ESR in a disordered network of nanographene sheets

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Abstract. Randomly networked nanographene sheets have been studied by electron spin resonance (ESR) technique at 20 GHz (K-band) and 35 GHz (Q-band). Nanographene has spin-polarized non-bonding π-electron states (edge-state spins) localized in the zigzag edge region. We have investigated the temperature dependence of an ESR signal of activated carbon fibers at two different microwave powers for each frequency. The signal intensity smoothly increases with decreasing temperature at any microwave power. The line width of ESR signal with a Lorentzian line shape decreases linearly upon cooling, and then increases steeply after taking a minimum at about 20 K irrespective of microwave power. The former is interpreted as the Korringa relation in the localized edge spins and conduction π carriers. The latter may be caused by inhomogeneous line broadening of the ESR signal from randomly distributed nanographene sheets with different sizes due to the suppression of electron hopping between nanographene sheets, i.e. electron localization. The discontinuous line broadening and the signal intensity drop at around 20 K reported in the previous X-band ESR at 1 µW were not observed, probably because of either higher microwave power than 1 µW or some amount of oxygen adsorption in our sample in the present study.

1. Introduction
Nanosized materials have attracted considerable attention due to their unconventional electronic features depending on the sizes, shapes, surface conditions and so on. In particular, nanosized graphite (nanographene) with open edges is intriguing [1], because the spin-polarized non-bonding π-electronic states, namely edge-state spins, were predicted to appear at the zigzag edge region and not at the arm-chair edge region [2, 3], and were confirmed by scanning tunneling microscope (STM) and scanning tunneling spectroscopy (STS) experiments [1, 4, 5, 6, 7]. The presence of edge-state spins, therefore, results in a variety of magnetism in nanographene, depending on its shape.

The edge-state spins in the zigzag edge region are ferromagnetically coupled with the interaction of the order of $10^3$ K ($J_0$), and the inter-zigzag chain interaction via the arm-chair edges mediated by conduction π electrons has a strength of $10^{-1} \sim 10^{-2}$ of $J_0$ (the order of 10 ~ 100 K) with either positive or negative sign depending on the mutual relation between the zigzag edges, resulting in forming ferrimagnetic spins in each nanographene sheet.

Activated carbon nanofiber (ACF), which consists of a three-dimensional disordered network of loosely stacked 3-4 nanographene sheets with a mean in-plane size of 2-3 nm, has internanographene domain interactions with the magnitude of a few Kelvin originating from hopping integral among domains. This electron transport in the network is governed by the
Coulomb-gap type variable range hopping [8], and thus strong electron localization was expected due to the suppression of electron hopping at low temperatures and was observed below about 20 K in the ACFs [9]. In Ref. 9, the electron-localization-induced magnetic state of the edge-state spins in the ACFs sample were observed below 20 K from X-band electron spin resonance (ESR), magnetic susceptibility and electrical conductivity experiments. In the present study, we further investigate whether this behavior is observed or not in high-frequency ESR.

2. Experimental
Phenol-based ACFs (FR-20, Kuraray Chemicals) were heat-treated at 473 K for 48 h in vacuum (10^{-8} torr) after evacuating at room temperature for five days to remove the adsorbed foreign gas species. The ACF sample was sealed into a high quality quartz (Sprasil) tube in vacuum. K- and Q-band ESR measurements were carried out at temperatures between 1.5 K and 80 K by utilizing a 16 T superconducting magnet (Oxford Instruments, UK), a vector network analyzer (ABmm, France) and home-made ESR cryostats with cylindrical resonant cavities at KYOKUGEN, Osaka University. We used the second (K-band) and the third (Q-band) harmonics of the fundamental microwave (8-18 GHz) generated with an internal YIG oscillator in the vector network analyzer equipped with Shottky diode devices and attenuators. Since we do not have a power meter, we only know the relative power reduction when using the attenuators.

3. Results and discussion
Figures 1 (a) and (b) show the temperature dependences of Q-band (34.8 GHz) ESR signals without (×1) and with power attenuation (×1/3), respectively. All the ESR signals can be fitted with a Lorentzian function, and hence the line widths of the signals are extracted from the fittings. For the sake of simplicity, the fittings on several signals are drawn with open circles in the figures. The resonance field does not shift much and the $g$-value is close to 2.0 which is associated with a small spin-orbit interaction of carbon. Similar ESR signals at K-band (19.7 GHz) without (×1) and with power attenuation (×1/10) are obtained as shown in Figs. 2 (a) and (b). A hole-burning effect, namely irregular feature in the ESR signal, which appeared in the previous X-band ESR, was not observed at 15 K.

The temperature dependences of the signal intensity (relative intensity normalized by the magnitude at 1.5 K) and the line width at Q-band are shown in Figs. 3 (a) and (b), respectively. The signal intensity increases monotonically with decreasing temperature like magnetic susceptibility without a sudden drop below 20 K observed in the previous X-band ESR at 1 µW. The line width decreases linearly upon cooling from 80 K and increase steeply after taking a minimum at around 20 K. Similar temperature dependences of the signal intensity and the line width are obtained at K-band as depicted in Figs. 4 (a) and (b).

Since the magnetic susceptibility of our ACFs obeys the Curie-Weiss law with a small negative Weiss temperature of -2~3 K [9], a monotonous increase of the ESR signal intensity upon cooling is consistent with our expectation in the paramagnetic state. The line width above 20 K proportional to the temperature is probably caused by the Korringa relation $1/T_{1,\text{eff}} \propto T$, where $T_{1,\text{eff}}$ represents the effective spin-lattice relaxation time, in the localized edge-state spins and conduction $\pi$ carriers. Here, the line width $\Delta H$ has the relation of $\Delta H \propto 1/T_{1,\text{eff}}$ and the $1/T_{1,\text{eff}}$ is given as $1/T_{1,\text{eff}} = 1/T_{nn}(T_{nn}/T_{\pi L})$, where $T_{nn}$, $T_{nn}$, and $T_{\pi L}$ are the relaxation times of from the edge-state spin to the $\pi$ carrier, from the $\pi$ carrier to the edge-state spin, and from the $\pi$ carrier to the lattice, respectively [10]. The $T_{nn}$ is give by the Korringa relation and the other two relaxation times are nearly temperature independent as described in Ref. 9. A considerably long $T_{\pi L}$ causes the bottleneck effect and makes the ESR signal sharpen.

The conductivity due to the Coulomb-gap type variable range hopping decreases abruptly below about 20 K [9], and then the suppression of carrier hopping may cause weakening the internanographene domain interactions among the nanographene sheets. As a consequence,
Figure 1. Temperature dependence of ESR signals at Q-band (a) without and (b) with power attenuation (×1/3). Open circles represent a fitting of the experimental data to a Lorentzian function.

Figure 2. Temperature dependence of ESR signals at K-band (a) without and (b) with power attenuation (×1/10). Open circles represent a fitting of the experimental data to a Lorentzian function.

Ferrimagnetic edge-state spins on each nanographene sheet behave independently. Kittle and Abrahams [11] calculated ESR resonance lines in crystals having lattice points populated at random by identical paramagnetic ions. Then, it was found that for fractional magnetic population $f<0.01$ the line shape is approximately Lorentzian with a width proportional to $f$. In our sample, the fractional magnetic population of edge-state spins on each graphene sheet
is evaluated to be $\sim 0.001$ (0.25 $\mu_B$ magnetic moment, namely a quarter of spin 1/2 with $g=2$, for 300 carbon sites on each nanographene sheet) [12]. This probably causes a line broadening owing to the superposition of the ESR signals from the edge-state spins on randomly distributed nanographene sheets with different sizes.

In the present high-frequency ESR studies, we did not observe any sudden changes of the line width and the signal intensity at about 20 K which were observed in the previous X-band ESR at 1 $\mu$W [9]. This discrepancy is probably caused by two plausible reasons. At sufficiently low microwave power, the relaxation time $T_{\pi L}$ may become short and temperature dependent. Then, the bottleneck effect is probably broken and thus the signal becomes broad at low temperatures. From this consideration, microwave power in our high-frequency ESR experiments may not be small enough to break the bottleneck effect. On the other hand, the feature of the ESR signal is extremely sensitive to the presence of oxygen molecules [9, 13] and the transition at about 20 K shifts to high temperature side and smears out at sufficiently low oxygen concentration. Therefore, our ACF sample in the present study may contain some absorbed oxygen molecules even though the careful treatment of evacuation and heating.

4. Conclusions
We have studied randomly networked nanographene sheets realized in activated carbon fibers by K- and Q-band ESR. The temperature dependence of ESR signal intensity shows a smooth increase as the temperature is decreased. The line width of ESR signal with a Lorentzian line shape decreases linearly upon cooling and then increases steeply after taking a minimum at about 20 K. The former behavior above 20 K is interpreted as the Korringa relation in the localized edge spins and conduction $\pi$ carriers, and the latter one below 20 K may be caused by the superposition of the ESR signals from ferrimagnetic edge-state spins on randomly distributed
nanographene sheets due to the suppression of electron hopping among the nanographene sheets. The temperature dependence of the ESR line width in this study is similar to that of the X-band data above 20 K at 1 $\mu$W, but the discontinuous line broadening was not observed at about 20 K.

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**References**

[1] Enoki T, Kobayashi Y and Fukui K 2007 *Int. Rev. Phys. Chem.* **26** 609
[2] Fujita M, Wakabayashi K, Nakada K and Kusakabe K 1996 *J. Phys. Soc. Jpn.* **65** 1920
[3] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 *Phys. Rev. B* **54** 17954
[4] Kobayashi Y, Fukui K I, Enoki T, Kusakabe K and Kusakabe K 2005 *Phys. Rev. B* **71** 193406
[5] Kobayashi Y, Fukui K I, Enoki T and Kusakabe K 2006 *Phys. Rev. B* **73** 125415
[6] Niimi Y, Matsui T, Kambara H, Tagami K, Tsukada M and Fukuyama H 2006 *Phys. Rev. B* **73** 085421
[7] Enoki T and Takai K 2009 *Solid State Commun.* **149** 1144
[8] Fung A W P, Wang Z H, Dresselhaus M S, Dresselhaus G, Pekala R W and Endo M 1994 *Phys. Rev. B* **49** 17325
[9] Joly V LK, Takahara K, Takai K, Sugihara K, Enoki T, Koshino M and Tanaka H 2010 *Phys. Rev. B* **81** 115408
[10] Hasegawa H 1959 *Prog. Theor. Phys.* **21** 483
[11] Kittel C and Abrahams E 1953 *Phys. Rev.* **90** 238
[12] Shibayama Y, Sato H, Enoki T, Bi X -X, Dresselhaus M S and Endo M 2000 *J. Phys. Soc. Jpn.* **69** 754
[13] Sumanasekera G U, Chen G, Takai K, Joly J, Kobayashi N, Enoki T and Eklund P C 2010 *J. Phys.: Condens. Matter.* **22** 334208