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EPR evidence of antiferromagnetic ordering in single-layer graphene

Maria A. Augustyniak-Jabłokow*, Krzysztof Tadyszak, Mariusz Maćkowiak, and Yurii V. Yablokov

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

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* Corresponding author: e-mail aldona@ifmpan.poznan.pl, Phone: +48 618695205

We report electron paramagnetic resonance (EPR) evidence of the antiferromagnetic ordering in pristine single-layer graphene. Temperature dependences of the parameters of EPR spectra obtained for vacuum-processed samples were studied within the temperature range of 4.2–300 K. Our experiment has confirmed recent theoretical predictions that in single-layer graphene the carrier-mediated exchange interaction leads to antiferromagnetic coupling. We note some quantitative discrepancies between the theory and experimental findings and discuss their origins.

1 Introduction Since its discovery [1], graphene has received unprecedented attention due to its two-dimensional crystal structure and unique electronic structure. The properties of single-layer hexagonal carbon sheets of graphene have stimulated a lot of theoretical research. Magnetism of carbon materials is of particular interest, since the application of new carbon-based magnetic materials is very promising in the design of nanoscale magnetic and spintronic devices. Theoretical studies suggest that the crucial role in determining the magnetic properties of graphene is played by the the localized electron states. Exchange between them is realized by the long-ranged Ruderman–Kittel–Kasuya–Yoshida (RKKY) interactions mediated by conducting electrons [2–6]. For the centres localized on the same sublattice, ferromagnetic order is expected, whereas interactions between centres localized on two various sublattices lead to antiferromagnetic ordering analogous to the state of a diluted antiferromagnet [2–4]. Several authors have demonstrated the importance of the edge states and single-atom point defects [5–8].

All these theoretical considerations lack experimental verification, which is mainly due to the amount of material necessary for the measurements of magnetic properties. One of the most sensitive methods for studying the magnetic properties and dynamics of spin systems in carbon structures, allowing also a distinction between various types of magnetic centres and the determination of spin concentration, is Electron Paramagnetic Resonance (EPR).

There have been already several attempts to apply this method to study graphene [9, 10]. One of them was performed on the mechanically exfoliated graphene flakes [9]. However, it was not possible to check whether all the flakes were of a single-layer type. The observed temperature dependences of the intensity and linewidth (increasing from 0.63 at RT up to 0.85 mT at liquid helium temperature) resembled those of graphite. The only difference was the isotropic *g*-factor in the samples studied. No signs of antiferromagnetic ordering were noticed. The other attempt of an EPR study of graphene was performed on a material obtained by the reduction of graphite oxide [10]. In that case, highly defected multilayer graphene was studied.

In this Letter we report EPR evidence of antiferromagnetic ordering in pristine monolayer graphene.

2 Experimental We have studied single-layer graphene produced by the substrate-free gas-phase synthesis with an average lateral size of ~550 nm, supplied by GrapheneSupermarket in the form of graphene suspension in pure ethanol. This material is reported to be free of functional groups and to have low defect concentration [11].

The sample for EPR measurements was prepared by deposition of the single-layer graphene on amorphous SiO_2 in argon atmosphere. The amount of graphene in the sample was estimated to be 0.02 mg. The as-prepared sample was EPR silent. A weak signal appeared only 60 hours after attaining high dynamic vacuum ($\sim 10^{-5}$ Pa). Several

days of sample storage under static vacuum in the closed ampoule resulted in a significant increase in signal intensity and in its narrowing. Later we found that storage of a graphene sample under much lower vacuum of ~5 Pa also produces a narrow EPR signal with the intensity sufficient for measurements. The results reported were obtained for a sample prepared by this procedure.

The EPR measurements were performed on a RADIOPAN SX spectrometer with Oxford CF935 cryostat allowing measurements in the temperature range of 4.2–300 K. The temperature was measured by a sensor located below the ampoule with graphene. The sample was held at each temperature for a time sufficient to reach the equilibrium state corresponding to the sensor reading. Depending on the temperature step and the temperature range, it took from 30 to 60 minutes.

Analysis of the dependence of the signal intensity on microwave power proved that the intensity decrease observed at a microwave power level of 1.35 mW was not caused by the resonance line saturation.

3 Results The EPR signal of graphene consists of a single isotropic line of Lorentzian shape. The room temperature g-factor is 2.00245 ± 0.00005, the linewidth $\Delta B_{pp} = 0.06$ mT is significantly lower than that observed in previous experiments [9, 10]. The spin content $N = 3.86 \times 10^{15}$ in the sample stored for two months was established by the use of the $K_3NbO_8:Cr^{5+}$ standard, and the estimated spin concentration was about $N = 4 \times 10^{20}$ spin/g. After another forty days of storage, the spin concentration decreased to $N = 2 \times 10^{20}$ spin/g.

The temperature dependences of the EPR signal intensity (corresponding to the paramagnetic susceptibility χ_{EPR}) for the sample with two different spin concentrations are shown in Fig. 1a. At $T \approx 35$ K (20 K in the sample with lower spin concentration), a bend in the $\chi_{EPR}(T)$ dependences is seen and below this temperature the signal intensity decreases. The observed temperature behaviour reminds that of an antiferromagnet. The observed temperature dependences can be fitted to the Curie–Weiss law, $\chi = C/(T + \Theta)$, with the Néel temperatures T_N equal to 36 K and 18 K and Θ equal to 15 K and 8 K for the spin concentrations $N = 4 \times 10^{20}$ spin/g and $N = 2 \times 10^{20}$ spin/g, respectively. These data indicate a linear dependence of the Néel temperature on spin concentration.

In the temperature interval 4.2–25 K, a very small decrease in the resonance field is observed, which above ~35 K is independent of temperature (Fig. 1b).

The linewidth, ΔB_{pp}, which at higher temperatures shows an approximately linear dependence on temperature, at low temperatures has a constant value of $\Delta B_{pp} = 0.022$ mT (Fig. 1c).

4 Discussion The small value of the linewidth and a very small deviation of the g-factor from the free-electron value suggest that spins do not originate from paramagnetic ion impurities but are inherent to carbon. Therefore,

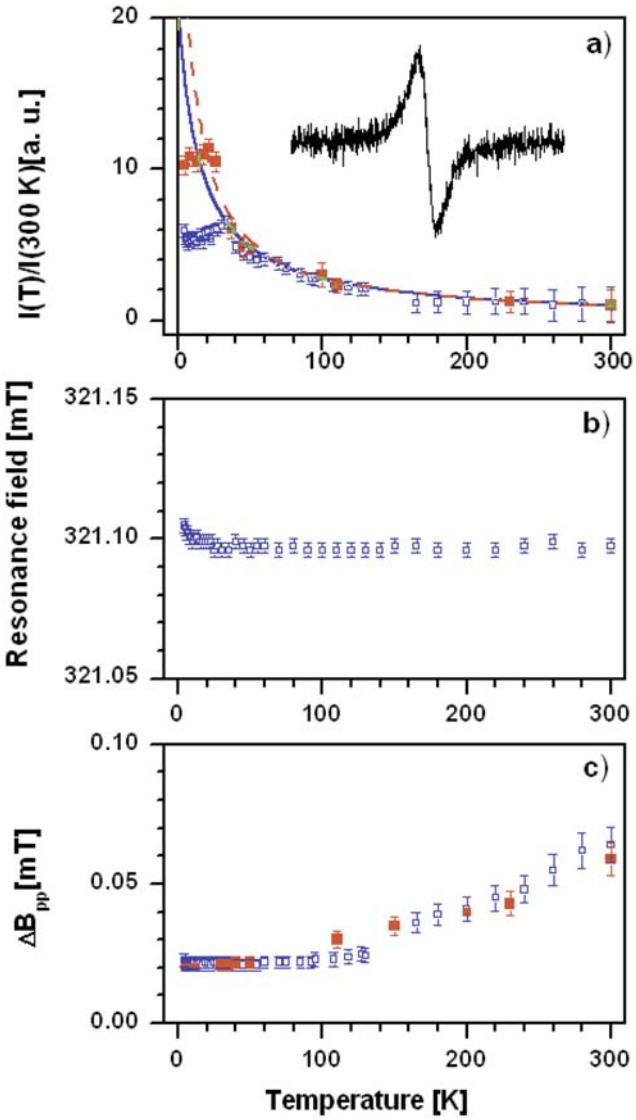

Figure 1 (online colour at: www.pss-rapid.com) (a) Temperature dependence of normalized integral intensity of the EPR spectrum in graphene for a sample with two different spin concentrations (open symbols: $N = 4 \times 10^{20}$, full symbols: $N = 2 \times 10^{20}$). The solid and dotted lines represent the best linear fit to the Curie–Weiss law with T_N: 36 K and 18 K and Θ: 15 K and 8 K, respectively. Inset: Spectrum recorded at 300 K with 32 accumulations. (b) Temperature dependence of the resonance field. (c) Temperature dependence of EPR linewidth ΔB_{pp}.

the magnetic properties reported here are considered to be intrinsic to the graphene samples.

The Curie–Weiss type temperature dependence of the signal intensity observed above the Néel temperature indicates that the EPR signal is mainly due to localized electrons. Experimental study [12] has shown that the number of conduction electrons in the vicinity of the neutrality point can be estimated for graphene as 4×10^{11} electrons per cm^2, corresponding to $N_e = 7 \times 10^{18}$ electrons/g, a number by two orders of magnitude lower than that of the ob-

served localized states. The presence of conducting electrons is manifested in the Lorentzian form of the homogeneously broadened EPR signal, which is a sign of some exchange process. In graphene, this exchange is realized by the fast transfer of electrons between localized and conducting states due to the proximity of their energies.

Another question is the origin of localized states seen by EPR in graphene. These are defects which possess magnetic moments, such as the zig-zag edge states, vacancies with the trapped electron, or adatoms such as hydrogen [2, 13]. The latter, due to the sample preparation and vacuum storage, should play no role in the case studied. The role of the zig-zag states in graphene nanoribbons is intensively discussed [3]. However, for large graphene flakes, the vacancies with spin $S = 1/2$ are expected to be the most probable source of magnetic moments [13, 14]. This hypothesis is supported by the fact that in the sample studied by us the number of spins decreases during graphene storage in vacuum at room temperature. This can be easily explained by a reconstruction of the vacancy sites [15]. The EPR active vacancies can be either created by vacuum or activated by detachment of the absorbed adatoms, which blocked the defect. To settle this problem we plan additional study with use of methods other than EPR.

The $\chi_{EPR}(T)$ dependence suggests the theoretically predicted [8] antiferromagnetic transition. However, for $p \sim 8\times10^{-4}$ and $p \sim 4\times10^{-4}$ corresponding to the estimated spin concentrations the observed Néel temperature is much higher than the predicted one. According to theoretical predictions, for the defect concentration $p = 10^{-2}$, the transition is expected at $T_N = 10$ K [8].

There can be several sources of such a discrepancy between theory and experiment. The linear dependence of T_N on p suggests an inhomogeneous distribution of defects in the graphene lattice resulting in the local increase in concentration of magnetic centres. But there are also other possibilities which should be taken into consideration. The most obvious is the simplified theoretical model of localized point-like magnetic impurities. A more realistic description should be able to take other factors into account. One of them is the increase in size of the vacancy defect due to transfer of the magnetic moment of the trapped electron on the neighbour carbon atoms. This can extend the range of the RKKY interactions, which can be also extended due to the presence of electron–electron interactions [16]. It was also shown that the formation of local magnetic moments leads to an interesting interplay between the spin correlation due to the RKKY interactions and the ripples, generating a variety of magnetic states [17]. To our knowledge, the theoretical considerations published hitherto have not distinguished between various types of defects. Differences between the edge states and vacancies and any other hypothetical magnetic states can multiply the number of sublattices and complicate the description.

Another problem which should be discussed, is the fact that the postulated transition weakly, or not at all, affects the temperature dependences of the resonant field and linewidth although the antiferromagnetic coupling is known to change the resonance conditions for the centres.

But the antiferromagnetic state in graphene, due to a very low spin concentration can differ significantly from such a state in concentrated or diluted antiferromagnets, where transition induced changes in the linewidth and resonance fields are due to the appearance of anisotropic fields, as well as various demagnetization effects. The influence of the last two factors, if they exist in graphene, can be smeared by irregular forms of the graphene flakes and nonstatistical distribution of magnetic moments. Intensity of the exchange field depends not only on the exchange integral but also on the concentration of the localized spins and conducting electrons. And in graphene both are very low. One should also consider that in graphene, except RKKY interactions there exists an additional, already mentioned, exchange interaction between localized states and the conducting electrons. We suppose that this exchange process is responsible for averaging of the resonance line parameters.

5 Conclusions EPR study confirms the existence of the theoretically predicted antiferromagnetic coupling between localized magnetic centres of concentration $\sim10^{20}$ spin/g in single-layer graphene. Linear dependence of T_N on the defect concentration suggests the inhomogeneous distribution of paramagnetic centres. Their most probable origin is the electrons trapped on the carbon atom vacancy. A more detailed study of the nature of the observed phenomena performed with the use of cw and pulsed EPR methods is necessary and is in progress.

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