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Thermoremanence and stable memory of single-domain hematites

Özden Özdemir and David J. Dunlop

Geophysics, Department of Physics, University of Toronto at Mississauga, Mississauga, Ontario, Canada

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[1] We report thermoremanent magnetization (TRM) intensities and thermal demagnetization behavior of seven samples of single-domain hematite (α Fe_2O_3) with grain sizes between 0.12 and 0.42 μm, before and after zero-field cycling through the low-temperature Morin transition ($T_M \approx$ 240 K). TRM was unaffected by 100 mT alternating field demagnetization and by 600°C thermal demagnetization. Most demagnetization occurred between 625°C and the Néel temperature of 680–690°C. The TRM memory recovered after low-temperature cycling was parallel to the original TRM and equally resistant to thermal demagnetization. TRM and TRM memory of single-domain hematites are mainly due to the hard spin-canted magnetism intrinsic to the crystal structure above the Morin transition, and not to the small and softer defect magnetism that survives below T_M. However, the defect magnetism may play a role in renucleating the spin-canted magnetism in a preferred direction during warming through T_M. TRM intensities are well predicted by Neél single-domain theory and increase in almost exact proportion to grain size. Although smaller than TRM intensities of multidomain hematites, single-domain TRMs are potent sources of remanent magnetic anomalies, particularly for larger grains (10–15 μm), and are likely to be more stable over geological time than multidomain hematite TRMs. *INDEX TERMS:* 1517 Geomagnetism and Paleomagnetism: Magnetic anomaly modeling; 1527 Geomagnetism and Paleomagnetism: Paleomagnetism applied to geologic processes; 1540 Geomagnetism and Paleomagnetism: Rock and mineral magnetism; 6225 Planetology: Solar System Objects: Mars. **Citation:** Özdemir, Ö., and D. J. Dunlop, Thermoremanence and stable memory of single-domain hematites, *Geophys. Res. Lett.*, *29*(18), 1877, doi:10.1029/2002GL015597, 2002.

1. Introduction

[2] The magnetism of hematite has received renewed attention since the discovery of large concentrations of >5–10 μm crystalline hematite in the equatorial Sinus Meridiani region of Mars [*Christensen et al.*, 2000] and intense magnetic anomalies in Mars' southern hemisphere, particularly in Terra Cimmeria and Terra Sirenum [*Connerney et al.*, 1999; *Acuña et al.*, 1999]. Multidomain hematite is one of the candidate source minerals for the anomalies [*Connerney et al.*, 1999; *Kletetschka et al.*, 2000]. Thermoremanent magnetization acquired when the ancient southern crust cooled below the Curie point soon after accretion of the planet at ~4.5 Ga is the probable process by which the anomalies formed [*Acuña et al.*, 1999].

[3] Hematite (α Fe_2O_3) exhibits a weak ferromagnetism arising from canted antiferromagnetic spin sublattices lying in the rhombohedral c-plane. Below the Morin transition at $T_M \approx 250$ K, the spins rotate to the c-axis and canting disappears [*Dzyaloshinsky*, 1958; *Moriya*, 1960]. However, a small "defect ferromagnetism", arising from microstructural defects and/or chemical impurities, is observed below T_M, and presumably exists above T_M as well although masked by the larger spin-canted magnetism.

[4] Most published hematite TRM data are for coarse grains or individual crystals [*Uyeda*, 1958; *Syono et al.*, 1962; *Dekkers and Linssen*, 1989], many larger than the critical size of ≈15 μm for single-domain (SD) behavior [*Dunlop and Özdemir*, 1997]. Multidomain (MD) hematites have intense TRM, comparable to the TRM of submicron magnetite [*Kletetschka et al.*, 2000; *Dunlop and Kletetschka*, 2001], but the long-term stability is likely lower. The few available data suggest that SD hematite has less intense TRM [*Dunlop*, 1971; *Clark*, 1983; *Kletetschka et al.*, 2000] but the stability against later magnetic field changes is orders of magnitude higher. The present paper is the first systematic study of TRM and its stability as a function of grain size in SD hematites.

[5] We measured the intensity and alternating-field (AF) and thermal demagnetization of TRM, and also of the TRM memory recovered after low-temperature cycling in zero field through the Morin transition, for hematites with mean sizes ranging from 0.12 μm to 0.42 μm. Although these are smaller sizes than observed for Martian hematites, the size dependence we document can be extrapolated to larger SD sizes.

[6] TRM memory after low-temperature cycling (LTC) is relevant to Mars because surface temperatures in many parts of the planet cycle diurnally or seasonally through T_M in the essentially zero present-day Martian field. Most published data on LTC in hematite are for saturation isothermal remanence (SIRM) of large grains and single crystals [*Néel and Pauthenet*, 1952; *Smith and Fuller*, 1967]. Much of the LTC memory of these MD hematites is a defect magnetism, which, being stress-sensitive, is arguably less stable over geological time than the spin-canted magnetism. One purpose of the present study is to investigate the stability and origin of TRM memory in SD hematites.

2. Sample Characterization

[7] We studied three sets of synthetic submicron hematites. Samples H1–H4 were prepared by heating cube-shaped magnetite crystals at 700°C in air for 18 hours. The heating produced rounded grains with average sizes ranging from 0.12 to 0.23 μm (Table 1). Samples H5 and H6, commercial hematite powders from Pfizer Inc., were heated in air for 5 hours at 500°C to convert any other forms

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Table 1. Sizes and Magnetic Properties of Hematite Samples

Sample	d (nm)	T_M (K)	μ_0H_C (mT)	M_{RS}/M	M (kA/m)
H1	234 ± 49	243	200	0.650	1.27
H2	193 ± 59	241	140	0.715	1.23
H3	165 ± 49	243	200	0.624	1.25
H4	117 ± 39	241	195	0.693	1.25
H5	360 ± 110	230	255	0.656	1.22
H6	420 ± 180	246	272	0.605	1.24
H7	60 × 520	248	150	0.500	1.19

of iron oxide to α Fe_2O_3. The median sizes after heating are 0.36 and 0.42 μm. Sample H7 contains acicular particles of average diameter 0.06 μm and length 0.52 ± 0.16 μm prepared by heating a Pfizer lepidocrocite at 700°C in air for 19 hours. Grain-size distributions were measured with a Hitachi S-4500 scanning electron microscope operated at 10 kV. The microcrystals were also examined with a Siemens D5000 X-ray diffractometer with Co Kα radiation. All samples had well-defined hematite diffraction patterns. No iron-containing impurities were detected.

[8] High-field thermomagnetic curves measured with a vibrating-sample magnetometer (VSM) gave hematite Néel temperatures of 680–690°C, in close agreement with thermal demagnetization curves of TRMs. Room-temperature hysteresis loops measured with the VSM did not close. The maximum field of 1.5 T was not enough to saturate the magnetization, so that M, M_{RS}, and H_C in Table 1 are non-saturation values of magnetization, isothermal remanence, and coercive force. They are nevertheless high. H_C ranges from 140 to 272 mT, 10^3–10^4 times typical terrestrial field strengths. M_{RS}/M for H1–H6 varies from 0.61 to 0.72, intermediate between expected SD values of 0.50 for uniaxial (magnetoelastic) anisotropy and 0.75 for triaxial (magnetocrystalline) c-plane anisotropy [*Dunlop*, 1971]. The very high H_C's imply that magnetoelastic anisotropy due to internal stresses is dominant because c-plane crystalline anisotropy is small, at least in large crystals [*Sunagawa and Flanders*, 1965; *Porath*, 1968]. However, only the acicular hematite (H7) has a purely uniaxial remanence ratio of 0.5.

[9] "Saturation" isothermal remanent magnetization (SIRM) produced in a 2.5 T field at 300 K was measured continuously during zero-field cooling to 20 K and back to 300 K with an MPMS-2 SQUID magnetometer (Figure 1). The remanence decreased precipitously in passing through T_M. 97–99% of the remanence is lost with the disappearance of spin-canting and the onset of c-axis antiferromagnetism. The defect remanence, which survives below T_M, is only 1–3% of the remanence above T_M and is constant between T_M and 20 K. There is no sign of a magnetite Verwey transition around T_V = 120 K, confirming that the samples are free of ferrimagnetic impurities.

[10] In warming back through T_M, ≈30% of the high-temperature remanence was recovered in its original direction. Since spin-canted ferromagnetism vanishes below T_M, the small defect remanence is likely responsible for renucleating this "memory" spin-canted remanence in a preferred direction in the warming half of the cycle. All the hematites showed well-defined Morin transitions with $T_M \approx$ 240–248 K in warming curves. These T_M values are less than the 250–260 K generally reported for large crystals of hematite, probably because of the fine particle size [*Muench et al.*, 1985]. Our samples also exhibit a thermal hysteresis: the values of T_M in cooling and in heating are different. This ΔT_M implies a thermal lag in the orientation of spins parallel or perpendicular to the c-axis.

[11] TRM experiments were carried out on 1 cm × 1 cm cylindrical samples containing 50% by weight α Fe_2O_3 dispersed in non-magnetic CaF_2. Samples were first heated to 705°C and cooled in zero field to establish a standard initial state. Samples were given TRMs by cooling from 705°C in a 1 mT field in a non-inductive furnace and were later thermally demagnetized in zero field in the same furnace. LTC was carried out by cooling freshly produced TRMs to 77 K in a dewar, allowing the temperature to equilibrate for 30 min, and warming back to room temperature, all in zero field in a 6-layer mu-metal shield. The resulting TRM memories were then thermally demagnetized.

3. TRM and TRM Memory

[12] TRM's were strong and very hard for all hematites. AF demagnetization to 100 mT had no effect. Thermal demagnetization had a minimal effect on TRM in heating steps up to 600°C (Figure 2). From ≈625°C, TRM decreased sharply, reaching zero at 680–690°C. TRM intensity M_{TRM} is 0.13–0.55 kA/m and increases with increasing grain size in the range 0.12–0.42 μm (Figure 3).

[13] LTC permanently demagnetized ≈60% of the original TRM (Figure 2). The memory fraction of TRM recovered after LTC was also very resistant to thermal demagnetization, with unblocking temperatures T_{UB} > 600–625°C. There was no decrease in the TRM memory, in fact a slight increase, in heating to 600°C (Figure 2). The original TRM direction was recovered after LTC, implying (as for SIRM) that defect remanence must be responsible for regenerating the memory.

4. Discussion

[14] The TRMs of all submicron hematites have stable SD properties: high intensities, unblocking temperatures, and AF coercivities. Evidence of the stable SD state is also

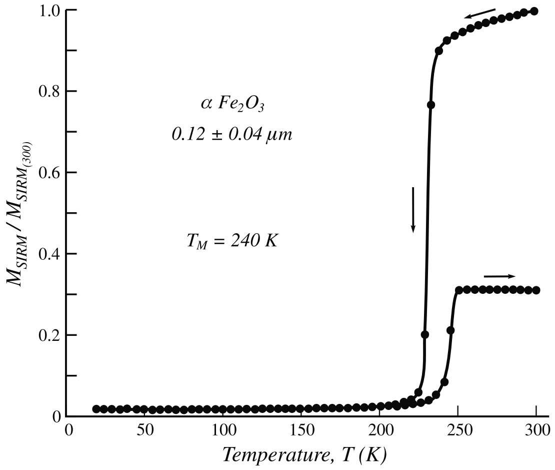

Figure 1. Normalized zero-field cooling and warming curves of SIRM for the 0.12 μm hematite (H4). T_M is obtained from the warming curve.

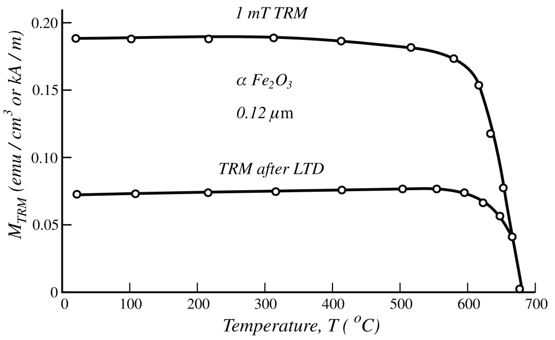

Figure 2. Stepwise thermal demagnetization of 1-mT TRM before and after LTD for the 0.12 μm hematite (H4). TRM and TRM memory both demagnetize mainly above 600°C.

clear in hysteresis results. A 1.5 T field was not enough to saturate the magnetization, and M_{RS}/M and H_C values were very high (Table 1). This hard SIRM, and presumably also the TRM, are controlled by the c-plane anisotropy, which combines uniaxial magnetoelastic and triaxial magnetocrystalline anisotropies.

[15] The TRM intensity in a field H = 1 mT ranges from 0.13 to 0.55 kA/m. The *Néel* [1955] theory of aligned uniaxial SD particles of volume V, blocking temperature T_B and spontaneous magnetization M_S (T) predicts a TRM intensity

$$M_{TRM} = M_{RS} \tanh[\mu_o V\, M_S(T_B) H/kT_b]. \qquad (1)$$

TRM intensities calculated from (1) using experimental values of M_{RS}, V, M and T_B agree well with measured M_{TRM} values (Figure 3). The small discrepancies may be due to differences between the model and the real assemblages (ranges of T_B, randomly oriented axes, non-uniaxial anisotropy).

[16] Equation (1) predicts an increase in M_{TRM} with increasing grain size. A bilogarithmic plot of M_{TRM} versus grain diameter d for our hematites (Figure 3) gives $M_{TRM} \propto d^n$ with n = 1.04 ± 0.03. M_{TRM} thus increases an order of magnitude for each decade increase in grain size.

[17] Some published TRMs in the 1–100 μm size range have an $M_{TRM} \propto$ d dependence similar to our data but values are an order of magnitude lower than our extrapolation [*Hartstra*, 1982; *Dekkers and Linssen*, 1989]. On the other hand, hematite crystals many hundred μm in size may contain only two major domains [*Halgedahl*, 1995], suggesting that the effective SD upper limit may be >15 μm. Although TRM intensities in submicron hematites are lower than MD TRMs (for H = 0.1 mT), it seems plausible that >5–10 μm SD hematites on Mars [*Christensen et al.*, 2000] could have TRMs as strong as MD hematites.

[18] After cycling through T_M, ≈40% of TRM and ≈30% of SIRM were recovered with their directions unchanged. Since all spin-canting disappears in cooling through the transition, as spins rotate from the rhombohedral c-plane to the c-axis, all memory should be lost. It is therefore remarkable that ≥30% of the remanences were recovered, in their original directions, in warming back through T_M. With a choice of several equivalent easy axes due to combined triaxial and uniaxial anisotropies within the c-plane and no external field acting, how do so many spin-canted moments remember their previous orientations? The connection is likely through the defect moments because only they survive below T_M. The TRM memory is very similar in its thermal stability to the original TRM (Figure 2), so this is not a case of selective removal of less stable remanence as in the case of LTC of magnetite through the Verwey transition. All the spin-canted moments are likely nearly equivalent in the strength of their pinning by c-plane anisotropy. Those that are able to couple to the much smaller defect moments recover their original directions and constitute the memory fraction.

[19] *Smith and Fuller* [1967] measured the temperature variation of SIRM of a large hematite crystal during LTC from 300 K to 213 K and back to 300 K. They observed that 35% of the SIRM was not demagnetized below T_M. This remanence is 52% of the SIRM memory at room temperature, leading them to suggest that the stable remanence of hematite below and above the Morin transition is basically due to a defect or structure-sensitive magnetism.

[20] We observe just the opposite. The surviving defect moment below T_M is only 1–3% of the room-temperature SIRM or 2–6% of the SIRM memory (Figure 1). The structure-sensitive moment by itself is an insignificant contributor to the observed TRM memory in our SD hematites. Its important role is as a "catalyst" in regenerating the memory during warming through the Morin transition. Stable TRM memory, with very high coercivities and no unblocking temperatures below 600°C, is overwhelmingly due to the hard spin-canted moment, pinned mainly by uniaxial magnetoelastic c-plane anisotropy.

5. Implications for Martian Magnetic Anomalies

[21] Present-day Mars is a very cold planet, surface temperatures averaging ≈220 K globally [*Jakosky and*

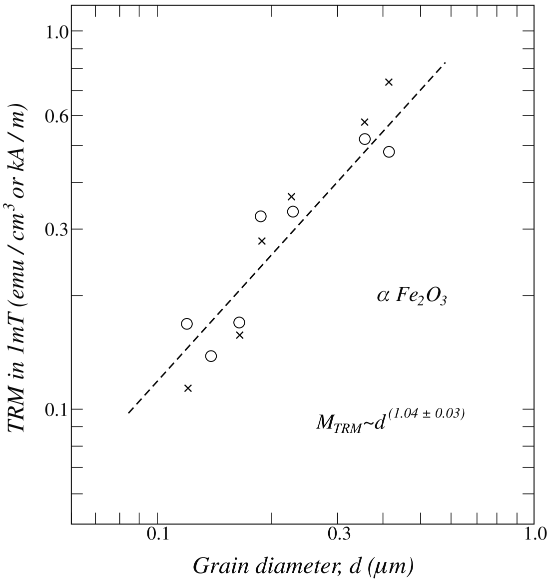

Figure 3. Grain-size dependence of TRM intensity for the present hematites. The dashed line has slope 1.04, showing that M_{TRM} is very nearly proportional to d. Open circles: experimental data points; crosses: theoretical TRM values from Néel single-domain theory.

Phillips, 2001]. Surface temperatures vary with time of day, season, and latitude from ≈148 K in the polar night to a maximum of ≈273 K at midday near the equator during the Martian summer [*Carr*, 1996]. Where surface temperatures are lower than the Morin transition (240–260 K), SD hematite will not contribute to Martian magnetic anomalies. Near the equator during Martian summer, the very stable magnetic memory of SD hematite, ≈40% of original TRM, could contribute partially to the Martian magnetic signal.

[22] The deep Martian crust has higher temperatures than the surface, although the thermal gradient is suggested to be only ≈10 K/km [*Hoffman*, 2000]. At the latitude of the major southern hemisphere anomalies (−30° to −80°), hematites in the deeper crust are more plausible anomaly sources than surface hematites which must have cycled repeatedly through the Morin transition. *Nagata et al.* [1961] showed that repeated cycling through T_M had only a very minor effect on TRM memory of synthetic hematite powders (grain size unspecified but probably similar to our SD hematites); the loss and recovery of TRM memory were almost perfectly reversible after the first cooling-warming cycle.

[23] Both SD and MD hematites have substantial memories (measured only for SIRM in the MD case, but assumed to be true for TRM also). The difference between the two is in the proportion of defect or structure-sensitive magnetism in the memory and the overall stability of remanence. *Haigh* [1957] made a careful separation of the magnetic behavior of the defect and spin-canted components of ferromagnetism (called by him the isotropic and anisotropic ferromagnetism, respectively). The spin-canted moment had a remanent coercivity H_{CR} = 480 mT, comparable to the H_C values we observe for our samples, while the defect moment was about ten times less coercive (H_{CR} = 43 mT). These are both substantial coercivities, certainly adequate to ensure stability of SD memory against later field changes, e.g., the death of Mars' dynamo field early in its history. The stability of MD hematites is lower. *Kletetschka et al.* [2000] found H_C = 2–10 mT for massive hematites, probably sufficient to ensure stability against field changes over geological times [*Dunlop and Kletetschka*, 2001]. However, the defect moment is potentially stress-sensitive and its stability against impact events in Martian history is less clear. This could be one reason for the lack of magnetic anomalies in cratered regions of the southern highlands, e.g., the Argyre and Hellas basins.

6. Conclusions

1. Single-domain hematites with sizes between 0.12 and 0.42 μm carry a strong and stable TRM.
2. The TRM memory after LTC is also very stable against thermal and AF demagnetization.
3. Stable TRM and memory with very high coercivities and unblocking temperatures are due to hard spin-canted ferromagnetism, not to defect ferromagnetism. However, the defect moment seems to couple to the spin-canted moment and renucleate memory in warming through T_M.
4. TRM of SD hematites in the Martian crust and on Mars' surface where temperatures exceed the Morin transition may contribute to Martian magnetic anomalies.

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Ö. Özdemir and D. J. Dunlop, Geophysics, Department of Physics, University of Toronto at Mississauga, Mississauga, Ontario L5L 1C6, Canada.