First-Principles Study of the Structural Phase Transition in Sn

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First-Principles Study of the Structural Phase Transition in Sn

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The dependence of phase transition temperature between the α and the β phases of tin (Sn) on pressure is examined through first-principles calculation. The temperature and the pressure-dependent thermodynamic quantities, such as the entropy, the Helmholtz free energy, and the Gibbs free energy, are estimated by employing the phonon density of states, which is calculated by using the frozen phonon approximation. The calculated structural phase transition is compared with experiment.

I. INTRODUCTION

The α phase and the β phase of tin are most commonly observed (crystal structures described in Fig. 1). The mass density of α-Sn is roughly 20 percent lower, and α-Sn is slightly more stable at low temperatures below T = 286 K, above which the β-Sn structure becomes more stable [2,3]. α-Sn is a diamond structure semiconductor with zero band gap while β-Sn has a tetragonal structure and is metallic. 'Gray tin' and 'white tin' are common names for the α phase and the β phase respectively, but α-Sn can be metastable against β-Sn by applying a pressure, and tin has been found to undergo successive phase transitions by further pressure increase [4,5]. The pressure-induced phase transitions of tin and other group-IV elements have been investigated both theoretically and experimentally [2–12]; however, little theoretical study of the pressure-induced phase transition at finite temperature exists.

First-principles calculations based on the density functional theory have been powerful in analyzing the physical properties of matters, but are confined to the ground state. A quasi-harmonic approach based on information on lattice vibration modes can be applied to investigate the finite-temperature state. Arbitrary pressure and temperature conditions can be described by using this approach with proper interpolation, and thermodynamic properties, such as the entropy, the Helmholtz free energy, and the Gibbs free energy can be determined. In this study, we theoretically investigated the dependence of the phase transition between α-Sn and β-Sn on both the pressure and the temperature by utilizing the calculated eigenfrequencies of the lattice vibration.

II. CALCULATION AND DISCUSSION

We used the Vienna ab initio simulation package (VASP) with the projector augmented wave (PAW) schemes [13] and the generalized gradient approximation (GGA) suggested by Perdew *et al.* [14]. The energy cutoff was taken as 241 eV. The k-points were chosen by using the Monkhorst-Pack method [15], and the k-point meshes were set as (5, 5, 5) for the α-Sn and (10, 10, 10) for the β-Sn. Many more k-points were necessary for the β-Sn calculation due to its metallic character to assure calculational convergence.
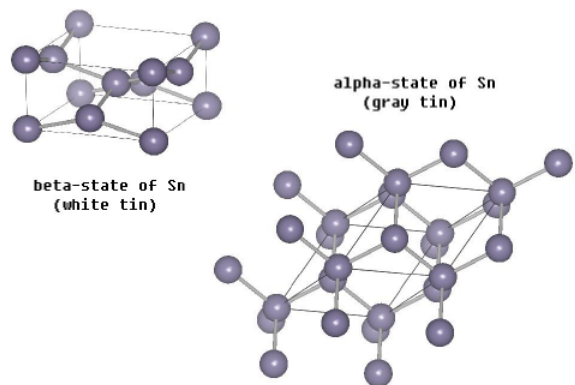

Fig. 1. (Color online) Crystal structures of two different states of tin : the α state and the β state. The α-Sn has a diamond structure, while the β-Sn has a tetragonal structure [1].

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Table 1. Comparison of the lattice constant and the bulk modulus of α-Sn and β-Sn with former calculations.

	α-Sn	β-Sn
	[lattice constant] in A	
our calculation	6.64	5.92
other calculations	6.38^1, 6.48^2, 6.55^3	5.70^1, 5.92^2, 5.85^3
	6.40^4, 6.47^5	5.70^4, 5.73^5
experiment	6.491^6	5.820^6
	[bulk modulus] in 10^9 Pa	
our calculation	47	57
other calculations	47^1, 42.1^2 , 44.7^3	61^1, 64.1^2, 54.4^3
	51.2^4, 45.6^5	60.5^4, 62.9^5
experiment	$(53)^7$	58.2^8
	[$\alpha \Leftrightarrow \beta$ transition temperature at zero pressure] in K	
our calculation	310	
other calculation	311	
experiment	286^9	

1-5 = Refs. 2–6, and 6-9 indicates Refs. 1, 16, 17, and 10.
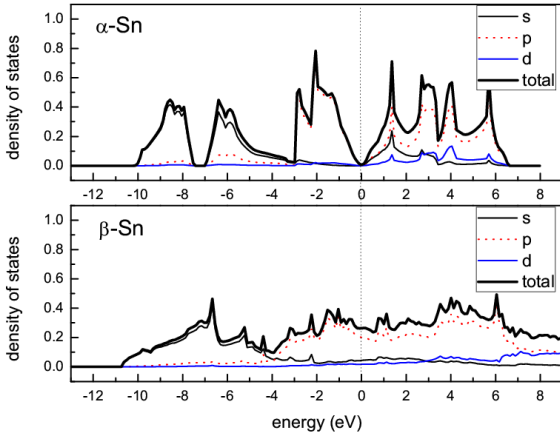
Fig. 2. (Color online) Electronic density of states of the α-Sn and the β-Sn.

The calculated results for the structural parameter are shown in Table I, along with the experimental data and the previously calculated results. The lattice constants of the two phases of tin were calculated to be 6.64 A and 5.92 A, respectively, for α-Sn and β-Sn in the ground state by minimizing the total energy. These are larger by 2 percent than the experimental values [1]. The bulk modulus of each phases were estimated as 47 GPa and 57 GPa. The bulk modulus experimental value for β-Sn is between 55 and 59 GPa [17,18] and is in agreement with our estimate, but experimental value for the α-Sn bulk modulus are scarce.

The calculated electronic density of states and band structure of α-Sn and β-Sn at the ground state are illustrated in Fig. 2 and Fig. 3, which show that α-Sn is a semiconductor with zero band gap and that the β-Sn is
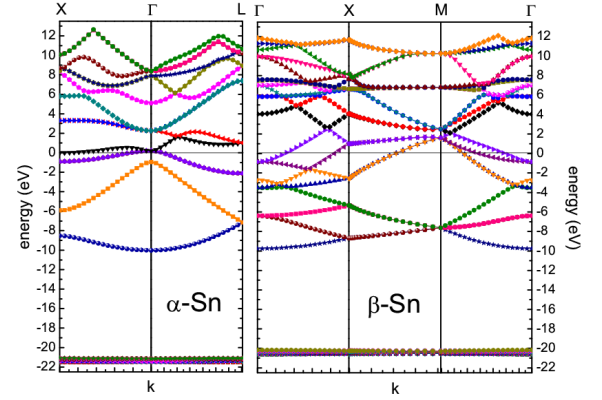
Fig. 3. (Color online) Electronic band structures of the α-Sn and the β-Sn.

metallic. The Sn-3d orbital states are located far below the Fermi level at about -21 or -20 eV for each of the two phases, as shown in Fig. 3. In the semiconducting α-phase, the bands of the s and the p orbitals are split around the Fermi level. This indicates that there is a strong hybridization between the s and the p orbitals in α-Sn, which raises the energy level of the anti-bonding states at the conduction band and lowers the the energy level of the bonding states at the valence band. This lowering of the electron-occupied bonding state can contribute to stabilization of the α-phase relatively to the β-phase.

We calculated the phonon frequency by solving the ω-$\vec{q}$ eigenvalue - eigenvector equation

$$det \left[\frac{1}{\sqrt{M_i M_j}} C_{ij}^{kl}(\vec{q}) - \omega^2 \right] = 0, \qquad (1)$$

where the indices i and j are for the two atoms concerned (displaced atom and target atom), and indices k and l are for the directions of the small displacement of the atom and of the direction of the resulting force on the target atom, and $\vec{q}$ is the wave vector of the vibrational mode. The interatomic force constant C_{ij}^{kl} is calculated by placing a small displacement on the i-th atom in the cell. Care should be taken to assign the amount of this small displacement so that the quasi-harmonic approach is valid; otherwise, too small or too large a displacement would result in failure to find the correct elastic constants and eventually the correct phonon frequencies. The choice of the cell size is often crucial. A larger cell size is desirable for low-frequency acoustic phonon calculation, but causes a quite longer calculation time. The cell multiplicities in this study were taken as $(3 \times 3 \times 3)$ for α-Sn and $(3 \times 3 \times 4)$ for β-Sn.

The calculated phonon dispersion relations for α-Sn and β-Sn are shown in Fig. 4. The phonon densities of the two states of Sn calculated by using uniform q-grid points $(10 \times 10 \times 10)$ in momentum space are shown in Fig. 5. The top two figures in Fig. 4 correspond to the phases under zero pressure, but the bottom figures
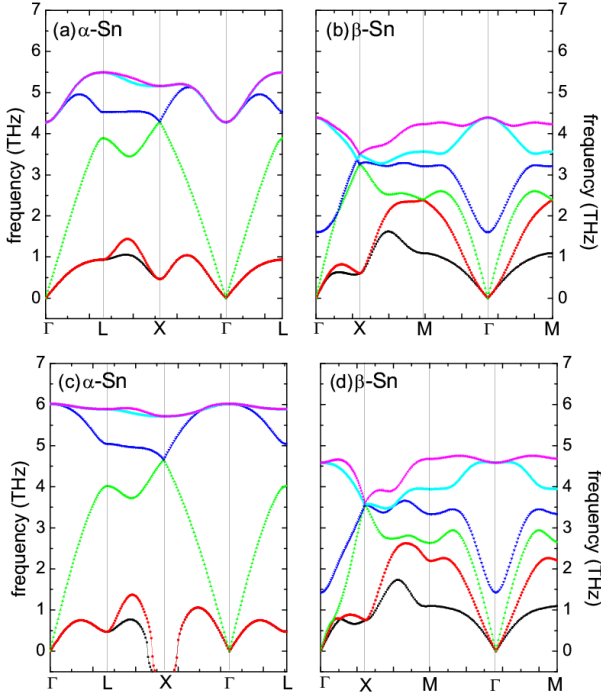
Fig. 4. (Color online) Calculated phonon dispersion curves of the α-Sn and the β-Sn. (a) and (b) are for the α-Sn and the β-Sn under zero pressure, and (c) and (d) correspond to the high pressure states (α-Sn at 2.8 GPa, β-Sn at 2.9 GPa).
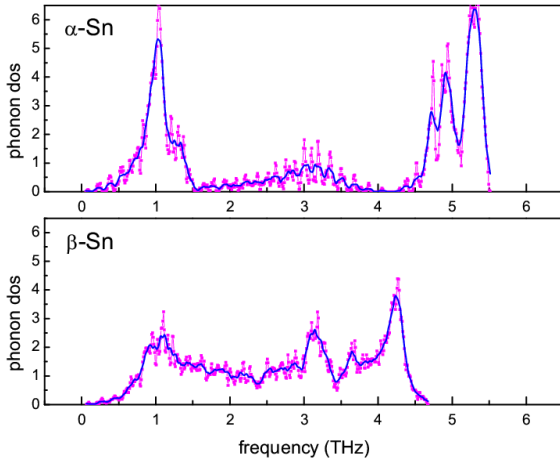

Fig. 5. (Color online) Phonon density of states of the α-Sn and the β-Sn.

correspond to the high pressure state. For the case of α-Sn, parts of the transverse acoustic phonon branch are bent downward with increasing pressure. This indicates phonon softening and has been discussed by Baroni *et al.* [12]. We found that this tendency grows as the pressure increases further. The overall vibrational frequencies of the β phase phonon, especially for the optical modes, are lower than or equal to those of the α phase. This discrepancy is related with the larger entropy and the lower free energy of β-Sn compared to α-Sn.
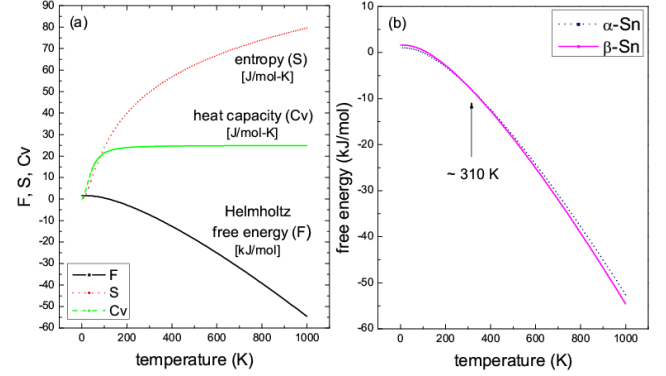

Fig. 6. (Color online) (a) Temperature dependence of the entropy, heat capacity, and Helmholtz free energy of the β-Sn at zero pressure, (b) Helmholtz free energies of the α-Sn and the β-Sn at zero pressure.

Thermodynamic quantities, such as the partition function Q, the Helmholtz free energy F, the internal energy U, the heat capacity C_v, and the entropy S can be calculated by using [19–22]

$$Q = \sum_{\vec{q},n} \exp\left[-\hbar\omega(n + \frac{1}{2})/kT\right], \tag{2}$$

$$F = -kTlnQ = \sum_{\vec{q}} \left[\frac{\hbar\omega}{2} + kTln\left(1 - \exp\left(-\hbar\omega/kT\right)\right)\right]$$

$$= \sum_{\vec{q}} ln\left[2\sinh\left(\frac{\hbar\omega}{2kT}\right)\right], \tag{3}$$

$$U = \sum_{\vec{q}} \left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1}\right]. \tag{4}$$

The entropy can be expressed as $S = -\dfrac{\partial F}{\partial T}$, and the heat capacity can also be expressed as $C_v = \dfrac{\partial U}{\partial T}$. The calculated F, S, and Cv of β-Sn at zero pressure are shown in Fig. 6, where the zero point energies were included. The two Helmholtz free energy curves for α-Sn and β-Sn cross at about 310 K, which is slightly higher than the experimental estimate of 13°C for the phase transition under ambient pressure. Our estimate of the $\alpha \Leftrightarrow \beta$ transition temperature as 310 K by using the GGA is almost identical to the former estimate of 311 K from the LDA calculation by Pavone *et al.* [2].

The pressure was estimated by adding two contributions - phonon contribution and electron contribution: $P = P_{ph} + P_{el} = -\left(\dfrac{\partial F_{ph}}{\partial T} + \dfrac{\partial F_{el}}{\partial T}\right)$. The free energy F is the sum of the two parts, F_{ph} and F_{el}. F_{ph} is the phonon contribution, i.e., lattice dynamical free energy, which was calculated by using Eq. (3) above, and F_{el} is the free energy of electronic contribution. The Gibbs
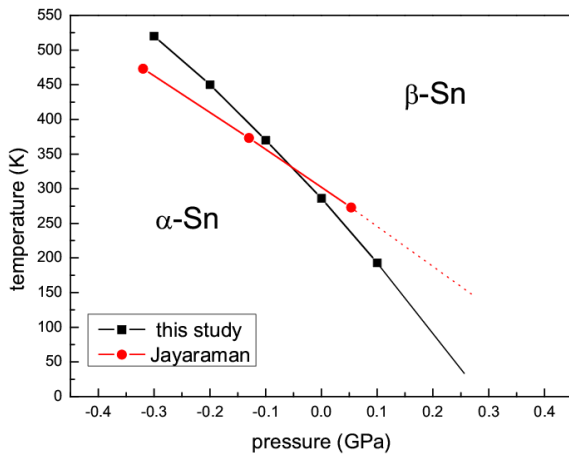
Fig. 7. (Color online) Calculated dependence of the phase transition temperature between the α-Sn and the β-Sn on the pressure is compared with an experimental estimate.

free energy $G = F + PV$ is the relevant thermodynamic quantity to determine the stable phase between neighboring phases.

The discrete Gibbs free energy values acquired for each of the two phases are interpolated. In Fig. 7, the pressure-dependent phase transition temperature is shown and compared with an experimental estimation by Jayaraman *et al.* [10]. Jayaraman used the Clapeyron equation to identify the slope dT/dP of the boundary. Our curve is slightly shifted so that it would be reconciled with the known transition temperature of 13 ^{o}C at zero pressure. We estimate the phase transition pressure at 0 K to be 0.3 GPa, which is in between the two previous theoretical estimates of 0.2 GPa by Christensen and Methfessel [4] and 0.8 GPa by Cheong and Chang [5]. The differences between these theoretical estimates should be ascribed to different calculation schemes.

III. CONCLUSIONS

First-principles calculations of the thermodynamic quantities for Sn were carried out in order to predict the structural phase transition. The phonon dispersion relations and the phonon density of states were calculated for two states of Sn. The Gibbs free energy and other thermodynamic properties were calculated for α-Sn and β-Sn by using phonon dispersion, by which the phase transition boundary between the two phases of tin was estimated.

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