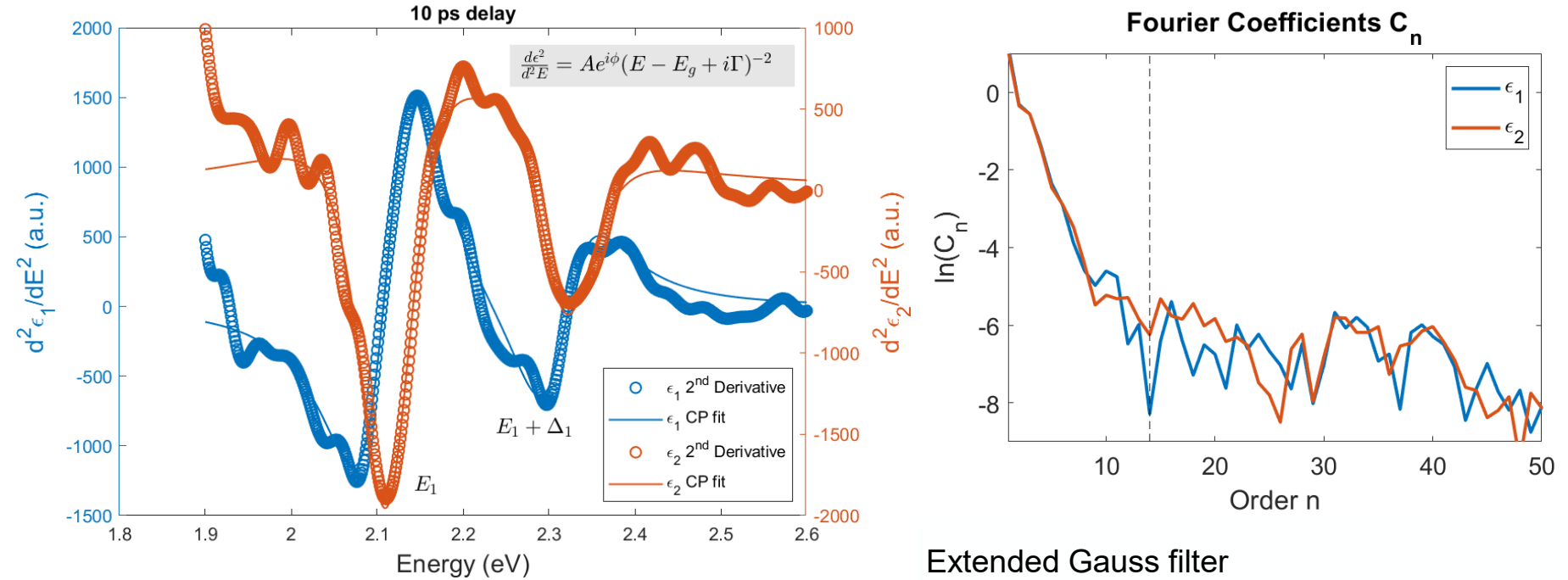
- 1.55 eV pump beam creates $N=4 \times 10^{21} \text{ cm}^{-3}$ electron-hole pairs near Γ -point.
- The E_1 and $E_1 + \Delta_1$ peaks decrease within the first two picoseconds and then recover:
Band filling, excitonic screening followed by diffusion, Auger, and radiative recombination.
- **Maybe a Fermi level singularity near 2.6 eV.**
- **Detailed modeling is required (Tanguy 2-D excitonic line shapes, including Fermi level singularity.)**

Ultrafast processes in photoexcited Germanium



- 1.55 eV pump beam creates $N=4 \times 10^{21} \text{ cm}^{-3}$ electron-hole pairs near Γ -point.
- The E_1 and $E_1 + \Delta_1$ peaks decrease within the first two picoseconds and then recover. (Band filling, excitonic screening followed by diffusion, Auger, and radiative recombination)
- Maybe a Fermi level singularity near 2.6 eV.
- **It looks like there is a redshift, but we need a line shape analysis with derivatives.**

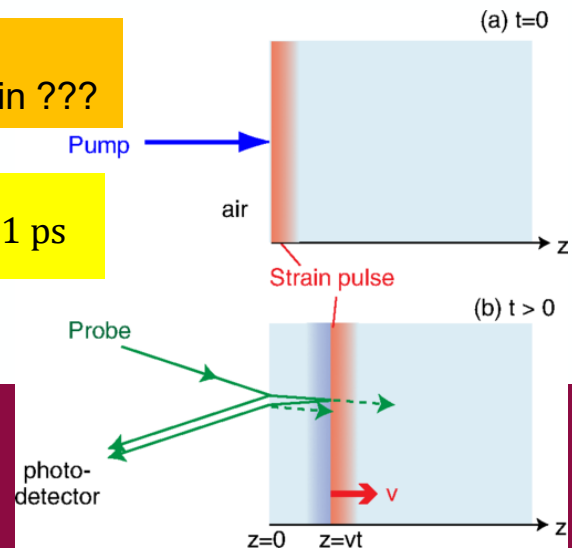
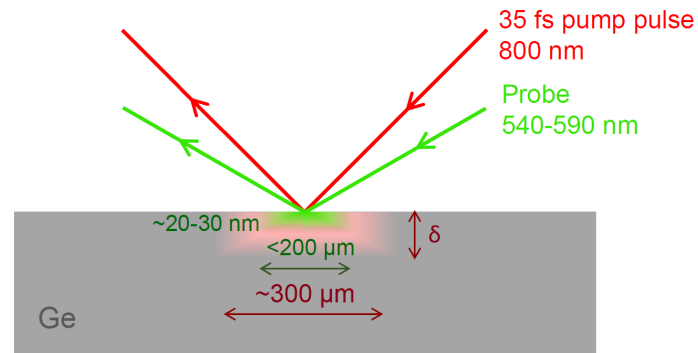
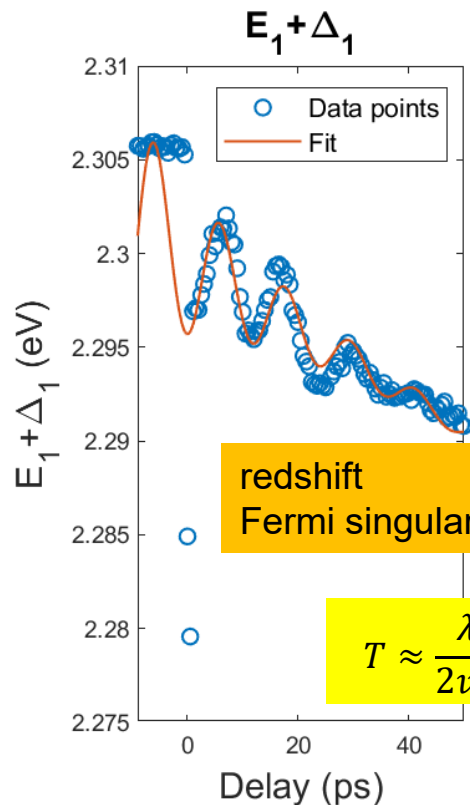
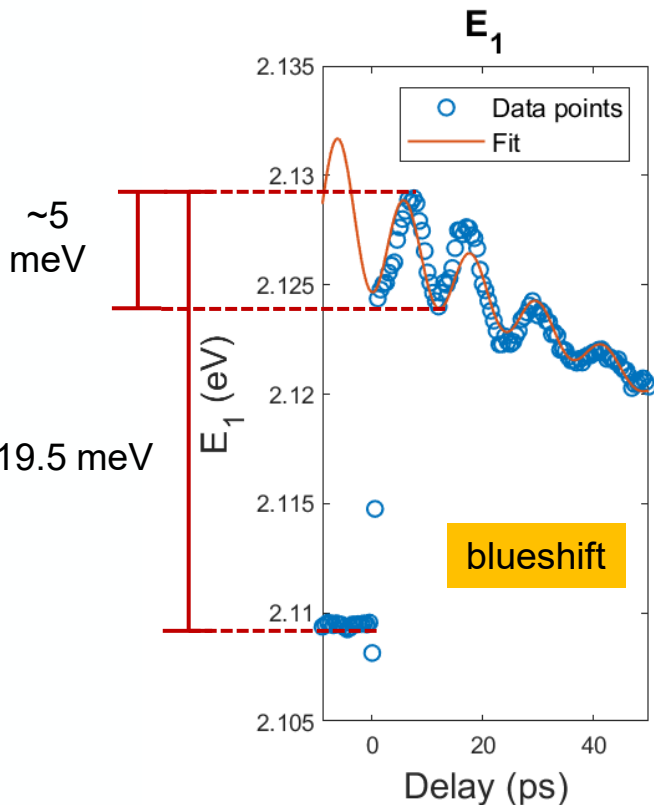
Derivative analysis: critical point parameters



Extended Gauss filter
Filter width determined from Fourier coefficients

Carlos Armenta, February 2023, unpublished.
Emminger *et al.*, PSS RRL **2022**, 2200058.
Le, JVST B **37**, 052903 (2019);

Coherent acoustic phonon oscillations

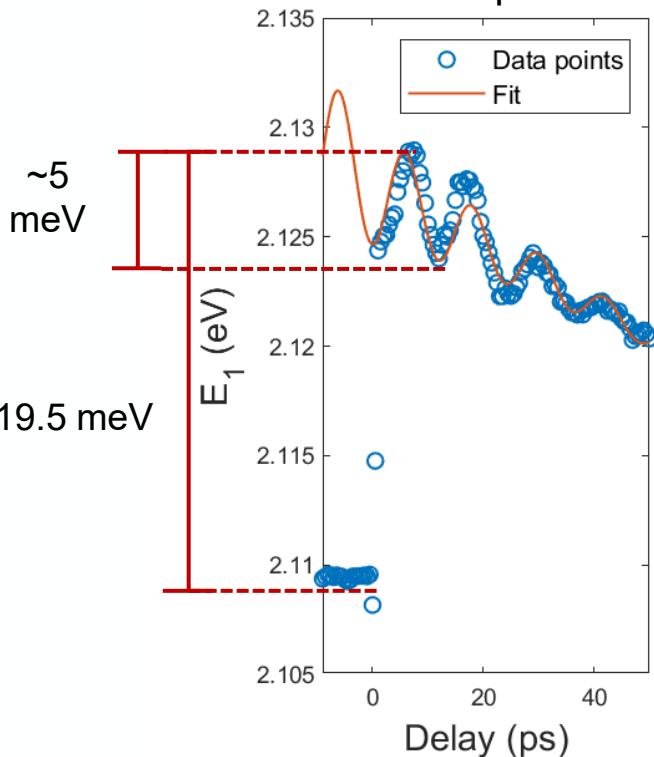


BE BOLD. Shape the Future.

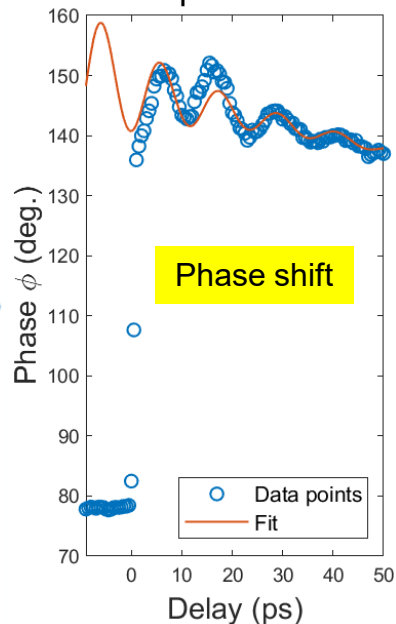
Carlos Armenta, February 2023, unpublished.
Emminger *et al.*, PSS RRL **2022**, 2200058.

Critical point parameters for E_1 and $E_1 + \Delta_1$

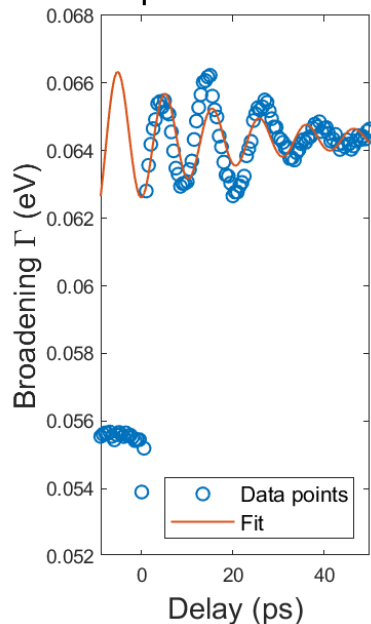
E_1



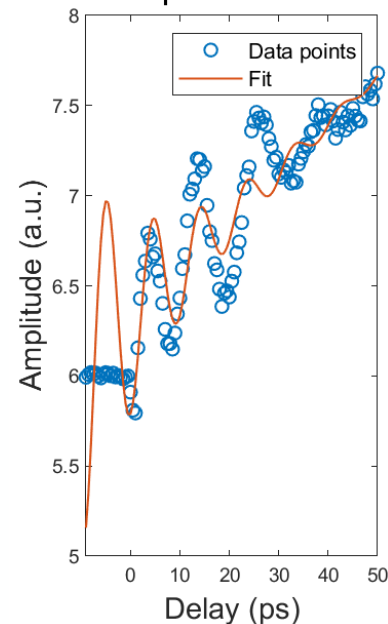
E_1 Phase ϕ



E_1 Broadening Γ



E_1 Amplitude



No red shift: phase angle changes. **Where is BGR?**

Conclusions

- Quantitative modeling of low-density optical processes is possible with basic physics and matrix elements from k.p theory:
 - **Photoluminescence in Ge**
 - **Indirect gap absorption in Ge**
 - **Direct gap absorption in Ge at low T**
 - More work is needed at high temperatures and for materials other than Ge.
- High carrier excitations:
 - **High electron doping density in Ge**
 - **Thermal excitation of electron-hole pairs in InSb**
 - **Femtosecond laser generation of electron-hole pairs in Ge (ELI Beamlines)**
 - Experimental data and qualitative explanations exist
- We need more experiments and more detailed theory and simulations.

Thank you!

Questions?

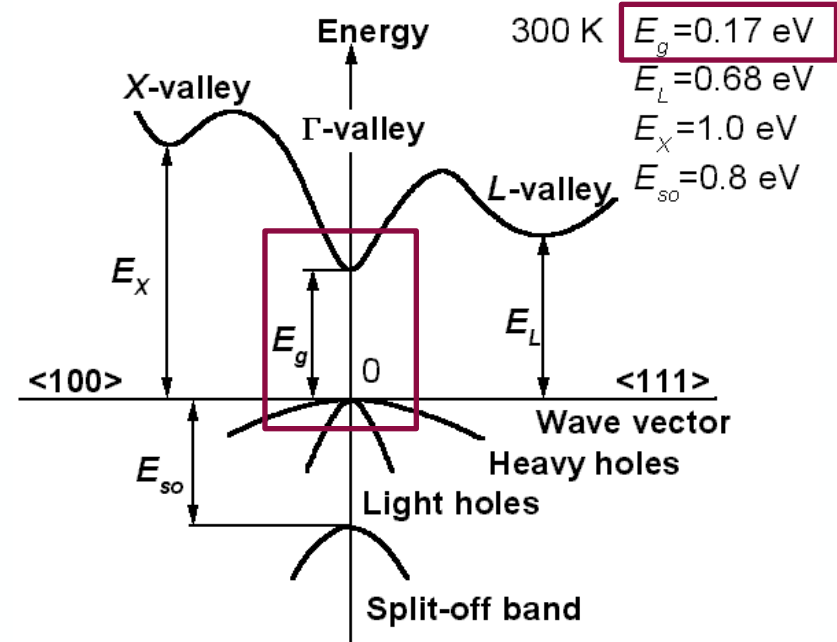


Direct band gap of InSb from 80 to 700 K

Measurement of the dielectric function of bulk InSb from 80 to 700 K near the direct band gap (E_0)



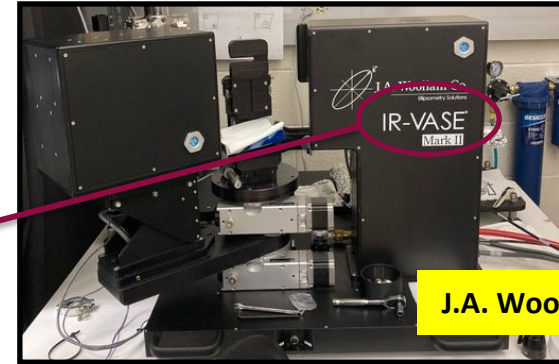
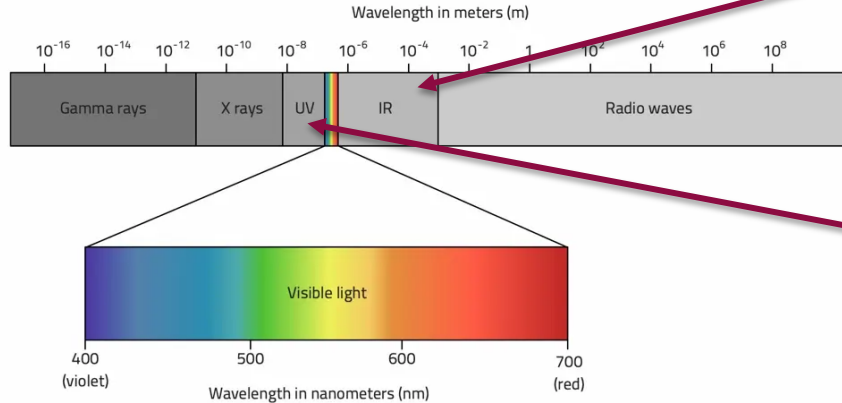
Bulk InSb: Commercial (MTI), (100) orientation, undoped, n-type, rough back side



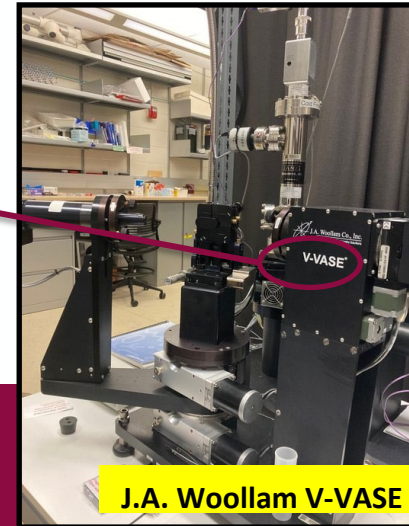
Direct Bandgap at 300 K: 0.17 eV

Ellipsometry from 190 nm to 40,000 nm

Two different instruments are used for measurements from the mid-infrared to the deep ultraviolet spectral range.



J.A. Woollam IR-VASE



J.A. Woollam V-VASE

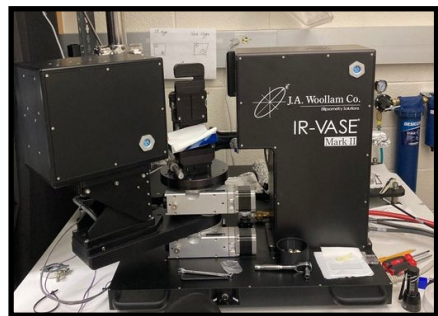


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SZ, Spectroscopic Ellipsometry from 10 to 700 K, Adv. Opt. Technol. 11, 117 (2022).

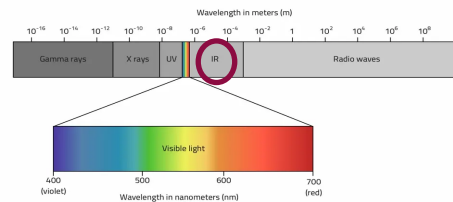
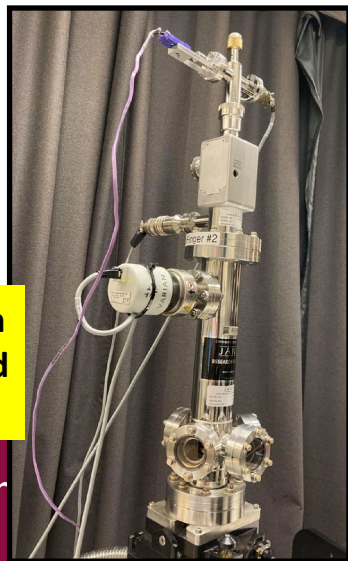
Temperature-dependent ellipsometry: 80-700 K

- Using FTIR spectroscopic ellipsometry in an ultra-high vacuum (UHV) cryostat with CVD diamond windows (Janis ST-400, Diamond Materials GmbH, Freiburg).
- Why diamond? Large transparency range and good vacuum seals, but expensive and high reflection losses.



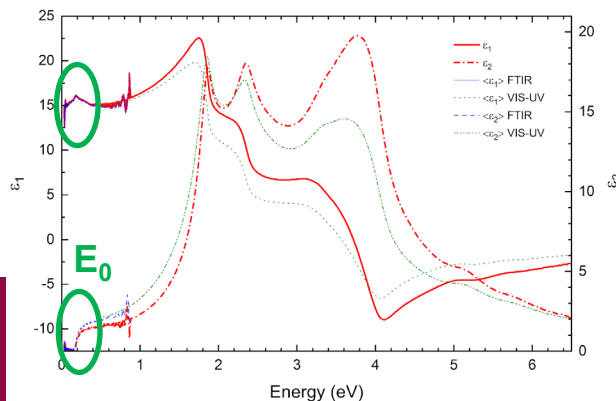
J.A. Woollam IR-VASE

Cryostat with
CVD diamond
windows



Energies: 30-40 meV to 1 eV

VIS-UV and FTIR spectra (dielectric functions) After oxide correction (25 Å)



Compare:
Aspnes, PRB **27**, 985 (1983)
Logothetidis, PRB **31**, 947 (1985).
Schaefer, JAP **127**, 165705 (2020).

SZ, Adv. Opt. Technol. **11**,
117 (2022).

InSb (100) sample preparation (cleaning)

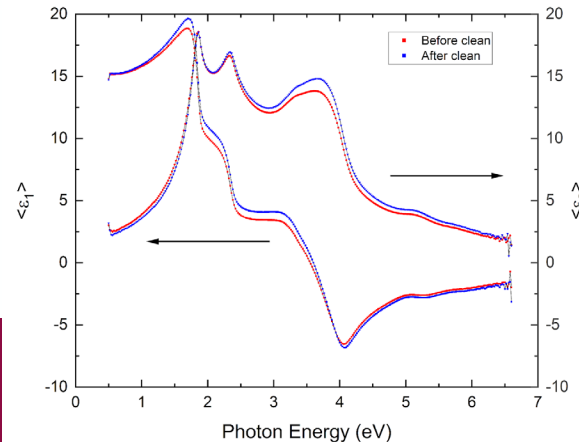
The InSb (100) sample was cleaned using **water** and **isopropanol** on the **ultrasonic cleaner** for 15 min on each to remove organic layers before the temperature dependent ellipsometry measurements.

Also: **Anneal sample at 450 K in UHV overnight** (degas)

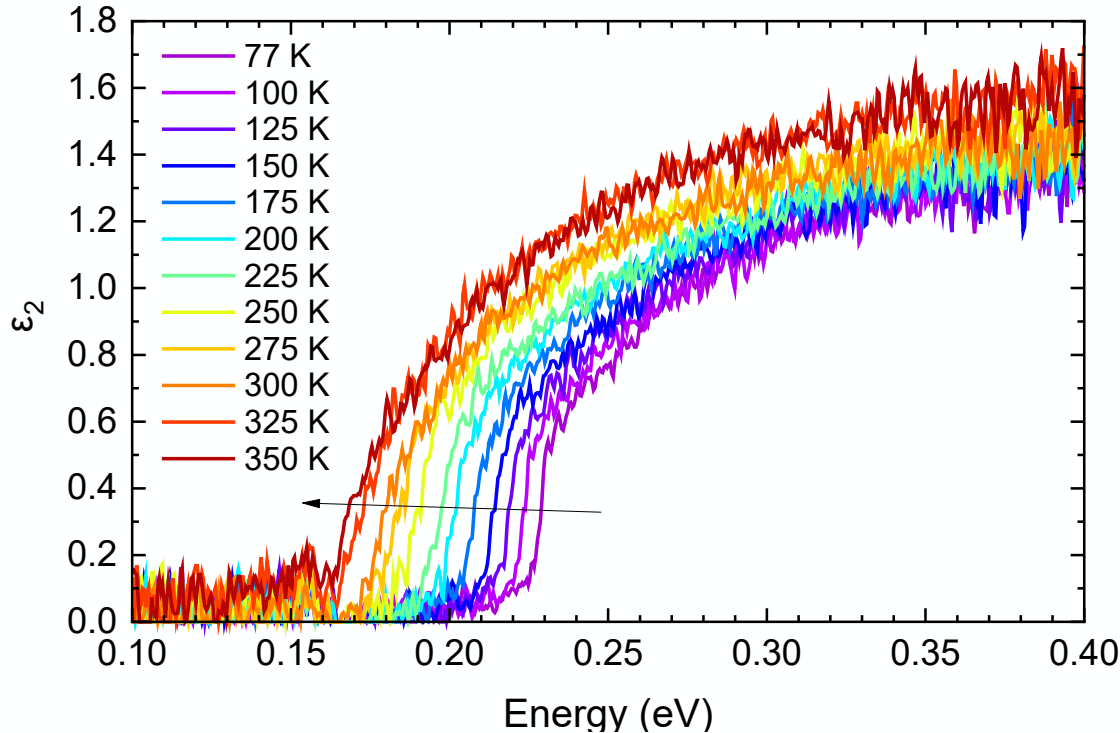
Not used: BrM, HCl-methanol (Aspnes/Studna 1983)



	Oxide Thickness (Å)
Before Clean	28.2
After Clean	22.5



InSb (100): Initial attempt was promising



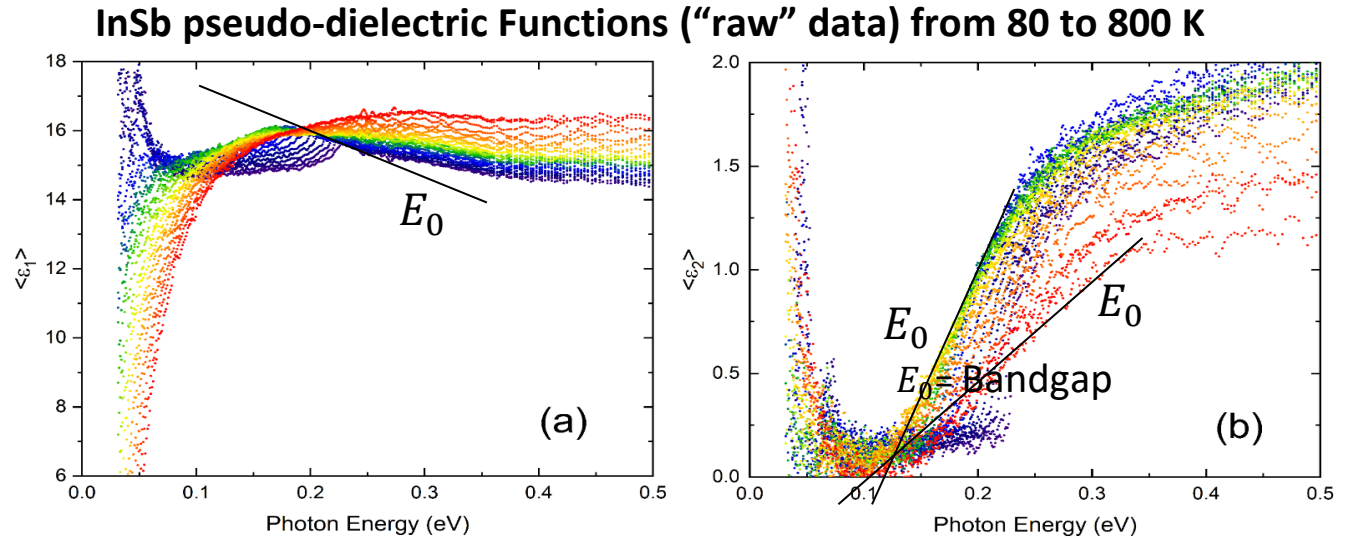
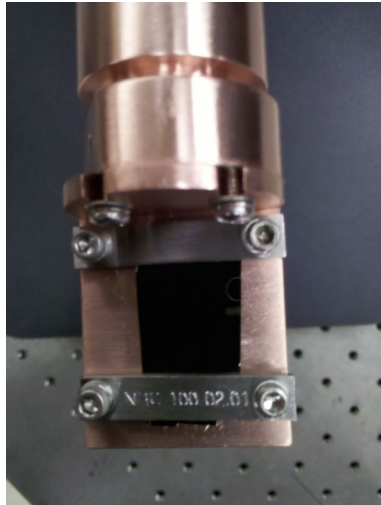
Multiple experimental issues:

- InSb sample cracks, melts, reacts with the Cu sample holder.
- Adhesive (carbon nanoparticles, silver paint) expands, evaporates, redeposits on the windows.
- Beam larger than sample: Depolarization from sample holder reflections.
- Black-body radiation, heat shield.
- Cryostat leaks, thermocouple breaks.

Initial result: **Clear redshift with increasing temperature (up to 450 K).**

Strange things happen above 450 K.

Data and oxide corrections (4 years later)



- Band gap reduced with increasing temperature (but only below 500 K)
- Drude response at high temperatures (thermally excited carriers)
- Depolarization artifacts at long wavelengths (below 300 K)

Band gap analysis

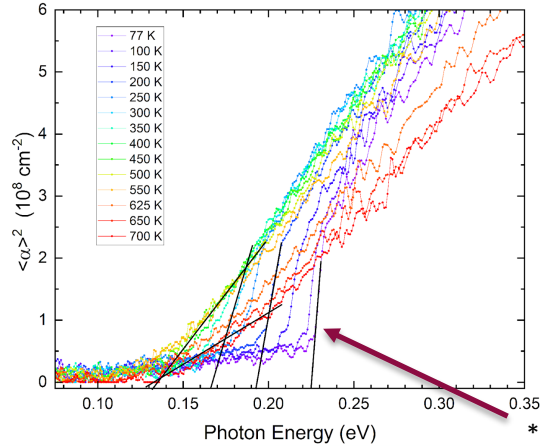
- How does the band gap of InSb change with temperature?

Tauc Plot:

$$\alpha(E) = A \sqrt{E - E_g}$$

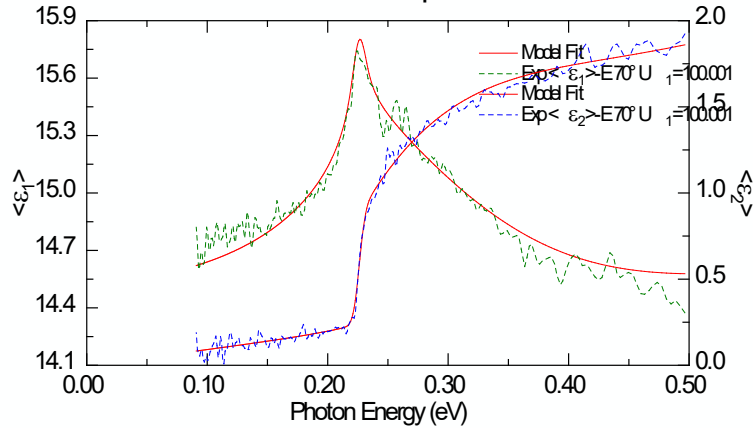


Need linear region, not possible



manual extrapolation

Parametric-Semiconductor Model:



Based on oscillator model

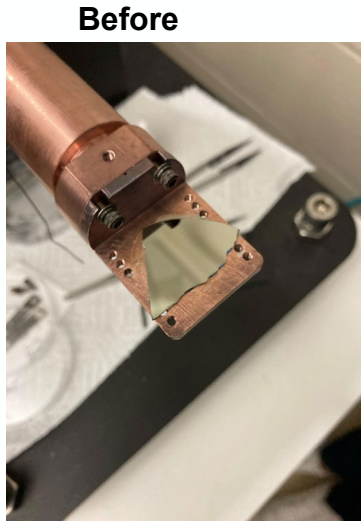
Parameter	Final Value
MSE	0.2958
En0.0	0.22615 ± 0.000889
Br0.0	4.7478 ± 1.32
Am0.0	0.31415 ± 124
Disc0.0	0.999 ± 788
RPos0.0	0.84009 ± 0.0264
RAmp0.0	1.8912 ± 0.191
PoleMag0.0	3.2469 ± 6.56
PoleMag2.0	1e-005 ± 0.000568

Conclusions

- Dielectric function of InSb measured from 80 to 700 K (with oxide correction of $25 \pm 5 \text{ \AA}$)
- Band gap is difficult to determine from a Tauc plot.
- Parametric semiconductor model shows great results for the band gap.
- Band gap shrinks with increasing temperature, but only up to 500 K.
- Band gap stays constant near 550 K and then increases again to 700 K.
- Drude tail due to thermal excitation of electron-hole pairs.
- Carrier concentration and mobility is reasonable (compared to Hall measurements).
- Detailed modeling requires Tanguy-Elliott theory of absorption by screened excitons, non-parabolicity, degenerate Fermi-Dirac statistics, k.p theory (in progress).
- InSb would behave as a topological insulator above melting point. Not possible.

Sad ending

- Unfortunately, the InSb sample melted at 750 K, but melting point is 800 K...
- Cannot become a topological insulator because it melts.



Future work:

Repeat experiment at high temperatures (below 750 K).

Increasing and decreasing temperature scans.