

## Theoretical study of high-pressure phases of tin

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High-pressure phases of Sn are investigated with use of the first-principles pseudopotential total-energy method. The  $T=0$  calculations accurately reproduce the structural parameters of the low-pressure modifications  $\alpha$ -Sn and  $\beta$ -Sn and predict a transition to either bcc or bct at high pressure. The calculated compression ratio of the body-centered phase at high pressure also agrees well with experiment.

Tin undergoes a phase transition at atmospheric pressure just below room temperature from gray tin ( $\alpha$ -Sn) to white tin ( $\beta$ -Sn). The  $\beta$ -Sn structure is then stable up to pressures of at least 9.5 GPa, where a phase change to a body-centered tetragonal (bct) phase with a  $c/a$  ratio of 0.91 has been reported by Olijnyk and Holzapfel.<sup>1</sup> In the pressure range from 35 to 50 GPa they find a transition to body-centered cubic (bcc), although the experimental characterization of this transition is presently under scrutiny.<sup>2</sup> The bcc phase remains stable at pressures up to at least 120 GPa.<sup>2</sup>

The  $\alpha$ -Sn (diamond structure) to  $\beta$ -Sn (double-bct) transition is especially interesting because the two structures are extremely close in energy at room temperature and normal pressure while having vastly different electronic properties. Gray tin is a zero-band-gap semiconductor and white tin is a metal. The fact that the  $\alpha$ -Sn $\rightarrow\beta$ -Sn transition takes place near atmospheric pressure in Sn whereas Si and Ge remain in the diamond phase up to 8.8–12.5 and 9.8–10.6 GPa, respectively, is thought to be primarily due to relativistic effects.<sup>3,4</sup> The present results, which include relativistic corrections, can be compared with nonrelativistic calculations<sup>5</sup> for a study of the importance of these effects in the determination of high-pressure phases of Sn.

The study presented here covers the pressure range up to approximately 100 GPa. The structures considered are diamond ( $\alpha$ -Sn),  $\beta$ -Sn, body-centered tetragonal (bct), body-centered cubic (bcc), and hexagonal close packed (hcp). Since entropy differences between the structures are ignored in this study, the results are valid for  $T=0$  only. *Ab initio* pseudopotentials<sup>6</sup> and a total-energy approach<sup>7</sup> are used. Only scalar-relativistic effects have been taken into account since the ground-state properties are not expected to change significantly within the precision of our calculations<sup>8</sup> and the addition of spin-orbit corrections requires significantly greater computational effort. The total energy is computed with use of the momentum-space formalism of Ihm, Zunger, and Cohen<sup>10</sup> within the local-density approximation (LDA) of density-functional theory using the exchange and correlation potential derived<sup>11</sup> from the Monte Carlo calculations of Ceperley and Alder.<sup>12</sup> We solve the Kohn-

Sham equations using a plane-wave basis determined by a cutoff in the kinetic energy  $(\mathbf{k} + \mathbf{G})^2$  of 30 Ry.<sup>13</sup> The charge density and potentials are represented by Fourier components up to  $G_{\max} = \max\{|\mathbf{G}|\} = 10.95$  a.u.<sup>-1</sup>. To obtain a good sampling of the Brillouin zone for the metallic high-pressure structures,  $\sim 100$ – $200$   $\mathbf{k}$  points are used in an irreducible zone. Only 10 special  $\mathbf{k}$  points<sup>14</sup> are required for the diamond phase because of the existence of a gap over essentially the whole Brillouin zone.

To estimate the static properties and transition pressures, the total energy is calculated for each candidate structure at several different volumes and the values are fitted with the Birch equation of state.<sup>15</sup> For the bcc, bct, and hcp structures the equation of state was fitted to data points at volumes between 25 and 50 a.u.<sup>3</sup>/electron.

With an energy cutoff of 30 Ry for the plane-wave basis, the energy per atom is calculated to within  $\sim 1$  mRy of its value corresponding to a complete set of plane waves. The relative energies between different structures at the *same volume* are calculated to within  $\sim 0.1$  mRy of its value for a complete basis set.

Equilibrium lattice parameters for  $\alpha$ -Sn and  $\beta$ -Sn are shown in Table I. The lattice constants for both phases agree to within 3% of the experimental values, and the  $c/a$  ratio for the  $\beta$ -Sn phase agrees to within less than 1%. Bulk moduli ( $B_0$ ) and their pressure derivatives

TABLE I. Calculated lattice parameters for the minimum-energy  $\alpha$ -Sn and  $\beta$ -Sn phases. Equilibrium lattice constants ( $a_0$ ) and the  $c/a$  ratio for  $\beta$ -Sn are shown. Experimental values are listed in parentheses. RT denotes a room-temperature measurement.

	$\alpha$ -Sn	$\beta$ -Sn
$a_0$ (Å)	6.341 (6.483 [90 K] <sup>a</sup> ) (6.491 [RT] <sup>c</sup> )	5.663 (5.812 [4.2 K] <sup>b</sup> ) (5.820 [RT] <sup>c</sup> )
$c/a$ (at $V_0$ )		$0.546 \pm 0.001$ (0.5455 <sup>c</sup> )

<sup>a</sup>Reference 16.<sup>b</sup>Reference 17.<sup>c</sup>Reference 18.

TABLE II. Calculated and experimental bulk moduli ( $B_0$ ) and their pressure derivatives ( $B'_0$ ) for  $\alpha$ -Sn,  $\beta$ -Sn, bcc, bct, and hcp phases. Experimental values are listed in parentheses. RT denotes a room-temperature measurement.

	$\alpha$ -Sn	$\beta$ -Sn	bcc	bct	hcp
$B_0$ (GPa)	50.5 (53[90 K] <sup>a</sup> )	63.7 (57.9[4.2 K] <sup>b</sup> ) (54.9[RT] <sup>c</sup> )	63.6 (76.4 <sup>d</sup> )	60.8	61.2
$B'_0$	4.64	4.52 (1.77 <sup>e</sup> )	4.43 (4.04 <sup>d</sup> )	4.42	4.35

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 20.

<sup>c</sup>Reference 21.

<sup>d</sup>Reference 2.

<sup>e</sup>Reference 22.

( $B'_0$ ) from the present calculation and experimental values are shown in Table II. We note an improvement of the calculated  $B_0(\alpha$ -Sn) over a previous nonrelativistic calculation<sup>5</sup> of 45.6 GPa.

The value of  $B_0$  for bcc underestimates the experimental value by 17%. The compression ratio at 120 GPa observed in Ref. 2 agrees well with the calculated value, 0.54 and 0.52, respectively; so it is possible that this difference arises from the small range of volume data available to the experimenters for their first-order fit to the Birch equation. In support of this, a fit to the calculated energies at only small volumes, up to the minimum in the  $E(V)$  curve, resulted in a higher bulk modulus,  $\sim$ 65 GPa, compared with 63.6 GPa obtained by fitting to data including higher volumes. Another possible explanation for the low estimate is that at the highest pressures considered, the cores are just beginning to overlap and neglecting this effect may contribute to the discrepancy between calculated and experimental values. This effect, however, would lead to larger estimates for the volume.

The transition pressures for the progression through the candidate structures are shown in Table III. The  $\alpha$ -Sn-to- $\beta$ -Sn structural transition is found to occur around 1 GPa. Estimates of the zero-point-motion energy based on experimental Debye temperatures<sup>23</sup> reduce the calculated transition pressure to about 0.80 GPa. At atmospheric pressure, the transition takes place at 13 °C. The slope of the  $\alpha$ -Sn-to- $\beta$ -Sn transition line can be estimated via the Clausius-Clapeyron equation to be  $-58$  °C/kbar,<sup>24</sup> and thus the  $T=0$  K transition pressure is expected to be  $\sim$ 0.5 GPa.

As is shown in Fig. 1, the total-energy curves for bcc, bct, and hcp lie so close in energy that their relative ordering cannot be determined within the margin of error. The three curves remain close down to a volume of 25 a.u.<sup>3</sup>/electron.

The calculated transition pressure from the  $\beta$ -Sn structure to the bcc or bct phase is  $\sim$ 25.0 GPa. Corrections due to the zero-point motion in the  $\beta$ -Sn and bcc phases yielded a transition pressure of about 23.5 GPa. The value of  $T_{\text{Debye}}$  for the bcc phase was estimated by scaling

the experimental  $T_{\text{Debye}}$  for  $\beta$ -Sn using calculated values of  $B_0$  and density.<sup>25</sup> Experimentally,<sup>1</sup> at room temperature  $\beta$ -Sn transforms to a bct phase at 9.5 GPa. A crude estimate of the  $T=0$  K transition based on the  $\beta$ -Sn-Sn-II (bct) boundary line in the phase diagram<sup>24</sup> gives a pressure of 15–20 GPa. In addition, according to the calculations a bct phase would have a  $c/a$  ratio ranging from 0.87 to 0.90 for pressures between 10 and 50 GPa, compared with the range 0.91–0.95 found in the experiment described in Ref. 1. At pressures between 40 and 56 GPa, the x-ray diffraction patterns show the coexistence of bct and bcc phases, and, above 56 GPa, Sn is pure bcc. Because of the limit on the energy resolution, we cannot differentiate between the bcc and bct phases in the range 25–100 GPa.

It is found experimentally<sup>2</sup> that tin is in the bcc phase

TABLE III. Calculated and experimental structural transition pressures at  $T=0$ . Structures considered in the calculation were  $\alpha$ -Sn,  $\beta$ -Sn, bct, bcc, and hcp. An estimate of the zero-point motion is included in the calculation of the first two transition pressures. All experimental values are at room temperature unless noted otherwise.

	Theoretical $P_t$ (GPa)	Experimental $P_t$ (GPa)
$\alpha$ -Sn $\rightarrow$ $\beta$ -Sn	0.8	$\sim 0$ $\sim 0.5$ (0 K) <sup>a</sup>
$\beta$ -Sn $\rightarrow$ (bcc, bct)	23.5	
(bcc, bct) $\rightarrow$ hcp	$> 90$	
$\beta$ -Sn $\rightarrow$ bct		9.5 <sup>b</sup> 15–20 (0 K) <sup>a</sup>
bct $\rightarrow$ bcc		$\sim 35$ –50 <sup>b</sup>
bcc $\rightarrow$ hcp		$> 120$ <sup>c</sup>

<sup>a</sup>Based on an extrapolation of the phase line in a pressure-temperature diagram (see text and Ref. 23).

<sup>b</sup>Reference 1.

<sup>c</sup>Reference 2.

from  $\sim 50$  GPa to at least 120 GPa, the highest pressure achieved. Although a pressure for the body-centered to hcp transition cannot be predicted from the present study, if stable, a high-pressure hcp phase would have a  $c/a$  ratio between 1.63 and 1.65.

The band structure for the  $\alpha$ -Sn phase at approximately the equilibrium volume is shown in Fig. 2. The calculated band gap in the diamond structure is actually negative (at  $\Gamma$  the first conduction band dips below the threefold-degenerate valence band). This can be attributed to the LDA and the neglect of spin-orbit effects. For the  $\beta$ -Sn lattice (for which the calculated band structure is not shown), the resulting density of states at the Fermi surface is large and hence this material is a good metal, as expected.

In conclusion, the calculated structural parameters for  $\alpha$ -Sn and  $\beta$ -Sn are in good agreement with experimental values. We reproduce the sequence  $\alpha$ -Sn $\rightarrow\beta$ -Sn $\rightarrow$ body-centered phase, and parameters for the high-pressure body-centered phase also reproduce experimental values.

The inclusion of zero-point-motion effects, even within our crude estimation scheme, improves substantially the agreement between predicted and measured transition pressures (corrected to 0 K). Since the high-pressure bcc, bct, and hcp phases lie so close in energy, the calculations do not determine their relative ordering or the critical pressures of transitions among them.

There are discrepancies between the results presented here and measurements at higher pressures. Experimentally, the determination of medium- to high-pressure structures of Sn is incomplete. At pressures near 35 GPa, the x-ray diffraction pattern contains extra lines in addition to the lower-pressure bct lines. All of these extra lines fit a bcc indexing. The bcc lines are the dominant features in the spectrum at about 56 GPa; yet bct lines have been observed at this pressure.<sup>1</sup> Contradicting this, Desgreniers, Vohra, and Ruoff<sup>2</sup> report that from  $\sim 50$  to 120 GPa tin is pure bcc. They see no lines at 52 GPa or above reminiscent of bct. The use of ice as a pressure medium in Ref. 1 has been criticized,<sup>2</sup> and could

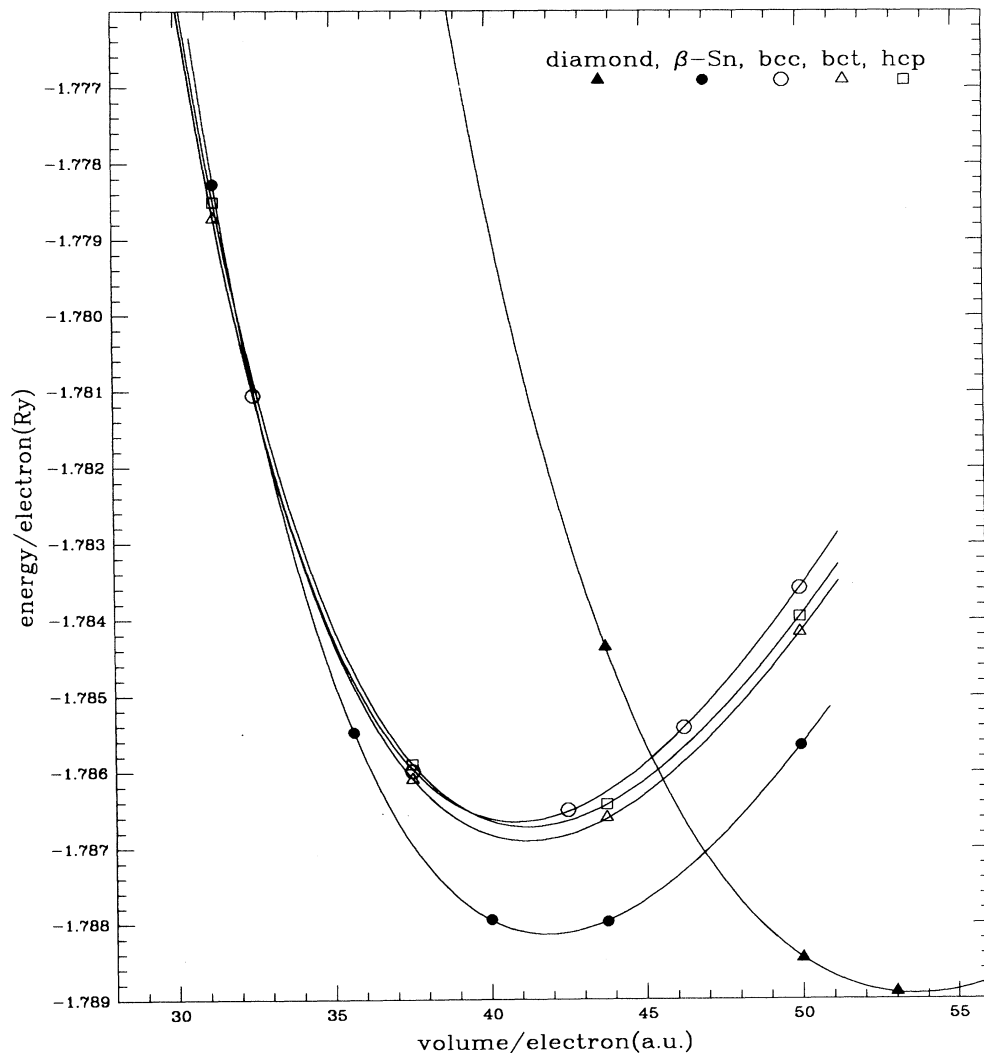


FIG. 1. Total-energy curves for the five structures considered in this work. The fits are to the Birch equation of state.

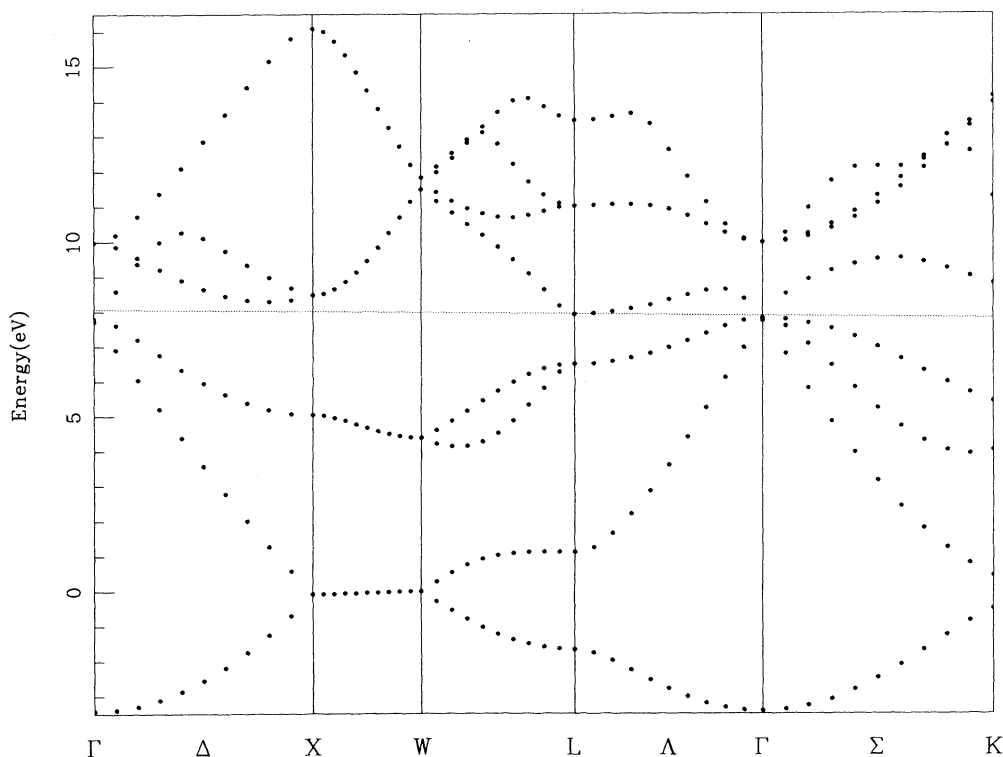


FIG. 2. Band structure for  $\alpha$ -Sn (diamond structure) at the equilibrium volume.

explain the large discrepancy between the calculated and observed  $c/a$  ratios for the bct phase, since above 18 GPa, ice is not a hydrostatic pressure medium.<sup>26</sup> Clarification of the experimental situation in this intermediate region as well as pressures above 120 GPa would provide more guidance in the further development of theory.

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