

Ferromagnetism of nanographite structures in carbon microspheres

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Carbon microspheres with unusual magnetic properties have been prepared by method of solid-phase pyrolysis where metal-free phthalocyanine was used as a precursor. The morphology, structure and magnetic properties of prepared samples were investigated using electron microscopy, magnetometry and electron paramagnetic resonance. Carbon microspheres with a mean diameter $d = 3.40 \pm 0.15 \mu\text{m}$ consist of graphitized nanocrystallites with a thickness of 5-15 graphene layers. The samples demonstrate a strong paramagnetism with the concentration of paramagnetic centers $\sim 5 \times 10^{19}$ spin/g. In the temperature range of 5-100 K a ferromagnetism was revealed with a maximum value of the saturation magnetization, $M_s \approx 0.03 \text{ emu/g}$ at $T = 25\text{K}$. The temperature-independent diamagnetism with susceptibility of $\chi^{\text{Dia}} = -1 \cdot 10^{-6} \text{ emu/g-Oe}$ was also measured.

Index Terms— carbon ferromagnetism, nanographite, phthalocyanine, solid-phase pyrolysis.

I. INTRODUCTION

In recent years, carbon magnetism attracted great interest from the point of view of both fundamental science and practical applications [1-3]. Search of magnetism based on light elements is of great importance, since these materials have a number of advantages: low density, biocompatibility, plasticity, transparency, etc. Among these elements carbon takes a specific place, especially after discovery of its novel nanoscopic modifications such as graphene, fullerenes, nanotubes and nanocapsules, nanographene ribbons, etc.

Transition from macroscopic sizes to nanoscopic ones can be very radical and may help to create new unique novel materials and devices. For instance, when the sizes of nanographites or nanographene are decreased to a few nanometers, the role of edge states with “zigzag” and “armchair” shapes in their electronic structure strongly increases. In edge states of zigzag-type the π -electrons are localized and strongly spin-polarized, which influences also the transport properties of electrons. Unusual magnetic and electronic properties of nanographite and nanographene are not only the manifestation of novel properties in the physics of condensed state but also an attractive area for potential applications in electronics, spintronics, quantum information processing, etc. [2,3]. In nanographites and nanographene not only edge states can play an essential role in appearance of magnetic and transport properties. Different defects such as vacancies, topological defects and doping with different elements and functional groups can also play a key role [3]. Defects in graphite/graphene lattices were introduced by various methods: intercalation of atoms and molecules, doping, proton irradiation, carbon implantation, etc [1,3,4]. Defect atoms (for instance, vacancies, substitution of carbon by nitrogen or hydrogen chemisorption) induce spin-polarized defect states [2,5].

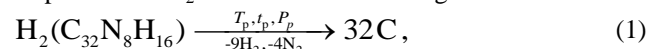
Among experimental works, related to the “defect” carbon magnetism caused by vacancies, one can mention [4], where a

room-temperature ferromagnetism was observed in highly oriented pyrolytic graphite (HOPG) irradiated with high-energy (2.25 MeV) protons. Among a large number of theoretical works in the field of carbon magnetism, one can underline the work [6] where a ferromagnetic Stoner criterion in narrow impurity bands for sp -electrons was derived and a possible realization of high-temperature ferromagnetism at relatively low electron concentrations was shown. In [7,8] by solid-phase pyrolysis of metal-free phthalocyanine ($\text{H}_2\text{Pc} \equiv \text{H}_2(\text{C}_{32}\text{N}_8\text{H}_{16})$) a carbon microspheres were obtained with an average diameter of about 3 μm , consisting of nanographite structures and exhibiting an intense electron paramagnetic resonance (EPR) signal. With a view to more in-depth study of the magnetic characteristics of the prepared microspheres in the present study we carried out magnetometer measurements in the temperature range of 10 K-300 K.

II. EXPERIMENTAL TECHNIQUE

For preparation of metal nanoparticles and nanoalloys, we developed a method of solid-phase pyrolysis in organic and organometallic compounds, as described in [8,9]. The advantage of this method: it is a single-stage, rather simple and provides a high yield of the final product. Previously using this technique we obtained various nanocomposites Ni/C, Cu/C, and nanoalloys $\text{Ni}_{1-x}\text{Cu}_x$ in different carbon matrices [9-11].

In this paper, pre-purified polycrystalline powders H_2Pc in a quartz ampoule with a volume $\approx 100 \text{ cm}^3$ were sealed in a vacuum of $\sim 10^{-6} \text{ MPa}$. The rapid heating of samples to temperatures above the 600°C results in thermal decomposition of H_2Pc molecules according to reaction



where T_p - pyrolysis temperature, t_p - time of pyrolysis, P_p - self-generated gas pressure in the ampoule. We selected

conditions pyrolysis $T_p = 700^\circ\text{C}$, $t_p = 30$ minutes at which the distribution of microspheres by the size occurs at the most narrow range $\langle d \rangle = 3.40 \pm 0.15 \mu\text{m}$. The structure, morphology and elemental composition of the samples are studied using a scanning electron microscope (SEM) Vega TS 5130 MM

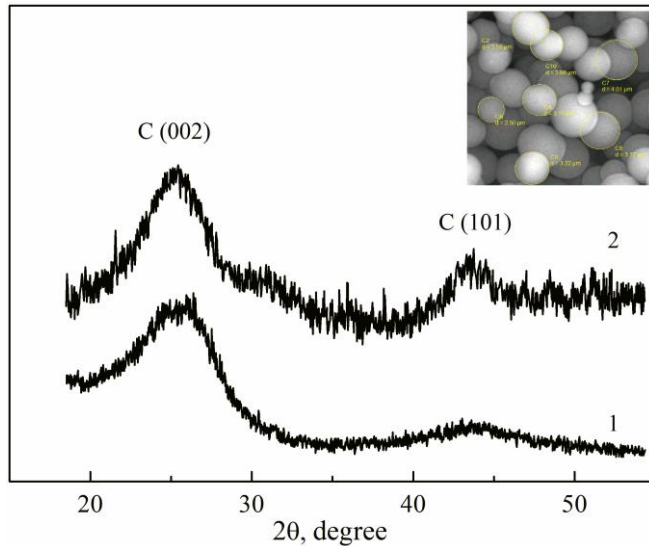


Fig. 1. X-ray diffraction spectra of carbon microspheres synthesized at 700°C , 30 min (1) and 900°C , 30 min (2) Inset – SEM images of carbon microspheres.

(Tescan) with a device for energy dispersive X-ray microanalysis INCA Energy 300. The magnetic characteristics of the carbon microspheres were taken on a vibrating magnetometer (VSM, Quantum Design) in magnetic fields to 60 kOe in a temperature range 5K-300K and ESR X-band spectrometer at 300K.

III. RESULTS AND DISCUSSIONS

Figure 1 presents the X-ray diffraction spectra of carbon microspheres obtained by pyrolysis at temperatures 700°C and 900°C and with pyrolysis time of 30 minutes. Two broad

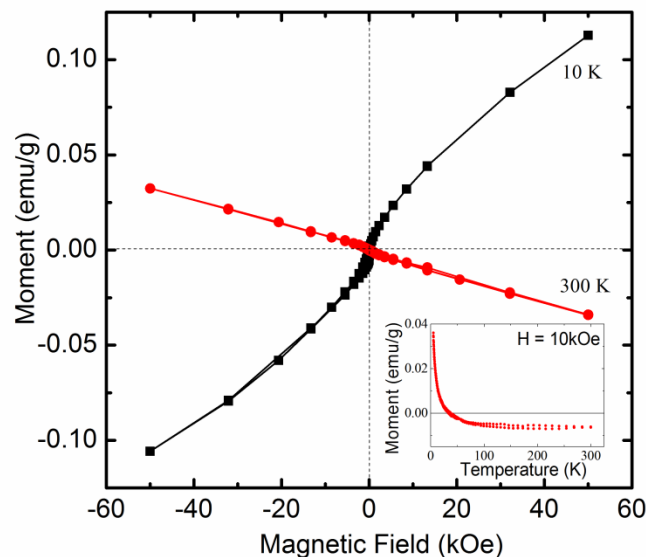


Fig. 2. M-H dependence of carbon microspheres at 10 and 300K. The inset: M-T dependence at $H=10$ kOe

peaks in the spectrum at $\sim 25^\circ$ и $\sim 43^\circ$ corresponds to graphite planes (002) and (101). Analysis of the spectra shows that the microspheres consist of carbon with weakly graphitized nanocrystallites with interplanar distance d_{002} from ≈ 0.345 nm to ≈ 0.357 nm (depending on the conditions of pyrolysis). The

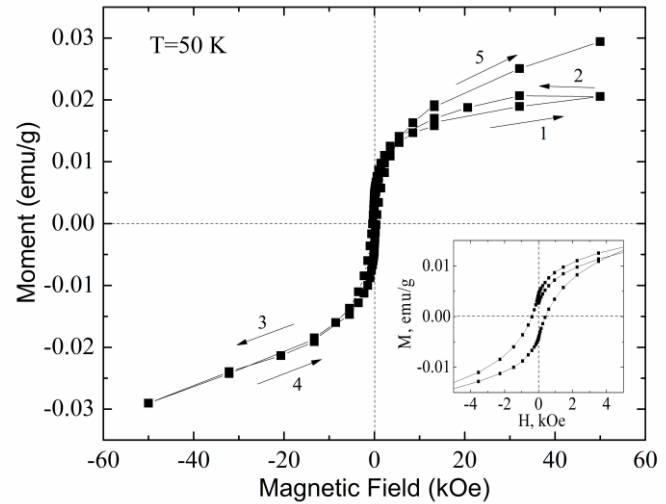


Fig. 3. M-H dependence and hysteresis loop (inset) of carbon microspheres at 50 K.

inset in Figure 1 shows the SEM image of product pyrolysis H_2Pc for sample 1 ($T_{\text{pyr}}=700^\circ\text{C}$). Similar microspheres were obtained in the case of sample 2 ($T_{\text{pyr}}=900^\circ\text{C}$).

Figure 2 shows the dependence of the magnetization of the magnetic field at temperatures of 10K and 300K. The inset in Figure 2 shows the dependence of M vs T at $H = 10$ kOe. Analysis of M-T and M-H curves shows the presence of paramagnetic centers with the concentration $n = 3 \cdot 10^{19}$ spin/g and temperature-independent diamagnetism with susceptibility of $\chi^{\text{Dia}} \approx -1 \cdot 10^{-6}$ emu/g·Oe.

The most important result in investigation of the magnetic properties of the pyrolysis products H_2Pc is a revelation of ferromagnetism at the temperatures rang from 5K-100K, along with paramagnetism and diamagnetism. The maximum value of the saturation magnetization is $M_s \approx 0.03$ emu/g at $T \approx 25\text{K}$.

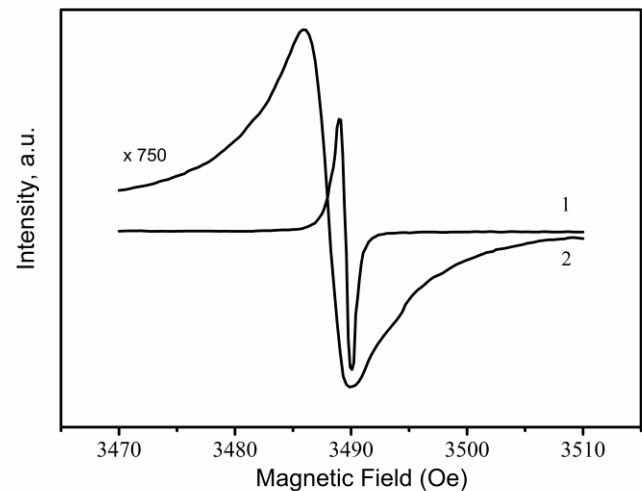


Fig. 4. EPR spectra of carbon microspheres prepared at 700°C (1) and 900°C (2).

When the temperature rises to $T \approx 100\text{K}$, there is a significant drop in M_s : $M_s(T=100\text{K}) \approx 0.002 \text{ emu/g}$. Figure 3 shows the dependence of M - H at $T=50 \text{ K}$, and inset shows the corresponding ferromagnetic hysteresis loop. The coercive force $H_c = 390 \text{ Oe}$ at $T=50 \text{ K}$. Unusual temperature behavior in ferromagnetic response as well as our element analysis in these samples is ruling out the presence of possible ferromagnetic impurities such as Fe, Ni, Co. Indeed, ferromagnetic nanoparticles of these elements have rather high Curie temperature $T_{\text{Curie}} \sim 1000 \text{ K}$ and, therefore, the saturation magnetization is remained practically unchanged up to the room temperature. Superparamagnetism of nanoparticles with these elements follows a Curie-Langevin $M \sim C / T$ temperature dependence without any hysteresis. Thus, observed in our samples unusual ferromagnetic behavior different from magnetism in Fe, Ni and Co nanoparticles. Notice also that the values of the magnetization of the first straight and the reversed magnetization cycles (arrows 1, 2 and 5) are somewhat different. This strange behavior requires further understanding of these differences and in-depth analysis of our magnetometer measurements.

Figure 4 provides the EPR spectra of samples obtained by pyrolysis at temperatures 700°C (sample 1) and 900°C (sample 2). The parameters of ESR spectrum of sample 1: the g -factor 2.0031 and intensity $\sim 5 \cdot 10^{19} \text{ spin/g}$. The ESR line width is only 0.8 Oe, which indicates a strong exchange narrowing. It is obvious that the observed strong paramagnetism and ferromagnetism are due to the edge centers such as "zigzag" and/or presence of nitrogen impurity atoms. On the essential role of nitrogen impurity atoms can be judged by comparing the integrated intensity of the ESR spectra of samples 1 and 2: $I_{700}/I_{900} \sim 200$. It is noteworthy to say that the sample 1 contains nitrogen impurity atoms with a concentration is about 10 atomic %, while in the case of the sample 2 the nitrogen concentration is only ~ 2 atomic %.

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