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Mechanical compression induced short-range ordering of nanographene spins

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Nanographene has electronic structure which depends crucially on its edge shape; that is, the zigzag edge has an edge state having a localized spin in spite of the absence of such a state in the armchair edge. Nanoporous activated carbon fibers, which consist of a three-dimensional random network of nanographite domains (stacked nanographene sheets), are investigated to clarify the magnetism of the edge-state spins in relation to Ar physisorption. In addition to the deviation of the susceptibility from the Curie-Weiss behavior, the electron spin resonance linewidth is found to increase abruptly below the boiling point (87 K) of Ar condensed in the nanopores. This is the evidence of mechanically induced magnetic short-range ordering of edge-state spins in the nanographite upon the condensation of Ar molecules.

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A sudden prominence of graphene (single-sheet graphite) has triggered booming research on graphene in condensed-matter physics and electronics device applications.[1–3] Recently, nanographene, which is defined nanosized graphene, has emerged as an important and intriguing target in the research on graphene.[4–8] What distinguishes essentially nanographene from infinite size graphene is edge-shape dependence of its electronic structure owing to the presence of edges in the former; that is, nonbonding π-electron state (edge-state) localized in the zigzag-shaped edge region exists, as confirmed by theoretical calculations,[4–6] and ultrahigh-vacuum scanning tunneling microscopy/spectroscopy of well-defined graphene edges.[9–11] Interestingly, it is relevant also to the problem on non-Kekulé structure of aromatic molecules in chemistry language.[12] Indeed, non-Kekulé molecules such as phenalenyl and trianglulene free radicals have open-shell nonbonding π-electron states with localized spins populated around the zigzag-shaped peripheral region at the Fermi level. Recent works have inspired us also to recognize the importance of the edge-state-inherent magnetism of nanographene, in relation to molecular magnetism.[13–19] Indeed, theoretical works suggest the presence of strong ferromagnetic interaction ranging several 10^3 K between the edge-state spins in the zigzag edge [Fig. 1(a)],[6] which can create carbon only ferromagnetism.[20] Experimental findings have revealed also unconventional phenomena of edge-state spin magnetism, such as spin glass,[7] edge-state-spin-based gas sensor probe,[13] and ON/OFF magnetic switching phenomenon.[14–18] Among these, the ON/OFF magnetic switching phenomenon, which is discussed in the present Rapid Communication, is of particular interest.

In the present work on the magnetic switching, we employed nanoporous activated carbon fibers (ACFs) as an experimental model system of edge-state spin. The primary structural unit of ACFs is a nanographite domain which consists of a stack of 3–4 nanographene sheets with a mean intrasheet size of approximately 3 nm and a mean intersheet distance of approximately 0.38 nm.[21] The intersheet distance that is considerably larger than the intersheet distance of bulk regular graphite (0.335 nm) suggests that the constituent nanographene sheets are loosely coupled with each other in the individual nanographite domain.[21] Then, the nanographite domains form a three-dimensional disordered network with the entire structure being soft and flexible. Interestingly, the nanopores created between the nanographite domains provide huge specific surface areas of $\sim 2000\ \mathrm{m}^2/\mathrm{g}$ and accommodate a huge amount of guest molecules through phys-

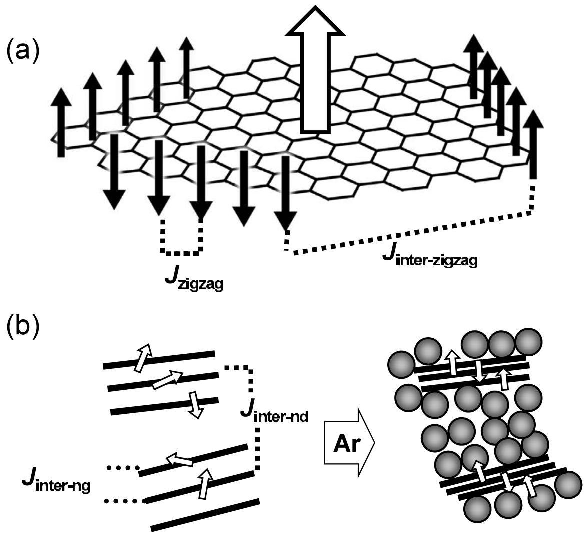

FIG. 1. (a) A nanographite domain with edge-state spins ferromagnetically arranged with intra-zigzag-edge ferromagnetic interaction J_{zigzag} in a zigzag edge. The net magnetic moment (open arrow) of a nanographene is determined after compensation between the ferromagnetic clusters of zigzag-edge spins interacting with each other through inter-zigzag-edge interaction $J_{\text{inter-zigzag}}$. (b) The inter-nanographene-sheet antiferromagnetic interaction $J_{\text{inter-ng}}$ in a nanographite domain and the inter-nanographite-domain antiferromagnetic interaction $J_{\text{inter-nd}}$. The compression by Ar molecules strengthens $J_{\text{inter-ng}}$. The arrow indicates the net magnetic moment in an individual nanographene sheet.

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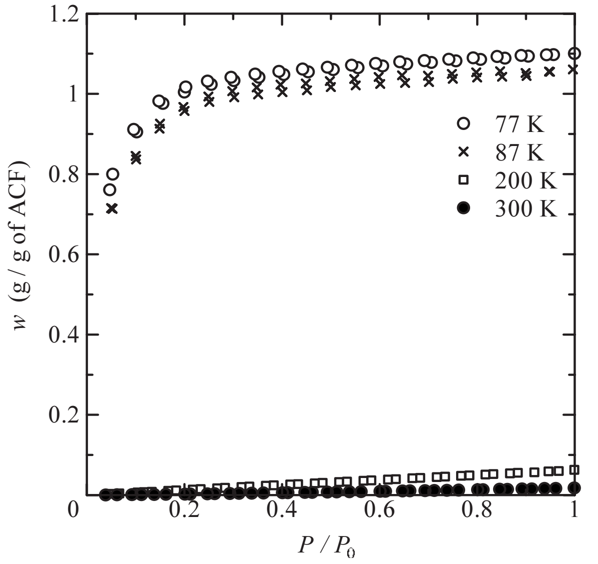

FIG. 2. Ar adsorption isotherms at four temperature points. P_0 is the saturation vapor pressure of Ar.

isorption. According to previous works on the magnetic switching phenomenon which has been observed as universal effect of guest molecules such as water,[14] organic molecules,[15] acids,[16] bromine,[17] etc., the effective pressure of the guest molecules condensed in the nanopores mechanically compresses the nanographite domains, with the intersheet distance being reduced, as evidenced by a decrease of 10% for water adsorption.[21] This enhances the internanographene-sheet antiferromagnetic interaction $J_{\text{inter-ng}}$ between the edge-state spins on the adjacent nanographene sheets in a nanographite domain, resulting in the occurrence of a transition from a high-spin state to low-spin one as shown in Fig. 1(b).[22] These experimental findings encourage us to investigate the magnetic switching effect using inert gas molecules which perturb the edge-state spins only mechanically with no chemical stimuli.

In the present experiments, the magnetic behavior of the edge-state spins in ACFs (FR-20, Kuraray Chemical Co. Ltd., specific surface areas of 2000 m^2/g) was investigated using susceptibility and electron spin resonance (ESR) in relation to Ar adsorption in the temperature range from room temperature to liquid-helium temperature. The samples for the magnetic measurements were vacuum sealed at room temperature in glass tubes, or sealed in Ar atmosphere (approximately 1 atm and purity higher than 99.999%) in glass tubes at room temperature after heat treatment at 473 K for 48 h at a vacuum level of $\sim 1\times10^{-6}$ Torr for removing remaining foreign gas contaminants. The Ar adsorption isotherms were investigated at 77, 87, 200, and 300 K.

Figure 2 shows the adsorption isotherms at four temperature points. In the temperature range well above the boiling point of Ar (87 K), the amount of the adsorbed Ar molecules is negligible whereas it becomes saturated below the boiling point. From the isotherms, the temperature dependence of the filling factor of Ar into the nanopores is obtained as shown in Fig. 3(b), in which the adsorption amount at 77 K is assumed to be that of saturation.

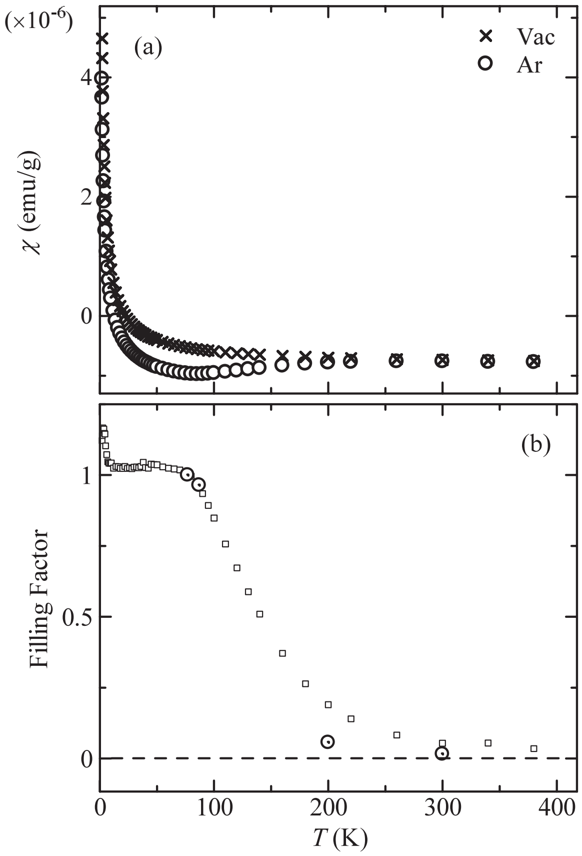

FIG. 3. (a) Temperature dependence of the susceptibilities for the nonadsorbed (vac) and Ar-adsorbed (Ar) samples. (b) Filling factor (circles) of Ar in the nanopores as a function of temperature. Squares are the absolute value of the difference in the susceptibilities between the nonadsorbed and Ar-adsorbed samples. The value is normalized with respect to the value at 77 K.

Figure 3(a) shows the temperature dependence of the susceptibility of the sample in vacuum and that with the nanopores saturated with physisorbed Ar molecules. The spin concentration is estimated as several spins per nanographite and almost the same between these two samples. The Ar adsorption decreases the susceptibility at temperatures below approximately 200 K from the Curie-Weiss behavior, in contrast to the Curie-Weiss susceptibility with the negative Weiss temperature of -2 to -3 K in vacuum. The decrease is owing to two factors; the change in the behavior of the edge-state spins and the diamagnetic susceptibility of the Ar molecules in the nanopores. Figure 3(b) exhibits the difference in the susceptibility between in vacuum and in Ar. This qualitatively tracks the filling factor obtained from the isotherms, suggesting the important contribution of the Ar diamagnetic contribution. However, the difference in the susceptibility is remarkably larger than the filling factor in the temperature range (200 and 300 K) above the boiling point of Ar. This indicates that the susceptibility of the edge-state spins in the Ar-adsorbed ACFs becomes considerably smaller than that expected from the molecular-field theory, demonstrating the importance of antiferromagnetic short-range spin fluctuations.

Figure 4 shows the temperature dependence of the ESR

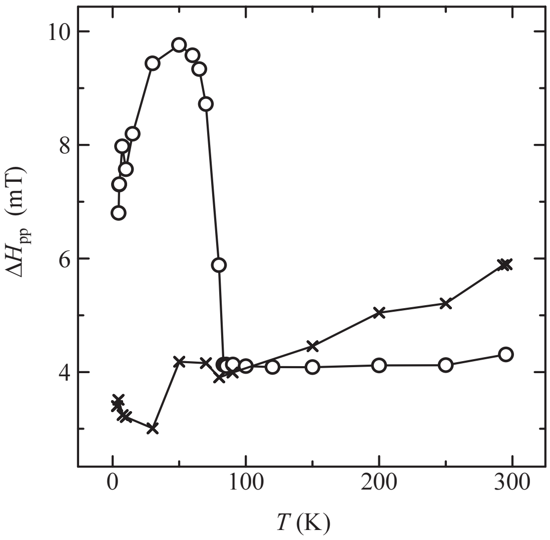

FIG. 4. Temperature dependence of the ESR linewidth ΔH_{pp} for the nonadsorbed (×) and Ar-adsorbed (○) samples. Solid lines are only guide for eyes.

linewidth ΔH_{pp} for the nonadsorbed and Ar-adsorbed samples. The ESR signal always exhibits a single Lorentzian line. ΔH_{pp} is 4 and 6 mT at room temperature for the nonadsorbed and Ar-adsorbed ACFs, respectively. They are smaller than those expected from the dipolar interaction and anisotropic exchange interaction, which are possible origins of the linewidth, in the entire temperature range investigated. Indeed, the dipolar field estimated with the geometry of the nanographite domain, nearest-neighbor edge-state spin distance (0.246 nm), and the mean spin density[7] gives a linewidth of approximately 20–30 mT. On the other hand, the anisotropic exchange interaction[23] expressed as $\sim(\Delta g/g)^2 J$ gives $\sim 10^3$ mT using the intra-zigzag-edge exchange interaction[6] $J_{\mathrm{zigzag}} \sim$ several 10^3 K and the g-value deviation of $(\Delta g/g) \sim 0.024$ for graphite.[24] The linewidth well narrowed from these expected values suggests the homogeneity of the edge-state spin system, in which the exchange narrowing mechanism operates between the localized spins.

The ESR linewidth ΔH_{pp} of the nonadsorbed sample is narrowing monotonically by 40% with lowering the temperature from 300 to 4 K. This indicates the presence of strong exchange coupling between the edge-state spins and conduction carriers (Korringa mechanism).[19] In contrast, that of the Ar-adsorbed one becomes abruptly broadened below about the boiling point (85 K), and then around 50 K it has a maximum whose value is indeed 2.4 times larger than the value above 85 K. The abrupt increase in the linewidth indicates the development of internal field affecting the edge-state spins in nanographite domains as the precursor of magnetic ordering.

The experimental findings presented above firmly demonstrate that the condensation of Ar molecules in the nanopores of ACFs triggers the development of magnetic short-range ordering in the edge-state spins. Here, taking into account the mechanical effect of water molecules in the magnetism of the water-adsorbed ACFs, we can recall the magnetic switching phenomenon[14–18] as a possible explanation for the anomalous change in the magnetism of the Ar-adsorbed ACFs; that is, the adsorbed Ar molecules in the nanopores compress the nanographite domains, resulting in strengthening the inter-nanographene-sheet antiferromagnetic exchange interaction $J_{\mathrm{inter\text{-}ng}}$ and eventually developing antiferromagnetic short-range ordering [see Fig. 1(b)] in a nanographite domain. Note that the decrease in ΔH_{pp} below approximately 50 K is associated with the successive relaxation of the mechanical compression due to the thermal contraction of the frozen Ar molecules in the nanopores upon the lowering of the temperature. The development of the short-range ordering is somewhat puzzling because the edge-state spin system is subjected to the disordered structure of the ACFs, which cannot create the uniform static internal field.

Here we unravel this puzzle on the basis of the microscopic feature of the edge state in the nanographite.[18,19] Figure 1 shows schematically the structure of a nanographite domain which is comprised of a stack of 3–4 nanographene sheets. A zigzag edge consisting of a small number of edge carbon atoms in a nanographene sheet has edge-state spins which are ferromagnetically arranged with strong ferromagnetic interaction J_{zigzag} (several 10^3 K) as exhibited in Fig. 1(a). Then the ferromagnetic clusters present in the zigzag-edge regions are interacting with each other on an individual nanographene sheet with inter-zigzag-edge interaction $J_{\mathrm{inter\text{-}zigzag}}$ that is mediated by the conduction π electrons. $J_{\mathrm{inter\text{-}zigzag}}$ is plus (ferromagnetic) or minus (antiferromagntic) with its strength of $10^{-1}-10^{-3} J_{\mathrm{zigzag}}$ depending on the mutual geometrical relation between the zigzag edges concerned. The strengths of the exchange interactions are summarized to be on the order of $J_{\mathrm{zigzag}} > J_{\mathrm{inter\text{-}zigzag}} > J_{\mathrm{inter\text{-}ng}} \geqslant J_{\mathrm{inter\text{-}nd}}$, where the smallest $J_{\mathrm{inter\text{-}nd}}$ is the inter-nanographite-domain interaction estimated as $-2-3$ K.[7]

The magnetic moment of the edge-state spin has features in between localized and itinerant electrons. Indeed, the strength of the magnetic moment is estimated as ~ 0.2 μ_{B} per site in the zigzag edge,[5] which is fractional in contrast to the pure localized spin system having 1 μ_{B}. It varies also depending on the geometrical details (the length of zigzag edge, environment, etc.). Thus, the random distribution of the zigzag edges and the spatially varying strengths of the magnetic moments cooperate to create ferrimagnetic structure[19] with a nonzero net magnetic moment in an individual nanographene sheet [Fig. 1(a)] taking into account the considerably small $J_{\mathrm{inter\text{-}ng}}$ and $J_{\mathrm{inter\text{-}nd}}$.

The edge-state spins can be described as weakly anisotropic Heisenberg spins since the magnetic anisotropy is considerably small due to the small spin-orbit interaction of carbon atom $(2\times 10^{-4}$ eV).[24] The two dimensionality and finiteness in size in the edge-state spin system of a nanographene sheet (3 nm) with the aid of the small magnetic anisotropy tend to enhance spin fluctuations at the expense of the stabilization of magnetic ordering. When the inter-nanographene-sheet antiferromagnetic interaction $J_{\mathrm{inter\text{-}ng}}$ is strengthened upon the mechanical compression of the nanographite domain by the condensed Ar molecules, the enhancement of the dimensionality can bring about the development of short-range ordering at the expense of the spin fluctuations [see Fig. 1(b)].

Here we have to bridge between the observed ESR line profile and the spin fluctuations. According to conventional theory on spin dynamics,[25,26] the line shape is governed by the competition between the static and dynamic parameters, for which the second moment associated with the anisotropic exchange and the dipolar interactions, and the isotropic exchange interaction are responsible, respectively. Indeed, the term given as Eq. (1),

$$\sum_k |F_k|^2 \langle S_k^z(\tau) S_{-k}^z \rangle^2 \qquad (1)$$

plays an essential role in the line profile, where the static contribution $|F_k|^2$ is the k component of the Fourier transform of the second moment, and dynamic contribution $\langle S_k^z(\tau) S_{-k}^z \rangle$ representing the spin fluctuations is the correlation function of S_k^z governed by the isotropic exchangeinteraction. As the temperature is lowered, the developing slow spin fluctuations related to wave number k specific to the magnetic ordering works to broaden the linewidth. The enhancement in the dimensionality by the mechanical compression makes the spin fluctuations slower and brings the spin system toward an ordered state. Eventually, the abrupt increase in ΔH_{pp} below the boiling point of Ar and the deviation of the susceptibility from the mean-field behavior are ascribed to mechanical compression induced short-range ordering of the edge-state spin system.

In summary, the mechanical compression of nanographite domains by Ar molecules condensed in the nanopores can induces magnetic short-range ordering of the edge-state spins in a nanographite domain. This unconventional nanomagnetism, whose behavior can be easily tuned by the mechanical process, is owing to the unique feature of the edge-state spins in the flexible network, in which nanographene sheets are incorporated.

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