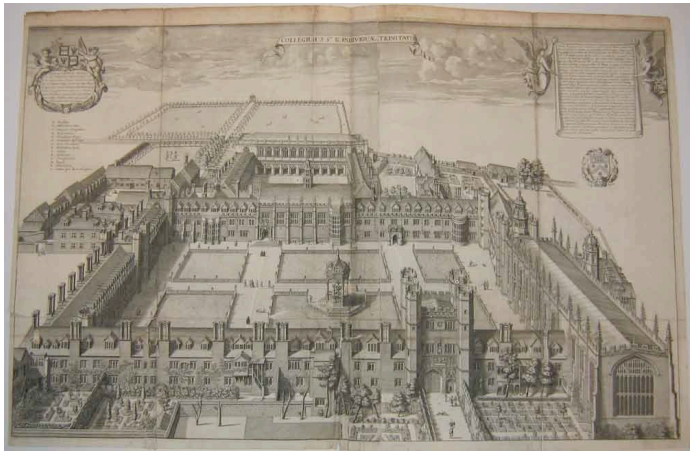

Simulation of a fast-ion conducting glass

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Acknowledgements

- Maria Mitkova, Michael Kozicki (Programmable metallization cell device)
- D. Tafen, former student who carried out early calculations PRB **72** 054206 (2005).
- S. R. Elliott, hospitality and advice
- **£££$**: U. S. NSF, Axon Technologies Corp

Roadmap

- Silver-doped chalcogenide glass materials
- Application as a computer memory device
- Scientific Puzzles
- Our modeling (a work in progress!)
- Results and prospects

Solid electrolytes

- High ionic conductivity, low electronic conductivity “solid electrolyte” or fast ion conductor.
- Usually, not always, cation conduction.
- Best conductivity Li^+ (smallest) or Ag^+ (most deformable)
- Applications: batteries, chemical sensors, supercapacitors and fuel cells…
- Basic process is thermally activated hopping

Glassy solid electrolytes

- Often have glasses with *higher* ionic conductivity than crystal (*eg.* : Lithium Borate: $Li_2B_4O_7$)
- Conduction is isotropic
- No grain boundaries
- Continuously variable compositions possible

Ag-doped chalcogenide glasses

- Silver doped chalcogenide glasses are solid electrolytes.
- Interesting photoresponse:
  - Photodissolution (light ‘dissolves’ surface Ag film into bulk)
  - Photoexsolution (light ‘extracts’ Ag from bulk to surface)

Photo-induced surface deposition

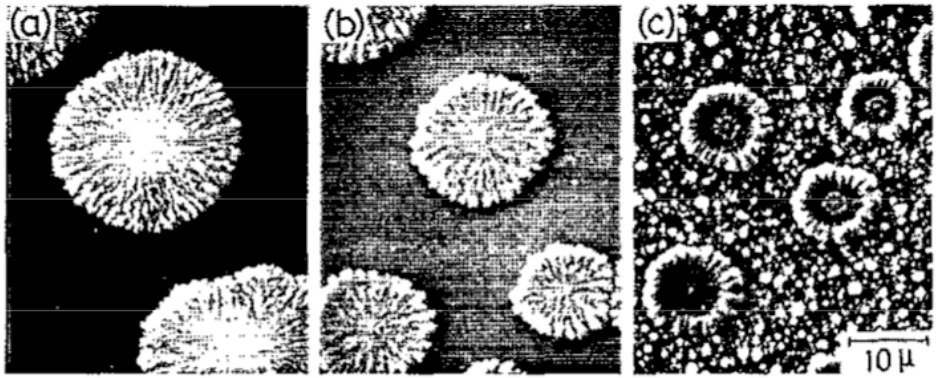
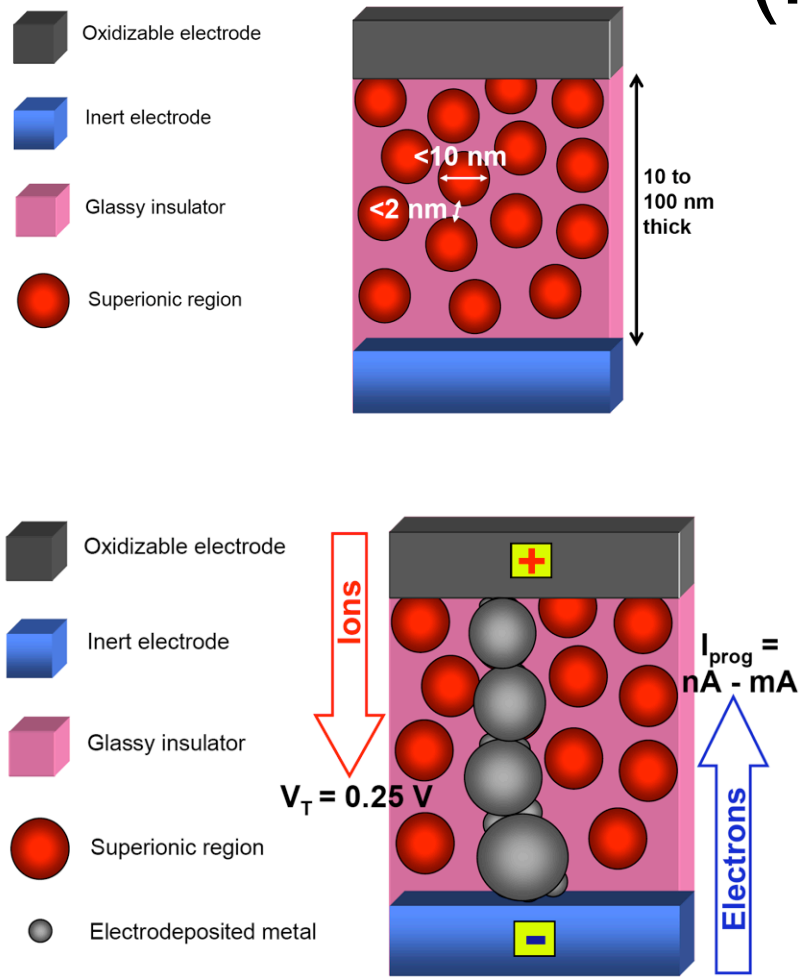


FIG. 3. SEM photographs of photodeposited Ag particles on $Ag_{45}As_{15}S_{40}$ ($x=45$) sample. The illuminations with lights of (a) 80, (b) 200, and (c) 530 mW/cm^2 were provided for 15 min at 21 °C.

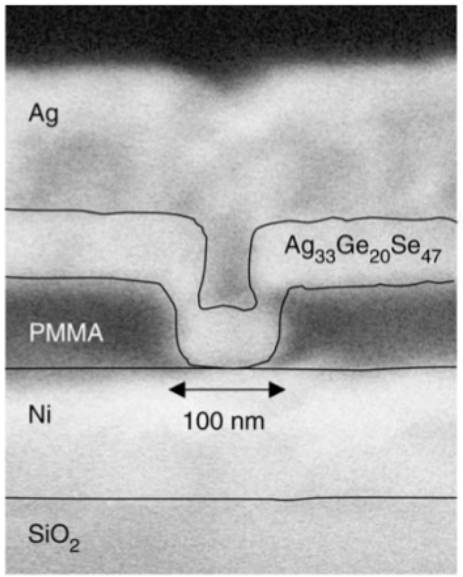
T. Kawaguchi and S. Maruno JAP **77** 628 (1995)
(Arsenic sulfide-based glass)
T. Kawaguchi, S. Maruno and S. R. Elliott
JAP **79** 9096 (1996) (S, Se-based glasses)

Programmable Metallization Cell (PMC)



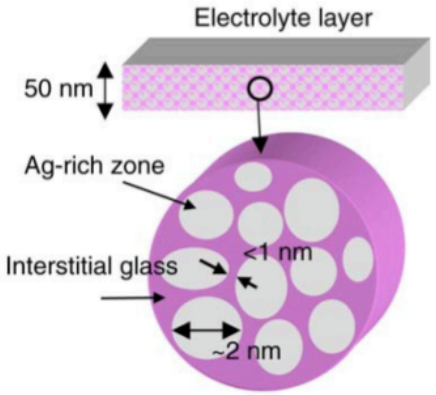
Figures courtesy of M. N. Kozicki, M. Mitkova, ASU

M.N. Kozicki et al. / Superlattices and Microstructures 34 (2003) 459–465



(a)

SEM image of device



(b)

PMC is nanostructured: Ag_2Se xtals in Ge-rich glass phase. Ag-rich crystallites *ca*. 2-7nm

PMC

- A promising technology:
  - Low voltages needed: ~*200 mV*
  - Low power consumption
  - Fast: under *20 ns* switch times
  - Good for at least 10^{12} cycles

See: *www.axontc.com*

Puzzles

- What is the structure of the bulk glass?
- Where does the Ag “sit”; and what is the nature of these traps?
- Why is the Ag so mobile?
- What is the mechanism of photo-induced surface deposition?

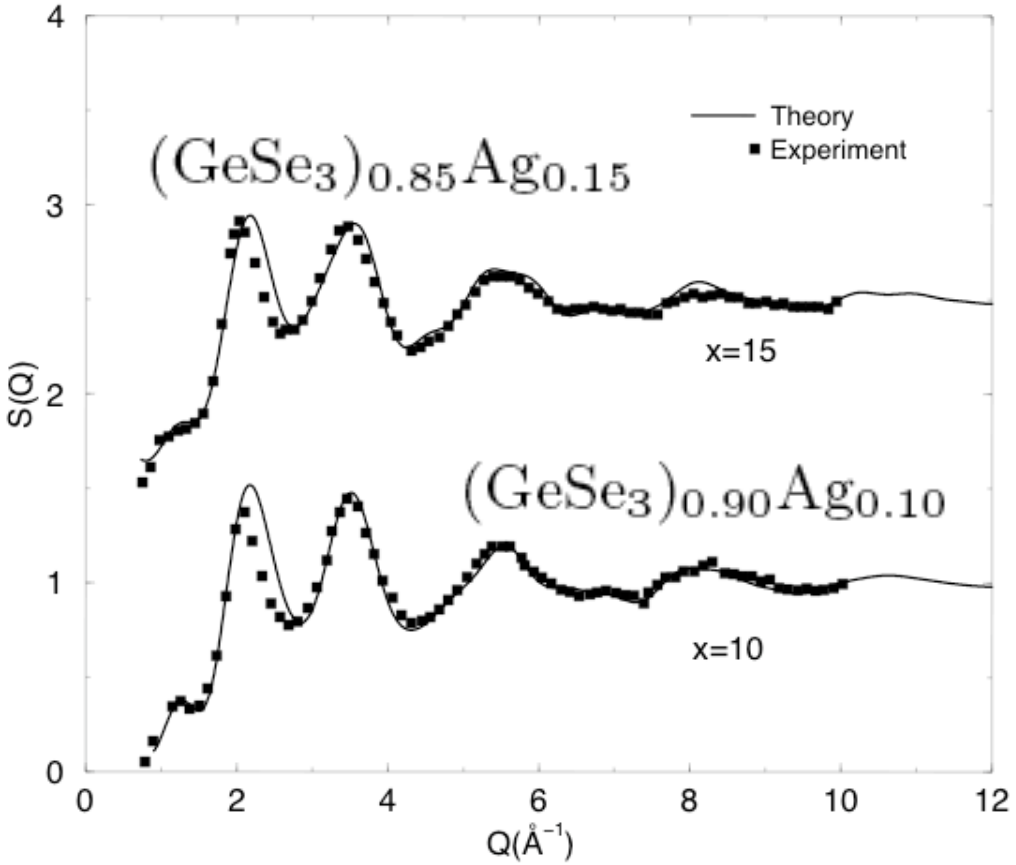
Approach

- We use *ab initio* MD to model: a-$(GeSe_3)_{.9}Ag_{.1}$ and a-$(GeSe_3)_{.85}Ag_{.15}$
- Hamiltonians: FIREBALL2000 (local orbital LDA), VASP (plane wave LDA)
- Models made by conventional melt quenching (equilibrate liquid, quench over 5ps, anneal)

Limitations

- Tiny models (~250 atoms)
- Short times (< 100 ps)
- Homogeneous systems only: not picking up phase separation effects, which may be relevant for PMC.
- No electrochemistry yet.

GeSe:Ag Models



Neutron total structure factors.

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

What does it mean?

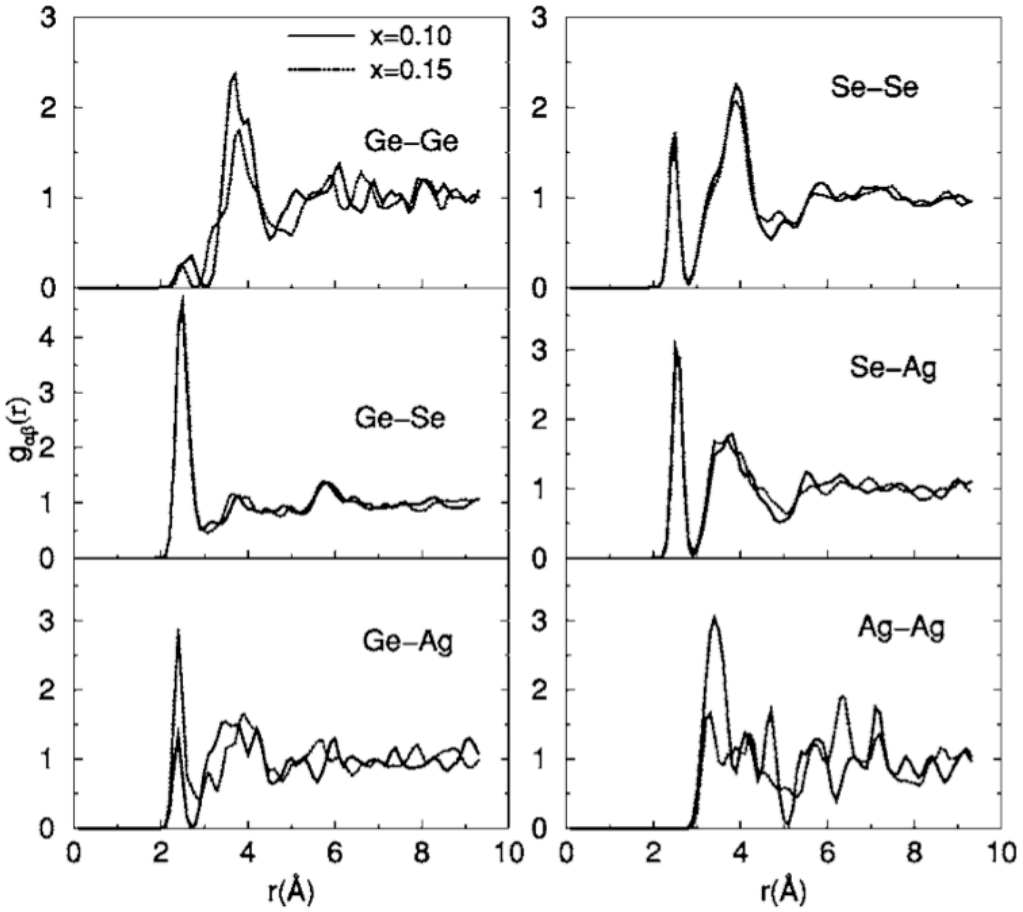
- Analysis of partials shows that first peak (near 1.1Å$^{-1)}$ is mostly due to Ge-Ge and Ag-Ag correlations. The peak becomes prominent with *increased* Ge and *decreased* Ag content.
- Continuous wavelet transform methods (Harrop, Taraskin, Elliott *et al.*) suggest that peaks near k~2.0Å^{-1}, 3.5Å^{-1} involve extended spatial correlations (up to 15-20Å)

Network Topology and Chemical Order

- Silver is mostly two-fold: 100% for x=0.1 and 86% for x=0.15 (remainder three-fold)

	Ge_4	Ge_3	Se_2	Se_3	Se_1	Ag_2	Ag_3
x=0.10	35 (65%)	17 (31.5%)	86 (53.1%)	56 (33.9%)	17 (11.8%)	24 (100%)	—
x=0.15	34 (66.7%)	13 (25.5%)	85 (55.6%)	57 (37.2%)	11 (7.2%)	31 (86.1%)	4 (11.1%)
	Ge-Se	Se-Se	Ag-Se	Ag-Ge			
x=0.10	64%	21%	13%	1.5%			
x=0.15	57.1%	19.2%	18.2%	5.2%			

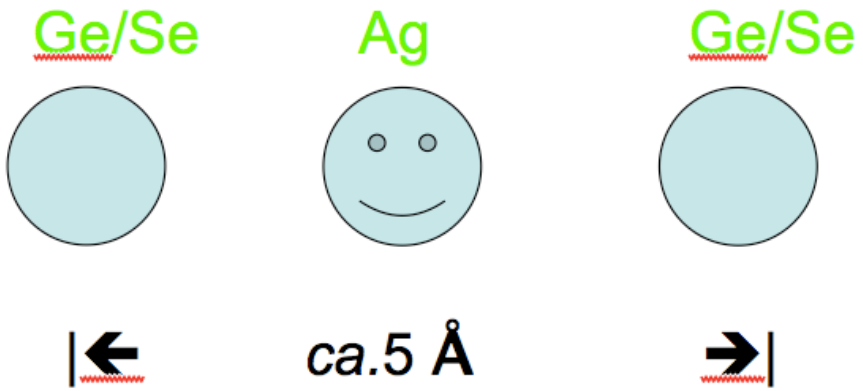
Partial RDFs



←Ag-Ag no clear correlations “random” for these *x. (nb.* limited statistics*)*

Traps: I

- Ag sits midway between host atoms separated by about 5Å. Call this a *trapping center* (TC).



- This emerged for FIREBALL and VASP from melt-quench models and for unbonded Ag introduced in the network: Ag ‘finds its way’ to the same form of TC.

Traps: II

- The TCs are distributed in the glass. Silver sits at isolated TC (32%) or in region with higher density of TC (68%) available.
- The Ag sub-system is a sort of “glass within a glass”. How does ‘melting’ proceed for trap system?

Electronic Density of States

SILVER TRANSPORT IN Ge_xSe_{1-x}:Ag MATERIALS:…

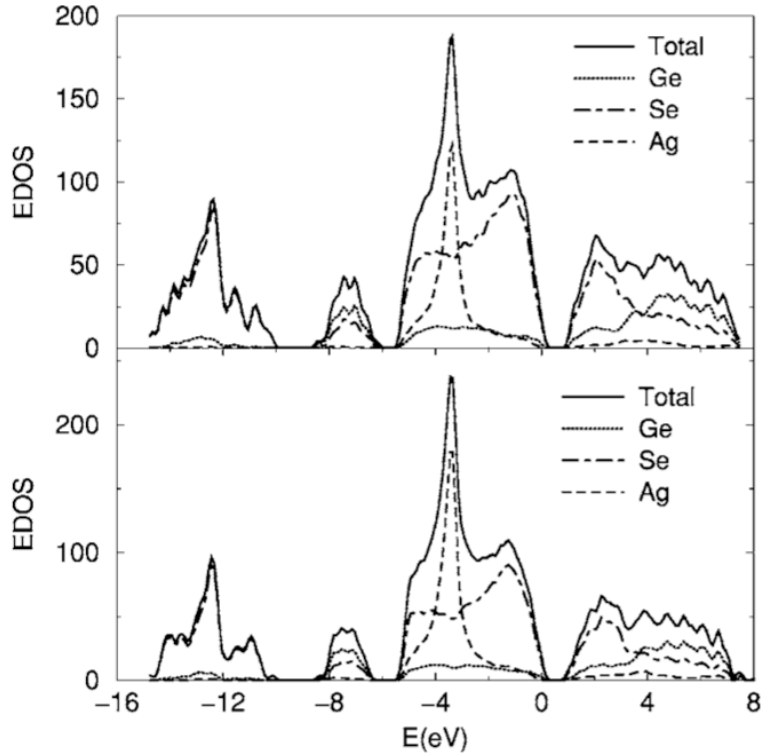


FIG. 5. Electronic density of states and species projected electronic density of states for Se, Ge, and Ag for $(GeSe_3)_{0.90}Ag_{0.10}$ (top panel) and $(GeSe_3)_{0.85}Ag_{0.15}$ (bottom panel) glasses.

Top valence band: Ge and Se p-states, Ag 4d. Band edges mostly due to Se 4p lone pairs

Tafen, Mitkova, DD PRB **72** 054206 (2005)

Electrons: II

- With VASP, we find electronic deep donor level for non-bonded Ag (~0.2eV below LUMO).
- In a simple picture of light-solid interactions, photodiffusion might be associated with (light-induced) occupation changes in these levels.

Ag dynamics (*x=0.15, T=1000K*)

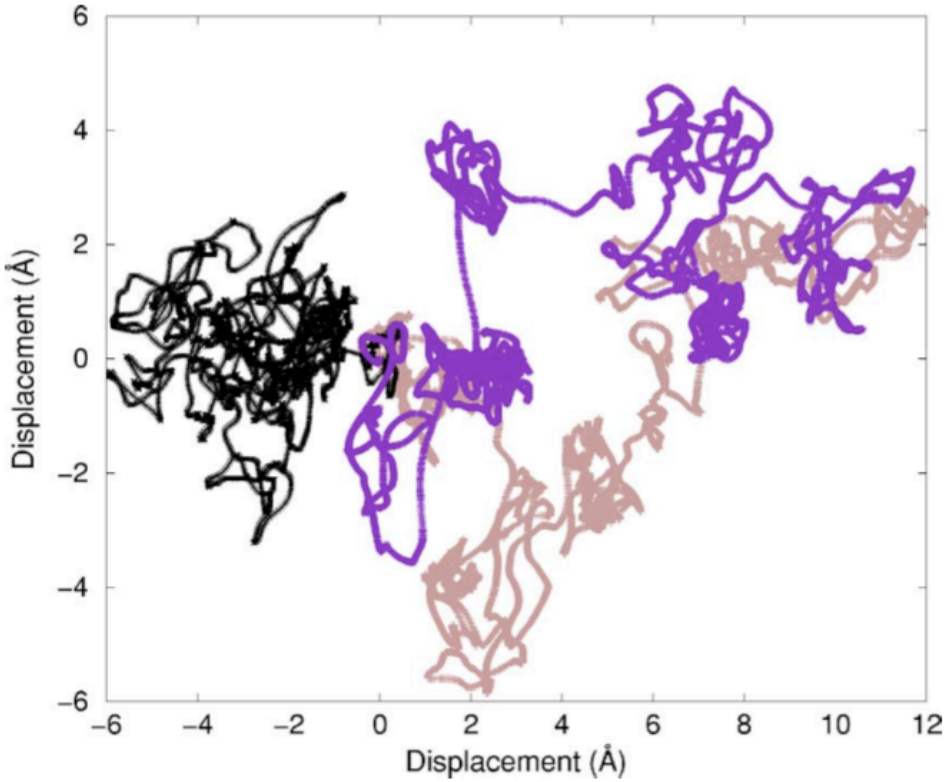
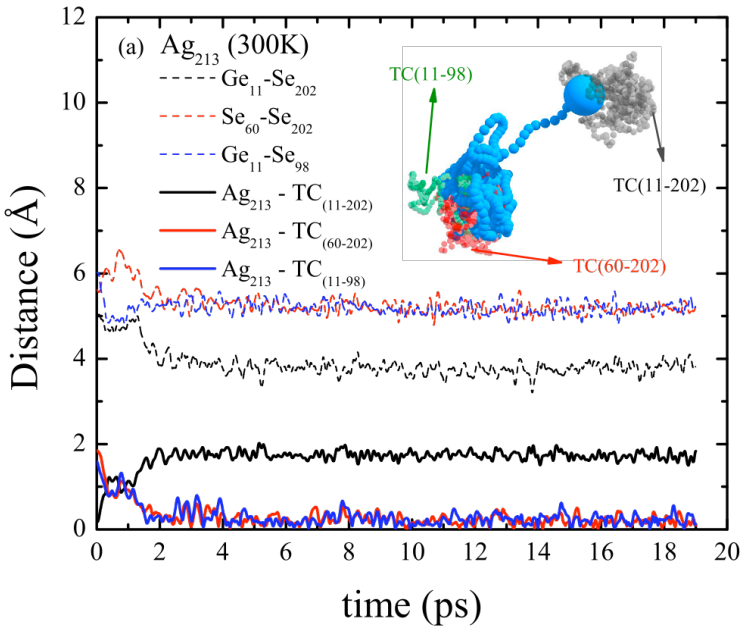


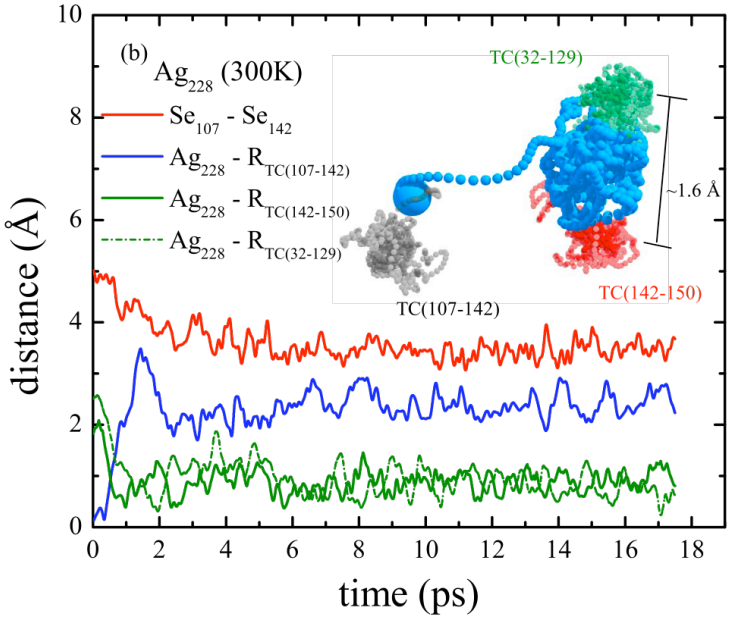
FIG. 8. (Color online) Trajectories of the most (indigo and brown) and least (black) mobile Ag atoms in $(GeSe_3)_{0.85}Ag_{0.15}$ glass ($T=1000$ K).

Ag trapping/diffusion

- Average trapping time: *ca*. 2-3 ps (1000K)
- From Einstein relation, D~1-2E−5 cm^2/s at T=1000K for both glasses. Short simulations: *caveat emptor.*
- Extrapolating to 300K gives D within in factor of ~10 of experiment (Urena *et al.*, 2005)

Examples of Hopping





Isolated trap “big hop”

Multiple traps

There is rapid hopping among the adjoining TCs for volumes with more TCs.

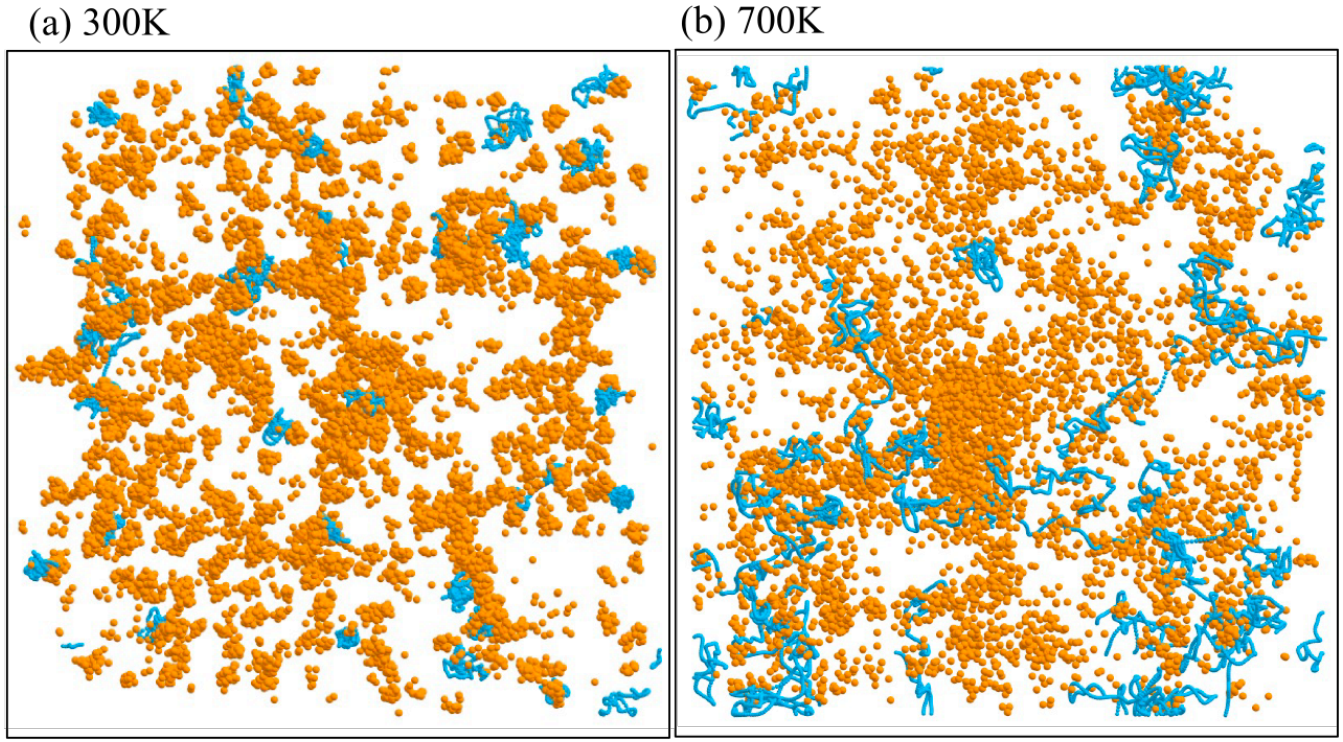
I. Chaudhuri, F. Inam, DAD Phys. Rev. B (in press, 2009)

Ag Dynamics

- “Supertraps” exist. Hopping is faster and shorter-ranged in parts of cell with higher trap density.
- “Long” hops from isolated traps.

Reminiscent of “diffusive” and “non-diffusive” processes of Middleton and Wales (PRB **64** 024205 2001).

Trap and Ag dynamics



Orange: traps
Blue: Ag

Silver dynamics

- At 300K the Ag and TCs are uniformly distributed in cell.
- At 700K the TC-network becomes more diffuse, and the Ag-network “melts” heterogeneously: large hops from isolated TCs, small, rapid hops from overlapping TCs.

Some inferences

- There are *trapping centers.* This is a direct observation of the Scher-Lax-Phillips[1] traps. Trap model is successful to explain relaxation data.
- Traps have a dynamic character: fill more of space at higher T.
- We need better statistics. Absorption and emission rates of cages, temperature dependence etc. In progress.
- Local basis (FIREBALL) and plane wave (VASP) produce very similar results.

[1] J. C. Phillips, Rep. Prog. Phys **59** 1133 (1996).

Whats next?

- Surface structure
- Phase separation, interfaces
- Photoresponse
- Electrochemistry and filament growth