Electron-phonon coupling and ultrafast dynamics of hot carriers in semiconductors.

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Collaborations

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R. Sen (post-doc)

L. Perfetti (ARPES, 2PPE)

Osaka, Japan:

K. Tanimura (ARPES, 2PPE)
J. Kanasaki (ARPES, 2PPE)

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OSAKA UNIVERSITY

Osaka
Metropolitan
University

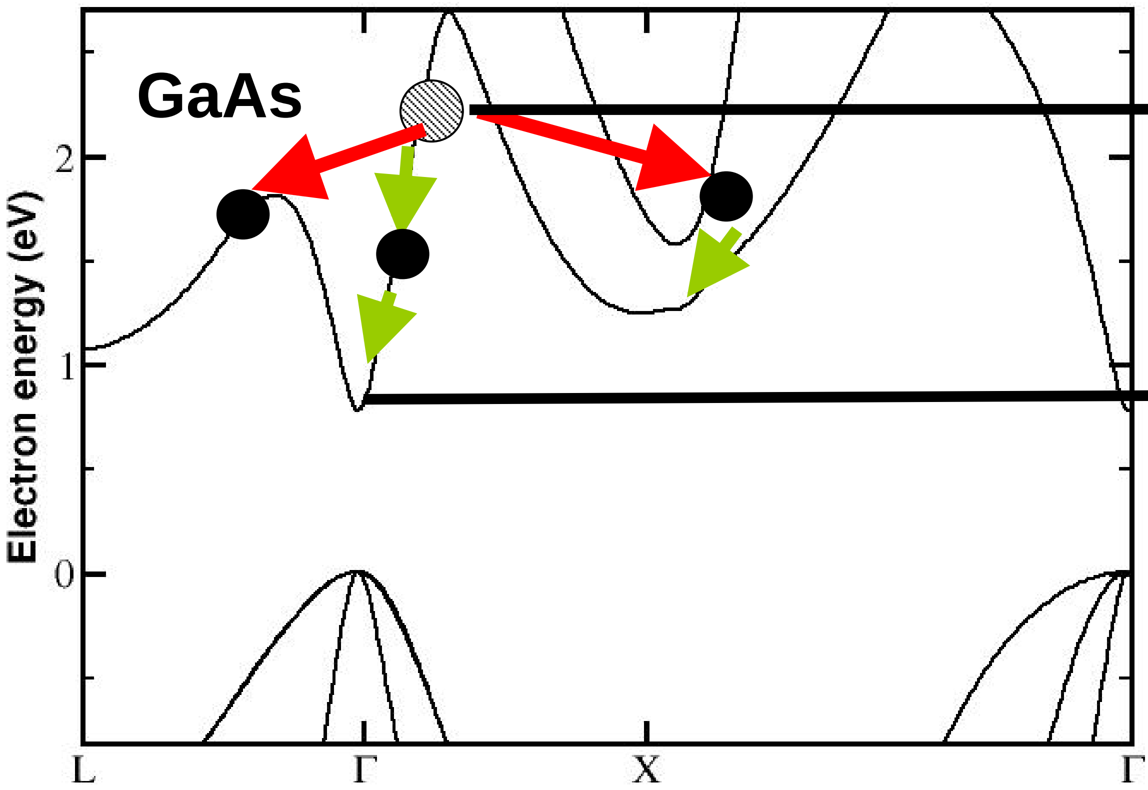
Outline

- ***Electron-phonon scattering for highly excited electrons: GaAs***

- ***Highly excited electron relaxation in Si and Ge***

- ***Photoexcited electron relaxation in InSe***

RELAXATION DYNAMICS OF HIGHLY EXCITED ELECTRONS

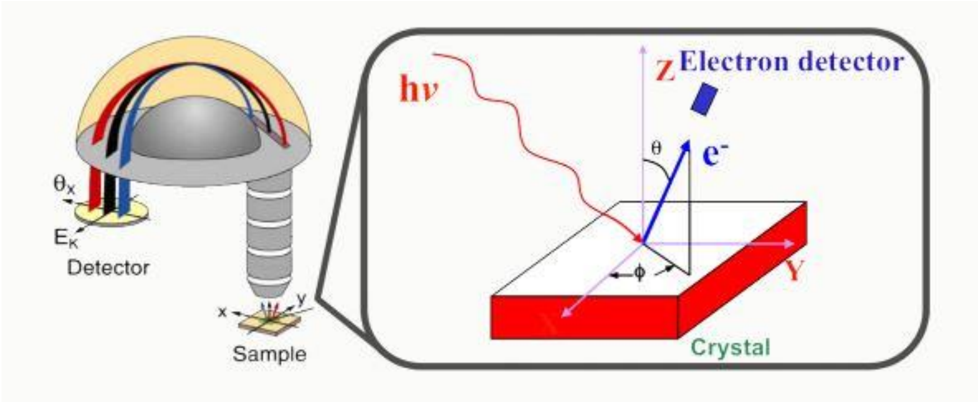


Excess energy: main parameter

highly non-thermal initial distributions

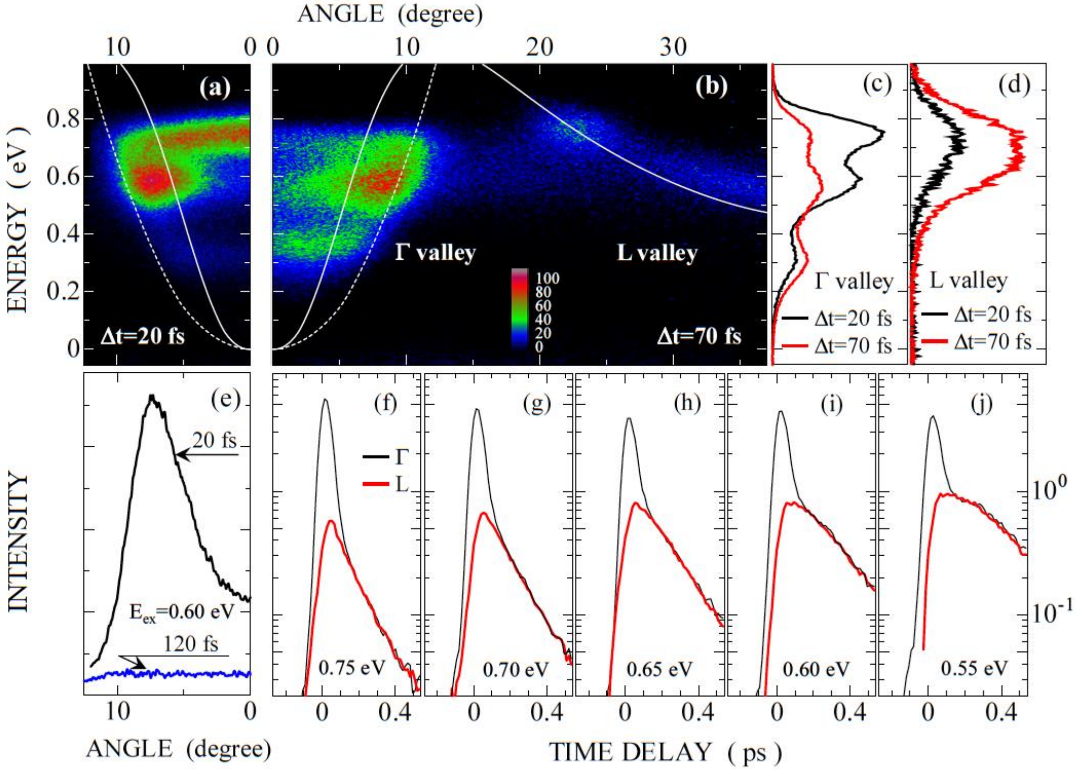
Sjakste, Tanimura, Barbarino, Perfetti, Vast, J. Phys: Cond. Mat. ***30****, 353001 (2018).*

EXPERIMENTS: ARPES



Pump and probe: 2 laser pulses at different time

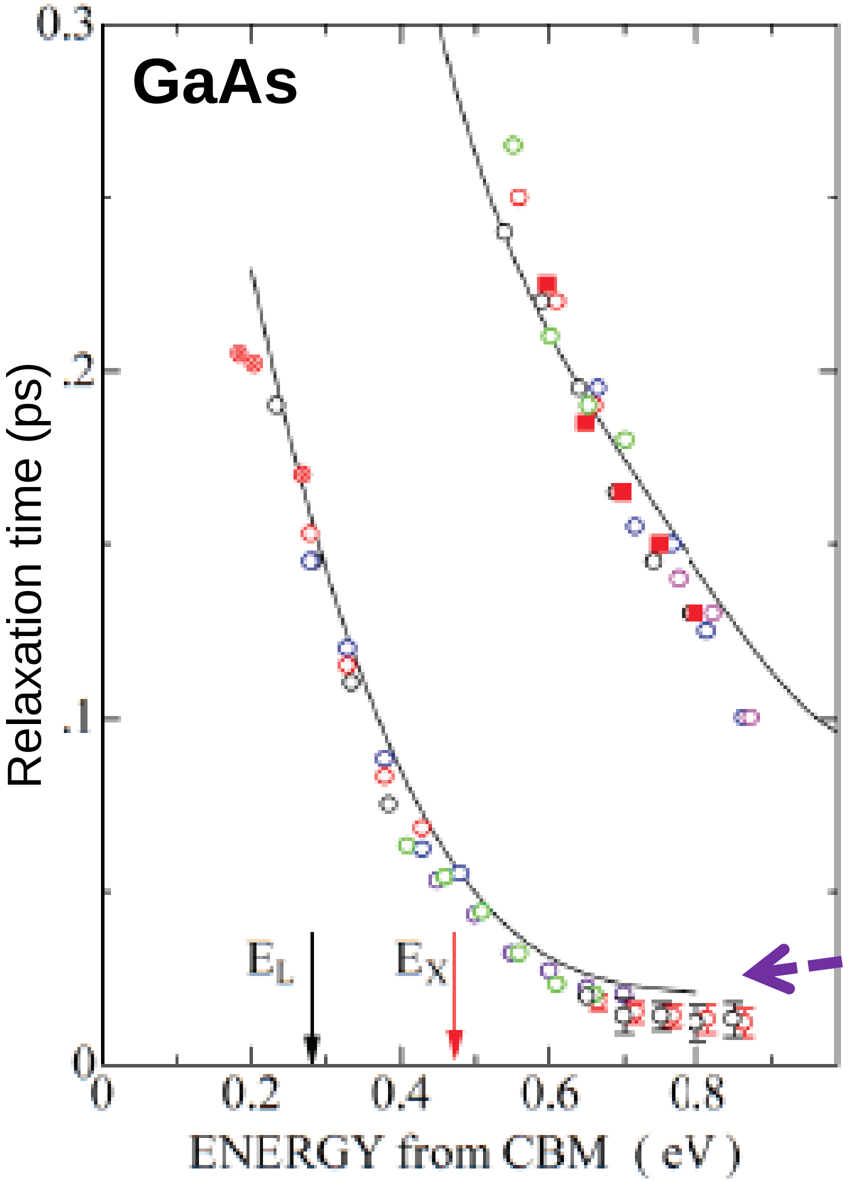
GaAs
300K

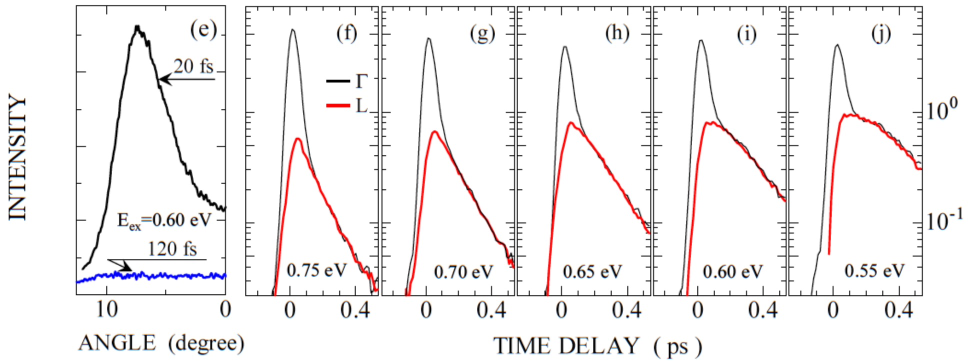


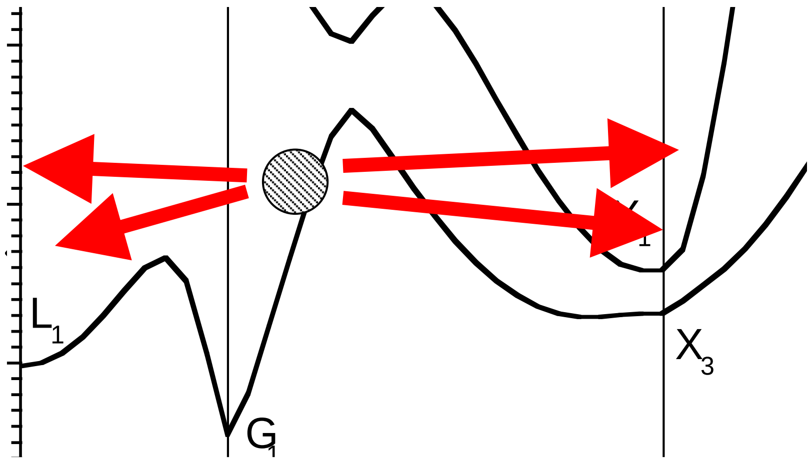
Two distinct relaxation regimes

H. Tanimura, J. Kanasaki, K. Tanimura, J. Sjakste, N. Vast, M. Calandra, F. Mauri, PRB 93 (2016) (R)

HOT ELECTRON ENSEMBLE (HEE)





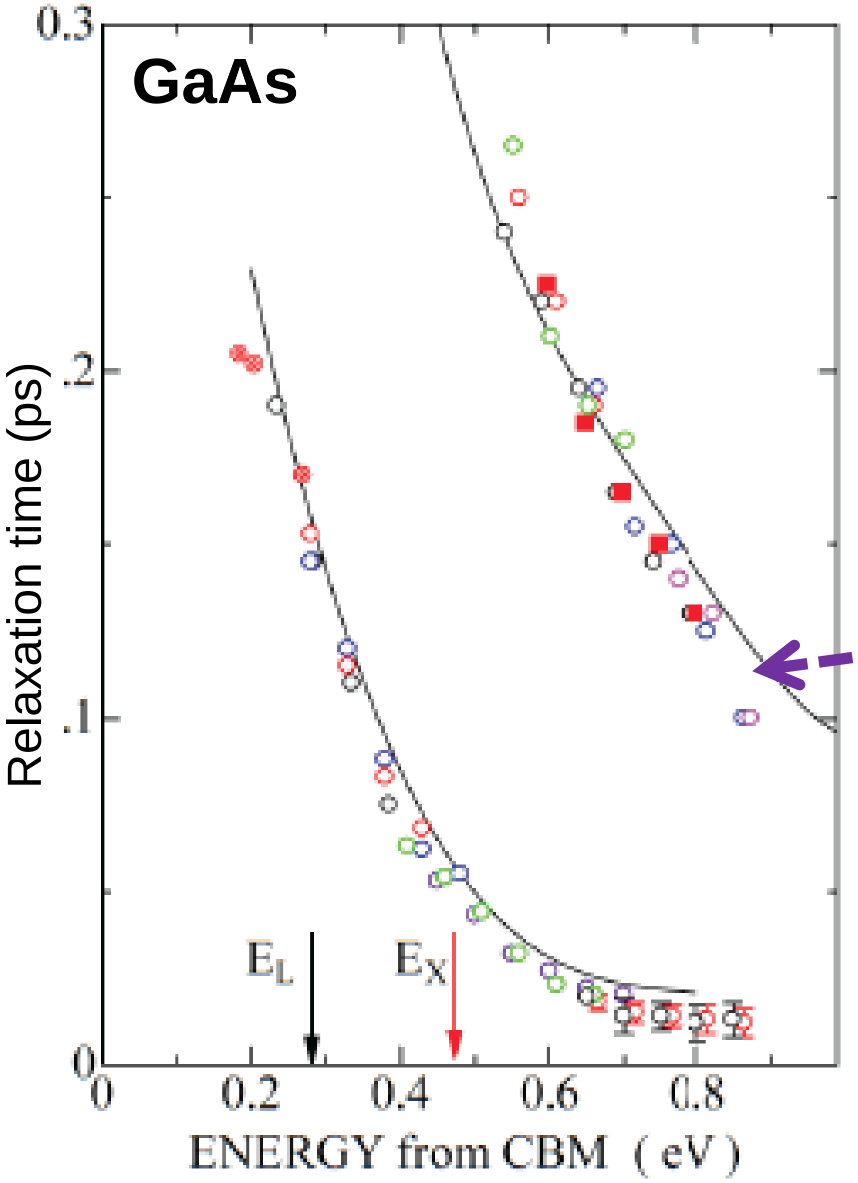


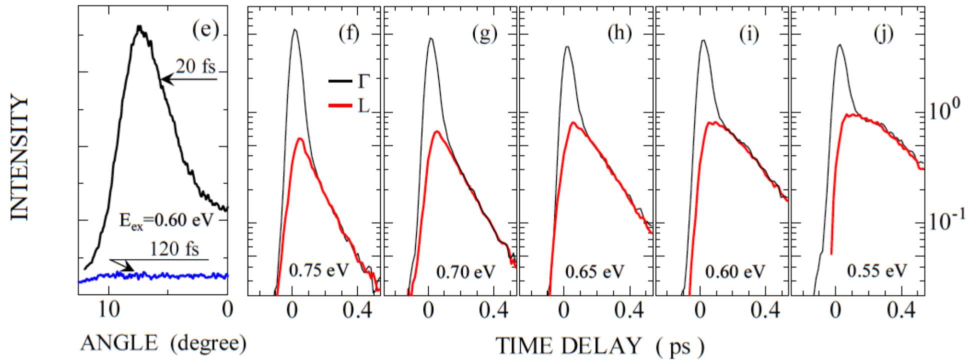
« Short » time: wavepacket spreads over BZ;
« isomerization »: total scattering rate, mostly intervalley transitions

Tanimura et al, PRB 93 (2016) 161203 (R).

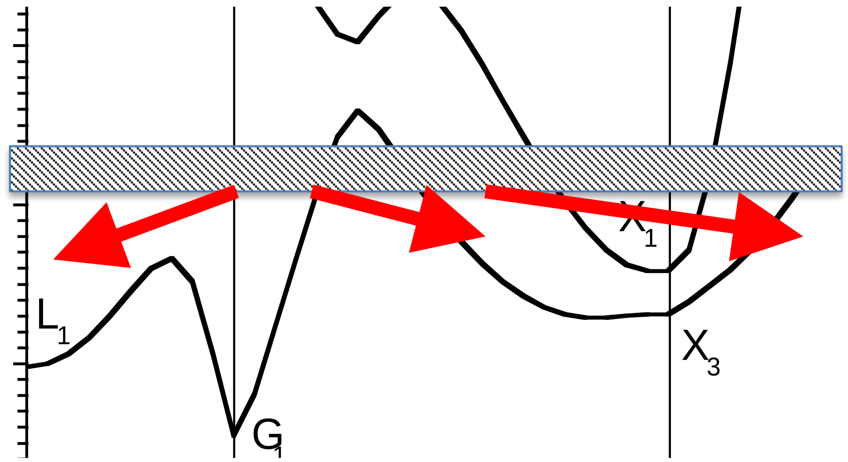
Sjakste et al, J. Phys: Cond. Mat. ***30****, 353001 (2018).*

HOT ELECTRON ENSEMBLE (HEE)





« long » time: energy transfer from electrons to phonons



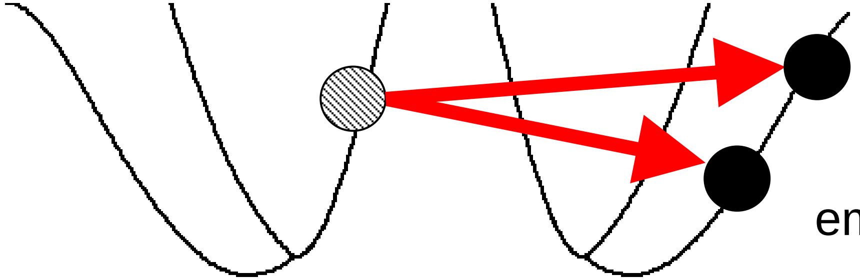
mostly intervalley transitions

Tanimura, Kanasaki, Tanimura, Sjakste, Vast, Calandra, Mauri, PRB 93 (2016) 161203 (R).

ELECTRON-PHONON COUPLING: DFPT+ Wanner

$$\langle \Psi_{n,k} | \Delta W_q^{\lambda} | \Psi_{n',k+q} \rangle$$

DFPT: Baroni et al, Rev. Mod. Phys. 2001



$$\Gamma_{n,\mathbf{k}} = \Gamma_{n\mathbf{k}}^{em} + \Gamma_{n\mathbf{k}}^{abs}$$

absorption+emission

$$\frac{d < E >}{dt} = \Gamma_{em}\omega_{em} - \Gamma_{abs}\omega_{abs}$$

emission-absorption

Wannier interpolation of the electron-phonon matrix elements:

J. Sjakste, N. Vast, M. Calandra, F. Mauri, PRB 92 (2015) 054307

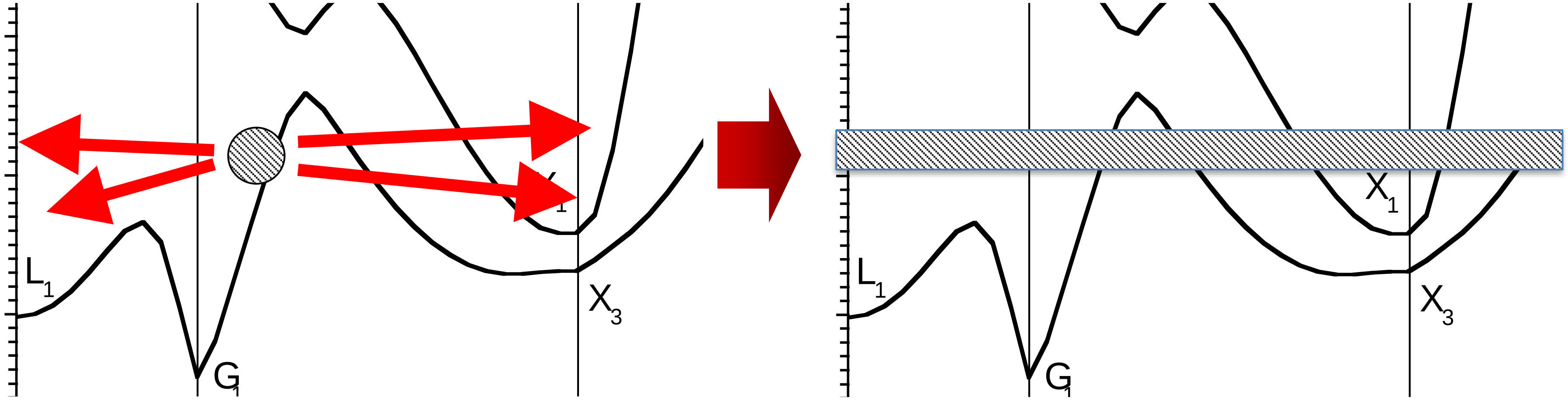
C. Verdi, F. Giustino, PRL 115 (2015) 176401

S. Poncé, E. R. Margine, C. Verdi, and F. Giustino, Comp. Phys. Commun. 209, 116 (2016).

ELECTRON-PHONON SCATTERING: HIGHLY EXCITED ELECTRONS

« Randomisation » of initial momentum

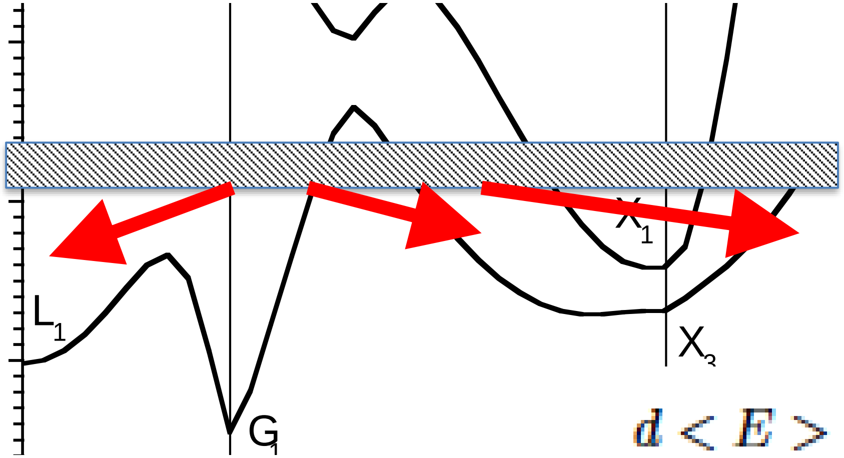
some fs - some tens of fs



$$\Gamma_{n,\mathbf{k}} = \Gamma^{em}_{n\mathbf{k}} + \Gamma^{abs}_{n\mathbf{k}}$$

Energy transfer to phonons

10 times slower

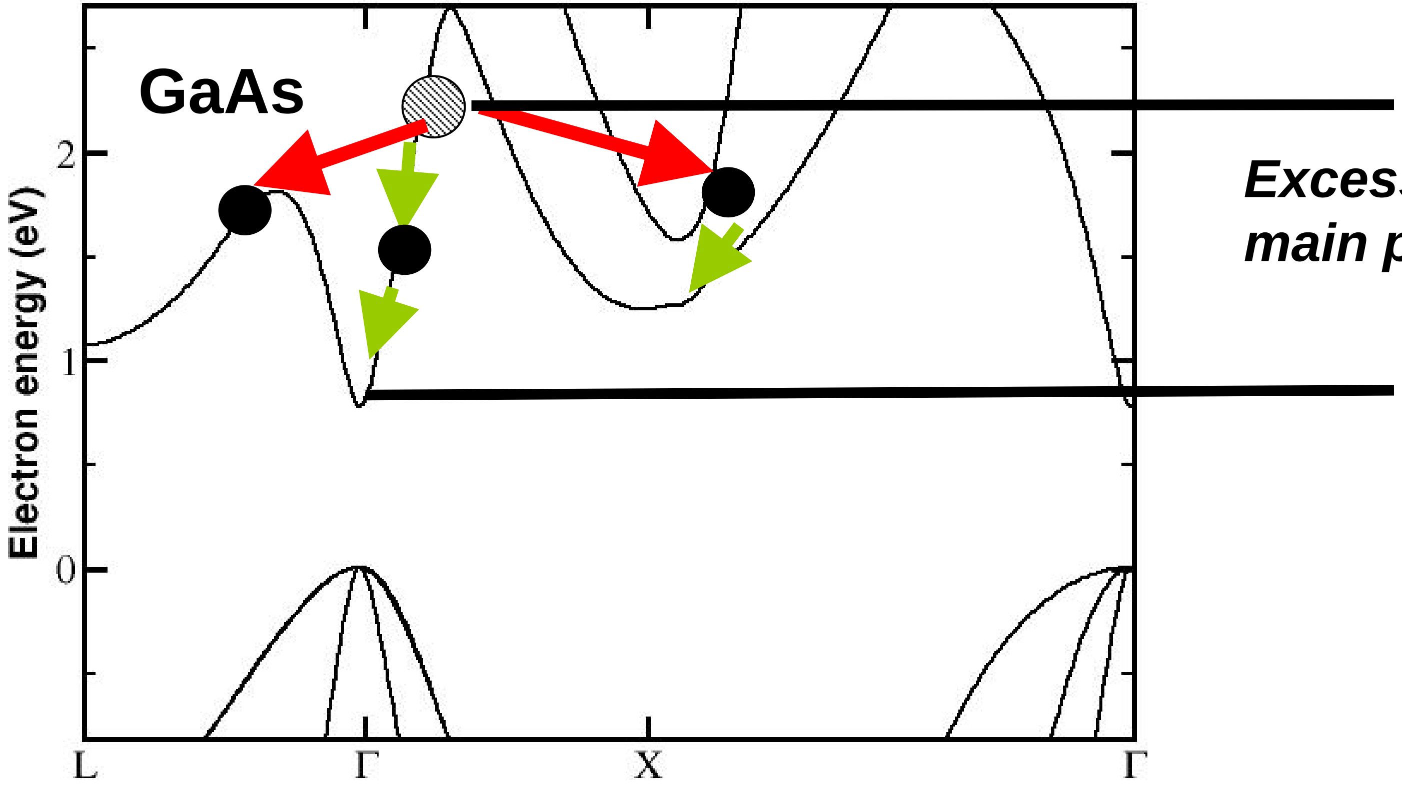


$$\frac{d<E>}{dt} = \Gamma_{em}\omega_{em} - \Gamma_{abs}\omega_{abs}$$

Tanimura et al, PRB 93 (2016) 161203 (R).

Sjakste et al, J. Phys: Cond. Mat. ***30****, 353001 (2018).*

MAIN SCATTERING CHANNELS



Excess energy: main parameter

- Below second CBM in polar materials : polar optical (Fröhlich) scattering
- Above second CBM: intervalley scattering

Sjakste, Tanimura, Barbarino, Perfetti, Vast, J. Phys: Cond. Mat. ***30****, 353001 (2018).*

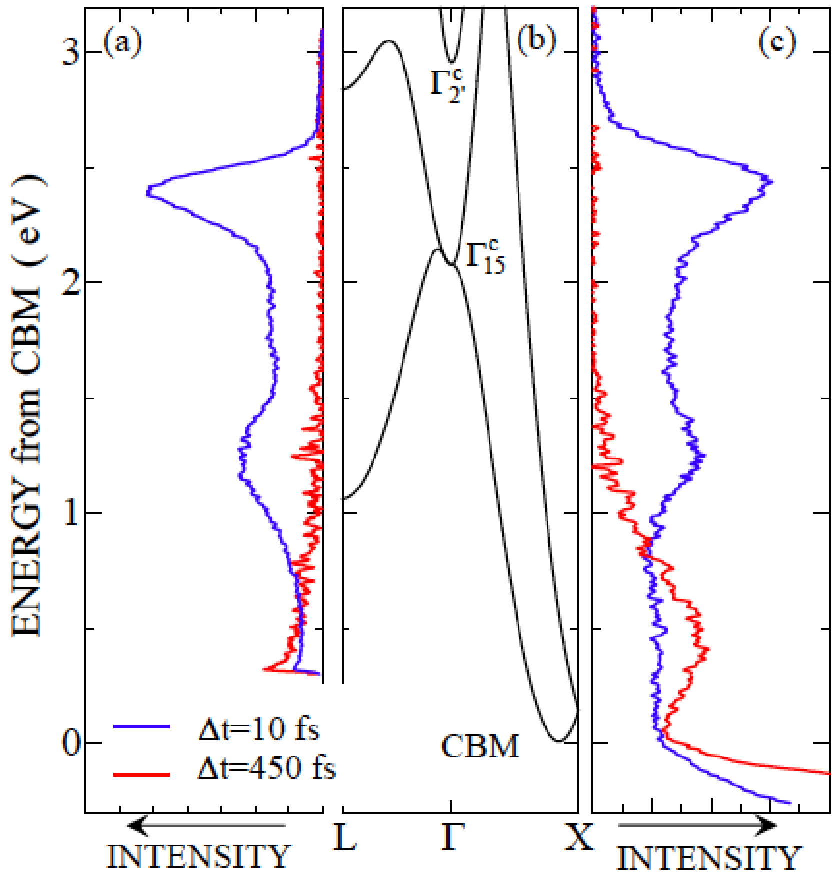
Outline

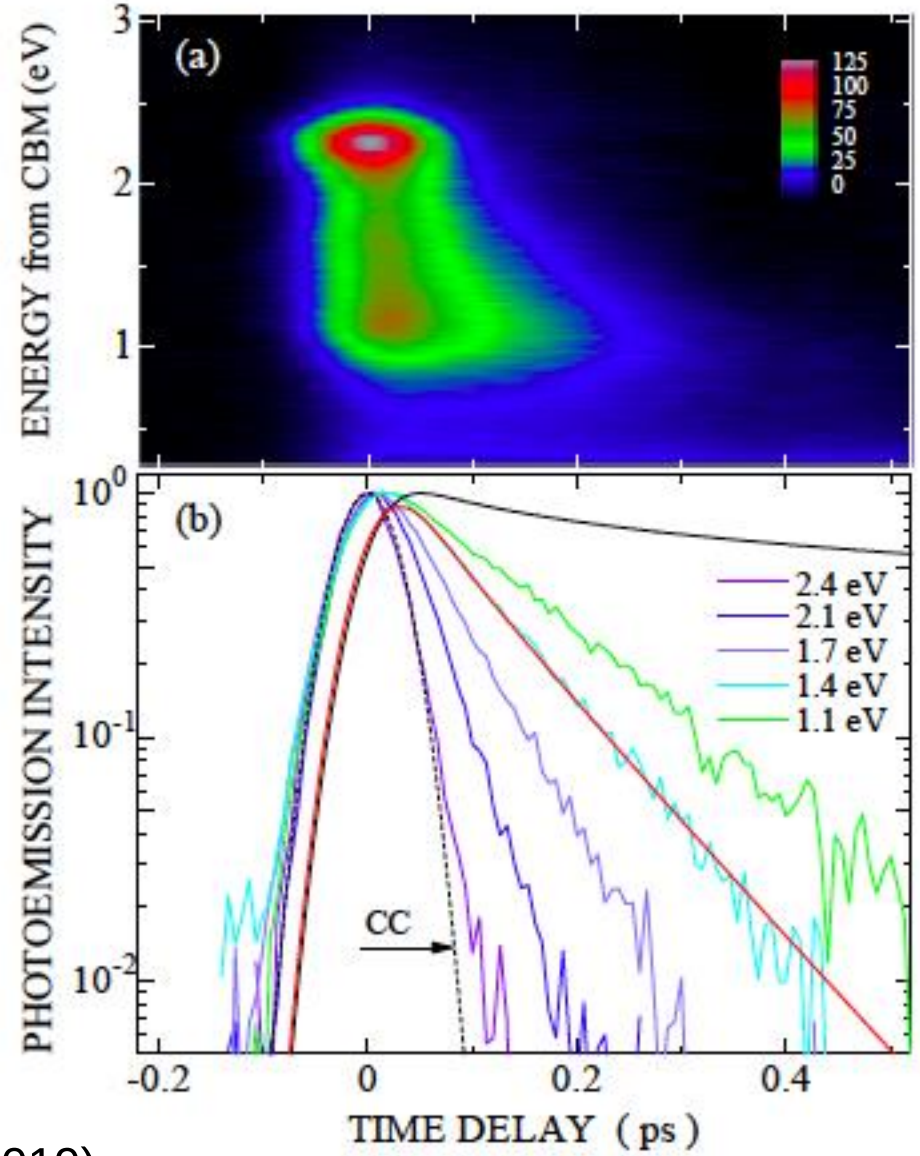
- Electron-phonon scattering for highly excited electrons

- Highly excited electron relaxation in Si and Ge

- Photoexcited electron relaxation in InSe

HIGHLY EXCITED ELECTRONS IN SILICON: 2PPE





Excess energies: 1-3 eV above CBM

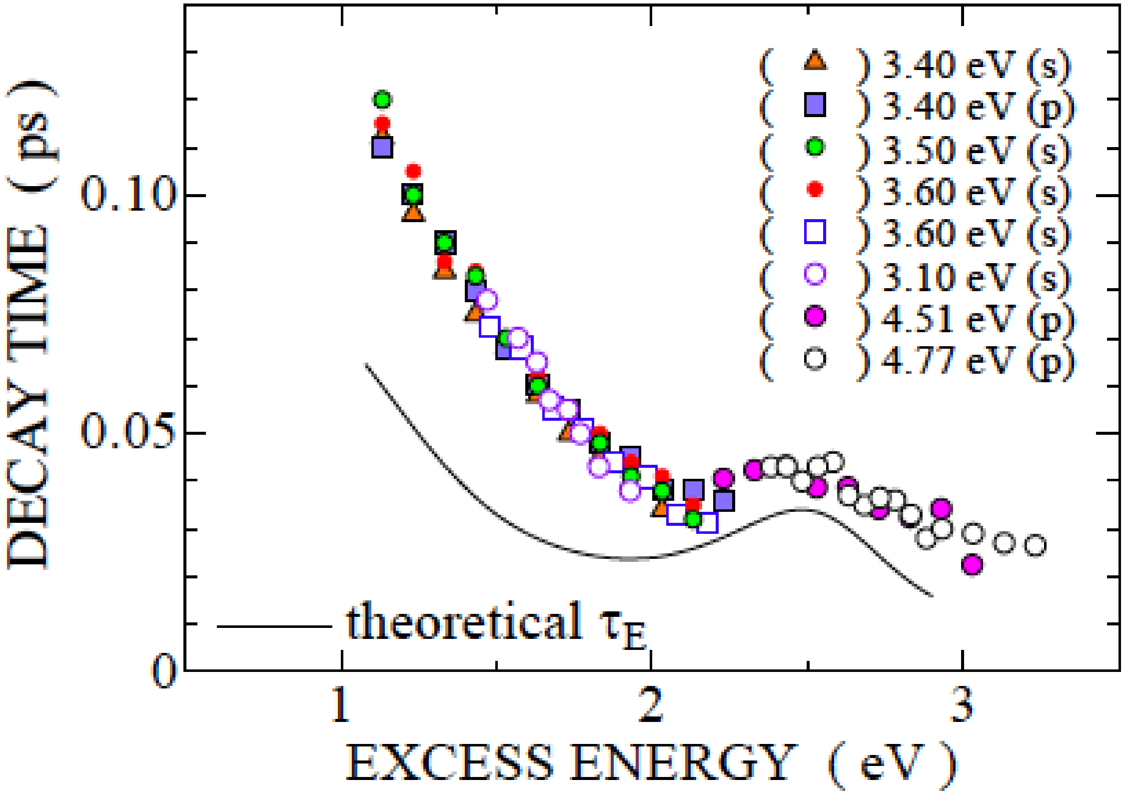
Tanimura et al, PRB **100**, 03520 (2019).

HIGHLY EXCITED ELECTRONS IN SILICON: INTERPRETATION PROBLEM

Previous work: conflict theory/experiment:

Measured relaxation times 10 times longer than calculated ones

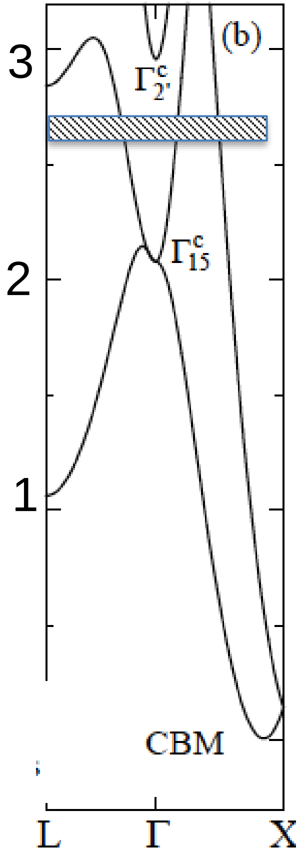
Ichibayashi *et al*, Phys. Rev. B 84, 235210 (2011).



This work: HEE idea

Initial relaxation:
too fast to be measured

Measured relaxation times:
energy loss



Tanimura, Kanasaki, Tanimura, Sjakste, Vast PRB **100**, 03520 (2019).

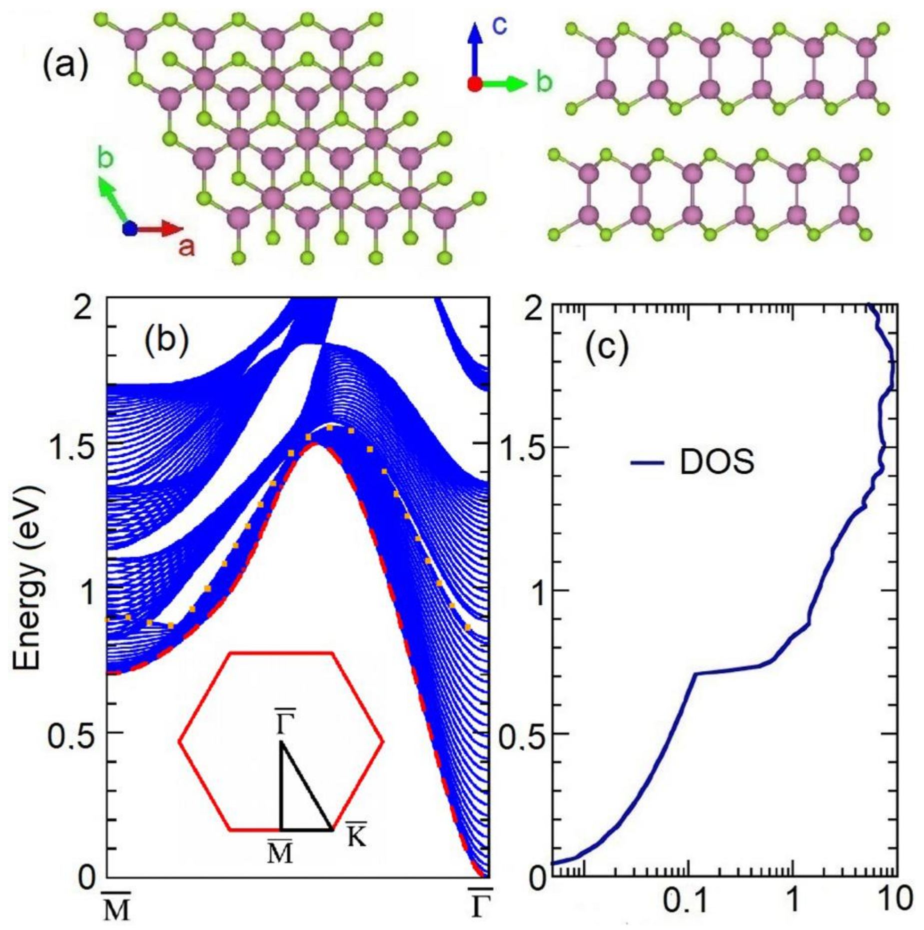
Outline

- ***Electron-phonon scattering for highly excited electrons***
- ***Highly excited electron relaxation in Si and Ge***
- ***Photoexcited electron relaxation in InSe***

Photoexcited electron relaxation in InSe

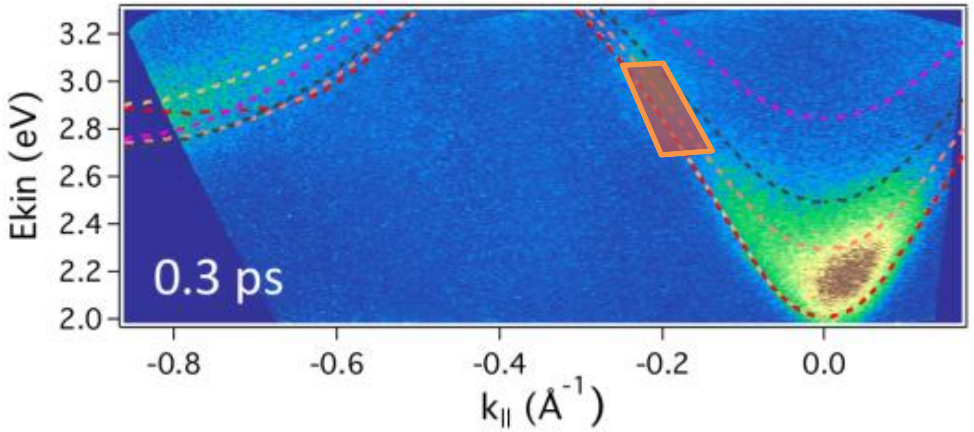
Luca PERFETTI
Zhesheng CHEN
Zailan ZHANG
Raphael CABOUAT
Jelena SJAKSTE
Cristine GIORGETTI
Valerie VENIARD
Abdelkarim Ouerghi
Hugo Henck

Evangelos PAPALAZAROU
Marino MARSI

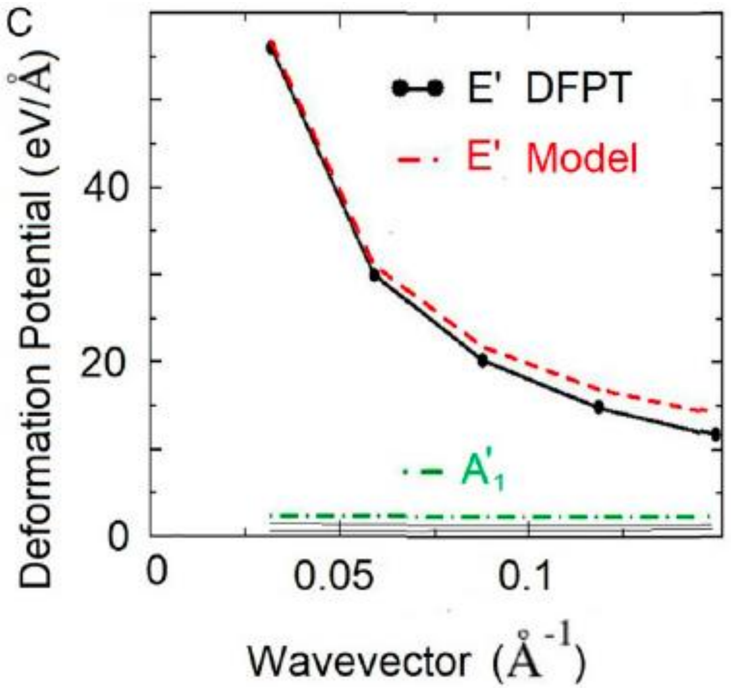


- Layered material
- Very narrow Γ valley
- Large M valley

InSe: energy relaxation in Γ valley



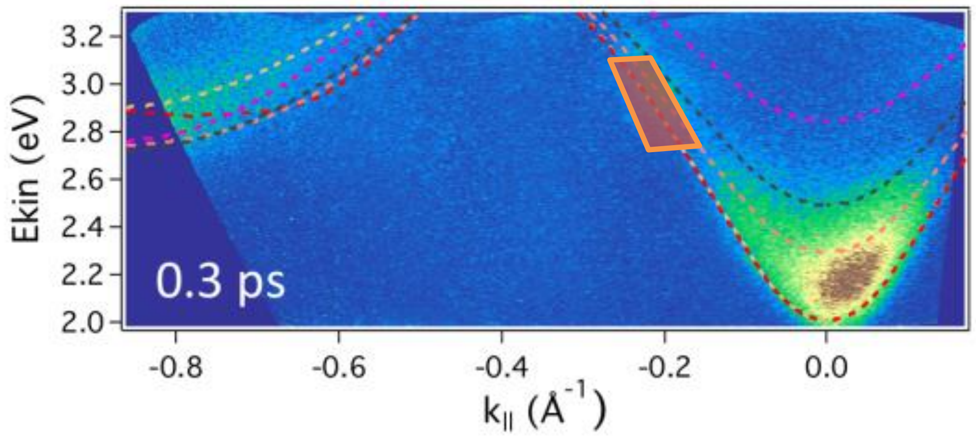
Excess energy below 0.7eV



- **no intervalley scattering**
- **very narrow Γ valley (q<0.2 ang.)**
- **Fröhlich scattering**
  (scatering by polar phonons)

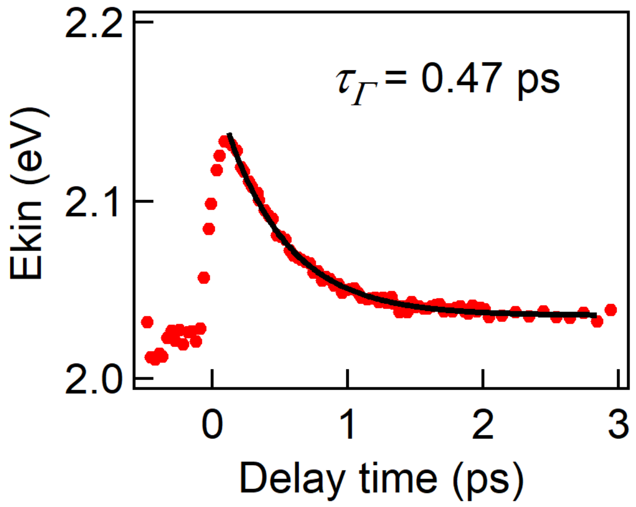
Chen, Giorgetti, Sjakste, Cabouat et al, PRB 97, 241201(R) (2018).

InSe: energy relaxation in Γ valley

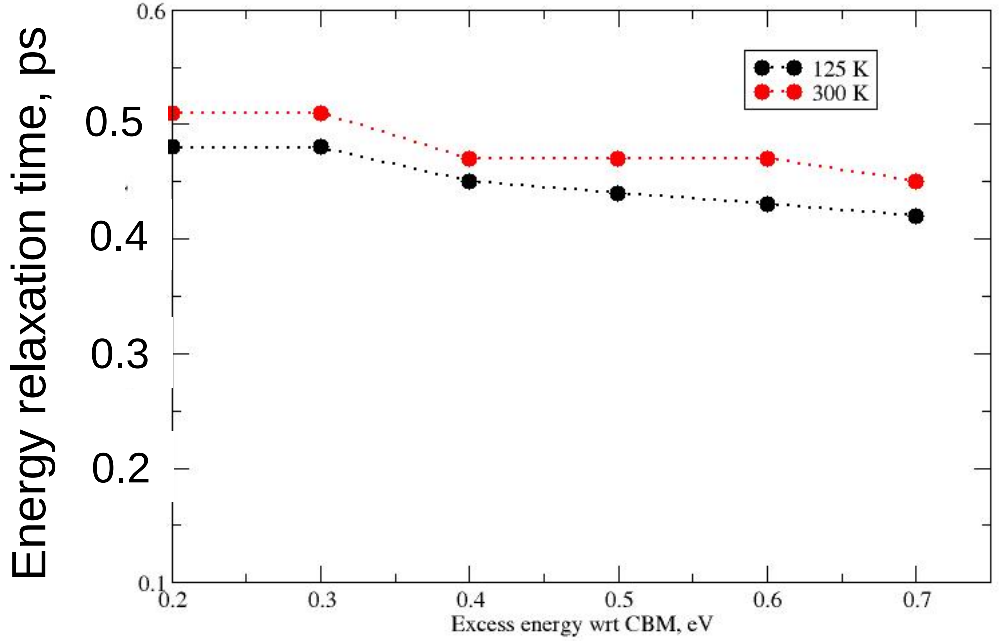


below 0.7 eV

Experiment



Theory: energy transfer due to coupling with polar phonons



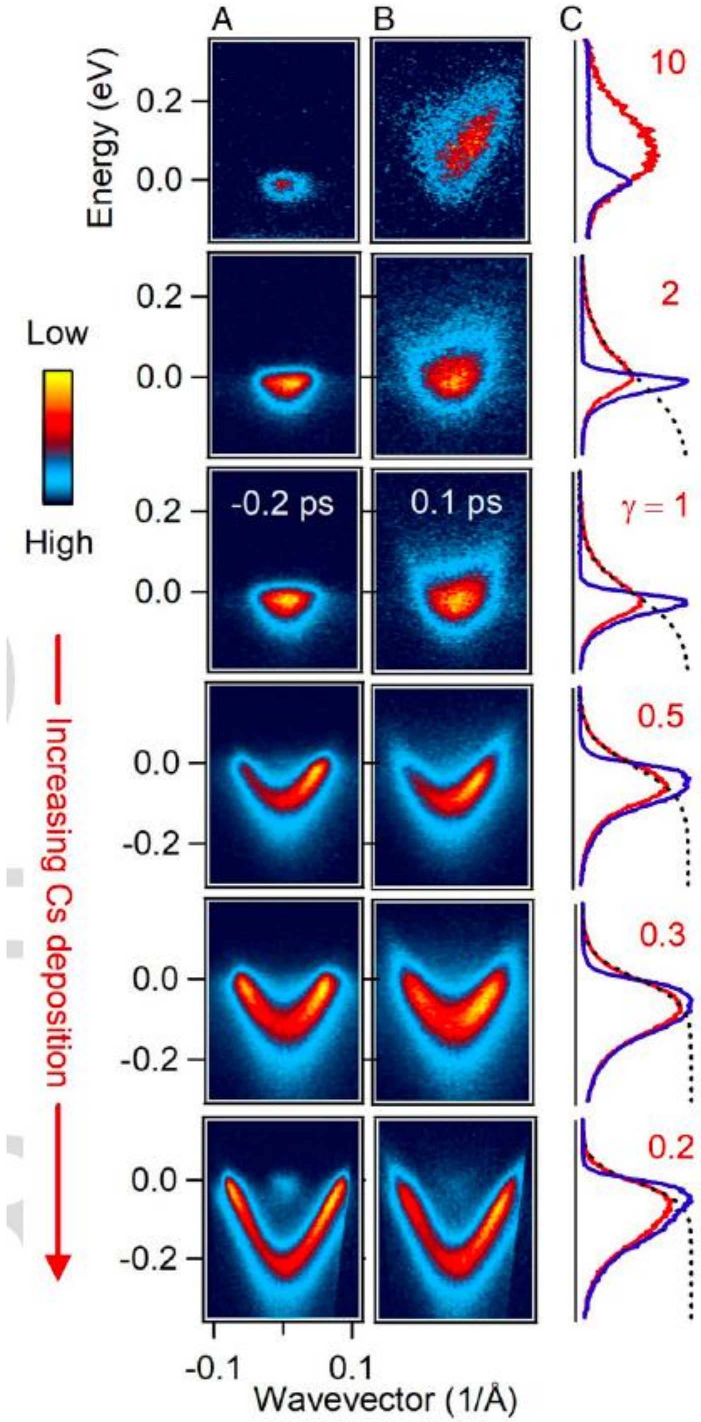
scattering by polar phonons

$$\frac{4\pi i e}{\varepsilon_\infty q^2} q_\mu \sum_\alpha Z_{\mu\lambda}(\alpha) e_\lambda(\alpha\hat{q})$$

Good agreement between theory and experiment.

Chen, Giorgetti, Sjakste, Cabouat et al, PRB 97, 241201(R) (2018).

Quasi-two-dimensional gas on InSe



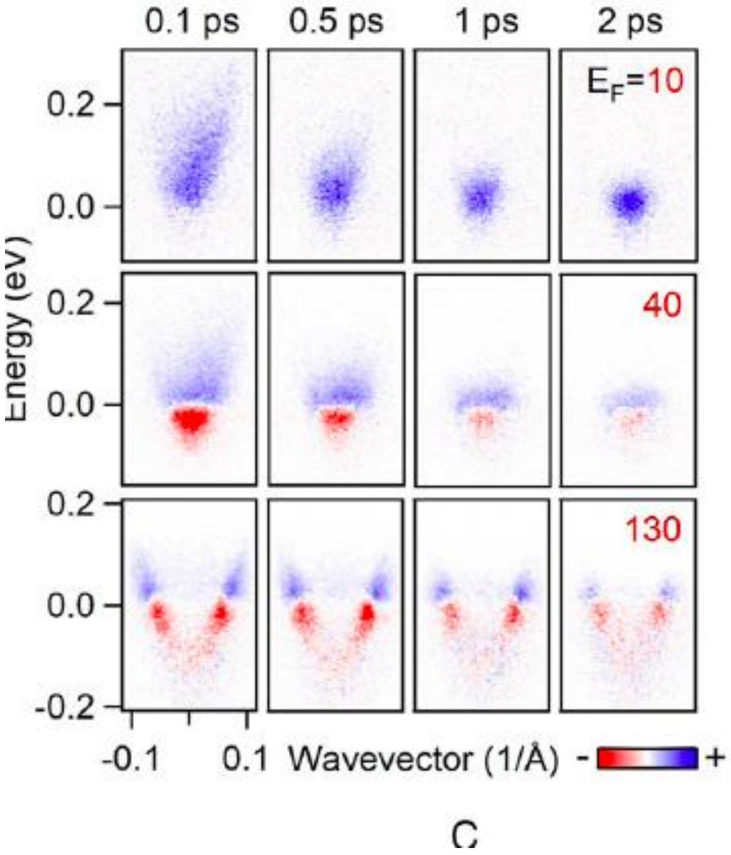
Experiment:

Zhesheng CHEN
Luca PERFETTI

Increasing Cs deposition on InSe surface

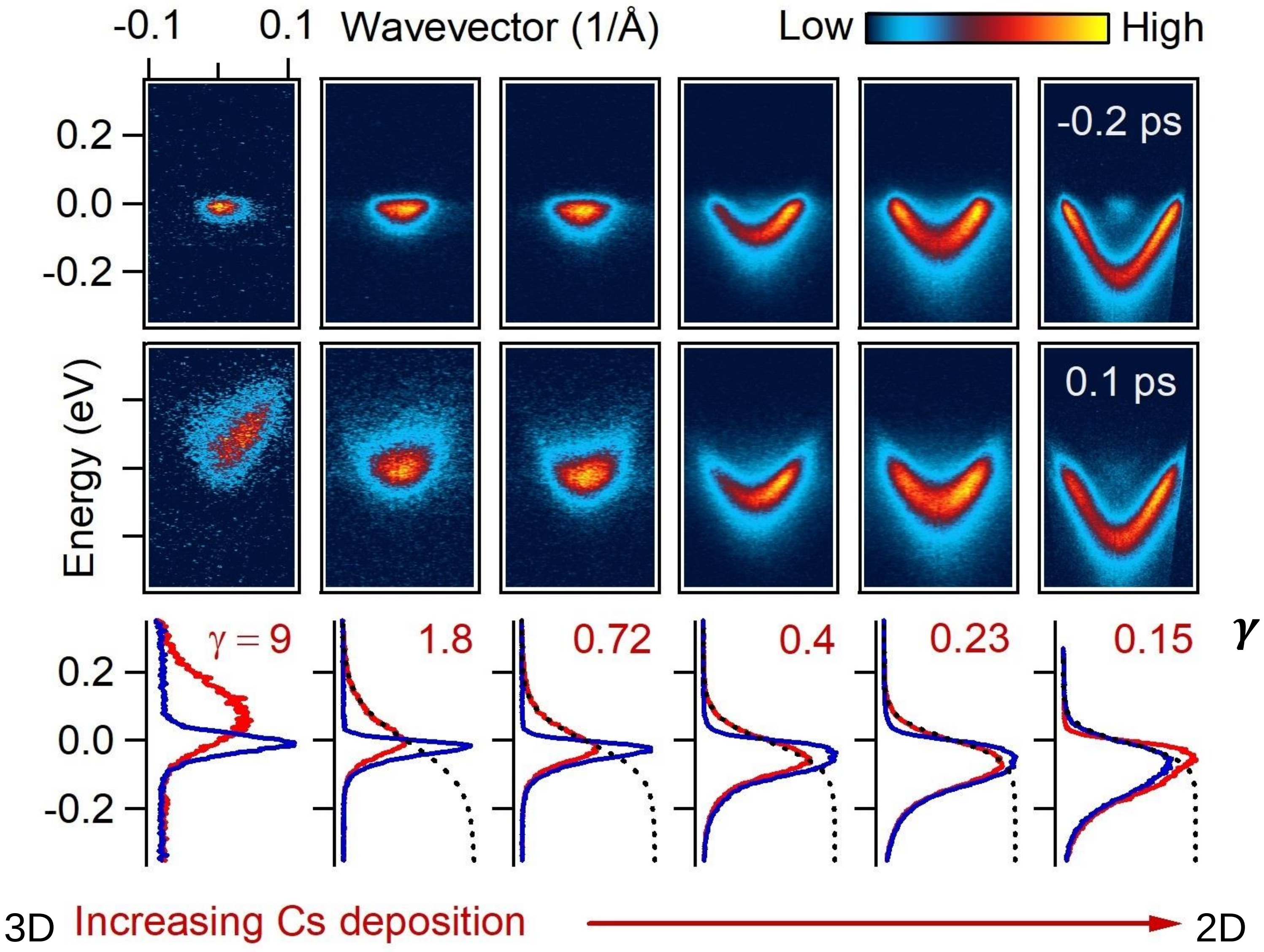
electron gas created on the surface

Dynamics of excited electrons studied by tr-ARPES

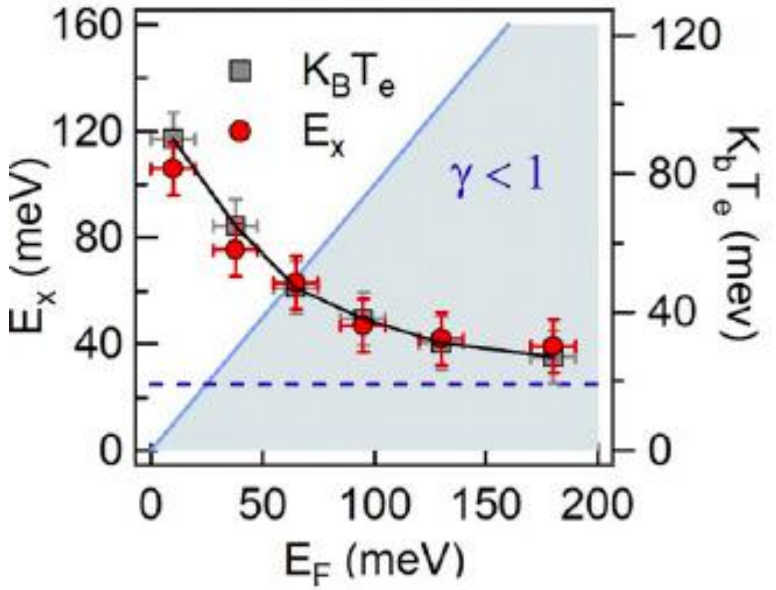


Chen, Sjakste et al, PNAS 117, 21962-21967 (2020)

Photoexcited electrons and 2D gas



$\gamma = T_e/E_F$

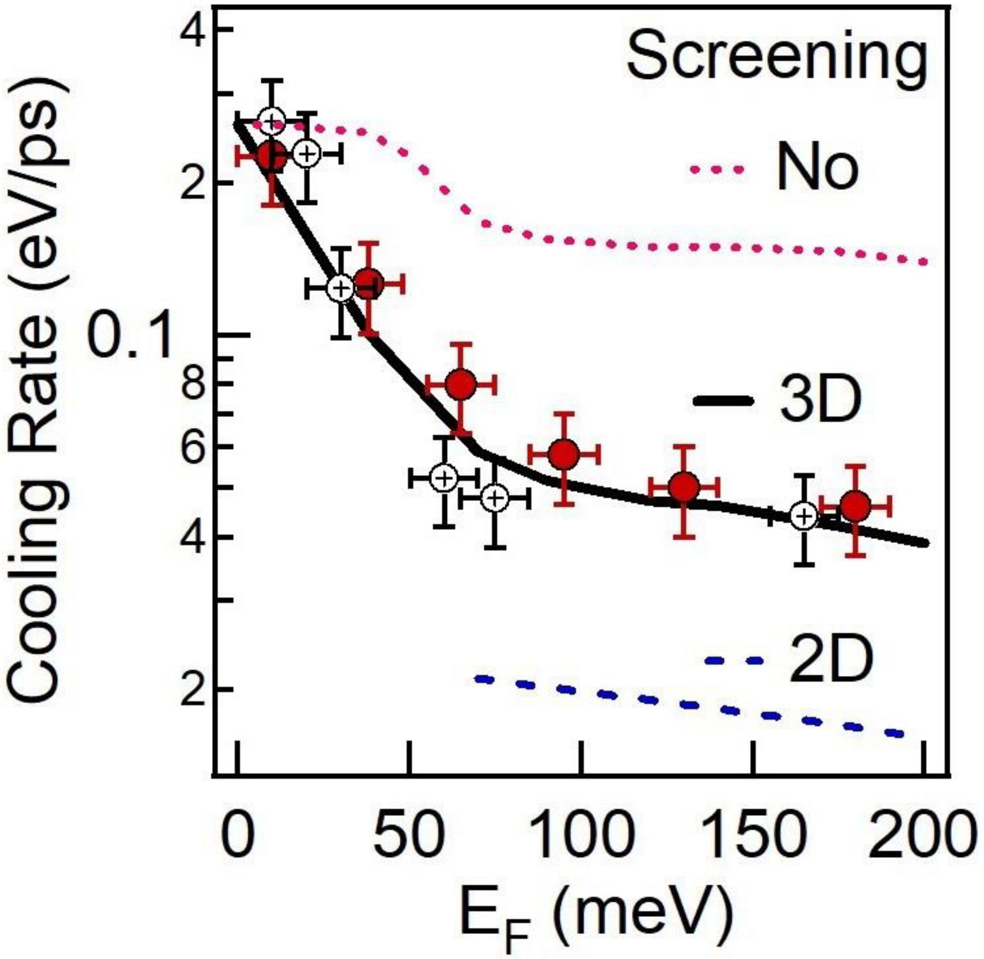


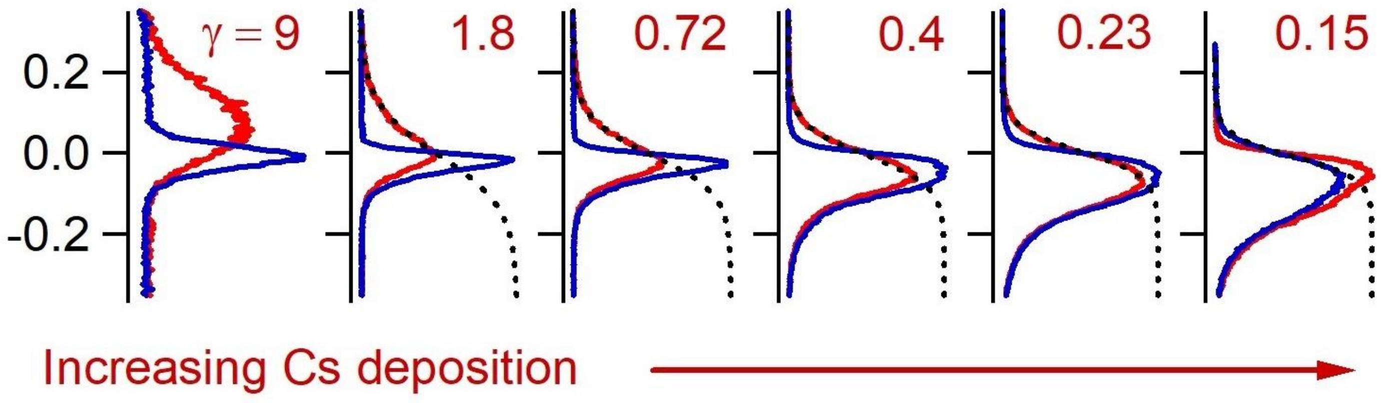
Low deposition: photoexcited electrons are non-thermal

High deposition: photoexcited electrons are thermalized

Chen, Sjakste et al, PNAS 117, 21962-21967 (2020)

Energy transfer in doped InSe





$$\gamma = T_e / E_F$$

Remote coupling of electrons to 3D phonons

Chen, Sjakste et al, PNAS 117, 21962-21967 (2020)

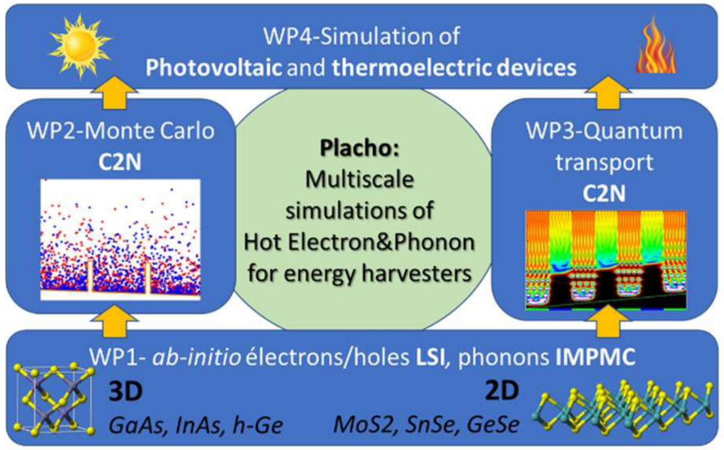
Conclusion

DFT-based calculations + time-resolved photoemission spectroscopy: powerful tools to study electron-phonon coupling

- *The concept of hot electron ensemble allowed us to interpret the relaxation times of highly excited electrons in several semiconductors.*

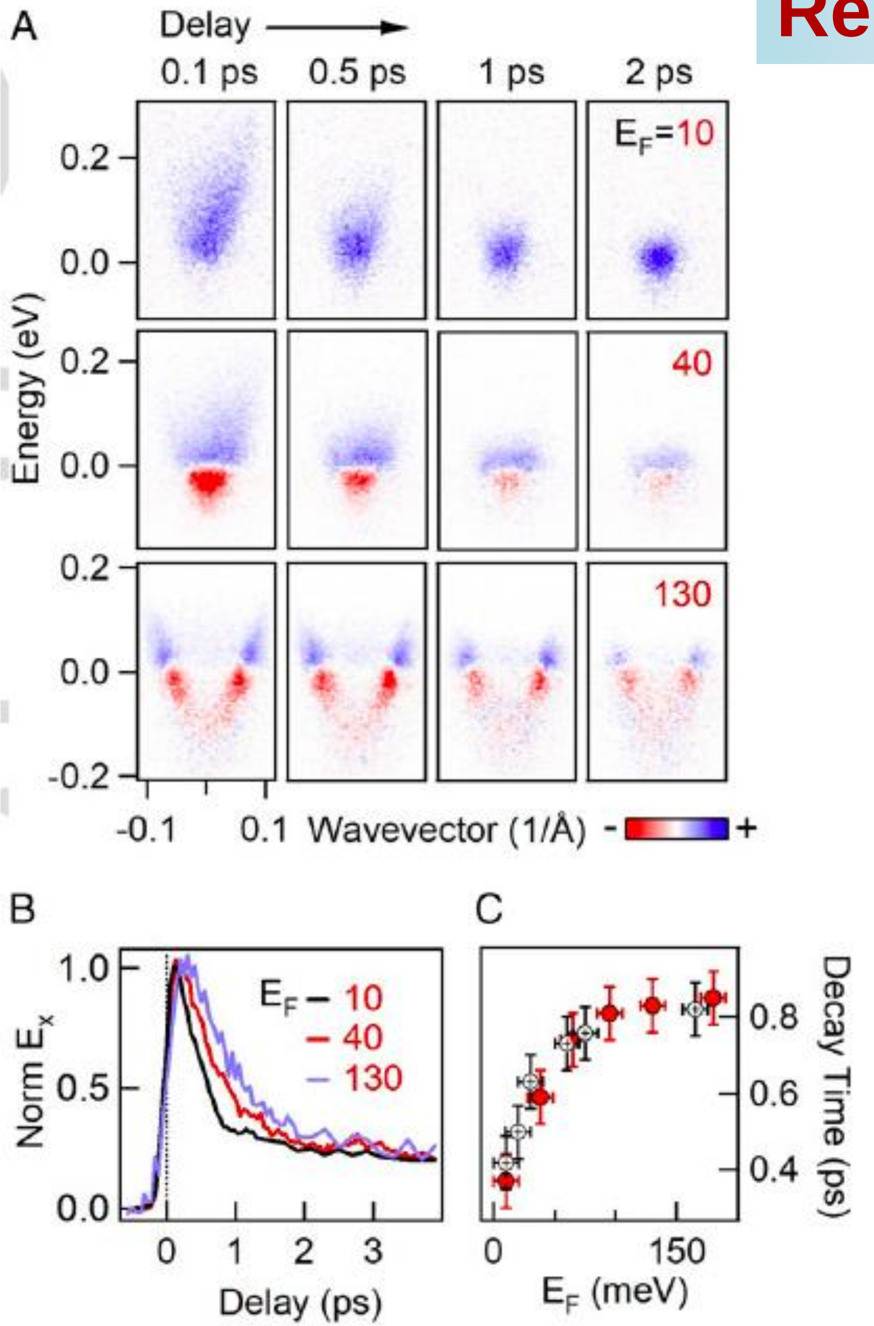
- *Doped InSe:*
  - *screening of polar coupling*
  - *remote coupling to 3D phonons*

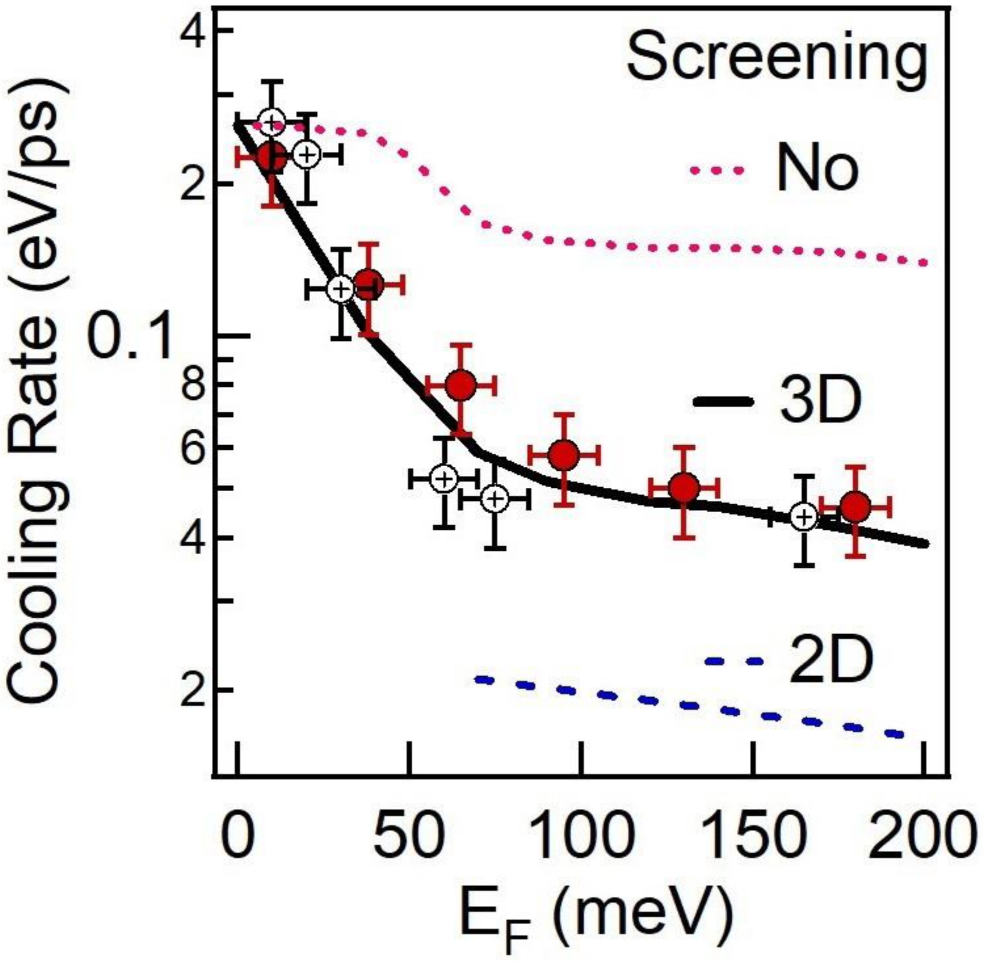
- *Hot carrier transport: probing the transient state*



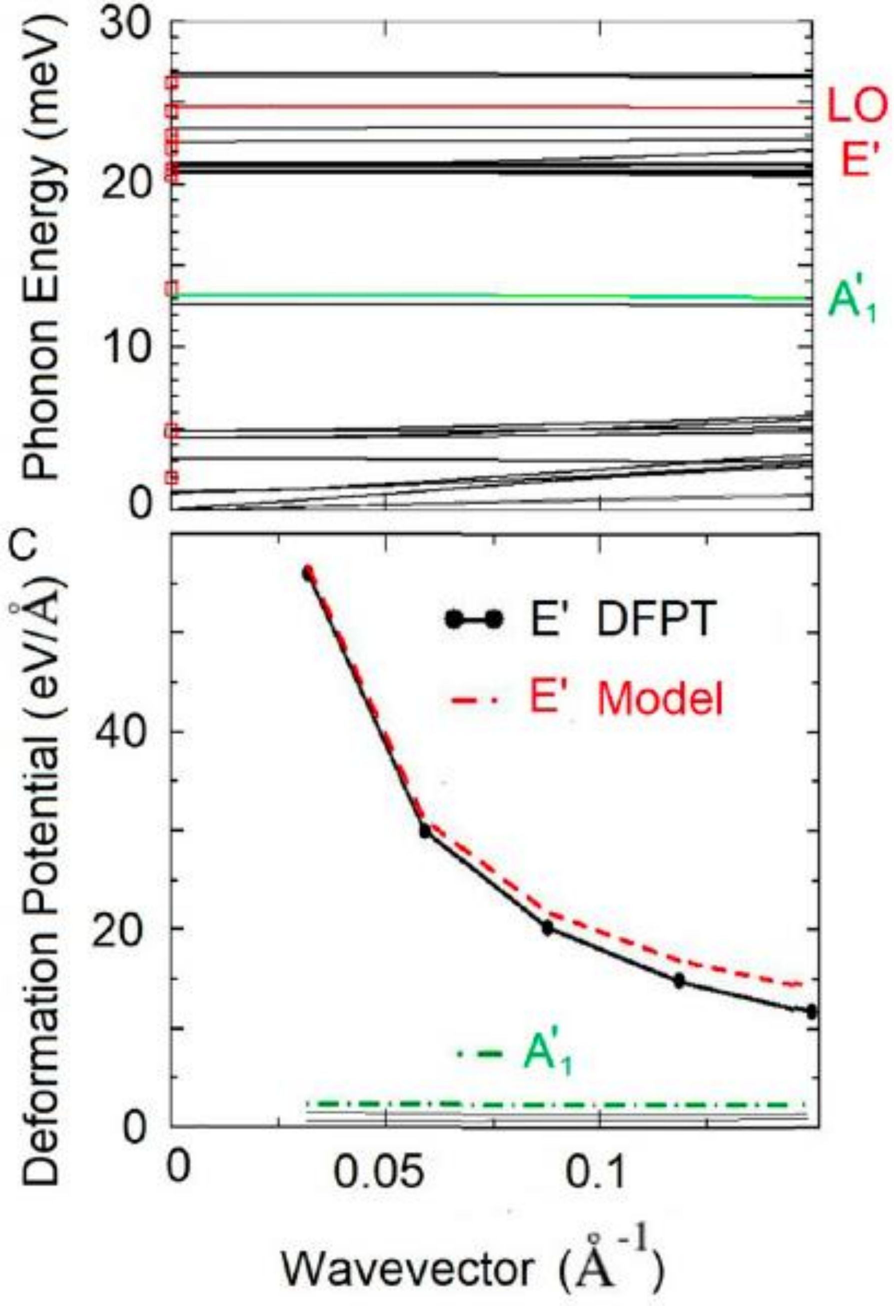
Thank you for your attention!

Relaxation dynamics of photoexcited electrons





Chen, Sjakste et al, PNAS 117, 21962-21967 (2020)



Calculation: screened Fröhlich interaction

3D model:

$$|g^{3D}_{fr}(\mathbf{q})| = \frac{4\pi e^2}{V\epsilon_{bulk}|\mathbf{q}|}\sum_{s}\sum_{\lambda'}\frac{q_{\lambda'}}{|\mathbf{q}|}Z_{\lambda'\lambda s}\mathbf{e}^s_{\lambda}(\mathbf{q})/\sqrt{2M_s\omega_{\mathbf{q}}}$$

Vogl, PRB 13 (1976).

3D screening:

$$\epsilon^{scr}_{bulk} = \epsilon_{bulk}\left(1+\frac{(q^{3D}_0)^2}{q^2}\right)$$

Thomas-Fermi

2D model:

$$|g^{2D}_{fr}(\mathbf{q})| = \frac{C_Z}{e^0_{eff}+r_{eff}|\mathbf{q_p}|}$$

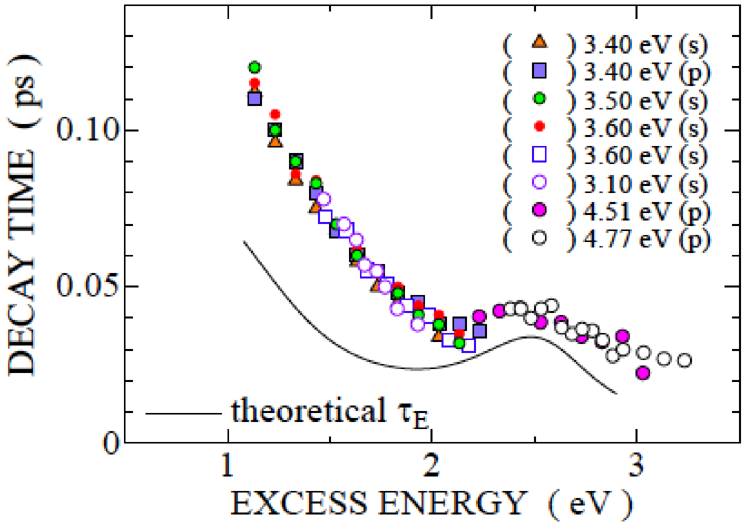
$$C_Z = \frac{2\pi e^2}{A}\times\sum_{s}\sum_{\lambda'}\frac{q_{\lambda'}}{|\mathbf{q_p}|}Z_{\lambda'\lambda s}\mathbf{e}^s_{\lambda}(\mathbf{q})/\sqrt{2M_s\omega_{\mathbf{q}}}$$

Sohier, Calandra, Mauri, PRB 94 (2016)

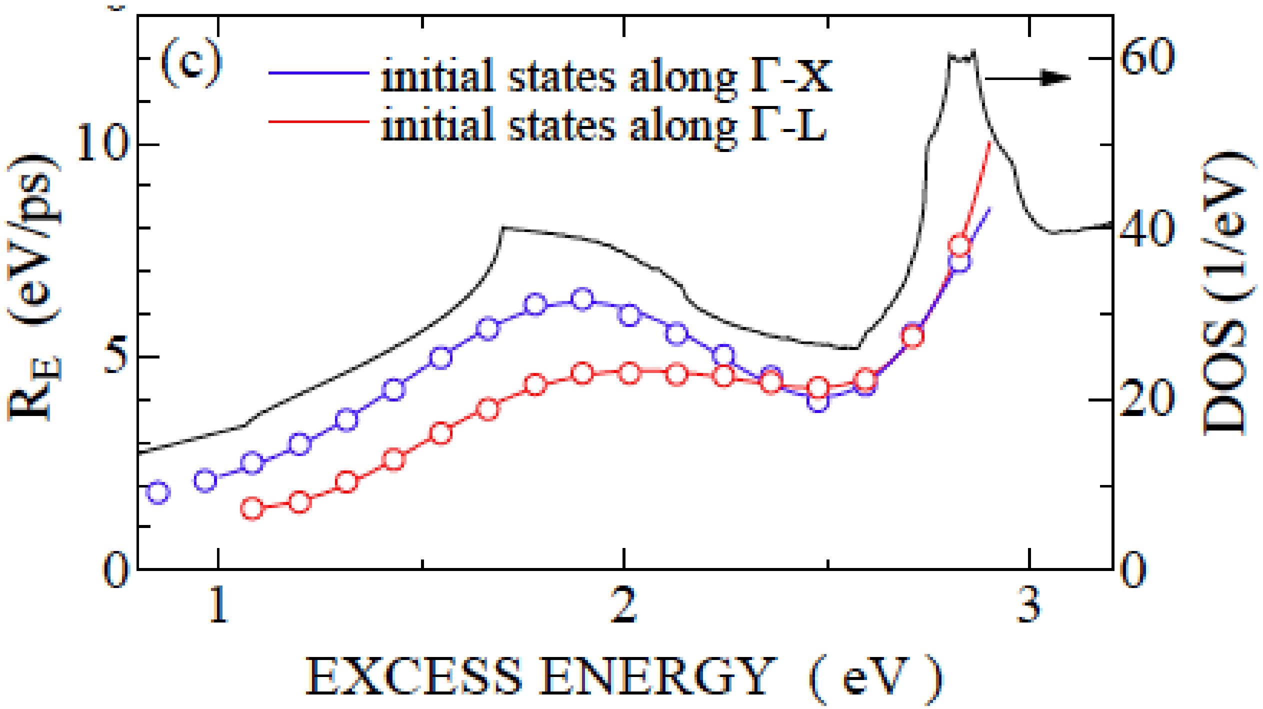
2D screening:

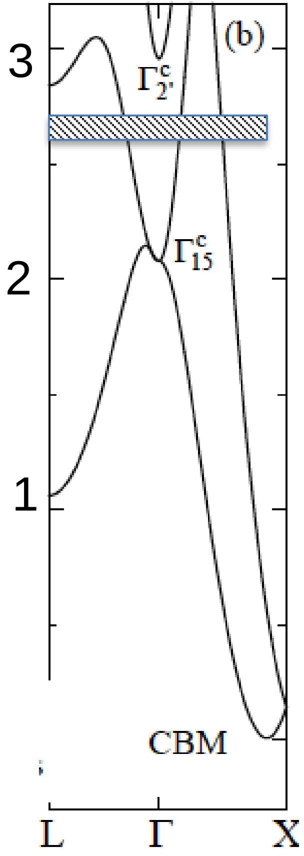
Stern, PRL 18, 546 (1967)

HIGHLY EXCITED ELECTRONS IN SILICON: ENERGY LOSS RATE



$$\frac{d<E>}{dt} = \Gamma_{em}\omega_{em} - \Gamma_{abs}\omega_{abs}$$

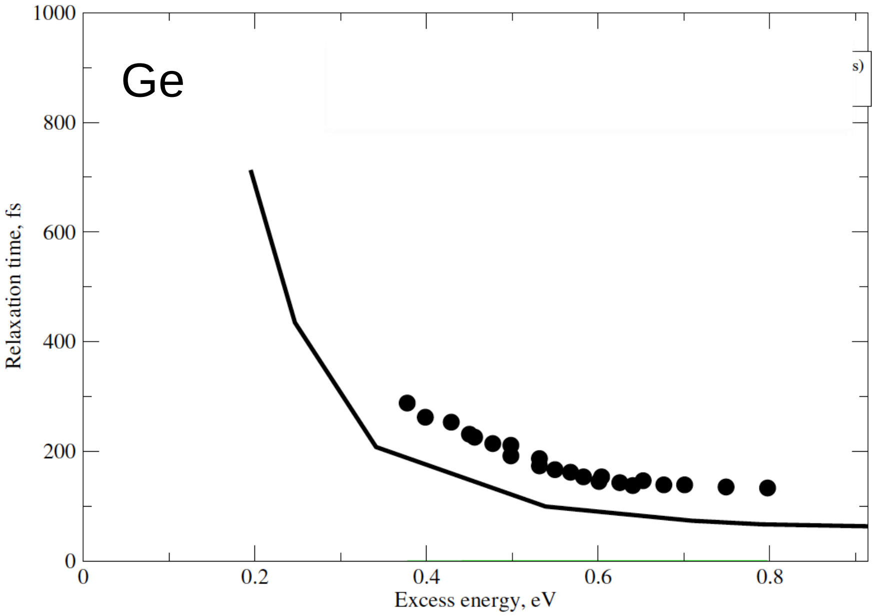


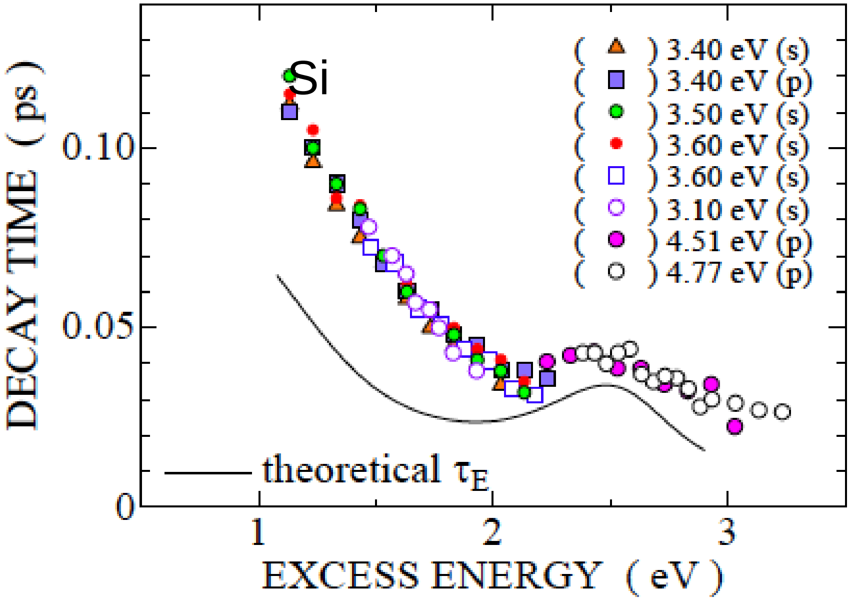


Energy loss rate:
Determined by DOS of final electronic states

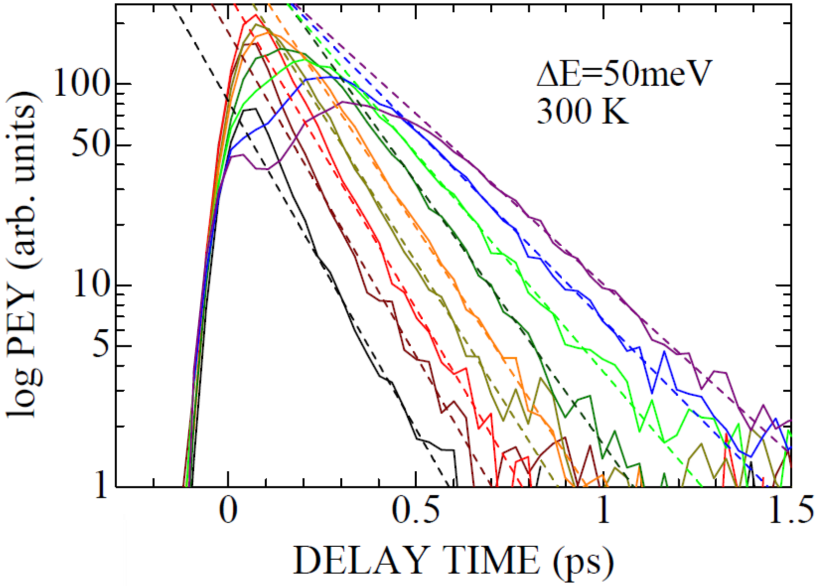
Tanimura, Kanasaki, Tanimura, Sjakste, Vast PRB **100**, 03520 (2019).

THE NEED FOR TIME PROPAGATION





PRB **100**, 03520 (2019)



Photoemission intensity (PEY) over energy interval ΔE:
Semi-logarithmic plot analysis, over several hundreds of fs.

ENERGY-DEPENDENT TIME PROPAGATION MODEL

$$\left.\frac{\partial f_{\mathbf{k}n}}{\partial t}\right|_{\text{coll}}^{\text{e-ph}} = -\frac{2\pi}{\hbar}\frac{1}{L^d}\sum_{\mathbf{q},\nu}\left|g^{\nu}_{\mathbf{k}'m,\mathbf{k}n}\right|^2\{f_{\mathbf{k}n}(1-f_{\mathbf{k}'m})N^{\nu}_{\mathbf{q}}$$
$$\times\delta(\varepsilon_{\mathbf{k}n}+\hbar\omega_{\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m})+f_{\mathbf{k}n}(1-f_{\mathbf{k}'m})(1+N^{\nu}_{-\mathbf{q}})$$
$$\times\delta(\varepsilon_{\mathbf{k}n}-\hbar\omega_{-\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m})-(1-f_{\mathbf{k}n})f_{\mathbf{k}'m}(1+N^{\nu}_{\mathbf{q}})$$
$$\times\delta(\varepsilon_{\mathbf{k}n}+\hbar\omega_{\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m})-(1-f_{\mathbf{k}n})f_{\mathbf{k}'n}N^{\nu}_{-\mathbf{q}}$$
$$\times\delta(\varepsilon_{\mathbf{k}n}-\hbar\omega_{-\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m})\}\,.$$

→

$$\left.\frac{\partial f}{\partial t}\right|_{coll}(\varepsilon,t)$$

k and q dependent expression can be replaced by excess-energy-dependent model:
Dos(ε), $f(\varepsilon,t)$ ω_{em} , ω_{abs} , g_{eff} *(effective coefficient)*

$$f(\varepsilon,t+\Delta t) = f(\varepsilon,t)\exp(-\Gamma(\varepsilon,t)(t+\Delta t))$$

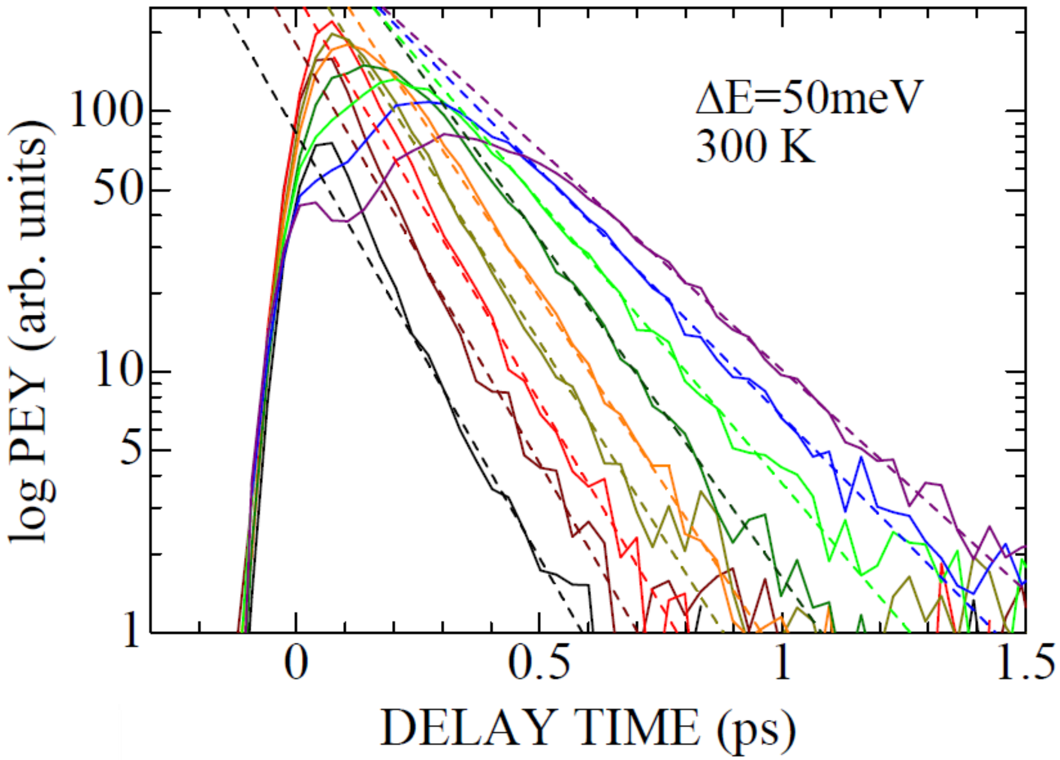
→

$$f(\varepsilon,t+\Delta t) = f(\varepsilon,t) - \Gamma(\varepsilon,t)f(\varepsilon,t)\Delta t$$

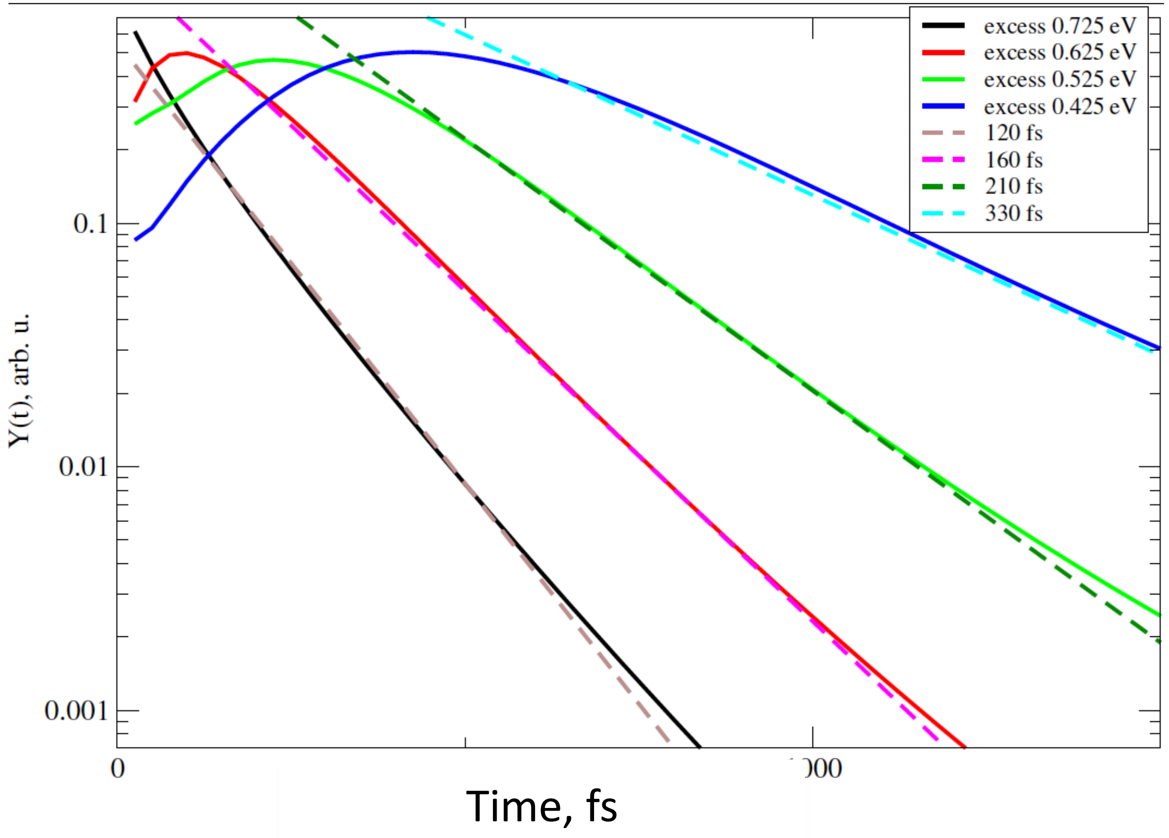
F. Caruso, J. Phys. Chem. Lett. 2021, 12, 6, 1734

TIME PROPAGATION OF ELECTRONIC DISTRIBUTIONS

Experiment

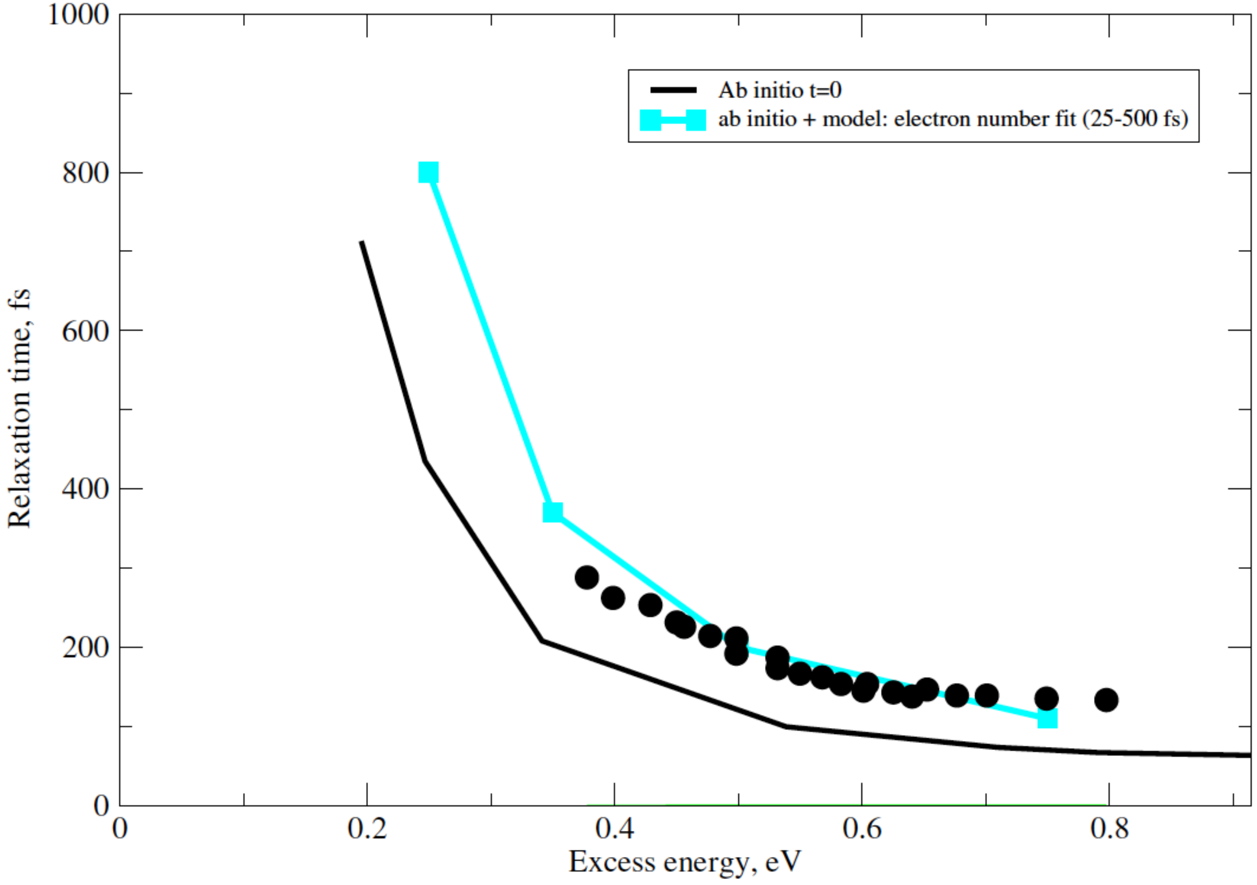


Theory $PEY(E,t) = \int_{E}^{E+\Delta E} f(\varepsilon,t)n(\varepsilon)d\varepsilon$



Semi-logarithmic plot analysis, over several hundred fs.

TIME PROPAGATION OF ELECTRONIC DISTRIBUTIONS



Time propagation of electronic distributions allows to improve the theory/experiment agreement

Outline

- ***Electron-phonon scattering for highly excited electrons***

- ***Highly excited electron relaxation in Si and Ge***

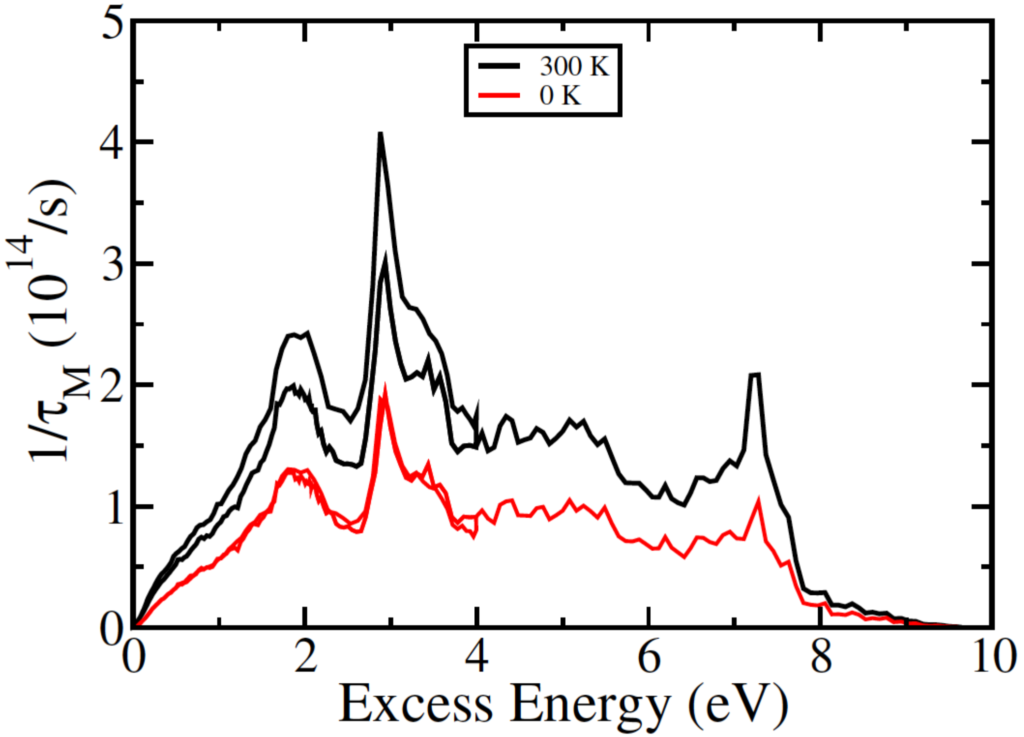
- ***Time propagation model***

- ***Photoexcited electron relaxation in InSe***

TEMPERATURE DEPENDENCE

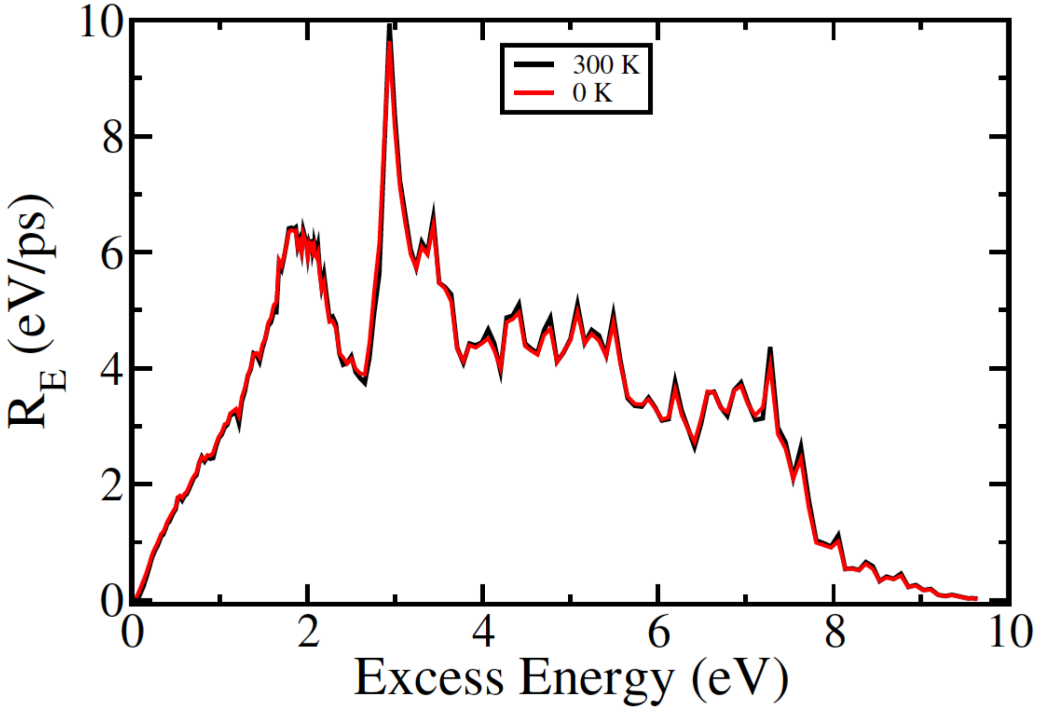
Raja Sen, post-doc

Total scattering rate, Si



Populations of acoustical phonons grow with temperature

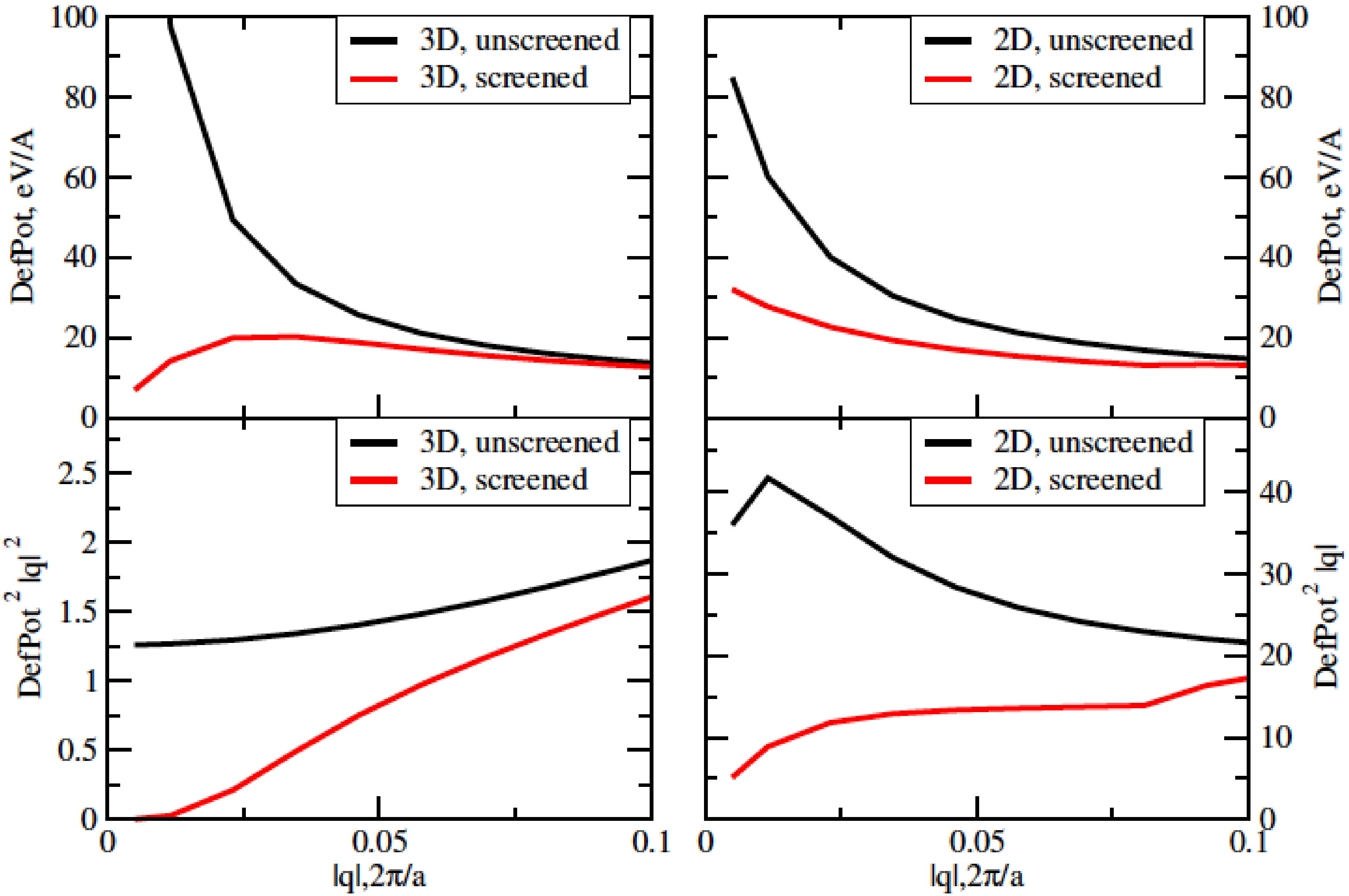
Energy loss rate, Si.



Negligible temperature dependence for energy loss rate

GaAs (Theory and experiment): *Sjakste et al, PRB* **97**, 064302 *(2018)*

The effect of 2D and 3D screening



Chen, Sjakste et al, PNAS 117, 21962-21967 (2020) (SI)

Stern model of 2D screening

$$\epsilon_{iso}^{scr} = \epsilon_{iso}(1 + q_0^{2D}/q_p), q_p \leq 2k_F$$

$$\epsilon_{iso}^{scr} = \epsilon_{iso}(1 + q_0^{2D}/q_p(1 - (1 - (2k_F/q_p)^2)^{1/2})),$$

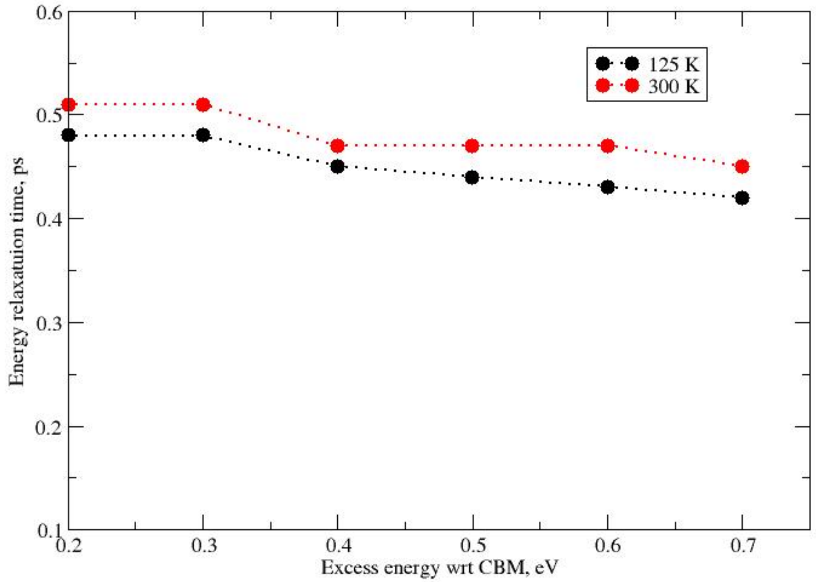
$$q_p > 2k_F$$

$$q_0^{2D} = 2m_{eff}e^2/\epsilon_{iso}\hbar^2$$

Stern, PRL 18, 546 (1967)

Excess energy

$$E_x = \frac{\int |f(E,T_e,\mu) - f_0(E,T)| E dE}{\int |f(\varepsilon,T_e,\mu) - f_0(E,T)| dE}$$



Energy loss rate:

$$\eta = \frac{d < E >}{dt} = \frac{\int |f(E,T_e,\mu) - f_0(E,T)| \left[(1 - f(E - \hbar\omega_{em}, T_e, \mu))\Gamma_{em}\omega_{em} - (1 - f(E + \hbar\omega_{abs}, T_e, \mu))\Gamma_{abs}\omega_{abs}\right] dE}{\int |f(E,T_e,\mu) - f_0(E,T)| dE}$$

Integral mean value theorem:

$$\eta = \frac{d < E >}{dt}(E_x) = (1 - f(E_x - \hbar\omega_{em}, T_e, \mu))\Gamma_{em}\omega_{em} - (1 - f(E_x + \hbar\omega_{abs}, T_e, \mu))\Gamma_{abs}\omega_{abs}$$

Hot electron tail:

$$\frac{d < E >}{dt} = \Gamma_{em}\omega_{em} - \Gamma_{abs}\omega_{abs}$$

Total scattering

$$\Gamma^{em}_{n\mathbf{k}} = \frac{2\pi}{\hbar}\sum_{n'}\sum_{\lambda}\frac{1}{L^d}\sum_{\mathbf{q}\in BZ}|\langle n',\mathbf{k}+\mathbf{q}|\Delta W^{\lambda}_{\mathbf{q}}|n,\mathbf{k}\rangle|^2\delta(\varepsilon_{n,\mathbf{k}}-\varepsilon_{n',\mathbf{k}+\mathbf{q}}-\hbar\omega^{\lambda}_{\mathbf{q}})(N^{\lambda}_{\mathbf{q}}(T)+1)$$

$$\Gamma^{abs}_{n\mathbf{k}} = \frac{2\pi}{\hbar}\sum_{n'}\sum_{\lambda}\frac{1}{L^d}\sum_{\mathbf{q}\in BZ}|\langle n',\mathbf{k}+\mathbf{q}|\Delta W^{\lambda}_{\mathbf{q}}|n,\mathbf{k}\rangle|^2\delta(\varepsilon_{n,\mathbf{k}}-\varepsilon_{n',\mathbf{k}+\mathbf{q}}+\hbar\omega^{\lambda}_{\mathbf{q}})N^{\lambda}_{\mathbf{q}}(T)$$

$$\Gamma_{n,\mathbf{k}} = \Gamma^{em}_{n\mathbf{k}} + \Gamma^{abs}_{n\mathbf{k}}$$

Energy loss

$$\omega_{em}\Gamma^{em}_{n,\mathbf{k}} = \frac{2\pi}{\hbar}\sum_{n'}\sum_{\nu}\frac{1}{L^d}\sum_{\mathbf{q}\in BZ}\omega^{\nu}_{\mathbf{q}}|g^{\nu}_{n,\mathbf{k}}(\mathbf{q})|^2\delta(E_{n,\mathbf{k}} - E_{n',\mathbf{k}+\mathbf{q}} - \hbar\omega^{\nu}_{\mathbf{q}})(N^{\nu}_{\mathbf{q}}(T) + 1)$$

$$\omega_{abs}\Gamma^{abs}_{n,\mathbf{k}} = \frac{2\pi}{\hbar}\sum_{n'}\sum_{\nu}\frac{1}{L^d}\sum_{\mathbf{q}\in BZ}\omega^{\nu}_{\mathbf{q}}|g^{\nu}_{n,\mathbf{k}}(\mathbf{q})|^2 \times \delta(E_{n,\mathbf{k}} - E_{n',\mathbf{k}+\mathbf{q}} + \hbar\omega^{\nu}_{\mathbf{q}})N^{\nu}_{\mathbf{q}}(T)$$

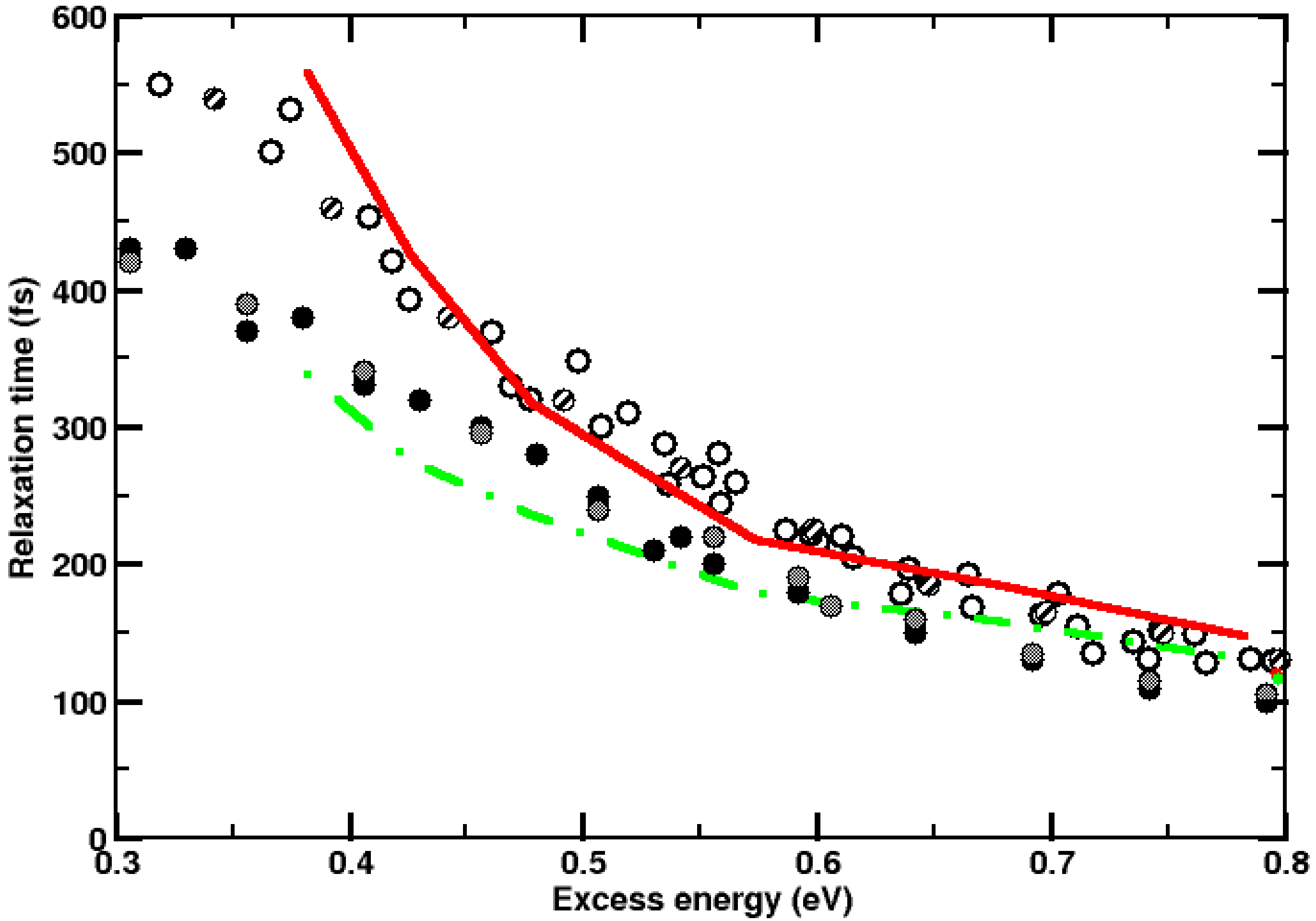
$$\frac{d < E >}{dt} = \Gamma_{em}\omega_{em} - \Gamma_{abs}\omega_{abs}$$

Ingredients: dos, matrix elements, phonon frequencies

Full expression of the collision term: out and in

$$
\begin{aligned}
\left.\frac{\partial f_{\mathbf{k}n}}{\partial t}\right|_{\mathrm{coll}}^{\mathrm{e-ph}} = -\frac{2\pi}{\hbar}\frac{1}{L^d}\sum_{\mathbf{q},\nu}\left|g^{\nu}_{\mathbf{k}'m,\mathbf{k}n}\right|^2 & \{ f_{\mathbf{k}n}(1-f_{\mathbf{k}'m})N^{\nu}_{\mathbf{q}} \\
& \times\delta(\varepsilon_{\mathbf{k}n}+\hbar\omega_{\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m}) + f_{\mathbf{k}n}(1-f_{\mathbf{k}'m})(1+N^{\nu}_{-\mathbf{q}}) \\
& \times\delta(\varepsilon_{\mathbf{k}n}-\hbar\omega_{-\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m}) - (1-f_{\mathbf{k}n})f_{\mathbf{k}'m}(1+N^{\nu}_{\mathbf{q}}) \\
& \times\delta(\varepsilon_{\mathbf{k}n}+\hbar\omega_{\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m}) - (1-f_{\mathbf{k}n})f_{\mathbf{k}'n}N^{\nu}_{-\mathbf{q}} \\
& \times\delta(\varepsilon_{\mathbf{k}n}-\hbar\omega_{-\mathbf{q}\nu}-\varepsilon_{\mathbf{k}'m}) \} \,.
\end{aligned}
$$

Energy relaxation of hot electrons in GaAs



ELECTRON-PHONON COUPLING: DFPT

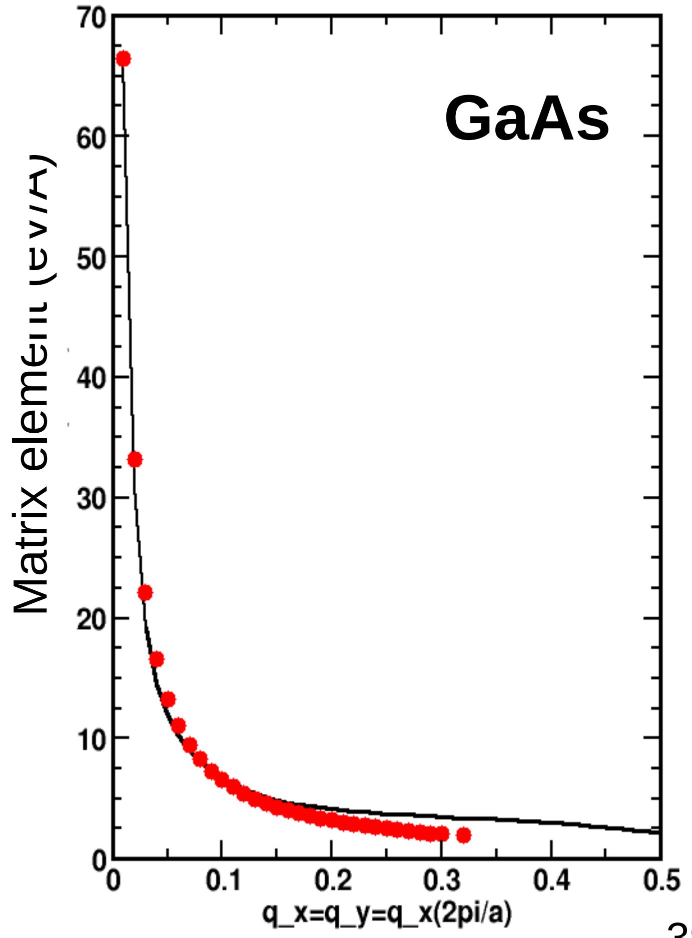
$$\left\langle \Psi_{n,k} \middle| \Delta W_q^{\lambda} \middle| \Psi_{n',k+q} \right\rangle$$

DFPT: Baroni et al, Rev. Mod. Phys. 2001

FRÖHLICH INTERACTION

$$|g_{fr}^{3D}(\mathbf{q})| = \frac{4\pi e^2}{V \epsilon_{bulk} |\mathbf{q}|} \sum_{s} \sum_{\lambda'} \frac{q_{\lambda'}}{|\mathbf{q}|} Z_{\lambda' \lambda s} \mathbf{e}_{\lambda}^{s}(\mathbf{q}) / \sqrt{2 M_s \omega_{\mathbf{q}}}$$

model based on ab inito parameters:
dielectric constant , effective charges



Vogl, PRB 13 (1976).

J. Sjakste et al, Annual Review of Heat Transfer, Begell House, Vol. 17 (2014).

CALCULATIONS: DFPT+Wannier

Reciprocal space
Bloch functions
Initial grid

$$\left\langle \Psi_{n,k} \middle| \Delta W_q^{\lambda} \middle| \Psi_{n',k+q} \right\rangle$$

- Non-local part (if polar)

Real space
Maximally localized Wannier functions
Interpolation on dense grid

Reciprocal space
Bloch functions
Dense grid

$$\left\langle \Psi_{n,k} \middle| \Delta W_q^{\lambda} \middle| \Psi_{n',k+q} \right\rangle$$

+ Non-local part (if polar)

J. Sjakste, N. Vast, M. Calandra, F. Mauri, PRB 92 (2015) 054307

C. Verdi, F. Giustino, PRL 115 (2015) 176401

MAIN CHANNELS: IMPORTANT FOR MONTE CARLO

Raja Sen

"Hot electrons in Si lose energy mostly to optical phonons": Truth or myth?

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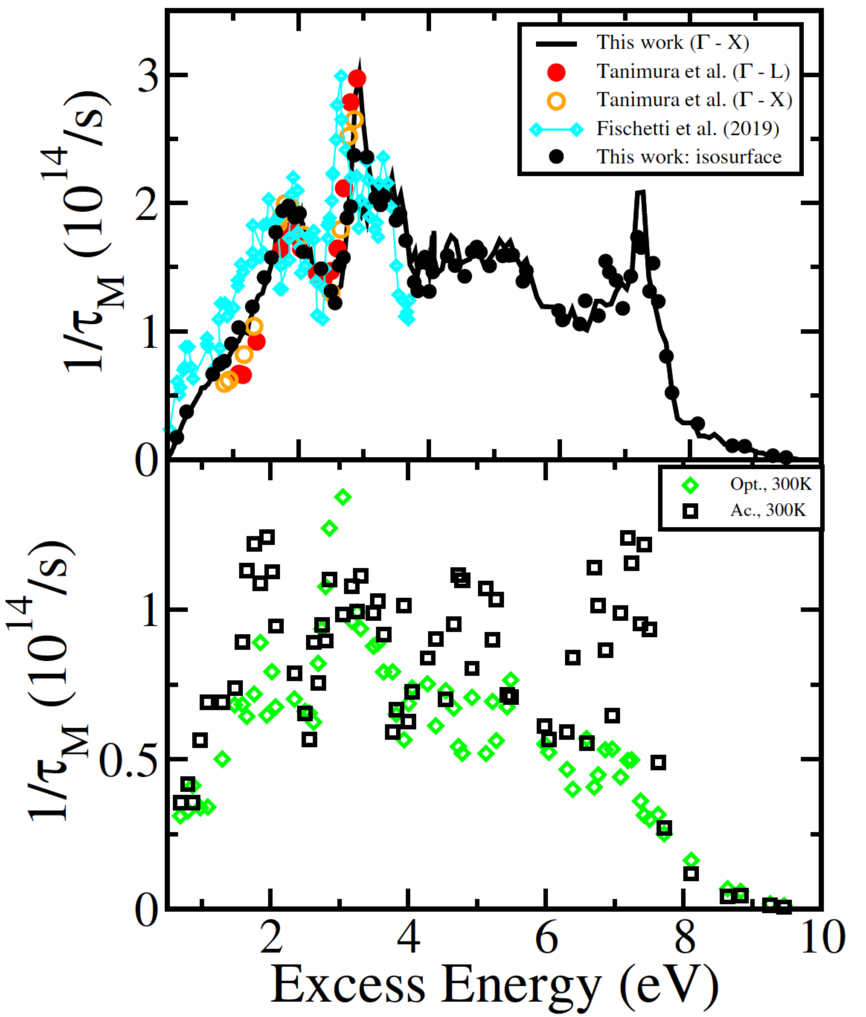
Si, 300 K



Total scattering rate:
acoustical phonons are dominant (at 300K)

EPW code, EPIK code: identical results

Also: *Bernardi at al, PRL (2014)*

MAIN CHANNELS: IMPORTANT FOR MONTE CARLO

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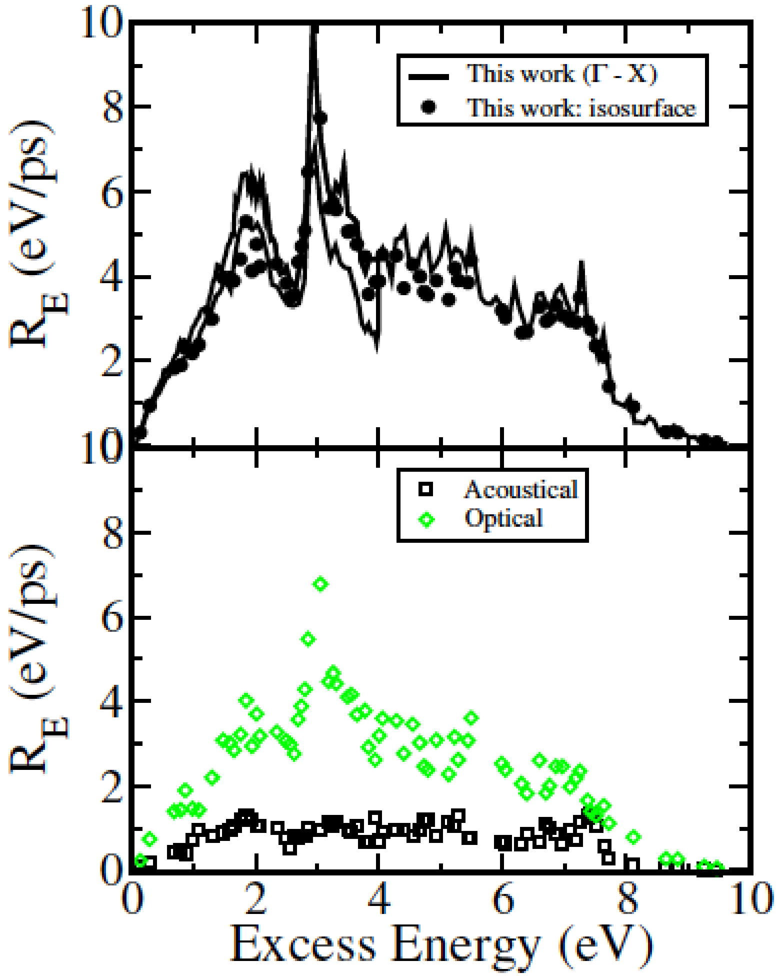

Energy loss rate:
optical phonons are dominant

Not unexpected:
Ahmad et al, Phys. Stat. Sol. 40:631 (1970)

Temperature-dependent contribution of acoustical phonons cancels out of energy loss

EPW code, EPIK code: identical results