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Electron spin dynamics and electron spin resonance in graphene

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A theory of spin relaxation in graphene including intrinsic, Bychkov-Rashba, and ripple spin-orbit coupling is presented. We find from spin relaxation data by Tombros et al. [Nature 448, 571 (2007)] that intrinsic spin-orbit coupling dominates over other contributions with a coupling constant of 3.7 meV. Although it is 1-3 orders of magnitude larger than those obtained from first principles, we show that comparable values are found for other honeycomb systems, MgB2 and LiC6; the latter is studied herein by electron spin resonance (ESR). We predict that spin coherence is longer preserved for spins perpendicular to the graphene plane, which is beneficial for spintronics. We identify experimental conditions when bulk ESR is realizable on graphene.

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Introduction. The discovery of graphene [1] stimulated enormous interest due its fundamentally and technologically important properties. One potential application is in spintronics [2], i.e. when the electron spin degree of freedom is utilized as information carrier. The principal parameter governing spintronic usability is the spin relaxation time (also referred to as spin-lattice relaxation time), \( \tau_s \), which characterizes how an injected non-thermal equilibrium spin state decays. For realistic applications, \( \tau_s \) longer than 10-100 ns is required. A general, often cited concept is that "pure materials made of light elements” can reach this limit. The huge mobility of charge carriers in graphene (approaching \( 10^6 \text{ cm}^2/\text{Vs} \)) is the momentum relaxation time) are proportional: \( \tau_s = \alpha_{\text{DyP}} L^2_{\text{DyP}} / \Gamma \), where \( \alpha_{\text{DyP}} \approx 1 \).

A link between the EY and the DyP was found recently [3]: for metals with inversion symmetry but rapid momentum scattering, the generalization of the EY theory leads to \( \Gamma_s = \alpha_i L^2 / \Delta^2 + 1 \), which gives a DyP like spin relaxation when \( \Gamma > \Delta \).

Three sources of SOC are present in graphene: intrinsic, BR type (due to the symmetry breaking by a perpendicular electric field), and the ripple related (which is due to the inevitable ripples in graphene). However, the role and magnitude of these SOC parameters is a debated issue. For the intrinsic SOC ranges two orders of magnitude; 0.9-200 \( \mu \text{eV} \) [4,5], whereas value of the BR SOC appears to be settled to 10-36 \( \mu \text{eV} \) per \( \mu \text{m} \) (Refs. [6] and [7], respectively). The effect of the substrate for the spin relaxation is also unsettled [8]. Given this debate, a description is required which enables comparison with the spin transport data.

Here, we present the theory of spin relaxation in graphene including intrinsic, BR, and ripple spin-orbit coupling. We analyze the spin transport data from Refs. [6,7,18] and we find that the intrinsic SOC dominates the relaxation with a large, unexpected magnitude. We discuss two similar honeycomb systems; MgB2 and LiC6, and show that they exhibit similar intrinsic SOC. The result predicts a strong anisotropy of the spin relaxation time. We study the feasibility of bulk electron spin resonance (ESR) spectroscopy on graphene and pinpoint experimental conditions when it is possible. ESR would allow a direct, spectroscopic measurement of \( \tau_s \) (Ref. [19]), which underlines its importance [20].

Experimental. We prepared Li intercalated HOPG graphite by the "immersion into molten Li” method [21]. The golden color of the samples attested the LiC6 intercalation level [22]. Freshly cleaved samples were sealed under He in quartz tubes for the ESR experiment.

Spin relaxation in graphene. Low energy excitations around the \( K \) point of the Brillouin zone are described by a two-dimensional Dirac equation:

\[
H = v_F (\sigma_x p_x + \sigma_y p_y),
\]
with the $v_F \approx 10^6$ m/s Fermi velocity [1]. The spin-orbit interaction in graphene is given by [14]:

$$H_{SO} = L_i \sigma_z S_z + \frac{L_{BR} + L_{\text{ripple}}(r)}{2}(\sigma_x S_y - \sigma_y S_x),$$

(2)

where $L_i$, $L_{BR}$, and $L_{\text{ripple}}$ are the SOC’s of the intrinsic, BR, and ripple terms, respectively. $L_{\text{ripple}}(r)$ is Gaussian correlated random variable, $\langle L_{\text{ripple}}(r)L_{\text{ripple}}(r') \rangle \sim \delta (r - r')$.

The spin relaxation rates induced by these SOC’s are additive in lowest order provided $\max(L_i, L_{BR}, L_{\text{ripple}}) \ll \max(\Gamma, \mu)$:

$$\Gamma_s = \Gamma_{s,i} + \Gamma_{s,\text{BR}} + \Gamma_{s,\text{ripple}}$$

(3)

The contributions from the intrinsic ($\Gamma_{s,i}$), BR ($\Gamma_{s,\text{BR}}$), and ripple ($\Gamma_{s,\text{ripple}}$) relaxation rates are obtained using the Mori-Kawasaki formula similar to that used in Ref. [23] considering the conical band structure and the $K$, $K'$ degeneracy:

$$\Gamma_{s,i} = \delta_{\nu,||} \frac{L_i^2}{2\pi \mu \Gamma} \arctan(\mu / \Gamma),$$

(4)

$$\Gamma_{s,\text{BR}} = \frac{(2\delta_{\nu,||} + \delta_{\nu,\perp}) L_{\text{BR}}^2}{16 \pi \mu \Gamma} \left[ 1 + \left( \frac{\mu}{\Gamma} + \frac{\mu}{\Gamma} \right) \arctan \left( \frac{\mu}{\Gamma} \right) \right],$$

(5)

$$\Gamma_{s,\text{ripple}} = \frac{(2\delta_{\nu,||} + \delta_{\nu,\perp}) \pi}{32} L_{\text{ripple}}^2 \rho(\mu, \Gamma)$$

(6)

$\nu = ||$, or $\perp$ is the spin polarization direction with respect to the graphene plane; e.g. $\nu = ||$ in the spin transport experiments [6]. Here, $\mu$ is the chemical potential and $\mu(\mu, \Gamma) = -\frac{e}{\hbar} \ln \left( \frac{\mu^2 + \mu^2}{\mu^2} \right) + |\mu| \left( 1 - \frac{\pi}{2} \arctan \left( \frac{\mu}{\Gamma} \right) \right)$ is the pseudo chemical potential ($D \approx 3$ eV is the cutoff in the continuum theory) which appears in the expression of the density of states (DOS), $\rho(\mu, \Gamma)$, with finite $\mu$ and $\Gamma$:

$$\rho(\mu, \Gamma) = \frac{2A_c \mu^2}{\pi \hbar^2 v_F^2}$$

(7)

with $A_c = 5.24 A^2/(2 \text{ atoms})$ being the elementary cell and $\rho(\mu, \Gamma)$ is measured in units of states/eV·atom.

The intrinsic contribution disappears when spins are polarized perpendicular to the plane and the BR and ripple terms have a 2:1 anisotropy for the $||$ directions. For the intrinsic part, $\Gamma_{s,i} \approx \frac{L_i^2}{2\pi \mu \Gamma} \Gamma$ when $\mu \gg \Gamma$, which is an Elliott-Yafet like result with $\alpha_i = 1$ since the band-band separation, $\Delta = 2\mu$. In the vicinity of the Dirac point, DP, (i.e. $\mu \approx 0$ and $\Gamma$ finite) it returns a Dyakonov-Perel like result of $\Gamma_{s,i} = \frac{L_i^2}{4 \ln(\mu / \Gamma)}$. This is in agreement with the generalized Elliott-Yafet theory which predicts a similar crossover when the momentum scattering rate overcomes other energy scales [13]. Interestingly, the intrinsic contribution can be well fitted with a Lorentzian: $\Gamma_{s,i} \approx \alpha_i \frac{L_i^4}{\pi \mu^2 \Gamma^2}$, where $\alpha_i \approx 0.2..0.4$ and $\Gamma / \Gamma \approx 1..2$ for typical values of $\mu$ and $\Gamma$.

The BR term is only present if a perpendicular electric field, $E$, is applied, which induces a BR SOC of $L_{BR} = \kappa E$ with $\kappa$ values between 10 [15] and 36 μeV/(V nm) [14]. The electric field changes $\mu$ through: $\mu = \sqrt{n \pi \hbar^2 v_F^2}$ where $n = \beta E$ is the carrier density and $\beta = 0.22$ (V·nm)$^{-1}$ for SiO$_2$ gate insulator [24]. This yields the BR SOC as a function of $\mu$: $L_{BR}(\mu) \propto \kappa \mu^2 \cdot \frac{\sqrt{\mu}}{\sqrt{\hbar^2 v_F^2}}$.

The ripple relaxation contribution depends on $\Gamma$ only if $\mu \ll \Gamma$, where it resembles an EY relaxation: $\Gamma_{s,\text{ripple}} \propto L_{\text{ripple}}^2 \Gamma \ln(\mu / \Gamma)$.

Analysis of the spin transport data. In the following, we analyze the available spin transport data [6, 7, 18] in the framework of the above calculation. Values of $\tau_z = 60..125$ ps were found around the charge neutrality point (depending on the sample), with a typical $\Gamma \approx 75$ meV [18]. Fig. 1 shows the measured and calculated spin relaxation rate data for $\nu = ||$: $\Gamma = 75$ meV, that is independent of $\mu$, was used for the calculated curves. First principles calculations of the intrinsic SOC scatter more than two orders of magnitude with values of $0.9 \mu$eV [14] 250, 24 μeV [15], and 200 μeV [16]. Values for the BR SOC, $L_{BR} = \kappa E$, vary between $\kappa = 10..36 \mu$eV/(V nm). This gives rise to the minimal
and maximal estimates for both types of the contributions as shown in Fig. 1. The ripple SOC was estimated to be 17 µeV in Ref. [14].

Clearly, the first principles based relaxation rates fall short of explaining the experimental observation. Of the three contributions, only the intrinsic one has a µ dependence that mimics the experiment, whereas the other two shows the opposite. It may appear that a fit to the data is ill defined, given the relatively large number of free parameters (Γ and 3 L’s). However to our surprise, the fit consistently yields the same, robust set of parameters, irrespective of starting values or the method used (least squares fitting or combined with a simulated annealing), which are: \( L_i = 3.7(1) \) meV, \( L_{BR} = L_{ripple} = 0 \), \( \Gamma = 120(5) \) meV. This robustness originates from the qualitative difference between the µ dependence of the different contributions. The obtained values satisfy the criterion for the perturbative approach and the value of Γ determined herein is in agreement with that obtained in Ref. [18].

The intrinsic SOC opens a bandgap of \( L_i \) in the excitation spectrum [15, 16] therefore it is natural to ask: why is not this gap observed experimentally? Two interrelated answers are in order: first, best quality samples to date are ballistic only in order: first, best quality samples to date are ballistic on the submicron scale, giving a momentum scattering rate of the order of meV’s (or bigger), which can mask the gap [27]. Second, charge inhomogeneities (the so-called puddles) prevent us from reaching the Dirac point, the average minimal charge density is estimated [28] as \( 10^{-3} \) cm\(^{-2} \), which gives an average \( \mu \sim 4 \) meV, capable of overwhelming the obtained gap.

The present analysis allows for the design of graphene based spintronic devices. For spins polarized perpendicular to the graphene plane, the intrinsic contribution vanishes thus resulting in a substantially longer spin relaxation time. For spins polarized in the graphene plane, Fig. 1 shows that around the Dirac point purer samples (i.e. smaller Γ) decreases \( \tau_s \) rather than increasing it, thus deteriorating performance. This, somewhat counterintuitive phenomenon, is the consequence of the Dyakonov-Perel like behavior of the intrinsic contribution around the DP.

The large value obtained for the intrinsic SOC is surprising as it is an order of magnitude larger than the largest theoretical estimate [15] and up to 3 orders of magnitude larger than other results [14, 25, 26]. However, given that the experimental µ dependence of \( \Gamma_i \) dictates the dominant role of the intrinsic coupling, \( L_i \) yields necessarily a large value. In the following, we consider two similar systems, MgB\(_2\) and Li doped graphite and show that therein similar values of the intrinsic coupling are obtained.

In MgB\(_2\), the boron atoms form a honeycomb lattice with four p-shell electrons, such as in graphene, which highlights the similarity of the two materials. Therein, an intrinsic SOC of \( L_i(\text{MgB}_2) = 2.8 \) meV of the \( \pi \) orbitals was found [23]. It was shown by Grüneis and coworkers [29] and confirmed [30] that alkali atom intercalated graphite is an excellent model system of biased graphene as the two-dimensional electron dispersion is retained due to the weak interlayer coupling. The Li intercalated stage I graphite compound LiC\(_6\) [22] is particularly suitable to determine the intrinsic SOC as Li is the lightest alkali metal and its contribution to the spin relaxation is undetectable [4].

In Fig. 2, we show the temperature dependent ESR linewidth, \( \Delta B \), for an HOPG LiC\(_6\) along with previous data on a powder LiC\(_6\) sample [31] and schematics of the band structure. A linear fit to the data yields \( \Delta B = 0.205 \) [mT] + \( T \times 6 \cdot 10^{-5} \) [mT/K]. Of these terms, the temperature dependent one is associated with the homogeneous broadening, \( \Delta B_{hom} \), due to SOC, which gives \( \Gamma_{hom} = gB\mu_B\Delta B_{hom} \) (\( g \approx 2 \) is the g-factor, \( \mu_B \) is the Bohr magneton) and is \( \Gamma_s = 2.1 \cdot 10^{-3} \) eV at 300 K. Since Li doped graphite resembles biased graphene [29, 30], the above theory of the intrinsic SOC applies, i.e. \( \Gamma_i = \frac{\pi}{2} \Gamma_s \). With the values of \( \Delta = 1.65 \) eV [30] and a typical \( \Gamma(300 \text{ K}) = 4.4 \) meV [22], we obtain \( L_i(\text{LiC}_6) = 1.1 \) meV. Although it is debated whether SOC in graphite is applicable for graphene [14], the similar result for these three systems leads us to conclude that the intrinsic SOC is properly determined in graphite.

**Detectability of ESR on graphene.** With the SOC parameters and the theory of spin relaxation at hand, we assess the feasibility of ESR spectroscopy on graphene. It is determined by the sample amount, the magnitude of the spin-susceptibility, and the ESR linewidth. The ESR signal is proportional to the amount of magnetic moments: \( \chi_0 VB/\mu_0 \) where \( B \) is the magnetic field, \( \chi_0 \) is the volume spin-susceptibility (dimensionless in SI units), \( V \) is the sample volume, and \( \mu_0 \) is the permeability of vacuum. For graphene with area \( A \), the amount of magnetic moments is \( \chi_{0,gr}AB/\mu_0 \) with \( \chi_{0,gr} \) having a unit of meters. The Pauli spin-susceptibility of graphene is \( \chi_{0,gr} = \mu_0B^2(\mu, \Gamma)/\pi^2N \), \( N \) is the number of carbons and the DOS, \( \rho(\mu, \Gamma) \), is given above.

ESR spectrometer performance is given by the limit-of-
FIG. 3: Limit of ESR detection for graphene as a function of $\mu$ and $\Gamma$ in units of the graphene area (upper panel) for an in-plane magnetic field. Arrows show the maximum chemical potential by gate bias and by chemical doping and solid curve indicate the 100 mm$^2$ area border. Expected ESR linewidth, $\Delta B_1$ (lower panel), solid lines show two selected linewidths, 1 and 10 mT.

development (LOD$_0$) i.e. the number of $S = 1/2$ non-interacting spins at 300 K which give a signal-to-noise of $S/N = 10$ ratio for $\Delta B = 0.1$ mT linewidth, and 1 sec/spectrum-point time constant. For state-of-the-art spectrometers LOD$_0 = 10^{10}$ spins/0.1 mT. The spin-susceptibility of such spins is $\chi_{\text{Curie}} = \frac{\mu_0 \mu_B^2}{2}(\hbar g\tau)$, where $N_s$ spins occupy a volume of $V$, which gives an LOD for graphene:

$$\text{LOD}_{gr} = \text{LOD}_0 \cdot \frac{f(\Delta B)}{26 \text{ meV} \times \rho(\mu, \Gamma)} \quad (8)$$

in units of number of carbons. Here, 26 meV is the thermal energy at 300 K and the $f(\Delta B = 0.1 \text{ mT}) = 1$ function describes that the ESR $S/N$ decreases as $1/\Delta B$ if $\Delta B < 1$ mT (the typical magnetic field modulation limit) and as $1/(\Delta B)^2$ if $\Delta B \geq 1$ mT. For $\mu > \Gamma$, the DOS is well approximated by $\rho(\mu) = 0.0385\mu^2/\text{states/eV atom}$ which yields a compact result: $\text{LOD}_{gr} \approx 1000 \text{LOD}_0 \cdot f(\Delta B)/\mu$ with $\mu$ in eV units.

Clearly, a sizeable DOS and narrow linewidth are prerequisites to observe ESR on graphene. Large DOS can be achieved by moving $\mu$ away from the DP or by inducing defects. The latter yields, however, increased scattering thus larger linewidth. Shifting $\mu$ by a gate bias is limited to $\sim 0.2$ eV due to breakdown in the most common SiO$_2$ insulator around $E \approx 0.1$ V/mm. With chemical doping using K, up to $\mu \sim 1.35$ eV can be achieved [29]. The ESR linewidth is expected to be strongly anisotropic with a minimum, $\Delta B_1$, for a perpendicular magnetic field, its magnitude however remains unknown. In Fig. 3, we show the calculated LOD for graphene as a function of $\mu$ and $\Gamma$ in units of the graphene area along with the calculated linewidth for an in-plane magnetic field. The LOD can be two orders of magnitude smaller for a perpendicular magnetic field if the corresponding ESR linewidth is an order of magnitude smaller. Therefore ESR experiments should be attempted with the perpendicular orientation first. This experiment would yield directly the magnitude of the BR and ripple relaxation contributions from $\Delta B_1$.

An important benchmark, that indeed the intrinsic ESR signal of graphene is observed, is an angular dependence of the ESR linewidth: $\Delta B(\theta) = \sin^2(\theta) \Delta B_1 + \cos^2(\theta) \Delta B_2$ as a function of the azimuth angle, $\theta$. Finally, we note that the anisotropy could reconcile the narrow ESR linewidth in the perpendicular geometry [20] with the short $\tau_s$ in the spin transport experiment [6].

In conclusion, we presented a theory of spin relaxation in graphene which takes into account intrinsic, Bychkov-Rashba, and ripple spin-orbit coupling induced spin relaxation. Analysis of spin relaxation data show that the intrinsic contribution dominates the relaxation with a coupling constant that is orders of magnitude larger than theoretical estimates but it is not unusually large compared to other honeycomb systems. The result predicts a large anisotropy of the spin relaxation. We presented under what circumstances bulk ESR spectroscopy can be observed in graphene.

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