Magnetism in non-stoichiometric goethite of varying total water content and surface area

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SUMMARY
In this work, the magnetic properties of four non-stoichiometric goethites with varying total water content and surface area have been investigated. The samples were prepared using two different hydrothermal methods, deriving either from Fe(II) precursors or from Fe(III) precursors. The effects of both agitation during mixing solutions and drying time during synthesis upon the physical properties of the final products were also studied. The samples were characterized by XRD, TGA, BET, $^{57}$Fe Mössbauer spectrometry at 300 K, 77 K and 4.2 K, ZFC and FC curves, and magnetization curves. The goethites synthesized from the Fe(II) precursors result less crystalline, contain higher water content than those prepared from the Fe(III) precursor. In addition, ferrous precursor goethites exhibit superparamagnetic relaxation effects, while the ferric precursor goethites exhibit magnetic ordering of clusters. It is found that the stirring process during synthesis can affect the total water content and the magnetic behaviour of the goethites. Our results suggest that structural water content decreases the magnetic hyperfine field at 4.2 K. The adsorbed water content also affects this parameter as suggested by in situ annealing cycles of the goethites in a Mössbauer cryofurnace. Finally, we propose an unique 2-D phase diagram to describe all the magnetic properties of present goethites observed as a function of temperature, surface area (or particle size) and total water content.

Key words: crystallinity, goethite, magnetic properties, surface area, water content.

1 INTRODUCTION
Goethite ($\alpha$-FeOOH) is a fascinating iron oxyhydroxide. Indeed, it is commonly found in natural ecosystems and is by far the most common iron oxyhydroxide in terrestrial soils, sediments and clays (Schwertmann & Cornell 1991; Cornell & Schwertmann 1996; De Grave et al. 2002; Guyo et al. 2003). It was previously ignored in palaeomagnetic and rock magnetic studies until it was discovered that it could carry a stable remanence (Strangway et al. 1968; Hedley 1971; Dekkers 1989a,b). Since then, increasing efforts have been put forward in order to fully understand the physical origin of the complex magnetism exhibited by this sample. Goethite is generally thought to be the source of disturbing secondary magnetizations in sediments. This iron phase has been used to quantify the corrosion of iron and steel, which can drive them protective properties (Lee et al. 2001). Goethite is sometimes used as a starting material to produce maghemite, which is used as magnetic pigment (Nuñez et al. 2000). It can also be used as a ferrofluid, thanks to its interesting magnetic properties (Lemaire et al. 2002).

Previous investigations have demonstrated that the crystallographic and the magnetic unit cell of goethite have the same size (Forsyth et al. 1968), and that below the Néel temperature (about 400 K), the iron moments are collinear in a two sublattice antiferromagnetic (AFM) structure and lie parallel to the $c$-axis (space group Pbnm). However, other authors (Coey et al. 1995) have reported that goethite orders in a non-collinear four sublattice AFM structure, with a canting angle of ±13° with respect to the $c$-axis. This value was obtained by refinements of the structural parameters and moment in spin modes on the powder neutron diffraction data of a natural fibrous goethite from Cary Mine, Ironwood, Michigan. The canting angle in this goethite is not related to a magnetic transition like the Morin transition in haematite, but it seems to be permanent and related to the presence of impurities and imperfections in the lattice of the sample.

Most of the natural and synthetic goethites exhibit rather poor crystallinity and rather small particle size. Their specific areas, for instance, may range from 8 to 200 m$^2$ g$^{-1}$ (Schwertmann et al. 2006).
1985; Cornell & Schwertmann 1996). As a consequence they have a
defective structure, which influences all their physical properties,
especially the magnetic ones. First of all, they contain more wa-
ter than the amount predicted by the theoretical formula. In order
to account for this additional water content a general formula for
goethite has been proposed, namely, \( \alpha - (\text{Fe})_{1-y} \cdot (\text{OH})_{y} \), in
which \( y/3 \) represents the fraction of Fe replaced by 3 H\(^{+}\) (Schulze &
Schwertmann 1984; Wolska & Schwertmann 1993). Secondly, many
structural defects occur in the goethite crystals, such as point defects
and intergrowths. Schulze & Schwertmann (1984) have found that
the presence of structural defects makes the hydrogen bonds weaker,
decreases the temperature of dehydroxylation, increases the amount
of hydroxyl and water content, reduces the crystal size and increases
the dissolution rate in acid.

Among the physical properties of goethite, the magnetic prop-
erties remain the most difficult to interpret. Indeed, various models
have been put forward in order to account for the magnetic be-
haviour, but some models still remain controversial. The strongest
magnetic interaction between nearest-neighbours Fe ions is AFM.
In the simplest case, this results in the creation of two magnetic
sublattices, both having the same temperature-dependent sublattice
magnetization \( M(T) \). To our knowledge, three types of theoretical
models describing \( M(T) \) have been at least put forward: all of them
are expected to be valid over the entire temperature ranging from
0 K up to the transition temperature, the main difference between
them being the mechanism involved in the magnetic ordering.
The first model considers the magnetic ordering of spins (De Grave &
Vandenberghne 1986; Van der Woude & Dekker 1966; Kilcoyne &
Ritter 1997), the second considers the ordering of magnetic clusters
(Bocquet et al. 1992; Bocquet & Kennedy 1992) while the third con-
siders the ordering of interacting magnetic particles (Morup et al.
1983). In the cluster coupling model, the particles themselves may
be considered as being made up of interacting magnetic clusters,
with an ordering temperature of \( T_N \), whereas in the particle cou-
ping model the particles themselves as a whole interact with their
neighbours. However, those models do not fully satisfy the magnetic
properties of all the samples. As a rule of thumb, it seems that both
the particle size and the degree of crystallinity are the main fac-
tors determining the type of mechanism involved in the magnetic
ordering. Barrero et al. (1999) have tried to classify the magnetic
behaviour of the goethites according to their particle sizes. In con-
trast, the degree of crystallinity in a sample is usually more difficult
to quantify. On the other hand, the temperature dependence of the
magnetization at the surface of nanoparticles has been found to be
much steeper than that in the core. Yamamoto et al. (1993) have
calculated this dependence using the Brillouin function assuming
the surface spin being equal to \( 5/2 \) and the surface exchange field
to be reduced with respect to the core exchange field.

In spite of the simplifying efforts, the actual experiments on
the magnetic behaviour of goethites are even more complicated.
For example, several authors have reported that natural and synthetic
goethites possess a small net magnetic moment (Strangway et al.
1968; Hedley 1971; Broz et al. 1990; Coey et al. 1995; Özdemir
& Dunlop 1996; Broz & Sedlak 1991; De Boer & Dekkers 1998;
Guyodo et al. 2003). The WFM was found to be also parallel to
the crystallographic c-axis, while the Curie point \( (T_C) \) was found to
be equal to the Neél point \( (T_N) \) ( Özdemir & Dunlop 1996). Other
features like reduction and distribution of the transition temperatures
and of the exchange interactions, as well as lowering of the saturation
magnetization have been observed in these systems and explained
on the basis of surface effects, structural defects or the presence of
impurities (Murad 1996).

From this literature review, one concludes that the magnetic prop-
erties of \( \alpha \)-FeOOH are strongly affected by both the particle size and
the degree of crystallinity. However, most of the work has been re-
lated to the particle size, which is rather easy to measure. In contrast,
the degree of crystallinity in a sample is usually more difficult to
quantify. The usual way derives from the mean coherence length
in a certain crystallographic direction, which is determined from
the line broadening of the corresponding X-ray reflection. However,
this term is very complex because it includes mixed contributions
coming from small particle size and non-stoichiometry, which is
essentially due to the presence of \( \text{H}_2\text{O} \) and/or \( \text{OH}^{-} \) bound into
the structures. In this work, the degree of non-stoichiometry and the
surface area will be related to the degree of crystallinity of the
sample. To the best of our knowledge, there is a lack of work related
to the effect of total water content on the magnetic properties of
non-stoichiometric goethite: this is the main purpose of the present
investigation. For completeness, the surface areas and grain sizes of
the samples are also considered in this work.

2 EXPERIMENTAL PART

To obtain goethites with a broad range of water contents, four dif-
ferent samples were prepared according to literature procedures,
but introducing small variations in some steps as follows. Two of
them were precipitated from Fe(II) precursors according to the pro-
cedure described in Section 5.3. of Schwertmann & Cornell (1991).
Aqueous solutions of \( \text{FeCl}_2 \cdot 4\text{H}_2\text{O} \) and \( \text{NaHCO}_3 \) were mixed under
a constant flux of air and once the oxidation was completed, the
product was filtrated, washed several times, and dried in an oven
at 40 °C. The powdered samples dried for 24 hr and 48 hr were named
GOE24H and GOE48H, respectively. The other two samples were
prepared from Fe(III) precursors by mixing \( \text{Fe(NO}_3)_2 \cdot 3\text{H}_2\text{O} \) and
KOH aqueous solutions following procedure 5.2.1. described in the
reference above. The reaction after mixture took place at 70 °C for
60 hr. The samples were named GONOSA and GONITRA. During
the reaction, for the first sample the mixture was left in repose inside
the oven, whereas for the second case the mixture was constantly
stirred with a magnetic bar encased in chemically inert Teflon. Fi-
ally, the products were filtrated, washed several times, and dried in
an oven at 40 °C. According to Schwertmann and Cornell (1991),
the particle shape of the goethites from Fe(III) precursors is acic-
ular, and consist of several domains along the needle axis. Those
goethites from Fe(II) precursors are of lower crystallinity and consist
of agglomerated grains of acicular-like shapes.

All the powdered samples were characterized using several tech-
niques. X-ray diffraction (XRD) measurements was performed on a
BRUKER AKS D8 ADVANCE equipped with a PSD detector and a Co tube. The scans were done in the range of 10°–80°(2θ) at
0.014° per second. Thermogravimetric analysis (TGA) was done in
a TA Instruments 2950 TGA HR V6.1A. The curves were obtained
using about 15 mg of sample submitted to a flux of 100 mL min⁻¹ of
\( \text{N}_2 \) UAP and a heating rate of 10 °C min⁻¹ from room temperature
till 900 °C. BET analysis with \( \text{N}_2 \) was performed in a ASAP 2010
V4.00 D. All induced magnetization measurements were performed
by using a commercial SQUID magnetometer (MPMS—Quantum
Design). Zero-field-cooled (ZFC) magnetization curves were ob-
tained by cooling in zero field from a high temperature (300 K) to
a low temperature and then measuring the magnetization at stepwise
increasing temperatures, from 2 K to 400 K, in a small applied field
\( (B = 50 \text{ mT}) \). The sample was again cooled, in the same field, and
field cooled (FC) magnetization curves were obtained by measuring

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at stepwise increasing temperatures. An additional induced magnetization curve was obtained by cooling the sample in a field of 1 T and measuring in the same field at stepwise increasing temperature up to 400 K. Mössbauer spectrometry at 300 K, 77 K and 4.2 K were obtained in a conventional spectrometer working in the transmission mode, with a constant acceleration drive using a 25 mCi Co$^{57}$/Rh source and a cryofurnace (77–680 K) to perform temperature and in situ temperature cycling measurements. Analysis of the spectra was performed by using least-square fitting programs. Quadrupolar doublets and magnetic sextets composed of Lorentzian lines were considered. The isomer shift values are quoted to that of α–Fe at 300 K.

Mössbauer spectrometry was also used to perform several in situ annealing cycles applied to some samples with the purpose of removing the adsorbed water content. For GOE48H, in the first cycle, the sample was heated for 30 min at 380 K, below the temperature of the phase transition into haematite. Afterwards, the sample was cooled down inside the cryofurnace to 77 K to get in situ Mössbauer spectrum (MS). In a second cycle, the temperature was raised again to 370 K for 90 min and lately the MS was collected again at 77 K. For GONOSA and GONITRA, several cycles at 365 K, 370 K, 375 K and 380 K for 30 min were performed and each corresponding MS was recorded in situ Mössbauer spectrum (MS). In the case of sample GOE48H, one observes in addition to peaks clearly attributed to goethite, another small peak located at about 17 °, which is assigned to the lepidocrocite phase. The formation of this phase might be related to a larger than expected rate of oxidation. In spite of this, we are assuming that the presence of lepidocrocite in the goethites prepared from Fe(II) precursors does not affect noticeably the interpretation of final results, because of its minor relative amount (less than ~10 weight per cent). As we will see later, room temperature and 77 K MS support this idea. Fig. 1 reveals that the Bragg peaks for sample GOE48H are broader than those of GONITRA: this broadening has to be attributed to both the poor degree of crystallinity and the lower crystalline grain size of the samples prepared from the Fe(II) precursors in comparison to those prepared from Fe(III). In fact, this is reflected in the different average grain sizes of the samples as determined from the X-ray patterns (see Table 1).

Table 1. Adsorbed (per cent H$_2$O), structural (per cent OH) and total (per cent ΔOH) water content, as well as values for the non-stoichiometric parameter (γ) and surface area (S) for all samples, and Néel ($T_N$) and blocking temperatures ($T_B$). The numbers in parenthesis indicate the uncertainty in the last digit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Per cent H$_2$O</th>
<th>Per cent OH</th>
<th>Per cent ΔOH</th>
<th>γ</th>
<th>S (m$^2$ g$^{-1}$)</th>
<th>(Per cent ΔOH)/S</th>
<th>Grain size (nm)</th>
<th>$T_N$ (K)</th>
<th>$T_B$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOE24H</td>
<td>0.97(3)</td>
<td>19.4(1)</td>
<td>20.4(1)</td>
<td>0.76(1)</td>
<td>135.6(4)</td>
<td>0.15</td>
<td></td>
<td>310(2)</td>
<td>279(2)</td>
</tr>
<tr>
<td>GOE48H</td>
<td>1.36(3)</td>
<td>18.7(1)</td>
<td>20.1(1)</td>
<td>0.63(1)</td>
<td>153.4(4)</td>
<td>0.13</td>
<td></td>
<td>310(2)</td>
<td>262(2)</td>
</tr>
<tr>
<td>GONITRA</td>
<td>0.11(3)</td>
<td>13.4(1)</td>
<td>13.3(1)</td>
<td>0.25(1)</td>
<td>27.8(1)</td>
<td>0.48</td>
<td></td>
<td>387(2)</td>
<td>—</td>
</tr>
<tr>
<td>GONOSA</td>
<td>0.10(3)</td>
<td>11.8(1)</td>
<td>11.7(1)</td>
<td>0.13(1)</td>
<td>32.5(2)</td>
<td>0.36</td>
<td></td>
<td>387(2)</td>
<td>—</td>
</tr>
</tbody>
</table>
Figure 2. Thermogravimetric curves for all samples.

GÖE24H, GÖE48H, GONITRA, and GONOSA, respectively. This phenomenon is mainly assigned to the departure of surface water (per cent H₂O) (Schwertmann et al. 1985; Özdemir & Dunlop 2000). The second and most important region of weight loss, which is associated to the departure of structural hydroxyl (per cent OH), is relatively more abrupt for the Fe(III) goethites than for the Fe(II) goethites. For the first two samples, it ends at about 700 K, whereas for the others, it finishes at about 900 K. Above this temperature the weight remains rather constant. The shape of these curves could be related to the lower degree of crystallinity of the goethites from Fe(II) precursors in comparison to the goethites from Fe(III) precursors (Schwertmann & Cornell 1991).

The chemical formula for non-stoichiometric goethite is given by α-Fe₁₋₀.₃(OH)₁₋₀.₇O₂₋₀.₆, where y represents the non-stoichiometric parameter. The per cent OH can be related to the hydroxyl content in the goethite’s formula through the following equation (Schulze & Schwertmann 1984; Wolska & Schwertmann 1993):

\[
\text{per cent OH} = \frac{93.56(1 + y)}{9.24 - 1.83y}.
\] (1)

On the other hand, the total water content (per cent ΔOH) is given by:

\[
\text{per cent } \Delta\text{OH} = \text{per cent OH} + \text{per cent } \text{H}_2\text{O}. \tag{2}
\]

From the calculated data listed in Table 1, one can conclude that goethites prepared from the Fe(II) precursors contain more structural (and thus more vacancies) and surface water and hence more total water molecules than goethites prepared from the Fe(III) precursors. Additionally, the present results suggest that the stirring process during synthesis may improve the incorporation of OH groups into the goethite structure. Indeed, the agitation of the mixture of reactants makes probably the solution more homogeneous and thus favours a much more effective incorporation of the ions into the crystalline structure.

3.2 Magnetic characterization

Fig. 3 shows the ZFC/FC induced magnetization curves for each one of the samples. One observes that the FC values are higher than the ZFC ones, suggesting a small net moment in the samples, the origin of which will be discussed later. On the other hand, the shapes of the curves and the magnetization are similar for the two goethites obtained from Fe(II) precursors (Figs 3a and b). For samples GÖE24H and GÖE48H (Figs 3a and b), there are different temperatures at which the ZFC branches present a bending upwards. Since the Néel temperatures, \(T_N\), are above room temperature (see discussion below), these maxima can be associated to the blocking process of small magnetic clusters, thus determining the onset of superparamagnetic (SPM) behaviour, according to the small grain sizes. The blocking temperatures, \(T_B\), estimated as the maximum of these peaks, were located at 279 and 262 ± 2K for GÖE24H and GÖE48H, respectively.

In contrast, the shapes of the curves for goethites from Fe(III) precursors are different from each other and from the previous ones. In the case of GONITRA, the ZFC and FC curves do not practically show irreversibility (see Fig. 3c). Such a behaviour is consistent with the 300 K MS, a well-resolved sextet. Both features indicate that static magnetic ordering prevails the SPM relaxation phenomena, because the clusters exhibit a larger size than those of previous case. Here, it is worth mentioning that Barrero et al. (1999) have adequately fitted the temperature dependence of the average
magnetic hyperfine field with this model. One also observes that the ZFC curve exhibits a relatively sharp peak at around 30 K, which may be associated to a cluster glass ordering below this temperature. On the contrary, the FC/ZFC curves for GONOSA start to separate above 360 K, while the low-temperature sharp peak is found to be much broader (see Fig. 3d). This broadening could be related to the fact that the temperatures for both cluster glass ordering and magnetic ordering of clusters are closer for GONOSA than for GONITRA.

The induced magnetization $M$ scales of Figs 3(a) and (b) for samples from Fe(II) precursors are very similar. In contrast, the $M$ scale for GONITRA is at least two and four orders of magnitude larger than those for GONOSA and the goethites from Fe(II) precursors, respectively. This behaviour for the Fe(II) goethites could be ascribed to a strong surface effects, which do not allow preferred magnetic orientation of the iron ions located at these sites. Indeed, the average net contribution of the grain boundaries to the total magnetization is very small while that of the crystalline grains is also very small due to the dominant AFM character. On the other hand, the large $M$ values found for GONITRA in comparison to those for GONOSA, probably originate from larger amount of antiferromagnetically uncompensated sites in each magnetic cluster. This explanation is in agreement with the larger OH content and thus more vacancies are observed for GONITRA. Another possible explanation could come from different average cluster sizes.

Finally, the relative separation of the ZFC curve with respect to the FC one is larger for GONITRA than for GONOSA. This phenomenon could be related to different degrees of intercluster coupling, larger in the case GONITRA. In fact, it is expected that the higher the average magnetization per cluster, the larger would be the intercluster interaction.

Fig. 4 shows the induced magnetization curves for all samples, obtained under an applied field of 1 T. This field is enough to overcome any SPM fluctuations, and thus it is expected that any variation in the curve is due to intrinsic properties of the material close to the Néel point. It is possible to see that the shapes of the magnetization versus temperature ($T$) curves are similar for the goethites from Fe(II) precursors. The insert in Fig. 4 shows $dM/dT$ versus $T$ curves from which the minimum observed at about 310 K could be associated to the Néel temperatures ($T_N$) for both samples. The large reduction in $T_N$ value for these samples as compared to that reported for well-crystallized large-particle goethite of about 400 K, is due to mutual contributions coming from low crystallinity, high surface area, high concentration of defects, and large total water content. On the other hand, GONITRA and GONOSA have a $T_N$ of about 387 K, evidencing better crystallinity and larger grain sizes of these samples as compared to the others. The $T_N$ perhaps coincides with the onset of magnetic ordering of clusters. Another interesting behaviour could be seen in the magnetization curve for GONOSA: the magnetization goes through a maximum at a temperature of about 387 K, evidencing better crystallinity and larger grain sizes of these samples as compared to the others. This peak has been also observed in some natural and synthetic goethites (Hedley 1971; Broz & Sedlak 1991), but its origin is not yet clearly understood, to our knowledge. For single domain particles, this maximum can be due to the different temperature dependencies of the magnetization and anisotropy. There is no agreement in the literature as to whether the spontaneous magnetization is based on coherent rotation in a single domain particle or in the clusters, or even if the rotation is not coherent.

Fig. 5 shows the hysteresis loops for GOE48H at different temperatures. The magnetization of this sample is proportional to the applied field at 300 K and 400 K, suggesting a paramagnetic (PM) behaviour. Moreover, the loops show that the magnetization is not saturated at 7 T, as is reported by Rochette & Fillion (1989), and exhibits a extremely low coercive field, in contrary to that at 10 K. In addition, the centre of the loop is shifted towards negative fields by an amount of $H_c = ~0.6$ T (see the insert in Fig. 5), which can be due to the existence of an exchange bias between the weak ferromagnetic and AFM phases, which are present in this defective goethite. Let us remember that the WFM in goethite, which has been widely discussed in the literature, has been shown to be oriented parallel to crystallographic $c$-axis. Thermoremanence experiments (TRM) performed on oriented crystals of goethite clearly showed that the WFM of goethite is parallel to the AFM spin axis, which is also the $c$-axis (Figs 3 and 4 of Özdemir & Dunlop 1996). Various explanations of its origin have been reported. Moreover, it is well established that the balance of exchange interactions is modified at the surface because of missing iron neighbours. Néel (1962) has suggested that for small irregular particles containing $n$ moments, the number of unbalanced spins is $n^{1/2}$. Thus, the average particle moment is given by $m(n^{1/2})$, where $m$ is the average particle moment.
moment per iron atom. This model was applied by Strangway et al. (1968) to explain the thermoremanence magnetization observed in natural goethites when cooling in the presence of an external field. According to Broz et al. (1990; 1991), the net moment may also arise from the presence of unpaired chains at the surface. On the other hand, an iron neighbour can also be lost due to the presence of impurities, vacancies, and structural defects. In the case of the aluminium impurities, Hedley (1971) and Pollard et al. (1991) suggested that these ions may be preferentially located in one of the two magnetic sublattices, thus producing uncompensated spins. Finally, Coey et al. (1995) proposed that the origin of the small net moment may also originate from a hydrogen order. We conclude that the considerable amount of vacancies, and of structural defects, and the high surface areas are the main causes of the net moment in present Fe(II) goethites.

Fig. 6 shows the hysteresis loops for GONITRA at different temperatures. The shape of the loop at 300 K suggests a ferromagnetic-like behaviour in comparison to that at 400 K, but the ferromagnetism is more evident at 10 K. The hysteresis loops also show that the magnetization is not saturated at 7 T. The exchange bias is also net magnetic more evident at 10 K. The hysteresis loops also show that the loops were obtained after cooling in a 7 T field.

All samples are magnetically ordered. The MS and the derived hyperfine parameters at this latter temperature are reported elsewhere (Betancur et al. 2004).

We have performed multiple linear regression analysis between the water content and the hyperfine field at 4.2 K $B_{hf}(4.2 \text{ K})$. It is found that the variations of this parameter are poorly described when only one of the structural properties is taken into account. For example, the linear correlation coefficients between $B_{hf}$ and per cent H$_2$O is 0.12; between $B_{hf}$ and $S$ is 0.70, between $B_{hf}$ and per cent $\Delta$OH is 0.87, and between $B_{hf}$ and parameter $y$ is 0.62, etc. However, the linear correlation is noticeably improved when two physical properties are taken into account. The equation with the best correlation coefficient, where both parameter $y$ and surface area $S$ are considered, is expressed as:

$$B_{hf}(4.2 \text{ K}) = 50.8 - 0.6433y - 0.0023S \ (n = 13, \ R^2 \approx 0.91),$$

in which $n$ is the number of data points, and $R^2$ is the linear correlation coefficient. In order to calculate this equation we have considered the data reported by Schwertmann et al. (1985). It is worth mentioning that they did neither report equation similar to those presented here, nor calculate the $y$ values. Quantities $y$ and $S$ are commonly referred to as the degree of crystallinity. It is reasonable to assume that the effect of surface water content on $B_{hf}(4.2 \text{ K})$ is reflected by the surface area, because both are directly correlated, that is, the larger the surface, the higher the surface water content is.

As expected, $B_{hf}(4.2 \text{ K})$ decreases with increasing water content, mainly the structural water content. Indeed, the replacement of the Fe ions (magnetic ions) by hydroxyl groups (non-magnetic ions) and hence the presence of more vacancies (Schulze & Schwertmann 1984; Wolska & Schwertmann 1993), weaken the magnetic interactions. It is evident that both surface water and hydroxyl excess have some influence on the lattice parameters and consequently play a substantial role in the magnitude of the hyperfine field. Of course, these additional structural parameters are mainly determined by goethite formation factors such as crystallization, rates, temperature, etc.

The water content was also followed by performing several in situ annealing treatments to the samples inside the cryofurnace. Fig. 7 compares the spectrum at 77 K of GOE48H before and after a first annealing at 380 K for 30 min. One observes that the lines of the spectrum become more asymmetrically broadened after the treatment, and that the splitting between the first and sixth lines is reduced. This is reflected in the reduction by 9 T of the average hyperfine field $\langle B_{hf} \rangle$ (from 47.1 T before treatment to 38.1 T after treatment) (see Table 3). After the second annealing for 90 min at 370 K, a reduction is again noticed but rather small (1.1 T). Those experiments allow to conclude that most of the water is evaporated during the first cycle. In addition, the results for GOE24H are very similar.

3.3 Mössbauer characterization

Room temperature MS for the goethites prepared from Fe(II) precursors consist of a doublet. In contrast, both room temperature MS of GONITRA and GONOSA consist of broadened lines, which can be described by means of a distribution of sextets. The refined values of the hyperfine parameters are listed in Table 2. At 4.2 K,
obtained on GOE48H for which treatment for both samples. These latter results contrast with those hyperfine parameters were observed during the second annealing physical properties of the products. No appreciable changes in the total water content of GONOSA is less than that for GONITRA, about 0.8 T (see Table 3). From Table 1, one concludes that the change at 77 K is about 5.5 T, whereas for GONOSA this change is only controversially broadened after the treatment, however, in a lesser extent in comparison to GOE48H. The reduction for GONITRA of its \( \langle B_{hf} \rangle \) at 77 K is about 5.5 T, whereas for GONOSA this change is only about 0.8 T (see Table 3). From Table 1, one concludes that the total water content of GONOSA is less than that for GONITRA, as reflected by the reduction of the hyperfine field. Again, there is an evidence that the magnetic stirring during synthesis affects the physical properties of the products. No appreciable changes in the hyperfine parameters were observed during the second annealing treatment for both samples. These latter results contrast with those obtained on GOE48H for which \( \langle B_{hf} \rangle \) progressively decreases after each cycle.

Table 3. Hyperfine parameters at 77 K for samples before and after the annealing and rehydration treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \delta ) (mm s(^{-1}))</th>
<th>( 2\varepsilon ) (mm s(^{-1}))</th>
<th>( \langle B_{hf} \rangle ) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOE48H</td>
<td>0.47</td>
<td>-0.24</td>
<td>47.1</td>
</tr>
<tr>
<td>GONITRA</td>
<td>0.49</td>
<td>-0.28</td>
<td>49.8</td>
</tr>
<tr>
<td>GONOSA</td>
<td>0.46</td>
<td>-0.23</td>
<td>49.6</td>
</tr>
<tr>
<td>Hyperfine parameters after annealing treatments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GOE48H(^1)</td>
<td>0.47</td>
<td>-0.21</td>
<td>38.1</td>
</tr>
<tr>
<td>GOE48H(^2)</td>
<td>0.47</td>
<td>-0.20</td>
<td>37.0</td>
</tr>
<tr>
<td>GONITRA(^3)</td>
<td>0.44</td>
<td>-0.23</td>
<td>44.3</td>
</tr>
<tr>
<td>GONOSA(^4)</td>
<td>0.47</td>
<td>-0.22</td>
<td>48.8</td>
</tr>
<tr>
<td>GONOSA(^5)</td>
<td>0.47</td>
<td>-0.23</td>
<td>48.3</td>
</tr>
<tr>
<td>Hyperfine parameters after rehydration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GOE48H</td>
<td>0.49</td>
<td>-0.23</td>
<td>45.2</td>
</tr>
</tbody>
</table>

1: First cycle at 380 K for 30 min; 2: Second cycle at 380 K for 90 min; 3: First cycle at 380 K for 90 min; 4: first cycle at 380 K for 90 min; 5: second cycle at 380 K for 90 min.

At first, we tried to correlate all these data by means of a multiple linear regression analysis between the average reduced hyperfine field at 77 K, \( \langle B_{hf,77K} \rangle \), as defined below on one hand, and either per cent OH, per cent \( \Delta \)OH, per cent \( H_2O \) or per cent \( \Delta \)OH/S on the other hand. \( \langle B_{hf,77K} \rangle \) is defined as the difference between the average hyperfine fields obtained from the 77 K MS for the untreated sample, \( \langle B_{hf,untreated} \rangle \), and the sample after the first cycle, \( \langle B_{hf,first-cycle} \rangle \), with respect to the first one, according to the following equation:

\[
\langle B_{hf,77K} \rangle = \frac{\langle B_{hf,untreated} \rangle - \langle B_{hf,first-cycle} \rangle}{\langle B_{hf,untreated} \rangle}.
\] (4)

The reason to propose eq. 4 is that it takes into account a reference value, \( \langle B_{hf,untreated} \rangle \), which is the average hyperfine of the sample without any thermal treatment. In other words, \( \langle B_{hf,77K} \rangle \) is a weighted or ponderated value referred to \( \langle B_{hf,untreated} \rangle \). The best linear correlation coefficients \( R^2 \) are obtained for \( \langle B_{hf,77K} \rangle \) versus per cent OH \( (R^2 = 0.94) \) and for \( \langle B_{hf,77K} \rangle \) versus per cent \( \Delta \)OH \( (R^2 = 0.93) \).

We also tried exponential relationships between \( \langle B_{hf,77K} \rangle \) and per cent OH, and also between \( \langle B_{hf,77K} \rangle \) and per cent \( \Delta \)OH, which lead to correlation coefficients of \( R^2 = 1 \). Nevertheless, because of the low number of data points, it is difficult to decide which of the two relations, is the correct one. However, the linear and exponential relations suggest that the reduction in the hyperfine field is as large as the total water content is high. Indeed, we can expect that at the temperatures of annealing only adsorbed water content, that is, per cent \( H_2O \), should be released. However, the correlation coefficients (for the exponential as well as the linear equations) are much better for per cent OH than for per cent \( H_2O \).

Two possible mechanisms can be thus put forward. The first one considers the rupture of some goethite particles into a broad distribution of lower particle sizes because of the water pressure. Such an explanation is consistent with the reduction in the average hyperfine field and the asymmetrical broadening of the lines. A second scenario consists in the replacement of the water molecules and of some
hydroxyl groups by vacancy sites. According to the TGA results, at the annealing temperature, most of absorbed water is expected to be evaporated, while some hydroxyl groups can be also ejected, particularly for the Fe(II) goethites. More specifically, the temperature for the departure of adsorbed water occurs in the range of about $330 \pm 10 \text{K}$ for all samples. Average weight loss values of $0.37 \pm 0.03$ per cent, $0.39 \pm 0.04$ per cent, $2.0 \pm 0.2$ per cent and $2.7 \pm 0.3$ per cent for GONOSA, GONITRA, GOE24H and GOE48H, respectively, are obtained in the temperature range from 365 K to 380 K. Thus, the goethites with large surface areas are expected to possess proportionally an high water content. In the case of Fe(III) goethites, the evaporated water could escape not only from the particle surface but also from the cluster frontiers. During the thermal treatment, a part of the water is evaporated, allowing a release of the hydroxyl and/or water groups, provoking thus the creation of vacancies. Because the interaction between the magnetic iron ions in goethite is mediated by these groups, a decrease of the magnetic interaction is expected, when they are released. This second hypothesis seems to be more realistic: indeed, after removing the sample from the cryofurnace and exposing to room atmosphere for a few hours, a MS was recorded at 77 K is again collected. As listed in Table 3, the hyperfine parameters of the untreated sample are almost recovered, in agreement with a rehydration of the samples.

### 3.4 Magnetic phase diagram for goethite

As mentioned earlier, Barrero et al. (1999) have made an attempt to classify the magnetic behaviour of goethite but only as a function of particle size (and hence surface area). However, the magnetic properties observed in goethite are much more complex and depend on more structural and chemical properties. Thus, we have attempted to incorporate in a unique phase diagram all the magnetic behaviours observed as a function of temperature, $T$, surface area, $S$ (or particle size) and total water content, $\Delta \text{OH}$. $\Delta \text{OH}$ takes into account the non-stoichiometric parameter $y$ and the adsorbed water content, as given by eqs (1) and (2). A new schematic magnetic phase diagram is thus proposed in Fig. 9. Ideal goethite ($\Delta \text{OH}$/S values above $\sim0.50$ per cent/m$^2$ g$^{-1}$), has which never been reported, with low $S$ (or large particle goethite) and stoichiometric, that is, $y = 0$, below and above $T_N$ is AFM and PM, respectively. As $\Delta \text{OH}$/S decreases, and below $T_N$, goethite exhibits AFM, WFM and magnetic ordering of clusters (MOC). Above $T_N$, goethite is PM. It is interesting to mention that for certain $\Delta \text{OH}$ values and below certain temperatures (e.g. 30 K), goethite can exhibit cluster glass-like ordering (CG). As $\Delta \text{OH}$/S decreases further, there are certain critical values, which strongly depend on particle size (surface area), for which goethite becomes SPM. Above certain $S$ values, the magnetic properties are related to surface area properties. Of course, a precise line separating the different regions remains difficult to establish, but the present diagram shows some tendency (see the dotted lines in Fig. 9). It is important to emphasize that further investigations are needed to better characterize these regions.

### 4 CONCLUSIONS

We have studied the effect of the total water content and the surface area on the magnetic hyperfine properties of several non-stoichiometric goethites. It is found that these properties strongly depend on the synthesis conditions. Our results support the magnetic cluster ordering and SPM models depending upon the surface area and thus on the crystalline domain sizes. We also found that the drying time after the chemical reaction of the solutions does not appreciably affect the magnetic properties of the final products prepared from Fe(II) precursors. In contrast, the agitation during the mixture of the solutions in the goethites from Fe(III) precursors, provides significant effects on the properties of the products. In this case, more structural and adsorbed water content, slightly low surface area, cluster glass like with perhaps low magnetic coupling, and the lack of Hopkinson effect are some interesting characteristics of these goethites. We have proposed and explained two phenomenological equations, one linear and the other exponential, which relate the effect of water and/or hydroxyl contents on the average magnetic hyperfine field at low temperatures.

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