Interactions between goethite particles subjected to heat treatment

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Abstract
We have studied the effect of heating on the magnetic properties of particles of nanocrystalline
goethite by use of Mössbauer spectroscopy. Heating at 150 °C for 24 h leads to a change in the
quadrupole shift in the low-temperature spectra, indicating a rotation of the sublattice
magnetization directions. Fitting of quantiles, derived from the asymmetrically broadened
spectra between 80 and 300 K, to the superferromagnetism model indicates that this change is
due to a stronger magnetic coupling between the particles.

1. Introduction

Goethite (α-FeOOH) is a common mineral, which is often present as a very fine-grained material in soils and sediments [1, 2]. It controls the geochemistry of plant nutrients and pollutants by coprecipitation and surface reactions and records characteristic components of past environments. For example, the discovery of goethite on the surface of Mars [3] gives credibility to the claim that liquid water was present in the past.
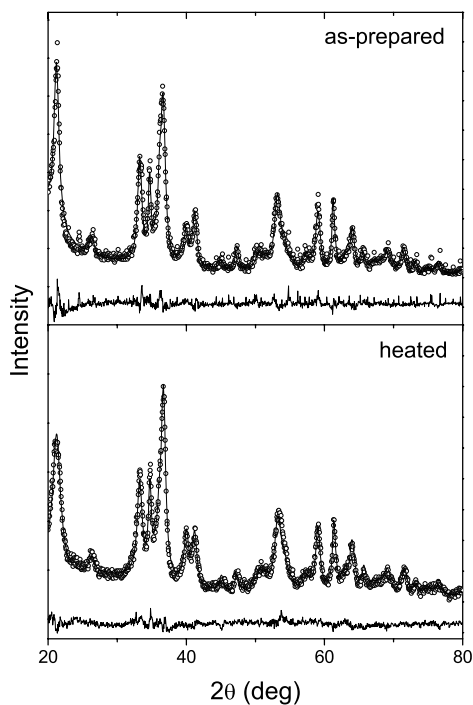
Goethite has an orthorhombic unit cell with space group *Pnma*[4]. It is antiferromagnetic with a Néel temperature of about 400 K [4, 5]. The bulk magnetic structure has been suggested to consist of four sublattices, where the spins are inclined $\pm 13°$ with respect to the [010] direction [6]. The particles are usually found to be elongated along the [010] direction. Mössbauer spectra of fine-grained goethite usually show line broadening, which is attributed to fluctuations of the magnetization directions of the grains.

If heated to temperatures above approximately 200 °C, goethite transforms into hematite (α-Fe$_2$O$_3$). Previous studies of goethite have shown that heating at *lower* temperatures can also affect the magnetic properties. Koch *et al* [7] studied

samples of goethite heated in air at temperatures from 60 to 105 °C and the results indicated an increase in the strength of the inter-particle interactions. This was suggested to be due to desorption of water from the surface of the particles, leading to a stronger coupling between the particles. In another study, Mørup *et al* [8] heated a sample at 150 °C for 24 h, and observed that the heating induced rather prominent changes in the Mössbauer spectra as the lines became broader and the hyperfine field decreased. They attributed this to a reduction of the average volume of the particles. These differences in behavior are believed to correlate with the synthesis conditions determining the initial aggregation of the crystallites [9]. Betancur *et al* [10] also studied goethite particles synthesized with different methods, and observed upon heating to 107 °C considerable changes in the Mössbauer spectra. In this case the average hyperfine field was also found to decrease as a result of the heat treatment. The authors suggested a model where the heating leads to additional vacancies due to evaporation of water. They suggested that this may lead to a reduction of the magnetic interactions as the hydroxyl groups are mediators of the exchange coupling between the Fe^{3+} ions. Thus, different samples of goethite seem to be affected differently upon heating.

In this work we have studied particles of goethite subjected to heat treatment, with special focus on low-temperature Mössbauer data and quantitative analysis of the

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[4] It should be noted that some authors use the space group *Pnmb* which results in a different indexing of directions and lattice planes.

Figure 1. XRD data for the as-prepared and heated samples. The fit residue from the Rietveld analysis is shown below each plot.

Table 1. Lattice parameters and particle dimensions (in nm) obtained from the Rietveld analysis of the XRD data. Numbers in parenthesis indicate uncertainty on last digit.

Sample	a	b	c	$d_{[100]}$	$d_{[010]}$	$d_{[001]}$
As-prepared	0.947(1)	0.3026(3)	0.462(1)	12(2)	20(2)	7(1)
Heated	0.959(1)	0.3021(3)	0.461(1)	9(2)	16(2)	3(1)

for calibration at room temperature. Temperatures above 80 K were obtained with a liquid nitrogen cryostat, whereas measurements below 80 K were performed in a closed cycle helium refrigerator. Temperatures above 320 K were obtained in a specially designed oven. Samples were re-measured at 20 K after being measured at elevated temperatures in order to confirm that no changes had been induced during the measurement.

Powder x-ray diffraction (XRD) data were obtained with a Philips PW1820 diffractometer using Cu Kα radiation. Rietveld refinements were carried out using the Fullprof software package [11].
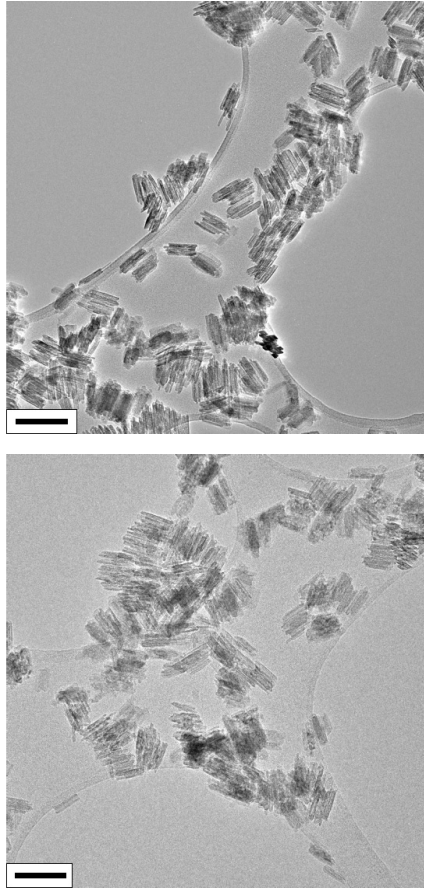
Transmission electron microscopy (TEM) images were obtained with a JEOL 3000 FEG microscope equipped with a Gatan 16 Mpix CCD camera. The samples for TEM were ultrasonically dispersed in demineralized water before being transferred (just a few droplets) to a holey carbon film where they were allowed to dry.

3. Results

Figure 1 shows XRD data for the two samples. All peaks correspond to those expected for goethite and no other phases are discernible. A Rietveld refinement of the XRD data was carried out to estimate the particles sizes. The refinement was done with the *Pnma* space group, which yielded the lattice parameters listed in table 1. These values are very close to those reported for bulk goethite [12]. In the analysis the shape of the particles was assumed to be ellipsoidal. The resulting dimensions of the crystallites are also reported in table 1.

Figure 2 shows TEM images of the two samples. No significant differences between the two samples could be observed. For both samples, a number of agglomerates are found, each consisting of several smaller rod-like entities bundled together. The dimensions of each rod is approximately 5 nm × 50 nm. It was not possible to determine whether each of these rods constituted a single goethite crystal. It is noteworthy that the sizes obtained from the Rietveld refinement are much different from those found by TEM. This seems to be a common observation for goethite, as it has also be demonstrated in a comparison by Bocquet *et al* [13] between numerous samples of different origin. The discrepancies may be explained by (imperfect) oriented attachment of particles, which is common in goethite samples [14–16], and which can make it difficult to define the crystal size in a unique way.

Figure 3 shows Mössbauer spectra of the two samples obtained at different temperatures. At the lowest temperatures the spectrum consists of a single sextet with narrow lines. As the temperature is increased, these lines become asymmetrically broadened as often observed for nanoparticles of goethite. The development with temperature is similar

hyperfine field distributions of the spectra obtained a higher temperatures in order to further elucidate this topic. We find that the magnitude of the quadrupole shift of the heated sample at low temperature is reduced, indicating that the increased degree of inter-particle interactions has led to a rotation of the sublattice magnetization directions. Moreover, when analyzing the individual quantiles of the magnetic hyperfine field distributions of Mössbauer spectra obtained over a range of temperature with the superferromagnetism model [5] we obtain quantitative results for the anisotropy energy barriers and the strength of the inter-particle interactions. These results support the conclusion concerning increased inter-particle interactions after heating.

2. Experimental details

Goethite was prepared by acid hydrolysis of an iron nitrate solution. 1.4 mol Fe(NO$_3$)$_3$ was dissolved in 700 ml 2 M HNO$_3$ and mixed with 2.8 mol NaOH in 2.8 l of water. The mixture was allowed to age at 285 K for approximately 3900 days with periodic stirring. The precipitate was washed in dilute HNO$_3$ three times followed by extensive washing in water. Finally, the sample was dried in air at room temperature. The resulting sample will in the following be referred to as the as-prepared sample.

A sample was heated in air at 150 °C for 24 h and will be referred to as the heated sample. As a bulk reference we used a natural well-crystallized sample from Cornwall, UK (the same as the one used by Mørup *et al* [5]).

The ^{57}Fe Mössbauer spectra were obtained in a conventional transmission geometry in the constant acceleration mode. The source was ^{57}Co in Rh. A foil of α-Fe was used
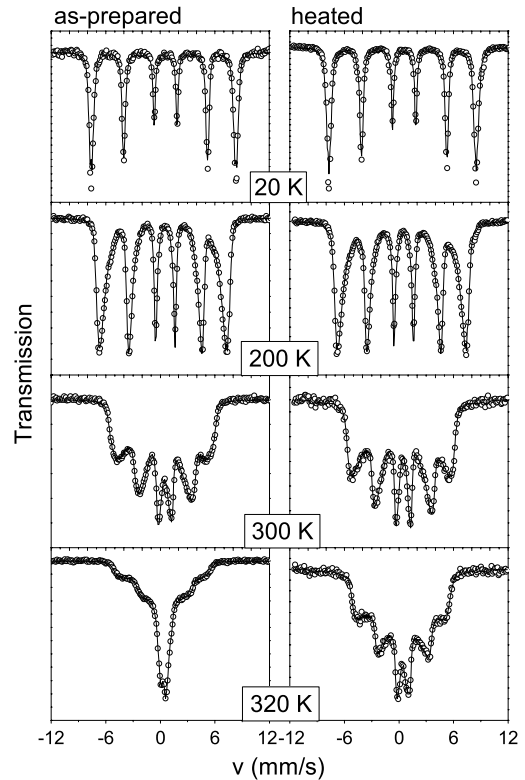
Figure 2. TEM images of the as-prepared (top) and heated (bottom) samples. The bar in the lower left corner corresponds to 100 nm.

Figure 3. Mössbauer spectra of the as-prepared (left) and heated (right) samples. The lines are fits using a distribution of sextets.

for both samples and the differences are only obvious at the highest temperatures. At 320 K the sextet component is most prominent in the spectra of the heated sample. Further spectra were obtained at temperatures up to 368 K. At these temperatures, the spectra of both samples contained a single doublet with narrow lines (data not shown).

4. Analysis of the Mössbauer spectra

The low-temperature (20–80 K) Mössbauer spectra could be well fitted with a single sextet with narrow lines. Figure 4 shows the variation of the isomer shift δ, the quadrupole shift ε, and the hyperfine field B_{hf} for the as-prepared and heated samples as a function of temperature. Data for the bulk sample are shown for comparison. Compared to the as-prepared sample, data for the heated sample indicate that the isomer shift is slightly smaller, the absolute value of the quadrupole shift is decreased, and the magnetic hyperfine field remains essentially unaffected.

As the temperature is increased above 80 K, the fits with only a single sextet become increasingly unsatisfactory due to the asymmetrical broadening of the lines. As a consequence we have fitted the spectra with a distribution of sextets, all with the same value of the isomer shift and the quadrupole shift, but with different hyperfine fields [17]. Figure 3 shows the

resulting fits. We have for comparison also fitted the 20 K spectra using a distribution. However, as one may observe this does not lead to very satisfactory fits, due to the small number of steps within such a narrow distribution. As a consequence, the analysis presented in this section is only based on data from 80 K and up.

At 368 K, the spectra of both samples could be satisfactory fitted using a single doublet with an quadrupole splitting ΔE_Q of 0.50 ± 0.01 mm s^{-1}. At this temperature the isomer shifts and quadrupole splittings obtained for the two samples were identical within the experimental uncertainty.

Figure 5 shows the hyperfine field distributions, obtained for the spectra shown in figure 3. At the highest temperatures, the emerging doublet component becomes apparent in the distributions as a sextet component with a small (<5 T) hyperfine field. Based on the hyperfine field distributions, $p[B_{hf}(T)] dB_{hf}$, we could follow the temperature dependence of certain f-quantiles, $B_f(T)$, defined by the relation

$$f = \int_0^{B_f(T)} p[B_{hf}(T)] \, dB_{hf}. \qquad (1)$$

These temperature dependences were analyzed with the model of 'superferromagnetism' [5, 18, 19]. In this model each particle is assumed to be coupled to its neighbors through ordinary exchange interactions. In the absence of this coupling, each particle is assumed to exhibit fast superparamagnetic relaxation, but the interactions result in an (at least local) ordering of the (sublattice) magnetization directions of the particles below a temperature T_p.
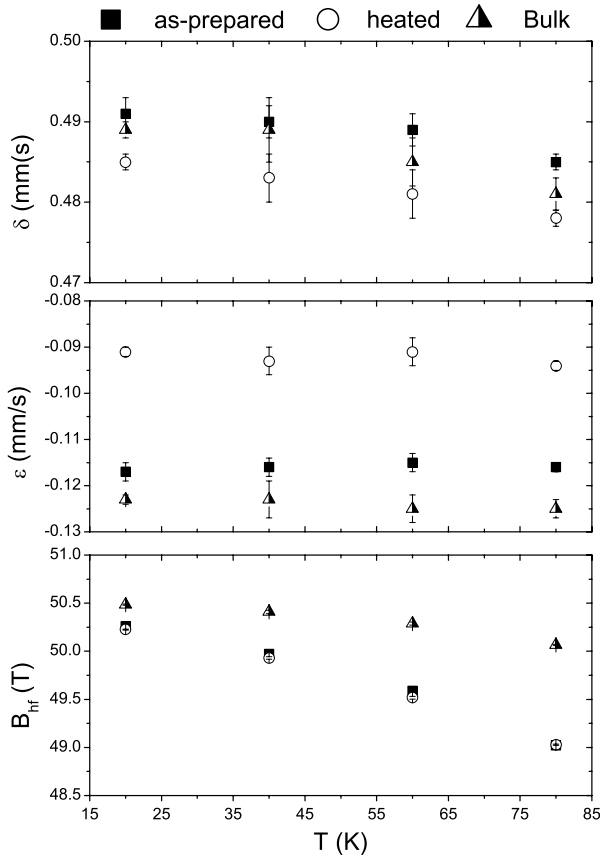
Figure 4. Isomer shift (δ), quadrupole shift (ε), and magnetic hyperfine field (B_{hf}) as a function of temperature for the as-prepared, heated, and bulk samples.

Figure 5. Magnetic hyperfine field distributions obtained from fits to a number of the Mössbauer spectra shown in figure 3.

The interaction energy between two crystallites i and j may be written [18]

$$E_{ij} = -\vec{M}_i(T) \cdot K_{ex}^{ij} \vec{M}_j(T), \qquad (2)$$

where K_{ex} is an exchange coefficient, which depends on the coupling strength between the two particles. Summing over all neighbors we arrive at

$$E_i = -\vec{M}_i(T) \cdot \sum_j K_{ex}^{ij} \vec{M}_j(T), \qquad (3)$$

which in a mean-field approximation reduces to

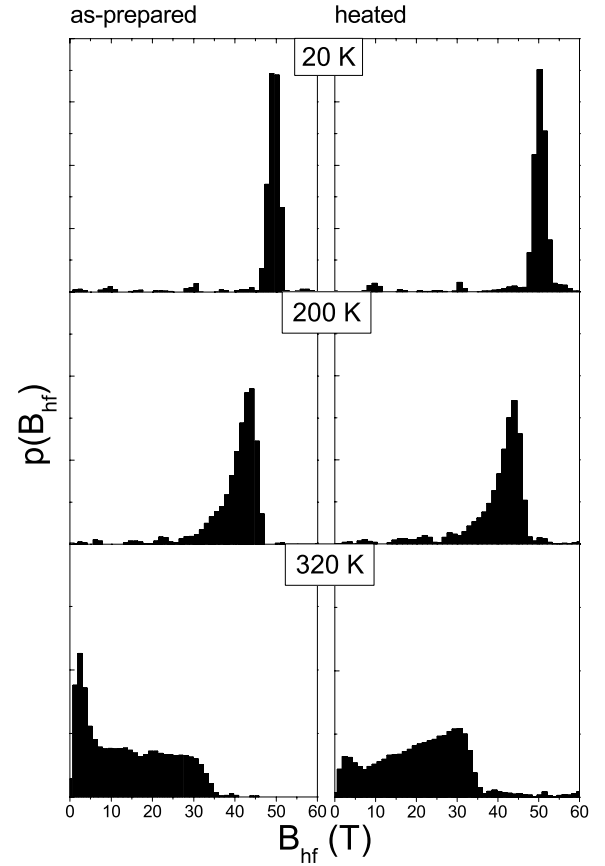$$E_i = -K_m \vec{M}_i(T) \cdot \langle \vec{M}(T) \rangle, \qquad (4)$$

where $K_m \langle \vec{M}(T) \rangle$ is the mean field from the all neighboring crystallites, and K_m is the effective exchange coefficient.

Introducing the order parameter

$$b(T) \equiv \frac{|\langle \vec{M}(T) \rangle|}{M_0(T)}, \qquad (5)$$

where $M_0 = |\vec{M}_i|$ is the saturation value of the (sublattice) magnetization, (4) may be rewritten

$$E_i = -K_m M_0^2(T) b(T) \cos \varphi, \qquad (6)$$

where φ is the angle between $\vec{M}_i$ and $\langle \vec{M}(T) \rangle$. As a result we write the total magnetic energy of crystallite i as

$$E_{tot} = -E_a \cos^2 \theta - K_m M_0^2(T) b(T) \cos \varphi \qquad (7)$$

where $E_a = KV$ is the anisotropy energy barrier, K is the anisotropy constant, V is the volume of the particle, and θ is the angle between M and the magnetic easy axis (a uniaxial anisotropy has been assumed).

Nanoparticles in close contact often exhibit oriented attachment, i.e., they are oriented along common crystallographic orientations. This has been observed in studies of TiO$_2$ [20], α-Fe$_2$O$_3$ [21], and goethite [14–16]. In this case, the easy axes of magnetization must be pointing in almost the same direction. As a first approximation one may therefore assume that $\langle \vec{M}(T) \rangle$ is parallel to the easy axis of particle i [19] and the above expression reduces to
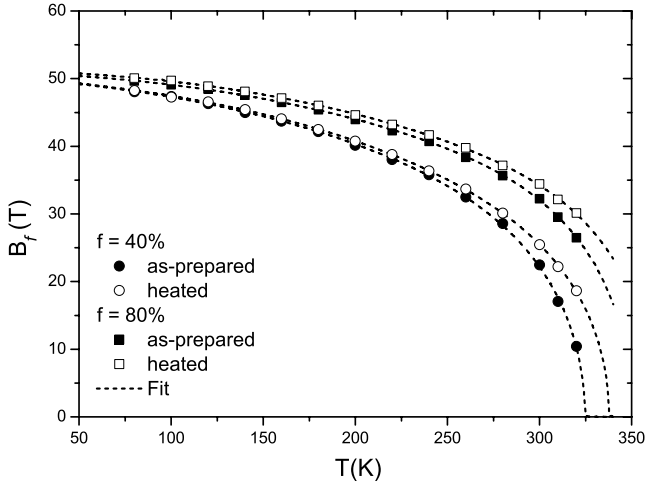
$$E_{tot} = -E_a \cos^2 \theta - K_m M_0^2(T) b(T) \cos \theta. \qquad (8)$$

The resulting temperature variation is found using Boltzmann statistics as

$$b(T) = \frac{\int_0^\pi \exp(-\beta E_{tot}) \sin \theta \cos \theta \, d\theta}{\int_0^\pi \exp(-\beta E_{tot}) \sin \theta \, d\theta}, \qquad (9)$$

where $\beta = (k_B T)^{-1}$. This expression for the temperature dependence of $b(T)$ can be solved numerically. In the absence

Figure 6. B_f versus T for $f = 40$ and 80% extracted from the hyperfine field distributions. The fits to the superferromagnetism model are shown as lines.

of anisotropy, (9) yields

$$b^0(T) = \mathscr{L}\left(\beta K_\mathrm{m} M_0^2(T) b^0(T)\right),$$ (10)

where $\mathscr{L}(x)$ is the Langevin function. The resulting ordering temperature in the absence of anisotropy may be expressed as [18]

$$T_\mathrm{p}^0 = \frac{K_\mathrm{m} M_0^2(T_\mathrm{p}^0)}{3k_\mathrm{B}}.$$ (11)

We will in the following report results in terms of $E_\mathrm{int} = K_\mathrm{m} M_0^2(T_\mathrm{p}^0) = 3k_\mathrm{B} T_\mathrm{p}^0$ and E_a. In our case, we fitted (9) to the experimentally found order parameter

$$b_f(T) = \frac{B_f(T)}{B_0(T)},$$ (12)

where $B_0(T)$ is the hyperfine field for the bulk sample, in order to obtain values of the interaction strength and the anisotropy energy barrier for each quantile. In previous studies of goethite particles [5, 7], the *average* hyperfine fields were fitted with the same model, but the estimated magnetic anisotropy was in that case found to be negligible. As discussed by Hansen *et al* [19] the influence of the anisotropy energy may be averaged out if only the average hyperfine field is considered.

Figure 6 shows the fits for selected quantiles. We have only considered quantiles between 40 and 80% as the noise in the derived hyperfine field distributions leads to less reliable quantiles outside this range. The superferromagnetism model is found to fit the data very well.

Figure 7(a) shows the obtained interaction strengths. A slightly larger value ($\sim$60 K on average) of $E_\mathrm{int}/k_\mathrm{B}$ is observed for the heated sample compared to the as-prepared sample. Figure 7(b) shows the anisotropy energy barriers. The values of $E_\mathrm{a}/k_\mathrm{B}$ are found to be very similar for the two samples, and all increase with increasing f, from close to 400 K at $f = 40\%$ to $\approx$1600 K at $f = 80\%$.
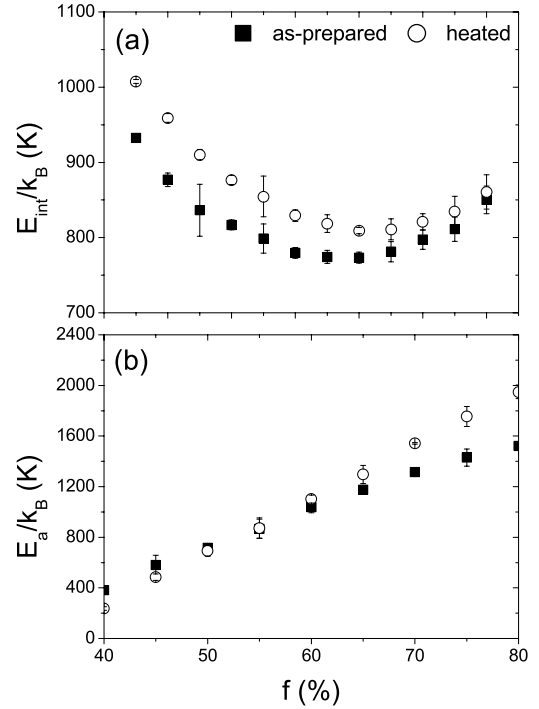
Figure 7. (a) Interaction strength (E_int) and (b) anisotropy energy barrier (E_a) as a function of f. Both are shown in units of K.

5. Discussion

From the TEM images, we see that in our case the heating has little, if any, effect on the morphology of the particles. The XRD data also confirm the absence of new phases, hence no phase transformation has taken place. This is also indicated by the observation that δ and B_hf at the lowest temperatures are very similar for the two samples. The finding that almost the same value of the barrier (except for the highest quantiles) is found for the two samples also indicates that the heating has not resulted in a volume change.

The sizes obtained from XRD differ and the particle dimensions seem to be reduced as a result of the heating. However, no such change could be inferred from the TEM images. These differences could be due to the fact that microstrain was not included in our Rietveld refinement of the XRD data.

From figure 4 it can be concluded that the heat treatment results in a change in the quadrupole shift ε. In general, the magnitude of the quadrupole *shift* depends on parameters (V_{zz}, η) pertaining to the electric field gradient (EFG) of the material, and the angles between the principal component of the EFG and the magnetic hyperfine field. On the other hand, the quadrupole *splitting* (ΔE_Q) depends only on V_{zz} and η. As the quadruple splittings at high temperature were identical, the observed change cannot be attributed to differences in the EFG, but must be related to the angles between the EFG and the hyperfine field. Frandsen and Mørup [22] also observed a similar change in ε when the interactions between 8 nm particles of hematite (α-Fe$_2$O$_3$) were varied. In the case of hematite, the value of ε depends on the angle ϕ between the

magnetization and the EFG (assuming uniaxial symmetry) as

$$\varepsilon = \varepsilon_0 (3 \cos^2 \phi - 1)/2. \tag{13}$$

It was suggested that the particle interactions result in a rotation of the sublattice magnetization directions. Although the EFG in goethite is more complex [23] we suggest that a similar effect is in play here. The mechanism behind this spin rotation was in the case of hematite suggested to be interactions between particles with non-aligned lattice planes [22]. Because of the exchange coupling between the particles, the sublattice magnetization in each particle is slightly rotated.

The magnetic anisotropy constant of goethite is on the order of 5×10^4 J m^{-3} [6, 13]. With a particle volume on the order of 500–1000 nm^3 (table 1), one finds that $KV \gg k_B T$ at room temperature. Therefore, one should not expect relaxation of the sublattice magnetization directions of a particle as a whole. However, high-resolution TEM (HRTEM) studies of the as-prepared sample have shown that the rod-shaped particles contain many low-angle grain boundaries [24]. The net exchange interaction between neighboring grains may be weak because of the magnetic mismatch in the grain boundary, and therefore the (sublattice) magnetization directions in the grains may fluctuate. This can explain the relaxation effects seen in the Mössbauer spectra. The magnetic mismatch may also result in magnetic frustration and a related spin-canting near a grain boundary. The present Mössbauer data show that the heating results in some suppression of the magnetic fluctuations and also leads to a larger spin rotation. Both effects can be explained by a stronger exchange coupling across the interfaces between the grains, which could be related to, for example, some structural relaxation in the grain boundaries or to evaporation of impurities such as water.

The Néel temperature, T_N, of bulk goethite is close to 400 K. In our as-prepared sample, the sextet has almost completely collapsed to a doublet at 320 K. It has been debated whether this collapse should be attributed to fast superparamagnetic relaxation or to a reduction of T_N [25]. If the particles are not superparamagnetic to begin with, the observed changes after heating could also be explained by an increase in T_N. As the heating does not seem to cause an increase of the particle volume, such a change in T_N would imply stronger magnetic interactions, possibly through a change in the number of imperfections in the crystal structure. Bocquet and Hill [26] have found such a correlation between T_N and the number of vacancy defects. Although it is plausible that sample heating results in a change in the number of lattice defects, it is observed that, upon heating our sample, the value of ε moves *away* from the bulk value, rather than approach it as one would expect from such a correlation. We therefore do not find that such a mechanism can explain the effects observed in our current study.

6. Summary

We have studied samples of goethite before and after heat treatment. We find that the quadrupole shift at low temperatures is markedly different in the heated sample, indicating a rotation of the sublattice magnetization directions.

Using the model of superferromagnetism to analyze the spectra at elevated temperatures, we find that the heating increases the inter-particle interaction, in agreement with previous studies. We conclude that this is the probable cause of the rotation of the sublattice magnetization directions.

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