High-temperature electrical measurements and thermodynamic properties of \( \text{Fe}_3\text{O}_4-\text{FeCr}_2\text{O}_4-\text{MgCr}_2\text{O}_4-\text{FeAl}_2\text{O}_4 \) spinels

JOHAN NELL, BERNARD J. WOOD
Department of Geology, University of Bristol, Bristol BS8 1RJ, Great Britain

ABSTRACT

Electrical conductivity and thermopower measurements have been made on \( \text{Fe}_3\text{O}_4-\text{FeCr}_2\text{O}_4, \text{Fe}_3\text{O}_4-\text{MgCr}_2\text{O}_4, \) and \( \text{Fe}_3\text{O}_4-\text{FeCr}_2\text{O}_4-\text{FeAl}_2\text{O}_4 \) spinel solid solutions at 600 °C to 1400 °C and 1 atm. Our analysis of the data indicates that these are \( n \)-type small polaron conductors, as in \( \text{Fe}_3\text{O}_4 \), with electron hopping confined to the octahedral sites. If \( \text{Cr}^{3+} \) is not involved in the conduction mechanism (i.e., \( \text{Fe}^{2+}-\text{Fe}^{3+} \) hopping only) then, with octahedral site hopping, the combined thermopower-electrical conductivity technique enables high-temperature cation distributions to be obtained.

On the \( \text{Fe}_3\text{O}_4-\text{FeCr}_2\text{O}_4 \) join we have found, from measurements of the independent density of states, that hopping is octahedral and involves \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) only at compositions with 40% or more of \( \text{Fe}_3\text{O}_4 \), but that \( \text{Cr}^{3+} \) becomes involved in the conduction process at very \( \text{FeCr}_2\text{O}_4 \)-rich compositions. We have therefore excluded data on very \( \text{Cr}^{3+} \)-rich compositions, which also exhibit high activation energies, from our estimates of cation distributions.

The thermopower and electrical conductivity data were combined with earlier results on the joins \( \text{Fe}_3\text{O}_4-\text{MgFe}_2\text{O}_4, \text{Fe}_3\text{O}_4-\text{FeAl}_2\text{O}_4, \) and \( \text{Fe}_3\text{O}_4-\text{MgAl}_2\text{O}_4 \) to estimate cation distributions for compositions within the geologically important system \( (\text{Mg}^{2+},\text{Fe}^{3+})-(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})r\text{O}_4 \). The cation distributions were then combined with activity-composition relations and interphase partitioning data to derive a complete thermodynamic model for the complex system \( (\text{Mg}^{2+},\text{Fe}^{2+})-(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})r\text{O}_4 \). The model, which takes explicit account of order-disorder relations, produces and successfully predicts a wide range of macroscopic thermodynamic measurements that have been made on simple and complex spinels. A computer program to generate cation distributions and activities is available from B. J. Wood.

INTRODUCTION

The importance of spinels as furnace smelting products and as petrogenetic indicators in a wide range of igneous and metamorphic rocks has been emphasized in many studies of their thermodynamic properties (e.g., Sack, 1982; Buddington and Lindsey, 1964; Irvine, 1965; Mattioli and Wood, 1988). We recently reported high-temperature thermopower and electrical conductivity measurements on \( \text{Fe}_3\text{O}_4-\text{MgFe}_2\text{O}_4, \text{Fe}_3\text{O}_4-\text{FeAl}_2\text{O}_4, \) and \( \text{Fe}_3\text{O}_4-\text{MgAl}_2\text{O}_4 \) spinel solid solutions (Nell et al., 1989) and used the results to estimate cation distributions from the model of Mason (1987). The cation distributions were subsequently combined with activity-composition relations and interphase partitioning data to develop an internally consistent thermodynamic model for \( (\text{Mg}^{2+}, \text{Fe}^{2+})-(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})r\text{O}_4 \) spinels (Nell and Wood, 1989). Application of the model to natural spinels is limited, however, since most geologically important systems contain \( \text{Cr}_2\text{O}_3 \) or \( \text{TiO}_2 \) components. We have therefore extended our electrical measurements to \( \text{Cr}_2\text{O}_3 \)-bearing spinels in the system \( (\text{Mg}^{2+},\text{Fe}^{3+})-(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})r\text{O}_4 \) which closely approximate the compositions of many naturally occurring members of the spinel group.

Characterization of order-disorder relations is central to the understanding of the thermodynamic properties of spinels (O'Neill and Navrotsky, 1983, 1984; Nell et al., 1989). In the system \( (\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})r\text{O}_4 \), \( \text{Fe}^{2+}, \text{Mg}^{2+}, \) and \( \text{Al}^{3+} \) disorder between tetrahedral and octahedral sites, whereas \( \text{Cr}^{3+} \), by virtue of its size and crystal field stabilization, resides on octahedral sites only (O'Neill and Navrotsky, 1983, 1984). Although \( \text{Cr}^{3+} \) is ordered, its presence influences the partitioning of the other cations between octahedral and tetrahedral sites, as will be discussed further below. In this study, we report high-temperature thermopower and electrical conductivity data on \( \text{Fe}_3\text{O}_4-\text{FeCr}_2\text{O}_4, \text{Fe}_3\text{O}_4-\text{MgCr}_2\text{O}_4, \) and \( \text{Fe}_3\text{O}_4-\text{FeAl}_2\text{O}_4-\text{FeCr}_2\text{O}_4 \) spinel solid solutions in an attempt to characterize high-temperature order-disorder relations in \( (\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})r\text{O}_4 \) solid solutions. Cation distributions determined from quenched samples are subject to great uncertainties because of reordering during quenching (O'Neill and Navrotsky, 1983) so that in situ, high-temperature measurements are required. These have been attempted for several spinel systems (e.g., Wu and Mason, 1981; Mason, 1987; Nell et al., 1989) by measuring thermopower and electrical conductivity and assum-
Table 1. Sample characterization

<table>
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<tr>
<th></th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;&lt;sub&gt;1−2y&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;Mg&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;&lt;sub&gt;1−2y&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</th>
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<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
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<tr>
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</tr>
<tr>
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</tr>
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<td>(3)</td>
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<tr>
<td>% density</td>
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<td>93.6</td>
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|                  | Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Al<sub>1−2z</sub>Cr<sub>1−z</sub>O<sub>4</sub> | Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Al<sub>1−2z</sub>Cr<sub>1−z</sub>O<sub>4</sub> | Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Al<sub>1−2z</sub>Cr<sub>1−z</sub>O<sub>4</sub> |
|                  | x = 0.25                                        | x = 0.50                                        | x = 0.75                                        |
| FeO              | 34.71                                          | 33.53                                           | 32.40                                           |
| FeO<sub>2</sub>  | 19.50 (0.89)                                    | 38.33 (0.34)                                    | 53.95 (0.58)                                    |
| MgO              | 0.00                                           | 0.00                                            | 0.00                                            |
| Al<sub>2</sub>O<sub>3</sub> | 19.08 (0.13)                                    | 12.00 (0.15)                                    | 5.08 (0.13)                                     |
| Cr<sub>2</sub>O<sub>3</sub> | 26.62 (0.46)                                    | 16.83 (0.29)                                    | 8.42 (0.16)                                     |
| Total            | 99.91                                          | 100.69                                          | 100.59                                          |
| No. of analyses  | 6                                              | 5                                               | 5                                               |
| Fe<sup>3+</sup> + Mg / Fe<sup>2+</sup> | 1.0                                            | 1.0                                             | 1.0                                             |
| Fe<sup>2+</sup> + Al + Cr | 8.3162                                         | 8.3398                                          | 8.3836                                          |
| Cell edge        |                                                |                                                |                                                |
| (Å)              | (4)                                            | (6)                                            | (7)                                            |
| % density        | 89.0                                           | 87.5                                           | 92.4                                           |

Note:
- FeO<sub>2</sub> calculated from stoichiometry. Standard deviations are for total Fe.
- Numbers in parentheses are ±1 for the final decimal place.
- Percentage of theoretical density.

Experimental Methods

Solid solutions containing x = 0.25; 0.50 and 0.75 in Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Cr<sub>2</sub>O<sub>4</sub>; Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Mg<sub>2−x</sub>Cr<sub>2−2y</sub>O<sub>4</sub>; and Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Al<sub>1−x</sub>Cr<sub>1−x</sub>O<sub>4</sub>, as well as x = 0.25 and 0.50 in Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Al<sub>3−2z</sub>Cr<sub>1−z</sub>O<sub>4</sub> and Fe<sup>3+</sup>Fe<sup>2+</sup><sub>1−2y</sub>Al<sub>3−2z</sub>Cr<sub>1−z</sub>O<sub>4</sub>, were used for the electrical measurements. High-density polycrystalline samples were prepared from oxide starting mixes with repeated cycles of firing and grinding in a controlled gas atmosphere. Starting materials were reagent grade FeO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub>. The MgO and Al<sub>2</sub>O<sub>3</sub> were obtained from the decarbonation and dehydration of MgCO<sub>3</sub> and Al(OH)<sub>3</sub>, at 1200°C, respectively. The FeO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> were dried at 400°C. All oxides were stored in a desiccator.

Stoichiometric oxide mixtures were pressed into pellets and reacted at a temperature of 1300°C in a vertical tube furnace through which a gas stream with a CO/CO<sub>2</sub> ratio of 0.3/100 was passed at a flow rate of approximately 1 linear cm/s (log P<sub>CO</sub> = -4.7). Samples were reacted for 10 h at a time and, after 4 cycles of grinding and firing, single phase spinels were produced for every composition. Once prepared, the samples were crushed in a vi-
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bratory mill (using alumina grinding medium) and iso-
statically cold pressed into pellets at a pressure of 2.75 \times 10^8 Pa. The pellets were subsequently densified through sintering at 1300 °C under an atmosphere with \( \log P_{O_2} = -4.7 \) for 24 h. Final cell edges and percentages of the theoretical densities for each composition are reported in Table 1.

Thermopower (Q) and electrical conductivity (\( \sigma \)) measurements were conducted using a four-point measurement technique outlined by Nell et al. (1989). At all times, a gas mixture with a CO/CO\(_2\) ratio of 0.3/100 was passed through the furnace at a flow rate of 1 linear cm/s. Measurements were made at 50–100 °C intervals, commencing at 1400 °C after 12 h of annealing to stabilize grain growth, down to approximately 600 °C and up again to 1400 °C. Values were recorded once thermal voltages were stable to \( \pm 1\% \) over at least 30 min. Measurements taken in sequence from high to low T generally agreed with those recorded from low to high T, suggesting that equilibrium values were measured.

On the completion of the electrical measurements, the samples used for the measurements were mounted and polished for analysis by electron microprobe. Compositions are given in Table 1. Concentrations of Fe\(^{3+}\) have been calculated from stoichiometry. All the samples were chemically homogeneous single-phase spinel. No chemical zoning was observed and potential Fe depletion resulting from assimilation by thermocouple beads could not be detected. Most samples were slightly contaminated with Al\(_2\)O\(_3\) derived from the alumina grinding medium used in the vibratory mill. The level of contamination rarely exceeds 1% by mass and is sufficiently low not to affect the electrical measurements.

RESULTS

Thermopower (Q) results for the systems Fe\(^{2+}\)Fe\(^{3+}\)Cr\(^{3+}\)O\(_4\), Fe\(^{2+}\)Mg\(^{2+}\)Fe\(^{3+}\)Cr\(^{3+}\)O\(_4\), Fe\(^{2+}\)Mg\(^{2+}\)Fe\(^{3+}\)Cr\(^{3+}\)Al\(^{3+}\)O\(_4\), Cr\(^{3+}\)Fe\(^{3+}\)O\(_4\), Fe\(^{2+}\)Fe\(^{3+}\)Al\(^{3+}\)Fe\(^{3+}\)O\(_4\), and Fe\(^{2+}\)Fe\(^{3+}\)Al\(^{3+}\)Fe\(^{3+}\)O\(_4\) are presented in Figures 1A, 2A, 3A, 4A, and 5A, respectively. Results obtained for Fe\(^{3+}\)O\(_4\) by Nell et al. (1989) are presented on each of the diagrams for comparison. Error bars on the data points correspond to a \( \pm 7\% \) uncertainty in the absolute value of Q and represent an uncertainty of \( \pm 1\% \) in the maximum temperature gradient for every measurement (Nell et al., 1989). Repeated heating and cooling cycles always produced the same result within experimental uncertainty and, in that sense, the data are reversible. In Fe\(_2\)O\(_4\)-FeCr\(_2\)O\(_4\) and Fe\(_2\)O\(_4\)-FeAl\(_2\)O\(_4\)-FeCr\(_2\)O\(_4\), solid solutions, there is a systematic decrease in the absolute value of thermopower with Fe\(_2\)O\(_4\) dilution (Figs. 1A, 3A, 4A, and 5A). Given the assumption of octahedral Fe\(^{2+}\)-Fe\(^{3+}\) hopping, this decrease results from the substitution of Fe\(^{3+}\) by Cr\(^{3+}\) and Al\(^{3+}\), which decreases the ratio Fe\(^{3+}\)/Fe\(^{2+}\) on octa-
hedral sites. In Fe\(_2\)O\(_4\)-MgCr\(_2\)O\(_4\), solid solutions Fe\(^{2+}\) and Fe\(^{3+}\) are replaced by Mg\(^{2+}\) and Cr\(^{3+}\), respectively, and the ratio Fe\(^{3+}\)/Fe\(^{2+}\) on octahedral sites, as well as ther-

Fig. 1. (A) Thermopower measurements in the system Fe\(_2\)O\(_4\) (mt)-FeCr\(_2\)O\(_4\) (ch) as a function of temperature. Solid and open symbols in Figures 1-5 are down and up temperature measurements, respectively. Data for pure Fe\(_2\)O\(_4\) in this and subsequent figures are from Nell et al. (1989). (B) Electrical conductivity data in Fe\(_2\)O\(_4\)-FeCr\(_2\)O\(_4\) solid solutions as a function of temperature.
Fig. 2. (A) Thermopower measurements in Fe$_3$O$_4$ (mt)-MgCr$_2$O$_4$ (pc) solid solutions as a function of temperature. Notice the change in sign in the temperature derivative of $Q$ at high temperatures in the sample (mt)$_{0.25}$ (pc)$_{0.75}$. Error bars on the data have been omitted for clarity. Uncertainties are still, however, $\pm 70$% of the absolute value of $Q$. (B) Electrical conductivity measurements in Fe$_3$O$_4$-MgCr$_2$O$_4$ solid solutions as a function of temperature.

Thermopower and conductivity data were fit to the following polynomials:

\[ Q = a + b\left(10^4/T\right) + c\left(10^4/T\right)^2 \text{ $\mu$V/K} \quad (1) \]

and

\[ \ln \sigma T = A + B\left(10^4/T\right) \text{ (2)} \]

The statistical significance of the second-degree term ($c$) in Equation 1 has been tested with the F-ratio and is only used for the compositions Fe$^{2+}$Fe$^{3+}$Cr$^{3+}$O$_4$ and Fe$^{2+}$Fe$^{3+}$Mg$^{2+}$Cr$^{3+}$O$_4$ where the confidence level for a quadratic relative to a linear relationship exceeds the 90% confidence level (Bevington, 1969, p. 200). It should be pointed out that, in the small polaron limit of a system with fixed carrier concentration, thermopower is independent of temperature. In Fe$_3$O$_4$ and Fe$_2$O$_3$ solid solutions, however, the carrier concentrations depend on temperature because of the disordering of Fe$^{2+}$ and Fe$^{3+}$ between octahedral and tetrahedral sites, and it is the temperature dependence of carrier concentration that is reflected by the polynomial to which thermopower has been fitted in Equation 1. The coefficients $a$, $b$, $c$, $A$, and $B$ are reported in Table 2, and the resulting regression curves are presented as the solid lines in Figures 1-5. Error bars on the lines in Figures 1B, 2B, 3B, 4B, and 5B are $\pm 15$% of the mean values calculated from Equation 2 and represent the observed scatter in conductivity data.

The coefficient $B$ in Equation 2 is proportional to the apparent activation energy ($E_a$)

\[ B = \frac{-E_a \cdot e_o}{k \cdot 10^4} \quad (3) \]

where $k$ is Boltzmann's constant, $e_o$ is the electronic charge, and $E_a$ is the apparent hopping energy in eV obtained from the conductivity data when temperature and compositional dependencies of carrier concentrations are neglected ($\sigma = \exp[A - (E_a \cdot e_o/kT)/T]$). Values of $E_a$ are reported in Table 2.

**ELECTRICAL BEHAVIOR AND NONSTOICHIOMETRY**

In order to interpret our results, it is first necessary to be sure that the concentrations of the conducting species,
Fe$^{2+}$ and Fe$^{3+}$, are known precisely. The total Fe content is, of course, known from the starting mixture and from microprobe analysis. The Fe$^{2+}$/Fe$^{3+}$ ratios of single phase spinels depend on $f_{O_2}$, however, and we wished to maintain essentially the ideal spinel stoichiometry of three cations to four O atoms. Dieckmann (1982) has determined deviations from stoichiometry of pure Fe$_2$O$_4$ and, as a starting point, we applied his equations for magnetite to estimate the stoichiometry of our complex spinel solutions. The deviation from stoichiometry, $\delta [= (\text{cation vacancies - Fe interstitials}) \text{ per lattice molecule}]$, is derived as follows:

$$
\delta = \frac{(\text{Fe}^{2+} - \delta)^3}{(\text{Fe}^{3+} + 2\delta)^2} K_v (a_{O_2}^{-2/3}(a_{\text{Fe}^{3+}}))^{-1/3}
$$

$$
- \frac{(\text{Fe}^{2+} + 2\delta)^3}{(\text{Fe}^{3+} - \delta)^2} K_i (a_{O_2}^{-2/3}(a_{\text{Fe}^{3+}}))^{1/3}
$$

where $K_v$ is the vacancy equilibrium constant, $K_i$ the
INTERSTITIAL EQUILIBRIUM CONSTANT, AND THE SUB- AND SUPER-SCRIPTS SS REFER TO THE SOLID SOLUTION OF INTEREST. AS AN INITIAL APPROXIMATION, K₁ AND K₂ WERE ASSUMED TO BE INDEPENDENT OF COMPOSITION AND THE f₀ FOR WHICH δ Eq. ZERO WERE CALCULATED USING THE EQUILIBRIUM CONSTANTS GIVEN BY DIECKMANN (1982) FOR PURE MAGNETITE. IT WAS FOUND THAT A CO/CO₂ RATIO OF APPROXIMATELY 0.3/100 WOULD ALWAYS YIELD f₀ WITHIN ABOUT TWO LOG UNITS OF THE f₀ AT WHICH δ EQ. ZERO FOR THE SOLID SOLUTION COMPOSITIONS OF INTEREST TO US IN THIS STUDY. THIS SHOULD PLACE THE EXPERIMENTS IN A PLATEAU REGION OF NEAR ZERO DEVIATION FROM STOICHIOMETRY (DIECKMANN, 1982). THE ASSUMPTION OF VACANCY AND INTERSTITIAL EQUILIBRIUM CONSTANTS THAT ARE INDEPENDENT OF COMPOSITION IS QUESTIONABLE, HOWEVER. IN ORDER TO ASSESS THE APPLICABILITY OF THE APPROXIMATION, WE CONDUCTED THERMOPOWER AND CONDUCTIVITY MEASUREMENTS ON A DILUTE SOLID SOLUTION CONTAINING 25% Fe₂O₃ AND 75% MgAl₂O₄ AT 900 °C OVER A RANGE OF f₀, OF SIX LOG UNITS. THIS COMPOSITION AND TEMPERATURE WAS SELECTED BECAUSE OF THE AVAILABILITY OF Fe₂O₃ ACTIVITY DATA (MATTIOLI AND WOOD, 1988) AND BECAUSE IT REPRESENTS THE MOST DEPLETED MAGNETITE CONCENTRATIONS EXAMINED IN OUR STUDY.

Thermopower and conductivity results are compared with the calculated defect concentration profile as a function of temperature in Figures 6A–6C, respectively. Thermopower follows the defect concentration profile closely while conductivity remains constant within uncertainty over the f₀ range of our measurements (note that f₀ more oxidizing than approximately 10⁻⁹ are difficult to achieve with CO-CO₂ mixtures at 900 °C). The pertinent observation is that there is, as in Fe₂O₃, a well-defined plateau in which both thermopower and electrical conductivity are insensitive to variations in f₀. This plateau extends over approximately five log units in f₀ and corresponds to |δ| ≤ 1 x 10⁻³. The observed correspondence between thermopower and the calculated δ agrees with that expected for small polaron conduction in which Q depends on Fe³⁺/Fe²⁺ (see Eq. 5 below). The correspondence between the calculated δ and thermopower suggests that neither K₁ nor K₂ varies greatly with composition, a condition also reported by Erickson and Mason (1985) for the Fe₂O₃-CoFe₂O₄ system.

In solid solutions where Fe³⁺ is replaced, but Fe²⁺ content is unchanged, e.g., Fe₂O₃-FeCr₂O₄, the plateau region is displaced toward more reduced log f₀ values by a factor of ½ log X₃Fe₂O₄ (Nell and Wood, unpublished data; Aragon and McCallister, 1982) if nonstoichiometry is associated only with the Fe₂O₃ component of the solid solution. The width of the plateau region should remain the same, however, at five log units in f₀ at 900 °C. In a solid solution containing 25% Fe₂O₃ and 75% FeCr₂O₄, for example, the f₀ at which δ equals zero at 900 °C is at log f₀ = -12.6 while it is at -10.2 for a 25% Fe₂O₃-75% MgAl₂O₄ solid solution (Fig. 6C). This is to be compared with the values for pure Fe₂O₃ (log f₀ = -11.1) and the gas mixture we used that gives a log f₀ at 900 °C of -11.0. We conclude therefore that a gas mixture with a CO/CO₂ ratio of 0.3/100 should be in equilibrium with Fe₂O₃ solid solutions in which the deviation from stoichiometry is less than approximately 0.1% even when Fe₂O₃ content is diluted to 25%. As a check on this assumption, we always varied the gas composition slightly in solid solutions containing 25% Fe₂O₃ in order to test for fluctuations in the value of the thermoelectric coefficient that would serve as an indicator of deviations from stoichiometry approaching the shoulders of the plateau. None were observed. We consider, there-
fore, that our thermopower and conductivity data refer to stoichiometric spinels of the appropriate compositions, and that, in the region of interest, deviations from stoichiometry yield effects that are within experimental uncertainty (Figs. 6A, 6B). One of the reviewers also commented that the CO/CO₂ equilibrium is strongly temperature dependent and that use of a constant gas mixture could lead to \( f_{O_2} \) values not on the plateau at lower temperatures. The relations given by Dieckmann (1982) indicate, however, that curves of constant \( \delta \) are essentially parallel to \( \text{CO}-\text{CO}_2 \) isopleths on a \( \log P_{O_2} \) vs. temperature diagram, and that it is therefore appropriate to use a fixed gas mixture. We should also point out that our thermopower results for Fe₂O₄ (Nell et al., 1989), using a fixed gas composition, agree with the study of Wu and Mason (1981) in which great care was taken to preserve exact Fe₂O₄ stoichiometry over the temperature range 600–1500 °C.

**THERMOPOWER AND CONDUCTIVITY THEORY**

Electrical conductivity and thermopower measurements on spinels, although of some inherent mineralogical interest, are of most value if they can be used to cast light on the distribution of charge carriers in the crystal structure. This requires a correct interpretation of the conductivity mechanism, something that is difficult to do meaningfully in these complex phases. However, in the temperature range of our study (600–1400 °C), the measured activation energy of approximately 0.12 eV for electrical conduction in magnetite coupled with the low carrier mobility has been used by many authors to infer a small polaron mechanism. This will be discussed in more detail below.

We begin, however, with a brief review of conduction behavior in Fe₂O₄ at low temperature, where the results are more ambiguous. Kuipers and Brabers (1979) observed thermally activated drift mobilities above and be-

![](image)

**Table 2.** Polynomial fit parameters for the thermopower and conductivity data sets

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<th>System</th>
<th>Fe⁺⁺⁺Fe⁺⁺Cr₁₋₂₋₂O₄</th>
<th>Fe⁺⁺⁺⁺Mg⁺⁺⁺⁺Fe⁺⁺Cr₁₋₂₋₂O₄</th>
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</tbody>
</table>

**Fig. 6.** (A) Thermopower measurements in a solid solution containing 25% Fe₂O₄ and 75% MgAl₂O₄ at 900 °C as a function of \( \log P_{O_2} \). (B) Electrical conductivity measurements in Mg₀.₇₅Fe₀.₃₅Al₁₋₂₋₂O₄ as a function of \( \log P_{O_2} \). (C) Defect profile for Mg₀.₇₅Fe₀.₃₅Al₁₋₂₋₂O₄ as a function of \( \log P_{O_2} \).
low the Verwey transition (~120 K) and ascribed conduction to phonon-assisted tunnelling or hopping possibly caused by small polaron formation. Chakraverty (1980), on the other hand, proposed bipolaron formation as a result of ordering between neighboring Fe²⁺-Fe³⁺ pairs, whereas Ihle and Lorenz (1986) interpreted the electrical conductivity in terms of the superposition of small polaron band and small polaron hopping conduction. They noted however that, above 350 K, the small polaron band conduction decreases rapidly in favor of the hopping mechanism. Aragon and Honig (1988) found that the main features of the electrical conductivity and thermoelectric power measurements at temperatures above and below the Verwey transition can be described with a small polaron model when the thermal dependence of the density of states is taken into account. Other mechanisms that have been proposed include intermediate polaron formation with long-range ordered Fe²⁺-Fe³⁺ pairs being responsible for conduction and charge density waves where itinerant electrons are the charge carriers (Goodenough, 1980). Following this analysis, Ghose (1988) also considered the possibility of intermediate polaron formation at low temperatures in his discussion of the electrical conduction of ilvaite. At temperatures above 310 K, however, the gradual loss of long-range order destroys the Fe²⁺-Fe³⁺ pairs, and at temperatures above 405 K, all long-range order is lost and conduction is dominated by small polaron hopping.

Most of the possible low-temperature conduction mechanisms are excluded at the high temperatures (600–1400 °C) at which our experiments were conducted. The loss of long- and short-range Fe²⁺-Fe³⁺ and Fe²⁺-Fe²⁺ order with increasing temperature argues against the presence of intermediate polaron and bipolarons, respectively; whereas, itinerant electron conduction is inconsistent with the small activated drift mobilities observed for magnetite (Dieckmann et al., 1983) and magnetite solid solutions at high temperatures (e.g., Nell et al., 1989). The transition temperature from band type behavior (see below) to hopping motion for small polarons has been estimated to be approximately θ/2 where θ is the Debye temperature (Austin and Mott, 1969). This agrees with the result of Ihle and Lorenz (1986) that conduction resulting from hopping dominates in Fe₂O₃ above 350 K given that θ for Fe₂O₃ is approximately 605 K (Grønvold and Sveen, 1974). Small polaron hopping should therefore dominate in the temperature range of our study, a conclusion reached on the basis of the moderate activation energy and low drift mobility observed by Verwey et al. (1947), Tannhauser (1962), Dieckmann et al. (1983), and Mason and Bowen (1981), among others. The remaining question, however, is whether electron hopping takes place between octahedral sites only, between tetrahedral sites only, or involves both types of sites.

In a study of intervalence charge transfer in silicates, Amthauer and Rossman (1984) found that small polaron hopping between Fe²⁺ and Fe³⁺ only occurs if these ions occupy equivalent or geometrically similar nearest-neighbor sites that share common edges or faces to form infinite chains, sheets, or three-dimensional networks. This observation was explained by the molecular orbital calculations of Sherman (1987) who investigated several mixed valence Fe-O clusters with edge-sharing cation polyhedra. In the case of Fe²⁺ and Fe³⁺ octahedra sharing an edge, the atomic orbitals of the two ions overlap to some extent, giving partial metal-metal bonding thereby facilitating electron transfer. In the spinel structure, octahedral sites form infinite edge-sharing networks with one another, but share corners with tetrahedral sites. The tetrahedral sites are isolated from one another. Therefore in spinel, octahedral-octahedral electron hopping is favored over octahedral-tetrahedral or tetrahedral-tetrahedral transfer.

High-temperature electrical conductivity data for Fe₂O₃ were correlated with the product of the concentrations of Fe²⁺ and Fe³⁺ on octahedral sites only by Tannhauser (1962), Dieckmann et al. (1983), and Mason and Bowen (1981) while Verwey et al. (1947) and Banerjee et al. (1967) also interpreted their conductivity results in terms of electron hopping on octahedral sites based on the assumption (now known to be a poor approximation) of inverse cation distributions at high temperatures. In all studies, the hopping energy was found to be approximately 0.12 eV. Independent evidence for electron hopping between octahedral sites in magnetite has been provided by Mössbauer studies where absorption ascribed to Fe³⁺ on the octahedral sites is observed (e.g., Kündig and Hargrove, 1969). Thermally activated electron hopping on octahedral sites was also observed by Lotgering and Van Diepen (1977) in a Mössbauer study of Zn-Ti ferrites between 78 K and 300 K. We infer therefore that experimental and theoretical evidence is heavily in favor of octahedral hopping in pure Fe₂O₃ and presumably also in ferrites close to magnetite in composition.

The assumption of electron hopping on octahedral sites only enabled Wu and Mason (1981) to estimate the partitioning of Fe²⁺ and Fe³⁺ between octahedral and tetrahedral sites in magnetite from their measurements of the thermoelectric coefficient. Given that there is no local Fe²⁺-Fe³⁺ order in the structure and that electron-electron repulsion is sufficiently large to prevent double occupancy of a given site, the thermoelectric coefficient (Q) for an n-type small polaron conductor is given by

$$Q = -\frac{k}{e_o} \left[ \ln \left( \frac{2 \left[ \frac{\beta \text{Fe}^{3+}}{\alpha \text{Fe}^{2+}} \right]}{\left[ \frac{\beta \text{Fe}^{2+}}{\alpha \text{Fe}^{3+}} \right]} \right) + A \right] \frac{V}{K}$$  \hspace{1cm} (5)

(Chaikin and Beni, 1976; Wu and Mason, 1981; Austin and Mott, 1969) where k is Boltzmann's constant, e is the electronic charge, and A is the vibrational entropy associated with the ions surrounding a polaron on a given site. If conduction takes place in systems where the conducting sites all have approximately the same energy (e.g., the octahedral spinel sublattice) A is assumed to be negligibly small (Austin and Mott, 1969; Emin, 1975). From Equation 5 it is clear that the thermoelectric coefficient...
directly gives the ratio (Fe$^{3+}$/Fe$^{2+}$) on octahedral sites, provided the conditions of disorder and single occupation are fulfilled. In that case $Q$ is sufficient to fully characterize cation distributions in Fe$_2$O$_3$ and in solid solutions such as Fe$_2$O$_3$-FeCr$_2$O$_4$ where only Fe$^{2+}$ and Fe$^{3+}$ are disordered between octahedral and tetrahedral sites. Wu and Mason (1981) measured the thermoelectric coefficient of magnetite at high temperature and, based on the assumption of octahedral site electron hopping, showed that the Fe$^{2+}$-Fe$^{3+}$ distribution changes as anticipated from almost completely inverse (low [Fe$^{3+}$/Fe$^{2+}$]) at low temperatures to essentially completely disordered at temperatures close to 1500 °C. As Fe$_2$O$_3$ is diluted by other components, the same conduction mechanism should apply at least over limited ranges of solid solution, enabling cation distributions to be determined in more complex spinels. In Fe$_2$O$_3$-MgCr$_2$O$_4$ and Fe$_2$O$_3$-FeAl$_2$O$_3$-FeCr$_2$O$_4$ solid solutions, however, three cations (Fe$^{2+}$, Fe$^{3+}$, Mg$^{2+}$ and Fe$^{2+}$, Fe$^{3+}$, Al$^{3+}$, respectively) are disordered and additional information is required to derive the intersite cation distributions. In these cases, measurement of the electrical conductivity ($\sigma$) provides the required data if the conduction mechanism is unchanged.

In the adiabatic limit of small polaron transport, the probability that an electron will respond rapidly enough to a coincidence event to execute a successful hop is approximately equal to 1 (Holstein, 1959; Tuller and Nowick, 1977), and the electrical conductivity for the small polaron conductor in this limit is given by

$$\sigma = \frac{Nc'(1 - c')g^2a^2v_s\exp\left(-\frac{E_H}{kT}\right)}{kT} \text{ (Ocm)}^{-1}$$

(Tuller and Nowick, 1977; Dieckmann et al., 1983), where $g$ is a geometric factor that is constant for a given system, $a$ is the jump distance (cm), $v_s$ is the lattice vibration frequency, $N$ is the density of conducting sites (cm$^{-3}$), $c'$ is the fraction of conducting sites occupied by charge carriers, $(1 - c')$ is the fraction of available jump sites, $E_H$ is the hopping energy, and the remaining terms have their usual meaning. In the case of spinels with electron hopping on octahedral sites only, $c' = [00]Fe^{2+}/([00]Fe^{3+} + [00]Fe^{2+})$, $(1 - c') = [00]Fe^{3+}/([00]Fe^{2+} + [00]Fe^{3+})$, and $N$ becomes the total concentration $[00]Fe^{2+} + [00]Fe^{3+}$. By normalizing the electrical conductivity of a mixed spinel to that of pure Fe$_2$O$_3$ ($N = 2.0$), the total concentration of $[00]Fe^{2+} + [00]Fe^{3+}$ can be calculated for the composition of interest (Mason, 1987; Nell et al., 1989). Measurement of $[00]Fe^{3+}/[00]Fe^{2+}$ and $[00]Fe^{3+}/[00]Fe^{2+} + [00]Fe^{3+}$ allows complete calculation of cation distributions in Fe$_2$O$_3$-MgCr$_2$O$_4$ and Fe$_2$O$_3$-FeAl$_2$O$_3$-FeCr$_2$O$_4$ solid solutions.

In our previous work (Nell et al., 1989) on the joins Fe$_2$O$_3$-MgFe$_2$O$_4$, Fe$_2$O$_3$-FeAl$_2$O$_3$, and Fe$_2$O$_3$-MgAl$_2$O$_3$, we found that dilution of Fe$_2$O$_3$ with the additional components brought changes in $Q$ and $\sigma$ which are consistent with the conduction mechanism remaining unchanged from $X_{Fe_2O_3}$ of 1.0 down to at least 0.25. By assuming that only octahedral hopping occurs and using Equations 5 and 6, we obtained cation site occupancies and activation energies that varied monotonically with composition. Furthermore, partitioning of Fe$^{3+}$ and Fe$^{2+}$ between octahedral and tetrahedral sites was found to closely obey the spinel model of O'Neill and Navrotsky (1983, 1984), which was derived from a wide variety of data on a large number of unary and binary spinels. Our results are therefore consistent with octahedral hopping only of Fe$^{2+}$-Fe$^{3+}$ in these systems.

Although octahedral hopping appears to dominate in spinels, application of Equations 5 and 6 may still become invalid if other electron donors or acceptors, such as Cr$^{3+}$ or Ti$^{4+}$, are present and involved in conduction. Bannerjee et al. (1967) and Verwey et al. (1947), for example, found evidence for a transition from octahedral site electron hopping between Fe$^{2+}$ and Fe$^{3+}$ to a different type of conduction mechanism with increasing magnetite dilution in the systems Fe$_2$O$_3$-Fe$_3$TiO$_4$ and Fe$_2$O$_3$-Mg$_2$Cr$_2$O$_4$, respectively. In both systems, inflection points in plots of the activation energy of hopping vs. composition indicate a transition from hopping of Fe$^{2+}$-Fe$^{3+}$ between octahedral sites (activation energies of approximately 0.15 to 0.25 eV) to a different type of conduction mechanism (activation energies of approximately 0.4-0.5 eV). In view of the large energy barriers expected for tetrahedral and mixed site electron hopping, the observed second conduction mechanisms can probably be attributed to electron hopping between Fe$^{2+}$ and Ti$^{4+}$ and Fe$^{2+}$ and Cr$^{3+}$, respectively (D. Sherman, personal communication).

Large compositional dependencies of activation energy are not, however, observed in any of the systems in which Fe$^{2+}$ and Fe$^{3+}$ are diluted by Mg$^{2+}$ and Al$^{3+}$ (Nell et al., 1989), presumably because neither of the latter ions can contribute to conduction.

Our data support the suggestion that Cr$^{3+}$ becomes involved in the electron hopping process. Figure 7 shows activation energy as a function of composition for the join Fe$_2$O$_3$-FeCr$_2$O$_4$. In the FeCr$_2$O$_4$-rich region of the join ($X_{FeCr_2O_4} \geq 0.75$), activation energies for conduction are constant at approximately 0.5 eV. In more Fe$_2$O$_3$-rich compositions, activation energy increases monotonically from 0.13 eV to 0.25 eV with increasing FeCr$_2$O$_4$ content. There appears to be a region of rapidly increasing activation energy between 0.6 and 0.75 $X_{FeCr_2O_4}$. Our provisional interpretation of the data was that in the region $0 \leq X_{FeCr_2O_4} \leq 0.6$, conduction is by octahedral hopping between Fe$^{2+}$ and Fe$^{3+}$ only, whereas the more Cr-rich compositions exhibit mixed Fe$^{2+}$-Fe$^{3+}$-Cr$^{3+}$ electron transfer. As a test of this hypothesis, we applied Equations 5 and 6 to the values of thermopower and electrical conductivity of Fe$_2$O$_3$-FeCr$_2$O$_4$ solid solutions. In this case, if octahedral hopping between Fe$^{2+}$ and Fe$^{3+}$ is the sole mechanism, then with Cr present only on octahedral sites, Equations 5 and 6 enable us to calculate $N$, the densities of conducting (Fe$^{2+}$ + Fe$^{3+}$) sites and to compare them with the expected values of 1.5, 1.0, and 0.5 for 75, 50, and 25 mol% Fe$_2$O$_3$, respectively. The data reveal excellent agreement between calculated and nominal $N$ values.
This study by Gillor et al. (1976) on the thermal properties of spinels presents data on the apparent hopping energies in the system Fe$_2$O$_3$-FeCr$_2$O$_4$ as a function of composition.

Over the entire temperature range 600 °C to 1400 °C for solid solutions containing 75 and 50% Fe$_2$O$_3$. For the composition containing 25 mol% Fe$_2$O$_3$, however, the data give physically impossible values requiring a change in conduction mechanism. We conclude therefore that octahedral Fe$^{2+}$-Fe$^{3+}$ hopping almost certainly occurs at Fe$_2$O$_3$ concentrations to 40% on this join but not at more FeCr$_2$O$_4$-rich compositions. We also consider that inflection points in plots of activation energy vs. composition (Fig. 7) are likely wherever there is a change in the conduction mechanism. Such inflections in activation energy were found in the binaries Fe$_2$O$_3$-FeCr$_2$O$_4$ and Fe$_2$O$_3$-MgCr$_2$O$_4$, and for two joins we studied in the Fe$_2$O$_3$-FeAl$_2$O$_4$-FeCr$_2$O$_4$ ternary (Table 2). In the case of MgCr$_2$O$_4$, unusual thermopower results were also observed in the 25% Fe$_2$O$_3$ composition (Fig. 2A).

In conclusion, we should state that we are unable to prove conclusively that octahedral Fe$^{2+}$-Fe$^{3+}$ hopping is the sole mechanism operating in the complex spinels we have studied. The experimental and theoretical evidence in favor of its operating in pure Fe$_2$O$_3$ is, however, overwhelming. Furthermore, conductivity results on the joins Fe$_2$O$_3$-FeAl$_2$O$_4$, Fe$_2$O$_3$-MgFe$_2$O$_4$, and Fe$_2$O$_3$-MgAl$_2$O$_4$ exhibit only small increases in activation energy with Fe$_2$O$_3$ dilution, and calculated cation distributions are crystallographically reasonable. On the Fe$_2$O$_3$-FeCr$_2$O$_4$ join, the assumption of Fe$^{2+}$-Fe$^{3+}$ hopping gives the correct concentration of (Fe$^{2+}$ + Fe$^{3+}$) on octahedral sites at up to 50% FeCr$_2$O$_4$ substitution, confirming octahedral Fe$^{2+}$-Fe$^{3+}$ hopping. Changes in conduction mechanism have also been recognized by sharp increases in activation energy and independently confirmed on the Fe$_2$O$_3$-FeCr$_2$O$_4$ join from the density of states calculations. We therefore believe that, after excluding data at 75% Cr$^{3+}$ substitution for Fe$^{2+}$, we are justified in using Equations 5 and 6 to estimate cation distributions in these complex spinels.

**CATION DISTRIBUTIONS**

Cation distributions in Fe$_2$O$_3$-FeCr$_2$O$_4$, Fe$_2$O$_3$-MgCr$_2$O$_4$, and Fe$_2$O$_3$-FeAl$_2$O$_4$-FeCr$_2$O$_4$ solid solutions were calculated from the mass-balance, charge-balance, and stoichiometry conditions listed in Table 3. At fixed mole fraction ($x$) of Fe$_2$O$_3$ in Fe$_2$O$_3$-FeCr$_2$O$_4$ solid solutions, only the thermoelectric coefficient is required to determine cation distributions since $N = \langle \text{Fe}^{2+} \rangle + \langle \text{Fe}^{3+} \rangle = 2x_{\text{Fe}_{2}\text{O}_{3}}$. In Fe$_2$O$_3$-MgCr$_2$O$_4$ and Fe$_2$O$_3$-FeAl$_2$O$_4$-FeCr$_2$O$_4$ solid solutions, $N$ was calculated from electrical conductivity measurements (Nell et al., 1989; Mason, 1987), which then allowed calculation of cation distributions.
through the relationships in Table 3. Uncertainties in the cation distributions were calculated by considering maximum uncertainties in the thermopower and conductivity measurements as outlined by Nell et al. (1989). Results for each system are presented in Figures 8A, 9, and 10 together with calculated distribution curves (see below).

**THERMODYNAMIC MODEL**

Our estimates of cation distributions may be combined with data on activity-composition relations and interphase partitioning to construct a thermodynamic model for \((\text{Mg}^{2+},\text{Fe}^{3+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})_{2}\text{O}_{4}\) spinels that makes explicit provision for all order-disorder relations. We will commence with outlining the approach. The thermodynamic properties were formulated as an extension of our previous work on \((\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})_{2}\text{O}_{4}\) solid solutions (Nell and Wood, 1989). There are ten independent fictive normal and inverse reference components in \((\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})_{2}\text{O}_{4}\) solid solutions that were used to derive mixing properties (Table 4). The reference components are related through three independent compositional exchange vectors, \(\text{Fe}^{2+}(\text{Mg}^{2+})_{1-}\), \(\text{Al}^{3+}(\text{Fe}^{3+}+\text{Cr}^{3+})_{1-}\), and \(\text{Cr}^{3+}(\text{Al}^{3+}+\text{Fe}^{3+})_{1-}\), and three compositional parameters are required to express the bulk chemical composition of any particular phase. These parameters are labeled \(r_1\), \(r_2\), and \(r_3\) and are defined as follows:

\[
\begin{align*}
 r_1 &= 1 - \left(\frac{6}{5}\right)X_{\text{Cr}} + 2\left(\frac{6}{5}\right)X_{\text{Mg}} \\
 r_2 &= \frac{1}{2}\left(\frac{6}{5}\right)X_{\text{Al}} + 2\left(\frac{6}{5}\right)X_{\text{A}} \\
 r_3 &= \frac{6}{5}X_{\text{Cr}}
\end{align*}
\]

where \(X_{\text{Cr}}\) refers to the atomic fraction of \(\text{Cr}^{3+}\) on octahedral sites. There are also four intersite cation exchange reactions between the reference end-member components, three of which are independent. The three selected order parameters are labeled \(s_1\), \(s_2\), and \(s_3\), and are defined as follows (\(s_1\) was formulated as an absolute rather than a difference quantity in order to facilitate comparison between the series expansion model and our earlier O'Neil-Navrotsky formalism, Nell et al., 1989):

\[
\begin{align*}
 s_1 &= \frac{6}{5}X_{\text{Al}} - \frac{1}{2}\left(\frac{6}{5}\right)X_{\text{A}} \\
 s_2 &= \frac{6}{5}X_{\text{Al}^3+} - \frac{1}{2}\left(\frac{6}{5}\right)X_{\text{Fe}^{3+}} \\
 s_3 &= \frac{6}{5}X_{\text{Mg}}
\end{align*}
\]

**TABLE 3. Compositional relations and constraints in \(\text{Fe}_2\text{O}_4-\text{FeCr}_2\text{O}_4\), \(\text{Fe}_2\text{O}_4-\text{MgCr}_2\text{O}_4\), and \(\text{Fe}_2\text{O}_4-\text{FeAl}_2\text{O}_4-\text{FeCr}_2\text{O}_4\) solid solutions**

<table>
<thead>
<tr>
<th>System</th>
<th>Structural formula</th>
<th>((\text{Fe}_2\text{O}_4),(\text{FeCr}_2\text{O}_4))</th>
<th>((\text{Fe}_2\text{O}_4),(\text{MgCr}_2\text{O}_4))</th>
<th>((\text{Fe}_2\text{O}_4),(\text{MgCr}_2\text{O}_4),(\text{FeAl}_2\text{O}_4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{System})</td>
<td>(\text{Structural formula})</td>
<td>((\text{Fe}_2\text{O}_4),(\text{FeCr}_2\text{O}_4))</td>
<td>((\text{Fe}_2\text{O}_4),(\text{MgCr}_2\text{O}_4))</td>
<td>((\text{Fe}_2\text{O}_4),(\text{MgCr}_2\text{O}_4),(\text{FeAl}_2\text{O}_4))</td>
</tr>
<tr>
<td>(d + e + n = 2)</td>
<td>(2(a + d) + 3(b + e + n) = 8)</td>
<td>(b + e = 2x)</td>
<td>(a + b + c = 1)</td>
<td>(2(a + d) + 3(b + e + n) = 8)</td>
</tr>
</tbody>
</table>
Six parameters are thus required to characterize composition and order in \((\text{Mg}^{2+}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+})_6\text{O}_8\) spinels. The coordinates of the reference components in the six parameter space are in Table 4, and cation fractions per structural formula unit are in Table 5. From the information in Table 5, the configurational entropy of a solid solution \((S_{\text{conf}})\) may be expressed as a function of order and compositional parameters through the equation

\[
S_{\text{conf}} = -R \sum \sum n_{ia} X_{ia} \ln(X_{ia})
\]

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

The vibrational part of the Gibbs free energy \((G^*)\) is obtained from a second-degree Taylor series expansion in terms of compositional and order parameters (Thompson, 1969; Sack, 1982; Nell and Wood, 1989):

\[
G^* = C_0 + C_1 R \sum X_{ia} \ln(X_{ia}) + C_2 \sum \sum \sum n_{ia} X_{ia} \ln(X_{ia}) + C_3 \sum \sum \sum n_{ia} X_{ia} R \ln(X_{ia}) + C_4 \sum \sum \sum n_{ia} X_{ia} R^2 \ln(X_{ia})
\]

Nonideal mixing in the second-degree expansion can be identified with symmetric binary interaction parameters and reciprocal reaction terms (Thompson, 1969; Nell and Wood, 1989). In our previous paper, we derived a solution set for the 21 series expansion coefficients that do not involve the \(r_i\) parameter. By considering the 17 possible binary solid solutions involving reference components \(\text{FeCr}_2\text{O}_4\) and \(\text{MgCr}_2\text{O}_4\) (Table 4), the coefficients involving the \(r_i\) parameter were likewise determined. The complete set for the series expansion coefficients expressed in terms of on-site regular symmetric interaction parameters and reciprocal reaction energies is given in Appendix I. The subscripts to the reciprocal reaction terms refer to the reference end-member components defined in Table 4, whereas the formulation of the reciprocal reaction terms and the interaction parameters were discussed in detail in our previous paper (Nell and Wood, 1989).

### Equilibrium conditions

Equilibrium in \((\text{Mg}^{2+}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+})_6\text{O}_8\) solid solutions is achieved when, at fixed temperature, pressure and composition, the following conditions are satisfied:

\[
\frac{\partial G}{\partial s_1} = 0,
\]

\[
\frac{\partial G}{\partial s_2} = 0,
\]

\[
\frac{\partial G}{\partial s_3} = 0.
\]

Substituting Equations 9 and 10 into 11 and differenti-
ating gives the equilibrium conditions in terms of expansion coefficients and cation site fractions:

\[
\begin{align*}
\frac{\partial G}{\partial s_1} &= g_1 + 2g_{12}s_1 + g_{12}r_1 + g_{12}r_2 + g_{13}r_3 \\
+ g_{12}s_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
\frac{\partial G}{\partial s_2} &= g_{12} + 2g_{12}s_2 + g_{12}r_1 + g_{12}r_3 + g_{13}r_3 \\
+ g_{12}s_1 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Mg^{2+}]}{[Mg^{3+}]} \right) \\
\frac{\partial G}{\partial s_3} &= g_{12} + 2g_{13}s_2 + g_{12}r_1 + g_{12}r_3 + g_{13}r_3 \\
+ g_{12}s_1 + g_{13}s_2 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
0 &= g_1 + 2g_{12}r_1 + g_{12}r_2 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
0 &= g_2 + 2g_{12}r_2 + g_{12}r_1 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
0 &= g_3 + 2g_{12}r_3 + g_{12}r_1 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_3 + g_{13}s_2 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right)
\end{align*}
\]

Equations 13–15 were used to calculate intersite cation distributions in \((Mg^{2+},Fe^{2+},Fe^{3+},Al^{3+},Cr^{3+})O_4\) spinels after the following substitutions for the compositional parameters \(r_1\) to \(r_3\) were made:

\[
\begin{align*}
r_1 &= X_{FeO_4} + X_{FeAlO_4} + X_{FeCrO_4} \\
r_2 &= X_{FeAlO_4} + X_{MgAlO_4} \\
r_3 &= X_{FeCrO_4} + X_{MgCrO_4}
\end{align*}
\]

All but the \(g_{r_1}, g_{r_2}, \text{ and } g_{r_3}\) parameters in Equations 13–15 were derived in our previous study (Nell and Wood, 1989). The new coefficients \(g_{r_1}, g_{r_2}, \text{ and } g_{r_3}\) describe the effects of \(Cr^{3+}\) substitution on intersite partitioning involving \(Fe^{2+}-Al^{3+}, Fe^{3+}-Fe^{3+}\), and \(Fe^{2+}-Mg^{2+}\), respectively. It follows therefore that, unless all these parameters are equal to zero, the substitution of \(Cr^{3+}\) must affect cation distributions despite the fact that it does not, itself, disorder.

**Activity-composition relations**

There are six compositional series expansion coefficients available to model activity-composition relations along the 15 binary solid solutions in the trigonal prism \(Fe_2O_4, FeAl_2O_4, MgFe_2O_4, MgAl_2O_4, FeCr_2O_4, MgCr_2O_4\). The values of three of these coefficients were determined from our work in the quaternary \((Mg^{2+},Fe^{2+})(Fe^{3+},Al^{3+})O_4\) (Nell and Wood, 1989). Three additional coefficients \((g_{r_1}, g_{r_2}, \text{ and } g_{r_3})\) are required to describe activity-composition relations along the eight binary Cr-bearing solid solutions where the \(r_3\) compositional exchange vector is operative.

Substituting Equations 9 and 10 into Equation 11 and differentiating with respect to \(r_1, r_2, \text{ and } r_3\) gives

\[
\begin{align*}
\frac{\partial G}{\partial r_1} &= g_1 + 2g_{12}r_1 + g_{12}r_2 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[!Al^{2+}]} \right) \\
0 &= g_2 + 2g_{12}r_2 + g_{12}r_1 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
0 &= g_3 + 2g_{12}r_3 + g_{12}r_1 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_3 + g_{13}s_2 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right)
\end{align*}
\]

and

\[
\begin{align*}
\frac{\partial G}{\partial r_2} &= g_1 + 2g_{12}r_2 + g_{12}r_1 + g_{13}r_3 + g_{13}s_1 \\
+ g_{12}r_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
0 &= g_2 + 2g_{13}s_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right) \\
0 &= g_3 + 2g_{13}s_2 + g_{13}s_3 + RT \ln \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Al^{3+}]}{[Al^{2+}]} \right)
\end{align*}
\]

Chemical potentials of fictive reference components are obtained by partial differentiation of the free energy with respect to each of the order and compositional parameters:

\[
\mu_{a,b,c,d,e,f} = G + \left( a - r_1 \right) \left( \frac{\partial G}{\partial r_1} \right) + \left( b - r_2 \right) \left( \frac{\partial G}{\partial r_2} \right) + \left( c - r_3 \right) \left( \frac{\partial G}{\partial r_3} \right) + \left( d - s_1 \right) \left( \frac{\partial G}{\partial s_1} \right) + \left( e - s_2 \right) \left( \frac{\partial G}{\partial s_2} \right) + \left( f - s_3 \right) \left( \frac{\partial G}{\partial s_3} \right)
\]

where the coefficients \(a-f\) are coordinates of a phase in \(r_1-r_2-r_3-s_1-s_2-s_3\) space. Chemical potentials of the reference end-member components obtained from Equation 20 are presented in Table 6. Reference components 1–8 are, of
A, MgFe$_2$O$_4$ relative to disordered pure end-member standard states at the temperature and pressure of interest as well as the activities of FeCr$_2$O$_4$ and MgCr$_2$O$_4$ relative to normal standard state end-members are in Table 7.

**Constraint of model parameters**

Values of the coefficients involving the $r_1$ parameter were derived as an extension of the parameters obtained in our earlier work (Nell and Wood, 1989). The $g_{3}$, and $g_{3}$, parameters were constrained from our cation distribution data for Fe$_2$O$_3$-FeAl$_2$O$_3$-FeCr$_2$O$_4$ and Fe$_2$O$_3$-FeAl$_2$O$_3$ solid solutions, respectively. Data for Fe$_2$O$_3$-MgCr$_2$O$_4$ solid solutions suggest that the $g_{3}$ parameter is effectively equal to zero, indicating that the substitution of Cr$^{3+}$ does not affect the partitioning of Fe$^{2+}$ and Mg$^{2+}$ between octahedral and tetrahedral sites (Eq. 15).

The $g_{3}$ parameter was constrained from activity-composition relations in Fe$_2$O$_3$-FeCr$_2$O$_4$ solid solutions at 1227 °C (Katsura et al., 1975) and 1400 °C (Petric and Jacob, 1982a). The $g_{3}$ coefficient was determined from Al$^{3+}$-Cr$^{3+}$ partitioning experiments between clinopyroxene and MgAl$_2$O$_4$-MgCr$_2$O$_4$ solid solutions at 1100 °C (Webb and Wood, 1986), whereas $g_{3}$ was estimated from experiments on the partitioning of Fe$^{2+}$-Mg$^{2+}$ between olivine and MgAl$_2$O$_4$-FeAl$_2$O$_3$-FeCr$_2$O$_4$ solid solutions at 800 °C and 900 °C (Engi, 1983). The fitted values of the $g_{3}$, $g_{3}$, $g_{3}$, $g_{3}$, $g_{3}$, and $g_{3}$ parameters were finally tested and refined by comparing observed and calculated cation distributions, activity-composition relations, and interphase partitioning coefficients in Fe$_2$O$_3$-FeCr$_2$O$_4$, Fe$_2$O$_3$-MgCr$_2$O$_4$, Fe$_2$O$_3$-FeAl$_2$O$_3$, MgAl$_2$O$_4$-MgCr$_2$O$_4$, MgAl$_2$O$_4$-FeCr$_2$O$_4$, and Fe$_2$O$_3$-FeCr$_2$O$_4$ solid solutions. The standard state chemical potentials of the reference end-member components were set to zero and the values of the $g_{0}$, $g_{1}$, $g_{2}$, and $g_{3}$ coefficients were subsequently constrained to be consistent with the values of the higher order expansion coefficients. These values are reported in Table 8 together with the values of the coefficients obtained in our earlier study (Nell and Wood, 1989). The estimated uncertainties in Table 8 reflect ranges over which the values may be varied while preserving a reasonable fit to the data. The coefficients are highly correlated (Nell and Wood, 1989) and the uncertainties are not intended to represent those correlations.

**Application of the model to FeCr$_2$O$_4$- and MgCr$_2$O$_4$-bearing solid solutions**

Cation distributions and activity-composition relations in Fe$_2$O$_3$-FeCr$_2$O$_4$, Fe$_2$O$_3$-MgCr$_2$O$_4$, Fe$_2$O$_3$-FeAl$_2$O$_3$-FeCr$_2$O$_4$, and MgAl$_2$O$_4$-MgCr$_2$O$_4$ solid solutions were calculated from the values of the expansion coefficients in Table 8. Equations 13–15 were used to calculate cation distributions for a given temperature. A Newton-Raphson method (e.g., Gerald and Wheatley, 1984, p. 133–159) was used to solve the nonlinear equations resulting in the solid lines in Figures 8A, 9, 10, and 11A. In all four systems, the data were used to constrain model pa-
Table 6. Chemical potentials of reference end-member components

\[
\begin{align*}
\mu_{\text{Fe}^3\text{O}_4} &= \mu_{\text{Fe}^3\text{O}_4}^0 - 2 \ln (\text{Fe}^3\text{O}_4) = -3.633 \text{J mol}^{-1} \\
\mu_{\text{FeAl}_2\text{O}_4} &= \mu_{\text{FeAl}_2\text{O}_4}^0 - 2 \ln (\text{FeAl}_2\text{O}_4) = -3.633 \text{J mol}^{-1} \\
\mu_{\text{MgFe}_2\text{O}_4} &= \mu_{\text{MgFe}_2\text{O}_4}^0 - 2 \ln (\text{MgFe}_2\text{O}_4) = -3.633 \text{J mol}^{-1} \\
\mu_{\text{MgAl}_2\text{O}_4} &= \mu_{\text{MgAl}_2\text{O}_4}^0 - 2 \ln (\text{MgAl}_2\text{O}_4) = -3.633 \text{J mol}^{-1} \\
\mu_{\text{FeC}r_2\text{O}_4} &= \mu_{\text{FeC}r_2\text{O}_4}^0 - 2 \ln (\text{FeC}r_2\text{O}_4) = -3.633 \text{J mol}^{-1} \\
\mu_{\text{MgC}r_2\text{O}_4} &= \mu_{\text{MgC}r_2\text{O}_4}^0 - 2 \ln (\text{MgC}r_2\text{O}_4) = -3.633 \text{J mol}^{-1}
\end{align*}
\]

Parameters, and the calculated lines are thus fitted. \(\text{Fe}_2\text{O}_3\), \(\text{FeAl}_2\text{O}_4\), \(\text{MgFe}_2\text{O}_4\), \(\text{MgAl}_2\text{O}_4\), \(\text{FeC}r_2\text{O}_4\), and \(\text{MgC}r_2\text{O}_4\) activities were calculated from the equations in Tables 6 and 7 and are presented as solid lines in activity-composition diagrams (Figs. 8B and 11B) and interphase partition plots (Figs. 12, 13A, and 13B). The data in Figures 8B and 13A were used to derive values of the model coefficients and the calculated lines in these figures are
Table 7. Activities of spinel, magnetite, hercynite, magnesioferrite, chromite and picrochromite relative end-member standard states at the temperature and pressures of interest

\[
\begin{align*}
\text{RT} \ln a_{\text{sp}-c} & = -g_{\text{sp}}r^2 - g_{\text{sp}}r^2 - g_{\text{sp}}s^2 - g_{\text{sp}}s^2 - g_{\text{sp}}s^2 \\
& - g_{\text{sp}}r^2 - g_{\text{sp}}r^2 - g_{\text{sp}}s^2 - g_{\text{sp}}s^2 - g_{\text{sp}}s^2 - g_{\text{sp}}s^2 \\
& + \text{RT} \left( 1 - s^2 \right) \left[ 2 \text{ ln } \left( \frac{\text{Fe}^2+}{\text{Mg}^2+} \right) + \text{ ln } \left( \frac{\text{Fe}^2+}{\text{Mg}^2+} \right) \right] \\
& + \text{RT} \left( 1 - s^2 \right) \left[ 2 \text{ ln } \left( \frac{\text{Fe}^2+}{\text{Mg}^2+} \right) + \text{ ln } \left( \frac{\text{Fe}^2+}{\text{Mg}^2+} \right) \right]
\end{align*}
\]

Note: 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 s1, s2, and s3 indicates values in pure disordered end-member spinels.
Fig. 12. Predicted values of ln $K_{Cr}^G$ [\(K_d = (X_{Cr}^{G_a-Cr})/(X_{Cr}^{G_a-Cr})\times(X_{G_d}^{G_d-Cr})\times(X_{cr}^{G_a-Cr})\)] compared to the data of Engi (1983) at 700 °C, 800 °C, and 900 °C. Calculations were performed at 700 °C and take account of the nonideality (\(W_n\) on a 1 atom basis) in olivine. Directions of approach to equilibrium in the experimental measurements are indicated by arrows on the error bars.

Fig. 13. (A) Calculated values of ln $K_{Cr}^G$ [\(K_d = (X_{Cr}^{G_a-Cr})/(X_{Cr}^{G_a-Cr})\times(X_{G_d}^{G_d-Cr})\times(X_{cr}^{G_d-Cr})\)] at 1100 °C compared to the data of Webb and Wood (1986) at 1000 °C and 1100 °C. Cr$^{3+}$-Al$^{3+}$ mixing in clinopyroxene is assumed to be ideal. (B) Predicted values of ln $K_{Cr}^G$ [\(K_d = (X_{Cr}^{G_a-Cr})/(X_{Cr}^{G_a-Cr})\times(X_{G_d}^{G_d-Cr})\times(X_{cr}^{G_d-Cr})\)] at 1050 °C compared to the data of Oka et al. (1984) at 1050 °C and 1250 °C. Nonideality in Al$_2$O$_3$-Cr$_2$O$_3$ solid solutions is modeled with asymmetric interaction parameters.

**TABLE 8.** Internally consistent values of the Taylor series expansion coefficients

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_1$</td>
<td>2.9 ± 5.5</td>
</tr>
<tr>
<td>$g_2$</td>
<td>7.1 ± 4.5</td>
</tr>
<tr>
<td>$g_3$</td>
<td>33.5 ± 19.8</td>
</tr>
<tr>
<td>$g_4$</td>
<td>35.5 ± 2.5</td>
</tr>
<tr>
<td>$g_5$</td>
<td>14.7 ± 0.5</td>
</tr>
<tr>
<td>$g_6$</td>
<td>44.5 ± 4.5</td>
</tr>
<tr>
<td>$g_7$</td>
<td>34.0 ± 2.5</td>
</tr>
<tr>
<td>$g_8$</td>
<td>-10.0 ± 1.0</td>
</tr>
<tr>
<td>$g_9$</td>
<td>-38.0 ± 2.0</td>
</tr>
<tr>
<td>$g_{10}$</td>
<td>-35.0 ± 2.0</td>
</tr>
<tr>
<td>$g_{11}$</td>
<td>-25.7 ± 1.5</td>
</tr>
<tr>
<td>$g_{12}$</td>
<td>-26.8 ± 1.3</td>
</tr>
<tr>
<td>$g_{13}$</td>
<td>-15.0 ± 3.0</td>
</tr>
<tr>
<td>$g_{14}$</td>
<td>10.0 ± 3.0</td>
</tr>
<tr>
<td>$g_{15}$</td>
<td>-0.5 ± 0.2</td>
</tr>
<tr>
<td>$g_{16}$</td>
<td>-7.1 ± 0.5</td>
</tr>
<tr>
<td>$g_{17}$</td>
<td>-25.0 ± 3.5</td>
</tr>
<tr>
<td>$g_{18}$</td>
<td>-15.0 ± 2.0</td>
</tr>
<tr>
<td>$g_{19}$</td>
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</tr>
<tr>
<td>$g_{20}$</td>
<td>5.5 ± 3.0</td>
</tr>
<tr>
<td>$g_{21}$</td>
<td>-16.6 ± 4.0</td>
</tr>
<tr>
<td>$g_{22}$</td>
<td>-11.9 ± 2.0</td>
</tr>
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<td>$g_{23}$</td>
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<tr>
<td>$g_{25}$</td>
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<tr>
<td>$g_{26}$</td>
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<td>$g_{27}$</td>
<td>-15.0 ± 3.0</td>
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<tr>
<td>$g_{28}$</td>
<td>-24.6 ± 2.0</td>
</tr>
</tbody>
</table>
the modeling of activity-composition relations along this binary is the $g_{\text{crsp}}$ coefficient which has been constrained by the mixing properties of $\text{Fe}_2\text{O}_3$-$\text{MgFe}_2\text{O}_4$ and $\text{MgAl}_2\text{O}_4$-$\text{FeAl}_2\text{O}_4$ solid solutions (Nell and Wood, 1989). $\text{Fe}^{2+}$-$\text{Mg}^{2+}$ partitioning between olivine (ol) and $\text{FeCr}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ solid solution (Crsp) is given by

$$
\ln K_{\text{ol-Crsp}} = \ln \frac{(X_{\text{FeCr}_2\text{O}_4})_{\text{Crsp}}(X_{\text{MgCr}_2\text{O}_4})_{\text{ol}}}{(X_{\text{MgCr}_2\text{O}_4})_{\text{Crsp}}(X_{\text{FeCr}_2\text{O}_4})_{\text{ol}}} - \frac{W_{\text{cr}}}{RT}
$$

where $K_{\text{ol-Crsp}}$ is the equilibrium for the olivine-spinel exchange reaction, $X_{\text{FeCr}_2\text{O}_4}$ is the mole fraction of chromite in the spinel solid solution, $\gamma_{\text{FeCr}_2\text{O}_4} = (\gamma_{\text{FeCr}_2\text{O}_4})_{\text{ol}}/(\gamma_{\text{FeCr}_2\text{O}_4})_{\text{Crsp}}$ is the activity coefficient of chromite in the spinel solid solution, and $W_{\text{cr}}$ is the regular solution interaction parameter for Fe-Mg olivine. Predicted $K_{\text{ol-Crsp}}$ values at fixed spinel composition were calculated from Equation 21 using $\gamma_{\text{FeCr}_2\text{O}_4}$ and $\gamma_{\text{MgCr}_2\text{O}_4}$ values from our activity-composition relations. The regular solution interaction parameter ($W_{\text{cr}}$) in olivine was assumed to be $4.5 \pm 1.0$ kJ/mol on a 1 atom basis (Nafziger and Muan, 1967; O'Neill and Wall, 1987) and the mean value for $K_{\text{ol-Crsp}}$ was calculated to be 3.0. Predicted $\ln K_{\text{ol-Crsp}}$ values at $700^\circ$C are in good agreement with experimental measurements at $700^\circ$C and $800^\circ$C (Fig. 12). Data at points of 900°C are, however, inconsistent with the lower temperature results and would require a much smaller value of the $g_{\text{crsp}}$ coefficient. The $g_{\text{crsp}}$ coefficient is given by $-W_{\text{MgCr}_2\text{O}_4}$ (Appendix 1) and our value of $-10.0 \pm 1.0$ kJ/mol is in good agreement with a recent estimate of approximately 8.2 kJ/mol for $W_{\text{FeCr}_2\text{O}_4}$ (Sack and Ghiorso, 1989). The three anomalous data points at 900°C are, therefore, in the context of our model, inconsistent with a wide range of activity-composition, as well as partitioning data summarized in our earlier paper (Jamieson and Roeder, 1984; Lehmann and Roux, 1986; Shishkov et al., 1980; and Trinel-Dufour and Perrot, 1977 summarized in Nell and Wood, 1989).

Data points at the intersection of the $\text{FeCr}_2\text{O}_4$-$\text{MgAl}_2\text{O}_4$ and $\text{MgCr}_2\text{O}_4$-$\text{FeAl}_2\text{O}_4$ tie lines were used to constrain the value of the $g_{\text{crsp}}$ parameter by formulating equilibria similar to Equation 21 for the $\text{FeCr}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ and $\text{MgAl}_2\text{O}_4$-$\text{FeAl}_2\text{O}_4$ components in equilibrium with olivine. Our model calculates equal ratios for $\ln \gamma_{\text{MgAl}_2\text{O}_4}$ and $\ln \gamma_{\text{FeAl}_2\text{O}_4}$, but the data are poorly reversed and do not provide a stringent test for our model.

**$\text{Fe}_2\text{O}_3$-$\text{FeCr}_2\text{O}_4$ solid solutions**

Calculated cation distributions at 1400°C (Fig. 8A) agree with our results obtained from thermopower measurements. Activity-composition relations calculated at 1227°C are shown in Figure 8B together with the data of Katsura et al. (1975) and Petric and Jacob (1982a). Uncertainties in the latter data were estimated from the experimental method in which spinel solid solutions and Pt-Fe alloys were equilibrated at a fixed $P_{\text{Fe}}$. The uncertainty in the value of $\log a_{\text{Fe}}$ is approximately $\pm 0.06$ log units (Nell and Wood, 1989) resulting in the error bars presented in Figure 8B.

**$\text{Fe}_2\text{O}_3$-$\text{MgCr}_2\text{O}_4$ and $\text{Fe}_2\text{O}_3$-$\text{FeAl}_2\text{O}_4$-$\text{FeCr}_2\text{O}_4$ solid solutions**

Cation distributions in $\text{Fe}_2\text{O}_3$-$\text{MgCr}_2\text{O}_4$ solid solutions calculated at 1000°C are compared with measured values in Figure 9. Measured and calculated cation distributions in $\text{Fe}_2\text{O}_3$-$\text{FeAl}_2\text{O}_4$-$\text{FeCr}_2\text{O}_4$ solid solutions along a pseudobinary section with the ratio of $\text{Cr}_2\text{O}_3/(\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ = 1/2 at 1100°C are in Figure 10. Data in this system were collected along three pseudobinary sections taken at constant ratios of $\text{FeAl}_2\text{O}_4/(\text{FeAl}_2\text{O}_4 + \text{FeCr}_2\text{O}_4)$ = 1/6, 1/1, and 5/6, respectively. This was done to facilitate integration of a three-component Gibbs-Duhem equation (Darken, 1950) for the excess partial molar entropy of $\text{Fe}_2\text{O}_3$ in solution that in turn was calculated using the thermopower-conductivity technique, and this provides a feasible, if ponderous, way of obtaining high-temperature cation distributions in such systems.

Activity-composition relations modeled for $\text{Fe}_2\text{O}_3$-$\text{FeAl}_2\text{O}_4$ solid solutions at 1100°C are compared to the measurements of Petric and Jacob (1982b) in Figure 11B. Error bars on the data points correspond to an uncertainty of $\pm 10\%$ in the measured activities.

**$\text{MgAl}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ solid solutions**

$\text{Al}^{3+}$-$\text{Cr}^{3+}$ partitioning experiments between spinel and clinopyroxene at 1100°C and 25 kbar pressure (Webb and Wood, 1986) were used to constrain activity-composition relations in $\text{MgAl}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ solid solutions. Assuming ideal mixing in clinopyroxene solid solutions, equilibrium between $\text{NaAl}_2\text{Si}_3\text{O}_8$-$\text{NaCr}_2\text{Si}_3\text{O}_8$ (cpx) and $\text{MgAl}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ (CrAlsp) is given by

$$
\ln K_{\text{cpx-CrAlsp}} = \ln \frac{(X_{\text{MgAl}_2\text{O}_4})_{\text{CrAlsp}}(X_{\text{MgCr}_2\text{O}_4})_{\text{cpx}}}{(X_{\text{MgCr}_2\text{O}_4})_{\text{CrAlsp}}(X_{\text{MgAl}_2\text{O}_4})_{\text{cpx}}}
$$

$$
= \ln K_{\text{cpx-CrAlsp}} + \ln \left(\frac{\gamma_{\text{MgAl}_2\text{O}_4}}{\gamma_{\text{MgCr}_2\text{O}_4}}\right).
$$

Theoretical $\ln K_{\text{cpx-CrAlsp}}$ values at fixed spinel compositions were calculated from our activity-composition re-
lations at 1100 °C and the results are shown in Figure 13A together with the data of Webb and Wood (1986). The mean value of $K_{\text{gCrAlSp}}$ was found to be 1.05.

The model was also used to predict $\text{Cr}^{3+}$-$\text{Al}^{3+}$ partitioning behavior between $\text{MgAl}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ and $\text{Al}_2\text{O}_3$-$\text{Cr}_2\text{O}_3$ solid solutions. Oka et al. (1984) crystallized $\text{Cr}$-$\text{Al}$ gels and reported partitioning data for this system based on their synthesis experiments at 1250, 1050, and 796 °C at 25 kbar pressure. Equilibrium between asymmetric sesquioxide solid solutions (cor) and symmetric Mg-$\text{Al}_2\text{O}_4$-$\text{Cr}_2\text{O}_3$ solid solutions (CrAlsp) is given by the following relationship:

$$
\ln K_{\text{gCrAlSp}} = \ln \left( \frac{W_{\text{CrAlSp}}}{W_{\text{MgCrAlSp}}} \right) (X_{\text{CrAlSp}}/X_{\text{MgCrAlSp}}) = \ln K_{\text{gCrAlSp}} + \frac{1}{2} \left( \frac{W_{\text{CrAlSp}}}{W_{\text{MgCrAlSp}}} \right) (X_{\text{CrAlSp}}/X_{\text{MgCrAlSp}})^2 + \frac{4W_{\text{CrAlSp}} - 2W_{\text{CrAlSp}}X_{\text{CrAlSp}}}{2RT}$$

where $W_{\text{CrAlSp}}$ and $W_{\text{MgCrAlSp}}$ are asymmetric interaction parameters in $\text{Al}_2\text{O}_3$-$\text{Cr}_2\text{O}_3$ solid solutions. We calculated $K_{\text{gCrAlSp}}$ values following the approach outlined above for $\text{FeCr}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ solid solutions. $W_{\text{CrAlSp}}$ values were obtained from Jacob (1978) and Chatterjee et al. (1982) while $K_{\text{gCrAlSp}}$ was set to zero. Our predicted partition coefficients at 1050 °C are in good agreement with data from Oka et al. (1984) at 1050 °C and 1250 °C given the range of possible values for the asymmetric interaction parameters in the sesquioxide (Fig. 13B).

**Conclusions**

We have presented a large body of thermoelectricity and electrical conductivity data on spinel in the systems $\text{Fe}_3\text{O}_4$-$\text{FeCr}_2\text{O}_4$, and $\text{Fe}_2\text{O}_3$-$\text{MgCr}_2\text{O}_4$ and the ternary $\text{Fe}_2\text{O}_3$-$\text{FeAl}_2\text{O}_4$-$\text{FeCr}_2\text{O}_4$. From both experimental data and theoretical calculations we have argued that most of the data are consistent with octahedral site electron hopping between $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ analogous to that which is observed in pure $\text{Fe}_3\text{O}_4$. Activation energies for conduction increase slowly and monotonically away from $\text{Fe}_3\text{O}_4$, and cation distributions calculated from the data are consistent with the formalism of O'Neill and Navrotsky (1983, 1984), which is a good description of ionic and binary spinels. On the $\text{Fe}_2\text{O}_3$-$\text{FeCr}_2\text{O}_4$ join, we were able to conduct an independent test of the $\text{Fe}^{3+}$-$\text{Fe}^{2+}$ hopping mechanism and found agreement between calculated and nominal concentrations of $\text{Fe}$ at $\text{FeCr}_2\text{O}_4$ contents between 0 and 60%. More $\text{Cr}$-rich compositions cannot, however, be described by this conduction mechanism, and we believe it likely that $\text{Cr}^{3+}$ is involved at more dilute concentrations of $\text{Fe}_3\text{O}_4$.

We used the data to calculate octahedral-tetrahedral cation distributions for these compositions where octahedral $\text{Fe}^{2+}$-$\text{Fe}^{3+}$ electron hopping appears to hold. The cation distribution data were then combined with activity-composition relations and interphase partitioning data for chrome-bearing spinels in a model that extends our previous work in $(\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+})_2\text{O}_4$ solid solutions (Nell and Wood, 1989) to the geologically important system $(\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})_2\text{O}_4$. We used a second-degree Taylor series expansion of the vibrational part of the Gibbs free energy in terms of order and composition parameters and constrained the values of the series expansion coefficients to be consistent with cation distribution data, activity-composition relations, and element partitioning data. The model reproduces the data from which the values of coefficients were obtained and also successfully predicts data that were not used to constrain the fit parameters.

A computer program in Fortran 77 has been written to calculate cation distributions and activities in the $(\text{Mg}^{2+},\text{Fe}^{2+})(\text{Fe}^{3+},\text{Al}^{3+},\text{Cr}^{3+})_2\text{O}_4$ system. It is available on diskette or tape from the second author.

**Acknowledgments**

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**References Cited**


Dieckmann, R. (1982) Defects and cation diffusion in magnetite (IV);
Non-stoichiometry and point defect structure of magnetite ($\text{Fe}_x\text{O}_y$). Berichte Bunsgesellschaft Physikalische Chemie, 86, 112-118.


Mattioli, G.S., and Wood, B.J. (1988) Magnetic activities across the $\text{MgAl}_2\text{O}_4$-$\text{Fe}_3\text{O}_4$ spinel join, with application to the thermobarometric estimates of upper mantle oxygen fugacity. Contributions to Mineralogy and Petrology, 98, 148-162.


Nell, J., and Wood, B.J. (1989) Thermodynamic properties in a multi-component solid solution involving cation disorder: $\text{Fe}_x\text{O}_y$-$\text{MgFe}_2\text{O}_4$-$\text{FeAl}_2\text{O}_4$-$\text{MgAl}_2\text{O}_4$-$\text{FeCr}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ solid solutions.

Nell, J., Wood, B.J., and Mason, T.O. (1989) High-temperature cation distributions in $\text{Fe}_x\text{O}_y$-$\text{MgFe}_2\text{O}_4$-$\text{FeAl}_2\text{O}_4$-$\text{MgAl}_2\text{O}_4$-$\text{FeCr}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ spinels from thermoporwer and conductivity measurements. American Mineralogist, 74, 339-351.


Petrie, A., and Jacob, K.T. (1982) Thermodynamic properties of $\text{Fe}_x\text{O}_y$-$\text{Fe}^{2+}$-$\text{Fe}^{3+}$-$\text{FeCr}_2\text{O}_4$ spinel solid solutions. Journal of the American Ceramic Society, 65, 117-123.

Trinel-Dufour, M.C., and Perrot, P. (1977) Thermodynamic study of solid solutions in the system $\text{Fe}_3\text{O}_4$-$\text{FeSiO}_3$-$\text{SiO}_2$. Contributions to Mineralogy and Petrology, 102, 41-68.


APPENDIX 1.

Thermodynamic coefficients in a second-degree Taylor series expansion for the vibrational part of the Gibbs free energy of $\text{Fe}_x\text{O}_y$-$\text{MgFe}_2\text{O}_4$-$\text{FeAl}_2\text{O}_4$-$\text{MgAl}_2\text{O}_4$-$\text{FeCr}_2\text{O}_4$-$\text{MgCr}_2\text{O}_4$ solid solutions.
\[ g_0 = \mu_0^g + \mu_0^f - \mu_0^s + W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + W_{\text{Mg}-\text{Fe}^{2+}} \]
\[ \quad - W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_1 = \mu_1^g - \mu_1^f + 2W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_2 = \mu_2^g - \mu_2^f + W_{\text{Mg}-\text{Fe}^{3+}} + W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_3 = \mu_3^g - \mu_3^f + 2W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{2+}} + W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{3+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_4 = \mu_4^g - \mu_4^f + W_{\text{Mg}-\text{Fe}^{3+}} + W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/2} = W_{\text{Mg}-\text{Fe}^{2+}} + W_{\text{Mg}-\text{Fe}^{3+}} + W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/1} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/3} = W_{\text{Mg}-\text{Fe}^{2+}} - W_{\text{Mg}-\text{Fe}^{3+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/4} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/5} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/6} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/7} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/8} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/9} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/10} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/11} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/12} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/13} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/14} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/15} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/16} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/17} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/18} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/19} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/20} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/21} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/22} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/23} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/24} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[ g_{r/25} = W_{\text{Mg}-\text{Fe}^{3+}} - W_{\text{Mg}-\text{Fe}^{2+}} + \Delta G_{34}^g - \Delta G_{34}^s \]
\[-W_{\mathrm{Mg}^{2+} \cdots \mathrm{Cr}} + \Delta G_{8}^{\alpha} + \Delta G_{16}^{\alpha} + \Delta G_{38}^{\alpha}\]

\[-\Delta G_{49}^{\alpha} - \Delta G_{12}^{\alpha} - \Delta G_{46}^{\alpha}\]

\[g_{ij2} = W_{(\mathrm{Mg},\mathrm{Al} \cdots \mathrm{Fe})^{2+}} - W_{(\mathrm{Fe}^{2+} \cdots \mathrm{Fe})^{2+}} - W_{(\mathrm{Al} \cdots \mathrm{Fe})^{2+}}\]

\[+ \frac{W_{(\mathrm{Mg} \cdots \mathrm{Fe})^{2+}} - W_{(\mathrm{Mg} \cdots \mathrm{Fe})^{2+}} - W_{(\mathrm{Fe} \cdots \mathrm{Fe})^{2+}}}{2}\]

\[+ \Delta G_{28}^{\alpha} - \Delta G_{45}^{\alpha} - \Delta G_{56}^{\alpha}\]

\[g_{ij3} = W_{\mathrm{Mg}^{2+} \cdots \mathrm{Mg}} - W_{\mathrm{Mg}^{2+} \cdots \mathrm{Fe}^{2+}} - W_{\mathrm{Al} \cdots \mathrm{Fe}^{2+}}\]

\[+ \frac{W_{\mathrm{Mg}^{2+} \cdots \mathrm{Mg}} - W_{\mathrm{Mg}^{2+} \cdots \mathrm{Fe}^{2+}} - W_{\mathrm{Mg}^{2+} \cdots \mathrm{Fe}^{2+}}}{2}\]

\[+ \Delta G_{16}^{\alpha} + \Delta G_{78}^{\alpha} - \Delta G_{34}^{\alpha} - \Delta G_{12}^{\alpha}\]