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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)Fe3O4–xFe2TiO4 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 (Fe3TiO4), 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), xFe3TiO4–(1–x)Fe2O4, 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 evidence7,8 for spinodal decomposition in magnetite (Fe3O4)-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 Fe3O4–Fe2TiO4 pseudobinary alloys in this study were made with the two endpoint materials, Fe3O4, was purchased commercially from Alfa Aesar, with 99.9% purity. Fe2TiO4 was synthesized by combining stoichiometric amounts of TiO2, Fe2O3, 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 Fe3TiO4.

Fe3TiO4 pellets were powdered and mixed with Fe3O4 by SPEX milling, then sintered at 1100 °C for 100 h. The sintering atmosphere was set to ~99.8% Ar and ~0.2% O2. 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 Fe2TiO4 to Fe3O4 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 (Fe1–xTiO4, 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. 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. 

Cation distributions can be represented as:

\[
0 < x < 0.5 \left[ Fe^{3+} \right]_A \left( Ti^{4+} Fe^{2+} \right)_{1-x} Fe^{3+}_{1-2x} O^{2-}, \tag{1}
\]

\[
0.5 < x < 1 \left[ Fe^{3+} Fe^{2+} \right]_A \left( Ti^{4+} Fe^{2+} \right)_{2-x} O^{2-}. \tag{2}
\]

This distribution yields a discontinuity in the composition dependence of the magnetization. The TM system has the inverse spinel structure, 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

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

\[
0.5 < x < 1 \left( x 0 + (2 - x)4 \right)_B
- \left[ (2 - 2x)5 + (2x - 1)4 \right]_A = 2 - 2x \mu_B. \tag{4}
\]

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.

Lattice parameters calculated using the Nelson and Riley method \cite{16} are consistent with Wechsler’s extrapolated data. 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 $\mu_0 M$ 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. 10K 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 \cite{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. \cite{17} $M_S$ values are in good agreement with the Neel 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. Published phase diagrams show Neel temperatures in TM solid solutions to vary linearly with composition. Akimoto and others 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. 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 the Akimoto model, compared to a linear model.

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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