

Physical properties of a GeS₂ glass using approximate *ab initio* molecular dynamics

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(Received 1 October 2002; published 17 March 2003)

With the use of *ab initio* based molecular dynamics simulations we study the structural, dynamical and electronic properties of glassy *g*-GeS₂ at room temperature. From the radial distribution function we find nearest neighbor distances almost identical to the experimental values and the static structure factor is close to its experimental counterpart. From the Ge-S-Ge bond angle distribution we obtain the correct distribution of corner and edge-sharing GeS₄ tetrahedra. Concerning the dynamical characteristics we find in the mean square displacement of the atoms discontinuous variations corresponding either to the removal of coordination defects around a single particle or to structural rearrangements involving a larger number of atoms. Finally we calculate the vibrational density of states, which exhibits two well separated bands as well as some features characteristic of the amorphous state, and the electronic density of states showing an optical gap of 3.27 eV.

DOI: 10.1103/PhysRevB.67.094204

PACS number(s): 61.43.Fs, 71.23.-k, 71.15.Pd

I. INTRODUCTION

Among chalcogenide glasses, glassy germanium disulfide (*g*-GeS₂) has been heavily studied for many years,¹ and was still the subject of recent experimental investigations^{2,3} because of its interesting physical properties. Chalcogenide materials can be used as sensitive media for optical recording, as light guides, as high-resolution inorganic photoresistors, or antireflection coatings.⁴ Moreover bulk glasses with, for example, Ag⁺ cations are good solid electrolytes with a high ionic conductivity at room temperature,⁵ and thin GeS₂ films are promising materials for submicron lithography when doped with silver.⁶ The high quantum efficiency of these glasses appears as a consequence of the relative high masses of the elements involved.⁷ All these potential applications of glassy GeS₂ have led many authors to study the physical properties of these chalcogenide glasses, and many experiments have been done on this topic.^{8,9} However, in order to understand the physical mechanisms occurring at the atomic scale and leading to the results observed in experiments, numerical simulations can be an alternative tool and more specifically molecular dynamics (MD) simulations. Although cluster modeling simulations were performed on *g*-GeS₂,¹⁰ it appears that GeS₂ compounds have not been the topic of extensive MD investigations yet, contrary to GeSe₂ (Ref. 11) or SiSe₂.¹² In order to perform such investigations one has to decide what kind of description (classical or *ab initio*) is adequate for GeS₂. Taking mostly (but not purely) covalent bonding into account in *g*-GeS₂ a first-principles approach seems appropriate. In this paper we therefore present a theoretical study of the structural, dynamical and electronic properties of *g*-GeS₂ using an approximate *ab initio* description based on the Sankey-Niklewski scheme¹³ and materialized in the so-called “FIREBALL96” MD code.¹⁴ This technique has been successfully used in the study of several different chalcogenide glasses,^{15,16} and in order to check its validity in the case of GeS₂ samples we have compared our

results with experimental results when those were available. Concerning the structure at 300 K, the nearest-neighbor distances as well as the static structure factor compare well with the experimental data. Using the angle distributions and the radial pair distribution functions we find the correct proportion of edge and corner sharing GeS₄ tetrahedra which are the basic building blocks of the germanium disulfide glass. Concerning the dynamics of the individual particles, we find in the mean square displacement (MSD) signatures of individual or collective atomic rearrangements corresponding to either the removal of “defects” or to the oscillation of large clusters which could be at the origin of the excess of modes seen at low frequency in the vibrational spectrum.

The paper is organized as follows: In Sec. II we present the theoretical foundation of the FIREBALL96 code as well as the approximations used. In Sec. III the results are presented for the structural, dynamical and electronic properties of the GeS₂ sample and Sec. IV gives the major conclusions.

II. MODEL

The theoretical framework of our work is the widely used density functional theory¹⁷ using *three* additional approximations.

First we use the well known local-density-approximation¹⁸ combined with the pseudopotential approximation, which replaces the core electrons by an effective potential acting on the valence electrons (Hamman-Schluter-Chiang pseudopotentials are used¹⁹). The electronic eigenstates are determined by a tight-binding-like linear combination of pseudoatomic orbitals (PAOs) that satisfy the atomic self-consistent Hohenberg-Kohn-Sham equations.²⁰ A minimal basis set of one *s* and three *p* confined pseudo-orbitals per site is required.

The second approximation was suggested by Harris.²¹ It consists in using a sum of neutral-atom spherical charge densities as a zeroth-order approximation to the self-consistent

density, keeping only the first-order changes from this density in the energy functional. This approximation avoids the necessity of iterating to self-consistency, so eigenvalues only need to be determined once instead of ≈ 10 times at each step. This approximation also avoids four-center Coulomb integrals in our calculations, which is a great simplification. The Harris functional has been used in many studies and has always given surprisingly good agreement with fully self-consistent calculations, except for highly ionic systems.^{15,22}

A third approximation is made to reduce the range of the tight-binding-like Hamiltonian matrix elements. To that purpose, the PAOs are slightly excited by imposing the boundary condition that they vanish outside a predetermined radius. This cut-off radius is chosen equal to $5a_0$, which represents a distance of 2.645 Å. Atoms do not overlap each other beyond twice this distance, so the number of neighbors of each atom is considerably reduced. All these approximations permit one to gain a considerable amount of CPU time compared to *ab initio* methods like the Car-Parrinello scheme,²³ and therefore one can perform longer simulation runs or study larger systems. Moreover, this method has proved to be a very efficient tool for a wide variety of problems, and has been used with success in many different investigations.^{15,16,24,25}

Concerning the details of the present simulation, all of our calculations were performed in the microcanonical ensemble (N , V , and E constants), with a time step of 2.5 fs, and using only the Γ point to sample the Brillouin zone. The initial configuration of our system was a crystalline α -GeS₂ sample containing 96 particles (32 Ge and 64 S) confined in a cubic cell of 13.82 Å to which periodic boundary conditions have been applied. This represents a density of 2.75 g cm⁻³, which is the usual experimental density.⁹ This crystalline configuration was then melted at 2000 K over approximately 2 ps and then equilibrated at 1000 K for an additional 1.5 ps. We then quenched the system (by velocity rescaling) through the glass transition ($T_g = 710$ K) to a target temperature of $T = 300$ K over 4 ps (for more details on similar systems, see Ref. 16). Starting from this configuration, we performed a very long thermal MD simulation at 300 K over 375 ps, i.e., 150 000 steps. During this time, we saved the configurations every 20 steps, and consequently all the results presented below have been averaged over these 7500 configurations.

III. RESULTS

A. Structural properties

The basic building blocks of glassy g -GeS₂ are GeS₄ tetrahedra, connected together within a random network. The structural unit disorder is reflected in the absence of long range order and in the wide distribution of bond lengths and bond angles. Structural information may be extracted from the radial pair correlation function $g(r)$. For a given α - β pair it is defined by

$$g_{\alpha-\beta}(r) = \frac{V}{4\pi r^2 N_\alpha dr} dn_\beta. \quad (1)$$

Results are shown in Fig. 1 for the three different pairs. The

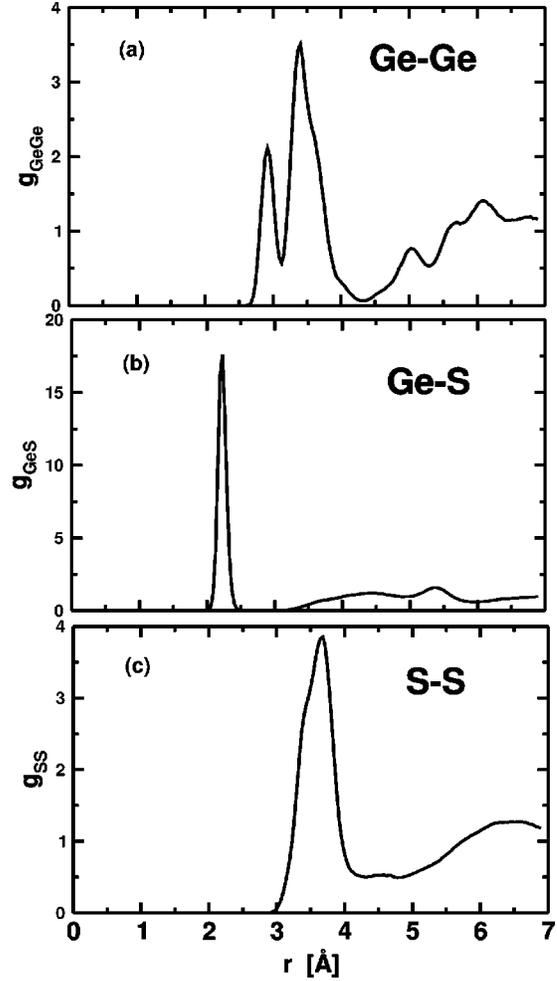


FIG. 1. Radial pair distribution functions (a) Ge-Ge, (b) Ge-S, and (c) S-S.

smallest distance appears for the Ge-S pairs [Fig. 1(b)] at 2.22 Å, and is in perfect agreement with the distance determined experimentally [2.21 (Ref. 8)]. The distance between two Ge atoms represents the intertetrahedral distance, and depends on the nature of the connection between the tetrahedra. The first peak at 2.91 Å in Fig. 1(a) is due to edge-sharing tetrahedra, while the second one, at 3.41 Å, is due to corner-sharing links as shown in Fig. 2. The experimental distances are respectively estimated at 2.91 Å and 3.42 Å,⁸ which is extremely close to our results. Finally the S-S pairs are responsible of the wide peak centered at 3.66 Å [Fig. 1(c)], which is also extremely close to the experimental first S-S distance of 3.64 Å.⁸

A complementary way to analyze the structure is to compute the static structure factor $S(q)$ [obtained by a Fourier transformation of $g(r)$] which can be directly compared to its experimental counterpart. In Fig. 3 we present the calculated $S(q)$ together with the one obtained by neutron diffraction experiments.²⁶ The good agreement between the two curves shows the quality of the model concerning the structural description of GeS₂ glasses. The first sharp diffraction peak (FSDP), which is a signature of the intermediate range order in amorphous states, appears at $\approx 1 \text{ \AA}^{-1}$ and is slightly

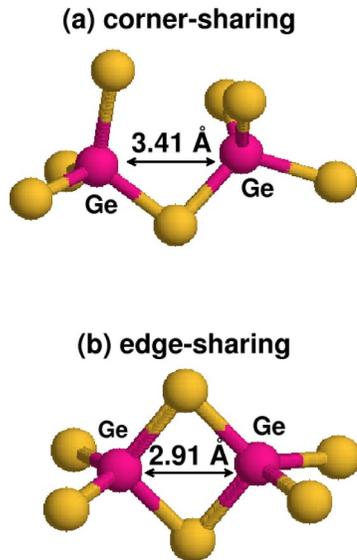


FIG. 2. Ge-Ge distances in corner and edge-sharing tetrahedra.

underestimated compared to the experimental one. This is probably a consequence of the small size of our system: 1 \AA^{-1} represents in real space a distance of 6.3 \AA and a sphere with such a radius provides a volume which is close to the total volume of our cell. Therefore the lack of statistics for these large distances can explain the underestimation of the FSDP in our simulation.

In order to analyze completely the medium-range structure we have also calculated the bond angle distributions and in particular the intratetrahedral $\widehat{S\text{GeS}}$ and intertetrahedral $\widehat{\text{GeSGe}}$ bond angles which are represented in Fig. 4. The intratetrahedral angle $\widehat{S\text{GeS}}$ is centered at 110° , which is close to the perfect tetrahedral angle of 109.47° . Its large distribution is a signature of the structural disorder of our glassy sample. The intertetrahedral bond angle $\widehat{\text{GeSGe}}$ is the angle *between* tetrahedra and includes two major contribu-

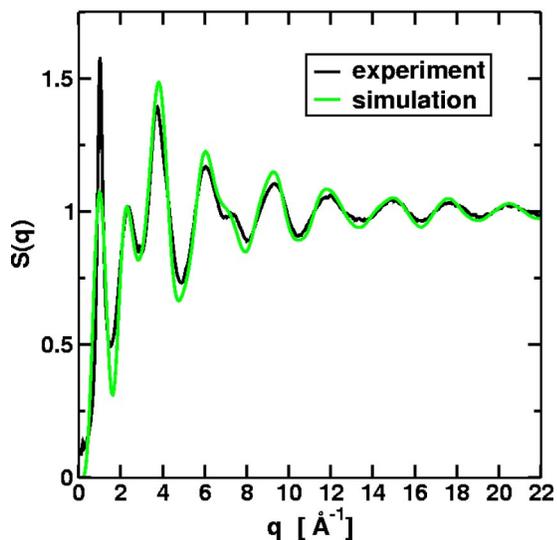


FIG. 3. Experimental and simulated static structure factor.

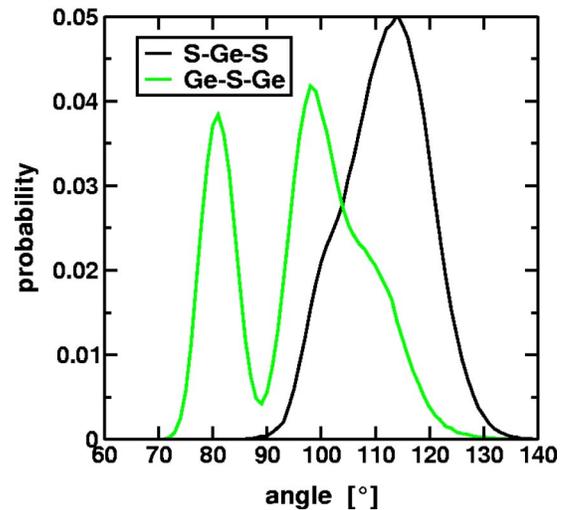


FIG. 4. Bond angle distributions.

tions. The first one, centered at 80° , is caused by edge-sharing tetrahedra. The second, at $\approx 100^\circ$, is due to corner-sharing tetrahedra. The integration of these two peaks permits to estimate the fraction of edge-sharing and corner-sharing connections which are respectively 18.6% and 81.4%. These results have also been confirmed by a direct counting of each type of connection in our sample. Experimental Raman scattering measurements in amorphous $g\text{-GeS}_2$ have given 16.6% of edge-sharing links and 83.4% of corner-sharing links³ which is relatively close to our results.

In view of all these data, we can safely say that the model describes correctly the structure of amorphous GeS_2 . It remains to be seen if this is also true for the dynamical properties which is the topic of Sec. III B.

B. Dynamical properties

The dynamical properties of glassy $g\text{-GeS}_2$ have been studied through the mean square displacement and the vibrational density of states. The MSD is defined as $\langle r^2(t) \rangle = \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$ where $\vec{r}_i(t)$ is the position of particle i at time t . We can deduce from the slope of the MSD the diffusion constant D , where $D = \frac{1}{6} \lim_{t \rightarrow \infty} r^2(t)/t$. In our calculation, D was found equal to zero; this means that the thermal energy at ambient temperature is not high enough to reach the diffusive regime during the time scale of our simulation (375 ps). Nevertheless during this time some specific structural rearrangements can occur which manifest themselves by a brutal increase of the total MSD or of the MSD of individual atoms. In this later case the “jumps” in the MSD are due to the removal of a coordination “defect” in the glassy system. An example of such a rearrangement is shown in Fig. 5: Fig. 5(a) represents the individual MSD of Ge^* , a particular germanium atom, with a dramatic increase from $\approx 0.5 \text{ \AA}^2$ (before the jump) to $\approx 2.5 \text{ \AA}^2$ (after the jump) around 100 ps. The jump can clearly be seen in Fig. 5(b), which shows the projection of the displacement of Ge^* on the x - z plane while the reason of the jump becomes apparent in Figs. 5(c) and 5(d), which illustrate the group of particles surrounding Ge^* just before and after the jump. Indeed we

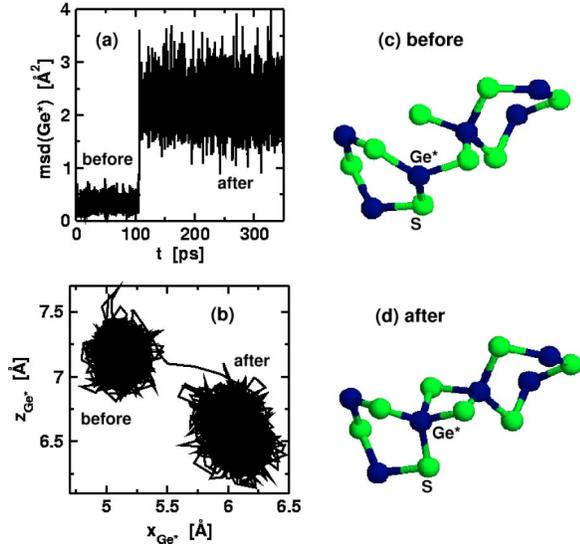


FIG. 5. (a) Mean square displacement of Ge^* before and after the jump. (b) Projection on the (x,z) plane of the trajectory of Ge^* . Atomic configuration around Ge^* before (c) and after (d) the jump.

see that the initially 3-coordinated Ge^* atom is linked with a terminal sulfur atom, thus creating two edge-sharing tetrahedra, which is a configuration energetically more favorable.

The second kind of rearrangement illustrated in Fig. 6 involves a larger number of particles and manifests itself by a “pulse” in the total MSD whose amplitude is more important for the sulfur atoms than for the germanium atoms as shown in Fig. 6(a). In that case a group of particles (≈ 20) in a certain configuration at t_1 [Fig. 6(b)] switches to a new state at t_2 [Fig. 6(c)] which can be called metastable since its lifetime is relatively short (≈ 10 ps) before the system comes back again to its original structure. Note that in this case no link has been broken or created. We observed such “oscillations” twice in our simulation with a time interval of

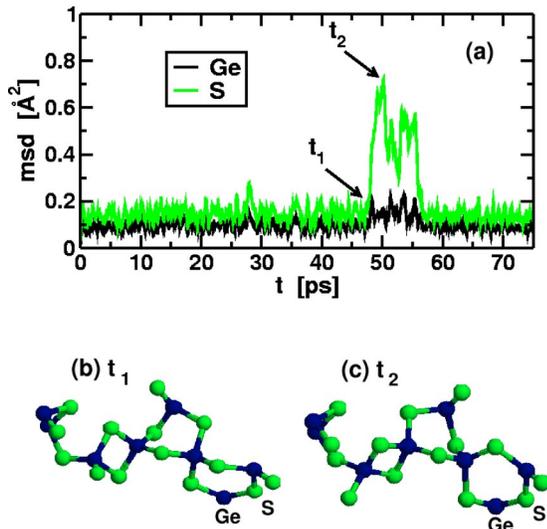


FIG. 6. (a) Total MSD for the S and Ge atoms displaying a pulse at t_1 . Structural arrangement of the most mobile atoms at t_1 (b) and t_2 (c).

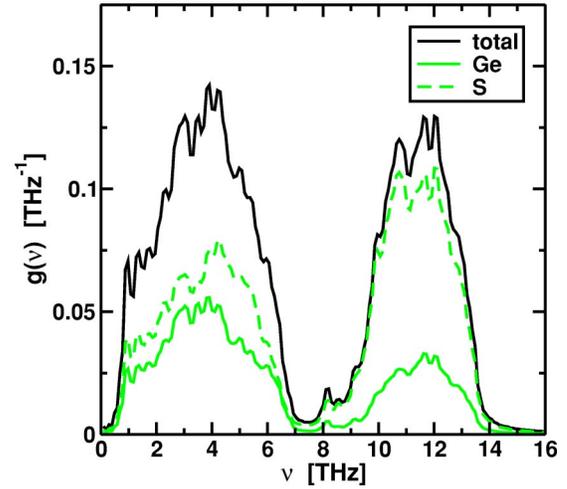


FIG. 7. Total and partial vibrational densities of states.

300 ps. Clearly our simulation time is too short to see if these oscillations repeat themselves at a well determined (low) frequency and to make a connection with the so-called “soft” modes²⁸ well known in amorphous systems.

To complete the study of the dynamical properties we have computed $g(\nu)$, the vibrational density of states (VDOS), via a Fourier transformation of the velocity auto-correlation function:

$$g(\nu) = \frac{1}{Nk_b T} \sum_i m_i \int_{-\infty}^{\infty} \exp(i\nu t) \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle dt. \quad (2)$$

The Fourier transformation has been calculated using the Wiener-Kinchin theorem²⁷ over the last 4096 steps of the simulation. The total spectrum as well as the partial contributions due to Ge and S are shown in Fig. 7. Despite serious efforts we could not find the experimental counterpart of the total spectrum since apparently no neutron diffraction studies have been performed on $g\text{-GeS}_2$. But, comparing our results with those obtained for analogous GeSe_2 glasses,¹⁶ the spectrum exhibits the same features. Mainly two bands can be distinguished: a low-energy acoustic band involving mainly extended interblock vibrations and a high-energy optic band consisting of more localized intrablock vibrations. The two main bands are clearly separated and have approximately the same width (7 THz).

In addition to the usual acoustic and optical bands, a small band can be seen close to 8 THz corresponding to the so-called A_1 mode.¹⁵ The A_1 mode is well known to be a tetrahedral breathing mode (in which a central Ge atom is stationary and its four S neighbors move radially relative to the fixed Ge). This feature is strongly revealed in Raman measurements,²⁹ because the mode is especially Raman active. In Raman measurements, there is a clear indication of a “two peak” structure to the A_1 band. In particular, one usually sees a high frequency peak or shoulder which is interpreted as arising from edge-sharing tetrahedra (see Fig. 2), and the main band from tetrahedra in corner-sharing conformations.³⁰ The A_1 and A_{1c} modes have also been resolved in inelastic neutron scattering studies of $g\text{-GeSe}_2$.³¹

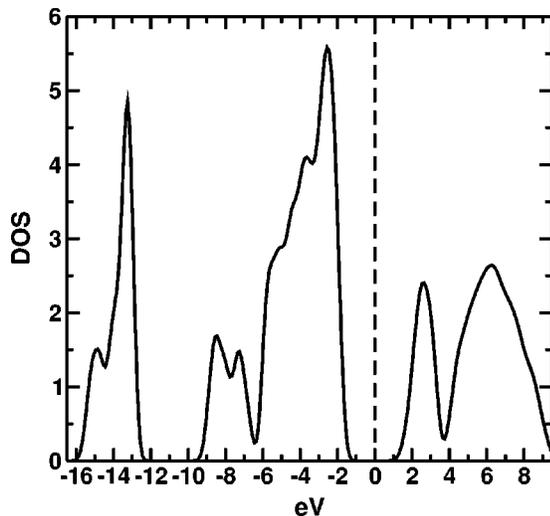


FIG. 8. Electronic density of states. The dashed vertical line is the Fermi energy. The optical gap is found to be 3.27 eV.

In our work the tetrahedral breathing band does show a clearly resolved splitting. It is possible that a direct analysis of the eigenvectors of the dynamical matrix³¹ would provide more information linking the observed spectral feature to microscopic vibrational excitations. At the low frequency end of the spectrum, a shoulder is present between 1 and 2 THz which is coherent with the existence of a “boson” peak found experimentally.³² The “boson” peak refers to an excess in the VDOS with respect to the Debye distribution and is located generally around 1.5THz.

C. Electronic properties

In Fig. 8 we present the electronic density of states, obtained by binning the density functional electron energy eigenvalues from the starting, fully relaxed model. The Γ point optical gap is 3.27 eV which compares very well with the experimental value of 3.2 eV obtained by resonant Raman-scattering spectroscopy.³² This good agreement is due to the opposite effects of the use of a minimal basis set which is well known to exaggerate the gap and of Kohn-Sham eigenvalues which tend to underestimate the gap. It should be noted that this gap is greater than that (2.3 eV) of *g*-GeSe₂. Another point from Fig. 8 is the lack of any localized states in the optical gap (the Fermi level is at $E=0$ in our calculation). This lack of gap states is realistic, since the density of gap states is very small in *g*-GeS₂.

IV. CONCLUSION

We find that the results obtained for our 96-atom GeS₂ model are in excellent agreement with all the corresponding

experimental results that are available. This realism is surprising since the size of our system is relatively small, and accurate MD simulations usually require larger systems.

The structural properties of *g*-GeS₂, which have been extensively studied, are all extremely realistic in our simulation. The pair-correlation functions lead to interatomic distances that are within 10^{-2} Å compared to the experimental values and the static structure factor is very similar to the one obtained from neutron diffraction studies. The small underestimation of the FSDP encourages us to use larger models, and we are currently preparing samples containing 258 atoms. The fraction of edge and corner-sharing tetrahedra, which can be deduced from the angular distribution, is also close to experiment. It should be mentioned that we don't find homopolar (Ge-Ge or S-S) bonds in the present investigation but their existence can not be excluded *a priori* in the 258-atom model. Probably a more in-depth study of the large system will permit to solve the apparent disagreement between two recent experimental studies on this point.^{2,3}

Concerning the dynamical properties of our sample we find discontinuous atomic displacements at ambient temperature, leading to jumps in the MSD. These jumps can either be due to the removal of coordination defects around a single atom or to oscillations of larger groups of atoms (≈ 20) between a stable and metastable configuration which could be at the origin of “soft” modes that are often seen in amorphous systems. The vibrational density of states of glassy GeS₂ could not be compared directly to the experimental spectrum, since to our knowledge it is not yet available in the literature. We find basically two bands separated by a “gap” in which exists a small structure due to the tetrahedral breathing modes. At low frequency we find at around 1 THz a shoulder corresponding to the famous boson peak present in many amorphous systems. Concerning the electronic properties we find an optical gap of 3.27 eV and no localized states in the gap which is in agreement with experimental data. These MD results obtained for *g*-GeS₂ with the use of the FIREBALL96 code show that one can have confidence in this “pseudo” *ab initio* scheme giving an excellent description of the physical characteristics of germanium disulfide for a relatively low computer load.

ACKNOWLEDGMENTS

P.J. would like to thank R. Jullien, A. Pradel, and M. Ribes for their help in initiating this project. We would also like to thank E. Bychkov for the data of the experimental structure factor of *g*-GeS₂ as well as Jun Li for advice in the early stages of this work. Part of the calculations were performed at the “Center Informatique National de l'Enseignement Supérieur (CINES)” in Montpellier. D.A.D. thanks the National Science Foundation for support under Grant Nos. DMR-0081006, 0074624, and 0205858.

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