Materials Research Express

Anomalous low-temperature saturation effects and negative thermal expansion in the c-axis of highly oriented pyrolytic graphite at the magic angle

Anomalous low-temperature saturation effects and negative thermal expansion in the c-axis of highly oriented pyrolytic graphite at the magic angle

Ayoub Taallah[a,b+], Gao Shuai[a,b+], Omololu Odunmbaku[a,b], Anna Corrias[c*] and Filippo S. Boi [a,b*].

a. College of Physics, Sichuan University, Chengdu, China 610064.
b. Sino-British Joint Materials Research Institute, Sichuan University, Chengdu, China 610064.
c. School of Physical Sciences, University of Kent, Canterbury, UK CT2 7NZ.

+ These authors contributed equally to this work (equally first authors)

email corresponding author: f.boi@scu.edu.cn, a.corrias@kent.ac.uk

Abstract

We report a novel T-XRD and Rietveld-refinement investigation of pyrolytic-graphite samples with high degree of graphene-layer-orientation and misfit-rotational-angle of ~ 0.8° in the T-range from 12 K to 298 K. An anomalous variation of the graphitic c-axis which involves firstly negative-thermal-expansion (from 12 K to ~50 K), a saturation-effect (from 50 K to ~160 K) and then a positive expansion (from ~180 K to 298 K) is evidenced. The reported trend is significantly different with respect to that expected by considering the standard-thermal-expansion α-parameter where no saturation-effect is present. SQUID-magnetometry revealed further presence of superconducting-like hysteresis which resemble those observed by Scheike et al.

1 Introduction

The recent discoveries of superconductivity in pure highly oriented pyrolytic graphite (HOPG) materials [1-10], water doped graphite [3] and twisted bilayer graphene [11] have attracted a significant attention in the fields of condensed matter physics and materials science. Formation of such granular superconductive features has been attributed to the existence of rotational misfits between the graphene layers in Bernal graphite systems and to possible formation of rhombohedral phases in interfacial contact with the hexagonal one. Superconductive phenomena in HOPG systems have been ascribed to formation of a network of line defects with flat bands (described by the Burgers–Bragg–Read–Shockley dislocation model [6]), which appears at the interfaces between slightly twisted graphite structures when the twist angle is small enough (for bilayer graphene, the defects emerge when $\theta_{twist} \sim 1°$ [6]). Recently, existence of Mott insulation in twisted bilayer graphene has been further proposed [11]. However, the possible existence of second order antiferromagnetic transition and its relation with the critical superconductive temperature remains still not well understood. Interestingly, anomalous high temperature c-axis shifts (i.e. much different than those expected considering the standard thermal expansion parameter of graphite [16]) have been also reported in HOPG samples characterized by misfit between the graphene layers in the order of ~ 0.8º, 0.5º and 1.5º by using high-T X-ray diffraction (XRD) and Rietveld refinement methods [15]. However, no low-temperature investigations of these types of samples have been yet reported. Interestingly, presence of a transition in the thermal expansion dynamics of the c-axis in the graphitic unit-cell of multiwalled carbon nanotubes was demonstrated in an early report from 300 K to 12 K [14]. It is therefore important to investigate further these systems at low temperature and understand the possible presence of structural transitions which may imply unexpected changes of magnetic ordering.

In this work we report a novel T-XRD investigation of the c-axis shifts in HOPG samples with rotational misfit in proximity of the first magic angle in the temperature range from 12 K to 298K. We focus our attention on samples with characteristic average misfit angle of approximately 0.8° (see ref. [15] for high resolution transmission electron microscopy, HRTEM analyses) which were identified by preliminary XRD with HOPG c-axis parallel to the substrate. The Rietveld refinement method was used to extract the variation of the c-axis with the temperature. Interestingly, the 002 diffraction peak shows a negative expansion effect at low temperature followed by an anomalous saturation like effect and then by a positive expansion. The observed structural transitions can not be explained on the basis of the standard thermal expansion parameter of graphite [16] and clearly evidence the presence of unexpected low-temperature characteristics in the thermal expansion properties of HOPG. As extracted by Rietveld refinements, the c-axis shift from 12 K to 298 K results in the value of 0.001365 nm which is much smaller than that of 0.005154 nm expected considering the tabulated thermal expansion parameter of graphite in 1/K ($26.7*10^{-6}$ 1/K). In addition, SQUID magnetometry measurements revealed presence of superconducting like hysteresis which resemble those observed by Scheike et al.[2,3].

2 Experimental

HOPG samples with dimensions of 5 x 5 x 1 mm, with mosaic angle values of 0.8°, ± 0.2° (sample 1 and 2) and 1.5°, ± 0.2° (sample 3) were purchased from XFNANO, INC China. Another HOPG sample (sample 4) was purchased from CFC CARBON with dimensions 3.5 x 3.5 x 1 mm and mosaic angle 0.8°, ± 0.2°. Note that the given values of mosaic angles are not an indicator of the rotational misfit in the graphene layers.

Preliminary XRD measurements were performed at room temperature by employing a PANalytical Empyrean powder X-ray diffractometer (Cu K-α1,2) with c-axis parallel to the substrate on all the 4 HOPG samples, to identify the variation in the intensity of 002/100 reflections. T-XRD measurements were then performed on HOPG with I002/I100 ratio of ~ 0.4, with c-axis orientation perpendicular to the substrate on another 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, from 12 K to 298 K (12 K, 20 K, 30 K, 40 K, 50 K, 60 K, 70 K, 80 K , 90 K, 100 K, 120 K, 140 K, 160 K, 180 K, 200 K, 220 K, 240 K, 260 K, 280 K and 298 K). SQUID measurements were performed at room temperature on the pristine as purchased samples with a Quantum Design system.

3 Results and Discussion

The structural characteristics of samples 1-4 were firstly investigated by means of XRD measurements performed with HOPG c-axis parallel to the substrate, as shown in Fig.1. This process allowed to identify the samples with higher level of graphene layer alignment. Significant differences in the structural characteristics of the HOPG structure of the 4 samples were found. As shown in Fig.1A-B, the first two types (samples 1 and 2) of HOPG revealed a very intense 100 reflection, which could be ascribed to the presence of a significant alignment between the graphite layers. Presence of weak 002, 101 and 004 reflections could be also detected. Differently, a systematic decrease in the relative intensity of the 100 reflection and an increase in that of the 002 were found in sample 3 and 4; such a structural variation was further evidenced by the 002/100 intensity ratios: ~ 0.4 for samples 1 and 2, 0.77 for sample 3 and 2.63 for sample 4. T-XRD measurements were then performed on the HOPG with 002/100 intensity ratio ~ 0.4 from 12 K to 298 K, as shown in the plots of Figs2-3. An unusual change in the c-axis values was found with the increase of the temperature. As evidenced in Fig.2, the position of the 002 diffraction peak was found to shift towards larger values of 2θ degrees in the T-range from 12 K to ~50 K. An anomalous saturation like effect was then observed from 50 K to ~ 160 K. Furthermore, expansion was found from ~180K to 298K with a shift of the 002 diffraction peak towards lower values of 2θ degrees. These structural transitions can not be explained on the basis of the standard thermal expansion parameter of graphite [16,17] where no saturation effect is present. As evidenced by Rietveld refinement analyses, see ESI Fig.Supp.1-39 and tables 1 and

2, the shifts in the position of the 002 reflection can be understood in terms of 1) a c-axis contraction from 12K to ~50K (negative thermal expansion [17]), 2) an anomalous saturation effect in the T-range from ~50 K to 160K, and 3) an expansion of the c-axis of HOPG in the T-range from ~180K to 298K, as shown in the plot of Fig.4A, which imply existence of a low temperature structural transition at approximately 160K (see table 1 in ESI). The extracted thermal expansion α-factor values can be found in Fig.4B. The investigation of the magnetic properties by SQUID measurements revealed a substantial difference between samples 1,2 and sample 3-4, as evidenced in Fig.5 (see also ESI Fig. Supp. 42-44 for additional magnetization data), A superconducting-like hysteresis (which resembles that reported by Scheike et al. [1-3]) could be detected in samples 1-3 (Fig.5A,B,D). Instead only diamagnetic signal could be detected in sample 4 (Fig.5C). Note that in this latter case, measurements were performed by changing the maximum field values from 300 Oe (Fig.5C) to 10000 Oe (ESI), without significant differences in the outcoming signal.

4 Conclusion

In conclusion, in this work we have reported a novel low T-XRD and Rietveld refinement investigation of the c-axis shifts in HOPG at the magic angle from 12 K to 298K. The c-axis parameter was found to contract from 12 K to ~50 K, anomalously saturate from 50 K to ~160K and expand from ~180K to 298K. SQUID magnetometry was also employed at room temperature and revealed presence of superconducting like hystereses in samples with 002/100 (intensity) ratios of ~ 0.4 and 0.77. Only diamagnetism was instead detected in samples with 002/100 I-ratio of ~ 2.63.

Acknowledgments

We acknowledge NSFC Grant Nº 11750110413 and Sichuan Province Grant Nº 2019YFH0080.

References

[1] 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.

[2] 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.

[3] Scheike T., Böhlmann W., Esquinazi P., Barzola-Quiquia J., Ballestar A., and Setzer A. Can Doping Graphite Trigger Room Temperature Superconductivity? Evidence for Granular High-Temperature Superconductivity in Water-Treated Graphite Powder. Adv. Mater. 2012; 24: 5826.

[4] Zoraghi M., Barzola-Quiquia J., Stiller M., Esquinazi P. D., Estrela-Lopis I. Influence of interfaces on the transport properties of graphite revealed by nanometer thickness reduction. Carbon 2018; 139: 1074-1084.

[5] 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

[6] 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.

[7] Volovik G. E. Graphite, Graphene, and the Flat Band Superconductivity. JETP Letters 2018; 107: 516-517

[8] Saad M., Gilmutdinov I. F., Kiiamov A. G., Tayurskii D. A., Nikitin S. I., Yusupov R. V. Observation of Persistent Currents in Finely Dispersed Pyrolytic Graphite. Jetp Lett. 2018; 107: 37-41.

[9] Ballestar A., Barzola-Quiquia J., Scheike T. and Esquinazi P. Josephson-coupled superconducting regions embedded at the interfaces of highly oriented pyrolytic graphite. New Journal of Physics 2013 ;15: 023024.

[10] Brihuega I., Mallet P., González-Herrero H., de Laissardière G. T., Ugeda M. M., Magaud L., Gómez-Rodríguez J. M., Ynduráin F., and Veuillen J.-Y. Unraveling the Intrinsic and Robust Nature of van Hove Singularities in Twisted Bilayer Graphene by Scanning Tunneling Microscopy and Theoretical Analysis. Phys. Rev. Lett. 2012; 109: 196802.

[11] 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.

[12] Flores M., Cisternas E., Correa J., and Vargas P. Moiré patterns on STM images of graphite induced by rotations of surface and subsurface layers. Chem. Phys. 2013; 423: 49.

[13] Warner J. H., Römmeli M. H., Gemming T., Büchner B., and Briggs G. A. D. Direct Imaging of Rotational Stacking Faults in Few Layer Graphene. Nano Lett. 2009; 9: 102.

[14] Boi F. S., Zhang X. and Corrias A. Temperature driven structural-memory-effects in carbon nanotubes filled with Fe_3C nano crystals. Materials Research Express 2018; 5: 025010.

[15] 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.

[16] Harb M., von Korff Schmising C., Enquist H., Jurgilaitis A., Maximov I., Shvets P. V., Obraztsov A. N., Khakhulin D., Wulff M., and Larsson J. The c-axis thermal conductivity of graphite film of nanometer

thickness measured by time resolved X-ray diffraction. Appl. Phys. Lett. 2012; 101: 233108.
[17] Kellett E. A. and Richards B. P. The Thermal Expansion Of Graphite Within The Layer Planes. Journal Of Nuclear Materials 1964; 12: 184-192.

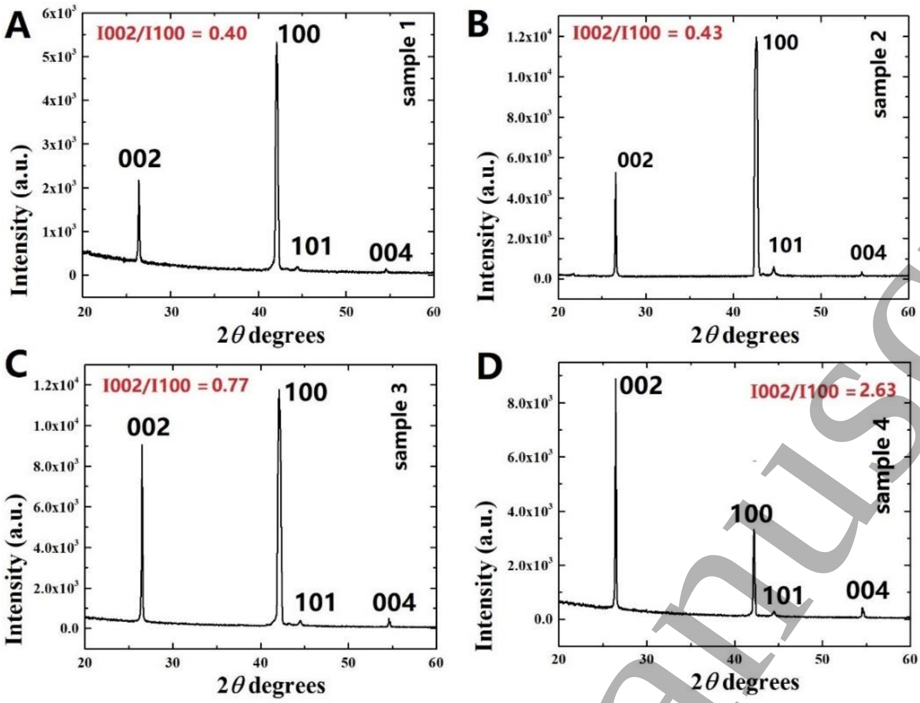

Figure 1: Room temperature XRD diffractograms measured with HOPG c-axis parallel to the substrate for sample 1(A), sample 2(B), sample 3(C) and sample 4(D). See supplementary materials for rocking curve analyses revealing presence of dislocations in samples 1-3 (ESI Fig.Supp.45-47).

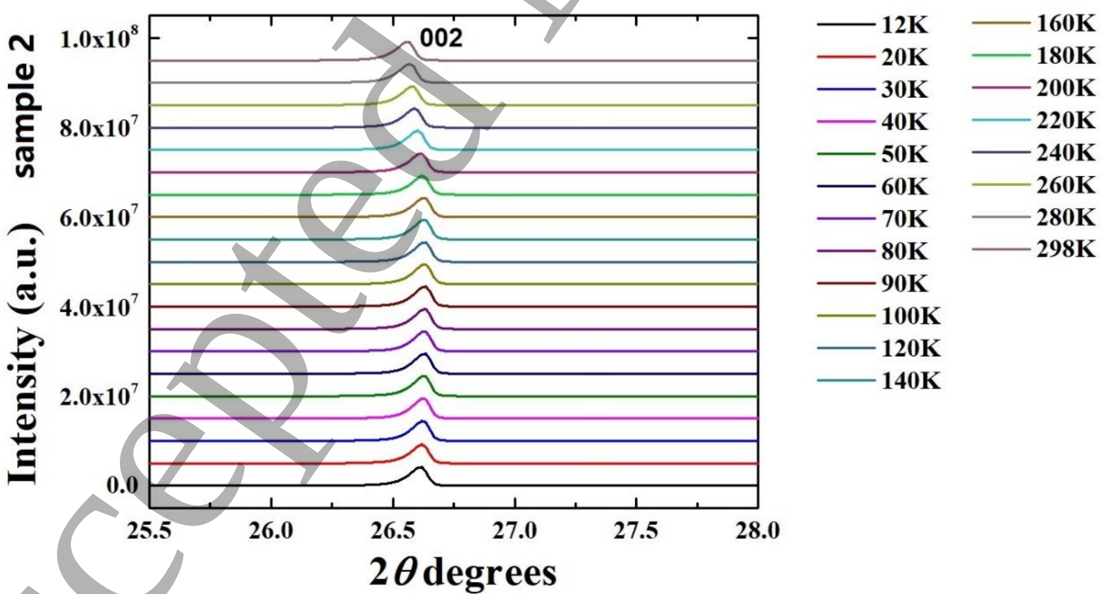

Figure 2: T-XRD diffractograms of HOPG sample 2 (~ 0.8 ° θ_{misfit} misfit-angle, see ref.15 for HRTEM and Moiré pattern analyses of this type of sample) measured with c-axis perpendicular to the substrate, showing the structural shifts of the 002 reflection as a function of the temperature from 12 K to 298 K.

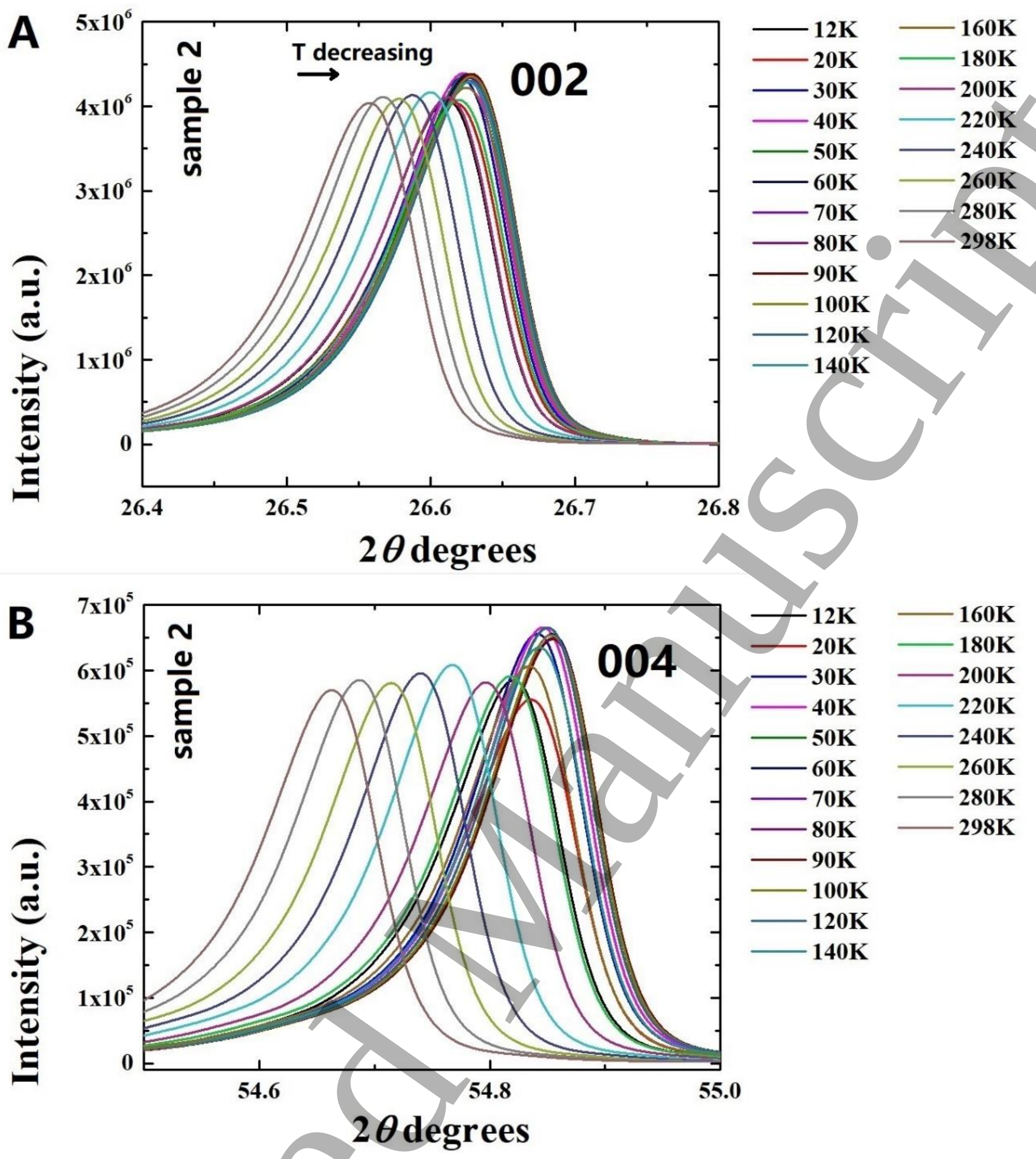

Figure 3: XRD diffractograms (c-axis perpendicular to substrate) showing with a higher detail the structural shifts of the 002 (A) and 004 (B) reflections of HOPG (~ 0.8 ° θ_{misfit} average misfit-angle) as a function of the temperature from 12 K to 298 K. Note that the possible variation in the relative intensity of the measured 004 reflection in comparison to the high temperature XRD data reported in ref [15] (performed with Rigaku Smart-lab powder X-ray diffractometer) can be ascribed to differences in sample preparation. In ref [15] the outer surface lamellae of the HOPG sample were removed by using scotch tape methods (in order to remove surface misoriented layers), while in the study reported here no removal of surface layers was performed.

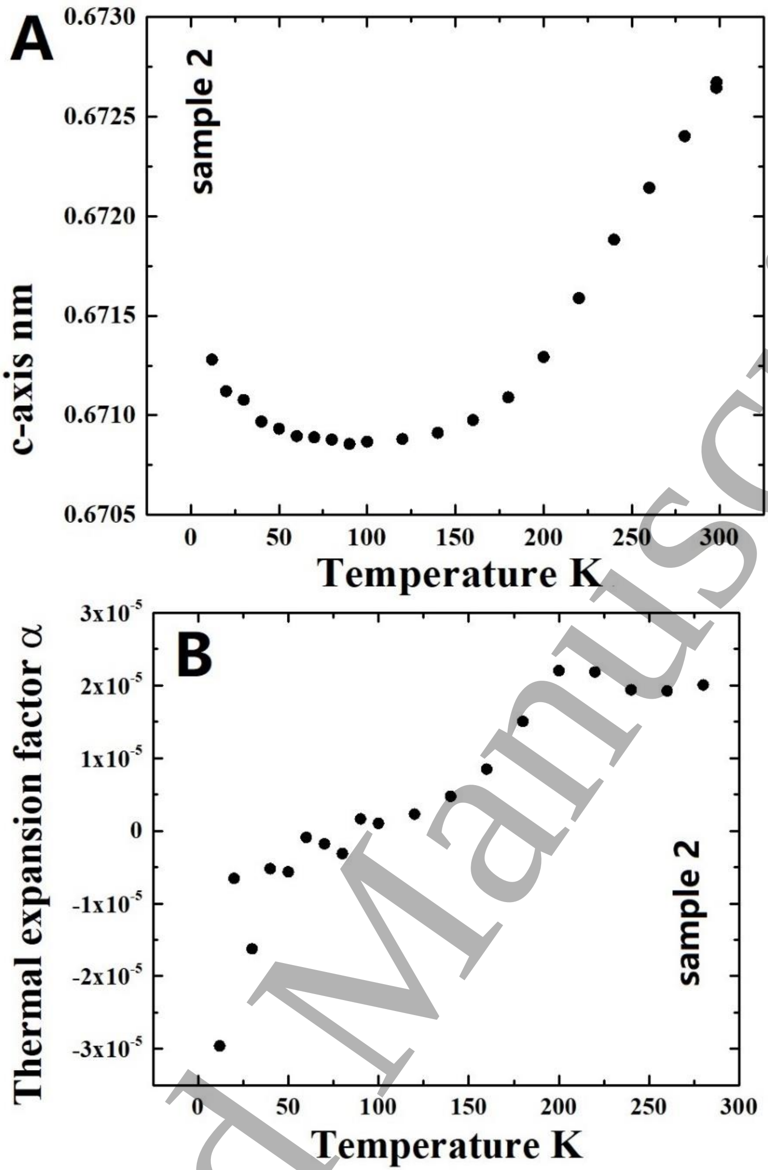

Figure 4: Plots showing in A the variation of the unit cell c-axis with temperature from 12K to 298K for HOPG samples with misfit-angle θ_{misfit} of ~ 0.8 º (as extracted from the Rietveld refinement analyses shown in ESI) and in B the calculated thermal expansion parameter as a function of the temperature. The thermal expansion parameter was obtained by applying the obtained c-axis values into the equation $1/L*(\Delta L/\ \Delta T)$.

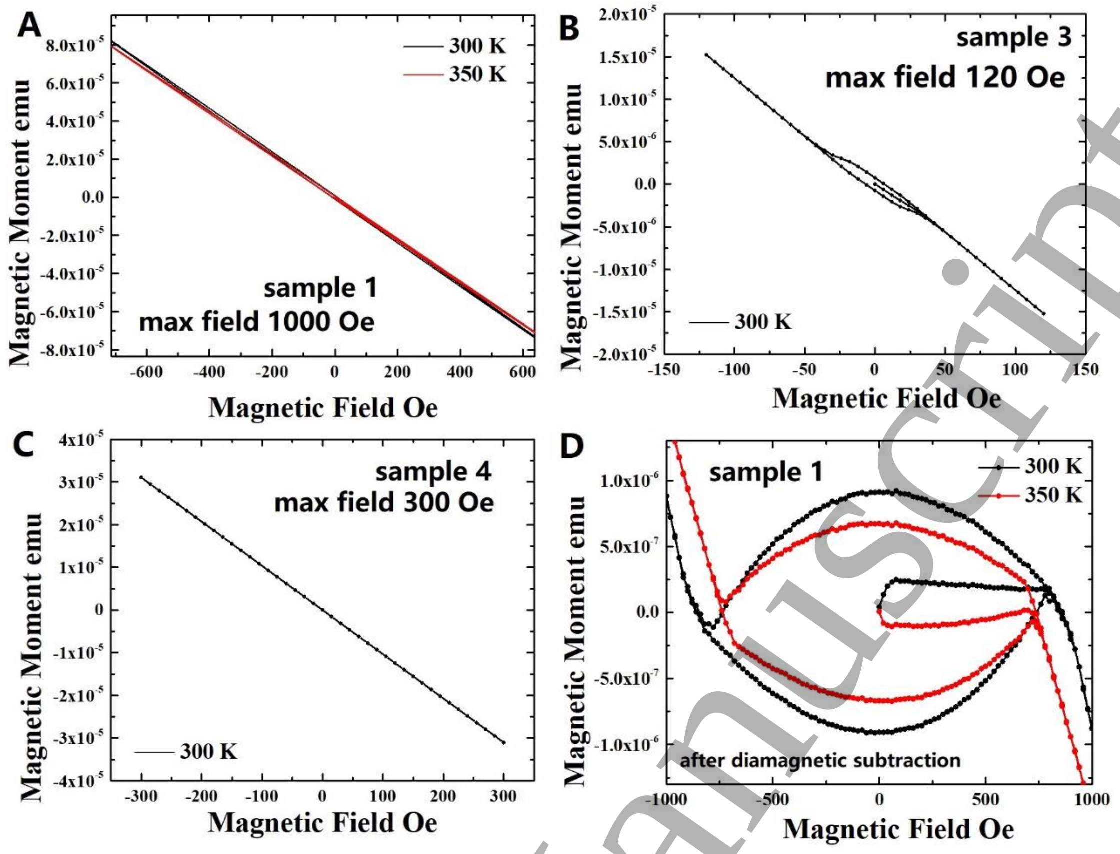

Figure 5: SQUID magnetometry measurements revealing significantly different magnetic signals in samples 1-4. A superconductive-like hysteresis which resembles that reported by Scheike et al. [2,3] was found in samples 1,2 and 3 (with weaker intensity). Instead only diamagnetic features could be detected in sample 4 as shown in Fig.5C and in ESI. The signals obtained after diamagnetic subtraction are shown in Fig.5D and in ESI Fig. Supp. 42-44 (for samples 3 and 4). Note that SQUID measurements were performed with field perpendicular to HOPG layers. In D a linear diamagnetic background was subtracted based on the method used in ref. [1-3]. The linear diamagnetic backgrounds from A were subtracted in D using $\chi = -1.15209*10^{-7}$emu/Oe at 300K and $\chi = -1.111209*10^{-7}$emu/Oe at 350 K.