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Synthesis and magnetic properties of single phase titanomagnetites

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The focus of this paper is the study of cation distributions and resulting magnetizations in titanomagnetites (TMs), $(1-x)Fe_3O_{4-x}Fe_2TiO_4$ solid solutions. TM remnant states are hypothesized to contribute to planetary magnetic field anomalies. This work correlates experimental data with proposed models for the TM pseudobinary. Improved synthesis procedures are reported for single phase Ulvöspinel (Fe_2TiO_4), and TM solid solutions were made using solid state synthesis techniques. X-ray diffraction and scanning electron microscopy show samples to be single phase solid solutions. M-H curves of TM75, 80, 85, 90, and 95 (TMX where X = at. % of ulvöspinel) were measured using a Physical Property Measurement System at 10 K, in fields of 0 to 8 T. The saturation magnetization was found to be close to that predicted by the Neel model for cation distribution in TMs. M-T curves of the remnant magnetization were measured from 10 K to 350 K. The remnant magnetization was acquired at 10 K by applying an 8 T field and then releasing the field. Experimental Neel temperatures are reported for samples in the Neel model ground state.
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I. INTRODUCTION

The pseudobinary titanomagnetites (TMs), xFe_2TiO_4 -$(1-x)Fe_3O_4$, are common magnetic spinel minerals on the earth,[1] the moon,[2] and Mars.[3] Their remnant magnetization contributes to planetary field anomalies, gives clues to geomagnetic evolution,[4] and argues for their importance in magnetic surveying.[5] Here we correlate experimental magnetization data with the proposed Neel Model for pseudobinary TM solid solutions that are precursors for studying spinodal decomposition in the systems.[6]

Previously, we presented evidence[7,8] for spinodal decomposition in magnetite (Fe_3O_4)-rich titanomagnetite solutions ($x > 0.5$), studied structural, magnetic, and thermal properties in solid solutions, and identified cation distributions by Mossbauer spectroscopy.[9] In these materials, there was also wüstite observed. In ulvöspinel rich solutions ($x > 0.5$), Neel temperatures fall in day to night temperature swings on Mars, suggesting identification with magnetic sensors based on their temperature dependent magnetization. Phase equilibria in oxidizing, inert, and reducing environments may impact the remnant state of the minerals in planetary environments.[10,11]

This work discusses experimental agreement of solid solution properties with the Neel model and its consequent cation distributions. A precise knowledge of Neel temperature dependence on composition will be important for interpreting magnetic data sent back from probes of the remnant state on Mars.

II. EXPERIMENTAL PROCEDURES

The mixtures used to synthesize the Fe_3O_4-Fe_2TiO_4 pseudobinary alloys in this study were made with the two endpoint materials. Fe_3O_4 was purchased commercially from Alfa Aesar, with 99.9% purity. Fe_2TiO_4 was synthesized by combining stoichiometric amounts of TiO_2, Fe_2O_3, and Fe sponge, with 0.072 wt. % excess of Fe to prevent Fe-deficiency and using SPEX milling to provide fine powders, where shorter diffusion lengths promote faster equilibration.[12] Pressed pellets were loaded into steel crucibles and heated in a tube furnace for 100 h at 1150 °C to ensure full reaction, in a pure Ar environment. Materials were characterized by X-ray diffraction (XRD) as being single phase Fe_2TiO_4.

Fe_2TiO_4 pellets were powdered and mixed with Fe_3O_4 by SPEX milling, then sintered at 1100 °C for 100 h. The sintering atmosphere was set to ~99.8% Ar and ~0.2% O_2. After sintering, the temperature was decreased to 750 °C from which the samples were quenched in cold water. The desired TM compositions were produced by varying the molar ratio of Fe_2TiO_4 to Fe_3O_4 in precursor mixtures. TM samples with x = 0.05, 0.1, 0.2 to 0.95 and 1.0, respectively, are designated TM5-100. We examine TM75, 80, 85, 90, and 95 samples, powdered to obtain XRD patterns, confirming them to be single phase solid solutions TMX ($Fe_{3-x}Ti_xO_4$, X = 100*x). Samples with ulvöspinel concentrations below 75% were found to form wüstite in our sintering atmosphere.

Hysteresis loops were measured using the Physical Property Measurement System (PPMS). Samples were cooled to 10 K and M(H) measured between −8 and 8 T. Remnant magnetization was measured by magnetizing samples in an 8 T applied field, and releasing the field. The decay of remnant magnetization was measured from 10– 350 K.

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III. RESULTS AND DISCUSSION

The Neel model predicts a discontinuous transition of cation distribution between magnetite and ulvöspinel in TMs. Magnetite, an inverse spinel, has Fe^{3+} on the A-site and both Fe^{3+} and Fe^{2+} on B-sites. Ti^{4+} is substituted exclusively on the B-sites.[13] The Neel model predicts that Ti^{4+} substitutes for Fe^{3+} on B-sites, simultaneously causing Fe^{3+} to an Fe^{2+} charge transfer at a different B-site. At the TM50 composition only Fe^{2+} remains on the B-sites. For TM50-100, as more Ti^{4+} is substituted on the B-sites, two A-site Fe^{3+} are converted to Fe^{2+}, to maintain charge balance.[14] [Fig. 1(a)] Cation distributions can be represented (x = mole fraction) as

$$0 < x < 0.5\ [Fe^{3+}]_A(Ti_x^{4+}\,Fe_{1+x}^{2+}\,Fe_{1-2x}^{3+})_B O_4^{2-}, \quad (1)$$

$$0.5 < x < 1\ [Fe_{2-2x}^{3+}\,Fe_{2x-1}^{2+}]_A(Ti_x^{4+}\,Fe_{2-x}^{2+})_B O_4^{2-}. \quad (2)$$

This distribution yields a discontinuity in the composition dependence of the magnetization. The TM system has the inverse spinel structure,[15] meaning A-site magnetic moments are aligned anti-parallel to the B-site moments. Assigning magnetic moments of Fe^{2+}, Fe^{3+}, and Ti^{4+} to be $4\mu_B$, $5\mu_B$, and $0\mu_B$, respectively, we predict the saturation magnetization of any TM composition, based on the Neel Model [Fig. 1(b)]

$$0 < x < 0.5\ \left((x)0 + (1+x)4 + (1-2x)5\right)_B - [5]_A = 4 - 6x\,\mu_B, \quad (3)$$

$$0.5 < x < 1\ \left((x)0 + (2-x)4\right)_B - [(2-2x)5 + (2x-1)4]_A = 2 - 2x\,\mu_B. \quad (4)$$

XRD results for TM75-95 (Fig. 2) show nominally single phase solid solutions. There is a small amount of excess iron, but the samples have less second phase oxides than previous experiments.[10]

Lattice parameters calculated using the Nelson and Riley method[16] are consistent with Wechsler's extrapolated data.[12] Their samples were reported to have 1–2 wt. % wüstite and some ilmenite.

A decrease in magnetization is observed as the ulvöspinel composition is approached. The data was corrected for $\mu_O M$

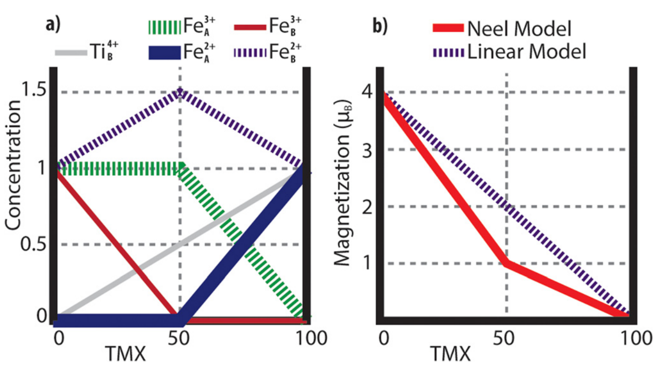

FIG. 1. (a) Depiction of Neel Model of cation distribution with respect to composition for titanomagnetite and (b) the magnetization vs composition of TM based on the Neel model.

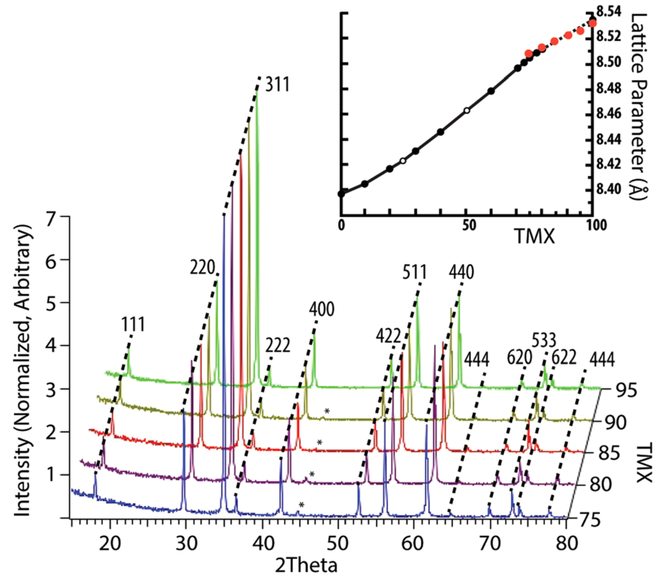

FIG. 2. XRD patterns for TM75-95. Indexed to spinel peaks (110 peaks of iron are starred). Inset shows lattice parameters based XRD data (red/grey) compared to published data (black).[12]

and rotation against exchange using a linear fit of high field data points, in order to estimate the saturation magnetization. This data is shown in the inset of Fig. 3. M_S agrees well with Neel model predictions. 10 K hysteresis loops display wasp-waisting, indicating there may be some coupling to second phases at the grain boundaries that are undetectable by XRD. Hysteresis loops taken at temperatures above 130 K did not indicate any wasp-waisting, suggesting that the coupling GB phase(s) have low Neel temperatures.

Prior Mossbauer spectroscopy[9] measurements indicated some deviations from the Neel model of cation distributions in TM solid solutions. In future work, we will conduct similar experiments on the higher purity samples. Mossbauer determined cation distributions for TM solid solutions indicated increased charge localization for compositions above TM75, with more A-site Fe^{2+}, and less of the 3+ than predicted. Similar results were found by Banerjee.[17] M_S values are in good agreement with the Neel model.

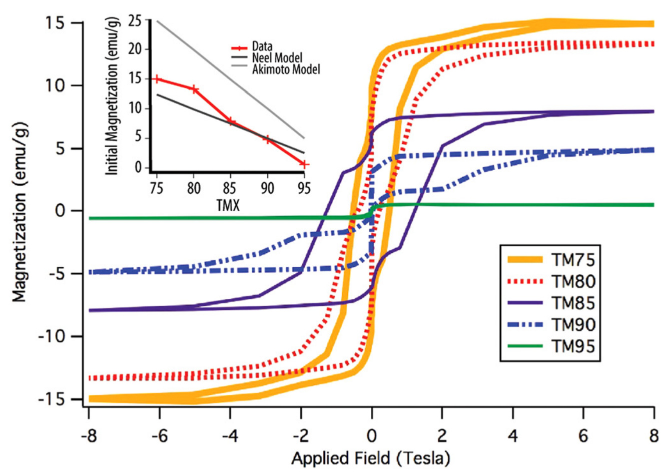

FIG. 3. Magnetization vs applied field for TM75-95. Inset displays data compared with Akimoto and Neel models.

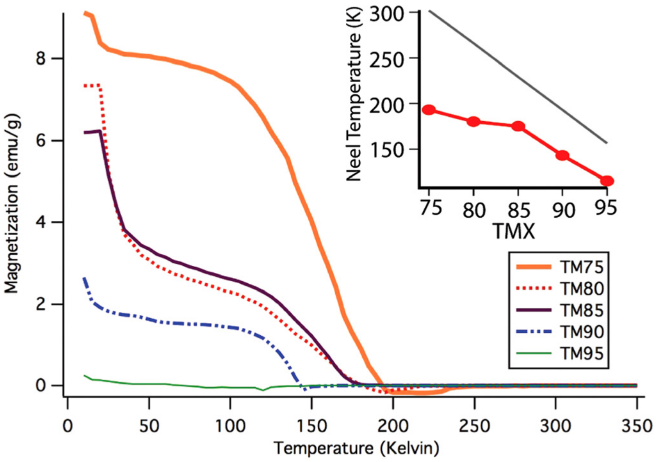

FIG. 4. Remnant magnetization of TM75-95 after applying an 8 T field, and its decay in zero field heating. Inset shows Neel temperatures determined from this model, compared to a linear model.

The remnant magnetization after applying an 8 T field at 10 K decayed in zero field as we increased the temperature to 350 K, Fig. 4. End member Neel temperatures are known to be 120 K for ulvöspinel and 853 K for magnetite.[18] Published phase diagrams show Neel temperatures in TM solid solutions to vary linearly with composition. Akimoto[19] and others[20] found a linear composition dependence of Neel Temperature. It has been suggested that the Akimoto model could be used for high temperature equilibrium (metastable low temperature) states, while the Neel Model is the true low temperature ground state.[20] Based on saturation magnetizations, our samples appear to approach low temperature Neel ground state configurations. In this Neel ground state, the Neel temperatures are smaller than those reported by Akimoto and exhibit a non-linear composition dependence. Our experimental data for TM95 is close to the known T_N value for ulvöspinel. As the titanium concentration is decreased, we find a greater deviation of the linear composition dependence of T_N in our data. T_N for TM75 is 195 K, which is much lower than the Akimoto model, which predicts 303 K. In Ginzburg-Landua theories of magnetic phase transitions, magnetic free energies scale as even powers of the magnetization; therefore, a power law dependence of the Neel temperature with magnetization might be expected and the lower observed Neel temperatures are consistent with the lower magnetizations in the Neel ground state.

At very low temperatures, M(T) curves display a low temperature sharp decrease in magnetization near 40–50 K. This is not observed when a 1 T applied field is used to prepare the remnant state (as opposed to the 8 T field). This is reminiscent of features seen in frozen spin liquid systems and activated by spin flop rotation against exchange interactions. The mechanism for pinning this state at low temperatures is still unknown at this time.

IV. CONCLUSIONS

We have inferred cation distributions for TM solid solutions from magnetizations. Our cation distributions for TM solid solutions are in good agreement with the Neel model. The Neel temperatures of the compositions are smaller than those predicted for random solid solution. This impacts the detection of TMs on the surface of Mars, where their Neel temperatures fall within the day to night temperature swing. For the compositions studied here, we predict distinct differences between solutions in a random Akimoto and ordered Neel state.

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[1]C. Klein and C. S. Hurlbut, *Manual of Mineralogy*, 21st ed. (John Wiley and Sons, New York, 1993).
[2]D. W. Strangeway, W. A. Gose, G. W. Pearce, and J. G. Cames, "Magnetism and the history of the moon," *Proceedings of the 18th Annual Conference on Magnetism and Magnetic Materials* (AIP, 1973) Pt. 2, pp. 1178–1197.
[3]D. Gubbins and E. Herrero-Bervera, *Encyclopedia of Geomagnetism and Paleomagnetism*, Encyclopedia of Earth Sciences Series Vol. XXVI (Springer, 2007).
[4]G. Kletetschka, P. J. Wasilewski, and P. T. Taylor, "Mineralogy of the sources for magnetic anomalies on Mars," Meteorit. Planet. Sci. **35**, 895–899 (2000).
[5]P. Kearey and M. Brooks, *An Introduction to Geophysical Exploration* (Blackwell Science Publications, 1991).
[6]A. F. Buddington and and D. H. Lindsley. "Iron-titanium oxide minerals and synthetic equivalents," J. Petrology **5**, 310–357 (1964).
[7]A. T. Wise, M. Saenko, A. M. Velázquez, D. E. Laughlin, M. Diaz-Michelena, and M. E. McHenry, "Phase evolution in the Fe_3O_4-Fe_2TiO_4 pseudo-binary system and its implications for remanent magnetization in martian minerals," IEEE Trans. Magn. **47**, 4124–4127 (2011).
[8]R. Sanz, M. Cerdan, A. T. Wise, M. E. McHenry, and M. Diaz-Michelena, "Temperature dependent magnetization and remanent magnetization in pseudo-binary $(Fe2TiO4)_x$-$(Fe3O4)_{1-x}$ $(0.30 < x < 1.00)$ titanomagnetites," IEEE Trans. Magn. **47**, 4128–4131 (2011).
[9]M. Sorescu, T. Xu, A. Wise, M. Diaz-Michelena, and M. E. McHenry, "Studies on structural, magnetic and thermal properties of xFe_2TiO_4-$(1-x)Fe_3O_4$ $(0 \leq x \leq 1)$ pseudo-binary system," J. Magn. Magn. Mater. **324**, 1453–1462 (2012).
[10]S. Lan, K. Grotschner, A. Wise, D. E. Laughlin, M. Diaz-Michelena, and M. E. McHenry. "Phase identification and temperature-Dependent magnetization of Ti-rich titanomagnetites $(0.5 < x < 1)$ in different atmospheres," IEEE Trans. Magn. **49**, 4314–4318 (2013).
[11]C. Grotschner, S. Lan, A. Wise, D. E. Laughlin, M. Diaz-Michelena, and M. E. McHenry, "The role of atmosphere on phase transformations and magnetic properties of ulvospinel," IEEE Trans. Magn. **49**, 4273–4276 (2013).
[12]B. A. Wechsler, D. H. Lindsley, and C. T. Prewitt, "Crystal structure and cation distribution in titanomagnetites $(Fe_{3-x}Ti_xO_4)$," Am. Minerologist **69**, 754–770 (1984).
[13]G. Blasse, "Crystal chemistry and some magnetic properties of mixed metal oxides with spinel structure," Philips Res. Rep., Suppl. **3**, 1–139 (1964).
[14]L. Neel, "Some theoretical aspects of rock-magnetism," Adv. Phys. **4**, 191–243 (1955).
[15]W. H. Bragg, "The structure of the spinel group of crystals," Philos. Mag. **30**, 305–315 (1915).
[16]J. B. Nelson and D. P. Riley, "An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals," Proc. Phys. Soc. **57**, 160 (1945).
[17]S. K. Banerjee, W. O'Reilly, T. C. Gibb, and N. N. Greenwood, "The behaviour of ferrous ions in iron-titanium spinels," J. Phys. Chem. Solids **28**, 1323–1335 (1967).
[18]R. Butler, "Ferromagnetic minerals," in *Paleomagnetism: Magnetic Domains to Geologic Terranes* (Blackwell Scientific Publications, 1992), Chap. II, pp. 16–30.
[19]S. Akimoto, "Thermomagnetic study of ferromagnetic minerals contained in igneous rocks," J. Geomagn. Geoelectr. **6**, 1–14 (1954).
[20]A. Stephenson, "The temperature dependent cation distribution in titanomagnetites," Geophys. J. R. Astron. Soc. **18**, 199–210 (1969).