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Origin of structural analogies and differences between the atomic structures of GeSe₄ and GeS₄ glasses: A first principles study

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First-principles molecular dynamics simulations based on density functional theory are employed for a comparative study of structural and bonding properties of two stoichiometrically identical chalcogenide glasses, GeSe₄ and GeS₄. Two periodic cells of 120 and 480 atoms are adopted. Both glasses feature a coexistence of Ge-centered tetrahedra and Se(S) homopolar connections. Results obtained for N = 480 indicate substantial differences at the level of the Se(S) environment, since Ge–Se–Se connections are more frequent than the corresponding Ge–S–S ones. The presence of a more prominent first sharp diffraction peak in the total neutron structure factor of glassy GeS₄ is rationalized in terms of a higher number of large size rings, accounting for extended Ge–Se correlations. Both the electronic density of states and appropriate electronic localization tools provide evidence of a higher ionic character of Ge–S bonds when compared to Ge–Se bonds. An interesting byproduct of these investigations is the occurrence of discernible size effects that affect structural motifs involving next nearest neighbor distances, when 120 or 480 atoms are used. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4926830>]

I. INTRODUCTION

Within the family of Ge_xX_{1-x} (X = S, Se) chalcogenide glasses, two specific compositions, $x = 0.33$ and $x = 0.2$, are representative of the atomic network structures for small values of x ($x \leq 0.33$). The network at $x = 0.33$ can be viewed as a highly chemically ordered one, with the large predominance of the tetrahedral fourfold Ge coordination.¹ For $x = 0.2$ instead, one expects chalcogenide X_n chains and a negligible number of Ge–Ge homopolar bonds, since the Ge atoms are accommodated in interconnected GeX₄ tetrahedra.²⁻⁴ To go beyond this generic picture, a wealth of experimental results have become available for glassy GeSe₂ (*g*-GeSe₂) and GeSe₄ (*g*-GeSe₄).^{1,5-10} The structure of these glasses is far from trivial, calling for the kind of quantitative understanding provided by first-principles molecular dynamics (FPMD) approaches based on density functional theory (DFT).

Taken together, experiments and theory concur to show that in glassy *g*-GeSe₂, a sizable departure from chemical order occurs.^{1,11-14} Both edge-sharing (ES) and corner-sharing (CS) connections are present, coexisting with miscoordinations (Ge not fourfold connected and Se not twofold connected) as well as Ge–Ge and Se–Se homopolar bonds. The topology of glassy *g*-GeSe₄ differs drastically from the one of glassy *g*-GeSe₂. Here, the network structure lies in between two opposite models, both compatible with a chemically ordered AB₄ network (where A and B are two different chemical species). In the first, Ge atoms are connected to one Se dimer in Ge–Se–Se triads (AB configurations). Alternatively, one can find AA, BB configurations corresponding to Ge–Se–Ge, Se–Se–Se triads, respectively. When all Se atoms are in AB motifs, BB and AA configurations are absent since no Se atoms are left available to form chains longer than Se₂

or to link two Ge atoms as nearest neighbors. On the contrary, when no AB connections exist, there is a phase separation between two coexisting domains having as compositions GeSe₂ and Se_n, leading to an equal amount of AA and BB units.¹⁵ Nowadays, there is a consensus on the existence of all three kinds of Se coordination units (Ge–Se–Se, Ge–Se–Ge, and Se–Se–Se), this conclusion being consistent with both nuclear magnetic resonance (NMR) data,¹⁶ FPMD calculations,¹⁷ and first principles analyses of NMR chemical shifts.¹⁸

It is of interest to establish whether or not the above arguments on the topologies of *g*-GeSe₂ and *g*-GeSe₄ can be applied to the case of *g*-GeS₂ and *g*-GeS₄. For the $x = 0.33$ case, the picture emerging from experiments and FPMD results point towards a short range order quite similar in glassy *g*-GeSe₂ and *g*-GeS₂.¹⁹⁻²¹ However, there are more edge-sharing connections and a higher ionic character for glassy *g*-GeS₂. This is consistent with the smaller number of homopolar bonds. Much less is known for *g*-GeS₄, for which FPMD data are unavailable so far. On the experimental side, there is a striking difference between *g*-GeS₄ and *g*-GeSe₄ in the low wavevector region ($k \approx 1 \text{ \AA}^{-1}$) of the total neutron structure factor (Fig. 1). As an indication of two distinct amounts of intermediate range order, the first sharp diffraction peak (FSDP) is prominent in one case (*g*-GeS₄) and much smaller in the other (*g*-GeSe₄).

To understand the microscopic origins of these behaviors and allow for a comparative analysis between *g*-GeSe₄ and *g*-GeS₄, we focus in this work on the atomic structure of glassy *g*-GeS₄. For the sake of consistency, new first-principles molecular dynamics data are produced also for glassy *g*-GeSe₄, by using two simulation cells with N = 120 and N = 480. It is worth pointing out that the availability of atomic models with two different sizes will provide hints on the sensitivity of

FIG. 1. Average mean-square displacements for Ge ($T = 900$ K black line, $T = 300$ K green line) and Se atoms ($T = 900$ K red line, $T = 300$ K blue line) of g -GeSe₄ with $N = 120$. Dashed lines correspond to linear regressions.

structural features to the dimensions of the periodic simulation box.

This paper is organized as follows. Section II is devoted to our theoretical model, organized in subsections providing details both on the generalities of our modelling framework and on the procedures employed to produce configurations for g -GeS₄ and g -GeSe₄ at $N = 120$ and $N = 480$. Results (Sec. III) are presented by beginning with the total neutron structure factors and the total pair correlation functions. Then, we move to the partial structure factors (reciprocal space) and to the partial pair correlation functions (real space). Through the identification of the main structural units, we are able to produce coordination numbers. In addition to the chain analysis, a ring analysis is carried out to establish a relationship between structural correlations in real space and the intensity of the first sharp diffraction peak in the total and in the partial neutron structure factors. On the side of the electronic properties, we discuss the electronic density of states (EDOSs) and the nature of the localized Wannier functions and centers. This allows to compare the bonding properties of the two glassy systems in terms of relative ionicity. Conclusions are collected in Sec. IV.

II. THEORETICAL MODEL

A. General framework

Our calculations are based on the FPMD Car-Parrinello²² molecular dynamics (CPMD) approach, as implemented in the CPMD code.²³ Within this framework, we employed models of g -GeS₄ and g -GeSe₄ made of $N = 480$ (96 Ge + 384 S/Se) and $N = 120$ (24 Ge and 96 S/Se) atoms. Recently, a study of size effects was carried out for liquid GeSe₂ ($N = 120$ and $N = 480$), by concluding that most structural properties do not change significantly when moving from $N = 120$ to $N = 480$.²⁴ This study is worth pursuing for glassy systems, since the statistical accuracies of the results are dissimilar when comparing averaged properties in the liquid and in the glass. To this purpose, we make available here data for $N = 120$ and $N = 480$.

For the four models under investigation, the system sizes allow to cover k values significantly smaller than the position of the FSDP, $k_{\text{FSDP}} \approx 1 \text{ \AA}^{-1}$.²⁵ FPMD was employed in conjunction with the Generalized Gradient Approximation (GGA) due to Becke (B) for the exchange energy and Lee, Yang, and Parr (LYP) for the correlation energy.^{26,27} The valence-core interaction is described by norm-conserving pseudopotential according to the prescription of Troullier and Martins.²⁸ The wave functions were expanded at the Γ point of the supercell on a plane wave basis set with an energy cutoff $E_c = 30$ Ry for g -GeS₄ and $E_c = 20$ Ry for g -GeSe₄. A fictitious electron mass of 1000 a.u. (i.e., in units of $m_e a_0^2$, where m_e is the electron mass and a_0 is the Bohr radius) was used throughout. Time steps ranging in between $\Delta t = 0.12$ fs and $\Delta t = 0.24$ fs were adopted to integrate the equations of motion. Temperature control was implemented for both the ionic and electronic degrees of freedom by using Nosé-Hoover thermostats.^{29–31}

As a general feature, all densities were calibrated by suitable variations of the volume at values close to 0 GPa. This is detailed below, together with a description of the quenching schedules used to produce a glass from the liquid.

B. Glassy GeS₄

For the largest system, $N = 480$, we used a periodically repeated cubic cell of $23.52 \text{ \AA}$ corresponding to the experimental density, ρ_0 , equal to $0.0317 \text{ atoms \AA}^{-3}$.^{6,32}

The initial coordinates were obtained by a configuration extracted from the fully equilibrated trajectories produced for g -GeS₂.¹⁹ To achieve the correct composition, the number of S atoms was changed to 384 by modifying the chemical identity of 96 randomly chosen Ge atoms. We produced a single trajectory for $N = 480$ in the NVT ensemble, by following a well documented setup having an extended record of reliability.^{19,33–37} Accordingly, to lose the memory of the initial configuration, the system was randomized at 2000 K during ≈ 25 ps and then quenched by steps of 500 K, lasting 10 ps each, the last step bringing the system from $T = 500$ K to $T = 300$ K. At this temperature, the value of the pressure associated with ρ_0 was non-negligible (1 GPa). By expanding the box size to $24.82 \text{ \AA}$ ($\rho_0^{\text{new}} = 0.0314 \text{ \AA}^{-3}$) and further relaxing the whole structure, we were able to lower the pressure to less than 0.1 GPa.

In the $N = 120$ case, the initial configuration was created by first selecting one configuration of liquid g -GeSe₄ and then by changing the chemical identity of the Se atoms to S. As a choice for the density, we took the one corresponding to ~ 0 pressure for $N = 480$ ($\rho_0^{\text{new}} = 0.0313 \text{ \AA}^{-3}$, see above). The thermal cycle reads as follows: 16 ps at 100 K, 10 ps at 300 K, 12 ps at 600 K, 33 ps at 900 K, 17 ps at 600 K, and 22 ps at 300 K.

C. Glassy GeSe₄

For $N = 120$, we carried out the calculations in the isothermal-isobaric (NPT) ensemble, by keeping fixed the shape of the simulation cell that adjusts to the imposed pressure in an isotropic manner. This was done by using the variable size version of the Parrinello-Rahman technique implemented

in the framework of CPMD.^{38–42} Working in the NPT ensemble was motivated by a recent study on *g*-GeSe₂, where residual pressures (non-negligible at the imposed experimental density) were found to affect the description of the structural properties.⁴³ Such investigation was a prerequisite to the study of glassy *g*-GeSe₂ under pressure, ultimately unraveling a density driven mechanism for a structural transformation of the network.³⁷ Within that investigation, only the size $N = 120$ was selected, due to the computational burden of considering a large set of different reduced densities and pressures. The availability of previous calculations³⁵ allowed us to start from a configuration representative of the amorphous state. After releasing the residual pressure at $T = 0$ K, with a new density found to be equal to $\rho_0^{new} = 0.0312 \text{ \AA}^{-3}$ and box size = 15.66 Å (initial values $\rho_0 = 0.0337 \text{ atom \AA}^{-3}$, box size 15.27 Å),³⁵ the model generated undertook a thermal cycle in the NPT ensemble. We allowed for isotropic variation of the cell dimensions by performing a thermal cycle encompassing two sets of trajectories. The first is devoted to heating (16 ps at 100 K, 14 ps at 400 K, 10 ps at 600 K, and 38 ps at 900 K) and the second one to cooling, followed by equilibration and annealing at room temperature (26 ps at 600 K and 81 ps at 300 K). Overall, the results presented hereafter for *g*-GeSe₄ are averaged over 60 ps. For $N = 480$, we changed the chemical identities of a glassy GeSe₂ model to make our system compatible with the new composition and we proceeded as in the case of glassy *g*-GeS₄, by using the same schedule for the thermal cycle. This allowed to lose memory of the initial configuration and produce a statistically meaningful trajectory. The density of the system was taken to be the one that corresponds to zero pressure in the $N = 120$ case ($\rho_0^{new} = 0.0312 \text{ \AA}^{-3}$).

D. Identification of the glassy state

For the four systems under investigation, one can invoke the notion of topologies configurationally arrested to characterize the dynamical behavior at $T = 300$ K. This concept is exemplified in Fig. 1 where we compare (case of *g*-GeSe₄, $N = 120$) the mean square displacements of Ge and Se calculated at $T = 900$ K (in the supercooled liquid regime) and at $T = 300$ K. The lack of any discernible diffusive behavior is particularly striking at $T = 300$ K, providing unambiguous evidence on the attainment of a glassy regime devoid of any detectable atomic mobility, at least on the time scale of our atomic-scale simulation approach.

E. Electronic structure localized tools

Analysis of the detailed electronic structure is performed in terms of the maximally localized Wannier functions.^{44,45} Following the standard procedure, the Wannier functions and the corresponding centers are obtained as unitary transformation *on the fly* of the Kohn-Sham orbitals $\psi_i(\mathbf{r})$. Specifically, among all the possible unitary transformations, we select the one that minimizes the spread (spatial extension) of the resulting Wannier orbitals $w_n(\mathbf{r})$,

$$\Omega = \sum_n \left(\langle w_n | \mathbf{r}^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2 \right). \quad (1)$$

This leads to an iterative scheme for computing the orbital transformation,

$$w_n(\mathbf{r}) = \sum_i \left[\prod_p \exp(-A_{i,n}^p) \cdot \psi_i(\mathbf{r}) \right], \quad (2)$$

where $A_{i,n}^p$ is a matrix generalization of the Berry phase connector, i is the wave vector, and p is the order of the iteration as specified in Ref. 45. The Wannier states provide in this way an unbiased method for partitioning the charge density and the electronic information then becomes contracted into four numbers, and the center of the orbital is then defined by

$$x_n = -\frac{L}{2\pi} \Im m \log \langle w_n | \exp(-i2\pi \cdot x/L) | w_n \rangle \quad (3)$$

with similar expressions along the other two cartesian directions and its related spread. Here, L is the length of the simulation cell along the x direction. The analysis of the Wannier function centers with respect to the nuclear positions allows gaining insight into the chemical bonding involved in a wealth of systems such as water,^{46,47} amorphous silicon,⁴⁸ oxides,⁴⁹ and complex electronic structure evolutions involving formation and breaking of chemical bonds.⁵⁰ This analysis has been also extended to several disordered chalcogenides.^{19,34}

III. RESULTS

A. Neutron total structure factor and total pair correlation function

The total neutron structure factor $S_T(k)$ is defined by

$$S_T(k) = \sum_{\alpha=1}^2 \sum_{\beta=1}^2 c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} \left[S_{\alpha\beta}^{FZ}(k) - 1 \right], \quad (4)$$

where α and β denote one of the two chemical species, respectively. c_{α} and b_{α} are the atomic fractions and coherent neutron scattering lengths of Ge, Se, or S, and $S_{\alpha\beta}^{FZ}(k)$ is a Faber-Ziman (FZ) partial structure factor.⁵¹ The coherent neutron scattering lengths, b_{α} , for Ge, Se, and S of natural isotopic abundance are equal to 8.185, 7.97, and 2.847 fm, respectively.⁵²

The corresponding real space information is given by the total pair correlation function,

$$\begin{aligned} g_T(r) - 1 &= \frac{1}{2\pi^2 n_0 r} \int_0^{\infty} dk k [S_T(k) - 1] \sin(kr) \\ &= \sum_{\alpha=1}^n \sum_{\beta=1}^n \frac{c_{\alpha} c_{\beta} b_{\alpha} b_{\beta}}{\langle b \rangle^2} [g_{\alpha\beta}(r) - 1], \end{aligned} \quad (5)$$

where n_0 is the atomic number density and $g_{\alpha\beta}(r)$ is a partial pair correlation function.

In Fig. 2, the calculated total neutron structure factors $S_T(k)$ are given for *g*-GeS₄ and *g*-GeSe₄ along with their experimental counterparts. The data are Fourier transformed from direct space through the calculation of the corresponding total pair correlation functions. The different intensities in the FSDP are indicative of dissimilar intermediate range order properties. We shall address this issue in more detail when describing the real space properties in Sec. III C. The improvement arising from the use of a larger model is particularly noticeable in

FIG. 2. Fourier transformed total neutron structure factors at 300 K for g -GeSe₄ (shifted upwards by +1.5) and g -GeS₄. For both systems, $N = 120$ atoms (green line), $N = 480$ atoms (blue line). Experimental measurements (solid black line with circles) for g -GeSe₄ from Refs. 5 and 6 and g -GeS₄ from Ref. 32.

the case of g -GeS₄. The sets of data relative to $N = 120$ and $N = 480$ sets of results differ between the peaks located at $k \sim 1 \text{ Å}^{-1}$ and $k \sim 4 \text{ Å}^{-1}$, the oscillations found for $N = 120$ being replaced by a largely steady profile. For g -GeSe₄, a spurious peak appears clearly at $k \approx 0.5 \text{ Å}^{-1}$, that is at the left of the FSDP region, located around $k \approx 1 \text{ Å}^{-1}$. The position of this peak bears no physical meaning, as being related to an artifact stemming from the Fourier transformation and/or to some persistent and yet not significant long range correlation.

Turning to the results in direct space, the calculated total pair correlation functions $g_T(r)$ are shown for g -GeSe₄ and g -GeS₄ in Fig. 3 along with the corresponding diffraction data. Experimental data were obtained by Fourier transforming the total neutron structure factors and using upper limits of integration $l_{int}(g\text{-GeSe}_4) = 19.95 \text{ Å}^{-1}$ for g -GeSe₄ and $l_{int}(g\text{-GeS}_4) = 49.95 \text{ Å}^{-1}$ for g -GeS₄.^{5,32} These limits result

FIG. 3. Total pair correlation functions at 300 K for g -GeSe₄ and g -GeS₄ (shifted upwards by +10). These quantities have been obtained by Fourier transform from reciprocal space by taking the experimental upper limits. For both systems, $N = 120$ (solid green line with circles), $N = 480$ (solid blue line) compared to the experimental measurements for g -GeSe₄ from Ref. 32 (black broken line) and g -GeS₄ from Refs. 5 and 6 (black broken line). In the case of $N = 480$, we also report the results obtained by direct calculation in real space (magenta lines).

from the finite measurement window function of the diffractometer and lead to oscillations at r less than $\sim 2 \text{ Å}$.

For the case of $N = 480$ and for both glasses, our results are obtained both by direct calculation of the total pair correlation function and by Fourier integration of the reciprocal space data. This has been done by adopting the experimental upper limits $l_{int}(g\text{-GeSe}_4)$ and $l_{int}(g\text{-GeS}_4)$. Focussing on g -GeSe₄, the best agreement for the intensity of the main peak is obtained when the experimental upper limit is used for the Fourier integration, namely, $l_{int}(g\text{-GeSe}_4) = 19.95 \text{ Å}^{-1}$. On the contrary, in the case of g -GeS₄, for which the upper limit of integration is much higher, ($l_{int}(g\text{-GeS}_4) = 49.95 \text{ Å}^{-1}$), the pair correlation function is quite insensitive to the procedure of calculations. A similar rationale was developed when comparing the results obtained for the total pair correlation functions of g -GeSe₄ and g -SiSe₄.³⁵ Overall, theory compares rather well to experiments, the differences being limited to the large bump found for $3 < r < 5 \text{ Å}$ in g -GeS₄. This feature is shifted at higher values, as shown by its maximum located at 3.59 Å , to be compared with the experimental data, 3.39 Å . In these glasses, the basic building blocks are the Ge-X₄ ($X = \text{S, Se}$) tetrahedra, the first peak in $g_T(r)$ being a signature of the intra-tetrahedra Ge-X ($X = \text{S, Se}$) bonds, while the second peak corresponds to the inter-tetrahedra interatomic distances.

B. Reciprocal space properties

1. Faber-Ziman partial structure factors

The calculated FZ partial structure factors of g -GeSe₄ and g -GeS₄ are shown in Fig. 4. For g -GeSe₄, the changes associated with the larger system size are limited to the intensities of the first peak and to the amplitude of the oscillations contributing to the third peak in $S_{\text{GeGe}}^{\text{FZ}}(k)$. In the g -GeS₄ case, it appears that for $N = 480$, the height of the FSDP intensities is reduced in the Ge-Ge partial structure factor, such feature taking a split pattern, mostly ascribed to statistical noise. The same reason can be invoked to rationalize the presence of the spurious peak at $k \approx 0.5 \text{ Å}^{-1}$ (observed in the total neutron structure factor) for which no sign is found in either $S_{\text{GeX}}^{\text{FZ}}(k)$ or $S_{\text{SeSe}}^{\text{FZ}}(k)$ of g -GeSe₄.

In both g -GeSe₄ and g -GeS₄, the intermediate range order (to be associated to features around $k \approx 1 \text{ Å}^{-1}$) is due to the Ge-Ge and Ge-Se (or Ge-S) correlations since no deviations from the baseline profiles of $S_{\text{XX}}^{\text{FZ}}(k)$ ($X = \text{Se, S}$) are found in the FSDP region. The higher intensity of the FSDP in g -GeS₄ when compared to g -GeSe₄, observed for the total neutron structure factor, corresponds to a more intense peak in $S_{\text{GeSe}}^{\text{FZ}}(k)$ (central panels, Fig. 4). This provides indirect evidence of the existence of Ge-Se correlations at distances typical of intermediate range order. We anticipate that a ring analysis will confirm this conjecture (Sec. III C 3).

C. Real space properties

1. Pair correlation functions

In Fig. 5, we display the calculated partial pair correlation functions $g_{\alpha\beta}(r)$ for g -GeS₄ and g -GeSe₄. For $N = 480$, the partial pair correlation functions $g_{\text{GeGe}}^{\text{GeS}_4}(r)$ and $g_{\text{GeGe}}^{\text{GeSe}_4}(r)$ exhibit

FIG. 4. The Faber-Ziman partial structure factors $S^{\text{FZ}}_{\text{GeGe}}(k)$ (top panel), $S^{\text{FZ}}_{\text{GeX}}(k)$ (middle panel), and $S^{\text{FZ}}_{\text{XX}}(k)$ (bottom panel) ($X = \text{Se}, \text{S}$). From left to right: $g\text{-GeSe}_4$ and $g\text{-GeS}_4$ models. $N = 120$ atoms (solid green line), $N = 480$ (solid blue line).

a first small peak at $r \approx 2.45$ Å, signature of the presence of homopolar Ge–Ge bonds. Such feature is absent in both systems for $N = 120$. At larger distances, the pair correlation functions have in common the peaks representative of ES and CS tetrahedra, located at $r \approx 2.9$ Å, $r \approx 3.6$ Å ($g^{\text{GeSe}_4}_{\text{GeGe}}(r)$) and $r \approx 3.0$ Å, $r \approx 3.72$ Å ($g^{\text{GeSe}_4}_{\text{GeGe}}(r)$), respectively. However, the height of the CS-related peak behaves differently when moving from $N = 120$ to $N = 480$, with a sharp increase in the $g\text{-GeS}_4$ case and a sharp decrease in the $g\text{-GeSe}_4$ case. The impact of a larger size on the pattern taken by $g^{\text{GeS}_4}_{\text{GeGe}}(r)$ and $g^{\text{GeSe}_4}_{\text{GeGe}}(r)$ is striking for $r > 5$ Å. Thus, in $g\text{-GeSe}_4$, a clear maximum appears around 6–6.5 Å for $N = 480$, in contrast with the oscillating profile where several maxima and minima are clearly discernible for $N = 120$. This is an unambiguous size effect to which the minority species (Ge) is particularly sensitive.

The partial correlation functions $g_{\text{GeS}}(r)$ and $g_{\text{GeSe}}(r)$ are very similar, differing only in the position of the first peak (2.22 Å–2.23 Å as a signature of the Ge–S bonds and 2.36 Å–2.37 Å as a signature of the Ge–Se bonds). These observations are consistent with the predominance of Ge-centered tetrahedral motif in these systems. Similarly, the first peaks at $r \approx 2.11$ Å–2.12 Å in g_{SS} and $r \approx 2.37$ Å–2.38 Å in g_{SeSe} are indicative of the presence of homopolar Se–Se and S–S bonds being part of chains. For $r > 3$ Å, g_{SS} and g_{SeSe} behave identically indicating a very similar short range Se/S sub-networks.

FIG. 5. Partial pair correlation functions $g_{\text{GeGe}}(r)$, $g_{\text{GeX}}(r)$ (shifted upward by +8.0) and $g_{\text{XX}}(r)$ ($X = \text{S}$ or Se) (shifted upward by +3.0) for $g\text{-GeSe}_4$ (top panel) and $g\text{-GeS}_4$ (bottom panel). We show both results for $N = 120$ (green line) and $N = 480$ (blue broken line).

The peaks at $r \approx 3.63$ Å in $g\text{-GeS}_4$ and at $r \approx 3.85$ Å–3.87 Å in the $g\text{-GeSe}_4$ glasses are the signatures of the intra-tetrahedral X–X ($X = \text{S}, \text{Se}$) connections.

2. Coordination numbers and structural units

The coordination numbers $\bar{n}_{\alpha\beta}$ are listed in Table I. These are defined as the mean number of nearest neighbors of type β located around an atom of type α . As an integration range, we have taken the first minimum of the total pair correlation function. The total coordination numbers for Ge and X (Se or S) are given by $\bar{n}_{\text{Ge}} = \bar{n}_{\text{GeGe}} + \bar{n}_{\text{GeX}}$ and $\bar{n}_{\text{X}} = \bar{n}_{\text{XX}} + \bar{n}_{\text{XGe}}$, respectively, where $\bar{n}_{\text{XGe}}/c_{\text{Ge}} = \bar{n}_{\text{GeX}}/c_{\text{X}}$. The average coordination number irrespective of the type of chemical species is given by the expression $\bar{n} = c_{\text{Ge}}(\bar{n}_{\text{GeGe}} + \bar{n}_{\text{GeX}}) + c_{\text{X}}(\bar{n}_{\text{XX}} + \bar{n}_{\text{XGe}})$.

The coordination numbers are consistent with networks made of high proportions of tetrahedra, the only noticeable deviation from this arrangement being the n_{GeGe} value (0.36) for $g\text{-GeSe}_4$, $N = 480$. The vanishing value of n_{GeGe} in $g\text{-GeS}_4$, $N = 480$ (0.03), together with the absence of such nearest-neighbor Ge–Ge contacts in the $N = 120$ models suggests two considerations. First, $g\text{-GeS}_4$ is more chemically ordered than $g\text{-GeSe}_4$. Second, the occurrence of homopolar bonds in the

TABLE I. The first peak position (FPP), second peak position (SPP) in $g_{\alpha\beta}(r)$ and nearest neighbor coordination numbers $\bar{n}_{\alpha\beta}$ calculated for g -GeS₄ and g -GeSe₄. The coordination numbers $\bar{n}_{\alpha\beta}$ were obtained by integrating the corresponding partial pair correlation ($g_{\alpha\beta}(r)$) functions for the GeX₄ models up to their first minimum.

$g_{\alpha\beta}(r)$	Model	FPP (Å)	SPP (Å)	$\bar{n}_{\alpha\beta}$
$g_{\text{GeGe}}(r)$	g -GeSe ₄ -120	...	2.97–3.69	...
	g -GeSe ₄ -480	2.47	3.70	0.36
	g -GeS ₄ -120	...	2.77–3.64	...
	g -GeS ₄ -480	2.47	2.89–3.60	0.03
$g_{\text{GeX}}(r)$	g -GeSe ₄ -120	2.36	3.58	3.96
	g -GeSe ₄ -480	2.37	3.67	3.85
	g -GeS ₄ -120	2.22	3.43	4.00
	g -GeS ₄ -480	2.23	3.43	3.98
$g_{\text{XGe}}(r)$	g -GeSe ₄ -120	2.36	3.58	0.99
	g -GeSe ₄ -480	2.37	3.67	0.96
	g -GeS ₄ -120	2.22	3.43	1.00
	g -GeS ₄ -480	2.23	3.43	0.99
$g_{\text{XX}}(r)$	g -GeSe ₄ -120	2.38	3.87	0.99
	g -GeSe ₄ -480	2.37	3.85	1.04
	g -GeS ₄ -120	2.11	3.63	1.00
	g -GeS ₄ -480	2.12	3.63	0.99
		$\bar{n}_{\text{Ge}}$	$\bar{n}_{\text{X}}$	$\bar{n}$
g -GeSe ₄ -120		3.96	1.99	2.386
g -GeSe ₄ -480		4.21	2.00	2.44
g -GeS ₄ -120		4.00	2.00	2.40
g -GeS ₄ -480		3.99	1.98	2.385

less chemically ordered system (GeSe₄) is prevented by the limited number of Ge atoms when $N = 120$ (24 Ge atoms only).

To provide a more complete description of the network, we calculated the average percentages of the individual $\bar{n}_{\alpha}(l)$ structural units where an atom of species α (Ge, X = S or Se) is l -fold coordinated to other atoms. To clarify this notation, Ge–GeS₃ represents a Ge atom that is connected to one Ge atom and 3 S atoms while Ge–S₄ represents a Ge atom that is connected to 4 S atoms. The percentage proportion of units $\bar{n}_{\alpha}(l)$ are summarized in Table II.

Tetrahedra Ge(X₄) motifs are largely predominant for both systems, even though in g -GeSe₄, $N = 480$ their percentage lowers due to the occurrence of homopolar bonds. Interestingly, the deviation from chemical order, found to be more important in g -GeSe₄, is confirmed by the presence of threefold Ge-coordinated units for both $N = 120$ and $N = 480$. These units are essentially absent in g -GeS₄ (none for $N = 120$ and 0.7% for $N = 480$). The only sizable deviation from chemical order manifests itself through the formation of fourfold Ge–GeX₃ units.

Focusing on the results for $N = 120$, we notice that AA, AB, and BB motifs occur with similar weights in g -GeS₄ and in g -GeSe₄, AB connections being by far more numerous (about 43%, more than 15% larger than the BB and AA ones). Not only the above percentages change when considering the $N = 480$ models, but notable differences also appear between the two sets of g -GeS₄ and g -GeSe₄ values. For both systems, AB linkages are by far less abundant. However, while in

TABLE II. Percentage $\bar{n}_{\alpha}(l)$ of the different coordination units in glassy g -GeS₄ and glassy g -GeSe₄. We also provide the percentage of Ge atom involved in homopolar bonds N_{GeGe} , the percentage of X atom (S or Se) involved in homopolar bonds N_{XX} as well as the percentages of Ge atoms making edge-sharing (ES) or corner-sharing (CS) connections. These quantities have been calculated including neighbors separated by a cutoff corresponding to the first minimum in the partial pair correlation functions.

		Proportion $\bar{n}_{\alpha}(l)$ (%)			
		g -GeSe ₄		g -GeS ₄	
		N = 120	N = 480	N = 120	N = 480
Ge atom					
$l = 2$	X ₂	...	4.8	...	0.4
$l = 3$	GeX ₂	...	...	...	...
	X ₃	3.6	3.6	...	0.7
$l = 4$	GeX ₃	...	6.2	...	2.0
	X ₄	96.4	85.0	99.9	96.7
$l = 5$	Ge ₂ X ₃	...	...	...	...
	GeX ₄	...	...	0.1	0.1
	X ₅	...	...	...	...
X atom					
$l = 1$	Ge	...	1.5	...	0.5
	X	1.0	1.7	...	1.3
$l = 2$	X ₂ (BB)	28.1	30.7	28.1	32.0
	XGe (AB)	43.6	38.2	43.8	33.9
	Ge ₂ (AA)	27.1	26.5	28.1	31.8
$l = 3$	X ₂ Ge	...	0.5	...	<0.1
	XGe ₂	0.1	0.3	...	0.2
	Ge ₃	...	0.3	...	0.2
$N_{\text{Ge-Ge}}$		0.0	6.2	0.2	2.7
$N_{\text{X-X}}$		71.9	70.1	71.9	67.4
$N_{\text{Ge}}(\text{ES})$		25	25.4	29.2	32.8
$N_{\text{Ge}}(\text{CS})$		75	68.3	70.6	64.6

g -GeSe₄, AB connections remain largely predominant (38 % against 31% BB and 27% AA), g -GeS₄ features close percentages of AA, AB, and BB connections, falling within 2% and lying in between ~32% and ~34%. We point out that statistical uncertainties reported in the past for the AA, AB, and BB populations are of the order of 3%. Therefore, we are confident on the realistic character of the differences found between the topologies of g -GeS₄ and g -GeSe₄ for $N = 480$. One can conclude that the system size $N = 120$ is insufficiently accurate to describe correlations involving triads of atoms (next-nearest neighbors), at least when one of the two species is present in small concentrations, as it is in the present case for g -GeS₄ and g -GeSe₄ with $N = 120$.

Turning to the relative weights of corner-sharing and edge-sharing connections, both networks are characterized by an unambiguous majority of Ge connected in a corner-sharing fashion. This is consistent with the relative intensities and widths of the second and third peaks in the corresponding

FIG. 6. Chains statistics and rings connectivity profiles (histogram), including standard deviations (thin lines), for g -GeS₄ and g -GeSe₄. The rings statistics was calculated using the RINGS method.^{53,54} (a) Number of chains of size n . (b) Evolution of the ring diameter as a function of the size of the ring n . (c) $R_c(n)$, proportion of rings of size n , i.e., number of rings of size n normalized to the total number of atoms in the model.

partial Ge–Ge pair correlation functions (see Fig. 5). We also note that the percentage of Ge atoms involved in edge-sharing connection are systematically higher in g -GeSe₄.

3. Rings analysis and the intermediate range order

Based on what exemplified so far, g -GeSe₄ and g -GeS₄ can be viewed as resulting from the coexistence of Ge-centered

FIG. 7. The electronic density of states extracted from the Kohn-Sham eigenvalues. Result for amorphous g -GeS₄ (solid black curve) is compared to that obtained for amorphous g -GeSe₄ (solid red curve). (Top) Systems with $N = 120$, (bottom) systems with $N = 480$. A Gaussian broadening of 0.08 eV has been employed.

tetrahedra and a large number of Se–Se (S–S) homopolar bonds. For each system, hints on a more detailed level of network organization can be found by resorting to the statistics of chains and rings, for which we display the main results on Fig. 6. The largest average distance (termed diameter) for rings of a given size is also provided. To implement the rings analysis, the connectivity profiles were obtained using the RINGS method.^{53,54} The method employs a shortest path search for rings using the King/Franzblau shortest paths criterion and allowing for homopolar bonds during the searching procedure.^{55,56} For the cutoff distances, we took the first minimum of the partial pair correlation functions. The quantity reported, R_c , is the number of rings containing n atoms, normalized to the total number of atoms.

Results are shown for $N = 480$. By looking at the distribution of X_n chains, one notices that X_2 and X_4 chains are more numerous in g -GeSe₄, while the occurrences are comparable in X_3 for both g -GeSe₄ and g -GeS₄. Overall, a slight tendency to favor longer chains (containing a number of atoms equal

FIG. 8. Partial pair correlation functions $g_{\text{GeW}}(r)$ (top panel) and $g_{\text{XW}}(r)$ (bottom panel). The results at $N = 120$ for g -GeSe₄-NVT (solid red lines) and g -GeS₄-NPT (solid black lines) models are compared.

FIG. 9. The distribution of the Wannier center spreads as a function of the distance between Se or S atoms and the Wannier centers. The top panel shows the distribution for all S (or Se) in the system, while in the lower panel, the distributions are obtained by selecting AA, AB, and BB configurations. Details of the local bonding environment in the case of $g\text{-GeS}_4$ and $g\text{-GeSe}_4$ are given by the corresponding configurations. Ge atoms are shown in red, whereas X atoms (S or Se) are in yellow. The Wannier centers are the blue spheres. Counterlines are shown for 2.5%, 5%, 10%, 20%, 50%, and 75%. For clarity, counterlines are plotted alternately in black and grey.

or large than 6 atoms) is recorded in $g\text{-GeS}_4$. We recall that no signature of intermediate range order was found in the Se–Se partial structure factor, suggesting that these specific motifs do not contribute to persisting correlations on distances significantly beyond nearest neighbors.

The distribution of rings is clearly marked by specific sizes occurring in both $g\text{-GeS}_4$ and $g\text{-GeSe}_4$, for instance, $n = 4$, 5, 6 if one focuses on $n < 8$. However, $n = 6$ is much more

frequent in $g\text{-GeS}_4$. Moreover, a global view of the largest occurrences provides evidence on the existence of specific ring sizes more abundant in $g\text{-GeS}_4$, namely, $n = 10$, 13, 15. These correspond to ring diameters well beyond 5 Å (i.e., the first two shells of neighbors). Such observation is instrumental to establish a correlation between the existence of these motifs and the more pronounced intermediate range order found in $g\text{-GeS}_4$. Therefore, Ge and S atoms separated by distances well

beyond nearest neighbors in high n rings are responsible for the appearance of a higher FSDP in $S_{\text{GeS}}^{\text{FZ}}(k)$.

D. Electronic properties

A view of the EDOS for $g\text{-GeS}_4$ and $g\text{-GeSe}_4$ ($N = 120$ and $N = 480$) is given in Fig. 7. The shape of the EDOS around the Fermi level can provide hints on the extent of the ionic character in the systems under consideration. In the present case, both sets of results ($N = 120$ and $N = 480$) point toward a larger gap for the case of $g\text{-GeS}_4$. Based on this observation, $g\text{-GeS}_4$ could be considered as bearing a more pronounced ionic character than $g\text{-GeSe}_4$.

It is of interest to substantiate this assertion, which is inline with the conventional Pauling bond ionicity definition⁵⁷ and more recent studies,^{58,59} by collecting further evidence through an analysis of the local electronic structure. This can be carried out in terms of maximally localized Wannier function centers and their spread (from hereafter labelled WFCs and Ω , respectively).^{44,45} The results shown in Figs. 8 and 9 were obtained by averaging over 50 uncorrelated configurations taken along the trajectory collected at 300 K.

The intrinsic localized distribution in space of these quantities allows to infer the extent of covalent vs. ionic nature of bonding. To this purpose, one can rely on the correspondence between the distances identified in the atom-centers pair correlation functions $g_{\text{GeW}}(r)$ (for $g\text{-GeS}_4$ or $g\text{-GeSe}_4$), $g_{\text{SeW}}(r)$ (for $g\text{-GeSe}_4$), $g_{\text{SW}}(r)$ (for $g\text{-GeS}_4$), and specific WFCs (the W label referring to these degrees of freedom). As shown in Fig. 8, three type of WFCs can be distinguished (see also Fig. 10).

The first type, labeled as W_B , refers to Ge–S or Ge–Se bonds. A clear fingerprint of these centers is the pronounced

main peak exhibited by $g_{\text{GeW}}(r)$ at around 1.3 Å. Looking at the patterns found in $g_{\text{Se(S)W}}(r)$, one can ascribe such bonds to the secondary peaks at ~ 0.9 Å ($g\text{-GeS}_4$, see inset) and ~ 1 Å ($g\text{-GeSe}_4$, see inset). The second type, labeled as W_H , refers to homopolar S–S or Se–Se bonds and it corresponds to the third peak in $g_{\text{SeW}}(r)$ (1.02 Å) or $g_{\text{SW}}(r)$ (1.18 Å) (see inset), as revealed by a one-to-one matching between those distances and the related centers. The third type, labeled as W_{LP} , indicates the lone pair (LP) valence electrons not participating to chemical bonds but remaining localized in the vicinity of the group VI atoms (S, Se). We ascribe to the lone pair the first peak at ~ 0.47 Å (in $g_{\text{SeW}}(r)$) and ~ 0.44 Å (in $g_{\text{SW}}(r)$) and the extended feature of $g_{\text{GeW}}(r)$ spreading around ~ 2.33 Å (in $g\text{-GeSe}_4$) and ~ 2.48 Å (in $g\text{-GeS}_4$). Given the above definitions, the first observation concerns the locations of the W_B centers with respect to the Ge atoms in $g_{\text{GeW}}(r)$ for $g\text{-GeS}_4$ or $g\text{-GeSe}_4$. These turn out to be rather close, since on average $\text{Ge}-W_B = 1.32 \pm 0.01$ Å and $\text{Ge}-W_B = 1.36 \pm 0.01$ Å for GeS_4 and GeSe_4 , respectively.

However, when looking at the separation between the maxima at around 1.3 Å and those lying at about ~ 2.3 Å (in $g\text{-GeS}_4$) and ~ 2.5 Å (in $g\text{-GeSe}_4$), a smaller value is found for $g\text{-GeS}_4$, pointing toward a tendency of the Wannier center to lay closer to the S sites. In a way consistent with this point, we remark that the W_B centers, analyzed on the basis of $g_{\text{SeW}}(r)$ and $g_{\text{SW}}(r)$, are closer to the origin (i.e., the Se or the S atom) in the case of S, since $\text{S}-W_B = 0.9 \pm 0.01$ Å and $\text{Se}-W_B = 1.0 \pm 0.1$ Å. Therefore, the relative position of the peaks in $g_{\text{GeW}}(r)$ for $g\text{-GeS}_4$ and $g\text{-GeSe}_4$ and the closer location to the origin for the secondary peaks in $g_{\text{SW}}(r)$ allow to conclude that $g\text{-GeS}_4$ has a higher ionic character than $g\text{-GeSe}_4$. This stems from the fact that the centers of electronic localization (related to heterogeneous bonding) are systematically closer to the S sites than to the Se sites. This analysis can be further developed by studying the correlation between two quantities, i.e., the delocalization (spread) of the WFCs (i.e., Ω) and the distance ($d = X(\text{Se}, \text{S}) - W$) separating the S or Se atoms and the WFCs. In the top panel of Fig. 9, this quantity is displayed by accounting for all $X-W$ distances within the range of 0–1.35 Å. We stress that we are dealing here with a distribution of values, giving rise to a three dimensional representation for which we display in Fig. 9 a two-dimensional view. For this purpose, a color code map is given on the top of Fig. 9. Following the same spirit, in the lower panels, we disentangle the contributions of the AA, AB, and BB units. As expected, the total distributions are made of three main regions in the $X\text{-WFCs}/\Omega$ two dimensional projected space. The first accounts for the W_{LP} centers ($g\text{-GeSe}_4$: $\sim(1.32, 0.47)$ and $g\text{-GeS}_4$: $\sim(1.17, 0.44)$). The second and the third stand for the WFCs characterizing the heteropolar ($g\text{-GeSe}_4$: $\sim(1.29, 1.0)$, $g\text{-GeS}_4$: $\sim(1.15, 0.9)$) and the homopolar ($g\text{-GeSe}_4$: $\sim(1.26, 1.17)$ and $g\text{-GeS}_4$: $\sim(1.06, 1.03)$) bonds within the AA, AB, and BB units.

Fig. 9 provides convincing evidence of the higher polarity in Ge–S bonding. Indeed, (a) the $\text{S}-W_{B/H/LP}$ distances are shorter than the $\text{Se}-W_{B/H/LP}$ ones, (consistently with the behavior of the pair correlation functions $g_{\text{GeW}}(r)$ and $g_{\text{Se(S)W}}(r)$), (b) the $\Omega_{B/H/LP}$ values are systematically lower for $g\text{-GeS}_4$, and (c) the spread of the Ω distributions is narrower (for all kinds of WFCs) in $g\text{-GeS}_4$.

FIG. 10. Details of the local bonding environment in the case of GeSe_4 (or GeS_4). Ge atoms are shown in red, whereas Se (or S) atoms are in yellow. The Wannier centers are the blue. To avoid confusion, only a few atoms are labeled along with representative Wannier centers.

FIG. 11. Snapshots of the most localized Kohn-Sham states close to the band gap of the 480-atom model of g -GeSe₄. Red and blue surfaces render the isosurfaces with a value of $+0.03$ ($\text{\AA}^{-3/2}$) and -0.03 ($\text{\AA}^{-3/2}$), respectively. Atoms and the bonding network are displayed by semitransparent spheres and lines. The states are mostly localized on the atoms highlighted with colored spheres; red spheres for Ge, yellow for S.

We also observe that the distribution corresponding to BB configurations is a fairly linear function of the $S(\text{Se})$ - W_B distance, that is, the smallest spread corresponds to the shortest $S(\text{Se})$ - W_B distances. Typically, these are found at opposite sides for a given chain, as if inner bonds were intrinsically less localized than outer ones.

We can also characterize the inner gap states appearing for $N = 480$ in g -GeSe₄ in terms of their localization inside the network, as done in Fig. 11. Our analysis focuses on the eigenstates LUMO (lowest unoccupied molecular orbital) and LUMO + 1 which are localized on configurations containing some short Se-Se bonds ($d_{\text{SeSe}} \leq 2$ Å). These defective bonds are only present in the g -GeSe₄ case $N = 480$ and in a very limited amount.

IV. CONCLUSIONS

First-principles molecular dynamics studies of glassy g -GeS₄ and glassy g -GeSe₄ have shown that both networks are characterized by tetrahedral connections interlinked with Se-Se or S-S homopolar bonds. Homopolar Ge-Ge bonds are found in g -GeSe₄ for the largest ($N = 480$) periodic simulation cell only, underlying a non-negligible size effect that occurs in multicomponent systems with a low concentration of the minority species. The occurrence of homopolar Ge-Ge bonds in

g -GeSe₄ is consistent with its lower ionic character, as showed by the Wannier centers analysis describing the electron localization. Also, the connectivity of the Se and S atoms (the relative weight of Ge-Se-Ge (Ge-S-Ge), Ge-Se-Se (Ge-S-S), or Se-Se-Se (S-S-S) configurations) is found to be sensitive to the system size. Two changes characterize the adoption of $N = 480$ instead of $N = 120$. There is a strong decrease of Ge-Se-Se (Ge-S-S) connections in both g -GeSe₄ and g -GeS₄, more specifically from about 44% to 38% (g -GeSe₄) and 34% (g -GeS₄). In g -GeSe₄, Ge-Se-Se linkages are by far the most important (38%) against Ge-Se-Ge (26%) and the Se-Se-Se (31%) ones. In g -GeS₄ instead, the three configurations are found to lie within 2%. We were able to ascribe the higher intensity of the first sharp diffraction peak in the total neutron structure factor of glassy g -GeS₄ to the corresponding FSDP in the Ge-S partial structure factor. This arises due to a substantially higher number of large size rings ($n > 8$) for glassy g -GeS₄. In these motifs, Ge and S atoms are separated by distances typical of intermediate range order. The higher ionicity of glassy g -GeS₄ when compared to g -GeSe₄ confirms a tendency already observed in g -GeS₂ vs g -GeSe₂.

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