

***Ab initio* determination of ion traps and the dynamics of silver in silver-doped chalcogenide glass**

I. Chaudhuri and F. Inam

Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA

D. A. Drabold

*Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA**and Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom*

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We present a microscopic picture of silver dynamics in $\text{GeSe}_3:\text{Ag}$ glass obtained from the *ab initio* simulation. The dynamics of Ag is explored at two temperatures: 300 and 700 K. In the relaxed network, Ag occupies trapping centers that exist between suitably separated host sites. At 700 K, Ag motion proceeds via a trapping-release dynamics between “supertraps” or cages consisting of multiple trapping center sites in a small volume. Our work offers a first-principles identification of trapping centers invoked in current theories, with a description of their properties and associated Ag dynamics. We compute the charge state of the Ag in the network and show that it is neutral if weakly bonded and Ag^+ if in a trapping center.

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One of the outstanding problems of solid-state ionics is the nature of the hopping of metal atoms in fast-ion conductors. As a step toward a general atomistic picture, we offer a detailed *ab initio* study of Ag dynamics in a glassy germanium selenide matrix. In agreement with a previous study,¹ we show that trapping centers exist and describe their atomistic nature in detail. Our work is also related to the theory of batteries, the prime technological application of solid electrolytes. Finally, the promising “programmable metallization cell,” another nonvolatile computer memory device,² is made from the materials we describe here.

Silver-doped Ge-Se glasses exhibit a fascinating range of phenomena: among them high ionic conductivity³ and photodoping⁴ connected with fast Ag diffusion.^{5,6} An empirical model of Elliott⁷ provided an estimate of the activation energies of ionic conductivities. In this model, the Ag ions are assumed to be surrounded by cations (Se) and Coulombic and polarization interactions give rise to the potential barriers, leading to the hopping dynamics of Ag. The first MD simulations, using an empirical potential, were due to Iyetomi *et al.*,⁸ who detected the phase separation of the Ag atoms in GeSeAg glasses. Recently, we have reported the existence of Scher-Lax-Phillips traps,⁹ in *ab initio* models of $(\text{GeSe}_3)_{1-x}\text{Ag}_x$ (for $x=0.10$ and $x=0.15$).¹ Our calculations are related to a recently published percolative free-volume model¹⁰ and provided microscopic identification of the trapping centers proposed by these and other authors. Our calculation only describes the dynamics in a homogeneous glass and does not reflect material interfaces and compositional fluctuations that may be important in some device applications

In this Rapid Communication, we find that Ag atoms sit preferentially near the midpoint of a line connecting between (Ge or Se) atoms separated by about 5.0 Å at $T=0$, and we name these energy minima as “trapping centers” or TC. For $T>300$ K, there is hopping between the TCs, but this is spatially nonuniform and temperature dependent. We find that the TCs are nonuniformly distributed in space. Volumes with a high concentration of TCs have longer trap lifetimes than volumes with few or no TCs. The barriers between TCs

that are close together tend to be small, enabling rapid hopping *within the high-density region*; but the effect of a collection of TCs in close proximity is to create a strong barrier for the Ag to escape to another volume. Thus, one can introduce the notion of “supertraps” or cages built from more than one fundamental TC. The collective behavior of a set of TCs in close proximity is very different than the case of an isolated TC. Our simulations reveal dynamics reminiscent of supercooled colloids¹¹ and diffusion of Li ions in silicate glass.^{12–14}

The results reported here are from the plane-wave *ab initio* code Vienna *ab initio* simulation package (VASP) (Ref. 15) at constant volume. Similar approximations have been used with success on GeSe_2 liquid¹⁶ and glass.¹⁷ We began with a 239 atom $(\text{GeSe}_3)_{0.85}\text{Ag}_{0.15}$ model (50 Ge, 153 Se, and 36 Ag atoms) generated with the local basis *ab initio* FIREBALL method,¹⁸ with a neutron structure factor close to experiment. We relaxed this with VASP and only small changes were noted. Details of coordination and structure are available elsewhere.¹ These models possess the interesting feature that all Ag atoms are found halfway between pairs of host atoms (Ge-Ag-Ge, Se-Ag-Se, or Ge-Ag-Se), with the exception of only one Ag. About 61% of Ag sites reside between a pair of Se; the rest involve one Ge. The distances between host pair atoms are between 4.7 and 5.2 Å and the bond length of the Ag to the atoms of the pair is in the range 2.4–2.6 Å. About 17% of Ag has twofold Se neighboring pair; the rest of the Ag host pairs are undercoordinated. To verify the existence of these traps in an independent way, we introduced unbonded Ag at a variety of locations in a 64-atom amorphous Se model¹⁹ at $T=300$ K, so that the Ag could “probe” the energy landscape in an unbiased fashion and without exception; the Ag became trapped between two Se host atoms with distances in the range we indicate above for the ternary glass.

Returning to the ternary material, we begin by reporting some electronic characteristics of the Ag in the solid state. We examined the charge state of Ag by removing all but one Ag.²⁰ It is found that the remaining Ag lost a charge of about one electron when moved from an isolated position to a TC.

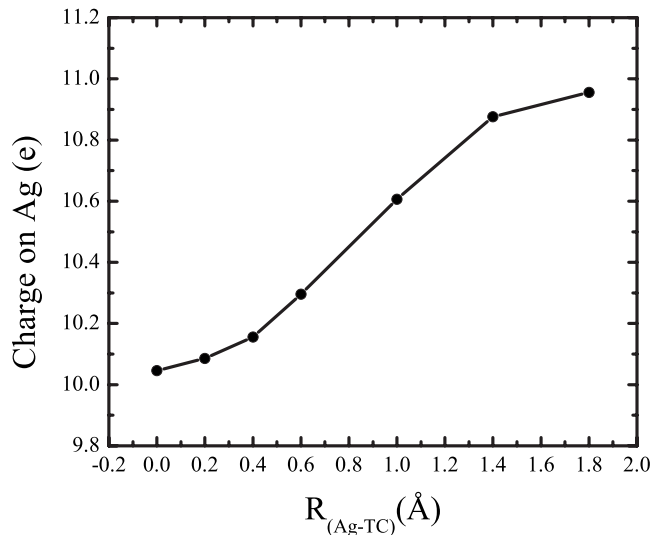


FIG. 1. Valence charge on Ag site with respect to the distance from the TC site (see text). The charge state of Ag changes from neutral when isolated to ionic near TC. Neutral silver has ten $3d$ and one $4s$ electrons.

Near a TC, Ag acts as a positive ion.⁴ At TC, about 65%–70% of the charge lost by Ag site is transferred to the neighboring pair sites. Thus, in the Born-Oppenheimer approximation²¹ (expected to be valid here), we find Ag to be uncharged while undergoing diffusive motion and in the Ag^+ state for bonded conformations (see Fig. 1).

We find that Ag in the network affects the electronic density of states near the optical gap. For nonbonded Ag, it is found that a silver-related level appears about 0.2 eV below the lowest-unoccupied molecular orbital (LUMO) level. With Ag placed at a TC, an increase in the valence edge level density is apparent, as the charge is transferred from the Ag site to the neighboring sites. Therefore, neighbors of Ag are found to contribute to the valence tail and the Ag creates levels near the conduction tail.

We also added an electron to occupy the LUMO, with Ag placed at TC. It is found that the total charge on Ag sites is increased and consequently the contribution of Ag to the conduction tail is enhanced. The increase in charge on Ag sites resulted in an increase in bond length (and therefore a weakened bond) between Ag and the neighboring pair sites. Light of an appropriate wavelength might induce electronic transitions between the valence tail and conduction tail states: both of which are Ag-related. Hellmann-Feynman forces associated with the light-induced occupation change may be large for the Ag and stimulate metal diffusion in a local-heating picture.²² Thus, the electron injection (closely related to light-induced occupation change) suggests weakened Ag bonding, lower barriers, and presumably more highly diffusive Ag.

Silver dynamics was studied by constant-temperature Nosé-Hoover dynamics at 300 and 700 K. Extended trajectories of 20 ps were obtained. At 300 K, silver is largely trapped: only six hopping events were observed. The silver traps fall into two categories. Type 1 (32%) is strongly bound: four Ag atoms sit at single TC with no neighboring

TC within a radius of 2.0 Å and seven Ag occupy two overlapping TCs with the host pairs making an angle of about 90° to each other. Type 2 (68%) is oscillating between two or three closely spaced TCs. Figure 2 reveals the dynamics of the two types of Ag. In the top panel of Fig. 2, dynamics of Ag_{213} (type 1) relative to the three TCs is shown. Initially, it is trapped at TC(11–202) (between Ge_{11} and Se_{202}), the gradual decrease in the Ge_{11} – Se_{202} distance pushes the Ag out, and it is eventually trapped at two overlapping TCs [TC(60–202) and TC(11–98)]. Note the stabilization in the Se_{60} – Se_{202} and Ge_{11} – Se_{98} distances after Ag is trapped between the host atom pair. The bottom panel of Fig. 2 illustrates type 2 Ag motion. Ag_{228} is initially trapped at TC(107–142). It becomes unstable due to the motion of TC(142–150) (initially at 1.8 Å from Ag_{228}) and then a decrease in the Se_{107} – Se_{142} distance moves it out of its initial TC. Eventually Ag_{228} is trapped between the two TCs [TC(142–150) and TC(32–129)] with an average distance of about 1.6 Å between them. The trajectory of Ag_{228} shows cage or “supertrapping” between two TCs. Note the larger fluctuations in the position of Ag as compared to type 1 Ag (trajectory of Ag_{213}). The hopping lengths between one TC to other TCs, in general, depend on the concentration of neighboring TCs. A larger number of neighboring TCs tends to confine the Ag in a smaller region (1.0 Å) as in the two cases discussed above, while larger jumps are observed for Ag with lower concentration of neighboring TCs.²³

The mean-squared displacement of Ag at 700 K shows a linear increase with time, illustrating the diffusive nature of the Ag dynamics, consistent with the previous studies.¹ The Ag dynamics consists of a gradual drift away from the initial (fully relaxed) TC configurations followed by hops between cages. There are 20 jumps observed—much larger than that for 300 K—as expected, with an average time period of approximately 7 ps between the hops. The hopping lengths vary between 1.5–4.0 Å. We characterize such hopping dynamics in terms of the variation in the concentration of TCs n_{TC} around Ag sites. Figure 3 shows the displacement of Ag_{213} at 700 K. The hopping is apparent in the form of abrupt changes in the displacement. To understand these jumps, we counted the number of TCs surrounding the Ag site in a radius of 4.0 Å. In Fig. 3, the concentration of neighboring TCs is also plotted with the displacement. A correlation between the hops and the decrease in n_{TC} is apparent. The jumps tend to occur at times when either n_{TC} is low or exhibits a sudden decrease. Also, the figure reveals the significant impact of thermal fluctuations on the TCs and their density. The trajectory of Ag_{213} along with the trajectories of three neighboring TCs (inset) in the trapped region gives further insight into the nature of the trap. At higher temperature, the Ag sites are more unstable because of thermal fluctuations in the neighboring network and their higher thermal energies. It would require a higher density of TCs to confine the Ag dynamics. The hops can be considered as a spontaneous event, which may be triggered by a decrease in the concentration of neighboring TCs.

Figure 4 illustrates Ag motion at both temperatures. In equilibrium, the Ag at 300 K is confined on or in between the dense regions spanned by the TCs. Note that the volume fraction containing no TC is large at 300 K. At 700 K, TC is

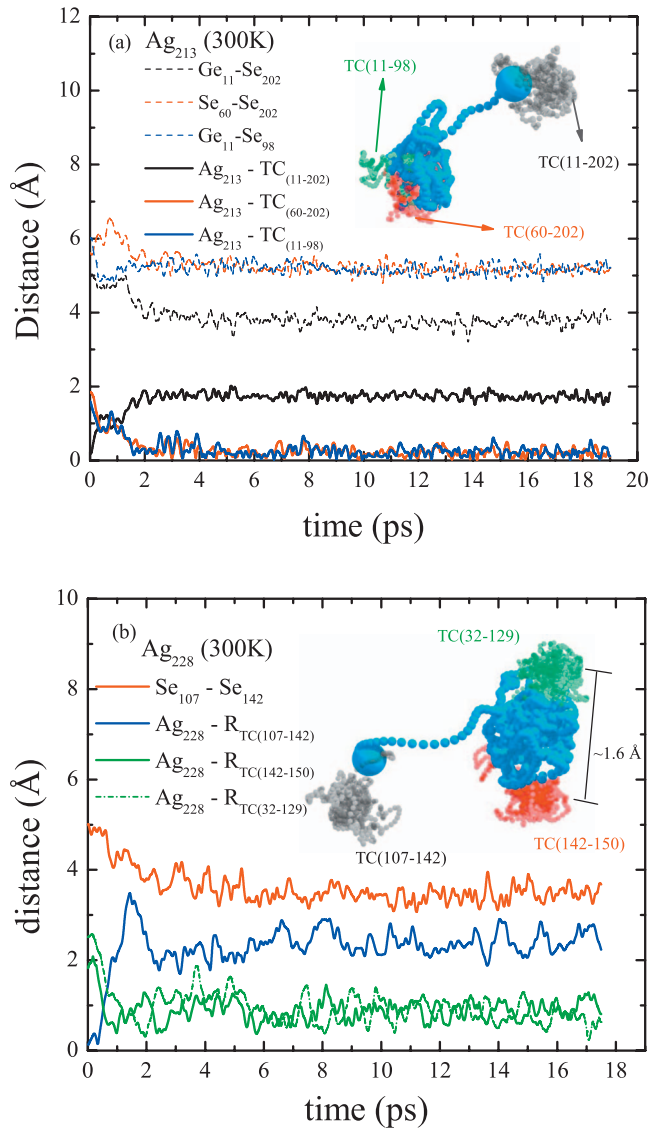


FIG. 2. (Color) Characteristic examples of silver dynamics: top: “type 1” trap, bottom “type 2” (see text). The inset shows the trajectories of Ag sites (blue) with the trajectories of neighboring TCs (gray, green, and red). The motion is crudely oscillatory within a TC and much more ballistic between traps.

less concentrated owing to the thermal fluctuations in the host network, thus enhancing Ag diffusion. The Ag jumps between dense TCs regions (cages) are apparent. Such dynamics is quite similar to the hopping dynamics suggested for Li ions in silicate glasses,^{12,13} where the high mobility of Li ions is correlated with the decrease in the volume fraction of voids, which decreases the local atomic density around ion.^{11,14} At 300 K, the TCs are relatively more stable and are distributed randomly as shown in Fig. 4 in the form of dense and dilute regions, similar to the Scher-Lax-Phillips traps.⁹ One can view Fig. 4 as a revealing a percolative process. At the higher temperature, the trapping basins become more extended and overlapping, until transport through the glass becomes possible.

In summary, we have presented a microscopic picture of

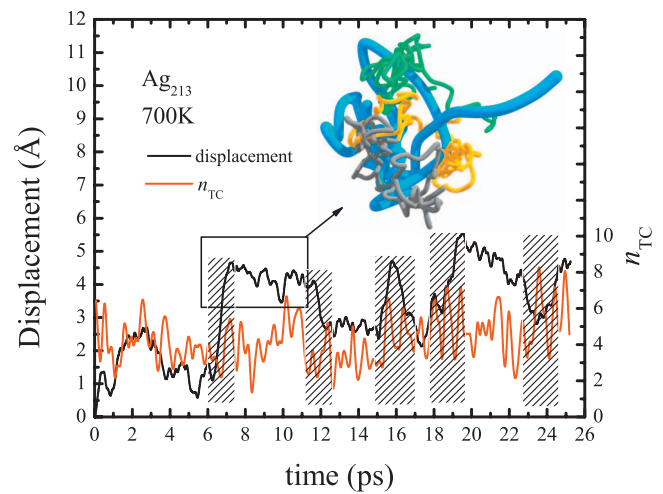


FIG. 3. (Color) Displacement of Ag_{213} from its initial starting position and the average number n_{TC} of trapping centers surrounding Ag_{213} (within the radius of 4.0 Å around the Ag atom). The shaded regions highlight the hops. The trajectory of Ag_{213} (blue) is shown along with those of three neighboring TCs (yellow, green, and gray) in the time during which Ag is trapped after making a “jump.” Observe the creation and annihilation of TCs at 700 K.

Ag dynamics in the $(GeSe_3)_{75}Ag_{15}$ glass at low and high temperatures. It is shown that the Ag is loosely bonded to the host network and the low-energy sites of Ag at 0 K are at the centers of the pairs of host sites, having distances of about 5.2 Å separating them. At low temperatures, the Ag is mainly trapped at or in between such trapping centers. At higher temperatures, the dynamics mainly consist of trapped motion followed by hops. The trapped region of Ag consists of higher concentration of TCs forming a cagelike network, which confine Ag dynamics in the cage. Large fluctuations in the concentration of TCs trigger hopping and allow the Ag to move between such cages.

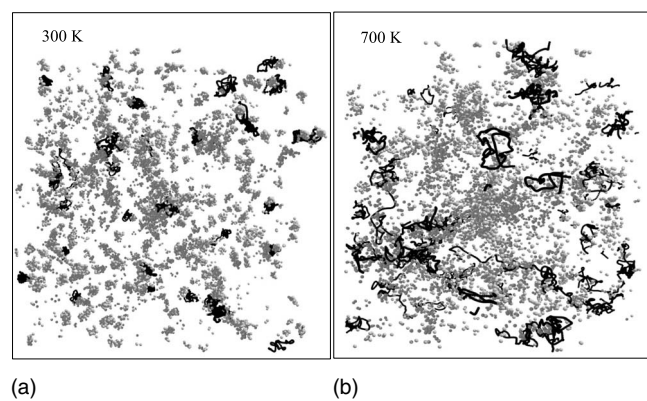


FIG. 4. Trajectories of TCs (gray) and all Ag (black) from MD simulation of about 6 ps length at (a) 300 K and (b) 700 K. Concentration of Ag sites around dense regions of TCs is apparent at 300 K and the Ag hops between the dense regions of TCs are clear at 700 K. Note the increase in the fraction of volume in the cell with TCs at 700 K relative to 300 K.

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