THE INFLUENCE OF PARTICLE AGGLOMERATION ON THE EFFECTIVE ANISOTROPY CONSTANT OF PARTICLES WITHIN MAGNETIC FLUIDS AS STUDIED BY MAGNETIC RESONANCE*

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The assumption of particle chains formation is used in order to derive an expression for magnetic resonance condition in magnetic fluids. Using this relation, the dependence of the effective anisotropy constant of particles within magnetic fluids on particles concentration is discussed. For a magnetic fluid with $Mn_{0.6}Fe_{0.4}Fe_2O_4$ particles dispersed in kerosene, a good agreement between the theoretical considerations and the experimental results is found. The obtained results allow us to assert that diluted magnetic fluids are necessary to be investigated in order to determine a more accurate value of the effective anisotropy constant of particles within magnetic fluids by means of ferromagnetic resonance measurements.

Key words: magnetic fluid; ferromagnetic resonance; effective anisotropy constant; chain like particle agglomerations.

1. INTRODUCTION

The magnetic fluids are stable colloidal systems consisting of single-domain ferro-ferrimagnetic particles coated with a surfactant and dispersed in a carrier liquid [1]. These remarkable magnetic systems have attracted interest of the scientific community because of their applications ranging from instrumentation to medicine. Moreover, the magnetic fluids are suitable systems in study of the properties of nanometric size particles.

The ferromagnetic resonance measurements are a powerful tool to investigate both the macroscopic properties of a magnetic fluid and the properties of individual single-domain particles within the fluid. The analysis of the colloidal stability of magnetic fluids [2–4] and the experimental determination of the effective anisotropy constant of particles within the fluid [5, 6] are only two examples in which the ferromagnetic resonance measurements can be successfully used.

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Electron microscopy picture [7], computer simulations [8] and magneto-optical measurements [9] revealed that in the presence of a static magnetic field, the particles from a magnetic fluid tend to associate, forming linear chains or stretched clusters parallel to the magnetic field.

In magnetic resonance spectrometers, the frequency of the microwave field rests constant and the static magnetic field increases slowly in a fixed range and in a settled time interval. For the above experimental arrangement, is possible that the particle agglomerations are forming during the magnetic resonance measurements, induced by the static magnetic field.

The aim of the present paper is to analyse both theoretical and experimental effect of particles concentration on the measured value of the effective anisotropy constant of particles within magnetic fluids, taking into account the possibility of particle chains formation during the ferromagnetic resonance measurements.

2. THEORETICAL CONSIDERATIONS

In the magnetic resonance experiments the static magnetic field at resonance is strong enough to saturate the magnetic fluid (≈ 3 kOe at a frequency of 9060 MHz for a magnetic liquid with magnetite particles [10]). Therefore the magnetization vectors of the particles can be assumed as being approximately parallel to the magnetic field in ferromagnetic resonance measurements.

As it is known [11], if the particles within magnetic fluids are large enough to agglomerates, in static magnetic fields two kinds of particle agglomerations one forms: a) drop like agglomerations, which are stretched on the magnetic field direction and b) chain like particle agglomerations, which are parallel to the magnetic field. In the following considerations is assumed that chain like particle agglomerations one forms during the ferromagnetic resonance measurements.

In paper [12] the particles chaining within a magnetic fluid was theoretically analyzed. As it was derived in [12], the equation (1) gives the mean number of particles in a chain, when the magnetic fluid is subjected to a very strong magnetic field.

$$N_{Av} = \left[1 - \frac{2\rho V_m}{3\lambda^2}\exp(2\lambda)\right]^{-1} \tag{1}$$

In this relation λ is the interaction parameter,

$$\lambda = \frac{m^2}{D^3 k_B T} \tag{2}$$

In the above relations V_m is the mean magnetic volume of the particles, ρ is the particle concentration within magnetic fluid, m is the mean magnetic moment of

the particles, k_B is the Boltzmann's constant, T is the temperature and D is the mean distance between the two neighbouring particles.

In case of a chain with N particles, each particle from the chain is subjected both to the external field and to the dipolar field of all others particles within the magnetic fluid. Neglecting the effect of the magnetic field produced by the particles from other chains, the intensity of the mean dipolar magnetic field, which acts on a particle, due to all others particles from the same chain, is given by relation (3). This relation was obtained assuming that the magnetic particles are identical balls with the diameter D and magnetic moment m.

$$\langle H_i \rangle = \begin{cases} 0, & \text{for } N = 1 \\ \dfrac{4m}{ND^3} \cdot \displaystyle\sum_{k=0}^{N-2} \dfrac{N-k-1}{(k+1)^3}, & \text{for } N \geq 2 \end{cases} \tag{3}$$

Computing the sum of relation (3) one obtains:

$$\langle H_i \rangle = \begin{cases} 0, & \text{for } N = 1 \\ \dfrac{4m}{ND^3} \cdot \left\{ \begin{array}{l} \dfrac{N}{2} \dfrac{\mathrm{d}^3}{\mathrm{d}N^3} \left[\ln\left(\Gamma(N)\right) \right] + \dfrac{\mathrm{d}^2}{\mathrm{d}N^2} \left[\ln\left(\Gamma(N)\right) \right] + \\ N \displaystyle\sum_{k=1}^{\infty} \dfrac{1}{k^3} - \dfrac{\pi}{6} \end{array} \right\}, & \text{for } N \geq 2 \end{cases} \tag{4}$$

where,

$$\Gamma(N) = \int_0^{\infty} \exp(-t) t^{N-1} \mathrm{d}t \tag{5}$$

is the gamma function of Euler. We define the function $f : \boldsymbol{R}^+ \setminus [0, 1) \to \boldsymbol{R}$,

$$f(y) = \frac{y}{2} \frac{\mathrm{d}^3}{\mathrm{d}y^3} \left[\ln\left(\Gamma(y)\right) \right] + \frac{\mathrm{d}^2}{\mathrm{d}y^2} \left[\ln\left(\Gamma(y)\right) \right] + y \sum_{k=1}^{\infty} \frac{1}{k^3} - \frac{\pi}{6} \tag{6}$$

Because the function f has a monotone behaviour, the definition domain of $\langle H_i \rangle$ (relation (4)) can be extended to the definition domain of function f. As a consequence, in relation (4) rational values of N_{Av} (as results from equation (1)) can be used to compute the intensity of the mean magnetic. The equation (4) will be used further in the fitting of experimental results.

$$\begin{aligned} \langle H_i \rangle = \frac{4m}{N_{Av} D^3} \cdot \Bigg\{ & \frac{N_{Av}}{2} \frac{\mathrm{d}^3}{\mathrm{d}N_{Av}^3} \left[\ln\left(\Gamma\left(N_{Av}\right)\right) \right] + \\ & + \frac{\mathrm{d}^2}{\mathrm{d}N_{Av}^2} \left[\ln\left(\Gamma\left(N_{Av}\right)\right) \right] + N_{Av} \sum_{k=1}^{\infty} \frac{1}{k^3} - \frac{\pi}{6} \Bigg\} \end{aligned} \tag{7}$$

The theoretical description of the magnetic resonance condition for a system consisting of single domain particles which forms chain aggregates is based on the analysis of the free magnetic energy of a single domain particle at its equilibrium position [13]. As it is shown in [13], starting from the equation of motion of the magnetization vector *M*, in the Landau-Lifshitz form, the resonant pulsation ω_{res} is given by the relation (8):

$$\omega_{res} = \frac{g\gamma\left(1+\alpha^2\right)^{1/2}}{M_S \sin\theta_0}\left(F_{\theta\theta}F_{\varphi\varphi} - F_{\varphi\theta}^2\right)^{1/2} \tag{8}$$

In relation (8) φ and θ are the angular coordinates of the magnetic moment of the particle; $F_{\theta\theta}$, $F_{\varphi\varphi}$ and $F_{\varphi\theta}$ are the second derivatives of the free energy density of a particle at the equilibrium position (θ_0, φ_0), where *F* has a minimum; *g* is the spectroscopic splitting factor; γ is the gyromagnetic electronic ratio; α is the damping parameter and M_S is the saturation magnetization of the bulk material of the particles.

For particles within the magnetic fluid having a spherical shape and uniaxial anisotropy, under the assumptions of particles chaining, the free magnetic energy density of a particle, is given by relation:

$$F = -\vec{H}\cdot\vec{M} - K\left(\vec{a}\cdot\frac{\vec{M}}{M_S}\right)^2 - \left\langle\vec{H}_i\right\rangle\cdot\vec{M} \tag{9}$$

In the above relation, *K* represents a uniaxial effective anisotropy constant, given by the shape anisotropy and the magnetocrystalline anisotropy and *a* is the unit vector, which defines the direction of the anisotropy axis. Also, *H* is the external static magnetic field, *M* is the magnetization of a particle and $\langle H_i \rangle$ is the intensity of the mean dipolar magnetic field acting on a particle due to all others particles from the same *N*-particle chain. After calculation of the free energy derivatives, $F_{\theta\theta}$, $F_{\varphi\varphi}$ and $F_{\varphi\theta}$ the resonance condition of the magnetic fluid becomes:

$$\omega_{res} = g\gamma\left(1+\alpha^2\right)^{1/2}\left[H + \frac{2K}{M_S} + \langle H_i\rangle\right] \tag{10}$$

The above relation can be rewritten in the usually form:

$$\omega_{res} = g\gamma\left(1+\alpha^2\right)^{1/2}\left[H + \frac{2K_{eff}}{M_S}\right] \tag{11}$$

where the effective anisotropy constant includes the effect of the dipolar interactions.

$$K_{eff} = K + \frac{M_S\langle H_i\rangle}{2} \tag{12}$$

Consequently, if the effective anisotropy constant is determined from the usual relation (11), its value depends on the particle concentration of particles within the magnetic fluid as in relation (12). In this relation, K is the effective anisotropy constant corresponding to a high dilution, for which the particle agglomerations and the interparticle interactions can be neglected.

3. SAMPLES

In order to prove the validity of the above theoretical conclusion, a magnetic fluid with $Mn_{0.6}Fe_{0.4}Fe_2O_4$ particles dispersed in kerosene and stabilised with oleic acid was investigated. The colloidal particles of $Mn_{0.6}Fe_{0.4}Fe_2O_4$ were obtained by chemical co-precipitation in aqueous solution.

The particle concentration of the initial magnetic fluid and the mean magnetic diameter were determined from the magnetization curve, using the Chantrell method [14], resulting $\rho = 4.46 \cdot 10^{16}$ cm^{-3} and $D_m = 12.8$ nm. From the initial magnetic fluid, 10 samples were obtained by successive dilution with kerosene, using a dilution ratio 2/3.

4. EXPERIMENTAL RESULTS AND DISCUSSIONS

The magnetic resonance measurements were performed at room temperature using an ESR spectrometer, which works at the frequency of 9060 MHz. The resonance absorption signal was recorded using a data acquisition system. The magnetic resonance spectra are presented in Fig. 1. It can be observed that the

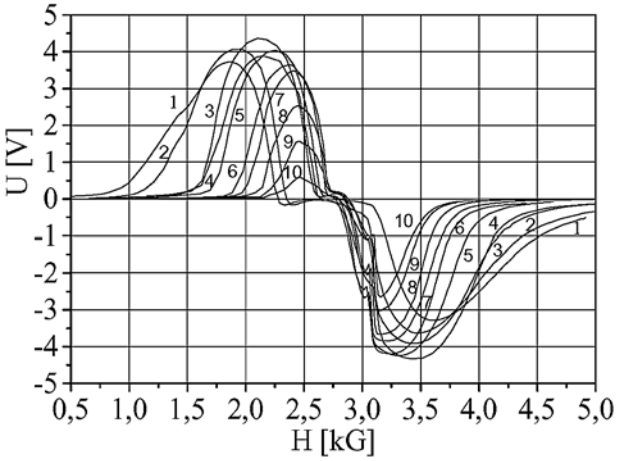

Fig. 1. – The magnetic resonance spectra of the investigated magnetic fluid (1 – for the undiluted magnetic fluid, 2 – for the first dilution and so on).

resonance spectra become narrower by decreasing the particle concentration from the magnetic fluid samples. This in qualitative agreement with the results obtained by Tronconi *et al.* [15] for a magnetic fluid with $MnFe_2O_4$ particles dispersed in water. Also, as it can be observed from the Fig. 1, the magnetic resonance line has a two-line pattern (a broader line superposed with a narrower one) for the investigated samples. In a theoretical paper [16], is demonstrated that a composed line is possible due to the chain like particle agglomerations induced by the static magnetic field at resonance. V. K. Sharma and F. Waldner [17] experimentally investigated some commercial magnetic fluids with magnetite particles and demonstrated that by dilution with trifluoroacetic acid, particle agglomerations occur in the investigated magnetic fluids and the narrow line vanished. Therefore, the shape of the magnetic resonance spectra (Fig. 1) allows us to assume that the investigated samples have particles in superparamagnetic state and a fraction of particles in agglomerations.

The resonance magnetic field H was computed, for each sample as $(H_1 + H_2)/2$, where H_1 and H_2 are respectively the first maximum and the last minimum of the resonance curves.

In order to determine K_{eff} using equation (11), we need to know the Lande factor of the magnetic material from which are made the particles within the magnetic fluid sample. The disposal of the magnetic ions in the tetrahedral position (A) in the octahedral position (B) of the spinell lattice of $Mn_{0.6}Fe_{0.4}Fe_2O_4$ ferrite is presented in formula below:

$$\left[Mn_x^{2+}Fe_{1-x}^{3+}\right]^A\left[Fe_{1-x}^{2+}Fe_{1+x}^{3+}\right]^B O_4^{2-} \tag{13}$$

where x is the concentration of the Mn^{2+} ions.

It is known that the Lande factor g_L for an isolated atom is given by equation (18):

$$g_L = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{14}$$

where J, S and L are the total, the spin and the orbital quantum numbers, respectively. Using equation (14) for the isolated atom applied to Fe^{3+}, Fe^{2+}, Mn^{2+} ions, the following values for the Lande factor were obtained: $g_L(Fe^{3+}) = 2$; $g_L(Fe^{2+}) = 1.5$ and $g_L(Mn^{2+}) = 2$. The Lande factor of a molecule of ferrite was computed as weighted mean value of the Lande factors corresponding to the ions from tetrahedral position (A) and ions from octahedral position (B). In case of the $Mn_{0.6}Fe_{0.4}Fe_2O_4$ ferrite, which has the chemical formula of a molecule given by equation (13), the Lande factor is:

$$g_L = \frac{1}{3}\Big[x \cdot g_L\left(\mathrm{Mn}^{2+}\right) + (1-x)\cdot g_L\left(\mathrm{Fe}^{3+}\right) + \\ + (1-x)\cdot g_L\left(\mathrm{Fe}^{2+}\right) + (1+x)\cdot g_L\left(\mathrm{Fe}^{3+}\right)\Big] \tag{15}$$

For the investigated sample, the value of the Mn^{2+} ions concentration is $x = 0.6$ and the Lande factor, computed with the equation (15) is $g_L = 1.93$. The spectroscopic splitting factor, g, which is correlated with the Lande factor, g_L, by relation $2 - g_L = g - 2$ [18] was computed and the obtained value is $g = 2.07$.

Using the calculated value of g and the measured values of the resonance field, H, the effective anisotropy constant, K_{eff}, was determined from Eq. (11). In this equation, the damping parameter was taken as $\alpha = 0.01$, which is an usual value for ferrimagnetic materials [18]. The dependence of the effective anisotropy constant of the particles within magnetic fluid, K_{eff}, on the particles concentration is presented in Fig. 2. As it can be observed from Fig. 2, the values of the effective anisotropy constant as measured by this technique decreases by dilution of the sample, tending to constant value. This value, $K = 6.25 \cdot 10^4$ erg/cm^3 corresponds to a high dilution, for which the particle agglomerations and the interparticle interactions can be neglected. The line is the theoretical dependence on concentration of the effective anisotropy constant of particles within the magnetic fluid (relation (12)). This dependence was computed based on the theoretical considerations presented in section 2. The used constants were: the saturation magnetization of the bulk material of the

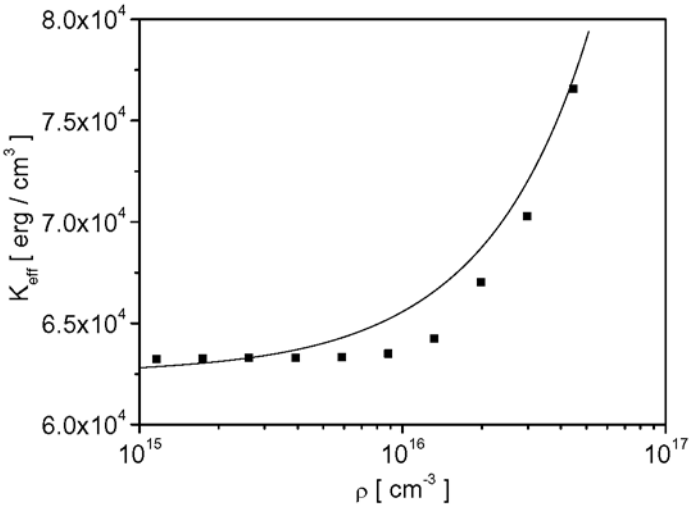

Fig. 2. – The dependence of K_{eff} on the particle concentration. The full line represents the theoretical dependence and the points (■) are experimental values.

particles, $M_S = 300$ G; the mean magnetic diameter of particles, $D_m = 12.8$ nm; the thickness of the nonmagnetic shell was considered as being 0.85 nm; the temperature, $T = 300$ K and the effective anisotropy constant of particles corresponding to high dilution, $K = 6.25 \cdot 10^4$ erg/cm^3.

5. CONCLUSIONS

The experimental results show that the effective anisotropy constant of particles within magnetic fluids, as determined by ferromagnetic resonance using the usual relation (11), depends on particle concentration. The values of the effective anisotropy constant as measured by this technique, decreases by dilution of the magnetic fluid, tending to constant value.

Taking into account the possibility of particle chains formation during the ferromagnetic resonance measurements, the theoretical analysis is in a good agreement with the experimental results.

The obtained result allows us to assert that diluted magnetic fluids are necessary to be investigated in order to determine a more accurate value of the effective anisotropy constant of particles within magnetic fluids by means of ferromagnetic resonance measurements.

REFERENCES

1. R. E. Rosensweig, *Ferrohydrodynamics,* Cambridge University Press, Cambridge, 1985.
2. P. C. Fannin, C. N. Marin, V. Socoliuc, G. M. Istrătucă, A. T. Giannitsis, *The effect of colloidal stabilization upon ferrimagnetic resonance in magnetic fluids in the presence of a polarizing magnetic field,* J. Phys. D: Appl. Phys., **36**, 1227 (2003).
3. C. N. Marin, I. Mălăescu, V. Socoliuc, *Study of the interparticle interaction effect on magnetic resonance line in ferrofluids*, Journal of Optoelectronics and Advanced Materials, 5, 227 (2003).
4. P. C. Fannin, C. N. Marin, V. Socoliuc, G. M. Istrătucă, A. T. Giannitsis, J. Magn. Magn. Matter., (in press).
5. P. C. Fannin, T. Relihan, S. W. Charles, *Investigation of ferromagnetic resonance in magnetic fluids by means of the short-circuited coaxial line technique*, J. Phys. D: Appl. Phys., 28, 2003 (1995).
6. I. Mălăescu, *A new method for determination of the effective anisotropy constant of the particles within ferrofluids,* Journal of Optoelectronics and Advanced Materials, 5, 233 (2003).
7. P. Goldberg, J. Hansford, P. J. van Heerden, *Polarization of light in suspensions of small ferrite particles in a magnetic field,* J. Appl. Phys. 42, 3874 (1971).
8. R. W. Chantrell, A. Bradbury, J. Popplewell, S. W. Charles, *Agglomerate formation in magnetic fluid,* J. Appl. Phys. 53, 2742 (1982).
9. V. Socoliuc, D. Bica, *Experimental investigation of magnetic induced phase-separation kinetics in aqueous ferrofluids,* Progress in Colloid & Polymer Science 117, 104 (2001).
10. I. Hrianca, I. Mălăescu, F. Claici, C. N. Marin, *The influence of particle concentration in ferrofluids on broadening of the magnetic resonance line,* J. Magn. Magn. Mater., 201, 126 (1999).

11. *Magnetic fluids and applications handbook*, Eds. B. Berkovski, V. Bashtovoy, Begell House Inc., New York-London, 1996.
12. P. G. de Gennes, P. Pincus, Phys. Kondens. Materie. 11, 189 (1970).
13. U. Netzelmann, *Ferromagnetic resonance of particulate magnetic recording tapes,* J. Appl. Phys., **68**, 1800 (1990).
14. R. W. Chantrell, J. Popplewell, S. W. Charles, IEEE Trans. Magn. 14, 975 (1978).
15. A. L. Tronconi, P. C. Morais, F. Pelegrini, F. A. Tourinho, *Electron paramagnetic resonance study of ionic water-based manganese ferrite ferrofluids,* J. Magn. Magn. Mater., 122, 90 (1993).
16. C. N. Marin, *The particle concentration effect on magnetic resonance linewidth for magnetic liquids with chain aggregates,* J. Magn. Magn. Mater., 250, 197 (2002).
17. V. K. Sharma and F. Waldner, *Superparamagnetic and ferrimagnetic resonance of ultrafine Fe_3O_4 particles in ferrofluids*, J. Appl. Phys., 48, 4298 (1977).
18. S. V. Vonsovski, *Magnetismul*, Ed. Stiintifica si Enciclopedica, Bucuresti, 1981.