Equation of state and phase diagram of tin at high pressures

K V Khishchenko
Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya 13/19, Moscow 125412, Russia
E-mail: konst@ihed.ras.ru

Abstract. A thermodynamic model of the free energy as a function of volume and temperature for tin with taking into account the polymorphic transformation and melting effects is proposed. Results of equation-of-state and phase-diagram parameters calculations for this metal are compared with available experimental data on static and shock compression at high pressures.

1. Introduction

Description of the thermodynamic properties and phase transitions of matter over a wide range of densities and temperatures is of essential interest for shock-wave physics [1–3].

In the present work a new multi-phase equation of state (EOS) for tin is presented. This EOS takes into account the polymorphic transformation and melting effects. Calculated results are compared with available experimental data at high pressures. The most essential static and shock compression experiments are described.

2. EOS model

The specific free energy of the substance is considered as a sum of three components [1],

\[ F(V, T) = F_c(V) + F_a(V, T) + F_e(V, T), \]  

(1)

providing for the condition \( F_c(V_0c) = E_{0c}. \) As can be readily seen, differentiation of the energy (2) with respect to volume yields an equation for the pressure \( P_c(V) = -dF_c/dV, \) which is

\[ F_c(V) = E_{0c} + a_0 V_0c \ln \sigma_c - 3 V_0c \sum_{i=1}^{6} \frac{a_i}{4} \left( \sigma_c^{-i/3} - 1 \right)^2 + 3 V_0c \sum_{i=1}^{2} \frac{b_i}{4} \left( \sigma_c^{-i/3} - 1 \right), \]  

(2)
analogous to the relation proposed previously [6] as an expansion of the Thomas–Fermi model in powers of the atomic cell radius \( r_c \sim \sigma_c^{-1/3} \).

The value of the coefficient \( b_2 \) in equation (2) is determined from the condition of coincidence with the model of degenerate ideal Fermi-gas of nonrelativistic electrons in the range of compressions above \( \sigma_c \sim 10^3 \div 10^4 \) [5]. In order to determine the coefficients \( b_1 \) and \( a_i \) in equation (2), one must solve the problem of minimization of the root-mean-square deviation of pressure at some points \( V = V_n, n = 1, \ldots, N \), in the interval \( \sigma_c = 50 \div 10^3 \) from the results of calculation by the Thomas–Fermi model with corrections [7] subject to the conditions for the pressure, bulk modulus and its derivative with respect to pressure at

\[
B_c^{(1)}(V_{0c}) = -V dP_c/dV = B_{0c} \quad \text{and} \quad B_c^{(1)}(V_{0c}) = dB_c/dP_c = B_{0c}' \quad \text{respectively.}
\]

The problem of conditional minimization is solved with the introduction of Lagrange factors [8]. The values of the parameters \( V_{0c}, B_{0c} \) and \( B_{0c}' \) are fitted by iterations so as to satisfy under normal conditions the tabular value of specific volume \( V_0 \) and the values of isentropic compression modulus \( B_S = -V(\partial P/\partial V)_S = B_{S0} \) and its pressure derivative \( B_S' = (\partial B_S/\partial P)_S = B_{S0}' \) determined by the data of static and shock compressibility measurements.

The energy on the cold curve of a solid phase in the rarefaction region \( (\sigma_c < 1) \) is given by the polynomial,

\[
F_c(V) = V_{0c} \sum_{i=1}^{3} \frac{c_i}{k_i} \sigma_c^{k_i} + E_{\text{sub}},
\]

which provides for the value of the sublimation energy \( F_c = E_{\text{sub}} \) at \( V \to \infty \). The requirement of continuity of the function \( F_c(V) \) and its three derivatives with respect to volume leaves only two free parameters, \( k_2 \) and \( k_3 \), in equation (3).

The thermal lattice component of the free energy for each solid phase is defined as follows,

\[
F_a(V, T) = RT \left( 3 \ln \left( 1 - e^{-\theta_a/T} \right) - D(\theta_a/T) \right),
\]

where \( R = k_B (Am_u)^{-1} \), \( k_B \) is the Boltzmann constant, \( m_u \) is the atomic mass unit (amu), \( A \) is the atomic mass (in amu), \( D \) is the Debye function [9], \( \theta_a = \theta_s(V) \) is the characteristic temperature of phonon spectrum [2, 4],

\[
\theta_s(V) = \theta_{s0} \sigma^{2/3} \exp \left( (\gamma_{s0} - 2/3) \frac{B_s^2 + D_s^2}{B_s} \arctan \frac{B_s \ln \sigma}{B_s^2 + D_s (\ln \sigma + D_s)} \right),
\]

where \( \sigma = V_0/V, \gamma_{s0} \) is the value of Grüneisen coefficient of the solid phase under normal conditions.

The energy of the liquid phase at \( T = 0 \) K is determined by the relations

\[
F_c^{(l)}(V) = F_c^{(l1)}(V) = V_{l0} \frac{2\sigma_l^2}{1 + \sigma_l^2} \left( d_0 + \frac{d_n}{n_l} \sigma_l^n \right) \quad \text{at} \quad \sigma_l \geq 1,
\]

\[
F_c^{(l)}(V) = V_{l0} \sum_{i=1}^{3} \frac{d_i}{k_i} \sigma_l^{n_i} + E_{\text{sub}} \quad \text{at} \quad \sigma_l < 1,
\]

where superscripts \( l1 \) and \( l \) denote the high-pressure solid phase and the liquid, \( \sigma_l = V_{l0}/V, V_{l0} \) is the specific volume of the liquid phase at a chosen point on the melting curve of phase \( l1 \) \( (P = P_{m0}, T = T_{m0}) \), the coefficients \( d_0 \) and \( d_n \) define the volume change under phase transition of \( l1 \) to the liquid at this point. The parameters of (7) are determined from the requirement of continuity of the function (6)–(7) and its three derivatives with respect to volume at \( \sigma_l = 1 \).
The contribution of thermal movement of heavy particles to the free energy of the liquid phase is defined in the form of equation (4), where \( \theta_a = \theta_l(V) + (T_a T_\sigma^2/3)^{1/2} \), \( T_a \) is a constant,

\[
\theta_l(V) = \theta_{l0}\sigma_l^{2/3} \exp \left( \frac{(\gamma_{l0} - 2/3)}{B_l} \right) \frac{B_l}{B_l^2 + D_l (\ln \sigma_l + D_l)}
\]

the parameter \( \theta_{l0} \) defines the enthalpy change under melting of phase \( s1 \) at \( P = P_{m0} \), \( \gamma_{l0} \) is the value of Gruneisen coefficient of the liquid phase at \( \sigma_l = 1 \).

3. Calculation results

Under the normal conditions (\( P = 0.1 \) MPa, \( T = 298 \) K), the white tin modification, \( \beta \)-Sn, is stable. The transformation of \( \beta \)-Sn to the body-centered tetragonal structure \( \gamma \)-Sn occurs under compression up to pressure of \( P = 9.4 \pm 0.4 \) GPa at \( T = 298 \) K [10,11]. Further compression up to \( P = 45 \pm 5 \) GPa at room temperature leads to the transformation of \( \gamma \)-Sn to the body-centered cubic structure \( \delta \)-Sn, which is stable up to maximal pressure of \( P = 120 \pm 10 \) GPa achieved in experiments with diamond anvil cells [12].

In the present work, EOS for \( \beta-\gamma \)-liquid tin system is constructed on the basis of the model developed. Calculated isotherm \( T = 298 \) K and principal Hugoniot of the metal in comparison with data on static [12,13] and shock [14–18] compression are presented in figure 1. One can see that the multi-phase EOS proposed for tin adequately describes the measurement results for compressibility of the considered polymorphs and liquid phase of tin in a wide range of pressures.

**Figure 1.** Static and shock compression of tin. Solid line corresponds to the calculated Hugoniot curve with accounting for the \( \beta-\gamma \) transition and melting, dashed line is the isotherm of \( \gamma \)-Sn at \( T = 298 \) K from present EOS. Experimental data: \( \circ \), [12]; \( \square \), [13]; \( \triangledown \), [14]; ■, [15]; \( \triangle \), [16]; \( \bigtriangleup \), [17]; •, [18].

**Figure 2.** Phase diagram of \( \beta-\gamma \)-liquid tin system. Solid line is the calculated Hugoniot; dash-dot lines are the phase boundaries; \( \diamond \) is the measured point of \( \beta-\gamma \) transition at \( T = 298 \) K [10,11]; \( \square \) is the melting point on the Hugoniot from EOS [19]; \( \circ \) marks points on the calculated melting curve [20].
Phase diagram of the $\beta$–$\gamma$–liquid tin system is shown in figure 2. The curves of the $\beta$–$\gamma$, $\beta$–liquid and $\gamma$–liquid phase equilibrium resulting from the present EOS are in a good agreement with available experimental data [10, 11] on the phase boundaries at pressures $P \lesssim 10$ GPa. The present melting curve of $\gamma$-Sn also agrees with results of calculations [19, 20]. The melting occurs on the obtained Hugoniot in the pressure range of $P = 50.3 \div 63.3$ GPa (see figure 2).

Thus the multi-phase EOS developed for tin provides a consistent description of the data of static and shock experiments, and it can be used in numerical simulation of processes at high pressures.

Acknowledgments
This work was done under financial support of the Russian Foundation for Basic Research, grant No. 06-02-17464.

References
[1] Zel’dovich Ya B and Raizer Yu P 1967 Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena (New York: Academic Press)
[2] Bushman A V, Fortov V E, Kanel’ G I and Ni A L 1993 Intense Dynamic Loading of Condensed Matter (Washington: Taylor & Francis)
[3] Kanel’ G I, Razorenov S V and Fortov V E 2004 Shock-Wave Phenomena and the Properties of Condensed Matter (New York: Springer)
[4] Bushman A V and Fortov V E 1988 Sov. Tech. Rev. B: Therm. Phys. vol 1, ed A E Scheindlin and V E Fortov (New York: Harwood Academic) p 219
[5] Khishchenko K V 2004 Tech. Phys. Lett. 30 829
[6] Kalitkin N N and Govorukhina I A 1965 Sov. Phys. Solid State 7 287
[7] Kalitkin N N and Kuz’mina L V 1975 Preprint No 35 (Moscow: Institute of Applied Mathematics, USSR Academy of Sciences)
[8] Bushman A V, Fortov V E and Lomonosov I V 1991 High Pressure Equations of State: Theory and Applications, ed S Eliezer and R A Ricci (Amsterdam: North-Holland) p 249
[9] Landau L D and Lifshitz E M 1980 Statistical Physics (Oxford: Pergamon Press)
[10] Young D A 1991 Phase Diagrams of the Elements (Berkeley, CA: University of California Press)
[11] Tonkov E Yu and Ponyatovsky E G 2005 Phase Transformations of Elements under High Pressure (Boca Raton, FL: CRC Press)
[12] Desgreniers S, Vohra Y K and Ruoff A L 1989 Phys. Rev. B 39 10359
[13] Liu M and Liu L 1986 High Temp.–High Press. 18 79
[14] Marsh S P (ed) 1980 LASL Shock Hugoniot Data (Berkeley, CA: University of California Press)
[15] Al’tshuler L V, Krupnikov K K and Brazhnik M I 1958 Sov. Phys. JETP 7 614
[16] Al’tshuler L V, Bakanova A A and Trunin R F 1962 Sov. Phys. JETP 15 65
[17] Walsh J M, Rice M H, McQueen R G and Yarger F L 1957 Phys. Rev. 108 196
[18] McQueen R G and Marsh S P 1960 J. Appl. Phys. 31 1253
[19] Mabire C and Hereil P L 2000 Shock Compression of Condensed Matter—1999, ed M D Furnish, L C Chhabildas and R S Hixon (New York: AIP Press) p 93
[20] Bernard S and Maillet J B 2002 Phys. Rev. B 66 012103