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A NEW METHOD FOR DETERMINATION OF THE EFFECTIVE ANISOTROPY CONSTANT OF THE PARTICLES WITHIN FERROFLUIDS

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A new method for determination of the effective anisotropy constant (magnetocrystalline, shape and surface), K_{eff}, of the colloidal particles within ferrofluids, from ferromagnetic resonance measurements and based on the theoretical values computed for the Lande factor (g) of the ferrite molecule, is described. Two ferrofluids samples (denoted F1 and F2), with magnetite particles dispersed in kerosene and stabilized with oleic acid, were used. In the proposed method only one measurement (magnetic resonance) is necessary in order to determine K_{eff}. The Lande factor of the magnetite molecule, having the chemical formula, $\left[Fe^{2+}O^{2-}\right]^{A}\left[Fe_2^{3+}\right]^{B}O_3^{2-}$, was computed that the weight mean value of the Landé factors corresponding to the three ions in the tetrahedral positions (A) and in the octahedral positions (B). The values obtained in this way for K_{eff} are compared to the ones determined from other measurements.

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1. Introduction

Ferrofluids, also known as magnetic fluids, are colloidal suspensions of single-domain ferro or ferrimagnetic particles, dispersed in water or kerosene, having a mean diameter of approximately 10 nm. They may be described as superparamagnetic systems of single-domain particles [1], [2] with dynamic response:

$$\chi = \chi_0 (1 + j\omega\tau)^{-1} = \chi' - \chi'' \qquad \left(j = \sqrt{-1}\right) \tag{1}$$

where χ_0 is the static magnetic susceptibility, ω is the angular frequency, τ is the relaxation time for the magnetization reversal of a particle and χ' and χ'' the real and the imaginary parts of the complex magnetic susceptibility χ. The magnetization of ferrofluids in a variable magnetic field takes place either by rotating the particles in the basic liquid or by rotating the magnetic moment in the solid phase [3], [4] and [5]. Two magnetic relaxation processes are possible in ferrofluids: Brown type, and Nèel type. The frequency dependence of the complex magnetic susceptibility on the ratio of the magnetic anisotropy energy to the thermal energy [6] is given by:

$$\sigma = \frac{K_{eff} V_m}{kT} \tag{2}$$

where K_{eff} is the effective anisotropy constant (magnetocrystalline, shape and surface) and V_m, is the magnetic volume of the particle. For $\sigma > 1$, the magnetic moment in the particle is "blocked"; i.e. the moment cannot surmount the energy barrier, $K_{eff} V_m$, to reverse the direction of magnetization during the measurement. This possibility has been studied theoretically by Raikher and Shliomis [7] and has

been shown to be dependent on the ratio σ. Under these conditions precession of the magnetic moment in the anisotropy field H^a, occurs with a pulsation of resonance ω_r:

$$\omega_r = \mu_0 \gamma H^a \tag{3}$$

where γ is the magnetogyric ratio and $\mu_0 = 4 \cdot \pi \cdot 10^{-7}$ H/m is the magnetic permeability of the vacuum.

The effective anisotropy constant of single-domain particles, from a ferrofluid differs from the anisotropy constant of the bulk material from which the particles results. Studies concerning the determination of the anisotropy constant of the colloidal particles from the ferrofluids are relatively recent [8], [9], [10], and [11]. P. C. Fannin et al. using wide-band magnetic susceptibility measurements [8] in zero and external applied magnetic fields, the values of internal anisotropy field, H^a, and effective anisotropy constant, K, were determined for ferrofluids with magnetite and *Ni-Zn* ferrite particles [9]. In papers [10], I. Malaescu et al, determined the values of the effective anisotropy constant for magnetite particles dispersed in ferrofluids, using static measurements and magnetic relaxation measurements. The effect of magnetic particle concentration on the effective anisotropy constant was studied by J. L. Dormann et al. [11] using AC measurements of magnetic susceptibility at different temperatures, for systems consisting of nanoparticle dispersed in solid or liquid medium.

This paper describes a new method for the determination of the effective anisotropy constant of colloidal particles within ferrofluids, from ferromagnetic resonance measurements and based on the theoretical values computed for the Landé factor (g) of the magnetite ferrite molecule, for two ferrofluids samples. Assuming a spherical shape of the particles and uniaxial effective anisotropy, in the proposed method only one measurement (magnetic resonance) is necessary in order to determine the effective anisotropy constant of the colloidal particles, unlike the radiofrequency measurements [10] or wide-band magnetic susceptibility measurements [8].

2. Preparation and characterization of samples

For measurements, were used two ferrofluids samples, denoted F_1 and F_2 with magnetite particles dispersed in kerosene. The difference between them consists only in the method used to obtain the particle, in concentration and the dimensions of the particles. The magnetite colloidal particles of ferrofluid F_1, were obtained by chemical co-precipitation of Fe^{2+} and Fe^{3+} ions, in aqueous solution [12] and were with technical oleic acid. The particles of sample F_2 were obtained by a new technique [13], namely chemical co-precipitation of bivalent and trivalent *Fe* salts with an excess of NH_3 in *25%* solution, at decreasing *pH*. The stabilization of magnetite particles was done by hydrofobization with oleic acid in the absence of dispersion medium (kerosene), at a temperature of $75\ ^oC$, followed by a thermal treatment at $100\ ^oC$ for *1.5* hours.

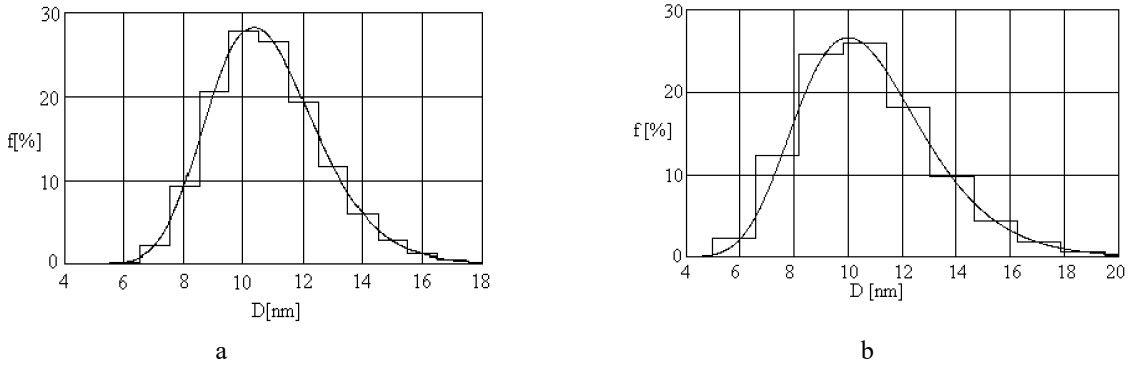


Fig. 1. The particle size distribution of magnetite particles, as resulted from electron micrograph in: a) - the ferrofluid F_1 and b) - the ferrofluid F_2

The electron micrograph analysis of the studied ferrofluids, allowed the determination of dimensional distribution of magnetite particles, which is shown in Fig. 1. a (for sample F_1) and

Fig. 1. b (for sample F_2), respectively. The diameter of the particles obeys a lognormal distribution with the mean value D_1=*11.4 nm* (for sample F_1) and D_2=*10.8 nm* (for sample F_2), and a standard deviation Δ_1 = *2.4 nm* and Δ_2 = *2.5 nm*, respectively. The resolution of the electron microscope was *0.7 nm*.

In order to determine the saturation magnetization of samples, the static magnetization measurements were performed using a ballistic galvanometer. The resulted values for the saturation magnetization of the investigated ferrofluids were $M_{\infty(F1)}$ = *12.63 kA/m* and $M_{\infty(F2)}$ = *36.34 kA/m*, respectively. The particle concentration of the ferrofluids (n) was determined from saturation magnetization and was based on the mean magnetic diameter resulting from the electron micrograph. The thickness of the solid non-magnetic shell was considered as being *0.84 nm* [14]. The values obtained are: n_1=*5.5* $\cdot 10^{22}$ m^{-3} and n_2=*19.16* $\cdot 10^{22}$ m^{-3}, respectively.

3. Method; results and discussions

For each studied sample, the magnetic resonance measurements were made at room temperature using a RPE spectrometer of type ART 5, which works at the frequency of *9060 MHz*. The resonance absorption signal was recorded using a data acquisition system. The ferromagnetic resonance spectra of the ferrofluids samples are shown in Fig. 2. It can be observed that the resonance line-width is larger for sample F_2 than for sample F_1, therefore the resonance spectra becomes narrower on decreasing the magnetite particle concentration from the ferrofluids. This is in qualitative agreement with the results obtained by A. L. Tronconi et. al [15] for ferrofluids with *Mn-Fe* particles, and to I. Hrianca et. al [16] for ferrofluids with magnetite and *Mn-Fe* particles.

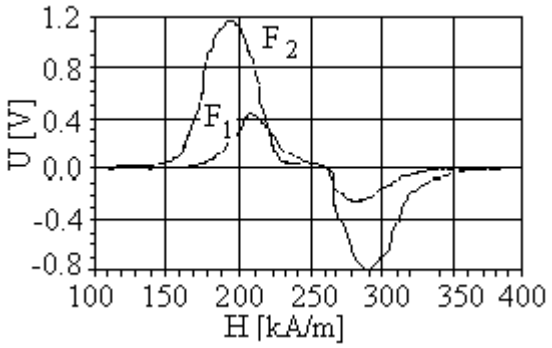


Fig. 2. Magnetic resonance spectrum for ferrofluid F_1 and ferrofluid F_2.

It is known [17] that for an ellipsoid with its principal axes parallel to the *Ox*, *Oy*, *Oz* coordinate axes and subjected to a static magnetic field, H_o, which is parallel to *oz* axis, the resonance condition is:

$$\omega_r = g_J \gamma \mu_0 \sqrt{\left[H_0 + \left(N_y - N_z + N_y^a\right)M_S\right]\left[H_0 + \left(N_x - N_z + N_x^a\right)M_S\right]} \tag{4}$$

In this relation, M_S is the saturation magnetization of the bulk material, N_x, N_y and N_z are the shape demagnetizing factors for each direction and N_x^a and N_y^a are the demagnetizing factors due to the effective anisotropy. Assuming a spherical shape of the particles ($N_x = N_y = N_z$) and uniaxial effective anisotropy with an easy axis along the *Oz* direction, $\left(N_x^a = N_y^a = \dfrac{2K_{eff}}{\mu_0 M_S^2}\right)$, the equation (4) becomes:

$$\omega_r = g_J \gamma \mu_0 \left(H_0 + H^a\right) \tag{5}$$

where,

$$H^a = \frac{2K_{eff}}{\mu_0 M_S} \tag{6}$$

is the anisotropy field.

The $H_o$value of the resonance magnetic field, was computed with the equation $(H_1+H_2)/2$, where H_1 and H_2 are the maximum and the minimum of the resonance curves, respectively (Fig. 2). The results obtained for H_o are presented in Table 1.

Table 1.

Samples	H_o [kA/m]	g_J	H^a [kA/m]	K_{eff} [J/m^3]
F_1	247	1.83	34.60	$10.30 \cdot 10^3$
F_2	240	1.83	41.60	$12.40 \cdot 10^3$

The distribution of the magnetic ions over the tetrahedral (A) and the octahedral positions (B) of the spinell lattice [18] in the investigated ferrofluids can be assumed to be as follows:

$$(F_1, F_2): \left[Fe^{2+}O^{2-}\right]^A \left[Fe_2^{3+}\right]^B O_3^{2-} \tag{7}$$

It is known that the Lande's factor g_J for an isolated atom [17], is given by the equation:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{8}$$

where J, S and L are the total, the spin and the orbital quantum numbers, respectively. Using equation (8) for the isolated atom applied to Fe^{3+} and Fe^{2+} ions, the following values for the Landé factor were obtained: $g_{J(Fe^{3+})} = 2$ and $g_{J(Fe^{2+})} = 1.5$, respectively. Considering that for the magnetite ferrite molecule having the chemical formula given by the equation (7), the Landé factor is the weight mean value of the Landé factors corresponding to the three ions over the tetrahedral (A) and the octahedral (B) position, it results:

$$g_{J(1,2)} = \frac{1 \cdot g_{J(Fe^{2+})} + 2 \cdot g_{J(Fe^{3+})}}{3} \tag{9}$$

The values $g_{J(1,2)}$ (for samples F_1 and F_2), computed with the equation (9), are given in Table 1. Using these values and the values for H_o for each sample of a ferrofluid (see Table 1), with the equations (5) and (6) H^a and K_{eff}, respectively, were computed. The values obtained for the anisotropy field H^a, and the effective anisotropy constant K_{eff}, of the colloidal particles in the studied ferrofluids, are presented in Table 1. For the saturation magnetization of magnetite the value $M_S = 477.5$ *kA/m*, was assumed [19]. The values obtained for the anisotropy field and for the effective anisotropy constant are close to the values determined by L. R. Bickford [20], for magnetite single-crystal and by I. Malaescu et. al [10] for ferrofluids with magnetite particles, from measurements of Néel relaxation times. It is also observed that the values for K_{1eff} and K_{2eff} differ, even though the colloidal particles from samples F_1 and F_2 are of the same type (magnetite). This is due to the fact that the effective anisotropy constant depends on magnetite particle concentration. As it is shown in paper [21], K_{eff}

shows small changes for particle concentration, between 10^{21} and 10^{22} m^{-3}. Increasing the particle concentration, K_{eff} is strongly changed, a fact that can be assigned to the magnetic interparticle interaction. It was also shown in [22], that K_{eff} depends on the surface effects and on the method used to obtain the colloidal particles.

4. Conclusions

In conclusion, using the ferromagnetic resonance measurements and based on the theoretical values computed for the Landé factor of magnetite ferrite molecule, the effective anisotropy constant was determined through a new method.

In the proposed method if it is considered a spherical shape of the particles and uniaxial effective anisotropy, only one measurement (magnetic resonance) is necessary in order to determine K_{eff}.

The Landé factor of the magnetite ferrite molecule was computed as the weight mean value of the Landé factors corresponding to the three ions in the tetrahedral and octahedral positions.

The results obtained for K_{eff}, are in agreement with the ones determined from other measurements.

References

[1] P. C. Fannin, B. K. P. Scaife, S. W. Charles, J. Phys.D: Appl. Phys. **21**, 533 (1988).
[2] M. Hanson, J. Magn. Magn. Mater. **96**, 105 (1991).
[3] P. C. Fannin, B. K. P. Scaife, S. W. Charles, J. Magn. Magn. Mater. **65**, 179 (1987).
[4] P. C. Fannin, B. K. P. Scaife, S. W. Charles, J. Magn. Magn. Mater. **122**, 159 (1993).
[5] I. Hrianca, I. Malaescu, J. Magn. Magn. Mater. **150**, 131 (1995).
[6] A. M. Konn, P. Laurent, P. Talbot, M. Le Floc'h, J. Magn. Magn. Mater. **140-144**, 367 (1995).
[7] Y. L. Raikher, M. I. Shliomis, Sov. Phys. JETP **40**, 526 (1975).
[8] P. C. Fannin, T. Relihan, S. W. Charles, J. Phys. D: Appl. Phys. **28**(10)**,** 2003 (1995).
[9] P. C. Fannin, S. W. Charles, IEEE Trans. Magn. **33**(5), 4251 (1997).
[10] I. Malaescu, I. Hrianca, J. Magn. Magn. Mater. **157/158**, 585 (1996).
[11] J. L. Dormann, D. Fiorani, E. Tronc, J. Magn. Magn. Mater. **202**, 251 (1999).
[12] D. Bica, R. Minea, RO Patent, 97556 (1989).
[13] I. Malaescu, L. Gabor, F. Claici, N. Stefu, J. Magn. Magn. Mater. **222**, 8 (2000).
[14] Y. L. Raikher, M. I. Shliomis, Adv. Chem. Phys. **87**, chap. 8 (1994).
[15] A. L. Tronconi, P. C. Morais, F. Pelegrini, F. A. Tourinho, J. Magn. Magn. Mater. **122**, 90 (1993).
[16] I. Hrianca, I. Malaescu, F. Claici, C. N. Marin, J. Magn. Magn. Mater. **201**, 126 (1999).
[17] C. Kittel, Phys. Rev. **73**, 155 (1948).
[18] R. V. Upadhyay, K. J. Davies, S. Wells, S. W. Charles, J. Magn. Magn. Mater. **132**, 249 (1994).
[19] E. Kneller, Ferromagnetismus, Berlin Springer, (1962).
[20] L. R. Bickford Jr., Phys. Rev. **78**, 449 (1950).
[21] C. N. Marin, I. Malaescu, A. Ercuta, J. Phys. D: Appl. Phys. **34**, 1466 (2001).
[22] D. Prodan, C. Chaneac, E. Tronc, J. P. Jolivet, R. Cherkaour, A. Ezzir, M. Nogues, J. L. Dormann, J. Magn. Magn. Mater. **203**, 63 (1999).