2A19

# Mechanism of ESR line-broadening in helium adsorbed ACF

**(Tokyo Institute of Technology) ○V. L. Joseph Joly, Katsunori Takahara, Kazuyuki Takai, Toshiaki Enoki**

## [Introduction]

Activated carbon fiber (ACF) is a unique disordered nanoporous carbon material, where the randomly oriented nanographite domains give it a large specific surface area. The surface area of ACF is attributed to the ultramicropores (size < 0.7 nm) and micropores that can accommodate a significant amount of guest gas species. The structural studies report that ultramicropores of ACF can have cage-type or wedge-shaped geometries and can accommodate only very small atoms like helium. The present studies on helium gas adsorbed ACF have revealed an anomalous ESR line-broadening, which is different from the usual pressure-induced effects of gas adsorption on magnetism. We will be discussing the ESR line broadening on the basis of a possible reversible structural change associated with the helium occupation into the cage-type ultramicropores, where the dimensionality of the nanographite domains is reduced towards two-dimensional (2D). Apart from the guest-gas-induced changes in magnetic properties of ACF, we have investigated the heat-treatment-induced structure modification and the related changes in magnetic properties.

## [Experimental]

Phenol-based ACF (FR-20, Kuraray Chemical) having specific surface area of ~2000 $m^2/g$ is used. For helium adsorption studies, ca. 3 mg of ACF is packed vertically into a quartz tube and evacuated to $2\times10^{-6}$ Torr followed by heat treatment at 473 K for 12 hrs and helium is introduced at room temperature at 100, 300, 600, and 1013 mbar (at room temperature). The temperature variation of ESR spectra is investigated from room temperature to liquid helium temperature, at each of the helium pressures. For the studies of high-temperature heat-treatment, ca. 1 mg of ACF is used in a special sample tube set up, which facilitates the heating up to 1200 $^oC$ in vacuum.

## [Results & Discussion]

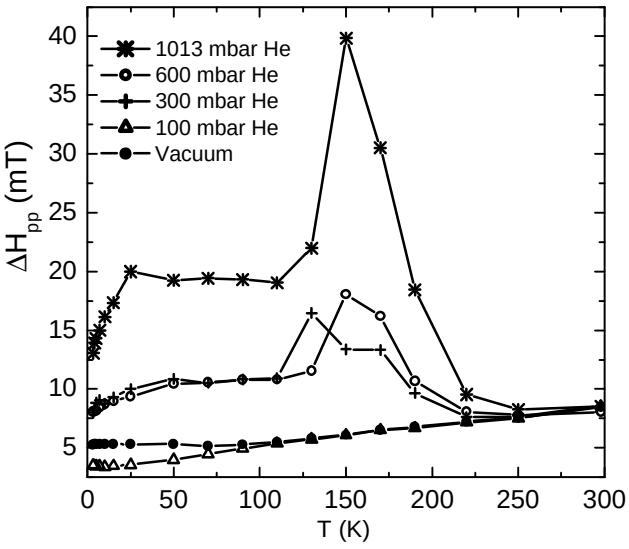


Fig.1 ESR line-width of ACF after 12 hrs heat-treatment in vacuum is compared with that after helium adsorption at 100, 300, 600 and 1013 mbar pressures. The line-broadening that is observed far above the boiling point of helium, is not present in vacuum and 100 mbar helium pressure.

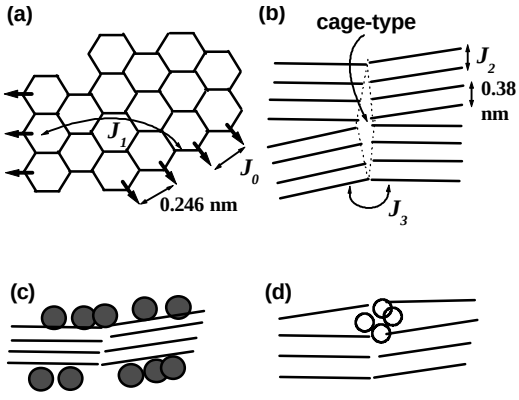


Fig.2(**a**) Nanographene sheet with localized magnetic moments on zigzag edge carbon and ferromagnetic exchange, $J_0$ between them. The inter-zigzag edge interaction is shown as $J_1$. **(b)** Parallel lines are nanographene sheets of nanographite with inter-sheet exchange, $J_2$ and inter-nanographite domain exchange, $J_3$. A cage-type ultramicropores is indicated. **(c)** On adsorbing bigger gas species (patterned circles) surrounding nanographite domains, inter-sheet separation is shorter. **(d)** An expansion in inter-sheet separation on adsorbing helium (circles) into the cage-type ultramicropore.

As shown in Fig.1, the ESR line-width of ACF is ca. 8 mT at room temperature irrespective of the presence or absence of helium in ACF. The line-width of ACF after helium adsorption increases anomalously for pressures above 300 mbar, below 250 K with a maximum about 150 K, in contrast to the

monotonous decrease in the case of ACF in vacuum. The line-width also increases with helium pressure, reaching a maximum of 40 mT in 1013 mbar. Interestingly, below 130 K the line is further narrowed

The line-width of ACF is governed by the spin-spin relaxation, since the spin-lattice relaxation rate is one to two orders of magnitude smaller than that of spin-spin relaxation due to a very small spin-orbit coupling of carbon. The contribution of spin-spin relaxation due to dipole-dipole interaction is estimated to be ~24 mT (assuming that the shortest inter-spin distance is 0.246 nm (as shown in Fig.2(a)) and the effective magnetic moment per edge-state carbon atom is 0.2 $\mu_B$). The fact that the contribution of dipole-dipole interaction is smaller than the observed maximum line-width requires other origin. In this connection, the strong ferromagnetic exchange interaction in the zigzag edge can be responsible for the spin-spin relaxation. Indeed, the contribution from anisotropic exchange interaction is estimated as $10^3$ mT using $(\Delta g/g)^2 J_{0,\mathrm{iso}}$, where $\Delta g$ (~0.024) is the anisotropy of the $g$ value, and $J_{0,\mathrm{iso}}$ is the isotropic term of the ferromagnetic interaction, $J_0$ (~$10^3$ K). The observed line-width of ACF in vacuum is less than 10 mT with Lorentzian line-shape in all temperature ranges (see Fig.1). Such reduction in line-width is possible with exchange narrowing.

The ESR line-width is expressed as follows

$$\frac{1}{c_0 T}\sum_k |F_k|^2 \left\langle S_k^z(t) S_{-k}^z(0)\right\rangle^2$$

where the static term $|F_K|^2$ is the $k$- component of the dipole-dipole interaction and anisotropic exchange interaction in the Fourier transform and the dynamical term $<S_k^z(t)\, S_{-k}^z(0)>$ is the spin correlation function. At elevated temperatures in a three-dimensional (3D) magnetic system, the dynamic term gives rise to the exchange narrowing phenomenon. However, the situation is complicated, when a low-dimensional antiferromagnetic system goes down to low temperatures, at which antiferromagnetic short-range ordering develops. Spin fluctuations related to the wave vector specific to the antiferromagnetic ordering works to broaden the line-width.

Helium adsorption occurs in two stages: The first stage is in the higher temperature region (150-250 K), where the cage-type ultramicropores (see Fig.2b) that have the highest adsorption potential are progressively filled. In the second stage, which occurs below 130 K, the adsorption occurs into the bigger micropores. The evidence for this two stage adsorption is obtained from the studies carried out with different cooling rates, where we have found that the first stage (high temperature stage) is controlled by the helium diffusion time. Here, the driving force that makes helium with high kinetic energy to adsorb is the enhanced potential for which the capillary effect is responsible. In fact, the functional groups can generate an induced electric dipole on the helium atoms. It should be noted that if the extremely small size of helium atom is taken into account, the interaction between induced electric dipole of helium atom and the dipole of the functional group can be in the range of 200 K.

If we consider the structural changes associated with helium adsorption, the line-broadening can be explained as follows: In the first stage, helium occupying the cage-type ultramicropores work to expand the inter-nanographene sheet distance, which is equivalent to the reduction in the dimensionality of the system towards 2D. This results in the progressive broadening of line-width down to 150 K. In the second stage nanographite domains are surrounded by helium atoms, compressing the system so that it partly returns to 3D state with sharper line.

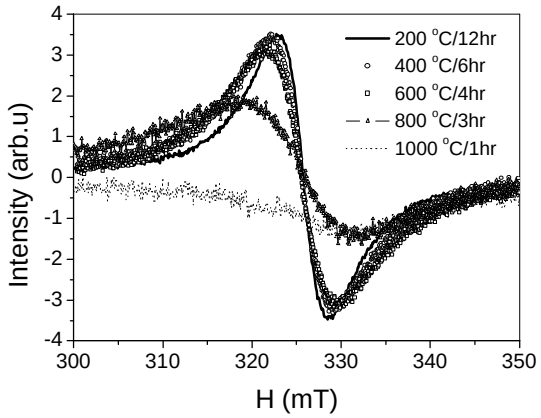


Fig.3 Room temperature ESR line-profile of ACF after vacuum heat-treatment at 200, 400, 600, 800, and 1000 °C.

The vacuum heat-treated ACF shows a systematic homogeneous broadening of the ESR line-width with increasing the heat-treatment temperature (see Fig.3). And eventually the ESR line is broadened out after heating above 1000 °C, which is far below the graphitization temperature, ca. 1700 °C. The vacuum heat-treatment of ACF at temperatures below the graphitization temperature can cause the removal of functional groups attached to the edges and thereby a better wave function overlap, which eventually results in phase transition from insulating to metallic phase on increasing the heating temperatures. Here, the line-broadening can be attributed to the enhancement in inter-nanographite domain magnetic interactions $J_3$, associated with the modification of the nanographite edges by heat-treatment.

In conclusion, the line-broadening phenomenon observed after helium adsorption is attributed to the enhanced spin fluctuations when the dimensionality of the system is reduced towards 2D. And the heat-treatment in vacuum up to 1000 °C enhances the inter-domain wave function overlap resulting in ESR line-broadening.