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Magnetic properties of iron–oxygen nanostructure doped with 4f elements

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Abstract

In the course of the studies of magnetic susceptibility of iron–oxygen two-dimensional nanostructures formed on the surface of silica, special state of these groups was discovered at the certain degree of filling of the first oxide layer. It was found that surface ordering of a ferromagnetic type takes place in a half filled layer. Influence of cerium and ytterbium atoms introduction on spin arrangement in deposited nanostructures was also discussed.

Keywords: Nanostructures; Magnetic susceptibility; Element–oxygen groups

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1. Introduction

Studies of physico–chemical and physical properties of nanostructures aimed at the development of human's concept of nanometer-size objects are vigorously conducted at the present time. However, if three-dimensional (especially metallic) nano-particles have been investigated comprehensively [1–3], systematic study of two-dimensional oxide substance (layers 5–50 Å) only starts because of the absence of scientific approach to the synthesis of such oxide structures. Literature devoted to the magnetic properties of small-size systems is concerned basically with three- and two-dimensional metallic systems, but there are almost no works dealing with two-dimensional oxide nanostructures [4]. One of the interesting aspects of magnetochemical study of oxide nanostructures is investigation of surface para- and ferromagnetism on diamagnetic matrix, which appear due to the orbitals transformation in superstructures.

In the present work the results are presented of magnetochemical study of oxygen groups, iron–oxygen nanolayers (3–15 Å), and nanostructures, containing cerium–oxygen and ytterbium–oxygen groups.

2. Experimental

Synthesis of element–oxygen groups and element–oxygen monolayers (n) (1–4 monolayers) on the surface of dispersed silica ($S=275$ m^2 g^{-1}) was carried out by the method of molecular layering [5], based on the performing of two or more alternating irreversible surface reactions between functional groups of silica and corresponding low-molecular compounds of element El:

$$m(\equiv\mathrm{Si-OH}) + \mathrm{ElCl}_n \rightarrow (\equiv\mathrm{Si-O-})_m\mathrm{ElCl}_{n-m} + m\mathrm{HCl}\uparrow \quad (1)$$

$$(\equiv\mathrm{Si-O-})_m\mathrm{ElCl}_{n-m} + (n-m)\mathrm{H_2O} \rightarrow (\equiv\mathrm{Si-O-})_m\mathrm{El(OH)}_{n-m} + (n-m)\mathrm{HCl}\uparrow \quad (2)$$

In our case, El is Fe, Ti, Yb, or Ce. As a result of a set of Eqs. (1) and (2) a monolayer of element–oxygen groups is formed at the surface of silica, number of such sets determines the number of deposited monolayers. To elucidate the influence of degree of surface filling with element–oxygen groups ($\theta=1$ for a sample, containing one monolayer of element–oxygen groups) on magnetic properties we have synthesized samples with degree of filling less than unity ($\theta<1$), equal to unity (monolayer), and samples with different number of deposited monolayers ($n=1$–4). Samples were synthesized in gaseous and liquid phases. Synthesis in gaseous phase was conducted in a Pyrex reactor on a flow-type installation in the flow of dried nitrogen. Wide-pore silica-gel ($S=275$ m^2 g^{-1}, pore diameter 100–140 Å) used in the work was purified from admixtures and hydrated with water vapor at 200°C. Salts $\mathrm{TiCl_4}$ and $\mathrm{FeCl_3}$ were used as initial ElCl_n reagents. In synthesized samples the content of $\mathrm{OH^-}$, $\mathrm{Cl^-}$, $\mathrm{Ti^{4+}}$, and $\mathrm{Fe^{3+}}$ was determined.

Synthesis in solution was carried on in the media of

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Table 1
Composition of metal–oxygen groups deposited on SiO_2 surface

Fe content, mmol g^{-1} SiO_2	Yb content, mmol g^{-1} SiO_2	Ce content, mmol g^{-1} SiO_2	θ M/OH^-, mol mol^{-1}
0.02			0.01
0.40			0.22
0.70			0.40
1.80			1.00
	0.03		0.01
	1.44		0.80
		0.02	0.01
		1.27	0.60
0.32	0.03		Fe/Yb 0.2/0.01
0.32	1.41		Fe/Yb 0.2/0.8
0.30		1.31	Fe/Ce 0.2/0.61

M – Fe, Yb, Ce.
θ is a degree of filling of SiO_2 surface.

thoroughly dried CH_3OH with $YbCl_3$ and $Ce_2(SO_4)_3$ as initial reactants. Sample characteristics are summarized in Table 1.

Magnetic susceptibility was measured according to Faraday method within the temperature range 90–293 K at different values of magnetic field strength: 4100, 5820, 7190, and 8280 Oersted. The precision of measurements is 2%.

3. Results and discussion

The analysis of magnetic data for samples containing Fe–O groups showed that χ_{gram} (emu g^{-1}) depends on the strength of magnetic field. Since there were no ferromagnetic admixtures in initial compounds, appearance of the dependence under question can originate from ferromagnetic character of interactions caused by parallel orientation of spins of iron atoms incorporated in =Fe–O– groups. According to [2] after four monolayers deposition synthesized layer of the substance corresponds to the structure of α-Fe_2O_3. At temperature higher than T_C (953 K) bulk oxide α-Fe_2O_3 is paramagnetic, whereas within the range 253 K–953 K a weak ferromagnetism is observed. Moreover, it is known, that decrease in particle size leads to the decrease of T_C, therefore the appearance of ferromagnetism in samples studied can be easily explained.

From Fig. 1, where the dependence of χ_{gram} on a number of iron–oxygen groups is sketched, it can be drawn, that at degree of filling $\theta = 0.4$ susceptibility of these groups is maximum, at further increase in amount of =Fe–O– groups it decreases and remains constant up to the maximum iron content (ferro-gel). The decrease in susceptibility with the increase in iron concentration can be

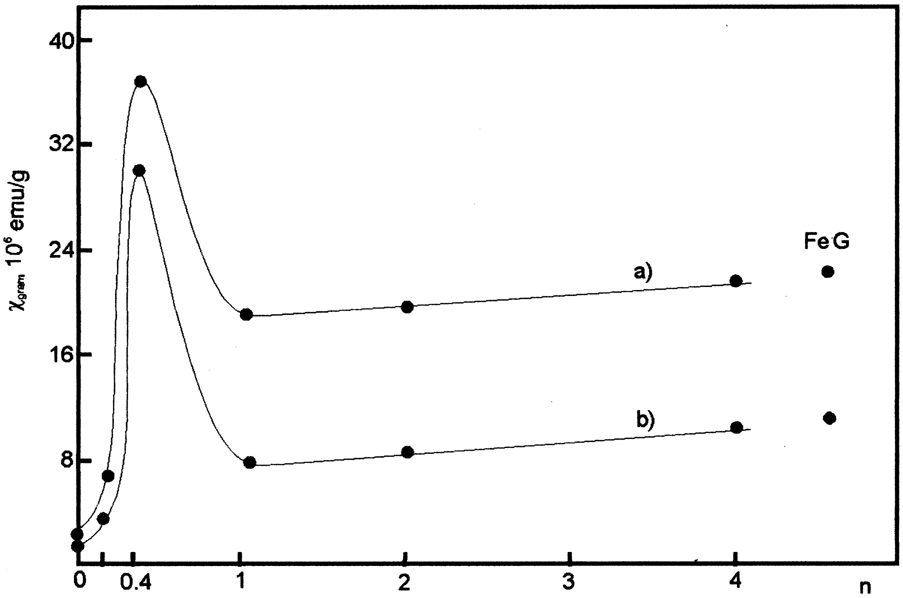

Fig. 1. Dependence of χ_{gram} on iron–oxygen groups content in samples (ferro-gel) at $H = 8280$ Oe, (a)90 K, (b)293 K, n – number of deposited iron–oxygen monolayers.

related with increase in amount of =Fe–O– groups, in which spins of iron atoms are parallel.

It is obvious that at iron–oxygen groups content corresponding to $\theta=0.4$ there is limited concentration of iron atoms and local environment of –Fe–O– groups does not prevent parallel spin orientation (mainly due to the orienting influence of bonds with silica core). Addition of separate groups to the surface of a sublayer should result in formation of coordination structures, the shape of which will depend as on the presence of oxy- or hydroxy-groups, as on polarizing influence of the core. These coordination groups will be identical, all other things being equal (surface state, Si–O–Si distance, etc.), and also direction of magnetic atom spin with regard to the sublayer should be the same. Synthesis of samples according to the method of chemical buildup promotes formation of practically identical surface iron–oxygen groups with respect to composition and structure that, in turn, enables unambiguous arrangement of magnetic atom spins. Analysis of magnetic data shows, that such spin arrangement is retained up to content of iron–oxygen groups corresponding to $\theta=0.4$. As the number of iron–oxygen groups further increases, distance between these groups becomes comparable with the length of Si–O–Si bonds in the surface layer of a sublayer, that causes origination of exchange interactions between iron atoms along the chain –Fe–O–Fe–.

Decrease in susceptibility at further increase of degree of filling testifies antiferromagnetic character of these interactions. Actual constancy of χ_{gram}, when number of the layers is greater than one, points out realization of transition to a massive substance in terms of properties. Negligible increase in susceptibility, which can be seen at extrapolation of χ_{gram} to the ferro-gel susceptibility, is due to incomplete compensation of ferro- and antiferromagnetic contributions.

It is worth to note, that analogous character of change of specific magnetic susceptibility with degree of filling and with the number of monolayers was observed for the samples, containing diamagnetic titanium–oxygen groups deposited on silica [5]. In this case maximum specific magnetic susceptibility occurs at degree of filling equal to 0.6. We assume this maximum is caused by the maximum value of one of the diamagnetic susceptibility components, namely by induced polarization paramagnetism, concerned with deformation of electronic shell of titanium atom under influence of surrounding (orienting influence of a sublayer). Similarity in magnetic behavior of dia- and paramagnetic samples testifies the existence of a peculiar state (from the viewpoint of magnetic ordering) of metal–oxygen groups at the degree of filling about 0.4–0.6, at which these groups can arrange on the surface rather freely and realization of the most favorable state at the interaction with the sublayer is possible.

Further increase in groups amount should inevitably result in formation of more complex surface structure. In this case the distortion of the shape and electronic structure of initially formed element–oxygen layers will occur.

For the detailed analysis of magnetic behavior of the samples, containing iron–oxygen groups, the dependence was studied of the reduced specific magnetization of the samples [σ, emu g^{-1}(Fe_2O_3)] on the magnetic field strength (i.e. specific magnetization was reduced to 1 g of Fe_2O_3 gross weight).

Analysis of the curves σ-H (Fig. 2) showed that this dependence for =Fe–O– monolayer and ferro-gel is extrapolated very close to zero, that is typical for paramagnetic compounds. For the sample with =Fe–O– groups content 0.4 the extrapolation gives a value 0.28 emu g^{-1}, i.e. the presence of spontaneous magnetization is characteristic for this state. Value of reduced spontaneous magnetization appears to be close to that for α-Fe_2O_3 (0.20 emu g^{-1}) [6]. Thus one can assume that our suggestion about the peculiar state of deposited iron–oxygen layers at $\theta=0.4$ is proved, because their ferromagnetic ordering is realized in this state.

The presence of spontaneous magnetization, which is comparable to weak ferromagnetism in α-Fe_2O_3 proves the specific state of iron atoms layer, i.e. orienting influence of the surface on the parallel ordering of spins. The ordering observed does not practically depend on temperature. Its appearance is not caused by the placement of the substance in magnetic field. This state occurs only at sufficiently complete filling of the surface of diamagnetic matrix and disappears upon deposition of the next layers, between which an antiferromagnetic interaction takes place.

It is of a special interest that value of spontaneous magnetization does not practically depend on temperature. This can be explained by the high stability of ferromagnetic ordering, created, apparently, as a result of silica-gel bond system. Thus the data obtained allows us to claim the existence of two-dimensional area of magnetization at a certain amount of iron–oxygen groups on the surface of diamagnetic sublayer.

To elucidate an influence of coordination environment

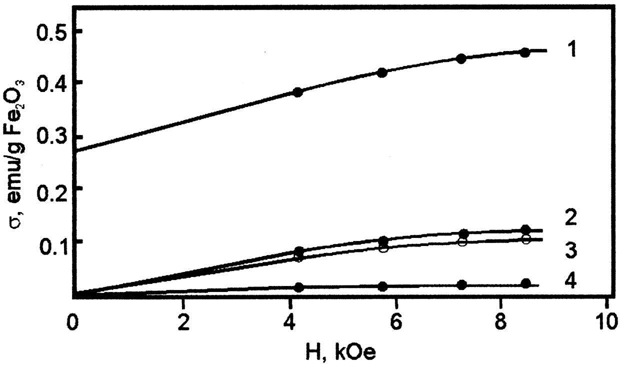

Fig. 2. Dependence of reduced specific magnetization (σ) on magnetic field strength for iron–oxygen containing samples at 293 K. Samples: (1)0.4 Fe, (2)0.22 Fe, (3)1.0 Fe, (4)ferro-gel.

on the appearance of peculiar electronic state of surface element–oxygen groups we studied oxide nanostructures, containing 4f-elements. We synthesized oxide nanostructures, containing Ce^{3+} ($4f^1$) and Yb^{3+} ($4f^{13}$). Choosing these elements we generate two probable cases of magnetic characteristics – dia- and paramagnetic, because both of the elements possess two oxidation states (Ce^{3+} and Ce^{4+}, Yb^{2+} and Yb^{3+}). Samples were synthesized containing either Yb–O or Ce–O groups in the surface monolayer, where some of Fe–O groups are substituted with Yb–O or Ce–O (Table 1). Values of χ_{gram} for Yb–O groups at 290 K were $-0.050 \cdot 10^{-6}$ ($\theta = 0.01$) and $-0.343 \cdot 10^{-6}$ emu g^{-1} ($\theta = 0.8$), i.e. these structures are diamagnetic and their diamagnetism increases with the degree of filling. The most reasonable explanation of such diamagnetism from our point of view is realization of Yb^{2+} oxidation state ($Yb^{3+} \rightarrow Yb^{2+}$ is probable due to redox reaction in methanol solution) in surface nanostructures. We can consider the reduction process of $Yb^{3+} \rightarrow Yb^{2+}$ analogous to elementary act of heterogeneous catalyst of oxidation, but nanostructure does not return in an initial state. The dependence of χ_{gram} on strength of magnetic field (H) is absent. In contrast to diamagnetic Ti–O groups, after deposition of metal, which electronic configuration is slightly affected by coordination environment, we register no areas of spin ordering. However the increase in diamagnetism with the increase in Yb content does point out the presence of orienting effect of sublayer on the symmetry of electronic cloud.

For Ce–O group at 290 K χ_{gram} is $0.230 \cdot 10^{-6}$ ($\theta = 0.01$) and $0.952 \cdot 10^{-6}$ emu g^{-1} ($\theta = 0.6$), therewith it does not depend on H. Susceptibility increases with Ce^{3+} content that can testify the parallel spin arrangement in the surface layer, which has the same origin as that in Fe–O groups deposited on SiO_2. Thus, orienting effects of sublayer displays itself in case of Ce–O groups too, however specificity of electronic configuration of f-elements prevents the formation of two-dimensional magnetization area, caused by collectivization of electrons.

Our suggestions are proved by the values of magnetic susceptibility of nanostructures with interlaced Fe–O and f-element–O groups. At introduction of Yb–O groups χ_{gram} of iron–oxygen nanostructures decreases [$0.508 \cdot 10^{-6}$ ($\theta = 0.01$) and $0.310 \cdot 10^{-6}$ emu g^{-1} ($\theta = 0.80$)] and its dependence on H disappears. When Ce–O groups are introduced χ_{gram} decreases ($1.82.10^{-6}$ emu g^{-1}), but its dependence on H retains. Consequently, introduction of diamagnetic f-ion leads to complete destruction of two-dimensional magnetization area, at the same time an addition of paramagnetic f-ion only reduces cooperative exchange.

So, structural-induced magnetic effects were observed in the case of d- as well as f-elements, and have two components: polarizing and orienting influence of silica-gel sublayer and peculiarities of electronic structure of the ion. From our viewpoint the presence of cooperative exchange interactions between element–oxygen groups is the necessary condition for appearance of peculiar state.

4. Conclusions

The study of oxide nanostructures showed that the presence of peculiar electronic state of iron– and f-element–oxygen groups on the surface of SiO_2 and appearance of two-dimensional area of ordering are due to the orienting influence of sublayer and indirect exchange between d-elements. In the case of f-elements the surface state is limited by structural-induced spin arrangement.

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