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Theory of Direct Band Gap Absorption in Highly Excited Semiconductors

AVS 2022, Pittsburgh, PA

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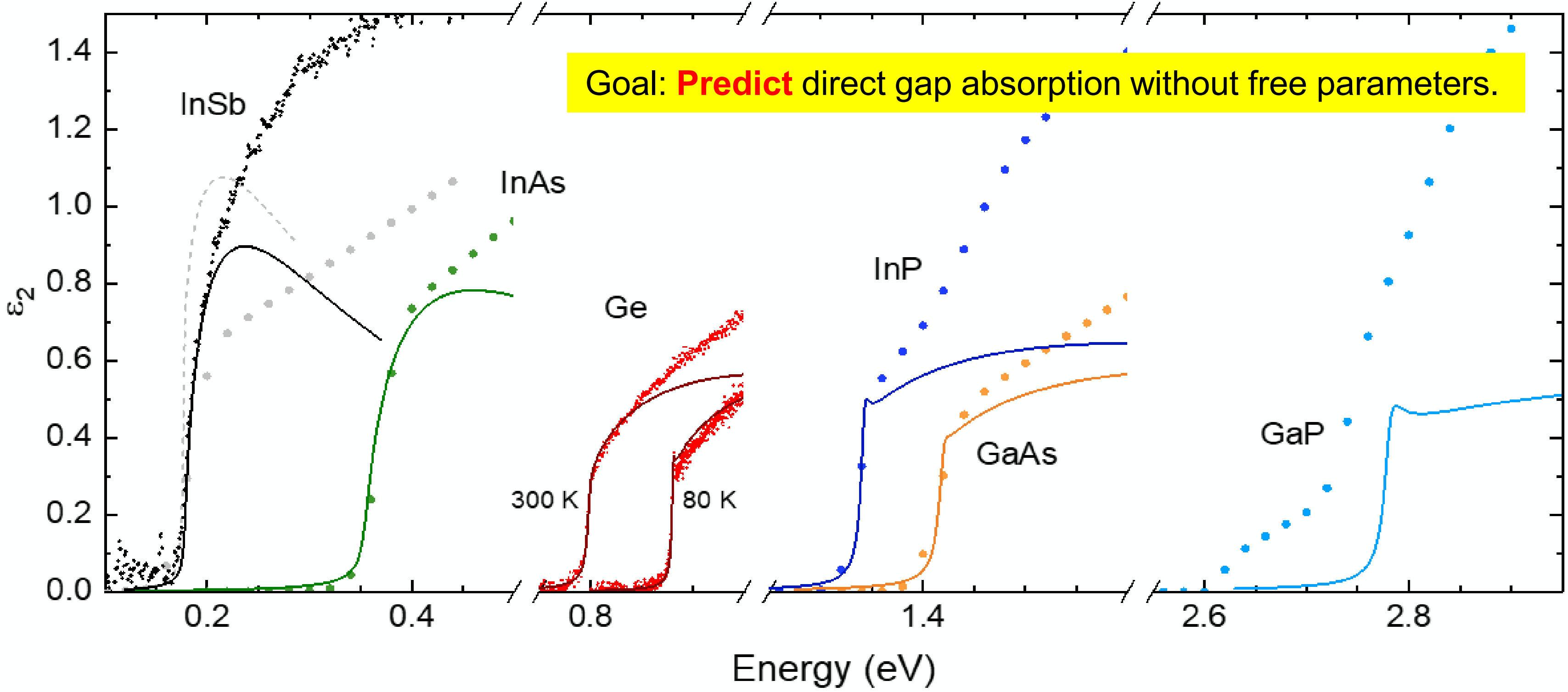
Problem Statement: Direct Gap Absorption



Goal: **Predict** direct gap absorption without free parameters.

Carola Emminger *et al.*, JAP **131**, 165701 (2022).

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
   - a) **In situ doping** or
   - b) **ultrafast lasers** or
   - c) **high temperatures**.

Goal: CMOS-integrated mid-infrared camera (thermal imaging with a phone).

Fermi's Golden Rule: Tauc Plot

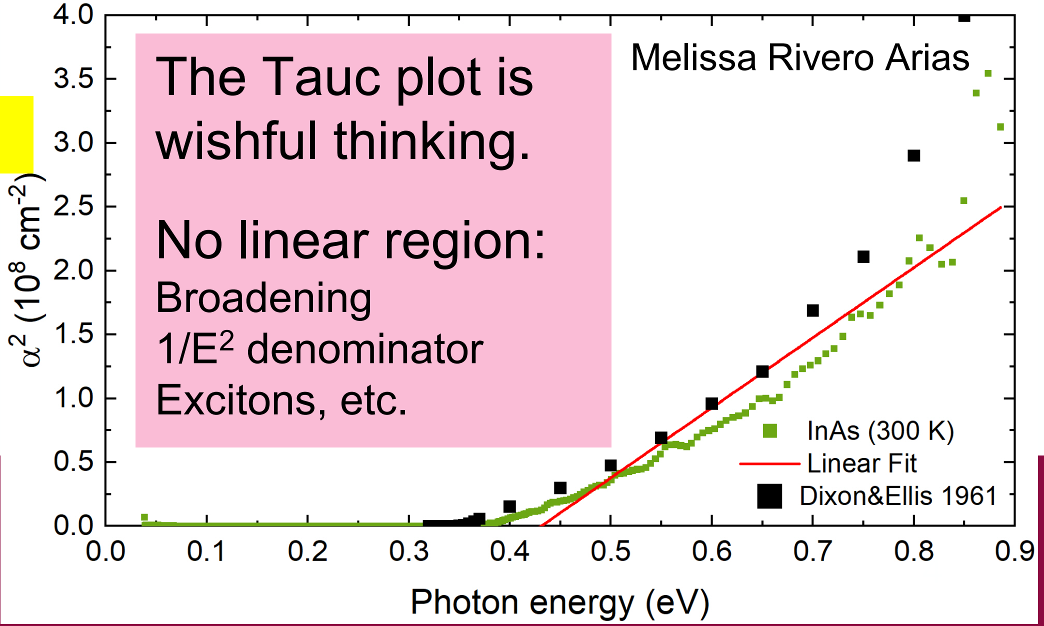
Direct band gap absorption

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

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

Use **k·p** matrix element *P*: $E_P=2P^2/m_0$

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



Melissa Rivero Arias

The Tauc plot is wishful thinking.

No linear region:

Broadening

1/E^2 denominator

Excitons, etc.

k·p Theory (Band Structure Method)

Schrödinger equation

$$H\Phi_{n\vec{k}} = \left(\frac{\vec{p}^2}{2m} + V\right)\Phi_{n\vec{k}} = E_{n\vec{k}}\Phi_{n\vec{k}}$$

Use Bloch's theorem: $\Phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r})$

Product rule

$$(fg)'' = f''g + 2f'g' + fg''$$

Solve equation for **k**=0. $$\left(\frac{\vec{p}^2}{2m} + \frac{\hbar^2\vec{k}^2}{2m} + \frac{\hbar\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{p}}}{\boldsymbol{m}} + V\right)u_{n\vec{k}} = E_{n\vec{k}}u_{n\vec{k}}$$

Treat red term in perturbation theory.

Outcomes:

Optical dipole matrix element, effective masses, exciton energies, nonparabolicity, **k-dependent matrix elements**

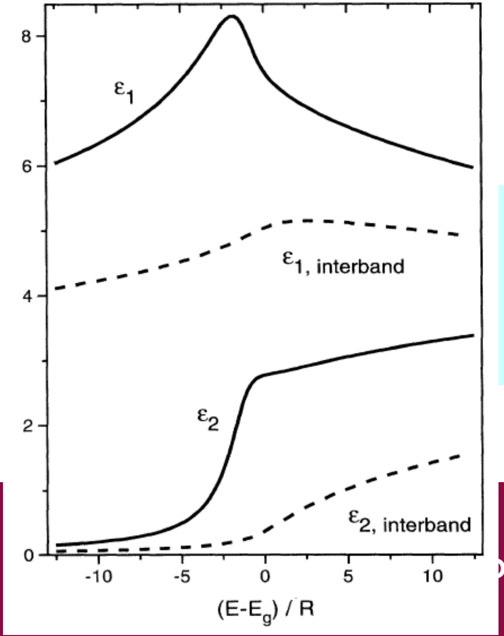
Yu & Cardona, Fundamentals of Semiconductors
Kane, J. Phys. Chem. Solids **1**, 249 (1957). Kane 1966.

Elliott-Tanguy Exciton Absorption

Direct band gap absorption

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

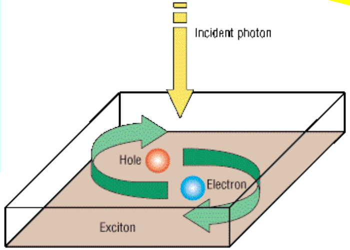
$$\varepsilon_2(\hbar\omega)=\frac{e^2\sqrt{m_0}\,\mu^{\frac{3}{2}}}{3\pi\sqrt{2}\,\varepsilon_0\hbar}\,\frac{E_P\sqrt{R}}{(\hbar\omega)^2}\left[\sum_{n=1}^{\infty}\frac{4\pi R}{n^3}\,\delta\left(\hbar\omega-E_0+\frac{R}{n^2}\right)+\frac{2\pi H(\hbar\omega-E_0)}{1-\exp\left(-2\pi\sqrt{{R}/{\hbar\omega-E_0}}\right)}\right]$$

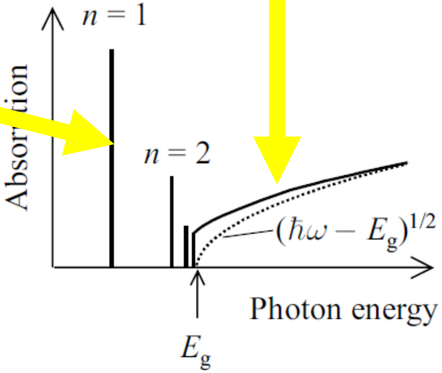


Tanguy's contributions:
- Add Lorentzian broadening
- Kramers-Kronig transform to get the real part.

bound excitons

exciton continuum enhancement





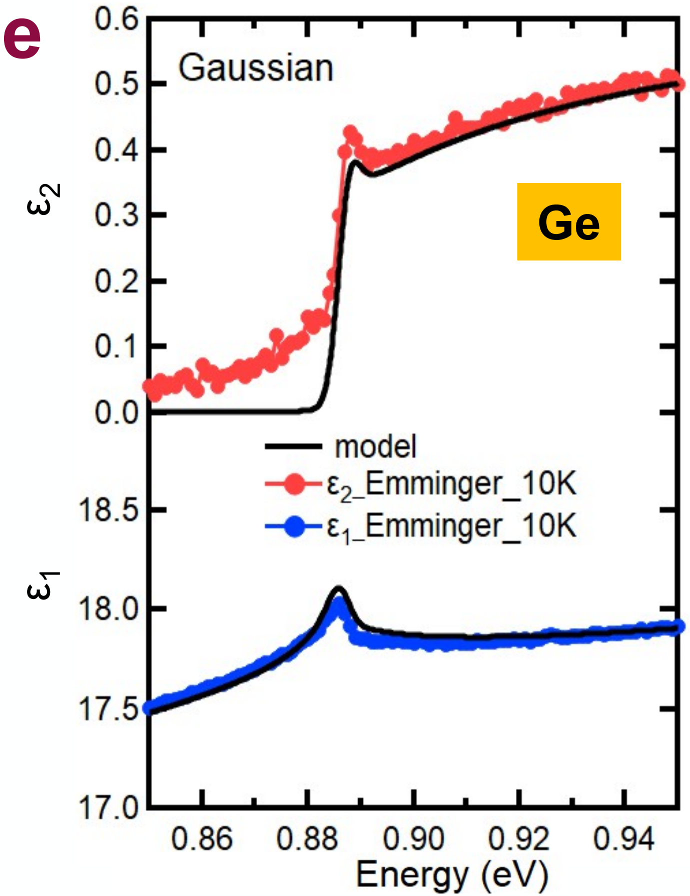
R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
Christian Tanguy, Phys. Rev. Lett. **75**, 4090 (1995) + (E)

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)

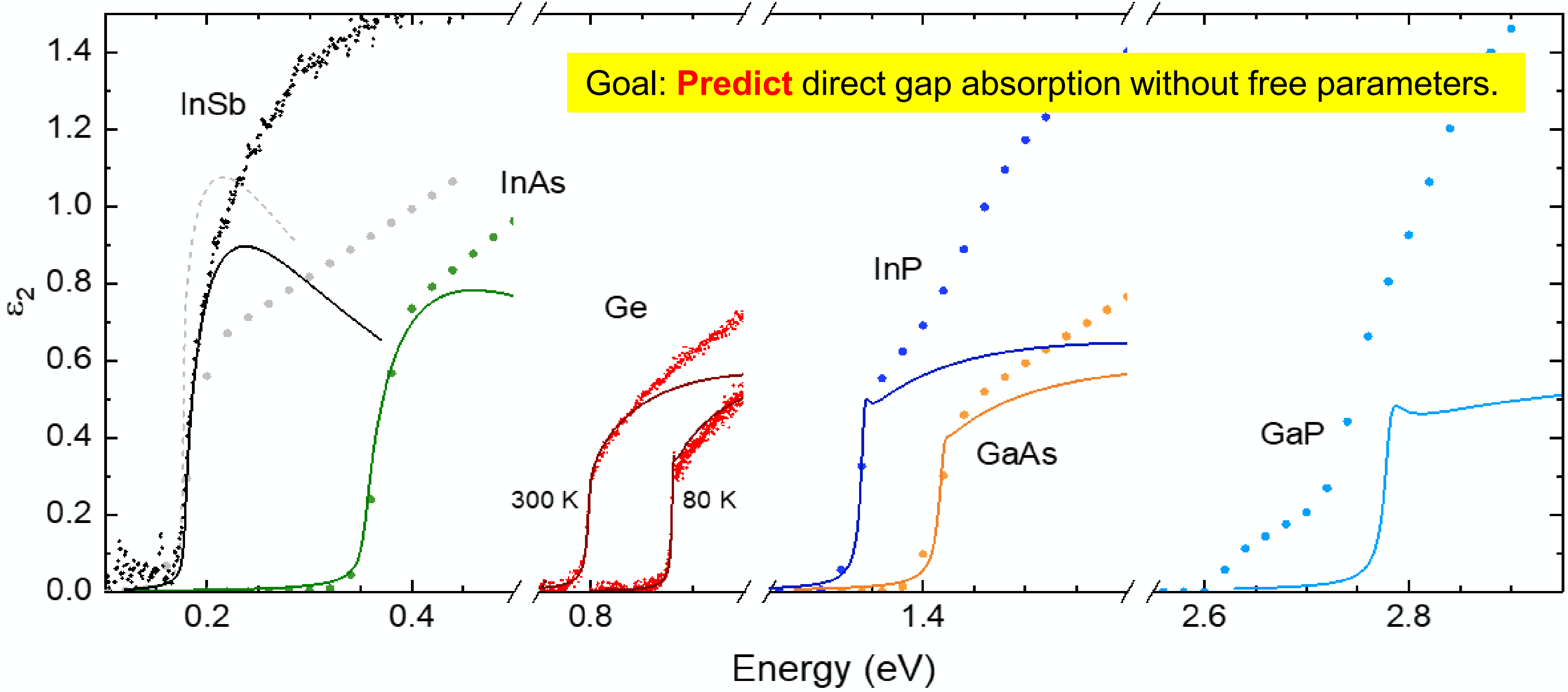
- **Adjustable parameters:**
- Broadening Γ: 2.3 meV
- Band gap E_0
- Linear background A_1 and B_1 (contribution from E_1 to real part of ε)

Quantitative agreement



Carola Emminger *et al.*, JAP **131**, 165701 (2022).

No success for other semiconductors



Goal: **Predict** direct gap absorption without free parameters.

Carola Emminger *et al.*, JAP **131**, 165701 (2022).

Kane’s 8x8 k·p Hamiltonian

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

Outcome:
Nonparabolicity,
k-dependent matrix elements.
Analytical solutions.

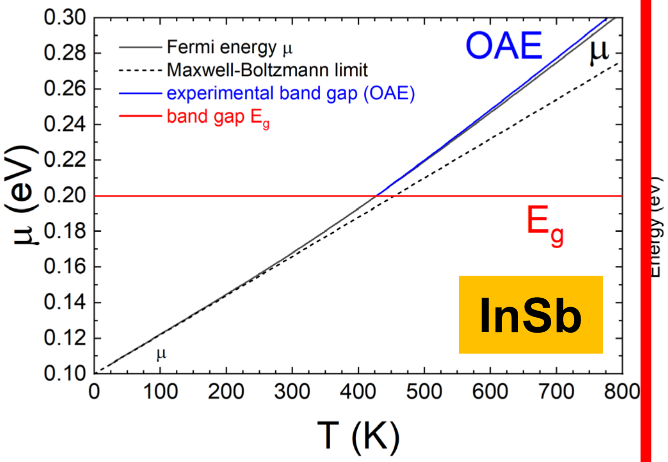
Characteristic equation is cubic:
Solve with Vieta’s method.

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

Approximations exist for small or large spin-orbit splittings but are not satisfactory.
We need a **perturbative solution** to the cubic equation for small wave vectors k.

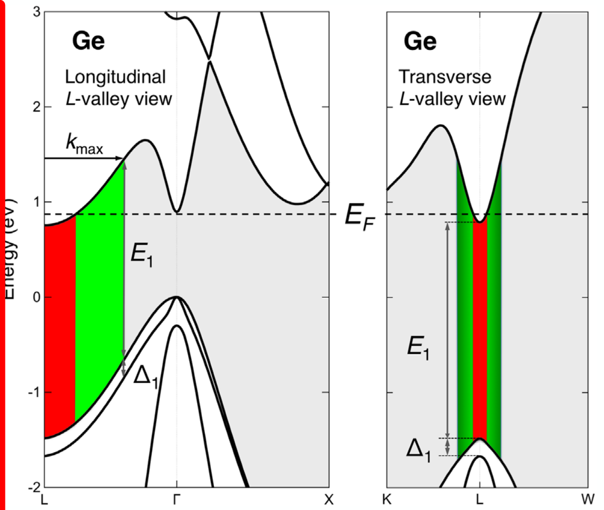
E. O. Kane, *Band Structure of InSb*, J. Phys. Chem. Solids **1**, 249 (1957).
E. O. Kane, 1966.

Optical Absorption at High Carrier Densities



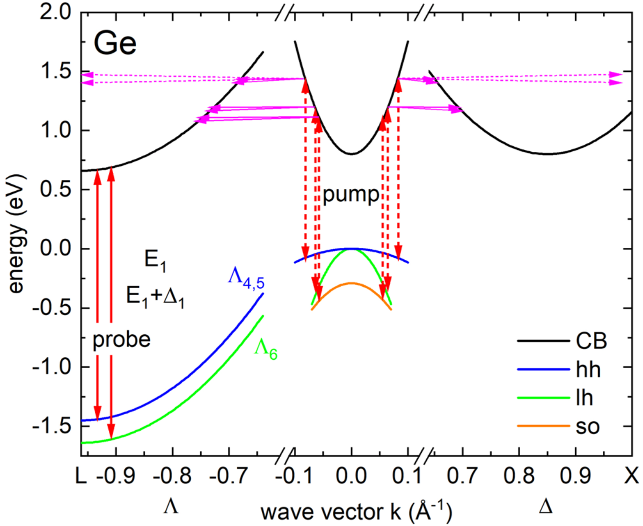
High temperature
(thermal excitation of e-h pairs)
constant m and E_g

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



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

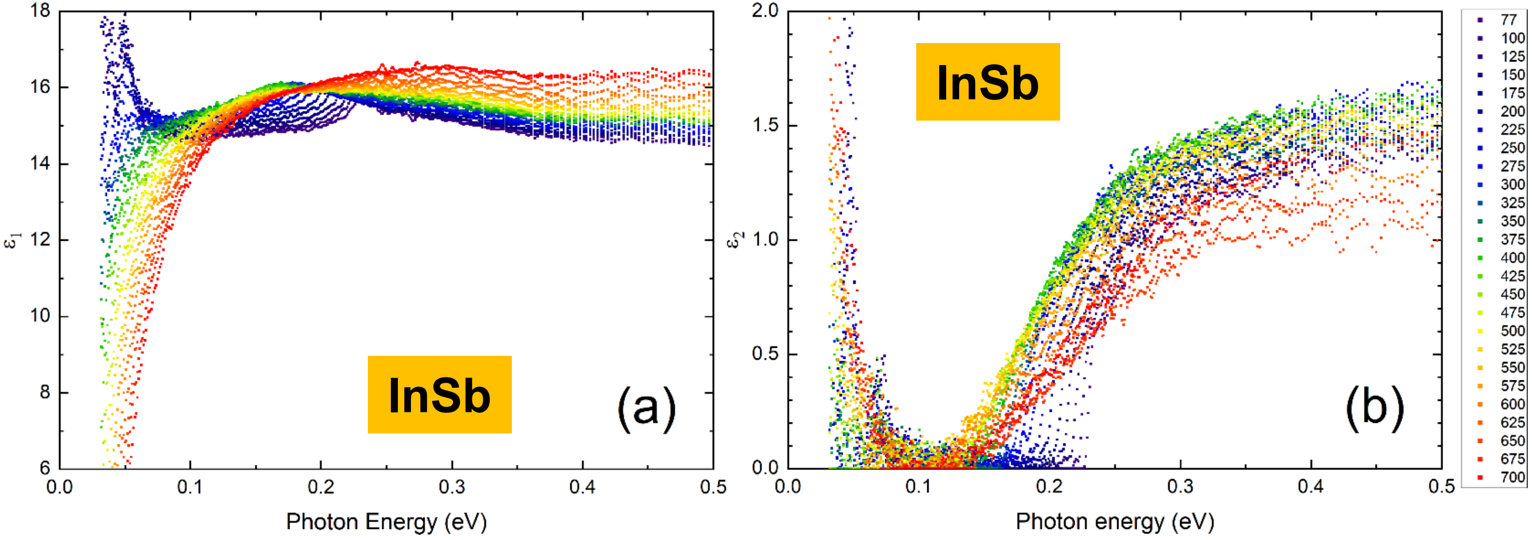
Xu et al., PRL **118**, 267402 (2017)

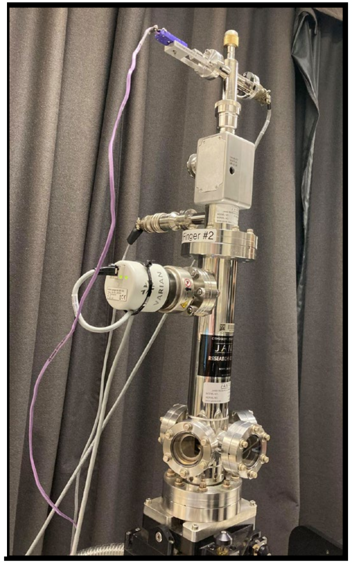


Intense femtosecond **laser excitation** (ELI Beamlines)
(electrons pile at L-point)

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

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).

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

Required model improvements: Screened Excitons

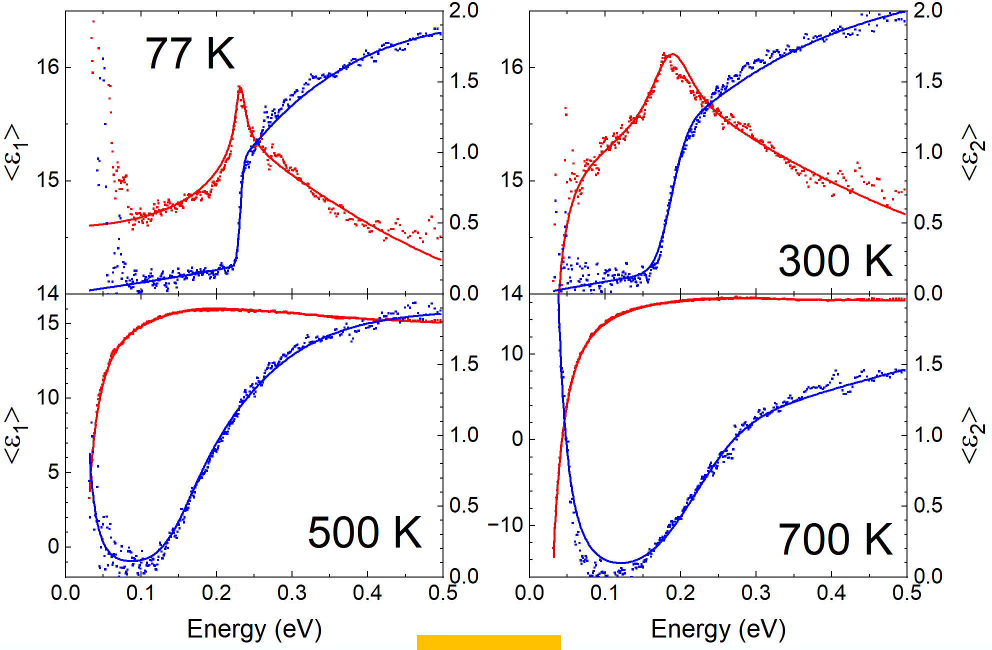
$$\varepsilon_2(E)=\frac{2\pi A\sqrt{R}}{E^2}\left\{\sum_{n=1}^{\sqrt{g}}\frac{2R}{n}\left(\frac{1}{n^2}-\frac{n^2}{g^2}\right)\delta\left[E-E_0+\frac{R}{n^2}\left(1-\frac{n^2}{g}\right)^2\right]+\frac{\sinh(\pi g k)\mathrm{H}(E-E_0)}{\cosh(\pi g k)-\cosh\left(\pi g\sqrt{k^2-\frac{4}{g}}\right)}\right\}[f_h(E)-f_e(E)]$$

- **Absorption by screened excitons** (Hulthen potential)
- **Screening parameter** $g=12/\pi^2 a_R k_{TF}$ (large: no screening)
- **Two terms for light and heavy excitons**
- **Numerical Kramers-Kronig transform** (Fermi factors)
- **Non-parabolicity and temperature-dependent mass** from k.p theory
- **Degenerate Fermi-Dirac statistics with nonparabolic DOS** to calculate f_h & f_e.
- **k-dependent matrix element *P***.
- 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
- **Band gap renormalization.**

Christian Tanguy, Phys. Rev. B **60**, 10660 (1999).
Jose Menendez, Phys. Rev. B **101**, 195204 (2020).
Carola Emminger, J. Appl. Phys. **131**, 165701 (2022).

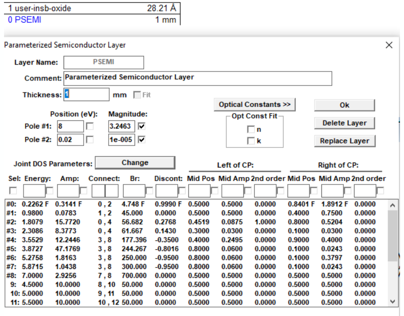
Band gap analysis for InSb

How does the band gap of InSb change with temperature?



InSb

Parametric-Semiconductor Model:



1 user-insb-oxide	28.21 Å
0 PSEMI	1 mm

Parameterized Semiconductor Layer

Layer Name: PSEMI

Comment: Parameterized Semiconductor Layer

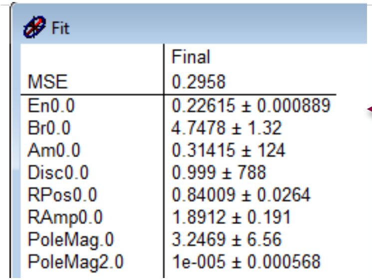
Thickness: 1 mm ☐ Fit

	Position (eV):		Magnitude:	
Pole #1:	8	☐	3.2463	☑
Pole #2:	0.02	☐	1e-005	☑

Opt Const Fit: ☐ n ☐ k

Joint DOS Parameters:

Sel:	Energy:	Amp:	Connect:	Br:	Discont:	Left of CP: Mid Pos	Left of CP: Mid Amp	Left of CP: 2nd order	Right of CP: Mid Pos	Right of CP: Mid Amp	Right of CP: 2nd order
#0:	0.2262 F	0.3141 F	0 , 2	4.748 F	0.9990 F	0.5000	0.5000	0.0000	0.8401 F	1.8912 F	0.0000
#1:	0.9800	0.0783	1 , 2	45.000	0.0000	0.5000	0.5000	0.0000	0.4000	0.7500	0.0000
#2:	1.8079	15.7720	0 , 4	56.682	0.2768	0.4519	0.0875	1.0000	0.8000	0.5204	0.0000
#3:	2.3086	8.3773	0 , 4	61.667	0.1430	0.3000	0.0300	0.0000	0.1000	0.0300	0.0000
#4:	3.5529	12.2446	3 , 8	177.396	-0.3500	0.4000	0.2495	0.0000	0.9000	0.4000	0.0000
#5:	3.8727	47.1769	3 , 8	244.267	-0.8016	0.8000	0.0600	0.0000	0.1000	0.0243	0.0000
#6:	5.2758	1.8163	3 , 8	250.000	-0.9500	0.8000	0.0600	0.0000	0.1000	0.3797	0.0000
#7:	5.8715	1.0438	3 , 8	300.000	-0.9500	0.8000	0.0600	0.0000	0.1000	0.0243	0.0000
#8:	7.0000	2.9256	7 , 8	700.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000
9:	4.5000	10.0000	8 , 10	50.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000
10:	5.0000	10.0000	9 , 11	50.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000
11:	5.5000	10.0000	10 , 12	50.000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000



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

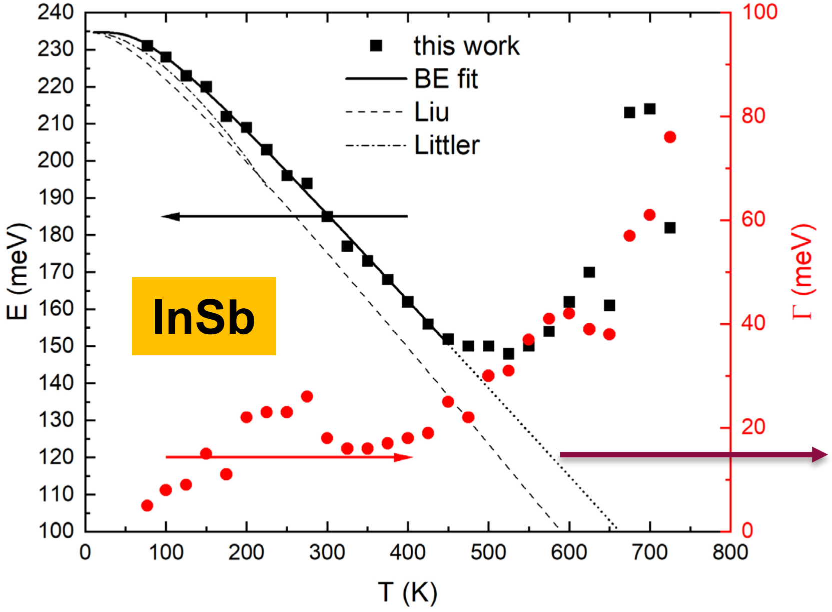
Also vary "shape parameters".

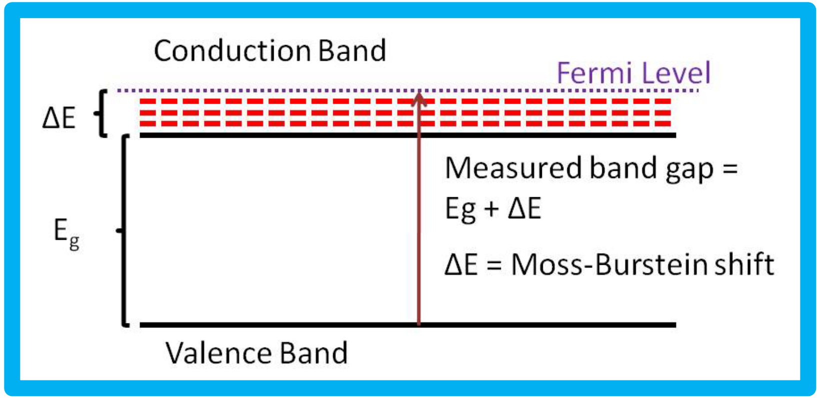
Asymmetric peak shape poorly described.

Try Tanguy oscillator for excitonic line shape.

C. M. Herzinger, B. Johs, et al., J. Appl. Phys. **83**, 3323 (1998)
Rivero Arias, JVSTB **41**, 022203 (2023)

Band gap of InSb from 80 to 800 K




Conduction Band

Fermi Level

ΔE

E_g

Measured band gap = Eg + ΔE

ΔE = Moss-Burstein shift

Valence Band

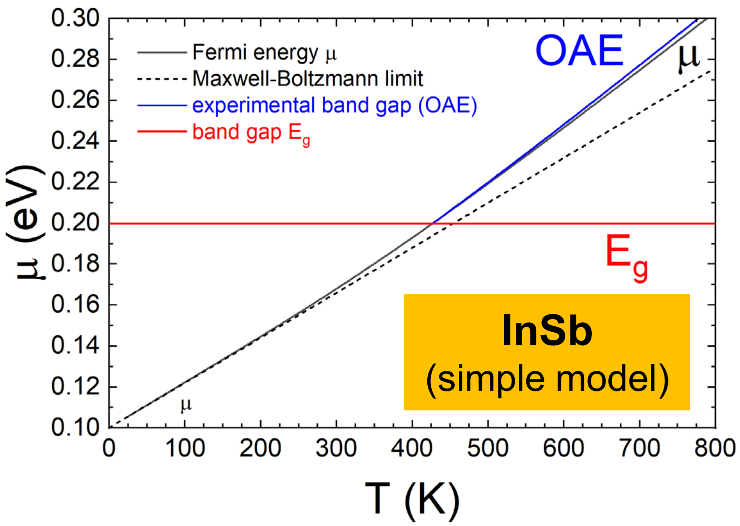
Bose-Einstein Model

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

- 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**

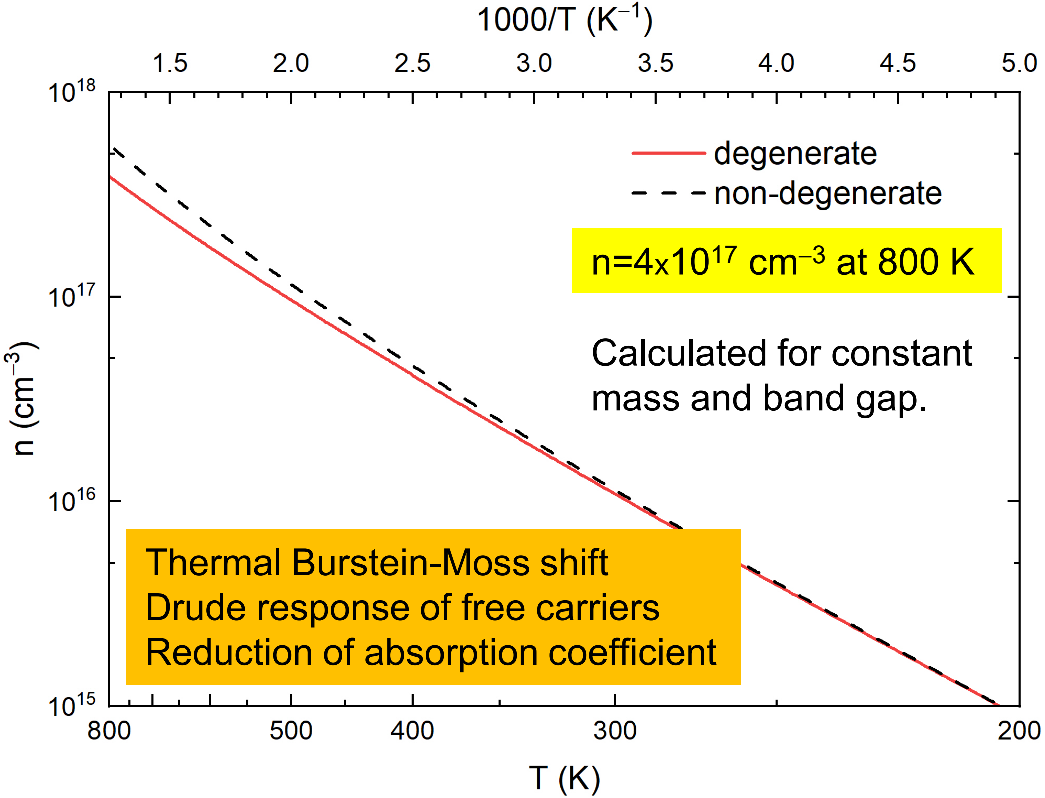
T.S. Moss, Proc. Phys. Soc. **67**, 775 (1954).
E. Burstein, Phys. Rev. **93**, 632 (1954).

Thermal excitations of electron-hole pairs in InSb



InSb
(simple model)

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



n=4x10^{17} cm^{-3} at 800 K

Calculated for constant mass and band gap.

Thermal Burstein-Moss shift
Drude response of free carriers
Reduction of absorption coefficient

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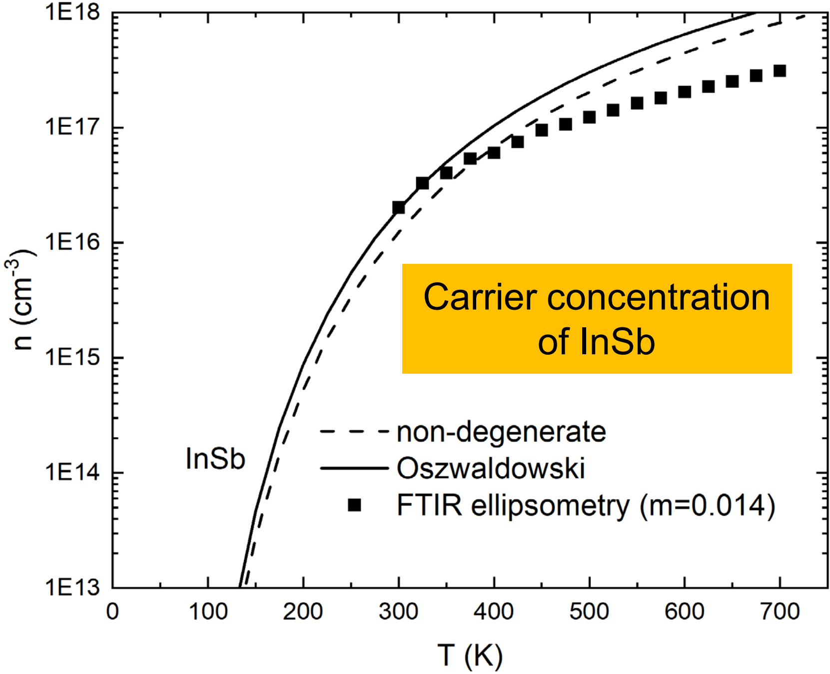
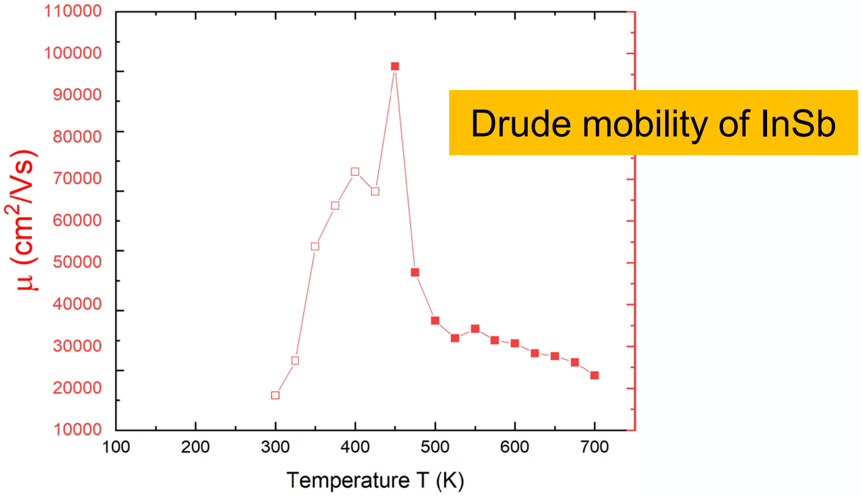
Rivero Arias, JVSTB **41**, 022203 (2023)

Carrier concentration and mobility from 80 to 800 K

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

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


Carrier concentration of InSb


Drude mobility of InSb

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

Oswaldowski/Zimpel, J. Phys. Chem. Solids **49**, 1179 (1988).
D. L. Rode, Phys. Rev. B **3**, 3287 (1971).

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 with input from k·p theory (nonparabolicity, matrix elements)
- High carrier excitations:
  - **High electron doping density in Ge** (Menendez)
  - **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?