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Magnetic vortex and unsaturated magnetization components in highly oriented pyrolytic graphite

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Abstract

Observation of ferromagnetic and granular superconductive features in highly-oriented-pyrolytic-graphite (HOPG) has recently attracted an important attention. We report a novel temperature dependent XRD and SQUID investigation of HOPG in the temperature range from 300.15 to 77.15 K. Unusual hysteresis features indicate the possible presence of vortex states in conditions of magnetic field approximately perpendicular to the HOPG layers. This interpretation is further supported by additional measurements performed on intermediate lamellae extracted by exfoliation. Evidence of a possible structural-transition in the c-axis of HOPG in the temperature range between 77 K and 100K is also provided by using the Rietveld refinement method.

ZFC and FC measurements performed at high field values of 5000-10000 Oe, together with mFC-mZFC subtraction, highlight absence of a sharp depletion of the difference between magnetization signals towards zero. These observations may indicate the possible presence of additional unsaturated weak features, which are ascribed to superconductive signals as previously predicted by Scheike et al. [8].

1 Introduction

Understanding the origin of magnetic ordering in pure carbon-based graphitic materials has recently become a crucial focus of research towards translation of these systems into technological applications. Graphite is a layered material with hexagonal symmetry (space group $P6_3/mmc$) characterized by delocalized π-electrons along the graphene layers and Van der Waals forces in between (layers) [1-15]. The stacking between graphene layers and the layer orientation have been shown to play a crucial role towards modifications of band gap and energy dispersion relation characteristics of these materials. In particular, formation of unusual superconductive features in bilayer graphene and highly oriented pyrolytic graphite (HOPG) has been recently reported for specific rotational angle, known as magic angle of rotation [1-15,23,25]. Presence of sequential stacking consisting of Bernal and rhombohedral phases has been also acknowledged as one of the possible factors governing such high temperature superconductive effects [4]. Interestingly, superconductive ordering in HOPG systems was already reported in early 2000 by Kopelevich et al. for certain conditions of annealing [1]. It was shown that formation of superconductive hysteresis could be triggered by high temperature annealing of as grown ferromagnetic HOPG samples [1]. These observations were further supported by the recent works of Scheike T. et al. and Esquinazi et al. [7,8] where existence of room temperature superconductive phenomena was reported in conditions of magnetic field perpendicular to HOPG layers and explained on the basis of the Burgers–Bragg–Read–Shockley (BBRS) dislocation model [5,6]. Existence of possible relationships between second order antiferromagnetic transitions and critical superconductive temperature in such magic angle Mott insulated superconductive systems has been also recently proposed [12a, 12b, 24]. In typical Mott insulator, the ground state is generally characterized by antiferromagnetic spin ordering below the Néel temperature [24, 12a, 12b]. In view of this important theory recently proposed in magic angle superconductivity, understanding the link between antiferromagnetic correlations and superconducting ordering is of crucial importance. The presence of temperature induced antiferromagnetic transitions has been recently reported also in electron paramagnetic resonance (EPR) studies of nanostructured graphite and multiwalled carbon nanotubes [17-19]. Possible correlation effects compatible with antiferromagnetic/ferromagnetic ordering were also shown through EPR studies in pristine HOPG [21]. Possible links between this magnetic transition and structural rearrangements of the graphitic c-axis in this type of Bernal systems (with A-B-A stacking) with the decrease of the temperature remain still unclear.

Interestingly, presence of transitions in the c-axis of the graphitic unit-cell has been reported in multiwalled carbon nanotubes in the range from 300K to 12 K (below room temperature) [20]. Furthermore, c-axis shifts have been reported in nanostructured graphite, carbon nanotubes, carbon onions and HOPG at higher temperatures, from 298 K to 673 K [20, 23,25]. However, further studies are needed in order to understand the possible relationship between such structural transitions and the magnetic correlation effects recently predicted for these systems at the magic angle. In contrast with those predictions [12a, 12b], it is also important to mention a recent theory which suggests the absence of Mott insulation characteristics and proximity to Wigner Crystallization in conditions close to first magic angle of rotation [16]. In addition, anomalous transitions have been predicted in graphite for large applied magnetic fields [26-29].

In this work we report a novel temperature dependent XRD and SQUID investigation of HOPG from 300.15 down to 77.15 K.

Magnetization vs Field measurements revealed the presence of unusual vortex-like magnetic hysteresis with characteristic sharp magnetization features at 250 K. Interpretation of this unusual type of signal was further supported by magnetization analysis performed on lamellae exfoliated from internal regions of the sample which revealed anomalous pinning features possibly attributable to onion and vortex states of the magnetization [35]. Additionally, zero field cooled (ZFC)-field cooled (FC) measurements appeared to suggest the possible absence of complete magnetic-moment-saturation in conditions of high applied magnetic field values of 5000 Oe and 10000 Oe. These observations were further corroborated by calculations performed using the mFC-mZFC subtraction methods reported in previous works [7,8]. Possible presence of additional magnetic components (i.e. weak superconductive regions/interfaces) at the origin of such unsaturated magnetization signal can not be excluded on the basis of recent experimental reports [7,8].

Evidence of a structural-transition in the c-axis of HOPG at temperatures between 100 to 77K is also demonstrated by means of Rietveld refinement. This transition was further investigated on turbostratic graphite and carbon nanotubes samples for comparison.

2 Experimental

HOPG samples with dimensions of 5 x 5 x 1 mm and mosaic angle of 0.5°, ± 0.2° and 0.8°, ± 0.2° were purchased from XFNANO, INC China. Commercial graphite powder was purchased from Xiya Reagents China Cas number 7782-42-5. Fe_5C_2/Fe_7C_3 filled CNTs were produced by pyrolysis of sulfur/ferrocene mixtures following the method reported in reference [19].

Temperature dependent XRD measurements were performed on a Rigaku Smart-lab powder X-ray diffractometer (Cu K-α , $\lambda = 0.15418$ nm) with Bragg- Brentano configuration under vacuum values below 7 Pa in the temperature range from 300.15 down to 77.15 K, with an Anton Paar TTK450 chamber. The HOPG samples were positioned with the c-axis perpendicular to the substrate holder. Additional measurements were performed on thin walled CNT samples on a PANalytical Empyrean powder X-ray diffractometer (Cu K-α1, 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, in the temperature range from 12 to 300K. TEM measurements were performed with a 200 kV American FEI Tecnai G2F20. Fourier transform analyses and Moiré pattern analyses were performed with the Digital Micrograph software (see ESI Fig.Supp.1-3). SQUID measurements were performed at maximum fields values of 5000 Oe and 10000 Oe in pristine as purchased samples, with a Quantum Design system.

3 Results and Discussion

The layered structure of the HOPG sample was firstly revealed by XRD measurements, as indicated in Fig.1, with the observation of preferred 002 and 004 reflections. Note that no peak features compatible with rhombohedral graphite were detected. By analyzing the temperature dependent XRD diffractograms in Fig.1, it is possible to notice that a significant temperature dependent shift in the position of the 002 and 004 diffraction peaks towards larger values of 2θ is present as the temperature decreases. This significant transition can be observed in more detail in Fig.2, where the 002 (Fig.2A) and 004 (Fig.2B) peak-shifts are shown as a function of the temperature. The Rietveld refinement method (see ESI) was used for extracting the corresponding c-axis values for each of the analyzed temperature point. As shown in Fig.2C a significant decrease in the c-axis value with the decrease of the temperature was found. By examining the plot in Fig.2C the presence of a non-linear trend could be observed. On the basis of the calculated c-axis values with tabulated thermal expansion parameters, a shift of -0.0040 nm would be expected [22]. Instead by extracting the c-axis shift in the temperature range from 300 to 77K with Rietveld refinement (see ESI for detailed analyses), our results show a much weaker value of c-axis shift, namely -0.0008 nm (see Fig.2C).

The right part of the plot shown in Fig.2C, could be ascribed to the possible presence of phonon-related thermal contributions (Grüneisen law for a periodic system). Note, this trend significantly deviates from the linear one shown in ref.25 at high temperature for HOPG samples containing rotational characteristics with comparable θ_{misfit} values.

Focusing then on the region of the plot comprised from 100K to 77K (Fig.2C), is then possible to notice a clear change in the step of the c-axis shift and a saturation-like effect which implies the presence of a transition in the value of thermal expansion parameter along the c-axis of HOPG. This is shown in Fig.2D where the thermal expansion α-parameter is plotted as a function of the temperature. This observation strongly diverges from the expected linear trend predicted by the tabulated thermal expansion parameter of nanostructured graphite [22]. Note also that no such saturation effect could be detected in the values of c-axis extracted in comparable temperature range from other turbostratic graphite-based samples which are shown in Figs.3 and 4 respectively (see also ESI for details of Rietveld refinement analyses), namely commercial turbostratic graphite (see Figs.3-4A) and thin walled carbon nanotubes (see Figs.3-4B). Additional structural information was then extracted by employing high resolution transmission electron microscopy (HRTEM). These analyses were performed with the electron beam parallel to the c-axis of the exfoliated lamellae. Interestingly, existence of Moiré periodicities was found, as shown in Fig.Supp1-3. By using the equation $a/2D=\sin(\theta/2)$ where a is the basal lattice constant (0.25239 nm) of HOPG and θ is the misfit angle, a misfit angle θ_{misfit} of ~1.5° between the graphitic layers was extracted.

Additional insight was obtained by SQUID magnetometry. As shown in Fig.5, presence of an unusual hysteresis was found in the magnetization vs field measurements performed at 250K in conditions of magnetic field approximately perpendicular to the graphitic layers (see Fig.5A before subtraction and B-C after diamagnetic subtraction using slightly different χ-values; note that due to the sample dimensions, the sample could be accommodated only with a tilted-like orientation within the measurement-capsule). Presence of unusual sharp magnetization pinning components in this system could be further detected. Particularly, note the presence of feature 1 and 2 in Fig.5B. which may imply the possible presence of vortex-like states in the analyzed sample. The variation of the shape of the magnetization signal after subtraction of a gradually increasing diamagnetic background is shown in Fig.5B,C. This subtraction evidences the presence of multiple components in the magnetization signal and therefore of complexities in the magnetic properties of the analyzed sample.

In the attempt to investigate the origin of these signals additional measurements were performed in lamellae extracted from internal intermediate regions (between surface and central regions) of the bulk HOPG sample. Note that analyses of lamellae exfoliated between surface and central regions of the main HOPG sample were not considered in order to avoid effects from surface-contamination or impurities. Indeed, a previous work has shown presence of contamination on surface layers of commercially available HOPG [37].

As shown in Fig.6, these investigations revealed the presence of anomalous unsaturated hysteresis signals with characteristic pinning features which could be ascribed to presence of onion and vortex magnetization states (see Fig.6A-D before diamagnetic subtraction and Fig.6E-F after subtraction) [35]. Particularly, the dynamics of vortex state formation could be described departing from an initial onion state (I) in analogy with the study reported in ref.35. Namely, onion state (phase I), distorted onion states (II) and (III), vortex state (IV), distorted vortex states (V) and (VI) and reversed-onion state (VII) [35]. Particularly, note also the possible presence of pair vortices in the phase IV (see also ref [36] for additional example of onion states and pair vortices).

Additional analyses were then sought by means of ZFC and FC in an attempt to investigate possible presence of multiple magnetic components, see Fig.7. These measurements were performed in two HOPG samples characterized by comparable XRD diffractograms. ZFC and FC measurements performed in conditions of high magnetic field of 5000 Oe (A) and 10000 Oe (B) revealed the presence of a significant transition as the temperature was decreased from 300K to 10K. The magnetization was found to be less negative as the temperature decreased to 10K (see Fig.7). Furthermore, no significant overlap between the FC and ZFC signals was observed, despite the used high fields values (i.e. significant overlap would be expected for a standard ferromagnetic component for applied fields above the $H_{saturation}$ [32-34]). Additional evidence was then sought by plotting the difference of the two magnetization signals (mFC-mZFC) following the method reported by Scheike et al.[7,8]. These analyses revealed a non-zero trend in conditions of large field values of 5000 Oe and 10000 Oe [32-34]. This observation seems to confirm the complex nature of the signal shown in Fig.5. Particularly, saturation would be typically expected to exist for maximum field values in the order 2000-3000 Oe. Literature reports have further shown that ferromagnetic saturation can require up 3000 Oe in certain type of pyrolytic graphite samples [34]. In those conditions, a saturated linear trend in proximity to zero values of mFC-mZFC is expected [34]. Interestingly in Fig.7B and .8B, the measurements performed at 10000 Oe do not show a saturated trend; This observation implies the existence of additional unsaturated magnetic complexities of possible superconductive origin in agreement with the report of Scheike et al. [7,8]. Further work will be still necessary for gaining deeper understanding of the nature of the observed multiple magnetization signals.

4 Conclusion

In conclusion, we have reported a novel temperature dependent XRD and SQUID investigation of HOPG from 300.15 to 77.15 K. Presence of unusual vortex states in the magnetization signals was demonstrated by hysteresis loop measurements performed on the bulk sample and on lamellae extracted by exfoliation methods. mFC-mZFC subtractions also revealed presence of unsaturated magnetization features at high fields of 5000 Oe and 10000 Oe possibly indicating presence of a weak superconductive component. Comparative measurements of c-axis shifts as a function of the temperature were further reported in turbostratic graphite and CNTs samples. Evidence of a possible structural-transition in the c-axis of HOPG in the temperature range between 77 K and 100K was also evidenced by means of Rietveld refinement.

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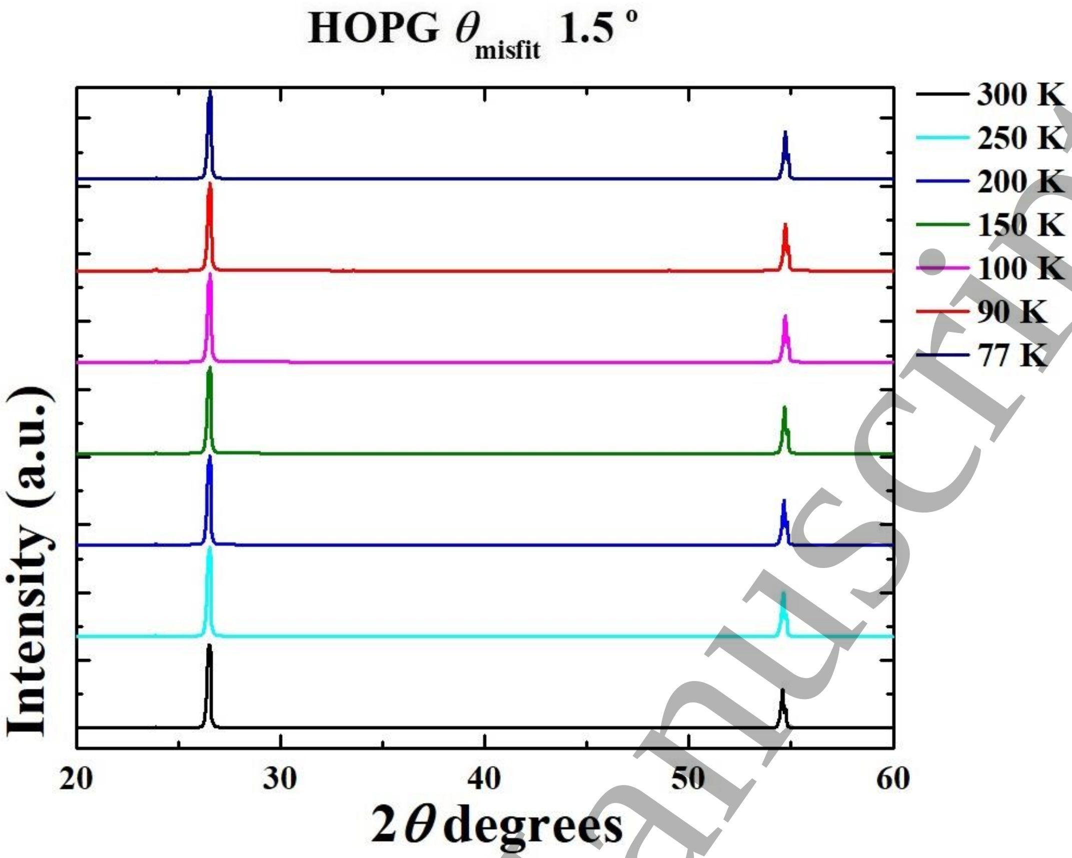


Figure 1. XRD diffractograms showing the structural shifts of the 002 and 004 reflections of HOPG as a function of the temperature from 300.15 to 77.15K.

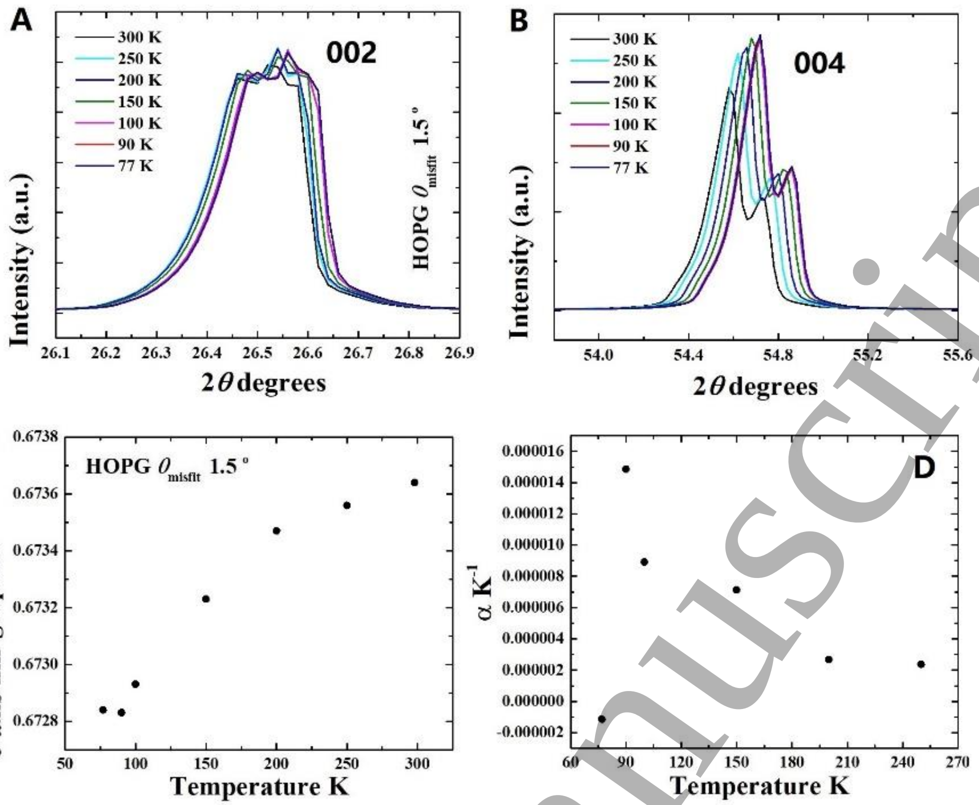


Figure 2. XRD diffractograms showing with a higher detail the structural shifts of the 002 (A) and 004 (B) reflections of HOPG as a function of the temperature from 300.15 to 77.15K. In C, D plots showing the variation of the unit cell c-axis of HOPG as extracted with the Rietveld refinement method (see ESI for detailed analyses) as a function of the temperature from 300.15 to 77.15K. The α-factor was also plotted as function of the temperature in D. Note the presence of a possible transition at the temperature of 100-77K.

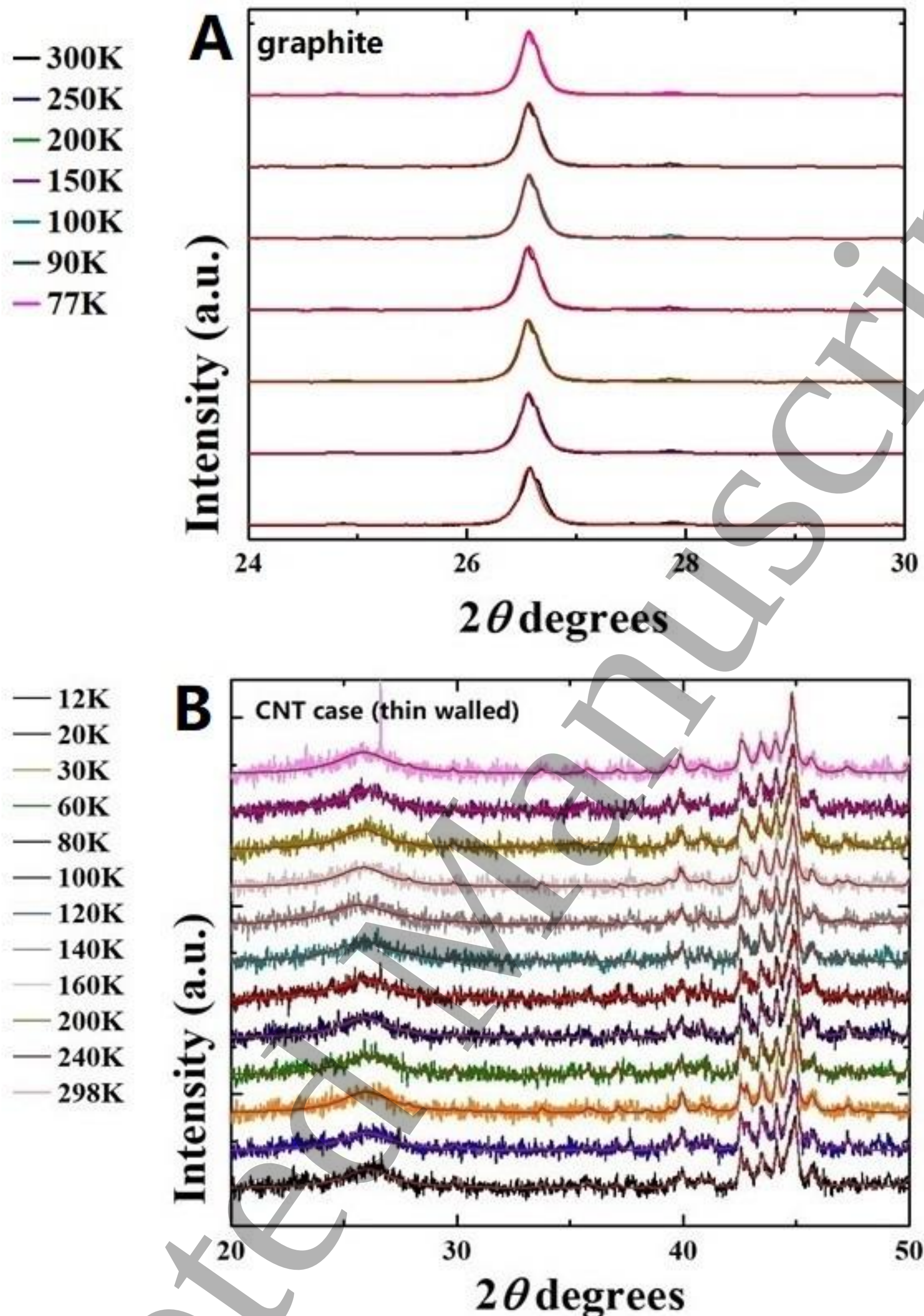


Figure 3: XRD patterns and Rietveld refinement (red line) obtained from a powder of graphite (turbostratic) in A (see experimental section for details of used instrumentation) and a powder of Fe_5C_2/Fe_7C_3 filled CNTs produced by pyrolysis of sulfur/ferrocene mixtures in B. See reference 30-31 for method of CNT-production and peak phase identification.

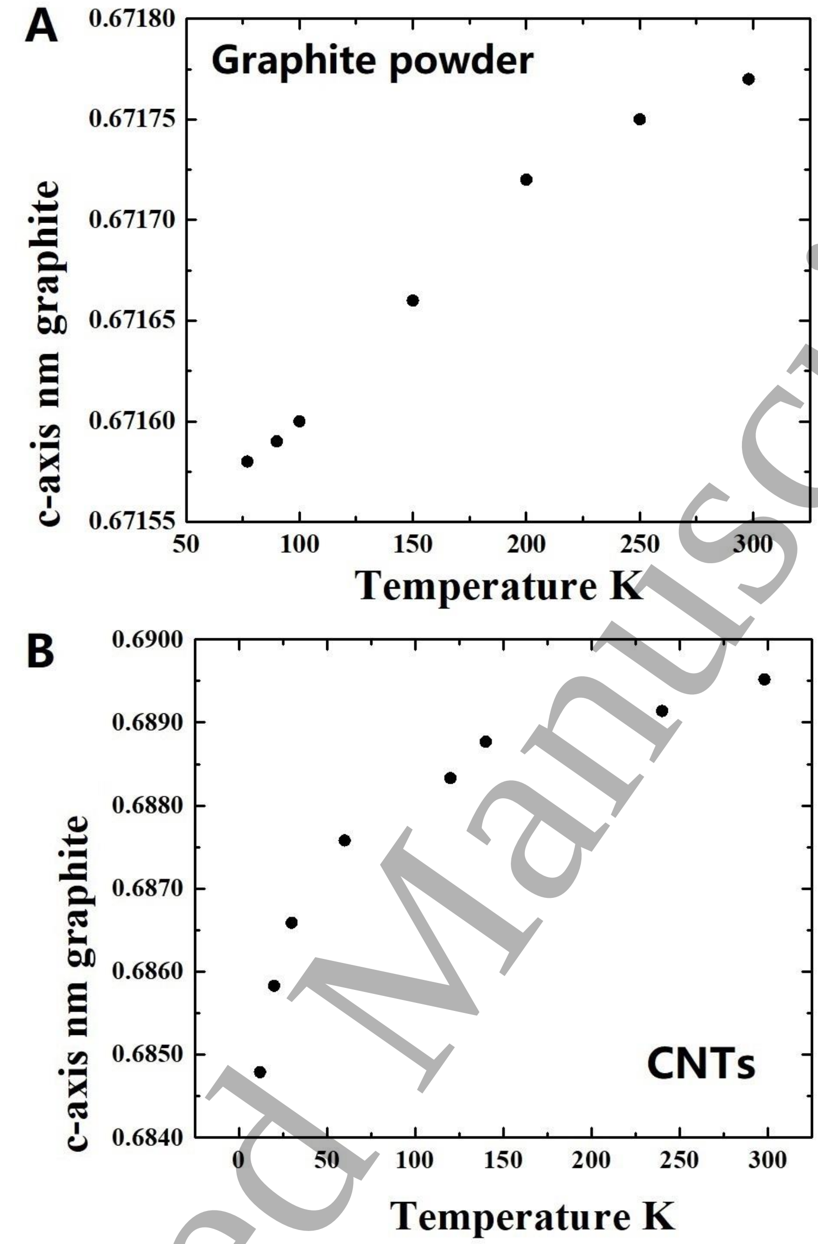


Figure 4. Plots showing the variation of the unit cell c-axis in A) for turbostratic graphite (Fig.3A) and B) for thin walled CNTs (Fig.3B), as extracted with the Rietveld refinement method as a function of the temperature from 300.15 to 77.15 K (graphite case) and from 300 to 12 K (CNT case). See Fig.3 for Rietveld refinement characterization of thin walled CNTs samples.

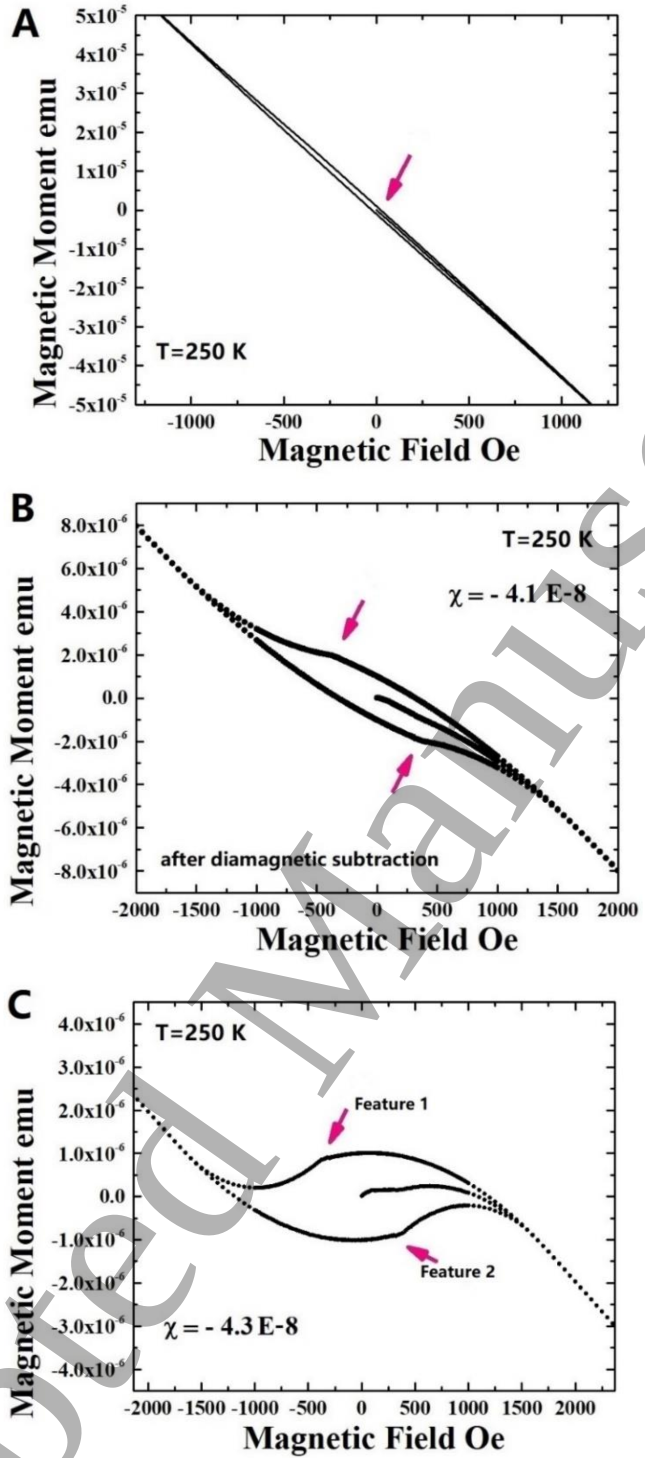


Figure 5. Magnetization vs Field measurements of HOPG at 250K showing the presence of an unusual hysteresis for magnetic field orientation approximately perpendicular (tilted orientation) to the HOPG layers (due to sample dimensions, only a tilted orientation could be achieved in the HOPG sample when encased in the SQUID capsule). In B and C the signal is shown after diamagnetic background subtraction using slightly different slopes obtained by fitting the linear diamagnetic background. Note the presence of two characteristics sharp features, as indicated by the magenta arrows, which can not be explained on the basis of standard ferromagnetic ordering.

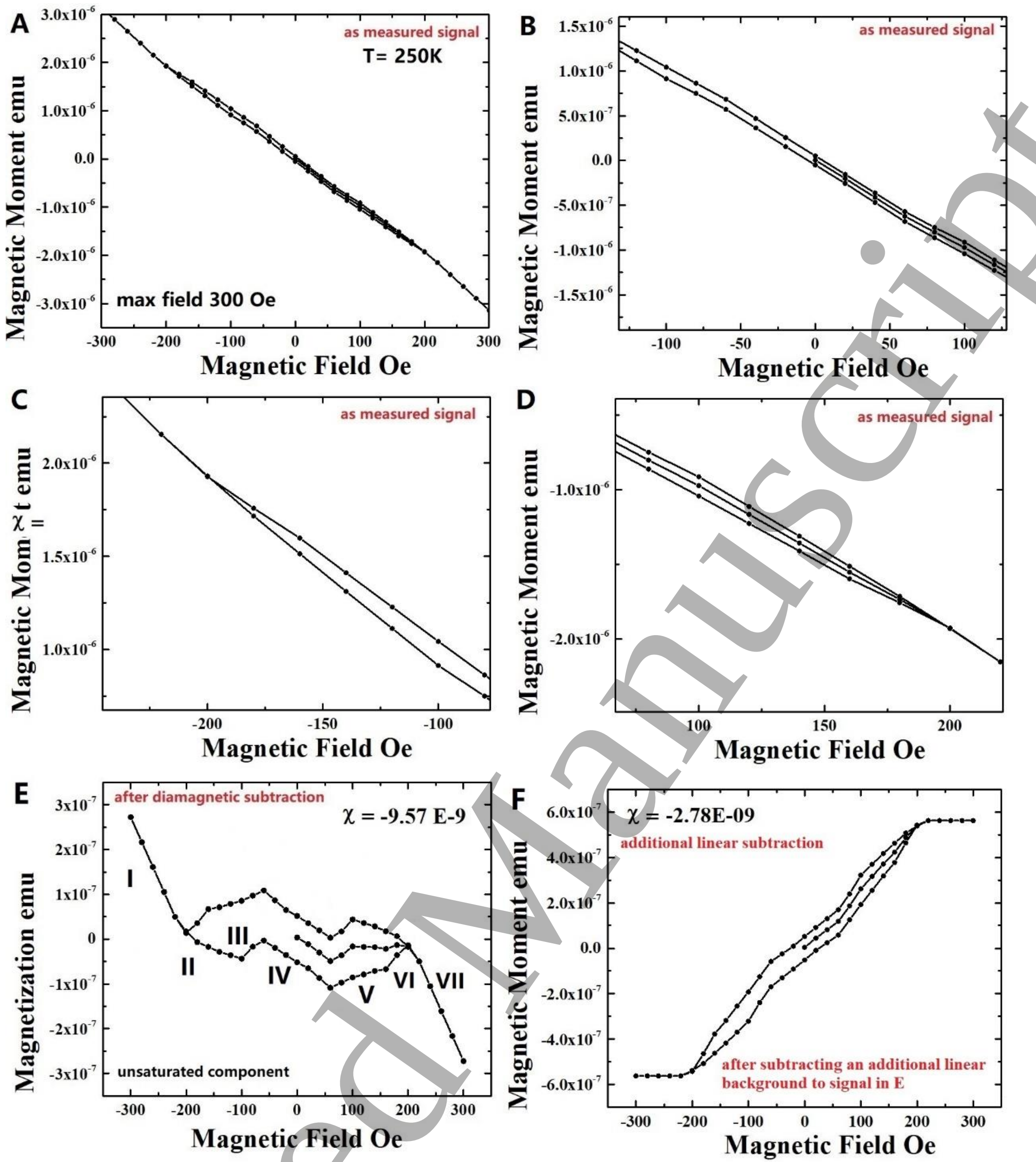


Figure 6. Magnetization vs Field measurements in A-D of an μm-thin lamellae extracted from the internal regions of the bulk HOPG sample by using tape-based exfoliation methods. The measured signal reveals the presence of an unusual hysteresis in conditions of magnetic field orientation perpendicular to the HOPG layers. Anomalous pinning features, could be clearly observed in E after diamagnetic subtraction (in E the signal is obtained by subtracting a linear diamagnetic background). By applying a second diamagnetic subtraction to the signal in E, an unusual magnetization signal can be found. The observed features indicate the presence of a transition from a onion-like magnetization state to a vortex-like one in conditions of max applied field of 300 Oe. The dynamics of vortex state formation can be described as onion state (phase I), distorted onion states (II) and (III), vortex state (IV), distorted vortex states (V) and (VI) and reversed-onion state (VII) [35] as highlighted in E.

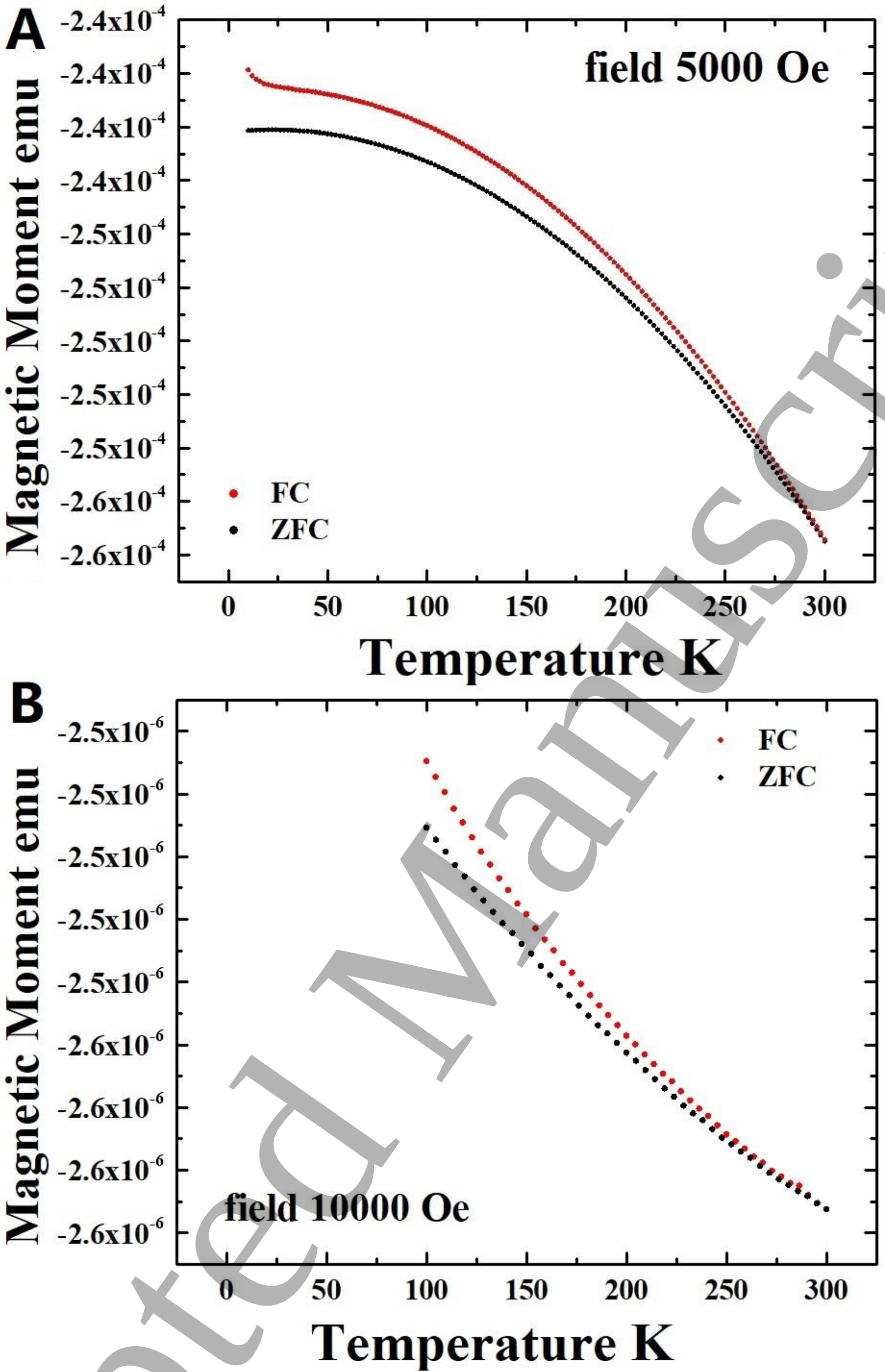
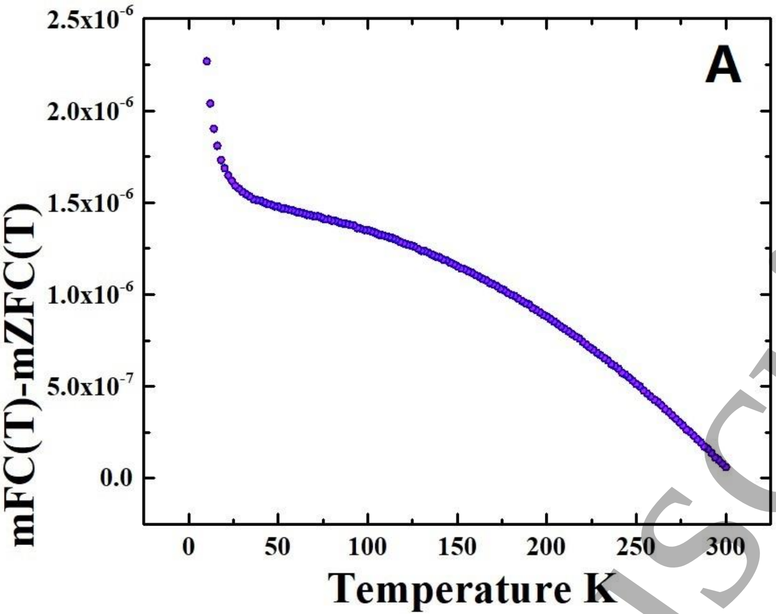


Figure 7. ZFC and FC magnetization plots of two HOPG samples with comparable structural characteristics. Note the presence of a significant transition as temperature approaches to 100 K. The magnetization is found to be less negative as the temperature decreases to 10K. Most importantly note the absence of saturation despite the use of large magnetic field values of 5000 Oe and 10000 Oe.



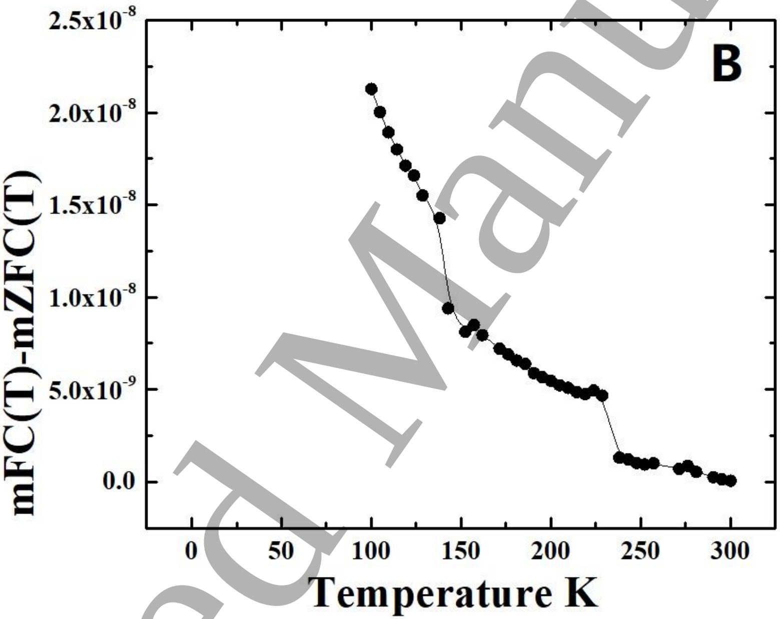


Figure 8. mFC -mZFC plots measured at 5000 Oe (A) and 10000 Oe (B) in two HOPG samples with comparable structural characteristics. Notice the non-zero positive contribution in both samples at large field values of 5000 Oe (A) and 10000 Oe (B) which can not be explained on the basis of the only ferromagnetic-vortex ordering. Previous works [32-34] have shown that a finite positive difference between mFC -mZFC can be possibly attributed as due to pinning of magnetic entities, superconducting vortices or magnetic domains in ferromagnets in conditions of low applied magnetic field values. Such a subtraction would be however expected to sharply decrease to zero in conditions of applied magnetic field larger than saturation-fields for $H > H_{saturation}$. The significant divergence observed below 300K in A and B indicates presence of unusual unsaturated components in agreement with previous observations of Scheike et al.[7,8].