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Simulation of phase change materials for data storage

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Atomistic simulations of phase change materials for data storage

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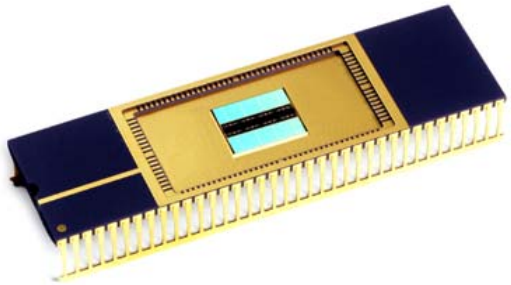
Phase Change Materials for electronic and optical data storage

Optical data storage: DVD



Electronic non-volatile memory: Phase Change Memory Cell

Chalcogenides alloys $Ge_2Sb_2Te_5$ (GST) , GeTe

fast and reversible change between crystalline and amorphous phases (50 ns)

Phase change Materials

Two states system → possibility of storing a "0" or "1" bit

Large difference in properties between the two phases
(crystal - metallic amorphous – semiconducting)

Resistivity changes by 3 orders of magnitude → PCM

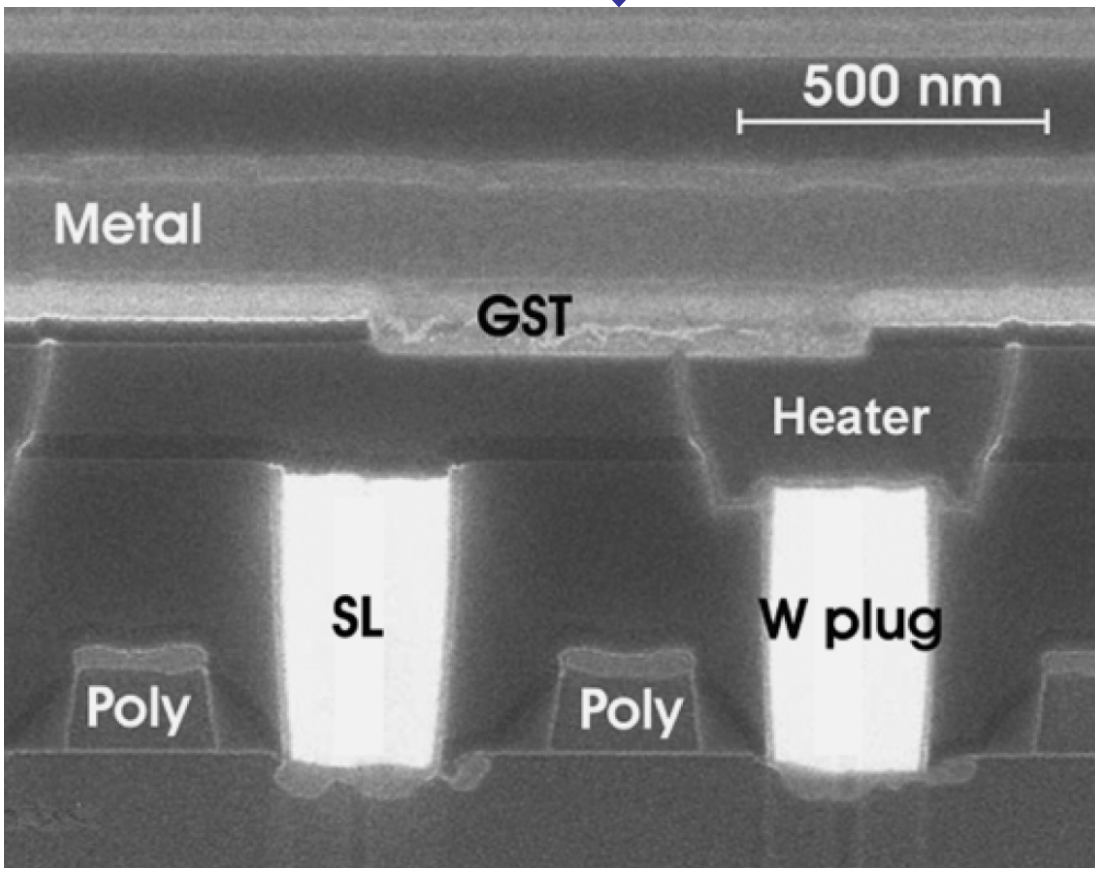
Reflectivity change 30 %: → optical storage (DVD)

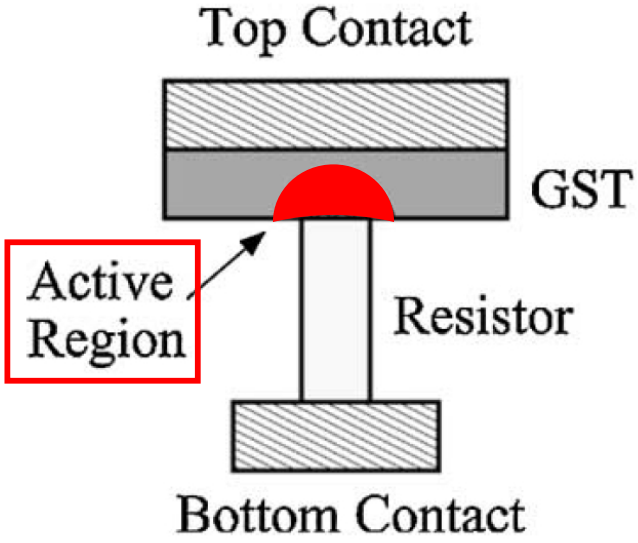
Transition induced by heating (Joule or laser irradiation)

The Phase–Change memory cell

Schematic representation

SEM cross section





- Active region: a small drop within GST film undergoes the phase transition
- Phase–change by heating via Joule effect

Concept first proposed by Ovshinsky in 1968

PCM faster and with better scalability than Flash

April 2010

Numonyx (now bought by Micron) commercialized 90 nm PCM device

Research center based in Agrate Brianza (Milano-Italy)

April 2011

First mobile phone with PCM inside commercialized by Samsung

July 2012

Micron: 45 nm devices in production

Open issues

- Structure of the amorphous phase
- Origin of optical contrast between amorphous and crystal
- Origin of resistivity contrast
- Mechanism of phase change

Wuttig and Yamada, Nat. Mat. 6, 824 (2007)

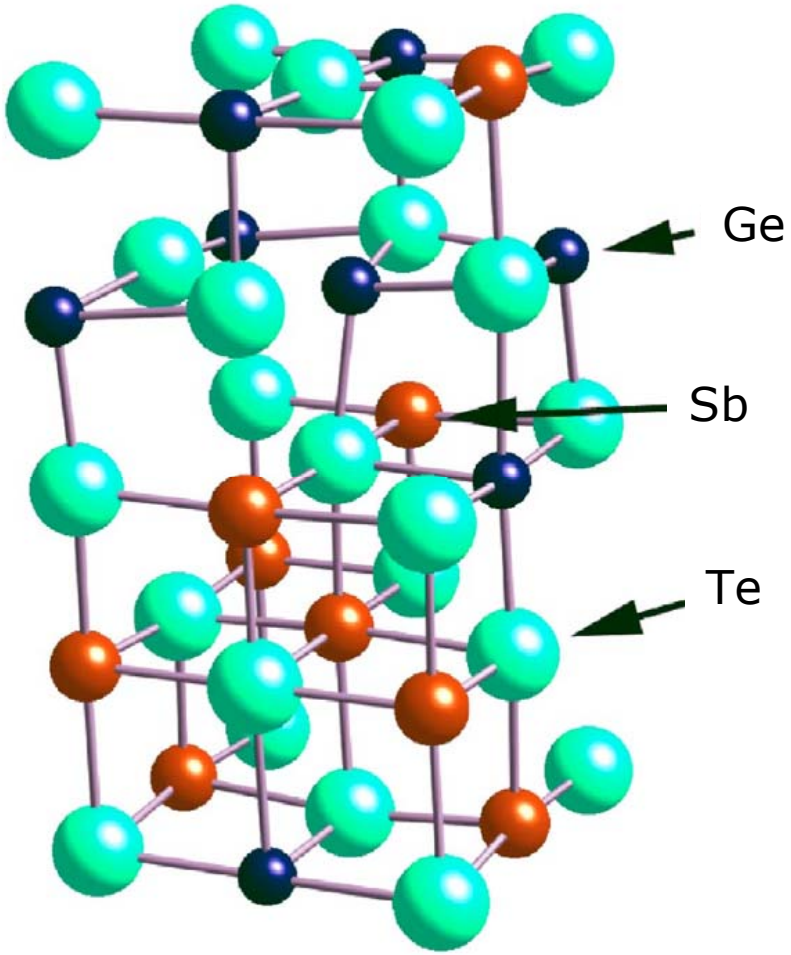
Lacaita and Wouters, Physica Status Solidi A 205, 2281 (2008)

Raoux, Annu. Rev. Mater. Res. 39, 25 (2009)

Raoux , Welnic, Ielmini, Chem. Rev. 110, 240 (2010)

Lencer, Salinga, Wuttig, Adv. Mater. 23, 2030 (2011)

GST crystalline phase: Rocksalt



- NaCl-type

$Ge_2Sb_2Te_5$

- One sublattice fully occupied by Te
- The other randomly occupied by Ge, Sb and 20% vacancies
- Octahedral environment

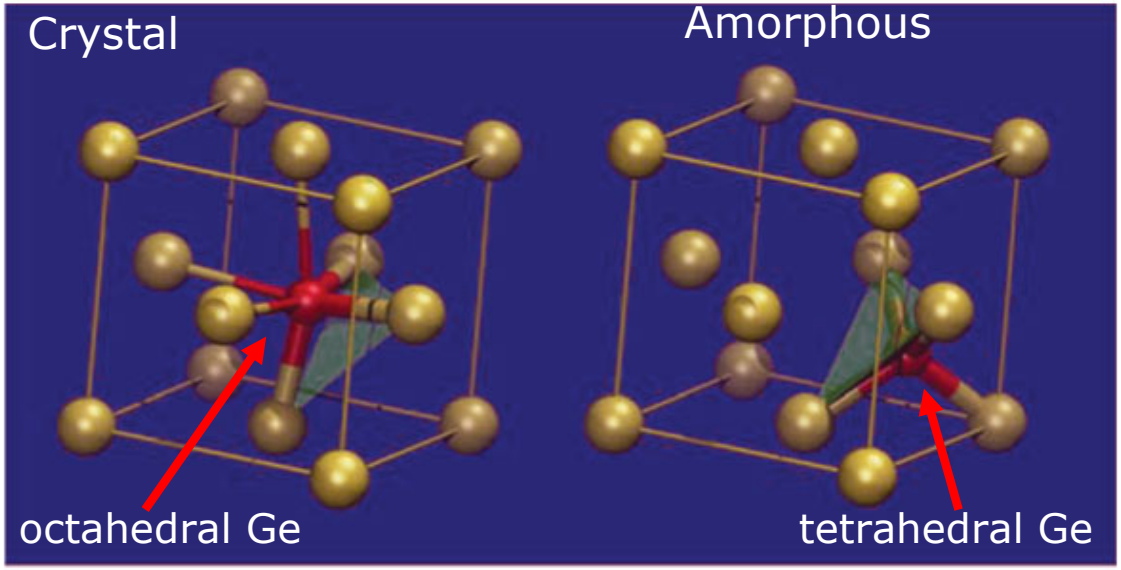
each atom 6-fold coordinated

Metastable phase: transition to hexagonal structure at ~250 °C

Structure of amorphous GST

- EXAFS/XANES data suggest 4-fold Ge coordination
- Ge in tetrahedral environment in amorphous GST
- Phase transition cubic ⇆ amorphous: octahedral ⇆ tetrahedral change of Ge environment

[Kolobov et al., *Nat. Mater.* **3,** 703 (2004)]



Octahedral ⇆ tetrahedral change responsible for electronic and optical contrast

Ab-initio models of amorphous GST

Model of amorphous GST generated by quenching from the melt in ab-initio molecular dynamics

- Caravati, Bernasconi, Kühne, Krack, and Parrinello, Appl. Phys. Lett. 91, 171906 (2007)
- Akola and Jones, Phys. Rev. B 76, 235201 (2007)
- Hegedus and Elliott, Nature Mater. 7, 399 (2008).
- Z. M. Sun et al, Appl. Phys. Lett. 93, 241908 (2008)
- M. Xu et al, Phys. Rev. Lett. 103, 195502 (2009)

Phase Change Materials from First Principles

- First principles molecular dynamics simulations
- Density Functional Theory (GGA-PBE + pseudopotentials)
- Code Quickstep, open source CP2K project www.cp2k.org
  Basis sets: Guassian (wavefunctions) + plane waves (elec. density)

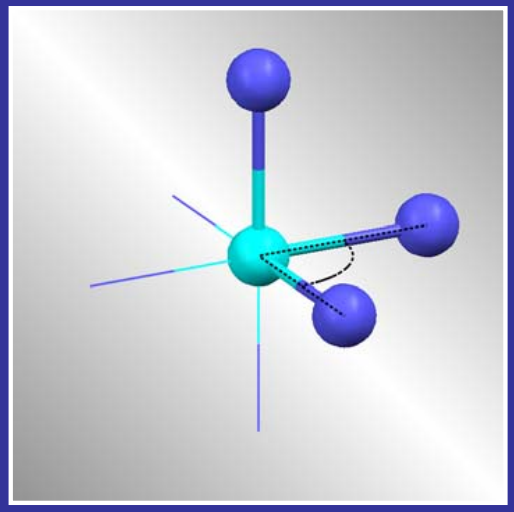
  Second generation Car–Parrinello method
  Factor 25 speed up with respect to conventional BO-MD CP2K
  (Kühne, Krack, Mohamed, Parrinello, PRL 2007)

  270-500 atoms, quenching from the melt in 80-100 ps

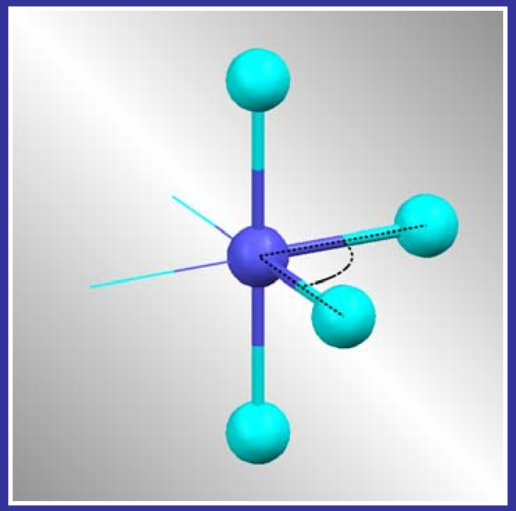
Coexistence of octahedra and tetrahedra in amorphous PCM

(defective) octahedral
Ge, Sb and Te

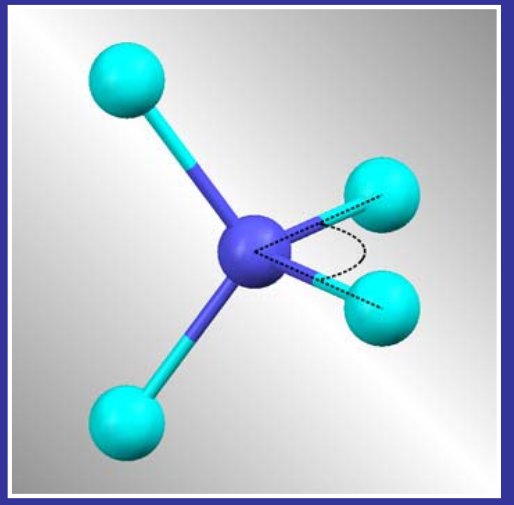
3–coor Te



4–coor Ge



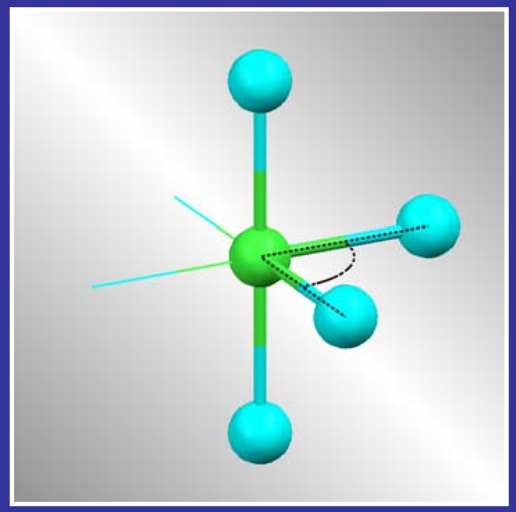
tetrahedral
4–coor Ge, 25 %



3+1 coordination

→p-bonding

only p valence states



4–coor Sb

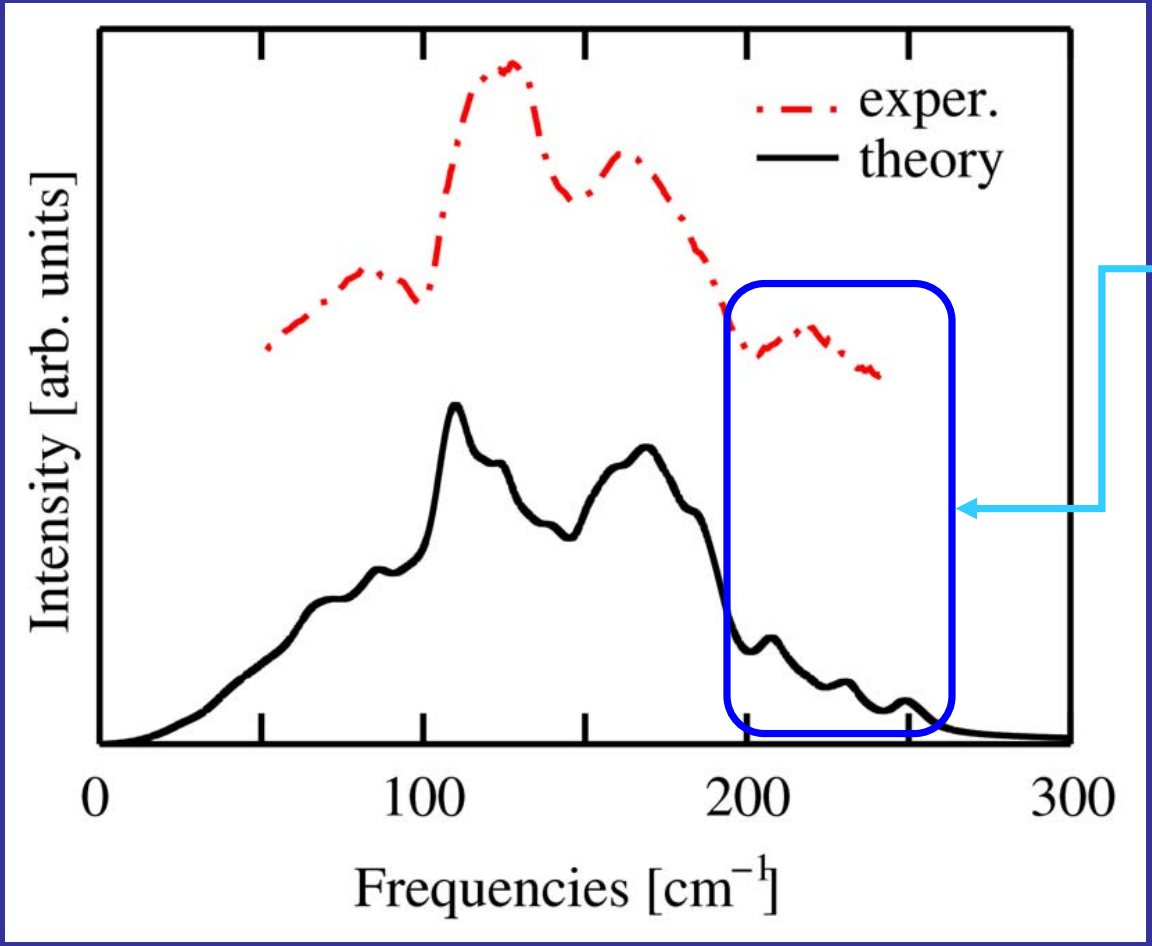
sp^3 bonding

s + p valence states

Caravati, Bernasconi, Kuhne, Krack, Parrinello, APL 2007

Tetrahedral Ge: vibrational fingerprint

Amorphous GeTe: Raman spectrum (Bond Polarizabilty Model)



Phonon freq. > 190 cm^{-1}:

- Localized on tetrahedral Ge

⇨ signature of tetrahedral Ge

Exp: Andrikopolous et al J. Phys. Chem. Solids (2007); De Bastiani et al PRB (2009).

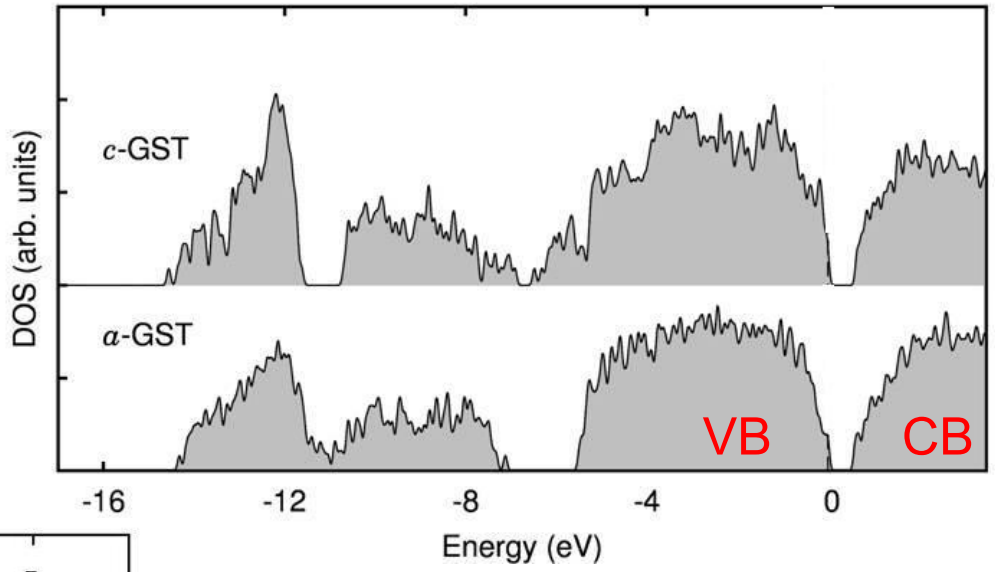
Mazzarello, Caravati, Angioletti, Bernasconi, Parrinello

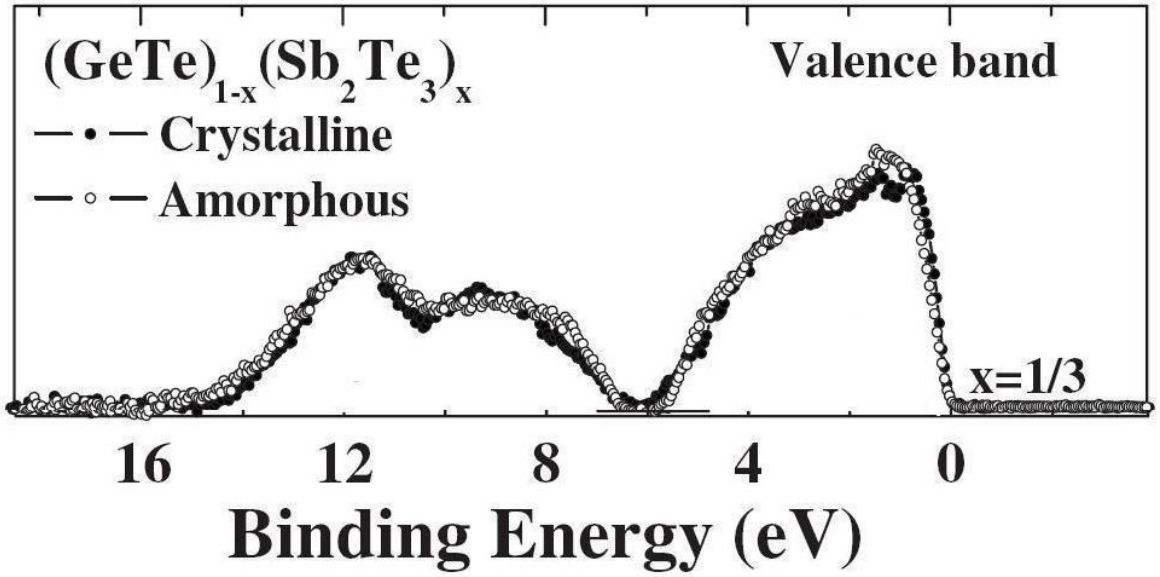
Phys. Rev. Lett. 104, 085503 (2010)

Electronic properties

Electronic Density of States very similar in amorphous and crystalline phases

Theory





Exp. Photoemission

J-J. Kim et al, PRB 07

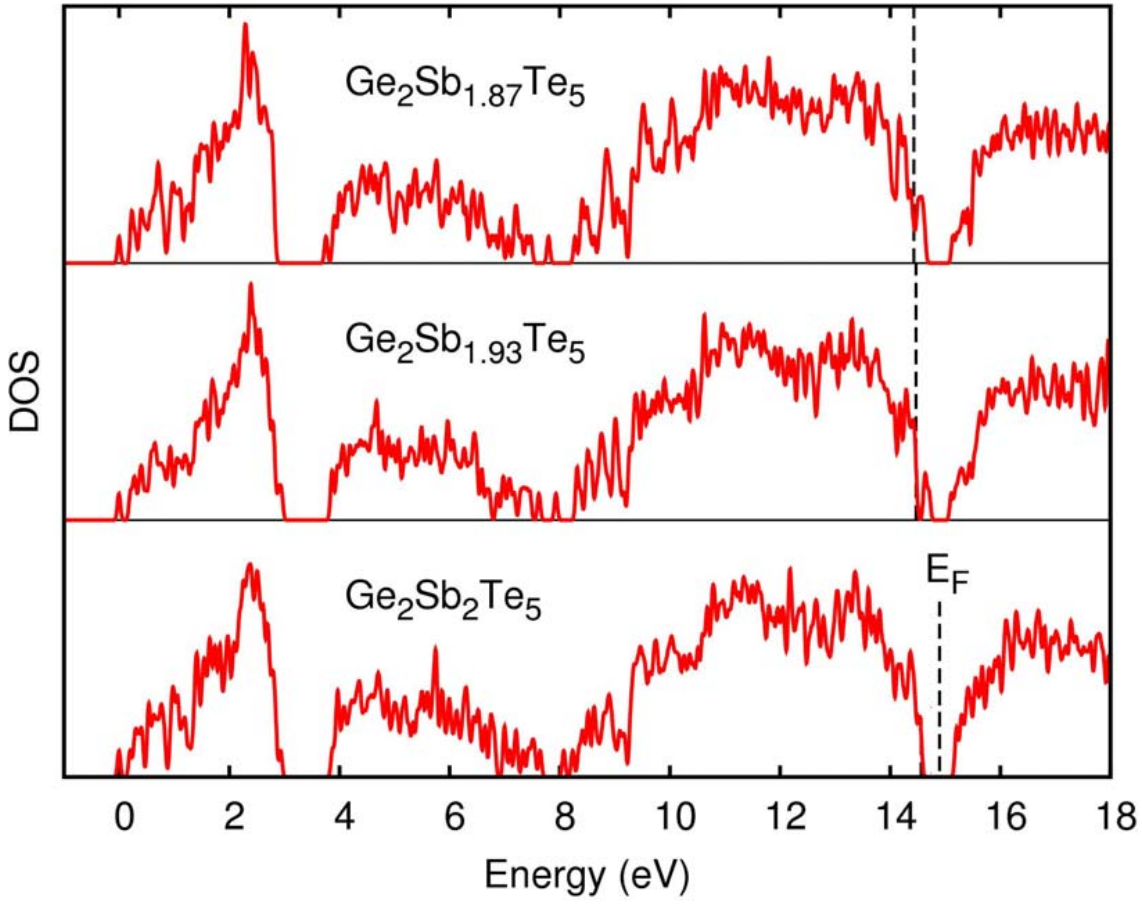
Optical Tauc gap:

c-GST → 0.5 eV

a-GST → 0.7 eV

Electronic properties: cubic crystal

GST stoichiometric crystal is semiconducting



Ge/Sb deficiency: → holes in VB

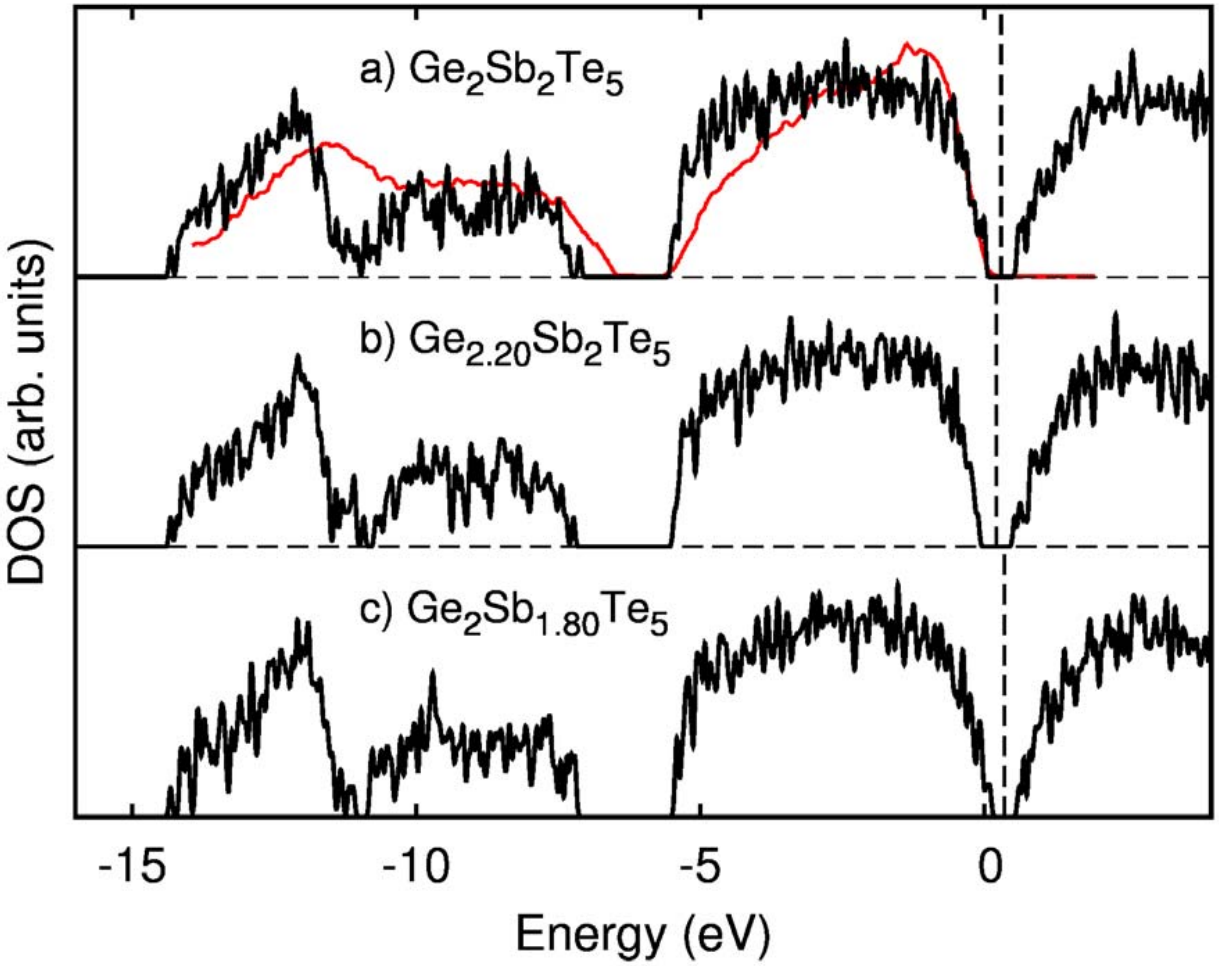
Ge/Sb excess: → electrons in CB

HSE hybrid functional

Degenerate p-type semiconductor due to Sb deficiency

Electronic Properties

Non-stoichiometric GST: amorphous phase



Crystal can be doped

Amorphous can not

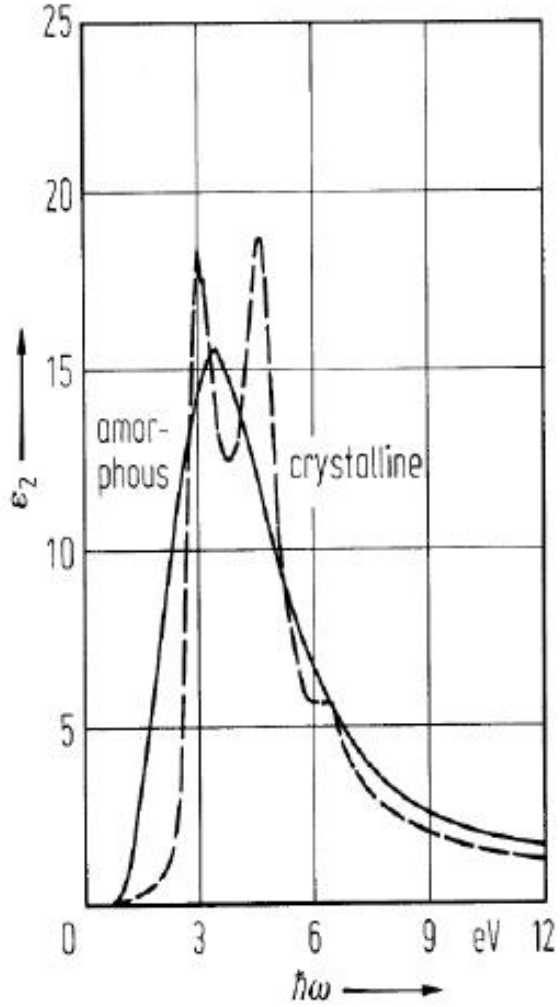
This explains electronic contrast (PCM)

Ge excess, Sb deficiency → E_f at midgap

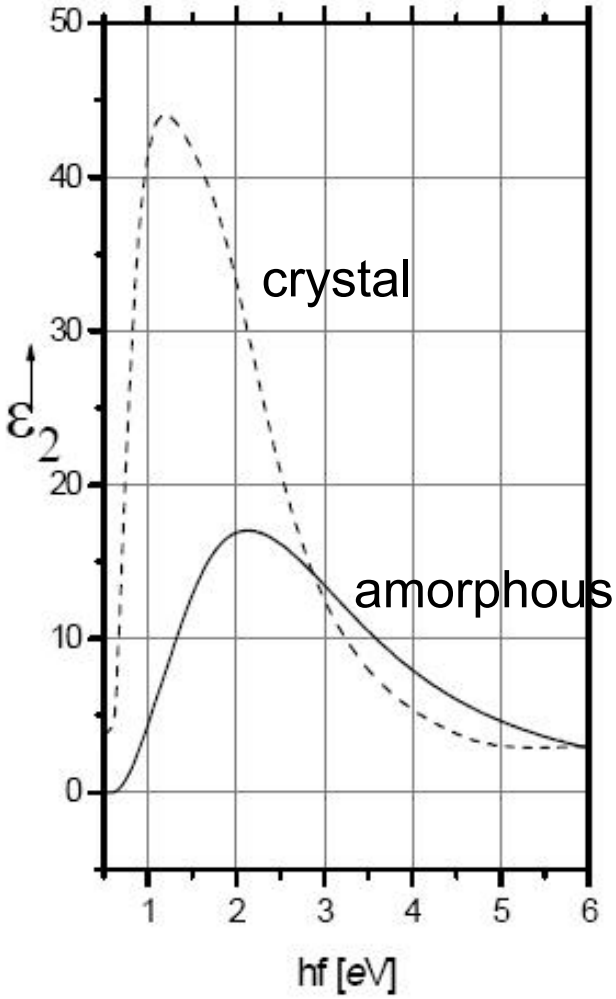
Caravati, MB, et al, J. Phys. Cond. Matt. 21, 255501 (2009)

Optical contrast between amorphous and crystal

GaAs



$Ge_2Sb_2Te_5$



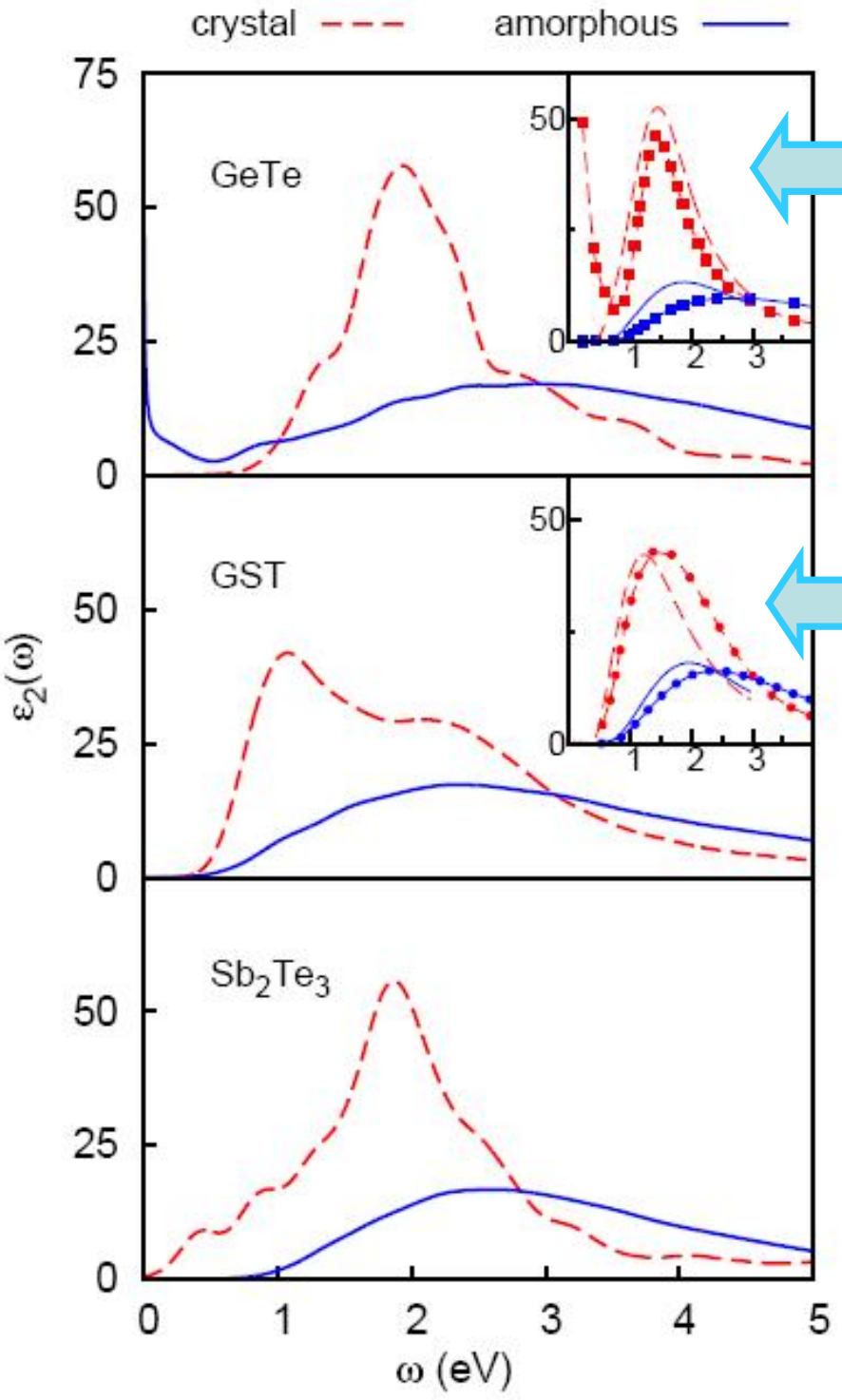
Optical constrast in PCM due to change in optical matrix elements

$$\epsilon_2(\omega) = \frac{8\pi^2}{3V_o N_{\mathbf{k}} \omega^2} \sum_{v,c,\mathbf{k}} |\langle c,\mathbf{k}|\mathbf{p}|v,\mathbf{k}\rangle|^2 \delta(\omega - E_{c,\mathbf{k}} + E_{v,\mathbf{k}})$$

- Presence of Ge tetrahedra
  (Welnic, Botti, Reining, Wuttig, PRL 2007)

- Angular disorder in p-bonding in amorphous phase
  Resonant valence bonds present in crystal and lost in amorphous

  Shportko, et al., Nat. Mat. 2008
  Huang and Robertson, PRB 2010



Exp. (Welnic 2007; Shportko 2008)

Optical contrast in PCM

Exp. (Welnic 2007; Orava 2008)

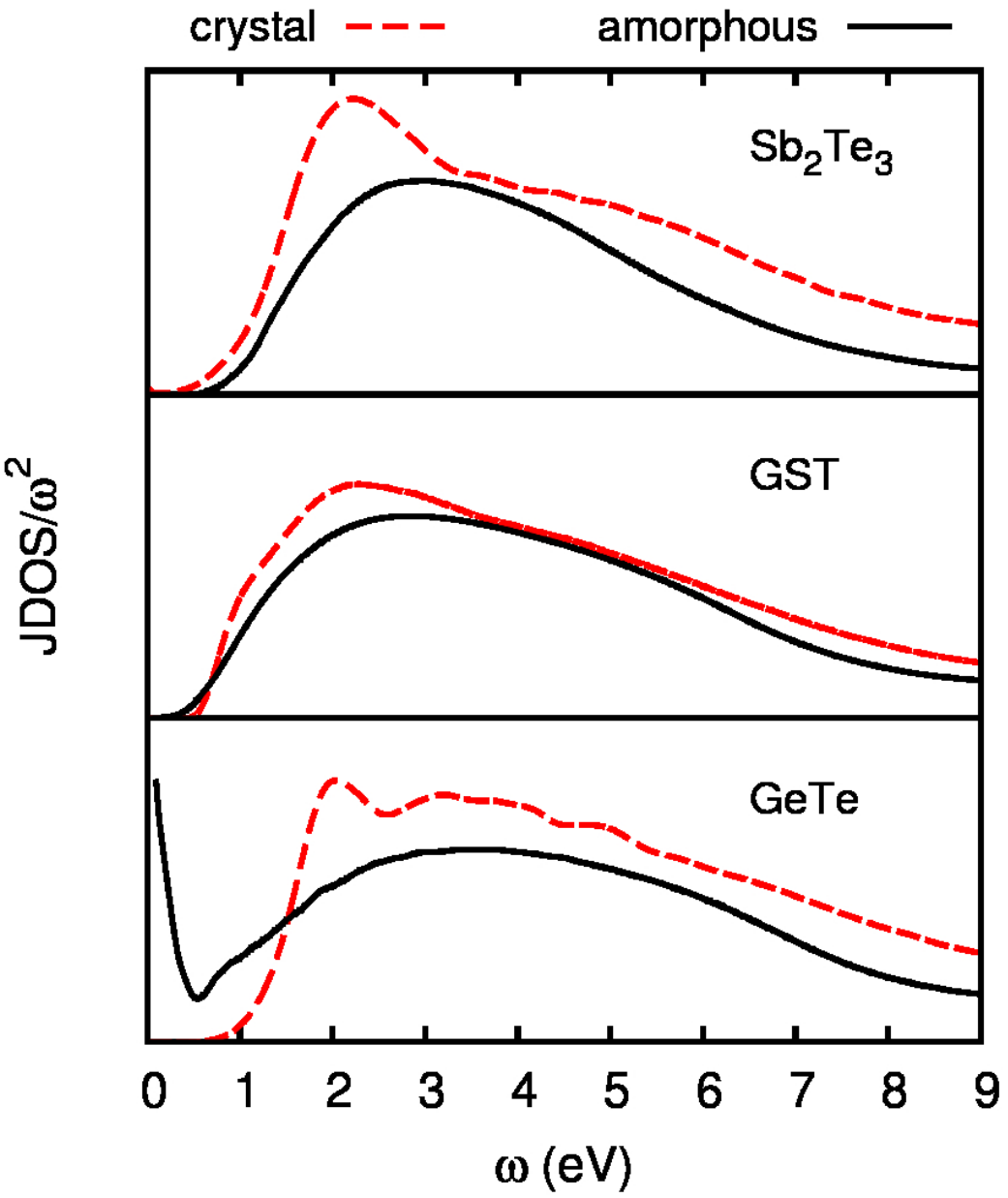
$\varepsilon_2(\omega)$ dielectric function

in RPA with hybrid functional HSE

Caravati, Bernasconi, Parrinello

J. Phys. Cond. Matt. 22, 315801 (2010)

Joint Density of States



(Huang and Robertson PRB 2010)

Angular disorder in p-bonds in amorphous phases

decrease of the optical matrix elements

optical contrast

This explains why DVDs work

Open issues

- Structure of the amorphous phase ✓
- Origin of resistivity contrast ✓
- Origin of optical contrast ✓

Origin of high crystallization speed

large simulations cells and long simulations time needed!

Large scale atomistic simulations of PCM

DFT results as database to develop interatomic potentials based on Neural Network to simulate 10^3 atoms for 10 ns

(Behler and Parrinello PRL 2007)

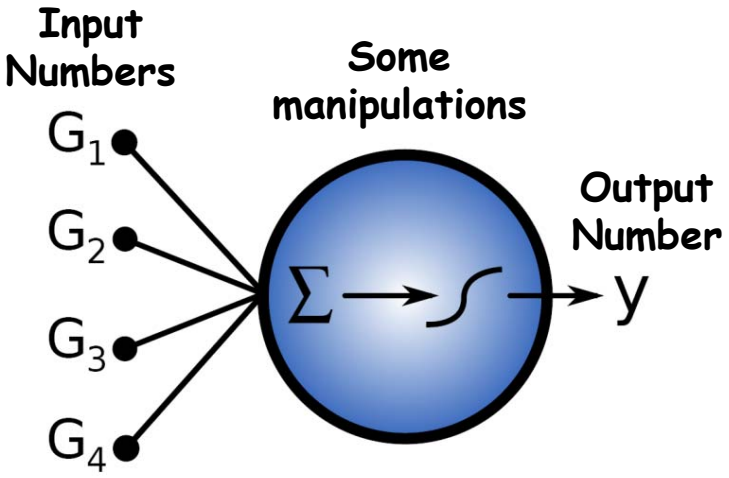
already applied to elemental carbon, silicon, sodium, ZnO

Neural Networks – Symmetry Functions

Total energy as sum of atomic energies $E=\Sigma_i E_i$

$$E_i = F(\{G(\bar{r})\})$$

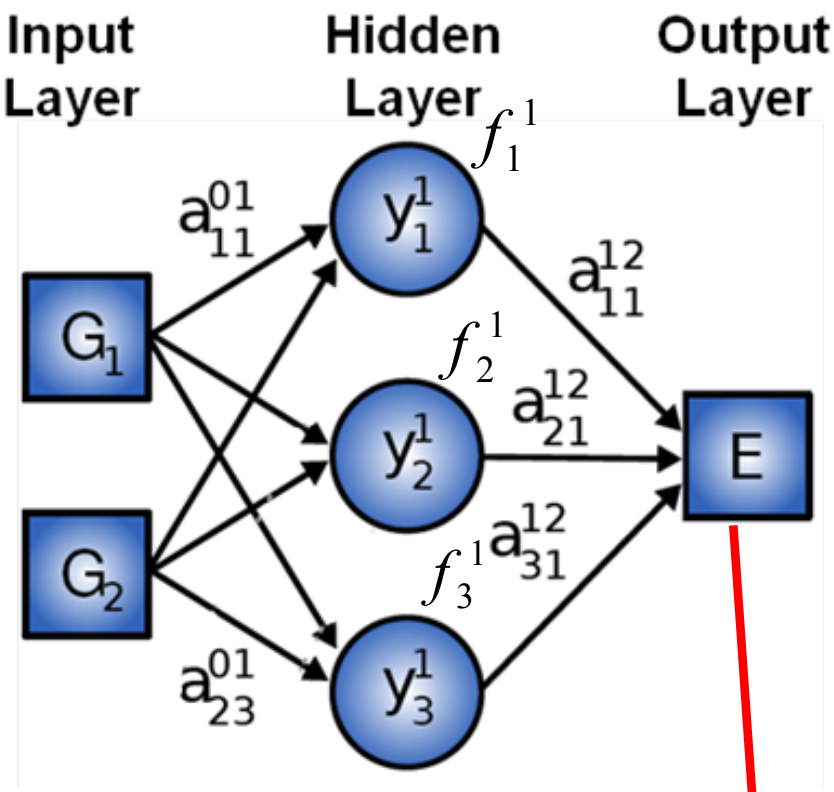
Symmetry functions {G}:
information on local atomic environment up to a certain cutoff radius



F is EXTREMELY complicated, but it IS analytic!

Input numbers: functions of atomic positions (symmetry functions)
Some manipulations: linear and non-linear combinations of input numbers
Output number: energy of the input configuration

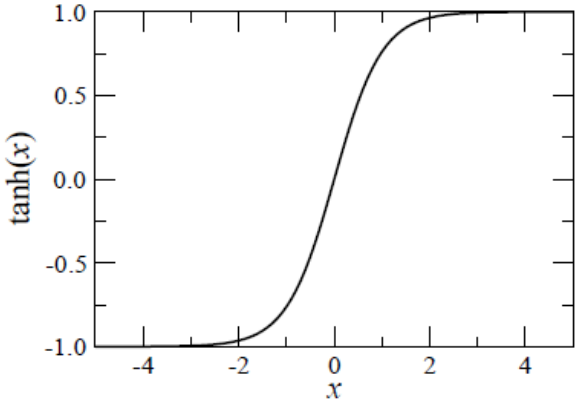
Neural Networks - The algorithm



A (VERY) simple example:

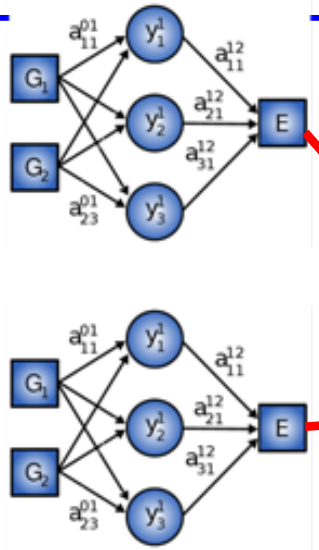
$$E_{atom} = f_1^2\left(b_1^2 + \sum_{j=1}^{3} a_{j1}^{12} \cdot f_j^1\underbrace{\left(b_j^1 + \sum_{i=1}^{2} G_i \cdot a_{ij}^{01}\right)}_{y_j^1}\right)$$

a_i^j , b_i^j = fitting parameters
G_i = Symmetry Functions
f_i^j = Activation Functions



another atom...

N other atoms!



Σ -> Total energy!

Neural Networks – GeTe

Building of the Neural Network Potential

159 symmetry functions for each atom
NN topology: 3 hidden layers of 20 nodes each
About 8000 fitting parameters.
No long range interactions
Code RuNNer (Bochum) + DL_Poly

DFT-PBE calculations of selected structures for NN fitting

(Quantum-Espresso code)

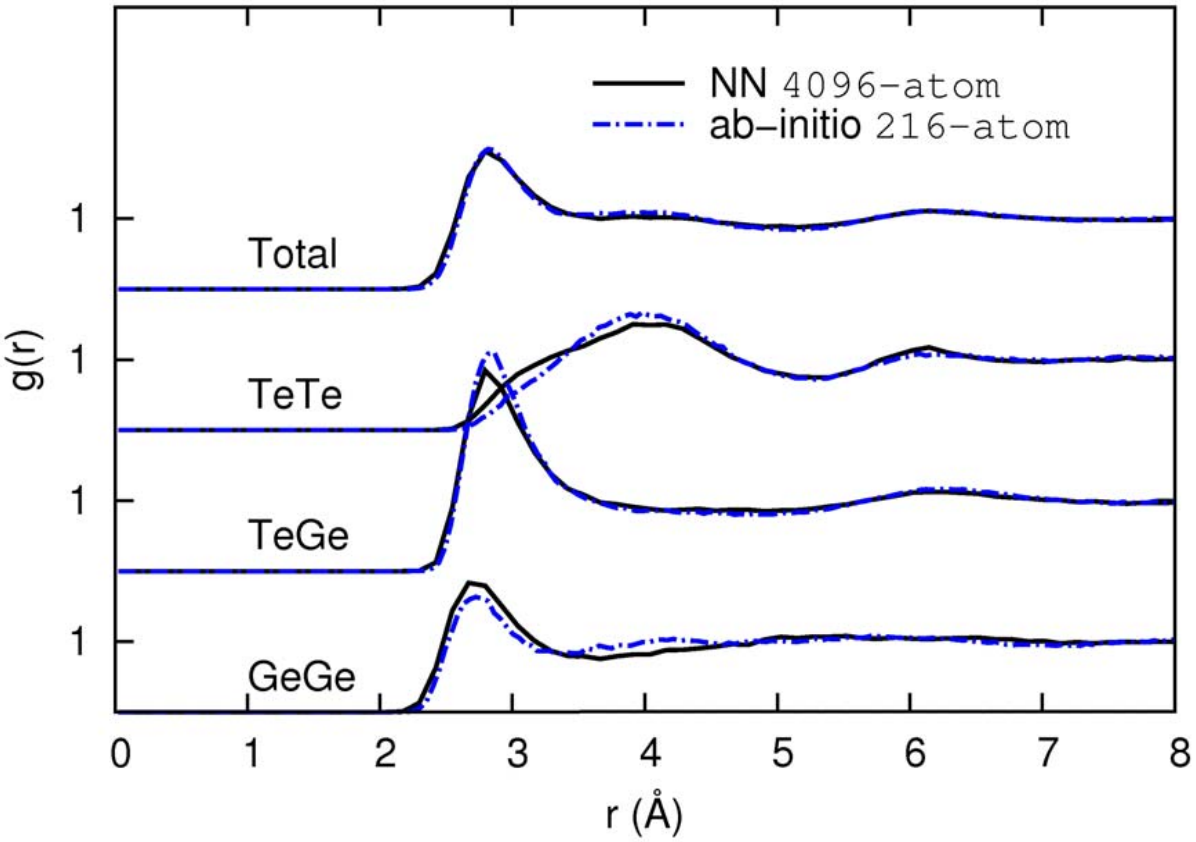
energy of 30000 structures (64- 128-atom cells, PBC) of crystalline, liquid and amorphous phases of GeTe at normal conditions and high pressure

DFT simulations of liquid and amorphous GeTe

216-atom cells CP2k code

Neural Network: liquid GeTe

pair correlation functions



NN: 4096-atom cell

Sosso, MB, et al. PRB 2012

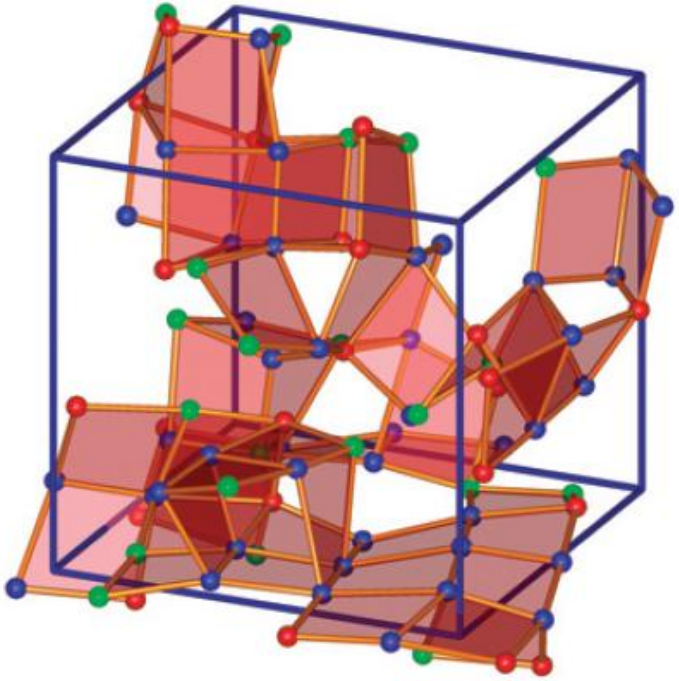
Diffusion coefficient

D= 4.29 10^{-5} cm^2/s

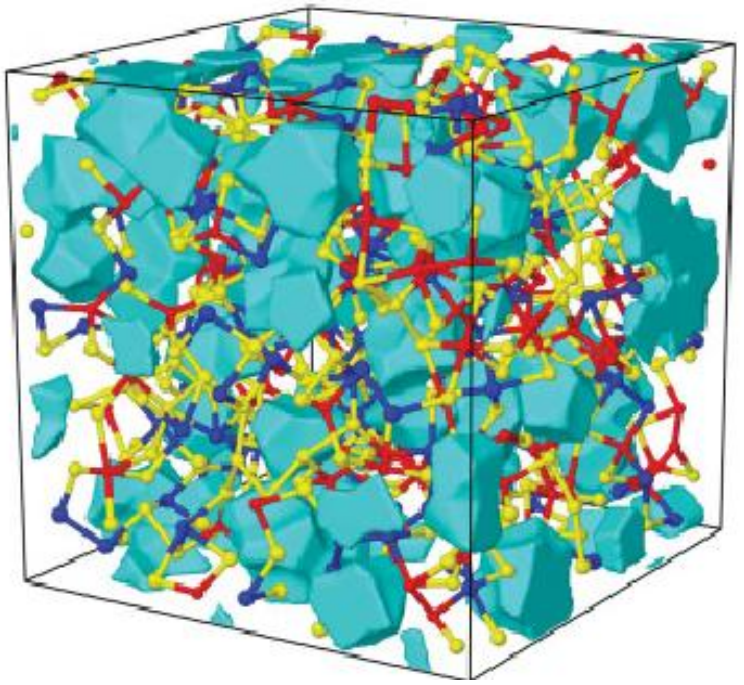
(DFT 4.29 10^{-5} cm^2/s)

NN 10^4 faster than DFT for 4000 atoms

Origin of fast crystallization of phase change materials



a-GST



Rings

(Hegedus, Elliott Nat Mat 2008)

Cavities

(Akola and Jones PRB 2007)

but what's about the supercooled liquid?

Classical nucleation theory

Nucleation rate $I_{ss} \propto D \exp(-G_c/(k_B T))$

D = diffusion coefficient

Free energy critical nucleus $G_c = 16\pi\sigma^3/(3\Delta\mu^2)$

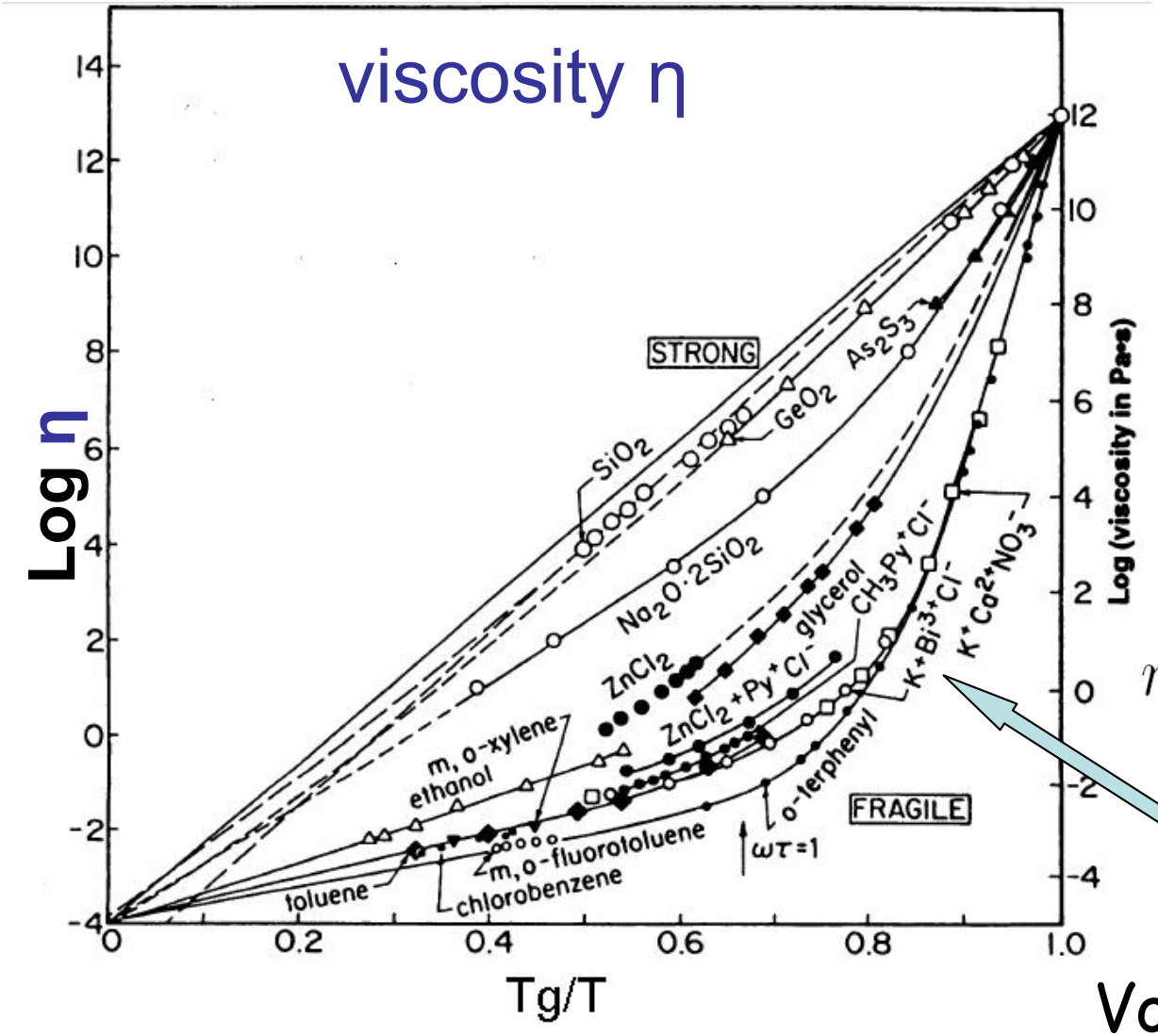
$\Delta\mu$ = free energy difference liquid & cryst

driving force for crystallization

Crystal growth speed $u \propto D(1 - e^{-\frac{\Delta\mu}{k_B T}})$

Supercooled liquids: fragile or strong

Angell, Science 267, 1924 (1995)



fragility index

Silica m =15

PVC m=195

$$m = d(log_{10}\eta)/d(T_g/T)\ |_{T=T_g}$$

$$\eta \sim e^{\frac{1}{A(T-T_k)}}$$

Vogel-Tammann-Fulcher

Are phase change materials fragile liquids?

NN molecular dynamics simulation of supercooled liquid GeTe

4096-atom cell

Simulation time of 2 ns

Melting temperature

Thermodynamic integration for free energy

$$F_{NN} - F_{ref} = \int_0^1 d\lambda \langle U(\lambda) \rangle \qquad U(\lambda) = \lambda U_{NN} + (1-\lambda) U_{ref}$$

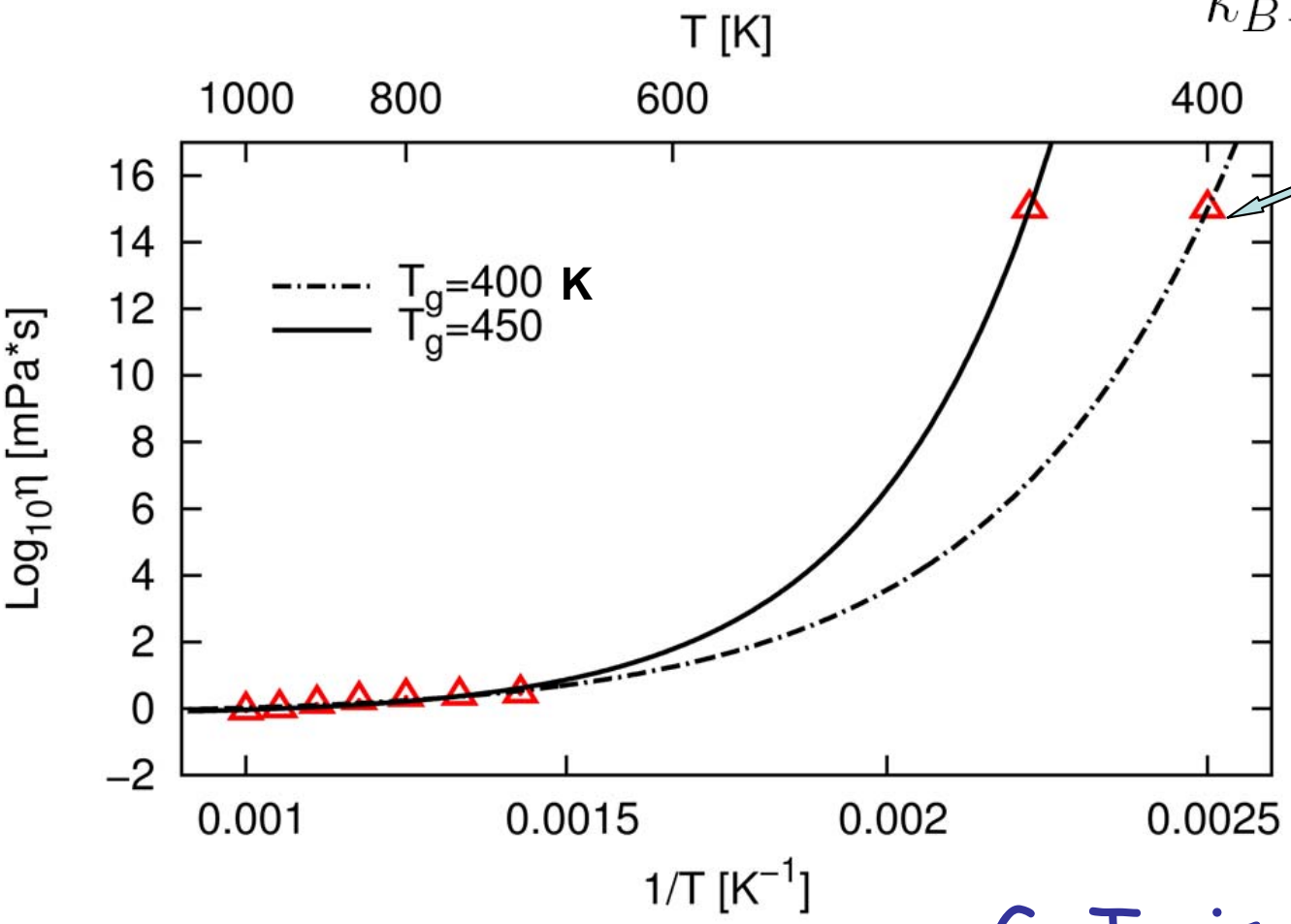
reference = harmonic crystal or LJ fluid

$$\mu_{liquid}(P, T_m) = \mu_{cryst}(P, T_m)$$

T_m =1001 K exp. 998 K GeTe

Viscosity of supercooled liquid GeTe

Green-Kubo $\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{xy}(t)\sigma_{xy}(0)\rangle dt$



T_g

modified VTF

(Mauroa PNAS 2009)

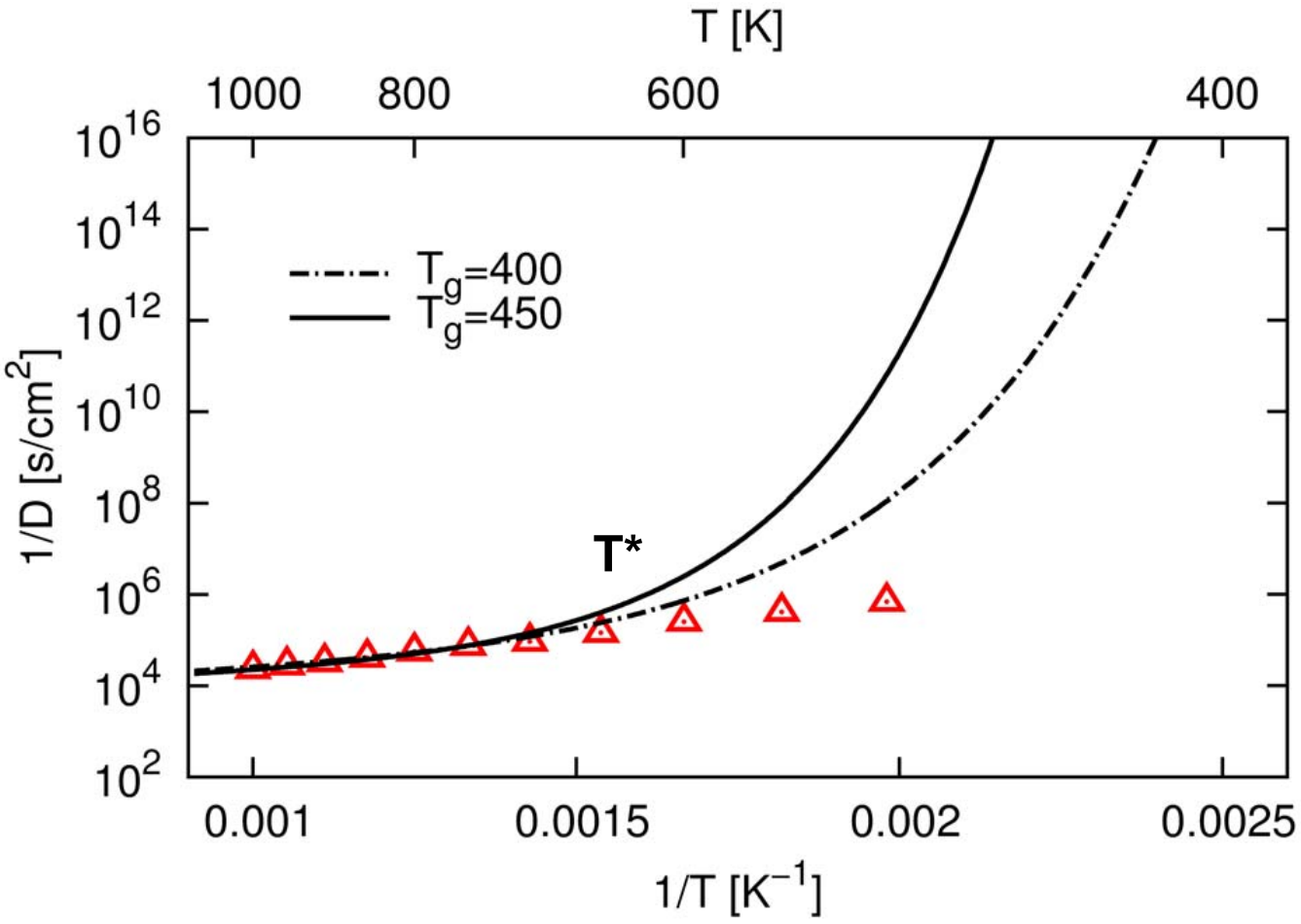
fragility index m=104

(Silica =15, PVC =195)

GeTe is a fragile liquid !

Sosso, Behler, Bernasconi, Phys. Stat. Sol. B 249, 1880 (2012) and submitted

Breakdown of Stokes-Einstein relation



$$D \propto \frac{T}{\eta}$$

not valid for

T < T*

$$D = 10^{-6} cm^2/s$$

at 500 K

Self diffusion coefficient D computed from mean square displ. over 50 ps

Decoupling of diffusivity from viscosity in fragile GeTe liquid

Fast crystallization of amorphous just above Tg

high diffusivity (fragility and breakdown of Stokes-Einstein) at high supercooling

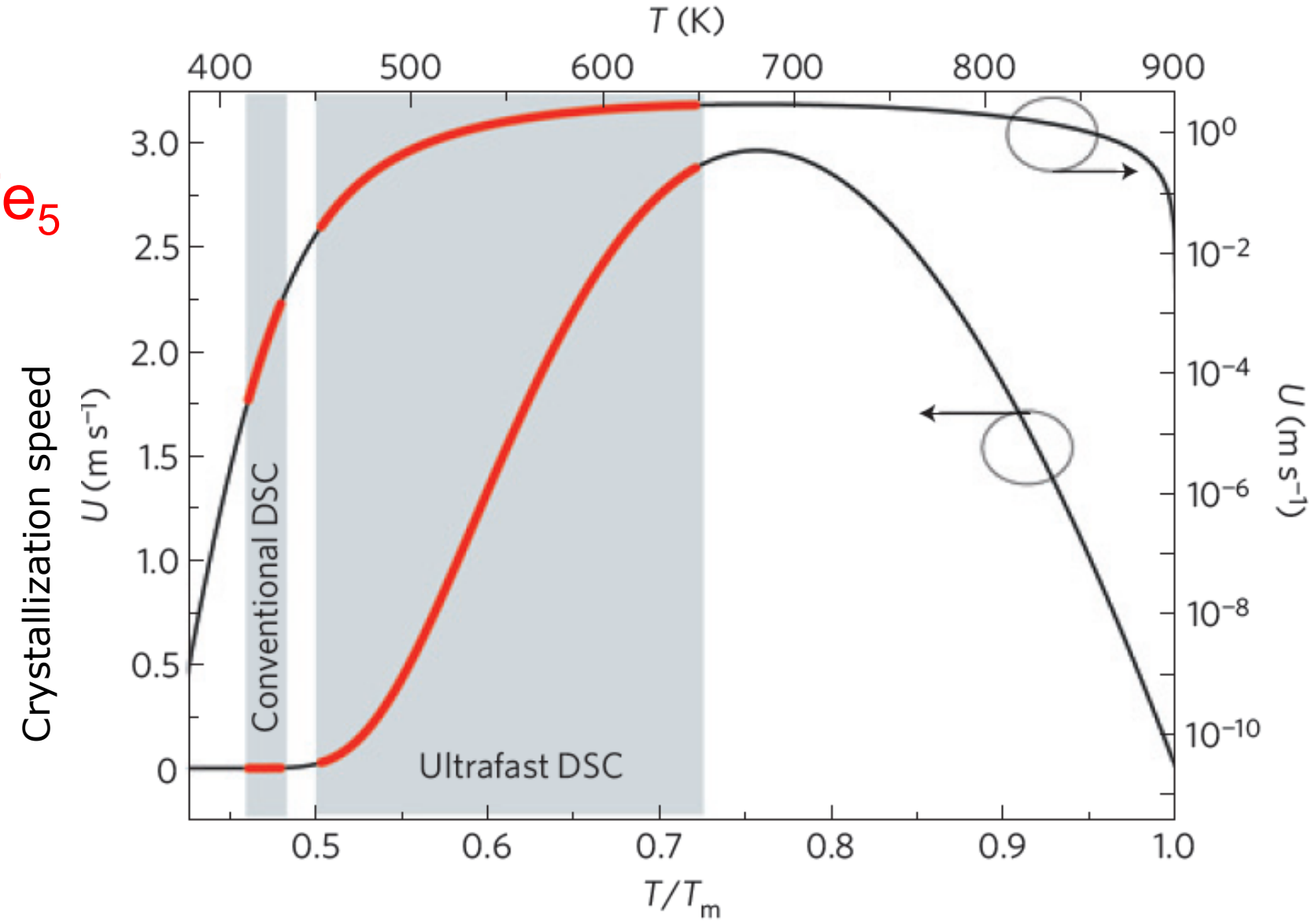
both large self-diffusion coefficient D and

large $\Delta\mu$ driving force for crystallization

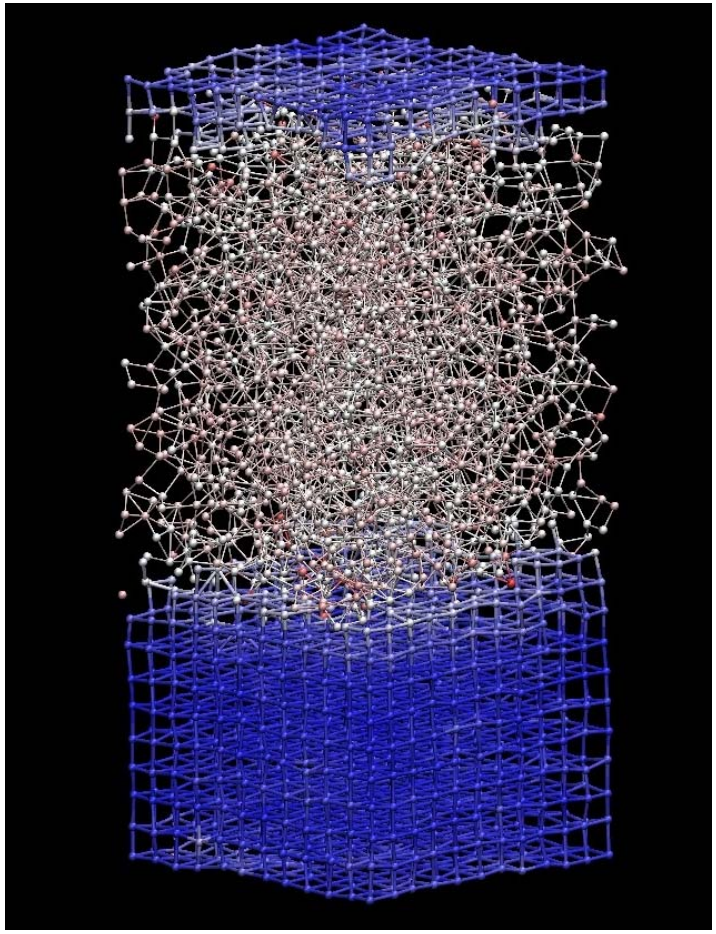
Ultrafast DSC (10^4 K/s)

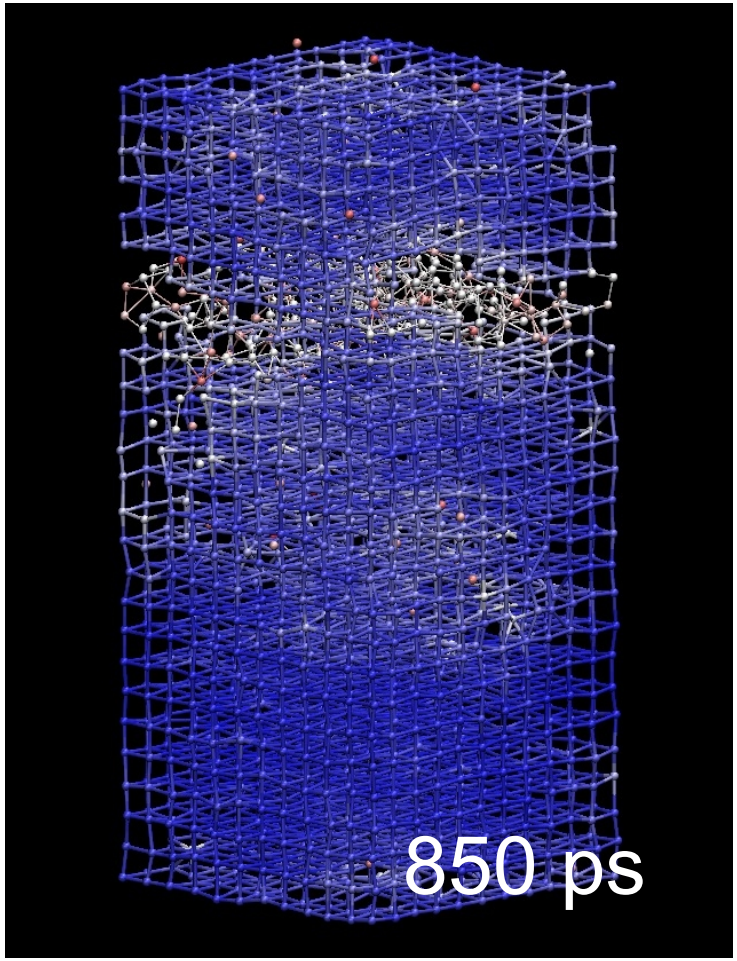
Orava, Greer et al, Nat. Mat. 11, 279 (12)

$Ge_2Sb_2Te_5$



Crystallization of supercooled GeTe at the liquid-amorphous interface





T= 600 K speed of crystal growth 2 m/s

Coworkers

Milano-Bicocca: G. Sosso,E. Spreafico,D. Colleoni,D. Mandelli
G. Miceli, S. Gabardi, S. Angioletti-Uberti

ETHZ, USI Lugano: S. Caravati, M. Parrinello

PSI-Villigen: M. Krack

Aachen University: R. Mazzarello

Bochum University: J. Behler

Mainz University: T. Kühne

Experimental colleagues at Micron (Agrate-Brianza)

Thank you for attention !

Publications

Caravati et al, Appl. Phys. Lett. 91, 171906 (2007);
Phys. Rev. Lett. 102, 205502 (2009) ; Phys. Rev. B 81, 014201 (2010) ;
J. Phys. Cond. Matt. 21, 255501 (2009); 22, 315801 (2010);
J. Phys. Cond. Matt. 23, 265801 (2011).

Sosso et al, J. Phys. Cond. Matt. 21, 095410 (2009); 21, 245401 (2009);
Phys. Rev. B 83, 134201 (2011); Phys. Rev. B 85, 174103 (2012);
Phys. Rev. B 86, 104301 (2012); Phys. Stat. Sol. B, 249, 1880 (2012).

Spreafico et al, Phys. Rev. B 83, 144205 (2011).

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Gabardi et al, J. Phys. Cond. Matt. 24, 385803 (2012).

Mandelli et al. Phys. Stat. Sol. B, 249, 2140 (2012).