



Simulations of some interesting amorphous materials

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Phase change materials

- Particular GeSbTe alloys are famous “phase change” materials: rapidly switching between **amorphous and crystalline phases**, of interest since Ovshinsky.
- Now the basis of commercial FLASH memory devices.
- *What can we say about this?*

Preliminary: the challenge of crystallization

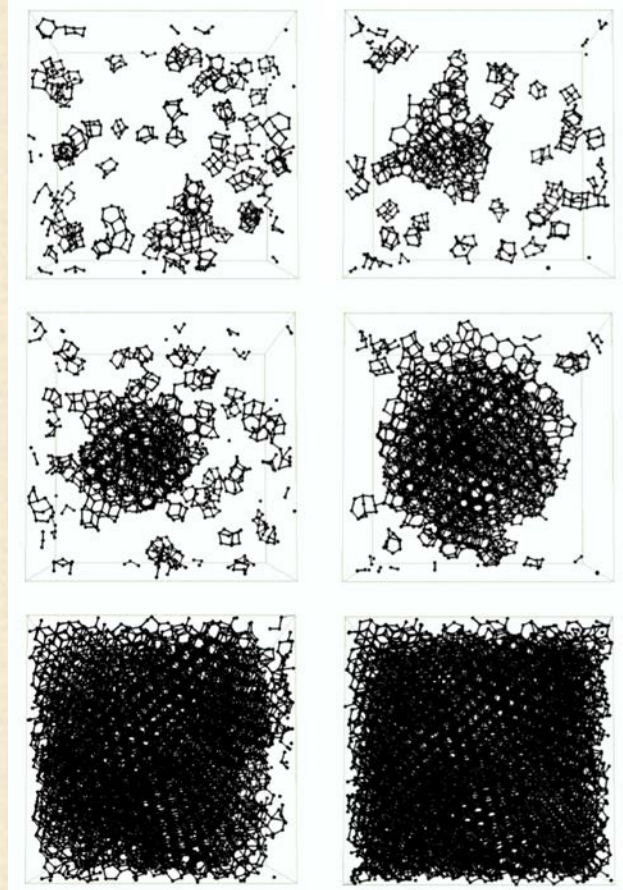
- The intrinsic time scale of these simulations is set by the MD time step: about 10^{-15} sec.
- Crystallization is devilishly hard – requiring typically *nanoseconds*¹, suggesting the need for millions of steps.

¹ P. Beaucage and N. Mousseau, PRB 71 094102 (2005)

Crystallization of Si (from liquid)

“Evolution of nucleation and crystallization during the liquid-crystal phase transition of SW Si at 1250K and 2.32 g/cm³. The configurations show atoms that belong only to crystalline structures at 0, 0.58, 0.86, 1.15, 1.44, and 1.73 ns”

“Thus, the critical cluster size should be around 175 atoms for Si at 1250 K, in agreement with the estimate of Uttormark *et al.*”



Now is the winter of our discontent...

- Chemistry of GST is more complex than elemental silicon.
- There are no credible empirical interatomic potentials.
- Beware size artifacts: these simulations use periodic boundary conditions, and calculations have shown that small cells crystallize faster.
- It would seem that we are in the “large, long-time, chemically complex” regime.



The Cambridge Crystallization

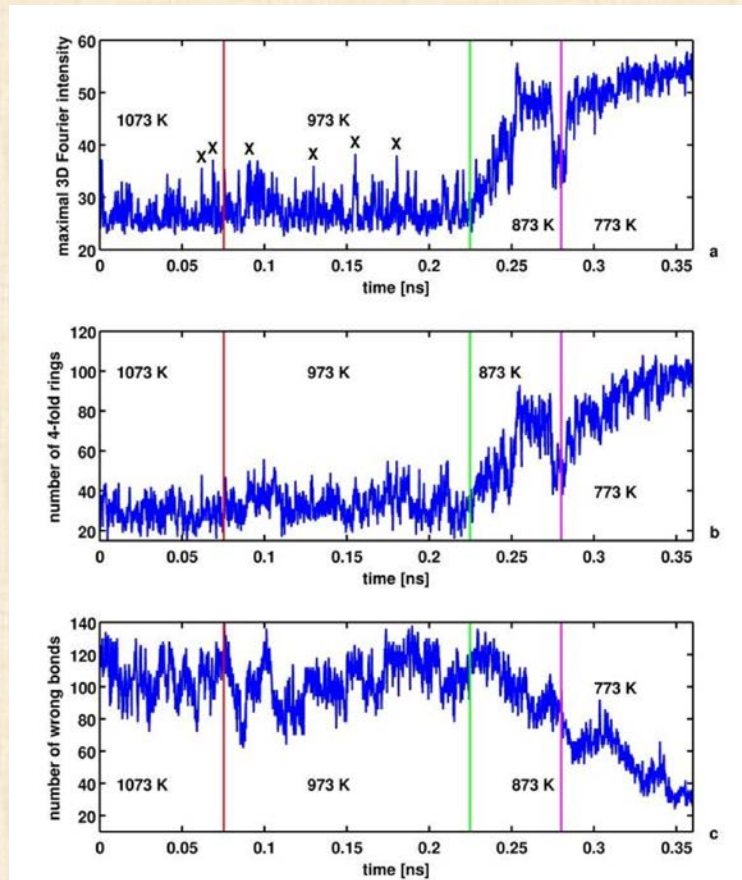
Microscopic origin of the fast crystallization ability of Ge–Sb–Te phase-change memory materials, J. Hegedüs & S. R. Elliott, Nat. Mats. (2008):

*Here, we describe for the first time how the entire write/erase cycle for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ composition can be reproduced using ab initio molecular-dynamics simulations. Deep insight is gained into the phase-change process; very high densities of connected square rings, characteristic of the metastable rocksalt structure, form during melt cooling and are also quenched into the amorphous phase. Their presence strongly facilitates the homogeneous crystal nucleation of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. **As this simulation procedure is general, the microscopic insight provided on crystal nucleation should open up new ways to develop superior phase-change memory materials, for example, faster nucleation, different compositions, doping levels and so on.***

Cambridge Recipe

- VASP *ab initio* MD code
- 63-90 atom models for GST-225,124 (now much improved and extended, esp. by Wuttig, Jones, Akola *et al.*)
- Cubic cells + periodic-boundary conditions
- Constant volume
- Quenching from melt + heating amorphous
- 6 month runs on 32 nodes of supercomputer (in 2008!)

E&H: The emergence of order amorphous → crystalline



Long range order: Maximum 3D Fourier intensity.

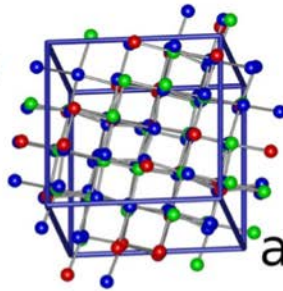
Rocksalt building blocks

Wrong bonds

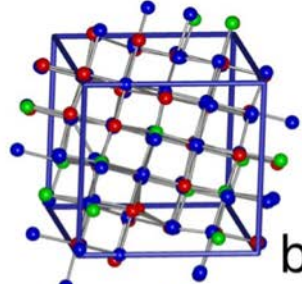
H&E: GST -124 and -225

Simulated Crystallization

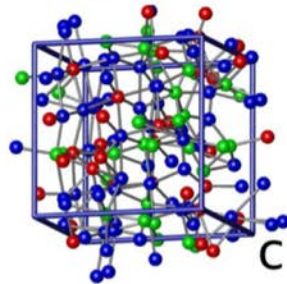
a) GST-225
(slow liquid-quenched)



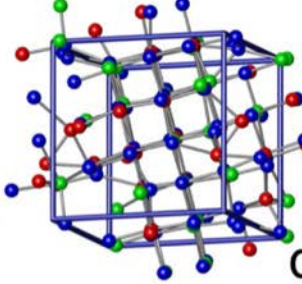
b) GST-124
(slow liquid-quenched)



c) a-GST-225
(fast liquid-quenched)

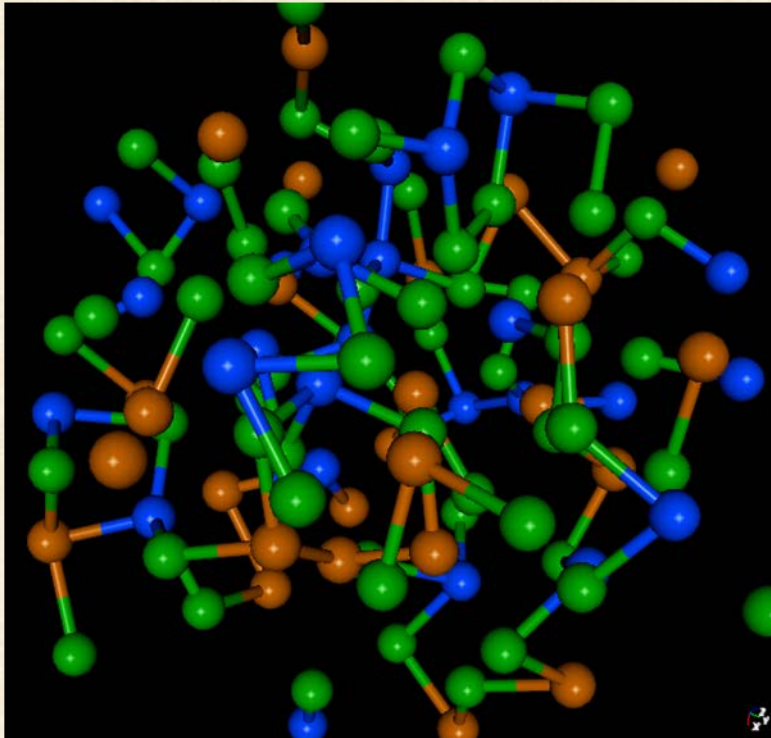


d) GST-225
(amorphous-annealed)



Ge= green; Sb= red; Te= blue

a-GST(225) \rightarrow c-GST(225) [the movie]



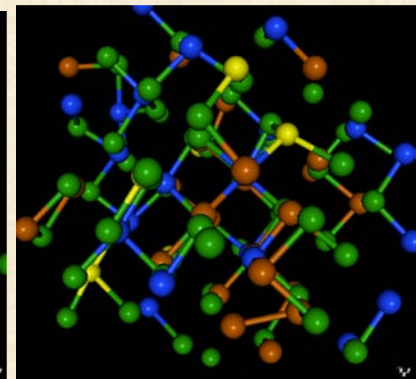
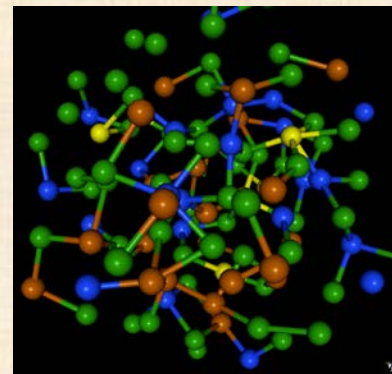
The heart of the problem is DYNAMICS.
650K anneal: 340 ps depicted here.

A video showing the process of crystallization in 225. *Merely a confirmation of H&E.*

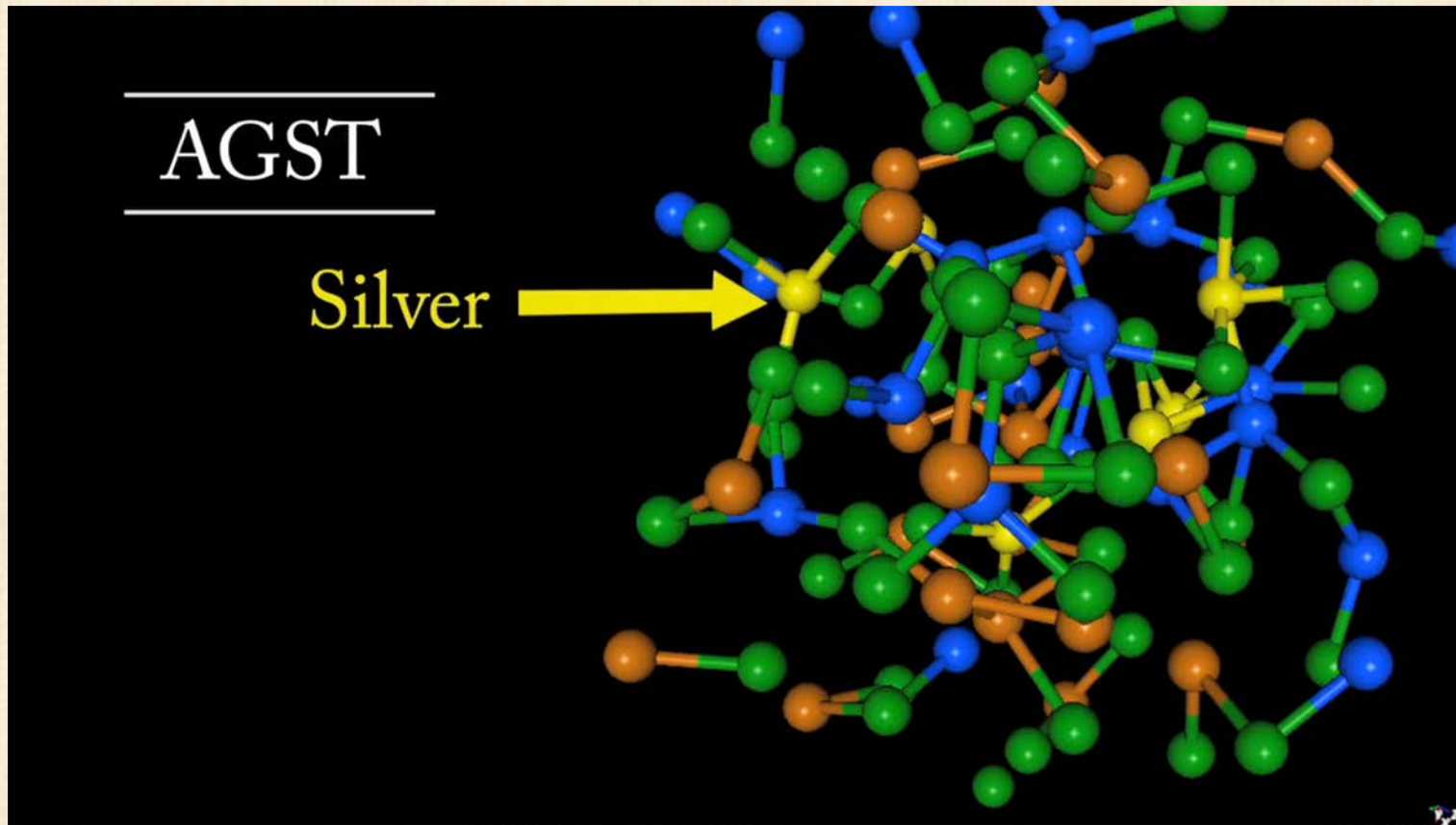
Key student: Binay Prasai

Snapshots near the beginning and near the end

Ge: blue, Sb: orange, Te: green



225+Ag: Dynamics



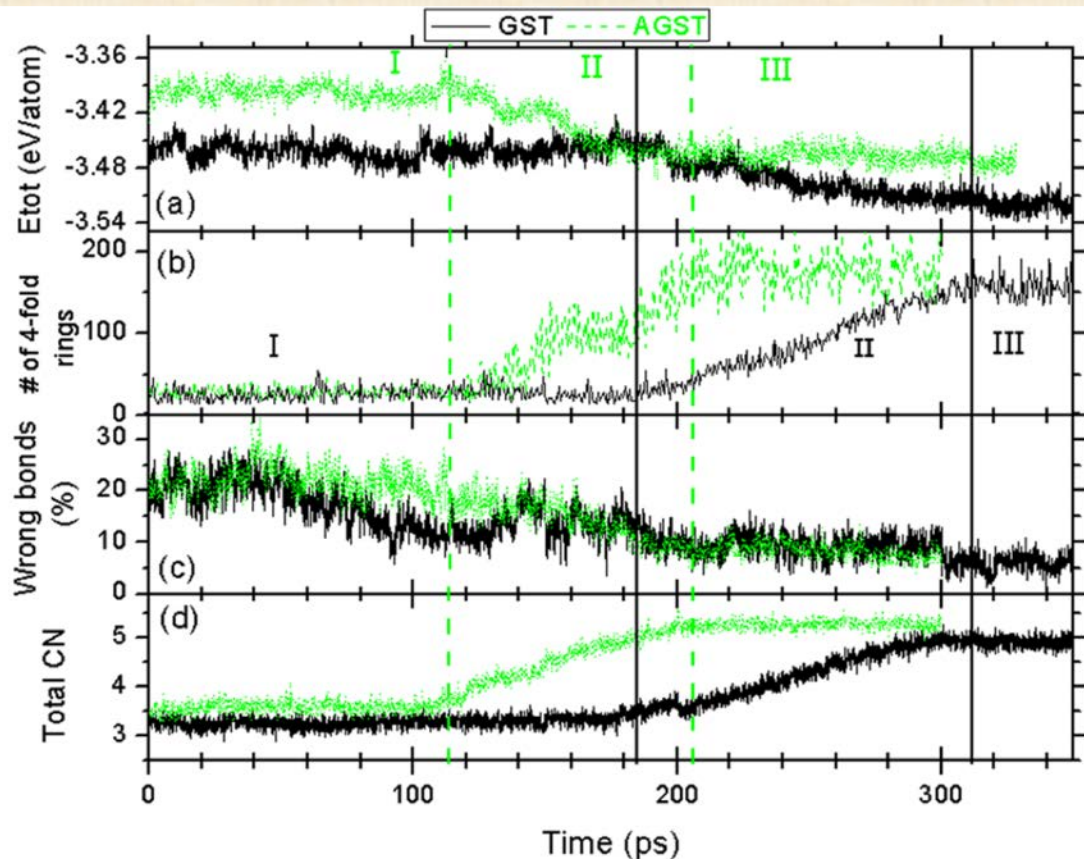
Crystallization compared

|← Crystallize →|

|← Incubation →|

|← Stabilization →|

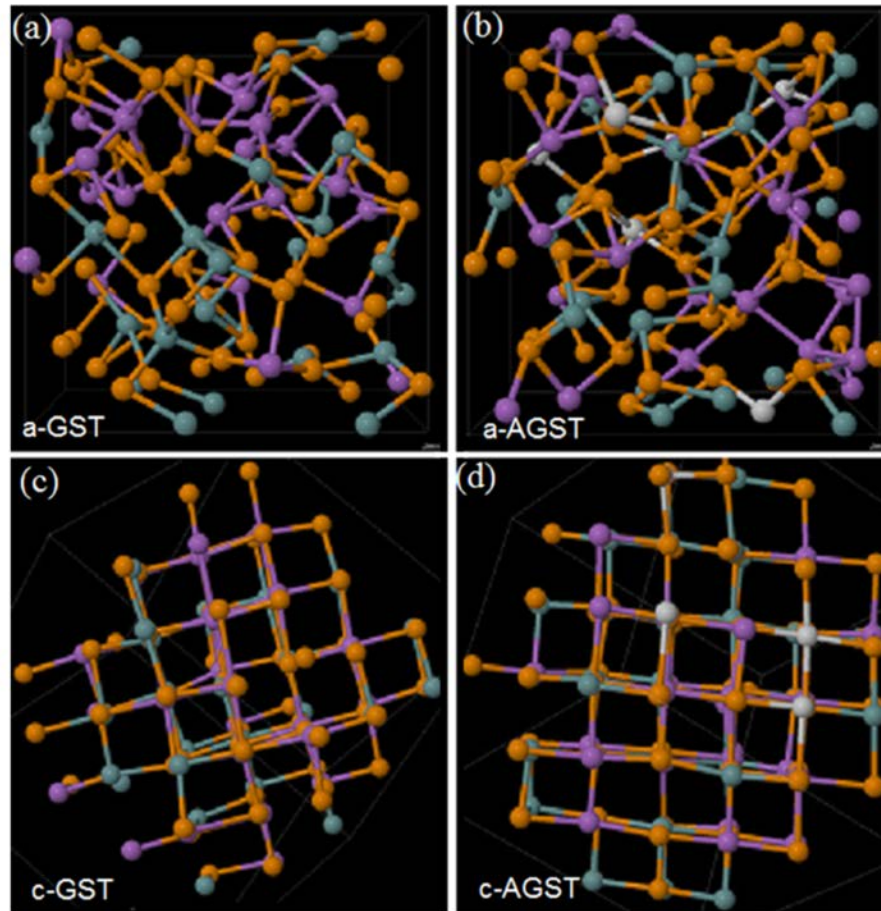
Nomenclature of H&E



What does it mean?

- Ag enters matrix substitutionally
- Repetitions suggest somewhat faster crystallization for Ag-doped GST (~ 200 ps) vs ~ 320 ps.
- The conductivity contrast is maintained, appears to be thermally stable.

Before and after: relaxed

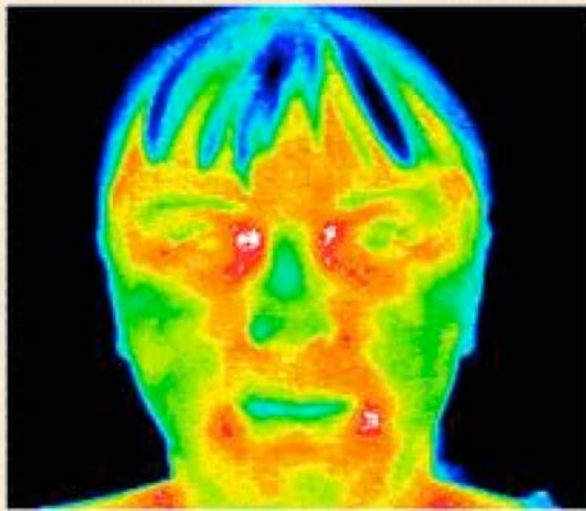
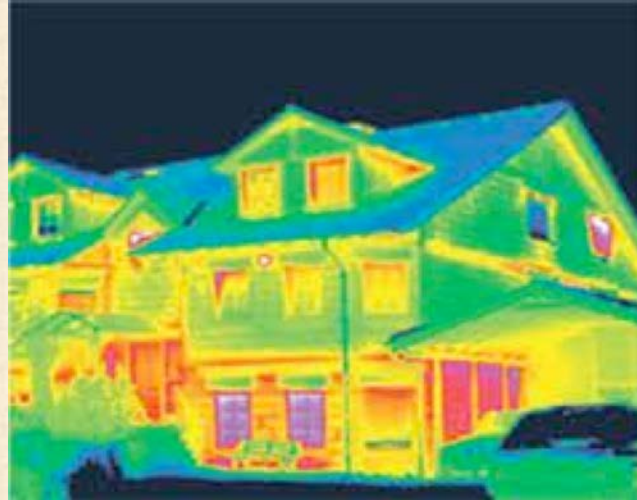


Color definitions: orange-Te, green-Ge, purple-Sb, and gray-Ag.

And now
for something
completely different...

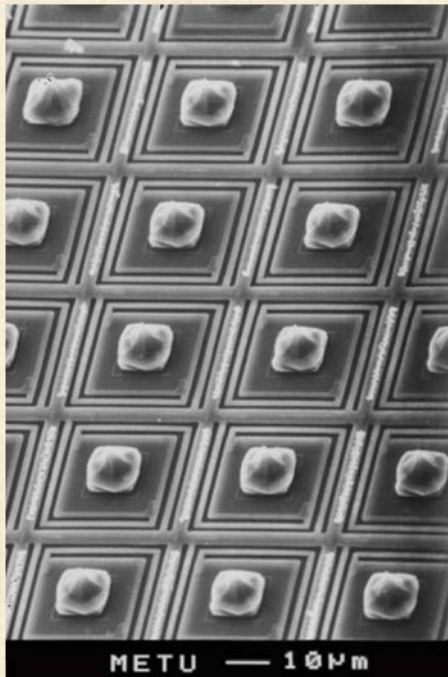


And now another application... Thermal imaging!



Thermal Imaging in a nutshell

Idea: probe the temperature pixel by pixel to get thermal image. **Strategy:** find material whose resistivity changes a lot with small change in T .



Micrograph of microbolometer at focal plane

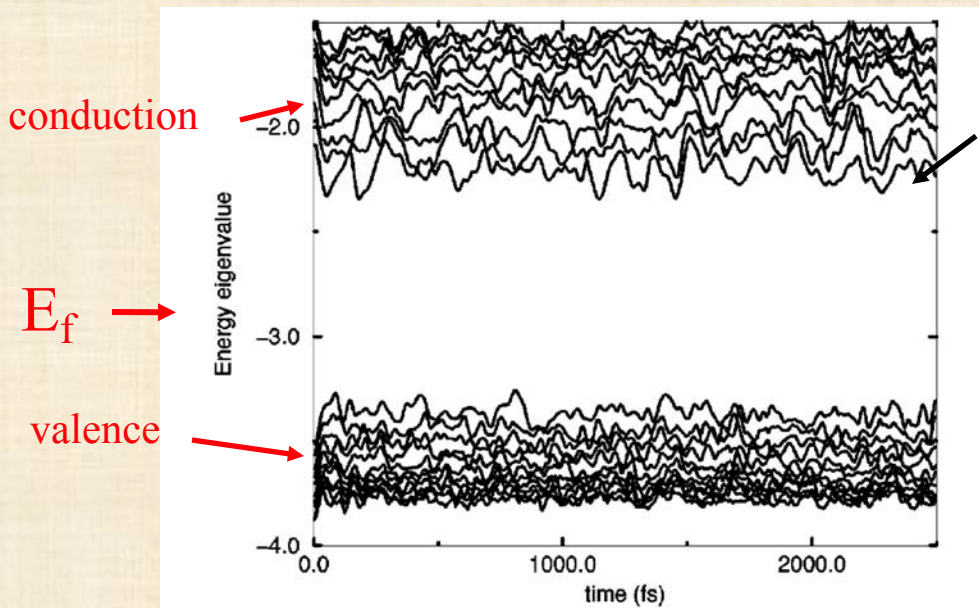
The key is a high resolution T-sensitive array

- Fact: doped a-Si:H and VOx are the best focal plane materials.
- Materials physics question: what determines the temperature coefficient of resistivity (TCR), and why these materials?
- $T > 0$ means moving atoms: so we estimate conductivity as function of temperature!

Science of TCR

States near gap are localized, sensitive to lattice vibrations. Consider **Amorphous Si**.

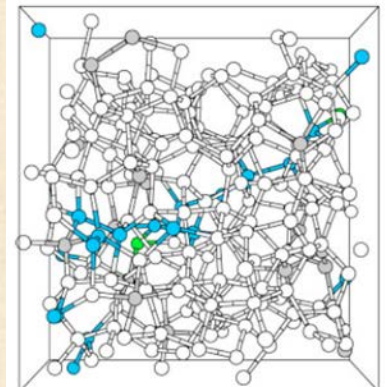
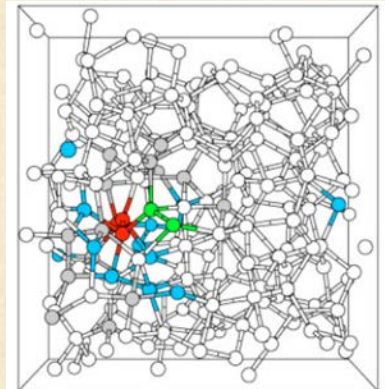
Simulation of network dynamics reveals that the electron eigenvalues and eigenfunctions near E_f are sensitive to phonons, and **vary by tenths of eV at 300K, an energy scale larger than kT.**



Simulation time (in fs= 10^{-15} s)

Thermal eigenvalue fluctuations, 300K
Large for localized States (DAD, PRL 1991)

States conjugate to fluctuating eigenvalues vary considerably (same state separated by 100fs)
DAD (Phys Rev B 2000)



Large TCR, why?

- In an adiabatic picture, thermal disorder strongly modulates electronic energy eigenvalues and eigenstates.
- The conductivity depends critically on these quantities. We routinely compute all of these.
- We use these quantities, obtained from believable atomistic models to estimate the T-dependence of the conductivity.
- Disorder (thus localization) amplifies the electron-lattice coupling, enhances T-dependence of conductivity.

Estimating the conductivity

Thus, DC conductivity may be computed as the zero frequency limit. To include the motion of the lattice (thus temperature dependence), we average over the motion of the atoms from a simulation.

DC conductivity:
$$\bar{\sigma}_{\alpha\alpha}(\varepsilon) = \frac{2\pi e^2 \hbar}{\Omega m^2} \sum_{ni} \overline{|\langle \psi_n^t | p_\alpha | \psi_i^t \rangle|^2 \delta(\varepsilon_n^t - \varepsilon) \delta(\varepsilon_i^t - \varepsilon)}$$

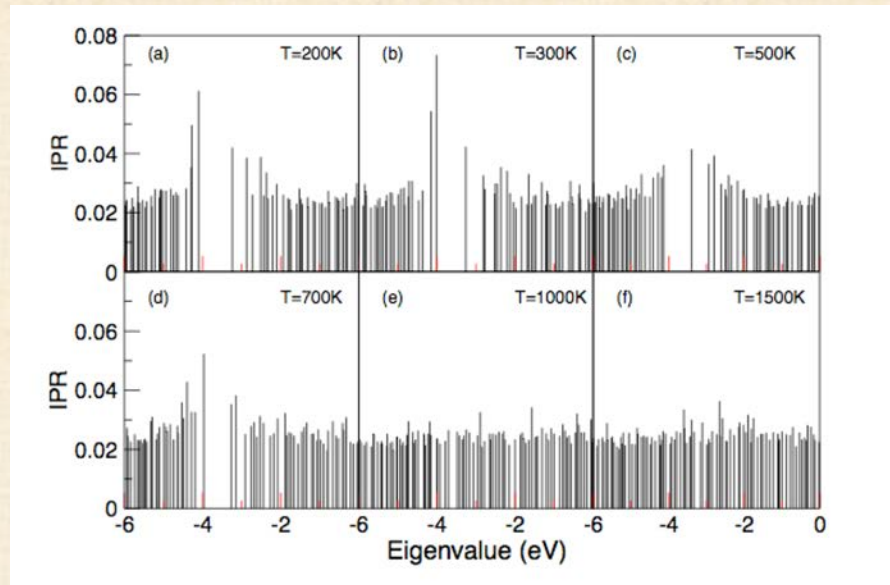
We compute all this for credible structural models. Main T-dependence is in the thermal (trajectory) average!

We have carried this out

- System needs to be well equilibrated.
- Small systems (*ca* 216 atoms) and simple approximations (minimal basis set) appear to pick up the observed effects.
- Calculations: average Kubo formula over many configurations at various T.

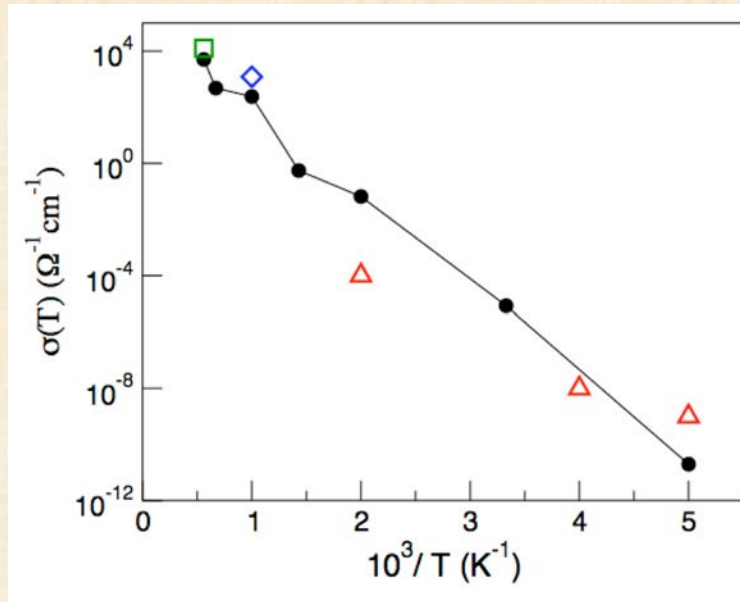
Results from Kubo study

a-Si (intrinsic material)

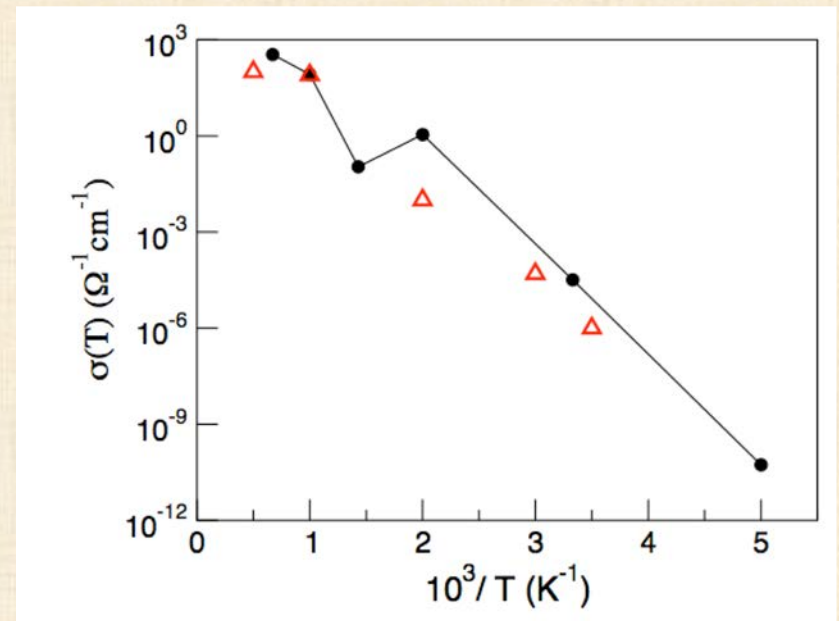


IPR [measure of localization]
as function of temperature

T-dependent conductivity



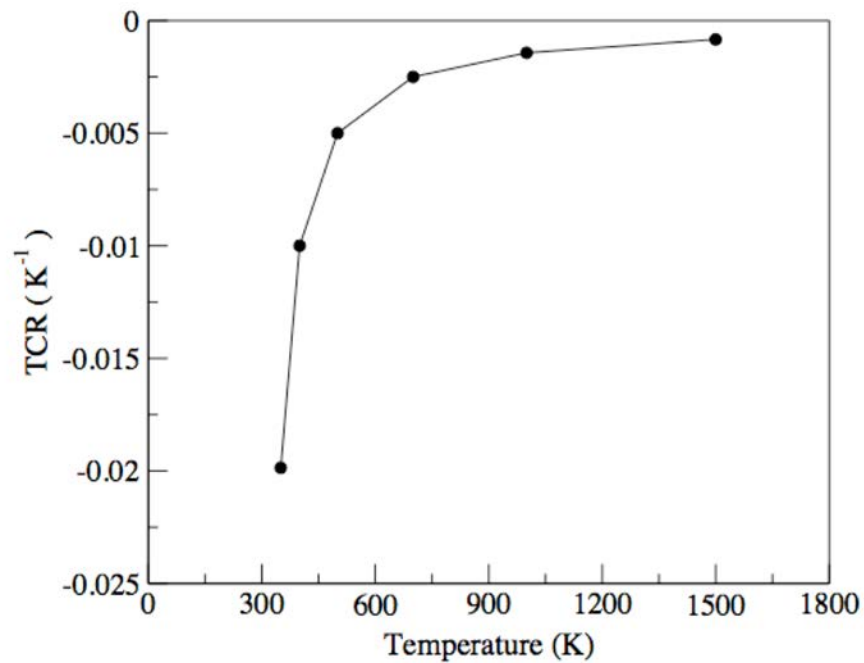
a-Si



a-Si:H

Symbols: experiment; connect-the-dots: calculation

TCR



$$TCR = \frac{1}{\rho_0} \frac{\rho - \rho_0}{T - T_0}$$

Note: TCR ~ -2.0%/K
Expt: -(2.0-5.0)%/K

So what does it mean?

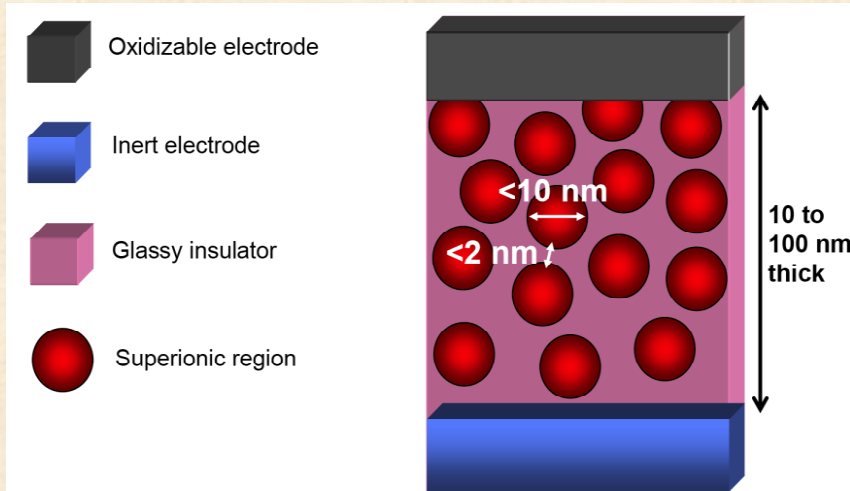
- The high TCR of a-Si is due to the high sensitivity of the states near the Fermi level to thermal distortions.
- Official buzz words: The electron-phonon coupling is large for localized states around the gap.
- Shift the Fermi level into these thermally fluctuating states and the conductivity (resistivity) varies greatly with T!

And now
for something
completely different...

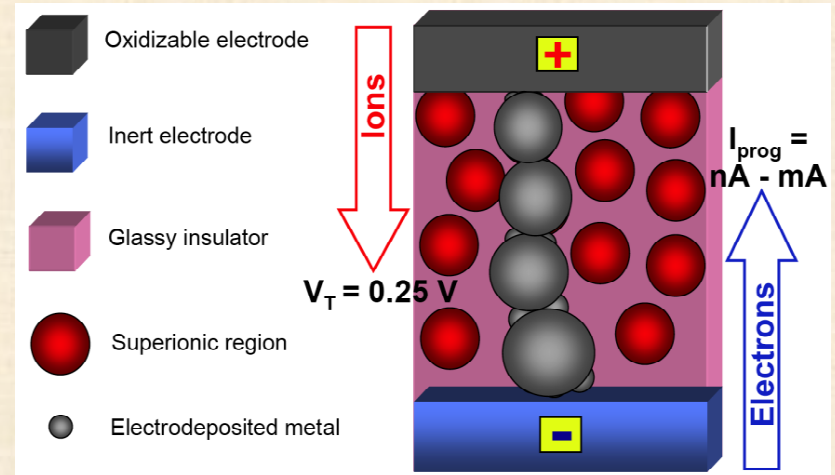


A different computer memory
material made from solid
electrolyte

Programmable Metallization Cell or “Conducting Bridge” Memory



High resistance state (Ag exists in the form of ions).



The cell is biased to grow metallic Ag filaments between cathode (bottom electrode) and oxidizable (Ag) anode (top). The resistance is nearly zero, because of the metallic filament.

Illustrations courtesy M. Mitkova, Boise State
M. N. Kozicki, Arizona State University

The basic idea

- Silver ions in S or Se glasses move quickly through the glass.
- The cell has two states, one with nearly zero (electrical) resistance and one with nearly infinite resistance. The “0” and “1” states....
- It is easy to change from one state to the other.
- Switching time is ~ 10 nanoseconds (0.00000001 seconds!).
- Devices have been grown on ~ 10 nanometers (0.00000001 m) scale.

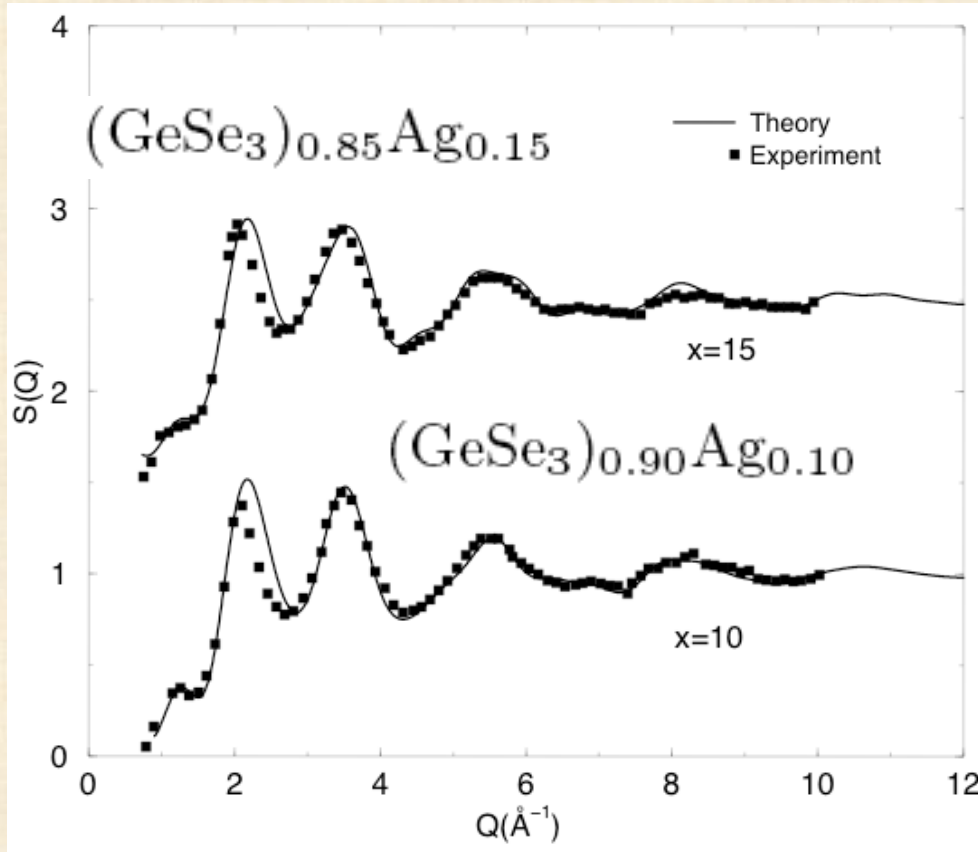
Our problem: what is happening at the atomic level?

- We make the first realistic models of the silver-doped glasses.
- We study the dynamics of the silver in detail.
- We discover atomic-level processes hard/impossible to infer from experiment.

Approach

- Use Fireball local orbital MD, subsequently with plane wave DFT.
- Cook and quench in conventional way, forming models of $a\text{-(GeSe}_3\text{)}_{.9}\text{Ag}_{.1}$ and $a\text{-(GeSe}_3\text{)}_{.85}\text{Ag}_{.15}$

GeSe:Ag Models (240 atoms)



Static structure factors.

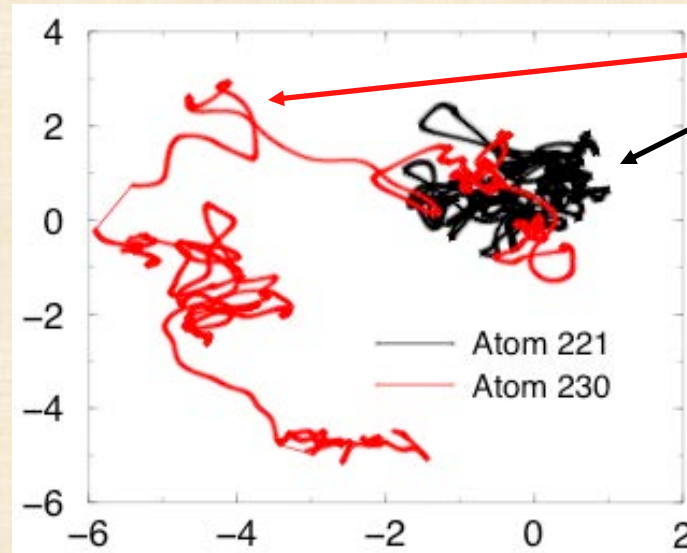
Experiment:

A. Piarristeguy, J.
Non-Cryst. Sol. **332**,
1 (2003).

Ag hopping from thermal MD

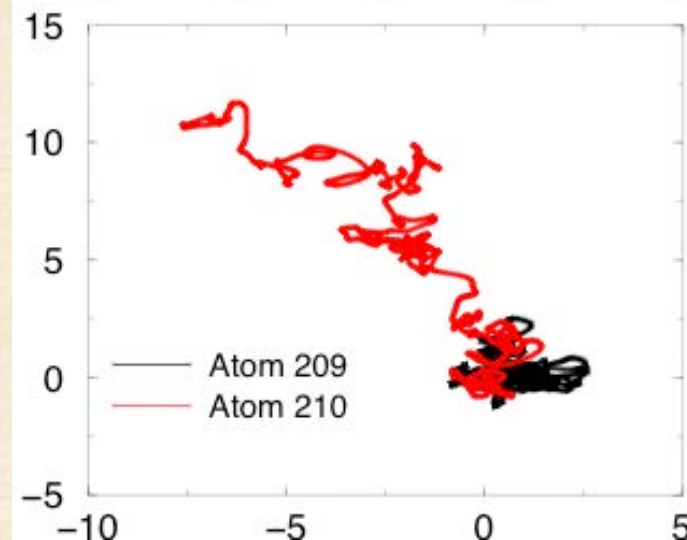
Thermal MD, constant T, 20 ps, *ab initio* interactions, 1000K.

D. N. Tafen, 2005

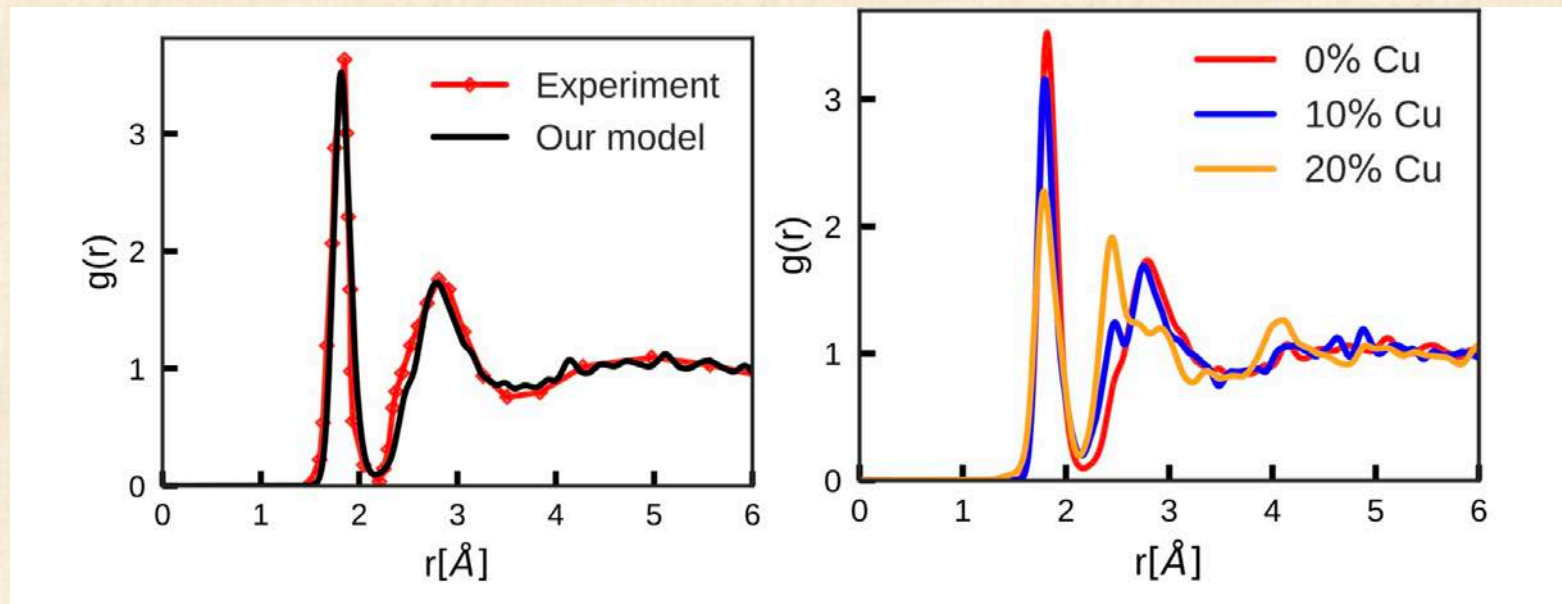


Most diffusive Ag atom

Least diffusive Ag atom



Another CBRAM system: $\text{Al}_2\text{O}_3 + \text{Cu}$ (~ 200 atoms, VASP)



Left: alumina: model and experiment¹ Right: $g(r)$ for 0, 10%, 20% Cu

¹P. Lamparter, R. Kneip, Physica B 234-6 405 (1997).

Cu clusters in Al₂O₃

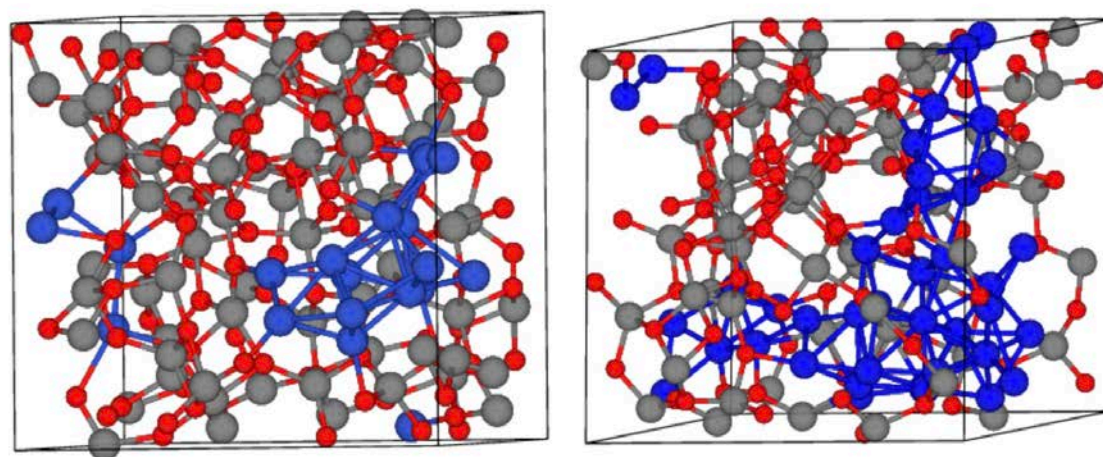


FIG. 2. Cu atoms (blue), O (red) and Al (grey) in (a-Al₂O₃)_{0.9}Cu_{0.1} (top) and (a-Al₂O₃)_{0.8}Cu_{0.2} (bottom). Note that the Cu clusters in the oxide matrix. Periodic boundary conditions are employed throughout.

Space-filling Cu cluster
for 20% broken for 10%

**Cu clustering in
Alumina, not in chalcs**

Computation of conduction paths

- For Cu-doped alumina and a Ag-doped GeSe_3 , we compute the path of the conduction from the Kubo-Greenwood formula. Details next lecture (if time allows!)

Bader projection of conduction onto atomic sites

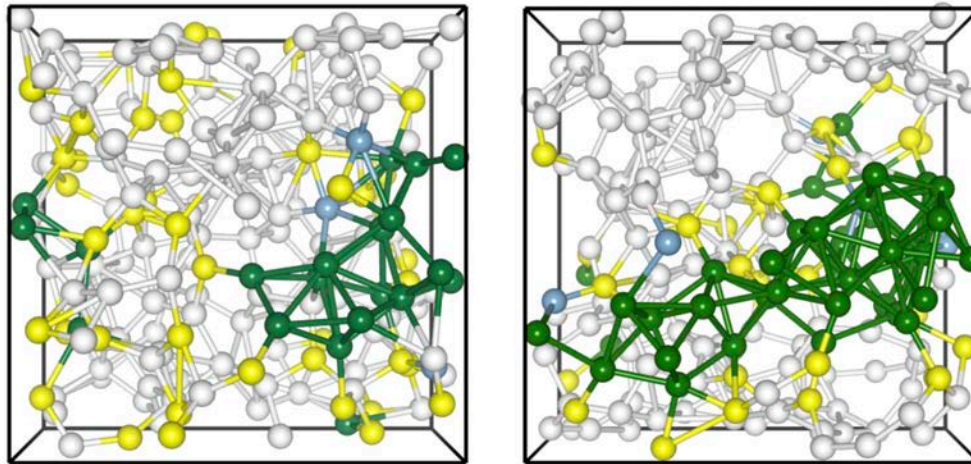


FIG. 4. Bader projection of SPC $\zeta(\mathbf{x})$ of oxides. Left: $\text{Al}_2\text{O}_3:\text{Cu}, 10\%$. Right: $\text{Al}_2\text{O}_3:\text{Cu}, 20\%$. The atoms with color represent the atoms with 95% of SPC[20]. Color nomenclature is green:Cu, yellow:O, blue:Al

Inferences

- There are *trapping defects*. Trap model is successful with relaxation data.
- There is free volume (reduced local density) for rapid diffusers.
- Some goals: provide the microscopic parameters for the trapping model, elucidate the microscopic (and dynamic) nature of the traps.
- Direct and realistic simulation of atomic diffusion: accessible with MD time scales (picoseconds).
- Cu (and Ag) cluster in alumina host, do *not* from the chalcogenide host. We compute/compare the conduction pathway.

And now
for something
completely different...



Materials by design

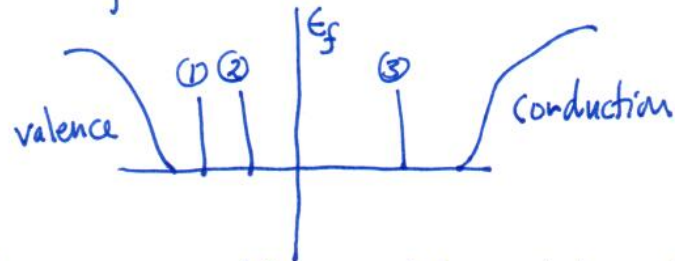
Engineering the gap

Key student: *Kiran Prasai*

Idea: We want a spectral region to include no electron states – we seek a model with a specified optical gap, or we want to impose *a priori* electronic information that an ideal model should have a particular gap...

Examples: band gap engineering for PV applications
: means to impose *a priori* optical info. in modeling

We have this density of electron states in our computer model:



(1)-(3) are unwanted gap states. Lets get rid of them! How?

Note: The total energy (in tight-binding) is:

$$\Phi = \underbrace{\sum_{n \text{ occ}} \lambda_n}_{\text{Band energy}} + \underbrace{U}_{\text{Repulsive term}}$$

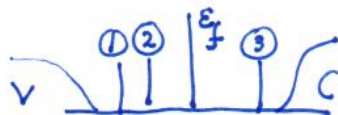
So the force is just

$$F_\alpha = -\frac{\partial \Phi}{\partial R_\alpha} = \sum_{n \text{ occ}} -\frac{\partial \lambda_n}{\partial R_\alpha} - \frac{\partial U}{\partial R_\alpha}$$

R_α : atomic coordinate

$$F_{\alpha} = - \sum_{n \text{ occ}} \frac{\partial \lambda_n}{\partial R_{\alpha}} - \frac{\partial U}{\partial R_{\alpha}}$$

Each term is a contribution to total force - eigenvalue by eigenvalue.



So any $\frac{\partial \lambda_n}{\partial R_{\alpha}}$ below ϵ_f provides a piece of the total force.

But... Consider $\partial \lambda_3 / \partial R_{\alpha}$, the gradient of $\lambda_3(R_1 - R_{3n})$. It indicates direction of maximum increase of λ_3 .

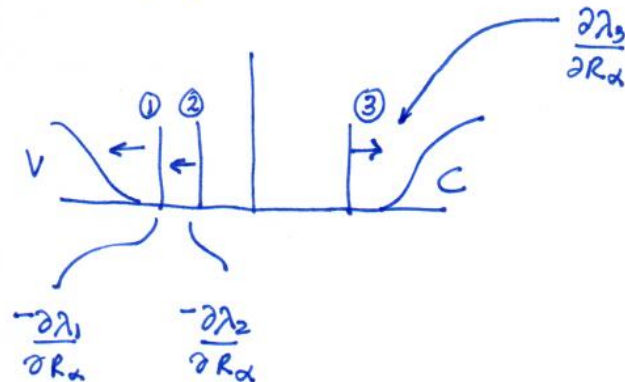
⇒ So to shift λ_3 toward conduction edge, move incrementally along $\vec{e} = \partial \lambda_3 / \partial R_{\alpha}$

Analogously, shift λ_1, λ_2 toward valence edge by moving along $-\partial \lambda_1 / \partial R_{\alpha}$ etc (- for valence).

OK, so these $\frac{\partial \lambda_n}{\partial R_\alpha}$ gradients point the way to optimizing the gap. They are byproducts of any simulation thanks to the Hellmann-Feynman theorem

$$\frac{\partial \lambda_n}{\partial R_\alpha} = \langle \psi_n | \frac{\partial H}{\partial R_\alpha} | \psi_n \rangle \quad H|\psi_n\rangle = \lambda_n|\psi_n\rangle \text{ etc}$$

Conceptually then, we add "gap-clearing forces" on states ①, ②, ③.



Practical implementation

Consider a Lagrangian $\mathcal{L} = T - \Phi$ in which T is the usual kinetic energy, and

$$\Phi(R_1, R_2, \dots, R_{3N}) = \sum_i f_i \langle \Psi_i | H | \Psi_i \rangle + U_r + \sum_i \gamma g(\lambda_n) (\langle \Psi_n | H | \Psi_n \rangle - \varepsilon_f)$$

Usual forces

“gap clearing” force

$g(\lambda_n)$ is picked to move valence (conduction) defect states into valence (conduction) tail.

Cooked up to push defect levels below E_f into the valence band, levels above E_f into conduction band.

Gap engineering: continued

Biased dynamics (with forces added to open gap) at diffusive temperatures leads to relaxed structures with engineered gap.

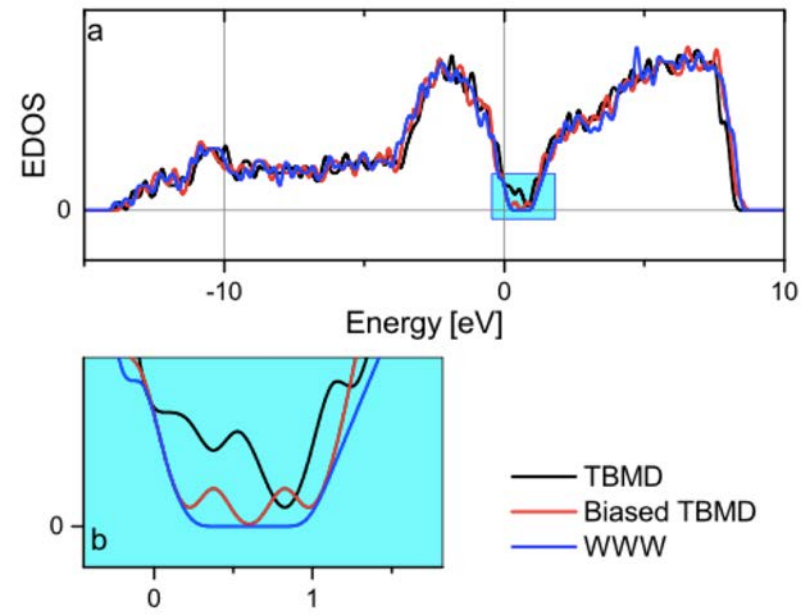
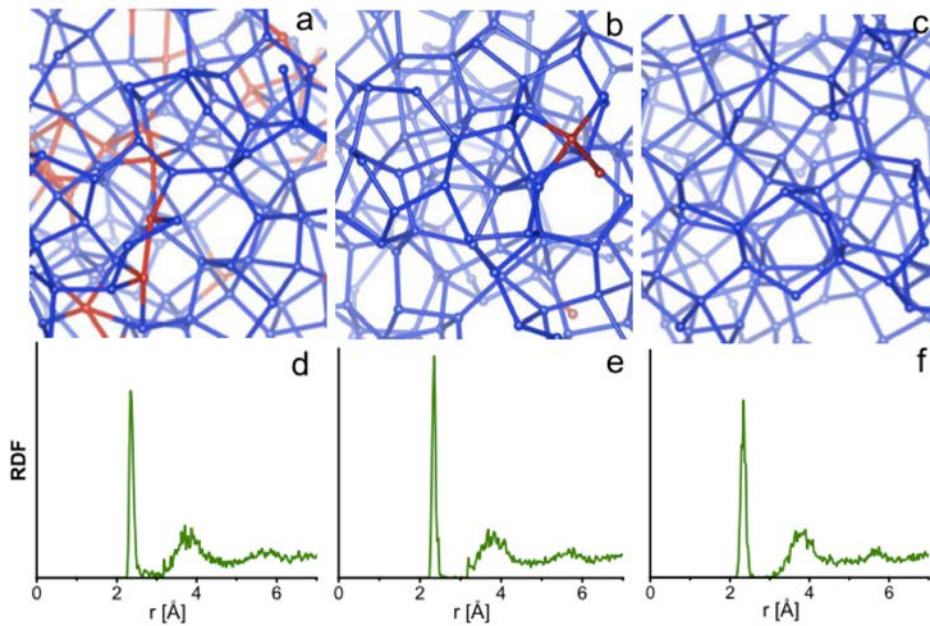
In practice we carry out the melt-quench segment of the simulation with biased forces. After dynamical arrest, we anneal and relax with physical forces and produce models with the desired optical gap.

Implemented with *ab initio* code (VASP) and tight-binding.

Results: a-Si

TBMD “gap force” WWW

Density of states

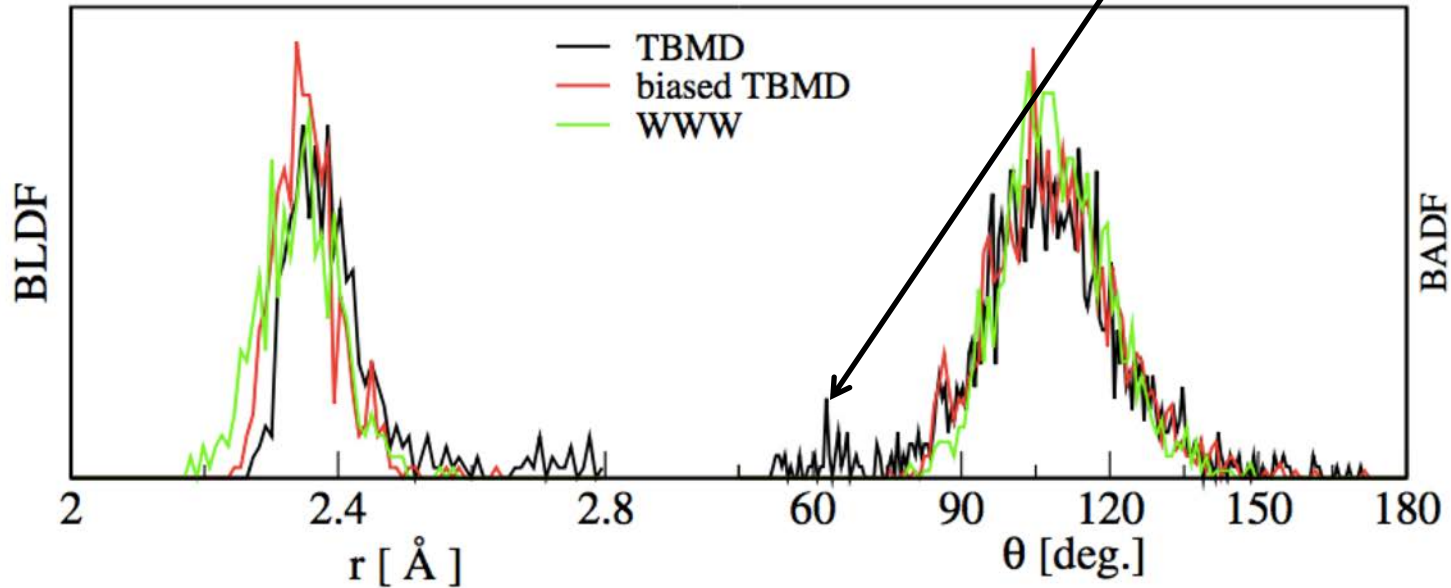


Red – coordination defects

97% fourfold (~87% tbmd)

Defects: structural
and electronic!

Results: a-Si



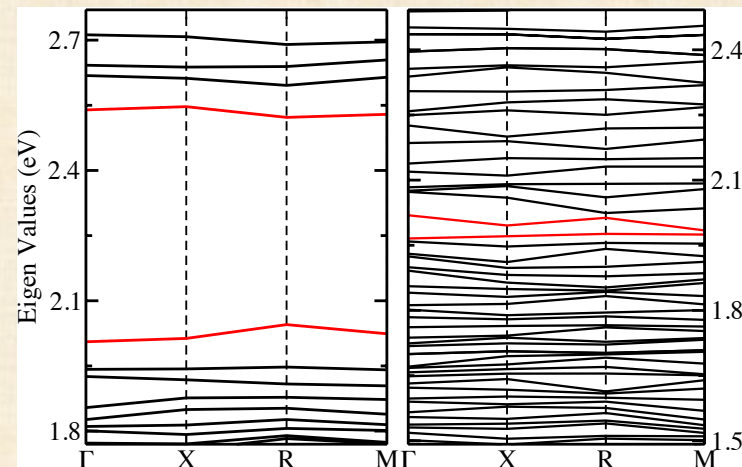
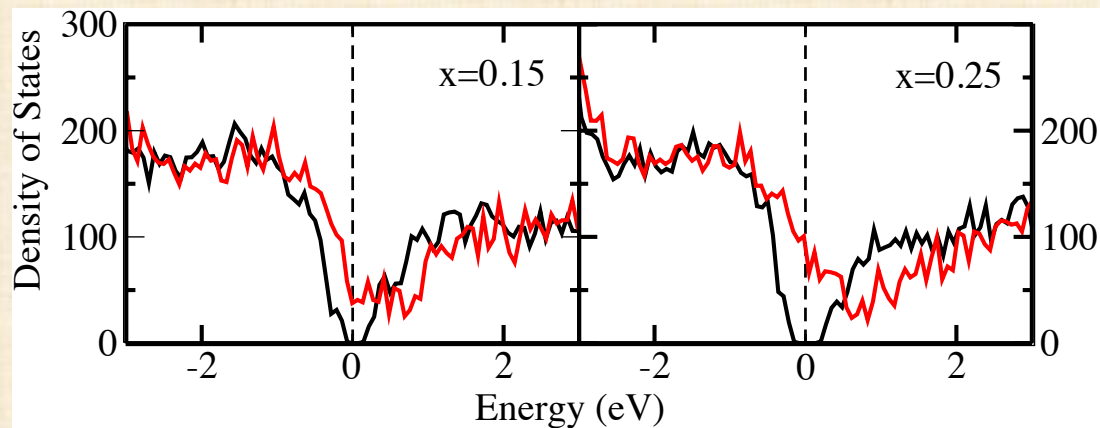
Note: STRUCTURAL features of “gap force” model is much better than TBMD, close to WWW. **Electronic *a priori* information improves the structure.**

a-(GeSe₃)_{1-x}Ag_x Materials

- Solid Electrolyte (incredibly mobile Ag in glassy host)
- Conducting bridge (FLASH) memory materials: insulating phase and conducting phase (real devices you can buy!)
- Unclear identity of **electronically** conducting phase (little Ag wires or something else?)
- **This Work:** Determination of electronically conducting phase at $x=0.15$ and 0.25 , about 0.04 eV/atom above best glass models. **Start from FEAR model**
- Amorphous forms with qualitatively different optical response. Seems consistent with G. Chen experiments.

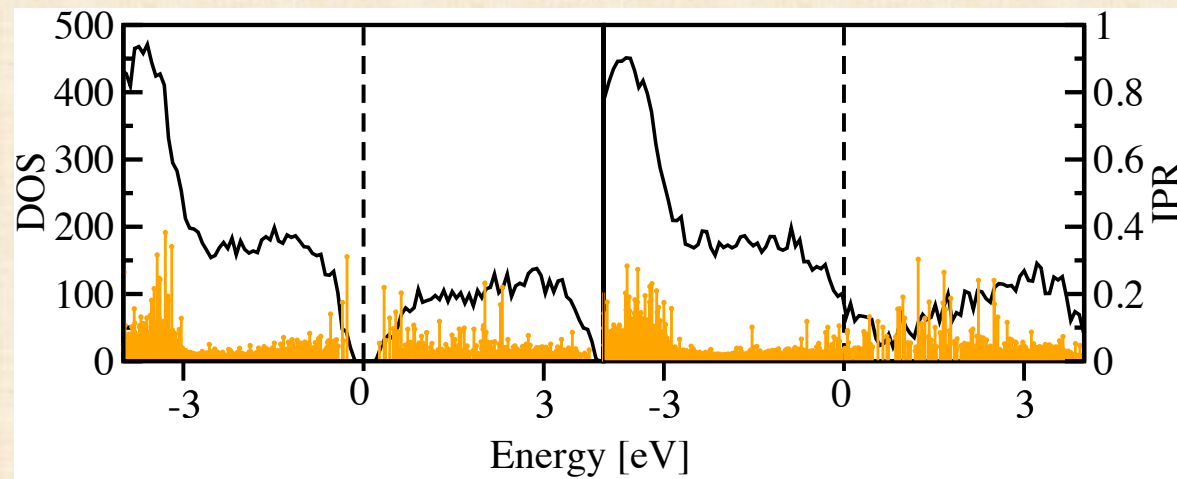
Electronic Structure: Metallic vs. Insulating

Black: Insulating, Red: Metallic



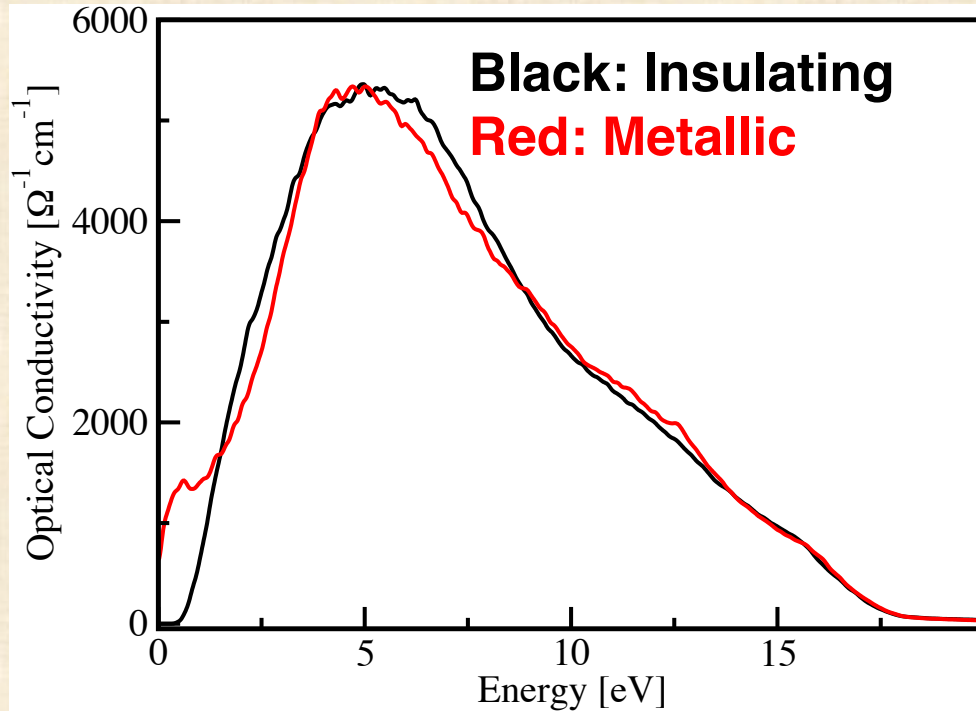
Red lines: HOMO-LUMO Levels

IPR: A measure of Localization



Optical Conductivity

Kubo-Greenwood Formula



DC Conductivity:

Insulating $\sim 10^{-6}$ S/cm

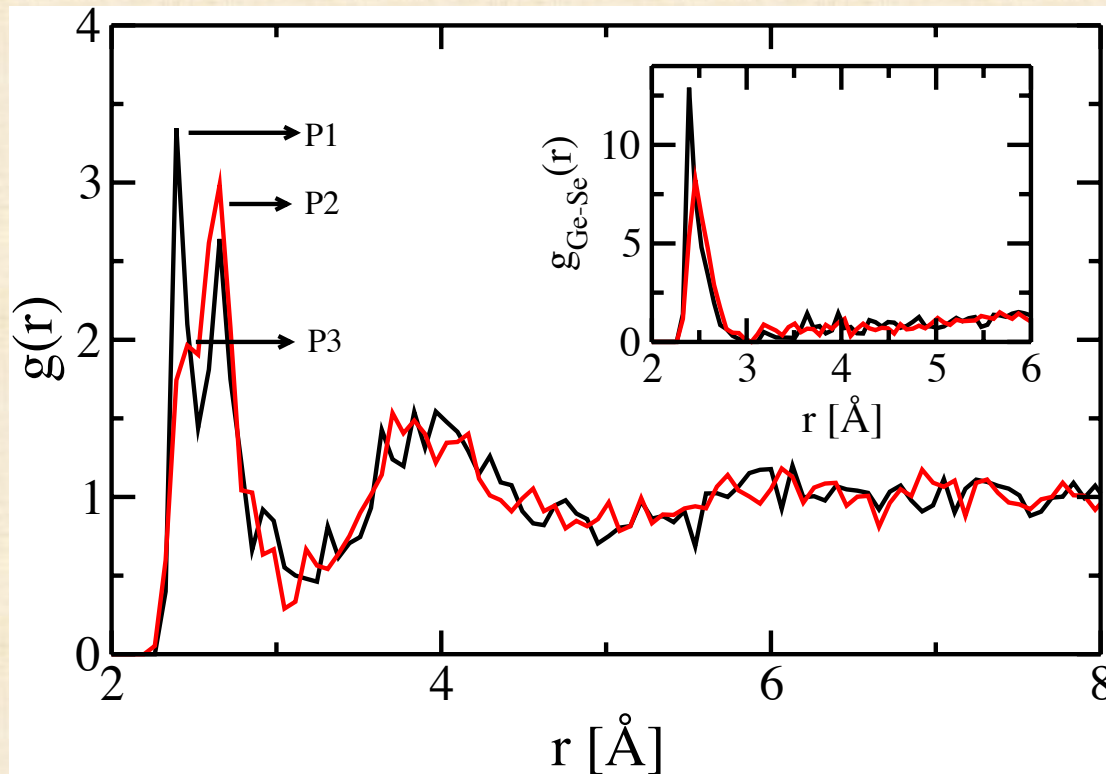
Metallic $\sim 10^2$ S/cm

Mechanism: impurity band hopping at Fermi-level, conduction Through Se p-orbitals **not** silver!

Pair Correlations

$(\text{GeSe}_3)_{1-x}\text{Ag}_x$: Ag_2Se and $\text{Ge}_t\text{Se}_{1-t}$

Black: Insulating, Red: Metallic



Gap engineering: conclusion

- We give a practical recipe to impose a desired gap. (potentially useful for applications).
- *Constraining the electronic structure has structural consequences.* We offer means to include complex but important information in making a model that agrees with our full knowledge base

Can determine new phases of useful materials with desired electronic properties

Comments on SIESTA

There are several ways to solve the Kohn-Sham equations.
The most popular are:

Spectral methods (some basis set and variational principle)

- Plane-wave methods (in the spirit of solid state theory)
- Local orbital methods (in the spirit of quantum chemistry)

Both methods are extremely useful, both have specific strengths and weaknesses.

I use VASP (plane waves) and SIESTA (local orbital).

A few words about SIESTA

Spanish Initiative for Electronic Structure of Thousands of Atoms

P. Ordejon, E. Artacho, J. Soler *et al.*

- Pseudopotentials
- Solution of Kohn-Sham equation on approximately complete basis
- Basis set: compact pseudoatomic orbitals “fireballs”
[O. F. Sankey]
- Flexible: User can select basis set from minimal to Fairly complete. Example for Si
- Single zeta (s+3p), double-zeta 2(s+3p), double-zeta
- Polarized 2(s+3p)+5d,

More SIESTA

Very well written and developed code, with most of the bells and whistles we expect, and some unusual possibilities for linear scaling computation and non-equilibrium Green's functions for transport (TRANSIESTA).

Vast experience now, applied to everything from nanowires to DNA.

Well documented and **FREE!**

SIESTA, more

Go to: <https://launchpad.net/siesta>

Key reference: J. M.Soler et al, JPCM 14, 2745 (2002)

Also:

<https://web.pa.msu.edu/people/tomanek/SIESTA-installation.html>

And to show how modern and cool I am, a Youtube video:

<https://www.youtube.com/watch?v=4QuSIf3vECQ>

From Emilio Artacho:

<http://www.psi-k.org/Psik-training/Bristol-September%202009/Emilio/ArtachoBristolSiestaTut09-2.pdf>

SIESTA discussion

Advantages:

- Can be much faster than plane
- Wave methods.
- Advantageous for very large systems.
- Free, many earlier calculations, excellent documentation.

Disadvantages:

- Even less of a “black box” than plane wave schemes.
- Basis set IS incomplete. Sometimes it matters sometimes not, *you have to check and understand.*
- In practice if one uses a full basis, it's as slow as plane waves.