Superconductivity and spin-glass like behavior in system with Pd sheet sandwiched between graphene sheets

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Abstract. Pd-metal graphite (Pd-MG) has a layered structure, where each Pd sheet is sandwiched between adjacent graphene sheets. DC magnetization and AC magnetic susceptibility of Pd-MG have been measured using a SQUID magnetometer. Pd-MG undergoes a superconducting transition at \( T_c = 3.63 \pm 0.04 \) K. The superconductivity occurs in Pd sheets. The relaxation of \( M_{ZFC} \) (aging), which is common to spin glass systems, is also observed below \( T_c \). The relaxation rate \( S(t) \) shows a peak at a characteristic time \( t_{cr} \), which is longer than a wait time \( t_w \). The irreversibility between \( \chi_{ZFC} \) and \( \chi_{FC} \) occurs well above \( T_c \). The susceptibility \( \chi_{FC} \) obeys a Curie-Weiss behavior with a negative Curie-Weiss temperature \( -13.1 \leq \Theta \leq -5.4 \) K. The growth of antiferromagnetic order is limited by the disordered nature of nanographites, forming spin glass-like behavior at low temperatures in graphene sheets.

PACS numbers: 74.80.Dm, 75.30.Kz, 75.50.Ee, 72.15.Rn

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1. Introduction

Magnetism and superconductivity are manifestations of two different ordered states into which metals can condense at low temperatures. In general these two states are mutually exclusive; they do not coexist at the same site in the system. The study of the interplay between these properties has recently been revitalized by the discovery of a family of high-$T_c$ boride carbides RNi$_2$B$_2$C (where R is a rare-earth element) [1, 2]. The R-C layers separated by Ni$_2$B$_2$ sheets are antiferromagnetically ordered below a Néel temperature $T_N$, while Ni$_2$B$_2$ sheets are superconducting below $T_c$. Like RNi$_2$B$_2$C, Pd-metal graphite (MG) has a layered structure [3-7]. Ideally, Pd monolayer is sandwiched between adjacent graphite sheets, forming a periodic c-axis stacking like graphite intercalation compounds (GIC’s). Each Pd layer consists of small islands formed of Pd nanoparticles with finite sizes. Pd nanoparticles would generate internal stress inside the graphite lattice, leading to the break up of adjacent graphene sheets into nanographites. It is expected that the superconductivity occurs in Pd sheets and that the antiferromagnetic (AF) short-range order occurs in nanographites in graphene sheets, leading to a spin glass-like behavior.

In the present work, we have undertaken an extensive study on the magnetic properties of Pd-MG from various kinds of measurement using SQUID magnetometer: the DC magnetization in the zero-field cooled (ZFC), field-cooled (FC), thermoremanent (TR), and isothermal remnant (IR) states, and the AC magnetic susceptibility (the dispersion and absorption). We show that this compound undergoes a superconducting transition at a critical temperature $T_c$ (= 3.63 ± 0.04 K). The superconductivity occurs in Pd sheets. The relaxation of ZFC magnetization $M_{ZFC}(t)$ is also observed below $T_c$. It depends on a wait time $t_w$, a time spent at constant temperature before the magnetic field is applied. This phenomenon is called aging and has been observed in spin glass (SG) systems. As far as we know, the aging effect has not been observed in usual superconductors. There is only one exception for a certain Bi$_2$Sr$_2$CaCu$_2$O$_8$ sample displaying a paramagnetic Meissner effect [8, 9]. In this sense, the aging behavior in Pd-MG is considered to be magnetic but not superconducting in origin. The FC susceptibility well above $T_c$ obeys a Curie-Weiss behavior with a negative Curie-Weiss temperature $\Theta$. The deviation of the ZFC susceptibility from the FC susceptibility starts to occur even at 298 K. These results suggest that an AF short-range order appears well above $T_c$. Based on these results, we propose a model that the superconductivity occurs in Pd sheets and that the AF short-range order occurs in graphene sheets. Although no long-range magnetic order below $T_c$ has been clearly confirmed from the present work, it is assumed that the possible interplay between the superconductivity and the SG-like behavior becomes significant below $T_c$.

Here we present experimental and theoretical backgrounds for the origin of the superconductivity in Pd sheets and the antiferromagnetism in nanographites. The absence of superconductivity in pristine Pd above 2 mK is mainly due to strong spin fluctuations [10]. Theoretically it is suggested that Pd without spin fluctuations should
be a superconductor \[11, 12\]. Experimentally, Stritzker \[13\] has reported that pure Pd films, evaporated between 4.2 and 300 K, can be transformed into superconductors by means of irradiation at low temperatures with He\(^+\) ions. The maximum transition temperature obtained is 3.2 K. A special kind of disorder produced by low temperature irradiation may lead to a smearing of the Fermi energy \(E_F\), and thus to a reduction of the density of states (DOS) at \(E_F\), \(N(E_F)\). This reduction of \(N(E_F)\) leads to a decrease in the Stoner enhancement factor. As a result, the strong spin fluctuations would be reduced and superconductivity might be possible. In fact, Meyer and Stritzker \[14\] have shown that the AC magnetic susceptibility of low-temperature irradiated Pd is strongly reduced in comparison to the annealed Pd metal.

Nanographites are nanometer-sized graphite fragments, forming a new class of mesoscopic system. Fujita et al. \[15\] and Wakabayashi et al. \[16\] have theoretically suggested that the electronic structures of finite-size graphene sheets depend crucially on the shape of their edges. Finite graphite systems having zigzag edges exhibit a special edge state. The corresponding energy bands are almost flat at \(E_F\), giving a sharp peak in \(N(E_F)\). The conduction electrons localized near the zigzag edge have magnetic moments \((= g\mu_B S\) with \(g = 2\) and \(S = 1/2\)). Harigaya \[17, 18, 19\] has theoretically predicted that the magnetism in nanographites with zigzag edge sites depends on the stacking sequence of nanographites. The structure of pristine graphite consists of hexagonal net planes of carbon stacked along the \(c\) axis in a staggered array usually denoted as \(ABAB\ldots\) \[20\]. There is a lateral shift on going from layer \(A\) to layer \(B\). There are two kinds of spin configurations depending on the stacking of nanographites. For the \(A-B\) stacking, there is no interlayer interaction at the edge site, giving rise to the AF spin alignment. The growth of AF spin order is greatly limited by the disordered nature of nanographites, forming AF short-range order. For the \(A-A\) type stacking, on the other hand, the magnetic moment per layer does not appear due to the interlayer interaction.

2. EXPERIMENTAL PROCEDURE

In a previous work \[7\] we have shown that there are two types of Pd-MG depending on the reduction condition in the sample preparation: the long-reaction time and the short-reaction time. The physical properties of these two systems are rather different: the ferromagnetic nature for the long-reaction time and the AF nature for the short-reaction time. The sample used in the present work (the short-reaction time) is the same as that used in the previous work \[7\]. Pd-MG samples based on natural graphite were prepared by heating PdCl\(_2\) GIC with mixed stages (2, 3, and 4) at 350 °C under hydrogen gas (flow rate 300 ml per minute) for 2 hours.

The detail of sample characterization for Pd-MG was presented in the previous papers \[3, 5\]. The average size of Pd nanoparticles was estimated as \((530 \pm 340)\) Å from the bright field transmission electron microscope photograph \[3\]. The existence of nanographites was confirmed from the Raman scattering \[5\]. The Raman spectrum shows a large peak at 1580 cm\(^{-1}\) assigned as the \(E_{2g}\) mode in pristine graphite (1582
cm$^{-1}$), and a small peak at 1360 cm$^{-1}$ assigned as the D-band (disordered induced modes) of graphite [5]. The size of nanographites can be estimated from an empirical law $L_a = 4.4 \times I_{1580}/I_{1350}$, where $I_{1580}$ and $I_{1360}$ are the intensities of the corresponding peaks. In fact, the size of nanographites is on the same order as that of Pd nanoparticles. There is no appreciable charge transfer between nanographites and Pd nanoparticles.

The Pd-MG sample consists of many small flakes. Each flake has a well-defined $c$ axis. If these flakes are carefully piled inside the sample capsule for the measurement, the $c$ axis of the whole sample could correspond to the $c$ axis of each flake. This is not the case for the present experiment. The present sample may be regarded as a powdered sample with the $c$ axis randomly distributed over all directions. Because of the small samples, the resistivity measurement could not be carried out. The mass of the sample used in the present work was 23.8 mg.

The DC magnetization and AC magnetic susceptibility of Pd-MG were measured using a SQUID magnetometer (Quantum Design, MPMS XL-5). Before setting up a sample at 298 K, a remnant magnetic field was reduced to less than 3 mOe using an ultra-low-field capability option. For convenience, hereafter this remnant field is denoted as the state $H = 0$. (i) DC magnetization. The sample was cooled from 298 to 1.9 K at $H = 0$. After an external magnetic field ($H$) was applied at 1.9 K, the zero-field cooled magnetization ($M_{ZFC}$) was measured with increasing $T$ from 1.9 to 60 K. The sample was kept at 70 K for 20 minutes. Then the field cooled magnetization ($M_{FC}$) was measured with decreasing $T$ from 60 to 1.9 K. (ii) A hysteresis loop of DC magnetization. The sample was cooled from 298 K to $T = 1.9$ or $3.3$ K at $H = 0$. Then DC magnetization at $T$ was measured as $H$ was varied from $H = 0$ to 1 kOe, from 1 to -1 kOe, and from -1 to 1 kOe in order. (iv) AC magnetic susceptibility ($\chi = \chi' + i\chi''$). The dispersion $\chi'$ and absorption $\chi''$ were simultaneously measured with increasing $T$ from 1.9 to 20 K with and without $H$, where the frequency and amplitude of the AC magnetic field were $f = 1$ Hz and $h = 2$ Oe, respectively. After each $T$ scan, $H$ was changed at 30 K. The sample was cooled from 30 to 1.9 K. Then the measurement was repeated with increasing $T$ from 1.9 to 20 K in the presence of $H$.

3. RESULT

3.1. $\chi'$ and $\chi''$

Figures 1 and 2 show the $T$ dependence of $\chi'$ for Pd-MG at various $H$, where $f = 1$ Hz and $h = 2$ Oe. The dispersion $\chi'$ at $H = 0$ slightly increases with decreasing $T$ at the high-$T$ side. It shows a peak at 3.8 K. Below 3.8 K, $\chi'$ drastically decreases with further decreasing $T$. The sign of $\chi'$ changes from positive to negative below 2.65 K. In contrast, the dispersion $\chi'$ for $5 \leq H \leq 350$ Oe still shows a positive peak, shifting to the low-$T$ side with increasing $H$. However, the sign of $\chi'$ changes from positive to negative below a zero-crossing temperature $T_0 (= 3.45$ K at $H = 5$ Oe). For $400 \leq H \leq 600$ Oe, no
Figure 1. $T$ dependence of the dispersion $\chi'$ for Pd-MG at $H = 0$ and 5 Oe. $f = 1$ Hz. $h = 2$ Oe.

Figure 2. (a) - (d) $T$ dependence of $\chi'$ for Pd-MG at various $H$. $f = 1$ Hz. $h = 2$ Oe. The solid lines in (c) and (d) are guides to the eyes.
Figure 3. (a) and (b) $T$ dependence of the absorption $\chi''$ for Pd-MG at various $H$. $f = 1$ Hz. $h = 2$ Oe. The solid lines are guides to the eyes.

An appreciable peak is observed in $\chi'$. The dispersion $\chi'$ starts to decrease with decreasing $T$ below $T_0$. The negative sign of $\chi'$ below $T_0$ for $H \geq 5$ Oe is related to a diamagnetic flux expulsion (the Meissner effect), giving a bit of evidence of the superconductivity at low temperatures. We find that the derivative $d\chi'/dT$ shows a peak, shifting to the low-$T$ side with increasing $H$. The peak temperature of $d\chi'/dT$ vs $T$ is regarded as a superconducting transition temperature $T_c(H) = T_2(H)$ (see section 4.1 for the definition of $T_2(H)$). Using the value of $\chi'$ at $1.9$ K ($\approx -2 \times 10^{-5}$ emu/g) and the density $\rho$ which is on the order of 1-2 g/cm$^3$, the fraction of flux expulsion relative to complete diamagnetism ($\chi_0 = -1/4\pi = -0.0796$ emu/cm$^3$) is estimated as only 0.05%, suggesting isolated superconducting islands.
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Figure 4. Hysteresis loop of DC magnetization $M$ for Pd-MG at (a) $T = 1.9$ K and (b) $3.3$ K. After the sample was cooled from 298 to 1.9 K at $H = 0$, the measurement was made with increasing $H$ from 0 to 1 kOe (closed circles), with decreasing $H$ from 1 to -1 kOe (open circles), and with increasing $H$ from -1 to 1 kOe (open triangles).

Figure 3 shows the $T$ dependence of the absorption $\chi''$ in the presence of $H$. The data at $H = 0$ were presented in the previous paper [7]. The absorption $\chi''$ at $H = 0$ increases with decreasing $T$. A drastic increase is observed around 3.5 K. In contrast, the $T$ dependence of $\chi''$ at $H \geq 20$ Oe is rather different from that at $H = 0$. It has a relatively sharp peak at a peak temperature. This peak shifts to the low-$T$ side with increasing $H$. The peak temperature is the same as $T_2(H)$. We notice that the peak temperatures of $\chi'$ and $\chi''$ at $H = 0$ are almost independent of AC frequency $f$ for $0.07$ Hz $\leq f \leq 1$ kHz as have been reported in the previous paper [7].

3.2. $M$-$H$ curve

Figure 4 shows the hysteresis loop of the DC magnetization $M(H)$ at $T = 1.9$ and 3.3 K, respectively. After the sample was cooled from 298 to 1.9 K at $H = 0$, the magnetization $M(H)$ was measured for $-1 \leq H \leq 1$ kOe. The magnetization curve at 1.9 K shows a non-typical hysteresis behavior. There are some anomalies at low-field region in the demagnetization and remagnetization curves at 1.9 and 3.3 K, which
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3.3. IRM and TRM

Figure 5 shows the $T$ dependence of the magnetization $M_{ZFC}$, $M_{IR}$, $M_{FC}$, and $M_{TR}$ for $H = 25$, 75, 150, and 200 Oe. The magnetization $M_{IR}$ is the isothermal remnant (IR) magnetization. During the process of ZFC measurement (with increasing $T$), $M_{ZFC}$ at each $T$ was measured at $H$ and $M_{IR}$ was measured at the same $T$ 10^2 sec later after setting $H$ to zero. The magnetization $M_{TR}$ is the thermoremnant (TR) magnetization. During the process of FC measurement (with decreasing $T$), $M_{FC}$ at

Figure 5. $H$ dependence of DC magnetization $M_{ZFC}$ for Pd-MG at (a) 1.9 K and (b) 3.3 K (closed circles). After the sample was cooled from 298 to 1.9 K at $H = 0$, the measurement was carried out with increasing $H$ from 0 to 200 Oe. The data around $H = 0$ at 1.9 K is slightly different from that shown in figure 4. Completely disappear at 5.5 K. In figures 5(a) and (b) we show the detail of the initial magnetization curve at 1.9 and 3.3 K. For the data at $T = 1.9$ K, the positive value of the initial magnetization $M_{int}$ around $H = 15$ Oe is sensitive to the condition of cooling from 298 to 1.9 K at $H = 0$. The negative value of $M_{int}$ for $38 \leq H \leq 190$ Oe gives a bit of evidence for the occurrence of the Meissner effect. The local-minimum field may be related to the lower critical field $H_{c1}$. At 3.3 K this negative local minimum disappears.
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Figure 6. T dependence of $M_{ZFC}$, $M_{IR}$, $M_{FC}$, and $M_{TR}$ for Pd-MG. (a) $H = 25$, (b) 75, (c) 150, and (d) 200 Oe. During the ZFC measurement, $M_{ZFC}$ at each $T$ was measured at $H$ and $M_{IR}$ was measured $10^2$ sec later after $H$ was set to zero field. During the FC measurement, $M_{FC}$ at each $T$ was measured at $H$. $M_{TR}$ was measured $10^2$ sec later after $H$ was set to zero field.

Each $T$ was measured at $H$ and $M_{TR}$ was measured at the same $T$ $10^2$ sec later after setting $H$ to zero. The magnetization $M_{TR}$ is larger than $M_{FC}$ and $M_{IR}$ is larger than $M_{ZFC}$ below a characteristic temperature $T_\alpha$ ($T_\alpha = 3.1$ K for $H = 75$ Oe), which are features common to the superconducting state. Similar behavior of $M_{TR}$ vs $T$ and $M_{FC}$ vs $T$ has been reported in high $T_c$ superconductors La$_2$CuO$_{4-y}$:Ba [21] and Bi$_2$Sr$_2$CaCu$_2$O$_y$ [8, 9]. This is due to the flux trapping after switching off the field, giving a strong evidence of the superconductivity at low temperatures. The value of $T_\alpha$ is a little lower than $T_2(H)$: $T_2(H) = 3.34$ K at $H = 75$ Oe. Above $T_\alpha$, $M_{FC}$ is larger than $M_{TR}$ and $M_{ZFC}$ is larger than $M_{IR}$, which are features common to spin systems with spin frustration effects. The derivatives $dM_{TR}/dT$ and $dM_{IR}/dT$ at $H = 75$ Oe exhibit negative local minima at 3.34 K and 3.45 K, respectively. The magnetization $M_{TR}$ decreases with increasing $T$ and reduces to a positive value above $T_c(H)$, suggesting the existence of AF short-range order. This is in contrast to the case of La$_2$CuO$_{4-y}$:Ba [21] and Bi$_2$Sr$_2$CaCu$_2$O$_y$ [8, 9]: $M_{TR}$ becomes zero above $T_c(H)$ ($= T_2(H)$), since no flux
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Figure 7. $T$ dependence of (a) $\chi_{ZFC}$ and (b) $\chi_{FC}$ for Pd-MG. $H = 1$ Oe.

trapping occurs.

3.4. $\chi_{ZFC}$ and $\chi_{FC}$

In the previous paper [7] we show the $T$ dependence of $\chi_{ZFC} (= M_{ZFC}/H)$ and $\chi_{FC} (= M_{FC}/H)$ for Pd-MG where $H = 1$ Oe and $1.9 \leq T \leq 298$ K. We find that the deviation of $\chi_{ZFC}$ from $\chi_{FC}$ starts to appear below 298 K, suggesting a behavior reminiscent of frustrated spin systems. In the present work, we have measured the $T$ dependence of $\chi_{ZFC}$ and $\chi_{FC}$ at low temperatures below 6 K. Figures 7 and 8 (a) - (d) show the $T$ dependence of $\chi_{ZFC}$ and $\chi_{FC}$ for Pd-MG at various $H$. At $H = 1$ Oe (see figure 7), a cusp-like peak is observed at 3.8 K for both $\chi_{ZFC}$ and $\chi_{FC}$. A local minimum is observed around 2.7 K in $\chi_{ZFC}$ and 3.4 K in $\chi_{FC}$. As shown in figure 8, the cusp-like peak shifts to the low-$T$ side with increasing $H$, becoming into a broader peak for $H \geq 100$ Oe. The local minimum of $\chi_{FC}$ at a temperature $T_{\text{min}}$ also shifts to the low-$T$ side with increasing $H$ for $1 \leq H \leq 50$ Oe. The increase of $\chi_{FC}$ below $T_{\text{min}}$ indicates the existence of AF short-range order at low temperatures. The resultant susceptibility arises from a competition between a negative diamagnetic susceptibility due to the Meissner effect and a positive AF susceptibility. Figure 9 shows the $T$ dependence of
Figure 8. (a) - (d) $T$ dependence of $\chi_{ZF C}$ and $\chi_{FC}$ for Pd-MG at various $H$.

Figure 9. $T$ dependence of the difference $\delta \chi (= \chi_{FC} - \chi_{ZFC})$ for Pd-MG at various $H$. The temperature ($T_\delta$) denoted by arrow is a characteristic temperature at which $\delta \chi$ starts to increase drastically with decreasing $T$. 
the difference $\delta \chi$ defined by $\delta \chi = \chi_{FC} - \chi_{ZFC}$. The difference $\delta \chi$ provides a measure for the irreversible effect of magnetization. The difference $\delta \chi$ is positive at least below 60 K for $1 \leq H \leq 500$ Oe. The growth of the AF spin correlation length is greatly limited by the disordered nature of nanographites, forming AF short-range order. Because of the frustrated nature, the system magnetically behaves like SG’s. Note that $\delta \chi$ starts to increase drastically with decreasing $T$ below a characteristic temperature $T_{\delta}$, which is nearly equal to the peak temperature $(T_1(H))$ of $\chi'$ vs $T$ (see section 4.1 for the definition of $T_1(H)$).

3.5. Aging effect

The relaxation of the ZFC magnetization was measured. The system was rapidly cooled from 50 K to $T$ (= 3.0, 3.2, and 3.6 K) in the absence of $H$. After the isothermal aging was carried out at $T$ and $H = 0$ for a wait time $t_w = 2.0 \times 10^3$ sec, the field $H$ (= 50 Oe) is switched on at $t = 0$. Figure 10(a) shows the time $(t)$ dependence of $m_{ZFC}(t, T) = \frac{\Delta M_{ZFC}(t, T)}{M_{ZFC}(t = 0, T)}$, where $\Delta M_{ZFC}(t, T) = M_{ZFC}(t, T) - M_{ZFC}(t = 0, T)$. The magnetization $m_{ZFC}(t, T)$ at $T = 3.0, 3.2$ K is almost proportional to $\ln t$ for $t < t_w$ and it deviates from the $\ln t$ dependence for $t > t_w$. The $t$ dependence of $m_{ZFC}(t, T)$ at $T = 3.6$ K is rather different from that at $T = 3.0$ and 3.2 K. Figure 10(b) shows the relaxation rate $S(t)$ defined by $S(t) = (1/H) \frac{dM_{ZFC}(t)}{d\ln t}$ at $T = 3.0$ and 3.6 K, which is calculated from the data shown in figure 10(a). The relaxation rate $S(t)$ exhibits a broad peak at a characteristic time $t_{cr}$. The time $t_{cr}$ linearly decreases with increasing $T$: $t_{cr}$ is longer than $t_w$ for $3.0 \leq T \leq 3.6$ K and is assumed to be equal to $t_w$ at $T = 3.78$ K. The width of the peak in $S(t)$ at 3.0 K is broader than that at 3.6 K, indicating a broader distribution of relaxation times as $T$ is lowered. This phenomenon is called aging and has been observed in SG’s [22, 23]. Similar $T$ dependence of $t_{cr}$ has been observed in the 3D Ising SG system Cu$_{0.5}$Co$_{0.5}$Cl$_2$-FeCl$_3$ graphite bi-intercalation compound (GBIC) [24], where $t_{cr}$ almost linearly decreases with increasing $T$ and becomes equal to $t_w$ at the spin freezing temperature $T_{SG}$. As far as we know, the aging behavior of $M_{ZFC}$ has never been observed in usual superconductors. However, there is only one exception for this. The aging, rejuvenation, and memory effects have been reported in a melt-cast Bi$_2$Sr$_2$CaCu$_2$O$_8$ sample displaying a phenomenon called paramagnetic Meissner (PME) effect ($M_{FC} > 0$ and $M_{ZFC} < 0$ below $T_c$) [8, 9]. In this case, the competing interactions between current loops (magnetic moments) give rise to a glassy low-temperature state, where the aging behavior is similar to that observed in SG’s. The aging behavior observed in Pd-MG is magnetic in origin, suggesting the existence of the SG-like behavior below $T_c$.

3.6. DC magnetic susceptibility at high fields

Figures 11 (a) and (b) show the $T$ dependence of $\chi_{FC}$ of Pd-MG for $H = 1 - 500$ Oe. Figure 12 shows the $T$ dependence of $\chi_{FC}$ at $H = 3$ kOe. The susceptibility obeys the Curie-Weiss law only at low temperatures ($5 \leq T \leq 30$ K). The least-squares fit of the
data $\chi_{FC}$ vs $T$ for each $H$ to

$$\chi_{FC} = \chi_0 + C_g/(T - \Theta),$$

yields the Curie-Weiss constant $C_g$, the Curie-Weiss temperature $\Theta$, and $T$-independent susceptibility $\chi_0$, which are listed in Table I. The values of $C_g$, $\Theta$, and $\chi_0$ are different for different $H$. The inset of figure 12 and figure 13 show the $T$ dependence of the corresponding reciprocal susceptibility $(\chi_{FC} - \chi_0)^{-1}$ for $H = 3 \text{kOe}$, and $1 \leq H \leq 500 \text{Oe}$, respectively. We find that $\Theta$ is negative for any $H$, suggesting the AF nature of the system. The inclusion of the data for $T \geq 30 \text{K}$ gives rise to a deviation of the
Figure 11. (a) and (b) $T$ dependence of $\chi_{FC}$ for Pd-MG at various $H$.

Figure 12. $T$ dependence of $\chi_{FC}$ for Pd-MG at $H = 3$ kOe. The inset shows the reciprocal susceptibility $(\chi_{FC} - \chi_0)^{-1}$. 
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Figure 13. $T$ dependence of the reciprocal susceptibility $(\chi_{FC} - \chi_0)^{-1}$ for Pd-MG at various $H$, where $\chi_0$ is a $T$-independent susceptibility determined from the least-squares fit of the data to the Curie-Weiss law \(^{(1)}\) for each $H$. The solid straight lines denote the fitting curves, where $C_g$, $\Theta$, and $\chi_0$ are listed in the table \(^{(1)}\).

| $H$ (Oe) | $C_g$ ($10^{-3}$ emu K/g) | $\Theta$ (K) | $\chi_0$ ($10^{-5}$ emu/g) |
|----------|--------------------------|-------------|---------------------------|
| 1        | 5.81                     | -6.9        | 4.02                      |
| 5        | 3.85                     | -9.4        | 3.94                      |
| 100      | 0.90                     | -13.1       | 3.72                      |
| 200      | 0.53                     | -12.4       | 3.40                      |
| 300      | 0.37                     | -11.5       | 3.47                      |
| 400      | 0.28                     | -10.6       | 2.76                      |
| 500      | 0.23                     | -9.8        | 2.63                      |
| 3000     | 0.05                     | -5.4        | 0.66                      |

This is in contrast to the paramagnetic susceptibility due to magnetic impurities, where the agreement of the data with \(^{(1)}\) becomes better as the data at higher $T$ are included. Since $\Theta$ is close to zero, hereafter we call this behavior the Curie-like behavior rather than Curie-Weiss like behavior. Such a Curie-like behavior is due to the localized conduction electrons near zigzag edge sites of nanographites. Each electron has the effective magnetic moment $P_{eff} = g[S(S+1)]^{1/2}$, where the Landé $g$ factor $g = 2$ and spin $S = 1/2$ of the conduction electron. Then the value of $N_g$, the number of spins of localized conduction electrons (per gram), can be estimated as $N_g = (3k_B C_g/\mu_B^2 P_{eff}^2) = 8.0 \times 10^{19}$ per gram, where we use $P_{eff} = \sqrt{3}$ and
Figure 14. $H$ dependence of $M_{ZF C}$ at 1.9 K for Pd-MG. After the sample was cooled from 298 to 1.9 K at $H = 0$, the measurement was carried out with increasing $H$ from 0 to 40 kOe. The inset shows the detail of $M_{ZF C}$ vs $H$ at low $H$. The solid lines are guides to the eyes.

$C_g = 4.98 \times 10^{-5}$ emu K/g for $H = 3$ kOe. This value of $N_g$ is a little larger than that reported by Shibayama et al. [25] for activated carbon fibers (ACF) composed of a disorder network of nanographites $[N_g = (0.39 - 4.2) \times 10^{19}$/g$]$. Figure 14 shows the $H$ dependence of $M_{ZF C}$ at 1.9 K for $0 \leq H \leq 40$ kOe. The magnetization $M_{ZF C}$ exhibits strong nonlinear $H$ dependence, and it reaches 0.13 emu/g at $H = 40$ kOe, which does not correspond to the saturation magnetization $M_s$. It is predicted that the ratio of the saturation magnetization $M_s (= N_g \mu_B g S)$ to $C_g$ is given by $3k_B/\mu_B g(S + 1)$, which is independent of $N_g$. When $g = 2$ and $S = 1/2$ for the conduction electron, the saturation magnetization $M_s$ is estimated as 0.74 emu/g. This value of $M_s$ is much larger than that of $M_{ZF C}$ at $H = 40$ kOe. The reason for such a large $M_s$ is not clear.

4. DISCUSSION

4.1. Possibility of a quasi-2D superconductivity in Pd sheets

Our results obtained above are summarized in the $H$-$T$ diagram of Pd-MG. In figure 15 we make a plot of the peak temperatures of $\chi'$ vs $T$, $d\chi'/dT$ vs $T$, $\chi''$ vs $T$, $d\chi_{ZF C}/dT$ vs $T$, and $d\chi_{FC}/dT$ vs $T$, the local-minimum temperatures of $d\delta\chi/dT$ vs $T$ and $\chi_{FC}$ vs $T$, and the characteristic temperature $T_\delta$ for $\delta\chi$ vs $T$, as a function of $H$. The data are classed in three groups: (i) the upper line for $\chi'$ vs $T$ and $\delta\chi$ vs $T$ (denoted as the line $H_1(T)$ or the line $T_1(H)$), (ii) the intermediate line for $d\chi'/dT$ vs $T$, $\chi''$ vs $T$, $d\chi_{ZF C}/dT$
Figure 15. $H$-$T$ diagram for Pd-MG, where the peak temperatures of $\chi'$ vs $T$ (closed triangle), $d\chi'/dT$ vs $T$ (closed circle), $\chi''$ vs $T$ (open circle), $d\chi_{ZFC}/dT$ vs $T$ (open square), and $d\chi_{FC}/dT$ vs $T$ (closed diamond), the local-minimum temperatures of $d\delta\chi/dT$ vs $T$ (closed square) and $\chi_{FC}$ vs $T$ (open triangle down), and $T_\delta$ for $\delta\chi$ vs $T$ (open triangle down), are plotted as a function of $H$. The superconducting transition temperature $T_c(H)$ coincide with the peak temperatures ($T_2(H)$) of $d\chi'/dT$ vs $T$ and $\chi''$ vs $T$. The solid lines are least-squares fitting curves. See the text in detail.
which is defined as a critical temperature for usual superconductors. The upper critical field $H_{c2}(T = 0 \text{ K})$ is roughly estimated from the slope of the line $H_2(T)$ at $T = T_c$: $(-dH_2/dT)_{T_c} = 180 \pm 20 \text{ Oe/K}$. Using the relation $H_{c2}(0) \approx -0.69T_c(dH_2/dT)_{T_c}$, the extrapolated $H_{c2}(0)$ is estimated as $450 \pm 50 \text{ Oe}$. The coherence length $\xi(0)$ is estimated as $\xi(0) = 850 \pm 10 \text{ Å}$, which is larger than the average size of Pd nanoparticles ($= 530 \pm 340 \text{ Å}$).

It is well known that the $H$-$T$ diagram of an ideal quasi-2D superconductors such high $T_c$ superconductors consists of a vortex lattice (Abrikosov lattice) phase, vortex glass phase, and a vortex liquid phase [29, 30]. The three lines ($H_{al}$, $H_{ag}$, and $H_{gl}$) merge into a multicritical point around $T^*$ and $H^*$, where the line $H_{al}$ is the boundary between the vortex lattice and the vortex liquid phase, the line $H_{ag}$ is the boundary between the vortex lattice phase and the vortex glass phase, and the line $H_{gl}$ is the boundary between the vortex glass phase and vortex liquid phase. Our $H$-$T$ diagram of Pd-MG is compared with that of typical quasi-2D superconductors. It seems that the lines $H_1$ and $H_2$ correspond to the lines $H_{gl}$ and $H_{ag}$, respectively. The line $H_1$ is the irreversibility line similar to the line $H_{gl}$. While the lines $H_{gl}$ and $H_{ag}$ merge at a multicritical point, the lines $H_1$ and $H_2$ do not merge even at $H = 0$. The absence of the multicritical point and the line $H_{al}$, suggests that the superconductivity in Pd-MG is quasi-2D.

So far we assume that the superconductivity occurs mainly in Pd sheets and that the AF short-range order occurs in nanographites (denoted by model I). There may be another possibility that the superconductivity occurs in nanographites and that the AF short-range order occurs in the Pd sheets (denoted by model II). This possibility can be ruled out for the following reason. Experimentally, Kopelevich et al. [31] have reported the superconducting-like magnetization hysteresis loops in highly oriented pyrolytic graphite (HOPG). Theoretically, González et al. [32] have predicted that a topological disorder in graphene sheets can trigger the instabilities for a possible $p$-wave superconductivity. Pd-MG exhibits the type-II superconductivity. There is a relationship between the upper critical field $H_{c2}$ and $T_c$: $H_{c2} = 124T_c$ in the units of K for $T_c$ and Oe for $H_{c2}$. This relation is in good agreement with an empirical law ($H_{c2} \approx 200T_c$) derived from the BCS (Bardeen-Cooper-Schrieffer) theory [27], suggesting that the conventional superconductivity occurs in Pd-MG. In this sense, the model I is preferable to the model II, in spite of the lack in our knowledge in the possible $p$-wave superconductivity in graphene sheets.

4.2. AF short-range order and SG-like behavior in graphene sheets

The nature of the AF short-range order is discussed. The existence of AF short-range order has been confirmed from the following results. (i) The susceptibility $\chi_{FC}$ obeys a Curie-Weiss law with a negative $\Theta$. The interactions between localized magnetic moments is antiferromagnetic. (ii) The irreversibility between $\chi_{ZF C}$ and $\chi_{FC}$ occurs well above $T_c$. The growth of spin order is greatly suppressed by the disordered nature of nanographites, forming the AF short-range order. Because of the frustrated nature
of AF interaction between nanographites, no long-range order can develop at any finite temperatures. We have found several results supporting that the AF short-range order below $T_c$ exhibits a SG-like behavior. (i) For an usual superconducting phase, $M_{TR}$ is larger than $M_{FC}$, and $M_{IR}$ is larger than $M_{IR}$ below $T_c(H)$. For Pd-MG, $M_{TR}$ is larger than $M_{FC}$, and $M_{IR}$ is larger than $M_{IR}$ for $T < T_\alpha < T_2(H)$, while $M_{TR}$ is smaller than $M_{FC}$, and $M_{IR}$ is smaller than $M_{IR}$ for $T_\alpha < T < T_2(H)$. The latter is a feature common to the SG systems having spin frustration effect. (ii) The aging dynamics of $M_{ZFC}(t)$ is observed below $T_c$, corresponding to a slow evolution of non-equilibrium spin configurations towards equilibrium ones. The relaxation rate $S(t) = (1/H)dM_{ZFC}/d\ln t$ shows a broad peak at $t_{cr}$ which is longer than $t_w$. Such an aging behavior is usually observed in SG systems. When the SG system is quenched from a high temperature above $T_{SG}$ to a low temperature $T$ below $T_{SG}$, the initial state is not thermodynamically stable and relaxes to more stable state. The aging behaviors depend strongly on their thermal history within the SG phase. Note that a SG-like behavior has been observed in $\chi_{FC}$ of ACF which is composed of disordered network of nanographites [25]. The susceptibility $\chi_{FC}$ of ACF shows a cusp around 4 - 7 K. This behavior is understood in terms of spin frustration effect arising from random strengths of the AF interactions between nanographites. As is discussed in section [4.1] the line $H_1(T)$ is assumed to be the irreversibility line for the magnetization in the superconductivity (the line $H_{gl}$). However, there is some possibility that the line $H_1(T)$ may correspond to the AT line for the SG-like behavior.

Harigaya [17, 18, 19] has theoretically predicted that the magnetism in nanographites with zigzag edge sites depends on the stacking sequence of nanographites. For the A-B stacking, there is no interlayer interaction $J_1$ at the edge site, where $J_1$ is the strength of the weak hopping interaction between neighboring layers. This gives rise to the finite magnetic moment. The AF spin alignment is favorable for strong on-site repulsion $U$. The local magnetic moments tend to exist at the edge sites in each layer due to the large amplitude of the wavefunctions at these sites. The number of up-spin electrons is larger than that of down-spin electrons in the first layer. The number of down-spin electrons is larger than that of up-spin electrons in the second layer, and so on. The system can be described by the AF Heisenberg model with the exchange interaction $J' (= 2J_1^2/U)$. For the A-A type stacking, on the other hand, the magnetic moment per layer does not appear due to the interlayer interaction. The up- and down-spin electrons are not magnetically polarized in each layer. Although there is no detailed structural study on the stacking sequence in Pd-MG, the AF order in Pd-MG may suggest that the A-B stacking is dominant compared to the A-A stacking. The spin correlation length along the $c$ axis is considered to be on the same order of the nearest neighbor interlayer distance between nanographites. Since the Pd sheet is sandwiched between graphene sheets, there is no net molecular field on Pd sheet from graphene sheets having the A-B stacking along the $c$ axis. This may lead to the coexistence of superconductivity and AF short-range order.
4.3. Effect of multilayered Pd sheets

In an ideal Pd-MG, there is one Pd sheet (monolayer) between adjacent graphene sheets. In reality, there are either monolayer or multilayers (2 - 4 layers) between graphene sheets. Multilayered Pd nanoparticles would generate internal stress inside the graphite lattice, leading to the break up of adjacent graphene sheets into nanographites. How does the spin fluctuation vary with the number of Pd layers in a quasi 2D-like Pd systems consisting of stacked Pd layers? Bouarab et al. [33] have predicted (i) no magnetic moment for \( n = 1 \), (ii) ferromagnetic moment for \( n = 2 - 5 \), and (iii) no magnetic moment for \( n > 5 \), where \( n \) is the number of Pd layers. The value of \( N(E_F) \) for \( n = 1 \) is smaller than that in the bulk Pd. The 2D effect increases the DOS in the middle of the energy band, whereas it decreases the DOS in the higher energy side where \( E_F \) exists. Because the Stoner criterion \( J_s N(E_F) > 1 \) is not satisfied, the Pd monolayer is non-magnetic, where \( J_s \) is an exchange parameter. The peak of the DOS, which is much below \( E_F \) for \( n = 1 \), moves towards \( E_F \) for higher \( n \). This prediction suggests that the Pd monolayer may be a superconductor because of the suppression of spin fluctuations. On the other hand, Pd layers with \( n = 2 - 5 \) may be a ferromagnet. In Pd-MG, at present it is not clear what is the minimum number of Pd layers \( (n_c) \) required for the ferromagnetic state. The value of \( n_c \) is dependent on the size of Pd nanoparticles. However, it is reasonable to conclude that Pd layers in Pd-MG is ferromagnetic for \( n \geq n_c \) corresponding to the sample with the long-reaction time and is superconducting for \( n < n_c \) corresponding to the sample with the short-reaction time [7].

5. CONCLUSION

Pd-MG undergoes a superconducting transition at \( T_c (= 3.63 \, \text{K}) \). A quasi-2D superconductivity occurs in Pd sheets. The AF short-range order appears well above \( T_c \) in graphene sheets. The growth of the AF short-range order is limited by the disordered nature of nanographites. Both the aging behavior of \( M_{ZFC}(t) \) and the \( T \) dependence of \( M_{ZFC}, M_{FC}, M_{IR}, \) and \( M_{TR} \) below \( T_c \) suggest the existence of a SG like behavior in nanographites. Further studies are required to understand the possible interplay between the superconductivity and SG-like behavior, including the nature of the irreversibility line \( H_1(T) \).

Acknowledgments

The authors would like to thank K. Harigaya for valuable discussions on the antiferromagnetism in nanographites. The work at Binghamton was supported by the Research Foundation of SUNY-Binghamton (contract number 240-9522A). The work at Osaka (J.W.) was supported by the Ministry of Education, Science, Sports and Culture, Japan [the grant for young scientists (No. 70314375)] and by Kansai Invention Center, Kyoto, Japan.
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