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LETTERS TO THE EDITOR

Magnetic Ordering in Nanofilms Containing 3*d* Elements

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Magnetic properties of nanofilms are of considerable research interest, as special features of layered structures with two-dimensional arrangement of ions at the substrate surface can give rise to novel properties [1–3]. Furthermore, studies of magnetic properties of thin films containing transition metal ions allows obtaining essential information concerning the nature of interactions between these ions both in a film plane and in the perpendicular direction. Unfortunately, such researches have not been systematic [1] and the lack of information prevents modeling the 3*d*-element ions behavior in two-dimensional surface systems. The phenomenon of the magnetization vector reorientation as function of temperature and layer thickness has been revealed in the studies of thin films of ferromagnetic metals. It has been suggested that in very thin films the surface uniaxial anisotropy favoring perpendicular magnetization can prevail over dipole-dipole interactions promoting orientation of spins in parallel to the substrate surface plane. At certain range of the layer thickness, temperature-dependent reorienttation of the magnetization direction is possible [2]. Hence, overall magnetic properties of the film should result from the competition between the two types of exchange interactions corresponding to the arrangement of spins at 90° (ferromagnetic, perpendicular to the substrate) and 180° (antiferromagnetic). It is not clear whether the above-described ordering is typical only of metal films or it can be observed in films of other compounds containing metal ions. Herein we report on comparison of magnetic properties of various nanofilms containing ions of 3*d*-elements.

In earlier studies of magnetic properties of oxide nanofilms consisting of M–O groups (M = Fe^{3+} or Ti^{4+}) deposited onto the surface of disperse silicon dioxide, we have found a complex dependence of magnetic properties on the magnetic field strength and on the degree of layer filling [3, 4]. The synthesis has been carried out via the molecular layering method, the number of monolayers ranging from 1 up to 4, and the film thickness being of 0.3–1.5 nm. A sharp increase in the magnetic susceptibility has been observed at the degree of a monolayer filling (θ) of 0.4–0.6 for both diamagnetic (Ti^{4+}) and paramagnetic (Fe^{3+}) ions. The specific magnetic susceptibility for Fe–O groups at 293 K is of 1.5×10^{-6} (θ = 0.02) and 31×10^{-6} (θ = 0.4) cm^3/g. With further θ increase, the susceptibility has decrease, its behavior corresponding to the antiferromagnetic exchange. Therefore, at small θ values the influence of neighboring M–O groups yet does not prevent the spin orientation perpendicular to the substrate (ferromagnetic exchange) but the further appearance of metal-oxygen groups leads to the stronger exchange interactions, the orientation interaction with the support, and the sharp decrease in the susceptibility (antiferromagnetic exchange). Thus, similarly to the metal films, the two-dimensional magnetic ordering with parallel or antiparallel ordering of the spins is possible for nanolayers of M–O groups. In the case of Ti^{4+} ions, the ordering is caused by the strong polarization by the substrate and is thus structurally induced. The observed weak ferromagnetism in the films based on diamagnetic ions well correlates with the similar phenomenon for VO_2 and SnO_2 films [5–7].

We extended the studies of magnetic properties on the Langmuir–Blodgett films of $Fe^{(III)}$ and $Fe^{(II)}$ stearates with the stearate fragments being in parallel orientation due to the hydrophobic interactions and

almost perpendicular to the substrate surface. Details of the films preparation and characterization are described elsewhere [8]; the film thickness was of 3 nm. We used the films deposited onto a glass substrate or the nanostructures obtained via collapse of stearic acid monolayers from the subphase containing metal salts.

Temperature dependence of magnetic susceptibility of Fe^{2+} and Fe^{3+} films coincided with the Curie–Weiss law only at 77–200 K (cf. [1] reporting on magnetic properties of similar films at 4.5–100 K). At higher temperature, the contribution of temperature-independent paramagnetism to the susceptibility was revealed, pointing at the electron delocalization within the film. The delocalization was possibly caused by redistribution of electrons between oxygen ions of carboxylic groups and iron ions, being enhanced with increasing temperature. The suggestion was supported by the fact that the temperature-independent paramagnetism values (800 cm^3/mol) for the films containing iron in different oxidation states (Fe^{2+} and Fe^{3+}) were close. Values of μ_{eff} calculated from the magnetic susceptibility were fairly low (0.8–2.6 μ_B for all the studied films irrespectively of the preparation method), likely due to both the low-spin state of iron ions and the presence of a strong indirect antiferromagnetic exchange involving stearate anions. The μ_{eff} increasing with temperature observed experimentally was typical of antiferromagnetic interaction; the exception was the case of collapsed structures containing Fe^{2+} ions with the magnetic moment decreasing from 1.75 to 1.0 μ_B at 77–300 K, typical for ferromagnetic interactions. Remarkably, the behavior of the latter sample was changed after drying and incubation during two months: the magnetic moment of the incubated film increased with temperature, similarly to the behavior of Fe^{3+} stearate. In view of that, we concluded that magnetic properties of the Langmuir-Blodgett stearate films were caused by a competition of two exchange modes, the predominant one depending on temperature. The assumption was supported by the earlier finding that magnetic hysteresis with almost zero residual magnetization was observed at 4.5 K for films containing manganese, iron, cobalt, or nickel ions, evidencing about the presence of weak ferromagnetic contribution to the interaction [1]. In summary, the independent data on different two-dimensional structures were essentially complementary and confirmed the model of magnetic ordering in nanofilms based on the presence of two types of interactions, ferro- and antiferromagnetic ones.

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