磁気エネルギーの定式化

[M.Hillert and M.Jarl : CALPHAD, 2(1978),227.]

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１．変数設定

$C_m(T)$	：磁気比熱
T_c	：キュリー温度
β	：１原子当たりの飽和磁化（単位はボーア磁子）
cfm	：Completely ferromagnetic state
cpm	：Completely paramagnetic state
eqm	：Equilibrium magnetic state（T_c 以下では強磁性状態。しかし cfm ではない。 T_c 以上では常磁性状態、しかし cpm ではない。）
$\Delta^\circ S^{cfm\to eqm}(T)$	：$cfm \to eqm$ における磁気エントロピー変化
$\Delta^\circ H^{cfm\to eqm}(T)$	：$cfm \to eqm$ における磁気エンタルピー変化
$\Delta^\circ G^{cfm\to eqm}(T)$	：$cfm \to eqm$ における自由エネルギー変化

また以下のように、各変数間の関係式を設定する。

$$\ln(\beta+1) = \frac{518}{675}\left(K^{lro} + \frac{3}{5}K^{sro}\right) = \frac{518}{675}K^{lro} + \frac{518}{1125}K^{sro}$$

$$K^{lro} = \frac{474}{497}\left(\frac{1-p}{p}\right)K^{sro}$$

より、

$$\frac{518}{675}K^{lro} = \frac{518}{675}\frac{474}{497}\left(\frac{1-p}{p}\right)K^{sro} = \frac{74}{225}\frac{158}{71}\left(\frac{1-p}{p}\right)K^{sro} = \frac{11692}{15975}\left(\frac{1-p}{p}\right)K^{sro}$$

したがって、

$$\ln(\beta+1) = \frac{518}{675}K^{lro} + \frac{518}{1125}K^{sro} = \frac{11692}{15975}\left(\frac{1-p}{p}\right)K^{sro} + \frac{518}{1125}K^{sro} = \left\{\frac{11692}{15975}\left(\frac{1-p}{p}\right) + \frac{518}{1125}\right\}K^{sro}$$

$$\therefore\ K^{sro} = \frac{1}{\dfrac{11692}{15975}\left(\dfrac{1-p}{p}\right) + \dfrac{518}{1125}}\ln(\beta+1) = \frac{1}{\alpha}\ln(\beta+1)$$

$$K^{lro} = \frac{474}{497}\left(\frac{1-p}{p}\right)K^{sro} = \frac{1}{\alpha}\frac{474}{497}\left(\frac{1-p}{p}\right)\ln(\beta+1)$$

ここで、

$$\alpha \equiv \frac{518}{1125} + \frac{11692}{15975}\left(\frac{1-p}{p}\right)$$

$p = 0.28,\qquad$ (for fcc)

$p = 0.40,\qquad$ (for bcc)

である。

２．磁気自由エネルギーの計算

まず完全に磁気規則化した状態（完全強磁性）をエネルギーの基準にとった場合の各種熱力学量について導出しよう。（なお、エネルギー基準をこのように取る理由は、各種熱力学量も計算において、温度 0(K)からの積分が行われるからである。）

まずキュリー温度T_c以上および以下における磁気比熱の関数形を、

$$\begin{aligned} C_m(T) &= 2K^{lro}R\left\{\left(\frac{T}{T_c}\right)^3+\frac{1}{3}\left(\frac{T}{T_c}\right)^9+\frac{1}{5}\left(\frac{T}{T_c}\right)^{15}\right\} \\ &= 2\frac{1}{\alpha}\frac{474}{497}\left(\frac{1-p}{p}\right)R\ln(\beta+1)\left\{\left(\frac{T}{T_c}\right)^3+\frac{1}{3}\left(\frac{T}{T_c}\right)^9+\frac{1}{5}\left(\frac{T}{T_c}\right)^{15}\right\}, \qquad (T<T_c) \end{aligned} \tag{1a}$$

$$\begin{aligned} C_m(T) &= 2K^{sro}R\left\{\left(\frac{T}{T_c}\right)^{-5}+\frac{1}{3}\left(\frac{T}{T_c}\right)^{-15}+\frac{1}{5}\left(\frac{T}{T_c}\right)^{-25}\right\} \\ &= 2\frac{1}{\alpha}R\ln(\beta+1)\left\{\left(\frac{T}{T_c}\right)^{-5}+\frac{1}{3}\left(\frac{T}{T_c}\right)^{-15}+\frac{1}{5}\left(\frac{T}{T_c}\right)^{-25}\right\}, \qquad (T>T_c) \end{aligned} \tag{1b}$$

のように近似する。磁気エントロピーは、

$$\Delta^\circ S^{cfm\to eqm}(T)=\int_{T'=0}^{T'=T}\frac{C_m(T')}{T'}dT' \tag{2}$$

にて定義されるので、式(1)を代入することによって、

$$\begin{aligned} \Delta^\circ S^{cfm\to eqm}(T) &= \int_{T'=0}^{T'=T}\frac{1}{T'}\frac{2}{\alpha}\frac{474}{497}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\left\{\left(\frac{T'}{T_c}\right)^3+\frac{1}{3}\left(\frac{T'}{T_c}\right)^9+\frac{1}{5}\left(\frac{T'}{T_c}\right)^{15}\right\}dT' \\ &= \frac{2}{\alpha}\frac{474}{497}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\int_{T'=0}^{T'=T}\frac{1}{T'}\left\{\left(\frac{T'}{T_c}\right)^3+\frac{1}{3}\left(\frac{T'}{T_c}\right)^9+\frac{1}{5}\left(\frac{T'}{T_c}\right)^{15}\right\}dT' \\ &= \frac{2}{\alpha}\frac{474}{497}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\frac{1}{T_c}\int_{T'=0}^{T'=T}\left\{\left(\frac{T'}{T_c}\right)^2+\frac{1}{3}\left(\frac{T'}{T_c}\right)^8+\frac{1}{5}\left(\frac{T'}{T_c}\right)^{14}\right\}dT' \\ &= \frac{2}{\alpha}\frac{474}{497}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\frac{1}{T_c}\left[\frac{T_c}{3}\left(\frac{T'}{T_c}\right)^3+\frac{T_c}{27}\left(\frac{T'}{T_c}\right)^9+\frac{T_c}{75}\left(\frac{T'}{T_c}\right)^{15}\right]_0^T \\ &= \frac{1}{\alpha}\frac{474}{497}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\left[\frac{2}{3}\left(\frac{T}{T_c}\right)^3+\frac{2}{27}\left(\frac{T}{T_c}\right)^9+\frac{2}{75}\left(\frac{T}{T_c}\right)^{15}\right], \qquad (T\le T_c) \end{aligned} \tag{3a}$$

$$
\begin{aligned}
\Delta^{\circ} S^{cfm\to eqm}(T) &= \Delta^{\circ} S^{cfm\to eqm}(T_c) + \int_{T'=T_c}^{T'=T} \frac{2}{T'\alpha} R\ln(\beta+1)\left\{\left(\frac{T'}{T_c}\right)^{-5} + \frac{1}{3}\left(\frac{T'}{T_c}\right)^{-15} + \frac{1}{5}\left(\frac{T'}{T_c}\right)^{-25}\right\} dT' \\
&= \Delta^{\circ} S^{cfm\to eqm}(T_c) + R\ln(\beta+1)\frac{2}{T_c\alpha}\int_{T'=T_c}^{T'=T}\left\{\left(\frac{T'}{T_c}\right)^{-6} + \frac{1}{3}\left(\frac{T'}{T_c}\right)^{-16} + \frac{1}{5}\left(\frac{T'}{T_c}\right)^{-26}\right\} dT' \\
&= \Delta^{\circ} S^{cfm\to eqm}(T_c) + R\ln(\beta+1)\frac{-2}{T_c\alpha}\left[\frac{T_c}{5}\left(\frac{T'}{T_c}\right)^{-5} + \frac{T_c}{45}\left(\frac{T'}{T_c}\right)^{-15} + \frac{T_c}{125}\left(\frac{T'}{T_c}\right)^{-25}\right]_{T_c}^{T} \\
&= \Delta^{\circ} S^{cfm\to eqm}(T_c) - \frac{1}{\alpha}R\ln(\beta+1)\left[\frac{2}{5}\left(\frac{T'}{T_c}\right)^{-5} + \frac{2}{45}\left(\frac{T'}{T_c}\right)^{-15} + \frac{2}{125}\left(\frac{T'}{T_c}\right)^{-25}\right]_{T_c}^{T} \\
&= \Delta^{\circ} S^{cfm\to eqm}(T_c) - \frac{1}{\alpha}R\ln(\beta+1)\left[\frac{2}{5}\left(\frac{T}{T_c}\right)^{-5} + \frac{2}{45}\left(\frac{T}{T_c}\right)^{-15} + \frac{2}{125}\left(\frac{T}{T_c}\right)^{-25} - \frac{518}{1125}\right], \qquad (T \ge T_c)
\end{aligned}
\tag{3b}
$$

温度が無限大では、

$$
\begin{aligned}
\Delta^{\circ} S^{cfm\to eqm}(\infty) &= \Delta^{\circ} S^{cfm\to eqm}(T_c) + \frac{518}{1125}\frac{1}{\alpha}R\ln(\beta+1) \\
&= \frac{1}{\alpha}\frac{474}{497}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\left[\frac{2}{3}+\frac{2}{27}+\frac{2}{75}\right] + \frac{518}{1125}\frac{1}{\alpha}R\ln(\beta+1) \\
&= \frac{1}{\alpha}\frac{11692}{15975}\left(\frac{1}{p}-1\right)R\ln(\beta+1) + \frac{518}{1125}\frac{1}{\alpha}R\ln(\beta+1) \\
&= \left(\frac{518}{1125} + \frac{11692}{15975}\left(\frac{1}{p}-1\right)\right)\frac{1}{\alpha}R\ln(\beta+1) \\
&= \left(\frac{518}{1125} + \frac{11692}{15975}\left(\frac{1}{p}-1\right)\right)\frac{1}{\alpha}R\ln(\beta+1) = \alpha\frac{1}{\alpha}R\ln(\beta+1) = R\ln(\beta+1)
\end{aligned}
$$

と計算される。次に、エンタルピーは、

$$
\Delta^{\circ} H^{cfm\to eqm}(T) = \int_{T'=0}^{T'=T} C_m(T')dT' \tag{4}
$$

にて定義されるので、式(1a,b)を代入することによって、

$$
\begin{aligned}
\Delta^{\circ} H^{cfm\to eqm}(T) &= \int_{T'=0}^{T'=T} \frac{474}{497}\frac{2}{\alpha}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\left\{\left(\frac{T'}{T_c}\right)^{3} + \frac{1}{3}\left(\frac{T'}{T_c}\right)^{9} + \frac{1}{5}\left(\frac{T'}{T_c}\right)^{15}\right\} dT' \\
&= \frac{474}{497}\frac{2}{\alpha}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\int_{T'=0}^{T'=T}\left\{\left(\frac{T'}{T_c}\right)^{3} + \frac{1}{3}\left(\frac{T'}{T_c}\right)^{9} + \frac{1}{5}\left(\frac{T'}{T_c}\right)^{15}\right\} dT' \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)R\ln(\beta+1)\left[\frac{T_c}{2}\left(\frac{T'}{T_c}\right)^{4} + \frac{T_c}{15}\left(\frac{T'}{T_c}\right)^{10} + \frac{T_c}{40}\left(\frac{T'}{T_c}\right)^{16}\right]_{0}^{T} \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1)\left[\frac{1}{2}\left(\frac{T}{T_c}\right)^{3} + \frac{1}{15}\left(\frac{T}{T_c}\right)^{9} + \frac{1}{40}\left(\frac{T}{T_c}\right)^{15}\right], \qquad (T \le T_c)
\end{aligned}
\tag{5a}
$$

$$
\begin{aligned}
\Delta^\circ H^{cfm\to eqm}(T) &= \Delta^\circ H^{cfm\to eqm}(T_c) + \int_{T'=T_c}^{T'=T} \frac{2}{\alpha} R\ln(\beta+1)\left\{\left(\frac{T'}{T_c}\right)^{-5} + \frac{1}{3}\left(\frac{T'}{T_c}\right)^{-15} + \frac{1}{5}\left(\frac{T'}{T_c}\right)^{-25}\right\} dT' \\
&= \Delta^\circ H^{cfm\to eqm}(T_c) + \frac{2}{\alpha} R\ln(\beta+1)\int_{T'=T_c}^{T'=T}\left\{\left(\frac{T'}{T_c}\right)^{-5} + \frac{1}{3}\left(\frac{T'}{T_c}\right)^{-15} + \frac{1}{5}\left(\frac{T'}{T_c}\right)^{-25}\right\} dT' \\
&= \Delta^\circ H^{cfm\to eqm}(T_c) - \frac{1}{\alpha} RT_c \ln(\beta+1)\left[\frac{1}{2}\left(\frac{T'}{T_c}\right)^{-4} + \frac{1}{21}\left(\frac{T'}{T_c}\right)^{-14} + \frac{1}{60}\left(\frac{T'}{T_c}\right)^{-24}\right]_{T_c}^{T} \\
&= \Delta^\circ H^{cfm\to eqm}(T_c) - \frac{1}{\alpha} RT_c \ln(\beta+1)\left[\frac{1}{2}\left(\frac{T}{T_c}\right)^{-4} + \frac{1}{21}\left(\frac{T}{T_c}\right)^{-14} + \frac{1}{60}\left(\frac{T}{T_c}\right)^{-24} - \frac{1}{2} - \frac{1}{21} - \frac{1}{60}\right] \\
&= \Delta^\circ H^{cfm\to eqm}(T_c) - \frac{1}{\alpha} RT \ln(\beta+1)\left[\frac{1}{2}\left(\frac{T}{T_c}\right)^{-5} + \frac{1}{21}\left(\frac{T}{T_c}\right)^{-15} + \frac{1}{60}\left(\frac{T}{T_c}\right)^{-25} - \frac{79}{140}\left(\frac{T_c}{T}\right)\right], \quad (T \ge T_c)
\end{aligned} \tag{5b}
$$

温度が無限大では、

$$
\begin{aligned}
\Delta^\circ H^{cfm\to eqm}(\infty) &= \Delta^\circ H^{cfm\to eqm}(T_c) + \frac{79}{140}\frac{1}{\alpha} RT_c \ln(\beta+1) \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT_c \ln(\beta+1)\left[\frac{1}{2}+\frac{1}{15}+\frac{1}{40}\right] + \frac{79}{140}\frac{1}{\alpha} RT_c \ln(\beta+1) \\
&= \frac{71}{120}\frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT_c \ln(\beta+1) + \frac{79}{140}\frac{1}{\alpha} RT_c \ln(\beta+1) \\
&= \left(\frac{71}{120}\frac{474}{497}\left(\frac{1}{p}-1\right) + \frac{79}{140}\right)\frac{1}{\alpha} RT_c \ln(\beta+1) \\
&= \frac{79}{140}\left(\frac{1}{p}-1+1\right)\frac{1}{\alpha} RT_c \ln(\beta+1) = \frac{79}{140}\frac{1}{p}\frac{1}{\alpha} RT_c \ln(\beta+1)
\end{aligned}
$$

また、

$$
\begin{aligned}
&\Delta^\circ H^{cfm\to eqm}(T_c) - T\Delta^\circ S^{cfm\to eqm}(T_c) \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT_c \ln(\beta+1)\left[\frac{1}{2}\left(\frac{T_c}{T_c}\right)^{3} + \frac{1}{15}\left(\frac{T_c}{T_c}\right)^{9} + \frac{1}{40}\left(\frac{T_c}{T_c}\right)^{15}\right] \\
&\quad - T\,\frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) R\ln(\beta+1)\left[\frac{2}{3}\left(\frac{T_c}{T_c}\right)^{3} + \frac{2}{27}\left(\frac{T_c}{T_c}\right)^{9} + \frac{2}{75}\left(\frac{T_c}{T_c}\right)^{15}\right] \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT_c \ln(\beta+1)\left[\frac{1}{2}+\frac{1}{15}+\frac{1}{40}\right] - \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT \ln(\beta+1)\left[\frac{2}{3}+\frac{2}{27}+\frac{2}{75}\right] \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT \ln(\beta+1)\left(\frac{71}{120}\frac{T_c}{T} - \frac{518}{675}\right) = -\frac{474}{497}\left(\frac{518}{675} - \frac{71}{120}\frac{T_c}{T}\right)\frac{1}{\alpha}\left(\frac{1}{p}-1\right) RT \ln(\beta+1)
\end{aligned}
$$

である。

さて、自由エネルギーは、

$$
\Delta^\circ G^{cfm\to eqm}(T) = \Delta^\circ H^{cfm\to eqm}(T) - T\Delta^\circ S^{cfm\to eqm}(T) \tag{6}
$$

にて定義されるので、以上から、

$$\begin{aligned}\Delta^\circ G^{cfm\to eqm}(T) &= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1)\left[\frac{1}{2}\left(\frac{T}{T_c}\right)^3+\frac{1}{15}\left(\frac{T}{T_c}\right)^9+\frac{1}{40}\left(\frac{T}{T_c}\right)^{15}\right]\\
&\quad -\frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1)\left[\frac{2}{3}\left(\frac{T}{T_c}\right)^3+\frac{2}{27}\left(\frac{T}{T_c}\right)^9+\frac{2}{75}\left(\frac{T}{T_c}\right)^{15}\right]\\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1)\left[\left(\frac{1}{2}-\frac{2}{3}\right)\left(\frac{T}{T_c}\right)^3+\left(\frac{1}{15}-\frac{2}{27}\right)\left(\frac{T}{T_c}\right)^9+\left(\frac{1}{40}-\frac{2}{75}\right)\left(\frac{T}{T_c}\right)^{15}\right]\\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1)\left[-\frac{1}{6}\left(\frac{T}{T_c}\right)^3-\frac{1}{135}\left(\frac{T}{T_c}\right)^9-\frac{1}{600}\left(\frac{T}{T_c}\right)^{15}\right],\qquad (T\le T_c)\end{aligned}\tag{7a}$$

$$\begin{aligned}&\Delta^\circ G^{cfm\to eqm}(T)\\
&=\Delta^\circ H^{cfm\to eqm}(T_c)-T\Delta^\circ S^{cfm\to eqm}(T_c)\\
&\quad -\frac{1}{\alpha}RT\ln(\beta+1)\left[\frac{1}{2}\left(\frac{T}{T_c}\right)^{-5}+\frac{1}{21}\left(\frac{T}{T_c}\right)^{-15}+\frac{1}{60}\left(\frac{T}{T_c}\right)^{-25}-\frac{79}{140}\left(\frac{T_c}{T}\right)\right]\\
&\quad +\frac{1}{\alpha}RT\ln(\beta+1)\left[\frac{2}{5}\left(\frac{T}{T_c}\right)^{-5}+\frac{2}{45}\left(\frac{T}{T_c}\right)^{-15}+\frac{2}{125}\left(\frac{T}{T_c}\right)^{-25}-\frac{518}{1125}\right]\\
&=\Delta^\circ H^{cfm\to eqm}(T_c)-T\Delta^\circ S^{cfm\to eqm}(T_c)\\
&\quad +\frac{1}{\alpha}RT\ln(\beta+1)\left[\begin{array}{l}\frac{2}{5}\left(\frac{T}{T_c}\right)^{-5}+\frac{2}{45}\left(\frac{T}{T_c}\right)^{-15}+\frac{2}{125}\left(\frac{T}{T_c}\right)^{-25}-\frac{518}{1125}\\ -\frac{1}{2}\left(\frac{T}{T_c}\right)^{-5}-\frac{1}{21}\left(\frac{T}{T_c}\right)^{-15}-\frac{1}{60}\left(\frac{T}{T_c}\right)^{-25}+\frac{79}{140}\left(\frac{T_c}{T}\right)\end{array}\right]\\
&=\Delta^\circ H^{cfm\to eqm}(T_c)-T\Delta^\circ S^{cfm\to eqm}(T_c)\\
&\quad +\frac{1}{\alpha}RT\ln(\beta+1)\left[\left(\frac{2}{5}-\frac{1}{2}\right)\left(\frac{T}{T_c}\right)^{-5}+\left(\frac{2}{45}-\frac{1}{21}\right)\left(\frac{T}{T_c}\right)^{-15}+\left(\frac{2}{125}-\frac{1}{60}\right)\frac{2}{125}\left(\frac{T}{T_c}\right)^{-25}+\frac{79}{140}\left(\frac{T_c}{T}\right)-\frac{518}{1125}\right]\\
&=\Delta^\circ H^{cfm\to eqm}(T_c)-T\Delta^\circ S^{cfm\to eqm}(T_c)\\
&\quad +\frac{1}{\alpha}RT\ln(\beta+1)\left[-\frac{1}{10}\left(\frac{T}{T_c}\right)^{-5}-\frac{1}{315}\left(\frac{T}{T_c}\right)^{-15}-\frac{1}{1500}\left(\frac{T}{T_c}\right)^{-25}+\frac{79}{140}\left(\frac{T_c}{T}\right)-\frac{518}{1125}\right],\quad (T\ge T_c)\end{aligned}\tag{7b}$$

となる。

さて、次に完全常磁性状態から磁気的平衡状態への自由エネルギー変化量$\Delta^\circ G^{cpm\to eqm}(T)$を求めよう。磁気的平衡状態の自由エネルギーについて、

$$\begin{aligned}{}^\circ G^{eqm}(T) &= {}^\circ G^{cfm}(T)+\Delta^\circ G^{cfm\to eqm}(T)\\ {}^\circ G^{eqm}(T) &= {}^\circ G^{cpm}(T)+\Delta^\circ G^{cpm\to eqm}(T)\end{aligned}\tag{12}$$

が成立する。また物理的に、

$$
\begin{aligned}
{}^{\circ}G^{cpm}(T) - {}^{\circ}G^{cfm}(T) &= \Delta^{\circ}H^{cfm\to eqm}(\infty) - T\Delta^{\circ}S^{cfm\to eqm}(\infty) \\
&= \frac{79}{140}\frac{1}{p}\frac{1}{\alpha}RT_c\ln(\beta+1) - RT\ln(\beta+1) \\
&= -\left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1)
\end{aligned}
\tag{13}
$$

であることを考慮すると、$\Delta^{\circ}G^{cpm\to eqm}(T)$ は、

$$
\begin{aligned}
&\therefore\ {}^{\circ}G^{cfm}(T) + \Delta^{\circ}G^{cfm\to eqm}(T) = {}^{\circ}G^{cpm}(T) + \Delta^{\circ}G^{cpm\to eqm}(T) \\
&\Delta^{\circ}G^{cpm\to eqm}(T) = \Delta^{\circ}G^{cfm\to eqm}(T) - \{{}^{\circ}G^{cpm}(T) - {}^{\circ}G^{cfm}(T)\} \\
&\qquad = \Delta^{\circ}G^{cfm\to eqm}(T) + \left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1)
\end{aligned}
\tag{14}
$$

と表されることがわかる。式(14)に式(7a,b)を代入することによって、

$$
\begin{aligned}
&\Delta^{\circ}G^{cpm\to eqm}(T) = \Delta^{\circ}G^{cfm\to eqm}(T) + \left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1) \\
&= \frac{474}{497}\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1)\left[-\frac{1}{6}\left(\frac{T}{T_c}\right)^{3} - \frac{1}{135}\left(\frac{T}{T_c}\right)^{9} - \frac{1}{600}\left(\frac{T}{T_c}\right)^{15}\right] + \left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1) \\
&= \frac{1}{\alpha}\left[\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T} - \frac{474}{497}\left(\frac{1}{p}-1\right)\left\{\frac{1}{6}\left(\frac{T}{T_c}\right)^{3} + \frac{1}{135}\left(\frac{T}{T_c}\right)^{9} + \frac{1}{600}\left(\frac{T}{T_c}\right)^{15}\right\}\right]RT\ln(\beta+1), \quad (T \le T_c)
\end{aligned}
\tag{15a}
$$

$$
\begin{aligned}
&\Delta^{\circ}G^{cpm\to eqm}(T) = \Delta^{\circ}G^{cfm\to eqm}(T) + \left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1) \\
&= \Delta^{\circ}H^{cfm\to eqm}(T_c) - T\Delta^{\circ}S^{cfm\to eqm}(T_c) \\
&\quad + \frac{1}{\alpha}RT\ln(\beta+1)\left[-\frac{1}{10}\left(\frac{T}{T_c}\right)^{-5} - \frac{1}{315}\left(\frac{T}{T_c}\right)^{-15} - \frac{1}{1500}\left(\frac{T}{T_c}\right)^{-25} + \frac{711}{1260}\left(\frac{T_c}{T}\right) - \frac{518}{1125}\right] + \left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1) \\
&= -\frac{474}{497}\left(\frac{518}{675} - \frac{71}{120}\frac{T_c}{T}\right)\frac{1}{\alpha}\left(\frac{1}{p}-1\right)RT\ln(\beta+1) \\
&\quad + \frac{1}{\alpha}RT\ln(\beta+1)\left[-\frac{1}{10}\left(\frac{T}{T_c}\right)^{-5} - \frac{1}{315}\left(\frac{T}{T_c}\right)^{-15} - \frac{1}{1500}\left(\frac{T}{T_c}\right)^{-25} + \frac{711}{1260}\left(\frac{T_c}{T}\right) - \frac{518}{1125}\right] + \left(\alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right)\frac{1}{\alpha}RT\ln(\beta+1) \\
&= \frac{1}{\alpha}RT\ln(\beta+1)\left[\frac{711}{1260}\frac{T_c}{T} - \frac{518}{1125} - \frac{474}{497}\left(\frac{518}{675} - \frac{71}{120}\frac{T_c}{T}\right)\left(\frac{1}{p}-1\right) + \alpha - \frac{1}{p}\frac{79}{140}\frac{T_c}{T}\right] \\
&\quad - \frac{1}{\alpha}RT\ln(\beta+1)\left[\frac{1}{10}\left(\frac{T}{T_c}\right)^{-5} + \frac{1}{315}\left(\frac{T}{T_c}\right)^{-15} + \frac{1}{1500}\left(\frac{T}{T_c}\right)^{-25}\right] \\
&= -\frac{1}{\alpha}\left[\frac{1}{10}\left(\frac{T}{T_c}\right)^{-5} + \frac{1}{315}\left(\frac{T}{T_c}\right)^{-15} + \frac{1}{1500}\left(\frac{T}{T_c}\right)^{-25}\right]RT\ln(\beta+1), \qquad (T \ge T_c)
\end{aligned}
\tag{15b}
$$

を得る。ここで、

$$\frac{711}{1260}\frac{T_c}{T}-\frac{518}{1125}-\frac{474}{497}\left(\frac{518}{675}-\frac{71}{120}\frac{T_c}{T}\right)\left(\frac{1}{p}-1\right)+\alpha-\frac{1}{p}\frac{79}{140}\frac{T_c}{T}$$
$$=\frac{711}{1260}\frac{T_c}{T}-\frac{518}{1125}-\frac{474}{497}\frac{518}{675}\left(\frac{1}{p}-1\right)+\frac{474}{497}\frac{71}{120}\frac{T_c}{T}\left(\frac{1}{p}-1\right)+\alpha-\frac{1}{p}\frac{79}{140}\frac{T_c}{T}$$
$$=\frac{79}{140}\frac{T_c}{T}-\frac{518}{1125}-\frac{11692}{15975}\left(\frac{1}{p}-1\right)+\frac{79}{140}\frac{T_c}{T}\left(\frac{1}{p}-1\right)+\alpha-\frac{1}{p}\frac{79}{140}\frac{T_c}{T}$$
$$=\frac{79}{140}\frac{T_c}{T}+\frac{79}{140}\frac{T_c}{T}\left(\frac{1}{p}-1\right)-\frac{1}{p}\frac{79}{140}\frac{T_c}{T}=0$$

である。以上をまとめて、最終的に

$$G^{mg}=RT\ln(\beta+1)\cdot f(\tau)$$
$$f(\tau)=1-\frac{1}{\alpha}\left\{\frac{79\tau^{-1}}{140p}+\frac{474}{497}\left(\frac{1}{p}-1\right)\left(\frac{\tau^3}{6}+\frac{\tau^9}{135}+\frac{\tau^{15}}{600}\right)\right\},\qquad(\tau<1)$$
$$f(\tau)=-\frac{1}{\alpha}\left(\frac{\tau^{-5}}{10}+\frac{\tau^{-15}}{315}+\frac{\tau^{-25}}{1500}\right),\qquad(\tau>1)$$
$$\alpha\equiv\frac{518}{1125}+\frac{11692}{15975}\left(\frac{1}{p}-1\right)$$
$$p=0.28,\qquad(\text{for fcc})$$
$$p=0.40,\qquad(\text{for bcc})$$
$$\tau=T/T_c$$

を得る。

合金の場合、β と τ が組成の関数となる。例えば、A-B-C３元合金では、

$$T_{Curie}(c_A,c_B,c_C)={}^{\circ}T_Ac_A+{}^{\circ}T_Bc_B+{}^{\circ}T_Cc_C$$
$$+T_{AB}(c_A,c_B)c_Ac_B+T_{BC}(c_B,c_C)c_Bc_C+T_{CA}(c_C,c_A)c_Cc_A+T_{ABC}c_Ac_Bc_C$$
$$T_{ij}(c_i,c_j)=\sum_k {}^{\circ}T_{ij}(c_i-c_j)^k$$

$$\beta(c_A,c_B,c_C)={}^{\circ}\beta_Ac_A+{}^{\circ}\beta_Bc_B+{}^{\circ}\beta_Cc_C$$
$$+\beta_{AB}(c_A,c_B)c_Ac_B+\beta_{BC}(c_B,c_C)c_Bc_C+\beta_{CA}(c_C,c_A)c_Cc_A+\beta_{ABC}c_Ac_Bc_C$$
$$\beta_{ij}(c_i,c_j)=\sum_k {}^{\circ}\beta_{ij}(c_i-c_j)^k$$

と表される。${}^{\circ}T_X$ は純成分 X のキュリー温度で、${}^{\circ}\beta_X$ は純成分 X の１原子当たりの飽和磁化（ボーア磁子単位で、絶対 0 度における値）である。純鉄では ${}^{\circ}T_{Fe}^{bcc}=1043(K)$ および ${}^{\circ}\beta_{Fe}^{bcc}=2.22$ となる。