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

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

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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 \( \theta_{\text{tw}} \sim 1° \) [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 [12]) have been also reported in HOPG samples characterized by misfit between the graphene layers in the order of ~0.8°, 0.5° and 1.5° by using high-T x-ray diffraction (XRD) and Rietveld refinement methods [13]. 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 298 K. We focus our attention
on samples with characteristic average misfit angle of approximately 0.8° (see [13] 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 [12] 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 [12]. 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 × 5 × 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 × 3.5 × 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 [16, 17].

Preliminary XRD measurements were performed at room temperature by employing a PANalytical Empyrean powder x-ray diffractometer (Cu K-α 1, 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 I002/1100 ratio of ~0.4, with c-axis orientation perpendicular to the substrate on another PANalytical Empyrean powder x-ray diffractometer (Cu K-α 1, λ = 0.15406 nm), equipped with a primary Johansson monochromator, an Oxford Cryosystems Phenix cryostat operating under vacuum below 10⁻⁷ Pa, and a Xcelerator 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.

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 figure Supp.45–47).
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 figure 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 figures 1(A)–(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 figures 2–3. An unusual change in the c-axis values was found with the increase of the temperature. As evidenced in figure 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 ~180 K to 298 K 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 [12, 15] where no saturation effect is present. As evidenced by Rietveld refinement analyses, see ESI figure Supp.1–39 and tables 1 and 2 is available online at stacks.iop.org/MRX/7/015614/mmedia, the shifts in the position of the 002 reflection can be understood in terms of (1) a c-axis contraction from 12 K to ~50 K (negative thermal expansion [15]), (2) an anomalous saturation effect in the T-range from ~50 K to 160 K, and (3) an expansion of the c-axis of HOPG in the T-range from ~180 K to 298 K, as shown in the plot of figure 4(A), which imply existence of a low temperature structural transition at approximately 160 K (see table 1 in ESI). The extracted thermal expansion α-factor values can be found in figure 4(B).

The investigation of the magnetic properties by SQUID measurements revealed a substantial difference between samples 1,2 and sample 3–4, as evidenced in figure 5 (see also ESI figure Supp. 42–44 for additional

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**Figure 4.** Plots showing in A the variation of the unit cell c-axis with temperature from 12 K to 298 K for HOPG samples with misfit-angle θ_mis of ~0.8° (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/k (ΔL/ΔT).
magnetization data), a superconducting-like hysteresis (which resembles that reported by Scheike et al [1–3]) could be detected in samples 1–3 (figures 5(A), (B), (D)). Instead only diamagnetic features could be detected in sample 4 (figure 5(C)). Note that in this latter case, measurements were performed by changing the maximum field values from 300 Oe (figure 5(C)) to 10000 Oe (ESI), without significant differences in the outcome 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 298 K. The c-axis parameter was found to contract from 12 K to ~50 K, anomalously saturate from 50 K to ~160 K and expand from ~180 K to 298 K. 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.

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