The effect of adsorbed molecules on electronic structure and magnetic properties of nanographites

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Abstract. The results of investigation of changes in electronic structure and magnetic properties of multilayer graphene nanoclusters (nanographites) during their interaction with adsorbed chlorine molecules are presented. The decrease in both the density of states of current carriers \(D(E_F)\) at the Fermi level \(E_F\) and the concentration of localized spins is revealed. The former can be explained by the spin splitting of edge \(\pi\)-electron states in nanographites induced by the enhancement of electron-electron interactions due to increase of \(D(E_F)\) at partial transfer of the electron density from nanographites to chlorine adatoms. The latter indicates that at the interaction of nanographites with adatoms the electron spins of \(3p\)-orbitals of chlorine and unpaired \(\pi\)-orbitals of edge carbon atoms are coupled, i.e. the edge covalent compound of nanographite with chlorine forms. The changes in the spin-relaxation characteristics of the current carriers during chlorination of samples are also consistent with the above model of interaction between nanographites and adatoms.

1. Introduction

According to both theoretical and experimental studies near the zigzag edges of honeycomb carbon structures the specific edge \(\pi\)-electronic band forms, whose energy of electronic state density peak is only \(\approx 25 \pm 5\) meV less than the Fermi energy [1, 2]. The peripheral \(\pi\)-electronic band significantly modifies the electronic structure and magnetic properties of nanoscale carbon structures [1, 2]. The study of this band change at the interaction of nanocarbons with different adatoms is of great interest from both fundamental and practical points of view. This paper presents the results of investigation of changes in electronic structure and magnetic properties of multilayer graphene nanoclusters (nanographites) at their interaction with the chlorine molecules.

2. Experiment

The nanoscale turbostratic graphite particles, which are building blocks of activated carbon fibers (ACFs) [1, 2], have been chosen as multilayer graphene nanoclusters (nanographites) for investigations. The changes in their electronic structure and magnetic properties at interaction with acceptor molecules have been studied by methods of electron spin resonance (ESR) and magnetic susceptibility measurements.

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 was studied at 3 and 300 K; dependence of static magnetic susceptibility on temperature was measured in the range from 2 to 300 K at magnetic field of 1 T.

The 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 were 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\(\cdot\)LiF, respectively.

In the ESR experiments, samples have been placed in one-zone quartz reactor inserted into the resonance cavity of the spectrometer, which was evacuated before the measurements to \(\approx 10^{-6}\) Torr. The gaseous chlorine passed through magnesium perchlorate to remove water molecules before penetrating into reactor with the sample. The gaseous chlorine has been introduced into the reactor by several approximately equal portions. The ESR spectrum of the sample has been measured \(\approx 5\) min after introducing each portion of chlorine into reactor.

3. Results and discussions

Regardless of vacuum degree the ESR spectrum of ACFs consists of two signals (Fig. 1 a), which have different widths but the same value of g-factor \((= 2.0027 \pm 0.0001)\). With decreasing temperature, the integral intensity of broad-spectrum component is invariable, while that of narrow component varies approximately according to the Curie law. On this basis, the broad signal can be attributed to spin resonance on conduction electrons and the narrow one can be regarded as spin resonance on the localized magnetic moments. It should be noted that the integral intensity of the CESR signal is proportional to the density of states \(D(E_F)\) of current carriers at the Fermi level \(E_F\) [3].

![Fig. 1. The ESR spectrum at 120 K (a) and temperature dependences of the widths \(\Delta B\) of its components for the initial (1, 2, 3, 4) and chlorinated (5, 6) samples (b). 1 and 2 – the data for the broad component of the ESR spectrum for the non-evacuated and evacuated samples, respectively; 5 – the data for the broad component of the ESR spectrum for the chlorinated sample; 3, 4 and 6 – the data for the narrow component of the ESR spectrum for the non-evacuated, evacuated and chlorinated samples, respectively.](image)
magnetic moments are by $\approx 60\%$ and $\approx 35\%$ less than those for the original sample, respectively.

During the saturation of ACFs by chlorine, the spin relaxation rate of current carriers, which is proportional to the width of the CESR signal, decreases (Fig. 3) and the value of $g$-factor of conduction electrons increases (Fig. 3, inset). At the same time, the width of the resonance on localized magnetic moments decreases by $\approx 0.05$ mT without changing the value of its $g$-factor.

At cooling of chlorinated sample, the spin relaxation rate of current carriers (the width of signal) increases by $\approx 55\%$ from its value at room temperature (Fig. 1 b). The width of signal from the localized magnetic moments is invariable within the measurement error (Fig. 1 b).

Evacuation of chlorinated ACFs leads to the increase of integral intensity of the CESR signal to its value in the original sample. However, complete restoration of the ESR spectrum occurs only in the evacuation carried out at $T > 425$ K. This fact indicates the presence of halogen atoms covalently bonded with carbon atoms in chlorinated samples.

![Fig. 2. The change of $D(E_\parallel)$ during adsorption of chlorine molecules by nanographites (a) and a schematic explanation of this phenomenon (b)]. b1, b2 and b3 correspond to the edge $\pi$-electronic band before and after adsorption of molecules by nanographites and subsequent spin splitting of this band. $I_0$ – the intensity of the CESR signal of reference sample Li:LiF.

The temperature dependences of specific magnetic susceptibility for both initial and chlorinated ACFs are qualitatively similar and well approximated by the sum of the paramagnetic and diamagnetic components: $\chi = C/(T-\Theta)+\chi_0$, where the Curie constant $C = 1 \times 10^3$ cm$^3$/K/g, the Curie temperature $\Theta = -1.2$ K and the diamagnetic contribution to the susceptibility $\chi_0 = -5.5 \times 10^4$ cm$^3$/g in chlorinated sample. The value of Curie constant corresponds to the concentration of localized spins $N_i = 1.6 \times 10^{19}$ spin/g, which is $\approx 30\%$ less than that in the initial sample. The change in $N_i$ during the interaction of ACFs with chlorine molecules correlates well with decrease in intensity of ESR signal for localized spins and indicates pairing of electron spins on unoccupied ("dangling") $\sigma$-orbitals of edge carbon atoms with electron spins on $3p$-orbitals of chlorine atoms. In other words, the formation of edge covalent compounds of nanographites with chlorine occurs. However, the preservation of nature of broad component in the ESR spectrum at chlorination proves that the edge $\pi$-electron states are still present.

At the interaction with graphene, the chlorine adatoms attract a portion of the electron density [4]. Therefore, the expected result of interaction of chlorine adatoms with nanographene stack (nanographite) is the enhancement of $D(E_\parallel)$ (Fig. 2 b), which contradicts the experimental data (Fig. 2 a). The reasons for that can be spin splitting of the edge $\pi$-electronic states, induced by increasing of electron-electron interactions due to enhancement of $D(E_\parallel)$ during the transfer of the part of electron density from nanographite to chlorine adatoms (Fig. 2 b). The mentioned point of view on the nature of considered phenomenon agrees with the recent results by scanning probe microscopy of the oxidized and protonated zigzag edges of honeycomb carbon networks [5, 6].

![Fig. 3. The dependences of spin relaxation rate $1/T_1$ and shift $\Delta g$ of $g$-factor (in the inset) for current carriers on the number of chlorine portions $n$ introduced into the reactor with evacuated ACFs. $\Delta g = g-g_c$, where $g_c$ is the free-electron $g$-factor.]

4. Conclusions

The electronic structure near the Fermi level and the properties of nanoscale honeycomb carbon structures are strongly influenced by the edge $\pi$-electron states formed near zigzag parts of their edges. The research data show that the values of $D(E_\parallel)$, $N_i$ and spin relaxation rate of current carriers for nanographites in the chlorine atmosphere differ significantly from the values of these parameters for initial sample. It is shown, that the change in $D(E_\parallel)$ can be attributed to the spin splitting of edge $\pi$-electron states induced by increasing of electron-electron interactions due to enhancement of $D(E_\parallel)$ while a part of the electron density is transferred from nanographites to chlorine adatoms. The decrease of $N_i$ during the interaction of nanographites with chlorine indicates pairing of the electron spins on unoccupied ("dangling") $\sigma$-orbitals of nanographite edge atoms with the electron spins on $3p$-orbitals of chlorine atoms, that is the formation of edge covalent compound of nanographites with chlorine. The changes in the spin-relaxation characteristics of the current carriers during chlorination of samples are also consistent with the above model of interaction of nanographites with chlorine.

References