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1994 J. Phys.: Condens. Matter 6 3081

(http://iopscience.iop.org/0953-8984/6/16/013)

J. Phys.: Condens. Matter 6 (1994) 3081–3090. Printed in the UK

Ultrafine maghemite particles: I. Studies of induced magnetic texture

P V Hendriksen†, F Bødker‡, S Linderoth†, S Wells‡ and S Mørup
Physics Department, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received 7 January 1994

Abstract. A sample with an orientational magnetic texture was prepared by freezing a ferrofluid containing maghemite particles in a magnetic field. The degree of alignment of the easy directions obtained by field-cooling was examined by Mössbauer spectroscopy for varying strengths of the freezing field. We compare the results with the predictions of a simple model assuming that the intrinsic magnetic anisotropy in the particles is uniaxial and that the particles are non-interacting. Good agreement between the experimental results and the theoretical model is found. This allows a determination of the magnetic anisotropy energy constant of the particles, which is an important parameter in the model. The anisotropy energy constant is also determined from the reduction of the magnetic hyperfine field relative to the saturation value caused by collective magnetic excitations, as well as from a decay of remanence measurement. Good agreement between the estimates of the anisotropy energy constant by the three methods is found.

1. Introduction

Samples with magnetic texture can be prepared by freezing suspensions of single-domain particles (ferrofluids) in a magnetic field. The orientation of the magnetic moments along the applied magnetic field will enforce a degree of alignment on the easy directions of the particles. The equilibrium orientation of the easy directions is frozen-in when the carrier medium solidifies. Several studies of the orientational magnetic texture induced in this way have been reported in the literature [1–5]. In most of these studies the magnetic texture was examined by magnetization measurements. Here, as in [5], we measure the induced texture by Mössbauer spectroscopy. This method allows information on the orientational distribution of the magnetic moments to be obtained in the case of zero applied field, which is not possible by magnetization measurements. (Magnetization measurements probe the mean value of the cosines of the angles between the magnetic moments and the direction of the applied field, whereas Mössbauer spectroscopy probes the squared cosine of this angular distribution. Due to the invariance of the magnetic anisotropy energy in fine particles to a 180° *rotation of the magnetic moment even non-random orientations of the easy directions* in a particulate sample may have zero magnetization.)

Hartmann and Mende [4] have given a theoretical treatment of the induced magnetic texture in a field-cooled ferrofluid. They considered the orientational effect of a magnetic field on an ensemble of single-domain magnetic particles that were free to rotate, taking into

† Present address: Materials Department, Risø National Laboratory, DK-4000 Roskilde, Denmark.
‡ Chemistry Department, University College of North Wales, Bangor, Gwynedd, LL57 2UW, UK.

0953-8984/94/163081+10$19.50

account the interplay between the Zeeman energy, the magnetic anisotropy energy of the particles and the thermal energy. It is the purpose of this study to perform an experimental test of their predictions by using Mössbauer spectroscopy. Furthermore, samples with frozen-in magnetic texture are useful for studying, for example, the origin of the incomplete spin alignment observed in fine maghemite particles in large applied fields [6]. In the following paper [7] the magnetically textured samples studied here are utilized for a study of the spin structure in the particles.

The degree of alignment of the easy directions obtained by freezing the samples in a field depends strongly on the value of the magnetic anisotropy energy constant, K. An estimate of the anisotropy energy constant is obtained from a comparison of the theoretically expected orientation in the field-cooled samples with those observed experimentally. The magnitude of the anisotropy constant is further estimated by two other methods: (i) from the reduction relative to the saturation value of the magnetic hyperfine splitting in the 15 K Mössbauer spectrum, caused by collective magnetic excitations, and (ii) from a determination of the distribution of blocking temperatures found by a decay of remanence measurement.

2. Experimental

The ferrofluid was prepared by a chemical co-precipitation of Fe(II) and Fe(III). An aqueous solution of $FeSO_4$ and $Fe(NO_3)_3$, with a concentration ratio of 1:2, was slowly added to an ammonium-hydroxide solution, resulting in the formation of a precipitate of colloidal magnetite. The particles were subsequently coated with oleic acid, washed and suspended in heptane. To separate the magnetite particles from large needle-shaped goethite crystals, which are also formed in small numbers during preparation, the sample was centrifuged at 35 000 RPM (70 000 g). Electron micrographs of the sample revealed that after centrifuging the needle-shaped particles constitute less than 2% of the particles (by volume). When the prepared ferrofluid was exposed to air the particles transformed to γ-Fe_2O_3 (maghemite). The particle size distribution of the sample was investigated by electron microscopy using a Philips EM301 electron microscope. The particle size distribution was estimated by using a Zeiss particle size analyser.

The magnetization curve of the sample was obtained at room temperature using a vibrating sample magnetometer (VSM). The magnetic size distribution was extracted by the method of Chantrell and co-workers [8]. An estimate of the anisotropy constant of the particles was obtained from a decay of remanence measurement between 4–50 K, again using a VSM [9].

Mössbauer spectra were obtained in a closed-cycle helium refrigerator allowing spectra to be obtained at temperatures down to 15 K. A 50 mCi source of ^{57}Co in rhodium was used. Isomer shifts are given relative to α-iron at room temperature. The sample was kept in a disk-shaped plexiglass container. The texture-inducing field was applied perpendicular to the disk plane during cooling of the sample. The cooling rate was approximately 30 K min^{-1} at the freezing point of the carrier medium (heptane, 182 K).

3. Sample characterization

3.1. Particle size distribution

The particle size distribution in ferrofluids prepared in the described manner is normally well described by a log–normal distribution, which in a normalized form ($y = D_r/\bar{D}_r$) is

$$f(y) = \frac{1}{\sqrt{2\pi}\sigma_r y} \exp\left(-\frac{\ln^2 y}{2\sigma_r^2}\right) \tag{1}$$

where D_r is the particle diameter, $\bar{D}_r$ the median diameter and σ_r the standard deviation of $\ln y$. The results of both magnetization measurements and Mössbauer spectroscopy depend on the volume-weighted particle size distribution rather than the number-weighted size distribution, as directly obtained from TEM micrographs. If the number-weighted particle size distribution is log–normal, the volume-weighted distribution will also be log–normal. The parameters of the two distributions are related by $\bar{D}_v = \bar{D}_r \exp(3\sigma_r^2)$ and $\sigma_v = 3\sigma_r$ [10], where the subscript v denotes the parameters of a volume-weighted particle volume distribution. (When we refer to the volume distribution, $f(V)$, we mean the volume-weighted particle volume distribution). By analysing the particle size data obtained from the electron micrographs in terms of a normalized log–normal distribution we find a median diameter of $\bar{D}_r = 6.8\,\text{nm}$ and a standard deviation σ_r equal to 0.31. This corresponds to a volume distribution with a median diameter of $\bar{D}_v = 8.8\,\text{nm}$ and a standard deviation of $\sigma_v = 0.93$.

The volume distribution of the sample can also be derived from the room temperature magnetization curve [8]. The particle volume distribution estimated by this method is referred to as the magnetic volume distribution in the following discussion. The method probes the distribution of magnetic moments in the sample, which is proportional to the volume distribution assuming that the magnetization is independent of particle size.

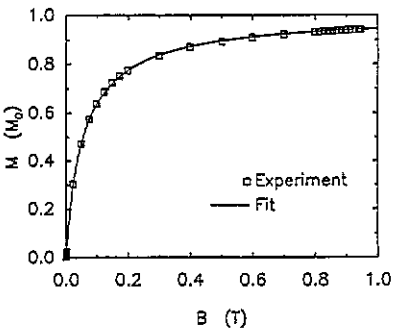

Figure 1. The room temperature magnetization curve of the sample. The squares are the experimental data points. The full curve is a best fit curve using the model of Chantrell and co-workers [8], with $\bar{D}_v = 9.0$ nm and $\sigma_v = 1.05$.

At room temperature the particles are superparamagnetic. For a mono-dispersed ensemble of particles the magnetization induced by application of a magnetic field is given by the Langevin function (if the magnetic anisotropy can be considered negligible [11]). The existence of a particle size distribution modifies the response relative to the Langevin function and will be given by a volume-weighted sum of the responses of all different particle volumes. Chantrell and co-workers [8] have developed a method by which the parameters of an assumed log–normal volume distribution can be derived from the measured magnetization curve. The magnetization curve of the sample is shown in figure 1. A best-fit curve obtained from the model, taking the particle size distribution into account, is shown as a full curve in figure 1. By this method we find $\bar{D}_v = 9.0\,\text{nm}$ and $\sigma_v = 1.05$. The saturation magnetization of the particles was assumed to be equal to that of bulk maghemite at room temperature ($M = 3.66 \times 10^5\,\text{J T}^{-1}\,\text{m}^{-3}$). The parameters describing the particle volume distribution derived from the magnetization curve are in good agreement with the parameters obtained from the electron micrographs. The standard deviation of the magnetic volume distribution is usually found to be larger than the standard deviation of the volume distribution derived

from the electron micrographs [8]. The difference might stem from the sensitivity of the former to magnetic interparticle interactions in the sample [9]. As shown in [7], 17% of the spins in the investigated particles do not align with a large applied magnetic field at 15 K. Hence, the saturation magnetization of the particles is reduced relative to the value for bulk maghemite. As the fraction of the spins that do not align in large applied fields decreases with increasing temperature [7] the saturation magnetization at room temperature is reduced by no more than 17% relative to the bulk value. Using a saturation magnetization, reduced by 17% relative to the bulk value, we find a median particle size of $\bar{D}_v = 9.5$ nm.

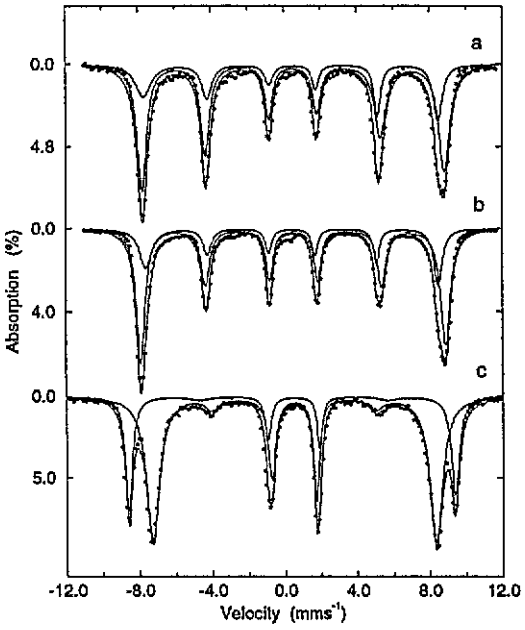

Figure 2. Mössbauer spectra of the investigated sample, obtained at 15 K. Spectra (a) and (b) were obtained in zero field and spectrum (c) in a field of 4.35 T. In (a) the sample was frozen in zero field and in (b) it was frozen in a magnetic field of 2.25 T perpendicular to the sample plane, i.e. parallel to the γ-beam. Best fit curves as well as the components of the fits are shown with thin full curves.

3.2. Characterization by Mössbauer spectroscopy

Mössbauer spectra obtained at 15 K of the sample frozen in zero field and in a field of 2.25 T, both measured in zero field, are shown in figure 2(*a*) and 2(*b*), respectively. The spectrum shown in figure 2(*c*) was obtained in a magnetic field of 4.35 T applied parallel to the γ-ray. The spectra are typical of ultrafine maghemite particles. The spectra can be well fitted with two sextets representing the two different sites in the spinel lattice. The best fit curves as well as the A- and B-site subspectra are shown with full curves in figure 2. The two spectra obtained in zero field are asymmetric (lines one, two and three are more intense than lines four, five and six, respectively) due to the different magnetic hyperfine fields and isomer shifts of the A- and B-site subspectra. In addition to this asymmetry each absorption line is seen to be asymmetric (inwardly broadened) which is typical of ultrafine magnetic particles [12, 13]. The deviation from a pure Lorentzian lineshape is most clearly seen on the outer flanks of lines 1 and 6, where deviations between the experimental spectra and the Lorentzians of the best-fit curves are evident. Presumably intrinsic finite-size effects, such as variations of the magnetic hyperfine field in the particles as well as relaxation phenomena like collective magnetic excitations, are the main causes for the asymmetric

line broadening [12–14]. Some absorption, which cannot be ascribed to maghemite, is seen in the spectra around zero velocity (in figures 2(*a*) and 2(*b*)) and at $-2.5\,\mathrm{mm\,s^{-1}}$ (cf. figure 2(*b*)). The absorption near zero velocity in figures 2(*a*) and 2(*b*) is due to iron in the beryllium windows of the cryostat used for these measurements. The origin of the absorption at $-2.5\,\mathrm{mm\,s^{-1}}$ has not been established. Since it constitutes less than 1% of the total absorption it is of no consequence to the data analysis and it is neglected in the following discussion.

The reduction of the hyperfine field, B_{obs}, relative to the saturation value, B_0, due to collective magnetic excitations can, for particles with uniaxial anisotropy, be written as [13, 14]

$$B_{\mathrm{obs}} = B_0\left(1 - \frac{k_{\mathrm{B}}T}{2KV}\right) \tag{2}$$

where K is the anisotropy energy constant, k_{B} is the Boltzmann constant, T is the temperature and V is the particle volume. If a large magnetic field is applied the collective magnetic excitations will be blocked, and the saturation value of the hyperfine field can be determined. The order of magnitude of the anisotropy constant can thus be determined from the Mössbauer spectra by comparing the hyperfine field (B_0) measured in a large magnetic field and that obtained in zero field at the same temperature [13, 14]. The values of B_0 for the A- and B-site components, determined from the Mössbauer spectrum obtained in a magnetic field of 4.35 T at 15 K (figure 2(*c*)), are 51.5 and 52.9 T, respectively. The values found from the spectrum obtained at the same temperature in zero field (figure 2(*a*)) are 49.8 and 52.0 T, respectively. Using the volume-weighted median volume determined from the magnetization measurements, the anisotropy energy constant is found to be $K = (1.2 \pm 0.4) \times 10^4\,\mathrm{J\,m^{-3}}$.

3.3. Decay of remanence measurements

The anisotropy constant can also be determined from a measurement of the decay of remanence with temperature [9, 15]. The sample is cooled to 4 K in zero field, a saturating field (1.0 T) is applied and subsequently switched off. After 100 s the remanent magnetization is measured. The procedure is then repeated at higher temperatures.

The remanent magnetization decays with time due to thermally driven fluctuations of the magnetic moments. Assuming that the relaxation can be described by Néel's theory [16], the relaxation time can be written as

$$\tau = \tau_0 \exp(KV/k_{\mathrm{B}}T) \tag{3}$$

where KV is the energy barrier and τ_0 is a characteristic relaxation time, normally assumed to be of the order of 10^{-10}–10^{-13} s. The blocking temperature, T_{B}, is defined as the temperature below which the magnetic relaxation is slow compared with the characteristic measuring time ($\tau_{\mathrm{m}} = 100\,\mathrm{s}$). A distribution of particle volumes exists in the sample, resulting in a distribution of blocking temperatures. A mean blocking temperature, $\langle T_{\mathrm{B}}\rangle$, at which half of the magnetic volume is superparamagnetic, can be extracted by fitting the measured temperature dependence of the remanence with the expression [15]

$$\bar{M}_{\mathrm{r}}(T) = \frac{M_{\mathrm{r}}}{M_{\mathrm{s}}} = \bar{M}_{\mathrm{r}}(0)\int_{T/\langle T_{\mathrm{B}}\rangle}^{\infty} f(T_{\mathrm{r}})\,\mathrm{d}T_{\mathrm{r}}. \tag{4}$$

Here $\bar{M}_{\mathrm{r}} = M_{\mathrm{r}}/M_{\mathrm{s}}$ signifies the reduced remanence, $\bar{M}_{\mathrm{r}}(0)$ is the reduced remanence at 0 K, M_{s} is the saturation magnetization, $T_{\mathrm{r}} = T_{\mathrm{B}}/\langle T_{\mathrm{B}}\rangle$ is the reduced blocking temperature

and $f(T_r)$ is the normalized distribution of blocking temperatures. The integral in (4) equals the volume-weighted fraction of the particles that are blocked at a given temperature T. Assuming that the anisotropy constant is independent of particle size, the blocking temperature is proportional to the particle volume. To describe the blocking temperature distribution we thus use a log–normal distribution with a variance equal to the one determined in section 3.1. The mean blocking temperature is treated as a parameter.

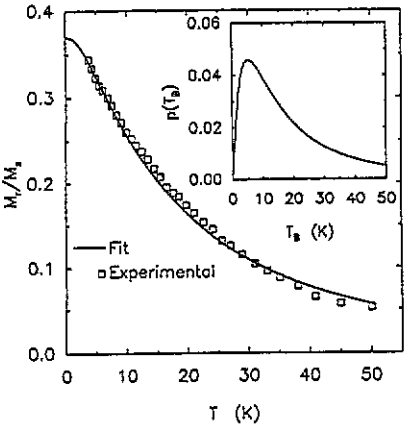

Figure 3. The temperature dependence of the reduced remanence. The full curve is a best fit with a theoretical model for the temperature dependence of the remanence (see text). The inset shows the distribution of blocking temperatures given by the temperature derivative of the fitted remanence curve.

The decay of remanence curve of the sample is shown in figure 3. The reduced remanent magnetization of a sample with random orientation of the easy axes should tend to 0.5 as T approaches 0 K [17], but clearly this is not the case in figure 3. Such behaviour was also observed in [9], where possible causes for the reduction of M_r relative to the theoretical value of $\bar{M}_r(0) = 0.5$ were discussed. If we treat $\bar{M}_r(0)$ as a free parameter, a good fit of the experimental data by (4) can be obtained. The best fit was obtained for $\langle T_B \rangle = 17$ K ($\bar{M}_r(0) = 0.37$). The best fit curve is shown in figure 3 as a full curve, and the corresponding distribution of blocking temperatures, calculated as the derivative of the fitted remanence curve with respect to temperature (cf. (4)), is shown in the inset.

An estimate of the anisotropy constant can now be obtained from (3) by inserting the mean blocking temperature, $\langle T_B \rangle$, and the median volume, $\bar{V}$, determined in section 3.1. By this method we find a magnetic anisotropy constant $K \approx 1.9 \times 10^4\,\mathrm{J\,m^{-3}}$, (taking $\tau_m = 100$ s and $\tau_0 = 10^{-12}$ s). There are some experimental uncertainties associated with this determination. The uncertainty in τ_0 alone ($\tau_0 = 10^{-10}$–10^{-13} s) results in an uncertainty in K of about 15%. Furthermore there is some experimental uncertainty in the median volume (±5%) and in the blocking temperature. If we fit the experimental data by (4) with $\bar{M}_r(0) = 0.5$ we find best correspondence between the experimental data and the theoretical curve for a mean blocking temperature of 12 K. Taking the deviation between the two estimates of the blocking temperature discussed above as an estimate of the uncertainty in this quantity, the total uncertainty in K estimated by this method amounts to about 50%, i.e. $K = (1.9 \pm 1.0) \times 10^4\,\mathrm{J\,m^{-3}}$. Taking into account the experimental uncertainties this value is in accordance with that determined from the low-temperature Mössbauer spectra.

4. Magnetic texture

4.1. Theory

When a ferrofluid is frozen in a magnetic field the equilibrium orientation of the easy

axes at the melting point can be frozen-in, and a sample with a magnetic texture prepared. Hartmann and Mende [4] have treated this problem applying Boltzmann statistics.

The orientational energy, U, of a magnetic particle with uniaxial magnetic anisotropy in a uniform magnetic field, B, is given by

$$U = KV \sin^2 \alpha - \mu B \cos \beta \tag{5}$$

where α is the angle between the magnetic moment, μ, and the anisotropy axis, and β is the angle between the applied field and the magnetic moment. The extent to which the magnetic moments of the particles in a ferrofluid will align along an applied magnetic field depends on the ratio of the Zeeman energy to the thermal energy, $p = \mu B / k_B T$. The alignment of the moments will also lead to a degree of alignment of the easy axes, which depends on the ratio of the anisotropy energy to the thermal energy, $q = KV/k_B T$. The equilibrium orientational distribution function of the easy axes can be found applying Boltzmann statistics [4].

The relative areas, $A_{i,j}$, of the six lines in the magnetically split Mössbauer spectrum depend on the angle, η, between the γ-ray and the magnetic hyperfine field [18]:

$$\begin{aligned} A_{1,6} &= 3(1 + \cos^2 \eta) \\ A_{2,5} &= 4 \sin^2 \eta \\ A_{3,4} &= 1 + \cos^2 \eta. \end{aligned} \tag{6}$$

If the sample is oriented such that the γ-ray direction is parallel to the direction of the freezing field when obtaining the Mössbauer spectrum, and the temperature is so low that the magnetic moment can be assumed to lie along the easy axis, η will be equal to the angle between the easy axis and the freezing field (θ). To evaluate the area ratio of the lines in the Mössbauer spectrum, we thus need to calculate the statistically averaged value of $\cos^2 \theta$. Hartmann and Mende have shown [4] that $\langle \cos^2 \theta \rangle = g(p, q)$ can be written

$$g(p, q) = \tfrac{1}{3}\left[1 + 2\xi(q)\left(1 - 3p^{-1} L(p)\right)\right] \tag{7}$$

where

$$\xi = \frac{3}{4q}\left(\frac{q^{1/2} \exp(q)}{\phi(q^{1/2})} - 1\right) - \frac{1}{2} \tag{8}$$

and

$$\phi(q^{1/2}) = \int_0^{q^{1/2}} \exp x^2 \, \mathrm{d}x \tag{9}$$

and $L(p)$ is the Langevin function.

The degree of frozen-in alignment of the easy axes, expressed in terms of $\langle \cos^2 \theta \rangle$, is calculated by inserting the values of p and q at freezing conditions in (7). Due to the distribution of particle sizes in the sample it cannot be characterized by just one set of (p, q) values. An integration over the particle size distribution must be performed:

$$\overline{g(p, q)} = \int_0^\infty g(p, q) f(V) \, \mathrm{d}V \tag{10}$$

where $f(V)$ is the particle volume distribution function. When evaluating (10) we assume that the magnetization and the anisotropy constant K are independent of particle size. The area ratio of the lines in the Mössbauer spectrum of the magnetically textured sample is then evaluated from (6) using the volume-weighted thermal mean value of $\cos^2 \theta$, calculated from (10).

4.2. Results and discussion

The Mössbauer spectrum obtained at 15 K in zero field of a sample that was frozen in a magnetic field of 2.25 T, is shown in figure 2(*b*). The Mössbauer spectrum was obtained with the γ-ray direction perpendicular to the sample plane, i.e. in the direction of the freezing field. The partial alignment of the magnetic moments is clearly seen by the reduced absorption in lines 2 and 5 as compared with the spectrum of the zero-field cooled sample in figure 2(*a*). At 15 K the magnetic moment can be assumed to be along the easy direction, and hence the spectrum reflects the orientation of the easy axes.

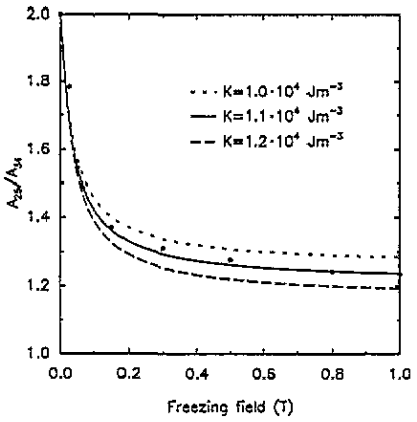

Figure 4. The orientation of the magnetic moments expressed by the area ratio, x, of lines 2 and 5 to lines 3 and 4 in the Mössbauer spectrum as a function of the freezing field. The Mössbauer spectra were obtained at 15 K in zero field. The full circles are experimental observations, corrected for the fraction of canted spins (see text). The full curves are calculated from (9), (10) and (13) for different values of the anisotropy constant.

We have investigated the degree of alignment as a function of freezing field. The results are summarized in figure 4, where the measured area ratio, $x = A_{2,5}/A_{3,4}$, is shown as a function of the freezing field. The values of x plotted in the figure are not those directly observed in the experiments. Full alignment of all spins in the sample is not obtained even in a large magnetic field. This is clearly revealed by spectrum (c) in figure 2, where some absorption in lines 2 and 5 is seen to prevail despite the applied magnetic field of 4.35 T. As discussed in [7] this is due to spin-canting of a fraction of the spins. Assuming that the canting angles are random, it can be estimated that approximately 17% of the spins in the particles are canted [7]. The experimental values plotted in figure 4 have been corrected for the influence of canted spins.

The sample was cooled at the same rate ($\approx 30\,\mathrm{K\,min^{-1}}$) for all freezing fields, and was kept in liquid nitrogen until the time of measurement. The full curves in figure 4 are theoretical curves for the area ratio calculated from (6), (7) and (10). In calculating the theoretical curves, the magnetic volume distribution $f(V)$ determined from the magnetization measurement was used. The induced alignment is seen to saturate; increasing the freezing field by a factor of five beyond 0.2 T, only reduces the area ratio by 10%. This is in accordance with previous studies [5] of the effects of freezing ferrofluids in a magnetic field. The saturation indicates that regardless of whether the magnetic moments are fully aligned along the freezing field, the ratio of the anisotropy energy to the thermal energy in the system is insufficient to enforce the same degree of alignment on the easy directions. Theoretical curves for three different values of the anisotropy energy constant are shown in figure 4. They show, in agreement with the above argument, that the obtained degree of alignment is quite sensitive to the value of the anisotropy energy constant.

The correspondence between the measured area ratios for different freezing fields and the theoretical prediction is very good. Hence, the theory of Hartmann and Mende for non-interacting particles [4] seems to account very well for the degree of alignment of the easy directions obtained by field-cooling a ferrofluid. The Mössbauer spectrum of the textured sample yields a direct measure of the distribution of easy directions in the sample. Hence, it allows a more direct test of the predictions of the theory of Hartmann and Mende than measurements of the magnetization of the textured sample. The good agreement between the experimental data and the theoretical curve allows an independent determination of the anisotropy constant. The best agreement is found for $K = 1.1 \times 10^4\,\mathrm{J\,m^{-3}}$. This value has an uncertainty due to the experimental uncertainty on the volume distribution. If we use the volume distribution determined from the electron micrographs instead of that determined from the magnetization measurements, best agreement is found for $K = 1.4 \times 10^4\,\mathrm{J\,m^{-3}}$. Assuming the deviation between the two values to be a measure of the experimental uncertainty on K determined by this method, we find that $K = (1.1 \pm 0.3) \times 10^4\,\mathrm{J\,m^{-3}}$. The value is in agreement with the values found by the two other methods, within the experimental uncertainty.

The particles in a ferrofluid have a tendency to agglomerate due to the magnetic interaction between them [19]. This tendency depends on the ratio of the interaction energy to the thermal energy and increases when a magnetic field is applied [20–22]. The order of magnitude of the magnetic dipolar interaction, E, between two single-domain particles with magnetic moments μ, separated by a distance D is $E = \mu^2\mu_0/2\pi D^3$, where μ_0 is the permeability of free space. Inserting the magnetic moment of 9 nm maghemite particles and assuming a centre-to-centre distance between the particles of 11 nm (the particles are separated by the oleic acid coating) the interaction energy is found to be equal to the thermal energy, $k_B T$, at around 200 K. This is quite close to the freezing temperature of heptane. Hence, some agglomerates of the largest particles are probably formed in the field-cooled samples. However, we do not see the influence of the interparticle interactions in the orientation experiments. That is, the field dependence of the induced alignment of the easy directions can be fully accounted for by the simple model neglecting interparticle interactions.

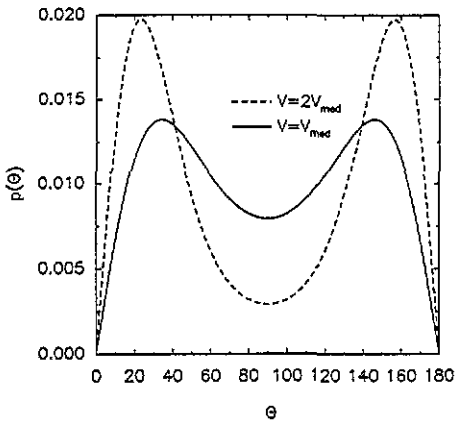

Figure 5. The equilibrium distribution of angles between the easy axis and an applied field of 1 T, calculated from the theory of Hartmann and Mende [4], for an ensemble of magnetic particles with a moment of $1.4 \times 10^{-19}\,\mathrm{J\,T^{-1}}$ (the median magnetic moment of the investigated sample) and for an ensemble with a magnetic moment twice as large. The uniaxial anisotropy constant was assumed to be $1.1 \times 10^4\,\mathrm{J\,m^{-3}}$. The distributions were calculated at a temperature of 182 K, which is the melting point of the carrier medium (heptane).

The partial alignment of the easy axes induced by field-cooling of the ferrofluid is illustrated in figure 5. The equilibrium angular distribution of easy directions in a field of 1 T at 182 K (melting point of heptane) is plotted for an ensemble of particles with an

anisotropy constant of $1.1 \times 10^4\,J\,m^{-3}$, and with a volume equal to the median volume or twice the median volume, of the investigated sample. (The expression for the angular distribution of easy axes derived in [4] was evaluated using standard numerical techniques). The degree of alignment increases with increasing particle size. The improved alignment obtained for the larger particles stems from the stronger coupling of the magnetic moment to the easy direction due to the enhanced anisotropy energy, KV.

5. Conclusion

By freezing a ferrofluid in a magnetic field, a partial alignment of the easy directions is obtained and a sample with a magnetic texture can be prepared. The degree of alignment observed experimentally is in good agreement with the predictions of a simple theory of the behaviour of non-interacting particles with uniaxial magnetic anisotropy.

We have determined the anisotropy energy constant of the investigated maghemite particles in three different ways. Analysing the reduction of the hyperfine field relative to the saturation value at 15 K in terms of a model of collective magnetic excitations yielded $K = (1.2 \pm 0.4) \times 10^4\,J\,m^{-3}$. From the decay of remanence measurements we found $K = (1.9 \pm 1.0) \times 10^4\,J\,m^{-3}$, and from the dependence of the area ratio A_{25}/A_{34} in the Mössbauer spectrum of the textured samples on the freezing field $K = (1.1 \pm 0.3) \times 10^4\,J\,m^{-3}$ was found. The values found by the different methods are, considering the experimental uncertainties, in good agreement.

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