Thermoremanence and Néel Temperature of Goethite

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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 (α-FeOOH). Susceptibility χ⊥ measured perpendicular to the c-axis was almost temperature independent between 50 and 300 K, while χ∥ 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⊥ and χ∥ data trends to their point of intersection gives an estimate for the AFM Néel temperature TN of (120 ± 2)°C. TRM's produced by cooling in a weak field applied either parallel or perpendicular to the c-axis had intensities of 2.4 x 10⁻⁴ Am²/kg and 1.2 x 10⁻⁵ Am²/kg, respectively. Since (M_TRM)⊥ is only 5% of (M_TRM)∥, 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 ± 2)°C. Thus the ferromagnetic Curie point TC coincides with TN 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 (α-FeOOH), 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 TN 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 TN, 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 thermoremanence 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 H₀ 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 comparison between the AFM Néel temperature TN (from susceptibility measurements) and the ferromagnetic (FM) Curie temperature TC (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-Kα radiation and a silicon standard gave numerous reflections characteristic of goethite. The orthorhombic unit cell dimensions were determined to be a = 4.6 Å, b = 9.9 Å, and c = 3.0 Å, 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 TN from these M(T) data. Much more prominent is the drop in magnetization beginning around 250°C, as the goethite dehydrates to hematite (α-Fe₂O₃) (Francombe and Rooksby, 1959).

Temperature Dependence of High-Field Susceptibility

Magnetic susceptibility χ in a field H₀ = 0.1 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∥) or perpendicular (χ⊥) to H₀ (produced by a superconducting solenoid).

Table 1. Reported Néel and Curie Temperatures of Goethite

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>TN or TC (°C)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic</td>
<td>70, 100</td>
<td>χ-T curves</td>
<td>Szytula et al. (1966)</td>
</tr>
<tr>
<td>Synthetic</td>
<td>85</td>
<td>Mössbauer</td>
<td>Bocquet &amp; Kennedy (1992)</td>
</tr>
<tr>
<td>Synthetic</td>
<td>91</td>
<td>Mössbauer</td>
<td>Koch et al. (1985)</td>
</tr>
<tr>
<td>Synthetic</td>
<td>94</td>
<td>Mössbauer</td>
<td>Dézi &amp; Fodor (1966)</td>
</tr>
<tr>
<td>Synthetic</td>
<td>97</td>
<td>Mössbauer</td>
<td>Hryniewicz &amp; Kuligawczuk (1963)</td>
</tr>
<tr>
<td>Synthetic</td>
<td>105</td>
<td>TRM blocking</td>
<td>Banerjee (1970)</td>
</tr>
<tr>
<td>Natural</td>
<td>120</td>
<td>TRM blocking</td>
<td>Strangway et al. (1967)</td>
</tr>
<tr>
<td>Natural</td>
<td>120</td>
<td>Mössbauer</td>
<td>Van der Woude &amp; Dekker (1966)</td>
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<td>TRM unblocking</td>
<td>This paper</td>
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<tr>
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<td>130</td>
<td>Mössbauer</td>
<td>Forsyth et al. (1968)</td>
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<tr>
<td>Synthetic</td>
<td>170</td>
<td>χ-T curves</td>
<td>Van Oosterhout (1965)</td>
</tr>
</tbody>
</table>

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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 dehydration transformation.

Susceptibility $\chi_\perp$ perpendicular to the AFM spin axis is due to rotation of the spin sublattices by the torque of $H_\parallel$, and should be almost temperature independent (Nagamiya et al., 1955). In agreement with this prediction, our measured variation of $\chi_\perp$ with temperature was almost flat (Figure 2). Susceptibility $\chi_\parallel$ parallel to the AFM spin axis is theoretically zero because the torque $\mu_0 VM \times H_\parallel$ vanishes. However, above 0 K, thermal energy increasingly perturbs the sublattice magnetizations $M_A$ and $M_B$ out of perfect parallelism or antiparallelism with $H_\parallel$ and $\chi_\parallel$ is predicted to be proportional to $T$. Our data between 50 and 300 K confirm this prediction (Figure 2).

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

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

### Thermomagnetic Susceptibility (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 $H_\parallel$ applied either parallel or perpendicular to the $c$-axes of the goethite crystals. $(M_{\text{TRM}})_r$ had an intensity of $2.4 \times 10^{-4}$ Am²/kg, about 20 times greater than $(M_{\text{TRM}})_c$ (intensity of $1.2 \times 10^{-5}$ Am²/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 $H_\parallel$. We conclude that the FM $M_A$ vector in goethite lies along the $c$-axis, parallel to the AFM spin directions or sublattice magnetizations $M_A$ and $M_B$.

Figure 2. Antiferromagnetic susceptibility measured at 10 K intervals during heating from 10 K to 300 K. $\chi_\parallel, \chi_\perp, \chi_{\text{powder}}$ were measured parallel and perpendicular to the goethite $c$-axis, respectively. $\chi_{\text{powder}}$ was measured for randomly oriented crystallites in a powdered subsample. The intersection of linear extrapolations of the $\chi_{\parallel}, \chi_{\perp}$ and $\chi_{\text{powder}}$ data pinpoints the Néel temperature: $T_N = (120 \pm 2)^\circ$C.
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 showed a sharp decrease, reaching zero at (120 ± 2)°C. M_TRM decreased 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 ± 2)°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 ± 2)°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). Bouquet and Kennedy (1992) reported T_N = 85°C for a synthetic goethite of submicron (12 μm x 49 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 μm crystallites to 92°C for 0.2 μm crystallites. It seems likely that these synthetic goethites were poorly crystallized.

Our data demonstrate that 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^{4+}, because of their significantly different ionic radii, would distort the goethite lattice. For example, Al^{3+} has an ionic radius of 0.54 Å, much smaller than that of Fe^{3+} (0.645 Å), and would cause a reduction of the unit cell-edge parameter. Our measured X-ray cell-edge dimensions are in
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 \( \mathbf{M}_N - \mathbf{M}_B \).

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 detect 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 \( \chi_1 \) and \( \chi_\alpha \) data, is \( 120 \pm 2 \)°C.

3. The observed very stable TRM’s parallel and perpendicular to the spin axis both had maximum unblocking temperatures of \( 120 \pm 2 \)°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: \( 120 \pm 2 \)°C. The anti ferromagnetism and ferromagnetism must have a common origin.

5. The ferromagnetism of \( \alpha \)-FeOOH is not due to spin canting as in \( \alpha \)-Fe\(_2\)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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References


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