Structure of amorphous Ag/Ge/S alloys: Experimentally constrained density functional study

J Akola,1,2 B Beuneu,3 R O Jones,4,5 P Jóvári,6 I Kaban,7 J Kolář,8 I Voleská,8 and T Wágner8

1 Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland
2 COMP Centre of Excellence, Department of Applied Physics, Aalto University, FI-00076 Aalto, Finland
3 Laboratoire Léon Brillouin, CEA-CNRS, CEA-Saclay, F-91191 Gif-sur-Yvette, France
4 Peter-Grünberg-Institut PGI-1 and JARA/HPC, Forschungszentrum Jülich, D-52425 Jülich, Germany
5 German Research School for Simulation Sciences, FZ Jülich, D-52425 Jülich, Germany
6 Research Institute for Solid State Physics and Optics, P.O. Box 49, H-1525 Budapest, Hungary
7 Institute for Complex Materials, IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany
8 Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Náměstí Československých legii 565, CZ-53210 Pardubice, Czech Republic

E-mail: jaakko.akola@tut.fi, r.jones@fz-juelich.de, jovari.pal@wigner.mta.hu

Abstract.
Density functional/molecular dynamics simulations have been performed to determine structural and other properties of amorphous Ag/Ge/S and Ge/S alloys. In the former, the calculations have been combined with experimental data (x-ray and neutron diffraction, extended x-ray absorption fine structure). Ag/Ge/As alloys have high ionic conductivity and are among the most promising candidates for future memristor technology. We find excellent agreement between the experimental results and large-scale (500 atoms) simulations in Ag/Ge/S, and we compare and contrast the structures of Ge/S and Ag/Ge/S. The calculated electronic structures, vibrational densities of states, ionic mobilities, and cavity distributions of the amorphous materials are discussed and compared with data on crystalline phases where available. The high mobility of Ag in solid state electrolyte applications is related to the presence of cavities and can occur via jumps to a neighbouring vacant site.

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1. Introduction

The need to replace flash memory by highly scalable, rapid, low-power and durable non-volatile alternatives has focused on a range of devices often referred to as resistive random access memories (RRAM). The information is stored as states of different resistivities that can be programmed by appropriate physical mechanisms, and almost all involve amorphous chalcogenides. Well-known examples are provided by phase change materials (PCM), which are based on the extremely rapid and reversible transformation between the amorphous and crystalline forms of nanosized bits in a very thin polycrystalline layer of a semiconductor. Phase changes are achieved by laser light or resistive heating and can be monitored by changes in resistivity or optical properties and form the basis of rewriteable optical storage (digital versatile disk DVD, Blu-ray Disc) and electronic applications based on phase-change RAM (PC-RAM) [1]. The best studied PC materials are alloys of the GST family (GeTe)$_x$(Sb$_2$Te$_3$)$_{1-x}$, particularly Ge$_2$Sb$_2$Te$_5$, and Sb-rich compounds, including Ag/In/Sb/Te (AIST) alloys. The past decade has seen considerable progress in understanding the phase change mechanism, in particular for the speed of crystallization. Molecular dynamics simulations based on density functional theory have played an essential role [2].

Another promising candidate for non-volatile memory is based on a metal-insulator-metal (MIM) electrochemical cell [3]. In this case, the resistance change results from the formation or removal of conducting pathways (filaments) in the electrolyte, depending on the polarity of the electrodes. The dendritic growth of Ag filaments in As$_2$S$_3$, the polarity dependence of the switching, and the memory function were recognized many years ago [4], and devices using this phenomenon are referred to as electrochemical metallization cells (EMC) or conductive bridge memory (CBM) [5]. The active electrode is often Ag or Cu, the inert electrode W, and the favoured electrolytes are amorphous Ge chalcogenides, with Ge-S playing a prominent role. The structure of the electrolyte is complicated by the formation of crystalline diffusion products [6], although recent work has shown that it is possible to control the size of Ag$_2$S nanocrystals in GeS$_2$ matrix composites [7]. The ternary system Ag/Ge/S is the focus of the present work.

Chalcogenide glasses containing Ag have many applications and have been studied extensively [8–12]. They are among the best ionic conductors, but our understanding of the conduction mechanism is hampered by a lack of detailed knowledge of the structure. Studies of the alloy system (Ag$_2$S)$_x$(GeS$_2$)$_{1-x}$, which forms a glass in the range $x = 0 - 0.55$ and has its maximum conductivity at $x = 0.55$, include Raman spectroscopy [13], extended x-ray absorption fine structure (EXAFS) [14], x-ray absorption spectroscopy, small angle and anomalous wide angle x-ray scattering [15], and isotope-substitution neutron diffraction (ND) with and without reverse Monte Carlo analysis [16, 17]. These measurements indicated that the basic framework comprises GeS$_4$ tetrahedra. For Ag$_2$GeS$_4$ ($x = 0.5$), the proposed structure is a chain of corner-linked tetrahedra similar to that found in crystalline Ag$_8$GeS$_6$ (argyrodite, $x = 0.8$) [18], and the high conductivity of Ag$^+$ ions might be associated with chainlike medium-range
order [17]. Changes in the strength of the first sharp diffraction peak were consistent with the presence of voids (cavities) [19].

The above measurements have focused on \((\text{Ag}_2\text{S})_x(\text{GeS}_2)_{1-x}\) compositions, and it is important to study other regions of the Ag/Ge/S phase diagram. XRD and ND studies of \(\text{Ge}_x\text{S}_{1-x}\) alloys with \(0.333 \leq x \leq 0.467\), sometimes termed as “Ge-rich” because they have a larger Ge/S ratio than in \(\text{GeS}_2\), showed different structural patterns from those found in \(\text{GeS}_2\) [20]. Rátkai et al. [21] have performed a reverse Monte Carlo analysis of XRD, ND, and EXAFS data on \(\text{GeS}_3\) doped with up to 25 at. % Ag. Ge has mainly S neighbours in \(\text{GeS}_3\), but Ge-Ge and Ag-Ag bonds appear already in \((\text{GeS}_3)_{0.85}\-\text{Ag}_{0.15}\), and the S-Ag coordination number increases with increasing Ag content. These techniques are applied in the present work to Ag-doped \(\text{Ge}_{42}\text{S}_{58}\), which has a much higher Ge/S ratio, and complemented by extensive density functional (DF) calculations. The combination of RMC analysis and DF calculations was described by Biswas et al. [22] and applied to glassy \(\text{GeS}_2\) [23], and we have used it to determine the structure of amorphous forms of \(\text{Ge}_2\text{Sb}_2\text{Te}_5\) [24], \(\text{Ag}_{3.5}\text{In}_{3.8}\text{Sb}_{75.0}\text{Te}_{17.7}\) [25], \(\text{Ga}_{11}\text{Ge}_{11}\text{Te}_{78}\) [26], \(\text{Ge}_{15}\text{Te}_{85}\) [27], and \(\text{AsS}_2\) and \(\text{Ag-AsS}_2\) [28]. The DF calculations are particularly valuable in avoiding structures with unphysical properties. Without this constraint, for example, RMC fitting to XRD, XPS, and EXAFS data led to a metallic, not semiconducting structure of amorphous \(\text{Ge}_2\text{Sb}_2\text{Te}_5\) [29]. We shall extend these DF calculations to study filament formation in Ag-doped chalcogenides in the presence of an electrostatic field. The role of an electric field on diffusion of a Cu interstitial in \(\alpha\)-cristobalite \(\text{SiO}_2\) has been simulated by Zelený et al. [30], and Cu filament formation in Cu-amorphous \(\text{SiO}_2\)-Cu in the presence of a field has been simulated very recently using classical force fields [31].

2. Methods

2.1. Experimental

Glasses of the composition \(\text{Ag}_x(\text{Ge}_{0.42}\text{S}_{0.58})_{100-x}\) with \(x=0\) (Ge/S) and 20 at. % (Ag/Ge/S) were prepared from 5N purity elements. The components of total mass of 10 g were inserted into quartz ampoules, which were then evacuated to a pressure of \(10^{-3}\) Pa, sealed, and placed in a rocking furnace. The glasses were synthesized with a well-defined heating profile at a maximum temperature of 1000°C for 12 h. The ampoules were quenched in iced water and then annealed for 3 h at 50°C below the respective glass transition temperature. The mass densities at room temperature, determined with an accuracy of 0.15 % using the Archimedean method by weighing samples in air and in toluene, were 3.187 g cm\(^{-3}\) (0.03908 atoms Å\(^{-3}\)) for \(x=0\), and 4.878 cm\(^{-3}\) (0.04827 atoms Å\(^{-3}\)) for \(x=0.20\).

X-ray diffraction (XRD) measurements of flat samples (~ 2 mm thick) were carried out in transmission geometry at the BW5 beamline at HASYLAB (DESY, Hamburg, Germany). The incident beam had an energy of 100 keV and a cross section of 2 mm\(^2\). The scattered intensity was recorded by a Ge solid-state detector, and the raw
data were corrected for background, absorption, polarization, detector dead-time, and variations in detector solid angle [32]. The neutron diffraction (ND) experiments were performed with the 7C2 diffractometer at the Laboratoire Léon Brillouin (CEA-Saclay, France) using a neutron beam with wavelength 0.714 Å. The samples were ground and inserted into thin-walled (70 µm) vanadium containers of 7 mm diameter. The diffraction data were corrected for detector efficiency, empty instrument background, scattering from the sample holder, multiple scattering [33], and absorption [34] using standard procedures [35].

The Ge and Ag K-absorption edge EXAFS measurements were carried out at the X1 experimental station at HASYLAB in transmission mode. The glassy alloys were finely ground, mixed with cellulose, and pressed into tablets. The quantity of powder was selected to provide transmission near 1/e for the particular composition and absorption edge. EXAFS spectra were obtained in steps above the absorption edge, and the measuring time was k-weighted during data collection. The X-ray absorption cross sections \( \mu(E) \) were converted to \( \chi(k) \) by standard procedures using the program Viper [36].

2.2. RMC analysis

The starting structures for DF/MD simulations were produced by applying the reverse Monte Carlo (RMC) method [37,38], in which the atoms are moved randomly to optimize the fit to high energy XRD, ND, and Ag and Ge K-edge EXAFS data. Further RMC refinement of structures can be carried out based on local minima in the energy surface determined by DF/MD calculations. Electronic structure and other information can be incorporated by constraining coordination numbers or bond angle distributions, and the bond angles (Ge-S-Ge, S-Ge-S, S-Ag-S, Ag-S-Ag, and Ag-Ag-S) and minimum distances (Ge-Ge: 2.35 Å, Ge-S: 2.05 Å, Ge-Ag: 2.45 Å, S-S: 1.9 Å, S-Ag: 2.3 Å, and Ag-Ag: 2.85 Å) were constrained to be close to those found in DF simulations. The maximum displacement of an atom in a move was 0.05 Å for each coordinate, and refinement was discontinued after \( \sim 5000 \) accepted moves. The total energy of the final RMC fit was 0.13 eV/atom higher than the DF energy minimum in Ag/Ge/S. The use of DF optimized structures as RMC input is particularly advantageous in these systems, where the scattering of x-rays and neutrons is much weaker in one element (S) than in the others.

2.3. Density functional calculations

The DF/MD simulations \( (NVT, \text{i.e., constant particle number } N, \text{ volume } V, \text{ and temperature } T) \) used the CPMD program package [39]. Born-Oppenheimer molecular dynamics, where the Kohn-Sham orbitals are optimized after each MD step, enable us to use much longer time steps (3.025 fs, 125 a.u.) than in standard Car-Parrinello simulations. The PBEsol approximation [40] for the exchange-correlation energy is a modification of the popular PBE functional [41] that is intended to improve equilibrium
properties for extended systems, and we used it also in recent calculations on Ag/As/S [28] and Ge/Sb/Te [42] alloys. The electron-ion interaction was described by scalar-relativistic pseudopotentials of Troullier-Martins form [43] with valence configurations Ag: 4d\(^{10}\)5s, Ge: 4s\(^{2}\)4p\(^{2}\), and S: 3s\(^{2}\)3p\(^{4}\). We used periodic boundary conditions with a single point (k=0) in the Brillouin zone, and the kinetic energy cutoffs of the plane wave basis set were 60 Ry (Ag/Ge/S) and 30 Ry (Ge/S). The temperature was controlled by a Nosé-Hoover thermostat (frequency 800 cm\(^{-1}\), chain length 4) [44]. The cubic simulation cells contained 500 atoms (Ag\(_{100}\)Ge\(_{168}\)S\(_{232}\) and Ge\(_{210}\)S\(_{290}\)) with box sizes 21.799 Å and 23.38865 Å, corresponding to the measured densities.

The time scale of traditional melt-quench simulations is much too short for physical processes that can take hours in these materials, and we start from atomic models based on structures generated by applying the RMC method to the experimental data set. Several structures were then optimized by the DF method in order to select promising starting points for MD annealing, which allows local diffusion and relaxation at temperatures below the melting point. The selected Ag/Ge/S structures were heated to 500 K and cooled to 300 K over 142 ps in steps of 50 K. Data were collected at 300 K for 32.6 ps (10800 time steps), and the structures optimized. Additional NVT runs at 500 K (112.1 ps, 37071 time steps) and 600 K (39.9 ps, 13200 time steps) were carried out to investigate Ag dynamics. The glass temperatures of (Ag\(_{2}\)S\(_{x}\)(GeS\(_{2}\))\(_{1-x}\); 0.1 ≤ x ≤ 0.4 lie in the range 570-600 K [45].

The XRD and ND results for Ge/S could be reproduced well by RMC without constraints. However, in contrast to our experience with Ag/Ge/S, Ag-AsS\(_{2}\), and AgS\(_{2}\), and elsewhere, extensive attempts to find a structure with a DF energy within 100 meV/atom of the minimum value did not succeed. Since our main criterion for a starting structure is relative stability, we have taken the one with the lowest total energy of all that we tested. The sample with this structure was cooled from 600 K to 300 K in steps of 50 K (201.9 ps, 66800 time steps), with final data collection over 30.4 ps (10050 time steps). We require that both ND and XRD measurements are reproduced well, and the unusual problems in Ge/S may arise from the relatively low concentration of S and the fact that its bound coherent nuclear scattering length (2.847 fm) is much less than in Ge (8.185 fm) [46].

The power spectra (vibrational densities of states) and their projections onto the elements were calculated from the Fourier transform of the velocity-velocity autocorrelation functions from the final trajectories, and the instantaneous diffusion coefficients \(D_\alpha(t)\) were determined from the time-dependence of the atomic mean square displacements (MSD) using

\[
D_\alpha(t) = \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle,
\]

where \(r(t)\) are the coordinates of an atom of type \(\alpha\) at time \(t\). Cavities are assigned by determining domains that are farther from any atom than a given cutoff (here 2.5 Å, spherical test particle) and building cells around their centers according to the Voronoi construction [29].
3. Results and Discussion

3.1. Neutron and x-ray diffraction structure factors, EXAFS

The structure factors \( S(Q) \) for Ag/Ge/S (XRD, ND, calculated) are shown in Fig. 1, and the overall agreement between theory and experiment is very satisfactory. Excellent agreement is also found for the amplitude and phase of the Ge- and Ag-K-edge EXAFS spectra of \( a\)-Ag/Ge/S (Fig. 2), which shows that the local configuration around Ag and Ge (particularly the corresponding bond distances) are described very well.

![Figure 1. (Colour online) Structure factors \( S(Q) \) for amorphous Ag/Ge/S (XRD, ND). Black line: Experiment, red line: calculated (DF+RMC fit). The upper curve is displaced by 1 unit.](image)

3.2. Structures: pair distribution functions, coordination numbers

The optimized structures of amorphous Ge/S and Ag/Ge/S [Fig. 3(a,b)] show clearly the lower density in the former. The corresponding partial pair distribution functions (PDF) \( g_{\alpha\beta}(r) \) are shown in Fig. 4 (Ge-S, Ge-Ge, S-S) and Fig. 5 (Ag-Ag, Ag-S, Ag-As in Ag/Ge/S). The first maximum, the first minimum, and the bond cutoff for each curve are given in Table 1. Ge-S bonds are dominate in the covalent network, but
Ge-Ge bonds also contribute significantly in Ag/Ge/S. For Ge/S, the Ge-Ge PDF is significantly weaker, and few S-S bonds ("wrong bonds") occur around 2.07 Å, as in Ag/Ge/S. Silver forms bonds mostly with sulphur as demonstrated by the sharp Ag-S peak at 2.55 Å. The Ag-Ge PDF has a well-defined first peak, which differs from the weak shoulder for Ag-As found in Ag-AsS$_2$ [28]. The average coordination numbers in Ge/S and Ag/Ge/S are given in Table 2.

The dominant configurations are given in Tables 3 (a-Ge/S) and 4 (a-Ag/Ge/S) and provide interesting details of the local coordination. Ge atoms favour fourfold coordination in Ge/S, although threefold coordination is not uncommon. Ag atoms favour coordination numbers between 5 and 7 in Ag/Ge/S (sixfold on average), and Ge atoms are mainly fourfold coordinated (with Ge–AgS$_3$ as the most prominent configuration). There is an interesting anti-correlation between Ge-Ge and Ag-Ge bonds.

The most common environments of S atoms involve Ag and Ge and three- and fourfold coordination: S–AgGe$_2$ and S–Ag$_2$Ge$_2$. Ag shows a variety of configurations where bonding with S is preferred over Ge, and over 90% of the configurations involve Ag-Ag bonds. There are few terminal S atoms in the Ge/S network, which differs markedly from Ag-AsS$_2$. The S atoms in the Ge-S network are chemically saturated by covalent bonds, and the weaker Ag-S bonds should enhance Ag mobility.
Table 1. The first maxima of the partial PDF \( g_{\alpha\beta} \) of \( a\text{-Ag/Ge/S} \) and \( a\text{-Ge/S} \) at 300 K. All distances in Å.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha )</th>
<th>( \beta = \text{Ge} )</th>
<th>S</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/Ge/S</td>
<td>Ge</td>
<td>2.53</td>
<td>2.32</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>2.32</td>
<td>2.08</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>2.62</td>
<td>2.55</td>
<td>2.93</td>
</tr>
<tr>
<td>Ge/S</td>
<td>Ge</td>
<td>2.53</td>
<td>2.26</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>2.26</td>
<td>2.07</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2. The average coordination number \( N_{\alpha\beta} \) in \( a\text{-Ag/Ge/S} \) and \( a\text{-Ge/S} \) at 300 K. Bond cutoff distances: Ge-Ge: 2.8, Ge-S: 2.8, Ge-Ag: 3.0, S-S: 2.3, Ag-S: 3.2, Ag-Ag: 3.5.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha )</th>
<th>( N_{\alpha\text{Ge}} )</th>
<th>( N_{\alpha\text{S}} )</th>
<th>( N_{\alpha\text{Ag}} )</th>
<th>( N_{\alpha\text{tot}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/Ge/S</td>
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<td>0.60</td>
<td>2.86</td>
<td>0.55</td>
<td>4.01</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>2.07</td>
<td>0.07</td>
<td>1.52</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>1.68</td>
<td>3.52</td>
<td>0.92</td>
<td>6.13</td>
</tr>
<tr>
<td>Ge/S</td>
<td>Ge</td>
<td>0.32</td>
<td>3.24</td>
<td>–</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>2.35</td>
<td>0.10</td>
<td>–</td>
<td>2.44</td>
</tr>
</tbody>
</table>

Table 3. Percentage of atoms of element \( \alpha \) with coordination number \( N_\alpha \), and dominant configurations in \( a\text{-Ge/S} \) at 300 K (DF/MD simulations, three most frequent configurations, values under 1% are excluded). Bond cutoffs as in Table 2. Boldface: total coordination number.

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( N_\alpha=2 )</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>2.4</td>
<td>43.9</td>
<td>52.8</td>
</tr>
<tr>
<td>S2: 2.4</td>
<td>S3: 37.1</td>
<td>GeS2: 6.7</td>
<td>GeS3: 19.5</td>
</tr>
<tr>
<td>S</td>
<td>59.7</td>
<td>38.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Ge2: 52.3</td>
<td>Ge3: 37.1</td>
<td>Ge2S: 1.5</td>
<td>Ge4: 1.5</td>
</tr>
</tbody>
</table>
3.3. Angular distributions, coordination numbers

The angular distributions near Ag-S and Ge-S bonds (DF/MD simulations, 300 K, Fig. 6) show features similar to those found in Ag-AsS$_2$. A striking exception is the Ag-Ag-Ag distribution, where the peak at 60° is much more pronounced in Ag/Ge/S. These correspond to triangular configurations and indicate increased connectivity among Ag atoms, despite the smaller concentration (20%) relative to the chalcogenide host. The S-Ag-S angles have a maximum at $\sim$90°, indicating octahedral (sixfold) coordination. The maxima at 100° in S-Ge-S in both alloys is related to the coexistence of tetrahedral (threelfold) and octahedral Ge coordination, where the Ge atoms coordinated to Ag are of the latter type. The S-Ge-S angles are affected more by the presence of Ag, and the
corresponding peak is narrower and shifted to lower angles.

There are no crystallographic data for the constituent phases of compounds of the compositions studied here, but several crystalline forms of the family \((\mathrm{Ag}_2\mathrm{S})_x(\mathrm{GeS}_2)_{1-x}\) are known: \(\mathrm{GeS}_2\) \((x = 0)\), \(\mathrm{AgGeS}_3\) \((x = 0.5 [47])\), \(\mathrm{Ag}_8\mathrm{GeS}_6\) \((x = 0.8\), argyrodite [18]\), and \(\mathrm{Ag}_2\mathrm{S}\) \((x = 1\), argentite, acanthite). The basic structural units of glassy \(\mathrm{GeS}_2\) are \(\mathrm{GeS}_4\) tetrahedra connected via corner- and edge-sharing. Slightly distorted \(\mathrm{GeS}_4\) tetrahedra (mean \(\mathrm{Ge}-\mathrm{S}\) bond length 2.212 Å) are also present in crystalline \(\mathrm{Ag}_8\mathrm{GeS}_6\), with two further \(\mathrm{S}\) atoms without bonds to \(\mathrm{Ge}\) atoms. These units are linked via Ag atoms, which show three types of \(\mathrm{S}\)-coordination: strongly distorted tetrahedra (4), near-planar threefold coordination (3), and a near-linear S-Ag-S structure (1). The Ag-S distances are \(2.56 - 2.94\) Å, \(2.49 - 2.76\) Å, and \(2.42 - 2.44\) Å, respectively. All Ag atoms have at least one Ag near neighbour between \(2.93 - 3.11\) Å. Short Ag-S bonds are also found in \(\mathrm{AgGeS}_3\) (2.377 Å), with additional bonds in the range \(2.502 - 2.746\) Å. Ge-S bonds range from \(2.150\) to \(2.356\) Å. The distortions from tetrahedral symmetry are substantial in this case [47]. The Ag-S and Ge-S bond distances can be compared
Figure 5. (Colour online) Partial PDF $g_{\alpha\beta}(r)$ for Ag-β distances in a-Ag/Ge/S: black: Ag-S, red: Ag-Ge, blue (thick): Ag-Ag. Inset: Coordination number as function of bond cutoff distance.

Table 4. Percentage of atoms of element $\alpha$ with coordination number $N_\alpha$, and dominant configurations in a-Ag/Ge/S at 300 K (DF/MD simulations, three most frequent configurations, values under 1% are excluded). Bond cutoffs as in Table 2. Boldface: total coordination number.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$N_\alpha=2$</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>20.0</td>
<td>63.7</td>
<td>14.2</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>6.3 GeS: 5.6</td>
<td>40.3</td>
<td>41.1</td>
<td>11.2</td>
<td>1.0</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ag</td>
<td>7.3 GeS: 2.2</td>
<td>27.0</td>
<td>34.4</td>
<td>21.7</td>
<td>7.4</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

with our results 2.55 Å and 2.32 Å, respectively (Table 1).

3.4. Electronic structure, density of states

The calculated electronic densities of states (DOS) and their projections onto elements and atomic orbitals are shown in Fig. 7. The calculated band gaps at the Fermi energy are 0.54 eV (Ag/Ge/S) and 1.15 eV (Ge/S). These may be compared with the experimental band gaps in Ag$_8$GeS$_6$ (1.37 eV [48]), GeS$_2$ (3.425 eV [49]), and the
Figure 6. (Colour online) Angular distributions in Ge$_{42}$S$_{58}$ (“bin.”) and Ag/Ge/S. The dashed lines denote the reference values $60^\circ$, $90^\circ$, and $109.47^\circ$ (tetrahedral).

The calculated band gaps are nevertheless consistent with semiconducting behaviour throughout the simulations, and there were no numerical instabilities that sometimes accompany gapless (metallic) or small band gap simulations.

Our calculations show prominent peaks at $-13$ eV (S 3s states) and $-4.1$ eV (Ag 4d states), as well as a band from $-7$ to $-11$ eV (Ge 3s, S 4s). The hump at the top of the valence band has contributions from Ag (4d), Ge (3p), and S (3p) antibonding states. This picture is similar to that found for Ag and S in the calculated DOS and the photoelectron energy distributions found in Ag$_2$S [51]. Effective charges in Ag/Ge/S have been computed by the method of Bader [52,53] to be $+0.29e$ for Ag, $+0.10e$ for Ge, and $-0.20e$ for S. Despite the low effective charges, the cationic nature of Ag$^+$ is clear. The effect of adding Ag atoms is similar to our findings for Ag-AsS$_2$ and AsS$_2$ [28].
3.5. Cavity distributions

The distributions of cavities, defined as in [29] with the parameters given above, are dramatically different in Ge/S and Ag/Ge/S [Fig. 3(c,d)]. The density is much lower in the former, and the cavity volume correspondingly much greater. The cavity volumes vary during the simulations, for Ag/Ge/S from 6.7% shortly (100 time steps) after the beginning to 4.6% at the end, for Ge/S 42.2% to 41.6%. A decrease in the number of cavities and other “defects” is expected as the samples age. In Ag-AsS$_2$ and AsS$_2$ the final values were 4.8% and 37.8%, respectively [28].

The pair distribution functions involving cavities are given in the Supplementary Information (Fig. SF1 [54]). In terms of neighboring atoms, cavities are typically surrounded by 7.4 atoms, and S has the largest contribution (50%). Each cavity is
linked to at least one Ag atom, which suggests that Ag atoms have neighbouring sites available for diffusion. The cavity-cavity distribution shows reduced weight at shorter distances, i.e., fewer connections, indicating that the cavities comprise single “trapping sites” consistent with the small total volume [Fig. 3(d)]. The overall picture is similar to that in Ag-AsS₂.

3.6. Dynamical properties

The ranges of vibrational frequencies to be expected can be found from studies of solids containing the component elements. Crystalline $\beta$-GeS₂ shows bands of Raman active modes up to 170 cm$^{-1}$ and from 338 – 445 cm$^{-1}$ [55]. Raman and Brillouin light scattering measurements on amorphous GeS₂ show peaks at 20 cm$^{-1}$ and 100 cm$^{-1}$ and shoulders near 200 cm$^{-1}$ and 250 cm$^{-1}$ [56]. Infrared reflectivity measurements on crystalline $\beta$-Ag₂S at 4.2 K show peaks at 40 and 70 cm$^{-1}$, shoulders at 90 and 140 cm$^{-1}$, a broad band near 230 cm$^{-1}$ and a strong peak at 270 cm$^{-1}$ [57]. Absorption spectra of Ag₈GeS₆ show peaks around 123 cm$^{-1}$ [48].

The calculated power spectra (vibrational densities of states, vDOS) and their projections onto the elements at 300 K are shown for α-Ge/S and α-Ag/Ge/S in Fig. 8. The vDOS shows all frequencies with equal weights and does not reflect the actual intensities of Raman and IR active modes. The qualitative features in Ge/S can readily be identified: S-S vibrations with frequencies above 350 cm$^{-1}$, a broad distribution with a maximum near 300 cm$^{-1}$ (Ge-S vibrations), and a broad low energy peak involving modes with several atoms. The frequency range of the S-S vibrations covers the frequencies found in sulphur chains [58]. Apart from the low-frequency modes involving Ag (maximum at $\sim$ 40 cm$^{-1}$), the power spectrum for Ag/Ge/S (Fig. 8) shows a broad, uniform spectrum. The presence of Ag changes the vibrational properties of S, since there are numerous Ag-S bonds and fewer S-S bonds than in Ge/S.

The high mobility of Ag ions is a crucial feature of Ag-doped semiconductors in technical applications. The motion of Ag atoms is much more pronounced than in Ge and S atoms in the present Ag/Ge/S simulations, and it is perhaps the most interesting dynamical property. The instantaneous diffusion coefficient $D$ is determined from Eq. (1), and the plot of $D$ against inverse time is given in the Supplementary Information (SI) [Fig. SF2 [54]]. Simulations at 500 K and 600 K are near or below the glass transition temperature and will not reach equilibrium on the time scale available for such simulations (or experiment), and the slow approach to equilibrium is often described by a “stretched exponential” function [59]. Extrapolation to 1 ns of the Ag/Ge/S results between 10 ps and 112 ps lead to a value of $D$ of $0.015 \times 10^{-5}$ cm$^2$s$^{-1}$ (Fig. SF2).

More information about the mechanism of enhanced Ag mobility can be found by studying the motion of the most mobile Ag atoms, including their mean square displacement MSD. In Fig. 9 we show 110 ps trajectories in Ag/Ge/S at 500 K of three highly mobile Ag ions with final MSD values (a) 94.4 Å$^2$, (b) 38.8 Å$^2$, and (c) 52.1 Å$^2$. The Ge and S atoms are much less mobile than Ag atoms, and we show them in the
starting configuration. During the first 40 ps of the simulation, the system is far from equilibrium and changes rapidly. The individual MSD are more settled for longer times, but show occasional jumps to a neighbouring vacant site, i.e., an Ag atom exchange places with a vacancy.

The correlation between the mobility of Ag atoms and the presence of cavities is consistent with the “free volume” picture of Ag mobility (see Ref. [60] and references therein) and the concept of “trapping centres” for Ag ions diffusing in Ag-GeSe$_3$ [9,10], where the most mobile ions moved through the regions of lowest density. Correlated motion of Ag ions, which was proposed in a “caterpillar” model of Ag chalcogenides [61], has not been observed, but could occur in much longer simulations.


4. Conclusions

The combination of MD/DF simulations and experimental measurements using RMC refinement has been applied successfully to glassy GeSe$_2$ [23], amorphous Ge$_2$Sb$_2$Te$_5$ [24], and Ag-AsS$_2$ [28] and is used here to study amorphous Ag/Ge/S alloys. There is excellent agreement between DF/MD calculations (500 atoms in the unit cell) and experiment (structure factors, EXAFS spectra, DF energy) in ternary Ag/Ge/S. The calculated self-diffusion constants show that Ag ions are much more mobile than Ge and S ions, and the vibrational density of states shows marked low-frequency modes associated with Ag that further emphasize the enhanced mobility.

There are interesting differences between the results for Ag-GeS$_3$ [21] and those found here for compounds with a higher Ge:S ratio. The higher S content in the former means that S-S bonds are significant for all Ag concentrations investigated. The coordination numbers characterizing the host covalent network (e.g. Ge-Ge, Ge-S, S-S) do not depend on the composition between 15–25% Ag content (Table 3 of [21]).
suggesting that Ag occupies the free volume of the covalent network without breaking it, as found in the present work. However, a strong network rearrangement for Ag content below 15% is manifest in the formation of Ge-Ge bonds. Another remarkable structural feature of Ag-GeS\textsubscript{3} glasses is the violation of chemical order: S-S bonds survive the formation of Ge-Ge pairs, although homonuclear bonding is generally not favoured in binary Ge-S glasses. The formation of S-S bonds is facilitated by the addition of Ag, e.g., by the formation of larger voids around low-coordinated S atoms. These differences from the results in Ag-AsS\textsubscript{2} must be due to the differences in composition and valency, since the covalent radii of Ge and As are similar (Ge: 1.25 Å, As: 1.15 Å [62]).

Cavities are an important feature of the chalcogenide host material, particularly in Ge/S, where they make up 42% of the total volume. Over 50% of Ag ions in Ag/Ge/S have neighbouring vacant sites that provide trapping sites and migration channels for Ag cations, and we observe Ag ion motion occurring by jumps to such vacant sites. Understanding the role of an applied electric field in these ionic conductors will require extensive simulations in the presence of such a field. A prerequisite for such simulations is a thorough understanding of the basic structures of the disordered materials. This we have provided here for Ag/Ge/S alloys.

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and executables are available at
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