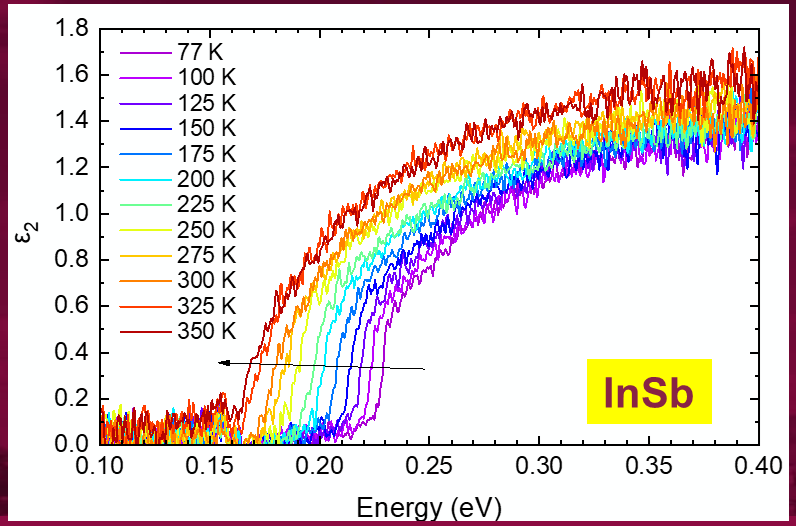
2024 Nebraska Ellipsometry Lecture Mini Series

FA9550-20-1-0135 AFOSR
NSF DMR-2235447 NSF

Matrix elements and excitonic effects in the direct gap absorption of semiconductors



Stefan Zollner

with:
Carola Emminger (Uni Leipzig and HU Berlin, Germany)
Jose Menendez (Arizona State University, Tempe, AZ)

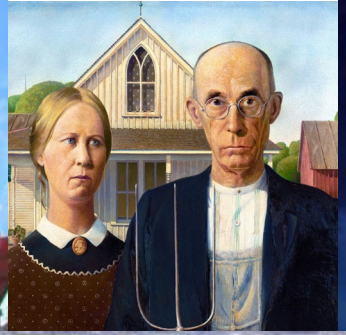
Email: zollner@nmsu.edu. WWW: http://femto.nmsu.edu.

BE BOLD. Shape the Future.

College of Arts and Sciences, Department of Physics
New Mexico State University, Las Cruces, NM, USA

Biography

Regensburg/Stuttgart
Germany



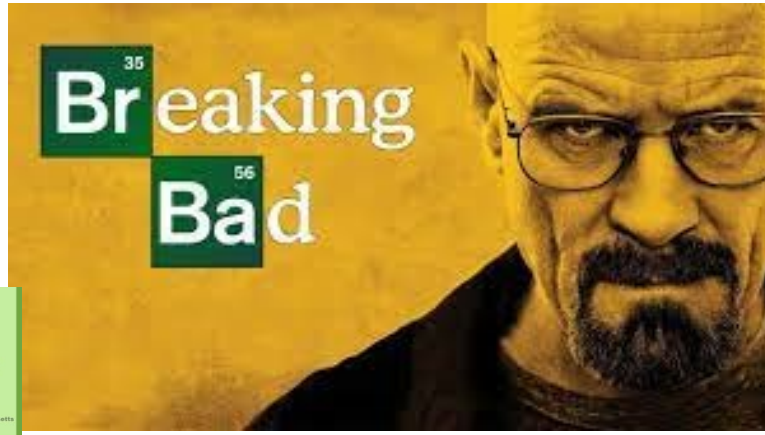
Motorola (Mesa, Tempe)
Arizona, 1997-2005

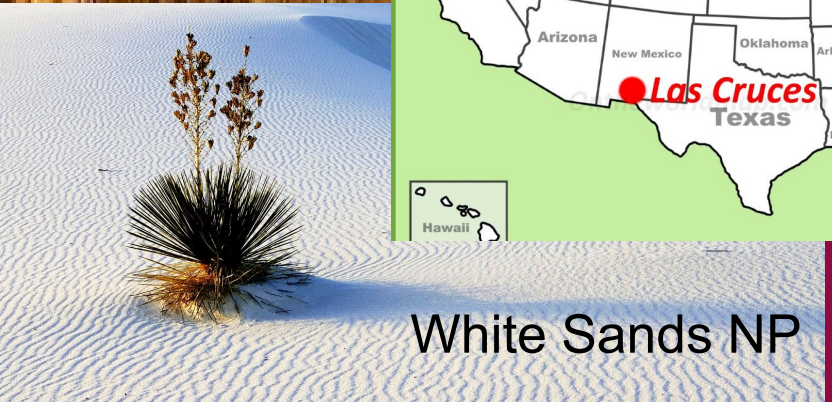
Freescale, IBM
New York, 91-92; 07-10

NMSU
Las Cruces, NM
Since 2010

Motorola, Freescale
Texas, 2005-2007

Where is Las Cruces, NM ???





New Mexico State University, Las Cruces

Land grant institution, Carnegie R2 (soon to be R1)
Comprehensive: Arts and Sciences, Education, Business, Agriculture
Ph.D. programs in sciences, engineering, agriculture; Ag extension

14,000 students (11,500 UG, 2,500 GR), 1000 faculty

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

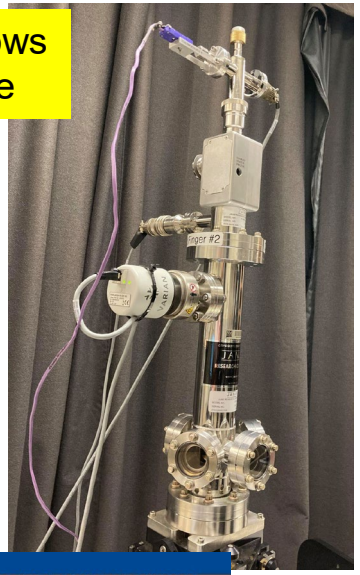
Military-friendly institution (Army and Air Force ROTC programs)

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

Physics: BS/BA, MS, PhD degrees. 71 UG and 37 GR students.
12 faculty (HE Nuclear and Materials Physics), **1.7 M$ expenditures.**
ABET-accredited BS in Physics and BS in Engineering Physics

Ellipsometry at NMSU

diamond windows
closed-cycle He

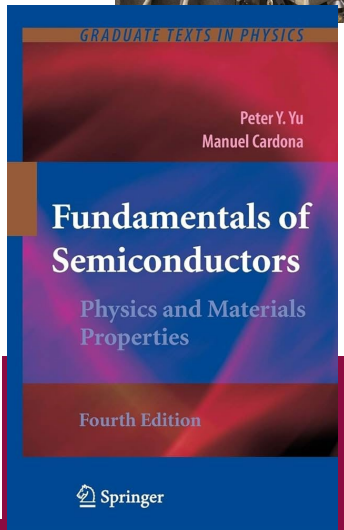


Ellipsometry on anything (inorganic, 3D)

- Metals, insulators, semiconductors
- Mid-IR to vacuum UV
- 10 to 800 K

Ellipsometry tells us a lot about materials quality (not necessarily what we want to know).

Optical critical points of thin-film $Ge_{1-y}Sn_y$ alloys: A comparative $Ge_{1-y}Sn_y$ / $Ge_{1-x}Si_x$ study VR D'costa, CS Cook, AG Birdwell, CL Littler, M Canonico, S Zollner, ... Physical Review B 73 (12), 125207	429	2006
Growth and strain compensation effects in the ternary $Si_{1-x-y}Ge_xC_y$ alloy system K Eberl, SS Iyer, S Zollner, JC Tsang, FK LeGoues Applied physics letters 60 (24), 3033-3035	404	1992
Ge–Sn semiconductors for band-gap and lattice engineering M Bauer, J Taraci, J Tolle, AVG Chizmeshya, S Zollner, DJ Smith, ... Applied physics letters 81 (16), 2992-2994	322	2002



Problem statement

(1) Achieve a **quantitative** understanding of **absorption** and **emission** processes.

- Our **qualitative** understanding of excitonic absorption 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 (femtosecond) lasers*** or
  - **high temperatures (narrow-gap or gapless semiconductors)**
- **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

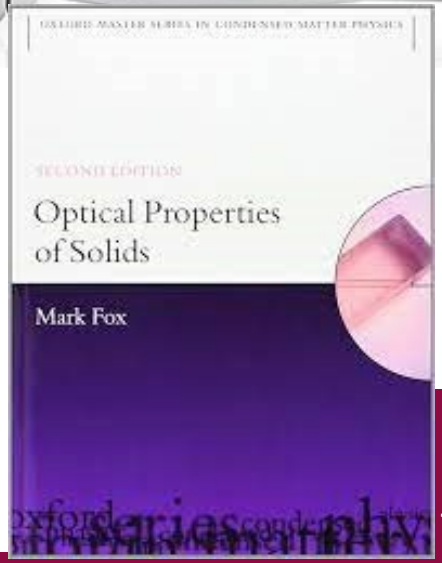
R. J. Elliott
Phys. Rev. **108**, 1384 – Published 15 December 1957

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 **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 **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.

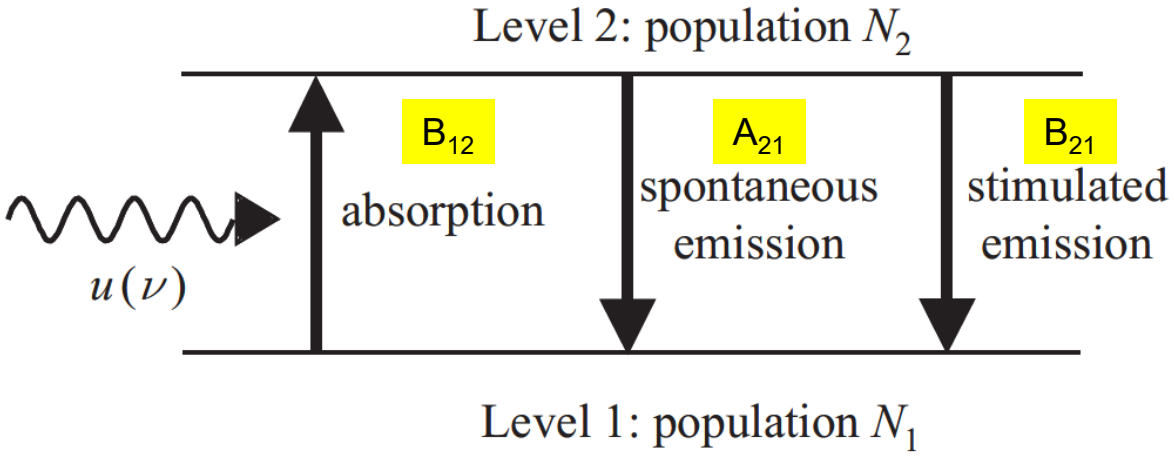
Received 9 April 1957



Matrix elements and excitonic effects in the direct gap absorption of 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
  - Intravalence band absorption in topological insulators (**α-tin**)
  - *Optical constants of **highly excited germanium***
    (femtosecond ellipsometry at ELI Beamlines in Prague) – Carlos Armenta F'24.
- Conclusion and Outlook

Einstein coefficients



One coefficient is sufficient:

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

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

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

$$B_{12} N_1 u(\hbar\omega) = A_{21} N_2 + B_{21} N_2 u(\hbar\omega)$$

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

Albert Einstein, *Strahlungs-Emission und Absorption nach der Quantentheorie*, DPG Verh. **18**, 318 (1916); Phys. Z. **18**, 121 (1917). See also Mark Fox.

Fermi's Golden Rule: Tauc plot

Direct band gap absorption

constant **k**·**p** matrix element

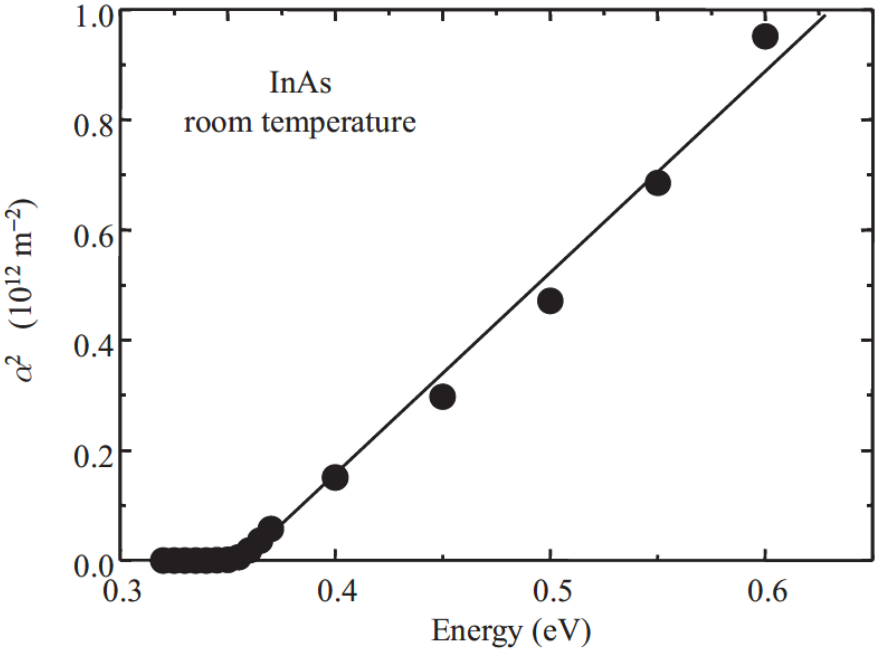
$$\frac{1}{\tau} = \frac{2\pi}{\hbar}\int_{i,f} |\langle f|H_{eR}|i\rangle|^2 \delta\left(E_f - E_i - \hbar\omega\right) = \frac{2\pi}{\hbar}|\langle f|H_{eR}|i\rangle|^2 g_{fi}(\hbar\omega)$$

Joint DOS parabolic bands

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

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

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



Fermi's Golden Rule: Tauc plot

Direct band gap absorption

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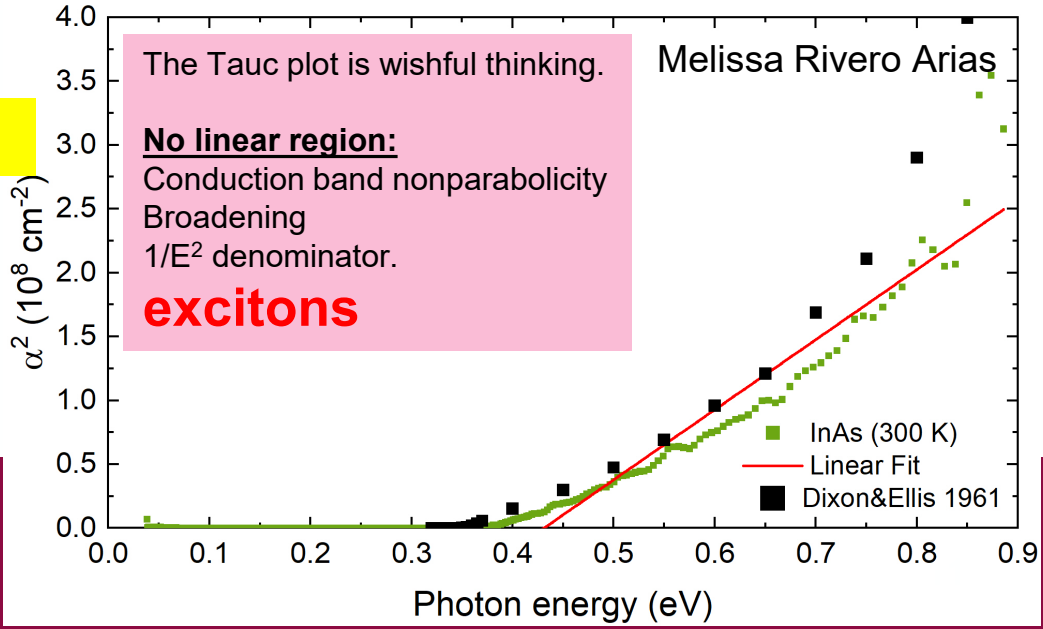
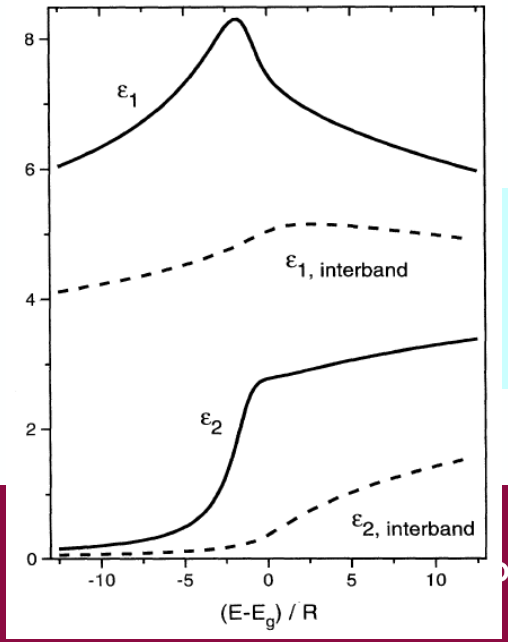


Elliott-Tanguy exciton absorption

Direct band gap absorption

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

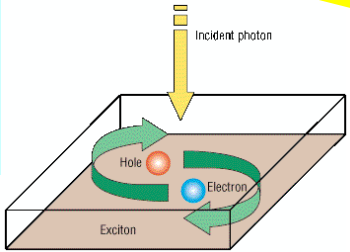
$$\varepsilon_2(\hbar\omega) = \frac{e^2\sqrt{m_0}\mu^{\frac{3}{2}}}{3\pi\sqrt{2}\varepsilon_0\hbar}\frac{E_P\sqrt{R}}{(\hbar\omega)^2}\left[\sum_{n=1}^{\infty}\frac{4\pi R}{n^3}\delta\left(\hbar\omega - E_0 + \frac{R}{n^2}\right) + \frac{2\pi H(\hbar\omega - E_0)}{1 - \exp\left(-2\pi\sqrt{R/\hbar\omega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

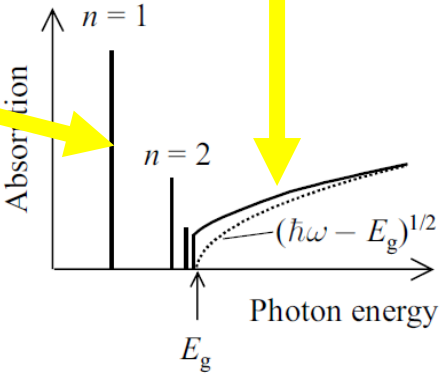


bound excitons

exciton continuum enhancement

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

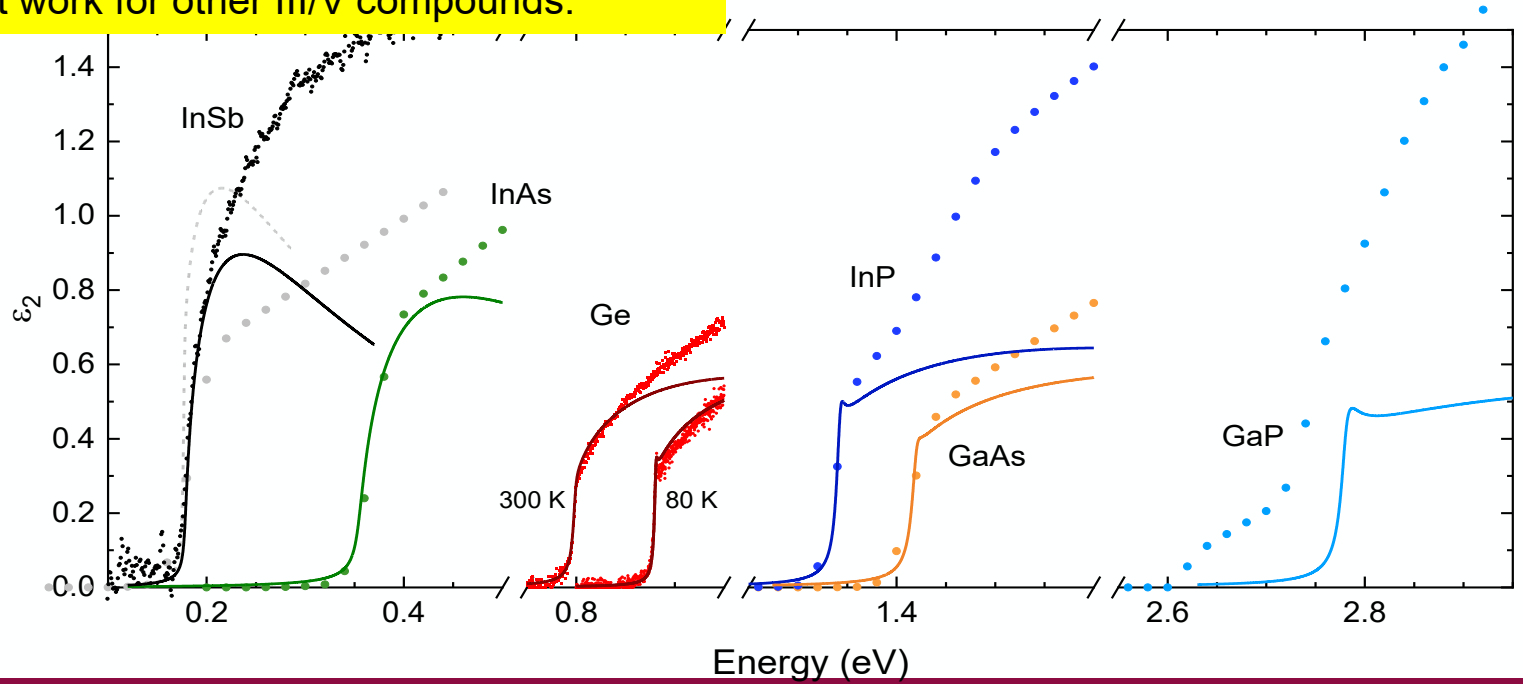




R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
Christian Tanguy, Phys. Rev. Lett. **75**, 4090 (1995) + (E)

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.



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

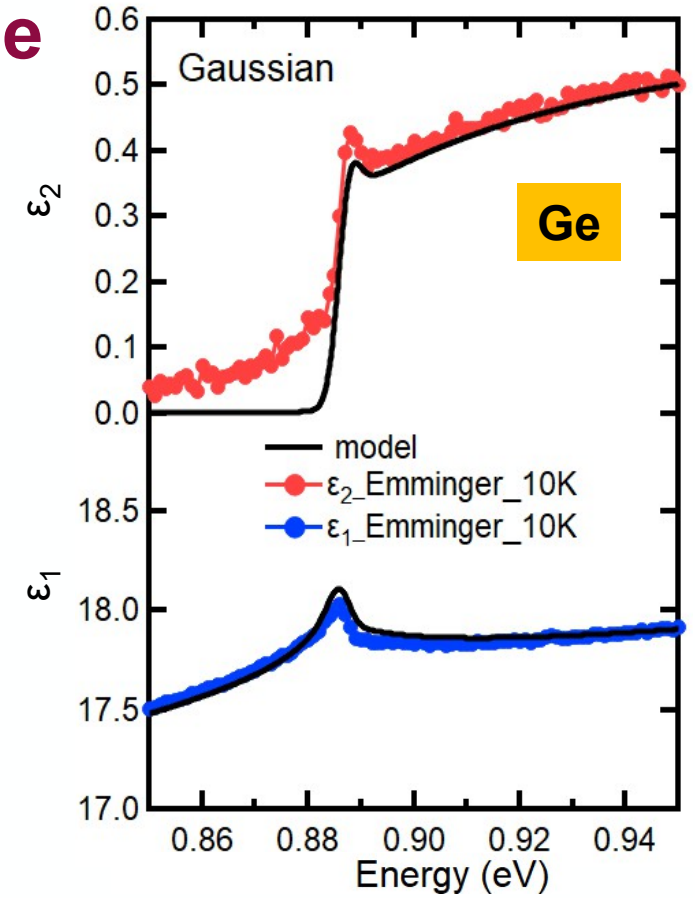
Elliott-Tanguy theory applied to Ge

- **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

- **Problems:**
- Broadening below the gap (band tail, oxide correction)



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

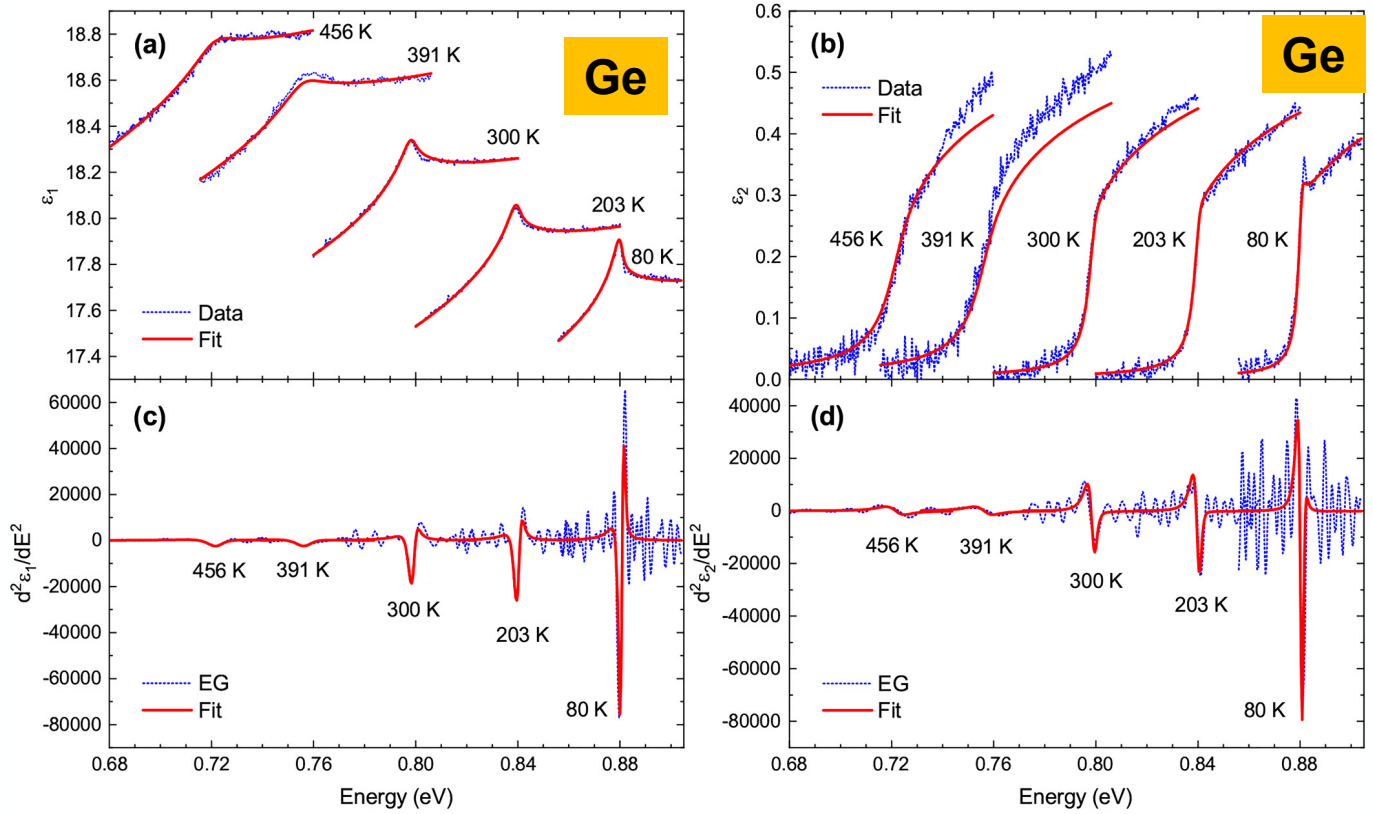
Elliott-Tanguy theory applied to Ge

Good agreement at low temperatures.

Model also describes second derivatives.

Potential problems:

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



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

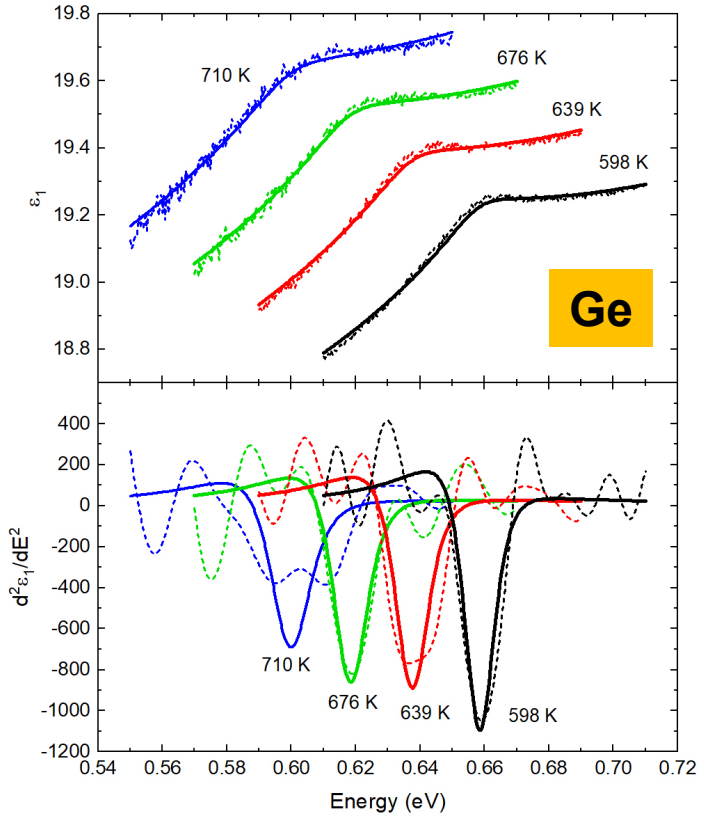
Elliott-Tanguy theory: problems for Ge at high T

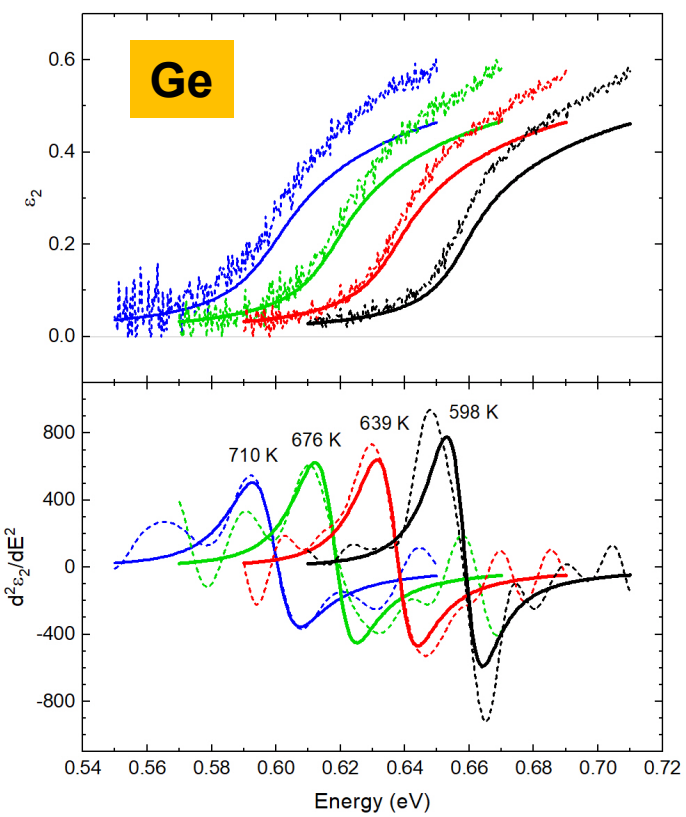
Good agreement at low temperatures.

Model also describes second derivatives.

Potential problems:

- Matrix element k-dependent
- Nonparabolicity
- Resonant indirect absorption
- Temperature dependence of the effective mass.





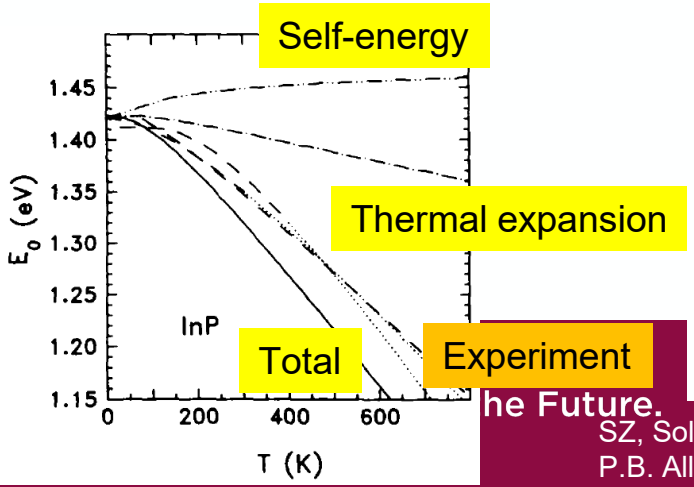
Temperature dependence of the effective mass

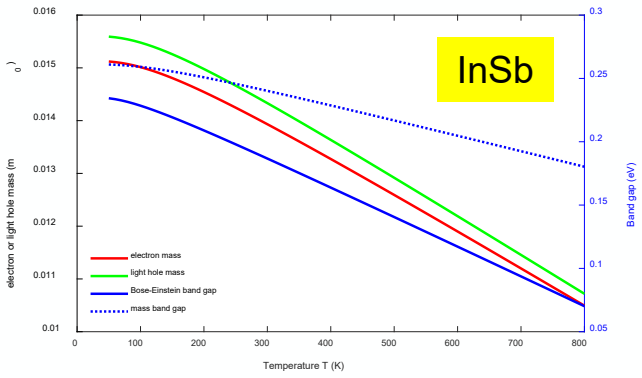
- Effective electron mass given by k·p theory

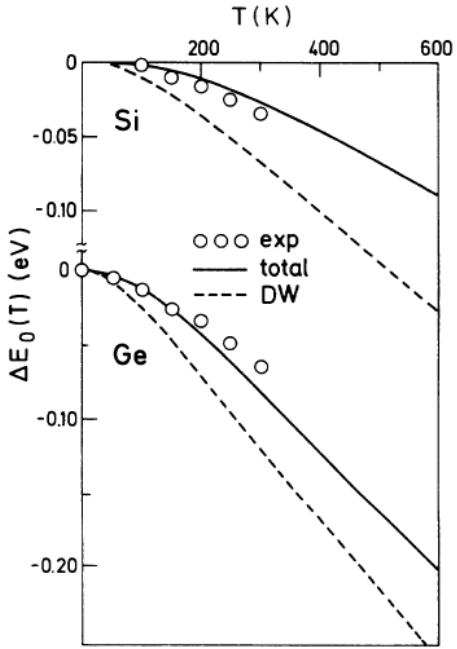
$$\frac{1}{m_e(T)} = 1 + \frac{E_P}{3}\left(\frac{2}{E_0(T)} + \frac{1}{E_0(T)+\Delta_0}\right)$$

E_0: direct band gap
k·p matrix element *P*: $E_P = 2P^2/m_0$

- Temperature dependence of the direct band gap has two contributions:
  - Thermal expansion of the lattice
  - Electron-phonon scattering (Debye-Waller term and self-energy)
- "Mass band gap" should **only include the thermal expansion**.
- **TBD:** Polaron effects on effective mass in III/V materials.



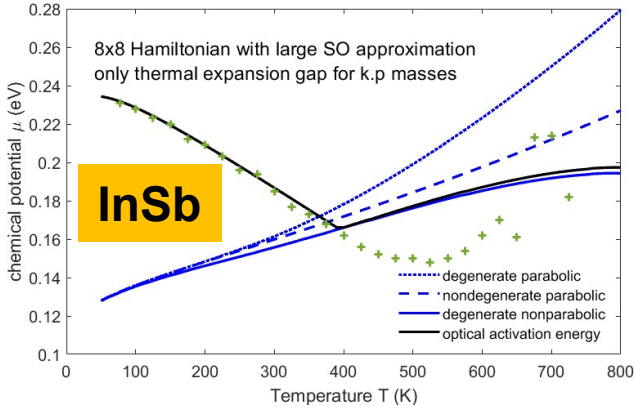


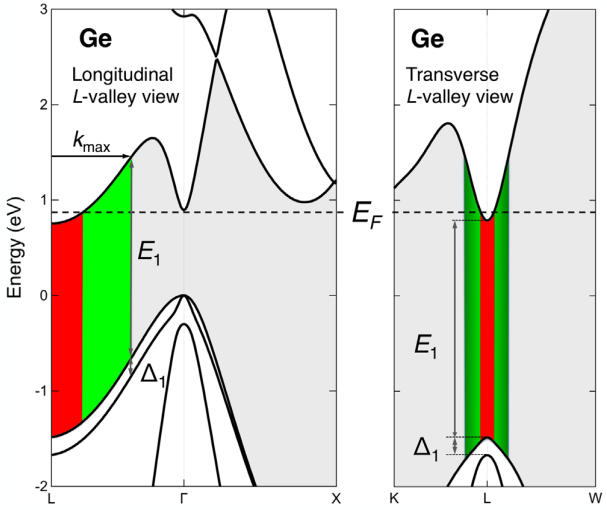


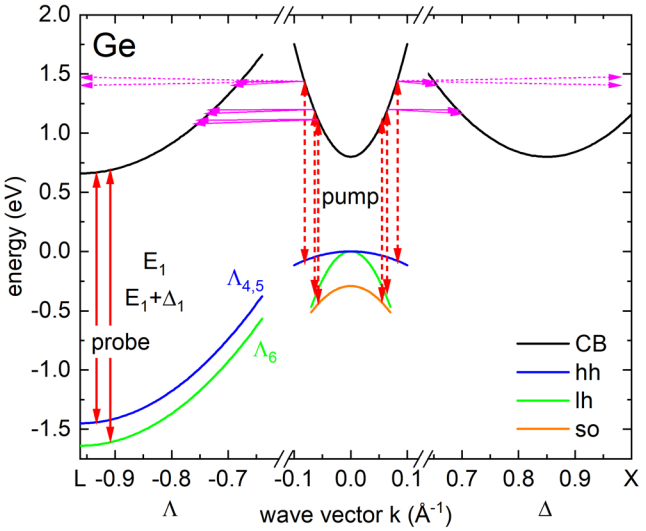
he Future.

SZ, Solid State Commun. **77**, 485 (1991).
P.B. Allen and M. Cardona, Phys. Rev. B **27** 4760 (1983).

Optical Absorption at High Carrier Densities







High temperature
(thermal excitation of e-h pairs)
constant m and E_0

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

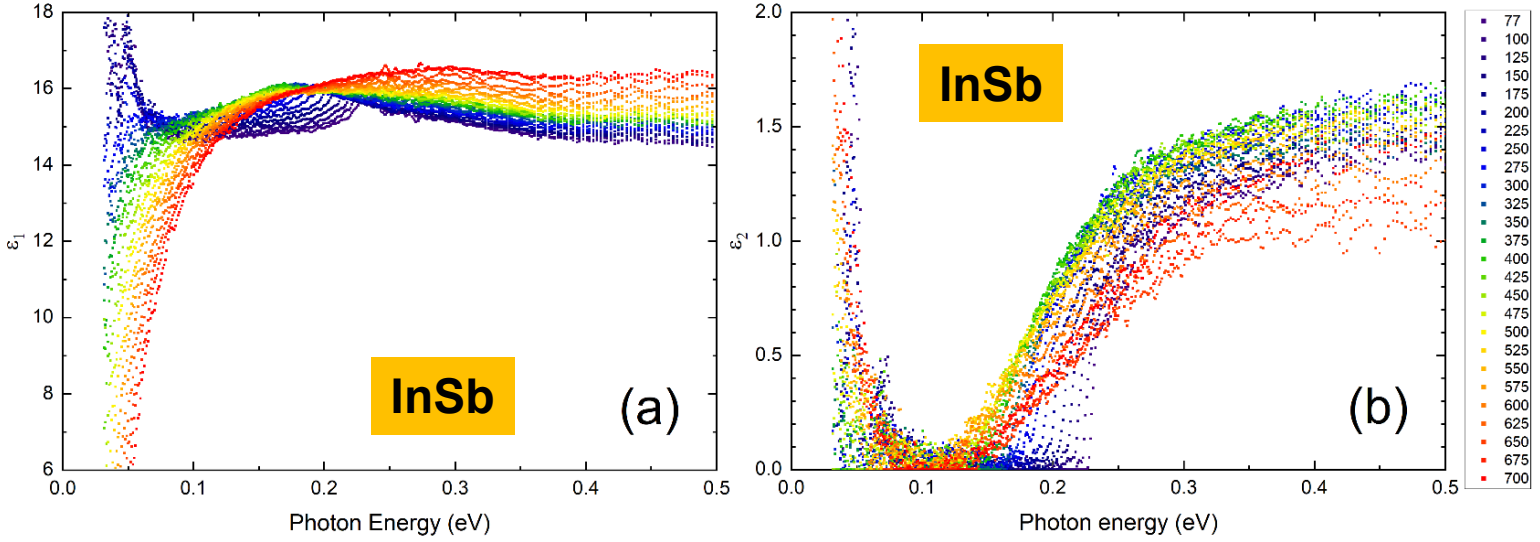
Intense femtosecond **laser excitation** (ELI Beamlines)
(electrons pile at L-point)

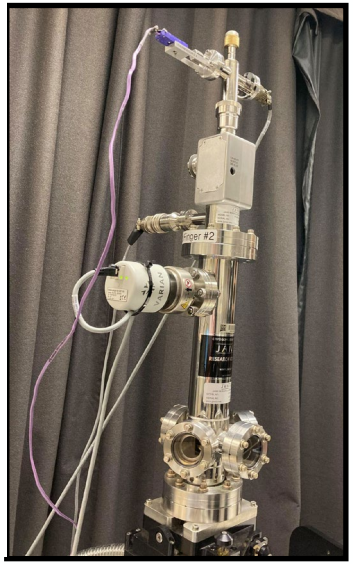
Rivero, JVSTB **41**, 022203 (2023)

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

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

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



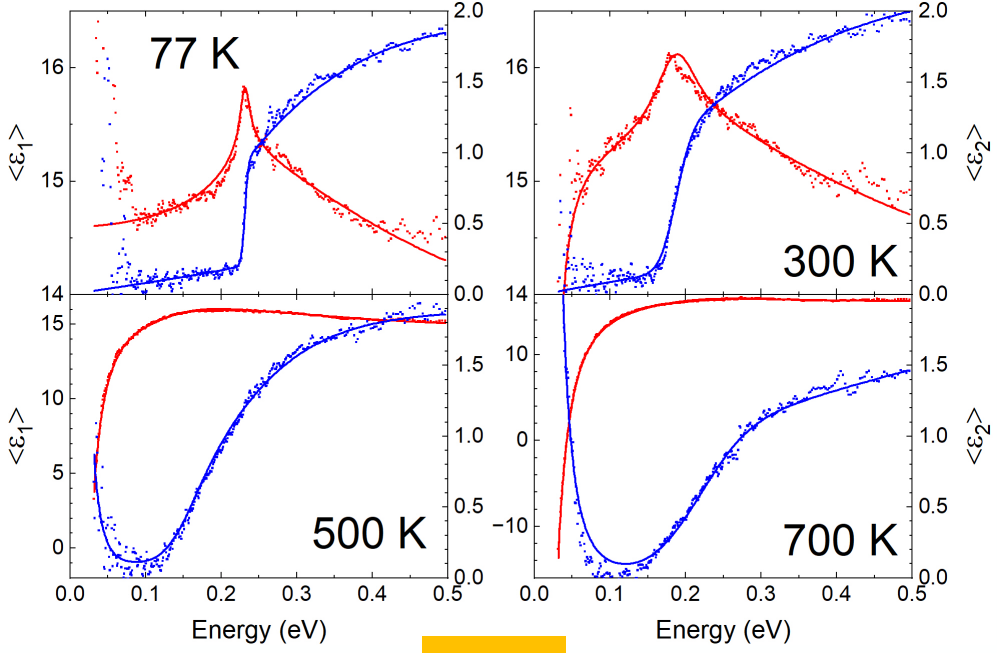


- **Band gap** changes with temperature (but only below 500 K).
- **Amplitude reduction at high temperatures (Pauli blocking, bleaching)**
- **Drude response** at high temperatures (thermally excited carriers).
- Depolarization artifacts at long wavelengths (below 300 K).

Woollam FTIR-VASE cryostat with CVD diamond windows

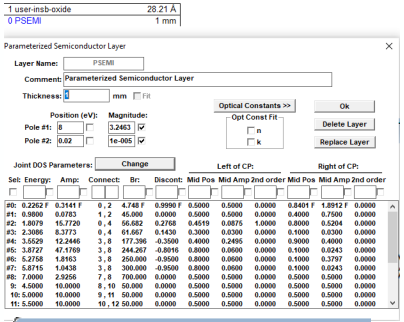
Band gap analysis for InSb

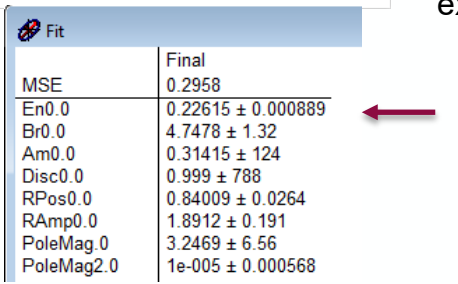
How does the band gap of InSb change with temperature?



InSb

Parametric-Semiconductor Model:





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

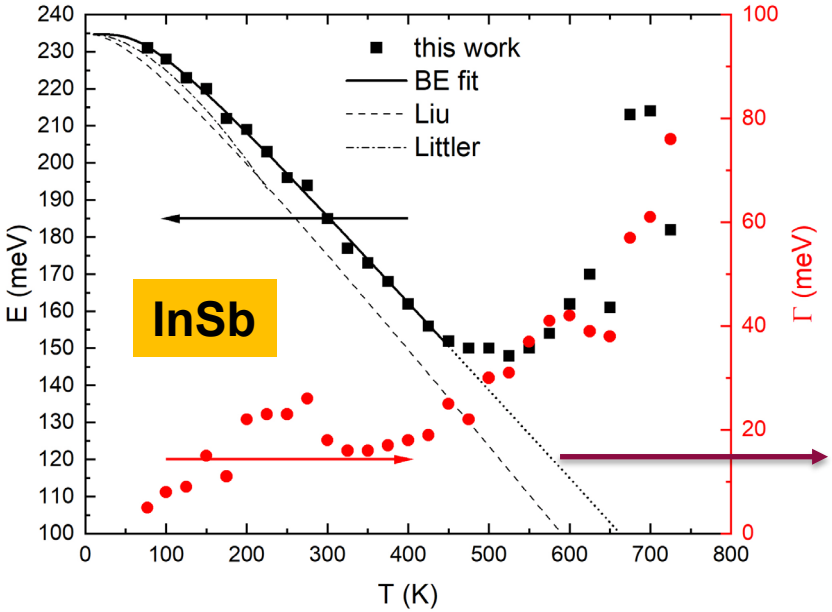
Also vary "shape parameters".

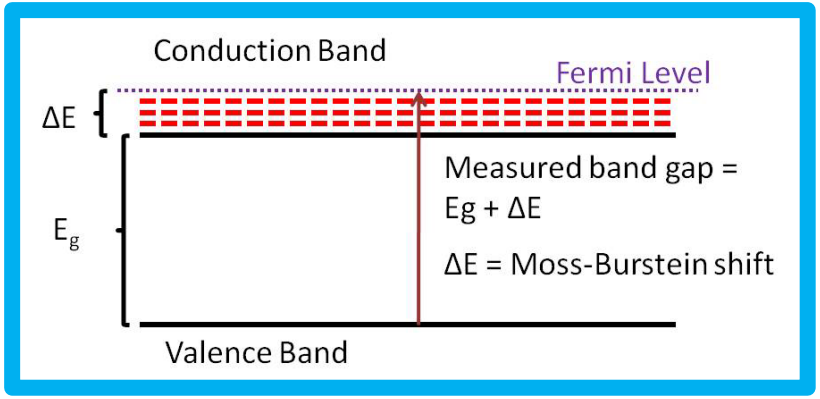
Asymmetric peak shape poorly described.

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





Bose-Einstein Model

$$E_0(T) = E^{\mathrm{un}} - b\left[1 + \frac{2}{\exp\left(\Omega/k_B T\right)}\right]$$

- 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).

k·p theory (band structure method)

Schrödinger equation

$$H\Phi_{n\vec{k}} = \left(\frac{\vec{p}^2}{2m_0} + V\right)\Phi_{n\vec{k}} = E_{n\vec{k}}\Phi_{n\vec{k}}$$

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.

$$\left(\frac{\vec{p}^2}{2m_0} + \frac{\hbar^2\vec{k}^2}{2m_0} + \frac{\hbar\vec{k}\cdot\vec{p}}{m_0} + V\right)u_{n\vec{k}} = E_{n\vec{k}}u_{n\vec{k}}$$

Eliminate green free-electron term with substitution of variables (Kane 1957).

Then treat red term in perturbation theory.

Works very well for semiconductors with local V(**r**) potentials.

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

Nonparabolicity of InSb conduction band from k·p theory

Kane 8x8 k·p Hamiltonian:

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

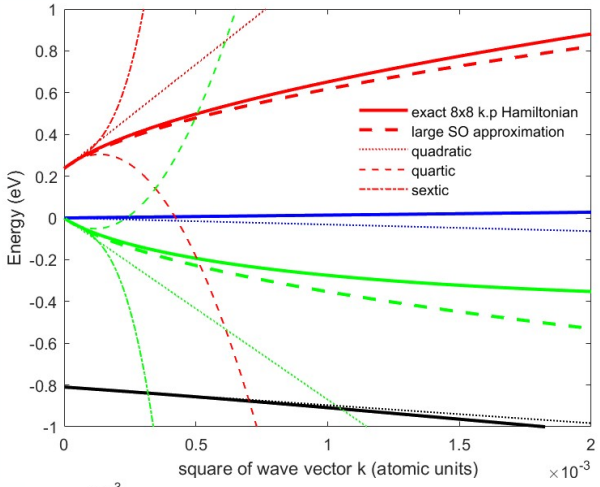
Cubic characteristic equation:

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

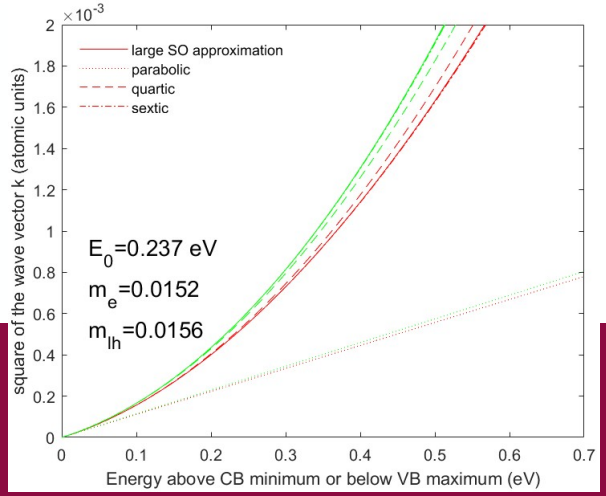
Large spin-orbit approximation:

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

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



Energy versus k



Density of CB states

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

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

Chemical potential in intrinsic InSb

$$n_\Gamma(T) = N_e(T)\left[F_{\frac{1}{2}}\left(\frac{\mu - E_0^{\exp}}{k_B T}\right) + \frac{15}{4}\alpha_e k_B T F_{\frac{3}{2}}\left(\frac{\mu - E_0^{\exp}}{k_B T}\right)\right],$$

with the prefactor[39,40]

$$N_n(T) = \frac{1}{4}\left(\frac{2m_0 m_n^* k_B T}{\pi\hbar^2}\right)^{3/2}.$$

$$p_{lh}(T) = N_{lh}(T)\left[F_{\frac{1}{2}}\left(-\frac{\mu}{k_B T}\right) + \frac{15}{4}\alpha_{lh} k_B T F_{\frac{3}{2}}\left(-\frac{\mu}{k_B T}\right)\right]$$

$$p_{hh}(T) = N_{hh}(T) F_{\frac{1}{2}}\left(-\frac{\mu}{k_B T}\right)$$

$$p_{so}(T) = N_{so}(T) F_{\frac{1}{2}}\left(\frac{-\Delta_0 - \mu}{k_B T}\right),$$

$$n_L(T) = 4N_L(T) F_{\frac{1}{2}}\left(\frac{\mu - E_L^{\exp}}{k_B T}\right),$$

$$n_X(T) = 3N_X(T) F_{\frac{1}{2}}\left(\frac{\mu - E_X^{\exp}}{k_B T}\right).$$

Intrinsic condition: n=p.
Find chemical potential as a function of T.

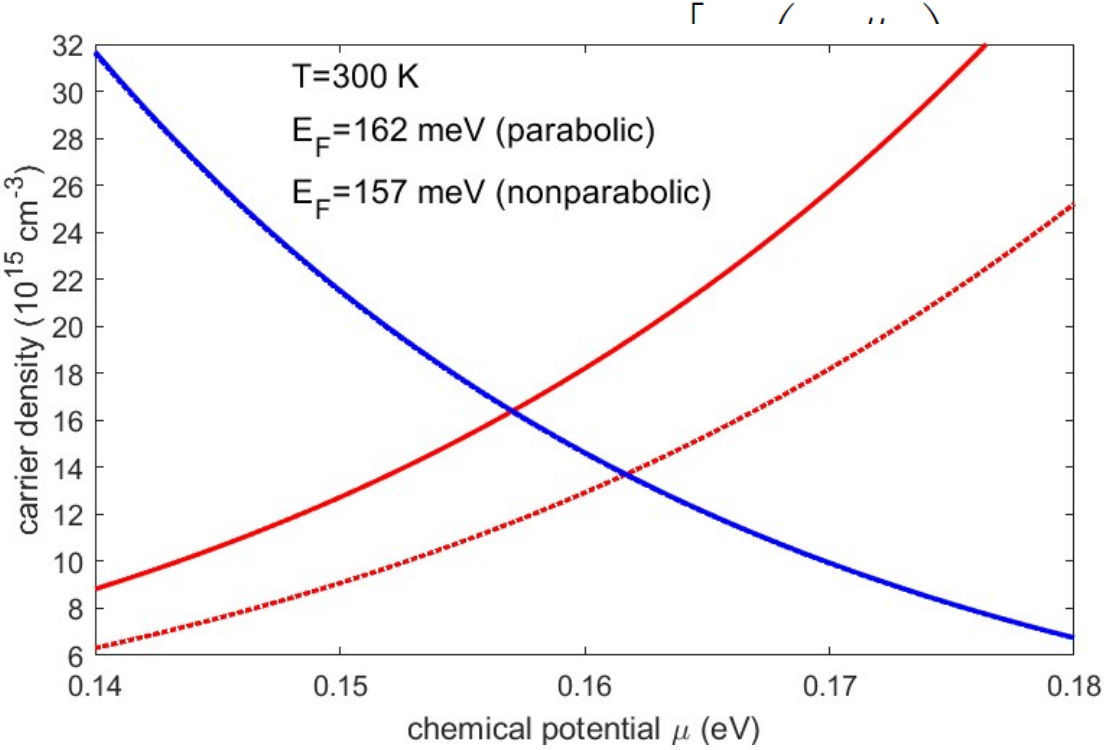
S. Zollner and J. Menendez (unpublished).

Chemical potential in intrinsic InSb

$$n_\Gamma(T) = N_e(T)\left[F_{\frac{1}{2}}\left(\frac{\mu - E_0^{\exp}}{k_B T}\right) + \frac{15}{4}\alpha_e k_B T F_{\frac{3}{2}}\left(\frac{\mu - E_0^{\exp}}{k_B T}\right)\right]$$

with the prefactor[39,40]

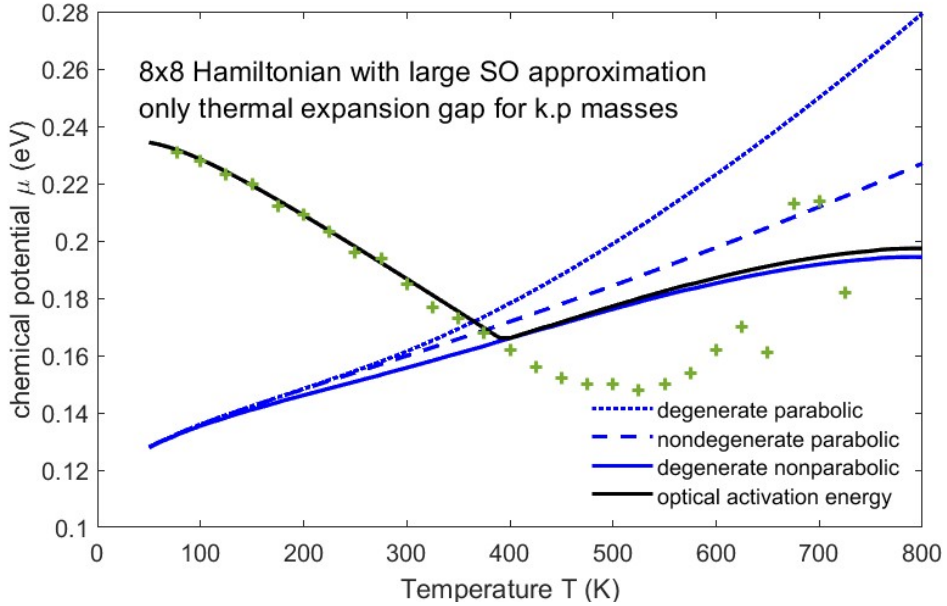
$$N_n(T) = \frac{1}{4}\left(\frac{2m_0 m_n^* k_B T}{\pi\hbar^2}\right)^{3/2}.$$

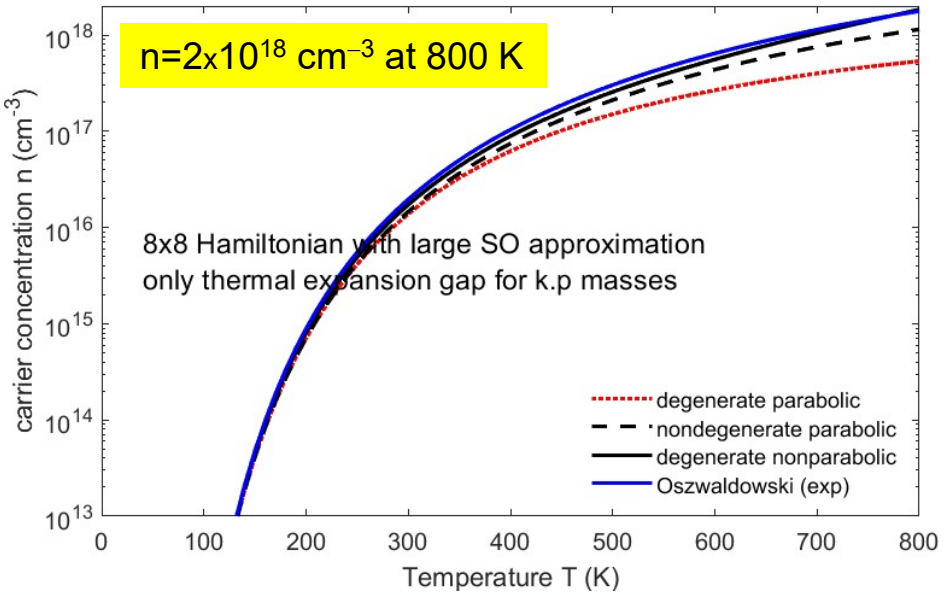


Intrinsic condition: n=p.
Find chemical potential as a function of T.
Degenerate Fermi-Dirac statistics.
Nonparabolicity of conduction band.

S. Zollner and J. Menendez (unpublished).

Thermal excitations of electron-hole pairs in InSb





$k_B T = E_g/4$ at 600 K
Fermi level above
conduction band edge above 450 K.

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

M. Rivero Arias *et al.*, JVSTB **41**, 022203 (2023).
Oswaldowski/Zimpel, J. Phys. Chem. Solids **49**, 1179 (1988).
D. L. Rode, Phys. Rev. B **3**, 3287 (1971).

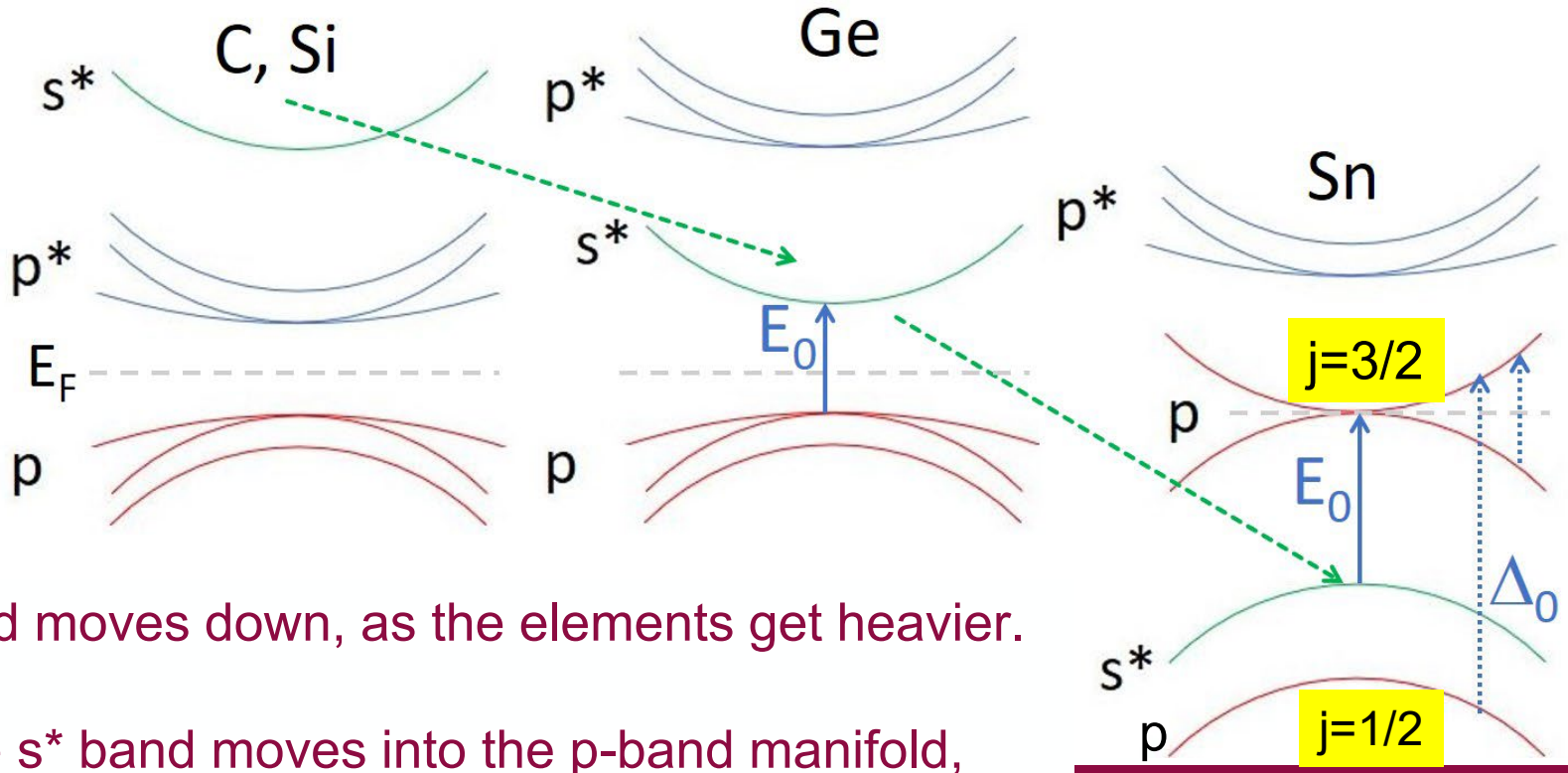
Optical constants model: screened excitons

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

- **Absorption by screened excitons** (Hulthen potential)
- **Degenerate Fermi-Dirac statistics** to calculate f_h and f_e.
- Numerical Kramers-Kronig transform (need occupation factors)
- 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)
  Sommerfeld enhancement persists well above the Mott density.
- **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

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

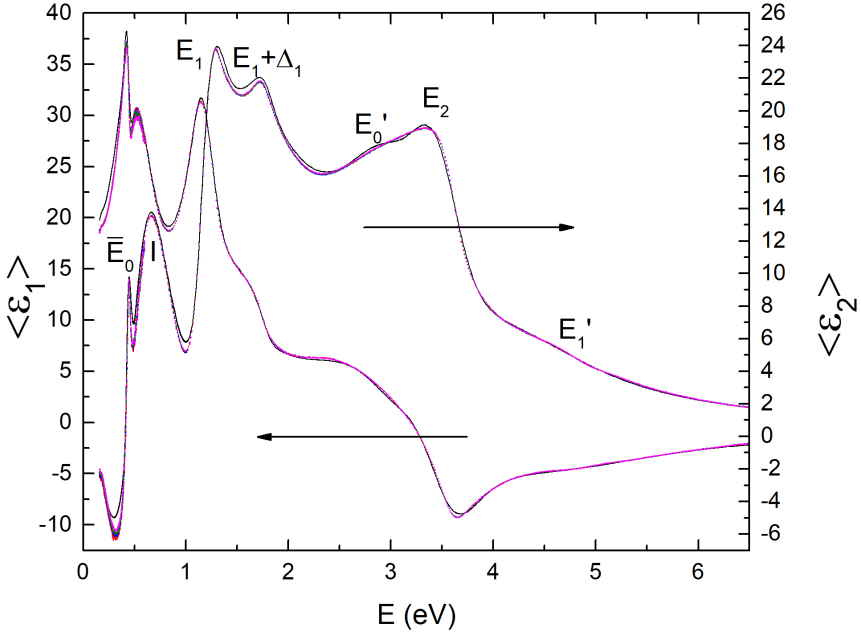
Relativistic Effects: Darwin Shift: C, Si, Ge, Sn

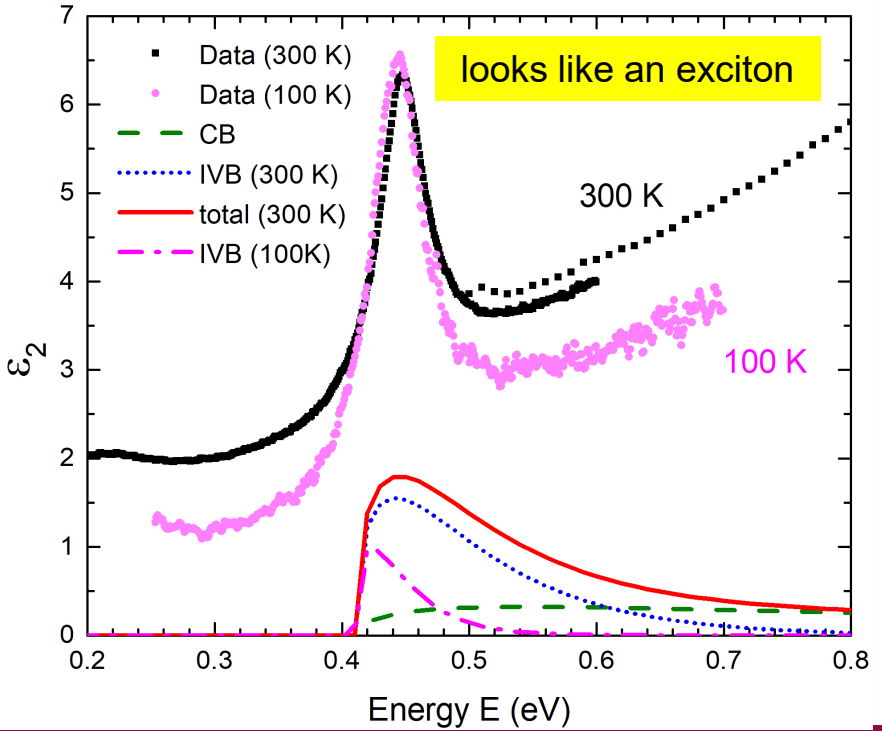


The s* band moves down, as the elements get heavier.

In α-tin, the s* band moves into the p-band manifold, between the j=1/2 and j=3/2 states.
This makes α-tin an (**inverted**) **gapless** semiconductor.

Intravalence band absorption in gapless topological insulators (α-tin)





R.A. Carrasco, APL **113**, 232104 (2018).

All gapless (inverted) semiconductors should have this peak.
Theory with same model as Ge IVB (Kaiser 1953, Kahn 1955).

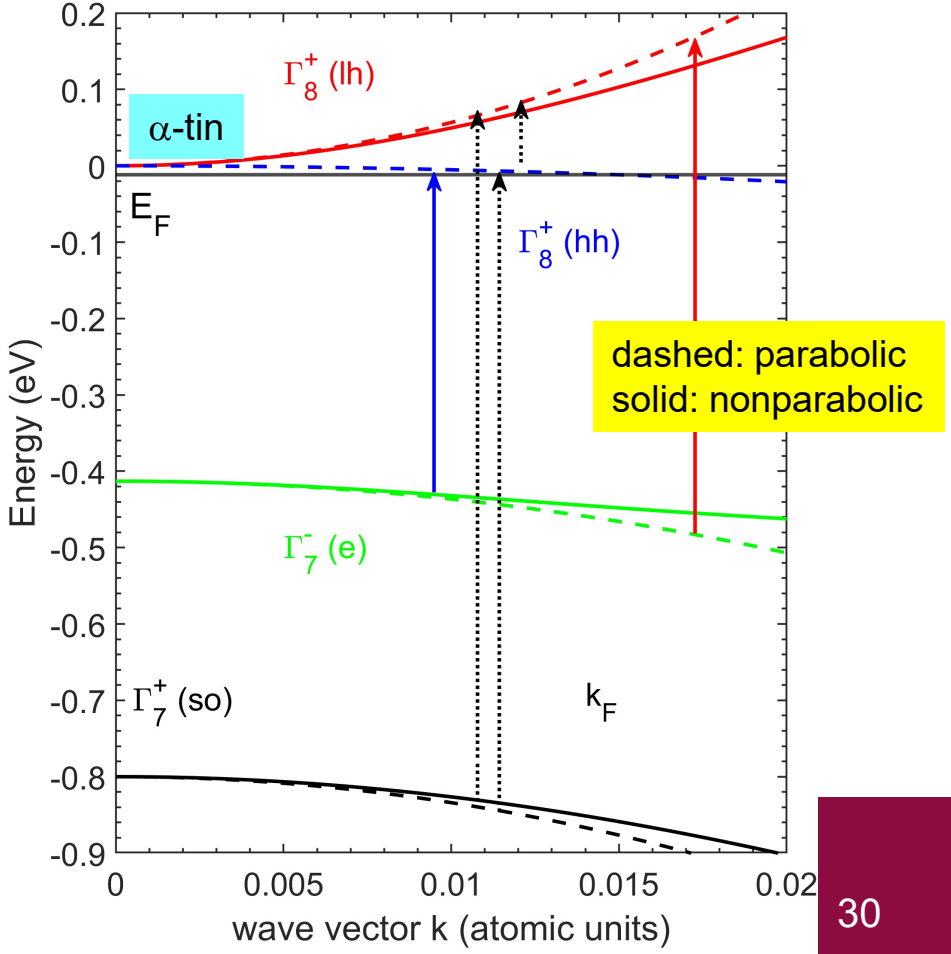
Simple 8x8 k·p band structure of α-tin (Kane)

Kane 8x8 k·p Hamiltonian:

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

Cubic characteristic equation:

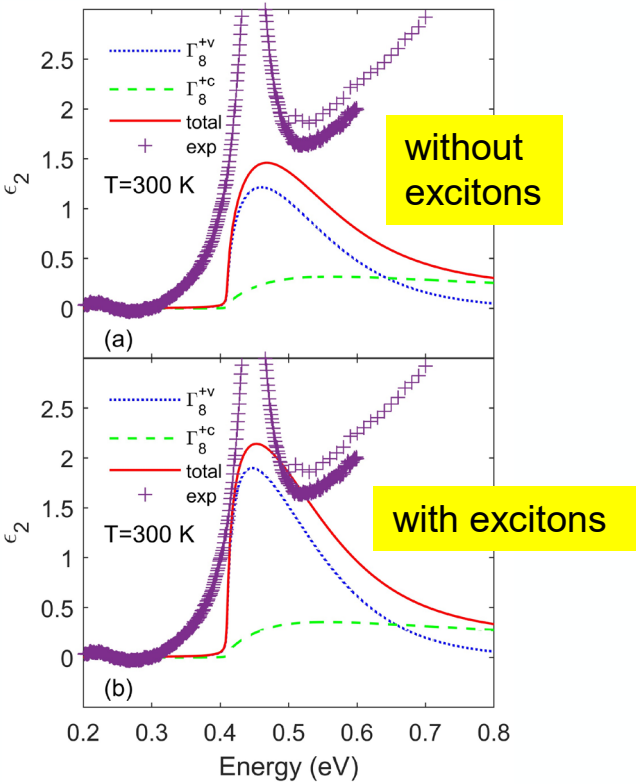
$$\tilde{E}\left(\tilde{E}-E_0\right)\left(\tilde{E}+\Delta_0\right)-\frac{\hbar^2k^2E_P}{2m_0}\left(\tilde{E}+\frac{2\Delta_0}{3}\right)=0$$



S. Zollner, JVST 2024 (in print).

e Future.

Excitonic intravalence band absorption in α-tin

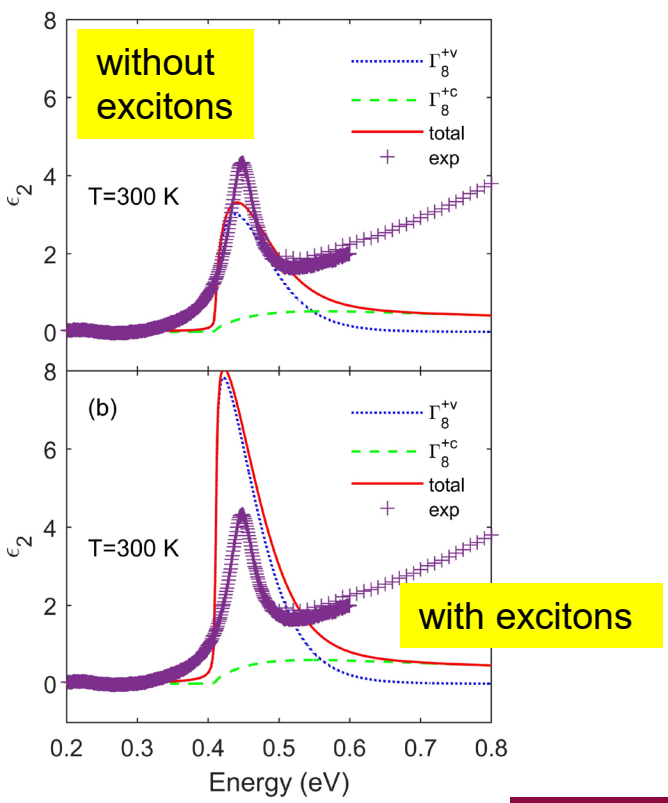


Screening:

$$r_s = \frac{1}{a_x}\sqrt[3]{\frac{3}{4\pi n}}$$

$$V(r) = -k\frac{\exp(-r/\lambda_D)}{r}$$

$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{pe^2}} = \frac{1}{k_D}$$



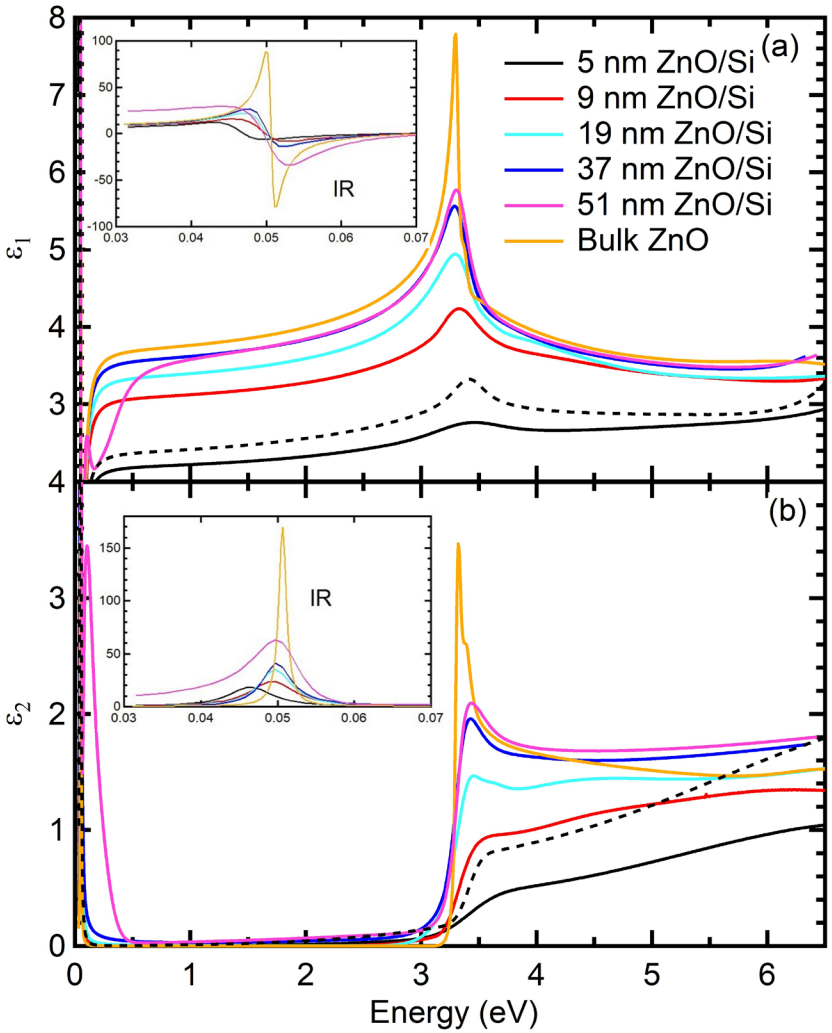
Parabolic bands

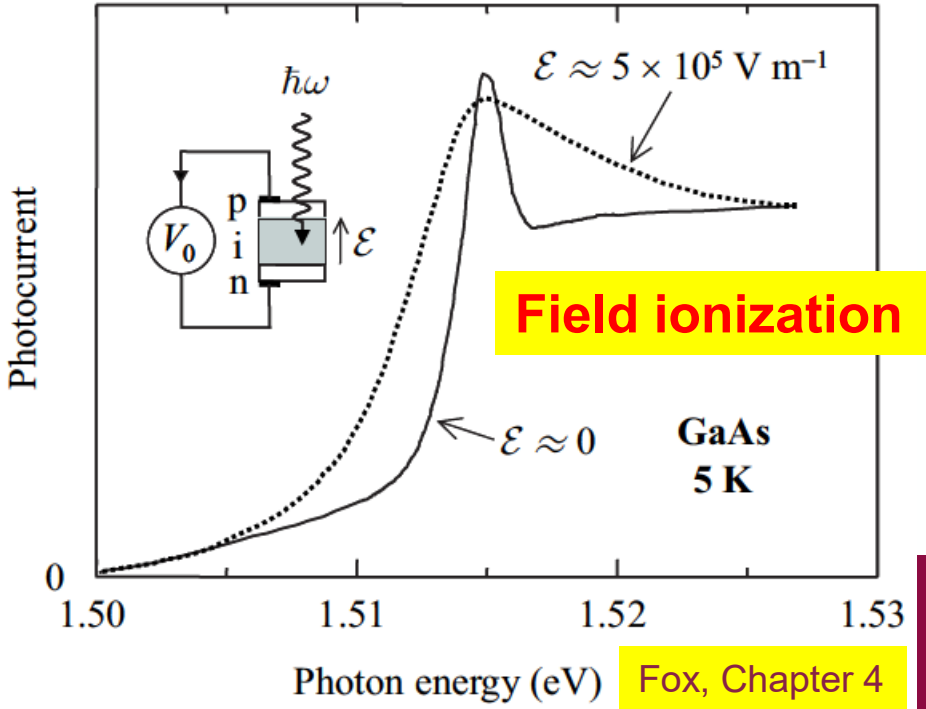
nonparabolicity affects exciton radius (screening)

S. Zollner, JVST 2024 (in print).

Thickness dependence of excitonic absorption

ZnO on Si with different thicknesses.
This might be an electric field effect.
(Samarasingha, Sudeshna Chattopadhyay, SZ, JVSTB 2020)





Field ionization

Fox, Chapter 4

Conclusions

- Quantitative modeling of low-density optical processes is possible with basic physics and matrix elements from k.p theory:
  - Photoluminescence in Ge (Menendez)
  - Indirect gap absorption in Ge (Menendez)
  - **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 and α-tin.**
  - ~~*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?

Many students contributed to this project.