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First-principles simulation on pressure-dependent local structure change of AsS melt

Tingkun Gu [a],*, Yuanhua Qi [b]

[a] Shandong Provincial Key Laboratory of UHV Transmission Technology and Equipment, School of Electrical Engineering, Shandong University, Jinan 250061, China
[b] School of Physics, Shandong University, Jinan 250061, China

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ABSTRACT

The local structure of AsS melt has been investigated by the first-principles method. At ambient pressure, As_4S_4 molecules remain in liquid AsS similar to that of crystal As_4S_4(II). Structural analyses based on the first and second coordination shell indicate that the local structure of AsS melt undergo two sudden change processes with increasing pressure from 0.0 to 6.9 GPa: the first is from 1.5 to 2.9 GPa that the AsS melt transforms from molecular into polymeric liquid, the second is from 4.3 to 5.6 GPa where the coordination number of the first shell for As and S change apparently. Our calculated results and conclusion for the structural change of AsS melt under compression are very different from those of previous report (Phys. Rev. B 84, 224202). Corresponding to the local structure change, the dynamical properties, such as diffusion coefficients and velocity-velocity autocorrelation function, also show apparent transformation in theses pressure intervals. On the basis of the calculated results, we concluded that the local structure changes of AsS melt should be consistent with its liquid-liquid phase transition under compression.

1. Introduction

Liquid-liquid phase transition is a controversial scientific issue, and phase transitions in simple isotropic liquids were not attracted extensive attention in the scientific researches before 1990, except for a few theoretical works [1]. Within the latest three decades, the liquid-liquid phase transition of elementary substances, oxides, and halogenides under high pressure had been investigated extensively because of the rapid development in high pressure technology [2–13]. Generally, both changes in structures (the short-range and intermediate-range order structures) and physical properties occur synchronously in the transformation process in melts under compression, and these changes can be smooth or sharp. Researchers always deduce the structural transformations under compression in melts on the basis of the experimental data of the physical properties, such as, the viscosity, electric resistivity, *etc.* It is thought generally that the sudden changes in the data of physical properties under pressure should correspond to the manifest structural change. However, there are two factors to disturb the definition of the phase transition in melts, the first is the diverse experimental data of physical properties, for example, very large divergent viscosity data for some melts were reported by different researchers in previous scientific literatures, the second is that some difficulties should be overcome when analyzing the liquid structure in detail because only the total pair correlation function or structure factor could be obtained from X-ray diffraction experiments, if extracting the partial pair correlation functions or structure factors of binary melts, the expensive neutron scattering experiment should be employed.

Chalcogenide substances undergo a great number of phases under variations of pressure and temperature. Under compression, Se and S show structural phase transformations accompanied by insulator-metal transitions both in solid and liquid states [7–9]. $GeSe_2$ compound exhibits a series of phase transitions under compression in the crystalline state, as well as a significant modification of the intermediate-range order structure in the melt [14]. A remarkable experimental observation of two phase transformations under compression in the AsS melt was reported on the basis of the obviously variations of the physical properties in narrow pressure intervals. The structure factor and the pair correlation function of liquid AsS under different pressure obtained by the energy-dispersive x-ray diffraction (EDXD) method indicate that there is short-range order structure change along with the phase transition, but the details are still unclear since the partial structure factor or pair correlation function cannot extracted from EDXD method [15]. To understand the correlation between the local structure change and phase transition, the parameters related to the short-range order structure change under compression are investigated by first-principles method for AsS melt.

2. Computational details

All calculations were performed by using the Vienna *ab initio* simulation program (VASP) in which the first principle calculations are

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* Corresponding author.
E-mail address: gutk@sdu.edu.cn (T. Gu).

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based on the density functional theory [16,17]. The projector augmented-wave (PAW) method and the generalized gradient approximation (PW91) were adopted to describe the interaction between the ions and electrons, and the electron-exchange effect, respectively [18,19]. To simulate the local structure change of AsS melt under pressure, the same temperature of 1073 K was set in the calculating process. In the simulations, we used a canonical ensemble with a Nosé thermostat for temperature control, the different pressure values were obtained by adjusting the densities of AsS melt (see Fig. 1), and the equation of motion was solved *via* the velocity Verlet algorithm with a time step of 3 fs. Plane-wave bases set with a cutoff energy of 400 eV and the Γ point alone to sample the Brillouin zone of the supercell for each of AsS melt were used. The initial configuration was chosen as 200 atoms randomly distributed in a cubic supercell, then the system was equilibrated for 3000 steps at a high temperature of 2000 K in order to remove the memory effect. After that, the system was gradually cooled down to 1073 K. Finally, after equilibration taking about 6 ps at 1073 K, structure information was acquired during another 30 ps period in which the energy conservation was excellent and the drift was smaller than 0.5 meV/atom/ps.

3. Results and discussion

3.1. Validation of the calculated results

In a molecular dynamics simulation of liquid state, The partial structure factors $S_{ij}(k)$ are defined by

$$S_{ij}(k) = \frac{1}{N_i N_j}\left\langle \sum_{\mu=1}^{N_i}\sum_{\gamma=1}^{N_j} e^{ik(r_\mu - r_\gamma)}\right\rangle \tag{1}$$

The positions of ions $\{r_\mu\}$ are obtained by *ab initio* MD simulations, N_i is the number of ions of the ith species, and the angular brackets $< >$ mean the time average. The total structure factor is then expressed as a linear combination of the partial structural factors $S_{ij}(k)$ normalized by the neutron scattering lengths of As and S,

$$S(k) = \sum_i \sum_j c_i^{1/2} c_j^{1/2} \frac{b_i b_j}{c_i b_i^2 + c_j b_j^2} S_{ij}(k) \tag{2}$$

where neutron scattering lengths are: $b_{\mathrm{As}} = 6.58$ and $b_{\mathrm{S}} = 2.847$. c_i is the number concentration.

Generally, the structure factor is extracted from diffraction experiments directly. It is a better way to validate the calculated results by comparing the calculated structure factors with those of experimental results. Both the calculated and experimental structure factors of AsS melts under different pressures are shown in Fig. 2 where the excellent agreements between calculated and experimental structure factors in the first peak and the left shoulder are observed.

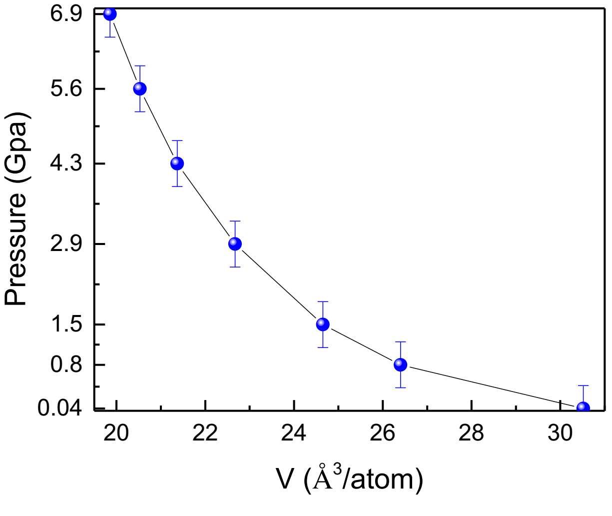

Fig. 1. pressure as a function of volume for AsS melt at 1073 K.

3.2. Pair correlation functions

To get the local structure information of AsS melt, partial pair correlation functions ($g_{AsAs}(r)$, $g_{AsS}(r)$ and $g_{SS}(r)$) of AsS melts are calculated and shown in Fig. 3. For comparison, the partial pair correlation functions of crystal As_4S_4(II) which is obtained by quenching the AsS melt [20] are also shown in Fig. 3. The first and second peak positions of $g_{\alpha\beta}(r)$ of AsS melt at ambient pressure (0.04 GPa) are consistent with those of crystal As_4S_4(II). For $g_{AsAs}(r)$, both the first peak and the first minimum positions are nearly invariant under compression, while its first peak height decreases and the first minimum becomes shallow with increasing the external pressure evidently. For the $g_{AsS}(r)$, its first peak position don not shifts under compression, the first peak height is reduced apparently with increasing pressure. As pressure less than 2.9 GPa, The first minimum and second peak in $g_{AsS}(r)$ are visible, but both of them disappear as the pressure above 2.9 GPa. As for $g_{SS}(r)$, its first peak shifts to the left hand, and the small hump located around 2.0 Å which means some S atoms are in molecular state (the S—S bond length is about 2.05 Å in S_8 state [21]) fades away with increasing pressure. The first peak and minimum positions of $g_{SS}(r)$ are nearly identical to those of the second peak and minimum of $g_{AsAs}(r)$ and $g_{AsS}(r)$, respectively. This means that the first shell of S is only occupied by As atoms similar to that of crystal As_4S_4(II). Apparent variations of $g_{\alpha\beta}(r)$ in Fig. 3 imply the liquid structure change in AsS melt under compression. By checking the nearest neighbor distance of $g_{\alpha\beta}(r)$ [the first-peak positions of $g_{\alpha\beta}(r)$, $r_{\alpha\beta}$], we cannot get explicit changing trends for r_{AsS} and r_{AsAs}. As for r_{SS}, its value decreases equably with increasing pressure which is very different from that of previous report [22]. We found that the changing trends of $g_{SS}(r)$ and $g_{AsAs}(r)$ in Ref 22 are in reverse order with our present results. Especially for $g_{SS}(r)$, it is illogical that the first peak of $g_{SS}(r)$ becomes much broader and shifts to larger r with increasing pressure in AsS melt which also conflict with the calculated results of liquid As_2S_3 published early by the identical author

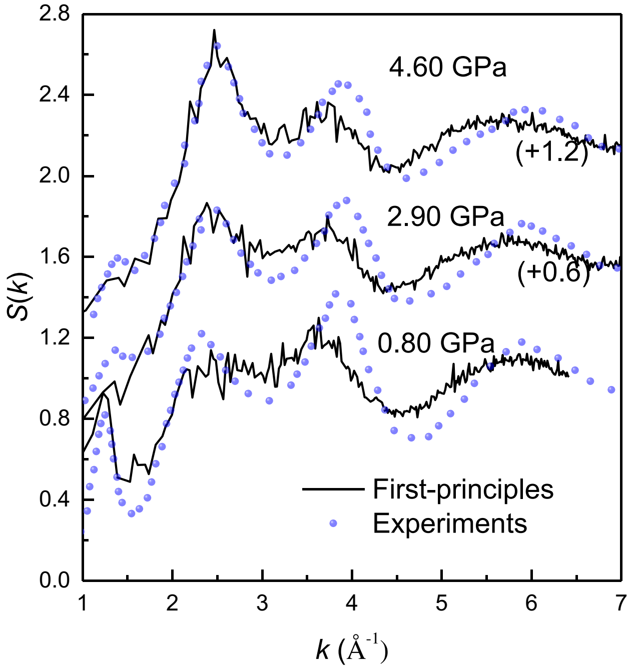

Fig. 2. Calculated total structure factors of AsS melts compared with experimental results.