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# On spin-canting in maghemite particles

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The degree of alignment of the magnetic moments of $Fe^{3+}$ ions in ultrafine maghemite particles has been studied in samples with induced magnetic texture. The textured samples were prepared by freezing ferrofluids, containing 7.5 nm maghemite particles, in a magnetic field. Mössbauer spectroscopy studies of the textured samples in large magnetic fields demonstrate that the lack of full alignment is not an effect of large magnetic anisotropy, as suggested recently, but that the effect is rather due to canting of individual spins.

## I. INTRODUCTION

The lack of full aligment of the spins in ultrafine maghemite particles in large applied fields was demonstrated by Coey[1] more than 20 years ago. He found, by using Mössbauer spectroscopy, that even a magnetic field of 5 T was insufficient to align all spins in 6 nm $\gamma$-$Fe_2O_3$ particles. The spin structure of the particles was suggested to be noncollinear due to competing antiferromagnetic exchange interactions, most likely at the surfaces of the particles.[1] The observations by Coey also explain why the saturation magnetization of small magnetic particle systems is smaller than that of the bulk material. The phenomenon of canting of spins in nominally ferrimagnetic particles has later been observed in other oxides[2–4] as well as for thin oxide layers on metallic iron.[5]

The suggestion[1] that spin canting is a surface phenomenon has been supported by several later studies, e.g., by $^{57}$Fe or $^{57}$Co surface enrichment of maghemite particles.[6–8] However, recent Mössbauer studies of maghemite particles, with and without surface enrichment with $^{57}$Fe, have indicated[9] that spin canting is not a surface effect, but rather a finite-size effect that is uniform throughout the whole volume of the particles. Also, lately, Pankhurst and Pollard[10] have shown that the observation of nonzero $\Delta m=0$ Mössbauer line intensities may be explained by the response of a randomly oriented ferrimagnetic powder to a large magnetic field when the individual particles are assumed to have a large uniaxial anisotropy, i.e., they suggest that the so-called spin canting effect is due to the lack of full alignment of all the spins in the particles. Hence, the lack of full alignment of spins is a matter of continuing dispute, despite the long history of the discussion and the great importance of maghemite particles in, for example, magnetic recording media and ferrofluids.

We have devised a simple experiment in order to clarify whether the incomplete spin alignment in ultrafine maghemite particles is an effect of specific spins being canted relative to the field direction or, as suggested by Pankhurst and Pollard,[10] that it stems from the inability of the applied field to make the magnetization vector overcome the magnetic anisotropy of the particles. The idea of our experiment is that if full alignment of the magnetic moments is hindered by the volume anisotropy of the particles, then the degree of alignment will depend on the angular distribution of the anisotropy directions with respect to the applied field. A non-random distribution of easy axes (magnetic texture) can be obtained by freezing a ferrofluid in an applied magnetic field. The degree of texture is a function of the magnetic moment of the particles, the intensity of the applied magnetic field, the magnetic anisotropy, and the freezing temperature of the ferrofluid.[11,12] Here, we will show, results of studies of magnetically textured samples of 7.5 nm $\gamma$-$Fe_2O_3$ particles. Recently, we performed similar experiments on 9.0 nm maghemite particles.[13] The advantage of studying 7.5 nm maghemite particles is, as will be shown, that the so-called spin canting effect is more prominent in the smaller particles.

## II. EXPERIMENT

Magnetite particles were prepared by coprecipitation of Fe(II) and Fe(III) from an aqueous solution. Leaving the prepared ferrofluid in air resulted in oxidation of the magnetite ($Fe_3O_4$) into maghemite ($\gamma$-$Fe_2O_3$).

Magnetization measurements were carried out by using a vibrating-sample magnetometer. Mössbauer spectroscopy studies were performed by using a conventional constant acceleration spectrometer with a $^{57}$Co source in rhodium. Magnetic fields between zero and 4.35 T could be applied parallel or perpendicular to the $\gamma$-ray direction. Transmission electron microscopy was performed using a Philips EM301 electron microscope.

Energy dispersive x-ray diffraction spectra were obtained by measuring the energy spectrum of scattered white x-ray radiation. From the line broadening of the diffraction peaks an estimate of the mean crystallite size could be deduced.

## III. RESULTS AND DISCUSSION

Figure 1 shows the magnetization versus applied magnetic field at room temperature. The solid line is a fit, following the method of Chantrell *et al.*,[14] to the magnetization curve, assuming a lognormal distribution of particle size.

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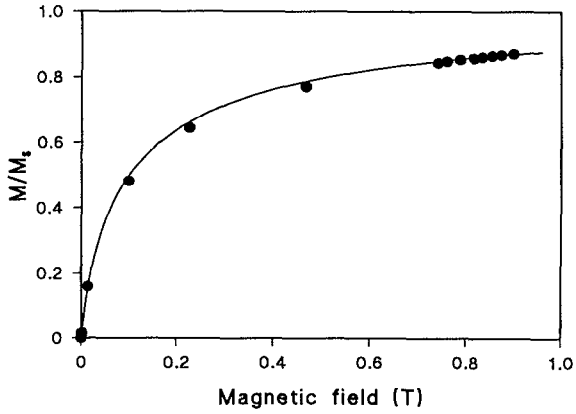


FIG. 1. The magnetization, at room temperature, as a function of applied magnetic field. The full curve is the best fit obtained using the method of Chantrell *et al.*[14]

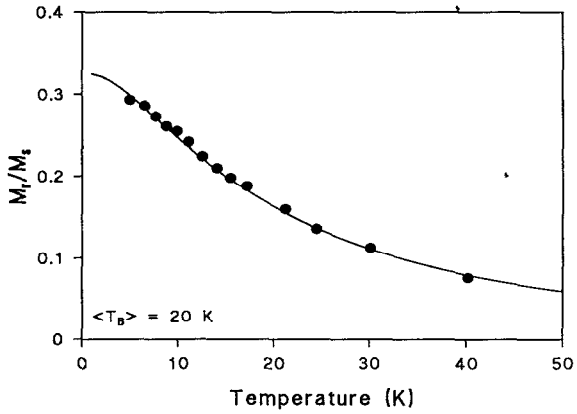


FIG. 2. The temperature dependence of the remanent magnetization. The circles are the experimental data and the solid lines are the best fits, using Eq. (1), for different chosen $\langle T_B \rangle$ values. The distribution of $T_B$ has been assumed to be lognormal (see the text).

From electron micrographs, Mössbauer spectroscopy, x-ray diffraction, and magnetization measurements, the volume-weighted mean particle diameter was found estimated to be $\bar{D}=7.5\pm1.0$ nm.

From the decay of remanence the mean superparamagnetic blocking temperature, $\langle T_B \rangle$, can be extracted by fitting with the following expression:

$$\overline{M_r}(T)=\frac{M_r}{M_s}=\overline{M_r}(0)\int_{T/\langle T_B\rangle}^{\infty} f(T_r)dT_r, \tag{1}$$

where $\overline{M_r}$ is the reduced remanence, $M_r(0)$ is the reduced remanence at 0 K, $T_r=T_B/\langle T_B \rangle$ is the reduced blocking temperature, and $f(T_r)$ is the normalized distribution of blocking temperatures. Assuming the effective magnetic anisotropy constant, $K_{\text{eff}}$, to be size independent, $f(T_r)$ will follow a lognormal distribution. The best fit of Eq. (1) to the $\overline{M_r}(T)$ curve (see Fig. 2) was found for $\langle T_B \rangle \approx 20$ K. From

$$\tau_m=\tau_0 \exp(K_{\text{eff}}V/k_BT_B), \tag{2}$$

where $V=\pi/6\bar{D}$, and $\tau_m$ and $\tau_0$ are the measuring time (100 s) and the minimum relaxation time ($10^{-10}$–$10^{-12}$ s),[15–17] respectively, $K_{\text{eff}}$ is deduced to be $(3-4)\times10^4$ J m$^{-3}$.

Mössbauer spectra of the ferrofluid, frozen in a magnetic field of 4.35 T applied parallel or perpendicular to the sample plane, are shown in Fig. 3. The spectra were obtained at 5 K in a remanence field of 0.06 T perpendicular to the sample plane. The spectra are typical for ultrafine maghemite particles,[18] the spectra are asymmetric with lines 1, 2, and 3 more intense than lines 4, 5, and 6, respectively, and with an inward broadening of each of the absorption lines. As evident from Fig. 3, the spectra have different absorption intensities in the line pair 2 and 5 (the spectra have been normalized to the same maximum absorption intensity in line 1). The relative intensity of the absorption lines 2 and 5 depends on the direction of the magnetic hyperfine field, acting at the absorbing Mössbauer nuclei, relative to the direction of the gamma rays. When the hyperfine field is parallel to the $\gamma$-ray direction, the intensity of lines 2 and 5 will be zero, while a spin orientation perpendicular to the $\gamma$-ray direction will result in the relative line intensities 3:4:1:1:4:3. The different intensities of lines 2 and 5 for the two sample preparation fields thus reveal different average orientations of the magnetic moments, i.e., it demonstrates the induced texture of the samples. The lower part of Fig. 3 shows the difference spectrum.

Increasing the magnitude of the magnetic field applied during the measurements results in a change of the relative areas of lines 2 and 5. Already for fields below 1 T, a saturation is found in the orientation of the magnetic moments in the direction of the applied field. Mössbauer spectra of 7.5 and 9.0 nm samples, when measured in a magnetic field of 4.35 T applied parallel with the $\gamma$-ray direction, are shown in Fig. 4. The line intensities of lines 2 and 5 were found to be independent of the direction of the induced texture. The intensities of lines 2 and 5 have decreased considerably, but

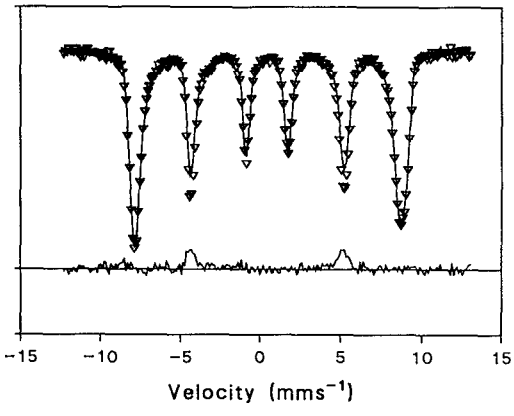


FIG. 3. Mössbauer spectra of samples with frozen-in magnetic texture. The freezing field was 4.35 T. The spectrum of the sample frozen in a field perpendicular to the sample plane is given by a solid line, while the triangles denote the sample frozen with the field applied parallel to the sample plane. The Mössbauer spectra were obtained at 5 K in a field of 0.06 T along the $\gamma$-ray direction. The spectra have been normalized to the same maximum absorption in line 1. The lower part of the figure shows the difference spectrum.

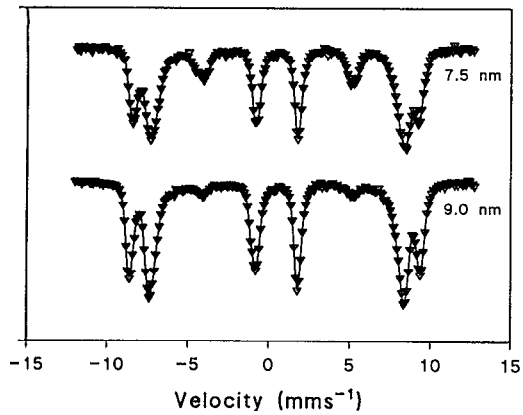


FIG. 4. Mössbauer spectra of 7.5 nm (the upper spectrum) and 9.0 nm maghemite[13] particles in a magnetic field of 4.35 T parallel to the $\gamma$-ray direction. The spectra were obtained at 5 and 15 K, respectively.

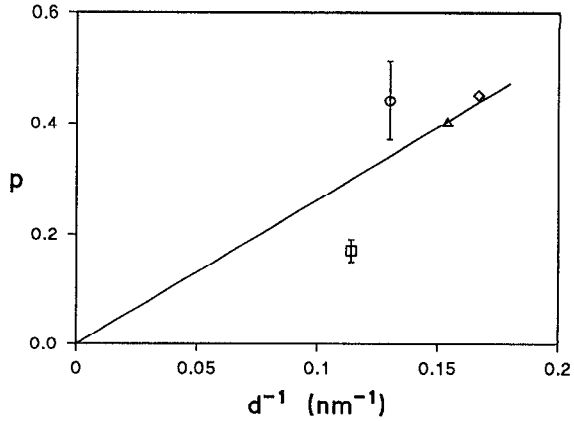


FIG. 5. The fraction of canted spins, $p$, versus the inverse of the particle diameter of maghemite particles (◇,[1] △,[4] □,[13] and ○, present study) as found, by Mössbauer spectroscopy, at about 5 K and in an applied field of 4–5 T.

they have not achieved the value of zero as they should if all spins were aligned by the field. This observation is similar to that made by Coey.[1] If the model of Pankhurst and Pollard (the PP model) was correct, one should expect that the degree of spin alignment in the 4.35 T field should differ for the 7.5 and the 9.0 nm samples. The fact that relatively low fields, applied during the measurements, are able to align the particle magnetic moment, but with some spins retaining an angle relative to the applied field, is consistent with the concept of spin canting.

Furthermore, the magnetic anisotropies of the studied maghemite particles are much smaller than would be necessary to account for the lack of full alignment by the model of Pankhurst and Pollard.[10] We find $K_{\text{eff}}=(3–4)\times10^4$ J m$^{-3}$, while in the PP model an effective magnetic anisotropy constant about an order of magnitude larger is needed to explain the observed incomplete alignment.

The degree of spin canting depends on the particle size. As shown in Fig. 4, the intensity of lines 2 and 5 is largest for the 7.5 nm particles. When assuming the area ratio of line pairs (2,5) and (1,6) in the Mössbauer spectra to be $\frac{2}{3}$ for canted spins and zero (in an applied field of 4–5 T) for noncanted spins, the fraction, $p$, of the spins being canted may be found. In Fig. 5, $p$ is plotted for different samples as a function of the inverse particle diameter. It is clear that the degree of spin canting increases with decreasing particle size. This is expected, both when assuming the spin canting to be a surface effect and when assuming it to be a finite size effect uniform throughout the particle. If the spin canting is due to spin canting of a certain surface layer with thickness $t$, then the plot of $p$ vs $d^{-1}$ should, in a first-order approximation, follow a straight line. From the straight-line fit in Fig. 5, $t\approx0.9$ nm is deduced. However, the data suggest that other parameters than the particle size influence the degree of spin canting in ultrafine maghemite particles.

When fitting the Mössbauer spectrum of the 7.5 nm particles in Fig. 4 with single lines, the deduced magnetic hyperfine field derived from the positions of lines 2 and 5 is found to be about 1 T smaller than that deduced from lines 1 and 6. This observation cannot be accounted for by the PP model, because the incomplete alignment is ascribed to the incomplete alignment of all spins, whereas the observation can be understood in the model of spin canting, because the canting of the spins must originate from the surroundings of the spins being different from that of the average spin (on either the A site or the B site). A similar observation has been made for the 9.0 nm maghemite particles.[13]

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