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Oxidation-induced magnetism in Nano-graphite

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[Introduction]

The study of carbon nano-structures have received considerable reattention since the discovery of graphene in 2004. This rekindled the passion for intense research in this area. This is largely because of the unusual physical and chemical properties exhibited by these carbon nano-structures. The members of this family include fullerenes, carbon nanotubes and graphene. Compared to the closed shell counterparts, the open shell nanostructures such as nanographene shows unconventional electronic and magnetic properties. The edges of a nanographene sheet can be described in terms of armchair and zigzag edges. Nanographene sheets with edges terminated with armchair are similar to the closed shell counter parts such as fullerenes in terms of their magnetic properties whereas sheets terminated with zigzag edges show edge state magnetism due to the presence of nonbonding electrons of π origin. There are several attempts to bring in additional magnetic centers apart from the edge state spins. The first report in this direction is the ferromagnetism observed by the irradiation of highly oriented pyrolytic graphite with proton. Recently, it has been established that defects can induce magnetism in carbon nano-structures which also leads to edge state magnetism. The adjacent carbon atoms in a graphene sublattice carries opposite spins. When functional groups are connected to adjacent carbon atoms, equal number of carbon atoms are missing from different sublattices. This leads to a net zero magnetic moment. When alternate carbon atoms carry the functional groups, carbon atoms are removed from the same sublattice. This leads to a sublattice imbalance and a net nonzero magnetic moment. With graphene oxide as a target material, we varied the degree of oxidation in order to increase the number of defects. The robust nature of graphite towards conventional mild chemical reactions made us to select oxidation as the preferred method for introducing defects. The electronic and magnetic properties of nanographene oxide were investigated for activated carbon fibers (ACF), which consist of 3D disordered network of nanographite domains (stacked nanographene sheets).

[Experiment]

A series of nanographite oxide samples were prepared by modified Hummer's method using ACFs as the graphite precursor, varying the degree of oxidation (O/C) by changing KMnO_4/ACF ratio from 1 to 4. Nanographite oxide samples with $\text{O/C} > 0.6$ were dispersible in water whereas samples with $\text{O/C} < 0.6$ were insoluble. These samples were characterized by ESR, SQUID, NEXAFS and elemental analysis. The ESR measurements were done at room temperature using X-band spectrometer. The magnetic susceptibilities were measured with a SQUID magnetometer in the temperature range 2-300 K with an applied magnetic field of 1T. The magnetization measurements were done at 2K, 10K and 300K in the field range from 0 to 7T. Carbon K-edge NEXAFS measurements were done at the X-ray beam line BL-7A at Photon Factory-Institute of Materials Structure Science, KEK Tsukuba.

[Results and Discussion]

The NEXAFS spectrum of the pristine ACFs before oxidation is described in terms of the π^* conduction band contribution (285.7 eV) and the nonbonding edge state contribution (284.5 eV), the latter of which is positioned around the Fermi level. On the basis of the analysis with the deconvolution, the NEXAFS spectrum of the nanographite oxide revealed the presence of an additional state (oxidation induced state) (285.1 eV) near the Fermi level apart from the edge states. This oxidation-induced state is suggested to have nonbonding nature as it is positioned at the Fermi level. The intensity of the π^* peak of the conduction electrons decreased from 2.1 to 0.78 (the ratio of π^* peak intensity to edge jump intensity at 340 eV is taken as the intensity, see Fig.1a) upon increasing the degree of oxidation. This implies that the robust π network can be destroyed locally by employing modified Hummers method. The intensity of the edge state decreased from 0.62 to 0.16. The intensity of the oxidation-induced state increased from 0.0 to 0.34 as we increased the degree of oxidation. It should be noted that the contribution of the oxidation-induced state surpasses around $\text{O/C} = 0.3$.

The observed susceptibility is described in terms of Curie-Weiss type spin susceptibility χ_s with a negative Weiss temperature and the temperature independent orbital susceptibility χ_{orb} for all the samples having different oxygen contents. From the analysis of the susceptibility, as we move from O/C~0.04 to 0.6, the absolute value of χ_{orb} decreased from $8 \times 10^{-7} \text{ emu.g}^{-1}$ to $1 \times 10^{-7} \text{ emu.g}^{-1}$. This indicates that the extended π -electronic structure is destroyed successively as the oxidation proceeds, in good agreement with the NEXAFS results which indicates the decrease in the contribution of the π^* conduction band (Fig. 1a). The spin density (N_s) increased steeply from $0.4 \times 10^{20} \text{ g}^{-1}$ to $5 \times 10^{20} \text{ g}^{-1}$, which is more than ten time of that of pristine ACFs, and the absolute value of Weiss temperature decreased from 5 K to 2 K (Fig. 1c). Taking account of the presence of a crossover point, at which the major contribution of the magnetic nonbonding state is changed from the edge state to the oxidation-induced state, the steep increase in the spin concentration is caused by the creation of nonbonding states induced by oxidation, while the contribution of the edge state is declining (Fig. 1a). The decrease in the Weiss temperature upon oxidation is understood by that the edge state spins having itinerant nature are interacting with each other through conduction π -electron-mediated exchange interaction, whereas the localized spins of the oxidation-induced state are isolated and free from exchange interaction. This difference is observed in the ESR line width change upon oxidation (Fig. 1f). The peak to peak width (ΔH_{pp}) decreased from 2 mT to 0.7 mT as we move from O/C~ 0.04 to 0.6. This suggests that the edge-state spins coupled through exchange interaction are affected by spin fluctuations, in contrast to the negligible such effect in the spins of oxidation-induced state.

For the oxidized samples, the observed magnetization curves deviates from the behavior of noninteracting $S=1/2$, and has values larger than those expected from $S=1/2$ Brillouin curve in the low field range below ca.20000 Oe in Fig.2. This trend is emphasized upon the increase in the degree of oxidation. This suggests the presence of ferromagnetic interaction acting between localized spins of oxidation-induced nonbonding states. In the sample most highly oxidized O/C=0.6, the average strength of the ferromagnetic interaction is estimated as the coefficient of internal field, $\alpha=1.9 \times 10^3 \text{ Oe.emu}^{-1}.\text{g}$. It is considered that the spins strongly coupled through ferromagnetic interaction are free from the surrounding. Selective hydroxylation of benzenoid rings and unzipping of all-benzenoid nanographene sheets into oxygen-joined fragments are the possible candidates for the observed magnetism.

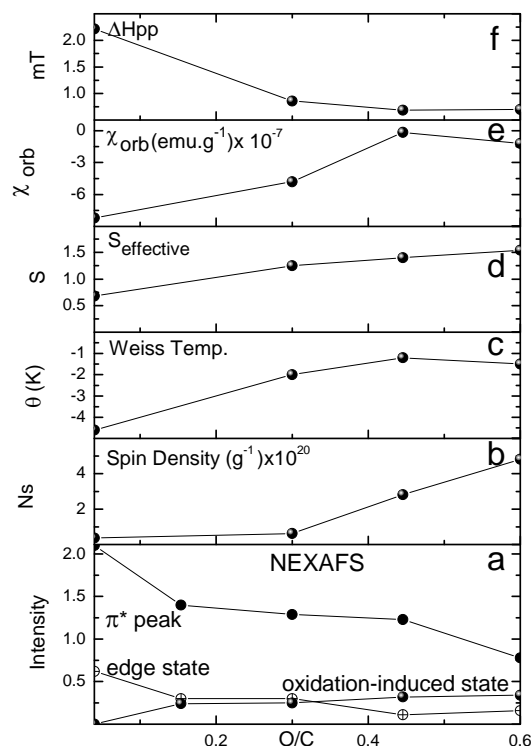


Figure 1. The variation of the edge state, oxidation-induced state, π^* peak, spin density, Weiss temperature, orbital susceptibility and peak to peak width (ΔH_{pp}) with O/C ratio.

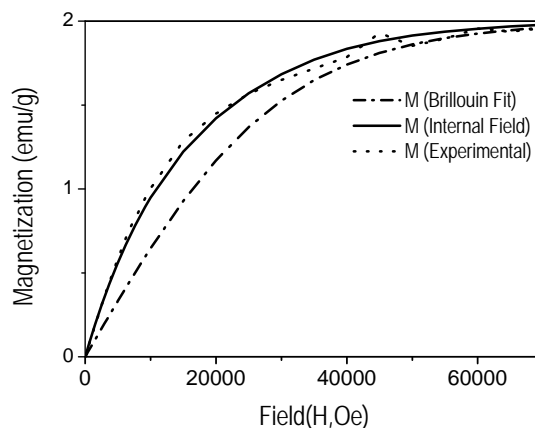


Figure 2. The black dots show the experimental magnetization data for nanographite oxide sample with O/C=0.6. The solid line shows the fit using ferromagnetic internal field of $\alpha=1.9 \times 10^3 \text{ Oe.emu}^{-1}.\text{g}$. The dashed line shows the fit with Brillouin function assuming $S=1/2$.