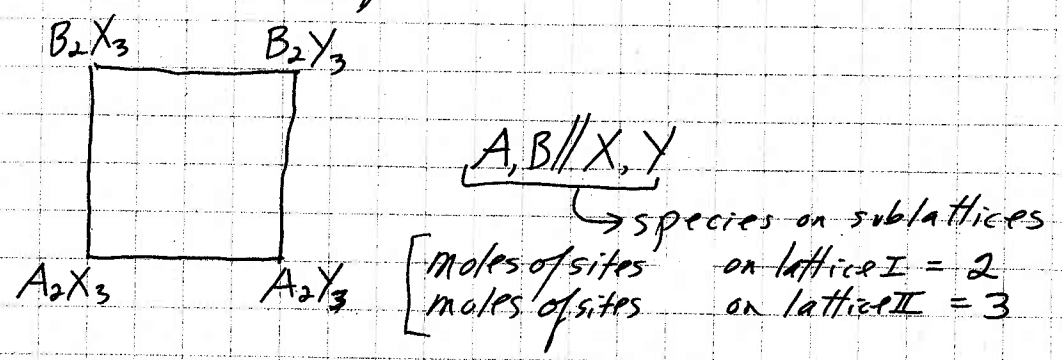


COMPOUND ENERGY FORMALISM (CEF)

Example for 2 sublattices

Always a fixed number of sites per lattice.



$$\begin{aligned}
 g(\text{per mole}) = & (y_A y_X g_{A_2X_3}^0 + y_A y_Y g_{A_2Y_3}^0 + y_B y_X g_{B_2X_3}^0 + y_B y_Y g_{B_2Y_3}^0) \\
 & + RT (y_A \ln y_A + y_B \ln y_B) + 3RT (y_X \ln y_X + y_Y \ln y_Y) \\
 & + \sum_i L_{AB|X} (y_A - y_B) y_X y_Y + \sum_i L_{AB|Y} (y_A - y_B) y_X y_Y + \sum_i L_{A|XY} (y_X - y_Y) y_A y_X y_Y \\
 & + \sum_i L_{B|XY} (y_X - y_Y) y_B y_X y_Y + \sum_i L_{AB|XY} y_A y_B y_X y_Y
 \end{aligned}$$

(compare to Eqs. (1-119) in the chapter in Phase Transformations in Materials)

where:

$$\begin{cases}
 y_A = \frac{\text{molar}}{\text{site}} \text{ fraction} = M_A / (M_A + M_B) = 1 - y_B \\
 y_X = \frac{\text{molar}}{\text{site}} \text{ fraction} = M_X / (M_X + M_Y) = 1 - y_Y
 \end{cases}$$

Not to be confused with Equivalent Fractions X_i which are not used in the CEF. (In my notation $y_i = X_i$)

$g_{A_2X_3}^0$ = molar Gibbs energy of one mole of A_2X_3 (not one equivalent)

A_2X_3, A_2Y_3, \dots are "end-members"
There is one end-member for each lattice pair.

Ex: $A, B, C // X, Y, Z, W$ (Number of end-members) = $3 \times 4 = 12$

- Extension to 3 or more sub-lattices is evident.

Δg_{AB}) at $X_A = X_B = 1/2$. Suppose now that the experimental data indicate that the extremum in G^E occurs, for example, close to $X_B = 1/4$ rather than at $X_B = 1/2$. We could shift the extremum in the usual way by making Δg_{AB} a linear function of composition (sub-regular model). However, this can often result in poor fitting of the partial properties at compositions near $X_B = 1.0$. For example, in the case where $G^E < 0$, if we wish to shift the minimum to $X_B = 1/4$ by using the sub-regular model, then we must set $G^E = a + bX_B$ where $a < 0$ and $b > 0$. This causes the partial excess Gibbs energy of component B to increase, and even to become positive, at high values of X_B .

Another way to shift the composition of the minimum without this undesirable side-effect is to keep Δg_{AB} constant and to choose Z_A and Z_B such that $Z_B/Z_A = 3$. Examples are given for the Mn-Y and Ce-Mn systems in Sections 3.1 and 3.3.

2.2 Solid Solutions

All solid solutions were modeled using the well-known Compound Energy Formalism (CEF) [2001Hil]. For example, the Laves phase $(\text{Mg}, \text{Y})_2^a [\text{Mg}, \text{Y}]_1^b$ has two sublattices, the a and b lattices, with Mg and Y on both lattices. Its Gibbs energy in the CEF is given by

$$\begin{aligned}
 G = & y_{\text{Mg}}^a y_{\text{Mg}}^b G_{\text{Mg:Mg}} + y_{\text{Mg}}^a y_{\text{Y}}^b G_{\text{Mg:Y}} + y_{\text{Y}}^a y_{\text{Mg}}^b G_{\text{Y:Mg}} + y_{\text{Y}}^a y_{\text{Y}}^b G_{\text{Y:Y}} \\
 & + 2RT \left(y_{\text{Mg}}^a \ln y_{\text{Mg}}^a + y_{\text{Y}}^a \ln y_{\text{Y}}^a \right) + RT \left(y_{\text{Mg}}^b \ln y_{\text{Mg}}^b + y_{\text{Y}}^b \ln y_{\text{Y}}^b \right) \quad (\text{Eq 7}) \\
 & + \sum_{i,j,k} y_i^a y_j^a y_k^b L_{ij:k} + \sum_{i,j,k} y_k^a y_i^b y_j^b L_{k:ij}
 \end{aligned}$$

where y_i^a , y_i^b are site fractions of component i on each sublattice, $G_{i:j}$ is the Gibbs energy of end-member $(i)_2^a [j]_1^b$. A Gibbs energy $G_{i:j}$ is required for every possible end-member pair. $L_{ij:k}$ and $L_{k:ij}$ are interaction parameters between components i and j on one sub-lattice when the other sub-lattice is occupied only by k .

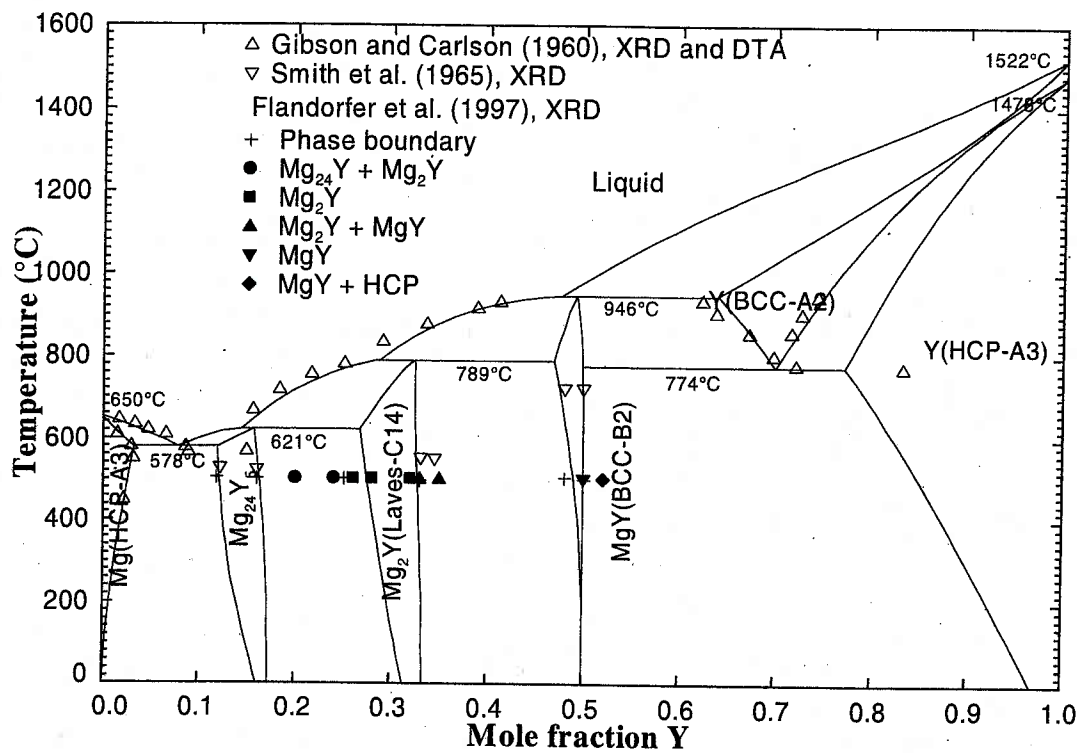


Fig. 17 Optimized phase diagram of the Mg-Y system.

Table 2. Optimized model parameters of all binary phases in the Mg-Ce-Mn-Y system (J/mole)

Liquoid Alloy			
Coordination Numbers ^(a)			
<i>i</i>	<i>j</i>	<i>Z_{ij}ⁱ</i>	<i>Z_{ij}^j</i>
Ce	Mg	6	2
Ce	Mn	6	3
Ce	Y	6	6
Mg	Mn	6	6
Mg	Y	3	6
Mn	Y	2	6
Laves-C14 (MgZn₂-type): (Ce, Mg, Mn, Y)₂[Ce, Mg, Mn, Y]			
<i>G</i> (Ce:Ce)	= 3 <i>G</i> (Ce,FCC-A1) + 30,000		
<i>G</i> (Ce:Mg)	= 2 <i>G</i> (Ce,FCC-A1) + <i>G</i> (Mg,HCP-A3) + 41,840		
<i>G</i> (Ce:Mn)	= 2 <i>G</i> (Ce,FCC-A1) + <i>G</i> (Mn,CBCC-A12) + 41,840		
<i>G</i> (Ce:Y)	= 2 <i>G</i> (Ce,FCC-A1) + <i>G</i> (Y,HCP-A3) + 41,840		
<i>G</i> (Mg:Ce)	= 2 <i>G</i> (Mg,HCP-A3) + <i>G</i> (Ce,FCC-A1) - 43,264.73 + 10.35 <i>T</i>		
<i>G</i> (Mg:Mg)	= 3 <i>G</i> (Mg,HCP-A3) + 15,000 ^(b)		
<i>G</i> (Mg:Mn)	= 2 <i>G</i> (Mg,HCP-A3) + <i>G</i> (Mn,CBCC-A12) + 83,680		
<i>G</i> (Mg:Y)	= 2 <i>G</i> (Mg,HCP-A3) + <i>G</i> (Y,HCP-A3) - 37,548.96 + 6.6 <i>T</i>		
<i>G</i> (Mn:Ce)	= 2 <i>G</i> (Mn,CBCC-A12) + <i>G</i> (Ce,FCC-A1) + 41,840		
<i>G</i> (Mn:Mg)	= 2 <i>G</i> (Mn,CBCC-A12) + <i>G</i> (Mg,HCP-A3) + 83,680		
Laves-C15 (Cu₂Mg-type): (Ce, Mg, Mn, Y)₂[Ce, Mg, Mn, Y]			
<i>G</i> (Ce:Ce)	= 3 <i>G</i> (Ce,FCC-A1) + 62,760		
<i>G</i> (Ce:Mg)	= 2 <i>G</i> (Ce,FCC-A1) + <i>G</i> (Mg,HCP-A3) + 41,840		
<i>G</i> (Ce:Mn)	= 2 <i>G</i> (Ce,FCC-A1) + <i>G</i> (Mn,CBCC-A12) + 41,840		
<i>G</i> (Ce:Y)	= 2 <i>G</i> (Ce,FCC-A1) + <i>G</i> (Y,HCP-A3) + 41,840		
<i>G</i> (Mg:Ce)	= 2 <i>G</i> (Mg,HCP-A3) + <i>G</i> (Ce,FCC-A1) - 47,449 + 10.35 <i>T</i>		
<i>G</i> (Mg:Mg)	= 3 <i>G</i> (Mg,HCP-A3) + 15,000 ^(b)		
<i>G</i> (Mg:Mn)	= 2 <i>G</i> (Mg,HCP-A3) + <i>G</i> (Mn,CBCC-A12) + 49,340		
<i>G</i> (Mg:Y)	= 2 <i>G</i> (Mg,HCP-A3) + <i>G</i> (Y,HCP) - 20,920		
<i>G</i> (Mn:Ce)	= 2 <i>G</i> (Mn,CBCC-A12) + <i>G</i> (Ce,FCC-A1) + 41,840		
<i>G</i> (Mn:Mg)	= 2 <i>G</i> (Mn,CBCC-A12) + <i>G</i> (Mg,HCP-A3) + 49,340		

$G(\text{Mn}:\text{Mn}) = 3G(\text{Mn}, \text{CBCC-A12}) + 3,000^{(c)}$	$G(\text{Mn}:\text{Mn}) = 3G(\text{Mn}, \text{CBCC-A12}) + 83,680$
$G(\text{Mn}:\text{Y}) = 2G(\text{Mn}, \text{CBCC-A12}) + G(\text{Y}, \text{HCP-A3}) + 14,983.568 + 12.577$	$G(\text{Mn}:\text{Y}) = 2G(\text{Mn}, \text{CBCC-A12}) + G(\text{Y}, \text{HCP-A3}) - 7,200 + 12.577$
$G(\text{Y}:\text{Ce}) = 2G(\text{Y}, \text{HCP-A3}) + G(\text{Ce}, \text{FCC-A1}) + 41,840$	$G(\text{Y}:\text{Ce}) = 2G(\text{Y}, \text{HCP-A3}) + G(\text{Ce}, \text{FCC-A1}) + 41,840$
$G(\text{Y}:\text{Mg}) = 2G(\text{Y}, \text{HCP-A3}) + G(\text{Mg}, \text{HCP-A3}) + 67,548.96 - 6.67$	$G(\text{Y}:\text{Mg}) = 2G(\text{Y}, \text{HCP-A3}) + G(\text{Mg}, \text{HCP}) + 88,220$
$G(\text{Y}:\text{Mn}) = 2G(\text{Y}, \text{HCP-A3}) + G(\text{Mn}, \text{CBCC-A12}) + 23,936 - 12.577$	$G(\text{Y}:\text{Mn}) = 2G(\text{Y}, \text{HCP-A3}) + G(\text{Mn}, \text{CBCC-A12}) + 174,560 - 12.577$
$G(\text{Y}:\text{Y}) = 3G(\text{Y}, \text{HCP-A3}) + 15,000^{(d)}$	$G(\text{Y}:\text{Y}) = 3G(\text{Y}, \text{HCP-A3}) + 125,520$
$L_{\text{Mg}, \text{Y}:\text{Mg}} = L_{\text{Mg}, \text{Y}:\text{Y}} = 21,000^{(d)}$	
$L_{\text{Mg}:\text{Mg}, \text{Y}} = L_{\text{Y}:\text{Mg}, \text{Y}} = -21,000 + 7.57^{(d)}$	
BCC-B2 (CsCl-type): (Mg, Mn)[Ce, Mg, Y]	
$G(\text{Mg}:\text{Ce}) = G(\text{Mg}, \text{HCP-A3}) + G(\text{Ce}, \text{FCC-A1}) - 28,600 + 5.087$	$G(\text{Ce}, \text{HCP-A3}) = G(\text{Ce}, \text{FCC-A1}) + 5,230$
$G(\text{Mg}:\text{Mg}) = 2G(\text{Mg}, \text{HCP-A3}) + 8,368$	$L_{\text{Ce}, \text{Mg}} = -24,476.4$
$G(\text{Mg}:\text{Y}) = G(\text{Mg}, \text{HCP-A3}) + G(\text{Y}, \text{HCP-A3}) - 29,031.03 + 6.067$	$L_{\text{Ce}, \text{Mn}} = 62,760$
$G(\text{Mn}:\text{Ce}) = G(\text{Mn}, \text{CBCC-A12}) + G(\text{Ce}, \text{FCC}) + 83,680$	$L_{\text{Ce}, \text{Y}} = 0$
$G(\text{Mn}:\text{Mg}) = G(\text{Mn}, \text{CBCC-A12}) + G(\text{Mg}, \text{HCP-A3}) + 41,840$	$L_{\text{Mg}, \text{Mn}} = 37,148.1 - 1.81037^{(e)}$
$G(\text{Mn}:\text{Y}) = G(\text{Mn}, \text{CBCC-A12}) + G(\text{Y}, \text{HCP-A3}) - 836.8$	$L_{\text{Mg}, \text{Y}} = -27,031.25 + 13.957 - 2,836.21(X_{\text{Mg}} - X_{\text{Y}})^{(d)}$
	$L_{\text{Mn}, \text{Y}} = 62,760$
BCC-A2 : (Ce, Mg, Mn, Y)	
$L_{\text{Ce}, \text{Mg}} = -15,594.01 - 9.757 + 9,340.62(X_{\text{Ce}} - X_{\text{Mg}})$	$L_{\text{Ce}, \text{Mg}} = -9,273.15 - 2.077$

$L_{\text{Ce,Mn}}$	$= 35,982.4 + 4,184(X_{\text{Ce}} - X_{\text{Mn}})$	$L_{\text{Ce,Mn}}$	$= 41,840 + 6,276(X_{\text{Ce}} - X_{\text{Mn}})$
$L_{\text{Ce,Y}}$	$= 2,092$	$L_{\text{Ce,Y}}$	$= 0$
$L_{\text{Mg,Mn}}$	$= 83,680$	$L_{\text{Mg,Mn}}$	$= 83,680$
$L_{\text{Mg,Y}}$	$= -48,242.98 + 25.5T$	$L_{\text{Mg,Y}}$	$= 62,760$
$L_{\text{Mn,Y}}$	$= 62,760$	$L_{\text{Mn,Y}}$	$= 62,760$
DHCP-A3' : (Ce, Y)			
$G(\text{Ce})$	$= G(\text{Ce,FCC-A1}) - 1,200 + 4.2T$	$G(\text{Mg:Mg:Y})$	$= 28G(\text{Mg,HCP-A3}) + G(\text{Y,HCP-A3}) - 21,170.12$
$G(\text{Y})$	$= G(\text{Y,HCP-A3})^{(f)} + 6,276$	$G(\text{Mg:Y:Y})$	$= 24G(\text{Mg,HCP-A3}) + 5G(\text{Y,HCP-A3}) - 227,282.29$ $+ 36.53T^{(d)}$
$L_{\text{Ce,Y}}$	$= -8,840.34 - 4.2T$		

Stoichiometric compounds

Compound	$H_{298.15\text{K}}^{\circ}$ (J/mol)	$S_{298.15\text{K}}^{\circ}$ (J/mol·K)	C_p (J/mol·K)
CeMg_{12}	-139,880.0	377.01	$C_p = C_p(\text{Ce,FCC-A1}) + 12 \times C_p(\text{Mg,HCP-A3})$
$\text{Ce}_2\text{Mg}_{17}$	-215,906.0	591.63	$C_p = 2 \times C_p(\text{Ce,FCC-A1}) + 17 \times C_p(\text{Mg,HCP-A3})$
$\text{Ce}_5\text{Mg}_{41}$	-576,002.0	1,387.78	$C_p = 5 \times C_p(\text{Ce,FCC-A1}) + 41 \times C_p(\text{Mg,HCP-A3})$
CeMg_3	-76,000.0	140.97	$C_p = C_p(\text{Ce,FCC-A1}) + 3 \times C_p(\text{Mg,HCP-A3})$
Mn_{23}Y_6	-153,700.0	1,046.82	$C_p = 23 \times C_p(\text{Mn,CBCC-A12}) + 6 \times C_p(\text{Y,HCP-A3})$
Mn_{12}Y	-32,695.9	440.59	$C_p = 12 \times C_p(\text{Mn,CBCC-A12}) + C_p(\text{Y,HCP-A3})$

(a) For all pure elements (Ce, Mg, Mn and Y) $Z_{ii}^i = 6$; (b) [1998Agal]; (c) [1998Sau]; (d) [2003Fab]; (e) [2005Gro]; (f) $G(\text{Y,HCP-A3})$ from [2000Din]

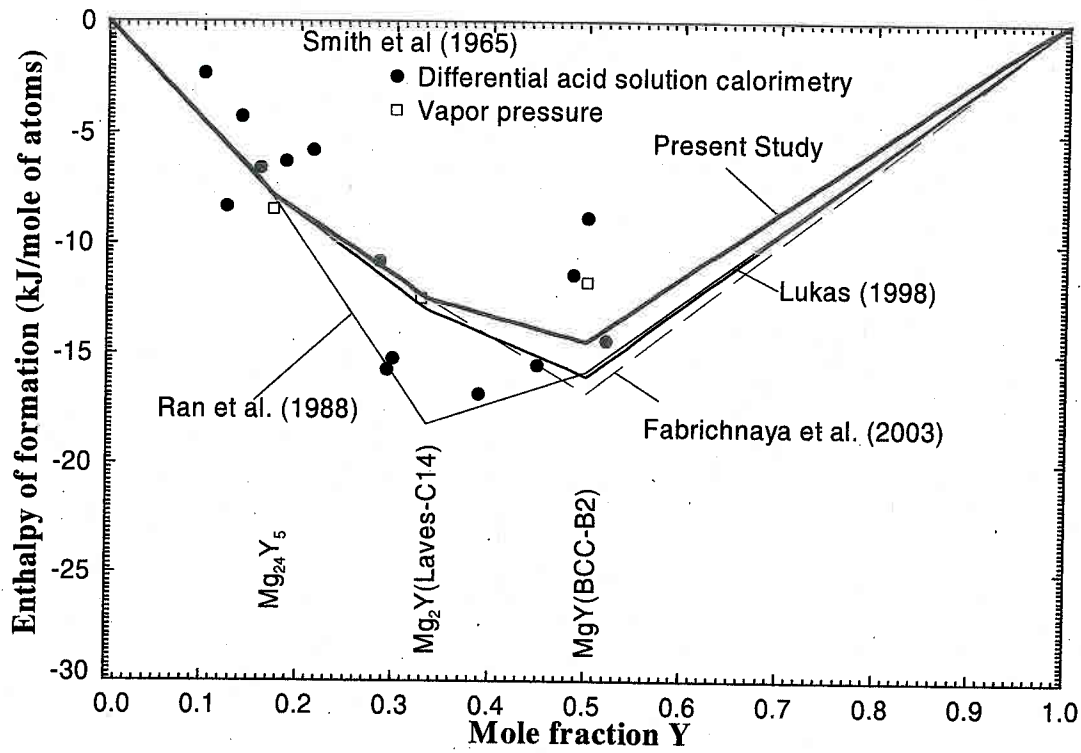
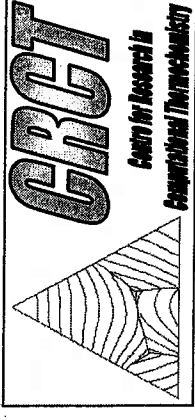


Fig. 22 Enthalpy of formation of intermetallic compounds in the Mg-Y system at 25°C.

Sublattice Model – Compound Energy Formalism



- Used for solid solutions

- Example: Spinel Solution (A^{2+} , A^{3+} , B^{2+} , C^{3+} , ...) [A^{2+} , A^{3+} , B^{2+} , C^{3+} , ...] O_4

$$G = \sum_i \sum_j Y'_i Y''_j G_{ij} - TS^{config} + G^E$$

where: Y'_i , Y''_j = site fractions on first and second sublattices

$$S^{config} = -R \left(\sum_i Y'_i \ln Y'_i + 2 \sum_j Y''_j \ln Y''_j \right) = \text{configurational entropy}$$

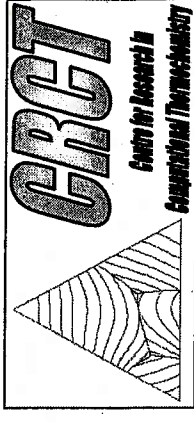
$$G^E = \sum_i \sum_j \sum_k Y'_i Y'_j Y''_k L_{ij:k} + \sum_i \sum_j \sum_k Y'_i Y''_j Y''_k L_{k:ij}$$

(usually $G^E = 0$ or contains only a very few small parameters L_{ijk})

G_{ij} = “end-member Gibbs energies” (one for each ion pair)

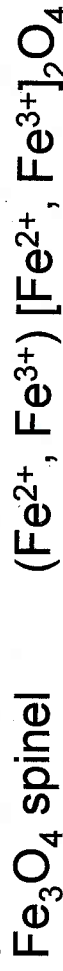
The G_{ij} are the main parameters of the formalism.

(Sublattice Model – Compound Energy Formalism)



- End-member Gibbs energies G_{ij} are the formalism parameters.
- Some may be equal to Gibbs energies of real compounds,
- In other cases, certain linear combinations of the G_{ij} have physical significance, and these combinations are the model parameters.

■ Example:



- Four end-member Gibbs energies:

$$G_{\text{Fe}^{2+}\text{Fe}^{2+}}, G_{\text{Fe}^{2+}\text{Fe}^{3+}}, G_{\text{Fe}^{3+}\text{Fe}^{2+}}, G_{\text{Fe}^{3+}\text{Fe}^{3+}}$$

$G_{\text{Fe}^{2+}\text{Fe}^{3+}}$ = Gibbs energy of hypothetical normal Fe_3O_4

$$I = G_{\text{Fe}^{3+}\text{Fe}^{3+}} + G_{\text{Fe}^{3+}\text{Fe}^{2+}} - 2G_{\text{Fe}^{2+}\text{Fe}^{3+}}$$

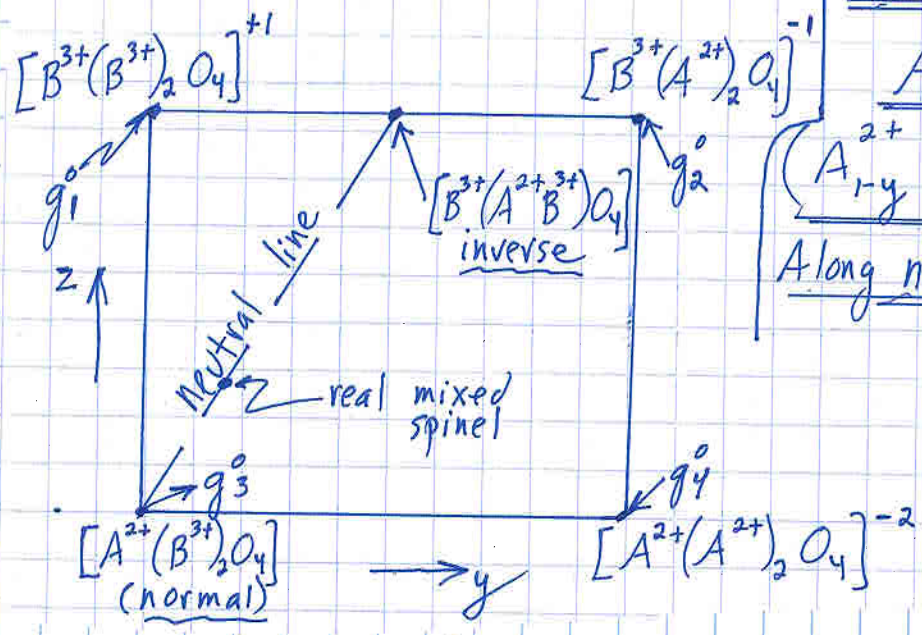
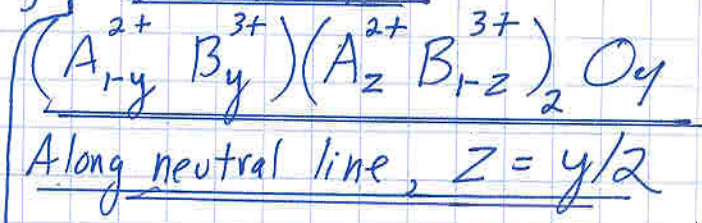
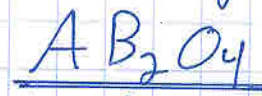
= model parameter related to degree of inversion

$$\Delta = G_{\text{Fe}^{2+}\text{Fe}^{2+}} + G_{\text{Fe}^{3+}\text{Fe}^{3+}} - G_{\text{Fe}^{3+}\text{Fe}^{2+}} - G_{\text{Fe}^{2+}\text{Fe}^{3+}}$$

= model parameter related to reciprocal exchange of nearest-neighbor pairs

($G_{\text{Fe}^{3+}\text{Fe}^{2+}}$ can be arbitrarily set equal to $G_{\text{Fe}^{2+}\text{Fe}^{3+}}$)

Mixed Spinel



$$g = [y(1-y/2)g_4^0 + y(y/2)g_2^0 + (1-y)(1-y/2)g_3^0 + (1-y)(y/2)g_1^0] + RT [y \ln y + (1-y) \ln (1-y)] + 2RT [y/2 \ln y/2 + (1-y/2) \ln (1-y/2)]$$

$$A_T^{2+} + B_O^{3+} = B_T^{3+} + A_O^{2+}; \Delta G^{\text{site exchange}} = (E_{A_O^{2+}} + E_{B_T^{3+}} - E_{A_T^{2+}} - E_{B_O^{3+}})$$

Arbitrarily set $(E_{A_T^{2+}}) = (E_{A_O^{2+}}) = (E_{B_O^{3+}}) = C$

where the E 's are site energies

where: $g_3^0 = [E_{A_T^{2+}} + 2E_{B_O^{3+}}] = 3C$ [Very simplified model.]

$g_2^0 = [E_{B_T^{3+}} + 2E_{A_O^{2+}}] = 3C + \Delta G^{\text{site exchange}}$

and similarly for g_1^0 and g_4^0

Then: $g = (1-y)(1-y/2)(3C) + (1-y)(y/2)(\Delta G^{\text{site xch}} + 3C) + y(1-y/2)(3C) + y(y/2)(\Delta G^{\text{site xch}} + 3C) + RT(\dots) + 2RT(\dots)$

$(dg/dy) = 0 \Rightarrow RT \ln \frac{y/(y/2)}{(1-y)(1-y/2)} + \Delta G^{\text{site xch}} = 0$

$y^2/(1-y)(2-y) = \exp(-\Delta G^{\text{site exchange}}/RT)$

Solve for y to get degree of inversion.

Then choose C so that $g = g_{AB_2O_4}(\text{real})$