Magneto-transport in Dilute Fluorinated Graphene

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\[
\rho(B)/\rho(B=0T) \quad B(T)
\]

\[
L_\Phi(nm) \quad T(K)
\]

Sample A

3.8x10^{17/cm^2}
2.5x10^{17/cm^2}
1.4x10^{17/cm^2}
1.1x10^{17/cm^2}
0.6x10^{17/cm^2}
Motivation

Engineering the properties of graphene with adatoms

• Electronic and optical properties (band gap opening, doping, luminescence)
• Functionalization (sensing, composite material)
• Magnetism

➢ Fully fluorinated graphene CF (graphene monofluoride)
  • ultrathin large bandgap insulator
  • photoluminescence due to defect states


Robinson et al, Nano Lett. 10, 3001 (2010)
Nair et al, Small 6, 2877 (2010)
Jeon et al, ACS Nano, 5, 1042 (2011)
…
Dilute fluorinated graphene (DFG): Is it magnetic?

Magneto-transport experiments in DFG reveal:

- Saturation of phase breaking length at low temperature
- Very large negative magneto-resistance

Hong et al, PRB 83, 085410 (2011)
Hong et al, submitted to PRL
The Team

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Atomic defects in graphene

- adatoms, vacancies, substitutes
  - F, H, OH, B, N, etc

- strong and short-ranged interaction with Dirac fermions
  - hybridize with the $\pi$ orbitals of graphene
  - sharp resonance in the DoS near the Dirac point
  - may carry a local magnetic moment-Kondo impurity
  - strong spin-orbit coupling

Hubbard model with onsite energy $U$ and hopping term $t$


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Adatom-induced magnetism

net spin $\sim \mu_B$

decay over a few lattice constants

“local moment”

- tunable adatom coverage
- tunable electron density and density of states

$tunable$ electron-moment, moment-moment interactions

graphene twist:

A-A: ferromagnetic, A-B: anti-ferromagnetic

Yazyev & Helm, *PRB* 75, 125408 (2007) and many others
Adatoms: resonant scattering center

\[ J_l(kr) \]
\[ Y_l(kr) \]

phase shift \( \delta_l(k) \)

\[ \sigma = \frac{2e^2}{\pi \hbar n_{\text{defect}}} \ln^2(k_F R_0) \]

Stauber et al, PRB 76, 205423 (2007)
Hentschel and Guinea, PRB 76, 115407 (2007)

Chen et al, PRL 102, 236805 (2009)
Ni et al, Nano Lett. 10, 3868(2010)

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Outline

- Introduction

- Dilute fluorinated graphene
  - Fabrication and characterization
  - Carrier density driven weak to strong localization
  - Weak localization regime: anomalous phase breaking
  - Strong localization regime: large negative magnetoresistance
  - Possible origins
Dilute fluorinated graphene

- Fluorination extremely dilute $n_F \sim 10^{12}$-$10^{13}$ /cm$^2$ (< 0.1%)

- Defluorination recovers high-quality graphene
  - Raman $I_D/I_G < 0.1$
  - mobility of several thousand cm$^2$/Vs
  - nice SdH oscillations

Clean and reversible fluorination

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Raman spectra of DFG and defluorinated DFG

\[ \frac{I_D}{I_G} \text{ ratio determines the fluorine density} \]

Lucchese et al, Carbon 48, 1592 (2010)
STM signature of F-adatoms on graphene

- mostly isolated fluorine
  - Three-fold
  - 30° rotated
  - $\sqrt{3}\times\sqrt{3}$ superlattice
  - Up to 10 lattice constants

- total about 900 defects
- average spacing 7 nm
- distribution uneven, clusters are rare

fluorine density $n_F \sim 2 \times 10^{12}/\text{cm}^2$, or 0.05% coverage
Adatoms are strong scatterers

midgap state fit
$R_0 = 3.7 \ \text{Å}$

sample A
200 K

DFG sample A
fluorine density:
$n_F = 7 \times 10^{11}/\text{cm}^2$

mobility:
$\mu \sim 1000 \ \text{cm}^2/\text{Vs}$

"midgap" state scattering

$$\sigma = \frac{2e^2}{\pi \hbar} \frac{n}{n_{\text{defect}}} \ln^2 (k_F R_0)$$

Stauber et al, PRB 76, 205423 (2007)
Hentschel and Guinea, PRB 76, 115407 (2007)
Conductivity shows strong temperature dependence

![Graph showing conductivity vs. gate voltage difference](image)

- Sample B
- $n_F = 2 \times 10^{12}/\text{cm}^2$

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KITP grapene UCSB, Jan 9, 2012
Density-driven strong to weak localization

Variable-range hopping

\[ \rho(T) \propto \exp \left[ \left( \frac{T_0}{T} \right)^{1/3} \right] \]

“Anderson localization”

increasing \( n \)

\[ \frac{\hbar}{2e^2} \sim n_F = 2 \times 10^{12}/\text{cm}^2 \]

“weak localization”

\[ \sigma(T) \propto \ln T \]

Elias et al., *Science* 323, 610 (2009)
Moser et al., *PRB* 81, 205445 (2010)
Outline

- Introduction
- Fabrication and characterization
- Carrier density driven weak to strong localization

Magneto-transport in DFG

- Weak localization regime: phase breaking length saturation
- Strong localization regime: large negative magnetoresistance

- Possible explanations
Magnetoresistance of pristine graphene

\[ \mu_{FE} = 16,000 \text{ cm}^2/\text{Vs} \]

\[ \nu = 94 \]

Shubnikov-de Haas oscillations
Magneto-resistance of DFG

$T = 5K$

$\rho / \rho(B=0)$

- Sample B
- $n_F = 2 \times 10^{12}/cm^2$
- $4.2 \times 10^{12}/cm^2$

- weak localization at high carrier density
Magneto-resistance of DFG

- Weak localization at high carrier density

![Graph showing the magneto-resistance of DFG with different carrier densities.]

Sample B: $n_F = 2 \times 10^{12}/\text{cm}^2$

- $1.4 \times 10^{12}/\text{cm}^2$
- $4.2 \times 10^{12}/\text{cm}^2$

Temperature: $T = 5K$
Magneto-resistance of DFG

- Weak localization at high carrier density
- Large negative magneto-resistance at low carrier density

Sample B

- $n_F = 2 \times 10^{12}/\text{cm}^2$
- $1.0 \times 10^{12}/\text{cm}^2$
- $4.2 \times 10^{12}/\text{cm}^2$
- $1.4 \times 10^{12}/\text{cm}^2$

$T=5\text{K}$

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Weak localization in DFG

\[ \frac{\pi h}{e^2} \Delta \sigma(B) = F\left(\frac{4l_B^{-2}}{L_{\Phi}^{-2}}\right) - F\left(\frac{4l_B^{-2}}{L_{\Phi}^{-2} + 2L_i^{-2}}\right) - 2F\left(\frac{4l_B^{-2}}{L_{\Phi}^{-2} + L_i^{-2} + L_*^{-2}}\right) \]

- \( L_{\Phi} \): phase breaking length
- e-e scattering
- e-phonon scattering
- sample boundary
- microwave radiation
- spin-flip scattering

- \( L_i \): intervalley scattering length
  - point defects

- \( L_* \): intravalley backscattering length
  - point defects
  - ripples and dislocations

\( n = 4.2 \times 10^{12}/cm^2 \)

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Unusual saturation of $L_\Phi$ at low-$T$

Dilute fluorinated graphene:
- High-$T$ regime follows e-e collision ($T^{-1/2}$)
- $L_\Phi$ saturates at $\sim 10$ K
- $L_{sat} \sim 140$ nm

Pristine graphene:
$L_\Phi \sim$ several $\mu$m at lower $T$

Tikhonenko et al, PRL, 100, 056802 (2008)
Ki et al, PRB, 78, 125409 (2008)

Unusual saturation of the phase breaking length in DFG
Temperature dependence of $L_\Phi$

Phase breaking scattering rate:

$$\tau_\Phi^{-1} = aT + bT^2 + \tau_{sat}^{-1}$$

spin-flip scattering due to fluorine?
Possible sources of phase breaking saturation

1. Sample size
2. Experimental issues
3. Magnetic contaminations
4. Unintentionally produced vacancies

Control sample: Defluorinated DFG
Control: Defluorinated DFG

Fluorine adatoms are responsible for the observed phase breaking length saturation.

\[ \tau_{\Phi}^{-1} = aT + bT^2 + \tau_{sat}^{-1} \]

\( \tau_{sat} \) in control sample at least 25 times longer than \( \tau_{sat} \) in fluorinated sample.

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KITP graphene UCSB, Jan 9, 2012
Tunability of phase breaking rate

Phase breaking rate tunable via carrier and fluorine density

fluorine density:

A and C: $n_F \sim 7 \times 10^{11}$/cm$^2$

B and D: $n_F \sim 2 \times 10^{12}$/cm$^2$

Higher $\tau_{\text{sat}}^{-1}$ at higher fluorine density

Higher $\tau_{\text{sat}}^{-1}$ at lower carrier density

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Spin-flip scattering due to fluorine

Nagaoka-Suhl formula:

$$\frac{1}{\tau_{sf}} = \frac{n_{mag}}{\pi \hbar N(E_F)} \frac{\pi^2 S(S+1)}{\pi^2 S(S+1) + \ln^2(T/T_k)}$$

$n_{mag}$: magnetic impurity density

$$T_k: \text{Kondo temperature}$$

$$\tau_{sf}^{-1} = \tau_{sat}^{-1} ; \quad n_{mag} = n_F ; \quad S = 1/2$$

The Kondo temperature $T_k$ up to 0.2 mK

$$T_k \propto \exp\left(-\frac{1}{N(E_F)J}\right)$$

exchange energy $J$ up to 5 meV

Pierre et al., PRB 68, 085413 (2003)
Sengupta et al, PRB 77, 045417(2008)


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Magneto-resistance of DFG

- weak localization at high carrier density
- large negative magneto-resistance in the variable-range hopping regime
  - Up to 40-fold reduction
  - Not yet saturated at 9 T

Comparable to CMR manganites, ferromagnetic semiconductors

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Temperature dependence of the MR

Large negative MR at low temperature
Temperature dependence of the MR at a fixed field

\[ n = 8 \times 10^{11} / \text{cm}^2 \]
Localization length $\xi$ in field

$$\rho(T) \propto \exp\left[\left(\frac{T_0}{T}\right)^{1/3}\right]$$

$$T_0 = \frac{13.8}{k_B N(E_F) \xi^2}$$

$\xi$ enhanced by a factor of 4 at 9 T
Temperature dependence of the MR

Staircase MR at low temperature

$n=8 \times 10^{11}/\text{cm}^2$
Staircase-like field dependence at low temperature
Staircase-like field dependence at low temperature

\[ \frac{\rho(B)}{\rho(0T)} \]

- \(0.8 \times 10^{12}/\text{cm}^2\)
- \(1.3 \times 10^{12}/\text{cm}^2\)
Staircase-like field dependence at low temperature
Staircase-like field dependence at low temperature

\[
\frac{\rho(B)}{\rho(0T)}
\]

- Black line: $0.8 \times 10^{12}/\text{cm}^2$
- Red line: $1.3 \times 10^{12}/\text{cm}^2$
- Green line: $1.4 \times 10^{12}/\text{cm}^2$
- Blue line: $2.0 \times 10^{12}/\text{cm}^2$

$B$ (T)
Staircase-like field dependence at low temperature

- Reproducible
- Seen in multiple samples
- NOT periodic in B (AB effect)
- NOT periodic in 1/B (SdH)
- NOT universal conductance fluctuation

$$\Delta \sigma \sim 0.001-0.1 \text{ e}^2/\text{h}$$

Discrete energy levels or length scales probed by the magnetic field?
Large negative MR NOT due to the following mechanisms

- Classical MR (positive)
- Wave function shrinking in B-field (positive)
- Zeeman effect (isotropic)

Hypothesis: quantum interference induced Anderson localization?

Magnetic field breaks time reversal symmetry and suppresses phase coherent backscattering.

Theory and exp. in quasi-1D: universal doubling of $\xi$ in strong field.

2D and 3D: no good theory
ten-fold MR observed in $\text{In}_2\text{O}_{3-x}$ film

Difficulty with current data:

- $\xi(0) = 55 \text{ nm} \quad \Rightarrow \quad B_{\text{sat}} = 0.2 \text{ T}$
- no mechanism for staircase

Magneto-transport of DFG

- Anomalous phase breaking length saturation in weak localization regime
- Colossal magneto-resistance in variable-range hopping regime

Evidence of local moment

Explanations?
Hypothesis #2: magnetic polarons?

Exchange coupling between moments and localized electrons

A magnetic field aligns the polarons and enhances hopping.

Kaminski & Das Sarma, PRL 88, 247202 (2002)
Negative MR in CMR manganites and ferromagnetic semiconductors

Moca et al., *PRL* 102, 137203 (2009).

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Summary

- Clean, controlled, dilute fluorinated graphene
- Carrier density-driven weak to strong localization transition
- Anomalous phase breaking in weak localization regime
- Large negative magnetoresistance in hopping regime
- Theory needed

Hong et al, PRB 83, 085410(2011), Hong et al, submitted to PRL