Magnetic properties of the magnetite-spinel solid solution: Curie temperatures, magnetic susceptibilities, and cation ordering

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ABSTRACT

Curie temperatures ($T_C$) of the $(\text{Fe}_2\text{O}_4)_x(\text{MgAl}_2\text{O}_4)_{1-x}$ solid solution have been determined from measurements of magnetic susceptibility ($\chi$) vs. temperature. The trend in $T_C$ vs. composition extrapolates to 0 K at $x = 0.27$. This behavior is rationalized in terms of the trend in cation distribution vs. composition suggested by Nell and Wood (1989), with Fe occurring predominantly on tetrahedral sites for $x < 0.27$.

High-temperature $\chi$-$T$ curves are nonreversible because of the processes of cation ordering and exsolution, which occur in the temperature range 400–650 °C. The Curie temperature of single-phase material is shown to be sensitive to the state of nonconvergent cation order, with a difference in $T_C$ of more than 70°C being observed between a sample quenched from 1400 °C and the same sample after heating to 650 °C. This interaction between magnetic and chemical ordering leads to thermal hysteresis behavior such that $T_C$ measured during heating experiments is approximately 10 °C higher than that measured during cooling. The hysteresis is due to a reversible difference in the state of cation order during heating and cooling caused by a kinetic lag in the cation-ordering behavior.

Samples with compositions in the range $0.55 < x < 0.7$ undergo exsolution to a mixture of ferrimagnetic and paramagnetic phases after heating to 650 °C. Room-temperature hysteresis loops of the starting material and the high-temperature experiment products are compared. All starting materials are multidomain with coercivities $H_c < 1.26$ mT and $M_r/M_s < 0.051$. Samples that exsolved during the experiments have coercivities up to 20 mT and $M_r/M_s$ up to 0.36. This change in hysteresis properties is caused by grain subdivision during exsolution and implies a transition in the magnetic domain state from multi- to single-domain.

INTRODUCTION

The magnetic properties of solid solutions are sensitive to the processes of oxidation, cation ordering, and subsolidus exsolution. Both in nature and in laboratory experiments these processes can occur concurrently, resulting in complex microstructures and a magnetic signature that is characteristic of the mineral processes that occurred. In rock magnetism it is the magnetic properties of minerals responsible for natural remanent magnetization that are of interest. Studying the interaction between cation ordering, exsolution, and magnetism helps us to understand the acquisition, alteration, and stability of natural magnetizations over geological time. In mineral physics magnetic properties of complex solid solutions provide a sensitive probe for the study of intrinsic mineral properties and kinetic processes.

This paper is the second in a series detailing the magnetic properties of the magnetite-spinel solid solution $(\text{Fe}_2\text{O}_4)_x(\text{MgAl}_2\text{O}_4)_{1-x}$ (Harrison and Putnis 1995). The general aims of the project are to investigate the interaction between magnetism and the processes of subsolidus exsolution and nonconvergent cation ordering. Exsolution microstructures are often responsible for high coercivities in naturally occurring magnetic minerals such as the titanomagnetite solid solution (Tucker and O'Reilly 1980; Shive and Butler 1969; Price 1980; Evans and Wayman 1974). Although titanomagnetite is the most important cause of remanence in rocks, it is not possible to study the development of subsolidus exsolution microstructures in synthetic titanomagnetite because of the low temperatures required to produce spinodal decomposition. However, the general principles of the relationship between magnetism, chemical composition, microstructure, and cation ordering can be studied in related systems. The magnetite-spinel solid solution is a more suitable system in that the chemical solvus has a consolute point near 1000 °C (Mattioli and Wood 1988) and there are extensive changes in the degree of nonconvergent cation order as a function of temperature (Nell and Wood 1989; Nell et al. 1989).

In a previous paper (Harrison and Putnis 1995) we detailed low-temperature hysteresis properties of the homogeneous solid solution. The trend in saturation magnetization vs. composition can be understood in terms of the distribution of Fe atoms between tetrahedral (A) and...
octahedral (B) sites, the net magnetization being the difference between the A and B sublattice magnetizations (Brown et al. 1993). The results showed that for $x > 0.3$ the solid solution is ferrimagnetic with the B sublattice magnetization greater than the A sublattice magnetization. For $x < 0.3$ the solid solution is ferrimagnetic with the A sublattice magnetization greater than the B sublattice magnetization. The $x = 0.3$ composition is a compensation point corresponding to an antiferromagnetic spin structure with A and B sublattice magnetizations equal. The compensation point is associated with a pronounced peak in the coercivity of 700 mT, which is related to the presence of fine-scale heterogeneities in composition and degree of cation order.

There is a discrepancy between the position of the compensation point reported by Harrison and Putnis (1995) for samples quenched from 1400 °C and the position predicted by the Nell and Wood (1989) model for an equilibration temperature of 1400 °C. This discrepancy is due to cation reordering, which occurs when quenching from high temperatures. The position of the compensation point in quenched samples is a function of the kinetics of cation reordering and cannot be predicted directly from equilibrium models. The observed compensation point at $x = 0.3$ is consistent with Nell and Wood (1989) if a kinetic closure temperature of 1200 °C is assumed.

Other experimental work on this solid solution includes measurements of lattice parameters, activities, Curie temperatures, room-temperature low-field magnetization, and cation distribution vs. composition (Mattioli et al. 1987; Mattioli and Wood 1988; Nishitani 1981; Nell et al. 1989). This paper presents the results of alternating-field susceptibility measurements on synthetic samples of the magnetite-spinel solid solution, initially quenched from 1400 °C. We demonstrate that susceptibility measurements can be used to monitor changes in the Curie temperature associated with both compositional changes and changes in the degree of cation order.

Theoretical background

Crystal structure and cation distributions of magnetic spinels

Magnetite (Fe$^{2+}$Fe$^{3+}$O$_4$) and spinel (MgAl$_2$O$_4$) are both cubic spinels with space-group Fd3m and eight formula units per unit cell. The 32 O atoms per unit cell are in an approximately close-packed arrangement with cations occupying eight tetrahedral (A) sites and 16 edge-sharing octahedral (B) sites. At room temperature MgAl$_2$O$_4$ has the normal spinel cation distribution with 8 Mg atoms occupying A sites and 16 Al atoms on B sites. Fe$_2$O$_3$ has the inverse spinel cation distribution at room temperature with 8 Fe$^{3+}$ ions occupying A sites and 8 Fe$^{3+}$ + 8 Fe$^{2+}$ ions occupying B sites. At elevated temperatures cations become progressively disordered over both A and B sites (Peterson et al. 1991; Wood et al. 1986; Carpenter and Salje 1994; Trestman-Matts et al. 1983). The process of nonconvergent cation ordering is a common phenomenon in spinels and has been discussed in detail in the literature (Carpenter et al. 1994; O'Neill and Navrotsky 1984; Nell and Wood 1989; Sack and Ghiorso 1991; Stephenson 1969). The term nonconvergent means that there is no symmetry change involved in ordering cations between A and B sites.

The distribution of cations between octahedral and tetrahedral sites for the (Fe$_2$O$_3$)(MgAl$_2$O$_4$)$_x$ solid solution has been experimentally determined at 1000 °C (Nell et al. 1989), and a thermodynamic model describing the temperature dependence of cation distribution has been proposed (Nell and Wood 1989). The solid solution has a solvus at temperatures below 1000 °C (Mattioli and Wood 1988). Exsolution occurs within the quaternary system Fe$_2$O$_3$-FeAl$_2$O$_3$-MgFe$_2$O$_4$-MgAl$_2$O$_4$, but tie-lines joining Fe-rich and Fe-poor phases remain close to the binary join Fe$_2$O$_3$-MgAl$_2$O$_4$ (Lehmann and Roux 1986).

The spin-only magnetic moments associated with Fe$^{2+}$ and Fe$^{3+}$ ions are 4 and 5 $\mu_B$, respectively ($1 \mu_B = 9.27 \times 10^{-24}$ Am$^2$). Below the Curie temperature ($T_c$) of a magnetic spinel Fe atoms on B sites have their moments aligned parallel to each other but antiparallel to those on A sites. The net saturation magnetization is given by the difference between the octahedral and tetrahedral sublattice magnetizations (Stephenson 1972). If the sublattice magnetizations are unequal then the net magnetization is nonzero and the material is ferrimagnetic. For example, magnetite with the inverse cation distribution has a net moment of 4 $\mu_B$. If the sublattice magnetizations are equal, then the net magnetization is zero and the material is antiferromagnetic.

Temperature dependence of magnetic susceptibility ($\chi$)

Here we present a brief outline of the theory relevant to the interpretation of susceptibility-temperature curves. For a detailed description of rock and mineral magnetism the reader is referred to O'Reilly (1984). Magnetic susceptibility ($\chi$) describes the response of a material to an applied magnetic field. The magnetization per unit mass $M$ (Am$^2$/kg) acquired by a material in a field $H$ (A/m) defines susceptibility using the equation $\chi = M/H$ (m$^3$/kg). If $H$ is an alternating field, then the response of the material may not be in phase with the field. In this case $\chi$ has an imaginary component and hence $\chi = \chi' + i\chi''$. In the majority of cases only the real component of susceptibility is considered and this is denoted $\chi$ in what follows.

Below $T_c$ the temperature dependence of $\chi$ may be understood in terms of the relationship $\chi(T) \propto M_s(T)/K(T)$, where $M_s$ is the spontaneous magnetization and $K$ is the magnetic anisotropy. Both $M_s$ and $K$ decrease with increasing temperature. At low temperatures these two effects cancel and $\chi$ remains roughly constant. As $T \to T_c$ both $M_s$ and $K \to 0$. If $K$ decreases at a faster rate than $M_s$, then thermal fluctuations at $T$ close to $T_c$ lead to enhanced susceptibility (Dunlop 1974). This is known as the Hopkinson effect. Above $T_c$, $M_s$ is zero and the material displays only paramagnetic susceptibility, which falls to zero rapidly as $\chi \propto 1/(T - T_c)$. This sharp decrease
in \( x \) provides an accurate determination of \( T_c \) and hence an insight into changes in composition and degree of cation order that occur during the measurements.

**Experimental and Analytical Procedures**

**Synthesis**

The starting materials for all syntheses were 99.9% pure \( \text{Fe}_2\text{O}_3 \) and \( \text{MgO} \) and \( \text{Al}_2\text{O}_3 \) prepared by firing \( \text{AlCl}_3 \cdot 6\text{H}_2\text{O} \) for 2 h at 400 °C, 5 h at 700 °C, and 1 h at 900 °C. The oxides were weighed in stoichiometric proportions, ground together, and pressed into pellets. The pellets were then fired at 1400 °C for periods between 3 and 5 d in a vertical-tube gas-mixing furnace under controlled \( f\text{O}_2 \) (Nafziger et al. 1971). A value of \( \log f\text{O}_2 = -4.2 \) was chosen to yield stoichiometry in the magnetite component of the solid solution (Dieckmann 1982). Samples were quenched from 1400 °C by dropping directly from the furnace into water. Starting materials were characterized by X-ray diffraction, electron microprobe analysis, and SEM and TEM techniques. A detailed description of the synthesis technique and sample characterization is given by Harrison and Putnis (1995). All samples quenched from 1400 °C are single phase.

**Magnetic measurements**

Measurements of high-temperature alternating-field susceptibility were made in air using a KAPPA susceptibility bridge. Individual pellets of synthetic material with masses ranging from 9 to 46 mg were placed in an open test tube inside a water-cooled furnace. Measurements of susceptibility were made every 15–20 s while the temperature was ramped from room temperature to 650 °C and back to room temperature at a rate of 11 °C/min. Temperatures were measured with a Pt-Rh thermocouple placed directly next to the sample. The total time for each experiment is approximately 1.9 h. High-temperature experiments were performed on samples with \( x \approx 0.43 \), i.e., those with Curie temperatures near or above room temperature.

Measurements of low-temperature alternating-field susceptibility were made with a Lakeshore susceptometer. Several pellets of material (total sample mass between 81 and 126 mg) were packed in a gelatin capsule and placed in a sample chamber with a helium atmosphere. Temperature was controlled with a refrigerator unit. Measurements of both real and imaginary components of magnetic susceptibility were made in the temperature range 20–300 K (−253 to 27 °C). Only samples with Curie temperatures below room temperature were measured using the Lakeshore susceptometer.

Low-field DC magnetic behavior of samples SP9 and SP5 (see Table 1) was measured with a Quantum Design MPMS1 SQUID magnetometer. The samples were cooled to 20 K in zero field. For SP9, magnetization in a constant field of 5 mT was measured as a function of temperature in 10 K steps to 300 K. The temperature was equilibrated at each step prior to measurement. This measurement provided the only determination of \( T_c \) for sample SP9. For SP5 magnetization was measured in temperature-sweep mode with a heating rate of 5 °C/min. Susceptibility and low-field magnetization rapidly fall to zero above \( T_c \). Values of \( T_c \) were determined from the data sets by linearly extrapolating the \( x-T \) curves to the \( x = 0 \) axis. Extrapolation was performed by fitting a straight line by least squares to the data points immediately surrounding the point of inflection. This procedure was performed for both heating and cooling parts of the \( x-T \) curves.

Room-temperature hysteresis loops of starting materials with \( x \approx 0.5 \) and the products of high-temperature experiments displaying nonreversible \( x-T \) curves were measured using a vibrating sample magnetometer. All samples saturated in the maximum applied field of 800 mT. Values of the room-temperature saturation magnetization \( (M_s) \) were determined by linearly extrapolating the high-field portion of the loop to the \( H = 0 \) axis. The value of the saturation remanent magnetization \( (M_r) \) and coercivity \( (H_c) \) were taken directly from the hysteresis loops.

### Table 1. Curie temperatures of synthetic spinels

<table>
<thead>
<tr>
<th>Sample</th>
<th>( x^* )</th>
<th>Heating</th>
<th>Cooling</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP15</td>
<td>1</td>
<td>584.4</td>
<td>583.9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP18</td>
<td>0.9</td>
<td>517</td>
<td>517.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP14</td>
<td>0.81</td>
<td>470.7</td>
<td>488</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP17</td>
<td>0.71</td>
<td>355.3</td>
<td>515.4**</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP13</td>
<td>0.609</td>
<td>283.2</td>
<td>518.9**</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP20</td>
<td>0.55</td>
<td>170.6</td>
<td>517.8**</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP12</td>
<td>0.51</td>
<td>107.6</td>
<td>175.7, 502.6†</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP9</td>
<td>0.43</td>
<td>—</td>
<td>467.1**</td>
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<tr>
<td>SP10</td>
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<td>—</td>
<td>—</td>
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<tr>
<td>SP8</td>
<td>0.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Mole-fraction magnetite defined by ideal formula unit \( (\text{Fe}_3\text{O}_4)_{(\text{MgAl}_2\text{O}_4)}\... \)

** Susceptibility remains finite up to \(-525°C\).

† Sample remains two phase, both Curie temperatures given.
Figure 1. (a–f) Magnetic susceptibility per unit mass, $\chi$ (m$^3$/kg), vs. temperature (°C) for the (Fe$_3$O$_4$)$_x$((MgAl)$_2$O$_4$)$_{1-x}$ solid solution. Solid lines are for the first experiment, dashed lines are for the second experiment. Arrows indicate the directions of heating and cooling. (g) Magnetization in a field of 5 mT, $M$ (Am$^2$/kg), vs. temperature (°C) for sample SP9.
RESULTS AND DISCUSSION

Initial Curie temperatures of the homogeneous solid solution

$T_c$ data for all heating and cooling experiments are presented in Table 1. Selected $\chi$-$T$ curves and the low-temperature DC magnetization experiment for SP9 are presented in Figure 1. Figure 1a shows the behavior in the pure Fe$_3$O$_4$ end-member. A sharp decrease in $\chi$ occurs at the Curie temperature $T_c = 584.4$ °C (see Table 1). This value corresponds to the magnetic transition in stoichiometric magnetite (Readman and O'Reilly 1972), and hence we suggest that although oxidation at the rim of the sample pellet cannot be ruled out, the bulk of the sample remains unoxidized during the timescale of the experiments. This view is supported by the reversible nature of the magnetic transition after heating to 650 °C.

Figures 1b–1g show the behavior for selected intermediate members of the solid solution. If two experiments were performed on the same sample, the first experiment is shown as a solid curve and the second experiment as a dashed curve. The behavior of these samples is complicated because of the processes of cation ordering and exsolution that occur on heating. The rate of these two processes is slow below 400 °C, and hence the decrease in $\chi$ during the first heating experiment is associated with the magnetic transition in homogeneous material quenched from 1400 °C. Nonreversible changes in cation order and composition occur on heating above 400 °C resulting in complex $\chi$-$T$ behavior. These curves are discussed in detail in later sections.

Curie temperatures vs. composition for the first heating experiments are listed in Table 1 and are shown in Figure 2 along with the $T_c$ data of Nishitani (1981). Samples with $x < 0.3$ display only paramagnetic susceptibility at temperatures above 20 K (Fig. 1f). These samples exhibit hysteresis at 4.4 K (Harrison and Putnis 1995), and therefore we conclude that $T_c$ for $x < 0.3$ lies in the temperature range 4.4–20 K as indicated by the limits in Figure 2. There is a clear trend in the variation of $T_c$ with composition for $x > 0.3$. The solid line is a least-squares fit to the $T_c$-$x$ data ($x > 0.3$) with a third-order polynomial function $T_c (°C) = -853 + 2410x - 970x^2$. This function extrapolates to 0 K at $x = 0.27$. Nishitani (1981) measured $T_c$ on samples of the solid solution annealed and quenched from 1200 °C. Differences in the trend of $T_c$ vs. composition between the present work and that of Nishitani (1981) may reflect either differences in nonstoichiometry in the samples or differences in cation order due to quenching from 1200 °C as opposed to 1400 °C.

To interpret the variation of Curie temperature with composition (Fig. 2) we must first understand the nature of the interactions that are responsible for magnetic ordering. A detailed discussion of the atomic basis for magnetic ordering in oxide spinels is given by O'Reilly (1984). Fe$^{2+}$ and Fe$^{3+}$ ions have net magnetic moments because of the presence of unpaired d-orbital electrons. When the electron orbitals from neighboring atoms overlap, the magnetic moments interact to cause the energy of the moments to depend upon their relative orientation. This exchange interaction is described by the equation $E_{ex} = -2J^2\sin^2 \theta$, where $E_{ex}$ is the exchange energy, $J$ is the exchange constant for two identical atoms, $S$ is proportional to the magnetic moment of the atoms, and $\theta$ is the angle between the moments. If $J > 0$, then the moments align parallel to one another (ferromagnetic ordering), and if $J < 0$, then the moments align antiparallel (antiferromagnetic ordering). In magnetic spinels there is little direct overlap of Fe ion orbitals, but superexchange interactions do occur by means of O atoms. Fe atoms occur on both A and B sites, and hence we consider three superexchange constants: $J_{AA}$, $J_{AB}$, and $J_{BB}$. Magnetic ordering in Fe-rich spinels is dominated by the negative $J_{AB}$ interaction, which leads to the ferrimagnetic behavior discussed earlier.

The strength of the superexchange interaction determines the Curie temperature. The decrease in $T_c$ with increasing mole-fraction MgAl$_2$O$_4$ is due to dilution of the $J_{AB}$ interaction by nonmagnetic Mg and Al atoms. Similar behavior is seen in the titanomagnetite solid solution because of the dilution of Fe$_3$O$_4$ by nonmagnetic Ti atoms (Stephenson 1972). At $x = 0.3$ there is an abrupt change in the $T_c$-$x$ trend, which implies an abrupt change in the strength of the superexchange interaction. This composition has been previously identified with a compensation point in the trend of saturation magnetization vs. composition (Harrison and Putnis 1995). Assuming a kinetic closure temperature of 1200 °C for samples quenched from 1400 °C, the cation distribution suggested...
by Nell and Wood (1989) has Fe located predominantly on B sites for $x > 0.3$, leading to ferrimagnetic ordering. The compensation point at $x \approx 0.3$ has both magnetic sublattices equal and hence no net magnetization. For $x < 0.3$, Fe is distributed predominantly on A sites, causing a small increase in the net magnetization. The strength of the $J_{AA}$ interaction is very much less than that of the $J_{AB}$ interaction. The abrupt change in $T_c$ vs. $x$ at $x \approx 0.3$ is entirely consistent with the change in Fe distribution suggested by Nell and Wood (1989) and is caused by Fe atoms being located predominantly on tetrahedral sites, hence reducing the strength of the superexchange interaction.

Nonreversibility of high-temperature $\chi$-$T$ curves: Exsolution

The nonreversible behavior of the high-temperature $\chi$-$T$ curves can be understood in terms of the changes in composition and degree of cation order that occur at temperatures greater than approximately 400 °C. In Figure 1b (SP13 $x = 0.61$) the first decrease in $\chi$ at 283 °C is associated with $T_c$ for the homogeneous solid solution. The cooling curve, however, shows a single magnetic transition with $T_c = 519$ °C. Samples SP17 ($x = 0.71$) and SP20 ($x = 0.55$) show similar behavior (Table 1). The increase in $T_c$ observed in these samples after heating to 650 °C is caused by subsolvus exsolution, which results in an intergrowth of Fe-rich and Fe-poor phases. Sample SP20 was investigated by both XRD and TEM techniques. The microstructure in this sample after a single high-temperature susceptibility experiment is shown in Figure 3a and consists of intersecting lamellae parallel to $\{100\}$. A comparison of the 440 XRD peak profile for sample SP20 before and after the high-temperature experiment is shown in Figure 3b. The exsolved sample consists of three spinel phases corresponding to an Fe-rich phase, an Fe-poor phase, and the original bulk phase. If we assume that exsolution occurs close to the $(\text{Fe}_3\text{O}_4)_{x}(\text{MgAl}_2\text{O}_4)_{1-x}$ binary join, then the Fe-rich phase with $T_c = 519$ °C corresponds to a composition $x \approx 0.89$ (Fig. 2). $T_c$ for the Fe-poor phase is below room temperature.

Further demonstration of exsolution in these samples is provided by a comparison of room-temperature hysteresis properties before and after the high-temperature experiments. Hysteresis loops for sample SP13 are presented in Figure 4, and hysteresis parameters are listed in Table 2. All starting materials show multidomain behavior with $H_e \leq 1.26$ mT and $M_r/M_s \leq 0.051$. After heating, samples SP13, SP17, and SP20 display hysteresis properties similar to those of randomly oriented single-domain grains (Stoner and Wohlfarth 1948). $H_e$ is in the range 13.3–19.9 mT, and $M_r/M_s$ is in the range 0.28–0.36. The ideal value of the ratio $M_r/M_s$ for noninteracting single-domain grains is 0.5. The lower value observed here is probably caused by magnetostatic interaction between grains (Davis and Evans 1976). The pronounced Hopkinson susceptibility peak observed at $T_c$ for the exsolved phase is further evidence of single-domain behavior (Dunlop 1974). The transition from multi- to single-domain behavior in response to subsolvus exsolution was recognized earlier in natural titanomagnetite (Evans and Wayman 1974; Price 1980) and...
is caused by subdivision of large multidomain grains by \{100\} lamellae of a paramagnetic phase. This results in a cubic array of interacting magnetic grains with diameters below the threshold size for single-domain behavior. Estimates of the value of the multidomain to single-domain threshold size vary but are on the order of 0.05 \(\mu\)m (Dunlop 1973). However, this value may vary significantly if there is strong interaction between magnetic particles. The role of exsolution in producing technological materials with high coercivities has been well studied (Zijlstra 1982; Livingston 1981).

**Nonreversibility of high-temperature \(x-T\) curves:**

**Cation ordering**

The behavior of sample SP12 \((x = 0.51)\) is shown in Figure 1c. \(T_c\) for the homogeneous phase is initially 107.6 °C. After heating to 650 °C partial exsolution of an Fe-rich phase occurs with \(T_c = 502.6 °C\). Exsolution proceeds to a much lesser extent in this sample than for samples with \(x \geq 0.55\), and there is a strong magnetic signal from the remaining bulk phase. \(T_c\) for the remaining bulk phase measured during cooling is 175.7 °C. There is a difference of approximately 70 °C between \(T_c\) for the bulk phase measured during the first heating experiment and that measured after the sample was heated to 650 °C. Given that partial exsolution of an Fe-rich phase has occurred the composition of the remaining bulk phase is poorer in Fe than before. This should lead to a decrease in Curie temperature rather than the observed increase. There are no significant increases in \(H_c\) or \(M_{\chi}/M_s\) after the heating experiments (Table 2), implying that the bulk of the sample remains homogeneous. Hence, the increase in \(T_c\) is not produced by the change in the composition of the bulk phase. It is unlikely that the observed increase in \(T_c\) is caused by oxidation of the sample because, as discussed earlier, the \(x-T\) curve for pure Fe$_3$O$_4$ is reversible (Fig. 1a) and shows no evidence that bulk oxidation occurred during the experiments.

We conclude that the increase in \(T_c\) is due to a large difference in the state of nonconvergent cation order between the sample that is initially quenched from 1400 °C and the same sample subsequently heated to 650 °C. This interpretation requires careful consideration of the cation ordering and kinetic behavior of quenched samples. Our framework for the description of nonconvergent cation ordering in spinels follows that of Carpenter et al. (1994). We describe the state of cation order in terms of an order parameter \(Q\) that takes a value of \(Q = 0\) for complete cation disorder between A and B sites and a value of \(Q = 1\) for complete order at \(T = 0\) K. A sample annealed at 1400 °C is relatively disordered and has a low value of \(Q\). Significant cation reordering can occur during quenching from high temperatures (Wood et al. 1986; Milliard et al. 1992). It is found that spinels annealed at temperatures >900–1000 °C reorder during the quench to yield a constant value of \(Q\) equivalent to the equilibrium value.

**Table 2.** Hysteresis properties of synthetic spinels before and after high-\(T\) experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>(x^*)</th>
<th>(M_s (Am^2/kg))</th>
<th>(H_c (mT))</th>
<th>(M_{\chi}/M_s)</th>
<th>(M_s (Am^2/kg))</th>
<th>(H_c (mT))</th>
<th>(M_{\chi}/M_s)</th>
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<tbody>
<tr>
<td>SP15</td>
<td>1</td>
<td>94.4</td>
<td>0.82</td>
<td>0.008</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>SP18</td>
<td>0.9</td>
<td>72.2</td>
<td>0.78</td>
<td>0.009</td>
<td>61.6</td>
<td>2</td>
<td>0.011</td>
</tr>
<tr>
<td>SP14</td>
<td>0.81</td>
<td>56.2</td>
<td>1.22</td>
<td>0.013</td>
<td>49.2</td>
<td>13.33</td>
<td>0.282</td>
</tr>
<tr>
<td>SP17</td>
<td>0.71</td>
<td>38.6</td>
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<td>0.051</td>
<td>40.3</td>
<td>19.86</td>
<td>0.277</td>
</tr>
<tr>
<td>SP13</td>
<td>0.609</td>
<td>29.7</td>
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<td>33.1</td>
<td>16.19</td>
<td>0.364</td>
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<td>SP12</td>
<td>0.51</td>
<td>18.2</td>
<td>0.5</td>
<td>0.021</td>
<td>19.6</td>
<td>1.2</td>
<td>0.057</td>
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<td>0.43</td>
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<td>—</td>
<td>9.64</td>
<td>4.14</td>
<td>0.198</td>
</tr>
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</table>

* Mole-fraction magnetite defined by ideal formula unit (Fe$_3$O$_4$)$_x$(MgAl$_2$O$_4$)$_{1-x}$...
HARRISON AND PUTNIS: MAGNETITE-SPINEL MAGNETIC PROPERTIES

**FIGURE 5.** Schematic variation of nonconvergent cation order parameter, Q (solid lines), vs. temperature, T (°C), during temperature-sweep experiments (heating and cooling rate 10 °C/min). The solid curves are calculated values based on kinetic theory (Carpenter and Salje 1989). Dashed line is the equilibrium variation of Q with T (Carpenter and Salje 1994). Arrows indicate the directions of heating and cooling for first and subsequent experiments. T_r is the cation-distribution relaxation temperature, corresponding to a rapid increase in Q toward the equilibrium value.

at \( T \approx 900 \) °C. The initial value of Q in the susceptibility experiments is therefore lower than the equilibrium value at 650 °C, and there is a thermodynamic driving force for ordering. The kinetic behavior of Fe-rich spinels containing Mg and Al has been studied by Sujata and Mason (1992). Measurements of electrical resistivity on initially disordered material heated at a rate of 20 °C/min display enhanced resistivity at a characteristic relaxation temperature. The relaxation temperature is associated with the onset of rapid cation ordering. After heating above the relaxation temperature, Q may eventually reach its equilibrium value, which is maintained on cooling to room temperature.

For sample SP12 (\( x = 0.51 \)) relaxation of the cation distribution occurs after heating to 650 °C. The difference in Q before and after relaxation yields an increase in at approximately 70 °C, suggesting that there is strong interaction between magnetic and cation ordering in this system. This behavior contrasts with that of the titanomagnetite solid solution in which little variation in \( T_c \) for different degrees of cation order (Moskowitz 1987). The essential difference between the two systems is that the titanomagnetite solid solution contains nonmagnetic Ti atoms exclusively on B sites. The \( J_{AB} \) interaction is insensitive to variations in the distribution of \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) ions between A and B sites. In the magnetite-spinel solid solution Mg and Al atoms disorder between A and B sites, strongly affecting the \( J_{AB} \) interaction and hence \( T_c \).

For many samples with nonreversible \( \chi-T \) curves a second measurement was performed (dashed lines in Fig. 1). Sample SP13 (Fig. 1b) exsolved during the first experiment to yield an array of single-domain magnetic particles with \( T_c \) in the range 519–528 °C. The magnetic transition in this material displayed thermal hysteresis behavior during the second measurement experiment. \( T_c \) measured during heating is 528.3 °C. The value of \( T_c \) measured during cooling is 518.9 °C for experiment 1 and 518 °C for experiment 2. There appears to be a reversible difference between \( T_c \) measured when \( T \) is sweeping up and that measured when \( T \) is sweeping down. This thermal hysteresis behavior is observed in samples SP14, SP17, SP13, SP12, and SP9. The effect is most pronounced in sample SP14 (\( x = 0.81 \)), where the difference between \( T_c \) for heating and cooling is 24.5 °C. Thermal hysteresis is often observed in temperature-sweep experiments when the sample temperature is unable to change at the same rate as the furnace temperature (thermal lag). This is not the case in these experiments because no thermal lag is observed in samples SP15 and SP18. Because hysteresis is reversible the effect is probably the result of a reversible difference in the state of cation order during heating and cooling. The behavior of sample SP12 discussed above suggests that \( T_c \) is higher for larger values of Q (i.e., a more ordered cation distribution), and hence samples displaying hysteresis have \( Q_{\text{coating}} > Q_{\text{coating}} \).

A schematic representation of the changes in Q during heating and cooling at 10 °C/min is shown in Figure 5. This figure is the result of a computer simulation of cation ordering during constant heating- and cooling-rate experiments, using the kinetic theory of Carpenter and Salje (1989) and the thermodynamic description of ordering in MgAl_2O_4 given by Carpenter and Salje (1994). Kinetic changes in Q are defined by the Ginzburg-Landau equation

\[
\frac{dQ}{dt} = -\frac{\gamma \exp(-\Delta G^*/RT)\partial G}{\partial Q}
\]

where \( \gamma \) is a constant and \( \Delta G^* \) is the free energy of activation. \( G \) is the excess free energy due to ordering (relative to the disordered phase) given by

\[
G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{6}cQ^3
\]

where \( h, a, c, \), and \( T_c \) are constants. Substituting Equation 2 into Equation 1 and integrating we obtain

\[
\int_{Q_0}^{Q_f} -\frac{2RT}{\gamma \exp(-\Delta G^*/RT)} \left[-h + a(T - T_c)Q + \frac{1}{6}cQ^2\right] dQ
\]

which may be solved numerically to obtain the behavior during either isothermal annealing or temperature-sweep experiments. Further details of these calculations are given elsewhere. Values for the constants \( h, a, c, \) and \( T_c \) were...
taken from Carpenter and Salje (1994). Measured values for the kinetic constants $\gamma$ and $AG^*$ were not available. An approximate value for $\gamma = 3.84 \times 10^9 s^{-1}$ was derived by fitting the Landau model to the kinetic data of O’Neill (1994) for MgFe$_2$O$_4$. A value of $AG^* = 200 kJ/mol$ was then chosen to yield a relaxation temperature in the range 500–600 °C.

The dashed line in Figure 5 represents the equilibrium variation of $Q$ with $T$. The initial value of $Q$ is lower than equilibrium in material quenched from high temperatures. There is a large thermodynamic driving force for ordering, but below 400 °C $Q$ is prevented from increasing by kinetic constraints. As the temperature is swept above the range 500–600 °C $Q$ rapidly increases toward its equilibrium value. This increase corresponds to the relaxation temperature identified by Sujata and Mason (1992). In a temperature-sweep experiment $Q$ oversteps its equilibrium value because the rate of ordering tends to zero as equilibrium is approached. $Q$ relaxes toward its equilibrium value only as the rate of ordering increases at higher temperatures.

The variation of $Q$ with $T$ during cooling from the high-temperature equilibrium value is indicated by the arrows in Figure 5. As $T$ decreases, the rate of ordering becomes insufficient to allow $Q$ to follow the equilibrium pathway. Below 500 °C $Q$ remains constant and the degree of order is quenched. The large difference between the initial value of $Q$ and the value obtained after heating and cooling through the relaxation temperature is responsible for the increase in $T_c$ observed in sample SP12 (Fig. 1c). If a second experiment is performed on the sample with the new starting value of $Q$ then the hysteresis behavior is revealed. $Q$ begins to increase again when $T$ approaches the relaxation temperature. The equilibrium value of $Q$ is overstepped, and $Q$ eventually relaxes toward equilibrium at high temperatures. All subsequent heating and cooling cycles follow the same $Q$-$T$ path. If $T_c$ coincides with the temperature range where $Q_{\text{heating}} > Q_{\text{cooling}}$ then the magnetic transition also displays thermal hysteresis.

**Implications**

The large variation in $T_c$ with degree of cation order has implications for the calibration of $T_c$ vs. composition (Fig. 2). No conclusions about the composition of an unknown phase can be made from a measurement of $T_c$ unless $Q$ is known and a calibration of $T_c$ vs. $Q$ has been performed. This may be relevant for other spinels in which nonmagnetic ions disorder between A and B sites. In terms of natural magnetic spinels (titanomagnetite), it is generally assumed from crystal-chemical arguments that Ti$^{4+}$ ions exist only on octahedral B sites (Waychunas 1991). However, significant amounts of tetrahedrally coordinated Ti were suggested by Allan et al. (1989) in fully oxidized titanomagnetite (titanomaghemite). Hence, there may be more interaction between cation ordering and magnetism in this material, an effect that should not be ignored when interpreting the magnetic properties of naturally oxidized material. Significant amounts of Mg and Al can occur in titanomagnetite (Nishitani 1981). The presence of these cations on tetrahedral sites may also greatly affect magnetic properties.

This study has demonstrated that exsolution can be easily produced in the magnetite-spinel solid solution and that there is significant interaction between the resultant microstructures and the magnetic hysteresis properties. This has implications for rock magnetism because the microstructures are analogous to those often seen in natural titanomagnetites. A detailed study of subsolvus exsolution in the titanomagnetite solid solution has not been possible because of kinetic constraints. Current knowledge of the magnetic consequences of exsolution is based on a few studies of natural material. This work has studied a synthetic analog system with well-characterized starting material and known thermal histories.

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