Thermoremanent magnetization of multidomain hematite

Ozden Ozdemir and David J. Dunlop

Department of Chemical and Physical Sciences, University of Toronto at Mississauga, Mississauga, Ontario, Canada

Received 5 May 2005; revised 14 June 2005; accepted 28 June 2005; published 24 September 2005.

[i] We have studied thermoremanent magnetization (TRM) produced by fields of 10-140 u.T in the (0001) basal plane of a 10 x 6 x 2 mm natural single crystal of hematite, both before and after zero-field cycling through the Morin transition at T_M = 260 K. Stepwise thermal demagnetization of TRM indicated high-unblocking temperatures between 680°C and the Curie-Neel temperature T_N = 690°C. In contrast, TRM was easily demagnetized by alternating fields, TRM intensity decreasing exponentially with increasing field in typical multidomain fashion. The observed 100-μT WTRM is 1.1 kA/m. This strong TRM, almost equal to the saturation remanence, results from hematite's weak internal demagnetizing field. Domain walls move almost unhindered to their limiting positions, and TRM intensity approaches saturation. On cooling through *TM,* spins rotate to the antiferromagnetic *c* axis, and hematite's weak ferromagnetism is largely lost. However, on reheating in zero field through T_M, as the spins rotate back into the basal plane, a "memory" remanence is regenerated in the original TRM direction. This TRM memory was about 25% of M_{TRM} for our crystal and was even more resistant to thermal demagnetization than the original TRM. The 25% memory of TRM is similar to that of 0.12- to 0.42-μm single-domain hematites. High-unblocking-temperature TRM and TRM memory must be due to magnetoelastic pinning of spins in the basal plane by lattice defects, because both TRM and memory decrease with high-temperature treatment, which anneals out defects. The memory phenomenon seems to be in essence an amplification of residual magnetism that survives below the Morin transition. Remanence produced in a demagnetized sample below T_M and room temperature remanence that has been cooled through T_M increase in identical ways on warming through the transition. We propose that small regions of canted spins, pinned by crystal defects, remain below T_M when the bulk of spins have aligned with the antiferromagnetic *c* axis. These nuclei serve to regenerate room temperature domain structure and remanence in warming through T_M.

Citation: Ozdemir, O., and D. J. Dunlop (2005), Thermoremanent magnetization of multidomain hematite, *J. Geophvu. Res., Ill),* B09104, doi: 10.1029/2005JB003820.

1. Introduction

[2] Hematite (a-Fe_2O_3) is a common oxide mineral on Earth and Mars. It is antiferromagnetic (AF), the spin sublattices lying along the rhombohedral *c* axis at temperatures below the Morin transition (T_M = 260 K) and in the (0001) *c* plane above T_M. The basal plane of hematite's thin platy crystals is (0001).

[3] Hematite is of paleomagnetic interest because above T_M its antiferromagnetism is not perfect. Spins lie in the basal plane but are canted out of exact antiparallelism by a very small angle (~0.13°), creating a weak ferromagnetism (WF) in the basal plane perpendicular to the spin sublattices. The WF moment amounts to ~2 kA/m, ~0.2% of either sublattice magnetization. Triaxial magnetocrystalline anisotropy within the basal plane is usually overshadowed by uniaxial or triaxial anisotropy of magnetoelastic origin. This anisotropy governs WF remanence directions within the basal plane. A much stronger anisotropy binds the AF sublattices parallel or perpendicular to the *c* axis. *Neel and Pauthenet* [1952] measured an almost temperature-independent AF susceptibility of ~ 1.2 x 10^{-3} SI above' and below T_M, implying that a field of ~100 T would be required to pull antiparallel spins away from their preferred axis into ultimate alignment. Before this can happen, the spin lattices will rotate 90°, but this "spin flopping" itself requires a field of 16.2 T at temperatures well removed from T_M *[Foner and Shapiro.,* 1969; *Shapira,* 1969].

[4] Although hematite is, in principle, perfectly AF below T_M *[Dzyaloshinsky,* 1958], it has been known since the time *of Neel and Pauthenet* [1952] that some remanence survives below T_M when hematite crystals are cooled through the WF —> AF transition. In the present paper we will show that it is not necessary to magnetize the WF phase above T_M and to cool it through the transition: A field applied to a demagnetized sample at low temperature produces a remanence directly. In either case, wanning the sample through

0148-0227/05/2005JB003820S09.00

T_M in the absence of a field results in a spontaneous increase in the remanence (by a factor of 20–25 for the crystal studied in this paper).

[5] The remanence after warming through T_M is usually called the memory. What is being remembered is the low-temperature remanence, which nucleates or renucleates domains in the WF phase above T_M. One of the purposes of this paper is to shed light on the mechanism by which this occurs.

[6] Hematite is often a secondary mineral in oxidized sediments and sedimentary rocks, but it can also be a primary product of high-temperature oxidation of titanomagnetite in basaltic magmas or a product of high-temperature metamorphism. If the hematite is produced above its Curie-Néel temperature (T_N = 675°C–690°C), it will acquire thermoremanent magnetization (TRM) when cooled in the Earth's magnetic field. If hematite production continues below T_N, thermochemical remanent magnetization will result. If the hematite is produced close to ambient temperature, e.g., by inversion of low-temperature oxidation products like maghemite or titanomaghemite, chemical remanent magnetization results.

[7] In this paper we focus attention on TRM of hematite. In part, this is because of recent interest in hematite as a possible source of strong crustal magnetization on Mars [*Kletetschka et al.*, 2000; *Dunlop and Kletetschka*, 2001; *Özdemir and Dunlop*, 2002; *Dunlop and Arkani-Hamed*, 2005]. It is known that multidomain (MD) hematite can have unexpectedly intense TRM, but the long-term stability of that TRM to changing fields, heating, and cycling through T_M, all of which could happen in the Martian crust, is not well investigated. We contrast the TRM properties of MD hematite with the better known and understood properties of single-domain (SD) hematite [*Dunlop*, 1971].

2. Sample Characterization

[8] Magnetic measurements were carried out on a 10 × 6 × 2 mm natural crystal of hematite from Ontario and on subsamples of the same crystal. The 10 × 6 mm surfaces are (0001) crystal faces; they are smooth and mirror-like with a metallic luster. Five 0.05-mm-thick subsamples 1–3 mm in size were cleaved from the crystal. These flakes were used for thermomagnetic, electron microprobe, and X-ray analyses and for hysteresis and low-temperature cycling.

[9] X-ray powder diffraction using a Siemens D5000 diffractometer with Co Kα radiation gave hexagonal unit cell edge values a = 5.040 ± 0.002 Å and c = 13.742 ± 0.007 Å, in good agreement with standard values of 5.034 and 13.752 Å for hematite (American Society for Testing and Materials data file 13-534). The composition of the crystal was also determined using a Cameco SK-50 electron microprobe. The (0001) plane was probed for Fe, O, and seven other elements. Each element was measured at five different locations. The analyses gave 68.30 ± 0.25 wt % Fe, close to the theoretical value of 69.94%. The oxygen concentration was 31.56 ± 0.11 wt %. The crystal is almost stoichiometric hematite with no major impurities.

[10] A high-field thermomagnetic curve was measured on the third subsample using a Princeton Measurements Corporation microvibrating sample magnetometer (PMC micro-VSM). Saturation magnetization M_s was almost temperature-independent between 20°C and 500°C, then decreased strongly above 600°C, and disappeared around 690°C (Figure 1). This value agrees with the Mössbauer determination of the temperature at which the weak ferromagnetism disappears [*Freier et al.*, 1962] and with T_N as measured by *Kaye* [1961].

[11] The fourth subsample was cooled in nominally zero field (<300 nT) to 20 K, where it was given a saturation isothermal remanent magnetization (SIRM) by applying a 2.5-T field in the (0001) plane parallel to the sample's long axis and then warmed to 300 K in zero field. Magnetization was monitored during warming using a Quantum Design MPMS2 superconducting quantum interference device magnetometer. Between 20 and 250 K, M_{rs} was temperature-independent (Figure 2a). On warming through the Morin transition around T_M = 260 K a massive increase in remanence accompanies flopping of spins from the AF c axis to the (0001) basal plane. For convenience of comparison, Figures 2a and 2b are both normalized to magnetization at 300 K, but if Figure 2a were normalized instead to the 20-K SIRM, the jump would be to a value of ~25. The sharp remanence transition at a temperature close to T_M = 261.5 K, as measured by *Flanders* [1969] for pure synthetic hematite, shows that our crystal is stoichiometric hematite. Even small amounts of cation impurities would broaden the transition and lower T_M [*Morin*, 1950; *Haigh*, 1957; *Kaye*, 1962; *Besser et al.*, 1967]. In further warming above T_M the SIRM remained essentially constant.

[12] A different SIRM was produced by applying a 2.5-T field in the basal plane of the same subsample at room temperature. Subsequent zero-field cooling and warming curves are shown in Figure 2b. In cooling from 300 to 270 K the remanence was almost constant. At the Morin transition the magnetocrystalline anisotropy constants pass through zero and change sign, and spin-canted magnetism vanishes [*Besser et al.*, 1967]. By 260 K, 98% of the initial SIRM had disappeared. Between T_M and 20 K the residual 2% of the original remanence remained constant. As the crystal warmed from 20 K, the remanence retraced the cooling curve and then increased in crossing the Morin transition. There is a small thermal hysteresis: T_M is slightly higher on warming than on cooling. Above T_M, 37% of the original room temperature SIRM was recovered. This is a large SIRM memory. Submicron SD hematites have memory ratios of ~30% [*Özdemir and Dunlop*, 2002], and possibly less well crystallized natural hematites (from <5 μm to 100–150 μm in size) have 50–80% memories [*Hartstra*, 1982].

[13] After completion of TRM experiments, room temperature saturation hysteresis was measured in the (0001) plane of the 10 × 6 × 2 mm crystal using a Princeton Applied Research large-sample vibrating sample magnetometer in a maximum 1-T field. The measured saturation magnetization M_s was 0.38 A m^2/kg (2.0 kA/m), very close to M_s = 0.4 A m^2/kg for pure single-crystal hematites [*Flanders and Remeika*, 1965; *Voigt et al.*, 1971]. Large hematite crystals have low coercive forces H_c, 0.35–3.2 mT for synthetic crystals [*Flanders and Remeika*, 1965] and 1.1–6.5 mT for natural crystals with simple twins [*Sunagawa and Flanders*, 1965]. H_c = 2.8 mT for our crystal, relatively high for such a large crystal. Shape anisotropy is negligible because hematite has such a small

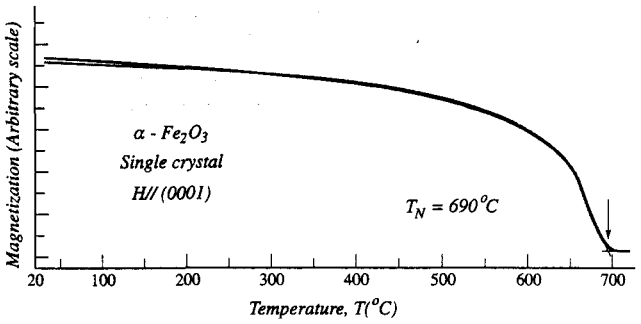

Figure 1. Strong field thermomagnetic curve for a 3-mm hematite crystal (subsample of the main crystal). The field was applied in the (0001) basal plane. See color version of this figure in the HTML.

M_s. The basal plane magnetocrystalline anisotropy of hematite crystals is also very small. The observed coercive force may be controlled by the triaxial basal plane anisotropy associated with multiple twins [*Porath and Raleigh*, 1967]. The saturation remanence ratio M_{rs}/M_s was 0.69, intermediate between 0.5–0.637 for uniaxial magnetoelastic anisotropy and 0.75–0.955 for planar triaxial anisotropy [*Dunlop and Özdemir*, 1997, chapter 11]. A mixture of both types of anisotropy is likely.

[14] An independent hysteresis loop was measured on the fifth subsample using a PMC micro-VSM (Figure 3). Fields were applied in the (0001) plane up to a maximum of 1.5 T. The measured parameters are M_s = 0.36 A m^2/kg, M_{rs}/M_s = 0.87, H_c = 8.7 mT, and H_{cr}/H_c = 1.07, where H_{cr} is remanent coercive force. The remanence ratio is significantly higher than that of the parent crystal and favors triaxial basal plane anisotropy.

[15] We make comparisons throughout the paper with a SD hematite, sample H1 of *Özdemir and Dunlop* [2002] (average grain size of 0.23 μm). H1 was prepared by heating cube-shaped magnetite crystals at 700°C in air for 18 hours. The rhombohedral unit cell dimensions a = 5.037 ± 0.002 Å and c = 13.757 ± 0.007 Å and the Néel temperature T_N = 685°C indicate that the sample is free of ferrous iron. The SD hematite showed a well-defined Morin transition with T_M = 243 K. This value is less than T_M = 260 K for our MD single crystal. This is probably because of fine grain size [*Bando et al.*, 1965], although almost defect-free 0.2-μm crystals can have T_M as high as 256 K [*Goya et al.*, 2005]. The hysteresis curve for the SD hematite is a minor loop even at 1.5 T. The nonsaturated hysteresis parameters are M_s = 0.24 A m^2/kg, M_{rs}/M_s = 0.65, and H_c = 200 mT.

3. TRM Experiments

[16] TRMs were produced parallel to the (0001) plane of the 10 × 6 × 2 mm crystal by cooling from 710°C, in fields ranging from 10 μT to 1 mT. TRM experiments for the 0.23-μm hematite were carried out on 1 × 1 cm cylindrical samples containing 50% by weight hematite dispersed in nonmagnetic CaF_2. TRMs were produced in a water-cooled noninductive resistance furnace within a set of Helmholtz coils, and their stability was tested by

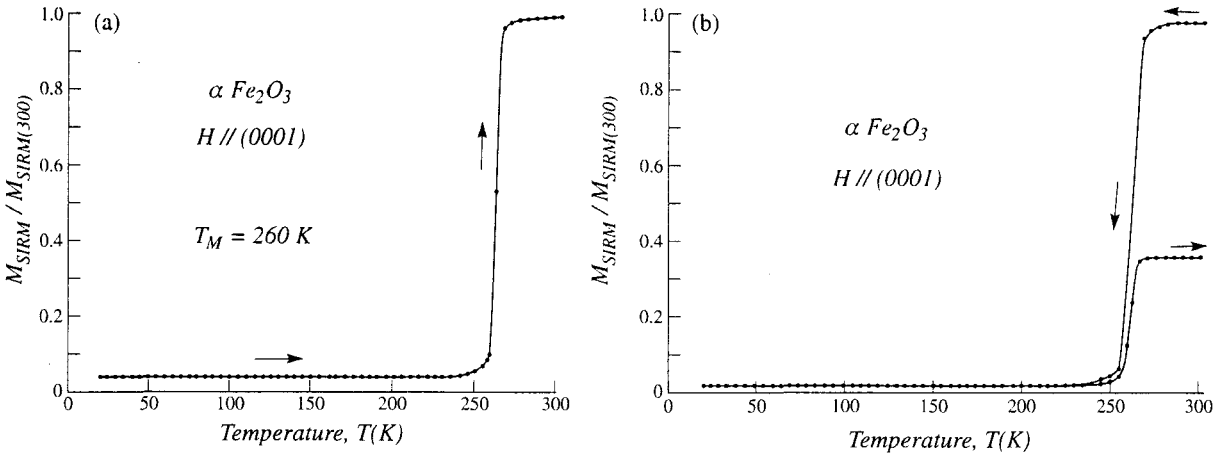

Figure 2. (a) Zero-field warming curve of saturation remanence M_{SIRM} for a 3.5-mm hematite crystal (subsample). The crystal was cooled in zero field from 300 to 20 K, where a 2.5-T field was applied parallel to (0001). The crystal acquired a remanence, although it is nominally in a purely antiferromagnetic state at 20 K. This low-temperature moment is probably due to a small fraction of spins that are not aligned with the antiferromagnetic c axis. A sharp increase in remanence at 260 K marks the onset of weak ferromagnetism in the basal plane. The high-temperature remanence is in the same direction as the much smaller 20-K saturation isothermal remanent magnetization (SIRM), which served to nucleate it. (b) Normalized temperature dependence of SIRM produced by a 2.5-T field applied in the (0001) basal plane of the same crystal at 300 K, during zero-field cooling from 300 to 20 K and warming back to 300 K. A large fraction of the initial SIRM demagnetized at T_M (260 K) with the disappearance of spin canting. The low-temperature remanence or defect moment, which survives below T_M is 2% of the original 300-K SIRM and is constant between T_M and 20 K. About one third of the initial remanence is recovered on warming through T_M. This memory phenomenon presumably originates in a coupling between weakly ferromagnetic nuclei below T_M and the spin-canted phase above T_M, similar to that evidenced in Figure 2a.

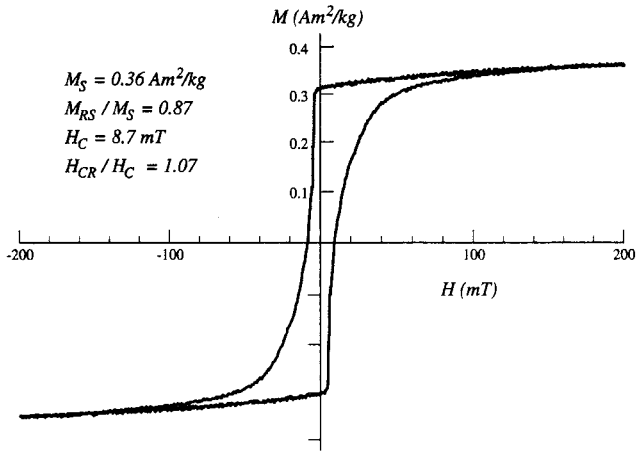

Figure 3. Saturation hysteresis measured at room temperature with a Princeton Measurements Corporation microvibrating sample magnetometer for a 3-mm flake of the main crystal. Fields were applied in the (0001) basal plane of the crystal.

alternating field and stepwise thermal demagnetization. Low-temperature demagnetization (LTD) was carried out by cooling freshly produced TRMs to 77 K in a liquid N_2 dewar, allowing the temperature to equilibrate for 30 min and warming back to room temperature, all in the zero-field (<10 nT) environment of a six-layer μ-metal shield. TRM memory, the remanence fraction surviving LTD, was then demagnetized thermally and by alternating fields.

[17] TRM intensity for the single crystal rises very rapidly with increasing field (Figure 4). When H = 20 μT, M_{TRM} has an intensity of 0.83 kA/m, about 50 times greater than SD TRM, which is limited by thermal fluctuations [*Özdemir and Dunlop*, 2002]. The rise to saturation is almost complete by 100 μT. The observed strong TRM in our MD crystal is due to hematite's weak spontaneous magnetization (M_s = 2.0 kA/m) and resulting weak self-demagnetizing field H_d. At saturation, H_d is only 0.8 mT, so domain walls move almost unhindered to their limiting positions and M_{TRM} approaches saturation ($M_{rs} \approx$ 1.4 kA/m) in quite small fields.

[18] Alternating field demagnetization of the 0.1-mT TRM of the large crystal reveals two distinct fractions (Figure 5a). The low-coercivity ("soft") fraction, representing about 75% of the TRM, decreases exponentially, which is characteristic MD behavior, and has a median destructive field of ~3.5 mT, about equal to H_c. The "hard" fraction, isolated above 20–40 mT, is hardly affected by fields of 100 mT. Its behavior is similar to that of the 0.23-μm SD hematite. *Syono et al.* [1962] observed a similar demagnetization curve of TRM for a large crystal of hematite. In their case the hard fraction isolated after 20-mT demagnetization was one third of the original TRM.

[19] About 25% of a freshly produced 0.1-mT TRM survives zero-field cycling to 77 K (Figure 5b). This is less than the SIRM memory of 37% for a 3.5-mm subsample of the same crystal (Figure 2b). Alternating field cleaning of the TRM memory reveals the same soft and hard fractions seen in the original TRM but in different proportions. The soft, exponentially decaying fraction is approximately two thirds of the TRM, and the hard fraction has increased to approximately one third.

[20] Thermal demagnetization had a minor effect on the TRM of the large crystal in heating steps up to 680°C (Figure 6). Ninety-five percent of the TRM unblocking temperatures T_{UB} are >683°C. The TRM memory after LTD was even more resistant to thermal demagnetization, with T_{UB} > 694°C. TRM and its memory are both univectorial remanences parallel to the applied field that produced the TRM.

[21] Annealing reduces the internal strains and stresses produced by crystal defects [*Gallon*, 1968; *Keeling*, 1972]. To study the effect of annealing on TRM and its memory, the large single crystal was heated in zero field (<100 nT) in air at 600°C for 3 and 5 hours using a Schonstedt thermal demagnetizer. The sequence of the annealing experiments was as follows: (1) thermally demagnetize the crystal at 705°C and anneal for 3 hours, (2) produce 0.1 mT TRM and measure M_{TRM}, (3) induce LTD by cooling the crystal to 77 K in liquid N_2 and measure the TRM memory, and (4) repeat 1 to 3 for 5-hour annealing experiments.

[22] The intensity of TRM decreased ~8% after 3 hours annealing (Figure 7). However, the intensity of the TRM memory was reduced much more, by ~30%. Five hours of annealing had little further effect. Annealing apparently reduced the number of strain centers but did not completely

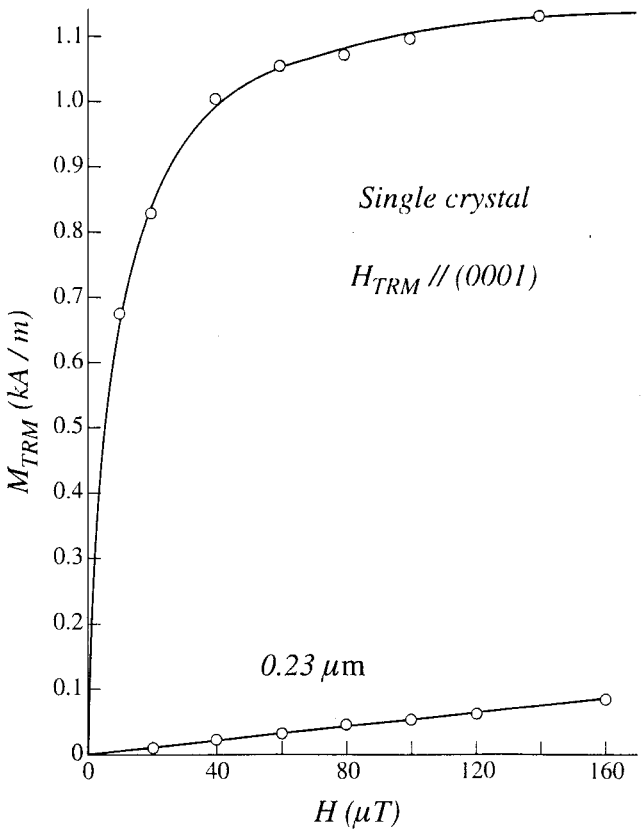

Figure 4. Acquisition of thermoremanent magnetization (TRM) in fields ranging from 10 to 160 μT, applied in the (0001) basal plane, for multidomain (MD) (10 × 6 × 2 mm crystal) and single-domain (SD) (0.23 μm) hematites. The MD crystal has a stronger TRM than the SD hematite at all fields and approaches saturation in 160 μT.

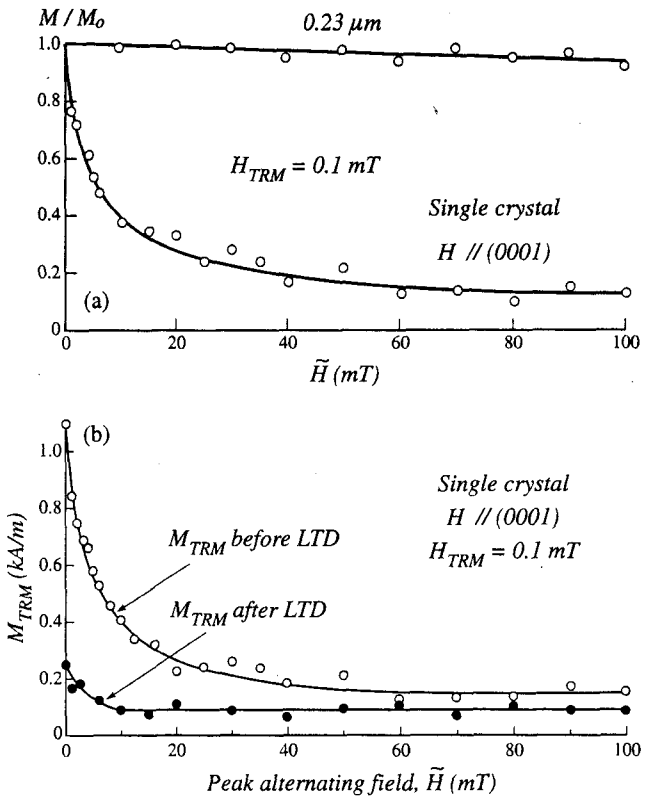

Figure 5. (a) Alternating field demagnetization of 0.1-mT TRMs for SD and MD (10 × 6 × 2 mm) hematites. SD TRM is very hard; fields up to 100 mT had no effect. MD TRM has two distinct regions: a soft, exponentially decreasing remanence due to loosely pinned domain walls and a hard fraction isolated above 30 mT. (b) Demagnetization of 0.1-mT TRM before and after low-temperature demagnetization (LTD) for the 10 × 6 × 2 mm hematite crystal. A large fraction of the exponentially decreasing low-coercivity component has been destroyed by LTD. However, the TRM memory has generally similar features to the original TRM, on a reduced scale.

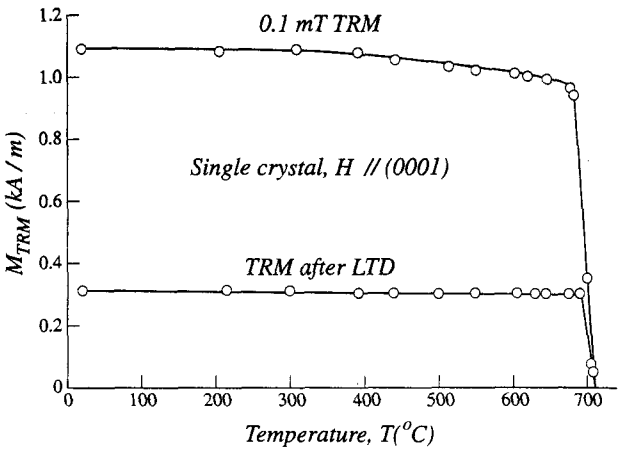

Figure 6. Stepwise thermal demagnetization of 0.1-mT TRM before and after LTD for the 10 × 6 × 2 mm hematite crystal. The TRM and its memory have no unblocking temperatures T_{UB} < 680°C.

remove all of them. The memory seems to be pinned magnetoelastically by dislocations or other crystal defects.

4. Discussion

4.1. TRM Before LTD

[23] With a magnetizing field of only 0.1 mT our large hematite crystal acquired a very strong TRM, M_{TRM} = 1.1 kA/m, ~80% of the saturation remanence produced at room temperature by much larger fields. Previous authors have reported a similar tendency for the TRM of MD hematite to approach saturation in weak fields similar to the Earth's magnetic field. Our TRM data, for the millimeter-sized crystal and for 0.23 μm SD hematite grains, are compatible with the variation found by *Hartstra* [1982] and *Kletetschka et al.* [2000] for natural hematites in the 1–1000 μm size range. The dashed line in Figure 8 shows the theoretical saturation TRM for MD hematite predicted by *Néel*'s [1955] theory [*Dunlop and Kletetschka*, 2001]. Our single-crystal TRM agrees well with the theory and with other experimental data.

[24] Weak field TRM is intense in MD hematite because the applied field is almost unopposed by self-demagnetization. The internal demagnetizing field $H_d = -NM_s$, where N is the demagnetizing factor (~1/3 in SI or $4\pi/3$ in cgs for equidimensional crystals). Because hematite's spontaneous magnetization M_s is so small (~2 kA/m (or ~2 emu/cm^3) for our crystal at room temperature T_0), H_d is correspondingly small, <1 mT at T_0 and even smaller in the TRM blocking range just below T_N. Domain walls can move far from their demagnetized positions in quite weak fields, and M_{TRM} approaches M_{rs} (Figure 4).

[25] The MD TRM was very hard. Thermal demagnetization had a minimal effect on TRM in heating steps up to 683°C (Figure 6). This must be due to strong domain wall pinning by crystal defects. The kinds of defects that can pin walls in natural single crystals of hematite are volume defects like voids and nonmagnetic inclusions [*Flanders*

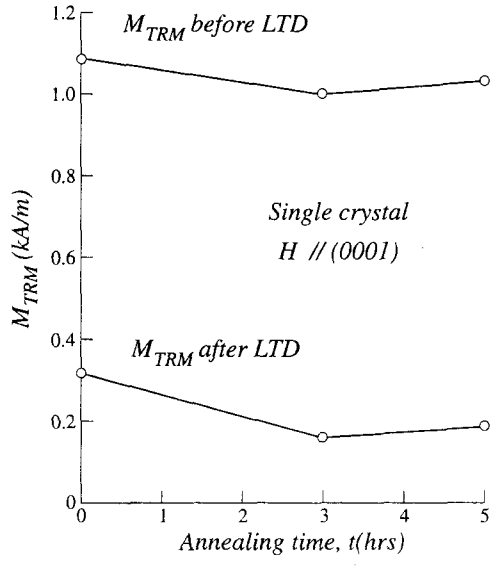

Figure 7. Intensity of 0.1-mT TRM before and after low-temperature demagnetization as a function of annealing time for the 10 × 6 × 2 mm hematite crystal.

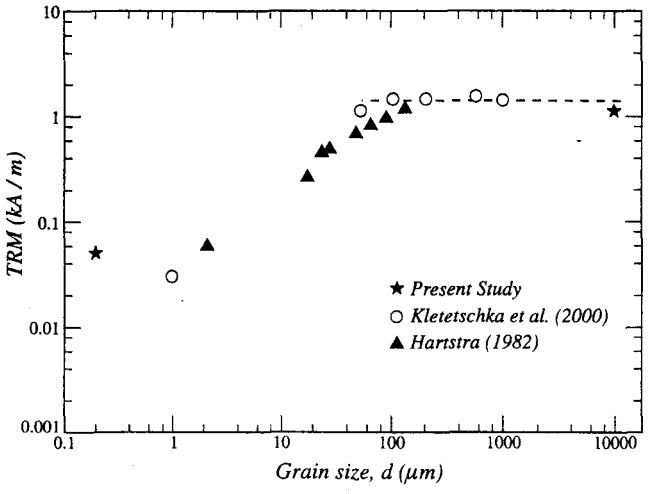

Figure 8. Grain size dependence of the intensity of 0.1-mT TRM in hematite. The dashed line is the saturation TRM for MD hematite predicted by *Néel*'s [1955] theory.

and Remeika, 1965], line and planar defects like screw dislocations [*Sunagawa*, 1960], twin boundaries, and irregularities such as misoriented crystallites. *Sunagawa and Flanders* [1965] found that natural hematites containing twinned and misoriented crystals have higher coercive forces and triaxial anisotropies. Growth and deformational twinning occur during crystal growth [*Putnis*, 1992]. *Halgedahl* [1998] observed that hard wall-pinning sites are associated with hematite platelets cleaved from larger parent crystals. These imperfections introduce a strain-stress distribution in the crystal. The weakly ferromagnetic moment is coupled magnetoelastically to the strain distribution.

[26] Nuclear magnetic resonance (NMR) studies of the WF phase confirm that a large fraction of domain walls are strongly pinned at localized strains [*Hirai et al.*, 1971; *Searle et al.*, 1972]. Strongly pinned 180° domain walls in hematite are responsible for the largest contribution to the positive phase NMR signal. Strong wall pinning is confirmed by magnetoelastic resonance experiments on synthetic single crystals of hematite [*Maartense and Searle*, 1971]. Coupling of the crystal's acoustic resonance modes with low-lying spin wave modes excited near local strains resulted in magnetoelastic waves. Strongly pinned domain walls are the presumed source of the hard TRM that demagnetizes only at very high temperatures in our crystal.

[27] Why is TRM so much less resistant to alternating fields than to heating (Figures 5a and 5b)? One possibility is that more walls nucleate in alternating fields than in TRM production. This is the case in titanomagnetite [*Halgedahl*, 1991] and may be so also in hematite. *Halgedahl* [1995] observed only one domain wall in a section perpendicular to the basal plane for a hematite crystal in an SIRM state, while *Eaton and Morrish* [1969, Figure 3] observed ~15 walls with an average spacing of ~150 μm in one section and reported spacings as small as 50 μm in other sections.

4.2. TRM After LTD

[28] Cycling our crystal in zero field through the Morin transition at T_M = 260 K resulted in the permanent loss of ~75% of the TRM (Figure 5b). This decrease below T_M is understandable because the WF domain walls should, in principle, vanish at T_M. As the *c* axis crystalline anisotropy constant passes through zero and changes sign at T_M, the spins rotate from the (0001) plane to the *c* axis, and spin canting disappears. Domain walls blocked by magnetocrystalline-controlled pinning become free to jump or disappear entirely. The mystery is why the domains which disappear on cooling below T_M, as observed by the Faraday effect [*Williams et al.*, 1958] or magnetic colloids [*Gallon*, 1968], should reappear on heating. The process appears to be one of renucleation, in which a small wall nucleus forms and then grows rapidly by propagation of the boundary. NMR measurements show a drop in signal on cooling and a recovery on heating; these effects are undoubtedly related to the disappearance and re-creation of domain walls [*Anderson*, 1966; *Hirai et al.*, 1971].

[29] *Eaton and Morrish* [1969, 1971] observed that on cooling, the transition occurs by separation into WF and AF regions separated by a boundary parallel to the growth layers in the crystal. A light diffuse colloidal line marks the boundary between the two phases. During cooling, the AF phase nucleates at the outermost growth layer and enlarges at the expense of the WF phase, which is ultimately swept out of the crystal. On warming through T_M the process is reversible; after nucleation the WF phase sweeps across the crystal, removing the AF phase.

[30] There is experimental evidence that domain structure persists below the Morin transition. *Gustard* [1967] and *Gallon* [1968] observed that some colloid patterns remained around defects in a natural crystal. When the crystal warmed through T_M, colloid patterns spread out from these nucleation sites into the body of the crystal. This is the likely mechanism of magnetic memory.

[31] The decrease that we observe in TRM memory with increasing annealing time for our crystal (Figure 7) is consistent with the observations of *Gallon* [1968], who found that annealing alters the domain structure. Above the transition, colloid patterns on the surface of annealed crystals were more extensive than before annealing. However, annealing the crystal at 1200°C reduced crystal defects so much that the colloid patterns were no longer present below the transition.

[32] The effectiveness of annealing in reducing crystal strain in hematite crystals is also seen in the results of *Hirai et al.* [1971] and [*Searle et al.*, 1972]. The NMR signal associated with strongly pinned domain walls was weakened by annealing although never completely eliminated.

4.3. Defect Moment and Magnetic Memory

[33] SIRM cooling and warming curves for our large crystal (Figure 2b) are similar to those of SD hematites [*Özdemir and Dunlop*, 2002, Figure 1]. They have a similar remanence loss at T_M (97–98% of the original SIRM), a similar moment below T_M (2–3% of initial SIRM), and similar memory (30–37% of initial SIRM). These facts suggest that in SD and MD hematites alike, magnetic memory is controlled by a small fraction (a few percent) of the spins which are unusually strongly pinned by crystal defects.

[34] The existence of a WF moment in the AF phase below T_M is indicated by colloid patterns observed well

below T_M [*Gustard*, 1967; *Gallon*, 1968; *Eaton and Morrish*, 1969, 1971] and implies that some spins do not participate in the general rotation from the rhombohedral *c* plane to the *c* axis on cooling through the Morin transition of the bulk crystal. The "defect moment" [*Smith and Fuller*, 1967; *Dunlop*, 1971] of these few spins serves to restore preferred WF spin directions and domains in parts of the crystal during warming through the Morin transition and is thus responsible for the memory phenomenon.

[35] Weak ferromagnetism persists even at very low temperatures, much below T_M. Applying a saturating field to our initially demagnetized hematite crystal at 20 K produced a substantial SIRM (Figure 2a). This SIRM did not change in zero-field warming to T_M but then spontaneously increased by a factor of ~25. Thus memory does not require cycling through T_M. The WF defect moment produced below T_M (Figure 2a) is just as effective in nucleating domain structure above T_M as are WF moments produced above T_M and cooled below the transition (Figure 2b). Low-temperature SIRM is actually more efficient than the $T < T_M$ residue of room temperature SIRM in generating large moments on warming through T_M. Room temperature remanence is ~25 times the low-temperature remanence in Figure 2a, while the ratio of room temperature memory to low-temperature remanence is ~20 in Figure 2b.

5. Conclusions

[36] TRM of a large MD crystal of natural hematite has an intensity of ~1 kA/m for an applied field of 40 μT, similar to the Earth's magnetic field. This weak field TRM is close to saturation remanence and is ~50% of the saturation magnetization M_s = 2.0 kA/m. Weak internal self-demagnetizing fields H_d resulting from the low M_s allow domain walls to be displaced close to their limiting positions by small applied fields just below the Curie-Néel temperature T_N.

[37] In order to thermally demagnetize the TRM it must again be heated close to T_N. Cleaning by alternating fields is much easier. A 20-mT field erases ~75% of the TRM, leaving a hard residue, which is unaffected by alternating fields as high as 100 mT.

[38] LTD also removes ~75% of the TRM. However, the TRM memory that remains does not correspond to the hard residue of TRM after alternating field cleaning. Only one third of the memory is resistant to alternating fields. The remaining two thirds is very soft and disappears in fields <10 mT. Both soft and hard parts of the memory have very high unblocking temperatures ≥690°C.

[39] The existence of memory is remarkable because spin canting in the basal plane, and with it the WF moment, should vanish with rotation of spins to the *c* axis in the AF phase below T_M. In practice, domain structure and weak ferromagnetism do not completely disappear below T_M. We were able to produce SIRM in a previously demagnetized sample even at 20 K, and this remanence, when warmed through T_M in null field, generated a large room temperature remanence (25 times larger) in the same direction.

[40] A small fraction (2%) of SIRM produced at room temperature also survives below T_M. On rewarming through the transition in zero field it plays the same role as remanence produced directly below T_M, renucleating domains and a memory of the original room temperature remanence with a reduced intensity (37%) but unchanged direction. Memory is reduced by annealing and must be related to internal stresses.

[41] We propose that the mechanism of memory is spins pinned magnetoelastically by lattice defects such as dislocations. These spins rotate only partially out of the basal plane during cooling through T_M. Some basal plane anisotropy, also magnetoelastic in origin, must remain below TM in order to guide the spin nuclei into the preferred orientations that they originally had above T_M on rewarming through the transition.

[42] This mechanism works equally well for remanence produced below *TM*, both in principle and in practice. The experimental ratio between room temperature remanence and the low-temperature "defect" remanence that nucleated it is 20-25 for our crystal, whether the original remanence was produced above or below T_M.

[43] **Acknowledgments.** These results were obtained during visits to the Institute for Rock Magnetism, University of Minnesota. We thank the IRM for visiting fellowships and Mike Jackson and Peat Solheid for help in setting up experiments and data handling. The IRM is supported by the National Science Foundation, Earth Sciences Division, and by the Keck Foundation. Two anonymous reviewers offered helpful suggestions. The large hematite crystal was kindly donated by Malcolm Back and Bob Ramik of the Royal Ontario Museum, Toronto. Our research is funded by the Natural Sciences and Engineering Research Council of Canada, grant A7709.

References

Anderson, D. H. (1966), Nuclear magnetic resonance of Fe^{57} in single-crystal hematite, *Phys. Rev., 151,* 247-257.

Bando, Y., M. Kiyama, N. Yamamoto, T. Takada, T. Shinjo, and H. Takaki (1965), Magnetic properties of a-Fe_2O3 fine particles, *J. Phvs. Soc. Jpn., 20,* 2086.

Besser, P. J., A. H. Morrish, and C. W. Searle (1967), Magnetocrystalline anisotropy of pure and doped hematite, *Phys. Rev., 153,* 632-640.

Dunlop, D. J. (1971), Magnetic properties of fine-particle hematite, *Ann: Geophys., 27,* 269-293.

Dunlop, D. J., and J. Arkani-Hamed (2005), Magnetic minerals in the Martian crust, *J. Geophys. Res.*, doi:10.1029/2005JE002404, in press.

Dunlop, D. J., and G. Kletetschka (2001), Multidomain hematite: A source of planetary magnetic anomalies?, *Geophvs. Res. Lett., 28,* 3345-3348.

Dun|op, D. J., and 6. Ozdemir (1997), *Rock Magnetism: Fundamentals and Frontiers,* 573 pp., Cambridge Univ. Press, New York.

Dzyaloshinsky, I. (1958), A thermodynamic theory of "weak" ferromagnetism of antiferromagnetics, *J. Phys. Chem. Solids, 4,* 241-255.

Eaton, J. A., and A. H. Morrish (1969), Magnetic domains in hematite at and above the Morin transition, *J. Appl. Phys., 40,* 3180-3185.

Eaton, J. A., and A. H. Morrish (1971), Magnetic domain structure of hematite, *Can. J. Phys., 49,* 2768-2777.

Flanders, P. J. (1969), Spin axis rotation in hematite, *J. Appl. Phys., 40,* 1247-1248.

Flanders, P. J., and J. P. Remeika (1965), Magnetic properties of hematite single crystals, *Philos. Mag., 11,* 1271-1288.

Foner, S., and Y. Shapira (1969), Magnetic phase transitions in pure a Fe_20_3, *Phys. Lett. A, 29,* 276-277.

Freier, S., M. Greenshpan, P. Hillman, and H. Shechter (1962), The antiferromagnetic Curie point in ct-Fe_2O_3, *Phys. Lett., 2,* 191-192.

Gallon, T. E. (1968), The remanent magnetization of haematite single crystals, *Proc. R. Soc. London. Ser. A, 303,* 511-524.

Goya, G. F., M. Veith, R. Rapalavicuite, H. Shen, and S. Mathur (2005), Thermal hysteresis of spin reorientation at Morin transition in alkoxide derived hematite nanoparticles, *Appl. Phys. A, SO,* 1523-1526.

Gustard, B. (1967), The ferromagnetic domain structure in hematite, *Proc. R. Soc. London, Ser. A, 297,* 269-274.

Haigh, G. (1957), The effect of added titanium and aluminum on the magnetic behaviour of a. ferric oxide, *Philos. Mag., 2,* 505-520.

Halgedahl, S. L. (1991), Magnetic domain patterns observed on synthetic Ti-rich titanomagnetite as a function of temperature and in states of thermoremanent magnetization,/. *Geophys. Res., 96,* 3943-3972.

Halgedahl, S. L. (1995), Bitter patterns versus hystereis behavior in small single particles of hematite, *J. Geophys. Res., 100,* 353-364.
Halgedahl, S. L. (1998), Barkhausen jumps in large versus small platelets of natural hematite, *J. Geophys. Res., 103,* 30,575-30,589.
Hartstra, R. L. (1982), Some rock magnetic parameters for natural iron-titanium oxides, Ph.D. thesis, 145 pp., Univ. of Utrecht, Utrecht, Netherlands.
Hirai, A., J. A. Eaton, and C. W. Searle (1971), Fe^{57} nuclear magnetic resonance and some dynamical characteristics of domain walls in ot-Fe_20_3, *Phys. Rev. B, 3,* 68-75.
Kaye, G. (1961), Temperature effects in domain patterns from single crystals of haematite (a-Fe_2O_3), *Proc. Phys. Soc. London, 78,* 869-877.
Kaye, G. (1962), The effect of titanium on the low temperature transition in natural crystals of haematite, *Proc. Phys. Soc. London, 80,* 238-243.
Keeling, R. 0., Jr. (1972), Mossbauer investigation of mechanically induced magnetic anisotropy in natural hematite, *J. Appl. Phys., 43,* 4736-4740.
Kletetschka, G., P. J. Wasilewski, and P. T. Taylor (2000), Unique thermoremanent magnetization of multidomain sized hematite: Implications for magnetic anomalies, *Earth Planet. Sci. Lett., 176,* 469-479.
Maartense, I., and C. W. Searle (1971), Domain wall and magnetoelastic resonance in hematite, *J. Appl. Phys., 42,* 2349-2355.
Morin, F. J. (1950), Magnetic susceptibility of aFe_20_3 and aFe_20_3 with added titanium, *Phys. Rev., 78,* 819-820.
Neel, L. (1955), Some theoretical aspects of rock magnetism, *Adv. Phvs., 4,* 191-243.
Neel, L., and R. Pauthenet (1952), Etude thermomagnetique d'un monocristal de Fe_2O_3a, *C. R. Hebd. Seances Acad. Sci., 234,* 2172-2174.
Ozdemir, 6., and D. J. Dunlop (2002), Thermoremanence and stable memory of single-domain hematites, *Geophys. Res. Lett.,* 2P(18), 1877, doi:10.1029/2002GL015597.
Porath, H., and C. B. Raleigh (1967), An origin of the triaxial basal-plane anisotropy in hematite crystals, *J. Appl. Phys., 38,* 2401-2402.
Putnis, A. (1992), *Introduction to Mineral Sciences,* 457 pp., Cambridge Univ. Press, New York.
Searle, C. W., S. Kupca, and J. H. Davis (1972), Nuclear magnetic resonance study of tightly pinned domain walls in a-Fe_2 O_3, *Phys. Rev. B, 5,* 3441-3445.
Shapira, Y. (1969), Ultrasonic behavior near the spin-flop transitions of hematite, *Phys. Rev., 184,* 589-600.
Smith, R. W., and M. Fuller (1967), Alpha-hematite: Stable remanence and memory, *Science, 156,* 1130-1133.
Sunagawa, I. (1960), Growth history of hematite, *Am. Mineral, 45,* 566-575.
Sunagawa, I., and P. J. Flanders (1965), Structural and magnetic studies in hematite single crystals, *Philos. Mag., 11,* 747—761.
Syono, Y, S. Akimoto, and T. Nagata (1962), Remanent magnetization of ferromagnetic single crystal, *J. Geomagn. Geoelectr., 14,* 113-124.
Voigt, C., S. Foner, and H. C. Praddaude (1971), Angular dependence of field-induced phase transition in a-Fe_20_3, *Phys. Lett. A, 36,* 255-256.
Williams, H. J., R. C. Sherwood, and J. P. Remeika (1958), Magnetic domains in a-Fe_20_3, *J. Appl. Phys., 29,* 1772-1773.

D. /. Dunlop and 0. Ozdemir, Department of Chemical and Physical Sciences, University of Toronto at Mississauga, Mississauga, Ontario L5L 1C6, Canada. (ozdemir@physics.utoronto.ca)