

Thermoremanence and Néel Temperature of Goethite

Özden Özdemir and David J. Dunlop

Geophysics, Physics, Erindale College, University of Toronto, Mississauga, Ontario, Canada

Abstract. We have measured thermoremanence (TRM) and the temperature dependence of high-field susceptibility χ , both parallel and perpendicular to the crystallographic c-axis, for a sample of well crystallized natural goethite (αFeOOH). Susceptibility χ_{\perp} measured perpendicular to the c-axis was almost temperature independent between 50 and 300 K, while χ_{\parallel} measured parallel to the c-axis increased almost linearly with temperature over the same range. These are the dependences expected for an antiferromagnetic (AFM) substance with sublattice magnetizations along the c-axis. Extrapolation of the χ_{\perp} and χ_{\parallel} data trends to their point of intersection gives an estimate for the AFM Néel temperature T_N of $(120 \pm 2)^{\circ}\text{C}$. TRM's produced by cooling in a weak field applied either parallel or perpendicular to the c-axis had intensities of $2.4 \times 10^{-4} \text{ Am}^2/\text{kg}$ and $1.2 \times 10^{-5} \text{ Am}^2/\text{kg}$, respectively. Since $(M_{\text{TRM}})_{\perp}$ is only 5% of $(M_{\text{TRM}})_{\parallel}$, the weak ferromagnetism of goethite must be parallel to the AFM spin axis, not perpendicular to it as in the case of hematite. The ferromagnetism is very hard: TRM was unaffected by AF demagnetization to 100 mT and by thermal demagnetization to 90°C . Above 90°C , TRM decreased sharply, reaching zero at $(120 \pm 2)^{\circ}\text{C}$. Thus the ferromagnetic Curie point T_C coincides with T_N , as in hematite. However, the weak ferromagnetism cannot be due to spin canting, as it is in hematite, because canting of the sublattices would produce a net moment perpendicular to the c-axis, rather than parallel to the c-axis as observed.

Introduction

Goethite (αFeOOH), although a minor carrier of stable paleomagnetic remanence, is common in nature as a weathering product of iron-bearing minerals, particularly in soils and sediments. Goethite is antiferromagnetic (AFM), the sublattice magnetizations lying along the crystallographic c-axis. Its Néel temperature T_N , determined from either the Mössbauer hyperfine field or the thermal variation of susceptibility, has been variously reported as 70°C to 170°C (Table 1).

Goethite also possesses a weak ferromagnetism below T_N , perhaps because of unbalanced numbers of spins resulting from crystal imperfections (Van Oosterhout, 1965) or the presence of impurities (Hedley, 1971). Strangway et al. (1967) and Banerjee (1970) showed that goethite can acquire a weak but very stable thermoremanent magnetization (TRM). The TRM blocking temperature range extended up to 105°C (Banerjee, 1970) or 120°C (Strangway et al., 1967). Neither study used oriented crystals.

In the present study, we measured both temperature-dependent susceptibility and TRM as a function of orientation of the applied field \mathbf{H}_0 with respect to the c-axis of goethite. Measurements on a single crystal or group of similarly oriented crystals are more informative than measurements on polycrystalline material because the ferromagnetism of goethite, like its antiferromagnetism, is highly anisotropic (Hedley, 1971). We were able to make a direct compari-

son between the AFM Néel temperature T_N (from susceptibility measurements) and the ferromagnetic (FM) Curie temperature T_C (from TRM). These proved to be identical: 120°C .

Sample Characterization

We used a museum-quality specimen of well crystallized natural goethite with obvious crystal elongation parallel to the c-axis. The orthorhombic goethite lattice is built of iron-centred oxygen octahedra linked in such a way as to form one-dimensional chains parallel to the c-axis. These chains are joined by sharing corners, such that each anion is common to three octahedra (Ewing, 1935). The hydroxyl bonds linking planes of oxygen atoms form zigzag chains, also parallel to the c-axis.

X-ray diffraction analysis of the sample using a Debye-Scherrer camera with Fe-K α radiation and a silicon standard gave numerous reflections characteristic of goethite. The orthorhombic unit cell dimensions were determined to be $a=4.6 \text{ \AA}$, $b=9.9 \text{ \AA}$ and $c=3.0 \text{ \AA}$, in close agreement with standard values (ASTM data file 17-536).

The thermomagnetic curve had a broad and ill-defined minor peak just above 100°C (Figure 1). It would be difficult to determine an accurate value for the AFM to paramagnetic (PM) transition temperature T_N from these $M(T)$ data. Much more prominent is the drop in magnetization beginning around 250°C , as the goethite dehydrates to hematite ($\alpha\text{Fe}_2\text{O}_3$) (Francombe and Rooksby, 1959).

Temperature Dependence of High-Field Susceptibility

Magnetic susceptibility χ in a field $\mathbf{H}_0=0.1 \text{ T}$ was measured every 10 K from 10 to 300 K using a superconducting susceptometer (MPMS at the Institute for Rock Magnetism, University of Minnesota). Goethite crystals were carefully oriented in two separate runs with their c-axes either parallel (χ_{\parallel}) or perpendicular (χ_{\perp}) to \mathbf{H}_0 (produced by a superconducting solenoid).

Table 1. Reported Néel and Curie Temperatures of Goethite

Type of sample	T_N or T_C ($^{\circ}\text{C}$)	Method	Reference
Synthetic	70, 100	χ -T curves	Szytula et al. (1966)
Synthetic	85	Mössbauer	Bocquet & Kennedy (1992)
Synthetic	91	Mössbauer	Koch et al. (1985)
Synthetic	94	Mössbauer	Dézi & Fodor (1966)
Synthetic	97	Mössbauer	Hryniewicz & Kulgawczuk (1963)
Synthetic	105	TRM blocking	Banerjee (1970)
Natural	120	TRM blocking	Strangway et al. (1967)
Natural	120	Mössbauer	Van der Woude & Dekker (1966)
Natural	120	Mössbauer	Mørup et al. (1983)
Natural	120	χ -T curves	This paper
Natural	120	TRM unblocking	This paper
Synthetic	130	Mössbauer	Forsyth et al. (1968)
Synthetic	170	χ -T curves	Van Oosterhout (1965)

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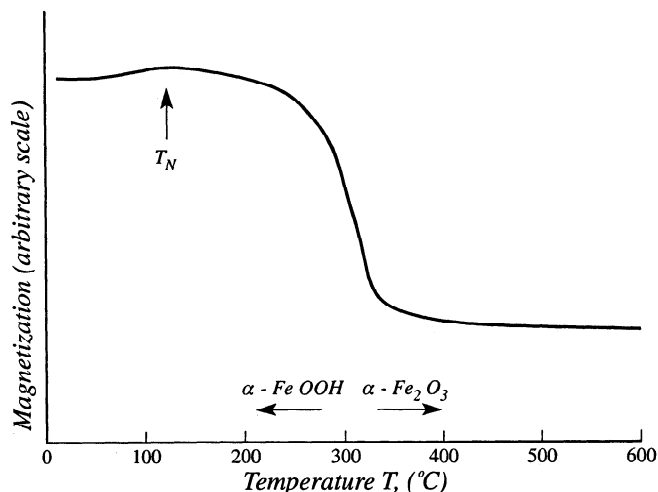


Figure 1. Thermomagnetic (strong-field magnetization vs. temperature) heating curve of a goethite subsample. The broad minor peak just above 100°C marks the AFM-PM transition, but does not pinpoint T_N very accurately. The strong decrease in magnetization between 250 and 320°C is due to the $\alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3$ dehydration transformation.

Susceptibility χ_{\perp} perpendicular to the AFM spin axis is due to rotation of the spin sublattices by the torque of \mathbf{H}_0 and should be in almost temperature independent (Nagamiya et al., 1955). In agreement with this prediction, our measured variation of χ_{\perp} with

temperature was almost flat (Figure 2). Susceptibility χ_{\parallel} parallel to the AFM spin axis is theoretically zero because the torque $\mu_0 \mathbf{VM} \times \mathbf{H}_0$ vanishes. However, above 0 K, thermal energy increasingly perturbs the sublattice magnetizations \mathbf{M}_A and \mathbf{M}_B out of perfect parallelism or antiparallelism with \mathbf{H}_0 and χ_{\parallel} is predicted to be proportional to T . Our data between 50 and 300 K confirm this prediction (Figure 2).

We also measured the susceptibility χ_{powder} of randomly oriented goethite crystallites in a powdered subsample (Figure 2). The predicted value of χ_{powder} at any temperature T is $(2/3)\chi_{\perp} + (1/3)\chi_{\parallel}$. Our data obey this relation when $T > 150$ K, but are biased toward χ_{\perp} when $T < 150$ K.

Linear extrapolations of the χ_{\perp} , χ_{powder} and χ_{\parallel} data above 300 K intersect at a common point, pinpointing the AFM-PM transition. The Néel temperature T_N indicated by this method is $(120 \pm 2)^\circ\text{C}$.

Thermoremanent Magnetization (TRM)

Total TRM's were produced in two separate runs by cooling a cm-size goethite sample from 150°C to room temperature with a 1-mT (10-Oe) field \mathbf{H}_0 applied either parallel or perpendicular to the c-axes of the goethite crystals. $(M_{\text{TRM}})_{\parallel}$ had an intensity of $2.4 \times 10^{-4} \text{ Am}^2/\text{kg}$, about 20 times greater than $(M_{\text{TRM}})_{\perp}$ (intensity of $1.2 \times 10^{-5} \text{ Am}^2/\text{kg}$). The capacity for TRM acquisition is very much greater parallel to the c-axis than perpendicular to it. In fact, TRM at the 5% level might be explained by minor misalignment of crystal axes perpendicular to \mathbf{H}_0 . We conclude that the FM \mathbf{M}_s vector in goethite lies along the c-axis, parallel to the AFM spin directions or sublattice magnetizations \mathbf{M}_A and \mathbf{M}_B .

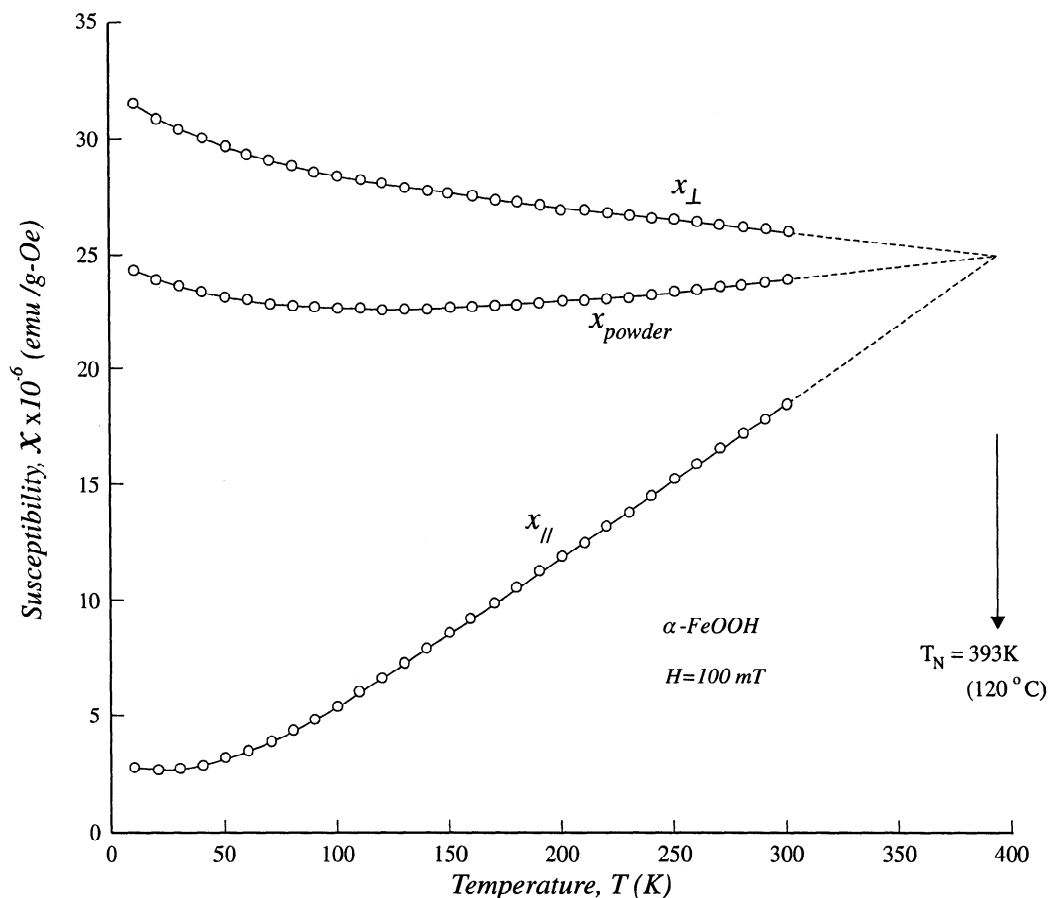


Figure 2. Antiferromagnetic susceptibility measured at 10 K intervals during heating from 10 K to 300 K. χ_{\parallel} , χ_{\perp} were measured parallel and perpendicular to the goethite c-axis, respectively. χ_{powder} was measured for randomly oriented crystallites in a powdered subsample. The intersection of linear extrapolations of the χ_{\parallel} , χ_{\perp} and χ_{powder} data pinpoints the Néel temperature: $T_N = (120 \pm 2)^\circ\text{C}$.

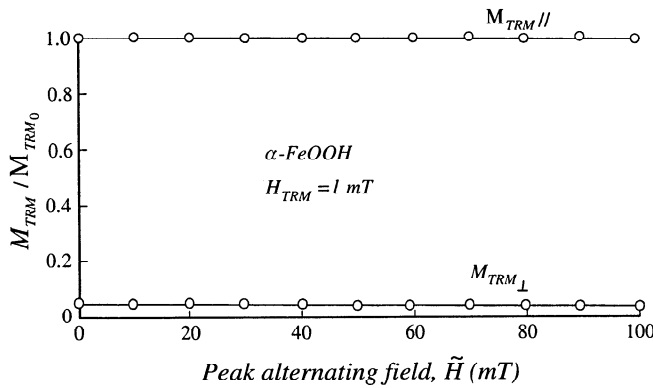


Figure 3. Attempted AF demagnetization of TRM's produced parallel and perpendicular to the goethite c-axis. Neither TRM was affected by AF's ≤ 100 mT. Note that $(M_{TRM})_{\perp}$ is only 5% as intense as $(M_{TRM})_{\parallel}$.

Both TRM's were very hard. AF demagnetization to 100 mT had no effect (Figure 3). Stepwise thermal demagnetization likewise had a minimal effect on either TRM for heating runs up to 90°C (Figure 4). After heating above 90°C, $(M_{TRM})_{\parallel}$ showed a sharp decrease, reaching zero at $(120 \pm 2)^{\circ}\text{C}$. $(M_{TRM})_{\perp}$ dropped to zero at the same temperature. We assume that the maximum unblocking temperatures observed fall very close to the FM Curie temperature T_C , which is therefore also $(120 \pm 2)^{\circ}\text{C}$.

Although there have been a number of previous determinations of T_N and of T_C for goethite (Table 1), this is the first time to our knowledge that both have been measured in independent experiments on the same crystals and shown to be identical. There can be no doubt that the weak ferromagnetism of goethite has its origin in the much stronger antiferromagnetism, and not in trace impurities of some other mineral.

Discussion

Our T_N and T_C values of $(120 \pm 2)^{\circ}\text{C}$ for goethite are in good agreement with previous determinations of either T_N or T_C using

natural goethites (e.g., Van der Woude and Dekker, 1966; Strangway et al., 1967; Mørup et al., 1983). Synthetic goethites, however, have given widely dispersed estimates of T_N (Table 1). Bocquet and Kennedy (1992) reported $T_N = 85^{\circ}\text{C}$ for a synthetic goethite of submicron ($12\text{ nm} \times 49\text{ nm}$) crystallite size, attributing the low T_N value to the presence of lattice vacancies. Yamamoto (1968) reported size-dependent T_N values, ranging from 127°C for $<< 1\text{ }\mu\text{m}$ crystallites to 92°C for $0.2\text{ }\mu\text{m}$ crystallites. It seems likely that these synthetic goethites were poorly crystallized.

Our data demonstrate that $\geq 95\%$ of TRM in goethite is acquired parallel to the c-axis, which is the AFM spin axis. Although the production of TRM in goethite is well documented, the crystallographic control of TRM orientation is a new finding.

The weak ferromagnetism must have a different origin than the weak ferromagnetism of hematite. Above the Morin transition in hematite, M_A and M_B lie in the c-plane. Ferromagnetism results from a slight canting of M_A and M_B out of exact antiparallelism (Dzyaloshinsky, 1958). The FM spontaneous magnetization M_S of hematite therefore lies in the c-plane, perpendicular to M_A and M_B .

In goethite, the strong TRM anisotropy we have observed proves that M_S is parallel to the A and B sublattice magnetizations M_A and M_B . Spin-canting is therefore ruled out. Moriya (1960) has proposed on theoretical grounds that some orthorhombic crystals, specifically NiF_2 , can exhibit spin-canting. The experimental evidence is in conflict, however, neutron diffraction indicating that M_A and M_B are deflected slightly away from the c-axis (Erickson, 1953) while nuclear magnetic resonance data imply that M_A and M_B are almost perpendicular to the c-axis (Moriya, 1960). Thus, spin-canting in orthorhombic crystals is unproven in general, and can definitely be ruled out in goethite on the basis of our measurements.

At the same time, the fact that $T_C = T_N$ shows that the ferromagnetism and antiferromagnetism of goethite have a common origin. A magnetic impurity phase would have a T_C different from T_N and cannot be the cause of the ferromagnetism. In any case, non-magnetic impurities, such as Al^{3+} or Mn^{3+} , because of their significantly different ionic radii, would distort the goethite lattice. For example, Al^{3+} has an ionic radius of 0.53 \AA , much smaller than that of Fe^{3+} (0.645 \AA), and would cause a reduction of the unit cell-edge parameter. Our measured X-ray cell-edge dimensions are in

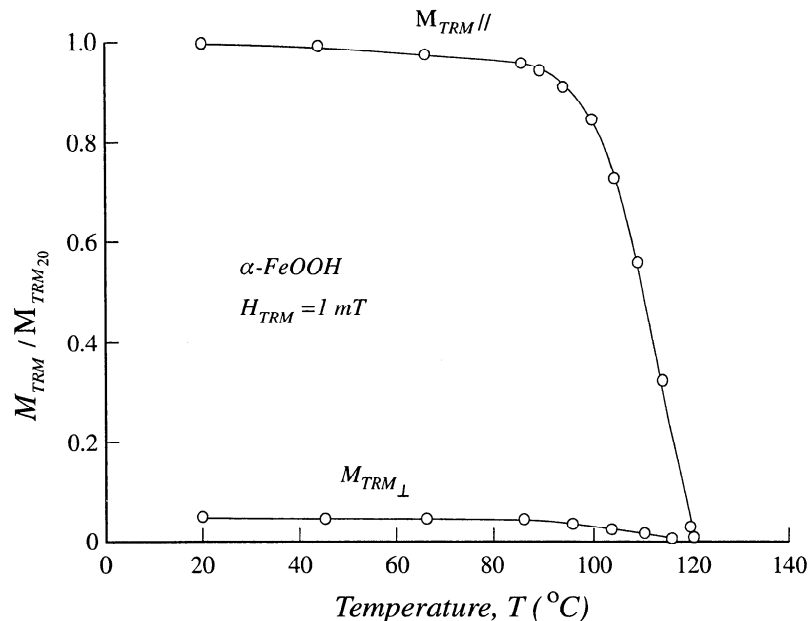


Figure 4. Stepwise thermal demagnetization of TRM's produced parallel and perpendicular to the goethite c-axis. Both TRM's are unaffected by zero-field heating to 90°C but demagnetize completely when heated to 120°C. From these data, the best estimate of the goethite Curie temperature is $(120 \pm 2)^{\circ}\text{C}$.

excellent agreement with standard values, however (see sample characterization section), showing that impurities are insignificant in our samples.

The likeliest mechanism for the parasitic ferromagnetism of goethite is spin imbalance, caused by lattice vacancies distributed randomly between the A and B sublattices. Although the vacancies are not ordered on a superlattice as in maghemite or pyrrhotite, random spin imbalance could still produce a measurable net magnetization $|\mathbf{M}_A - \mathbf{M}_B|$.

Several specific mechanisms have been proposed.

- i) The substitution of cations like Mn^{3+} or Al^{3+} in the FeOOH lattice would tend to destroy the perfect AFM balance between sublattices (Néel, 1949). Hedley (1971) found that increasing Al^{3+} content did correlate with larger FM moment in natural goethites, but even "pure" goethites had a measurable moment.
- ii) Van Oosterhout (1965) suggested that goethite has a defect structure caused by water molecules in the crystal. The chains of AFM coupled ferric ions are interrupted by hydroxyl bonds.
- iii) Banerjee (1970) proposed that weak ferromagnetism could result from broken links in the continuous AFM iron-oxygen-iron chains by lattice vacancies. Since the vacancies occur randomly, some of the broken links contain an odd number of antiparallel iron spins. Such links are responsible for the spin imbalance moment.

Conclusions

1. The weak ferromagnetism of our natural goethite sample is crystallographically oriented parallel to the c-axis, which is also the AFM spin axis.
2. The AFM Néel temperature T_N of goethite, estimated by extrapolation of 10-300 K χ_{\parallel} and χ_{\perp} data, is $(120 \pm 2)^{\circ}\text{C}$.
3. The observed very stable TRM's parallel and perpendicular to the spin axis both had maximum unblocking temperatures of $(120 \pm 2)^{\circ}\text{C}$. This is our best estimate of the FM Curie temperature T_C of goethite.
4. T_N and T_C are identical for goethite: $(120 \pm 2)^{\circ}\text{C}$. The antiferromagnetism and ferromagnetism must have a common origin.
5. The ferromagnetism of αFeOOH is not due to spin canting as in $\alpha\text{Fe}_2\text{O}_3$. It is probably due to unbalanced numbers of spins on the A and B sublattices, resulting from random lattice vacancies.

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Özden Özdemir and David J. Dunlop, Department of Physics, Erindale College, University of Toronto, 3359 Mississauga Road North, Mississauga, Ontario, Canada L5L 1C6. (e-mail: ozdemir@physics.utoronto.ca)

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