

## Model of spin localization in activated carbon fibers

Mateusz Kempniński

*Institute of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*

Wojciech Kempniński<sup>a)</sup> and Jacek Kaszyński

*Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland*

Małgorzata Śliwińska-Bartkowiak

*Institute of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*

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Mechanisms of spin localization in graphitic nanoparticles of activated carbon fibers (ACFs) are discussed. Electronic properties of ACFs are described by the model which is the fusion of two approaches: Langevin paramagnetism represented by Curie law in electron paramagnetic resonance measurements and granular metal model used to describe conducting properties of separated fibers according to metal-insulator transition. This approach shows the possibility of changing the electronic properties of ACFs by temperature or adsorbed molecules as a main factors. © 2006 American Institute of Physics. [DOI: 10.1063/1.2187416]

The structure of an activated carbon fibers (ACF) consists of nanographitic units (NGU), each approximately 2.5 nm in diameter and several graphene layers thick.<sup>1,2</sup> These units are linked structurally; however, the mechanical linkage is not necessarily electrically good. This structure constitutes porous system; the mean pore size between NGU is approximately 1.4 nm. The molecules confined in ACFs' micropores may show behavior of bulk material as well as nanoscale particles system depending on different factors.<sup>3-6</sup> In presented electron paramagnetic resonance (EPR) experiments, pure ACFs were compared to those with adsorbed C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> molecules. If there is a charge transfer between NGU and guest molecules, the hyperfine interaction of electron spin with N or H nuclei<sup>7</sup> can give additional information about host-guest interaction. There is also an influence of the size of a nanoparticle on the value of spectroscopic splitting factor  $g$  — by applying theory of EPR of small metal particles<sup>8</sup> mean grain size of ACFs' nanoparticles was determined as 2.7 nm.<sup>2</sup>

EPR experiments showed that the integral intensity of the signal  $I$ , which is proportional to the number of spins, increases with lowering temperature in ACFs. If there is a constant number of noninteracting localized spins, the integral intensity of the EPR signal is described by Curie law resulting from Langevin paramagnetism.<sup>9</sup> Our electric conductivity measurements show that for ACFs it is allowed to modify Curie law, because the number of free carriers changes during the adsorption process and depends on temperature as in the granular metal model,<sup>10</sup> where different conduction mechanisms are observed: Coulomb-gap conduction, charge-energy-limited tunneling and variable-range hopping conduction.<sup>11</sup> To describe electronic properties of ACFs, we propose the model of localization of spins at NGU which is a fusion of two approaches: Curie law behavior studied by EPR and granular metal model observed in conductivity measurements of a single fiber.

Electric resistivity measurements were performed by the four-probe method with Picowatt RV-Elektronikka OY

AVS-47 resistance bridge, equipped with helium-flow cryostat, in the temperature range of 20–295 K. EPR spectra of ACFs were acquired with Radiopan ES/X spectrometer, equipped with an Oxford Instruments gas flow helium cryostat, in the temperature range of 4.2–300 K. Fibers were acquired from Osaka Gas Chemicals Co. Ltd, Japan. ACFs samples were evacuated at 200 °C by pumping with a turbomolecular pump at 10<sup>-4</sup> mbar for 1 h, to ensure that the pores are empty. The fitting of conductivity and EPR experimental data was performed using SigmaPlot curve fitter which uses the Marquardt–Levenberg algorithm to find the coefficients (parameters) of the independent variables that give the best fit between the equation and the data, both in conductivity and EPR experiments. The quality of the fit is expressed by the coefficient of determination  $r^2$ .

The electrical resistivity  $\rho$  of ACFs strongly depends on temperature  $T$ . This process is shown in Fig. 1, where  $\rho$  rapidly increases in temperatures below 100 K to reach the value of one order of magnitude greater at 35 K.  $\rho(T)$  dependence in the low-temperature region is consistent with transport model proposed for granular metal:

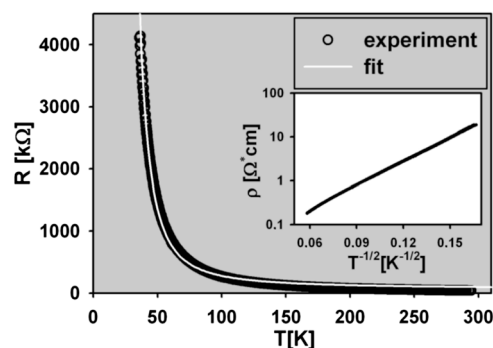


FIG. 1. Temperature dependence of ACFs' resistance together with the fitting line:  $r^2=0.998$ . The insert shows logarithmic resistivity  $\rho$  vs  $T^{-1/2}$  — linear dependence is consistent with granular metal model; activation energy  $T_0$  for carrier hopping equals 316 K.

<sup>a)</sup>Electronic mail: wojkem@ifmpan.poznan.pl

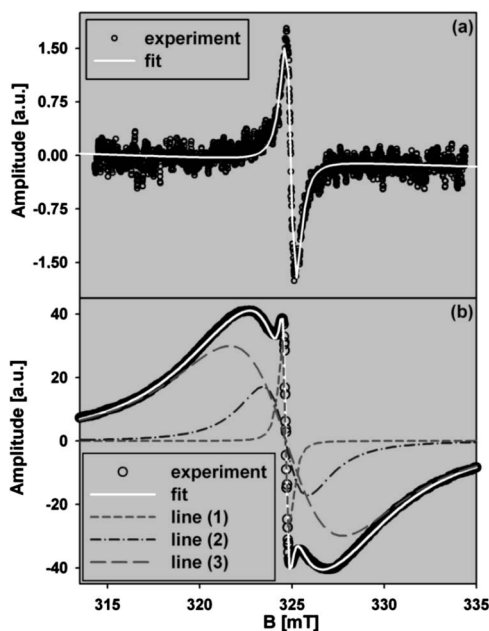


FIG. 2. EPR spectra of ACFs recorded at 20 K. (a) Spectrum of pure ACFs fitted with single Lorentzian line; (b) deconvoluted spectrum of ACFs with adsorbed  $C_6H_5NO_2$ . Fit of the spectrum ( $r^2=0.999$ ) consists of three Lorentzian lines. Adsorption of guest molecules strongly modifies nanographitic units' structure — signal gain in (b) is ten times lower than in (a).

$$\rho(T) = \rho_0 \exp(T_0/T)^{1/2}, \quad (1)$$

where  $\rho_0$  is the proportionality constant and  $T_0$  is the activation energy for hopping processes between two neighboring NGU.<sup>1,10</sup>

Fitting of the experimental data to Eq. (1) gives  $r^2$  coefficient equal to 0.998 and  $T_0=316$  K. ACFs' electrical properties evolve with decreasing temperature, according to description presented in Refs. 11 and 12 from half-metallic to nearly insulating.

EPR spectra of studied samples are observed below 100 K. It is the result of the ACFs' electrical transport properties which can be compared to the granular metallic system described by Mott's law (1).<sup>1,11</sup> The spectrum of pure ACFs consists of single Lorentzian line — Fig. 2(a). The line is recorded at  $g=2.0031$ , which is equal to the perpendicular spectroscopic splitting factor  $g_{\perp}$  of graphite.<sup>13</sup> The EPR spectrum changes after adsorption of  $C_6H_5NO_2$  — broader component appears as it is shown in Fig. 2(b). Deconvolution procedure helps to find that the spectrum consists of three Lorentzian lines. Line (1) is the same as observed for pure ACFs, but its amplitude is much greater than the amplitude of pure ACFs' line. Linewidth and  $g$ -factor of line (1) are temperature independent. The amplitude of this line is about 20 times greater than in pure ACFs—compare Figs. 2(a) and 2(b). It is the result of significant modifications which appear in the structure of NGU after guest molecules adsorption inside ACFs' micropores.<sup>14–16</sup> Two additional lines, marked as lines (2) and (3) in Fig. 2(b), are also related to the nanographitic structure of ACFs.<sup>2</sup> Line (2) originates from NGU (host), tightly surrounded by molecules (guest) captured in pores. Its linewidth and  $g$ -factor are temperature independent, whereas the linewidth and  $g$ -factor of component (3) of the observed spectrum strongly depend on temperature.<sup>2</sup> The behavior of line (3) can be explained as a surface effect. Strong instabilities of the paramagnetic cen-

ters at the fiber's surface or in its larger pores give the temperature dependence. Integral intensities of all three lines increase with lowering the temperature. This fact, as well as no visible hyperfine splitting arising from interaction of unpaired electron with nuclear spins of H or N, allow us to regard ACFs as a system with paramagnetic centers strongly localized within the NGU in low-temperature region.

According to Langevin paramagnetism, the magnetization  $\mathbf{M}$  of paramagnetics increases as the temperature is lowered, due to the increased number of spins  $N$  oriented along the external magnetic field  $\mathbf{H}$ . The relation  $\mathbf{M}=\chi\mathbf{H}$  gives magnetic susceptibility  $\chi$  which is proportional to integral intensity  $I$  of the EPR signal. As a result,  $I$  holds the Curie law:

$$\chi = \frac{N\mu^2}{3kT} = \frac{C}{T} \propto I, \quad (2)$$

where  $\mu$  is the magnetic moment of a paramagnetic center,  $k$  is the Boltzmann's constant, and  $C$  is the Curie constant.<sup>9</sup> This behavior is characteristic of materials having a constant number of localized spins that can be ordered in the external field. For ACFs, the description is different as the number of localized spins in the system changes with temperature. It has been well manifested in transport properties of ACFs that resistivity of a single fiber increases with lowering temperature. Such behavior is consistent with granular metal model introducing the metal-insulator transition and can be described by the Eq. (1).

A simple model of conductivity shows that resistivity can also be represented as a reciprocal value of conductivity:  $\rho=\sigma^{-1}=(N_c e \nu)^{-1}$ , where  $\sigma$  is the electric conductivity,  $N_c$  is the number of charge carriers,  $e$  is the electron charge value, and  $\nu$  is the mobility of carriers.<sup>11</sup> If there is a change in  $N_c$ , then the number of spins  $N$  in Curie law [Eq. (2)] cannot be considered constant. Conductivity of ACFs decreases with lowering temperature as the charge transport between NGU decays. This is due to a stiffening of the nanoparticles' structure — when there is an increase in the height of the potential barrier, hopping processes become less probable. Also thermal excitations are weaker — the number of carriers with energy comparable to the activation energy  $T_0$  decreases. Because of the Coulomb-gap effect, carriers from conducting band become localized on NGU and are visible in EPR phenomenon, giving rise to a higher integral intensity value of the EPR signal. It means that the total number of spins observed in the EPR experiment increases with lowering temperature. Consequently, Curie law has to be modified by an additional spin localization process connected with the granular metal properties of ACFs.

We show different results of fitting the three components of EPR spectra of ACFs with adsorbed  $C_6H_5NO_2$ . When fitting line (1), one can only get a rough agreement with Curie law, especially at temperatures below 50 K — see Fig. 3(a) — coefficient  $r^2$  for the whole temperature range is about 0.959. A similar fit can be proposed for lines (2) and (3), as shown in Figs. 3(b) and 3(c), with  $r^2=0.971$  and 0.995, respectively.

To assume additional mechanism (metal-insulator transition<sup>1</sup>) of increasing the spin number, we get much better fit for the line (1) —  $r^2$  equals to 0.997. The following equation has been used, taking into account the spin number increase related to the changes of resistivity:

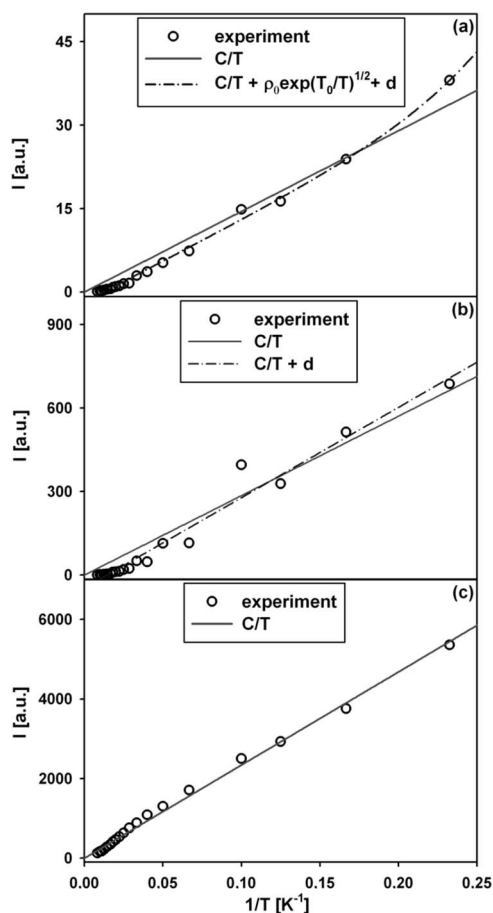


FIG. 3. Fit results for integral intensity  $I$  for: (a) Line (1) with  $T_0=323$  K, (b) Line (2), and (c) Line (3). There is no modification of Curie law in case of lines (2) and (3), because ACFs' nanounits are electrically pre-separated by guest molecules. Additional constant  $d$  appearing in the case of Lines (1) and (2) gives better fit for high-temperature region, where thermal activation modulates Coulomb gaps between nanocrystallites.

$$I \propto C/T + \rho_0 \exp(T_0/T)^{1/2} + d. \quad (3)$$

A result of this improvement is shown in Fig. 2(a).

In the cases of lines (2) and (3), the increase in spin number results only from Langevin's paramagnetic behavior as ACFs' nanocrystallites are electrically pre-separated by guest molecules. For these lines, Curie law modification is not necessary. The additional constant  $d$  appearing in Eq. (3) gives a better fit for high-temperature region, where thermal activation can modulate Coulomb gaps in the system of linked NGU. For line (1), this modulation is rather weak, ( $d=-2$ ). A stronger effect, with  $d=-47$ , appears in the case of line (2), where the  $d$  parameter is also needed for fit improvement. It seems to be obvious when host-guest interaction is appreciable in the system. No additional constant is needed in fitting line (3). The Curie law is observed in this case — Fig. 3(b).

As was shown in papers,<sup>14,17</sup> NGU size can be reduced by interaction with guest molecules; accordingly, the potential barrier for hopping of charge carriers between NGU in-

creases. This implies that temperature dependence of lines (2) and (3) will follow Curie law. In the case of line (1), the activation energy  $T_0$  for carrier hopping is equal to 323 K, what is in good agreement with the value obtained from fitting the conductivity data to Eq. (1) and with the published data.<sup>11</sup>

EPR experiments show that integral intensities of EPR spectra of ACFs increase with lowering temperature. There are two possible mechanisms responsible for such changes. The first one agrees with Langevin paramagnetism and follows the Curie law. The second one refers to localized spin number increase which is consistent with the electrical transport model for granular metals, that is likely to be used for ACFs. As the conductivity of ACFs is reduced with the lowering of temperature, charge carriers from conducting band are trapped at localized states and, as a consequence, resistivity and number of localized spins recorded in EPR increase. Results of our studies show that the number of localized states in ACFs can be modified, or even controlled in future experiments, by temperature changes or adsorption of chosen guest molecules. Both factors could allow one to manipulate the system of Coulomb gaps in a nanoparticle matrix. In such a case, the nanographitic arrangement with well-defined Coulomb gaps between graphitic nanoparticles could possibly serve as a quantum-dot matrix.

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