Thermodynamic properties of stable and metastable phases of Pt metal

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Abstract: Isometric heat capacity c_v and isobaric heat capacity c_p of Pt with stable and metastable phases were calculated by using pure element systematic theory. These results are in excellent agreement with of SGTE (Scientific Group Thermodata Europe) database and JANAF (Joint Army-Navy-Air Force) experimental values. The calculation results of c_v and c_p of Pt metal in natural state are in good agreement with those calculated by FP(first-principles) method. It is found that the electron devotion to heat capacity is important to adjust in OA(one-atom) method while calculating heat capacity. The full information about thermodynamic properties of Pt metal with stable and metastable phases, such as entropy(S), enthalpy(H) and Gibbs energy(G) were calculated from 0 K to random temperature. The results are in good agreement with JANAF experimental value. In contrast to SGTE database, the thermodynamic properties from 0 K to 298.15 K are implemented.
Key words: Pt; heat capacity; thermodynamic property

1 Introduction

There are many methods[1−5], such as experimental evaluations and theoretic calculations, to get thermodynamic data of pure metals. In these methods, SGTE (Scientific Group Thermodata Europe) pure element database[6] contains thermodynamic data for around 78 elements in the stable and all metastable phases over 298.15 K. With 30 years of work, Prof. XIE has finally established the framework of systematic sciences of alloys(SSA) which is constituted by pure element systematic theory, physics and chemistry, and statistics thermodynamics of alloys. The core of systematic science of alloys is the one-atom(OA) theory of pure elements[7−12]. In order to keep the integrity of thermodynamic properties of SGTE pure element database, in this work, pure element systematic theory is adopted to calculate isometric heat capacity c_v, isobaric heat capacity c_p and thermodynamic properties of Pt metal and the results are compared with those of SGTE database, JANAF(Joint Army-Navy-Air Force) and FP (first-principles) method.

2 Principles and methods

Generally, there is a relationship between isobaric heat capacity c_p and isometric heat capacity c_v:

$$c_p = c_v + TBV\beta'^2 \tag{1}$$

where T is temperature; V is molar volume; B is isothermal bulk modulus; and β' is the coefficient of volume thermal expansion. According to Debye-Grüneisen model[13], $\beta'=3\alpha$.

$$\alpha = \frac{c_v}{3Q[1 - K(U/Q)]^2} \tag{2}$$

$$c_v = 3R\left[12\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{y^3 \mathrm{d}y}{\exp y - 1} - \frac{3\theta_D/T}{\exp(\theta_D/T) - 1}\right] \tag{3}$$

$$U = \int_0^T c_v \, \mathrm{d}T \qquad (4)$$

The relationship between constant K, Q and microscopic quantity has been conducted by MAI potential-energy function[8]:

$$K = \frac{2\pi\theta_D k_B r_0}{3hj}(2n-1)\sqrt{\frac{m}{n(n-1)E_c}} + \frac{1}{2} \qquad (5)$$

$$Q = \frac{m\left(\dfrac{4\pi\theta_D k_B r_0}{3hj}\right)^2}{\dfrac{1}{3}\left(\dfrac{\theta k_B r_0}{hj} \cdot \sqrt{\dfrac{m}{E_c} \cdot \dfrac{n}{n-1}} + 1\right)} \qquad (6)$$

$$\theta_D = \frac{3hj}{(2n-1)2\pi\theta_D k_B}(K-\frac{1}{2})\sqrt{\frac{n(n-1)E_c}{r^2 m}} =$$

$$K'\sqrt{\frac{E_c}{v^{2/3}}} \qquad (7)$$

Once heat capacity is known, other thermodynamic properties, such as enthalpy(H), entropy(S) and Gibbs energy(G) can be calculated by Eq.(8):

$$\begin{cases} H = \int_0^T c_p \, \mathrm{d}T + H(0\,\mathrm{K}) \cdot \\[2mm] \quad \int_0^T c_p \, \mathrm{d}T - \int_0^{298.15} c_p \, \mathrm{d}T + H(298.15\,\mathrm{K}) \\[2mm] S = \int_0^T \dfrac{c_p}{T} \, \mathrm{d}T + S(0\,\mathrm{K}) \\[2mm] G = H - TS \end{cases} \qquad (8)$$

where U is the internal energy; j is the multiple of the half cutoff wavelength; θ_D is Debye temperature; R is gas constant; k_B is Boltzman's constant; r_0 is average effective bond length of the crystal in equilibrium; m is atomic mass; n is the exponent of the MAI potential-energy function; E_c is cohesive energy; v is atomic volume; and h is Planck's constant, respectively.

3 Temperature dependence of isometric heat capacity and isobar heat capacity

In order to keep the integrity of thermodynamic property for SGTE pure element database, isometric heat capacity c_v and isobaric heat capacity c_p of Pt metal with FCC, HCP, BCC structures and in liquid state were calculated by pure element systematic theory. Calculation results are shown in Fig.1. The results of SGTE database and experimental value of JANAF are

provided for comparison. Calculation results by FP method[14] are shown in Fig.2.

From Figs.1 and 2, isometric heat capacity c_v in natural state calculated by OA method is in good agreement with calculation results by FP method[15]. Isobaric heat capacities c_p in natural state and liquid state are in good agreement with JANAF experimental values, results of SGTE database, and calculation results by FP method. At the same time, it reinforces the results from 0 to 298.15 K for SGTE database. Even though FP method cannot calculate heat capacity of metastable phases, it can show contributions to heat capacity $c_v(e)$ made by electrons. This indicates that OA method needs to be revised while calculating heat capacity. Contributions to heat capacity $c_v(e)$ made by electrons cannot be neglected.

4 Temperature dependence of entropy, enthalpy and Gibbs energy

When the thermodynamic property of FCC-Pt at 0 K is taken as referred standard, that is, $S^f=0$, $H^f=564$ kJ/mol[16], temperature dependence of the thermodynamic properties of Pt metal with FCC, HCP, BCC structures and in liquid state are shown in Figs.3 and 4 accordingly. From these figures, compared with SGTE database, it reinforces thermodynamic properties from 0 to 298.15 K at low temperatures, making the information of pure metal more integral. At the same time, the thermodynamic properties of metastable phases can be calculated and the values of its own melting point can be obtained, respectively.

5 Conclusions

1) Isometric heat capacity c_v and isobaric heat capacity c_p of Pt metal with stable and metastable phases were calculated by using pure element systematic theory. The results are in good agreement with those calculated by FP method and JANAF experimental values.

2) Specific heat calculated by OA method needs to be revised. Contributions to specific heat made by electrons can not be neglected.

3) The complete information about thermodynamic properties of Pt metal, such as entropy S, enthalpy H and Gibbs energy(G) from 0 K to any temperature can be calculated and the results are in good agreement with JANAF experimental values. Compared with SGTE database, it reinforces thermodynamic properties from 0 K to 298.15 K.
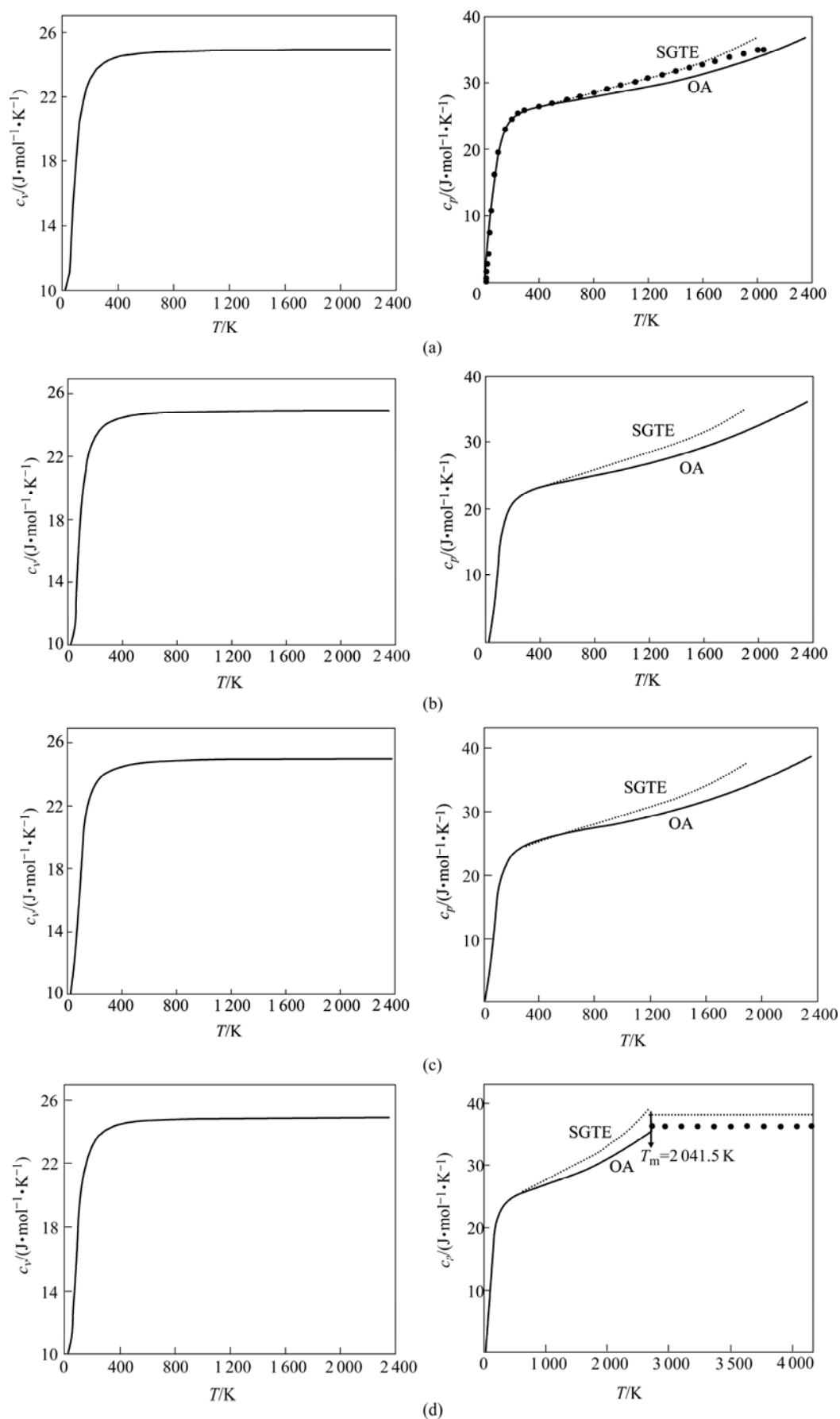
Fig.1 Curves of c_v—T and c_p—T of Pt metal with FCC (a), HCP (b), BCC (c) structures and in liquid state (d) calculated by OA method (●─Experimental value[15])
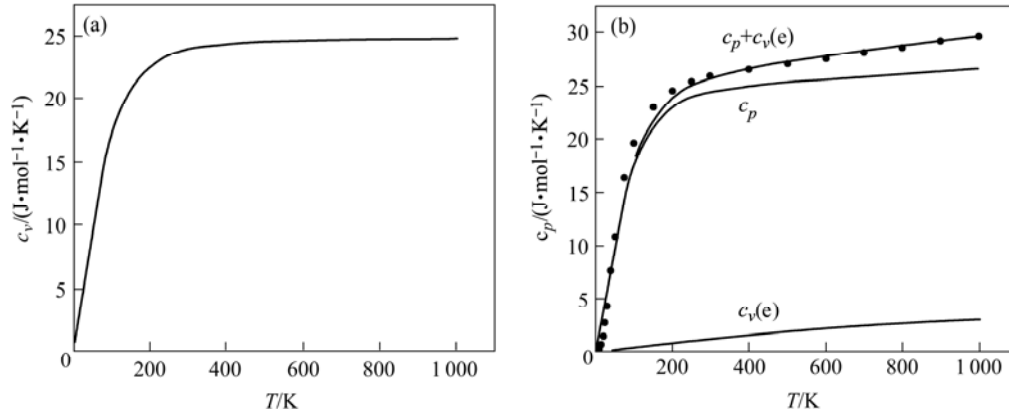
Fig.2 Curves of c_v—T and c_p—T of Pt metal in natural state calculated by FP method (●—Experimental value[15])
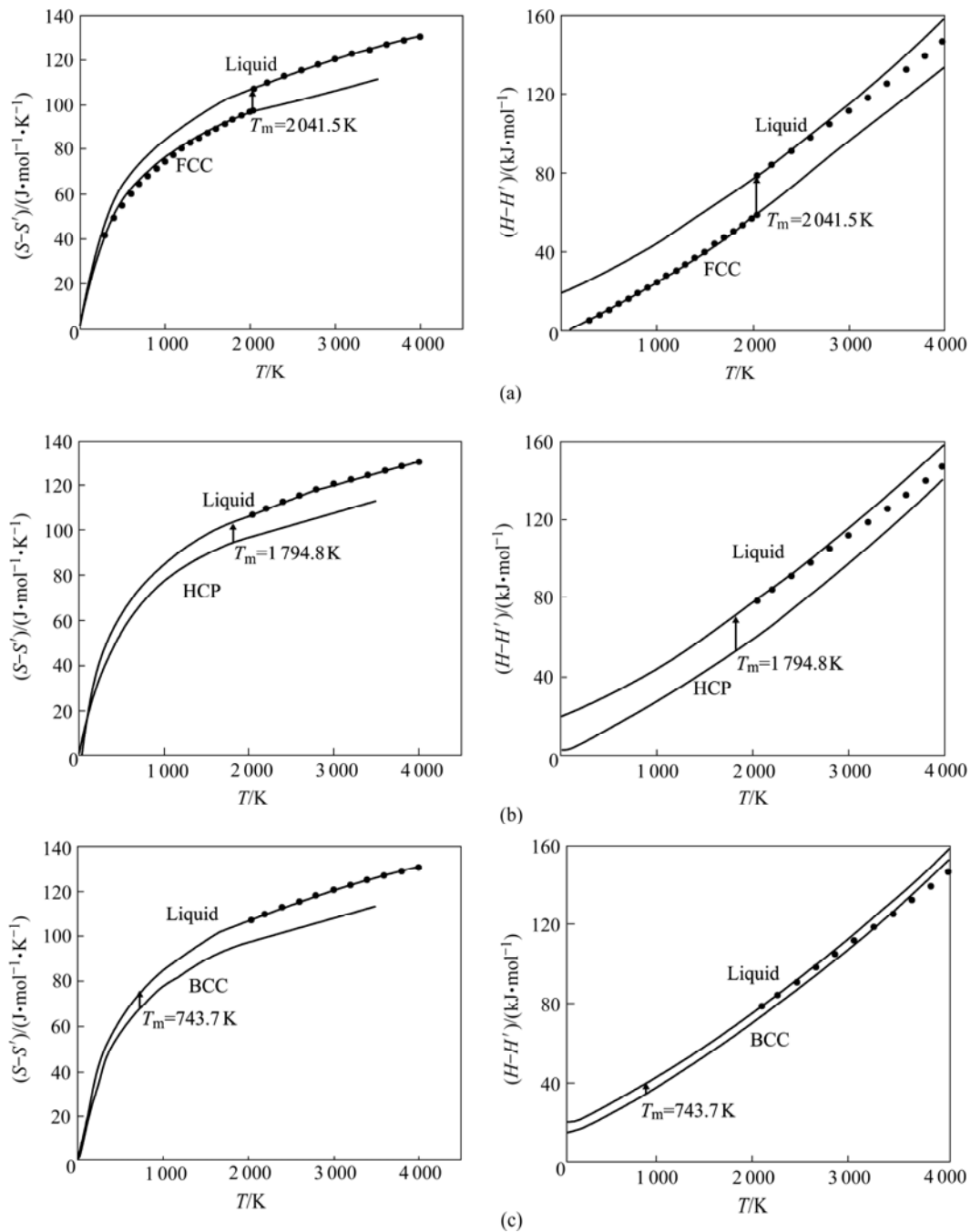

Fig.3 Curves of S—T and H—T of Pt metal with FCC (a), HCP (b), BCC (c) structures and in liquid state (●—Experimental value[15])
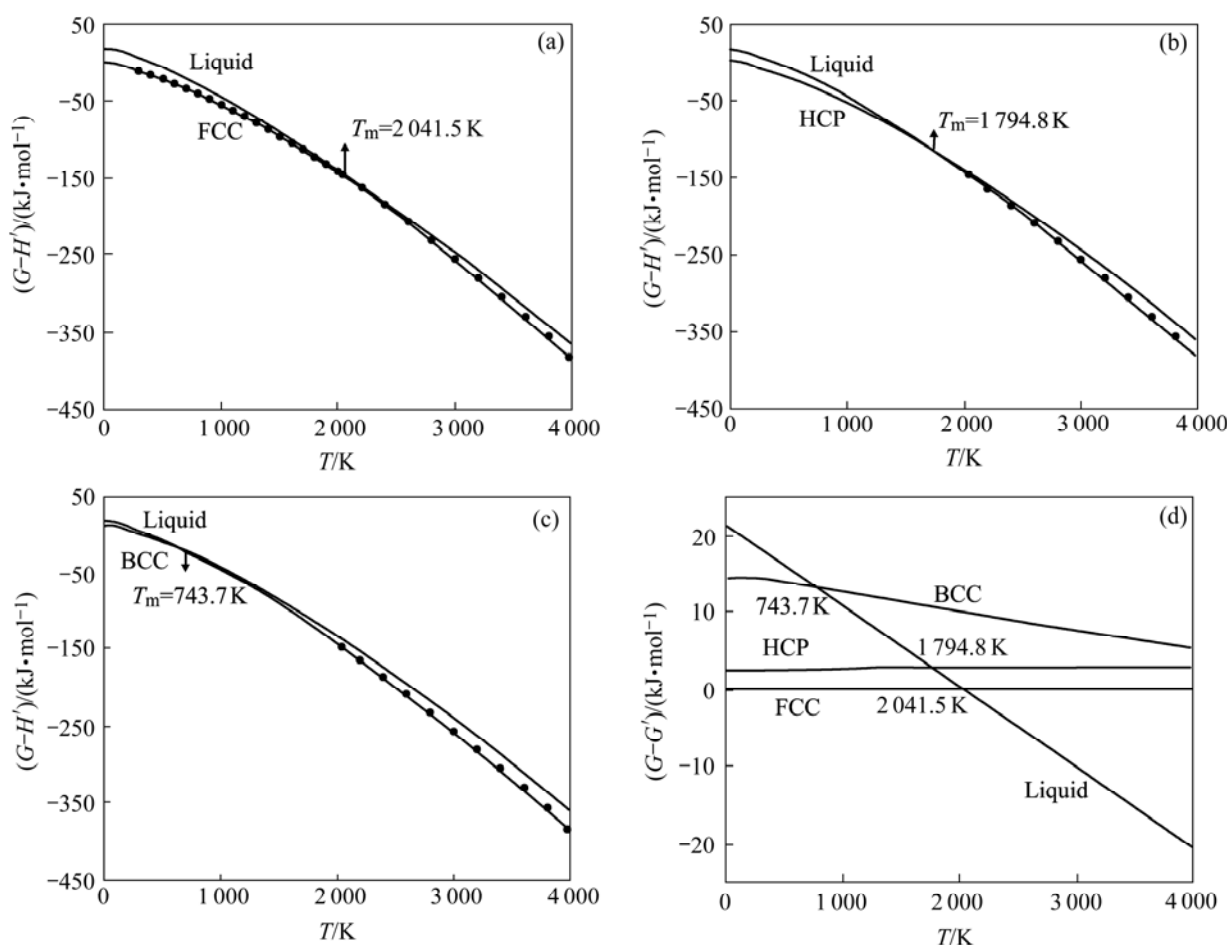
Fig.4 Curves of $G—T$ and total Gibbs energy (d) of Pt metal with FCC (a), HCP (b), BCC (c) structures and in liquid state (●—Experimental value[15])

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