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Thermodynamic determination of the cation distribution in $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ ferrites

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Abstract

The cation distribution in the spinel ferrite system $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75$ and $\gamma = 0.137$) has been calculated analytically in complete form as a function of thermodynamic parameters. A generalized theoretical framework based on the O'Neill–Navrotsky model and Newton methods was used to solve a multicomponent system for up to 10 cation species. The relationship between the cation distribution and composition is given. The results are shown to agree with the available experimental results.

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1. Introduction

Because the theoretical interpretation of the chemical and physical properties (e.g., magnetic, semiconducting, catalytic) of spinel ferrites strongly depends on the sites assigned to the cations, determination of the cation distribution between the tetrahedral and octahedral sites for these compounds has been investigated extensively [1–5].

The calculation, using thermodynamics, of the cation distribution in the structure of spinel oxides such as $\text{A}_{1-\gamma}\text{B}_{2+\gamma}\text{O}_4$ has been attempted by several authors. Schmalzried [6] first employed the defect chemical scheme to calculate the cation distribution as a function of the thermodynamic parameters. This method included the following equations: mass-balance, site-ratio-balance, charge-balance, cation site exchange reaction equilibrium between the tetrahedral and octahedral sublattices, valence exchange equilibrium among multi-valent cations, and external equilibrium with the atmosphere. O'Neill et al. [7] developed a thermodynamic model with non-linear change in enthalpy for a binary spinel solid solution. Mason et al. [8] replaced one of the internal equilibrium constraints by thermoelectric power and solved for the six-cation species. When the number

of unknowns increases to eight, the algebra appears too involved to be handled analytically even with the addition of the thermoelectric power information.

In the case of the $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ system, the number of unknowns increases to ten since two kinds of cations (Fe and Mn) with two oxidation states (+2 and +3) and one fixed nickel valence (+2) are distributed over the two sublattices. In this paper, we demonstrate that thermodynamic parameters can appropriately be used to study the distribution of cations between tetrahedral and octahedral sites if a reasonable assumption is made.

2. Theory

We start with the interchange reaction:



where A and B denote different ions, parentheses () the tetrahedral sites and brackets [] the octahedral sites. If we define y as the fraction of B ions in the tetrahedral sites, the reaction equilibrium constant K is:

$$K = \frac{y^2}{(1-y)(2-y)} \quad (2)$$

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and the free energy ΔG of the cation distribution is

$$\Delta G = -RT \ln K = -RT \ln \left(\frac{y^2}{(1-y)(2-y)} \right). \quad (3)$$

It is well known that

$$\Delta G = \Delta U - T\Delta S + \Delta(PV), \quad (4)$$

where ΔU is the internal energy change, ΔS the non-configurational entropy change, T temperature, and $\Delta(PV)$ is the change of the product of pressure (P) and volume (V). Because the values of ΔS and $\Delta(PV)$ are very small [7], they can be ignored when we calculate ΔG .

Dunitz and Orgel [9] showed that a number of the observed cation distributions in spinels can be explained by crystal field theory. A transition metal ion will generally have a crystal field stabilization energy (CFSE) in octahedral coordination greater than that in tetrahedral coordination, and the difference in CFSE, ΔU_S , is given simply as a linear function of y : $\Delta U_S = y(\Delta\text{CFSE}(A) - \Delta\text{CFSE}(B))$. From lattice and electrostatic energy considerations, O'Neill et al. [10] showed that ΔU_S has a quadratic dependence on y and takes the form

$$\Delta U_S = \alpha y + \beta y^2, \quad (5)$$

where the constants α and β depend on the relative site preference of the cations involved, and O'Neill et al. also related the internal energy ΔU to ΔU_S by

$$\Delta U = \partial(\Delta U_S)/\partial y. \quad (6)$$

Substituting Eqs. (6) and (5) into Eqs. (4) and (3), we obtain

$$\ln K = \ln \left(\frac{y^2}{(1-y)(2-y)} \right) = -\frac{\alpha + 2\beta y}{RT}. \quad (7)$$

We note that Eq. (7) was also derived differently, as follows, by O'Neill et al. [10] using the configurational entropy appropriate to an assumption of complete random mixing of ions on each site:

$$S_c = -R \sum b^s N_i^s \ln N_i^s, \quad (8)$$

where N_i^s is the fraction of species i in site s and b^s is the number of sites of type “ s ” per formula unit. Writing Eq. (8) for AB_2O_4 spinel:

$$S_c = -R[y \ln y + (1-y) \ln(1-y) + y \ln(y/2) + (2-y) \ln(1-y/2)]. \quad (9)$$

O'Neill et al then obtained Eq. (7).

3. Results and discussion

The spinel formula unit of $Ni_xMn_{1-\gamma-x}Fe_{2+\gamma}O_4$ can be represented by the formula

$$(\text{Ni}_a^{2+} \text{Mn}_b^{2+} \text{Fe}_c^{2+} \text{Mn}_d^{3+} \text{Fe}_e^{3+}) \times [\text{Ni}_f^{2+} \text{Mn}_g^{2+} \text{Fe}_h^{2+} \text{Mn}_i^{3+} \text{Fe}_j^{3+}] \text{O}_4, \quad (10)$$

where again the parentheses enclose the tetrahedral sites and brackets the octahedral sites. Oxygen non-stoichiometry is ignored since the cation distribution is insensitive to the oxygen partial pressure under thermodynamic equilibrium at elevated temperature [11]. According to the defect chemical approach, the following equations can be derived. Here we differ from previous work [8] by including 10 rather than 6 variables.

The two site balance equations are

$$\sum_{k=a}^e k = 1 \quad (\text{Tetrahedral}) \quad (11)$$

and

$$\sum_{k=f}^j k = 2 \quad (\text{Octahedral}). \quad (12)$$

The charge balance equation is

$$2(a + b + c + f + g + h) + 3(d + e + i + j) = 8 \quad (13)$$

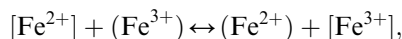
The mass balance equations are, using x for the mole fraction of NiFe_2O_4 :

$$a + f = x \quad (14)$$

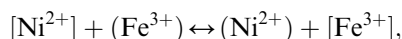
and

$$b + d + g + i = 1 - x - \gamma \quad (15)$$

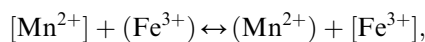
Eqs. (11)–(15) represent conservation reactions. Only two site constraints are established independently and consequently the three mass balance equations (Mn, Ni and Fe) become redundant. If the three mass balance equations were taken independently instead, the two site balance constraints would become redundant. Using Eqs. (11)–(15), we can rewrite the formula unit (formula (10)) in terms of the variables b, c, d, e and g only (x and γ must be given). Therefore, we need another five independent equations to solve the problem. Table 1 lists the resulting expressions for each species in the formula unit, from which the following five distribution reactions can be derived using the same notation convention for the sublattices.



$$K_1 = \frac{cj}{eh} = \frac{c(1+x+b+g-e+\gamma)}{e(1-x-b-c-g)}, \quad (16)$$



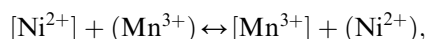
$$K_2 = \frac{aj}{ef} = \frac{(1-b-c-d-e)(1+x+b+g-e+\gamma)}{e(x+b+c+d+e-1)}, \quad (17)$$



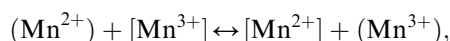
$$K_3 = \frac{bj}{eg} = \frac{b(1+x+b+g-e+\gamma)}{eg}, \quad (18)$$

Table 1
Species concentrations per formula unit

Ions	Tetrahedral	Octahedral	Total
Ni ²⁺	$a = 1 - b - c - d - e$	$f = x + b + c + d + e - 1$	x
Mn ²⁺	b	g	$b + g$
Fe ²⁺	c	$h = 1 - x - b - c - g$	$1 - x - b - g$
Mn ³⁺	d	$i = 1 - x - b - d - g - \gamma$	$1 - x - b - g - \gamma$
Fe ³⁺	e	$j = 1 + x + b + g - e + \gamma$	$1 + x + b + g + \gamma$
Total	1	2	3



$$K_4 = \frac{ia}{df} = \frac{(1-x-b-d-g-\gamma)(1-b-c-d-e)}{d(x+b+c+d+e-1)}, \quad (19)$$



$$K_5 = \frac{gd}{bi} = \frac{gd}{b(1-x-b-d-g-\gamma)}. \quad (20)$$

Combining Eqs. (11)–(20), we can draw the conclusion that, if K_1, K_2, K_3, K_4 , and K_5 are known, the overall cation distribution of $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ can be derived, in principle. However, the values of these cation distribution constants are not available for the mixed spinel ferrites. Fortunately, it has been proposed that the α and β terms for a given interchange reaction (Eq. (1)) are composition-independent in mixed spinels [7,8,11], and therefore we can use the distribution constants of end member compounds to resolve the problem.

Using Eq. (7) and expressing energy in kJ mol^{-1} , O'Neill et al. [10] showed: $-RT \ln K_1 = 25 - 2 \times 20e$, $-RT \ln K_2 = -28 + 0.009T - 2 \times 20e$, $-RT \ln K_3 = 32.42 - 2 \times 17.04e$, and $-RT \ln K_4 = 25.1 - 2 \times 20.1d$. We also need a value for K_5 and, in the absence of any other published values, we take the value of K_5 derived by Pelton et al. [12] from the high-temperature phase equilibria: $K_5 = \exp(-83.6 \text{ kJ}/RT)$, where RT is also in kJ mol^{-1} units.

In order to solve the equations, we use Newton's method. Setting

$$F(b, c, d, e, g) = \begin{cases} K_1 e h - c(1 + x + b + g - e + \gamma) \\ K_2 e(x + b + c + d + e - 1) \\ -(1 - b - c - d - e)(1 + x + b + g - e + \gamma) \\ K_3 e g - b(1 + x + b + g + \gamma) \\ K_4 d(x + b + c + d + e - 1) \\ -(1 - x - b - d - g - \gamma)(1 - b - c - d - e) \\ K_5 b(1 - x - b - d - g - \gamma) - gd \end{cases} \quad (21)$$

and

$$F'(b, c, d, e, g) = \begin{bmatrix} \frac{\partial f_1}{\partial b} & \frac{\partial f_1}{\partial c} & \dots & \frac{\partial f_1}{\partial e} \\ \frac{\partial f_2}{\partial b} & \frac{\partial f_2}{\partial c} & \dots & \frac{\partial f_2}{\partial e} \\ \dots & \dots & \dots & \dots \\ \frac{\partial f_5}{\partial b} & \frac{\partial f_5}{\partial c} & \dots & \frac{\partial f_5}{\partial e} \end{bmatrix} \quad (22)$$

the iteration formulae are

$$\phi(x) = x - (F'(b, c, d, e, g))^{-1} F(b, c, d, e, g) \quad (23)$$

and

$$F'(b, c, d, e, g) \nabla x^k = -f(b, c, d, e, g). \quad (24)$$

After solving for ∇x^k , we calculate a new x^{k+1} by letting $x^{k+1} = x^k + \nabla x^k$. The process is repeated until convergence is obtained.

The values of γ were investigated by Han-ill Yoo et al. [11]. With $\gamma = 0.137$, all compositions correspond to a cubic structure in the spinel single-phase field.

So, using computer-assisted solution of the above equations, the cation distributions which are given in Tables 2 and 3 were uniquely determined for $\gamma = 0.137$ at temperature 900°C and 1200°C respectively.

For $x = 0$ and $\gamma = 0.137$ at 900°C , the distribution we find:

$$(\text{Mn}_{0.2692}^{2+} \text{Fe}_{0.0707}^{2+} \text{Fe}_{0.6600}^{3+}) \times [\text{Mn}_{0.5347}^{2+} \text{Mn}_{0.0700}^{3+} \text{Fe}_{0.1364}^{2+} \text{Fe}_{1.2700}^{3+}] \quad (25)$$

is consistent with the distribution determined by Han-ill Yoo et al. using experimental thermoelectric power [11]:

$$(\text{Mn}_{0.268}^{2+} \text{Fe}_{0.061}^{2+} \text{Fe}_{0.671}^{3+}) [\text{Mn}_{0.515}^{2+} \text{Mn}_{0.081}^{3+} \text{Fe}_{0.118}^{2+} \text{Fe}_{1.286}^{3+}]. \quad (26)$$

The agreement for the site occupancies is exceptionally good—within 16% for each site but generally much closer—justifying our application of thermodynamic determination of the cation distributions.

As can be seen in the plots of the cation distributions for 1200°C (Fig. 1), in most cases the cation distributions have nearly linear composition dependence on Ni content. It can also be seen that the fraction of tetrahedral Fe^{3+} ions increases at both temperatures, whereas the fraction of octahedral Fe^{3+} ions decreases

Table 2
Cation distribution for $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ ($\gamma = 0.137$) spinel using thermodynamic method (1200°C)

x	Tetrahedral					Octahedral				
	Ni^{2+}	Mn^{2+}	Fe^{2+}	Mn^{3+}	Fe^{3+}	Ni^{2+}	Mn^{2+}	Fe^{2+}	Mn^{3+}	Fe^{3+}
0	—	0.0790	0.2309	0.000	0.6901	—	0.3851	0.3049	0.3989	0.9111
0.25	0.0004	0.0900	0.1492	0.000	0.7604	0.2496	0.3731	0.1375	0.1499	1.0899
0.5	0.0013	0.0799	0.0866	0.000	0.8322	0.4987	0.2681	0.0632	0.0148	1.1552
0.75	0.0129	0.0201	0.1071	0.000	0.8599	0.7371	0.0589	0.0640	0.0340	1.1060

Table 3
Cation distribution for $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ ($\gamma = 0.137$) spinel using thermodynamic method (900°C)

x	Tetrahedral					Octahedral				
	Ni^{2+}	Mn^{2+}	Fe^{2+}	Mn^{3+}	Fe^{3+}	Ni^{2+}	Mn^{2+}	Fe^{2+}	Mn^{3+}	Fe^{3+}
0	—	0.2692	0.0707	0.0000	0.6601	—	0.5237	0.1364	0.0701	1.2698
0.25	0.0020	0.0890	0.1389	0.0000	0.7701	0.2480	0.4110	0.1111	0.1130	1.1169
0.5	0.0024	0.0510	0.1465	0.0000	0.8001	0.4976	0.2047	0.0977	0.1073	1.0927
0.75	0.0034	0.0041	0.1526	0.0000	0.8399	0.7466	0.0134	0.0800	0.0956	1.0644

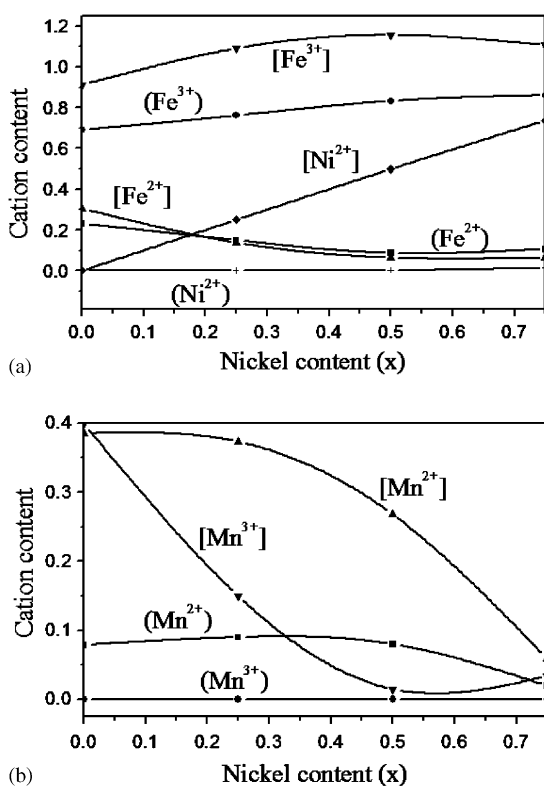


Fig. 1. 1200°C cation distributions for (a) iron and nickel species and (b) manganese species. The parentheses () enclose the tetrahedral species and brackets [] the octahedral species. Continuous lines are added to guide the eye between the calculated results—symbols at $x = 0, 0.25, 0.5$, and 0.75 .

at 900°C and increases at 1200°C as the nickel to manganese ratio increases. The number of Mn^{2+} ions in tetrahedral sites is quite small and remains constant.

Ni^{2+} is shown to be a predominantly octahedral divalent cation, as previously proved [10]. Mn^{3+} ions in octahedral sites increase sharply and Mn^{2+} ions in octahedral sites decrease with increasing temperature because the reaction equilibrium constants vary with temperature.

Many of the measurements of the physical properties, which depend on the cation distribution, are made at room temperature on spinels quenched from high temperature. The errors in the results of thermodynamic calculations based on such measurements are determined by how far this assumption is justified as well as by the accuracy of the measurements.

4. Conclusions

The cation distribution for 10 variables in the ternary compound $\text{Ni}_x\text{Mn}_{1-\gamma-x}\text{Fe}_{2+\gamma}\text{O}_4$ has been calculated accurately using the thermodynamic parameters in conjunction with the framework of O'Neill–Navrotsky. This method can be applied to ternary compounds if the thermodynamic parameters are available.

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