Midterm project

20120778

Subin Lee

Department of Materials Science & Engineering
Pohang University of Science & Technology

Problem

- Postechium (Ps)과 Kaistium (Ks) 2 원계에 대한 실험 정보는 다음과 같이 발표되어있다. 이를 바탕으로 Liquid, fcc, bcc 각 상에 대한 열역학 수식화를 수행하고 Ps-Ks 2 원계 상태도를 계산하시오.

- 순수 Ps, Ks 의 Gibbs energy:

$$\Delta^{o}G_{Ps}^{fcc\rightarrow liquid} = 15000 - 10\ T$$

$$\Delta^{o}G_{Ks}^{bcc\rightarrow liquid} = 16250 - 12.5\ T$$

$$\Delta^{o}G_{Ps}^{fcc\rightarrow bcc} = 10000$$

$$\Delta^{o}G_{Ks}^{bcc\rightarrow fcc} = 7500$$

1) Determine solution model
2) Calculate chemical potentials and complete the phase diagram

Liquid phase

Enthalpy of mixing

$$\Delta H_M = \Omega X_A(1 - X_A)$$

For sub-regular solution

$$\Omega = a + bX_A + cX_A^2 + dX_A^3 + \cdots$$

$$= a + bX_A$$

$$= L_0 + L_1 X_A$$

$$\Delta H_M = X_A(1 - X_A)(L_0 + L_1 X_A)$$

$$\therefore y = \frac{\Delta H_M}{X_A(1 - X_A)} = L_0 + L_1 X_A$$

Activity

$$RT \ln a_A = RT \ln X_A + L_0 + 2L_1 X_A$$

$$\Omega = a + bX_A + cX_A^2 + dX_A^3 + \cdots$$

$$= a + bX_A$$

$$= L_0 + 2L_1 X_A$$

$$RT \ln a_A = RT \ln X_A + (1 - X_A)^2 (L_0 + 2L_1 X_A)$$

$$\therefore y = \frac{RT \ln(\frac{a_A}{X_A})}{(1 - X_A)^2} = L_0 + 2L_1 X_A$$

$$(14894.23 - 7.9913T) + (-4794.93 - 0.01123T) X_{Ks}$$

FCC phase

- Enthalpy of formation

$$\Delta H_f^F = X_{Ks}\Delta G_{Ks}^{B\to F} + \Omega^F X_{Ps} X_{Ks} = X_{Ks}\Delta G_{Ks}^{B\to F} + (L_0 + L_1 X_{Ks}) X_{Ps} X_{Ks}$$

$$\frac{\Delta H_f^F - X_{Ks}\Delta G_{Ks}^{B\to F}}{(1 - X_{Ks}) X_{Ks}} = L_0 + L_1 X_{Ks}$$

- Activity

$$\Delta G_{Ks}^F = \mu_{Ks}^F = \Delta G_{Ks}^{B\to F} + X_{Ps}^2 (\Omega^F + \frac{d\Omega^F}{dX_{Ks}} X_{Ks}) + RT \ln X_{Ks}$$

$$= \Delta G_{Ks}^{B\to F} + RT \ln a_{Ks} (wrt.F)$$

$$= RT \ln a_{Ks} (wrt.B)$$

$$\frac{RT \ln(\frac{a_{Ks}(wrt.B)}{X_{Ks}}) - \Delta G_{Ks}^{B\to F}}{X_{Ps}^2} = \Omega^F + \frac{d\Omega^F}{dX_{Ks}} X_{Ks} = L_0 + 2L_1 X_{Tk}$$

$$(12597.61 - 4.9970T) + (-7199.98 - 0.02249T) X_{Ks}$$

BCC phase

Liquid
- Heat of Mixing
L0: 14894.230619, L1: -4794.925467, r2: 0.999997

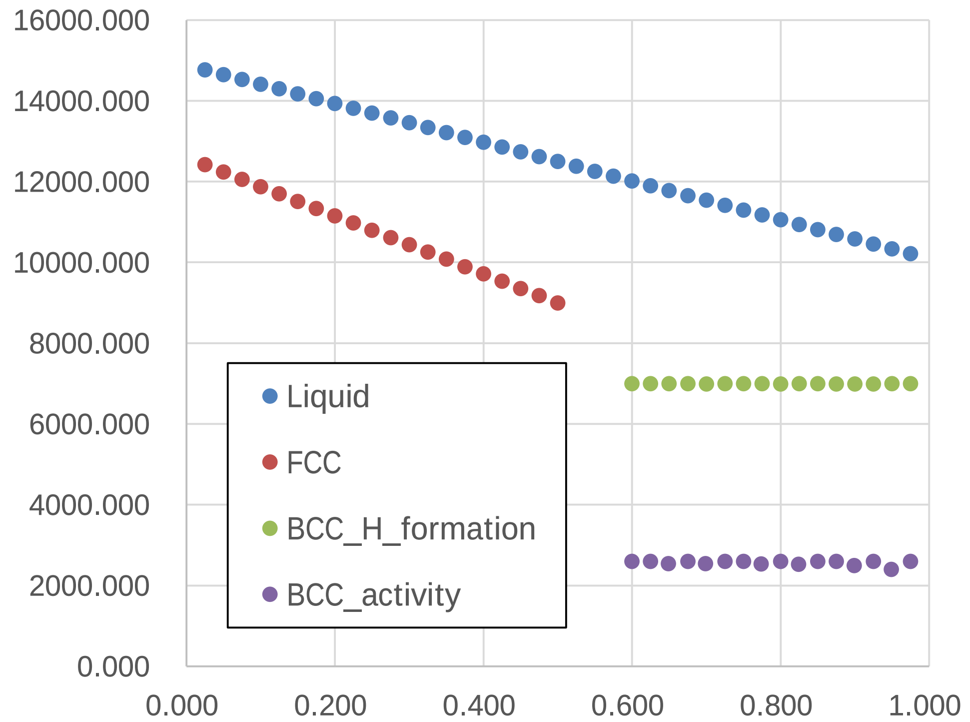
- Activty
L0: 2907.165742, L1: -9623.552212, r2: 0.999975

======================
FCC
- Heat of Mixing
L0: 12597.609462, L1: -7199.977924, r2: 0.999997

- Activity
L0: 7100.870170, L1: -14350.482517, r2: 0.999903

======================
BCC
- Heat of Mixing
L0: 7000.896856, L1: -6.654231, r2: 0.090489

- Activity
L0: 2688.268626, L1: -155.440435, r2: 0.111885



Regular solution model

$$6995.65 - 2.953T$$

Equilibrium conditions

$$\begin{cases}\mu_A^L = \mu_A^{FCC} \\ \mu_B^L = \mu_B^{FCC}\end{cases} \quad \begin{cases}\mu_A^L = \mu_A^{BCC} \\ \mu_B^L = \mu_B^{BCC}\end{cases} \quad \begin{cases}\mu_A^{FCC} = \mu_A^{BCC} \\ \mu_B^{FCC} = \mu_B^{BCC}\end{cases}$$

Liquid	$(14894.23 - 7.9913T) + (-4794.93 - 0.01123T)X_{Ks}$
FCC	$(12597.61 - 4.9970T) + (-7199.98 - 0.02249T)X_{Ks}$
BCC	$6995.65 - 2.953T$

$$\mu_{Ps}^L = \Delta G_{Ps}^{F\to L} + (X_{Ks}^L)^2 \left\{L_0 + L_1(2X_{Ks}^L - 1)\right\} + RT\ln(1 - X_{Ks}^L)$$

$$\mu_{Ks}^L = \Delta G_{Ks}^{B\to L} + (1 - X_{Ks}^L)^2 \left\{L_0 + 2L_1 X_{Ks}^L\right\} + RT\ln(X_{Ks}^L)$$

$$\mu_{Ps}^F = (X_{Ks}^F)^2 \left\{L_0 + L_1(2X_{Ks}^F - 1)\right\} + RT\ln(1 - X_{Ks}^F)$$

$$\mu_{Ks}^F = \Delta G_{Ks}^{B\to F} + (X_{Ks}^F)^2 \left\{L_0 + 2L_1 X_{Ks}^F\right\} + RT\ln(X_{Ks}^F)$$

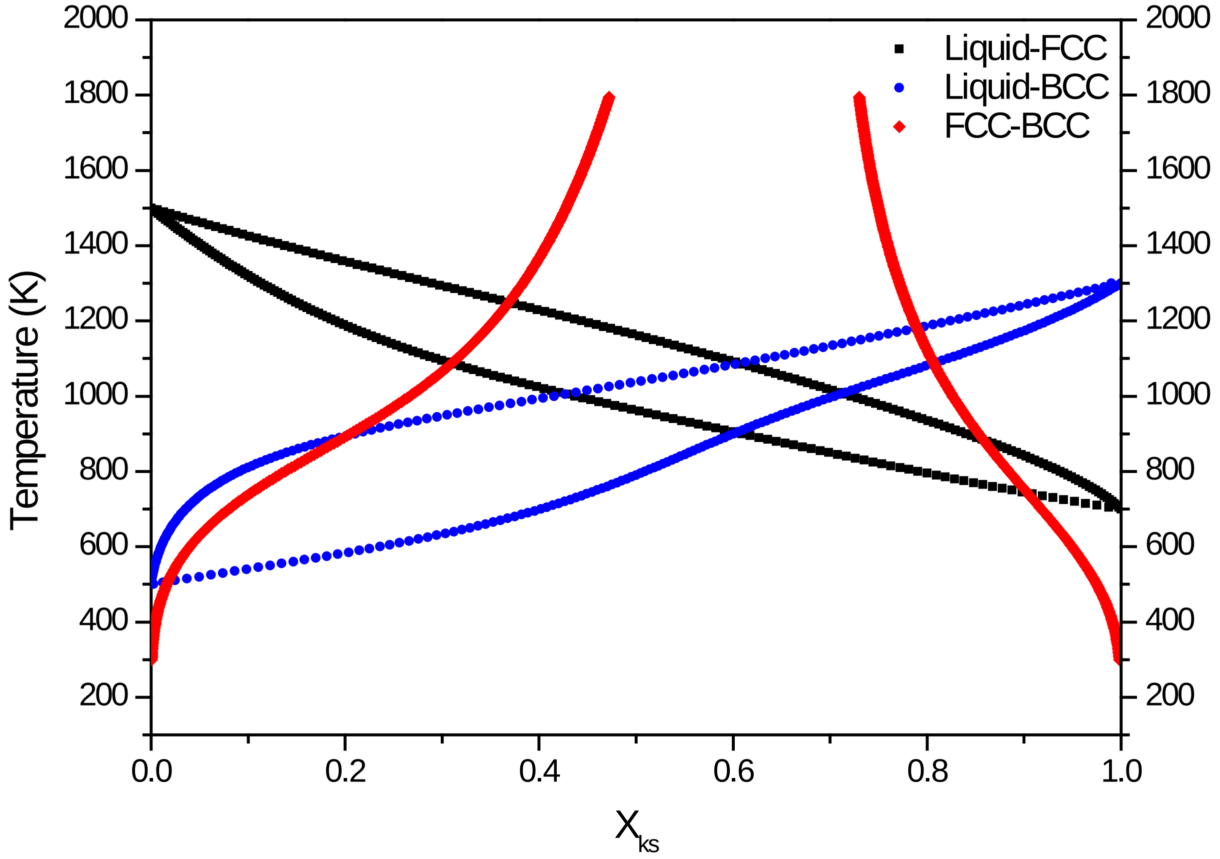
$$\mu_{Ps}^B = \Delta G_{Ps}^{F\to B} + L_0 (X_{Ks}^B)^2 + RT\ln(1 - X_{Ks}^B)$$

$$\mu_{Ks}^B = L_0 (1 - X_{Ks}^B)^2 + RT\ln(X_{Ks}^B)$$

Solve the non-linear equations system by Newton method

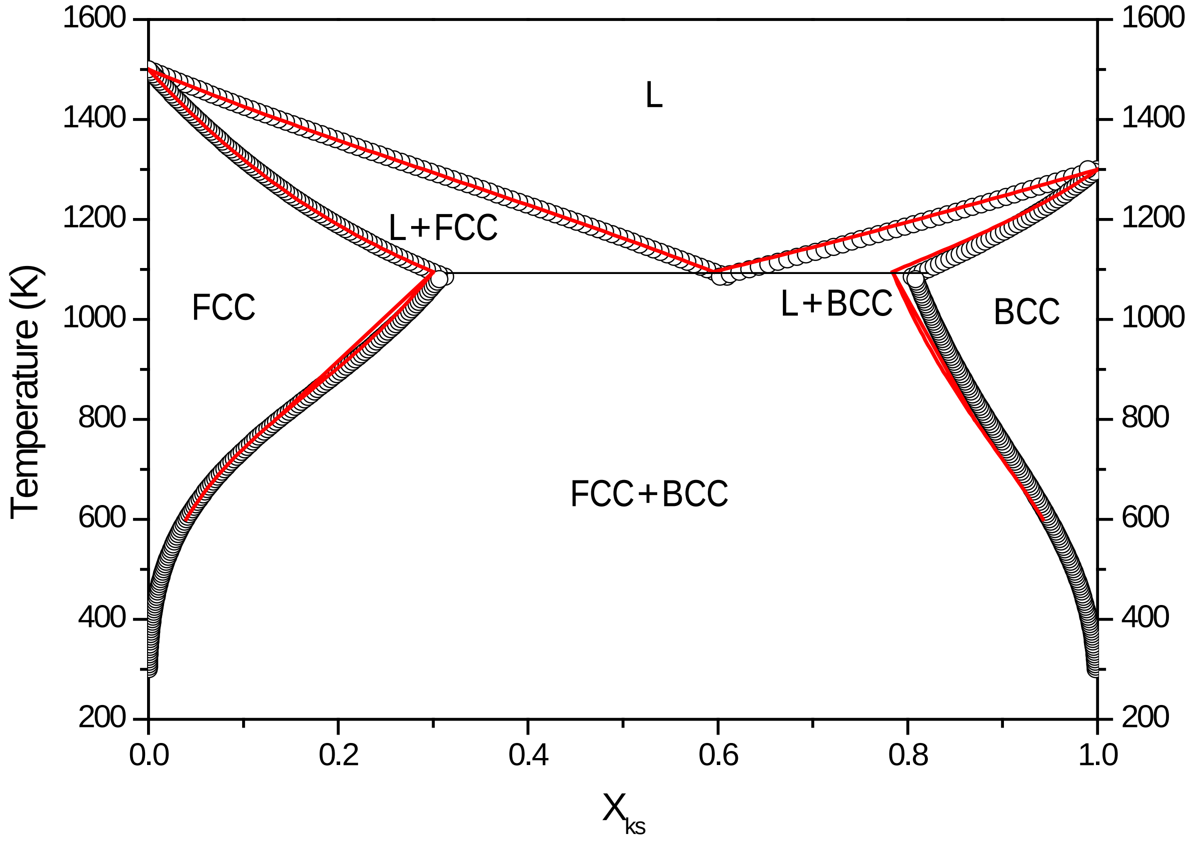
$$P_{(k)} = P_{(k-1)} - [J(P_{(k-1)}]^{-1} F(P_{(k-1)})$$

Results



Liquid-FCC
Liquid-BCC
FCC-BCC
Temperature (K)
2000
1800
1600
1400
1200
1000
800
600
400
200
0.0
0.2
0.4
0.6
0.8
1.0
X_{ks}

Results



L
L+FCC
FCC
L+BCC
BCC
FCC+BCC
Temperature (K)
X_{ks}
1600
1400
1200
1000
800
600
400
200
0.0
0.2
0.4
0.6
0.8
1.0