

The effect of colloidal stabilization upon ferrimagnetic resonance in magnetic fluids in the presence of a polarizing magnetic field

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Abstract

The complex magnetic susceptibility of two magnetic fluids, with different degrees of colloidal stabilization, has been measured over the frequency range 100 MHz to 6 GHz. The colloidal stabilization of the magnetic fluids has been investigated using magneto-optical measurements. Based on complex magnetic susceptibility measurements, $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$, the dependence of the maximum absorption frequency at resonance, f_{\max} , and of line width, Δf , on an external magnetic polarizing field, H , over the range 0–1.45 kOe, has been examined for both magnetic fluids. The experimental results have been interpreted in terms of magnetic interparticle interactions and particle agglomeration.

1. Introduction

Magnetic fluids are stable colloidal systems consisting of magnetic single domain particles dispersed in a carrier liquid. In order to preserve the colloidal stabilization, the particles are coated with a surfactant [1]. Particle agglomeration may occur within magnetic fluids [1] depending on a number of factors including the type of stabilization, particle size distribution, temperature and the strength of an applied magnetic field. Since magnetic resonance measurements are very sensitive to changes in the local magnetic field, these can be used for the investigation of structural changes in magnetic fluids.

As is well known, two experimental arrangements are used for magnetic resonance measurements. In the conventional

magnetic resonance technique, the sample is placed within a resonant cavity, the frequency of the microwave field remains constant and the static magnetic field increases slowly over a fixed range and in a settled time interval. The recorded signal is the power absorbed by the sample as a function of the polarizing magnetic field. In the second experimental arrangement, the magnetic resonance phenomenon is determined from measurements of complex magnetic susceptibility, $\chi(\omega)$, at a constant polarizing field [2], resonance being indicated by a transition in the value of real part of complex magnetic susceptibility, $\chi'(\omega)$, from a positive to a negative quantity at the resonance frequency.

Investigations concerning the effect of interparticle interactions within magnetic fluids on the magnetic resonance line have been performed in papers [3–6] based on conventional ferromagnetic resonance techniques. Sharma

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and Waldner [3] were the first to experimentally approach the subject of the influence of interparticle interactions on the magnetic resonance line within magnetic fluids. They observed that the addition of a flocculent agent to the sample led to an increase in magnetic resonance line width. In later works [4–6], the authors revealed that the magnetic resonance line width as well as the shape of magnetic resonance line depends on particle concentration.

Based on the measurements of $\chi(\omega)$ as a function of a constant polarizing field over the range 0–1.45 kOe, this paper reports on the effect which the degree of colloidal stabilization has on the maximum absorption frequency, f_{\max} , at resonance and also on the line width, Δf , for two magnetic fluids.

2. Theoretical considerations

The theoretical description of the magnetic resonance condition for a system consisting of single domain particles is based on the analysis of the free magnetic energy per unit volume of a representative particle. As it is shown in [7], starting from the equation of motion of the magnetization vector \mathbf{M} of the representative particle, in the Landau–Lifshitz form, relations (1) and (2) give the resonance condition ($\omega_{0,R}$) and the line width ($\Delta\omega_R$), as:

$$\omega_{0,R} = \frac{g\gamma(1 + \alpha_R^2)^{1/2}}{M_S \sin \theta_0} (F_{\theta\theta} F_{\varphi\varphi} - F_{\varphi\theta}^2)^{1/2} \quad (1)$$

$$\Delta\omega_R = \frac{g\gamma\alpha_R}{M_S} \left(F_{\theta\theta} + \frac{F_{\varphi\varphi}}{\sin^2 \theta_0} \right) \quad (2)$$

In equations (1) and (2), M_S is the saturation magnetization of the bulk material of the particle; g is the spectroscopic splitting factor; γ is the gyromagnetic electronic ratio and α_R is the damping parameter. φ and θ are the angular co-ordinates of the magnetization of the particle whilst $F_{\theta\theta}$, $F_{\varphi\varphi}$ and $F_{\varphi\theta}$ are the second derivatives of the free energy per unit volume of the representative particle, at the equilibrium position of magnetization of the particle (φ_0, θ_0), where F has a minimum.

The susceptibility χ_R is given by [7]:

$$\chi_R = \frac{\gamma^2 g^2 (1 + \alpha_R^2)}{\omega_{0,R}^2 - \omega^2 + i\omega\Delta\omega_R} \left[l^2 \left(F_{\theta\theta} + \frac{i\omega\alpha_R M_S}{\gamma g (1 + \alpha_R^2)} \right) + s^2 \left(\frac{F_{\varphi\varphi}}{\sin^2 \theta_0} + \frac{i\omega\alpha_R M_S}{\gamma g (1 + \alpha_R^2)} \right) + 2ls \frac{F_{\varphi\theta}}{\sin \theta_0} \right] \quad (3)$$

The parameter l and s are:

$$l = \sin \delta \sin(\varphi_0 - \lambda) \quad (4)$$

$$s = \cos \theta_0 \sin \delta \cos(\varphi_0 - \lambda) - \cos \delta \sin \theta_0 \quad (5)$$

In the above relations δ and λ are the angular co-ordinates of the microwave magnetic field, \mathbf{h} (see figure 1).

As reported by Scaife [8], the resonance frequency, f_{res} , and the frequency of maximum absorption, f_{\max} , are always different, only for pure resonance (i.e. null damping parameter) is $f_{\text{res}} = f_{\max}$. From relation (3) it can be easily observed that $\omega_{0,R}$ is the angular frequency corresponding to the maximum of the $\chi''(\omega)$ component. Therefore in the following

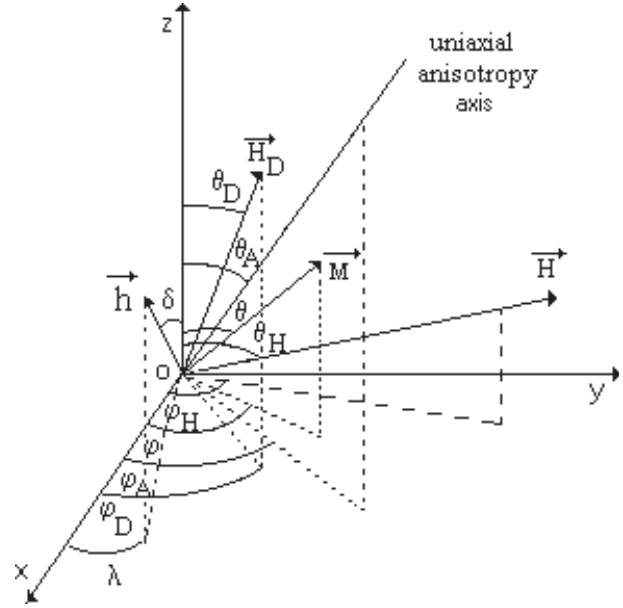


Figure 1. The definition of the angles that determine the orientation of the external magnetic field \mathbf{H} , the mean dipolar interaction magnetic field, \mathbf{H}_D , the magnetization, \mathbf{M} , of uniaxial anisotropy axis and of the microwave field, \mathbf{h} .

considerations $\omega_{0,R} = 2\pi f_{\max,R}$ and $\Delta\omega_R = 2\pi \Delta f_R$ (Δf_R being twice the deviation in frequency from the maximum of the imaginary part of complex magnetic susceptibility at which χ''_R has dropped to half its maximum).

Assuming that the particles within the sample have uniaxial anisotropy, the free magnetic energy per unit volume of the representative particle is:

$$F = -M_S H (\vec{e} \cdot \vec{e}_H) - M_S H_D (\vec{e} \cdot \vec{e}_D) - K (\vec{e} \cdot \vec{e}_A)^2 \quad (6)$$

In equation (6), H is the intensity of the static external magnetic field (the polarizing field), H_D is the intensity of the dipolar magnetic field acting on the representative particle due to all other particles in the sample and K represents the effective uniaxial anisotropy constant; \vec{e} , \vec{e}_H , \vec{e}_D and \vec{e}_A are the unit vectors which define, respectively, the direction of magnetization, of the static polarizing magnetic field, of the dipolar magnetic field and of the anisotropy axis.

Calculation of $f_{\max,R}$ and of Δf_R with relations (1) and (2), respectively, requires knowledge of the equilibrium position of the magnetization of the representative particle at which the free magnetic energy, F , is a minimum. Conditions for minimum of F are:

$$\frac{\partial F}{\partial \theta}(\theta_0, \varphi_0) = 0, \quad \frac{\partial F}{\partial \varphi}(\theta_0, \varphi_0) = 0, \quad (7)$$

$$d^2 F(\theta_0, \varphi_0) > 0$$

The last condition of the system (7) is fulfilled if the eigenvalues of the Hessian matrix of the form $d^2 F(\theta_0, \varphi_0)$ are all strictly positive. This system has to be solved in order to find the equilibrium position of magnetization of the representative particle. For the two limiting cases (a) and (b) the system (7) is easily solved: case (a) concerns small anisotropy field and small interactions by comparison with the polarizing field,

H , whilst case (b) concerns small interactions by comparison with the anisotropy field and zero polarizing field.

2.1. Strong polarizing field

Under the assumption of small anisotropy field, $2K/(M_S H) \ll 1$, and small interactions, $H_D/H \ll 1$, the magnetization of the representative particle at the equilibrium position is approximately parallel to the static magnetic field. Also, assuming that the static magnetic field is parallel to the oy direction, after calculation of the free energy derivatives, $F_{\theta\theta}$, $F_{\varphi\varphi}$ and $F_{\varphi\theta}$, equation (1) becomes:

$$f_{\max,R} = \frac{g\gamma(1 + \alpha_R^2)^{1/2}}{2\pi} \left\{ \left[H + H_D \sin \theta_D \sin \varphi_D - \frac{2K}{M_S} (\cos^2 \theta_A - \sin^2 \theta_A \sin^2 \varphi_A) \right] \times \left[H + H_D \sin \theta_D \sin \varphi_D - \frac{2K}{M_S} \sin^2 \theta_A \cos(2\varphi_A) \right] - \frac{4K^2}{M_S^2} \sin^2 \theta_A \cos^2 \theta_A \cos^2 \varphi_A \right\}^{1/2} \quad (8)$$

In the above equation (θ_D , φ_D) and (θ_A , φ_A) are, respectively, the angular co-ordinates of the dipolar magnetic field and the angular co-ordinates of the unit vector which define the direction of the anisotropy axis (see figure 1). In case of small anisotropy field and small interactions, the terms $(H_D/H)^2$, $2KH_D/(M_S H^2)$ and $(2K/HM_S)^2$ can be neglected and using the approximation $(1 + x)^{1/2} \cong 1 + x/2$ (for $x < 0.5$), equation (8) becomes:

$$f_{\max,R} = \frac{g\gamma(1 + \alpha_R^2)^{1/2}}{2\pi} \left[H + H_D \sin \theta_D \sin \varphi_D + \frac{K}{M_S} (2 \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \cos^2 \varphi_A \sin^2 \theta_A) \right] \quad (9)$$

Using the same approximations, the line width of the representative particle is:

$$\Delta f_R = \frac{g\gamma\alpha_R}{\pi} \left[H + H_D \sin \theta_D \sin \varphi_D + \frac{K}{M_S} (2 \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \cos^2 \varphi_A \sin^2 \theta_A) \right] \quad (10)$$

As can be observed from relations (9) and (10), the resonance condition and the line width depend on local dipolar field and on the orientation of the anisotropy axis of the particle. In a magnetic fluid, both the local magnetic field and the orientation of anisotropy axis generally differ from one particle to another. The measured susceptibility is in fact a result of the contribution of all particles within the sample. As reported in [9], in the presence of a static magnetic field the orientation of the anisotropy axes of the particles obey an orientation distribution. Also, because the magnetic particles within a magnetic fluid obey a dimensional distribution and as the neighbours of first order make the most important contribution to the dipolar field, we can assume an orientation distribution and strength distribution of the dipolar field. Therefore, a

spread of values $f_{\max,R}$ and Δf_R will result. In order to find f_{\max} of the magnetic fluid, the susceptibility given by relation (3) has to be averaged over all particle sizes, over all orientations of the anisotropy axes and over all orientations of the dipolar field. Because this averaging can only be performed numerically, the best approximation we can make for f_{\max} is obtained by averaging equation (9) over all particle sizes, over all orientations of the anisotropy axes and over all orientations of the dipolar field.

$$f_{\max} = \frac{g\gamma(1 + \alpha^2)^{1/2}}{2\pi} \left(H + a \frac{m}{d_{\text{mean}}^3} + b \frac{2K}{M_S} \right) \quad (11)$$

Also, we have to expect that the damping parameter of the magnetic fluid, α , will be different from the damping parameter of the representative particle, α_R , because α_R determines the intrinsic line width of the representative particle whilst the line width of the magnetic fluid is extrinsic being determined by the spread of the value of $f_{\max,R}$. In equation (11) H is the intensity of the polarizing field, m is the mean magnetic moment of a particle and d_{mean} is the mean distance between the particles. The term am/d_{mean}^3 is the mean dipolar interparticle interaction field and the last term in equation (11) is the mean anisotropy field. The parameter a depends on the local structure of the system, whilst the parameter b depends on the orientation of the anisotropy axes, both a and b depending on the polarizing field. An evaluation of the parameters a and b is possible only if the orientation distribution of dipolar field (i.e. the local structure of the system) and of anisotropy axes are known. An analytical relation for a can only be found for particular cases. For example, in [6], the mean dipolar term was calculated for the case of strong polarizing field and small particle concentration, when the magnetic particles within the magnetic fluid are disposed in chain like particle agglomerations assuming that the particles are identical balls and interact only with the particles from the same chain. Evaluation of the mean dipolar term at polarizing fields smaller than the saturation field, by taking into account the size distribution of the magnetic particles within the magnetic fluid, the particle agglomeration (other than chain like aggregates) and the interparticle interaction between the particles from different clusters, can only be performed numerically. Concerning the parameters a and b , an analytical relation can only be found for particular cases. For example, in [9] the orientation distribution function of the anisotropy axes of the magnetic particles within a magnetic fluid in the presence of an external field, is calculated for the case of identical particles, without interparticle interaction. For the same approximations as in [9], for magnetite particles having uniaxial anisotropy ($K = 1.1 \times 10^5$ erg cm $^{-3}$ and $M_S = 480$ Gauss) with magnetic diameter of 10 nm, at $T = 300$ K, a value of $b = 0.14$ is obtained at a polarizing field of 1.4 kOe. At constant temperature, for particles from a given material, the parameter b is as close to one for large particles and strong polarizing fields [9].

As we have mentioned, equation (10) gives the line width of one particle within the sample, but the measured line width is essentially due to the spread of the value of $f_{\max,R}$ (see equation (9)). Based on Van Vleck's method of moments [10], the line width is given by:

$$\Delta f = 2.35(\langle f_{\max,R}^2 \rangle - \langle f_{\max,R} \rangle^2)^{1/2} \quad (12)$$

Using equation (9) and assuming a constant value of ratio K/M_S , equation (12) becomes:

$$\Delta f = \frac{2.35g\gamma(1+\alpha_R^2)^{1/2}}{2\pi} \times \left\{ \langle H_D^2 \sin^2 \theta_D \sin^2 \varphi_D \rangle - \langle H_D \sin \theta_D \sin \varphi_D \rangle^2 + \frac{K^2}{M_S^2} [(2 \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \cos^2 \varphi_A \sin^2 \theta_A)^2] - (2 \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \cos^2 \varphi_A \sin^2 \theta_A)^2 \right\} + \frac{2K}{M_S} \langle H_D \sin \theta_D \sin \varphi_D (2 \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \cos^2 \varphi_A \sin^2 \theta_A) \rangle - \frac{2K}{M_S} \langle H_D \sin \theta_D \sin \varphi_D \rangle \times (2 \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \cos^2 \varphi_A \sin^2 \theta_A) \quad (13)$$

In the case of a constant dipolar field, for uniform orientation distribution of the dipolar field and of the anisotropy axes, if the co-ordinates (φ_D, θ_D) and (φ_A, θ_A) can be considered as being independent, one obtains:

$$\Delta f = \frac{2.35g\gamma(1+\alpha_R^2)^{1/2}}{2\pi} \left(0.33H_D^2 + 0.8 \frac{K^2}{M_S^2} \right)^{1/2} \quad (14)$$

Another interesting case is that of the dipolar field parallel to the direction of the polarizing field. In this case, if the dipolar field is not constant and does not depend on the co-ordinates (φ_A, θ_A) , relation (12) becomes:

$$\Delta f = \frac{2.35g\gamma(1+\alpha_R^2)^{1/2}}{2\pi} \left\{ \langle H_D^2 \rangle - \langle H_D \rangle^2 + \frac{K^2}{M_S^2} [\langle \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \sin^2 \theta_A \cos(2\varphi_A) \rangle^2] - \frac{K^2}{M_S^2} (\langle \sin^2 \theta_A \sin^2 \varphi_A - \cos^2 \theta_A - \sin^2 \theta_A \cos(2\varphi_A) \rangle)^2 \right\}^{1/2} \quad (15)$$

For uniform orientation distribution of the anisotropy axes one obtains:

$$\Delta f = \frac{2.35g\gamma(1+\alpha_R^2)^{1/2}}{2\pi} \left(\text{Disp}(H_D) + 0.8 \frac{K^2}{M_S^2} \right)^{1/2} \quad (16)$$

In relation (16), $\text{Disp}(H_D) = \langle H_D^2 \rangle - \langle H_D \rangle^2$ is the dispersion of values of the dipolar field. For a magnetic fluid without particle agglomerations, the dispersion of values of the dipolar field is smaller than that corresponding to a magnetic fluid with particle agglomerations. Therefore, the line width of a magnetic fluid with particle agglomeration will be larger than the line width of a magnetic fluid without particle agglomerations.

For a magnetic fluid, evaluation of equation (12) by taking into account the orientation distribution of anisotropy axes as well as the local structure is not an easy matter because both the orientation distribution of anisotropy axes and the local structure of the magnetic fluid depends on the degree of colloidal stabilization of the magnetic fluid and on the strength

of polarizing field. However it is expected that the line width of a magnetic fluid will have a value proportional to the anisotropy field and also to the interaction term m/d_{mean}^3 , giving,

$$\Delta f \approx \Delta f \left(\frac{m}{d_{\text{mean}}^3}, \frac{2K}{M_S} \right) \quad (17)$$

2.2. Zero polarizing field

Under the assumption of zero polarizing field and small interactions (by comparison with the anisotropy field), the magnetization of the representative particle at the equilibrium position is approximately parallel to the anisotropy axis. Therefore, using equation (6) with $H = 0$, from equations (1) and (2) we obtain for the representative particle:

$$f(0)_{\text{max,R}} = \frac{g\gamma(1+\alpha_R^2)^{1/2}}{2\pi} \left(\frac{2K}{M_S} + H_D \sin \theta_D \sin \varphi_D \right) \quad (18)$$

$$\Delta f(0)_R = \frac{g\gamma\alpha_R}{\pi} \left(\frac{2K}{M_S} + H_D \sin \theta_D \sin \varphi_D \right) \quad (19)$$

Under the same considerations as those pertaining in the case of a strong polarizing field, the value of f_{max} for the magnetic fluid in zero polarizing field, can be written as:

$$f(0)_{\text{max}} = \frac{g\gamma(1+\alpha^2)^{1/2}}{2\pi} \left(a \frac{m}{d^3} + \frac{2K}{M_S} \right) \quad (20)$$

The measured line width is mainly due to the spread of $f(0)_{\text{max,R}}$ values (see equation (18)). Following the same Van Vleck's method of moments, one obtains:

$$\Delta f(0) = \frac{2.35g\gamma(1+\alpha_R^2)^{1/2}}{2\pi} \times [(\langle H_D^2 \sin^2 \theta_D \sin^2 \varphi_D \rangle - \langle H_D \sin \theta_D \sin \varphi_D \rangle^2)]^{1/2} \quad (21)$$

In the case of a constant dipolar field having a uniform orientation distribution,

$$\Delta f(0) = 0.215g\gamma(1+\alpha_R^2)^{1/2} H_D \quad (22)$$

The measured line width of the magnetic fluid in zero polarizing fields will be a function of dipolar interaction term,

$$\Delta f(0) \approx \Delta f \left(\frac{m}{d_{\text{mean}}^3} \right) \quad (23)$$

3. Samples

The investigated magnetic fluids were two magnetic fluids with magnetite particles dispersed in kerosene and stabilized with oleic acid. The colloidal particles of magnetite were obtained by chemical co-precipitation of Fe^{2+} and Fe^{3+} ions, in aqueous solution [11]. The salts of Fe^{2+} and Fe^{3+} ions together with the ammoniac solution and oleic acid with technical purity were introduced in the chemical reactor and heated. The resulting suspension was filtered and the particles divided into two parts. The particles from one part were washed, dried and then dispersed in kerosene. The dispersion was filtered in a magnetic field gradient with magnetic wool (as in [12]), resulting in a magnetic fluid denoted as sample A. The unwashed particles from the second part were dried and then dispersed in kerosene. The dispersion was filtered in a

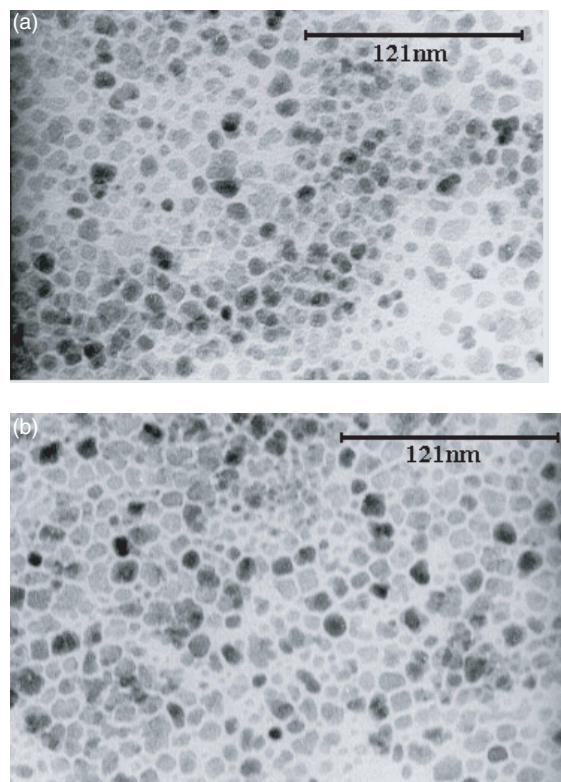


Figure 2. The electron micrograph for investigated samples: (a) sample A and (b) sample B.

magnetic field gradient with magnetic wool [12], the resulting magnetic fluid being denoted as sample B.

From the electron micrographs of the samples (presented in figure 2) we found that samples A and B have the same particle size distribution. This result was as expected since the nucleation and growth processes of the magnetite particles from both magnetic fluid samples were the same. From the statistic analysis of the size of particles a mean physical diameter of the particles of $D = 10.3$ nm and standard deviation $\sigma = 2.48$ nm, was obtained for both samples. The particle size distribution, obtained by electron microscope analysis, is presented in figure 3.

The saturation magnetization of the samples, measured in an alternating magnetic field at a frequency of 50 Hz, were found to be $M_\infty = 317$ Gauss, for sample A and $M_\infty = 268$ Gauss, for sample B.

4. Results and discussion

In order to investigate the degree of colloidal stabilization of samples A and B, dichroism measurements and optical microscopy investigations were carried out. Direct visualization through the optic microscope demonstrates that sample B undergoes magnetic induced phase condensation when subjected to magnetic fields. Figure 4 shows the optical micrograph of the condensed phase drops formed in sample B in a 150 Oe magnetic field at $t = 30^\circ\text{C}$ (details of the experimental procedures can be found in [13]). The elongated drops (stripes like in figure 4) are oriented parallel to the direction of the magnetic field. The majority of the condensed

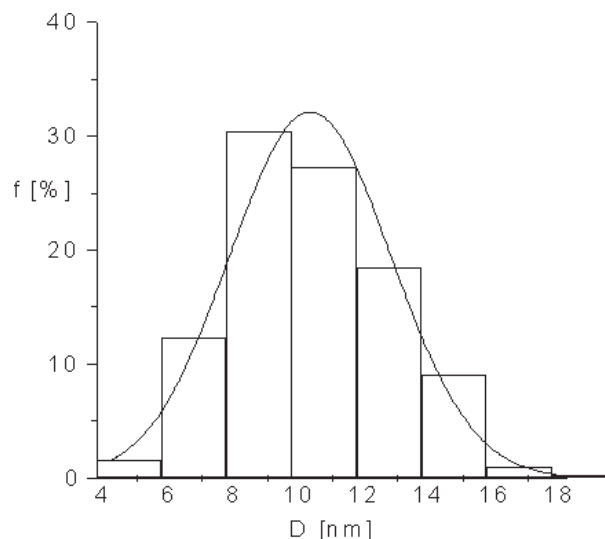


Figure 3. The histogram of the particle size distribution of the investigated samples. The full line is the normal curve associated to the histogram.

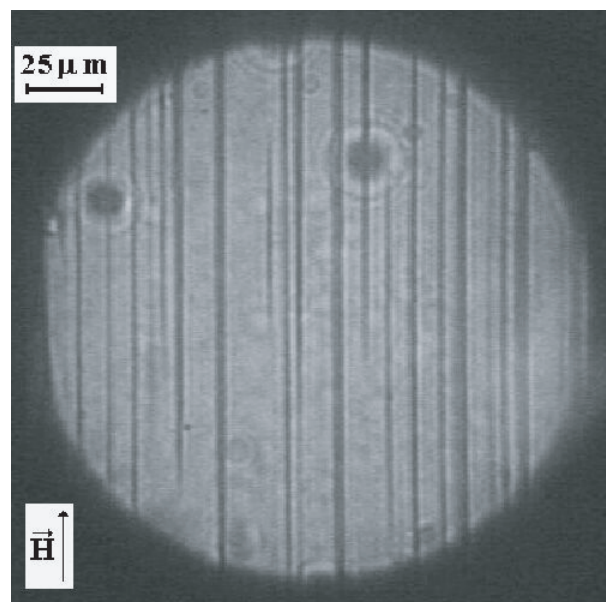


Figure 4. Condensed phase drops formed in a 150 Oe magnetic field at $t = 30^\circ\text{C}$ in sample B.

phase drops have a thickness of 2–5 μm and a length greater than 100 μm .

For sample A, no phase condensation was observed by optic microscopy, therefore light scattering measurements were performed (details on the experimental procedures can be found in [13]). In the case of sample A no light scattering was observed for an applied field intensity up to 3 kOe; this suggests that no phase condensation occurs.

In order to detect the existence of small magnetic particle clusters, magnetic linear dichroism was measured for sample A (details on the experimental procedures can be found in [14]) and figure 5 shows the field dependence of the reduced dichroism obtained for sample A. The reduced dichroism was calculated as the dichroism $\Delta\text{Im}(n) = \text{Im}(n_l - n_r)$ (where n_l and n_r are the sample complex refractive indexes for light

polarized parallel and perpendicular to the field direction) divided by the sample's volume fraction Φ . The theoretical expression of the magnetic induced dichroism in the magnetic fluid is [15, 16]:

$$\frac{\Delta \text{Im}(n)(H)}{\Phi} = \frac{n}{2} \Delta \text{Im}(\chi) \int g(d) \left(1 - \frac{3L(\xi)}{\xi}\right) \delta d \quad (24)$$

where $\Delta \text{Im}(\chi) = \text{Im}(\chi_l - \chi_r)$, is the scatterer mean dielectric anisotropy and n is the refractive index of the carrier. χ_l and χ_r are, respectively, the dielectric susceptibilities of the scatterer parallel and perpendicular to the long axis of the scatterer. The scatterers can be isolated particles, linear chains, clusters, or chains of clusters. $g(d) = d^3 f(d) / \int d^3 f(d) \delta d$ is the scatterer volume distribution function, where $f(d)$ is the scatterer diameter distribution function. $L(\xi)$ is the Langevin function: $\xi(d, H) = v_m M_S H / kT$ where M_S is the magnetite saturation magnetization, H is the magnetic field strength, T is the temperature, k is Boltzmann's constant and v_m is the scatterer magnetic volume, which is smaller than the physical volume due to the existence of the nonmagnetic layer at the surface of the particles.

The experimental curve of figure 5 was fitted to equation (24) in order to calculate the scatterer mean diameter. Assuming that for sample A no particle agglomerations occur, a log-normal distribution with the same standard deviation as the size distribution of the magnetic particle was used for the fit. If no particle agglomerations are present within the sample A, the mean scatterer diameter, d resulting from the fit has to be smaller than the mean particle diameter, D , obtained from electron microscopy analysis (due to the existence of the nonmagnetic layer at the surface of the particles). The volume fraction Φ was calculated using $D = 10.3$ nm, the measured value of $M_\infty = 317$ Gauss and assuming that a nonmagnetic shell of thickness 0.84 nm existed at the surface of the magnetite particles [17]. For the resulting volume fraction of $\Phi = 8.7\%$, the mean scatterer diameter determined from the best fit of the experimental dichroism curve with equation (24) was estimated as $d = 15.1$ nm. One can observe that the scatterers mean diameter is significantly greater than the particle mean diameter of $D = 10.3$ nm, obtained from electron microscopy. Therefore, one can conclude that small

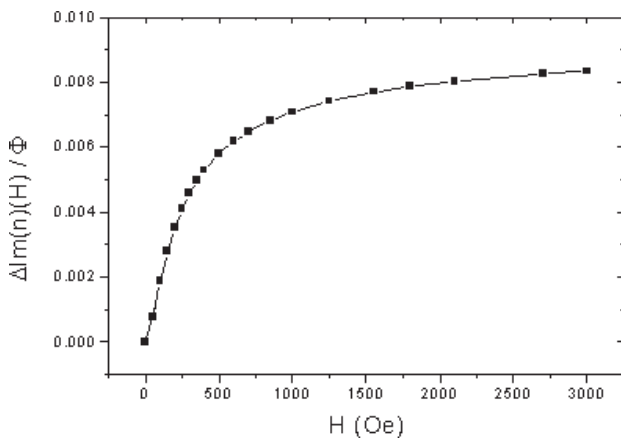


Figure 5. Magnetic field dependence of the reduced dichroism of sample A ($\Phi = 8.7\%$) measured at $t = 30^\circ\text{C}$.

particle agglomerations still occur within sample A when it is subjected to a magnetic field and because of their small dimensions we can assume that the particle agglomerations are chain like.

The complex magnetic susceptibility measurements were performed using the short-circuited coaxial transmission line technique [2], with the frequency ranged within 100 MHz and 6 GHz. The coaxial short-circuited transmission line containing the magnetic fluid sample was placed between the poles of an electromagnet, the axis of the coaxial line being perpendicular to the magnetic field. For each magnetic fluid sample the measurements were performed at 11 different constant values of polarizing magnetic field, over the range 0 and 1.45 kOe. For both samples a resonance phenomenon, indicated by the transition of the real part of complex magnetic susceptibility, χ' , going from a positive to a negative quantity, is observed. The measured values of the real part, χ' and imaginary part, χ'' of the complex magnetic susceptibility of the two magnetic fluid samples are displayed in figures 6 and 7 for three values of polarizing field. The plotted values are normalized to the values corresponding to 100 MHz. From figures 6 and 7 one can observe that an increase in the polarizing field leads to an increase of resonance frequency, f_{res} , as well as of the frequency of maximum absorption, f_{max} , for both samples.

In figures 8 and 9 are presented the dependences of f_{max} on the polarizing field for samples A and B, respectively. For both samples the dependence of f_{max} on the intensity of polarizing field is linear as in the case of a strong polarizing field (equation (11)). The linearity of this dependence can be observed even for small values of the polarizing field, a fact that is explainable based on the structure of the samples. As has already been discussed, in the case of sample A, the magneto-optical measurements revealed that the polarizing field induced chain like particle agglomerations whilst in the case of sample B, the polarizing field induced drop like particle agglomerations, stretched in the direction of the polarizing field. Therefore, in both samples the mean dipolar interparticle interaction field is strong and is approximately parallel to the polarizing field even for small values of the polarizing field. Consequently, for the small anisotropy case, the magnetization

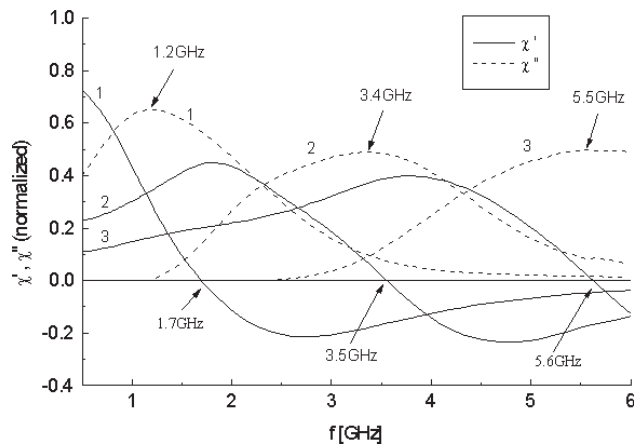


Figure 6. Plot of χ' and χ'' against frequency for sample A, at three values of polarizing field ($H_1 = 0$ Oe, $H_2 = 713.6$ Oe, and $H_3 = 1.434$ kOe).

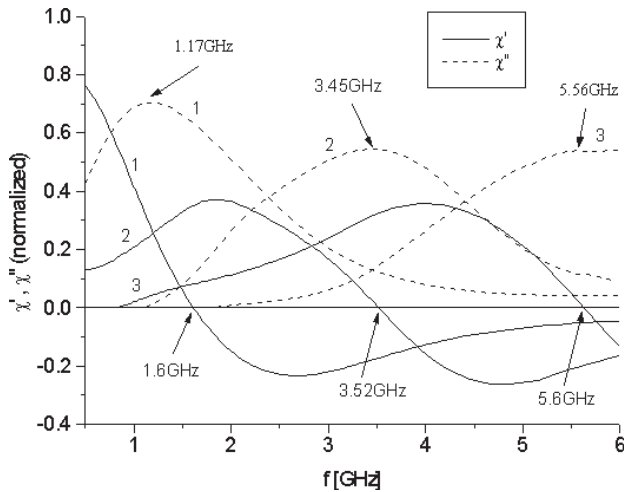


Figure 7. Plot of χ' and χ'' against frequency for sample B, at three values of polarizing field ($H_1 = 0$ Oe, $H_2 = 713.6$ Oe, and $H_3 = 1.434$ kOe).

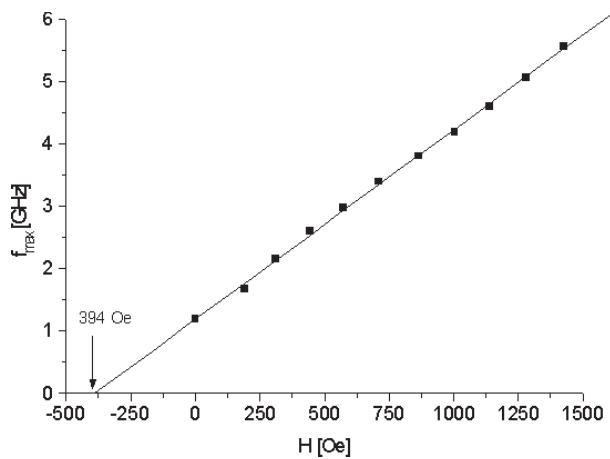


Figure 8. The dependence of f_{\max} on polarizing field for sample A.

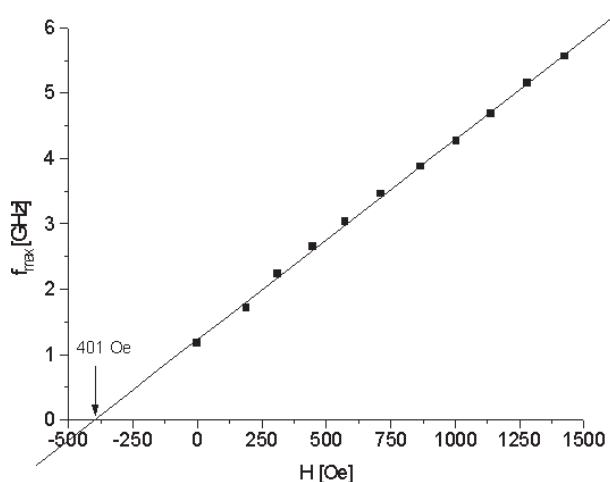


Figure 9. The dependence of f_{\max} on polarizing field for sample B.

of the representative particle at the equilibrium position is approximately parallel to the static magnetic field and to the dipolar field. Assuming (as in the strong polarizing field case) that the static magnetic field is parallel to the oy direction, upon

calculation of the free energy derivatives, $F_{\theta\theta}$, $F_{\varphi\varphi}$ and $F_{\varphi\theta}$, equation (1) becomes:

$$f_{\max,R} = \frac{g\gamma(1 + \alpha_R^2)^{1/2}}{2\pi} \times \left\{ \left[H + H_D - \frac{2K}{M_S} (\cos^2 \theta_A - \sin^2 \theta_A \sin^2 \varphi_A) \right] \times \left[H + H_D - \frac{2K}{M_S} \sin^2 \theta_A \cos(2\varphi_A) \right] - \frac{4K^2}{M_S^2} \sin^2 \theta_A \cos^2 \theta_A \cos^2 \varphi_A \right\}^{1/2} \quad (25)$$

In equation (25) we can factor the sum of the polarizing field and the dipolar field and then by neglecting the term $(2K/(H + H_D)M_S)^2$ and using the approximation $(1 + x)^{1/2} \cong 1 + x/2$ (for $x < 0.5$), equation (25) becomes a linear function on H . Therefore, for magnetic fluids with particles having small anisotropy, which form particle agglomerations, equation (11) is valid even for small values of the polarizing field.

Fitting the dependence of f_{\max} on the intensity of polarizing field with the linear dependence (11), the resulting values of the slope and of the intercept for samples A and B are as follows: slope(A) = 3.018×10^6 Oe $^{-1}$, intercept(A) = 1.19 GHz, slope(B) = 3.048×10^6 Oe $^{-1}$ and intercept(B) = 1.22 GHz (see figures 8 and 9). Using the values of the slope obtained for samples A and B, the effective spectroscopic splitting factor $g_{\text{eff}} = g(1 + \alpha^2)^{1/2}$ can be calculated, resulting in $g_{\text{eff}}(A) = 2.16$ and $g_{\text{eff}}(B) = 2.18$. These values are close to the value of spectroscopic splitting factor measured by Bickford [18] on natural crystal of magnetite at room temperature, $g_{\text{eff}} = 2.17$. We can observe that $g_{\text{eff}}(B) > g_{\text{eff}}(A)$ and because samples A and B have particles from the same material and identical particle size distributions, the difference between the values of the effective spectroscopic splitting factor is due to the different values of the damping parameters of the investigated samples. Therefore, the damping parameter of sample B is larger than the damping parameter of sample A. This result is correlated with the structure of the samples in the presence of an external field, being in agreement with the magneto-optical results, which revealed that the polarizing field induces large particle agglomerations in sample B. Consequently, the dipolar interparticle interactions in sample B are stronger than those in sample A (where only small particle agglomerations occur in the presence of an external field); therefore the damping parameter of sample B is stronger than that of sample A. In conclusion, evaluation of the effective spectroscopic splitting factor supplies information on the strength of the interparticle interaction in the investigated sample, a large value of this parameter being a sign of particle agglomeration in the magnetic fluids.

Another useful parameter for the evaluation of the strength of interparticle interactions is that of the ratio between the intercept and the slope of the plot of the dependence of f_{\max} against the polarizing field, H . From relation (11) this ratio is found to be:

$$R = a \frac{m}{d_{\text{mean}}^3} + b \frac{2K}{M_S} \quad (26)$$

Evaluation of this ratio from the fit of the experimental dependence of f_{\max} against H with a linear dependence,

leads to the values $R(A) = (394 \pm 5.1) \text{ Oe}$ and $R(B) = (401 \pm 5.5) \text{ Oe}$. We can observe that $R(B)$ and $R(A)$ have approximately the same value, in the limit of experimental errors. Taking into account that the particles within the investigated samples are from the same material and have the same particle size distribution, and also that the saturation magnetization of sample A is larger than that of sample B, this then results in the particle concentration within sample A, $\rho(A)$, being larger than that within sample B, $\rho(B)$, and in the ratio $\rho(A)/\rho(B) = M_\infty(A)/M_\infty(B) = 1.18$. Therefore, if the particles within the samples are well dispersed and no particle agglomeration occurs, the mean distance between the particles, d_{mean} has to be smaller for sample A than for the sample B and the first term from relation (26) has to be larger for sample A than for the sample B. The second term from relation (26) has to be the same for the investigated samples because the magnetic particles within the samples have the same size distribution, the particles are from the same material and the measurements were performed for the same range of polarizing field. Consequently, if no particle agglomeration occurs within the samples, $R(A)$ has to be larger than $R(B)$, but we have found experimentally that $R(A)$ and $R(B)$ have approximately the same value. This means that the particles within sample B are disposed in a structure more compact than that within sample A, corresponding to stronger interparticle interaction in sample B than within sample A. This result is also in agreement with the results of magneto-optical measurements which revealed that within sample B the particle agglomerations are larger than those within sample A, in the presence of the polarizing field.

In paper [6], the theoretical dependence of the magnetic resonance line width, ΔH , on particle concentration within a magnetic fluid with chain like particle agglomerations is discussed. It is shown that the larger the particle agglomeration, the larger is the line width, ΔH . Also, in papers [4] and [5] it is shown that the line width ΔH increases by decreasing the mean distance between the particles within magnetic fluid samples, the dependence of ΔH on $1/d_{\text{mean}}^3$ being linear in magnetic fluids with particle concentrations larger than 10^{16} cm^{-3} .

Relations (14), (16), (17), (22) and (23) show that the line width Δf will have a value directly proportional to the dipolar field and therefore with the mean value of interaction term m/d_{mean}^3 . As has already been mentioned, the particle concentration within sample A is larger than the particle concentration within sample B, indicating that if the particles within the samples are well dispersed, the mean distance between the particles, d_{mean} has to be smaller for sample A than for sample B. Taking into account that the magnetic particles within the samples are from the same material and obey the same size distribution, then the mean value of the interaction term has to be larger for sample A than for the sample B. Therefore, in case of no particle agglomeration occurrence within the samples, the line width of sample A has to be larger than the line width of sample B, for the same value of the polarizing field.

In the case of this paper, the dependence of the line width Δf on the polarizing field is presented in figure 10, for both investigated samples. We can observe that in the case of sample B the values of Δf are larger than those obtained for

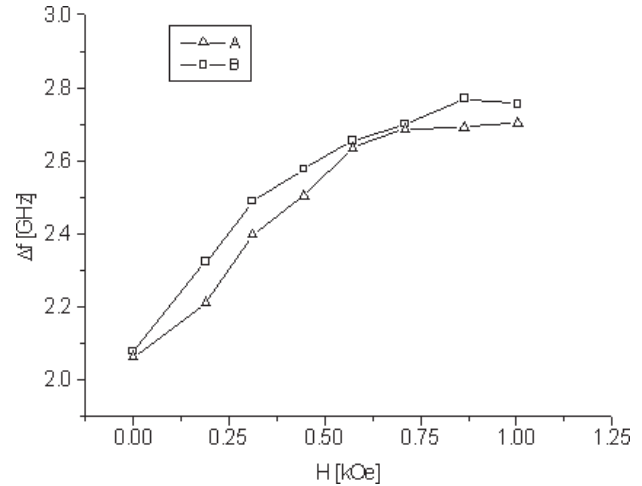


Figure 10. The dependence on polarizing field of the line width for the investigated samples.

sample A, at each value of polarizing field. This result can be explained based on the obtaining process of the magnetic fluid samples. As we have already mentioned, the particles from the sample B have been not washed after co-precipitation. Consequently, the resulting magnetic fluid (sample B) is colloiddally unstable in the presence of a magnetic field, large particle agglomerations within the magnetic fluid sample being induced by the magnetic field, as was confirmed by magneto-optical measurements. This means that the particles within sample B are disposed in a structure more compact than that of sample A, at a given value of polarizing field (corresponding to stronger interparticle interaction in sample B than within sample A). This fact results in values of the mean dipolar interaction term m/d_{mean}^3 being larger for sample B than for sample A, and therefore to values of line width of sample B being larger than those obtained for sample A, at each value of polarizing field. Moreover, because in zero polarizing field the line width of sample B is larger than the line width of sample A, we can assume that particle agglomerations are formed in sample B even in the absence of an external magnetic field.

5. Conclusion

Magnetic resonance measurements are a useful experimental method for obtaining important information concerning the magnetic dipolar interparticle interactions and the stability of the magnetic fluids, both in the presence and absence of an external magnetic field. Large values of the effective spectroscopic splitting factor g_{eff} , of the parameter, R , and of the line width, Δf , are correlated with large values of interparticle magnetic interactions within the investigated samples. Notwithstanding this, it is recognized that magnetic resonance measurements cannot supply precise information on the type of particle agglomerations within the magnetic fluids, unlike the magneto-optical measurement technique, which remains an important experimental technique for the analysis of magnetic field induced instability within the magnetic fluids.

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