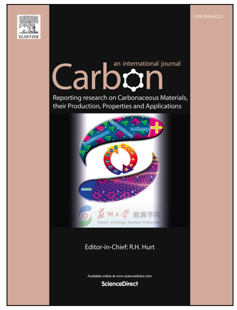
Journal Pre-proof



Unusual butterfly-shaped magnetization signals and spin-glass-like behaviour in highly oriented pyrolytic graphite

Ayoub Taallah, Jiqiu Wen, Shanling Wang, Salvatore Grasso, Yi He, JiaChen Xia, Gao Shuai, Omololu Odunmbaku, Anna Corrias, Filippo S. Boi

PII: S0008-6223(20)30545-5

DOI: https://doi.org/10.1016/j.carbon.2020.05.104

Reference: CARBON 15373

To appear in: *Carbon*

Received Date: 6 March 2020

Revised Date: 20 May 2020

Accepted Date: 30 May 2020

Please cite this article as: A. Taallah, J. Wen, S. Wang, S. Grasso, Y. He, J. Xia, G. Shuai, O. Odunmbaku, A. Corrias, F.S. Boi, Unusual butterfly-shaped magnetization signals and spin-glass-like behaviour in highly oriented pyrolytic graphite, *Carbon* (2020), doi: https://doi.org/10.1016/j.carbon.2020.05.104.

Unusual butterfly-shaped magnetization signals and spin-glass-like behaviour in highly oriented pyrolytic graphite

Ayoub Taallah[a], Jiqiu Wen[b], Shanling Wang[b], Salvatore Grasso[c], Yi He[b], JiaChen Xia[a], Gao Shuai[a], Omololu Odunmbaku[a], Anna Corrias[d] and Filippo S. Boi [a*].

a. College of Physics, Sichuan University, Chengdu, China

b. Analytical and Testing Center, Sichuan University, Chengdu, China

c. Southwest Jiaotong University, Department of Material science and Engineering, Chengdu, China

d. School of Physical Sciences, University of Kent, Canterbury, UK

Corresponding author: f.boi@scu.edu.cn

Abstract

We report a novel investigation on the relationship between magnetic-ordering and graphitic-structure in highly-oriented-pyrolytic-graphite (HOPG). By employing orientation-dependent-X-ray-diffraction, Raman-spectroscopy and temperature-dependent-superconductive-quantum-interference-device (T-SQUID) we examined the presence of ferromagnetic- and superconductive-ordering in HOPG systems with 1) disordered (HOPG1, containing carbon-vacancy-rich weak-Bernal-stacking and Moiré-superlattices with θ_{misfit} ~ 0.5^o) and 2) ordered (HOPG2, containing higher-degree of Bernal-stacking and Moiré-superlattices with θ_{misfit} ~ 0.5^o, 0.8^o, 11^o) graphitic-layer-arrangement. A perfect-HOPG is expected to exhibit a diamagnetic-response to an applied-magnetic-field. Instead, additional 1) ferromagnetic-signals presenting a characteristic width-enhancement with the field increasing in HOPG1 and 2) complex butterfly-shaped ferromagnetic signals in HOPG2, are demonstrated. Temperature-dependent-magnetometry evidenced further the presence of randomly oriented ferromagnetic clusters originating from topological disorder in both HOPG1 and HOPG2. These magnetic signals were explained on the basis of the percolative-type model.

Understanding and controlling the intrinsic magnetic characteristics of carbon based materials has recently become an important research topic in materials science, chemistry and physics. This could lead to development of functional devices for technological applications, such as magnetic tunnel junctions and superconductive/ferromagnetic systems. Previous studies have indicated the presence of lattice defects as important factors which can induce a spontaneous magnetic ordering in graphite and graphene [1-6]. Ferromagnetic ordering has been demonstrated in presence of vacancies and 2D networks of point defects [1,4,6]. Existence of superconducting ordering has been reported in highly oriented pyrolytic graphite (HOPG) under certain conditions of thermal annealing [2]. Granular superconductive features at room temperature have been demonstrated for commercially available HOPG samples and attributed to the high dislocation density within certain interfaces [7-9]. The stacking between the graphitic layers and the layer orientation with respect to the c-axis (rotational orientation) have been also indicated as some of the critical factors which can influence the formation of intrinsic magnetization features in HOPG [10-12] and bilayer-graphene [13-15]. Particularly, the recent observation of negative thermal expansion effects in dislocation-rich (HOPG) samples suggests that relative graphitic layers rotation has significant influence on the intrinsic physical properties of these systems [12].

In this letter, with the aim of investigating further the properties of HOPG materials, we considered a possible correlation between magnetic ordering and graphitic layers orientation in two types of commercially available HOPG systems. By employing orientation dependent X-ray diffraction (O-XRD) and temperature dependent superconductive quantum interference device (T-SQUID) we have investigated the presence of magnetic ordering in 1) disordered and 2) ordered HOPG materials (namely HOPG1 and 2).

Ferromagnetic-signals with a characteristic hysteresis-width enhancement with the field increasing were detected in HOPG1. Observation of these unusual features is attributed to an antiferromagnetic-coupling effect between ferromagnetic multilayers, in presence of both rotational misorientation and vacancy defects (as confirmed by Raman spectroscopy). Differently, complex butterfly-shaped ferromagnetic signals are shown in HOPG2.

Temperature-dependent-magnetometry evidenced the presence of a magnetization M(T,H) irreversibility in both HOPG1 and HOPG2 possibly arising from topological disorder [24]. These signals evidence the presence of magnetic contributions from randomly oriented ferromagnetic clusters that can be explained on the basis of the percolative-type picture reported in ref. [24-31], together with possible antiferromagnetic correlations competing with the ferromagnetic ordering [24].

Experimental details, additional structural and compositional characterization analysis are given in the electronic supplementary information (ESI). The layered arrangement of the HOPG samples was firstly confirmed by XRD as shown in Fig.1A. Data were collected with the HOPG c-axis oriented parallel with respect to the used substrate. Significant layer-misorientation characteristics could be detected in the HOPG1, as indicated by the weak 100 reflection in Fig.1A and by the appearance of Moiré superlattice features (i.e. fringes) in TEM investigations (on exfoliated-lamellae) in conditions of electron beam parallel to the sample c-axis (Fig.1B). As an additional indicator of the disorder in the sample, a vacancy rich lattice-arrangement could be probed by Raman spectroscopy, this is shown in Fig.1C, where the ratio ID/ID' was ~ 6. Instead, a highly oriented arrangement characterized by an intense 100 reflection could be found in HOPG2 (Fig.1D) [12,16]. Presence of ferromagnetic hysteresis was revealed by magnetization vs field measurements of HOPG1 with the c-axis perpendicular to the applied field (Fig.2A-C). The as measured signals were found to exhibit a characteristic diamagnetic background, as shown in Fig.2A. In Fig. 2B, a characteristic hysteresis width enhancement with the field increasing was found. By comparing the observed signal to the one reported by ref. [17] for antiferromagnetically-coupled ferromagnetic multilayers, the possible presence of antiferromagnetism within a portion of the HOPG interfaces can not be excluded. This observation agrees also with a previous work in ref.18 where a gradual antiferromagnetic transition was reported.

Weak magnetization signals were further measured when the sample orientation was rotated and positioned with the HOPG1 layers perpendicular to the applied field, in Fig.2D. In this latter case, presence of a much weaker hysteresis with a squared like shape was found. Possible influences of rotational disorder and therefore non-uniform c-axis orientation within HOPG1, cannot be excluded (see ref.[12] for example of rotational disorder on lamellae extracted from surface regions of HOPG).

Comparative measurements were then sought on HOPG2 which exhibited a higher degree of Bernal stacking (see 100 reflection in Fig.1D). The result of these measurements performed with the magnetic field approximately perpendicular to the HOPG2 layers is shown in Fig.3. The as measured signal at the temperature of 250 K is evidenced with an increasing level of detail in Fig.3A-C and after diamagnetic background subtraction in Fig.3D-F. Note the presence of a complex ferromagnetic butterfly-shaped hysteresis signal in Fig.3F, indicating possible coexistence of multiple magnetization components. By comparing this signal with those reported in ref.19-20, multiple contributions arising from possible onion-vortex spin states (black arrows in Fig.3F) can not be excluded. It is important to notice that the observed hysteresis can be explained on the basis of the percolative-type picture reported in ref.[24-31], with the presence of pre-existing ferromagnetic clusters. No superconductive components were detected, implying possible absence of superconductivity in HOPG2 [2,16]. In order to confirm the origin of the butterfly shaped signal shown in Fig.3F, additional analyses were performed on μm-sized lamellae exfoliated from the inner regions of the HOPG2 structure. In Fig.4A, a typical XRD pattern of an inner exfoliated lamellae is shown; note the presence of an intense 100 reflection which is an indicator of the high degree of Bernal ordering within the lamella. Interestingly, magnetization measurements of the individual exfoliated lamellae (field orientation perpendicular to graphitic layers) revealed only ferromagnetic signals, as shown in Fig.4B,C and Fig.4D (after background subtraction) where the evolution of the ferromagnetic signal as the temperature is increased from

2K to 300K is shown. Most importantly note the presence of Moiré superlattices with θ_{misfit} ~0.5^o (see ESI Fig.S10) in analogy with HOPG1 (Fig.1B). The variation in the values of coercivity and saturation magnetization is shown in Fig.4E,F. These results suggest a non-uniform distribution of the magnetization states observed in Fig.3F in HOPG2. In further investigating presence of dislocations as the origin-factor of the butterfly-shaped signal in Fig.3, additional rocking curve measurements were acquired from as exfoliated lamellae (from HOPG2), as shown in Fig.5A,B (see ESI Fig.S8,S9 for Moiré superlattice analyses revealing θ_{misfit} ~0.8^o and ~11^o). Note the presence of non-monotonic features (Fig.5B) which are a clear indicator of rotational misfit between the graphitic layers. ZFC and FC measurements of as exfoliated (i.e not yet exposed to magnetic field) dislocation rich inner lamellae from inner regions of the sample were then considered. As shown in Fig.5C and Fig.5D a spin-glass-like behaviour was found [21,22,24]. This observation highlights the existence of non-trivial spin arrangements in the sample and seems to exclude presence of superconductive transitions [23]. In particular, the magnetization M(T,H) irreversibility shown in Figs.5D and Fig.5F evidences the possible presence of topological disorder in both HOPG1 and HOPG2 [24].

According to the percolation-type picture reported in ref.[24-31], uncorrelated ferromagnetic clusters are formed below a temperature T^*, leading to finite values of M_s(T,H), M_{rem}(T,H), and ΔM(T,H) [24,25]. As the temperature decreases, ferromagnetic correlations develop on a larger scale, and eventually a long-range ferromagnetic order emerges. It is possible to identify the T≈150 K for HOPG1 as a transition temperature below which an enlargement of pre-existing ferromagnetic cluster contribution takes place [24].

The ZFC-FC magnetization irreversibility shown in Fig.5F for HOPG1, together with the ferromagnetic hysteresis loops measured at T = 250 K in Fig. 2 provide evidence that 1) ferromagnetic clusters may exist up to T ~ 300 K and 2) an enlargement of pre-existing ferromagnetic clusters takes place below 150K.

Similarly, the enhanced ZFC-FC magnetization irreversibility below T ~ 150 K in Fig. 5D evidences existence of randomly oriented ferromagnetic clusters for T < 150 K in HOPG2, in agreement with the observed ferromagnetic hysteresis at 250K in Fig.3.

Further, it is important to note that the random orientation of the magnetic moments associated to different ferromagnetic clusters can be stabilized in presence of competing antiferromagnetic correlations, leading to a spin-glass-like behaviour [24].

In conclusion, we have investigated the relationship between magnetic ordering and graphitic layers orientation in HOPG systems with a disordered and ordered graphitic-layer arrangement. Presence of ferromagnetic hysteresis with a characteristic hysteresis-width-enhancement with the field increasing was demonstrated in HOPG1 and attributed to antiferromagnetic-coupling between ferromagnetic multilayers. A butterfly-shaped ferromagnetic hysteresis was instead evidenced in HOPG2. Temperature-dependent-magnetometry revealed presence of a magnetization M(T,H) irreversibility in both HOPG1 and HOPG2, evidencing presence of magnetic contributions from randomly oriented ferromagnetic clusters together with possible antiferromagnetic correlations competing with the ferromagnetic ordering.

Acknowledgments
The authors acknowledge research support from NSFC funds 11750110413, 11950410752 and Sichuan Province fund 2019YFH0080. We also acknowledge Prof. Lei Li. SG was supported by Thousand Talents Program of China and Sichuan Province.

References

[1] Esquinazi, Pablo (Ed.). Basic Physics of Functionalized Graphite. Springer Series in Materials Science, Volume 244. ISBN 978-3-319-39353-7. Springer International Publishing Switzerland, 2016.

[2] Kopelevich Y., Esquinazi P., Torres J. H. S., Moehlecke S. Ferromagnetic- and Superconducting-Like Behavior of Graphite. Journal of Low Temperature Physics 2000; 119: 691-702.

[3] Yazyev O. V., Helm L. Defect-induced magnetism in graphene. Phys. Rev. B 2007; 75: 125408.

[4] Faccio R., Pardo H., Denis P. A., Yoshikawa Oeiras R., Araújo-Moreira F. M., Veríssimo-Alves M., Mombrú A. W. Magnetism induced by single carbon vacancies in a three-dimensional graphitic network. Phys. Rev. B 2008; 77: 035416.

[5] Coey J. M. D., Venkatesan M., Fitzgerald C. B., Douvalis A. P., Sanders I. S. Ferromagnetism of a graphite nodule from the Canyon Diablo meteorite. Nature 2002; 420: 156–159.

[6] Červenka J., Katsnelson M.I. and Flipse C.F.J. Room-temperature ferromagnetism in graphite driven by 2D networks of point defects. Nature Physics 2009; 5:840-844

[7] Scheike T., Esquinazi P., Setzer A., and Böhlmann W. Granular superconductivity at room temperature in bulk highly oriented pyrolytic graphite samples. Carbon 2013; 59:140-149.

[8] Precker C. E., Esquinazi P. D., Champi A., Barzola-Quiquia J., Zoraghi M., Muiños-Landin S., Setzer A., Böhlmann W., Spemann D., Meijer J., Muenster T., Baehre O., Kloess G. and Beth H. Identification of a possible superconducting transition above room temperature in natural graphite crystals. New J. Phys. 2016;18: 113041

[9] Esquinazi P., Heikkilä T. T., Lysogorskiy Y. V., Tayurskii D. A., and Volovik G. E. On the Superconductivity of Graphite Interfaces. JETP Letters 2014; 100: 336–339.

[10] Kuwabara M., Clarke D. R., and Smith D. A. Anomalous superperiodicity in scanning tunneling microscope images of graphite. Appl. Phys. Lett. 1990; 56: 2396.

[11] Boi F. S, Liu M., Xia J., Odunmbaku O., Taallah A., Wen J. Anomalous c-axis shifts and symmetry enhancement in highly oriented pyrolytic graphite at the magic angle. Carbon 2019; 150: 27-31.

[12] Taallah A., Shuai G., Odunmbaku O., Corrias A. and Boi F. S. Anomalous low-temperature saturation effects and negative thermal expansion in the c-axis of highly oriented pyrolytic graphite at the magic angle. Materials Research Express 2020; 7: 015614.

[13] Cao Y., Fatemi V., Fang S., Watanabe K., Taniguchi T., Kaxiras E. and Jarillo-Herrero P. Unconventional superconductivity in magic-angle graphene superlattices. Nature 2018; 556: 43–50.

[14] Cao Y., Fatemi V., Demir A., Fang S., Tomarken S. L., Luo J. Y., Sanchez-Yamagishi J. D., Watanabe K., Taniguchi T., Kaxiras E., Ashoori R. C. and Jarillo-Herrero P. Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. Nature 2018; 556: 80–84.

[15] Padhi B., Setty C., and Phillips P. W. Doped Twisted Bilayer Graphene near Magic Angles: Proximity to Wigner Crystallization, Not Mott Insulation. Nanoletters 2018; 18: 6175-6180

[16] Boi F.S., Xia J., Shuai G., Taallah A., Wang S., He Y., Odunmbaku O., Wen J. Magnetization signals in μm-thin lamellae of highly oriented pyrolytic graphite: a field-dependent study. Materials Research Express 2019; 6: 126101.

[17] Hellwig O., Kirk T. L., Kortright J. B., Berger A. and Fullerton E. E. A new phase diagram for layered antiferromagnetic films. Nature Materials 2003; 2: 112-116.

[18] Kausteklis J., Cevc P., Arčon D., Nasi L., Pontiroli D., Mazzani M., and Riccò M. Electron paramagnetic resonance study of nanostructured graphite. Physical Review B 2011; 84: 125406.

[19] Montoncello F., Giovannini L., Nizzoli F., Tanigawa H., Ono T., Gubbiotti G., Madami M., Tacchi S., and Carlotti G. Magnetization reversal and soft modes in nanorings: Transitions between onion and vortex states studied by Brillouin light scattering. Physical Review B 2008; 78: 104421.

[20] Lai M.F., Chen Y.-J., Liu D.-R., Lo C.-K., Hsu C.-J., Liao C.-N., Lee C.-P., Chiu Y.-H., and Wei Z.-H. Influence of different onion states on magnetization reversal processes in permalloy rings. IEEE Transactions on Magnetics 2010; 46: 179-182.

[21] Tackett R. J., Bhuiya A. W. and Botez C. E. Dynamic susceptibility evidence of surface spin freezing in ultrafine NiFe2O4 nanoparticles. Nanotechnology 2009; 20: 445705.

[22] Nagata S., Keesom P. H., Harrison H. R. Low-dc-field susceptibility of CuMn spin glass. Physical Review B 1979; 19: 1633-1638.

[23] Suzuki M., Suzuki I. S., Walter J. H-T phase diagram and the nature of Vortex-glass phase in a quasi-two-dimensional superconductor: Sn-metal layer sandwiched between graphene sheets. Physica C: Superconductivity 2004; 402: 243-256.

[24] Kopelevich Y., da Silva R. R., Torres J. H. S., Penicaud A., and Kyotani T. Local ferromagnetism in microporous carbon with the structural regularity of zeolite Y. Phys. Rev. B 2003; 68: 092408

[25] Theodoropoulou N., Hebard A. F., Overberg M. E., Abernathy C. R., Pearton S. J., Chu S. N. G., and Wilson R. G. Unconventional Carrier-Mediated Ferromagnetism above Room Temperature in Ion-Implanted (Ga, Mn)P:C. Phys. Rev. Lett. 2002; 89: 107203.

[26] Uehara M., Mori S., Chen C. H., and Cheong S.-W. Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites. Nature 1999; 399: 560-563.

[27] Salamon M. B., Lin P. and Chun S. H. Colossal Magnetoresistance is a Griffiths Singularity. Phys. Rev. Lett. 2002; 88: 197203.

[28] Kaminski A. and Das Sarma S. Polaron Percolation in Diluted Magnetic Semiconductors. Phys. Rev. Lett. 2002; 88: 247202.

[29] Mayr M., Alvarez G., and Dagotto E. Global versus local ferromagnetism in a model for diluted magnetic semiconductors studied with Monte Carlo techniques. Phys. Rev. B 2002; 65: 241202(R).

[30] Alvarez G., Mayr M., and Dagotto E. Phase Diagram of a Model for Diluted Magnetic Semiconductors Beyond Mean-Field Approximations. Phys. Rev. Lett. 2002; 89: 277202.

[31] Burgy J., Dagotto E., and Mayr M. Percolative transitions with first-order characteristics in the context of colossal magnetoresistance manganites. Phys. Rev. B 2003; 67: 014410.

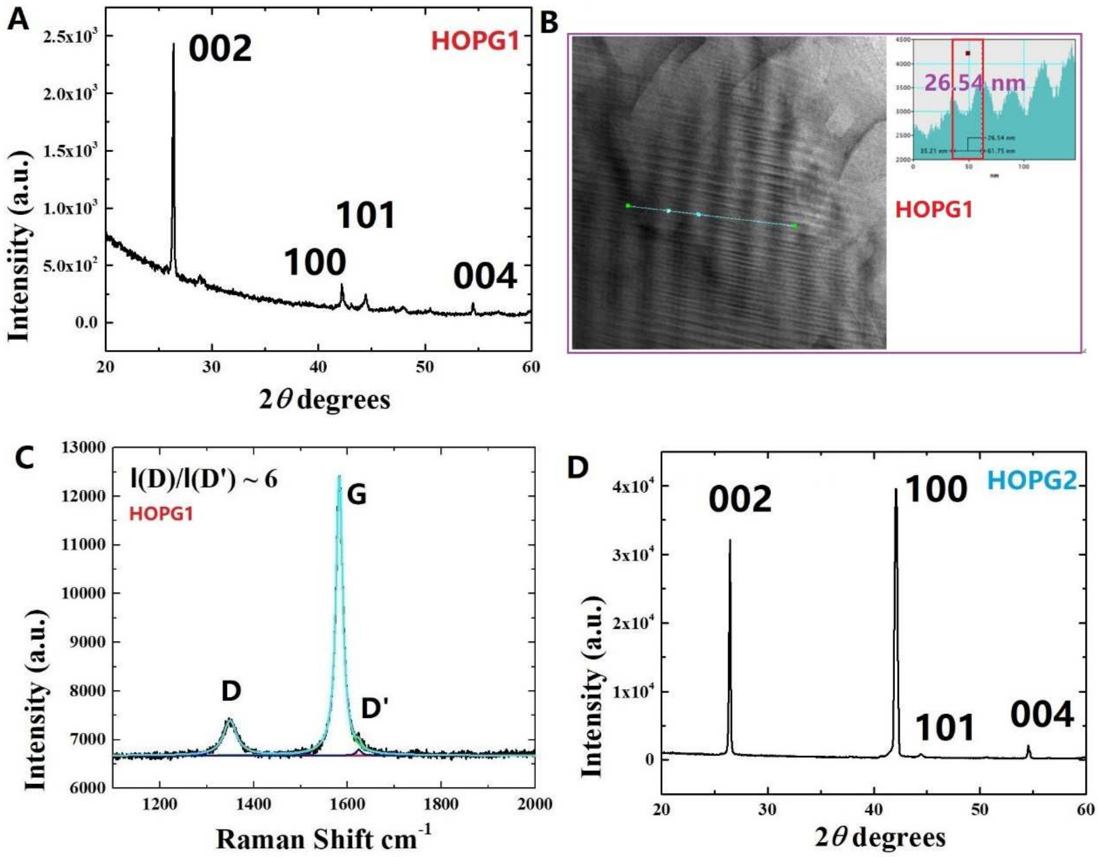


Fig.1: XRD patterns of HOPG1 and 2, performed with c-axis orientation parallel to the substrate and parallel to the beam. In A I002/I100 = 7.54. In D I002/I100 = 0.82. See ESI for EDX analyses of the sample 1 shown in A revealing presence of C and O elemental species. In B and C TEM and Raman spectroscopy measurements of HOPG1 are shown. By using the equation $a/2D = \sin(\theta/2)$ where a is the basal lattice constant corresponding to 0.247 nm, and D is the periodicity of the Moiré pattern, a θ_{twist} of approximately 0.53 degrees can be extracted. See also Fig.S1,S2 in ESI.

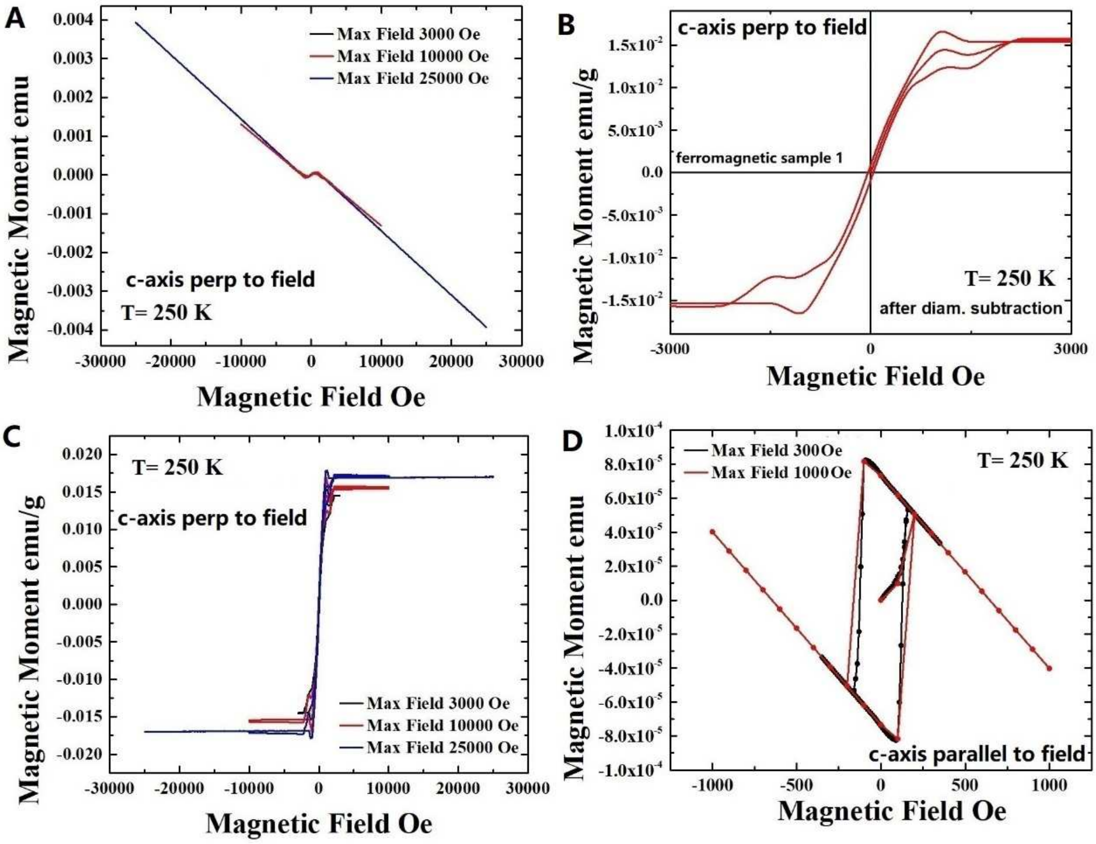


Fig.2: In A-C ferromagnetic hystereses measured in HOPG 1 at 250K showing the presence of a magnetization pinning feature. Note that the surface layers of the sample were removed before the measurement, in order to avoid possible influence from superficial impurities. In addition, notice that no metal-traces could be detected in the sample by EDX measurements (see ESI). In D, presence of weak ferromagnetic hysteresis for magnetic field orientation perpendicular to the HOPG layers (c-axis parallel to field) is shown.

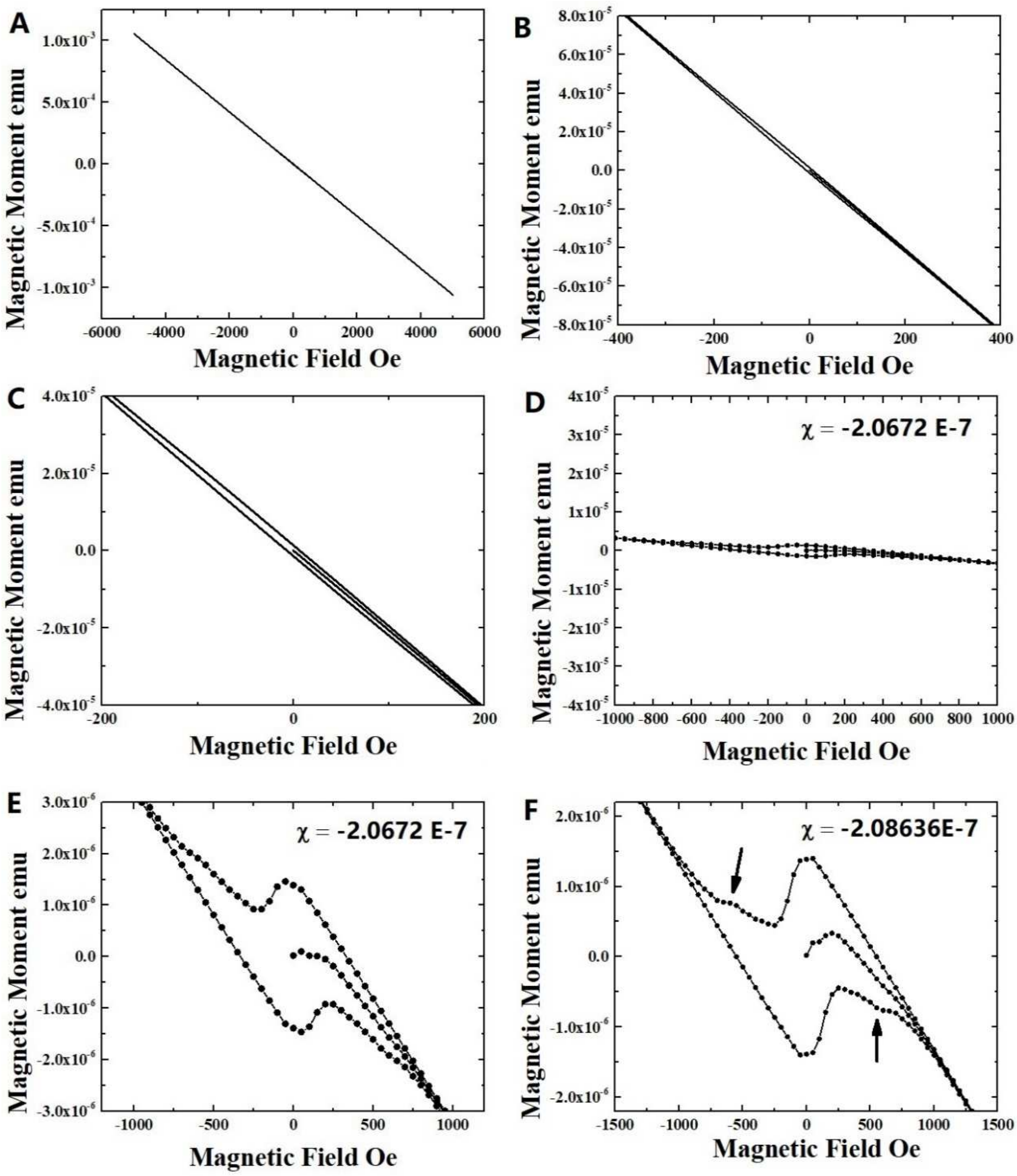


Fig.3: As measured butterfly-shaped hysteresis at 250K in the HOPG2 before (A-C) and after (D-F) background subtraction. Due to the sample dimensions (compared to the measuring capsule) only a tilted orientation with respect to the applied magnetic field could be achieved (field approximately perpendicular to graphitic layers). Note the significant difference with respect to the hysteresis shown in Fig.2. The possible coexistence of multiple signals components can not be excluded [19,20]. The observed hysteresis can be explained on the basis of the percolative-type picture reported in ref.[24-31], with the presence of pre-existing ferromagnetic clusters [24].

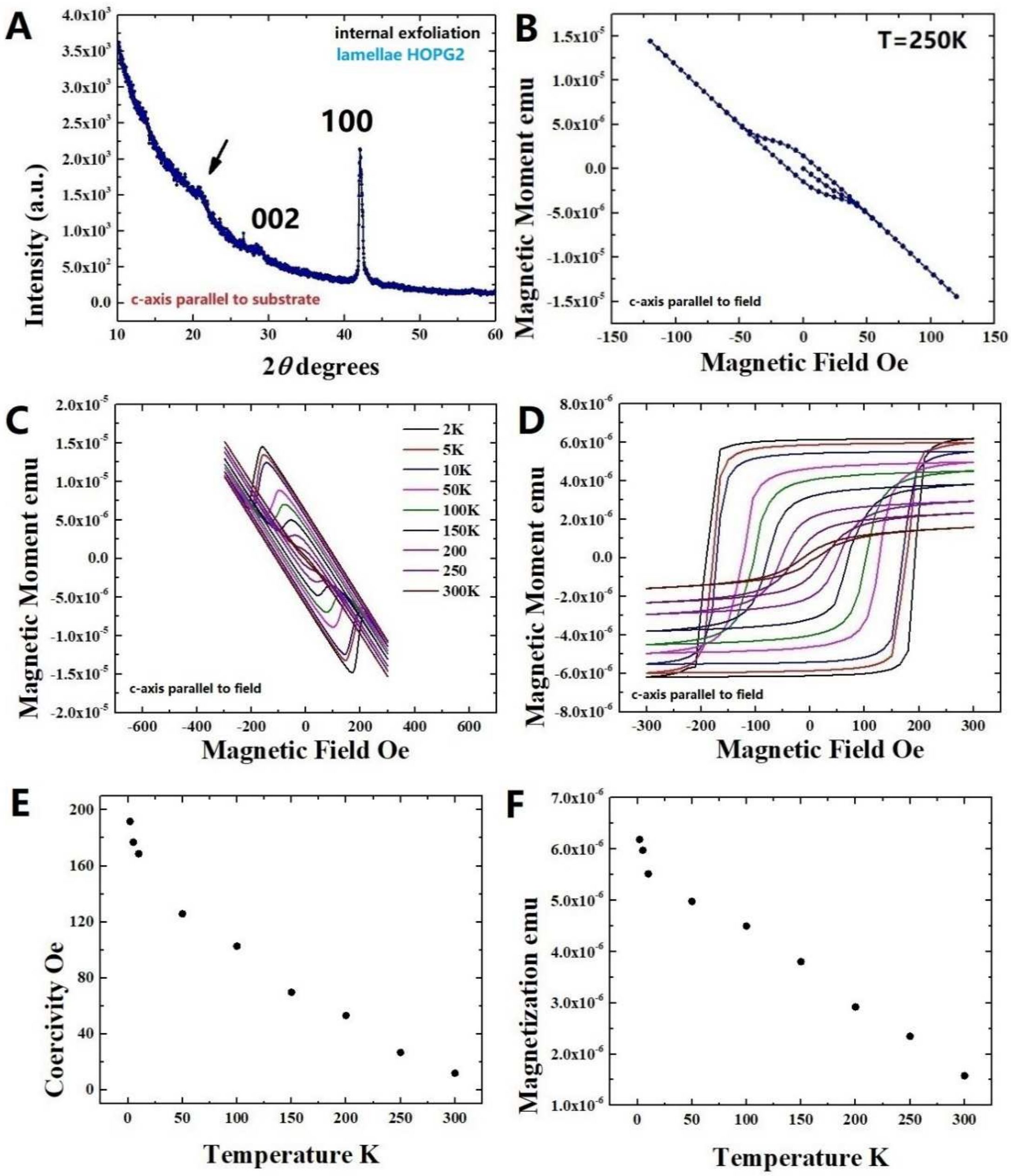


Fig.4: In A typical O-XRD analysis of a lamellae exfoliated from inner regions of HOPG 2. In B-C magnetization signals revealing the presence of ferromagnetic hystereses in the temperature range from 2K to 300K for c-axis parallel to the applied field (field perpendicular to graphitic layers). In D the signals are shown after diamagnetic substraction. In E,F plots showing the variation in the coercivity and saturation magnetization with temperature. See ESI Fig.S10 for TEM analyses of lamellae analysed in C,D where a θ_{misfit}~ 0.5^{o} could be extracted. See also ESI Fig.S7, for Raman spectroscopy analyses of the same lamellae.

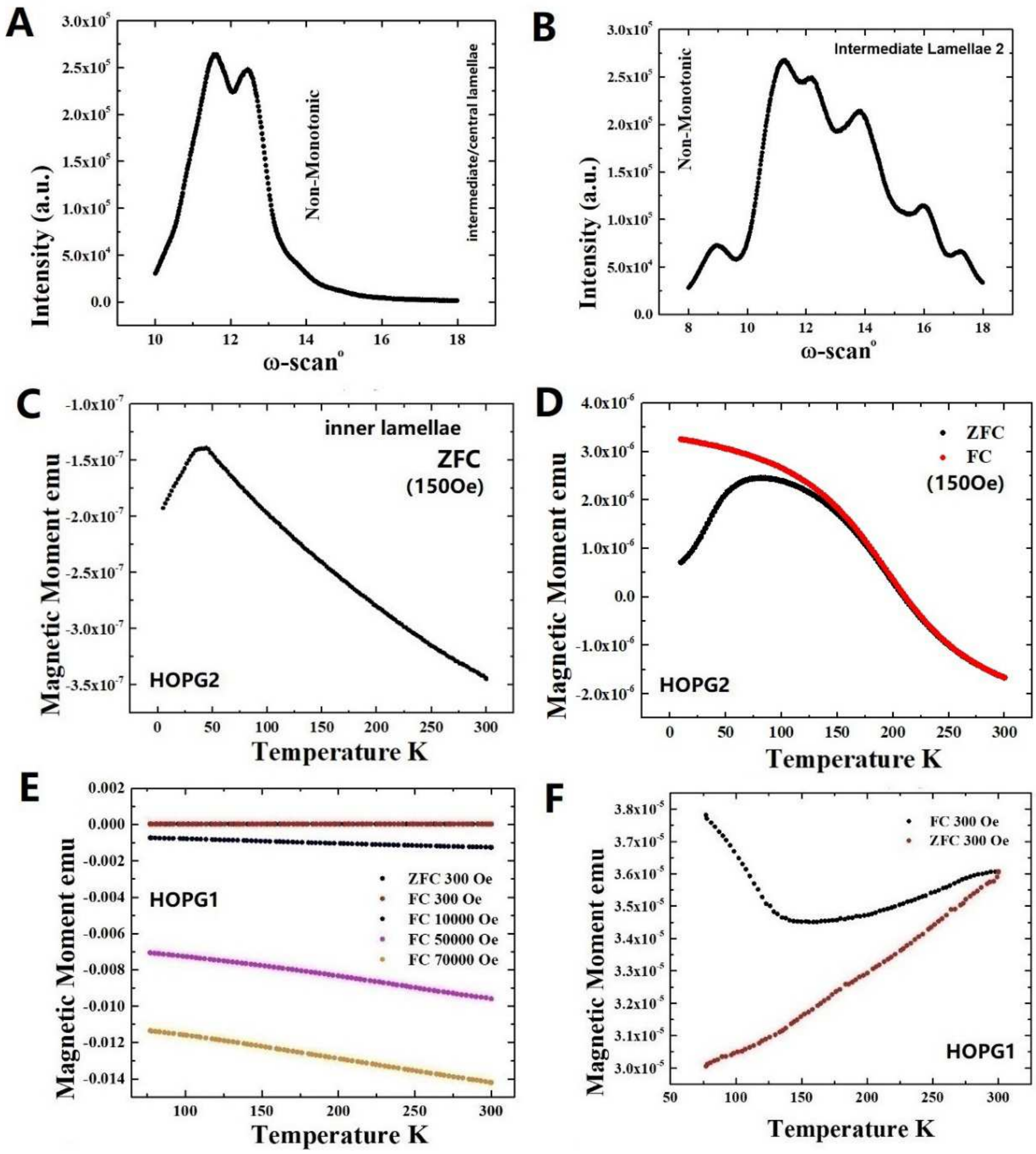


Fig.5: In A,B rocking curve measurements revealing presence of misfit rotational features between graphitic layers in as exfoliated lamellae from inner and inner/central regions of HOPG2. In C,D additional ZFC and ZFC-FCmeasurement performed in two as exfoliated lamellae with field orientation perpendicular to graphitic layers (see ESI Fig.S8,S9 for TEM analyses of the lamellae, revealing rotational misorientation θ_{misfit} ~ 0.8^o and ~11^o). The magnetization M(T,H) irreversibility shown in Figs.5D and Fig.5F indicates presence of topological disorder in both HOPG2 and HOPG1 and may originate from randomly oriented ferromagnetic clusters. The random orientation of the magnetic moments associated to different ferromagnetic clusters can be stabilized in presence of competing antiferromagnetic correlations, leading to a spin-glass-like behaviour [24].

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: