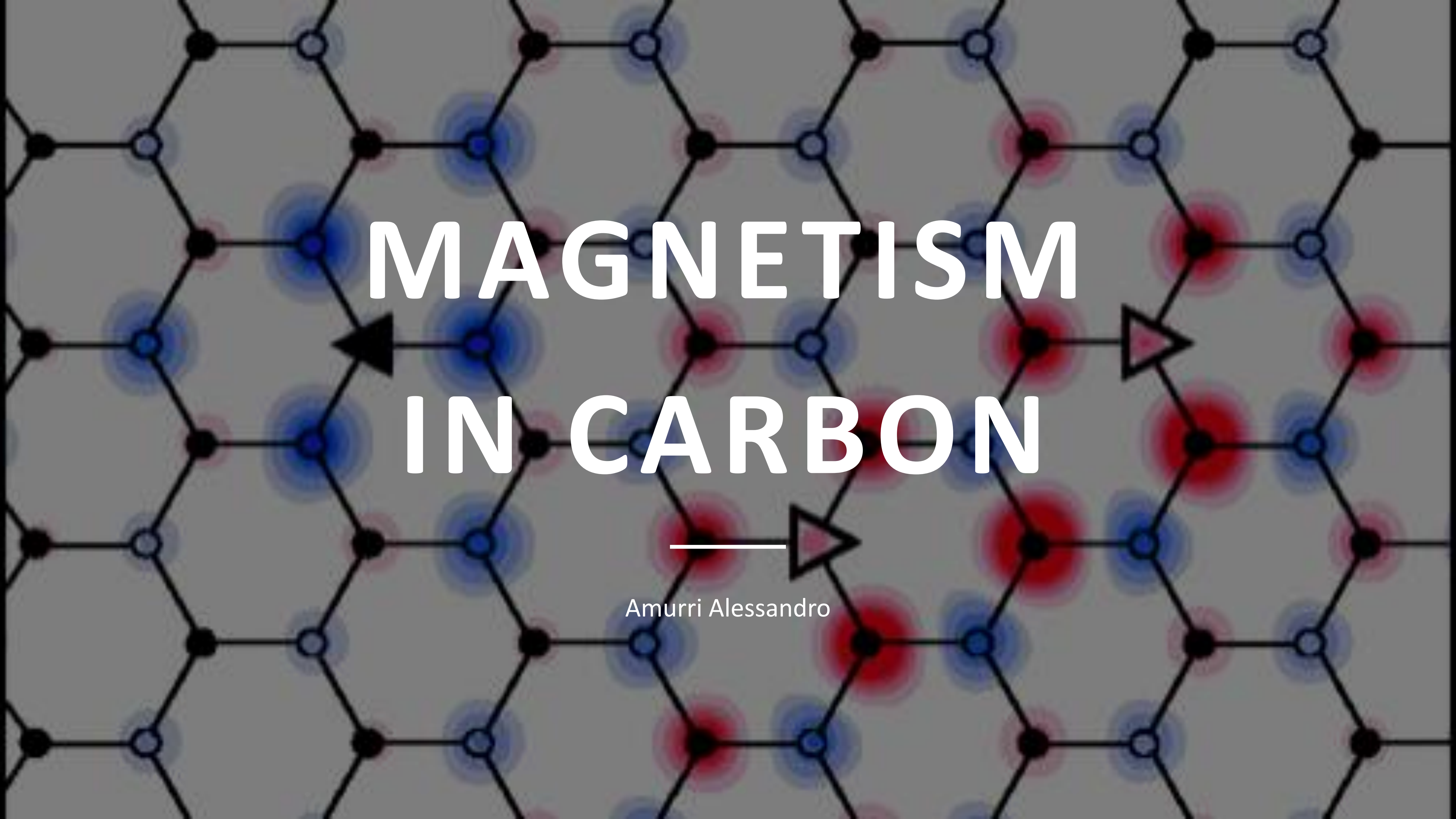


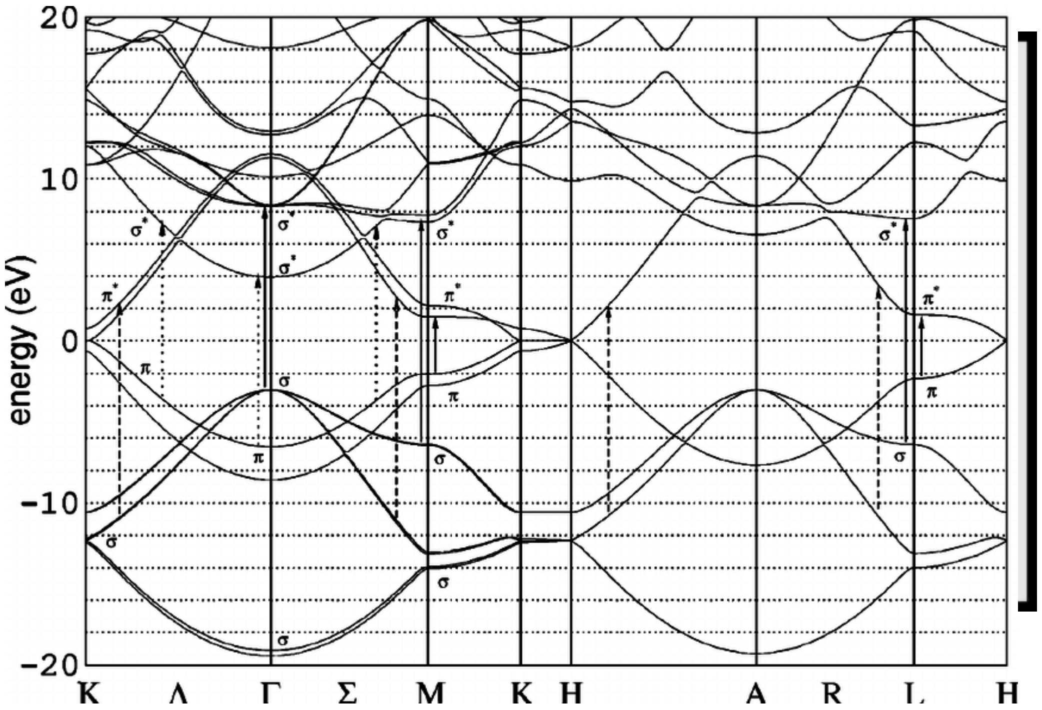
MAGNETISM IN CARBON

Amurri Alessandro

INTRODUCTION

INGREDIENTS FOR MAGNETISM

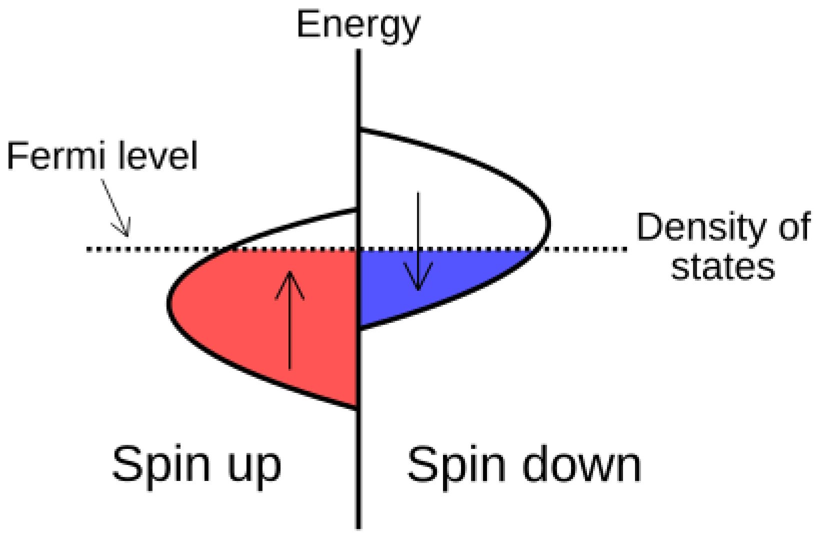
- Conventional magnetism: d and f elements
- Partially filled and localized orbitals
- Strong exchange
- Broken spin degeneracy
- In graphite and graphene no unpaired electrons
- Strong overlap of orbitals
- No exchange
- Low DOS at Fermi level



MARINOPOULOS, AG. et al. 2004 PHYSICAL REVIEW B

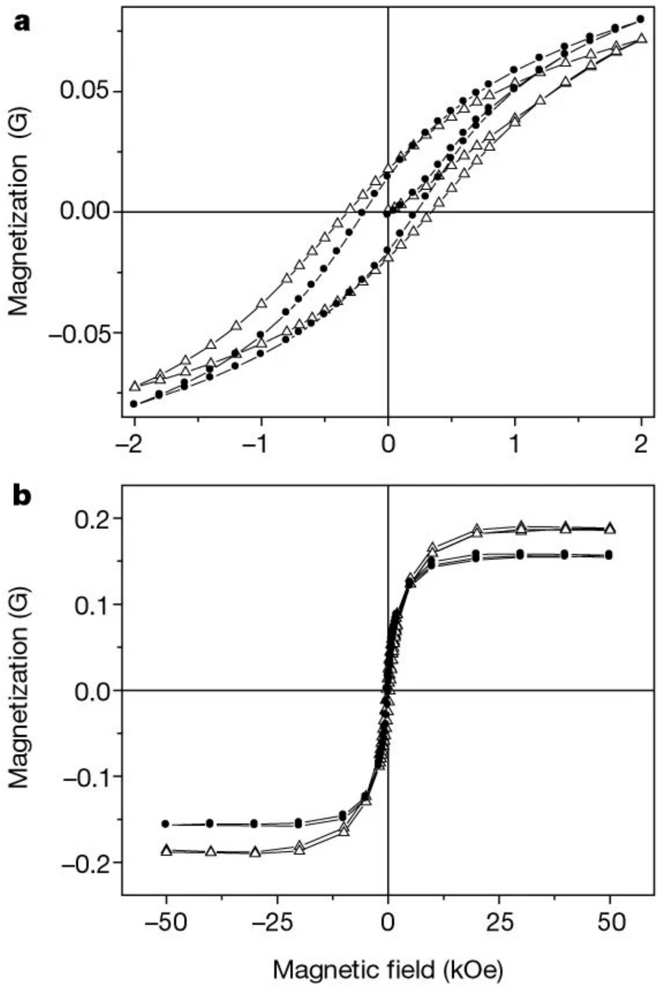
WHEN CAN P ELEMENTS BE MAGNETIC?

- Delocalized p electrons → no magnetism
- Defects can induce a localization of π states
- Localization + electron-electron interaction →unpaired spins
- Broken symmetry lifts spin degeneracy
- High DOS at Fermi level



FIRST (CONTROVERTIAL) EVIDENCE

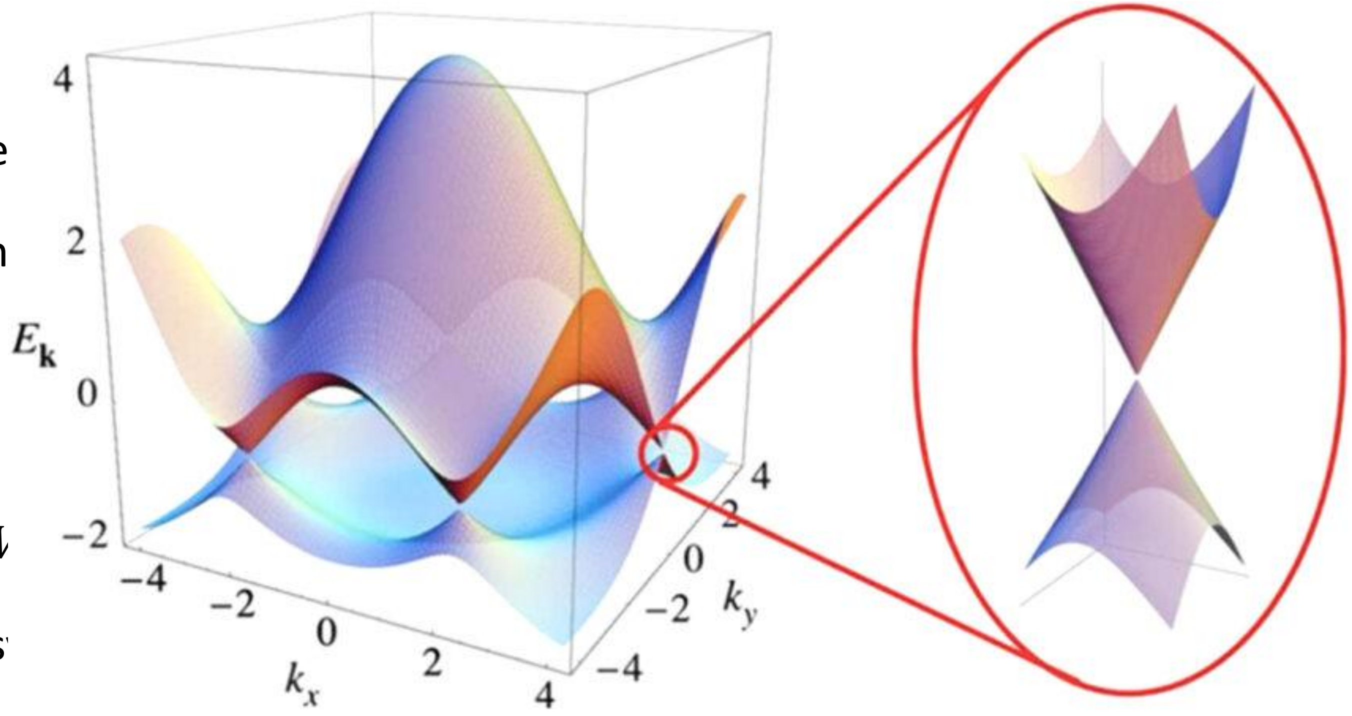
- 2001 – Makarova et al., “Magnetic carbon” (Nature)
  - Claimed RT ferromagntism in polymerized fullerenes
- The article was retracted
- Sparked interest in magnetism in carbon
- New evidences of defect-induced magnetism



T.L. Makarova et al. Nat. (2006) 413(6857)

THEORY

THEORETICAL FRAMEWORK



- $\mathcal{H}_0$: first ne
- Only π-sym
- $t \simeq -2{,}7eV$
- Half-filled s
- $\mathcal{H}_0$ exhibits electron-hole symmetry

THEORETICAL FRAMEWORK

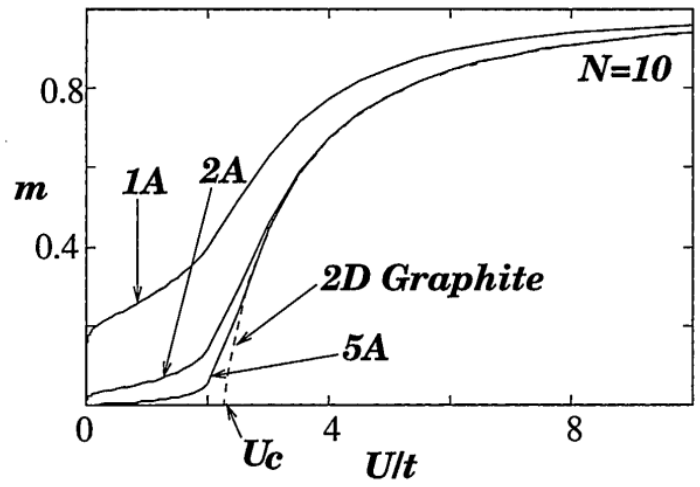
$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' = -t \sum_{\langle i,j\rangle,\sigma} \left[c_{i\sigma}^{\dagger} c_{j\sigma} + h.c.\right] + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

- $\mathcal{H}'$: on-site Coulomb interactions between electrons
- $U > 0$: Coulomb repulsion parameter of π-electrons
- Mean-field approximation is used

$$\mathcal{H}'_{mf} = U \sum_{i} [n_{i\uparrow}\langle n_{i\downarrow}\rangle + n_{i\downarrow}\langle n_{i\uparrow}\rangle - \langle n_{i\uparrow}\rangle\langle n_{i\downarrow}\rangle]$$

THEORETICAL FRAMEWORK

- Self-consistent solution $M_i = \frac{\langle n_{i\uparrow}\rangle - \langle n_{i\downarrow}\rangle}{2} \rightarrow S = \sum_i M_i$
- The solution is controlled by the ratio U/t



M. Fujita et al. J. Phys. Soc. Jpn (1996) Vol 65, No. 7

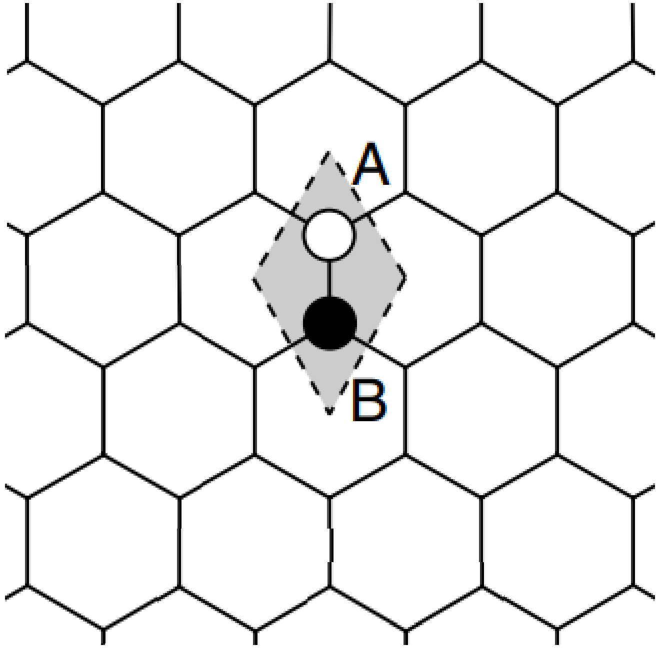
THEORETICAL FRAMEWORK: COUNTING RULES

- From honeycomb lattice (benzenoid) group theory the number of zero energy states (ZES) is

$$\eta = 2\alpha - N$$

- Stoner criterion controls the onset of magnetism $U\rho(E_f) > 1$
- Lieb's theorem determins the total spin

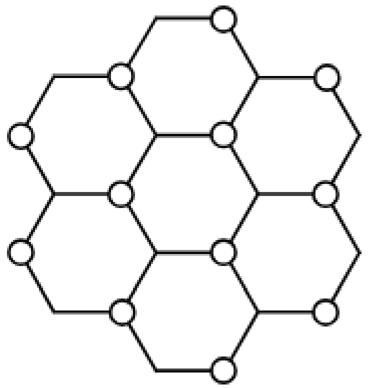
$$S = \frac{1}{2}|N_A - N_B|$$



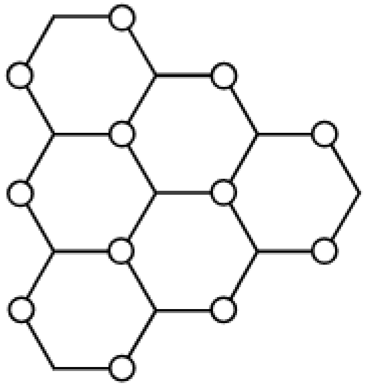
Yazyev O V Rep. Prog. Phys. 73 (2010) 056501

THEORETICAL EXAMPLE: FINITE FRAGMENTS

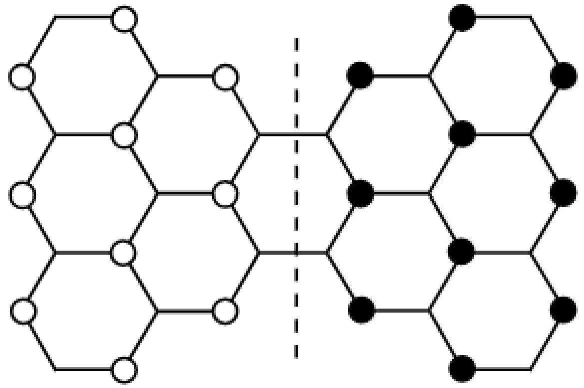
- Hexagonal finite gaphene fragments



corenene



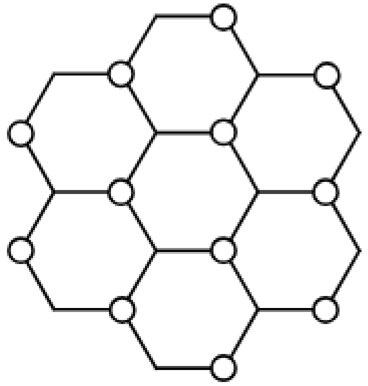
triangulane



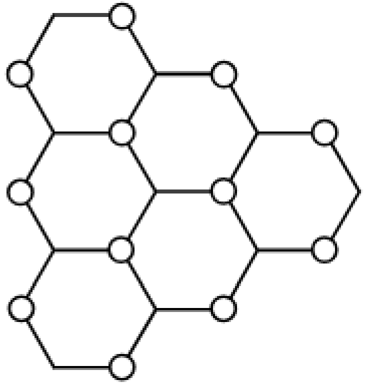
bow-tie

Yazyev O V Rep. Prog. Phys. 73 (2010) 056501

THEORETICAL EXAMPLE: FINITE FRAGMENTS



$$N_A = N_B = 12$$
$$\alpha = 12$$
$$\eta = 0$$
S=0



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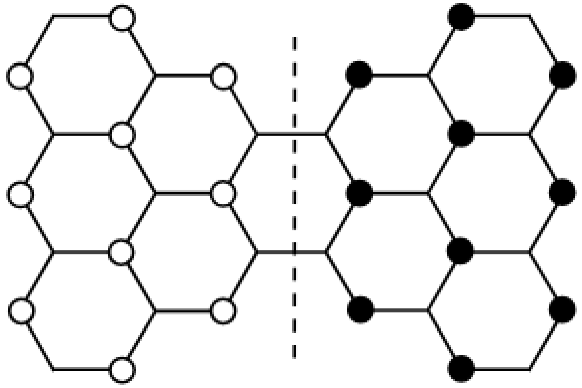

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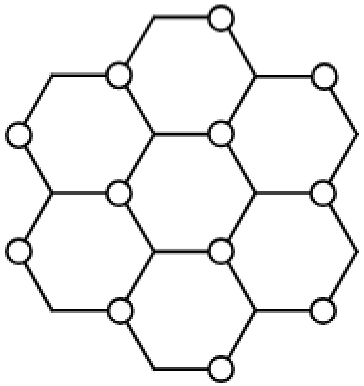
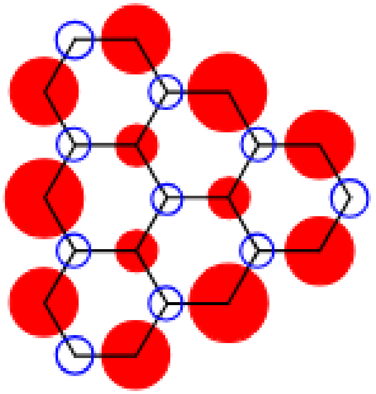
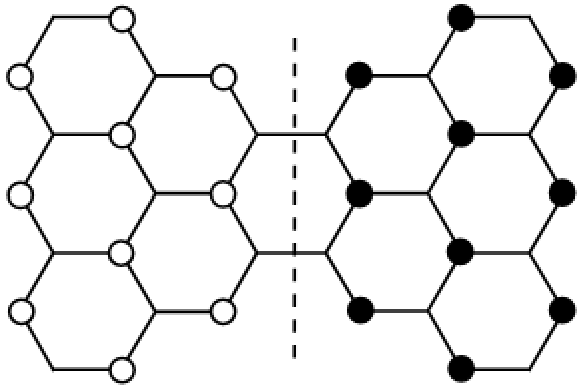
THEORETICAL EXAMPLE: FINITE FRAGMENTS



corenene



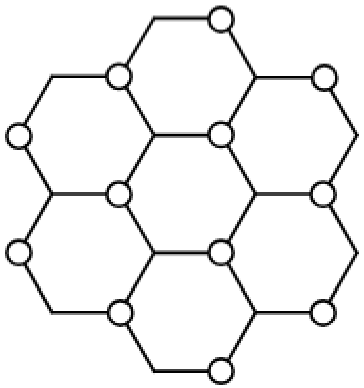
$$N_A - N_B = 2$$
$$\alpha = 12$$
$$\eta = 2$$
$$S = 1$$
$$m = 2\mu_B$$



bow-tie

Yazyev O V Rep. Prog. Phys. 73 (2010) 056501

THEORETICAL EXAMPLE:FINITE FRAGMENTS



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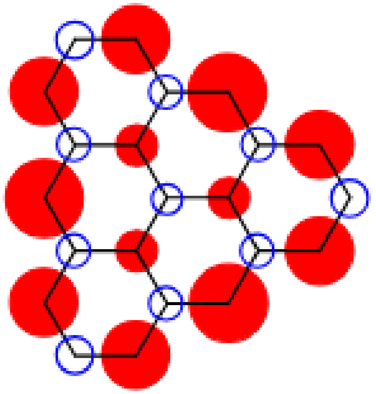
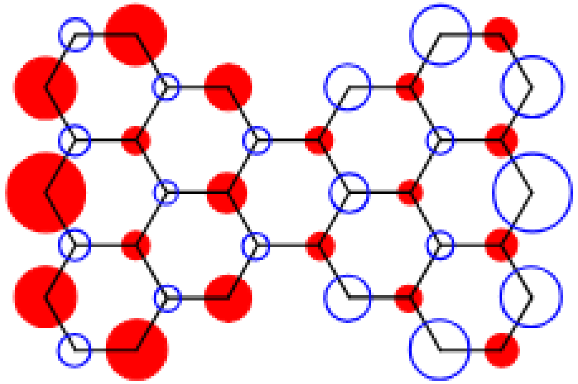


triangulane



$$N_A = N_B = 19$$
$$\alpha = 20$$
$$\eta = 2$$
$$S = 0$$

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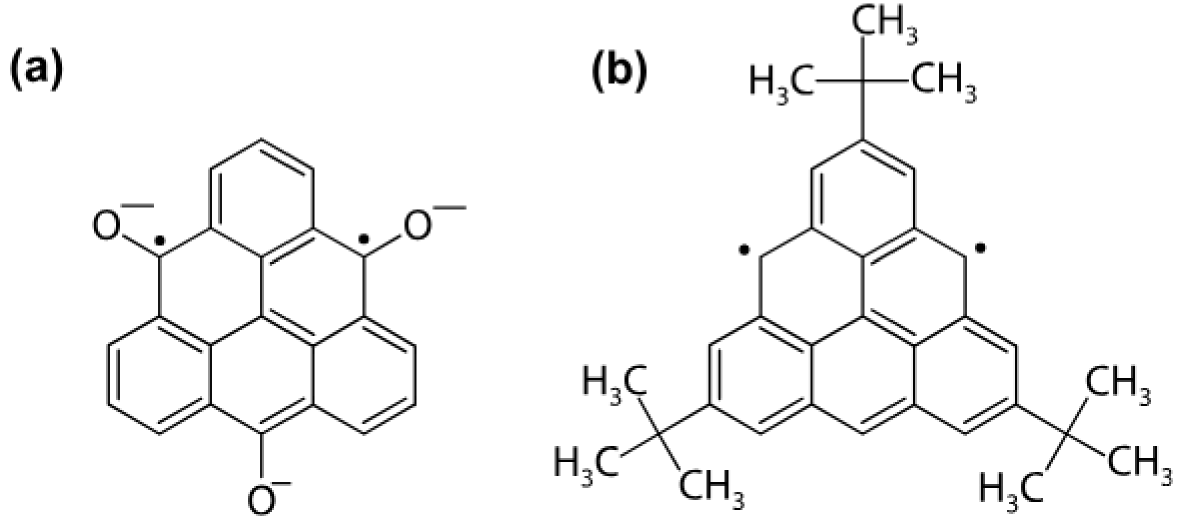
THEORETICAL EXAMPLE:FINITE FRAGMENTS

- Attempts to synthesize these molecule failed

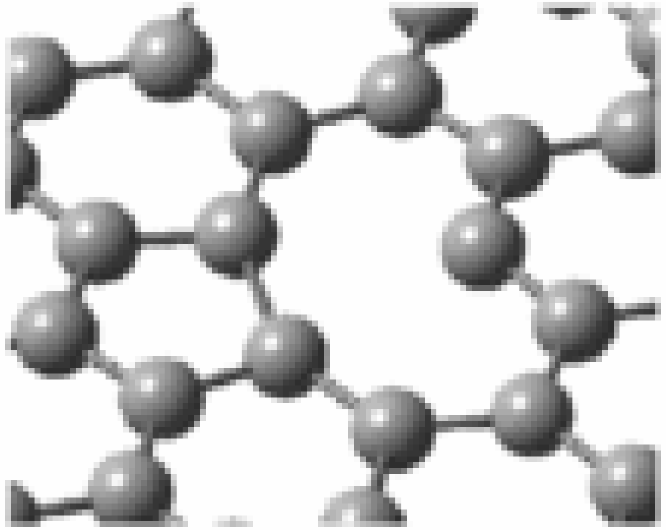


Yazyev O V Rep. Prog. Phys. 73 (2010) 056501

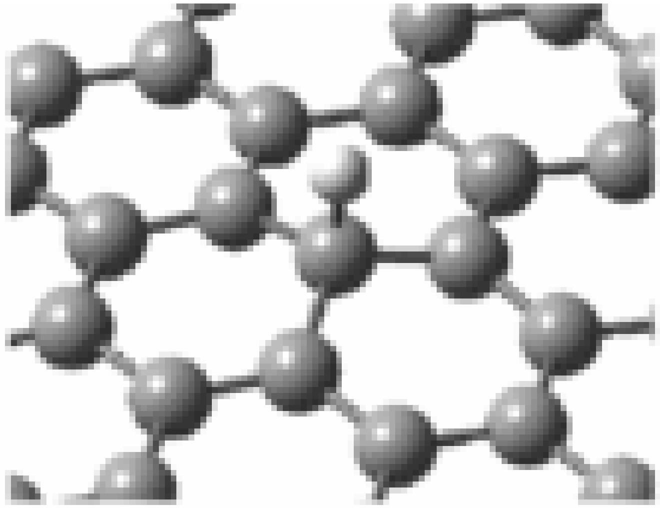
DEFECTS INDUCED MAGNETISM

- Imbalance in sublattices leads to magnetism $N_I \equiv |N_A - N_B| \geq 0$
- Simple defects in graphene

VACANCY



HYDROGEN CHEMISORPTION



Yazyev O V 2008b Phys. Rev. Lett. 101 037203

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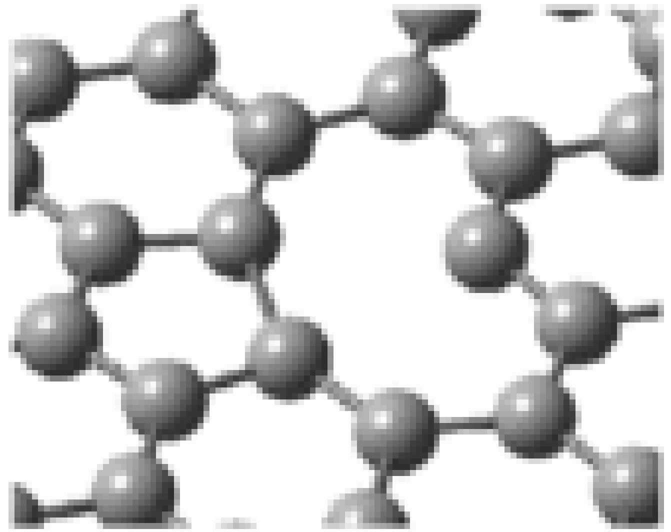

- One carbon is removed
- A dangling bond is unsaturated
- Jahn-Teller distortion
- Inbalance in the sublattices

Yazyev O V 2008b Phys. Rev. Lett. 101 037203

DEFECTS INDUCED MAGNETISM

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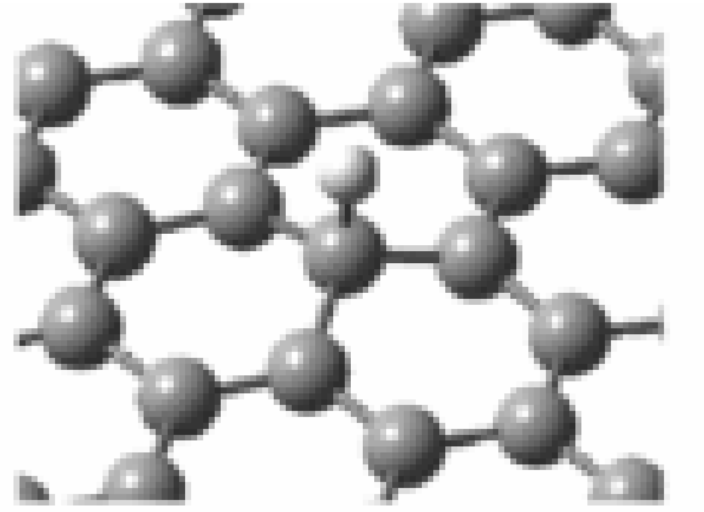
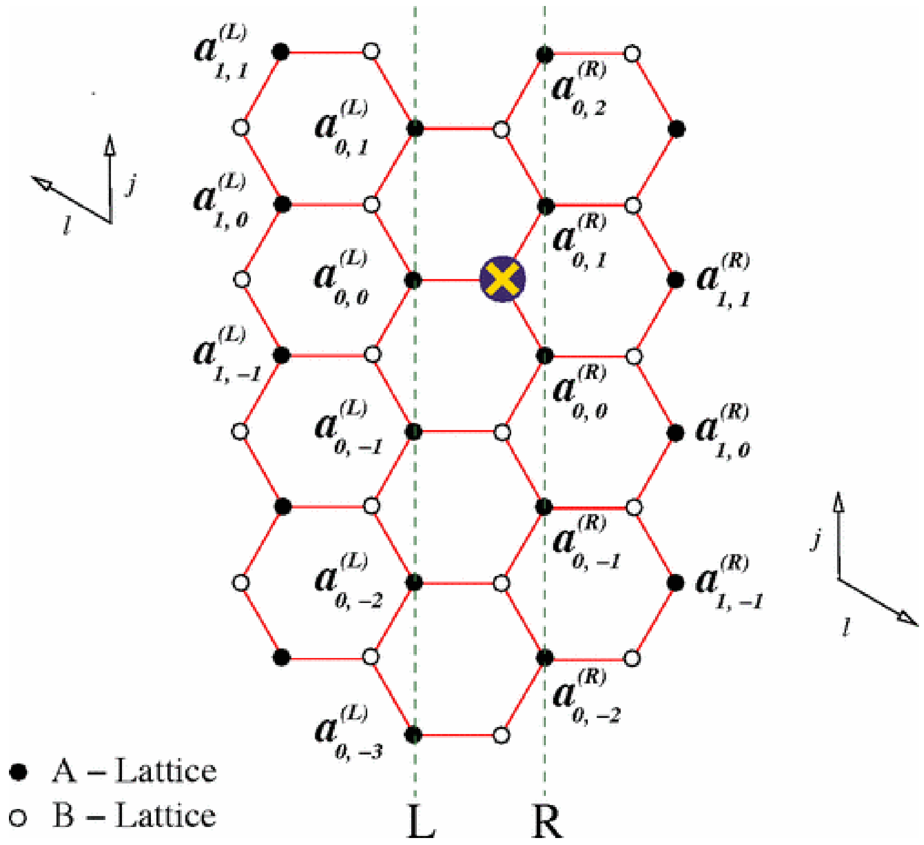
HYDROGEN CHEMISORPTION



- Hydrogenated carbon: $sp^2 \rightarrow sp^3$
- Removal of the p_z orbital
- Protrusion of the carbon
- Acts like a vacancy

Yazyev O V 2008b Phys. Rev. Lett. 101 037203

QUASI-LOCALISED STATES NEAR VACANCIES

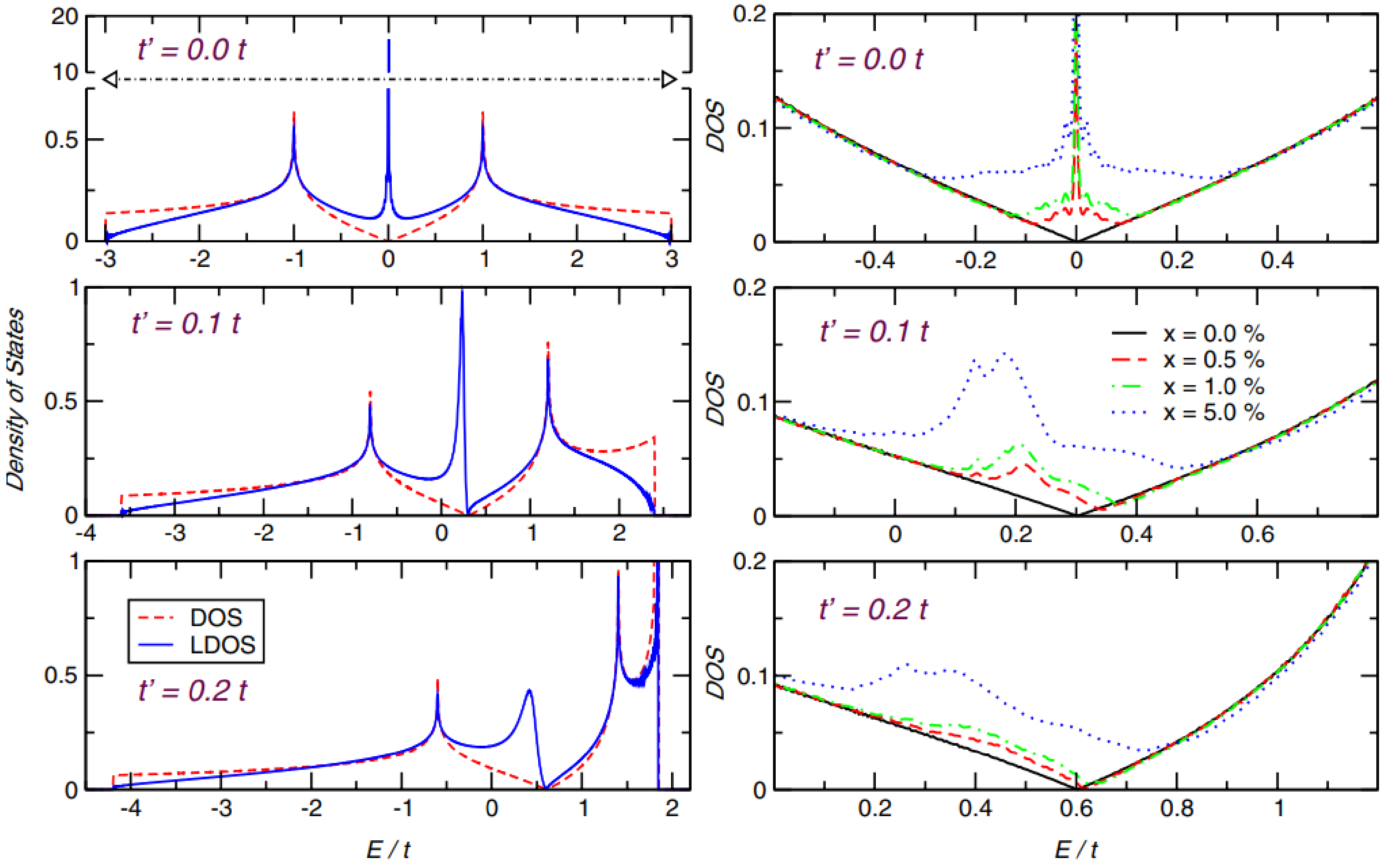


$$\mathcal{H} = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j - t' \sum_{\langle\langle i,j \rangle\rangle} c_i^\dagger c_j + h.c.$$

- t' is the next-nearest-neighbour hopping enegy
- ZES are found
- $\Psi_{ZES}(r)$ is quasi-localised
- Power low decay: $\Psi_{ZES}(r) \propto 1/r$

V. M. Pereira et al. Phys. Rev. Lett.96, 036801 (2006).

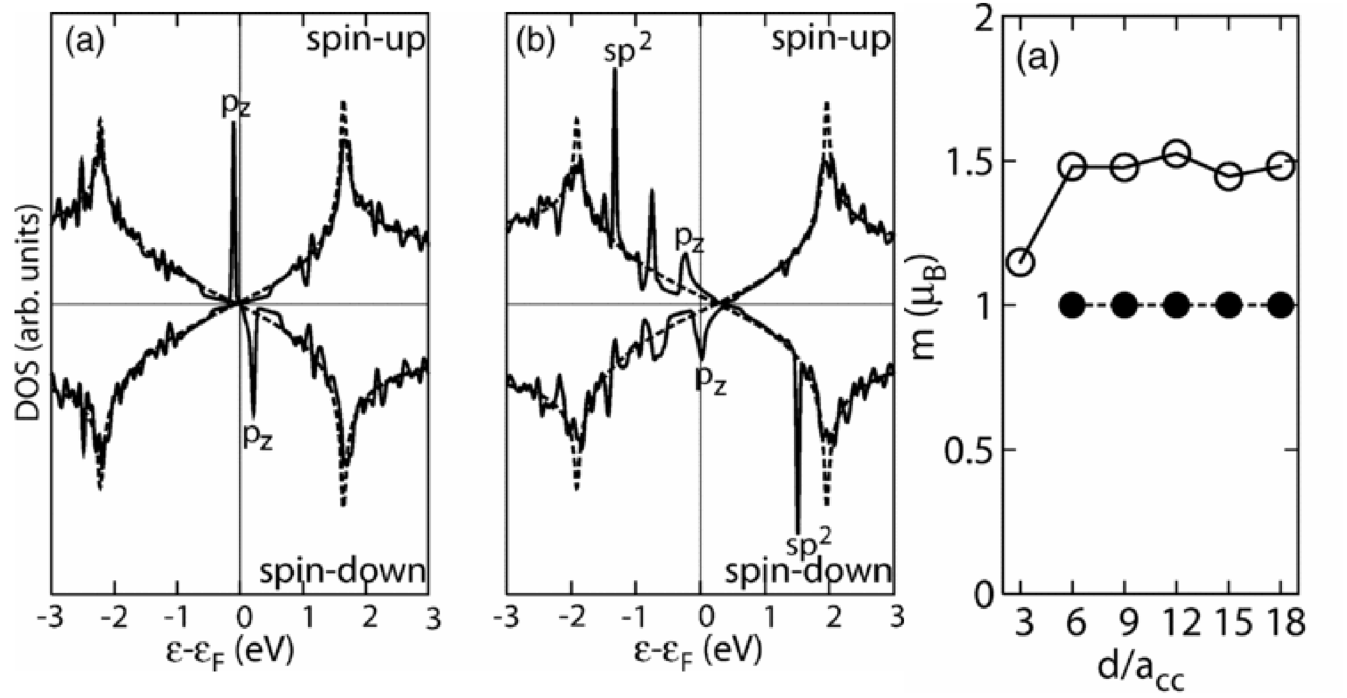
LDOS OF QUASI-LOCALISED STATES



V. M. Pereira et al. Phys. Rev. Lett.96, 036801 (2006).

ONSET OF MAGNETISM

- DFT calculations on a periodical 2D superlattice of defects
- Magnetism from both chemisorption and vacancies



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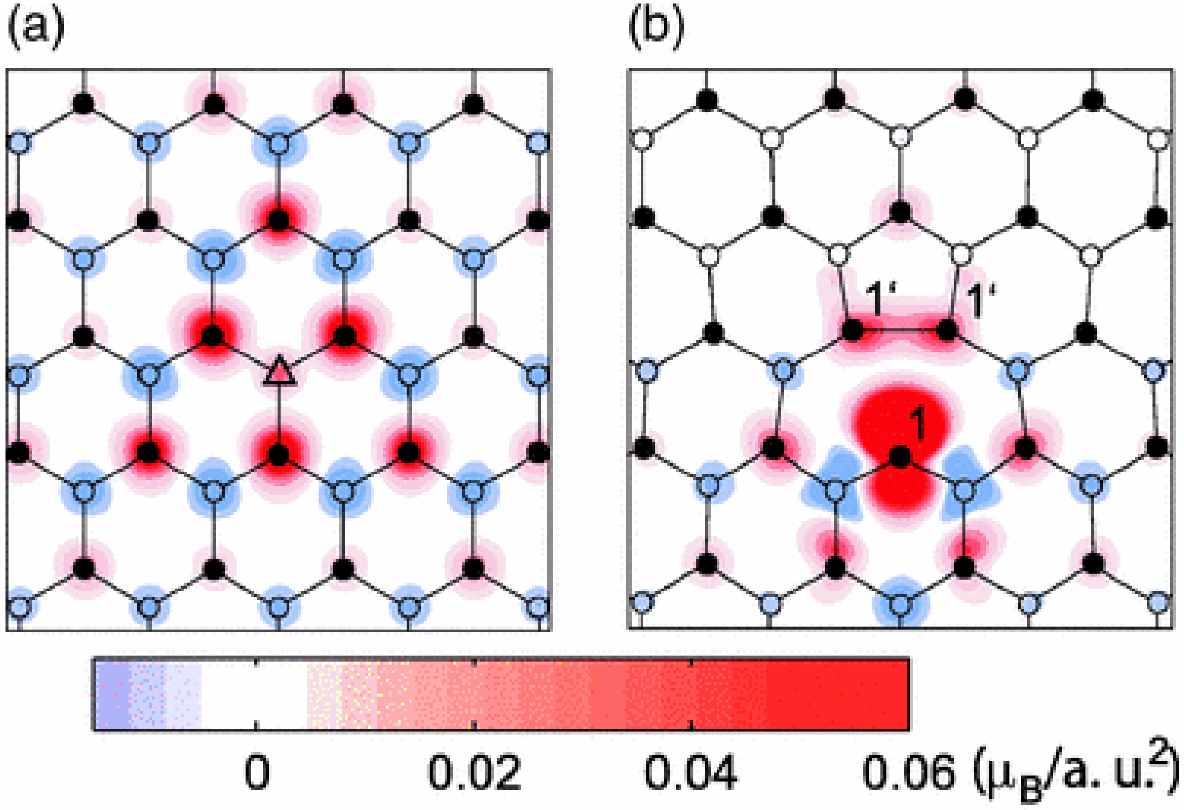
ONSET OF MAGNETISM

- Spin distribution near the defects



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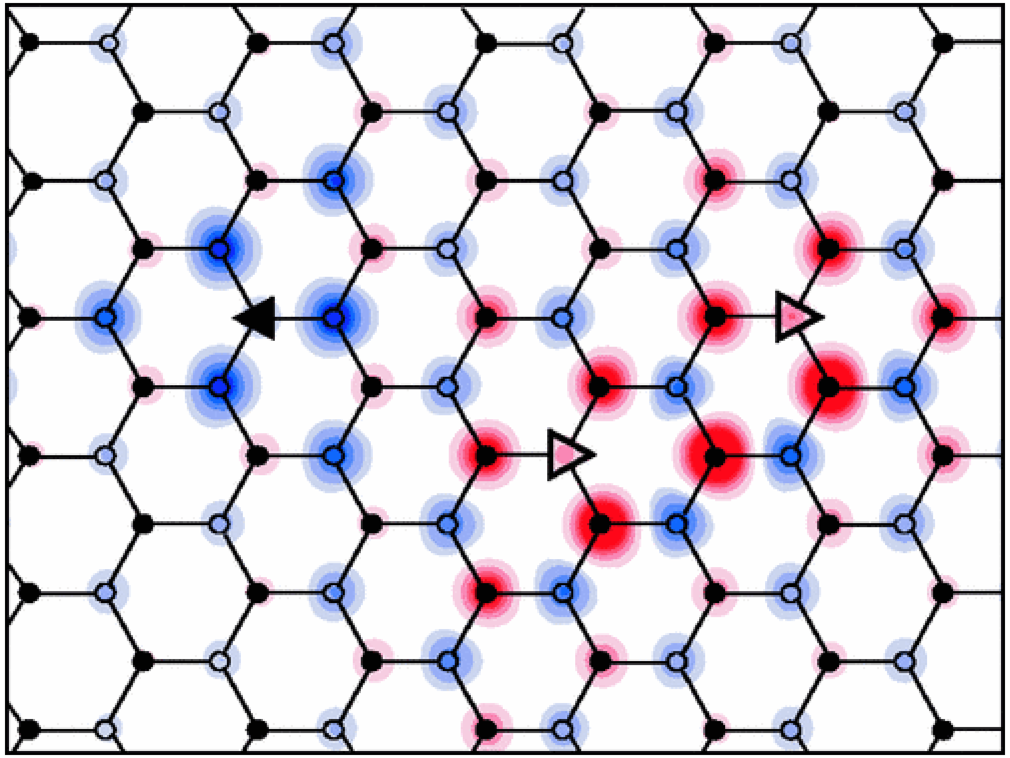
ONSET OF MAGNETISM

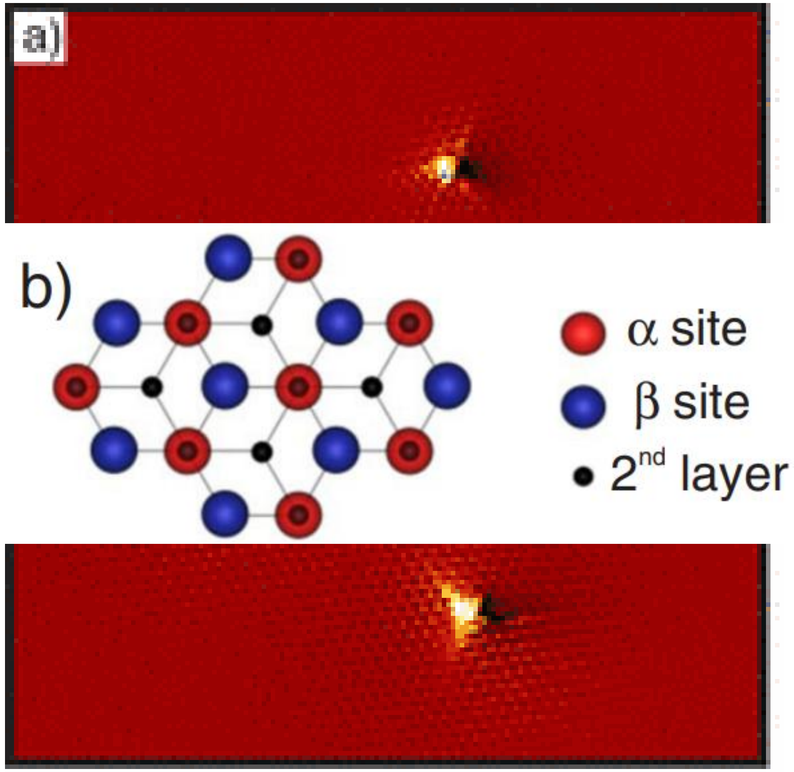
- Studying defects on both sublattices



Yazyev O V 2008b Phys. Rev. Lett. 101 037203

EXPERIMENTAL EVIDENCE

- HOPG with AB Bernal stacking
- Vacancies in exfolieted HOPG by irradiating with 140 eV Ar^{+}ions
- Annealing the sample gave single vacancies
- LT-STM was used to study the LDOS



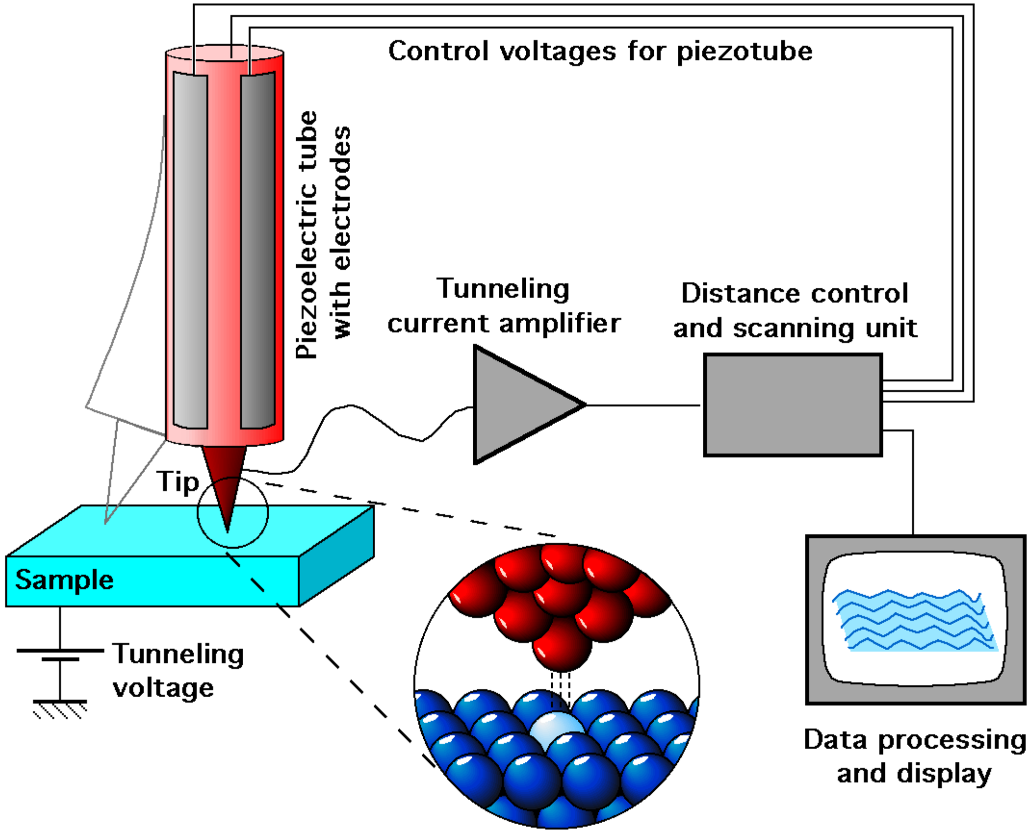
M. M. Ugeda Phys. Rev. Lett. **104**, 096804

LT-SCANNING TUNNELING MICROSCOPY

- STM is base on quantum tunneling
- Measurements done in UHV and LT
- Measures the LDOS

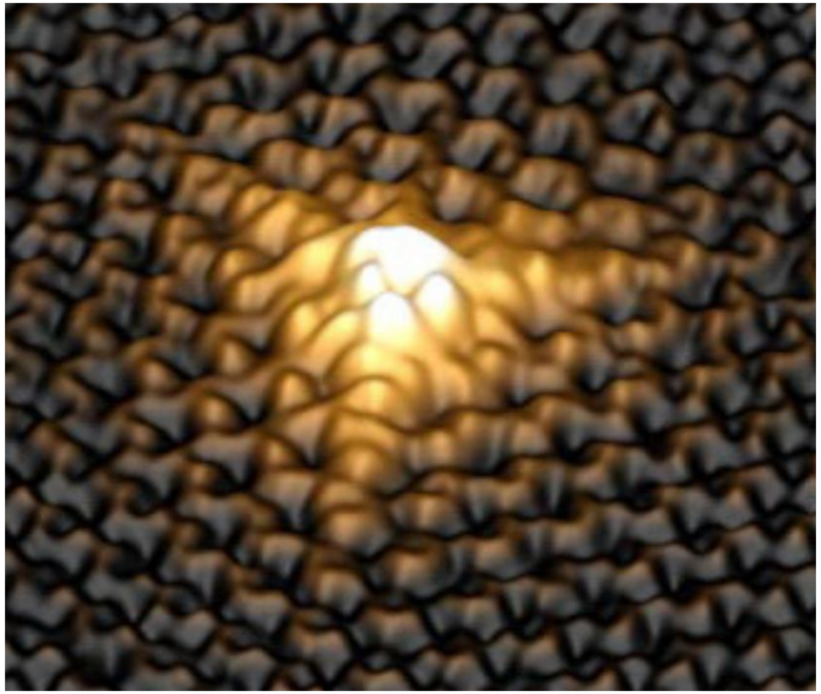
$$I_t = \int_0^{eV} \rho_{sample}(E, r_0)\, \rho_{tip}\, |M|^2 dE$$

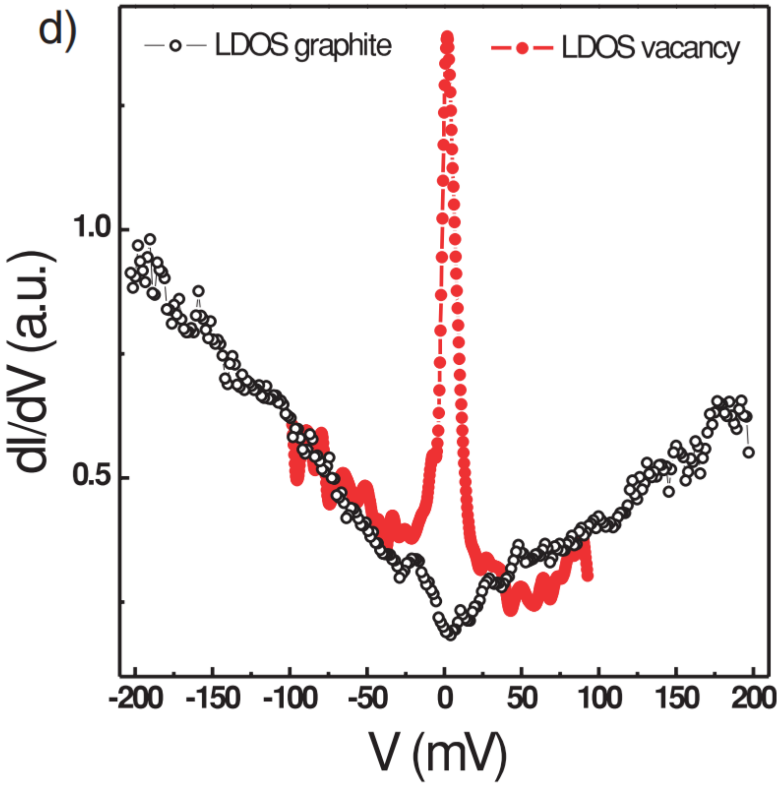
$$\frac{dI_t(V)}{dV} \propto \rho_{sample}(E = eV, r_0)$$



A. Pasha Arch Appl Mech (2020) 90:1893–1917

LT-SCANNING TUNNELING MICROSCOPY

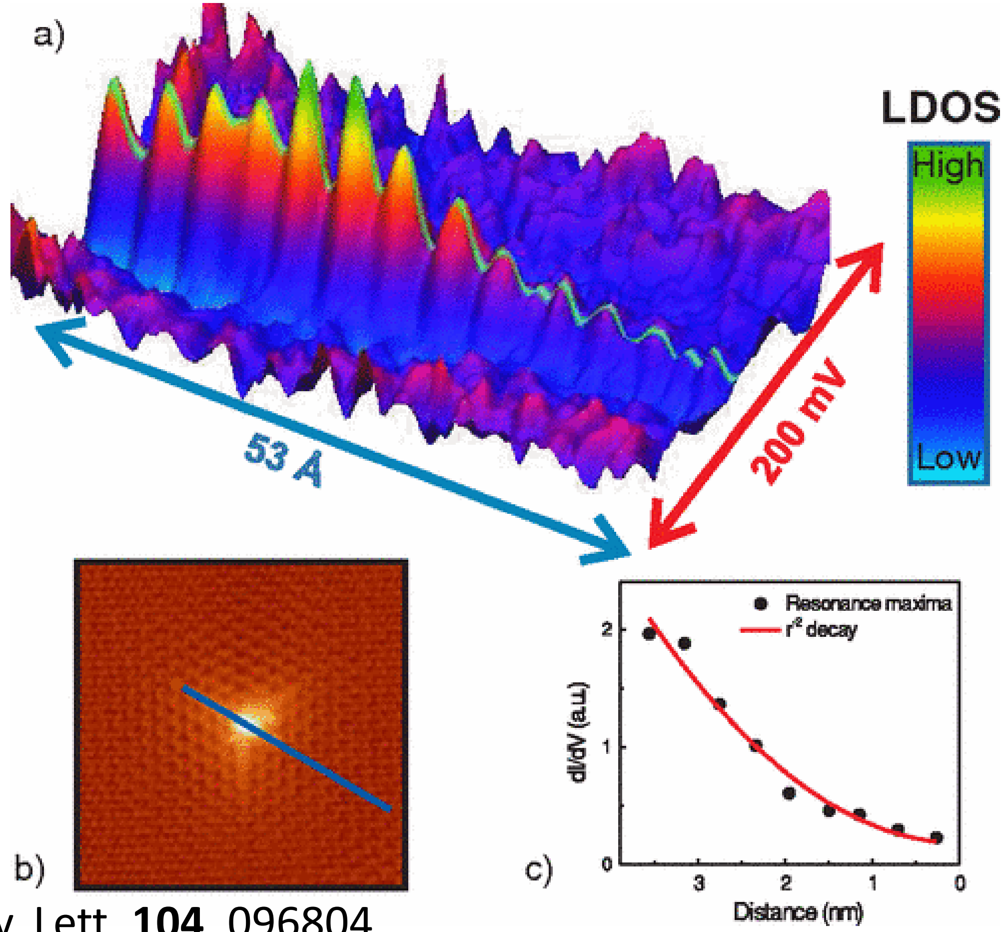




M. M. Ugeda Phys. Rev. Lett. **104**, 096804

EXPERIMENTAL EVIDENCE

- Local LDOS map around a single vacancy
- Shows a peak around E_F
- Peaks maxima vs position is consistent with r^{-1} decay

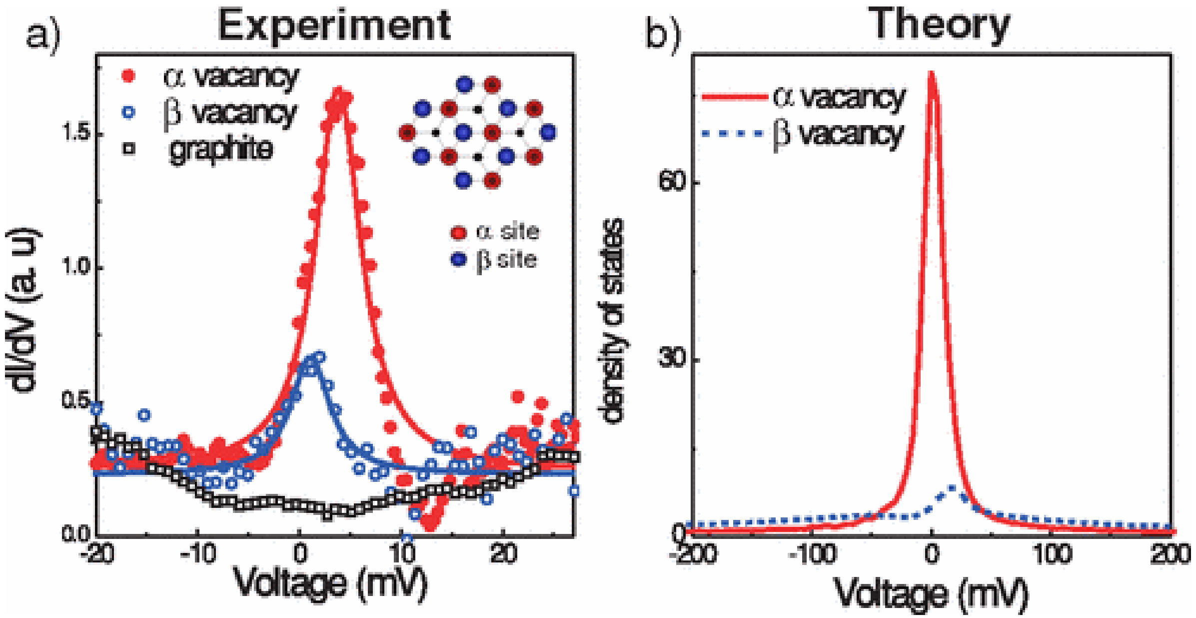


M. M. Ugeda Phys. Rev. Lett. **104**, 096804

AB BERNAL STACKING

- Sublattices are not equivalent
- LDOS peak changes
- In agreement with theory prediction
- Ferrimagnetism arise
- Curie Temperature can be estimate

$$T_C \approx e^2 \sqrt{n_\nu}$$

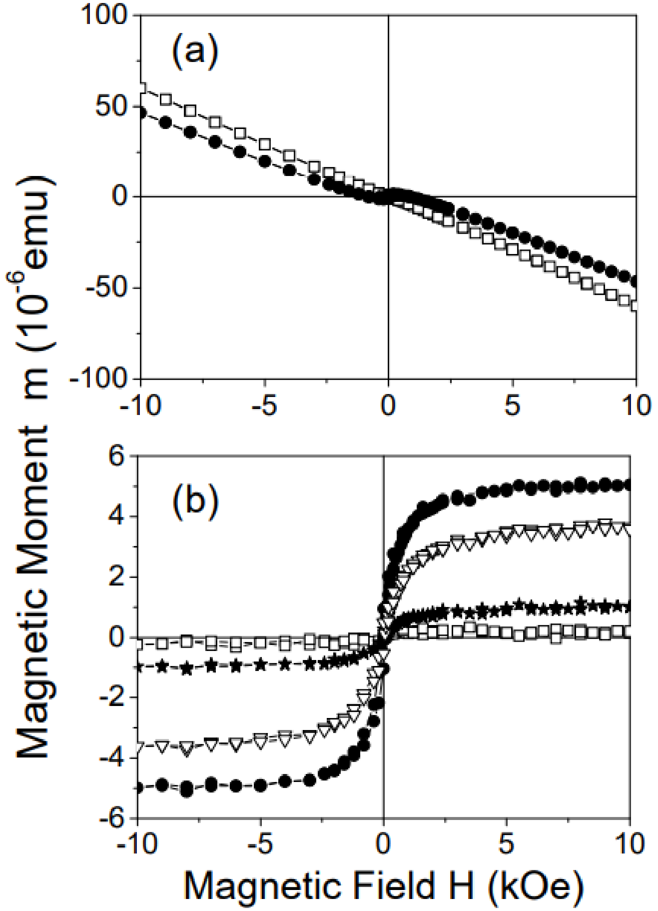


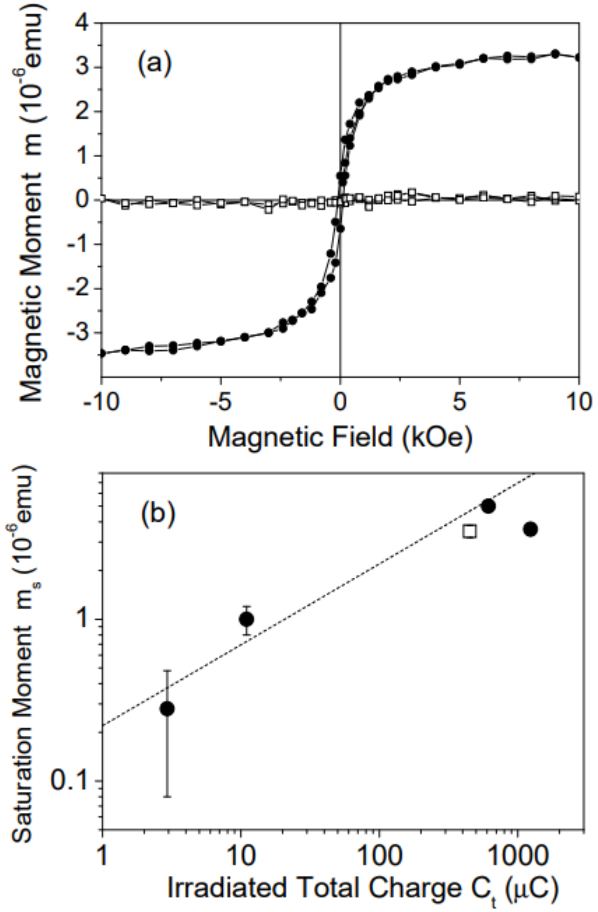
M. M. Ugeda Phys. Rev. Lett. **104**, 096804

BULK DEFECTS

- HOPG irradieted with 2.25 MeV protons
- Different types of defects
- Concentration of defects changes with number of irradiation cycles
- Hysteresis loops were measured at different temperatures 5 K, 300 K, 380 K
- Ferromagnetic at RT
- Curie Temperature above 400K

BULK DEFECTS

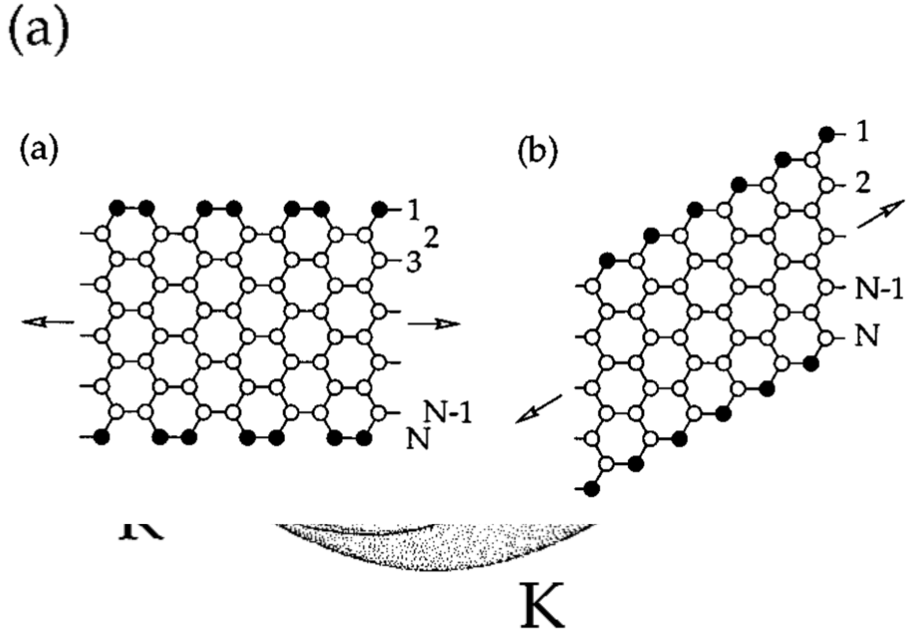




Esquinazi P. et al. 2003 Phys. Rev. Lett. 91 227201

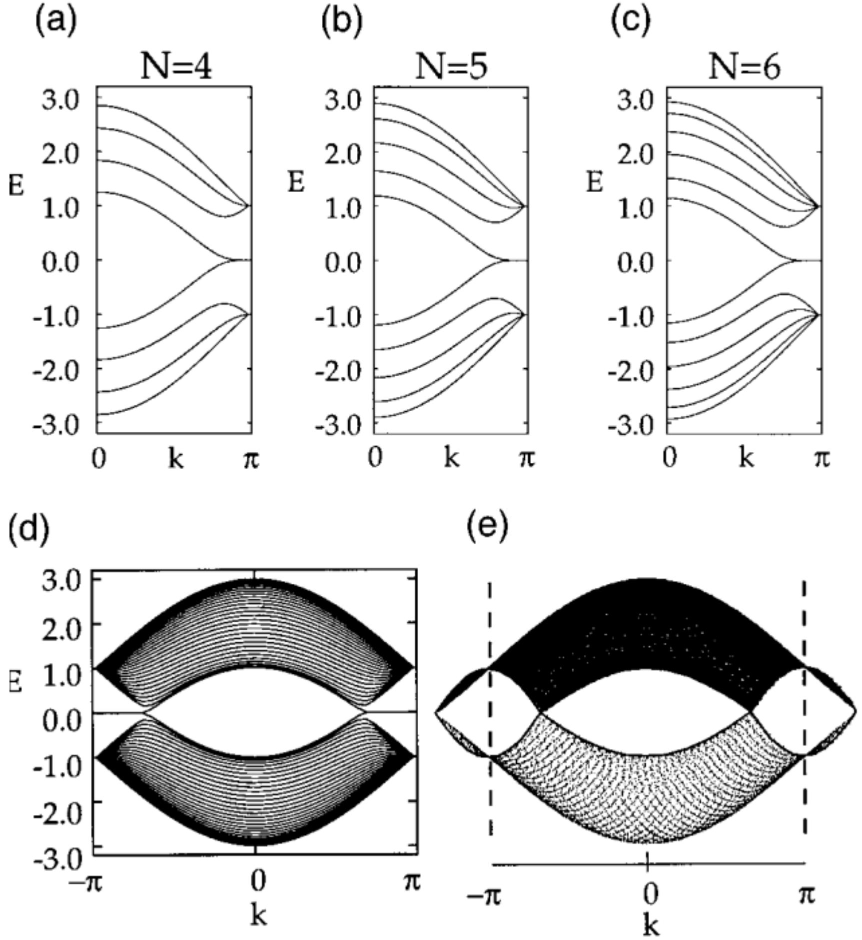
EDGE MAGNETISM

- Graphene is a zero-gap semiconductor
- Nanometric size changes the band structure
- Graphene nanoribons: finite-size 1D system
- Two possible edges
- Magnetism decreases with the increase of size

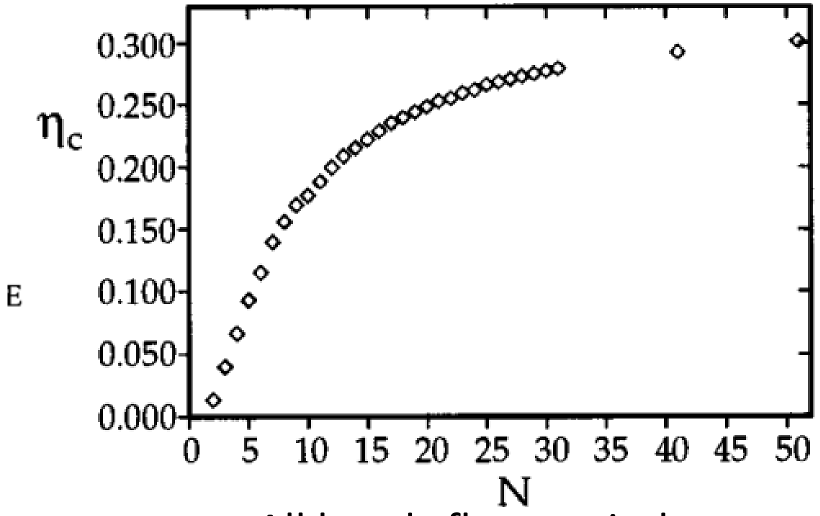


M. Fujita et al. 1996 Phys. Rev. Lett. B S0163-1829(96)11048-1

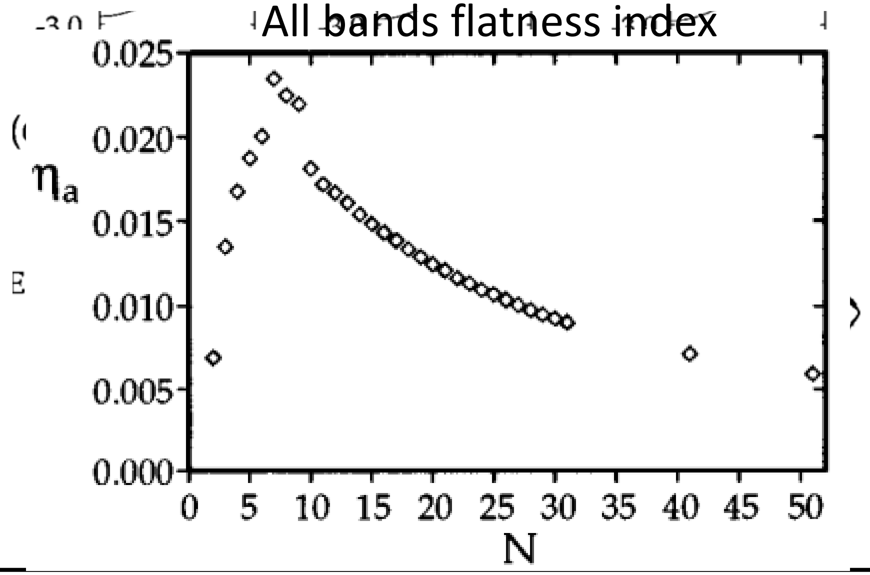
EDGE MAGNETISM



Center band flatness index



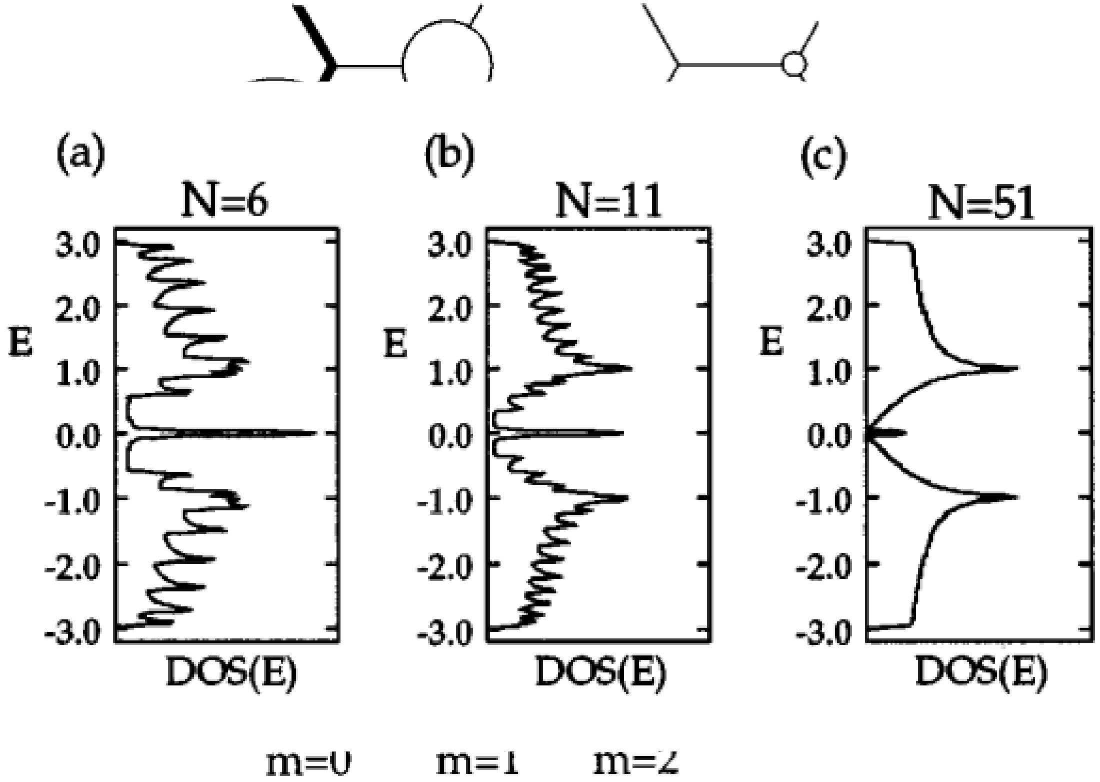
All bands flatness index



M. Fujita et al. 1996 Phys. Rev. Lett. B S0163-1829(96)11048-1

EDGE MAGNETISM:THEORY

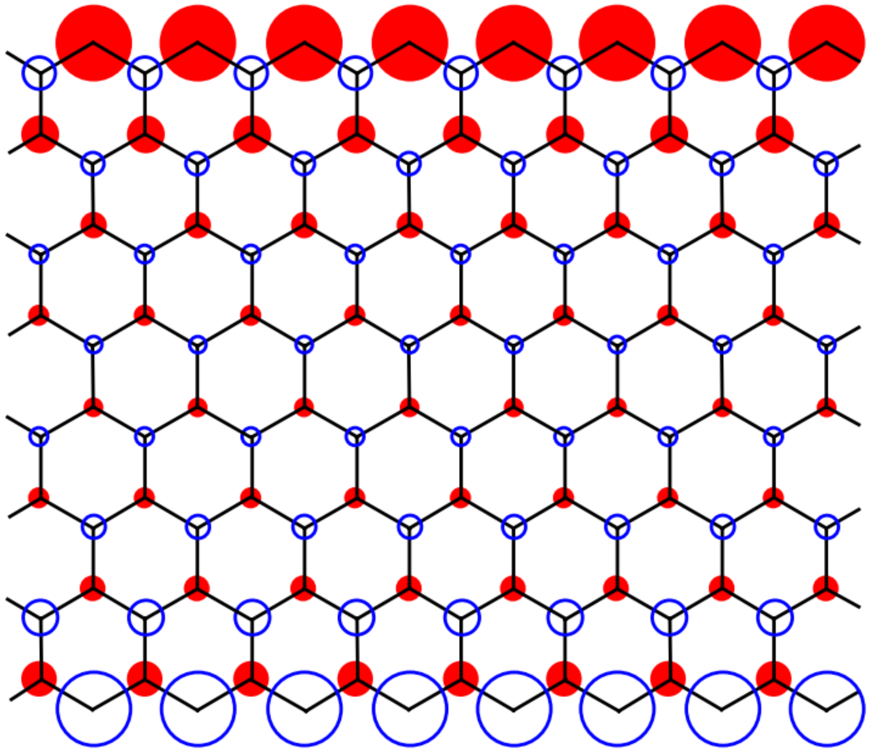
- Semi-infinite graphene plane with zig-zag edge
- Tight-binding of LCAO is used
- Spacially localized states are found
- States localised on a single sublattice
- $\psi_s(r)$ has an exponential decay

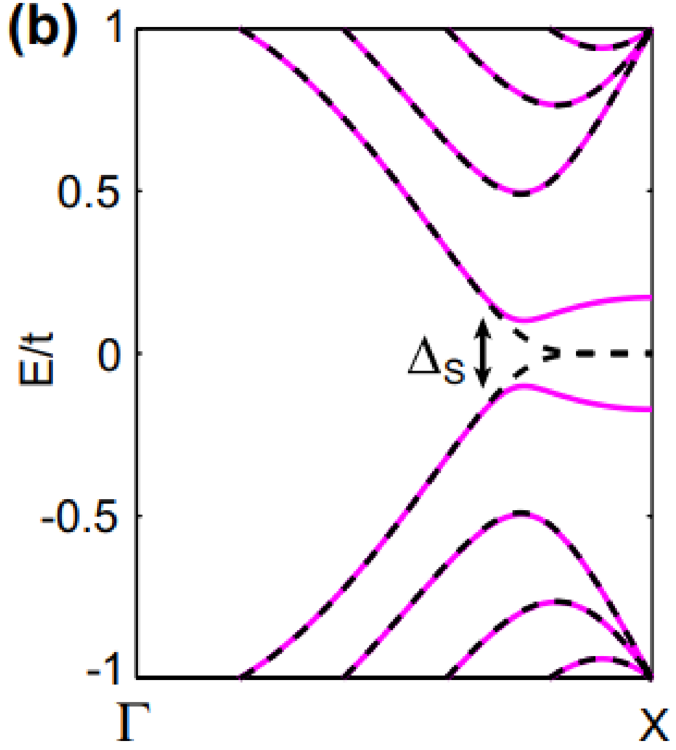


M. Fujita et al. 1996 Phys. Rev. Lett. B S0163-1829(96)11048-1

EDGE MAGNETISM: THEORY

Considering the interaction between elecotrons using the Hubbard model

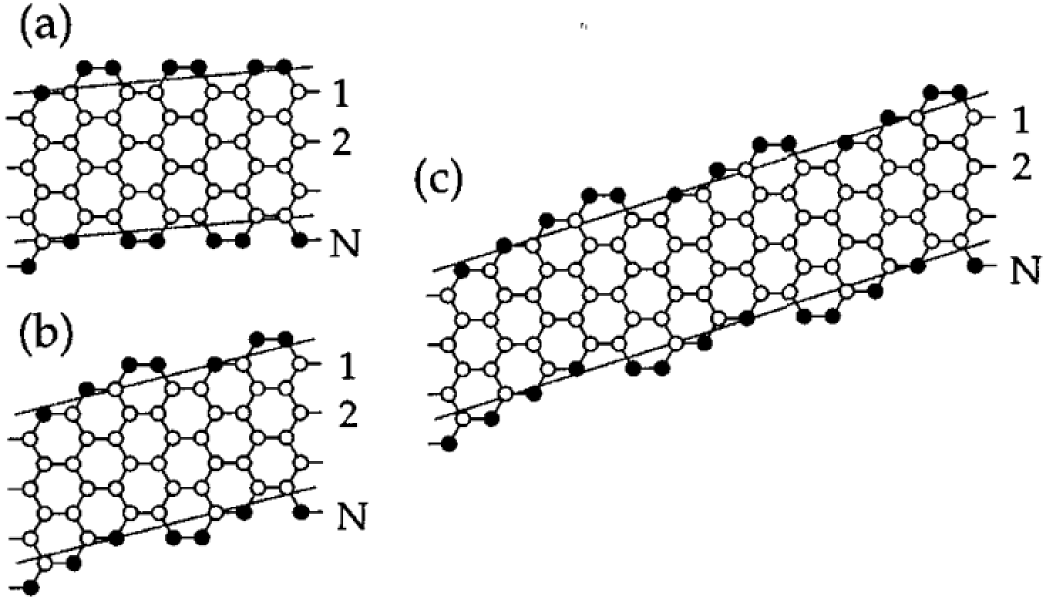




Yazyev O V 2008b Phys. Rev. Lett. 101 037203

EDGE MAGNETISM:REAL EDGES

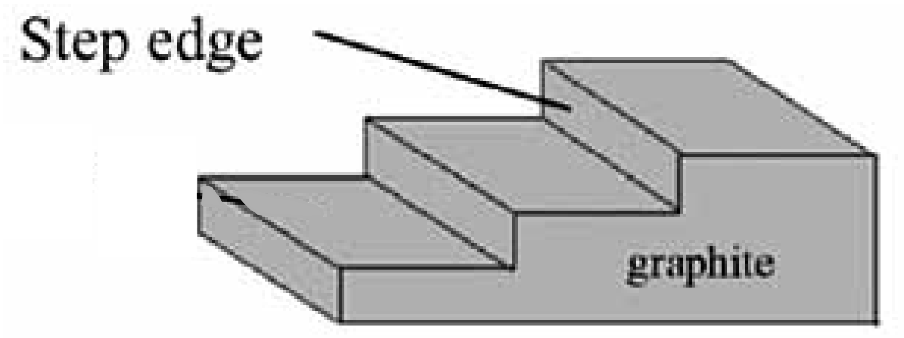
- Real edges are of both types
- The ratio can be different
- Spacially localized states are still found



M. Fujita et al. 1996 Phys. Rev. Lett. B S0163-1829(96)11048-1

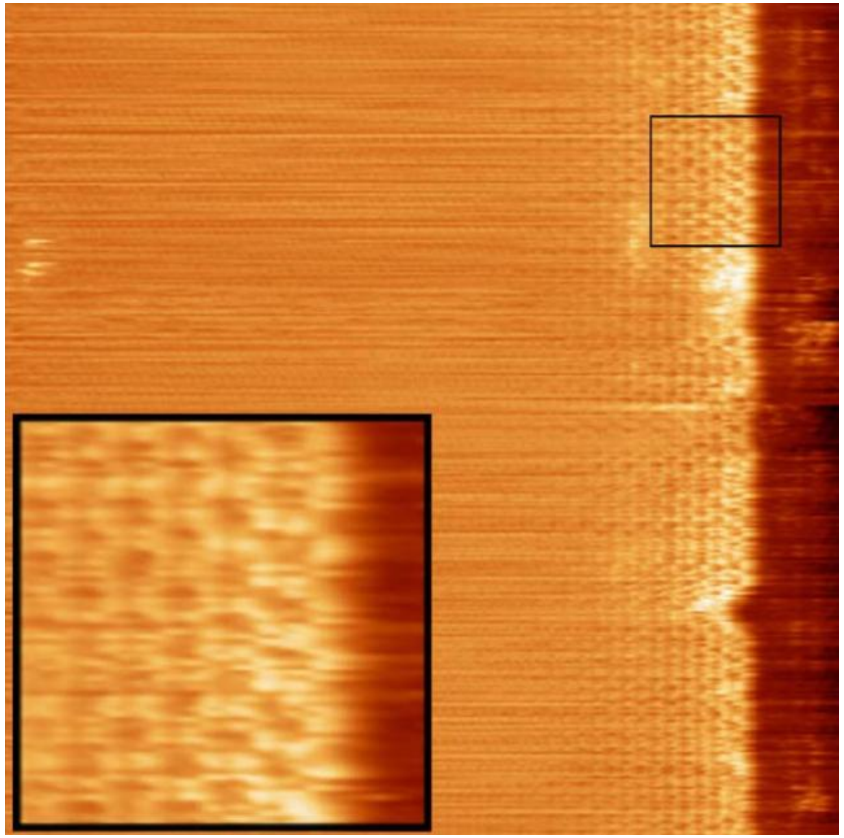
EDGE MAGNETISM:EXPERIMENTS

- UHV-STM was used on step edges of HOPG
- Brightness of the images is proportional to LDOS
- Theoretical predictions were confirmed

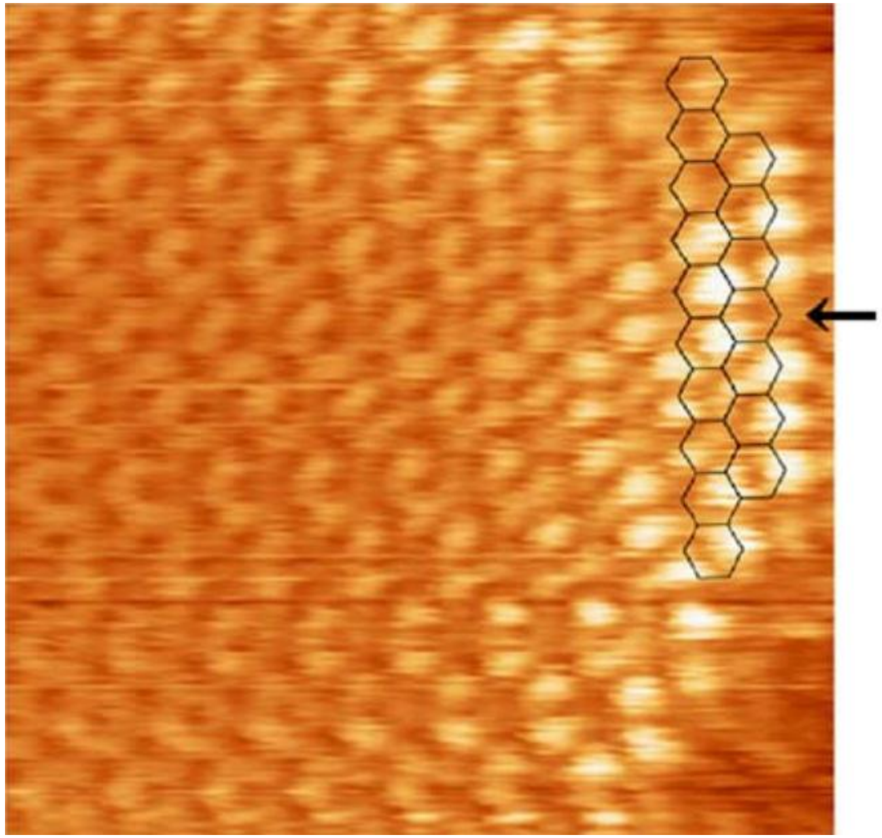


EDGE MAGNETISM:EXPERIMENTS

Armchair edge

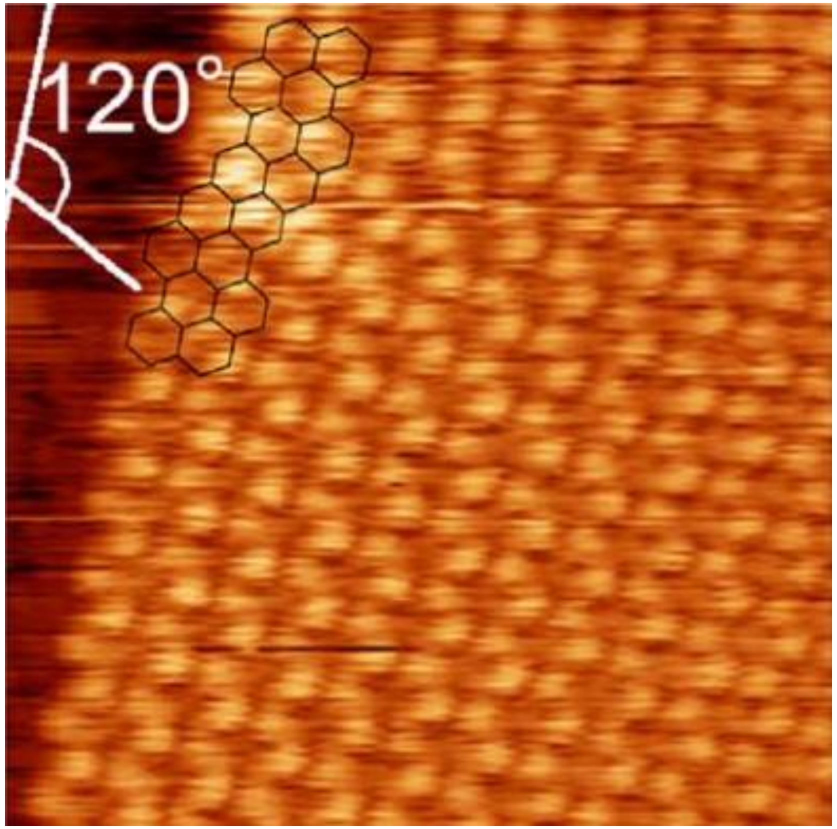


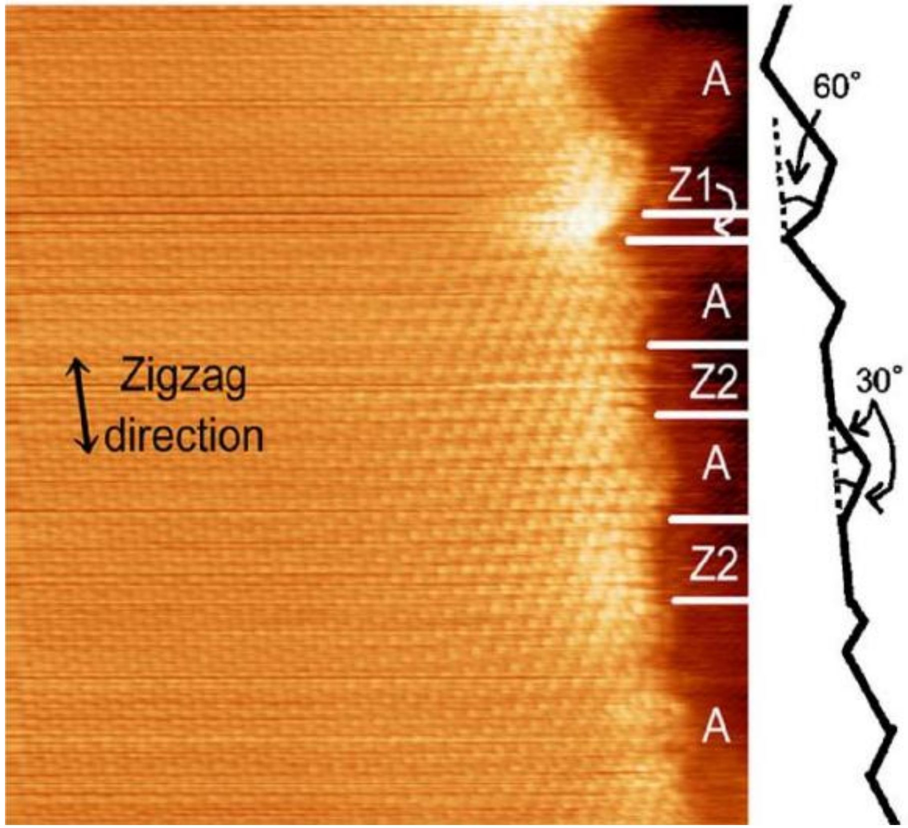
Zigzag edge



Kobayashi Y, Fukui K i, Enoki T and Kusakabe K 2006 Phys. Rev. B 73 125415

EDGE MAGNETISM:EXPERIMENTS



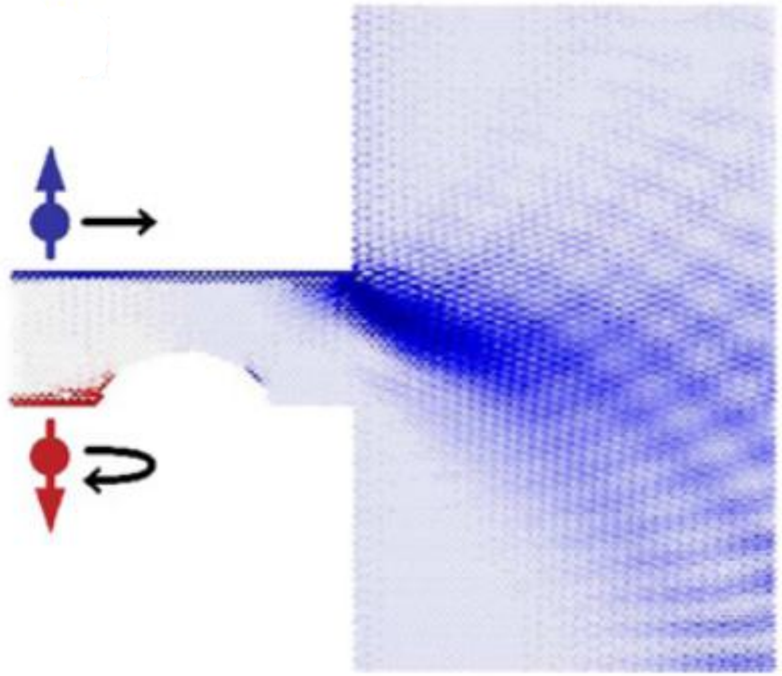


Kobayashi Y, Fukui K i, Enoki T and Kusakabe K 2006 Phys. Rev. B 73 125415

APPLICATIONS

APPLICATIONS: SPINTRONIC

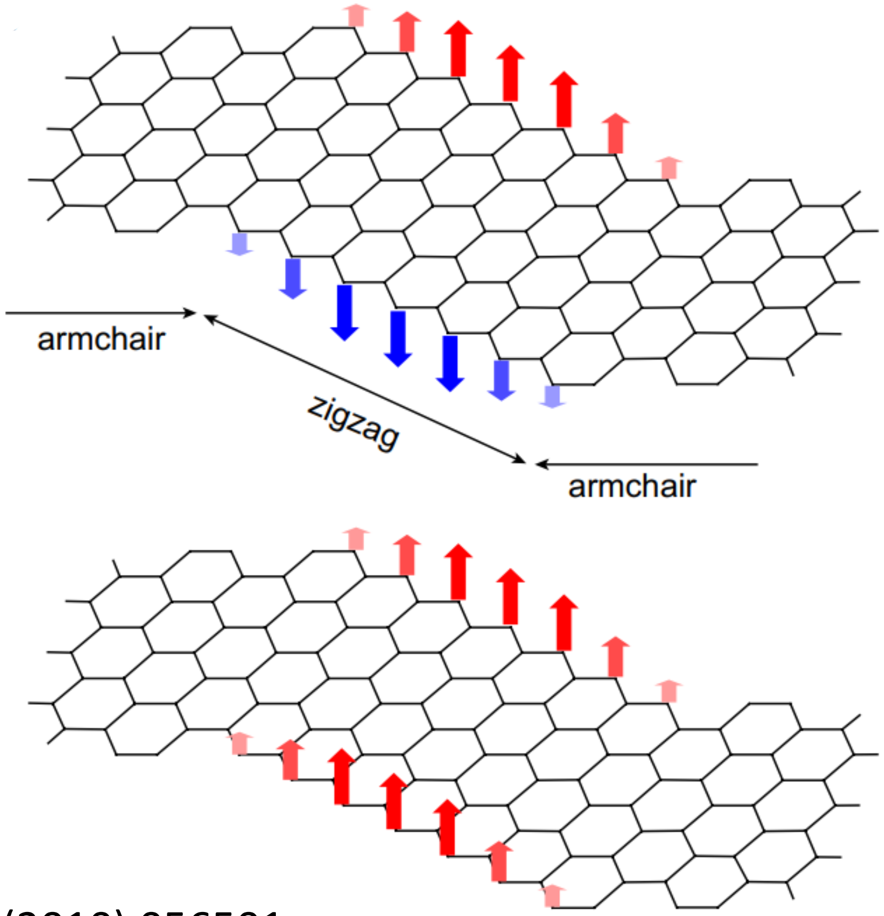
- Electrically or defect induced half-metallicity in zigzag graphene nanoribbons
- Nanoribbon attached to a graphene layer
- Spin-polarised electron are injected into the graphene sheet
- An exeted defect is introduced



Yazyev O V Rep. Prog. Phys. 73 (2010) 056501

APPLICATIONS: MAGNETORESISTIVITY

- Graphene nanostructure in magnetoresistive junctions
- High MR
- An all graphene-based device
- Low resistivity state with magnetic field
- High resistivity without



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REFERENCES

- [1] Yazyev O V Rep. Prog. Phys. 73 (2010) 056501
- [2] Yazyev O V 2008b Phys. Rev. Lett. 101 037203
- [3] Kobayashi Y, Fukui K i, Enoki T and Kusakabe K 2006 Phys. Rev. B 73 125415
- [4] Esquinazi P, Spemann D, H¨ohne R, Setzer A, Han K H and Butz T 2003 Phys. Rev. Lett. 91 227201
- [5] V. M. Pereira, F. Guinea, J. M. B. Lopes dos Santos,N. M. R. Peres, and A. H. Castro Neto, Phys. Rev. Lett.96, 036801 (2006).
- [6] M. M. Ugeda Phys. Rev. Lett. **104**, 096804