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# Magnetic Ordering of Iron–Oxygen and Iron–Organic Nanostructures on a Diamagnetic Matrix

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**Abstract**—The study of the magnetic susceptibility of iron–oxygen quasi-two-dimensional nanostructures (nanolayers) showed that the dependence of the susceptibility on the number of iron–oxygen groups deposited on a silica support is nonmonotic. It was found that a two-dimensional magnetization region arises at a certain number of iron–oxygen groups in the surface layer of the support.

Recent studies show that a substance having nanodimensions (nanostructure) acquires new properties compared to a bulk solid [1–3]. The physicochemical properties of three-dimensional oxide nanostructures (nanoparticles) have been studied in sufficient detail, whereas the properties of quasi-two-dimensional oxide nanostructures (nanolayers) are still not clearly understood [4]. An examination of published data on magnetic properties of nanostructures [5–8] shows that virtually no papers deal with the magnetic properties of two-dimensional oxide nanostructures.

An interesting aspect of the magnetochemical study of two-dimensional oxide nanostructures in the study of the surface magnetism, resulting, e.g., from rehybridization of orbitals. Note that, until recently (1980s), doubt was cast on the possibility that the surface of a solid can have magnetic properties. However, as noted in [9], recent achievements in the theory and experiment in this field show that both the surface magnetism and surface phase transitions associated with the changes in magnetic properties can be observed.

Certain ideas on how to accomplish a two-dimensional ferromagnetic organization were proposed in the literature [10]. The principle of a two-dimensional organization of unpaired electrons (or magnetic moments) is schematically shown in Fig. 1. It follows from this figure that all large moments (thick arrows) are oriented in one direction, and all small moments (thin arrows) are directed to the opposite side (owing to the fact that the energy of the exchange between the neighbors is negative). Such an organization of magnetic moments provides the surface ferromagnetism, or, to be more specific, the ferrimagnetism.

Our preliminary experiments [11, 12] point to the existence of the two-dimensional magnetism.

Here we report the results of magnetochemical and Mössbauer spectroscopic study of samples containing various amounts of iron–oxygen or iron–organic groups in the surface monolayer or various amounts of iron–oxygen monolayers on a silica support. Some characteristics of the samples are given in Table 1.

The starting silica support is a diamagnetic material ($\chi_g$ $-0.277 \times 10^{-6}$ cm$^3$/g).

The measurements of the specific magnetic susceptibility ($\chi_g$) of the samples with various contents of iron–oxygen groups in the surface monolayer ($\theta$) and with various numbers of the deposited monolayers ($n$) showed that $\chi_g$ depends on the magnetic field strength ($H$) for all the samples. The dependence of $\chi_g$ on the field strength is conventionally attributed

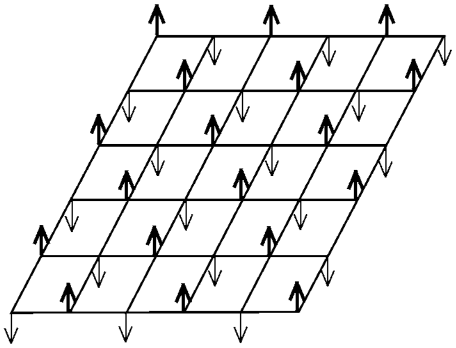

**Fig. 1.** Scheme of the two-dimensional ferrimagnetic organization of magnetic moments. Arrows show the directions of magnetic moments of metal ions.

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either to ferromagnetic impurities or to ferromagnetic ordering. However, in our case this dependence is not associated with impurities, because the starting substances were free of ferromagnetic impurities. According to [13], for the ferromagnetism to arise, spins of the neighboring iron atoms should retain their parallel orientation in spite of thermal excitation. Hence, we presumed that the observed effect may result from the parallel orientation of spins of iron atoms incorporated in the surface iron–oxygen groups.

The plot of $\chi_g$ vs. iron concentration (the number of iron–oxygen groups) on the surface is given in Fig. 2. It is seen that, when the content of Fe–O groups on the surface corresponds to the degree of filling $\theta = 0.4$, the plot passes through a maximum. As the number of Fe–O groups is increased further, the susceptibility decreases and then remains almost constant up to the maximal iron content (the ferro gel sample). We believe that the comparison of magnetic properties of the synthesized samples with ferro gel instead of $\alpha$-$Fe_2O_3$ is more justified, because the temperature of the sample synthesis (260°C) is much lower than the temperature of $\alpha$-$Fe_2O_3$ preparation.

The growth of $\chi_g$ with an increase in the number of iron–oxygen groups fixed on the diamagnetic matrix suggests that the spins of iron atoms have a parallel orientation. We emphasize that this arrangement is energetically advantageous, since in many cases a pair of neighboring atoms with parallel moments has a lower energy than that with antiparallel moments [13, 14]. However, when the content of Fe–O groups corresponds to $\theta$ ~0.5, the limiting concentration of iron atoms is apparently reached, at which the local surrounding of the Fe–O groups does not prevent the parallel orientation of the spins; this is associated to a greater extent with an orienting effect of the silica framework on the (≡Si–O–Fe≡) bonds.

This conclusion is supported by the data of [15] on the possibility of transmission of the effect of various groups located near the surface of Si and O atoms along the system of overlapping *p* and *d* orbitals. The theoretical calculations carried out in [16, 17] show that such an exchange interaction is possible and it can involve adsorbed ions located at distances of tens of interatomic distances.

Addition of separate groups to the surface in the course of chemisorption results in an increase in the size of the regions of magnetic ordering, and, consequently, in the growth of the accompanying separate magnetic moments. As the content of Fe–O is increased further ($\theta > 0.5$, up to $\theta = 1$), the distances between these groups become comparable to the lengths of the Si–O–Si bonds in the surface layer of the support, i.e., ~3 Å. In this case, various interactions between the surface iron–oxygen complexes are possible, as well as the exchange interactions between iron atoms along the (≡Si–O–Fe=) bond of one group and through the surface (≡Si–O–Si≡) bonds to another (≡Si–O–Fe=) bond. This is confirmed by the observed decrease in the susceptibility at $\theta > 0.5$ and points to the antiferromagnetic character of these interactions.

**Table 1.** Characteristics of iron-containing nanostructures on a silica matrix[a]

| Sample | | *S*, $m^2/g$ | $Fe^{3+}$ content, mmol/g of $SiO_2$ | $\theta$ | *n* |
|---|---|---|---|---|---|
| no. | designation | | | | |
| | Silica gel ($SiO_2$) | 275 | | | |
| 1 | 0.01Fe–O/$SiO_2$ | 274 | 0.02 | 0.01 | |
| 2 | 0.22Fe–O/$SiO_2$ | 270 | 0.40 | 0.22 | |
| 3 | 0.36Fe–O/$SiO_2$ | 269 | 0.62 | 0.36 | |
| 4 | 0.4Fe–O/$SiO_2$ | 271 | 0.70 | 0.4 | |
| 5 | 0.7Fe–O/$SiO_2$ | 270 | 1.26 | 0.7 | |
| 6 | 1Fe–O/$SiO_2$ | 267 | 1.8 | 1 | 1 |
| 7 | 2Fe–O/$SiO_2$ | 248 | 2.4 | | 2 |
| 8 | 4Fe–O/$SiO_2$ | 198 | 3.47 | | 4 |
| 9 | 1Fe–$O_{impregnation}$/$SiO_2$ | 214 | 1.84 | | |
| 10 | 4Fe–$O_{impregnation}$/$SiO_2$ | 107 | 3.54 | | |
| 11 | 0.02Fe$R_2$/$SiO_2$ | 270 | 0.01 | 0.02 | |
| 12 | 0.3Fe$R_2$/$SiO_2$ | 270 | 0.13 | 0.3 | |
| 13 | 0.59Fe$R_2$/$SiO_2$ | 268 | 0.26 | 0.59 | |
| 14 | 1Fe$R_2$/$SiO_2$ | 259 | 0.44 | 1 | 1 |

[a] ($\theta$) Degree of the substitution of Fe–O groups for OH groups; (*n*) number of deposited monolayers.

The fact that $\chi_g$ is almost constant for the samples with $n > 1$ shows that these samples approach in their characteristics the properties of compact ferro gel containing Fe–O groups.

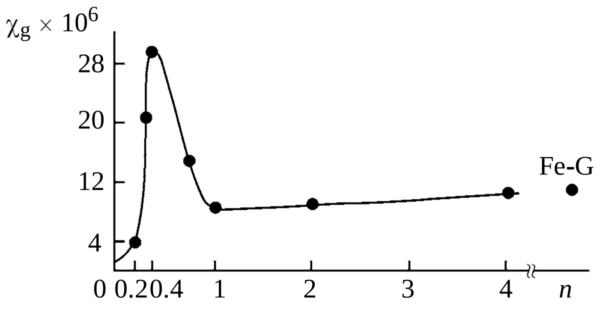


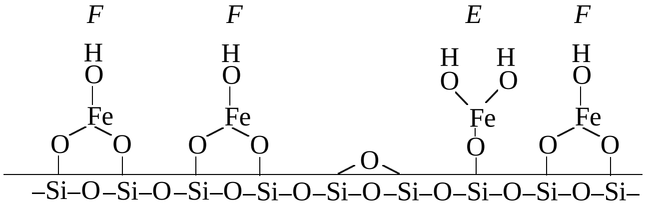
**Fig. 2.** Plot of $\chi_g$ ($cm^3/g$) vs. content of iron–oxygen groups at $H = 8.28$ kOe and $T = 293$ K. (*n*) Number of deposited monolayers; (Fe-G) ferro gel.

**Table 2.** Parameters of Mössbauer spectra of iron-containing nanostructures

| Series | Sample |  | $\alpha$-$Fe_2O_3$ |  |  |  | Amorphous magnetic phase |  |  |  | Paramagnetic phase |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | no. | designation | % | δ, mm/s | *E*, mm/s | *H*, kOe | % | δ, mm/s | *E*, mm/s | *H*, kOe | % | δ, mm/s | *E*, mm/s |
| 1 | 1 | 0.01Fe–O/$SiO_2$ |  |  |  |  |  |  |  |  | 87.9 | 0.14 | 0.57 |
|  |  |  |  |  |  |  |  |  |  |  | 12.1 | 0.44 | 1.07 |
|  | 2 | 0.36Fe–O/$SiO_2$ |  |  |  |  | 87.7 | 0.37 | 0.105 | 400 | 8.3 | 0.12 | 0.58 |
|  |  |  |  |  |  |  |  |  |  |  | 4.0 | 0.36 | 0.77 |
|  | 3 | 0.4Fe–O/$SiO_2$ | 39.4 | 0.38 | 0.23 | 510 | 47.4 | 0.38 | 0.14 | 420 | 8.8 | 0.12 | 0.59 |
|  |  |  |  |  |  |  |  |  |  |  | 4.4 | 0.37 | 0.78 |
|  | 4 | 1Fe–O/$SiO_2$ | 57.7 | 0.37 | 0.20 | 516 | 23.8 | 0.29 | 0.28 | 453 | 3.1 | 0.21 | 0.48 |
|  |  |  |  |  |  |  |  |  |  |  | 15.4 | 0.37 | 0.78 |
|  | 5 | 4Fe–O/$SiO_2$ | 78.1 | 0.37 | 0.22 | 515 | 17.6 | 0.38 | 0.13 | 480 | 4.3 | 0.20 | 0.73 |
| 2 | 6 | $\alpha$-$Fe_2O_3$ | 100 | 0.37 | 0.23 | 521 |  |  |  |  |  |  |  |
| 3 | 7 | 1Fe–O/$SiO_{2\ \text{impregnation}}$ | 100 | 0.40 | 0.23 | 520 |  |  |  |  |  |  |  |
|  | 8 | 4Fe–O/$SiO_{2\ \text{impregnation}}$ | 100 | 0.37 | 0.23 | 520 |  |  |  |  |  |  |  |
| 4 | 9 | 0.02$FeR_2/SiO_2$ |  |  |  |  |  |  |  |  | 100 | 0.12 | 0.59 |
|  | 10 | 0.3$FeR_2/SiO_2$ |  |  |  |  |  |  |  |  | 83.4 | 0.09 | 0.53 |
|  |  |  |  |  |  |  |  |  |  |  | 16.6 | 0.06 | 1.34 |
|  | 11 | 0.59$FeR_2/SiO_2$ |  |  |  |  |  |  |  |  | 82.7 | 0.13 | 0.55 |
|  |  |  |  |  |  |  |  |  |  |  | 17.3 | 0.35 | 1.08 |
|  | 12 | 1$FeR_2/SiO_2$ |  |  |  |  |  |  |  |  | 65.5 | 0.10 | 0.55 |
|  |  |  |  |  |  |  |  |  |  |  | 34.5 | 0.26 | 0.64 |

The Mössbauer parameters (δ, the isomer shift; *E*, quadrupole splitting; *H*, effective ultrafine magnetic field) for the samples under study are given in Table 2 where two states of iron in these samples (magnetically ordered and paramagnetic) were considered separately.

Let us consider the paramagnetic state of iron atoms. The Mössbauer spectra of the samples with θ 0.01 and 0.36 show the absence of magnetically ordered iron. When the filling of the silica surface with iron–oxygen groups is low, two forms of iron corresponding to two doublets, *E* and *F* (see scheme; Table 2) coexist in the nonmagnetic state.



With such a content of Fe–O groups on the surface, we can speak about isolated iron(3+) atoms. The values of the quadrupole splitting suggest that the *E* doublet corresponds to a more symmetrical surrounding of $Fe^{3+}$ with ligands. Such a complex can form by the reaction of $FeCl_3$ molecules with an OH group of the silica surface by reaction (1) and then by reaction (1'):

$$\equiv Si–OH + FeCl_3 \longrightarrow \equiv Si–O–FeCl_2 + HCl\uparrow, \quad (1)$$

$$\equiv Si–O–FeCl_2 + 2H_2O \longrightarrow \equiv Si–O–Fe(OH)_2 + 2HCl\uparrow. \quad (1')$$

The less symmetrical surrounding of iron atoms described by the *F* doublet results from the reaction of $FeCl_3$ with two surface OH groups:

$$2(\equiv Si–OH) + FeCl_3 \longrightarrow (\equiv Si–O)_2–FeCl + 2HCl\uparrow, \quad (2)$$

$$(\equiv Si–O)_2–FeCl + H_2O \longrightarrow (\equiv Si–O)_2–FeOH + HCl\uparrow. \quad (2')$$

When more than one monolayer of Fe–O groups is deposited, the *F* doublet disappears.

The magnetically ordered state is manifested in the Mössbauer spectra as an amorphous magnetically ordered phase and as an $\alpha$-$Fe_2O_3$ phase, with the Mössbauer parameters of the latter being in good agreement with the published data [18]. Table 2 shows that, as the content of $Fe^{3+}$ on the silica surface in sample nos. 1–5 (series 1) increases, the fraction of $\alpha$-$Fe_2O_3$ grows, and the fraction of the amorphous magnetically ordered phase decreases, which suggests that this phase is formed in the initial stage of the synthesis.

**Table 3.** Dependence of the specific magnetic susceptibility $\chi_{gFe}$ on the number of iron–oxygen (nos. 1–4) and iron–organic (nos. 5–8) groups on silica; $H$ = 8280 Oe, $T$ = 90 K

| No. | Content of [–Fe(OH)$_2$], mmol/g | θ | $\theta_{Fe}$, cm$^3$/g | No. | Content of [–Fe(R)$_2$], mmol/g | θ | $\theta_{Fe}$, cm$^3$/g |
|---|---|---|---|---|---|---|---|
| 1 | 0.02 | 0.01 | 188 | 5 | 0.01 | 0.02 | 11.0 |
| 2 | 0.40 | 0.22 | 144 | 6 | 0.13 | 0.3 | 23.0 |
| 3 | 0.70 | 0.4 | 978 | 7 | 0.26 | 0.59 | 53.4 |
| 4 | 1.80 | 1 | 243 | 8 | 0.44 | 1 | 23.4 |

The spectrum of the sample with θ = 0.4 suggests the presence of a certain amount (39.4%) of iron ions on the silica surface, which are in a surrounding similar to that in α-$Fe_2O_3$ (hematite). As the number of Fe–O groups increases further (θ > 0.4, i.e., sample 1Fe), they become incorporated not into the surface monolayer of isolated iron–oxygen groups but into bulk regions approaching α-$Fe_2O_3$ in their structure. This means that a microphase (α-$Fe_2O_3$) appears on the surface. Note that, for the samples obtained by impregnation (1Fe–O$_{\text{impregnation}}$ and 5Fe–O$_{\text{impregnation}}$ in Table 1), with the concentration of Fe–O groups close to that in 1Fe–O and 4Fe–O samples, the parameters of the Mössbauer spectra are identical to those of the three-dimensional α-$Fe_2O_3$ phase (Table 2, series 2 and 3).

These results suggest that the sample with θ = 0.4 contains iron ions (iron–oxygen groups) on the silica surface in the following states.

(1) Isolated iron ions (*E* and *F* types).

(2) Iron ions that, after attaining a certain concentration of iron on the surface (~0.7 mmol/g), may interact with the same neighboring groups along the ≡Si–O–Fe bonds (along =Fe–O–Si–O–Si–O–Fe= chains). According to magnetic measurements, these ions form separate surface areas of magnetization with a random spin orientation. Such a specific state of the layer of iron ions is also possible, apart from other reasons, owing to an orienting effect of the support surface on the parallel ordering of spins of these atoms.

(3) Iron ions separated by a distance comparable with the Si–O–Si bond length in the surface layer of the support, after the iron concentration on the surface becomes higher than 0.7 mmol/g. In this case, the interaction of iron–oxygen groups with the same neighboring groups may involve additional exchange interactions between iron atoms, which results in the appearance of Mössbauer parameters close to those of the α-$Fe_2O_3$ phase. However, the effective ultrafine magnetic field (Δ*H*) is slightly lower, which suggests that iron ions in this sample still do not form microcrystals of the α-$Fe_2O_3$ phase.

As the phase formation complicates the control of the composition, structure, and properties of the synthesized two-dimensional oxide nanostructures, we studied iron–organic groups which show no tendency to phase formation in a monolayer [19]. The chemical composition of samples (nos. 11–14) with the iron–organic groups is given in Table 1, and the parameters of the Mössbauer spectra of samples with iron diacetylacetonate groups are given in Table 2.

It follows from Table 2 that, in the case of the samples with iron–organic groups (sample nos. 9–12), only a doublet is observed, which is indicative of the predominant presence of separate iron–organic groups on the silica surface.

Table 3 contains the data on the dependence of $\chi_{gFe}$ (cm$^3$/g Fe) on the number of iron-containing groups in a monolayer, with a certain degree of substitution of surface OH groups (θ) corresponding to each concentration of iron ions in the surface [=FeOH] and [–Fe($C_5H_7O_2$)$_2$] groups. The quantity $\chi_{gFe}$ is the

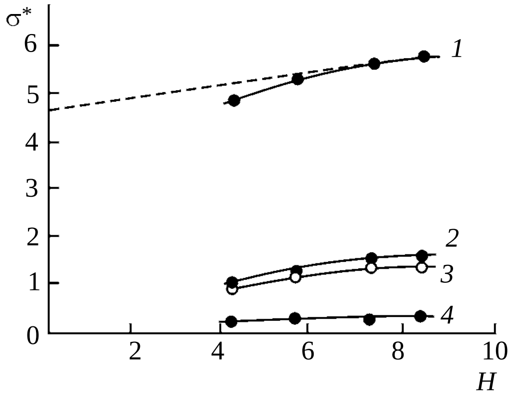


**Fig. 3.** Reduced specific magnetization σ* (A m$^2$/kg $Fe_2O_3$) vs. the magnetic field strength *H* (kOe) for the samples with iron–oxygen groups. Sample: (*1*) 0.4Fe–O/$SiO_2$, (*2*) 0.22Fe–O/$SiO_2$, (*3*) 1FeO/$SiO_2$, and (*4*) ferro gel.

specific magnetic susceptibility related to 1 g of iron and calculated by the formula $\chi_{gFe} = \chi_g(1/C + M_{gr})/(1/M_{Fe})$, where $\chi_g$ is the measured magnetic susceptibility (cm$^3$/g); $C$, concentration of $Fe^{3+}$ ions on the surface (mmol/g $SiO_2$); $M_{gr}$, molecular weight of an iron-containing group; and $M_{Fe}$, atomic weight of iron. Table 3 shows that, for both series of samples containing iron–oxygen and iron–organic groups, $\chi_{gFe}$ passes through a maximum at the degree of surface filling with these groups in the region of $\theta$ ~0.5.

The observed increase in $\chi_{gFe}$ with increasing content of the [–Fe(OH)$_2$] groups, beginning from $\theta$ 0.02 mmol/g $SiO_2$, is due to an increase in the number of Fe–O groups with parallel orientation of iron spins. As the number of Fe–O groups increases further, the influence of the nearest neighbors starts to be manifested in the appearance of the exchange magnetic interaction.

When [–FeR$_2$] groups are present on the surface of samples with $\theta$ ~0.5, the distance between the neighboring iron atoms is greater than that with the [–Fe(OH)$_2$] groups [24], and the interactions become antiferromagnetic. In fact, according to Table 2, in the case of the [–Fe(OH)$_2$] groups even at $\theta$ = 0.4 the cooperative interactions are manifested in the spectra as a sextet corresponding to the structure similar to that of $\alpha$-$Fe_2O_3$.

With the [–FeR$_2$] groups, even at $\theta$ = 1, a doublet typical for isolated Fe–O groups is still observed. In fact, bulky organic ligands prevent the generation of magnetically ordered structures.

For a more detailed examination of the magnetic behavior of the samples with iron–oxygen groups, we calculated the specific magnetization $\sigma = \chi_g H$ (cm$^3$/g). Then, we reduced $\sigma$ to the unit weight of $Fe_2O_3$ contained in the samples in the form of iron–oxygen groups ($\sigma^* = \sigma C$, where $C$ is the relative weight content of $Fe_2O_3$, which was calculated from the data of Table 1). The dependences of $\sigma^*$ on the magnetic field strength are plotted in Fig. 3. The $\sigma^*$–$H$ curves for the iron-containing samples show (Fig. 3) that, for the monolayer of Fe–O groups and for ferro gel, the dependence of $\sigma^*$–$H$ is extrapolated to $\sigma^*$ ~0, which is typical for paramagnetics [14]. The extrapolation for the sample with $\theta$ = 0.4 results in $\sigma^*_{sp,293K}$ = 4.64 A m$^2$/kg $Fe_2O_3$, i.e., this sample is characterized by spontaneous magnetization. For comparison, $\sigma^*_{sp,293K}$ for $\alpha$-$Fe_2O_3$ is 0.2 A m$^2$/kg $Fe_2O_3$ [20].

Let us consider how the magnetization varies with increasing $\theta$ and with depositing two and four monolayers of Fe–O groups. At $\theta$ = 0.01, we cannot speak about collective interaction of the atoms on the surface, as the spontaneous magnetization is absent. The increase in $\theta$ to 0.22 results in the formation of separate surface regions of magnetization with a random spin orientation. Only at $\theta$ ~0.4 the limiting concentration of iron atoms seems to be reached, at which the local surrounding of the Fe–O groups does not prevent the parallel orientation of spins within the surface atom layer and the formation of a two-dimensional magnetization area.

Additional Fe–O groups ($\theta$ > 0.4) in a monolayer give rise to the antiferromagnetic exchange, as instead of single groups on the surface the formation of greater entities, such as “islets” and “bands” of Fe–O groups, is possible. Such a possibility is supported by a theoretical analysis [21] of the dependence of the differential heat of chemisorption ($q$) on $\theta$ with regard to the mutual influence of atoms on the surface. It was shown in [21] that the groups uniformly arranged on the surface up to $\theta$ ~0.35–0.4 are single. Further chemisorption ($\theta$ ~0.45–0.5) is accompanied by the formation of clusters of two or three groups, which then join together to give (at $\theta$ > 0.55) greater “islets” and “bands.”

The antiferromagnetic exchange is also typical for the samples with one, two, and four iron–oxygen monolayers, with the coordination number of iron ion increasing in this case at the expense of the interaction between the neighboring iron atoms linked by an oxygen Fe–O–Fe bridge. Therefore, our assumption about a special state of Fe–O groups at $\theta$ ~0.4 is confirmed: specifically at this or close content of Fe–O groups their ferrimagnetic ordering is realized. Note also that the reduced spontaneous magnetization of a magnetically ordered layer remains almost unchanged in the temperature range 90–293 K ($\sigma^*_{sp,90K} = \sigma^*_{sp,293K}$ = 4.63 A m$^2$/kg $Fe_2O_3$), i.e., all the characteristics of magnetic exchange are ensured by the covalent bonding of iron–oxygen groups with the support. This fact is very important, because, according to [22, 23], the thermal excitation ($T \neq 0$) prevents a particular spin orientation in an applied magnetic field. In our case, the ferrimagnetism occurs only when the interaction between the neighboring iron ions is so strong that their spins retain the parallel orientation in spite of the thermal action. The data obtained point to a specific state of iron ion monolayer with $\theta$ ~0.4, which is due, among other factors, to the orienting effect of the support surface on the parallel orientation of spins of these ions.

On the whole, the data obtained in this work suggest that the magnetic ordering arises at a certain content of Fe–O groups deposited on the surface of a diamagnetic support. Two sources of the effect responsible for the magnetic state are indisputable: the orienting effect of the silica support on the iron–oxygen groups bound to it by covalent bonds and the possibility of exchange interactions between the neighboring iron–oxygen groups (in particular, via the silica support).

## EXPERIMENTAL

The Fe–O and Fe–OR (R is an organic group) groups and Fe–O monolayers (1–4 monolayers) on the surface of dispersed silica (ShSK silica gel, $S_{sp}$ = 275 $m^2/g$, pore diameter 100–140 Å) were prepared at 200–275°C by the molecular deposition technique [24, 25], also known as atomic layer epitaxy (ALE) [26]. The synthesis of oxides by this technique is based on two alternating irreversible surface reactions between functional groups of silica (e.g., silanol ≡Si–OH) and appropriate low-molecular-weight compounds.

$$m(\equiv\text{Si–OH}) + \text{ECl}_n \longrightarrow (\equiv\text{Si–O–})_m\text{ECl}_{n-m} + m\text{HCl}, \quad (3)$$

$$(\equiv\text{Si–O–})_m\text{ECl}_{n-m} + (n - m)\text{H}_2\text{O} \longrightarrow (\equiv\text{Si–O–})_m\text{E(OH)}_{n-m} + (n - m)\text{HCl}. \quad (4)$$

In the case of the reaction with $FeCl_3$, the replacement of all the OH groups on the silica surface by the cycle of reactions (3) and (4) yields a monolayer of iron–oxygen groups chemically bound to the silica framework. The number of such cycles determines the number of deposited monolayers. Since the samples with a monolayer of iron–oxygen (Fe–O) groups contain the maximal number of these groups, we take the degree of replacement of OH groups by iron–oxygen groups (θ) to be unity (θ = 1) for such samples. The samples with the content of Fe–O groups less than unity ($\theta < 1$) were obtained by performing reaction (3) with silica gel containing various amounts of surface OH groups. Such silica gel was prepared by heat treatment at 200–1000°C. The content of OH groups was maximal in the sample with the fully hydroxylated surface ($T_{tr}$ = 200°C): 3.3 mmol OH/g $SiO_2$, and the minimal content was 0.03 mmol OH/g $SiO_2$.

The samples were prepared in a flow of thoroughly dried argon (dew point –80°C) in a flow-through Pyrex reactor using the installation described previously [27]. Silica gel was first treated to remove impurities ($Fe^{3+}$, $Al^{3+}$) with 3 N HCl; then it was washed with water to remove chloride ions and hydrated with water vapor at 200°C. As reagents in reaction (3) we used vapors of anhydrous $FeCl_3$ and $FeCl(C_5H_7O_2)_2$, which were formed when the reagents were sublimed in a flow of argon. After carrying out reactions (3) and (4), we analyzed the product for the OH groups (by the reaction with $CH_3MgI$) and for the chloride, $Fe^{3+}$, and $Fe^{2+}$ ions (by photocolorimetry).

Ferro gel (FeOOH) was prepared by the reaction of $FeCl_3$ with $NH_4OH$, following the procedure in [28], and heated at 250°C.

The magnetic susceptibility of the samples $\chi_g$ ($cm^3/g$) was measured by the Faraday method at the Institute of Chemistry, St. Petersburg State University. The measurements were carried out in the temperature range 90–293 K at four magnetic field strengths: 4100, 5820, 7190, and 8280 Oe. The $\chi_g$ values were determined using nickel sulfate ($NiSO_4 \cdot 10H_2O$) obtained from the Institute of Standardization and Metrology (St. Petersburg) as a reference substance with $\chi_g = 16.910 \times 10^{-6}$ $cm^3/g$. The measurement accuracy was 2%. The Mössbauer spectra were recorded on a Wissel spectrometer. The $^{57}Co$ isotope in a rhodium matrix was the source of γ-quanta. We used metallic iron (α-Fe) as a reference for calibrating the chemical shifts (δ) and determining all the Mössbauer parameters. All the measurements were carried out at room temperature. The X-ray phase analysis was performed on a DRON-2 diffractometer by the powder method. The specific surface area of the samples was determined by the Brunauer–Emmett–Teller method, from low-temperature air adsorption.

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