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Optical properties of nickel ferrite ferrofluids

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Abstract

We investigate magneto-optical properties of chemically synthesized ionic ferrofluids based on nickel ferrite nanoparticles. These new ferrofluids with potential biological applications become birefringent under low magnetic fields. Both a static and a dynamic probing are here presented. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Ferrofluids; Magneto-optical birefringence

1. Introduction

In the years to come, one of the most important developments for the magnetic liquids or ferrofluids will be the biological domain. A successful grafting of antibodies to maghemite nanoparticles have already been performed [1] and checked by optical birefringence measurements. The long-term purpose of such associations is to transport drugs or antibodies together with the magnetic particles directly inside the human body. Nevertheless, to test a biodistribution in vivo of maghemite nanoparticles would be difficult to handle. Maghemite is an iron ferrite and in a titration process, the iron coming from the particles could not be distinguished from iron haemoglobin. A ferrofluid based on a different and nontoxic material is therefore necessary to realize such biological in vivo experiments.

We present here an optical study of new ionic aqueous ferrofluids based on nickel ferrite particles. Recent papers [2] have shown that colloidal dispersions of magnetic particles made of ball-milled nickel ferrite present anomalous magnetic behaviors. The low temperature (4 K) magnetization curve of these ball-milled particles exhibits an open hysteresis loop even for very large magnetic fields (13 000 kA m^{-1}). Their magnetization under a 5600 kA m^{-1} magnetic field is still time dependent. The authors explain these observations by strong surface effects inside the particles, related to the existence of a surface layer of disordered spins.

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In our work, we use magnetic particles chemically synthesized according to Massart's method [3]. It has been shown [4] that these particles as the ball-milled ones, present magnetization heterogeneities with a magnetic monodomain ordered core and a disordered surface layer. Ferromagnetic resonance experiments realized on the same chemically synthesized particles have shown their magnetic uniaxiality [5]. We investigate here static and dynamic magneto-optical properties of their dispersion in a liquid at room temperature. The aim of such experiments is to check the suitability of these particles for optical titration in biological applications.

2. Chemical synthesis and particle characterization

Two steps are required to prepare nickel ferrite ferrofluids. First, magnetic particles are produced and secondly, they are dispersed in a liquid carrier. To synthesize the nanosized magnetic particles, a polycondensation method is used. A co-precipitation of an aqueous solution of $NiCl_2$ and $FeCl_3$ in an alkaline medium leads to nanoparticles of $NiFe_2O_4$ coated with hydroxoligands. Using low polarizing counterions, the precipitated particles can then be dispersed in a polar medium. The amphoteric hydroxyl groups adsorbed on the surface of the particles, introduce an electrostatic interparticle repulsion which prevents the solution from aggregation under the magnetic dipolar and van der Waals interactions. The obtained dispersion is a magnetic colloid electrostatically stabilized. It can be dispersed in different polar liquids, here water or glycerine. The volume fraction Φ of $NiFe_2O_4$ material is determined by chemical titration of iron. Three samples with different volume fractions Φ are prepared: $\Phi = 0.23\%$, 0.45% and 0.75%. Φ is small enough ($\Phi < 1\%$) for the solutions to remain in the dilute range where the interparticle interactions are negligible [6]. The average interparticle distance ranges from 5 to 10 particle diameters. The colloid can be considered as a 'gas' of isolated grains, the solution containing eventually some aggregates of a few particles [6].

From electronic microscopy a direct image of the magnetic particles is obtained and presented in Fig. 1. It clearly indicates that the particles are roughly spherical and that their average diameter d_{EM} is ranging from 3 to 5 nm. Moreover, the lines indexation of the electron beam diffraction pattern shows that the particles have a spinel structure [4]. An X-rays diffraction experiment has also been performed on the nickel ferrite particles. The powder diagram presented in the Fig. 2 exhibits peaks which are characteristic of the spinel structure. The [3 1 1] line provides a determination of a mean diameter, found equal to $d_{RX} = 4.5$ nm in good agreement with the electronic microscopy.

3. Magneto-optical measurements

Beside this crystalline characterization we have performed an optical probing of the solutions at $\lambda_0 = 632.8$ nm. At this wavelength, the optical absorption coefficient α (coming from the Beer–Lambert law) of $NiFe_2O_4$ presents a minimum [7]. With our fine particle systems, we determine experimentally $\alpha = 0.44 \times 10^4$ cm^{-1}, to be compared to 10^4 cm^{-1}, the value found for thin films in Ref. [7]. Besides, the solution exhibits magneto-optical properties. Submitted to a static magnetic field, it behaves as an optically uniaxial plate [8–11]. The results of a static birefringence experiment [12] performed on a dilute aqueous solution may be interpreted in terms of a Langevin formalism

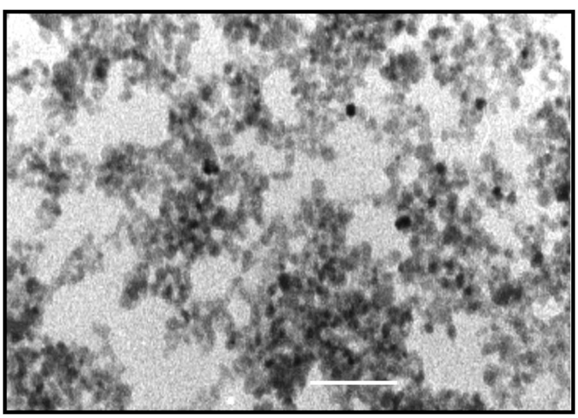

Fig. 1. Electronic microscopy picture of a chemically synthesized ferrofluid sample made of nickel ferrite particles. The bar corresponds to 50 nm.

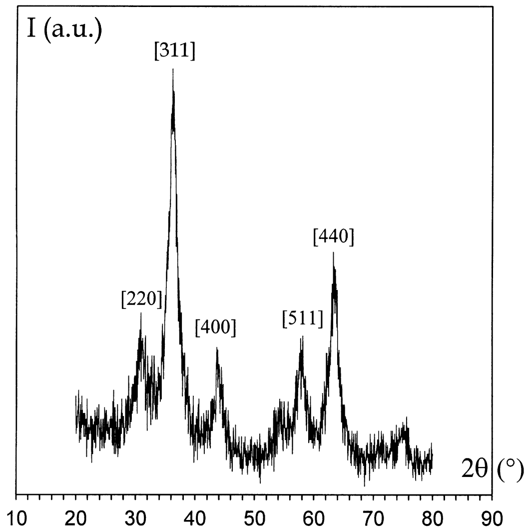

Fig. 2. X-rays diffraction spectrum of a chemically synthesized ferrofluid sample made of nickel ferrite particles.

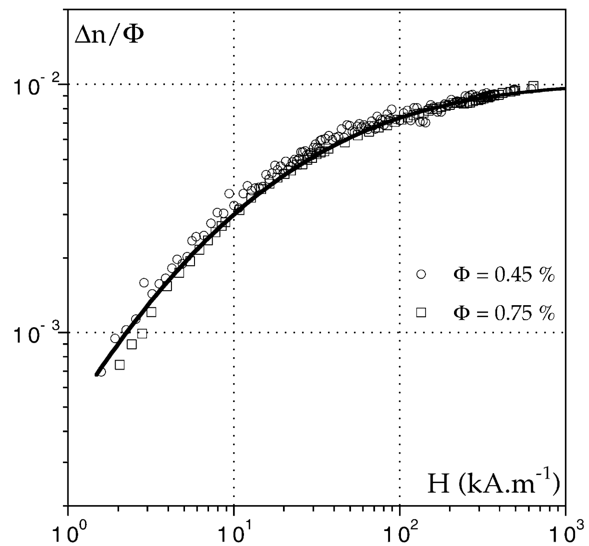

Fig. 3. Reduced static birefringence as a function of applied magnetic field for two volume fractions $\Phi = 0.45\%$ and 0.75%. The full line is the best fit of the experimental data with the second Langevin function coupled with a log-normal distribution.

with an optical anisotropy of individual particles $\delta n_0 = 0.10$:

$$\frac{\Delta n}{\delta n_0 \Phi} = \frac{\int L_2(\xi) d^3 P(d) dd}{\int d^3 P(d) dd},$$

ξ being the Langevin parameter, ratio of the magnetic energy of a particle to the thermal energy, $L_2(\xi) = 1 - (3/\xi^2)(\coth \xi - 1/\xi)$, the second Langevin function and $P(d)$ the diameter distribution of the nanoparticles. The experimental static birefringence $\Delta n(H)$ of two solutions, of volume fractions $\Phi = 0.45\%$ and 0.75%, is presented in Fig. 3 in a reduced representation, as a function of the applied magnetic field. We assume a log-normal distribution of roughly spherical particles and a magnetization of the nickel ferrite material equal to its bulk value $m_S = 270\ \mathrm{kA\ m^{-1}}$. A best fit of the experimental data, gives a distribution of characteristics $d_{mp} = 5.5$ nm and $s = 0.4$ very close to the electronic microscopy and X-rays characterizations. In future it would be interesting to investigate experimentally the magnetic dichroism of the solution. In principle, it should present similar field variations as magnetic birefringence [8,10,13].

A dynamic probing is also performed in a birefringence measurement, under a low alternating magnetic field, as a function of the field frequency. The experimental set-up is presented in the Fig. 4. The ferrofluid sample, dispersed in glycerine, is put in a glass cell of thickness e, submitted to an alternating field $H_A = 16\ \mathrm{kA\ m^{-1}}$ produced by Helmholtz's coils (B_1, B_2). The beam of an He–Ne weak power laser (L) of wavelength $\lambda_0 = 632.8$ nm, goes successively through a polarizer (P), the sample cell and an analyzer (A). A photodiode (D) detects the transmitted intensity. A lock-in amplifier (LIA) using the field frequency as a reference, gives the module and the phase of the 2ω part of the signal $I_{2\omega} \propto \Delta n^2$.

The field frequency is experimentally ranging from 1 Hz to 1 kHz. As a function of frequency, we present in Fig. 5 two parameters respectively proportional to the real and to the imaginary part of the birefringence normalized at 1 Hz: $\Delta n/\Delta n(1\ \mathrm{Hz})$. The imaginary part presents a maximum at $f = 15$ Hz. We compare in Fig. 6 the experimental results to a standard Debye relaxation $\Delta n/\Delta n(1\ \mathrm{Hz}) = 1/(1 + i\omega\tau)$. Such a model expresses that at low frequencies the particle optical axis follows the oscillations of the magnetic field. As the

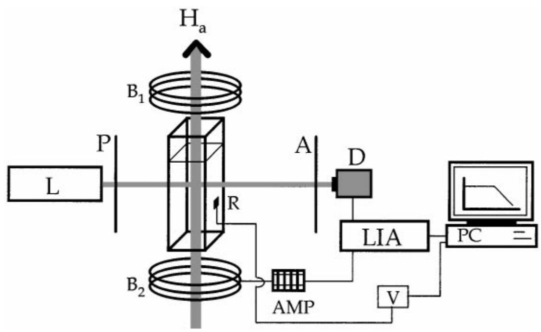

Fig. 4. Experimental set-up for the measurements under alternating magnetic fields.

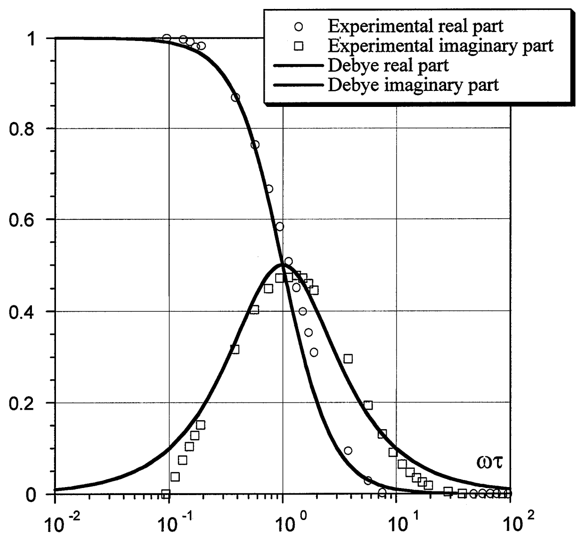

Fig. 5. Real and imaginary parts of the birefringence of the ferrofluid solution as a function of frequency. The full lines correspond to the real and the imaginary parts of the Debye relaxation.

frequency increases the phase-lag between the field and the particle axis progressively increases and in the high frequency limit the particle does not oscillate anymore. Identifying the frequency of the maximum of the imaginary part to the condition $\omega\tau = 1$ allows a comparison of the model to the experiment as a function of the reduced parameter $\omega\tau$. The characteristic time resulting from this adjustment is $\tau = 10$ ms. This Debye relaxation time corresponds to a Brownian time of rotational diffusion $\tau = 3\eta V_h/k_B T$, V_h being the hydrodynamic volume of the particles ($V_h = \pi d_h^3/6$; d_h the hydrodynamic radius of the particles). We find here $d_h = 30$ nm to compare with the low field average of static birefringence [12] $d_{LF} = d_0 \exp(6s^2) \cong$ 20 nm and with a transient measurement after a pulse of magnetic field in an aqueous sample made of the same particles: $\tau_{Pulse} = 27$ μs and $d_h(\text{pulse}) \cong 40$ nm. These large values of d_h have to be correlated to the large width of the particle distribution in the sample and to the low field value (1.6 kA m^{-1}) used in the experiment.

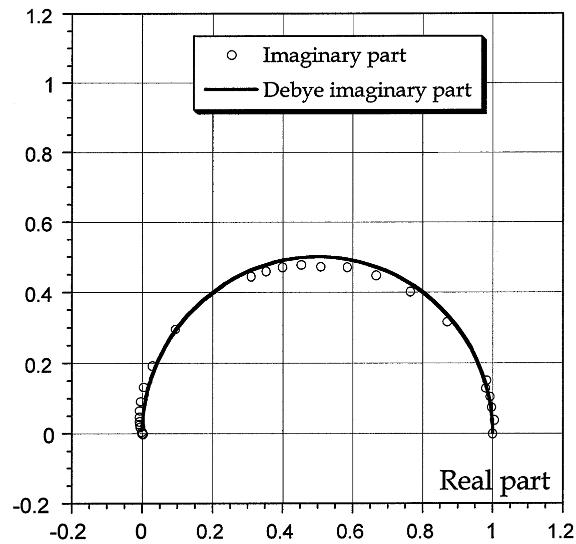

Fig. 6. Cole–Cole plot of the experimental birefringence. The full line corresponds to the Debye relaxation curve.

4. Conclusions

In conclusion, the chemically synthesized nickel ferrites particles used here present optical characteristics very similar to the ones of γ-Fe_2O_3 with a slightly larger absorption. However, standard birefringence dynamic investigations are possible and a probing in large magnetic fields would be interesting to perform. These $NiFe_2O_4$ particles will be used in future for biomedical applications providing an improvement of the width of the size distribution.

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