How do rewritable DVDs work?

Optical properties of phase-change materials

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Outline

1. Introduction to Phase Change Materials (PCMs)

2. Open questions for Phase Change Materials optimization
   - Local structural changes upon amorphization
   - Optical spectra: from crystalline to amorphous

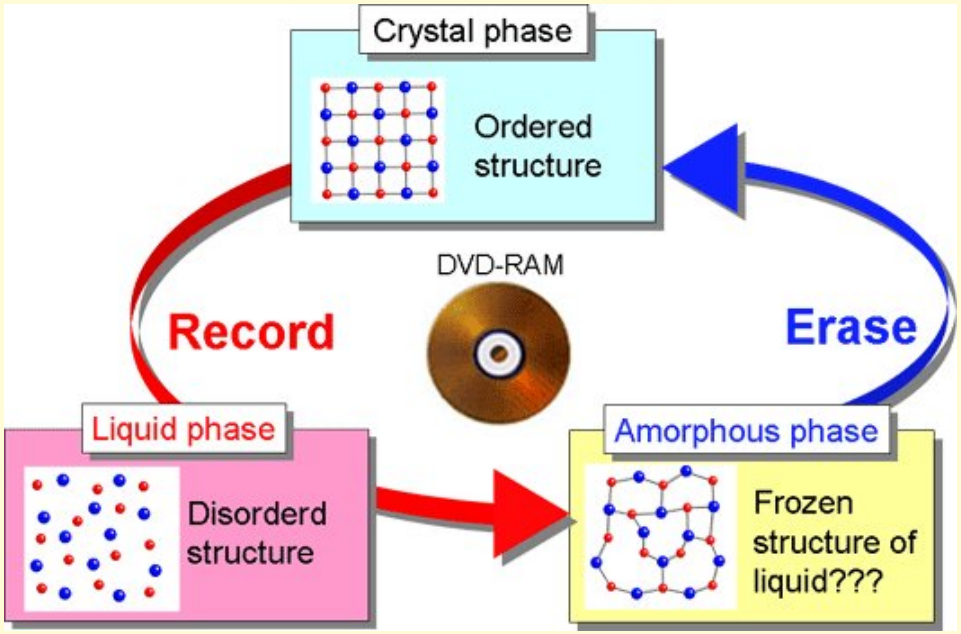
3. Answers to the open questions

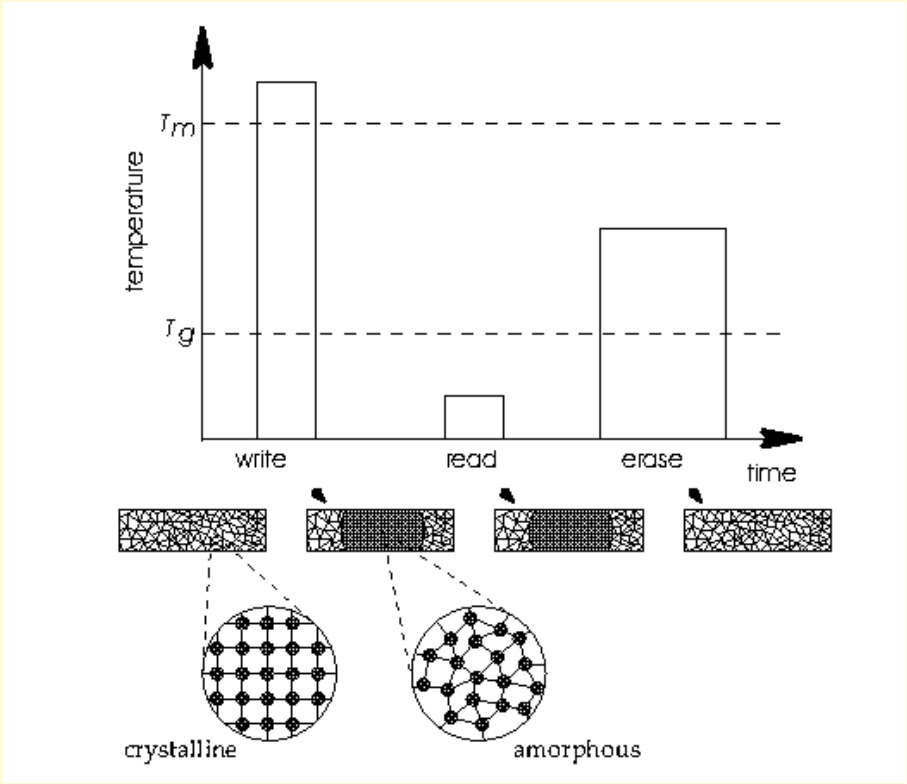
Outline

Need for next generation memories

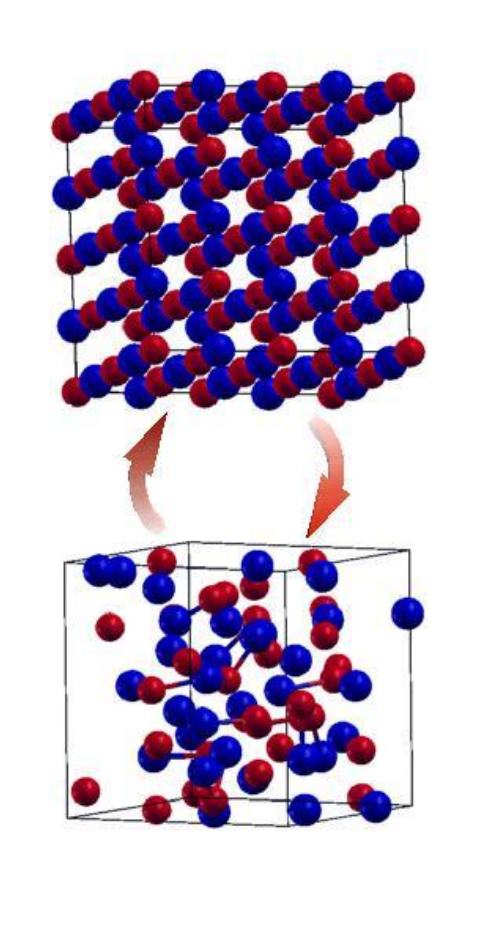
Phase Change Materials (PCMs) are already employed in optical data storage, e.g. in rewritable DVD's.
The resistivity contrast could be used in phase change random access memories.

Writing, reading and erasing a DVD



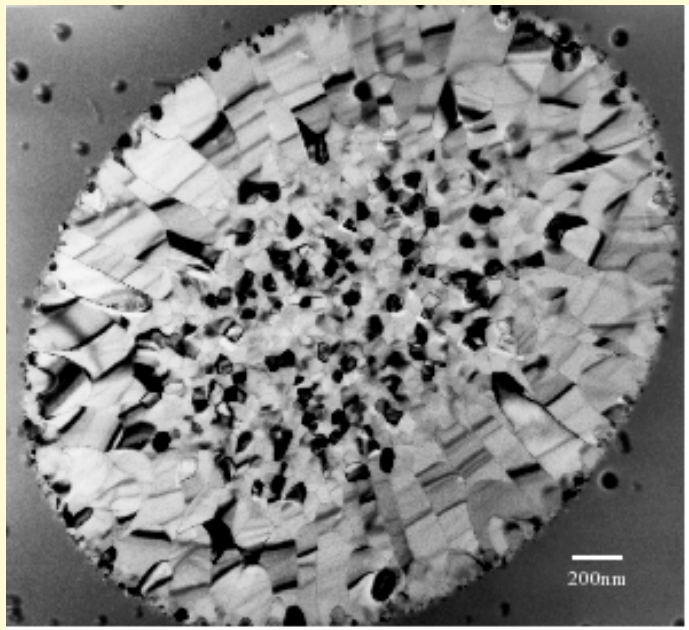


Reversible phase transitions in PCMs

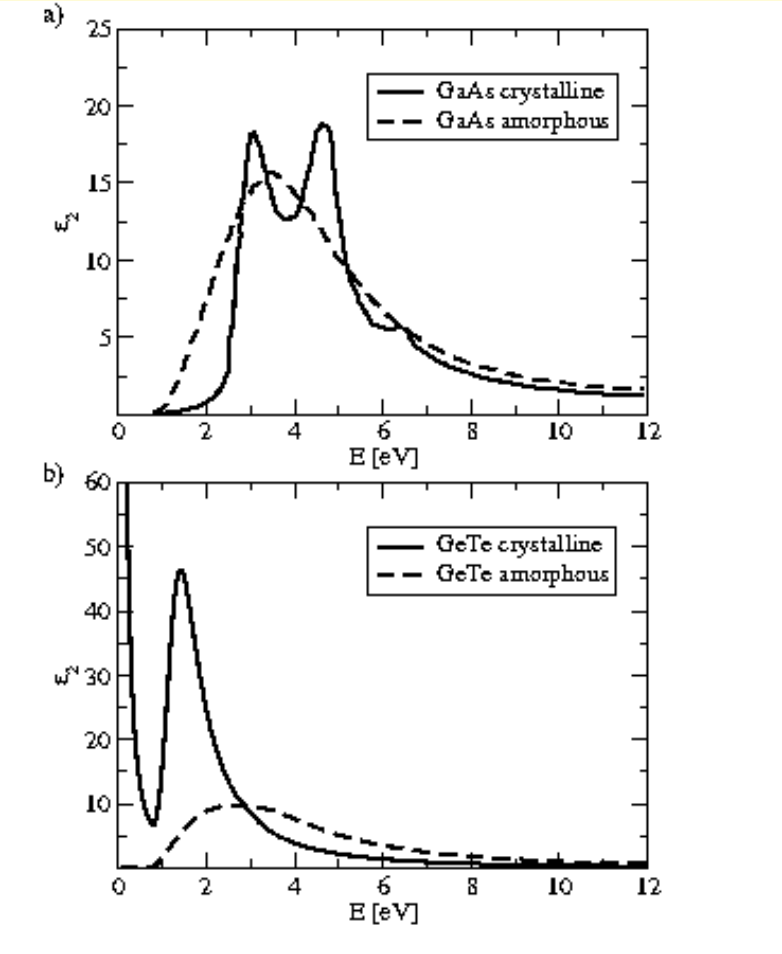


GeSbTe alloys:

- pronounced structural differences
- rapid transitions (10-100 ns)
- large optical and electric contrast
- already applied but still not well understood



Optical spectra of semiconductors

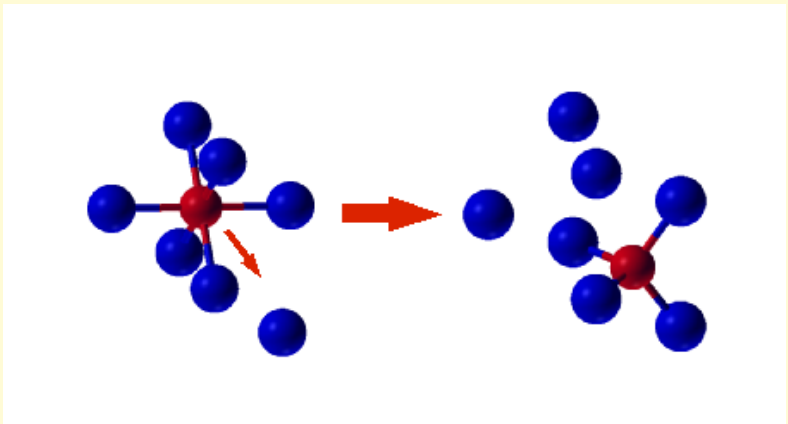


- GaAs: absorption in crystalline and amorphous phase similar
- GeSbTe alloys: strong optical contrast

GeSbTe alloys are suitable for data storage!

Outline

Local order of GeSbTe alloys in the amorphous phase



Ge in red
Te in blue

- Experiment: a fraction of Ge becomes tetrahedrally coordinated
- Such a phenomenon has never been observed for conventional covalent semiconductors
- Contradiction to continuous random network model
- Correlation between local order and optical properties?

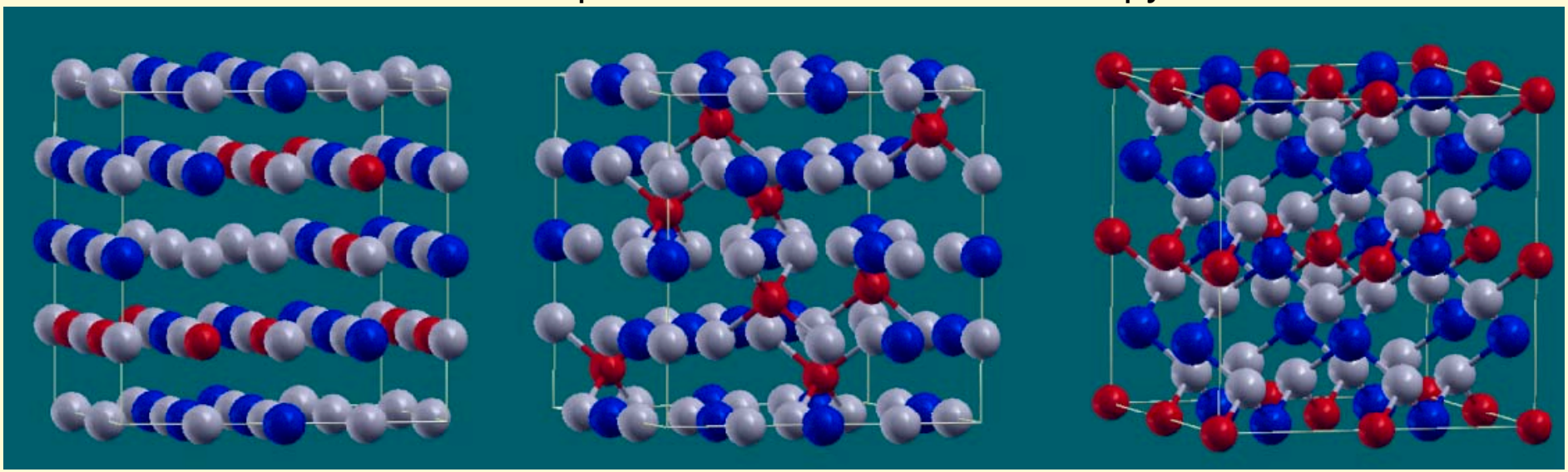
Kolobov et al. Nature Materials **3**, 703 (2004)

Open problems for PCMs optimization:

1. Can a change in local order explain the strong optical contrast?
2. Is this contrast due to a change in the electronic energy levels?
3. Can we tune the optical contrast?

Crystalline structures of GeSbTe alloys

Rocksalt - octahedral coor. Spinel - mixed coor. Chalcopyrite - tetrahedral coor.

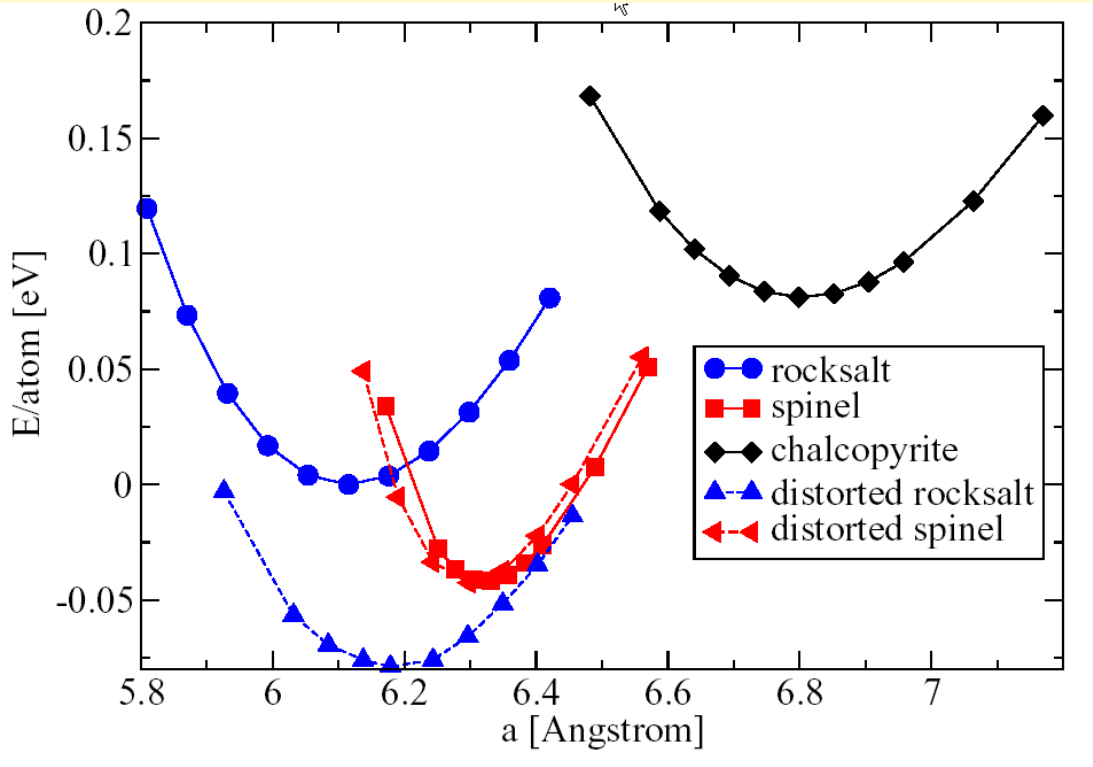


Te in gray, Sb in blue, Ge in red

Rocksalt structure relaxes in slightly distorted state

DFT total energies

Spinel (mixed coordination) suitable model for amorphous short range order



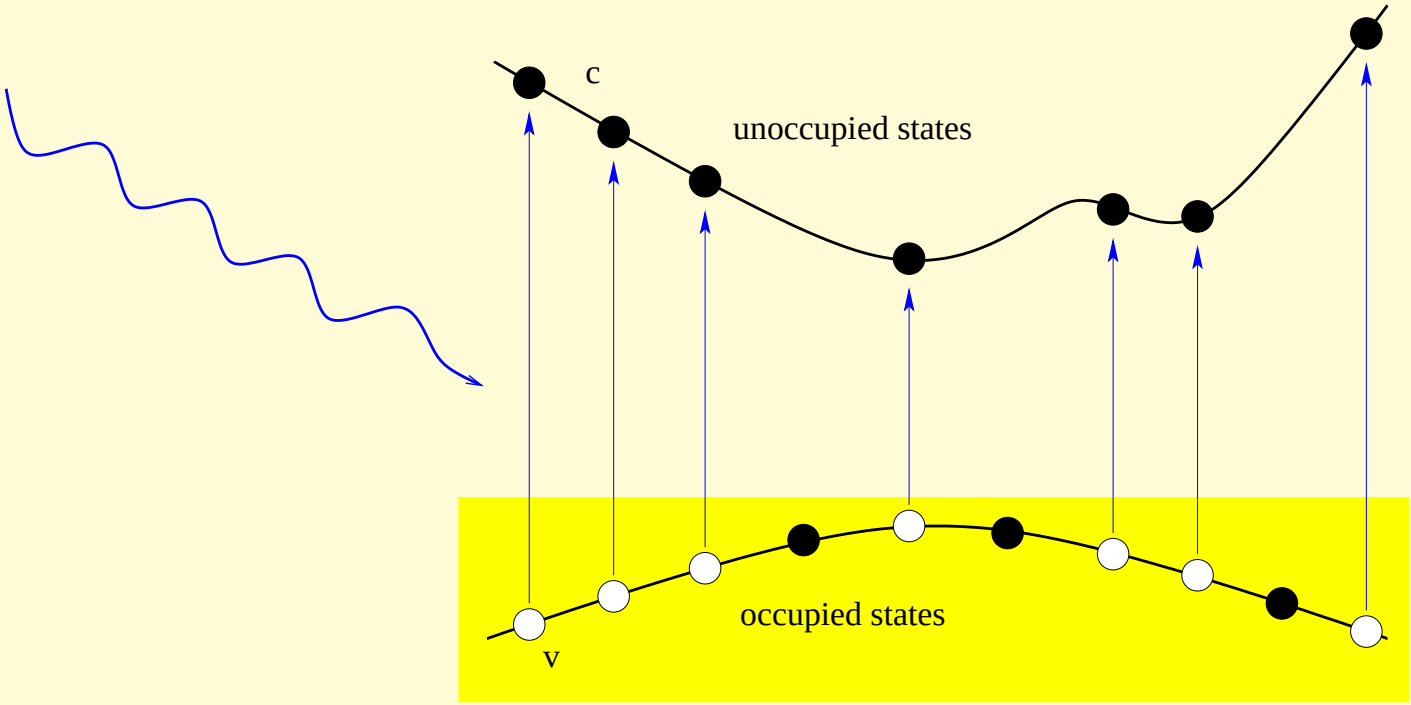
volume increase 5-10%
energy difference 30 meV
increase of bulk modulus

W. Welnic et al. Nature Materials **5**, 56 (2006)

From experimental observation to our models

- If all Ge atoms were in tetrahedral positions the volume increase would be $\geq$ 30% (experiment: 5-10%)
- Models for amorphous GeTe:
  - 64 atoms supercell
  - octahedral coordination except for 2, 4 or 8 Ge with tetrahedral short range order
- Models for amorphous $Ge_1Sb_2Te_4$:
  - 56 atoms supercell
  - either 4 or 8 Ge with tetrahedral short range order
- All models still exhibit long rang order!

Optical absorption: approximations within DFT

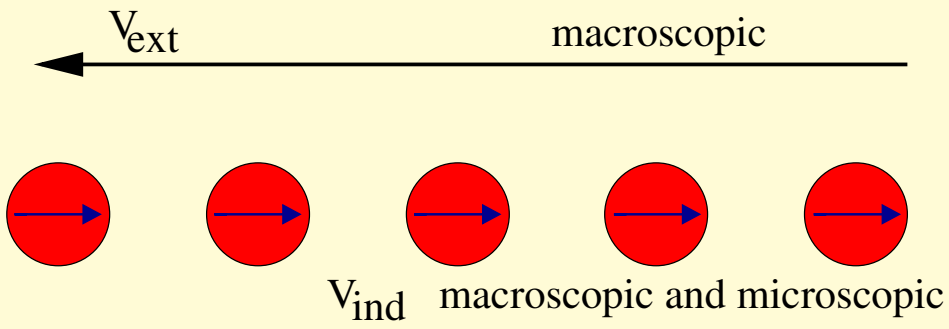


$$\epsilon_2(\omega) = 2\frac{4\pi^2}{\Omega N_{\mathbf{k}}\omega^2}\lim_{q\to 0}\frac{1}{\mathbf{q}^2}\sum_{v,c,\mathbf{k}}\left|m_{v,c,\mathbf{k}}\right|^2\delta(\epsilon_{c\mathbf{k}}-\epsilon_{v\mathbf{k}}-\omega)$$

$$m_{v,c,\mathbf{k}} = \langle c\,|\mathbf{q}\cdot\mathbf{v}|\,v\rangle$$

Independent-particle $\rightarrow$ GW $\rightarrow$ e-h interaction

Linear response functions within TDDFT



$$\bar{\chi} = \chi^0 + \chi^0 \left(\bar{v} + f_{\rm xc}\right) \bar{\chi}$$

$$\varepsilon_{\rm M} = \lim_{q \to 0} \left[1 - v_0(q) \bar{\chi}_{00}(q, \omega)\right]$$

- Independent-particle ($\bar{v} = 0$, $f_{\rm xc} = 0$)
- RPA ($f_{\rm xc} = 0$)
- TDLDA ($f_{\rm xc} = \frac{dV_{\rm xc}^{\rm LDA}}{d\rho} \delta(\mathbf{r} - \mathbf{r}')$)

Open problems for PCMs optimization:

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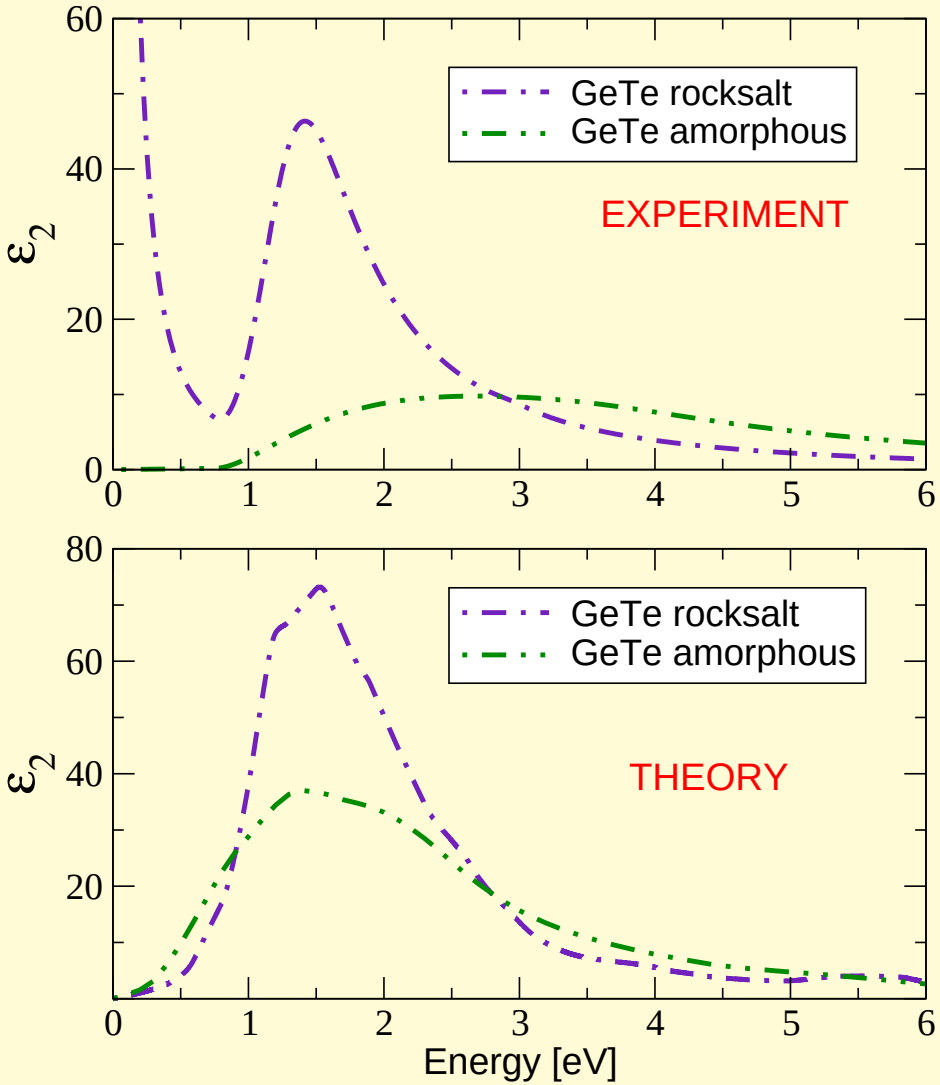
2. Is this contrast due to a change in the electronic energy levels?
3. Can we tune the optical contrast?

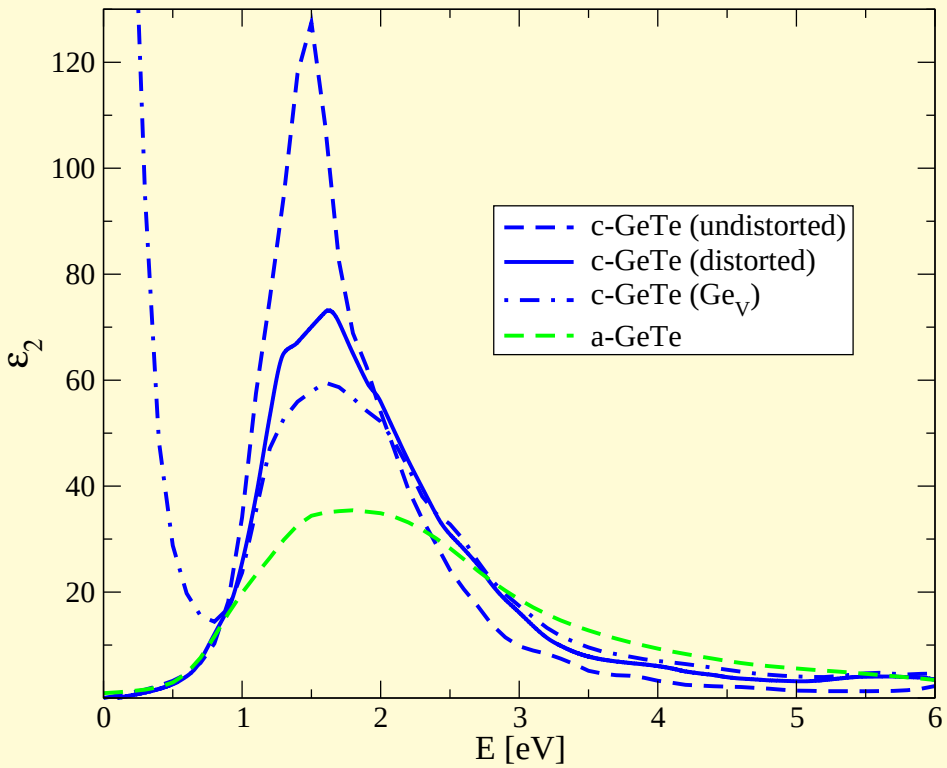
GeTe: experiment vs. RPA calculation



- Main features of the optical contrast well reproduced
- Spectroscopy on polycrystalline thin films of GeTe
- Presence of Ge vacancies in the sample
- Our models still exhibit long range order

Experimental results obtained in RWTH Aachen University

GeTe: effect of distorsion and Ge vacancies

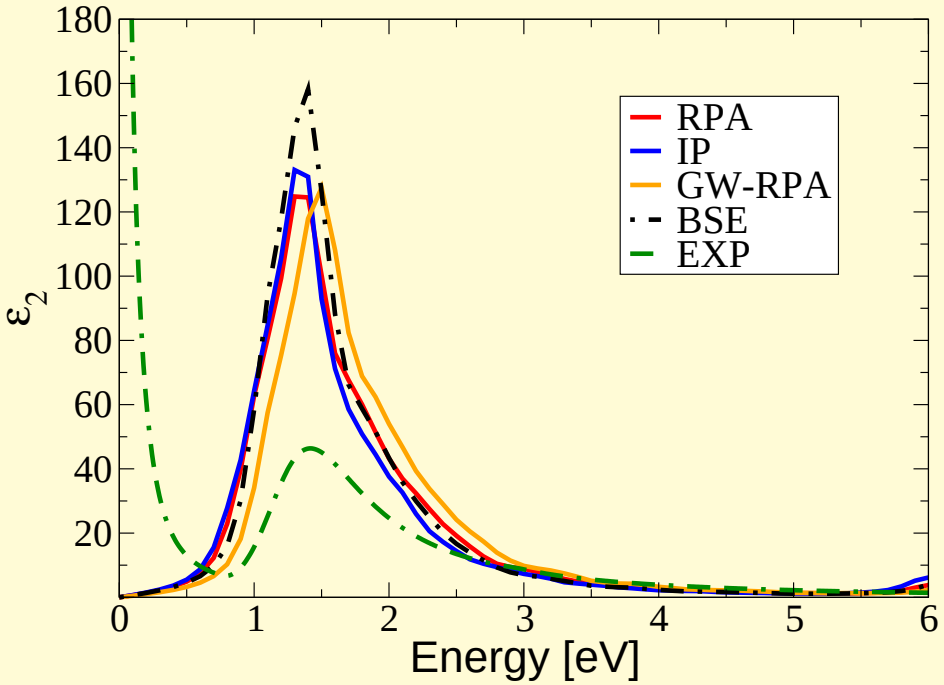


- Distorsion: no more 6 equivalent neighbours
- Ge Vacancies:
  - Drude peak well reproduced
  - Intensity of the main peak decreases
- Distorsion and vacancies reduce the number of Ge-Te bonds

Calculations within RPA approximation

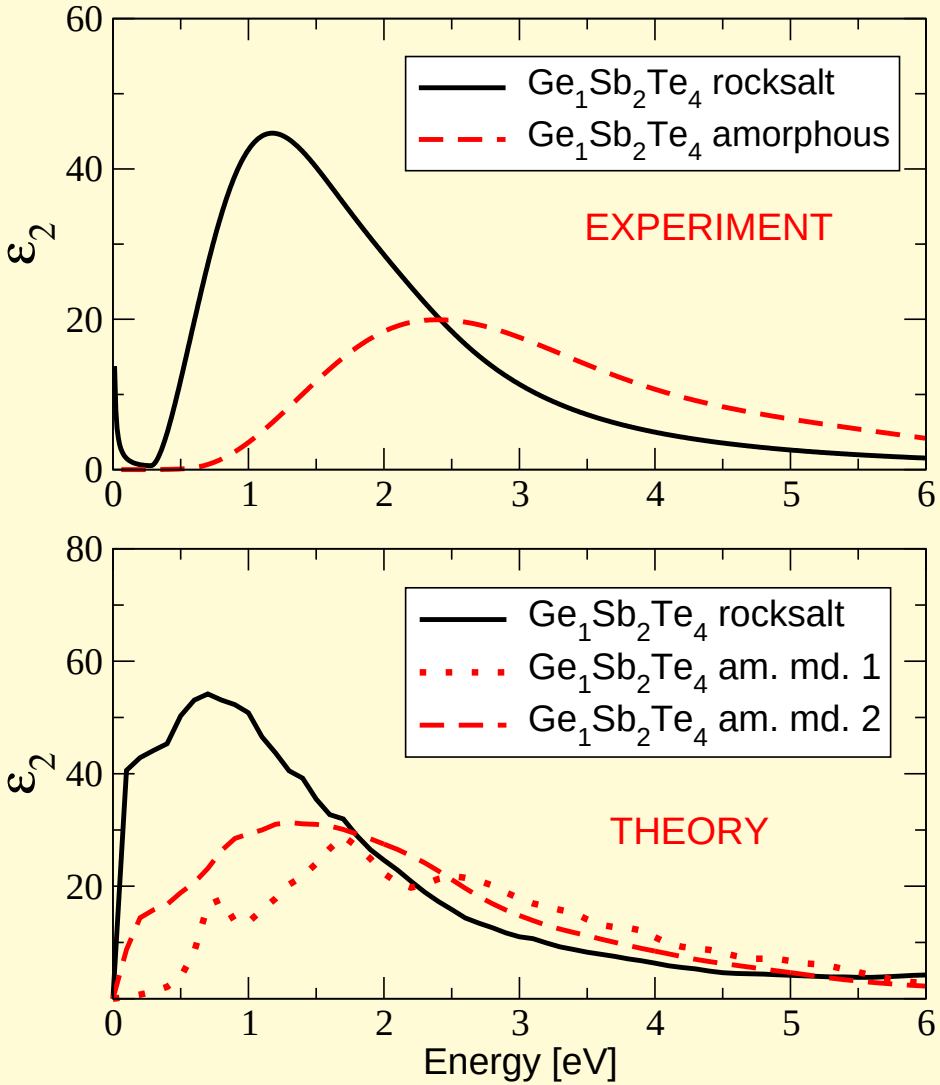
TDLDA, GW & BSE

- TDLDA and RPA give the same result
- Better agreement with experiment using many-body calculations?



- GW shifts gap by 0.15 eV
- Small excitonic effect compensate for GW correction
- RPA is enough for our purposes!

GeSbTe: experiment vs. RPA calculation



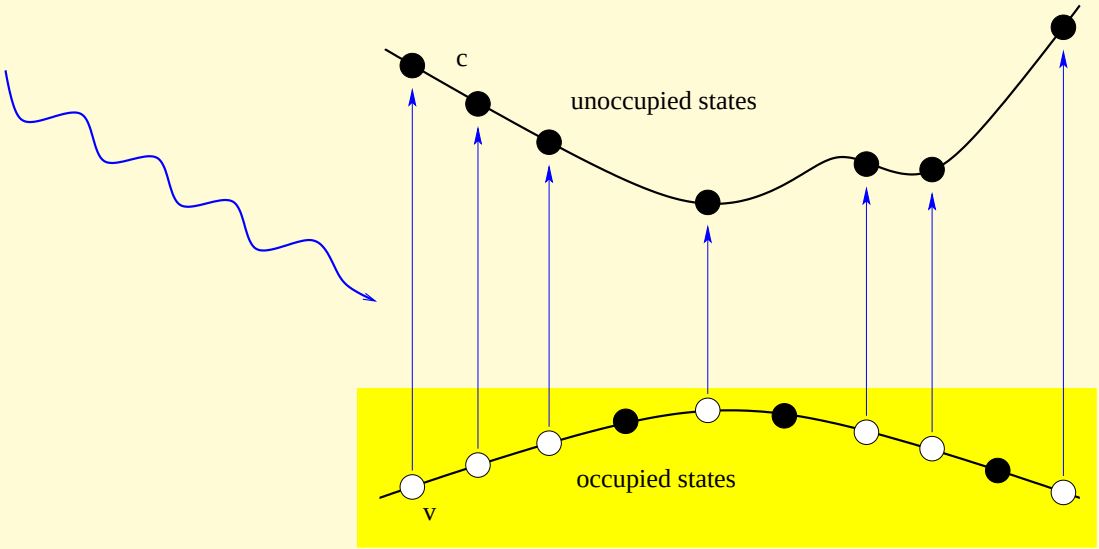
- again main features of the optical contrast well reproduced
- we conclude that a change in local order can explain the strong optical contrast

Experimental results obtained in RWTH Aachen University

Open problems for PCMs optimization:

1. Can a change in local order explain the strong optical contrast?
2. Is this contrast due to a change in the electronic energy levels (JDOS)?
3. Can we tune the optical contrast?

Optical absorption

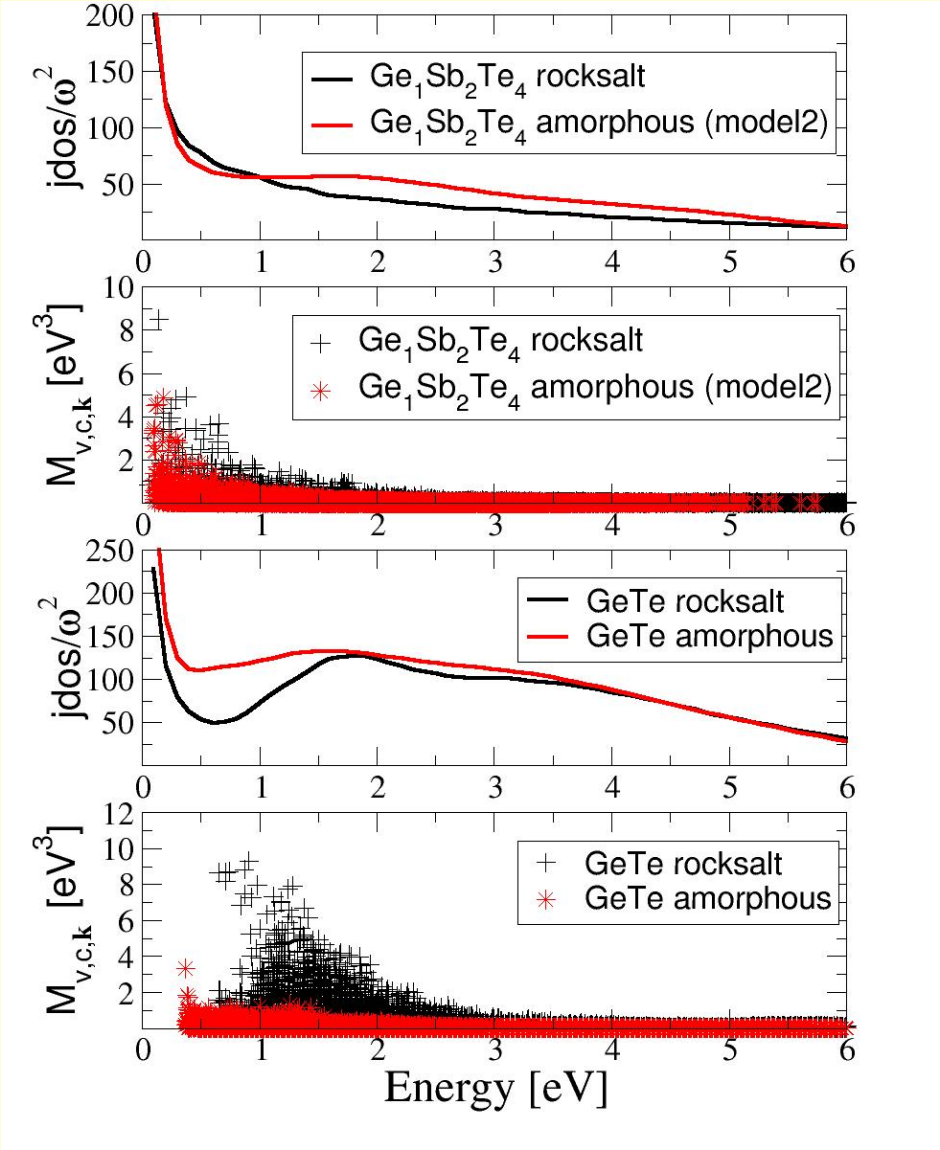


$$\epsilon_2(\omega) = 2\frac{4\pi^2}{\Omega N_{\mathbf{k}}\omega^2}\lim_{q\to 0}\frac{1}{\mathbf{q}^2}\sum_{v,c,\mathbf{k}}\left|m_{v,c,\mathbf{k}}\right|^2\delta(\epsilon_{c\mathbf{k}}-\epsilon_{v\mathbf{k}}-\omega)$$

$m_{v,c,\mathbf{k}} = \langle c\,|\mathbf{q}\cdot\mathbf{v}|\,v\rangle$ velocity matrix elements

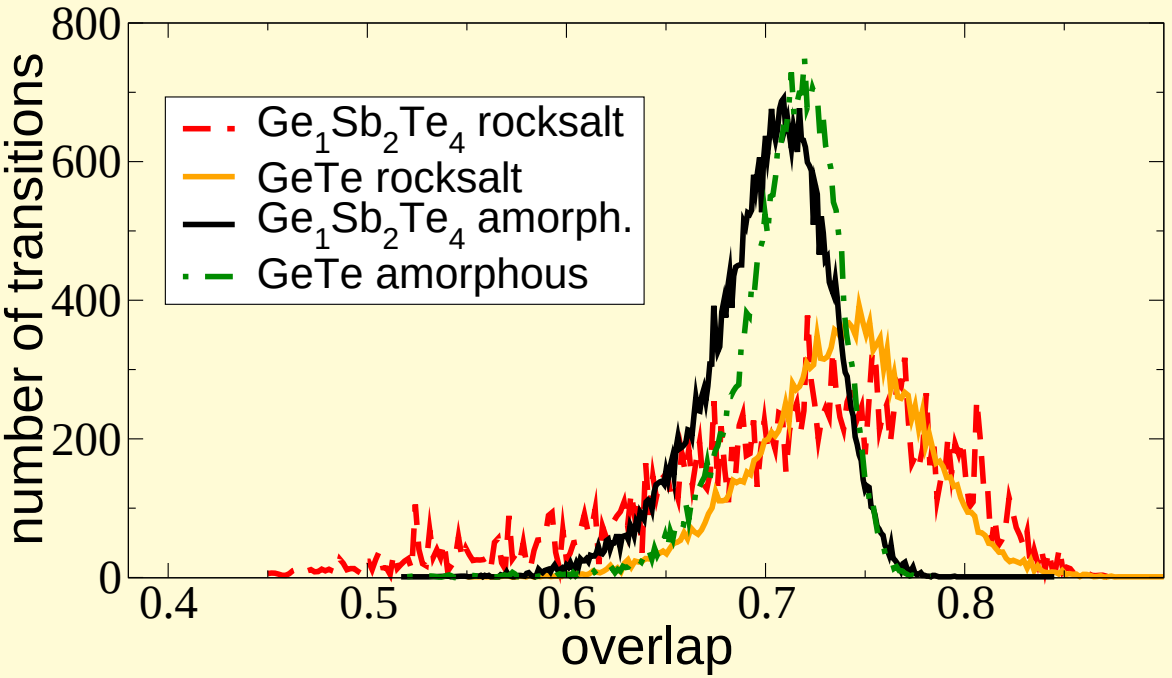
$$JDOS/\omega^2 = \frac{1}{N_{\mathbf{k}}\omega^2}\sum_{v,c,\mathbf{k}}\delta(\epsilon_{c\mathbf{k}}-\epsilon_{v\mathbf{k}}-\omega)$$

Origin of the optical contrast



- No significant changes in JDOS
- With constant matrix elements one wouldn't expect any optical contrast
- Optical contrast is determined by changes in transition matrix elements

Understanding the optical contrast



- Changes in local structure cause changes in spatial dispersion of wavefunctions
- Overlap changes $\rightarrow$ matrix elements change

Open problems for PCMs optimization:

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2. Is this contrast due to a change in the electronic energy levels?
3. Can we tune the optical contrast?

Contribution from distorsion and vacancies

- Decrease of coordination and inclusion of vacancies: reduce the number of Ge-Te bonds
- Decrease of coordination and distorsions: reduce the overlap of the wavefunctions
- Optical properties in PCM can be tuned by modifying these contributions!

Outline

Conclusions

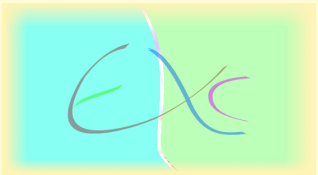
- Calculation of optical properties of PCMs from first principles
- Optical contrast in PCMs understood!
- Change in local order origin of optical contrast
- Optical contrast governed by changes in spatial overlap of wavefunctions which lead to smaller transition matrix elements
- The model explains how to change the optical contrast by tuning the number of Ge-Te bonds (vacancies, distortions, composition)

Acknowledgments

- Ground state and GW calculations: `www.abinit.org/`

- TDDFT for periodic systems: `theory.polytechnique.fr/codes/`

- BSE for periodic systems: `theory.polytechnique.fr/codes/`



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W. Welnic, S. Botti, L. Reining, and M. Wuttig,
Origin of the optical contrast in phase change materials
Phys. Rev. Lett. **98**, 236403 (2007).


W. Welnic, M. Wuttig, S. Botti, and L. Reining,
Local atomic order and optical properties in amorphous and laser-crystallized GeTe
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