

Multilayer graphene nanoclusters: structure, electronic and magnetic properties

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Abstract. The data on atomic and electronic structure and some magnetic properties of graphite domains in activated carbon fibers (ACFs) are presented. It has been established that they have nanometer sizes in all three dimensions, and consist of three turbostratic packed nanographenes on average. In ACFs the graphite domains form disordered system and are separated from each other by the nanopores and/or sp^3 -amorphous carbon phase. The data of magnetic methods point out that the density of electronic states at the Fermi level of nanographites exceeds the value of respective parameter for macroscopic ordered graphite by more than an order.

1. Introduction

The effect of the surface and edge atoms on electronic structure increases with decreasing sizes of particles and depends on the geometry of the positions of the peripheral atoms [1]. According to calculations [2], the specific π -electronic band forms near the zigzag edges of honeycomb carbon networks, which can significantly affect their electronic structure near the Fermi level in nanoscale samples. This paper presents the results of investigation of multilayer graphene nanoclusters (nanographites) by various physical methods with an emphasis on their atomic picture and features of electronic structure near the Fermi level.

2. Experiment

The graphite particles forming a disordered network in polyacrylonitril-based activated carbon fibers (ACFs) with specific surface area $\approx 2000 \text{ m}^2/\text{g}$ have been chosen as the object of this study.

The average sizes and values of structure parameters of graphite domains in ACFs have been determined from X-ray diffraction profiles, obtained with Bruker D8 diffractometer (Germany) in Bragg-Brentano geometry with source $\text{CuK}\alpha$ ($\lambda_{\text{xr}} = 0.15417 \text{ nm}$). Small angle X-ray scattering profiles of ACFs have been acquired with KRM-1 diffractometer (Russia) with source $\text{FeK}\alpha$ ($\lambda_{\text{xr}} = 0.19373 \text{ nm}$).

The Raman spectrum of ACFs has been recorded with confocal Raman spectrometer WITec Alpha 500 (Germany) with wavelength $\lambda_{\text{R}} = 531.8 \text{ nm}$.

The data on magnetization and static magnetic susceptibility have been obtained using Quantum Design MPMS-5S SQUID magnetometer (USA). Dependence of the magnetization on magnetic field has been studied at 3 and 300 K; dependence of static magnetic susceptibility on temperature has been measured in the range from 2 to 300 K at magnetic field of 1 T.

The electron spin resonance (ESR) spectra have been acquired with Bruker EMX-6/1 X-band spectrometer (Germany). The integral intensities and g -factor values of the resonance signals have been determined using the intensity and value $g = 2.002293 \pm 0.000003$ of the conduction electron spin resonance (CESR) signal of lithium particles in reference sample Li:LiF, respectively, which do not change in range from 2 to 400 K.

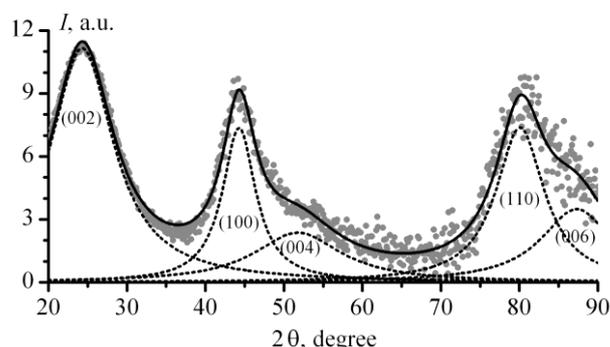


Fig. 1. The X-ray diffraction profile of ACFs and its decomposition into five Lorentzians corresponding to (002), (100), (004), (110) and (006) reflections.

3. Results and discussions

The X-ray diffraction profile of ACFs contains a number of broad components, whose positions do not depend on the direction of X-ray beam with respect to fiber orientation (Fig. 1). It can be represented as sum of five Lorentzians, corresponding to (002), (100), (004), (110) and (006) reflections (Fig. 1). Using standard methods of calculation the average graphite domain size in the direction perpendicular to carbon layers $L_c \approx 0.8 \text{ nm}$ and the average interlayer spacing $d_c \approx 0.366 \text{ nm}$ were estimated from the width and position of (002) reflection. In the same way, the average graphite domain size in basal plane $L_a \approx 3 \text{ nm}$ was calculated from the width and position of (100) reflection.

For the initial ACFs and for the samples whose pores are filled with water and palladium the dependences of the intensity of X-ray small-angle scattering I on s ($s = s(2\theta) = (2\sin\theta)/\lambda_{\text{xr}}$, where 2θ is scattering angle) are qualitatively similar. In particular, all dependences in logarithmic scale exhibit slightly visible maximum near $s \approx 0.38 \text{ nm}^{-1}$. Mass distribution function of inhomogeneities by size $D_m(r)$ calculated for these dependences by standard techniques are bell-shaped with close peak positions. Intensity of maximum in $D_m(r)$ at $r \approx 1.2 \text{ nm}$ among ACFs with pores occupied by atmosphere, water and palladium, correlates with the contrast between nanographite and substance contained in the pores of the sample. This correlation allows to attribute the inhomogeneities of specified size to the micropores in the fiber.

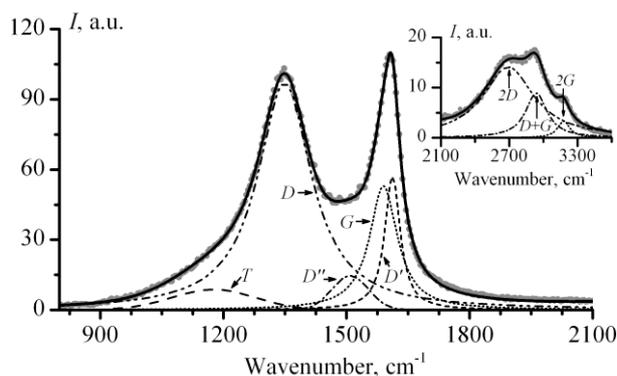


Fig. 2. The Raman spectrum of ACFs and its decomposition into three Lorentzians (G , D and D') and two Gaussians (T and D''). In the inset the overtone spectrum and its decomposition into three Lorentzians ($2D$, $D+G$ and $2G$) are presented.

The Raman spectrum of ACFs (Fig. 2) is qualitatively close to corresponding spectra of defective and nanocrystalline graphites [3]. In the range of 800 to 2100 cm^{-1} (main spectra) it can be approximated by the sum of three Lorentzians (G -, D - and D' - bands) and two Gaussians (T - and D'' - bands) (Fig. 2). Overtone spectrum observed in the range of 2100 to 3600 cm^{-1} can be represented by the sum of three Lorentzians $2D$, ($D+G$) and $2G$ (the inset in Fig. 2). The results of semiquantitative analysis of Raman spectroscopy data of ACFs are in good agreement with results of X-ray diffraction profile analysis and in consideration of data on small angle X-ray scattering they provide evidence that fibers contain disordered system of turbostratic nanographites separated from each other by nanopores and/or sp^3 -amorphous carbon phase.

The temperature dependence of specific magnetic susceptibility for ACFs (Fig. 3) is well approximated by the sum of paramagnetic and diamagnetic components with Curie constant $C = 1.3 \times 10^{-5} \text{ cm}^3 \cdot \text{K/g}$, Curie temperature $\Theta = -0.9 \text{ K}$ and diamagnetic contribution to susceptibility $\chi_0 = -6 \times 10^{-6} \text{ cm}^3/\text{g}$. The value of Curie constant corresponds to one localized spin per ≈ 2400 carbon atoms.

Regardless of vacuum degree the ESR spectrum of ACFs consists of two signals, which have different widths but the same value of the asymmetry parameter A/B ($= 1.15$) and the g -factor ($= 2.0027 \pm 0.0001$) (the inset in Fig. 3). With decreasing temperature the integral intensity

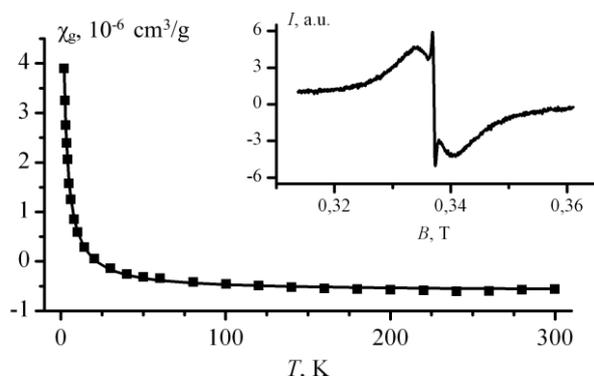


Fig. 3. The temperature dependence of the specific magnetic susceptibility for ACFs. Dots correspond to the experimental values, equation of the solid line: $\chi_g = 1.3 \times 10^{-5}/(T+0.9) - 0.6 \times 10^{-6}$. In the inset, the ESR spectrum of the same ACFs at 120 K is shown.

of narrow spectrum component varies approximately according to the Curie law (Fig. 4), while that of broad component is invariable (the inset in Fig. 4). On this basis the broad signal can be attributed to spin resonance on conduction electrons and the narrow one can be regarded as resonance on the localized magnetic moments.

The intensity of CCSR signal is proportional to the density of states $D(E_F)$ of current carriers at the Fermi level E_F [4]. Therefore, using the concentration of localized spins in ACFs the value of $D(E_F)$ in nanographites can be easily estimated by comparing the intensities of the resonance signals of different nature. Such calculations show that the value of $D(E_F)$ for the studied ACFs exceeds by more than an order the value of respective parameter for macroscopic ordered graphite. This estimation is in good agreement with the calculations of the electronic structure of nanographenes and nanographites with zigzag edges [2].

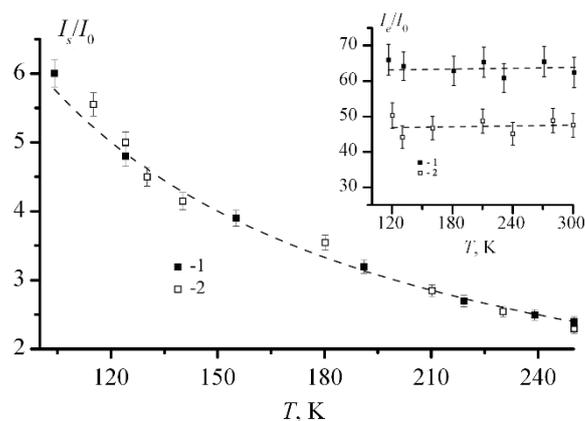


Fig. 4. The temperature dependences of integral intensity of narrow and broad (in the inset) components of the ESR spectrum for ACFs. 1 and 2 – the data for evacuated and non-evacuated samples, respectively. I_0 – the intensity of the CCSR signal of reference sample $\text{Li}:\text{LiF}$. Lines are presented as guides for the eye only.

4. Conclusions

The data set of structural research methods for chosen ACFs indicates the presence of disordered system of turbostratic nanographites separated from each other by nanoscale pores and/or sp^3 -carbon amorphous phase. Due to turbostratic packing of nanographenes, the average distance between them ($\approx 0.366 \text{ nm}$) is significantly larger than the distance between the carbon layers in the macroscopic ordered graphite. According to data of magnetic research methods, the density of states at the Fermi level of nanographites significantly exceeds the corresponding values for the macroscopic graphite.

References

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