Temperature dependence of the atomic structure of liquid As_2Se_3: *ab initio* molecular dynamics simulations

Temperature dependence of the atomic structure of liquid As₂Se₃: *ab initio* molecular dynamics simulations

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Abstract. The structural and electronic properties of liquid As_2Se_3 mixtures are studied by *ab initio* molecular dynamics simulations. We detail the temperature dependence of the atomic structure by calculating the correlation functions in a real space as well as in a reciprocal space. It is found that the network structure changes to a chain-like structure by bond breaking with increasing temperature, and that there are triangular atomic configurations in the chain-like structure at higher temperatures. We also investigate the relation between the semiconductor–metal transition and the structural change.

1. Introduction

The structure of solid arsenic triselenide consists of As_2Se_3 layers, which are parallel to the (010) plane [1]. In each layer, AsSe spiral chains parallel to the *c*-axis are connected by Se atoms (see figure 1). Each As atom is surrounded by three Se atoms, and each Se atom is surrounded by two As atoms. On melting, the short-range atomic arrangement in the solid is preserved [2], though the layer structure is disrupted. In the liquid phase, the As and Se atoms have basically threefold and twofold coordinations, respectively, and the heterocoordination is preferred. The electronic structure of this liquid mixture is semiconducting in character near the triple point due to the preservation of a covalent bonding [3].

The optical absorption measurement [4] revealed that the optical gap decreases rapidly with increasing temperature and it vanishes at about 1000 °C. This means that liquid As_2Se_3 has metallic properties above that temperature. X-ray diffraction [5] and extended x-ray absorption fine-structure (EXAFS) [6] measurements showed that the local environment around the As atom changes substantially and As–As covalent bonds are formed when the semiconductor–metal (SC–M) transition occurs in liquid As_2Se_3. The electrical conductivity and thermoelectric power of liquid As–Se mixtures were also measured for a wide range of temperature and pressure including the SC–M transition [7].

Recently, we have carried out *ab initio* molecular dynamics (MD) simulations for liquid As_2Se_3 to investigate the microscopic mechanism of metallization [8]. It is found that, with increasing temperature, As atoms which have twofold coordination increase, and p-like non-bonding states that are almost half-filled are generated around the twofold-coordinated As atoms, which causes the metallic state.

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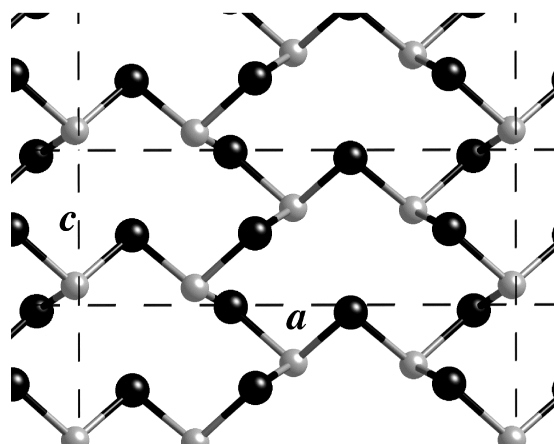
Figure 1. The atomic configuration in one layer of crystalline As_2Se_3 (projected on the (010) plane). The grey and black balls show the positions of As and Se atoms, respectively. The dashed lines show the unit cell as well as the c- and a-axes.

In this paper, we detail the results of our *ab initio* MD simulations for liquid As_2Se_3 mixtures. We focus mainly on the temperature dependence of the atomic structure, and discuss the structural change in connection with the microscopic mechanism of the SC–M transition. In section 2, the method of *ab initio* MD simulations used here is briefly described. The results of our simulations and discussions are given in section 3. Finally we summarize our work in section 4.

2. Method of calculation

Our calculations were performed within the framework of the density functional theory, in which the generalized gradient approximation [9] was used for the exchange–correlation energy. The electronic wavefunctions were expanded in the plane-wave (PW) basis set. The energy functional was minimized using an iterative scheme based on the preconditioned conjugate-gradient method [10–12]. For the valence electron–ion interaction, we used the ultrasoft pseudopotentials [13] obtained from the electronic structure calculations for $As(4s^2 4p^3 4d^0)$ and $Se(4s^2 4p^4 4d^0)$ atoms. The scheme for the pseudization of the wavefunctions and that for the calculation of the augmentation functions are described in reference [14]. The PW cut-off energies for the wavefunctions and the charge density are 11 and 55 Ryd, respectively.

To check the accuracy of our method, we have applied it to As_2 and Se_2 dimers. The bond length r_e and the vibrational frequency ω_e were obtained as $r_e = 2.12$ Å and $\omega_e = 432$ cm^{-1} for As_2, and $r_e = 2.19$ Å and $\omega_e = 379$ cm^{-1} for Se_2, which are in good agreement with the experimental values [15], $r_e = 2.10$ Å and $\omega_e = 430$ cm^{-1} for As_2, and $r_e = 2.17$ Å and $\omega_e = 385$ cm^{-1} for Se_2.

In the simulation of liquid As_2Se_3, we used the cubic supercell which contains 80 atoms (32 As + 48 Se). The simulations were carried out for four thermodynamic states; the temperatures and densities are (800 K, 4.30 g cm^{-3}), (1000 K, 4.19 g cm^{-3}), (1300 K, 4.03 g cm^{-3}), and (1700 K, 3.95 g cm^{-3}), which are taken from the experiment [5]. Using the Nosé–Hoover thermostat technique [16], the equations of motion were solved via the velocity Verlet algorithm with a time step $\Delta t = 2.2$–3.1 fs. The Γ point was used for the Brillouin zone
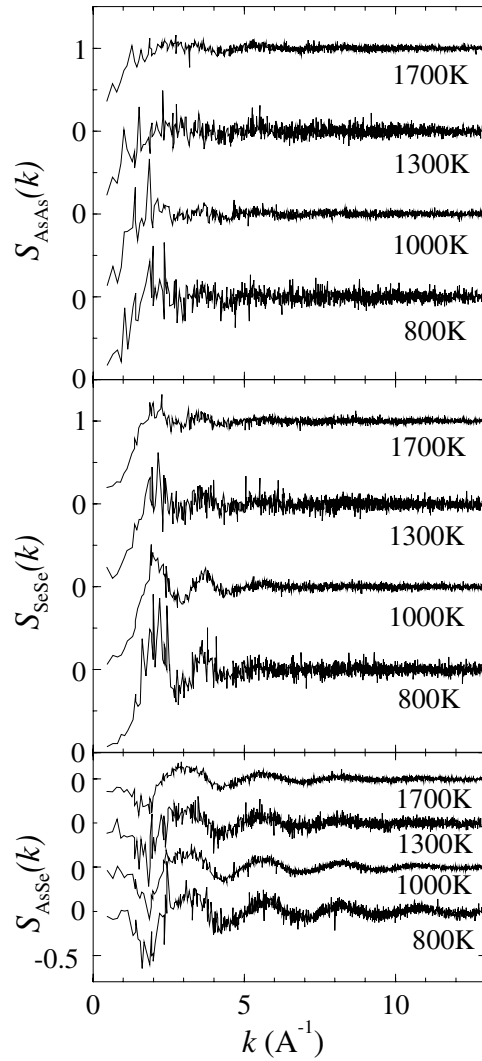
Figure 2. The temperature dependence of the Ashcroft–Langreth partial structure factors $S_{\alpha\beta}(k)$ of the liquid As$_2$Se$_3$ mixture.

sampling. The quantities of interest were obtained by averaging over 5.5 ps after the initial equilibration taking 3 ps.

3. Results

3.1. Structure factors

In this section, we investigate the temperature dependence of the atomic structure in a reciprocal space. The Ashcroft–Langreth partial structure factors [17] $S_{\alpha\beta}(k)$ are defined as

$$S_{\alpha\beta}(k) = (N_\alpha N_\beta)^{-1/2} \left[\left\langle \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \exp\left\{-i\mathbf{k} \cdot (\mathbf{r}_{\alpha i} - \mathbf{r}_{\beta j})\right\} \right\rangle - (N_\alpha N_\beta)^{1/2}\delta_{k,0} \right] \tag{1}$$

where N_α is the total number of α-type atoms, and $\boldsymbol{r}_{\alpha i}$ is the position of ith α-type atom. It is seen, from figure 2, that the $S_{\mathrm{AsAs}}(k)$ is structureless at any temperatures, although there is a broad peak around $k = 2$ Å^{-1} at lower temperatures. In the $S_{\mathrm{SeSe}}(k)$, the first and second peaks are clearly seen at $k = 2$ and 3.5 Å^{-1}, respectively, at the lower temperatures, while these peaks become unclear with increasing temperature. $S_{\mathrm{AsSe}}(k)$ has a negative dip at $k = 1.8$ Å^{-1} and oscillating behaviour over a wide range of k. These structures in the $S_{\mathrm{AsSe}}(k)$ remain even at higher temperatures. The total structure factors $S(k)$ calculated from the $S_{\alpha\beta}(k)$ using the atomic scattering factors for x-rays [18] are in good agreement with the experimental results [5] as was shown in figure 1 of reference [8]. While $S_{\mathrm{SeSe}}(k)$ and $S_{\mathrm{AsAs}}(k)$ give the first peak at 2.5 Å^{-1} and the second peak at 3.5 Å^{-1} of $S(k)$, $S_{\mathrm{AsSe}}(k)$ causes the oscillating behaviour at $k > 5$ Å^{-1} in $S(k)$.

The Bhatia–Thornton concentration–concentration structure factor [19] is defined as

$$S_{CC}(k) = c_{\mathrm{As}} c_{\mathrm{Se}} \left\{ c_{\mathrm{Se}} S_{\mathrm{AsAs}}(k) + c_{\mathrm{As}} S_{\mathrm{SeSe}}(k) - 2(c_{\mathrm{As}} c_{\mathrm{Se}})^{1/2} S_{\mathrm{AsSe}}(k) \right\} \tag{2}$$

where c_{As}, c_{Se} are the concentrations of As and Se atoms, respectively. In figure 3, the $S_{CC}(k)$ for liquid As$_2$Se$_3$ for four temperatures are presented. Due to the contribution from the dips of the $S_{\mathrm{AsSe}}(k)$, the positions of the first and second peaks of $S_{CC}(k)$ are about 2.0 and 4.0 Å^{-1}, respectively, which are slightly different from the peak positions of the $S(k)$. The first peak of $S_{CC}(k)$ is large when the temperature is low, and becomes broader with increasing temperature.
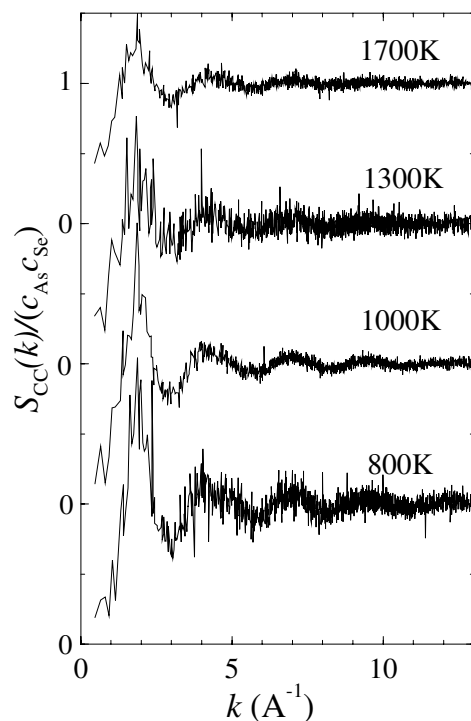

Figure 3. The temperature dependence of the Bhatia–Thornton concentration–concentration structure factor $S_{CC}(k)$ of the liquid As$_2$Se$_3$ mixture.
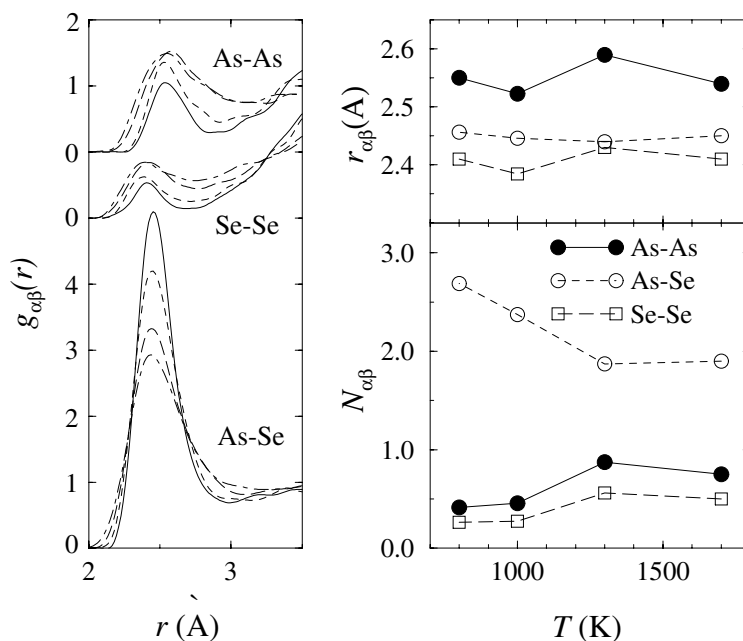
Figure 4. The temperature dependence of (a) the partial pair distribution functions $g_{\alpha\beta}(r)$, (b) the first-peak positions $r_{\alpha\beta}$ of the $g_{\alpha\beta}(r)$, and (c) the coordination numbers $N_{\alpha\beta}$ of the liquid As₂Se₃ mixture.

3.2. Pair distribution functions

Figure 4(a) shows the partial pair distribution functions $g_{\alpha\beta}(r)$ of liquid As₂Se₃ for four temperatures. The temperature dependences of the first-peak positions $r_{\alpha\beta}$ of $g_{\alpha\beta}(r)$ and the coordination numbers $N_{\alpha\beta}$ are shown in figures 4(b) and 4(c), respectively. $N_{\alpha\beta}$ is the average number of nearest-neighbour β-type atoms around an α-type atom, and is calculated as $2\rho_\beta \int_0^{r_{\alpha\beta}} 4\pi r^2 g_{\alpha\beta}(r)\,dr$ with ρ_β being the number density of β-type atoms. We see that the value of r_{AsAs} is larger than those of r_{AsSe} and r_{SeSe}. Since the difference between r_{AsSe} and r_{SeSe} is quite small, it would be hard to distinguish between them by experimental measurements. In fact, the appearance of As–As bonds was observed by EXAFS measurement [6], though Se–Se bonds were not observed. Since $r_{\alpha\beta}$ corresponds to the bond length between α- and β-type atoms, it is natural that $r_{\alpha\beta}$ depends weakly on the temperature. On the other hand, the temperature dependence of $N_{\alpha\beta}$ is noticeable as is seen in figure 4(c). With increasing temperature, N_{AsSe} decreases from about 3 at 800 K to about 2 at 1300 K, and $N_{\alpha\beta}$ for like atoms increases slightly. This behaviour is understandable because the As and Se atoms are distributed more randomly in the network structure at higher temperatures. It is, however, interesting to notice that the $N_{\alpha\beta}$ do not decrease monotonically, but remain almost unchanged when the temperature is increased from 1300 K to 1700 K.

3.3. Coordination number distribution functions

The coordination number (n) distribution function $P_\alpha(n)$ is defined as the probability of finding n atoms around an α-type atom. In a similar way, $P_{\alpha\beta}(n)$ is defined as the probability of finding n β-type atoms around an α-type atom. We calculated $P_\alpha(n)$ and $P_{\alpha\beta}(n)$ simply by counting the number of atoms inside a sphere of radius R centred at each α-type atom. We used $R = 2.7$ Å.

Note that the $P_\alpha(n)$ and $P_{\alpha\beta}(n)$ are normalized as

$$\sum_n P_\alpha(n) = 1 \qquad \text{and} \qquad \sum_n P_{\alpha\beta}(n) = 1.$$

The $P_\alpha(n)$ and $P_{\alpha\beta}(n)$ are displayed in figure 5. While $P_{As}(n)$ has a peak at $n = 3$ when the temperature is below 1000 K, more twofold-coordinated As atoms exist than threefold-coordinated ones at 1300 and 1700 K. This is caused by the fact that the number of Se atoms around As atoms decreases as shown in figure 5(d); $P_{AsSe}(3)$ decreases, $P_{AsSe}(2)$ remains almost unchanged, and $P_{AsSe}(1)$ increases. From the temperature dependence of $P_{Se}(n)$, we see that, with increasing temperature, twofold-coordinated Se atoms decrease and onefold-coordinated Se atoms increase in number, because the number of As atoms around Se atoms decreases as shown in figure 5(e). $P_{Se}(2)$ has the largest value at all temperatures, which is consistent with the fact that the chalcogen atoms are likely to form a twofold chain-like structure. As observed in the temperature dependence of the coordination numbers $N_{\alpha\beta}$, the probability of finding like atoms around each atom increases with increasing temperature as shown in figures 5(c) and 5(f), although more than half of the atoms have no neighbouring like atom. It should be emphasized that, in the distribution of the $P_\alpha(n)$ at higher temperatures, $P_\alpha(2)$ has the largest values for both As and Se atoms, which means that the major part of this liquid mixture consists of twofold chain-like structures. Note also that $P_{Se}(1)$ has fairly high values, implying that the chains are terminated by Se atoms.
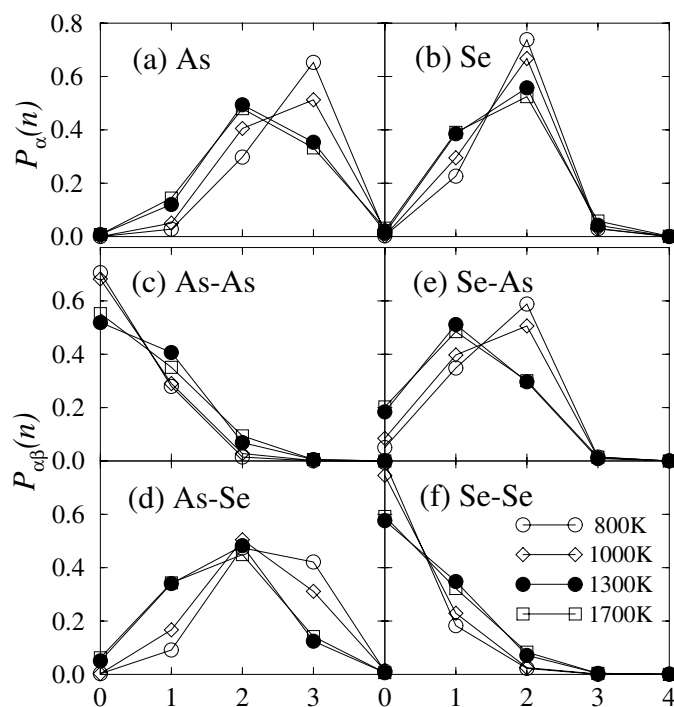

Figure 5. The temperature dependence of the coordination number (n) distribution functions $P_\alpha(n)$ for $\alpha =$ (a) As and (b) Se, and $P_{\alpha\beta}(n)$ for α–$\beta =$ (c) As–As, (d) As–Se, (e) Se–As, and (f) Se–Se of the liquid As_2Se_3 mixture.

3.4. Three-body bond-angle distribution functions

The three-body bond-angle distribution function $B_{\alpha\beta\gamma}(\theta)$ is defined as the probability of finding the three-body bond angle between θ and $\theta + \Delta\theta$. To obtain the $B_{\alpha\beta\gamma}(\theta)$, we found α- and γ-type atoms inside a sphere of radius R centred at each β-type atom, and the three-body bond angles around each β-type atom were calculated. Figure 6 shows the temperature dependence of the $B_{\alpha\beta\gamma}(\theta)$, which are normalized with the integral of the $B_{\alpha\beta\gamma}(\theta)$ over the angle θ proportional to the total number of the triplet $\alpha-\beta-\gamma$ in liquid mixtures. From figures 6(b) and 6(d), the $B_{\alpha\beta\gamma}(\theta)$ for 'correct' Se–As–Se and As–Se–As distribute triplets from 60° to 140° with a peak around 100°, which should be compared with bond angles in the solid phase: 93–105° around As atoms and 86–92° around Se atoms. The $B_{\alpha\beta\gamma}(\theta)$ for other triplets also have a peak around 100° at 800 K, and spread over a wider range of angle at higher temperatures. It is interesting to note that, with increasing temperature, another peak at 60° in the $B_{\alpha\beta\gamma}(\theta)$ grows when at least one of the three atoms is As. This means that those three atoms form triangles in liquid mixtures. When the temperature increases, the network structure changes to a chain-like structure by bond breaking. Since As atoms prefer threefold coordination to lower ones, the triangle structure would be formed so as to have threefold coordination locally in a single chain.
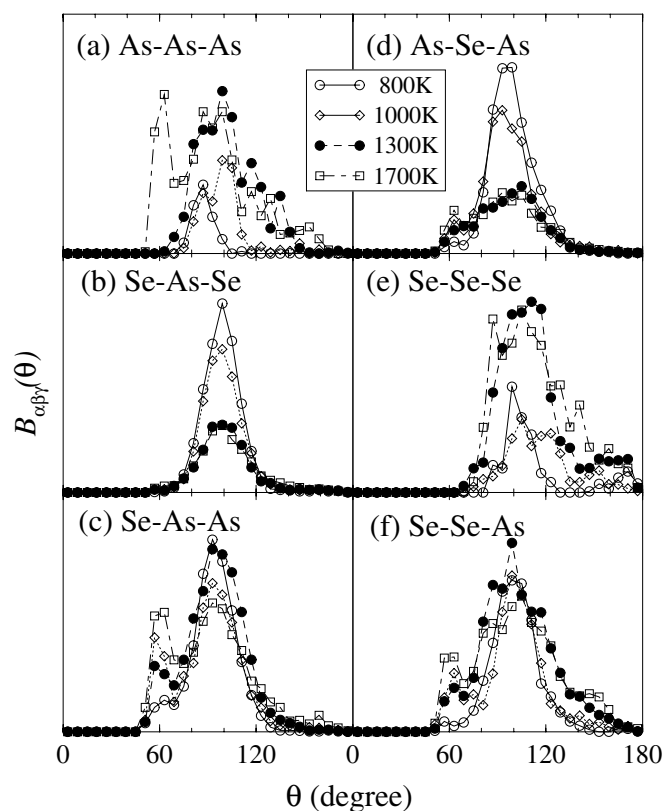

Figure 6. The temperature dependence of the three-body bond-angle distribution functions $B_{\alpha\beta\gamma}(\theta)$ of the liquid As$_2$Se$_3$ mixture.
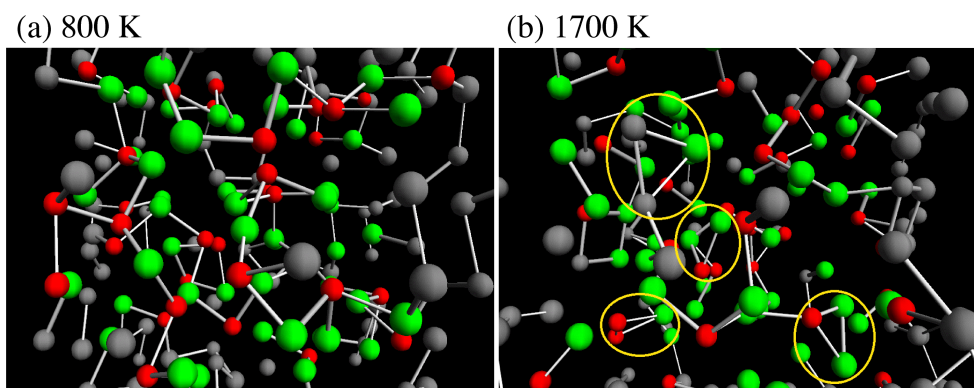
Figure 7. Atomic configurations of the liquid As_2Se_3 mixture for two temperatures: (a) 800 and (b) 1700 K. The red and green balls show the positions of As and Se atoms, respectively, in the supercell. The grey balls show the positions of image atoms outside the supercell. Two atoms, whose distance apart is smaller than 2.7 Å, are connected by the bond. The yellow circles in (b) indicate the triangle structures at high temperatures.
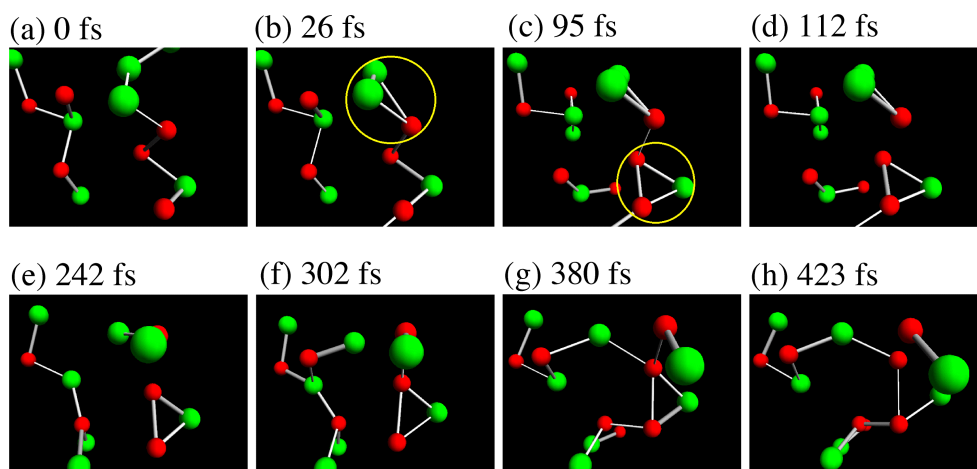

Figure 8. The time evolution of local atomic configurations at 1700 K. The red and green balls show the positions of As and Se atoms, respectively. Two atoms, whose distance apart is smaller than 2.7 Å, are connected by the bond. The yellow circles show the new triangle structures.

3.5. Spatial atomic configurations

The features in the temperature dependence of the atomic structure stated above are confirmed by directly viewing the atomic configuration. Snapshots of the atomic configurations for two temperatures, 800 and 1700 K, are shown in figures 7(a) and 7(b), respectively. The red and green balls show the positions of As and Se atoms, respectively, in the supercell. The grey balls show the positions of image atoms outside the supercell. Two atoms, whose distance apart is smaller than 2.7 Å, are connected by the bond.

It is seen from figure 7(a) that, at 800 K, the As and Se atoms have mainly threefold and twofold coordinations, respectively, and the heterocoordinations are preferred to the homocoordinations, which means that the liquid has the three-dimensional network structure.

On the other hand, at 1700 K, both As and Se atoms have mainly twofold coordination as shown in figure 7(b), indicating that the liquid has the chain-like structure. We can see that most of the chains are terminated by Se atoms. As described in the previous section, there are triangle structures at high temperatures, which are indicated by the yellow circles in figure 7(b). The lifetime of such triangle structures is less than several hundreds of fs.

To see how the triangle structures are formed at high temperatures and how the atomic structure evolves with time, we examine the local structure at 1700 K as a function of time and show a typical example in figure 8, where the red and green balls show the positions of As and Se atoms, respectively. In figure 8(a), two chains are shown. We focus on the right-hand chain in which there are both Se–Se and As–As bonds. After 26 fs, a triangle structure, which includes one As atom and two Se atoms, appears in the right-hand chain as indicated by a yellow circle in figure 8(b), and the As atom at the corner of the triangle becomes threefold coordinated. At 95 fs, another triangle structure appears in the same chain as indicated by a yellow circle in figure 8(c). In this case, the triangle is formed by two As atoms and one Se atom. At this configuration, three As atoms in the chain focused on are threefold coordinated. It is interesting that bonds connecting these triangles are broken and two isolated triangles appear as shown in figures 8(d) and 8(e). At about 300 fs, just after two triangles are connected with each other by forming a new As–As bond, one of them (the upper triangle) deforms its structure (figure 8(f)). At 380 fs, two new bonds are formed so as to associate the triangle with the left-hand chain; in figure 8(g), we can see one fourfold-coordinated As atom as well as twofold- and threefold-coordinated ones. Since the fourfold-coordinated As is not stable, rearrangement of the atomic configuration must take place as displayed in figure 8(h). At this final configuration, no triangle structure exists. Thus we can consider the local triangle structure as a transient local structure, which appears during the structural change of the chain structure.

3.6. Relation between the structural change and the SC–M transition

As described in the previous paper [8], the system that we have simulated by *ab initio* MD simulations has semiconducting and metallic properties at lower and higher temperatures, respectively, which is in agreement with the experimental observations [4]. In this section, we discuss the relation between the SC–M transition and the temperature dependence of the atomic structure.

To investigate the electronic structure near the Fermi level E_F, we calculated the partial electronic densities of states (DOS) $D_\alpha(E)$ [8] for the As and Se atoms, and decomposed the $D_\alpha(E)$ with respect to the coordination number as shown in figure 9. From this figure, we see that the dips in the $D_\alpha(E)$ at E_F are gradually filled up with increasing temperature, and the contributions to $D_\alpha(E)$ from lower-coordinated atoms precede those from higher-coordinated atoms for increasing value at E_F. This fact clearly indicates that the electronic states around lower-coordinated atoms are important for the metallization.

Figure 10 shows the spatial distribution of the electronic wavefunctions with the eigenenergies near E_F as well as the chain-like atomic configurations. We can see that the electronic wavefunctions have a large amplitude around the twofold-coordinated As (indicated by arrows in figure 10) and Se atoms. This spatial distribution is similar to that of the p-like non-bonding orbitals in liquid chalcogens [20]. As shown in figure 10, the electronic wavefunctions also have an amplitude around the onefold-coordinated atoms, i.e. the ends of chains, which is related to the stabilization of antibonding states by the bond breaking as was discussed for liquid Se [20].
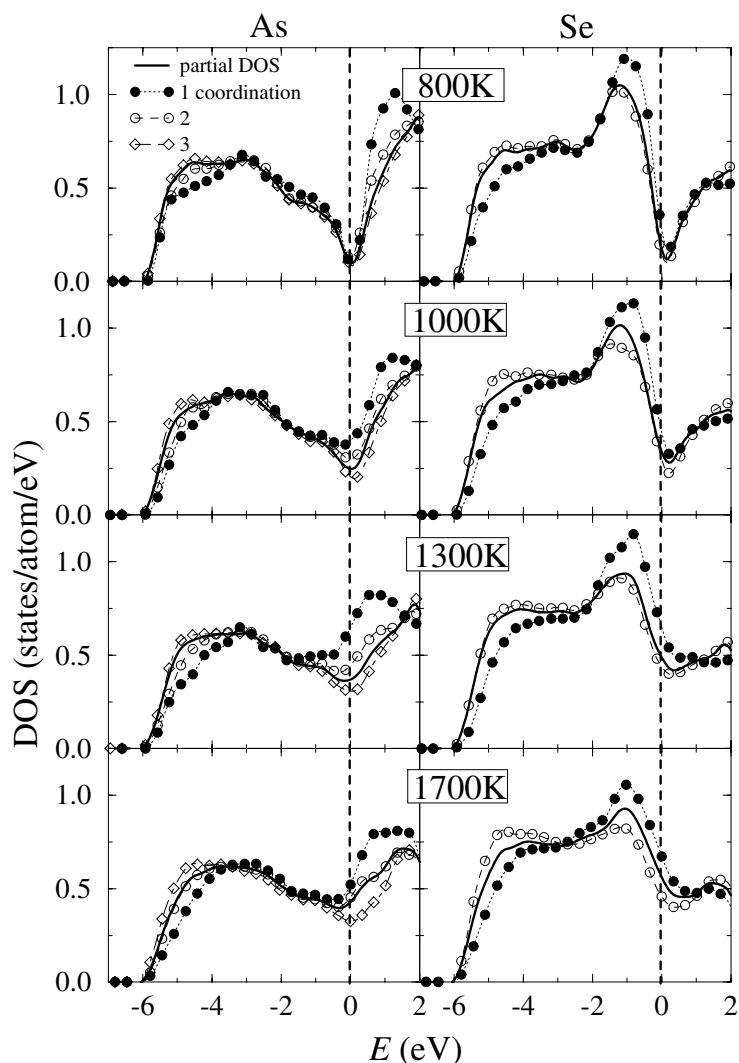
Figure 9. The temperature dependence of the electronic density of states (DOS) of the liquid As_2Se_3 mixture. The solid line shows the partial DOS for As atoms (left-hand portion) and for Se atoms (right-hand portion). The solid circles, open circles, and diamonds show the partial DOS corresponding to onefold-, twofold-, and threefold-coordinated atoms, respectively. The origin of the energy is taken to be the Fermi level ($E_F = 0$).

4. Summary

The structural and electronic properties of liquid As_2Se_3 mixtures have been investigated by *ab initio* molecular dynamics simulations. We have detailed the temperature dependence of the atomic structure by calculating the correlation functions in the real space as well as in the reciprocal space. The coordination number (n) distribution function $P_\alpha(n)$ gives us highly detailed information about the local atomic configuration; $P_\alpha(2)$ has the largest values for both As and Se atoms at higher temperatures, which means that the major part of this liquid mixture consists of twofold chain-like structures. By investigating the three-body bond-angle
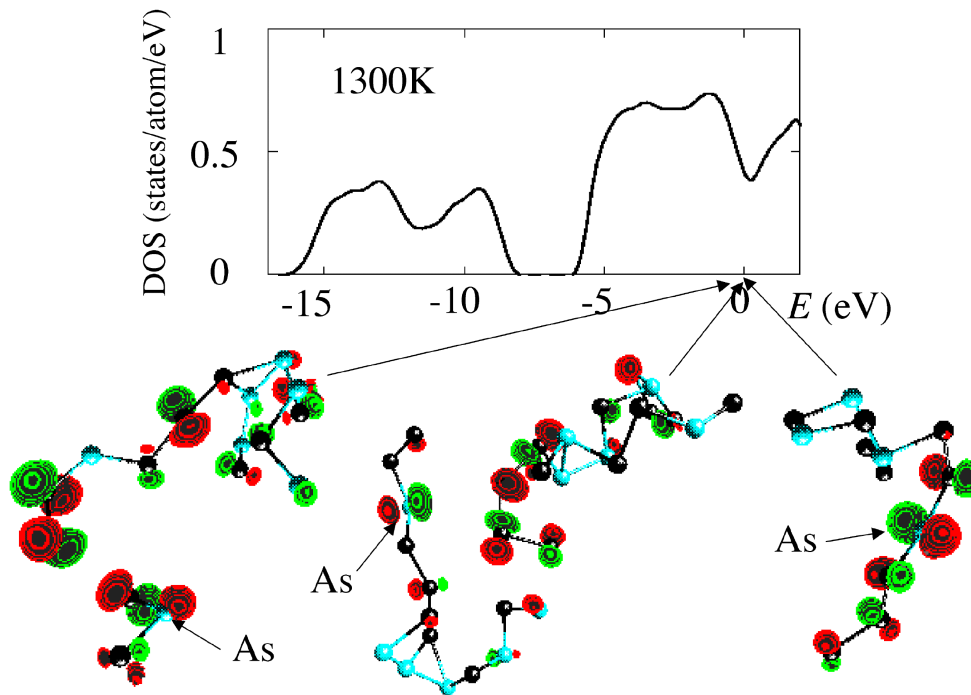
Figure 10. Upper graph: the total electronic density of states of the liquid As$_2$Se$_3$ mixture at 1300 K. Lower illustration: the atomic configuration and spatial distribution of the electronic wavefunctions with the eigenenergies near the Fermi level (the origin of the energy). The blue and black balls show the positions of As and Se atoms, respectively. Two atoms, whose distance apart is smaller than 2.7 Å, are connected by the bond. The green and the red contour curves show the wavefunctions with different signs.

distribution functions, it has been found that there are triangular atomic configurations in the chain-like structure at higher temperatures. We have also investigated the relation between the semiconductor–metal transition and the structural change. From the partial electronic density of states and the spatial distribution of the electronic wavefunctions, it has been clarified that the electronic states around lower-coordinated, i.e. onefold- and twofold-coordinated, atoms are important for the metallization.

Acknowledgments

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