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Structure and bonding of liquid Se

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Abstract. *Ab initio* molecular dynamics based on density functional theory has been used to study liquid Se at three temperatures: 570, 870 and 1370 K. The calculated $g(r)$ is in very close agreement with neutron diffraction data, except in the region of the first minimum at ~ 2.9 Å. We have examined the effect of including gradient corrections in the density functional description, and we find that they give a substantial improvement in the agreement with experiment near the first minimum. We analysed the bonding topology and we find a significant fraction of onefold- and threefold-coordinated Se atoms at the highest temperature.

1. Introduction

At ambient conditions, the stable crystal structure of Se is composed of atoms that are bonded into infinite chains, with a rather weak interaction between chains. From neutron and x-ray diffraction measurements it is believed that the mean coordination number remains close to 2.0 in the liquid even up to temperatures and pressures close to and beyond the critical point (1903 K, 380 bar) [1–3]. The high viscosity and low diffusion coefficient at temperatures near the melting point (494 K) are also consistent with the persistence of the chain structure in the liquid state. If the temperature is increased to over 1000 K, a drop of more than an order of magnitude is observed in the viscosity [4], and the diffusion coefficient increases by a factor of ~ 10 [5]. It seems likely that the chain structure is strongly disrupted at high temperatures as suggested by recent computer simulations [6–8], but it is difficult to be certain of this from diffraction data alone [9].

In the present paper we report the results of *ab initio* molecular dynamics (AIMD) simulations of high-temperature l-Se. Previous *ab initio* simulations of liquid selenium at low [8] and high temperatures [10] have been reported; however, all of them consistently reported pair correlation functions that are too large in the region of the first minimum, in disagreement with experimental data. These simulations were all based on the local density approximation (LDA) for evaluating the exchange–correlation energy. It is now generally recognized that the LDA fails to describe weak bonds accurately [11–13] and it has been shown that the introduction of gradient corrections (GC) to the LDA may help to solve this problem. This is particularly true for Se where GC improve the agreement with experimental data for the trigonal phase [12]. Here we show that the introduction of GC substantially improves the agreement with experiment for the liquid phase.

2. Simulation methods

The simulations that we have performed are based on *ab initio* molecular dynamics (AIMD), using density functional theory either within the LDA [14] or using the generalized gradient

approximation (GGA) [15]. The calculations have been performed using the VASP (Vienna *ab initio* simulation program) code [16]. The valence orbitals were expanded in a basis of plane waves and we used a pseudopotential to represent the core electrons. In contrast to our previous simulations [10], this work is based on the use of Vanderbilt ultra-soft pseudopotentials [17], which allows the use of a much smaller plane-wave basis set without loss of accuracy. At every step of the simulation, we solve the one-electron Kohn–Sham equations self-consistently by minimizing the one-electron energies using an iterative matrix-diagonalization method and an efficient charge-density mixing. From the knowledge of the ground state, the forces on the atoms are calculated using the Hellmann–Feynman theorem. The forces are then used to integrate the classical equations of motion of the ions. More details of the methods used and the code may be found elsewhere [16].

The system that we simulated was composed of 69 atoms in a cubic cell with periodic boundary conditions. The wavefunctions at the Γ point were expanded in a plane-wave basis with a cut-off energy of 11 Ryd. Test calculations done on crystalline selenium (c-Se) have shown that this cut-off is enough to reproduce the lattice parameters to within a few per cent [12]. The simulations have been performed at 570, 870 and 1370 K, at densities of 3.91 [18], 3.57 and 3.08 g cm⁻³ [19]. These densities correspond to experimental conditions under pressures of 1, 10 and 100 bar respectively for which neutron [1, 2] and x-ray [3] diffraction measurements on l-Se have been carried out. All of the simulations were done in the canonical ensemble by introducing a Nosé thermostat [20]. All of the simulations were first initialized by an equilibration run of 3.0–5.0 ps followed by a production run of 3.0–6.0 ps depending on temperature.

3. Results and discussion

First we shall concentrate on the pair correlation function at 870 K. In figure 1(a) we compare several experimental curves with the results of our simulations within the LDA and the GGA. As far as the position and amplitude of the peaks are concerned, both results reproduce the experimental data very well. We note however that in the region of the first minimum the LDA curve is in serious disagreement with experimental data. This is consistent with earlier LDA-based simulations of l-Se [8, 10]. The pair correlation function from our simulation with GC has a much lower minimum in far better agreement with all of the experimental data. The importance of the improvement may be gauged by comparing the coordination numbers. From the LDA curve we get a coordination number of 2.28, whereas one gets 2.03 from GGA curve, in much better agreement with experiment.

A more direct comparison with experimental results is achieved through the static structure factor. In figure 1(b) we compare the structure factor from our LDA and GGA simulations at 870 K with the experimental results from x-ray diffraction [3] and neutron scattering [2] measurements for the same conditions. These results clearly show that the introduction of GC to the LDA is essential if a more detailed agreement with experimental data has to be achieved. Therefore the rest of the results presented will be based on the GGA simulations only.

In figure 2 we compare the pair correlation functions obtained from our GGA simulations for 570, 870 and 1370 K with the experimental results. The overall agreement with the diffraction data is good at all three temperatures. Again we stress that the region of the first minimum is much lower than those predicted by LDA calculations [8, 10]. Examination of the peaks in figure 2 shows that their position and amplitude are relatively close to the corresponding experimental values. We note that the first-neighbour distance is essentially identical to the distance found in trigonal Se (2.37 Å). The second-neighbour distance is

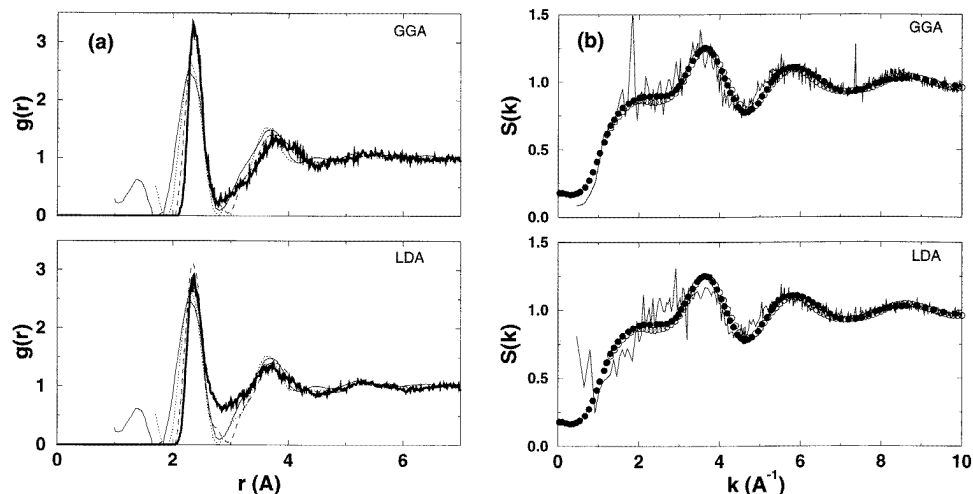


Figure 1. Comparison of our simulated pair correlation functions (a) and total structure factors (b) at 870 K obtained using the LDA and the GGA with experimental results. (a) The thick lines are the theoretical results, the thin lines and the long-dashed lines are data from neutron diffraction experiments [1, 2], and the dotted lines are results from x-ray diffraction experiments [3]. (b) The continuous lines are the theory. The filled and empty circles are experimental results from neutron scattering and x-ray diffraction experiments respectively.

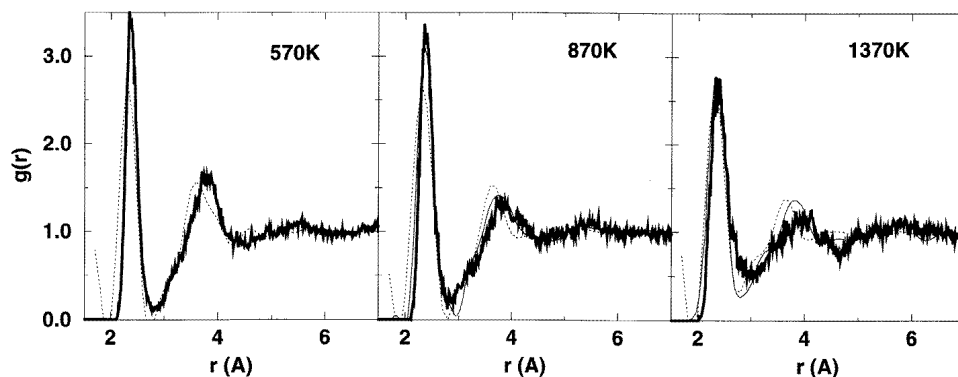


Figure 2. The pair correlation functions of liquid Se from our GGA-based simulations at 570, 870 and 1370 K, compared with experimental data. Thick lines are results of our simulations. The thin continuous lines are results of neutron diffraction measurements at 873 and 1373 K under pressures of 10 and 100 bar respectively [2]. The dotted lines are from x-ray diffraction data at 573, 873 and 1473 K [3].

however substantially larger in the liquid than in the crystal (3.44 Å).

In table 1 we show the nearest-neighbour coordination numbers N_c . We find that for 570 and 870 K selenium has an average coordination very close to 2, in good agreement with experimental results. Therefore at these temperatures, the chain structure of c-Se survives, at least partially, in the liquid state. A slightly higher coordination number is found at 1370 K. This suggests that at higher temperature the chain structure starts to be disrupted, with a

Table 1. Averages and distributions of coordination numbers N_c at 570, 870 and 1370 K. The cut-off radius r_c is taken to be the first minimum in $g(r)$, i.e. 2.83, 2.87 and 3.02 Å for the first, second and third temperature respectively. We show the average percentage of atoms with coordination N_c .

T (K)	570	870	1370
$\langle N_c \rangle$	2.00	2.03	2.23
$N_c = 1$	3.1	3.1	7.4
2	94.9	91.6	67.9
3	2.0	5.3	23.1
4	0.0	0.0	1.6

substantial penetration of inter-chain second neighbours into the first coordination shell. This is confirmed by examining the distribution of first-neighbour coordination numbers found in our simulations, also reported in table 1. At low temperatures the majority of atoms are twofold coordinated, concurring with the presence of chains in the liquid. There is however a significant rise in the number of onefold- and threefold-coordinated atoms with increasing temperature. Hence a large proportion of threefold-coordinated atoms is not incompatible with a coordination number close to 2.

4. Conclusions

We have shown that the introduction of gradient corrections to the local density approximation dramatically improves the agreement with diffraction data. On the basis of these findings we have presented results for the pair correlation functions and static structure factors at 570, 870 and 1370 K, in excellent agreement with several diffraction data. Analysis of the simulated $g(r)$ gives a mean coordination number close to 2, but we find significant fractions of onefold- and threefold-coordinated atoms, particularly at 1370 K, so the simple chain-like structure characteristic of the crystal is considerably disrupted.

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