Localized states in nanocarbons

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Abstract. Localization phenomenon is studied in different modern nanocarbon materials: pristine C_{60}, C_{60}-fullerides, carbon nanotubes and graphene-based structures in the form of activated carbon fibers built of quantum dot-like basic structural units. Two experimental methods are used to define the localization and population control of spins (charge carriers) in the nanocarbon materials – electron paramagnetic resonance (EPR) and direct current (d.c.) electrical conductivity measurements. Results are discussed in the frame of the possible applications of the aforementioned materials in the molecular electronics or spintronics.

Key words: activated carbon fibers (ACF) • carbon nanotubes • electron paramagnetic resonance (EPR) • fullerenes

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Introduction

Localization of spins (charge carriers) is of current interest because the quantum transport in the various nanoscale systems is defined by the conditions observed when hopping and tunneling are the main contribution to electrical transport in the systems with localized states, where strong Coulomb interactions are observed.

There are several definitions of localization, depending on the used methods and observed parameters. From the point of view of the d.c. conductivity, the simplest definition can be given for conductivity vanishing at $T = 0$. More precisely, we can say that an electron is localized if it does not diffuse away from some volume which is large enough to satisfy the uncertainty principle. More general definition says that wave function of the electron should exponentially decrease outside the region of localization [2].

From the point of view of electron paramagnetic resonance (EPR), localization is defined by the Curie law. The Langevin approach shows that the magnetization of paramagnetics increases with the lowering of the temperature T due to the increased number of spins parallel to the external magnetic field. The magnetic susceptibility χ is proportional to the integral intensity I of the EPR signal and I holds the Curie law [9]

$$(1) \qquad \chi = \frac{N\mu^2}{3kT} = \frac{C}{T} \propto I$$

where N – number of spins, μ – magnetic moment of a paramagnetic center, k – Boltzmann's constant and C – Curie constant. If the EPR integral intensity is

described by the Curie law, we can say that spins in the studied system are localized.

We can summarize the above into the most general definition which would say that the region of localization can be treated as a potential well, beyond which the wave function of a localized particle vanishes exponentially. This is the reason that in some cases we can describe the region of localization as a quantum dot.

## C_{60} fullerenes and fullerides

Stankowski's model of paramagnetic centres in C_{60} locates the holes (or electrons) at the surface of the C_{60} in the vicinity of the molecule equator [12]. The reason for such location is that a hole (or electron) moving at the surface of C_{60} creates a polaronic state. Such a state generates some deformation of the C_{60} surface. The easiest way to create any deformations in this case is to locate them in a region of the lowest curvature of the strongly symmetrical C_{60} molecule – the C_{60} equator (see Fig. 1 inset). Well defined C_{60}^{+} as a positive radical in pristine C_{60} [6] or C_{60}^{n-} ($n = 1$ or 3) as a negative radical observed for C_{60} doped with alkali metals (K or Rb) [7, 8, 11] prove this interpretation. Curie behaviour of C_{60}^{+} is presented in Fig. 1.

Doped C_{60} shows superconductivity at temperature T_C which depends on the distance between the molecules in the crystal lattice. Localization of spins within the single C_{60} molecule for fullerides gives the coherence length comparable with the size of the molecule [4].

Doping process which leads to the superconductivity of C_{60}-fullerides shows that a single C_{60} molecule can easily absorb electrons in the charge transfer process. This feature prompted the choice of the C_{60} to create the single-molecule quantum dot for studying the Kondo effect [10].

Carbon nanotubes

One of the main components of the EPR spectrum of carbon nanotubes is the broad line from catalysts [3]. Purification process helps to remove the impurities but creates some defects at the surface of nanotubes, which can be the source of paramagnetic centres observed
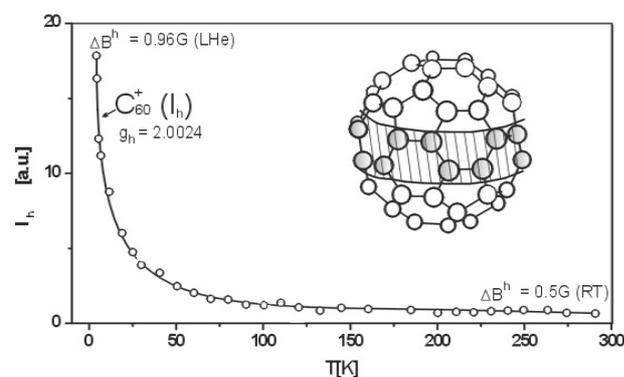
Fig. 1. Curie law behaviour for C_{60}^{+} radical. EPR parameters, g and ΔB are shown for room temperature (RT) and low temperature region (LT). Inset shows equatorial location of hole (h).
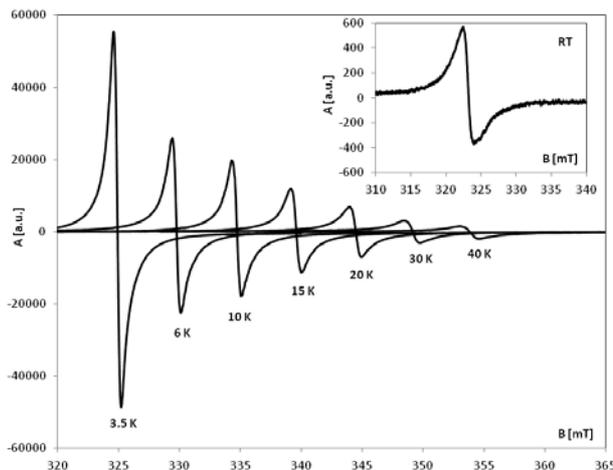

Fig. 2. Curie law behaviour at low temperature region for the powder sample of multi-wall carbon nanotubes. For clarity, the EPR spectra at different temperatures are shifted at the scale of B by a factor of 5 mT (the B-axis scale belongs to the 3.5 K spectrum). The inset shows the room temperature EPR spectrum (RT) with the Dysonian line shape.

by EPR. EPR is the perfect method to distinguish between the localized and conducting electrons and helps to determine the conducting properties of the carbon nanotubes. The Dysonian shape of the EPR line or Pauli paramagnetism point at the presence of the conduction electrons in the studied system. When spins become localized they come under the Langevin paramagnetism which is described by the Curie law Eq. (1). Figure 2 shows the evolution of the EPR spectrum during the lowering of the temperature of the well purified multi-wall carbon nanotubes (a powder sample). The EPR line at high temperatures has the Dysonian shape. It means that the thermally excited electrons can easily overcome the potential barriers separating the single nanotubes in the studied system. At low temperatures, the EPR spectrum changes its shape to Lorenzian with only slight asymmetry (adduct of the Dysonian component). It means that the spins become localized within the single nanotubes when thermal excitations are too low to induce hopping of charge carriers. Localization of spins within the low temperature region, similarly to the C_{60} fullerides, is defined by the Curie-like behaviour and is shown for the powdered sample of carbon nanotubes in Fig. 2.

Activated carbon fibers

Description of the electrical conductivity in activated carbon fibers (ACFs) bases on the model proposed for granular metals [1]. For ACFs, this model has a strong support from EPR experiments, where the localization phenomenon is detected via the Curie-like behaviour [5]. The model of localization in ACFs enables us to treat the system of conducting carbon nanographitic particles as the quantum dot matrix [5]. Spin population control in such system can be crucial for the future molecular electronics or spintronics application. Nanographitic particles in ACF are linked structurally and form the porous system. In such system the conducting properties strongly depend on the potential barriers
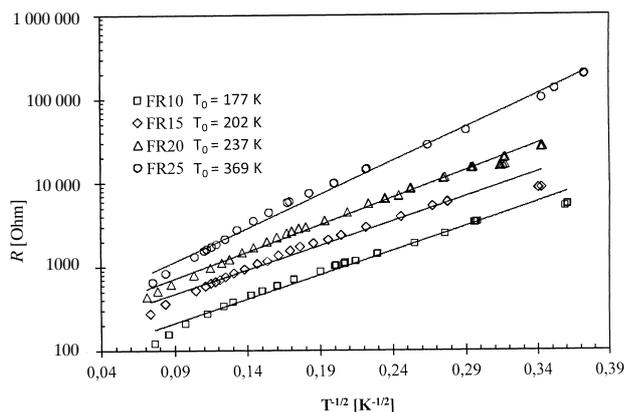
Fig. 3. T_0 parameter observed for different porosity of activated carbon fibers. □ – denotes FR10 with pore radius 9 Å, ◇ – denotes FR15 with pore radius 12 Å, △ – denotes FR20 with pore radius 16 Å, ○ – denotes FR25 with pore radius 22 Å. For clarity, the starting values of R have been vertically shifted.

between the nanoparticles [1]. Control of the potential barriers for charge carrier hopping within the ACF would be possible if we could get information on the nanographitic linkages and influence them. This could be possible with the adsorption of the guest molecules inside the pores [5] but the most important is the initial arrangement of the nanoparticles and their linkages which can be macroscopically defined by measuring the porosity of ACFs. Figure 3 shows how the T_0 parameter [1, 5] depends on the level of porosity for the set of Kuraray Chemical Co. ACFs filled with water. T_0 parameter defines the energy which is necessary to overcome the potential barrier in hopping processes observed in ACFs. The higher value of T_0 for the larger pores in the FR25 sample suggests that this type of ACF could be the most interesting from the point of view of designed quantum dot matrix.

Conclusion

We show that the localization processes observed in modern nanocarbon materials lead to local quantum transport of spins or carriers. Well-defined ways of localization could help in the future attempts to design the molecular electronics nanodevices. It seems that carbon nanostructures will have a large contribution to these attempts.

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