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Local Superconductivity and Ferromagnetism Interplay in Graphite-Sulfur Composites

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The superconductivity of graphite-sulfur composites is highly anisotropic and associated with the graphite planes. The superconducting state coexists with the ferromagnetism of pure graphite, and a continuous crossover from superconducting to ferromagnetic-like behavior could be achieved by increasing the magnetic field or the temperature. The angular dependence of the magnetic moment m(α) provides evidence for an interaction between the ferromagnetic and the superconducting order parameters.

An interplay between ferromagnetic (FM) and superconducting (SC) behavior of graphite and related systems has recently been observed [1, 2] and theoretically analyzed [3, 4]. In particular, it has been demonstrated that the SC of graphite-sulfur (C-S) composites occurring within some sort of "grains" or domains [5, 2] is highly anisotropic and associated with the graphite planes [2]. The SC domains coexist with the FM of pure graphite [1], and a continuous crossover from SC to FM-like behavior could be achieved increasing either the applied magnetic field H or the temperature T.

Here we focus our attention on the highly anisotropic nature of the SC state of the C-S composites, which was explored by means of the angular dependence of the sample magnetic moment m(α, T, H), where α is the angle between the applied magnetic field H and the largest sample surface. The main conclusion of this work is that SC and FM order parameters interact in such a way that the FM component of m(α, T, H) is rotated by 90° below the SC transition temperature T_c(H).

The here studied graphite-sulfur sample was thoroughly characterized in Ref. [2]. In summary, the C-S sample was prepared using graphite rods from Carbon of America Ultra Carbon, AGKSP grade, ultra "F" purity (99.9995%) (Alfa-Aesar, # 40766) and sulfur chunks from American Smelting and Refining Co. that are spectrographically pure (99.999+ %). A pressed pellet (ϕ = 6 mm, $\sim$7000 lb) of graphite was prepared by pressing graphite powder, the graphite powder was produced by cutting and grinding the graphite rod on the edge and side area of a new and clean circular diamond saw blade. The graphite pellet was encapsulated with sulfur chunks (mass ratio $\sim$ 1:1) in quartz tube under 1/2 atmosphere of argon and heat treated in a tube furnace at 400 °C for one hour and then slowly cooled (4 °C/h) to room temperature. X-ray diffraction measurements (θ-2θ geometry and rocking curves) of the reacted sample yielded a spectrum with only the superposition of the (00ℓ) diffraction peaks of graphite with the orthorhombic peaks of sulfur with no extra peak due to a compound, second phase or impurity. The c-axis lattice parameter (c = 6.72Å) of the sample is equal to the pristine graphite powder pellet, which testifies against sulfur intercalation. The diffraction pattern also shows a strong (00ℓ) preferred orientation, which was confirmed by rocking curve scans that give a $\Delta\theta$ = 6° (FWHM) for the (002) peak, due to the highly anisotropic (plate-like) shape of the graphite grains. The sample ($\sim 5 \times 2.5 \times 1.7 mm^3$) was cut from the reacted pellet and used for the magnetic moment measurements as well as the above described analyses. The m(α, T, H) has been measured using SQUID magnetometers MPMS5 (Quantum Design). All the magnetic moments presented here were normalized to the sample mass. The angular dependences of the magnetic moment of our sample were measured with the MPMS5 magnetometer where a horizontal sample rotator insert (Quantum Design) was placed in the regular sample holder space and controlled by the QD CPU board special EPROM (S3) rotational transport software. The rotator has a substrate capable to rotate 360° around the horizontal axis and on this substrate the largest surface of the samples were glued with Duco cement in such a way that the graphite c-axis can rotates around the substrate horizontal axis while the applied magnetic field is always vertical and perpendicular to the rotator axis. The measurements were performed with the step of 10°. The background signal of the rotator without a sample but with Duco cement is paramagnetic with a susceptibility $\chi_b \sim 3.6 \times 10^{-8}$ emu/Oe, this is at least one order of magnitude smaller than our sample signal. All the dc magnetic moment measurements were made using a scan length of 1.5 cm.

The SC characteristics of our C-S sample were presented in details in Ref. [2]. In Fig. 1(a) is shown the temperature dependence of the ZFC (zero field cooled) magnetic moment m(T) after the subtraction of the magnetic moment measured at T = 10 K, m(10K), i.e. in the normal state, for several magnetic fields applied perpendicular to the largest surface of the sample (H$\|$c). ZFC measurements were made on heating after the sample was cooled in zero applied field to low temperatures and the desired magnetic field was applied. From Fig. 1(a) we can see that the SC transition temperature $T_c = 9$K and that the SC signal $|$m(T) - m(10K)$|$, increases bellow this temperature. The m(T) measurements with the applied magnetic field parallel to the main sample surface (H$\|$a) present a completely different magnetic response. Fig. 1(b) shows the temperature dependence of the magnetic moment m(T) measured by ZFC for various applied fields, as indicated in the figure, when H$\|$a. No sign of a SC transition could be detected within the data noise of $\sim 5 \times 10^{-6}$ emu/g and the range of temperatures measured, down to 2.0 K (not shown in Fig. 1(b)). Note that the scale ranges in Figs. 1(b) and 1(a) are almost the same. These results indicate that the SC state is highly anisotropic and is associated with the graphite planes. Fig. 2 shows the hysteresis loops m(H) - m_o (H) measured with the ZFC procedure (H$\|$c) for T = 7, 8, 9 and 10 K, after subtraction of the diamagnetic background signal $m_o = \chi$ H, where $\chi = -7.12 \times 10^{-6}$ emu g^{-1} Oe^{-1} for all these measured temperatures (for more details see [2]). Fig. 2(a) shows at T = 7 K a characteristic type II SC hysteresis loop. As the temperature rises above T_c = 9 K, the hysteresis loops resemble that known for FM materials, Fig. 2 (d). For temperatures at and just below T_c, the presence of both SC and FM contributions to the measured signal can be seen, Fig. 2 (b,c).

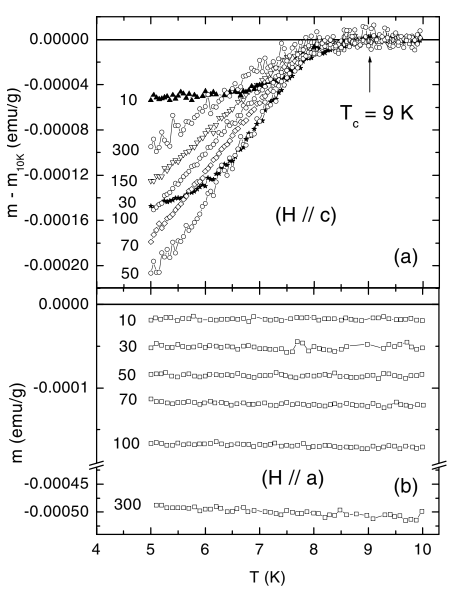

Figure 1. (a) Temperature dependences of the superconducting diamagnetic moment measured by zero-field-cooled after the subtraction of the normal magnetic moment at 10 K, m_{10K}, at various fields: (▲), H = 10 Oe; (⋆), H = 30 Oe; (○), H = 50 Oe; (◇), H = 70 Oe; (○), H = 100 Oe; (▽), H = 150 Oe; (○), H = 300 Oe, with H$\|$c. (b) Temperature dependences of the magnetic moment measured by zero-field-cooled with H$\|$ a and at different magnetic fields, as indicated in oersteds next to each curve.

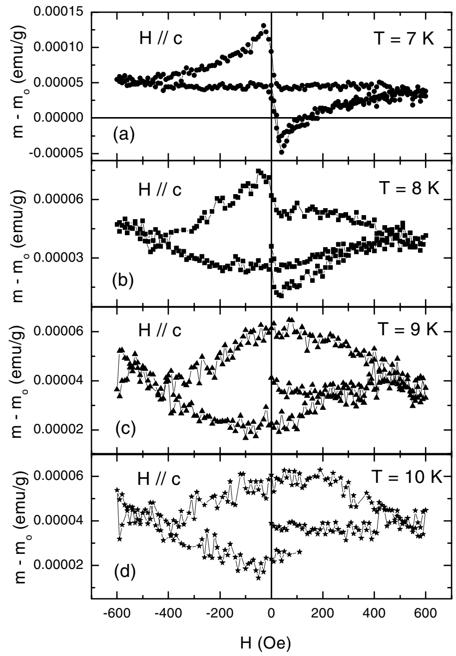

Figure 2. Zero-field-cooled magnetic moment hysteresis loops m(H), after the subtraction of the diamagnetic background signal ($m_o = \chi$H, where χ = -7.12 × 10^{-6} emu g^{-1} Oe^{-1}), with H$\|$ c and for (a) T = 7 K, (b) T = 8 K, (c) T = 9 K and (d) T = 10 K (the last part of this hysteresis loop was not measured). For details see text.

In other words, the results presented in Fig. 2 provide evidence for the coexistence of SC and FM in the C-S. A similar conclusion has been drawn in Ref. [2] based on the isothermal m(H) measurements at $T < T_c$ in a broader field range.

Again, for the m(H) measurements with the applied magnetic field parallel to the graphite planes (H$\|$a) a different magnetic response is obtained. Fig. 3(a-c) shows the ZFC magnetic moment hysteresis loops m(H) for T = 5, 7 and 9 K after subtraction of the linear diamagnetic background signal ($m_o = \chi$H, where χ(5 K) = χ(7 K) = χ(9 K) = -2.25 × 10^{-6} emu g^{-1} Oe^{-1}), for details see [2]. From these plots, fig. 3(a-c), we can clearly see three almost identical FM-like hysteresis loops obtained both below and above T_c.

These hysteresis loops are typical of FM materials and are similar to those observed before [1] in HOPG graphite samples. The FM behavior of both HOPG and C-S persists well above the room temperature [1,2]. At the same time, no noticeable change or anomaly was observed in the hysteresis loops around 9 K (H$\|$a). So, our samples show a FM-like behavior for all temperatures bellow the Curie temperature ($\sim$750 K) [2] in both H$\|$a and H$\|$c field configurations, and for $T < T_c$(H) and low fields the FM coexists with a SC state.

We also studied in details the angular dependence of m(α) for magnetic fields up to 10000 Oe. These high field m(α) measurements [6] are not directly related to the point under discussion but support the low field angular dependences observed. All these measurements were made by

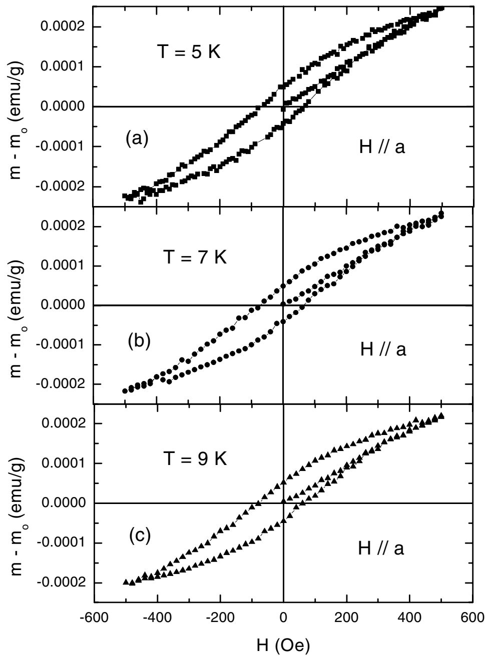

Figure 3. Zero-field-cooled hysteresis loops m(H), after the subtraction of the diamagnetic background signal ($m_o = \chi H$, where χ = -2.25 $\times$ 10^{-6} emu g^{-1} Oe^{-1}), with H$\|$ a and for (a) T = 5 K, (b) T = 7 K and (c) T = 9 K. For details see text.

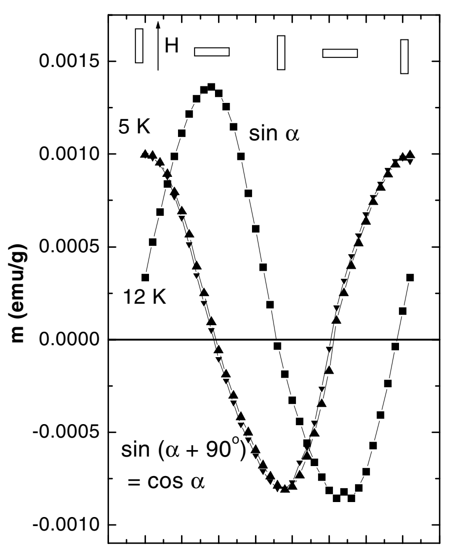

Figure 4. Angular dependences of the magnetic moment m(α) between 0° and 360° in the superconducting state (T = 5 K, (▲ = increasing, ▼ = decreasing magnetic field)) and in the normal state (T = 12 K, (■)) for H = 30 Oe. The applied magnetic field direction is shown. At the top of figure is also shown schematically the sample cross section position in relation to the magnetic field for α values of $\sim$ 0° (H$\|$a), 90° (H$\|$ c), 180° (H$\|$ a), 270° (H$\|$ c) and 360° (H$\|$ a).

initially zero field cooling (ZFC) the sample until 5 K (or 12 K) with the sample largest surfaces approximately vertical (α = 0° or H$\|$a). The angle α given here is the value as determinate by the QD software and depends only of the initial position. We allways tried to align as close as possible the initial position (α = 0°) of the sample so that the magnetic field is parallel to their largest surfaces (H$\|$a). The magnetic moments were measured with increasing and decreasing α from 0° to 360° and back in steps of 10°. Fig. 4 shows the angular dependences of the magnetic moment m(α) in the SC state (▲, T = 5 K) and the normal state (■, T = 12 K) when H = 30 Oe. For T = 5 K is also shown the magnetic moments measured with increasing (▲) and decreasing (▼) α, demonstrating the reversible m(α). The applied magnetic field direction is shown in figure 4. At the top of Fig. 4 we also show schematically the sample cross section position in relation to the magnetic field for α values of $\sim$ 0° (H$\|$a), 90° (H$\|$c), 180° (H$\|$ a), 270° (H$\|$c) and 360° (H$\|$a). Several new and interesting observations can be made from these measurements. From Fig. 4 we can see that the m(α) $\sim$ $sin\alpha$ for T = 12 K and m(α) $\sim$ $sin(\alpha$ + 90°) = cosα for T = 5 K. These observations imply that the magnetic response of the sample can vary from paramagnetic (or ferromagnetic) to diamagnetic depending simply on the sample/field configuration used during the measurement. The m(α, T, H) behavior of this graphite-sulfur sample in the normal state, T = 12 K, is essentially the same as found in pure HOPG graphite samples, which were also studied in great details and will be published elsewhere [6]. The m(α) dependence for T = 5 K suggests that the paramagnetic (or ferromagnetic) m(α, T, H) is confined to the graphite planes (or parallel to the sample largest surfaces) and rotates with the sample rotation in the applied field. For T = 12 K, or in the normal state, the magnetic moment is also paramagnetic (or ferromagnetic) but is perpendicular to the graphite planes (or 90° out of phase as compared to the measurements performed at T = 5 K) and also rotates with the sample rotation. We have shown before that this sample presents a superconducting behavior for T = 5 K ($T < T_c$). Noting, however, that at H = 30 Oe and T = 5 K the SC diamagnetic signal is only $\sim$ 10% (see Fig. 1(a)) of the magnetic moment values of Fig. 4. So, at 5 K the SC signal is masked by a larger FM moment. Also, the "diamagnetic" signals observed in the normal state for H$\|$c and H$\|$a [2] and as shown in Fig. 1(b) (H$\|$ a) are in fact a result of the superposition of the FM moment pointing against the applied magnetic field and/or when 180° $\leq \alpha \leq$ 340° in Fig. 4 (T = 12 K).

It is reasonable to assume that the main cause of the different m(α) behavior between T = 5 and 12 K at low fields originates from the occurrence of SC bellow 9 K. In spite of the total SC signal is rather weak, the occurrence of SC grains within the graphite planes for $T < T_c$ may result in an interaction between SC and FM order parameters turning the FM moment direction by 90° and confining it into the graphite planes. One may speculate on the appearance at $T < T_c$ of spin-polarized currents associated with spintriplet SC [3,4]. Then, these currents will exert a torque on the preexisting FM moment, leading to its rotation [8,9]. A more detailed discussion of this interesting possibility will be given in Ref. [6].

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