Equilibrium and Thermodynamic Properties of Grey, White, and Liquid Tin

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The thermodynamic properties of various phases of tin are calculated employing the method of adiabatic switching with modified embedded atom method (MEAM) potentials. The experimental $\alpha \rightarrow \beta$ and $\beta \rightarrow$ liquid transition temperatures are reproduced within an 11% accuracy. Good agreement with experiments is also obtained for other thermodynamic quantities. We demonstrate the versatility and accuracy of MEAM by how well it reproduces both metallic and covalent phases of tin over a wide temperature range and over a wide range of densities. [S0031-9007(97)04144-6]

The structural, electronic and thermodynamic properties of tin have been the subjects of considerable interest to the scientific community from both experimental [1,2] and theoretical [3–5] camps. The reasons are mostly due to the sensitivity of its properties to temperature and pressure changes. This in turn is due to the location of Sn in the periodic table. Tin belongs to group IV of the periodic table together with C, Si, Ge, and Pb. Above Sn, the elements C, Si, and Ge tend to form a diamond structure with strong covalent bonds, while below Sn the stable phase for Pb is metallic and fcc. It turns out that Sn is borderline between covalent and metallic bonding. This behavior is apparent in its phase diagram at atmospheric pressure: Below 286 K, Sn crystallizes into a grey material with a diamond cubic structure (α Sn) with a zero band gap [1]. Above this temperature, Sn is metallic and crystallizes into a white structure with a tetragonal crystal structure called β Sn. The β phase melts at a relatively low temperature: 505 K. So far, a microscopic description of the $\alpha \rightarrow \beta$ transition, as well as $\beta \rightarrow$ liquid, is not available. Considerable progress has been achieved within the past decade in calculations of zero temperature properties of real materials from first-principles quantum mechanical theory. Although in principle this type of calculation could be extended to finite temperature, an accurate description of thermodynamic properties from first principles is still a formidable computational task. Theoretical studies of Sn have been limited to studies of pressure-induced phase transitions of the solid phase at zero temperature [4,5].

In this paper, we report on molecular dynamics (MD) calculations of the thermodynamic properties of α, β, and liquid Sn as a function of temperature. We have evaluated the free energy and entropy of these phases by employing the method of adiabatic switching [6] with isothermal simulations. The atomic interactions are given by modified embedded atom method (MEAM) potentials [7]. Using a single set of MEAM functions, we reproduce a wide set of elastic and mechanical properties of Sn as well as more delicate quantities such as the α to β

transition temperature which defines a transition from a semiconducting to a metallic phase. We are also able to reproduce the experimental melting temperature of Sn within an 11% accuracy and many of the liquid properties.

There is no reason to expect that a classical model can predict both metallic and covalent bonding, as well as liquid properties, with a single set of interatomic potentials. The accurate description of the properties of a material such as Sn over a wide range of temperatures shows that MEAM is a robust method which can be used to describe metallic as well as covalently bonded materials.

The embedded atom method (EAM) has been shown over the past decade to be a reliable semiempirical method of calculation for a large class of metallic materials [8]. Recently Baskes *et al.* have introduced a modification to the EAM to extend the application of the method to materials with directional bonding, e.g., group IV elements: C, Si, Ge, and Sn [7,9]. The modified EAM (MEAM) includes the angular forces that result from directional bonding by modifying the background electron density from the spherically averaged density used in EAM. A detailed description of the model is provided in Refs. [7,10]. Because of space constraints, we include here a very brief description. The total energy E of a monatomic system is

$$E = \sum_i \left(F(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) \right), \qquad (1)$$

where $\phi(r_{ij})$ is a pair potential. The embedding function $F(\bar{\rho})$ is taken as $F(\bar{\rho}) = A E_c \frac{\bar{\rho}}{\rho_0} \ln(\frac{\bar{\rho}}{\rho_0})$. A is an adjustable parameter, E_c is the cohesive energy, and ρ_0 is a scaling parameter.

Unlike EAM, where the electron density is assumed to be spherically symmetric, MEAM assumes that the background electron density at a specific site $\bar{\rho}_i$ is a function of angle dependent "partial electron densities,"

$$\bar{\rho} = \frac{2\rho^{(0)}}{1 + e^{-\Gamma}}, \qquad (2)$$

where $\Gamma = \sum_{h=1}^{3} t^{(h)}(\rho^{(h)}/\rho^{(0)})^2$. $\rho^{(0)}$ is the spherically symmetric electron density, $t^{(h)}$ are constants, and $\rho^{(h)}$ are sums of simple exponentials with decay constants $\beta^{(h)}$ with x, y, and z projections of the distances between atoms.

The MEAM parameters for tin are obtained by fitting to the cohesive energy, lattice and elastic constant of α Sn, the lattice constants and vacancy formation energy of β Sn and the energy difference between various forms of Sn at 0 K. The resultant parameters using an fcc reference structure for Sn are given in Table I. Angular screening was implemented using the method detailed in Ref. [10] with $C_{\min} = 0.8$ and $C_{\max} = 2.8$.

We found that the $\alpha \rightarrow \beta$ transition temperature is quite sensitive to the structural energy difference between α and β phases. Ihm and Cohen [3] estimated the energy difference at 0 K between grey and white tin to be 0.04 eV/atom from nonrelativistic *ab initio* calculations and 0.015 eV/atom from the integration of the experimental C_p values. Cheong and Chang [4] used a first-principles total-energy pseudopotential method within the local density approximation to obtain a value of 0.034 eV/atom. More recent full-potential linear muffin-tin-orbital calculations have obtained a value of 0.0098 eV/atom for the structural energy difference between α and β tin [5]. Given the variation in the energy difference, we opted in this paper to vary the parameters in the potential to improve our calculated $\alpha \rightarrow \beta$ transition temperature at a cost of not fitting the $\alpha - \beta$ structural energy difference, since it was felt that the transition temperature was known more accurately than the energy difference. The value we obtain from this procedure is 0.055 eV/atom, which is higher than from previous calculations.

The resultant structural and elastic properties are given in Table II. In general there is excellent agreement with experiment with the exception of C_{44} for β Sn, where the calculation is almost an order of magnitude smaller than experiment. Note that the elastic constants for β Sn are a prediction of the model. The structural details of the tetragonal distortion are reproduced exactly (c/a), but not the elastic details. Experimentally, it is seen that the lattice is slightly stiffer in the c direction ($C_{33} > C_{11}$), but we calculate the opposite. In contrast, we predict the correct relationship between C_{12} and C_{13}.

The free energy of the α, β, and liquid Sn were evaluated employing the method of adiabatic switching in a molecular dynamics formalism. The method is based on Kirkwood's idea for evaluating the free energy of a system relative to a reference system by integrating the derivative of the free-energy difference between the systems along a reversible thermodynamic path which connects the system of interest with the reference system whose free energy is known [6]. An effective Hamiltonian is constructed from both systems such that

$$H_{\text{eff}}(\lambda) = (1 - \lambda)H_0 + \lambda H_1 = H_0 + \lambda \Delta H, \quad (3)$$

where H_0 is the Hamiltonian of the actual system, H_1 is the Hamiltonian of the reference system, and $0 \le \lambda \le 1$. The free-energy difference can be written as the integral over the thermodynamic path connecting both systems,

$$\Delta F = \int_0^1 \frac{\partial H_{\text{eff}}(\lambda)}{\partial \lambda} d\lambda = \int_0^1 \langle \Delta H \rangle_\lambda d\lambda. \quad (4)$$

Watanabe and Reinhardt [11] suggested the integral be carried out dynamically by allowing λ to be a function of time. In our free-energy calculations, we allow λ to vary linearly with time. The free-energy difference is then computed from the MD time average of ΔH over a time interval τ much longer than the natural vibrational period:

$$\Delta F = F_1 - F_0 = \frac{1}{\tau} \int_0^\tau \Delta H dt = \langle H_1 \rangle - \langle H_0 \rangle, \quad (5)$$

where $\langle \rangle$ means MD time averaging.

In the calculations of the free energy of the α and β phases, the chosen reference system was a harmonic solid with N-identical oscillators with a spring constant $k_{\text{eff}} = 2.0$ eV/atom and a zero motion energy of -3.14 eV/atom. The spring constant was chosen to match the average root-mean-squared (rms) displacement of the Sn atoms at 300 K and to obtain an average Einstein frequency in the harmonic solid which would correspond to a mean frequency of Sn ($\omega \sim 8$ meV). The rms displacement in the β phase was found to be larger than the rms of the α phase by as much as a factor of 2. The chosen value of the spring constant represents a compromise between these two criteria and between the two phases. The same value of k_{eff} was used at all sampled temperatures. The computational cell consisted of 1400 atoms for β Sn and 1720 for α Sn. The systems were equilibrated for about 5.0 ps using isothermal-isobaric MD [12,13] at various temperatures in the range 50–600 K and at zero external pressure. The equilibrated samples were then switched to a harmonic solid using isothermal MD. Convergence was checked by varying the switching time interval. We found that a switching time of 10 ps was sufficient to obtain an accuracy in the free energy of about 1–3 meV/atom.

TABLE I. MEAM parameters of tin. E_c is the cohesive energy, r_0 is the nearest-neighbor distance, and $\alpha^2 = 9\Omega B/E_c$, with B = bulk modulus and Ω the atomic volume of the reference structure (fcc Sn).

E_c (eV)	A	r_o (Å)	α	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$
3.08	1.0	3.44	6.20	6.2	6.0	6.0	6.0	4.5	6.5	-0.183

TABLE II. Calculated elastic and structural properties of α and β tin compared to experiment. Quantities in parentheses are from first-principles calculations.

Quantity	α (calc.)	α (expt.)	β (calc.)	β (expt.)
Ecoh (eV/atom)	−3.140	−3.140[a]	−3.085	(−3.10)[b], (−3.13)[c]
V (Å^3/atom)	34.05	34.05[d]	28.34	27.07[d]
a (Å)	6.483	6.483[d]	5.92	5.8313[d]
c/a	...	...	0.546	0.546[d]
B (eV/Å^3)	0.263	0.266[e]	0.40	0.356[e]
C_{11} (eV/Å^3)	0.458	0.431[e]	0.683	0.458[e]
C_{33} (eV/Å^3)	...	...	0.673	0.566[e]
C_{12} (eV/Å^3)	0.166	0.133[e]	0.360	0.374[e]
C_{13} (eV/Å^3)	...	...	0.217	0.244[e]
C_{66} (eV/Å^3)	0.244	0.266[e]	0.167	0.149[e]
C_{44} (eV/Å^3)	...	...	0.016	0.137[e]

[a]Ref. [17], [b]Ref. [3], [c]Ref. [5], [d]Ref. [18], [e]Ref. [19].

The liquid Sn was obtained by equilibrating the β structure at 600 K for 30 ps at isobaric-isothermal conditions with a zero external pressure. This sample was then used to obtained liquid Sn at other temperatures in the range 300–900 K using isothermal-isobaric MD. The free energy of the liquid phase was calculated using two different thermodynamic paths. We switched isothermally to an ideal gas by "turning off" all interactions. The final configuration was an ideal gas at the same volume and temperature as the starting liquid. The second path involved two steps. First, we switched isothermally to a Weeks-Andersen-Chandler (WAC) liquid [14]. The WAC potential is a Lennard-Jones potential with no attractive piece: $\Phi(r) = \varepsilon[(\frac{r_0}{r})^6 - 1]^2$ for $r \leq r_0$, and $\Phi(r) = 0$ for $r > r_0$. Its liquid structure is almost identical with the Lennard-Jones liquid [15]. The parameters ε and r_0 were chosen to match the internal energy and density of the Sn liquid at the appropriate temperature. This step gives the free energy difference between liquid Sn and the WAC liquid at the appropriate density and temperature. In the second step, the WAC liquid was then expanded isothermally to the ideal gas limit, and the free-energy difference between the WAC liquid and the ideal gas was calculated from the integral,

$$\Delta F = \int_{V_0}^{\infty} (P - P_I)\, dV, \qquad (6)$$

where P is the pressure of the system and P_I is the ideal gas pressure [15]. The expansion was carried out by imposing an isotropic strain rate of 0.01 ps^{-1} and expanding for 220 ps. Both methods give the same free energy of liquid Sn at 900 and 600 K within 3–5 meV/atom, with the pressure integration method being the one with a larger statistical error.

Figure 1 shows the free energy and entropy of the α, β, and liquid phases as a function of temperature. For the sake of clarity, the differences $(F_\alpha - F_\beta)$ and $(F_\beta - F_l)$ are shown. From the free-energy difference, the $(\alpha \rightarrow \beta)$ transition takes place at 283 K, in good agreement with the known experimental value of 286.3 K

[16], while the $(\beta \rightarrow$ liquid) transition occurs at 453 K. This melting temperature is 11% lower than the known experimental value of 505 K. This difference is consistent with the accuracy of our free-energy calculations of the liquid phase, where the relative error is of the order of 5 meV/atom, sufficient to create an error of about 50 K in the melting temperature.

Good agreement with experiment is also found for the specific heat at constant pressure. The values of C_p as well as other thermodynamic properties are shown in Table III. Overall, the agreement with experimental values is good, except for the change in enthalpy at the $\alpha \rightarrow \beta$ transition and at the melting point. The former is more than twice the experimental value. This is probably
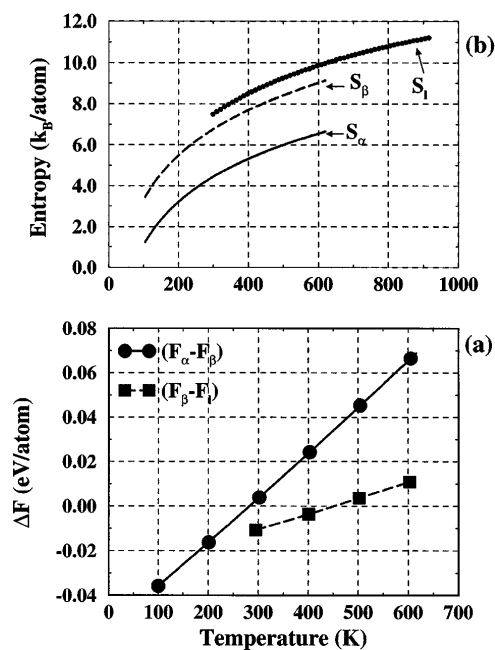

FIG. 1. (a) free-energy difference between α and β tin (solid line) and β and liquid tin (dashed line) as a function of temperature. (b) Entropy of α, β, and liquid phases obtained from the temperature derivative, $S = -(\partial F / \partial T)$, of least-square fits to the free energies corresponding to each phase. Note the large entropy difference between the α and β phases.

TABLE III. Calculated thermodynamics properties. Unless otherwise noted, values are at theoretical and experimental transition points.

Quantity	This work	Experiment
T_t	283 K	286 K[a]
T_m	453 K	505 K[b]
ΔH_t	0.056 eV/atom	0.022 eV/atom[b]
ΔH_m	0.032 eV/atom	0.073 eV/atom[b]
S_β (298.15 K)	13.35 cal/mol K	12.32 cal/mol K[b]
C_α (298 K)	6.12 cal/mol K	6.11 cal/mol K[c]
C_β (295 K)	6.35 cal/mol K	6.33[c], 6.45[d], cal/mol K
C_l (600 K)	7.088 cal/mol K	6.90 cal/mol K[d]
V_β (453 K)	29.03 Å^3/atom	27.40[e]
$\Delta V_m/V_\beta$	2.26%	2.3%[c]
α_α (273 K)	1.38×10^{-5} K^{-1}	1.99×10^{-5} K^{-1} [c]
α_β (300 K)	1.77×10^{-5} K^{-1}	2.35×10^{-5} K^{-1} [e]
$\alpha_\beta \parallel c$-dir (300 K)	2.09×10^{-5} K^{-1}	2.84×10^{-5} K^{-1} [c]
$\alpha_\beta \perp c$-dir (300 K)	1.37×10^{-5} K^{-1}	1.58×10^{-5} K^{-1} [c]
$\alpha_l(T_m)$	1.87×10^{-5} K^{-1}	2.92×10^{-5} K^{-1} [c]

[a]Ref. [16], [b]Ref. [20], [c]Ref. [21], [d]Ref. [22], [e]Ref. [19].

due to the structural energy difference our model predicts between the α and β phases at 0 K, which is higher (0.055 eV/atom) than the average estimated value for this energy difference (0.015 eV/atom) [3].

Other quantities in Table III are the specific volumes and the thermal expansion coefficients. The calculated volume discontinuity at melting $\Delta V_m/V_\beta$ agrees well with experiment, but the thermal expansion coefficients are underestimated by as much as 35% in the case of the liquid. However, the relative ratio of the liquid to solid (β) expansion coefficients is better reproduced, with the calculated ratio being off by only 15% with respect to the experimental value. The model also reproduces the anisotropy in the expansion coefficient of the β phase which has a lower value in the direction perpendicular to the c axis than in the parallel direction.

In conclusion, we have calculated the thermodynamic properties of the α, β, and liquid phases of tin as a function of temperature using a single modified embedded atom method potential for all phases. The resultant agreement with experiment over a wide range of temperatures demonstrates that MEAM is a robust method which can be used to describe metallic and covalently bonded materials accurately. Its versatility will be most useful in mixed systems, such as metal-semiconductor interfaces, where first-principles methods are difficult to apply.

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