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Macroscopic behavior and microscopic magnetic properties of nanocarbon

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ABSTRACT

Here are presented investigations of powder and glass-like samples containing carbon nanoparticles, not intentionally doped and doped with Ag, Au and Co. The neutron diffraction study reveals an amorphous structure of the samples doped with Au and Co, as well as the magnetic scattering due to a long-range FM order in the Co-doped sample. The composition and molecular structure of the sample doped with Au is clarified with the NMR investigations. The temperature dependence of the magnetization, $M(T)$, exhibits large irreversibility in low fields of $B=1-7$ mT. $M(B)$ saturates already above 2 T at high temperatures, but deviates from the saturation behavior below ~ 50 (150 K). Magnetic hysteresis is observed already at 300 K and exhibits a power-law temperature decay of the coercive field, $B_c(T)$. The macroscopic behavior above is typical of an assembly of partially blocked magnetic nanoparticles. The values of the saturation magnetization, M_s , and the blocking temperature, T_b , are obtained as well. However, the hysteresis loop in the Co-doped sample differs from that in other samples, and the values of B_c and M_s are noticeably increased.

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1. Introduction

A broad variety of carbon-based materials attracts attention due to unusual magnetic properties, including ferromagnetic (FM) behavior with evidence for a possibility of a long-range magnetic order [1,2]. Some of them are characterized by FM Curie temperature, T_C , lying above the room temperature [1–4]. Possible utilization of such materials stretches from spintronics and light magnets in technical devices to applications for biological and medical purposes [1,2].

Most known bulk modifications of carbon, as ordered graphite and diamond with negligible concentration of intrinsic defects, exhibit a pronounced diamagnetism [1,2,5]. However, introduction of additional defects has shown that the material acquires FM-like properties, which takes place e.g. in proton-irradiated graphite [2,6,7]. Generally, it is widely believed that unconventional

magnetism of carbon materials is connected with formation of defects or disorder in an ordered host matrix [1,2]. On the other hand, possible role of magnetic impurities in triggering the FM order still cannot be excluded unambiguously [1,2], although evidence of a π -electron ferromagnetism in metal-free carbon samples has been established [8,9]. Hence, investigations of carbon structures with metallic atoms, magnetic or not, which have been introduced in the material intentionally, is interesting question for clarification the role of such atoms in formation of the magnetic properties of the material, as well as for application purposes [7–13].

Intrinsic magnetism of carbon materials has been predicted also in extensive theoretical investigations. It has been shown a possibility of FM behavior on a graphite surface with negative Gaussian curvature [14], in a mixture of carbon atoms with alternation of sp^2 and sp^3 bonds [15], in the presence of the graphene zigzag edges [16,17] and in disordered graphite with randomly distributed single-atom defects, preserving the ordered stacking of the graphene layers [18]. A possibility of the ferrimagnetic order in

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a three-dimensional network of single-atomic vacancies in graphite has been found to persist for distances between the vacancies up to 1 nm, whereas localized magnetic moments $\mu_1 = 1.72 \mu_B$ still can be formed even at a larger separation of vacancies [19]. Similar values of magnetic moments per vacancy site, $\mu_1 = 1.12 - 1.53 \mu_B$, were predicted in graphene [20]. The values of $\mu_1 \sim 0.2 - 1.5 \mu_B$ per defect of a grain boundary, similar to the predictions above, were observed in highly-oriented pyrolytic graphite at a distance between defects $\sim 0.5 - 4$ nm [21,22]. Eventually, the role of atomic hydrogen absorption at graphite surface in formation of the room-temperature ferromagnetism should be mentioned [9,23].

According to the nature of carbon-based magnetism, attributable to disorder and intrinsic defects, an assembly of small carbon particles is expected to be a promising object with interesting magnetic behavior due to numerous surfaces defects and high surface-to-volume ratio.

In this work, we investigate magnetic and structural properties of the system of carbon nanoparticles, not intentionally doped or doped with Ag, Au and Co. The purpose is to obtain macroscopic data on the behavior of the magnetic irreversibility, hysteresis and saturation magnetization. In addition, microscopic information on structural and magnetic properties of the investigated material is obtained with the neutron powder diffraction and NMR study.

2. Materials and methods

Investigations were performed using not intentionally doped powder nanocarbon sample (# 1) and glass-like carbon samples, doped with 4.55 mass% of Ag (# 2), 1.70 mass% of Au (# 3) and 0.117 mass% of Co (# 4). The preparation details of # 2–4 are described in [24].

The atomic force microscopy (AFM) investigations have revealed the presence of carbon particles with a broad size distribution, characterized by the average, $R_{av} \sim 60$ nm, and the maximum, $R_{max} \sim 110$ nm particle radii, R [24].

The neutron powder diffraction study was carried out using the PNPI superpositional diffractometer. The patterns were measured at 2.6 and 300 K in the superposition mode, using monochromatic neutrons with a wave length $\lambda = 1.7526$ Å in the angular range of $4^\circ \leq 2\theta \leq 145^\circ$.

Solid-state NMR spectra were recorded under magic angle spinning conditions at ambient temperature, using the spectrometer AVANCE II-500WB (Bruker). Single-contact $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization (CP) technique with 3 ms contact time was applied for ^{13}C CP-spectra recording with high power proton decoupling at frequency of 100 kHz. For ^{13}C direct polarization spectrum, 2.3 μs pulse ($\pi/4$) was used with repetition time of 6 s and proton decoupling at frequency of 100 kHz. All chemical shifts are given in ppm from tetramethylsilane.

Magnetic properties were investigated by measurements of the *dc* magnetization $M(T, B)$ with a SQUID magnetometer. In particular, $M(B)$ was measured in fields $-5 \text{ T} \leq B \leq 5 \text{ T}$ by increasing and decreasing the field. $M(T)$ was measured in a field of 1 mT–5 T after cooling the sample from 300 K down to 3 K in zero (M_{ZFC} or zero field-cooled magnetization) or in non-zero (M_{FC} or field-cooled magnetization) field. Thermoremanent magnetization (TRM) was investigated after cooling the sample from 300 K down to 3 K in non-zero field and then reducing the field to zero. The magnetization data are presented below after subtraction of the diamagnetic contribution.

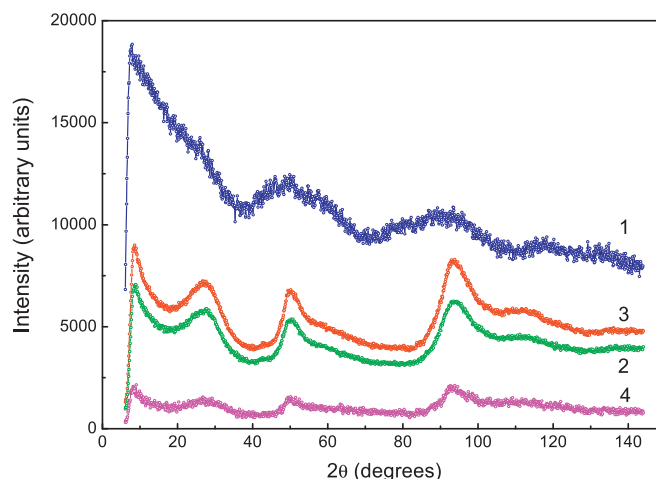


Fig. 1. The neutron diffraction patterns, obtained at 300 K for # 3 (curve 1), and at 300 K (curve 2) and 2.6 K (curve 3) for # 4. The curve 4 is the difference of the curves 3 and 2.

3. Results and discussion

3.1. Neutron powder diffraction

In Fig. 1 are displayed the diffraction patterns of # 3 and # 4 at room temperature and of # 4 at $T = 2.6$ K. A picture typical of an amorphous structure is observed for both samples, because the width of the diffraction peaks is increased considerably with respect to a crystalline state. It can be seen that the lines in # 4 are noticeably narrowed. This suggests a larger size of structural clusters formed in # 4 with respect to # 3. On the other hand, positions of the main maxima are almost identical for both samples, indicating a close internal cluster structure. In # 4, the peak amplitudes increase with cooling from 300 K down to $T = 2.6$ K, which follows from the differential signal (curve 4). This means magnetic scattering, connected with a long-range FM order in # 4. The influence of the temperature factors on the neutron diffraction patterns is much smaller than the observed difference.

3.2. NMR with magic-angle spinning

To clarify the composition and molecular structure of the material, we obtained the NMR spectra of hydrogen (^1H) and carbon (^{13}C) nuclei under the MAS conditions. The main peaks in ^1H spectrum (see the top panel of Fig. 2) correspond to the aliphatic (2.3 ppm) and the aromatic (6.8 ppm) groups. The signal coming from the aromatic groups demonstrates considerable chemical shift anisotropy (CSA), expectable for the aromatic protons. The aromatic to aliphatic signal ratio ~ 4 was obtained.

The ^{13}C CPMAS spectrum displayed in Fig. 2 (bottom panel) contains four main lines, which can be interpreted as follows: (i) the 126 ppm line is attributable to polynuclear aromatics; a half-width of the peak, constituting only 15 ppm, looks too narrow for such systems, pointing out to a high isotropy of an environment; (ii) the 137 ppm line is connected to substituted aromatics with a bent structure; (iii) the 153 ppm line is attributable to an oxygen-substituted aromatic, belonging probably to carbonyls; (iv) the 36 ppm line is pertinent of aliphatic chains (corresponding to the peak at 2 ppm of the ^1H spectrum in the top panel of Fig. 2).

Using CPMAS spectrum at lower spin frequency (4.5 kHz) [25], we found the main components of the CSA tensor of the 126 ppm line: $\delta_{11} = 219.17$, $\delta_{22} = 145.18$ and $\delta_{33} = 11.25$. These values are typical of the carbon atoms with the sp^2 -type of a chemical bond in the aromatic compounds (such as benzene, graphite etc.),

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