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ARTICLE *in* JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS · SEPTEMBER 2001

Impact Factor: 1.97 · DOI: 10.1016/S0304-8853(01)00389-4

ELSEVIER

Journal of Magnetism and Magnetic Materials 234 (2001) 499–504

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Magnetic volcanos in gadolinium Langmuir–Blodgett films

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Received 29 November 2000; received in revised form 23 May 2001

Abstract

Magnetic, structural and electronic properties of Langmuir–Blodgett films with incorporated Gd^{3+} ions has been detected using a scanning DC SQUID microscope, scanning electron microscope and X-ray diffraction. The magnetic images of 28 and 50 layer thick films at 77 K have been obtained after in-plane and out-of-plane pre-magnetization in a field of 1.4 T at 300 K. Randomly placed "magnetic volcanos" with a remanent magnetic moment of the order of $10^{-13}\,A\,m^2$ was observed. A decay of the remanent magnetization with a characteristic time of about 120 h was observed. It is suggested that the magnetic order is relatively long ranged, and that topological defects (vortices) lead to the observed out-of-plane field lines, and are responsible for the magnetic volcanos. Finally, it is hypothesized that a similar topology of field lines is responsible for superconductivity as observed in ceramic high-T_C superconductors.

PACS: 68.18; 75.70.K; 75.30.Pd

Keywords: Gadolinium; Langmuir–Blodgett films; SQUID microscope; Magnetic image; Scanning electron microscope; X-ray diffraction

1. Introduction

During the last few decades it became possible to investigate the magnetic properties of the thin films with thickness less than 100 metallic layers [1–3]. Generally, the magnetic behavior of thin films is different from bulk magnetism. The magnetic ordering temperature [3,4], the value of the saturation moment and orientation [5], and the critical field at phase transitions depend on the film thickness. Further, the magnetic properties of thin film depend on the conditions and methods of preparation (for example, on chemical, geometrical and epitaxial effect [3]). Three main regimes of magnetic behavior have been emphasized [3]. A thick-film limit (thickness more than 100 Å), where epitaxial strains dominate, an epitaxial crystal regime (thickness range 10–100 Å), and an interfacial limit (film thickness up to few monolayers). The surface of epitaxial Gd films deposited at room temperature has a multiple-terraced structure with crevices, and the first monolayer (ML) of the epitaxial Gd film is reconstructed with a superstructure consisting of a rectangular (7 × 14) atomic cell [6].

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0304-8853/01/$ -see front matter
PII: S0304-8853(01)00389-4

Langmuir–Blodgett (LB) films offer the possibility for experimental studies of magnetism in thin systems, and ultimately in two-dimension. LB films have a near perfect monoatomic structure and can be prepared with various distances between the magnetic layers. Often the influence of the substrate is negligible [7]. Magnetism of Mn stearate LB films has been reviewed [8]. For example, in the case of Mn ions the films have antiferromagnetic ordering and the Neel temperature, T_N, is about 2 K. LB films containing magnetic rare-earth ions have been found to be magnetic by electron paramagnetic resonance measurements [7]. The study suggests the existence of a transition from the paramagnetic to a magnetic state at relatively high temperature near 490 K. Recently, magnetic ordering has also been found for LB films containing ferri–ferrocyanide [9] and polyoxometalates [10]. In the present work, direct imaging of the magnetic order in the LB films has been conducted using a scanning DC SQUID microscope operating at 77 K. A structure of magnetic field lines resembling volcanos is observed.

2. Experimental details

Multilayer Gd-containing LB films were formed using ligand exchange approach [11,12] with Gd acetate solution (10^{-4} M, pH 5.2) as aqueous subphase. LB films with 28 and 50 layers of Gd ions, respectively, were formed on each side of a [1 0 0] oriented 0.3 mm thick oxidized commercial silicon-wafer. A $3 \times 8\,mm^2$ sample was cut from the wafer. Chemical reagents used in the deposition process were of GR grade purity. The stearic acid (CH_3–$(CH_2)_{16}$–COOH) and gadolinium acetate were obtained from the Serva Company and used without further purification. The water used was purified by a Milli-Q system (Millipore) The ML deposition was carried out with the utilization of conventional Teflon through computer control [11]. A floating ML on the aqueous subphase was compressed by a mobile Teflon barrier at a speed of 3 $Å^2$/(stearic acid molecule min) and was transferred to the silicon substrate at a constant surface pressure (about 30 mN/m) using the vertical dipping method. Chemical analysis of the films was subsequently performed by inductively coupled plasma emission spectroscope.

Small-angle X-ray scattering experiments were performed with a modified "Rigaku D/max-RC" diffractometer (X-ray wavelength $\lambda = 1.5405$ Å, power of X-ray source 12 kW).

Scanning electron microscopy measurements were carried out with the use of Philips XL-20 device (accelerating voltage 0.8–30 kV, magnification 10–1,000,000).

The detailed information about the general construction of the scanning HTS DC SQUID-based magnetic microscope (SSM) has been published previously [13]. The sample and a thin film calibration loop are deposited adjacent to silicon-wafers. Map of the magnetic field distribution from the sample is measured as the SQUID probe scans across the sample. The separation between the SQUID and the sample is about 100 μm and is calibrated by the signal from the calibration loop. The effective pick-up area of the SQUID is about 3000 μm^2 [13]. The DC SQUID electronics were operated in a standard flux-locked mode and detects changes in the magnetic field, B_z, perpendicular to the SQUID plane. The field sensitivity is 100 pT/$Hz^{1/2}$ at 1 Hz and 100 pT/$Hz^{1/2}$ at 200 Hz.

3. Experimental results

X-ray diffraction in the small angle range (SAXS) was employed to detect the periodic structure of LB films formed. Fig. 1 shows the typical SAXS pattern obtained from the multilayer (50 Gd layers) LB films formed using gadolinium acetate solution as a subphase. This figure demonstrates a well-defined perfect layered structure with several narrow Bragg reflections. The number of registered peaks was determined only by original X-ray beam intensity. The width of either diffraction peak ($\sim 0.1°$) yields a positional coherence length $D > 100$ nm evaluated using Scherrer's formula. The layered structure period d was determined to be 52 Å. Thus, our X-ray diffraction dates indicate that LB films studied

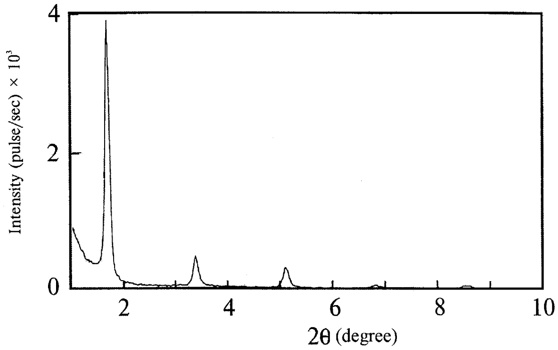

Fig. 1. X-ray diffractogram of LB film (50 bilayers) formed by the deposition of stearic acid mono layer from gadolinium acetate containing aqueous subphase (1×10^{-4} M gadolinium acetate in subphase, pH = 5.5) on the surface of polished silicon substrate with natural oxide layer. $T = 295$ K.

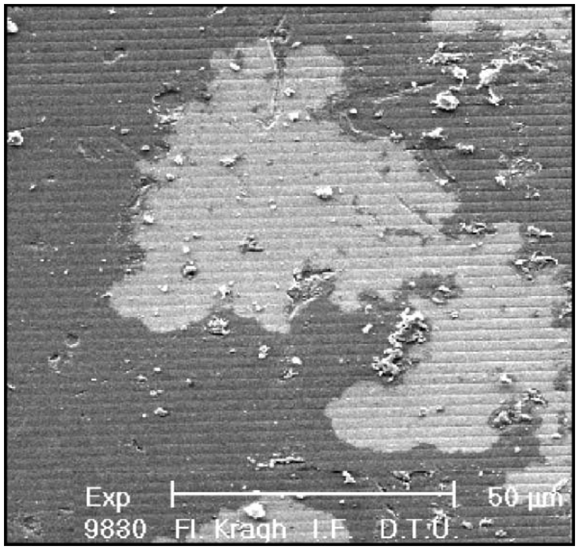

Fig. 2. Scanning electron microscopy image of multilayer Gd-containing LB films formed (50 Gd layers).

have perfect layered structure with Gd atoms arranged in two-dimensional monoatomic layers.

The low-intensity SEM measurements of natural Gd-containing multilayer LB films (50 Gd layers) have been conducted without sample surface treatment. The evidence of domain structure has been found. One can see planar domains of the characteristic size of the order of 100 µm with sharply different brightness (see Fig. 2). This picture points to the complex morphology and to the coexistence of regions with substantially different electric properties in the LB films formed. In our opinion the strong difference in electric conductivity inside of domains can be the possible reason of observed contrast on SEM images. The morphological base for conductivity differences can be the nonhomogeneus structure of Gd two-dimensional layers in LB films and the presence of areas with different Gd cations density and packing. This in turn can be a result of LB film formation procedure, where the floating stearic acid monolayer with adsorbed Gd cations is deposited on the substrate surface. The natural coexistence in the Langmuir monolayer of solid and liquid phase domains with different cation binding characteristics cause corresponding differences in arrangement of bound Gd cations in LB film.

Before film depositions all substrates have been tested by SSM at $T = 77$ K. No magnetic signals above noise level of the SSM was detected. Following magnetic experiments, including measurements of both samples (28 and 50 layers), have been made after film depositions. For these experiments substrates and samples have been cooled from the room to nitrogen temperature in the dewar remanent magnetic field which was close to 1 µT. A magnetizing field of 0.1 and 5.0 mT were applied perpendicular and parallel to the film surface, respectively, at 77 K. The SSM measurement showed that in this case none of the samples had any magnetic fields lines perpendicular to the surface. Therefore, for the first measurements only an apparently random magnetic signal was detected in the perpendicular direction to the films seen by the SQUID.

When the SSM is in operation the largest magnetic field that can be applied to the sample is about 5 mT. Thus, the following set of experiments after a field of 1.4 T produced by an electromagnet was applied to the samples located at room temperature, perpendicular and parallel to the surface of the sample for 5 min, respectively. Subsequently, the SSM images were taken at 77 K after cooling of the sample in the dewar of the SSM instrument.

For the case when the pre-magnetization was perpendicular to the sample surface before measurement the gray-scale magnetic image of local part ($\sim 3\times 4\,mm^2$) of the surface of LB film with 28 incorporated layers of Gd ions is shown in Fig. 3. Due to the relative large thickness of the substrate (close to 0.3 mm) the signal is mainly produced by Gd layers, which were located on the top surface of the substrate. There are five local maxima of the magnetic field (the darker areas inside the field isolines): Three of them are located close to the edges of the sample surface, and two in the interior. The values of the magnetic fields in two interior maxima are about -25 and -40 nT. It can be shown, as estimation, that the field of about 40 nT could be produced at the distance of about 100 μm by a dipole magnetic moment in the film plane equal to $5\times 10^{-13}\,A\,m^2$ and oriented perpendicular to the surface of the film.

Subsequent measurements showed that the value of the magnetic field in the five peaks decay with time. It decayed by an approximate factor of three over a time period of 5 days. The peaks became quite small and disappeared in random noise after one month. Thus, the characteristic relaxation time of the remanent magnetization is about 120 h.

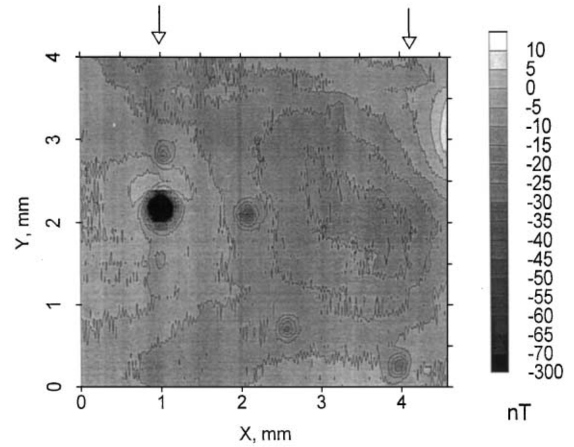

Fig. 3. Gray scale magnetic image of the surface of Langmuir–Blodgett film with 28 layers of Gd in remanent magnetic field (about 1 μT) and at temperature $T = 77\,K$. The positions (along of axis X) of the edges of the film in scan area of the SSM are shown by arrows. Before measurements magnetizing field equal to 1.4 T was applied for 5 min perpendicular to the plane of the film.

In case when a pre-magnetization field being applied before measurement in a direction parallel to the sample surface then pairs of field anomalies of different sign have appeared. The average distance between these magnetic anomalies is approximately close to 200 μm. Thus, after perpendicular and parallel magnetization of the film we found the evidence of the existence of the macroscopic regions with magnetic ordering in these films.

Fig. 4 depicts the magnetic image of the $3\times 2\,mm^2$ part of the LB film with 50 layers of the Gd ions. This image has been taken after a pre-magnetization in a perpendicular magnetic field of 1.4 T was applied in the opposite direction in comparison with one presented in Fig. 3. The main anomalies have positive values now. The amplitudes of the four maxima, placed relatively far from the substrate edges, are spread from 30 up to 80 nT. Experiments with the LB films, containing 25 incorporated layers of Gd ions, gave similar results.

4. Discussion of results

The first of our experiment has been made without pre-magnetization at room temperature. No significant magnetization of the sample was

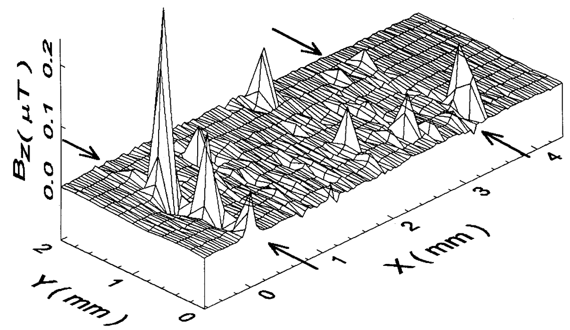

Fig. 4. Three-dimensional image of the surface of Langmuir–Blodgett film with 50 layers of Gd in remanent magnetic field (about 1 μT) and at temperature $T = 77\,K$. The positions (along axis X) of the edges of the film in scan area of the SSM are shown by arrows. Before measurements magnetizing field equal to 1.4 T was applied for 5 min perpendicular to the plane of the film.

observed indicating negligible magnetization. One possibility would be that the magnetic domains are smaller than about 50–100 μm with random in-plane orientations of the magnetization.

When the sample is pre-magnetized at room temperature a peculiar remanent magnetization exists at 77 K. In the following we discuss the origin of this magnetization and derive a possible model for the magnetization which identifies a novel type of magnetic ordering hitherto not considered.

The finite temperature properties of ultrathin ferromagnetic films, with special emphasizes to influence different interactions between spins in the film on the ground state configuration, the spin wave spectrum, and the ordering temperature have been detailedly considered in the work [14]. Essential role of anisotropy and dipolar coupling between spins, in the thermodynamic properties of two-dimensional magnetic films has been concluded. It is shown that anisotropic terms in the spin Hamiltonian suppress the large amplitude, long wavelength spin fluctuations [14]. In accordance with Mermin–Wagner theorem these fluctuations can destroy long-range order in two-dimensional Heisenberg ferromagnet with isotropic exchange coupling only. Thus, anisotropy can stabilize a long-range order of two-dimensional systems.

The existence of an out-of-plane magnetization component in the surface layer of Gd was reported [15–17]. It has been predicted [18] that a domain structure of ultra thin films with perpendicular anisotropy can have the following (based upon a stripe-domain structure) phases: smectic crystal, Ising nematic and tetragonal liquid. The Monte Carlo simulation [19] suggests the novel intermediate phase (with no long-range order but well-defined irregular domains) between striped domain state and fully disordered phase.

Our experimental data show that the LB film images demonstrate both directions of remanent in- and out-of-plane magnetization (perhaps, due to competition of different type of anisotropy).

If one assume the existence of an in-plane ferromagnetic coupling the obtained order is limited by the lower dimensionality of the system. At low but finite temperature a hexatic phase will exist where field-lines will run together at vortices. However, individual crystalline domains of the LB film may be smaller than the typical distances between vortices. In this case, one can consider the individual crystalline domains to be small ferromagnets that interact with each other. However, they are prohibited to form long-range order. Instead a hexatic structure with vortices will form. At vortices the field lines runs together, and as magnetic monopoles does not exists the lines must turn out of the plane. Vortices can therefore be identified (in SQUID measurements) by the volcano-like structure of field lines coming out of the film. We hypothesize that this is the cause for the observed field pattern. It is interesting to note that the field strength in a volcano will grow quadratic with the average distance between vortices. One may wonder if such vortices with strong field lines play a role in other systems. For the ceramic high T_C superconductors' field lines coming out of one vortex could end at a vortex in the adjacent magnetic layer. A vortices tunnel structure from layer to layer would have been formed. As the field increase quadric with in-plane distance between vortices at sufficiently low temperature the vortices field would be strong enough to trap an electron due to interaction with its spin. As two conducting layers are cutting each vortices tunnel an electron from each layer could be trapped forming the basis for electron-pair formation. If such electron pairs, where the basis for the observed superconductivity would explain the relatively short coherence length, and because of the two electron having parallel spin the observed d-wave symmetry occurs (see e.g. Ref. [20]). It would also explain why the superconducting phase is often seem to be adjacent to a phase with long-range magnetic order, where no vortex tunnels could exist. In relation to the current work it opens the question if one can construct high T_C superconducting films based on the LB film technique.

A question of interest is to what extent the behavior of other thin magnetic films will be characteristic for rare-earth LB films as well. Two possible cases may be considered: epitaxial layers, a few monolayers thick, and the surface of magnetic crystals. Epitaxial Gd/W(1 0 0) monolayer is one of the good model system for the two-dimensional Ising model (perhaps, due to large out-of-plane type of anisotropy [21]). Two monolayers of Gd exhibit a Curie point, $T_C \approx 260$ K. For films less than one monolayer thick a spin glass behavior with transition point $T_g \leqslant 50$ K was found [3]. The earlier results [16] demonstrate that the surface of the magnetic layer of Gd (0 0 0 1) film behaves differently from bulk, and that the Curie temperature of the surface layer is elevated about 60 K. It is shown, that the highest T_C values were obtained in the purest films and that it can be reduced by surface roughness [16], simultaneously the transition point of the Mn LB films increases as layer roughness decreases [22]. It is necessary to note that the discussion about enhanced Curie point for the surface layers of Gd is not yet conclusive, see for example many contributed papers in Ref. [23]. If the interaction between Gd layers in the LB films is considered minor, then the behavior of LB films containing Gd ions may be similar to surface atomic layer of epitaxial Gd. Thus, it may not be surprising that LB Gd films might be magnetic up to about 200 K above the bulk transition point. In the same time the significant role of anisotropy to stabilize the ordering can be also suggested.

Acknowledgements

The authors thank Yu.A. Koksharov for useful discussions and S.N. Polyakov for the help in the investigation of crystalline structure. The work was supported by the NATO Linkage Grant No. PST. CLG.976539 and INTAS Grant No. 97-0894.

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