

Effect of nonstoichiometry on the magnetic and electrical properties of synthetic single crystal $Fe_{2.4}Ti_{0.6}O_4$

B.J. Wanamaker and Bruce M. Moskowitz

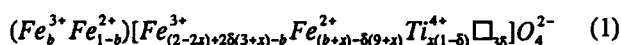
Department of Geology and Geophysics and Institute for Rock Magnetism, University of Minnesota, Minneapolis, Minnesota

Abstract. A single crystal of titanomagnetite $Fe_{2.4}Ti_{0.6}O_4$ (TM60) was synthesized using the floating zone technique. The Curie temperature, saturation magnetization at 5 K, and thermopower were measured for several pieces of the crystal as grown and following high temperature annealing at different oxygen fugacities within the stability field of the TM60. The magnetic and electrical data indicate that long-range ordering in TM60 is a function of nonstoichiometry with higher cation vacancy concentrations producing a more random cation distribution. This effect may explain the differences among cation distribution models for TM developed previously by other workers.

Introduction

The titanomagnetite (TM) solid solution series is an important mineral system in petrology and geophysics. Yet, there is still disagreement about major crystal chemical aspects of this mineral system [e.g., *Lindsley, 1991*]. Questions regarding the extent of nonstoichiometry and its effects on magnetic and thermodynamic properties are largely unexplored. Variations in intrinsic magnetic properties caused by changes in the crystal chemistry of titanomagnetite lead to subtle but complex changes in magnetic domain states, magnetic remanence and its stability. A complete understanding of the magnetic and thermochemical properties of titanomagnetites is essential for a proper interpretation of the paleomagnetic behavior of rocks containing this phase and its oxidized products.

Titanomagnetites ($Fe_{3-x}Ti_xO_4 \equiv (1-x)Fe_3O_4 \cdot xFe_2TiO_4$) form a complete solid solution with the spinel structure above approximately 600°C between the end members magnetite (Fe_3O_4) and ulvöspinel (Fe_2TiO_4), although intermediate compositions may be metastably preserved to lower temperatures by quenching. In addition, titanomagnetites often deviate from ideal 4/3 oxygen/cation stoichiometry by the formation of cation vacancies. At high temperatures (>1000°C), TM can accommodate a finite degree of nonstoichiometry of a few percent within its stability field [*Hauptman, 1974; Aragon and McCallister, 1982*]. A generalized formula for the cation distribution for any nonstoichiometric titanomagnetite can be given in terms of one distribution parameter (b) and two compositional parameters (x, δ) [*O'Reilly, 1984*]



where $()$ and $[\]$ denote A (tetrahedral) and B (octahedral) sites respectively, b is the number of Fe^{3+} ions on A sites, δ is the vacancy concentration, and \square represents a cation

vacancy. The nonstoichiometry parameter δ increases as a function of temperature and oxygen fugacity, theoretically varying between $0 < \delta < (1+x)/(9+x)$ [*Dieckmann, 1982; Aragon and McCallister, 1982*]. Experimental estimates for the maximum degree of nonstoichiometry at 1300°C for TM60-70 are $\delta_{max} \approx 0.01-0.02$ [*Hauptman, 1974; Senderov et al., 1993*]. The oxide spinel model of *O'Neill and Navrotsky [1984]* characterizes the cation distribution for TM at stoichiometry by a distribution coefficient K_{cd} for the exchange reaction $(Fe^{2+})_A + [Fe^{3+}]_B \rightleftharpoons (Fe^{3+})_A + [Fe^{2+}]_B$

$$K_{cd} = \frac{(Fe^{3+})_A [Fe^{2+}]_B}{(Fe^{2+})_A [Fe^{3+}]_B} = \frac{b(x+b)}{(1-b)(2-2x-b)} \quad (2)$$

When $K_{cd} = 0, 1,$ or ∞ , the cation distribution is respectively normal ($b=0$), random ($b=(2-2x)/(3-x)$), or inverse ($b=1, x \leq 0.5; b=2(1-x), x \geq 0.5$).

Although nonstoichiometry and short range ordering have been suggested before as possible explanations for the disparate magnetic results obtained on the TM series by numerous investigators [e.g., *Wechsler et al., 1984; Moskowitz, 1987*], there has yet to be definitive experimental confirmation of these hypotheses. Here we describe a method for synthesizing large single crystals of titanomagnetite and a series of magnetic and electrical measurements that may be used to investigate the effects of variations in point defect stoichiometry on the mineral physics of this material.

Synthesis of Single Crystals

A large (5-9 mm wide and 5 cm long) single crystal of TM60 was grown by the floating zone technique using a halogen lamp image furnace [*Brice, 1986*]. A feed rod of polycrystalline TM60 was synthesized by mixing hematite and titanium oxide powders in the appropriate proportions, cold pressing, and then sintering at approximately 1350°C in a reducing atmosphere for 24 hours.

In the image furnace, the feed rod is successively melted by mechanically translating it through the hot spot produced at the focal point of a gold plated ellipsoidal mirror containing two halogen lamps. Melting is initiated in the feed rod by gradually increasing the lamp power and the single crystal is then grown by recrystallizing the molten part of the feed rod onto a seed as the feed rod moves through the hot zone. The feed rod and seed are enclosed in a gas-tight quartz tube which allows the atmosphere to be controlled during crystal growth. Unlike the method of *Brabers et al. [1984]*, this feature allows us to produce crystals with different "grown in" stoichiometries. We used a gas mix of 10 CO₂:1 CO for TM60. Although the temperature inside the image furnace is not measured, the temperature gradient away from the focal point of the lamps is very steep. The feed rod and

single crystal outside of the melt zone are nevertheless maintained at some elevated temperature due to thermal conduction of the gas in the quartz tube. Examination of the crystal using the optical microscope, scanning electron microscope, electron microprobe, thermomagnetic analysis, and Laue back-reflection camera shows it to be single crystal, single phase, and chemically homogeneous except for a small gradient in Ti/Fe along the growth dimension due to the different melt-solid distribution coefficients of these species. Two slices, one near the top (tc) and one towards the bottom (bc), separated by 4 cm along the growth direction were cut from the crystal. Chemical compositions obtained from electron microprobe analysis are $x=0.61$ and $x=0.58$ for tc and bc, respectively. Fifty separate spot analyses were made across the diameter of the samples and errors in the x -parameter were estimated to be ± 0.01 . The resultant chemical gradient for the crystal of TM60 along the growth direction is ≈ 0.75 mole% Ti/cm and is negligible for the small (1-2 mm thick) samples used in the experiments.

Magnetic Measurements

Curie Temperature

Thermomagnetic curves for pieces from bc (first grown) and tc (last grown) are shown in Figure 1. Magnetization was measured in He gas using a vibrating sample magnetometer. The Curie temperatures (T_c) are 229°C (bc) and 176°C (tc). This variation in T_c is much greater than that expected for the small difference in composition and must be at least partly the result of a difference in the nonstoichiometry of the two samples [Hauptman, 1974]. Because the $f\text{O}_2$ of the 1/10:CO/CO₂ gas mix becomes increasingly more oxidizing relative to the TM60 stability field as temperature decreases, the earlier grown (bottom) part of the crystal may partially re-equilibrate to more oxidizing fugacities as it cools during continued growth of the crystal. Direct evidence of the effect of $f\text{O}_2$ on T_c is provided by subsequently annealing a piece from bc in the same 1/10:CO/CO₂ gas mix at 1300°C for 24 hrs., which caused T_c to decrease to 203°C (sample ba in Fig. 1). Further annealing of ba at 1300°C just inside the

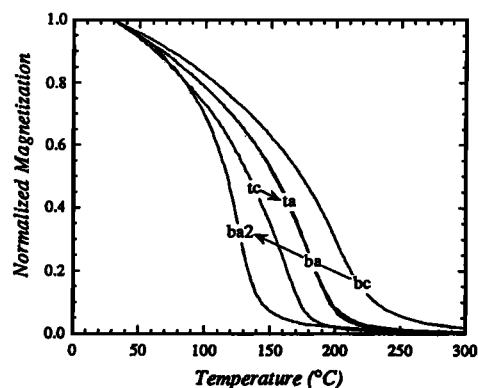


Figure 1. Normalized magnetization versus temperature for pieces from the top (tc, last grown) and bottom (bc, first grown) of a synthetic single crystal of TM60 "as grown." Samples ba and ba2 are pieces from bc subsequently annealed at 1300°C for 24 hrs. at oxygen fugacities of $10^{-2.7}$ and 10^{-4} Pa, respectively; ta is tc subsequently annealed at 1300°C for 24 hrs. at an $f\text{O}_2=10^{-1.3}$ Pa.

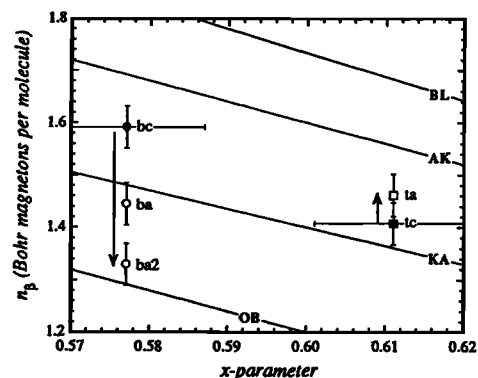


Figure 2. Magnetization (n_B) versus composition (x) for pieces of the synthetic TM60 crystal with different degrees of nonstoichiometry (δ) compared with that predicted by various cation distribution models. Samples bc, ba, ba2, tc, and ta are the same as in Fig. 1. Distribution models are BL (Bleil, 1971); AK (Akimoto, from O'Reilly, 1984); OB (O'Reilly and Banerjee, 1965); KA (Kakol et al., 1991).

reducing boundary of the TM60 stability field ($f\text{O}_2=10^{-4}$ Pa) reduced T_c to 145°C (sample ba2 in Fig. 1). The decrease in T_c correlates with the decrease in δ of the TM60 and is similar to that found by Hauptman [1974]. Oxidizing a piece from tc produced the opposite effect (sample ta in Fig. 1).

Saturation Magnetization

Magnetization measurements were made with a SQUID susceptometer (Quantum Design MPMS1) at 5 K in fields from 3 to 5.5 T, after cooling from 300 K in a 5.5 T field. Samples were thin disks cut parallel to {100} and oriented in the magnetometer so that the magnetic field was applied parallel to this plane, which contains the $\langle 100 \rangle$ easy axis of magnetization for TM60 [e.g., O'Reilly, 1984]. Saturation magnetization was calculated by extrapolating H^2 to infinite field. Although samples were not oriented with respect to their easy axes, the moments at 5.5 T were within 1% of the extrapolated value confirming that saturation was achieved. The moment at 5 K is plotted as a function of x and $f\text{O}_2$ of high temperature annealing in Figure 2 and compared with four cation distribution models for supposedly stoichiometric TM [O'Reilly and Banerjee, 1965; Bleil, 1971; O'Reilly, 1984; Kakol et al., 1991]. The moment n_B decreases with decreasing $f\text{O}_2$ (and δ) during annealing.

The cation distribution problem in titanomagnetite consists of dividing $[(2-2x)+2\delta(3+x)]\text{Fe}^{3+}$, $[(1+x)-\delta(9+x)]\text{Fe}^{2+}$, and $x(1-\delta)\text{Ti}^{4+}$ cations and 3δ vacancies between the A and B sites. Assuming simple A-B collinear magnetic interaction and B-site only Ti^{4+} and vacancies [e.g., O'Reilly, 1984; Collyer et al., 1988] reduces the cation distribution problem to partitioning Fe^{3+} and Fe^{2+} between the A and B sites, and the saturation magnetization in Bohr magnetons per formula unit at absolute zero for known δ and x is

$$n_B = 6(1-\delta)(1-x) - 2b \quad (3)$$

Unlike the data shown in Figure 2, (3) predicts that, for constant b , n_B should decrease with increasing $f\text{O}_2$ (and δ) and that the magnitude of this decrease is $\sim 1/5$ that observed for the sample pair ba,ba2, even for the largest change in nonstoichiometry permitted ($\delta_{\text{max}}=0.02$) [Senderov et al.,

1993]. The changes in magnetization of the bottom piece as a result of the annealing and quenching are not consistent with previous hypotheses that faster quench rates or higher quench temperatures (samples ba and ba2) would lead to an Akimoto-like distribution and slower quench rates or lower quench temperatures (sample bc) to an O'Reilly-Banerjee-like distribution [Trestman-Matts *et al.*, 1983; Stephenson, 1969; Bleil, 1971]. Instead, we hypothesize that the differences among the various cation distribution models result from differences in nonstoichiometry. At low temperatures, a decrease in nonstoichiometry apparently increases the degree of long range order (LRO) or, in other words, decreasing $f\text{O}_2$ (and δ) produces an apparent increase in b and hence, a lower net magnetization in (3).

Electrical Measurements

Electrical transport properties in ferrospinels, including TM, are primarily determined by small polaron conduction between octahedral Fe ions [e.g. Wu and Mason, 1981]. Thermoelectric power (Q), therefore, is a direct measure of the octahedral $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio [e.g., Wu and Mason, 1981] and can be used to obtain b as a function of temperature and δ

$$Q \cong -\frac{k}{e} \ln \frac{2[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = -\frac{k}{e} \ln \left(2 \frac{(2-2x) + 2\delta(3+x) - b}{x + b - \delta(9+x)} \right) \quad (4)$$

where k is Boltzmann's constant and e is electronic charge.

Thermopower was calculated from the slope of the EMF versus ΔT as the sample was moved in the temperature gradient of the furnace using the experimental setup described by Duda *et al.* [1990]. The thermopower of samples from the top part of the TM60 crystal was measured at 1200°C and oxygen fugacities of 10^{-3} , 10^{-4} , and 10^{-5} Pa and is shown in Figure 3. Near the reduction boundary, our value for $Q_{\text{TM60}} \cong -44 \mu\text{V}/\text{deg}$ agrees well with the results of Trestman-Matts *et al.* [1983] and suggests that, using the accepted site occupancy model in (1), the inverse-like cation distribution ($b \rightarrow 1$) of TM60 at low temperature changes toward a more normal-like distribution ($b \rightarrow 0$) at high temperatures. In addition, we find a small but reproducible and reversible decrease in Q with increasing oxygen fugacity above 10^{-4} Pa at 1200°C. As written, (4) is appropriate for B-site only hopping and vacancies and requires a decrease in the $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ on the B-site to explain the observed decrease in ther-

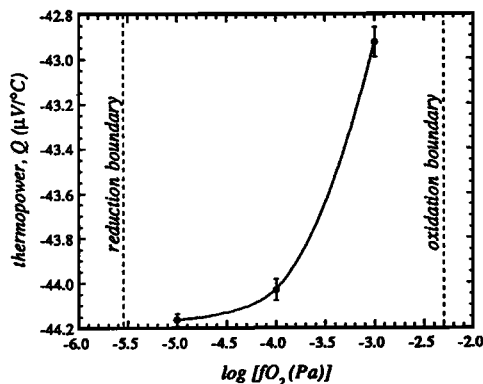


Figure 3. Thermopower (Q) versus $\log f\text{O}_2$ for the synthetic TM60 crystal at 1200°C.

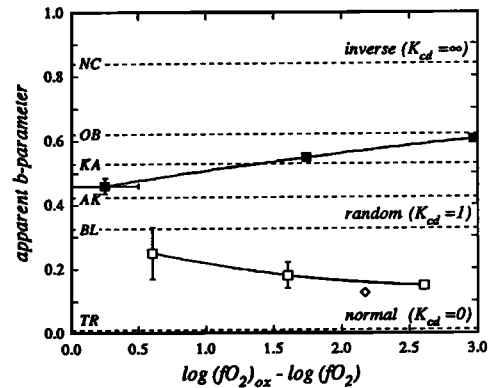


Figure 4. Apparent b calculated from the low temperature magnetization (solid symbols) and high temperature thermopower measurements (open symbols) versus relative oxidation defined as the difference between the $f\text{O}_2$ of the oxidation boundary of the TM60 crystal and the $f\text{O}_2$ imposed during high temperature annealing. The open diamond is calculated from the thermopower extrapolated to 1200°C for supposedly stoichiometric TM60 [Trestman-Matts *et al.*, 1983]. The cation distribution models shown are: NC (Néel-Chevallier), BL (Bleil), AK (Akimoto), OB (O'Reilly-Banerjee), KA (Kakol), and TR (Trestman-Matts *et al.*, 1984).

mopower, even though $[\text{Fe}^{3+}]$ in the crystal as a whole should increase with increasing $f\text{O}_2$. Although a more complicated expression than (4) is necessary should these constraints be relaxed, the thermopower measurements corroborate that b is sensitive to changes in nonstoichiometry and exhibits an apparent increase with increasing δ at high temperature.

Discussion and Summary

The $f\text{O}_2$ -dependence of T_c is similar to that obtained by Hauptman [1974] who also calculated δ as a function of $f\text{O}_2$ after quenching. Recent estimates of δ as a function of $f\text{O}_2$ by Senderov *et al.* [1993] are similar to those of Hauptman [1974] and suggest much higher degrees of nonstoichiometry in Ti-rich TM than previously hypothesized by Aragon and McCallister [1982], who assumed that vacancies are restricted to the magnetite component of TM.

The apparent changes in b as a function of $f\text{O}_2$ for both the magnetic and electrical measurements assuming only B-site vacancies and octahedral hopping are summarized in Figure 4. The high temperature b parameters are the average of a lower limit (using $\delta=0$) and an upper limit (using δ estimated from Senderov *et al.* [1993]) calculated from the thermopower data using (4). The low temperature b parameters are calculated in a similar manner from the magnetization data using (3). In terms of the cation distribution models shown in Figure 4, $K_{cd}=\infty$ corresponds to the Néel-Chevallier model; $K_{cd}=1$ corresponds to the Bleil [1971] model; and, $K_{cd}=0$ corresponds to the high temperature distribution of Trestman-Matts *et al.* [1983]. If it is further assumed that B-sites can accept a maximum of one Fe^{3+} ion, then $K_{cd}=1$ corresponds to the Akimoto model. The O'Reilly-Banerjee and Kakol models arise from $1 < K_{cd} < \infty$. Both the low temperature and high temperature measurements indicate that the cation distribution of TM60 becomes more random with increasing

oxidation/nonstoichiometry. At the low temperatures for which these models were developed, the O'Reilly-Banerjee model closely approximates b determined for the single crystals under reducing conditions while the Akimoto model is a better approximation under oxidizing conditions. If A-site vacancies are allowed, the apparent changes in b with increasing oxidation are smaller than shown in Figure 4, reducing the apparent increase in b calculated from (4) by 10% at most and canceling or even reversing the apparent decrease in b calculated from (3).

The relative changes in b at low and high temperatures as a function of oxidation suggest that cation vacancies stabilize a more random cation distribution than would otherwise be obtained for stoichiometric or reduced TM60. The production of cation vacancies must be compensated by the production of an appropriate number of positively charged species, for example, Fe^{3+} . If vacancies are more easily accommodated on A sites at high temperatures, they may also be accompanied by a greater than normal concentration of Fe^{3+} on A sites (higher b) either for local charge balance or due to defect association. At low temperatures, these vacancies would "return" with their accompanying Fe^{3+} to B sites, resulting in a lower b value relative to reduced TM60. This model requires electron hopping between A and B sites and that cation vacancy diffusion between A and B sites in the same unit cell is rapid enough to prevent complete quenching of the high temperature distribution of these defects. The differences among the various experimental cation distribution models may thus be explained by a previously unaccounted for variation in nonstoichiometry of the samples used by the different research groups.

The data presented above underscore the discrepancies between theoretical models of the cation and vacancy distributions in titanomagnetite and those necessary to explain our experimental measurements of electrical and magnetic behavior. Our preliminary single crystal data show that changes in nonstoichiometry may have a profound influence on LRO and resulting magnetic behavior of TM60 and titanomagnetites in general. Further measurements of the electrical and magnetic properties of titanomagnetites under strictly controlled thermodynamic conditions are necessary to construct a model more compatible with the experimental data and test the hypotheses suggested by our preliminary work.

Acknowledgments. The single crystal used in these experiments was grown using the Nichiden Machinery, Ltd. arc image furnace (model SC-35HD) maintained by the Department of Earth Sciences at Lawrence Livermore National Laboratory. Electrical experiments were also performed at LLNL through the generosity and assistance of Dr. Al Duba. The authors gratefully acknowledge reviews by T. Mason and Ö. Özdemir. This research is supported by NSF contracts EAR-901789 and EAR-9219621 and is contribution 9401 of the Institute for Rock Magnetism. The IRM is funded by grants from the Keck and National Science Foundations and the University of Minnesota.

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B. Wanamaker and B. Moskowitz, Dept. of Geology and Geophysics, 310 Pillsbury Dr., S.E., University of Minnesota, Minneapolis, MN 55455. (e-mail: bwana@maroon.tc.umn.edu)

(Received February 7, 1994; accepted March 4, 1994.)