

## Thermodynamic properties in a multicomponent solid solution involving cation disorder: $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4\text{-FeAl}_2\text{O}_4\text{-MgAl}_2\text{O}_4$ spinels

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### ABSTRACT

The spinel quaternary  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4\text{-MgFe}_2\text{O}_4\text{-MgAl}_2\text{O}_4$  is petrologically important but difficult to deal with thermodynamically because of complex order-disorder relations. We have used our recent measurements of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  site occupancies together with measured activity-composition relations, interphase cation distributions, and solvi to develop an internally consistent thermodynamic model for this system. The model is based on a second-degree Taylor series expansion of the vibrational part of the Gibbs free energy in terms of order and compositional parameters. It can readily be related to the familiar Margules parameters,  $W_{ij}^G$ , and reciprocal interactions commonly used to represent activities in multisite solid solutions.

With appropriate simplifications, the model reduces to the Navrotsky-Kleppa ( $-RT \ln K_D$  is constant) or O'Neill-Navrotsky ( $-RT \ln K_D$  is a function of order parameters) models of octahedral-tetrahedral disorder. Although neither of these simpler models provides a complete description of cation distributions in the quaternary, the O'Neill-Navrotsky formalism works well over wide ranges of composition.

### INTRODUCTION

Spinel is an important petrogenetic indicator in igneous and metamorphic rocks of both crustal and mantle origin. The wide compositional ranges of multivalent cations in spinels may, in principle, be used to constrain the values of the intensive variables that operated during their formation. Spinel chemistry is particularly sensitive to oxygen fugacity and temperature (e.g., Buddington and Lindsley, 1964; Irvine, 1965; Mattioli and Wood, 1988), and the  $\text{Fe}_3\text{O}_4$  contents of both aluminous spinels and titanomagnetites are commonly used for oxygen barometry in natural systems. In general, however, application of experimental calibrations to more complex natural systems requires either projection of the mineral compositions into simple systems or application of an activity-composition model to the multicomponent phases. Because of its generality, the latter approach is preferable, but is difficult to implement because of the lack of information on both macroscopic thermodynamic and microscopic order-disorder properties of the solid solutions. The purpose of this paper is to address the microscopic and macroscopic properties of spinels in the quaternary  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4\text{-FeAl}_2\text{O}_4\text{-MgAl}_2\text{O}_4$ .

Experimental calibrations of spinel equilibria mainly involve measurement of cation partitioning between this phase and others such as rhombohedral oxide (Buddington and Lindsley, 1964), silicate (Jamieson and Roeder, 1984), and fluid (Lehmann and Roux, 1986). In addition,

there are direct activity-composition measurements for binaries such as  $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$  (Mattioli and Wood, 1988),  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$  (Petric et al., 1981), and  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4$  (Shishkov et al., 1980). The activity data may be extended in temperature and composition space and integrated with the phase relations and cation-partitioning data in order to derive a reasonable entropy model for spinel solid solutions. The task is complicated, however, by the varying degrees of disorder of the major cations ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) between octahedral and tetrahedral spinel sites and the fact that these distributions are extremely difficult to quench from high temperature (Wood et al., 1986). Recently a thermopower and conductivity technique (Wu and Mason, 1981; Mason, 1987) has been developed for the in situ determination of  $\text{Fe}^{2+}\text{-Fe}^{3+}$  disorder in spinels at high temperature. Use of this technique to characterize the temperature and composition dependence of octahedral-tetrahedral partitioning provides most of the information necessary to link together activity-composition and cation-distribution data. In a previous paper (Nell et al., 1989) we employed the thermopower-conductivity technique to measure intersite cation distributions in  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$ , and  $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$  solid solutions and used the data to evaluate the applicability of commonly used cation-distribution models to spinels. We found that the join  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4$  fits reasonably well to either the Navrotsky-Kleppa (1967) model (both  $-RT \ln K_D^{\text{Fe}^{2+}\text{-Fe}^{3+}}$  and  $-RT \ln K_D^{\text{Mg-Fe}^{3+}}$  constant) or to the O'Neill-Navrotsky (1983, 1984) model in which the intersite cation distributions ( $-RT \ln K_D$ ) are linear functions of the degree of inversion of the solid solution. In  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$  solid

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**TABLE 1.** "Fictive" end-member components of normal and inverse spinels in  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  solid solutions expressed in terms of compositional and order parameters

Parameter	$\text{Mg}(\text{Al})_2\text{O}_4$ 1	$\text{Al}(\text{MgAl})\text{O}_4$ 2	$\text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$ 3	$\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$ 4	$\text{Fe}^{2+}(\text{Al})_2\text{O}_4$ 5	$\text{Al}(\text{Fe}^{2+}\text{Al})\text{O}_4$ 6	$\text{Mg}(\text{Fe}^{3+})_2\text{O}_4$ 7	$\text{Fe}^{3+}(\text{MgFe}^{3+})\text{O}_4$ 8
$r_1$	0	0	1	1	1	1	0	0
$r_2$	1	1	0	0	1	1	0	0
$s_1$	1	0	0	0	1	0	0	0
$s_2$	0	0	1	0	0	0	1	0
$s_3$	0	1	0	0	0	0	0	1

Note: Species in parentheses reside on octahedral sites. The number below each component is the number by which that component is identified in equations.

solutions, however, we found that the compositional dependence of  $-RT \ln K_{\text{Fe}^{2+}, \text{Al}}^{\text{tet}}$  is more complex than that given by either of these simple models. Representation of the properties of spinels in the quaternary  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  requires consideration of this complexity and generation of an internally consistent thermodynamic model that describes and predicts both microscopic and macroscopic phenomena.

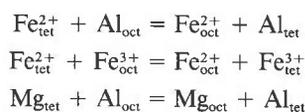
This paper presents a model that uses a Taylor series expansion of the vibrational part of the Gibbs free energy of the solid solution in terms of both order and compositional parameters. This approach was originally introduced by Thompson (1969) and has subsequently been extensively applied to the description of the thermodynamic properties of solid solutions (e.g., Sack, 1982; Hill and Sack, 1987; Andersen and Lindsley, 1988).

### FORMULATION

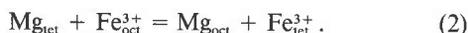
The composition of any spinel in the system  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  can be described in terms of the fictive normal and inverse components given in Table 1. These end-members will serve as reference components that will be used to derive the mixing properties of  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  solid solutions. There are two independent compositional exchange vectors ( $\text{Fe}^{2+}\text{Mg}^{-1}$  and  $\text{Fe}^{3+}\text{Al}^{-1}$ ) in the system of interest, and two compositional parameters are thus required to express the bulk chemical composition of any given solid solution. These are labeled  $r_1$  and  $r_2$  and are defined as follows:

$$\begin{aligned} r_1 &= 1 - (X_{\text{Mg}}^{\text{tet}} + 2X_{\text{Mg}}^{\text{oct}}) \\ r_2 &= 1/2(X_{\text{Al}}^{\text{tet}} + 2X_{\text{Al}}^{\text{oct}}), \end{aligned} \quad (1)$$

where  $X_{\text{Mg}}^{\text{tet}}$ , etc., refers to the atomic fraction of Mg on the tetrahedral site. In addition there are four intersite cation-exchange reactions between the reference end-member components, namely:



and



Only three of these reactions are independent, and we use the following order parameters ( $s_1$ ,  $s_2$ , and  $s_3$ ) to charac-

terize the cation distributions in the solid solution:

$$\begin{aligned} s_1 &= X_{\text{Al}}^{\text{oct}} - 1/2X_{\text{Al}}^{\text{tet}} \\ s_2 &= X_{\text{Fe}^{3+}}^{\text{oct}} - 1/2X_{\text{Fe}^{3+}}^{\text{tet}} \\ s_3 &= 2X_{\text{Mg}}^{\text{oct}}. \end{aligned} \quad (3)$$

There are therefore a total of five independent parameters that are needed to completely characterize any solid solution in the  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  system. Values of these five parameters in the pure fictive end-members are given in Table 1, and species concentrations per structural formula unit are given in Table 2. The configurational entropy of a solid solution ( $S_{\text{conf}}$ ) may then be expressed as a function of order and compositional parameters through the equation

$$S = -R \sum_a \sum_i n_a X_{i,a} \ln(X_{i,a}), \quad (4)$$

where  $n_a$  is the number of sites ( $a$ ) per formula unit and  $X_{i,a}$  is the mole fraction of component  $i$  on site  $a$ .

The Gibbs free energy of a solid solution ( $G$ ) is obtained by combining Equation 4 with an expression for the vibrational part of the Gibbs free energy ( $G^*$ ) through the relation

$$G = G^* - TS_{\text{conf}}. \quad (5)$$

We formulate the vibrational part of the Gibbs free energy using a Taylor series expansion in terms of the selected composition and order parameters. The first-degree terms in such an expansion describe equilibrium conditions in an ideal solid solution, and nonideality must be taken care of by higher-order terms (Thompson, 1969).

### Second-degree Taylor series expansion of $G^*$

We obtained the vibrational part of the Gibbs free energy from a second-degree Taylor series expansion:

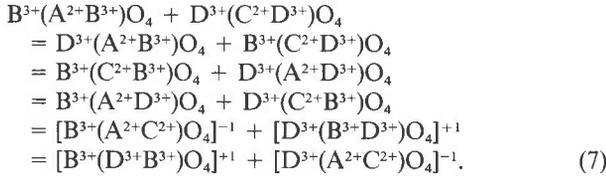
$$\begin{aligned} G^* &= g_0 + g_{r_1}r_1 + g_{r_2}r_2 + g_{s_1}s_1 + g_{s_2}s_2 \\ &+ g_{s_3}s_3 + g_{r_1r_1}r_1^2 + g_{r_2r_2}r_2^2 + g_{s_1s_1}s_1^2 \\ &+ g_{s_2s_2}s_2^2 + g_{s_3s_3}s_3^2 + g_{r_1r_2}r_1r_2 + g_{r_1s_1}r_1s_1 \\ &+ g_{r_1s_2}r_1s_2 + g_{r_1s_3}r_1s_3 + g_{r_2s_1}r_2s_1 + g_{r_2s_2}r_2s_2 \\ &+ g_{r_2s_3}r_2s_3 + g_{s_1s_2}s_1s_2 + g_{s_1s_3}s_1s_3 + g_{s_2s_3}s_2s_3, \end{aligned} \quad (6)$$

where the  $g_n$  parameters are the series expansion coefficients. The second-degree expansion allows for two types

**TABLE 2.** Species concentrations per structural formula unit expressed in terms of composition parameters ( $r_1$  and  $r_2$ ) and order parameters ( $s_1$ ,  $s_2$ , and  $s_3$ ).

Ion	Tetrahedral site	Octahedral site	Sum
Mg	$1 - r_1 - s_3$	$s_3$	$1 - r_1$
Al	$r_2 - s_1$	$r_2 + s_1$	$2r_2$
Fe <sup>2+</sup>	$r_1 + s_1 + s_2 + s_3 - 1$	$1 - s_1 - s_2 - s_3$	$r_1$
Fe <sup>3+</sup>	$1 - s_2 - r_2$	$1 + s_2 - r_2$	$2 - 2r_2$
Sum	1	2	3

of term to describe the excess free energy of mixing. These are (1) symmetric binary interaction parameters and (2) reciprocal reaction terms. Reciprocal reactions are present in all but 4 (binaries 1-5, 1-7, 3-5, and 3-7) of the possible 28 binary solid solutions between the eight reference end-member components. Denoting octahedral sites with parentheses, we write the following general reciprocal reactions between two fictive end-member components B<sup>3+</sup>(A<sup>2+</sup>B<sup>3+</sup>)O<sub>4</sub> (*a*) and D<sup>3+</sup>(C<sup>2+</sup>D<sup>3+</sup>)O<sub>4</sub> (*b*):



The standard state (pure phases at *P* and *T* of interest) free energy of the reciprocal reaction ( $\Delta G_{ab}^0$ ) is defined as

$$\Delta G_{ab}^0 = \mu_n^0 + \mu_m^0 - \mu_a^0 - \mu_b^0, \quad (8)$$

where  $\mu_n^0$  and  $\mu_m^0$  are used to denote standard-state chemical potentials of linearly dependent or independent "fictive" end-member components derived from reference

components *a* and *b* through any one of the reciprocal relations in Reactions 7. In all, an additional 26 linearly dependent fictive end-member components are implied by relations such as those given in Reactions 7; 20 of these components are charge unbalanced. The use of charge-unbalanced end-member components is valid given the additional constraint of equal amounts of oppositely charged species in order to satisfy electroneutrality (Wood and Nicholls, 1978).

Symmetric binary interaction parameters between the reference end-member components may be interpreted in terms of excess on-site microscopic interaction parameters. For a solid solution containing mole fractions *x* and (1 - *x*) of components B<sup>3+</sup>(A<sup>2+</sup>B<sup>3+</sup>)O<sub>4</sub> (*a*) and D<sup>3+</sup>(C<sup>2+</sup>D<sup>3+</sup>)O<sub>4</sub> (*b*), respectively, we express the regular symmetric interaction parameter ( $W_G^{ab}$ ) as follows:

$$\begin{aligned}
 W_G^{ab} &= (x)(1-x)W_{\text{BD}}^{\text{tet}} + 2\left(\frac{1-x}{2}\right)\left(\frac{x}{2}\right) \\
 &\quad \cdot [W_{\text{AC}}^{\text{oct}} + W_{\text{BD}}^{\text{oct}} + W_{\text{AD}}^{\text{oct}} + W_{\text{BC}}^{\text{oct}}] \\
 &\quad + 2\left(\frac{x}{2}\right)^2 W_{\text{AB}}^{\text{oct}} + 2\left(\frac{1-x}{2}\right)^2 W_{\text{CD}}^{\text{oct}} \\
 &\quad - \frac{x}{2} W_{\text{AB}}^{\text{oct}} - \frac{1-x}{2} W_{\text{CD}}^{\text{oct}} \\
 &= (x)(1-x) \left[ W_{\text{BD}}^{\text{tet}} + \frac{W_{\text{AC}}^{\text{oct}}}{2} + \frac{W_{\text{BD}}^{\text{oct}}}{2} + \frac{W_{\text{AD}}^{\text{oct}}}{2} \right. \\
 &\quad \left. + \frac{W_{\text{BC}}^{\text{oct}}}{2} - \frac{W_{\text{AB}}^{\text{oct}}}{2} - \frac{W_{\text{CD}}^{\text{oct}}}{2} \right], \quad (9)
 \end{aligned}$$

where  $W_{\text{BD}}^{\text{tet}}$ , etc., refers to the excess free energy of mixing of 1 mol of B<sup>3+</sup> and 1 mol of D<sup>3+</sup> on tetrahedral sites and

**TABLE 3.** Thermodynamic coefficients in a second-degree Taylor series expansion for the vibrational part of the Gibbs free energy of Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions

$g_0 = \mu_4^0 + \mu_1^0 - \mu_5^0 + W_G^{47} - W_G^{15} - W_G^{34} + \Delta G_{27}^0 - \Delta G_{34}^0 - \Delta G_{57}^0$
$g_{r_1} = \mu_5^0 - \mu_1^0 + 2W_G^{15} + W_G^{34} - W_G^{47} + \Delta G_{34}^0 - \Delta G_{47}^0 + \Delta G_{57}^0$
$g_{r_2} = \mu_6^0 - \mu_4^0 + W_G^{67} + W_G^{28} + W_G^{34} - W_G^{47} - W_G^{26} + \Delta G_{28}^0$
$g_{s_1} = \mu_5^0 - \mu_6^0 + W_G^{56} + W_G^{45} + W_G^{15} - W_G^{16} - W_G^{28} + \Delta G_{56}^0 + \Delta G_{45}^0 - \Delta G_{16}^0 - \Delta G_{28}^0$
$g_{s_2} = \mu_3^0 - \mu_4^0 + 2W_G^{34} + W_G^{15} - W_G^{47} + 2\Delta G_{34}^0 - \Delta G_{47}^0$
$g_{s_3} = \mu_8^0 + \mu_5^0 - \mu_1^0 - \mu_4^0 + W_G^{34} + W_G^{12} + W_G^{45} + W_G^{26} + 2W_G^{15} - W_G^{16} - W_G^{47} - W_G^{28} + \Delta G_{34}^0 + \Delta G_{12}^0 + \Delta G_{45}^0 - \Delta G_{16}^0$ $- \Delta G_{47}^0 - \Delta G_{28}^0 - \Delta G_{28}^0 + \Delta G_{58}^0 + \Delta G_{57}^0$
$g_{r_1 r_1} = -W_G^{15}$
$g_{r_2 r_2} = -W_G^{28} - \Delta G_{28}^0$
$g_{s_1 s_1} = -W_G^{56} - \Delta G_{56}^0$
$g_{s_2 s_2} = -W_G^{34} - \Delta G_{34}^0$
$g_{s_3 s_3} = W_G^{15} + W_G^{58} - W_G^{12} - W_G^{45} - W_G^{15} - W_G^{26} + \Delta G_{16}^0 + \Delta G_{58}^0 - \Delta G_{12}^0 - \Delta G_{45}^0 + \Delta G_{26}^0 - \Delta G_{58}^0$
$g_{r_1 r_2} = W_G^{38} + W_G^{47} - W_G^{67} - W_G^{34}$
$g_{r_1 s_1} = W_G^{16} - W_G^{15} - W_G^{56} + \Delta G_{16}^0 - \Delta G_{56}^0$
$g_{r_1 s_2} = W_G^{47} - W_G^{15} - W_G^{34} + \Delta G_{47}^0 - \Delta G_{34}^0$
$g_{r_1 s_3} = W_G^{24} + W_G^{58} - 2W_G^{15} - W_G^{58} - W_G^{45} + W_G^{14} - W_G^{18} + \Delta G_{24}^0 + \Delta G_{58}^0 + \Delta G_{16}^0 - \Delta G_{58}^0 - \Delta G_{12}^0 - \Delta G_{45}^0$
$g_{r_2 s_1} = W_G^{28} + W_G^{56} - W_G^{45} + \Delta G_{28}^0 + \Delta G_{56}^0 - \Delta G_{45}^0$
$g_{r_2 s_2} = W_G^{36} - W_G^{28} - W_G^{34} + \Delta G_{36}^0 - \Delta G_{28}^0 - \Delta G_{34}^0$
$g_{r_2 s_3} = W_G^{18} + W_G^{56} - W_G^{12} - W_G^{45}$
$g_{s_1 s_2} = W_G^{17} + W_G^{28} - W_G^{45} - W_G^{36} + \Delta G_{28}^0 - \Delta G_{45}^0 - \Delta G_{36}^0$
$g_{s_1 s_3} = W_G^{15} + W_G^{58} - W_G^{45} - W_G^{15} - W_G^{26} - W_G^{58} + \Delta G_{16}^0 + \Delta G_{58}^0 - \Delta G_{45}^0 + \Delta G_{26}^0 - \Delta G_{58}^0 - \Delta G_{58}^0$
$g_{s_2 s_3} = W_G^{16} + W_G^{58} - W_G^{12} - W_G^{45} - W_G^{15} - W_G^{26} + W_G^{78} - W_G^{34} + \Delta G_{16}^0 + \Delta G_{58}^0 - \Delta G_{12}^0 - \Delta G_{45}^0 + \Delta G_{26}^0 - \Delta G_{58}^0 + \Delta G_{78}^0 - \Delta G_{34}^0$

the factor 2 takes account of the two octahedral sites per formula unit.

The coefficients in the second-degree Taylor series expansion were determined by sequentially setting the composition of the solid solution to each of the 28 binary joins between the eight reference end-member components defined in Table 1. This gives, in each case, a value for  $G^*$  in terms of the coefficients in the power series. The expressions may then be equated with an equivalent relationship for  $G^*$  in terms of  $\Delta G_{ab}^0$  and  $W_G^{ab}$  that may then be used to solve for the power-series coefficients. For example, the free energy along the join 4-6 [ $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4\text{-Al}(\text{Fe}^{2+}\text{Al})\text{O}_4$ ] is given by

$$\begin{aligned} G^* &= g_0 + g_{r_1} + g_{r_2} + g_{r_1 r_1} + g_{r_2 r_2} + g_{r_1 r_2} \\ &= r_2(\mu_6^0 - \mu_4^0 + W_G^{46} + \Delta G_{46}^0) \\ &\quad + \mu_4^0 + r_2^2(-W_G^{46} - \Delta G_{46}^0). \end{aligned} \quad (10)$$

From Equation 10 it immediately follows that

$$\begin{aligned} \mu_6^0 - \mu_4^0 + W_G^{46} + \Delta G_{46}^0 &= g_{r_2} + g_{r_1 r_2} \\ -W_G^{46} - \Delta G_{46}^0 &= g_{r_2 r_2} \end{aligned}$$

and

$$\mu_4^0 = g_0 + g_{r_1} + g_{r_1 r_1}.$$

Applying Equations 7 and 9 we obtain the following expressions for  $\Delta G_{46}^0$  and  $W_G^{46}$ , respectively:

$$\begin{aligned} \Delta G_{46}^0 &= \mu_{\text{Fe}^{3+}(\text{Fe}^{2+}\text{Al})\text{O}_4}^0 + \mu_{\text{Al}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4}^0 - \mu_4^0 - \mu_6^0 \\ &= \mu_{[\text{Fe}^{3+}(\text{AlFe}^{3+})\text{O}_4]^{+1}}^0 + \mu_{[\text{Al}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4]^{-1}}^0 - \mu_4^0 - \mu_6^0 \\ &= \mu_{[\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4]^{-1}}^0 + \mu_{[\text{Al}(\text{AlFe}^{3+})\text{O}_4]^{+1}}^0 - \mu_4^0 - \mu_6^0 \end{aligned}$$

and

$$W_G^{46} = W_{\text{Fe}^{3+}\text{Al}}^{\text{tet}} + W_{\text{Fe}^{2+}\text{Al}}^{\text{oct}}/2.$$

The excess free energy contributions to the resultant solution set (Table 3) are not uniquely defined, however, since the system of equations used to solve for the values of the coefficients is overdetermined. Reciprocal excess free-energy terms are related to one another within the framework of possible reciprocal reactions that exist for the binary solid solutions. In solid solutions with multiple reciprocal relations (for example the join 4-6 as shown above),  $\Delta G_{ab}^0$  must be independent of the way in which the possible reciprocal reactions between components  $a$  and  $b$  are formulated, thus implying that  $\mu_n^0 + \mu_m^0 = \mu_{n'}^0 + \mu_{m'}^0$  where  $n$ ,  $m$ ,  $n'$ , and  $m'$  are end-members formed through reciprocal relations between components  $a$  and  $b$ . The symmetric nature of the expansion furthermore requires that  $\Delta G_{46}^0 = \Delta G_{28}^0 = -\Delta G_{26}^0 = -\Delta G_{48}^0$  and that  $W_{\text{MgAl}}^{\text{oct}} = W_{\text{MgFe}^{3+}}^{\text{oct}} = W_{\text{Fe}^{2+}\text{Al}}^{\text{oct}} = W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{oct}}$ .

Given these relationships between the excess free-energy terms, the solution set of the thermodynamic coefficients in the second-degree Taylor series expansion (Table 3) is consistent with the free-energy expressions of all 28 binary solid solutions between the end-member components defined in Table 1.

## Equilibrium conditions

Equilibrium in  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4\text{-FeAl}_2\text{O}_4\text{-MgAl}_2\text{O}_4$  solid solutions is established when at fixed temperature, pressure, and composition the following conditions are satisfied:

$$\begin{aligned} \left(\frac{\partial G}{\partial s_1}\right)_{T,P,r_1,r_2,s_2,s_3} &= \left(\frac{\partial G}{\partial s_2}\right)_{T,P,r_1,r_2,s_1,s_3} \\ &= \left(\frac{\partial G}{\partial s_3}\right)_{T,P,r_1,r_2,s_1,s_2} \\ &= 0. \end{aligned} \quad (11)$$

Substituting Equations 4 and 6 into 5 and differentiating gives the following equilibrium conditions:

$$\begin{aligned} \left(\frac{\partial G}{\partial s_1}\right)_{T,P,r_1,r_2,s_2,s_3} &= g_{s_1} + 2g_{s_1 s_1} s_1 + g_{r_1 s_1} r_1 + g_{r_2 s_1} r_2 + g_{s_1 s_2} s_2 \\ &\quad + g_{s_1 s_3} s_3 + RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Al}_{\text{oct}})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Al}_{\text{tet}})} \\ &= 0 \end{aligned} \quad (12)$$

$$\begin{aligned} \left(\frac{\partial G}{\partial s_2}\right)_{T,P,r_1,r_2,s_1,s_3} &= g_{s_2} + 2g_{s_2 s_2} s_2 + g_{r_1 s_2} r_1 + g_{r_2 s_2} r_2 + g_{s_1 s_2} s_1 \\ &\quad + g_{s_2 s_3} s_3 + RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Fe}_{\text{oct}}^{3+})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Fe}_{\text{tet}}^{3+})} \\ &= 0 \end{aligned} \quad (13)$$

and

$$\begin{aligned} \left(\frac{\partial G}{\partial s_3}\right)_{T,P,r_1,r_2,s_1,s_2} &= g_{s_3} + 2g_{s_3 s_3} s_3 + g_{r_1 s_3} r_1 + g_{r_2 s_3} r_2 + g_{s_1 s_3} s_1 \\ &\quad + g_{s_2 s_3} s_2 + RT \ln \frac{(\text{Mg}_{\text{oct}})(\text{Fe}_{\text{tet}}^{2+})}{(\text{Mg}_{\text{tet}})(\text{Fe}_{\text{oct}}^{2+})} \\ &= 0. \end{aligned} \quad (14)$$

## Application of equilibrium conditions

Equations 12 to 14 are applicable to the calculation of intersite cation distributions in  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4\text{-FeAl}_2\text{O}_4\text{-MgAl}_2\text{O}_4$  solid solutions. First we applied the equilibrium conditions to pure magnetite, hercynite, magnesioferrite, and spinel. From Equation 12 it follows that for pure  $\text{FeAl}_2\text{O}_4$ ,

$$\begin{aligned} -RT \ln \frac{(\text{Fe}_{\text{oct}}^{2+})(\text{Al}_{\text{tet}})}{(\text{Fe}_{\text{tet}}^{2+})(\text{Al}_{\text{oct}})} &= -(g_{s_1} + g_{r_1 s_1} + g_{r_2 s_1}) \\ &\quad - 2g_{s_1 s_1} s_1 \\ &= (\mu_6^0 - \mu_4^0 - W_G^{56} - \Delta G_{56}^0) \\ &\quad + 2(W_G^{56} + \Delta G_{56}^0) s_1 \\ &= (\mu_6^0 - \mu_4^0 - W_{\text{AlFe}^{2+}}^{\text{tet}} \\ &\quad - W_{\text{AlFe}^{2+}}^{\text{oct}} - \Delta G_{56}^0) \\ &\quad + 2(W_{\text{AlFe}^{2+}}^{\text{tet}} + W_{\text{AlFe}^{2+}}^{\text{oct}} \\ &\quad + \Delta G_{56}^0) s_1. \end{aligned} \quad (15)$$

Similarly, Equation 13 gives the equilibrium condition for pure  $\text{Fe}_3\text{O}_4$ :

$$\begin{aligned} -RT \ln \frac{(\text{Fe}_{\text{oct}}^{2+})(\text{Fe}_{\text{tet}}^{3+})}{(\text{Fe}_{\text{tet}}^{2+})(\text{Fe}_{\text{oct}}^{3+})} &= -(g_{s_2} + g_{r_{1s_2}}) - 2g_{s_2s_2} \\ &= (\mu_4^0 - \mu_3^0 - W_G^{34} - \Delta G_{34}^0) \\ &\quad + 2(W_G^{34} + \Delta G_{34}^0)s_2 \\ &= (\mu_4^0 - \mu_3^0 - W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{tet}} \\ &\quad - W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{oct}} - \Delta G_{34}^0) \\ &\quad + 2(W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{tet}} + W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{oct}} \\ &\quad + \Delta G_{34}^0)s_2. \end{aligned} \quad (16)$$

The equilibrium conditions for spinel and magnesioferrite were obtained from linear combinations of Equations 14 and 12 and Equations 14 and 13, respectively. For  $\text{MgAl}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ , respectively, we find that

$$\begin{aligned} -RT \ln \frac{(\text{Mg}_{\text{oct}})(\text{Al}_{\text{tet}})}{(\text{Mg}_{\text{tet}})(\text{Al}_{\text{oct}})} &= (g_{s_3} + g_{r_{2s_3}} + 2g_{s_3s_3} \\ &\quad - g_{s_1} - g_{r_{2s_1}} - g_{s_1s_3}) \\ &\quad + 2(g_{s_1s_3} - g_{s_1s_1} - g_{s_3s_3})s_1 \\ &= (\mu_2^0 - \mu_1^0 - W_G^{12} - \Delta G_{12}^0) \\ &\quad + 2(W_G^{12} + \Delta G_{12}^0)s_1 \\ &= (\mu_2^0 - \mu_1^0 - W_{\text{MgAl}}^{\text{tet}} \\ &\quad - W_{\text{MgAl}}^{\text{oct}} - \Delta G_{12}^0) \\ &\quad + 2(W_{\text{MgAl}}^{\text{tet}} + W_{\text{MgAl}}^{\text{oct}} \\ &\quad + \Delta G_{12}^0)s_1 \end{aligned} \quad (17)$$

and

$$\begin{aligned} -RT \ln \frac{(\text{Mg}_{\text{oct}})(\text{Fe}_{\text{tet}}^{3+})}{(\text{Mg}_{\text{tet}})(\text{Fe}_{\text{oct}}^{3+})} &= (g_{s_3} - g_{s_2} + 2g_{s_3s_3} - g_{s_2s_3}) \\ &\quad + 2(g_{s_2s_3} - g_{s_3s_3} - g_{s_2s_2})s_2 \\ &= (\mu_8^0 - \mu_7^0 - W_G^{78} - \Delta G_{78}^0) \\ &\quad + 2(W_G^{78} + \Delta G_{78}^0)s_2 \\ &= (\mu_8^0 - \mu_7^0 - W_{\text{MgFe}^{3+}}^{\text{tet}} \\ &\quad - W_{\text{MgFe}^{3+}}^{\text{oct}} - \Delta G_{78}^0) \\ &\quad + 2(W_{\text{MgFe}^{3+}}^{\text{tet}} + W_{\text{MgFe}^{3+}}^{\text{oct}} \\ &\quad + \Delta G_{78}^0)s_2. \end{aligned} \quad (18)$$

A comparison of Equations 15 to 18 with the O'Neill-Navrotsky (1983, 1984) formalism ( $-RT \ln[(A_{\text{oct}}^{2+})(B_{\text{tet}}^{3+})/(A_{\text{tet}}^{2+})(B_{\text{oct}}^{3+})] = -RT \ln K_D = \alpha + 2\beta B_{\text{tet}}^{3+}$ ) shows that for pure end-member spinels the O'Neill-Navrotsky model is equivalent to a second-degree Taylor series expansion of the vibrational free energy [note that for the end-member components,  $s_1$  and  $s_2$  are equal to  $(1 - B_{\text{tet}}^{3+})$ ]. The thermodynamic interpretations of the  $\alpha$  and  $\beta$  energy pa-

rameters used in the O'Neill-Navrotsky model are thus as follows:

$$\begin{aligned} \alpha_{\text{Fe}^{2+}\text{Al}} &= \mu_6^0 - \mu_5^0 + W_{\text{AlFe}^{2+}}^{\text{tet}} + W_{\text{AlFe}^{2+}}^{\text{oct}} + \Delta G_{56}^0 \\ \beta_{\text{Fe}^{2+}\text{Al}} &= -W_{\text{AlFe}^{2+}}^{\text{tet}} - W_{\text{AlFe}^{2+}}^{\text{oct}} - \Delta G_{56}^0 \\ \alpha_{\text{Fe}^{2+}\text{Fe}^{3+}} &= \mu_4^0 - \mu_3^0 + W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{tet}} + W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{oct}} + \Delta G_{34}^0 \\ \beta_{\text{Fe}^{2+}\text{Fe}^{3+}} &= -W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{tet}} - W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{oct}} - \Delta G_{34}^0 \\ \alpha_{\text{MgAl}} &= \mu_2^0 - \mu_1^0 + W_{\text{MgAl}}^{\text{tet}} + W_{\text{MgAl}}^{\text{oct}} + \Delta G_{12}^0 \\ \beta_{\text{MgAl}} &= -W_{\text{MgAl}}^{\text{tet}} - W_{\text{MgAl}}^{\text{oct}} - \Delta G_{12}^0 \\ \alpha_{\text{MgFe}^{3+}} &= \mu_8^0 - \mu_7^0 + W_{\text{MgFe}^{3+}}^{\text{tet}} + W_{\text{MgFe}^{3+}}^{\text{oct}} + \Delta G_{78}^0 \\ \beta_{\text{MgFe}^{3+}} &= -W_{\text{MgFe}^{3+}}^{\text{tet}} - W_{\text{MgFe}^{3+}}^{\text{oct}} - \Delta G_{78}^0. \end{aligned} \quad (19)$$

As a first approximation, O'Neill and Navrotsky (1983, 1984) suggested that the  $\beta$  parameter could be treated as constant for 2-3 spinels with a value of about  $-20$  kJ/mol. Neglecting the reciprocal terms in Equations 19, a constant  $\beta$  parameter would imply that  $W_{\text{AlFe}^{2+}}^{\text{tet}} + W_{\text{AlFe}^{2+}}^{\text{oct}} = W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{tet}} + W_{\text{Fe}^{2+}\text{Fe}^{3+}}^{\text{oct}} = W_{\text{MgAl}}^{\text{tet}} + W_{\text{MgAl}}^{\text{oct}} = W_{\text{MgFe}^{3+}}^{\text{tet}} + W_{\text{MgFe}^{3+}}^{\text{oct}} = 20$  kJ/mol. In binary and more complex solid solutions, the O'Neill-Navrotsky formalism is not, as will be shown below, equivalent to the second-degree expansion unless simplifications are made.

The equilibrium conditions for end-member spinels (Eqs. 15 to 18) are reduced to the Navrotsky-Kleppa (1967) formalism ( $-RT \ln K_D = \text{constant}$ ) when all excess free energy of mixing parameters are set to zero. Second-degree expansion terms are thus eliminated, and first-order expansion coefficients are simplified to include chemical potential terms only. Intersite cation distribution coefficients for hercynite, magnetite, spinel, and magnesioferrite, respectively, are then given by the following equations in terms of simplified first-order expansion coefficients ( $s'_1$ ,  $s'_2$  and  $s'_3$ ):

$$\begin{aligned} -RT \ln \frac{(\text{Fe}_{\text{oct}}^{2+})(\text{Al}_{\text{tet}})}{(\text{Fe}_{\text{tet}}^{2+})(\text{Al}_{\text{oct}})} &= -g_{s'_1} = \mu_6^0 - \mu_5^0 \\ -RT \ln \frac{(\text{Fe}_{\text{oct}}^{2+})(\text{Fe}_{\text{tet}}^{3+})}{(\text{Fe}_{\text{tet}}^{2+})(\text{Fe}_{\text{oct}}^{3+})} &= -g_{s'_2} = \mu_4^0 - \mu_3^0 \\ -RT \ln \frac{(\text{Mg}_{\text{oct}})(\text{Al}_{\text{tet}})}{(\text{Mg}_{\text{tet}})(\text{Al}_{\text{oct}})} &= g_{s'_3} - g_{s'_1} = \mu_2^0 - \mu_1^0 \\ -RT \ln \frac{(\text{Mg}_{\text{tet}})(\text{Fe}_{\text{oct}}^{3+})}{(\text{Mg}_{\text{oct}})(\text{Fe}_{\text{tet}}^{3+})} &= g_{s'_3} - g_{s'_2} = \mu_8^0 - \mu_7^0. \end{aligned} \quad (20)$$

The constants in the Navrotsky-Kleppa formalism are therefore equal to the chemical-potential differences between inverse and normal spinel end-members.

The equilibrium conditions (Eqs. 12 to 14) may now be applied to calculate cation distributions in binary spinel solid solutions. For examples we use the  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  systems as these have been previously dealt with using the O'Neill-Navrotsky formalism (Nell et al., 1989). For  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  solid solutions, it follows from Equations 13 and 14 through the

substitution of appropriate values for the order and composition parameters that

$$-RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Fe}_{\text{oct}}^{3+})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Fe}_{\text{tet}}^{3+})} = g_{s_2} + 2g_{s_2s_2}s_2 + g_{r_1s_2}X_{\text{Fe}_3\text{O}_4} + g_{s_2s_3}s_3 \quad (21)$$

and

$$-RT \ln \frac{(\text{Mg}_{\text{oct}})(\text{Fe}_{\text{tet}}^{2+})}{(\text{Mg}_{\text{tet}})(\text{Fe}_{\text{oct}}^{2+})} = g_{s_3} + 2g_{s_3s_3}s_3 + g_{r_1s_3}X_{\text{Fe}_3\text{O}_4} + g_{s_2s_3}s_2 \quad (22)$$

Similarly, for  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  solid solutions, we find from Equations 12 and 13 that

$$-RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Al}_{\text{oct}})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Al}_{\text{tet}})} = g_{s_1} + g_{r_1s_1} + 2g_{s_1s_1}s_1 + g_{r_2s_1}X_{\text{FeAl}_2\text{O}_4} + g_{s_1s_2}s_2 \quad (23)$$

and

$$-RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Fe}_{\text{oct}}^{3+})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Fe}_{\text{tet}}^{3+})} = g_{s_2} + g_{r_1s_2} + 2g_{s_2s_2}s_2 + g_{r_2s_2}X_{\text{FeAl}_2\text{O}_4} + g_{s_1s_2}s_1 \quad (24)$$

Equilibria in quaternary  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  solid solutions are obtained from Equations 12, 13, and 14 as follows:

$$-RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Al}_{\text{oct}})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Al}_{\text{tet}})} = g_{s_1} + 2g_{s_1s_1}s_1 + g_{r_1s_1}(X_{\text{Fe}_3\text{O}_4} + X_{\text{FeAl}_2\text{O}_4}) + g_{r_2s_1}(X_{\text{MgAl}_2\text{O}_4} + X_{\text{FeAl}_2\text{O}_4}) + g_{s_1s_2}s_2 + g_{s_1s_3}s_3 \quad (25)$$

$$-RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})(\text{Fe}_{\text{oct}}^{3+})}{(\text{Fe}_{\text{oct}}^{2+})(\text{Fe}_{\text{tet}}^{3+})} = g_{s_2} + 2g_{s_2s_2}s_2 + g_{r_1s_2}(X_{\text{Fe}_3\text{O}_4} + X_{\text{FeAl}_2\text{O}_4}) + g_{r_2s_2}(X_{\text{MgAl}_2\text{O}_4} + X_{\text{FeAl}_2\text{O}_4}) + g_{s_1s_2}s_1 + g_{s_2s_3}s_3 \quad (26)$$

and

$$-RT \ln \frac{(\text{Mg}_{\text{oct}})(\text{Fe}_{\text{tet}}^{2+})}{(\text{Mg}_{\text{tet}})(\text{Fe}_{\text{oct}}^{2+})} = g_{s_3} + 2g_{s_3s_3}s_3 + g_{r_1s_3}(X_{\text{Fe}_3\text{O}_4} + X_{\text{FeAl}_2\text{O}_4}) + g_{r_2s_3}(X_{\text{MgAl}_2\text{O}_4} + X_{\text{FeAl}_2\text{O}_4}) + g_{s_1s_3}s_1 + g_{s_2s_3}s_2 \quad (27)$$

Equations 25 to 27 may also be used to calculate intersite cation distributions in  $\text{Fe}_3\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  and  $\text{FeAl}_2\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  solid solutions, these binary systems being degenerate simplifications of quaternary solid solutions in which  $r_1 = 1 - r_2 = X_{\text{Fe}_3\text{O}_4}$ .

The Navrotsky-Kleppa (1967) and O'Neill-Navrotsky

formalisms for the functional form of the intersite distribution coefficients in binary and quaternary spinel solid solutions are readily derived from Equations 21 to 27 by introducing appropriate simplifications. Navrotsky-Kleppa expressions for the intersite distribution coefficients are obtained when all excess energy of mixing terms are zero. Intersite distribution coefficients in solid solutions are thus identical to those in pure end-members as given by Equations 20.

O'Neill-Navrotsky expressions for the intersite cation-distribution coefficients in complex solid solutions are obtained when the combined order and composition expansion coefficients ( $g_{r_1s_1}$ ,  $g_{r_1s_2}$ ,  $g_{r_1s_3}$ ,  $g_{r_2s_1}$ ,  $g_{r_2s_2}$ , and  $g_{r_2s_3}$ ) are set to zero. The distribution coefficients are simplified to be functions of order parameters only and this formalism is therefore equivalent to a second-degree Taylor series expansion in which combined order and composition coefficients are neglected. The expressions for the cross-order coefficients ( $g_{s_1s_2}$ ,  $g_{s_1s_3}$ , and  $g_{s_2s_3}$ ) in the Taylor series expansion (Table 3) are, of course, different from the energy terms in the O'Neill-Navrotsky model (Nell et al., 1989), the latter being linearly dependent combinations of pure end-member  $\beta$  energy parameters (Eqs. 19) rather than uniquely defined series expansion coefficients.

#### Activity-composition relations

There are three second-order composition coefficients available to describe activity-composition relations on the six binary joins in the quaternary  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$ - $\text{MgFe}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$ . Excess free-energy contributions for  $\text{Fe}^{2+}$ - $\text{Mg}$  mixing in both  $\text{Fe}_3\text{O}_4$ - $\text{MgFe}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  solid solutions are required to be identical in value and are modeled with the  $g_{r_1r_1}$  coefficient. A similar situation applies to  $\text{Fe}^{3+}$ - $\text{Al}$  mixing in  $\text{Fe}_3\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  solid solutions where the  $g_{r_2r_2}$  coefficient is used. Mixing in  $\text{Fe}_3\text{O}_4$ - $\text{MgAl}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ - $\text{FeAl}_2\text{O}_4$  solid solutions is a function of the  $g_{r_1r_1}$ ,  $g_{r_2r_2}$ , and  $g_{r_1r_2}$  coefficients where the latter coefficient serves as a third adjustable parameter.

Substituting Equations 4 and 6 into Equation 5 and differentiating with respect to  $r_1$  and  $r_2$  gives

$$\left(\frac{\partial G}{\partial r_1}\right)_{T,P,r_2,s_1,s_2,s_3} = g_{r_1} + 2g_{r_1r_1}r_1 + g_{r_1r_2}r_2 + g_{r_1s_1}s_1 + g_{r_1s_2}s_2 + g_{r_1s_3}s_3 + RT \ln \frac{(\text{Fe}_{\text{tet}}^{2+})}{(\text{Mg}_{\text{tet}})} \quad (28)$$

and

$$\left(\frac{\partial G}{\partial r_2}\right)_{T,P,r_1,s_1,s_2,s_3} = g_{r_2} + 2g_{r_2r_2}r_2 + g_{r_1r_2}r_1 + g_{r_2s_1}s_1 + g_{r_2s_2}s_2 + g_{r_2s_3}s_3 + RT \ln \frac{(\text{Al}_{\text{tet}})(\text{Al}_{\text{oct}})}{(\text{Fe}_{\text{tet}}^{3+})(\text{Fe}_{\text{oct}}^{3+})} \quad (29)$$

TABLE 4. Chemical potentials of reference end-member components

$\begin{aligned} \mu_{\text{Al}(\text{MgAl})\text{O}_4} = & g_0 + g_{r_2} + g_{s_3} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 - g_{r_1 s_1} r_1 s_1 - g_{r_1 s_2} r_1 s_2 - g_{s_1 s_2} s_1 s_2 \\ & + (2g_{r_2 r_2} + g_{r_2 s_3}) r_2 + (g_{r_1 r_2} + g_{r_1 s_3}) r_1 + (g_{r_2 s_1} + g_{s_1 s_2}) s_1 + (g_{r_2 s_2} + g_{s_2 s_3}) s_2 \\ & + (2g_{s_3 s_3} + g_{r_2 s_3}) s_3 - g_{r_1 r_2} r_1 r_2 - g_{r_2 s_1} r_2 s_1 - g_{r_2 s_2} r_2 s_2 - g_{r_1 s_3} r_1 s_3 - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + RT \ln(\text{Al}_{\text{tet}}/\text{Al}_{\text{oct}})(\text{Mg}_{\text{oct}}) - 2 \ln 2 \end{aligned}$
$\begin{aligned} \mu_{\text{Mg}(\text{AlAl})\text{O}_4} = & g_0 + g_{r_2} + g_{s_1} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 - g_{r_1 s_2} r_1 s_2 - g_{r_1 s_3} r_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + (2g_{r_2 r_2} + g_{r_2 s_1}) r_2 + (g_{r_1 r_2} + g_{r_1 s_1}) r_1 + (g_{r_2 s_1} + 2g_{s_1 s_1}) s_1 + (g_{r_2 s_2} + g_{s_1 s_2}) s_2 \\ & + (g_{s_1 s_3} + g_{r_2 s_3}) s_3 - g_{r_1 r_2} r_1 r_2 - g_{r_2 s_1} r_2 s_1 - g_{r_2 s_2} r_2 s_2 - g_{r_1 s_3} r_1 s_3 \\ & - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + RT [2 \ln(\text{Al}_{\text{oct}}) + \ln(\text{Mg}_{\text{tet}}) - 2 \ln 2] \end{aligned}$
$\begin{aligned} \mu_{\text{Fe}^{3+}(\text{Fe}^{3+}\text{Fe}^{3+})\text{O}_4} = & g_0 + g_{r_1} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 + 2g_{r_1 r_1} r_1 + g_{r_1 r_2} r_2 + g_{r_1 s_1} s_1 \\ & + g_{r_1 s_2} s_2 + g_{r_1 s_3} s_3 - g_{r_1 r_2} r_1 r_2 - g_{r_1 s_1} r_1 s_1 - g_{r_2 s_1} r_2 s_1 - g_{r_1 s_2} r_1 s_2 - g_{r_2 s_2} r_2 s_2 \\ & - g_{s_1 s_2} s_1 s_2 - g_{s_2 s_3} s_2 s_3 - g_{r_1 s_3} r_1 s_3 - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_3} s_1 s_3 \\ & + RT \ln(\text{Fe}_{\text{oct}}^{3+}/\text{Fe}_{\text{tet}}^{3+})(\text{Fe}_{\text{oct}}^{2+}) - 2 \ln 2 \end{aligned}$
$\begin{aligned} \mu_{\text{Fe}^{2+}(\text{Fe}^{3+}\text{Fe}^{3+})\text{O}_4} = & g_0 + g_{r_1} + g_{s_2} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 + (2g_{r_1 r_1} + g_{r_1 r_2}) r_1 + (g_{r_1 r_2} + g_{r_2 s_2}) r_2 \\ & + (g_{r_1 s_1} + g_{s_1 s_2}) s_1 + (g_{r_1 s_2} + 2g_{s_2 s_2}) s_2 + (g_{r_1 s_3} + g_{s_2 s_3}) s_3 - g_{r_1 r_2} r_1 r_2 - g_{r_1 s_1} r_1 s_1 - g_{r_2 s_1} r_2 s_1 - g_{r_1 s_2} r_1 s_2 \\ & - g_{r_2 s_2} r_2 s_2 - g_{s_1 s_2} s_1 s_2 - g_{s_2 s_3} s_2 s_3 - g_{r_1 s_3} r_1 s_3 - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_3} s_1 s_3 \\ & + RT [2 \ln(\text{Fe}_{\text{oct}}^{3+}) + \ln(\text{Fe}_{\text{tet}}^{2+}) - 2 \ln 2] \end{aligned}$
$\begin{aligned} \mu_{\text{Al}(\text{Fe}^{2+}\text{Al})\text{O}_4} = & g_0 + g_{r_1} + g_{r_2} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 + (2g_{r_1 r_1} + g_{r_1 r_2}) r_1 \\ & + (2g_{r_2 r_2} + g_{r_1 r_2}) r_2 + (g_{r_1 s_1} + g_{r_2 s_1}) s_1 + (g_{r_1 s_2} + g_{r_2 s_2}) s_2 + (g_{r_1 s_3} + g_{r_2 s_3}) s_3 - g_{r_1 r_2} r_1 r_2 - g_{r_1 s_1} r_1 s_1 \\ & - g_{r_2 s_1} r_2 s_1 - g_{r_1 s_2} r_1 s_2 - g_{r_2 s_2} r_2 s_2 - g_{s_1 s_2} s_1 s_2 - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + RT \ln(\text{Fe}_{\text{oct}}^{2+}/\text{Al}_{\text{oct}})(\text{Al}_{\text{tet}}) - 2 \ln 2 \end{aligned}$
$\begin{aligned} \mu_{\text{Fe}^{2+}(\text{AlAl})\text{O}_4} = & g_0 + g_{r_1} + g_{r_2} + g_{s_1} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 + (2g_{r_1 r_1} + g_{r_1 r_2}) r_1 \\ & + (2g_{r_2 r_2} + g_{r_1 r_2} + g_{r_2 s_1}) r_2 + (2g_{s_1 s_1} + g_{r_1 s_1} + g_{r_2 s_1}) s_1 + (g_{r_1 s_2} + g_{r_2 s_2} + g_{s_1 s_2}) s_2 + (g_{r_1 s_3} + g_{r_2 s_3} + g_{s_1 s_3}) s_3 \\ & - g_{r_1 r_2} r_1 r_2 - g_{r_1 s_1} r_1 s_1 - g_{r_1 s_2} r_1 s_2 - g_{r_1 s_3} r_1 s_3 - g_{r_2 s_1} r_2 s_1 - g_{r_2 s_2} r_2 s_2 - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_2} s_1 s_2 - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + RT [2 \ln(\text{Al}_{\text{oct}}) + \ln(\text{Fe}_{\text{tet}}^{2+}) - 2 \ln 2] \end{aligned}$
$\begin{aligned} \mu_{\text{Fe}^{3+}(\text{Fe}^{3+}\text{Mg})\text{O}_4} = & g_0 + g_{s_3} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 + g_{r_1 s_3} r_1 + g_{r_2 s_3} r_2 + g_{s_1 s_3} s_1 + g_{s_2 s_3} s_2 \\ & + 2g_{s_3 s_3} s_3 - g_{r_1 r_2} r_1 r_2 - g_{r_1 s_1} r_1 s_1 - g_{r_1 s_2} r_1 s_2 - g_{r_1 s_3} r_1 s_3 - g_{r_2 s_1} r_2 s_1 - g_{r_2 s_2} r_2 s_2 - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_2} s_1 s_2 - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + RT \ln(\text{Fe}_{\text{tet}}^{3+}/\text{Fe}_{\text{oct}}^{3+})(\text{Mg}_{\text{oct}}) - 2 \ln 2 \end{aligned}$
$\begin{aligned} \mu_{\text{Mg}(\text{Fe}^{3+}\text{Fe}^{3+})\text{O}_4} = & g_0 + g_{s_2} - g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} s_3^2 + g_{r_1 s_2} r_1 + g_{r_2 s_2} r_2 + g_{s_1 s_2} s_1 + 2g_{s_2 s_2} s_2 + g_{s_2 s_3} s_3 \\ & - g_{r_1 r_2} r_1 r_2 - g_{r_1 s_1} r_1 s_1 - g_{r_1 s_2} r_1 s_2 - g_{r_1 s_3} r_1 s_3 - g_{r_2 s_1} r_2 s_1 - g_{r_2 s_2} r_2 s_2 - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_2} s_1 s_2 - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_2 s_3 \\ & + RT [2 \ln(\text{Fe}_{\text{oct}}^{3+}) + \ln(\text{Mg}_{\text{tet}}) - 2 \ln 2] \end{aligned}$

The chemical potential of any component is obtained by partial differentiation of the free energy of the solid solution with respect to each of the order and compositional parameters:

$$\begin{aligned} \mu_{a,b,c,d,e} = & G + (a - r_1) \left( \frac{\partial G}{\partial r_1} \right)_{T,P,r_2,s_1,s_2,s_3} \\ & + (b - r_2) \left( \frac{\partial G}{\partial r_2} \right)_{T,P,r_1,s_1,s_2,s_3} \\ & + (c - s_1) \left( \frac{\partial G}{\partial s_1} \right)_{T,P,r_1,r_2,s_2,s_3} \\ & + (d - s_2) \left( \frac{\partial G}{\partial s_2} \right)_{T,P,r_1,r_2,s_1,s_3} \\ & + (e - s_3) \left( \frac{\partial G}{\partial s_3} \right)_{T,P,r_1,r_2,s_1,s_2} \end{aligned} \quad (30)$$

The coefficients  $a$  to  $e$  in Equation 30 refer to the coordinates of the component of interest in  $r_1$ - $r_2$ - $s_1$ - $s_2$ - $s_3$  space. We present in Table 4 the results for each of the reference end-member components. The reader should note that these reference components are perfectly ordered or inverse and hence do not refer to pure "real"

$\text{MgAl}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeAl}_2\text{O}_4$ , and  $\text{MgFe}_2\text{O}_4$  at the conditions of interest. In order to obtain chemical potentials relative to partially disordered "real"  $\text{MgAl}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeAl}_2\text{O}_4$ , and  $\text{MgFe}_2\text{O}_4$  at the conditions of interest, it is necessary to insert appropriate values of the respective order parameters into Equation 30. The activities of  $\text{MgAl}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeAl}_2\text{O}_4$ , and  $\text{MgFe}_2\text{O}_4$  relative to standard states of the disordered pure end-members at the temperature and pressure of interest are then given by the following expressions:

$$\begin{aligned} RT \ln a_{\text{MgAl}_2\text{O}_4} = & -g_{r_1 r_1} r_1^2 - g_{r_2 r_2} (r_2 - 1)^2 \\ & - g_{s_1 s_1} [s_1 (s_1 - 2 + 2s_3) - s_1^2 (s_1^0 - 2 + 2s_3^0)] \\ & - g_{s_2 s_2} s_2^2 - g_{s_3 s_3} (s_3 - s_3^0)^2 \\ & - g_{r_1 r_2} r_1 (r_2 - 1) - g_{r_1 s_1} r_1 (s_1 + s_3^0 - 1) \\ & - g_{r_1 s_2} r_1 s_2 - g_{r_1 s_3} r_1 (s_3 - s_3^0) \\ & - g_{r_2 s_1} (r_2 - 1) (s_1 + s_3^0 - 1) \\ & - g_{r_2 s_2} s_2 (r_2 - 1) \\ & - g_{r_2 s_3} (r_2 - 1) (s_3 - s_3^0) \\ & - g_{s_1 s_2} s_2 (s_1 + s_3^0 - 1) \\ & - g_{s_1 s_3} (s_3 - s_3^0) (s_1 + s_3^0 + 1) \\ & - g_{s_2 s_3} s_2 (s_3 - s_3^0) \end{aligned}$$

$$\begin{aligned}
 & + RT \left\{ (1 - s_3^0) \right. \\
 & \quad \left. \cdot \left[ 2 \ln \frac{(Al_{oct})^{ss}}{(Al_{oct})^{sp}} + \ln \frac{(Mg_{tet})^{ss}}{(Mg_{tet})^{sp}} \right] \right\} \\
 & + RT \left\{ s_3^0 \ln \frac{[(Al_{tet})(Al_{oct})(Mg_{oct})]^{ss}}{[(Al_{tet})(Al_{oct})(Mg_{oct})]^{sp}} \right\} \quad (31)
 \end{aligned}$$

$$\begin{aligned}
 RT \ln a_{Fe_3O_4} = & -g_{r_1 r_1} (r_1 - 1)^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 \\
 & - g_{s_2 s_2} (s_2 - s_2^0)^2 \\
 & - g_{s_3 s_3} s_3^2 - g_{r_1 s_1} s_1 (r_1 - 1) \\
 & - g_{r_1 s_2} (r_1 - 1) (s_2 - s_2^0) - g_{r_1 s_3} s_3 (r_1 - 1) \\
 & - g_{r_2 s_1} r_2 s_1 - g_{r_2 s_2} r_2 (s_2 - s_2^0) \\
 & - g_{r_2 s_3} r_2 s_3 - g_{s_1 s_2} s_1 (s_2 - s_2^0) \\
 & - g_{s_1 s_3} s_1 s_3 - g_{s_2 s_3} s_3 (s_2 - s_2^0) \\
 & + RT \left\{ s_2^0 \left[ 2 \ln \frac{(Fe_{oct}^{3+})^{ss}}{(Fe_{oct}^{3+})^{mt}} + \ln \frac{(Fe_{tet}^{2+})^{ss}}{(Fe_{tet}^{2+})^{mt}} \right] \right\} \\
 & + RT \left\{ (1 - s_2^0) \right. \\
 & \quad \cdot \ln \frac{[(Fe_{oct}^{3+})(Fe_{tet}^{3+})(Fe_{oct}^{2+})]^{ss}}{[(Fe_{oct}^{3+})(Fe_{tet}^{3+})(Fe_{oct}^{2+})]^{mt}} \left. \right\} \quad (32)
 \end{aligned}$$

$$\begin{aligned}
 RT \ln a_{FeAl_2O_4} = & -g_{r_1 r_1} (r_1 - 1)^2 - g_{r_2 r_2} (r_2 - 1)^2 \\
 & - g_{s_1 s_1} (s_1 - s_1^0)^2 - g_{s_2 s_2} s_2^2 \\
 & - g_{s_3 s_3} s_3^2 - g_{r_1 r_2} (r_1 r_2 - r_1 - r_2 + 1) \\
 & - g_{r_1 s_1} (r_1 - 1) (s_1 - s_1^0) \\
 & - g_{r_1 s_2} s_2 (r_1 - 1) - g_{r_1 s_3} s_3 (r_1 - 1) \\
 & - g_{r_2 s_1} (r_2 - 1) (s_1 - s_1^0) \\
 & - g_{r_2 s_2} s_2 (r_2 - 1) - g_{r_2 s_3} s_3 (r_2 - 1) \\
 & - g_{s_1 s_2} s_2 (s_1 - s_1^0) \\
 & - g_{s_1 s_3} s_3 (s_1 - s_1^0) - g_{s_2 s_3} s_2 s_3 \\
 & + RT \left\{ s_1^0 \left[ 2 \ln \frac{(Al_{oct})^{ss}}{(Al_{oct})^{hc}} + \ln \frac{(Fe_{tet}^{2+})^{ss}}{(Fe_{tet}^{2+})^{hc}} \right] \right\} \\
 & + RT \left\{ (1 - s_1^0) \right. \\
 & \quad \cdot \ln \frac{[(Al_{oct})(Al_{tet})(Fe_{oct}^{2+})]^{ss}}{[(Al_{oct})(Al_{tet})(Fe_{oct}^{2+})]^{hc}} \left. \right\} \quad (33)
 \end{aligned}$$

$$\begin{aligned}
 RT \ln a_{MgFe_2O_4} = & -g_{r_1 r_1} r_1^2 - g_{r_2 r_2} r_2^2 - g_{s_1 s_1} s_1^2 \\
 & - g_{s_2 s_2} [s_2 (s_2 - 2 + 2s_3^0) \\
 & \quad - s_2^0 (s_2^0 - 2 + 2s_3^0)] \\
 & - g_{s_3 s_3} (s_3 - s_3^0)^2 \\
 & - g_{r_1 s_1} r_1 s_1 - g_{r_1 s_2} r_1 (s_2 + s_3^0 - 1) \\
 & - g_{r_1 s_3} r_1 (s_3 - s_3^0) - g_{r_2 s_1} r_2 s_1 \\
 & - g_{r_2 s_2} r_2 (s_2 + s_3^0 - 1) - g_{r_2 s_3} r_2 (s_3 - s_3^0) \\
 & - g_{s_1 s_2} s_1 (s_2 + s_3^0 - 1) \\
 & - g_{s_1 s_3} s_1 (s_3 - s_3^0) \\
 & - g_{s_2 s_3} (s_3 - s_3^0) (s_2 + s_3^0 - 1) \\
 & + RT \left\{ (1 - s_3^0) \right. \\
 & \quad \cdot \left[ 2 \ln \frac{(Fe_{oct}^{3+})^{ss}}{(Fe_{oct}^{3+})^{mf}} + \ln \frac{(Mg_{tet})^{r}}{(Mg_{tet})^{mf}} \right] \left. \right\}
 \end{aligned}$$

**TABLE 5.** Internally consistent values of the Taylor's series expansion coefficients

Coefficient	Value (kJ/mol)
$g_{s_1}$	14.7 ± 0.5
$g_{s_2}$	44.5 ± 4.5
$g_{s_3}$	34.0 ± 2.5
$g_{r_1 r_1}$	-10.0 ± 1.0
$g_{r_2 r_2}$	-38.0 ± 2.0
$g_{s_1 s_1}$	-25.7 ± 1.5
$g_{s_2 s_2}$	-26.6 ± 1.3
$g_{s_3 s_3}$	-15.0 ± 3.0
$g_{r_1 r_2}$	10.0 ± 3.0
$g_{r_1 s_1}$	-7.1 ± 0.5
$g_{r_1 s_2}$	-25.0 ± 3.5
$g_{r_1 s_3}$	-15.0 ± 2.0
$g_{r_2 s_1}$	5.5 ± 3.0
$g_{r_2 s_2}$	-16.6 ± 4.0
$g_{r_2 s_3}$	-11.9 ± 2.0
$g_{s_1 s_2}$	-16.0 ± 12.0
$g_{s_1 s_3}$	-15.0 ± 3.0
$g_{s_2 s_3}$	-24.6 ± 2.0

$$+ RT \left\{ s_3^0 \ln \frac{[(Fe_{tet}^{3+})(Fe_{oct}^{3+})(Mg_{oct})]^{ss}}{[(Fe_{tet}^{3+})(Fe_{oct}^{3+})(Mg_{oct})]^{mf}} \right\}, \quad (34)$$

where the superscripts ss, sp, mt, hc, and mf refer, respectively, to solid solutions, pure spinel, pure magnetite, pure hercynite, and pure magnesioferrite, whereas the superscript 0 on the order parameters  $s_1$ ,  $s_2$ , and  $s_3$  refers to the values of these parameters in pure disordered end-member spinels.

#### CONSTRAINT OF MODEL PARAMETERS

Values of the order and combined order and composition coefficients in the Taylor series expansion (Table 5) were obtained from least-squares fits to available cation-distribution data for magnetite (Wu and Mason, 1981), spinel (Wood et al., 1986), and magnesioferrite (Pauthenet and Bochirol, 1951; Kriessman and Harrison, 1956; Epstein and Frackiewicz, 1958; Mozzi and Paladino, 1963; Blasse, 1964; Tellier, 1967) and from the  $Fe_3O_4$ - $MgFe_2O_4$  and  $Fe_3O_4$ - $FeAl_2O_4$  solid solutions measured by Nell et al. (1989). Cation disordering in hercynite is poorly constrained (Bohlen et al., 1986), and as an initial approximation, we assumed that  $Fe^{2+}$ -Al disordering in  $FeAl_2O_4$  is identical to Mg-Al disordering in  $MgAl_2O_4$  (Wood et al., 1986). Such disordering behavior in hercynite is in agreement with measured  $Fe^{2+}$ -Al distributions in  $Fe_3O_4$ - $FeAl_2O_4$  solid solutions (Nell et al., 1989), whereas the resultant small absolute value of the  $g_{s_1 s_1}$  coefficient facilitates fitting of the macroscopic thermodynamic measurements in  $FeAl_2O_4$ - $MgAl_2O_4$ ,  $Fe_3O_4$ - $MgFe_2O_4$ , and  $Fe_3O_4$ - $MgAl_2O_4$  solid solutions.

First, cation-distribution data for magnetite, magnesioferrite, and spinel were fitted to Equations 16 to 18, respectively, thus fixing the value of the  $g_{s_2 s_2}$  coefficient and constraining the values of the quantities ( $g_{s_2} + g_{r_1 s_2}$ ), ( $g_{s_3} + g_{r_2 s_3} + 2g_{s_3 s_3} - g_{s_1} - g_{r_2 s_1} - g_{s_1 s_3}$ ), ( $g_{s_1 s_3} - g_{s_1 s_1} - g_{s_3 s_3}$ ), ( $g_{s_3} - g_{s_2} + 2g_{s_3 s_3} - g_{s_2 s_3}$ ), and ( $g_{s_2 s_3} - g_{s_3 s_3} - g_{s_2 s_2}$ ), whereas the assumed disordering of hercynite implied that  $g_{s_1 s_3} =$

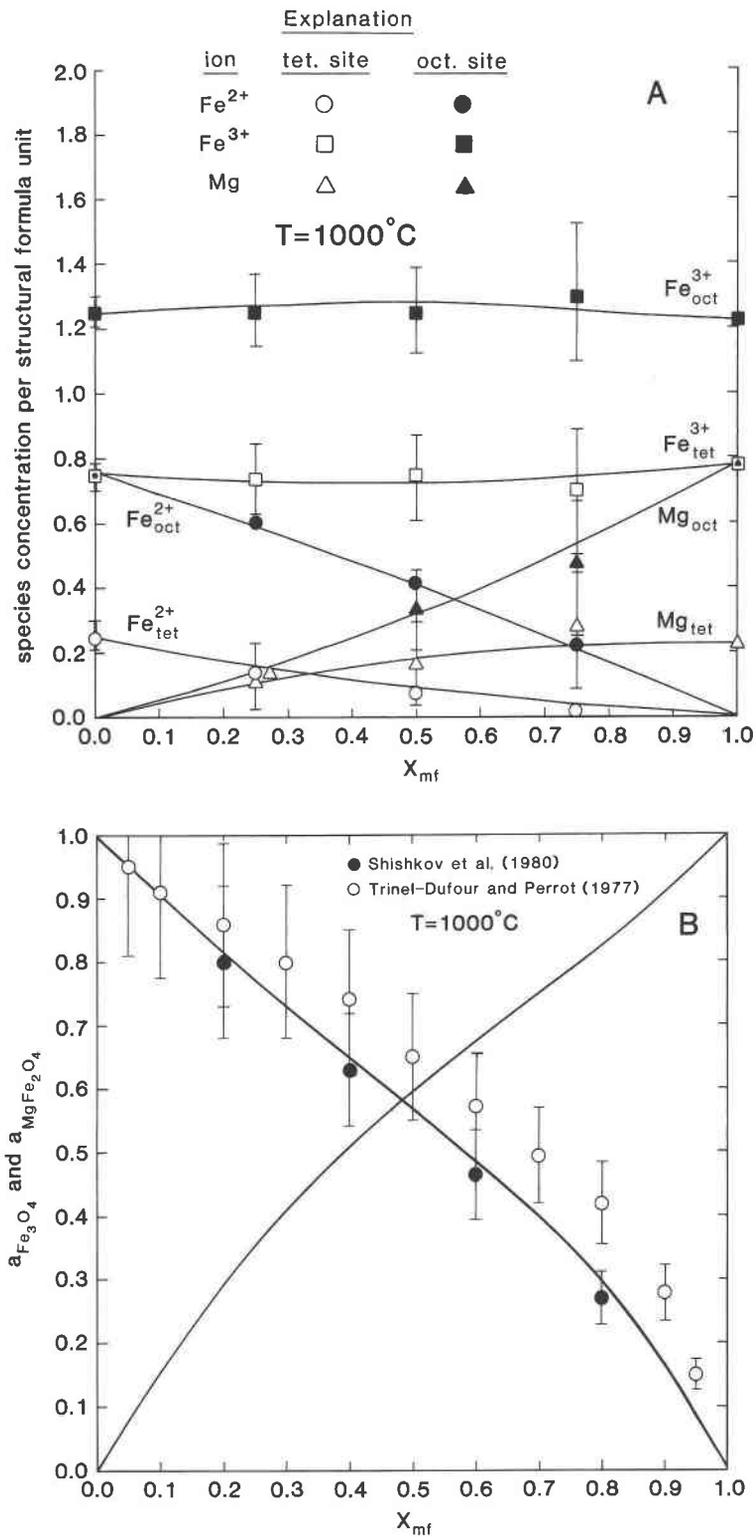


Fig. 1. (A) Cation distributions on the join  $Fe_3O_4$ - $MgFe_2O_4$  at 1000 °C (Nell et al., 1989) plotted as a function of mole fraction of  $MgFe_2O_4$  ( $X_{mf}$ ). Solid curves are values calculated from the model (see text). (B) Activity-composition relations for the  $Fe_3O_4$ - $MgFe_2O_4$  join at 1000 °C. Solid curves are values calculated from the model.

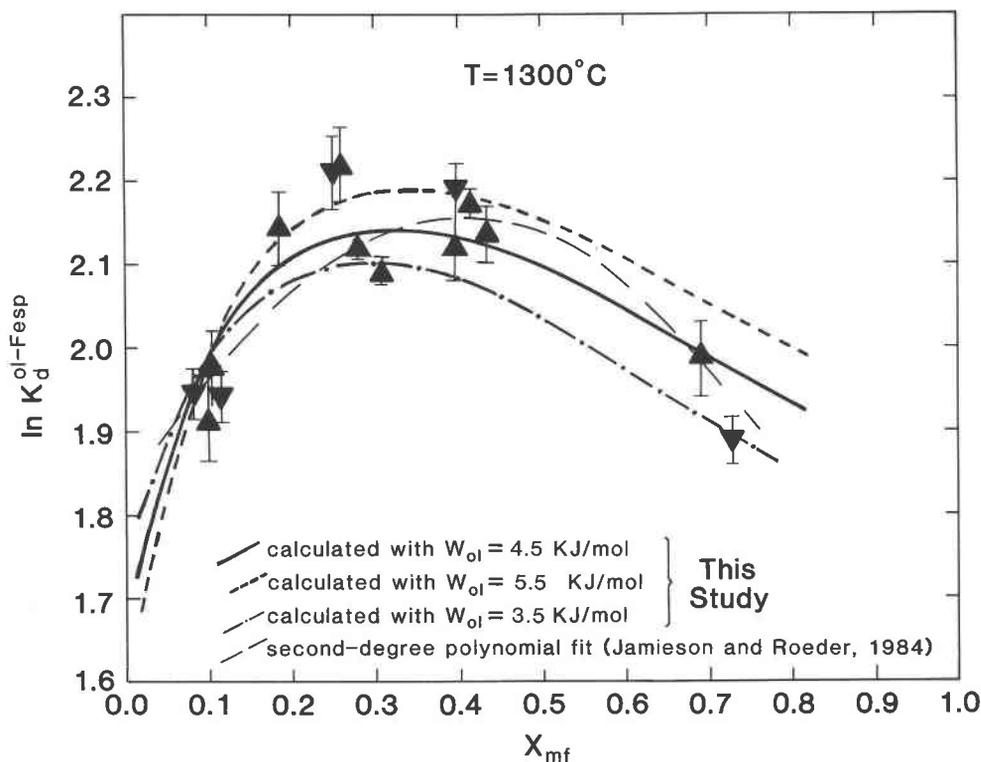


Fig. 2. Calculated values of  $\ln K_d^{ol-Fesp}$  [ $K_d = ((X_{Fe_3O_4}^{Fesp})(X_{MgSi_0.5O_2}^{ol})) / ((X_{MgFe_2O_4}^{Fesp})(X_{FeSi_0.5O_2}^{ol}))$ ] compared to the measurements of Jamieson and Roeder (1984) at 1300 °C. The calculations take account of the nonideality in olivine ( $W_{ol}$  on a 1-atom basis) and the probable uncertainty in the regular-solution parameter. Direction of approach to equilibrium in the experimental measurements is indicated by arrows on the error bars.

$g_{s_3s_3}$  and  $g_{r_1s_1} = g_{s_1s_3} - g_{s_3} - g_{r_2s_3} - 2g_{s_3s_3}$ . Next, Fe<sup>2+</sup>-Mg distributions in Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> were fitted to Equation 22 to obtain values for  $g_{r_1s_3}$ ,  $g_{s_3}$ ,  $g_{s_1s_3}$ , and  $g_{s_3s_3}$ . Consistency with the constraints imposed by the fits to magnetite and magnesioferrite then allowed the calculation of  $g_{s_2s_3}$ ,  $g_{s_2}$  and  $g_{r_1s_2}$ . Similarly, Fe<sup>2+</sup>-Al distributions in Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solutions were fitted to Equation 23, fixing  $g_{r_2s_1}$ , and  $g_{s_1} + g_{r_1s_1}$ , and  $g_{r_2s_2}$  was obtained from the Fe<sup>3+</sup>-Fe<sup>2+</sup> distribution in Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solutions through Equation 24. The values of all but three ( $g_{s_1}$ ,  $g_{r_2s_3}$ , and  $g_{r_1s_1}$ ) of the Taylor series expansion coefficients in Equations 12 to 14 were thus determined. The  $g_{s_1}$  and  $g_{r_1s_1}$  coefficients could be obtained by fitting Equation 12 to Fe<sup>2+</sup>-Al distributions in FeAl<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>, FeAl<sub>2</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub>, or Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions. The Fe<sup>2+</sup>-Al intersite distributions in these solid solutions are, however, not amenable to direct measurement, and in order to estimate the values of  $g_{s_1}$  and  $g_{r_1s_1}$ , we fitted Equation 12 to an assumed linear relationship between the Al-Fe<sup>2+</sup> distribution coefficient and composition in FeAl<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions.

Values of the composition parameters in the Taylor series expansion were determined from activity-composition relations and phase-equilibrium experiments in Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub>, and MgAl<sub>2</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> spinels. The value of the  $g_{r_2r_2}$  param-

eter was determined from the experimentally observed solvus in Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solutions, which has a consolute temperature of  $860 \pm 15$  °C (Turnock and Eugster, 1962). The  $g_{r_1r_1}$  parameter was determined from activity-composition measurements in Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> solid solutions at 1000 °C (Shishkov et al., 1980; Trinel-Dufour and Perrot, 1977) and Fe<sup>2+</sup>-Mg partitioning experiments between olivine and spinel solid solutions at 1300 °C (Jamieson and Roeder, 1984) and a chloride aqueous solution and spinel at 800 °C (Lehmann and Roux, 1986). Finally, the value of  $g_{r_1r_2}$  was constrained from activity-composition relations in Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions at 1000 °C (Mattioli and Wood, 1988).

The coefficients  $g_0$ ,  $g_{r_1}$ , and  $g_{r_2}$  determine absolute values of end-member chemical potentials and are not required for activity-composition calculations (Eqs. 31 to 34). These parameters were therefore set to zero. Finally, the derived values of the order, compositional, and combined order and composition parameters were tested and refined by comparing calculated cation-site fractions, activity-composition relations, and partitioning coefficients with experimentally measured cation distributions, activity-composition relations, and partitioning data in Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>, MgAl<sub>2</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>, and Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions. The refined values for the expansion coefficients and their estimated uncertainties are

reported in Table 5. The values are not unique since the expansion coefficients are highly correlated. The estimated uncertainties are not intended to reflect these correlations but rather to indicate ranges over which the refined values may be varied while preserving a satisfactory fit to the experimental data.

#### APPLICATION OF THE MODEL TO Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> SOLID SOLUTIONS

Theoretical cation distributions and activity-composition relations in Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>, MgAl<sub>2</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub>, and Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions were calculated using the values of the expansion coefficients in Table 5. Cation distributions were calculated from Equations 21 to 27. The nonlinear simultaneous equations were solved using a Newton-Raphson method (e.g., Gerald and Wheatley, 1984, p. 133–159), and the results are presented as solid lines in Figures 1A, 3A, and 4A. Activities of spinel, magnetite, hercynite, and magnesioferrite were calculated from Equations 31 to 34, respectively, and the results are presented as solid lines in Figures 1B, 3B, and 4B.

#### Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> solid solutions

Calculated cation distributions at 1000 °C (Fig. 1A) are in excellent agreement with experimental results obtained from the combined thermopower and conductivity technique (Nell et al., 1989). Activity-composition relations at 1000 °C display a positive deviation from ideality intermediate between the data of Shishkov et al. (1980) and Trinel-Dufour and Perrot (1977) (Fig. 1B). Error bars on the data points in Figure 1B represent an estimated uncertainty of ±10% in the measured activities. Jamieson and Roeder (1984) performed Fe<sup>2+</sup>-Mg exchange experiments between olivine and Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> solid solutions at high temperatures. We used their data to constrain Fe<sub>3</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub> activities at 1300 °C. The Fe<sup>2+</sup>-Mg exchange equilibrium between olivine (ol) and Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> solid solutions (Fesp) is given by

$$\begin{aligned} \ln K_a^{\text{ol-Fesp}} &= \ln \frac{(X_{\text{Fe}_3\text{O}_4}^{\text{Fesp}})(X_{\text{MgSi}_{0.5}\text{O}_2}^{\text{ol}})}{(X_{\text{MgFe}_2\text{O}_4}^{\text{Fesp}})(X_{\text{FeSi}_{0.5}\text{O}_2}^{\text{ol}})} \\ &= \ln K_a^{\text{ol-Fesp}} + \ln \frac{\gamma_{\text{MgFe}_2\text{O}_4}}{\gamma_{\text{Fe}_3\text{O}_4}} \\ &\quad - \frac{W_{\text{ol}}}{RT} + \frac{2W_{\text{ol}}}{RT} X_{\text{MgSi}_{0.5}\text{O}_2}^{\text{ol}} \end{aligned} \quad (35)$$

where  $K_a^{\text{ol-Fesp}}$  is the equilibrium constant for the olivine-spinel exchange reaction,  $X_{\text{Fe}_3\text{O}_4}^{\text{Fesp}}$  is the mole fraction of magnetite in the spinel solid solution,  $\gamma_{\text{Fe}_3\text{O}_4}$  ( $= a_{\text{Fe}_3\text{O}_4} / X_{\text{Fe}_3\text{O}_4}^{\text{Fesp}}$ ) is the activity coefficient of magnetite in spinel solid solution, and  $W_{\text{ol}}$  is the regular-solution parameter for Fe-Mg olivine. Theoretical  $K_a^{\text{ol-Fesp}}$  values at fixed spinel compositions were calculated from Equation 35 using  $\gamma_{\text{Fe}_3\text{O}_4}$  and  $\gamma_{\text{MgFe}_2\text{O}_4}$  values obtained from our calculated

activity-composition relations. Assuming a value of  $4.5 \pm 1.0$  kJ/mol on a 1-atom basis for the regular-solution interaction parameter ( $W_{\text{ol}}$ ) in olivine (Nafziger and Muan, 1967; O'Neill and Wall, 1987), the mean value for  $\ln K_a^{\text{ol-Fesp}}$  over the compositional range  $0.1 < X_{\text{MgFe}_2\text{O}_4} < 0.75$  was estimated to be 1.80. As can be seen from Figure 2, the calculated  $\ln K_a^{\text{ol-Fesp}}$  values are in good agreement with the experimental measurements within the range of likely values of  $W_{\text{ol}}$ .

#### Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solutions

Phase-equilibrium experiments at 2-kbar pressure (Turnock and Eugster, 1962) indicate the presence of a solvus at a composition of 55 mol% FeAl<sub>2</sub>O<sub>4</sub> and a consolute temperature of  $860 \pm 15$  °C in this system. Only these data were used as constraints on the mixing properties on this join, and our model calculates a solvus in almost perfect agreement with the experimental data. Calculated cation distributions and activity-composition relations at 1300 °C are presented in Figures 3A and 3B, respectively. There is excellent agreement with the measured cation distributions, and the predicted activity-composition relations are within the uncertainties in the data of Petric et al. (1981). Petric et al. determined activities by equilibrating spinel with Pt-Fe solid solutions at fixed  $P_{\text{O}_2}$ . Their data give an uncertainty of ±0.06 log units in  $\log a_{\text{Fe}}$  in the metal solution, and this uncertainty results in the error bars given in Figure 3B.

#### Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions

The combined thermopower and conductivity technique used to determine cation distributions in Fe<sub>3</sub>O<sub>4</sub>-MgFe<sub>2</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solutions (Nell et al., 1989) does not provide information on the intersite distributions of Mg and Al in Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions. In our earlier paper (Nell et al., 1989), we combined thermopower-conductivity measurements on Fe<sub>3</sub>O<sub>4</sub>-MgAl<sub>2</sub>O<sub>4</sub> solid solutions with the O'Neill-Navrotsky model to estimate the amount of tetrahedral Al. In the present study we opted to use the Gibbs-Duhem equation to calculate partial molar spinel entropies from our measured partial molar entropies of Fe<sub>3</sub>O<sub>4</sub>. These were then solved to obtain a model-independent concentration of Al on tetrahedral sites. Uncertainties in the calculated values of  $\text{Al}_{\text{tet}}$  arising from the integration of the Gibbs-Duhem equation were assessed by calculating  $\text{Al}_{\text{tet}}$  in Fe<sub>3</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solutions through the use of a similar procedure and then by comparing the result with the actual measured values of  $\text{Al}_{\text{tet}}$ . The results and uncertainties at 1000 °C are shown in Figure 4A together with theoretical cation-distribution curves. Cation distributions in this system were not used to constrain the values of the expansion coefficients, and the calculated cation distributions are therefore entirely predicted.

Calculated activity-composition relations are compared to the data of Mattioli and Wood (1988) in Figure 4B. The calculated solvus has a consolute temperature of about 1025 °C at a composition of 56 mol% Fe<sub>3</sub>O<sub>4</sub>. The

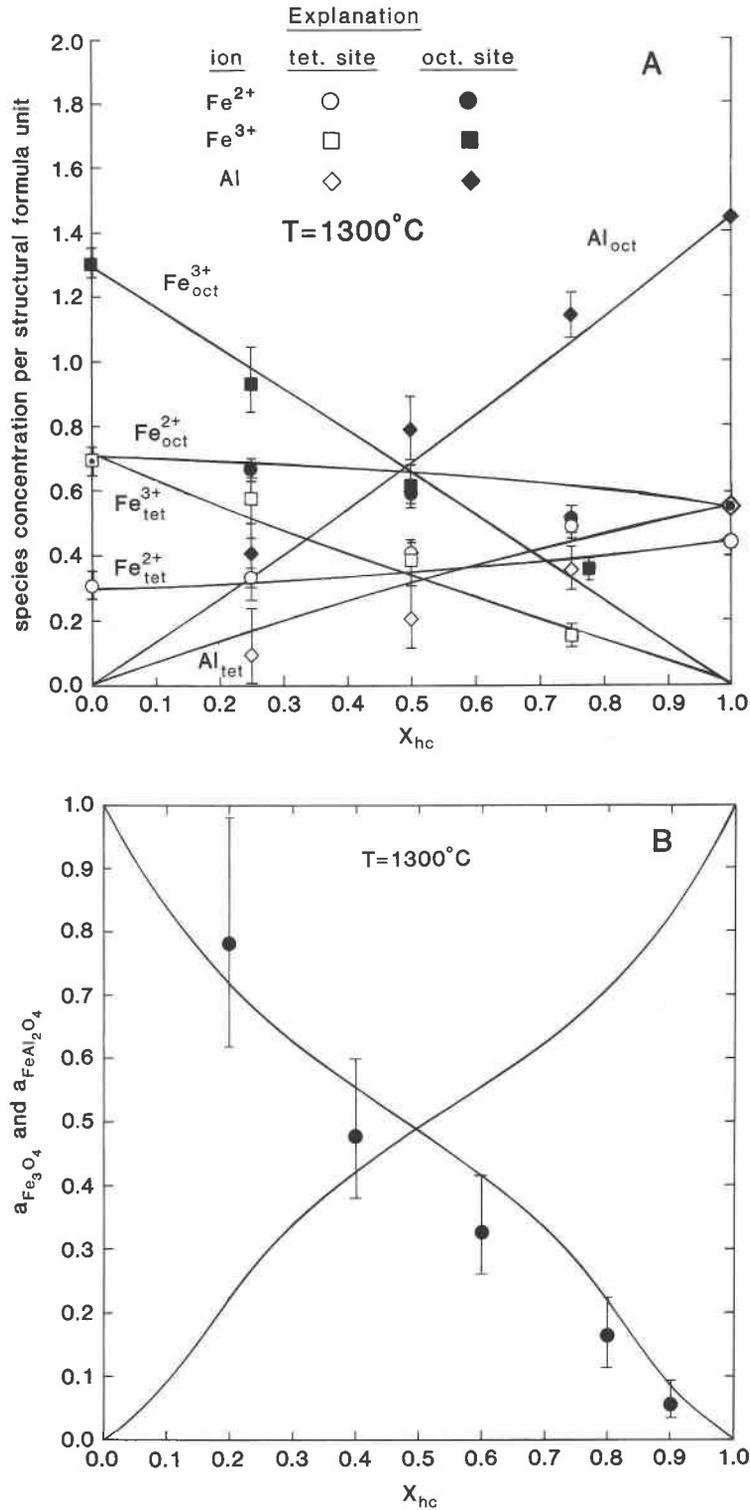
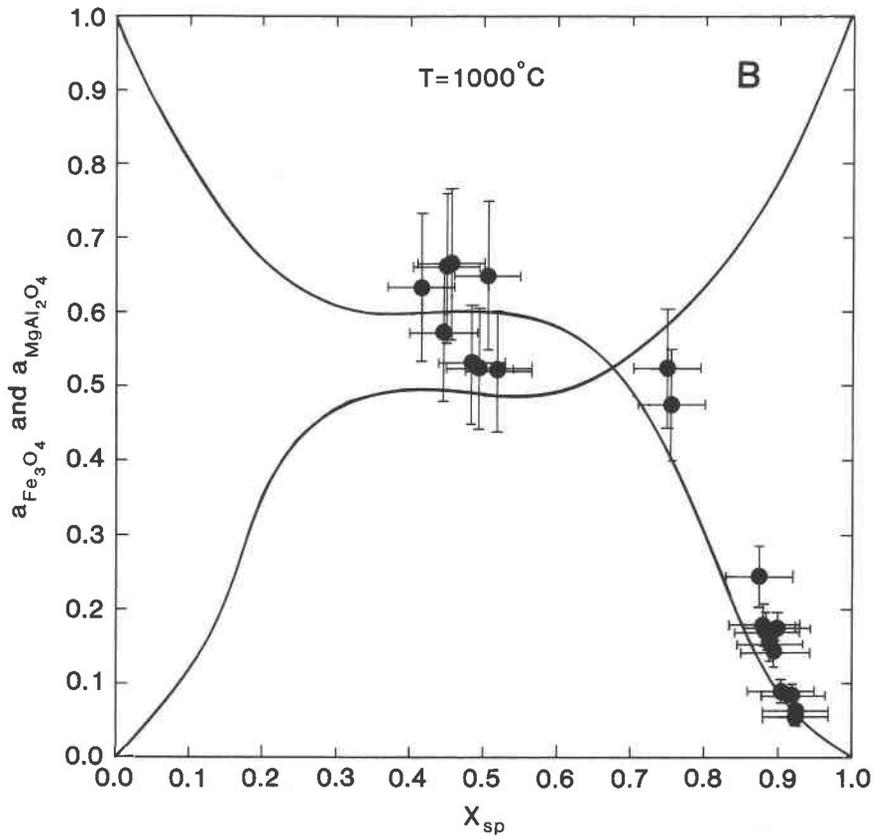
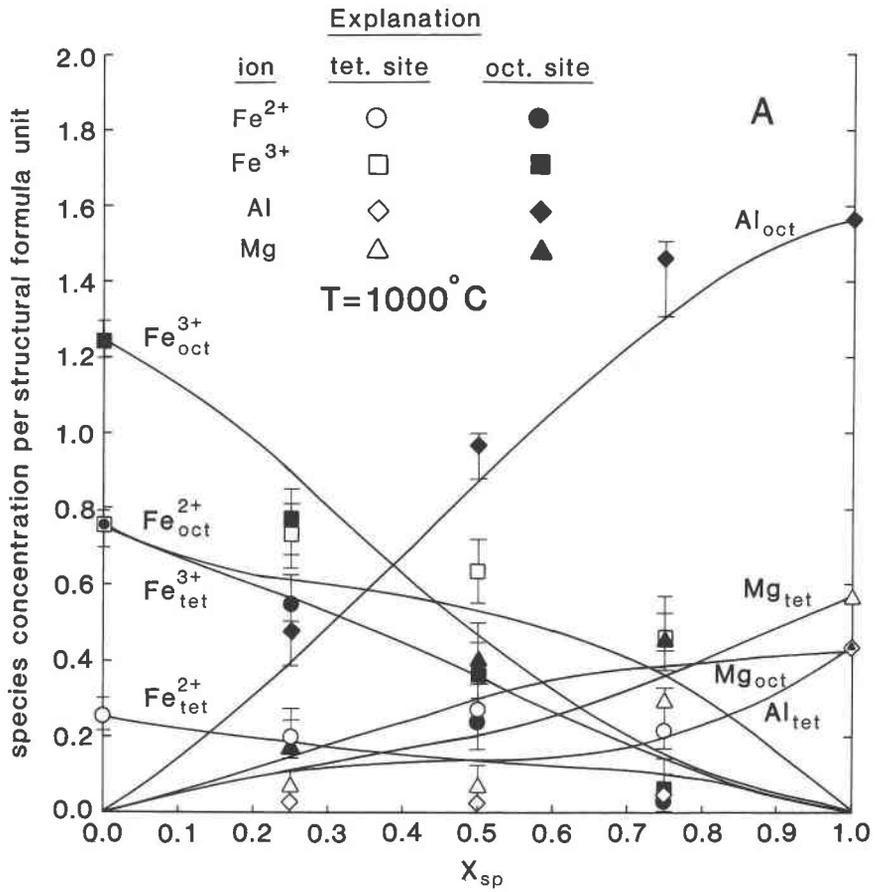


Fig. 3. (A) Calculated cation distributions on the join  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$  at  $1300^{\circ}\text{C}$  plotted as a function of mole fraction of  $\text{FeAl}_2\text{O}_4$  ( $X_{hc}$ ). Experimental data are from Nell et al. (1989). (B) Predicted activity-composition relations in  $\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$  spinels at  $1300^{\circ}\text{C}$  compared to the measurements of Petric et al. (1981).



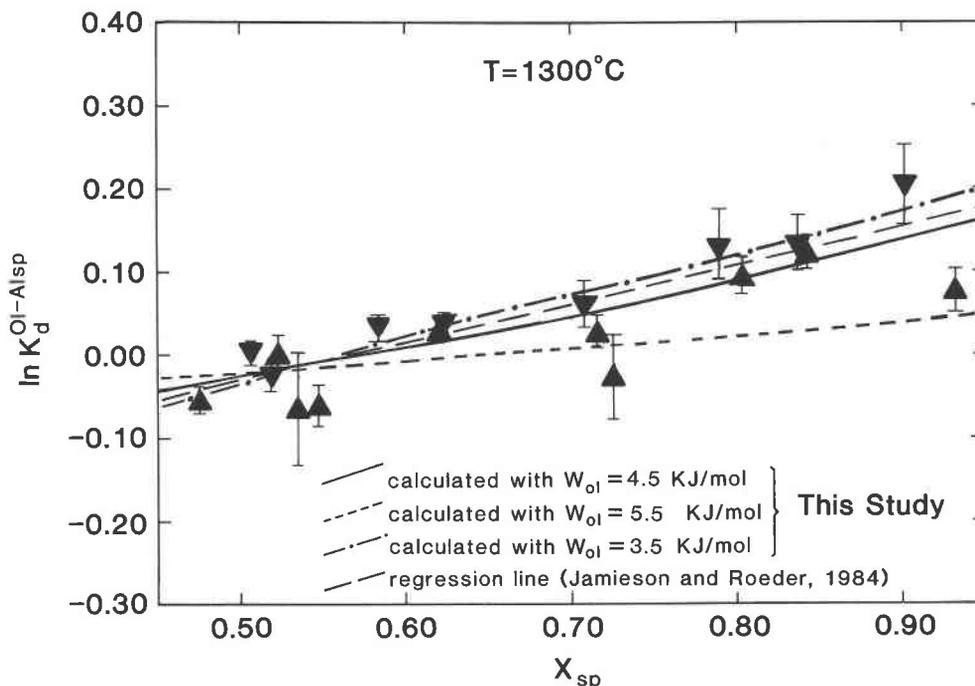


Figure 5. Calculated values of  $\ln K_d^{\text{Ol-Alsp}}$  ( $K_d^{\text{Ol-Alsp}} = [(X_{\text{MgAl}_2\text{O}_4}^{\text{Alsp}})(X_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Ol}})] / [(X_{\text{FeAl}_2\text{O}_4}^{\text{Alsp}})(X_{\text{MgSi}_{0.5}\text{O}_2}^{\text{Ol}})]$ ) for the join  $\text{FeAl}_2\text{O}_4\text{-MgAl}_2\text{O}_4$  compared to the measurements of Jamieson and Roeder (1984) at 1300 °C. Calculated distribution coefficients favor a value of about 3.5 kJ/mol on a 1-atom basis for the regular solution interaction parameter in olivine ( $W_{\text{ol}}$ ). Direction of approach to equilibrium in the experimental measurements is indicated by arrows on the error bars.

solvus predicted by our model is a compromise between the model of Lehmann and Roux (1986), who calculated a wider miscibility gap at 1000 °C, and the results of Mattioli and Wood (1988), who estimated the consolute temperature to be between 900 and 1000 °C.

#### $\text{MgAl}_2\text{O}_4\text{-FeAl}_2\text{O}_4$ solid solutions

Activity-composition relations were estimated from  $\text{Fe}^{2+}\text{-Mg}$  exchange experiments between olivine and spinel (Jamieson and Roeder, 1984) at 1300 °C and aqueous chloride solution and spinel at 800 °C (Lehmann and Roux, 1986). The equilibrium between olivine (ol) and  $\text{MgAl}_2\text{O}_4\text{-FeAl}_2\text{O}_4$  solid solutions (Alsp) is expressed as

$$\begin{aligned} \ln K_d^{\text{Ol-Alsp}} &= \ln \frac{(X_{\text{MgAl}_2\text{O}_4}^{\text{Alsp}})(X_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Ol}})}{(X_{\text{FeAl}_2\text{O}_4}^{\text{Alsp}})(X_{\text{MgSi}_{0.5}\text{O}_2}^{\text{Ol}})} \\ &= \ln K_a^{\text{Ol-Alsp}} + \ln \frac{\gamma_{\text{FeAl}_2\text{O}_4}}{\gamma_{\text{MgAl}_2\text{O}_4}} \\ &\quad - \frac{W_{\text{ol}}}{RT} + \frac{2W_{\text{ol}}}{RT} X_{\text{FeSi}_{0.5}\text{O}_2}^{\text{Ol}} \end{aligned} \quad (36)$$

Following the procedure outlined above for  $\text{Fe}_3\text{O}_4\text{-MgFe}_2\text{O}_4$  solid solutions, we used a value of  $W_{\text{ol}}$  of  $4.5 \pm 1.0$  kJ/mol on a 1-atom basis and found a mean value of  $\ln K_a^{\text{Ol-Alsp}}$  over the composition range  $0.5 < X_{\text{MgAl}_2\text{O}_4} < 0.9$  to be  $-0.02$ . Calculated values of  $\ln K_d^{\text{Ol-Alsp}}$  are in excellent agreement with the measured values of Jamieson and Roeder (1984) (Fig. 5).

Equilibrium between an ideal chloride aqueous solution (fl) and  $\text{MgAl}_2\text{O}_4\text{-FeAl}_2\text{O}_4$  solid solutions (Alsp) is given by the following relationship:

$$\begin{aligned} \ln \frac{(X_{\text{FeAl}_2\text{O}_4}^{\text{Alsp}})(X_{\text{MgCl}_2}^{\text{fl}})}{(X_{\text{MgAl}_2\text{O}_4}^{\text{Alsp}})(X_{\text{FeCl}_2}^{\text{fl}})} &= \ln K_a^{\text{fl-Alsp}} \\ &+ \ln \frac{\gamma_{\text{MgAl}_2\text{O}_4}}{\gamma_{\text{FeAl}_2\text{O}_4}} \end{aligned} \quad (37)$$

The agreement between our calculated activities and the data of Lehmann and Roux (1986) is excellent (Fig. 6). The mean value of  $\ln K_a^{\text{fl-Alsp}}$  is calculated to be  $-1.4$ .

#### CONCLUSIONS

A second-degree Taylor series expansion of the vibrational part of the Gibbs free energy was used to model

Fig. 4. (A) Predicted cation distributions on the join  $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$  at 1000 °C plotted as a function of mole fraction of  $\text{MgAl}_2\text{O}_4$  ( $X_{\text{sp}}$ ).  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  site-occupancy data are from Nell et al. (1989). Al and Mg intersite distributions were calculated by using the Gibbs-Duhem method (see text). (B) Calculated activity-composition relations for the  $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$  join at 1000 °C. Experimental measurements are from Mattioli and Wood (1988).

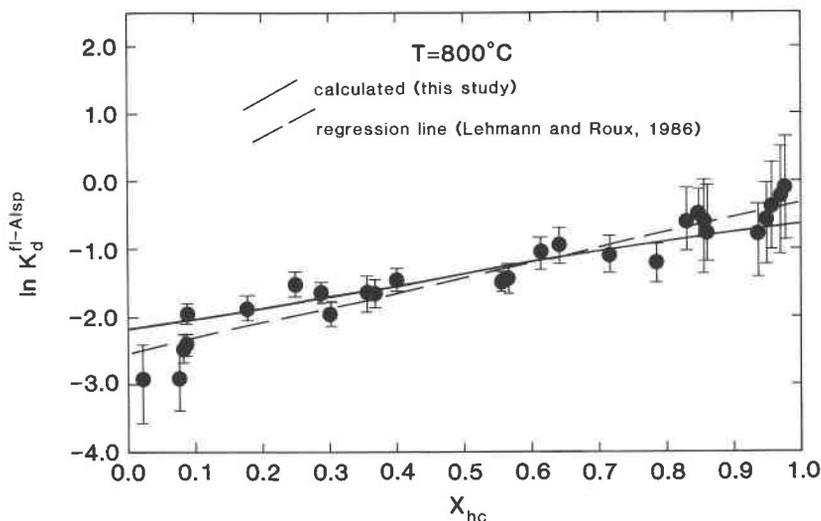


Fig. 6. Calculated values of  $\ln K_d^{(f)-Alsp}$  ( $K_d^{(f)-Alsp} = [(X_{FeAl_2O_4}^{Alsp})(X_{MgAl_2O_4}^{Fe})]/[(X_{MgAl_2O_4}^{Alsp})(X_{FeAl_2O_4}^{Fe})]$ ) for the join  $FeAl_2O_4$ - $MgAl_2O_4$  compared to the measurements of Lehmann and Roux (1986) at 800 °C.

cation distributions and activity-composition relations in  $Fe_3O_4$ - $MgFe_2O_4$ - $FeAl_2O_4$ - $MgAl_2O_4$  solid solutions. The resulting expression for the Gibbs free energy is symmetric with respect to order, composition, and combined order and composition parameters. Activity-composition relations and intersite cation distributions are thus treated with symmetric excess mixing energies. The Taylor series expansion coefficients are overdetermined, and as a result, certain relationships exist between the excess free-energy terms in the solution set of expansion coefficients. The Navrotsky-Kleppa (1967) model ( $-RT \ln K_D = \text{constant}$ ) for intersite cation distributions is obtained from the Taylor series expansion when all excess mixing energies are set to zero. The constants used in this formalism are shown to be differences between chemical potentials of reference end-member components. The O'Neill-Navrotsky (1983, 1984) model ( $-RT \ln K_D = \alpha + 2\beta B_{tet}^{+}$ ) for intersite cation distributions in pure end-member spinels is identical to the second-degree Taylor series expansion with the  $\beta$  energy parameter given by the regular symmetric interaction parameter between divalent and trivalent cations on tetrahedral and octahedral sites. In binary and quaternary solid solutions, the O'Neill-Navrotsky formalism corresponds to a second-degree series expansion in which the combined order and composition parameters are equal to zero.

The values of the series expansion coefficients were constrained from measured cation distributions and activity-composition relations in  $Fe_3O_4$ - $MgFe_2O_4$ ,  $Fe_3O_4$ - $FeAl_2O_4$ ,  $MgAl_2O_4$ - $FeAl_2O_4$ ,  $MgFe_2O_4$ - $MgAl_2O_4$ , and  $Fe_3O_4$ - $MgAl_2O_4$  solid solutions. The resultant data set allows calculation of internally consistent cation distributions and activity-composition relations in  $Fe_3O_4$ - $MgAl_2O_4$ - $MgFe_2O_4$ - $FeAl_2O_4$  solid solutions.

Application of the model to calculate cation distributions and activity-composition relations in  $Fe_3O_4$ -

$MgFe_2O_4$ ,  $Fe_3O_4$ - $FeAl_2O_4$ ,  $MgAl_2O_4$ - $FeAl_2O_4$ , and  $Fe_3O_4$ - $MgAl_2O_4$  solid solutions shows good agreement between the calculated values and experimental measurements. Regular symmetric interaction parameters adequately describe mixing in  $Fe_3O_4$ - $FeAl_2O_4$ ,  $MgAl_2O_4$ - $FeAl_2O_4$ ,  $Fe_3O_4$ - $MgFe_2O_4$ , and  $Fe_3O_4$ - $MgAl_2O_4$  solid solutions, and a solvus with consolute temperature of about 1025 °C is generated in the latter system.

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