Materials Research Express

PAPER

Percolative magnetic correlation and competing-antiferromagnetism in highly oriented pyrolytic graphite with hexagonal Moiré superlattices at the magic-angle

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Abstract
Occurrence of magnetic-correlation-phenomena in multi-layered carbon materials has recently attracted an important attention for applications in magnetic devices and spintronics. In this study, exfoliated highly-oriented-pyrolytic-graphite (HOPG) lamellae exhibiting hexagonal-Moiré-supperlattices, with periodicity of \(~\sim 13\) nm (1st category, \(\theta_{\text{rot}} \sim 1.09^\circ\)) and \(~\sim 36\) nm (2nd category, \(\theta_{\text{rot}} \sim 0.39^\circ\)) were investigated. Raman-spectroscopy evidenced weak D, D’ and intense G bands. In 1st category, magnetization versus field, ZFC–FC magnetic-curves from 2 K to 300 K and T-ESR revealed presence of uncorrelated and correlated ferromagnetic clusters at \(T^* \sim 150\) K together with a critical transition at \(T_c \sim 50\) K, compatible with percolative-ferromagnetic-correlation. Comparative measurements on the 2nd category, revealed an analogue trend, with at \(T^* \sim 50–60\) K together with an irreversibility at \(T_c \sim 40\) K, indicative of competing ferromagnetic/antiferromagnetic-correlations.

Introduction
Occurrence of magnetic correlation phenomena in multi-layered carbon materials has recently attracted an important attention for possible fabrication of magnetic-based devices. Magnetic correlation signals have been observed in pyrolytic carbon [1], highly oriented pyrolytic graphite (HOPG) [2, 3], turbostratic graphite [4, 5], amorphous carbon [6], carbon with large surface area [7, 8], \(C_{60}\) [9], polymerized \(C_{60}\) [10–12] and recently twisted graphene bilayer/s (TGB/TGBs) [13–15]. Important values of saturation magnetizations have been reported in presence of topological defects in the form of pentagon/heptagons [16–19]. A particular role (for the creation of magnetic correlation) has been attributed to disclinations and topological disorder [18]. Experiments performed on glassy carbon [16] highlighted the important role of the graphitization process in inducing topological-defects-formation and consequent ferromagnetic correlation.

Theoretical analyses have also predicted the occurrence of antiferromagnetic and superconducting instabilities in presence of topological disorder [17]. In particular, the concept of ferromagnetic correlation was described on the basis of the percolative theory of ferromagnetism [18].

According to this theory, uncorrelated clusters located in topologically disordered areas can be formed below a certain temperature \(T^*\) [18–20]. As the temperature decreases, ferromagnetic correlations develop and give rise to long-range ferromagnetic ordering at a certain critical temperature \(T_c\). Together with these observations, other works by Kuwabara et al.[21], Patil et al.[22], Flores et al.[23] and Brihuega et al.[24] (in graphite and multilayer graphene) have reported significant effects of layer rotation on the electronic structure of these materials, with appearance of singularities in the density of states [24]. Hexagonal Moiré superlattices with the following large super-periodicities D were reported in ref. [21–24], namely: D \(\sim 7.7\) nm (\(\theta_{\text{rot}} \sim 1.8^\circ\),
Kuwabara et al [21], D ∼ 6.8 nm, 8.4 nm, 9.2 nm (θrot ∼ 2.07°, 1.67° and 1.53°) Patil et al [22], D ∼ 4.85 nm, 1.5 nm (θrot ∼ 2.9°, 9.4° Flores et al [23], and D ∼ 1.48 nm, 2.24 nm, 4.1 nm, 10.11 nm (θrot ∼ 9.6°, 6.4°, 3.5°, 1.4° Brihuega et al [24].

Despite these important findings reported in literature, additional work is needed in order to elucidate the physical mechanism that induces magnetic ordering in graphite. A significant role of local-graphene-layer rotation in such a magnetic correlation process can not be excluded. Interestingly a recent work by Seo et al has shown the existence of an exotic ferromagnetic state for θrot ∼ 1.8° in TGBs [15]. The latter finding opens new directions towards the possible existence of multiple magnetic ordering features, controllable by graphene layer rotation.

In this letter we report a novel study on exfoliated HOPG lamellae exhibiting two categories of hexagonal Moiré superlattices with periodicity of ∼13 nm (1st category, θrot ∼ 1.09°) and ∼36 nm (2nd category, θrot ∼ 0.39°). By applying the equation a/2D = sin(θ/2) [21] where a is the basal lattice constant of HOPG (∼0.247 nm), D is the period of the Moiré pattern and θ is the rotational angle, rotational angles θrot of 1.09° and 0.39° could be identified. The observed super–periodicities have analogy with those reported by Kuwabara et al [21], Patil et al [22] and Brihuega et al [24]. Raman spectroscopy evidenced presence of weak D and D’ bands compatible with those expected for graphene layer rotation [25], together with an intense G band. Magnetization versus field measurements at 2 K, revealed unsaturated and progressively saturated ferromagnetic signals from 50 Oe to 150 Oe in the 1st category. Further, magnetization versus field, zero field cooled (ZFC) and field cooled (FC) measurements of the magnetization from 2 K to 300 K and T- electron spin resonance (ESR) revealed presence of uncorrelated and correlated ferromagnetic clusters at T ∼ 150 K together with a critical transition at Tc ∼ 50 K, compatible with percolative-ferromagnetic-correlation, in agreement with the percolative theory reported by Kopelevich et al [18].

Comparative measurements on the 2nd category, revealed an analogue trend, with at T ∼ 50–60 K together with an irreversibility at Tc ∼ 40 K; this latter observation provides evidence of a spin-glass-like behaviour, which we ascribed to the existence of additional competing antiferromagnetic correlations arising at low temperature (T ∼ 59 K). No superconductive-transition was found in the analysed temperature range [26–28].

Experimental

HOPG samples with dimensions of 5 × 5 × 1 mm and mosaic angle of 0.5°, ± 0.2° (grade A) were purchased from XFNANO, INC China. TEM measurements were performed with a 200 kV American FEI Tecnai G2F20. Note that the topmost surface layers of the as purchased HOPG samples were removed in order to exclude contribution from surface impurities. See ESI figures S.3–5 (available online at stacks.iop.org/MRX/7/125602/mmedia) for energy dispersive x-rays (EDX) measurements revealing also presence of minor Ca-based impurities in some of the as exfoliated lamellae. SQUID magnetometry measurements were performed with a Quantum design instrument. Raman Spectroscopy were collected in a custom-built Raman system using a triple grating monochromator (Andor Shamrock SR-303i-B, EU) with an attached EMCCD (ANDOR Newton DU970P-UVB, EU), excitation by a solid-state laser at 532 nm (RGB lasersystem, NovaPro 300 mW, Germany) and collection by a 100 ×, 0.90 NA objective (Olympus, Japan). Additional characterization can be found in the electronic supplementary information (ESI).

Results and discussion

Examples of the 1st and 2nd categories of Moiré superlattices are shown in figures 1–2 by high resolution transmission electron microscopy (HRTEM). As shown in figures 1, 2(A)–(D) with an increasing magnification, hexagonal Moiré superlattices with periodicity of ∼13 nm (θrot of ∼ 1.09°) and ∼36 nm (θrot of ∼0.39°) were found in two separate exfoliated lamellae. The observed superlattice resembles those reported by Kuwabara et al [21], Patil et al [22] and Brihuega et al [24]. In figure 1(E) Raman spectroscopy analyses performed in multiple areas of the lamella revealed presence of weak D and D’ bands and intense G bands. Comparable D, D’ bands and intense G bands were found in the 2nd category sample, as shown in figure 2(E). See also ESI figure S.1 for typical deconvolution analyses of these signals.

Magnetization versus field signals were then acquired by employing superconducting quantum interference device (SQUID) magnetometry. A typical example of magnetization signal obtained at 2 K in 1st category, is shown in figure 3(A), in conditions of maximum applied fields of ∼50 Oe. Interestingly an unsaturated signal was found. Field dependent zero field cooled (ZFC) and field cooled (FC) measurements of the magnetization were considered in order to elucidate the type of magnetic ordering in the sample. The signals were acquired from 2 K to 300 K at the fields of 10 Oe, 30 Oe and 50 Oe. According to the percolation-type picture outlined above and reported in ref. [18], uncorrelated ferromagnetic clusters can be formed below a certain temperature...
leading to finite values of \( M_s(T,H) \), \( M_{\text{rem}}(T,H) \), and \( \Delta M(T,H) \) [18–20]. As the temperature decreases, ferromagnetic correlations develop on a larger scale, and eventually a long-range ferromagnetic order emerges.

It is possible to identify \( T^* \sim 50 \) K as a transition temperature below which an enlargement of pre-existing ferromagnetic cluster contribution takes place [18–20]. The ZFC-FC magnetization irreversibility shown in figures 3(B)–(D) evidences an enlargement of pre-existing ferromagnetic clusters below 50 K.
This interpretation was further supported by additional analyses involving the subtraction of the magnetic moment of the ZFC signal to the magnetic moment of the FC signal (i.e. mFC-mZFC analytical method) as shown in figure S6. Note in figures 3(A)–(C) the presence of a field dependent percolative ferromagnetic correlation effect, with the ZFC and FC magnetic curves that converge and approximately overlap at 50 Oe. The observed trend can be explained by the existence of progressively saturated correlated ferromagnetic clusters in agreement with the percolative theory outlined in ref. [18]. In order to validate this interpretation and verify
possible existence of superconductive components arising from graphene-layer rotation [13, 14, 26, 27], additional characterization was sought through field dependent magnetization versus field measurements at $T \sim 2$ K. The signals were acquired at maximum applied fields of 50 Oe, 100 Oe and 150 Oe. As shown in figures 3(E), (F) no superconductive signals could be detected. A transition from an unsaturated hysteresis-like signal to a ferromagnetic hysteresis was found from 50 Oe to 150 Oe, for lamellae-layers orientation perpendicular and parallel to the applied field (figures 3(E), (F)). The evolution of the magnetization versus field signals with the temperature is then shown in figure 4. In figure 4(A) the signals observed at 2 K and 3 K, with the lamella layers respectively oriented perpendicular and parallel to the applied field, are evidenced. The evolution of the signal at higher temperatures is further shown in figures 4–(E) before and after diamagnetic subtraction. Note the significant weakening of the ferromagnetic signal at $T \sim 150$ K (above the $T_c$ temperature and in proximity of $T^*$ temperature [18]) in figure 4(D), (E), implying the existence of mixed correlated and uncorrelated ferromagnetic clusters at this temperature as predicted by the percolative theory [18].

Figure 3. Magnetization versus Field measurements acquired from 1st sample category, revealing in figure 3(A) an unusual unsaturated hysteresis. In figures 3(B)–(D) field dependent ZFC and FC magnetic curves. The signals were acquired from 2 K to 300 K at the fields of 10 Oe (B), 30 Oe (C) and 50 Oe (D). As shown in figures 3(B)–(D) a significant transition was found at $T_c \sim 50$ K, implying existence of magnetic correlation [18]. By analysing the ZFC and FC signal it appears evident the presence of a ferromagnetic correlation effect, with the ZFC and FC magnetic curves that converge and approximately overlap as the field is increased to 50 Oe. The observed trend can be explained on the basis of the percolative theory of ferromagnetism [18]. In figures 3(E), (F) field dependent magnetization versus field measurements acquired from 1st sample category, at $T \sim 2$ K. The signals were acquired at maximum applied fields of 50 Oe, 100 Oe and 150 Oe. As shown in figures 3(E), (F) a transition from an unsaturated signal to a ferromagnetic hysteresis was found as the field is increased from 50 Oe to 150 Oe.
observation was further confirmed by T-ESR in figure 4(F), where a significant shift in the differential absorption peak was found at ∼150 K from \( g \sim 1.99 \) to \( g \sim 1.98 \) (as the temperature was increased from ∼77 K to ∼300 K).

Comparative measurements were then sought in the 2nd sample-category exhibiting Moiré superlattices with period \( D \sim 36 \text{ nm}, \theta_{\text{rot}}\) of ∼0.39°.

As shown in figures 5(A)–(B) (see also ESI figure S2), ZFC and FC magnetization versus temperature measurements revealed an analogue \( T^* \sim 50–60 \text{ K} \), together with a magnetization irreversibility at ∼40 K. The latter being compatible with a spin-glass-like behaviour induced by competing ferromagnetic and antiferromagnetic electron-correlation events [18]. It is possible to identify the \( T_c \sim 40 \text{ K} \) as a critical irreversibility temperature below which coexistence of multiple competing components may take place. In order to better analyse this aspect, the mFC-mZFC subtraction method was applied to the signal in figure 5(A).

Interestingly, as shown in figure 7 a ferromagnetic transition could be probed at ∼40 K. The presence of a ferromagnetic transition was further confirmed by orientation-dependent magnetization versus field measurements in figures 3(C)–(F) (before and after diamagnetic background subtraction). Note the presence of a possible \( T^* \sim 50–60 \text{ K} \), while no superconductive-transition could be detected in the analysed temperature range [26–28]. This observation implies that superconductivity in graphite may originate from other unknown
defect features (as recently suggested by Arnold et al [28]) or may require different experimental conditions in order to be detected [14]. By comparing the mFC-mZFC subtraction-signals shown in figures S-6, 7 for the type 1 and 2 lamellae (see figure S8) it is also important to highlight an additional magnetic contribution arising below 17 K only for the lamella containing the \( \theta_{rot} \sim 1.09^\circ \) (D \( \sim 13 \) nm, figure S6).

The possible presence of variable periodic stacking between twisted layers may play also a role in inducing shifts in the expected value of the magic angle required for observation of orbital ferromagnetic ordering (expected value for TBG \( \theta_{rot} \sim 1.2^\circ \) [29]) or for superconductivity (expected value for TBG \( \theta_{rot} \sim 1.09^\circ \) [13]). This interesting aspect was computed by Khalaf et al in ref. [30]. It was shown that significant shifts in the value of the magic-angle may exist with the increase of sample thickness, especially for systems characterized by an alternate stacking of twisted multilayer graphene components. For \( n_s \) sequences, a shift by a factor of \( 2\cos (\pi' k/ n + 1) \) with \( k = 1, \ldots, n_s \) was found with respect to the original value of the magic angle [13, 24].
Conclusion

In conclusion, we have reported a novel investigation on the magnetic ordering in exfoliated HOPG lamellae exhibiting hexagonal Moiré superlattices with periodicity of $\sim 13$ nm, $\theta_{\text{rot}} \sim 1.09^\circ$ and $\sim 36$ nm, $\theta_{\text{rot}} \sim 0.39^\circ$. Raman Spectroscopy evidenced presence of weak D and D' bands compatible with those expected for rotated graphene layers, together with an intense G band in both sample-categories.

Magnetization versus field at 2 K, revealed unsaturated and saturated ferromagnetic signals in the 1st category. Field dependent, ZFC and FC magnetization versus temperature from 2 K to 300 K at the fields of 10 Oe, 30 Oe and 50 Oe revealed a transition at $T_c \sim 50$ K, compatible with ferromagnetic correlation. Comparative magnetometry measurements on the 2nd sample category revealed an analogue critical ferromagnetic transition at $T_c \sim 40$ K together with a spin-glass-like behaviour indicating existence of competing antiferromagnetic correlations at $\sim 59$ K.

Acknowledgments

Prof. Filippo Boi acknowledges research support from NSFC funds 11750110413 and 11950410752. Prof. Shanling Wang acknowledges research support from Sichuan University funding (SCU201208). We also acknowledge Prof. Lei Li for the help in the Raman spectroscopy measurements.

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References

[1] Mizogami S, Mizutani M, Fukuda M and Kawabata K 1991 Abnormal ferromagnetic behavior for pyrolytic carbon under low temperature growth by CVD method Synth. Met. 43 3271–4
[2] Esquinazi P, Setzer A, Höhne R, Semmelhack C, Kopelevich Y, Spemann D, Butz T, Kohlstrunk B and Lõesche M 2002 Ferromagnetism in oriented graphite samples Phys. Rev. B 66 024429
[3] Kopelevich Y, Esquinazi P, Torres J H S and Moehlecke S 2000 Ferromagnetic- and superconducting-like behavior of graphite J. Low Temp. Phys. 119 691–702
[4] Wang Y, Liu Z X, Zhang Y L, Li F Y and Jin C Q 2002 Evolution of magnetic behaviour in the graphitization process of glassy carbon Surf. Sci. 556 43–50
[5] Mukai Y, Ishii C, Hasegawa Y and Kaneko K 1995 Ferromagnetic behavior of superhigh surface area carbon J. Phys. Chem. 99 5743–5
[6] Ishii C, Shindo N and Kaneko K 1995 Random magnetism of superhigh surface area carbon having minute graphitic structures Chem. Lett. 242 196–201
[7] Yusuf M, Al-Mahdi M and Qureshi T 2009 Magnetic properties of graphene and graphite Int. J. Phys. Sci. 5 2864–8
[8] Narozhnyi V N, Müller K-H, Eckert D, Teresiak A, Dunsch L, Davydov V A, Kashevarova L S and Rakhmanina A V 2003 Ferromagnetic and superconducting-like behavior of graphite J. Phys. Condens. Matter 15 1031–22
[9] Kopelevich Y, Esquinazi P, Torres J H S and Moehlecke S 2000 Ferromagnetic- and superconducting-like behavior of graphite J. Phys. Condens. Matter 12 3044–52
[10] Makarova T L, Sundqvist B, Höhne R, Esquinazi P, Setzer A, Kopelevich Y, Spemann D, Butz T, Kohlstrunk B and Lösche M 2002 Ferromagnetism Nature 413 716–8
[11] Wood B A, Lewis M H, Lees M R, Bennington S M, Cain M G and Kitamura N 2002 Ferromagnetic fullerenes J. Phys. Condens. Matter 14 1385–91
[12] Narozhnyi V N, Müller K-H, Eckert D, Teresiak A, Dunsch L, Davydov V A, Kashevarova L S and Rakhmanina A V 2003 Ferromagnetic carbon with enhanced Curie temperature Physica B 329-333 1217–8
[13] Colin J, Paterni F, Fang S, Watanabe K, Taniguchi T, Kaxiras E and Jarillo-Herrero P 2018 Unconventional superconductivity in magic-angle graphene superlattices Nature 556 43–50
[14] Arora H S et al 2020 Superconductivity in metallic twisted bilayer graphene stabilized by WS22 Nature 583 379–84
[15] Seo K, Koton V N and Uchoa B 2019 Ferromagnetic mott state in twisted graphene bilayers at the magic angle Phys. Rev. Lett. 122 246402
[16] Wang X, Liu Z X, Zhang Y L, Li F Y and Jin C Q 2002 Evolution of magnetic behaviour in the graphitization process of glassy carbon J. Phys. Condens. Matter 14 10265
[17] González J, Guineu G, Pescia F and Mazdiyan M A 2001 Electron–electron interactions in graphene sheets Phys. Rev. B 63 134421
[18] Kopelevich Y, da Silva R R, Torres J H S, Penicaud A and Kyotani T 2003 Local ferromagnetism in microporous carbon with the structural regularity of zeolite Y Phys. Rev. B 68 094208
[19] Thedoporopoulou N, Hebard A F, Overberg M E, Abernathy C R, Pearton S J, Chu S N G and Wilson B G 2003 Unconventional Carrier-mediated ferromagnetism above room temperature in Ion-Implanted (Ga, Mn)P:Phys. Rev. Lett. 89 107203
[20] Taallah A, Wen J, Wang S, Grasso S, He Y, Xia J, Shuai G, Odumubaku O, Corrias A and Boi F S 2020 Unusual butterfly-shaped magnetization signals and spin-glass-like behaviour in highly oriented pyrolytic graphite Carbon 167 85–91
[21] Kuwabara M, Clarke D R and Smith D A 1990 Anomalous superperiodicity in scanning tunneling microscopy images of graphite Appl. Phys. Lett. 56 2396
[22] Patil S, Kolekar S and Deshpande A 2017 Revisiting HOPG superlattices: Structure and conductance properties Surf. Sci. 658 55–60
[23] Flores M, Cisternas E, Correa J and Vargas P 2013 Moiré patterns on STM images of graphite induced by rotations of surface and subsurface layers Chem. Phys. 423 49
[24] Brihuega I, Mallet P, González-Herrero H, de Laissardière G T, Ugeda M M, Magaud L, Gómez-Rodríquez J M, Ynduráin F and Veuillen J-Y 2012 Unraveling the intrinsic and robust nature of van Hove singularities in twisted bilayer graphene by scanning tunneling microscopy and theoretical analysis Phys. Rev. Lett. 109 196802

[25] Ramnani P, Neupane M R, Ge S, Balandin A A, Lake R K and Mulchandani A 2017 Raman spectra of twisted CVD bilayer graphene Carbon 123 302–6

[26] Scheike T, Esquinazi P, Setzer A and Böhlmann W 2013 Granular superconductivity at room temperature in bulk highly oriented pyrolytic graphite samples Carbon 59 148–9

[27] Esquinazi P, Heikkilä T T, Lysogorskiy Y V, Tayurskii D A and Volovik G E 2014 On the superconductivity of graphite interfaces JETP Lett. 100 336–9

[28] Arnold F, Nyéki J and Saunders J 2018 Superconducting sweet-spot in microcrystalline graphite revealed by point-contact spectroscopy JETP Lett. 107 577–8

[29] Sharpe A L, Fox E J, Barnard A W, Finney J, Watanabe K, Taniguchi T, Kastner M A and Goldhaber-Gordon D 2019 Emergent ferromagnetism near three-quarters filling in twisted bilayer graphene Science 365 605–8

[30] Khalaf E, Kruchkov A J, Tarnopolsky G and Vishwanath A 2019 Magic angle hierarchy in twisted graphene multilayers Phys. Rev. B 100 085109