Excitonic effects at the direct band gap of Ge

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Analysis of Femtosecond Pump-Probe Ellipsometry Data of Ge and Si

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Outline

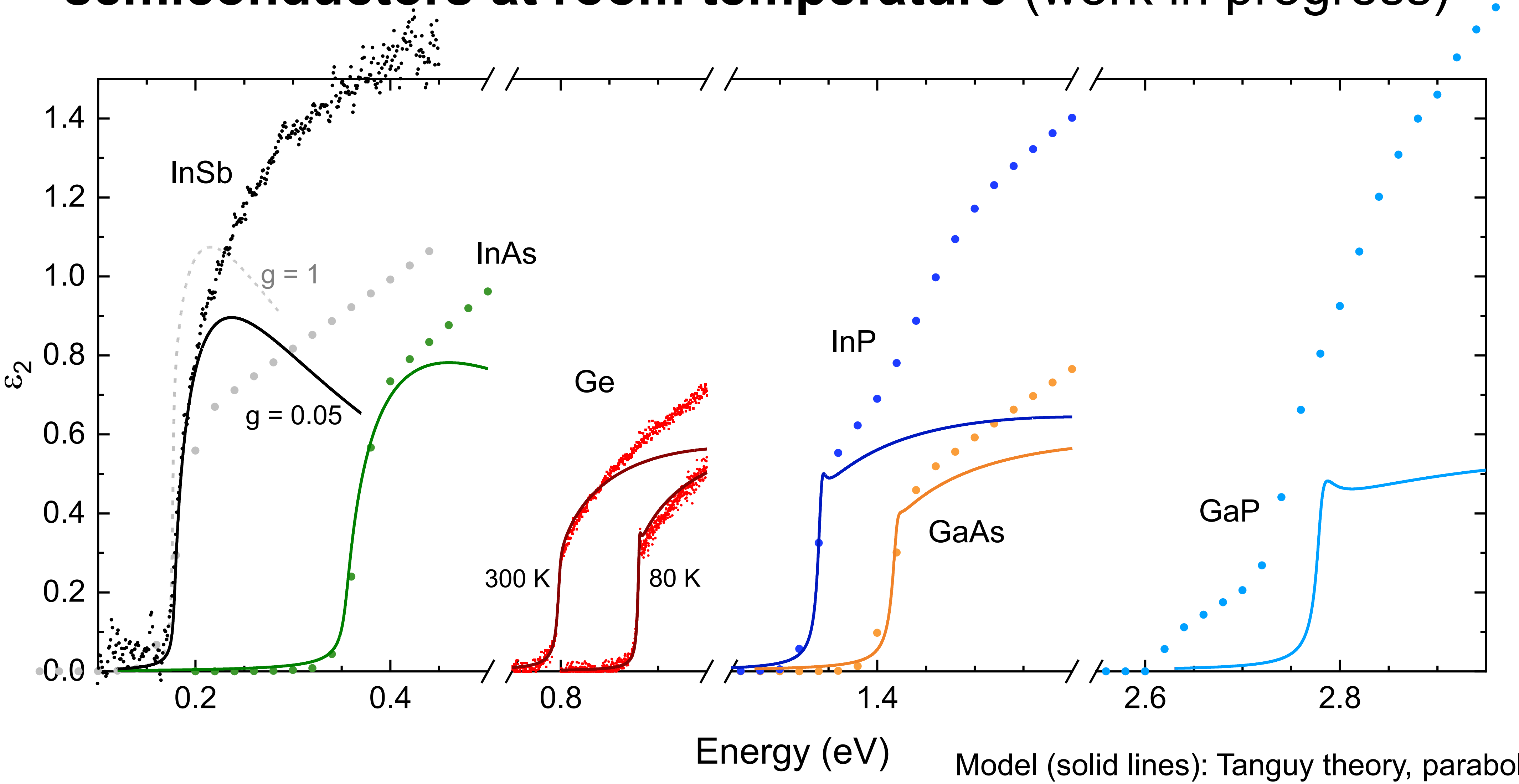
Part 1: Excitonic effects at the direct band gap of Ge

- Second derivative analysis using linear filters
- Tanguy-Elliott model with parameters from $k \cdot p$ theory
- Fit results: Energies and broadening as function of temperature

Part 2: Analysis of the transient dielectric function of Ge and Si from pump-probe spectroscopic ellipsometry

- Critical point parameters as functions of delay time
- Coherent acoustic phonon oscillations

Motivation: Model of the direct band gap of various semiconductors at room temperature (work in progress)



Model (solid lines): Tanguy theory, parabolic bands
Symbols: Experimental data from NMSU and UNL

C. Tanguy, Phys. Rev. B **60**, 10660 (1999)
J. Menéndez, D. J. Lockwood, J. C. Zwinkels, M. Noël, Phys. Rev. B **98**, 165207 (2018)
P. Yu and M. Cardona, *Fundamentals of Semiconductors*, (Springer, Heidelberg, 2010)

Tanguy-Elliott model to consider excitonic effects

R. J. Elliott, Phys. Rev. **108**, 1384 (1957)
C. Tanguy, Phys. Rev. B **60**, 10660 (1999)

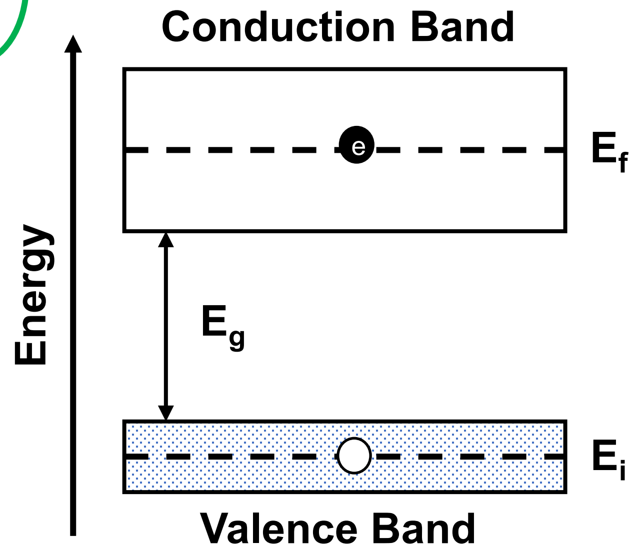
$$\epsilon(E) = \frac{A\sqrt{R}}{(E+i\Gamma)^2}\left[\tilde{g}\big(\xi(E+i\Gamma)\big) + \tilde{g}\big(\xi(-E-i\Gamma)\big) - 2\tilde{g}(\xi(0))\right]$$

$$\tilde{g}(\xi) = -2\psi\left(\frac{g}{\xi}\right) - \frac{\xi}{g} - 2\psi(1-\xi) - \frac{1}{\xi}$$

unbound, bound, interband

$$\xi(z) = \frac{2}{\left(\frac{E_0 - z}{R}\right)^{1/2} + \left(\frac{E_0 - z}{R} + \frac{4}{g}\right)^{1/2}}$$

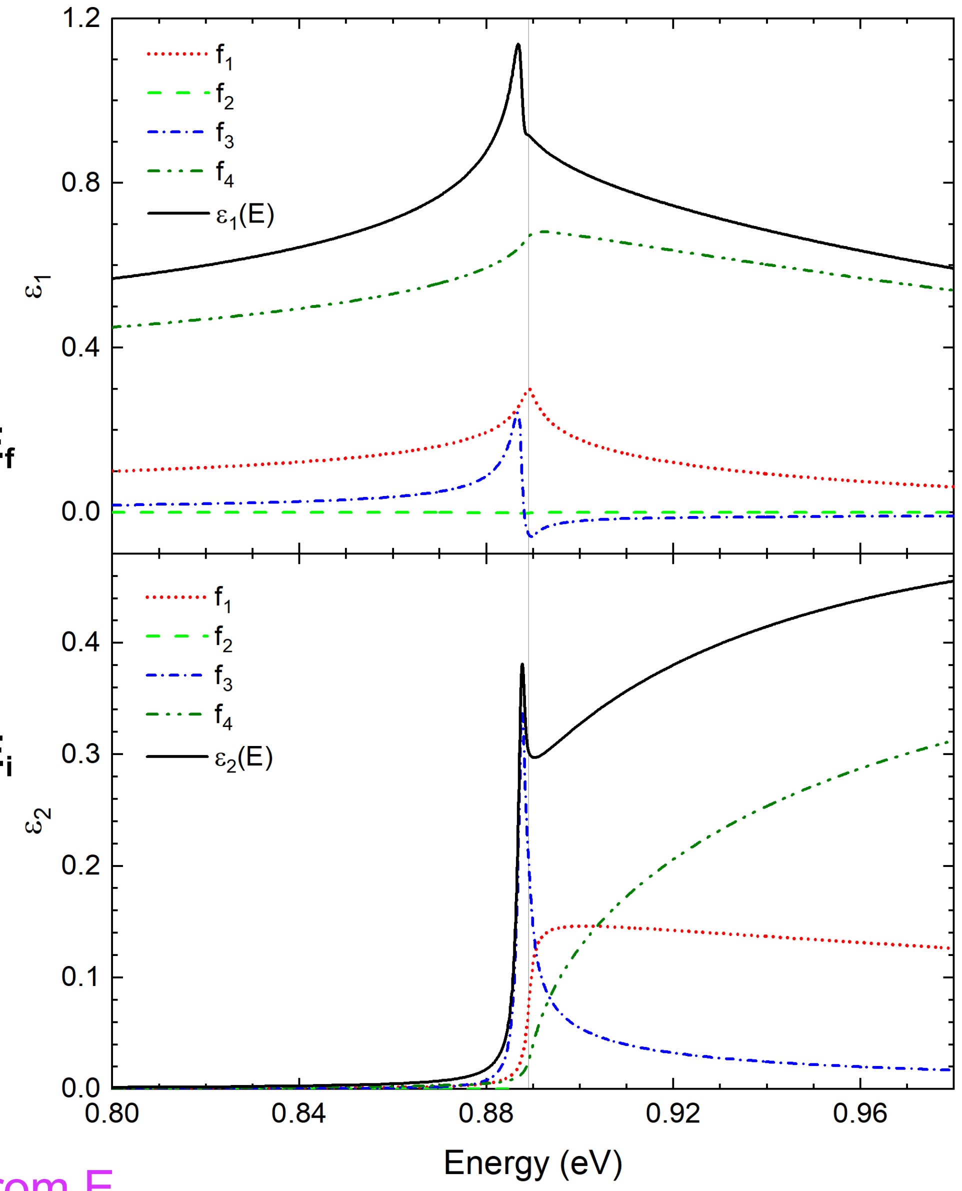
$$\psi(x) = \frac{d \ln \Gamma(x)}{dx}$$ (Digamma function)



Heavy hole (hh) and light hole (lh):

$$\epsilon(E) = \epsilon_{hh}(E) + \epsilon_{lh}(E) + 1 + \frac{A_1}{1 - B_1 E^2}$$

Sellmeier term to consider contributions from E_1



Parameters from k·p theory for semiconductors

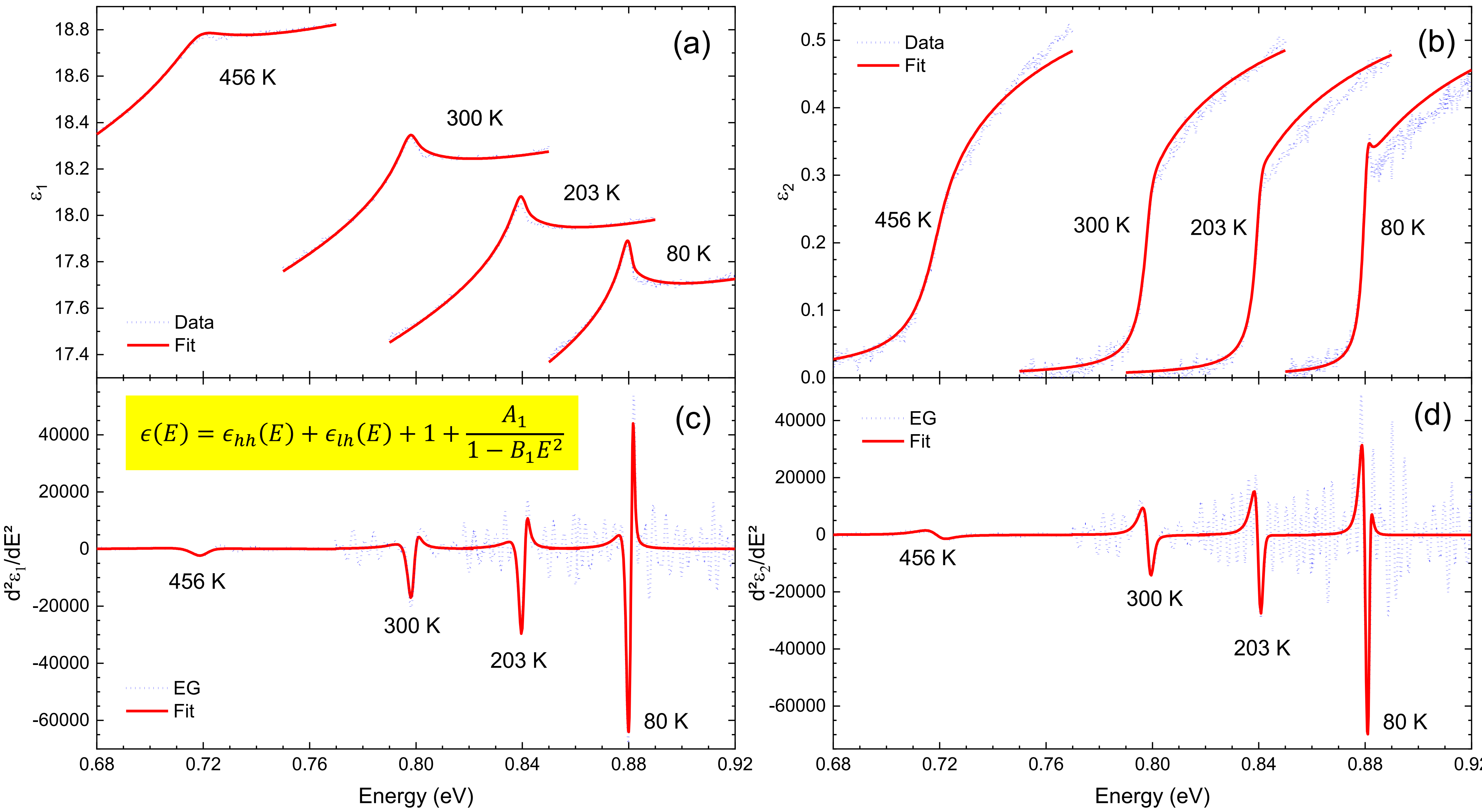
- **Effective masses**: $\frac{1}{\mu_{hh}} = \frac{1}{m_{hh}} + \frac{1}{m_e}$ and $\frac{1}{\mu_{lh}} = \frac{1}{m_{lh}} + \frac{1}{m_e}$
- **Excitonic binding energy**: $R_{hh} = \frac{\mu_{hh}}{\epsilon_r^2} 13.6\ \mathrm{eV}$

  $R_{hh} \approx 2\ \mathrm{meV}$ and $R_{lh} \approx 1\ \mathrm{meV}$ at 10 K
- **Matrix element** $E_P = \frac{2P^2}{m_0}$ calculated via $\frac{1}{m_e} = \frac{1}{m_0} + \frac{E_P}{3m_0}\left[\frac{2}{E_0} + \frac{1}{E_0+\Delta_0}\right]$
- Amplitude: $A_{hh} = \frac{e^2\sqrt{m_0}}{\sqrt{2}\pi\epsilon_0\hbar}\mu_{hh}^{3/2}\frac{E_P}{3}$ with $E_P \approx 25\ \mathrm{eV}$
- Parameters at 10 K:

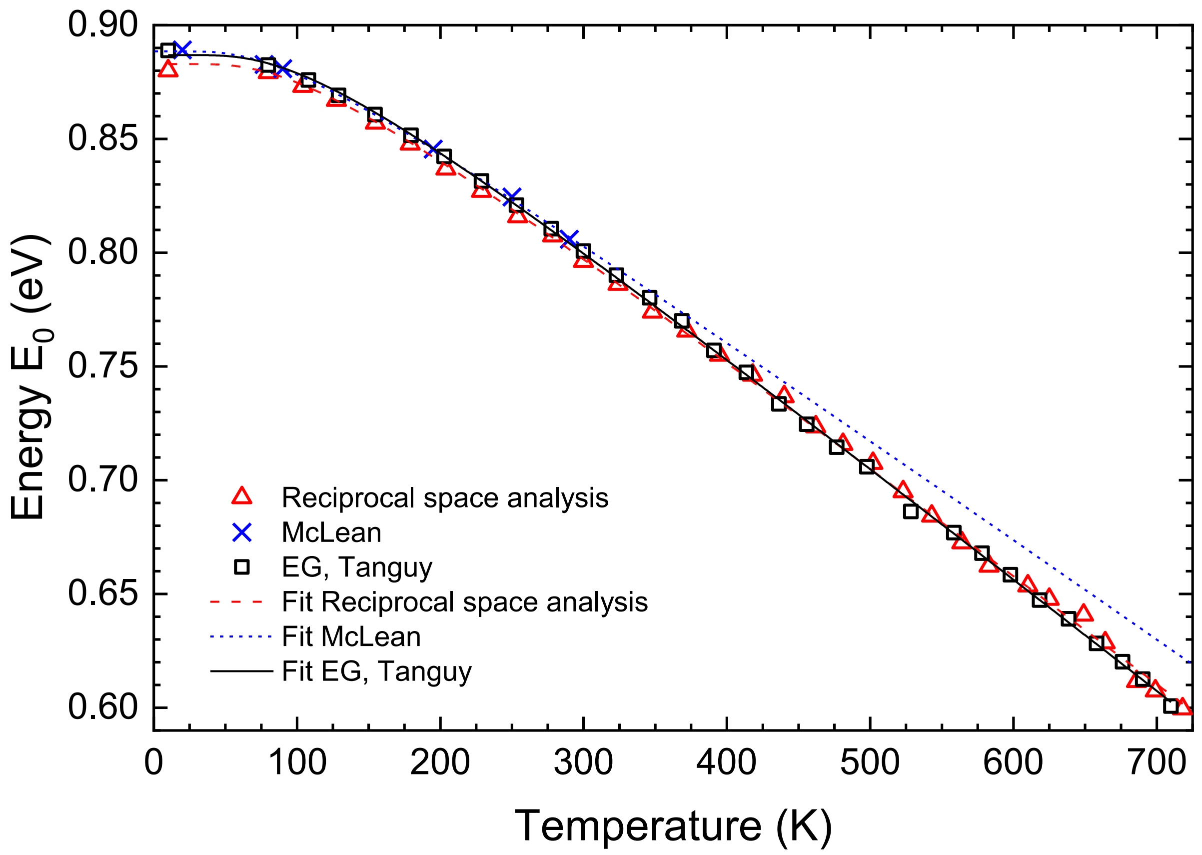
$m_{e\Gamma}$	m_{hh}	m_{lh}	μ_{hh}	μ_{lh}	A_{hh}	A_{lh}	R_{hh} (meV)	R_{lh} (meV)
0.037	0.42	0.045	0.034	0.020	0.78	0.36	1.9	1.1

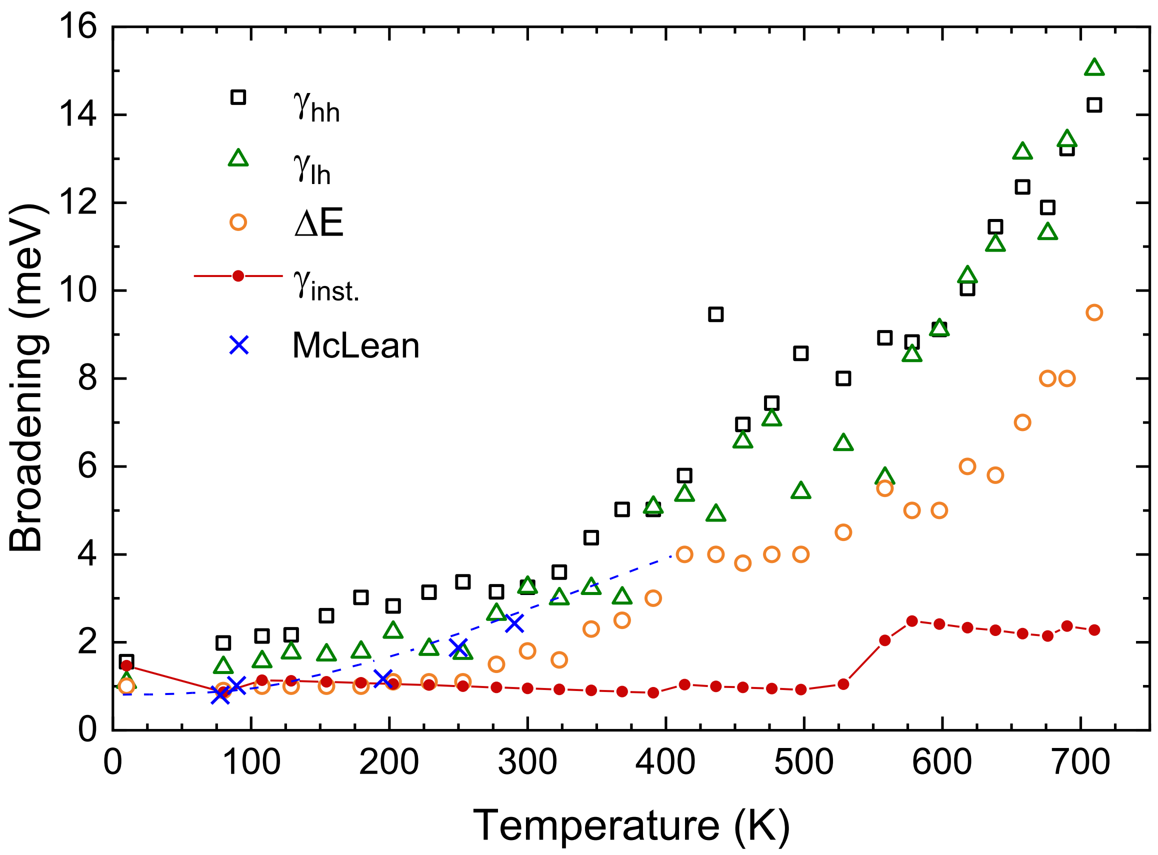
J. Menéndez, D. J. Lockwood, J. C. Zwinkels, M. Noël, Phys. Rev. B **98**, 165207 (2018)
P. Yu and M. Cardona, *Fundamentals of Semiconductors*, (Springer, Heidelberg, 2010)

Fit results for Ge



Temperature dependence of the direct band gap of Ge





$$E(T) = E_a - E_b\left[\frac{2}{e^{\frac{E_{ph}}{kT}} - 1} + 1\right]$$

$$\Gamma(T) = \Gamma_a + \Gamma_b\left[\frac{2}{e^{\frac{E_{ph}}{kT}} - 1} + 1\right]$$

L. Viña, S. Logothetidis, M. Cardona, Phys. Rev. B **30**, 1979 (1984)
C. Emminger, F. Abadizaman, N.S. Samarasingha, T.E. Tiwald, S. Zollner, J. Vac. Sci. Technol. B **38**, 012202 (2020)
T. P. McLean, *Progress in Semiconductors*, (Heywood, London, 1960);
T. P. McLean and E. G. S. Paige, J. Phys. Chem. Solids **23**, 822 (1962)

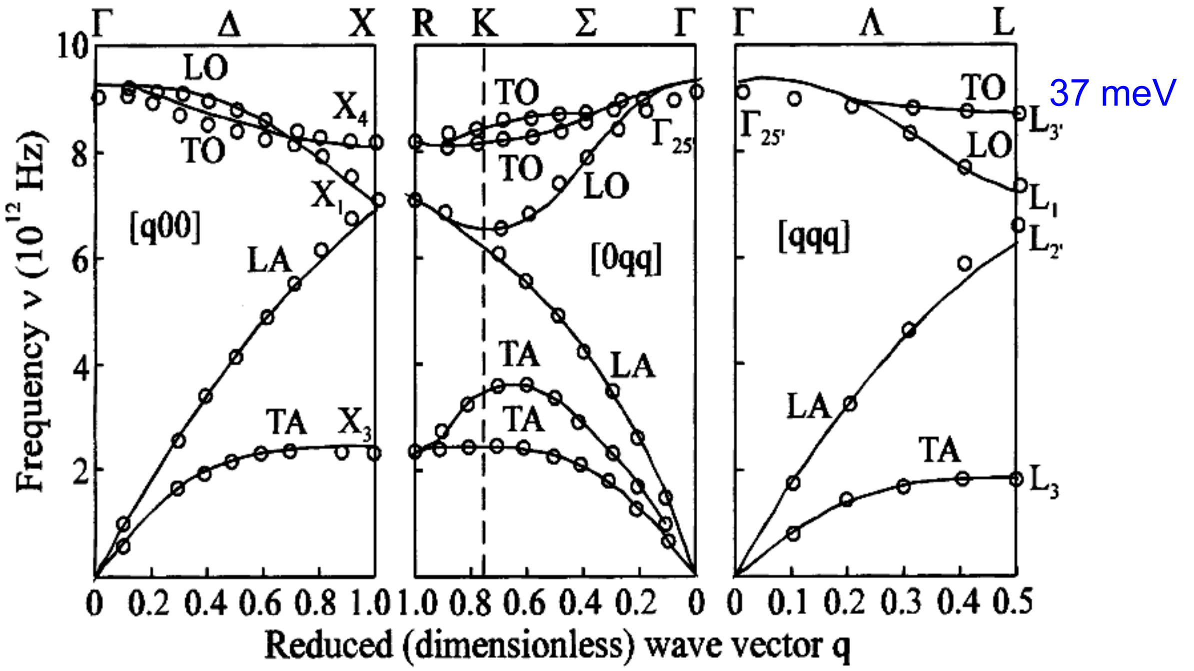
Electron-LA phonon and hole-optical phonon intravalley scattering

Scattering mechanism	**Scattering/relaxation time** *Normalizing constant*
Acoustic phonon	
Deformation potential	$\tau_{ac} = 2(2\pi)^{1/2}\rho\hbar^4 s^2[3E_1^2 m^{*3/2}(300k_B)^{3/2}]^{-1}$

$E_1 = 11.4\ \text{eV}$
$\rho = 5.32\ \text{g/cm}^3$
$s = \frac{u_{lo}}{3} + \frac{2u_{tr}}{3} = 3.9 \times 10^3\ \text{m/s}$ … ellipsoidal & warped bands
$m_{e\Gamma} = 0.037\ m_0$ … effective mass of the electron at Γ

Optic phonon	
Nonpolar	$\tau_{op} = 2(2\pi)^{1/2}\rho\hbar^3\omega_o[\exp(\theta_0/300) - 1] \times [3D_o^2 m^{*3/2}(300k_B)^{1/2}]^{-1}$

$m_{lh} = 0.045\ m_0$
$m_{hh} = 0.42\ m_0$
$a = 5.66$ Å
$d_0 = 37\ \text{eV}$ (Pötz and Vogl 1981)
$D_0 = d_0/a = 7.53$ eV/Å
$\omega_0 = 9\ \text{THz} = 37\ \text{meV}$



Weber W., Phys. Rev. **B15**, 10 (1977) 4789-4803.

	10 K		300 K		800 K	
Scattering	τ (fs)	Γ (meV)	τ (fs)	Γ (meV)	τ (fs)	Γ (meV)
Electrons-LA phonons	$5\text{x}10^5$	$6\text{x}10^{-4}$	3500	0.093	1400	0.23
hh-optical phonons	10^{21}	10^{-19}	180	1.8	35	9.5
lh-optical phonons	10^{22}	10^{-21}	5900	0.056	1400	0.23

W. Pötz and P. Vogl, Phys. Rev. B **24**, 2025 (1981)
L. Reggiani, *Hot-Electron Transport in Semiconductors* (Springer, Berlin, 1985)
R. R. Alfano, *Semiconductors Probed by Ultrafast Laser Spectroscopy Vol. 1*, (Academic Press, London, 1984), chapter by B. R. Nag

Scattering of electrons with LA phonons at the L-point

Scattering rate for intervalley scattering (Conwell 1967): $\frac{1}{\tau} = N_V \frac{D^2 m_{\text{eff}}^{1.5}}{\sqrt{2}\pi\hbar^2 \rho E_{\text{ph}}} \sqrt{\Delta E - E_{\text{ph}}} \left(1 + \frac{2}{e^{\frac{k_B E_{\text{ph}}}{T}} - 1}\right)$

m_{eff}: effective electron mass for final state for a single valley

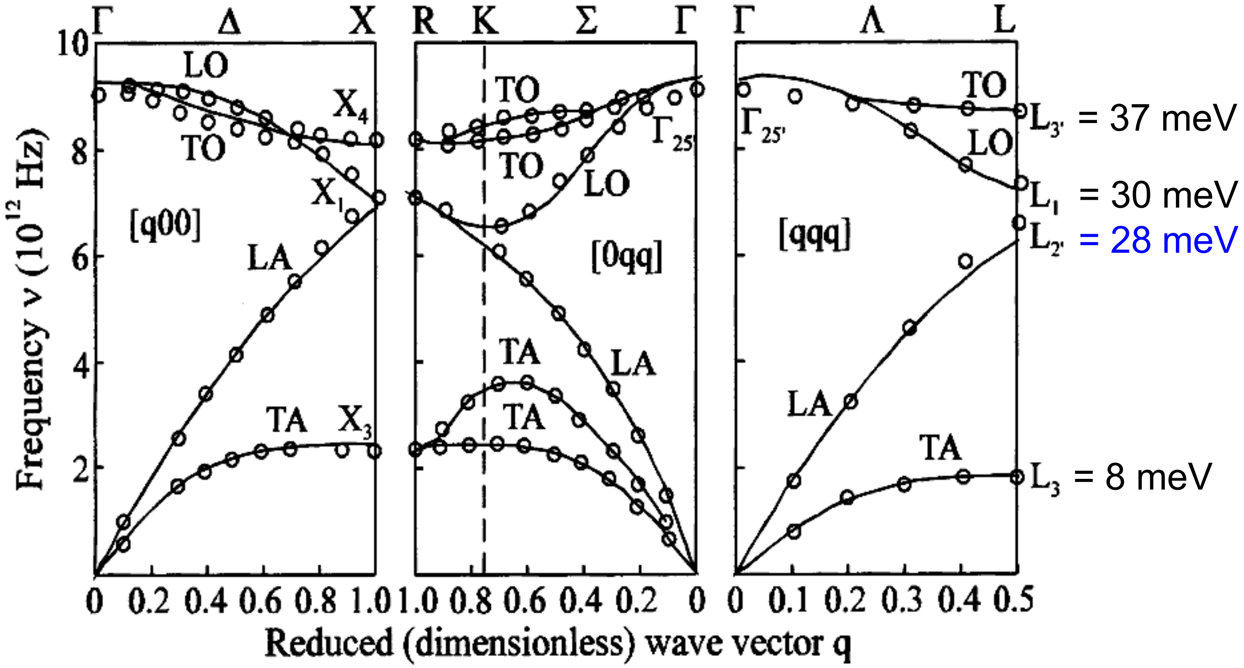
$$m_{\text{eff}} = (m_l m_t^2)^{\frac{1}{3}} = (1.6 \cdot 0.08^2)^{\frac{1}{3}}\ m_0 = 0.22\ m_0$$

$\Delta E = 0.8\ \text{eV} - 0.66\ \text{eV} = 0.139\ \text{eV}$ at RT
$\Delta E = 0.889\ \text{eV} - 0.742\ \text{eV} = 0.147\ \text{eV}$ at low T

$D = 6.5\ \text{eV/Å}$ at RT
$D = 3.0\ \text{eV/Å}$ at low T

$\rho = 5.32\ \text{g/cm}^3$
$E_{\text{ph}} = 28\ \text{meV}$
$N_V = 4$

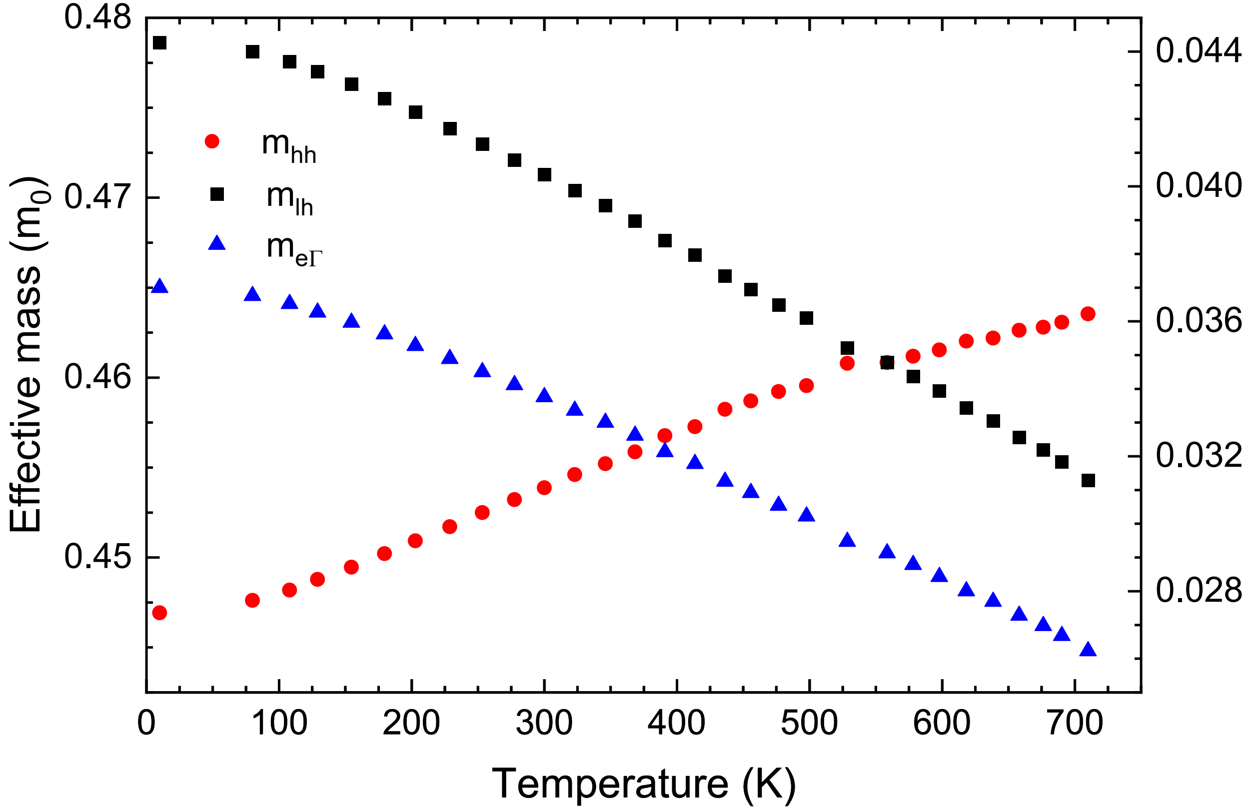
	300 K	10 K
τ (fs)	470	1050
Γ (meV)	0.70	0.31

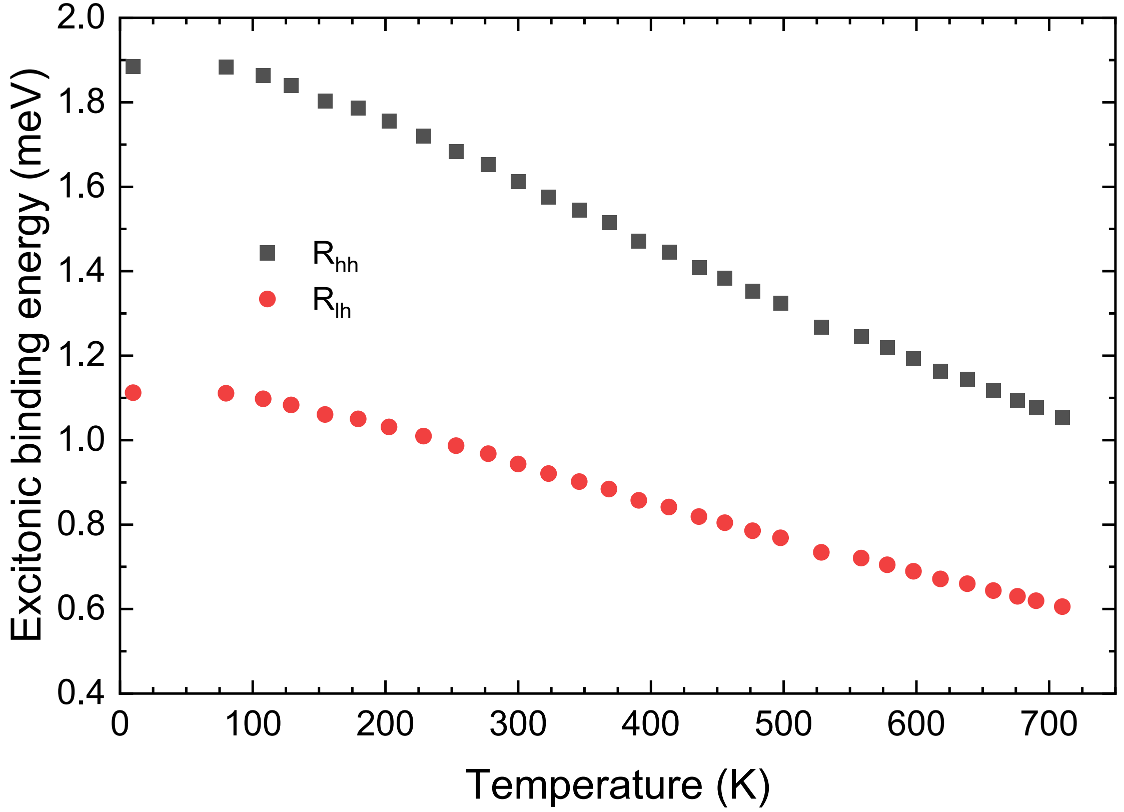


Weber W., Phys. Rev. **B15,** 10 (1977) 4789-4803.

E. M. Conwell, *High Field Transport in Semiconductors* (Academic, New York, 1967)

Temperature dependence of the effective masses and Rydberg energies





$$\frac{1}{m_{e\Gamma}} = \frac{1}{m_0} + \frac{E_P}{3m_0}\left[\frac{2}{E_0} + \frac{1}{E_0 + \Delta_0}\right]$$

$$\frac{1}{m_{hh}} = \frac{1}{\hbar}\left[-2A + 2B\left(1 + \frac{2|C|^2}{15B^2}\right)\right]$$

$$\frac{1}{m_{lh}} = \frac{1}{\hbar}\left[-2A - 2B\left(1 + \frac{2|C|^2}{15B^2}\right)\right]$$

$$A = 1 - 1/3\left[\frac{E_P}{E_0} + \frac{2E_Q}{E_0'}\right]$$

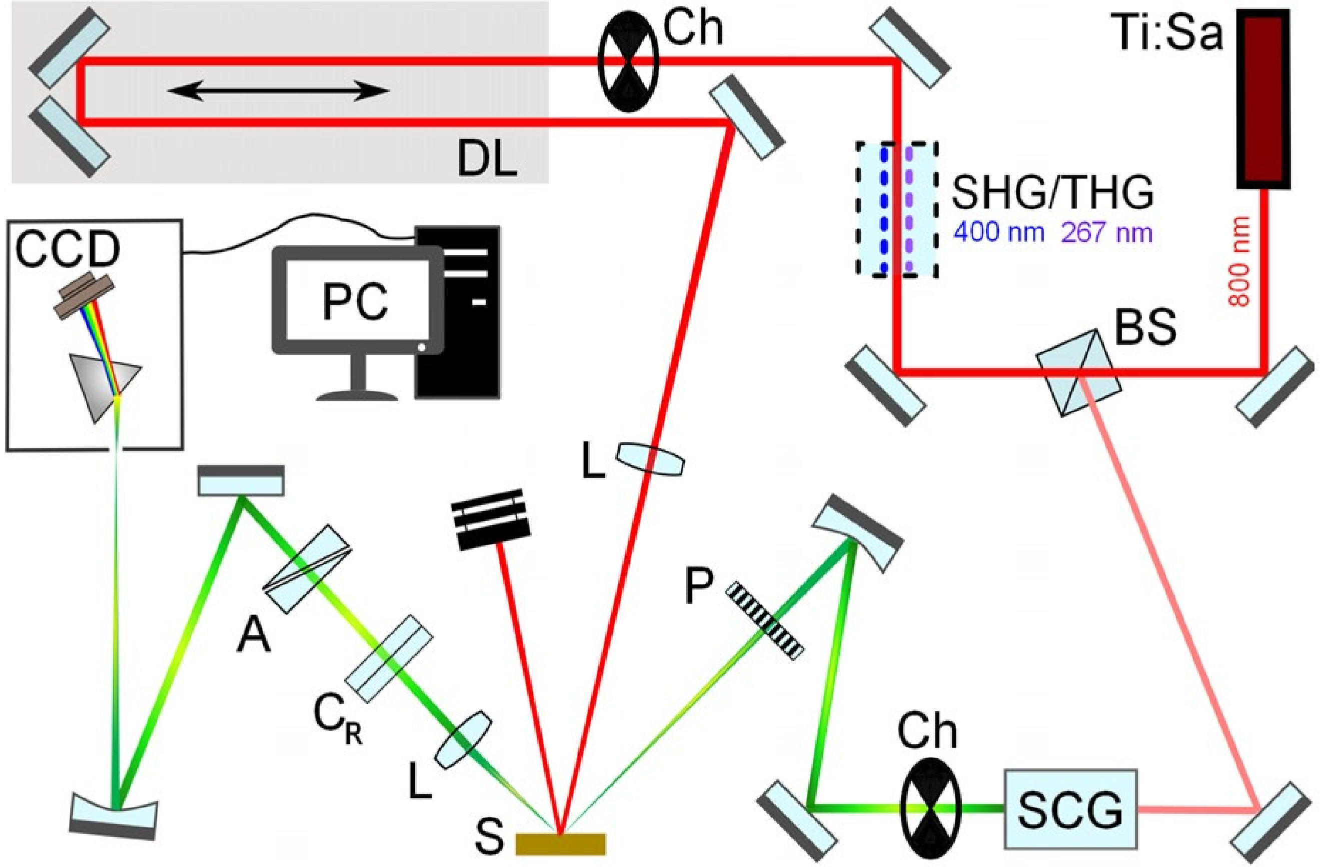
$$B = 1/3\left[-\frac{E_P}{E_0} + \frac{E_Q}{E_0'}\right]$$

$$C^2 = \frac{4E_P E_Q}{3E_0 E_0'} + \Delta$$

G. Dresselhaus, A. Kip, C. Kittel, Phys. Rev. **98**, 368 (1955)
J. Menéndez, D. J. Lockwood, J. C. Zwinkels, M. Noël, Phys. Rev. B **98**, 165207 (2018)
P. Yu and M. Cardona, *Fundamentals of Semiconductors*, (Springer, Heidelberg, 2010)

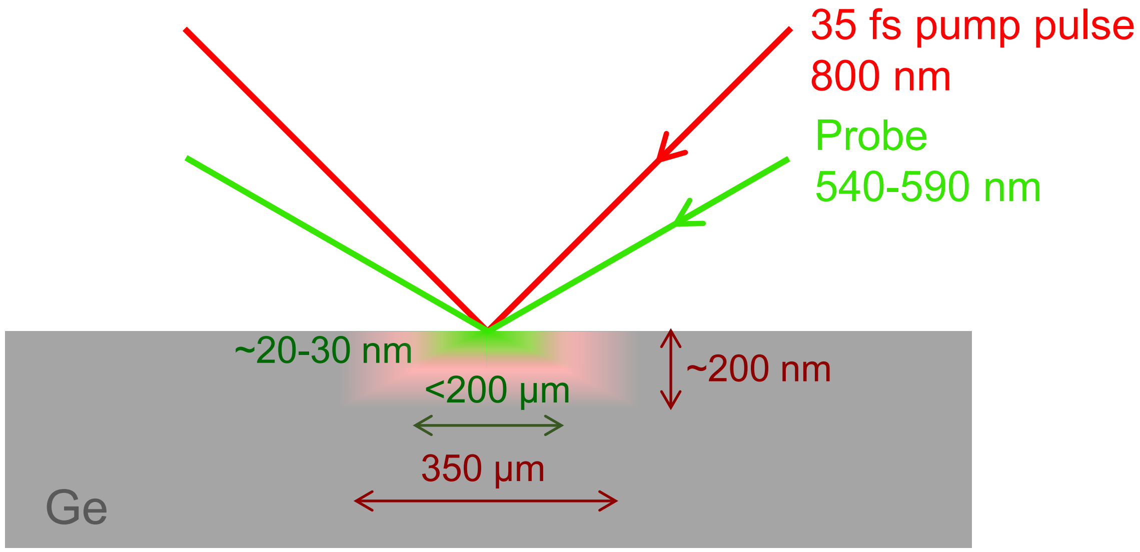
Pump-probe spectroscopic ellipsometry setup

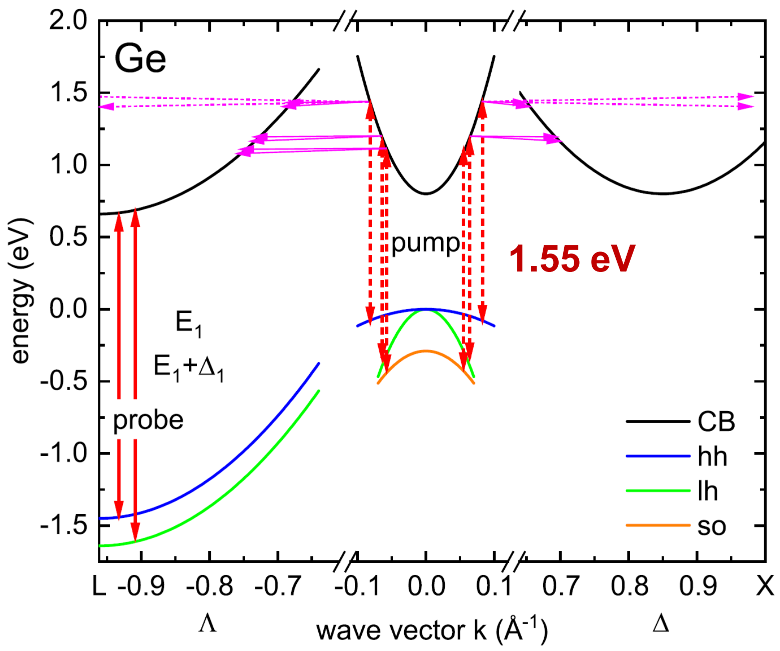
- Pump pulse: 266, 400, and 800 nm
- 35 fs laser pulses
- Repetition rate: 1 kHz
- Pulse energy: up to 6 mJ
- Carrier density: $10^{20}\ \mathrm{cm}^{-3}$
- Time resolution: 120 fs (oblique incidence)
- Spectral range: 1.7 – 3.5 eV
- Probe beam diameter <200 μm
- Pump beam diameter ~350 μm



S. Espinoza, S. Richter, M. Rebarz, O. Herrfurth, R. Schmidt-Grund, J. Andreasson, and S. Zollner, Appl. Phys. Lett. **115**, 052105 (2019)
S. Richter, M. Rebarz, O. Herrfurth, S. Espinoza, R. Schmidt-Grund, and J. Andreasson, Rev. Sci. Instrum. **92**, 033104 (2021)

Penetration depth of probe and pump beams

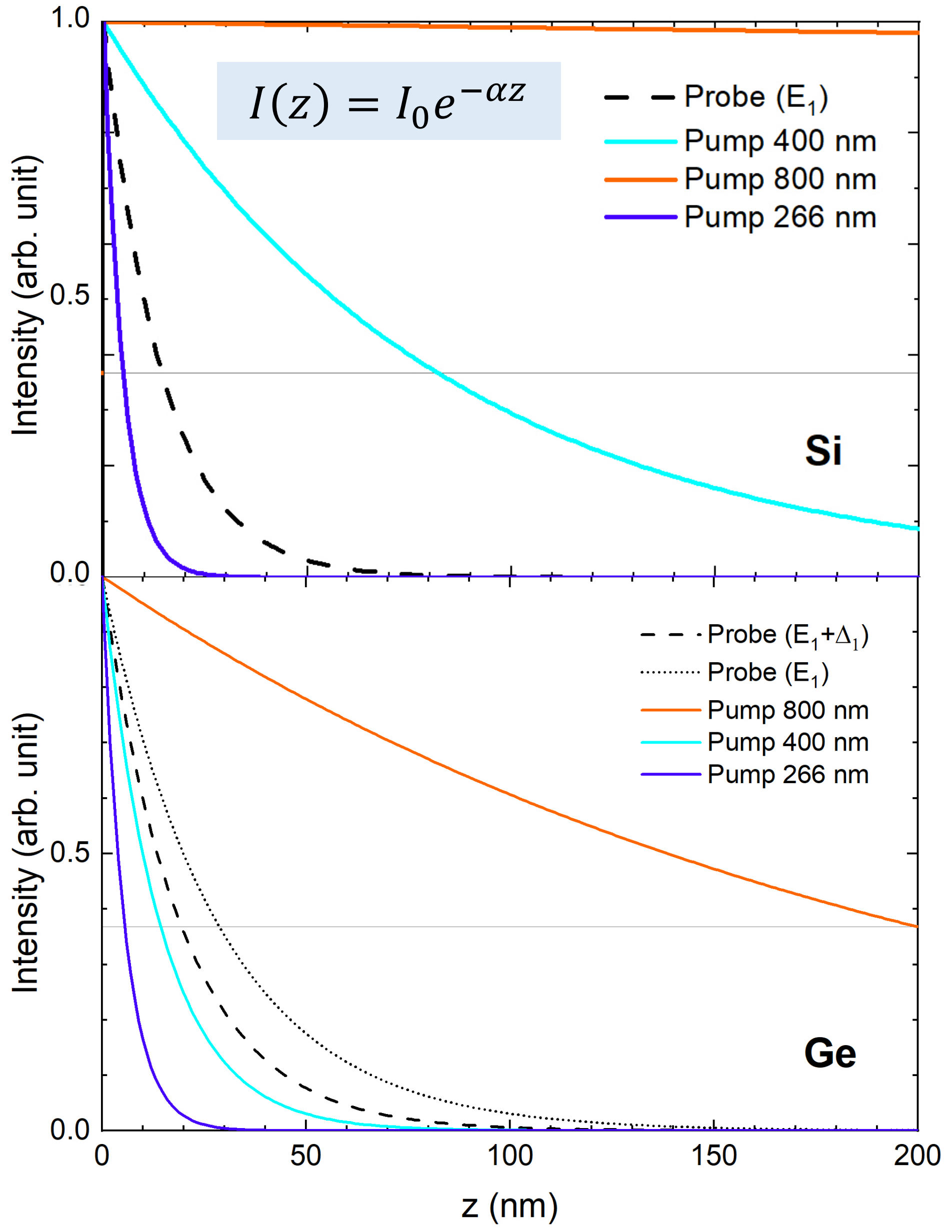




Carrier density:

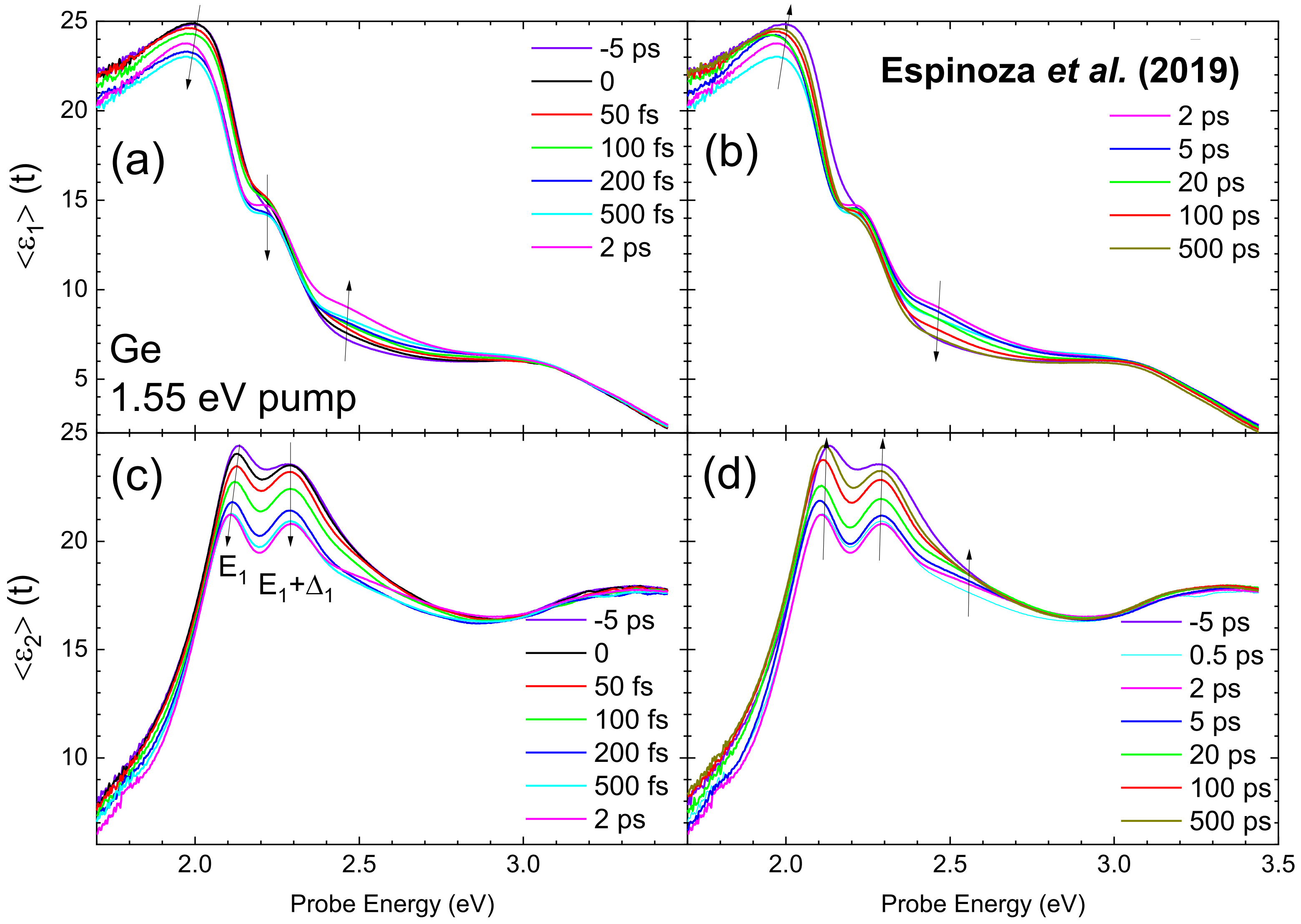
$10^{20}\ \mathrm{cm}^{-3}$

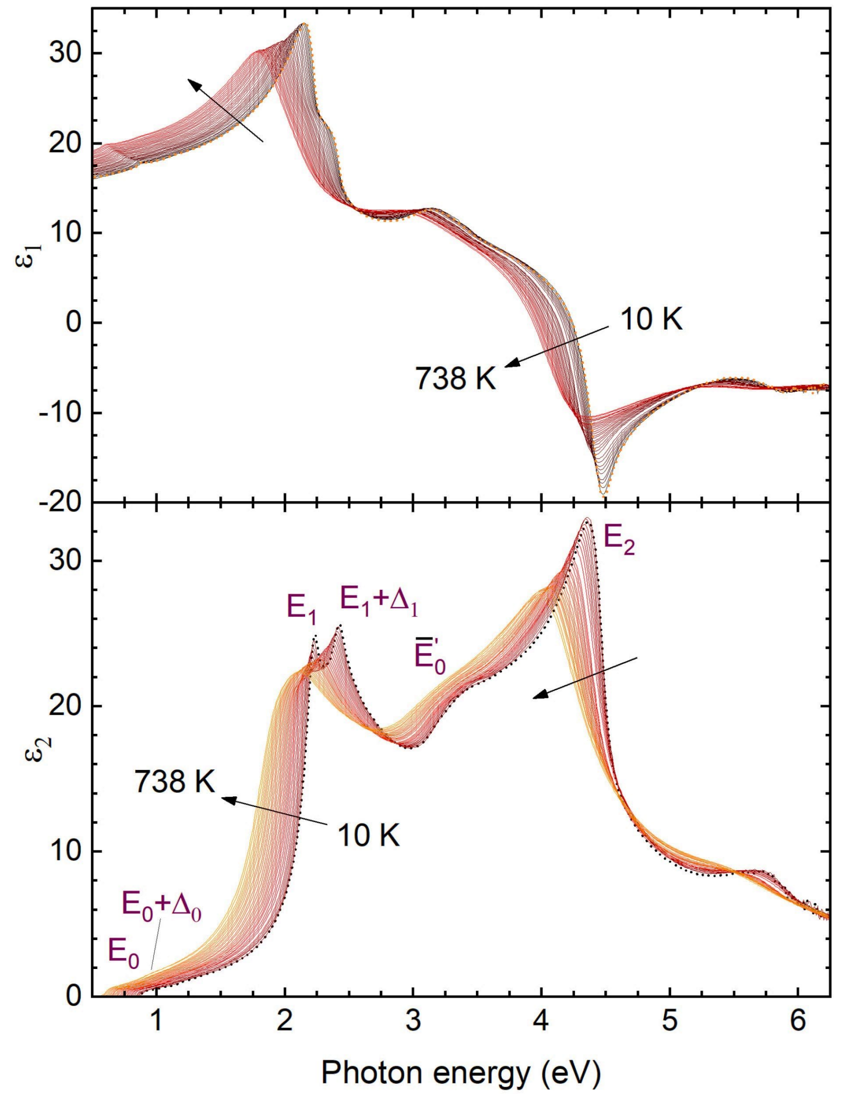
Electrons scatter from Γ to X and L



Transient pseudodielectric function from pump-probe spectroscopic ellipsometry

Temperature dependent dielectric function from spectroscopic ellipsometry





S. Espinoza, S. Richter, M. Rebarz, O. Herrfurth, R. Schmidt-Grund, J. Andreasson, S. Zollner, Appl. Phys. Lett. **115**, 052105 (2019).
C. Emminger, F. Abadizaman, N.S. Samarasingha, T.E. Tiwald, S. Zollner, J. Vac. Sci. Technol. B **38**, 012202 (2020).

Critical point analysis: Second derivatives from linear filters

Ge: E_1 and E_1+Δ_1
- EG filter width: 12-15 meV
- Fit: 2D-lineshape

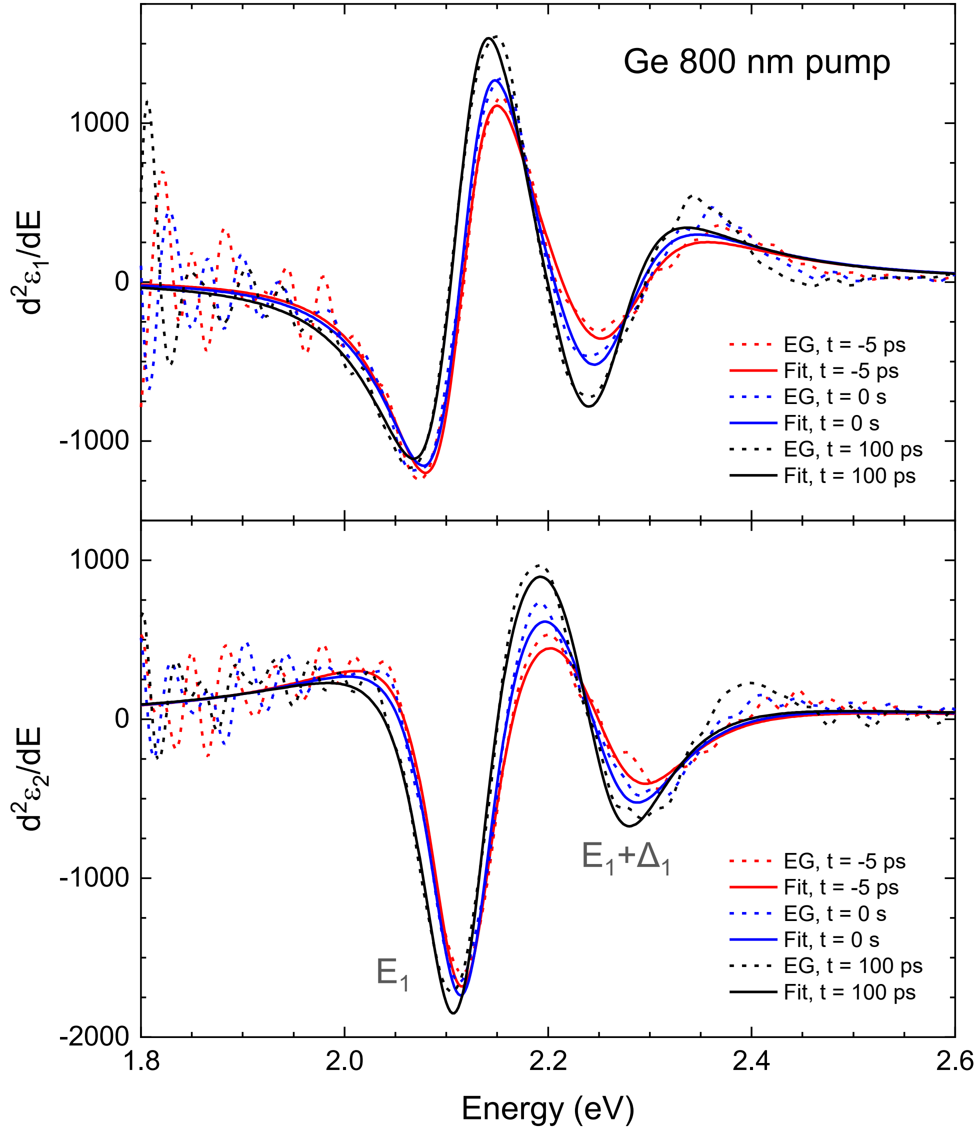
$$\epsilon_{2D}(E) = B - Ae^{i\varphi}\ln\left(E - E_g + i\Gamma\right)$$

Si: E_1
- EG filter width: 20 meV
- Fit: 0D-lineshape

$$\epsilon_{0D}(E) = B - \frac{Ae^{i\varphi}}{E - E_g + i\Gamma}$$

GaSb: E_1 and E_1+Δ_1
- EG filter width: 10-15 meV
- Fit: 2D-lineshape

=> Better: Lineshape considering bandfilling effects

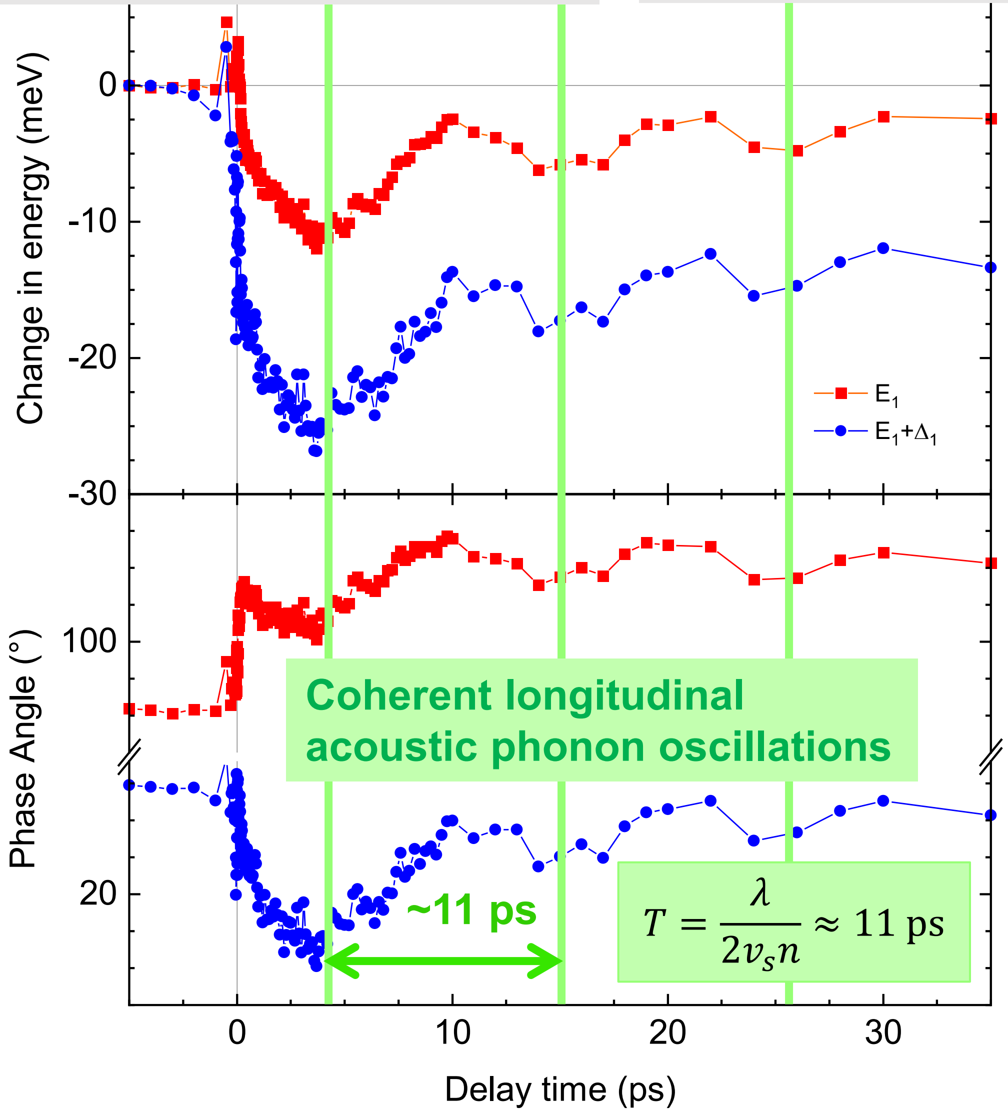


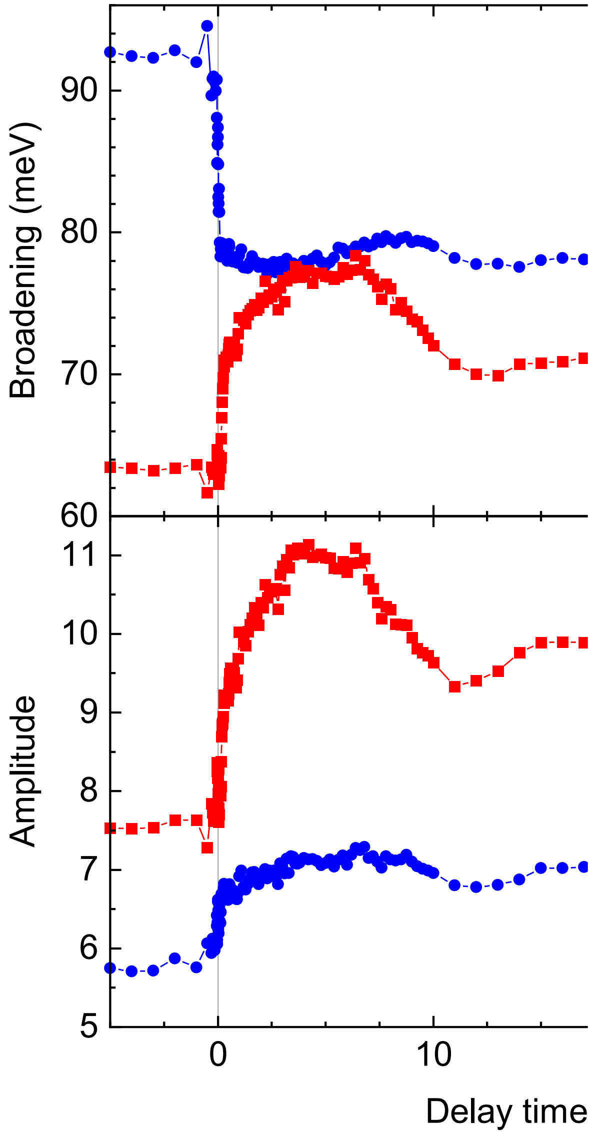
D. E. Aspnes, *Handbook on Semiconductors*, (North-Holland, Amsterdam, 1980)

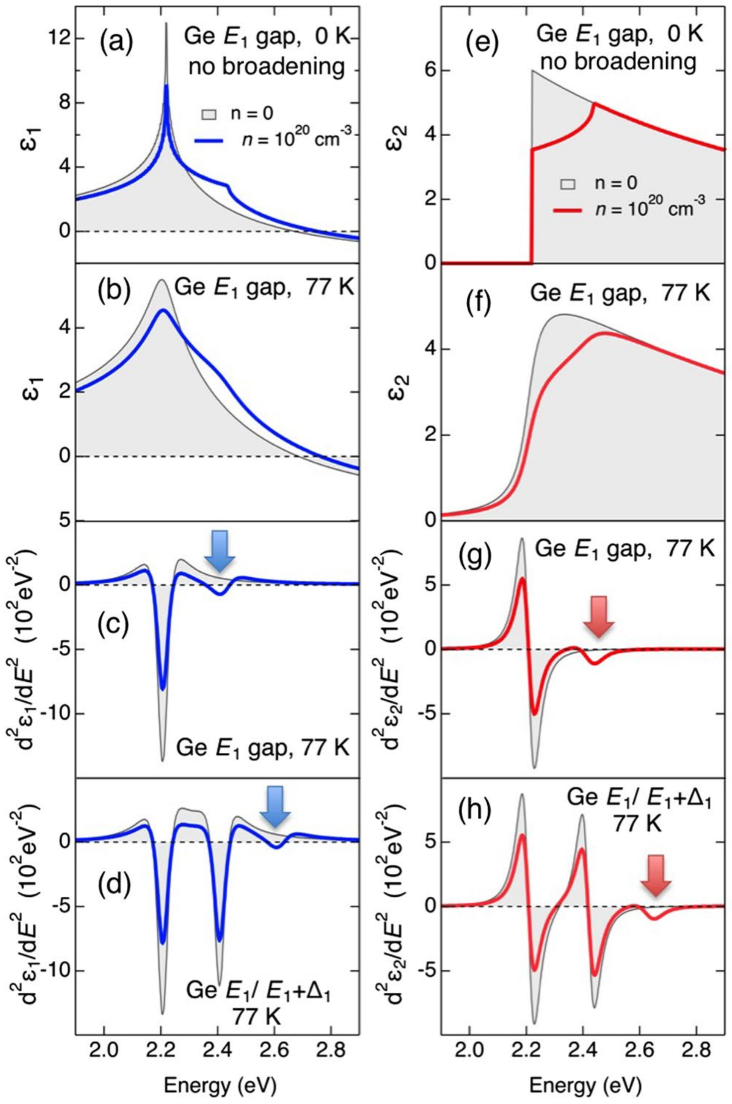
Critical point parameters as functions of delay time – Ge 800 nm pump

$\Delta E_1 \approx -10$ meV => $\Delta T \approx 20$ K
$\Delta(E_1+\Delta_1) \approx -25$ meV => $\Delta T \approx 40$ K

$$\Delta T \approx \frac{E(1-R)}{cV\rho} \approx 25\ \text{K}$$







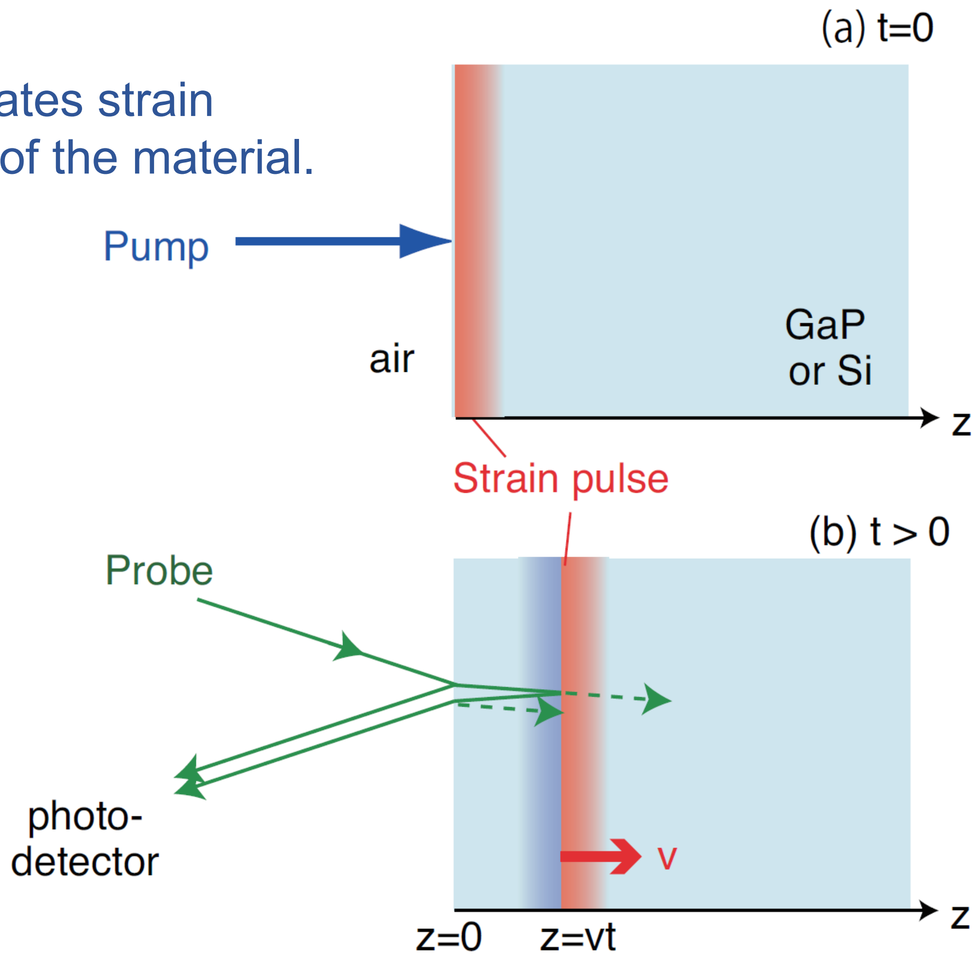
C. Xu, N. S. Fernando, S. Zollner, J. Kouvetakis, and J. Menéndez, Phys. Rev. B **118**, 267402 (2017).

C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc, Phys. Rev. B 34, 4129 (1986)

Creation and propagation of a strain pulse

The pump pulse creates strain close to the surface of the material.

The probe pulse gets reflected by the strain pulse, which moves through the crystal.

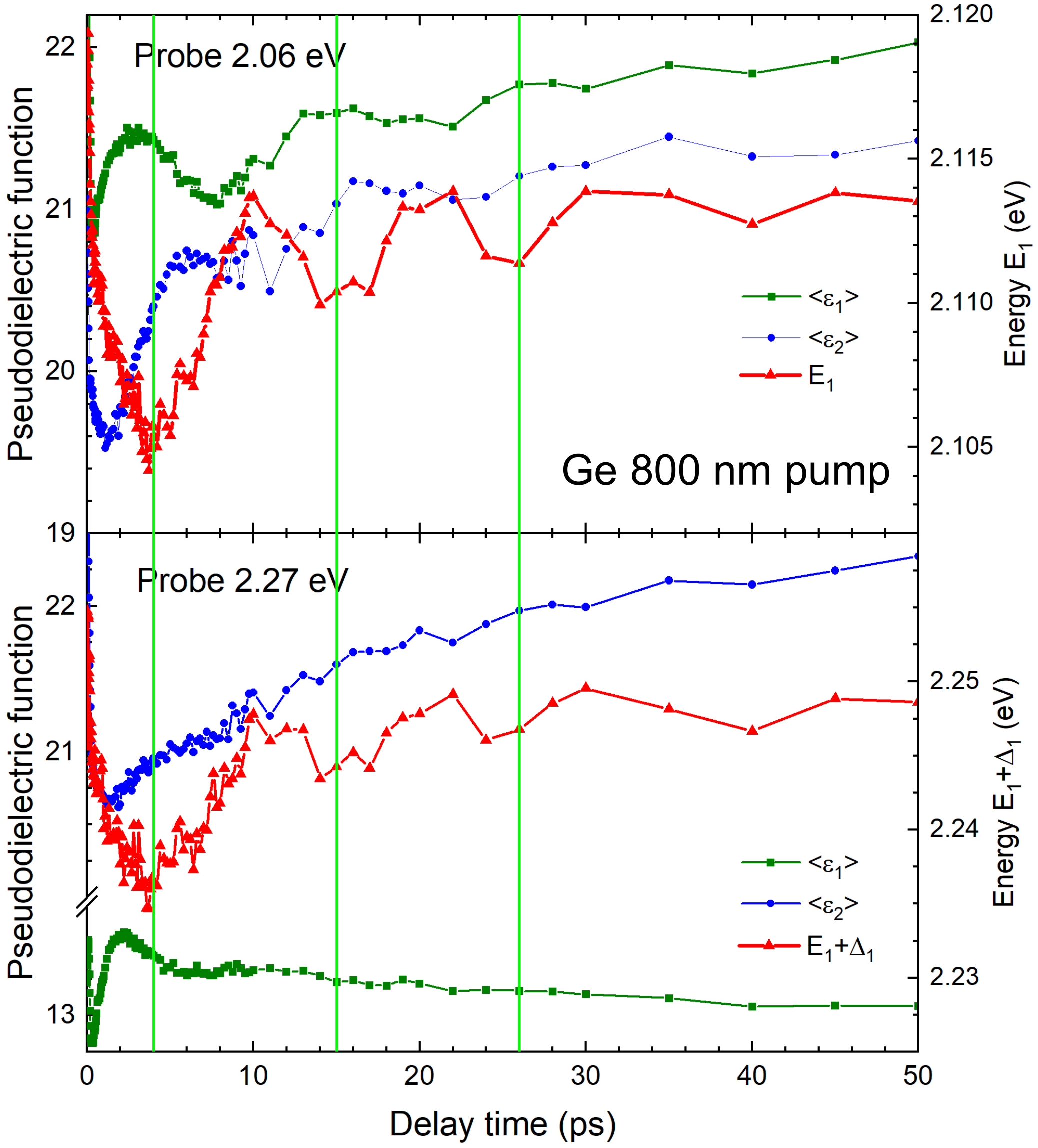


Period: $$T = \frac{\lambda}{2 v_s n}$$

λ …. probe wavelength
v_s … longitudinal sound velocity
n …. refractive index

K. Ishioka, V. Rustagi, U. Höfer, H. Petek, and C. J. Stanton, Phys. Rev. B **95**, 035205 (2017).

Coherent longitudinal acoustic phonon oscillations



→ Oscillations in the CP parameters more pronounced than in the dielectric function

Expected period in various materials:

Ge

E_1
$\lambda = 585$ nm
$n = 5.65$
$v_s = 4.87 \times 10^5$ cm/s
$T = \frac{\lambda}{2 v_s n} \approx 11$ ps

$E_1+\Delta_1$
$\lambda = 550$ nm
$n = 5.16$
$v_s = 4.87 \times 10^5$ cm/s
$T = \frac{\lambda}{2 v_s n} \approx 11$ ps

Si

$\lambda = 365$ nm
$n = 6.52$
$v_s = 8.43 \times 10^5$ cm/s
$T = \frac{\lambda}{2 v_s n} \approx 3.3$ ps

InP

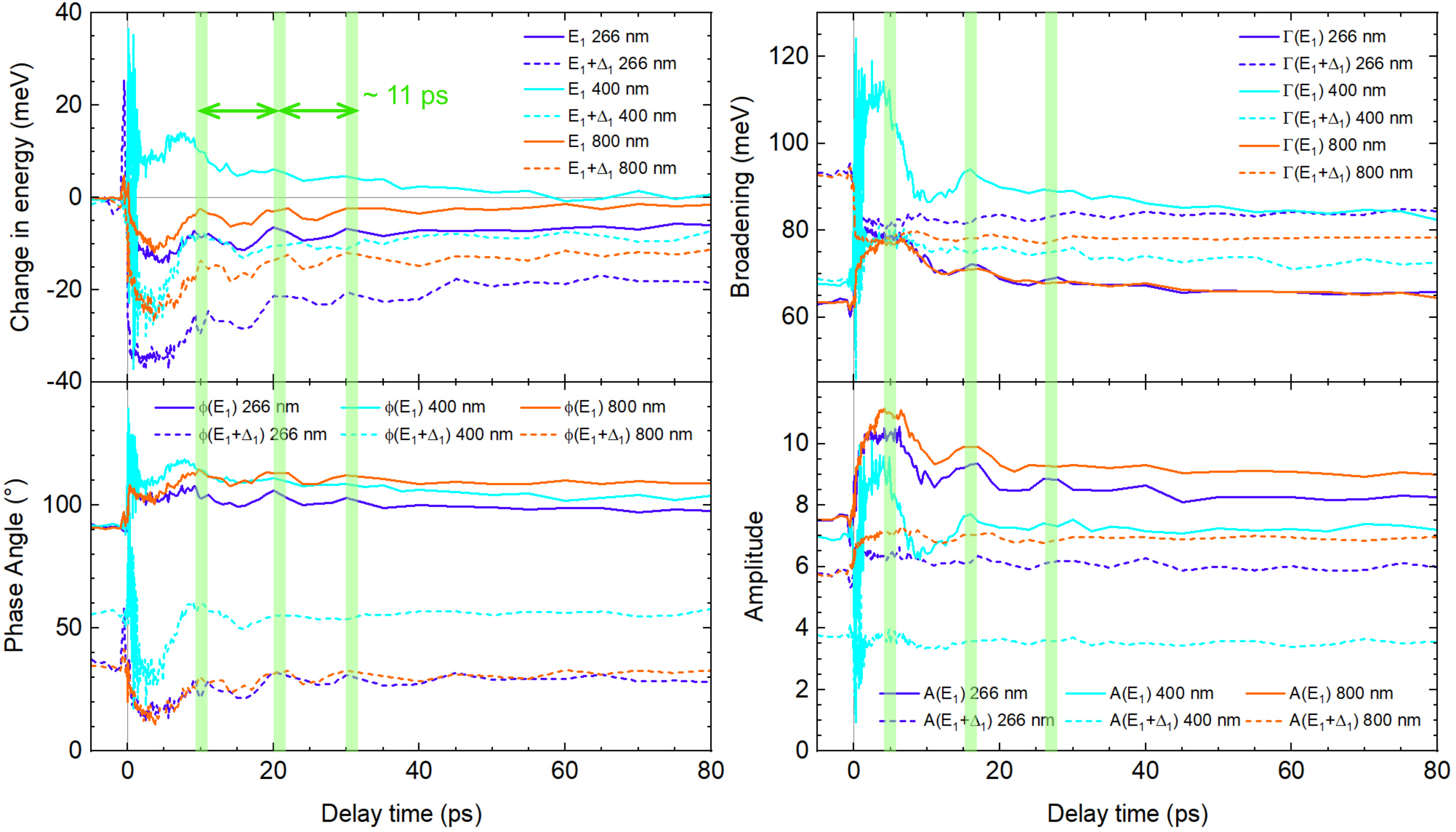
$\lambda = 390$ nm
$n = 3.98$
$v_s = 4.58 \times 10^5$ cm/s
$T = \frac{\lambda}{2 v_s n} \approx 11$ ps

GaSb

E_1
$\lambda = 620$ nm
$n = 5.24$
$v_s = 4 \times 10^5$ cm/s
$T = \frac{\lambda}{2 v_s n} \approx 15$ ps

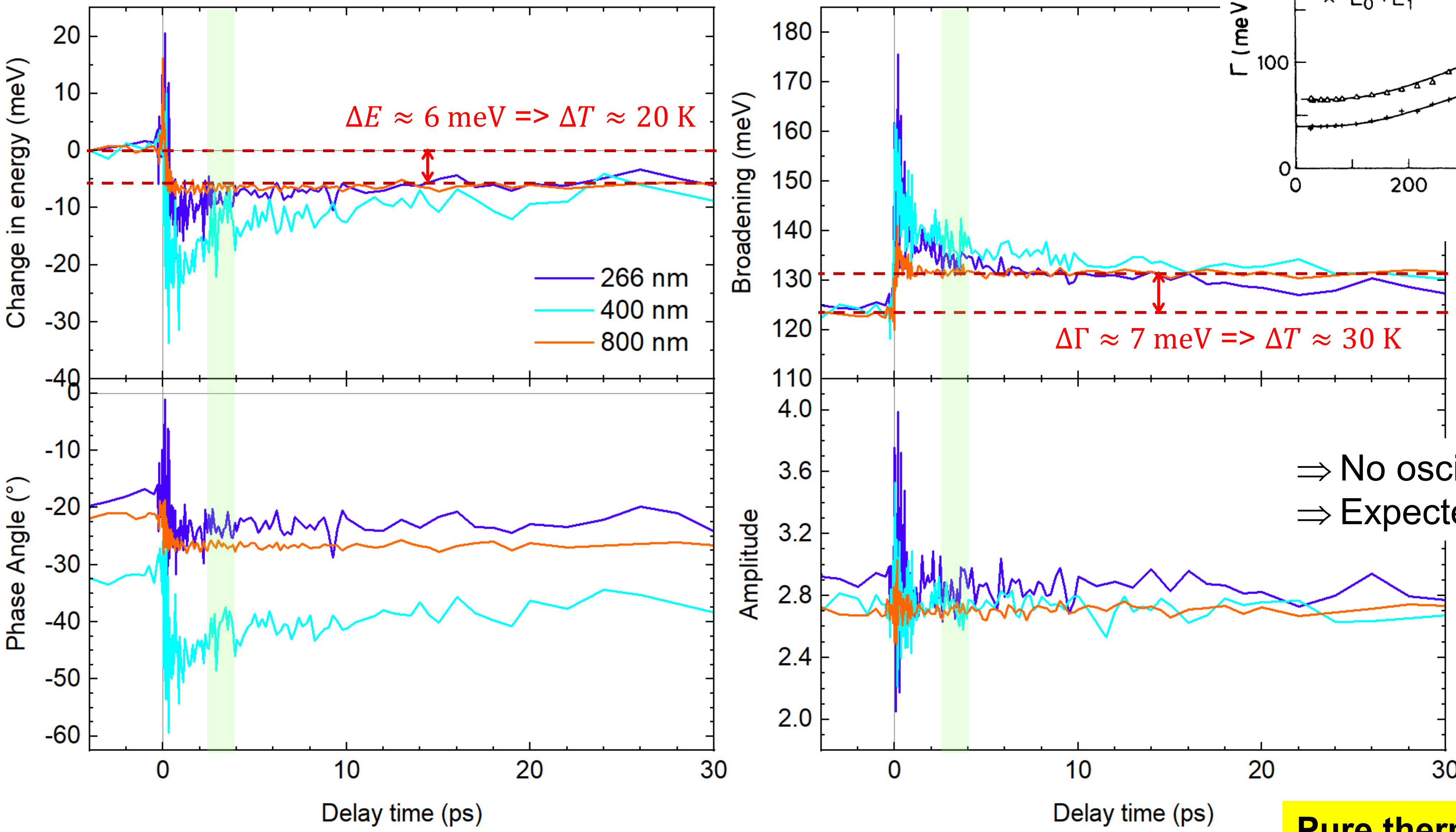
$E_1+\Delta_1$
$\lambda = 510$ nm
$n = 4.45$
$v_s = 4 \times 10^5$ cm/s
$T = \frac{\lambda}{2 v_s n} \approx 14$ ps

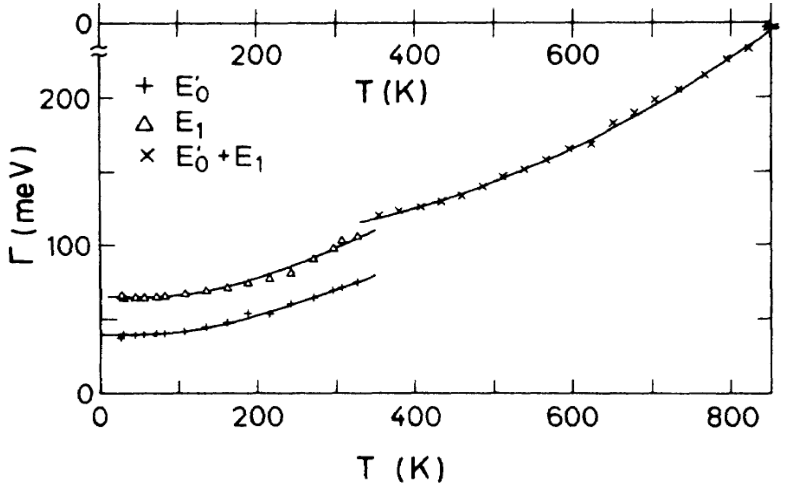
Critical point parameters of Ge (266, 400, and 800 nm pump)



=> Oscillations present in all Ge data sets (266, 400, and 800 nm pump)

Critical point parameters of Si (266, 400, and 800 nm pun





⇒ No oscillations detected

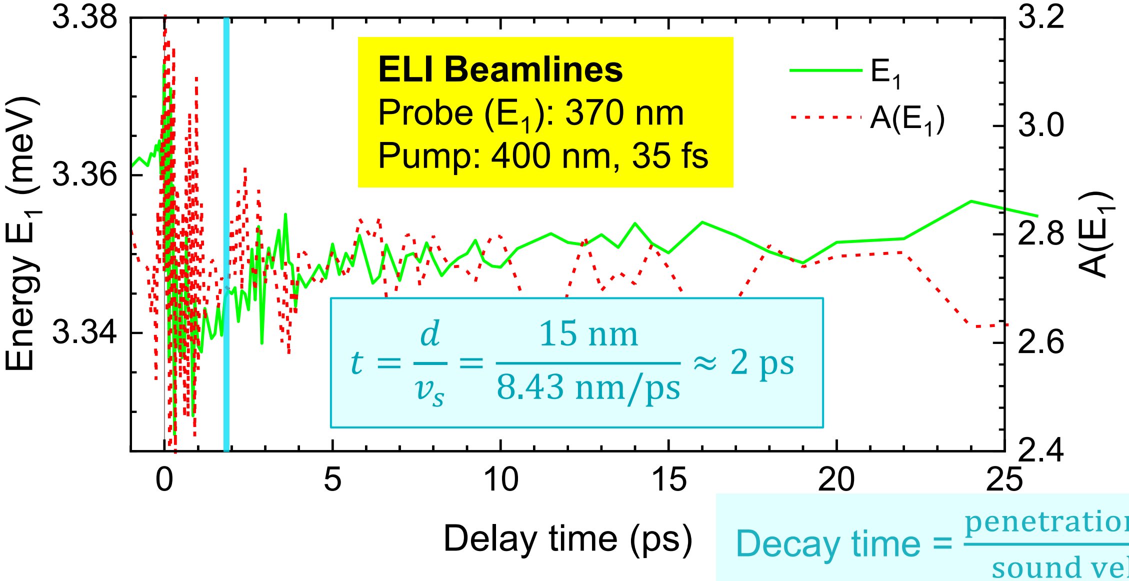
⇒ Expected period:

$$T = \frac{\lambda}{2 v_s n} \approx 3 \text{ ps}$$

Pure thermal effect

P. Lautenschlager, M. Garriga, L. Viña, and M. Cardona, Phys. Rev. B **36**, 4821 (1987).
K. Ishioka, V. Rustagi, U. Höfer, H. Petek, and C. J. Stanton, Phys. Rev. B **95**, 035205 (2017).

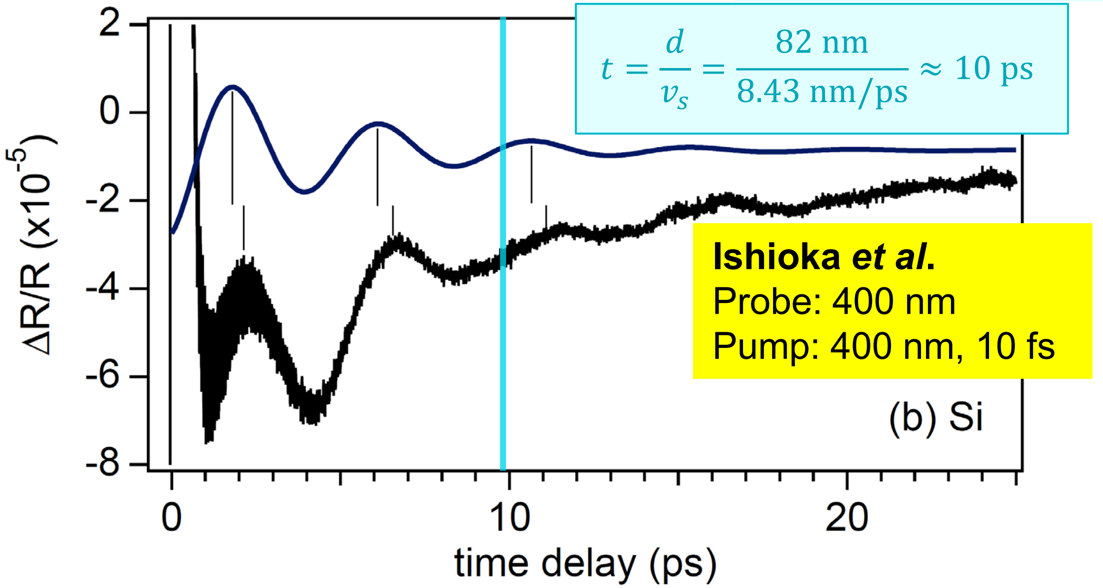
Coherent longitudinal acoustic phonon oscillations in Si

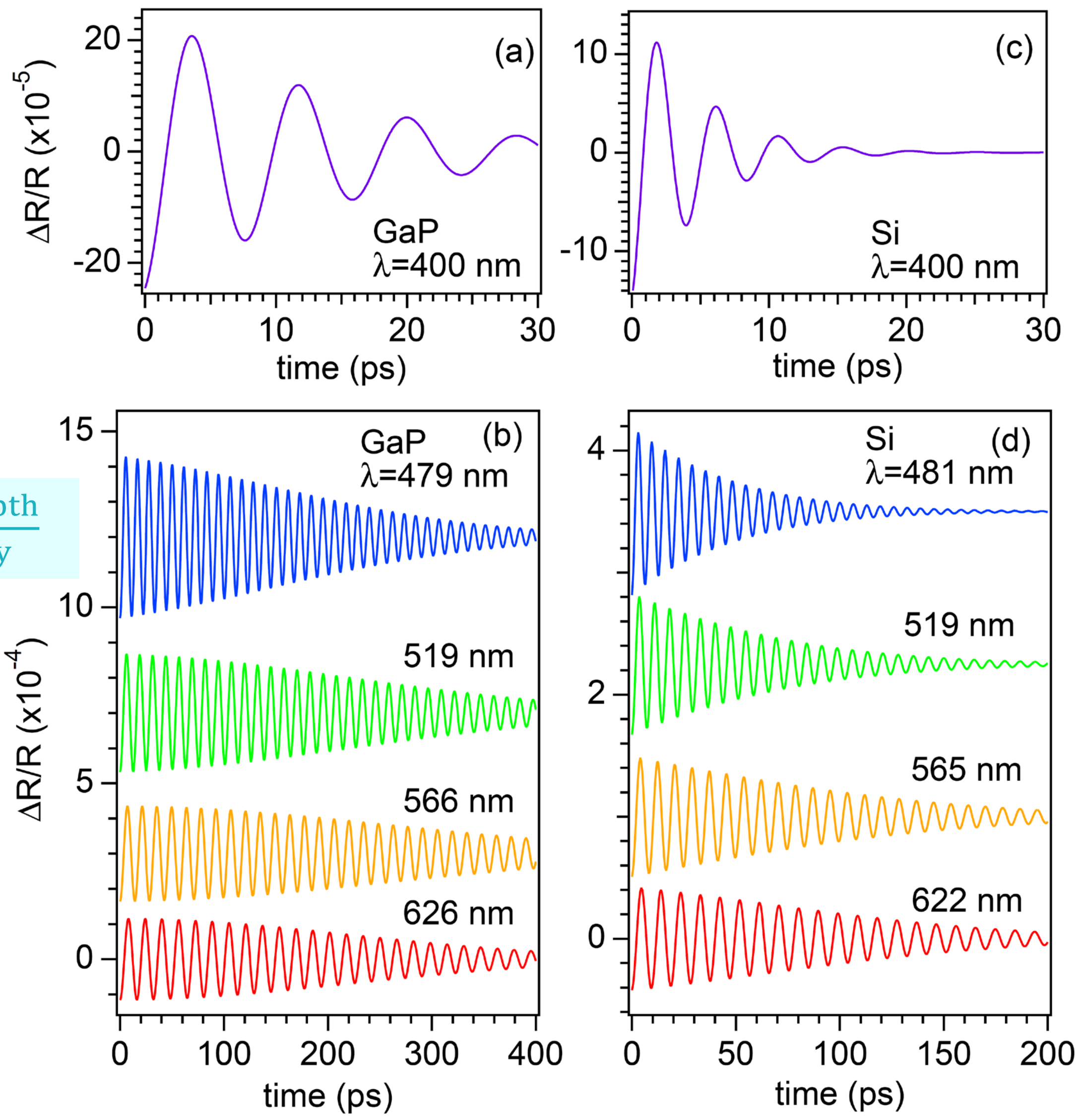


$$t = \frac{d}{v_s} = \frac{15\ \mathrm{nm}}{8.43\ \mathrm{nm/ps}} \approx 2\ \mathrm{ps}$$

$$\text{Decay time} = \frac{\text{penetration depth}}{\text{sound velocity}}$$

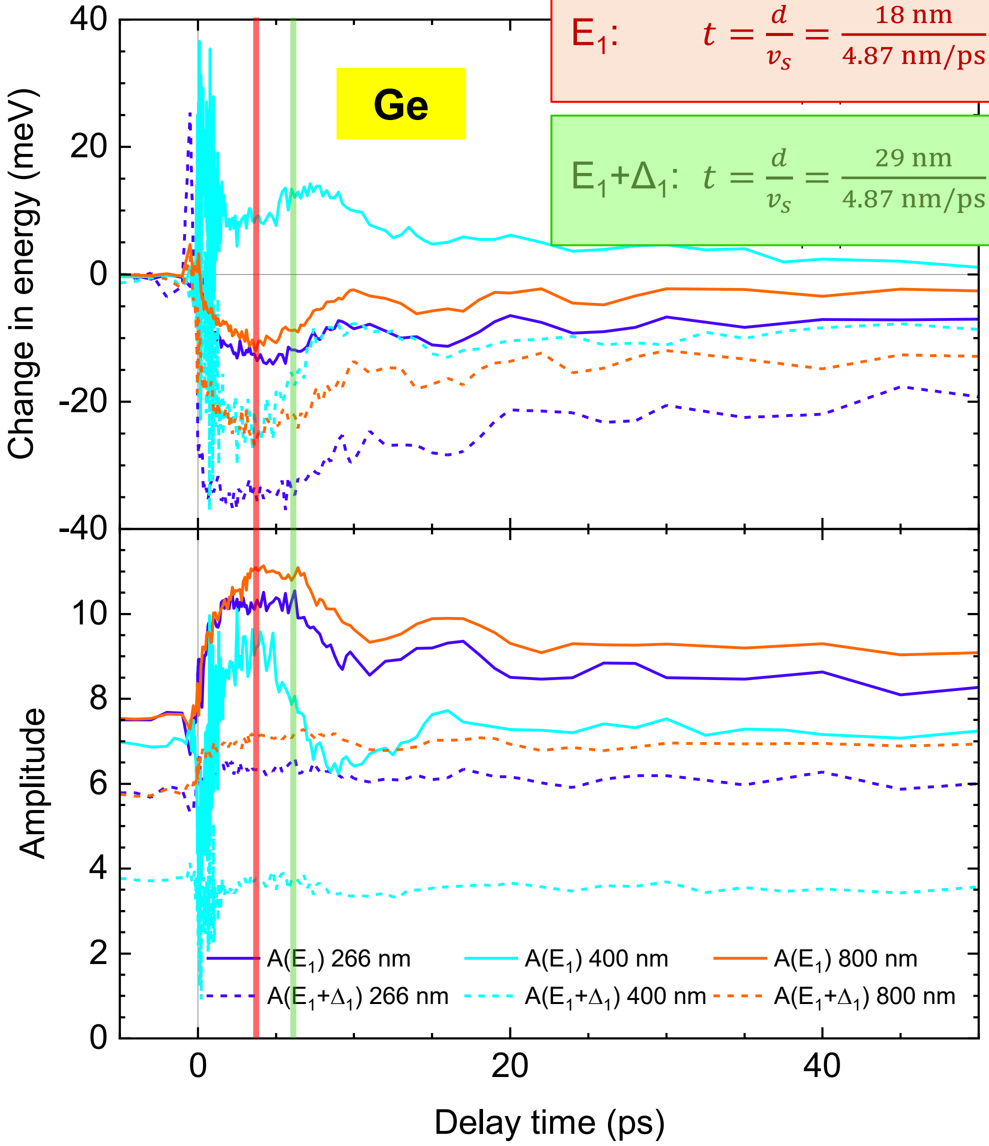
$$t = \frac{d}{v_s} = \frac{82\ \mathrm{nm}}{8.43\ \mathrm{nm/ps}} \approx 10\ \mathrm{ps}$$





K. Ishioka, V. Rustagi, U. Höfer, H. Petek, and C. J. Stanton, Phys. Rev. B **95**, 035205 (2017).

Propagation of strain pulses in Ge

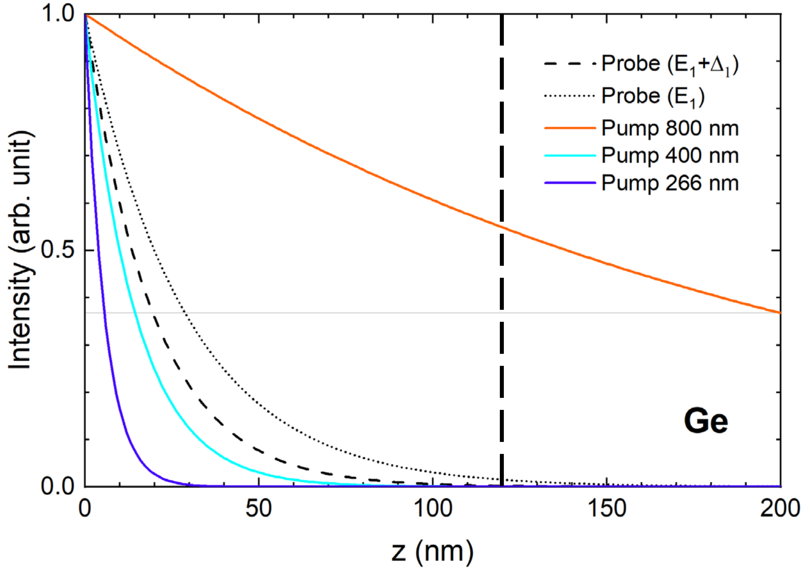


E_1: $t = \frac{d}{v_s} = \frac{18\ \text{nm}}{4.87\ \text{nm/ps}} \approx 4\ \text{ps}$

$E_1+\Delta_1$: $t = \frac{d}{v_s} = \frac{29\ \text{nm}}{4.87\ \text{nm/ps}} \approx 6\ \text{ps}$

Oscillations in the CP parameters seen up to about 25 ps:

$$d = 25\ \text{ps} \cdot 4.87 \frac{\text{nm}}{\text{ps}} \approx\ 120\ \text{nm}$$



Next step: Determine expected amplitude of coherent LA phonon oscillations

Summary

Part 1

- **Excitonic effects at the direct band gap E_0 of Ge**
  - Good agreement between model and data despite having only two fit parameters (energy and broadening).
  - Possible application to other semiconductors.

Part 2

- **Temporal evolution of E_1 and E_1+Δ_1 in Ge**
  - Oscillations in CP parameters due to coherent longitudinal acoustic phonons.
- **Temporal evolution of CP parameters in Si**
  - No phonon oscillations detected.
- **Outlook & future work**
  - Taking new data with time steps targeted to resolve phonon oscillations.
  - Tunable pump wavelength.
  - Investigating bandfilling effects.

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