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Published in:
Physical Review B

Link to article, DOI:
10.1103/PhysRevB.55.11064

Publication date:
1997

Document Version
Publisher's PDF, also known as Version of record

Evidence for magnetic ordering in ultrathin gadolinium Langmuir-Blodgett films

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(Received 24 October 1996)

Magnetic ultrathin Langmuir-Blodgett films containing rare earths are investigated. Electron paramagnetic resonance measurements suggest the possible existence of a transition from a paramagnetic to a magnetically ordered state. In Langmuir-Blodgett films with one hundred layers of Gd, a transition takes place at $T_0 \approx 490$ K. [S0163-1829(97)11517-X]

Recently, properties of the ultrathin films were systematically reviewed by Gasgnier,[1] Heinrich and Cochran,[2] and Flynn and Salamon,[3] and there have been attempts to study surface magnetism with photon beams from synchrotron sources.[4,5] From a theoretical viewpoint, the existence of magnetic ordering in a two-dimensional (2D) system depends on the nature of the magnetic interactions. In the isotropic Heisenberg approximation long-range magnetic order at $T>0$ is not allowed,[6] while for the 2D Ising model a magnetic structure can exist at nonzero temperatures.[7] Further, the competition between long-range dipolar interaction and low-dimensionality effects can give rise to magnetism in ultrathin films which is different from that in bulk.[8,9] The strong fluctuations in the 2D Heisenberg systems lead to a change of magnetization from an out-of-plane to an in-plane orientation under increasing temperature.[8] The value of T_c for epitaxially grown Gd monolayers depends on the nearest-neighbor coordination and is around 20 K below the bulk value. The significance of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction for monolayer magnetism is demonstrated by the value of $g=1.97$.[10] While two monolayers of Gd exhibit a $T_c \approx 260$ K and a saturation of magnetization at the field $H=50$ Oe, films of less than one monolayer demonstrate a spin-glass behavior with $T_g<50$ K.[3]

In a 2D Ising system with random and nonrandom interactions a spin glass with a finite freezing temperature T_g can arise.[11] The RKKY interaction in a Heisenberg spin glass can also lead to a nonzero transition temperature.[12] At room temperature, such systems can display an antiferromagnetic, a superparamagnetic, and an in-plane ferromagnetic phase.[13] Superparamagnetism has also been observed in Co/Cu(100) films,[14] and the magnetic structure above the Curie temperature was ascribed to 2D Heisenberg spin blocks.[15]

One interest in Langmuir-Blodgett (LB) films with magnetic ions is their possible use for testing different theoretical models of order in 2D magnets. LB films have some advantages in comparison with epitaxial films. These are, for example, their planar structure, the possibility to change the distance between magnetic layers, and their negligible substrate effects. Attempts have been made to study 2D magnetism.[16–23] The results have manifested the existence of an antiferromagnetic structure within layers of Mn LB film with Néel point $T_N \leqslant 10$ K.[17–20] Powders of Ferric stearate are superparamagnetic in the temperature range from 60 to 295 K.[21] The shift of the electron paramagnetic resonance field and the splitting of the Mössbauer spectrum indicates a time-dependent structure at $T<60$ K. In this paper we describe experiments which suggest the possible existence of magnetic ordering in Gd LB films.

The electron paramagnetic resonance (EPR) technique was employed to study the magnetism in LB films with from one Gd layer up to one hundred. Surface pressure-monolayer area (PA) isotherm measurements were carried out on an automatic Teflon trough at 18–20 °C. To form the Langmuir monolayer, stearic acid was dissolved in Chloroform (2×10^{-4} M) and spread on to Milli-Q purified water or on to an aqueous subphase containing 5×10^{-4} M Gd^{3+}, at pH from 4.6 up to 4.8. After complete solvent evaporation the floating monolayer on the subphase was compressed by a mobile teflon barrier at a speed of about 5 Å^2/(molecule×min). Polished silicon and quartz were used as substrate materials for LB film formation. Monolayers were deposited by a vertical lift method at 30 mN/m surface pressure.

Preliminary small-angle x-ray-scattering data showed the absence of 3D inclusions in the multilayer structure, and revealed the distance between layers of Gd ions to be about 50 Å. A stearic acid monolayer containing gadolinium ions was transferred to a graphite substrate by Schaefer's horizontal lifting method and studied with scanning tunneling microscopy. A relatively smooth surface with about a 5 Å distance between the tops was observed, presumably the image of the gadolinium atoms.

We formed samples of A and B types; type A was constructed by transfer of the gadolinium monolayer directly to the surface of a silicon wafer. Samples of type B were formed in two stages: first, the silicon substrates were covered by stearic acid buffer layers without metal cations, then the substrates were used for deposition of the Gd LB film. Actually, the structure incorporates two stearate sheets be-

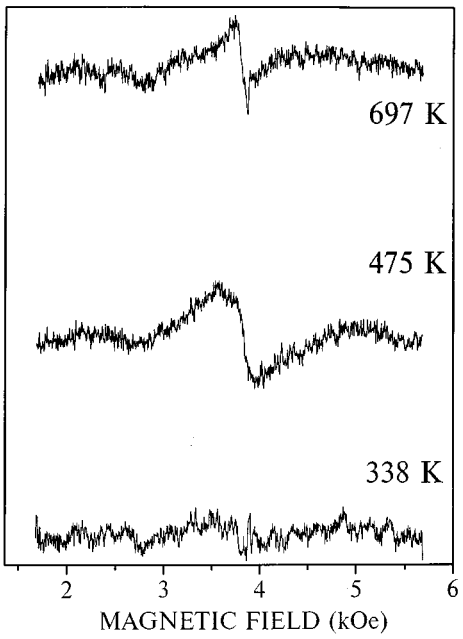

FIG. 1. EPR spectra of Gd- containing Langmuir-Blodgett film (sample A) during heating. The plane of the film is perpendicular to the external magnetic field.

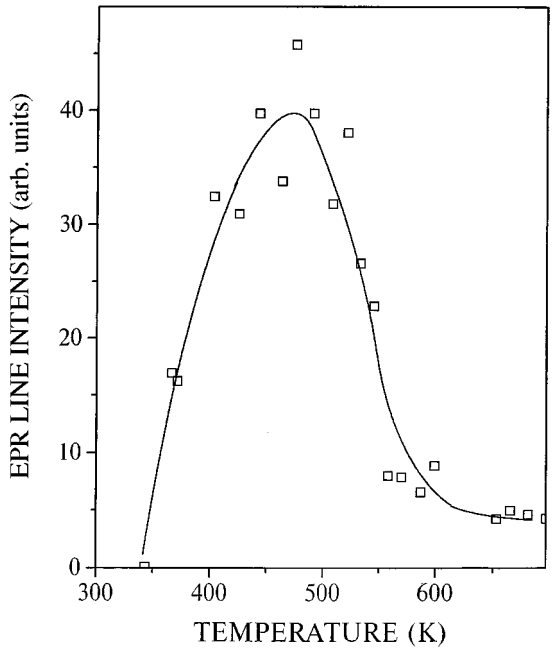

FIG. 2. Temperature dependencies of the EPR signal intensity in Gd-containing LB film (sample A) during heating. Solid lines are guides for the eye.

tween the Gd magnetic layers. Chemical analysis (using ICAP-61) showed that gadolinium was present in the quantitative ratio of three stearic acid molecules per two Gd^{3+} ions. The requirement of charge balance in the film implies that hydroxy-Gd stearates are included in the structure. The Gd-LB films have significant thermal stability and were reversibly heated up to 650 K without any apparent changes in properties. Our EPR experiments have shown that Gd^{3+} ions have been present in a water subphase in the desired concentration without other magnetic ions being present. All measurements of microwave absorption were recorded using an EPR spectrometer Varian E-4.

There was a noticeable EPR signal at room temperature (RT) in the sample A, while no EPR signal were detected at RT from samples of type B. We attribute the small signal in sample A to Gd^{3+} ions absorbed on the silicon substrate surface. For samples of type B, the silicon substrate was previously covered with a number of pure stearic acid layers. This changes the chemical nature of the surface and the covered surface is probably more flat than the original substrate. As a result, all the Gd ions were included in a quasi-2D structure as no EPR signal was detected. It is worth noting that after heating up to 700 K the sample A also becomes EPR silent at RT. Figure 1 shows characteristic experimental EPR spectra, observed during the study of sample A (100 Gd layers). As the temperature increases, a detectable gadolinium EPR signal appears at about 400 K. The EPR line intensity versus temperature has a broad maximum near a temperature of $T=500$ K (Fig. 2). The dependence on temperature of the linewidth ΔH of the EPR spectra (Fig. 3) demonstrates temperature hysteresis and line broadening with decreasing temperature. This is in contrast to the usual paramagnetic behavior of EPR spectra. Besides, on heating the sample the resonance field has a marked tendency to increase (see Fig. 3). The temperature-dependent shift in the value of g (Fig. 4) and the corresponding linewidth changes suggest magnetic ordering in Gd-LB films near 500 K. The magnetic ordering in the LB films containing gadolinium was confirmed by field hysteresis of the microwave absorption signal. For comparison, a ferrimagnetic film of γ-Fe_2O_3 was investigated; it had the same hysteresis characteristics. The hysteresis appeared to a greater extent in a film

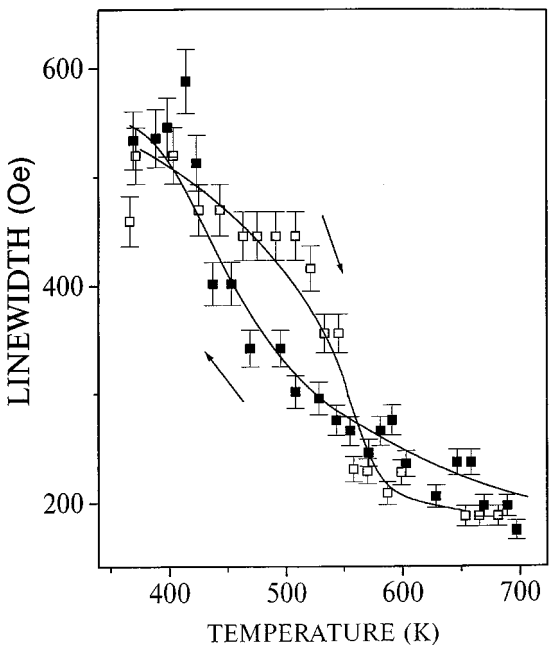

FIG. 3. The linewidth of the EPR line as a function of temperature in Gd-containing LB film (sample A). Open and closed squares denote temperature increasing and decreasing processes correspondingly.

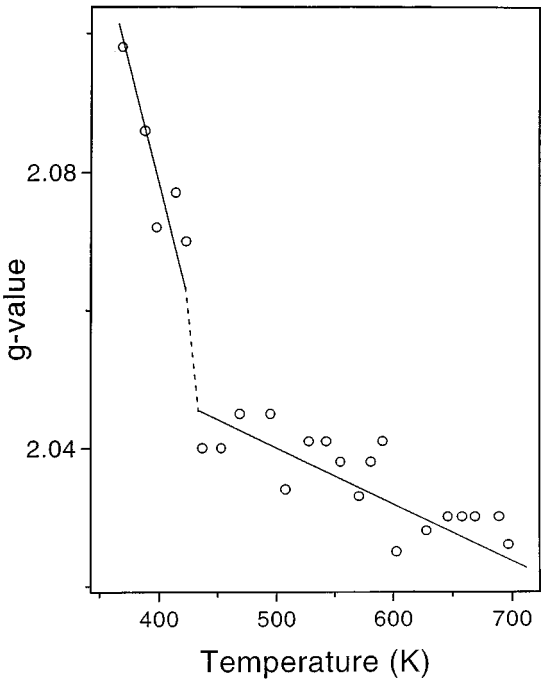

FIG. 4. The g value of the EPR line in Gd-containing LB film (sample A) as a function of temperature during cooling.

with 50 layers of Gd than in a sample with 24 layers and was practically undetectable in samples with a single Gd layer. Further, the films revealed a remnant absorption signal after the removal of the external magnetic field. Cooling down to 77 K caused an increase in the hysteresis. The magnetic ordering in a single layer of gadolinium ions incorporated in a multilayer stearic acid LB film could not be detected, possibly due to the weakness of the absorption signal.

A number of questions remain open about the magnetic order. What type of a magnetic order takes place in Gd-containing LB films: long- or short-range order? If long-range order exists, what is its magnetic structure? Is it ferromagnetic, ferrimagnetic, simple antiferromagnetic, or more complex? If the magnetic order is short ranged, is it a spin glass, exchange-bonded clusters, or is it superparamagnetic? What is the effective dimensionality of the Gd magnetic system in the films? In short, there are four experimental effects which relate to the magnetic ordering in the studied LB films. (i) The EPR signal is practically invisible at room temperature (see Fig. 1). The EPR intensity as a function of temperature has a rather broad maximum near 500 K (see Fig. 2). (ii) The linewidth ΔH increases about three times when the temperature is lowered from 550 K down to 400 K (see Fig. 3). (iii) The g factor is increased upon cooling, and its derivative dg/dT changes suddenly below 500 K (see Fig. 4). (iv) Field hysteresis of microwave absorption is observed at room and liquid nitrogen temperatures.

The first two phenomena are typical of magnetic ordering both in ferromagnets or in antiferromagnets.[24,25] In bulk magnets, below the ordering temperature (T_0) the intensity of the nonshifted EPR line decreases[10] and the signal becomes very small.[24] This results from a shifting of the intrinsic EPR signal to low fields in ferromagnets and to rather high fields in antiferromagnets. The shifting occurs because of the internal magnetic field. The internal field in ultrathin films may be too small to significantly shift the resonance line. The main reason for the linewidth broadening is the short-range order above the critical temperature T_0 and the magnetic fluctuations in the vicinity of T_0. As a rule, the EPR line starts to broaden at a temperature which is higher than the one where long-range order occurs.[24] Further, $\Delta H(T)$ demonstrates no anomaly at the Curie or Néel temperature.[24] The linewidth increases upon cooling in spin-glass systems as well as in systems with long-range order.[26] Therefore, it cannot be excluded that the magnetic order in the studied Gd LB films is a spin glass. Spin-glass behavior is typical of diluted magnetic compounds, such as magnetic impurities in a diamagnetic matrix,[26] and of frustrated magnets. A hexagonal 2D antiferromagnetic system is frustrated, but the magnetic hysteresis suggests ferromagnetic interactions to be most probable, and the sudden change in the temperature behavior of the EPR line near 500 K is not consistent with ordinary spin-glass behavior. As for the bonded cluster system (including exchange-bonded pairs, for example), which also often reveal anomalous EPR spectra behavior,[27] we believe that the observed temperature dependency of the EPR data cannot be due to the existence of Gd^{3+}-Gd^{3+} pairs: in this case the maximum of the EPR intensity (Fig. 2) should be much wider in temperature, as strong broadening of the EPR line within a relatively small temperature interval is not typical for bond cluster systems. The observed temperature dependent changes in the EPR spectrum of Gd-LB films therefore suggests the existence of a ferromagnetic component in the magnetic ordering. The structure of the Gd containing LB films seem to promote two-dimensional properties. In systems with reduced dimentionality it can be expected that there is a smoothing of all temperature anomalies.[28] In the multilayer structure of fatty acid LB film, multivalent metal ions can form interlayer ''salt bridges'' resulting in the enhancement of film stability and ordering. This effect should have a maximum for three-valent rare-earth cations. In the case of salts of Gd the dipole-dipole and isotropic indirect exchange interaction are most important. In chlorides, for instance, the $Gd^{3+}-Gd^{3+}$ interaction leads to a low transition, $T_C=2.2$ K, as in $GdCl_3$ with a distance between Gd ions of 4.105 Å.[24] The isotropic Hamiltonian of the exchange interaction cannot determine the magnetization direction, but when the dipolar energy overcomes the surface and interface anisotropy, the magnetization has an in-plane orientation. The magnetization direction in epitaxial Gd films changes with thickness, and a canted state on the surface of a thick film has been observed.[28]

The crystal structure of the rare-earth LB film has not been investigated. As a first guess, it is reasonable to assume the existence of hexagonal point symmetry of the magnetic layers. In the isotropic mean-field approximation the value of the exchange interaction J inside a ferromagnetic layer can be approximately estimated from the magnetic ordering temperature. For a hexagonal layer we may estimate J as $\approx 0.7 \times 10^{-3}$ eV. This estimate should be correct for the case when the interaction between layers is small enough to be ignored. A number of theoretical papers have been devoted to the study of the interlayer exchange coupling across nonmagnetic and nonmetallic spacers, see for example Refs. 29–

33. For insulating spacers, the value of the exchange interaction can decay exponentially with the thickness of the insulator layer.[32] Quasi-two-dimensional systems are close to 2D systems at $T \gg J_i/k_B$ and to 3D systems at $T \ll J_i/k_B$, where J_i is the interlayer exchange energy and k_B is the Boltzmann constant.[29] It means that if the magnetic order of the Gd LB films is near to being two dimensional at the transition point then $J_i \ll 0.7 \times 10^{-3}$ eV. However, high-temperature magnetic ordering can arise as a result of hard covalent bonds between Gd ions, as well as from layer anisotropy. Further, because of the method of preparation, it is possible that the Gd ions occupy two different sites. Therefore, it may be necessary to invoke a crystalline model with two sublattices.

In conclusion, the possibility of magnetic order at moderately high temperatures is observed in rare-earth Langmuir-Blodgett films. Many questions concerning the type of magnetic structure and exchange interactions still need to be explored and discussed and, in order to unambiguously interpret the EPR measurements and to verify the magnetic order of the films, more work on characterizing the films is needed. It is necessary to investigate the films for structural, chemical, and electronic transformations with temperature, and to study films with nonmagnetic rare-earth ions. Rare-earth Langmuir-Blodgett films with room-temperature magnetic order may be of technological interest in developing magnetic media applications and in nanostructure devices.

This work was supported by the Russian Fund of Fundamental Research (Grant Nos. 96-02-18127a and 96-03-333766a) and INTAS.

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