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Thermodynamic properties of FCC interstitial alloy AuSi with defects

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Abstract. The analytic expressions for free energy, concentration of the equilibrium vacancies and thermodynamic quantities such as the isothermal compressibility, thermal expansion coefficient and heat capacities at constant volume and at constant pressure of FCC interstitial alloy AB with defects under pressure are derived by the statistical moment method. The theoretical results are applied to AuSi interstitial alloy. Our calculated results for main metal Au are compared with the experimental data.

1. Introduction

The point defects in crystals, including vacancies, is widely investigated and plays an important role in many properties of a material. Thus an investigation of the point defects in solid is of special interest [1, 2].

The melting curve of Au was studied by experiments [3, 4] and calculations [5, 6]. Thus, when we study the point defects in crystals, Au is one of the most important research topics [7, 8].

There are various methods to investigate the defective crystals, among which the statistical moment method (SMM) is a modern one. In this paper, using SMM [9-11] we derive the analytic expressions of the concentration of equilibrium vacancies, the free energy and the thermodynamic quantities for FCC interstitial alloy AB with defects, under pressure. We then applied these results to the AuSi interstitial alloy.

2. Method

Considering the interstitial alloy AB with FCC structure, where the main atoms A are in the corners and face centers, the interstitial atoms B are in body centers. The closest atoms to the atom B are called A_1. The second closest atoms to the atom B are called A_2. When the interstitial alloy AB has N atoms and n vacancies in lattice points, from the minimum condition of real Gibbs thermodynamic potential $\left(\frac{\partial G_{AB}^{R}}{\partial n_v}\right)_{P,T,N} = 0$, we can find the equilibrium vacancy concentration n_v as follows

$$n_v = \frac{n}{N} = \exp\left(-\frac{g_{vAB}^{f}}{k_{Bo}T}\right) = \exp\left(-\frac{g_{vAB}^{f}}{\theta}\right), \quad (1)$$

where k_{Bo} is the Boltzmann constant, g^f_{vAB} is the change of Gibbs thermodynamic potential when a vacancy is formed and is determined by the distribution of atomic concentrations c_X

$$g^f_{vAB} = \sum_X c_X g^f_{vX} \ (X = A, B, A_1, A_2),\ c_B = \frac{N_B}{N},\ c_{A_1} = 6c_B,\ c_{A_2} = 8c_B,\ c_A = 1 - 15c_B. \tag{2}$$

When P = 0, we have

$$n_v(0,T) = \exp\left(-\frac{\sum_X c_X g^f_{vX}(0,T)}{\theta} \right),$$

$$g^f_{vX}(0,T) = \frac{n_1(\psi^0_X - \psi^1_X) + \Delta\psi^0_X}{N} = \frac{n_1(\psi^0_X - \psi^1_X) + (B_X - 1)\psi^0_X}{N},\ B_X \approx 1 + \frac{Nu^0_{0X}}{4\psi^0_X}, \tag{3}$$

where ψ^1_X / N is the free energy of an atom X on the first coordination sphere with the vacancy as the center of sphere, ψ^0_X / N is the free energy of an atom X in perfect crystal, n_1 is the number of atoms on the first coordination sphere (for FCC lattice, n_1 = 12) and $\Delta\psi^0_X / N$ is the change of free energy when the atom X releases from the lattice point to form a vacancy. If we set $x^i_X = \frac{\hbar}{2\theta}\sqrt{\frac{k^i_X}{m_X}}$, $X^i_X = x^i_X \coth x^i_X$, $Y^i_X = x^i_X / \sinh x^i_X$ (i = 0, 1), the free energy ψ^i_X has the form

$$\psi^i_X \approx \frac{N}{2}u^i_{0X} + 3N\theta\left[x^i_X + \ln(1 - e^{-2x^i_X}) \right] + 3N\left\{ \frac{\theta^2}{k^{i\,2}_X}\left[\gamma^i_{2X} X^{i\,2}_X - \frac{2\gamma^i_{1X}}{3}\left(1 + \frac{X^i_X}{2} \right) \right] + \right.$$

$$\left. + \frac{2\theta^3}{k^{i\,4}_X}\left[\frac{4}{3}\gamma^{i\,2}_{2X} X^i_X \left(1 + \frac{X^i_X}{2} \right) - 2\left(\gamma^{i\,2}_{1X} + 2\gamma^i_{1X}\gamma^i_{2X} \right)\left(1 + \frac{X^i_X}{2} \right)\left(1 + X^i_X \right) \right] \right\}, \tag{4}$$

where m_X is the mass of atom X, the cohesive energy u^i_{0X} and the crystal parameters k^i_X, γ^i_{1X}, γ^i_{2X} for atom X in perfect alloy (i = 0) and defective alloy (i = 1) are determined in [11].

When $P \neq 0$, if v^*_{AB} is the activation volume [12] we have

$$n_v(P,T) = n_v(P,0)\exp\left(-\frac{Pv^*_{AB}}{\theta} \right), \tag{5}$$

By using the equation of state of the interstitial alloy AB with FCC structure at 0 K and pressure P

$$Pv^i = -r^i_1\left(\frac{1}{6}\frac{\partial u^i_{0X}}{\partial r^i_{1X}} + \frac{\hbar\omega^i_X}{4k^i_X}\frac{\partial k^i_X}{\partial r^i_{1X}} \right), \tag{6}$$

we can find the nearest neighbor distance of atom X from the following formula

$$y^i_X(P,T) = \sqrt{\frac{2\gamma^i_X(P,0)\theta^2 A^i_X(P,0)}{3k^{i\,3}_X(P,0)}}, \tag{7}$$

$$r^i_{1B}(P,T) = r^i_{1B}(P,0) + y^i_{A_1}(P,T), r^i_{1A}(P,T) = r^i_{1A}(P,0) + y^i_A(P,T),$$

$$r^i_{1A_1}(P,T) \approx r^i_{1B}(P,T), r^i_{1A_2}(P,T) = r^i_{1A_2}(P,0) + y^i_B(P,T). \tag{8}$$

The mean nearest neighbor distance between two atoms in perfect interstitial alloy AB with FCC structure is approximately determined by

$$r_{AB}^0(P,T) = r_{AB}^0(P,0) + y_{AB}^0(P,T),$$
$$r_{AB}^0(P,0) = (1-c_B)r_{1A}^0(P,0) + c_B\sqrt{2}r_{1B}^0(P,0),$$
$$y_{AB}^0(P,T) = \left(1-15c_B\right)y_A^0\left(P,T\right) + c_B y_B^0\left(P,T\right) + 6c_B y_{A_1}^0(P,T) + 8c_B y_{A_2}^0(P,T). \quad (9)$$

Approximately, the nearest neighbor distance between atoms, in an alloy with defects, is equal to that of an ideal alloy.

The thermal expansion coefficient of real alloy has the form [11]

$$\alpha_{AB}^R = \sum_X c_X(\alpha_X^0 + n_v n_1(\alpha_X^1 - \alpha_X^0) + n_v\Delta_X\alpha_X^0), \quad \alpha_X^i = \frac{y_X^i}{r_{01X}^i T}\left(1 + \frac{\theta}{2r_{1X}^i}\frac{dr_{1X}^i}{d\theta}\right). \quad (10)$$

The heat capacity at constant volume for the real alloy is determined by [11]

$$C_{VAB}^R = \sum_X c_X(C_{VX}^0 + n_v n_1(C_{VX}^1 - C_{VX}^0) + n_v\Delta_X C_{VX}^0),$$

$$C_{VX}^i = 3Nk_B\left\{Y_X^{i\,2} + \frac{2\theta}{k_X^{i\,2}}\left[\left(2\gamma_{2X}^i + \frac{\gamma_{1X}^i}{3}\right)X_X^i Y_X^{i\,2} + \frac{\gamma_{1X}^i}{3}\left(1+Y_X^{i\,2}\right) - \gamma_{2X}^i\left(Y_X^{i\,4} + 2X_X^{i\,2}Y_X^{i\,2}\right)\right]\right\}. \quad (11)$$

The heat capacity at constant pressure for the real alloy is determined by [11]

$$C_{PAB}^R = C_{VAB}^R + \frac{9TV_{AB}\alpha_{TAB}^R}{\chi_{TAB}^R}. \quad (12)$$

3. Numerical results

For AuSi alloy, we use the *n*-*m* pair potential where potential parameters are given in Table 1 [13]

$$\varphi(r) = \frac{D}{n-m}\left[m\left(\frac{r_0}{r}\right)^n - n\left(\frac{r_0}{r}\right)^m\right]. \quad (13)$$

Table 1. The parameters *m*, *n*, *D*, r_0 for Au and Si materials [13].

Material	*m*	*n*	D (10^{-16}erg)	r_0 (10^{-10} *m*)
Au	5.5	10.5	6462.540	2.8751
Si	6	12	45128.34	2.295

Approximately,

$$\varphi_{\text{Au-Si}} \approx \frac{1}{2}\left(\varphi_{\text{Au-Au}} + \varphi_{\text{Si-Si}}\right) \quad (14)$$

Our numerical results are illustrated in Fig.1 to Fig.10. When the concentrations $c_{\text{Si}} \to 0$, we obtain thermodynamic quantities of Au as shown in tables from Table 2 to Table 7 and figures from Figure 1 to Figure 4.

In Table 3, the EXPT1 is from the linear extrapolation of thermal expansion, the EXPT2 is from the differential dilatometry, the EXPT3 is from the specific heat, the EXPT4 is the volume and lattice parameter of quenched samples, the EXPT5 is the quenched-in enthalpy and the EXPT6 is from the microscopic observations of quenched samples.

Table 2. Temperature dependence of the equilibrium vacancy concentration $n_v(T)$ in Au at zero pressure determined by the SMM, the CAL [7] and the EXPT [14].

Method	T (K)	973	1023	1073	1123	1173	1223	1273	1323	1337
SMM	n_v (10^{-4})	0.50	0.91	1.58	2.62	4.16	6.38	9.48	13.71	15.14
CAL[7]		0.77	1.30	2.09	3.22	4.79	6.89	9.64	13.15	15.00
EXPT[14]		0.3	0.6	1.2	2.1	2.4	3.3	4.8	6.6	7.2

Table 3. The equilibrium vacancy concentration n_v in Au at the melting temperature (T_m = 1337K) from the SMM and the EXPT1-5 [8].

Method	SMM	EXPT1	EXPT2	EXPT3	EXPT4	EXPT5	EXPT6
n_v (10^{-4})	15.14	14	7	40	7	20	3

Table 4. The dependence of the volume ratio V/V_0 on pressure, for Au, with defects at 300K calculated by the SMM and the first-principles CAL [15].

Method	P (GPa)	2	4	6	8	10	12
SMM	V/V_0	0.9912	0.9805	0.9706	0.9614	0.9529	0.9450
CAL[15]		0.9885	0.9779	0.9679	0.9586	0.9499	0.9416

Table 5. The dependence of the nearest neighbor distance r_{Au}(10^{-10} m) on the temperature, for Au, with defects at zero pressure calculated by the SMM and from the EXPT [17].

T (K)	293	574	676	777	875	971	1075	1179	1280	1324
SMM	2.8536	2.8655	2.8700	2.8745	2.8790	2.8835	2.8885	2.8936	2.8988	2.9011
EXPT [17]	2.8793	2.8928	2.8970	2.9013	2.9062	2.9112	2.9168	2.9232	2.9281	2.9310

Table 6. The dependence of thermal expansion α_T(10^{-6} K^{-1})and the heat capacity at constant pressure C_P (cal.mol^{-1}.K^{-1}) on temperature, for Au, with defects at zero pressure calculated by the SMM and from the EXPT [19].

Method	T (K)	300	400	500	600	700	800	1000	1200
SMM	α_T	14.44	15.00	15.53	16.06	16.62	17.20	18.47	19.94
EXPT[19]		14.1	14.5	15.0	15.4	15.9	16.5	17.9	19.5
SMM	C_p	6.00	6.10	6.18	6.25	6.32	6.40	6.56	6.76
EXPT[19]		6.07	6.18	6.28	6.40	6.52	6.65	6.90	7.15

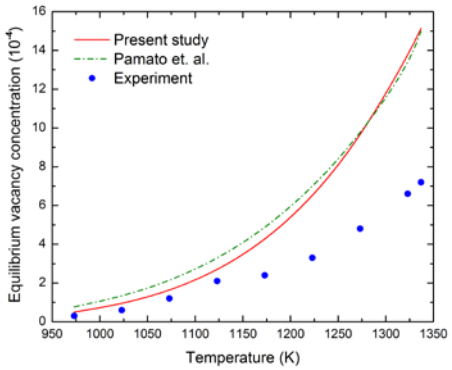

Figure 1. n_v (T) of Au at P = 0 from the SMM, the CAL [7] and the EXPT [14].

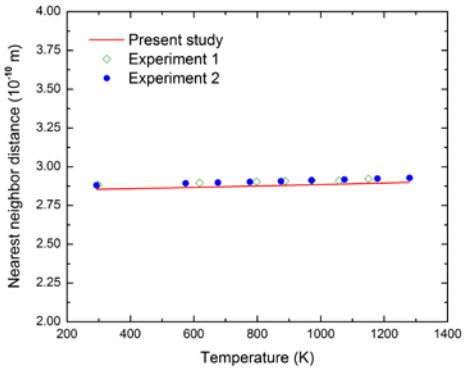

Figure 2. r_{Au} (T) of Au with defects at P = 0 from the SMM, EXPT 1 [16] and EXPT 2 [17].

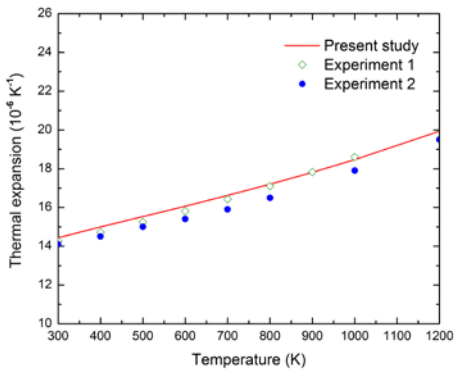

Figure 3. α_T (T) of Au with defects at P = 0 from the SMM, EXPT 1 [18] and EXPT 2 [19].

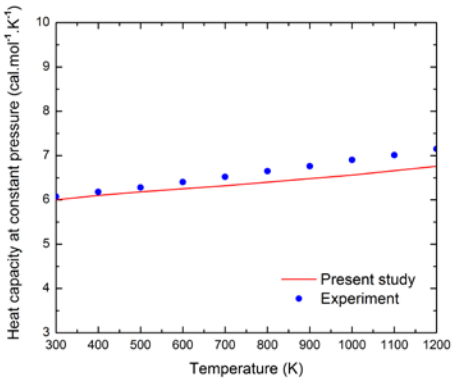

Figure 4. C_p (T) of Au with defects at P = 0 from the SMM and the EXPT [19].

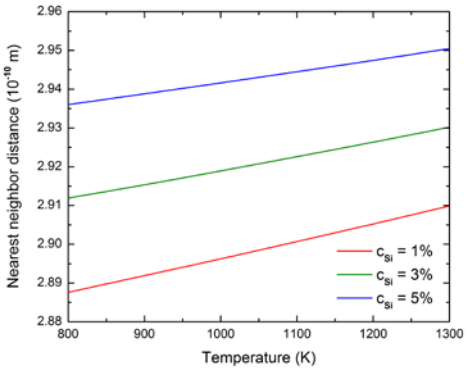

Figure 5. r_{AuSi} (T) of alloy AuSi with defects at P = 0, c_{Si}= 1%, 3%, 5% from the SMM.

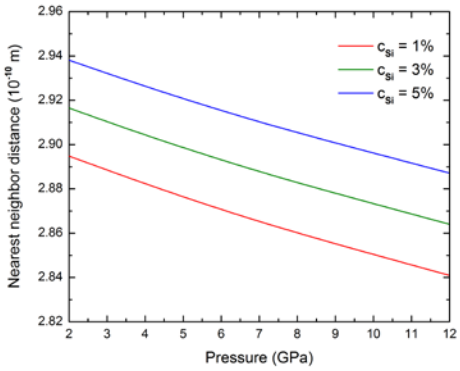

Figure 6. r_{AuSi} (P) of alloy AuSi with defects at T = 1200 K, c_{Si} = 1%, 3%, 5% from the SMM.

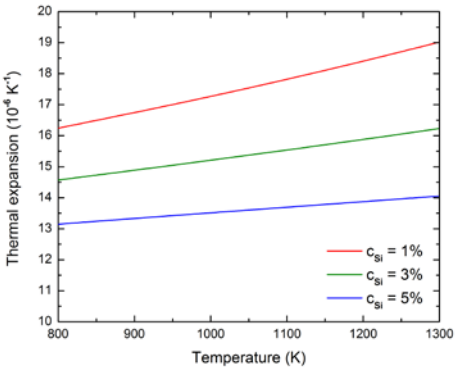

Figure 7. α_T (T) of alloy AuSi with defects at P = 0, c_{Si}= 1%, 3%, 5% from the SMM.

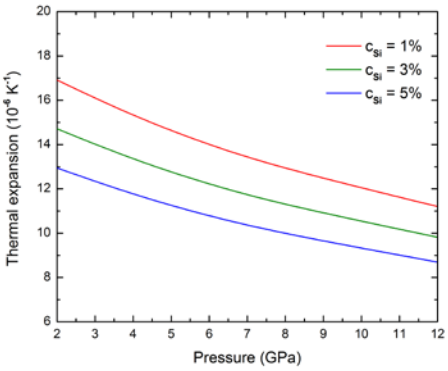

Figure 8. α_T (P) of alloy AuSi with defects at T = 1200 K, c_{Si} = 1%, 3%, 5% from the SMM.

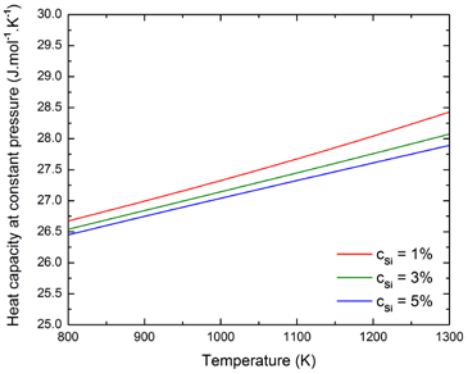

Figure 9. $C_P(T)$ of alloy AuSi with defects at $P = 0, c_{Si}$= 1%, 3%, 5% from the SMM.

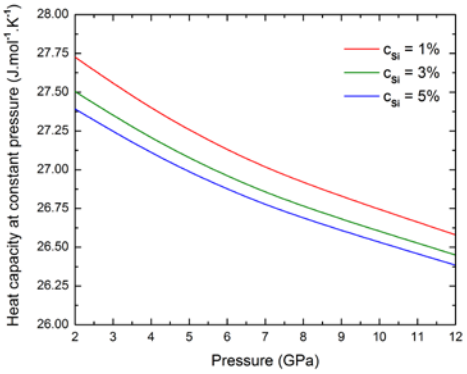

Figure 10. C_P (P) of alloy AuSi with defects at T = 1200 K, c_{Si} = 1%, 3%, 5% from the SMM.

4. Conclusion

Our results of the thermodynamic theory for interstitial alloys with vacancy and FCC structure based on the SMM are applied to AuSi alloy in the 300 to 1337 K interval of temperature, in the interval of concentration of interstitial atoms from 0 to 5% and in the interval of pressure from 0 to 12 GPa. The calculated results for the nearest neighbor distance, the thermal expansion coefficient and the heat capacity at constant pressure for an alloy with vacancies are more similar to the experimental results than in the case of an ideal alloy. The calculated results for the equilibrium vacancy concentration, the nearest neighbor distance, the volume ratio, the thermal expansion coefficient, the heat capacity at constant pressure of the main metal Au are in good agreement with experiments and other calculations. That proves that the point defects has a significant contribution on the thermodynamic quantities of an interstitial alloy, at high temperatures.

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