# Optical Properties of Solids: Lecture 9


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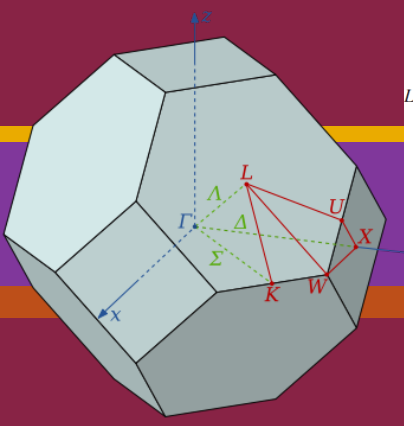
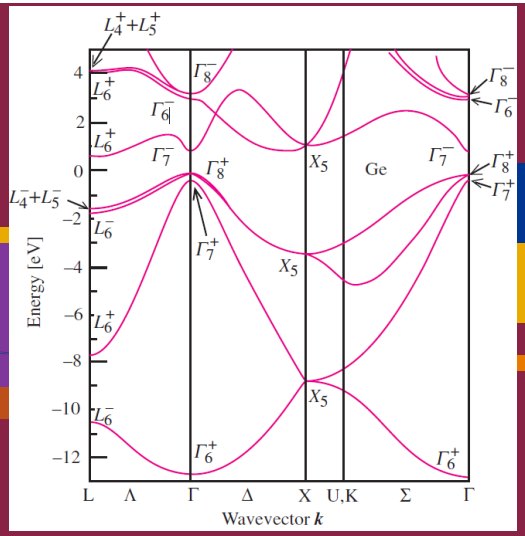
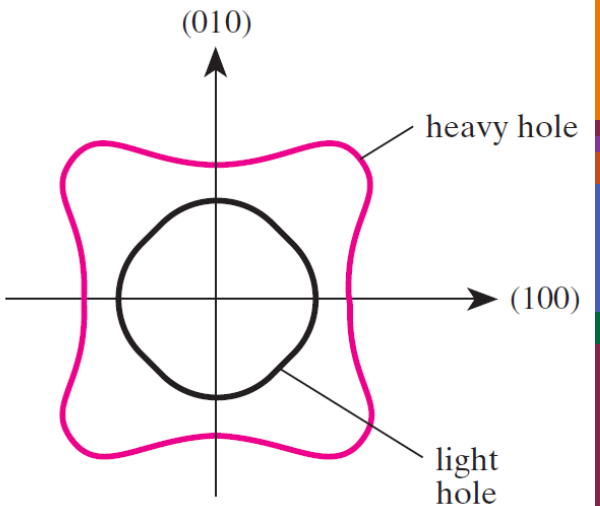
# Optical Properties of Solids: Lecture 7+8+9

Electronic Band Structure
Direct and indirect band gaps
Empty lattice, pseudopotential, k.p band structures
Optical interband transitions, Fermi's Golden Rule
**Absorption coefficient for** direct and **indirect gaps**
Tauc plot
**Van Hove singularities**



# References: Band Structure and Optical Properties

## Solid-State Theory and Semiconductor Band Structures:

- Mark Fox, Optical Properties of Solids
- Ashcroft and Mermin, Solid-State Physics
- Yu and Cardona, Fundamentals of Semiconductors
- Dresselhaus/Dresselhaus/Cronin/Gomes, Solid State Properties
- Cohen and Chelikowsky, Electronic Structure and Optical Properties
- Klingshirn, Semiconductor Optics
- Grundmann, Physics of Semiconductors
- Ioffe Institute web site: NSM Archive
  http://www.ioffe.ru/SVA/NSM/Semicond/index.html

# Outline

Band structure and optical interband transitions

Einstein coefficients, population inversion, optical gain, lasers

Fermi's Golden Rule

Joint density of states, optical mass

Direct gap absorption in InAs, PbS, and InSb; Tauc plot

**Indirect gap absorption in Si and Ge**

**Experimental techniques to measure absorption**

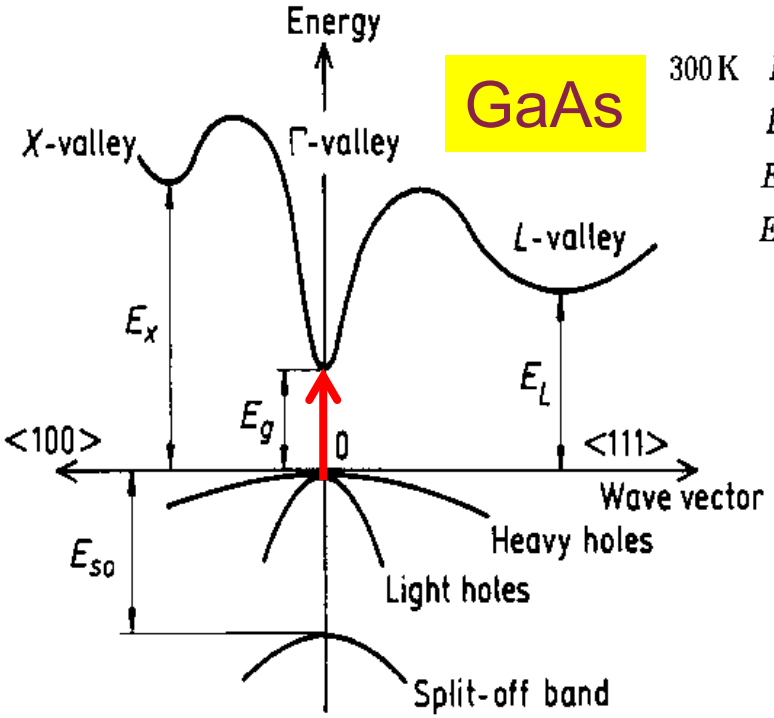
**Van Hove singularities**

**Critical points in the dielectric function**

**Analytical lineshapes to fit Savitzky-Golay derivative**

**Parametric oscillator model**

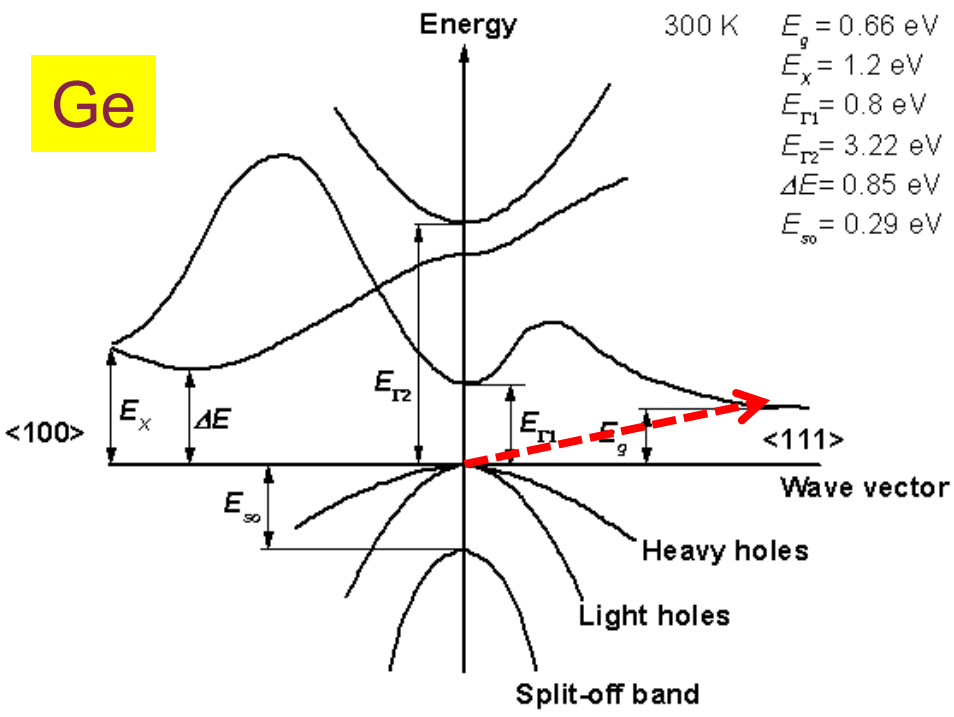
# Semiconductor Band Structures




GaAs

300 K $E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

Δk=0




Ge

300 K $E_g = 0.66$ eV
$E_X = 1.2$ eV
$E_{Γ1} = 0.8$ eV
$E_{Γ2} = 3.22$ eV
$\Delta E = 0.85$ eV
$E_{so} = 0.29$ eV

Δk≠0

**Direct transition:**

Initial and final electron state have **same** wave vector.

**Indirect transition:**

Initial and final electron state have **different** wave vector.

http://www.ioffe.ru/SVA/NSM/Semicond/index.html

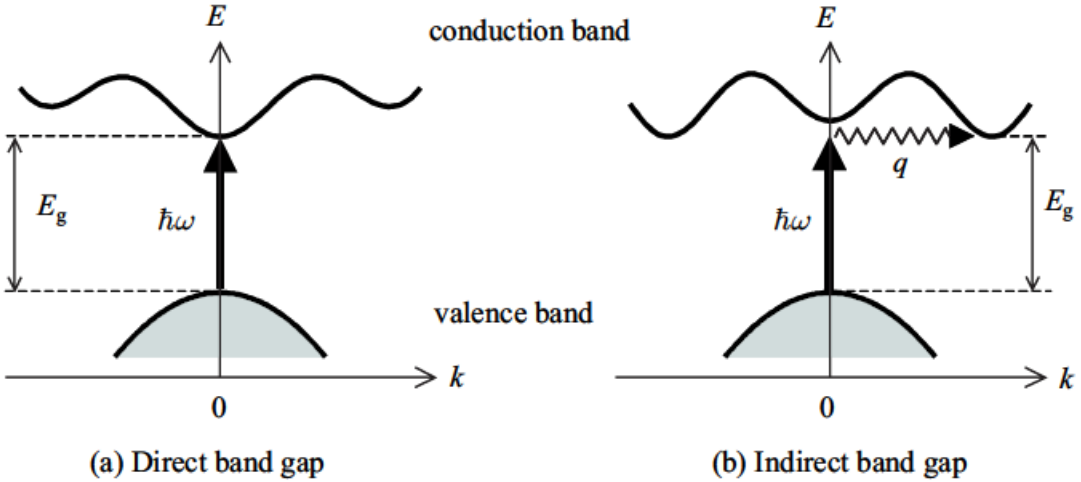
# Indirect Interband Transitions

Indirect transitions require phonon absorption or emission to conserve **crystal momentum k**.

Consider *Umklapp* processes (±**G RLV**).

Also possible: **Impurity**-assisted or **alloy** scattering

Also must conserve energy.

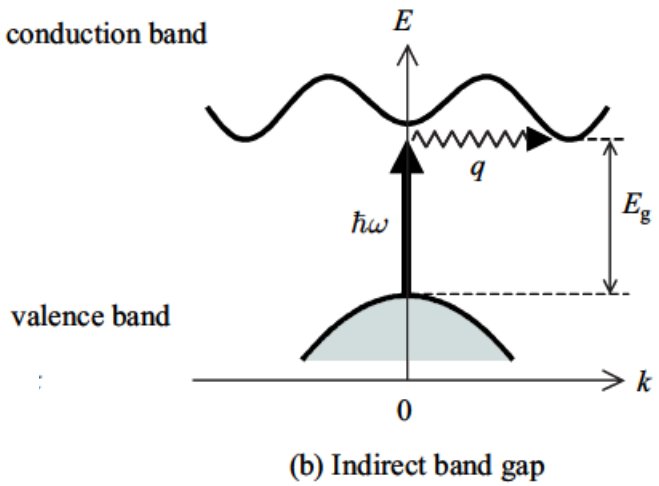



$$\vec{k}_f = \vec{k}_i \pm \vec{Q} \pm \vec{G}$$

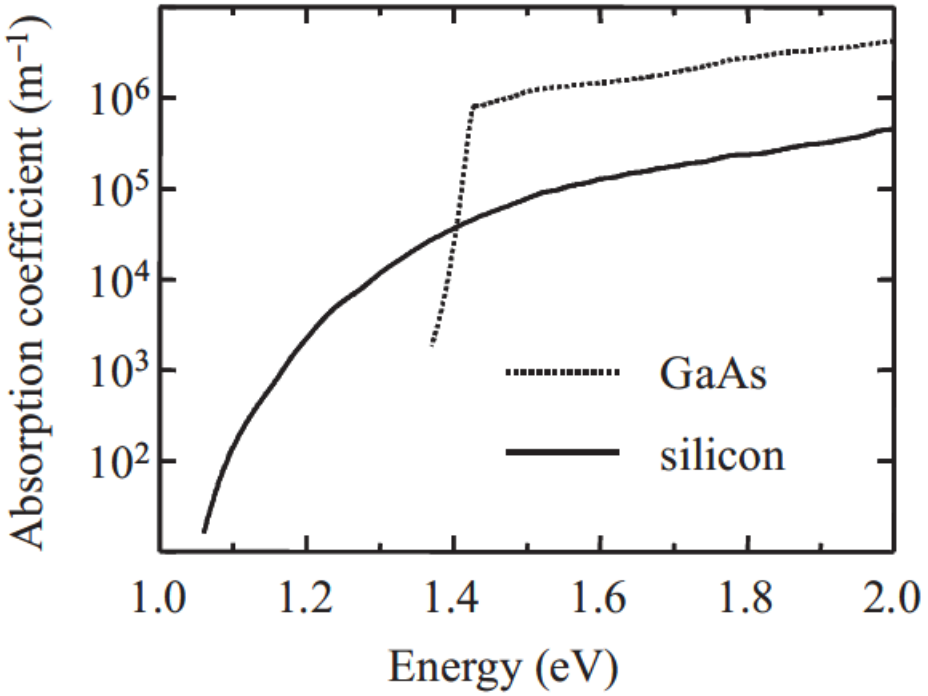
$$\vec{k}_f = \vec{k}_i$$

Fox, Chapter 3

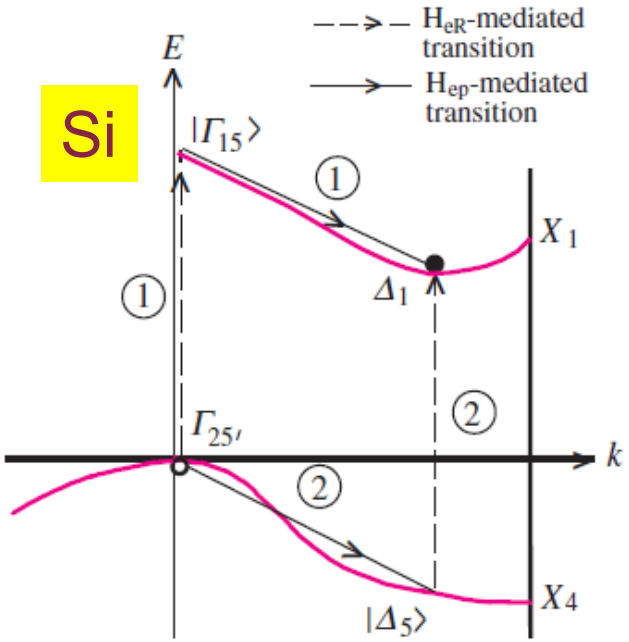
# Indirect transitions in Si



(b) Indirect band gap




Si




$$E_f = E_i + \hbar\omega \pm \hbar\Omega$$

energy

$$\hbar\vec{k}_f = \hbar\vec{k}_i \pm \hbar\vec{Q} \pm RLV$$

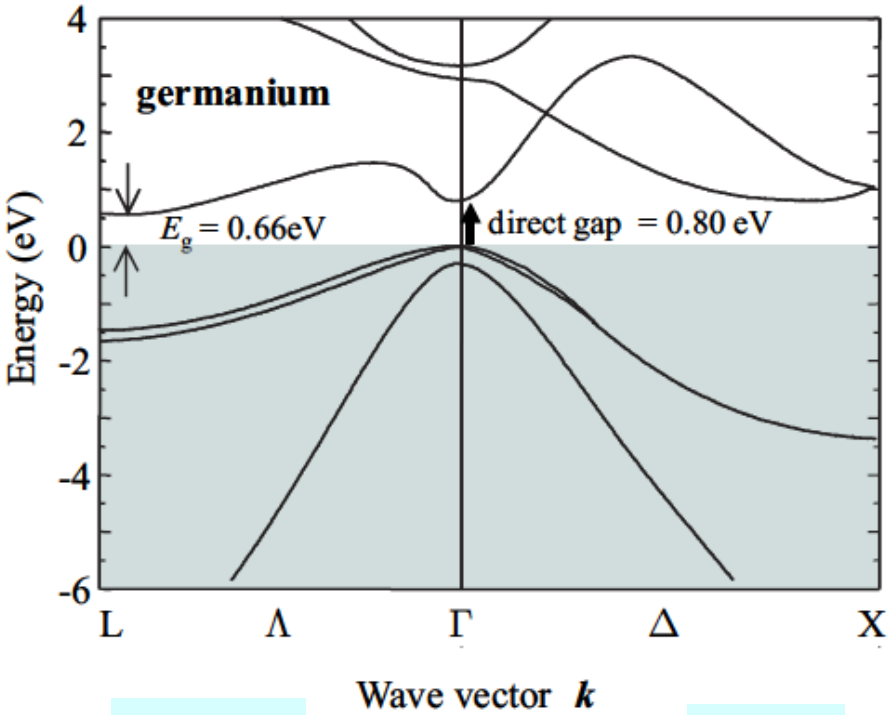
crystal momentum

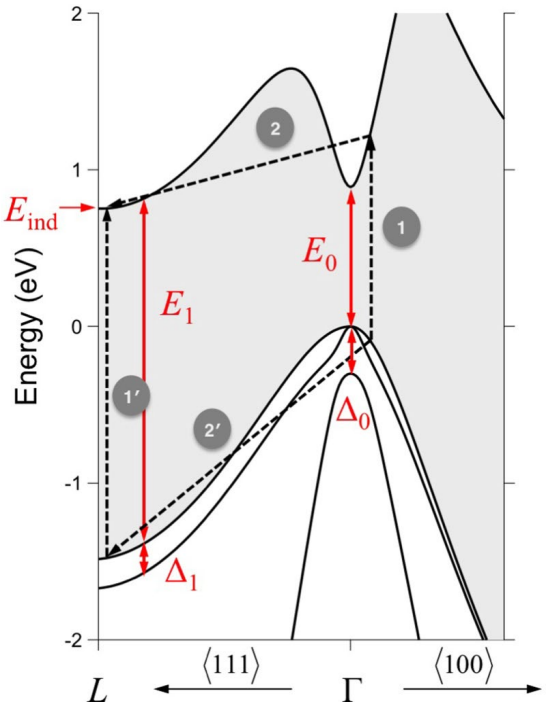
$$\alpha(\hbar\omega) \propto \left(\hbar\omega - E_g \mp \hbar\Omega\right)^2$$

Tauc plot: $\alpha^{1/2}$ increases linearly with energy

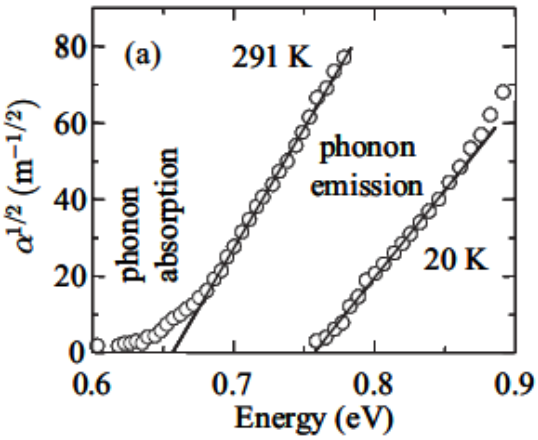
Fox, Chapter 3
Yu & Cardona

# Indirect transitions in Germanium

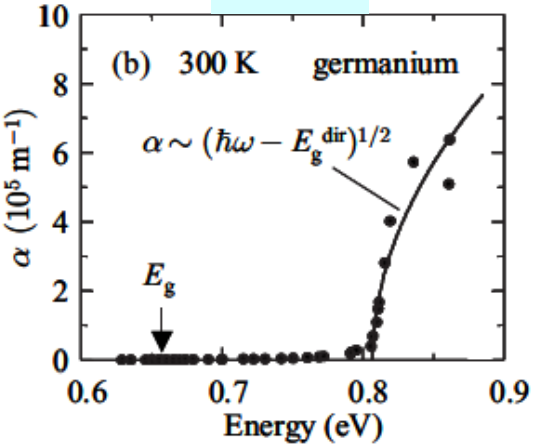



indirect




direct



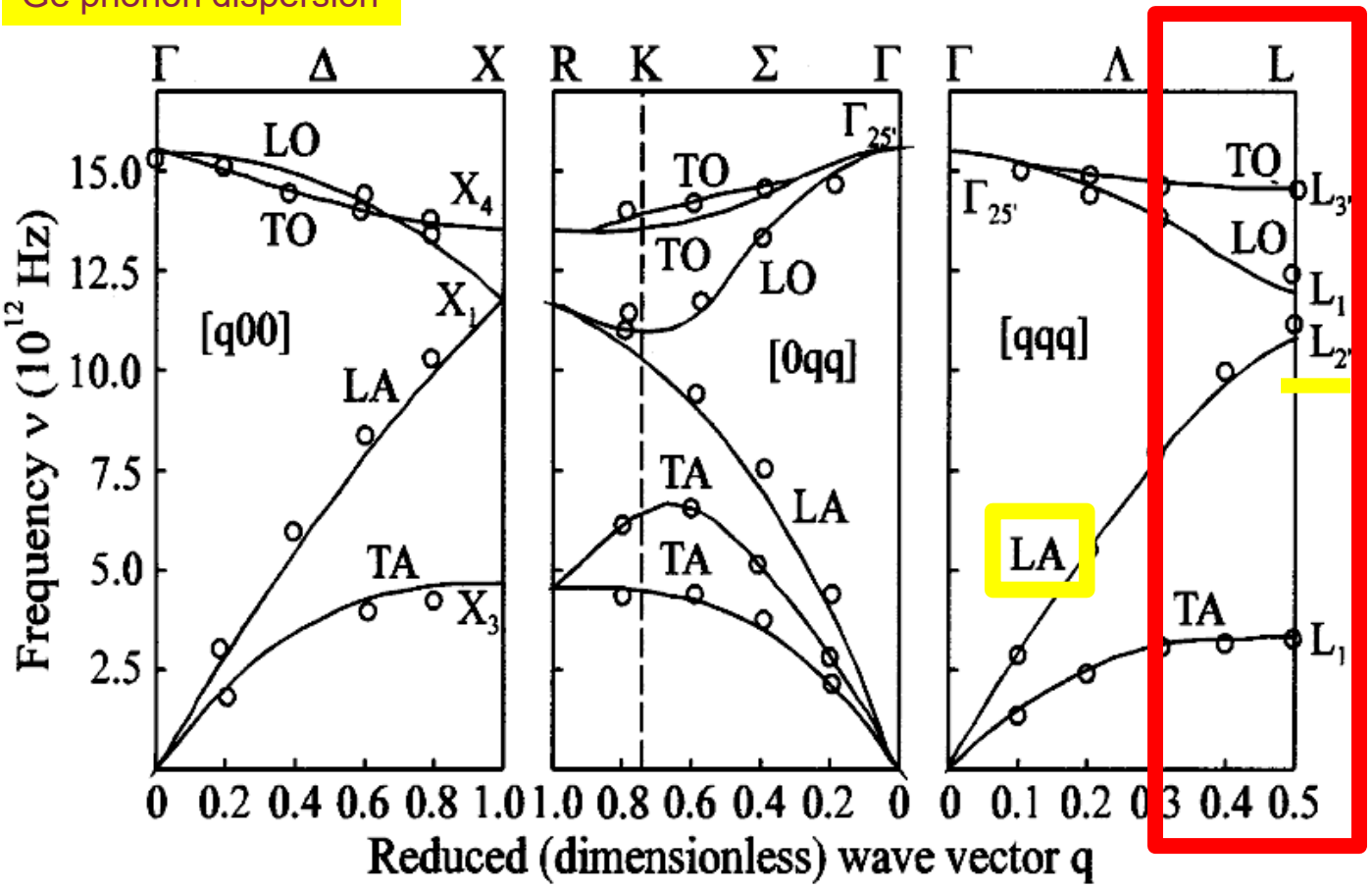

$$\hbar\vec{k}_f = \hbar\vec{k}_i \pm \hbar\vec{Q} \pm RLV$$

$$E_f = E_i + \hbar\omega \pm \hbar\Omega$$

Fox, Chapter 3
Yu & Cardona

# Which phonons assist with indirect transitions?

Ge phonon dispersion




Several branches at each k-point:

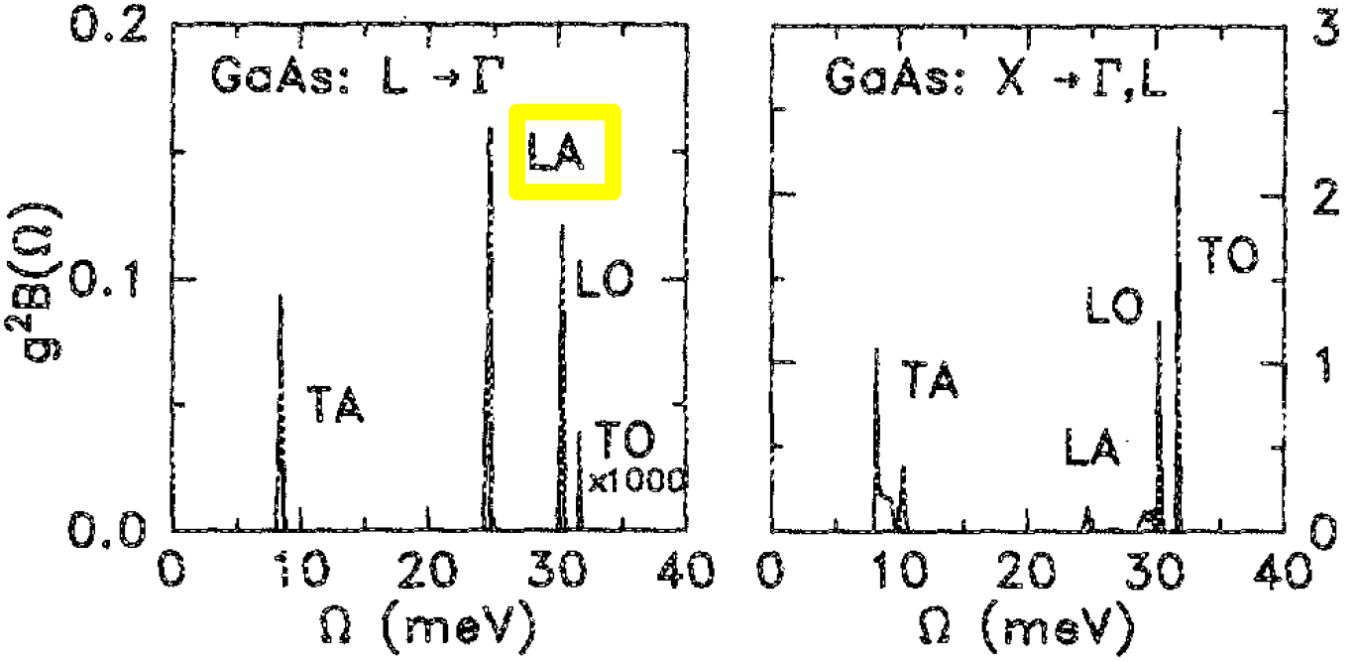
Transverse Optical
Longitudinal Optical
**Longitudinal Acoustic**
Transverse Acoustic

We know that **q**=L, because the CB minimum is at the L-point.

$\Gamma_{2'} \otimes L_1 = L_{2'}$

J. Birman, PR **127**, 1093 (1962)

# Which phonons assist with indirect transitions?




Several branches at each k-point:

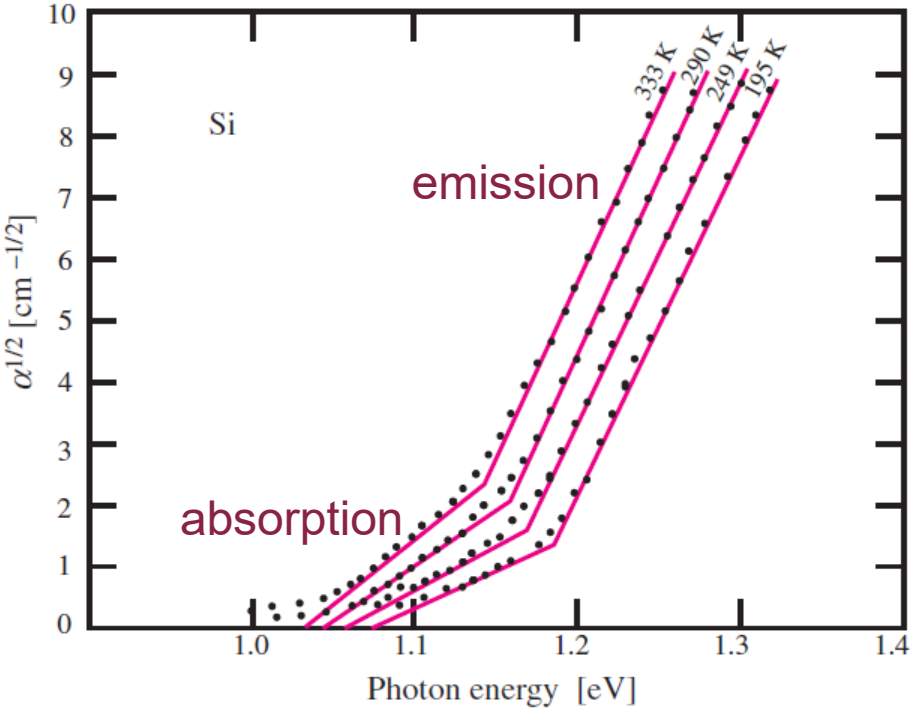
Transverse Optical
Longitudinal Optical
Longitudinal Acoustic
Transverse Acoustic

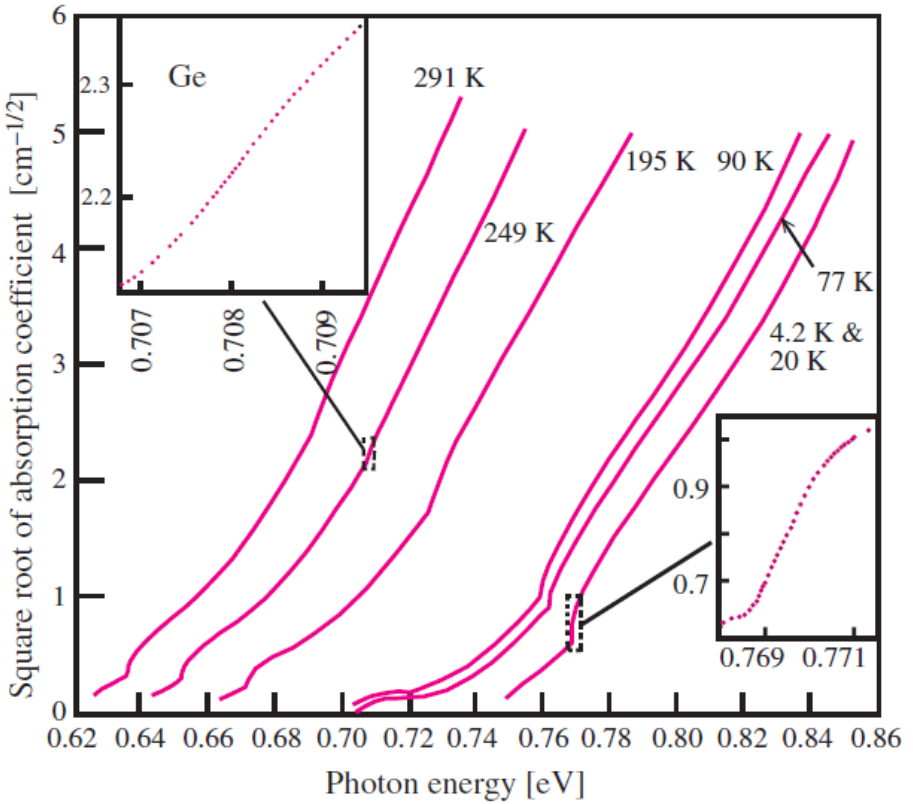
Quantitative description with intervalley spectral functions.

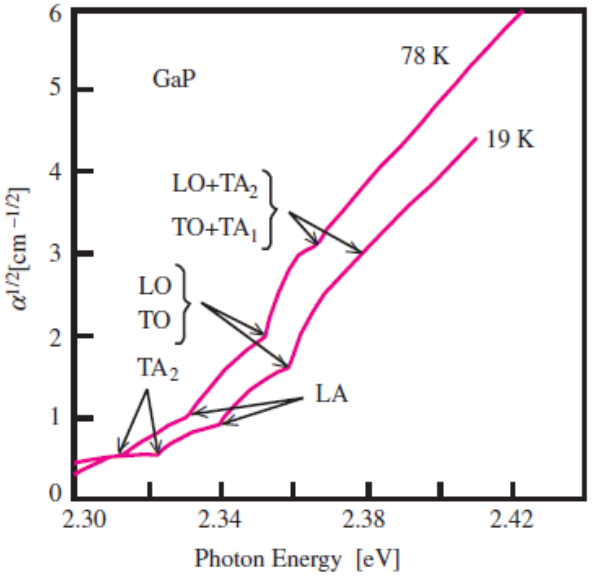
LA-assisted scattering is dominant in Ge for electrons, but we need LO phonons for holes. This ignores the k-dependence of the intervalley scattering matrix element.

Zollner, JAP **68**, 1682 (1990)
Krishnamurthy, JAP **74,** 2117 (1993)

# Indirect transitions: Phonon replica



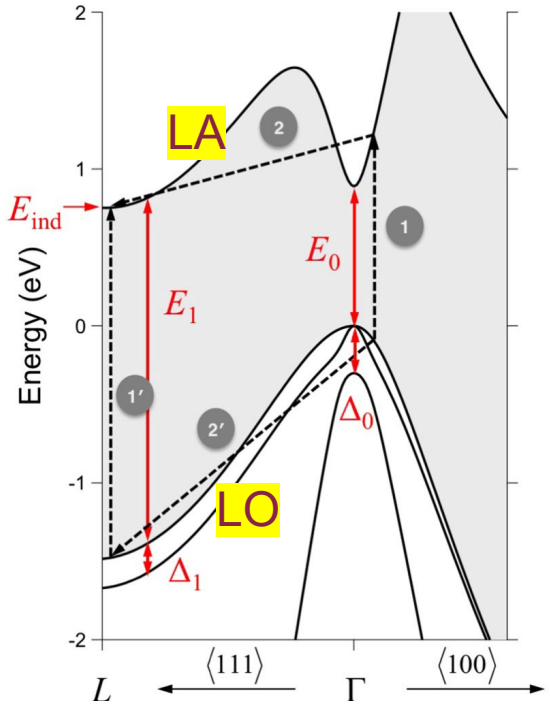




Phonon absorption and emission.
Different phonons can contribute.
Excitonic corrections may be needed.

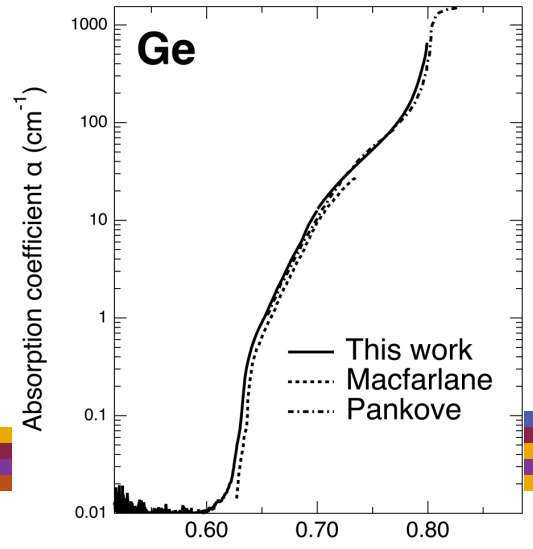
$$\hbar\vec{k}_f = \hbar\vec{k}_i \pm \hbar\vec{Q} + RLV$$

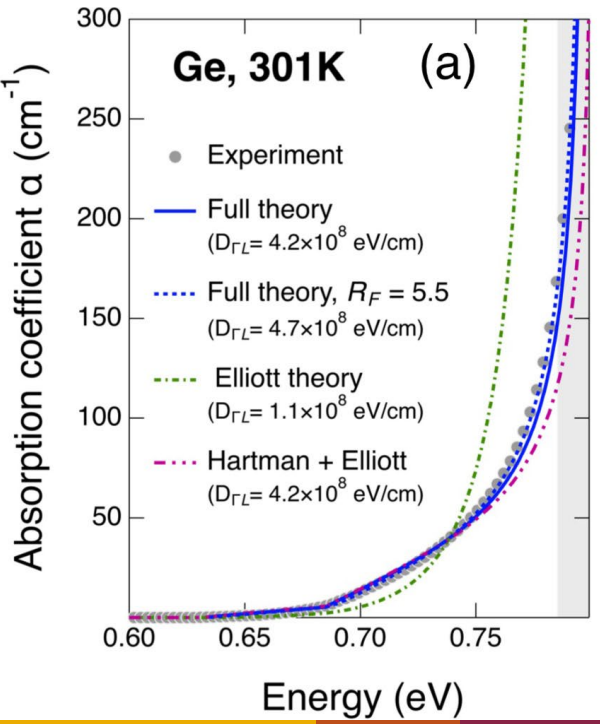
Yu & Cardona
Nishino, JPSJ **37** (1974): wavelength modulation

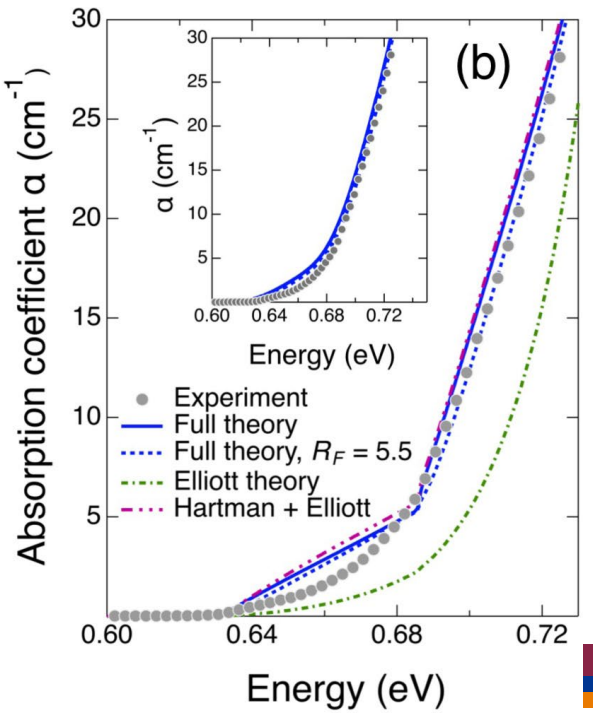
# Indirect transitions in Germanium




New experiments (α of Ge at 301 K)
New theory: all details of band structure, excitonic corrections
Only fit parameter: electron-phonon coupling parameter $D_{\Gamma L}$=4.2 eV/Å.

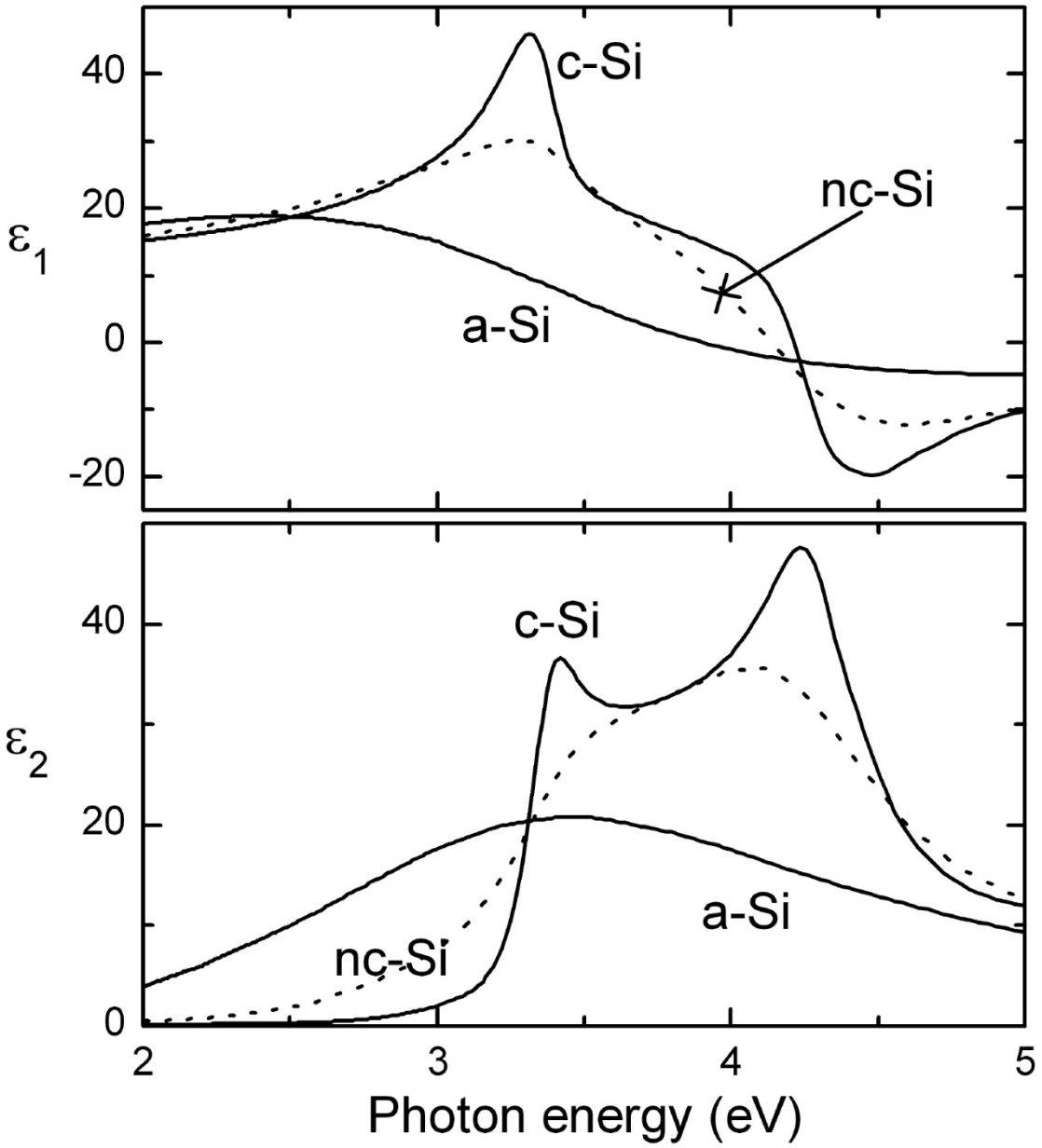



Menendez, PRB (2018); Hartman, PR (1962); Elliot, PR (1957)

# Indirect transitions: Weak or Strong ???



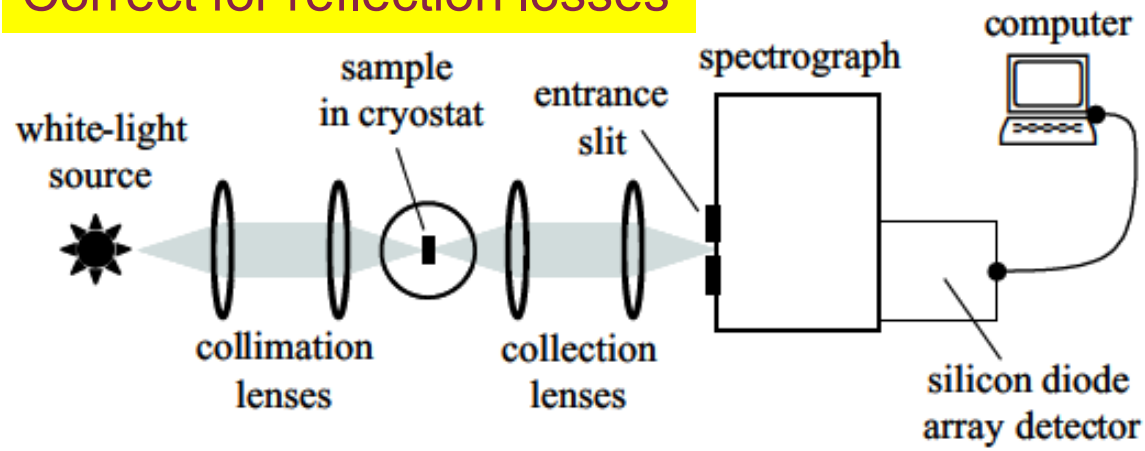

c-Si: All absorption below 3.4 eV is indirect.

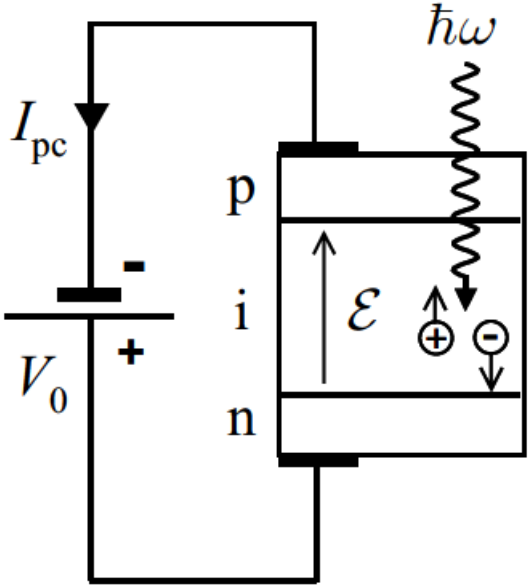
a-Si, nc-Si: Loss of periodicity increases strength of indirect absorption.

Peter Petrik, 2012

# Absorption measurements

Correct for reflection losses

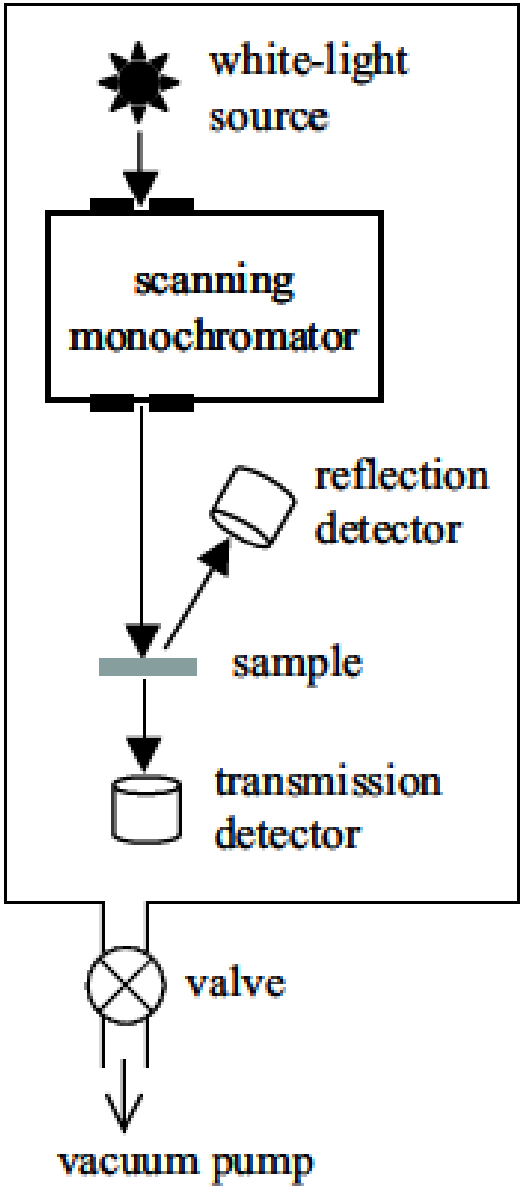



Best for small α

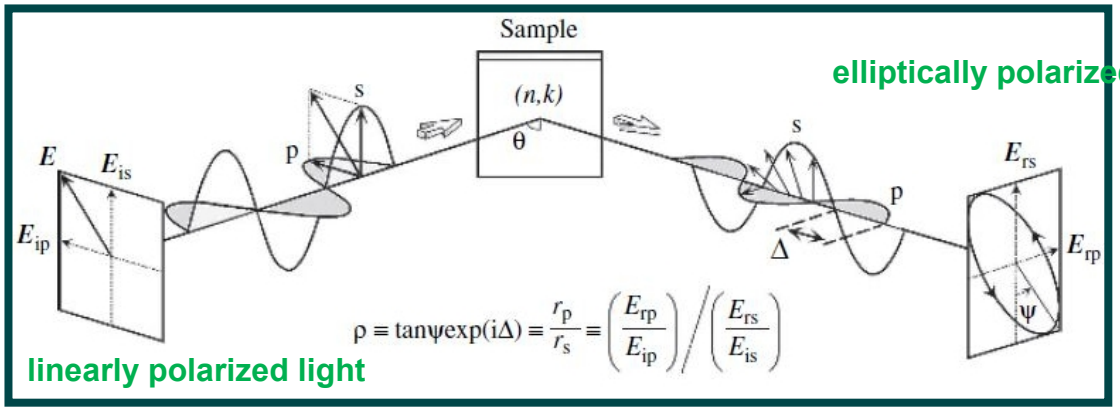
$$I_{PC} = e\eta \frac{P}{\hbar\omega}\left(1 - e^{-\alpha l}\right)$$

Photocurrent




Fox, Chapter 3

# Absorption measurements: Ellipsometry




Best for large α

Fresnel reflectance ratio, Ellipsometric angles

$$\rho = \frac{R_p}{R_s} = \frac{E_{rp}}{E_{ip}} \cdot \frac{E_{is}}{E_{rs}} = \tan\Psi\, e^{i\Delta}$$

$$\tilde{\varepsilon} = \sin^2\varphi \left[1 + \tan^2\varphi \cdot \left(\frac{1-\rho}{1+\rho}\right)^2\right]$$

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$

Complex dielectric function

Monochromator or Interferometer (λ)

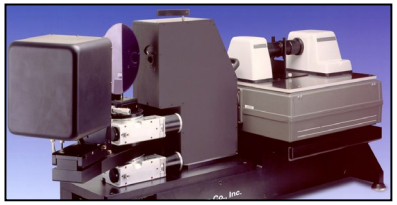
detector

polarizer

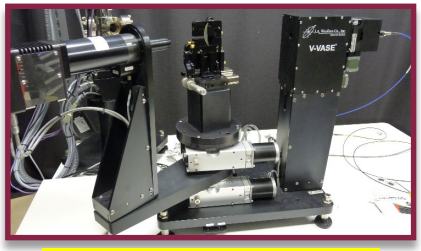
analyzer

Φ

Bulk sample

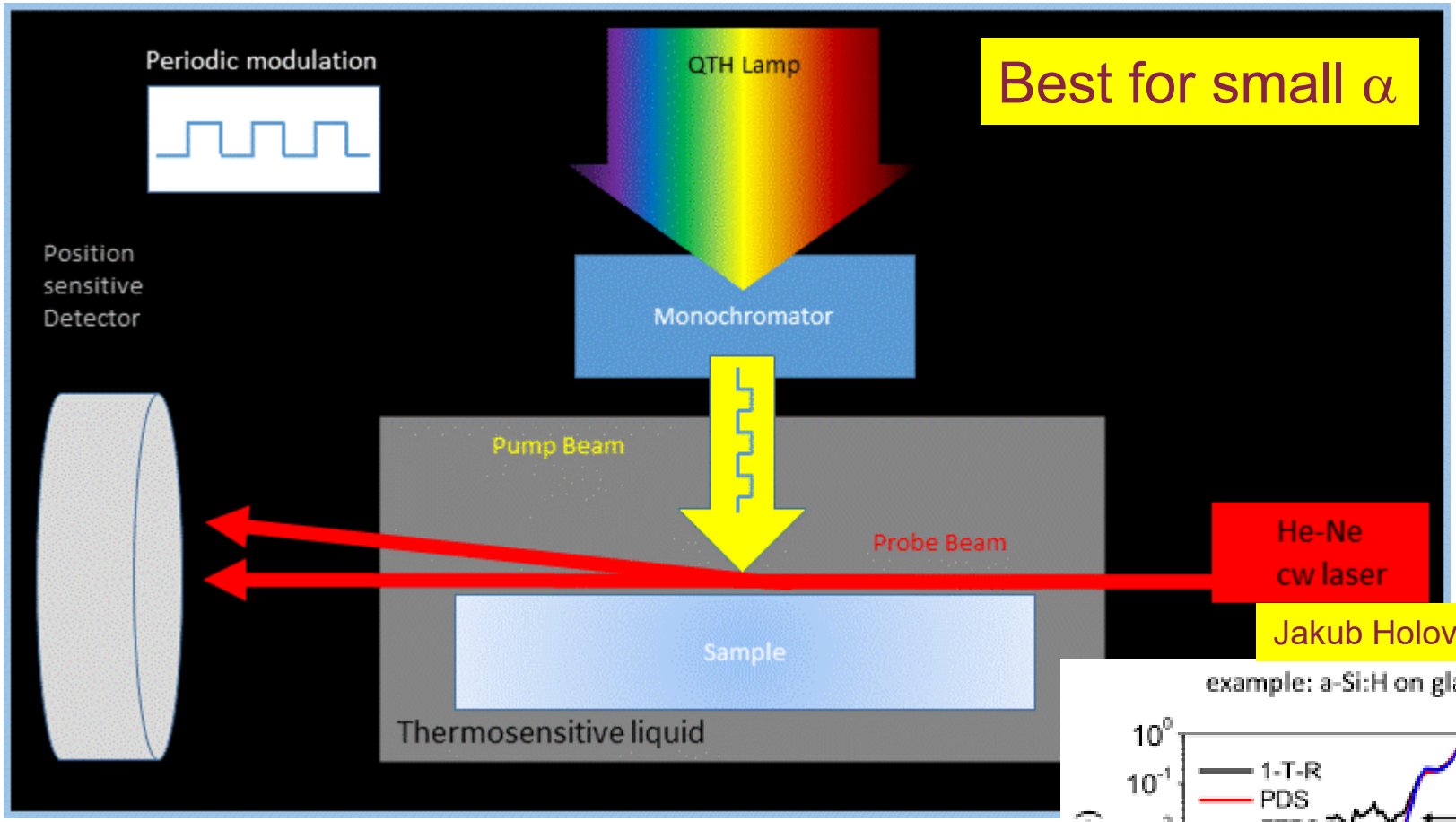


FTIR

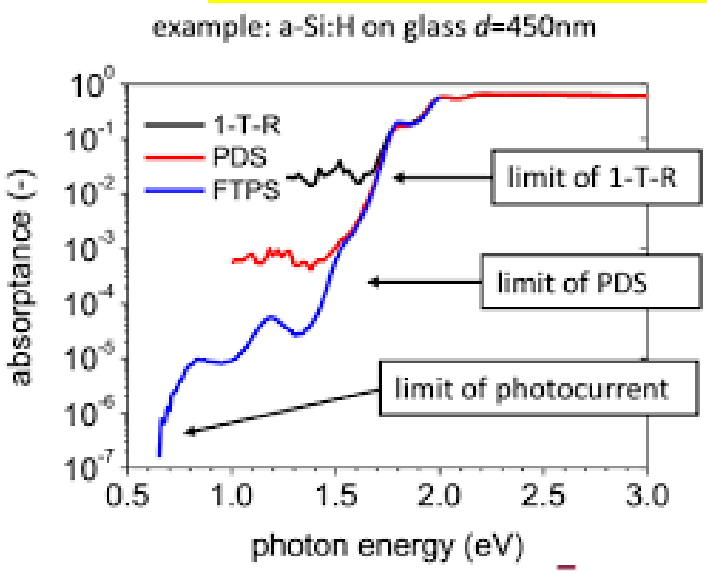



NIR-VIS-QUV

# Absorption measurements: Photothermal deflection




Jakub Holovsky, CTU Praha

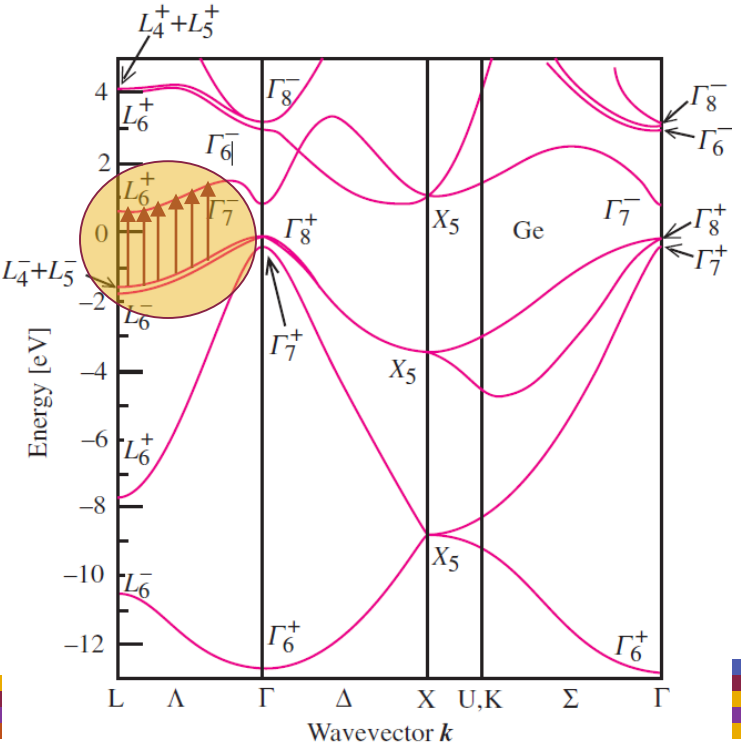


# Van Hove Singularities: Beyond effective-mass approximation

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

Consider two spin states for each **k**.

$$g_{fi}(\hbar\omega) = \iiint_{i,f} \frac{d^3\vec{k}}{4\pi^3}\delta\left(\hbar\omega - E_{fi}(\vec{k})\right) = \frac{1}{4\pi^3}\oiint_{\hbar\omega=E_{fi}} \frac{dS}{|\vec{\nabla}_{\vec{k}} E_{fi}(\vec{k})|}$$




Van Hove singularity: Parallel bands

**Use Taylor expansion around $k_0$:**

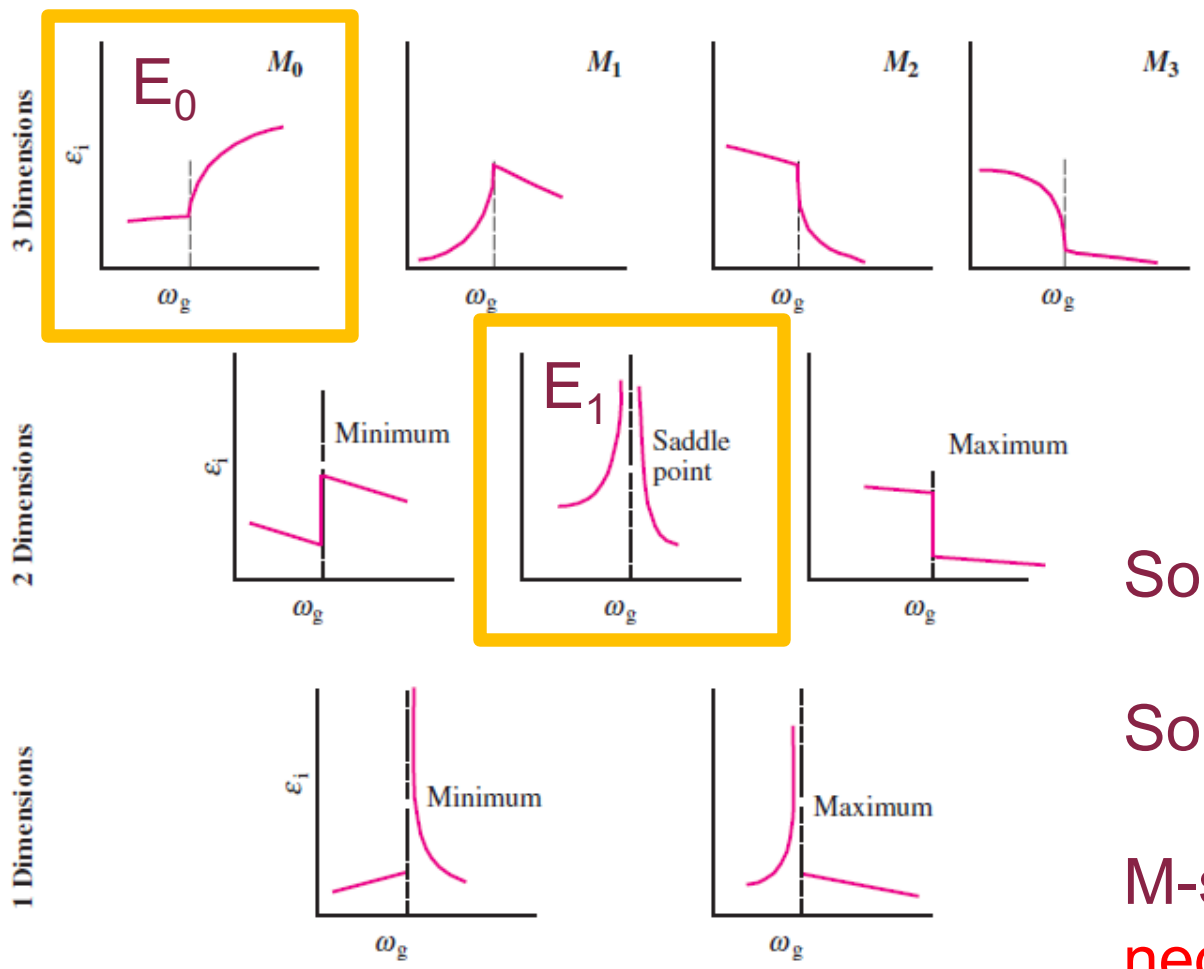
$$E_{fi}(\vec{k}) = E_{fi}(\vec{k}_0) + \sum_{i=1}^{3} a_i (k_i - k_{0i})^2$$

Some $a_i$ small or zero: 1D, 2D, 3D

Some $a_i$ positive, some negative

Ashcroft & Mermin, Chapter 8
Dresselhaus, Chapter 17

# Critical Points




$$E_{fi}(\vec{k}) = E_{fi}(\vec{k}_0) + \sum_{i=1}^{3} a_i (k_i - k_{0i})^2$$

Some $a_i$ small or zero:
1D, 2D, 3D

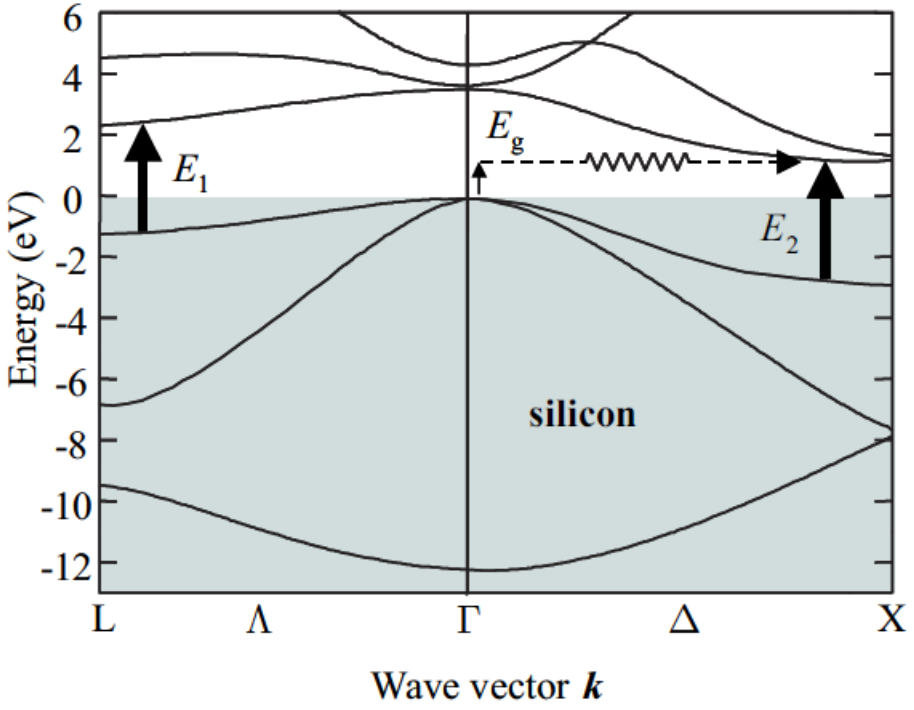
Some $a_i$ positive,
some negative

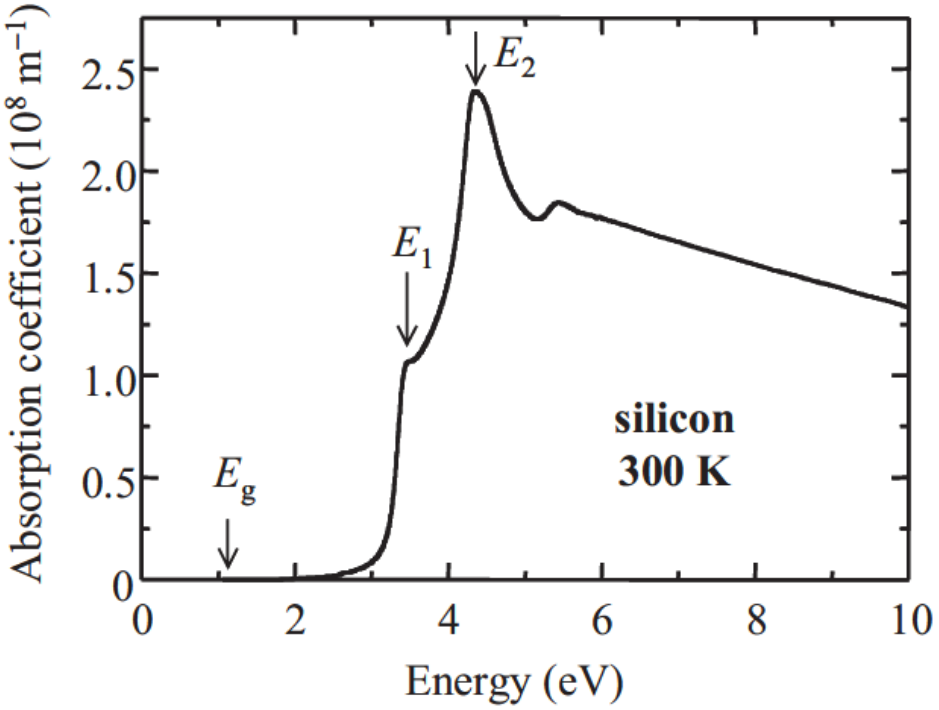
M-subscript: Number of negative mass parameters

| | Type | $D_j$ | |
|---|---|---|---|
| | | $E < E_0$ | $E > E_0$ |
| Three dimensions | $M_0$ | 0 | $(E - E_0)^{1/2}$ |
| | $M_1$ | $C - (E_0 - E)^{1/2}$ | $C$ |
| | $M_2$ | $C$ | $C - (E - E_0)^{1/2}$ |
| | $M_3$ | $(E_0 - E)^{1/2}$ | 0 |
| Two dimensions | $M_0$ | 0 | $C$ |
| | $M_1$ | $-\ln(E_0 - E)$ | $-\ln(E - E_0)$ |
| | $M_2$ | $C$ | 0 |
| One dimension | $M_0$ | 0 | $(E - E_0)^{-1/2}$ |
| | $M_1$ | $(E_0 - E)^{-1/2}$ | 0 |

Yu&Cardona
Dresselhaus, Chapter 17

# Critical points in silicon



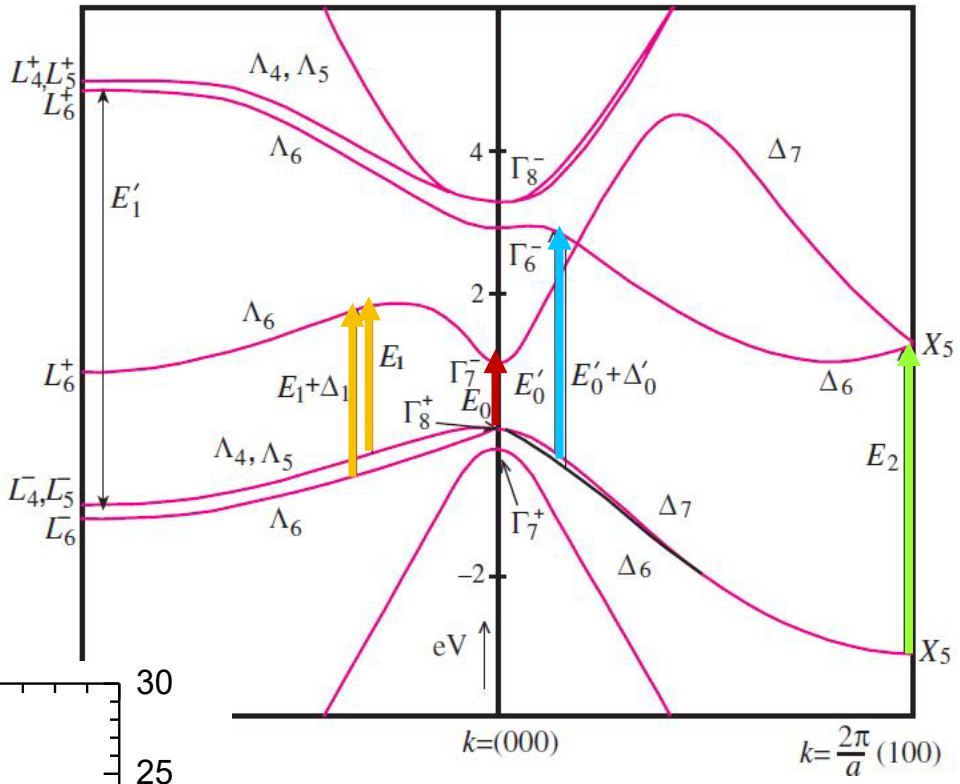

- Direct gap (3.4 eV) is much larger than indirect gap (1.1 eV).
- Si is almost transparent up to 3 eV.
- Spin-orbit splitting is small (no splittings).

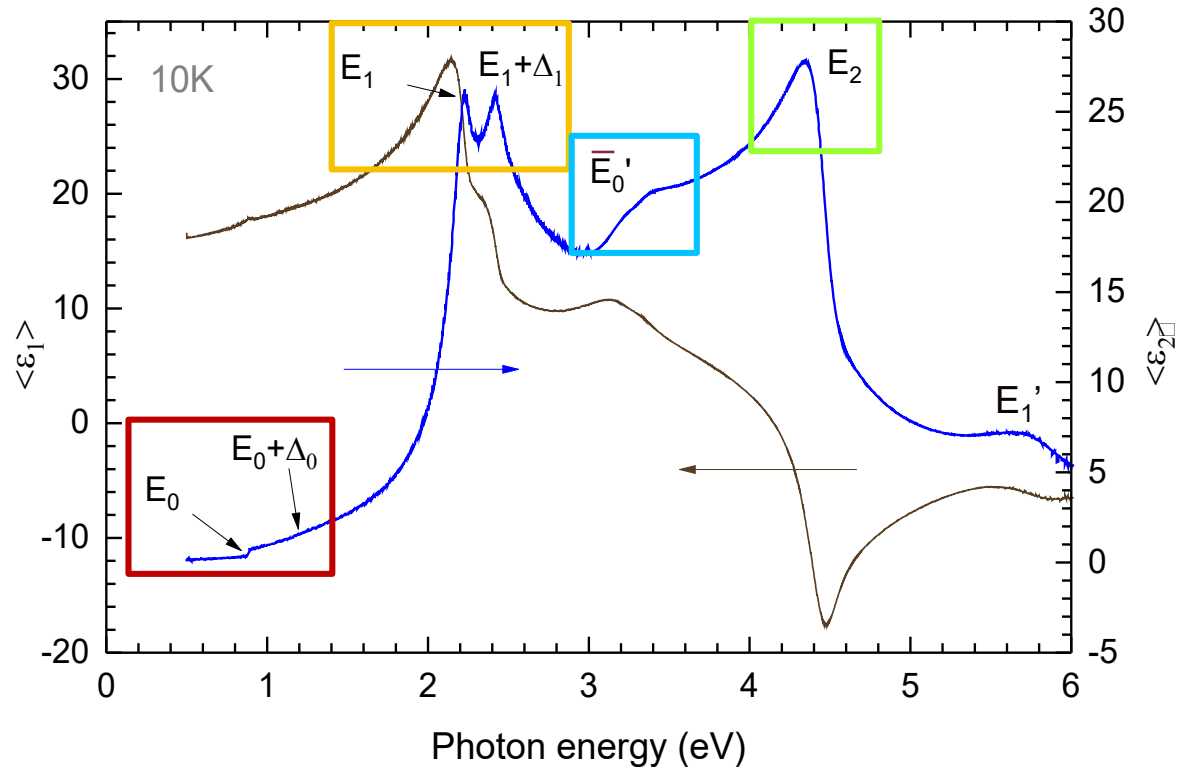
Fox, Chapter 3

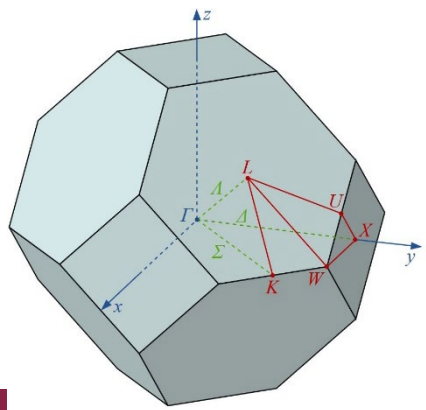
# Critical Points in Germanium

- Structures in the dielectric function due to interband transitions
- Joint density of states
- Van Hove singularities

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



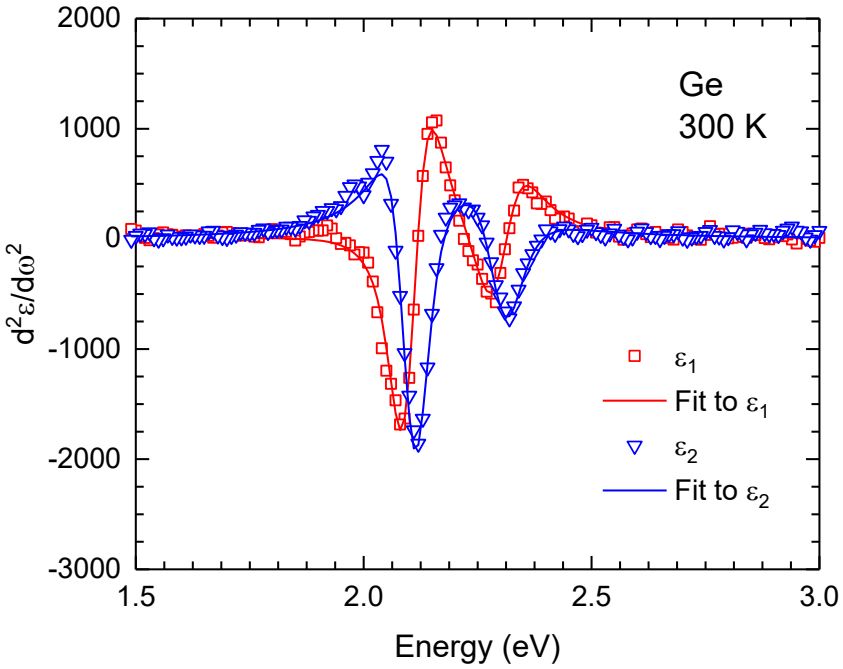



C. Emminger, ICSE-2019

# Critical-point lineshapes

| Type | | $D_j$ | |
|---|---|---|---|
| | | $E < E_0$ | $E > E_0$ |
| Three dimensions | $M_0$ | 0 | $(E - E_0)^{1/2}$ |
| | $M_1$ | $C - (E_0 - E)^{1/2}$ | $C$ |
| | $M_2$ | $C$ | $C - (E - E_0)^{1/2}$ |
| | $M_3$ | $(E_0 - E)^{1/2}$ | 0 |
| Two dimensions | $M_0$ | 0 | $C$ |
| | $M_1$ | $-\ln(E_0 - E)$ | $-\ln(E - E_0)$ |
| | $M_2$ | $C$ | 0 |
| One dimension | $M_0$ | 0 | $(E - E_0)^{-1/2}$ |
| | $M_1$ | $(E_0 - E)^{-1/2}$ | 0 |

Savitzky-Golay derivative of ellipsometry spectra




General expression (1D, 3D):

$$\varepsilon(\hbar\omega) = C + Ae^{i\Phi}(\hbar\omega - E_0 + i\Gamma)^{(n-2)/2}$$

General expression (2D):

$$\varepsilon(\hbar\omega) = C + Ae^{i\Phi}\ln(\hbar\omega - E_0 + i\Gamma)$$

| | |
|---|---|
| A | amplitude |
| $\Phi$ | excitonic phase angle |
| $\Gamma$ | broadening |

$E_1$ and $E_1+\Delta_1$ critical points, fitted with analytical lineshapes

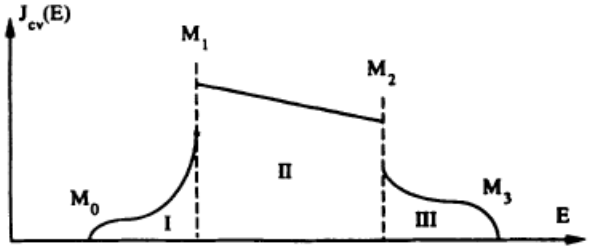
M. Cardona, Modulation Spectroscopy (Academic Press, 1966)
D.E. Aspnes, Surf. Sci. **37**, 418 (1973)

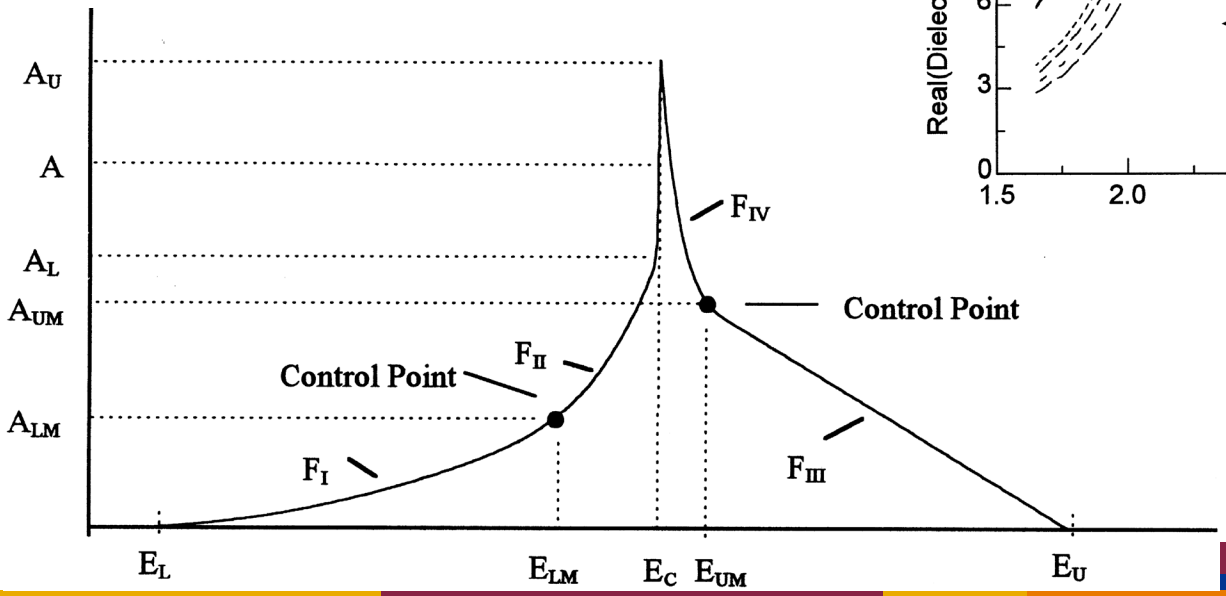
# Parametric oscillator (PSEMI) model

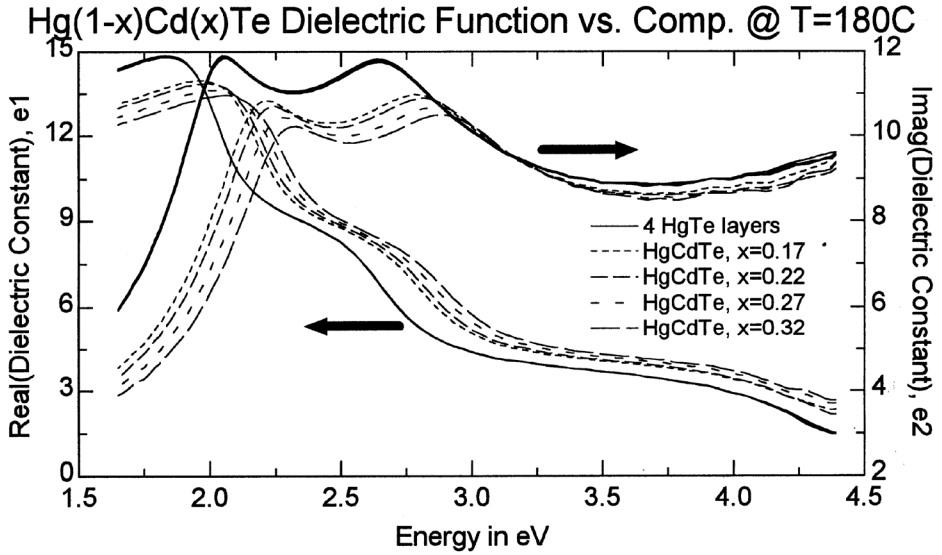
Critical points only valid near $E_{CP}$ (Taylor expansion around $E_{CP}$, parabolic bands, constant matrix elements), work well to fit derivatives.

To fit $\varepsilon$, we need to add more parameters in the wings.

Many parameters.




B. Johs, C.M. Herzinger, Thin Solid Films **313-314**, 137 (1998).
C.C. Kim, J.W. Garland, Phys. Rev. B **45**, 11749 (1992).

# Summary

Indirect gap absorption in Si and Ge

Experimental techniques to measure absorption

Van Hove singularities

Critical points in the dielectric function

Analytical lineshapes to fit Savitzky-Golay derivative

Parametric oscillator model

# What's next ???

**10: Excitons,**
**photoluminescence,**
**quantum confinement, wells, wires, dots**

**11: Applications I**
**What would you like to see ?**
**Please send email to zollner@fzu.cz**

**12: Applications II**
**Properties of thin films,**
**stress/strain, deformation potentials**