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Magnetism of adsorbed oxygen at low coverage

Igor S. Altman,[1,2] Peter V. Pikhitsa,[1,*] Young-Jeong Kim,[1] and Mansoo Choi[1,†]
[1]*National CRI Center for Nano Particle Control, Institute of Advanced Machinery and Design, School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, Korea*
[2]*School of Environmental Engineering, Faculty of Environmental Sciences, Griffith University, Brisbane, 4111, QLD, Australia*

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We report the magnetic measurement for oxygen adsorbed on different substrates at low coverage. An intriguing behavior of the oxygen magnetization against the applied magnetic field has been found. We demonstrate that it is an interplay between the substrate orientation of oxygen molecules and a weak antiferromagnetism of unit spins occurring via the substrate that shows such a behavior. The conclusion is made that the interaction of the oxygen molecules with the substrate (being neglected in previous work) plays a crucial role on the physical properties of the system.

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I. INTRODUCTION

The study of magnetic properties of oxygen adsorbed on a surface has a long history. The interest particularly is caused by the ability of oxygen to create a magnetic phase at low temperatures.[1–6] Being adsorbed on different substrates oxygen can form amorphous layers which are a convenient ground to test theoretical models describing magnetic systems. At the same time, despite many years of study of oxygen magnetism, many important aspects of its behavior remain open. So, for low oxygen coverage the careful measurements of oxygen magnetization are lacking. Note that in the papers devoted to the study of magnetism of oxygen adsorbed on different substrates the main attention was paid to the study of the $M-T$ curves,[7–13] which may bring only the general information on magnetic behavior. Such details as the characteristics of the oxygen spin-spin interaction and its interaction with the substrate could be extracted from peculiarities of the $M-H$ curves at low temperatures appearing against paramagnetic saturation. However, such experiments have not been done yet. It is worth mentioning that for the analysis of the oxygen magnetization measurements the reliable information on the orientation distribution of oxygen molecular axes is needed. The best case for the analysis is the one when all the axes are parallel. However, such a case is unlikely achieved in the experiment due to the usual nonperfect parallelism of the adsorbing surfaces.[2,6] The possible tilt angle (as well as its distribution) of the oxygen molecule on the surface also leads to a lack of the oxygen axis parallelism. Another possible case, which can be analyzed, is realized at the random orientation distribution of the oxygen molecular axes. This is easily achieved at the random orientation distribution of the adsorbing surfaces.

In the present work we carefully investigate the magnetization of oxygen adsorbed on the surface of onionlike carbon nanoparticles at low oxygen coverage. These particles consist of contiguous graphitic shells (which are the ideal substrate for oxygen adsorption). The choice of the onionlike carbon nanoparticles for this research is caused by the particle purity and uniformity that is crucial for an analysis of the experimental results. Let us emphasize that the randomness of the graphitic shells orientations yields the randomness of the oxygen molecular axis orientations.

The onionlike carbon nanoparticles are synthesized utilizing the same experimental setup as we used to control the size, morphology, and crystalline phase of silica and titania nanoparticles during their formation in flames.[14–17] The particles were generated as a result of the acetylene conversion in a co-flow oxy-hydrogen diffusion flame that is irradiated by the laser beam. The detail description of the particle synthesis is going to be done in a forthcoming paper. The transmission electron microscope (TEM) images of the particles are shown in Fig. 1. As one can see in Fig. 1 the synthesized particles are identical in structure and do not have any impurities.

II. EXPERIMENTAL APPROACH

The magnetization of oxygen adsorbed on a substrate can be derived from the experimental data as follows. First, the magnetization of the substrate is measured in an applied magnetic field. Then it is subtracted from the magnetization of the same substrate having been exposed to some oxygen dose. The obtained difference is ascribed to the magnetization of adsorbed oxygen. In order to succeed such a procedure the accuracy of measurements should be very high, especially when low oxygen coverage is studied. However, if the sample is sealed in a container for the measurements (as is usually done), an imperfection of making the exactly same

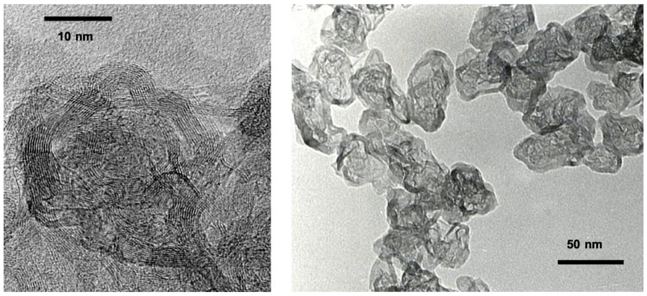

FIG. 1. TEM images of the onionlike carbon nanoparticles.

sealing for both cases (with and without oxygen) does not allow one to extract the oxygen magnetization unambiguously at least at low coverage. At the same time if the substrate is exposed to oxygen adsorption just inside the measuring system, then the problem related to the magnetization variation from a sealing substance disappears, and therefore the additional magnetization coming from the adsorbed oxygen can be measured very precisely. Although the described method does not allow one to know the exact amount of oxygen adsorbed, the experimental data on oxygen magnetization at low coverage can be treated in a proper way described below.

Let us describe our experiment in detail. The magnetization measurements were carried out with a commercial SQUID (superconducting quantum interference device) magnetometer (Quantum Design, MPMS 7). In order to adsorb oxygen on the surface of particles we utilized a device peculiarity of the SQUID system containing a little amount of oxygen inside the sample chamber due to a leakage.[18] The carbon nanoparticles were put in a gelatin capsule attached to the transport rod by a straw. The mass of carbon nanoparticles in the experiment we report was $m = 16.22$ mg. We found out that if such a sample is kept inside the SQUID at a fixed temperature ranged from about 55 K to about 100 K its magnetic moment at an applied magnetic field increases with time. At temperatures below 55 K the magnetic moment did not change with time. No change of the sample magnetic moment was found in the case when the gelatin capsule did not contain any carbon nanoparticles. We concluded that oxygen precipitated on the capsule being a liquid at temperatures above 55 K could penetrate the gelatin capsule and be adsorbed on the surface of the carbon nanoparticles leading to the increase of the magnetic moment. At temperatures below 55 K the adsorption does not occur likely due to oxygen freezing. Then if the sample is maintained at a temperature above 55 K and then cooled down, the additional magnetic moment at low temperatures comes from the adsorbed oxygen. Since the magnetic moment before and after oxygen adsorption is measured for the same sample, the high precision in determination of the additional magnetic moment is easily achieved that allows one to study low oxygen coverage accurately.

We introduced the sample into the SQUID at about 5 K and measured its magnetic moment at the temperatures not exceeding 55 K, which was used as a reference value. Then the sample was heated up to 60 K and was maintained at this temperature for a different time to provide different oxygen doses adsorbed. After this the sample was cooled down and its magnetization was measured again. Subtracting the data we obtained $M-T$ (magnetic moment vs temperature) curves and $M-H$ (magnetic moment vs applied magnetic field) curves at the different temperatures for the magnetization coming from the adsorbed oxygen at different coverage values. Since we do not know the actual amount of oxygen adsorbed hereinafter we present data with the magnetic moment instead of the magnetization of adsorbed oxygen commonly used.

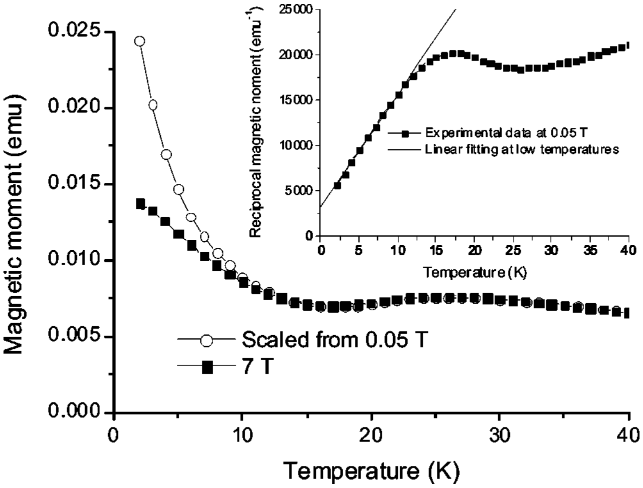

FIG. 2. The $M-T$ curves measured for the same oxygen dose adsorbed on carbon nanoparticles at different magnetic fields. The magnetic moment at 0.05 T is multiplied by 140 for an easy comparison. The inset shows the Curie plot for the magnetic moment at 0.05 T.

III. RESULTS AND DISCUSSION

In order to demonstrate the occurrence of paramagnetic saturation we plotted in Fig. 2 the $M-T$ curves measured for the same oxygen dose at different magnetic fields (0.05 and 7 T). The $M-T$ curve at the low magnetic field is scaled for a comparison. As one can see at the low temperatures the magnetic moment at the high magnetic field is much smaller than that (being scaled) at the low magnetic field. It certainly comes from the paramagnetic saturation. Note that the low temperature part of the $M-T$ curve at a low magnetic field can be represented by the Curie-Weiss law $[M = C/(T-\theta)]$ with the Weiss temperature, θ, about -3 K, which is extracted from the linear $M^{-1}-T$ dependence (see the inset in Fig. 2). As one can see the Curie-Weiss dependence is violated at temperatures above about 12 K. The latter temperature is the same as that for the magnetic transition recently reported for monobilayer oxygen adsorbed on the graphite.[4]

For a careful analysis of the paramagnetic saturation we studied $M-H$ curves measured at different temperatures for the same oxygen dose. The typical $M-H$ curve at 2 K is shown in Fig. 3. As we mentioned earlier we could not control the exact amount of oxygen coverage. At the same time it is clear, that, for instance, the value of the magnetic moment M_0 at the maximal magnetic field H_0 (7 T in our experiment) increases with coverage increase. Then it can characterize the coverage. Moreover, we found out a scaling of the $M-H$ curves, which means that after multiplication of the magnetic moment by a corresponding factor all $M-H$ curves exactly coincide (see the inset in Fig. 3 where the data for minimal and maximal coverage are presented). It allows one to claim that M_0 is proportional to the oxygen coverage. Since M_0 was varied in about 44 times in our experiment (from 0.000 64 emu to 0.028 emu), then the oxygen coverage was also changed in the same manner. The absolute value of the coverage will be discussed below. The $M-H$ curve

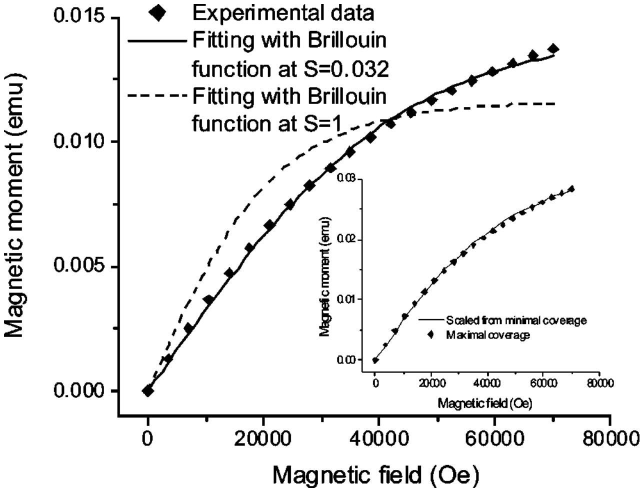

FIG. 3. The typical $M-H$ curve measured at 2 K for oxygen adsorbed on carbon nanoparticles. The different fittings are also presented. The inset demonstrates the scaling of the magnetic moment. The magnetic moment at minimal coverage is multiplied by the factor of 44 for a comparison.

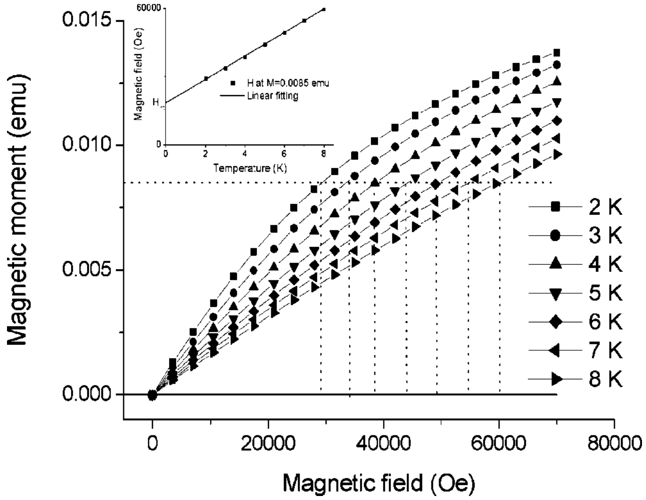

FIG. 4. The $M-H$ curves measured at different temperatures for oxygen adsorbed on the carbon nanoparticles. The procedure of the extraction of the $H_{int}(M)$ dependence with the assumption of the strong antiferromagnetic interaction in the system (see text) is illustrated. The inset demonstrates a possibility of the procedure suggested.

shown in Fig. 3 exhibits a saturating trend at high magnetic field conventional for paramagnetic systems. Such a behavior might be described by the Brillouin (B_S) function as[19]

$$M = NgS\mu_B B_S(\xi), \tag{1}$$

where N is the number of paramagnetic centers, g is their g factor, and S is the value of the spin; $\xi = gS\mu_B H/(k_B T)$, μ_B and k_B are the Bohr magneton and the Boltzmann constant. Hereinafter we use the value of $g=2$. The best fit to the experimental data (see Fig. 3) corresponds to $S=0.032$. So small a spin value of an oxygen molecule (which has unity spin in the ground state) is unrealistic even taking into account the spin reduction for a two-dimensional (2D) oxygen system discussed elsewhere.[6] The fit with the value of $S=1$ is also presented in Fig. 3 for a comparison. The impossibility to fit the data with a realistic value of spin might be related to the occurrence of antiferromagnetic interaction in the system. In this case instead of the applied magnetic field H in Eq. (1) the effective one H_{eff} should be substituted in the expression for ξ. Usually it is written as $H_{eff} = H - H_{int}$ with the interaction field (in the mean-field approximation) $H_{int} = \alpha M$. Instead of finding out the constant α that gives the best fit, we extracted the actual $H_{int}(M)$ dependence, which would lead to the $M-H$ curves observed in the experiment. The idea we applied is very simple. It is illustrated in Fig. 4 where the $M-H$ curves at different temperatures are given. If Eq. (1) with H_{eff} works then the points with the same M but at the different temperatures correspond to the same values of H_{eff}/T. From the experimental data we can derive the values of H yielding the same magnitudes of the magnetic moment M at the different temperatures. Then due to the perfect linearity of H against T (see the inset in Fig. 4), the intercept of the $H(T)$ dependence at a certain value of M with Y axis gives the value of H_{int} at this value of the moment, while the slope of the dependence gives the value of H_{eff}/T. The $H_{int}(M)$ dependence extracted in this way is presented in Fig. 5. We are not aware of any model being able to give such a dependence of the antiferromagnetic exchange field upon the magnetic moment. We claim that the dependence in Fig. 5 is rather apparent than the real one. It likely comes from the incorrect consideration of the oxygen spin behavior made above.

Indeed, using Eq. (1) to fit the experimental data we implicitly assume that all oxygen molecules contributing to the magnetic moment have spins parallel to the magnetic field. It may be correct only in the case of free molecules. However, it is undoubtedly wrong in the case of oxygen molecules attached to the surface since the spin direction of an oxygen molecule is determined by its molecular axis. Let us find out more realistic expression of magnetic moment.

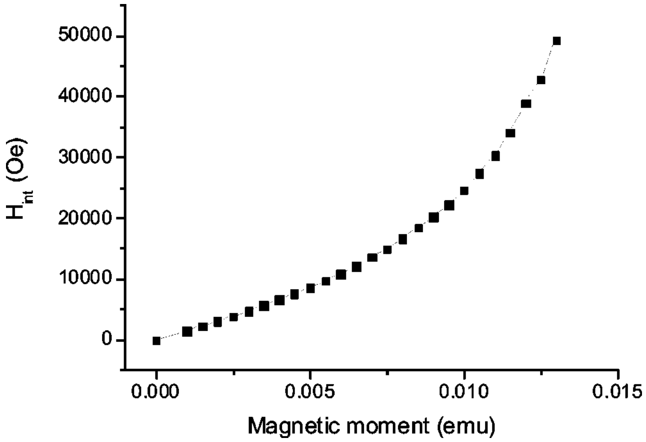

FIG. 5. The $H_{int}(M)$ dependence extracted from the experimental $M-H$ curves at different temperatures for oxygen adsorbed on the carbon nanoparticles with the assumption of the strong antiferromagnetic interaction in the system (see text).

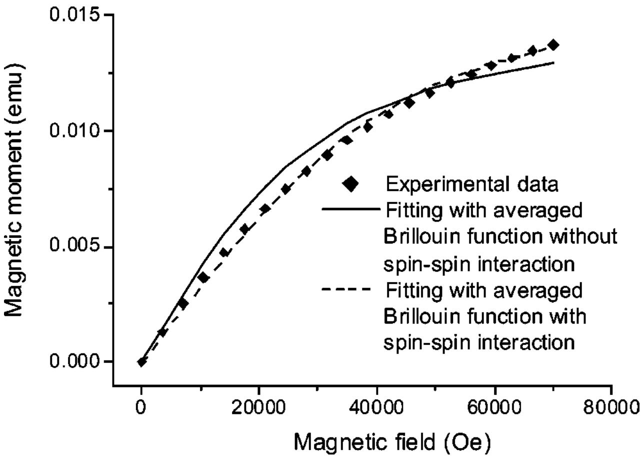

FIG. 6. The typical $M-H$ curve measured at 2 K for oxygen adsorbed on the carbon nanoparticles. The fittings using the averaged Brillouin function with and without spin-spin interaction are also shown.

In the case of the random distribution of the molecular axis directions the expression

$$\overline{B_S(\xi)}=\frac{\int_0^{\pi/2} B_S[\xi\cos(\theta)]\cos(\theta)\sin(\theta)d\theta}{\int_0^{\pi/2}\sin(\theta)d\theta} \tag{2}$$

should be used in Eq. (1) instead of $B_S(\xi)$. As one can easily see the averaging according to Eq. (2) leads to the reduction of the magnitude of the magnetic moment compared to that given by Eq. (1) at the same values of all the parameters. The reduction at a low magnetic field is three times while at a high magnetic field it is two times. We will discuss these numbers below. The fit using the $\overline{B_S(\xi)}$ function is given in Fig. 6 showing much better agreement with the experimental data than the fit with the $B_S(\xi)$ function.

Although the idea about the random spin distribution for noninteracting adsorbed oxygen molecules might explain the straightening of the experimental $M-H$ curve compared with that for the free spins described by the $B_S(\xi)$ function, it does not fit the $M-H$ curve in detail. Furthermore, the $M-T$ dependence at the low magnetic field calculated using the expression $M=NgS\mu_B\overline{B_S(\xi)}$ obeys the Curie law but not the Curie-Weiss one. It means that some additional assumptions are needed to match the experimental data (it would be possible if the fitting function is more straightened than the one with $S=1$).

In order to improve the fitting we may introduce a spin-spin interaction. The spin Hamiltonian can be expressed as

$$\hat{H}_{int}=-2\sum_{i>j} J_{ij}\vec{S}_i\vec{S}_j. \tag{3}$$

It is worth noting that in the system like ours the rigorous description of the spin-spin interaction is clumsy even for neighbor spins. The latter comes from the nonparallelism of the oxygen molecules due to the tilt angle on the surface. Since we want only to check the influence of the spin-spin interaction on the fitting but not to fit the experimental data precisely we can limit ourselves by the simplest case of the interaction of the nearest-neighbor spins considering them as the parallel ones. In the latter case the product can be easily calculated. Then taking into account $\hat{H}_{int}$ for the system with $S=1$ we obtain the following expression for the magnetic moment at the random spin distribution choosing $J_{ij}=J=\text{const}$:

$$M(H,T)=NgS\mu_B\frac{\int_0^{\pi/2} M_\theta(H,T)\sin(\theta)d\theta}{\int_0^{\pi/2}\sin(\theta)d\theta}, \tag{4}$$

where

$$M_\theta(H,T)=\frac{2\left[\sinh\left(\frac{4\mu_B H\cos(\theta)}{k_B T}\right)\exp\left(\frac{-A}{T}\right)+\sinh\left(\frac{2\mu_B H\cos(\theta)}{k_B T}\right)\cosh\left(\frac{A}{T}\right)\right]\cos(\theta)}{2\cosh\left(\frac{4\mu_B H\cos(\theta)}{k_B T}\right)\exp\left(\frac{-A}{T}\right)+4\cosh\left(\frac{2\mu_B H\cos(\theta)}{k_B T}\right)\cosh\left(\frac{A}{T}\right)+2\cosh\left(\frac{A}{T}\right)+\exp\left(\frac{2A}{T}\right)} \tag{5}$$

and $A=-2J/k_B$.

As one can see at $A=0$ the magnetic moment given by Eq. (4) exactly coincides with that following from Eq. (1) using the $\overline{B_S(\xi)}$ function instead of the $B_S(\xi)$ one at $S=1$. The use of Eq. (4) at $A=0.9$ K allows one to improve the fit of $M-H$ curve significantly (see Fig. 6). The sign of A corresponds to the antiferromagnetic interaction. Then the introduction of the antiferromagnetism explains the observed Curie-Weiss temperature dependence of the magnetic moment. It is worth noting finally that the straightening of the $M-H$ curves due to the random distribution of the spin directions is much stronger than that coming from the spin-spin interaction.

The specific surface area of the carbon nanoparticles, a_S, estimated from the TEM image is about 100 m^2/g. Using Eq. (4), which fits the experimental $M-H$ curves we can extract the number of the oxygen molecules N contributing to the magnetic moment. Then the oxygen coverage ρ represented as

$$\rho=\frac{N}{ma_S\cdot 6.36\times 10^{18}(\mathrm{m}^{-2})} \tag{6}$$

can be easily calculated. The factor 6.36×10^{18} (molecules/m^2) in the denominator in Eq. (6) characterizes the density of $\sqrt{3}\times\sqrt{3}$ oxygen structure. We found out that in our experiment the oxygen coverage calculated according to Eq. (6) varied from about 0.0077 to about 0.34 while its value at the state shown in Figs. 2–4 and 6 was about 0.165. We have to reiterate that at the low temperatures both $M-H$ curves and $M-T$ curves exhibited scaling at different coverage.

Our experiment undoubtedly demonstrates the randomness of the spin directions of the oxygen molecules adsorbed on the surface. Then the geometrical averaging reduces the Curie constant of such a system compared to that for the free spins. The reduction is about 3 for not very high magnitude of the applied magnetic field. Such a reduction could be distinguished even in the previous papers devoted to the study of the magnetization of adsorbed oxygen[7,11] if the low-temperature susceptibility were carefully examined. Then a comparison of the Curie constant for adsorbed oxygen with that for free spin oxygen (but not with the reduced value) that had been done in the recent papers on the oxygen magnetization has no sense.

The found scaling of the $M-H$ curves (which means an independence of their shape on the coverage) comes from an independence of spin-spin interaction on the coverage, i.e., on the distance between the oxygen molecules. It leads us to infer that the spin-spin interaction between the oxygen molecules does not occur directly but is likely realized via a substrate. The weakness of the constant A needed in order to match the experimental dependence supports this suppose. In this case the constant of the spin-spin interaction should depend on the substrate substance. In order to check such a hypothesis we additionally examined two substrates, namely, multiwalled carbon nanotubes (MWNT's) and MgO nanoparticles, which also may provide the randomness of the oxygen molecular axis orientations. The magnetization of oxygen adsorbed on MWNT's did not show any difference from that for the carbon nanoparticles while some dissimilarity was found in the case of oxygen adsorbed on the MgO nanoparticles confirming our assumption.

The Weiss temperature for oxygen adsorbed on the MgO nanoparticles was found from the $M-T$ curve to be about -2 K unlike the value of -3 K for oxygen on the carbon nanoparticles. The $M-H$ curves for both cases (oxygen on carbon and oxygen on MgO) are shown together in Fig. 7 clearly exhibiting the difference. The magnetization curve described by the expression $M=NgS\mu_B\overline{B_S(\xi)}$ is also plotted in Fig. 7 for a comparison. All the curves are scaled to the same value of M_0. The fitting of the $M-H$ curves for the MgO case (see Fig. 7) gave us the value of $A=0.5$ K unlike the value of $A=0.9$ K for carbon. We have to remind that the curve $M=NgS\mu_B\overline{B_S(\xi)}$ corresponds to zero value of the constant A. It is worth noting that the absolute values of the constant of the spin-spin interaction are in agreement with the values of the Weiss temperatures, i.e., the absolute value of the Weiss temperature increases with the A increase.

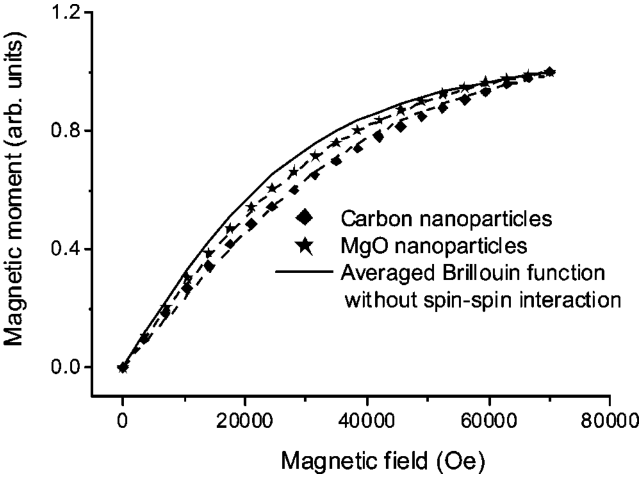

FIG. 7. The typical $M-H$ curves measured at 2 K for oxygen adsorbed on the carbon nanoparticles and on the MgO nanoparticles. The dashed lines fit the $M-H$ curves using the averaged Brillouin function with spin-spin interaction. The averaged Brillouin function without spin-spin interaction is plotted for a comparison.

Although Eq. (4) perfectly fits the experimental $M-H$ dependence at a given temperature it fails to fit the $M-T$ dependence at a given applied magnetic field in detail. So, the ratio $M_0(2\ \mathrm{K})/M_0(8\ \mathrm{K})$ extracted from the experiment with oxygen on the carbon nanoparticles is about 1.42 while its value obtained using Eq. (4) is about 1.97. We believe that this discrepancy likely comes from the spin reduction effect known for the 2D oxygen system.[6] Indeed, the magnitude of the spin reduction (and therefore the spin itself) may depend on the temperature yielding some temperature dependence of the value considering as the constant in Eq. (4). However, the analysis of this spin reduction lies beyond the scope of the present paper.

Summarizing, we found an intriguing behavior of the magnetic moment of oxygen adsorbed on different substrates at very low coverage. The analysis of corresponding $M-H$ and $M-T$ curves led to a conclusion that it is an interplay between the substrate orientation of the oxygen molecules and a weak antiferromagnetism of unit spins occurring via the substrate that shows such a behavior. This conclusion brings in the idea that the interaction of the oxygen molecules with the substrate (being neglected in previous work) plays a crucial role (at least at low coverage) on the physical properties of the system.

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[*] On leave from Physics Institute, Odessa National University, Odessa, Ukraine.

[†] Corresponding author. Email address: mchoi@plaza.snu.ac.kr

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