Ab-initio simulation of phase change materials

Marco Bernasconi

Department of Materials Science
University of Milano-Bicocca, Milano, Italy

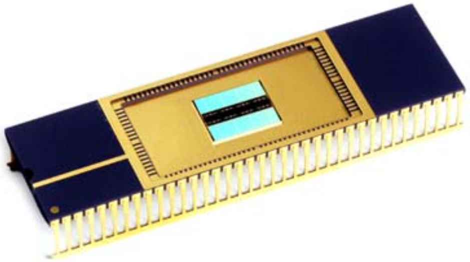
Projects: PHASEMAT (DECI-3) PHASEALL (DECI-4)

ETH Zurich c/o USI Lugano: S. Caravati, R. Mazzarello,
M. Parrinello (PI)

PSI, Villigen (CH): M. Krack

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)**

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 – insulating)

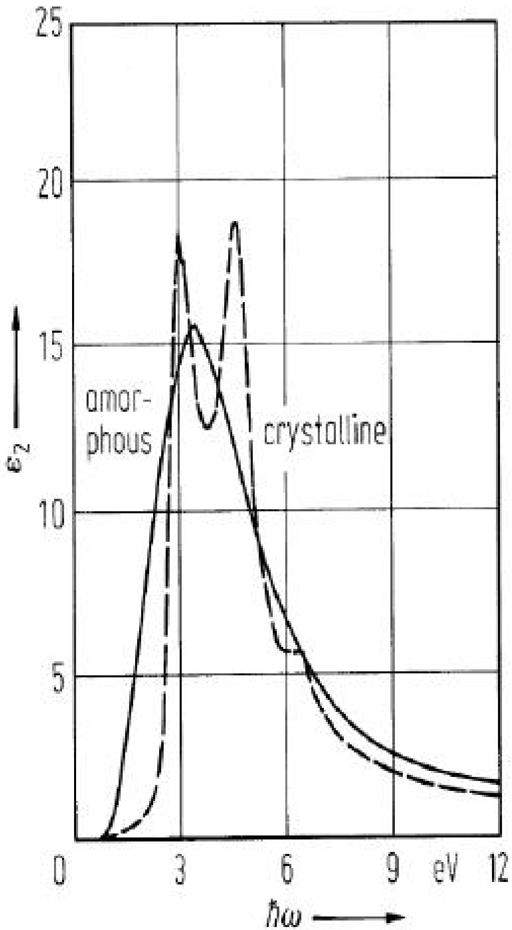
Resistivity changes by 3 orders of magnitude → PCM

Reflectivity change 30 %: → optical storage (DVD–RAM)

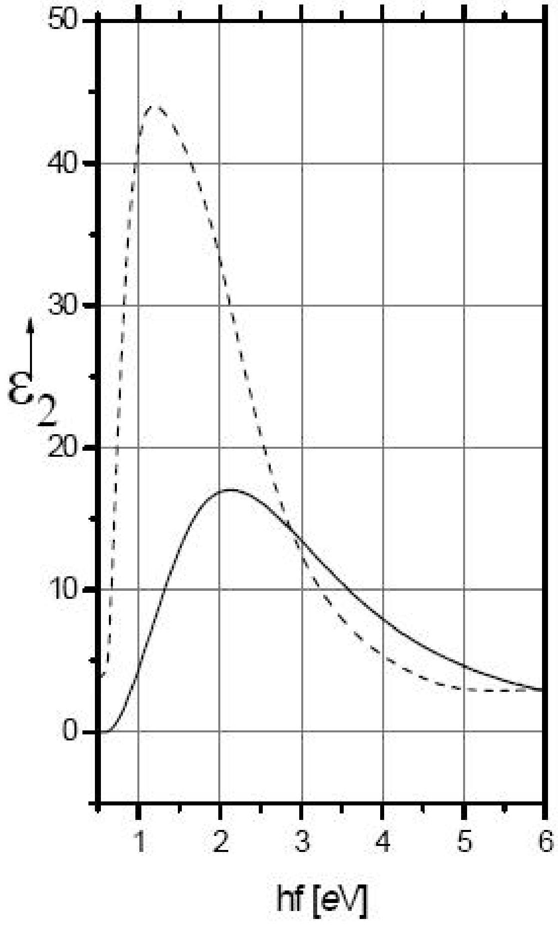
Transition induced by heating

Optical contrast between amorphous and crystal

GaAs



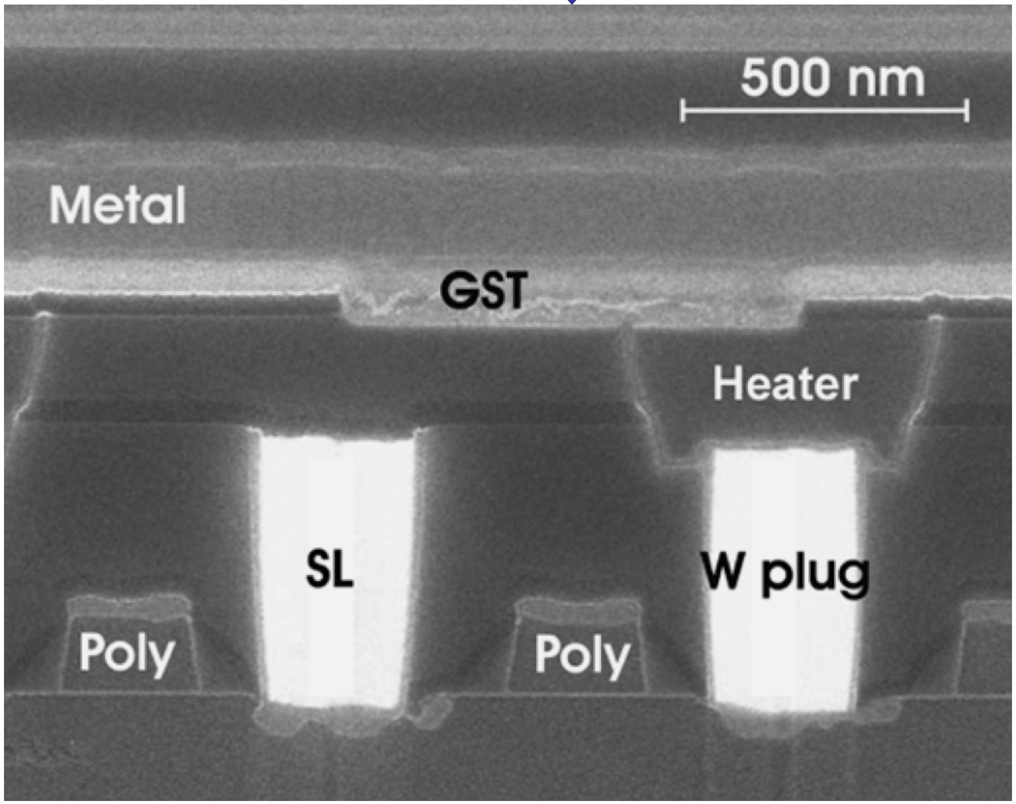
$Ge_2Sb_2Te_5$



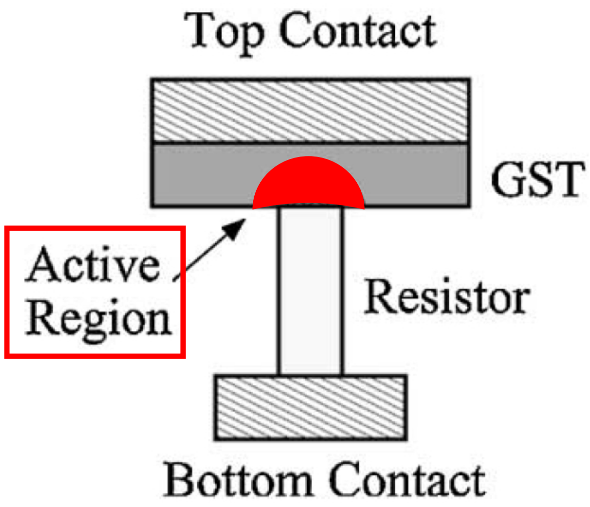
The Phase–Change memory cell

Schematic representation

SEM cross section



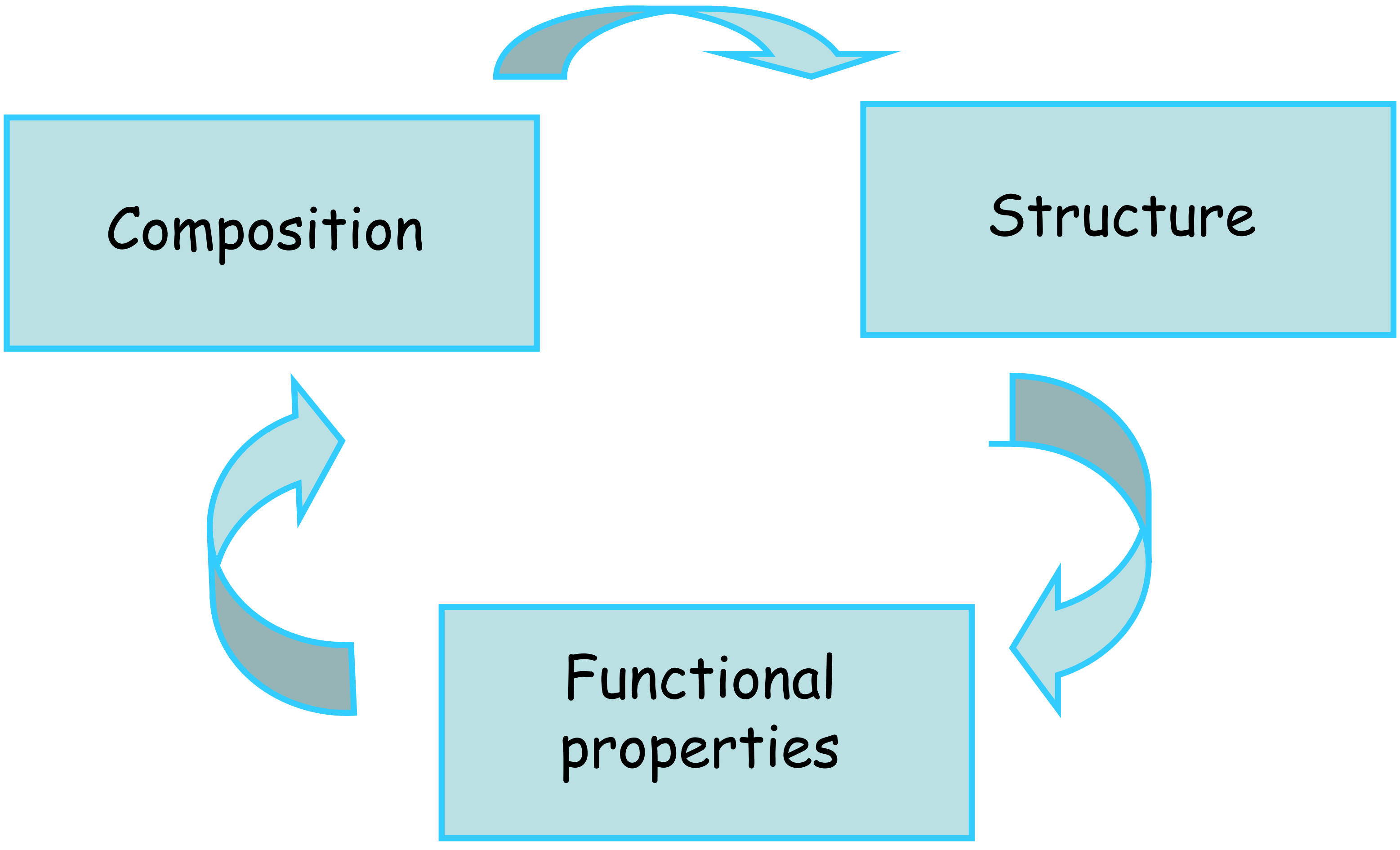
Collaboration with Numonyx



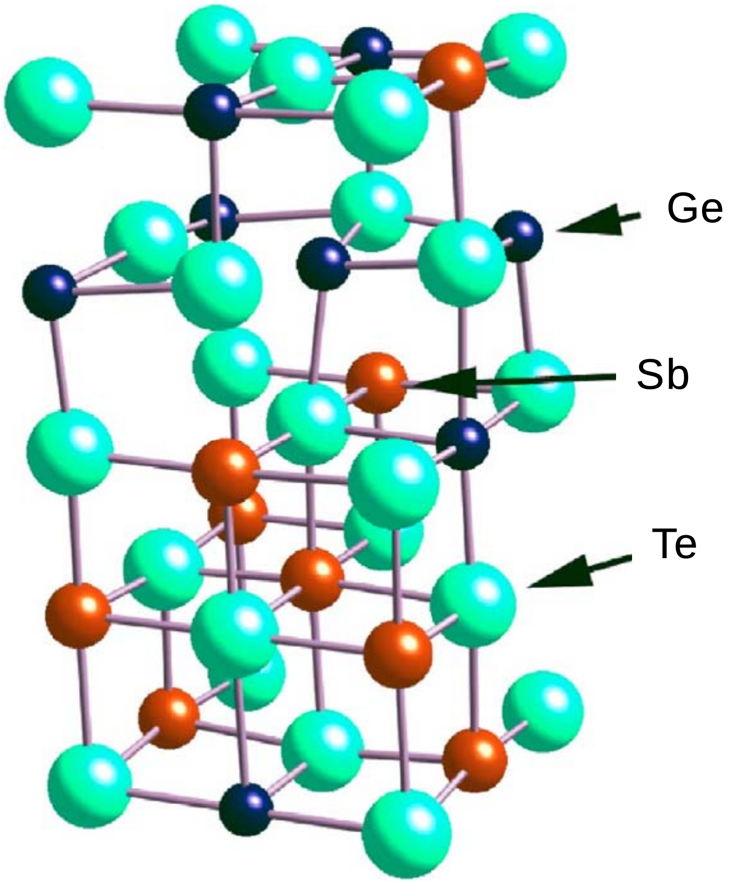
- Active region: a small drop within GST film undergoes the phase transition
- Phase–change by heating via Joule effect

Needs for better performing materials for PCM

e.g. automotive applications require stability of amorphous at high temperature



GST crystalline phase: Rocksalt



❖ NaCl-type

$Ge_2Sb_2Te_5$

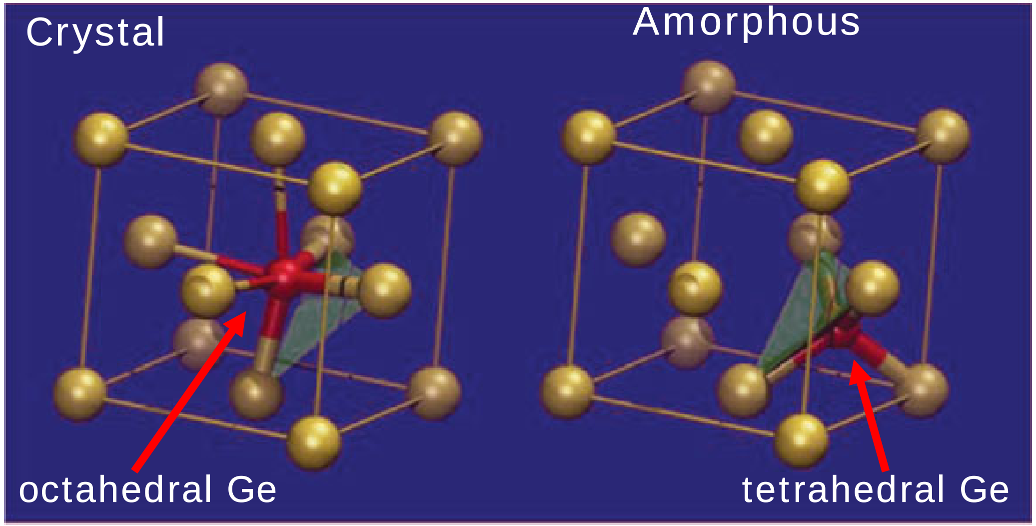
- One sublattice fully occupied by Te
- The other randomly occupied by Ge, Sb and 20% vacancies
- Octahedral environment

each atom 6-fold coordinated

The Kolobov's picture 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** (2004)]



Octahedral ⇆ tetrahedral change responsible for electronic and optical contrast

Phase Change Materials from First Principles

- Ab-initio (Car-Parrinello) atomistic molecular dynamics simulations
- Density Functional Theory (GGA + pseudopotentials)

  Second generation Car–Parrinello method (Kühne et al, PRL 2007)
  Factor 25 speed up with respect to conventional ab-initio MD
- Models of amorphous phase (200-500 atoms) generated by quenching from the melt on 100 ps time scale
  (1 ps → 2 hours on 256 processors)
- Code Quickstep, open source CP2K project http://cp2k.berlios.de
  Basis sets: Guassian (wavefunctions) + plane waves (elec. density)
- Sites: Juelich (JSC), Garching (RGZ-MPG) Ibm sp6 Deci-3
  Finland (CSC) Cray XT4/XT5 Deci-4

$Ge_2Sb_2Te_5$ (GST) GeTe Sb_2Te_3

$InGeTe_2$ (IGT) (high $T_{crys,}$ Morikawa *et al*, IEEE 2007)

- Structural Properties
- Vibrational properties
- Optical properties (DVDs)
- Electronic properties (PCM)

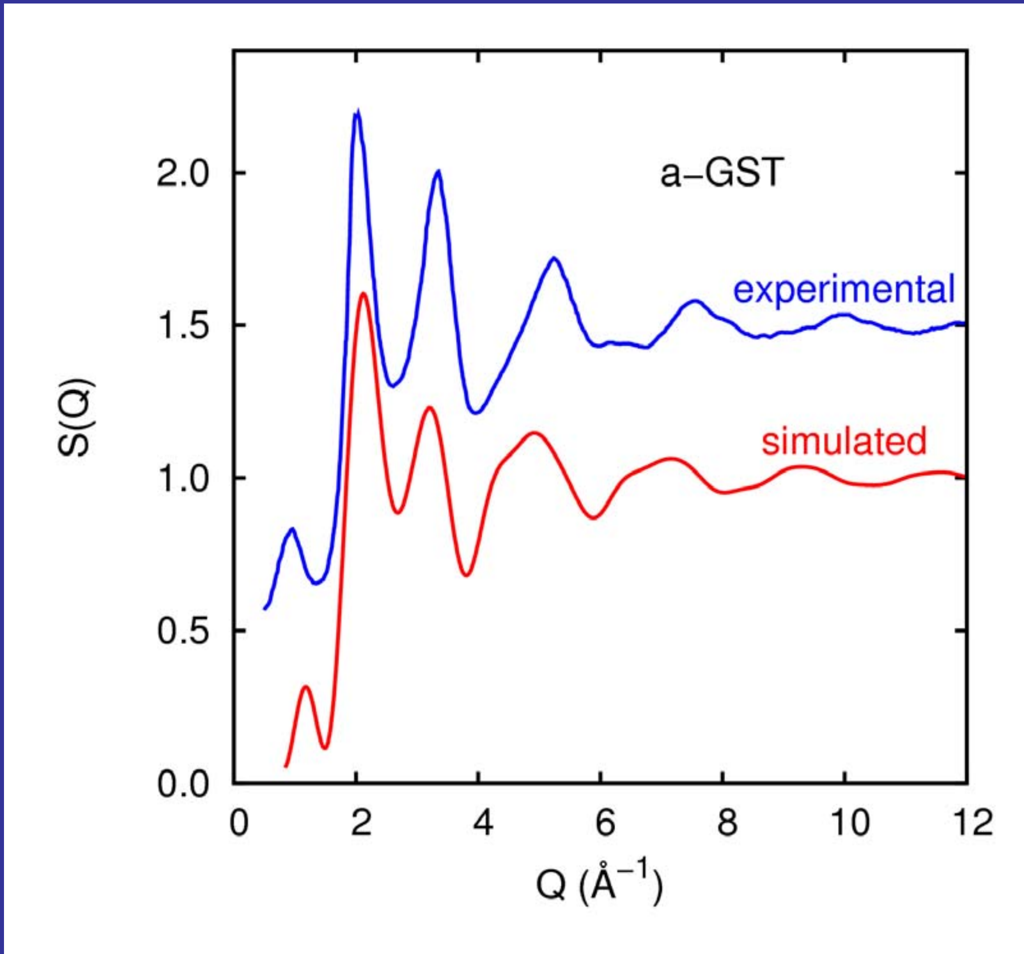
GST: amorphous model

Structure Factor

Liquid equilibrated at 990 K
(270 atoms)

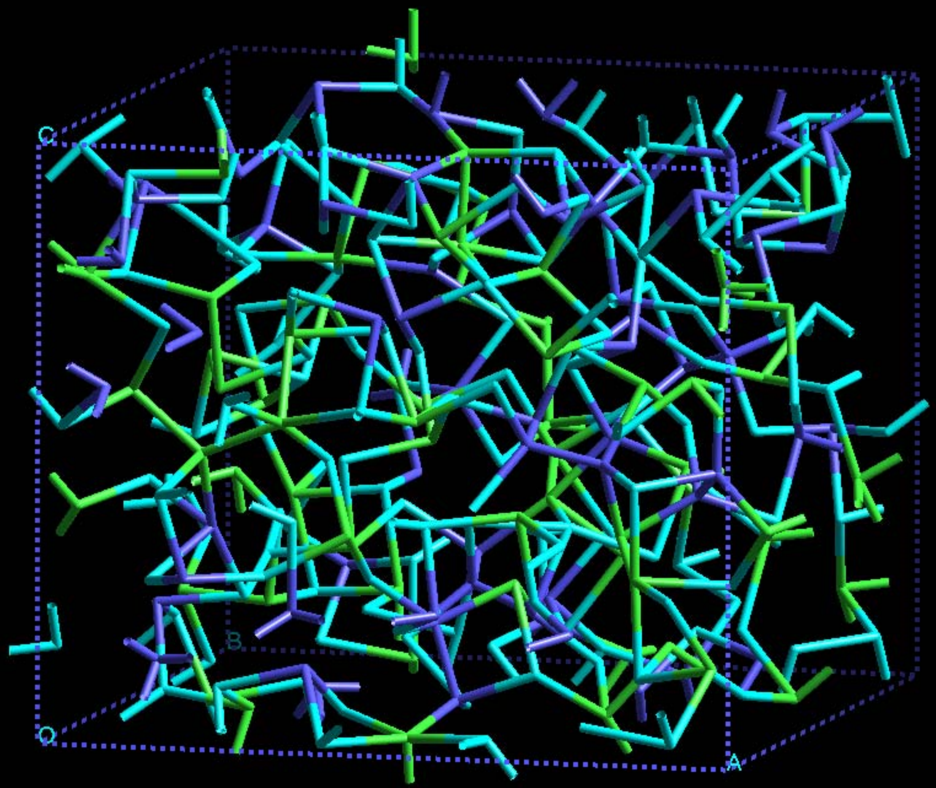
Liquid quenched to 300 K

(in 80 ps)



experimental neutron data:
Jovari et al., PRB 2007.

GST: amorphous model

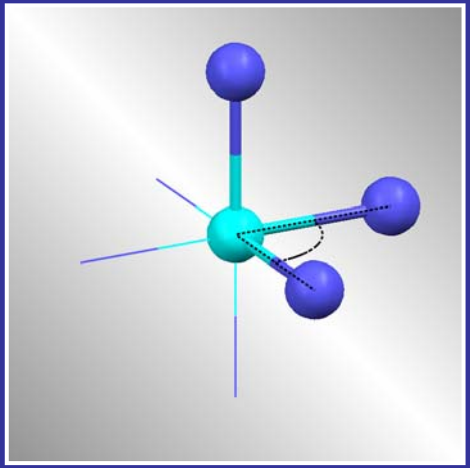


Ge Sb Te

Coexistence of octahedra and tetrahedra in amorphous PCM

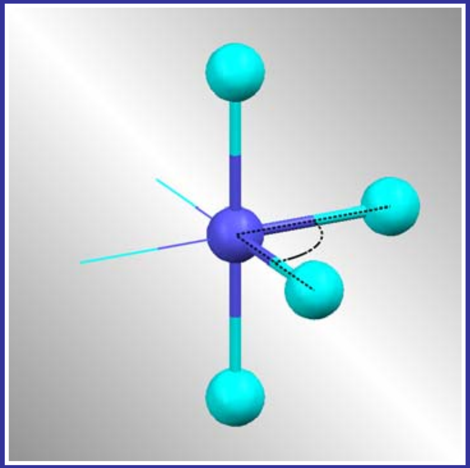
(defective) octahedral Ge, Sb and Te

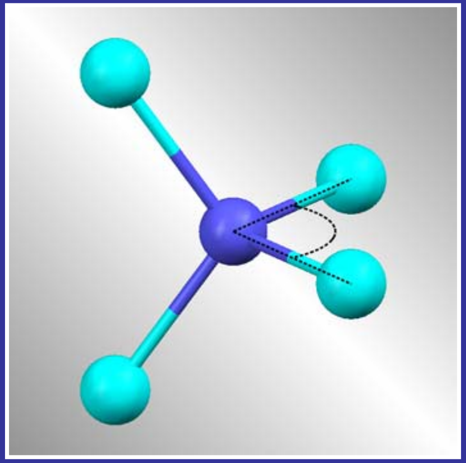
3–coor Te



tetrahedral 4–coor Ge

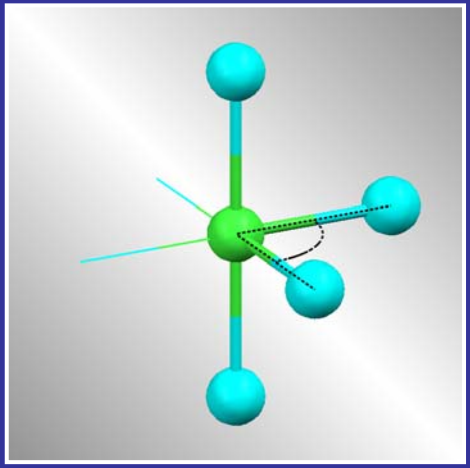
4–coor Ge





3+1 coordination

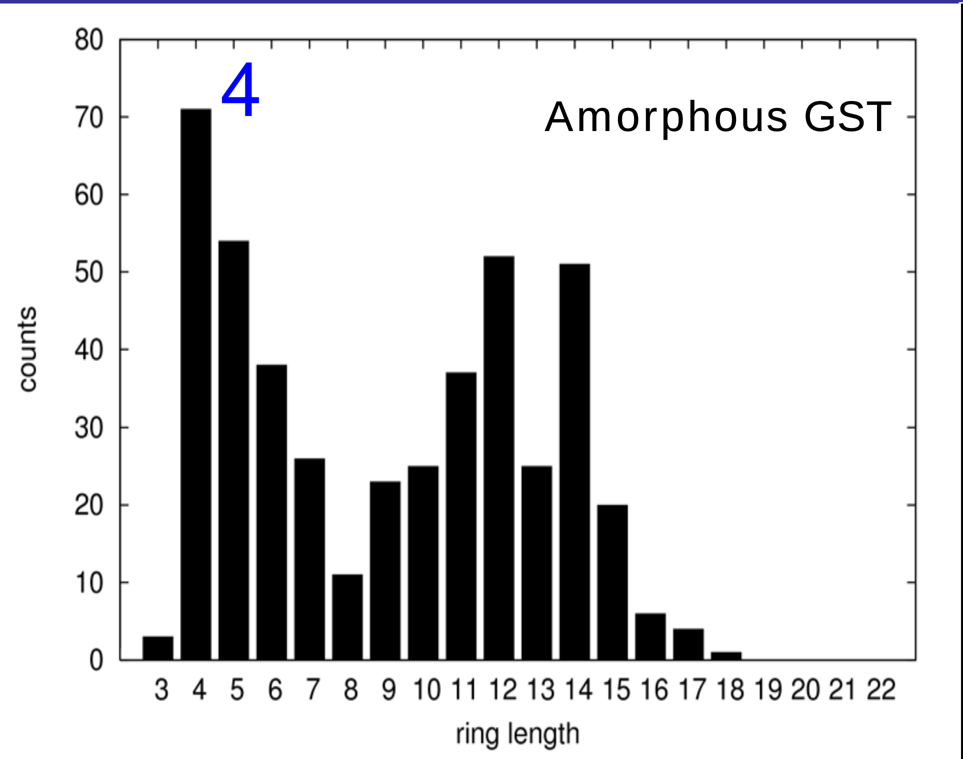
→ p-bonding



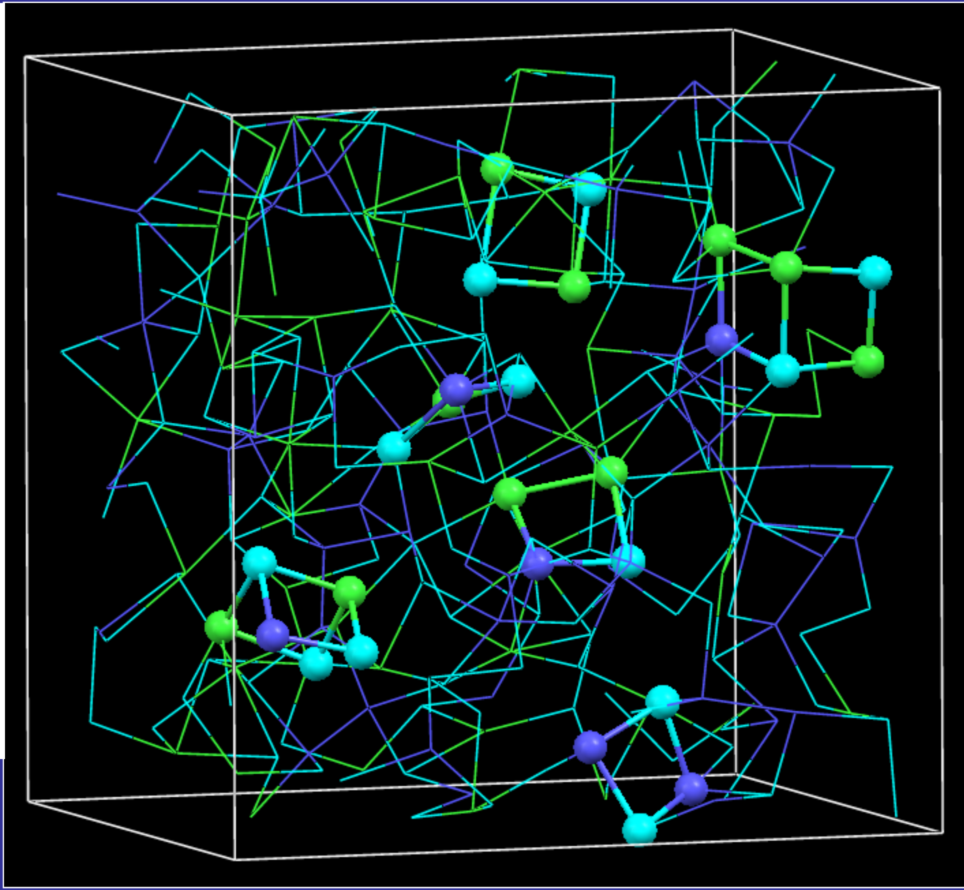
4–coor Sb

sp^3 bonding

4–fold rings (squares)



Ring distribution

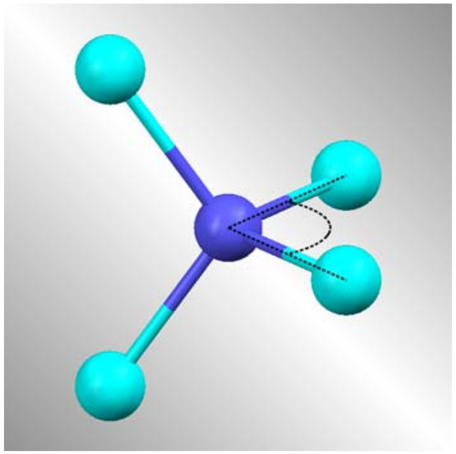


Caravati et al, APL 2007; J. Phys. Cond. Matt. 2009 ; PRL 2009; PRB 2010

Akola and Jones PRB 2007; Hegedus and Elliott, Nat. Mater. 2008

Tetrahedral sites

Ge-Ge and Ge-Sb bonds promote
Ge tetrahedral geometry



concentration of tetrahedral Ge:

- **GST: 27** % of Ge
- **GeTe: 22 % of Ge**
- **$InGeTe_2$: 19 % of Ge**

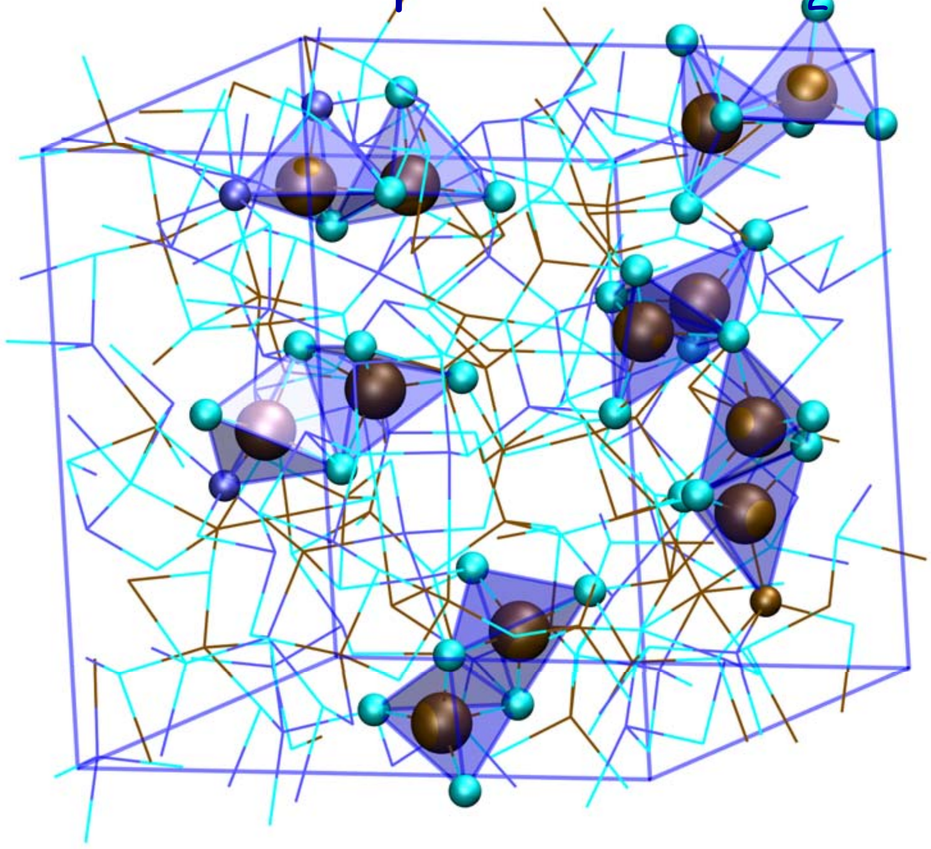
Sb_2Te_3 : only defective octahedral sites (No Ge)

$InGeTe_2$: In 60 % in tetrahedral sites !

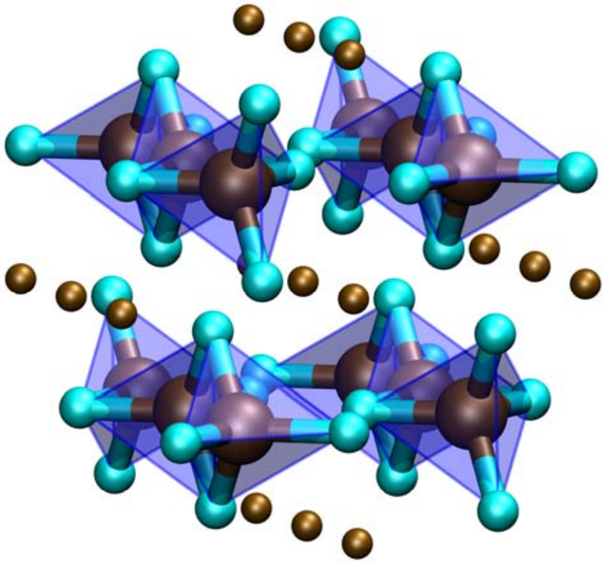
Caravati, Bernasconi, Parrinello Phys. Rev. B 81, 014201 (2010)

$InTe_4$ tetrahedra in a-IGT

Amorphous $InGeTe_2$



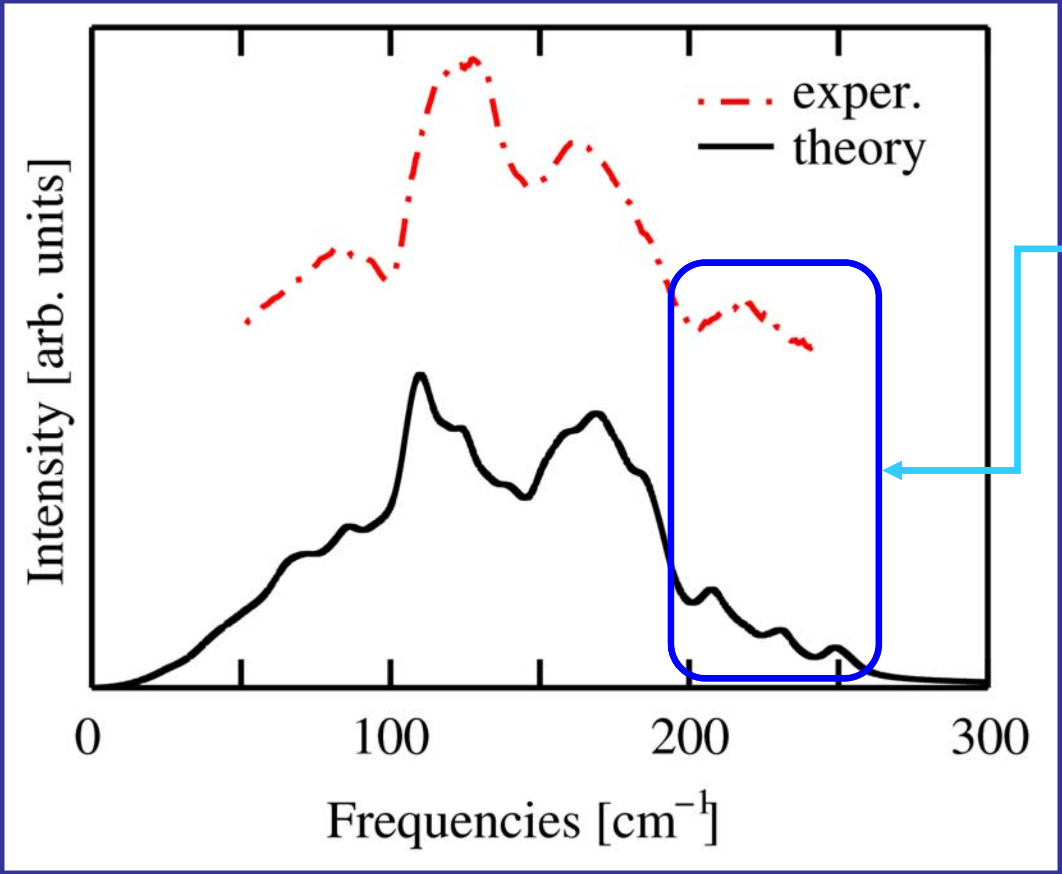
InTe crystal



Edge-sharing $InTe_4$ tetrahedra in crystalline InTe and In_2Te_5

Tetrahedral Ge: vibrational fingerprint

Amorphous GeTe: Raman spectrum



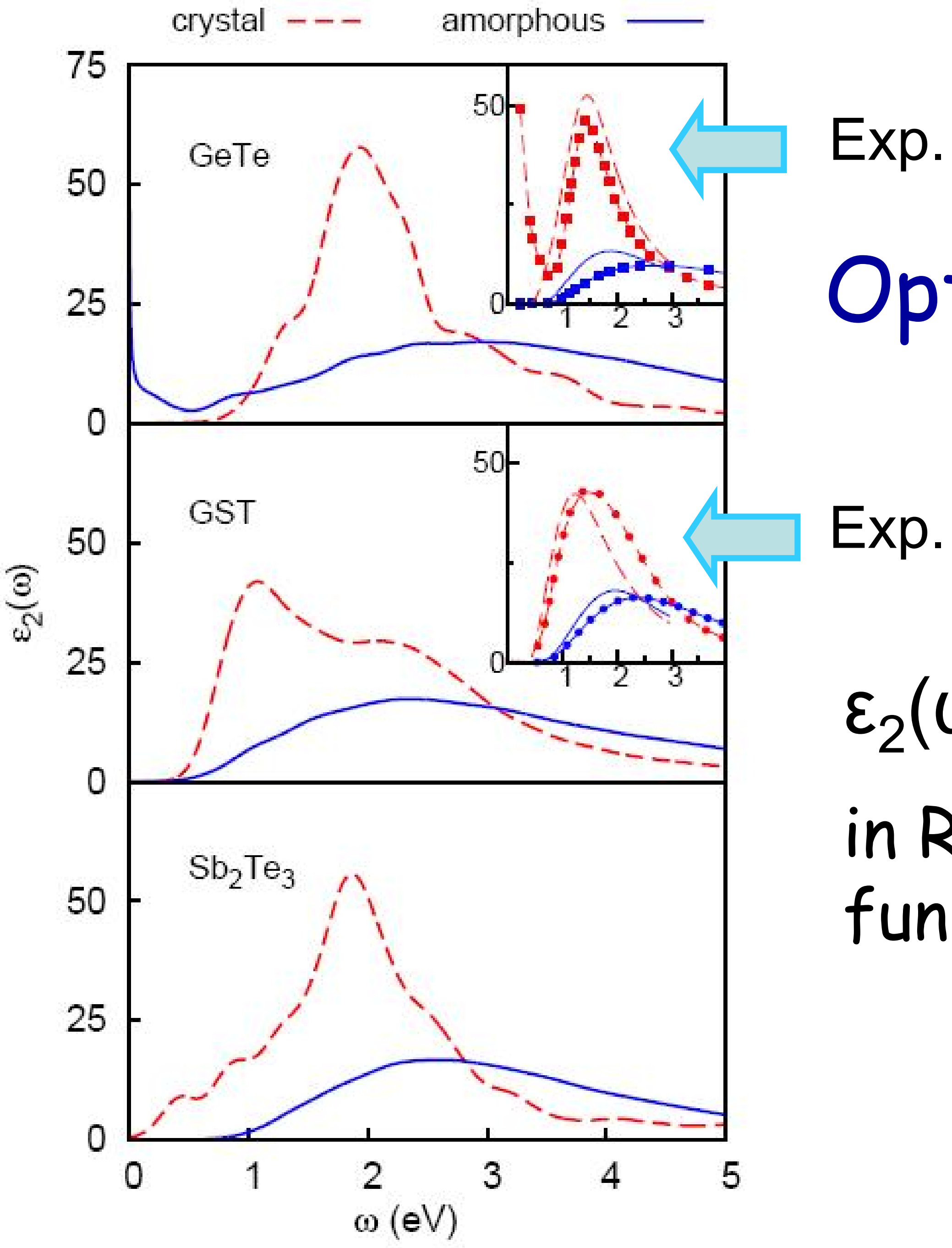
Phonon freq. > 190 cm^{-1}:

- Localized on tetrahedral Ge

⇨ signature of tetrahedral Ge

Mazzarello, Caravati, Angioletti, Bernasconi, Parrinello

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



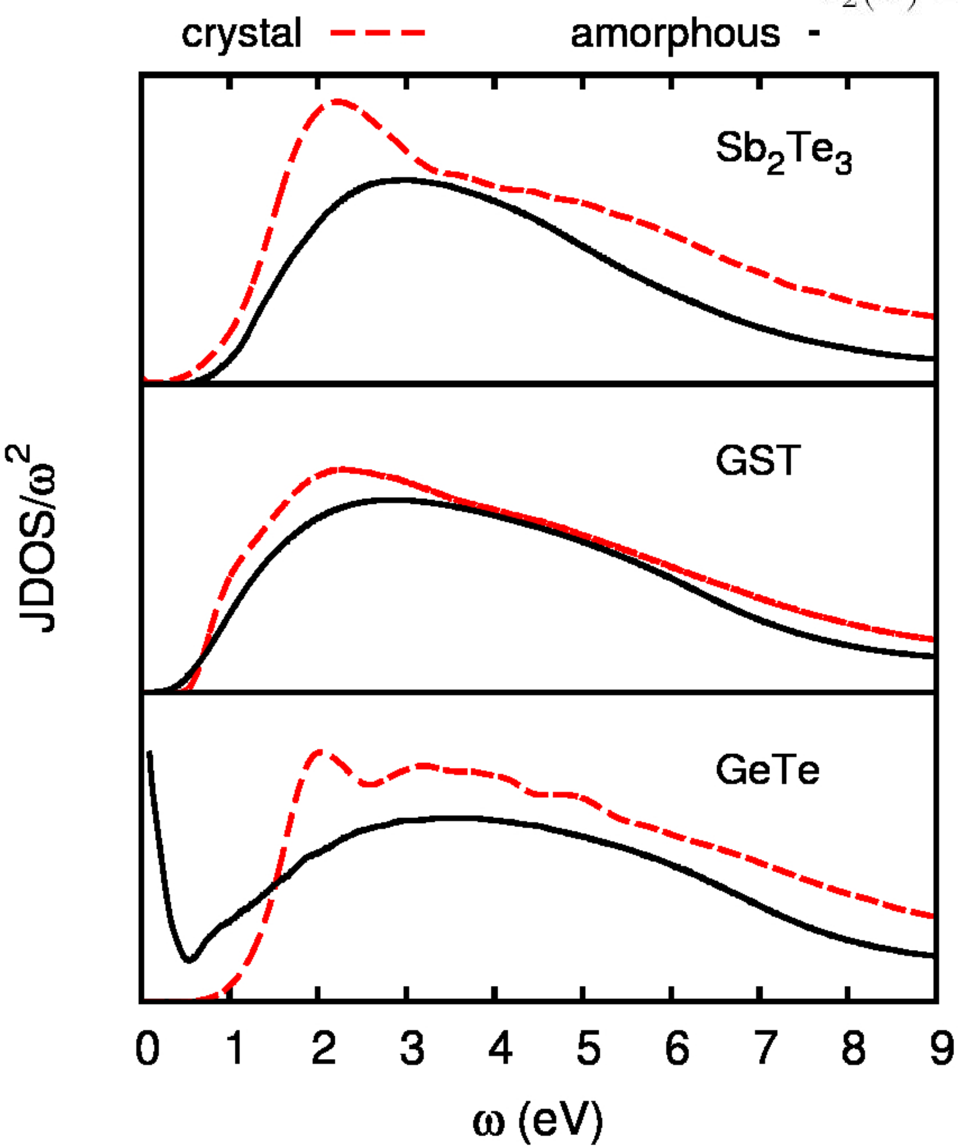
Optical contrast in PCM

$\varepsilon_2(\omega)$ dielectric functions

in RPA with hybrid functional HS03

Joint Density of States

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



(Huang and Robertson PRB 2010)

Angular disorder in p-bonds in amorphous phases

↓

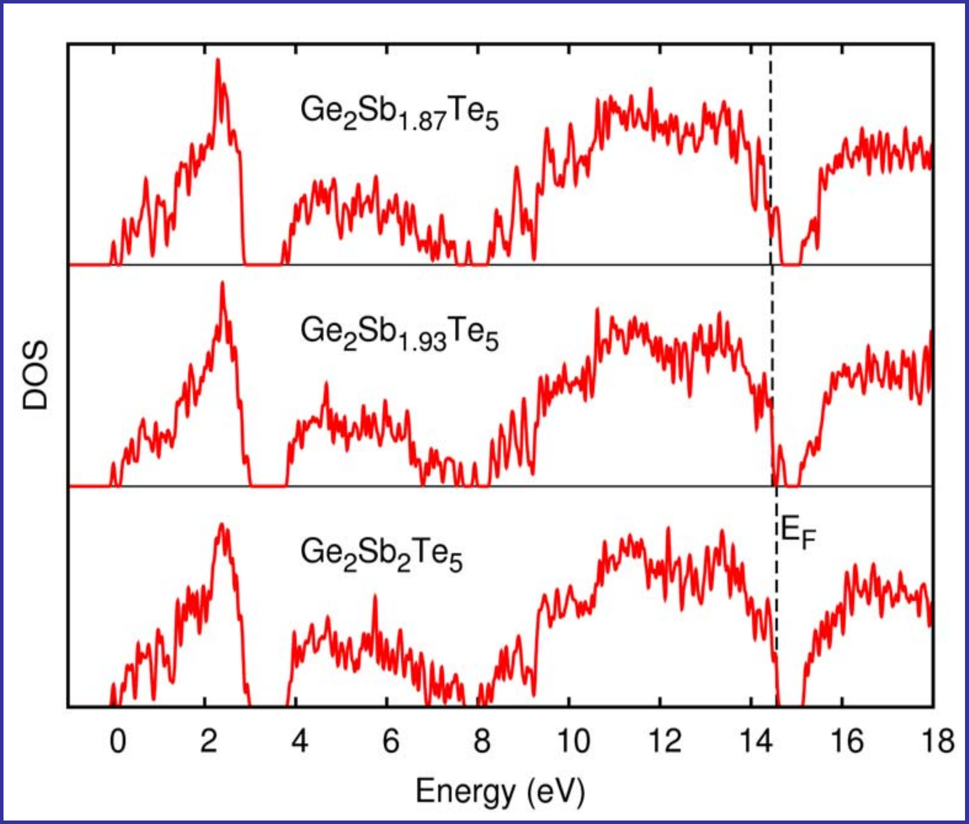
decrease of the optical matrix elements

↓

optical contrast

Electronic properties

GST stoichiometric crystal is semiconducting



Ge/Sb deficiency: → holes in VB

Ge/Sb excess: → electrons in CB

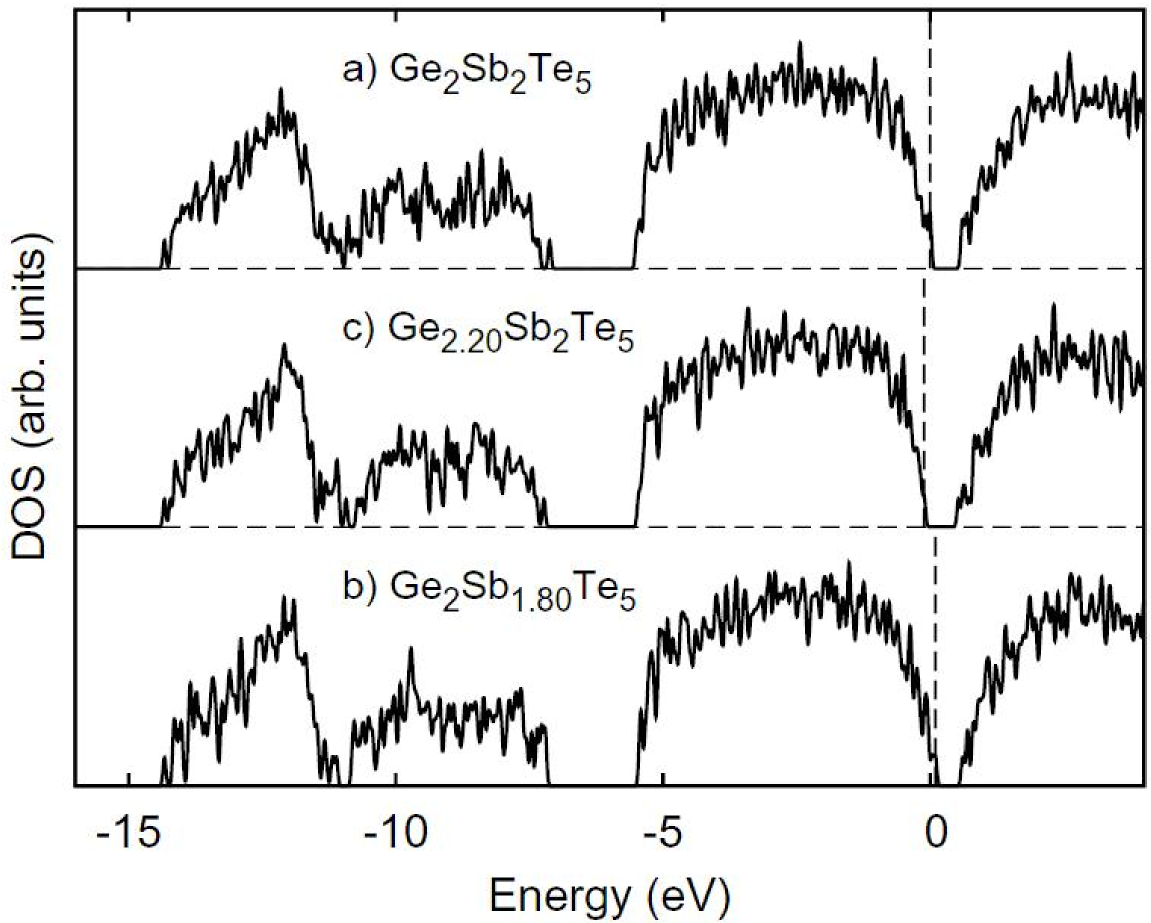
HS03 hybrid functional

S. Caravati, M. Bernasconi, T. D. Kühne, M. Krack, and M. Parrinello,

J. Phys. Condensed Matter 21, 255501 (2009)

Electronic Properties

Non-stoichiometric GST: amorphous phase



Semiconductor:

Band gap ~0.6 eV

Ge excess, Sb deficiency → No shift of E_f

Electronic properties

- Sb vacancies turn the cubic crytal into degenerate p-type semiconductor
- Electronic structure of amorphous phase is robust with respect to small change in composition

Conclusions

Ab-initio molecular dynamics simulations provided crucial insights on the properties of phase change materials

Structural properties of amorphous phases elucidated:

coexistence of defective octahedra and tetrahedra for Ge and In

$Ge_2Sb_2Te_5$ GeTe Sb_2Te_3 $InGeTe_2$

Angular disorder in p-bonding as microscopic origin of optical contrast exploited in DVD

Difference in conductivity partially due to different response of the two phases to defects in stoichiometry

Aknowledgments

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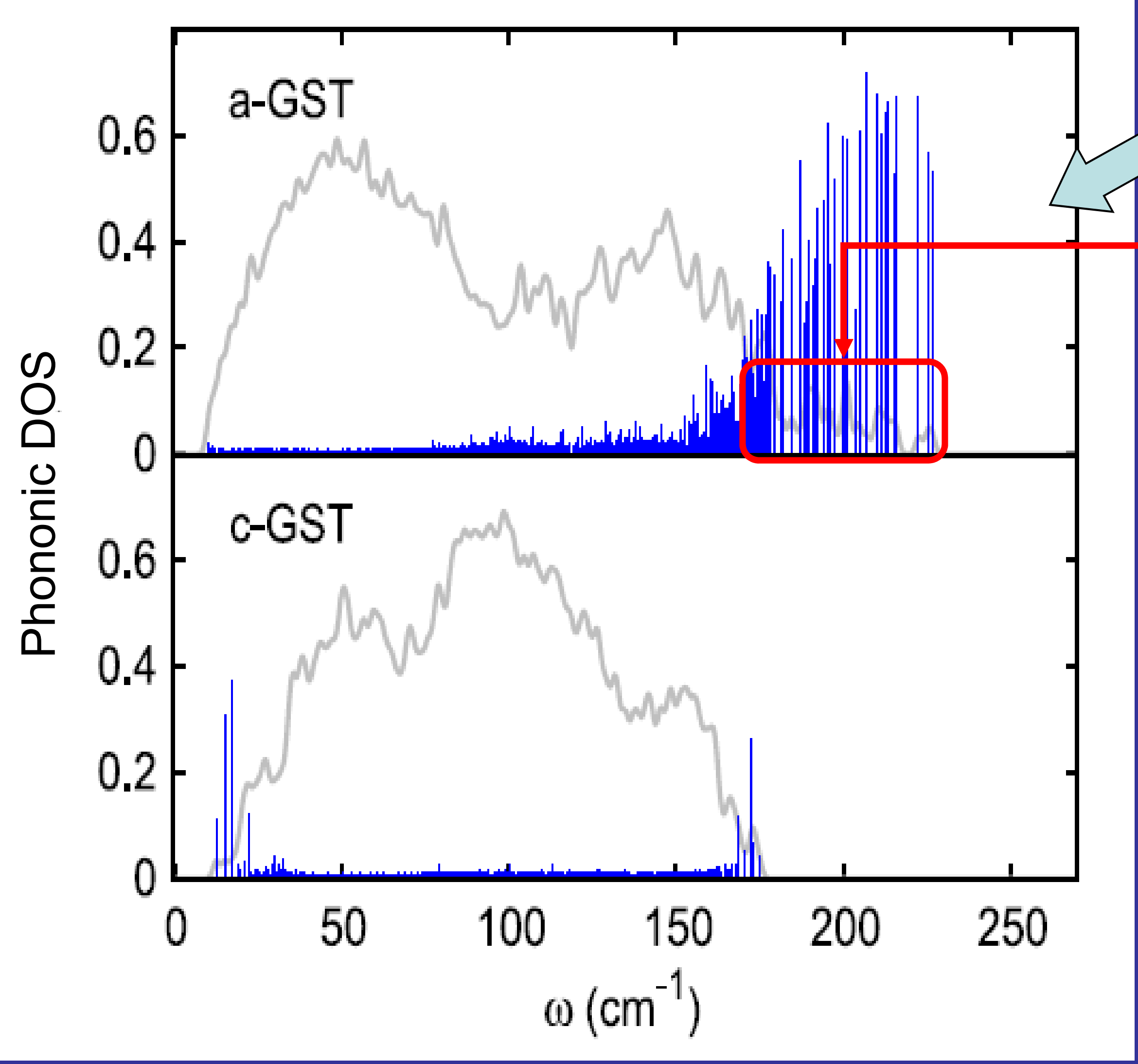
- PSI-Villigen: M. Krack

Support by DEISA: DECI-3 and DECI-4 projects
CSCS, Manno (CH)

Thank you for attention !

Tetrahedral Ge: vibrational fingerprint



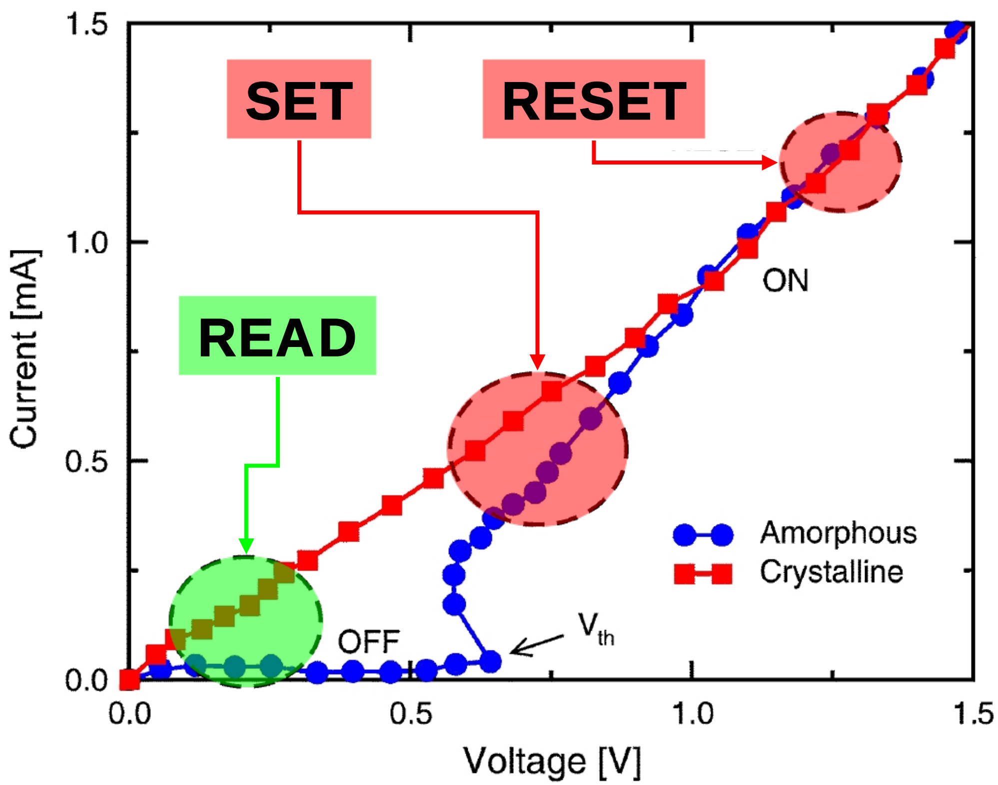
Inverse Partecipation Ratio

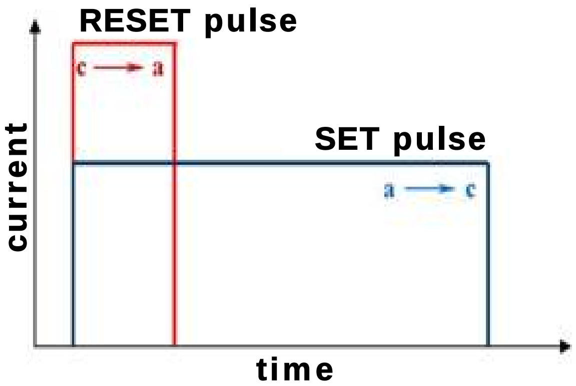
Phonons localized on Ge tetrahedra

Similar results in GeTe

I(V) characteristic: threshold switching behavior

- cell readout: performed at low bias ($V<V_{th}$)
- set/reset: bias higher than threshold ($V>V_{th}$)





➢ RESET:
higher current &
shorter pulse

crystal → amorphous

➢ SET:
lower current &
longer pulse:

amorphous → crystal