First-principles modeling of phase change materials

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Plan of Talk

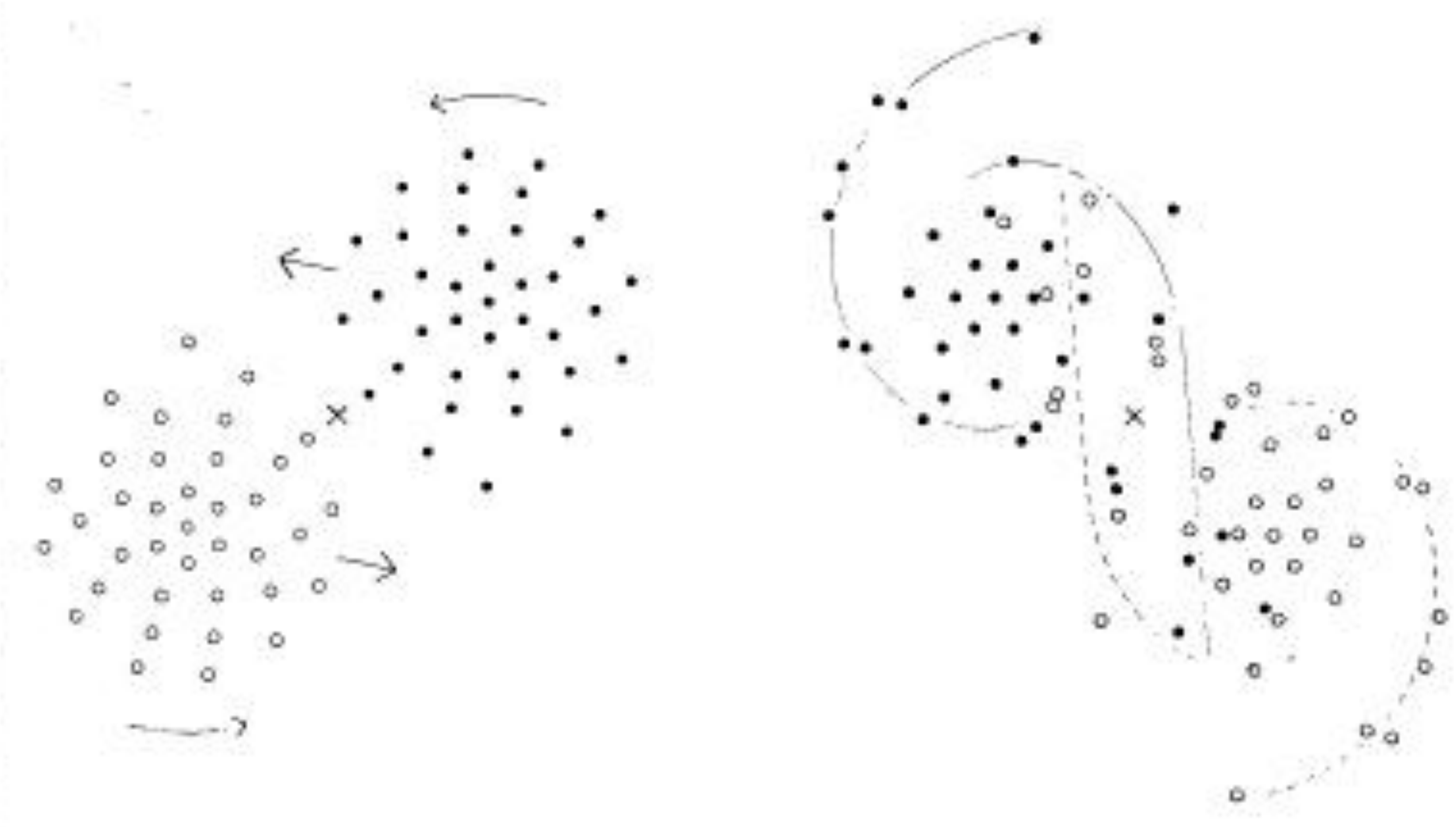
- A little history
- Modeling Phase Change Materials
- The Cambridge Crystallization
- Electronic Structure and Fluctuations
- Doping: Transition Metals
- Conclusions

The first MD simulation

Erik Holmberg (1908-2000), an astronomer at Uppsala, performed the first MD simulation to simulate galaxy collisions in 1941:

Starting with two “galaxies” (each with 37 “stars” represented by lamps), he simulated a galaxy-galaxy collision by attaching Se photocells to measure light intensity (which falls off like $1/r^2$, as does the gravitational force), evolved lamp coordinates according to equations of motion and optically inferred forces!

Results: Galaxy merger



E. Holmberg, Ap. J. **94** 385 (1941)

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation".

(Dirac, 1929)

$$i\hbar \partial\psi / \partial t = H(t)\psi$$

$$\boxed{\hat{H}(\{\vec{r}_i\},\{\vec{R}_\nu\},t) = \hat{T}_e + \hat{V}_{e-e} + \hat{T}_N + \hat{V}_{N-N} + \hat{V}_{e-N} + \hat{H}_{ext}}$$

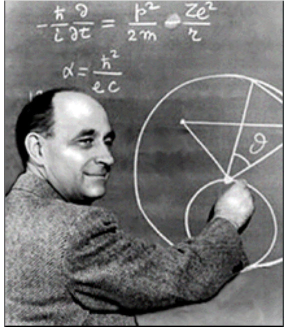
$$\hat{T}_e = \sum_{i=1}^{NZ_a} \frac{p_i^2}{2m}, \quad \hat{T}_N = \sum_{\nu=1}^{N} \frac{P_\nu^2}{2M} \quad \text{… kinetic energies}$$

$$\hat{V}_{e-e} = \frac{1}{2}\sum_{i\neq j}^{NZ_a} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad \hat{V}_{N-N} = \frac{1}{2}\sum_{\nu\neq\mu}^{N} \frac{Z_a^2 e^2}{|\vec{R}_\nu - \vec{R}_\mu|}, \quad \hat{V}_{e-N} = -\sum_{i=1}^{NZ_a}\sum_{\nu=1}^{N} \frac{Z_a e^2}{|\vec{r}_i - \vec{R}_\nu|}$$

… potential energies

Kohn argues that it *does not even make sense* to compute the many-body wave function for more than ca. 100 electrons. The "exponential wall".

The insight



- **Thomas/Fermi:** Electron density determines energy: Ground state energy = F [ρ] (input: electron density; output: energy of inhomogeneous electron gas)

- **Density functional theory** (Slater, **Kohn**, Hohenberg, Sham)

  Solve *single-particle* Schrödinger equation, potential is approximately known and depends upon the charge density. Mathematical structure of Hartree equations.

Ab initio MD in a slide

$$\{\frac{-\hbar^2}{2m}\nabla^2 + V_{ext}(x) + V_{Hartree}(\rho[x]) + V_{xc}(\rho[x])\}\psi_i = \lambda\psi_i$$

Adopt pseudopotentials, pick a representation:

$$|\psi_i> = \sum_{\vec{G}\neq 0} a^i_G |\vec{G}>$$

PLANE WAVES

$$|\psi_i> = \sum_{\mu} a^i_\mu |\mu>$$

LOCAL ORBITALS

Diagonalize (obtain $\{\psi\}$), compute the density matrix $\rho_{\mu\nu}$. Then:

$$E_{bs} = Tr(\rho H)$$

$$n(\vec{R}) = <\vec{R}|\hat{\rho}|\vec{R}>$$

$$F^\alpha_{bs} = -\nabla_\alpha E_{bs}$$

The quantity F_{bs} is the difficult, non-local part of the interatomic force

Some possibilities

Once we possess reliable forces, many simulations are possible. For example:

- Remove kinetic energy to find a local PE minimum;
- Simulate microcanonical, canonical or other dynamics.
- “Anneal” to crystallize an amorphous phase
- Try different materials, add impurities, add templates…

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 *nano*seconds[1], suggesting the need for millions of steps.

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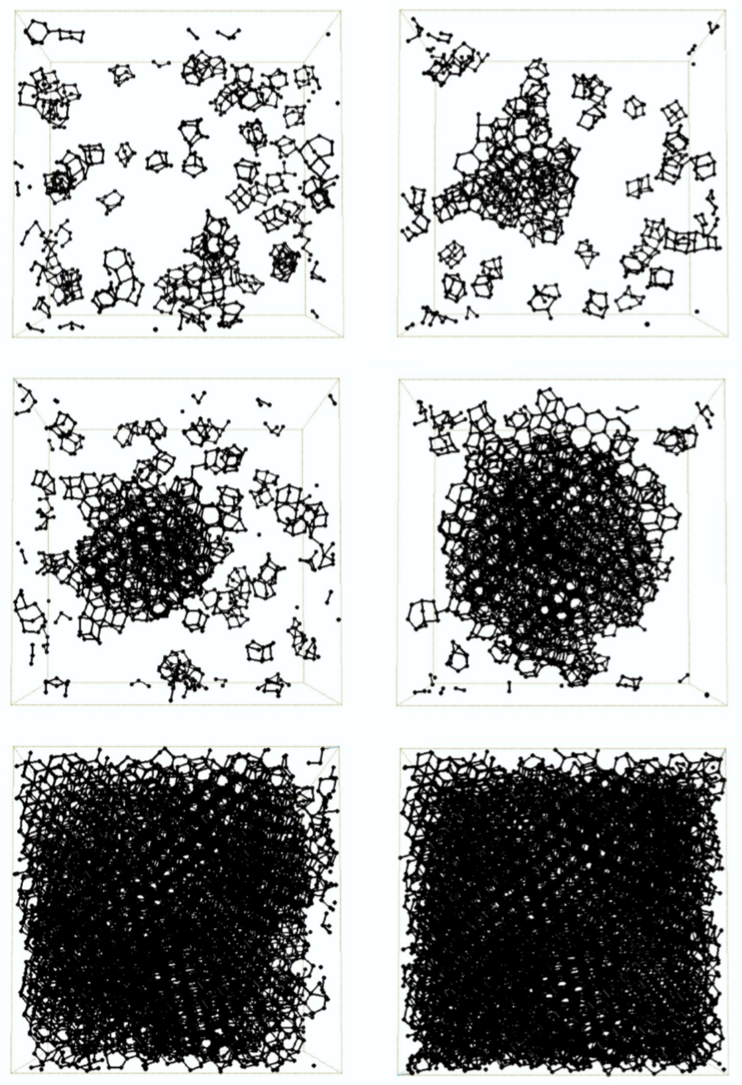
[1] P. Beaucage and N. Mousseau, PRB 71 094102 (2005)

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/cm^3. 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."

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

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

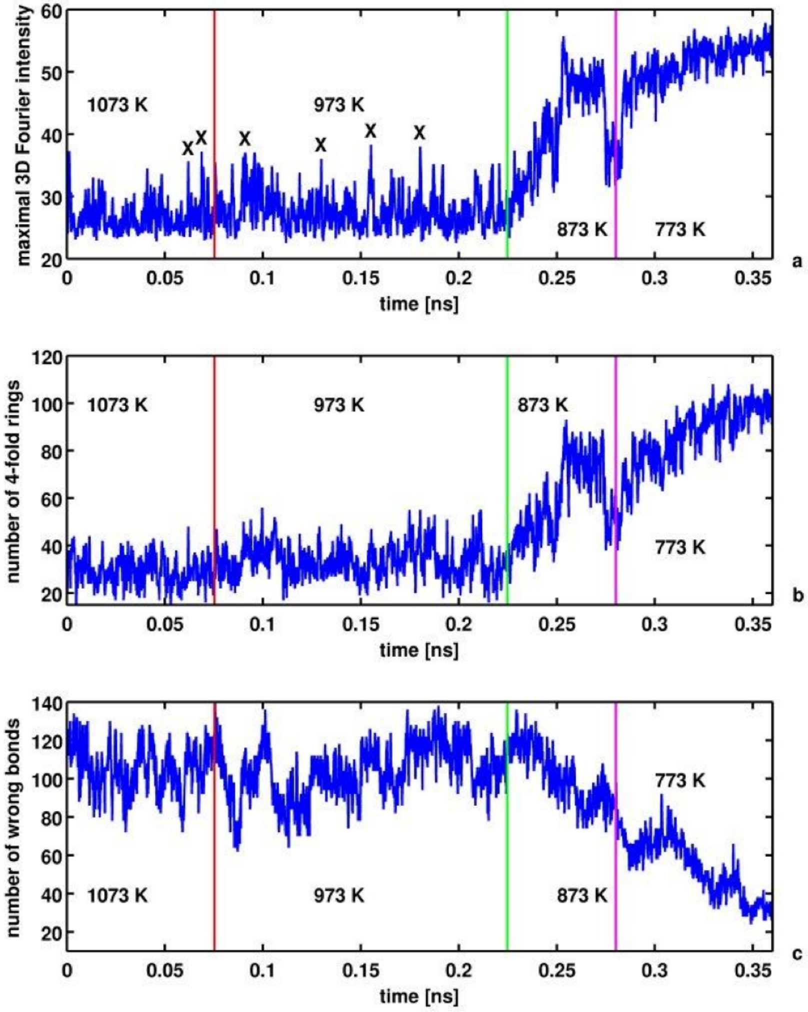
Microscopic origin of the fast crystallization ability of Ge–Sb–Te phase-change memory materials, J. Hegedüs & S. R. Elliott, Nat. Mats. (2008):

Here, we describe for the first time how the entire write/erase cycle for the $Ge_2Sb_2Te_5$ *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* $Ge_2Sb_2Te_5$*. 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.*

H&E Recipe

- VASP *ab initio* MD code
- 63-90 atom models for GST-225,124
- 150 atom models for GS, Sb
- Cubic cells + periodic-boundary conditions
- Constant volume
- Quenching from melt + heating amorphous
- 6 month runs on 32 nodes of supercomputer

E&H: The emergence of order amorphous → crystalline



Long range order: Maximum 3D Fourier intensity.

Rocksalt building blocks

Wrong bonds

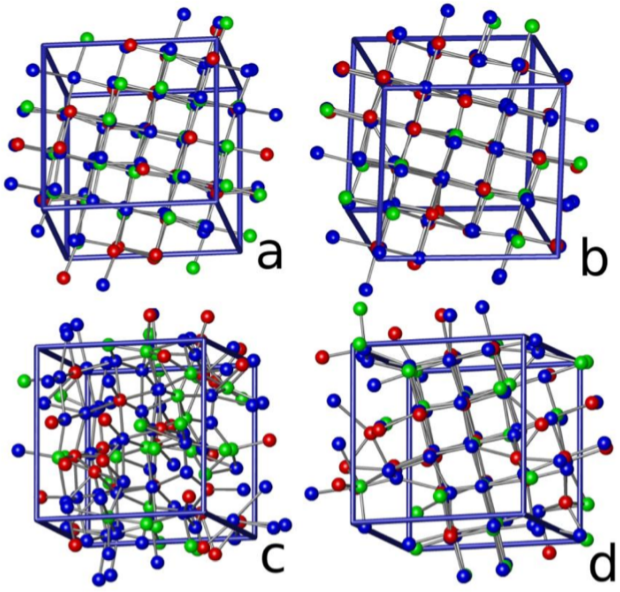
Credit: SRE – purloined from a lecture given in Jan 2009 found on the internet.

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)

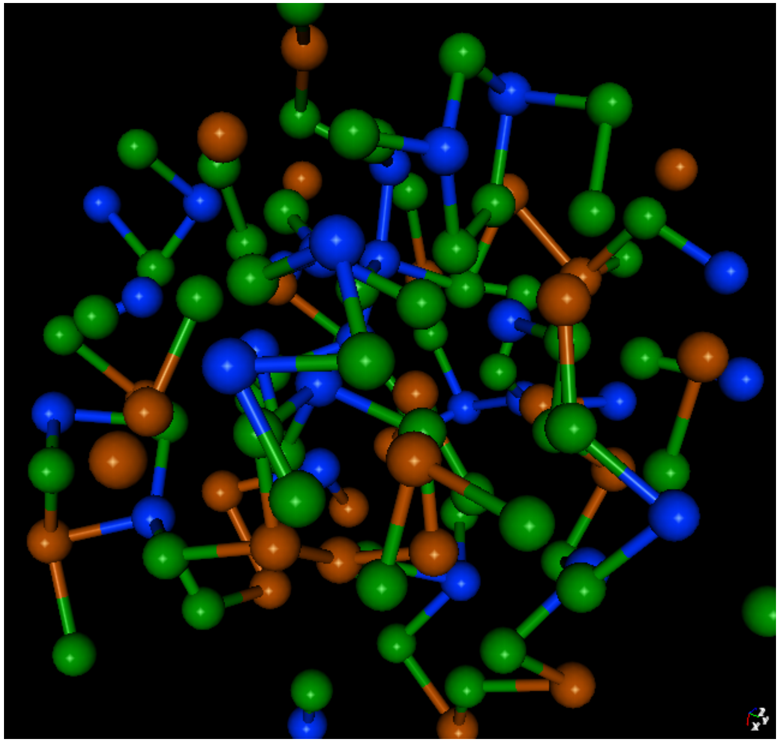
Ge= green; Sb= red; Te= blue

Hegedus & SRE, Nature Materials, **7**, 399 (2008)

H&E: Summary

- The NM paper opened up the field. Many interesting subsequent studies along these lines.
- The work has implications beyond our immediate interests – a truly realistic simulation to improve understanding of nucleation, and aspects of phase transitions.

a-GST(225) → c-GST(225) [the movie]



Ge: blue, Sb: orange, Te: green

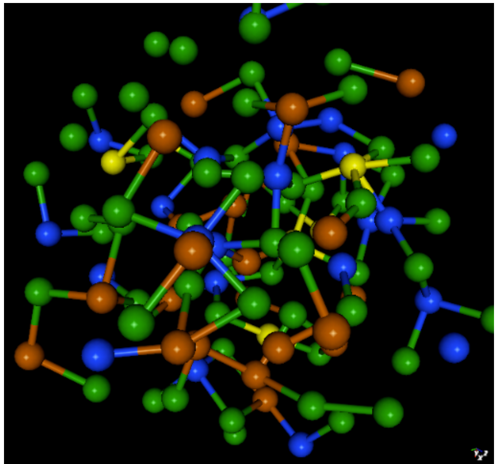
B. Prasai, G. Chen, DAD, APL **102** 041907 (2013).

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

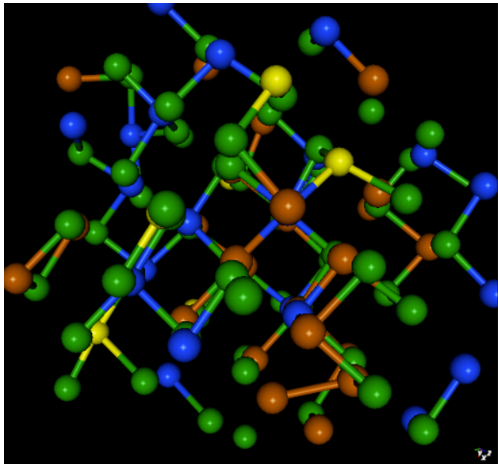
A video showing the process of crystallization in 225. *Merely a confirmation of H&E.*

Snapshots

Near the beginning

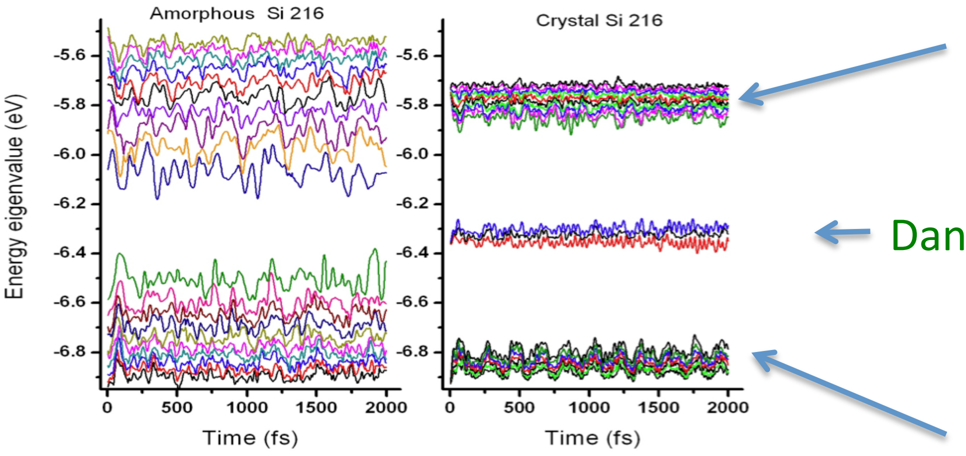


Near the end



Thermal effects: dynamic band tails

structural fluctuations→electronic fluctuations



Conduction band

Dangling bond

Valence band

Phonon-induced fluctuations amorphous and xtal **Si**. Both at T=300K.

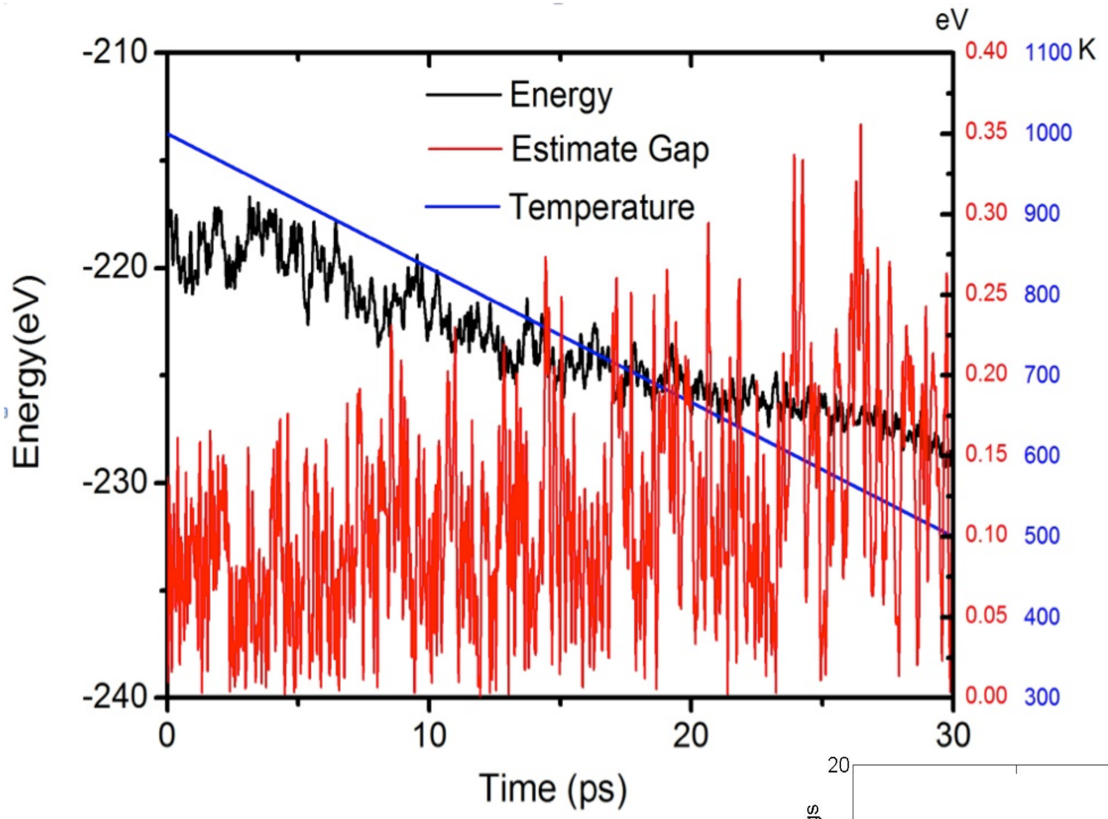
This must impact the conductivity, reflectivity etc.:

$$\sigma(T) = -\frac{1}{3}\sum_{\alpha} \int_{-\infty}^{\infty} \sigma_{\alpha\alpha}(\varepsilon)\frac{\partial f_F(\varepsilon)}{\partial \varepsilon}d\varepsilon, \qquad \bar{\sigma}_{\alpha\alpha}(\varepsilon) = \frac{2\pi e^2\hbar}{\Omega m^2}\sum_{ni}\overline{|\langle\psi_n^t|p_\alpha|\psi_i^t\rangle|^2\delta(\varepsilon_n^t-\varepsilon)\,\delta(\varepsilon_i^t-\varepsilon)}$$

Moral: Thermally average the Kubo-Greenwood formula

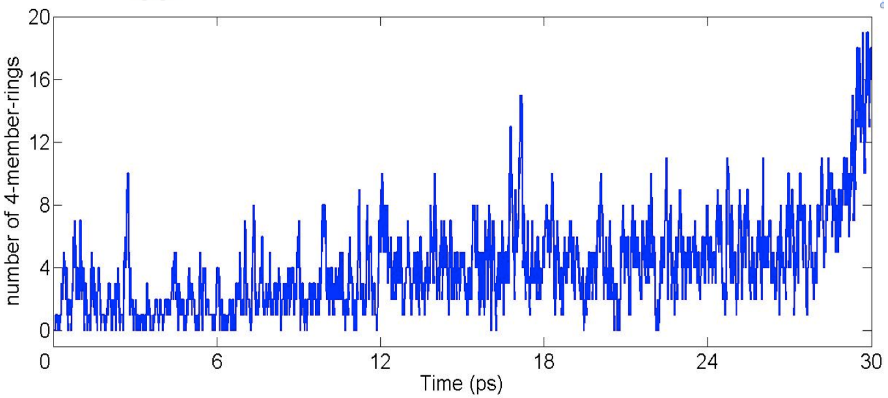
T. Abtew, M. Zhang, DAD Phys. Rev. B **76** 045212 (2007); MZ, DAD, PRL **105** 186602 (2010)
Experiments (a-Si): S. Aljishi *et al.*, PRL **64** 2811 (1990); PRL **67** 2179 (1991).

Thermal effects: the gap



Gap slowly (and noisily!) opens as amorphous phase emerges from liquid state.

4-fold rings



B. Cai, S. R. Elliott and DAD, APL **97** 191908 (2010)

Structural-electronic fluctuations

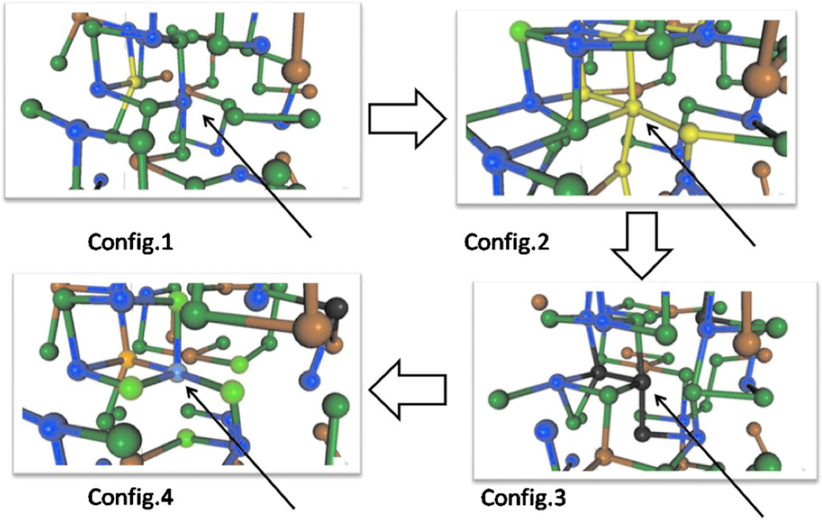
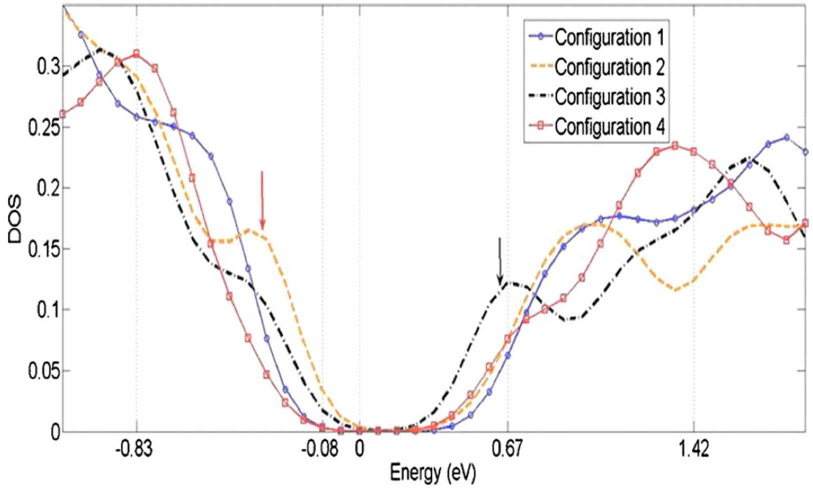


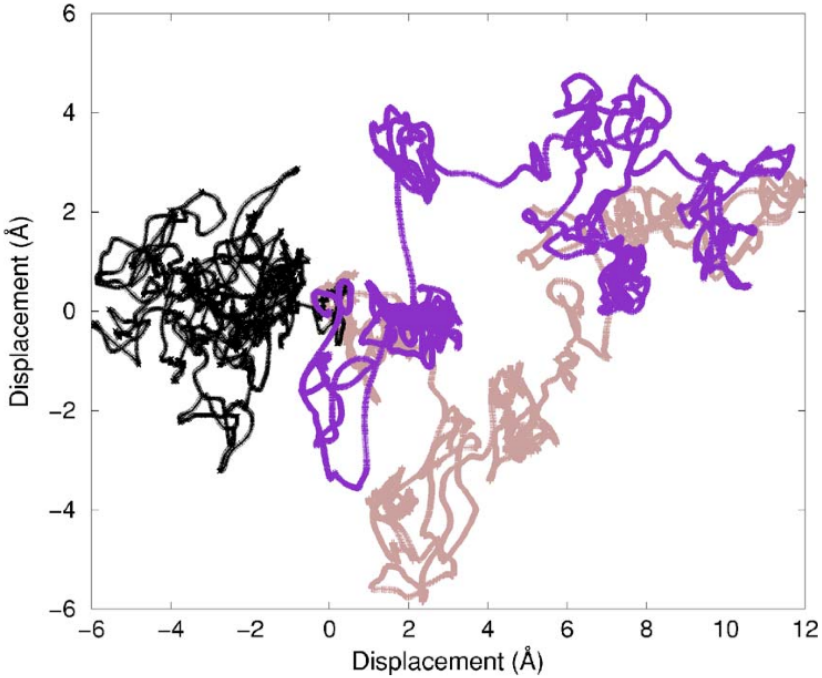
FIG. 4. (Color online) Snapshots of topology changes for one Ge atom and its six neighbors (Ge, blue/darkest; Sb, brown/next darkest; and Te, green/light). The central Ge atom is identified by black arrows. In monochrome: for Config. 2, the valence tail states are localized on the lightest (yellow) atoms connected to the central atom and in Config. 3 conduction tail states are localized on dark (black) atoms connected to the central atom.



Small structural fluctuations alter the gap (as system equilibrates to 500K).
structural fluctuations around Ge, lead to electronic fluctuations near the gap.
caveat emptor: small cell – 63 atoms, and Hartree-Fock to "amplify" the gap.

Cai *et al., opt. cit.*

Dopants



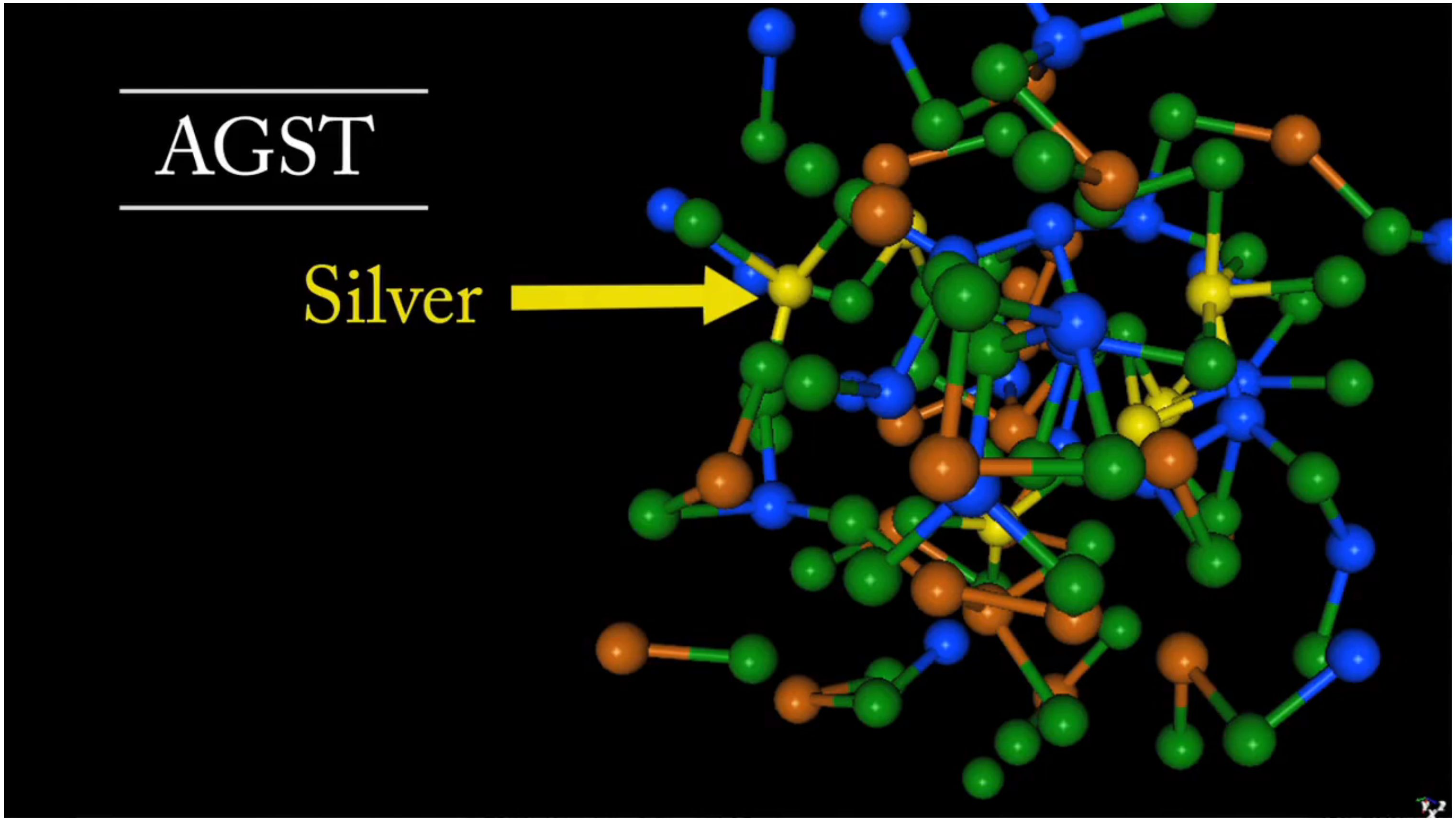
Silver is implicated in interesting processes in other chalcogenide systems.
It is extremely diffusive, big photo-response etc.

Least and most diffusive Ag atoms in $(GeSe_3)_{0.85}Ag_{0.15}$ at 1000K.

Tafen, Mitkova, DAD PRB 72 054206 (2005)

Lets add it to GST225

225+Ag: Dynamics

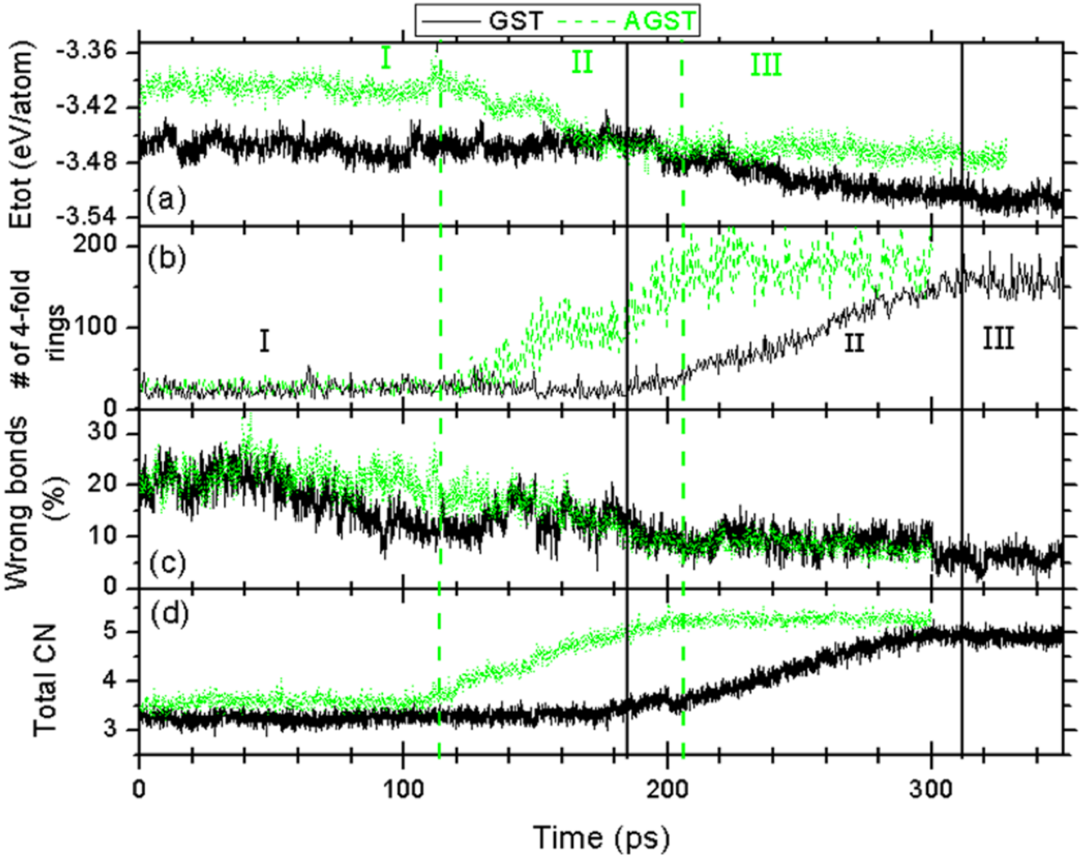


Crystallization compared

|← Crystallize → |

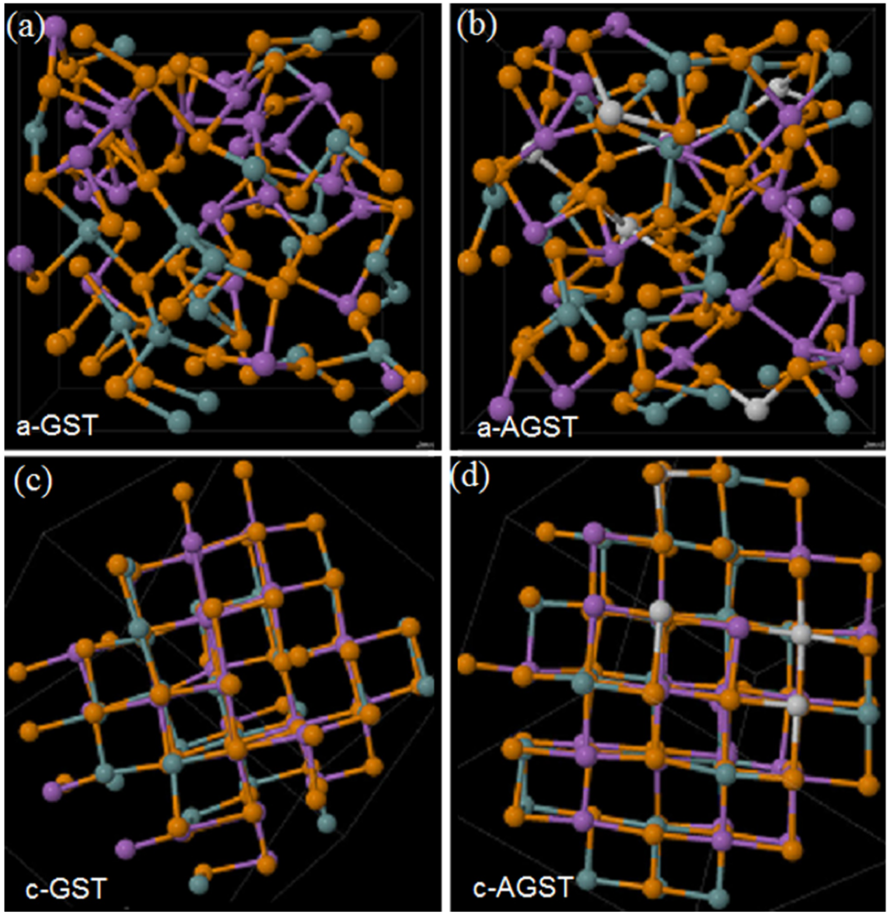
|← Incubation →| |← Stabilization →

Nomenclature of H&E



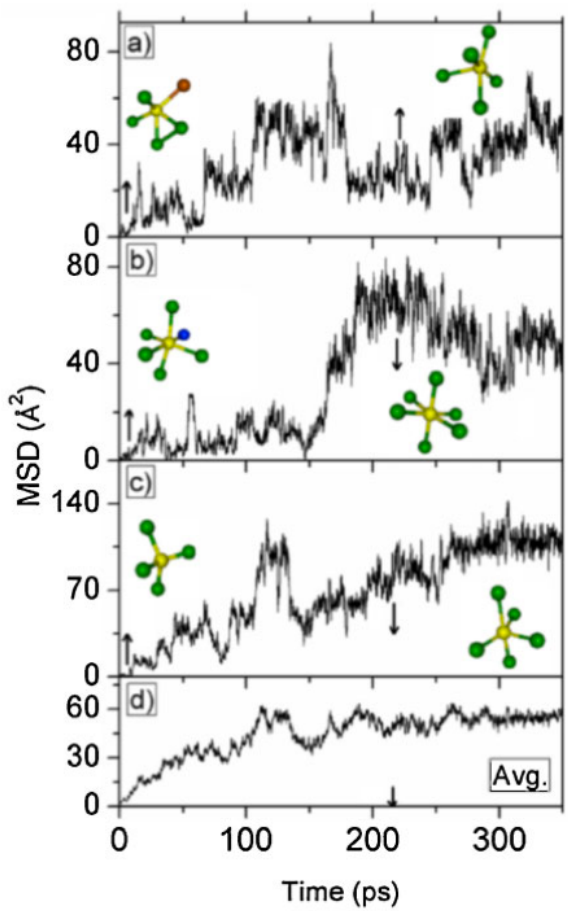
Prasai, Chen, DAD

Before and after: relaxed



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

Silver hopping in GST124



Mean-squared displacements of representative Ag at 650K. Thermally driven trap-release process. Higher (octahedral) coordination, less hopping.

As in other chalcs, Ag is highly mobile.

B. Prasai, M. Kordesch, G. Chen, DAD PSSb **250** 1785 (2013).

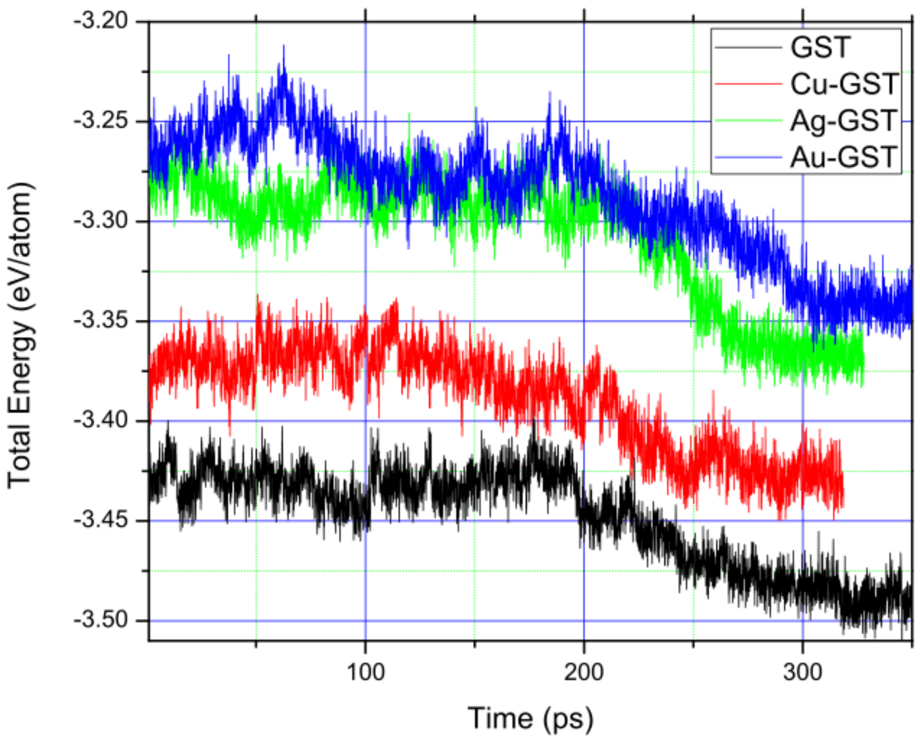
What does it mean?

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

Throwing darts at the periodic table

- Interesting behaviour for Ag, suggests that we should try other impurities. All rather preliminary *but*:
- For ~2% Cu optical contrast is reduced, tends to prefer non-octahedral sites.
- Au, Cu: no advantage in crystallization time.

225+Au, Ag, Cu



Caveat emptor
Only three repetitions!

All annealed at 650K

BP, DAD (unpublished)

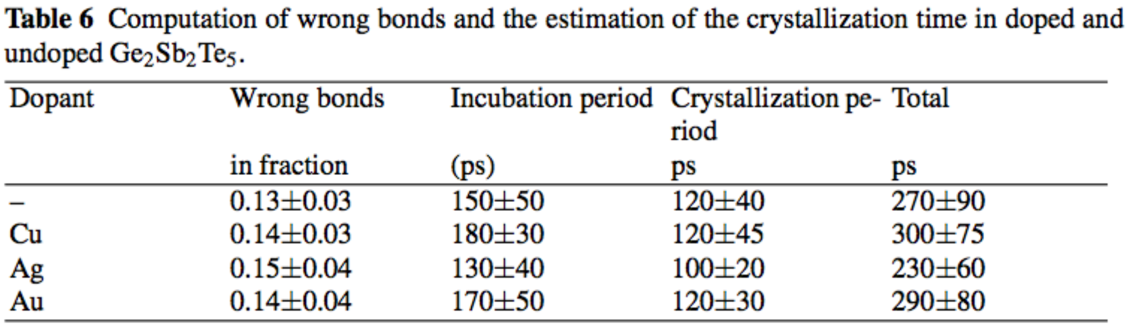
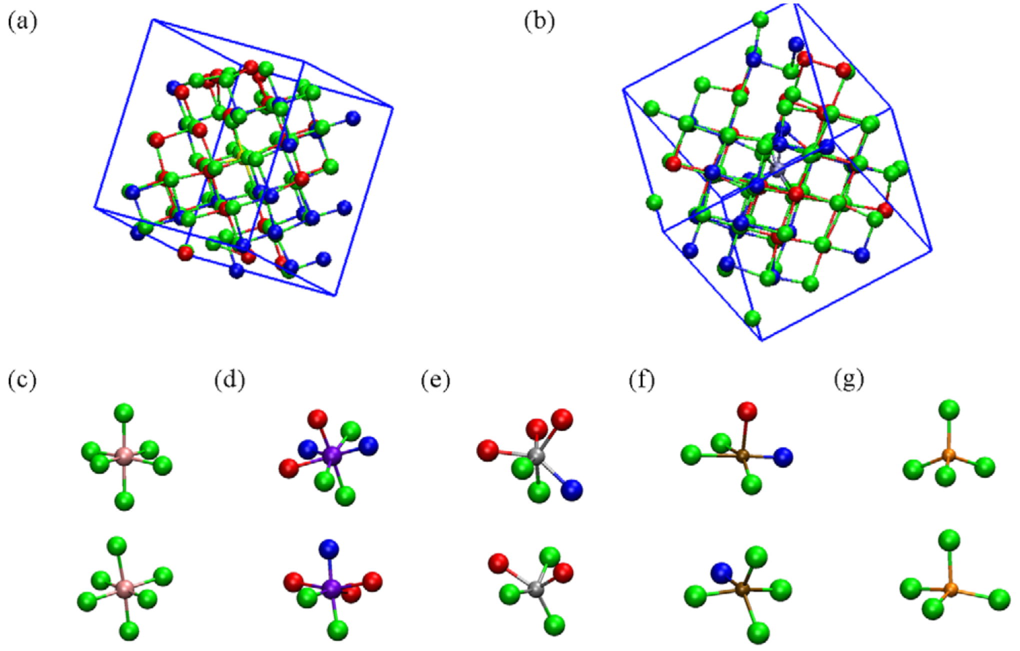


Table 6 Computation of wrong bonds and the estimation of the crystallization time in doped and undoped $Ge_2Sb_2Te_5$.

Dopant	Wrong bonds in fraction	Incubation period (ps)	Crystallization period ps	Total ps
–	0.13±0.03	150±50	120±40	270±90
Cu	0.14±0.03	180±30	120±45	300±75
Ag	0.15±0.04	130±40	100±20	230±60
Au	0.14±0.04	170±50	120±30	290±80

First row transition metals (Skelton and Elliott)



Crystalline GST
+ Sc and V

Amorphous

Crystalline

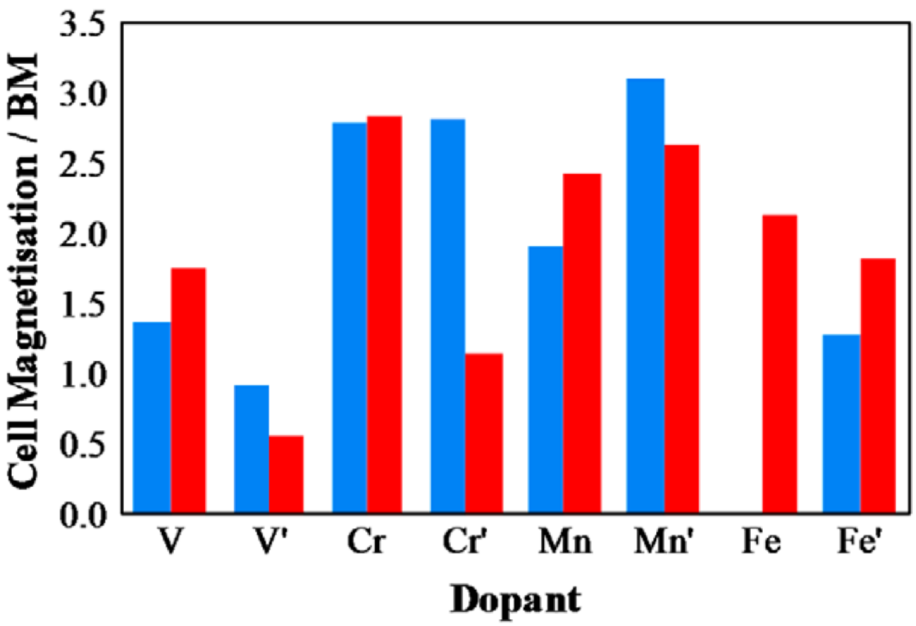
Cr Co Ni Cu Zn

First row TMs in 225: How the impurities “fit in” across the first row.

JPCM 25 205801 (2013)

Looking ahead: spin polarization

J. Phys.: Condens. Matter **25** (2013) 205801



Low energy magnetic states

amorphous, blue

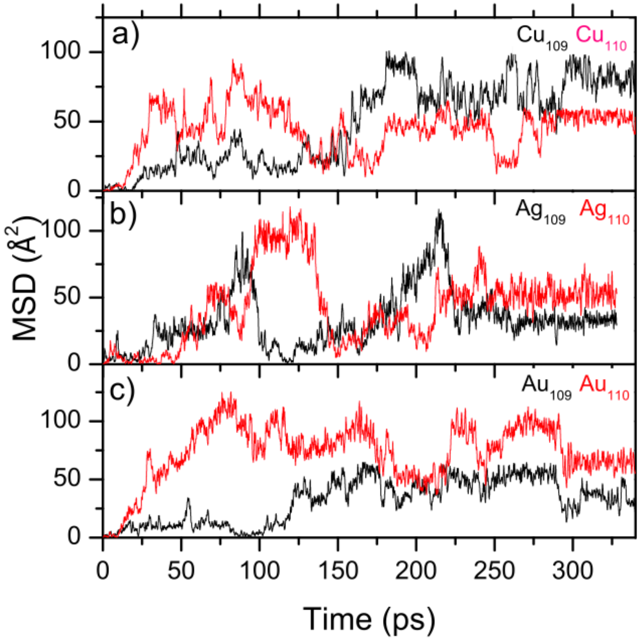
crystal, red

prime and "unprimed" bars
two different simulations

Sc, Ti, Co, Ni, Zn – no spin polarization

S&E, *opt. cit.*

Dance of the Noble Metals



TM impurities are mobile, a result
Also noted by S&E.

Less diffusive when octohedral
Ag and Au, no hopping after crystallization
Cu 109 hops even after crystallization

Big *caveat*: the statistics are clearly inadequate.

Prasai and DAD, unpublished.

Conclusions

- Thanks to Hegedus and Elliott, we have an effective new tool to explore PCMs. Simulations provide **direct insight** into important processes.
- Doping is one promising avenue to explore. Ag doping seems helpful.
- There are other fronts opening up: different materials, new concepts like templating etc.
- ***Mea culpa***: we need to improve our statistics. Need many long runs with varying initial conditions. High throughput approaches [Brian Hayden], bigger computers, better algorithms needed (as always)….
- An interesting context for "Materials by Design": algorithms that search for compositions, structures with desired properties. Currently a pipe dream, but getting closer…