Magnetic and electronic structures of nanographene and fluorinated nanographene with an interplay of edge-state spins and dangling bond spins

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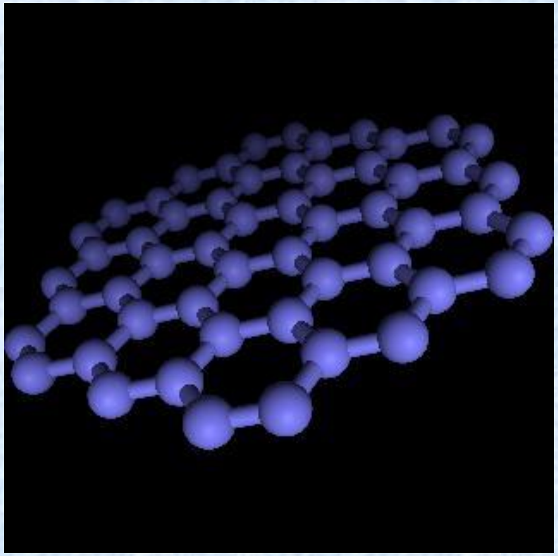
graphene 2012

April 10-13, 2012 · Brussels (Belgium)

graphene



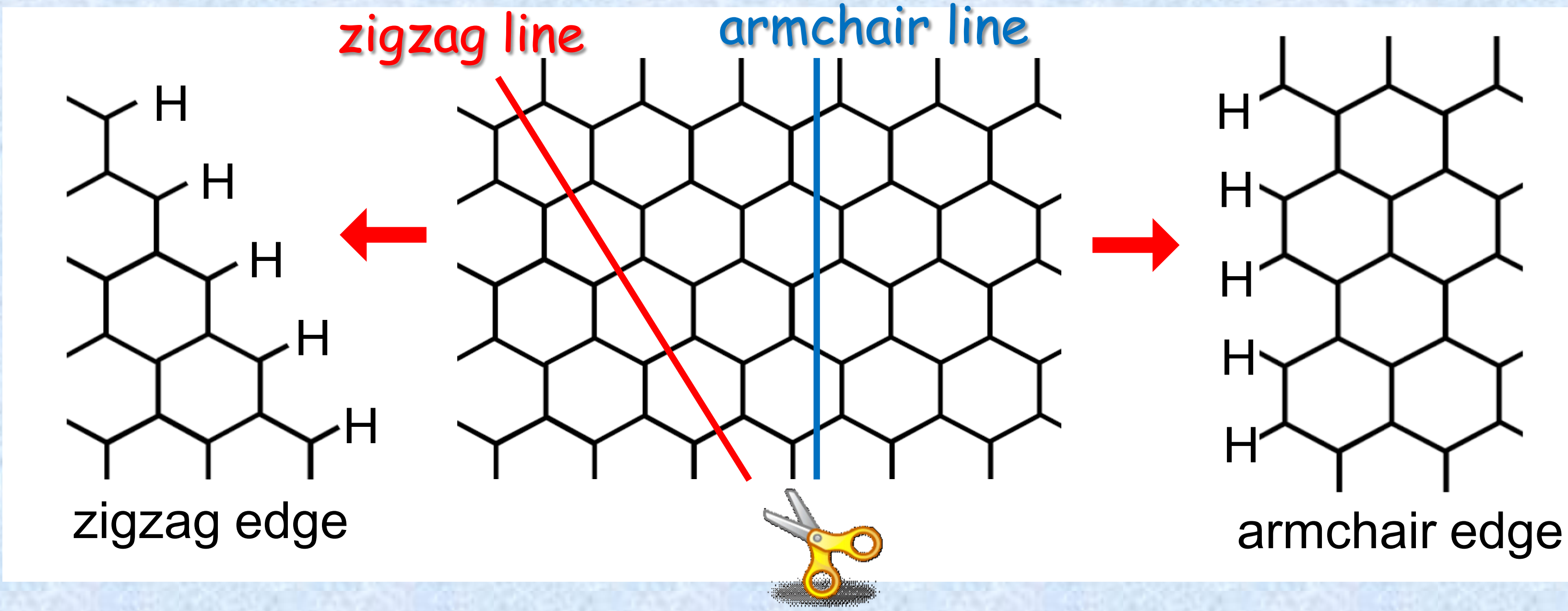
nanographene

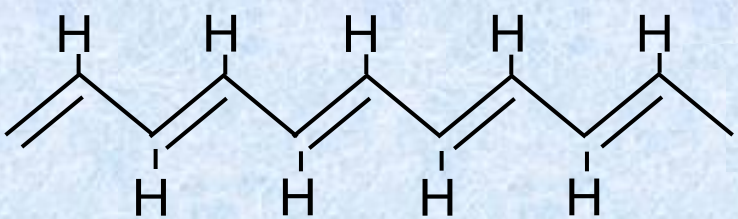
open edge

magnetic properties

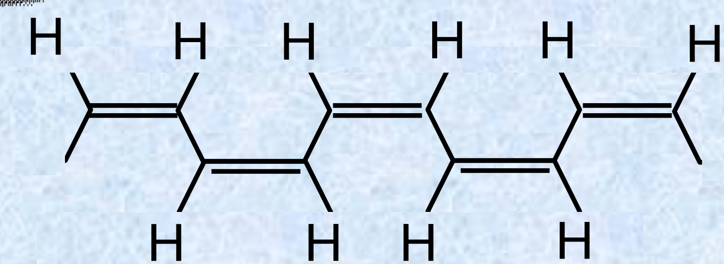
polycyclic aromatic molecules

T. Enoki, *Physica Scripta T* **146**, 014008 (2012).





trans-polyacetylene



cis-polyacetylene

Edge modifies the electronic structure in two manners

edge shape dependent (zigzag/armchair)

electron scattering/interference at the edge

superlattice pattern (STM)

Raman G-band (C-C stretching; 1600 cm^{-1})

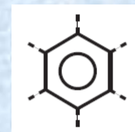
localized non-bondings π state at the edge (edge state)

graphene and edge effect for chemists and physicists

chemistry aspect

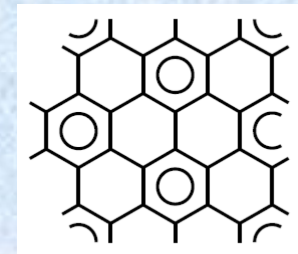
aromaticity

Clar's aromatic sextet rule



aromatic sextet

graphene



aromaticity 1/3

chemically active

physics aspect

massless Dirac fermion (relativistic wave equation)
in the bipartitie lattice

zero-gap semiconductor
with linear bands ($\propto \mathbf{p}$)

$$\mathscr{H} = v_F \sigma \mathbf{p}$$

momentum $\mathbf{p}$

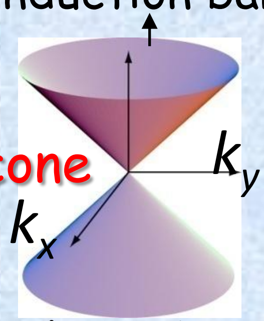
Fermi velocity $v_F \approx (1/300)c$

pseudo-spin σ ↑↓

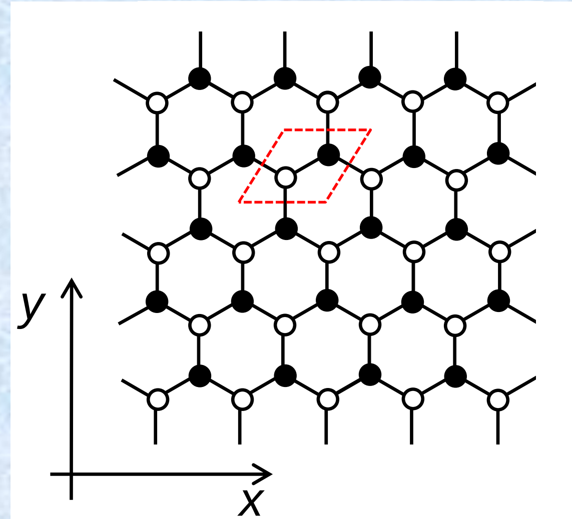
degree of freedom; 2

conduction band

Dirac cone



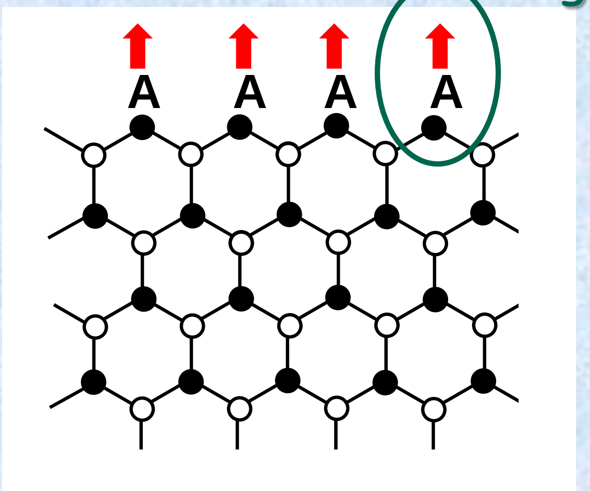
valence band



two sublattices A; ●, B; ○
two sites in the unit cell

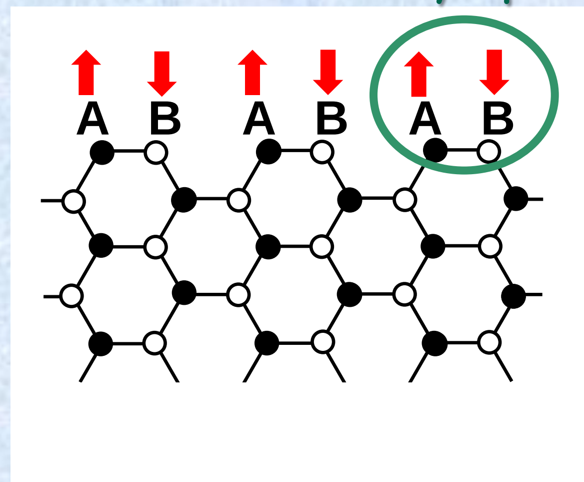
How physicists understand the edge state

edge state



zigzag edge

always paired



armchair edge

edge state (magnetic)

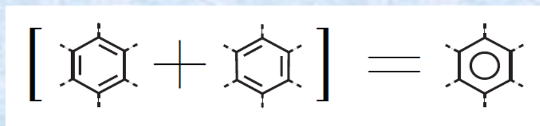
only one of the sublattices (A, B) exists in the zigzag edge

broken symmetry of the pseudo-spin ↑ in Dirac fermion

Clar's aromatic sextet rule (# of sextets) most stable structure

maximal number of the sextets separated by the entirely empty rings

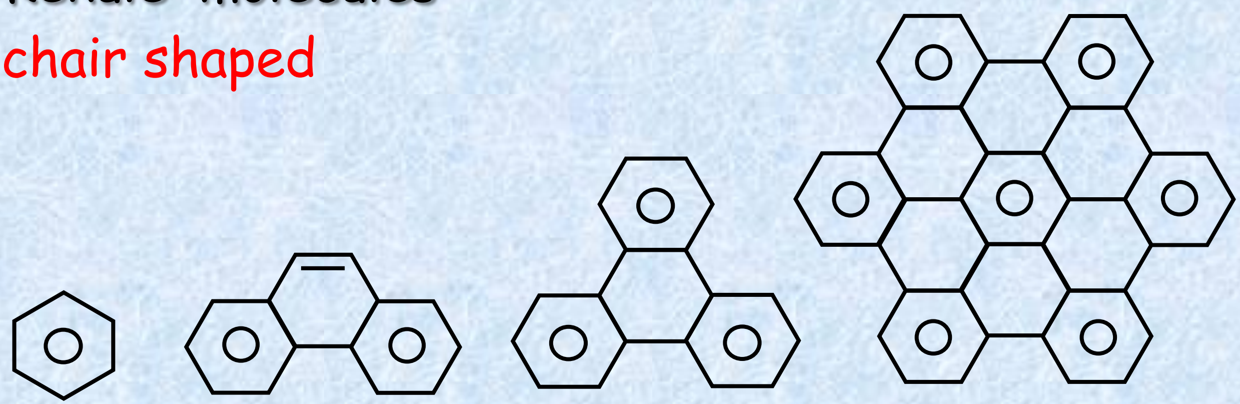
well stabilized



sextet
benzene ring with C atoms
singly bonded to the surrounding

aromatic Kekulé molecules

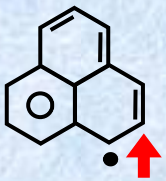
armchair shaped



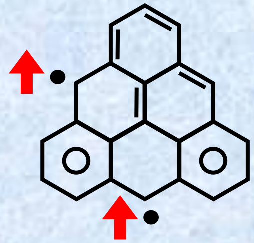
(1) (2) (3) (7)

non Kekulé molecules (non-bonding π-state (π-radical))

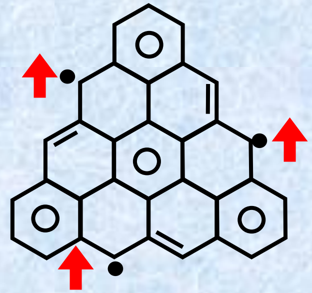
zigzag shaped



S=1/2
(1)



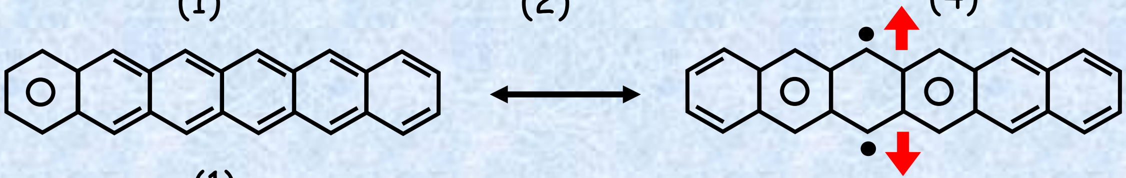
S=1
(2)



S=3/2
(4)

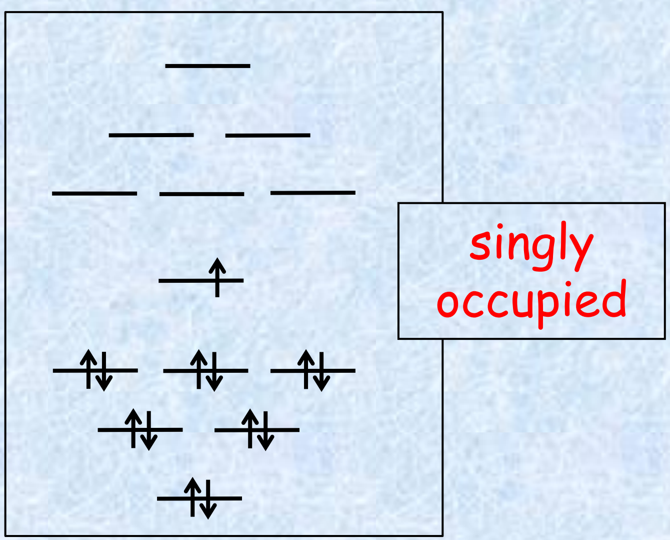
less stabilized
ferromagnetic

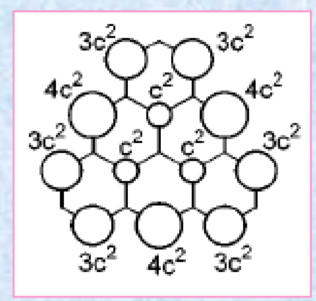
Hund rule



(1)

less stabilized
antiferromagnetic
(open shell singlet)

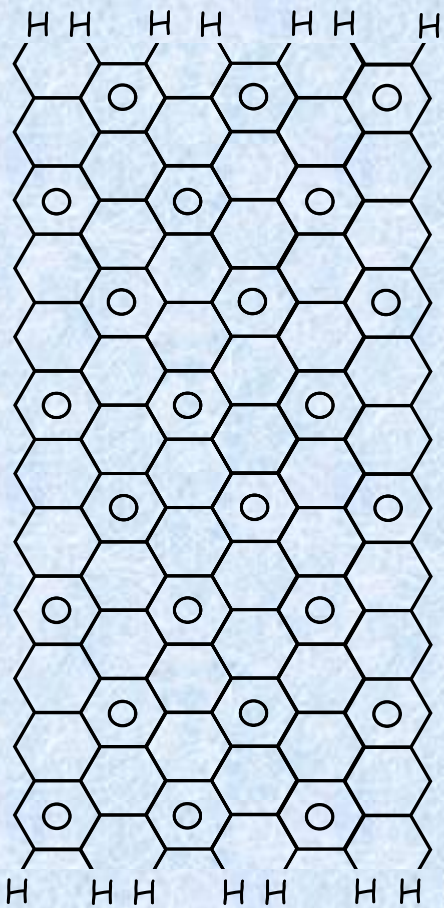




localized around
zigzag edges

edge state

nanographene ribbon   Clar's sextet formula



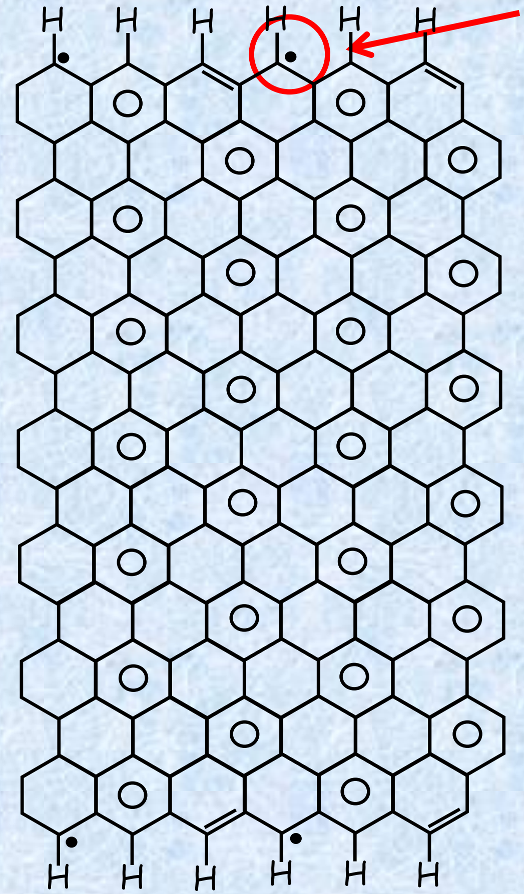
armchair edge

same to infinite graphene

nonmagnetic

radical spins at zigzag edges

magnetically
electronically
chemically
active



$\sqrt{3} \times \sqrt{3}$

superlattice
in the interior

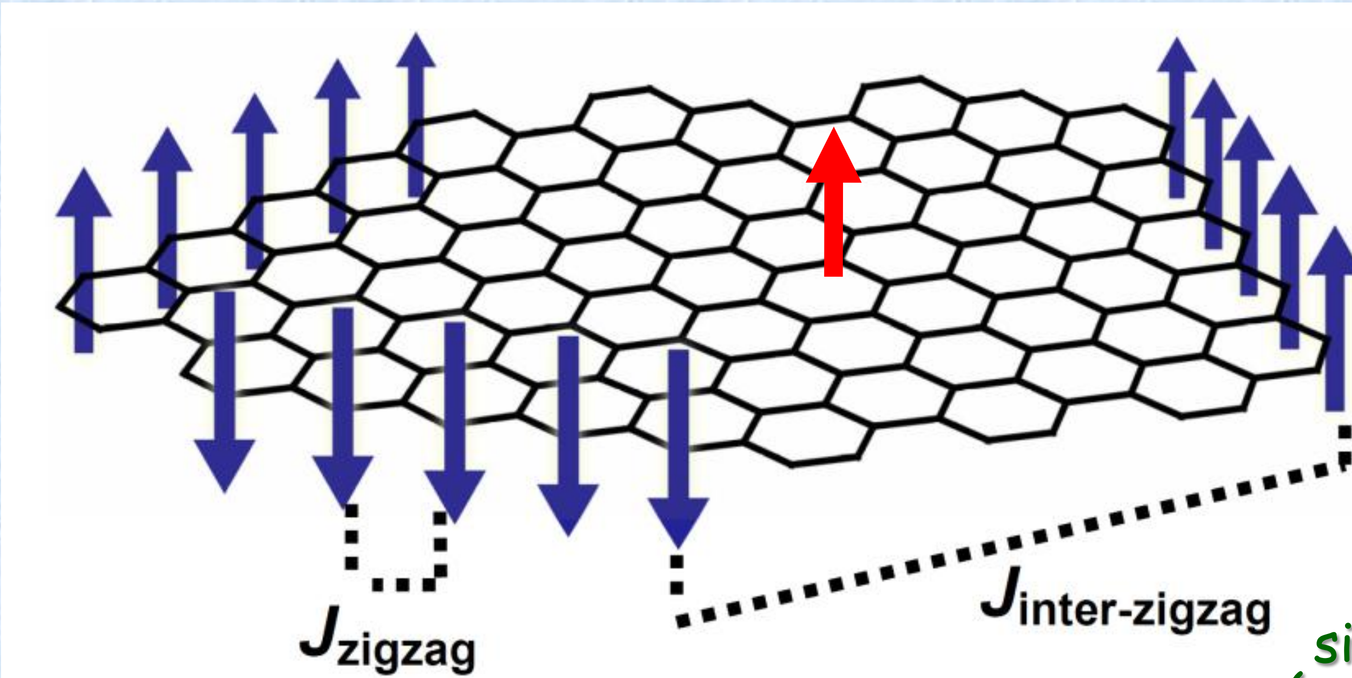
zigzag edge

magnetic (edge-state spins)

Wassmann, Mauri, et al. *JACS* (2010)

detailed magnetic structure in a nanographene sheet

isotropic Heisenberg spin (small spin-orbit interaction (~5 cm^{-1}) of C atom)



inter-zigzag int.
similar to RKKY int.
(conduction-electron-mediated)

J_{zigzag} ~ several 10^3 K ferromagnetic

$J_{inter\text{-}zigzag}$ ~ 10^{-1} – 10^{-2} J_{zigzag} ferro- or antiferromagnetic depending on the geometrical relation

effective magnetic moment

ferrimagnetic structure

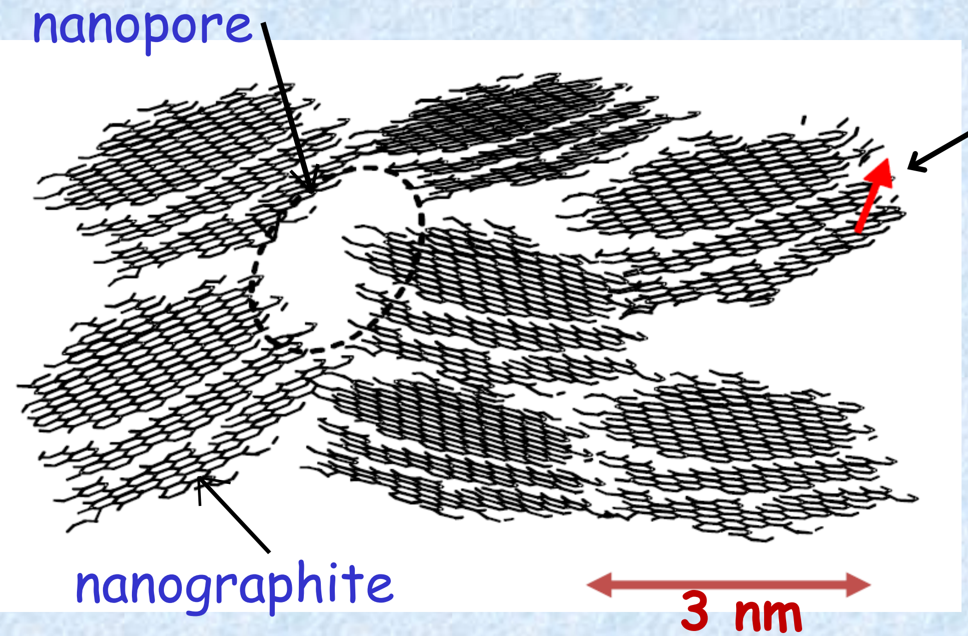
V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev. B* **81**, 115408 (2010)

electronic structure of edge state of π-electron origin

NEXAFS & ESR

Joly, Kiguchi, Terrones, Dresselhaus, Takai, Enoki, et al. *Phys. Rev.* **B81**, 245428 (2010)

Our target activated carbon fiber (ACF)
nanographene-based nanoporous carbon



localized edge-state spin

3-4 nanographene sheets stacked

ca.300 C atoms /nanographene sheet

3D random network of nanographite domains
soft and flexible network

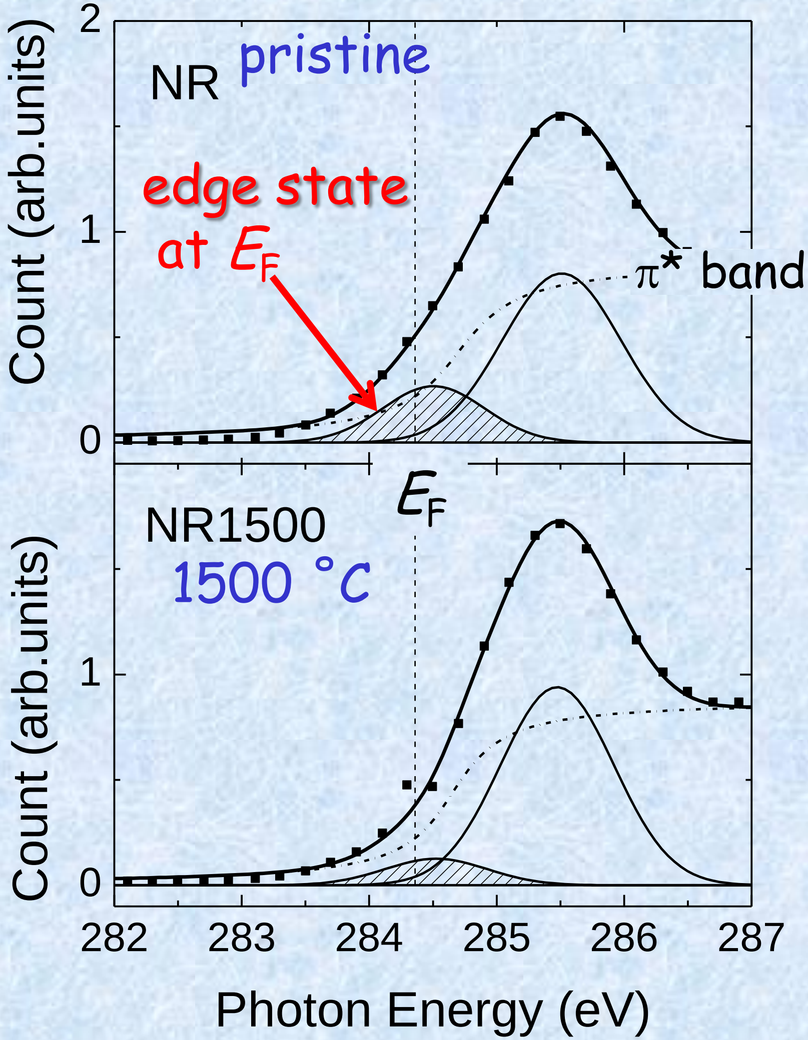
nanopores adsorption of guest molecules

edge-state spins spin concentration expected from Clar's rule

NEXAFS (near edge x-ray absorption fine structure)

graphene nanoribbon C 1s to π* peak under different annealing conditions

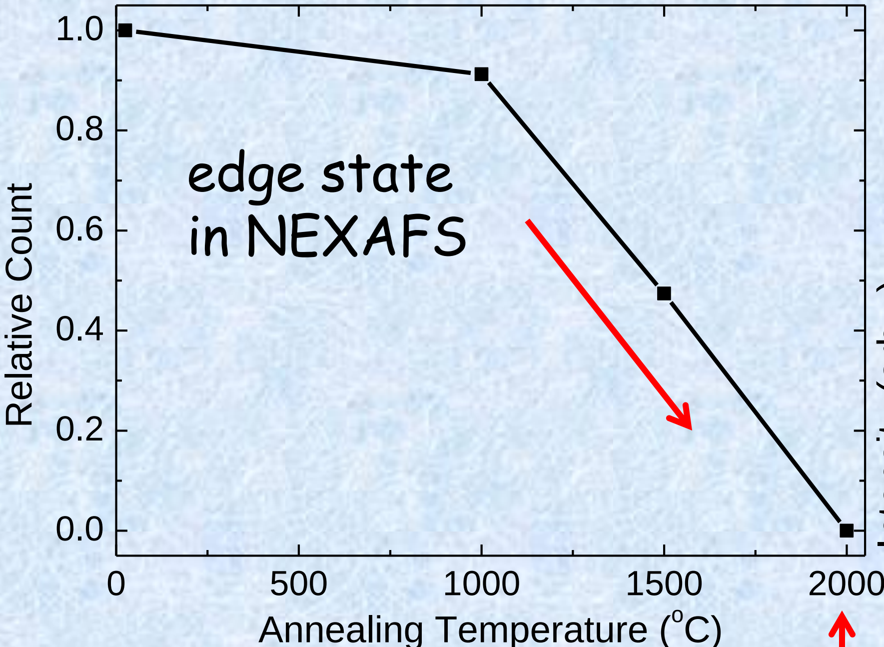
Joly, Kiguchi, Terrones, Dresselhaus, Takai, Enoki, et al. *Phys. Rev.* **B81**, 245428 (2010)



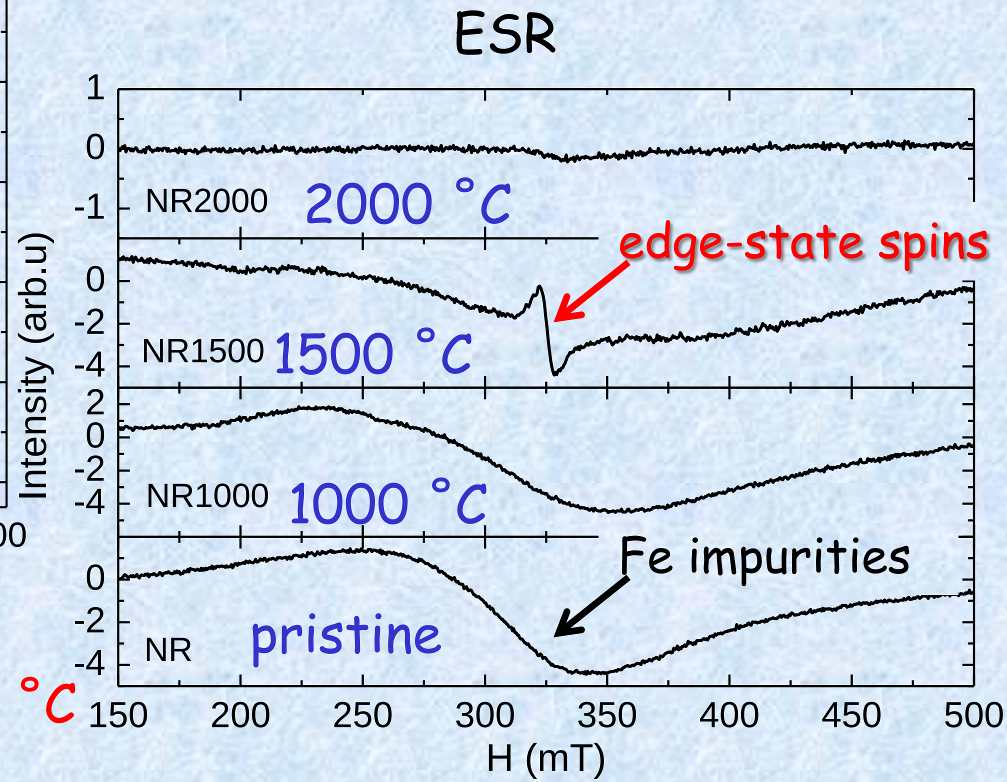
edge state decreases with HTT and disappears at HTT=2000 °C

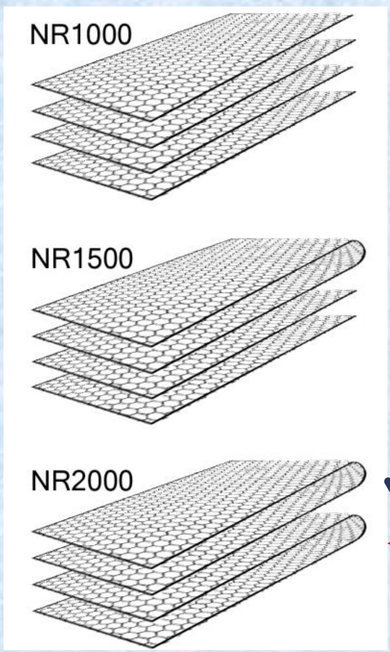
heat treatment above 2000 °C (> graphitization temperature)

edge state contribution in the $C\ 1s$ to π^* vs ESR intensity



2000 °C





loop formation
edge disappears

no edge state

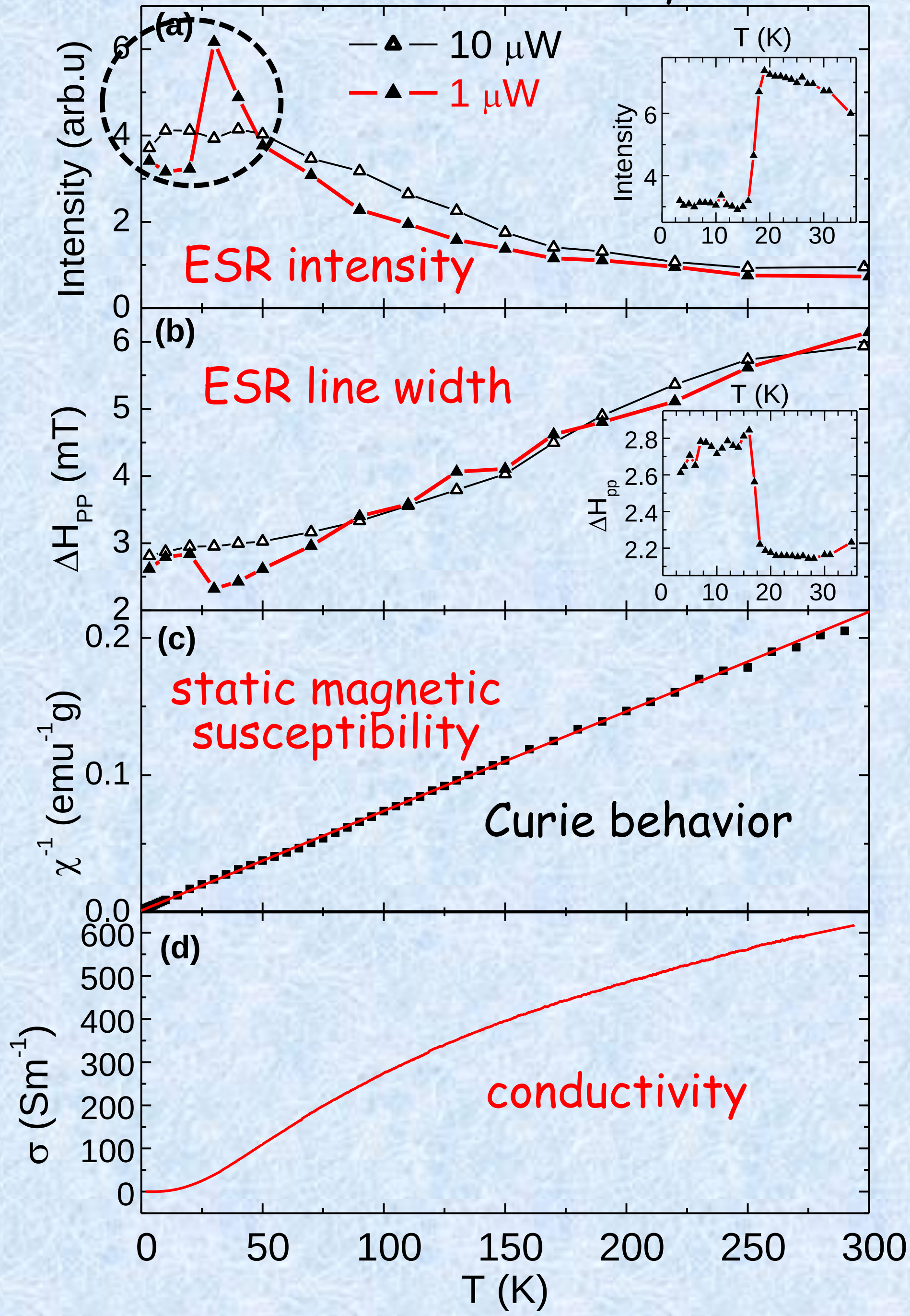
edge state is magnetic

magnetic structure of edge-state spin system

V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev. B*.**81**, 115408 (2010)

T. Enoki, Many Facets of Graphene, VCH, (2012), in press

V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev. B*.**81**, 115408 (2010)



dynamical behavior of the edge-state spin system

by ESR and electron transport investigations

ESR intensity
Curie type behavior of edge-state spins down to ca.30 K

drops below 30 K in disagreement with the static susceptibility

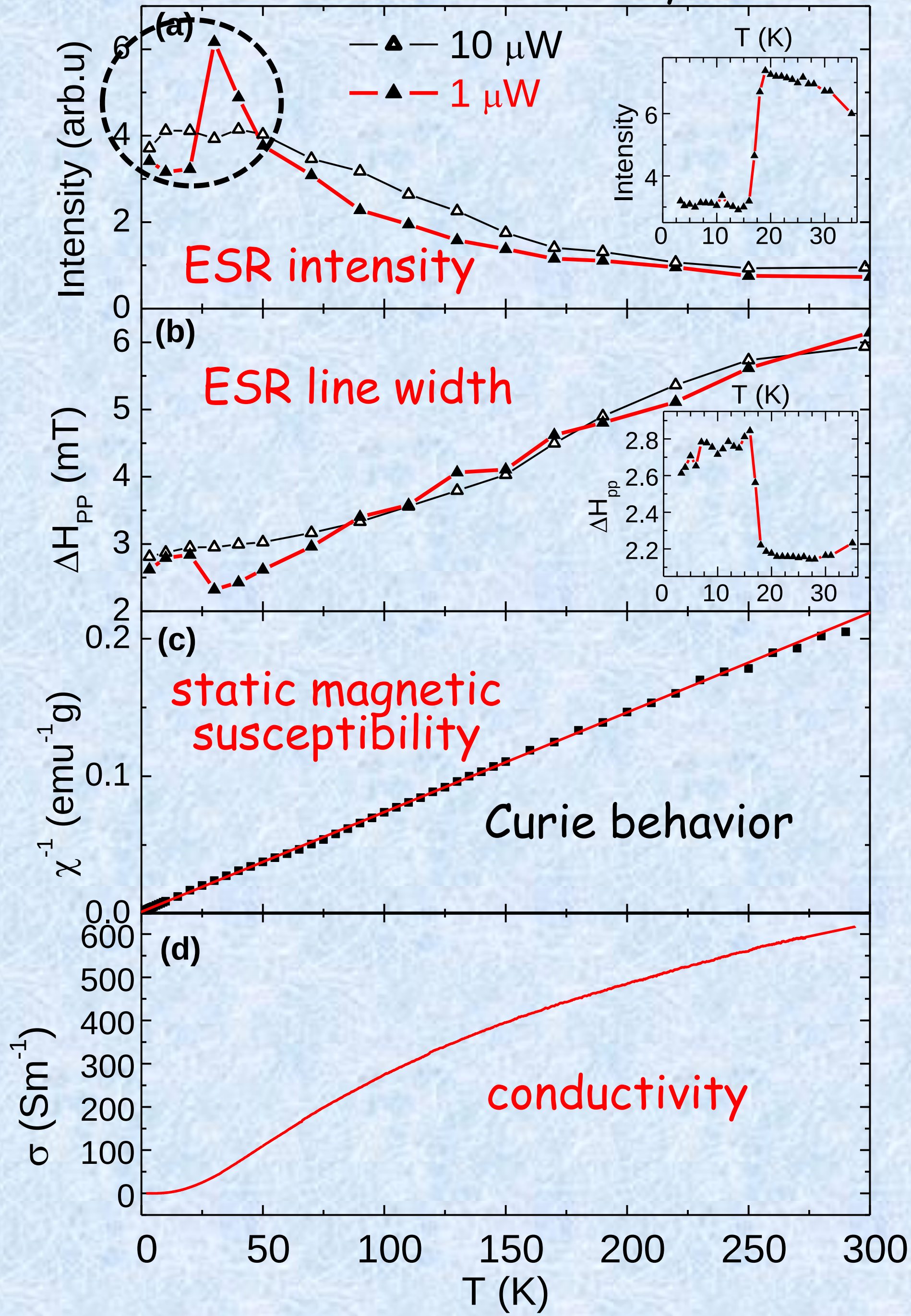
ESR line width
linear decrease with the lowering of the temperature down to ca.30 K

upsurge below ca.30 K

microwave power dependence

dynamical process governs

V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev. B.* **81**, 115408 (2010)



dynamical behavior of the edge-state spin system

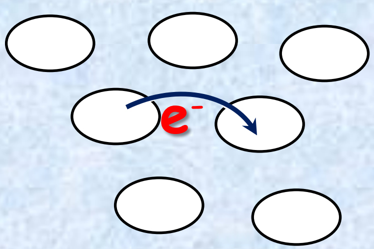
by ESR and electron transport investigations

dynamical process governs

conductivity decreases
with lowering of the temperature

Coulomb-gap variable range hopping
inter-nanographite-domain transport

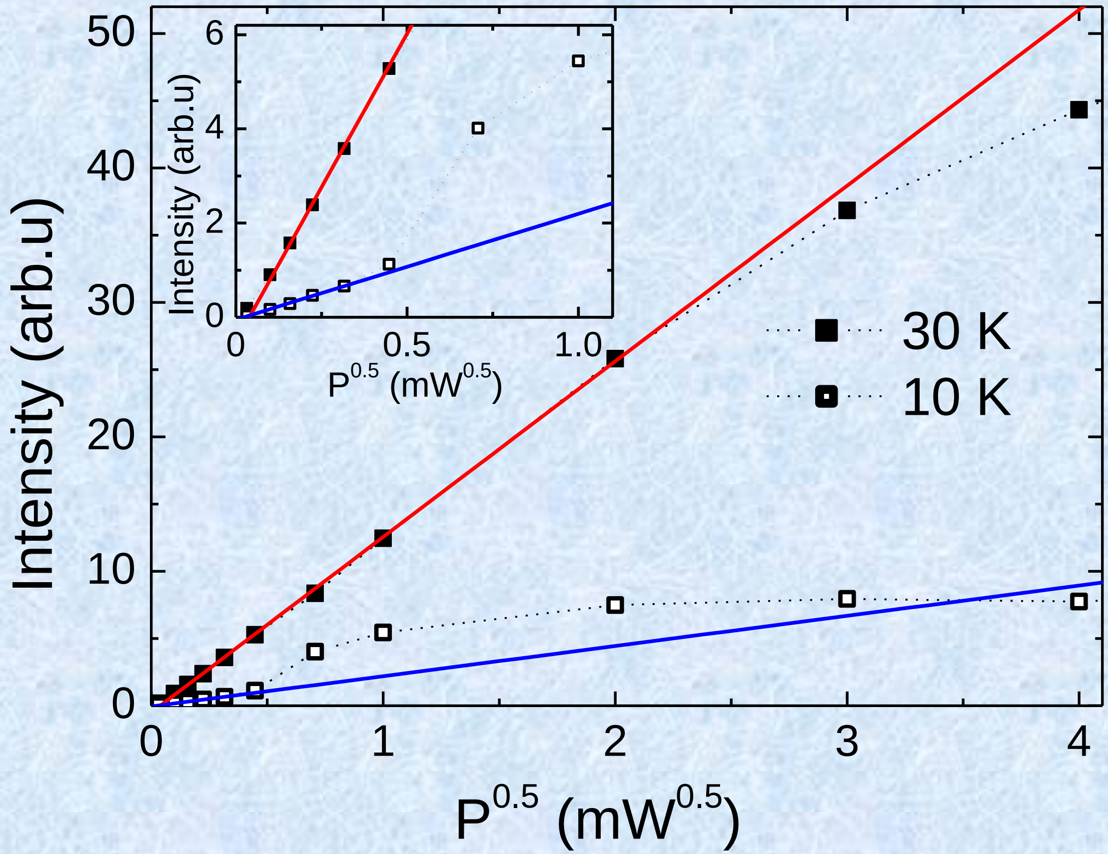
$$\sigma \propto \exp\left[-\left(T_0 / T\right)^{1/2}\right]$$

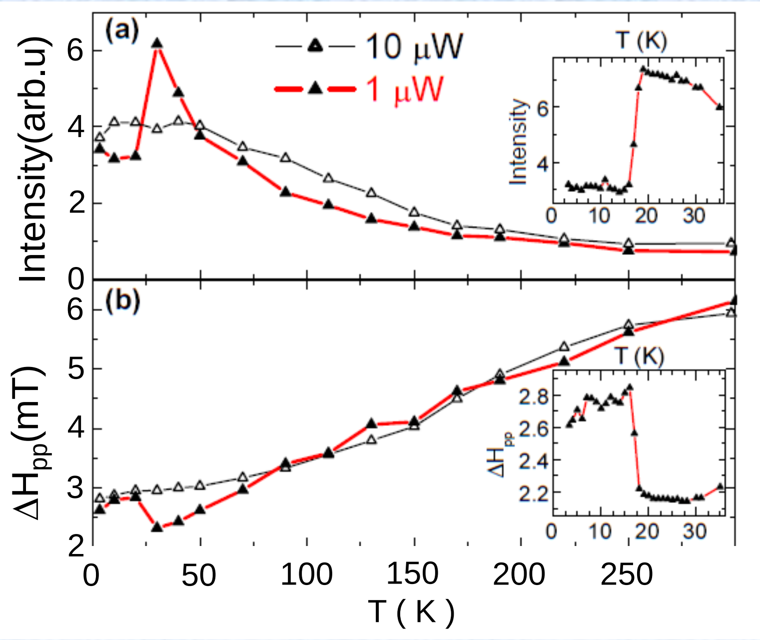


charging effect

electron localiztion at low *T*

ESR saturation curves (intensity vs $\sqrt{\text{microwave power}}$)



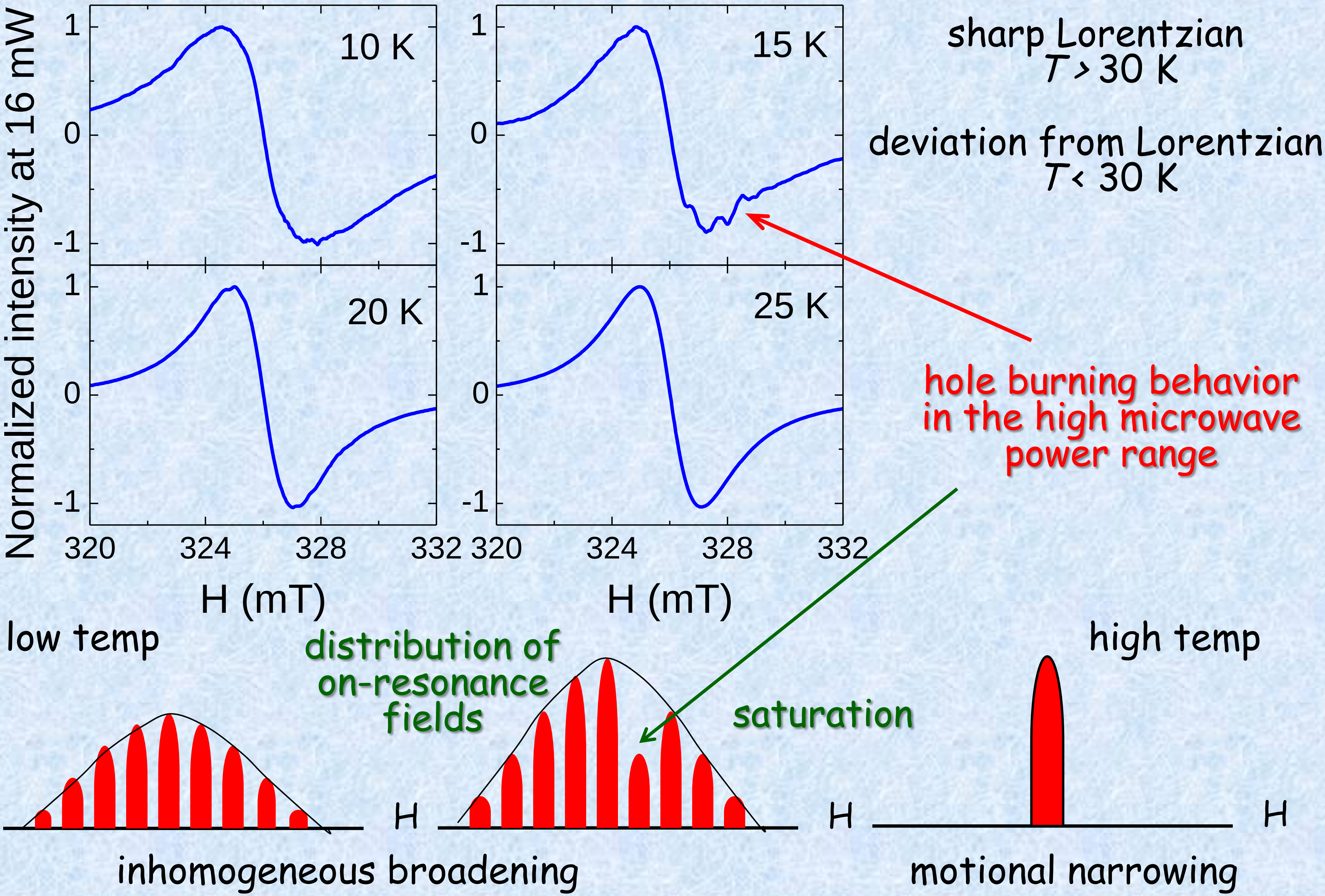


T > 30 K
less saturated

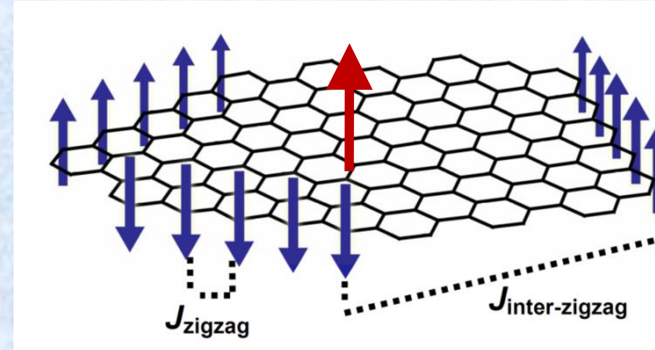
T < 30 K
strong saturation

inhomogeneous spin state
in the low temperature regime (*T* < 30 K)

ESR line shape at high microwave power (16 mW)



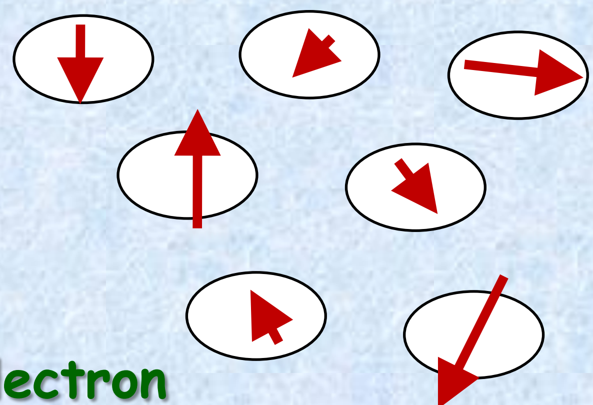
nanographene/nanographite domain



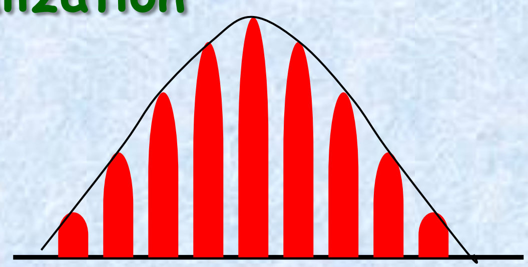
ferrimagnetic
a non-zero magnetic moment
with its value varying randomly

distribution of on-resonance fields

low temp

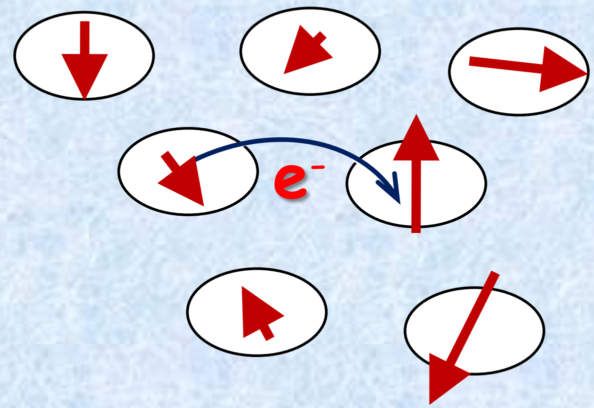


electron localization

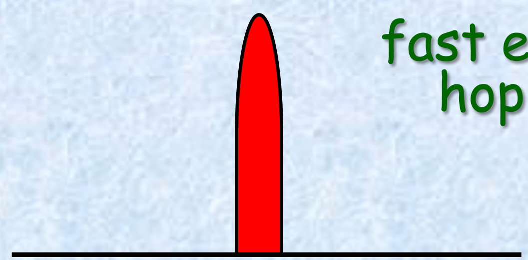


inhomogeneous broadening

high temp



fast electron hoppings

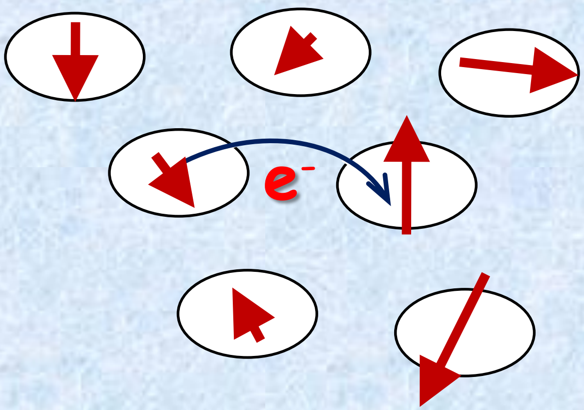


motional narrowing

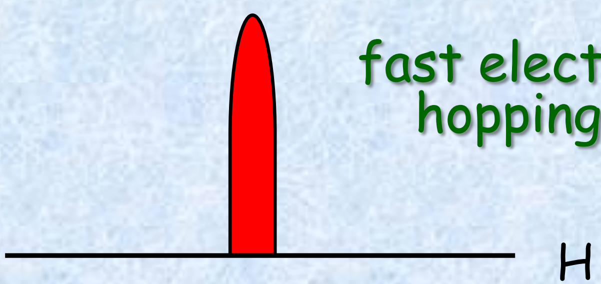
nanographene/nanographite domain

ferrimagnetic
a non-zero magnetic moment with its value varying randomly

high temp



fast electron
hoppings



motional narrowing

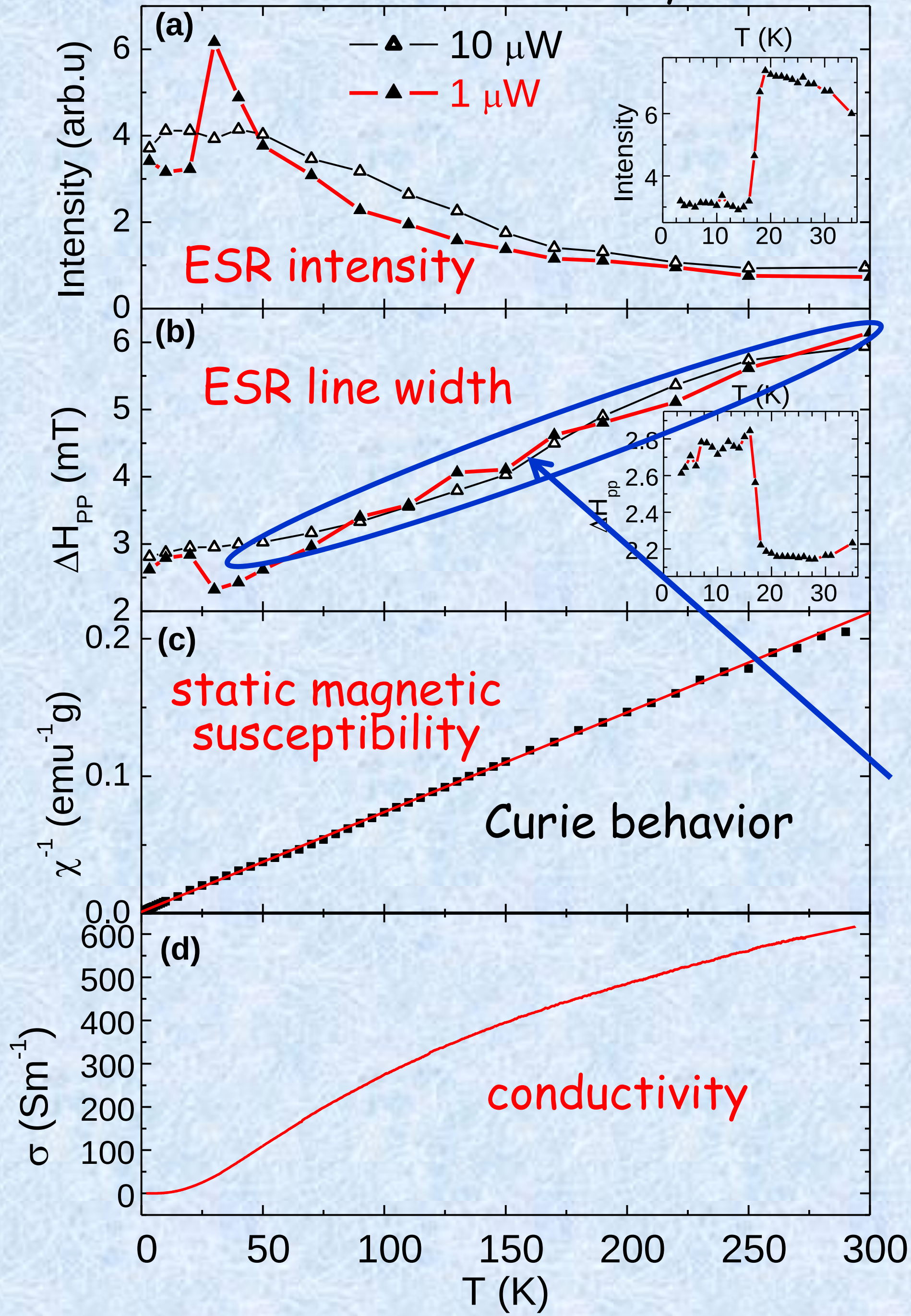
inhomogeneous broadening at low *T*

⬇

important evidence of ferrimagnetic structure
with varying net magnetic moments

each nanographite domain behaves
as independent superparamagnetic particle
in **electron localization state** at low *T*

V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev. B* **81**, 115408 (2010)



behavior at high temperature
T > 30 K

ESR signal

motional narrowing

intrinsic information on the individual nanographene

high T(>30 K) linear T dependent ΔH

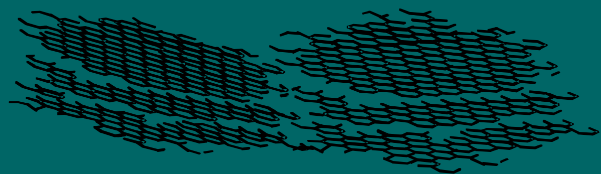
$$\Delta H \propto \frac{1}{T_{\text{edge-}\pi}} = \left(\frac{4\pi}{\hbar}\right) J_{\text{edge-}\pi}{}^{2} D(\varepsilon_{\mathrm{F}})^{2} k_{\mathrm{B}} T$$

Korringa relation

$J_{\text{edge-}\pi}$ exchange interaction

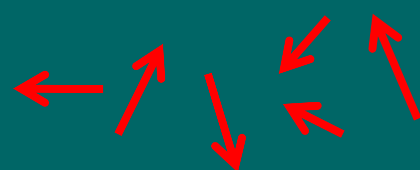
edge-state spin & cond. carrier coupled

What happens in the magnetism when heat treated ?



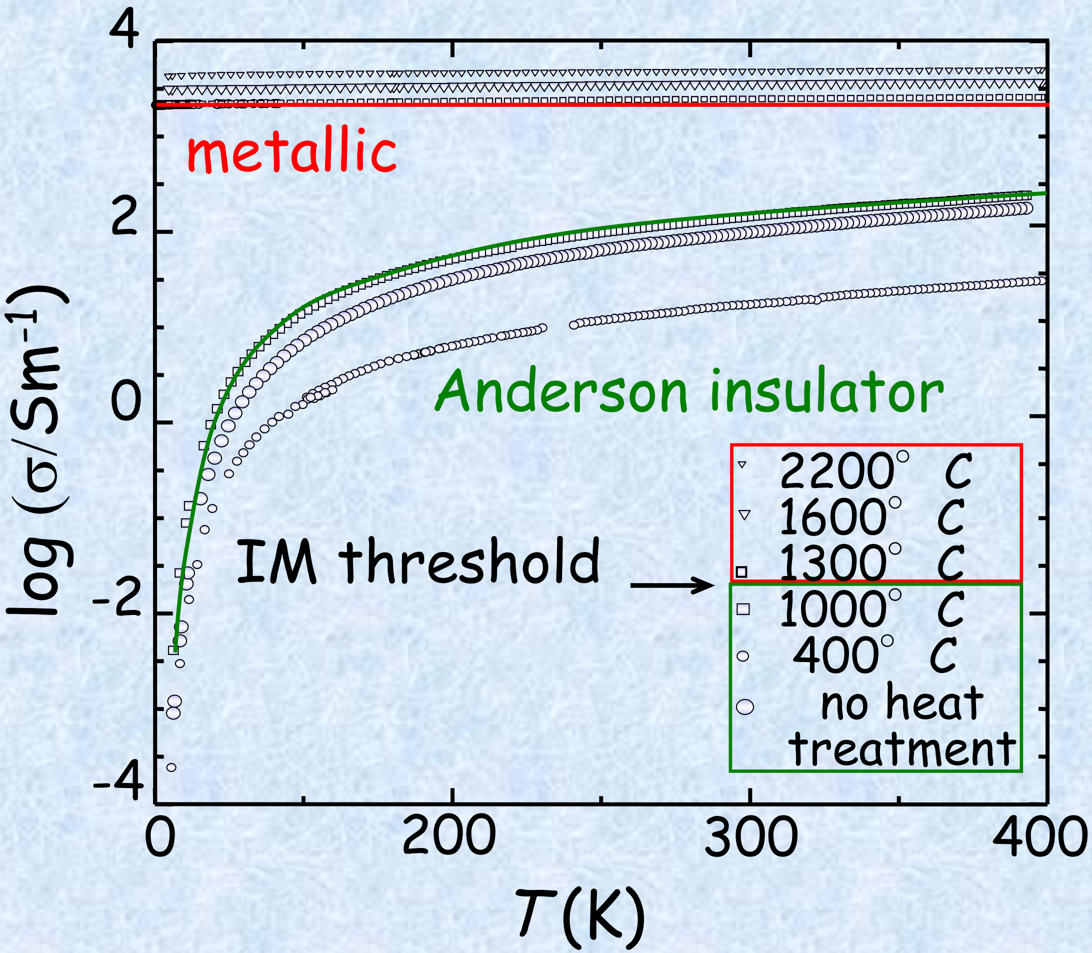
inter-nanographene
interaction strengthened

spin glass



Y. Shibayama, T. Enoki, et al. *Phys. Rev. Lett.* **84**, 1744 (2000).

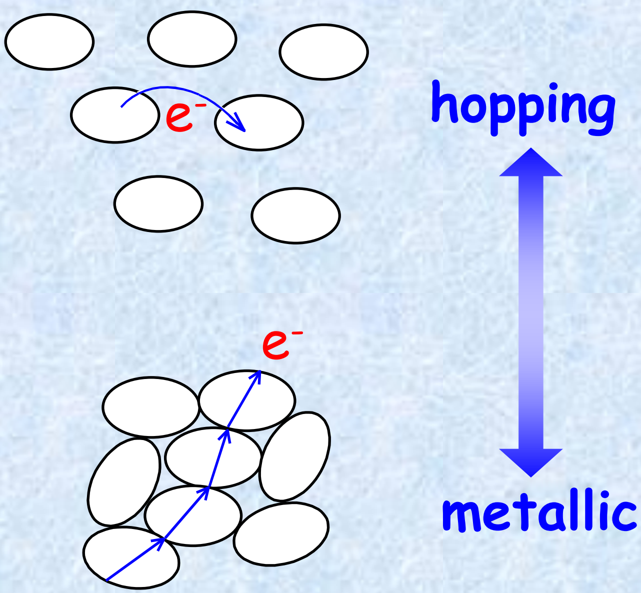
heat-treatment effect on conductivity



inter-nanographite-domain interaction enhanced by heat-treatment

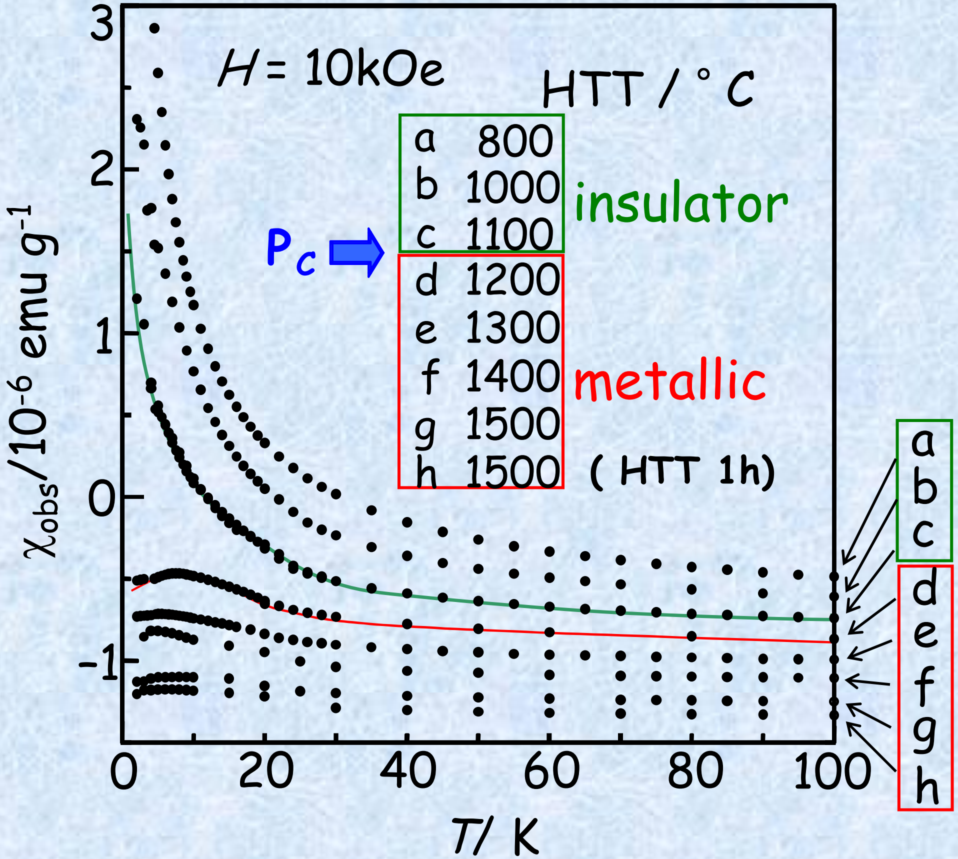
percolation threshold P_c

→ ca. HTT 1200° C



insulator-metal transition

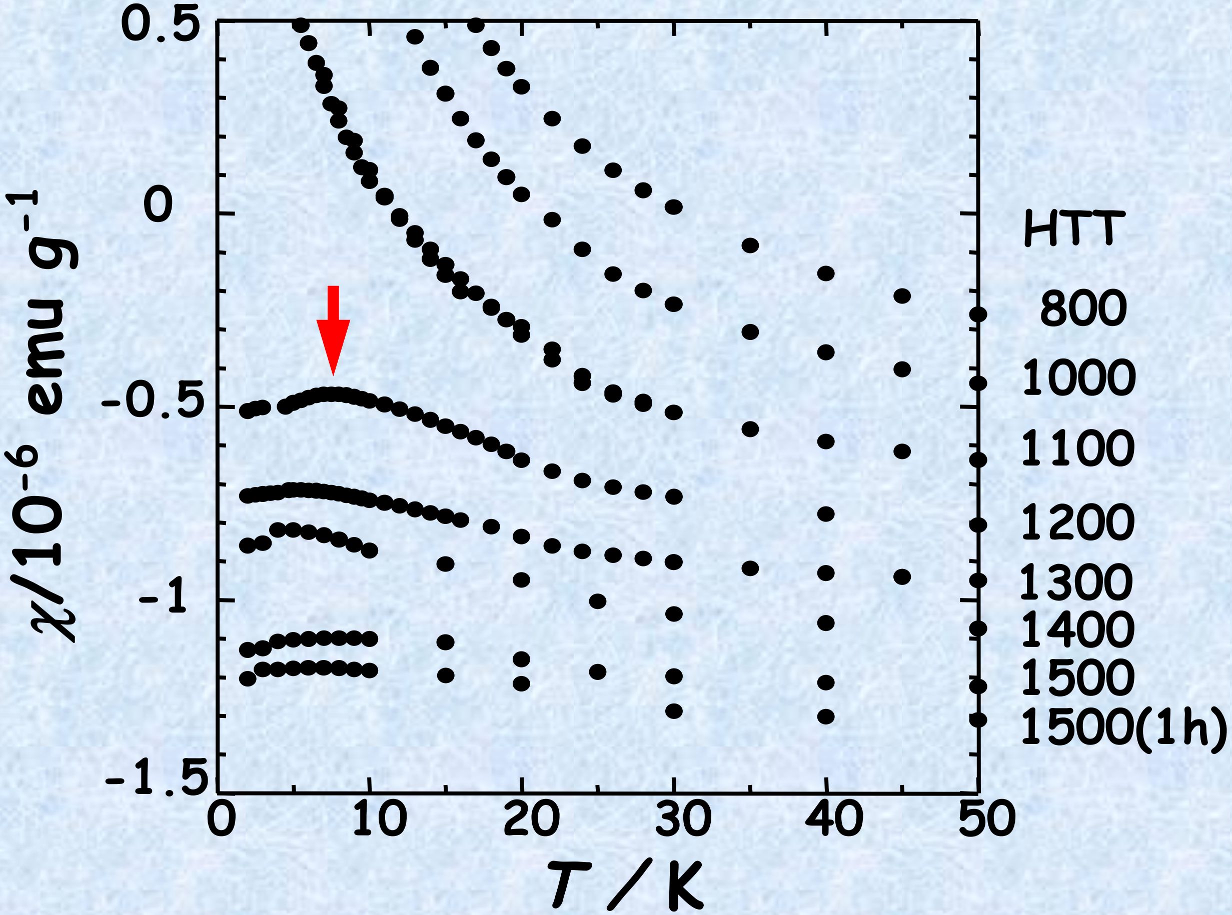
heat-treatment effect on magnetic susceptibility



HTT < P_C
Curie-Weiss behavior with localized spins and negative Weiss temperature

HTT > P_C
less temp. dependent enhanced diamagnetism

magnetism around the percolation threshold region



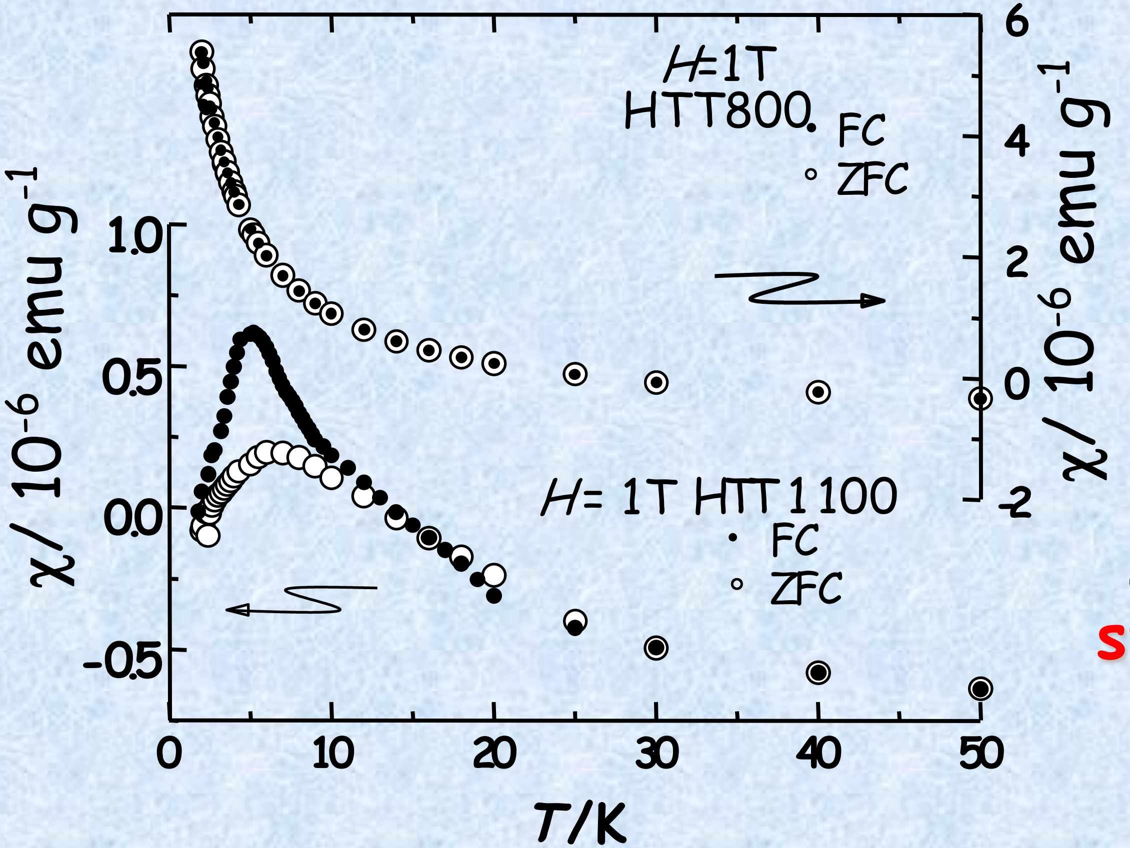
susceptibility peak ~ 7K

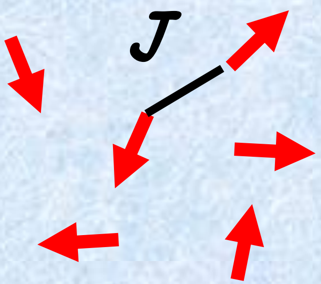
antiferromagnetic ordering?

negative Weiss temperature

field cooling effect

large field cooling effect around the MI threshold





disordered magnetism
spin-glass-like behavior

exchange interaction random distribution $\left|\sqrt{\langle \Delta J^2 \rangle}/\langle J \rangle\right| \sim 0.8$

edge state of π-electron origin
topological origin from the pseudo-spin in Dirac fermion

σ-dangling bond
defect origin in the sp^3 backbone

What difference?

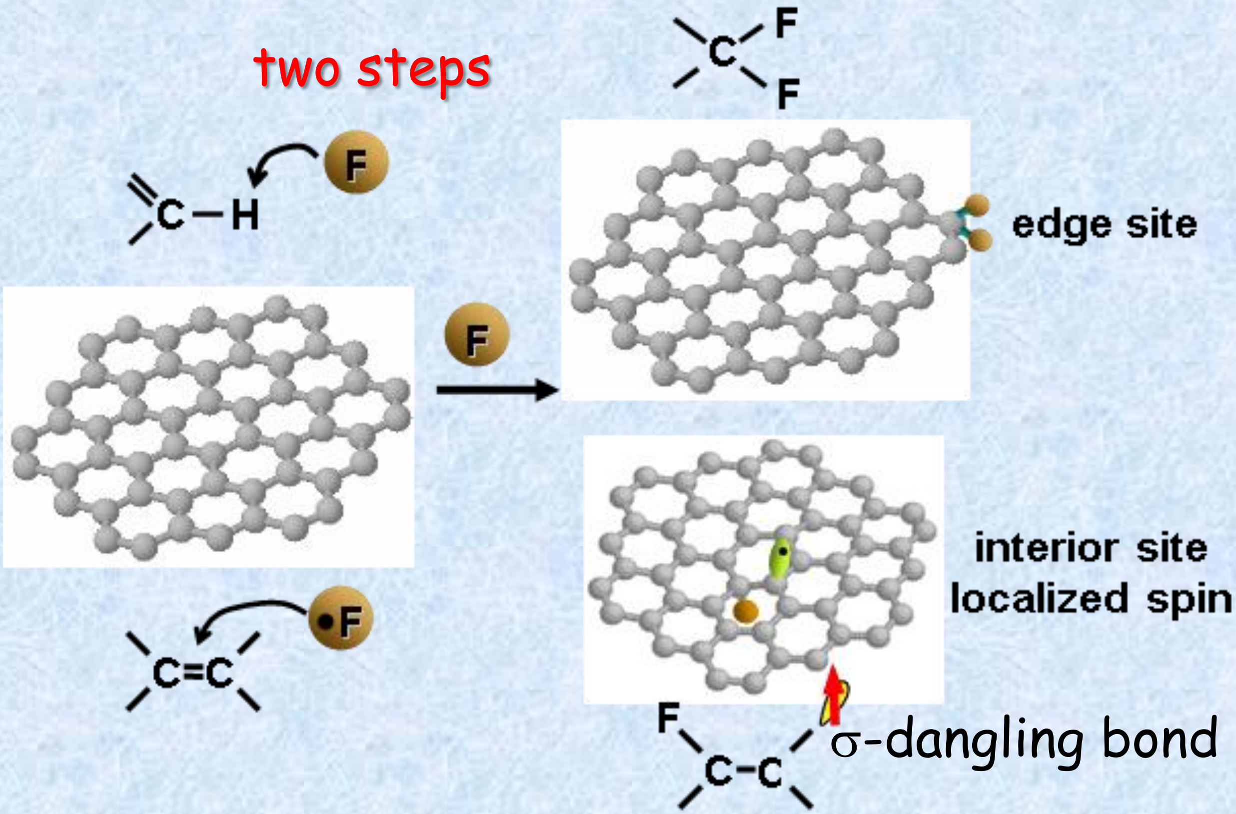
fluorination of nanographene

M. Kiguchi, V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev.* B84, , 045421 (2011)
T. Enoki, *Bull. Chem. Soc. Jpn.* 85, 249264 (2012)

fluorination of nanographene

two kinds of nonbonding state having localized spin

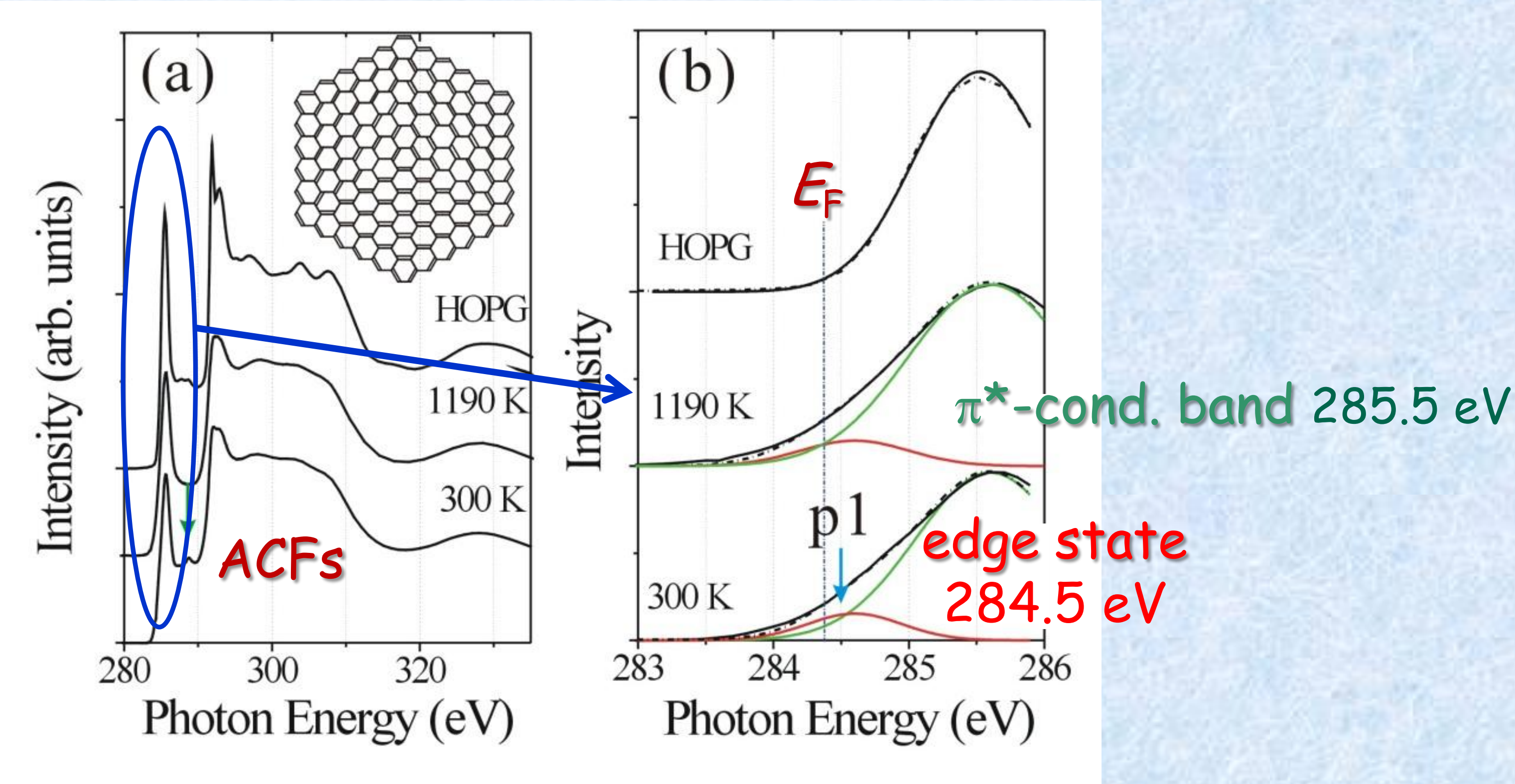
edge state of π-electron
σ-dangling bond of defect



electronic structure & magnetism

M. Kiguchi, V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev.* B84, , 045421 (2011)

fluorination of nanographene



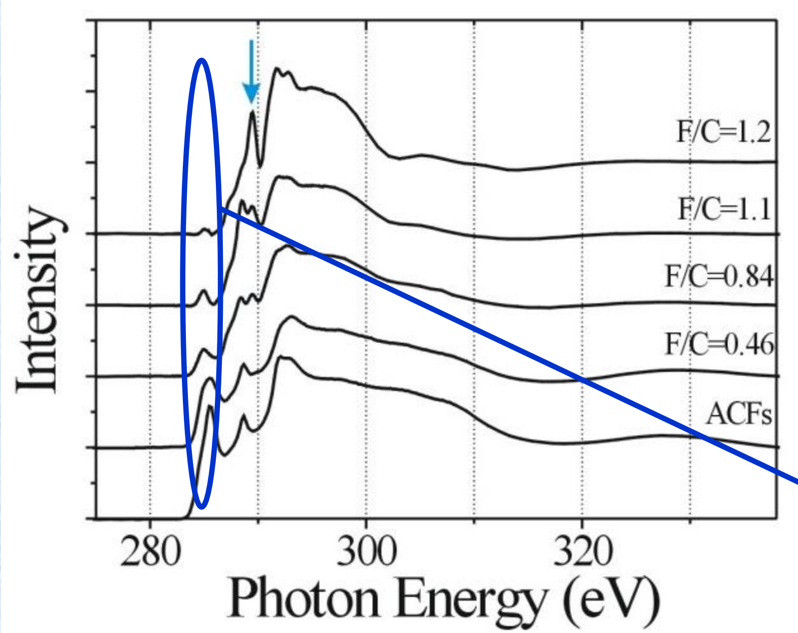
near edge X-ray absorption fine structure (NEXAFS)

nanographene in activated carbon fibers (ACF)

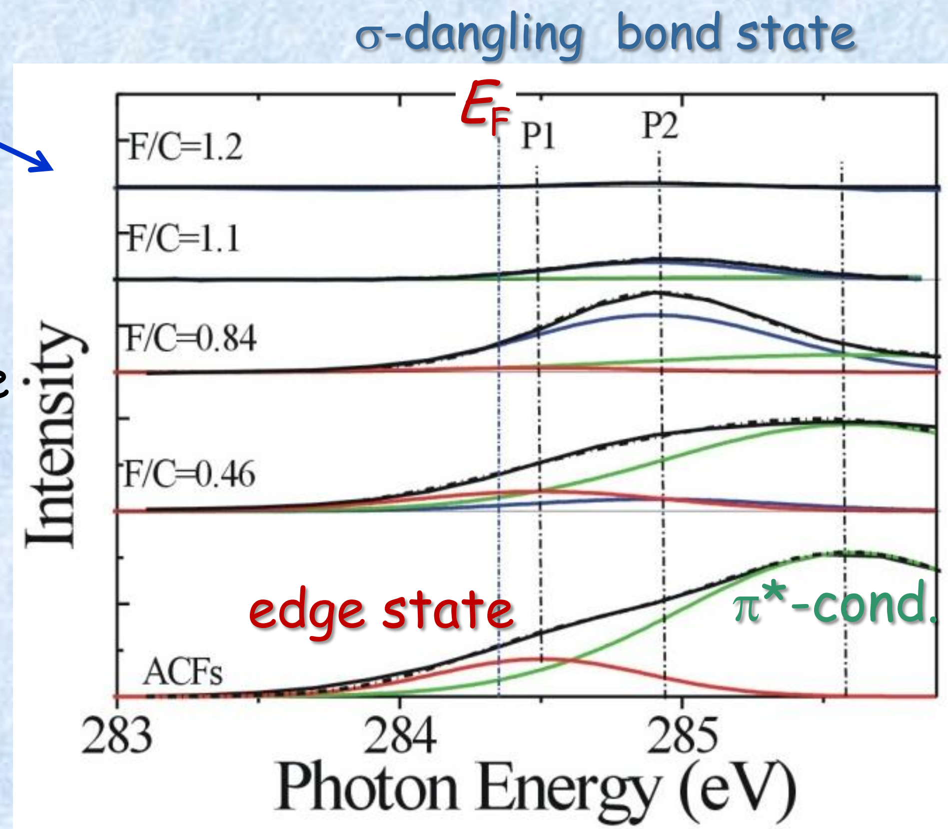
pristine ACFs heat-treated ACFs (1190 K)

M. Kiguchi, V. L. J. Joly, K. Takai, T. Enoki, et al., *Phys. Rev.* B84, , 045421 (2011)

NEXAFS fluorinated ACFs (F/C= 0 – 1.2)



σ-dangling bond state (284.9 eV)
appears independent from edge state
0.4 < F/C < 1.2
with a maximum intensity at F/C ~ 0.8

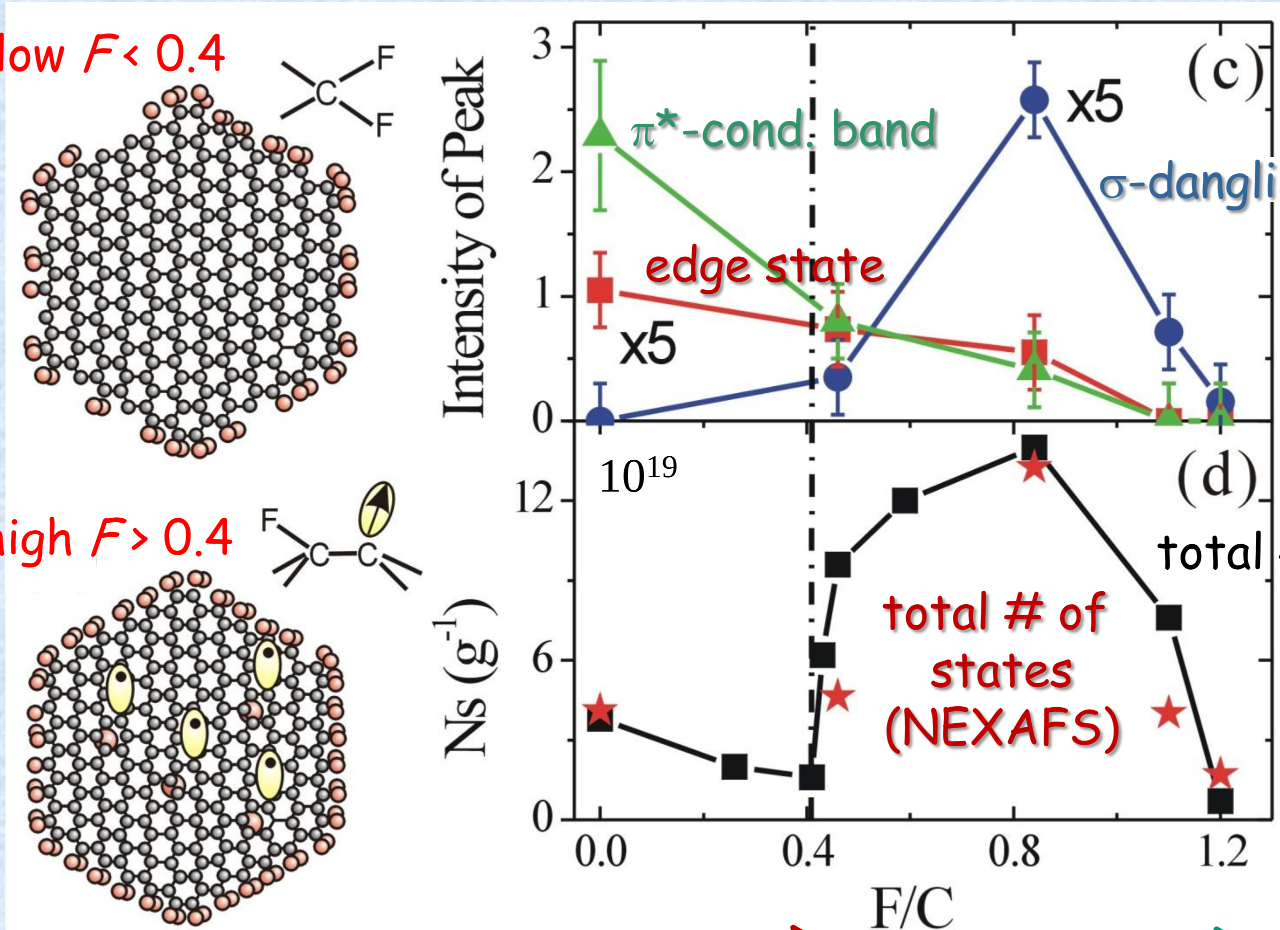


edge state of π-electron
chem. shift 284.5 eV more negative
from π* conduction band
large screening effect
large local density of states

σ-dangling bond
chem. shift 284.9 eV less negative
weak screening effect

fluorine concentration dependence of NEXAFS intensity and localized spin

of Carbon atoms ~200~300 (nanographene 2-3 nm)



electronic state
NEXAFS

magnetism

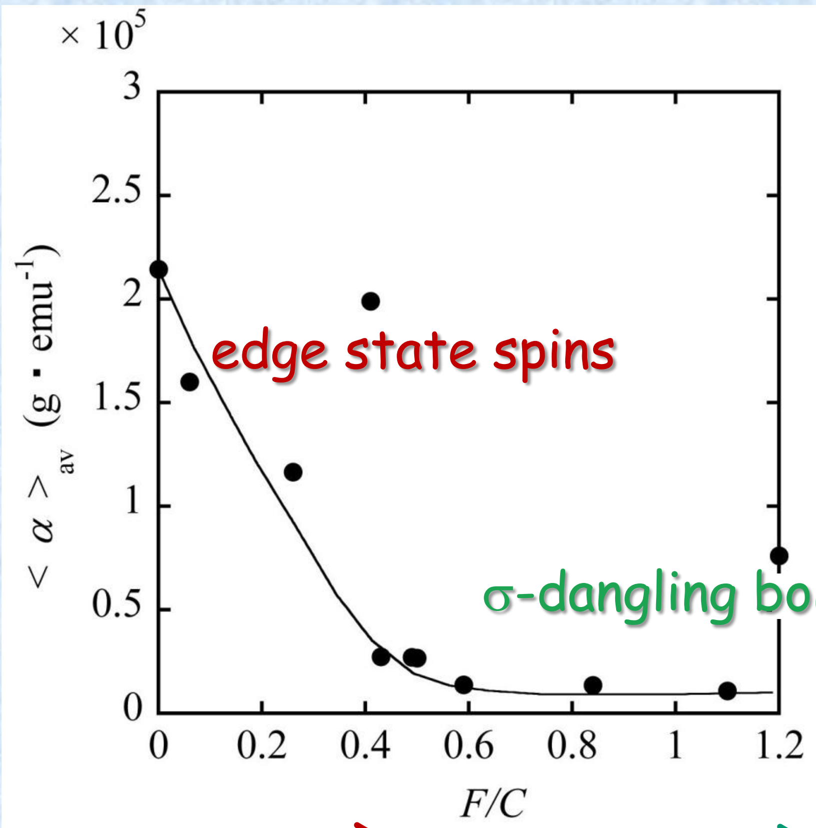
total # of localized spins
(magnetism)

edge C → interior C → fluorinated

max conc. of dangling bond spins at *F/C*~0.8

1/2 of interior C atoms fluorinated

magnetism; edge state and σ-dangling bond state internal exchange field



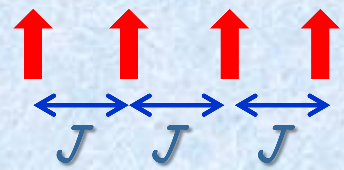
σ-dangling bond spins

edge C   interior C   fluorinated

edge state spins

topological origin

interacting with each other through exchange interaction



σ-dangling bond spins

defect origin

isolated with no interaction

isolated

K. Takai, H. Sato, T. Enoki, N. Yoshida, F. Okino, H. Touhara, M. Endo, *J. Phys. Soc. Jpn.* **70**, 175 (2001).

Summary

nanographene magnetic

depending on the edge chirality;
zigzag and armchair

edge state of π-electron origin at zigzag edge

σ-dangling bond state at defects

a variety of magnetism
ferromagnetic/antiferromagnetic/ferrimagnetic/spin glass

molecular magnetism & spintronics device applications

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