# Edge state and unconventional magnetism of nanographene/nanographite

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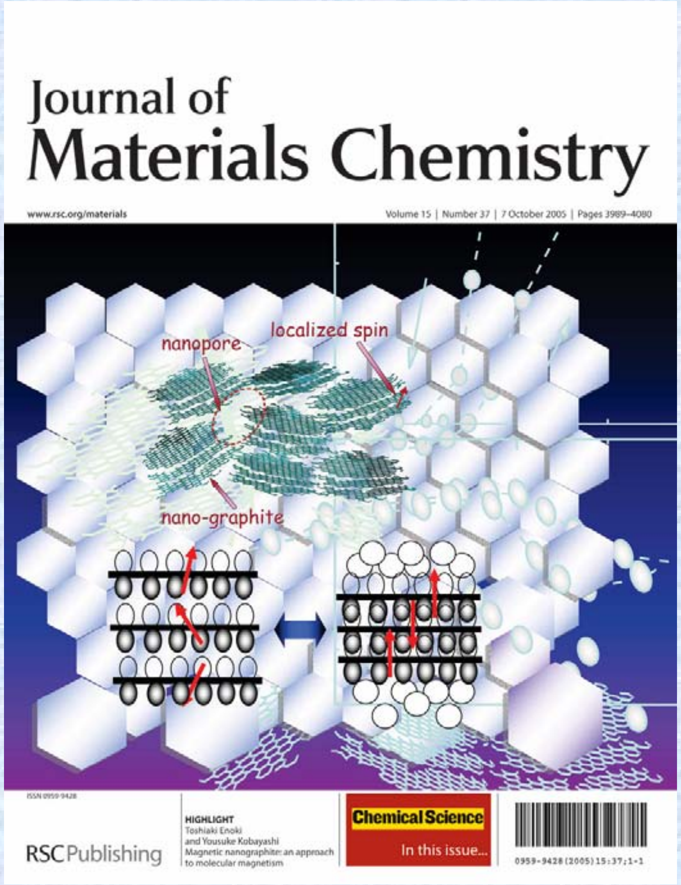
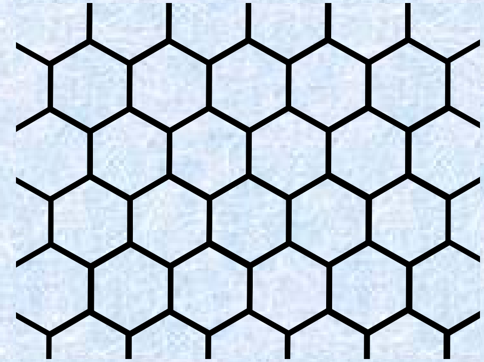



**NT06, Nagano**

**June 18-23, 2006**

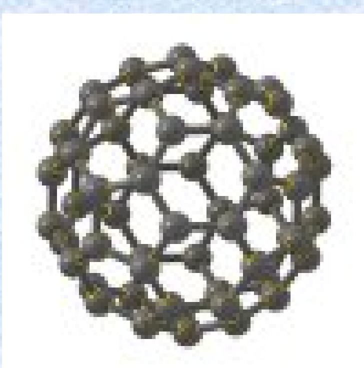
nanographite



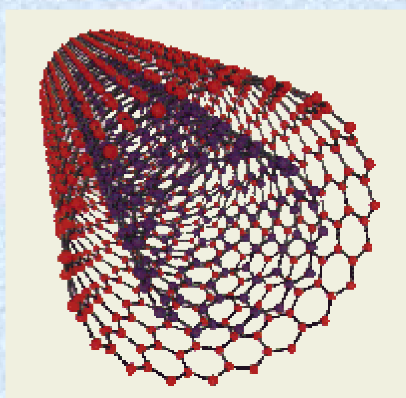
aromatic molecules — bulk graphite

nanographite $\pi$-electron system
with open edges

$\updownarrow$

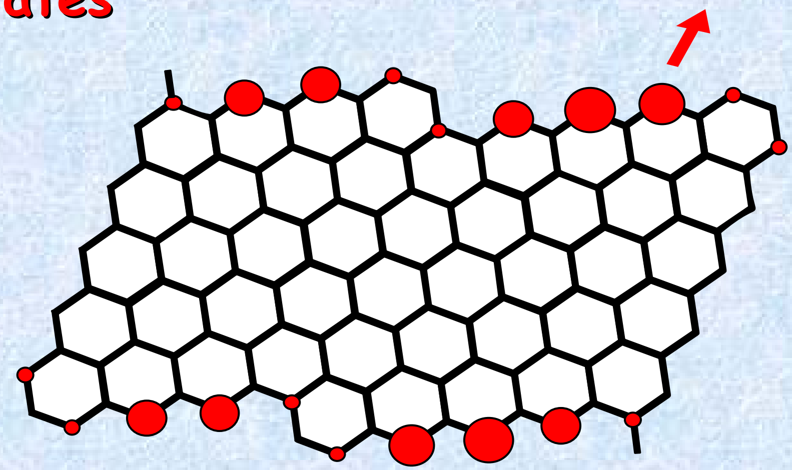


fullerenes
carbon nanotubes
closed $\pi$-electron system



## nanographite (nanographene)

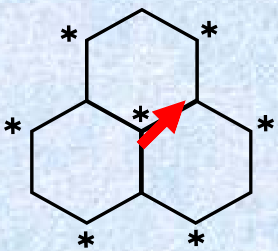
# shape effect → edge states



localized π-spins

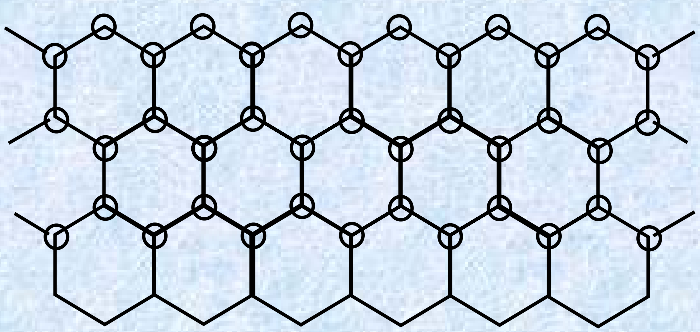
enhanced magnetism

Yamabe et al.
Fujita et al.

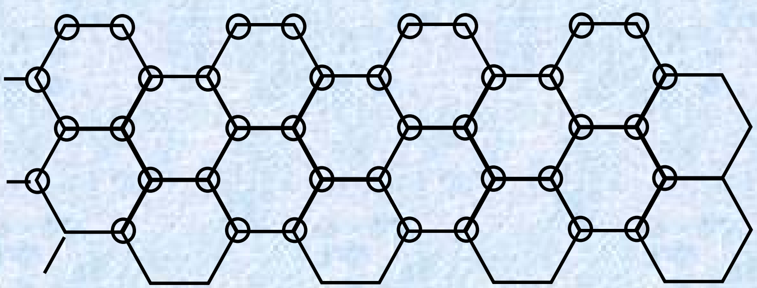


non-Kékule str.

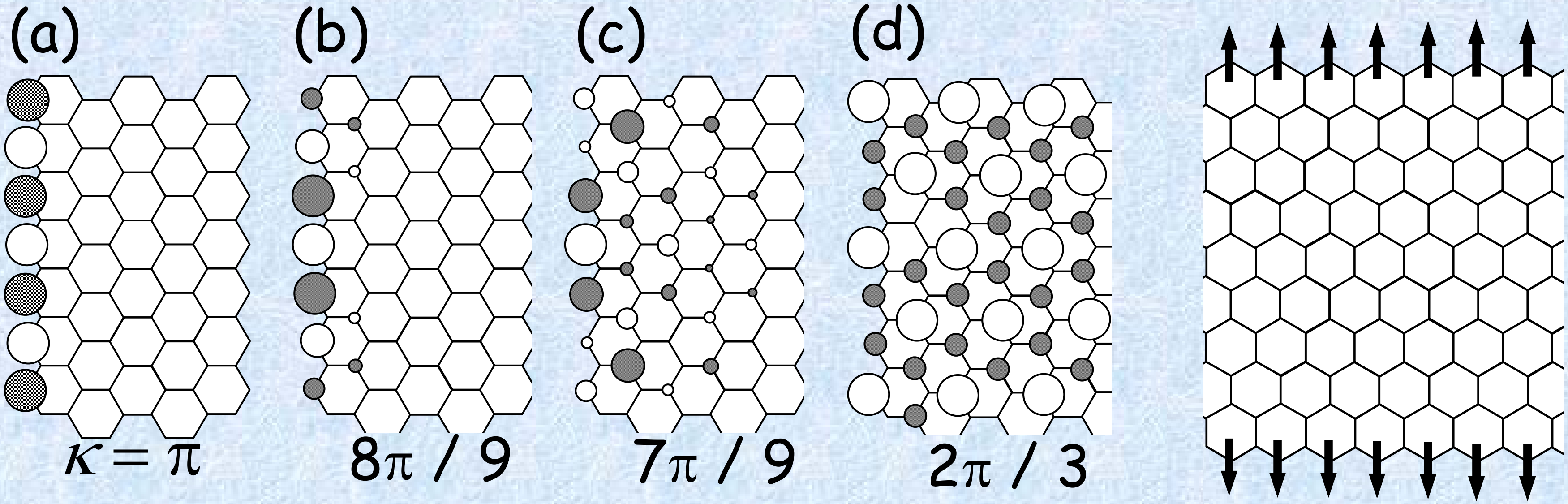
nonbonding π-state
($s$=1/2)



zigzag edge

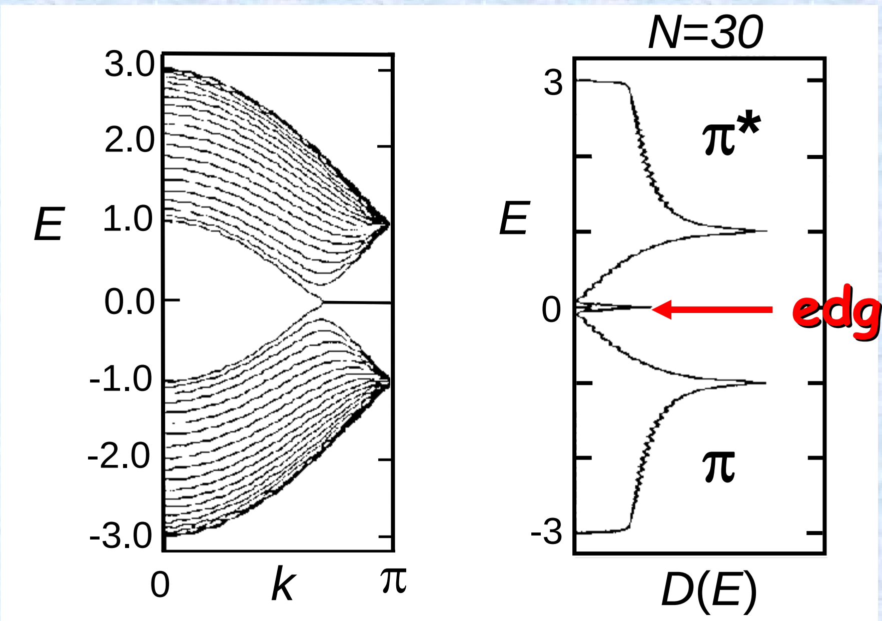


armchair edge




**ferromagnetic**

(Fujita et al.)




**edge state**

**zig-zag edge** → **edge state**

nonbonding π-state

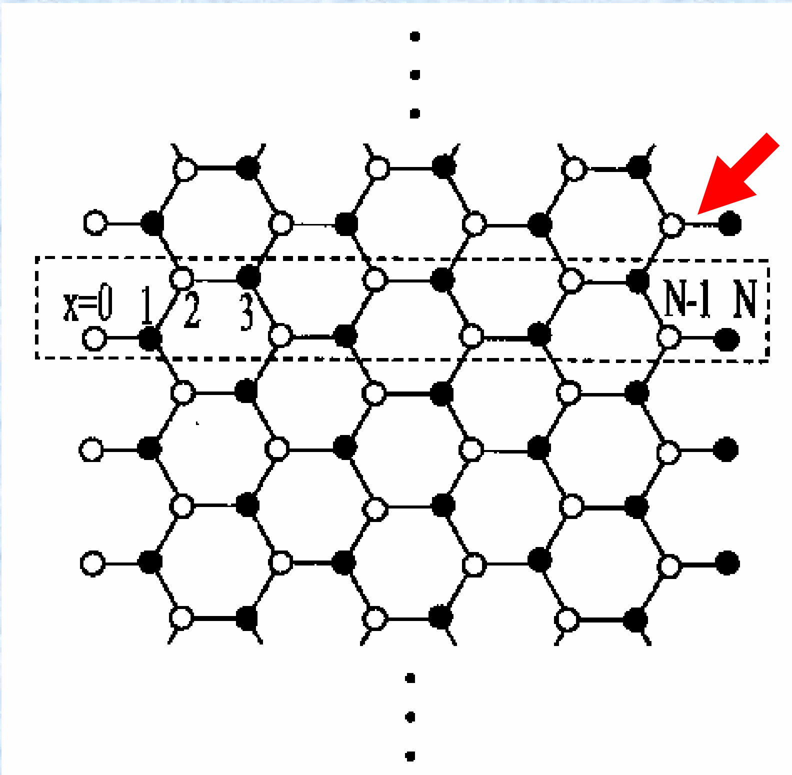
large density of states (DOS)

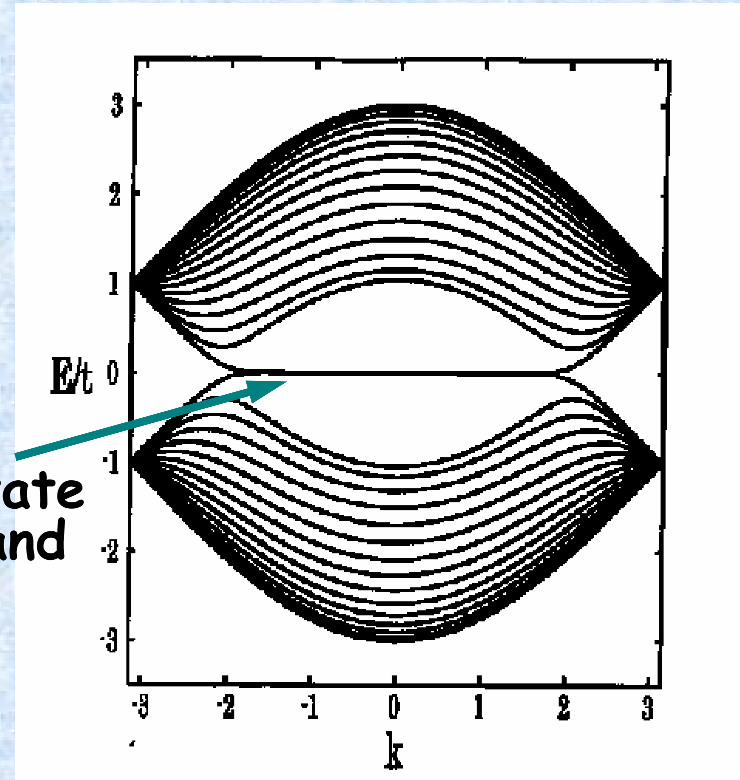
spin paramagnetism

contrast to bulk graphite

Klein edge

extra π-bond connected to the carbon atom at a zigzag edge

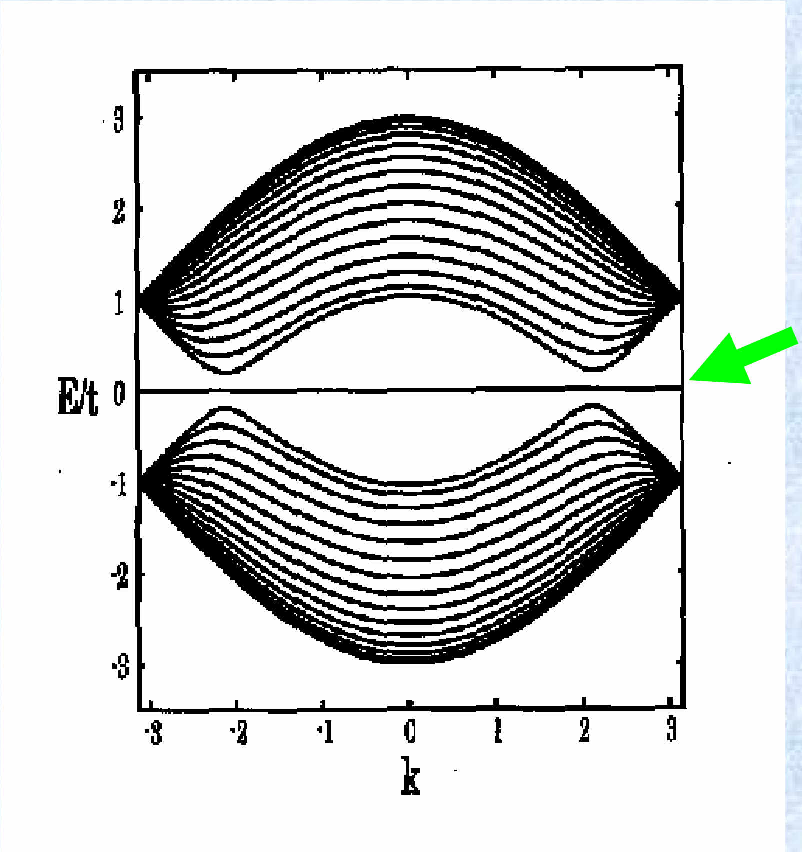


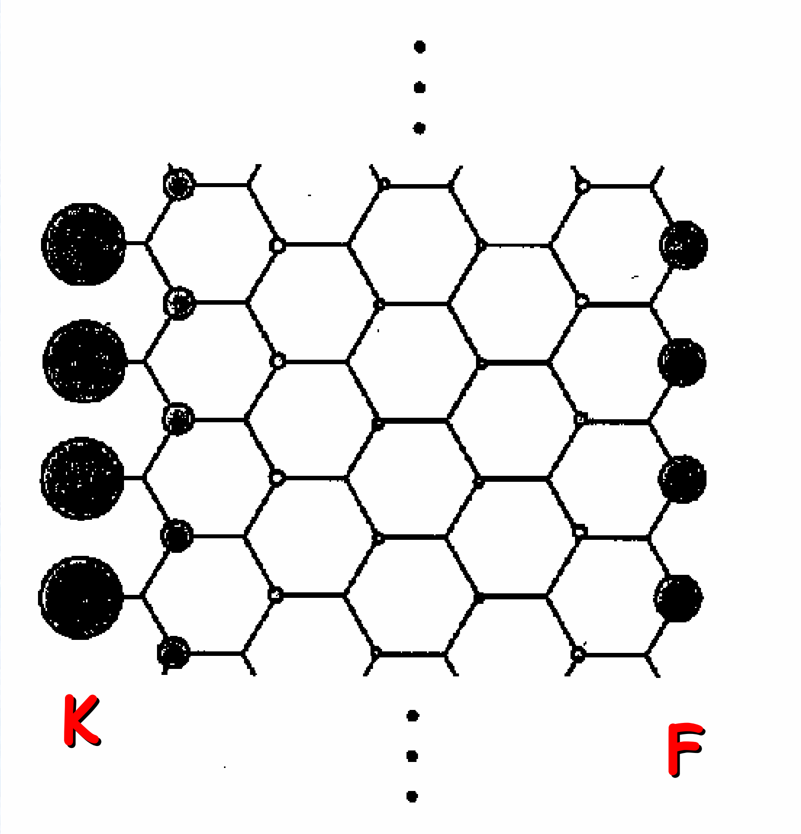




edge states with localized spins appear at $-2/3 < k < 2/3$

K. Kusakabe, et al. 2001

# combination of Fujita's and Klein's edges




completely localized edge state appears at $E_F$

**nano-magnetism**

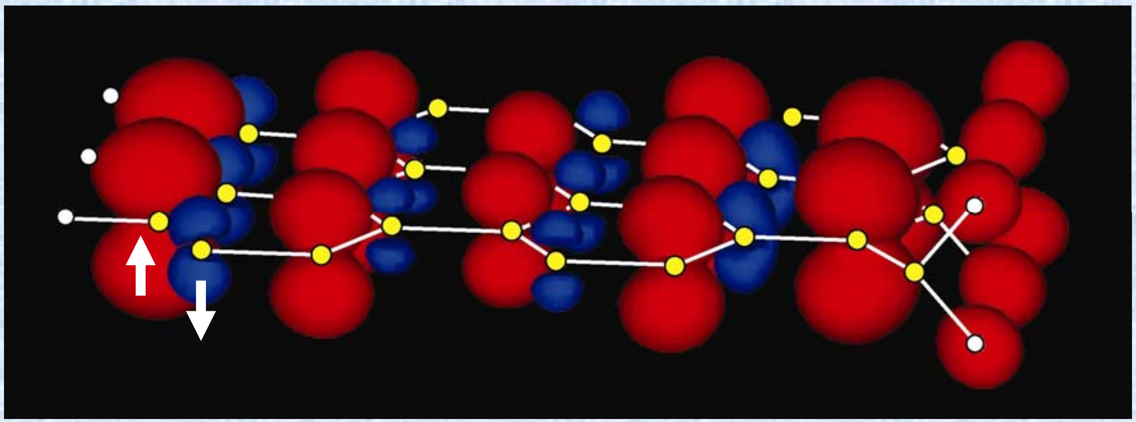
K. Kusakabe, et al. 2001

Kusakabe et al.

# Carbon-only ferromagnet

HC<

Fujita edge

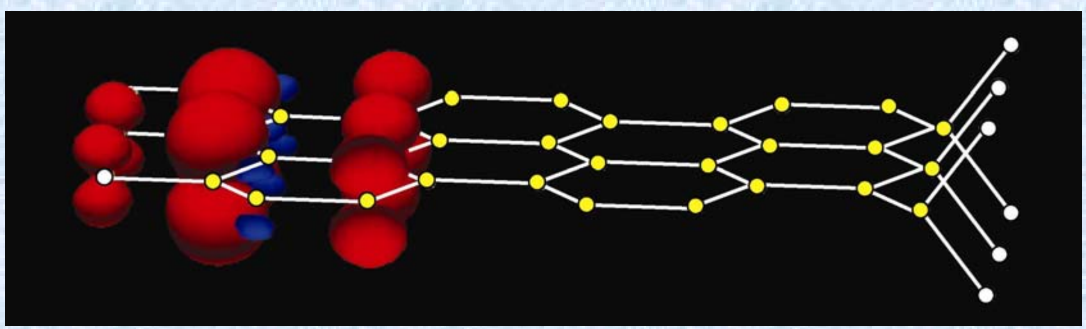


$-CH_2$

Klein edge

FC<

Fujita edge



$-CF_2$

Klein edge

spatially maldistributed ferromagnetism

# Present talk

## # Nanographene

# single nanographene sheet
nanodiamond
electrophoretic technique + heat-treatment

# nanographene ribbon
resonance Raman experiments

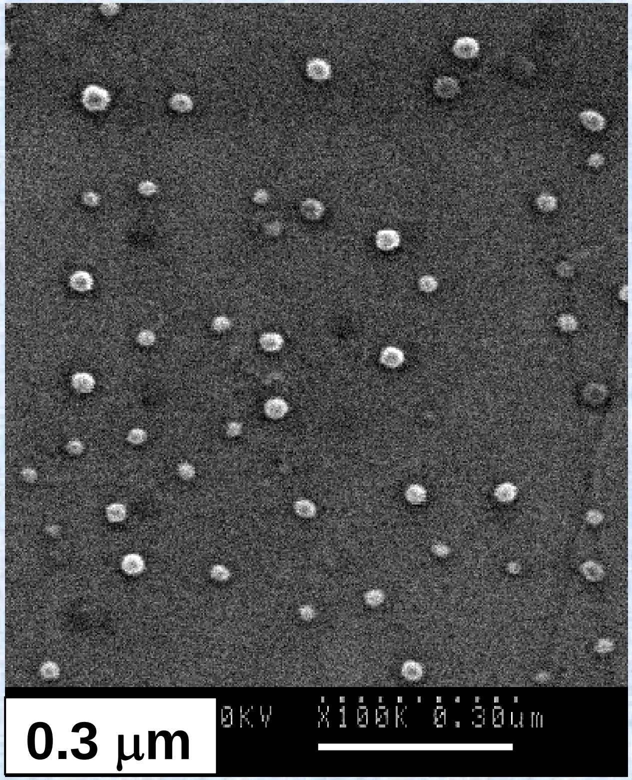
# electronic structure of **edge state**
at edges hydrogen-terminated

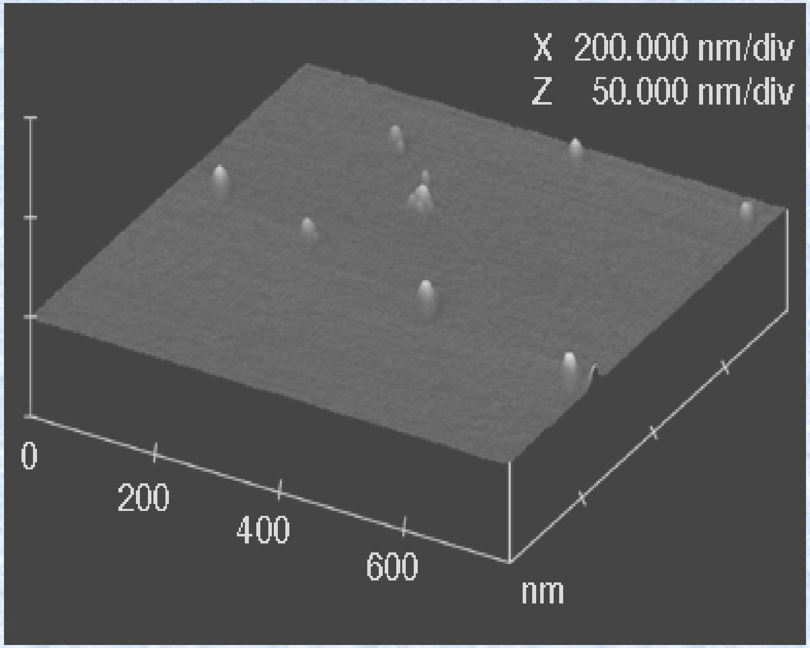
## # Controllable nanoscopic magnetism

**gas-adsorption induced magnetic switch**

# single nanographene sheet

# SEM and AFM images of diamond nanoparticles.



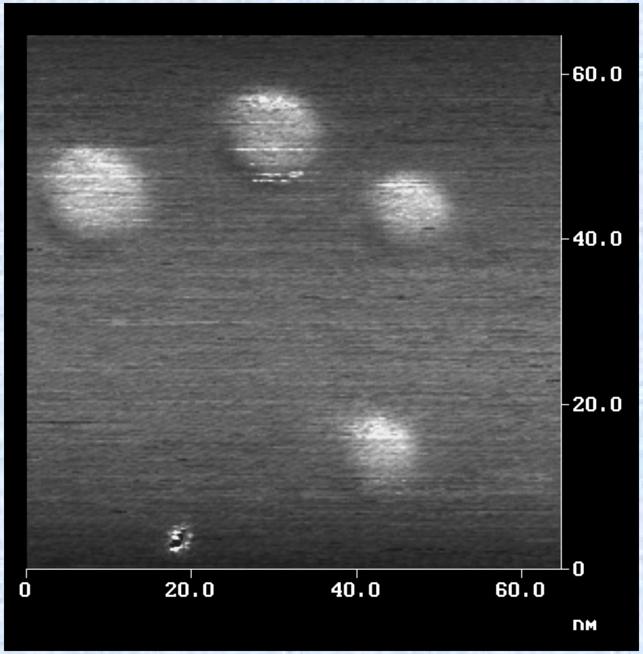



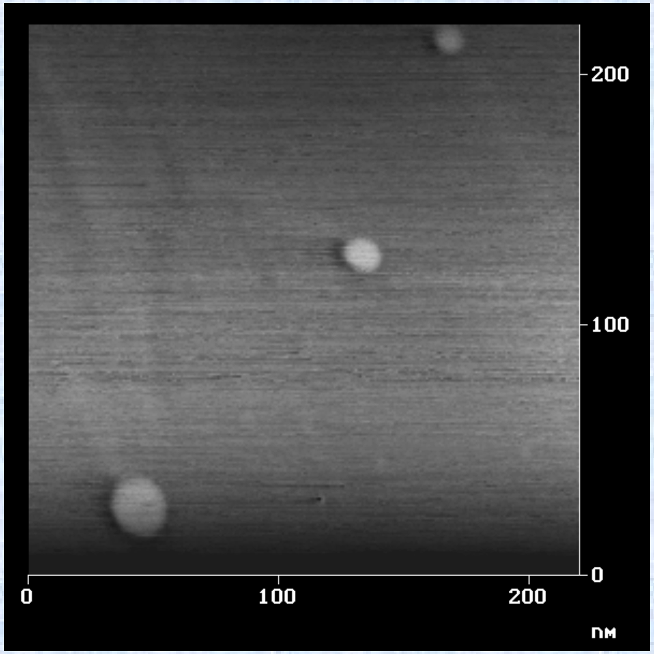

**nanodiamond particles (ca. 5 nm) deposited by electrophoretic technique**

spherical shape with particle sizes larger than those observed by TEM

**absorbed solvent molecules on the surface of particles**

# nanographene and STM analysis



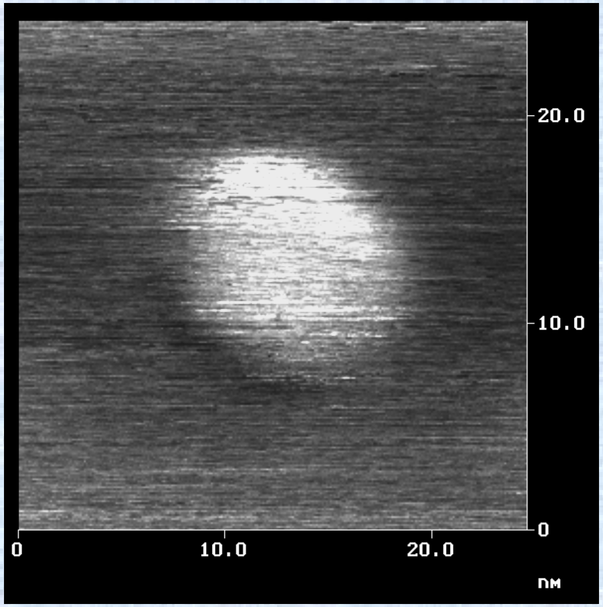



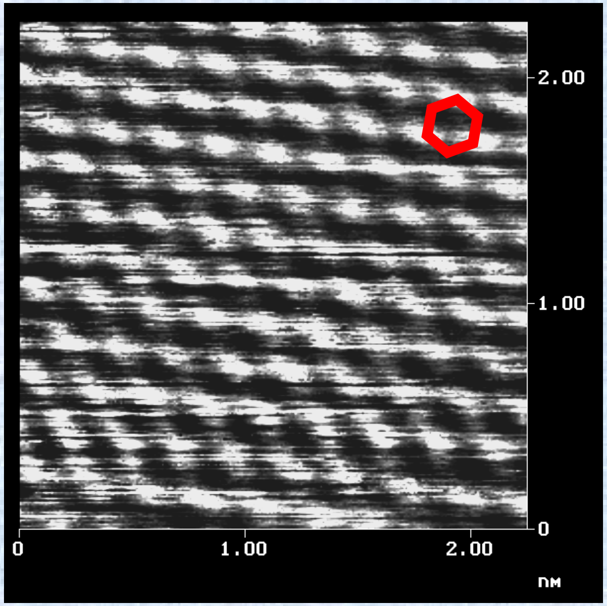

**STM images after heat-treatment at 1600 °C**

nanographene ⇨ flat single layer sheet

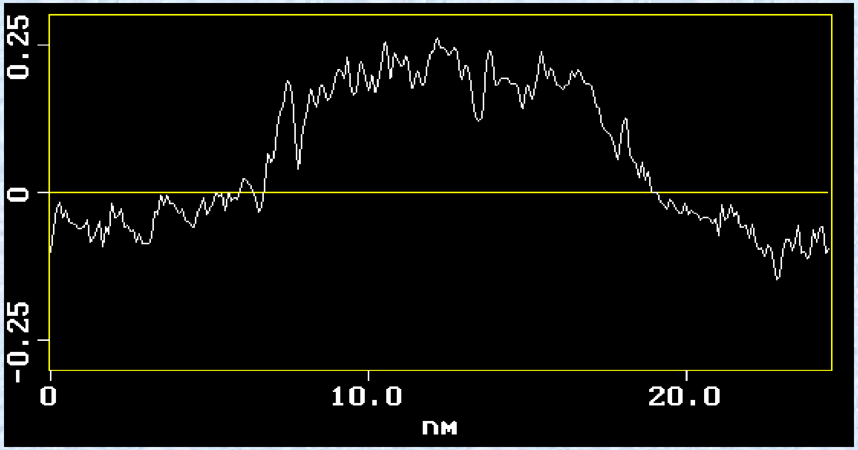
mean in-plane size of 10nm

# nanographene on HOPG substrate and STM Analysis

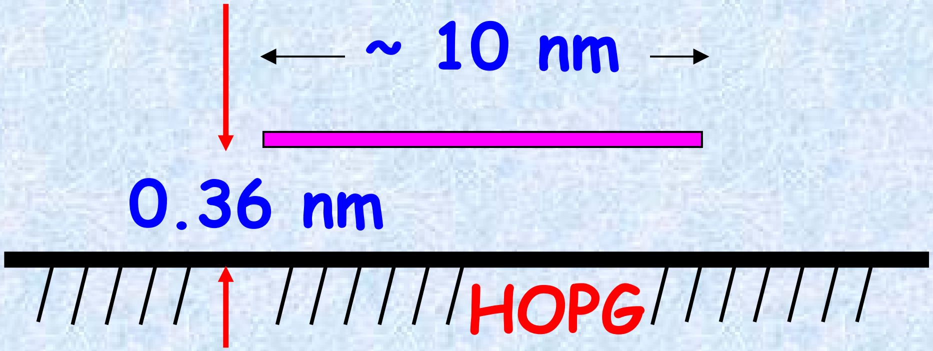



current image




cross-sectional profile

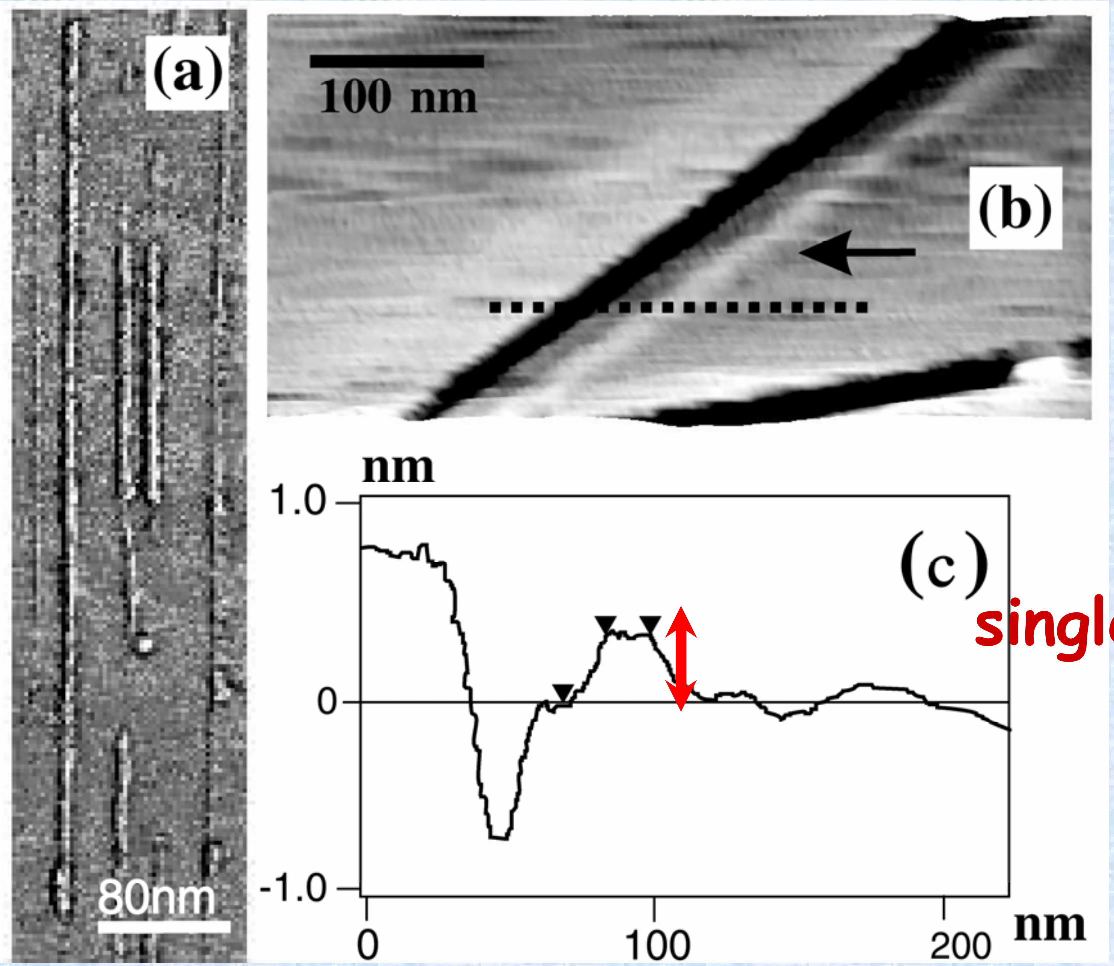



monolayer of nanographene

## nanographene ribbon observed by resonance Raman experiments

# AFM image of single nanographene ribbon

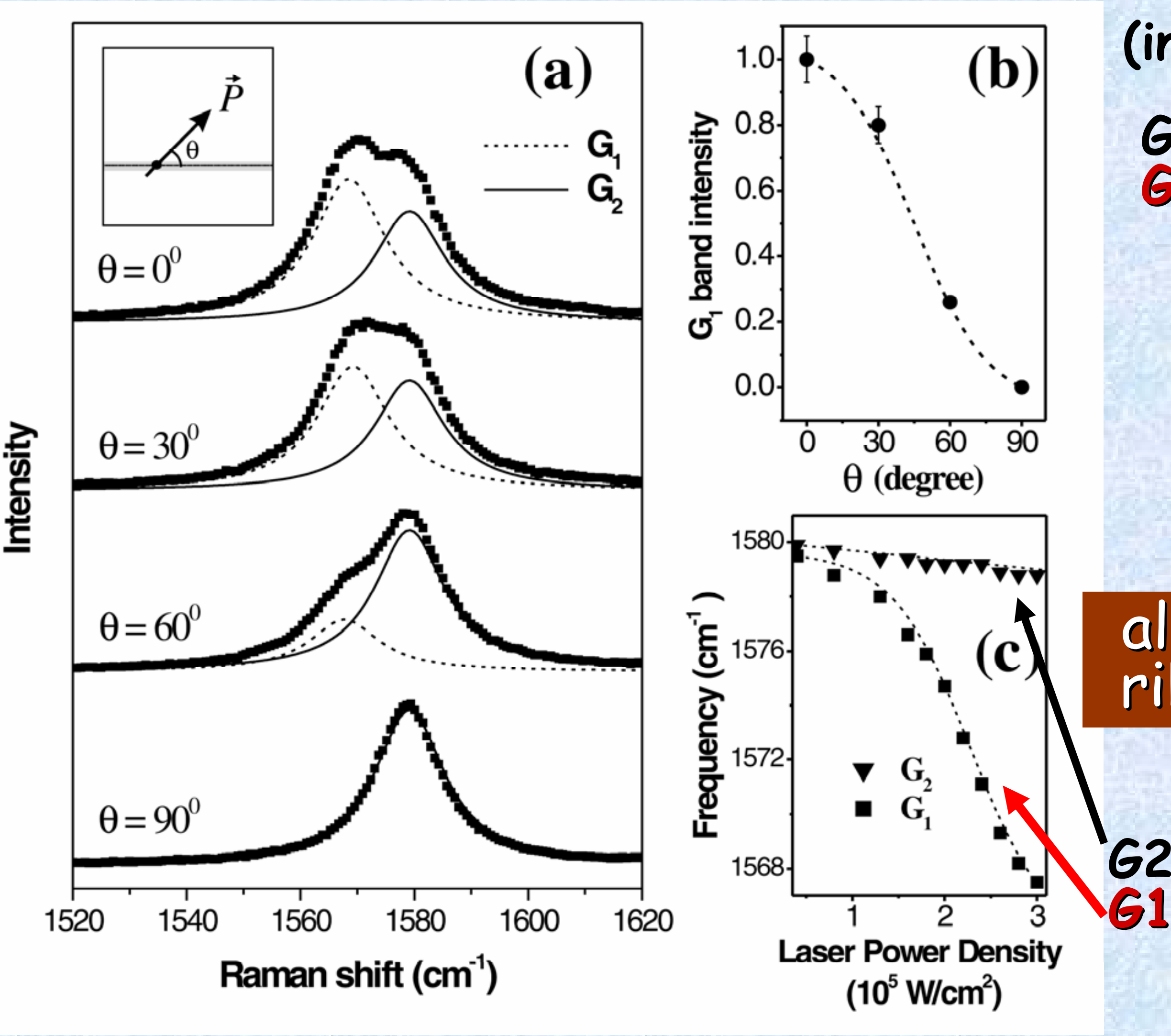
single sheet of nanographene ribbon at a step edge




ribbon size

8 nm x >1 μm

# Resonance Raman experiments with polarized light

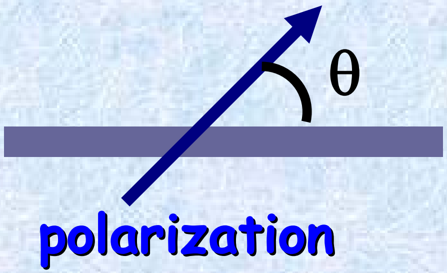



G band

(intralayer C-C stretching)

G2: substrate HOPG

G1: nanographene ribbon




alignments of individual ribbons are determined

small nanographene ribbon can be easily heated by laser beam edge states

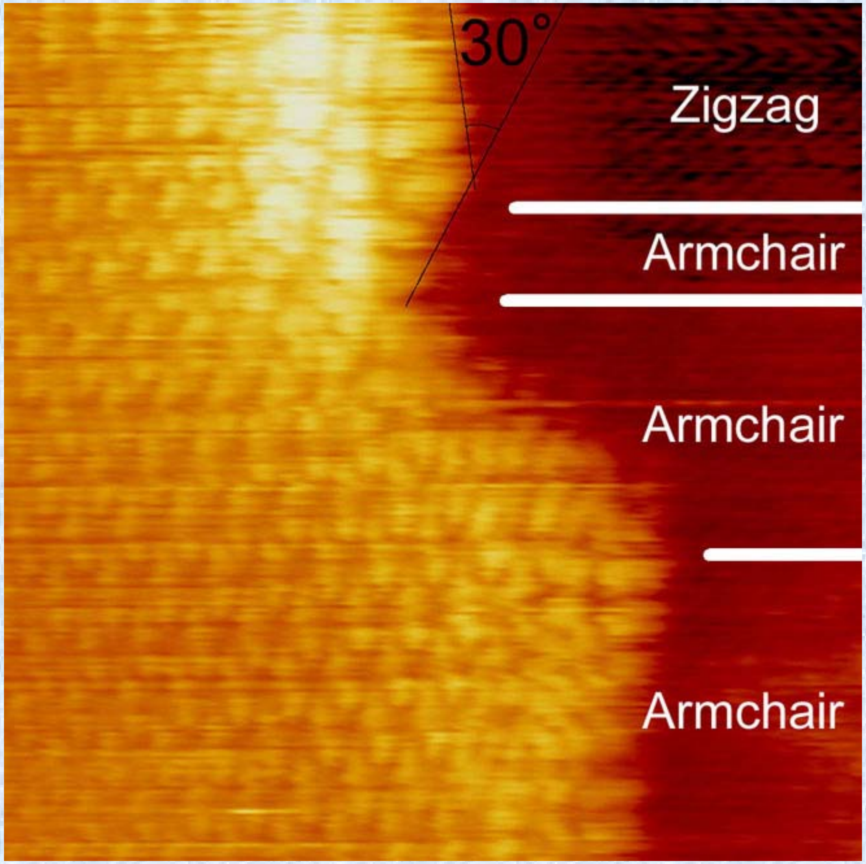
observed by STM/STS

and

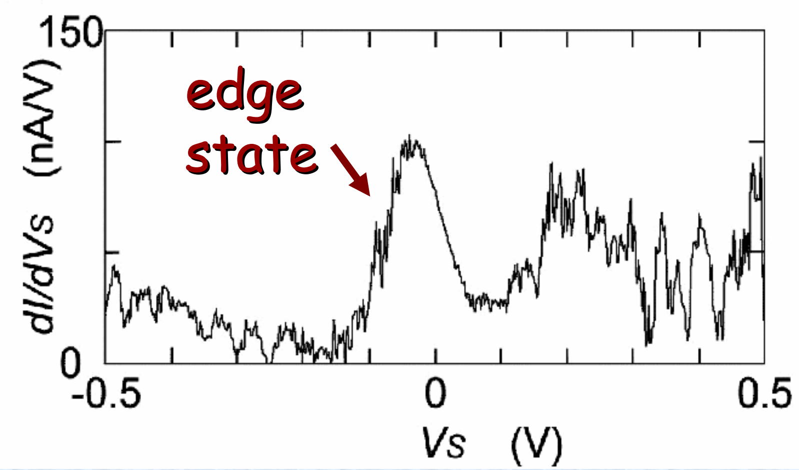
analyzed by tight-binding calculations

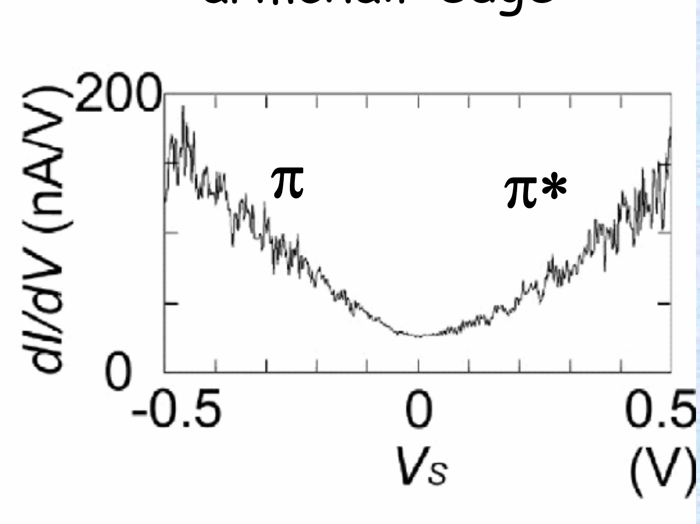
electronic state of graphene edges

experimental evidence of edge state

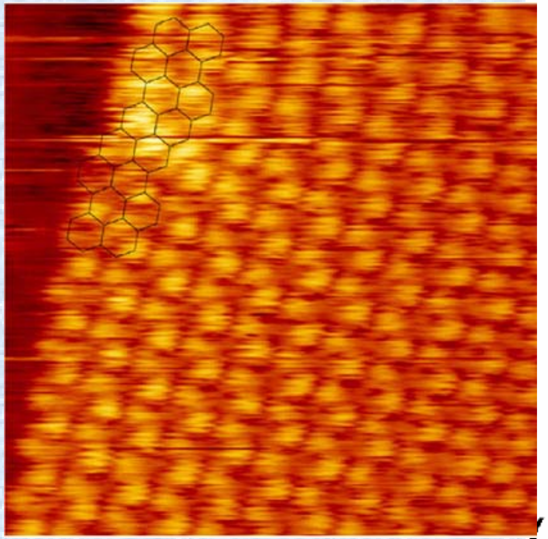


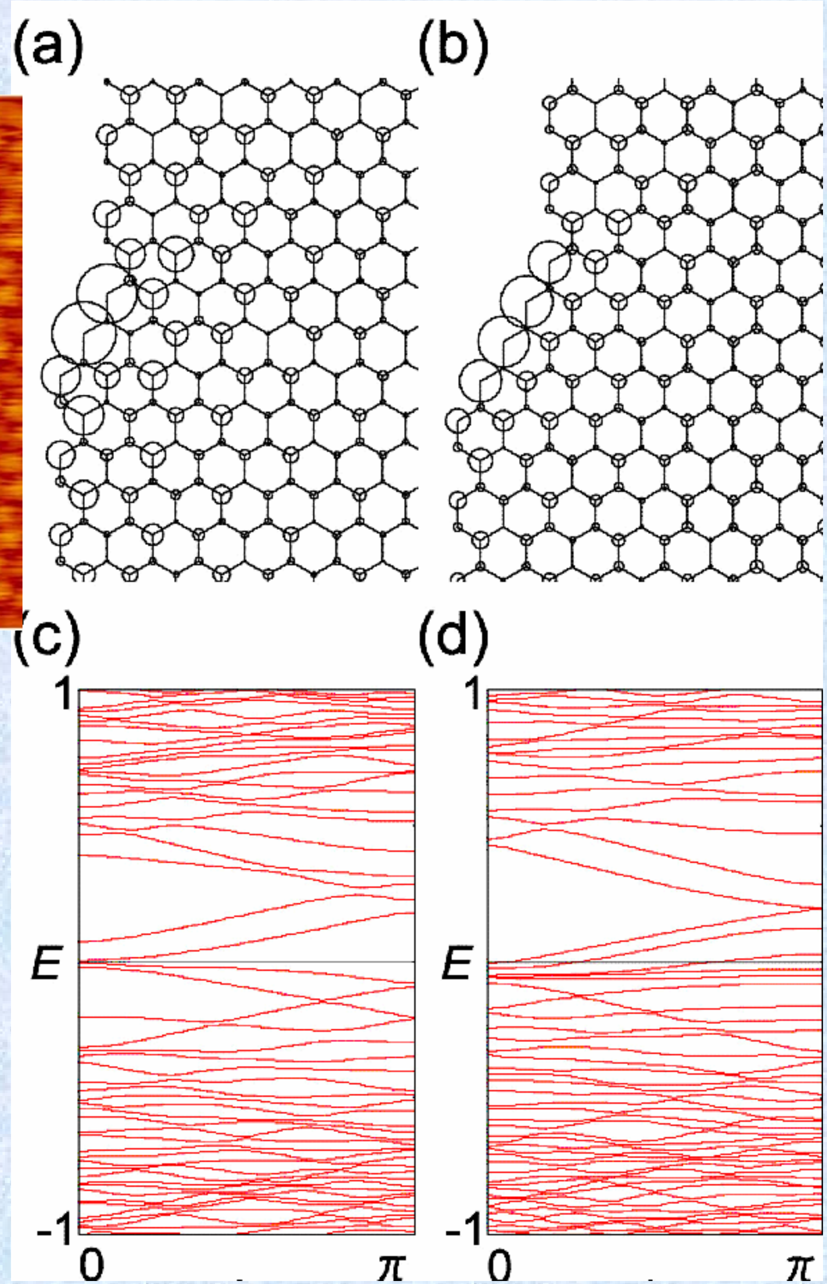

zigzag edge

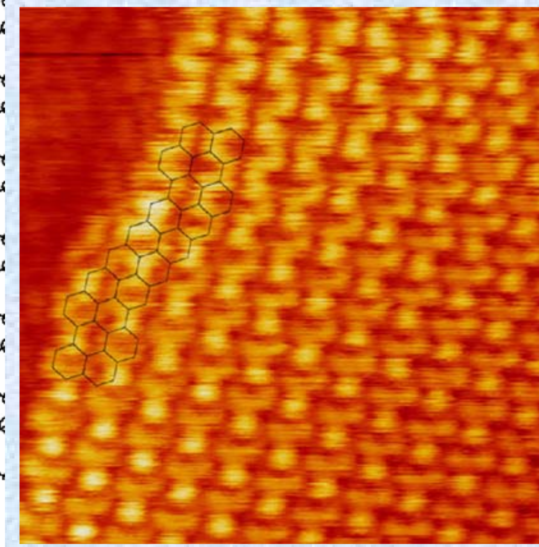



zigzag edge: short and defective, energetically unstable





3 zigzag carbon sites

5 zigzag carbon sites

finite length zigzag edge

edge state

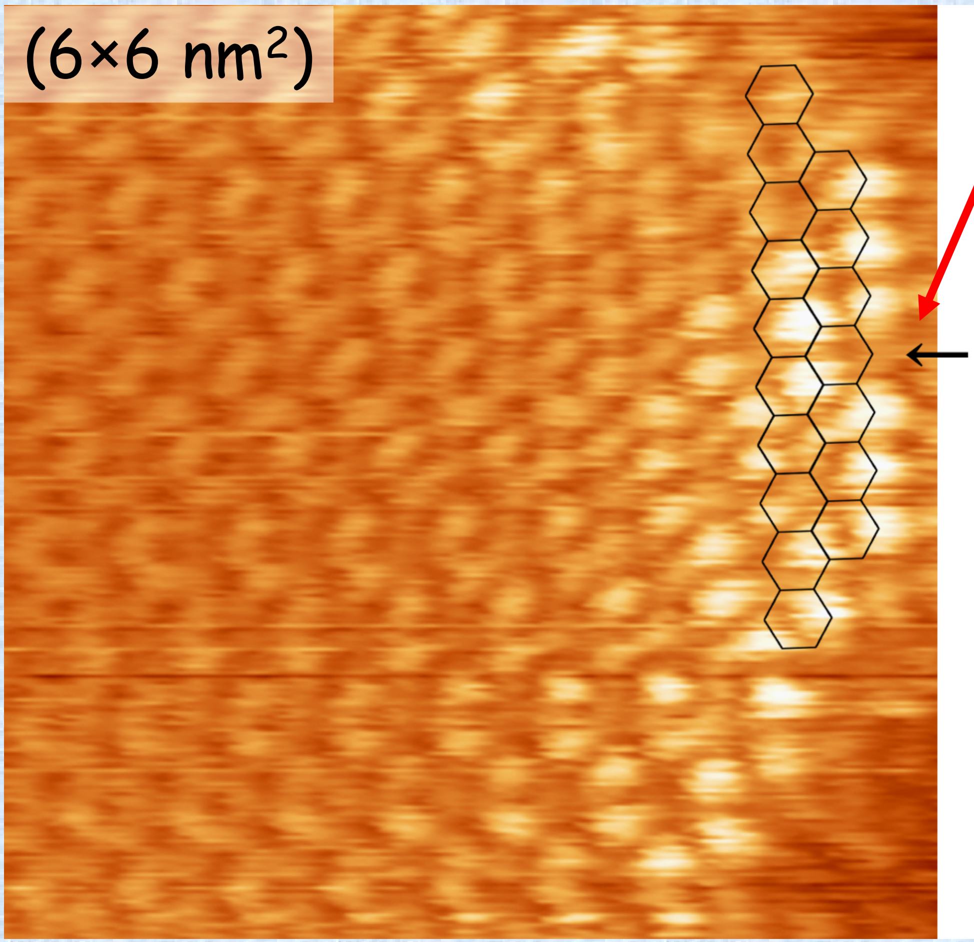
band structure

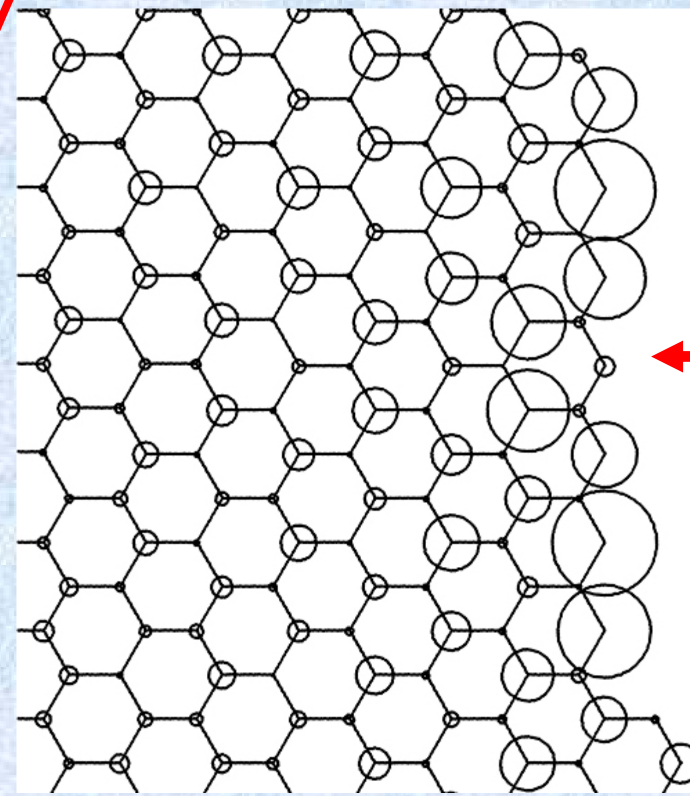
localized edge state

tight binding calculation

# electron confinement effect in zigzag edges

edge-state-absent site at zigzag edge
(small local density of states (LDOS))



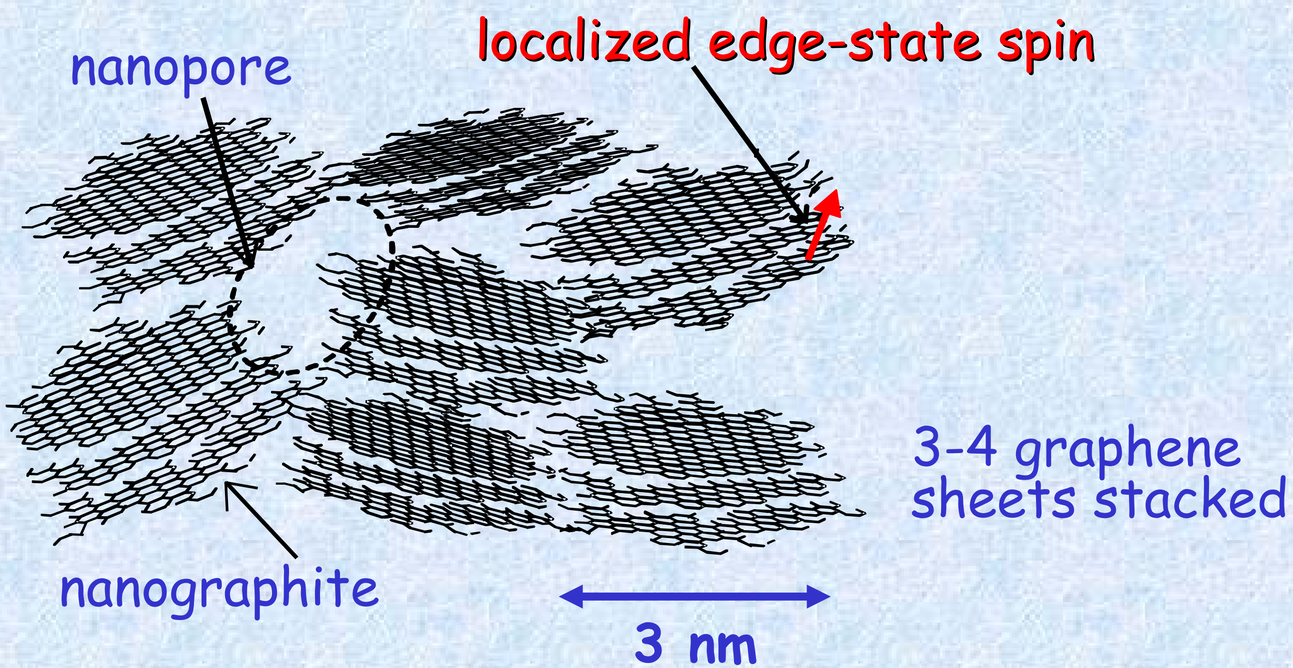



small
LDOS

node of the wave function

# magnetic switch of nanographite

# Activated carbon fibers (ACFs )

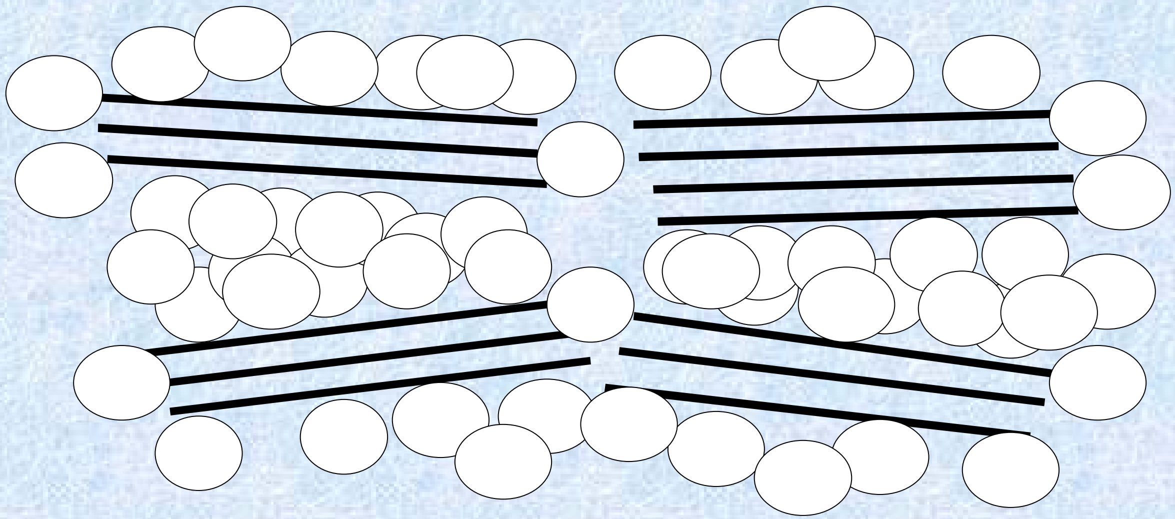



3D random network of nanographite domains

nanopores — adsorption of guest molecules

edge-state spins

## Gas physisorption ($O_2$,$N_2$,$H_2O$ etc.) in ACF nanopore space



guest molecules → effective pressure

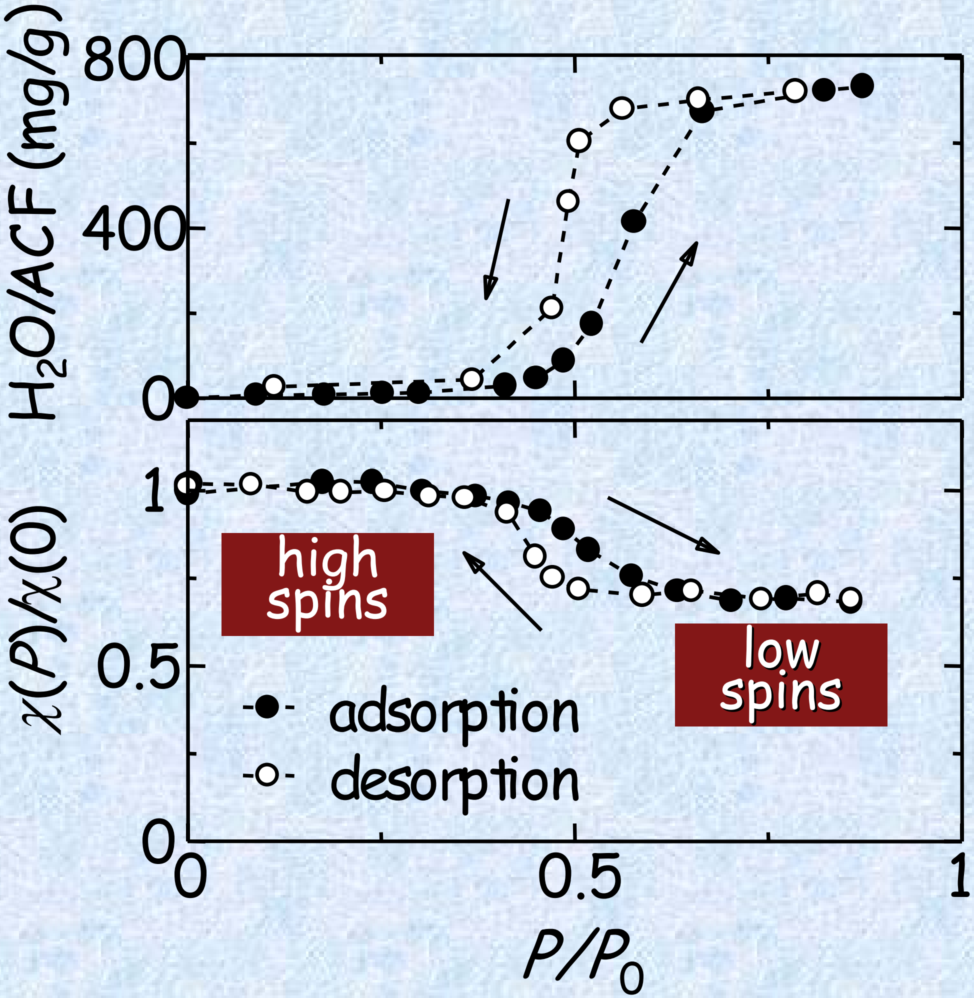
⇩

inter-nanographene layer distance reduced

**What effect on magnetism ?**

nanographite + $H_2O$

# Comparison between $H_2O$ adsorption isotherm and magnetic susceptibility




**# physisorption isotherm**

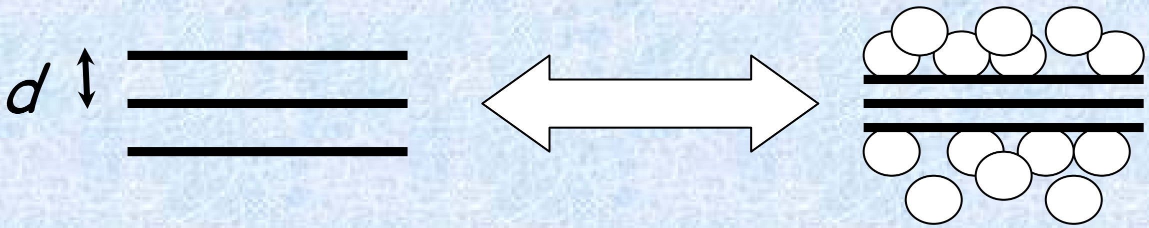
**adsorption threshold at $P/P_0 \sim 0.5$ (hydrophobic pore)**

**# magnetic susceptibility**

**drops at $P/P_0 > 0.5$**

**ON/OFF magnetic switch**

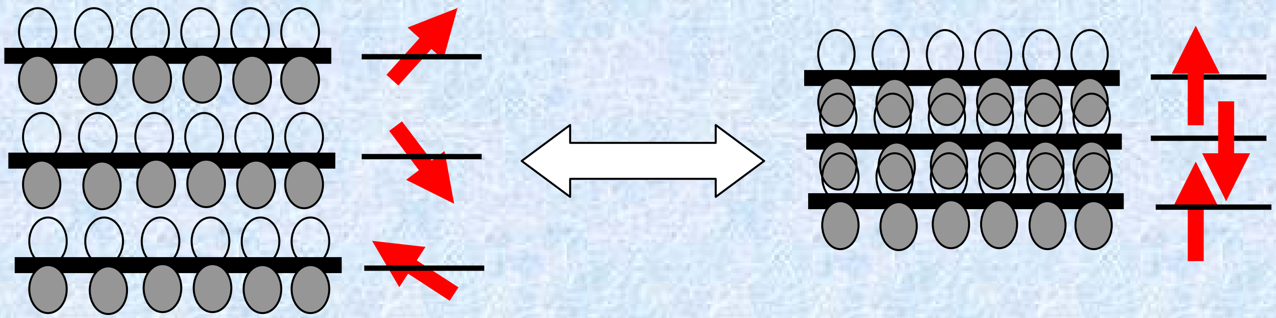
## effective pressure induced by $H_2O$ guests




$d$ ~0.38 nm $d$ ~ 0.34 nm

T.Suzuki et al., Carbon(1988)

**change in magnetism (high spin – low spin transition)**



**inter-graphene interaction $J \sim t^2/U$ enhanced**
**effective magnetic moment reduced**

**controllable nanoscopic magnetism in nanographite**

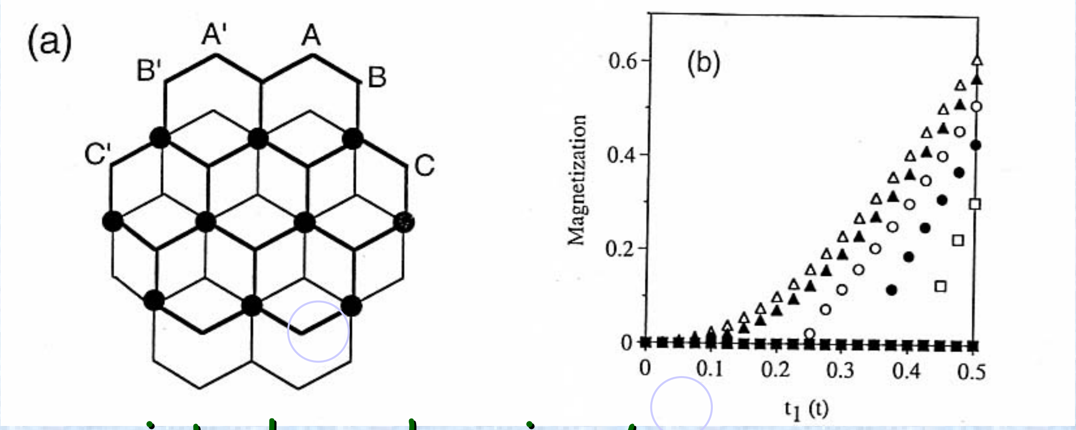
# Analysis by the Hubbard type model

**intralayer transfer int.: $t$**

**on-site Coulomb int.: $U$**

# closed shell electron case:

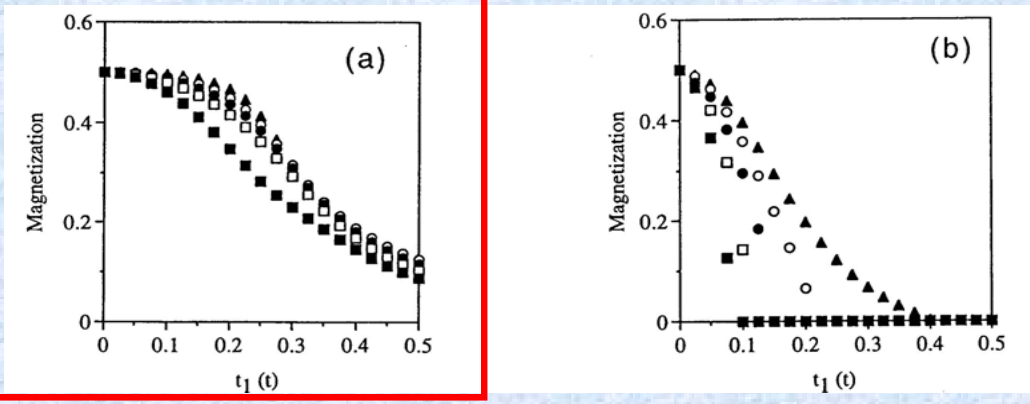
increase of interactions → increase of total magnetic moment




interlayer hopping $t_1$

# open shell electron case:

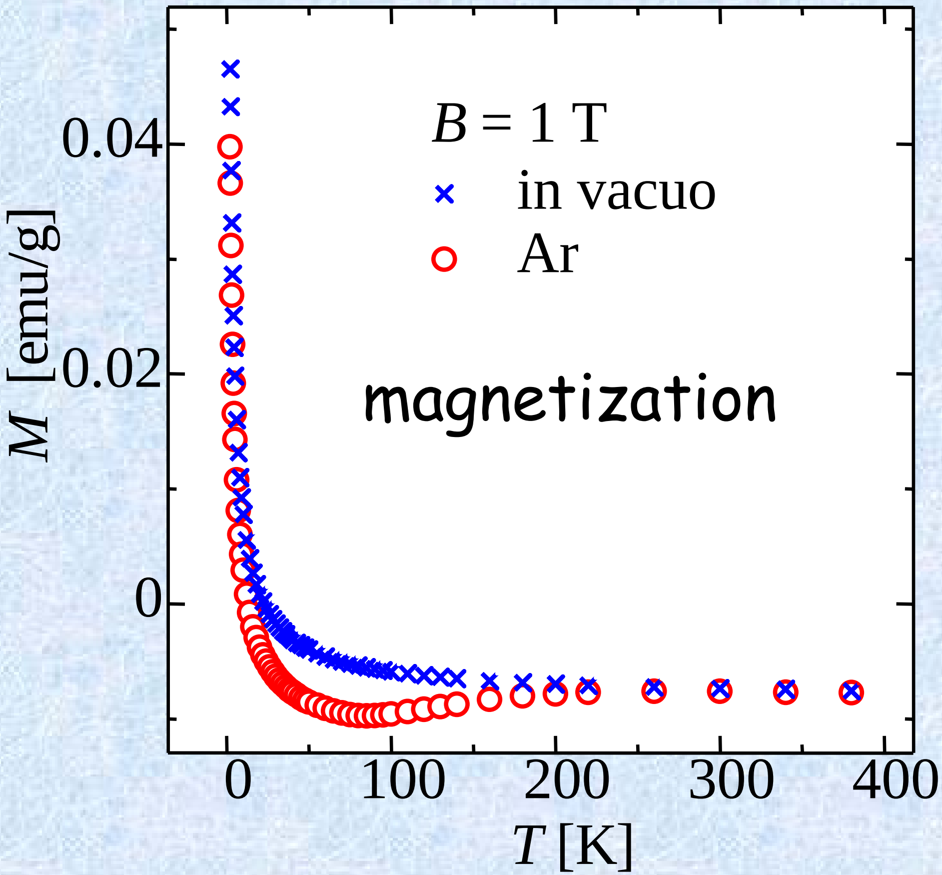
increase of interactions → decrease of total magnetic moment

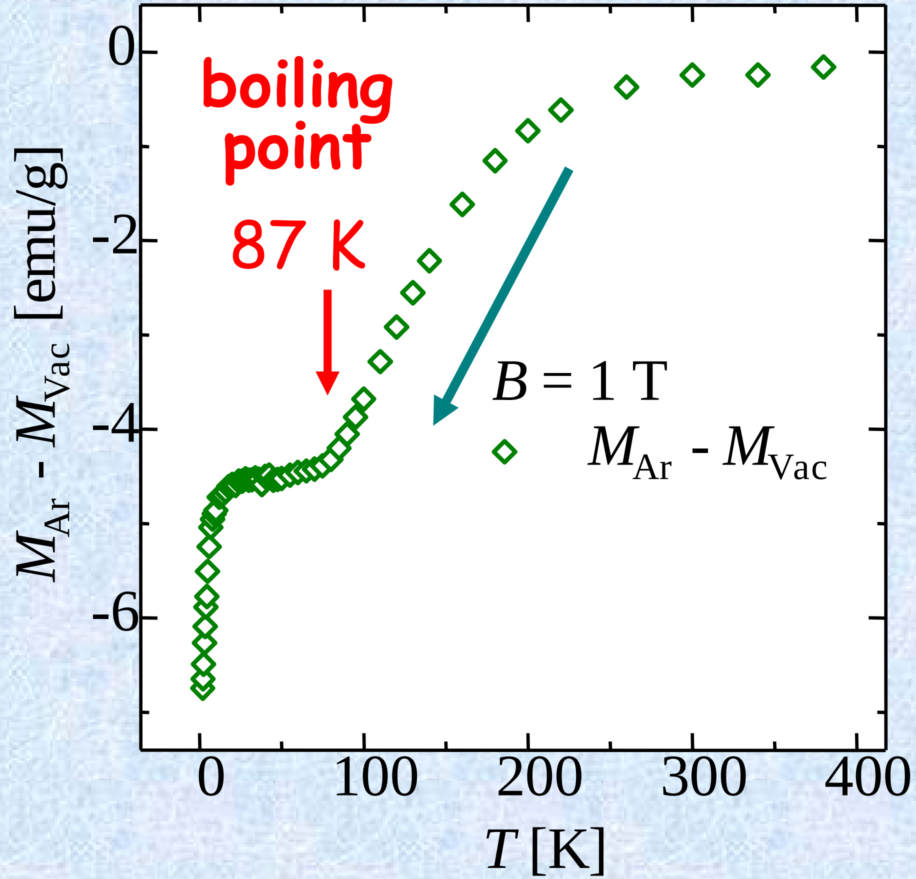



→ in agreement with experiments

K. Harigaya, J. Phys.: Condens. Matter 13, 1295 (2001);
K. Harigaya, Chem. Phys. Lett. 340, 123 (2001);
K. Harigaya and T. Enoki, Chem. Phys. Lett. 351, 128 (2002).

# Ar adsorption in micropores




magnetization affected well above the boiling point

**Ar guest atoms (diamagnetic) adsorbed well above the boiling point**

# zero-field muon spin relaxation (ZF-$\mu$SR) in Ar

- $T$>130 K (above $T_b$=87 K)

$$\exp(-\lambda t) = \exp\left(-\frac{(\gamma_\mu \sigma_B)^2}{\nu_{ex}} t\right)$$

exchange narrowing

$\sigma_B$: dipolar field

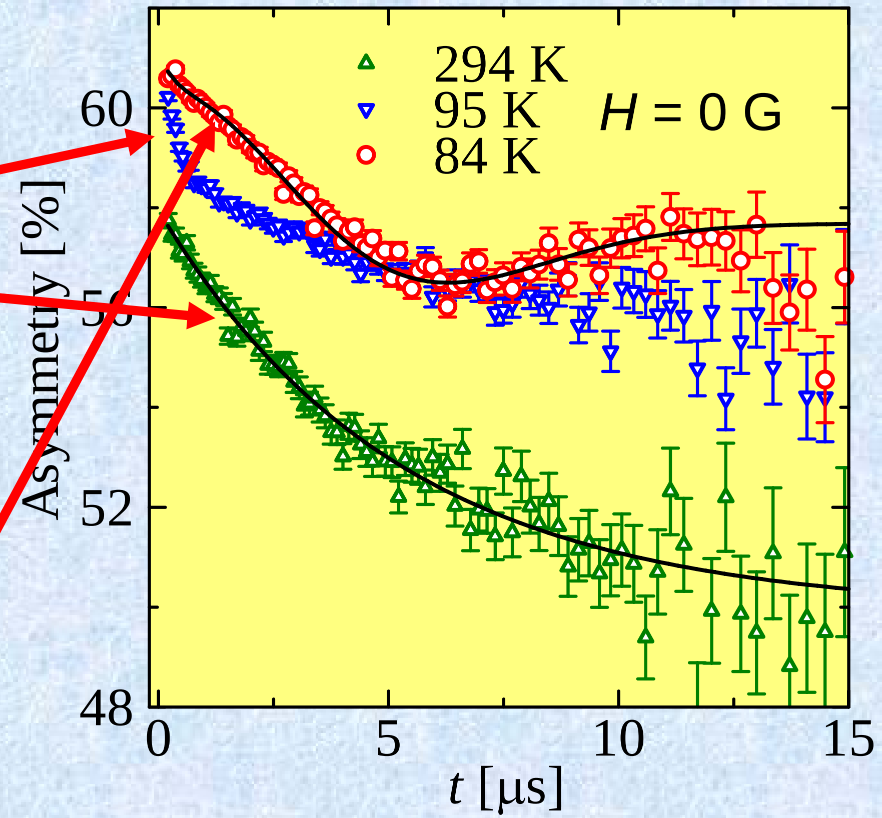
$\nu_{ex}$: exchange frequency

- $T$< 84 K (below $T_b$)

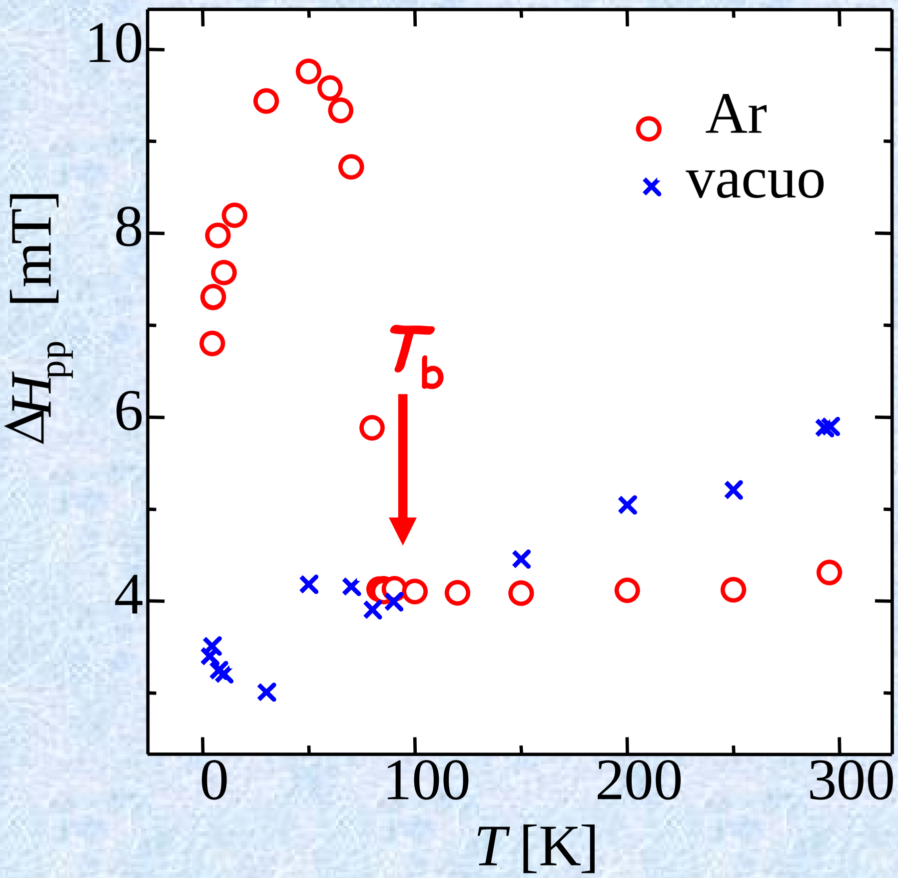
Kubo-Toyabe formula

$$\frac{1}{3} + \frac{2}{3}\left\{1-(\gamma_\mu\sigma_B)^2 t^2\right\}\exp\left\{-\frac{1}{2}(\gamma_\mu\sigma_B)^2 t^2\right\}$$

inhomogeneous broadening due to the dipolar field




exchange narrowing suppressed upon Ar adsorption




**ESR line width** $\Delta H \sim \left\langle \Delta H_d^{\ 2} \right\rangle / H_{ex}$

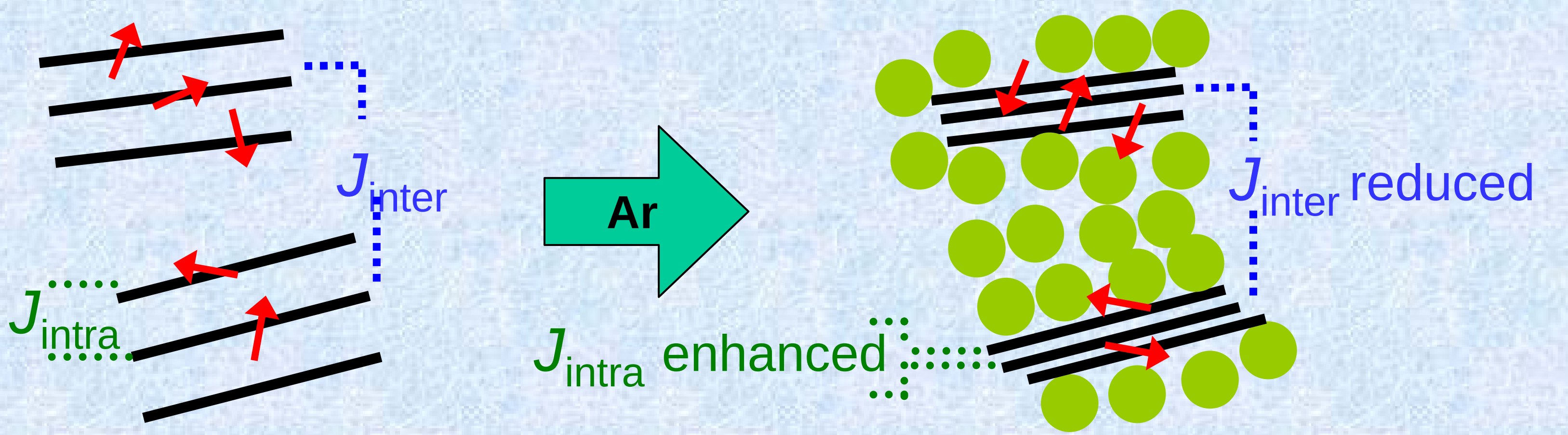
$\Delta H_d$: dipolar field

$H_{ex}$: exchange filed

**exchange narrowing suppressed below $T_b$**

**consistent with μSR**

magnetic switching effect



# Summary

## Nanographene/Nanographite

importance of geometry of edges

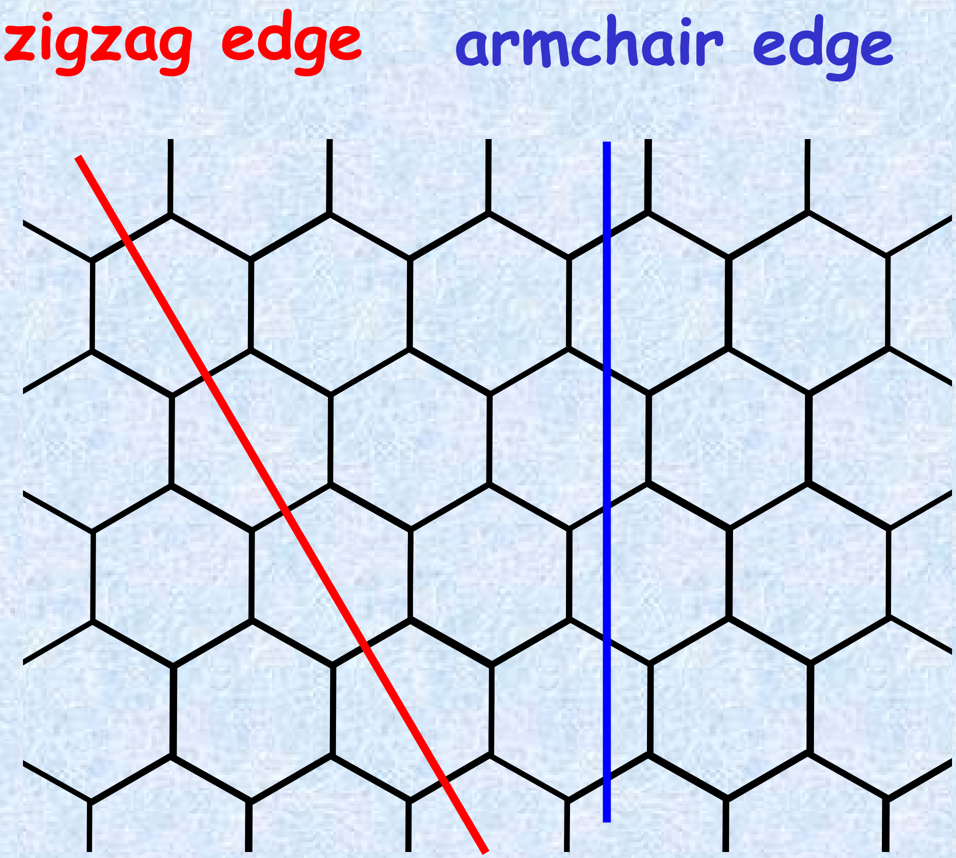
non-bonding $\pi$-electron state (edge state)

STM/STS observations
for well defined edges

nanoscopic magnetism

spin glass
magnetic switch
gas sensor

# Nanographene-based molecular devices




**electron beam lthography**

magnetic line

**chemical modifications**

CH itinerant magnetism

$CH_2$ localized magnetism

CF nonmagnetic

C=O conducting line

**future promising molecular devices**

**(compared with nanotubes)**

Contributors

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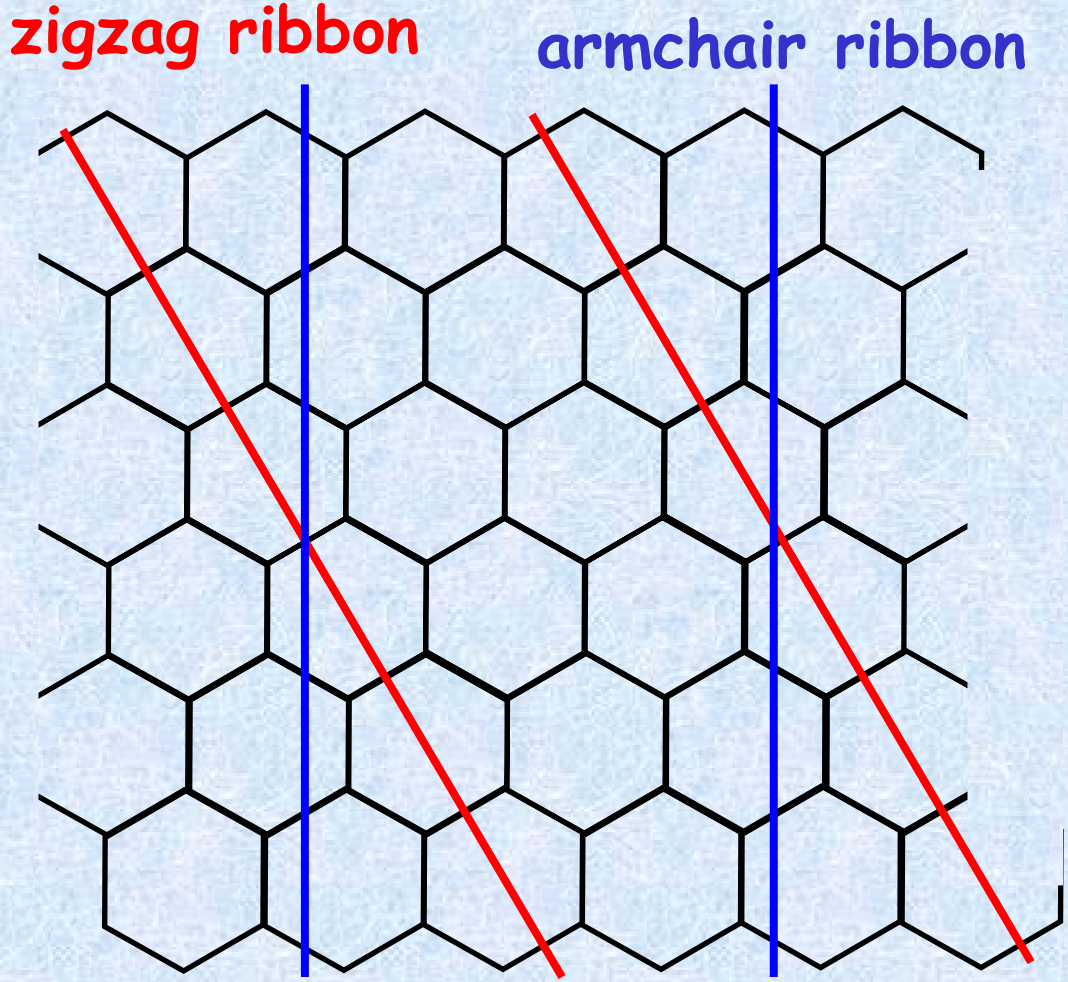
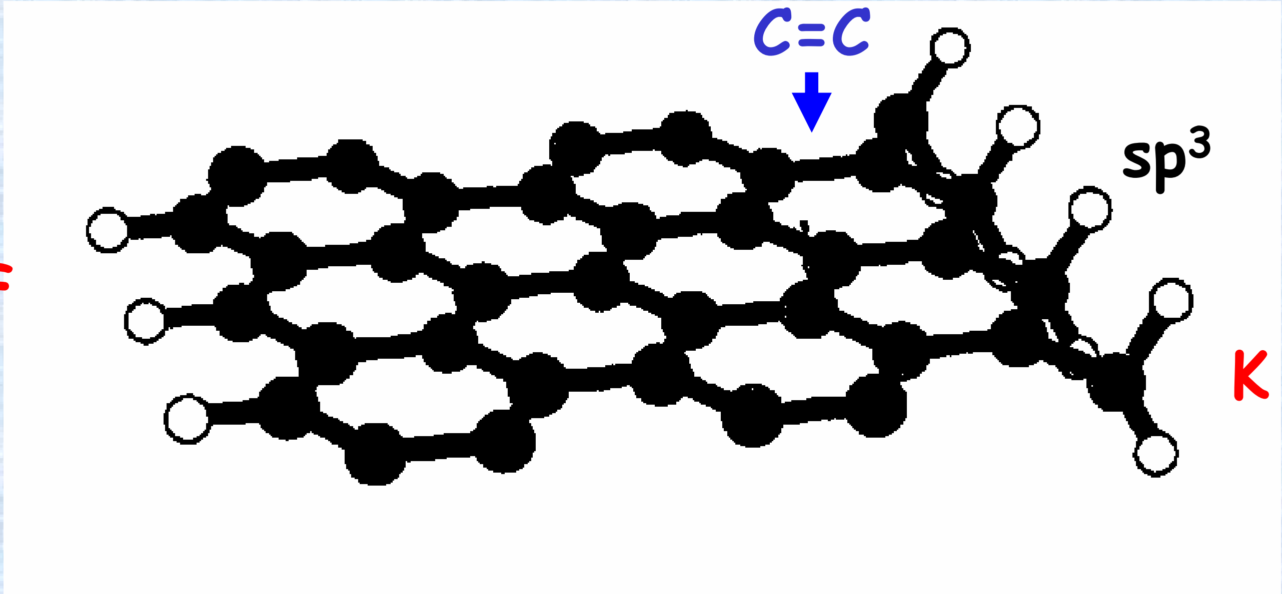
SARCO

## Nanographene ribbon



# magnetic nanocarbons with Klein and Fujita edges

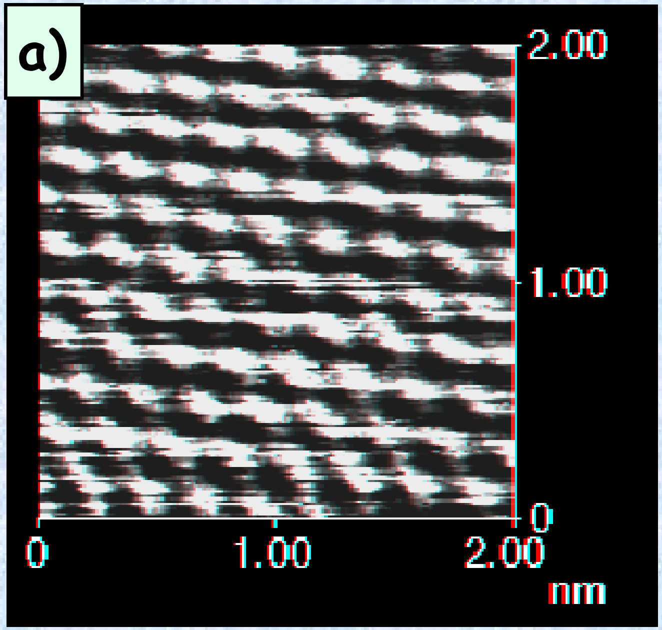



**nanocarbon-based ferromagnetism**

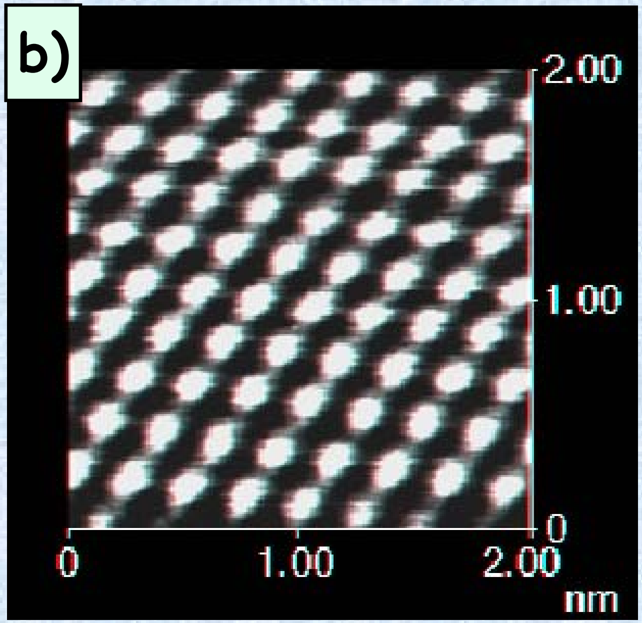
- F(or H)-terminated edge
- graphite-diamond interface

K. Kusakabe, et al. 2001

# triangular lattice image on a particle




Particle



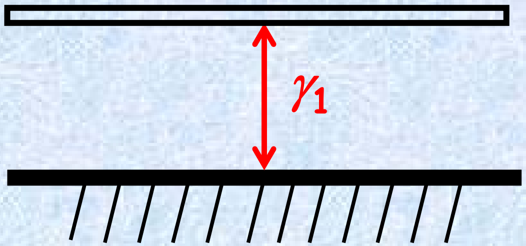

Substrate

★same A-B stacking mode with HOPG substrate
★small irregularity

# Electronic properties

- **graphene sheet-substrate interaction**

interlayer distance 0.35-0.37 nm




interlayer resonance integral

$\gamma_1$ = 0.20-0.29eV

(bulk $\gamma_1$ =0.39 eV)

- **quantum size effect**

$N$ ~ 3000 largest polycyclic aromatic molecule

band width $W = 6\gamma_0$

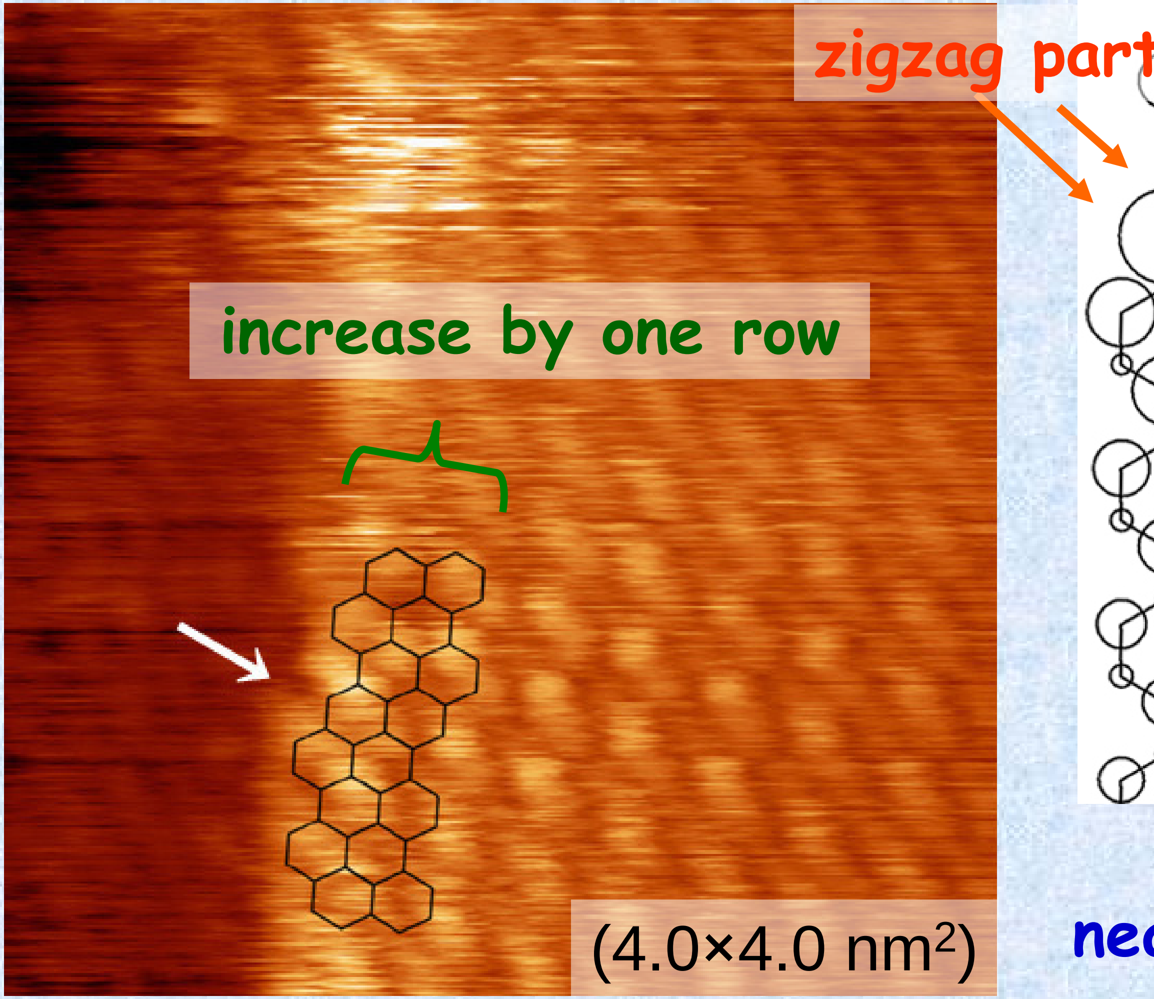
in-plane resonance integral $\gamma_0$ =3.16 eV

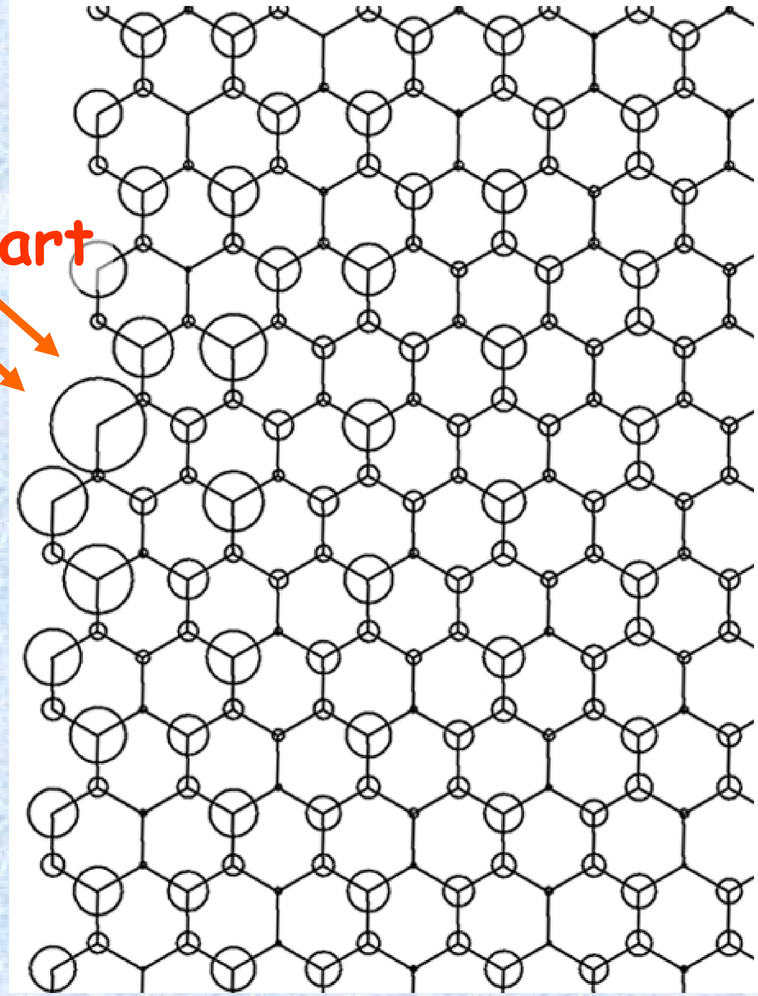
energy discreteness $N/W$ ~75 K

- **edge state effect**

scanning tunneling spectroscopy experiment

one zigzag edge atom
in armchair edge

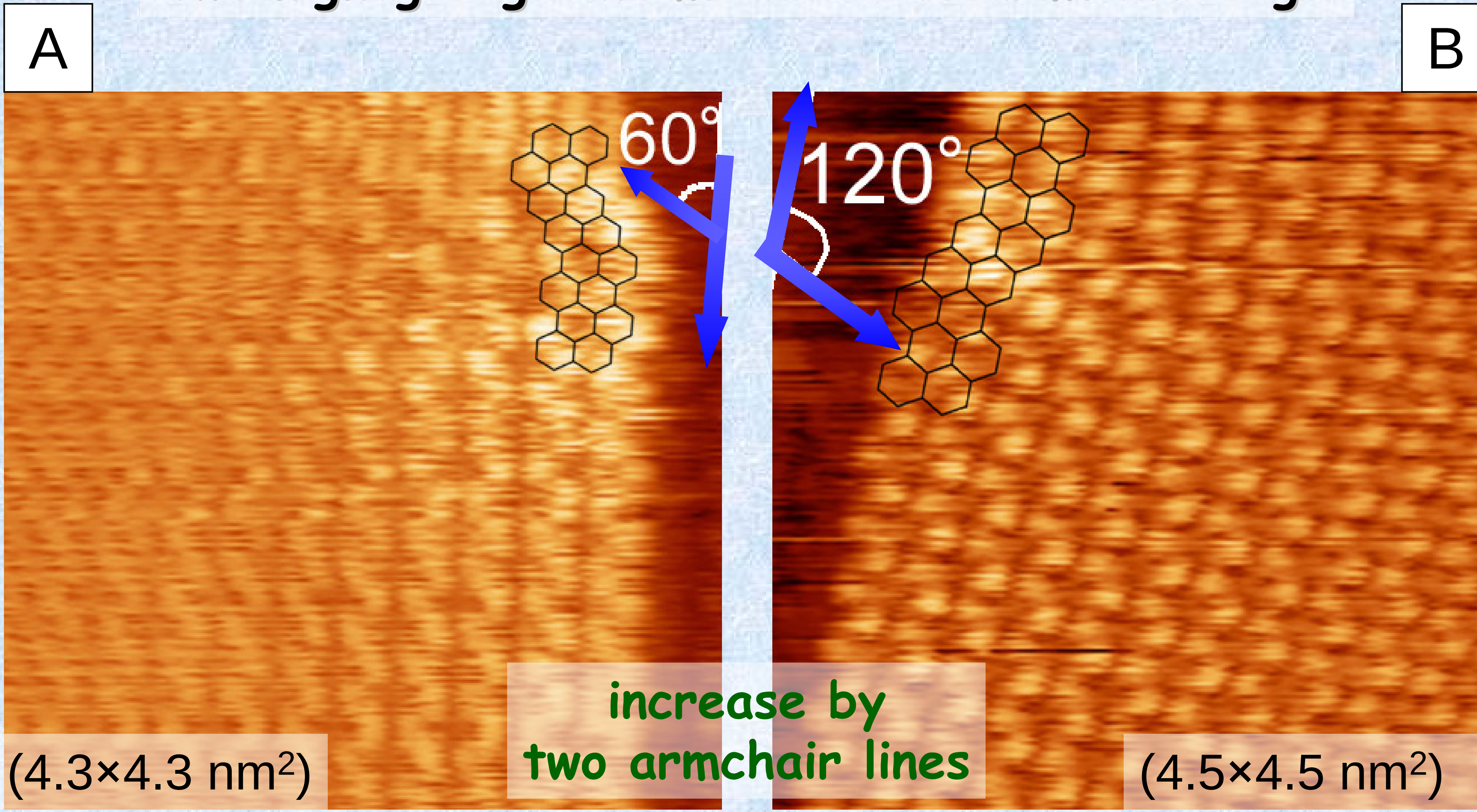


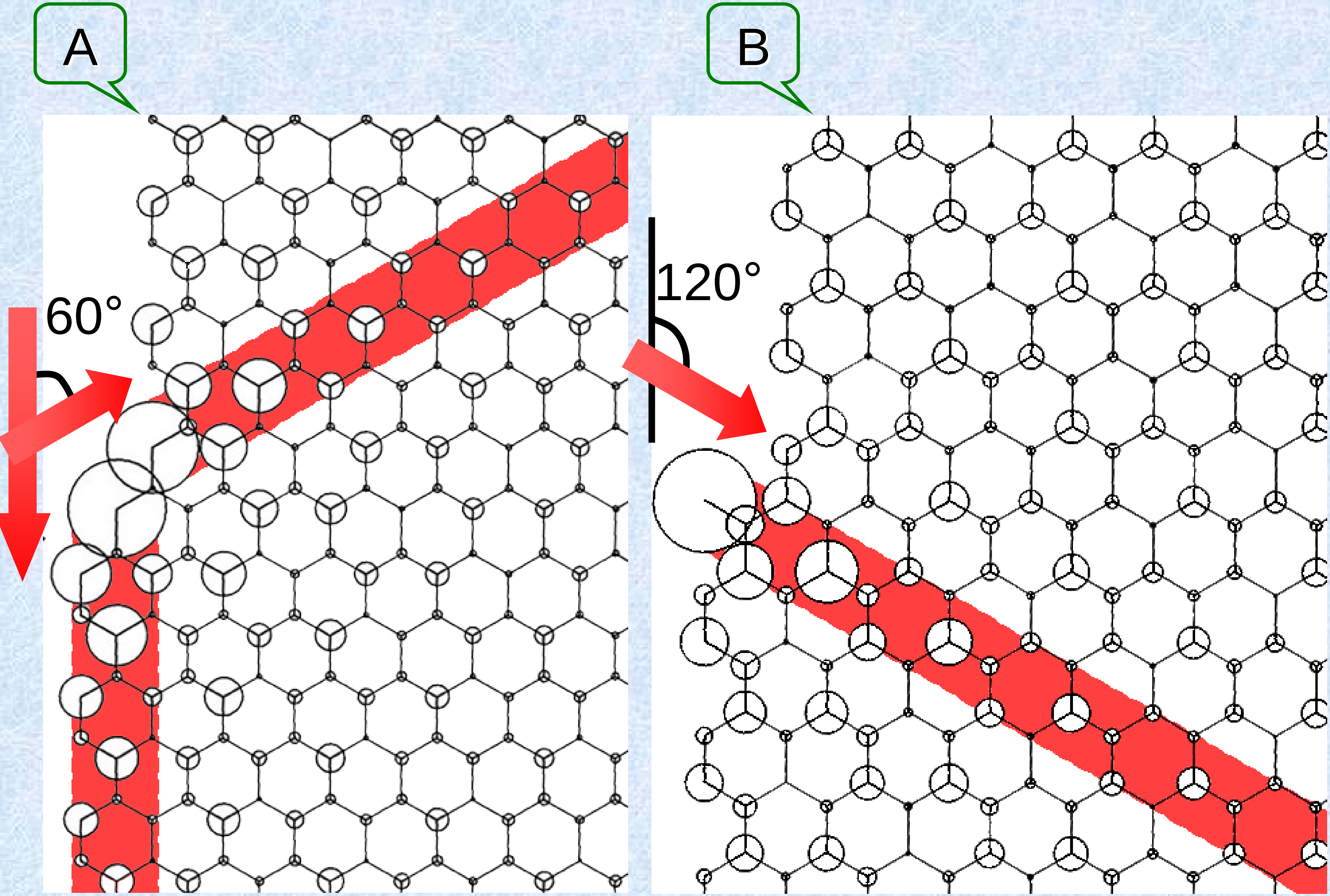
calculated LDOS
near the defect point

dispersed LDOS near the defect point
at which an armchair line is added

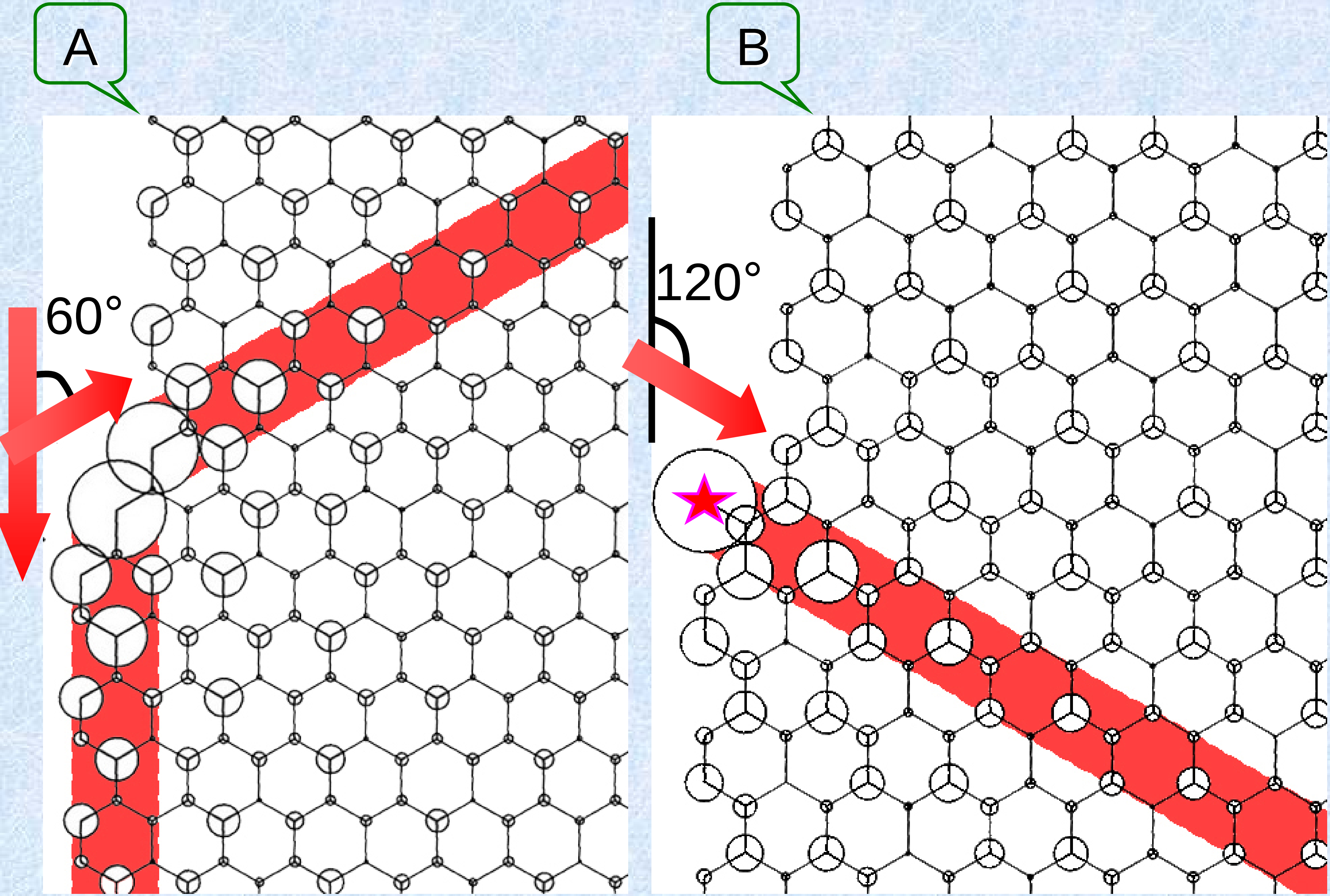
# two zigzag edge atoms added to armchair edge




arrays of bright spots near defects run in different directions

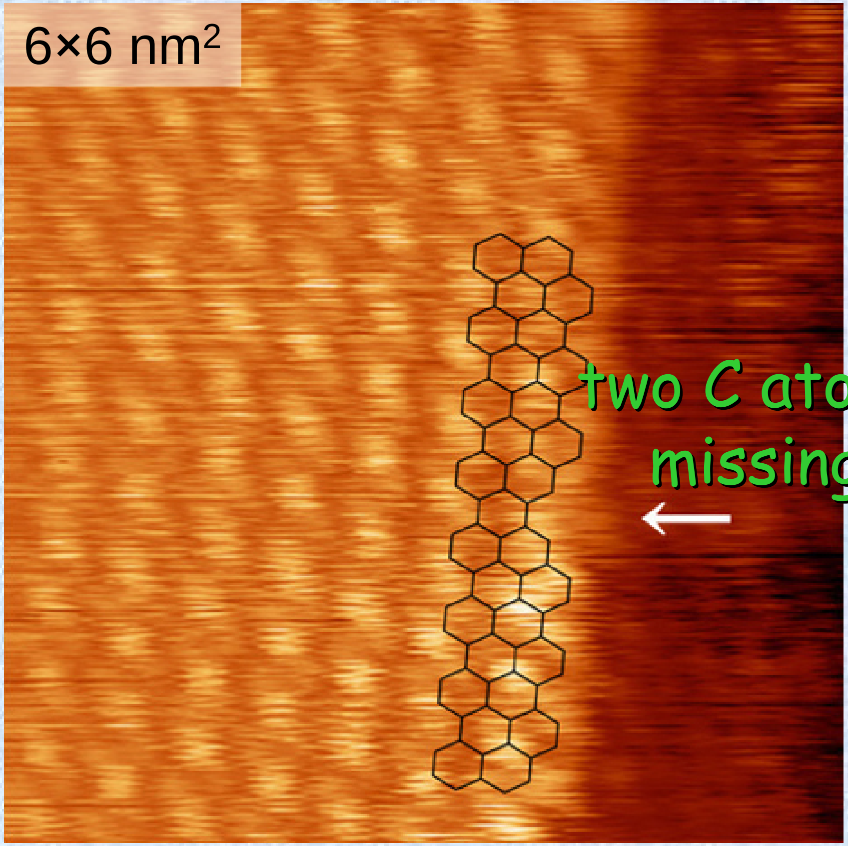



calculated LDOS near the defect point

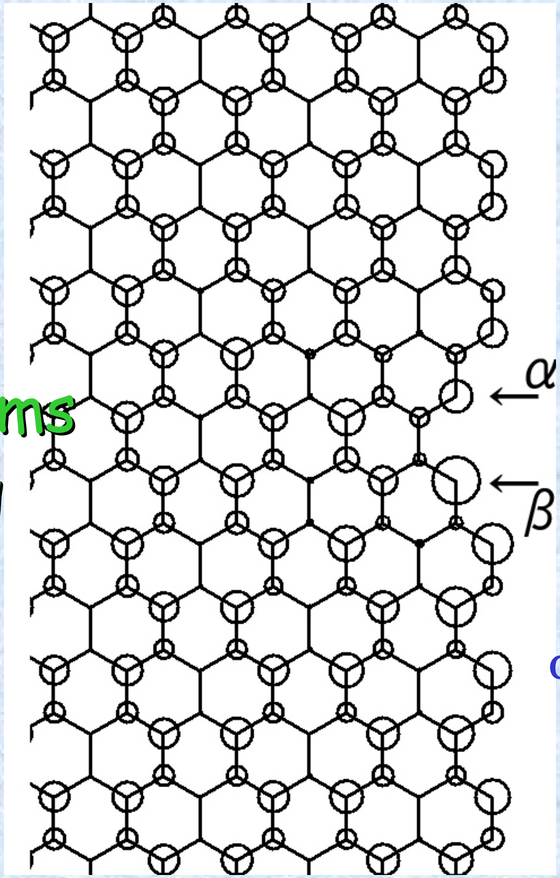



the difference comes from one extra-carbon atom

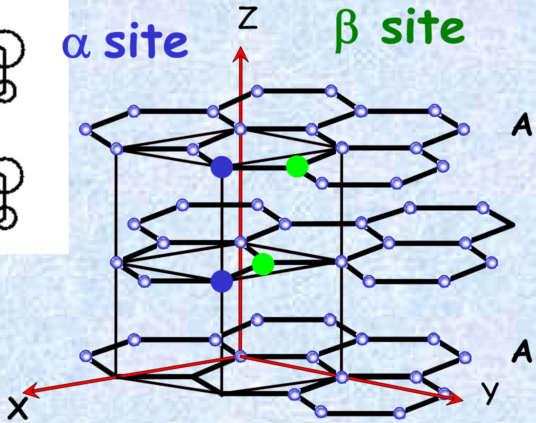
# effect of inter-graphene layer interaction on the edge state



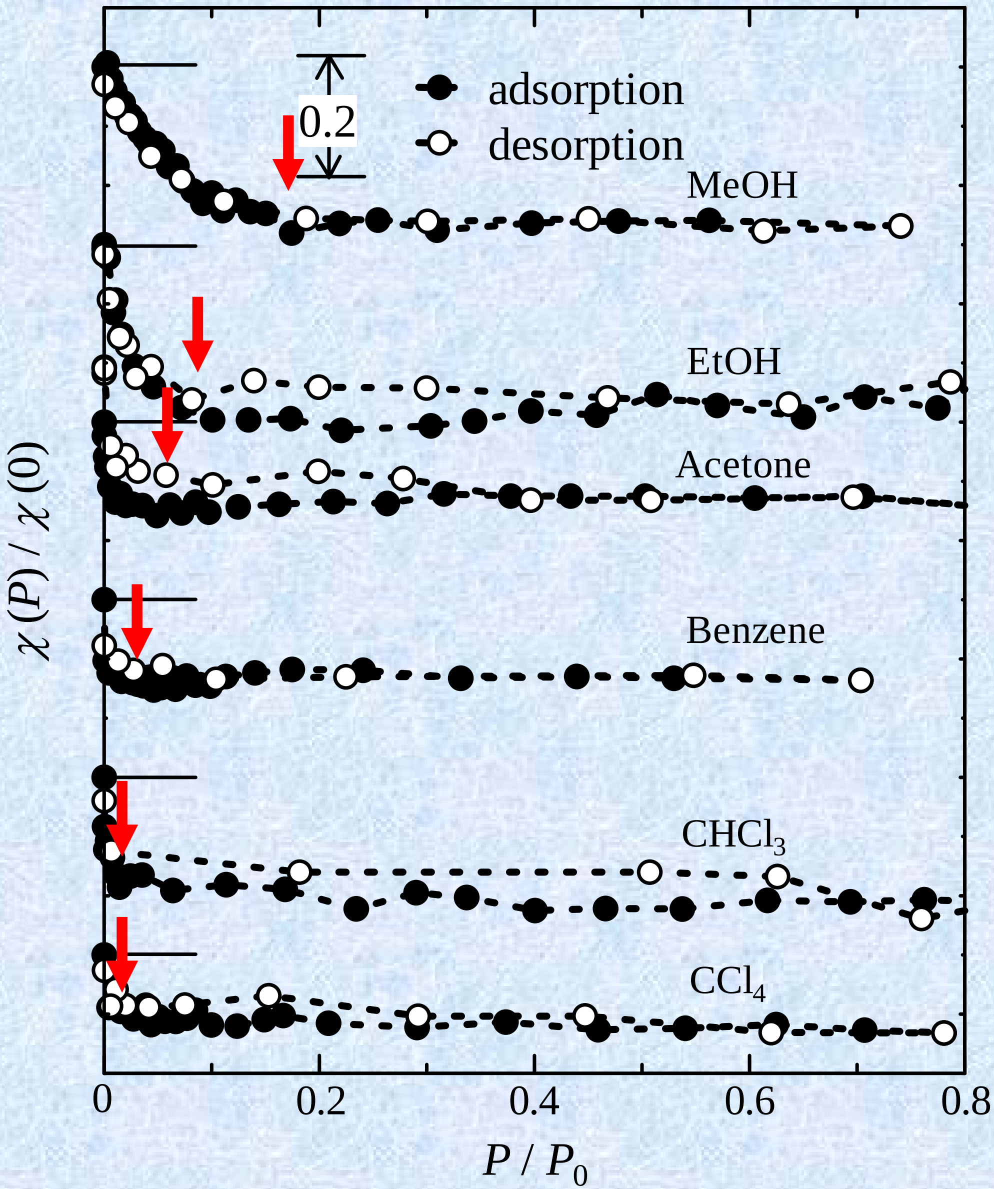

2D LDOS mapping



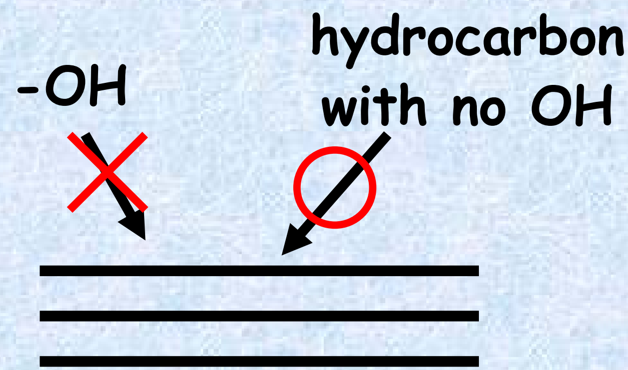

**edge state at a defect point**



# effect of various physisorbed molecules on nanomagntism

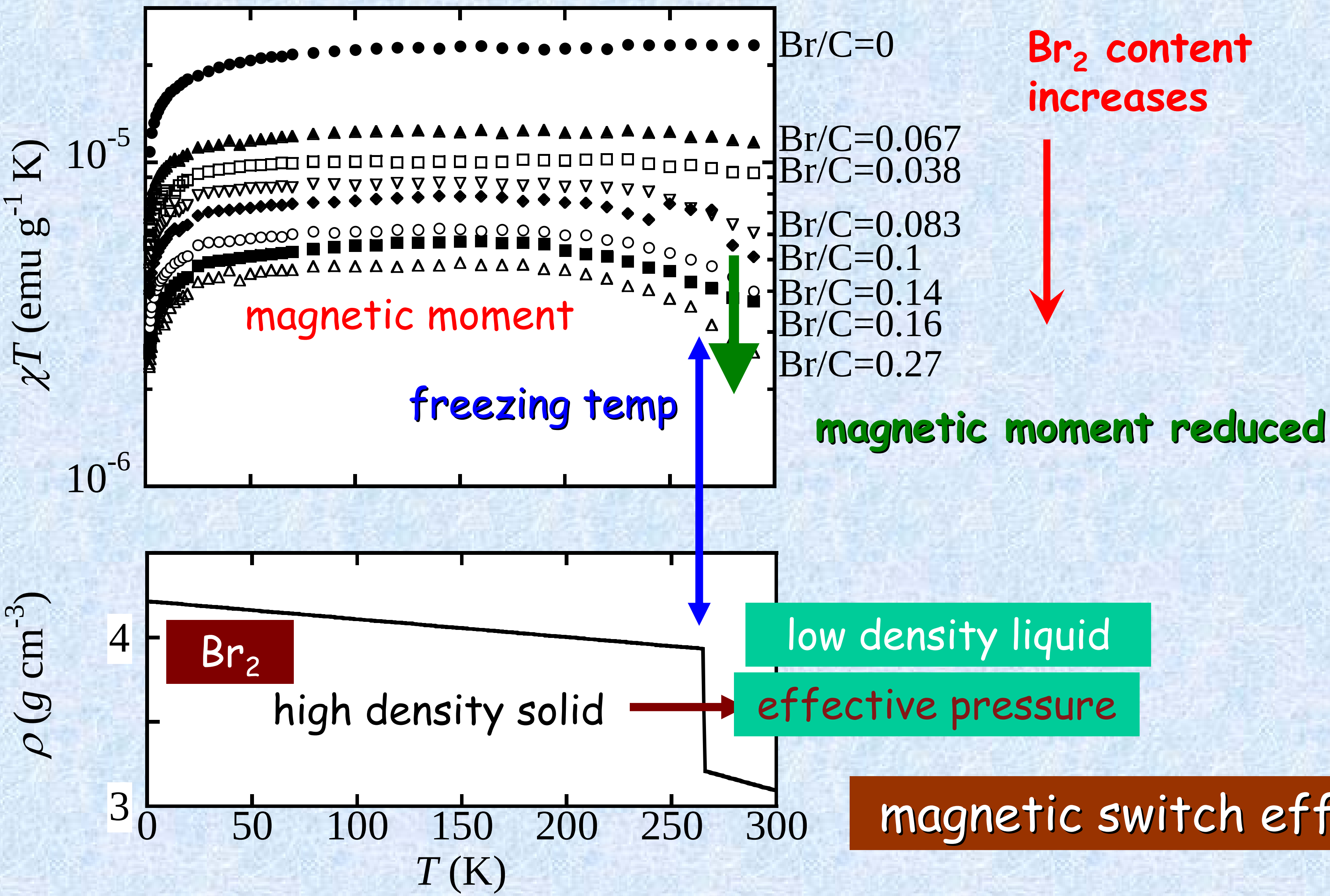



hydrophobic graphene surface



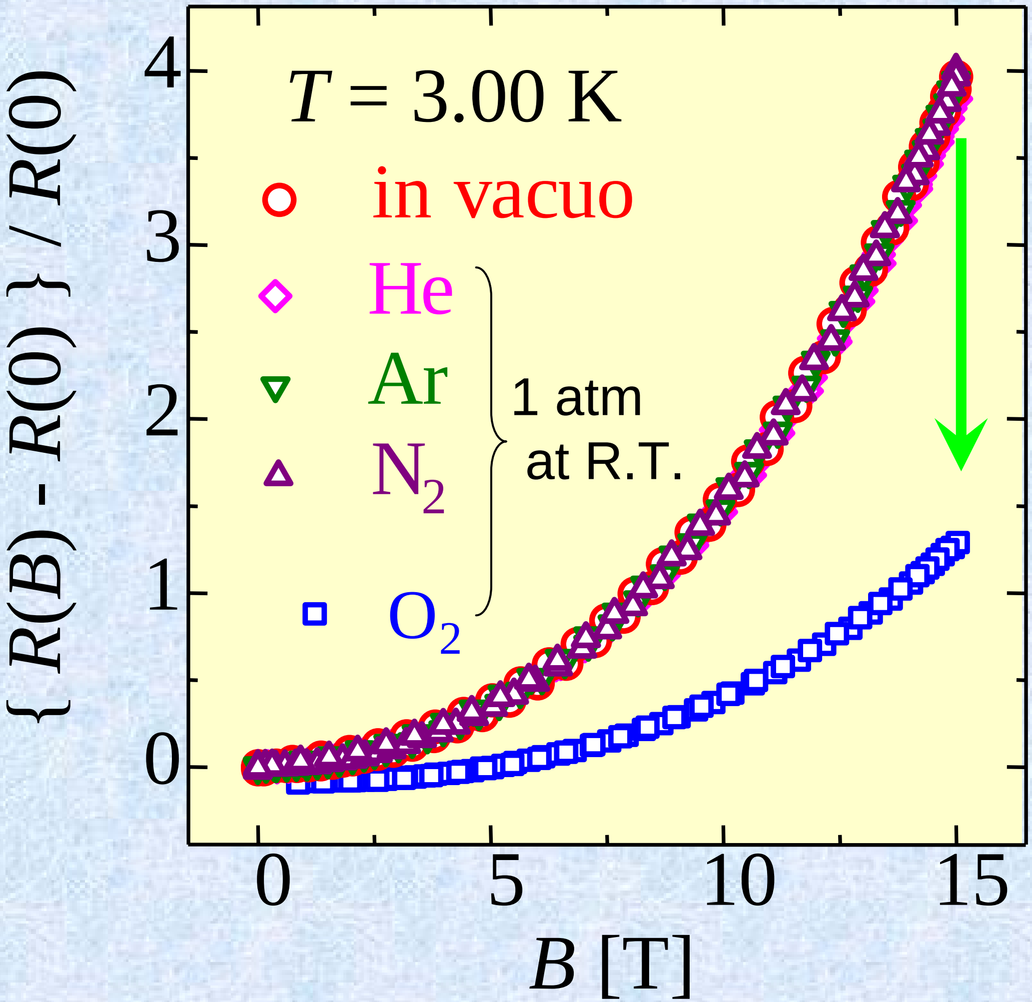

threshold pressure of magnetic switch effect is lowered upon the decrease in the weight of OH

# magnetic switch effect created at the solid-liquid transition of $Br_2$ guests

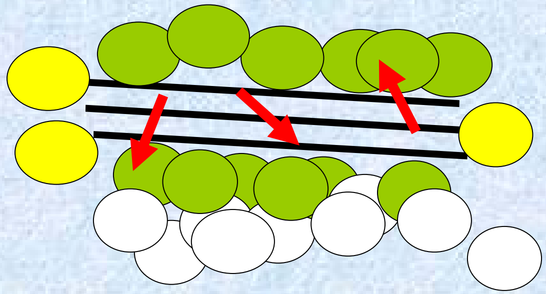



magnetic switch effect

# magnetoresitance with paramgnetic $O_2$ molecules




$O_2$ molecules $S$=1



wave function overlap with graphitic π-electron
**strong exchange int.**

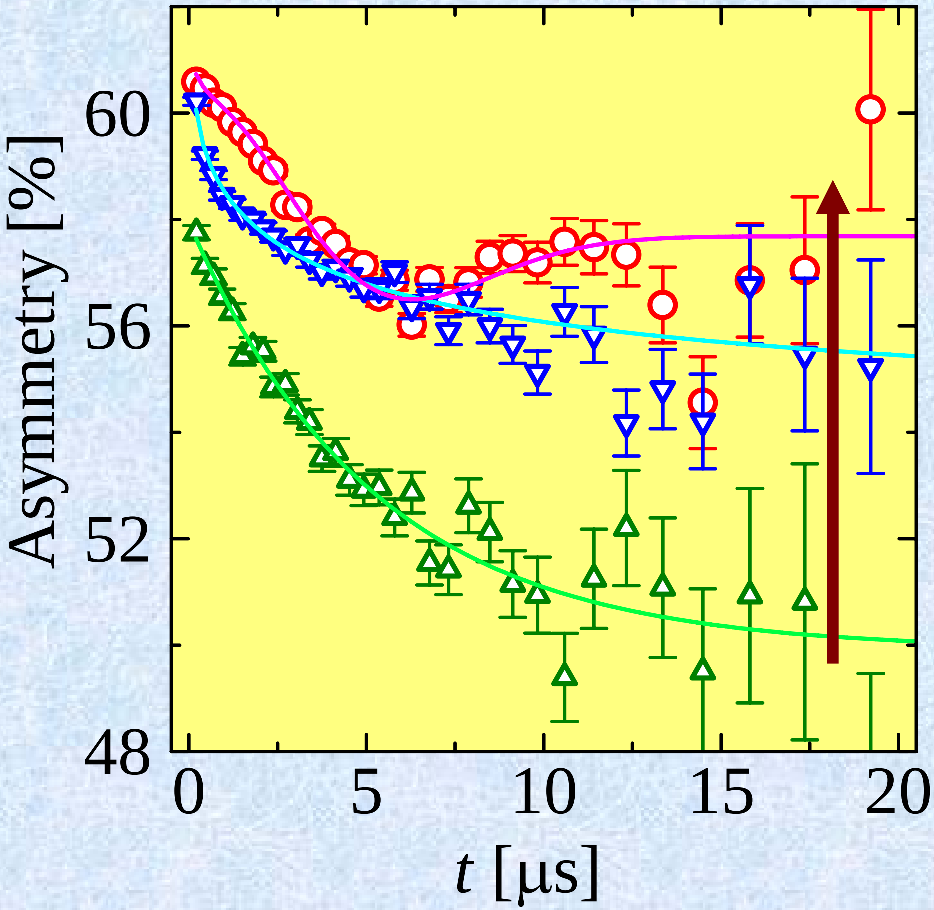
chemical bond with $S$=0 singlet state

physisorbed weak dipole-dipole int.

exchange int. between $O_2$ spins and edge-state spins

internal field from $O_2$ molecules ~20 K

# Zero field muon spin relaxation (μSR) in Ar atmosphere




Ar pressure:
~ 1 atm at 87 K (B.P.)

○: 84 K
▽: 95 K
△: 294 K

Freezing P. 84 K
Boiling p. 87 K

increase of the static component is prominent below the F.P. of Ar

freezing of Ar condensed in the nanopores
→ modification of the magnetism of the edge-state spins

## nano-graphite network

☆Coulomb blockade effect
☆spin-glass

**Activated carbon fibers**

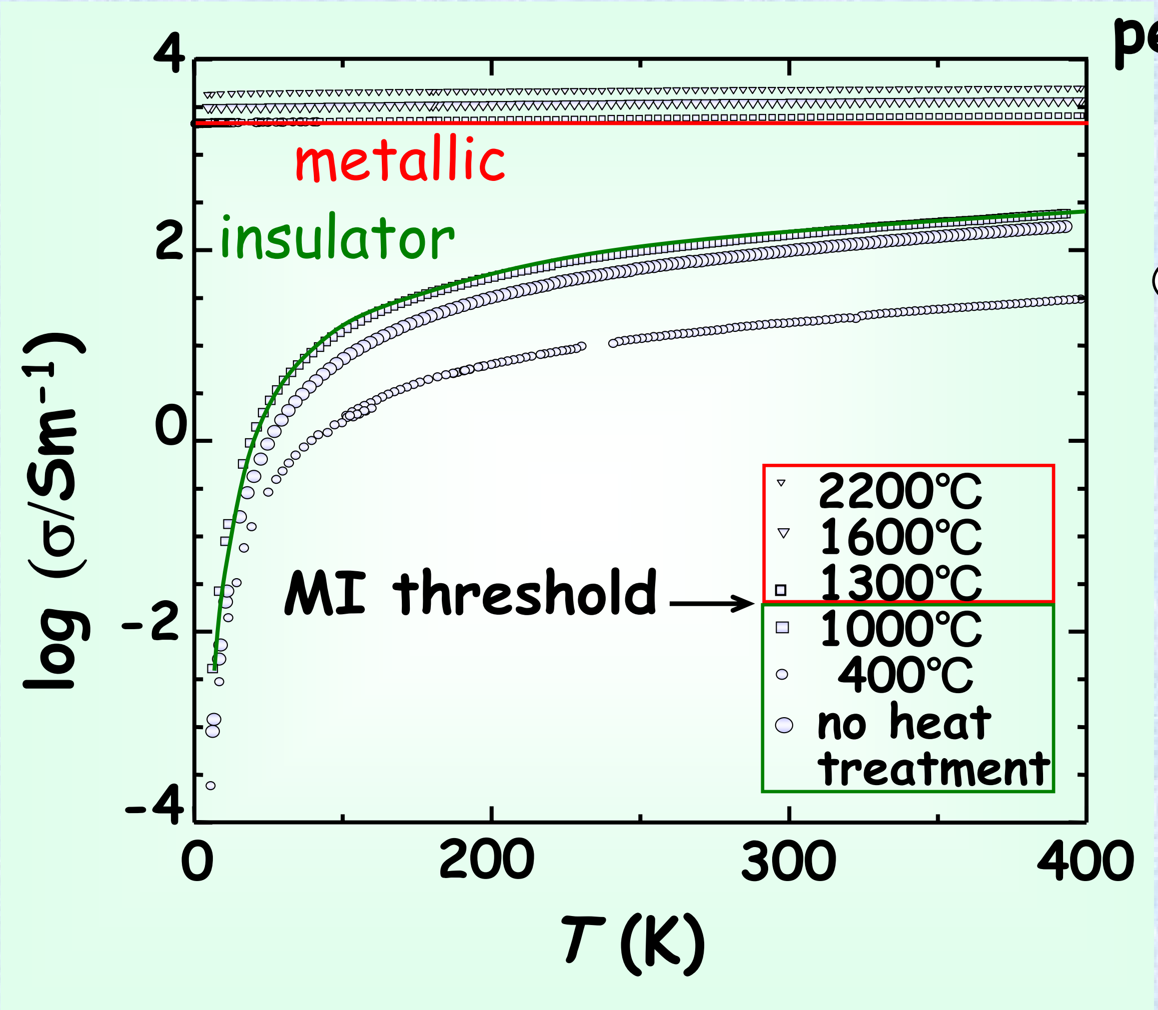
3D nano-graphite network

heat treatment

↓

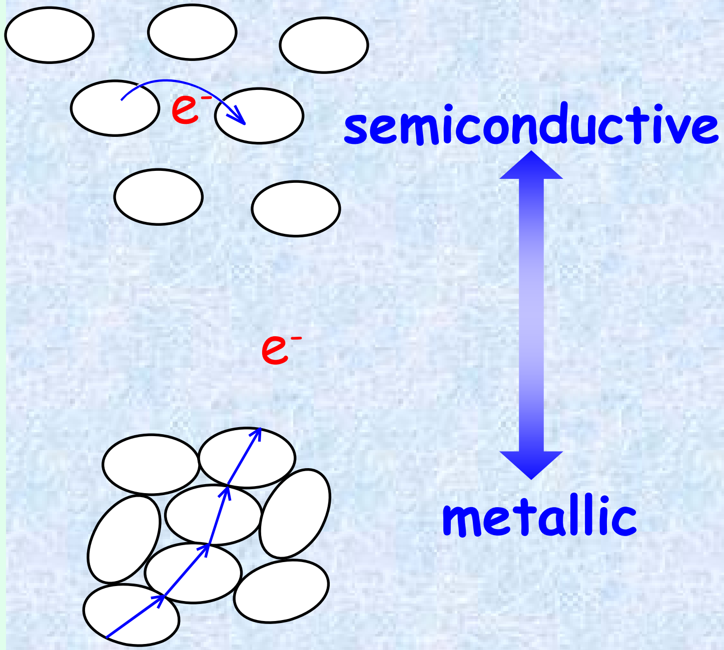
insulator-metal transition

# Heat-treatment effect on conductivity




percolation threshold $P_c$

→ ca. HTT 1200°C

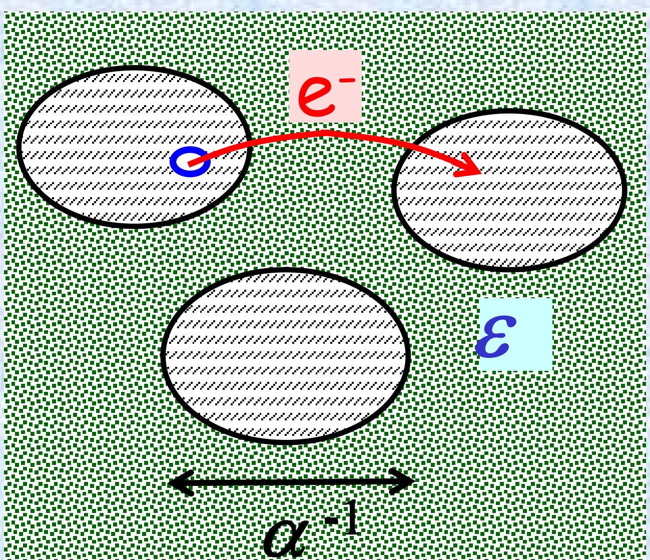


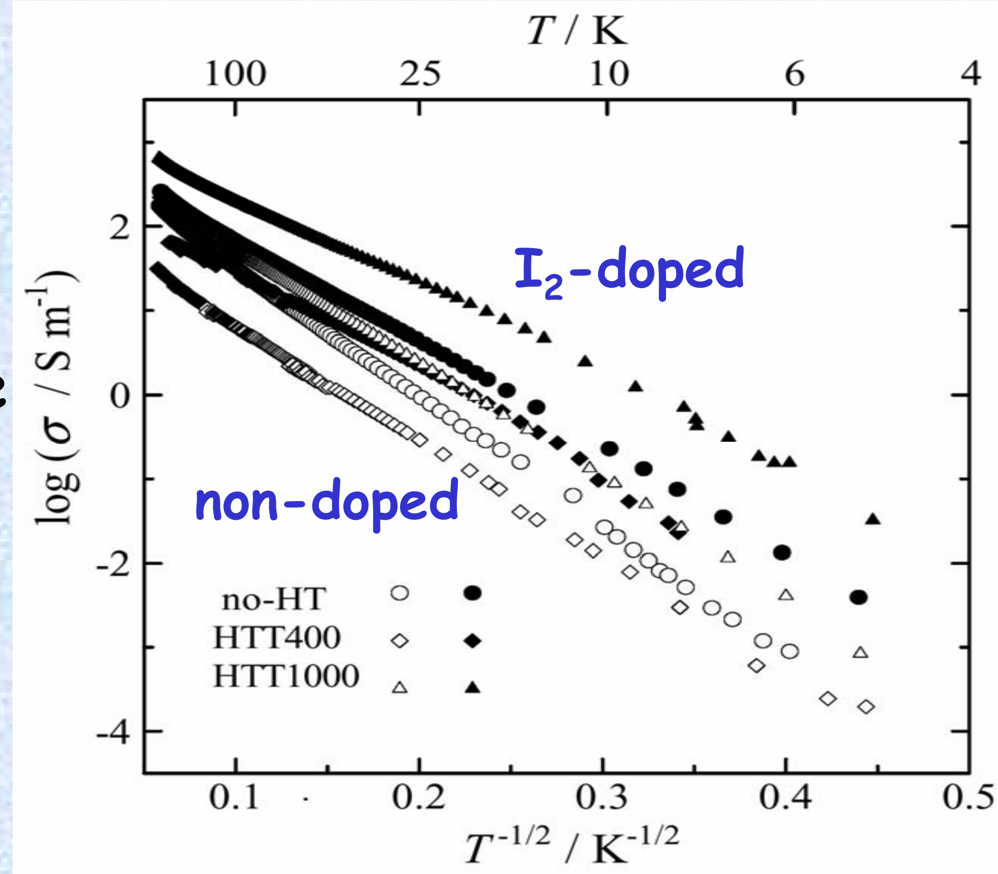
## semiconductive region

conductivity of ACFs
and iodine-doped ACFs

Coulomb gap variable-range
hopping conduction

**charging effect** $\dfrac{e^2}{\varepsilon r}$



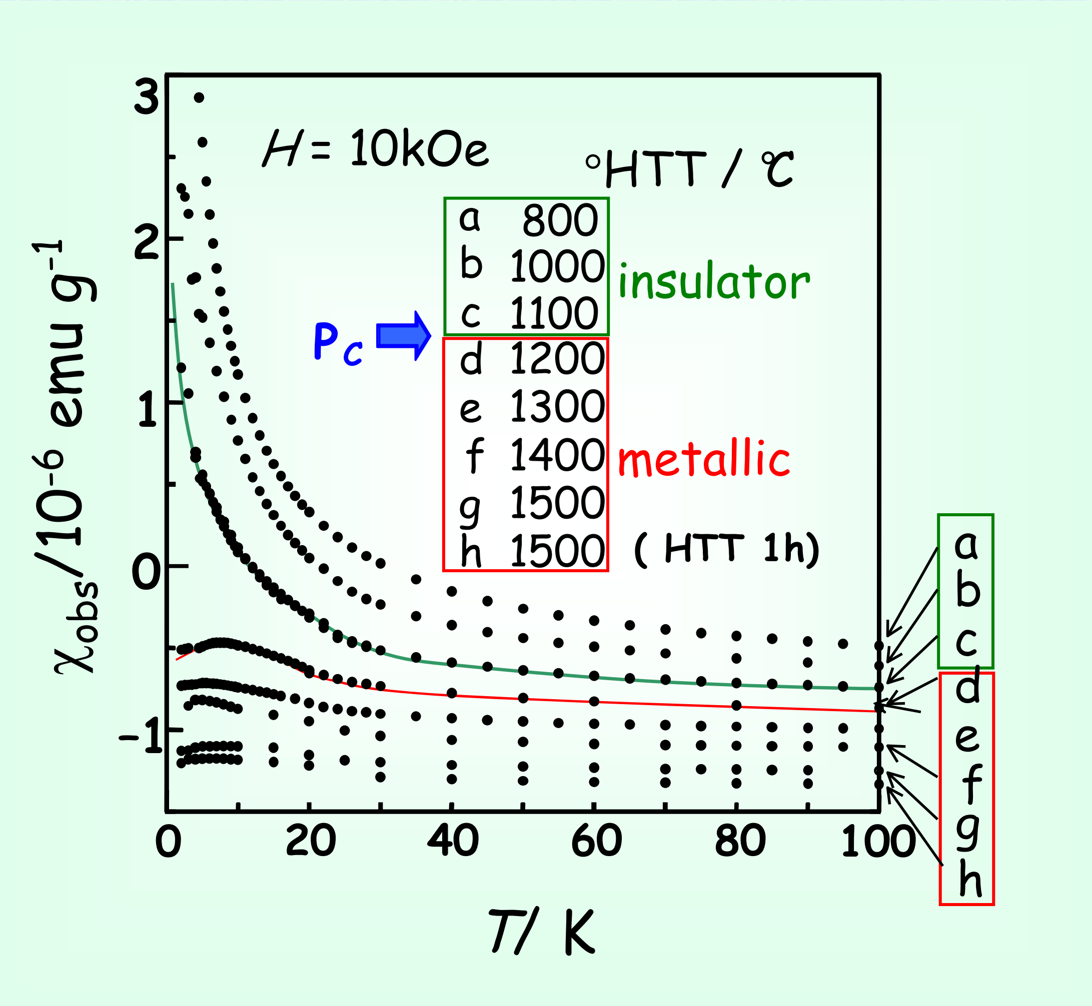

$$\sigma = \sigma_0 \exp[\ (T_0 / T)^{1/2}]$$

$$T_0 = \frac{6e^2}{\pi k_B} \frac{1}{4\pi\varepsilon} \frac{1}{\alpha^{\ 1}}$$

$\varepsilon$: dielectric constant

$\alpha^{-1}$: localization length

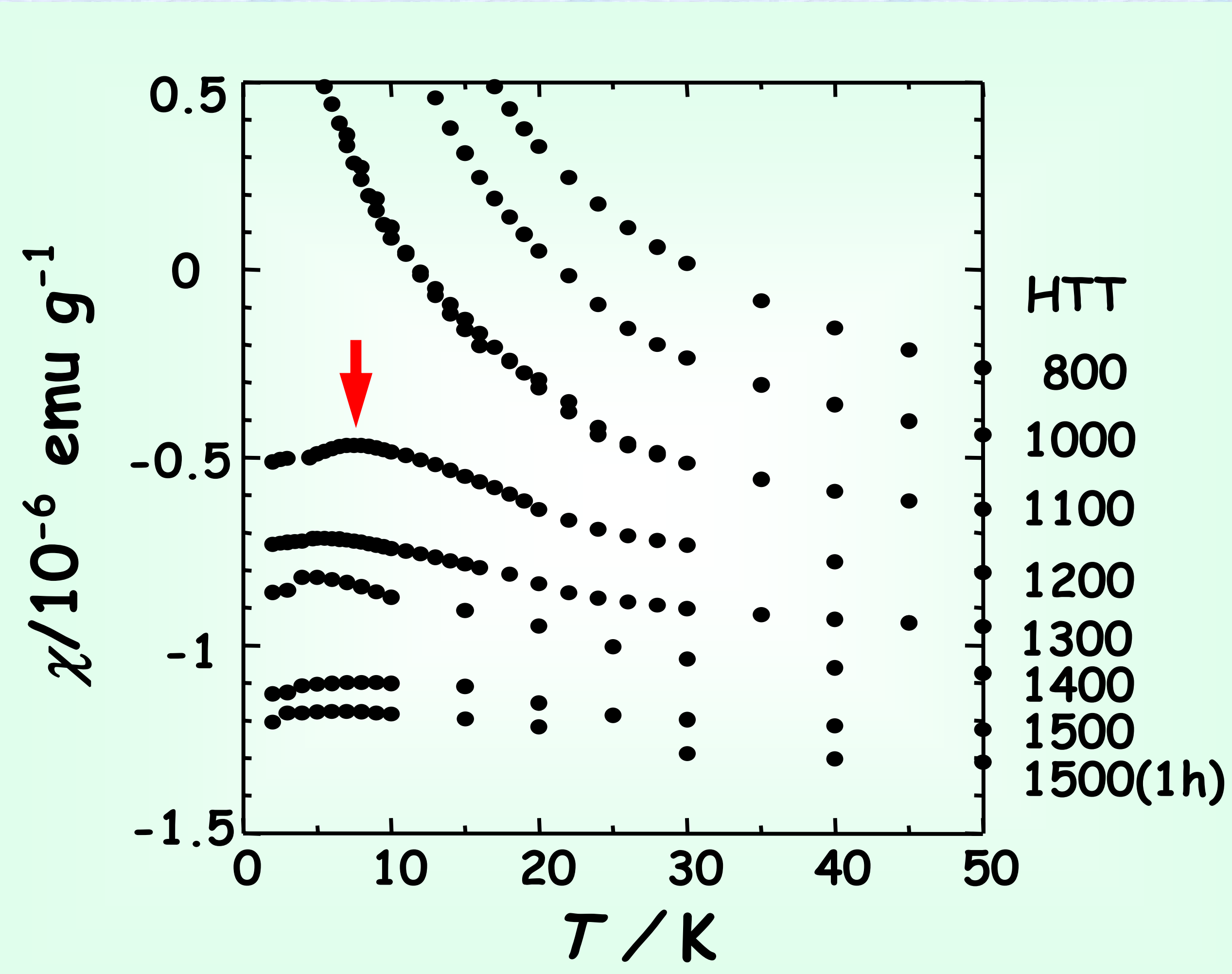
# Heat-treatment effect on magnetic susceptibility




**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



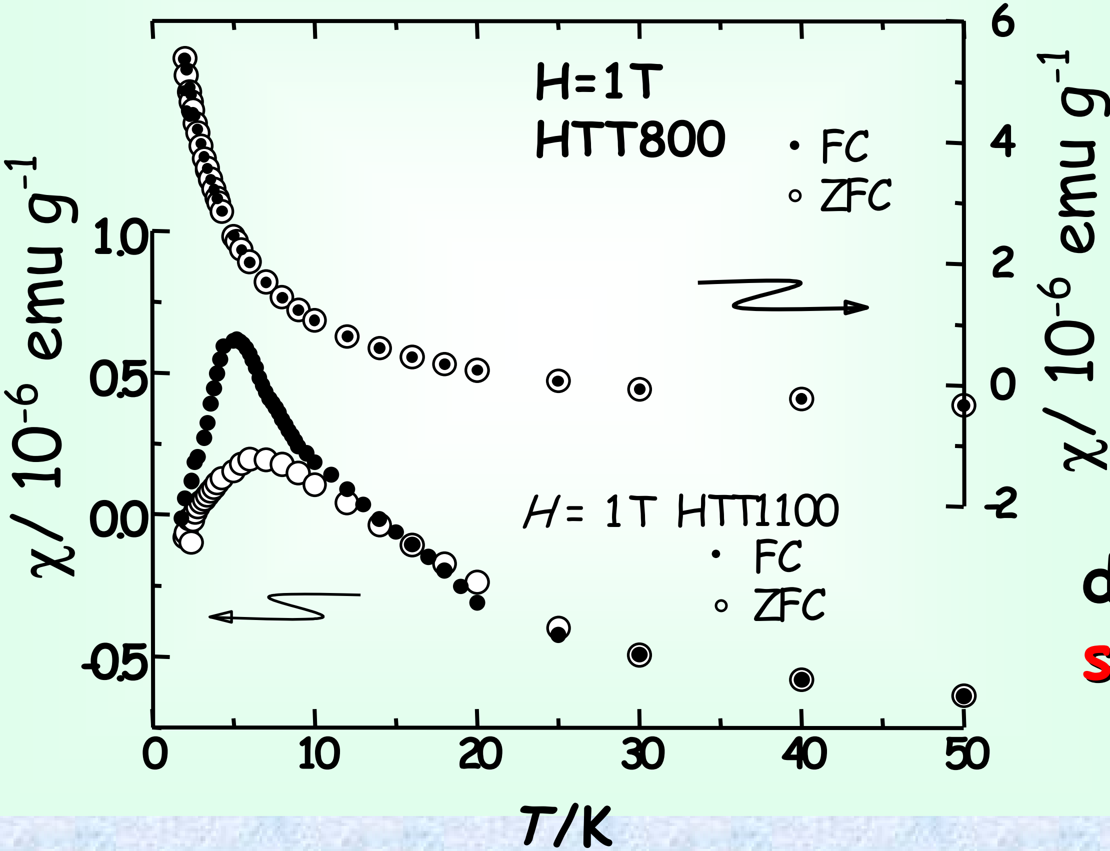

susceptibility peak ~ 7K

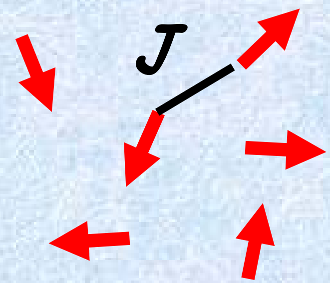
antiferromagnetic ordering?

negative Weiss temperature

# Field cooling effect

**large field cooling effect around the MI threshold**



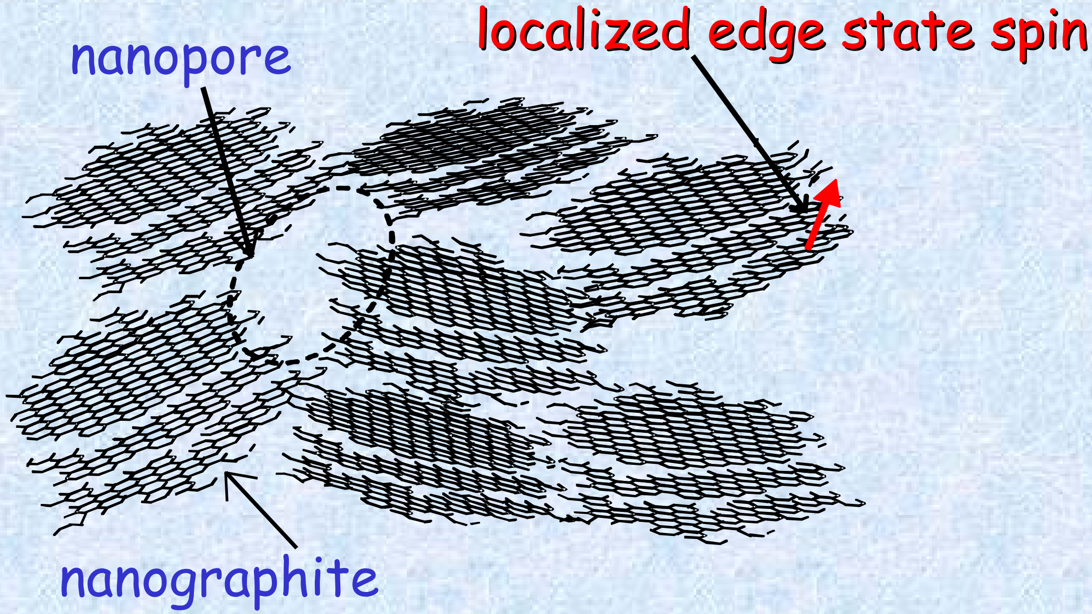




disordered magnetism

spin-glass-like behavior

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

# ACFs




# 3D random network of nanographite domains

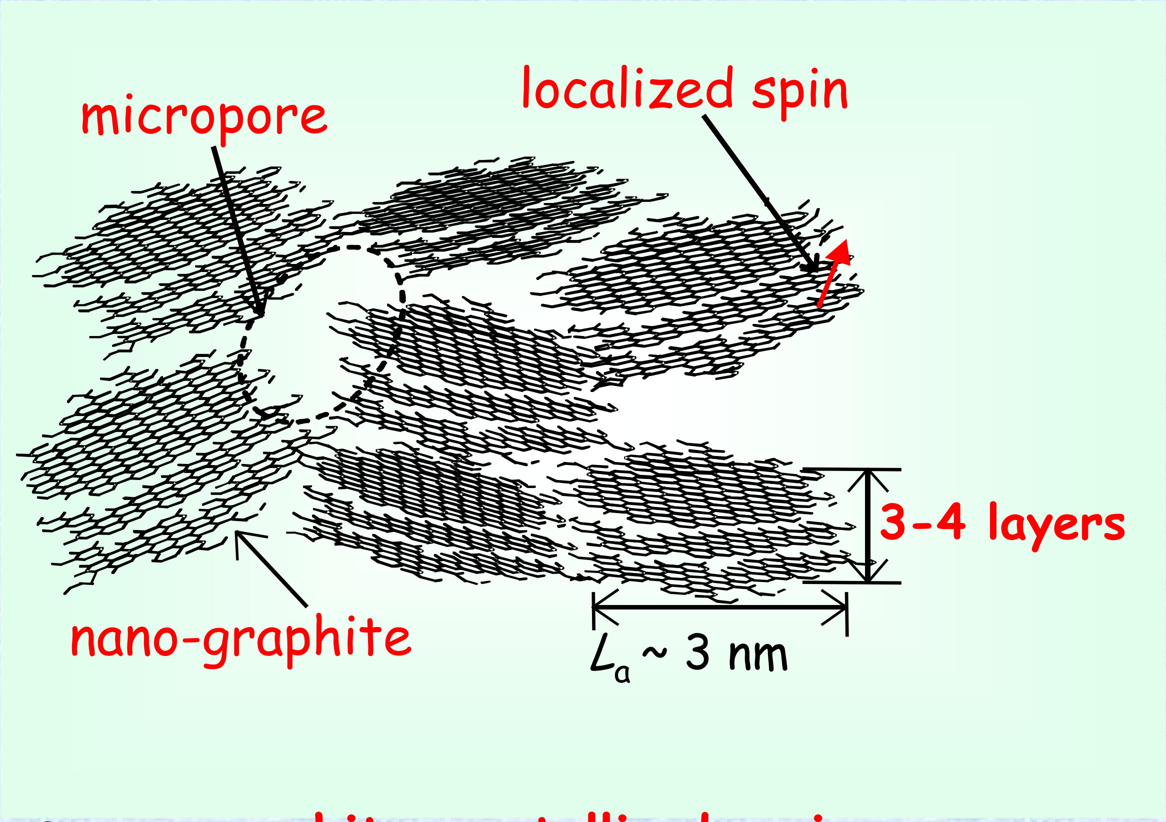
# nanopores

# edge-state spins

# Huge helium condensation in micropores

# Activated carbon fibers (ACF)

**3D random network of nanographites**




**edge spin probe**

◎ **nanographite; metallic domain**

**3-4 graphene sheets with in-plane size 2-3nm**

◎ **localized spins of edge origin** → several spins / nanographite

◎ **micropores** **~ 1-2nm, networked**

## ⟨Helium in micropores⟩

ACF; specific surface areas ~3000 $m^2/g$

☆ **gas adsorption**

He, Ne, Ar, $H_2$, $N_2$, $O_2$

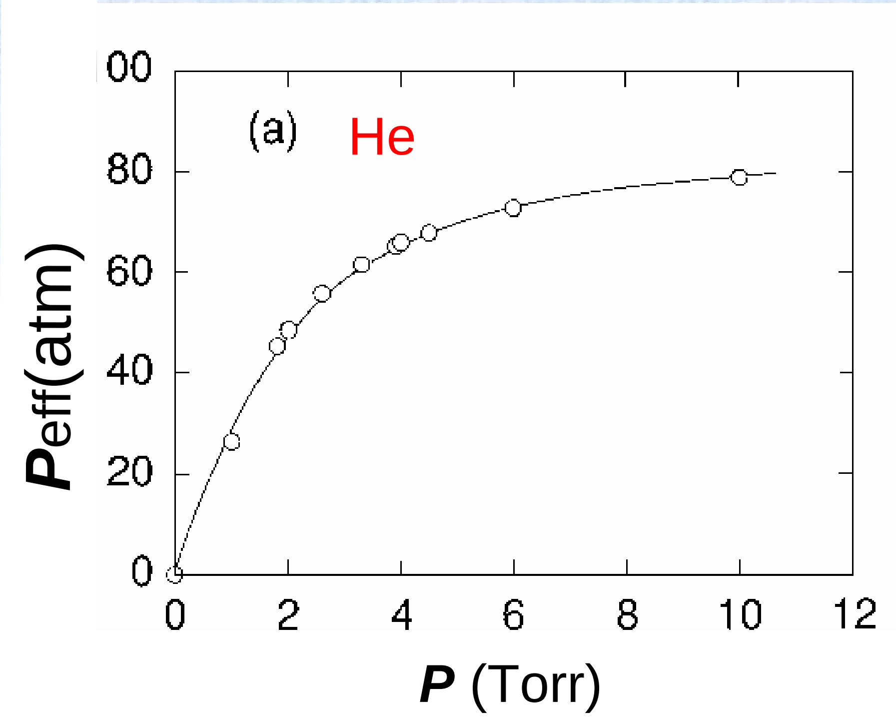
☆ **ESR spin-lattice relaxation**

saturation technique

**edge-localized spins**

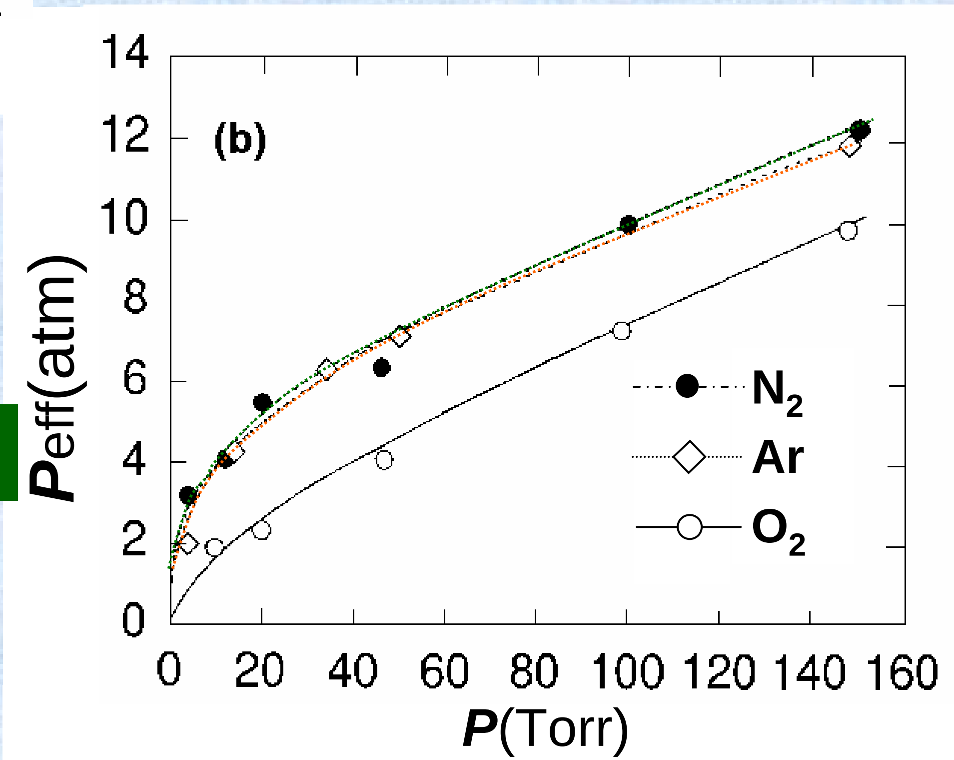
**probe for guest-host int.**

$$
\begin{tikzcd}
\hbar\omega \arrow[r] & \boxed{\text{spin system}} \arrow[d, "T_1"] \\
& \boxed{\text{lattice}}
\end{tikzcd}
$$




effective pressure in micropores at room temp.

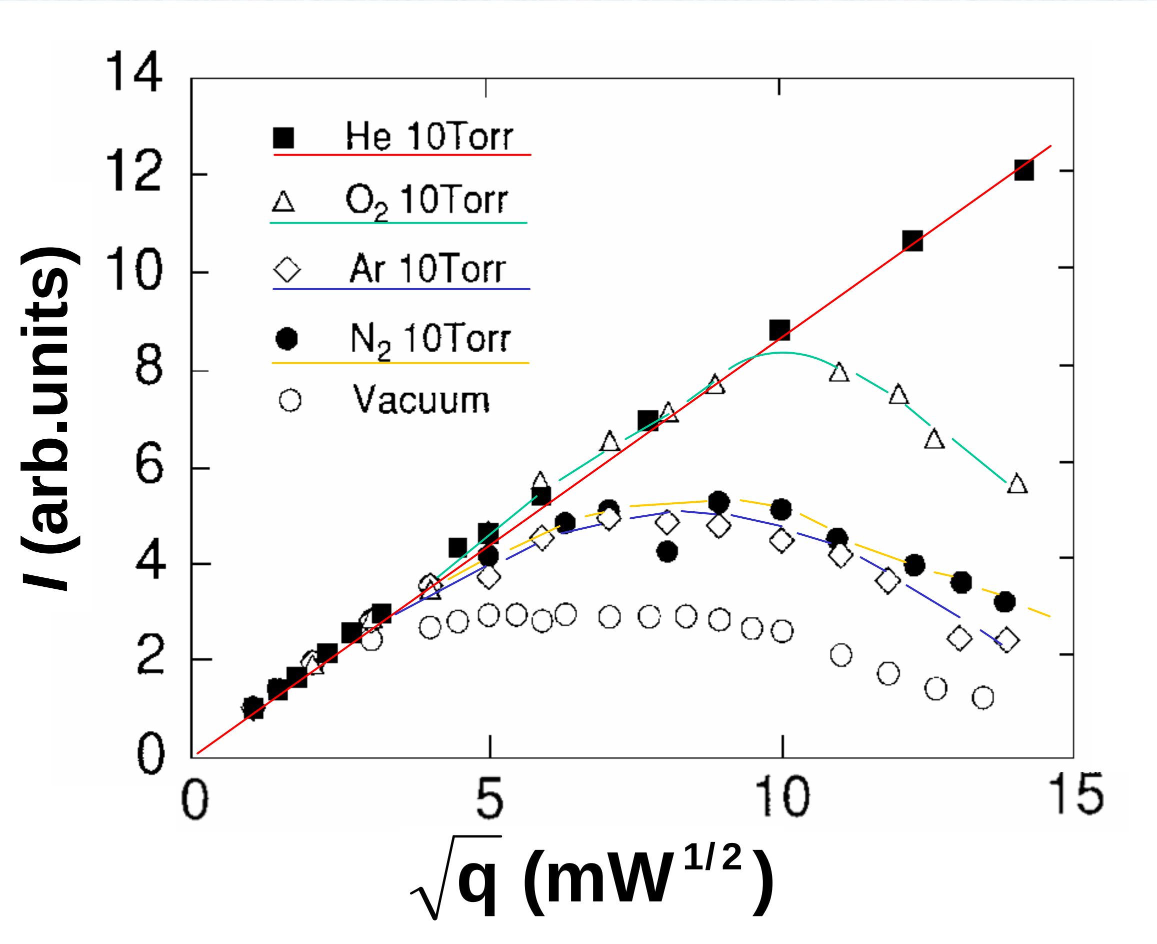
large condensation of guest gaseous species




extremely large condensation ~ $10^4$ times

He atom, exceptional nature

# ESR saturation curves with guest gases



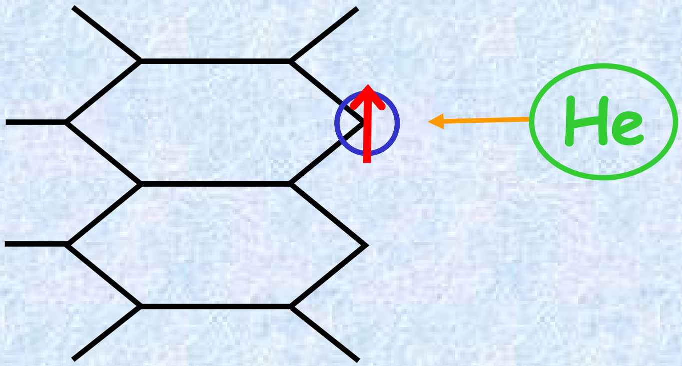

**independent of internal degree of freedom**

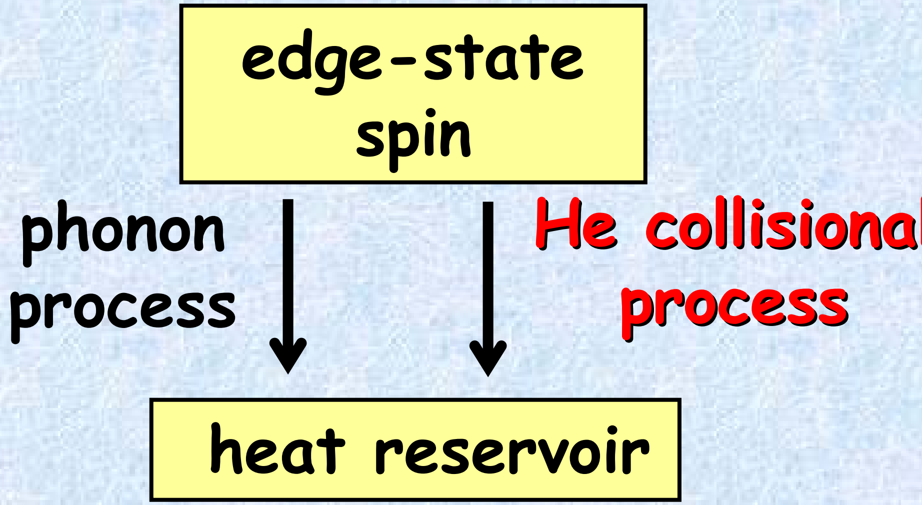
rotation / vibration

spin-lattice relaxation rate $T_1^{-1}$ is accelerated by gas uptake

**remarkable enhancement in He atmosphere**

# spin-lattice relaxation rate $T_1^{-1}$




electric dipole-dipole int
(van der Waals)

$$1/T_1 = n\sigma\upsilon$$

$n$: density of helium atoms

$\sigma$: cross section related to the spin-flop process

$\upsilon$: velocity of an He atom

$$\sqrt{\langle \upsilon^2 \rangle} = \sqrt{\frac{3RT}{M}}$$

$$1/T_1 \sim n\sqrt{T}$$

$$\frac{1}{T_1} = \frac{6.05}{9(2\pi)^{1/2}\hbar^4}\, n M^{3/2} \left(\frac{p}{\Delta E}\right)^2 \frac{\left(e^2 I J\right)^4}{R_0^{\,6}}\, w\left(k_B T\right)^{1/2}$$

$M$: mass of He atom, $R_o$: min.dist.(He atom and edge spin)

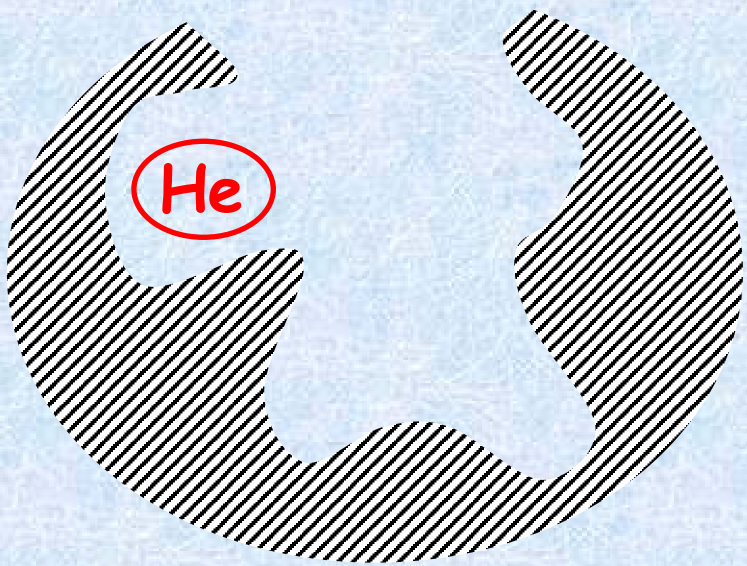
$\lambda$: spin-orbit int. of carbon p state, D: difference ( gr. and ex. states of C)

$\Delta E$: difference ($^1$P and $^1$S states of He atom)

$p = \lambda / \Delta$ $\quad I = \int \Psi_{1s}\Psi_{2pz} dr$ $\quad J = \int \Psi_{2s}\Psi_{2pz} dr$ $\quad \Psi$: He wave function

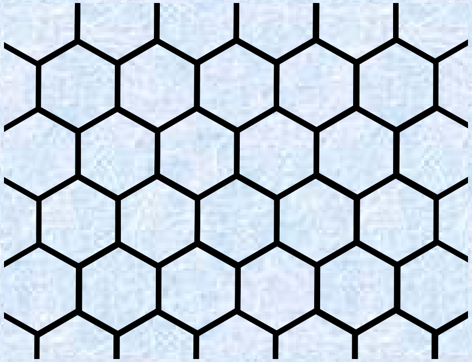
**helium atoms in activated carbon fibers**

- extremely large condensation at room temperature
- remarkable acceleration of $T_1^{-1}$




**He atom in ultra-micropore**

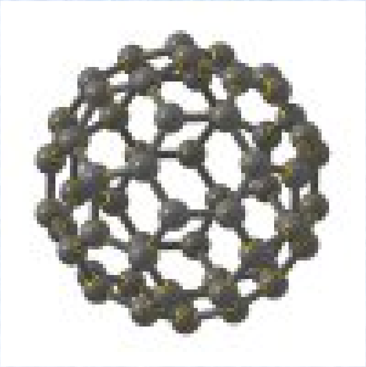
**enhanced interaction He-nanographite**



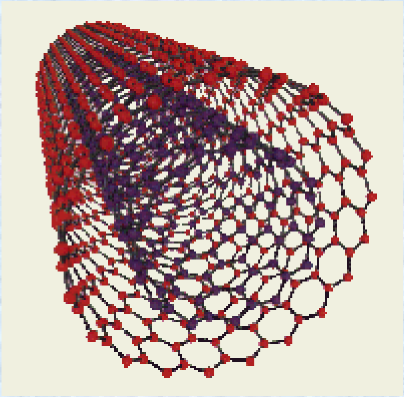
nano-graphite

aromatic molecules — bulk graphite

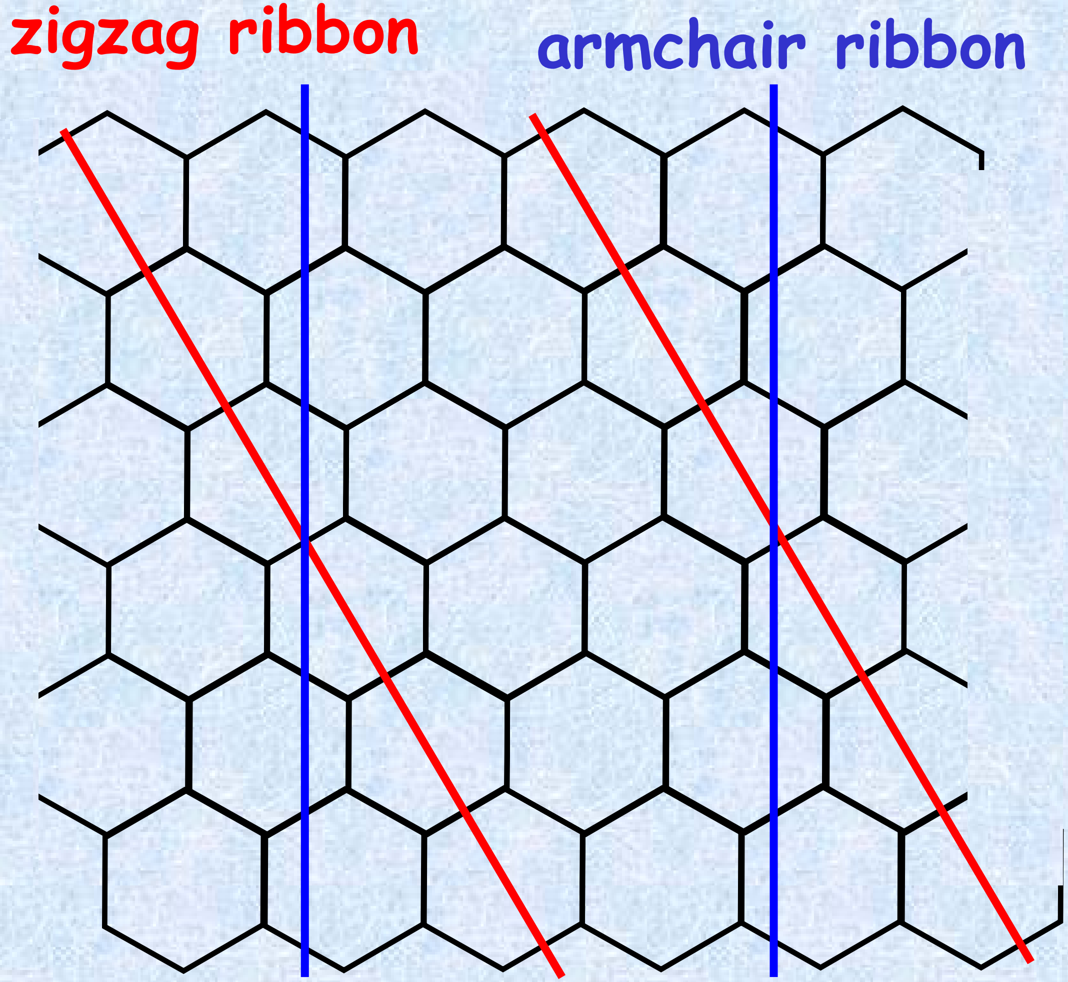
**nano-graphite π-electron system with open edges**



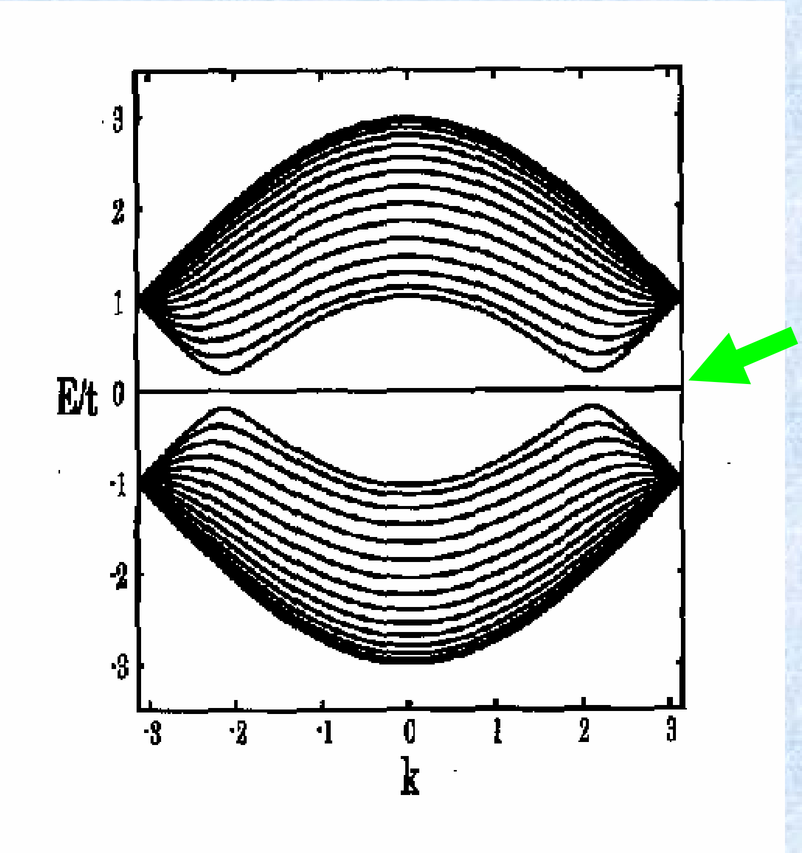
fullerenes
carbon nanotubes
closed π-electron system

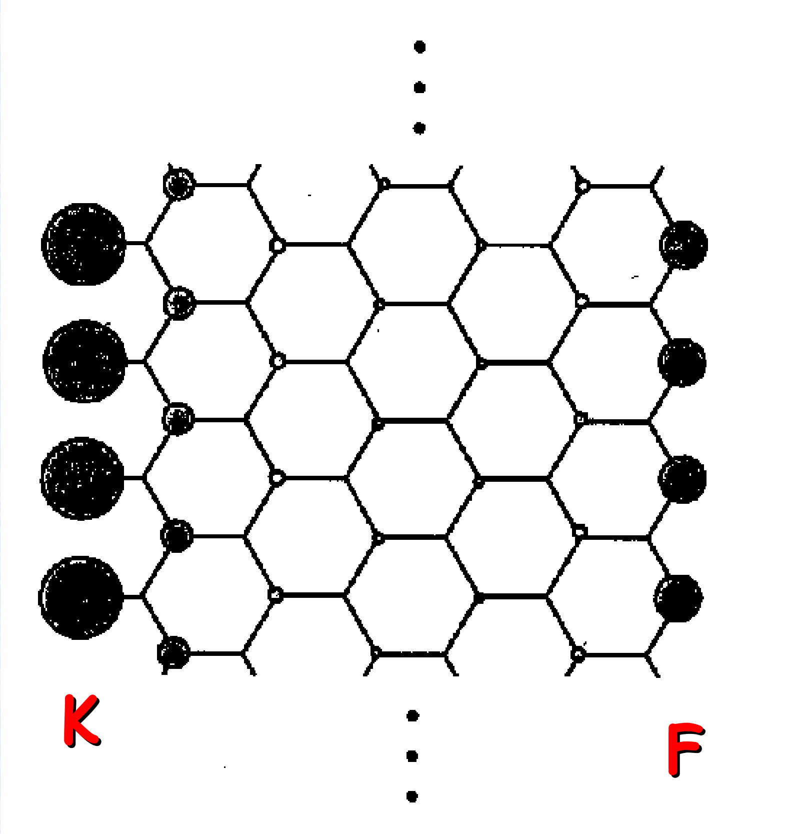


# Nanographene ribbon



# combination of Fujita's and Klein's edges



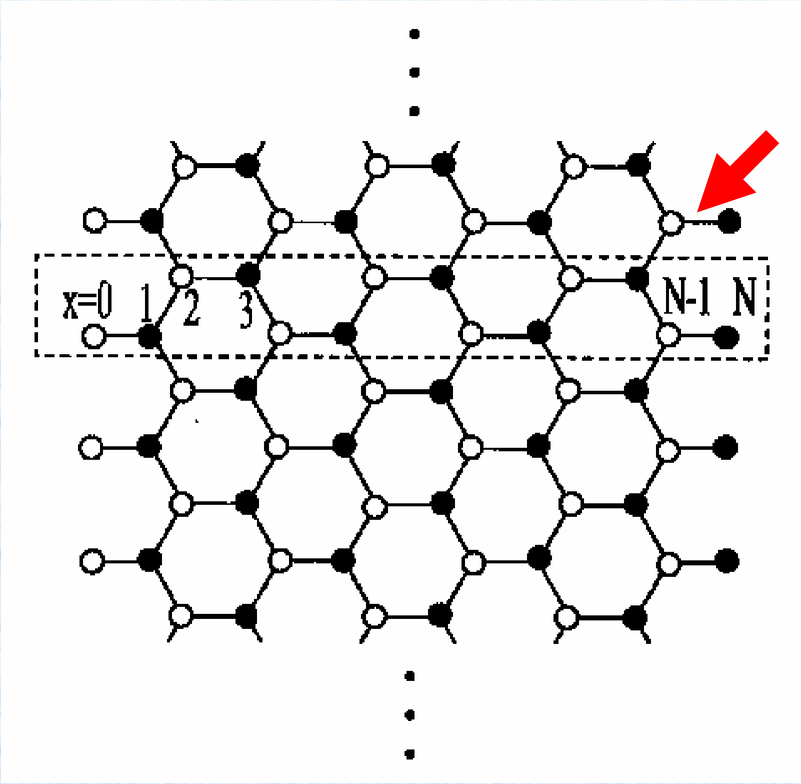

**completely localized edge state appears at $E_F$**

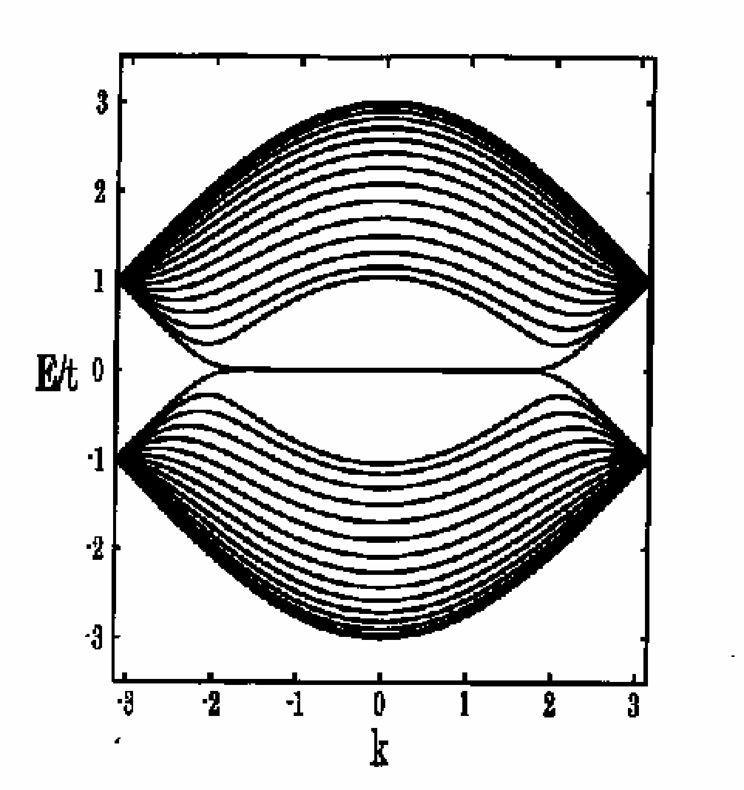
**nano-magnetism**

K. Kusakabe, et al. 2001

Klein edge

π-bond connected to the carbon atom at a zigzag edge

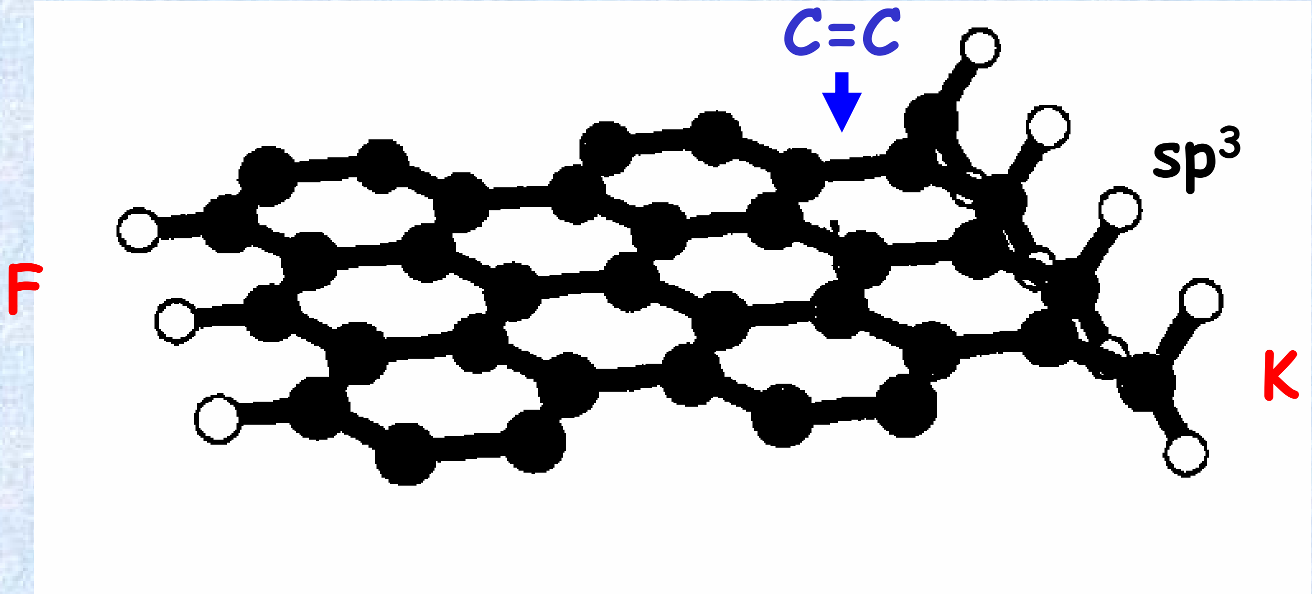



edge states with localized spins appear at $-2/3 \leqq k < 2/3$

K. Kusakabe, et al. 2001

# magnetic nanocarbons with Klein and Fujita edges




**nanocarbon-based ferromagnetism**

- F(or H)-terminated edge
- graphite-diamond interface

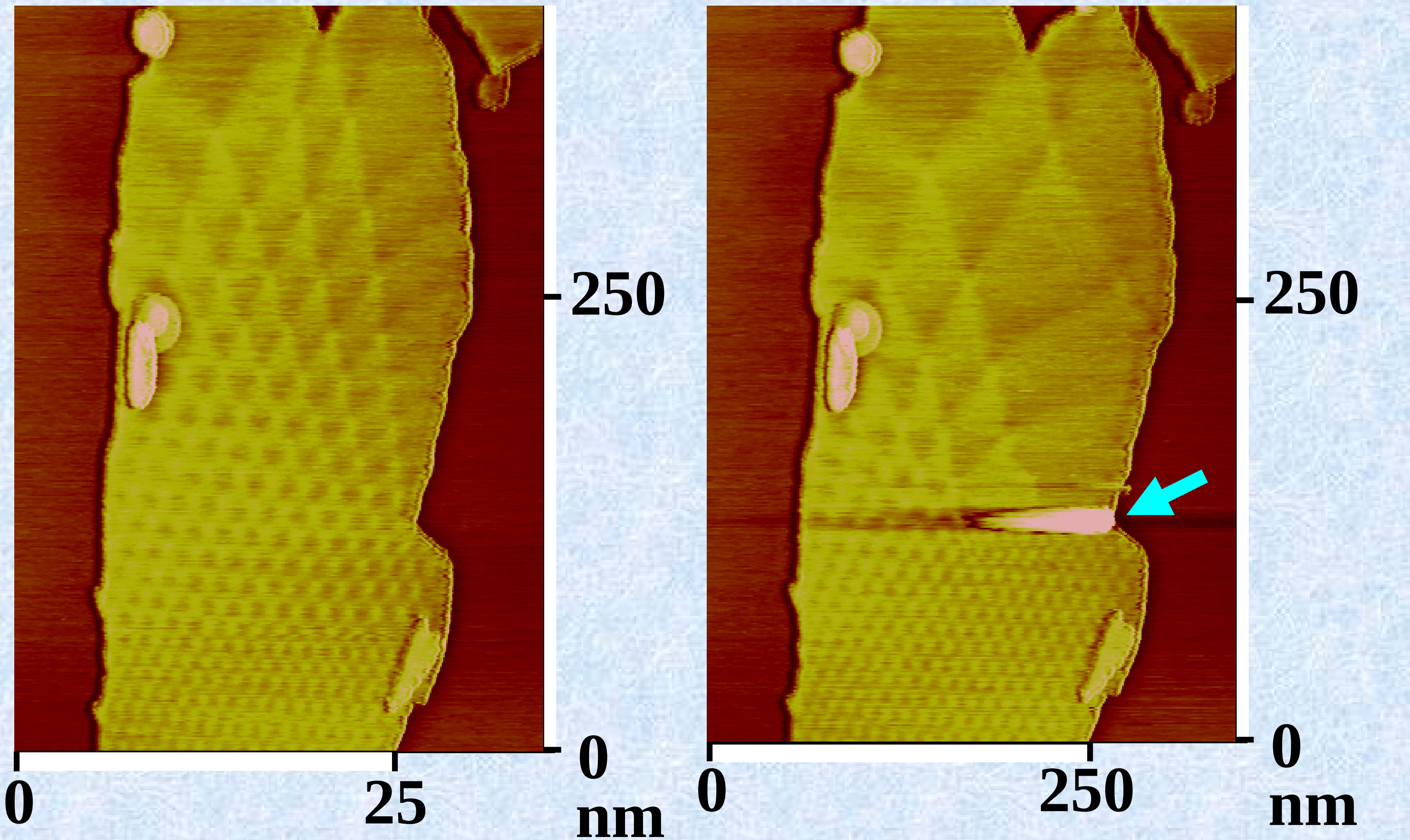
K. Kusakabe, et al. 2001

# Electron wave diffractions by STM

wave function **diffraction patterns** observed by **STM**

theoretical characterization

# Variations in diffraction period




V=200(mV)   I=0.7(nA)

**Diffraction patterns of electron waves**

graphene sheet

tilted with respect to the substrate

**potential gradient on the graphene plane**

free electron model

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)+V_{\mathrm{well}}(x)-F\cdot y\right]\psi(x,y)=E\psi(x,y)$$

linear potential

# Electron density by the k· p model

Hamiltonian around K-point

$$H = \begin{pmatrix} -F \cdot y & -i\gamma\frac{\partial}{\partial x} - \gamma\frac{\partial}{\partial y} \\ -i\gamma\frac{\partial}{\partial x} + \gamma\frac{\partial}{\partial y} & -F \cdot y \end{pmatrix}$$

linear potential

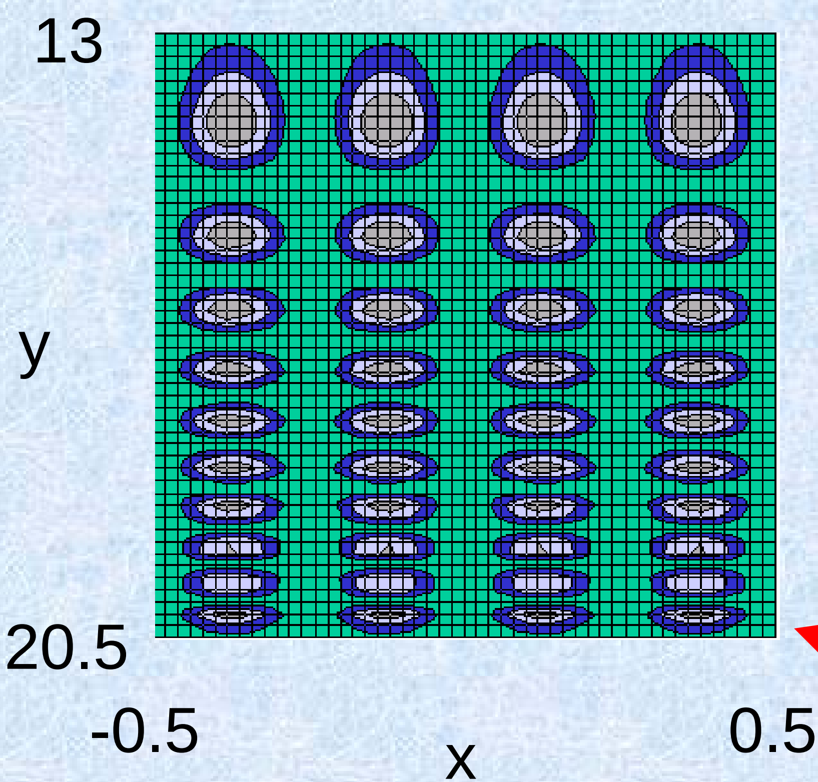
Solution with the infinite well

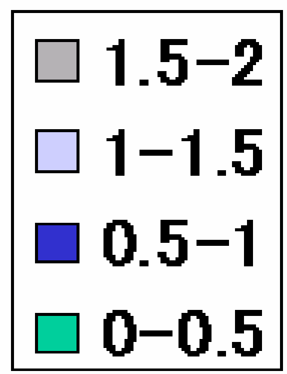
$$\Psi = 2A \begin{pmatrix} \sin\left(\frac{E_n x}{\gamma}\right) \sin\left[\frac{1}{\gamma}\left(\tilde{E}y + \frac{1}{2}Fy^2\right)\right] \\ -i\cos\left(\frac{E_n x}{\gamma}\right) \cos\left[\frac{1}{\gamma}\left(\tilde{E}y + \frac{1}{2}Fy^2\right)\right] \end{pmatrix}$$

electron density at the A-sublattice

$$|\psi_A(\boldsymbol{R}_A)|^2 = 4A^2 \sin^2\left(\frac{n\pi x}{d}\right) \times \left\{1 + \cos[(\boldsymbol{K} - \boldsymbol{K}') \cdot \boldsymbol{R}_A - \eta] \sin\left[\frac{2}{\gamma}\left(\tilde{E}y + \frac{1}{2}Fy^2\right)\right]\right\}$$

envelope function as a long range component




Local density of states

$$\sin^2\left(\frac{n\pi x}{d}\right)\left[\text{const.} + \sin\left(\frac{Fy^2}{\gamma} - \frac{2n\pi}{d}y\right)\right]$$

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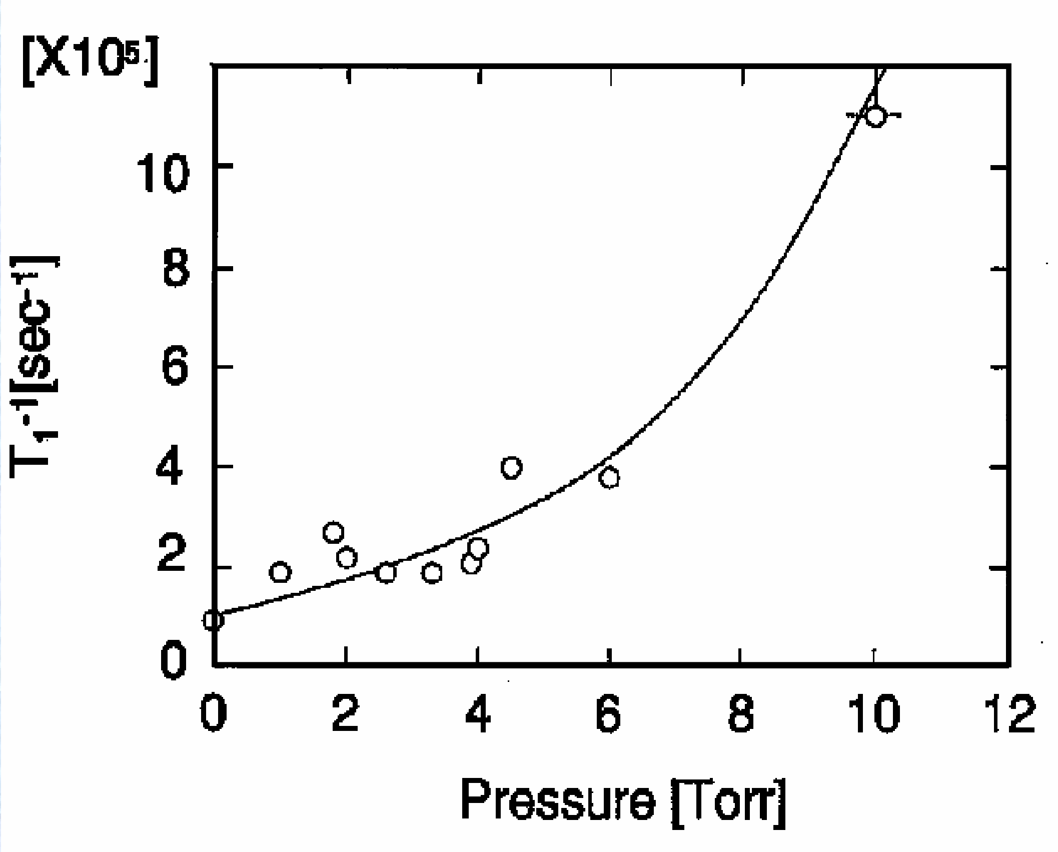
# He pressure dependence of spin-lattice relaxation rate at room temperature




**enhancement of $T_1^{-1}$**

**collisional process of He atom**

# Present talk

## # Nano-graphite

heat treatment of nano-diamond at 1600°C

electrophoretic technique

☆ single nano-graphene sheet

☆ electronic structure

## # Nano-graphite network

activated carbon fibers (ACF)

☆ Coulomb blockade effect

☆ spin-glass

## # Controllable nanoscopic magnetism

water-adsorption induced magnetic switch