Structures of liquid selenium at high pressures

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Abstract. Ab initio molecular dynamics simulation in the framework of the density functional theory is applied for investigation of selenium in the region of the liquid–liquid phase transition. The usability of the method for the problem is examined. Thermodynamic, structural and electronic properties are investigated. The phase transition is not observed on phase diagram, and probably could not be. The structure and electronic analysis suggests that all points may belong to one phase. The absence of phase transition can be result of underestimation of atom attraction that is typical for the exchange-correlation functional chosen.

1. Introduction

Liquid–liquid phase transition of selenium is observed experimentally in pressure–temperature region of 1–4 GPa and 900–1300 K [1]. Along with a minor jump of density, metallization is registered; the conductivity increases by several orders with the rise of pressure. The phenomenon takes place among other elements, such as sulphur, bismuth, tellurium, iron [1]. The nature of such phenomenon varies for different elements [2]. The selenium is supposed to form chains, which length decreases with the rise of pressure and temperature. The destruction of chains is assumed to cause abrupt behavior of properties.

The simulation of liquid selenium is carried out in [3–6]. Temperatures and densities in [3–5] are chosen to match earlier experiments [7, 8], where the region of phase transition is not investigated in detail. Temperatures and densities in [6] are chosen to follow melting curve obtained in [1]. The gap in electronic density of states (DOS) at lower temperatures (the evidence of semiconducting state) and its absence at higher (the evidence of conducting state) are obtained [3,5,9], although the data in [3,5] are sparse and cannot reveal the transition; the abrupt behavior of DOS changing is indicated only in [9]. The conductivity is not calculated directly in all these works.

This paper focuses on narrower region near liquid–liquid phase transition supposed according to data [1]. One can see figure 1, which represents points at phase diagram that are chosen in this work in comparison with those are chosen in [3,5,6]. Two isotherms of 800 and 1000 K containing 7 points each are calculated. The method of calculation is described in section 2. Section 3 presents the results of the study and is divided into five parts: thermodynamic properties, pair correlation function, chain structure analysis, Se–Se bond lifetime and dielectric properties. Discussion is provided in section 4; section 5 summarizes primary findings.
2. Methods

The simulation is carried out in the framework of DFT using VASP (*Vienna Ab Initio Simulation Package*) [10–12]. Periodic cell contains 128 atoms (448 Kohn–Sham bands), \(k\)-mesh includes 8 points (2 \(\times\) 2 \(\times\) 2 Monkhorst pack). The basis of plane waves is cut down by \(E_{\text{cut}} = 263\) eV. PAW pseudopotential and Perdew–Wang (PW91) exchange-correlation potential are used. Electronic selfconsistency loop breaks if total (free) energy change \(\Delta E < 10^{-7}\). The temperature is maintained by Nose–Hoover thermostat. The system was relaxing for 8 ps with the 2 fs time step starting from cubic structure. All following averaging are based on next 6 ps. This is a conventional approach, which is applied to study thermodynamic properties [13–15].

The applicability of VASP for high pressure and temperature calculations is discussed in [16, 17]. Since the temperatures and densities in this paper are much less than restrictions introduced in [16, 17], the method can be applied for the problem.

3. Results

3.1. Thermodynamic properties

Two isotherms of 1000 and 800 K are calculated. Each isotherm contains 7 points of different densities: 5.426, 5.316, 5.209, 5.156, 5.104, 5.003, 4.904 g/cm\(^3\) (figure 2).

Despite the selenium is observed experimentally in solid state at 800 K [1], at the simulation it is still liquid. The 800 K isotherm is smooth, while 1000 K isotherm has minor deviation from smooth behavior at \(\rho = 5.209\) g/cm\(^3\). But it does not exceed standard deviation, and could not be interpreted as an evidence of the phase transition. Probably, the density change is too small to be observed with chosen simulation parameters.

3.2. Pair correlation function

The first maximum of pair correlation function locates at \(r_{\text{max},1} \approx 2.4\) Å, that corresponds to Se–Se distance within chain (figure 3). With the rise of pressure and temperature \(r_{\text{max},1}\) and...
Figure 2. Selenium density-pressure phase diagram. Red points correspond to 1000 K isotherm, blue points correspond to 800 K isotherm. Error bars show standard deviation of pressure distribution over MD-steps.

Figure 3. Pair correlation function \(g(r)\). Red line—\(\rho = 5.426 \text{ g/cm}^3\), \(T = 1000 \text{ K}\); yellow line—\(\rho = 4.904 \text{ g/cm}^3\), \(T = 1000 \text{ K}\); blue line—\(\rho = 5.426 \text{ g/cm}^3\), \(T = 800 \text{ K}\); green line—\(\rho = 4.904 \text{ g/cm}^3\), \(T = 800 \text{ K}\).

\(r_{\text{min,1}}\) are shifting to the right. Alongside with shifting the first maximum becomes lower. The lowering of the first peak can be interpreted as decreasing of concentration Se–Se bonds, i.e. destruction of chains.
3.3. Selenium chains
In order to analyze the chain structure of selenium it is necessary to specify the definition of chain. We consider atoms \( i, j \) bonded together if the distance between them \( r_{ij} < r \), where \( r \) is given in advance parameter. With such geometric conception atoms are able to group not only linear structures (chains), but branched ones (i.e. structures with atoms that have at least three bond simultaneously). The choice of parameter \( r \) sufficiently influence the amount of such structures as well as size of the structures in general. To define the length of chains we should find a way how to take into account branched structures. The first way is to set such \( r \), so part of three-fold atoms will be negligible quantity. The second way is simply do not take into account other bonds, if one atom already has two of them (in practice there are almost no atoms with more then three bonds). Thus, all atoms get grouped in either linear structures, which length is defined as number of atoms in it, or stay single, that is a special case of chain with the length equals to one. These two ways quantitatively are different, but qualitatively are similar (figure 4).

At \( r = 2.5 \) Å, part of atoms that grouped in non-linear structures less 5%; they were neglected. At \( r = 2.7 \) Å, the second approach is used. It results in longer chains. But the general behavior keeps as well as for \( r = 2.5 \) Å: chains become shorter with the rise of temperature and pressure, that agrees with initial assumption. But even with high \( r \) the average length does not exceed 10 atoms, although chains in semiconductor region could consist of up to 1000 atoms. Probably, all observed points are in conducting region.

3.4. Bond lifetime
Consider the next value:

\[
F(t, r) = \frac{\langle f_{ij}(0)f_{ij}(t) \rangle}{\langle f_{ij}(0)f_{ij}(0) \rangle},
\]

where \( f_{ij} = \begin{cases} 1 & \text{for } r_{ij} < r, \\ 0 & \text{for } r_{ij} > r, \end{cases} \) \( r_{ij} \) is distance between \( i, j \) atoms.

Angular brackets \( \langle \ldots \rangle \) represent averaging over pairs of atoms and original time [3]. The physical meaning of \( F(t, r) \) is probability to keep bond between atoms at time \( t \), given they were bonded at \( t = 0 \). Figure 5 demonstrates \( F(t) \) for different \( r \), for \( \rho = 5.316 \) g/cm\(^3\), \( T = 1000 \) K.
Vibration of atoms results in oscillation of $F(t, r)$. Considering start of pair correlation function at 2.1 Å and absence of $F(t, r)$ oscillation at 2.7 Å we can conclude that Se–Se bond oscillates near 2.4 Å with an amplitude of $\approx 0.3$ Å.

The right $F(t, r)$ tail can be approximated with $(1 + t/\tau)^{-1}$. For $r = 2.7$ Å, $\tau = 476$ fs, which has a physical meaning of bond lifetime.

3.5. Electrical conductivity

Electrical conductivity is defined from frequency dependent dielectric matrix. In order to increase accuracy, 64 $k$-points ($4 \times 4 \times 4$ Monkhorst pack) are used for these calculations. Other parameters are the same as it is described in 2. The calculation algorithm is based on Kubo–Greenwood formula [18, 19] and does not take into account effective electron-ion collision, so conductivity is equal to zero at frequency $\omega = 0$. To determine static conductivity the dielectric function is extrapolated to zero. The outcome is averaged over 3–4 configuration for each density. Figure 6 represents the result.

The phase transition should be accompanied by the rise of conductivity be several orders of magnitude [1], but the growth is linear and all values are typical for conductors. Most likely all points belong to one phase.

4. Discussion

All approaches do not reveal the liquid–liquid phase transition. According to [1], the density change is approximately 8%. It is too minor to be observed via phase diagram due the high standard deviation. Probably, 8 ps simulation time is not enough to reach equilibrium state.

The chain length and conductivity analysis suggests that all points are referred to the same state. Low chain length and high conductivity are characteristic for the conducting state. Short chain structure may be a result of underestimation of attraction between atoms, that is typical for the chosen exchange-correlation potential PW91. The exchange-correlation potential does not take into account dispersion forces, unlike, for example, vdW-DF2 [20]. Since the structure
of selenium defines its physical properties, the choice of the potential is crucially important and seems to be the main reason of the discrepancy between this work and the experiment [1].

The abrupt behavior of properties changing is obtained only in [9]. In [9], electronic density of states is calculated and a gap at Fermi level is revealed at densities $\rho = 5.2 \, \text{g/cm}^3$ and lower, and temperature $T = 1000 \, \text{K}$. Perhaps, our computation results for dielectric matrix differ from [9] due to the lack of number of $k$-points: 768 in [9], while in this work 64 $k$-points are used. The convergence with respect to other parameters also should be examined. Especially, the number of particles is needed to be checked, as it has significant impact on possibility to form chains in selenium.

5. Conclusion
DFT simulation of selenium was carried out at the region of the liquid–liquid phase transition supposed according to [1]. Isotherms do not behave abruptly and it is probably impossible to observe phase transition at the equation of state. Depending on way of constructing chains they have average length 2–7 atoms. Se–Se bond oscillates near 2.4 Å with an amplitude of 0.3 Å, bond lasts approximately 480 fs. Conductivity values indicate conducting state at all densities.

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