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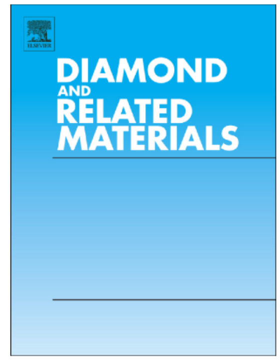


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# Unusual magnetic transition and enhanced diamagnetism in highly oriented pyrolytic graphite with long-range stacking-order

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## Abstract

The recent observations of unusual superconductive effects in highly oriented pyrolytic graphite (HOPG) and twisted bi-layer, tri-layer and multilayer graphene materials have attracted an important attention. In this work we present a novel investigation on the relationship between structural ordering and magnetism in HOPG. Orientation dependent X-ray diffraction and temperature dependent magnetometry allowed for the identification of those HOPG samples exhibiting a long-range ordering along the c-axis. ZFC and FC magnetic curves acquired from T~ 2K to 300K revealed a significant temperature-dependent variation of the diamagnetic component. By analyzing the ZFC/FC magnetic-curves (through magnetic moment subtraction methods) we identify the presence of a weak magnetic transition in the T range from 200K to 2K. The possible origin of the observed magnetization-trend is interpreted in relation to contributions arising from 1) disorder-rich locally-twisted-interfaces and 2) those internal graphitic sublattices exhibiting negative thermal expansion. Interestingly, magnetization against field measurements acquired at T~50K (max. field of 150 Oe) revealed the presence of a weak ferromagnetic-like hysteresis. Disappearance of the unusual ZFC/FC signal-splitting was instead found in those magnetic curves acquired from other HOPG samples with higher degree of disorder (short-range-ordering along the c-axis). This second category of samples was found to exhibit a disorder-mediated re-entrant spin-glass-like ferromagnetic behavior.

# 1 Introduction

The recent observations of unusual superconductive and magnetic effects in highly oriented pyrolytic graphite (HOPG) [1-9] and twisted bi-layer, tri-layer and multilayer graphene materials [10-16] have attracted a lot of attention in several research areas (i.e. physics, materials science and chemistry).

HOPG materials have been frequently described by referring to a system of dislocations (on the basis of the Burgers–Bragg–Read–Shockley dislocation model) consisting of rotated and/or tilted graphitic grains, with quasi-two-dimensional (2D) characteristics [4,5,17]. Noticeably, the tilting angle of the graphitic-grains ($\theta_{c\text{-axis}}$) in crystalline HOPG has been reported to have values $\lesssim 0.4°$ for the highest oriented grain-configuration [4,5]. Appearance of moiré superlattices and logarithmic van Hove singularities in this type of complex system has been recently demonstrated in presence of certain twisted-configurations (of the quasi-two-dimensional interfaces), namely for $1° \leq \theta_{twist} \leq 10°$ values [4,5,9,10-16,18]. Hexagonal moiré superlattices can be carefully identified by employing scanning tunnelling microscopy (STM) and high-resolution transmission electron microscopy (HRTEM) techniques [10,17,18]. Identification of the twist-angle value has been shown on the basis of the equation $a/2D=\sin(\theta/2)$, with $a$ being the basal lattice constant of HOPG (~ 0.247 nm), D the period of the moiré superlattice and $\theta$ the twisting-angle [4,5,18].

Presence of high dislocation densities in HOPG has been also shown to generate anomalous magnetic effects, under the application of an external magnetic field. A reversible splitting of zero field cooled (ZFC) and field cooled (FC) magnetization curves was interestingly reported by Scheike et al. [4], together with an unusual T-dependent enhancement of the diamagnetic behavior. The conditions for superconductivity in these materials have been described by referring to an interplay of edge dislocation (if $\theta_{c\text{-axis}} \neq 0$) and screw dislocations (if $\theta_{twist} \neq 0$) parameters [4,5]. The presence of interfacial contacts between Bernal (ABA) and rhombohedral (ABCA) phases has been indicated also as an important factor that could trigger superconductive ordering in these systems [6-8].

Together with these observations, the recent findings on the negative thermal expansion phenomena, at low temperature, in HOPG materials exhibiting long-range-crystalline-ordering, are of importance [17,18]. However, the relationship between such an unusual thermal expansion effect and the magnetic properties of these systems remains not fully understood and it requires further investigations.

Recent analyses performed by employing STM/STS (scanning tunnelling spectroscopy) and HRTEM have demonstrated the possible coexistence of multiple sublattice components within the multilayered structure of HOPG [18]. Modification of those interfaces has been further demonstrated in exfoliated systems, with an unusual distortion of moiré superlattices [18].

In this work, in the attempt of gaining a better understanding of the relation between structural characteristics and magnetic/superconductive transitions in those HOPG materials exhibiting long-range-ordering along the c-axis, we performed an in-depth investigation by employing orientation dependent X-ray diffraction (XRD) and superconductive quantum interference device (SQUID) magnetometry. Preliminary XRD analyses allowed the identification of the long-range ordered HOPG (HOPG with grade A,B), with structural characteristics comparable to those analyzed in Ref. [17,18]. Temperature dependent zero field cooled (ZFC) and field cooled (FC) magnetometry acquisitions from T~ 2K to T~300K revealed an unusual temperature-dependent variation of the diamagnetic component with the decrease of the temperature. We highlight the discovery of an anomalous splitting of the magnetic curves below T~200K. The observed transition is not compatible with a spin-glass behavior and instead resembles the anomalous trend reported by Scheike et al. in dislocation rich HOPG, in Ref.[4]. By analyzing the ZFC/FC magnetic-curves (through magnetic moment subtraction methods, namely mFC-mZFC) we identify the presence of a weak magnetic transition in the T range from 2 to 200K. Also, through re-interpretation of the temperature dependent $2\theta$-dataset reported in Ref. [17], we discuss the origin of the observed magnetic transition and the possible contributions arising from the internal Bernal (untwisted) and other twisted-graphitic-sublattices of HOPG. Interestingly, magnetization vs field measurements allowed for the

identification of a weak ferromagnetic hysteresis, after subtraction of a dominant linear diamagnetic background. The origin of the observed magnetization signal is further interpreted in relation to possible contributions arising from disorder-rich locally-twisted interfaces. Disappearance of the anomalous magnetic-curve-splitting was instead observed in those HOPG samples exhibiting a short-range ordering (i.e structural disorder).

## 2 Experimental

HOPG samples of grade A and B (purity >99.99%) with dimensions of 5 x 5 x 1 mm (mosaic angles of 0.5° and 0.8°, ± 0.2°) were purchased from XFNANO, INC China. TEM, HRTEM investigations were performed on exfoliated lamellae by employing a 200 kV American FEI Tecnai G2F20. Fourier transform analyses were performed by using the software Digital Micrograph. SQUID ZFC/FC and magnetization vs field signals were acquired with a MPMS-XL-5 Quantum Design instrument.

The T-XRD measurements were performed by employing a PANalytical Empyrean powder X-ray diffractometer (Cu K-α, λ =0.15406 nm), equipped with a primary Johansson monochromator, an Oxford Cryosystems PheniX cryostat operating under vacuum below $10^{-2}$ Pa, and a X'celerator linear detector, varying the temperature from 12 K to 298 K. Room temperature XRD characterization was further performed by employing an Empyrean PANalytical diffractometer (Cu Kα radiation).

## 3 Results and Discussion

The structure of ten as purchased HOPG samples was firstly analyzed using room temperature XRD measurements performed with the c-axis perpendicular to the substrate-stage, as indicated in Fig.1A-C. The number of samples was chosen to gain an explicit correlation between structure and magnetic properties. It is noticeable the presence of preferred (002) and (004) reflections of graphitic carbon with space group P63/mmc. The analyzed signals could be divided into two main categories, namely a first one (category 1, long range order) exhibiting a long-range-ordering along the c-axis (i.e. intense 004 and 100 reflections see Fig.1 and Fig.S1-S2, see ordered HOPG-1,2,3) and a second one (category 2, short range order) exhibiting instead a

shorter range-ordering, with significantly weaker 100 and 004 diffraction signals.

The ordered HOPG samples shown in Fig.1A-C were found to exhibit particularly intense 002 and 004 reflections, indicative of a long-range structural Bernal ordering along the c-axis. This interpretation was confirmed by orientation dependent analyses (performed with the c-axis parallel to the substrate) which revealed the presence of preferred 100 and 110 reflections (see ESI Fig.S1).

An unusual splitting of the 004 diffraction-peak into multiple components was also found. A two-component splitting of the 004 peak-reflection was identified in the ordered samples (see Fig.1B,C and Fig.S2). Instead, splitting into 3 to 5 components was observed in disordered HOPG, as shown in Fig.1A-C and Fig.S2,S3. This observation indicates the presence of multiple coexisting sublattices with varying unit-cell parameters.

Extended investigations were then sought by employing SQUID magnetometry. Temperature dependent zero field cooled (ZFC) and field cooled (FC) measurements of the magnetization performed on the ordered-1 sample (see Fig.1, for XRD analyses of the ordered-1-sample) from T~ 2K to T~300K revealed an unusual temperature-dependent variation of the diamagnetic component (Fig.2A, applied field of 150 Oe), which resembled the behavior previously reported by Tang et al. in low dimensional superconductors [20] and by Boi et al. in sulfur doped HOPG [23].

By analyzing the temperature dependent variation of the ZFC and FC signals, an anomalous reversible splitting of the magnetic curves was found below T~200K.

The observed signal splitting-transition appears to be not compatible with a spin-glass behavior and instead resembles the superconducting-like trend previously reported by Scheike et al. in dislocation rich-samples (see Ref. [4]). The field dependent variation of the ZFC magnetic-curves is further presented in Fig.2B (ZFC-susceptibility) and Fig.3A-C (field-dependent, magnetic-moment vs temperature, ZFC curves).

By analyzing the splitting of the ZFC/FC magnetic-curves (signals in Fig.2A, analyzed through magnetic moment subtraction methods, namely mFC-mZFC [4,19]) in Fig.4A, we were able to identify a weak magnetic transition in the T range from 200K to 2K.

The origin of the observed weak irreversibility, may possibly be ascribed to intrinsic contributions which arise from a small fraction of the sample´s volume. This interpretation is sensible, given the weak nature of the observed signal, when compared to the strong diamagnetic contribution presented in Fig.2A.

By comparing the mFC- mZFC analysis presented in Fig.4A with those reported by Kopelevich et al. [19] (for ferromagnetic/antiferromagnetic spin-glass-like systems), it is possible to note the presence of a significantly different temperature-dependent trend. This observation seems to suggest a different origin of the signal reported in this work.

Noticeably, in another work reported by Lehtinen et al [28], the presence of spins and magnetic moment contributions (in graphitic systems) was theorized to occur in presence of dangling bonds, which relate to vacancies and other structural defects. Together with these possibilities, other effects arising from diamagnetic responses can not be excluded. In an attempt to gain further insights on the observed magnetic transition, extended characterization was sought through re-interpretation of the temperature dependent 2$\theta$-dataset reported in Ref. [17], in those category-1 HOPG samples exhibiting negative thermal expansion.

The variation in the 2$\theta$-position of the 004 reflection with temperature in Fig.4B-E evidences a structural transition involving a saturation effect in the T-range from 180K to 50K and a negative thermal expansion from T~50K to T~12K. It is interesting to notice that the observed structural-transition happens in a comparable temperature range to that presented in Fig.4A (mFC-mZFC). Instead, no contributions from rhombohedral phases were found (Fig.4F).

Together with these observations, it is of importance to comment on possible additional magnetic contributions from locally twisted sublattices, which have been recently identified through both STM/STS and HRTEM (see Ref.[18]).

In particular, typical examples of frequently observed hexagonal superlattice periodicities are shown in Fig.5A-F, where the coexistence of D ~ 12.1 nm and D ~ 1.8 nm is presented. In Fig.5B, the Fourier transform analyses confirm the presence of the two coexisting super-periodicities of the superlattice. A local variation in the D

(period) value is also shown, as demonstrated in Fig.5A with D~15.8 nm, Fig.5C with D~15.9 nm, Fig.5D with D~ 13.7 nm, Fig.5E with D ~ 14.7 nm and Fig.5F with D ~ 15.7 nm. Additional analyses of locally twisted interfaces with variable periodicity are further shown in Figs.6,7. The twist-disorder parameter within the moiré superlattice was investigated through profile and Fourier transform analyses by employing the software Digital Micrograph [18,22,23].

Possible antiferromagnetic and/or ferromagnetic contributions arising at low temperature from the observed twisted sublattices cannot be excluded and may depend on the regularity of the twisted interfaces [13]. A previous work by Khalaf et al. [21] has indeed investigated theoretical predictions on possible shifts in the magic-value ($\theta_{twist}$ ~1.1°) of the twist-angle with the increase of the sample thickness. This was done by employing a system-model with $n_e$ sequences of twisted interfaces [21]. By multiplying the value of the magic angle to ~ 2cos (π∗k/ n+1) (with k = 1,…..,$n_e$) a shift of the expected twist angle towards $\sqrt{2}$ for n = 3 and 2 as n → ∞ was reported [21]. This observation appears to imply that existence of orbital magnetic components and/or superconductivity may be linked to the regularity as well as to the thickness of the analyzed twisted sublattices, in absence of twist angle disorder [13,21]. A significant fragility within correlated states in presence of twist-angle disorder has been indeed shown [13]. Noticeably, presence of ferrimagnetism has been recently shown by our group in exfoliated samples, in presence of twist-angle-disorder [29].

In an attempt to verify the possible presence of ferrimagnetic contributions in the analyzed sample, additional characterization was sought through hysteresis-loop acquisition (magnetization vs field measurements) at T~50K, with the max applied field value of 150Oe. As shown in Fig.8, these measurements revealed the coexistence of two type of magnetic signals, consisting of 1) a significant diamagnetic contribution, in agreement with the ZFC/FC measurements in Fig.2 and 2) an extremely weak ferromagnetic hysteresis, which could be identified after subtraction of a linear diamagnetic component, as shown in Fig.8A-C.

A disappearance of the reported unusual ZFC/FC splitting was then found in those HOPG samples exhibiting shorter range c-axis ordering (see Fig.9A). In this latter case, SQUID magnetometry analyses of the susceptibility parameter revealed a different type of irreversibilities compatible with a re-entrant spin-glass-like behaviour, in analogy with the interpretation of Kopelevich et al. [19]. An analogous susceptibility trend was interestingly found also in exfoliated lamellae (Fig.9B), possibly a consequence of structural transitions caused by changes in the stacking order [22,23]. Further, it is important to highlight the observation of comparable ZFC and FC spin-glass-like irreversibilities in other disclination-rich conductive graphite films (grafoil, see Fig.9C-F). In the latter case, we indicate the additional presence of oxygen-rich regions which seem to enhance the ferromagnetic response of the samples, with possible contributions arising from C-O and C=O rich interfaces (see ESI Fig.S4-7) [24]. Interestingly, the observed magnetization results acquired from the grafoil sample differ also from those recently reported on superconductive-like oxygen-rich graphite [25-27].

## Conclusion

In conclusion, in this work we investigated the relation between structural characteristics and magnetic ordering in HOPG materials exhibiting long-range ordering. Orientation dependent XRD and T-SQUID magnetometry allowed for the identification of those samples with long-range ordering (HOPG with grade A,B). Temperature dependent ZFC and FC magnetometry from T~ 2K to T~300K revealed an unusual temperature-dependent variation of the diamagnetic component with the decrease of the temperature. We highlighted the discovery of an anomalous splitting of the magnetic curves below T~200K. By analyzing the ZFC/FC magnetic-curves (through magnetic moment subtraction methods) we identified the presence of a weak magnetic transition in the T range from 200K to 2K. The possible origin of the observed magnetization-trend was discussed in relation to contributions arising from 1) disorder-rich locally twisted interfaces and 2) those internal graphitic sublattices exhibiting negative thermal expansion. Interestingly, magnetization vs field

measurements revealed the presence of a particularly weak ferromagnetic hysteresis (which appears to support the presence of a disordered-mediated magnetism) in coexistence with the dominant diamagnetic response. Disappearance of the unusual ZFC/FC signal-splitting was then found in magnetic curves acquired from HOPG samples with shorter-range ordering. A comparable spin-glass magnetic trend was also detected in exfoliated lamellae (as a consequence of structural disorder caused by the exfoliation process) and in disclination-rich conductive graphite films (grafoil).

## Acknowledgments

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## Data Statement

The data that supports the findings of this study are available within the article and its supplementary material.

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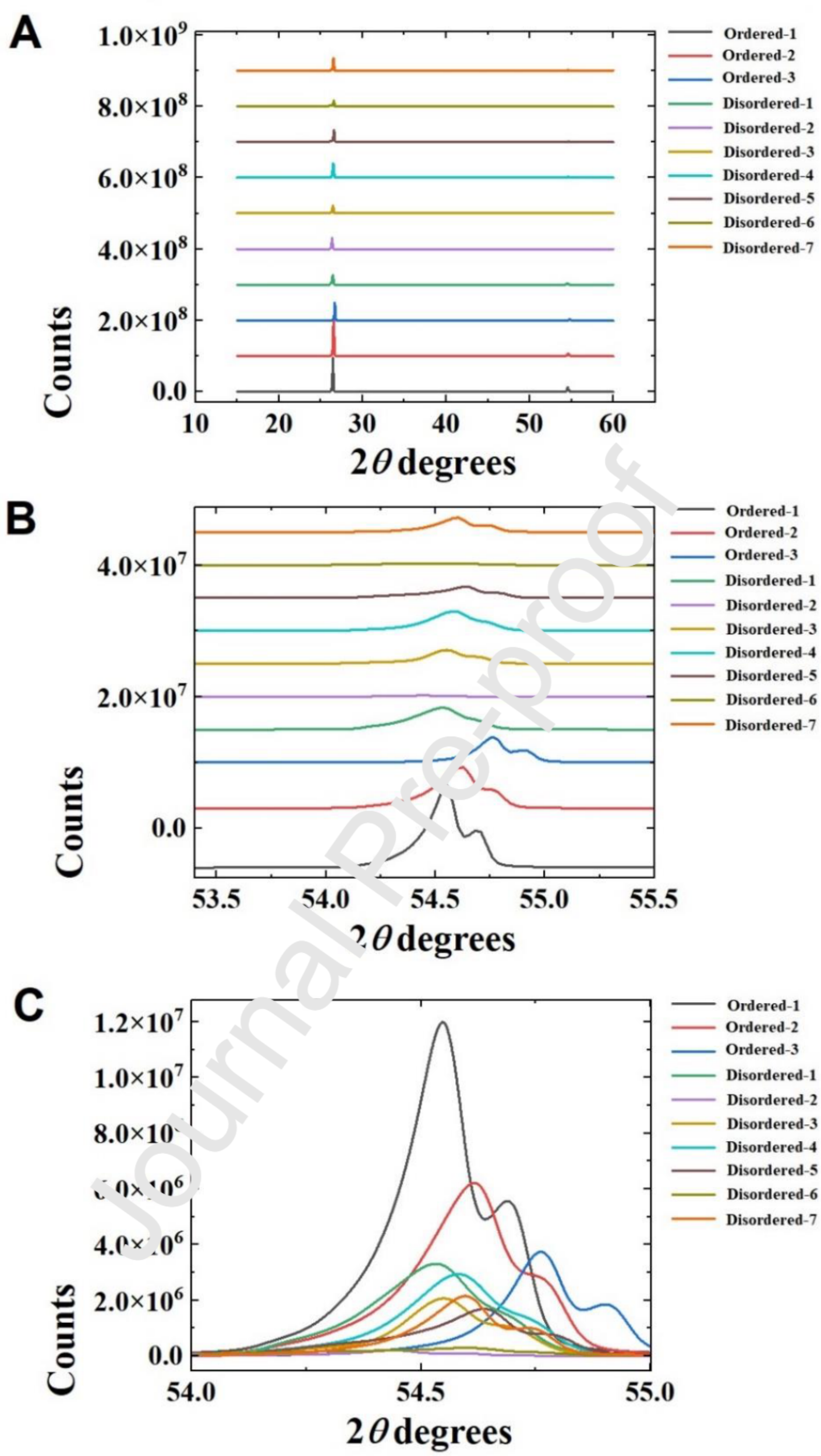
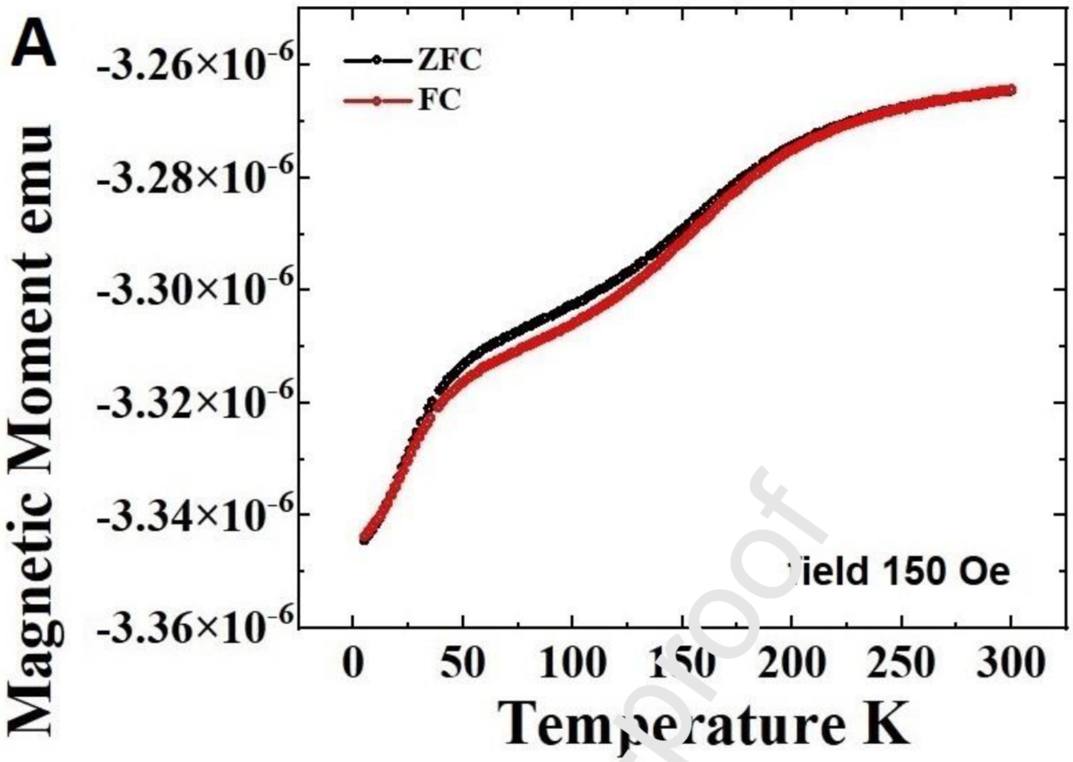



Figure 1: X-ray diffractograms acquired from ten as purchased HOPG samples and revealing a significant variation in the structural regularity and ordering of the c-axis parameter. Note in B,C the presence of an enhanced 004 reflection for the ordered-HOPG samples, indicative of the presence of an enhanced long range ordering along the c-axis of the analyzed samples.



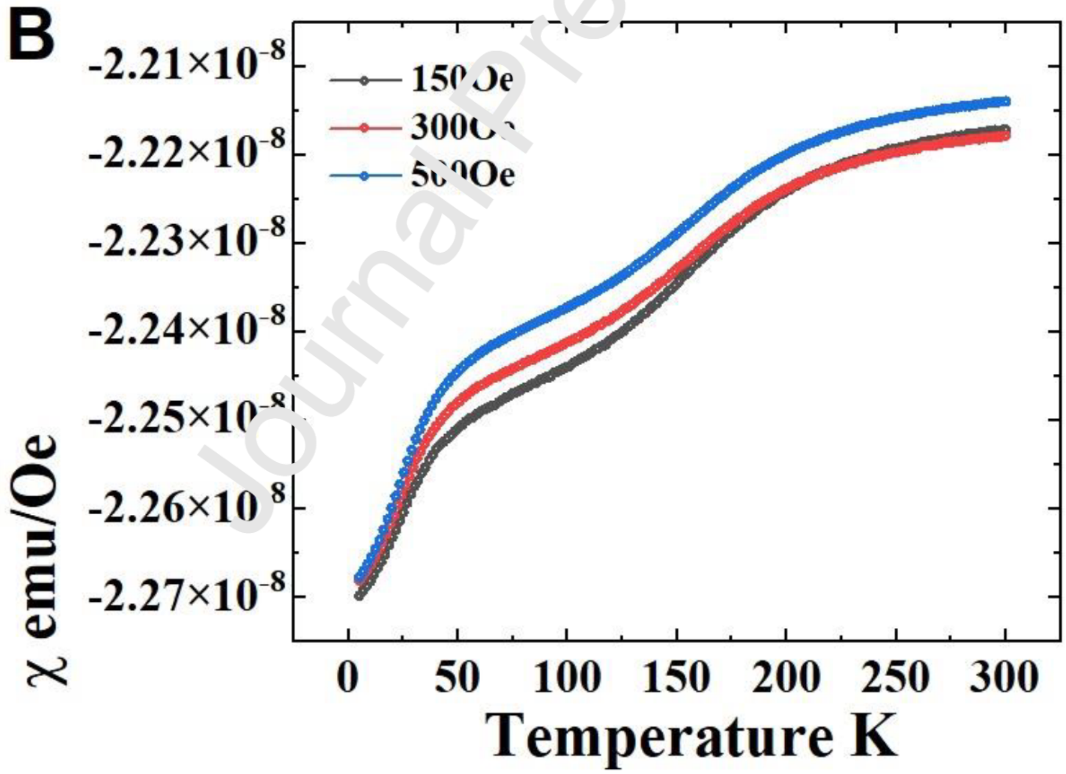




Figure 2: In A ZFC and FC magnetic curves (magnetization curves) acquired at the applied field of 150Oe from the ordered-1 HOPG sample (in Fig.1). In B, field-dependent ZFC-susceptibility curves. Noticeably, the signals presented in A evidence an unusual temperature dependent enhancement of the negative magnetization component together with a reversible signal splitting (A). The latter is indicative of a magnetic transition in the sample.

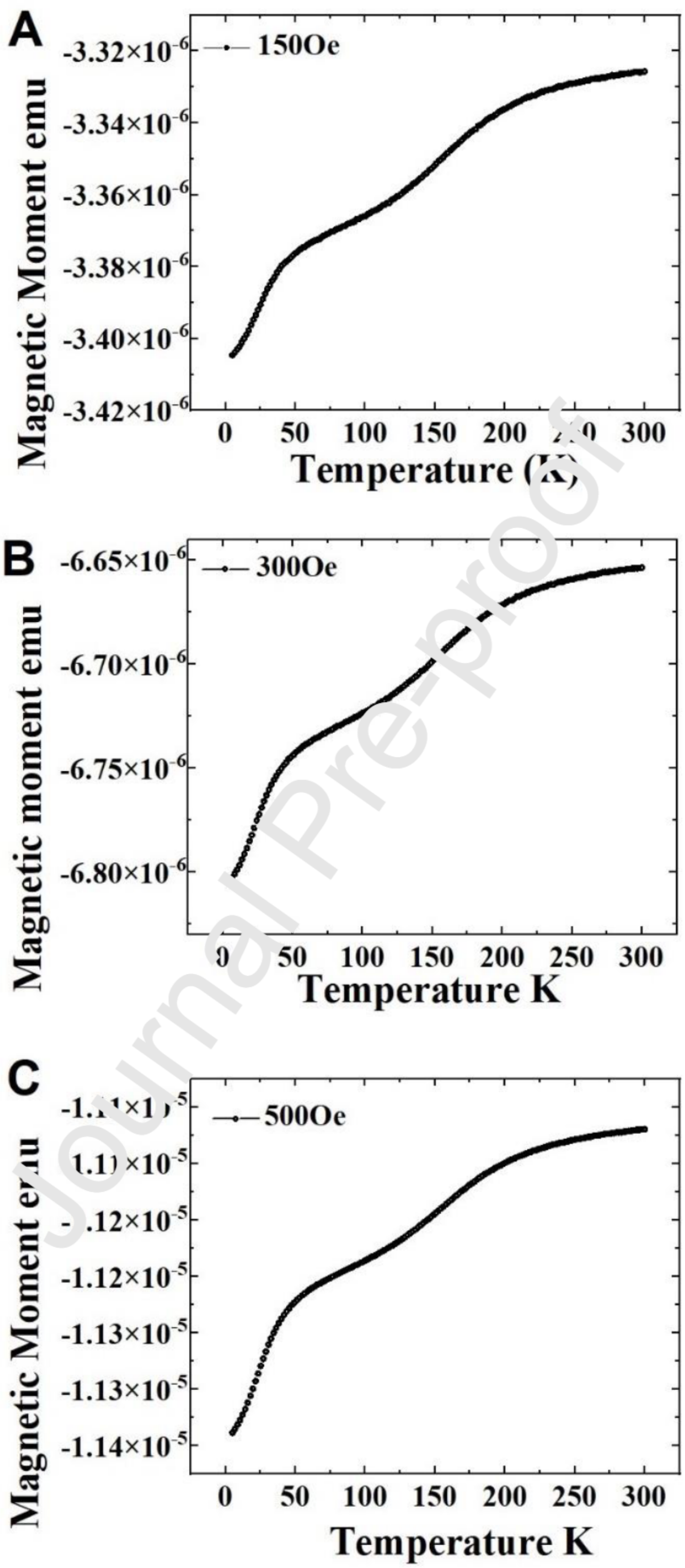



Figure 3: ZFC magnetic curves (magnetizations curves in A,B,C) evidencing the variation of the unusual temperature dependent negative magnetization component as the field value was increased from 150Oe to 500Oe (measurements acquired from ordered-1 HOPG sample).

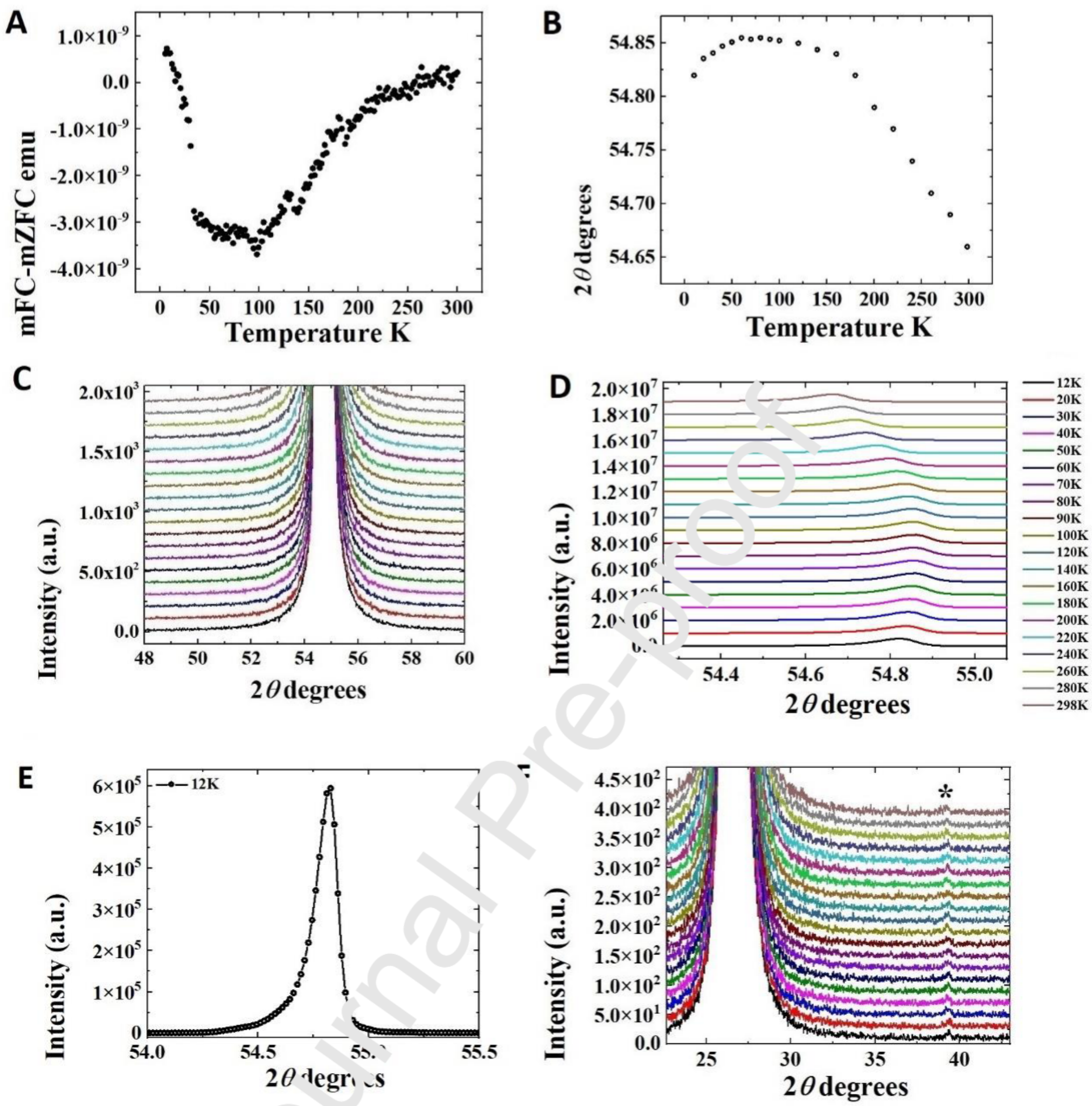



Figure 4: In A, analyses of ZFC/FC magnetic-curves (through magnetic moment subtraction methods, namely mFC-mZFC of the signal in Fig.2A), revealing the presence of a weak magnetic transition in the T range from 200K to 2K. In B-D re-investigation of the temperature dependent XRD dataset reported in Ref. [17] in those categories of HOPG samples exhibiting negative thermal expansion (category 1, long-range-ordering). Noticeably the variation of the 004 $2\theta$-position with temperature (B-D) evidences a structural transition involving a saturation effect in the T-range from 180K to 50K and negative thermal expansion from T~50K to T~12K. Note that the observed transition-trend in A happens in a comparable temperature range. The enhancement in diamagnetism shown below 50K in Fig.2,3 may possibly relate to the observed negative thermal expansion effect from T~50K to T~12K. In E the structural regularity and the long-range ordering of the analysed samples is evidenced by the sharpness of the 004 reflection and absence of signal-splitting. In F no contributions were found to arise from rhombohedral phases.

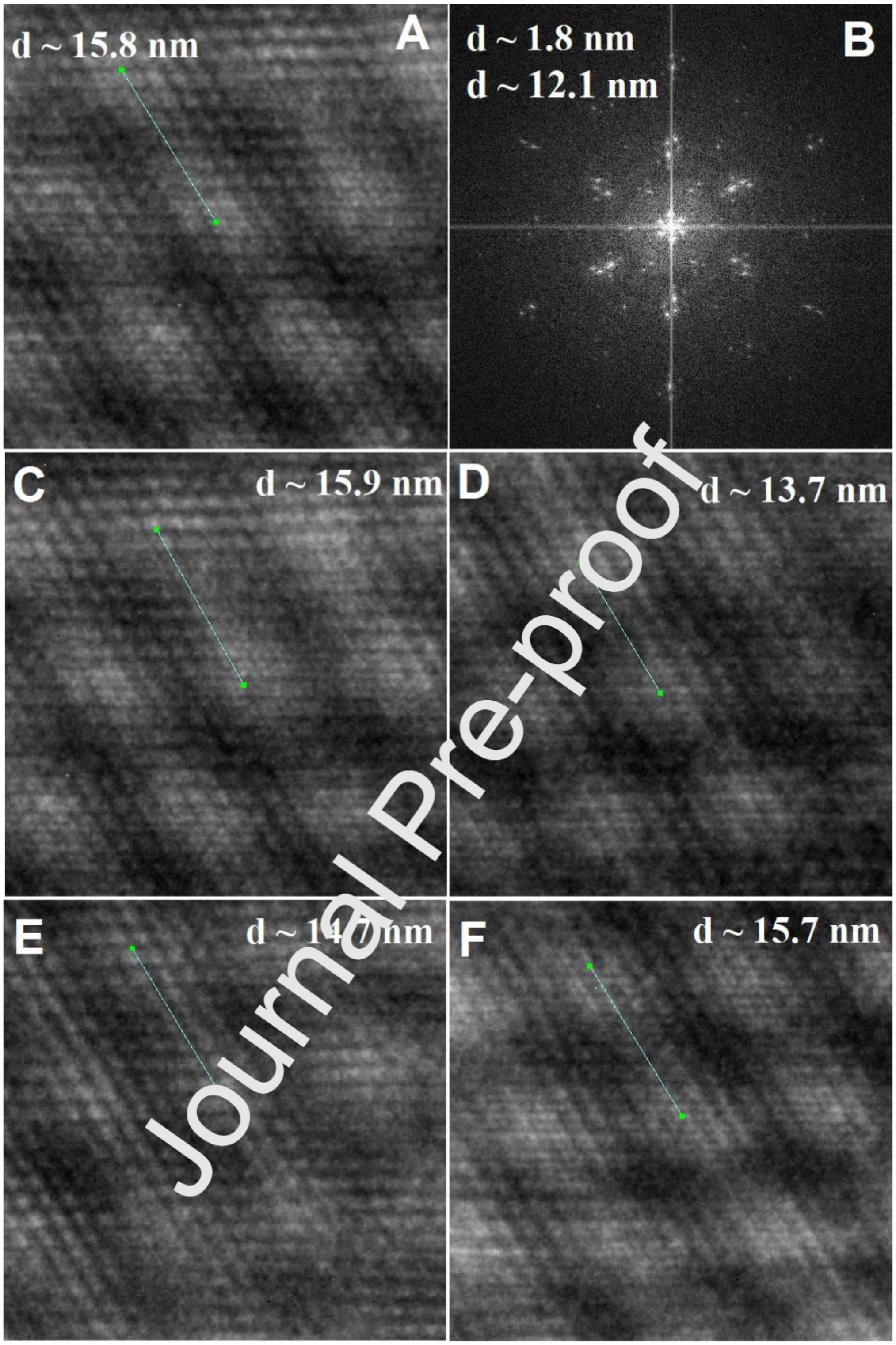





Figure 5: In A-F typical examples of frequently observed hexagonal superlattice periodicities (resulting from locally twisted sublattices), by employing HRTEM. The frequent coexistence of D ~ 12.1 nm and D ~ 1.8 nm periodicities was revealed by Fourier transform analyses in Fig.5B. It is also important to highlight a local variation in the D (period) value, as demonstrated in Fig.5A with D~15.8 nm, Fig.5C with D~15.9 nm, Fig.5D with D~ 13.7 nm, Fig.5E with D ~ 14.7 nm and Fig.5F with D ~ 15.7 nm (twist-angle-disorder possibly a consequence of the exfoliation process).

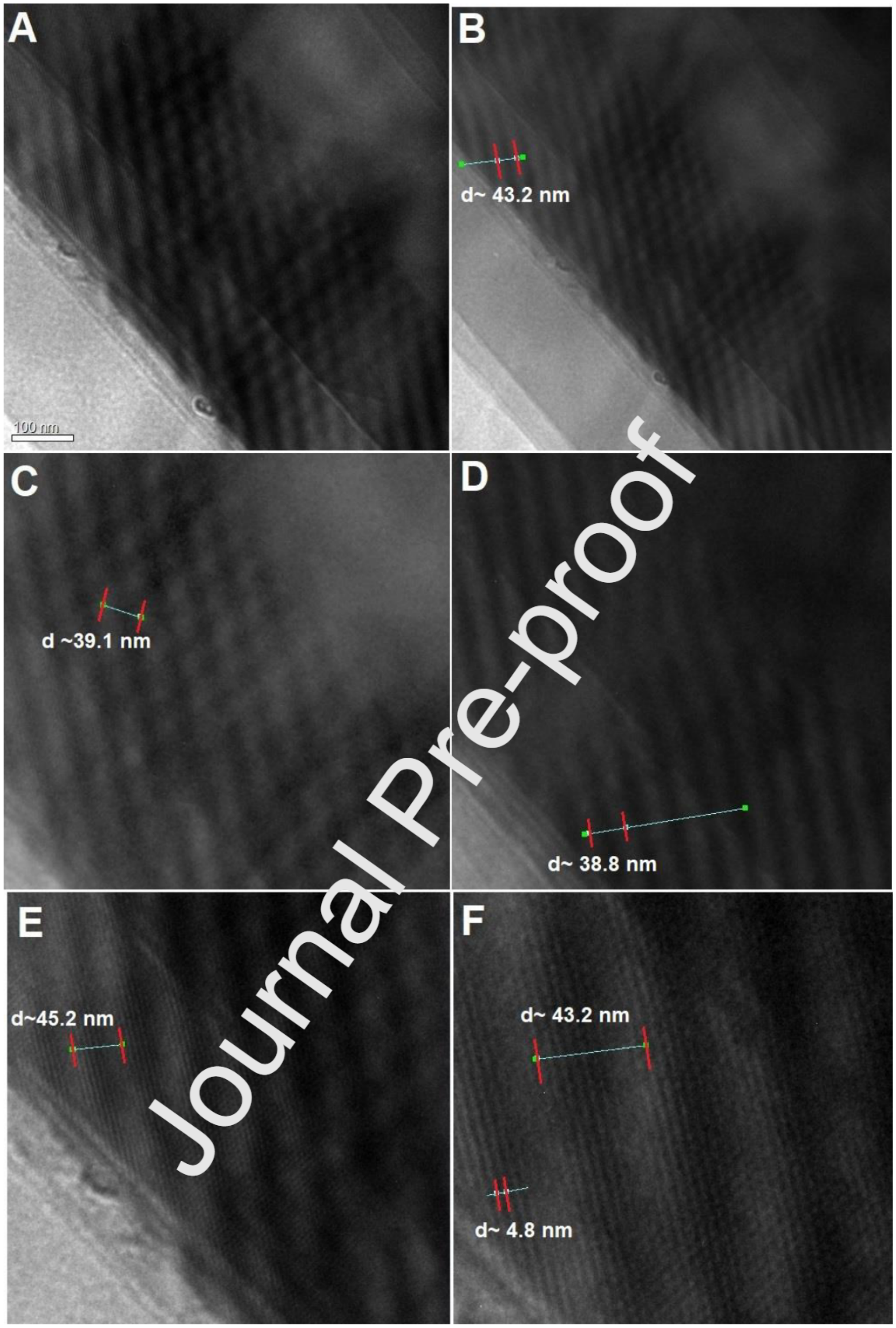



Figure 6: In A-F additional examples of frequently observed hexagonal superlattice periodicities (resulting from locally twisted sublattices), acquired by employing HRTEM. Noticeably, the coexistence of D ~ 39.1 nm and D ~ 4.8 nm periodicities was revealed by Fourier transform and profile analyses performed with the software Digital Micrograph.

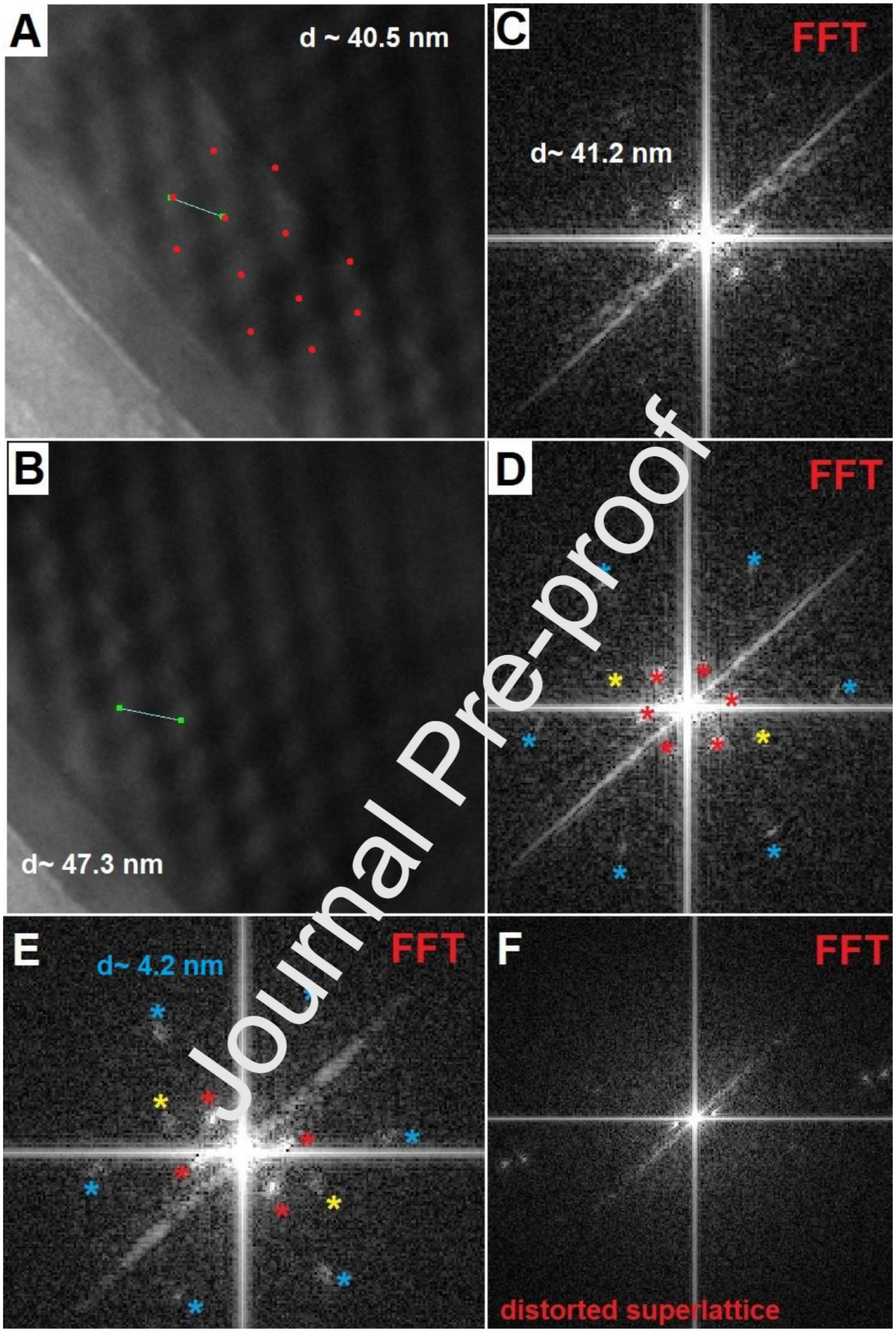



Figure 7: In A-F additional HRTEM and Fourier transform analyses revealing the frequent coexistence of D ~ 39.1 nm and D ~ 4.8 nm super-periodicities. The significant variation in the observed superlattice periodicity is indicative of twist angle disorder in the sample.

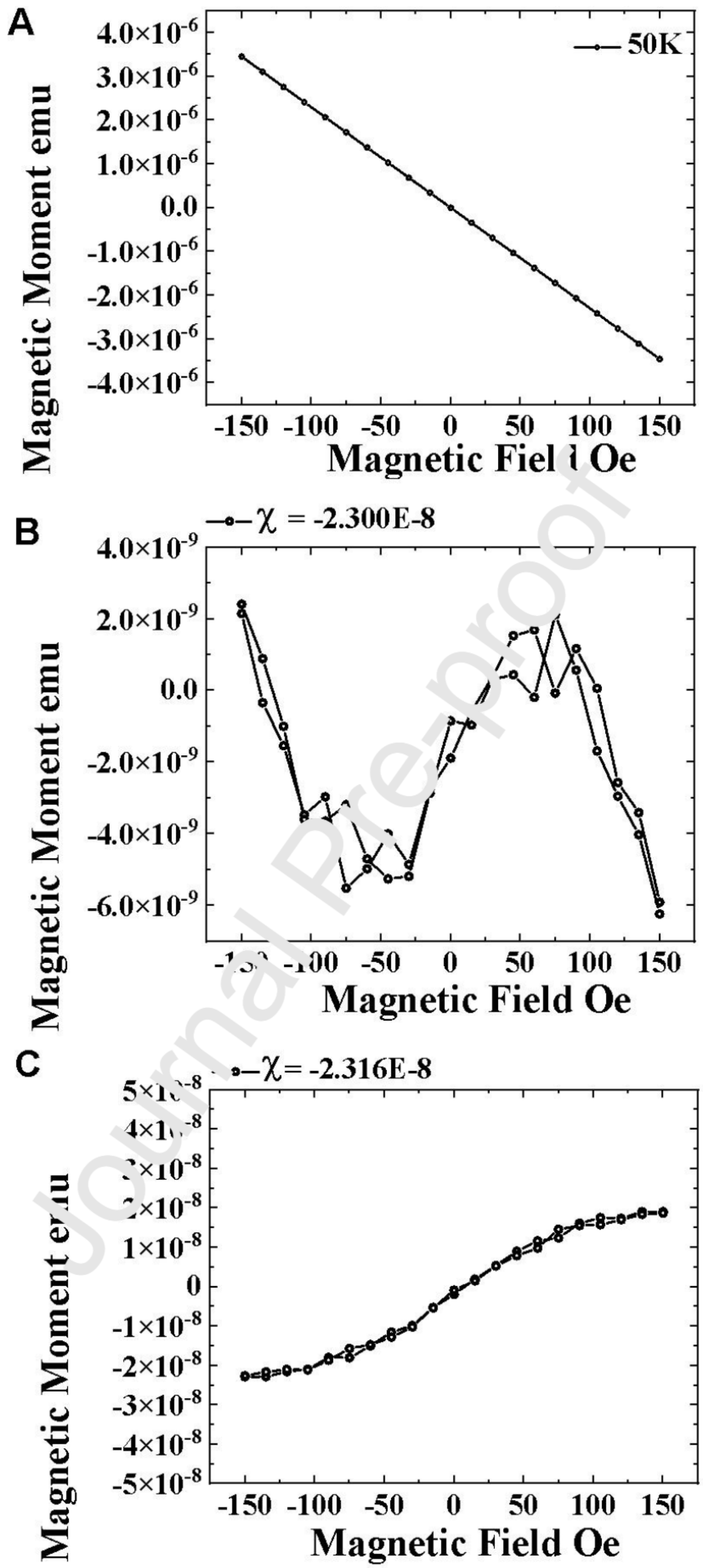



Figure 8: Magnetization vs applied-field signal, acquired at T~50K, revealing the coexistence of diamagnetic and ferromagnetic components. In B,C the signal subtracted from A with an increasing linear diamagnetic component is shown. The final subtracted signal in C evidences a weak ferromagnetic ordering in the sample.

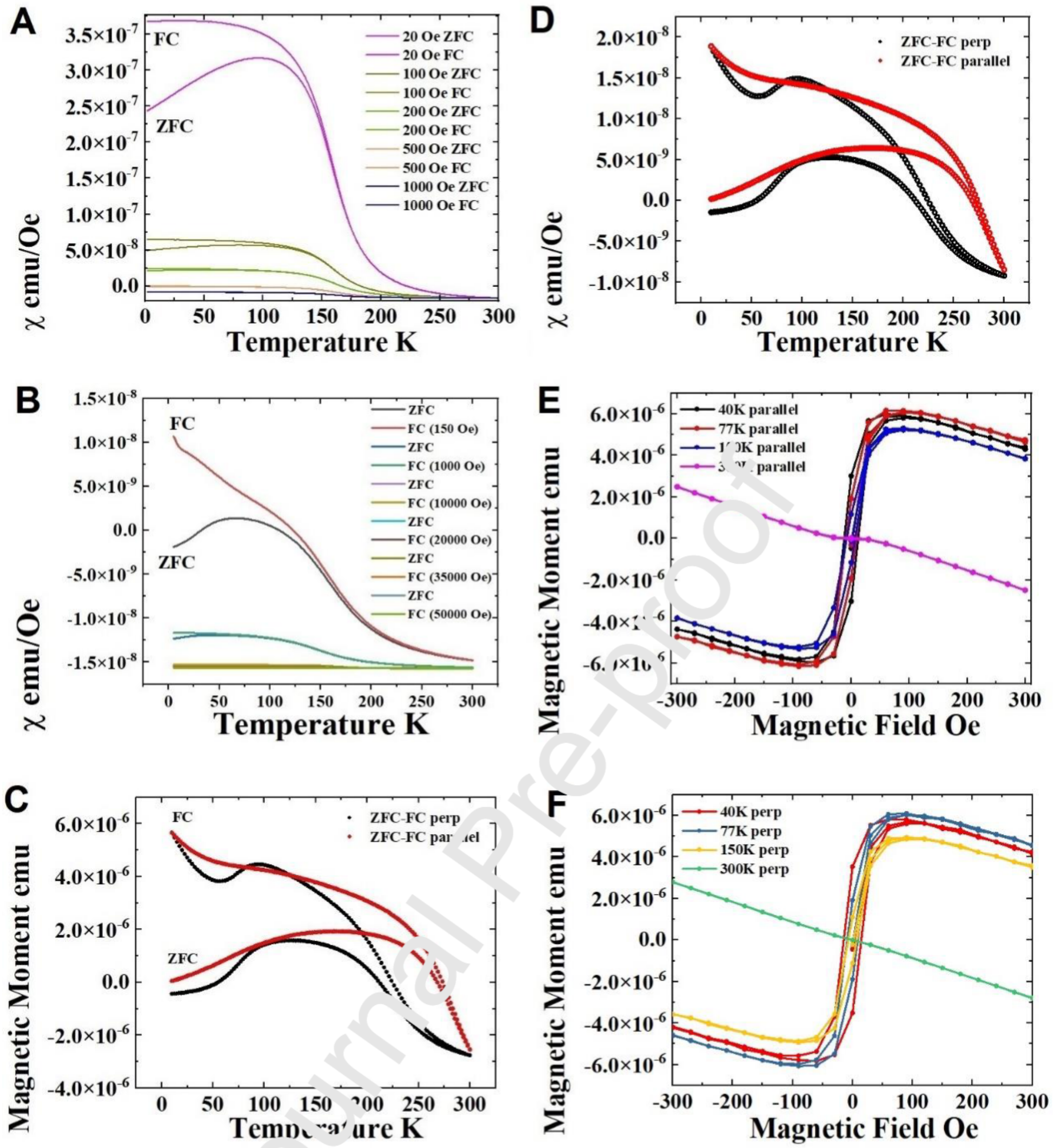
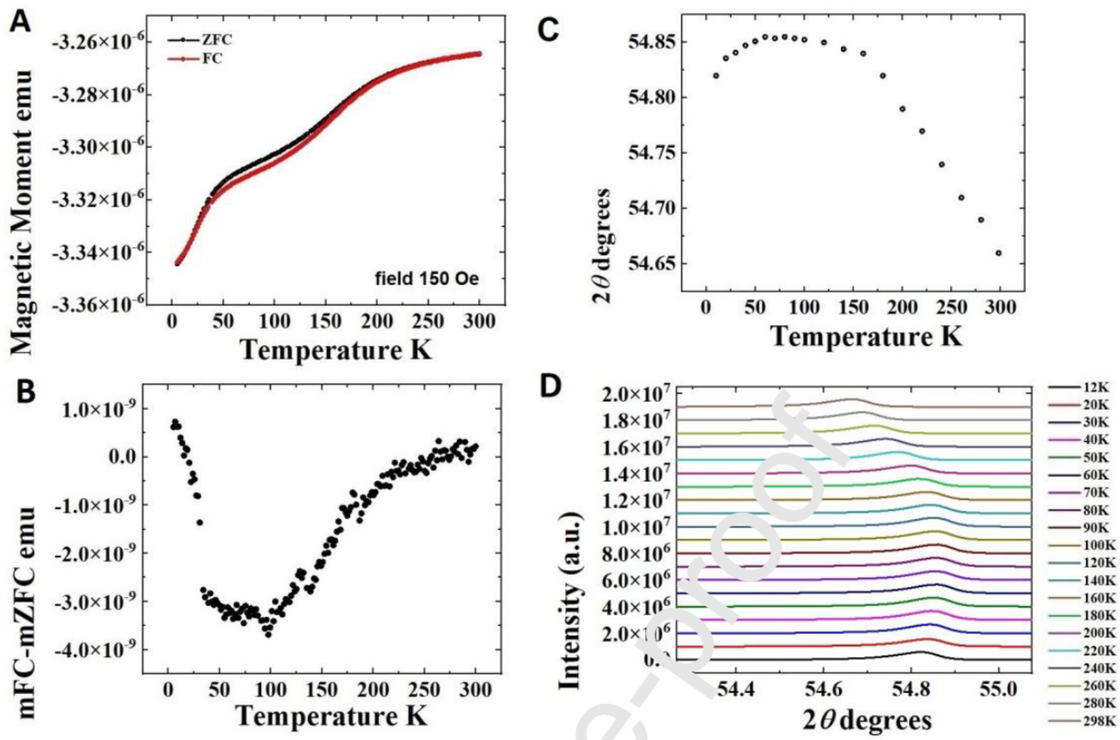



Figure 9: Extended SQUID magnetometry analyses acquired from a category 2 HOPG sample (weak 004 reflection, short-range-ordering) in A and revealing a re-entrant spin-glass-behaviour. In B and C-E, additional magnetic analyses performed on an exfoliated lamella (B) and in a highly conductive graphite film sample (grafoil, C-F). A re-entrant spin-glass behaviour was found in all the three cases shown in A-D. Particularly it is important to consider also possible contributions from C-O and C=O rich interfaces, which have been reported to generate spin-glass-like magnetization components in a recent report by Boi et al. [24] (see also Fig.S4-7 for additional characterization performed on grafoil).

Graphical abstract



Highlights

We present a novel investigation on HOPG samples exhibiting a long-range ordering along the c-axis.

ZFC and FC magnetic curves from T~ 2K to 300K revealed a temperature-dependent variation of the diamagnetic component.

We identify the presence of a weak magnetic transition in the T range from 200K to 2K.

Disappearance of the unusual signals-splitting was found in HOPG samples with higher degree of disorder.

**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:

**Contribution Statement**

The contributions to the work performed in this article were as follows. Prof. Filippo Boi designed the project. Prof. Filippo Boi, Prof. Anna Corrias, Prof. Salvatore Grasso and Mr. Jiaxin Song contributed to the preparation of the manuscript. Characterization experiments were performed by Mr. Jiaxin Song with the help of Prof. Filippo Boi (XRD, TEM and Magnetometry Characterization analyses), Prof. Salvatore Grasso (data analyses and interpretation), Prof. Shanling Wang (TEM/HRTEM measurements), Prof. Anna Corrias (temperature dependent X-ray measurements and analyses), Mr. Zhiquan Dai, Prof. Yi He, Milad Kermani, Shuai Gao, (characterization analyses), Prof. Jiqiu Wen, Dr. Aiqun Gu (X-ray diffraction analyses).