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Anomalous electronic and magnetic interactions in activated carbon fibers under controlled atmosphere

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[Introduction]

Activated carbon fiber (ACF) is a disordered carbon material having a huge specific surface area. The disordered matrix of ACF is randomly integrated with metallic nanographite domains having a large number of non-bonding edge states. These edge state spins are sensitive to the environment as they exist in the periphery of the nanographite domains. Also it is reported that the magnetic exchange interaction between nanographene layers is affected by the pressure of the adsorbed gas species. Helium is an interesting candidate to study the physisorption effect on the magnetism, especially because ACF has a significant amount of ultra-micropores, which only very small helium atoms can accommodate. We are reporting the results of ESR and magnetic susceptibility studies on helium adsorption in low pressure regime and vacuum condition, which is less understood in the literature.

[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 2×10^{-6} Torr followed by heat treatment at 473 K for different durations. Helium is introduced at room temperature into the 12 hrs heat-treated ACF. Initially a very small pressure (0.3 mbar) is added, which is increased in several steps up to 1013 mbar (at room temperature). Also we have studied the only vacuum-heat-treated samples with different durations at 473 K. The temperature variation of ESR spectra and susceptibility are investigated from room temperature to liquid helium temperature.

[Results & Discussion]

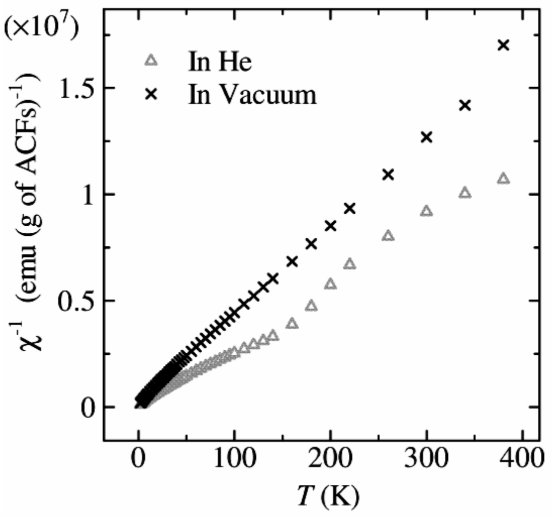

Fig.1 Temperature dependence of inverse magnetic susceptibility of ACF sample in 1013 mbar helium atmosphere and in vacuum.

A comparison between the magnetic susceptibilities of ACF in vacuum and 1013 mbar pressure of helium is shown in Fig. 1. The helium adsorbed sample shows a clear indication of an increase in the magnetic moment below 150 K, which is far above the boiling point of helium. This could be attributed to the fact that there is a sudden increase in the amount of adsorbed helium around 150 K. This argument is supported by the results of ESR studies (see Fig. 2). Such an increase in the adsorbed helium can cause mechanical effect on the nanographene stacks, reducing the inter-sheet aniferromagnetic exchange interaction.

Fig.2 shows the ESR line-widths (**a**) and intensities (**b**) of helium adsorbed ACF at different pressures. The temperature variation of line-width shows identical trend in the pressure range of 0.3-100 mbar. In contrast, for 300 mbar helium pressure the line-width increases anomalously below 220 K and this becomes more prominent at higher helium pressures (Fig. 2(**a**)). This phenomenon, happening well above the boiling-point of helium, is explained by a helium collision assisted spin-lattice relaxation mechanism. This indicates the possibility of a critical helium pressure in the range of 100-300 mbar, above which this anomaly appears. The samples show line-broadening in the temperature range of 150-220 K due to the increased spin-lattice relaxation rate. But, below 150 K the spin-lattice relaxation is not efficient due to the restricted mobility of the adsorbed helium atoms. On the other hand, with the increase in adsorption of helium the contribution from spin-spin relaxation increases. i.e., the weakening of the inter nanographene exchange results in slight broadening of the line-width below 150 K. The corresponding intensities given in Fig. 2(**b**), do not have any discontinuity around 150 K, consistent with static susceptibility, except for the sample in 1013 mbar helium. The weak temperature dependence in the ESR intensity for 1013 mbar case indicates the ineffectiveness of the spin-lattice relaxation mechanism.

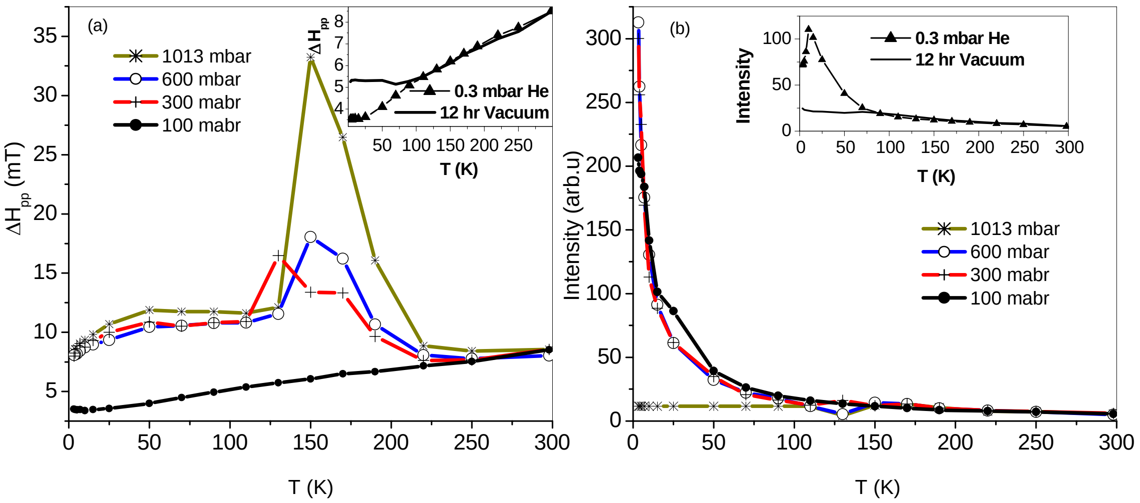

Fig. 2 ESR line-width (**a**) and intensity (**b**) of ACF after 12 hrs heat-treatment followed by helium adsorption at 100, 300, 600 and 1013 mbar pressures at room temperature. Inset: the comparison between 12 hr heat-treated without helium and after adding 0.3 mbar helium.

Fig. 3 shows the temperature dependence of the ESR line-widths and intensities of the sample heat-treated for different durations. Interestingly, we notice that all the samples in vacuum show some line-width broadening at low temperatures and it becomes more prominent as the duration of heat-treatment is increased. We attribute this to the spin fluctuations, since the line-width broadening is accompanied by the anomalies in the intensity as shown in Fig. 3 (**b**). The adsorption of helium at low pressure helps to reduce these spin fluctuations, resulting in sharpening of ESR signal at low temperatures, as shown in the insets of Fig.2. The low-power ESR studies confirm that this anomaly does not originate from microwave heating on the other hand there is a possibility of thermally driven structural changes at the nanographite edge, facilitating more magnetic ordering.

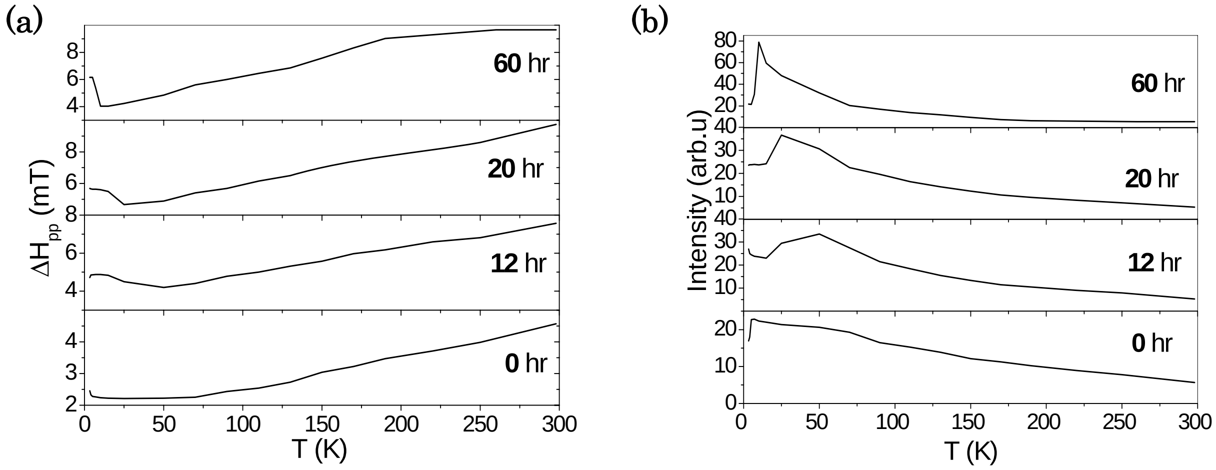

Fig. 3. (**a**) ESR line-width and (**b**) intensity of ACF after heat-treated for 0, 12, 20, 60 hrs at 473 K and at a vacuum of 2×10^{-6} Torr.

In conclusion, there is a critical pressure of helium above 100 mbar, at which the anomalous behaviour around 150 K begins to appear. The anomaly in magnetic susceptibility is due to the structural modification induced by the adsorbed helium. Whereas the ESR line-broadening is attributed to the helium collision induced spin-lattice relaxation mechanism.