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Structure of Liquid Tin under High Pressure by *ab initio* molecular-dynamics simulation

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Abstract. Pressure-induced structural change of liquid tin was studied by constant-pressure *ab initio* molecular-dynamics simulations from 0 to 4 GPa. We have found that with increasing pressure the liquid tin is not compressed uniformly but very gradually changes from complex anisotropic structures to more simple isotropic close-packed structure.

1. Introduction

It is well known that liquid tin has complex local structures whose character is shown by the side peak at the high- k side of the structure factor $S(k)$ [1]. On the other hand, liquid tin crystallizes in a β -Sn structure(Sn-II, white-tin) at the melting temperature of 505 K under ambient pressure. At higher pressure above 2.9 GPa, the solid phase Sn-III emerges, which is in a body-centered tetragonal(bct) structure[3].

In relation to these solid phase transitions, it is interesting to study the structural change in liquid phase under high pressure. Recently, Di Cicco *et al* [2] found gradual changes of liquid structure under high pressure by x-ray absorption spectroscopy and x-ray diffraction. They reported from the analyses of reverse Monte Carlo(RMC) method that, under ordinary pressure the local structure of liquid tin is composed of tetrahedral and close-packed configurations. On the other hand at high pressure, the close-packed structure becomes to be dominant. Furthermore they found that undercooled liquid does not crystallize to the Sn-II phase but to the Sn-III metastable solid phase even below the transition pressure between Sn-II and Sn-III of 2.9 GPa.

Inspired by these experimental results, in this paper we carry out *ab initio* molecular-dynamics(MD) simulations and investigate detailed structural change of liquid tin under wide range of pressures.

2. Method of simulation

Our *ab initio* calculation is based on the density functional theory with the generalized gradient approximation(GGA)[4] for the exchange-correlation energy. The projector augmented wave(PAW) potentials [5, 6] were employed for the electron-ion interaction with four valence electrons $5s^25p^2$. The electronic wavefunctions were expanded by a plane wave basis set with

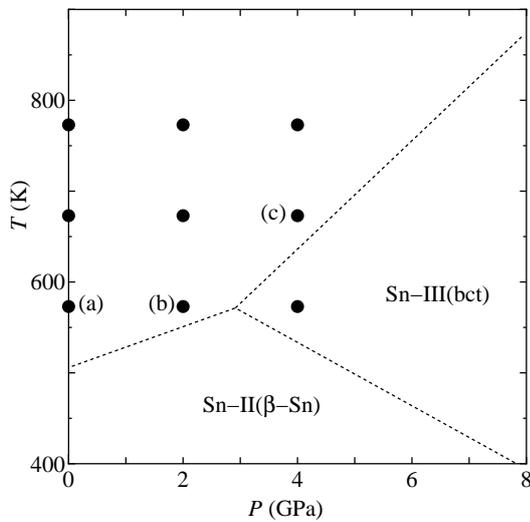


Figure 1. Phase diagram of tin schematically drawn from the references[2, 3]. The Dots show the thermodynamic states studied in this paper.

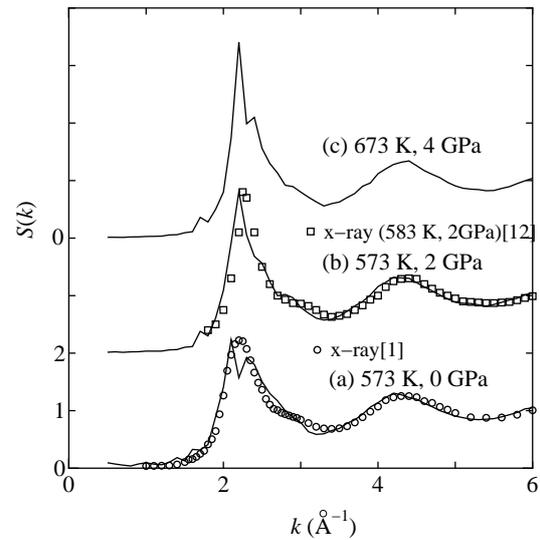


Figure 2. Calculated structure factors $S(k)$ for the three states. X-ray diffraction data are also shown by the circles[1] and squares[12].

a cutoff energy of 10 Ryd. The Γ point was only used to sample the Brillouin zone of the MD supercell. Since the crystal structures of Sn-II and Sn-III are tetragonal, we took a tetragonal MD cell with periodic boundary conditions instead of an ordinary cubic cell, though liquid structure should not depend on the shape of the MD cell. The constant-temperature and constant-pressure simulations[7, 8, 9] were performed employing 64 tin atoms for 4000 ~ 8000 steps with a time step of 3.6 fs at each thermodynamic state. Note that during the simulation the MD cell is allowed to change its shape with keeping it tetragonal.

To study the structural change of liquid tin with temperature and pressure variations we have performed the simulations at nine thermodynamic states as shown in figure 1 *i.e.* at the temperatures of 573, 673 and 773 K and at the pressures of 0, 2, 4 GPa. The structure factor $S(k)$, radial distribution function $g(r)$, three body angle distribution function $g^{(3)}(r_c, \theta)$ and the distribution of the coordination number $p(n_c)$ were calculated by averaging over 3500 ~ 7500 steps after the system reached the equilibrium state.

3. Results and Discussions

First we have analyzed temperature dependence of structure with constant pressure of 0 GPa and found that the short range structure of liquid tin does not so much depend on the temperature. This feature was also shown in the previous studies [10, 11] in which the structural change of liquid tin was investigated in a wider range of the temperature from 773 K to 1873 K.

In the following we focus on the pressure dependence of the structure in liquid tin especially by taking the three states along the experimentally reported melting curve, (a) 573 K, 0 GPa, (b) 573 K, 2 GPa and (c) 673 K, 4 GPa.

From the constant-pressure MD simulations, average volume of the MD cell V_{ave} is obtained as $V_{ave} = (L_a L_b L_c)_{ave}$, where $L_{a,b,c}$ are the lengths of the sides of the MD cell. The results of the average number densities and the average lengths of the MD cell ($n \text{ \AA}^{-3}$, $L_{ave} \text{ \AA}$) are (0.0312, 12.7), (0.0336, 12.4) and (0.0349, 12.2) at the states of (a), (b) and (c), respectively.

Figure 2 shows the calculated structure factors of liquid tin $S(k)$ at the three states (a),(b) and

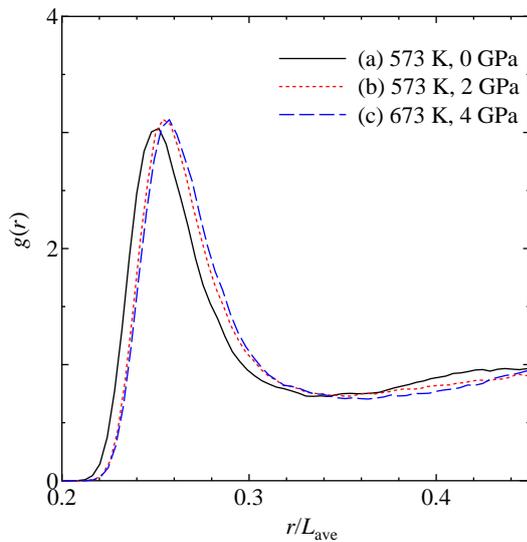


Figure 3. Radial distribution functions $g(r)$ scaled by the average length of the MD cell L_{ave} .

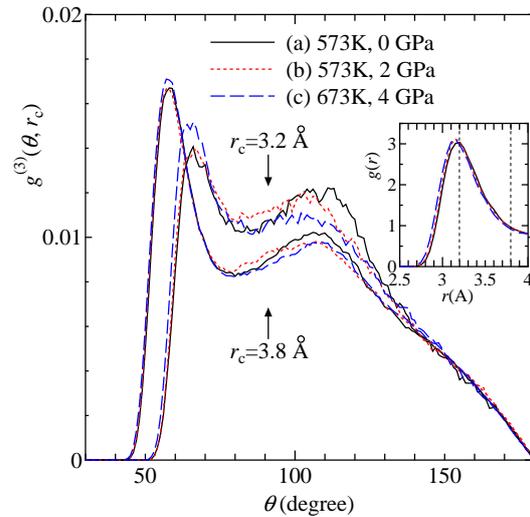


Figure 4. Three-body angle distribution functions $g^{(3)}(r_c, \theta)$ at the three states. The inset shows the cutoff distances r_c in $g(r)$.

(c) with the x-ray diffraction data[1, 12]. The wave number vector calculated by the simulation is given by the equation, $\mathbf{k} = 2\pi \times (l_a/L_a, l_b/L_b, l_c/L_c)$, where $l_{a,b,c}$ and $L_{a,b,c}$ are integers and lengths of the MD cell for the three sides, respectively. Since the values of $L_{a,b,c}$ vary during a constant-pressure simulation, the values of $S(k)$ were averaged over a range of 0.1\AA^{-1} . The calculated structure factors $S(k)$ are in very good agreement with the experimental data. The ratio of the wave number of the first peak k_1 to that of the second peak k_2 , k_2/k_1 , is almost 2 within statistical error. From the scattered data of $S(k)$ it is difficult to discuss whether the liquid tin is compressed uniformly or not as discussed in the experimental results[12, 13].

In figure 3, we show the pressure dependence of the radial distribution functions $g(r)$ scaled by the average length of the MD cell L_{ave} . Though the scaled $g(r)$ shifts to a larger r value with increasing pressure from the state (a) to the state (b), that is almost unchanged from (b) to (c). Judging from this result only, the structure of liquid tin seems to change in a way of more than uniform contraction from (a) to (b) and at above 2 GPa that seems to be compressed almost uniformly.

To examine the pressure dependence of the structure more in detail, we show normalized three-body angle distribution functions $g^{(3)}(r_c, \theta)$ at the three states (a), (b) and (c) in figure 3. The three-body angle is formed by a pair of vectors drawn from a reference atom to any other two atoms within the cutoff radius r_c . In figure 4 the cutoff distances r_c are selected as 3.2 and 3.8 Å, which corresponds to the first peak position of $g(r)$ and that of $g(r) \simeq 1$ after the first peak position (see inset in figure 4). When the interatomic interaction is isotropic and the atoms are closely packed, $g^{(3)}(r_c, \theta)$ should show a peak around 60° and consequently a hump around 120° . For the state (a), $g^{(3)}(r_c = 3.2\text{\AA}, \theta)$ has a peak around 60° and also the other clear peak around 110° . Since the peak around 110° is close to the tetrahedral bond angle of 109° , this peak implies the existence of complex local structures due to anisotropic interactions in liquid tin. With increasing pressure, from (a) to (b) the peak around 110° shifts to smaller angles, and then from (b) to (c) the peak becomes to be depressed and the peak around 60° becomes larger. For the larger cutoff distance of 3.8 Å, though the amount of change is smaller, a similar tendency is also observed.

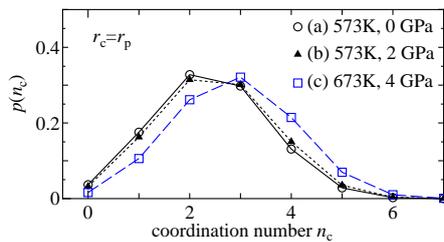


Figure 5. Distribution of the coordination number $p(n_c)$ at the three states.

In figure 5 we show the distributions of coordination number $p(n_c)$ which is calculated by counting the number of atoms around an atom within the distance r_p , the first peak position of $g(r)$. With increasing pressure, while the distribution $p(n_c)$ is almost unchanged from (a) to (b), that clearly shifts to larger values from (b) to (c). Average coordination numbers n_c^{ave} are estimated by $n_c^{\text{ave}} = 2 \times 4\pi n_{\text{ave}} \int_0^{r_p} g(r)r^2 dr$ or $n_c^{\text{ave}} = 2 \sum n_c p(n_c)$. The results of n_c^{ave} are 4.8, 5.0 and 5.7 for the states of (a), (b) and (c), respectively.

4. Conclusions

We have investigated pressure-induced structural change of liquid tin up to 4 GPa by *ab initio* molecular-dynamics simulations. From the results of $g(r)$, $g^{(3)}(r_c, \theta)$ and n_c it is concluded that, with increasing pressure the liquid tin is not compressed uniformly but very gradually changes from complex anisotropic structures to more simple isotropic close-packed structure.

5. Acknowledgments

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