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Local ferromagnetism in microporous carbon with the structural regularity of zeolite Y

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Magnetization $M(H,T)$ measurements have been performed on microporous carbon (MC) with a three-dimensional nanoarray structure corresponding to that of a zeolite Y supercage. The obtained results unambiguously demonstrate the occurrence of high-temperature ferromagnetism in MC, probably originating from a topological disorder associated with curved graphene sheets. The results provide evidence that the ferromagnetic behavior of MC is governed by isolated clusters in a broad temperature range, and suggest the occurrence of percolative-type transition with the temperature lowering. A comparative analysis of the results obtained on MC and related materials is given.

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During the past approximately 15 years, various research groups have reported on the occurrence of room-temperature ferromagnetism in materials made solely of carbon. Thus, high-temperature ferromagnetic (FM) behavior has been observed in pyrolitic carbon,[1] amorphous-like carbon prepared by direct pyrolysis,[2] superhigh surface area carbon with micro-graphitic structures,[3,4] C_{60} under photoassisted oxidation,[5] highly oriented pyrolitic graphite (HOPG),[6,7] extraterrestrial graphite,[8] and polymerized rhombohedral (rh)-C_{60}.[9–11] Certainly, an understanding of mechanism(s) behind the magnetic behavior of the carbon-based materials as well as an engineering of novel FM carbon structures should have a wide impact.

It appears that the largest among reported low-temperature values of the spontaneous magnetization M_s ($\sim$0.05, . . . ,0.5 emu/g)[12] take place in nearly graphitized materials which contain amorphous and/or fullerene-like carbon fragments.[1,9–11] Indeed, the high-temperature ferromagnetism in rh-C_{60} compounds[9–11] occurs only in samples prepared very close to the temperature at which fullerene cages collapse and an amorphous carbon forms. The presence of amorphous carbon in nominally rh-C_{60} and its possible decisive role in the magnetic behavior of this material has been pointed out in Ref. 11. On the other hand, experiments performed on a glassy carbon (GC) (Ref. 13) indicate that ferromagnetism emerges during the graphitization process, and a possibility that topological defects trigger ferromagnetism has been suggested.[13] In fact, the occurrence of FM, antiferromagnetic (AFM), and superconducting (SC) instabilities due to a topological disorder in graphitic sheets has been predicted theoretically.[14] The analysis given in Ref. 14 assumes the formation of pentagons and heptagons, i.e., disclinations in the graphene honeycomb lattice. The low-lying electronic states of an isolated graphitic sheet can be well approximated by Dirac equations in $(2+1)$ dimensions. Then, according to Ref. 14, a random distribution of topological defects described in terms of a random gauge field can lead to an enhancement of the density of states of Dirac fermions $N(E)$ at low energies E, and hence lead to magnetic or SC instabilities. Compounds with curved graphene layers have been proposed as promising materials for both FM and SC occurrence.[14]

The aforesaid experimental as well as theoretical results motivate us to explore magnetic behavior of the microporous carbon (MC) with a three-dimensional (3D) nanoarray structure whose arrangement matches that of supercages of zeolite Y. Details of preparation of the MC samples and their characterization are given elsewhere.[15,16] Briefly, the MC has been prepared by the following template technique. Powder zeolite Y was impregnated with furfuryl alcohol (FA) and FA was polymerized inside the zeolite channels by heating the FA/zeolite composite at 150 °C under N_2 flow. The resultant polyfurfuryl alcohol/zeolite composite was heated to 700 °C in N_2. As soon as the temperature reached 700 °C, propylene chemical vapor deposition (CVD) was performed for further carbon deposition. After the CVD, the composite was further heat-treated at 900 °C under a N_2 flow. The resultant carbon was liberated from the zeolite framework by acid washing. The obtained MC possesses a very high surface area of 3600 m^2/g and consists of a curved 3D graphene network which may contain randomly distributed pentagons and heptagons. The carbon particle size ranges from 1000 Å to 4000 Å.[16] Spectrographic analysis of the MC samples reveals magnetic impurity contents of Fe (64 ppm), Co (4.4 ppm), and Ni (3.5 ppm).

We performed dc magnetization $M(H,T)$ measurements on two MC samples from the same batch with masses $m_1 = 10.82$ mg (labeled as MC1) and $m_2 = 8.7$ mg (labeled as MC2) in the temperature range 2 K$\leqslant T \leqslant$300 K and applied magnetic field up to $\mu_0 H = 5$ T using the SQUID magnetometer MPMS5 (Quantum Design).

The obtained results unambiguously demonstrate the occurrence of ferromagnetism in our MC samples. The results also provide evidence that the sample FM behavior is governed by isolated or weakly interacting clusters (droplets) in a broad temperature range $T_c \leqslant T \leqslant T^*$, where $T^* > 300$ K and $T_c \approx 30$ K. Below T_c, FM magnetization suddenly increases suggesting a percolative-type transition associated

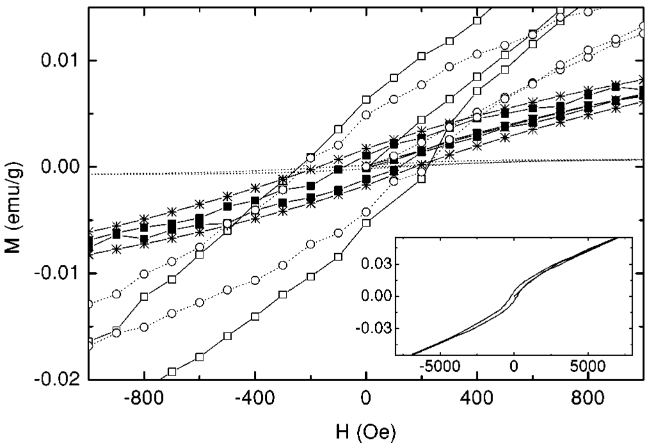

FIG. 1. Low-field portions of $M(H)$ obtained for MC1 sample in the field range -50 kOe$\leqslant H \leqslant 50$ kOe and $T=2$ K (□), 5 K (○), 30 K (*), and 300 K (■); dotted line corresponds to $M(H)$ measured for HOPG sample at $T=5$ K. Inset depicts $M(H)$ at $T=5$ K for MC1 sample on a larger field scale.

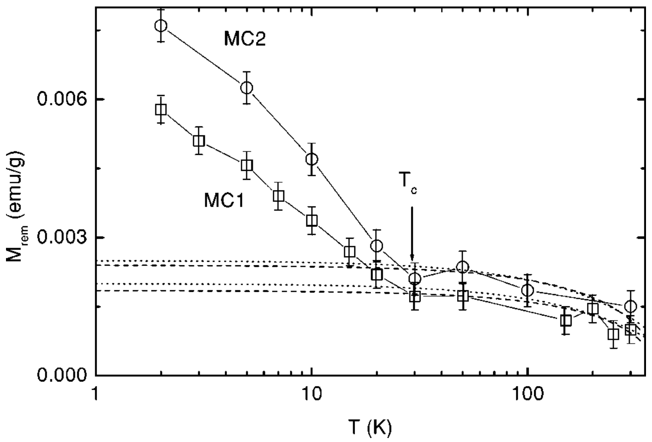

FIG. 2. Remanent magnetization, $M_{rem}(T)$ obtained for MC1 and MC2 samples. Dotted and dashed lines correspond to the dependence $M_{rem}(T) \sim (1-T/T^*)^n$ with $n=1$ (1/2) and $T^*=600$ (400) K, respectively. Arrow indicates the temperature T_c associated with the percolative-like FM transition.

with growing in size and/or interacting FM clusters. At yet lower temperatures $T \leqslant T_\times \approx 10$ K, a magnetization anomaly seemingly associated with competing AFM order has been observed.

Figure 1 presents low-field portions of $M(H)$ isotherms recorded for the MC1 sample in the field range -50 kOe $\leqslant H \leqslant 50$ kOe and $T \leqslant 300$ K, providing evidence for the FM hysteresis loops occurrence at all measuring temperatures. The inset in Fig. 1 exemplifies the $M(H)$ measured at $T=5$ K on a larger field scale, which demonstrates that $M(H)$ becomes reversible at $H \geqslant 5$ kOe, as well as that $|M(H)|$ continuously increases with the field increasing, so that $M(H)=M_s+\chi H$, where $M_s(5\text{ K})=0.02$ emu/g is the spontaneous magnetization obtained from the extrapolation of the linear $M(H)$ region to $H=0$, and $\chi(5K)=5.1\times 10^{-6}$ emu/gOe is the paramagnetic susceptibility. Additionally, in Fig. 1 we have plotted M(H) obtained for HOPG sample[6] at $T=5$ K and H applied parallel to the sample basal planes. The spontaneous magnetizations $M_s^{HOPG}(5\text{ K})=0.0007$ emu/g obtained for HOPG sample testifies that FM is drastically enhanced in the MC as compared to the HOPG. We stress that because the MC exhibits a very high surface area, the iron impurities should be (1) present as very small particles and (2) finely dispersed on the surface of MC. Then, since the HOPG sample contains ~100 ppm of Fe,[6] which exceeds the total magnetic impurity contents in our MC, the inequality $M_s^{MC} \gg M_s^{HOPG}$ cannot be accounted for by the impurity effect (see also below).

The remanent magnetization $M_{rem}(H=0)=[M^+(H=0)-M^-(H=0)]/2$ versus temperature obtained for both MC1 and MC2 samples, where $M^+(H=0)$ and $M^-(H=0)$ are zero-field positive and negative magnetizations measured after the field cycling is shown in Fig. 2. As Fig. 2 demonstrates, the $M_{rem}(T)$ steeply increases at $T \leqslant T_c \approx 30$ K. The steep increase of the magnetization below 30 K can also be seen in Fig. 3(a–d) where $M(H,T)$ measured for the MC2 sample in both zero-field-cooled (ZFC) and field-cooled (FC) on cooling regimes at various applied fields are given; the magnetization data corresponding to the ZFC regime, $M_{ZFC}(T,H)$, were taken on heating after the sample cooling at $H=0$, and the magnetization in the FC regime, $M_{FC}(T,H)$, was measured as a function of decreasing temperature in the applied field. The difference between $M_{ZFC}(T,H)$ and $M_{FC}(T,H)$ magnetizations, which is apparent from Fig. 3, suggests that the MC possesses a disordered magnetism similar as, for instance, diluted FM semiconductors (DFMS),[17,18] doped LaMnO$_3$ ("manganites"),[19] and TDAE-C$_{60}$.[20] The salient feature of the data presented in Fig. 3 is the negative sign of the difference $\Delta M(T,H)=M_{FC}(T,H)-M_{ZFC}(T,H)$ observed at $H=10$ kOe and $T<10$ K [see Fig. 3(d)], which is a rare phenomenon occurring, however, in the presence of metastable magnetic phases.[21,18]

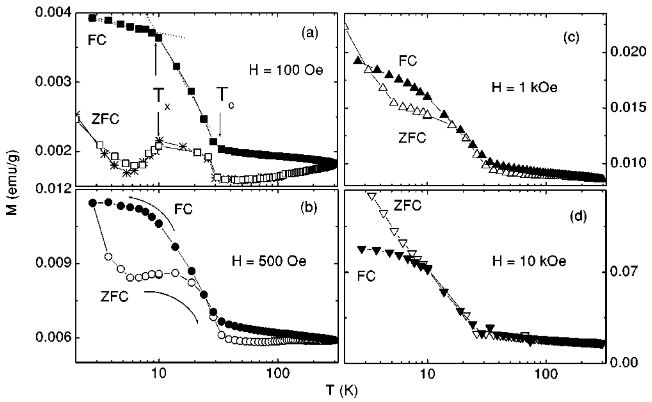

FIG. 3. (a–d) $M(T,H)$ measured for MC2 sample in both ZFC (open symbols) and FC (solid symbols) regimes at various applied magnetic fields; see text for meaning of T_c and $T_\times$(a), dotted lines are a guide for the eye. $M_{ZFC}(T,H=100\text{ Oe})$ (*) measured independently for 2 K$\leqslant T \leqslant$100 K is included in (a) for completeness.

We proceed with a discussion of the results noting a certain similarity between the magnetic behavior of MC and that of DFMS and manganites, where an occurrence of the percolative-type FM transition has been documented.[17,22–27] According to the percolation picture, uncorrelated FM clusters are formed below a temperature T^*, leading to finite although small values of $M_s(T,H)$, $M_{rem}(T,H)$, and $\Delta M(T,H)$.[17] As the temperature decreases, FM correlations develop on a larger scale, and eventually a long-range FM order emerges at the critical temperature $T_c<(\ll)T^*$. The random orientation of M_s corresponding to different FM clusters can be stabilized in the presence of quenched disorder and/or competing AFM correlations leading to the spin-glass-like behavior.[28,29] Note, that the magnetization anomaly at $T=T_\times\approx 10$ K, viz., both the steps in $M_{ZFC}(T)$ and the kink in $M_{FC}(T)$, see Fig. 3(a), is consistent with the occurrence of AFM correlations competing with the FM order.[30] The applied magnetic field aligns FM clusters diminishing $\Delta M(T,H)$, as experimentally found ($H>500$ Oe) (Fig. 3). However, $\Delta M(T,H)<0$ observed at high enough fields and $T<T_c$, see Fig. 3(d), may be associated with coexisting metastable AFM and FM phases, as well as with a first-order nature of the percolative transition.[27]

Adopting here the percolative-type picture, we tend to identify $T_c\approx 30$ K with a transition temperature below which an enlargement of preexisting FM clusters takes place. At the same time, because the experimental data indicate a coexistence of different magnetic states, the T_c should not be associated with a global FM phase transition temperature. Furthermore, as Fig. 2 shows, $M_{rem}(T)$ can be well approximated by the dependence $M_{rem}(T)\sim(1-T/T^*)^n$ at $T\geqslant T_c$, where $n=1$ (1/2) and $T^*=600$ (400) K can be associated with the temperature below which isolated FM clusters are formed. Note, that the linear M_{rem} vs T dependence has been observed for HOPG (Ref. 6,7) and graphite-sulfur composites[31] in a broad temperature range.

Apparently, the above phenomenology describes well the experimental results. At the same time, the observation of curved graphene sheets in our MC, presumably containing pentagons and heptagons,[15] is consistent with the theoretical expectations of the occurrence of both FM and AFM instabilities in topologically disordered graphitic layers;[14] at low energies, density of states of Dirac fermions diverges as $N(E)\sim E^{-1+2/z}$ (the dynamical exponent z depends on disorder) or $N(E)\sim E^{-1}\exp(-|\ln E^{2/3}|)$,[32,33] leading to the observed electronic instabilites. It is also possible that a peak in the $N(E)$ at $E=0$ (Ref. 34) triggers further instabilities. Since HOPG has a small number (if any) of topological defects,[14] the experimental observation that $M_s^{HOPG}\ll M_s^{MC}$ (see above) is not unexpected. On the other hand, there exists both experimental and theoretical evidence that fullerene-like fragments with positive and/or negative curvature should be a common feature of microporous carbons.[35] Such fragments should naturally appear also in rh-C_{60} samples with partially destroyed C_{60} molecules.[36,9–11]

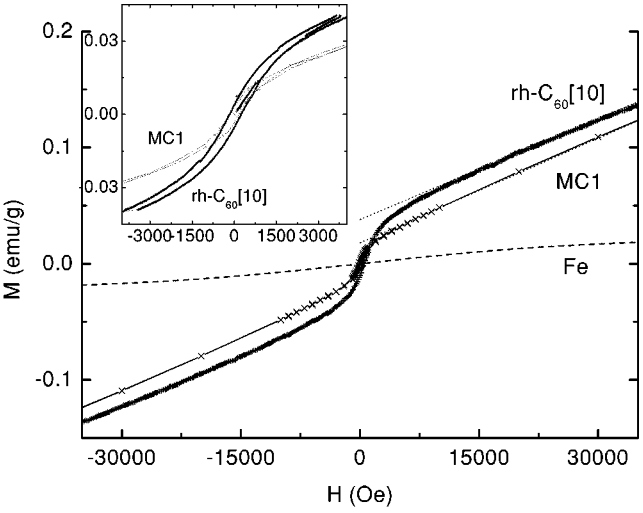

FIG. 4. $M(H)$ measured at $T=10$ K for rh-C_{60}[10] and MC1 samples; dotted lines are obtained from the equation $M(H)=M_s+\chi H$, where $M_s=0.018$ emu/g (MC1), $M_s=0.038$ emu/g (rh-C_{60}), and $\chi\approx 3\times 10^{-6}$ emu/gOe for both rh-C_{60} and MC1 samples; inset demonstrates the $M(H)$ at low fields. Dashed line corresponds to the calculated magnetization $M_{Fe}(H,T=10\text{ K})$ for Fe (64 ppm) impurities using a Brillouin function, see text.

A comparative analysis of the data obtained on MC1 and rh-C_{60} sample synthesized at the pressure 9 GPa and $T=800$ K (Ref. 10) (Fig. 4) reveals a striking correspondence between $M(H)$ measured in these materials. As follows from Fig. 4, the high field portion of the magnetization curves measured at $T=10$ K can be fitted by the equation $M(H)=M_s+\chi H$, where $M_s=0.018$ emu/g (MC1), $M_s=0.038$ emu/g (rh-C_{60}), and $\chi\approx 3\times 10^{-6}$ emu/gOe is the paramagnetic susceptibility for both materials. The remanent magnetizations measured in MC1, $M_{rem}=0.0034$ emu/g and rh-C_{60}, $M_{rem}=0.0047$ emu/g samples, see inset in Fig. 4, also practically coincide. To be more specific, we included in Fig. 4 the calculated magnetization due to Fe impurities (64 ppm) $M_{Fe}(H)=N\mu\tanh(\mu H/k_BT)$, where $T=10$ K, N is the number of Fe ions per gram, and $\mu=gJ\mu_B$, taking the Lande factor $g=2$ and the spin $J=2.5$ for Fe^{3+}. It is evident from Fig. 4 that magnetic impurities cannot account for the measured magnetization.

On the other hand, larger values of $M_s(10\text{ K})\approx 0.2\ldots 0.4$ emu/g and "saturated" character of FM hysteresis loops were reported for rh-C_{60} samples synthesized at the pressure of 6 GPa and $T=1020,\ldots,1050$ K.[9,11] This can be understood assuming a stronger coupling between FM clusters in 6 GPa-rh-C_{60} samples[9,11] as compared to that in MC and 9 GPa-rh-C_{60} compounds,[10] in a close analogy with the magnetization behavior in other inhomogeneous ferromagnets.[17,24] Actually, our recent measurements performed on 6 GPa-rh-C_{60} samples synthesized at $T=1073,\ldots,1123$ K, revealed a magnetic behavior characteristic of inhomogeneous ferromagnets,[37] suggesting that the sample (rh-C_{60}) preparation conditions control an interaction strength between FM clusters and/or their size.

To summarize, we reported on the observation of high-temperature ferromagnetism in microporous carbon consisting of curved graphitic layers. The results provide evidence that FM behavior of MC is governed by isolated clusters in a broad temperature range, and suggest the occurrence of percolative-type transition with the temperature lowering. We pointed out that ferromagnetism in both MC and rh-C_{60} compounds can be associated with fullerene-like fragments with positive and/or negative curvature.

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