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R. Sanz

Instituto Nacional de Técnica Aeroespacial, Spain

M. F. Cerdan

Instituto Nacional de Técnica Aeroespacial, Spain

Adam Wise

Carnegie Mellon University, adamwise@cmu.edu

Michael E. McHenry

Carnegie Mellon University, mm7g@andrew.cmu.edu

M. Diaz-Michelina

Instituto Nacional de Técnica Aeroespacial, Spain

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Temperature dependent Magnetization and Remanent Magnetization in Pseudo-binary $x(\text{Fe}_2\text{TiO}_4)-(1-x)(\text{Fe}_3\text{O}_4)$ ($0.30 < x < 1.00$) Titanomagnetites

R.Sanz¹, M. F. Cerdán¹, A. Wise², M. E. McHenry^{2,*} and M. Díaz-Michelena^{1*}, *Senior Member IEEE*

¹Space Programs and Space Sciences Department, INTA, Spain.

²Materials Science and Engineering Department, Carnegie Mellon University, Pittsburgh, PA 15213 USA

In this work we present preliminary results on magnetization and remanence of synthetic pseudo-binary $x(\text{Fe}_2\text{TiO}_4)-(1-x)(\text{Fe}_3\text{O}_4)$ ($0.30 < x < 1.00$). Magnetic characterization was performed at temperature ranges from 100 K up to 400 K. The final objective is to characterize the magnetic response as a function of temperature in order to foresight the future magnetic measurements of the magnetometer included into Met-Net mission to Mars. Samples present ferromagnetic behavior with Néel temperatures above the minimum Martian temperature. An increased remanence for sample with $x=0.65$ has been measured possibly originated by pinning mechanism which might offer a partial explanation as to the crustal magnetism of Mars.

Index Terms— Magnetism in solids, Mars, Titanomagnetites

I. INTRODUCTION

THE study of planetary magnetism provides insight into the validity of various models of the geological evolution of planets and satellites and thus of Solar System. The Mars Global Surveyor mission's results showed the first unambiguous measurements of the magnetic field on Mars [1]. These results showed that Mars presently has no active geologic dynamo and its global magnetic field is of crustal origin even though studies of Martian meteorites indicate that fields as large as 3000 nT may have once existed on the surface of Mars. Mapping of the Martian magnetic field reveals anomalous regions of intense magnetization [2] distributed in "stripes" of alternating polarity.

Paleomagnetic minerals, like magnetite and the magnetotitanates are crucial in explaining Martian field anomalies since minerals with a stable remanent magnetization comparable to magnetite could explain field anomalies as large as 200 nT [3]. Such minerals would necessarily be monodomain particles and have a mechanism for pinning the magnetization to prevent superparamagnetic switching [4,5]. Both composition and nanostructure of these minerals contribute to their remanent magnetic properties, being these characteristics associated to sintering conditions and later influence of environmental evolution, and formation and environmental conditions change at planetary distances.

The philosophy of former exploration probes launched to Mars was to deploy mobile instruments in rovers. Unless these rovers have movement capacity they are unable to obtain statistical data over planetary distances. In order to supply real statistical data a new kind of exploration missions can be designed. These new missions should be small and cheap platforms with the capacity to perform a net over the Martian surface, as small meteorological stations employed on Earth. This is the chosen philosophy for Met-Net mission.

One of the Met-Net mission [6] objectives is to obtain in-

situ magnetic data in the Martian environment. One of the mission payloads is a miniaturized magnetometer based on a commercial off-the shelf (COTS) AMR sensor of a $\pm 2 \cdot 10^5$ nT range and 10 nT resolution. Due to the weight and power limitations for payloads of this type of missions it will be unable to perform an exhaustive magnetic characterization of minerals over the field. These limitations mean that no controllable external magnetic field can be applied. However this magnetometer will be able to measure the temperature dependence of magnetic remanent state of crustal minerals in the Martian night to day temperature swing between -135 up to 20 °C. The evolution of this magnetic signal could be interpreted as a signature of the minerals found in the environment around the probe.

Important among the abundant mineral types on Mars are ferrites and titanomagnetites. Due to their abundance on the Martian surface, these may be important in understanding the geomagnetism of Mars. The magnetic properties of these mineral families have been widely studied. Previous studies often did not have access to state of the art ceramic processing, large fields and low temperatures required to fully characterize the magnetic properties of the materials and the sub-solidus miscibility gap is not fully characterized, in particular the region of spinodal decomposition.

This and a companion paper [7] begin new studies of synthesis \rightarrow structure \rightarrow magnetic properties relationships in the titanomagnetites. Reference [7] details magnetic probes of phase evolution in the sub-solidus phase diagram and the kinetics of exsolution. This paper reports on low temperature magnetic properties of these minerals sintered in similar conditions as expected occurred in Martian crust. The compositional dependence of the remanent magnetization for pseudo-binary $\text{Fe}_2\text{TiO}_4\text{-Fe}_3\text{O}_4$ solid solutions is reported. This is important for future interpretation of data collected on Mars.

II. EXPERIMENTAL METHODS

An $x(\text{Fe}_2\text{TiO}_4)-(1-x)(\text{Fe}_3\text{O}_4)$ ($0.30 < x < 1.00$) series was produced by solid state synthesis [7]. Nearly pure Fe_2TiO_4 was made from Fe_2O_3 , and TiO_2 mixed in stoichiometric

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proportions with 5.4% excess Fe sponge. Components were ground with a mortar and pestle, pressed into pellets, loaded into Fe crucibles and heated for 60h at 1050 °C in an Ar atmosphere to prevent oxidation. The resulting material was verified by XRD to be Fe₂TiO₄ less than 3% ilmenite.

Fe₂TiO₄ precursor pellets were ball-milled again to produce powders of an appropriate size for mixing with commercial Fe₃O₄ powder. This powder was mixed with commercial Fe₃O₄ powder in different proportions to produce the series studied here. Each composition was put in the SPEX mill for 10 min. to reduce the particle size and homogenize the powder and then pressed into pellets of 0.5 inches in diameter and ~0.15 inches thick. The pellets were placed in 1010 steel crucibles into an Ar furnace at 950°C for a 60 hour bake. Powders were furnace cooled under the Ar atmosphere to 400°C, then removed to air-cool to room temperature. Powders were verified to be single-phase solid solutions by XRD performed with an XPERT-PRO diffractometer (CuKα). Microstructures were determined by TEM [7].

Magnetic characterization of the samples reported here employed an ADE Magnetics magnetometer (model EV-7 VSM) with a temperature control unit. Before measurements all samples were submitted to degaussing process (alternating exponential decreasing field from 2T). The temperature dependence of the remanence, Mr, was measured applying and initial external field 1 T from room temperature and then decreasing temperature to 100 K where the field was removed and the temperature increased. Magnetization at a fixed 1T applied field, M(1T), was measured from 100 K to 400 K under field cooling (FC) conditions. Virgin magnetization curves of x=0.65 samples up to 2 T applied field were measured at temperatures ranging from 120 to 373 K.

III. RESULTS AND DISCUSSION

With the exception of the antiferromagnetic ulvospinel [8] all of the solid solutions in the pseudobinary titanomagnetite system are ferrimagnetic. Cation distributions reflect the fact that each Ti⁴⁺ ion substituted for a Fe³⁺ ion requires the conversion of a second Fe³⁺ ion to Fe²⁺[9]. Titanomagnetites can deviate from ideal stoichiometries due to (i) exsolution as discussed in [7], (ii) non-stoichiometry at high and low temperatures and (iii) cation impurities [10]. Cation impurities are a consideration in extraterrestrial minerals but not in compounds synthesized from relatively pure species in the laboratory. While a thermally activated degree of inversion in titanomagnetite spinels has been described [10], its activation energy barrier is similar to that for atomic diffusion by a Frenkel defect mechanism and therefore also consistent with exsolution. Given a small difference in the spinel lattice constants across the series [11], it is difficult to detect and therefore rule out early exsolution through spinodal decomposition. Fully developed 2-phase mixtures have been detected by x-rays [7] in samples annealed for extended times at 600 °C. Exsolution is considered in the companion article [7], here we report only on solid solutions.

XRD characterization (not shown) revealed all samples to be nominally solid solutions with the caveats described above. There were small amounts of ilmenite detected in x=0.50, 0.85, 0.90 and 0.95 samples, typical of samples approaching

the ulvospinel. The XRD pattern of the sample with x=0.65 had a slight shift to larger 2θ angles, indicating a slight contraction of its lattice constants, though two phases could not be detected. There was not evidence of 2-phases resulting from exsolution and we thus consider the samples solid solutions but can not rule out early spinodal decomposition.

Since Ti⁴⁺ is non-magnetic this results in a monotonic decrease in the saturation magnetization [9] and Néel temperature in moving toward the ulvospinel. The analysis of saturation moments and Néel temperatures are complicated by the fact that the materials are not easily saturated and depend on the crystal defect concentrations [12]. Prior works used saturating fields of only tenths of T (a few kG). We have measured to fields of 8T without saturating in the Fe₂TiO₄ rich compositions. This complication can be attributed to rotation against superexchange as in the P-type magnetization and is observed in other systems where a non-magnetic cation is substituted into the spinel structure [13,14]. Analysis of the canted spin problem [15] that gives rise to non-saturating behavior will be considered in subsequent work.

To compare the compositional and temperature dependent magnetic properties with previous literature we consider a nominally “saturating” 1 T field. Figure 1 shows M(1T) for temperatures between 100 to 400 K. Magnetic moments show ferrimagnetic behavior with increasing content of Fe₂TiO₄. A monotonic decrease in the moment is observed for larger x.

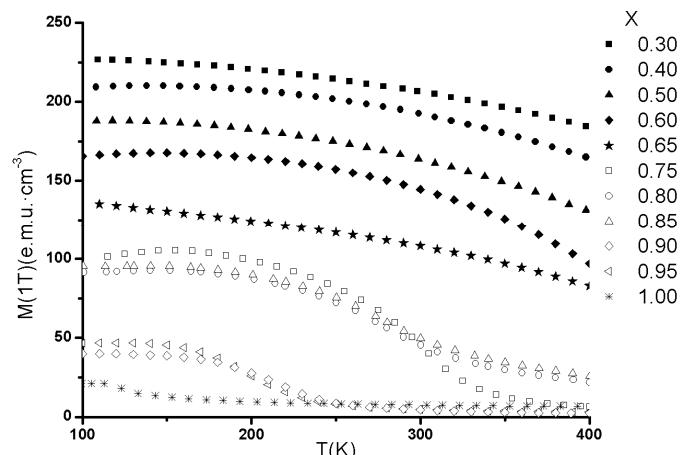


Fig. 1. 1T applied field magnetization as a function of temperature.

The variation of the magnetic response with composition in Figure 1 reflects the variation in site occupancies for Fe³⁺ and Fe²⁺ in tetrahedral and octahedral sites [16,17]. Magnetic behaviour of M(1T) has been associated to ferrimagnetic P-Type temperature dependence. This implies that the sublattice occupied by the cation with the smaller magnetic moment has a smaller net superexchange interaction than that occupied by the larger one. This superexchange mechanism is accompanied by a contraction of the lattice constant.

The Néel Temperature (T_N) of samples was determined by extrapolation using power law fitting methods (Figure 2). Samples with x higher than 70 had T_N in the measured temperature range. T_N was fit with a linear x dependence, T_N(x)=(-9.5±0.5)x+(1100±30)(K), in agreement with previously reported values [15] for similar composition range. Note that pure Fe₃O₄ T_N value from [18] has been included in figure 2, although its synthesis is different, for comparison. The x=0.65

sample showed a large deviation from this line. All the calculated T_N values are above the minimum temperature reached at Mars surface.

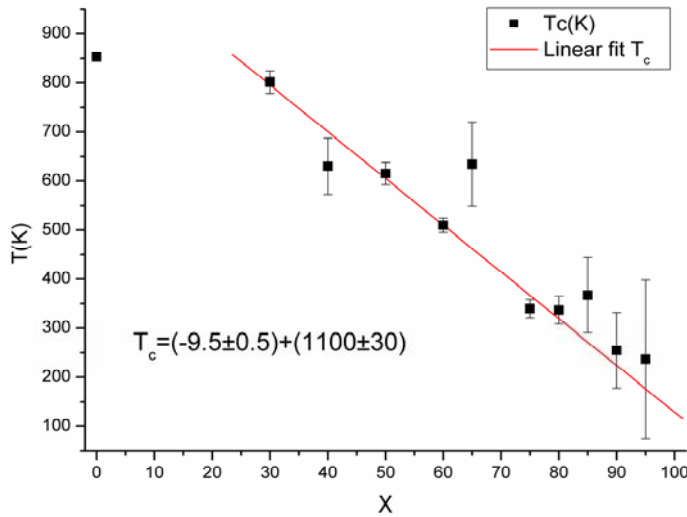


Fig. 2. Fits of T_N vs. composition for $(x) \text{Fe}_2\text{TiO}_4-(1-x)\text{Fe}_3\text{O}_4$.

Reduced remanent magnetization, $M_r/M(1T)$, ratios are illustrated in Figure 3. In all cases these were below 0.10 with the exception of the $x=0.65$ sample, which presents a value of ~ 0.25 ratio, the highest for all measured samples and temperatures. Substantial increases in the remanent magnetization in the titanomagnetites have been ascribed to finer grains [19]. The results for $M_r/M(1T)$ shown in Figure 3 would be consistent the existence of a smaller grain size. A fine modulated structure [20] will result from spinodal decomposition in the composition range between the spinodes of the regular solution model. This would be consistent with prior reports of an asymmetric miscibility gap in the pseudo-binary system [21, 22] with a consolute temperature of 600 °C. It is conceivable that compositions near those associated with the consolute temperature could have some early spinodal decomposition while furnace cooling to 400 °C.

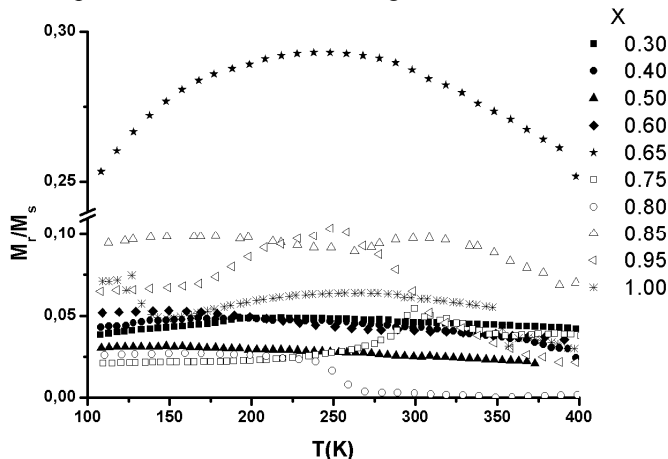


Fig.3. M_r/M_s ratios as a function of temperature.

Figure 4 shows virgin magnetization curves of the $x=0.65$ sample obtained in a temperature range from 153 to 373 K. The $M(1T)$ values for each temperature in these curves present a similar behavior but higher values to those obtained under FC conditions in Figure 1. The analysis of the curves allows calculating an (angularly averaged) effective anisotropy constant (K_{eff}) shown in the inset.

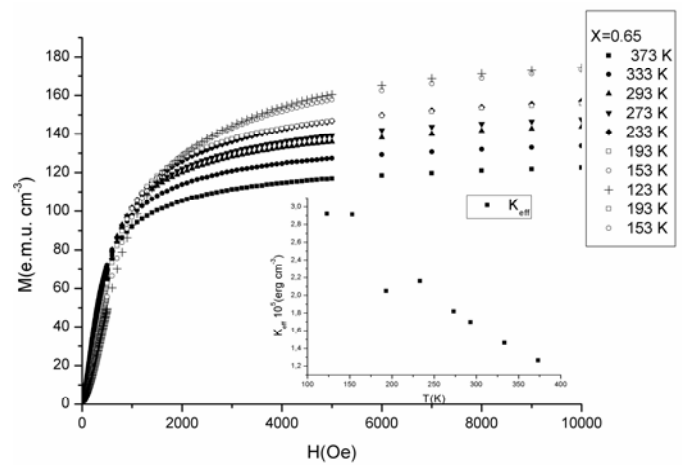


Fig. 4. Magnetization curves for the $x=0.65$ sample and calculated K_{eff} .

The non-saturating behavior of the $M(H)$ curves is thought to have its origin in the superexchange interaction and rotation of non-collinear spins [13-15], however in the geomagnetic community it has been ascribed to an effective anisotropy [19]. Calculated values of the effective anisotropy, K_{eff} are on the same order of magnitude [19] and tend to decrease linearly with decreasing temperature. The observation of microstructures of natural crystals in similar systems [17] consists of magnetite cubes surrounded by thin lamellar of ulvospinel where pinning of magnetic layers with non-collinear structures might be possible. Such a microstructure may explain, in the case of $x=0.65$ sample, the stabilization of remanent magnetization by an exchange bias pinning mechanism. Under this mechanism the M_r/M_s response with the temperature would be modulated by the behavior of the ferrimagnetic material surrounding the magnetite cubes. This ferrimagnetic material could explain the maximum in M_r/M_s signal at 250 K for $x=0.65$. If these preliminary results are confirmed, a mechanism at nanoscale might explain one of the reasons for the crustal anomalies observed at planetary scale on Mars. More detailed structural studies and synthesis of similar mineral families under slightly different conditions are being performed to confirm the existence of this mechanism.

IV. CONCLUSION

Preliminary studies of the magnetization and remanence in synthetic $x(\text{Fe}_2\text{TiO}_4)-(1-x)(\text{Fe}_3\text{O}_4)$ ($0.30 < x < 1.00$) pseudo-binary solid solutions have been reported. Magnetic characterization between 100 and 400 K indicate a monotonic decrease in the moment and linear decrease in the Néel temperature, T_N , for larger x . Samples exhibit ferrimagnetic behavior with Néel temperatures above the minimum Martian temperature. An increased remanence for a sample with $x=0.65$ has been measured and postulated as originating from an interfacial pinning mechanism. Larger remanent magnetization in titanomagnetites may offer a partial explanation as to the crustal magnetism of Mars.

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