Field induced two-dimensional ferromagnetic ordering in a gadolinium stearate Langmuir-Blodgett film

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Magnetic properties of materials confined to nanometer length scales are providing important information regarding low dimensional physics. Using gadolinium based Langmuir-Blodgett films, we have shown that a two-dimensional short range ferromagnetic order with no spontaneous magnetization occur as the field is applied along the normal to the growth (in-plane) direction. However, along the growth (out-of-plane) direction, we observe expected paramagnetic behavior down to a temperature of 2 K and a field of up to 70 kOe. We found that in-plane saturation moment increases and the field required to get this saturation decreases with decreasing temperature. These results are consistent with the theoretical predictions on isolated two-dimensional spin system having critical point at $T=0$. We have provided preliminary explanations of the observed field induced two-dimensional ferromagnetic ordering by considering asymmetric exchange coupling.

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I. INTRODUCTION

The role of dimensionality in magnetic ordering has remained an active field of research since the first argument of Bloch[1] in 1930 followed by theoretical work of Mermin and Wagner[2] in 1966. Recently, Bruno[3] has extended these results for more general spin-spin interactions. Advances in growth and characterization techniques of nanomaterials—materials confined to nanometer length scales in one, two, or all three dimensions—have enabled investigation of the effect of dimensionality on the magnetic ordering in general and ferromagnetism in particular.[4–12] Pomerantz *et al.*[11] demonstrated for the first time that one can form literally isolated two-dimensional (2D) magnets using Langmuir-Blodgett (LB) films. Using LB film growth technique, one can form 2D hexagonal lattice of metallic ions and multilayer stack of these 2D lattices can be kept separated by organic chains[13,14] [Fig. 1(a)]. Although several magnetic ions like manganese,[15] iron,[16] and cobalt[17] have been used to form LB films, clear signature of 2D ferromagnetic ordering has not been observed in these systems.

Recently, signature of magnetic ordering was observed in gadolinium based LB films at unusually high temperature.[18] But due to doubtful stoichiometry and absence of systematic low temperature magnetic measurements, the nature of ordering could not be established. The magnetic properties of solids based on gadolinium, a lanthanide metal, are primarily determined by the localized $4f$ moments. One can observe long-range magnetic ordering here provided the exchange coupling is mediated by the hybridized $6s$ and $5d$ conduction electrons.[19,20] On the other hand, one expects to observe paramagnetism[21] in gadolinium compounds due to absence of conduction electrons. In a recent systematic angle-resolved photoemission measurements of oxygen-induced magnetic surface states of lanthanide metals, it was shown[22] that gadolinium forms GdO instead of nonmetallic sesquioxide Gd_2O_3. The remaining one valence electron of $(5d6s^2)$ hybridized state was found to be responsible for mediating exchange coupling to form magnetic ordering. In the present study we have demonstrated that large stack of (basically) noninteracting 2D molecular magnetic planes with Gd-ions can be formed by a simple deposition technique.

II. EXPERIMENTAL DETAILS

Gadolinium Stearate LB films, having 9–101 monolayers (ML), were deposited on 1 mm thick Si(001) substrates using an alternating trough (KSV5000) from a monolayer of stearic acid on Milli-*Q* (Millipore) water subphase containing 5×10^{-4} M Gd^{3+} ions, obtained from dissolved gadolinium acetate. The surface pressure was maintained at 30 mNm^{-1} during deposition, and the dipping speed was 5 mm min^{-1}. The silicon substrates were cleaned and hydrophilized according to RCA cleaning procedure, first heating with 30% NH_3:30% $H_2O_2=1:1$ by volume for ten minutes followed by a rinsing with acetone and alcohol and finally washed with purified water. Grazing incidence x-ray reflectivity and diffuse scattering measurements were performed using a rotating anode x-ray setup (ENRAF, Nonius) to characterize the structure of deposited LB films.[13] In Fig. 1(a) we have shown the model of out-of-plane and in-plane structure of GdSt LB films on hydrophilic substrate.

The dc magnetization measurements were carried out using a 12-T commercial (Oxford Instruments) vibrating sample magnetometer as a function of magnetic field and temperature down to 2 K. Magnetization isotherm measurements (M vs H at a fixed temperature) over all four quadrants including the virgin curve were carried out as a function of magnetic field up to ±70 kOe, applied parallel (in-plane) as well as perpendicular (out-of-plane) to the film

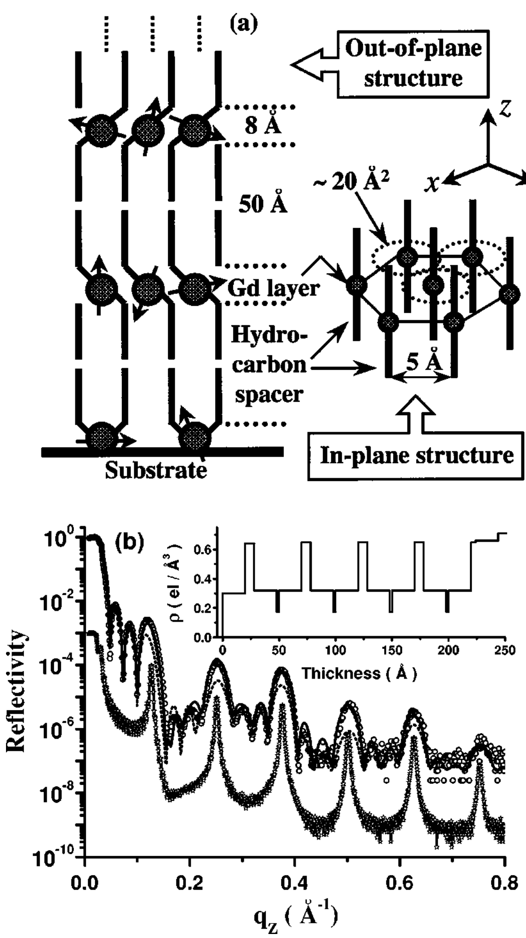

FIG. 1. (a) Model of out-of-plane and in-plane structure of GdSt molecule based Langmuir-Blodgett film. The number density of Gd ($=1\times10^{-3}$ Å^{-3}) in this model is consistent with the results of structural and magnetization measurements presented here. (b) Open circles are the experimental x-ray reflectivity data points for 9 ML GdSt LB film and solid line is the curve calculated with an electron-density profile (shown in the inset) of the model shown in (a). The dashed line is the calculated reflectivity curve corresponding to a model where three stearic acid tails are attached to a gadolinium ion. Reflectivity data of a 51 ML sample (line+star) are also shown for comparison. This data have been shifted down for clarity (refer text). Here $q_z=4\pi\sin\theta/\lambda$, where θ is the angle of incidence at specular condition and λ is the wavelength of x-ray radiation.

plane at several temperatures down to 2 K. All isotherm magnetization measurements were carried out by cooling the sample from 300 K to the desired temperature of measurement under zero magnetic field. Field-cooled M vs T magnetization measurements were also carried out over 2–100 K under 500 Oe in the cooling cycle.

III. RESULTS AND DISCUSSION

In Fig. 1(b) we have shown the measured and calculated specular x-ray reflectivity data of 9 ML GdSt LB film. In this data the presence of both Bragg peaks and Kiessig fringes corresponding to out-of-plane metal-metal distance and total film thickness, respectively,[23] are evident. For films with large number of layers, Bragg peaks become strong and Kiessig fringes could not be resolved properly [refer 51 ML data in Fig. 1(b)]. The measured 9 ML data matche quite well with the theoretical reflectivity calculated from the electron-density profile [refer inset of Fig. 1(b)] of the model shown in Fig. 1(a). The organic portion of film has electron density of 0.32 el Å^{-3} and dips going to the value of 0.17 el Å^{-3}, as observed earlier.[23] We have also shown the calculated reflectivity data in Fig. 1(b) assuming that three tails are attached to single gadolinium ion. The essential difference between two density profiles being the change of electron density in the metal plane from 0.64 el Å^{-3} to 0.48 el Å^{-3}. From these curves, we conclude that out of three valence electrons in gadolinium only two electrons participate in bonding. Diffuse scattering data of these films show clearly that the 2D metal planes are conformal in nature and have logarithmic in-plane correlation, as observed earlier.[24] The interfacial roughness comes out to be around 2 Å.

Figure 2(a) depicts the observed magnetization data for the 101 ML LB film as a function of applied field. Some kind of magnetic ordering is evident in the raw data itself despite the presence of a diamagnetic signal from the Si(001) substrate. By studying the other samples, we found that the magnetization value scales with the number of monolayers deposited where the nature of magnetic ordering is found to be independent of the number of monolayers. Silicon background was subtracted from all the data consistently before performing data analysis. The M vs T curves measured under 500 Oe field in two in-plane (xy) directions, obtained by rotating the film by 90°, and in the out-of-plane (z) direction exhibited paramagnetic behavior [Fig. 2(b)]. However, at lower temperatures the nature of the out-of-plane data were found to be different from that of in-plane data indicating different spin response in the in-plane directions, as we shall discuss later.

Figure 2(c) shows out-of-plane magnetization data measured at 5 K, 10 K, and 20 K temperatures. All the magnetization data plotted against (H/T) collapse to a single curve as expected for paramagnetism or superparamagnetism.[25] The data were fitted with the expression $M=M_s \mathrm{B}_s(g\mu_B SH/k_B T)$, where $M_s(=\mathrm{N}g\mu_B S/\mathrm{V})$ is the saturation magnetization and B_s is the Brillouin function defined as[8]

$$B_s(x)=\frac{2S+1}{2S}\coth\left(\frac{(2S+1)x}{2S}\right)-\frac{1}{2S}\coth\left(\frac{x}{2S}\right). \quad (1)$$

We obtained the value of spin S as 2.75 instead of expected 3.5 of the $4f$ moment for gadolinium. The value of M_s was found to be 1.29×10^{-5} emu/mm^2. This value corresponds well with the number of gadolinium per unit area ($\sim2.53\times10^{14}$ mm^{-2}) as obtained from fitting of the specular reflectivity data [refer Fig. 1(b)].

We have shown in Fig.2(c) magnetization data taken at various temperatures by applying field in a fixed in-plane direction. It is interesting to note that the slope of the curves as well as the respective saturation magnetization M_s values decreases as the temperature is increased. As a result, the in-plane magnetization curves do not collapse to a single

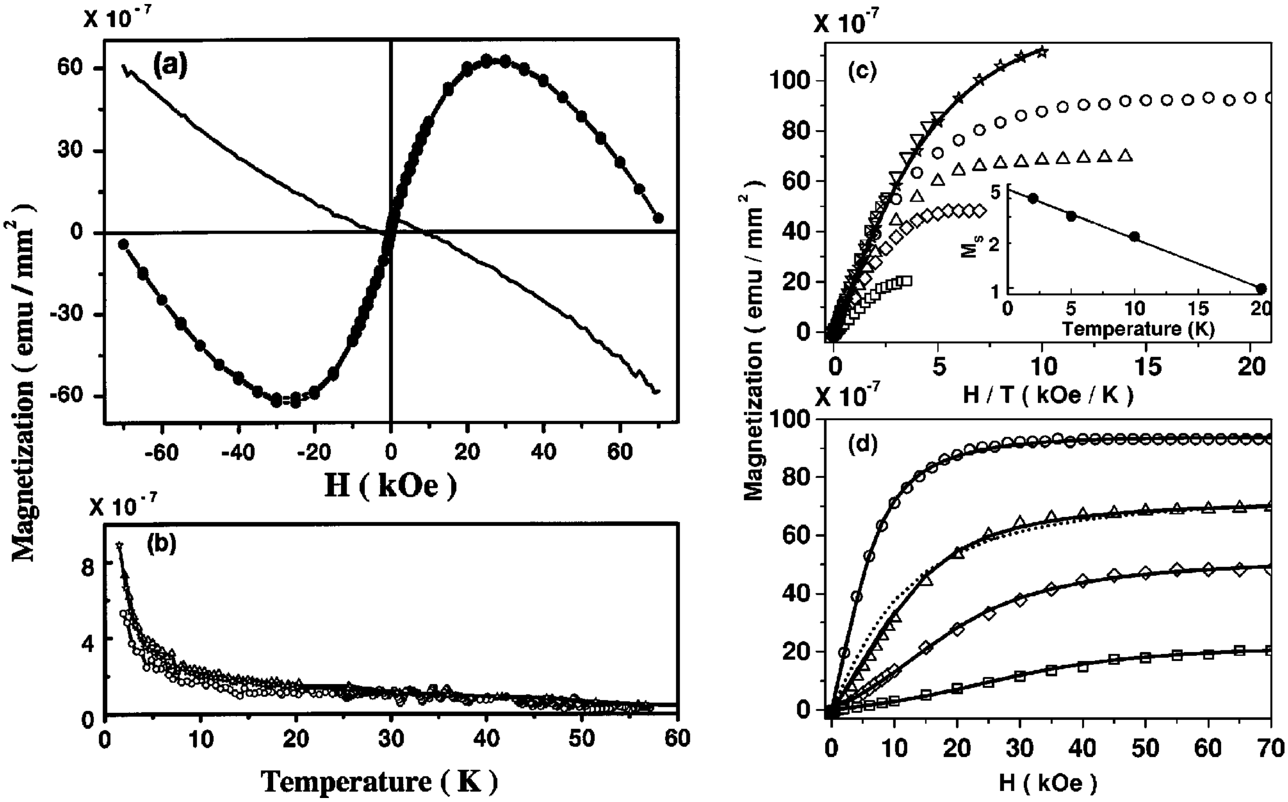

FIG. 2. (a) Raw data of in-plane magnetization as a function of applied magnetic field taken at 5 K for 101 ML GdSt LB film (line+solid circle) and for bare Si substrate used here (solid line). (b) The in-plane magnetization data in two orthogonal directions (line+star) and (line+triangle), respectively and out-of-plane magnetization data (line+circle) measured as a function of temperature T with an applied field H of 0.5 kOe. (c) Magnetization curves as a function of H/T for the out-of-plane direction measured at 5 K (open star), 10 K (open down-triangle), and 20 K (crossed square) with fit (solid line) using Eq. (1), and for the in-plane direction measured at 2 K (open circle), 5 K (open up-triangle), 10 K (open diamond) and 20 K (open square).The inset shows log-linear plot of the in-plane saturation magnetization M_s expressed in Bohr magneton per gadolinium ion at various temperatures and solid line is the linear fit. (d) In-plane magnetization data as shown in (b) are plotted against field with the corresponding fit (line) using Eq.(4). The dotted line is the best-fitted Brillouin function with field independent exchange (refer text).

curve like the out-of-plane data ruling out the existence of normal paramagnetism or superparamagnetism in these 2D planes.

However, like in out-of-plane data, no hysteresis (i.e, zero remanent magnetization and zero coercive field) was observed here. It should be noted here that field values H_s at which saturation of magnetization sets in was found to decrease with decreasing temperature and we obtained values of 10.2, 21.9, 34.6, and 57.2 kOe for sample temperatures of 2, 5, 10, and 20 K, respectively. This type of field induced ferromagnetism has been observed earlier.[26] Field induced ferromagnetism is also a characteristic feature of magnetic systems that exhibit metamagnetism.[27] In these systems field induced ferromagnetic ordering settles from initial antiferromagnetic phase as the applied field is increased. However, results of field-cooled and zero-field-cooled measurements performed on these LB films do not support the existence of metamagnetism in this system.

The field induced saturation magnetization was found to exhibit exponential dependence with temperature ($\log_{10} M_s = 0.66 - 0.034$ T) [refer inset of Fig. 2(c)]. Here M_s is expressed in the unit of μ_B/Gd and the projected value of M_s at 0 K comes out to be 4.57 μ_B/Gd. This value is less than the value of 5.5 obtained from the fitting of out-of-plane data. It is expected[28,29] that for 2D spin systems having continuous symmetry, the magnetization diverges exponentially as the temperature is reduced, and only at $T=0$ one expects long-range ferromagnetic alignment of the spins due to exchange coupling. At a finite temperature the spins become correlated only on a finite length scale ξ. This correlation length ξ increases exponentially[12,28,29] as the temperature goes to absolute zero and effective moment can be written as $\xi^2 g \mu_B S$. Although our data are consistent with this picture, more measurements at sub-Kelvin temperature are required before extracting meaningful physical parameters from fit as shown in inset of Fig. 2(c). Moreover, below 0.5 K the dipolar interaction of the gadolinium spin will become important[30] and we expect to observe interesting interplay between dipolar and exchange interactions. Although detailed modeling of the nature of ferromagnetic ordering and associated phase transition,[31] if any, will require the results of these future magnetization measurements and neutron diffuse scattering studies,[32] we can propose here a preliminary explanation of our observations based on a mean-field-like model. Absence of spin-spin interaction when the field is applied in the out-of-plane (z) direction is accommodated in this model by considering *anisotropic exchange*

$$J\ \mathbf{S}_i\cdot\mathbf{S}_j = J_x S_i^{(x)} S_j^{(x)} + J_y S_i^{(y)} S_j^{(y)} + J_z S_i^{(z)} S_j^{(z)} \qquad (2)$$

with $J_z=0$. As LB films are essentially powder in the 2D plane having about 100 Å domain size, we further assume that in the xy plane the exchange is isotropic $J_{||}=J_x=J_y$.

Brillouin function as used in ferromagnetism[8] can be utilized to write magnetization in the in-plane direction noting that $J_z=0$ and by neglecting spin fluctuations $(S_i-\langle S_i\rangle)\times(S_j-\langle S_j\rangle)$,

$$M = M_s \mathrm{B}_s\left(\frac{S}{k_B T}\left[g\mu_B H + J_{||}\langle S_j\rangle^{||}\sum_j \cos\theta_{ij}\right]\right), \qquad (3)$$

where θ_{ij} is the in-plane angle between spins S_i and S_j. The thermal averaged value of the in-plane component $\langle S_j\rangle^{||}$ will increase to the maximum value of S with the field H applied in an in-plane direction and we approximated this component as $CH\langle S_j\rangle$. With increasing applied field the *sum of cosines* in Eq. (3) also gets maximized. All these relationships can be used to write a simplified transcendental equation for in-plane magnetization as

$$M = M_s B_s\left(\frac{SH}{k_B T}\mu_B(g + J_{||}CM)\right). \qquad (4)$$

The constant C used in this linear approximation will depend on the angle, if any, between H and the xy plane of the LB film. If H is applied normal to the xy plane, C will become zero and from Eq. (4) we get back paramagnetism as shown in Eq. (1). The value of C is also expected to depend on temperature. It should be noted here that without invoking this field dependent exchange term the data couldn't be analyzed. We have tried fitting the data with a Brillouin function with constant exchange and the best fit was obtained [refer dashed curve in Fig. 2(d)] with 1.27×10^6 kOe mm^{2}emu^{-1} for the 5 K data.

In Fig. 2(d) we have plotted measured M along with the fitted curves obtained by using Eq. (4) for 2, 5, 10, and 20 K data. In this analysis we have used $S=3.5$ and only fitting parameter was $(J_{||}C)$, which increases with increasing temperature. The values come out to be 2.45×10^4, 8.82 $\times10^4$, 2.15×10^5, and 8.28×10^5 mm^{2}emu^{-1} at 2, 5, 10, and 20 K temperatures, respectively. It is expected that the exchange will not increase from 2 K to 20 K temperature, and hence with increasing temperature C increases making field induced in-plane spin alignment easier at elevated temperatures.

IV. SUMMARY AND CONCLUSION

In conclusion, we have demonstrated that multilayer GdSt LB films can provide an easy-to-form 2D ferromagnetic system where effect of substrate interaction can be neglected. Although out-of-plane magnetization resembles paramagnetic behavior down to a temperature of 2 K and a field of up to 70 kOe, field-induced ferromagnetic ordering was observed here in the in-plane direction. We found that the field H_s required to get the saturation magnetization decreases with decreasing temperature. Instead of exhibiting a finite-temperature critical point, the saturation magnetization in the in-plane direction was found to diverge exponentially indicating continuous increase in the correlation length ξ of the observed short-range ferromagnetic order as the temperature is reduced. This behavior is consistent with a critical point at $T=0$, expected for isolated 2D spin systems with continuous symmetry. The absence of remanence in the in-plane ferromagnetic ordering provides experimental validity of Mermin-Wagner theorem.[2,3] It is interesting to note here that long-range ferromagnetic ordering observed in magnetic monolayers[4–6,12] could not be achieved in the measured temperature range. We plan to investigate the effect of dipole interaction and the nature of spin fluctuations using sub-Kelvin magnetization and diffuse neutron scattering measurements, respectively. It is important to decipher the role of low-dimensionality, competing interactions, and positional disorder of Gd ions in hindering long-range ferromagnetism here.

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