Magnetic Properties of Carbon Nanospheres at low temperatures

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Abstract. The magnetic and electrical properties of Nitrogen doped carbon nanospheres can be probed using Electron Spin Resonance (ESR) techniques. Previous ESR measurements showed large peak on nitrogen doped spheres, implying that N forms paramagnetic impurities within the graphitic lattice. Low temperature measurements with continuous wave ESR, revealed different interactions of conduction electrons with nitrogen impurities and acoustic phonons hence two different spin relaxation mechanisms, Elliot-Yafet and D'yakonov-Perel' compete in the whole temperature range[5-300K].

1. Introduction

Among carbon nanostructures, the carbon nanospheres (CNS) have also shown to possess unique properties and have potential to be used in many applications. Although most researchers have come up with different techniques to synthesize and characterize these materials only few have tried to understand the mechanisms of spin and charge transport of CNS. Since carbon nanospheres are made of spherical graphene layers packed along the z-axis as in turbostratic-graphite, some properties of these spheres could related to these carbons. Carbon nanospheres of our interest contain different amount of nitrogen atoms forming local structures. Other carbon nanospheres [1] containing nitrogen has shown to possess a number of local structures as defects and/or impurities: pyridine-like, quaternary and pyrrole-like, etc. The effects of the local structures (impurities) is investigated in the range of temperature [5-300K] using the electron spin resonance spectrometer (ESR).

Taking into account large amount disorder induced by nitrogen addition in CNS; we expect spin relaxation to be dominated by electron-impurity momentum scattering via Elliot-Yafet (EY) mechanism in a broad range of temperature. However, lattice distortion induced by randomly distributed impurities in graphene (sp^2C changed into sp^3 C) have been argued to significantly enhances Rashba spin-orbit field [2, 3, and 4] more than what one might expect in extrinsic Rashba field [2 and 5]. Rashba spin-orbit field $\boldsymbol{b}(\boldsymbol{k}) = \lambda \boldsymbol{z} \times \boldsymbol{k}$ is seen in crystals lacking inversion symmetry; however it can also be induced by applying electric field perpendicular to 2D layer such graphene. Since both Elliot-Yafet and D'yakonov-Perel' mechanisms can occur with almost equal probabilities in nitrogen doped carbon nanospheres; a distinguishing feature of the D'yakonov-Perel'(DP) relaxation mechanisms $1/\tau_s = \left(\lambda/\hbar\right)^2 \tau_k$ is the smaller spin relaxation rate in disordered systems since impurity scattering causes electron spin to precess in different direction along $\boldsymbol{k}$-dependent effective fields $\boldsymbol{b}(\boldsymbol{k})$ as momentum scattering rate increases. Hyperfine interaction in the sample investigated is assumed very small to influence spin relaxation due to our failure to get any reasonable ^{13}C NMR signal on the CNS.

2. Theoretical Model

We analyze coupled charge and spin transport on a 2D system using a model of non-interacting electrons described by effective-mass Hamiltonian where electrons move in randomly distributed short-range spin-independent impurity potential. Since strong Rashba spin-orbit in semiconductors can be induced by impurity atoms rather external electric fields, electrons therefore also experience this spin-orbit field in some ranges of temperature [5]. The single-particle Hamiltonian could be used to described this 2D system, $H = H_0 + H_i$ where

$$H_0 = \sum_{k\sigma\sigma'} \left(\frac{\boldsymbol{k^2}}{2m} - \mu + \lambda \hat{z}.[\boldsymbol{\tau_{\sigma\sigma'}} \times \boldsymbol{k}]\right) c^{\dagger}_{k\sigma\sigma'} c_{k\sigma\sigma'} \qquad (1)$$

is the effective-mass Hamiltonian which can be interpreted as coupling of Zeeman to $\boldsymbol{k}$-dependent effective magnetic field. Second term is impurity Hamiltonian,

$$H_i = \int \sum_\sigma V_i(\boldsymbol{r}) \Psi_\sigma^\dagger(\boldsymbol{r}) \Psi_\sigma(\boldsymbol{r}) = \frac{1}{V} \sum_{kk'\sigma} V_i(\boldsymbol{k}-\boldsymbol{k}') c_{k\sigma}^\dagger c_{k'\sigma} \qquad (2)$$

and represents electron scattering with impurity potential $V_i = \mu_0 \sum_a \delta(\boldsymbol{r}-\boldsymbol{r_a})$. When Rashba term in an effective-mass Hamiltonian H_0 is negligible, spin relaxation of degenerate electrons with is dominated by EY mechanism via momentum-scattering (impurities or phonons) and can be represented by a relation,

$$\frac{1}{\tau_s(E_{\boldsymbol{k}})} = K \frac{1}{\tau_k(E_{\boldsymbol{k}})} \qquad (3)$$

where $\tau_k(E_{\boldsymbol{k}})$ is the momentum scattering time at energy $E_{\boldsymbol{k}}$, and K its constant determine by energy gap (assumed finite and small), nature of dominant EY relaxation mechanism via momentum scattering (charged or neutral impurity, phonon or electron-hole).

The relevance of Elliot-Yafet mechanism could be decided by dependence of momentum relaxation time τ_k on levels of doping and/or temperature. Since there is a relationship between momentum scattering τ_k and spin-relaxation time τ_s; temperature and doping dependence of spin-relaxation time in EY mechanism follows that of momentum. Theory describing dependency of spin relaxation on temperature via momentum scattering (impurities, surface and acoustic phonons) have been done using Monte-Carlo simulation on graphene embedded on the SiO_2 substrate [5]. Their analysis of momentum scattering (impurities, surface and acoustic phonons) in the range of temperature investigated showed the dominant of the temperature independent electron-impurity scattering rate and by deductions, the temperature dependence of the overall spin relaxation rate,

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{ac}} + \frac{1}{\tau_{sph}} + \frac{1}{\tau_{imp}}, \qquad (4)$$

is determined by surface and acoustic phonons spin relaxation rates which changes quadratically and linearly with temperature, respectively.

3. Sample preparation

Samples used were prepared in the School of Chemistry at Wits. These nitrogen containing CNS were prepared from burning pyridine (sample-NK6) and mixture of toluene and pyridine in a chemical vapor deposition system(CVD).Sample NK7 and NK9 were prepared by burning 10% and 90% of pyridine plus 90% and 10% of toluene, respectively. Elemental analyses show nitrogen content for these CNS: NK6, Nk7 and NK9 have 5.00, 3.52 and 1.48 percentage of nitrogen content, respectively. Details of the CNS syntheses and characterization can be obtained from N. Kunjuzwa theses [7].

4. Experimental set-up

Continuous wave (cw) ESR measurements were performed using Bruker spectrometer, ESP300E model operating at X-band (~ 9.5GHz) and equipped with a high Q cavity and Oxford continuous flow cryostat variable temperature accessory. The carbon nanospheres (CNS) samples labeled: NK6, NK7 and NK9 contained in an NMR tubes made out of Pyrex which is a type of borosilicate glass that is resistant to heat and chemical reactions. The measurements were taken at low microwave power to avoid ESR signal saturation. Liquid Nitrogen was used to vary the temperature of the sample in the range, 5-300K.

5. Results and Analysis

Temperature dependence of spin-lattice relaxation T_1 or spin relaxation τ_s could qualitatively described in the continuous wave mode ESR by resonance linewidth [6]. Peak-to-peak ESR amplitude of NK9 (not shown in this paper) shows that electrons are localized below about 140K. Therefore different constant peak-to-peak linewidth in this temperature range suggest the presence of different nitrogen paramagnetic impurities with different relaxation rates and dominated in different ranges of temperature shown in the **Fig. 1**. Above 140K, there is no clear relationship between momentum τ_p and spin relaxation time τ_s, this implies the overall spin-relaxation $1/\tau_s$ is the results of a sum of spin

relaxations of individual paramagnetic components whose proportionality with the sum of momentum scatterings(corresponding to different paramagnetic components) does not follow either DP or EY mechanism. Amplitude power saturation (shown in **Fig. 2**) confirms this conjecture; different paramagnetic impurities making the overall resonance line follow the microwave power individually.

Spin relaxation of CNS labelled NK7 and NK6, as shown in **Fig. 3** and **Fig. 4**, are dominated by EY via impurity and acoustic phonon momentum scattering at low temperatures (before a transition temperature is reached).

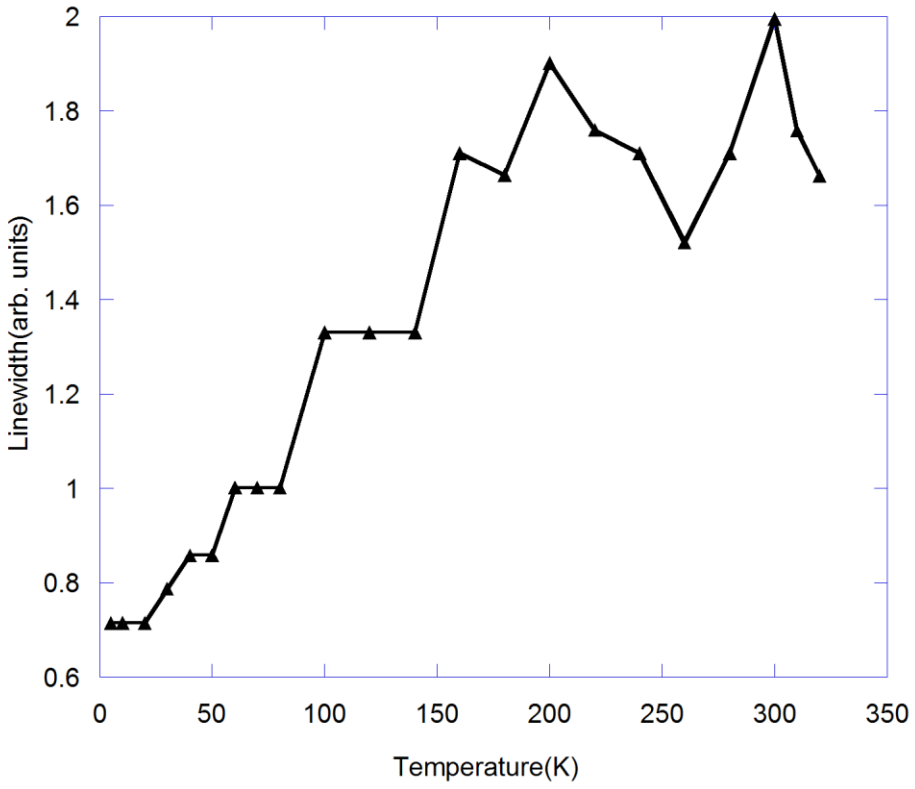

Figure 1. Linewidth describing scattering dominated by different impurities.

As temperature increases a critical temperature (about 180K for NK6 and NK7) is reached whereby dependent of linewidth on temperature is now opposite, this implies another relaxation mechanism starts to dominate. Above the critical temperature (around 180K), DP relaxation mechanisms dominate. At high temperatures, above 200K, the linewidth of both NK6 and NK7 are nearly independent of temperature. Since the DP spin relaxation is limited by spin-orbit strength λ and momentum scattering time τ_k , the weak temperature dependency of DP spin relaxation could be attributed to the perfect counterbalance between λ and τ_k as temperature increases.

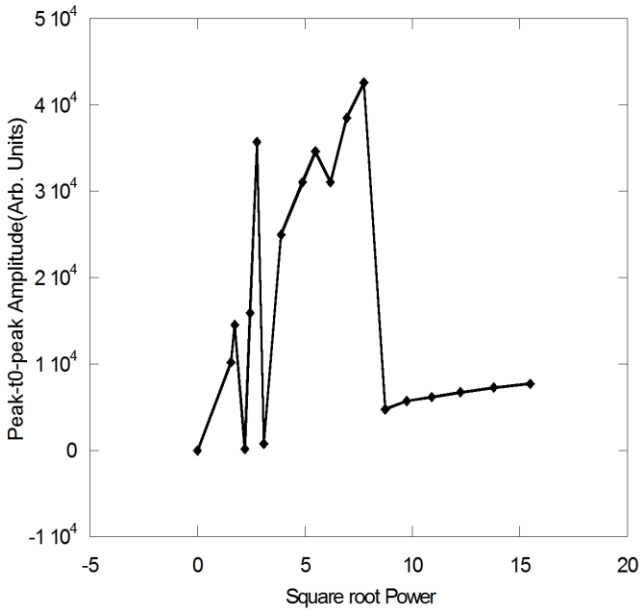

Figure 2. Different paramagnetic impurities follow microwave power individually.

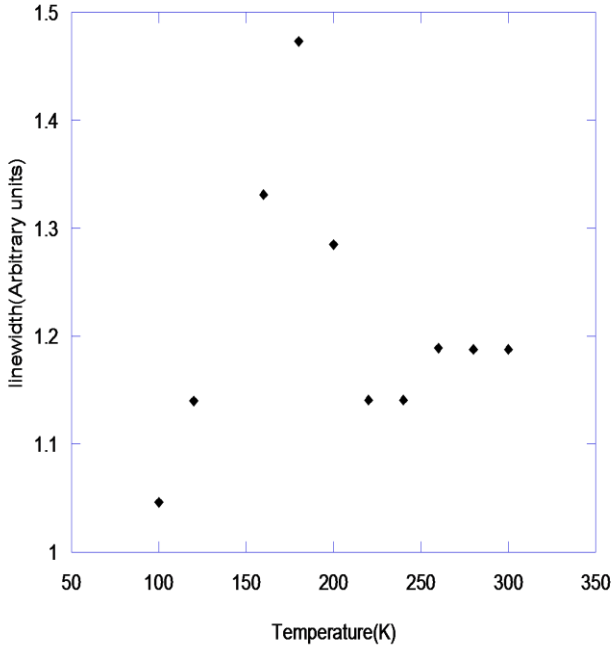

Figure 3. Different relaxation mechanisms dominate in different ranges of temperature.

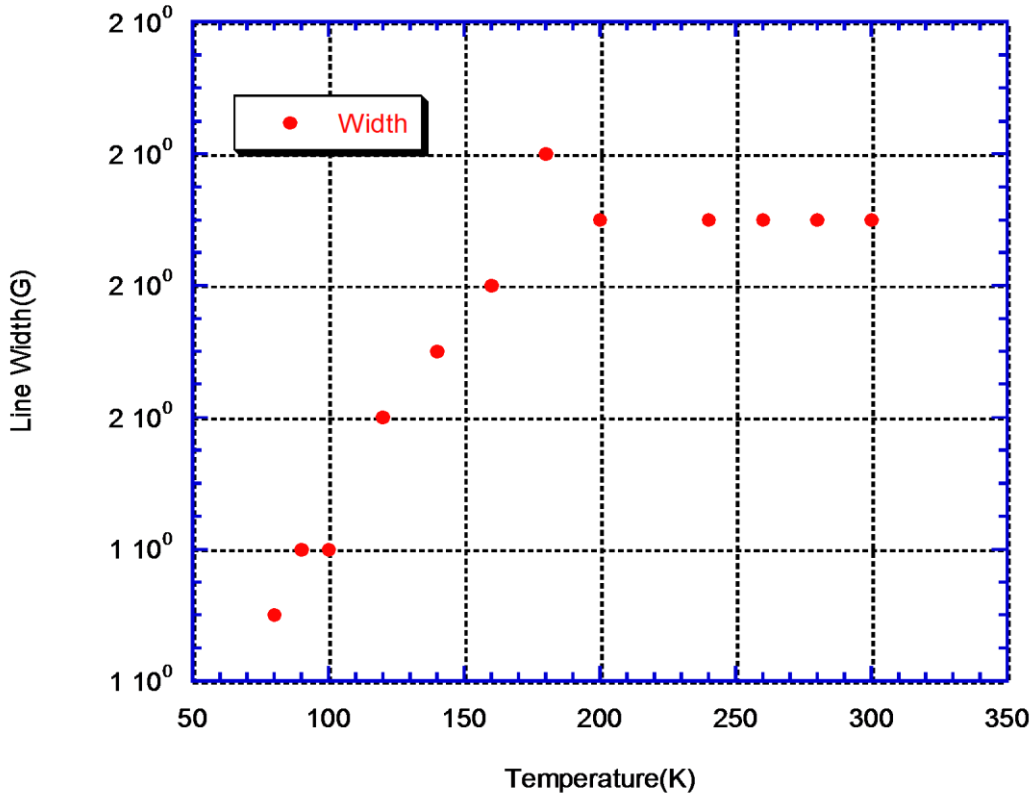

Figure 4. Different relaxation mechanisms dominate in different ranges of temperature.

6. Concluding Summary

The spin transport in CNS shows some similarities in behaviour with model formulated for charge and spin transport in graphene [5]. Our results show that spin relaxation in CNS can be tuned by controlling the amount of nitrogen impurities which seem to induce Rashba spin-orbit field at high temperatures. Since continuous wave mode ESR cannot directly gives accurately spin relaxation times, ESR operating at pulse mode should be used in the whole range of temperature investigated.

7. Acknowledgement

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