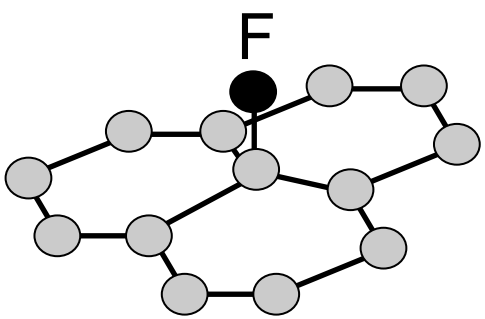
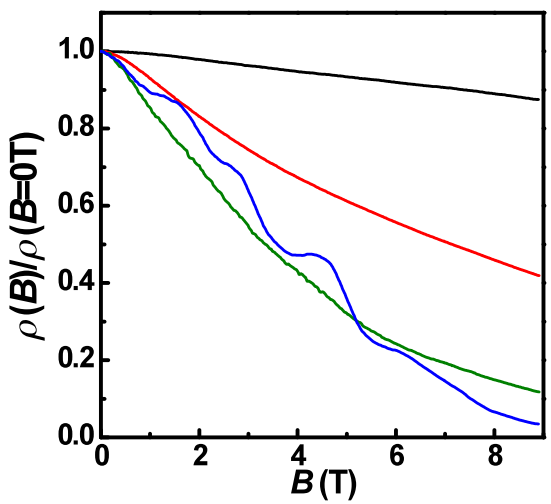
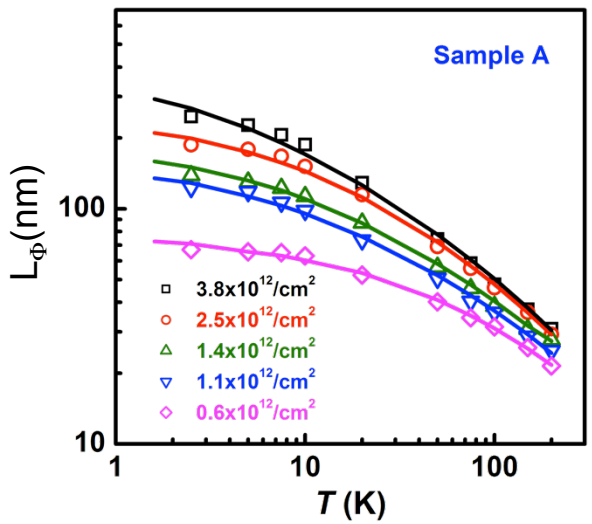
Magneto-transport in Dilute Fluorinated Graphene

Jun Zhu

Department of Physics
The Pennsylvania State University







Motivation

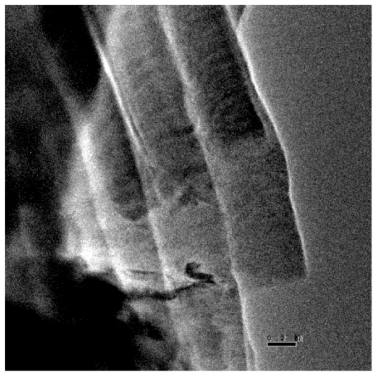
Engineering the properties of graphene with adatoms

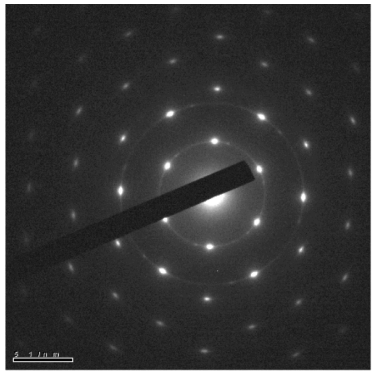
- Electronic and optical properties (band gap opening, doping, luminescence)
- Functionalization (sensing, composite material)
- Magnetism

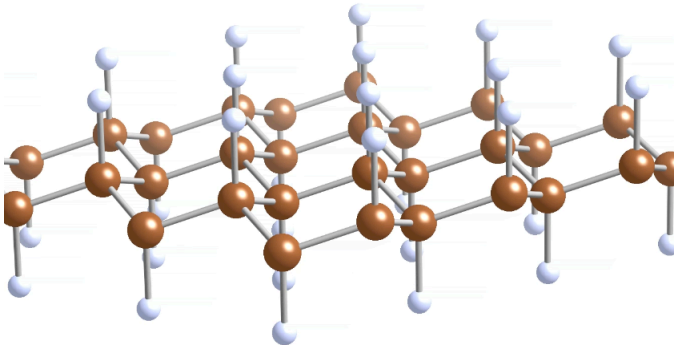
➢ Fully fluorinated graphene CF (graphene monofluoride)

- ultrathin large bandgap insulator
- photoluminescence due to defect states

Cheng et al, Physical Review B **81**, 205435 (2010).
Wang et al, Appl. Phys. Lett. **97**, 141915 (2010)

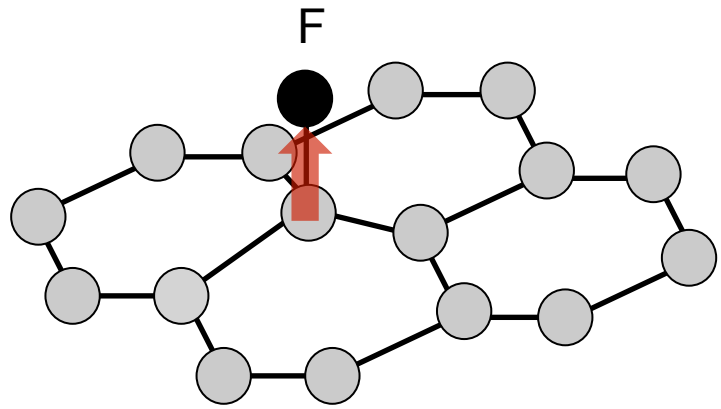






Robinson et al, Nano Lett. **10**, 3001 (2010)
Nair et al, Small **6**, 2877 (2010)
Jeon et al, ACS Nano, **5**, 1042 (2011)
…

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

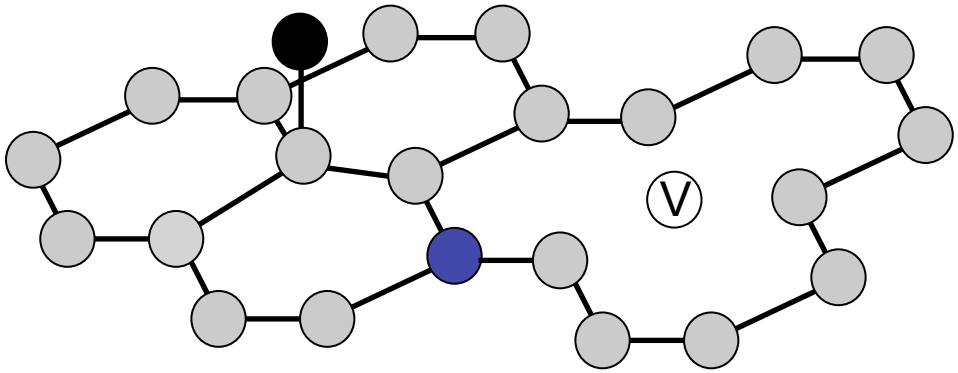
Dr. Xia Hong (now U. Nebraska-Lincoln)

Carina Herding

Ke Zou

Shih-Ho Cheng

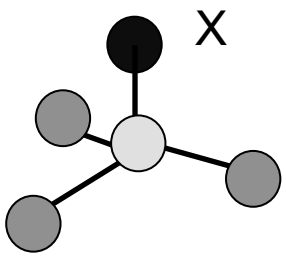
Atomic defects in graphene



adatoms, vacancies, substitutes

F, H, OH, B, N, etc

strong and short-ranged interaction with Dirac fermions



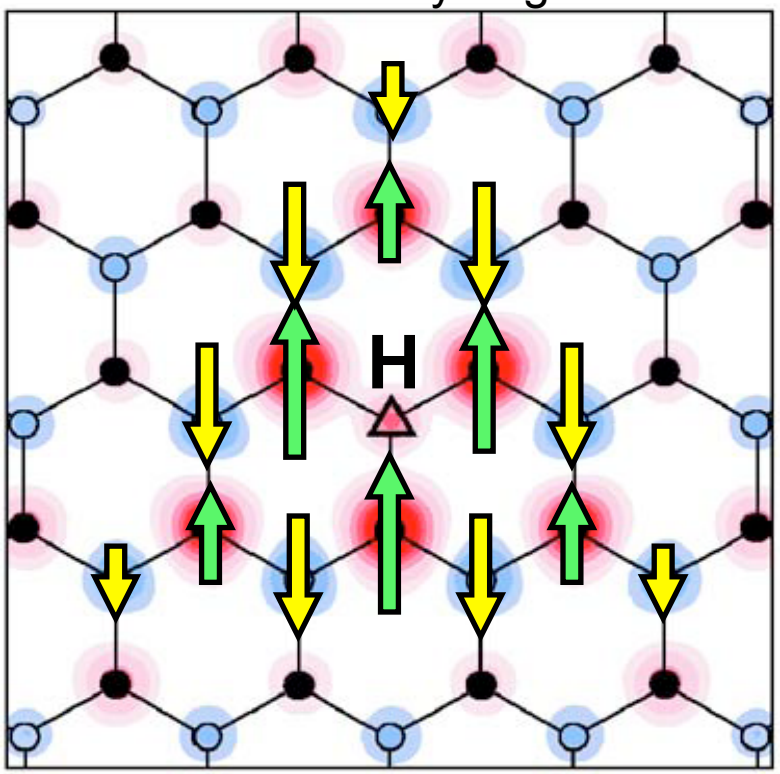
- hybridize with the π orbitals of graphene
- sharp resonance in the DoS near the Dirac point
- may carry a local magnetic moment-Kondo impurity
- strong spin-orbit coupling

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

Yazyev, Rep. Prog. Phys. **73** 056501 (2010)

Adatom-induced magnetism

chemisorbed hydrogen



Yazyev & Helm, *PRB* 75, 125408 (2007)
and many others

net spin ~ μ_B

decay over a few lattice constants

"local moment"

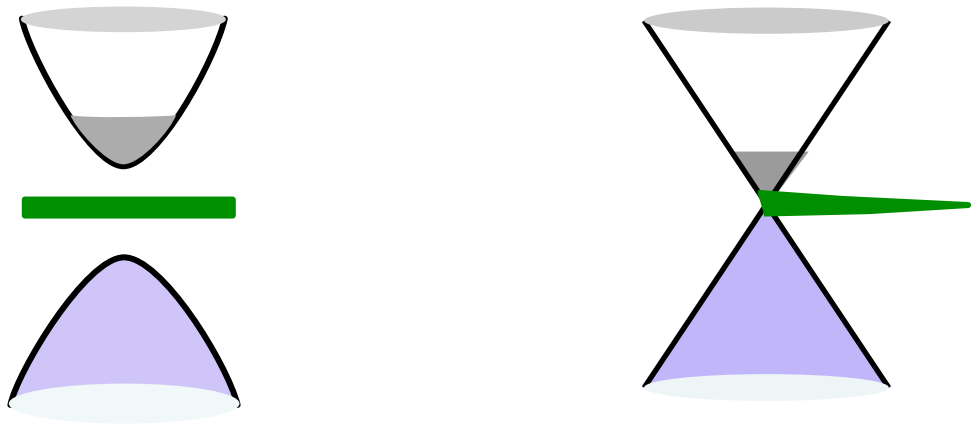
- tunable adatom coverage
- tunable electron density and density of states

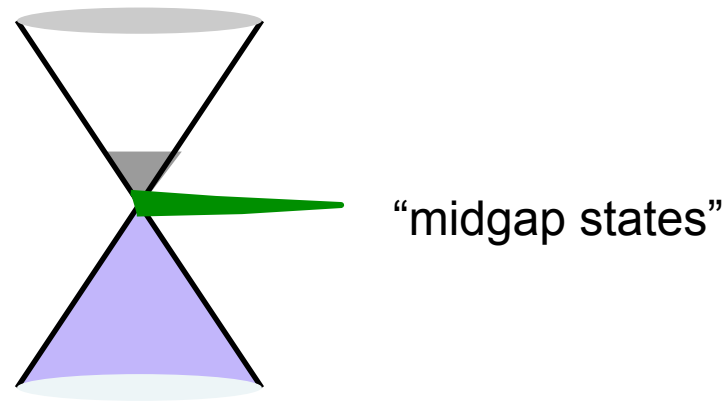
tunable electron-moment, moment-moment interactions

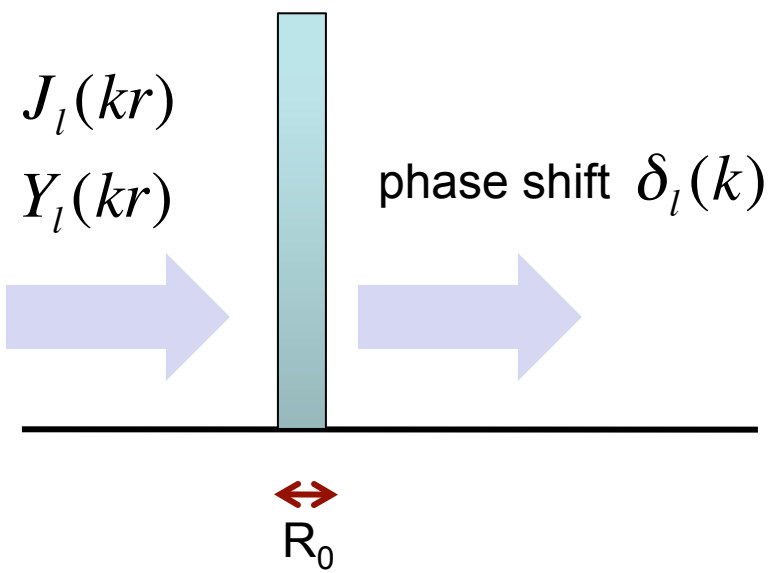
graphene twist:

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

Adatoms: resonant scattering center







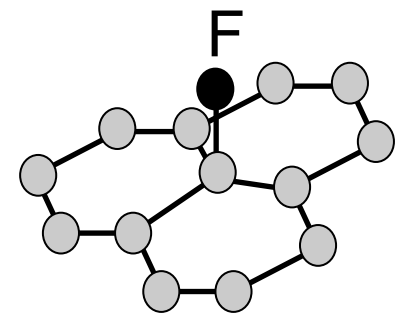
$$\sigma = \frac{2e^2}{\pi h}\frac{n}{n_{defect}}\ln^2(k_F R_0)$$

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

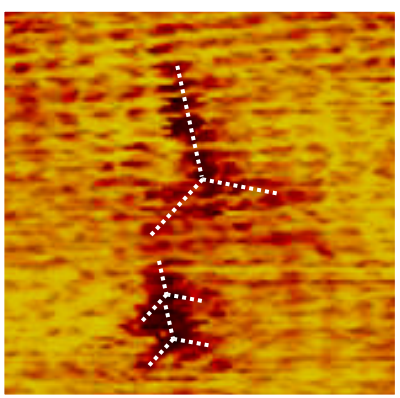
Chen et al, PRL **102**, 236805 (2009)
Ni et al, Nano Lett. **10**, 3868(2010)

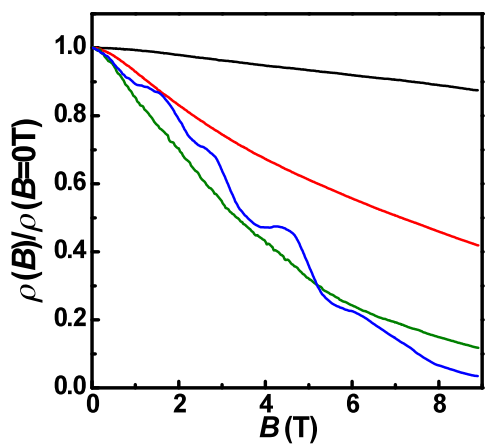
Outline

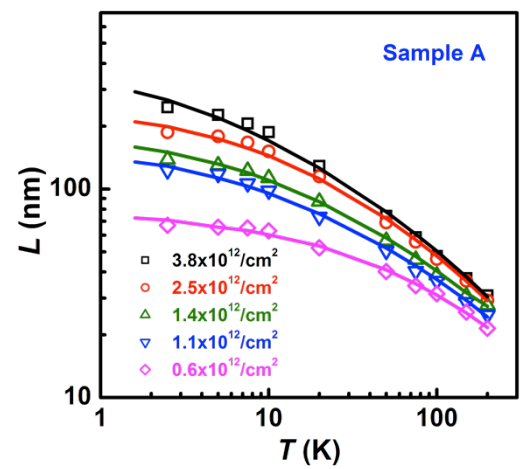
- Introduction



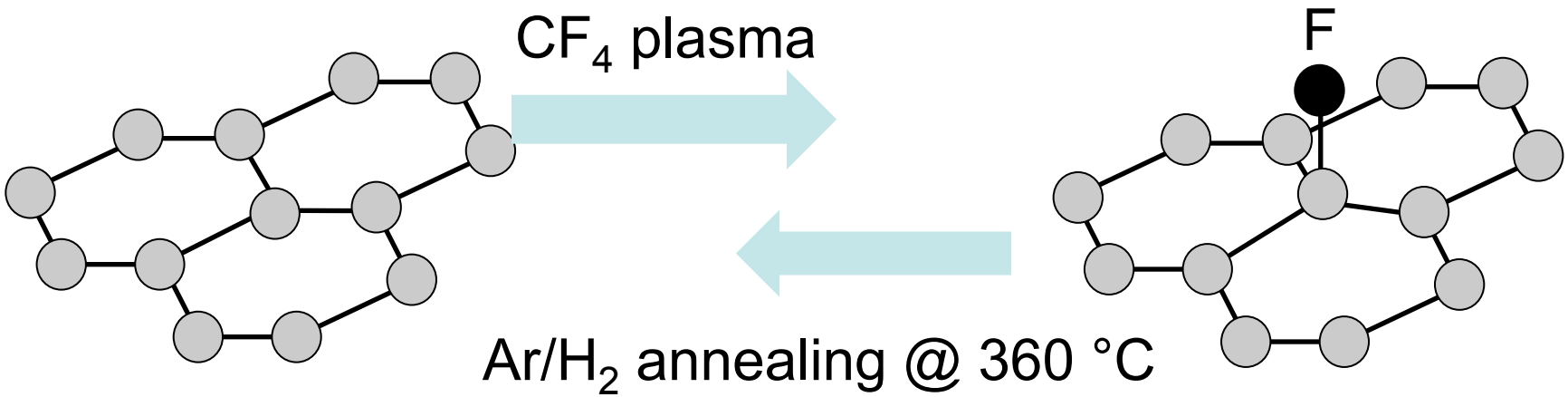
- Dilute fluorinated graphene
  - Fabrication and characterization
  - Carrier density driven weak to strong localization
  - Weak localization regime: anomalous phase breaking
  - Strong localization regime: large negative magnetoresistance
  - Possible origins







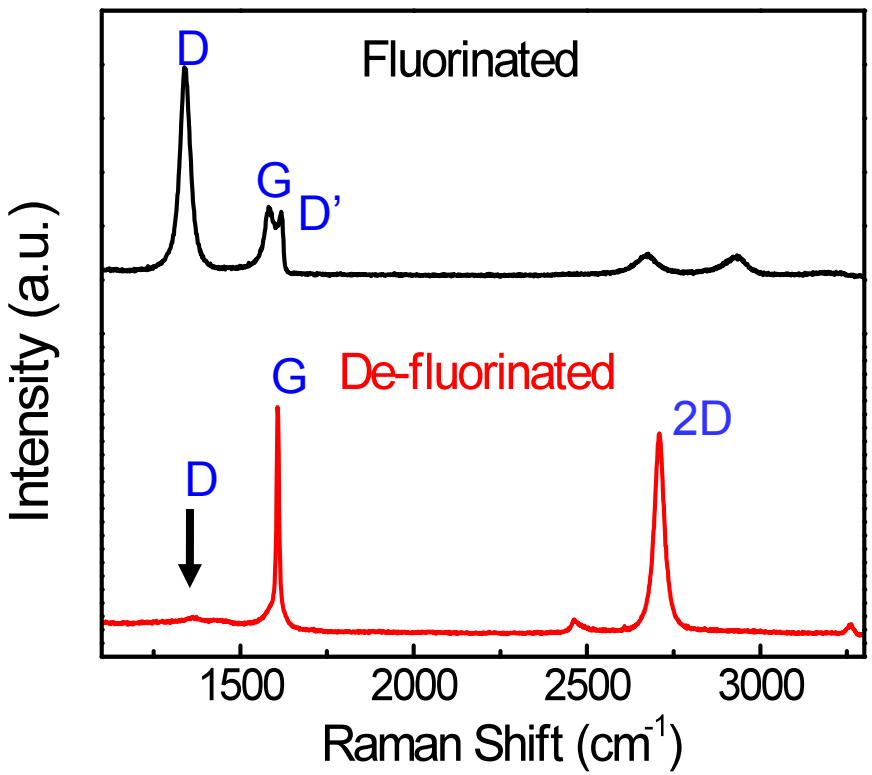
Dilute fluorinated graphene

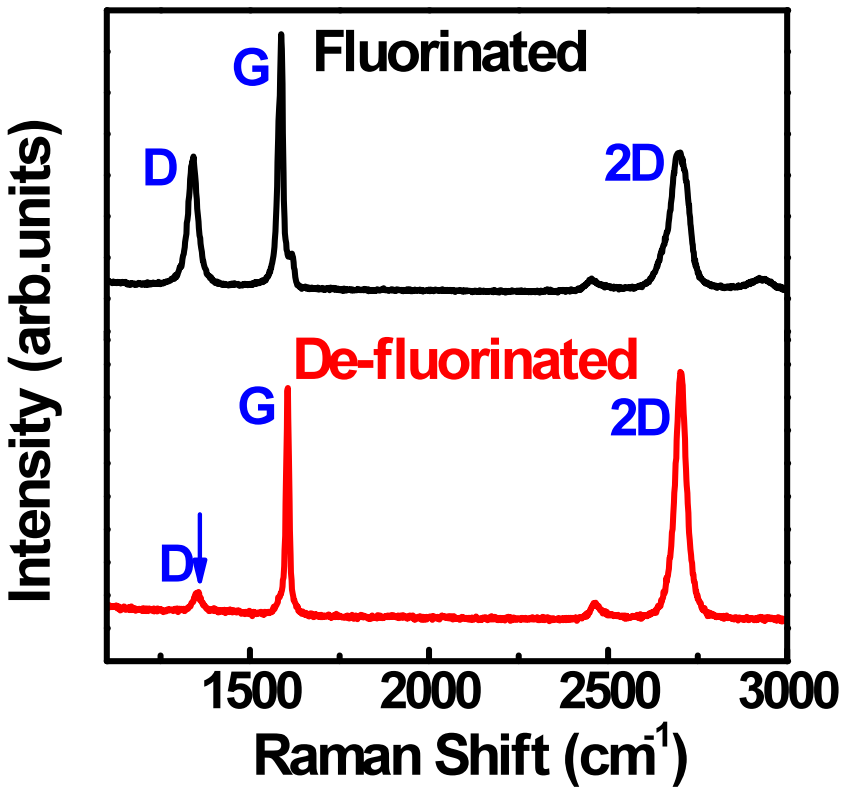


- Fluorination extremely dilute $n_F \sim 10^{12}$-10^{13} /cm^2 (< 0.1%)
- Defluorination recovers high-quality graphene
  - Raman $I_D/I_G < 0.1$
  - mobility of several thousand cm^2/Vs
  - nice SdH oscillations

Clean and reversible fluorination

Raman spectra of DFG and defluorinated DFG

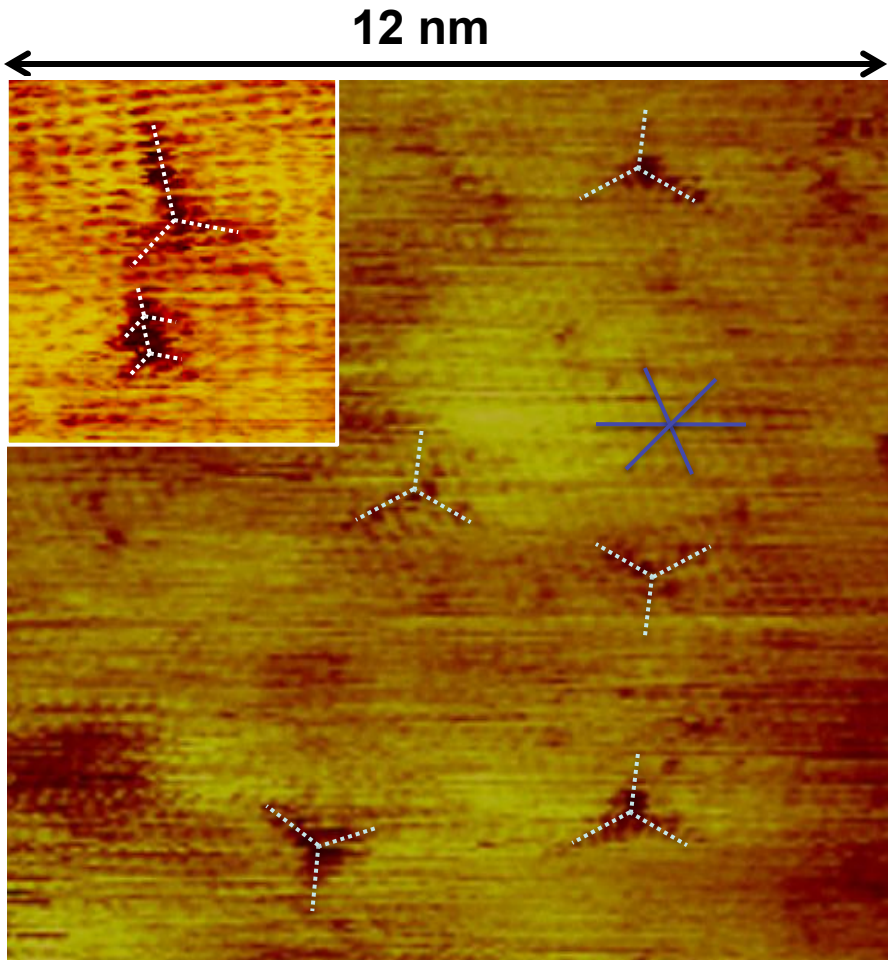




I_D/I_G ratio determines the fluorine density

Lucchese et al, Carbon 48, 1592 (2010)

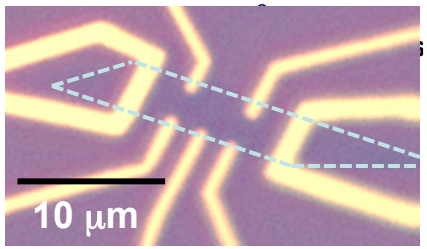
STM signature of F-adatoms on graphene

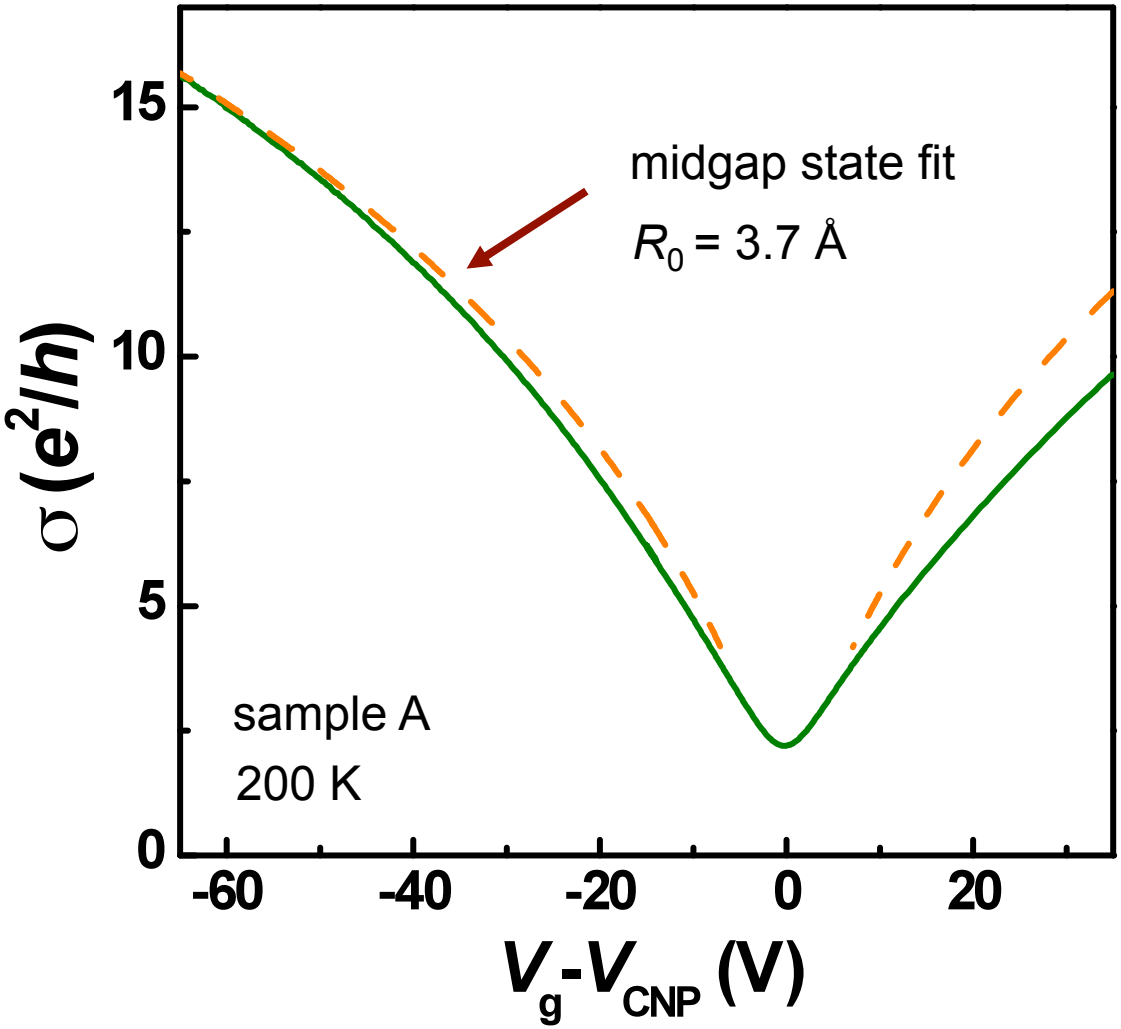


- **mostly isolated fluorine**
  - Three-fold
  - 30° rotated
  - √3x√3 superlattice
  - Up to 10 lattice constants
- total about 900 defects
- average spacing 7 nm
- distribution uneven, clusters are rare

fluorine density n_F~2x10^{12}/cm^2, or 0.05% coverage

Adatoms are strong scatterers





DFG sample A

fluorine density:

$n_F = 7\times10^{11}/\mathrm{cm}^2$

mobility:

$\mu \sim 1000\ \mathrm{cm}^2/\mathrm{Vs}$

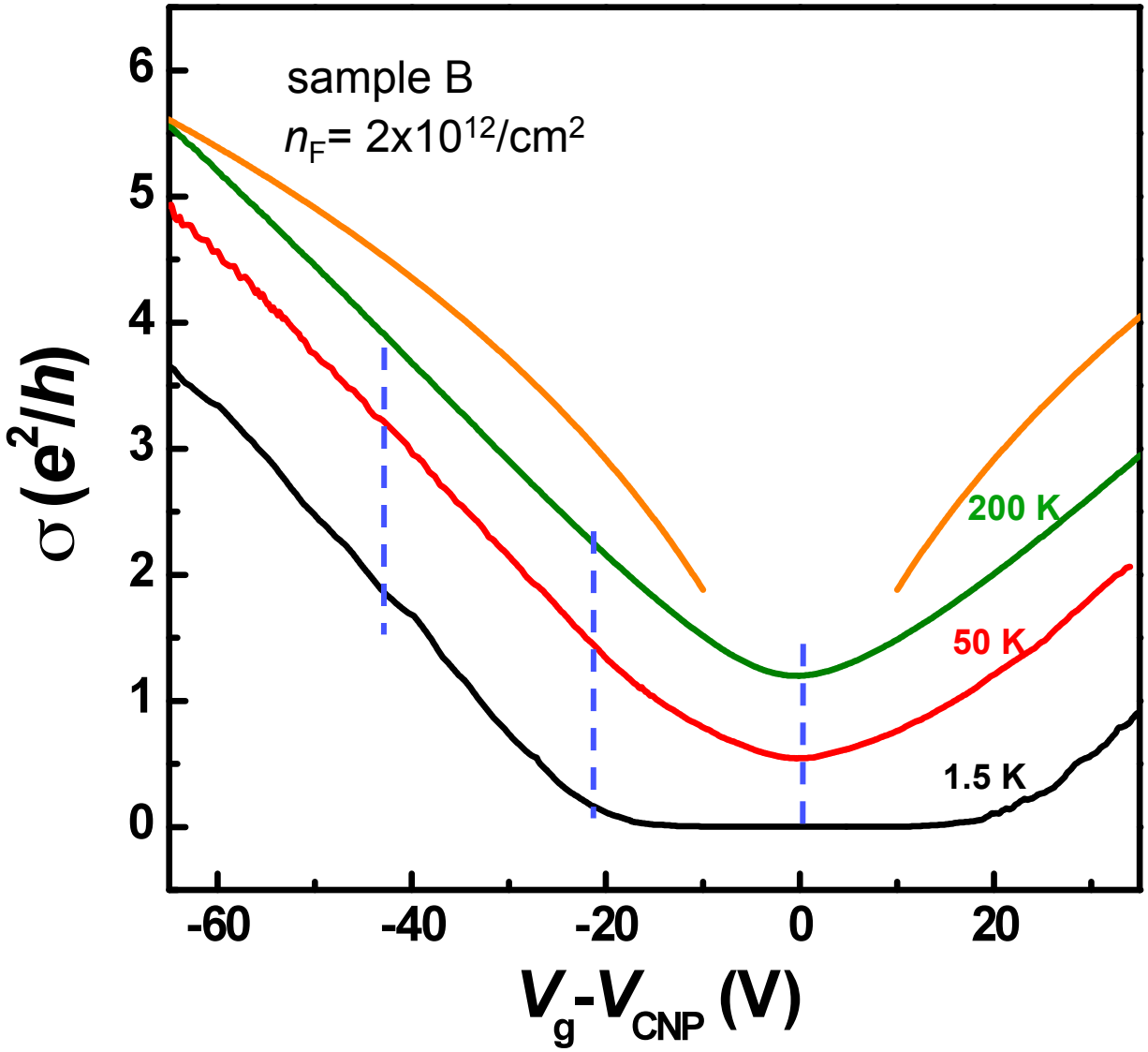
"midgap" state scattering

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

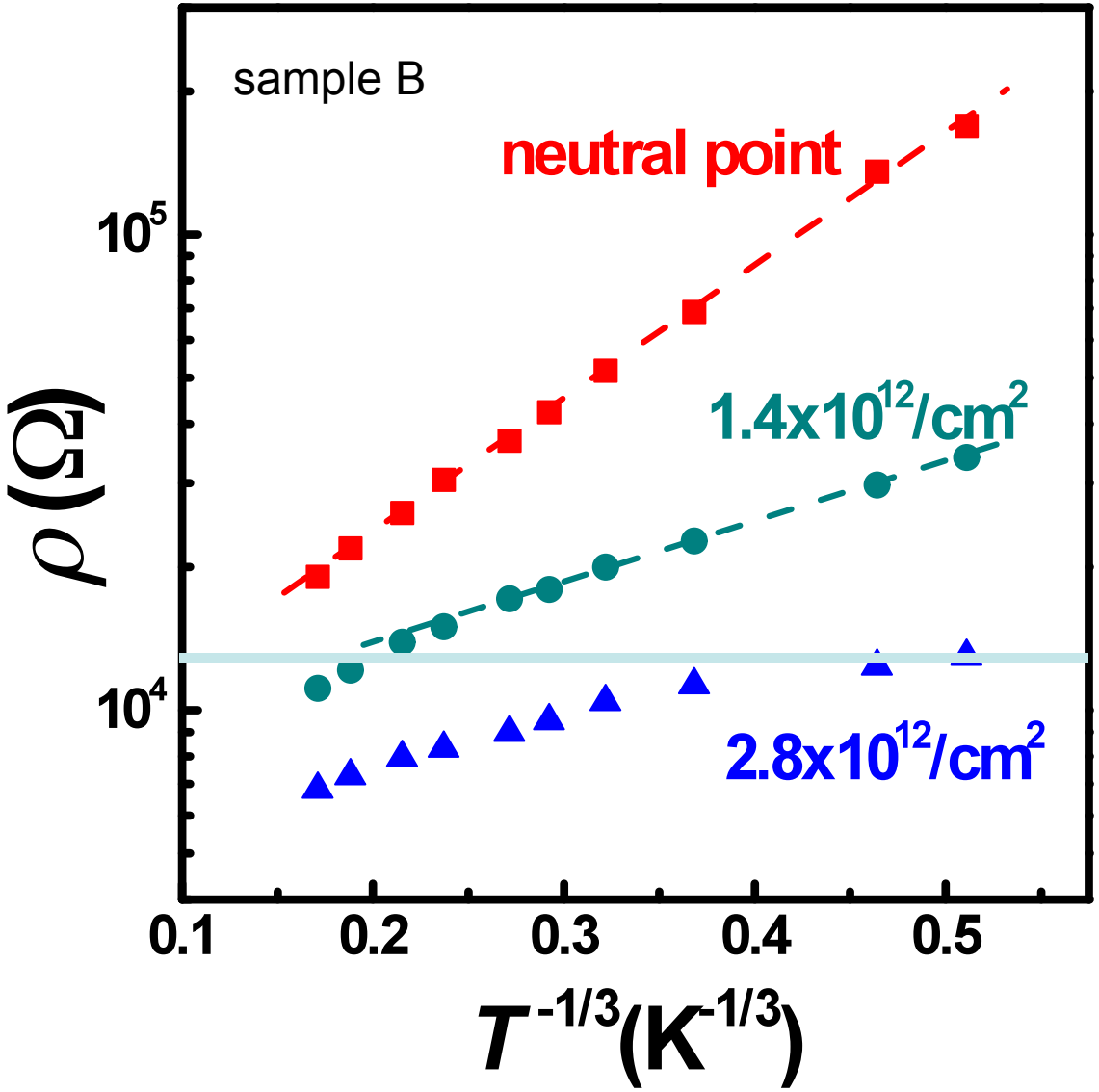
Stauber et al, PRB **76**, 205423 (2007)

Hentschel and Guinea, PRB **76**, 115407 (2007)

Conductivity shows strong temperature dependence



Density-driven strong to weak localization



Variable-range hopping

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

"Anderson localization"

increasing n

$$\frac{h}{2e^2}$$

~ $n_F = 2\times10^{12}/cm^2$

$$\sigma(T) \propto \ln T$$

"weak localization"

Elias et al., *Science* **323**, 610 (2009)
Wither et al, PRB **82**, 073403 (2010)
Moser et al., *PRB* **81**, 205445 (2010)

Jun Zhu, jzhu@phys.psu.edu

Outline

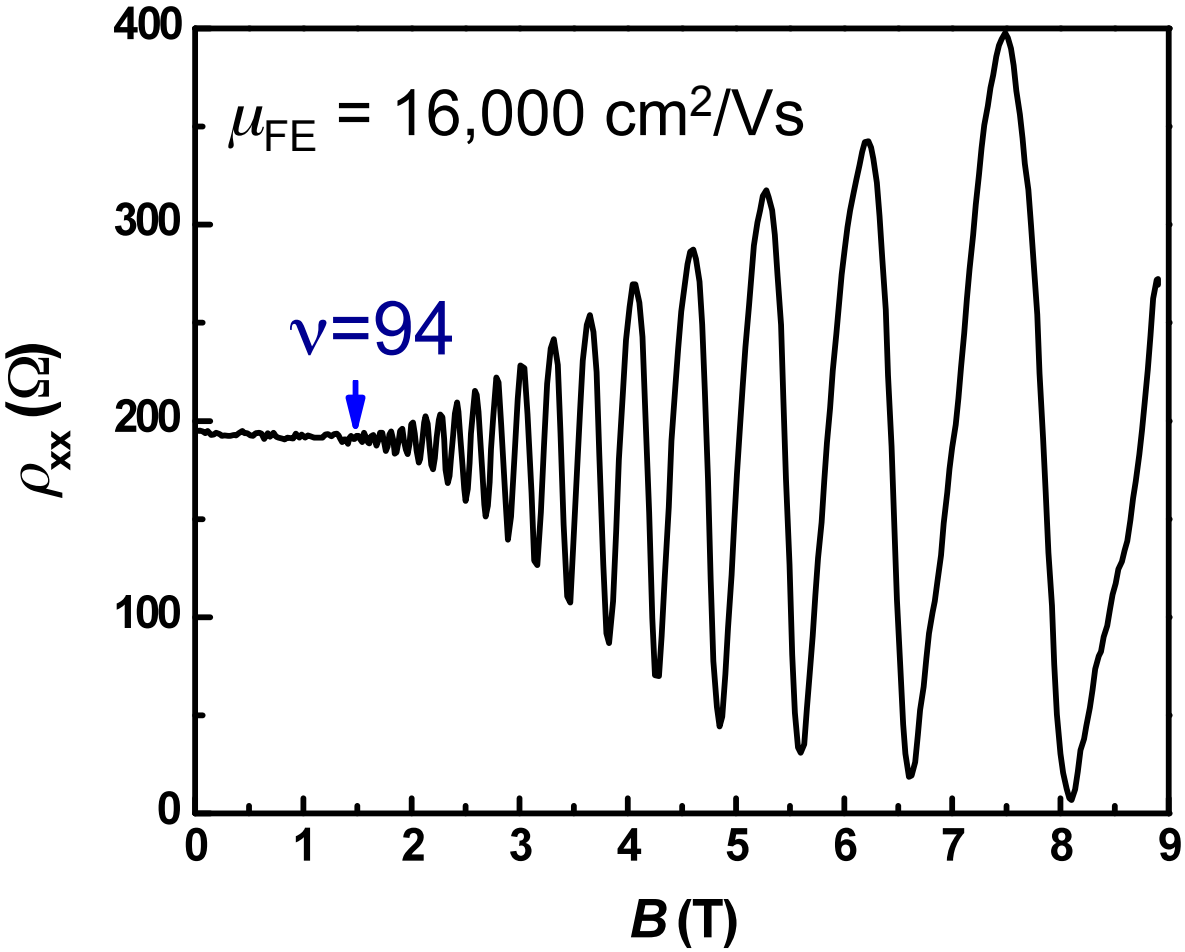
- Introduction
- Fabrication and characterization
- Carrier density driven weak to strong localization

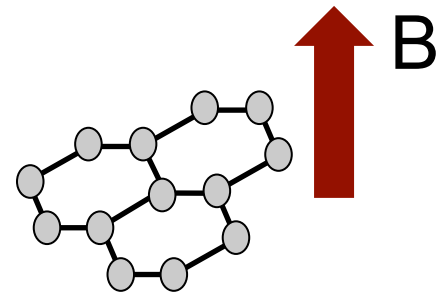
Magneto-transport in DFG

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

- Possible explanations

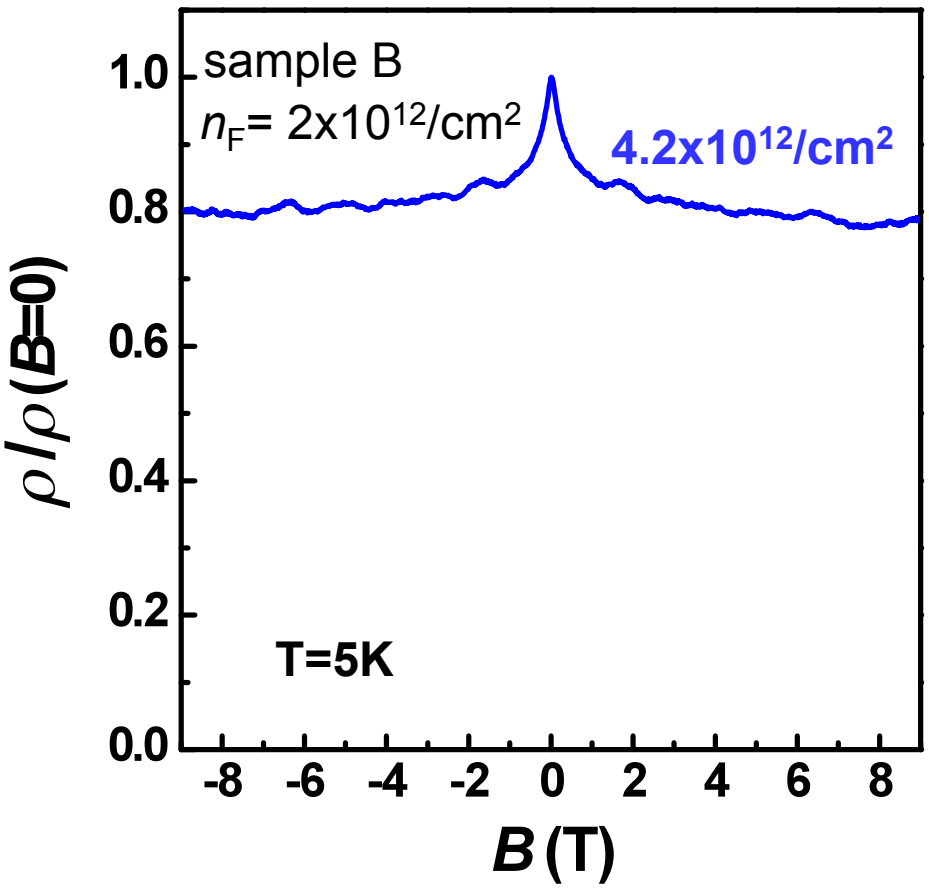
Magnetoresistance of pristine graphene

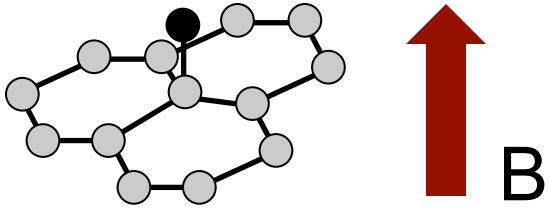




Shubnikov-de Haas oscillations

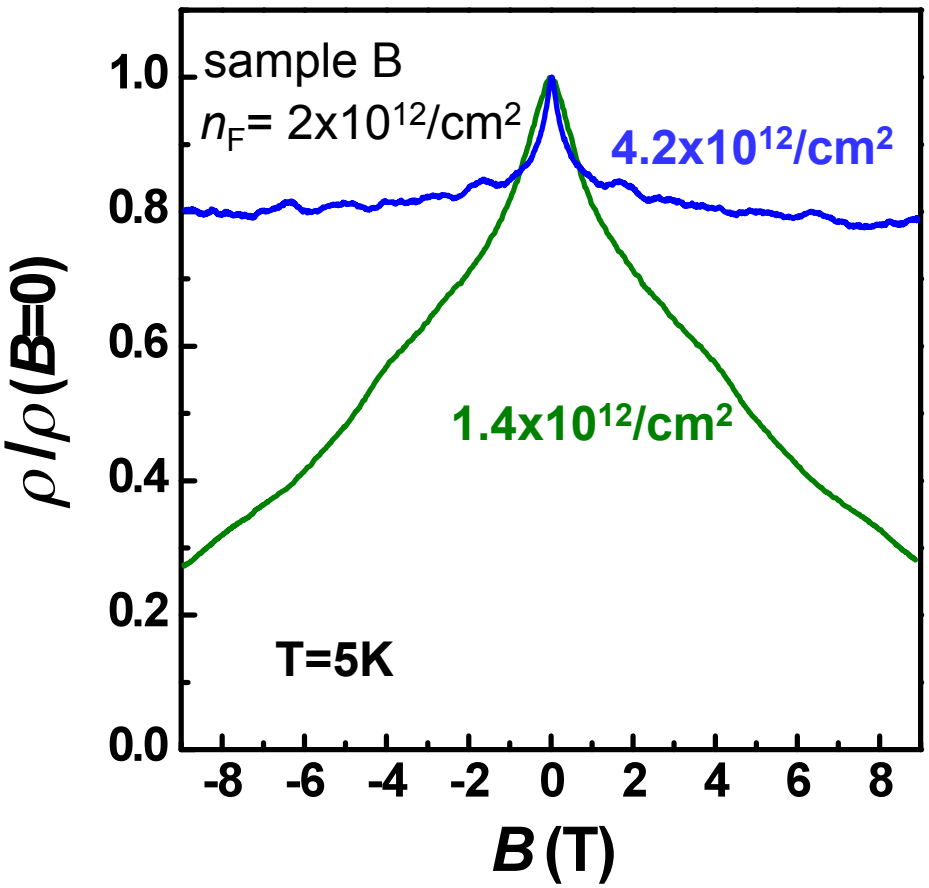
Magneto-resistance of DFG

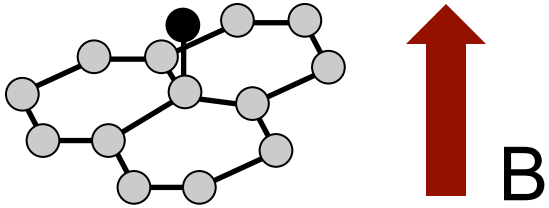




➢weak localization at high carrier density

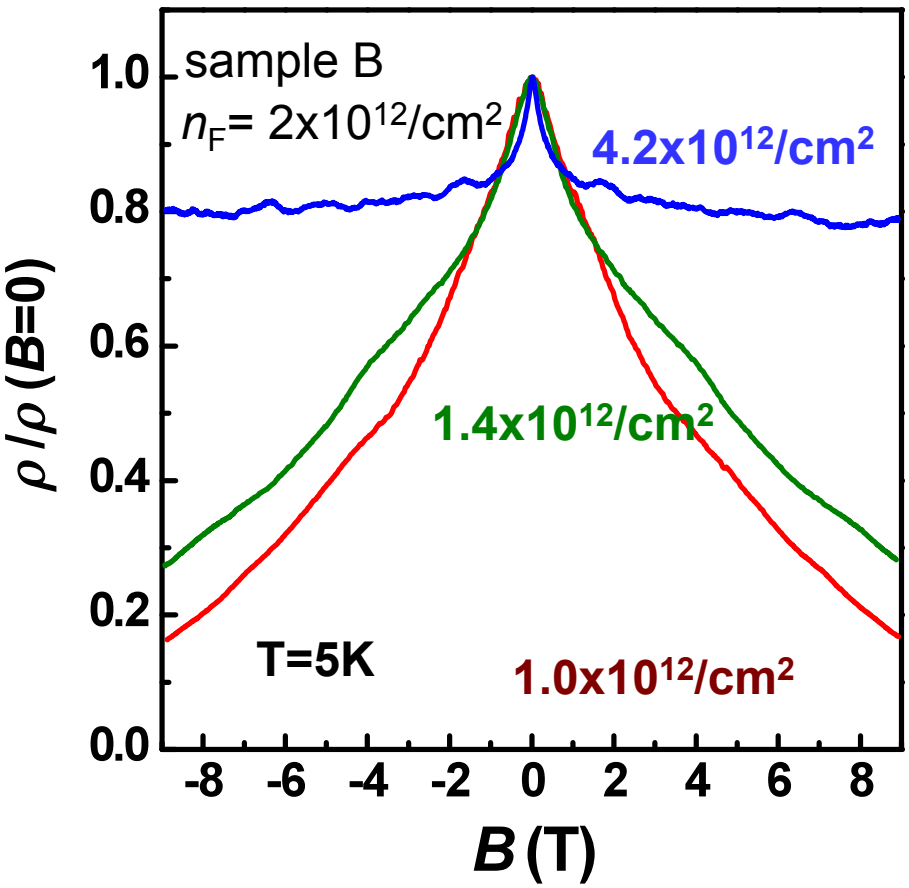
Magneto-resistance of DFG

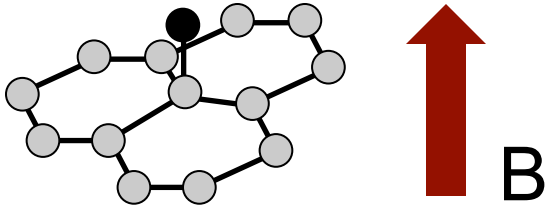




- weak localization at high carrier density

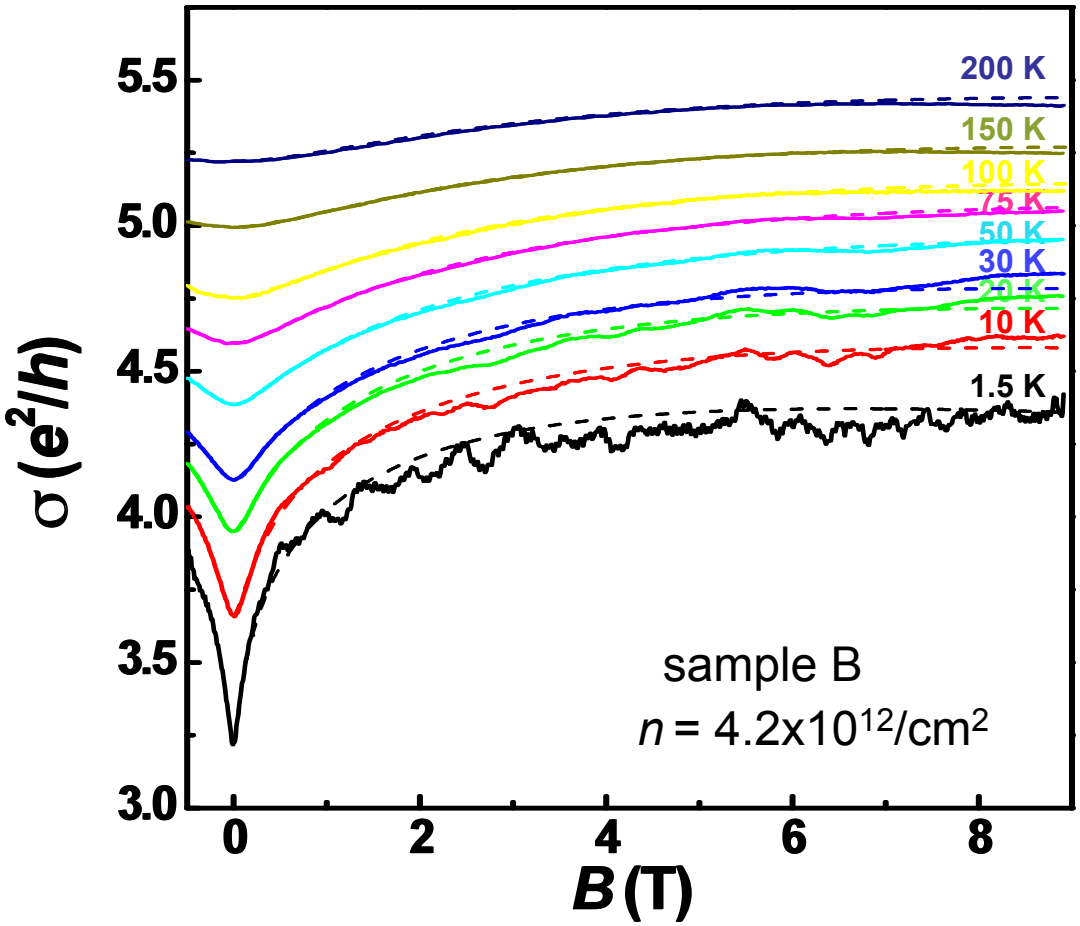
Magneto-resistance of DFG





- weak localization at high carrier density
- large negative magneto-resistance at low carrier density

Weak localization in DFG



L_Φ: phase breaking length

- e-e scattering
- e-phonon scattering
- sample boundary
- microwave radiation
- spin-flip scattering

L_i: intervalley scattering length

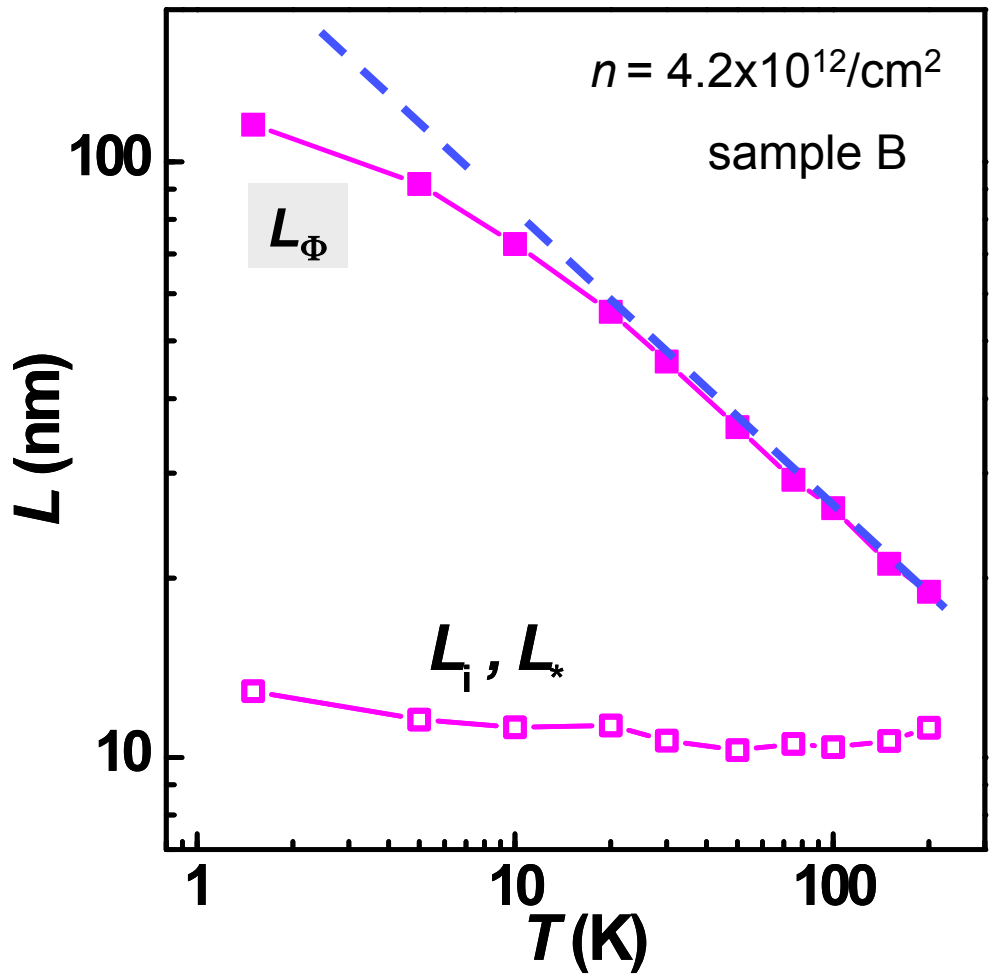
- point defects

L_*: intravalley backscattering len.

- point defects
- ripples and dislocations

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

Unusual saturation of L_Φ at low-T



Dilute fluorinated graphene:

- High-T regime follows e-e collision ($T^{-1/2}$)
- L_Φ saturates at ~ 10 K
- L_{sat} ~ 140 nm

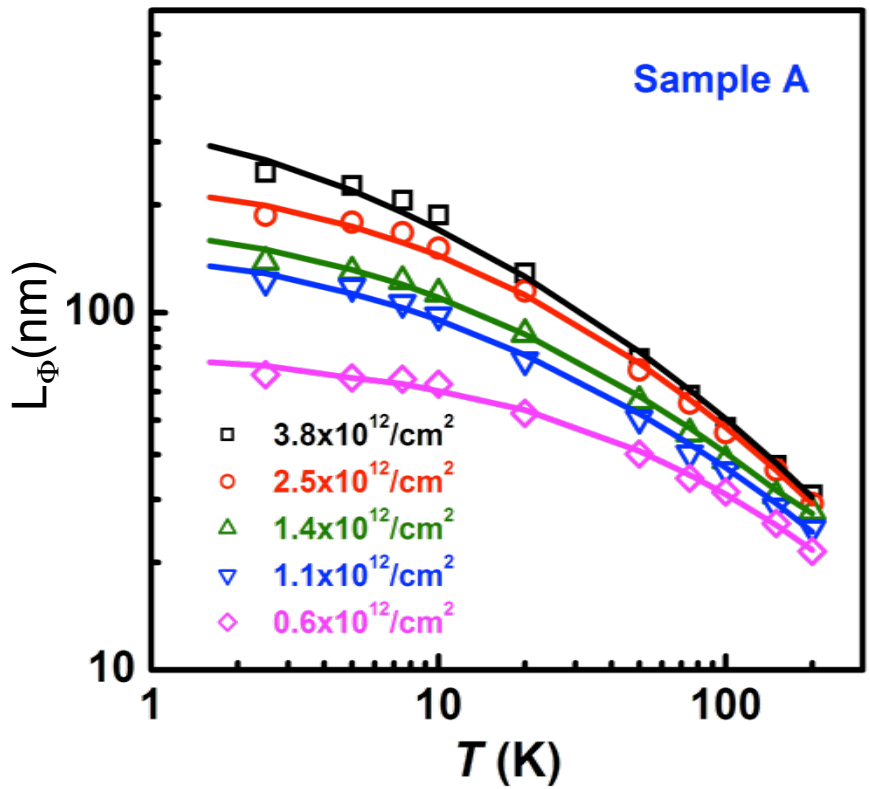
Pristine graphene:

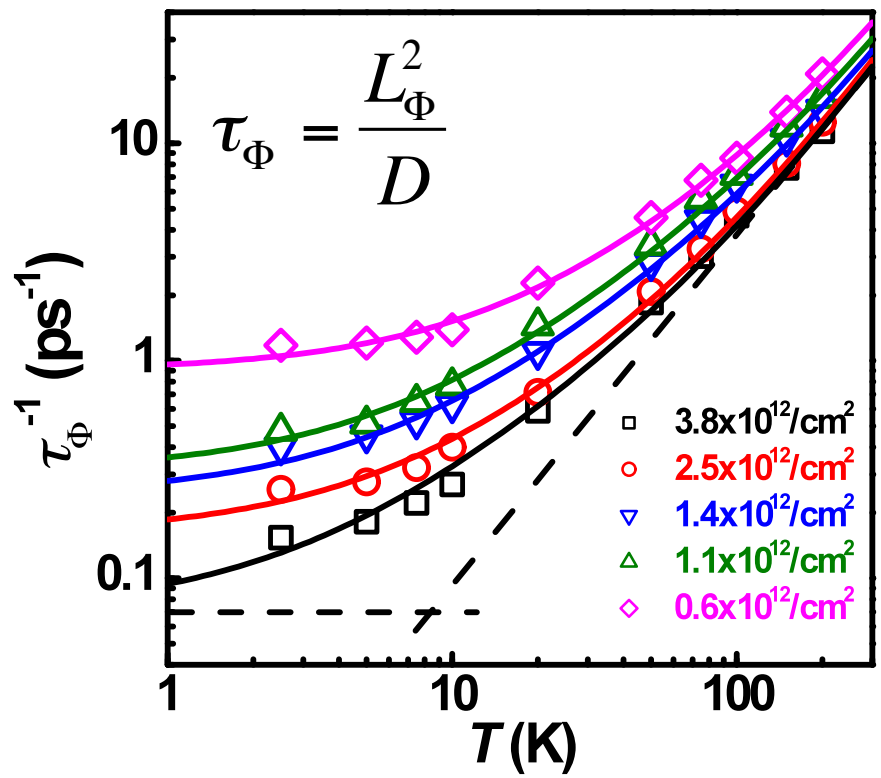
L_Φ ~ several μm at lower T

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_Φ





Phase breaking scattering rate:

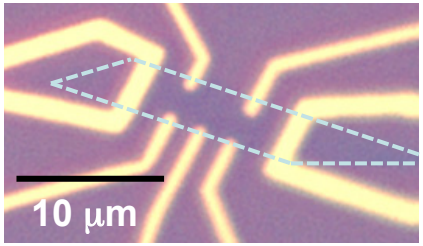
$$\tau_\Phi^{-1} = aT + bT^2 + \tau_{sat}^{-1}$$

e-e collision

spin-flip scattering due to fluorine?

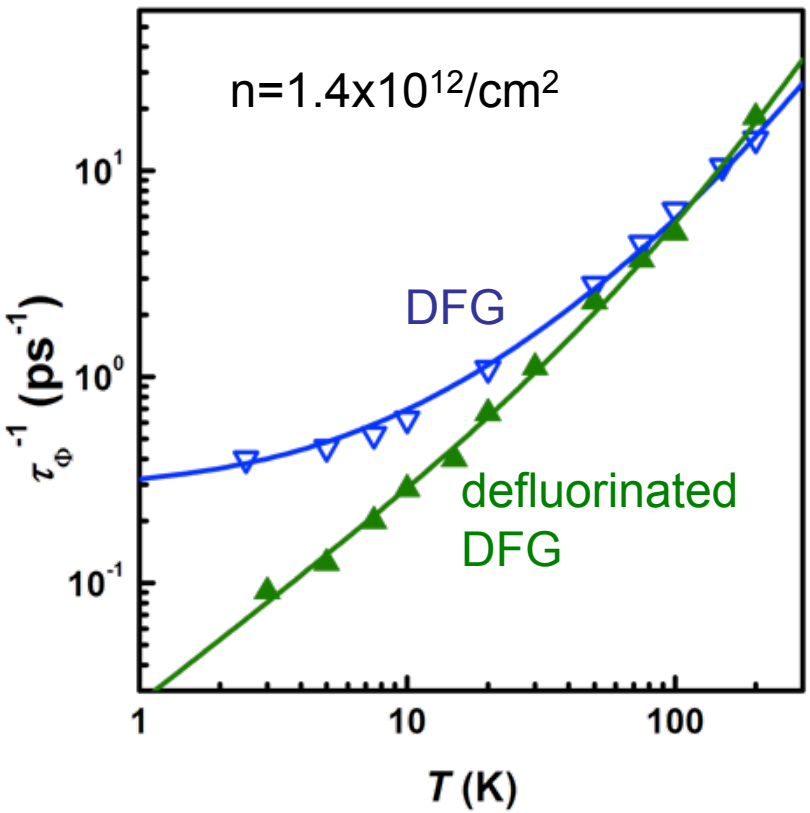
Possible sources of phase breaking saturation

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



Control sample: Defluorinated DFG

Control: Defluorinated DFG

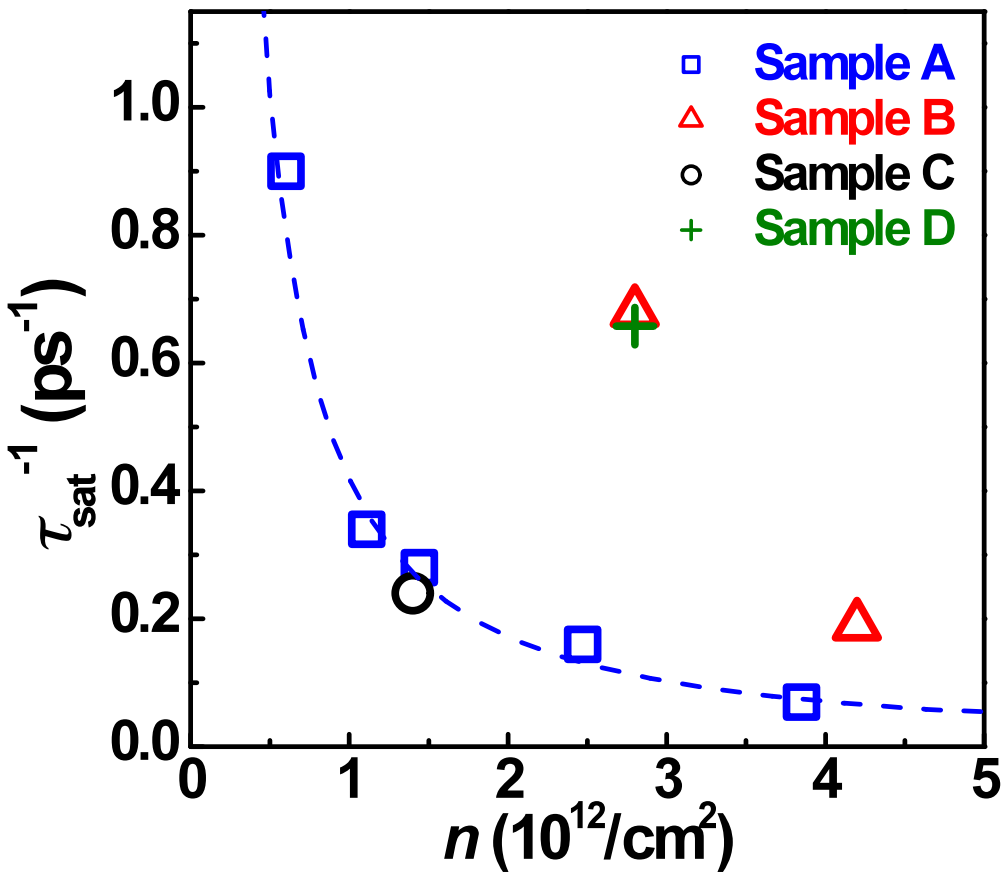


$$\tau_\Phi^{-1} = aT + bT^2 + \tau_{sat}^{-1}$$

τ_{sat} in control sample at least 25 times longer than τ_{sat} in fluorinated sample

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

Tunability of phase breaking rate



fluorine density:

A and C: $n_F \sim 7\times10^{11}/cm^2$

B and D: $n_F \sim 2\times10^{12}/cm^2$

Higher τ_{sat}^{-1} at higher fluorine density
Higher τ_{sat}^{-1} at lower carrier density

Phase breaking rate tunable via carrier and fluorine density

Spin-flip scattering due to fluorine

PENNSTATE PHYSICS

Nagaoka-Suhl formula:

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

n_{mag}: magnetic impurity density

T_K: Kondo temperature

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

→ The Kondo temperature T_k up to 0.2 mK

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

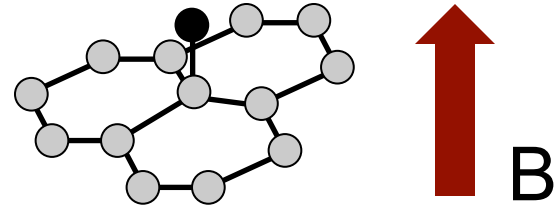
→ exchange energy J up to 5 meV

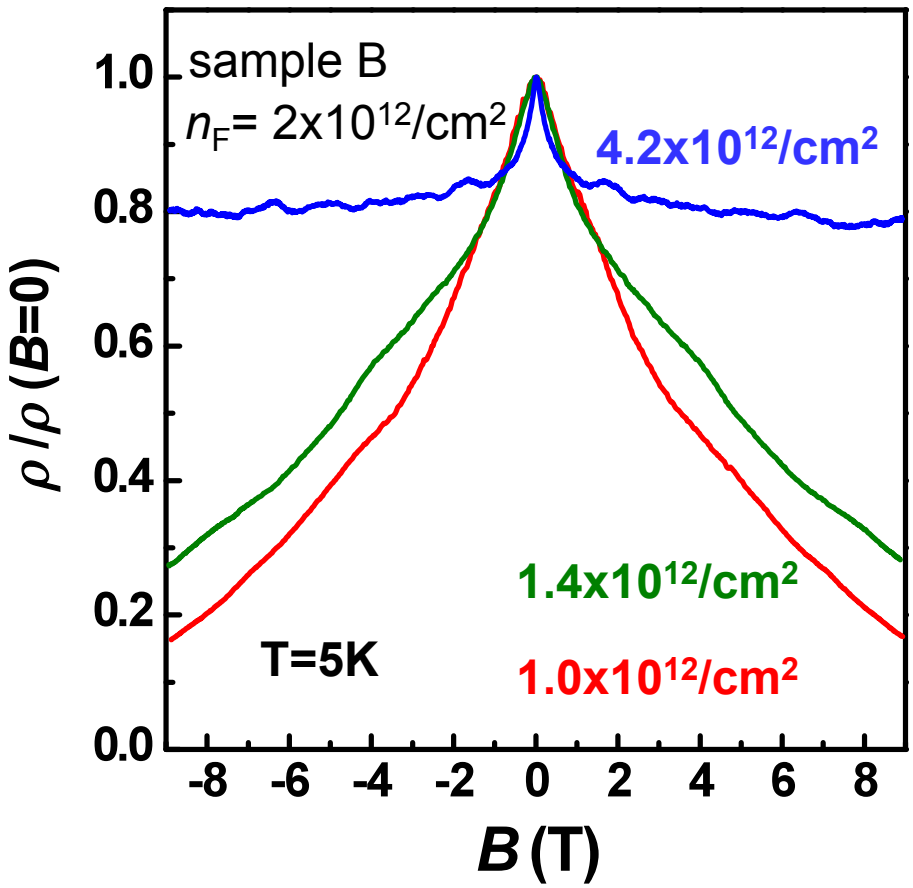
Pierre et al., *PRB* **68**, 085413 (2003)

Sengupta et al, PRB **77**, 045417(2008)

Chen et al, Nat. Phys., **7**, 535 (2011)

Magneto-resistance of DFG

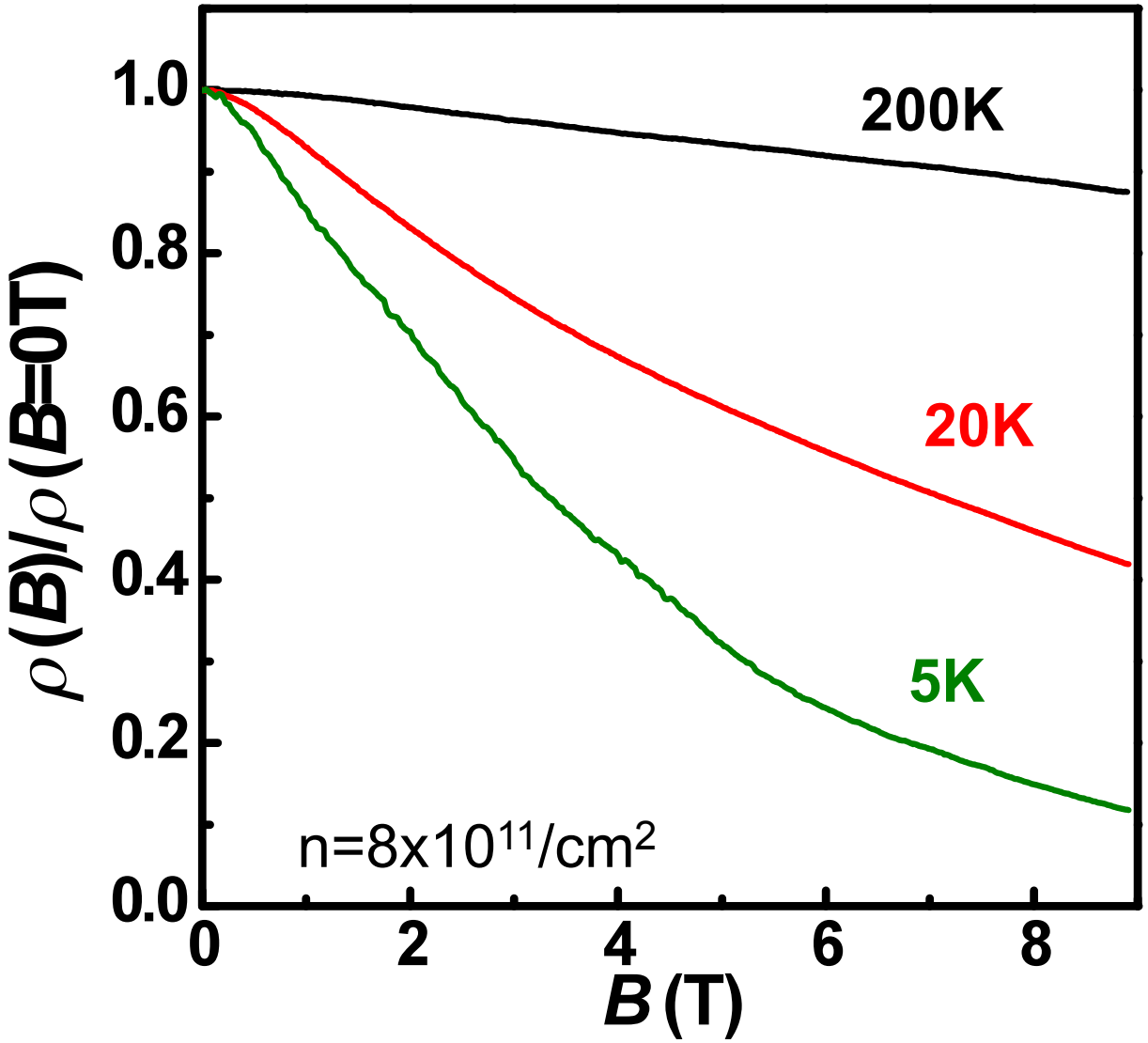




- weak localization at high carrier density
- large negative magneto-resistance in the variable-range hopping regime
  - Up to 40-fold reduction
  - Not yet saturated at 9 T

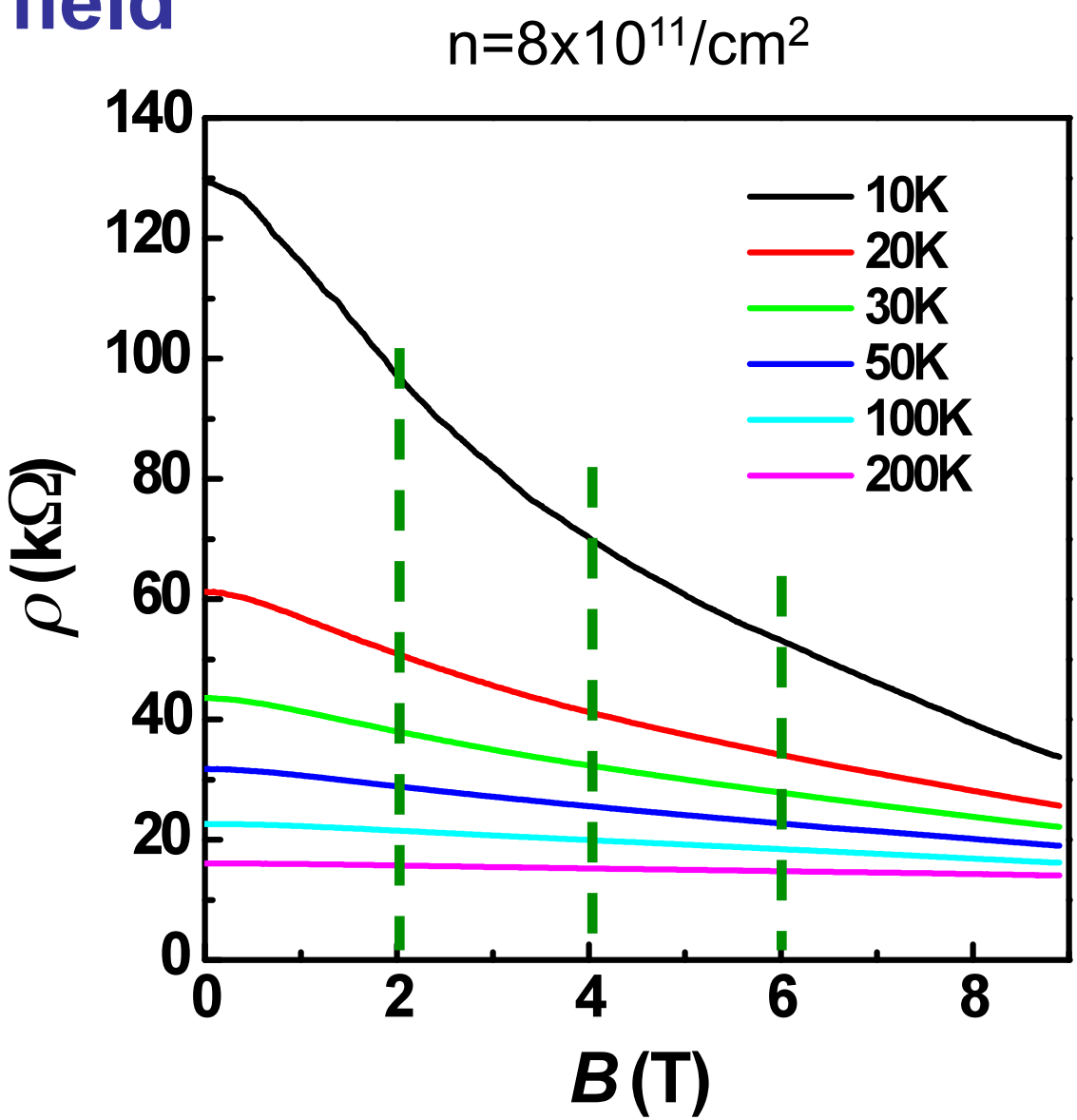
comparable to CMR manganites, ferromagnetic semiconductors

Temperature dependence of the MR

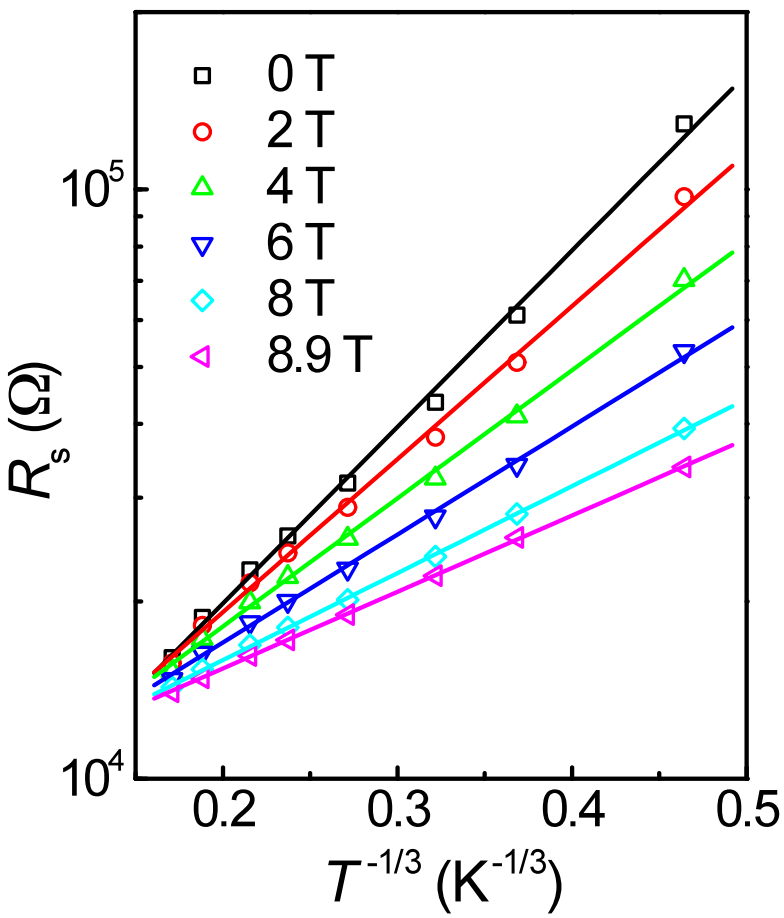


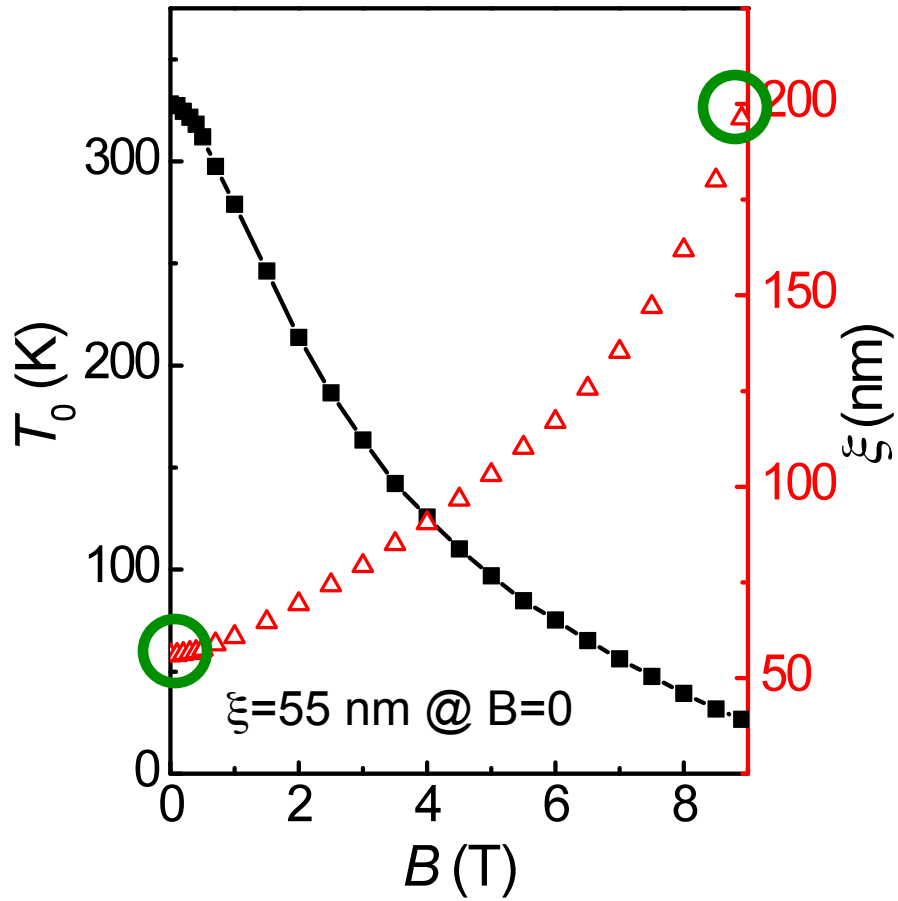
Large negative MR at low temperature

Temperature dependence of the MR at a fixed field



Localization length ξ in field



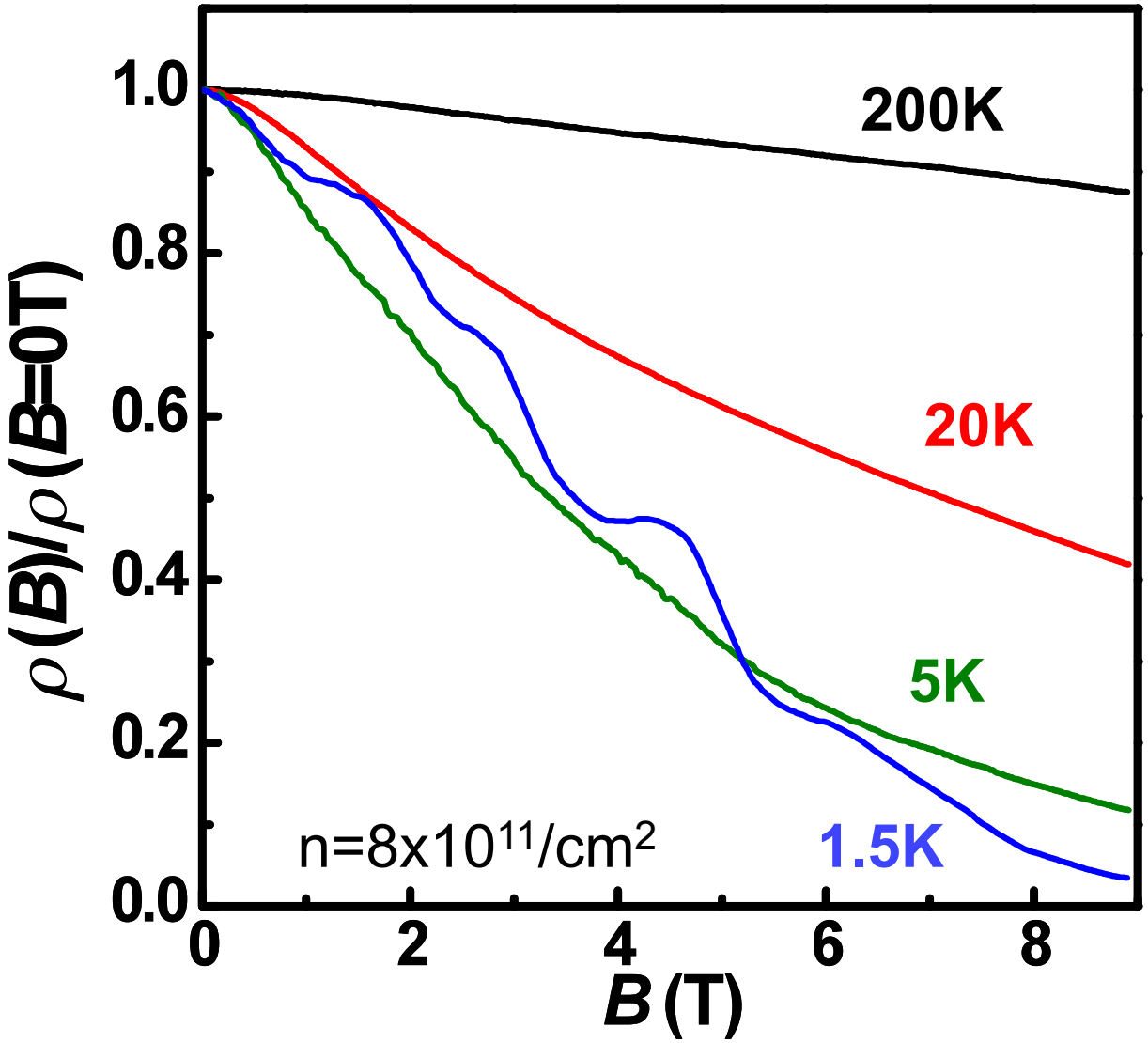


$$\rho(T) \propto \exp\left[(T_0/T)^{1/3}\right]$$

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

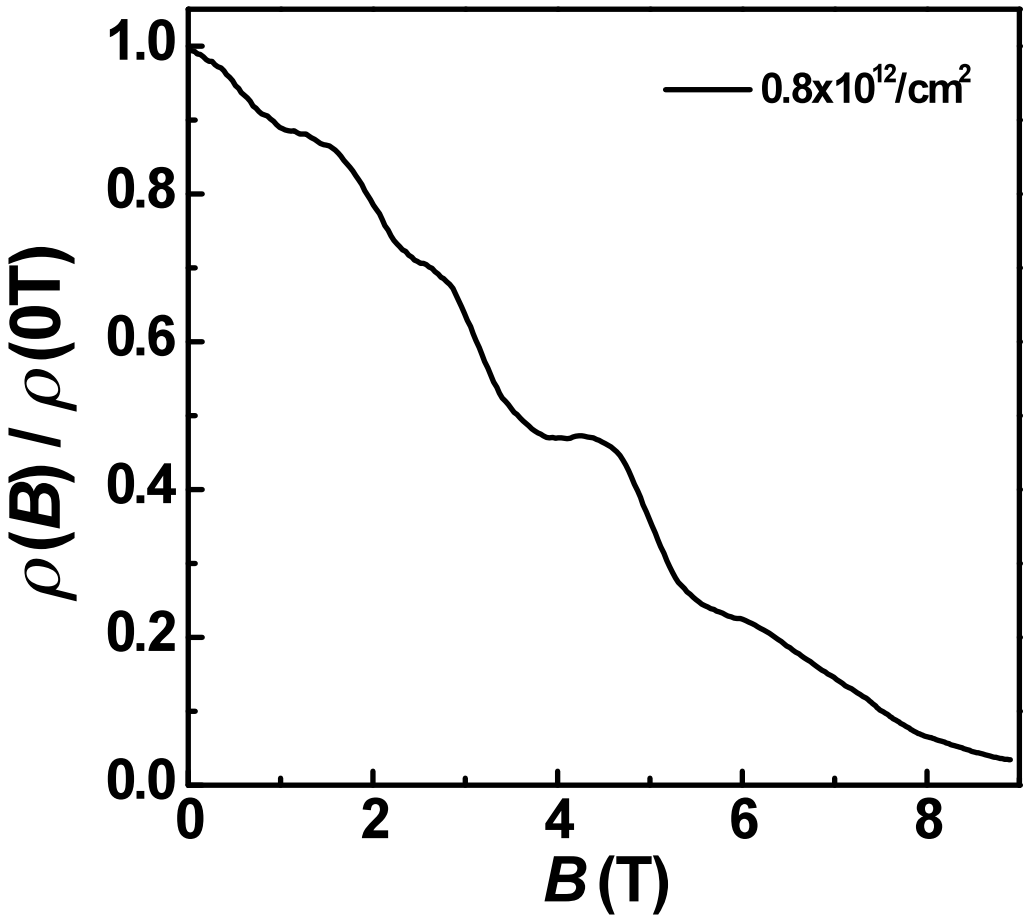
ξ enhanced by a factor of 4 at 9 T

Temperature dependence of the MR

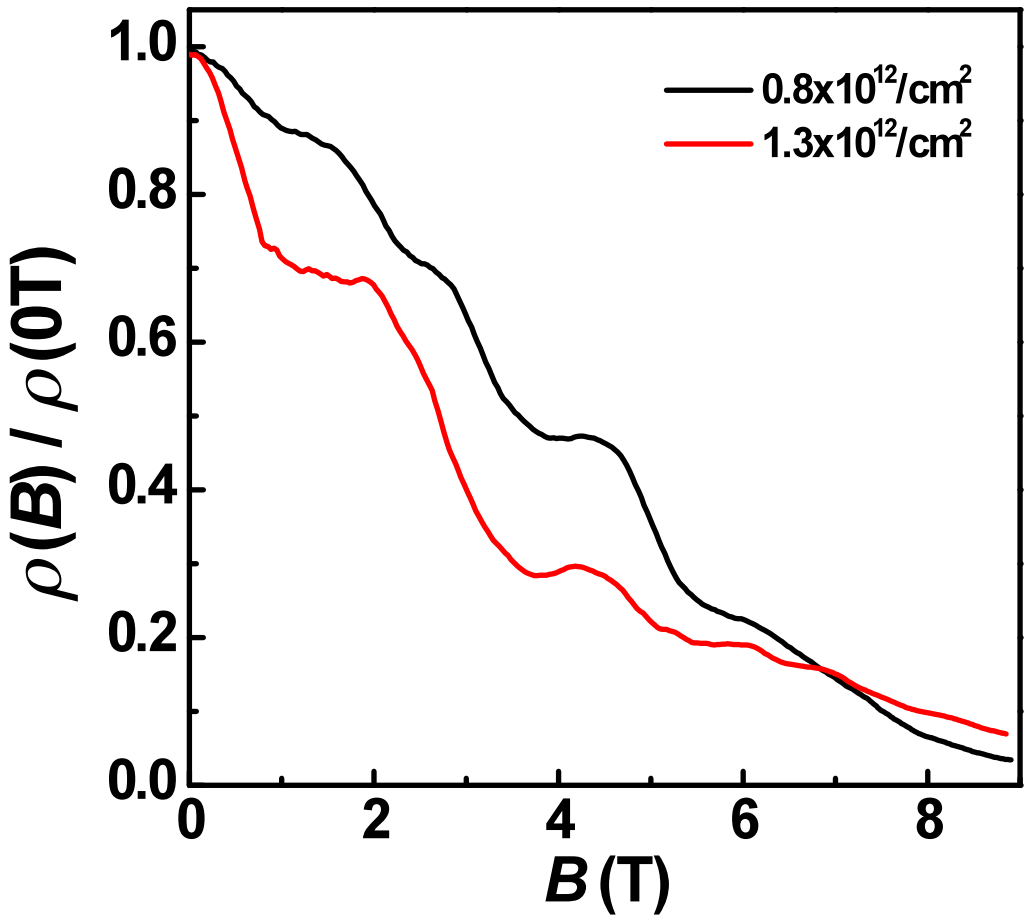


Staircase MR at low temperature

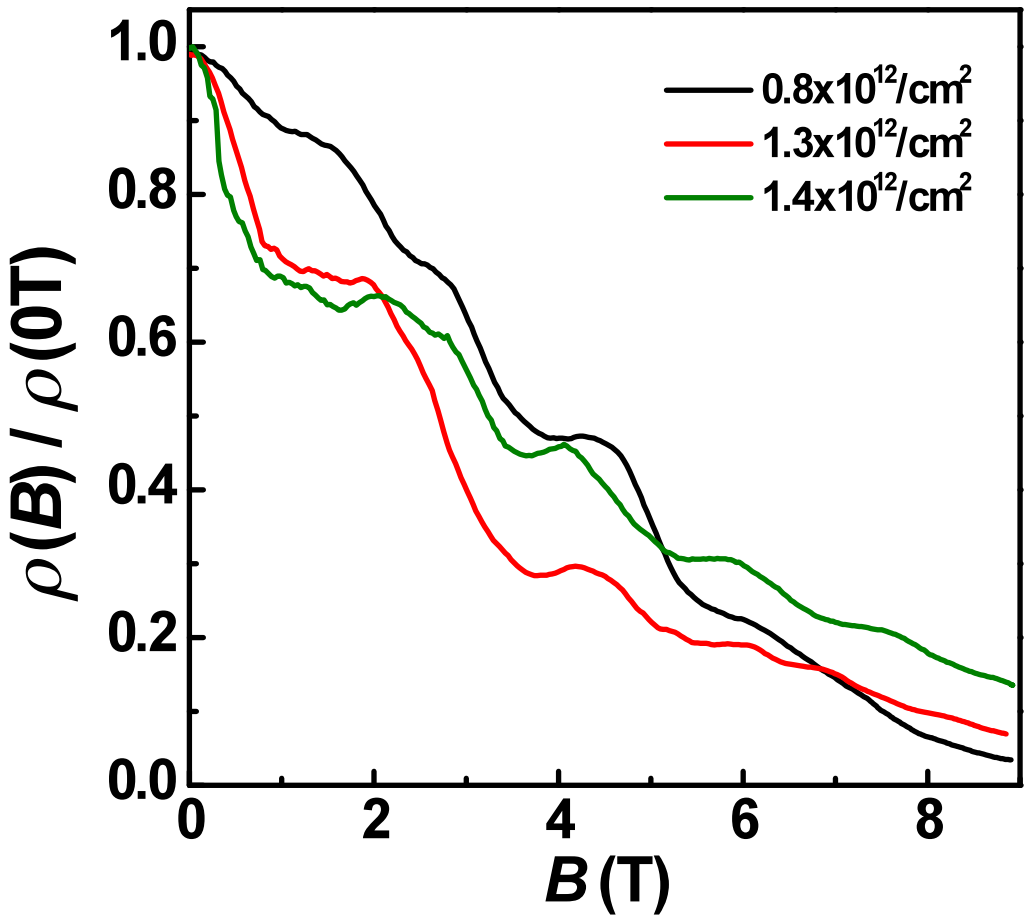
Staircase-like field dependence at low temperature



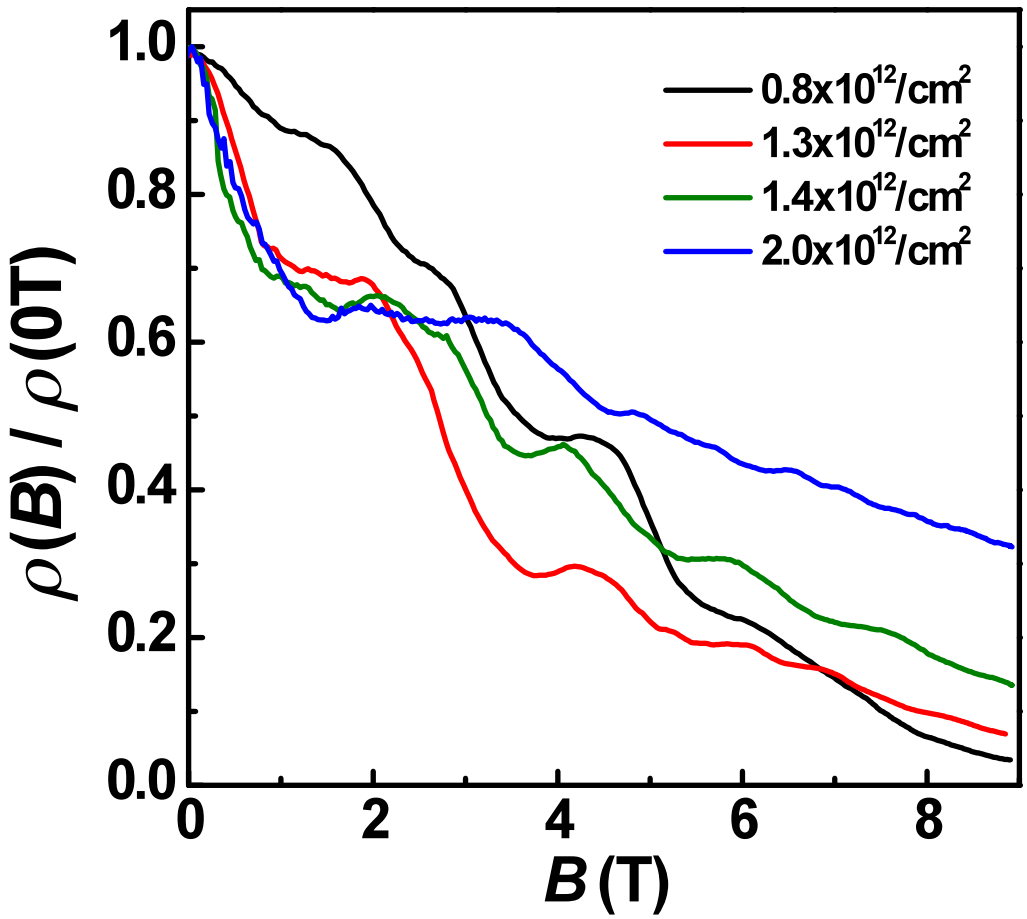
Staircase-like field dependence at low temperature



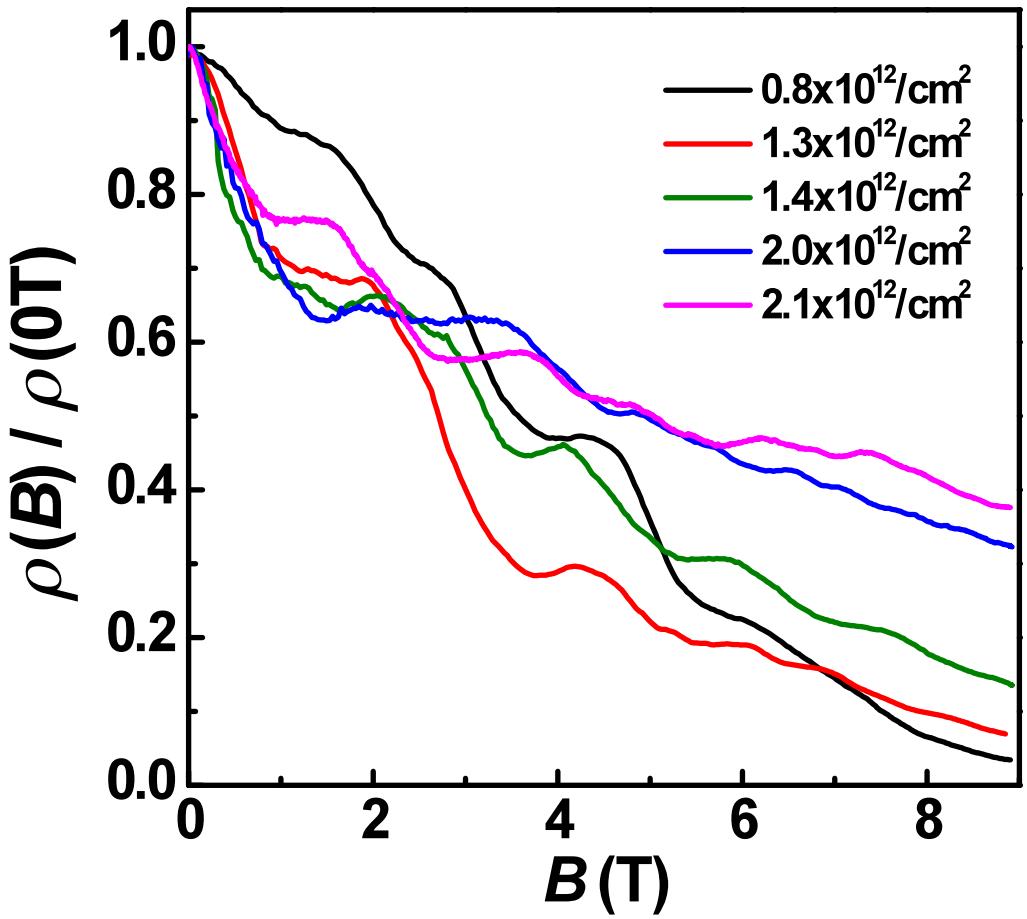
Staircase-like field dependence at low temperature



Staircase-like field dependence at low temperature



Staircase-like field dependence at low temperature



- reproducible
- seen in multiple samples

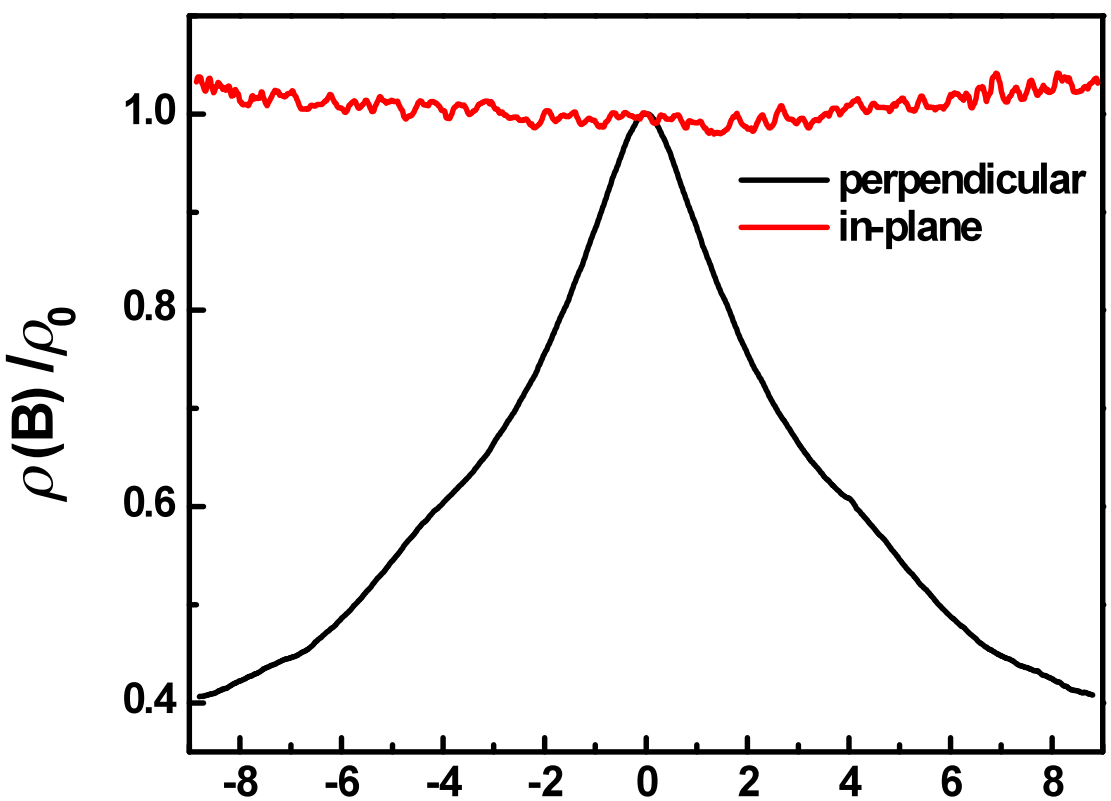
- **NOT** periodic in B (AB effect)
- **NOT** periodic in 1/B (SdH)
- **NOT** universal conductance fluctuation

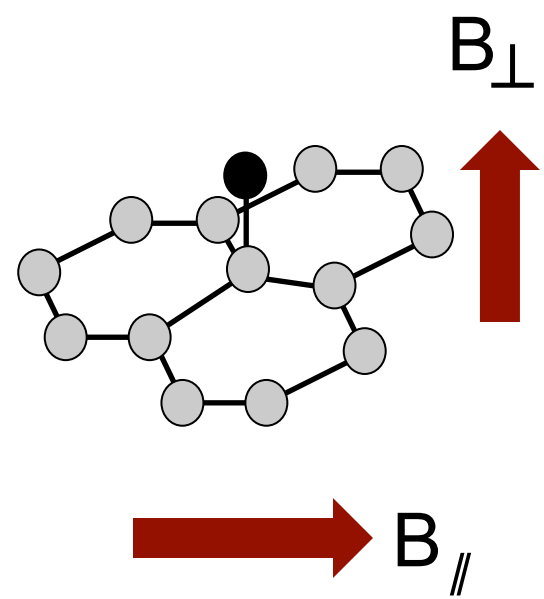
$\Delta\sigma \sim 0.001\text{–}0.1\ e^2/h$

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)

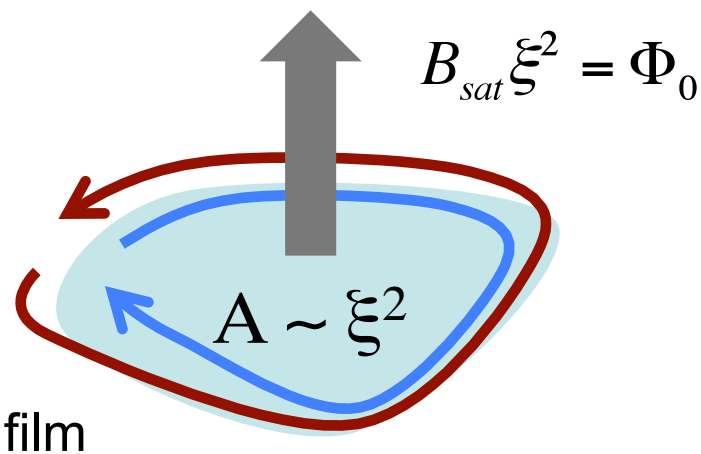




Fukuyama and Yosida, Negative Magnetoresistance in the Anderson Localized States, J. Phys. Society of Japan, **46**, 102, (1979)

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 ξ in strong field.

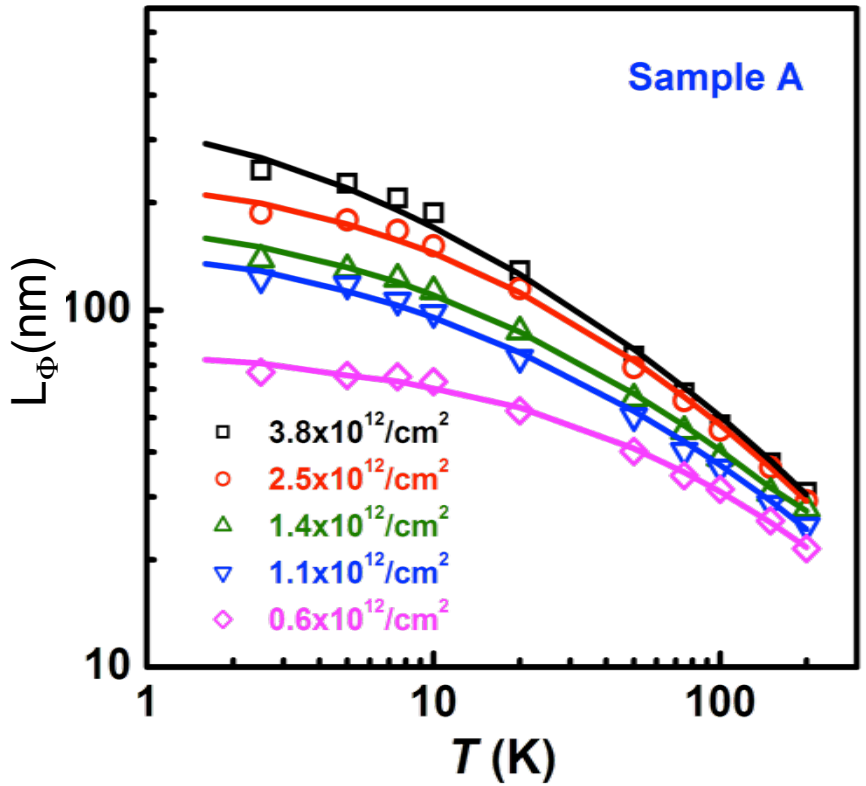
2D and 3D: no good theory
ten-fold MR observed in In_2O_{3-x} film

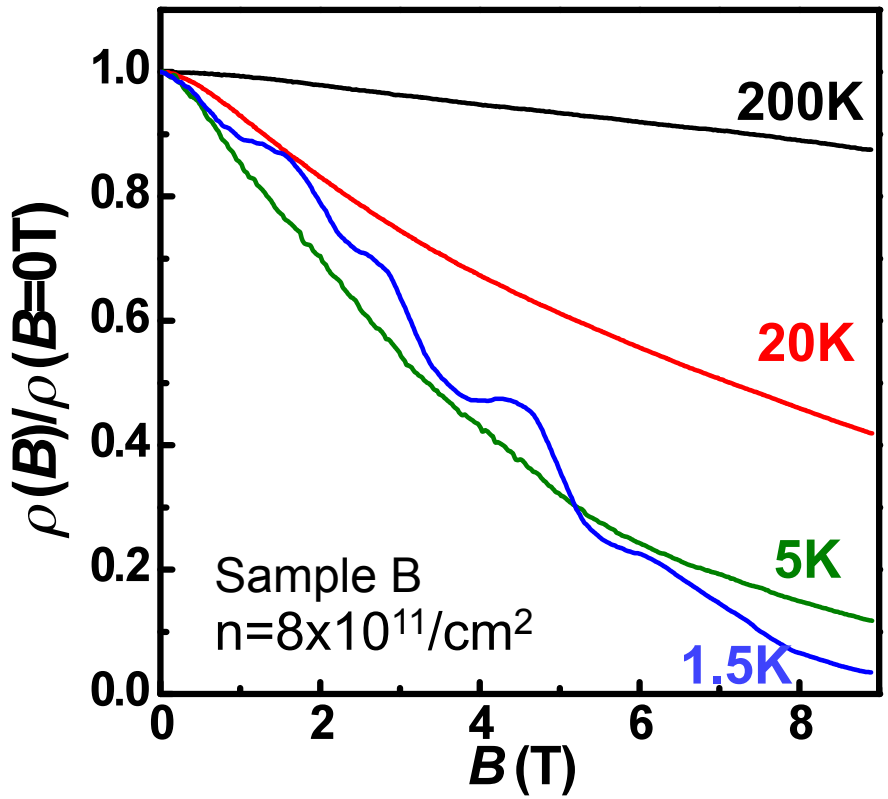
Difficulty with current data:

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

Pichard et al, Physical Review Letters **65**, 1812 (1990).
Lerner and Imry, Europhysics Letters **29**, 49 (1995).
Gershenson et al, PRL, 79, 725(1997)
Frydman and Ovadyahu, Solid State Comm. **94**, 745 (1995).

Magneto-transport of DFG





- Anomalous phase breaking length saturation in weak localization regime

- Colossal magneto-resistance in variable-range hopping regime

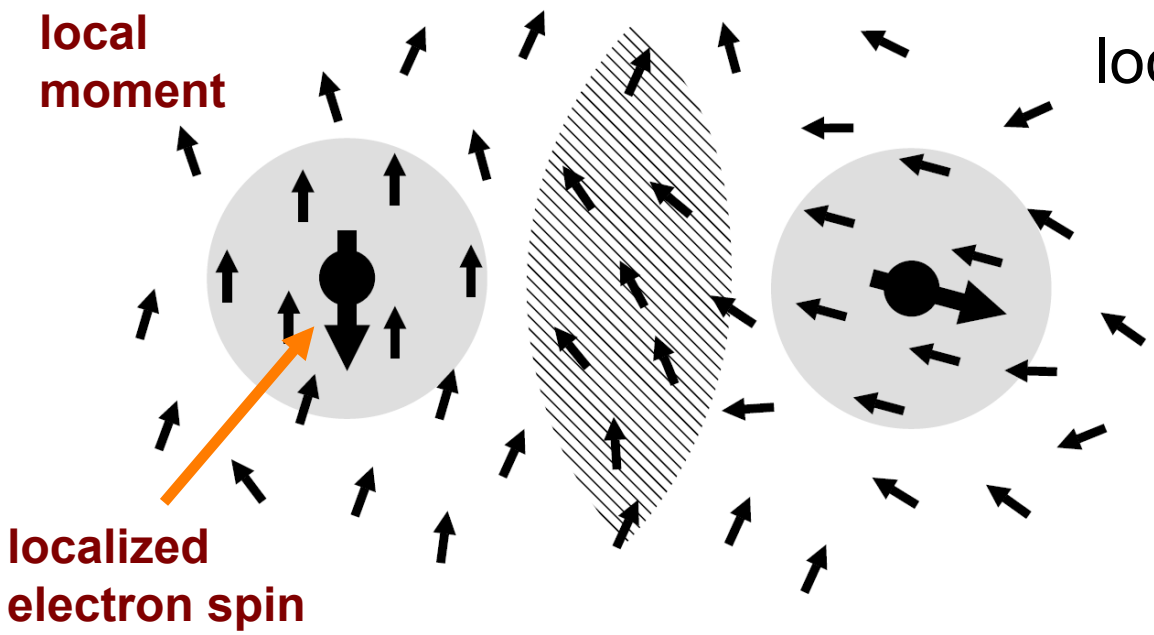
Evidence of local moment

Explanations?

Hypothesis #2: magnetic polarons?

Exchange coupling between moments and localized electrons

enhanced self-trapping



Kaminski & Das Sarma, *PRL* **88**, 247202 (2002)

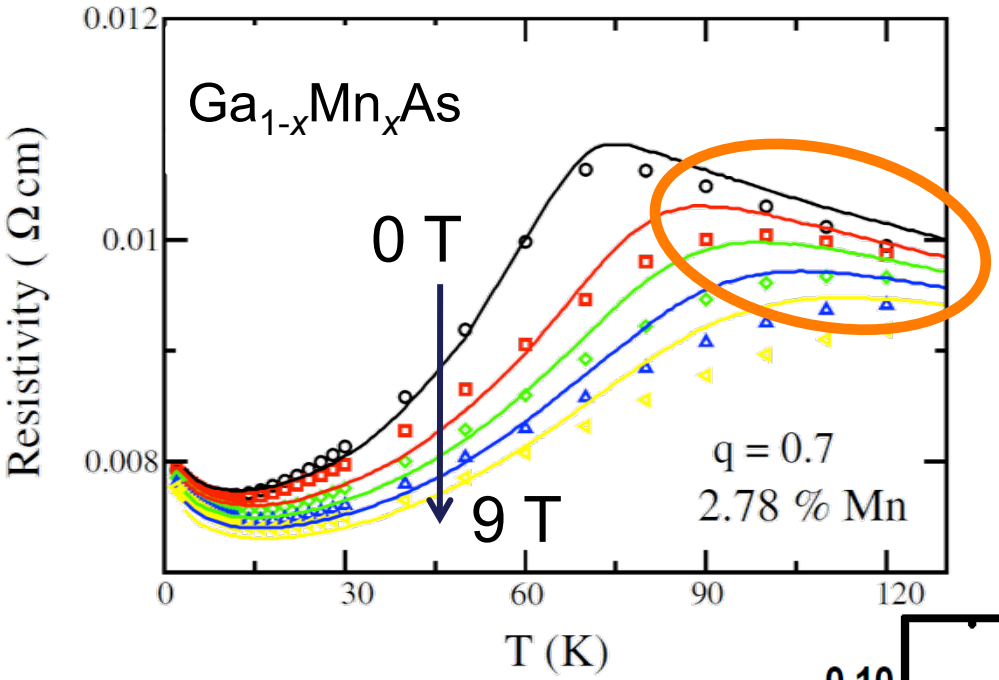
localization length ξ= 55 nm

F-F spacing 7 nm

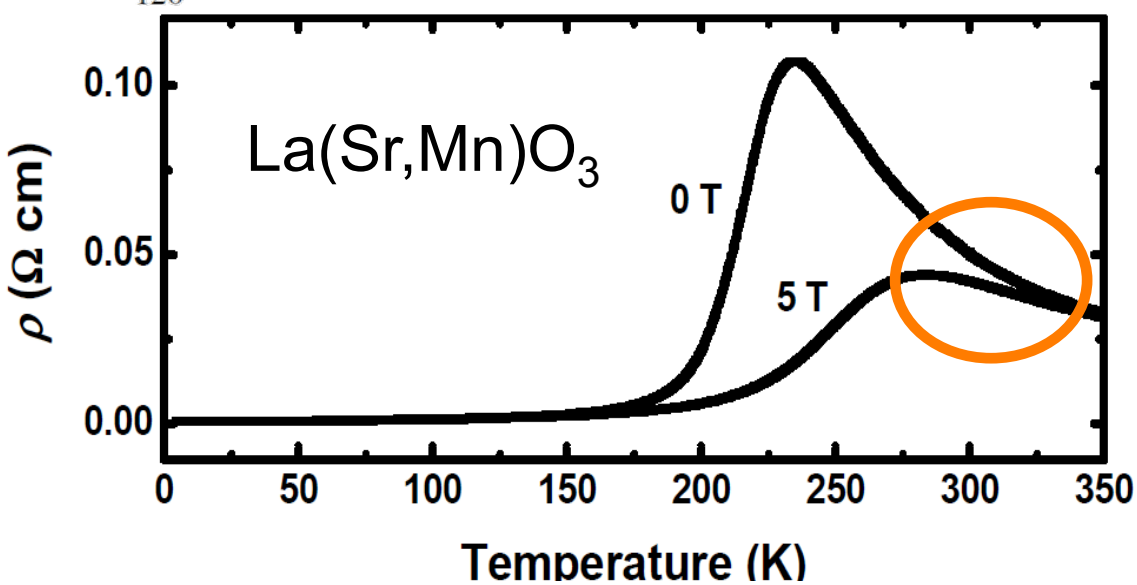
one electron localized over many F adatoms

A magnetic field aligns the polarons and enhances hopping.

Negative MR in CMR manganites and ferromagnetic semiconductors

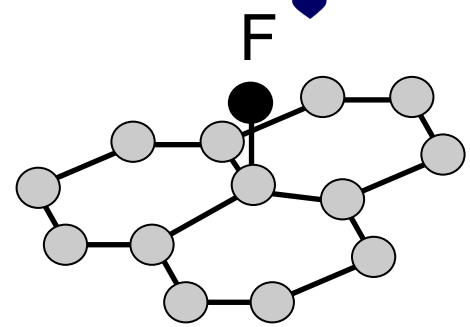


Moca et al., *PRL* **102**, 137203 (2009).

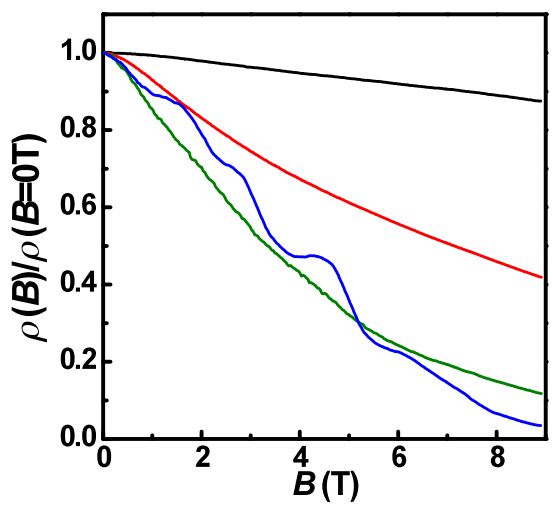


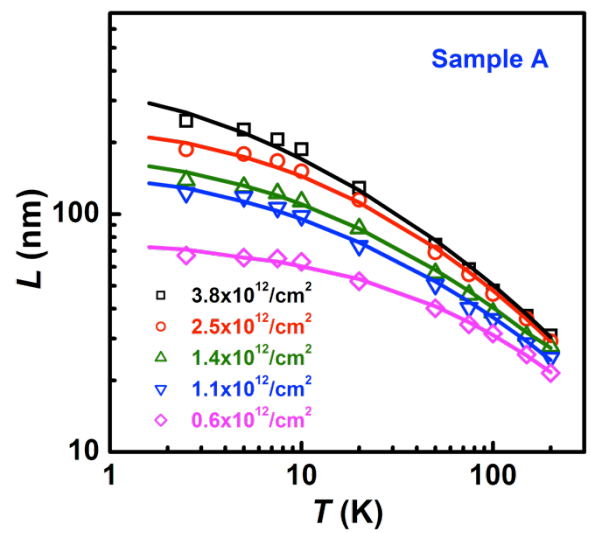
Dietl, *Semicond. Sci. Technol.* 17, 377 (2002)

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