Two-dimensional Induced Ferromagnetism

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(Dated: March 22, 2022)

Magnetic properties of materials confined to nanometer length scales are providing important information regarding low dimensional physics. Using gadolinium based Langmuir-Blodgett films, we demonstrate that two-dimensional ferromagnetic order can be induced by applying magnetic field along the in-plane (perpendicular to growth) direction. Field dependent exchange coupling is evident in the in-plane magnetization data that exhibit absence of hysteresis loop and show reduction in field required to obtain saturation in measured moment with decreasing temperature.

PACS numbers: 75.70.Ak, 75.60.Ej, 75.50.Xx

The role of dimensionality in magnetic ordering has remained an active field of research since the first argument of Bloch in 1930 followed by theoretical work of Mermin and Wagner in 1966 [1,2]. Recent advances in growth and characterization techniques of nanomaterials - materials confined to nanometer length scales in one, two or all three dimensions - has enabled investigation of magnetic ordering in general and ferromagnetism in particular in three dimensions - has enabled investigation of magnetic ordering. The exchange coupling is mediated by the hybridized 6s and 5d conduction electrons [13,14]. On the other hand, one expects to observe paramagnetism in gadolinium compounds due to absence of conduction electrons. However, in a recent systematic angle resolved photoemission measurements of oxygen-induced magnetic surface states of lanthanide metals, it was shown that gadolinium forms GdO instead of nonmetallic sesquioxide Gd$_2$O$_3$ [21]. The remaining one valence electron of (5d6s$^2$) hybridized state was found to be responsible for mediating exchange coupling to form magnetic ordering. The temperature dependence of the energy splitting of the oxygen-induced states has confirmed this possibility.

Here we present evidence of 2D ferromagnetism that can be induced by external magnetic field applied along the metallic planes in gadolinium stearate (GdSt) LB film. The gadolinium ions show normal paramagnetism due to absence of conduction electrons. However, in a recent systematic angle resolved photoemission measurements of oxygen-induced magnetic surface states of lanthanide metals, it was shown that gadolinium forms GdO instead of nonmetallic sesquioxide Gd$_2$O$_3$ [21]. The remaining one valence electron of (5d6s$^2$) hybridized state was found to be responsible for mediating exchange coupling to form magnetic ordering. The temperature dependence of the energy splitting of the oxygen-induced states has confirmed this possibility.

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. Grazing incidence x-ray reflectivity and diffuse scattering measurements were performed using a rotating anode x-ray set up, to characterize the structure of deposited LB films [12].

We have presented magnetization data of 101 ML LB film as a function of T and H measured using a vibrating sample magnetometer (Oxford Instruments). The nature of magnetic ordering was found to be independent
of number of monolayers deposited but in 101 ML sample the ordering was evident in the raw data itself despite the presence of diamagnetic signal of Si(001) substrate (refer Fig. 1(a)). 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 plane at several temperatures down to 2 K. All these measurements were carried out by cooling the sample from 300 K to the desired temperature of measurement under zero magnetic field. No hysteresis was found in these M vs. H curves. Field-cooled (FC) M vs. T measurements were carried out over 2 to 100 K under 500 Oe in the cooling cycle. We also found that the magnetization values scale with number of monolayers deposited.

Silicon background was subtracted from all the data consistently before performing data analysis. Fig. 1(b) depicts M vs. T curves measured with 500 Oe field in two in-plane directions, obtained by rotating the film by 90°, and in an out-of-plane direction. Paramagnetic behavior in all three directions is evident. However, at lower temperatures the nature of the out-of-plane data was found to be different from that of in-plane data (Fig. 1(b)) indicating different spin response in the in-plane directions as we shall discuss later. In Fig. 1(c) we have shown the 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, are evident. For films with large number of layers, Bragg peaks become strong and Kiessig fringes could not be resolved (refer 51 ML data in Fig. 1(c)). The measured 9 ML data matches quite well with the calculated reflectivity obtained from a simple model electron density profile shown in the inset. 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 [22]. The electron density of the head region takes a value of 0.64 el Å⁻³ to produce the strong Bragg peaks observed in reflectivity data. This value of electron density in the metal-plane corresponds to a molecular structure where two stearic acid tails (having 20 Å² area) are attached to a single gadolinium ion [12]. We have also shown the calculated reflectivity data and corresponding electron density profile in Fig. 1(c) 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 [22]. The interfacial roughness comes out to be around 2 Å.

Figure 2(a) shows out-of-plane magnetization data measured at 5K, 10K and 20K temperatures. All the magnetization data plotted against (H / T) collapses to a single curve as expected for paramagnetism or superparamagnetism [24]. The data were fitted with the expression 

\[ M = M_s B_s (g \mu_B SH / k_B T) \]

where \( M_s = \pm \frac{Ng \mu_H S}{V} \) is the saturation magnetization and \( B_s \) is the Brillouin function defined as [7]

\[ B_s (x) = \frac{2S + 1}{2S} \coth \left( \frac{(2S + 1)x}{2S} \right) - \frac{1}{2S} \coth \left( \frac{x}{2S} \right) \] (1)

We obtained the value of spin S as 2.75 instead of expected 3.5 of the 4f moment for gadolinium. \( M_s \) was found to be 1.29 × 10⁻⁵ emu/mm². This value corresponds well with the number density of gadolinium 2.53 × 10⁻⁶ mm⁻². Here, each gadolinium ion was assumed to be at the center of a cylinder of 20 Å² cross section and length 50 Å, as obtained from fitting of the specular reflectivity data shown in Fig. 1(c).

In Fig. 2(b) in-plane magnetization data taken at temperatures of 2K, 5K, 10K and 20K are shown. 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 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. This type of field-induced ferromagnetism has been observed earlier [25]. 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 20K, respectively. The saturation magnetization was found to exhibit exponential dependence with temperature (\( \log M_s = 0.66 - 0.034T \)) (refer inset of Fig. 2(b)). Here \( M_s \) is expressed in a unit of \( \mu_B / \text{Gd} \) and the projected value of \( M_s \) at 0K comes out to be 4.57 \( \mu_B / \text{Gd} \). This value is less than the value of 5.5 obtained from the fitting of out-of-plane data. It is interesting to note that the magnetization curves taken in the out-of-plane direction do not show this saturation behavior, which implies strong anisotropy in GdSt LB film. In fact, effect of strong anisotropy in ferromagnetism and possible existence of even direction dependent Curie temperature has been discussed earlier [26]. We have used an anisotropic exchange to explain the induced ferromagnetism in the in-plane direction – such an exchange was noted to be sufficient to stabilize ferromagnetism in 2D systems [2].

In this formalism it is expected that increase in applied magnetic field in a particular in-plane (xy) direction will increase the effective exchange field provided \( J_x, J_y \gg J_z \).
The existence of saturation in magnetization only in the in-plane direction corroborates this assumption.

We could analyze all the in-plane data by using Brillouin function as used in ferromagnetism:

\[ M = M_s B_s \left( \frac{S}{k_B T} [g \mu_B H + J_{||} \langle S \rangle \sum_j \cos \theta_{ij}] \right) \]  \hspace{1cm} (2)

where \( J_{||} = J_x = J_y \) are in-plane exchange (assumed to be symmetric on the basis of data shown in Fig.1(b)) and \( \theta_{ij} \) is the in-plane angle between spins \( S_i \) and \( S_j \).

With applied field the sum of cosines, in Eq. (2), gets maximized. This relationship can be used to write a simplified expression for in-plane magnetization

\[ M = M_s B_s \left( \frac{S H \mu_B}{k_B T} (g + \xi M) \right) \] \hspace{1cm} (3)

In Fig. 3 we have plotted measured \( M \) along with the fitted curves obtained by using Eq.(3) for 2, 5, 10 and 20K data. In this analysis we have used \( S = 3.5 \) and only fitting parameter was \( \xi \), which increases with increasing temperature. The values come out to be 2.45 \times 10^4, 8.82 \times 10^4, 2.15 \times 10^5 and 8.28 \times 10^5 mm^2emu^{-1} at 2, 5, 10 and 20K temperatures respectively. It should be noted here that without invoking this field dependent exchange interaction (\( \xi(H) \) the data couldn’t be analyzed. We have tried fitting the data with a Brillouin function with constant exchange in place of \( \xi \). The best fit was obtained (refer dashed curve in Fig. 3) with \( \xi(H) = 1.27 \times 10^6 \) kOe mm^2emu^{-1} for the 5K data. Only field dependent (liner) exchange could explain the observed magnetization data (refer Fig. 3).

It will be interesting to investigate the roles of various models of ferromagnetism for gadolinium and 2D dipole interactions to explain the observed reduction of \( H_s \) and increase of \( M_s \) as temperature decreases. Lower saturation value of magnetization (\( M_s \)) in the in-plane direction can be simply due to non-participation of few gadolinium planes, located near substrate/film and film/air interfaces, in 2D ferromagnetic ordering. However, strong asymmetry arising from lower spin value (2.75) in the out-of-plane direction and lower \( M_s \) value with expected spin of 3.5 in the in-plane direction need systematic microscopic measurements to elucidate the effect of anisotropic g-factor for spins.

In conclusion, we have demonstrated that GdSt LB films can provide an easy-to-form 2D ferromagnetic system. We have shown that out-of-plane magnetization resembles paramagnetic behavior down to a temperature of 2K and a field of up to 70 kOe. However, field induced ferromagnetic ordering was observed in the in-plane direction and the field \( H_s \) required to get the saturation magnetization decreases with decreasing temperature. The attachment of two stearic acid tails with single gadolinium ion and the presence of field induced ferromagnetic state in GdSt, found here, are consistent with the reported results of recent photoemission studies. The absence of remanence in the in-plane ferromagnetic ordering, observed perhaps for the first time here, provides experimental validity of Mermin-Wagner theorem which has been extended recently for the metallic two-dimensional systems.

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Figure captions:

FIG. 1: (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 with an applied field of 0.5 kOe. (c) 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) assuming two stearic acid tails attached to a gadolinium ion. The dashed line is the calculated reflectivity curve with the expected electron density profile corresponding to a model where three stearic acid tails attached to a gadolinium ion. Reflectivity data of a 51 ML sample (line+circle) is also shown for comparison. This data has been shifted down for clarity (refer text).

FIG. 2: Magnetization curves as a function of (H/T) for the (a) out-of-plane direction measured at 5K (open circle), 10K (solid circle) and 20K (star) with fit using Eq. (1) (solid line), and for the (b) in-plane direction measured at 2K (solid triangle), 5K (open circle), 10K (solid circle) and 20K (star). In-plane data shows the absence of scaling observed in (a). The inset shows log-linear plot of the in-plane saturation magnetization (M_s) expressed in Bohr magnetron per gadolinium ion at various temperatures and solid line is the linear fit (refer text).

FIG. 3: In-plane magnetization as a function of applied field for 101ML GdSt LB film measured at temperatures 2K (solid triangle), 5K (open circle), 10K (solid circle) and 20K (star). Solid line is the corresponding fit with the modified Brillouin function as given in Eq. (3). The dashed line is the best-fitted Brillouin function with field independent exchange (refer text).
Magnetization (emu/mm²) vs. Field (kOe)

- Linear scale
- magnetization values range from 0 to 100
- field values range from 0 to 70 kOe

Graph shows different curves for varying magnetization levels with markers for specific conditions.