Modelling of Phase Separation in Iron-based Ternary Alloys

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Background

1. Numerical simulations

   Fe-Cr-Mo & Fe-Cr-Ni systems

2. Asymptotic behavior of Mo or Ni

Extension of CH equation into ternary sytems

$$\frac{\partial c_i}{\partial t} = M_i \nabla^2 \left(\frac{\partial f_0}{\partial c_i} - K_i \nabla^2 c_i - \sum_{j=1}^{3} (1 - \delta_{ij}) L_{ij} \nabla^2 c_j \right)$$

M_i :mobility

Interaction parameters

$$L_{\text{Fecr}} = 18.6\text{kJ/mol}$$

$$L_{\text{FeMo}} = 35.7 - 0.0027T - (5.23 - 2.32)/1000\text{kJ/mol}$$

$$L_{FeNi} = -0.957 - 0.0013T + (1.79 - 0.002T)(C_{Fe} - c_{Ni})$$

$$L_{CrNi} = 17.12 - 0.0012T + (34.4 - 0.0012T)(C_{Cr} - C_{Ni})$$

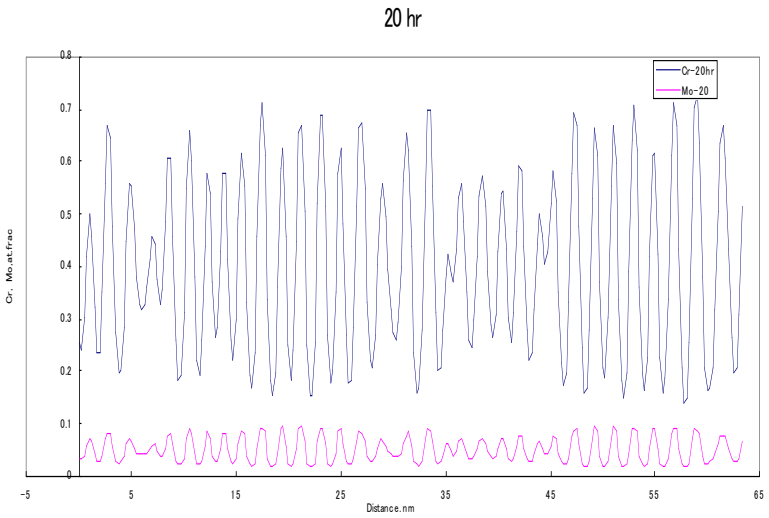
Diffusion coefficients(cm2/s)

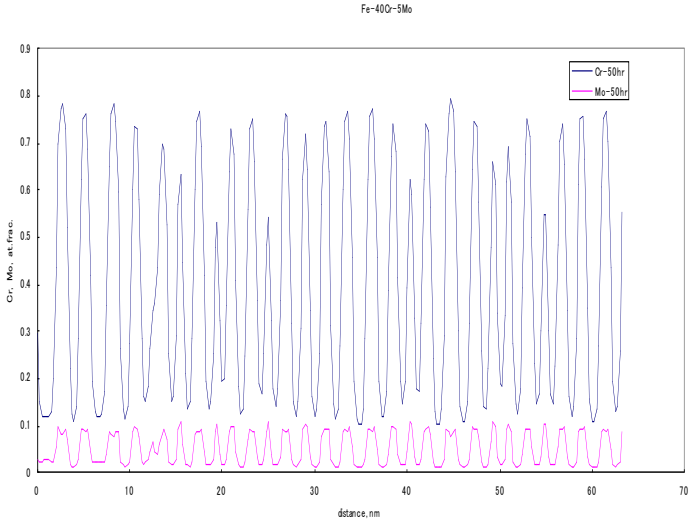
$$D_{Cr} = 0.19 \exp\left(-\frac{246000}{RT}\right)$$

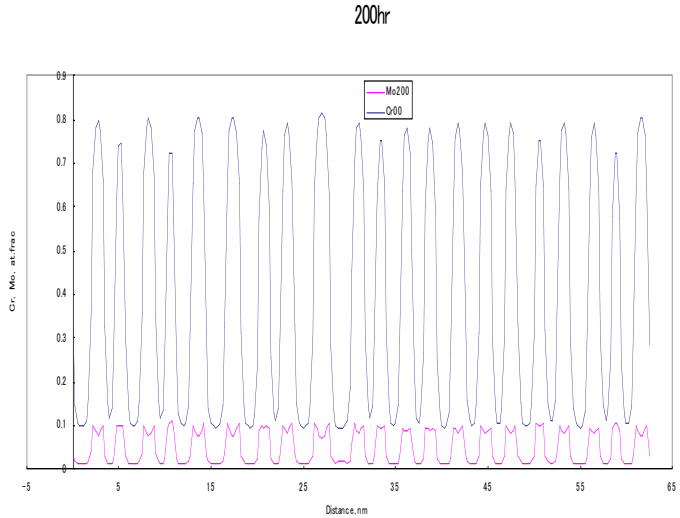
$$D_{Mo} = 0.29 \exp\left(-\frac{264000}{RT}\right)$$

$$D_{Ni} = 1.4 \exp\left(-\frac{245800}{RT}\right)$$

Fe-40Cr-5Mo



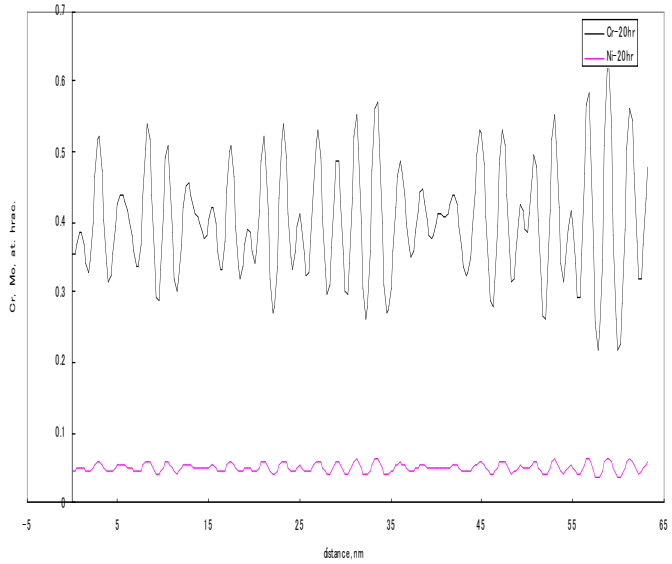




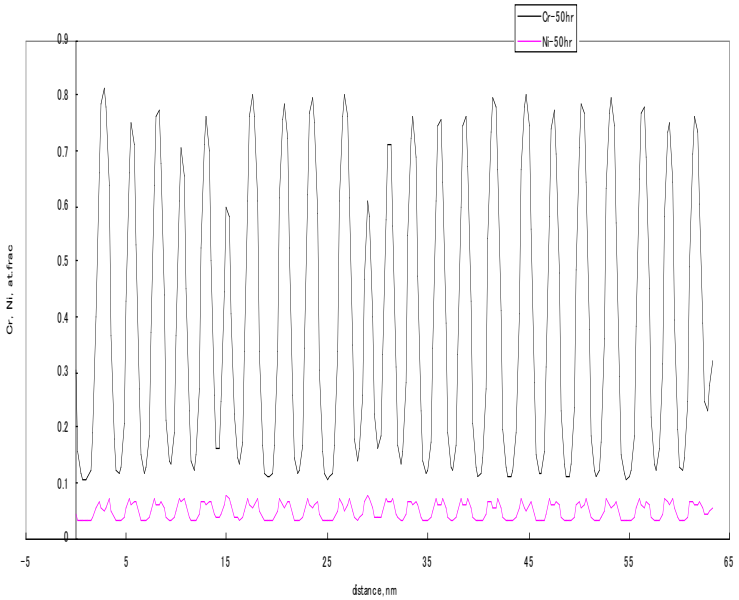
Bifurcation of Mo peaks along the trajectry of peak tops of Cr

Fe-40Cr-5Ni

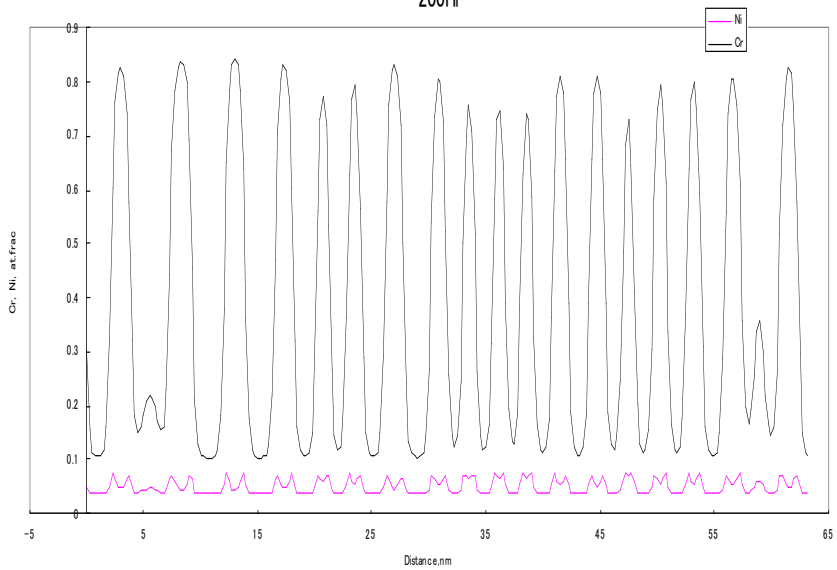
20Hri



50 Hr



200Hr



Decarese of
Ni concentration
along the trajectry of
peak tops of Cr

Behavior of Mo concentration along the trajectory of peak top of Cr

Increase at the beginning and then bifurcation of peak occurs

Behavior of Ni along the trajectory of peak top of Cr

Decrease of peak occurs

Mechanism ?

Purpose of present study

Fe－Cr-X ternary alloys

Behavior of X concentration along the trajectory of peak tops of Cr

Mechanism of the bifurcation of the peak of the concentration X

One-dimensional case

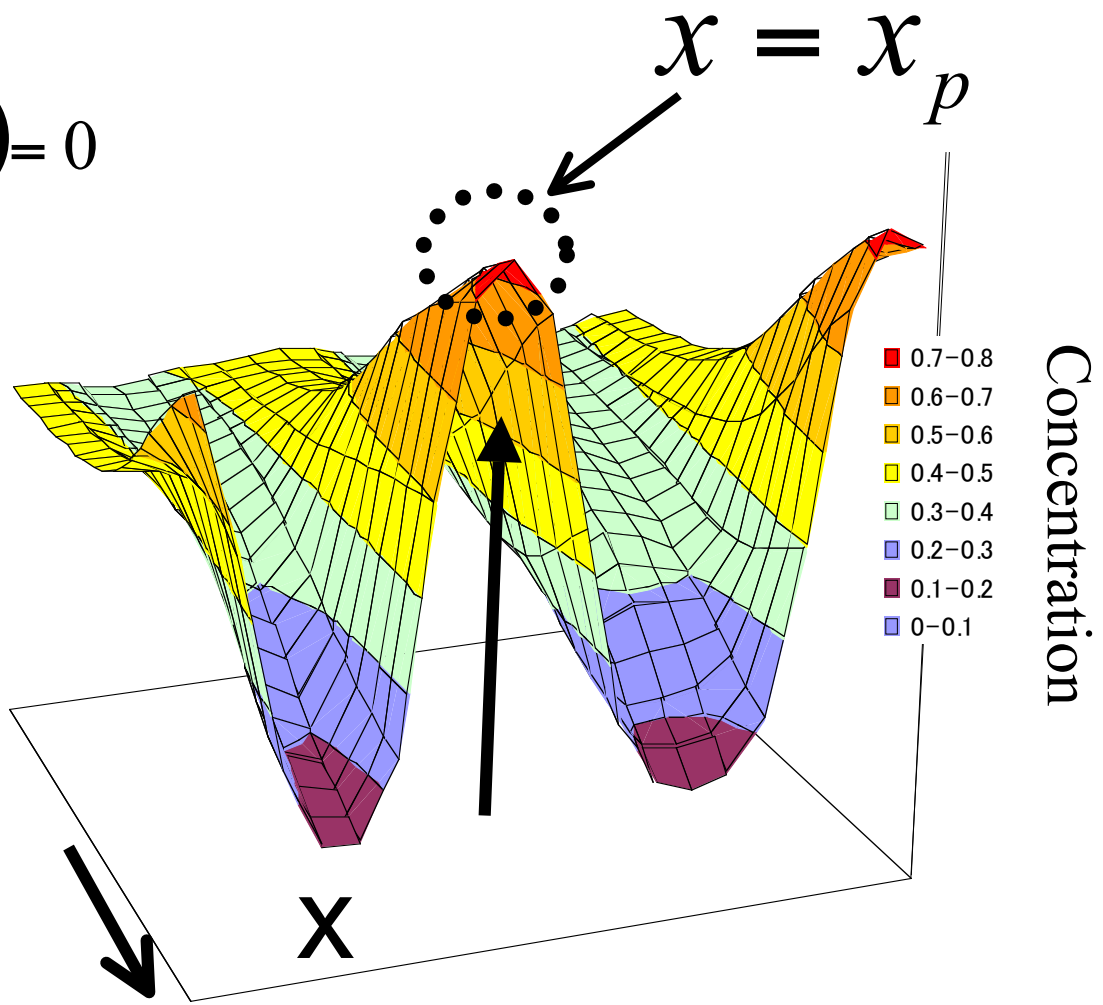
$$\frac{\partial \mathbf{c}_X}{\partial t} = \mathbf{M}_1 \left[\frac{\partial^2 \mathbf{f}_0}{\partial \mathbf{c}_X{}^2} \frac{\partial^2 \mathbf{c}_X}{\partial \mathbf{x}^2} + \frac{\partial^2 \mathbf{f}_0}{\partial \mathbf{c}_X \partial \mathbf{c}_Y} \frac{\partial^2 \mathbf{c}_Y}{\partial \mathbf{x}^2} \right.$$

$$+ 2 \frac{\partial^3 \mathbf{f}_0}{\partial \mathbf{c}_X^2 \partial \mathbf{c}_Y} \frac{\partial \mathbf{c}_X}{\partial \mathbf{x}} \frac{\partial \mathbf{c}_Y}{\partial \mathbf{x}} + \frac{\partial^3 \mathbf{f}_0}{\partial \mathbf{c}_X^3} \left(\frac{\partial \mathbf{c}_X}{\partial \mathbf{x}} \right)^2$$

$$\left. + \frac{\partial^3 \mathbf{f}_0}{\partial \mathbf{c}_X \partial \mathbf{c}_Y^2} \left(\frac{\partial \mathbf{c}_Y}{\partial \mathbf{x}} \right)^2 - \mathbf{K}_1 \frac{\partial^4 \mathbf{c}_X}{\partial \mathbf{x}^4} - \mathbf{L}_{12} \frac{\partial^4 \mathbf{c}_Y}{\partial \mathbf{x}^4} \right]$$

At peak top position p(x_p,t)

$$\frac{\partial c_{Cr}}{\partial x}\left(x_p, t\right) = 0$$



At the peak top position

- Peak top position of the i-element $c_{Cr}(x_p)$

$$\left[\frac{\partial c_{Cr}}{\partial x}\right]_{x=x_p} = 0, \quad \left[\frac{\partial^2 c_{Cr}}{\partial x^2}\right]_{x=x_p} < 0 \quad \cdots(2.1)$$

- Initial time ($t = 0$)

$$\overline{c_{Cr}} > \overline{c_X}, \quad \frac{\partial^2 f_0}{\partial c_{Cr}^2} < 0, \quad \frac{\partial^2 f_0}{\partial c_X^2} > 0 \quad \cdots(2.2)$$

Mean value theorem for differential calculus

$$\frac{f(a)-f(b)}{(a-b)}=\frac{df}{dx}(c),\quad a>c>b$$

Mean value theorem for compound function

(R. Courant and F.John: Introduction to Calculus and Analysis I, Springer(1989) ,pp.222-223)

$$G\left(t,x_p,0,\frac{\partial^2 c}{\partial x^2}(x_p,t),\cdots\right)-G\left(t,x_p,0,0,\cdots\right)$$

$$=\frac{\partial G}{\partial(\partial^2 c/\partial x^2)}\left(t,x_p,0,\varsigma,\cdots\right)\frac{\partial^2 c}{\partial x^2}(x_p,t)$$

$$\left[0>\varsigma>\frac{\partial^2 c}{\partial x^2}(x_p,t)\right]$$

Assumption

- $x = x_p$ Behavior of component X

$$\left(\frac{\partial c_X}{\partial x}\right)^2 << \left|\frac{\partial^2 c_{Cr}}{\partial x^2}\right|, \qquad \left|\frac{\partial c_{Cr}}{\partial x}\right| = 0$$

(After peak or bottom formation)

$$\frac{\partial^4 c_{Cr}}{\partial x^4}, \frac{\partial^4 c_X}{\partial x^4}$$

Negligible small

Behavior of element X along the trajectory of peak top of element Cr

$$\frac{d c_X}{d t}\left(x_p, t\right) \cong M_X \frac{\partial^2 f_0}{\partial c_{Cr} \partial c_X} \frac{\partial^2 c}{\partial x} \frac{\partial^2 c_{Cr}}{\partial x^2} < 0$$

$$\frac{\partial^2 f}{\partial c_{Cr}\partial c_X} = {}^0L_{CrX} - {}^0L_{FeCr} - {}^0L_{Fe}$$

$$- 2\left[{}^1L_{CrX}\left(c_{Cr} - c_X\right) + {}^1L_{CrX}\left(1 - c_{Cr} - 3c_X\right)\right]$$

$$+ RT\frac{1}{\left(1 - c_{Cr} - c_X\right)}$$

$$\frac{d}{dt}\left(\frac{\partial^2 f}{\partial c_X \partial c_{Cr}}\right) = \frac{RT}{(1-c_{Cr}-c_X)^2}\left(\frac{dc_{Cr}}{dt}+\frac{dc_X}{dt}\right)$$

$$\frac{dc_{Cr}}{dt} > 0, \quad \frac{dc_X}{dt} > 0$$

$$\frac{d}{dt}\left(\frac{\partial^2 f}{\partial c_{Cr} \partial c_X}\right) > 0$$

$$\left(\frac{\partial^2 f}{\partial c_{Cr} \partial c_X} \right) < 0$$

$$\frac{dc_{Cr}}{dt} > 0, \quad \frac{dc_X}{dt} > 0$$

$$\frac{d}{dt}\left(\frac{\partial^2 f}{\partial c_{Cr} \partial c_X} \right) > 0$$

$$\left(\frac{\partial^2 f}{\partial c_{Cr} \partial c_X} \right) < 0$$

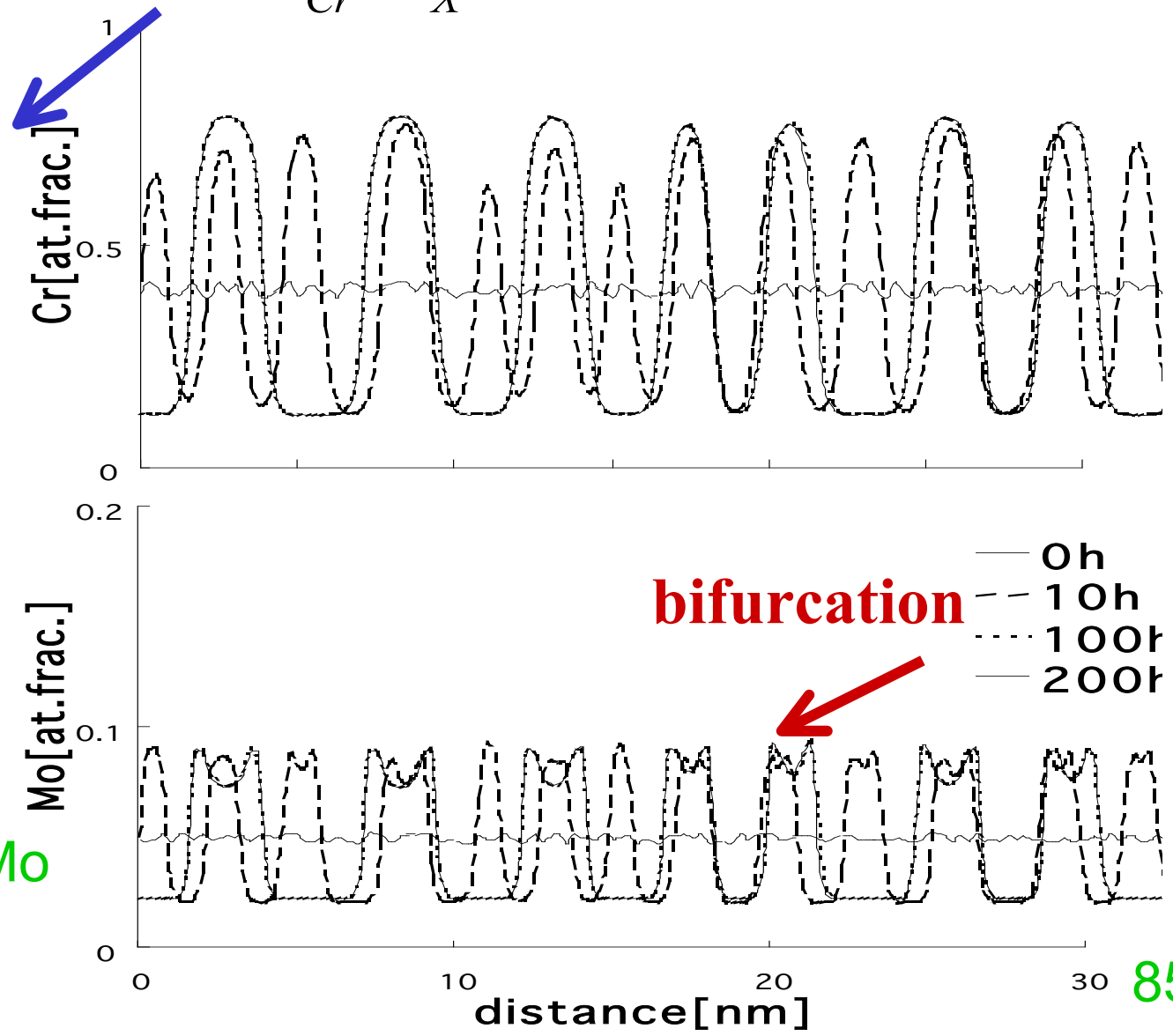
$$\left(\frac{\partial^2 f}{\partial c_{Cr} \partial c_X} \right) > 0 \rightarrow \frac{dc_X}{dt}$$

Bifurcation

Group1 $\partial^2 f_0/\partial c_i \partial c_j > 0$
$(c_i > c_j, \partial^2 f_0/\partial c_i^2 < 0, \partial^2 f_0/\partial c_j^2 > 0)$

Group2 $\partial^2 f_0/\partial c_i \partial c_j < 0 \quad (0 < t < \infty)$
$(c_i > c_j, \partial^2 f_0/\partial c_i^2 < 0, \partial^2 f_0/\partial c_j^2 > 0$

$$\frac{\partial^2 f_0}{\partial c_{Cr}\partial c_X} < 0, \quad \frac{dc_{Cr}}{dt} > 0, \frac{dc_X}{dt} > 0$$



Fe40Cr5Mo

850K

850K

Summary of numerical simulation of 1-dimentional C-H equation

- **Asymptotic behavior of minor element X in a Fe-Cr-X ternary alloy along the trajectory of a peak top of the major element Cr is classified into three groups according to the sign of the second derivative of the chemical free energy with respect to the concentration of Cr and the concentration of X.**

N-dimentional cases?

If at a position $\mathbf{x}=\mathbf{x}^0$ and a time $t_1>0$ a function $\alpha=c_X(\mathbf{x},t_1)$ has a peak top which is characterized by

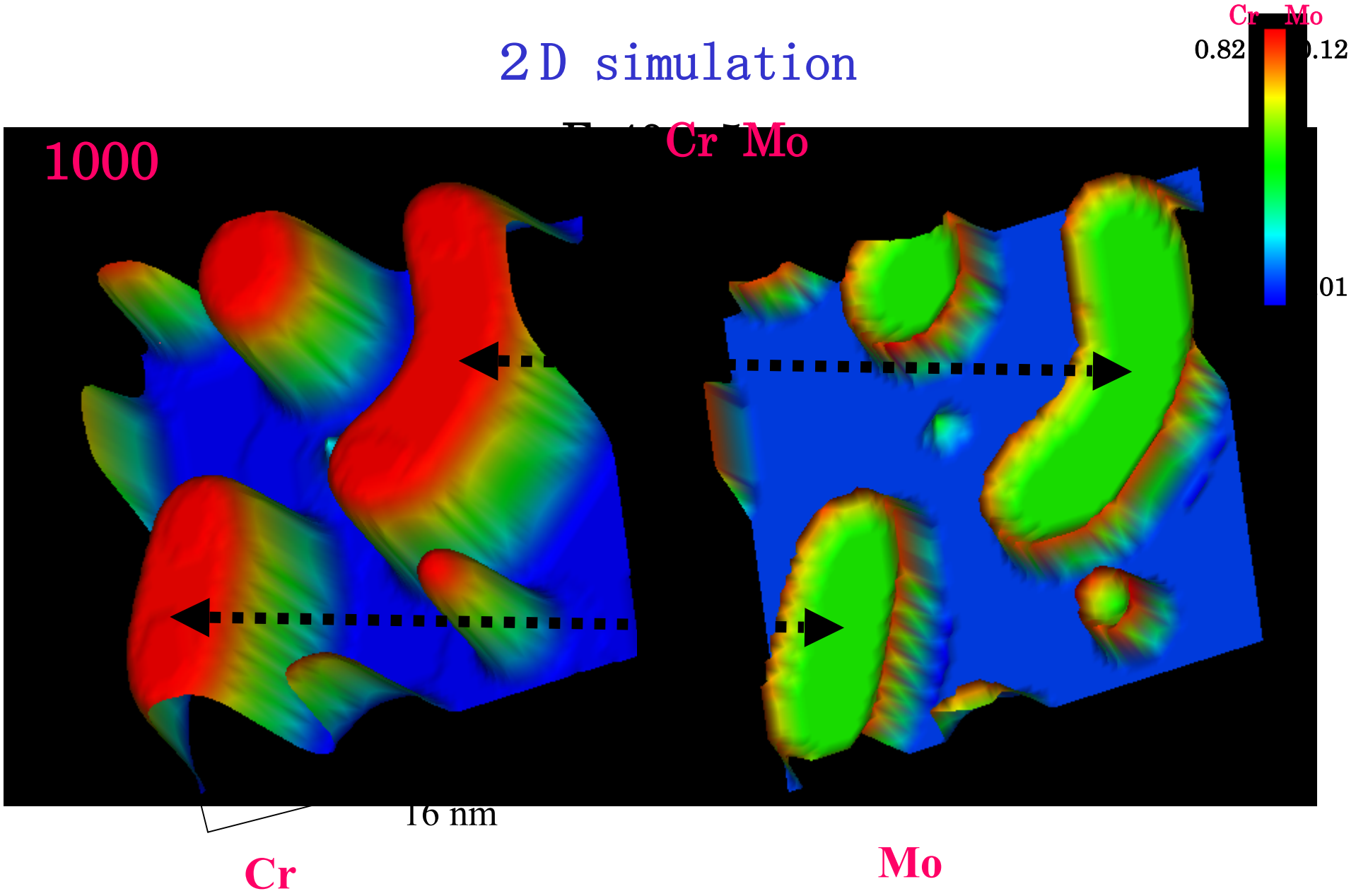
$$\partial \boldsymbol{c}_X / \partial \boldsymbol{x}_i(\mathbf{x}^0, \boldsymbol{t}_1) = 0$$

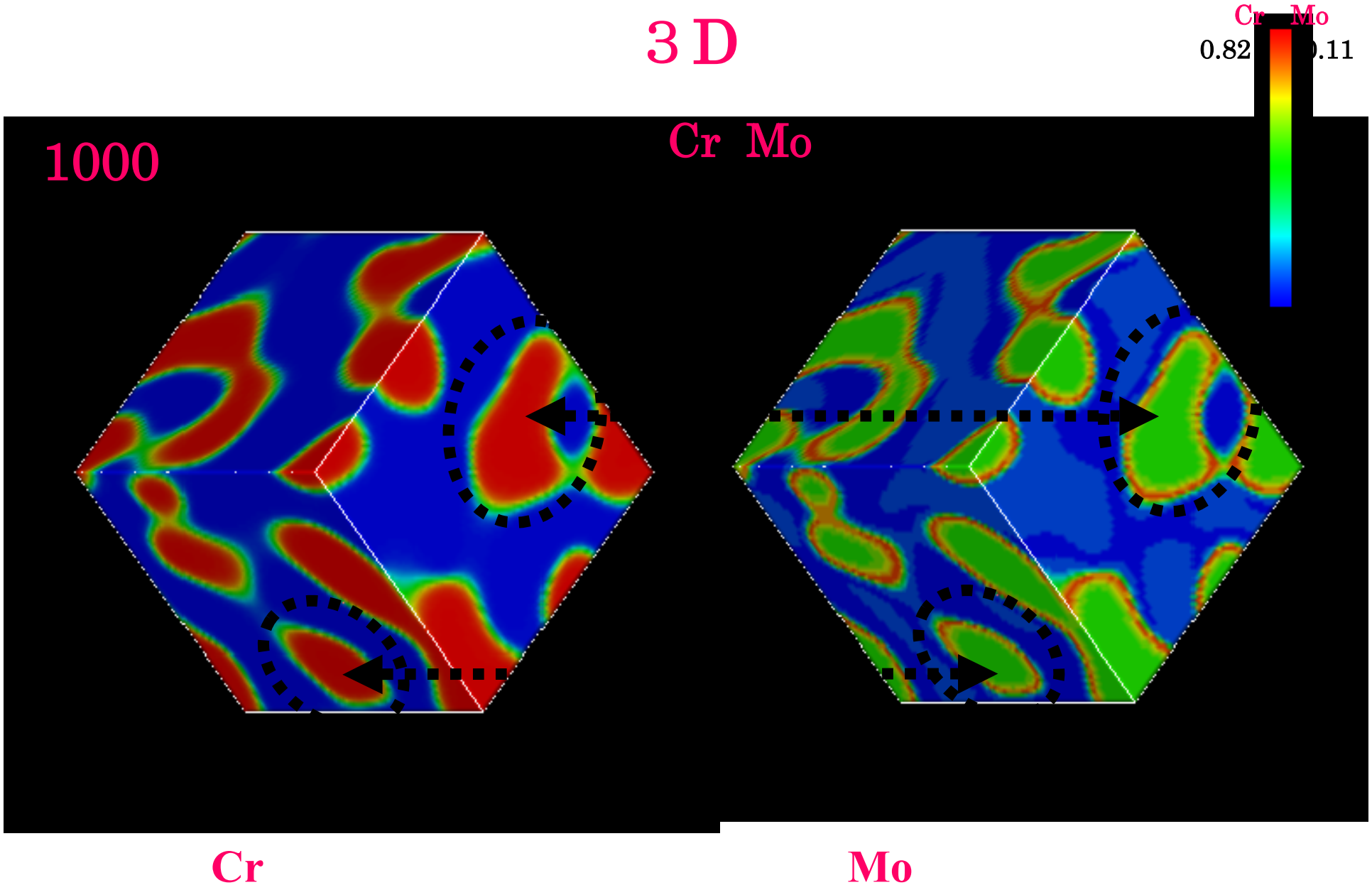
and negative definiteness of the Hessian

Then according to the general discussion on the solution of non-linear equation(A.Kitada,1994)

there exit an implicit function $\mathbf{g}(t)$, $\mathbf{x}^0=\mathbf{g}(t_1)$ such that

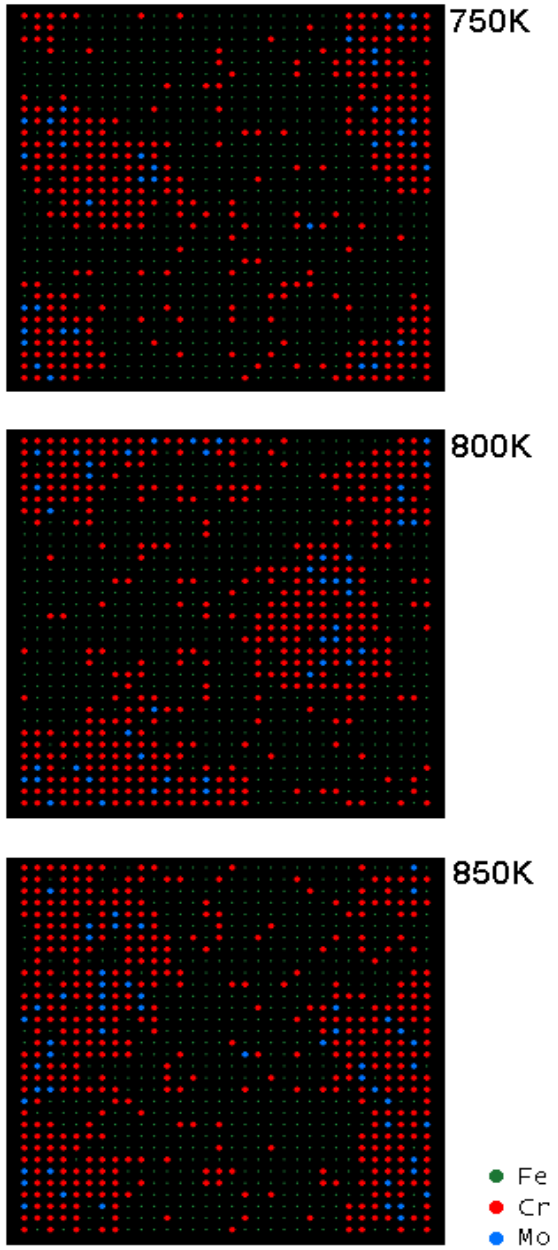
$$\frac{\partial \boldsymbol{c}_X(\boldsymbol{g}(\boldsymbol{t}),\boldsymbol{t})}{\partial \boldsymbol{x}_i} = 0, \quad \frac{\partial \boldsymbol{c}_X{}^2(\boldsymbol{g}(\boldsymbol{t}),\boldsymbol{t})}{\partial \boldsymbol{x}_i{}^2} < 0$$


2D simulation
Cr Mo
1000
Cr Mo
0.82
.12
01
16 nm
Cr
Mo

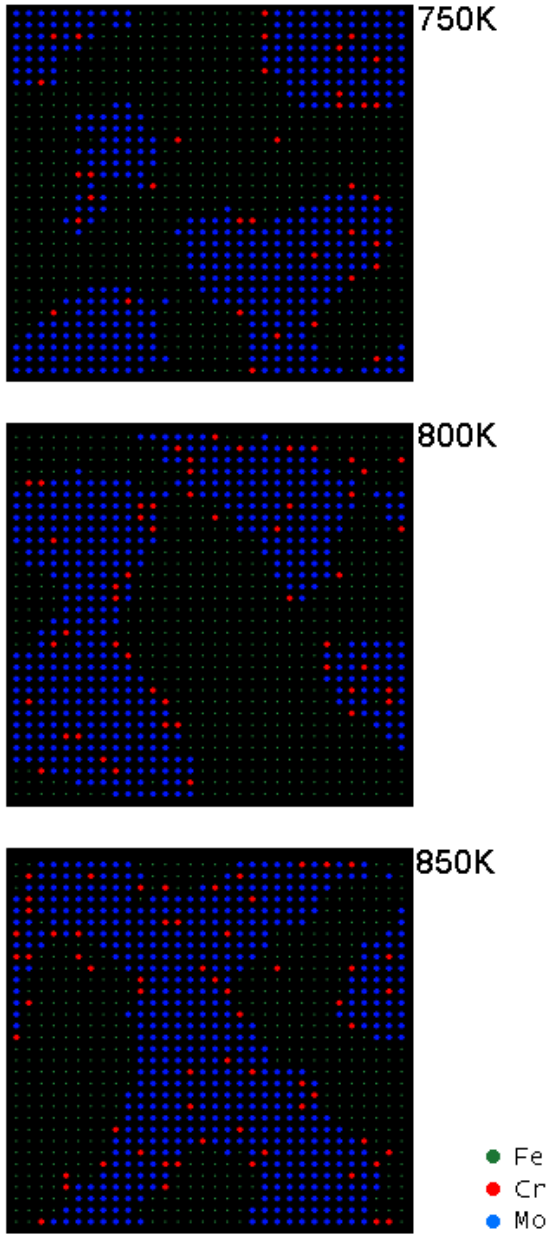

3 D
Cr Mo
0.82
.11
1000
Cr Mo
Cr
Mo

Monte Carlo Simulation

ϕ

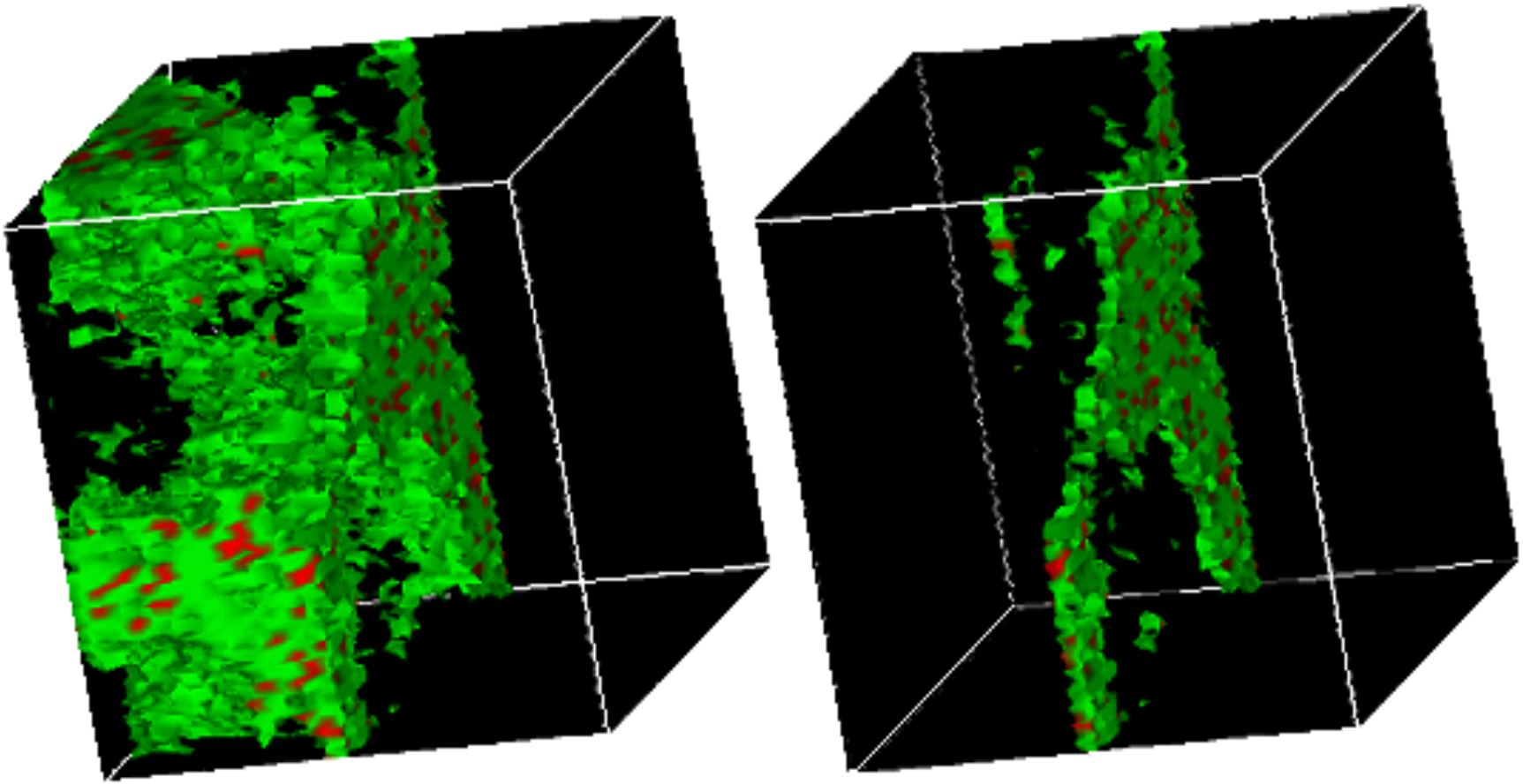


Fe-40Cr-5Mo

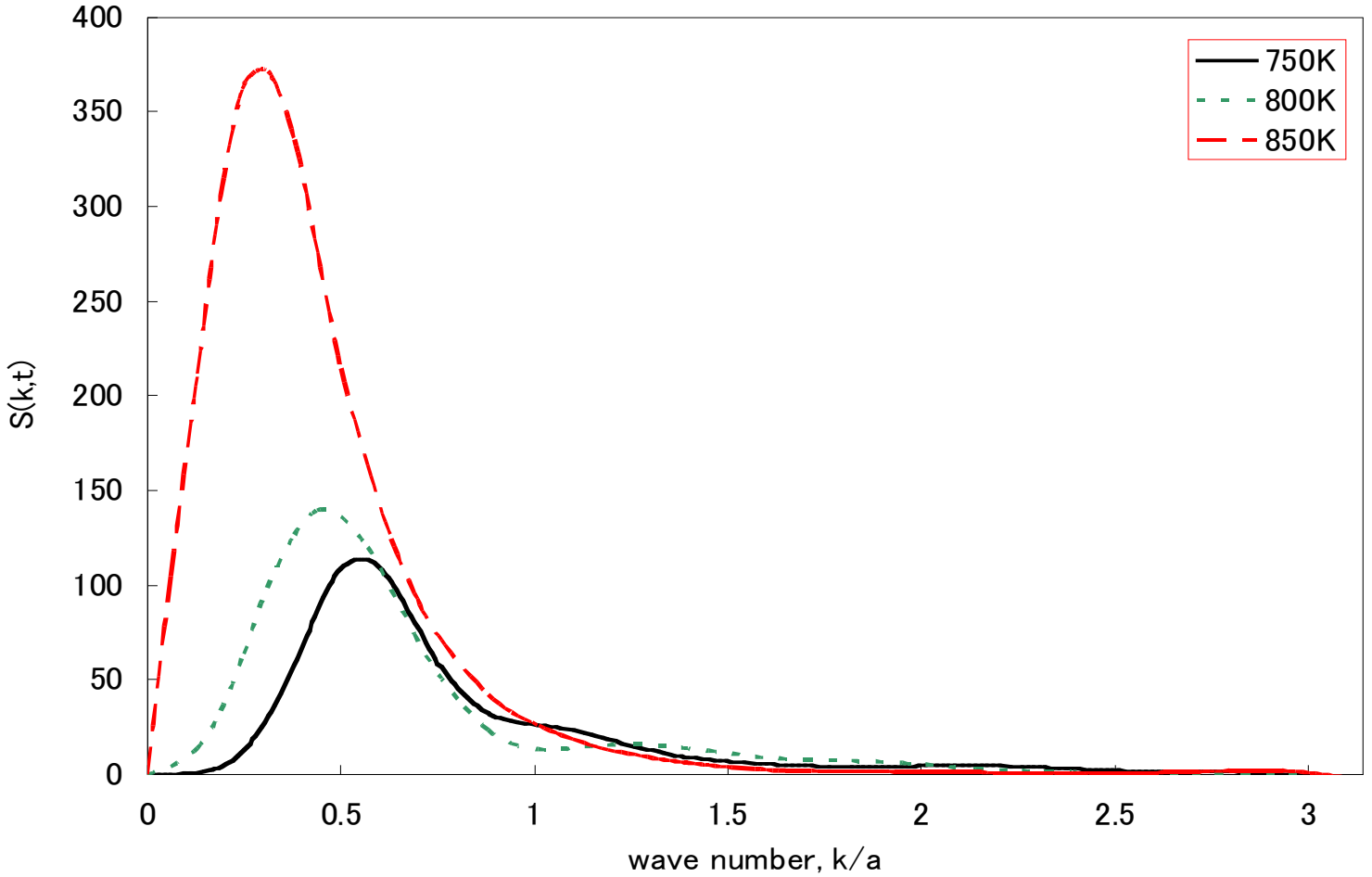


Fe-40Mo-5Cr

Monte Carlo Simulation



Variation of structure factor



Problems

Simulations

Temporal evolution of the structure

factor

Observations

X-ray diffraction

3D atom probe?(POSAP)

Thank you for your attention

ϕ

Fe-Cr-X ternary alloys(X=Mo,Ti,Ni etc.)

$$G_m^{\phi} = x_{Fe}\,{}^{0}G_{Fe}^{\phi} + x_{Cr}\,{}^{0}G_{Cr}^{\phi} + x_X\,{}^{0}G_X^{\phi} + RT\left(x_{Cr}\ln x_{Cr} + x_X \ln x_X\right)$$

$$+ {}^{E}G_m^{\phi} + {}^{mo}G_m^{\phi}$$

Excess Gibbs energy

$${}^{E}G_m^{\phi} = x_{Fe}x_{Cr}L_{FeCr}^{\phi} + x_{Fe}x_X L_{FeX}^{\phi} + x_{Cr}x_X L_{CrX}^{\phi}$$

$$+ x_{Fe}x_{Cr}x_X L_{FeCrX}^{\phi}$$

Gibbs energy due to the magnetic ordering

$${}^{E}G_m^{\phi} = RT\ln(\beta^{\phi}+1)f(\tau)$$

L_{ij}^{ϕ} binary interaction parameter
Between components i and j in phase ϕ