Thermodynamic properties of interstitial alloy FeC with BCC structure under pressure

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Abstract. The analytic expressions for the thermodynamic quantities such as the mean nearest neighbor distance, the free energy, the isothermal compressibility, the thermal expansion coefficient, the heat capacities at constant volume and at constant pressure of binary interstitial alloy with body-centered cubic (BCC) structure and the small concentration are derived by the statistical moment method. The theoretical results are applied to the interstitial FeC alloy in the interval of temperature from 50 to 1000K and in the interval of interstitial atom concentration from 0 to 5%. In special cases, we obtain the thermodynamic quantities of the main Fe metal. Our calculated results for the thermal expansion coefficient and the heat capacity under constant pressure of main metal Fe are in good agreement with experiments.

1. Introduction
Research on iron-based alloys is one of the topical issues for materials science and engineering. Especially, carbon is seen as the most importance alloying element in iron. The iron-carbon equilibrium phase diagram is experimentally and theoretically investigated more than any other binary systems [1]. The changes in the properties and microstructures at various temperatures shown in this diagram plays a crucial role in studying the behavior of a large variety of complex alloy steels. Many different potentials such as EAM [2, 3] and ABO [4] have been proposed to consider the physical characteristics of the iron-carbon system. Notably, in recent years, the high-pressure iron-carbon phase diagram is constructed to assess the role of carbon-rich phases during core crystallization in Earth [5].

In this paper, the high-pressure thermodynamic properties of the iron-carbon alloy (FeC) having body-centered cubic (BCC) structure is investigated thanks to the statistical moment method (SMM) [6]. By applying this method, we can easily consider the relationship between pressure, temperature, alloying element and thermodynamic properties of the FeC alloy.

2. Method
To analyze the physical properties of the FeC alloy, we use the interstitial alloy model illustrated in figure 1. In figure 1, A and B correspond to Fe and C, respectively. We assume that the atom B only interacts with the atoms A which closest to it (A₁ and A₂). If \( N_B \) atoms B are added into the crystal lattice of A, we will have \( 2N_B \) atoms A₁, \( 4N_B \) atoms A₂ and \( (N - 7N_B) \) atoms A, where \( N \) is the total atomic number of the system. The cohesive energy \( u_{0X} \), the concentration of alloying element \( c_X \) and the alloying parameters \( k_X, \alpha_X, \gamma_{1X}, \gamma_{2X}, \gamma_X \) (X = A, B, A₁, A₂) were carefully defined in our previous works [7].
The nearest neighbor distance \( a_x(P,0) \) for atom X can be derived by solving the following equation

\[
P_{\nu X} = -a_x \left( \frac{1}{6} \frac{\partial u_{0X}}{\partial a_x} + \frac{\hbar \omega_x}{4k_x} \frac{\partial k_x}{\partial a_x} \right)
\]  

(1)

where \( v_x \) is the atomic volume. Then, the average atomic displacement \( y_x(P,T) \) is given by

\[
y_x(P,T) = \left( \frac{2y_x(P,0)\theta^2}{3k_x(P,0)A_x(P,0)} \right)^{0.5}
\]

(2)

where \( \theta = k_BT \), \( k_B \) is the Boltzmann constant and \( A_x(P,0) \) was defined as in [8]. After that, the nearest neighbour distance \( a_x(P,T) \) for atom X at pressure \( P \) and temperature \( T \) is determined by

\[
a_x(P,T) = a_x(P,0) + y_x(P,T)
\]

(3a)

\[
a_y(P,0) + y_y(P,T)
\]

(3b)

\[
a_A(P,T) = a_y(P,0) + y_y(P,T)
\]

(3c)

\[
a_A(P,T) = a_y(P,0) + y_y(P,T)
\]

(3d)

Subsequently, the mean nearest neighbor distance in the interstitial AB alloy can be written as

\[
a_{AB}(P,0) = a_{0,AB} = (1-c_A)a_y(P,0) + c_B\sqrt{3}a_y(P,0)
\]

(4a)

\[
a_{AB}(P,T) = a_{AB}(P,0) + \sum_x c_x y_x(P,T)
\]

(4b)

The isothermal compressibility of the interstitial AB alloy has the form

\[
\chi_{TAB} = \frac{3 \left( a_{AB}/a_{0,AB} \right)^3}{2P + \sqrt{3} \frac{1}{4a_{AB} N} \left( \frac{\partial^2 \psi_{AB}}{\partial a_{AB}^2} \right)_T}
\]

(5a)

\[
\left( \frac{\partial^2 \psi_{AB}}{\partial a_{AB}^2} \right)_T = \sum_x c_x \left( \frac{\partial^2 \psi_x}{\partial a_x^2} \right)_T = \sum_x c_x \left\{ \frac{N}{2} \frac{\partial^2 \mu_{0X}}{\partial a_x^2} + \frac{3N\hbar\omega_x}{4k_x} \left[ \frac{\partial^2 k_x}{\partial a_x^2} - \frac{1}{2k_x} \left( \frac{\partial k_x}{\partial a_x} \right)^2 \right] \right\}
\]

(5b)

The thermal expansion coefficient of the interstitial AB alloy has the form
\[
\alpha_{TAB} = -\frac{k_B \chi_{TAB}}{3} \left( \frac{a_{0AB}}{a_{AB}} \right)^2 \frac{\partial^2 \psi_{AB}}{\partial \theta \partial a_{AB}}
\]  
(6a)

\[
\frac{\partial^2 \psi_{AB}}{\partial \theta \partial a_{AB}} = \sum_x c_x \frac{\partial^2 \psi_{x}}{\partial \theta \partial a_x}
\]  
(6b)

\[
\frac{\partial^2 \psi_x}{\partial \theta \partial a_x} = \frac{3}{2k_x \partial a_x} \frac{x_x^2}{\sinh^2 x_x} + 60x_x^2 \frac{\gamma_{lx}}{3k_x \partial a_x} \left( 2 + \frac{x_x^2 \coth x_x}{\sinh^2 x_x} \right) - \frac{1}{6} \frac{\partial \gamma_{lx}}{\partial x_x} \left( 4 + x_x \coth x_x + \frac{x_x^2}{\sinh^2 x_x} \right) - \frac{2\gamma_{lx}}{k_x \partial a_x} \left( \frac{x_x^2 \coth x_x}{\sinh^2 x_x} \right)
\]  
(6c)

The entropy of the interstitial AB alloy is determined by

\[
S_X = S_{0X} + \frac{3Nk_B}{k_x^2} \left[ \frac{\gamma_{lx}}{3} \left( 4 + x_x \coth x_x + \frac{x_x^2}{\sinh^2 x_x} \right) - 2\gamma_{lx} \frac{x_x^2 \coth x_x}{\sinh^2 x_x} \right]
\]  
(7a)

\[
S_{0X} = 3Nk_B \left[ x_x \coth x_x - \ln \left( 2 \sinh x_x \right) \right]
\]  
(7b)

The heat capacity at constant volume of interstitial alloy AB is determined by

\[
C_{vAB} = \sum_x c_x C_{vX}
\]  
(8a)

\[
C_{vX} = 3Nk_B \left[ \frac{x_x^2}{\sinh^2 x_x} + \frac{2\theta}{k_x^2} \left( 2\gamma_{lx} + \frac{\gamma_{lx}}{3} \right) \frac{x_x^2 \coth x_x}{\sinh^2 x_x} + \frac{2\gamma_{lx}}{3} \frac{x_x^2}{\sinh^2 x_x} + \frac{2x_x^2 \coth^2 x_x}{\sinh^2 x_x} \right]
\]  
(8b)

The heat capacity at constant pressure of the interstitial AB alloy is determined by

\[
C_{PAB} = C_{vAB} + \frac{9TV_{AB} \alpha_{TAB}^2}{\chi_{TAB}}
\]  
(9)

The adiabatic compressibility of the interstitial AB alloy has the form

\[
\chi_{SAB} = \frac{C_{vAB}}{C_{PAB}} \chi_{TAB}
\]  
(10)

3. Numerical results

For the Fe-Fe interaction, we use the Mie-Lennard-Jones pair potential as

\[
\varphi = \frac{D}{n-m} \left[ m \left( \frac{r_0}{r} \right)^n - n \left( \frac{r_0}{r} \right)^m \right]
\]  
(11)

where \( D \) is the dissociation energy, \( r_0 \) is the equilibrium value of \( r \), and \( m \) and \( n \) are taken empirically [9].

To describe the Fe-C interaction, we use the Finnis-Sinclair potential as follows

\[
U = -A \left( \frac{1}{r} \right) \rho(r) + \frac{1}{2} \sum_{ij} \Phi(r_{ij})
\]  
(12a)

\[
\rho(r) = \rho_1 \left( \frac{r}{R_1} \right)^2 + \rho_2 \left( \frac{r}{R_1} \right)^3 \quad \left( r < R_1 \right)
\]  
(12b)

\[
\Phi(r) = \left( \frac{r}{R_2} \right)^2 \left( k_1 + k_2 \frac{r}{R_1} + k_3 r^2 \right) \quad \left( r > R_2 \right)
\]  
(12c)

where \( \rho(r) \) is the embedded potential and \( \Phi(r_{ij}) \) is the pair potential. The Finnis-Sinclair parameters were introduced in Ref. [2].

Our numerical results for the thermal expansion coefficient and the heat capacity at constant pressure of the FeC alloy are described by figures from figure 2 to figure 9. When the concentration we obtain thermodynamic quantities of the main Fe metal. Our calculated results illustrated in Figures 2, 3 and 7 are in relatively good agreement with experiments.
Figure 2. $\alpha_T(T)$ of Fe at zero pressure obtained from the SMM, DFT [10] and EXPT [11].

Figure 3. $\alpha_T(c_C)$ of FeC at 300 K and zero pressure obtained from the SMM and EXPT [12].

Figure 4. $\alpha_T(T)$ of FeC at $c_C = 1, 3, 5$ % and zero pressure obtained from the SMM.

Figure 5. $\alpha_T(c_C)$ of FeC at $T = 100, 300, 500$ K and zero pressure obtained from the SMM.

Figure 6. $\alpha_T(P)$ of FeC at $T = 300$ K and $c_C = 1, 3, 5$ % obtained from the SMM.

Figure 7. $C_p(T)$ of FeC at zero pressure obtained from the SMM, DFT [10] and EXPT.
Figure 8. $C_p(cC)$ of FeC at zero pressure and $T = 100\%\ 300\%\ 500\ K$ obtained from the SMM.

Figure 9. $C_p(T)$ of FeC at $cC = 1\%$ and $P = 0, 10\ GPa$ obtained from the SMM.

For the FeC alloy at the same temperature and pressure when the concentration of interstitial atoms increases, the thermal expansion coefficient $\alpha_T$ and the heat capacity at constant pressure $C_p$ decrease. For example at $T = 1000K, P = 0$ when $cC$ increases from 0 to 5%, $\alpha_T$ decreases from $18.61.10^{-6}$ to $9.98.10^{-6}$ K$^{-1}, C_p$ decreases from 26.68 to 25.07 J/ (mol.K).

For the FeC alloy at the same pressure and concentration of interstitial atoms when temperature increases, the thermal expansion coefficient $\alpha_T$ and the heat capacity at constant pressure $C_p$ increase. For example at $P = 0, cC = 5\%$ when $T$ increases from 100 to 1000K, $\alpha_T$ increases from $3.14.10^{-6}$ to $9.98.10^{-6}$ K$^{-1}, C_p$ increases from 9.13 to 25.07 J/ (mol.K).

For the FeC alloy at the same temperature and concentration of interstitial atoms when pressure increases, the thermal expansion coefficient $\alpha_T$ and the heat capacity at constant pressure $C_p$ decreases. For example at $T = 300K, cC = 5\%$ when $P$ increases from 0 to 10 GPa, $\alpha_T$ decreases from $7.6.10^{-6}$ to $6.87.10^{-6}$ K$^{-1}, C_p$ decreases from 21.92 J/ (mol.K) to 21.66 J/ (mol.K).

4. Conclusion
The statistical moment method is applied to investigate the high-pressure thermodynamic properties of the FeC alloy having a body-centered cubic structure. The analytic expressions for thermodynamic quantities of the FeC alloy are given in the explicit forms. Our numerical results in the limited cases are consistent with experimental data and DFT calculations. These obtained results prove the effectiveness of the statistical moment method in prediction high-pressure thermodynamic characteristics of the complex iron-based alloys.

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