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Study of magnetite nanoparticles embedded in lyotropic liquid crystals

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Abstract

A study about the magnetic behaviour of magnetite nanoparticles diluted in lyotropic liquid crystals was carried out. It was corroborated that micellar phases of the liquid crystal suppressed the superparamagnetism of the nanoparticles by rising the blocking temperature beyond the room temperature. Phase transitions in the lyotropic mixtures can be determined from M *vs.* T curves of the ferrolyotropic. When the liquid crystal is in the nematic discotic phase, the magnetization and the susceptibility of the mixture mimics the behaviour of the orientational order parameter of the phase.

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1. Introduction

Lyotropic liquid crystals (LLC) show a low diamagnetic susceptibility anisotropy ($|\Delta\chi|\sim 0.7\times10^{-8}$ cgs units), being necessary high magnetic fields ($H\sim10^4$Oe) for orienting the liquid crystalline matrix. In a pioneering work, Brochard and de Gennes [1] proposed to introduce long rodlike ferromagnetic particles (~100nm) inside the liquid crystal (LC) (the so-called "ferronematic" mixture) in order to reduce this field by a factor 10^3. The first realization of a ferronematic was a thermotropic liquid crystal (p-methoxybenzyledene-p-butylaniline) doped with long γ-Fe_2O_3 magnetic grains (0.35μm) [2]. However, the doping of LC with nearly spherical ferromagnetic particles of around 10nm (typical dimension of particles in actual ferrofluids) was achieved only in LLC [3]. Intriguingly, ferro or ferrimagnetic nanoparticles (NP) of such size are *superparamagnetic* at room temperature (in solid compounds and magnetic colloids) but they continue magnetically blocked (i.e, they remain ferro or ferrimagnetic at room temperature) when diluted in nematic LC [4] or polymer thermotropic LC [5]. The physical process that produces this blocking is an open problem in nanomagnetism. Previous works suggested that clusters or aggregates of NP's [6] could account for the observed magnetic blocking when they are immersed in the LC, through an increase of the effective magnetic anisotropy k_{eff}. However, such aggregates never were experimentally observed. In this paper we

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report on the magnetic behavior of NP's of magnetite diluted in LLC as a function of the temperature between 282 and 350 K.

In our study, two types of LLC's were used: the first one was formed by the binary mixture of water and potassium laurate (KL), and the second one was obtained by mixing water, KL and decanol (DeOH).

2. Experimental

The LLC investigated in this work was mixtures of KL and water MilliQ (binary LLC) or KL, water MilliQ and DeOH (ternary LCC). DeOH (purity better than 99%) was purchased from Aldrich, whereas KL was synthesized in our laboratory from lauric acid via neutralization with potassium hydroxide, it was further recrystallized several times with ethanol (all these chemical compounds come from Merk). The ferrofluid used was EMG605 from Ferrotech Co. and it consist in an aqueous suspension of nanoparticles of magnetite (Fe_3O_4), with mean diameter of 10 nm, coated with a double layer of oleic acid as surfactant agent. A sample of pure ferrofluid was prepared by diluting the original ferrofluid in water until reaching a concentration of around 10^{14} nanoparticles/cm^3 (this sample is called FF in Table I).

Table 1: Composition (wt. %) and phase at room temperature (~297 K) for the samples studied. Each sample was doped with 10^{14} nanoparticles of magnetite per cm^3.

Sample	H_2O	KL	DeOH	Phase at RT
FF	100	-	-	isotropic liquid
B_1	99.94	0.06	-	molecular isotropic
B_2	90.90	9.10	-	micellar isotropic
N	67.00	26.00	7.00	discotic nematic

The ferronematic samples were prepared by careful doping of the lyotropic with the ferrofluid, reaching the mentioned concentration of Fe_3O_4 nanoparticles. This value (10^{14} nanoparticles/cm^3) is above the minimum concentration required in order to orient the nematic liquid crystal in the preparation of the corresponding ferronematic [7-8]. On the other hand, at this concentration, it was estimated that the ferrolyotropic has around 10^5 micelles by magnetic NP, and it is much less than 1% in volume fraction. The composition of each sample is given in Table I. The binary sample B_1 was prepared with a percentage of KL below the critical micellar concentration (CMC), and then in B_1 the soap molecules did not form micelles. Differently, B_2 was prepared with a concentration of soap higher than CMC. In the range of temperatures studied B_1 (B_2) remains in the molecular (micellar) isotropic phase. Finally, sample N corresponds to a ternary doped LLC and this sample present two phase transitions as determined by optical measurements: the first one at (285±3) K (from micellar isotropic to discotic nematic), and the second one at (315±3) K (from discotic nematic to micellar). The magnetization *versus* temperature measurements were performed from 282 to 350 K, under zero-field cooling (ZFC) and field cooling (FC) conditions, with applied field of 50 Oe, by using a SQUID magnetometer (Quantum Design). The samples were mounted in little quartz cylinders (internal diameter: 3 mm and height: 2 cm) and seals with resin.

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