Pressure Induced Phase Transition in Tin: \textit{ab-initio} Calculations

Debojyoti Mukherjee, K.D. Joshi, and Satish C. Gupta
Applied Physics Division, Bhabha Atomic Research Centre, Mumbai
India 400085

E-mail: debojyoti@barc.gov.in

Abstract. First principles total energy calculations as a function of unit cell volume have been performed on \(\alpha\) (diamond structure), \(\beta\) (double bct), bct, bcc and hcp structures of tin. The comparison of total energies of these structures at various volumes suggests high pressure structural transitions of \(\alpha \rightarrow \beta \rightarrow \text{bct} \rightarrow \text{bcc}\) at pressures of \(\sim 0.15\) GPa, \(2.7\) GPa and \(28\) GPa. Also, \(300\) K isotherm up to maximum pressures of \(\sim 400\) GPa has been determined for this metal. Using theoretical isotherm, shock Hugoniot of tin has been derived. Further, theoretically evaluated volume dependent Gruneisen parameter in conjunction with Lindeman melting law has been used to determine the pressure dependent melting of tin. The intersection of the theoretical melting curve with theoretically determined temperature rise with shock pressure reveals that this metal will melt at shock pressure of \(\sim 38\) GPa (temperature \(\sim 1428\) K) in good agreement with experimental value of \(39\) GPa (\(1550\pm100\) K).

1. Introduction
The group IV A element tin exists in double bct (\(\beta\)) structure at ambient conditions. In past, a number of investigations have been performed on this metal to examine its structural stability under pressure \([1-7]\). For example, in a high pressure x-ray diffraction measurements up to \(10\) GPa on tin Bernett \textit{et al.} \[1\] reported a \(\beta \rightarrow \text{bct}\) transition at \(9.8\) GPa with the \(c/a\) ratio measured to be \(\sim 0.91\). Subsequently, in high pressure energy dispersive x-ray diffraction study Olijnyk and Holzapfel \[2\] observed the \(\beta \rightarrow \text{bct}\) structural transitions at \(10\) GPa and \(35\) GPa. In another high pressure x-ray diffraction study using diamond anvil cell (DAC) Liu and Liu \[3\] reported \(\beta \rightarrow \text{bct} \rightarrow \text{bcc} \) phase transitions at \(\sim 9.7\) GPa and \(40\) GPa respectively. Later, Desgreniers \textit{et al.} \[4\] in a high pressure study up to \(120\) GPa reported the same structural sequence and demonstrated that the bcc phase remains stable up to \(120\) GPa. In a theoretical study, using ab-initio pseudopotential method Corkill \textit{et al.} \[5\] reported the structural transition sequence of \(\alpha \rightarrow \beta \rightarrow \text{bct} \rightarrow \text{bcc} \rightarrow \text{hcp}\) at pressures of \(0.8\) GPa, \(23.5\) GPa and \(90\) GPa, respectively. The \(\beta \rightarrow \text{bct}\) transition pressure of \(23.5\) GPa reported in this study does not agree with experiments. Also, the \(\text{bct} \rightarrow \text{hcp}\) transition predicted by these authors is not observed up to \(120\) GPa (the maximum pressure reached) in experimental study by Desgreniers \textit{et al.} \[4\]. In another study based on full potential linear muffin-tin orbital (FP-LMTO) calculations Christensien and Methfessel \[6\] reported \(\alpha \rightarrow \beta \rightarrow \text{bct} \rightarrow \text{bcc} \) transition sequence at pressures of \(0.2\) GPa, \(10.4\) GPa and \(50\) GPa, respectively. However, subsequently, Chun \textit{et al.} \[7\] using Cambridge Serial Total Energy Package (castep) which is again a total energy pseudopotential calculation method suggested the high pressure structural sequence of \(\alpha \rightarrow \beta \rightarrow \text{bct} \rightarrow \text{bcc} \rightarrow \text{hcp}\) in tin at pressures of \(0.7\) GPa, \(12\) GPa, \(45\) GPa and \(160\) GPa. Recently, using non local ultra soft pseudopotential method
within generalised gradient approximations (GGA) Shouxin Cui et. al. [8] have determined the enthalpies of various high pressure phases of this metal and reported the \( \alpha \rightarrow \beta \rightarrow \text{bcc} \) transition pressures to be 1.9 GPa, 13 GPa and 32 GPa, respectively. Further, in contrast to Chun et. al. [7], these authors do not find \( \text{bcc} \rightarrow \text{hcp} \) up to maximum theoretical pressure of 200 GPa.

In addition to the pressure induced structural phase transitions, the room pressure melting and pressure effect on melting temperature of tin has also attracted the attention of researchers [9-11]. For example, Ravelo and Basakes [9] in their molecular dynamics calculations determined thermodynamic properties of tin at room pressure. On the basis of the calculated free energy differences between \( \alpha \) and \( \beta \), and between \( \beta \) and liquid phase, these authors reported the room pressure \( \alpha \rightarrow \beta \) and \( \beta \) to liquid phase transition at 283 K and 453 K, respectively. Similarly, through optimal potential method, which is a combination of both the first principle and classical molecular dynamics, Bernard and Maillet [10] determined the room pressure melting temperature of tin as 450 K as compared to experimental value of 510 K. Further, they determined the shock Hugoniot and pressure effect on melting up to 200 GPa and 50 GPa, respectively. The pressure dependence of melting temperatures determined by these authors is not in agreement with the melting line measured through DAC experiments [11]. In past experimental studies under shock compressions have also been reported on this metal [12-15]. Though a large body of Hugoniot data have been generated by these experiments, the \( \text{bct} \rightarrow \text{bcc} \) phase transition have remained undetected as the volume change associated with this transition is very small \( \sim 0.8 \% \) [3]. Recently, sound velocity measurements have been performed using velocity interferometer system for any reflector (VISAR) in plate impact experiments carried out in reverse impact geometry configuration [16]. In this study Hu et. al. [16] have reported shock induced \( \text{bct} \rightarrow \text{bcc} \) and \( \text{bcc} \rightarrow \text{melting transitions as 34 \pm 2 GPa and 39 \pm 2 GPa, respectively.} \)

In the present work, we have performed first principles total energy calculations as a function of hydrostatic compression on \( \alpha, \beta, \text{bct}, \text{bcc} \) and \( \text{hcp} \) phases of tin and analysed its structural stability under pressure. Also, we have determined the 300 K isotherm up to \( \sim 400 \) GPa after adding the finite temperature contributions to the total energy calculated at 0 K. Further, the Hugoniot of tin has been derived from the theoretical isotherm up to \( \sim 380 \) GPa. Additionally, using theoretically evaluated volume dependent Gruneisen parameter in Lindeman melting law, the pressure dependent melting of tin has been determined. The shock induced melting of tin has been determined from the theoretical melting curve and temperature rise along Hugoniot.

2. Theoretical Procedure

The total energy calculations have been performed as a function of hydrostatic compression on \( \alpha, \beta, \text{bct}, \text{bcc} \) and \( \text{hcp} \) phases of tin employing full potential linearised augmented plane wave method (FP-LAPW) method (WIEN 97 package) [17] within GGA [18] for exchange - correlation energy. The \( \alpha \) phase is diamond structure and the \( \beta \) phase is tetragonal distortion of the \( \alpha \) phase having double bct structure with \( c/a \) ratio 0.546. The calculation of \( \alpha \) and \( \beta \) phase were performed in double bct cell having four atoms located at (000), \((0 \ ½ \ ½), (½ \ 0 \ ¼) \) and \((½ \ ½ \ ½) [19] \) or equivalently at \((0 \ ¼ \ 1/8), (½ \ ½ \ 3/8) (½ \ ½ \ 5/8) \) and \((0 \ ½ \ 7/8) \) (site 4a). It may be noted that for \( c/a =1.414, \) the cell becomes \( \alpha \) structure. Similarly, the calculations of \( \text{bct} \) and \( \text{bcc} \) phases were carried out in bct cell. The bct phase has \( c/a \) ratio 0.91. The bct cell for \( c/a =1.0 \) corresponds to \( \text{bcc} \) structure. The muffin tin radius used for all the structures is 2.0 \ a.u. and the plane wave cut-off parameter \( R_{\text{Kmax}} \) is fixed at 10. Before doing the calculations a point convergence test is carried out at ambient volume. For this we varied the number of \( k \) points in the Brillouin zone from 2000 to 10000 and found that 5000 \( k \) points are sufficient to obtain energy convergence within 0.1 mRy/atom. Therefore, for further calculations a grid of 5000 \( k \) points is used for sampling of the full Brillouin zone. The structural stability analysis at 300 K is carried out by comparing the total free energy of \( \alpha, \beta, \text{bcc} \) and \( \text{hcp} \) phases under hydrostatic compression. The free energy \( (F) \) at \( T=300 \) K is determined using the expression

\[
F(V, T) = E(V, T) - TS(V)
\]
Where the entropy contribution ‘TS(V)’ and the total energy $E(V,T)$ at $T=300$ is determined using the procedure followed by Walsh et. al [20] and Godwal and Jeanloz [21]. The 300 K isotherm is determined using following expressions [21, 22]

$$E(V,T) = E_e(V) + E_r(V,T) + E_s(V,T)$$

(2)

$$P(V,T) = -\frac{\partial E_e(V)}{\partial V} + \frac{\gamma E_r}{V} + \frac{1}{2} \frac{\gamma}{V} E_s$$

(3)

$E_r(V,T)$ is thermal lattice contribution including zero point vibration energy and $E_e(V,T) = \frac{1}{2} \beta T^2$ is thermal electronic contribution to total energy. The various terms in these equations were determined using the procedures described by Godwal and Jeanloz [21] and Gupta et. al [22].

The shock Hugoniot of tin is determined using the Eqs (2) and (3) together with the Rankine – Huginot equation. The pressure effect on melting is determined for bcc phase using the procedure followed by Soma et. al [23]; according to which the melting temperature at any compression $y(V/V_0)$ is given by:

$$T_{mel}(y) = T_{mel}(1) \exp \left[ 2 \int_y^1 \frac{\gamma(y) - \frac{1}{3}}{y} dy \right]$$

(4)

The variation in melting temperature as a function of compression $y(V/V_0)$ is determined using theoretically determined $\gamma(y)$. The melting temperature is plotted as a function of compression or corresponding pressure. Finally, temperature rise along the Hugoniot and melting temperature as a function of pressure are plotted together and crossover of the two curves yielded the shock pressure and corresponding temperature at which melting of Tin occurs under shock compression.

3. Results and Discussions
Figure 1. Free energy versus volume for various phases of tin. The inset shows the relative energy of bct and hcp phase with respect to β phase.

Figure 2. The atomic rearrangements required for formation of bct and hcp cell from β cell in tin. (a) Atoms labelled by 1, 2, 3 and 4 in β cell are located at (0 0 0), (½ 0 ¼), (½ ½ ½) and (0 ½ ¾), respectively; (b) To form bct cell from β cell the atoms labelled as 2, 3 and 4 require to shuffle by (0 0 ¼), (0 0 ½) and (0 0 -¼), respectively; (c) the dotted cell so formed is bct cell and (d) displays the (110) plane of the bct cell with atoms shown by filled circles lie on the plane and those with open circle lie in above or below layers. The arrows in Fig 2(d) indicate the atoms shown by open circle need to be moved in order to have hcp stacking.

The free energy as a function of volume has been determined for α, β, bct, bcc and hcp phase of tin. The equilibrium lattice parameters determined for α, β and bct structures from the present calculations at ambient conditions have been compared with the available experimental data [1, 3, 24] in table 1. The 300 K free energy of α, β, bct, bcc and hcp phase of tin is plotted as a function of primitive cell volume in figure 1. It is clear from the figure that the α phase is stable at ambient conditions and it transforms to β phase at a pressure of ~ 0.15 GPa. The bct and hcp phases are close to each other (within the accuracy of the calculation ~ 0.1 mRy/atom). The free energy vs volume plot of β phase crosses the bct or hcp phase at volume V = 26.8 (Å³)/atom with corresponding pressure of ~ 2.7 GPa.
Therefore, based on this it is not possible to say whether the transformed structure will be bct or hcp. Since the pressure induced transformations are diffusionless in nature [25] it is possible to identify the path of various atoms involved in the transition. Energetically, the path taken by the atoms is the one which introduces the least activation barrier for the transition. This requires an extensive calculation in which the total energy surface is constructed in terms of all the independent variables describing the transformation. Qualitatively, however, it is expected that the path of the transition is the one which involves the least rearrangements or smallest displacements of atoms. To qualitatively examine which path of transition is more likely, we have estimated the atomic displacements required to form bct and hcp cells from β cell. As displayed in figure 2 the bct cell can be formed from β cell by (i) shifting atoms (0 ½ ¾), (½ 0 ¼) and (½½½ ½) by (0 0 -¼), (0 0 ¼) and (0 0 ½), respectively and (ii) simultaneous expansion along c-axis and compression along a axis to change the c/a ratio from 0.772 to 0.91. As shown in figure 2(d) for transformation of β cell to hcp structure the following steps are required: (i) Formation of the bct cell as described above; (ii) contraction of the bct cell along [001] direction so that the hcp basal plane angle 65.5° becomes 60°; (iii) shuffle of the atoms by 1/12[-1 1 0] in opposite direction in every alternate layer and (iv) adjustment of the interplanar spacing to get hcp c/a = 1.632. This analysis suggests that the rearrangement of atoms required for formation of hcp directly from β is more than that for formation of bct from β indicating that formation of bet phase is more likely. Upon further compression, the bet phase transforms to bcc structure at V~ 20.55 (Å³/atom) with corresponding hydrostatic pressure of ~ 28 GPa. In table 2, we have compared the theoretically determined transition pressures with the experimentally measured one.

Table 1. Equilibrium lattice parameters from the present calculations compared with available experimental and theoretical values.

| Phase | Present calculations | Experimental values |
|-------|----------------------|---------------------|
|       | Lattice constant a (Å) | c/a ratio | Lattice constant a (Å) | c/a ratio |
| α     | 6.643                | 6.491[24]         |
| β     | 5.921                | 0.546 [24, 5.833, 1] | 3.81 [1, 9.7 GPa] |
| bct   | 3.930                | 0.910 [1]         | 3.81 [1]         |

Table 2. The comparison of various structural phase transition pressures in tin

| Phase | Theory other sources | Theory present work | Experimental |
|-------|----------------------|---------------------|--------------|
| α → β | 0.8GPa [5], 0.2GPa [6], 0.7 GPa [7], 1.9 GPa [8] | 0.15GPa | 0 GPa [1] |
| β → bct | 23.5GPa [5], 10.4 GPa [6], 12 GPa [7], 13 GPa [8] | 2.7GPa | 9.8 GPa [1, 9.5 GPa [2, 9.7 GPa [3] |
| bct → bcc | 50 GPa [6], 45 GPa [7], 32 GPa [8] | 28GPa | 35 [2, 40 GPa [3] |
| bcc → hcp | 90 GPa [5], 160 GPa [7] | -- | --- |

---
In figure 3 we have displayed the theoretically determined 300 K isotherm along with experimental data. The theoretical isotherm agrees well with experimental data [2-4]. Figure 4 shows the Hugoniot of tin derived from theoretical 0 K isotherm along with available experimental data from various sources [12-15]. The agreement of the Hugoniot with experimental data up to ~ 230 GPa is quite well, however, it starts deviating systematically from experimental data above this pressure. This systematic deviation of theoretical Hugoniot from experimental data above ~ 230 GPa could be due to the fact that the melting (or vaporization) of the bcc phase is not considered in our calculations.

Our theoretically determined pressure dependence of melting point along with the theoretical shock temperatures is shown in figure 5. Also shown in the figure is experimental melting data determined in high pressure high temperature diamond anvil cell (DAC) experiments [11]. The experimental data show a good agreement with the theoretical melting line. This indicates that the Debye model along with Lindeman law gives correct description of melting behaviour of tin at high pressure and high temperature. The room pressure melting temperature required for determination pressure dependence of melting is taken to be 505 K from literature [26]. The crossover of the melting and shock temperature curves suggests that tin will melt under shock compression of ~38 GPa, which is in good agreement with the experimental value of 39 ± 2 GPa [16].
References
[1] Berrett Dean J., Bean E. Vern and Tracy Hall 1966 J. appl. Phys. 37 875; J. D. Barnett, R. B. Bennion, and H. T. Hall, Science 141, 1041 (1963).
[2] Olijnyk H. and Holzapfel W. 1984 J. Phys. (paris) Colloq. 45, suppl. 11, C8-153.
[3] Liu M. and Liu L. 1986 High Temp.-High press. 18 79.
[4] Desgreniers S., Vohra Yogesh K. and Ruoff Aurhter L. 1989 Phys. Rev. B 39 10359.
[5] Corkill Jennifer L., Garcia Alberto and Cohen Martin L. 1990 Phys. Rev. B 43 11.
[6] Christensen N.E. and Methfessel 1993 Phys. Rev. B 48 5797.
[7] Chun Yu, Juyan Liu, Hao Lu and Junmei Chen 2006 Solid. State Comm. 140 538.
[8] Cui S., Cai L., Feng W., Hu H., Wang C. and Wang Y. 2008 Phys. Stat. Sol. (b) 245 53.
[9] Ravelo R. And Basakes M. 1997 Phys. Rev. Lett. 79 2482.
[10] Barnard S. And Maillet J.B. 2002 Phys. Rev. B 66 012103.
[11] Kiefer B., Duffy T., Uchida T., Wang Y. 2002 Melting of tin at High Pressures APS User Activity Repor.
[12] Walsh J.M., Rice Mavin H., McQueen R.G. and Yarger F.L. 1957 Phys. Rev. 108 196.
[13] McQueen R.G. and Marsh S.P. 1960 J. Appl. Phys. 31 1253.
[14] Marsh S.P. (ed) LASL Shock Hugoniot Data 1980 (Berkeley CA: University of California Press).
[15] Al’ishuler L.V., Bakanova A.a. and Trunin R.F. 1962 Sov. Phys. JETP 15 65.
[16] Hu J., Zhou Xianming, Dai Chengda, Tan Hua and Li Jiabo 2008 J. Appl. Phys. 104 083520.
[17] Blaha P. Schwarz K. and Luitz J. WIEN97 (Technical University of Vienna).
[18] Perdew J.P. Burke S. and Ernzerhof M. 1996 Phys. Rev. Lett. 77 3865.
[19] Barnett D.J., Bennion Roy B., Hall T.H. 1963 141 3585.
[20] Wallace D.C., Thermodynamics of crystals 1972 Wiley New York.
[21] Godwal B.K. and Jeanloz R. 1989 Phys. Rev. B 40 7501.
[22] Gupta Satish C., Joshi K.D. and Banerjee S. 2008 Metall. Materials Trans. A, 39A, 1593.
[23] Soma T. et al., Phys. Sta. Sol. (b). 1983 116 673.
[24] R. W. G. Wyckoff, Crystal Structures, 2nd ed. (Inter-science, New York, 1963), Vol. 1, p. 26ff.
[25] Satish C. Gupta and R. Chidambram 1994 12 51.
[26] Charles Kittel, Introduction to Solid State Physics 1996 John Wiley & Sons New York.