Thermodynamic properties of BCC interstitial alloy FeH under pressure

T H Nguyen 1, Q H Nguyen2, G Coman3, V Dinh Quang2 and C Tran Dinh2

1University of Transport and Communications, 3 Cau Giay, Dong Da, Hanoi, Vietnam
2Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Hanoi, Vietnam
3Dunarea de Jos University of Galati, 47 Domneasca, Romania

nthoaly@utc.edu.vn

Abstract. The analytic expressions of the mean nearest neighbor distance, the free energy and the thermodynamic quantities for interstitial alloy AB with body-centered cubic (BCC) structure under pressure are derived by the statistical moment method. The theoretical results are applied to interstitial alloy FeH. Our calculated results for Fe as main metal are in good agreement with experiments.

1. Introduction
Thermodynamic and elastic properties of metals and interstitial alloys are very interesting to many theoretical and experimental researchers [1,2]. There are some recent investigations on the density [3], the compressibility [4] and the sound velocity [5] of solid FeH at high pressures.

In this paper, we built a thermodynamic model for interstitial alloy AB with bcc structure, under pressure, by using the statistical moment method (SMM) [6-8] and applied these results to the interstitial alloy FeH.

2. Method
In the model of interstitial alloy AB with the body-centered cubic (BCC) structure, the atoms A with large size stay in the corners and center of the unit cell, the interstitial atoms B with smaller size stay in the center of the faces of unit cell. In [6-8], we derived the analytic expressions of the nearest neighbor distance $r_1$, the cohesive energy $u_0$ and the alloy parameters $k$, $\gamma_1$, $\gamma_2$, $\gamma$ for atoms B, A, A₁ (the atom A in the center) and A₂ (the atom A in the corners). The equation of state for interstitial alloy AB with BCC structure at temperature $T$ and pressure $P$ is written in the form

$$Pv = -r_1 \left( \frac{1}{6} \frac{\partial u_0}{\partial r_1} + \theta x cth \frac{x}{2k} \frac{\partial k}{\partial r_1} \right).$$

At 0K, this equation has the form
If knowing the form of potential interaction $\varphi_{i0}$, eq. (2) permits us to determine the nearest neighbor distance $r_{iX}(P,0)$ ($X = B, A, A_i, A_0$) at 0K and pressure $P$. After knowing $r_{iX}(P,0)$, we can determine the alloy parameters $k_x(P,0), \gamma_{1x}(P,0), \gamma_{2x}(P,0), \gamma_x(P,0)$ at 0K and pressure $P$. After that, we can calculate the displacements $y_{0X}(P,T)$ as in [6-8]. From that, we derive the nearest neighbor distance $r_{iX}(P,T)$ at temperature $T$ and pressure $P$

$$r_{i\beta}(P,T) = r_{i\beta}(P,0) + y_{0\beta}(P,T), r_{iX}(P,T) = r_{iX}(P,0) + y_{0X}(P,T),$$

$$r_{i\delta}(P,T) \approx r_{i\beta}(P,T), r_{i\delta,\gamma}(P,T) = r_{i\delta}(P,0) + y_{\delta\beta}(P,T).$$

Then, we calculate the mean nearest neighbor distance in interstitial alloy AB by the expressions as follows

$$r_{i\delta}(P,T) = r_{i\delta}(P,0) + y_{0\beta}(P,T),$$

$$r_{i\lambda}(P,0) = (1-c_{\beta})r_{i\beta}(P,0) + c_{\beta}r'_{i\beta}(P,0),$$

$$r'_{i\lambda}(P,0) = \sqrt{3}r_{i\beta}(P,0),$$

$$y_{0}(P,T) = (1-7c_{\beta})y_{0\beta}(P,T) + c_{\beta}y_{0\beta}(P,T) + 2c_{\beta}y_{0\beta}(P,T) + 4c_{\beta}y_{0\beta}(P,T),$$

where $r_{i\delta}(P,T) \equiv a_{\delta\beta}(P,T)$ is the mean nearest neighbor distance between atoms A in interstitial alloy AB at pressure $P$ and temperature $T$; $r_{i\lambda}(P,0) \equiv a_{0\beta}(P,0)$ is the mean nearest neighbor distance between atoms A in interstitial alloy AB at pressure $P$ and $0K$; $r_{i\delta}(P,0)$ is the nearest neighbor distance between atoms A in clean metal A at pressure $P$ and $0K$; $r'_{i\lambda}(P,0)$ is the nearest neighbor distance between atoms A in the zone containing the interstitial atom B at pressure $P$ and $0K$ and $c_{\beta}$ is the concentration of interstitial atoms B.

The free energy of alloy AB with BCC structure and the condition $c_{\beta} << c_{\beta}$ has the form

$$\psi_{AB} = (1-7c_{\beta})\psi_A + c_{\beta}\psi_B + 2c_{\beta}\psi_A + 4c_{\beta}\psi_A - TS_c,$$

$$\psi_x \approx \frac{N}{2}u_{0x} + \psi_{0x} + 3N\left[\frac{\theta}{k^2} \gamma_{2x}^2 X_x^2 - \frac{2\gamma_{1x}^2}{3} \left(1+\frac{X_x}{2}\right)\right] +$$

$$+ \frac{2\theta}{k^2} \left[\frac{4}{3}\gamma_{2x}^2 X_x^2 \left(1+\frac{X_x}{2}\right) - 2\left(\gamma_{1x}^2 + 2\gamma_{1x}\gamma_{2x}\right) \left(1+\frac{X_x}{2}\right) \left(1+X_x\right)\right],$$

$$\psi_{0x} = 3N\theta \left[X_x + \ln(1-e^{-2x})\right], X_x \equiv X_x \ \coth x_x,$$

where $\psi_x$ is the free energy of atom $X$, $\psi_{AB}$ is the free energy of interstitial alloy AB, $S_c$ is the configuration entropy of interstitial alloy AB.

The isothermal compressibility of interstitial alloy AB has the form
The thermal expansion coefficient of interstitial alloy AB has the form

$$\alpha_{TAB} = -\frac{k_B \chi_{TAB}}{3} \left( \frac{a_{AB}}{a_{AB}} \right)^2 \frac{\partial^2 \psi_{AB}}{\partial a_{AB}^2}.$$  

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

$$C_{VAB} = (1 - 7c_B)C_{VA} + c_B C_{VB} + 2c_B C_{VA_i} + 4c_B C_{VA_2},$$

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

$$C_{PAB} = C_{VAB} + \frac{9T V_{AB} \alpha_{TAB}^2}{\chi_{TAB}}.$$  

3. Numerical results

For the interaction between two Fe atoms, we use the $n$ - $m$ potential as follows

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

where the potential parameters are shown in Table 1.

| Interaction | $m$ | $n$ | $D$(eV) | $r_0$(Å) |
|-------------|-----|-----|----------|---------|
| Fe – Fe     | 7.0 | 11.5| 0.4      | 2.4775  |

For the interaction between the Fe atom and the H atom, we use the Morse potential as follows

$$\varphi(r) = D \left[ e^{-\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right],$$

where the potential parameters are shown in Table 2.

| Interaction | $D$(eV) | $\alpha$(Å)$^{-1}$ | $r_0$(Å) |
|-------------|---------|-------------------|---------|
| Fe – H      | 0.32    | 1.34              | 1.73    |

Our numerical results for FeH alloy are described in Figure 1 to Figure 12. When the concentration $c_H \rightarrow 0$, we obtain the thermodynamic quantities of Fe. Our calculated results in Figure 3, Figure 4, Figure 8 and Figure 12 are in rather good agreement with experiments and other calculations.
**Figure 1.** $r_{FeH}(T)$ of alloy FeH at $P = 0$ and $c_H = 1, 3, 5\%$ calculated by the SMM.

**Figure 2.** $r_{FeH}(c_H)$ of alloy FeH at $P = 0$ and $T = 100, 300, 500$ K calculated by the SMM.

**Figure 3.** $r_{Fe}(T)$ of Fe at $P = 0$ calculated by the SMM and from EXPT [11].

**Figure 4.** The volume of the unit cell $v_{Fe}(P)$ of Fe at 300K obtained from the SMM, PAW-LDA [12], PAW-GGA [12], EXPT [12].

**Figure 5.** $\alpha_{T}(T)$ of alloy FeH at $P = 0$ and $c_H = 1, 3, 5\%$ calculated by the SMM.

**Figure 6.** $\alpha_{T}(c_H)$ of alloy FeH at $P = 0$ and $T = 100, 300, 500$ K calculated by the SMM.
4. Conclusion

By using SMM, with the minimum condition of cohesive energies and the method of three coordination spheres, we found the mean nearest neighbor distance, the free energy, the isothermal compressibility, the isothermal and adiabatic elastic modulus, the thermal expansion coefficient, the heat capacities at

Figure 7. $\alpha_T (P)$ of alloy FeH at $T = 300$ K and $c_H = 1, 3, 5\%$ calculated by the SMM.

Figure 8. $\alpha_T (T)$ of metal Fe at $P = 0$ obtained from SMM, DFT [13] and EXPT [14].

Figure 9. $C_p (T)$ of alloy FeH at $P = 0$ and $c_H = 1, 3, 5\%$ calculated by the SMM.

Figure 10. $C_p (c_H)$ of alloy FeH at $P = 0$ and $T = 100, 300, 500$K calculated by the SMM.

Figure 11. $C_p (T)$ of alloy FeH at $c_H = 1\%$, $P = 0$ and 10 GPa calculated by the SMM.

Figure 12. $C_p (T)$ of metal Fe at $P = 0$ obtained from the SMM, DFT [13] and EXPT [15].
constant volume and at constant pressure, the entropy of binary interstitial alloy with BCC structure with
the concentration of interstitial atoms which is very small. The obtained expressions of these quantities
depend on the temperature and concentration of interstitial atoms. At zero concentration of interstitial
atoms, the thermodynamic quantities of the alloy become ones of main metal in alloy. The theoretical
results are applied to interstitial alloy FeH. At zero concentration of H interstitial atoms, our calculated
results for the nearest neighbor distance, the thermal expansion coefficient and the heat capacity at
constant pressure are in rather good agreement with the experimental results.

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