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LETTER TO THE EDITOR

The microscopic mechanism of the semiconductor–metal transition in liquid arsenic triselenideFuyuki Shimojo[†], Shuji Munejiri[†], Kozo Hoshino[†] and Y Zempo[‡][†] Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan[‡] Sumitomo Chemical, 6 Kitahara, Tsukuba 300-3294, Japan

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Abstract. We have clarified the microscopic mechanism of the semiconductor–metal transition in liquid As_2Se_3 with increasing temperature and pressure by means of *ab initio* molecular-dynamics simulations. It is shown that, at higher temperatures, a major part of this liquid mixture consists of twofold chain-like structures, while, at lower temperatures, it mainly has a network structure, where As and Se atoms have threefold and twofold coordinations, respectively. Accompanying this structural change, p-like non-bonding states that are almost half-filled are generated around the twofold-coordinated As atoms, and cause the metallic state of liquid As_2Se_3 .

The liquid phase of chalcogens, such as Se, Te and their mixtures, consists of chain molecules [1]. The electronic properties of these liquids are strongly correlated with their structural features such as the arrangement, the average length, and the dynamics of the chain molecules. Though liquid Se exhibits semiconducting properties near the triple point, a metallic state appears with decreasing density when the temperature and the pressure are increased up to near the critical point [2]. The chain-like structure remains even in the metallic state [3, 4], although the average chain length decreases substantially. This shortening of Se chains is responsible for the metallization as was discussed recently by us [4]. In the case of liquid Te, it exhibits metallic properties near the triple point, since the transition from semiconducting to metallic states occurs in a supercooled liquid state. However, the electrical conductivity σ decreases on adding alkali elements from $2000 \Omega^{-1} \text{cm}^{-1}$ for pure liquid Te to only about $1 \Omega^{-1} \text{cm}^{-1}$ at 50% alkali concentration [5]. We showed that this change in σ occurs because the interchain interactions are suppressed and the Te chains are stabilized by the presence of the alkali elements [6].

In contrast to the liquid chalcogens, which have a chain structure, the liquid-As–chalcogenide mixtures, such as As_2S_3 , As_2Se_3 , and As_2Te_3 , have a three-dimensional network structure [7]; the As and chalcogen atoms have basically threefold and twofold coordinations, respectively, and the hetero-coordination is preferred. The electronic structure of these liquid mixtures is semiconducting in character near the triple point [8]. It was found for the first time by Hosokawa *et al* [9] that a semiconductor–metal (SC–M) transition in liquid As_2Se_3 occurs with increasing temperature and pressure in a similar way to that for the liquid chalcogens. They measured the optical absorption coefficient and found that the optical gap decreases rapidly with increasing temperature and vanishes at about 1000°C . This means that liquid As_2Se_3 has metallic properties above that temperature. To investigate the microscopic mechanism of this SC–M transition, it is very important to clarify how the three-dimensional network structure

changes with temperature and pressure, and how it is related to the change in the electronic structure. For such a purpose, Tamura and collaborators carried out x-ray diffraction [10] and extended x-ray absorption fine-structure (EXAFS) [11] measurements for liquid As_2Se_3 . They found that the local environment around the As atom changes substantially and As–As covalent bonds are formed when the SC–M transition occurs. So far, however, the relation between this structural change and the electronic properties, such as the mechanism of the metallization, has not been well understood, and theoretical study to clarify it is desirable.

In this letter, we investigate the structural and electronic properties of liquid As_2Se_3 by means of *ab initio* molecular-dynamics (MD) simulations. We clarify the temperature dependence of the three-dimensional network structure, and present a clear description of the microscopic mechanism of the SC–M transition.

Our calculations were performed within the framework of the density functional theory, in which the generalized gradient approximation [12] was used for the exchange–correlation energy. We used the ultrasoft pseudopotential [13, 14] for As($4s^24p^34d^0$) and Se($4s^24p^44d^0$). The electronic wavefunctions and the charge density were expanded in plane waves with cut-off energies of 11 and 55 Ryd, respectively. The energy functional was minimized using an iterative scheme [15–17]. The cubic supercell contains 80 atoms (32 As + 48 Se). The simulations were carried out for four thermodynamic states; the temperatures T (K) and densities ρ (g cm^{-3}) are $(T, \rho) = (800, 4.30), (1000, 4.19), (1300, 4.03),$ and $(1700, 3.95)$, which are taken from experiment [10]. Using the Nosé–Hoover thermostat technique [18], the equations of motion were solved with a time step $\Delta t = 2.2\text{--}3.1$ fs. The Γ point was used for the Brillouin zone

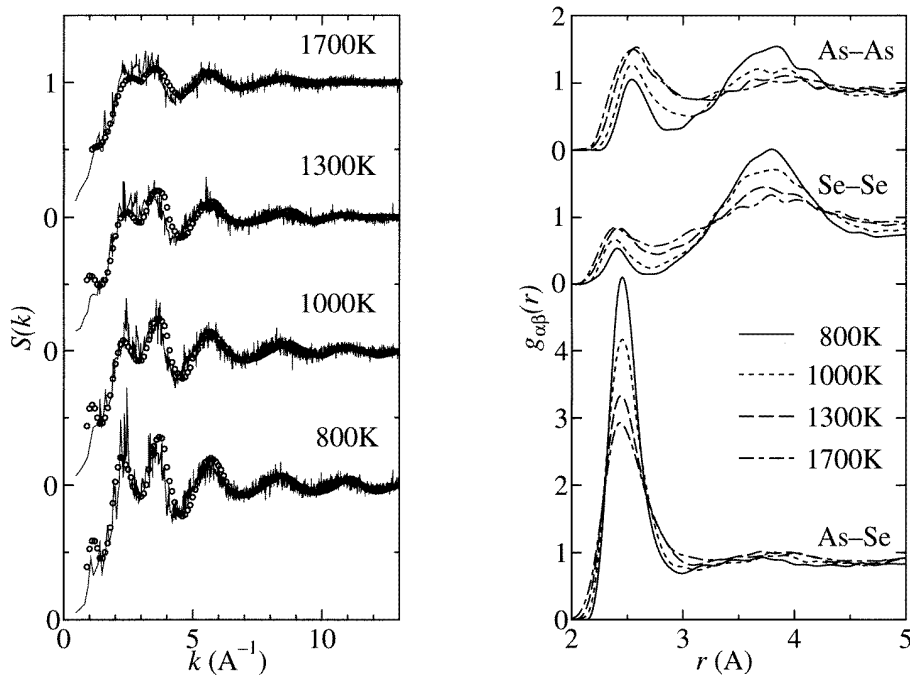


Figure 1. The temperature dependence of the total structure factor $S(k)$ of liquid As_2Se_3 . The solid curves show the calculated $S(k)$. The open circles show the results of x-ray diffraction measurements made by Hosokawa *et al* [10].

Figure 2. The temperature dependence of the partial pair distribution functions $g_{\alpha\beta}(r)$ of liquid As_2Se_3 .

sampling. The quantities of interest were obtained by averaging over 4 ps after the initial equilibration, which took 3 ps.

In figure 1, we show the calculated total structure factors $S(k)$ for four temperatures as well as the x-ray diffraction data for comparison. $S(k)$ was calculated from the partial structure factors $S_{\alpha\beta}(k)$ using the atomic scattering factors for x-rays [19]. We obtained the $S_{\alpha\beta}(k)$ on the basis of the following definition:

$$S_{\alpha\beta}(k) = \left\langle \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} e^{ik \cdot (r_i - r_j)} \right\rangle / \sqrt{N_\alpha N_\beta} \quad (1)$$

where N_α is the number of α -type ions and r_i the position of i th ion. We can see that the calculated $S(k)$ are in good agreement with the experiments. There is some structure in the calculated $S(k)$ at about 1 \AA^{-1} corresponding to the first sharp diffraction peak (FSDP) in the observed $S(k)$, which becomes less clear with increasing temperature. By investigating the contributions from the $S_{\alpha\beta}(k)$ to the $S(k)$, it is found that the FSDP is mainly determined by the $S_{\text{AsAs}}(k)$, while $S_{\text{SeSe}}(k)$ and $S_{\text{AsSe}}(k)$ are structureless around 1 \AA^{-1} .

The partial pair distribution functions $g_{\alpha\beta}(r)$ were calculated for four temperatures as shown in figure 2 to examine the atomic structure in real space. $g_{\text{AsSe}}(r)$ has a very large first peak at about 2.45 \AA , which means that the neighbours around each atom are mainly unlike atoms, thus being in accord with the experimental results. With increasing temperature, the height of the first peak becomes lower and the coordination number of unlike atoms decreases. On the other hand, though the first peaks of the $g_{\text{AsAs}}(r)$ and $g_{\text{SeSe}}(r)$ are much lower than that of $g_{\text{AsSe}}(r)$ at all temperatures, they become higher and the coordination number of like atoms increases when the temperature is increased. These facts can be explained as follows: at higher temperatures, the As and Se atoms are distributed more randomly in the network structure, and therefore the probability of finding like atoms around each atom increases. It should be emphasized that the first-peak position r_1 of $g_{\text{SeSe}}(r)$ is almost the same as that of $g_{\text{AsSe}}(r)$, i.e. $r_1 \sim 2.45 \text{ \AA}$, while r_1 for $g_{\text{AsAs}}(r)$ has a larger value, $\sim 2.55 \text{ \AA}$. Therefore, it would be very difficult to distinguish the Se–Se correlation from a total correlation function $F(r)$ obtained

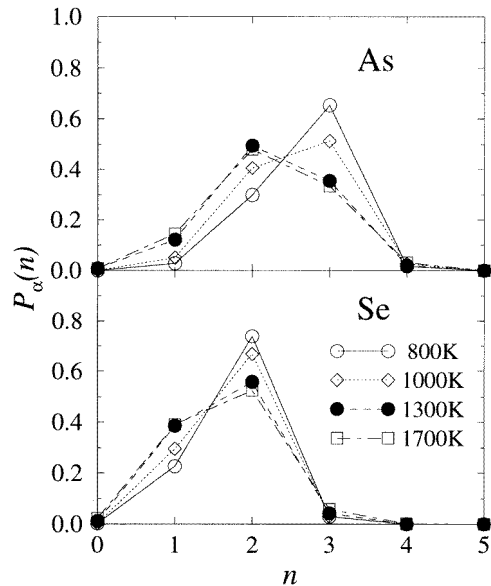


Figure 3. The temperature dependence of the coordination number (n) distribution functions $P_\alpha(n)$ of liquid As_2Se_3 .

by EXAFS measurements, since $F(r)$ is dominated by the As–Se correlation. This is why no Se–Se covalent bonds were observed at any temperature [11]. When the temperature is relatively high and the relative contribution of the As–As correlation to $F(r)$ becomes larger, the As–As correlation becomes extractable [11].

To see more clearly how the structural change occurs in liquid As_2Se_3 , we obtained the coordination number (n) distribution function $P_\alpha(n)$, which was calculated simply by counting the number of atoms inside a sphere of radius R centred at each α -type atom. Figure 3 displays $P_\alpha(n)$ calculated with $R = 2.7 \text{ \AA}$. $P_\alpha(n)$ depends somewhat on R ; e.g. $P_{\text{As}}(2)$ and $P_{\text{As}}(3)$ decrease and increase, respectively, by about 10%, when calculated with $R = 2.8 \text{ \AA}$. However, the following qualitative features of $P_\alpha(n)$ do not depend on R . While $P_{\text{As}}(2)$ is much smaller than $P_{\text{As}}(3)$ at 800 K, more twofold-coordinated As atoms exist at 1300 and 1700 K. As for the Se atoms, $P_{\text{Se}}(2)$ 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, though it decreases with increasing temperature. As a result, it is established that a major part of this liquid mixture consists of twofold chain-like structures at higher temperatures. This was confirmed by viewing directly the atomic configuration obtained by our *ab initio* MD simulation [20].

The total electronic densities of states (DOS) and the partial DOS for α -type ions are defined by

$$D(E) = \left\langle \sum_m \delta(E - E_m) \right\rangle \quad (2)$$

$$D_\alpha(E) = \left\langle \sum_m w_m^\alpha \delta(E - E_m) \right\rangle \quad (3)$$

respectively, where E_m is the eigen-energy of m th electronic state and w_m^α the weight of the m th electronic state for an α -type ion. $D(E)$ and $D_\alpha(E)$ were calculated by counting the number of electronic states within each interval of 0.27 eV and taking a time average of them. The errors at each interval estimated from the standard deviations for the distribution of the eigen-energies are less than 0.01 states $\text{eV}^{-1}/\text{atom}$. We obtained w_m^α by integrating the square norm of the wavefunction for the m th electronic state within a sphere of radius 1.2 \AA centred at each α -type atom, and normalized it such that $\sum_\alpha w_m^\alpha = 1$. The temperature dependence of the calculated DOS is shown in figure 4. The electronic states between -17 and -8 eV are s-like in character, and those above -6 eV are p-like. The p-like states of the Se atoms have similar features to those in liquid Se [4]: two peaks in $D_{\text{Se}}(E)$ at -4 and -1 eV correspond to p-like bonding and p-like non-bonding states, respectively, while the states above E_F are p-like anti-bonding states. The p-like states in $D_{\text{As}}(E)$ below E_F are mainly contributed by the threefold-coordinated bonding states.

At 800 K, $D(E)$ has a deep dip at E_F , which means that the system has semiconducting properties. With increasing temperature, the dip is gradually filled up, and the position of the dip shifts to higher energy, as shown by the arrows in figure 4 (right-hand panels). It should be noted that, above 1300 K, the dips in $D_{\text{As}}(E)$ and $D_{\text{Se}}(E)$ are located at lower and higher energies relative to E_F , respectively. When we investigated the spatial distribution of the electronic wavefunctions with eigen-energies near E_F at 1300 and 1700 K, we observed that they have a large amplitude around the twofold-coordinated As and Se atoms, forming p-like non-bonding orbitals, as well as around the onefold-coordinated atoms, i.e. the ends of chains [20].

As shown in figure 4, the system that we simulated has semiconducting and metallic properties at lower and higher temperatures, respectively. On the basis of the observations described above, two microscopic mechanisms of this SC–M transition are presented:

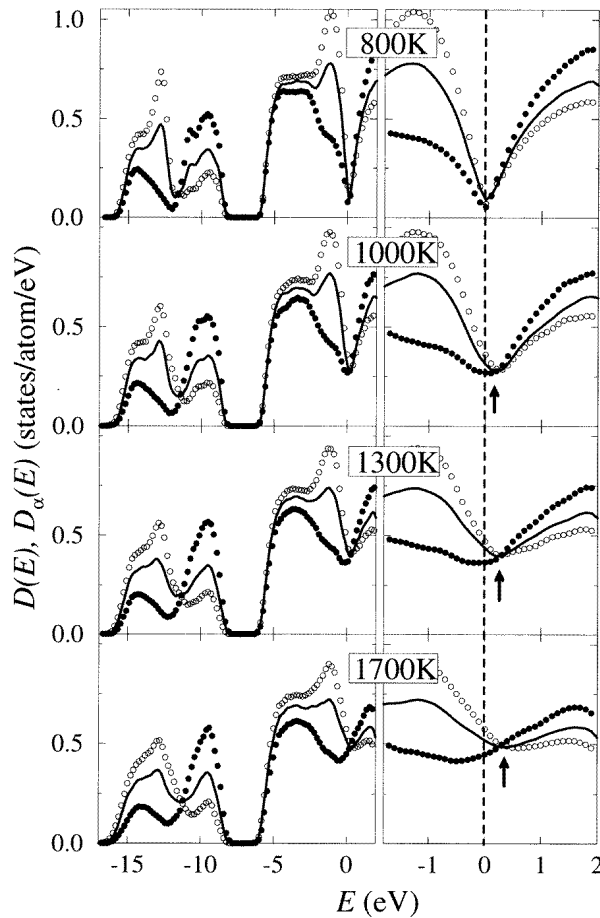


Figure 4. The temperature dependence of the electronic density of states (DOS) of liquid As_2Se_3 . The solid curves show the total DOS $D(E)$. The solid and open circles show the partial DOS $D_\alpha(E)$ for As and Se atoms, respectively. The origin of the energy is taken to be the Fermi level ($E_F = 0$). On the right-hand side at each temperature, the scale of the abscissa is enlarged around E_F . The arrows show the position of the dip in the total DOS in each case.

- (a) One is related to the electronic structure around the twofold-coordinated As atoms. The As atoms in the chain-like structure should have almost the same electronic states as those of the Se atoms, i.e. twofold-coordinated p-like bonding and p-like non-bonding states. To occupy these states, four p electrons per atom are needed, as is the case for the Se atoms. However, since the number of p electrons of the As atom is three, the p-like non-bonding states around the twofold-coordinated As atoms will not be completely occupied, which causes the metallic behaviour. Moreover, these p-like non-bonding states around the As atoms are considered to have electron eigen-energies that are nearly the same as those of the states around the Se atoms. Therefore, some of the electrons, which occupy p-like non-bonding states around the Se atoms, will transfer to the twofold-coordinated As atoms. This is why the dips in the partial DOS for As and Se are located on the lower- and higher-energy sides of E_F , respectively, at higher temperatures, which results in there being some electrons in the As energy bands and some holes in the Se energy bands.

- (b) The other is related to the electronic structure around the onefold-coordinated Se and also As atoms. If one of the two chemical bonds around an atom is broken in the chain-like structure, the p-like anti-bonding states are stabilized, and the states whose electronic wavefunctions have a large amplitude around the ends of chains would be generated near E_F . This is the same mechanism as those observed for liquid Se [4] as well as for the S_8 cluster [21].

In conclusion, we have clarified the microscopic mechanism of the SC–M transition in liquid As_2Se_3 by investigating the temperature dependence of its structural and electronic properties using *ab initio* MD simulations. We have found that, at higher temperatures, this liquid mixture has a major part consisting of twofold chain-like structures, while it has a network structure at lower temperatures. Accompanying this structural change, electronic states similar to those around chalcogen atoms are generated around the twofold-coordinated As atoms, and cannot be filled completely by the electrons originating from the p electrons of the As atoms. It has also been found that the number of onefold-coordinated Se and also As atoms increases with increasing temperature, and that, around the ends of chains, there exist electronic states with eigen-energies near E_F , which are similar to the metallic states in liquid chalcogens [4].

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