Sub-lattice モデルに基づく Ni-Al 合金の化学的自由エネルギー

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のフォロー

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１．不規則相の化学的自由エネルギー式

不規則相の化学的自由エネルギーは以下のように定式化される。

$$G_m^\phi - \sum_{i=A}^{B} x_i^\phi \,{}^\circ H_i^{SER}(298.15\mathrm{K}) = {}^{ref}G^\phi + {}^{id}G^\phi + {}^{ex}G^\phi$$

$${}^{ref}G^\phi = \sum_{i=A}^{B} x_i^\phi \{G_i^\phi - {}^\circ H_i^{SER}(298.15\mathrm{K})\}$$

$${}^{id}G^\phi = RT\sum_{i=A}^{B} x_i^\phi \ln x_i^\phi$$

$${}^{ex}G^\phi = x_A^\phi x_B^\phi L_{A,B}^\phi$$

$$L_{A,B}^\phi = \sum_{\nu=0}^{n} {}^\nu L_{A,B}^\phi (x_A^\phi - x_B^\phi)^\nu$$

$${}^\nu L_{A,B}^\phi = {}^\nu A_{A,B}^\phi + {}^\nu B_{A,B}^\phi T + \cdots$$

具体的に fcc-A1 の Ni-Al２元系について書き下して見ると、

$$\begin{aligned}
&G_m^\phi - \sum_{i=A}^{B} x_i^\phi \,{}^\circ H_i^{SER}(298.15\mathrm{K}) \\
&= {}^{ref}G^\phi + {}^{id}G^\phi + {}^{ex}G^\phi \\
&= \sum_{i=A}^{B} x_i^\phi \{G_i^\phi - {}^\circ H_i^{SER}(298.15\mathrm{K})\} + x_A^\phi x_B^\phi L_{A,B}^\phi + RT\sum_{i=A}^{B} x_i^\phi \ln x_i^\phi \\
&= x_{Ni}^{A1}(G_{Ni}^{A1} - {}^\circ H_{Ni}^{SER}) + x_{Al}^{A1}(G_{Al}^{A1} - {}^\circ H_{Al}^{SER}) + x_{Al}^{A1} x_{Ni}^{A1} L_{Al,Ni}^{A1} + RT(x_{Al}^{A1}\ln x_{Al}^{A1} + x_{Ni}^{A1}\ln x_{Ni}^{A1})
\end{aligned}$$

$$L_{Al,Ni}^{A1} = {}^0L_{Al,Ni}^{A1} + {}^1L_{Al,Ni}^{A1}(x_{Al}^{A1} - x_{Ni}^{A1}) + {}^2L_{Al,Ni}^{A1}(x_{Al}^{A1} - x_{Ni}^{A1})^2 + {}^3L_{Al,Ni}^{A1}(x_{Al}^{A1} - x_{Ni}^{A1})^3$$

[fcc-A1]

$${}^0L_{Al,Ni}^{fcc-A1} = -162407.750 + 16.212965T$$

$${}^1L_{Al,Ni}^{fcc-A1} = 73417.798 - 34.914000T$$

$${}^2L_{Al,Ni}^{fcc-A1} = 33471.014 - 9.837000T$$

$${}^3L_{Al,Ni}^{fcc-A1} = -30758.010 + 10.253000T$$

となる。

２．規則相の化学的自由エネルギー式

γ'相を例に取り、規則相の化学的自由エネルギー式を副格子モデルで記述しよう。まず、エネルギーを評価する１モル分子（化合物）を、

$$(A_{y_A^{(1)}} B_{y_B^{(1)}})_3 (A_{y_A^{(2)}} B_{y_B^{(2)}})$$

と置く。この化学的自由エネルギーは、

$$G_m^{ord} = {}^{ref}G^{ord} + {}^{id}G^{ord} + {}^{ex}G^{ord}$$

$$
\begin{aligned}
{}^{ref}G^{ord} &= \sum_{i=A}^{B}\sum_{j=A}^{B} y_i^{(1)} y_j^{(2)} G_{i:j}^{ord} \\
{}^{id}G^{ord} &= RT\left[\frac{3}{4}\sum_{i=A}^{B} y_i^{(1)} \ln y_i^{(1)} + \frac{1}{4}\sum_{i=A}^{B} y_i^{(2)} \ln y_i^{(2)}\right] \\
{}^{ex}G^{ord} &= \sum_{i=A}^{B}\sum_{j>i} y_i^{(1)} y_j^{(1)} \left(\sum_k y_k^{(2)} L_{i,j:k}^{ord}\right) + \sum_{i=A}^{B}\sum_{j>i} y_i^{(2)} y_j^{(2)} \left(\sum_k y_k^{(1)} L_{k:i,j}^{ord}\right) \\
&\quad + \sum_{i=A}^{B}\sum_{j>i}\sum_{k=A}^{B}\sum_{l>k} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} L_{i,j:k,l}^{ord}
\end{aligned}
$$

$$
\begin{aligned}
L_{i,j:k}^{ord} &= \sum_{\nu=0}^{n} {}^{\nu}L_{i,j:k}^{ord} (y_i^{(1)} - y_j^{(1)})^{\nu} \\
L_{k:i,j}^{ord} &= \sum_{\nu=0}^{n} {}^{\nu}L_{k:i,j}^{ord} (y_i^{(2)} - y_j^{(2)})^{\nu}
\end{aligned}
$$

にて与えられ、

$$
x_i = \frac{3}{4} y_i^{(1)} + \frac{1}{4} y_i^{(2)}
$$

が成立する。なお、不規則相の場合には、 $x_i = y_i^{(1)} = y_i^{(2)}$ となる。

これも具体的に Ni-Al 2 元系について書き下してみよう。

$$
\begin{aligned}
G_m^{ord} &= {}^{ref}G^{ord} + {}^{id}G^{ord} + {}^{ex}G^{ord} \\
&= \sum_{i=A}^{B}\sum_{j=A}^{B} y_i^{(1)} y_j^{(2)} G_{i:j}^{ord} + \sum_{i=A}^{B}\sum_{j>i} y_i^{(1)} y_j^{(1)} \left(\sum_k y_k^{(2)} L_{i,j:k}^{ord}\right) + \sum_{i=A}^{B}\sum_{j>i} y_i^{(2)} y_j^{(2)} \left(\sum_k y_k^{(1)} L_{k:i,j}^{ord}\right) \\
&\quad + \sum_{i=A}^{B}\sum_{j>i}\sum_{k=A}^{B}\sum_{l>k} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} L_{i,j:k,l}^{ord} + RT\left[\frac{3}{4}\sum_{i=A}^{B} y_i^{(1)} \ln y_i^{(1)} + \frac{1}{4}\sum_{i=A}^{B} y_i^{(2)} \ln y_i^{(2)}\right] \\
&= y_{Al}^{(1)} y_{Al}^{(2)} G_{Al:Al}^{L1_2} + y_{Al}^{(1)} y_{Ni}^{(2)} G_{Al:Ni}^{L1_2} + y_{Ni}^{(1)} y_{Al}^{(2)} G_{Ni:Al}^{L1_2} + y_{Ni}^{(1)} y_{Ni}^{(2)} G_{Ni:Ni}^{L1_2} \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} \left(y_{Al}^{(2)} L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)} L_{Al,Ni:Ni}^{L1_2}\right) + y_{Al}^{(2)} y_{Ni}^{(2)} \left(y_{Al}^{(1)} L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)} L_{Ni:Al,Ni}^{L1_2}\right) \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} y_{Al}^{(2)} y_{Ni}^{(2)} L_{Al,Ni:Al,Ni}^{L1_2} \\
&\quad + RT\left[\frac{3}{4}(y_{Al}^{(1)} \ln y_{Al}^{(1)} + y_{Ni}^{(1)} \ln y_{Ni}^{(1)}) + \frac{1}{4}(y_{Al}^{(2)} \ln y_{Al}^{(2)} + y_{Ni}^{(2)} \ln y_{Ni}^{(2)})\right]
\end{aligned}
$$

$$
\begin{aligned}
L_{Al,Ni:Al}^{ord} &= {}^{0}L_{Al,Ni:Al}^{ord} + {}^{1}L_{Al,Ni:Al}^{ord} (y_{Al}^{(1)} - y_{Ni}^{(1)}) \\
L_{Al,Ni:Ni}^{ord} &= {}^{0}L_{Al,Ni:Ni}^{ord} + {}^{1}L_{Al,Ni:Ni}^{ord} (y_{Al}^{(1)} - y_{Ni}^{(1)}) \\
L_{Al:Al,Ni}^{ord} &= {}^{0}L_{Al:Al,Ni}^{ord} + {}^{1}L_{Al:Al,Ni}^{ord} (y_{Al}^{(2)} - y_{Ni}^{(2)}) \\
L_{Ni:Al,Ni}^{ord} &= {}^{0}L_{Ni:Al,Ni}^{ord} + {}^{1}L_{Ni:Al,Ni}^{ord} (y_{Al}^{(2)} - y_{Ni}^{(2)}) \\
L_{Al,Ni:Al,Ni}^{ord} &= {}^{0}L_{Al,Ni:Al,Ni}^{ord}
\end{aligned}
$$

[$L1_2$]

$$u_{1Al,Ni} = -13415.515 + 2.0819247T$$
$$u_{4Al,Ni} = 7088.736 - 3.6868954T$$
$${}^{\circ}G_{Ni:Al}^{L1_2} - \frac{3}{4}{}^{\circ}G_{Ni}^{fcc-A1} - \frac{1}{4}{}^{\circ}G_{Al}^{fcc-A1} = 3u_{1Al,Ni}$$
$${}^{\circ}G_{Al:Ni}^{L1_2} - \frac{3}{4}{}^{\circ}G_{Al}^{fcc-A1} - \frac{1}{4}{}^{\circ}G_{Ni}^{fcc-A1} = 3u_{1Al,Ni}$$
$${}^{0}L_{Al,Ni:Al}^{L1_2} = {}^{0}L_{Al,Ni:Ni}^{L1_2} = 6u_{1Al,Ni}$$
$${}^{0}L_{Al:Al,Ni}^{L1_2} = {}^{0}L_{Ni:Al,Ni}^{L1_2} = 0$$
$${}^{1}L_{Al,Ni:Al}^{L1_2} = 3u_{4Al,Ni}$$
$${}^{1}L_{Al,Ni:Ni}^{L1_2} = 3u_{4Al,Ni}$$
$${}^{1}L_{Al:Al,Ni}^{L1_2} = u_{4Al,Ni}$$
$${}^{1}L_{Ni:Al,Ni}^{L1_2} = u_{4Al,Ni}$$

となる。また４副格子モデルでは、分子１モル（化合物）は、

$$(A_{y_A^{(1)}}B_{y_B^{(1)}})(A_{y_A^{(2)}}B_{y_B^{(2)}})(A_{y_A^{(3)}}B_{y_B^{(3)}})(A_{y_A^{(4)}}B_{y_B^{(4)}})$$

と表現されるので、化学的自由エネルギーは、

$$G_m^{ord} = {}^{ref}G^{ord} + {}^{id}G^{ord} + {}^{ex}G^{ord}$$

$${}^{ref}G^{ord} = \sum_{i=A}^{B}\sum_{j=A}^{B}\sum_{k=A}^{B}\sum_{l=A}^{B} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} G_{i:j:k:l}^{ord}$$

$${}^{id}G^{ord} = RT\left[\frac{1}{4}\sum_{i=A}^{B} y_i^{(1)}\ln y_i^{(1)} + \frac{1}{4}\sum_{i=A}^{B} y_i^{(2)}\ln y_i^{(2)} + \frac{1}{4}\sum_{i=A}^{B} y_i^{(3)}\ln y_i^{(3)} + \frac{1}{4}\sum_{i=A}^{B} y_i^{(4)}\ln y_i^{(4)}\right]$$

$$\begin{aligned}
{}^{ex}G^{ord} = & \sum_{i=A}^{B}\sum_{j>i} y_i^{(1)} y_j^{(1)}\left(\sum_{k,l,m} y_k^{(2)} y_l^{(3)} y_m^{(4)} L_{i,j:k:l:m}^{ord}\right) + \sum_{i=A}^{B}\sum_{j>i} y_i^{(2)} y_j^{(2)}\left(\sum_{k,l,m} y_k^{(1)} y_l^{(3)} y_m^{(4)} L_{k:i,j:l:m}^{ord}\right) \\
& + \sum_{i=A}^{B}\sum_{j>i} y_i^{(3)} y_j^{(3)}\left(\sum_{k,l,m} y_k^{(1)} y_l^{(2)} y_m^{(4)} L_{k:l:i,j:m}^{ord}\right) + \sum_{i=A}^{B}\sum_{j>i} y_i^{(4)} y_j^{(4)}\left(\sum_{k,l,m} y_k^{(1)} y_l^{(2)} y_m^{(3)} L_{k:l:m:i,j}^{ord}\right) \\
& + \sum_{i=A}^{B}\sum_{j>i}\sum_{k=A}^{B}\sum_{l>k} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)}\left(\sum_{p,q} y_p^{(3)} y_q^{(4)} L_{i,j:k,l:p:q}^{ord}\right) + \cdots \\
& + \sum_{i=A}^{B}\sum_{j>i}\sum_{k=A}^{B}\sum_{l>k}\sum_{p=A}^{B}\sum_{q>p} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} y_p^{(3)} y_q^{(3)}\left(\sum_{r} y_r^{(4)} L_{i,j:k,l:p,q:r}^{ord}\right) + \cdots \\
& + \sum_{i=A}^{B}\sum_{j>i}\sum_{k=A}^{B}\sum_{l>k}\sum_{p=A}^{B}\sum_{q>p}\sum_{r=A}^{B}\sum_{s>r} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} y_p^{(3)} y_q^{(3)} y_r^{(4)} y_s^{(4)} L_{i,j:k,l:p,q:r,s}^{ord}
\end{aligned}$$

と表される。

なお、規則相の化学的自由エネルギーは、不規則相の化学的自由エネルギーに規則化の過剰エネルギーを加算する形式

$$G_m = G_m^{dis}(x_i) + G_m^{ord}(y_i^{(1)}, y_i^{(2)}) - G_m^{ord}(x_i)$$

と定義される。

３．平衡規則度について

平衡規則度は、平衡副格子濃度によって一義的に定義することができる。平衡副格子濃度は、平均組成を固定した条件下にて、副格子濃度に対する化学的自由エネルギーの極値を求めることによって決定される。以下、具体的にγ'相について説明する。関係式は、

$$dG_m^{L1_2} = \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}}\right) dy_{Al}^{(1)} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}}\right) dy_{Ni}^{(1)} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}}\right) dy_{Al}^{(2)} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}}\right) dy_{Ni}^{(2)}$$

$$\begin{aligned}
G_m^{ord} &= y_{Al}^{(1)} y_{Al}^{(2)} G_{Al:Al}^{L1_2} + y_{Al}^{(1)} y_{Ni}^{(2)} G_{Al:Ni}^{L1_2} + y_{Ni}^{(1)} y_{Al}^{(2)} G_{Ni:Al}^{L1_2} + y_{Ni}^{(1)} y_{Ni}^{(2)} G_{Ni:Ni}^{L1_2} \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} \left(y_{Al}^{(2)} L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)} L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)} \left(y_{Al}^{(1)} L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)} L_{Ni:Al,Ni}^{L1_2} \right) \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} y_{Al}^{(2)} y_{Ni}^{(2)} L_{Al,Ni:Al,Ni}^{L1_2} + RT\left[\frac{3}{4}(y_{Al}^{(1)} \ln y_{Al}^{(1)} + y_{Ni}^{(1)} \ln y_{Ni}^{(1)}) + \frac{1}{4}(y_{Al}^{(2)} \ln y_{Al}^{(2)} + y_{Ni}^{(2)} \ln y_{Ni}^{(2)}) \right] \\
&= y_{Al}^{(1)} y_{Al}^{(2)} G_{Al:Al}^{L1_2} + y_{Al}^{(1)} y_{Ni}^{(2)} G_{Al:Ni}^{L1_2} + y_{Ni}^{(1)} y_{Al}^{(2)} G_{Ni:Al}^{L1_2} + y_{Ni}^{(1)} y_{Ni}^{(2)} G_{Ni:Ni}^{L1_2} \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} \left(y_{Al}^{(2)}\,{}^0L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)} \left(y_{Al}^{(1)}\,{}^0L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)}\,{}^0L_{Ni:Al,Ni}^{L1_2} \right) \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} y_{Al}^{(2)} y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2} \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} (y_{Al}^{(1)} - y_{Ni}^{(1)}) \left(y_{Al}^{(2)}\,{}^1L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)}\,{}^1L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)} (y_{Al}^{(2)} - y_{Ni}^{(2)}) \left(y_{Al}^{(1)}\,{}^1L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)}\,{}^1L_{Ni:Al,Ni}^{L1_2} \right) \\
&\quad + RT\left[\frac{3}{4}(y_{Al}^{(1)} \ln y_{Al}^{(1)} + y_{Ni}^{(1)} \ln y_{Ni}^{(1)}) + \frac{1}{4}(y_{Al}^{(2)} \ln y_{Al}^{(2)} + y_{Ni}^{(2)} \ln y_{Ni}^{(2)}) \right]
\end{aligned}$$

$$\begin{aligned}
\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}} &= y_{Al}^{(2)} G_{Al:Al}^{L1_2} + y_{Ni}^{(2)} G_{Al:Ni}^{L1_2} + \frac{3}{4} RT(\ln y_{Al}^{(1)} + 1) \\
&\quad + y_{Ni}^{(1)} \left(y_{Al}^{(2)}\,{}^0L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)}\,{}^0L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)} y_{Al}^{(2)} y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2} \\
&\quad + y_{Ni}^{(1)} (2y_{Al}^{(1)} - y_{Ni}^{(1)}) \left(y_{Al}^{(2)}\,{}^1L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)}\,{}^1L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)} (y_{Al}^{(2)} - y_{Ni}^{(2)})\,{}^1L_{Al:Al,Ni}^{L1_2}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}} &= y_{Al}^{(2)} G_{Ni:Al}^{L1_2} + y_{Ni}^{(2)} G_{Ni:Ni}^{L1_2} + \frac{3}{4} RT(\ln y_{Ni}^{(1)} + 1) \\
&\quad + y_{Al}^{(1)} \left(y_{Al}^{(2)}\,{}^0L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)}\,{}^0L_{Ni:Al,Ni}^{L1_2} + y_{Al}^{(1)} y_{Al}^{(2)} y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2} \\
&\quad + y_{Al}^{(1)} (y_{Al}^{(1)} - 2y_{Ni}^{(1)}) \left(y_{Al}^{(2)}\,{}^1L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)}\,{}^1L_{Al,Ni:Ni}^{L1_2} \right) + y_{Al}^{(2)} y_{Ni}^{(2)} (y_{Al}^{(2)} - y_{Ni}^{(2)})\,{}^1L_{Ni:Al,Ni}^{L1_2}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}} &= y_{Al}^{(1)} G_{Al:Al}^{L1_2} + y_{Ni}^{(1)} G_{Ni:Al}^{L1_2} + \frac{1}{4} RT(\ln y_{Al}^{(2)} + 1) \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)}\,{}^0L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)} \left(y_{Al}^{(1)}\,{}^0L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)}\,{}^0L_{Ni:Al,Ni}^{L1_2} \right) + y_{Al}^{(1)} y_{Ni}^{(1)} y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2} \\
&\quad + y_{Al}^{(1)} y_{Ni}^{(1)} (y_{Al}^{(1)} - y_{Ni}^{(1)})\,{}^1L_{Al,Ni:Al}^{L1_2} + y_{Ni}^{(2)} (2y_{Al}^{(2)} - y_{Ni}^{(2)}) \left(y_{Al}^{(1)}\,{}^1L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)}\,{}^1L_{Ni:Al,Ni}^{L1_2} \right)
\end{aligned}$$

$$\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}} = y_{Al}^{(1)} G_{Al:Ni}^{L1_2} + y_{Ni}^{(1)} G_{Ni:Ni}^{L1_2} + \frac{1}{4} RT(\ln y_{Ni}^{(2)} + 1)$$
$$+ y_{Al}^{(1)} y_{Ni}^{(1)}\, {}^0L_{Al,Ni:Ni}^{L1_2} + y_{Al}^{(2)} \left(y_{Al}^{(1)}\, {}^0L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)}\, {}^0L_{Ni:Al,Ni}^{L1_2} \right) + y_{Al}^{(1)} y_{Ni}^{(1)} y_{Al}^{(2)}\, {}^0L_{Al,Ni:Al,Ni}^{L1_2}$$
$$+ y_{Al}^{(1)} y_{Ni}^{(1)} (y_{Al}^{(1)} - y_{Ni}^{(1)})\, {}^1L_{Al,Ni:Ni}^{L1_2} + y_{Al}^{(2)} (y_{Al}^{(2)} - 2y_{Ni}^{(2)}) \left(y_{Al}^{(1)}\, {}^1L_{Al:Al,Ni}^{L1_2} + y_{Ni}^{(1)}\, {}^1L_{Ni:Al,Ni}^{L1_2} \right)$$

$$1 = y_{Al}^{(1)} + y_{Ni}^{(1)}, \qquad 0 = dy_{Al}^{(1)} + dy_{Ni}^{(1)}, \qquad \therefore dy_{Al}^{(1)} = -dy_{Ni}^{(1)}$$
$$1 = y_{Al}^{(2)} + y_{Ni}^{(2)}, \qquad 0 = dy_{Al}^{(2)} + dy_{Ni}^{(2)}, \qquad \therefore dy_{Al}^{(2)} = -dy_{Ni}^{(2)}$$
$$x_{Al} = \frac{3}{4} y_{Al}^{(1)} + \frac{1}{4} y_{Al}^{(2)}, \quad 0 = \frac{3}{4} dy_{Al}^{(1)} + \frac{1}{4} dy_{Al}^{(2)}, \quad \therefore dy_{Al}^{(2)} = -3dy_{Al}^{(1)}$$
$$x_{Ni} = \frac{3}{4} y_{Ni}^{(1)} + \frac{1}{4} y_{Ni}^{(2)}, \quad 0 = \frac{3}{4} dy_{Ni}^{(1)} + \frac{1}{4} dy_{Ni}^{(2)}, \quad \therefore dy_{Ni}^{(2)} = -3dy_{Ni}^{(1)}$$

となり、ここで、独立変数を $y_{Al}^{(2)}$ としよう。合金組成を固定した場合、

$$y_{Ni}^{(2)} = 1 - y_{Al}^{(2)}$$
$$y_{Al}^{(1)} = \frac{4}{3} x_{Al} - \frac{1}{3} y_{Al}^{(2)}$$
$$y_{Ni}^{(1)} = 1 - y_{Al}^{(1)} = 1 - \frac{4}{3} x_{Al} + \frac{1}{3} y_{Al}^{(2)}$$

であるので、 $y_{Al}^{(2)}$ が決まれば全ての量が決定できる。 $y_{Al}^{(2)}$ の平衡値は、

$$dG_m^{L1_2} = \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}} \right) dy_{Al}^{(1)} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}} \right) dy_{Ni}^{(1)} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}} \right) dy_{Al}^{(2)} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}} \right) dy_{Ni}^{(2)}$$
$$\frac{dG_m^{L1_2}}{dy_{Al}^{(2)}} = \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}} \right) \frac{dy_{Al}^{(1)}}{dy_{Al}^{(2)}} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}} \right) \frac{dy_{Ni}^{(1)}}{dy_{Al}^{(2)}} + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}} \right) + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}} \right) \frac{dy_{Ni}^{(2)}}{dy_{Al}^{(2)}}$$
$$= -\frac{1}{3} \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}} \right) + \frac{1}{3} \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}} \right) + \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}} \right) - \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}} \right) = 0$$
$$\therefore\ 3 \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}} \right) - 3 \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}} \right) = \left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}} \right) - \left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}} \right)$$

によって決定される。これに先の関係式を代入し整理しよう。

$$
\begin{aligned}
&3\left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(2)}}\right)-3\left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(2)}}\right)=\left(\frac{\partial G_m^{L1_2}}{\partial y_{Al}^{(1)}}\right)-\left(\frac{\partial G_m^{L1_2}}{\partial y_{Ni}^{(1)}}\right)\\
&3\left\{\begin{array}{l}
y_{Al}^{(1)}G_{Al:Al}^{L1_2}+y_{Ni}^{(1)}G_{Ni:Al}^{L1_2}+\frac{1}{4}RT(\ln y_{Al}^{(2)}+1)\\
+y_{Al}^{(1)}y_{Ni}^{(1)}\,{}^0L_{Al,Ni:Al}^{L1_2}+y_{Ni}^{(2)}\left(y_{Al}^{(1)}\,{}^0L_{Al:Al,Ni}^{L1_2}+y_{Ni}^{(1)}\,{}^0L_{Ni:Al,Ni}^{L1_2}\right)+y_{Al}^{(1)}y_{Ni}^{(1)}y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2}\\
+y_{Al}^{(1)}y_{Ni}^{(1)}(y_{Al}^{(1)}-y_{Ni}^{(1)})\,{}^1L_{Al,Ni:Al}^{L1_2}+y_{Ni}^{(2)}(2y_{Al}^{(2)}-y_{Ni}^{(2)})\left(y_{Al}^{(1)}\,{}^1L_{Al:Al,Ni}^{L1_2}+y_{Ni}^{(1)}\,{}^1L_{Ni:Al,Ni}^{L1_2}\right)
\end{array}\right\}\\
&-3\left\{\begin{array}{l}
y_{Al}^{(1)}G_{Al:Ni}^{L1_2}+y_{Ni}^{(1)}G_{Ni:Ni}^{L1_2}+\frac{1}{4}RT(\ln y_{Ni}^{(2)}+1)\\
+y_{Al}^{(1)}y_{Ni}^{(1)}\,{}^0L_{Al,Ni:Ni}^{L1_2}+y_{Al}^{(2)}\left(y_{Al}^{(1)}\,{}^0L_{Al:Al,Ni}^{L1_2}+y_{Ni}^{(1)}\,{}^0L_{Ni:Al,Ni}^{L1_2}\right)+y_{Al}^{(1)}y_{Ni}^{(1)}y_{Al}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2}\\
+y_{Al}^{(1)}y_{Ni}^{(1)}(y_{Al}^{(1)}-y_{Ni}^{(1)})\,{}^1L_{Al,Ni:Ni}^{L1_2}+y_{Al}^{(2)}(y_{Al}^{(2)}-2y_{Ni}^{(2)})\left(y_{Al}^{(1)}\,{}^1L_{Al:Al,Ni}^{L1_2}+y_{Ni}^{(1)}\,{}^1L_{Ni:Al,Ni}^{L1_2}\right)
\end{array}\right\}\\
&=\left\{\begin{array}{l}
y_{Al}^{(2)}G_{Al:Al}^{L1_2}+y_{Ni}^{(2)}G_{Al:Ni}^{L1_2}+\frac{3}{4}RT(\ln y_{Al}^{(1)}+1)\\
+y_{Ni}^{(1)}\left(y_{Al}^{(2)}\,{}^0L_{Al,Ni:Al}^{L1_2}+y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Ni}^{L1_2}\right)+y_{Al}^{(2)}y_{Ni}^{(2)}\,{}^0L_{Al:Al,Ni}^{L1_2}+y_{Ni}^{(1)}y_{Al}^{(2)}y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2}\\
+y_{Ni}^{(1)}(2y_{Al}^{(1)}-y_{Ni}^{(1)})\left(y_{Al}^{(2)}\,{}^1L_{Al,Ni:Al}^{L1_2}+y_{Ni}^{(2)}\,{}^1L_{Al,Ni:Ni}^{L1_2}\right)+y_{Al}^{(2)}y_{Ni}^{(2)}(y_{Al}^{(2)}-y_{Ni}^{(2)})\,{}^1L_{Al:Al,Ni}^{L1_2}
\end{array}\right\}\\
&-\left\{\begin{array}{l}
y_{Al}^{(2)}G_{Ni:Al}^{L1_2}+y_{Ni}^{(2)}G_{Ni:Ni}^{L1_2}+\frac{3}{4}RT(\ln y_{Ni}^{(1)}+1)\\
+y_{Al}^{(1)}\left(y_{Al}^{(2)}\,{}^0L_{Al,Ni:Al}^{L1_2}+y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Ni}^{L1_2}\right)+y_{Al}^{(2)}y_{Ni}^{(2)}\,{}^0L_{Ni:Al,Ni}^{L1_2}+y_{Al}^{(1)}y_{Al}^{(2)}y_{Ni}^{(2)}\,{}^0L_{Al,Ni:Al,Ni}^{L1_2}\\
+y_{Al}^{(1)}(y_{Al}^{(1)}-2y_{Ni}^{(1)})\left(y_{Al}^{(2)}\,{}^1L_{Al,Ni:Al}^{L1_2}+y_{Ni}^{(2)}\,{}^1L_{Al,Ni:Ni}^{L1_2}\right)+y_{Al}^{(2)}y_{Ni}^{(2)}(y_{Al}^{(2)}-y_{Ni}^{(2)})\,{}^1L_{Ni:Al,Ni}^{L1_2}
\end{array}\right\}
\end{aligned}
$$

となる。平衡規則度は、この式を解くことによって計算できる。実際の計算には、直接探索法やニュートン法が用いられる。

ところで、上式の係数の間には関係式が存在する。通常、規則-不規則変態は２次転移と扱えるので、不規則状態は常に、自由エネルギー曲線の極値を与える。なぜならば、不規則相が安定な場合には、当然、その状態が極小位置に対応し、一方、規則相が安定な場合には、不規則状態は極大位置に対応することになる。いずれにしても極値であるので、不規則状態を仮定すれば、上式は常に成立することになる。したがって、$y_i^{(j)}=x_i$ と置き直すと、

$$
\begin{aligned}
&3\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Al:Al} + x_{Ni}G^{L1_2}_{Ni:Al} + \frac{1}{4}RT(\ln x_{Al} + 1) \\
+x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\left(x_{Al}\,{}^{0}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{0}L^{L1_2}_{Ni:Al,Ni}\right) + x_{Al}x_{Ni}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Al,Ni:Al} + x_{Ni}(2x_{Al} - x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{1}L^{L1_2}_{Ni:Al,Ni}\right)
\end{array}\right\} \\
&-3\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Al:Ni} + x_{Ni}G^{L1_2}_{Ni:Ni} + \frac{1}{4}RT(\ln x_{Ni} + 1) \\
+x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Ni} + x_{Al}\left(x_{Al}\,{}^{0}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{0}L^{L1_2}_{Ni:Al,Ni}\right) + x_{Al}x_{Ni}x_{Al}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Al,Ni:Ni} + x_{Al}(x_{Al} - 2x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{1}L^{L1_2}_{Ni:Al,Ni}\right)
\end{array}\right\} \\
&=\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Al:Al} + x_{Ni}G^{L1_2}_{Al:Ni} + \frac{3}{4}RT(\ln x_{Al} + 1) \\
+x_{Ni}\left(x_{Al}\,{}^{0}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al:Al,Ni} + x_{Ni}x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Ni}(2x_{Al} - x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{1}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Al:Al,Ni}
\end{array}\right\} \\
&-\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Ni:Al} + x_{Ni}G^{L1_2}_{Ni:Ni} + \frac{3}{4}RT(\ln x_{Ni} + 1) \\
+x_{Al}\left(x_{Al}\,{}^{0}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Ni:Al,Ni} + x_{Al}x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Al}(x_{Al} - 2x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{1}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Ni:Al,Ni}
\end{array}\right\}
\end{aligned}
$$

を得る。これを整理して、

$$
\begin{aligned}
&3\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Al:Al} + x_{Ni}G^{L1_2}_{Ni:Al} \\
+x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al} + x_{Ni}(x_{Al}\,{}^{0}L^{L1_2}_{Al:Al,Ni} + {}^{0}L^{L1_2}_{Ni:Al,Ni} - x_{Al}\,{}^{0}L^{L1_2}_{Ni:Al,Ni}) + x_{Al}x_{Ni}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Al,Ni:Al} + x_{Ni}(2x_{Al} - x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{1}L^{L1_2}_{Ni:Al,Ni}\right)
\end{array}\right\} \\
&-3\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Al:Ni} + x_{Ni}G^{L1_2}_{Ni:Ni} \\
+x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Ni} + x_{Al}\left({}^{0}L^{L1_2}_{Al:Al,Ni} - x_{Ni}\,{}^{0}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{0}L^{L1_2}_{Ni:Al,Ni}\right) + x_{Al}x_{Ni}x_{Al}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Al,Ni:Ni} + x_{Al}(x_{Al} - 2x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al:Al,Ni} + x_{Ni}\,{}^{1}L^{L1_2}_{Ni:Al,Ni}\right)
\end{array}\right\} \\
&=\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Al:Al} + x_{Ni}G^{L1_2}_{Al:Ni} \\
+x_{Ni}\left(x_{Al}\,{}^{0}L^{L1_2}_{Al,Ni:Al} + {}^{0}L^{L1_2}_{Al,Ni:Ni} - x_{Al}\,{}^{0}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al:Al,Ni} + x_{Ni}x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Ni}(2x_{Al} - x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{1}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Al:Al,Ni}
\end{array}\right\} \\
&-\left\{\begin{array}{l}
x_{Al}G^{L1_2}_{Ni:Al} + x_{Ni}G^{L1_2}_{Ni:Ni} \\
+x_{Al}\left({}^{0}L^{L1_2}_{Al,Ni:Al} - x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Ni:Al,Ni} + x_{Al}x_{Al}x_{Ni}\,{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} \\
+x_{Al}(x_{Al} - 2x_{Ni})\left(x_{Al}\,{}^{1}L^{L1_2}_{Al,Ni:Al} + x_{Ni}\,{}^{1}L^{L1_2}_{Al,Ni:Ni}\right) + x_{Al}x_{Ni}(x_{Al} - x_{Ni})\,{}^{1}L^{L1_2}_{Ni:Al,Ni}
\end{array}\right\}
\end{aligned}
$$

$$
3\left\{\begin{array}{l}
x_{Al}(G^{L1_2}_{Al:Al}-G^{L1_2}_{Al:Ni}-{}^0L^{L1_2}_{Al:Al,Ni})+x_{Ni}(G^{L1_2}_{Ni:Al}+{}^0L^{L1_2}_{Ni:Al,Ni}-G^{L1_2}_{Ni:Ni})\\
+x_{Al}x_{Ni}({}^0L^{L1_2}_{Al,Ni:Al}+{}^0L^{L1_2}_{Al:Al,Ni}-{}^0L^{L1_2}_{Ni:Al,Ni}-{}^0L^{L1_2}_{Al,Ni:Ni}+{}^0L^{L1_2}_{Al:Al,Ni}-{}^0L^{L1_2}_{Ni:Al,Ni})\\
+x_{Al}x_{Ni}(x_{Ni}-x_{Al}){}^0L^{L1_2}_{Al,Ni:Al,Ni}\\
+x_{Al}x_{Ni}(x_{Al}-x_{Ni})({}^1L^{L1_2}_{Al,Ni:Al}-{}^1L^{L1_2}_{Al,Ni:Ni})\\
+x_{Ni}(2x_{Al}-x_{Ni})\left(x_{Al}\,{}^1L^{L1_2}_{Al:Al,Ni}+x_{Ni}\,{}^1L^{L1_2}_{Ni:Al,Ni}\right)-x_{Al}(x_{Al}-2x_{Ni})\left(x_{Al}\,{}^1L^{L1_2}_{Al:Al,Ni}+x_{Ni}\,{}^1L^{L1_2}_{Ni:Al,Ni}\right)
\end{array}\right\}
$$

$$
=\left\{\begin{array}{l}
x_{Al}(G^{L1_2}_{Al:Al}-G^{L1_2}_{Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Al})+x_{Ni}(G^{L1_2}_{Al:Ni}+{}^0L^{L1_2}_{Al,Ni:Ni}-G^{L1_2}_{Ni:Ni})\\
+x_{Al}x_{Ni}({}^0L^{L1_2}_{Al,Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Ni}+{}^0L^{L1_2}_{Al:Al,Ni}+{}^0L^{L1_2}_{Al,Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Ni}-{}^0L^{L1_2}_{Ni:Al,Ni})\\
+x_{Al}x_{Ni}(x_{Ni}-x_{Al}){}^0L^{L1_2}_{Al,Ni:Al,Ni}\\
+x_{Ni}(2x_{Al}-x_{Ni})\left(x_{Al}\,{}^1L^{L1_2}_{Al,Ni:Al}+x_{Ni}\,{}^1L^{L1_2}_{Al,Ni:Ni}\right)-x_{Al}(x_{Al}-2x_{Ni})\left(x_{Al}\,{}^1L^{L1_2}_{Al,Ni:Al}+x_{Ni}\,{}^1L^{L1_2}_{Al,Ni:Ni}\right)\\
+x_{Al}x_{Ni}(x_{Al}-x_{Ni})({}^1L^{L1_2}_{Al:Al,Ni}-{}^1L^{L1_2}_{Ni:Al,Ni})
\end{array}\right\}
$$

$$
3\left\{\begin{array}{l}
x_{Al}(G^{L1_2}_{Al:Al}-G^{L1_2}_{Al:Ni}-{}^0L^{L1_2}_{Al:Al,Ni})+x_{Ni}(G^{L1_2}_{Ni:Al}+{}^0L^{L1_2}_{Ni:Al,Ni}-G^{L1_2}_{Ni:Ni})\\
+x_{Al}x_{Ni}({}^0L^{L1_2}_{Al,Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Ni}+2\,{}^0L^{L1_2}_{Al:Al,Ni}-2\,{}^0L^{L1_2}_{Ni:Al,Ni})+x_{Al}x_{Ni}(x_{Ni}-x_{Al}){}^0L^{L1_2}_{Al,Ni:Al,Ni}\\
+x_{Al}x_{Ni}(x_{Al}-x_{Ni})({}^1L^{L1_2}_{Al,Ni:Al}-{}^1L^{L1_2}_{Al,Ni:Ni})+(4x_{Al}x_{Ni}-x_{Ni}x_{Ni}-x_{Al}x_{Al})(x_{Al}\,{}^1L^{L1_2}_{Al:Al,Ni}+x_{Ni}\,{}^1L^{L1_2}_{Ni:Al,Ni})
\end{array}\right\}
$$

$$
=\left\{\begin{array}{l}
x_{Al}(G^{L1_2}_{Al:Al}-G^{L1_2}_{Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Al})+x_{Ni}(G^{L1_2}_{Al:Ni}+{}^0L^{L1_2}_{Al,Ni:Ni}-G^{L1_2}_{Ni:Ni})\\
+x_{Al}x_{Ni}({}^0L^{L1_2}_{Al:Al,Ni}-{}^0L^{L1_2}_{Ni:Al,Ni}+2\,{}^0L^{L1_2}_{Al,Ni:Al}-2\,{}^0L^{L1_2}_{Al,Ni:Ni})+x_{Al}x_{Ni}(x_{Ni}-x_{Al}){}^0L^{L1_2}_{Al,Ni:Al,Ni}\\
+(4x_{Al}x_{Ni}-x_{Ni}x_{Ni}-x_{Al}x_{Al})(x_{Al}\,{}^1L^{L1_2}_{Al,Ni:Al}+x_{Ni}\,{}^1L^{L1_2}_{Al,Ni:Ni})+x_{Al}x_{Ni}(x_{Al}-x_{Ni})({}^1L^{L1_2}_{Al:Al,Ni}-{}^1L^{L1_2}_{Ni:Al,Ni})
\end{array}\right\}
$$

$$
\begin{array}{l}
x_{Al}(3G^{L1_2}_{Al:Al}-3G^{L1_2}_{Al:Ni}-3\,{}^0L^{L1_2}_{Al:Al,Ni})+x_{Ni}(3G^{L1_2}_{Ni:Al}+3\,{}^0L^{L1_2}_{Ni:Al,Ni}-3G^{L1_2}_{Ni:Ni})\\
-x_{Al}(G^{L1_2}_{Al:Al}-G^{L1_2}_{Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Al})-x_{Ni}(G^{L1_2}_{Al:Ni}+{}^0L^{L1_2}_{Al,Ni:Ni}-G^{L1_2}_{Ni:Ni})\\
+x_{Al}x_{Ni}(3\,{}^0L^{L1_2}_{Al,Ni:Al}-3\,{}^0L^{L1_2}_{Al,Ni:Ni}+6\,{}^0L^{L1_2}_{Al:Al,Ni}-6\,{}^0L^{L1_2}_{Ni:Al,Ni})+3x_{Al}x_{Ni}(x_{Ni}-x_{Al}){}^0L^{L1_2}_{Al,Ni:Al,Ni}\\
-x_{Al}x_{Ni}({}^0L^{L1_2}_{Al:Al,Ni}-{}^0L^{L1_2}_{Ni:Al,Ni}+2\,{}^0L^{L1_2}_{Al,Ni:Al}-2\,{}^0L^{L1_2}_{Al,Ni:Ni})-x_{Al}x_{Ni}(x_{Ni}-x_{Al}){}^0L^{L1_2}_{Al,Ni:Al,Ni}\\
+x_{Al}x_{Ni}(x_{Al}-x_{Ni})(3\,{}^1L^{L1_2}_{Al,Ni:Al}-3\,{}^1L^{L1_2}_{Al,Ni:Ni})+(4x_{Al}x_{Ni}-x_{Ni}x_{Ni}-x_{Al}x_{Al})(3x_{Al}\,{}^1L^{L1_2}_{Al:Al,Ni}+3x_{Ni}\,{}^1L^{L1_2}_{Ni:Al,Ni})\\
-(4x_{Al}x_{Ni}-x_{Ni}x_{Ni}-x_{Al}x_{Al})(x_{Al}\,{}^1L^{L1_2}_{Al,Ni:Al}+x_{Ni}\,{}^1L^{L1_2}_{Al,Ni:Ni})-x_{Al}x_{Ni}(x_{Al}-x_{Ni})({}^1L^{L1_2}_{Al:Al,Ni}-{}^1L^{L1_2}_{Ni:Al,Ni})=0
\end{array}
$$

$$
\begin{array}{l}
x_{Al}(-3G^{L1_2}_{Al:Ni}+G^{L1_2}_{Ni:Al}+2G^{L1_2}_{Al:Al}-3\,{}^0L^{L1_2}_{Al:Al,Ni}+{}^0L^{L1_2}_{Al,Ni:Al})+x_{Ni}(3G^{L1_2}_{Ni:Al}-G^{L1_2}_{Al:Ni}-2G^{L1_2}_{Ni:Ni}+3\,{}^0L^{L1_2}_{Ni:Al,Ni}-{}^0L^{L1_2}_{Al,Ni:Ni})\\
+x_{Al}x_{Ni}({}^0L^{L1_2}_{Al,Ni:Al}-{}^0L^{L1_2}_{Al,Ni:Ni}+5\,{}^0L^{L1_2}_{Al:Al,Ni}-5\,{}^0L^{L1_2}_{Ni:Al,Ni})\\
+x_{Al}x_{Ni}(x_{Al}-x_{Ni})(3\,{}^1L^{L1_2}_{Al,Ni:Al}-{}^1L^{L1_2}_{Al:Al,Ni}-3\,{}^1L^{L1_2}_{Al,Ni:Ni}+{}^1L^{L1_2}_{Ni:Al,Ni}-2\,{}^0L^{L1_2}_{Al,Ni:Al,Ni})\\
+(4x_{Al}x_{Ni}-x_{Al}^2-x_{Ni}^2)\{x_{Al}(3\,{}^1L^{L1_2}_{Al:Al,Ni}-{}^1L^{L1_2}_{Al,Ni:Al})+x_{Ni}(3\,{}^1L^{L1_2}_{Ni:Al,Ni}-{}^1L^{L1_2}_{Al,Ni:Ni})\}=0
\end{array}
$$

となり、これは恒等式であるので、

$$3G^{L1_2}_{Al:Ni} - G^{L1_2}_{Ni:Al} - 2G^{L1_2}_{Al:Al} + 3\,{}^0L^{L1_2}_{Al:Al,Ni} - {}^0L^{L1_2}_{Al,Ni:Al} = 0$$
$$3G^{L1_2}_{Ni:Al} - G^{L1_2}_{Al:Ni} - 2G^{L1_2}_{Ni:Ni} + 3\,{}^0L^{L1_2}_{Ni:Al,Ni} - {}^0L^{L1_2}_{Al,Ni:Ni} = 0$$
$${}^0L^{L1_2}_{Al,Ni:Al} - {}^0L^{L1_2}_{Al,Ni:Ni} + 5\,{}^0L^{L1_2}_{Al:Al,Ni} - 5\,{}^0L^{L1_2}_{Ni:Al,Ni} = 0$$
$$3\,{}^1L^{L1_2}_{Al,Ni:Al} - {}^1L^{L1_2}_{Al:Al,Ni} - 3\,{}^1L^{L1_2}_{Al,Ni:Ni} + {}^1L^{L1_2}_{Ni:Al,Ni} - 2\,{}^0L^{L1_2}_{Al,Ni:Al,Ni} = 0$$
$$3\,{}^1L^{L1_2}_{Al:Al,Ni} - {}^1L^{L1_2}_{Al,Ni:Al} = 0$$
$$3\,{}^1L^{L1_2}_{Ni:Al,Ni} - {}^1L^{L1_2}_{Al,Ni:Ni} = 0$$

を得る。ここで、

$$G^{L1_2}_{Al:Al} = G^{L1_2}_{Ni:Ni} = 0$$
$$G^{L1_2}_{Al:Ni} = u_1$$
$$G^{L1_2}_{Ni:Al} = u_2$$
$${}^0L^{L1_2}_{Al:Al,Ni} = u_3 + \frac{u_2}{2}$$
$${}^1L^{L1_2}_{Al:Al,Ni} = u_4$$
$${}^1L^{L1_2}_{Ni:Al,Ni} = u_5$$

と置くと、

$$3u_1 - u_2 + 3\left(u_3 + \frac{u_2}{2}\right) - {}^0L^{L1_2}_{Al,Ni:Al} = 0$$
$$-3u_2 + u_1 - 3\,{}^0L^{L1_2}_{Ni:Al,Ni} + {}^0L^{L1_2}_{Al,Ni:Ni} = 0$$
$${}^0L^{L1_2}_{Al,Ni:Al} - {}^0L^{L1_2}_{Al,Ni:Ni} + 5\left(u_3 + \frac{u_2}{2}\right) - 5\,{}^0L^{L1_2}_{Ni:Al,Ni} = 0$$
$$3\,{}^1L^{L1_2}_{Al,Ni:Al} - {}^1L^{L1_2}_{Al:Al,Ni} - 3\,{}^1L^{L1_2}_{Al,Ni:Ni} + {}^1L^{L1_2}_{Ni:Al,Ni} - 2\,{}^0L^{L1_2}_{Al,Ni:Al,Ni} = 0$$
$$3\,{}^1u_4 - {}^1L^{L1_2}_{Al,Ni:Al} = 0$$
$$3\,{}^1u_5 - {}^1L^{L1_2}_{Al,Ni:Ni} = 0$$

となり、始めの３式を足し合わせると、

$$4u_1 - 4u_2 + 8\left(u_3 + \frac{u_2}{2}\right) - 8\,{}^0L^{L1_2}_{Ni:Al,Ni} = 0$$
$$\therefore\ {}^0L^{L1_2}_{Ni:Al,Ni} = u_3 + \frac{u_1}{2}$$
$${}^0L^{L1_2}_{Al,Ni:Al} = 3u_1 - u_2 + 3\left(u_3 + \frac{u_2}{2}\right) = 3u_1 + \frac{u_2}{2} + 3u_3$$
$${}^0L^{L1_2}_{Al,Ni:Ni} = 3u_2 - u_1 + 3\,{}^0L^{L1_2}_{Ni:Al,Ni} = 3u_2 - u_1 + 3\left(u_3 + \frac{u_1}{2}\right) = 3u_2 + \frac{u_1}{2} + 3u_3$$

を得る。また後半の２式から

$$
\begin{aligned}
{}^{1}L^{L1_2}_{Al,Ni:Al} &= 3\,{}^{1}u_4 \\
{}^{1}L^{L1_2}_{Al,Ni:Ni} &= 3\,{}^{1}u_5
\end{aligned}
$$

である。さらに、４番目の式から

$$
\begin{aligned}
{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} &= \frac{1}{2}(3\,{}^{1}L^{L1_2}_{Al,Ni:Al} - {}^{1}L^{L1_2}_{Al:Al,Ni} - 3\,{}^{1}L^{L1_2}_{Al,Ni:Ni} + {}^{1}L^{L1_2}_{Ni:Al,Ni}) \\
&= \frac{1}{2}(9u_4 - u_4 - 9u_5 + u_5) = 4(u_4 - u_5)
\end{aligned}
$$

を得る。以上をまとめて、

$$
\begin{aligned}
G^{L1_2}_{Al:Al} &= G^{L1_2}_{Ni:Ni} = 0 \\
G^{L1_2}_{Al:Ni} &= u_1 \\
G^{L1_2}_{Ni:Al} &= u_2 \\
{}^{0}L^{L1_2}_{Al,Ni:Al} &= 3u_1 + \frac{u_2}{2} + 3u_3 \\
{}^{0}L^{L1_2}_{Al,Ni:Ni} &= 3u_2 + \frac{u_1}{2} + 3u_3 \\
{}^{0}L^{L1_2}_{Al:Al,Ni} &= u_3 + \frac{u_2}{2} \\
{}^{0}L^{L1_2}_{Ni:Al,Ni} &= u_3 + \frac{u_1}{2} \\
{}^{1}L^{L1_2}_{Al:Al,Ni} &= u_4 \\
{}^{1}L^{L1_2}_{Ni:Al,Ni} &= u_5 \\
{}^{0}L^{L1_2}_{Al,Ni:Al,Ni} &= 4(u_4 - u_5)
\end{aligned}
$$

となる。さらに、$G^{L1_2}_{Al:Ni} = G^{L1_2}_{Ni:Al} = u_1 = u_2$ を仮定すると、

$$
{}^{0}L^{L1_2}_{Al,Ni:Al} = {}^{0}L^{L1_2}_{Al,Ni:Ni}, \quad {}^{0}L^{L1_2}_{Al:Al,Ni} = {}^{0}L^{L1_2}_{Ni:Al,Ni}
$$

より、

$$G_{Al:Al}^{L1_2} = G_{Ni:Ni}^{L1_2} = 0$$
$$G_{Al:Ni}^{L1_2} = u_1$$
$$G_{Ni:Al}^{L1_2} = u_1$$
$$^0L_{Al,Ni:Al}^{L1_2} = 3u_1 + \frac{u_1}{2} + 3u_3 = 2u_1 + 3\left(u_3 + \frac{u_1}{2}\right) = 2u_1 + 3w_3$$
$$^0L_{Al,Ni:Ni}^{L1_2} = 3u_1 + \frac{u_1}{2} + 3u_3 = u_1 + 3\left(u_3 + \frac{u_1}{2}\right) = 2u_1 + 3w_3$$
$$^0L_{Al:Al,Ni}^{L1_2} = u_3 + \frac{u_1}{2} = w_3$$
$$^0L_{Ni:Al,Ni}^{L1_2} = u_3 + \frac{u_1}{2} = w_3$$
$$^1L_{Al:Al,Ni}^{L1_2} = u_4$$
$$^1L_{Ni:Al,Ni}^{L1_2} = u_5$$
$$^0L_{Al,Ni:Al,Ni}^{L1_2} = 4(u_4 - u_5)$$

となることがわかる。以上のように、各係数間には関係が存在し、任意に設定することはできない点に注意しなくてはならない。逆に、この関係を理解すれば、少ないフィッティングパラメータにて自由エネルギーを正確に導くことが出来る。