High-frequency EPR Studies of Spin-Spin Interaction between π-electronic Edge-Localized Spin States and Molecular Oxygen in Defective Carbon Onions

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Introduction

Zigzag edges of nanographene layers have continuous distribution of spin-polarized local magnetic moments (~0.1-0.15 Bohr magnetons) along the edge carbon atoms. Below 50 K the new paramagnetic complexes originating from zigzag edges weakly bound with oxygen ion-radicals $O_2^{\bullet}$ (S = 1/2) may appear at appropriate conditions (microwave/light irradiation) and then persist for a long time. At cryogenic temperatures these complexes are stable: despite weak ionic bond (binding energy <45 meV) spin-spin interaction between the oxygen ion-radical and collective polarized edge magnetic moments is not vanishing (<2 meV). Thus such complexes may be well observed by CW EPR. The objective of this research is studying the effect of applied magnetic field strength and excitation frequency on spin-spin coupling between the interacting agents.

Experimental

A quasi-optical EPR setup operating at 240 and 336 GHz in combination with a 12.5 T magnet was exploited for doing this research. Paramagnetic excited states related to weakly bound ionic complex "graphene zigzag edge – oxygen ion-radical" were generated by exposing the sample of defective carbon nano-onions (DCNOs) to intense microwave irradiation at T < 20 K. The sample consists of quasi-spherical and polyhedral-like multi-shell graphitic particles with a mean size ~6 nm and defective outermost shells. The temperature dependence of the spin susceptibility (for the EPR signal with line width 3.7 mT and g = 2.0015÷2.0020 characterizing these ionic complexes) was measured within the range 5-60 K at microwave frequencies of 240 and 336 GHz.

Results and Discussion

EPR data taken at 240 GHz excitation show that magnetic interaction between the oxygen ion-radical and edge localized spins has antiferromagnetic character with well featured downturn in spin susceptibility below 17 K (Fig. 1). Earlier such behavior was found by means of X-band EPR in setup with a resonator [1]. It seems that high applied magnetic field (~8.5 T and ~11.5 T) does not affect weak exchange coupling between the interacting spin agents – O_2^- S =1/2 spins and edge spins on the nanographene substrate. Such behavior may be well explained within the framework of a singlet-triplet model by means of the Bleaney-Bowers formula specially modified by an intentionally introduced co-multiplier related with the temperature dependence of the sticking coefficient s_c of chemisorbed O_2^- ionic complexes attached to the zigzag edges just at cryogenic temperatures. Here we suppose that s_c(T) = 1 below ~30 K and s_c(T) =0 above ~60 K through the irreversible desorption of O_2^- ions and decay of their ionic bonding to the substrate.

Conclusions

We found well featured antiferromagnetic interaction between the spins of oxygen ion-radical and zigzag edge spins of nanographene at T < 30 K in high magnetic field up to ~12 T. Such magnetic field does not modify substantially the magnetic interactions between the interacting agents.

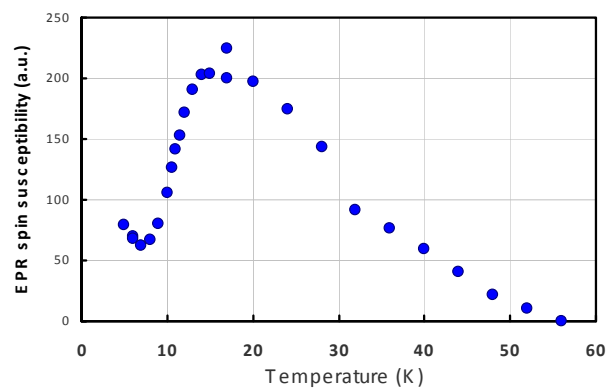

Fig. 1 Temperature dependence of EPR spin susceptibility of g = 2.0017 signal measured by means of quasi-optical MW set-up at ~240 GHz.

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References

[1] Shames, A.I., *et al.*, Carbon, **61**, 173-189 (2013).