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Ab initio molecular dynamics simulations of structural change in liquid $Se_{30}Te_{70}$ from low- to high-density phases

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ABSTRACT

The temperature dependence of atomic and electronic structures in liquid $Se_{30}Te_{70}$ is studied using *ab initio* molecular dynamics simulations. Our work verifies the structural change from low- to high-density phases observed in experiments. Moreover, we show that the structure of low-density liquid is an open twofold coordinated chain structure, which can be discussed by Peierls distorted local structures around both Se and Te atoms, and that of high-density liquid is a denser threefold coordinated structure. The structural change is due to the increasing interchain charge transfer with increasing temperature, which causes the breakup of Peierls distorted local structure. Our work also presents that a higher temperature is needed to destroy the Peierls distorted local structures around Se atoms than that around Te atoms. Thus, with increasing Se concentration in liquid Se_xTe_{1-x}, the percent of Peierls distorted local structures around Se atoms gradually increases and the structural change moves toward higher temperature. These results suggest that the collapse of the open atomic configuration plays an important role in the structural change in liquid Se–Te alloy, which shows a rough resemblance to that in liquid P and supercooled H_2O.

1. Introduction

It has been a widely accepted conventional view that the liquid structure varies gradually with temperature and/or pressure from the melting point to the critical point. However, growing evidences indicate that certain liquids such as P, C, H_2O, Si, S, Se, Te, and Ge–Te, Se–Te alloys can exist in phases with identical composition but different density and structure [1–15], and can undergo a liquid–liquid phase transition called polyamorphism during compression or quenching. Like the existence of a liquid–gas critical point, the liquid–liquid phase transition is also expected to terminate at a critical point in the P–T space, beyond which the high-density liquid (HDL) and low-density liquid (LDL) phases become indistinguishable. However, in liquid–liquid phase transition, the transition lines in the P–T space separating the stability regions for HDL and LDL phases usually have a negative Clapeyron slope, although exceptions are known to exist [16].

Density is considered to be the most important order parameter associated with liquid–liquid phase transitions or polyamorphism. If the liquid–liquid critical point is above the melting point, the phase transition exists in stable liquid state [17] and the isobaric density would abruptly decrease at transition temperature with lowering temperature. A well-document example is that the isobaric density of liquid P decreases about 35% at transition temperature when the pressure is 0.7 GPa [1–3]. However, in the case of glass-forming liquids, if the liquid–liquid critical point is located below the melting point, then the phase transition can be observed only in the supercooled liquid or amorphous glassy state [17]. In this case, the isobaric density of the liquid or glass is expected to go through a maximum followed by a minimum on lowering temperature [16]. Thermodynamic relations then predict that thermal expansion coefficient α_P, specific heat C_p, and isothermal compressibility K_T are all expected to go through a maximum at an intermediate temperature somewhere between those corresponding to the two density extrema [16]. Therefore, the anomalous temperature dependence of density and thermal expansion can serve as useful indicators of the existence of such phase transitions in the supercooled liquid or glassy state. Such as liquid H_2O, the maximum density occurs at 277 K, recent experimental studies have indicated the existence of high-density and low-density amorphous (HDA and LDA) phase transitions in amorphous H_2O [18]. Also, the results of neutron diffraction experiment imply a continuous transformation with increasing pressure from a low-density form of water to a high-density form of water at a temperature of 268 K [7]. The isobaric density

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extrema have also been observed in vitreous SiO_2, suggesting the existence of a polyamorphic phase transition in silica with a negative Clapeyron slope [19].

Besides H_2O and vitreous SiO_2, isobaric density extrema and the associated thermodynamic anomalies characteristic of liquid–liquid phase transition have also been experimentally observed in liquid Se–Te alloys [15]. For example, in liquid $Se_{30}Te_{70}$, the maximum and minimum of isobaric density are located at 933 and 673 K, respectively, and the maximum of α_P occurs at 773 K. Also, it should be mentioned that, at around 773 K, liquid $Se_{30}Te_{70}$ undergoes a semiconductor-metal (SC-M) transition observed in experiments [15]. With the increase of Se concentration, the transition temperature of liquid Se–Te alloy moves toward higher temperature. In the last 20 years, the analysis of the SC-M transition has been the focus of a large number of research papers. It is generally accepted that the SC-M transition is related to the structural change. In liquid–liquid phase transition of liquid P [1–3] and supercooled liquid H_2O [7] mentioned above, the collapse of the open tetrahedral atomic configuration plays an important role. However, the structural details of this transition from low-density to high-density liquid Se–Te alloys have so far been controversial. The density measurements for liquid Se–Te alloy [20] have shown a structural change from a Se-like loosely packed structure to a Te-like densely packed structure. Many neutron diffraction measurements [21] have indicated that this transition is a structural transition from a chain structure to a threefold coordinated one. However, Magana and Lannin [22] have carried out Raman measurements for liquid $Se_{30}Te_{70}$ and suggested that the effect of temperature is not one of changing the structure but rather of increasing disorder within chains.

Thus, to clarify these controversies about structural change from low- to high-density liquid Se–Te alloys, detailed investigations of the structural changes in the atomistic level are demanded. *Ab initio* calculation is an effective method to study the atomic and electronic structure of liquid metals and alloys from the first-principles perspective. Over the past several decades, *ab initio* calculations have been performed on many liquids, giving much useful information about microscopic structure of liquid metals and alloys [2,10,11,23]. However, to our knowledge, in contrast with the large number of *ab initio* investigations dedicated to pure liquid Se and Te [24–27], there is no *ab initio* calculations on the temperature-dependence of atomic and electronic properties in liquid Se–Te system, although the concentration-dependence of the microscopic structure and dynamics of liquid Se–Te alloys have been investigated [28].

The aim of the present work therefore was to verify the previous experimental work that indicates a structural change from low-density to high-density liquid $Se_{30}Te_{70}$ by *ab initio* molecular dynamics simulations, and to uncover the local atomic arrangements that occur in these two forms of liquid $Se_{30}Te_{70}$. Furthermore, we hope to find out the mechanism of the structural change associated with the SC-M transition in liquid Se–Te by understanding the microscopic atomic structure. It has been proved that *ab initio* technique is successful to great extent in modeling the structural and dynamic properties of liquid Se_xTe_{1-x} [28]. The paper is organized as follows: in Section 2, we describe the method of simulations; the results and corresponding discussions are reported in Section 3; a conclusion is given in Section 4.

2. Computational methods

Our density function theory (DFT) based calculations were performed in the generalized gradient approximation (GGA) using the Perdew and Wang [29,30] functional and the PAW [31,32] potentials as implemented in the VASP code [33]. Our canonical ensemble simulations were performed at six different temperatures from 613 to 1173 K with a Nosé thermostat for temperature control [34]. At each temperature the experimental atomic number densities [15] were used: 26.85 (613 K), 26.68 (673 K), 26.79 (733 K), 27.36 (833 K), 27.59 (973 K), 27.07 (1173 K) atoms/nm^3. We found that the calculated pressure at each temperature is close to zero and in the simulated temperature range from 613 to 1173 K the pressure difference is smaller than 0.95 kbar. We believe such a small pressure difference in our simulations will not bring significant errors for the comparison of structural properties at different temperatures. The system (24 Se+56 Te) was put in a simple cubic box with periodical boundary conditions. The Γ point was used to sample the Brillouin zone of the supercell. To check the *k*-point convergence on selected disordered structure, we have performed a fully converged calculation with a grid of $4\times4\times4k$ points (64*k* points). When Γ point is used, compared to a fully converged calculation with 64*k* points, the absolute error of average binding energy of per atom is 0.005 eV and the relative error is 0.002. The average binding energy is the average of potential energy for the 80 atoms system over 2000 configurations. We believe that such an error does not hamper our analysis on the temperature dependence of the structural properties of liquid $Se_{30}Te_{70}$. The electronic wave functions were expanded in the plane wave basis set, with an energy cutoff of 175 eV. The Verlet algorithm was used to integrate Newton's equations of motion and the time step of ion motion was 4 fs. A larger time step of 4 fs does not affect the simulated liquid structure as is evident from comparing our calculated structure factor with experimental results (shown in Fig. 1a).

The initial atomic configuration adopted was a random distribution of 80 atoms on the grid, which was constructed by dividing the supercell into $5\times5\times5$ square segments. At first, the system was heated up to 1373 K. After a run of 12 ps at this temperature, the system arrived at a hot liquid state. Whereafter, the hot liquid was gradually decreased to 1173 K and then the volume was adjusted to experimental value by scaling the box size manually. We noticed that the liquid was not in equilibrium after the box was adjusted. In order to obtain an equilibrium liquid at 1173 K, the equilibration time was performed for 4 ps. Then, the physical quantities of interest were obtained by averaging over another 8 ps period in which the energy conservation is excellent and the drift is smaller than 0.13 meV/atom/ps. For other temperatures, we only repeated this procedure and changed the final temperature into 973, 833, 733, 673, and 613 K, respectively.

3. Results and discussions

The structure factor $S(Q)$ is an important physical quantity, serving as a connection with experimental results. To compare with experimental results, the calculated $S(Q)$ at 733 K obtained by direct configuration sampling from the simulations and by Fourier transformation of the pair distribution function $g(r)$ are presented in Fig. 1(a), together with the experimental results at 748 K [28]. One can observe that Fourier transformed $S(Q)$ agrees completely with that obtained by direct configuration sampling, indicating that the errors in the calculation of Fourier transformed $S(Q)$ on our simulation box are negligible. More significant is the relatively good agreement between experiment and simulation except for a certain phase shift in the large-Q oscillations. As demonstrated in Ref. [28], this is most likely connected with the overestimation of the nearest neighbor distance in trigonal Te by