Ferrosmectics: A New Magnetic and Mesomorphic Phase

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We have realized new systems which consist of a periodic packing of a bidimensional magnetic liquid alternating with nonmagnetic fluid. These "ferrosmectic" phases are obtained by incorporating solid magnetic particles in lyotropic lamellar systems. Their existence has been proved by their optical properties and their anisotropic behavior in applied magnetic fields. This new system offers a large domain of investigation, both as a special bidimensional ferrofluid, and as an example—the first to our knowledge—of the compatibility between solid particles and structured liquids.

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Our purpose is to investigate the possibility of incorporating tiny solid particles into structured liquid phases, such as lyotropic mesophases. This problem is as yet totally unexplored, but may now be favorably considered, as, in recent years, swollen lamellar phases have been discovered and studied;[1-3] in these systems, layer thicknesses of the order of 100 Å may be easily obtained, which is in the same range as the sizes of colloid particles. In a first stage, we start with magnetic particles as they offer, *a priori*, specific advantages: Magnetic suspensions, called ferrofluids, are currently stabilized either in polar or apolar liquids;[4,5] the eventual incorporation of such solid particles in the lamellae may be revealed by important modifications of the optical magnetic properties of the system. Moreover, the ferrofluids are known to exhibit peculiar instabilities when submitted to a magnetic field;[5,6] one may expect that this confinement of the ferrofluid in layers will lead to new types of phenomena in applied magnetic fields.

In the following, we first describe the two components, ferrofluids, on the one hand, and lamellar phases, on the other, that we use as starting materials, and the way we elaborate the composite system. We then present and discuss the observations that permit us to conclude about the existence of ferrosmectic phases, and the first experiments relative to magnetic instabilities in those systems.

In principle, the problem of introducing solid particles in lamellar structures may look simple, but, in fact, it is rather complex from a physico-chemical point of view, as both ferrofluids and swollen lyotropic phases are by themselves multicomponent systems. The first necessary caution, when attempting to realize a mixed phase, is to look at the cross compatibility of the various ingredients of the two starting materials. This was our general guide for the choice of the constituents, as described below.

The ferrofluid we use is prepared with the method described in Ref. 4. It consists of maghemite Fe_2O_3-γ particles stabilized by adsorbed organophosphorated surfactant molecules in a lipidic medium. The saturation magnetization of the bulk ferrimagnetic material is 375 kA/m per unit volume. Recall that the ferrofluid dispersion is superparamagnetic due to the small sizes of the grains which are magnetic monodomains. The variation of the magnetization M with the applied magnetic field H obeys a Langevin-type law; the initial susceptibility χ_i and saturation magnetization M_s are proportional to the particle concentration. As for the continuous liquid medium, we choose cyclohexane, which is the lipidic constituent entering in the composition of the lyotropic phase described below. Notice that this ferrofluid dispersion contains free surfactant molecules, which are in equilibrium with those adsorbed on the surface of the particles. The surfactant concentration in oil is roughly proportional to the solid-particle concentration. The stability of the ferrofluid versus particle aggregation is tested by light scattering under magnetic field up to 10^4 G. The different samples are characterized by their volume fraction Φ in magnetic material; in the present experiments, Φ was varied from 0.1% to 6%. As for the size distribution of the particles, we assume a log-normal law, as it has been shown to be in good agreement with the experimental histograms:[7]

$$P(d)=\frac{1}{d\sigma(2\pi)^{1/2}}\exp\left[-\frac{1}{2\sigma^2}\ln^2\left(\frac{d}{d_0}\right)\right],$$

where d is the diameter of the particles, $\ln d_0$ is the mean value of $\ln d$, and σ is the standard deviation. The two characteristic parameters of the distribution are obtained by two independent experimental methods: analysis of the magnetization curve, described in Ref. 8, and small-angle x-ray scattering. The two determinations are in good agreement and lead to $d_0=80$ Å and $\sigma=0.4$.

The lyotropic system is a quaternary one, composed of water, cyclohexane, SDS (sodium dodecyle sulfate) as surfactant, and 1-pentanol as cosurfactant. This system

presents a lamellar phase[9] in a large domain of water and surfactant concentration at room temperature. Within this monophasic domain, the thickness of the lipidic layers may be varied from about 20 Å to more than 400 Å by changing the cyclohexane content, while keeping the water layer thickness constant. Starting from a nonswollen lamellar phase (water, SDS, 1-pentanol) we add cyclohexane containing pentanol at a concentration adjusted to maintain a constant composition of the SDS-pentanol interfaces. The lamellar structures are controlled by observing the typical oily-streak textures under a polarizing microscope; x-ray diffraction experiments confirm these results, and permit us to determine the smectic period of the phase. To prepare the composite system, we follow the same protocol, except that the cyclohexane is replaced by the ferrofluid described above. In a set of preliminary tests, we have varied Φ, the volume fraction of the particles in oil, and e, the oil-layer thickness, as they appear to be the two relevant parameters for the existence and stability of the phases. The different combinations of these two parameters that we have explored are summarized in Table I. The samples are prepared in glass tubes, carefully closed and kept at room temperature. They are compared to undoped lyotropic phases, i.e., lamellar phases of the same composition but without magnetic particles. We first ensure that the systems containing magnetic particles are stable and birefringent, as the initial undoped phases are. The phases that look birefringent and homogeneous at that macroscopic scale are then observed under a polarizing microscope, in sealed glass capillaries with rectangular cross section (100 μm × 1 mm).

The microscopic observations of the doped phases clearly demonstrate the existence of stable ferrofluid phases: Between crossed polarizers, large uniaxial domains appear, uniformly colored as the initial ferrofluid. The oriented domains are connected by the typical oily-streak defects of the lamellar phases (cf. Fig. 1). These stable ferrosmectic phases are observed for Φ and e values as indicated in Table I: $\Phi = 1.5\%$ and $e = 200$ and 250 Å, i.e., for the intermediate concentration and the larger thicknesses. As for the layer-thickness effect, it appears, as expected, that there is a matching condition between the particle size and oil-layer thickness e:

TABLE I. Physical characteristics and stability of the samples studied. Φ is the volume fraction in magnetic solid, and e is the oil-layer thickness.

Φ \ e	110 Å	160 Å	200 Å	250 Å
0.15%	Aggregates	Aggregates	Aggregates	Aggregates
1.5%	Aggregates	Aggregates	Stable	Stable
6%	Phase separation	Phase separation	Phase separation	Phase separation

The unstable-to-stable-regime transition is between $e = 160$ and 200 Å while the effective mean diameter of the particles including the surfactant steric hindrance is around 100 Å. Apart the polydispersity effects, this discrepancy indicates that a minimum "free volume" is required by each particle for the colloid to remain stable: This is perhaps related to the membrane fluctuations that have been predicted[10] and experimentally observed.[3] The thickness condition being fulfilled, each layer may accommodate one particle, thus realizing a bidimensional ferrofluid. In the present concentration conditions ($\Phi = 1.5\%$), the average distance between the particles in one layer is 300 Å, i.e., of the same order as the interlayer distance. Considering now the concentration effects, we observe that phase separation occurs for both very small or very large Φ values. However, the demixing processes are different: In the dilute regime ($\Phi = 0.15\%$), solid-particle aggregates, growing with time, separate from the lamellar phase; at high concentrations, several lamellar and/or isotropic phases coexist, differing by the magnetic-particle content. The interpretation of this effect is not straightforward, as it seems hardly understandable in terms of magnetic-particle concentration. In fact, a more reasonable explanation takes into account a critical effect of the surfactant equilibrium between bulk and interfaces. In the dilute case, the continuous oil medium is undersaturated so that the surfactant molecules slowly desorb from the solid surfaces, leading to a progressive aggregation and destabilization. On the other hand, in the case of high concentrations, the large quantities of surfactant in solution constitute a reservoir of molecules that interferes with the oil-water interface, thus modifying the phase diagram of the initial quaternary system and eventually leading to biphasic regions. It then seems possible to get more concentrated ferrosmectics, but this first implies a careful analysis of the evolution of the phase diagram.

Coming back to the stable ferrosmectic phases, we

FIG. 1. Oily-streak defects in the ferrosmectic phase. The brown color is due to the presence of Fe_2O_3 particles.

have studied their behavior under a magnetic field. This study has been carried out on oriented samples having the lamellae parallel to the limiting glass surfaces (homeotropic orientation). The magnetic field produced by an electromagnet is homogeneous with an accuracy of 1%. Two different geometries were studied, the magnetic field being either (a) parallel or (b) perpendicular to the lamellae (cf. Fig. 2), and the samples were observed via a polarizaing microscope. For the parallel-field configuration of Fig. 2(a), no modification occurs in the sample which remains uniformly dark between crossed polarizers when the field is applied. In the perpendicular geometry, a "fan-shaped" texture appears (cf. Fig. 3) for very low values of the applied field (less than 100 G). The initial homogeneous texture is rapidly recovered (a few minutes at 4000 G) when the sample is again turned in the field direction. In the absence of field, the texture is also recovered, but much more slowly (several hours). As the fan-shaped texture, in conventional smectics, indicates a preferential planar orientation of the "molecules" (i.e., lamellae normal to the limiting surface), we conclude that, in the present case, the magnetic layers tend to orient parallel to the applied field. This anisotropic behavior is a supplementary proof of the existence of the ferrosmectic phase; moreover, these magnetic effects imply a tight coupling between the particles and the lyotropic lamellae.

The fact that the instability in perpendicular geometry occurs for very low magnetic fields is at first sight surprising, if we compare to the usual smectics. Indeed, the predicted field threshold for the reorientation of the layers in conventional systems is very large (of the order of 10^5 G for a sample thickness of 100 μm) and difficult to observe experimentally. This remains true whatever the mechanism driving the instability: undulation modes as considered by Hurault and Helfrich,[11] or defect nucleation.[12] The present results are thus specific to the ferrosmectic phase which has to be considered as a smectic system exhibiting a very high magnetic anisotropy. This anisotropy may be understood in terms of a demagnetizing field, if the ferrosmectic is schematized as an alternate packing of thin magnetic films separated by nonmagnetic layers. Because of the pronounced shape anisotropy of the magnetic lamellae, the demagnetizing field due to the surface free poles appearing in an applied magnetic field is much higher for the perpendicular configuration than for the parallel one and the magnetic energy $E_{\parallel}$ is smaller than $E_{\perp}$. More precisely, we may write[5]

$$E_{\parallel,\perp} = -\tfrac{1}{2}\mu_0\chi_i H^2 \frac{1}{1+\chi_i D_{\parallel,\perp}}, \tag{1}$$

where χ_i and H have been defined previously, $\mu_0 = 4\pi \times 10^{-7}$ (SI units), and $D_{\parallel,\perp}$ is the demagnetizing factor in each geometry. In the limit of infinite slabs, $D_{\parallel}=0$ and $D_{\perp}=1$, so that the energy difference reduces to

$$\Delta E = -\tfrac{1}{2}\mu_0\chi_i^2 \frac{H^2}{1+\chi_i}. \tag{2}$$

In the present system ($\Phi = 1.5\%$), the initial susceptibility χ_i is of the order of 10^{-1} so that

$$\Delta E \simeq -\tfrac{1}{2}\mu_0\chi_i^2 H^2. \tag{3}$$

In order to get an estimation of the critical field value, we balance this magnetic energy with a typical energy of deformation for a smectic phase:[11]

$$E_{el} \simeq \pi K/\lambda d, \tag{4}$$

where K is the splay elastic constant, λ is a characteristic length of the order of one layer thickness, and d is the thickness of the sample. From expressions (3) and (4), one obtains

$$H_c \simeq \frac{1}{\chi_i}\left(\frac{2\pi K}{\mu_0\lambda d}\right)^{1/2}.$$

Using $K = 10^{-13}$ N as measured in conventional swollen lamellar phases,[3] and $\lambda = 20$ nm, one gets $H_c \simeq 5000$ A/m, i.e., of the order of 70 G. This is a very crude approximation, but it indicates that it is possible to obtain very-low-field instabilities, as experimentally observed.

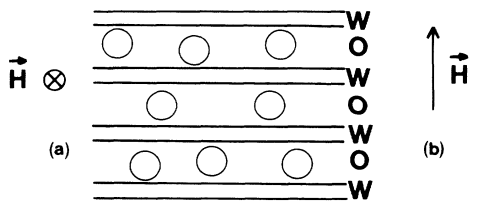

FIG. 2. The two geometries studied: (a) magnetic field parallel to the lamellae and (b) magnetic field perpendicular to the lamellae.

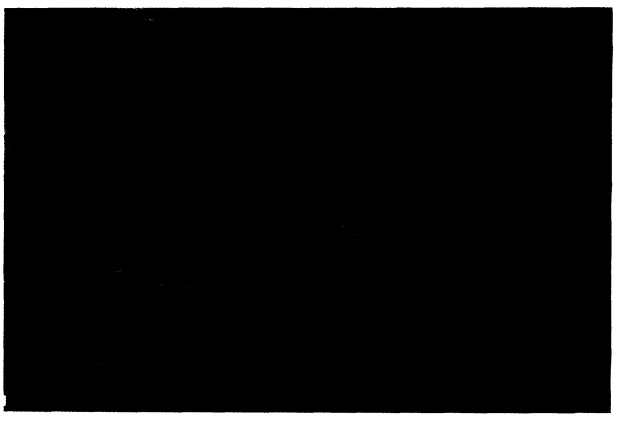

FIG. 3. Fan-shaped texture observed in an oriented ferrosmectic sample submitted to a magnetic field perpendicular to the lamellae.

Complementary experiments are currently under way in order to elucidate which mechanism—undulation or defect creation—governs the field-induced transition. Moreover, a quantitative study of the dynamics of the transition is a good approach for understanding the mechanical properties of these phases and their field dependence.

To conclude, we have proved that it is possible to dope a lamellar system with tiny solid particles, without disturbing the initial smectic structure. Moreover, the choice of ferrimagnetic grains as a dopant leads to a very specific object—that we have called a ferrosmectic —which allies mesomorphic features with a high superparamagnetic susceptibility. This is evidenced, in particular, by its anisotropic behavior in an applied magnetic field, which indicates a strong coupling between the magnetic component and the layered structure of the system. This specific feature results in a considerable lowering of the threshold-field value—compared to the usual smectics—for the reorientation of the lamellae in the field direction. More generally, we expect that these mixed systems will open the way to numerous theoretical and experimental studies. In particular, it would be interesting to investigate the influence of the incorporated solid particles on the membrane fluctuations[10] and flexibility and to study the magnetic interactions in this bidimensional configuration, using, for instance, light scattering and small-angle x-ray techniques.

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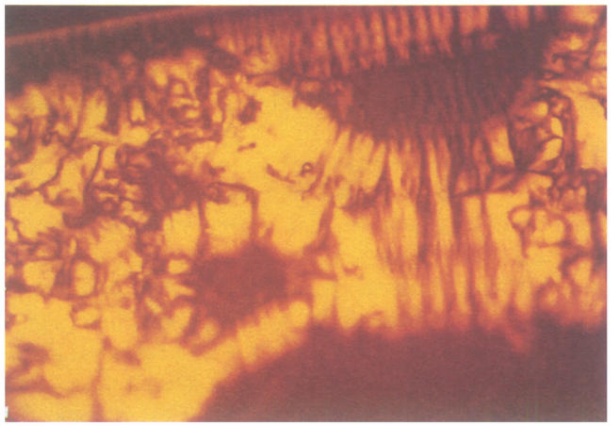

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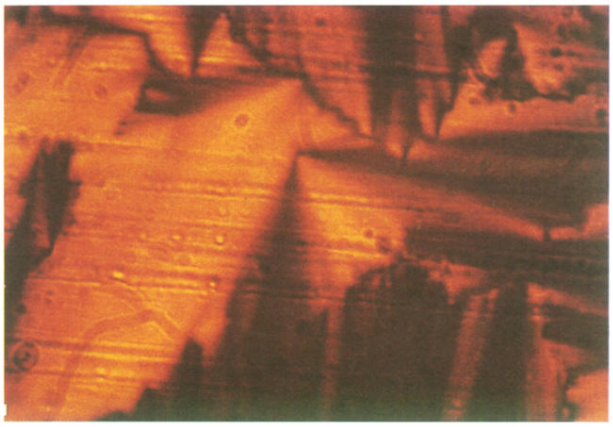

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