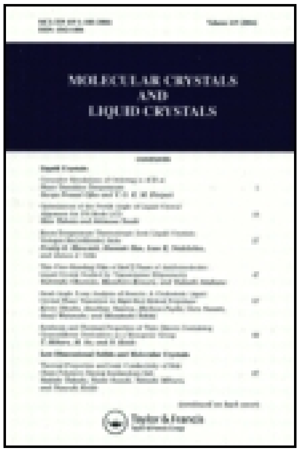

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Magnetic Properties of Adsorbed Oxygen in Microporous Carbon

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MAGNETIC PROPERTIES OF ADSORBED OXYGEN IN MICROPOROUS CARBON

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Abstract Microporous activated carbon fibers consisting of a disordered network of micrographites provide a micropore random network available for the adsorption of a large amount of gaseous materials. We investigate magnetic properties of oxygen molecules condensed in the micropore as a molecule-based random magnet. Magnetic susceptibility shows Curie-Weiss temperature dependence with the Weiss temperature of about -20K at low oxygen concentrations below 1% of the saturation concentration. The increase in the oxygen concentration makes the development of the second contribution to the susceptibility that has a broad hump around 60K. The magnetic behavior is explained in term of the formation of antiferromagnetic oxygen clusters on micrographitic domains, where the internal and marginal oxygen molecules in the cluster contribute to the susceptibility with a short range order hump and the Curie-Weiss susceptibility, respectively.

INTRODUCTION

In the condensed state of oxygen molecules, there are a large variety of phases due to the cooperation of translational, rotational and magnetic degrees of freedom in oxygen molecules.[1,2] Paramagnetic liquid phase is crystallized below T_f=54.4K. In the solid states, oxygen has three different phases depending on temperature. The highest temperature phase (γ) stabilized in the temperature range $43.8K<T<54.4K$ is described in terms of one dimensional antiferromagnetic chains where the rotational degree of freedom survives in an oxygen molecule. The lowering of temperature generates the β–phase having the features of a triangular frustrated spin system at $23.9<T<43.8K$. The lowest temperature phase (α) has antiferromagnetic long range ordering with the two sublattice structure below 23.9K. The introduction of oxygen molecules in a random microporous network is interesting from the view point of a random magnetic system based on molecules that is expected to have a totally different magnetic structure from that of the bulk oxygen system. In this respect, microporous carbon provides a good host in which oxygen molecules form a random condensed structure associated with the randomness and the restricted geometry of its random microporous network. In this paper, we investigate the magnetic properties of condensed oxygen molecules accommodated in activated carbon fibers (ACFs) with huge specific surface area (~3000m^2/g), which has a random network of micrographites consisting of the stacking of three to four graphene sheets with the dimension of $30 \times 30\,\text{Å}^2$. Oxygen molecules adsorbed on slit-shaped pores[3,4] associated with the narrows between graphene sheets of adjacent micrographites are expected to give interesting features of a molecular based random magnet.

EXPERIMENTAL

We employed phenol-based activated carbon fibers (FR20, Kurare Chemical Co. Ltd.) having specific surface areas of 2000m^2/g. About 20mg of ACFs loaded in a quartz tube cell was degassed through the heat-treatment at 200℃ in vacuum before oxygen adsorption. After the sample cell was loaded in the cryostat of Quantum Design SQUID magnetometer, we carried out the adsorption isotherm, magnetic susceptibility and magnetization measurements. Gas adsorption was performed at 60K up to the oxygen vapor pressure of $P_S = 5.4\text{Torr}$. Magnetic susceptibility was measured at 1T in the temperature range 2-60K and magnetization curves were measured up to 5.5T at 60K. In order to obtain the net values of the susceptibility and magnetization of adsorbed oxygen, we subtracted the contribution of ACFs from the observed data.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherm of oxygen at 60K. The adsorption isotherm shows a steep increase at low pressures below $P / P_S \approx 0.01$ where P_S is the vapor pressure of oxygen at 60K, and then saturates to the value of 600mg/g. In the case of oxygen adsorption on the surface of regular graphite, the isotherm shows a multi-step

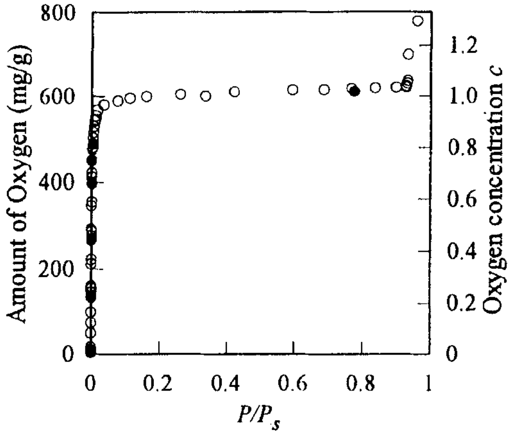

FIGURE 1 Oxygen adsorption isotherm at 60K where vapor pressure of oxygen P_s is 5.4Torr. Solid circles indicate the points where susceptibility and magnetization are measured.

structure caused by the successive development of layered structure on the surface.[5] The observed simple one-step saturation feature is considerably different from the multi-step adsorption isotherm for regular graphite with infinite flat surface. This indicates that oxygen molecules are adsorbed with random filling in micropores. Susceptibility and magnetization curves are investigated at the points indicated with solid circles in Figure 1, where oxygen concentration is expressed as the ratio c of the corresponding oxygen amount to the saturated amount.

Figure 2 (a) shows the temperature dependence of magnetic susceptibility of oxygen adsorbed on ACF with different concentrations. At low concentrations below about $c = 0.01$, the susceptibility obeys the Curie-Weiss law with the antiferromagnetic Weiss temperature ranging ~-20K. At higher concentrations, the increase of oxygen concentration makes the susceptibility reduced considerably. The temperature dependence indicates the development of the susceptibility contribution having a broad feature around 20-60K at the expense of the Curie-Weiss contribution at low temperatures with the increase of oxygen concentration. In order to discuss the magnetic structure, the susceptibility in the higher oxygen concentration region is decomposed into the Curie-Weiss contribution χ_{Curie} and the contribution χ_b having a broad feature around 20-60K as given in Figure 2 (b). It is worth comparing the feature of the susceptibility to that of bulk oxygen which is also shown in Figure 2 (b). The susceptibility of the oxygen

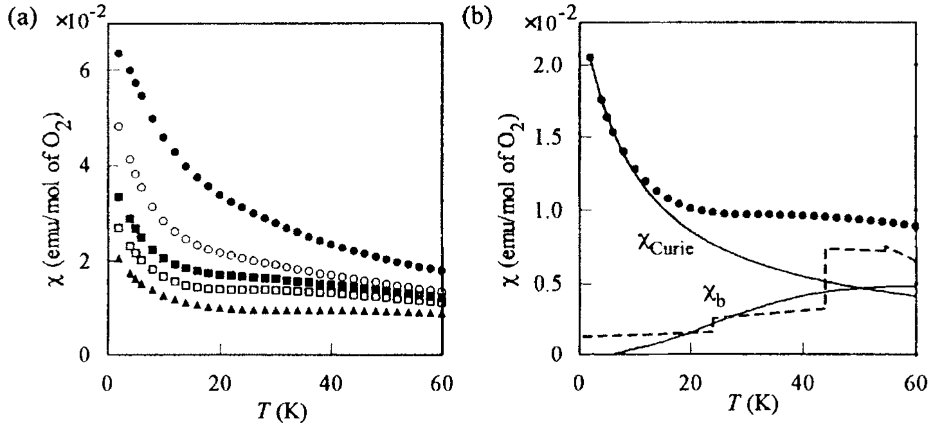

FIGURE 2 (a) Magnetic susceptibility of adsorbed oxygen at various concentrations; *c*=0.01, 0.21, 0.43, 0.65, 1.0 (from top to bottom). (b) The decomposition of the susceptibility at *c*=1.0 into the Curie-Weiss contribution χ_{Curie} and the contribution χ_b with a broad hump. A dashed line shows bulk oxygen after ref.2, where the oxygen concentration is adjusted to the amount of oxygen involved in χ_b.

condensed phase in the micropores reveals the absence of discontinuous changes associated with the phase transitions which ordinary bulk oxygen has. This finding proves the absence of definite phase transitions in oxygen condensed in the micropore network, resulting in random structural features below the freezing point. The feature of the susceptibility having the two contributions suggests the presence of two kinds of oxygen molecules surrounded by different environments. The Curie-type spins are related to isolated molecule from the surrounding, although they are affected by the weakly antiferromagnetic molecular field ranging ~-10K. The susceptibility having a broad hump is suggestive of the antiferromagnetic short range order behavior of oxygen spins interacting with each other through rather strong antiferromagnetic interaction and is considered to be associated with the modified structure of bulk oxygen caused by the randomness and the restricted geometry of the micropore network. Here, it is worth reminding the case of adsorbed oxygen on porous Vycor glasses that forms the similar phase to γ-phase of bulk solid oxygen,[4,5] where there is the coexistence of one dimensional antiferromagnetic chains and Curie-Weiss spins. Different from the oxygen on porous Vycor glasses, the behavior of the susceptibility χ_b is far from that of ordinary one dimensional antiferromagnet, but resembles the behavior of the bulk oxygen if the

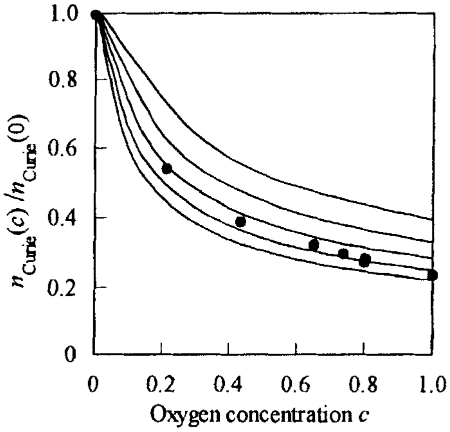

FIGURE 3 The number of Curie spins as a functions of adsorbed oxygen concentration. Solid lines denote the estimations with different oxygen cluster sizes; 29, 36, 43, 50 and 56Å from top to bottom.

discontinuous changes are neglected.

Next we discuss the local structure of an oxygen molecule randomly surrounded by neighboring oxygen molecules in a micropore in order to investigate the disordered feature of the magnetic structure on the basis of the adsorption on the surface of micrographitic domains. Figure 3 shows the number of Curie-type spins as a function of oxygen concentration which is obtained from the analysis of χ_{Curie}. The number of spins decreases steeply at low concentrations, and tends to saturate at higher concentrations. This indicates that antiferromagnetic clusters grow up on the surface of micrographites at the expense of the Curie-type spins with increasing the oxygen concentration, although the Curie-type spins still exist even at the saturated concentration. As mentioned in the Introduction, the structure of ACFs is explained in terms of the network of micrographites consisting of the stacking of three to four graphene sheets with the dimension of ca. $30 \times 30\,\text{Å}^2$. Therefore, the adsorption of oxygen molecules is governed by the surface of micrographites. In this connection, the oxygen adsorption on the surface of regular graphite is suggestive to the case of ACFs. On the regular surface of graphite, the two dimensional hexagonal arrangement of oxygen molecules are develops as the concentration increases where the molecular axis of an oxygen molecule is oriented perpendicular to the surface plane in order to achieve maximum packing in the ζ-phase.[8] On the contrary, the finiteness in the size of a micrographite domain modifies the arrangement of oxygen molecules in the micropores. Adsorbed oxygen molecules form the cluster on the surfaces of graphitic microdomains, where oxygen molecules around the marginal regions of the clusters are affected by the randomness of the peripheries of graphitic microdomains, resulting in more relaxed structure than that of regular graphite. Based on the idea mentioned above, the observed magnetic susceptibility is interpreted in terms of the contribution from the oxygen molecules in the hexagonal packed region and that in the marginal region, which correspond to χ_b and χ_{Curie}, respectively. Namely after the nucleation starts at a site on the graphitic surface, an oxygen cluster with the hexagonal structure develops on the basis of the nucleation site. Inside the cluster, the hexagonal structure is well stabilized, although the oxygen molecules located around the margin of the cluster have relaxed structure due to the deficiency of neighboring oxygen molecules, resulting in the deviation of the molecular axis from the direction perpendicular to the graphitic plane and the increase in the intermolecular distances. The situation in the oxygen cluster structure mentioned above gives a specific feature in its magnetic structure especially around the saturated concentration. The internal oxygen molecules densely packed with the hexagonal arrangement are coupled with each other through the antiferromagnetic exchange interactions with the same strength, while the spins of marginal oxygen molecules are weakly affected by the internal field associated with the spins of the oxygen molecules belonging to the densely packed region.

Here, we present a quantitative explanation for the analysis of the observed magnetic susceptibility. The following simple model gives the concentration of the Curie-Weiss spins as a function of oxygen concentration. At the beginning of the oxygen adsorption, a oxygen molecule is assumed to be adsorbed at the center of the surface of a micrographite domain having a regular hexagon shape with the diagonal distance of about 30Å. An oxygen cluster with hexagonal shape develops isotropically from the center where the number of nearest neighbors and the nearest neighbor distance are given to be $z=6$ and 3.3Å from the corresponding values of the ζ-phase on the regular graphite surface.[8] The calculation of the numbers of internal oxygen molecules n_b and surface ones n_c in the hexagonal cluster gives the concentration of Curie-type spins $n_b/(n_b+n_c)$, where the saturated concentration is defined as the concentration at which the hexagonal graphite domain is completely covered with oxygen molecules. The expected concentration dependence of the Curie spins is shown in Figure 3, where we employ five hexagonal oxygen cluster with different sizes; 29, 36, 43, 50 and 56Å. Comparison between the observed and calculated behavior is satisfactory, especially the case of 50Å is in good agreement with the experimental results. The deviation of the oxygen cluster size from the graphite size is considered to suggest the presence of additional rooms around side surfaces of micrographites for adsorbed oxygen molecules as well as the sites on graphitic planes.

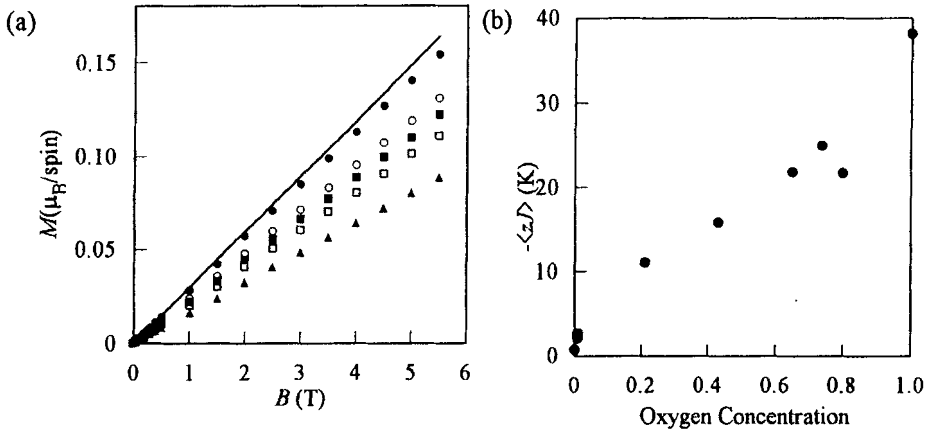

FIGURE 4 (a) Magnetization curves of adsorbed oxygen on ACF at various concentrations; c=0.01, 0.21, 0.43, 0.65, 1.0 (from top to bottom) at 60K. Solid line shows the Brillouin function for free spins (S=1). (b) Effective exchange interaction of adsorbed oxygen at 60K.

Figure 4 (a) shows magnetization curves of adsorbed oxygen at 60K. The magnitudes of magnetization decrease with oxygen concentration, indicating the effect of antiferromagnetic internal field from surrounding spins. Figure 4 (b) shows the oxygen concentration dependence of the effective molecular field estimated from the magnetization curves taken at 60K with the Brillouin function,

$$M = Ng\mu_B S B_S\left(\frac{g\mu_B S(H+H_i)}{kT}\right), \tag{1}$$

Here B_S is the Brillouin function with spin S, and H_i is the effective molecular field given by,

$$H_i = \frac{2\langle zJ\rangle}{N(g\mu_B)}M, \tag{2}$$

where J is the exchange coupling constant. The effective exchange interaction $\langle zJ \rangle$ averaged over the system increases linearly with oxygen concentration and reaches about 40K at the saturated concentration, which is similar to that of bulk liquid oxygen 30-34K,[2] but considerably reduced from the value of solid oxygen zJ=-120K at α-phase.[2] The similarity indicates that adsorbed oxygen in micropores has liquid-like structure at the saturated concentration at 60K.

CONCLUSION

We investigate the magnetic susceptibility and magnetization of adsorbed oxygen in random micropores of ACF as a molecule-based random magnet. The adsorption isotherm shows a simple saturation behavior which demonstrated that adsorbed oxygen form random structure due to the random micropore network of ACF. The magnetic properties are modified from bulk oxygen. The adsorbed oxygen has liquid-like structure around 60K where the exchange interactions between spins are averaged in space. With decreasing the temperature, the susceptibility indicates the coexistence two types of spins. At low oxygen concentrations below c=0.01, the susceptibility shows Curie-Weiss temperature dependence, while the susceptibility contribution having an antiferromagnetic short range order hump develops at higher oxygen concentrations. These findings prove that adsorbed oxygen molecules form two dimensional clusters on micrographite surfaces, where the internal molecules of the clusters form antiferromagnetic short range order structure and marginal molecules having relaxed structure gives the Curie-type contribution.

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