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Magnetic Moment Formation in Graphene Detected by Scattering of Pure Spin Currents

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Abstract

Hydrogen adatoms are shown to generate magnetic moments inside single layer graphene. Spin transport measurements on graphene spin valves exhibit a dip in the non-local spin signal as a function of applied magnetic field, which is due to scattering (relaxation) of pure spin currents by exchange coupling to the magnetic moments. Furthermore, Hanle spin precession measurements indicate the presence of an exchange field generated by the magnetic moments. The entire experiment including spin transport is performed in an ultrahigh vacuum chamber, and the characteristic signatures of magnetic moment formation appear only after hydrogen adatoms are introduced. Lattice vacancies also demonstrate similar behavior indicating that the magnetic moment formation originates from p_z -orbital defects.

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Many fascinating predictions have been made regarding magnetism in graphene including the formation of magnetic moments from dopants, defects, and edges [1–8]. While several experimental techniques provide insight into this problem [9–21], lack of clear evidence for magnetic moment formation hinders development of this nascent field. Studies based on bulk magnetometry [9–16] directly measure magnetic properties, but because it measures the total magnetic moment (not just the signal from graphene) it is difficult to rule out artifacts from environmental magnetic impurities. Transport [17–19] and scanning tunneling microscopy (STM) [20, 21] locally probe the graphene, but so far these measurements have been charge-based, so data are subject to various interpretations [22]. Thus, in order to convincingly demonstrate the formation of magnetic moments inside graphene due to dopants and defects, it is essential to employ techniques that directly probe the intrinsic spin degree-of-freedom of the magnetic moment while ensuring the signal originates from the graphene sheet under investigation.

In this Letter, we utilize pure spin currents to demonstrate that hydrogen adatoms and lattice vacancies generate magnetic moments in single layer graphene. Pure spin currents are injected into graphene spin valve devices and clear signatures of magnetic moment formation emerge in the non-local spin transport signal as hydrogen adatoms or lattice vacancies are systematically introduced in an ultrahigh vacuum (UHV) environment. Specifically, introduction of these point defects generate a characteristic dip in the non-local signal as a function of magnetic field. This feature is due to scattering (relaxation) of pure spin currents by localized magnetic moments in graphene and is explained quantitatively by a phenomenological theory based on spin-spin exchange coupling between conduction electrons and magnetic moments. Furthermore, we observe effective exchange fields due to this spin-spin coupling, which are of interest for novel phenomena and spintronic functionality [23–26] but have not been seen previously in graphene. Thus, these results provide the most clear and direct evidence for magnetic moment formation in graphene and demonstrate a method for utilizing localized magnetic moments to manipulate conduction electron spins.

For a systematic investigation, the spin transport measurement is first performed on a pristine single layer graphene (SLG) spin valve as a control measurement. Then, dopants/defects are controllably introduced to the SLG and the measurement is repeated. The sample remains in UHV during the entire process. Therefore, observed signatures of magnetic moment formation are caused by the adsorbed hydrogen or lattice vacancies.

Experiments are performed on non-local SLG spin valves [27–29] (Fig. 1a) consisting of two outer Au/Ti electrodes (a and d) and two ferromagnetic (FM) Co electrodes that make contact to SLG across MgO/TiO₂ tunnel barriers (b and c). The Co electrodes are capped with 5 nm Al₂O₃ to protect from hydrogen exposure. The tunnel barrier and capping layer are present only at the site of the FM electrodes, leaving the rest of the graphene uncovered. The device is fabricated on a SiO₂/Si substrate (300 nm thickness of SiO₂) where the Si is used as a back gate. Details of device fabrication are published elsewhere [29].

The charge and spin transport properties of pristine SLG spin valves are measured at 15 K using lock-in techniques. The gate dependent resistivity (ρ_G) of a representative sample A (black curve in Fig. 1b) exhibits a maximum at the gate voltage (V_G) of 0 V, which defines the Dirac point ($V_D = 0$ V). This sample exhibits mobility (μ) of 6105 cm²/Vs. To investigate spin transport in the SLG device (Fig. 1a), a current (I) is applied between electrodes b and a, injecting spin-polarized carriers into graphene directly below the FM injector, b. The spin population diffuses along the sample as a pure spin current (x -axis) and the spin density is measured at the FM spin detector, c, as a voltage difference (V) between electrodes c and d. An applied magnetic field ($B_{app,y}$) along the electrode magnetization direction (y -axis) is used to control the relative orientation of spin injector and detector magnetizations. For parallel alignment, the measured non-local resistance ($R_{NL} = V/I$) is positive whereas for antiparallel alignment R_{NL} is negative. The non-local spin signal is defined as the difference between parallel and antiparallel states ($\Delta R_{NL} = R_{NL}^P - R_{NL}^{AP}$). A typical scan of R_{NL} as a function of $B_{app,y}$ (Fig. 1c) displays discrete jumps as the electrode orientation changes between parallel and antiparallel. This sample exhibits a ΔR_{NL} of 8.8 Ω (sample A with $V_G - V_D = -15$ V). A constant spin-independent background is subtracted from all R_{NL} data presented in this study. Out-of-plane magnetic fields are applied to generate spin precession, and the resulting data (Fig. 1d, red for parallel, blue for antiparallel) are fit by the standard Hanle equation [28, 29] (solid curves) to determine the spin lifetime ($\tau_{so} = 479$ ps) and diffusion coefficient ($D = 0.023$ m²/s). The corresponding spin diffusion length is $\lambda = \sqrt{D\tau_{so}} = 3.3$ μm . Based on these values and a non-local spin signal of 8.8 Ω , the spin polarization of the junction current (P_J) is calculated to be 20% [30, 31].

Atomic hydrogen is introduced to spin valve devices at 15 K at a chamber pressure of 1×10^{-6} torr [31]. Following 2 s hydrogen exposure, the gate dependent ρ_G (red curve in Fig. 1b) is dramatically increased. An additional 6 s of exposure (8 s total) further increases

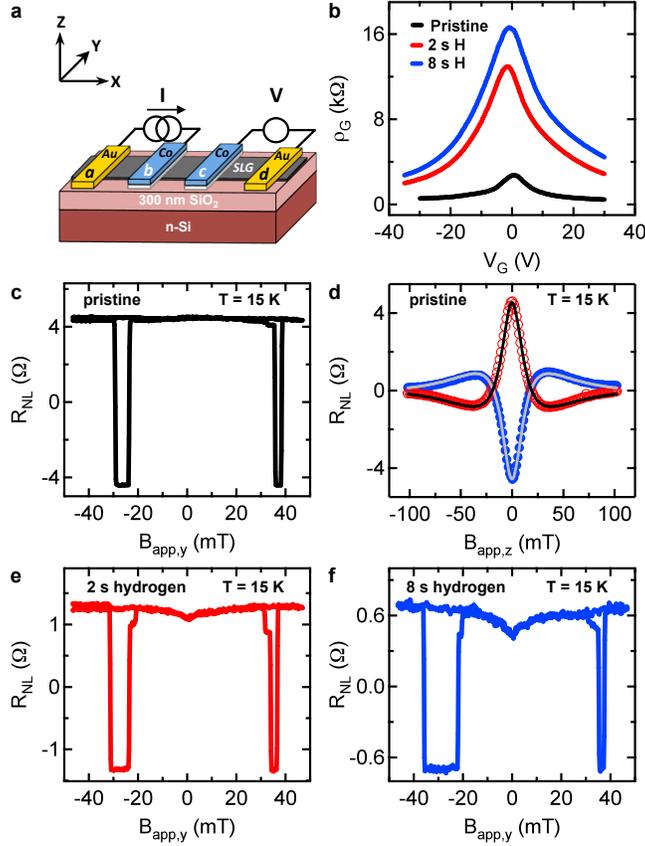


FIG. 1. The effect of hydrogen exposure on charge and spin transport in SLG at 15 K. (a) Schematic illustration of the non-local spin valve device. (b) Gate dependent resistivity for the pristine graphene (black) and following exposure to atomic hydrogen for 2 s (red) and 8 s (blue). Upon hydrogen doping, the Dirac point shifts from 0 V to -1 V. (c) Non-local spin transport measurement for pristine graphene. (d) Hanle spin precession measurement on pristine graphene. (e,f) Non-local spin transport measurements after atomic hydrogen exposure for 2 s and 8 s, respectively. Both curves exhibit a dip in R_{NL} at zero applied field, which is caused by spin relaxation induced by localized magnetic moments.

ρ_G (blue curve of Fig. 1b) and decreases the mobility to $495 \text{ cm}^2/\text{Vs}$. Based on the change in the resistivity, we make an order of magnitude estimate for the hydrogen coverage of 0.1% [31]. Accompanying the changes in charge transport are also changes in spin transport. Figures 1e and 1f display R_{NL} of sample A at $V_G - V_D = -15 \text{ V}$ as a function of $B_{app,y}$ following 2 s and 8 s of exposure, respectively. The initial ΔR_{NL} of $8.8 \text{ } \Omega$ is reduced to $2.6 \text{ } \Omega$ after 2 s of hydrogen exposure and further reduced to $1.4 \text{ } \Omega$ after 8 s. Interestingly, the

R_{NL} scans exhibit a dip centered at zero applied field. The dip in R_{NL} is prevalent for both up and down sweeps of $B_{app,y}$ at all measured gate voltages and has been reproduced on multiple samples following hydrogen exposure. The ratio of the dip magnitude to ΔR_{NL} is found to increase with increasing hydrogen exposure (comparing Fig. 1e and 1f), indicating the dip feature is dependent on the amount of adsorbed hydrogen.

To understand the origin of the dip in R_{NL} , we examine the expression for non-local resistance generated by spin transport [30],

$$R_{NL}^{(P/AP)} = \pm 2R_G e^{-L/\lambda} \prod_{i=1}^2 \left(\frac{P_J \frac{R_i}{R_G}}{1 - P_J^2} + \frac{P_F \frac{R_F}{R_G}}{1 - P_F^2} \right) \times \left[\prod_{i=1}^2 \left(1 + \frac{2 \frac{R_i}{R_G}}{1 - P_J^2} + \frac{2 \frac{R_F}{R_G}}{1 - P_F^2} \right) - e^{-2L/\lambda} \right]^{-1} \quad (1)$$

where $R_G = \rho_G \lambda / w$ is the spin resistance of graphene, w is the graphene width, $R_F = \rho_F \lambda_F / A_J$ is the spin resistance of the cobalt, ρ_F is the cobalt resistivity, λ_F is the cobalt spin diffusion length, A_J is the junction area, P_F is the spin polarization of cobalt, R_1 and R_2 are the contact resistances of the spin injector and detector, respectively, and L is the distance from injector to detector. This equation shows that the spin density at the detector electrode depends on both charge and spin properties. First, we confirm that the SLG resistivity does not change with magnetic field, so the dip is not related to changes in charge transport [31]. Second, we verify that the dip is not related to hydrogen-induced changes to the magnetic properties of the FM electrodes. Specifically, the effect of hydrogen exposure is reversible upon thermal cycling to room temperature and the anisotropic magnetoresistance of the Co electrodes are not affected by hydrogen exposure [31]. Next, we perform minor loop analysis on sample B (Fig. 2a) by reversing the magnetic field sweep immediately after the first magnetization reversal. The inversion of the dip in the antiparallel state (red curve) proves that the dip is due to increased spin relaxation at low fields. Furthermore, we rule out hyperfine coupling to nuclear spins as the origin of this increased spin relaxation [31].

As we discuss in the following, emergence of the dip following hydrogen adsorption identifies magnetic moment formation in graphene. The dip in R_{NL} is a characteristic feature of spin relaxation from exchange coupling with localized magnetic moments, and can be illustrated from a simple textbook example of two coupled spins in a magnetic field. The Hamiltonian is given by $H = A_{ex} \vec{S}_e \cdot \vec{S}_M + g_e \mu_B \vec{S}_e \cdot \vec{B}_{app} + g_M \mu_B \vec{S}_M \cdot \vec{B}_{app}$, where \vec{S}_e is the conduction electron spin, \vec{S}_M is the spin of the magnetic moment, g_e and g_M are the

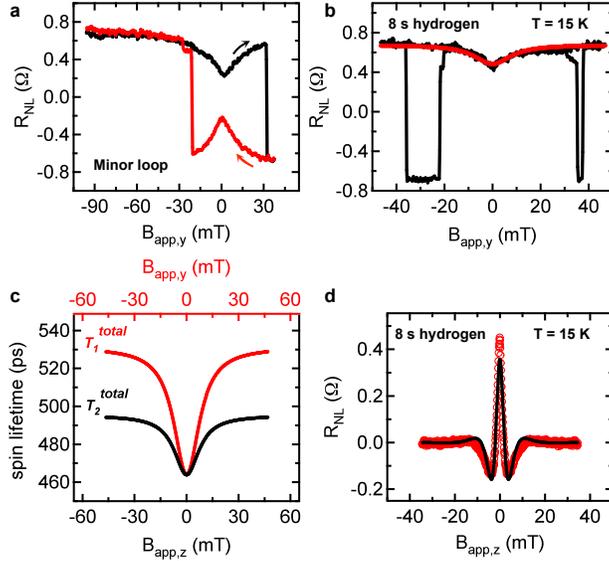


FIG. 2. (a) A minor loop scan shows that the dip in R_{NL} for parallel alignment (black) becomes a peak for antiparallel alignment (red), indicating the feature is due to increased spin relaxation, as opposed to an artifact of the background level. (b) Fitting the dip in R_{NL} based on the model of spin relaxation by paramagnetic moments (data in black, fit in red). (c) Field dependence of longitudinal (red) and transverse (black) spin lifetimes. (d) Hanle precession data following 8 s hydrogen exposure (red) is fit using equation 3 (black curve).

respective g -factors, and A_{ex} is the exchange coupling strength [32, 33]. Due to the presence of the exchange coupling, the individual spins are not conserved; only the total spin $\vec{S}_{tot} = \vec{S}_e + \vec{S}_M$ is conserved. For the case where both \vec{S}_e and \vec{S}_M are spin- $\frac{1}{2}$, the quantum mechanical eigenstates in zero magnetic field are the well-known singlet ($S_{tot} = 0$) and triplet ($S_{tot} = 1$) spin states [34]. At higher magnetic fields the Zeeman terms dominate and the two spins decouple so that the magnitudes and z -components of \vec{S}_e and \vec{S}_M become good quantum numbers, similar to the Paschen-Back effect [34]. Thus, the dip in R_{NL} is qualitatively explained by the non-conservation of \vec{S}_e at low fields due to the presence of exchange coupling with magnetic moments.

To quantitatively analyze the experimental data, we must consider that a conduction electron will interact with many localized magnetic moments. Thus, the terms in the Hamiltonian involving the conduction electron are given by $H_e = \eta_M A_{ex} \vec{S}_e \cdot \langle \vec{S}_M \rangle + g_e \mu_B \vec{S}_e \cdot \vec{B}_{app} = g_e \mu_B \vec{S}_e \cdot (\vec{B}_{ex} + \vec{B}_{app})$ where η_M is the filling density of magnetic moments. The averag-

ing $\langle \dots \rangle$ is over the ensemble of magnetic moments and the effective field generated by the exchange interaction is $\overline{\vec{B}}_{ex} = \frac{\eta_M A_{ex} \langle \vec{S}_M \rangle}{g_e \mu_B}$. As the spins diffuse through the lattice they experience varying magnetic moments which results in varying Larmor frequencies. In the local frame associated with the electrons this can be described by a time-dependent, randomly fluctuating magnetic field, $\vec{B}_{ex}(t) = \overline{\vec{B}}_{ex} + \Delta \vec{B}_{ex}(t)$. For the R_{NL} measurements, the longitudinal spin relaxation due to a fluctuating field is given by [35],

$$\frac{1}{\tau_1^{ex}} = \frac{(\Delta B)^2}{\tau_c} \frac{1}{\left(B_{app,y} + \overline{B}_{ex,y}\right)^2 + \left(\frac{\hbar}{g_e \mu_B \tau_c}\right)^2} \quad (2)$$

where ΔB is the rms fluctuation and τ_c is the correlation time [31]. The spin relaxation rate due to the exchange field is described by a Lorentzian curve which depends explicitly on the applied field, $B_{app,y}$, resulting in strong spin relaxation at low fields and suppressed spin relaxation at high fields. Due to the presence of $\overline{B}_{ex,y}$ in equation 2, ferromagnetic ordering will produce a dip in R_{NL} that is centered away from zero and is hysteretic, while paramagnetic ordering will produce a non-hysteretic dip centered at zero field. Thus, the magnetic moments measured in these experiments are paramagnetic. The total longitudinal spin lifetime, T_1^{total} , of conduction electrons is dependent on both the usual spin relaxation due to spin orbit coupling (τ_{so}) and longitudinal spin relaxation from the exchange field (τ_1^{ex}), such that $(T_1^{total})^{-1} = (\tau_1^{ex})^{-1} + (\tau_{so})^{-1}$. We apply the above model to the non-local spin transport data presented in Fig. 1f (sample A) and fit using equation (1), $\lambda = \sqrt{DT_1^{total}}$, and equation (2) [31]. The resulting fit (red line in Fig. 2b) replicates the shape and magnitude of the dip measured in R_{NL} (black line in Fig. 2b). The field dependent T_1^{total} (Fig. 2c), exhibits a minimum of 464 ps at zero field and increases asymptotically towards $\tau_{so} = 531$ ps for large $B_{app,y}$. The values obtained for ΔB and τ_c are 6.78 mT and 192 ps, respectively. The field-dependent spin relaxation following atomic hydrogen exposure, which emerges as a dip in R_{NL} , is a clear signature of paramagnetic moment formation.

Spin precession measurements provide further evidence for the presence of magnetic moments. Figure 2d shows spin precession data for sample A (8 s exposure, $V_G - V_D = -15$ V) with FM electrodes in the parallel alignment state. The Hanle curve has considerably narrowed compared to the precession measurements obtained prior to hydrogen adsorption (Fig. 1d). The sharpening of the Hanle curve results from the presence of an exchange field. The injected spins precess around a total field $B_{tot} = B_{app,z} + \overline{B}_{ex,z}$ (along z -axis) that includes not only the applied field, but also the exchange field from the paramagnetic mo-

ments. At 15 K and $B_{app,z} < 100$ mT, the magnetization is proportional to the applied field so that $\overline{B}_{ex,z} = kB_{app,z}$, where k is a proportionality constant. Thus, the spins precess about B_{tot} with frequency $\omega = g_e\mu_B B_{tot}/\hbar = g_e(1+k)\mu_B B_{app,z}/\hbar = g_e^*\mu_B B_{app,z}/\hbar$. To properly account for the enhanced g -factor induced by the magnetic moments, the Hanle equation must be modified to

$$R_{NL} = S \int_0^\infty \frac{e^{-L^2/4Dt}}{\sqrt{4\pi Dt}} \cos\left(\frac{g_e^*\mu_B B_{app,z}t}{\hbar}\right) e^{-t/T_2^{total}} dt \quad (3)$$

where T_2^{total} is the transverse spin lifetime. As shown in Fig. 2c, the T_2^{total} is related to, but different from T_1^{total} [31]. Using the field dependent T_2^{total} , the precession data (red circles of Fig. 2d) is fit to equation 3 (black line) to yield a value of $g_e^* = 7.13$. Physically, $g_e^* > 2$ corresponds to an enhanced spin precession frequency resulting from the exchange field. A detailed discussion of the Hanle fitting and the gate-dependent properties of the exchange field are provided in the supplementary information [31]. The dramatic narrowing of the Hanle peak combined with the emergence of a dip in R_{NL} provides the most direct evidence to date for the formation of magnetic moments in graphene due to the adsorption of atomic hydrogen.

We now turn our attention to lattice vacancy defects in graphene. Several theoretical works suggest the similarity of magnetism due to vacancies and hydrogen-doping [1, 4], as both should create magnetic moments inside graphene due to the removal/hybridization of p_z orbitals. To produce lattice vacancies in pristine SLG spin valves, we perform Ar-sputtering at low energies and examine the subsequent non-local spin transport. We again observe the emergence of a dip in R_{NL} and narrowed Hanle curve, indicating the formation of paramagnetic moments in graphene [31]. Given the very different chemical and structural properties of lattice vacancies compared to adsorbed hydrogen, the observation of similar features in the spin transport data provide strong evidence that the magnetic moments are created by the removal of p_z orbitals from the π -band, as predicted theoretically.

In conclusion, clear signatures of magnetic moment formation are observed in both the non-local spin transport and Hanle precession data, which emerge only after exposure to atomic hydrogen or lattice vacancies. The results and techniques presented here are important for future developments in magnetism and spintronics.

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