Structure, electronic, and vibrational properties of amorphous AsS$_2$ and AgAsS$_2$: Experimentally constrained density functional study

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Density functional/molecular dynamics simulations and experimental data (x-ray and neutron diffraction, extended x-ray absorption fine structure) have been combined to determine structural and other properties of amorphous As$_2$S$_2$ and AgAsS$_2$. These semiconductors represent the two small regions of the Ag-As-S ternary diagram where homogeneous glasses form, and they have quite different properties, including ionic conductivities. We find excellent agreement between the experimental results and large-scale (over 500 atoms) simulations, and we compare and contrast the structures of As$_2$S$_2$ and AgAsS$_2$. 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 coupled to the large cavity volume in As$_2$S$_2$ and local modifications of the covalent As-S network in the presence of Ag.

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I. INTRODUCTION

The electronic properties and applications of amorphous chalcogenide glasses along the Ag$-_x$As$_x$S$_y$ line have potential for ECM memory applications [7] and can be prepared as thin films by an optically induced solid state reaction [3]. Increasing the Ag concentration leads to dramatically increased conductivity in the range $9 < x < 15$, with Ag$^+$ ions playing a dominant role [8]. A combination of x-ray diffraction (XRD), neutron diffraction (ND), and x-ray absorption fine structure (EXAFS) has been used to study structural changes [9], and Raman [8,10] and scanning electron microscopy [10] measurements have been performed. The Ag-As-S ternary phase diagram shows only two regions where homogeneous glass formation occurs: near $x = 0$ (As$_2$S$_2$) and near $x = 25$ (AgAs$_2$S$_2$), the stoichiometric composition ($\text{As}_2\text{S}_3\text{Ag}_5\text{S}_2\text{S}_5\text{Ag}_5$) [11]. Glasses with $4 < x < 20$ segregate on a micrometer scale [10]. Crystalline forms of the silver sulfarsenide AgAs$_2$S$_2$ occur in nature as smithite (monoclinic) [12] and trechmannite (rhombohedral) [13], and refinement of the original structures [12,13] has resulted in significantly better R factors [14]. Glasses along the Ag$_2$S-$\text{As}_2$S$_3$ tie line, including AgAs$_2$S$_2$, have been studied by differential caloriometry and XRD [15], modulated differential scanning calorimetry and Raman spectroscopy [8], EXAFS [16], ND [17,18], and XRD [19]. Optical and photoemission studies [20] have been carried out on amorphous (a-) and crystalline (c-) AgAs$_2$S$_2$.

Understanding the properties of any glass, not only Ag-As-S, requires a detailed knowledge of its structure. This is provided here for As$_2$S$_2$ and AgAs$_2$S$_2$ by combining experimental measurements (EXAFS, XRD, and ND) with extensive density functional (DF)/molecular dynamics (MD) simulations of samples with more than 500 atoms. This experimentally constrained DF approach treats the geometrical and electronic structures on equal footings and has been applied successfully in semiconducting Ge$_2$Sb$_2$Te$_5$ [21], Ag$_{3.5}$In$_{1.3}$Sb$_{75}$Te$_{17.7}$ [22], and Ga$_{11}$Ge$_{11}$Te$_{78}$ alloys [23]. Electronic structure constraints proved to be crucial in semiconducting Ge$_2$Sb$_2$Te$_5$ [21], since reverse Monte Carlo analysis alone led to excellent agreement with XRD data, but an unphysical metallic band structure. The

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II. METHODS

A. Experiment

Samples of amorphous As$_2$ and AgAsS$_2$ were prepared from appropriate amounts of the high purity (99.999%) constituent elements and placed in silica ampoules that were then evacuated (residual pressure $\sim 10^{-4}$ Pa) and sealed. Oxide formation in As was avoided by sublimation of the sample before weighing. The samples were melted in a rocking furnace, held at 1223 K for 24 h, and quenched in air. The glassy samples were then annealed for 3 h near the glass transition temperature and kept under an inert atmosphere of N$_2$ after breaking the ampoules. The mass density was determined with an accuracy of 0.15% using the Archimedean method by weighing samples in air and in toluene.

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 [27]. The neutron diffraction (ND) experiments were performed with the 7C2 diffractometer at the Laboratoire Léon Brillouin (CEA-Saclay, France). The samples were ground and filled into thin-walled (0.1 mm) vanadium containers of 7 mm diameter. The diffraction data were corrected for detector efficiency, empty instrument background, scattering from the sample holder, multiple scattering [28], and absorption [29] using standard procedures [30].

The As 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 of 0.03 Å$^{-1}$ 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 [31].

B. Density functional calculations

The DF/MD simulations (constant particle number $N$, constant volume $V$) used the CPMD program package [32] with Born-Oppenheimer molecular dynamics (time step 3.025 fs, 125 a.u.) and the PBEsol approximation [33] for the exchange-correlation energy. The electron-ion interaction was described by scalar-relativistic pseudopotentials of Troullier-Martins form [34] with valence configurations Ag: 4d$^{10}$5s, As: 4s$^2$4p$^3$, and S: 3s$^2$3p$^4$. We use periodic boundary conditions with a single point ($k = 0$) in the Brillouin zone, and the kinetic energy cutoffs of the plane wave basis set were 60 Ry in AgAsS$_2$ and 25 Ry in AsS$_2$. The temperature is controlled by a Nosé-Hoover thermostat (frequency 800 cm$^{-1}$, chain length 4) [35].

The AgAsS$_2$ system comprised 560 atoms (140 Ag, 140 As, 280 S) and 3920 valence electrons. The size of the cubic box (23.122 Å) corresponds to a density of 0.0453 atoms/Å$^3$ (4.644 g/cm$^3$). The AsS$_2$ system has 540 atoms (180 As, 360 S, 3060 valence electrons) in a cubic box of size 24.0747 Å$^3$ (0.0388 atoms/Å$^3$, 2.968 g/cm$^3$). The simulations began at temperatures below the melting points, and the starting structures were generated by applying the reverse Monte Carlo method to the experimental data set (see below). The AgAsS$_2$ sample was heated to 500 K and cooled to 300 K over 125 ps in steps of 50 K. Data were collected at 300 K for 37.8 ps (12 500 time steps), and the structure was then optimized. The AsS$_2$ sample was cooled from 600 K in steps of 50 K. The cooling time to 300 K was 100 ps, and final data were collected over 30.3 ps (10 000 time steps).

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. The self-diffusion coefficients were determined from the time dependence of the atomic mean square displacements. Cavities are assigned by determining domains that are farther from any atom than a given cutoff (here 2.5 Å) and building cells around their centers according to the Voronoi construction [36].

C. RMC refinement

The starting structures for DF/MD simulations were produced by applying reverse Monte Carlo (RMC) simulation [37,38], in which the atoms are moved randomly to optimize the fit to high energy XRD and As K-edge EXAFS data in AsS$_2$. For AgAsS$_2$ we also used ND and Ag K-edge EXAFS data [9]. Several structures were optimized by the DF method in order to select promising starting points for MD annealing. 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 an atomic model based on some prior knowledge. We use MD to shake the system and allow local diffusion and relaxation without melting.

After the DF/MD simulations, the structure determined from the DF minimum energy was refined by RMC, where electronic structure and other information can be incorporated by constraining coordination numbers or bond angle distributions, and the bond angles here were constrained to be close to those of the unmodified DF structure. The minimum distances were As-As: 2.20 Å, As-S: 2.0 Å, and S-S: 1.85 Å, and the maximum displacement of an atom in a move was 0.01 Å along each coordinate. Refinement was stopped after ∼25 000 accepted moves. The total energy of the final RMC fit was 37 meV/atom higher than the DF energy minimum in AgAsS$_2$, and the measured mobility of Ag$^+$ and Cu$^+$ cations in Ge/Se liquids and glasses at several temperatures and have found that the most diffusive ions prefer low density regions of the networks (“trapping centers”). The ordering of oxygen vacancies may also play an essential role in the formation of conductive filaments in a TiO$_2$ resistive switching memory.
and 22 meV/atom higher in AsS₂. These energy differences are within the range of thermal fluctuations at 300 K (~k_B T), and the RMC refined structures are very close to the DF structures with minimum energy. 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.

III. RESULTS

A. Neutron and x-ray diffraction, EXAFS

The structure factors S(Q) for a-AsS₂ (XRD) and a-AgAsS₂ (XRD, ND) (Fig. 1) show halo patterns typical of disordered materials, and the oscillations extend well beyond 10 Å⁻¹. The prepeak at 1.0 Å⁻¹ in the AsS₂ XRD structure is typical for glassy materials and reflects the intermediate range ordering of coordination polyhedra, as seen in amorphous silica for a network of corner-sharing tetrahedra. The prepeak appears as a shoulder in the ND structure factor of AgAsS₂ and as a threshold in XRD and is reproduced by the calculations. The overall agreement between the measured and calculated curves is very good. The corresponding pair distribution functions (PDF) determined by Fourier transformation are presented as Supplementary Information (Fig. SF1) [39].

Excellent agreement is also found for the amplitude and phase of the As and Ag K-edge EXAFS spectra of a-AsS₂ (Fig. 2) and a-AgAsS₂ (Fig. 3), indicating that the local configurations around Ag and As (and the corresponding bond distances) are described well. These results show that all aspects of the experimental data set are satisfied by our atomic models.

FIG. 2. (Color online) Experimental As K-edge EXAFS spectra of a-AsS₂ (black) compared with DF-RMC refined model (red).

FIG. 3. (Color online) DF-RMC refined model Ag (green, thick line) and As (red line) K-edge EXAFS spectra of a-AgAsS₂ compared with experiment (black lines).
FIG. 4. (Color online) Structures of (a) and (b) α-AgAsS$_2$ and (c) and (d) α-AsS$_2$. The simulation boxes comprise 560 (side 23.1 Å) and 540 atoms (24.1 Å), respectively. (e) Ag atoms and (f) As and S atoms in α-AgAsS$_2$. Ag: gray, As: magenta, S: yellow.

B. Structure: Pair distribution functions, coordination numbers

Two views of the final structures of AsS$_2$ and AgAsS$_2$ are shown in Figs. 4(a)–4(d). Also shown for AgAsS$_2$ are the Ag atoms alone and the As-S network [Figs. 4(e) and 4(f)]. Ag forms stringlike metallic units, and over 90% of the Ag atoms have an Ag neighbor. The connectivity in the As-S network in AgAsS$_2$ differs from that in AsS$_2$ in having terminal sulfur atoms. AgAsS$_2$ has a higher density and is more densely packed than AsS$_2$. The partial PDF $g_{αβ}(r)$ for As-S, As-As, S-S in AsS$_2$ and AgAsS$_2$ are shown in Fig. 5 and for Ag atoms in AgAsS$_2$ (Ag-Ag, Ag-S, Ag-As) in Fig. 6. The first maximum and the first minimum (bond cutoff) of each curve are given in Table I. The Ag-As PDF has a weak shoulder, and the first maximum and minimum could not be assigned.

The local coordination shows many interesting details. In α-AsS$_2$, the As atoms are predominantly (98.8%) threefold coordinated, mainly as As-S$_3$ (81.8 %) and As-AsS$_2$ configurations (16.4 %), while S atoms are almost all twofold coordinated (39.9 % S-AsS, 49.8 % S-As$_2$). The average coordination numbers in AsS$_2$ and AgAsS$_2$ are given in Table II. The situation is more complicated in ternary AgAsS$_2$, where the dominant configurations are given in Table III. Ag atoms favor coordination numbers between 5 and 7 (mainly Ag-Ag$_2$S$_4$, Ag-AgS$_4$, Ag-AgS$_5$, and Ag-Ag$_2$S$_5$), which are significantly

![Table I](image)

![Table II](image)

![Table III](image)

FIG. 5. (Color online) Partial PDF $g_{αβ}(r)$ in α-AsS$_2$ (black line) and α-AgAsS$_2$ (red line). Vertical red bars show interatomic separations in trechmannite (c-AgAsS$_2$, Ref. [14]).
higher than the fourfold coordination found in earlier ND measurements [17]. As atoms are mainly threefold to fourfold coordinated (with As-S$_3$ as the most prominent configuration). The most prevalent environments of S atoms involve threefold to fivefold coordination: S-Ag$_3$As, S-Ag$_2$As$_2$, and S-AgAs$_2$ have almost equal weights, S-Ag$_4$As and S-Ag$_2$As$_2$ are less prominent.

The local atomic order in $\alpha$-AgAs$_2$ can be compared with that in the crystalline forms smithite (24 AgAs$_2$ units in the unit cell) and trechmannite (12 units), which have almost equal weights, S-Ag$_4$As and S-Ag$_2$As$_2$ are less prominent.

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Three such pyramids form an As$_3$S$_6$ ring with $\sim$C$_{1v}$ symmetry, higher than the symmetry of these rings in smithite ($\sim$C$_2v$). The As-S bond lengths inside the ring average 2.305 Å, and the external bonds are 2.233 Å. The structure of trechmannite can then be viewed as layers of As$_3$S$_6$ rings linked by AgS$_4$ tetrahedra. Other bond lengths of interest are: Ag-Ag: 3.656, 4.060, 4.212 Å; As-As: 3.543, 4.048 Å; Ag-As: 3.612, 3.723, 3.825, 3.838 Å; S-S: 3.329, 3.344, 3.440, 3.709, 3.760 Å [14].

All these interatomic separations are shown in Figs. 5 and 6.

Figures 5 and 6 and Table 1 show that short homonuclear bonds that occur in amorphous AgAs$_2$ are absent in the crystal. The weak S-S minimum at 2.06 Å is close to the S-S bond length in amorphous sulfur (2.05–2.06 Å) [40,41] and in small sulfur chains and rings [42]. The second peak in the As-As and Ag-Ag PDFs are in the same range as these atom separations in the crystal, and the S-As distance (2.28 Å) is close to As-S bonds measured in trechmannite [14] as well as in Ge-As$_2$ glasses and the corresponding crystals [43,44].

The sulfur coordination (Table II) is significantly higher in AgAs$_2$ ($\sim$3.6) than in As$_2$S$_3$ (twofold), due to Ag-S bonds and a different As-S network. As$_2$S$_3$ has a significant fraction of S-S bonds, which are almost absent in AgAs$_2$. These bonds are not compensated by covalent As-S bonds and lead to terminal S atoms (48% of all S atoms) in the As-S network [Fig. 4(f)]. The contribution of As-As bonds is small in both alloys, and the effect of Ag content on As coordination is quite subtle. The missing first peak in the As-Ag PDF indicates that bonds between As and Ag are not favored.

TABLE II. The average coordination number $N_{\alpha\beta}$ in $\alpha$-AgAs$_2$ and $\alpha$-As$_2$S$_3$ at 300 K. Cutoff distances as in Table 1.

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(N_{\alpha S})</th>
<th>(N_{\alpha S})</th>
<th>(N_{\alpha Ag})</th>
<th>(N_{\alpha \text{tot}})</th>
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</thead>
<tbody>
<tr>
<td>AgAs$_2$</td>
<td>As</td>
<td>0.12</td>
<td>2.95</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>1.48</td>
<td>0.06</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>0.17</td>
<td>4.14</td>
<td>1.81</td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>As</td>
<td>0.18</td>
<td>2.85</td>
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<tr>
<td></td>
<td>S</td>
<td>1.42</td>
<td>0.59</td>
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</table>

C. Angular distributions

The angular distributions of Ag-S and As-S bonds at 300 K are shown in Fig. 7 (DF/MD simulations). The broad distributions for Ag reflect metallic binding [Fig. 7(a)], and there is a maximum at 60° for Ag-Ag-Ag configurations corresponding to triangular clusters. The S-Ag-S distribution peaks at a relatively small angle (70°), whereas the Ag-S-Ag distribution has a maximum at 90° and less weight at smaller values.

The bond angles in the As-S network [Fig. 7(b)] differ little in As$_2$S$_3$ and AgAs$_2$. The angles around sulfur peak below 100°, whereas the S-As-S angles have maxima above 100° and more weight at larger values up to 135°. Both distributions indicate pyramidal configurations, and we note that stoichiometric c-As$_2$S$_3$ has bond angles near 99° for both elements. The coordination of As and S is less than four, which means that there is no contribution from tetrahedral configurations (109.47°). For As$_2$S$_3$, there is a small peak at 90° in S-As-S corresponding to configurations with nearly octahedral (cubic) bond angles. Despite the numerous S-S bonds there are few signs of triangular configurations (60°) in the As-S network.

D. Cavity distributions

The presence of cavities (vacancies, voids) and their distribution have significant effects on the properties of materials and have not yet been discussed in As$_2$S$_3$ and AgAs$_2$. We show the corresponding distributions in Fig. 8, calculated using a cutoff of 2.5 Å and the Voronoi construction [36]. As$_2$S$_3$ has a
TABLE III. Percentage of atoms of element $\alpha$ with coordination number $N_\alpha$, and dominant configurations in $\alpha$-AgAsS$_2$ at 300 K (DF/MD simulations, values under 1% are excluded). Bond cutoffs as in Table I. Boldface: total coordination number.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<th>9</th>
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<tr>
<td>As</td>
<td>81.2</td>
<td>17.8</td>
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<tr>
<td></td>
<td>S$_2$: 73.4</td>
<td>AgS$_3$: 11.9</td>
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<tr>
<td></td>
<td>As$_2$: 7.7</td>
<td>S$_2$: 3.1</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>6.0</td>
<td>28.3</td>
<td></td>
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<tr>
<td></td>
<td>As$_2$: 4.1</td>
<td>AgAs$_2$: 18.7</td>
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<tr>
<td></td>
<td>AsS$_2$: 8.7</td>
<td>Ag$_3$As$_2$: 18.9</td>
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<tr>
<td>Ag</td>
<td>1.0</td>
<td>40.8</td>
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<tr>
<td></td>
<td>Ag$_3$: 9.7</td>
<td>Ag$_4$: 46.4</td>
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<tr>
<td></td>
<td>S$_3$: 5.3</td>
<td>Ag$_5$: 8.0</td>
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<td></td>
<td>AgS$_4$: 2.8</td>
<td>Ag$_4$: 8.0</td>
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<td></td>
<td>As$_2$: 5.3</td>
<td>Ag$_5$: 1.0</td>
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much lower density and a much larger cavity volume (37.8 %) than AgAsS$_2$ (4.8%) and is clearly porous at the atomistic level. The cavity volume of $\alpha$-SiO$_2$ was 31.9% with the same parameter set [45].

The trechmaninite structure may be viewed as a defective PbS (galena) structure. The defects are vacancies: one on an Ag site surrounded by six S atoms, the second an S site surrounded by six As atoms. To test whether this effect occurs in the amorphous state, we have calculated partial PDF involving cavity centers, and they are shown in the Supplementary Information (Fig. SF4) [39], together with the corresponding coordination numbers (Table S1). All atom types have comparable PDF weights near the cavities, but the cavity-S coordination number is highest (2.4). The overall

![Figure 7](image)

**FIG. 7.** (Color online) Angular distributions in AsS$_2$ (bin.) and AgAsS$_2$. The dashed lines denote the values $60^\circ$, $90^\circ$, and $109.47^\circ$ (tetrahedral).

![Figure 8](image)

**FIG. 8.** (Color online) Cavities (red) in DF-RMC optimized structures of (a) $\alpha$-AsS$_2$, (b) $\alpha$-AgAsS$_2$. Yellow: S, purple: As, silver: Ag.
cavity coordination is close to sixfold as in trechmannite, but the nearest neighbors are mixed in $a$-$AgAsS_2$. In spite of the relatively high Ag concentration, many Ag cations (~40%) are adjacent to cavities, which would increase their mobility in the As/S matrix. The small cavity-cavity coordination number (<0.2) demonstrates the absence of multicavities, as opposed to the situation in $AsS_2$.

E. Dynamical properties

The high mobility of Ag in semiconducting materials is of particular technological interest, and analysis of the present MD trajectories gave the following values of the self-diffusion coefficient of Ag: 3.71 (at 600 K), 2.87 (500 K), 2.02 (450 K), and 1.31 (400 K), in units of $10^{-6}$ cm$^2$/s. These values are an order of magnitude higher than those in As and S. At 600 K, for example, we find 0.31 (As) and 0.45 (S), in the same units. As and S atoms are almost immobile at lower temperatures, while Ag atoms continue to diffuse.

The Raman and infrared active vibrational modes in crystalline $AgAsS_2$ have been studied by Slivka et al. [46]. There are numerous modes of each type in the range 20–400 cm$^{-1}$, and there are distinctive lines between 260 and 400 cm$^{-1}$ that are strong in Raman and fairly clear in the IR spectra. The frequencies of Raman active modes have been measured in $a$-$AsS_2$ and $a$-$AgAsS_2$ [8,10,47]. Adding Ag to AsS$_2$ leads to a new feature (~375 cm$^{-1}$) above the main feature in As$_2$S$_2$ (350 cm$^{-1}$). Infrared absorption and reflection spectra show transverse optical modes at 164 and 310 cm$^{-1}$ [48].

The calculated power spectra (vibrational densities of states, vDOS) and their projections onto the elements at 300 K are shown for $a$-$AsS_2$ and $a$-$AgAsS_2$ in Fig. 10, together with projections onto elements. All curves have the same maximum.

The calculated power spectra (vibrational densities of states, vDOS) of $AsS_2$ and $AgAsS_2$ at 300 K with projections onto elements. All curves have the same maximum.

FIG. 9. Computed vibrational density of states of amorphous $AsS_2$ and $AgAsS_2$ at 300 K with projections onto elements. All curves have the same maximum.

F. Electronic structure, density of states

The calculated electronic densities of states (DOS) of $AsS_2$ and $AgAsS_2$ are shown in Fig. 10, together with projections onto $s$-, $p$-, and $d$-atomic functions. The band gap in $AsS_2$ is 1.3 eV. There appear to be no crystalline forms of $AsS_2$, but the optical band gap in crystalline $AsS_2$ (orpiment) is 2.6 eV [49]. The calculated band gap in $a$-$AgAsS_2$ (1.0 eV) can be compared with the measured band gaps in the amorphous (1.95 eV) and crystalline (smithite, 2.1 eV) phases [50]. Density functional calculations with the PBEsol approximation commonly lead to gaps in the spectrum of Kohn-Sham eigenvalues that are less than measured optical band gaps. The superposition of x-ray spectra (fluorescent K bands and $\ell_{23}$ emission bands of S) on a common energy scale [19,51] provide information about the density of states in $c$-$AgAsS_2$ (smithite). There are prominent peaks at ~13 eV (S) and ~4.1 eV (Ag) that are also present in our results. Furthermore, the K-band spectra of amorphous and crystalline $AgAsS_2$ are very similar [19]. The origin of the peaks has been determined by electronic structure calculations [52] on clusters with the bulk crystalline (smithite) structure [51].

The differences in DOS between the two samples can readily be interpreted. The prominent peak at ~4 eV arises from the 4$d$ shell in Ag, while the more structured and narrower lower valence bands in $AgAsS_2$ are consistent with the reduced number of homopolar bonds ($s$-$s$ overlap). This effect has been found previously in $c$- and $a$-$Ge_2Sb_2Te_5$ [36]. The effective charges in $AgAsS_2$, evaluated using the Bader approach [53], are $Ag$: +0.37e, $As$: +0.12e, and $S$: −0.24e. The S charges are distributed in two “bands” around −0.10e and −0.35e, where the latter corresponds to terminal S atoms. The values for $AsS_2$, where there are no such atoms, are +0.10e (As) and −0.05e (S). The presence of the Ag cation causes a charge transfer to S as the covalent As-S network breaks up. The ionic character of Ag-S bonding is confirmed by the computed chemical bond orders (bond strengths), which lie in the range 0.2–0.5, while the covalent As-S bonds have values above unity (the value for
a single covalent bond). The terminal S atoms in AgAsS$_2$ are evident with higher values ($>1$) in the As-S bond orders. Plots of bond orders are given in the Supplementary Information (Figs. SF2 and SF3) [39].

IV. DISCUSSION AND CONCLUDING REMARKS

The combination of MD/DF simulations and experimental measurements using RMC refinement incorporates the electronic structure into structure determination. It has been applied successfully to amorphous Ge$_2$Sb$_2$Te$_5$ [21], Ag$_{1.5}$In$_{3.5}$Sb$_{75.7}$Te$_{17.7}$ [22], and Ga$_{1.1}$Ge$_{1}$Te$_{78}$ alloys [23], and has been used here to study amorphous As$_2$S$_2$ and AgAsS$_2$. The resulting models (540 atoms in As$_2$S$_2$, 560 atoms in AgAsS$_2$) are unusually large for combined DF/MD simulations, in order to reduce the effects of periodic boundary conditions and enable local density fluctuations. The models satisfy all criteria for agreement between theory and experiment (structure factors, EXAFS signals, DF energy, band gap) extremely well, and the calculated power spectra are in reasonable agreement with optical absorption and Raman spectra. The calculated self-diffusion constants show that Ag ions are much more mobile than As and S ions.

The As-S network and the cavities are crucial aspects to understand the atomic structure of As$_2$S$_2$ and AgAsS$_2$. As$_2$S$_2$ shows ideal twofold coordination for S and threefold coordination for As, with numerous S-S bonds (0.6). The As-S network differs in AgAsS$_2$; there are almost no S-S bonds, terminal S atoms coordinate with Ag, and the average coordination of S (3.6) is much larger. Furthermore, the abundant cavities in As$_2$S$_2$ (38%) are natural locations for Ag cations, and most are occupied by Ag in AgAsS$_2$. The calculated electronic DOS and the effective atomic charges support this picture.

The results suggest two main reasons for the high mobility of Ag$^+$ (and Cu$^+$) cations in solid state electrolytes: Cavities can act as trapping sites in the host material [24,25] and provide space for mobility, and cations can alter locally the bonding in the host. In the context of ECM/CBRAM materials, Ag$^+$ (Cu$^+$) can both move through the cavities in the host electrolyte and break covalent bonds in the material. We are extending the present calculations to quantify the role of Ag$^{+}$ in the electrical conductivity of Ag-doped semiconductors.

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[39] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.89.064202 for figures of (a) pair distribution functions and bond orders in AsS2 and AgAsS2, (b) partial PDF for cavities in AgAsS2, and (c) a table of cavity coordination numbers.


