Sub-lattice モデルに基づく
Ni-Al 合金の化学的自由エネルギー -
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 - 式は以下のように定式化される。

\[ G_m^\beta = \sum_{i=1}^{B} x_i^\beta \cdot H_i^\text{SER} \ (298.15K) = \ref G^\beta + \id G^\beta + \ex G^\beta \]

\[ \ref G^\beta = \sum_{i=1}^{B} x_i^\beta \cdot \{ G_i^\beta - \bar{H}_i^\text{SER} \ (298.15K) \} \]

\[ \id G^\beta = RT \sum_{i=1}^{B} x_i^\beta \ln x_i^\beta \]

\[ \ex G^\beta = x_A^\beta x_B^\beta I_{A,B}^\beta \]

\[ L_{A,B}^\beta = \sum_{\nu=0}^{B} \nu L_{A,B}^\beta (x_A^\beta - x_B^\beta) \nu \]

\[ \nu L_{A,B}^\beta = \nu A_{A,B}^\beta + \nu B_{A,B}^\beta T + \cdots \]

具体的に fcc-A1 の Ni-Al 2 元系について書き下して見ると、

\[ G_m^\beta = \sum_{i=1}^{B} x_i^\beta \cdot H_i^\text{SER} \ (298.15K) \]

\[ = \ref G^\beta + \id G^\beta + \ex G^\beta \]

\[ = \sum_{i=1}^{B} x_i^\beta \cdot \{ G_i^\beta - \bar{H}_i^\text{SER} \ (298.15K) \} + x_A^\beta x_B^\beta L_{A,B}^\beta + RT \sum_{i=1}^{B} x_i^\beta \ln x_i^\beta \]

\[ = x_{Al}^{A1} (G_{Ni}^{A1} - \bar{H}_{Ni}^\text{SER}) + x_{Al}^{A1} (G_{Al}^{A1} - \bar{H}_{Al}^\text{SER}) + x_{Al}^{A1} x_{Ni}^{Al} L_{Al,Ni}^{A1} + RT (x_{Al}^{A1} \ln x_{Al}^{A1} + x_{Ni}^{A1} \ln x_{Ni}^{A1}) \]

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

[fcc-A1]

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

\[ 1 L_{Al,Ni}^{fcc-A1} = 73417.798 - 34.914000T \]

\[ 2 L_{Al,Ni}^{fcc-A1} = 33471.014 - 9.837000T \]

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

となる。

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

\[ (A_{1/2}^{(1)} B_{1/2}^{(1)}) (A_{1/2}^{(2)} B_{1/2}^{(2)}) \]

と置く。この化学的自由エネルギー - 式は、

\[ G_m^\text{ord} = \ref G^\text{ord} + \id G^\text{ord} + \ex G^\text{ord} \]
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。

\[
G_{m}^{\text{ord}} = \text{ref } G^{\text{ord}} + \text{id } G^{\text{ord}} + \text{ex } G^{\text{ord}}
\]

\[ = \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(1)} y_j^{(2)} G_{E,ij}^{\text{ord}} + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(1)} y_j^{(1)} \left( \sum_k y_k^{(2)} L_{i,j,k}^{\text{ord}} \right) + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(2)} y_j^{(2)} \left( \sum_k y_k^{(1)} L_{i,j,k}^{\text{ord}} \right) + \sum_{i=A}^{B} \sum_{j=A}^{B} \sum_{k=A}^{B} \sum_{l=A}^{B} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} L_{i,j,k,l}^{\text{ord}} \]

\[ + \sum_{i=A}^{B} \sum_{j=A}^{B} \sum_{k=A}^{B} \sum_{l=A}^{B} y_i^{(1)} y_j^{(1)} y_k^{(2)} y_l^{(2)} L_{i,j,k,l}^{\text{ord}} + RT \left[ \frac{3}{4} \sum_{i=A}^{B} y_i^{(1)} \ln y_i^{(1)} + \frac{1}{4} \sum_{i=A}^{B} y_i^{(2)} \ln y_i^{(2)} \right] \]

\[ = y_{Al}^{(1)} y_{Al}^{(2)} G_{Al,Al}^{L_{12}} + y_{Al}^{(1)} y_{Ni}^{(2)} G_{Al,Ni}^{L_{12}} + y_{Ni}^{(1)} y_{Al}^{(2)} G_{Ni,Al}^{L_{12}} + y_{Ni}^{(1)} y_{Ni}^{(2)} G_{Ni,Ni}^{L_{12}} + y_{Al}^{(1)} y_{Al}^{(1)} L_{Al,Al,Al}^{L_{22}} + y_{Ni}^{(1)} y_{Ni}^{(1)} L_{Ni,Ni,Ni}^{L_{22}} + y_{Al}^{(1)} y_{Ni}^{(2)} L_{Al,Ni,Ni}^{L_{22}} + y_{Ni}^{(1)} y_{Al}^{(2)} L_{Ni,Al,Al}^{L_{22}} \]

\[ + \frac{3}{4} \left( y_{Al}^{(1)} \ln y_{Al}^{(1)} + y_{Ni}^{(1)} \ln y_{Ni}^{(1)} + \frac{1}{4} \left( y_{Al}^{(2)} \ln y_{Al}^{(2)} + y_{Ni}^{(2)} \ln y_{Ni}^{(2)} \right) \right] \]

\[ L_{Al,Al,Al}^{\text{ord}} = 0 L_{Al,Al,Al}^{\text{ord}} + 1 L_{Al,Al,Al}^{\text{ord}} \left( y_{Al}^{(1)} - y_{Ni}^{(1)} \right) \]

\[ L_{Al,Ni,Ni}^{\text{ord}} = 0 L_{Al,Ni,Ni}^{\text{ord}} + 1 L_{Al,Ni,Ni}^{\text{ord}} \left( y_{Al}^{(1)} - y_{Ni}^{(1)} \right) \]

\[ L_{Al,Al,Ni}^{\text{ord}} = 0 L_{Al,Al,Ni}^{\text{ord}} + 1 L_{Al,Al,Ni}^{\text{ord}} \left( y_{Al}^{(2)} - y_{Ni}^{(2)} \right) \]

\[ L_{Ni,Al,Ni}^{\text{ord}} = 0 L_{Ni,Al,Ni}^{\text{ord}} + 1 L_{Ni,Al,Ni}^{\text{ord}} \left( y_{Al}^{(2)} - y_{Ni}^{(2)} \right) \]

\[ L_{Al,Ni,Al}^{\text{ord}} = 0 L_{Al,Ni,Al}^{\text{ord}} + 1 L_{Al,Ni,Al}^{\text{ord}} \left( y_{Al}^{(2)} - y_{Ni}^{(2)} \right) \]

\[ \text{[L12]} \]
となる。また4副格子モデルでは、分子1モル（化合物）は、

\[
(A_x B_{1-x})_2(A_x B_{1-x})_2(A_x B_{1-x})_2(A_x B_{1-x})_2
\]

と表現されるので、化学的自由エネルギーは、

\[
G_m^{\text{ord}} = G_m^{\text{ref}} - \tau^{\text{ref}} + \Delta G_m^{\text{ord}} - G_m^{\text{ex}}
\]

\[
G_m^{\text{ref}} = \sum_{i=A}^{B} \sum_{j=A}^{B} \sum_{k=A}^{B} \sum_{l=A}^{B} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} G_{i;j;k;l}^{\text{ref}}
\]

\[
\Delta G_m^{\text{ord}} = RT \left( \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(1)} \ln y_i^{(1)} + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(2)} \ln y_i^{(2)} + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(3)} \ln y_i^{(3)} + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(4)} \ln y_i^{(4)} \right)
\]

\[
G_m^{\text{ex}} = \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(1)} y_j^{(2)} \sum_{k=A}^{B} y_k^{(3)} y_m^{(4)} L_{i;k;j;l;m}^{\text{ord}} + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(2)} y_j^{(3)} \sum_{k=A}^{B} y_k^{(4)} y_m^{(1)} L_{i;k;j;l;m}^{\text{ord}}
\]

\[
\sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(3)} y_j^{(4)} \sum_{k=A}^{B} y_k^{(1)} y_m^{(2)} L_{i;k;j;l;m}^{\text{ord}} + \sum_{i=A}^{B} \sum_{j=A}^{B} y_i^{(4)} y_j^{(1)} \sum_{k=A}^{B} y_k^{(2)} y_m^{(3)} L_{i;k;j;l;m}^{\text{ord}} + \cdots
\]

\[
\sum_{i=A}^{B} \sum_{j=A}^{B} \sum_{k=A}^{B} \sum_{l=A}^{B} \sum_{p=A}^{B} \sum_{q=A}^{B} \sum_{r=A}^{B} \sum_{s=A}^{B} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} y_p^{(1)} y_q^{(2)} y_r^{(3)} y_s^{(4)} L_{i;j;k;l;p;q;r;s}^{\text{ord}} + \cdots
\]

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

\[
G_m = G_m^{\text{dis}}(x_i) + G_m^{\text{ord}}(y_i^{(1)}, y_i^{(2)}) - G_m^{\text{ord}}(x_i)
\]
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ることによって決定される。以下、具体的にΔG相について説明する。関係式は、

\[
dG_{m}^{(1)} = \left( \frac{\partial G_{m}^{(1)}}{\partial y_{Al}^{(1)}} \right) dy_{Al}^{(1)} + \left( \frac{\partial G_{m}^{(1)}}{\partial y_{Ni}^{(1)}} \right) dy_{Ni}^{(1)} + \left( \frac{\partial G_{m}^{(1)}}{\partial y_{Al}^{(2)}} \right) dy_{Al}^{(2)} + \left( \frac{\partial G_{m}^{(1)}}{\partial y_{Ni}^{(2)}} \right) dy_{Ni}^{(2)}
\]

\[
G_{m}^{(m)} = \sum_{i=1}^{2} \sum_{j=1}^{2} \left( y_{Al}^{(i)} G_{Al}^{(i)} + y_{Ni}^{(i)} G_{Ni}^{(i)} \right) + \left( y_{Al}^{(2)} G_{Al}^{(2)} + y_{Ni}^{(2)} G_{Ni}^{(2)} \right) + RT \left[ \frac{3}{4} \left( y_{Al}^{(1)} \ln y_{Al}^{(1)} + y_{Ni}^{(1)} \ln y_{Ni}^{(1)} + \frac{1}{4} (y_{Al}^{(2)} \ln y_{Al}^{(2)} + y_{Ni}^{(2)} \ln y_{Ni}^{(2)}) \right) \right]
\]

\[
\frac{\partial G_{m}^{(1)}}{\partial y_{Al}^{(1)}} = y_{Al}^{(1)} G_{Al}^{(1)} + y_{Ni}^{(1)} G_{Ni}^{(1)} + \frac{3}{4} RT (\ln y_{Al}^{(1)} + 1)
\]

\[
\frac{\partial G_{m}^{(1)}}{\partial y_{Ni}^{(1)}} = y_{Al}^{(1)} G_{Al}^{(1)} + y_{Ni}^{(1)} G_{Ni}^{(1)} + \frac{3}{4} RT (\ln y_{Ni}^{(1)} + 1)
\]

\[
\frac{\partial G_{m}^{(1)}}{\partial y_{Al}^{(2)}} = y_{Al}^{(2)} G_{Al}^{(2)} + y_{Ni}^{(2)} G_{Ni}^{(2)} + \frac{1}{4} RT (\ln y_{Al}^{(2)} + 1)
\]

\[
\frac{\partial G_{m}^{(1)}}{\partial y_{Ni}^{(2)}} = y_{Al}^{(2)} G_{Al}^{(2)} + y_{Ni}^{(2)} G_{Ni}^{(2)} + \frac{1}{4} RT (\ln y_{Ni}^{(2)} + 1)
\]
\[
\frac{\partial G^{L1}_m}{\partial y^{(2)}_{Ni}} = y^{(1)}_d G^{L1}_d, y^{(1)}_N G^{L1}_N + \frac{1}{4} RT (\ln y^{(2)}_{Ni} + 1) + y^{(1)}_d y^{(1)}_N L^{L1}_{d,Ni} + y^{(2)}_d \left( y^{(1)}_d L^{L1}_{d,Al,Ni} + y^{(1)}_N L^{L1}_{N,Al,Ni} \right) + y^{(1)}_d y^{(1)}_N (y^{(1)}_d - y^{(1)}_N) L^{L1}_{d,Ni,Al} + y^{(2)}_d \left( y^{(2)}_d - 2 y^{(2)}_N \right) \left( y^{(1)}_d L^{L1}_{d,Al,Ni} + y^{(1)}_N L^{L1}_{N,Al,Ni} \right)
\]

1 = y^{(1)}_d + y^{(1)}_N, \quad 0 = dy^{(1)}_d + dy^{(1)}_N, \quad \therefore dy^{(1)}_d = -dy^{(1)}_N

1 = y^{(2)}_d + y^{(2)}_N, \quad 0 = dy^{(2)}_d + dy^{(2)}_N, \quad \therefore dy^{(2)}_d = -dy^{(2)}_N

\[x_{Ni} = \frac{3}{4} y^{(2)}_d + \frac{1}{4} y^{(2)}_N \quad 0 = \frac{3}{4} dy^{(1)}_d + \frac{1}{4} dy^{(1)}_N, \quad \therefore dy^{(1)}_d = -3dy^{(1)}_N
\]

\[x_{Ni} = \frac{3}{4} y^{(1)}_d + \frac{1}{4} y^{(2)}_d, \quad 0 = \frac{3}{4} dy^{(1)}_d + \frac{1}{4} dy^{(1)}_N, \quad \therefore dy^{(1)}_d = -3dy^{(1)}_N
\]

となり，ここで，独立変数を \( y^{(2)}_d \) としよう。合金組成を固定した場合，

\[y^{(2)}_{Ni} = 1 - y^{(2)}_d \]

\[y^{(1)}_d = \frac{4}{3} x_{Al} - \frac{1}{3} y^{(2)}_d \]

\[y^{(1)}_N = 1 - y^{(1)}_d \]

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

\[
dG^{L1}_d = \frac{\partial G^{L1}_d}{\partial y^{(1)}_d} dy^{(1)}_d + \frac{\partial G^{L1}_d}{\partial y^{(1)}_N} dy^{(1)}_N + \frac{\partial G^{L1}_d}{\partial y^{(2)}_d} dy^{(2)}_d + \frac{\partial G^{L1}_d}{\partial y^{(2)}_N} dy^{(2)}_N
\]

\[
dG^{L1}_N = \frac{\partial G^{L1}_N}{\partial y^{(1)}_d} dy^{(1)}_d + \frac{\partial G^{L1}_N}{\partial y^{(1)}_N} dy^{(1)}_N + \frac{\partial G^{L1}_N}{\partial y^{(2)}_d} dy^{(2)}_d + \frac{\partial G^{L1}_N}{\partial y^{(2)}_N} dy^{(2)}_N
\]

\[
m = -\frac{1}{3} \left( \frac{\partial G^{L1}_d}{\partial y^{(2)}_d} \right)_d + \frac{1}{3} \left( \frac{\partial G^{L1}_d}{\partial y^{(2)}_N} \right)_d + \frac{\partial G^{L1}_N}{\partial y^{(1)}_d} + \frac{\partial G^{L1}_N}{\partial y^{(1)}_N} - \frac{\partial G^{L1}_d}{\partial y^{(2)}_d} - \frac{\partial G^{L1}_d}{\partial y^{(2)}_N} = 0
\]

\[\therefore 3 \left( \frac{\partial G^{L1}_d}{\partial y^{(2)}_d} \right)_d - 3 \left( \frac{\partial G^{L1}_d}{\partial y^{(2)}_N} \right)_d = \left( \frac{\partial G^{L1}_N}{\partial y^{(1)}_d} \right)_d - \left( \frac{\partial G^{L1}_N}{\partial y^{(1)}_N} \right)_d
\]

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。
\[
\begin{align*}
3 \left( \frac{\partial G_{m}^{L_{1}}}{\partial y_{Al}^{(2)}} \right) - 3 \left( \frac{\partial G_{m}^{L_{1}}}{\partial y_{N_{i}}^{(2)}} \right) &= \left( \frac{\partial G_{m}^{L_{1}}}{\partial y_{Al}^{(i)}} \right) - \left( \frac{\partial G_{m}^{L_{1}}}{\partial y_{N_{i}}^{(i)}} \right) \\
&= \left\{ y_{Al}^{(i)} G_{Al}^{L_{1}} + y_{N_{i}}^{(i)} G_{N_{i}}^{L_{1}} + \frac{1}{4} RT (\ln y_{Al}^{(2)} + 1) \right\} \\
&\quad + y_{Al}^{(i)} y_{N_{i}}^{(i)} L_{Al,N_{i}}^{L_{1}} + y_{N_{i}}^{(i)} \left( y_{Al}^{(i)} L_{Al,N_{i}}^{L_{1}} + y_{N_{i}}^{(i)} L_{N_{i},N_{i}}^{L_{1}} \right) + y_{Al}^{(i)} y_{N_{i}}^{(i)} y_{N_{i}}^{(i)} L_{Al,N_{i}}^{L_{1}} \\
&\quad + y_{Al}^{(i)} L_{Al,N_{i}}^{L_{i}} \left( y_{Al}^{(i)} - y_{N_{i}}^{(i)} \right) L_{Al,N_{i}}^{L_{1}} + y_{N_{i}}^{(i)} \left( 2 y_{Al}^{(i)} - y_{N_{i}}^{(i)} \right) \left( y_{Al}^{(i)} L_{Al,N_{i}}^{L_{1}} + y_{N_{i}}^{(i)} L_{N_{i},N_{i}}^{L_{1}} \right)
\end{align*}
\]
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、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、
\[
\begin{align*}
&x_{AI} G_{AI}^{L_{11}} + x_{NI} G_{NI}^{L_{11}} + \frac{1}{4} RT(\ln x_{AI} + 1) \\
&+ x_{AI} x_{NI} 0 L_{AI}^{L_{11}} + x_{NI} \left(x_{AI} 0 L_{AI}^{L_{11}} + x_{NI} 0 L_{AI}^{L_{11}} + x_{AI} x_{NI} x_{AI} 0 L_{NI}^{L_{11}} + x_{AI} x_{NI} x_{AI} 0 L_{NI}^{L_{11}} \right) \\
&+ x_{AI} x_{NI} (x_{AI} - x_{NI}) \left(x_{AI} 1 L_{AI}^{L_{11}} + x_{NI} 1 L_{NI}^{L_{11}} \right) \\
&+ x_{AI} (x_{AI} - x_{NI}) \left(1 L_{AI}^{L_{11}} + x_{AI} (x_{AI} - 2 x_{NI}) \left(x_{AI} 1 L_{AI}^{L_{11}} + x_{NI} 1 L_{NI}^{L_{11}} \right) \right)
\end{align*}
\]

\[
\begin{align*}
&x_{AI} G_{AI}^{L_{12}} + x_{NI} G_{NI}^{L_{12}} + \frac{1}{4} RT(\ln x_{AI} + 1) \\
&+ x_{AI} x_{NI} 0 L_{AI}^{L_{12}} + x_{NI} \left(x_{AI} 0 L_{AI}^{L_{12}} + x_{NI} 0 L_{AI}^{L_{12}} \right) \\
&+ x_{AI} x_{NI} (x_{AI} - x_{NI}) \left(x_{AI} 1 L_{AI}^{L_{12}} + x_{NI} 1 L_{NI}^{L_{12}} \right) \\
&+ x_{AI} (x_{AI} - x_{NI}) \left(1 L_{AI}^{L_{12}} + x_{AI} (x_{AI} - 2 x_{NI}) \left(x_{AI} 1 L_{AI}^{L_{12}} + x_{NI} 1 L_{NI}^{L_{12}} \right) \right)
\end{align*}
\]

\[
\begin{align*}
&x_{AI} G_{AI}^{L_{12}} + x_{NI} G_{NI}^{L_{12}} + \frac{1}{4} RT(\ln x_{AI} + 1) \\
&+ x_{AI} x_{NI} 0 L_{AI}^{L_{12}} + x_{NI} \left(x_{AI} 0 L_{AI}^{L_{12}} + x_{NI} 0 L_{AI}^{L_{12}} \right) \\
&+ x_{AI} x_{NI} (x_{AI} - x_{NI}) \left(x_{AI} 1 L_{AI}^{L_{12}} + x_{NI} 1 L_{NI}^{L_{12}} \right) \\
&+ x_{AI} (x_{AI} - x_{NI}) \left(1 L_{AI}^{L_{12}} + x_{AI} (x_{AI} - 2 x_{NI}) \left(x_{AI} 1 L_{AI}^{L_{12}} + x_{NI} 1 L_{NI}^{L_{12}} \right) \right)
\end{align*}
\]

を得る。これを整理して、
\[
\begin{align*}
&x_{ai}(G_{ai;1}^{L_1} - G_{ni;1}^{L_1} - 0 L_{ai;1}^{L_1} + x_{ni}(G_{ni;1}^{L_1} + 0 L_{ni;1}^{L_1} - G_{ni;1}^{L_1})) \\
+ &x_{ai} x_{ni}(0 L_{ai;1}^{L_1} + 0 L_{ai;1}^{L_1} - 0 L_{ai;1}^{L_1} - 0 L_{ai;1}^{L_1} + 0 L_{ai;1}^{L_1} - 0 L_{ai;1}^{L_1}) \\
+ &x_{ai} x_{ni}(x_{ai} - x_{ni})(1 L_{ai;1}^{L_1} - 1 L_{ai;1}^{L_1} + 1 L_{ai;1}^{L_1} - 1 L_{ai;1}^{L_1} + 1 L_{ai;1}^{L_1} - 1 L_{ai;1}^{L_1}) \\
+ &x_{ai} x_{ni}(x_{ai} - x_{ni})(1 L_{ai;1}^{L_1} - 1 L_{ai;1}^{L_1} - 1 L_{ai;1}^{L_1} + 1 L_{ai;1}^{L_1} - 1 L_{ai;1}^{L_1} = 0 \\
\end{align*}
\]

となり、これは恒等式であるので、


\[
3G_{\text{Al,Al}}^{L_{12}} - G_{\text{Ni,Al}}^{L_{12}} - 2G_{\text{Al,Al}}^{L_{12}} + 3^0L_{\text{Al,Al,Ni}}^{L_{12}} - 0L_{\text{Al,Al,Ni}}^{L_{12}} = 0
\]

\[
3G_{\text{Ni,Al}}^{L_{12}} - G_{\text{Al,Al}}^{L_{12}} - 2G_{\text{Ni,Al}}^{L_{12}} + 3^0L_{\text{Ni,Al,Ni}}^{L_{12}} - 0L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

\[
0L_{\text{Al,Al,Ni}}^{L_{12}} - 0L_{\text{Al,Ni,Ni}}^{L_{12}} + 5^0L_{\text{Al,Al,Ni}}^{L_{12}} - 5^0L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

\[
3^1L_{\text{Al,Al,Ni}}^{L_{12}} - 1L_{\text{Al,Al,Ni}}^{L_{12}} - 3^1L_{\text{Ni,Al,Ni}}^{L_{12}} + 1L_{\text{Al,Al,Ni}}^{L_{12}} - 2^0L_{\text{Al,Al,Ni}}^{L_{12}} = 0
\]

\[
3^1L_{\text{Ni,Al,Ni}}^{L_{12}} - 1L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

\[
3^1L_{\text{Ni,Al,Ni}}^{L_{12}} - 1L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

を得る。ここで、

\[
G_{\text{Al,Al}}^{L_{12}} = G_{\text{Ni,Al}}^{L_{12}} = 0
\]

\[
G_{\text{Ni,Al}}^{L_{12}} = u_1
\]

\[
G_{\text{Ni,Ni}}^{L_{12}} = u_2
\]

\[
0L_{\text{Al,Al,Ni}}^{L_{12}} = u_3 + \frac{u_2}{2}
\]

\[
1L_{\text{Al,Al,Ni}}^{L_{12}} = u_4
\]

\[
1L_{\text{Ni,Al,Ni}}^{L_{12}} = u_5
\]

と置くと、

\[
3u_1 - u_2 + 3\left(u_3 + \frac{u_2}{2}\right) - 0L_{\text{Al,Al,Ni}}^{L_{12}} = 0
\]

\[
-3u_2 + u_1 - 3^0L_{\text{Ni,Al,Ni}}^{L_{12}} + 0L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

\[
0L_{\text{Al,Al,Ni}}^{L_{12}} - 0L_{\text{Al,Ni,Ni}}^{L_{12}} + 5\left(u_3 + \frac{u_2}{2}\right) - 5^0L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

\[
3^1L_{\text{Al,Al,Ni}}^{L_{12}} - 1L_{\text{Al,Al,Ni}}^{L_{12}} - 3^1L_{\text{Ni,Al,Ni}}^{L_{12}} + 1L_{\text{Al,Al,Ni}}^{L_{12}} - 2^0L_{\text{Al,Al,Ni}}^{L_{12}} = 0
\]

\[
3^1u_4 - 1L_{\text{Al,Al,Ni}}^{L_{12}} = 0
\]

\[
3^1u_5 - 1L_{\text{Al,Al,Ni}}^{L_{12}} = 0
\]

となり、始めの 3 式を足し合わせると、

\[
4u_1 - 4u_2 + 8\left(u_3 + \frac{u_2}{2}\right) - 8^0L_{\text{Ni,Al,Ni}}^{L_{12}} = 0
\]

\[
\therefore 0L_{\text{Ni,Al,Ni}}^{L_{12}} = u_3 + \frac{u_1}{2}
\]

\[
0L_{\text{Al,Al,Ni}}^{L_{12}} = 3u_1 - u_2 + 3\left(u_3 + \frac{u_2}{2}\right) = 3u_1 + \frac{u_2}{2} + 3u_3
\]

\[
0L_{\text{Ni,Al,Ni}}^{L_{12}} = 3u_2 - u_1 + 3^0L_{\text{Ni,Al,Ni}}^{L_{12}} = 3u_2 - u_1 + 3\left(u_3 + \frac{u_2}{2}\right) = 3u_2 + \frac{u_1}{2} + 3u_3
\]

を得る。また後半の 2 式から
\[ ^1L_{Al,Ne:Al}^{L12} = 3^1u_4 \]
\[ ^1L_{Al,Ne:Ni}^{L12} = 3^1u_5 \]

である。さらに、4番目の式から

\[
^0L_{Al,Ne:Al,Ni}^{L12} = \frac{1}{2}(3^1L_{Al,Ne:Al}^{L12} - ^1L_{Al:Al,Ni}^{L12} - 3^1L_{Al,Ne:Ni}^{L12} + ^1L_{Ni:Al,Ni}^{L12})
\]
\[= \frac{1}{2}(9u_4 - u_4 - 9u_5 + u_5) = 4(u_4 - u_5)\]

を得る。以上をまとめると、

\[ G_{Al:Al}^{L12} = G_{Ni:Ni}^{L12} = 0 \]
\[ G_{Al,Ni}^{L12} = u_1 \]
\[ G_{Ne:Al}^{L12} = u_2 \]
\[ ^0L_{Al,Ne:Al}^{L12} = 3u_1 + \frac{u_2}{2} + 3u_3 \]
\[ ^0L_{Al,Ne:Ni}^{L12} = 3u_2 + \frac{u_1}{2} + 3u_3 \]
\[ ^0L_{Al,Ni}^{L12} = u_3 + \frac{u_2}{2} \]
\[ ^0L_{Ne:Al}^{L12} = u_3 + \frac{u_1}{2} \]
\[ ^1L_{Al,Ne:Ni}^{L12} = u_4 \]
\[ ^1L_{Ni:Al,Ni}^{L12} = u_5 \]
\[ ^0L_{Al,Ne:Al,Ni}^{L12} = 4(u_4 - u_5) \]

となる。さらに、\[ G_{Al:Ne}^{L12} = G_{Ne:Al}^{L12} = u_1 = u_2 \]を仮定すると、

\[ ^0L_{Al,Ne:Al}^{L12} = ^0L_{Al,Ne:Ni}^{L12} = ^0L_{Ni:Al,Ni}^{L12} \]

より、
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。