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Ab initio molecular-dynamics simulation of liquid As_xSe_{1-x} alloys

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ARTICLE INFO

Article history: Received 3 March 2008 Received in revised form 13 April 2008 Accepted 18 April 2008

PACS: 61.20.Ja 61.25.Mv 71.15.Pd 71.22. + i

Keywords: Density of states Electronic structure Molecular dynamics simulation

1. Introduction

Arsenic, selenium, and their alloys are good examples of systems in which the fine interplay of microscopic structure and electronic properties provides an interesting test ground for theories. In particular, a great deal of work has been invested into the analysis of the semiconductor/metal (SC/M) transition [1–5,8]. The structure of liquid arsenic is found to be similar to its ground-state, rhombohedral crystal structure, with three-fold coordination [9,10]. The liquid phase of selenium consists of chain molecules [11] and the electronic properties are strongly correlated with its structural features. The chain-like structure remains even in the metallic state [12,13], although the average chain length decreases substantially. The liquid As-Se mixtures have a network structure composed of three-fold coordinated As atoms and two-fold coordinated Se atoms. The electronic structure of this liquid mixture is semiconducting in character near the triple point due to the preservation of a covalent bonding. The optical absorption measurement [14] revealed that the optical gap decreases rapidly with increasing temperature, and it vanishes at about 1000°C. This means that liquid As₂Se₃ has metallic properties above that temperature. 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 [5].

ABSTRACT

Ab initio molecular-dynamics simulations have been used to investigate the structure and dynamics properties of the liquid As_xSe_{1-x} at four compositions x = 0.2, 0.4, 0.5, and 0.6. We present results for the static structure factors, frequency spectra, and the electronic density of states. The results for the structure factor are in good agreement with the available experimental data. The vibrational density of states has two distinct bands for all compositions; the lower-energy band shifts to higher frequency while the higher-energy band shifts to lower frequency as the number of As atoms increases. The electronic density of states show that the liquid As_2Se_3 has semiconducting properties; increase or decrease As atoms will reduce the semiconducting character of the sample.

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As₂Se₃ displays an interesting character in the short-range environment. A similar bonding character of As₂Se₃ exists in the crystalline, glassy [6], and even the liquid states [7] from an analysis of radial distribution functions (RDFs) from scattering experiments. Recently, Shimojo et al. [8,15] have carried out ab initio molecular dynamics (MD) simulations for liquid As₂Se₃ mixtures and they 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. Structural studies for liquid As-Se alloy have extensively been made by means of X-ray and neutron diffractions [7,16,17], and extended X-ray absorption fine structure (EXAFS) techniques [4]; the structural information over a wider concentration has been received for this liquid alloy. However, to our knowledge the concentration dependence of the structural and electronic properties of liquid As-Se mixtures has not been studied from first principles yet. It is obvious that an *ab initio* investigation of the properties of these systems might provide valuable information to clarify the experimental results. Therefore, in this paper we intend to explore the capabilities of the DFT approach in the generalized gradient approximation (GGA) to provide a realistic picture of various liquid $As_x Se_{1-x}$ alloys (x = 0.2, 0.4, 0.5, and 0.6).

2. Computational methods

Our MD calculations have been performed at 800K by using the Vienna *ab initio* simulation program VASP [18,19] with the



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^{0921-4526/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.physb.2008.04.025

projector augmented wave (PAW) method [20,21]. The calculations presented here are based on density functional theory within the generalized gradient approximation (GGA). Our GGA calculations use the PW91 functional due to Perdew and Wang [22]. We have considered four concentrations of $As_x Se_{1-x}$: x = 0.2, 0.4, 0.5, and 0.6. In each case, we used a cubic 100-atom supercell with periodic boundary conditions. For this size cell, the actual numbers of As atoms in the five samples were 20, 40, 50, and 60. (Since the minority component in the 20% sample has only 20 atoms, the statistics will be quite poor and the results should be given greatest significance for the majority component in this case.) The atomic densities for the five concentrations were obtained from the measured density of I-As₂Se₃ at this temperature [3], together with Vegard Law. We use 215 and 462.8 eV cutoff for the energies of the plane waves and the electron density, respectively, and Γ -point sampling for the supercell Brillouin zone. For the electronic structure, we used Fermi-surface broadening corresponding to an electronic subsystem temperature of $k_{\rm B}T = 0.1$ eV. In calculating the electronic wave functions, at each concentration we include ten empty bands. We control the ionic temperature using the Nosé-Hoover thermostat [23]. The equations-of-motion are integrated by means of the Verlet algorithm, using an ionic time step of 3 fs. The initial atomic configuration adopted was a random distribution of 100 atoms on the grid for each concentration. Then, the system is heated up to 2000 K by rescaling the ionic velocities. After equilibration for 4 ps at this temperature, we gradually reduce the temperature to 800 K. The



Fig. 1. Atom-atom pair distribution functions $g_{ASAS}(r)$, $g_{SeSe}(r)$, and $g_{ASSe}(r)$ for $I-As_xSe_{1-x}$ at a temperature of 800 K. The graphs are vertically offset by six unit each for clarity.

physical quantities of interest were obtained by averaging over 10 ps after the initial equilibration taking 3 ps.

3. Structural properties

The atom–atom pair distribution functions obtained from the *ab initio* MD are depicted in Fig. 1. Our results for $g_{\alpha\beta}(r)$ at x = 0.4 are in close agreement with the recent calculation by Shimojo et al. [8]. The first peak of $g_{AsAs}(r)$ becomes higher while the first peak of $g_{SeSe}(r)$ becomes lower with increasing As concentration. Here it also can be appreciated that the As atoms induce a larger degree of short-range order than Se atoms and the g_{SeSe} for x = 0.6 sample has no obvious first peak. Since we are dealing with a mixture, in order to make a proper comparison with neutron scattering data, an average g(r) is obtained from the atom–atom distribution function $g_{\alpha\beta}(r)$ appropriately weighted with the atomic neutron scattering lengths,

$$g(r) = \frac{1}{\langle b \rangle^2} (x^2 b_{As}^2 g_{AsAs}(r) + (1-x)^2 b_{Se}^2 g_{SeSe}(r) + 2x(1-x) b_{As} b_{Se} g_{AsSe}(r)),$$
(1)

with $\langle b \rangle = xb_{As} + (1 - x)b_{Se}$ being *x* the fraction of As atoms, and the scattering lengths $b_{As} = 0.658 \times 10^{-14}$ m and $b_{Se} = 0.797 \times 10^{-14}$ m. The calculated total pair distribution functions for $As_x Se_{1-x}$ are shown in Fig. 2 in which we compare them with the experimental results. The calculated total g(r) is in reasonable agreement with the experiments; the first and second peak positions as well as the position of the first minimum of the



Fig. 2. Calculated total pair distribution functions for $1-As_xSe_{1-x}$ (full lines) compared with the experimental results (circles, Ref. [10]). The graphs are vertically offset by two unit each for clarity.

calculated g(r) are in good agreement with those of the experimental g(r). The Fourier transformation of the total pair distribution function leads to the Faber–Ziman structure factor, which we show in Fig. 3. Our calculated structure factors of $I-As_xSe_{1-x}$ are in good agreement with experimental structure factors obtained by neutron diffraction method. Given the partial pair distribution functions, it is possible to calculate the partial coordination numbers as

$$N_{\alpha\beta} = 2 \int_0^{R_{\text{max}}} 4\pi r^2 \rho_\beta g_{\alpha\beta}(r) \,\mathrm{d}r,\tag{2}$$

where R_{max} is the first maximum coordinate (the nearest-neighbor distanced) in $g_{\alpha\beta}$. The calculated nearest-neighbor distances and the partial coordination numbers of $1-As_xSe_{1-x}$ are listed in Table 1. We can see that the value of the average As–As bond length is larger than those of As–Se and Se–Se, and the difference between the average As–Se and Se–Se bond length is quite small. 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 *x*. On the other hand, the As concentration dependence of $N_{\alpha\beta}$ is noticeable as is seen in Table 1. The N_{AsAs} and N_{SeAs} increase while N_{AsSe} and N_{SeSe} decrease with increasing As atoms. The total coordination number of atom α in the alloy, N_{α} can be obtained from the sum of partial coordination numbers, such as $N_{\text{As}} = N_{\text{AsAs}} + N_{\text{AsSe}}$. Both N_{As} and N_{Se} in the liquid As–Se alloys decrease with increasing *x*.



Fig. 3. Calculated total structure factors for $1-As_xSe_{1-x}$ (full lines) compared with the experimental results (circles, Ref. [10]). The graphs are vertically offset by one unit each for clarity.

4. Dynamical properties

The dynamical properties are characterized by studying the velocity autocorrelation function C(t) defined as

$$C(t) = \frac{\langle \dot{\mathbf{r}}_i(t) \cdot \dot{\mathbf{r}}_i(0) \rangle}{\langle \dot{\mathbf{r}}_i(0) \cdot \dot{\mathbf{r}}_i(0) \rangle}.$$
(3)

Additionally, the Fourier transform of C(t) gives the frequency spectrum $Z(\omega)$, which will give us, among other things, information on the vibrational modes of the sample. The two functions for total and each atomic species are shown in Figs. 4 and 5 for the four systems under consideration. The velocity autocorrelation function and frequency spectra for pure liquid Se from the *ab initio* calculation [24] are also shown in the figures. We can see that the x = 0.2 sample has some of the same features as those in the pure l–Se. The general features of frequency spectra in all cases consist of two main bands. The lower-energy band (LEB) goes up to about

Table 1

The calculated nearest-neighbor distance r (in Å) and partial coordination number N for $1-As_x Se_{1-x}$

x	As-As		As–Se		Se–As		Se-Se	
	r	Ν	r	Ν	r	Ν	r	Ν
0.2	2.57	0.12	2.47	2.61	2.47	0.65	2.38	1.04
0.4 0.5	2.56 2.55	0.31 1.04	2.47 2.46	2.33 1.64	2.47 2.46	1.56 1.64	2.43 2.42	0.21
0.6	2.54	1.42	2.47	1.17	2.47	1.76	-	-



Fig. 4. Velocity autocorrelation function for $1-As_xSe_{1-x}$ alloys calculated by *ab initio* MD. The velocity autocorrelation function for liquid Se (circles) from Ref. [20].



Fig. 5. Frequency spectra for $1-As_xSe_{1-x}$ alloys in $1-As_xSe_{1-x}$ alloys calculated by *ab initio* MD. The frequency spectra of liquid Se (circles) from Ref. [20].

4 THz and the higher-energy band (HEB) decays after 8 THz. The vibrational modes in LEB is strongly correlated to the connectivity of the network [25], consisting of extended interblocks vibrations, in analogy with acoustic modes. The vibrational modes in HEB tend to strongly depend on the configurations of the building blocks, consisting of much more localized intrablock vibration: optical-like modes. The most relevant feature worth mentioning is the shift in the LEB toward higher frequency while the HEB toward lower frequency as the number of As atoms increases. This relative shift of frequency spectra is due to the change of the dominant building blocks. The effective valence force field undergoes a global change with the increasing of As concentration.

5. Electronic properties

The structural behavior of liquid alloys can be understood in terms of the electronic structure. In Fig. 6 we have plotted the change in the electronic density of states (DOS) as the As concentration increases. The pure l–As and l–Se are semiconducting and have been calculated to have deep minima in the electronic DOS at the Fermi energy (E_F) [2]. We see these features reflected in our simulations in Fig. 6. The valence band exhibits two broad features. The lowest band between about –16 and –8 eV originates from the atomic s-like states of As and Se. The next band above –6 eV contains p-like bonding states and p-like non-bonding states. These identifications agree with general expectations about the electronic structure of chalcogenide materials. The p-like states of the Se atoms have similar features



Fig. 6. The electronic density of states for $1-As_x Se_{1-x}$ alloys calculated by *ab initio* MD. The energy zero is taken at the Fermi level (vertical dotted line).

to those in liquid Se [13]: two peaks in DOS(E) at -4 and -1 eVcorrespond to p-like bonding and p-like non-bonding states, respectively, while the states above the Fermi level are p-like antibonding states. The generic features of the DOS for x = 0.4, i.e. liquid As₂Se₃, are consistent with previous results [15] and the DOS for liquid As₂Se₃ are very similar to those found for glassy As₂Se₃ [26]. Even though the DOS for the four concentrations are quite similar, we observe significant modifications as the As concentration is changed. First, the height of the peak from -2 eVto the Fermi level decreases with increasing As atoms. Second, the lowest band which is broad and has a single peak at x = 0.2 splits into two peaks at x = 0.4 then the two peaks become illegible as the *x* increases to 0.5 and 0.6. Finally, for x = 0.4 DOS(*E*) has a deep dip at $E_{\rm F}$, which means that the system has semiconducting properties while the dips are partly filled up for other As concentrations.

6. Conclusions

We have investigated the structure, dynamics properties, and electronic structure of liquid alloy As_xSe_{1-x} at 800 K. The nearestneighbor distances for $1-As_xSe_{1-x}$ depend weakly on the *x*; the calculated partial coordination numbers of $1-As_xSe_{1-x}$ change noticeable as the number of As atoms increases. The vibrational density of states has two distinct bands for all systems. The lowerenergy band shifts to higher frequency while the higher-energy band shifts to lower frequency as the number of As atoms increases. The electronic density of states has also two main bands in the valence range. The liquid As_xSe_{1-x} at x = 0.4 has semiconducting properties; increase or decrease *x* will reduce the semiconducting character of the sample.

Acknowledgment

Numerical calculation was carried out using the facilities of the Department of Physics in Nanjing Normal University.

References

- [1] H. Hoshino, R.W. Schmutzler, W.W. Warren Jr., F. Hensel, Philos. Mag. B 33 (1976) 255.
- [2] X.P. Li, Phys. Rev. B 41 (1990) 8392.
- [3] S. Hosokawa, Y. Sakaguchi, K. Tamura, J. Non-Cryst. Solids 150 (1992) 35.
- [4] K. Tamura, S. Hosokawa, M. Inui, M. Yao, H. Endo, H. Hoshino, J. Non-Cryst. Solids 150 (1992) 351.
- [5] H. Hoshino, T. Miyanaga, H. Ikemoto, S. Hosokawa, H. Endo, J. Non-Cryst. Solids 205-207 (1996) 43.
- [6] A.L. Renninger, B.L. Averbach, Phys. Rev. B 8 (1973) 1507.
- [7] O. Uemura, Y. Sagara, D. Muno, T. Satow, J. Non-Cryst. Solids 30 (1978) 55.
- [8] F. Shimojo, K. Hoshino, Y. Zempo, J. Phys.: Condens. Matter 12 (2000) 6161.
- [9] R. Bellissent, C. Bergman, R. Ceolin, J.P. Gaspard, Phys. Rev. Lett. 59 (1987) 661.
- [10] J. Hafner, Phys. Rev. Lett. 62 (1989) 784.

- [11] E. Gerlach, P. Grosse (Eds.), The Physics of Selenium and Tellurium, Proceedings of the International Conference on the Physics of Selenium and Tellurium, Königstein, Germany, Springer, Berlin, 1979.
- [12] K. Tamura, J. Non-Cryst. Solids 205-207 (1996) 239.
- [13] F. Shimojo, K. Hoshino, M. Watabe, Y. Zempo, J. Phys.: Condens. Matter 10 (1998) 1199. [14] S. Hosokawa, Y. Sakaguchi, H. Hiasa, K. Tamura, J. Phys.: Condens. Matter 3
- (1991) 6673.
- [15] F. Shimojo, S. Munejiri, K. Hoshino, Y. Zempo, J. Phys. Condens.: Matter 11 (1999) L153.
- [16] Y. Kameda, T. Usuki, O. Uemura, J. Non-Cryst. Solids 205-207 (1996) 130.
- [17] T. Usuki, K. Itoh, Y. Kameda, O. Uemura, Mater. Trans. JIM 39 (1998) 1135.
- [18] G. Kresse, J. Furthmller, Comput. Mater. Sci. 6 (1996) 15.
 [19] G. Kresse, J. Furthmller, Phys. Rev. B 54 (1996) 11169.
- [20] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
- [21] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758. [22] Y. Wang, J.P. Perdew, Phys. Rev. B 44 (1991) 1329.
- [23] S. Nosé, J. Chem. Phys. 81 (1984) 511;
- W.G. Hoover, Phys. Rev. A 31 (1985) 1695.
- [24] F. Kirchhoff, G. Kresse, M.J. Gillan, Phys. Rev. B 57 (1997) 10482.
- [25] N. Mousseau, D.A. Drabold, Eur. Phys. I. B 17 (2000) 667.
- [26] J. Li, D.A. Drabold, Phys. Rev. B 61 (2000) 11998.