

Composition (x) Dependence of Nonstoichiometry (δ) in Ferrite Spinel $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$

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The nonstoichiometry of spinel ferrite $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ has been measured as a function of oxygen activity (a_{O_2}) and Mg content (x) at 1000°C via coulometric titration. For a given Mg content, the nonstoichiometry varies with the oxygen activity as $\delta = [\text{V}]^\circ a_{\text{O}_2}^{-2/3} - [\text{I}]^\circ a_{\text{O}_2}^{-2/3}$, indicating metal vacancies at high a_{O_2} and metal interstitials at low a_{O_2} . As Mg content increases from $x = 0$ to $x = 0.29$, the defect parameter, $[\text{V}]^\circ$ decreases and $[\text{I}]^\circ$ increases, respectively, by 2–4 orders of magnitude. This is ascribed to the fact that magnesium ions remain at a fixed valence (Mg^{2+}) in the spinel. The Mg content dependencies of these defect parameters are discussed in the light of point defect thermodynamics. © 1998 Academic Press

1. INTRODUCTION

Magnesioferrous ferrite plays an important role in modern ferrite technology as an end member of the ferrites, particularly for high-frequency applications, e.g., Mg–Mn or Mg–Zn ferrites (1, 2). The electrical and magnetic properties of a ferrite are closely related to a number of factors such as oxygen nonstoichiometry, cation molecularity, microstructure, and phase purity (3–9). To prepare high-quality ferrites, therefore, knowledge of the effects of these factors on the ferrite properties is required.

Of these various factors, we have been examining the effect of nonstoichiometry, δ , as a measure of point defect concentrations on the electrical and magnetic properties of $(\text{Mg},\text{Mn},\text{Fe})_{3-\delta}\text{O}_4$ ferrite. For this purpose, information on the nonstoichiometry of this ferrite is required as a function of the ferrite composition, oxygen activity, and temperature.

The nonstoichiometry of spinel-type oxides such as $\text{Mn}_{3-\delta}\text{O}_4$, $\text{Fe}_{3-\delta}\text{O}_4$, $(\text{Co},\text{Fe})_{3-\delta}\text{O}_4$, and $(\text{Co},\text{Mn},\text{Fe})_{3-\delta}\text{O}_4$ has been extensively studied by Dieckmann *et al.* via thermogravimetry (10–14). For the systems of Mg–Mn ferrites, $(\text{Mg},\text{Mn},\text{Fe})_{3-\delta}\text{O}_4$, however, very few data are available.

In this work, the nonstoichiometry of $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ has been determined as a function of oxygen activity, a_{O_2}

($= P_{\text{O}_2}/\text{atm}$), and Mg content, x , at 1000°C by a coulometric titration technique. We report on the numerical values for δ and discuss, in the light of point defect thermodynamics, the dependencies of δ on the oxygen activity and Mg content.

2. EXPERIMENTAL

Ferrite samples, $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$, of three different compositions were prepared from the starting powders of MgO (99.999%, Aldrich Chemical Co., Inc.) and Fe_2O_3 (99.98%, Aldrich) via a conventional ceramic processing route. Sintering was carried out at 1350°C in an air atmosphere for 4 h. The cationic compositions were subsequently assayed as $x = 0.29, 0.24$, and 0.15 by ICP emission spectrophotometry, the errors of which were about 0.007.

Coulometric titration cells were constructed as schematically shown in Fig. 1. As a solid electrolyte, a disk of 8 mol % $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (8YSZ), 12.5 mm diameter \times 1.0–1.5 mm thick was used. Each disk was polished on both planar surfaces with assorted diamond pastes of grit size down to 1 μm . As gas electrodes, a piece of Pt gauze (no. 29809-3, 100 mesh, Aldrich), 2.5 mm \times 2.5 mm, was subsequently attached to each polished surface of a YSZ disk with the aid of Pt paste (no. 5542, unfluxed, Engelhard) by firing overnight at about 1000°C in an air atmosphere.

An alumina cup, measuring 10.5 mm o.d. \times 8 mm i.d. \times 3–4 mm high, served as a chamber to carry a ferrite specimen inside. As shown in Fig. 1, the ferrite specimen was supported by the tips of four alumina needles which were appropriately implanted on an alumina block. The needle-like sample supporters were used to minimize possible reaction with a ferrite specimen.

In stacking a disk of electrolyte upon the sample chamber, an alumina ring, 10 mm o.d. \times 8 mm i.d. \times 1 mm thick, and Pt annulus, 10 mm o.d. \times 8 mm i.d. \times 70 μm thick, were inserted as shown in Fig. 1. The former was for electrical insulation between the Pt-lead wire and the bare surface of the electrolyte, and the latter for electrical connection to the external circuitry.

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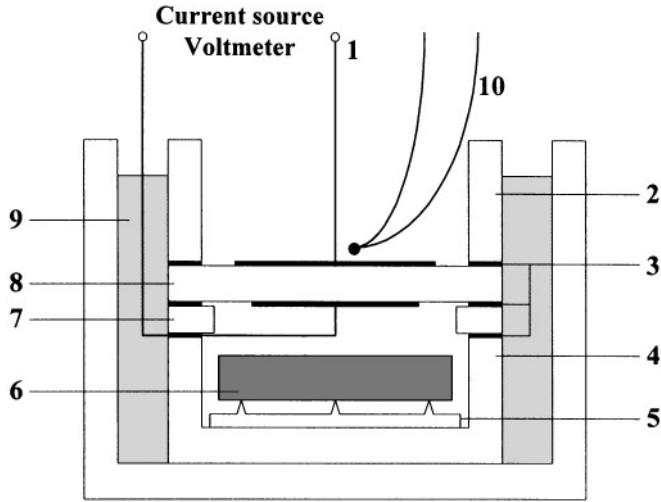


FIG. 1. Schematic view of the electrochemical cell. 1, Pt-lead wire; 2, YSZ ring; 3, Pt foil; 4, alumina cup; 5, alumina supporter; 6, specimen; 7, alumina ring; 8, YSZ disk; 9, silicate glass; 10, S-type thermocouple.

An as-assembled titration cell was placed inside an alumina crucible, 26 mm i.d. \times 18–20 mm high, and the empty space between the cell and the crucible was filled with glass powders of composition 49 wt% SiO_2 + 25 wt% BaO + 16 wt% B_2O_3 + 10 wt% Al_2O_3 . The entire assembly was heated to about 1100°C in a nitrogen atmosphere to fully melt the glass and then slowly cooled to the operating temperature, 1000°C. The melted glass provided a satisfactory gastight seal at 1000°C.

Coulometric titration was carried out as follows: a constant current, I , was passed through the YSZ electrolyte for a predetermined period of time, t , by using a dc current source (Keithley 224). The amount of molecular oxygen, ΔN_{O_2} , which was removed from or added to the sample chamber can be written as

$$\Delta N_{\text{O}_2} = \frac{It}{4F} \quad [1]$$

where F is the Faraday constant. ΔN_{O_2} involves the changes of oxygen content both in the ferrite sample, $\Delta N_{\text{O}_2}(\text{sp})$, and in the dead volume, $\Delta N_{\text{O}_2}(\text{gas})$; i.e.

$$\Delta N_{\text{O}_2} = \Delta N_{\text{O}_2}(\text{sp}) + \Delta N_{\text{O}_2}(\text{gas}). \quad [2]$$

If the gas inside the chamber is assumed to be ideal, then

$$\Delta N_{\text{O}_2}(\text{gas}) = \frac{V}{RT} \Delta P_{\text{O}_2}(\text{gas}), \quad [3]$$

where V denotes the dead volume of the sample chamber and $\Delta P_{\text{O}_2}(\text{gas})$ the change of oxygen partial pressure induced inside the chamber. In this experiment, the dead volume of the cell was about 10^{-7} m^3 and $\Delta P_{\text{O}_2}(\text{gas})$ was less than 10^{-3} atm in each titration run, so that $\Delta N_{\text{O}_2}(\text{gas})$ was about 10^{-9} mol at most. $\Delta N_{\text{O}_2}(\text{gas})$, on the other hand, was on the order of 10^{-7} mol . $\Delta N_{\text{O}_2}(\text{gas})/\Delta N_{\text{O}_2}$ was, therefore, less than 1%, and $\Delta N_{\text{O}_2}(\text{gas})$ can be ignored from the right-hand side of Eq. [2]. Accordingly,

$$\Delta N_{\text{O}_2}(\text{sp}) \approx \Delta N_{\text{O}_2} = \frac{It}{4F}. \quad [4]$$

When the oxygen content of the ferrite, of which the extent of metal deficit or nonstoichiometry is initially δ^* , i.e., $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta^*}\text{O}_4$, is increased by ΔN_{O} ($=2\Delta N_{\text{O}_2}$) so that the nonstoichiometry changes to δ , i.e., $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$, the change of the oxygen content of the ferrite can be related to the change of the nonstoichiometry, $\Delta\delta$ ($\equiv \delta - \delta^*$) as

$$\frac{\Delta N_{\text{O}}}{N_{\text{M}}} = \frac{4\Delta\delta}{(3-\delta)(3-\delta^*)}. \quad [5]$$

Here N_{M} is the number of moles of metallic component in the ferrite,

$$N_{\text{M}} = \frac{(3-\delta^*)m_0}{M_0}, \quad [6]$$

where m_0 and M_0 are the initial sample weight and the molar weight of $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta^*}\text{O}_4$, respectively. As δ is normally much smaller than 1, the change of the nonstoichiometry, $\Delta\delta$, can be calculated from Eqs. [4]–[6] as

$$\Delta\delta = \delta - \delta^* = \frac{3M_0It}{8m_0F} \quad [7]$$

Consequently, the nonstoichiometry of $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ can be controlled by passing a known amount of charge (It) through the electrolyte.

After the current was turned off, the open-circuit emf across the YSZ electrolyte was monitored with a digital multimeter (Keithley 197) to determine the equilibrium oxygen activity over the specimen, a_{O_2} , via the Nernst equation

$$E = \frac{RT}{4F} \ln \left(\frac{a_{\text{O}_2}}{a_{\text{O}_2}(\text{ref})} \right) \quad [8]$$

where E is the steady-state open-circuit emf and $a_{\text{O}_2}(\text{ref})$ the oxygen activity of the reference gas flowing outside the titration cell. In the present experiment, N_2/O_2 or CO_2/CO mixtures were employed as the reference gas, whose oxygen activity $a_{\text{O}_2}(\text{ref})$ was determined with a stabilized zirconia–oxygen concentration cell.

3. RESULTS AND DISCUSSION

In Fig. 2 are shown titration curves or nonstoichiometry isotherms, $\delta(a_{O_2})$, for the system $(Mg_xFe_{1-x})_{3-\delta}O_4$ for different cationic compositions $x = 0$ (ref 11), 0.15, 0.24, and 0.29 at 1000°C, and the numerical data are listed in Table 1. The nonstoichiometry isotherms show a hyperbolic sine behavior against $\log a_{O_2}$ in the spinel single-phase region and shift toward higher oxygen activity as Mg content x increases.

Extensive works on the nonstoichiometry (11–14), tracer diffusion (12–15), and cationic transference number (16) have shown that spinel ferrites have a Frenkel disorder as a majority ionic defect, that is, cation vacancies and interstitial cations. Therefore, the nonstoichiometry (δ) of spinel ferrite $(M_xFe_{1-x})_{3-\delta}O_4$ ($M = Fe, Mg, Mn, Zn, \text{etc.}$) corresponds to the difference between concentrations of cation vacancies and interstitial cations, or

$$\delta = [V] - [I] \quad [9]$$

In a spinel lattice, two types of cation vacancies and interstitials may be distinguished: one is octahedral and the other is tetrahedral. It has, however, been concluded for magnetite ($Fe_{3-\delta}O_4$) from Mössbauer (17) and TGA (11) studies that cation vacancies are predominantly present on octahedral lattice sites. It is thus assumed that $(Mg_xFe_{1-x})_{3-\delta}O_4$ spinel has also octahedral vacancies

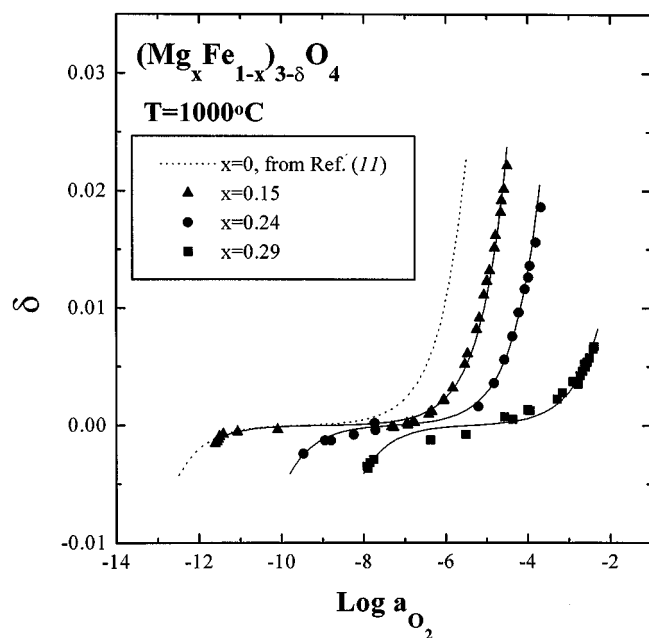


FIG. 2. Nonstoichiometry δ of $(Mg_xFe_{1-x})_{3-\delta}O_4$ vs oxygen activity a_{O_2} at 1000°C for different compositions. The curve for $x = 0$ (magnetite) is taken from ref 11.

TABLE 1
Nonstoichiometry δ as a Function of Oxygen Activity in $(Mg_xFe_{1-x})_{3-\delta}O_4$ at 1000°C: (a) $x = 0.15$, (b) $x = 0.24$, and (c) $x = 0.29$

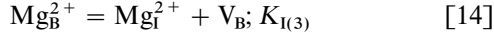
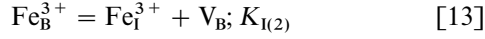
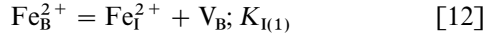
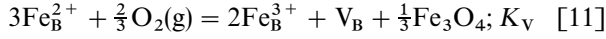
| (a) $x = 0.15$ | | | |
|----------------|------------------------|----------------|------------------------|
| $\log a_{O_2}$ | δ | $\log a_{O_2}$ | δ |
| -4.49 | 2.21×10^{-2} | -6.33 | 1.18×10^{-3} |
| -4.58 | 2.01×10^{-2} | -6.35 | 1.18×10^{-3} |
| -4.63 | 1.92×10^{-2} | -6.41 | 9.30×10^{-4} |
| -4.65 | 1.81×10^{-2} | -6.76 | 2.30×10^{-4} |
| -4.77 | 1.62×10^{-2} | -6.80 | 2.80×10^{-4} |
| -4.80 | 1.51×10^{-2} | -6.92 | 3.00×10^{-5} |
| -4.92 | 1.32×10^{-2} | -6.95 | 1.80×10^{-4} |
| -4.99 | 1.23×10^{-2} | -7.27 | -1.70×10^{-4} |
| -5.06 | 1.11×10^{-2} | -7.32 | -1.20×10^{-4} |
| -5.17 | 9.13×10^{-3} | -10.10 | -3.70×10^{-4} |
| -5.25 | 8.18×10^{-3} | -11.07 | -5.70×10^{-4} |
| -5.47 | 6.08×10^{-3} | -11.42 | -7.70×10^{-4} |
| -5.53 | 5.18×10^{-3} | -11.51 | -9.70×10^{-4} |
| -5.82 | 3.18×10^{-3} | -11.54 | -1.17×10^{-3} |
| -6.04 | 2.18×10^{-3} | -11.57 | -1.37×10^{-3} |
| -6.05 | 2.13×10^{-3} | -11.61 | -1.57×10^{-3} |
| (b) $x = 0.24$ | | (c) $x = 0.29$ | |
| $\log a_{O_2}$ | δ | $\log a_{O_2}$ | δ |
| -3.68 | 1.86×10^{-2} | -2.39 | 6.74×10^{-3} |
| -3.80 | 1.56×10^{-2} | -2.41 | 6.51×10^{-3} |
| -3.94 | 1.36×10^{-2} | -2.50 | 5.76×10^{-3} |
| -3.98 | 1.26×10^{-2} | -2.56 | 5.39×10^{-3} |
| -4.07 | 1.16×10^{-2} | -2.62 | 5.24×10^{-3} |
| -4.21 | 9.60×10^{-3} | -2.60 | 5.01×10^{-3} |
| -4.22 | 9.60×10^{-3} | -2.67 | 4.64×10^{-3} |
| -4.37 | 7.60×10^{-3} | -2.73 | 4.26×10^{-3} |
| -4.57 | 5.60×10^{-3} | -2.77 | 3.52×10^{-3} |
| -4.82 | 3.60×10^{-3} | -2.90 | 3.74×10^{-3} |
| -5.20 | 1.60×10^{-3} | -3.16 | 2.77×10^{-3} |
| -7.72 | -4.00×10^{-4} | -3.28 | 2.24×10^{-3} |
| -7.73 | -2.00×10^{-4} | -3.94 | 1.27×10^{-3} |
| -8.24 | -8.00×10^{-4} | -4.00 | 1.34×10^{-3} |
| -8.80 | -1.30×10^{-3} | -4.37 | 5.20×10^{-4} |
| -8.95 | -1.30×10^{-3} | -4.56 | 7.40×10^{-4} |
| -9.47 | -2.40×10^{-3} | -5.51 | 7.70×10^{-4} |
| | | -6.37 | -1.24×10^{-3} |
| | | -7.76 | -2.92×10^{-3} |
| | | -7.85 | -3.17×10^{-3} |
| | | -7.90 | -3.67×10^{-3} |
| | | -7.92 | -3.49×10^{-3} |

only, and tetrahedral vacancies are excluded. Furthermore, for the sake of simplicity, the distinction is not made between the tetrahedrally coordinated interstitial and the octahedrally coordinated interstitial.

With the foregoing assumptions, the nonstoichiometry of our system is expressed as

$$\delta = [V_B] - [Fe_i^{2+}] - [Fe_i^{3+}] - [Mg_i^{2+}], \quad [10]$$

and the following internal and external equilibria may be considered:



Here K_i [$i = \text{V}, \text{I}(1), \text{I}(2), \text{and I}(3)$] is the reaction equilibrium constant for the corresponding defect formation reaction, and the subscripts B and I represent an octahedral lattice site and an interstitial site, respectively. Applying the mass action law to Eqs. [11]–[14] on the assumption of ideal dilute solution, one can calculate the concentration of each defect as

$$[\text{V}_\text{B}] = \frac{[\text{Fe}_\text{B}^{2+}]^3}{[\text{Fe}_\text{B}^{3+}]^2} K_\text{V} a_{\text{Fe}_3\text{O}_4}^{-1/3} a_{\text{O}_2}^{2/3}, \quad [15]$$

$$[\text{Fe}_\text{I}^{2+}] = \frac{[\text{Fe}_\text{B}^{2+}]^2}{[\text{Fe}_\text{B}^{3+}]^2} \frac{K_{\text{I}(1)}}{K_\text{V}} a_{\text{Fe}_3\text{O}_4}^{1/3} a_{\text{O}_2}^{-2/3}, \quad [16]$$

$$[\text{Fe}_\text{I}^{3+}] = \frac{[\text{Fe}_\text{B}^{3+}]^3}{[\text{Fe}_\text{B}^{2+}]^3} \frac{K_{\text{I}(2)}}{K_\text{V}} a_{\text{Fe}_3\text{O}_4}^{1/3} a_{\text{O}_2}^{-2/3}, \quad [17]$$

$$[\text{Mg}_\text{I}^{2+}] = \frac{[\text{Mg}_\text{B}^{2+}][\text{Fe}_\text{B}^{3+}]^2}{[\text{Fe}_\text{B}^{2+}]^3} \frac{K_{\text{I}(3)}}{K_\text{V}} a_{\text{Fe}_3\text{O}_4}^{1/3} a_{\text{O}_2}^{-2/3}, \quad [18]$$

where $[\]$ denotes the concentration of the species therein and $a_{\text{Fe}_3\text{O}_4}$ is the activity of Fe_3O_4 in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ spinel. Replacing the right-hand side in Eq. [10] with those in Eqs. [15]–[18], the nonstoichiometry δ as a function of oxygen activity is

$$\delta = [\text{V}]^\circ a_{\text{O}_2}^{2/3} - [\text{I}]^\circ a_{\text{O}_2}^{-2/3}, \quad [19]$$

where

$$[\text{V}]^\circ = \frac{[\text{Fe}_\text{B}^{2+}]^3}{[\text{Fe}_\text{B}^{3+}]^2} K_\text{V} a_{\text{Fe}_3\text{O}_4}^{-1/3} \quad [20]$$

and

$$[\text{I}]^\circ = \left[\frac{[\text{Fe}_\text{B}^{2+}]^2}{[\text{Fe}_\text{B}^{3+}]^2} \frac{K_{\text{I}(1)}}{K_\text{V}} + \frac{[\text{Fe}_\text{B}^{3+}]^3}{[\text{Fe}_\text{B}^{2+}]^3} \frac{K_{\text{I}(2)}}{K_\text{V}} + \frac{[\text{Mg}_\text{B}^{2+}][\text{Fe}_\text{B}^{3+}]^2}{[\text{Fe}_\text{B}^{2+}]^3} \frac{K_{\text{I}(3)}}{K_\text{V}} \right] a_{\text{Fe}_3\text{O}_4}^{1/3} \quad [21]$$

Note that the nonstoichiometry (δ) of $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ spinel has the same oxygen activity dependence as other

spinel oxides (10–14) since cation redistribution and the activity of Fe_3O_4 in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ are insensitive to the oxygen activity if $\delta \ll 1$ (6, 20), which can be deduced from the structural similarity between them.

In a coulometric titration experiment, what is controlled or measured is changes of nonstoichiometry from a reference value (δ^*), $\Delta\delta$, not the absolute values of δ ; i.e.

$$\Delta\delta = \delta - \delta^* = [\text{V}]^\circ a_{\text{O}_2}^{2/3} - [\text{I}]^\circ a_{\text{O}_2}^{-2/3} - \delta^*. \quad [22]$$

Accordingly, to determine the absolute values of the nonstoichiometry, it is necessary to know the reference value, δ^* , first. To this end, the experimental data, $\Delta\delta$, were fitted to Eq. [22] to obtain $[\text{V}]^\circ$, $[\text{I}]^\circ$, δ^* , and subsequently the absolute values of δ . The absolute values on the ordinate in Fig. 2 were determined thereby, and solid lines in Fig. 2 are the best fit to Eq. [22].

The composition (x) dependencies of $[\text{V}]^\circ$ and $[\text{I}]^\circ$ are as shown in Figs. 3 and 4, respectively, and their numerical values are listed in Table 2. One can see that as x increases from 0 to 0.29, $[\text{V}]^\circ$ decreases and $[\text{I}]^\circ$ increases, respectively, by approximately 3 orders of magnitude. Qualitatively, these appreciable changes may be attributed to the fact that magnesium ions exist only as fixed-valent or Mg^{2+} in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$. For an oxide to accommodate a hyperstoichiometric amount of oxygen, some cations should oxidize to higher oxidation states. Increasing replacement of fixed-valent Mg for multivalent Fe, therefore, reduces the oxidation capacity of $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$. A similar trend is found for $(\text{Co}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ (14): as x increases, the δ isotherm shifts to increasingly high a_{O_2} . The latter may be attributed to the fact that the ionization potential of Co^{2+} to Co^{3+} is higher than that of Fe^{2+} to Fe^{3+} (18).

In Eqs. [20] and [21], one can immediately recognize that the defect parameters $[\text{V}]^\circ$ and $[\text{I}]^\circ$ are determined by cation redistribution. From the mass balance and electro-neutrality conditions for a lattice molecule $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$,

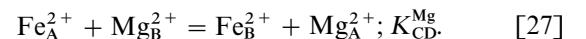
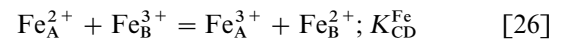
$$[\text{Mg}_\text{A}^{2+}] + [\text{Mg}_\text{B}^{2+}] = 3x, \quad [23]$$

$$[\text{Fe}_\text{A}^{2+}] + [\text{Fe}_\text{B}^{2+}] = 1 - 3x, \quad [24]$$

and

$$[\text{Fe}_\text{A}^{3+}] + [\text{Fe}_\text{B}^{3+}] = 2. \quad [25]$$

In the derivation of Eqs. [23]–[25], the concentrations of cation vacancies and interstitials were neglected since $\delta \ll 1$. Next, let us consider reaction of cation distribution between the tetrahedral and octahedral sites,



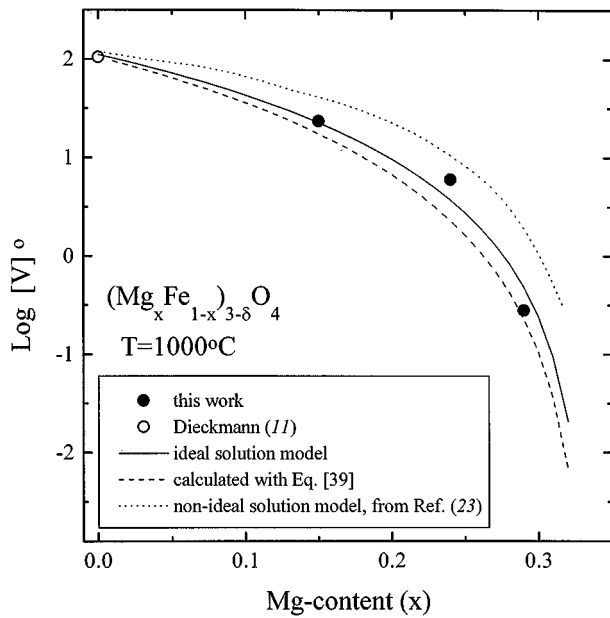


FIG. 3. Defect parameter $[V]^\circ$ as a function of Mg content, x , in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ at 1000°C . The data point for $x = 0$ (magnetite) is taken from ref (11).

Application of the mass action law to Eqs. [26] and [27] yields

$$K_{\text{CD}}^{\text{Fe}} = \frac{1}{\alpha} \frac{[\text{Fe}_A^{3+}]}{[\text{Fe}_B^{3+}]}, \quad [28]$$

$$K_{\text{CD}}^{\text{Mg}} = \frac{1}{\alpha} \frac{[\text{Mg}_A^{2+}]}{[\text{Mg}_B^{2+}]}, \quad [29]$$

where the distribution coefficient α is defined as

$$\alpha \equiv \frac{[\text{Fe}_A^{2+}]}{[\text{Fe}_B^{2+}]}. \quad [30]$$

Using Eqs. [23]–[25], [28], and [29], we write the following:

$$[\text{Fe}_B^{2+}] = \frac{1 - 3x}{1 + \alpha} \quad [31]$$

$$[\text{Fe}_B^{3+}] = \frac{2}{1 + \alpha K_{\text{CD}}^{\text{Fe}}} \quad [32]$$

$$[\text{Mg}_B^{2+}] = \frac{3x}{1 + \alpha K_{\text{CD}}^{\text{Mg}}} \quad [33]$$

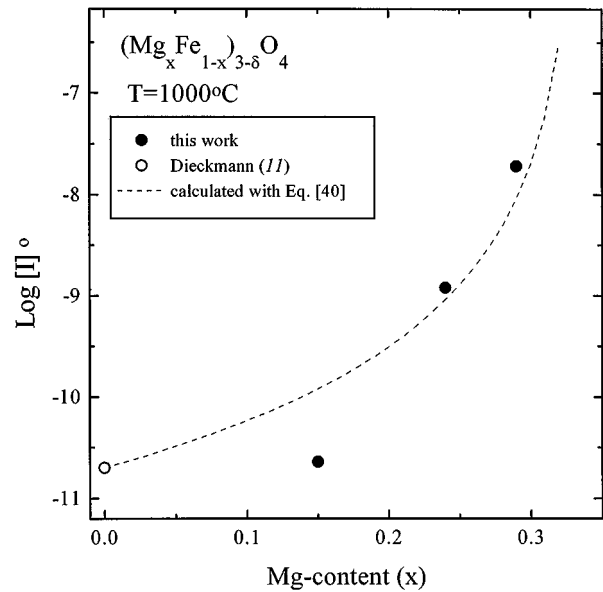


FIG. 4. Defect parameter $[I]^\circ$ as a function of Mg content, x , in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ at 1000°C . The data point for $x = 0$ (magnetite) is taken from ref 11.

Consequently, the defect parameters $[V]^\circ$ and $[I]^\circ$ in Eqs. [20] and [21] are

$$[V]^\circ = \frac{(1 - 3x)^2}{4} \frac{(1 + \alpha K_{\text{CD}}^{\text{Fe}})^2}{(1 + \alpha)^3} K_V a_{\text{Fe}_3\text{O}_4}^{-1/3} \quad [34]$$

and

$$[I]^\circ = \frac{4}{(1 - 3x)^2} \frac{(1 + \alpha)^2}{(1 + \alpha K_{\text{CD}}^{\text{Fe}})^2} \times \left[K_{\text{I}(1)} + \frac{2(1 + \alpha)}{(1 - 3x)(1 + \alpha K_{\text{CD}}^{\text{Fe}})} K_{\text{I}(2)} + \frac{3x(1 + \alpha)}{(1 - 3x)(1 + \alpha K_{\text{CD}}^{\text{Mg}})} K_{\text{I}(3)} \right] \frac{a_{\text{Fe}_3\text{O}_4}^{1/3}}{K_V}, \quad [35]$$

respectively.

TABLE 2
Defect Parameters $[V]^\circ$ and $[I]^\circ$ Obtained by Nonlinear Fittings of the Experimental Data for $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ at 1000°C to Eq. [22]

| x | $[V]^\circ$ | $[I]^\circ$ | δ^* |
|----------------|------------------|---------------------------------|-----------------------|
| 0 ^a | 105 | $2 \times 10 \times 10^{-11}$ | |
| 0.15 | 23.5 ± 0.4^b | $(2.5 \pm 0.6) \times 10^{-11}$ | 1.80×10^{-4} |
| 0.24 | 5.50 ± 0.15 | $(1.5 \pm 0.3) \times 10^{-9}$ | 2.00×10^{-4} |
| 0.29 | 0.28 ± 0.02 | $(1.9 \pm 0.3) \times 10^{-8}$ | 1.34×10^{-3} |

^aData from Dieckmann (11).

^bAll of the error values listed are fitting errors.

To explore the composition (x) dependencies of $[\text{V}]^\circ$ and $[\text{I}]^\circ$, the values for the equilibrium constants $K_{\text{CD}}^{\text{Fe}}$, $K_{\text{CD}}^{\text{Mg}}$, and K_{V} , for the distribution coefficient α , and for the activity of Fe_3O_4 in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ $a_{\text{Fe}_3\text{O}_4}$ are required. First, we will look into the composition dependence of $[\text{V}]^\circ$.

Let us assume $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ to be an ideal solution of Fe_3O_4 and MgFe_2O_4 . If this assumption is valid, then the activity of Fe_3O_4 in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$, $a_{\text{Fe}_3\text{O}_4}$, equals $1 - 3x$, and $K_{\text{CD}}^{\text{Fe}}$, K_{V} , and α are independent of the composition (x). Wu and Mason (19) measured the thermoelectric power of stoichiometric magnetite and calculated $K_{\text{CD}}^{\text{Fe}}$ as

$$\ln K_{\text{CD}}^{\text{Fe}} = \frac{2770}{T} - 1.61. \quad [36]$$

By a simple calculation, the distribution coefficient α for stoichiometric magnetite (Fe_3O_4) is related with $K_{\text{CD}}^{\text{Fe}}$ as

$$\alpha = \left[\left(\frac{1}{16} + \frac{1}{2K_{\text{CD}}^{\text{Fe}}} \right)^{1/2} \right] - \frac{1}{4}. \quad [37]$$

Furthermore, Dieckmann (11) has determined K_{V} for $\text{Fe}_{3-\delta}\text{O}_4$ from the temperature dependence of the nonstoichiometry, which is expressed as

$$\log K_{\text{V}} = \frac{10360}{T} - 5.53. \quad [38]$$

Now we have all the available data to calculate $[\text{V}]^\circ$ as a function of x in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ spinel. Using the data, we calculated $[\text{V}]^\circ$ as a function of x , which is shown in Fig. 3 as a solid line. There exists a rather good agreement between the calculated and experimental values, which means the experimental results are well explained by the ideal solution model.

Lu and Dieckmann (21) have performed a similar analysis on the dependence of $[\text{V}]^\circ$ and $[\text{I}]^\circ$ on the Me content x in $(\text{Me}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ ($Me = \text{Co}, \text{Mn}$) with the nonstoichiometry data which had been measured very precisely by them via thermogravimetry (10–14). They also assumed $(\text{Me}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ to be an ideal solution of $\text{Me}_{3-\delta}\text{O}_4$ and $\text{Fe}_{3-\delta}\text{O}_4$ and used the reaction constants for $\text{Fe}_{3-\delta}\text{O}_4$ to calculate the composition dependence of $[\text{V}]^\circ$ and $[\text{I}]^\circ$ in $(\text{Me}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$. In their analysis, however, the activity of Fe_3O_4 , $a_{\text{Fe}_3\text{O}_4}$, was not taken into account; in other words, $a_{\text{Fe}_3\text{O}_4}$ was set as 1. According to them, when Me exists only as Me^{2+} in the spinel structure, the defect parameter for the formation of cation vacancies, $[\text{V}]^\circ$, is expressed as

$$[\text{V}]^\circ = \frac{(1 - 3x)^3}{4} K_{\text{V}}, \quad [39]$$

where K_{V} has the same meaning as in Eq. [34]. The calculated values based on Eq. [39] are also shown in Fig. 3 as a dashed line. As can be seen in Fig. 3, the two calculated values (the solid line and the dashed line) show slight disagreement. The main differences between Eqs. [34] and [39] are the terms $(1 + \alpha K_{\text{CD}}^{\text{Fe}})^2 / (1 + \alpha)^3$ and $a_{\text{Fe}_3\text{O}_4}^{-1/3}$. Of the two terms, $(1 + \alpha K_{\text{CD}}^{\text{Fe}})^2 / (1 + \alpha)^3$, when it is calculated with Eqs. [37] and [38], is almost 1. The disagreement, therefore, mainly comes from $a_{\text{Fe}_3\text{O}_4}^{-1/3}$, which should have been considered in ref 21 for a more accurate analysis.

Up to now, the ideal solution model has been adopted to explain the composition dependence of $[\text{V}]^\circ$ in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ and it has been found to explain the experimental results quite well. In some literature, however, nonideality has been reported (22, 23). Trestman-Matts *et al.* (23) measured the thermoelectric power for the system Fe_3O_4 – MgFe_2O_4 to determine cation distributions. According to them, $K_{\text{CD}}^{\text{Fe}}$, and subsequently α , are a function of cationic composition, which have been assumed to be constant independent of the composition in the ideal solution model. Furthermore, they calculated the activity of Fe_3O_4 , $a_{\text{Fe}_3\text{O}_4}$, in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ and found that there is small positive deviation from ideality in the thermodynamic activity; i.e., $a_{\text{Fe}_3\text{O}_4} \neq 1 - 3x$. With the cationic distribution data and the activity of Fe_3O_4 reported by Trestman-Matts *et al.*, $[\text{V}]^\circ$ was calculated using Eq. [34], and the calculated results are demonstrated in Fig. 3 as a dotted line. Compared with the ideal solution model, the calculated values based on the data in ref 22 are a little overestimated.

As far as $[\text{I}]^\circ$ is concerned, no available data for the reaction constants K_i [$i = \text{I}(1), \text{I}(2), \text{and I}(3)$] and $K_{\text{CD}}^{\text{Mg}}$ in spinel ferrites have been reported. Furthermore, the interstitial-dominant regime (at low a_{O_2} , where $\delta < 0$) is not so clear as the cation vacancy-predominant regime (at high a_{O_2} , where $\delta > 0$) as demonstrated in Fig. 2, because only small concentrations of cation interstitials occur. This causes a relatively large error in $[\text{I}]^\circ$ compared with $[\text{V}]^\circ$ (Table 2). For magnetite, Dieckmann (11) failed to deconvolute $K_{\text{I}(1)}$ and $K_{\text{I}(2)}$ from $[\text{I}]^\circ$ and he concluded that it would only be possible on the basis of spectroscopic data or of extremely precise δ measurements which are practically not possible to perform. By this coulometric titration technique, it is also very difficult to get accurate values of $[\text{I}]^\circ$ in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ spinel by fitting of the experimental values of δ and to analyze the composition dependence of $[\text{I}]^\circ$. For this reason, a thorough discussion of the composition dependence of $[\text{I}]^\circ$ will not be done in this article. Instead, a simple comparison will be done between the experimental data and the analysis done by Lu and Dieckmann (21). According to Lu and Dieckmann, $[\text{I}]^\circ$ is expressed for $(\text{Me}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$, in which Me is present as Me^{2+} only, as

$$[\text{I}]^\circ = \frac{1}{(1 - 3x)^3} [\text{I}]_{\text{Fe}_3\text{O}_4}^\circ, \quad [40]$$

where $[I]_{\text{Fe}_3\text{O}_4}^\circ$ is the defect parameter for the formation of interstitial cations in magnetite, and the calculated values are shown as a dashed line in Fig. 4. The experimental values are in rather good agreement with the calculated values except for $x = 0.15$.

4. CONCLUSIONS

The nonstoichiometry (δ) of $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ has been measured as a function of oxygen activity (a_{O_2}) for different Mg contents (x) at 1000°C via coulometric titration. The nonstoichiometry isotherms vary sine-hyperbolically with $\log a_{\text{O}_2}$ and shift toward higher oxygen activity as Mg content increases. The oxygen activity dependence of δ is well explained in terms of Frenkel disorder: cation vacancies are predominant at high a_{O_2} and interstitial cations at low a_{O_2} . Absolute values of the nonstoichiometry for each composition at 1000°C were determined by fitting experimental data to the equation generally known for spinel oxides and may best be expressed as follows:

$$\delta = (23.5 \pm 0.4)a_{\text{O}_2}^{2/3} - (2.5 \pm 0.6) \times 10^{-11} a_{\text{O}_2}^{-2/3}$$

for $x = 0.15$

$$\delta = (6.0 \pm 0.1)a_{\text{O}_2}^{2/3} - (1.5 \pm 0.3) \times 10^{-9} a_{\text{O}_2}^{-2/3}$$

for $x = 0.24$

$$\delta = (0.28 \pm 0.02)a_{\text{O}_2}^{2/3} - (1.9 \pm 0.3) \times 10^{-8} a_{\text{O}_2}^{-2/3}$$

for $x = 0.29$

As can be seen in these equations, the defect parameters $[V]^\circ$ and $[I]^\circ$ change by 2–4 orders of magnitude with Mg content (x). In terms of point defect thermodynamics, the variation of $[V]^\circ$ with x was calculated with the assumptions that $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ is an ideal solution of Fe_3O_4 and MgFe_2O_4 : the reaction constants for the formation of cation vacancies and iron ion distribution in magnetite are the same in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$, and the activity of Fe_3O_4 in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ is $1 - 3x$. The experimental and calculated data were in good agreement, which means that the assumptions are valid. Because of the lack of the available data on the reaction constants for the formation of interstitial cations, a thorough analysis could not be carried out for $[I]^\circ$.

Qualitatively, the appreciable changes of $[V]^\circ$ and $[I]^\circ$ with Mg content are attributed to the fact that magnesium ions exist only as fixed-valent Mg^{2+} species in $(\text{Mg}_x\text{Fe}_{1-x})_{3-\delta}\text{O}_4$ and hence increasing amount of Mg reduces the oxidation capacity of the spinel ferrite.

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