Non-Thermal Phase Transition in Ge-Sb-Te Alloys: Role of Nonadiabatic Carrier Dynamics

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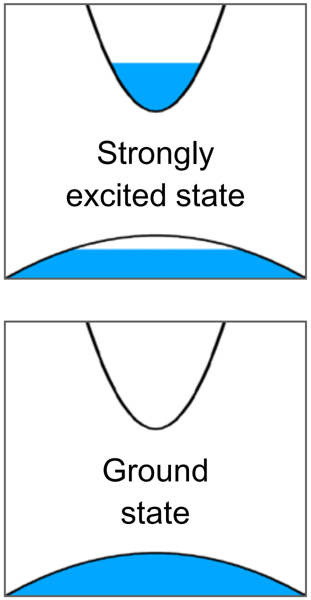
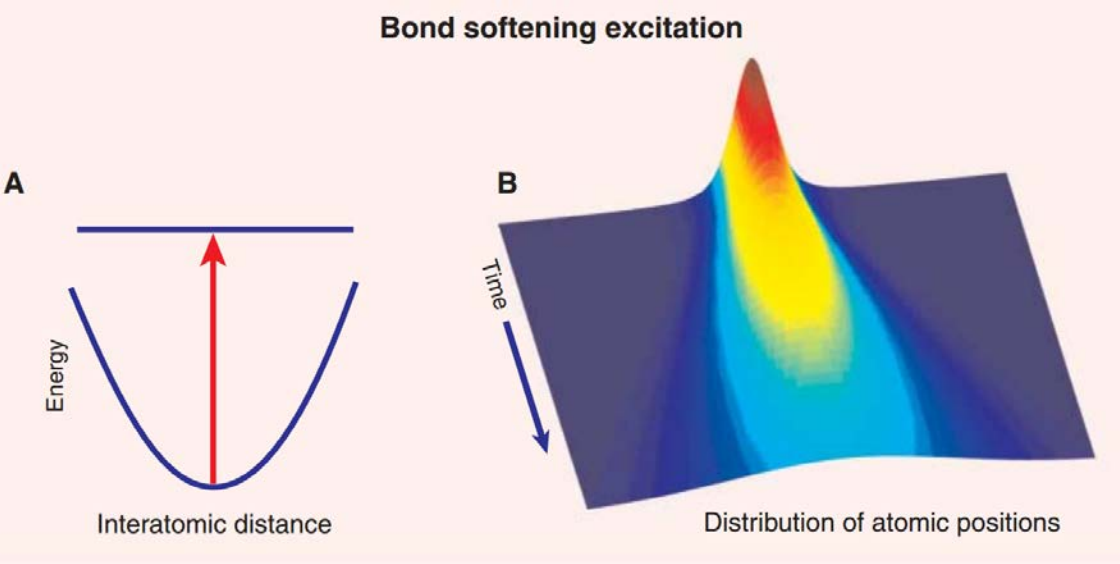
Non-Thermal Phase Transition

Excited carrier induced phase transition in low ionic temperature

Plasma annealing model J. A. Van Vechten (1979)

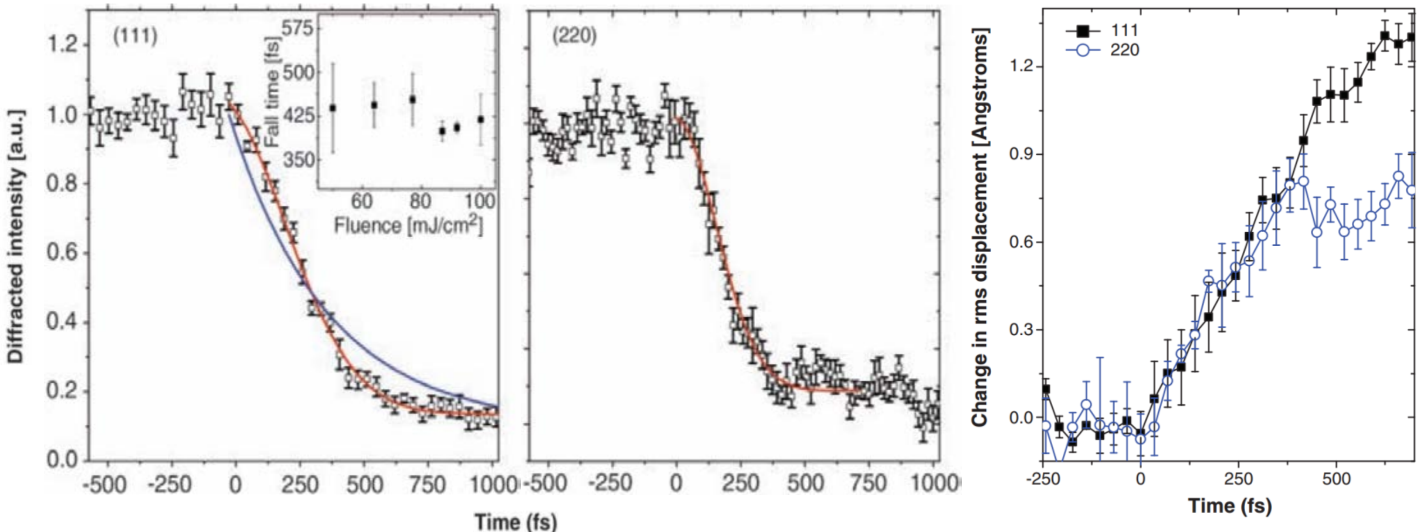




Science **316**, 1444 (2007)

Observation of Non-Thermal Phase Transition

Ultrafast time-resolved X-ray diffraction, InSb <111> <220> Bragg reflection



Science **308**, 392 (2005)

Debye-Waller model

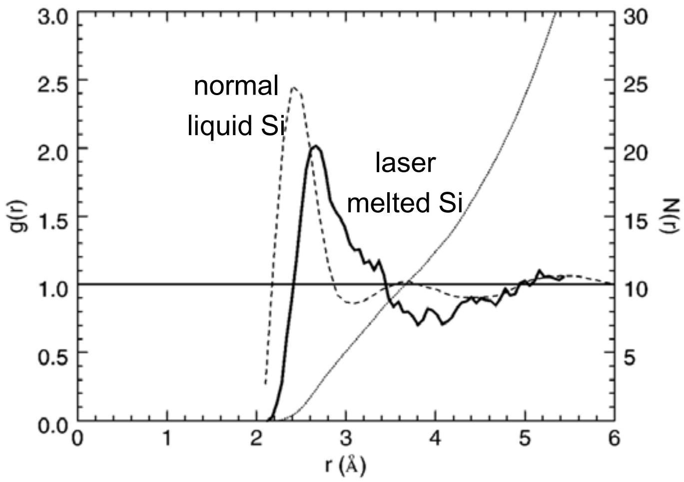
$$I(Q,t) = e^{-2W} = e^{-Q^2 \langle u^2(t) \rangle /3} \sim e^{-Q^2 v_{rms}^2 t^2 /3}$$

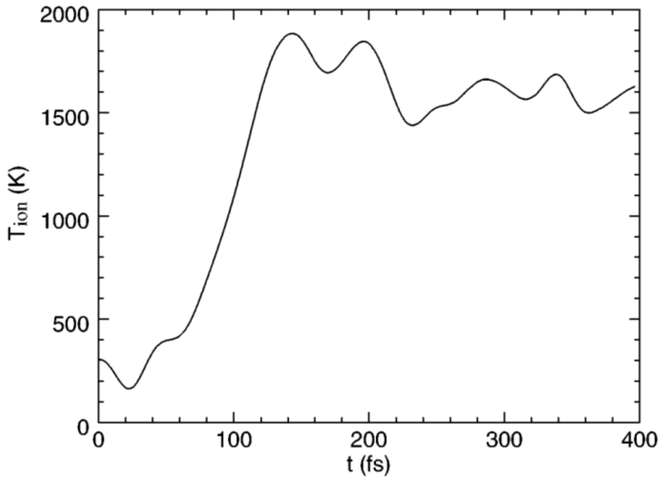
"Inertial motion" $\langle u^2(t) \rangle^{1/2} = v_{\mathrm{rms}} t$

DFT-MD Simulation

Using finite temperature density functional theory

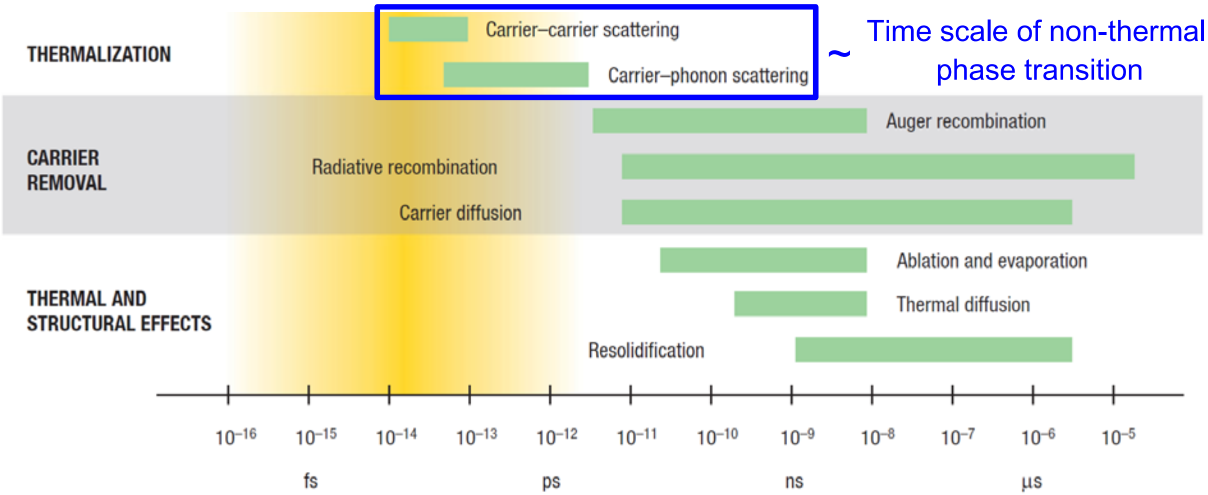
PRL **77**, 3149 (1996)



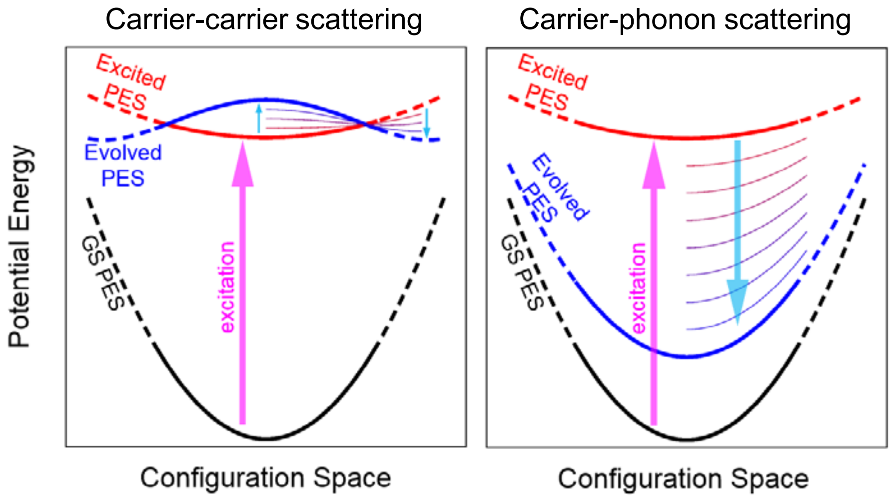


"Thermal activation"

Static Approximation in Previous Model

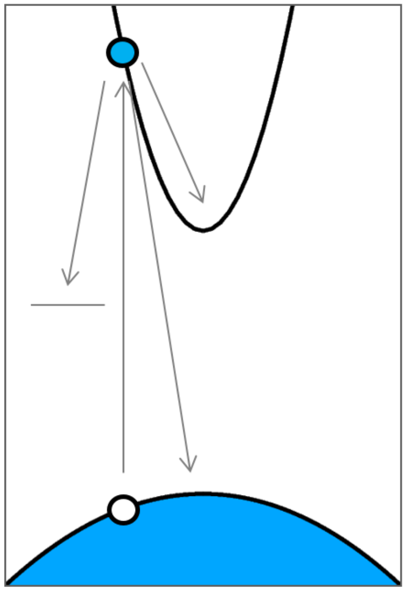


S. K. Sundaram and E. Mazur, Nature Mat. (2002)

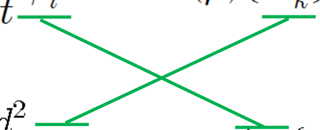


Beyond Quasi-Equilibrium: TDDFT-MD Simulation

Carrier Dynamics



- Real-time electronic and ionic dynamics
  - *ab-initio* molecular dynamics coupled with TDDFT
  - Ehrenfast dynamics



$$i\hbar\frac{\partial}{\partial t}\phi_i = H^{KS}(\rho,\{R_k\})\phi_i$$ Electron: Quantum mechanics

$$M_j\frac{d^2}{dt^2}R_j = -\nabla_j V(\rho,\{R_k\})$$ Ions: Classical mechanics

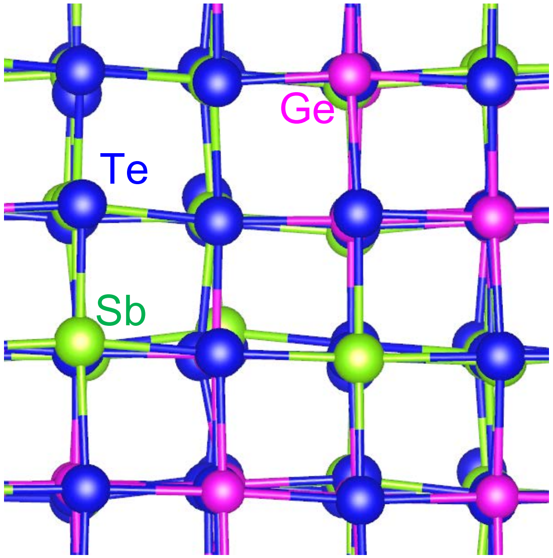
- TDDFT implemented in the SIESTA code
- Norm-conserving Troullier-Martins pseudopotentials
- PBE exchange-correlation functional
- Single-ζ polarized orbital basis set
- 96 atoms supercell
- Real-space grids
- Γ point for the Brillouin zone integration
- NVE ensemble

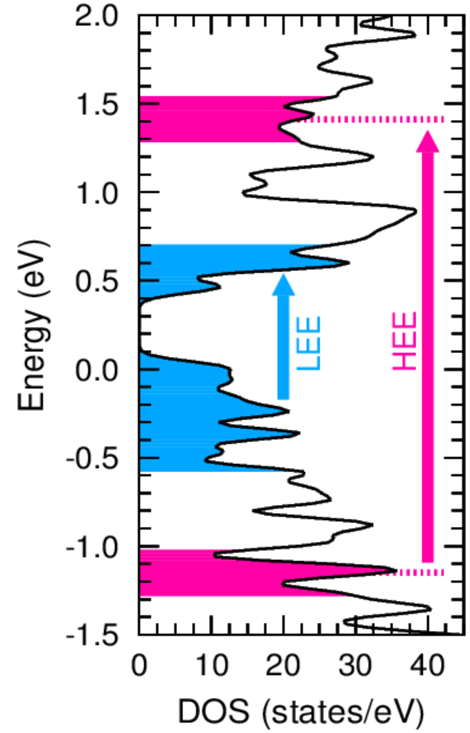
Atomic and Electronic Structures of GST

$Ge_2Sb_2Te_5$ rock-salt structure

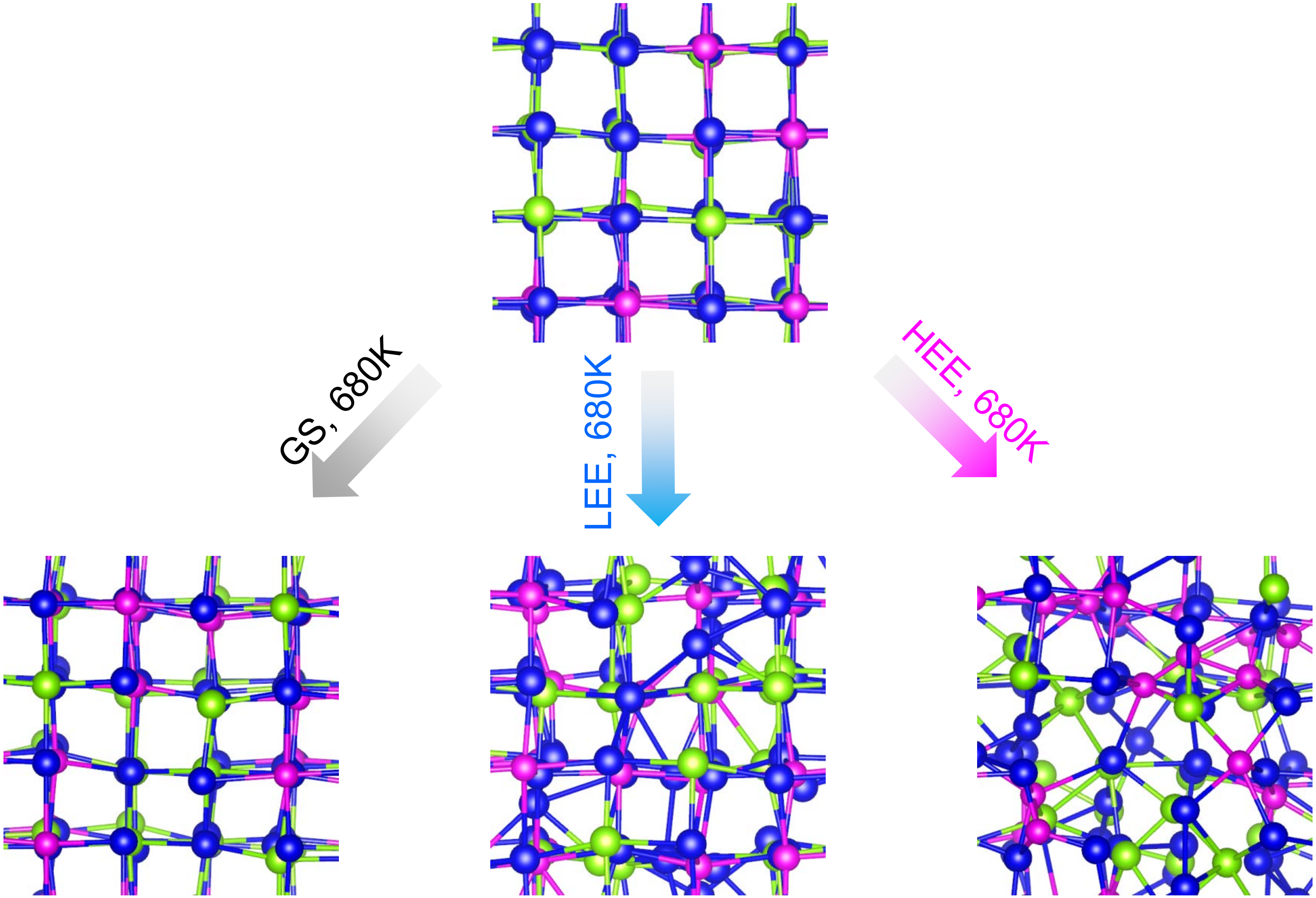
Cation — Anion

(Ge 2 : Sb 2 : Vac. 1) - Te 5

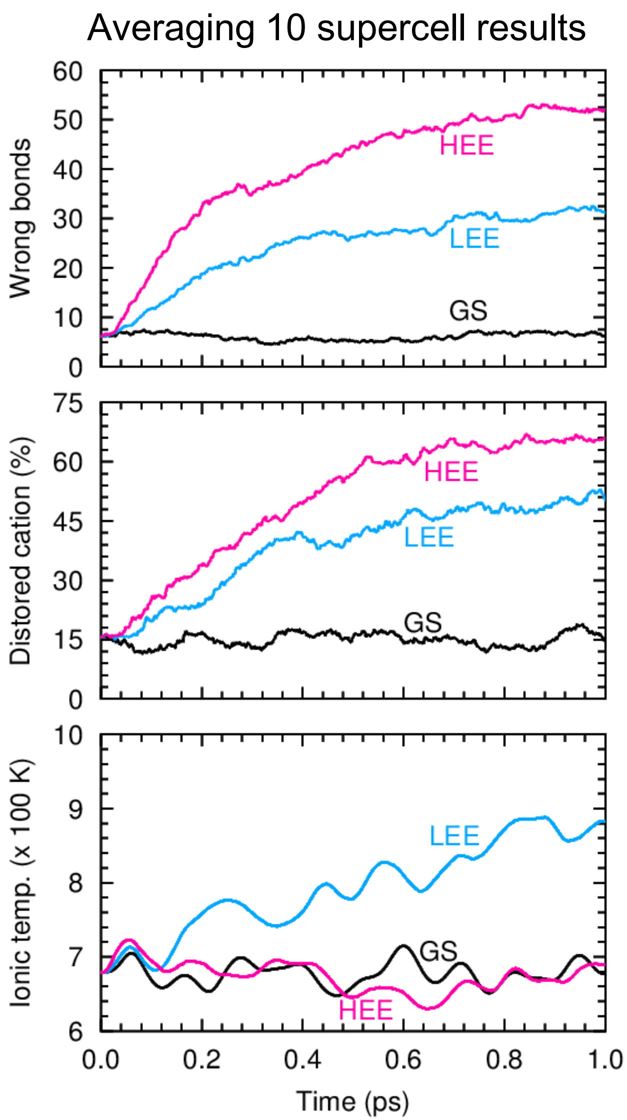




Structure Change by Excited Carriers



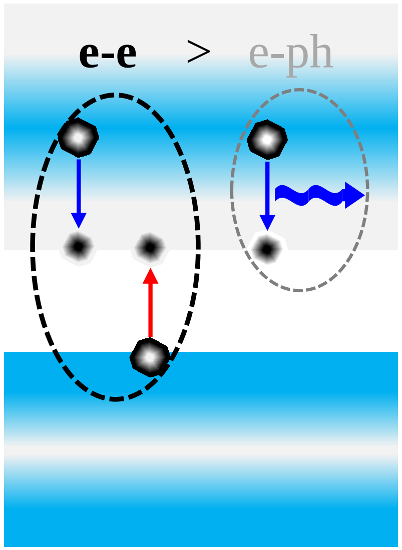
Non-Thermal Phase Transition in GST



Non-thermal effect
in high energy excitation

Carrier Scattering Processes

HEE



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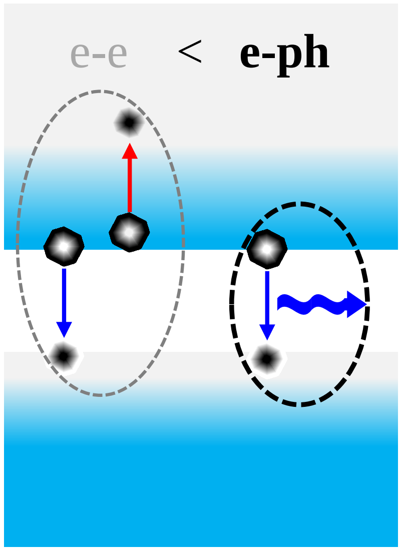
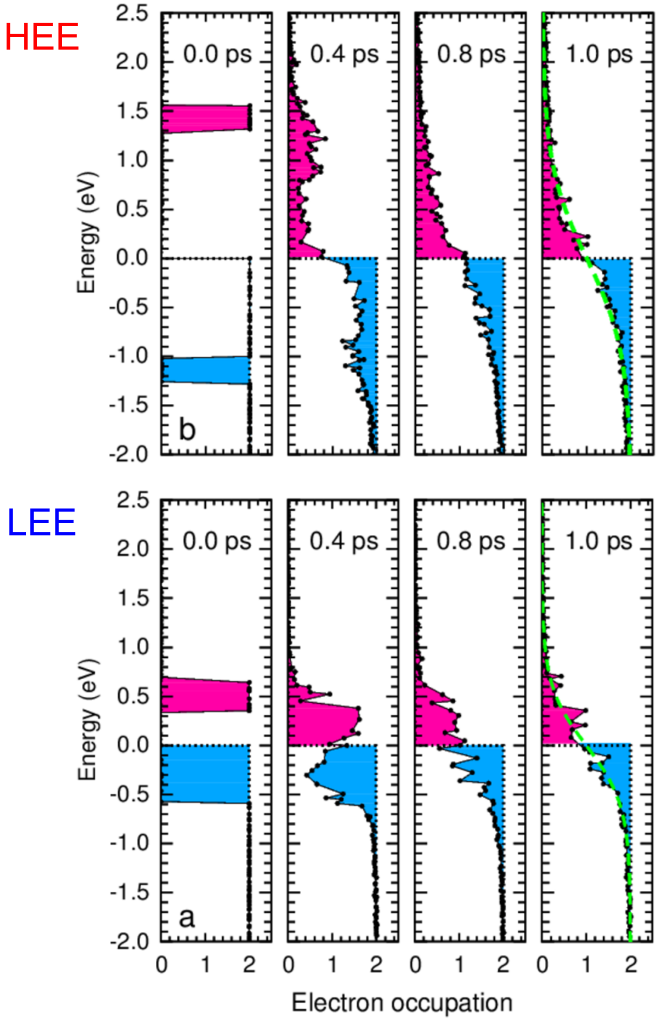
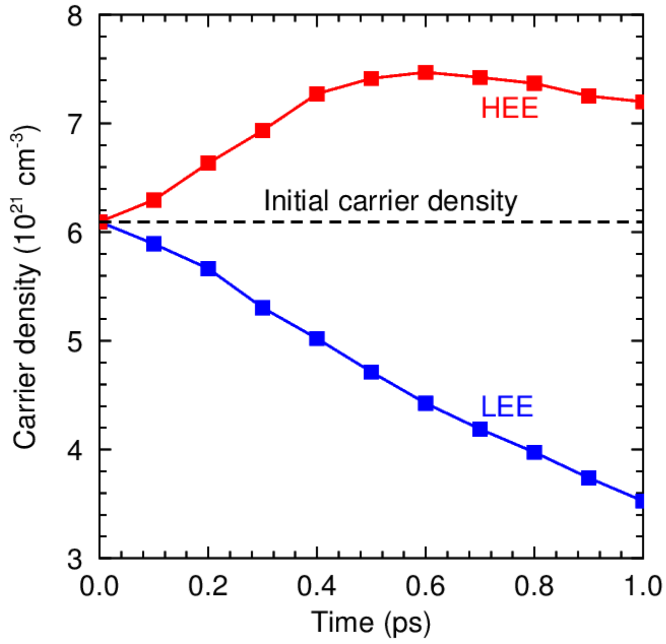
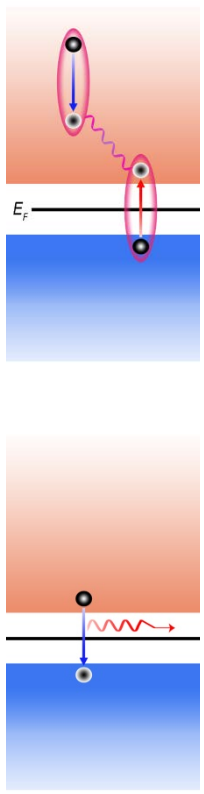


- Pauli blocking:
  "from occupied state to unoccupied state"
- Time scale: e-e coupling > e-ph coupling
- Equilibration: Lowering carrier energy

Carrier Multiplication and Non-Thermal Transition

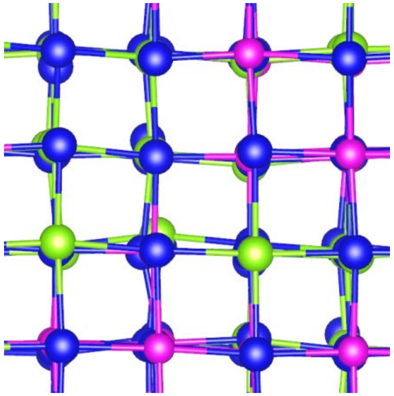






Summary: Energy Dependent Carrier Dynamics and Transitions

- Carrier recombination by strong e-ph coupling
- High ionic temperature
- Thermal phase transition with the aid of excited carriers



- Carrier multiplication by strong e-e coupling
- Low ionic temperature
- Nonthermal phase transition only by electronic effect

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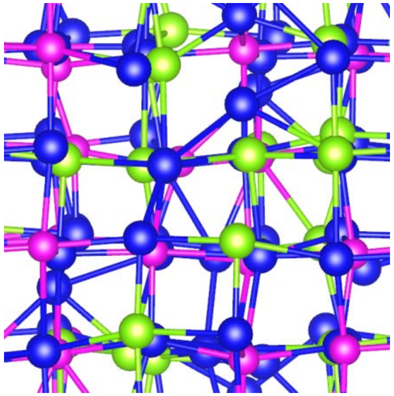

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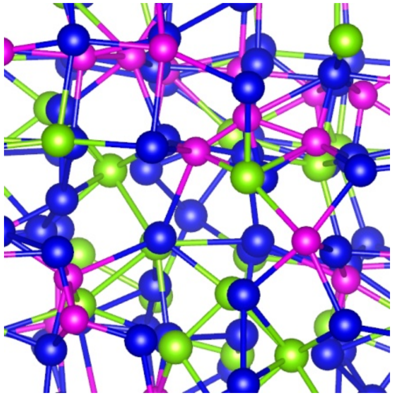


Revised Nonthermal Phase Transition Model

When carriers stay in quasi-equilibrium condition,

phase transition can be caused by a strong modification of the inter-atomic forces owing to excitation of a large fraction of the valence electron to the conduction band.

When carriers are in non-equilibrium condition,

along with the modification of the inter-atomic forces, phase transition can be enhanced by carrier multiplication or thermal activation depending on the carrier dynamics.

The effect of the non-equilibrium dynamics can be important
in small band gap or metallic system

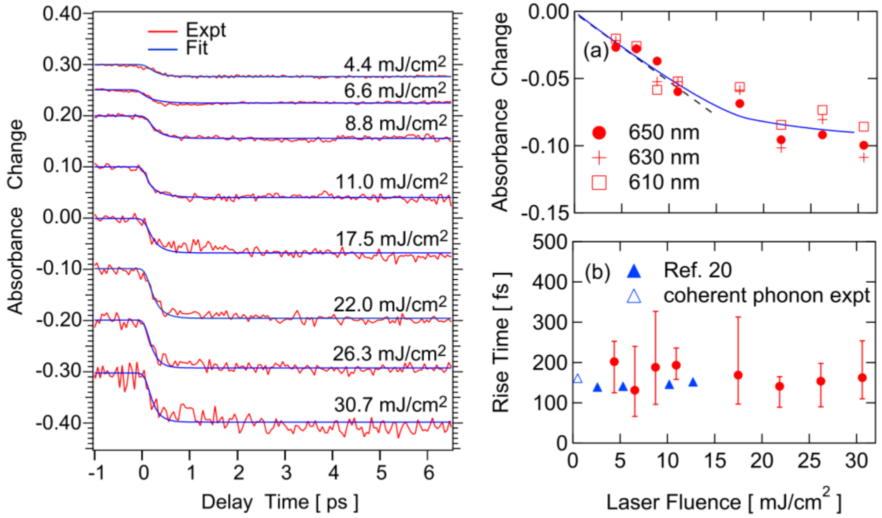
Within 1 ps ...

Evidence of Non-Thermal Effect in Experiments

- Ultrafast phase transition in GST
- Role of carrier density
- Evidence of non-thermal effect

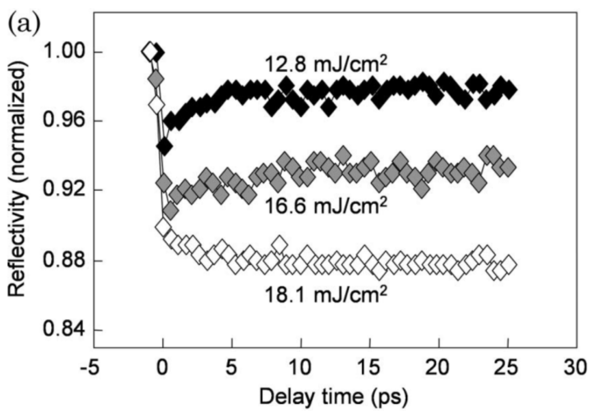
APL **104**, 261903 (2014)

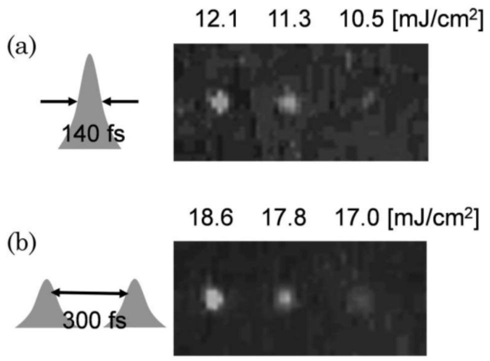
Sample: $Ge_2Sb_2Te_5$ 10 nm thickness

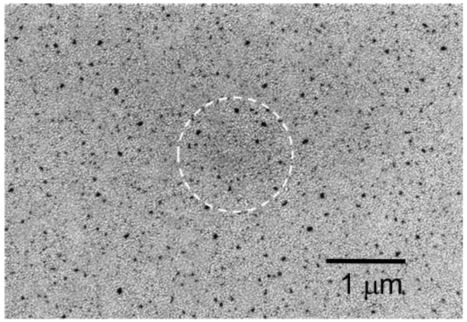


Appl. Opt. **49**, 3470 (2010)

Sample: $Ge_{10}Sb_2Te_{13}$ 20 nm thickness





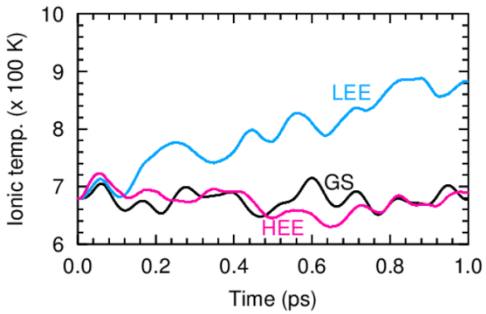


Limitations in Our Method

Ehrenfest dynamics

Spontaneous phonon emission $\langle n \rangle + 1$

Mean-field ionic potential $\langle n \rangle \sim 30$



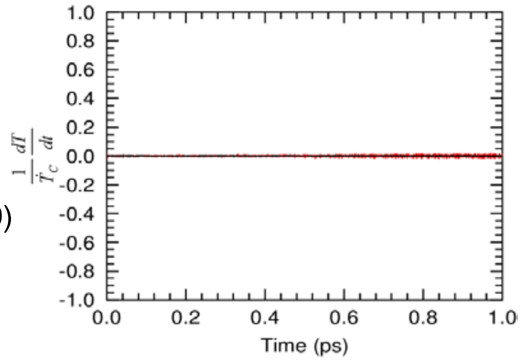
Local density approximation

Memory

$$\frac{dT}{dt} < \dot{T}_C$$

PRA **79**, 052503 (2009)

Band gap



It is currently reasonable approximations,
but it should be confirmed by future methods and experiments!

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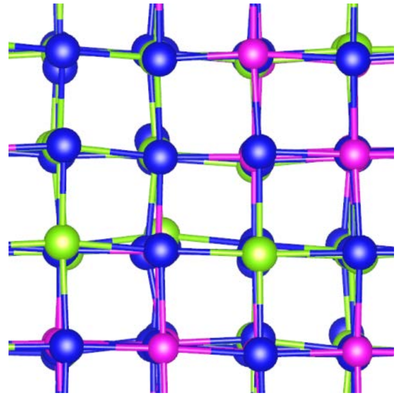

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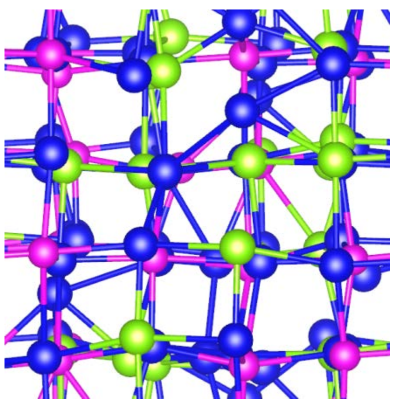

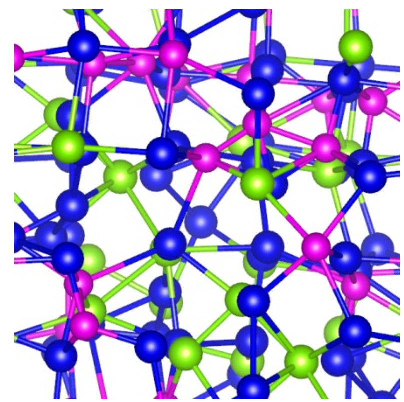

See more details in Phys. Rev. Lett. **117**, 126402 (2016)

Thank you for your attention!