

MAGNETIC PROPERTIES OF LANGMUIR-BLODGETT FILMS WITH IRON IONS

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Abstract. Stearate films with iron ions in various valence states (Fe^{2+} and Fe^{3+}) were fabricated by Langmuir–Blodgett (LB) method and slow monolayer collapse method. The composition and construction of nanostructures obtained were determined by surface pressure – area (p – a) method and mass-spectroscopy. Magnetic susceptibility of the two types of layered regular structures was measured. It should be noted that the temperature dependence of susceptibility does not show a Curie–Weiss behavior in the range 77 – 300K. In both types of films the low values of effective magnetic moments for both Fe^{2+} and Fe^{3+} were found. This can be explained by assuming the presence of low spin configuration of these ions. All anomalies of magnetic behavior are discussed within the framework of the model of film structuring. This process causes strong superexchange interactions of various (ferro- and antiferromagnetic) types. The coexistence of various exchange parameters opens new opportunities to design novel nanomaterials with required properties.

1. INTRODUCTION

Langmuir-Blodgett (LB) films containing ions of 3d-elements attract growing interest due to their nanotechnology application. The films are two-dimensional elements of regular molecular nanostructures and can be applied in new molecular devices, sensors, etc. They may be useful in producing ordered ultrafine multistructures in which molecular orientations and packing should be highly controlled. These properties determine the application of the films as nonlinear optical materials [1-3].

LB films of long-chain fatty acids and their 3d-element salts are also attractive as magnetic nanomaterials. In this case, the films contain magnetic and organic layers oriented two-dimensionally and present the multilayer regular nanostructure consisting of magnetic layers separated by non-magnetic layers. The inorganic ions or groups of

such ions can be included into multilayers to design new 2D magnetic hybrid materials based on polymetallic mixtures. There are several reports on the ferromagnetic properties of new hybrid organic-inorganic materials [4,5].

LB film is considered to mean not only a monomolecular layer of insoluble surface-active substance on an two phase interface (as a rule that is liquid-gas) but a regular multimolecular ensembles also obtained by consecutive transfer of such multistructures on solid substrate.

It is known that magnetic ions are responsible for the functional properties of the film. However, the spin state of these ions and their local surrounding is not yet ascertained.

In the present study, two types of layered regular nanostructures with Fe^{2+} and Fe^{3+} ions were synthesized: multistructures of iron stearate, which were

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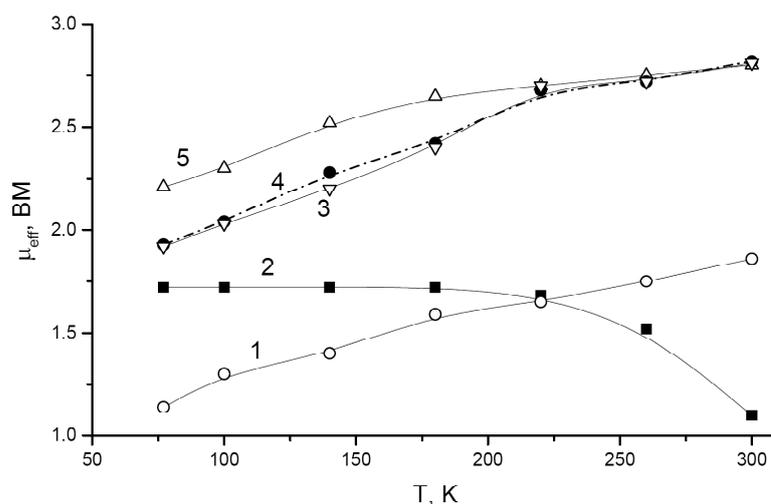


Fig. 1. Dependence of magnetic moment on temperature for collapsed multistructures: 1. collapsed stearate multistructures with Fe^{2+} ions after storage; 2. collapsed stearate multistructures with Fe^{2+} ions measured at once after synthesis; 3. collapsed stearate multistructures with Fe^{3+} ions measured at once after synthesis; 4. collapsed stearate multistructures with Fe^{3+} after storage; 5. collapsed multistructures prepared from previously prepared FeSt_3 .

obtained via consecutive transfer of iron stearate monolayers onto glass substrate (Langmuir – Blodgett method) and dispersions with the such chemical composition derived as a result of slow monolayers collapse.

The second type is the layered structure obtained by slow compression of monolayer. This causes a monolayer collapse and the parts of monolayer creeps one to another giving rise to collapsed multistructure. Such regular structure presents the small-size particles distributed in water phase (dispersion). This method permits to obtain the regular structures when difficulties in films preparing by LB technique take place.

Magnetic susceptibility of these nanostructures was studied. The results are discussed within the framework of superexchange interaction mechanism and nanostructuring process.

2. EXPERIMENTAL

Monolayers of iron stearate were fabricated by LB method by coating of the stearic acid solution in hexane (1.0 mg/ml) onto a aqueous subphases containing iron salts (FeCl_3 or Mohr salt). The transfer pressure was 20 mN/m. The rate of glass plate was 0.8 cm/sec. In the case of ferrous stearates, the water substrate component represents 10^{-4} M solution of Mohr salt. The low concentration of solution allows a physical adsorption of iron ions to be prevented. The study of Fe^{2+} fraction transferred from Mohr salt solution to a condensed monolayer was performed. It was found that the most portion of Fe^{2+}

transfers at $\text{pH} = 4$ [6]. The pH value was varied by the addition of HCl .

For ferric stearates, the water substrate is FeCl_3 with the same concentration of 10^{-4} mol/l but $\text{pH} = 3$ was used in this case because of the greater degree of hydrolyzation of Fe^{3+} ions. The described synthetic procedure resulted in obtaining of 60-layer samples.

For producing of multimolecular structures by slow collapse method the listed above subphases were used. The rate of monolayer pressing was 0.2% min. The particles are 0.1–0.4 mm in diameter. The composition and formation of nanostructures obtained were determined by surface pressure – area ($\pi - a$) method and mass-spectroscopy [6]. Magnetic susceptibility was measured by the Faraday method in temperature range 77 – 300K.

3. RESULTS AND DISCUSSION

Measured values of magnetic susceptibility were corrected for diamagnetism of constituent ions and glass substrate. The paramagnetic susceptibility per mole of iron ions, as well as the effective magnetic moment (μ_{eff}) was calculated for all measured temperatures.

It should be noted that the susceptibility of all films does not show the Curie–Weiss behavior in temperature range from 77 to 300K. This is a straight line up to 200K and then becomes practically temperature-independent. The appearance of contribution of temperature independent paramagnetism

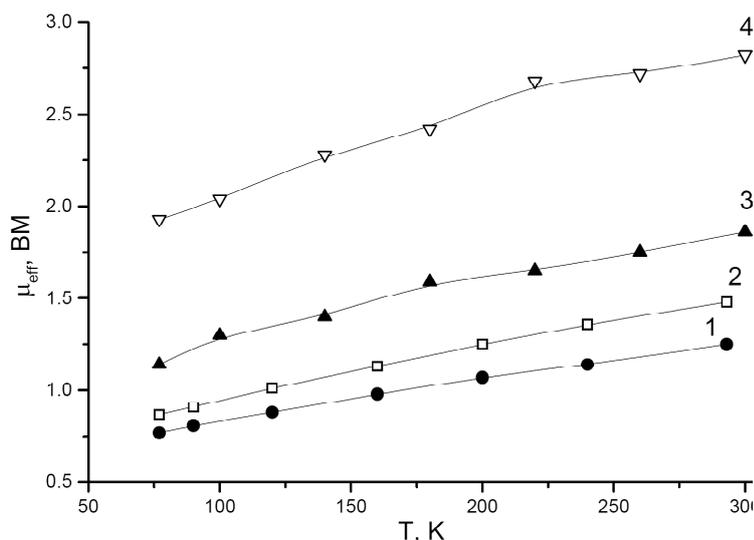


Fig. 2. Comparison of temperature dependence of effective magnetic moment of collapsed stearate multistripes and stearate LB films: 1. Fe²⁺ LB films; 2. Fe³⁺ LB films; 3. collapsed multistripes containing Fe²⁺ ions after storage; 4. collapsed multistripes containing Fe³⁺ after storage.

points to the effect of an electron delocalization in magnetic films.

The temperature dependence of effective magnetic moment of collapsed multistripes on temperature is shown in Fig. 1. Fig. 2 shows a similar dependence of μ_{eff} of LB films as well as the collapsed multistripes.

It is seen that the experimental moments of all stearates are in the region of 1.0 – 2.7 μ_B , regardless of method of their synthesis. These are too small in comparison with the theoretical values for Fe²⁺ (4.90 μ_B ; $S=2$) and Fe³⁺ (5.92 μ_B ; $S=5/2$). For Fe³⁺ stearates μ_{eff} is increasing from 1.8 up to 2.6 μ_B with temperature rise from 77 to 300K, while for Fe²⁺ stearates it is decreasing from 1.75 to 1.0 μ_B at the same temperature interval. The magnetic moment of Fe³⁺ ions should not depend on temperature [7].

It is evident, however, that for our Fe³⁺ samples such dependence does occur (samples №3, 4, and 5 in Fig. 1 and sample №2 in Fig. 2). For the samples №4 and 5, value of μ_{eff} is increasing from 1.8 up to 2.6 μ_B with temperature rise. They present the as-grown collapsed multistripes measured immediately after synthesis and those after storage during 2 month. A qualitative agreement between their magnetic moments points to the fact that these regular nanostructures have very high stability and their magnetic characteristics do not change in time.

For all stearates the range of magnetic moment variation are within the limits of theoretically calculated for low spin state (1.73 – 2.4 μ_B ; $S=1/2$). Because of this, the first explanation of small val-

ues of magnetic characteristics may be the presence of significant fraction of low spin Fe³⁺ ions.

According to X-ray data for Fe²⁺ films, the organic chains are arranged parallel to one another in a hexagonal unit cell [8]. In this environment the local symmetry of metal ions decreases. The realization of low spin state is possible because of additional splitting of iron ion levels under crystal-field effect of stearate ions.

Another reason, however, may cause the drop of magnetic characteristics, namely, the processes of film structuring. As a result, the partial antiferromagnetic aggregates (clusters) are produced since magnetic interaction between iron ions is possible. The distance between the magnetic ions in the films is about 5 nm, estimated from area of monolayer on water subphase. Therefore a superexchange magnetic interaction is possible only in these multistripes. It is known that character of such interaction is determined by the value of interaction angle. A superexchange term means the interaction of metal ions via nearest-neighbor oxygen ions. When the cation–anion–cation line forms an angle of 180°, the interaction is antiferromagnetic. In the 90° case, the superexchange should be ferromagnetic. If the hydrocarbon chains are aligned vertically to the film surface, the interaction between Fe³⁺ ions should be antiferromagnetic. The value of magnetic moment of the film must be less than those for isolated ions.

In order to check this assumption we measured the magnetic susceptibility of the sample obtained by the coating of previously prepared FeSt₃ on wa-

ter subphase. The behavior of temperature dependence does not change (curves 3 and 5) but the moment values are larger than those for collapsed samples obtained by coating of HSt on FeCl_3 aqueous solution.

When the films consist of FeSt_3 three bonds via stearate ions are in the multistructure. According to our mass spectroscopy data in the collapsed samples the hydroxosalts by type of FeOHSt_2 or $\text{Fe}(\text{OH})_2\text{St}$ is formed instead of FeSt_3 . Hence one or two bonds in the films are formed via hydroxyl groups. The size of such groups is less than that of stearate ions and a possibility of aggregation grows. Because of this, μ_{eff} decreases.

The collapsed layers of Fe^{2+} stearates have the following magnetic characteristics. Magnetic moment of the sample № 2 (Fig. 1), measured at once after coating, decreases from 1.75 to 1.0 μ_B in temperature range 77 – 300K. This does not correspond to theoretical values for all spin states of Fe^{2+} ions, and the experimental values cannot be explained by simple characteristics of isolated ions. According to our above-mentioned model the adequate explanation can be concurrent presence of low spin state of ions and strong superexchange interaction. As in the case of Fe^{3+} stearates, the hydroxosalts are formed in the process of coating. Due to absence of stearate group under the monolayer, exchange interlayer interaction and film structuring should be taken into account for interpretation of magnetic behavior.

It is interesting that after two-month storage of the films with Fe^{2+} , the temperature behavior of μ_{eff} is changed: μ_{eff} increases with increasing temperature. We observe a very important phenomenon confirming our suggestion about structuring of the film, the interval of moment values remains the same (1.0 – 1.8 μ_B). This fact points to the rearrangement of local environment of magnetic ions (change of exchange angle). The oxidation of Fe^{2+} to Fe^{3+} ions is also possible. Curve 1 in Fig. 1 demonstrates the antiferromagnetic behaviour, curve 2 ferromagnetic one.

In principle, the interaction can take place both within clusters of homo- or heterovalent ions and between isolated ions. In our opinion, however, the fact of total change of interaction character supports the first explanation. The variation of electronic and local arrangement goes on more simply within the clusters with strong exchange interaction. We analyzed the theoretical values of magnetic moments of any types of clusters containing homo- and heterovalent ions having various spin states. Our experimental results corresponds to values of μ_{eff} of

dimers as well as trimers with low and high spin ions. In order to clarify the mechanism of exchange interaction a more detailed investigation will be performed. These further investigations are in a progress.

Multimolecular layers of iron stearates having more regular structure than that of collapsed monolayers display essentially lower magnetic moments, Fig. 2. For Fe^{3+} and Fe^{2+} , the latter were in the range 0.86 – 1.40 μ_B and 0.77 – 1.25 μ_B , respectively. This can also be explained by our suggestion about the effect of two factors on magnetic properties of films. These are the presence of low spin configuration of Fe^{2+} and Fe^{3+} ions and the film structuring. It is clear that a regularity of structure is favoured by an exchange interaction, giving rise to lower magnetic moments of more regular structure.

The low values of magnetic moment of Fe^{2+} LB films on silicon were found previously [8]. The temperature dependence showed the Curie–Weiss behaviour. The magnetic moment value estimated from the Weiss constant was 1.0 μ_B . This value agrees with our data. In order to explain these results the authors suppose that the most of Fe^{2+} ions should have a low spin state with $S = 0$ and the antiferromagnetic interaction between iron ions. Unfortunately, they did not demonstrate a temperature dependence of μ_{eff} and there is no the possibility to perform a correlation between magnetic properties of the films coating on different substrates. Such new data might have advanced our understanding of electron transfer processes in two-dimensionally organized systems.

4. CONCLUSION

Stearate films as well as regular multistructures with iron ions were fabricated by LB method and the slow collapse method correspondingly. From the results of magnetic susceptibility measurements it was found that all stearates have the low values of effective magnetic moments for both Fe^{2+} and Fe^{3+} . The temperature dependence of susceptibility does not show a Curie–Weiss behavior in the range 77 – 300K. The contribution of temperature independent paramagnetism points to the effect of an electron delocalization in magnetic films.

All anomalies of magnetic behavior of LB films with various degree of regularity in ions arrangement have been explained within the framework of the model of film structuring (in other words, the processes of film self-organization). This process causes strong superexchange interactions of various (ferro- and antiferromagnetic) types. One of a

mechanism of self-organization can be the interaction between hydrophobic groups in process of film formation causing a various geometric peculiarities of condensed state constriction and producing the layers or tunnels for electron transfer. This offers considerable scope for application of LB films for fabrication of novel nanomaterials with required properties.

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