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Journal of Magnetism and Magnetic Materials 242–245 (2002) 572–574

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

$NiFe_2O_4$ nanoparticles in ferrofluids: evidence of spin disorder in the surface layer

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Abstract

We show that surface magnetic properties of $NiFe_2O_4$ nanoparticles constituting ionic ferrofluids can be investigated in macroscopic experiments. Cross-analysis of static magnetization and field-induced birefringence prove that the particles consist of a uniformly magnetized core and a spin-disordered surface layer of comparable thickness.

Keywords: Nanoparticles; Nickel ferrite; Magnetic fluids; Magnetic birefringence

Magnetic fluids or ferrofluids, being materials of great interest for engineering, are yet more fascinating with respect to biological applications. The latter, however, impose some special requirements. For example, the well-known γ-Fe_2O_3 ferrofluids become undesirable because their iron atoms are poorly distinguishable from those of hemoglobin. A conceivable solution is to use ferrites with another metal content. $NiFe_2O_4$ is a good candidate, and so one needs to know the principal properties of such ferrofluids. Among akin ferrites, $NiFe_2O_4$ is special: under size diminution, its particles, along with usual superparamagnetism, show strong reduction of magnetization with respect to that of the bulk ferrite. First, tests on grinded [1,2] and precipitated [3] fine grains attributed this decrease to the non-collinearity of the surface spins. Then, strong-field experiments at low temperatures [2–4] revealed opened hysteresis loops of nanoparticles even above 10^4 kA/m thus pointing out to the presence of a spin-glass-like structure. In result, a model of a $NiFe_2O_4$ nanoparticle as a spin-disordered layer wrapped around a uniformly magnetized core was proposed. Note that in the near past to prove the existence of such a layer in γ-Fe_2O_3 nanograins, several dynamic techniques were involved: AC-susceptibility [5], quasi-elastic neutron scattering [6], and ferromagnetic resonance [7].

In this paper, carrying on the idea of our work [8], we show that to detect the spin-disordered layer on nanograins and to estimate its thickness, it suffices to make *only two* basic measurements on a colloidal suspension of such particles, i.e., ferrofluid. In Ref. [8] we tested this on the samples with a constant mean particle size d. Hereby we analyze the case when d varies. Two ferrofluid samples obtained by a coprecipation method are employed. They have the same volume fractions of $NiFe_2O_4$—about 0.8 vol%—but differ in

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0304-8853/02/$ - see front matter
PII: S0304-8853(01)01122-2

the particle size. As measured by X-ray diffraction, for sample A the mean diameter is $d_{RX} = 4.4$ nm while for sample B $d_{RX} = 5.9$ nm.

As *the first test*, the static magnetization curve is measured. For interpretation we assume an assembly of independent single-domain grains with a magnetic moment $\mu = \pi I d^3/6$, where I is the magnetization of the particle. The liquid matrix with the suspended particles (whatever their magnetic anisotropy) behaves as an ideal superparamagnet [9] and the ferrofluid magnetization is given by the Langevin law:

$$M = I\Phi L(\xi), \quad L(\xi) = \coth\xi - \xi^{-1}, \quad \xi = \mu_0\mu H/kT, \tag{1}$$

with Φ being the ferrite volume fraction. Eq. (1) shows that at $\boldsymbol{H} = 0$ the magnetization equals zero. As the field $\boldsymbol{H}$ is turned on, the magnetic moments align with it so that in high fields M saturates at $I\Phi$. This model works fairly well for γ-Fe_2O_3 ferrofluids, one just has to set the nanoparticle magnetization I to be 75% of the bulk.

Magnetization curves of the samples A and B measured with a Foner device at room temperature and normalized with respect to Φ are shown in Fig. 1. Being in qualitative agreement with the superparamagnetic model (1) in weak to moderate fields, they go off it above 10^3 kA/m showing no saturation. Besides that, at 10^3 kA/m the values of M/Φ equal 95 (sample A) and 145 kA/m (B), i.e., are much lower than 270 kA/m, the bulk value of I at room temperature. This confirms the presence of spin-disordered regions in the particle. Inset in Fig. 1 shows (for sample A) the *ultima ratio* in favor of the spin-disorder hypothesis: a SQUID record at 5 K that shows an open magnetization loop.

Magnetic measurements indicate the presence of a spin disorder in the particles but do not localize it. To proceed, *the second test* is undertaken that measures the field-induced birefringence $\Delta n(H)$. For interpretation we use the model (1) extended by assumption that each particle, along with a magnetic anisotropy, has an optical one in the same direction, e.g. due to the anisometric shape. Then one has [10]

$$\Delta n = (\Delta n)_0[1 - 3L(\xi)/\xi], \quad (\Delta n)_0 = C\Phi f(\sigma), \tag{2}$$

where C depends on the particle refraction index and shape eccentricity. Function $f(\sigma)$ grows from 0 to 1 as its argument $\sigma = E_a/kT$ goes from zero to infinity; here E_a is the anisotropy energy. This model works well for γ-Fe_2O_3 and $CoFe_2O_4$ ferrofluids [10,11].

The setup and the method to measure the ferrofluid birefringence are described elsewhere [10]. Fig. 2 presents the $\Delta n(H)$ curves scaled by their maximum values. Note that contrary to the magnetization, the observed functions $\Delta n(H)$ are in *complete* qualitative agreement with the model (2): they readily saturate in high fields. Evaluating, as in Ref. [10], the most probable diameter and the dimensionless width of the log-normal distribution, one finds $d_{mp} = 4.7$ nm, $s = 0.55$ (sample A); $d_{mp} = 6.3$ nm, $s = 0.4$ (B).

Different high-field behavior of the functions $M(H)$ and $\Delta n(H)$ is a crucial fact. Enigmatic from other viewpoints, it easily interprets in terms of the core–shell model. Indeed, when the field is high enough, the Zeeman energy μH of the particle core exceeds kT, and the direction of the core magnetic moment $\boldsymbol{\mu}$ aligns with $\boldsymbol{H}$. Then the orientational effect of $\boldsymbol{H}$ (via internal

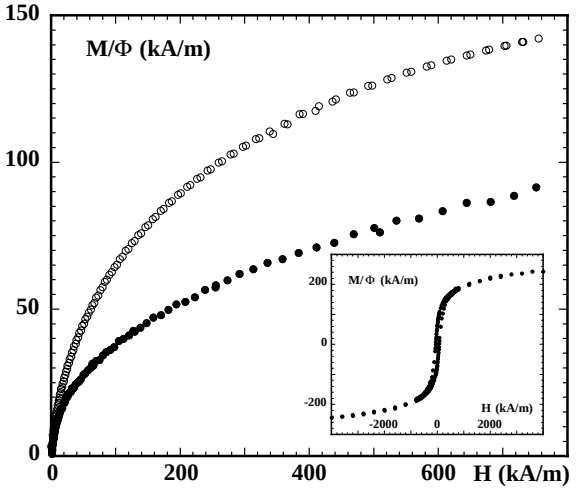

Fig. 1. Magnetization curves of the nickel ferrite ferrofluid samples A (full dots) and B (open dots). Inset: zero-field cooled hysteresis loop at 5 K of sample A.

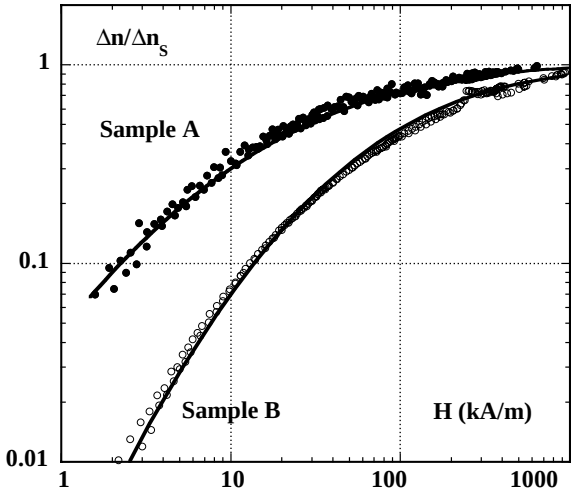

Fig. 2. Normalized magnetic birefringence versus applied field H; same symbols as in Fig. 1. Full lines are best fits of Eq. (2) weighted by a log-normal size distribution of diameters (see the text).

magnetic anisotropy) on the particle optical axis reaches its maximum resulting in saturation of the ferrofluid birefringence. With further increase of H, the magnetization process that continues (with no saturation) in the particle shell and remains well "visible" in the magnetization curve does not affect Δn.

Their saturation behavior has proven that the $\Delta n(H)$ dependences can be quantitatively interpreted with the aid of a polydisperse analog of Eq. (2), where ξ is defined with respect to the core. The fraction of spins included in the cores can be asserted as $\eta_c \sim M_{sat}^{(core)}/(\Phi I)$ with $M_{sat}^{(core)}$ evaluated through the ferrofluid histogram taken from the birefringence data. For example, $\eta_c \approx 23\%$ (sample A). Assuming identical spherical particles, by the order of magnitude one writes $\eta_c = (d_c/d)^3$, where d_c and d are, respectively, the core and total diameters of a particle. Identifying d_c with the value of $d_{mp} = 2.6$ nm, found when separating the core and surface contributions, we find $d = 4.2$ nm, that quite reasonably falls between the d_{mp} values 3.4 and 4.7 nm found by TEM and birefringence measurements. The effective thickness of the surface layer comes out ~ 0.9 nm that is comparable with 0.83 nm, the period of the $NiFe_2O_4$ crystal lattice.

The authors thank CAPEs and COFECUB for their financial support (Grant No. 292/99).

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