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Theoretical study of a melting curve for tin*

Xi Feng(习 锋)† and Cai Ling-Cang(蔡灵仓)

National Key Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, CAEP, Mianyang 621900, China

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The melting curve of Sn has been calculated using the dislocation-mediated melting model with the 'zone-linking method'. The results are in good agreement with the experimental data. According to our calculation, the melting temperature of γ-Sn at zero pressure is about 436 K obtained by the extrapolation of the method from the triple point of Sn. The results show that this calculation method is better than other theoretical methods for predicting the melting curve of polymorphic material Sn.

Keywords: melting temperature, thermodynamic property, phase transition, tin
PACC: 6155F, 6470D, 6250

1. Introduction

The study of melting temperatures of materials is of great interest in materials science and geophysics.[1−6] Tin (Sn) is a commonly used metal in daily life. Its special properties, however, make it useful for studies of a wide range of fundamental behaviours, including phase transformation mechanisms and kinetics. It has two readily accessible solid–solid phase transitions, with a low melting point and very different kinetic behaviours. There are a number of studies on its high-pressure behaviours. Mabire and Héreil[7] investigated its direct and reverse polymorphic transitions by shock compression measurements up to 50 GPa. Anderson *et al*[8] studied the phase transitions. Hu *et al*[9] measured sound velocities in Sn with the modified reverse-impact method in the range of 37–80 GPa. Hereil and Mabire[10] obtained the results of pyrometric measurements performed at the interface of an Sn target with a LiF window material in the range of 38 to 55 GPa. By performing extensive first-principles and classical molecular-dynamics (MD) simulations, Bernard and Maillet[11] calculated its melting curve up to 50 GPa and its Hugoniot curve up to 200 GPa by using an equilibrium MD technique, the so-called Hugoniotstate. Cox[12] suggested an empirical thermodynamically consistent equation of state (EOS), and a strength model for its β, γ, and liquid phases. Up to now, there is still a large discrepancy between experimental data and theoretical results on the melting curve of Sn. To find a theoretical model explaining this discrepancy is, therefore, a great challenge.

2. The dislocation-mediated melting model

Burakovsky *et al*[13,14] have given a model to determine the pressure dependence of the melting temperatures for various elements. We call this model the 'dislocation-mediated melting model'. According to this model, the melting temperature $T_{\rm m}(P)$ can be described as,

$$T_{\rm m}(P) = \frac{T_{\rm m}(0)}{\eta}\frac{G(P)}{G(0)}, \tag{1}$$

$$G(P) = G_0 + G_0'\frac{P}{\eta^{1/3}}, \tag{2}$$

$$G_0' \equiv (\mathrm{d}G/\mathrm{d}P)_0, \tag{3}$$

where $T_{\rm m}$ is the melting temperature; P is pressure; G is the shear modulus; $\eta = V_0/V$ is the compression; V is the specific volume; the subscript '0' refers to ambient conditions: $T \cong 300$ K and $P = 0$; G_0' is the pressure derivative of the shear modulus G. From Eqs.(1)–(3), we find that the main parameters in the dislocation-mediated melting model are the shear modulus $G(P)$ (which includes the two parameters G_0 and G_0') and the compression η. The compression η

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†Corresponding author. E-mail: hawk_0816@yahoo.com.cn

can be derived from Morse EOS[15] which is described as,

$$P = \frac{3B_0}{\alpha x^2}\left[e^{2\alpha(1-x)} - e^{\alpha(1-x)}\right], \quad (4)$$

$$\alpha = B_0' - 1, \quad (5)$$

$$x = \eta^{-1/3} = \left(\frac{V_0}{V}\right)^{-1/3}, \quad (6)$$

where, the parameters are the same as above. Finally, the melting curve $T_m(P)$ can be obtained by solving Eqs.(1)–(6) using the numerical method. In this paper, we try to predict the melting curve of Sn using the reasonable parameters in this dislocation-mediated melting model.

3. The melting curve of Sn

In predicting the melting temperatures at high pressures, researchers usually only investigate the melting temperatures at several small zones (with a number of critical points and phase boundaries) in an interested pressure and temperature range, and then link all results holistically.[12,16,17] We call this method the 'zone-linking method'. Based on the well-known phase diagram of Sn (Young[18]) and the 'zone-linking method', we divide the whole interesting temperature and pressure range of Sn into two zones: the β-Sn zone and the γ-Sn zone. Then we try to calculate the melting curve of Sn using the dislocation-mediated melting model in every zone, and link them as one melting curve of Sn holistically. We hope that through this calculation, we can find a way to calculate the melting curves of a polymorphic material, involving a solid–solid phase transition.

A good agreement of the room temperature isotherm of Sn between the calculated one from the Morse EOS and the experimental data,[19] can be seen in Fig.1. The parameters used in the Morse EOS, as listed in Table 1, are thus believed reasonable. Then, we can calculate the melting curve $T_m(P)$ of Sn by solving Eqs.(1)–(6) using the parameters listed in Table 1. This calculation includes four steps from the triple point of 2.9 GPa and 581 K.[18] First, the melting curve $T_m(P)$ of β-Sn is calculated using Eqs.(1)–(6); then the melting temperature ($T_{m0} \cong 436$ K) of γ-Sn at zero pressure can be obtained by direct extrapolation using Eqs.(1)–(6) from the triple point of Sn. Next, the melting curve $T_m(P)$ of γ-Sn is calculated using Eqs.(1)–(6) in the interested pressure range. Finally, according to the 'zone-linking method', the complete melting curve of Sn is obtained by linking the melting curves of β-Sn and γ-Sn at the triple point, as shown in Fig.2. For comparison, the theoretical results obtained previously[12] have also been shown in Fig.2.

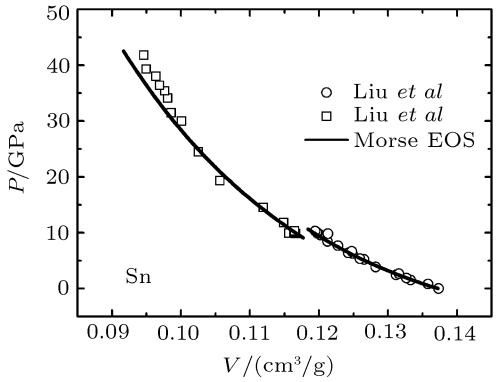


Fig.1. The room temperature isotherms of Sn.

Table 1. The parameters used for calculating the melting curve of Sn.

material	ρ_0/(g/cm^3)[12]	T_{m0}/K	G_0/GPa[12]	G'_0[20]	B_0/GPa[8]	B'_0[8]
β-Sn	7.287	505[12]	22.83	1.55	52.69	4.073
γ-Sn	7.579	436	11.62	1.55	66.37	3.217

From Fig.2, we see that the calculated melting curve of Sn is in good agreement with the diagrams given by Young[18] and Barnett *et al*,[21] respectively. Especially, the calculated melting curve of γ-Sn is in agreement with Hereil *et al*[10] within the experimental error, and is obviously better than that by C_{ox}.[12] In addition, our calculated melting temperature T_m (2300 K at 49 GPa) of Sn is also in agreement with the shock melting data, which has been obtained by Mabire *et al*[7] from experiments and theoretical method. At about 38 GPa obtained by Hereil *et al*,[10] the slope of the melting curve dT_m/dP obtained in

our calculation is about 30.27 K/GPa, which is almost double the 13.75 K/GPa obtained from C_{ox}.[12] Our results seem more reasonable and are in a better agreement with the experimental data than those of C_{ox}.

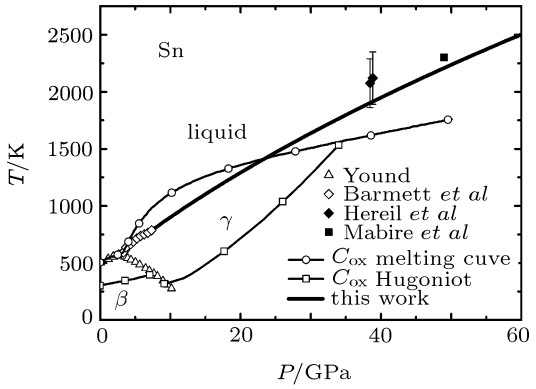


Fig.2. The melting curve of Sn.

4. Summary

To summarize, by choosing reasonable key parameters, the melting curve of a polymorphic material Sn can be predicted by using the dislocation-mediated melting model with the zone-linking method. The results are in good agreement with experimental data. By the extrapolation of the calculated results for β-Sn from the triple point of Sn, the melting temperature of γ-Sn at zero pressure is also obtained (at about 436 K). The results show that our calculated melting curve of polymorphic material Sn is in good agreement with experiments.

To verify this the suggested method needs more experimental and theoretical evidence on other polymorphic materials. In addition, the 'zone-linking method' is confirmed to be an effective way to determine the melting curves of the multi-state or multiphase materials if the corresponding 'critical points' and boundary conditions have been known.

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