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Ab-initio studies of advanced multifunctional materials

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Plan of the talk

- Introduction
- Theoretical methods
- Applications
  - (i) Diluted magnetic semiconductor for semiconductor spintronics
  - (ii) Graphene
- Summary

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Computational materials science (analysis and prediction)

Materials properties from ground state energy

Density Functional Theory (Walter Kohn, Noble Prize, 1998)

Total energy is a functional of density of electrons, E[n]
Explicit dependence of wavefunction avoided

Ab-initio theory - no adjustable parameters
(only input for structure and atomic species)

Computational challenge:
Modeling of large systems with many atoms in the unit cell
Accuracy: convergence with respect to k-points in the Brillouin zone, basis set size
Parallel implementation with MPI, large memory requirement
Multiscale modeling combining different length and time scales

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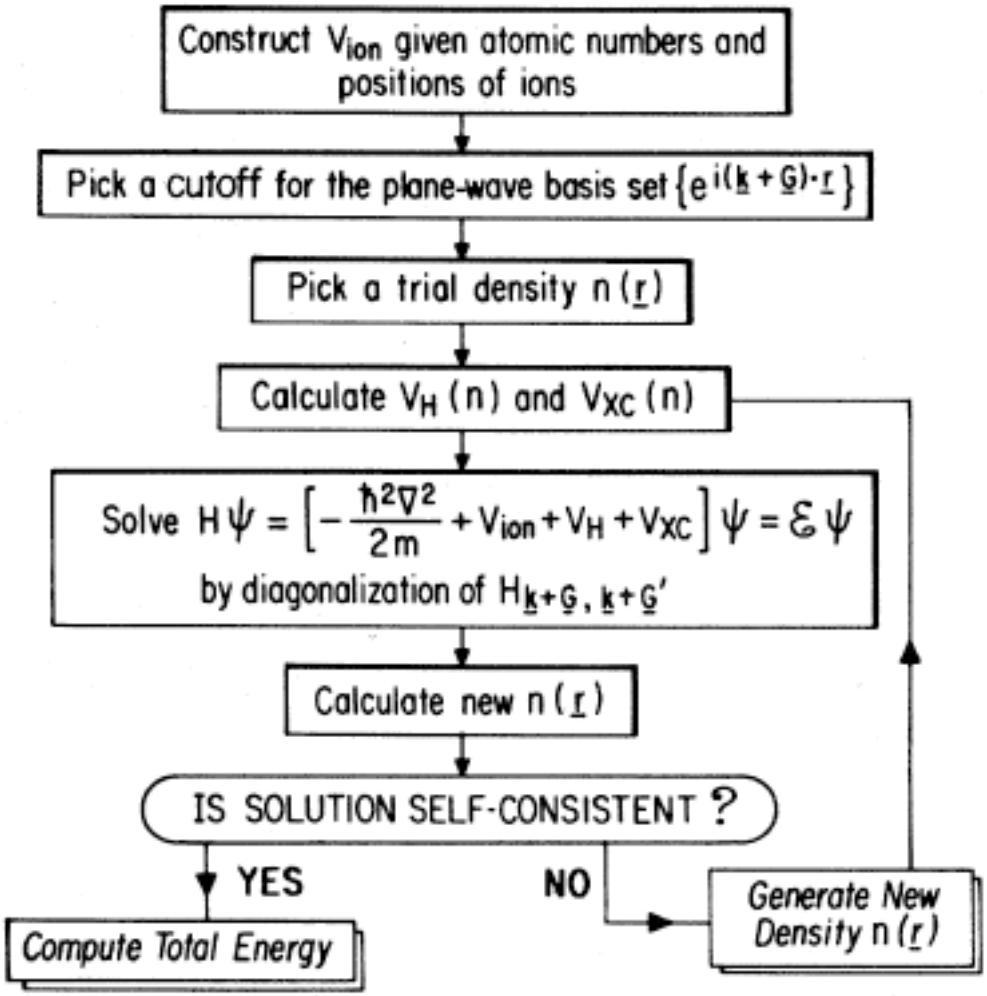
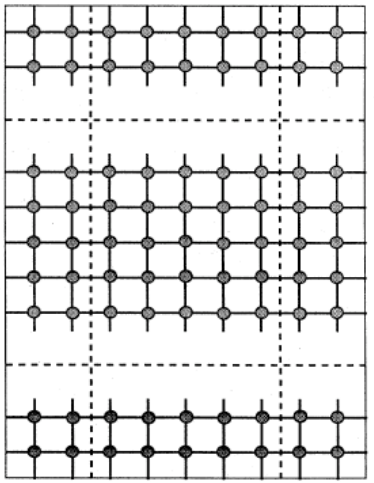
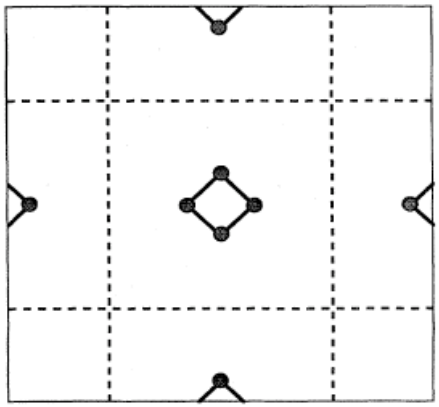
Self-consistency procedure





Surface



Molecule

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First principles modeling

1. Plane wave Projector Augmented Wave calculations (VASP): structural relaxations, clusters, total energy calculations of supercells (ordered system)
2. (a) Korringa-Kohn-Rostoker-Coherent Potential Approximation (KKR-CPA) calculations: disorder averaging, calculation of Heisenberg pair-exchange parameters using methodology of Liechtenstein *et al.*

$$H = -\sum_{i \neq j} J_{ij} \vec{e}_i . \vec{e}_j$$

J_{ij} > 0 (ferromagnetic)

< 0 (antiferromagnetic)

(b) Monte-Carlo simulations including disordered spins: magnetic percolation due to disorder

Metropolis algorithm

Determination of Curie temperature by the cumulant-crossing method

3. Atomistic spin dynamics simulations (magnetization dynamics)

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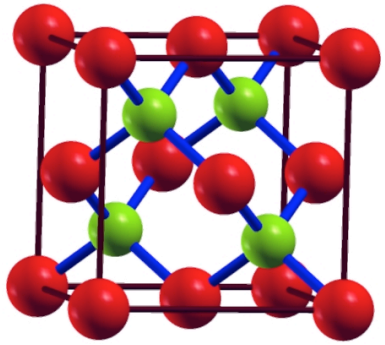
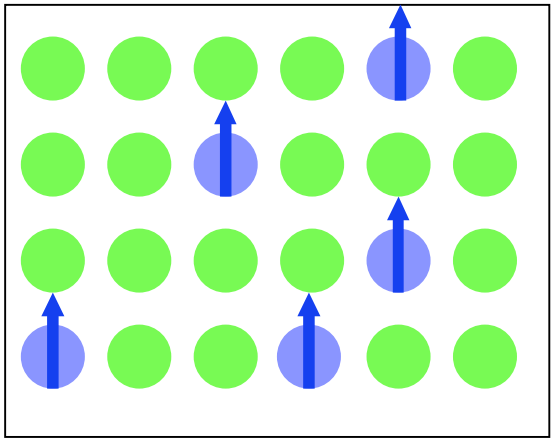
Semiconductor spintronics
Diluted magnetic semiconductors

Magnetic elements (Cr, Mn, Fe, Co) doped in semiconductors





- **Simultaneous properties of semiconductors and ferromagnets**
- **III-V DMS (Mn doped GaAs), II-VI DMS (Co doped ZnO)**
- **Manipulation of charge carriers by doping, electric field etc.**
- **Defects are obstacles**
- **Growth condition is crucial (often inhomogeneous distribution of dopants as well as formation of secondary phases)**

Appl. Phys. Lett. **89**, 212502 (2006)
Phys. Rev. B **74**, 235208 (2006)
Phys. Rev. B **68**, 205210 (2003)
J. Appl. Phys. **103**, 07D131 (2008)

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Complexities in DMS materials

- How do spins interact ?
- How do defects control the properties ?
- How can we increase the ordering temperatures (T_C) ?
- How do the electron-electron correlations affect the electronic and magnetic properties ?

Electronic structure and magnetic interaction

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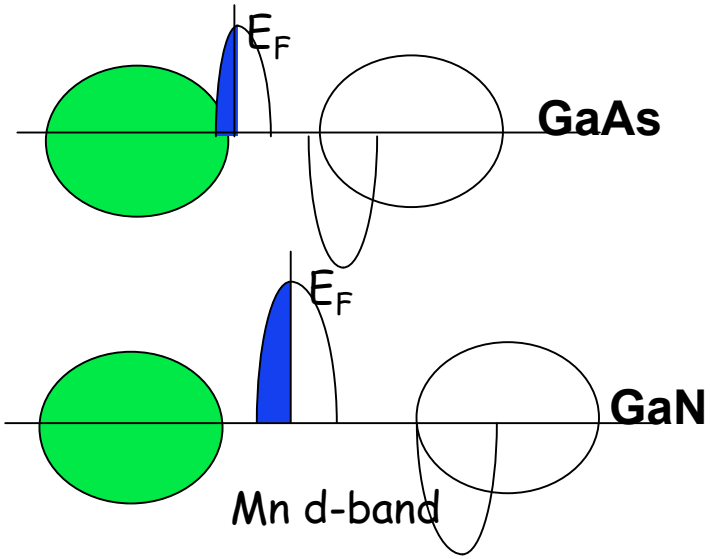
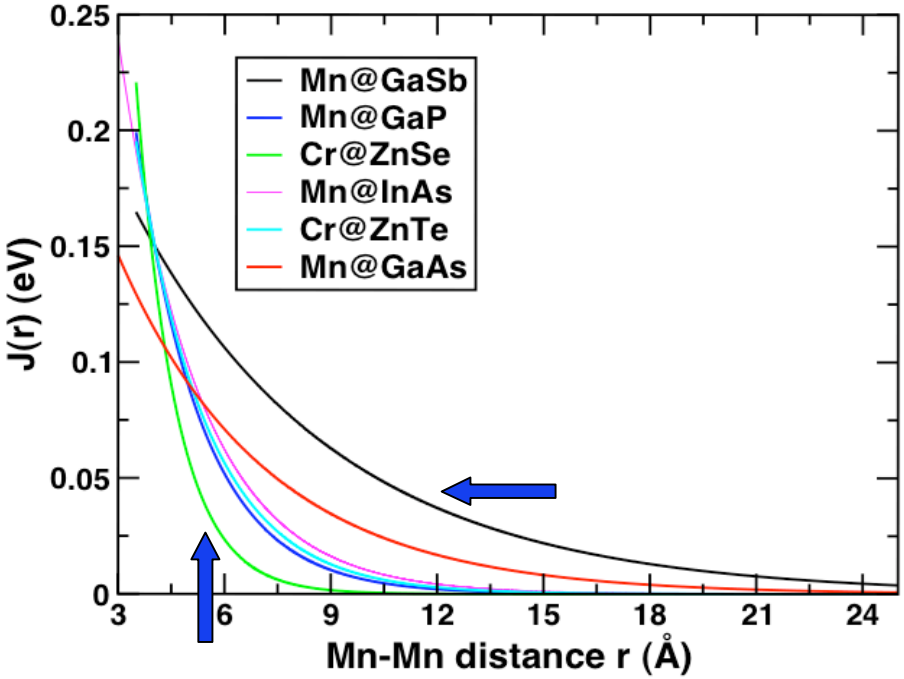
Electronic structure



Interaction between magnetic atoms



- Electronic structure and magnetic interaction are material-specific
- Correctly captured by ab-initio simulations

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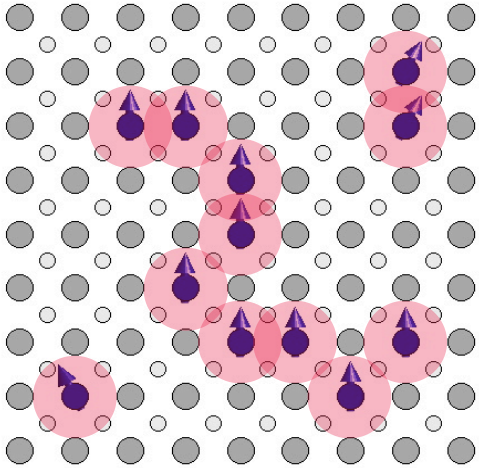
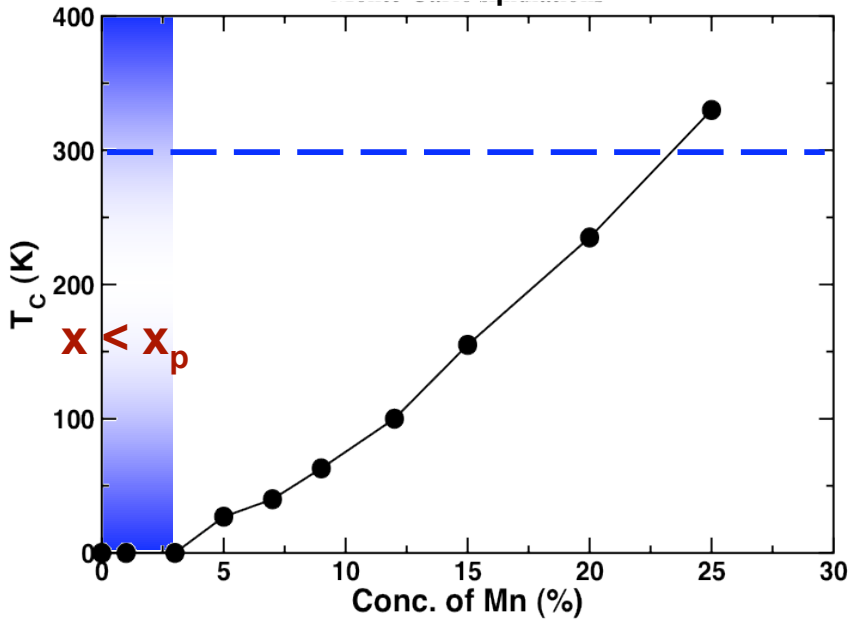
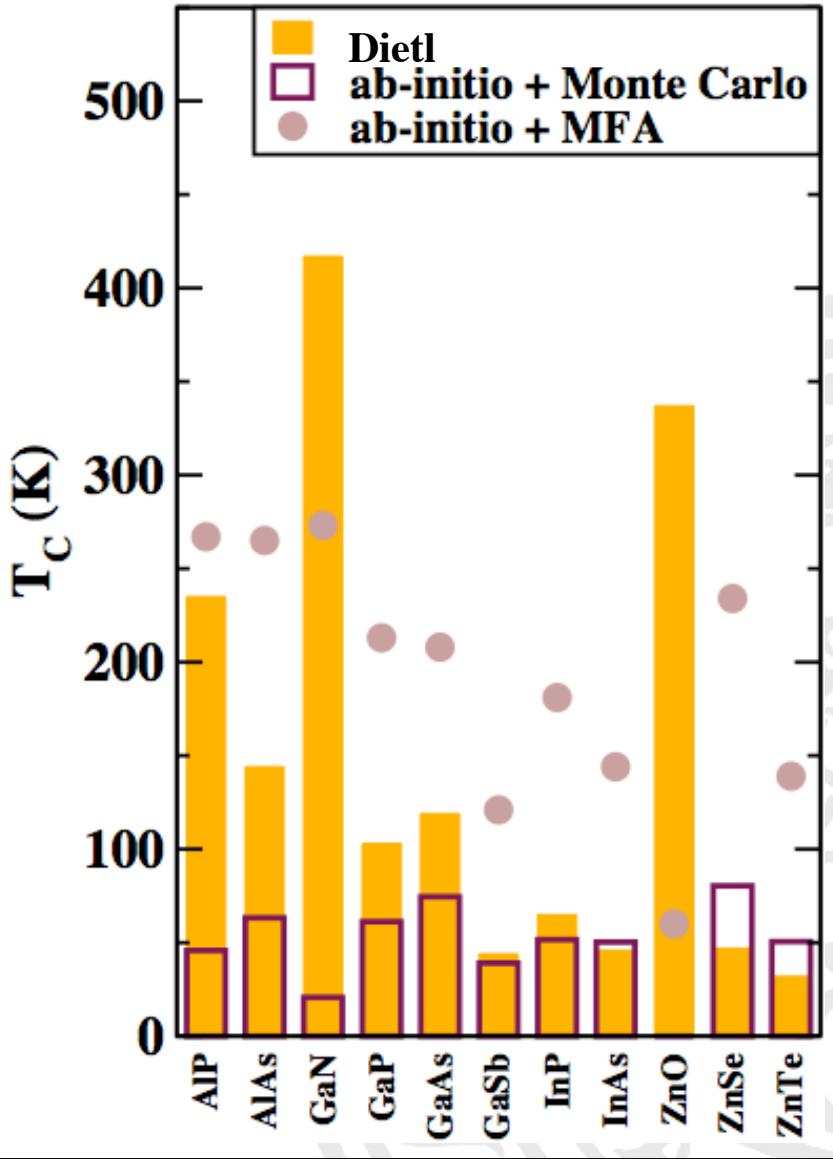
Magnetic percolation & T_C (Monte-Carlo Simulations)



Mn doped NiTiSn





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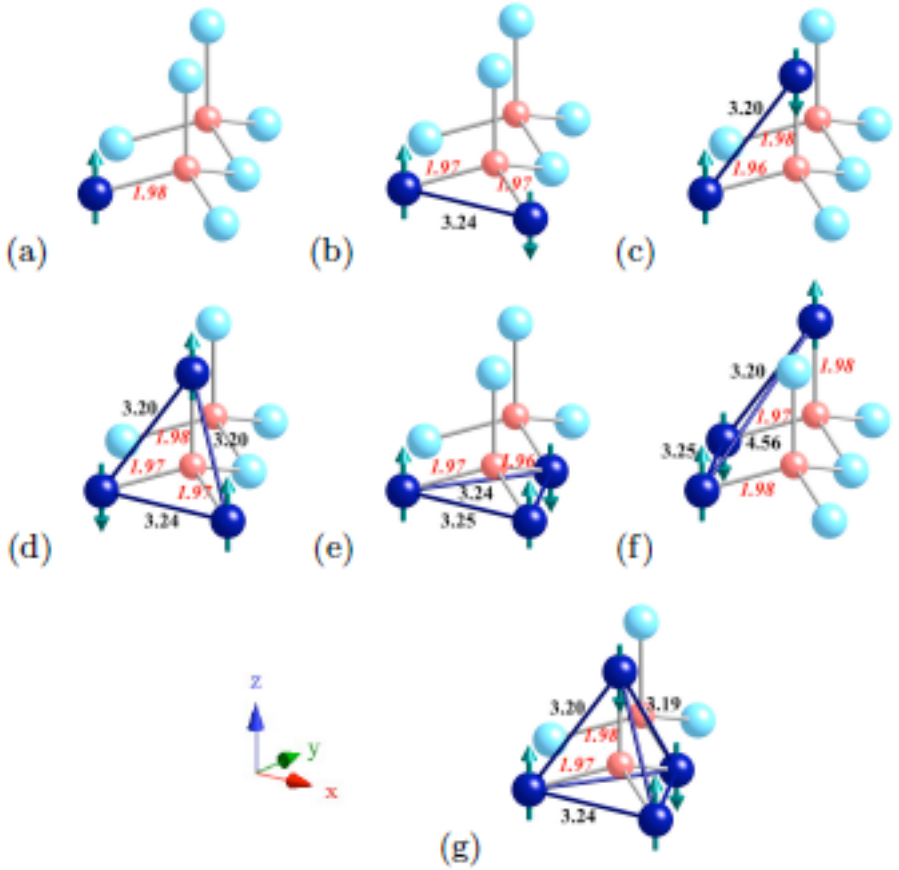
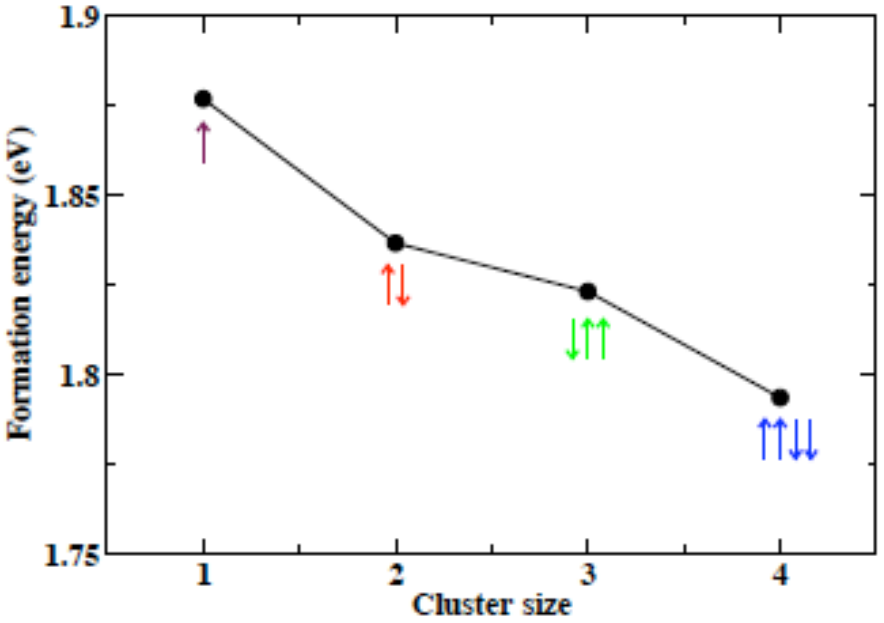
Co doped ZnO: microscopic picture

Chemical and magnetic structure



Probability of cluster formation



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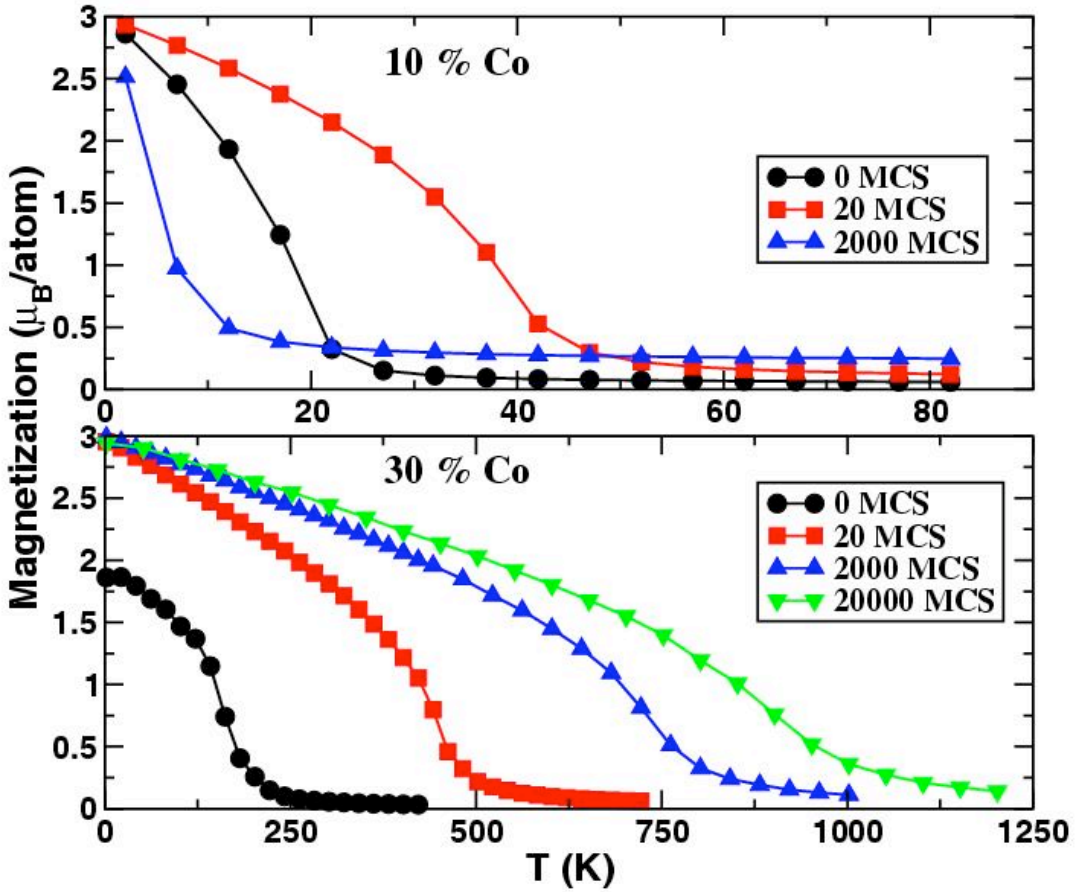
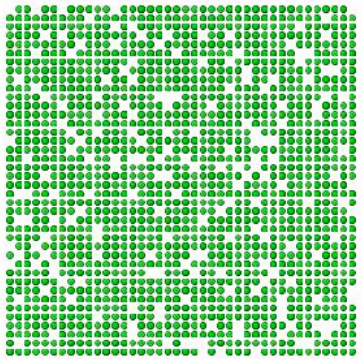
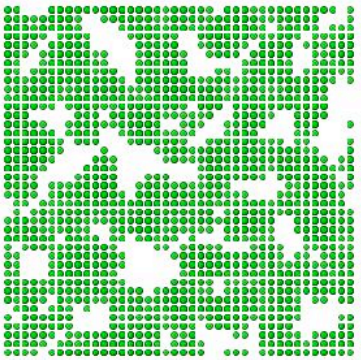
Inhomogeneties & Magnetism Co doped ZnO



10 % Co



Initial distribution



After 2000 MCS

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Atomistic spin dynamics

Equation of motion

$$\frac{d\mathbf{m}_i}{dt} = -\gamma \mathbf{m}_i \times [\mathbf{B}_i + \mathbf{b}_i(t)] - \gamma \frac{\alpha}{m} \mathbf{m}_i \times (\mathbf{m}_i \times [\mathbf{B}_i + \mathbf{b}_i(t)])$$

Effective field $\mathbf{B}_i = -\frac{\partial H}{\partial \mathbf{m}_i}$

$\mathbf{b}_i(t)$: Stochastic magnetic field

α : damping parameter

γ : electron gyromagnetic ratio

Exchange part (classical Heisenberg)

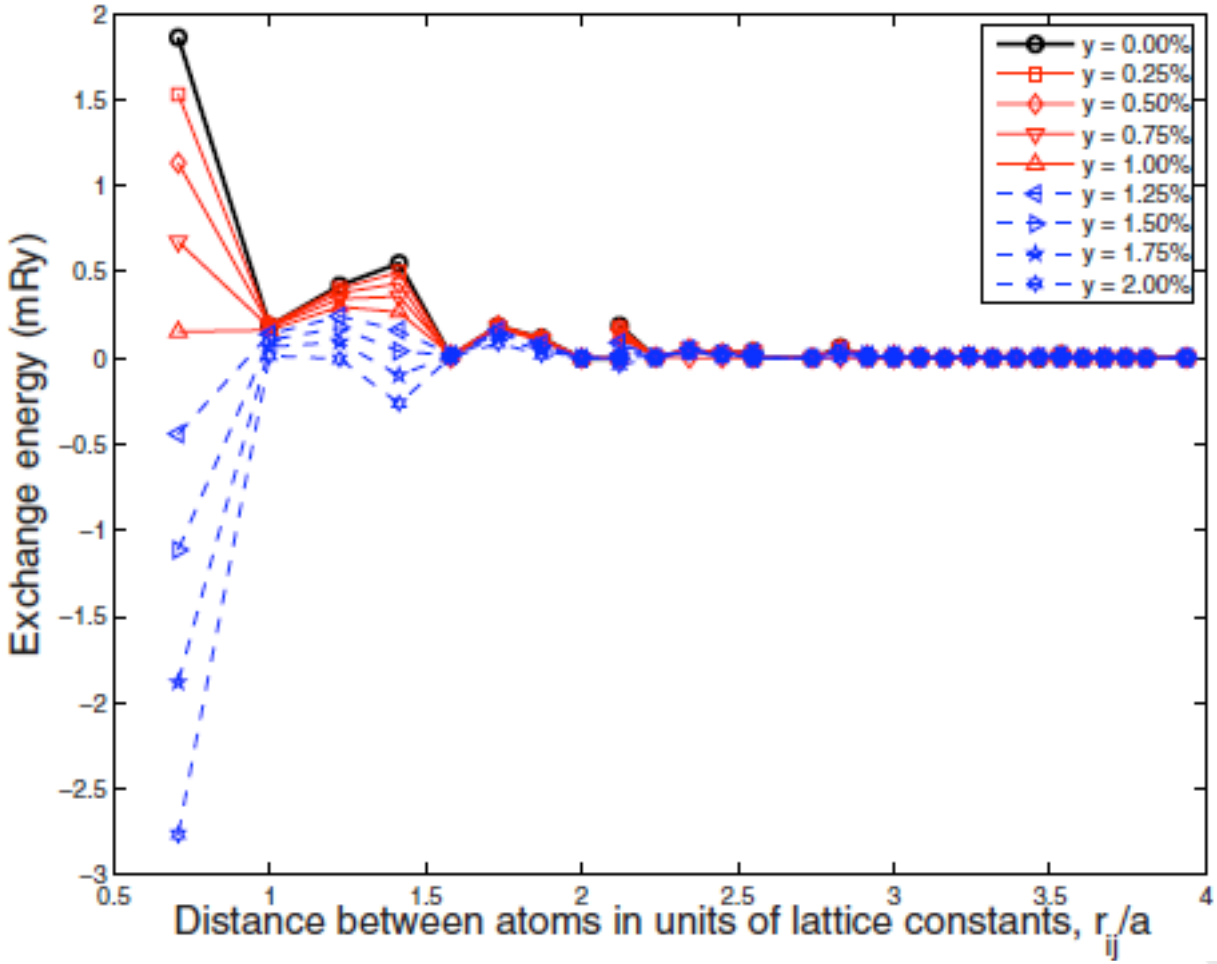
$$H_{ex} = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j$$

Skubic *et al.*, J. Phys: Condens. Matt. **20**, 315203 (2008)

Atomistic spin dynamics webpage: http://www.fysik.uu.se/cmt/asd

Exchange interactions (Mn doped GaAs, As antisites)

TB-LMTO-CPA calculations (Kudrnovsky et al.)



Ferromagnetic to antiferromagnetic exchange Interaction in presence of As antisites (double donor, hole killing)

Anisotropic exchange (strong in (110) direction)

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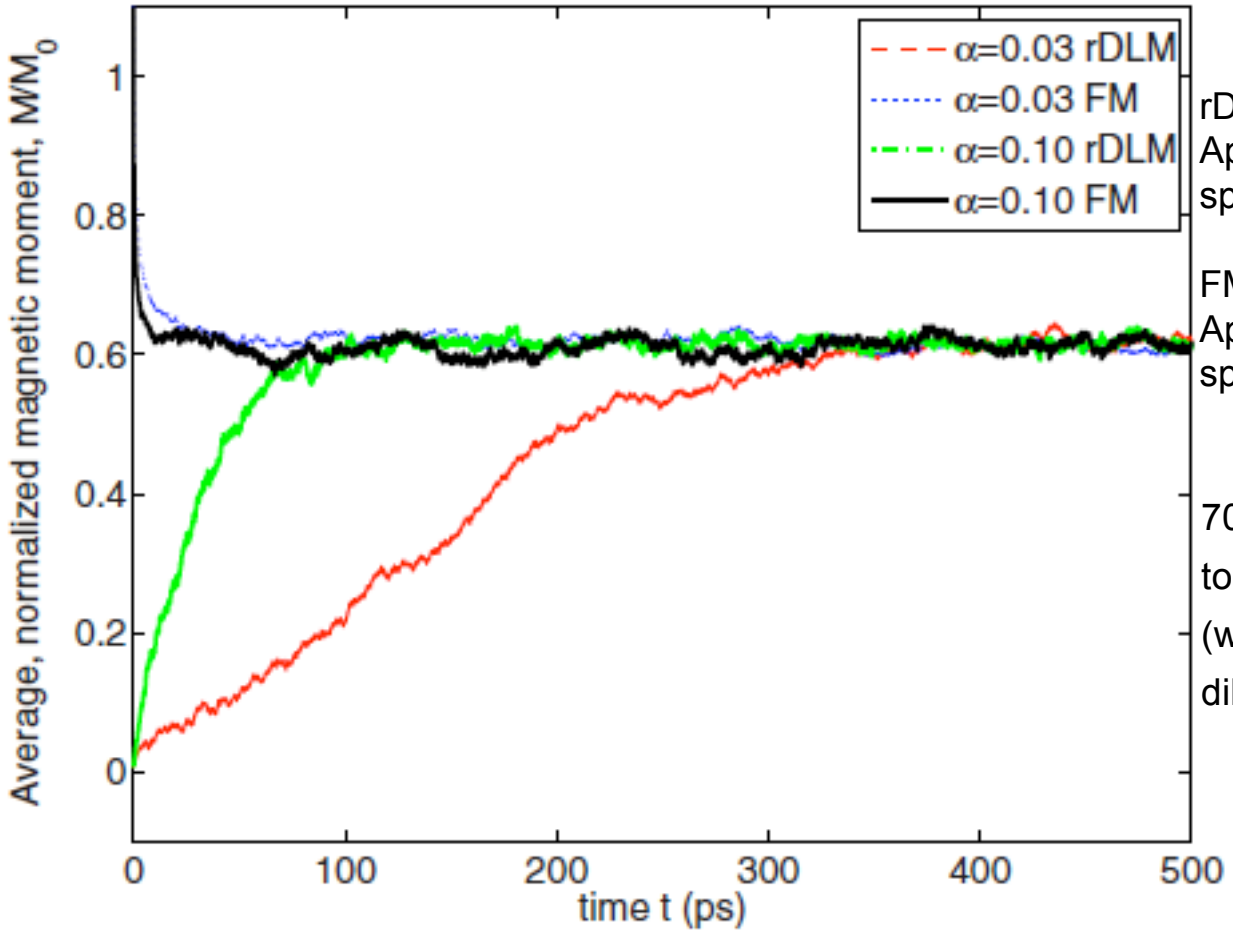
Dynamics of magnetization

L=40, T = 100K, As antisite conc. 0.25 %



rDLM: random disordered local moment
Approach to equilibrium:
spin precession and spin flipping

FM: ferromagnetic
Approach to equilibrium:
spin precession

70 % slower dynamics compared to bcc Fe
(weak local exchange field due to diluteness)

J. Hellsvik *et al.*,
Phys. Rev. B **78**, 144419 (2008)

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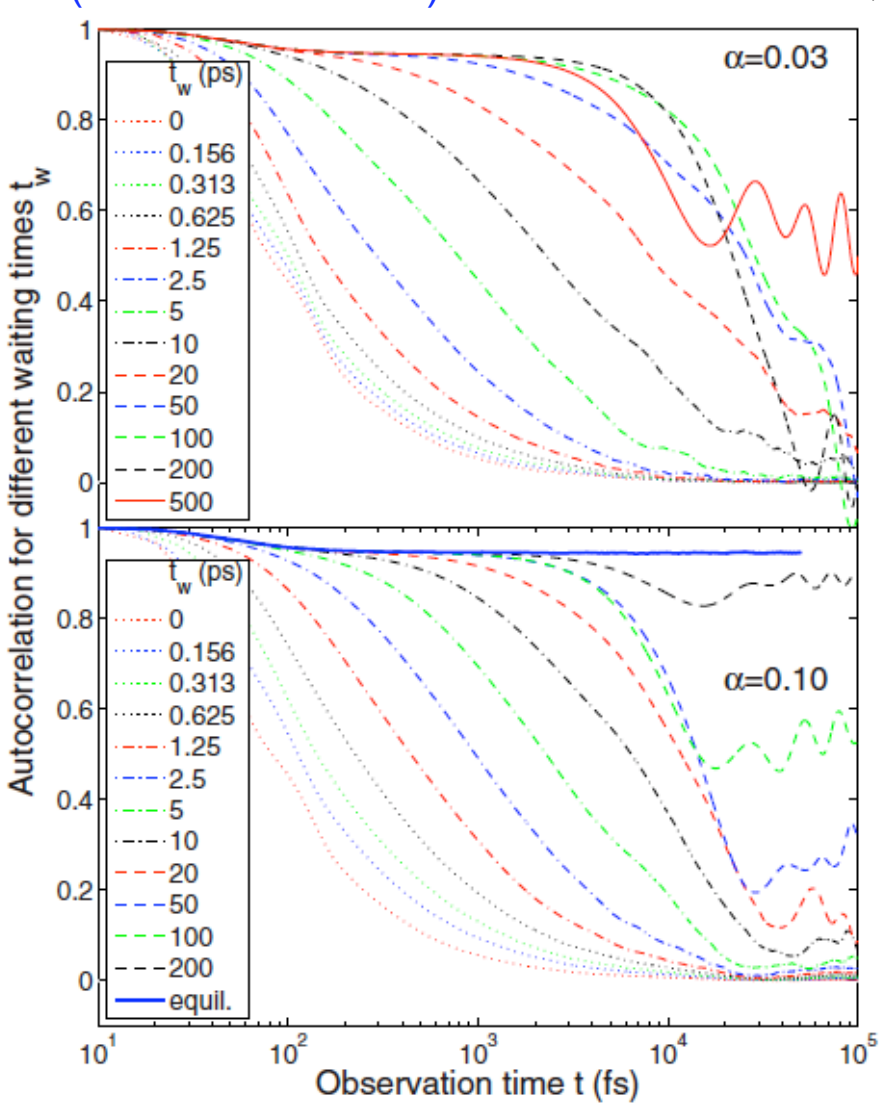
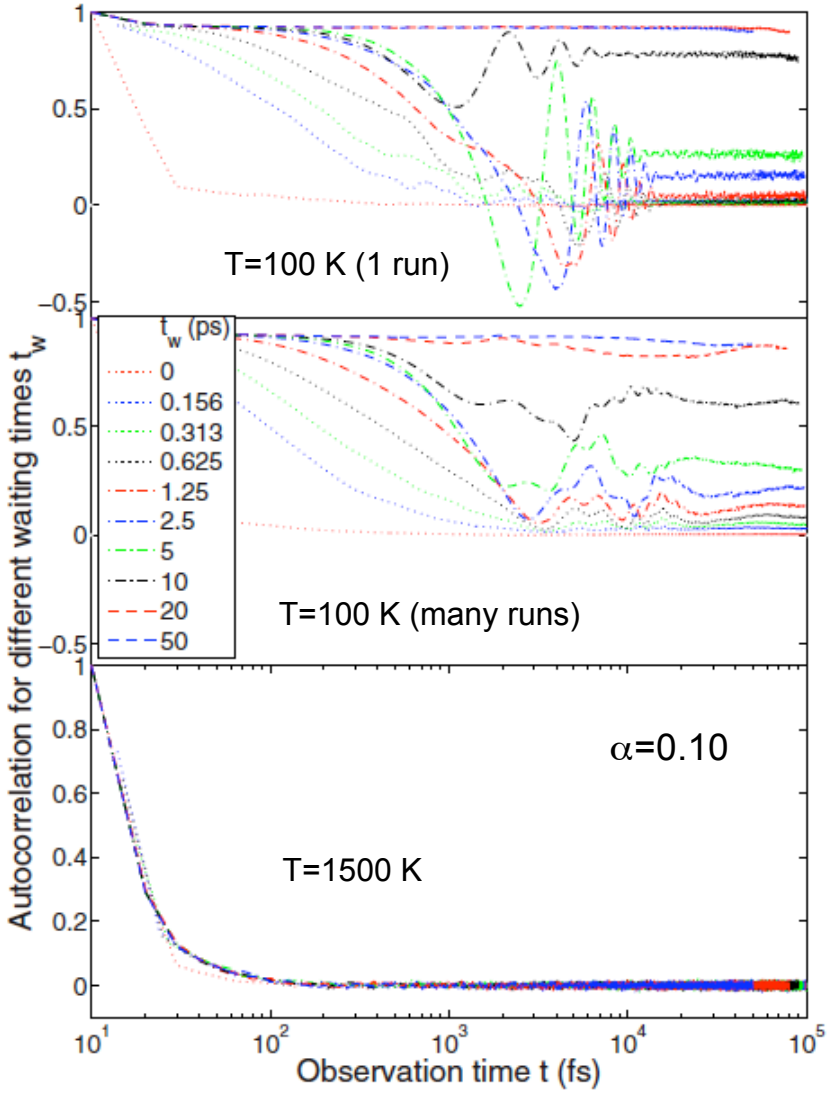
Is MnGaAs a spin glass ?

MnGaAs (0.25 % As antisite)

$$C_0(t_w + t, t_w) = \langle m_i(t_w) \cdot m_i(t_w + t) \rangle$$

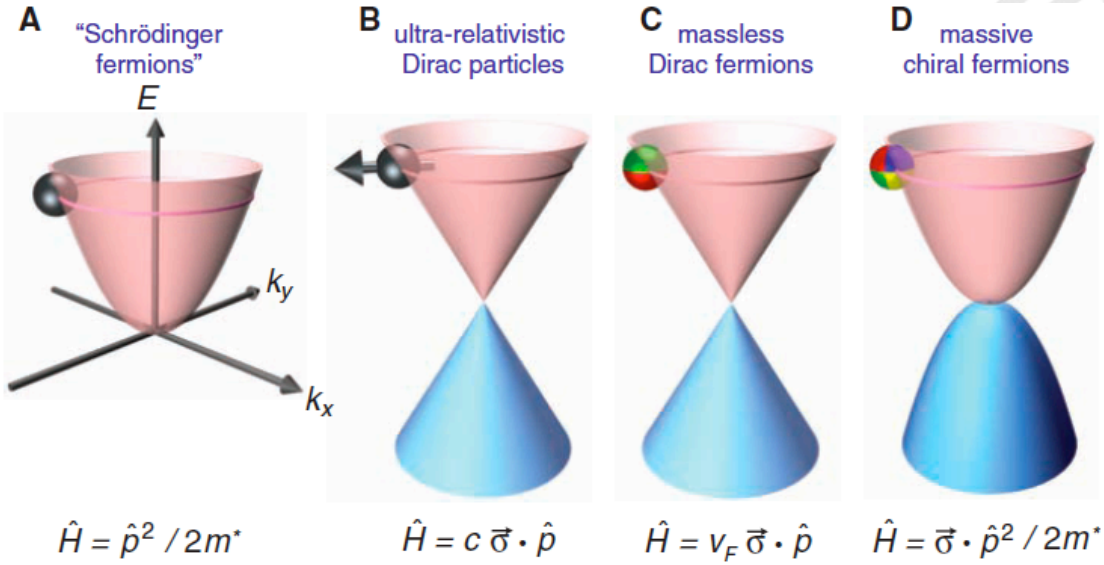
Bcc Fe





Exotic properties of graphene

- Existence of 2D crystal
- Similarity to QED (pseudospin & chirality) , massless Dirac Fermions
- Ambipolar electric field effect
- High mobility (almost independent of temperature)
- Anomalous quantum Hall effect
- Minimum quantum conductivity
- Applications: microprocessors, composites, hydrogen storage, gas-sensors, batteries, quantum computation, …….



Science **324**, 1530 (2009)

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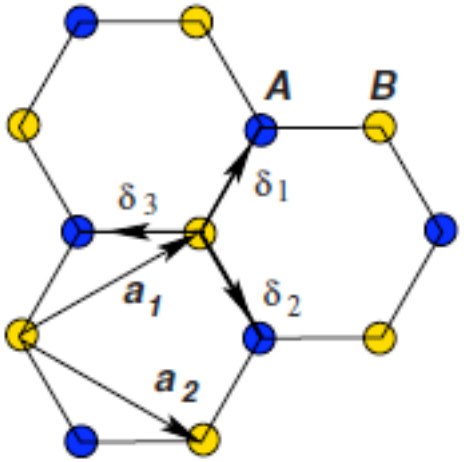
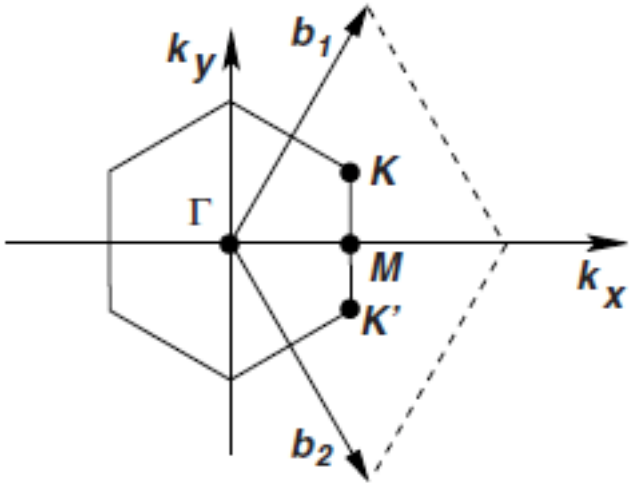
Electronic structure

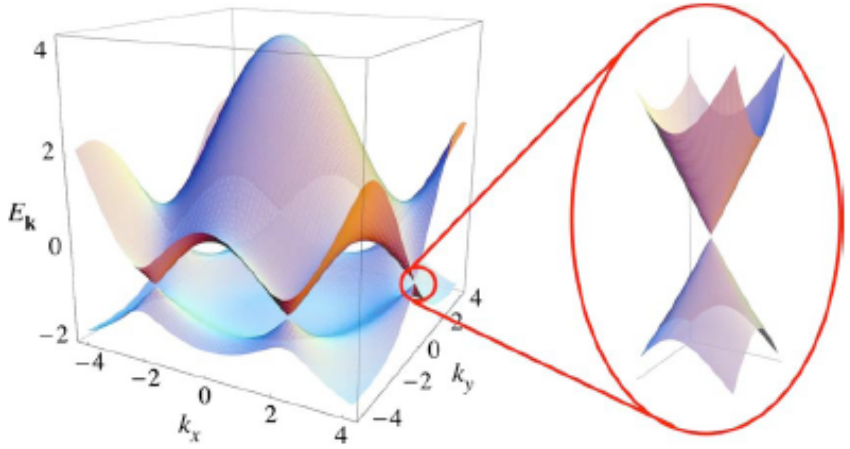


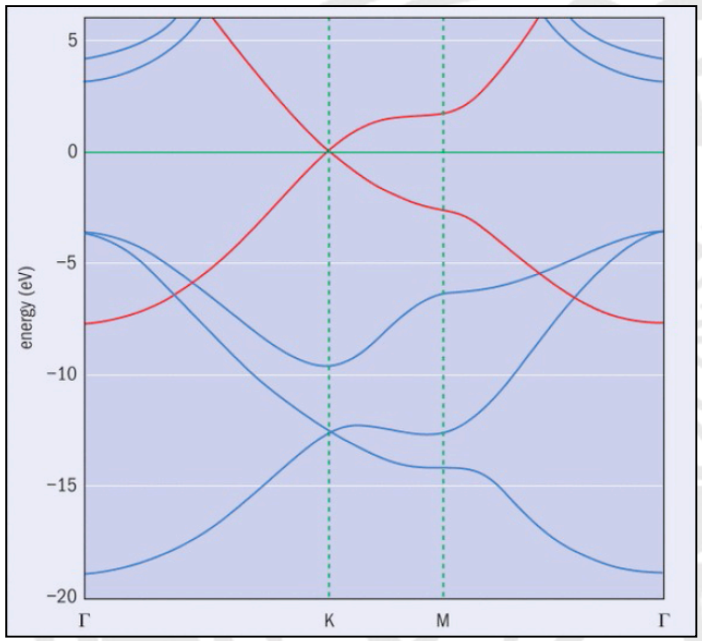


Linear dispersion around E=0 at K, K' (Dirac) pts.

$$E = \hbar v_F k$$

$$v_F = c/300$$





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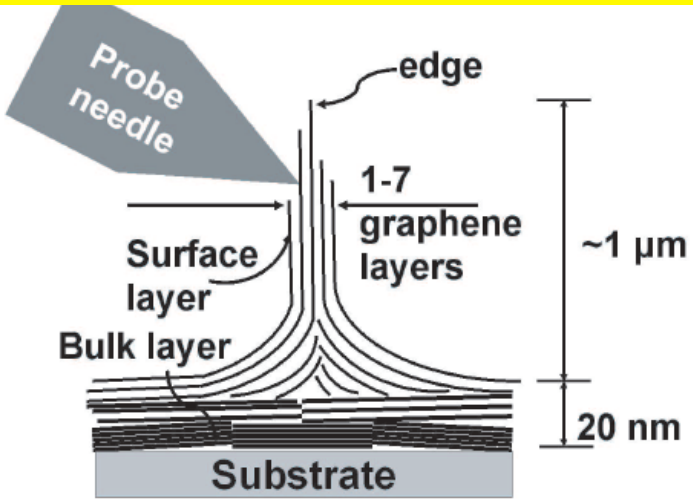
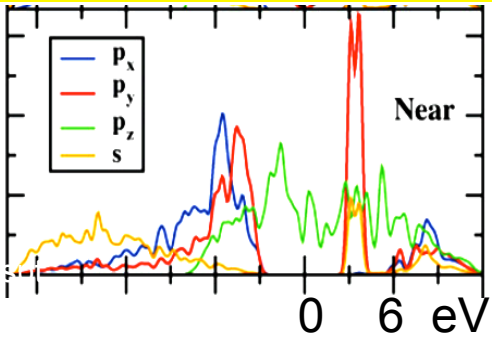
XAS on carbon nano-sheets

Schematic diagram of experiment



RF plasma-enhanced CVD --> introduction of defects by HCl treatment

DOS at neighborhood

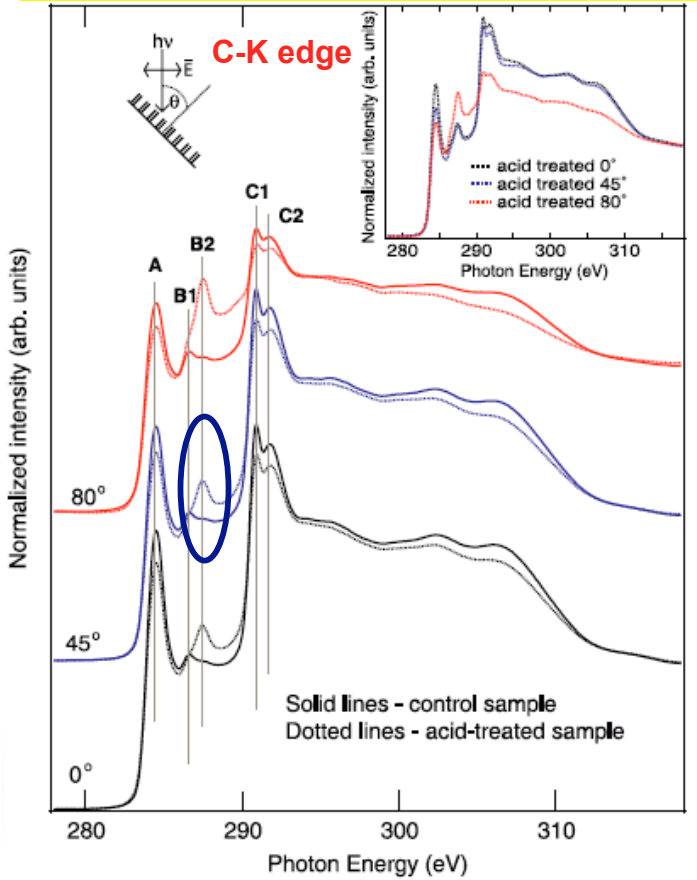


A -> π*

B1, B2 -> defect

C1,C2 -> σ*

X-ray absorption spectroscopy



Coleman et al., J. Phys. D: Appl. Phys. **41**, 062001 (2008)

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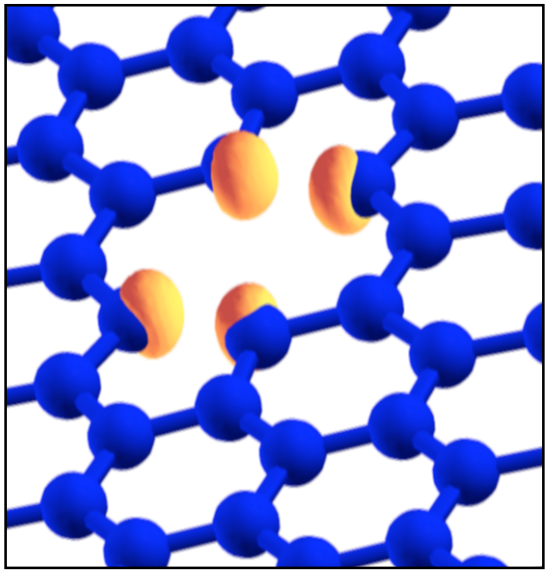
Graphene with a divacancy

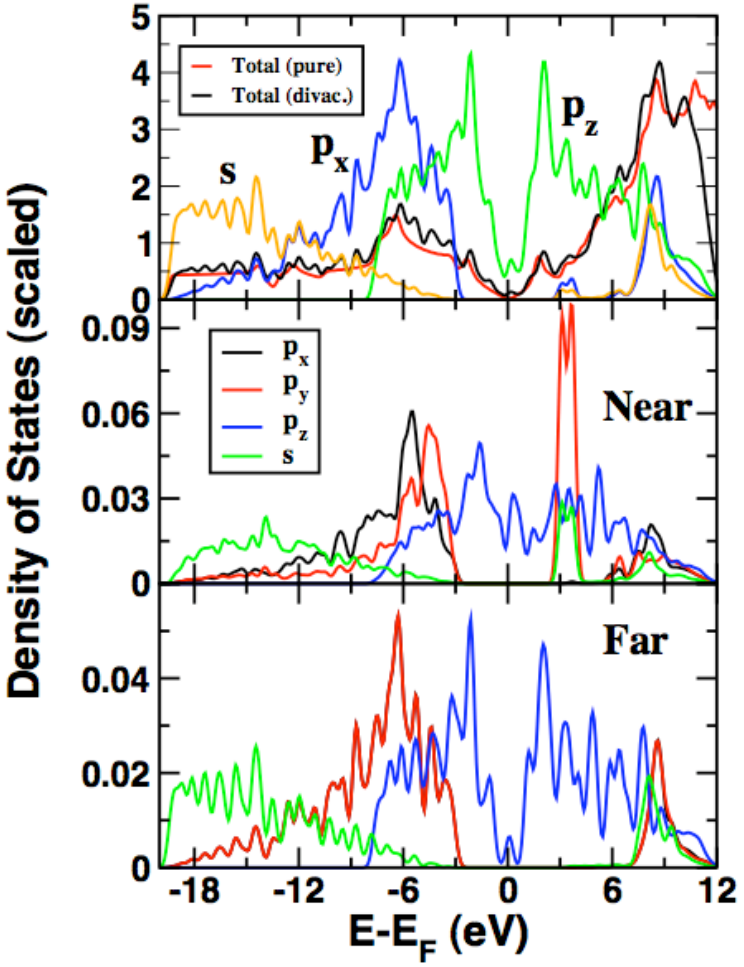
DFT supercell calculations



Defect induced peak in DOS

of in-plane σ^* character

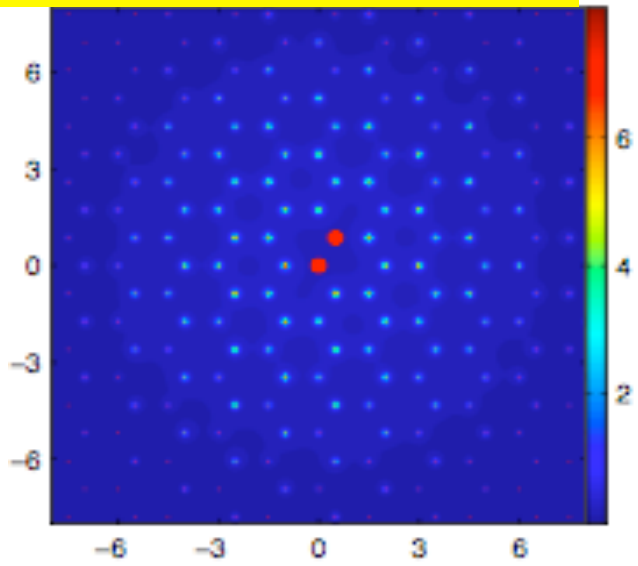
Increased DOS at Fermi level



Coleman et al., J. Phys. D: Appl. Phys. **41**, 062001 (2008)

Metallicity due to divacancy defects

Charge density distribution



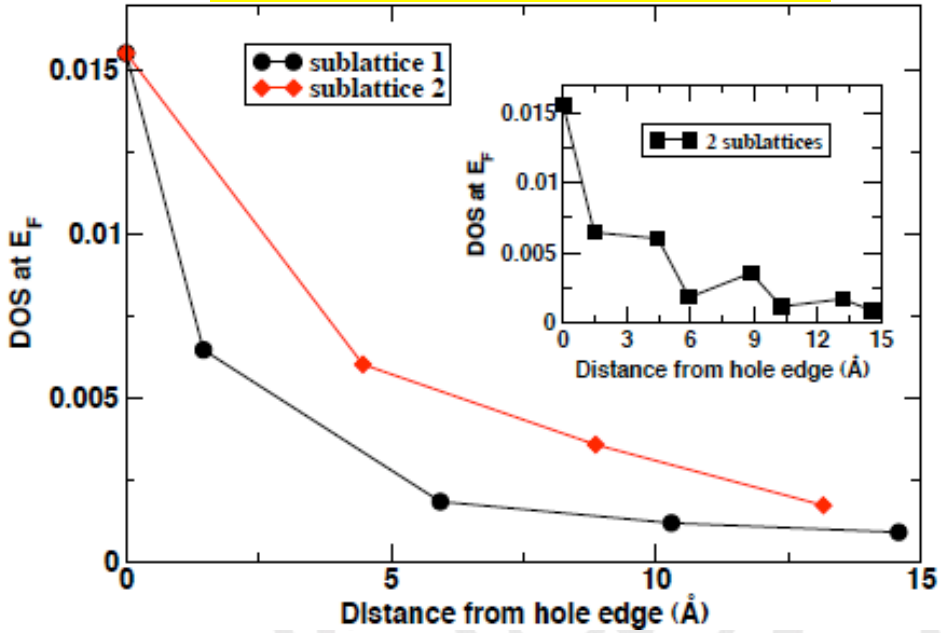
DFT-GGA
supercell calculations
(1.6 % vacancy)
Metallicity extends over
a large distance

Tight-binding Green's function calculations

Perturbed LDOS due to a vacancy at sublattice A

$$\delta N_B(r,E) = \frac{J_0^2(k_F|r-r_A|)}{4\pi\rho v_F^2}\,\mathrm{Im}\frac{(2D+i\pi)^2}{E\left[2\log(D/|E|)+i\pi\right]}$$

Metallic electronic structure



Engineering of defects
Controlling transport properties

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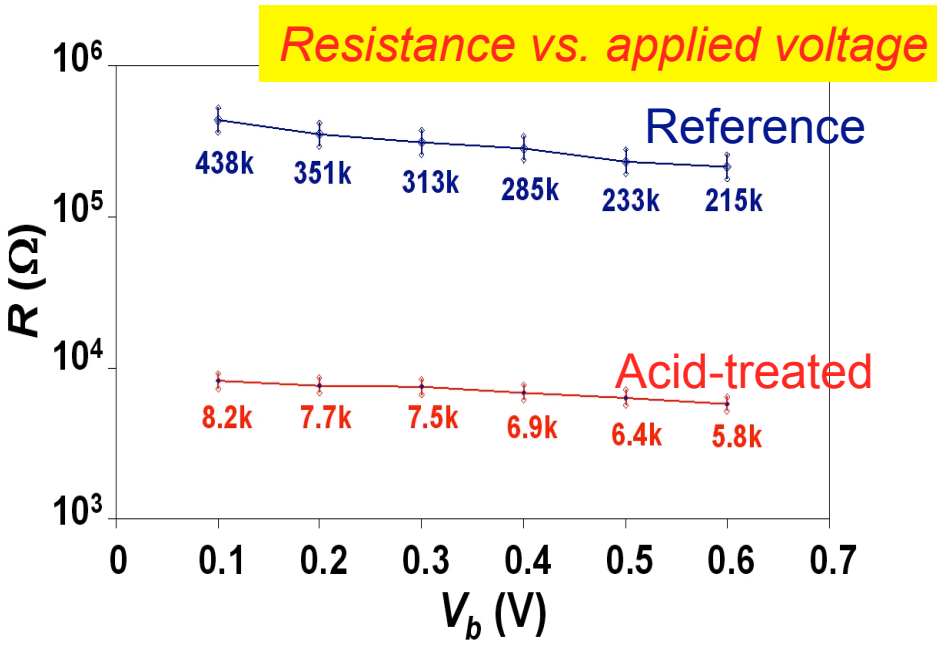
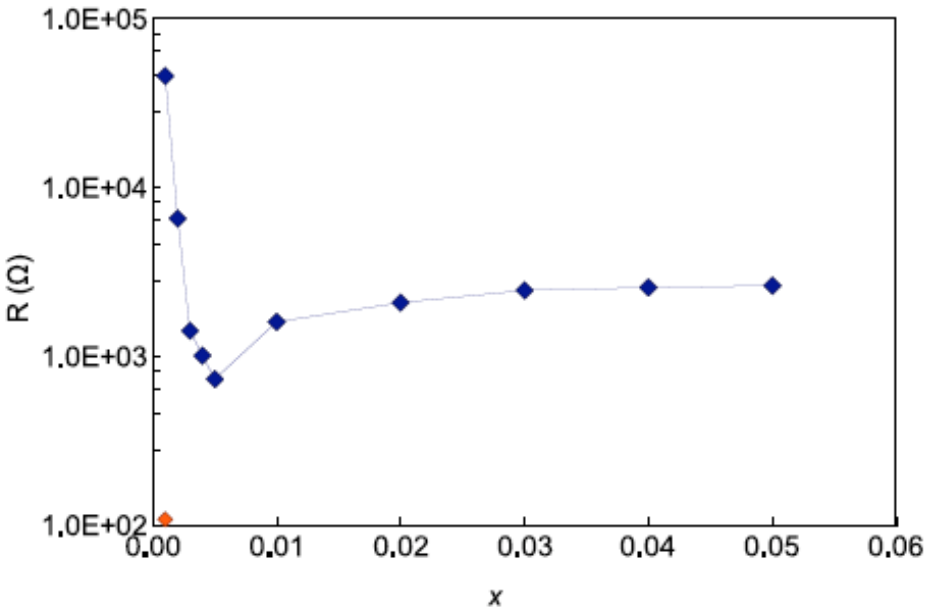
Experiment



With chemical treatment, 50 times decrease in resistance is observed.

J. Phys. D: Appl. Phys. (submitted)

Theory



TB-LMTO-ASA + CPA, Kubo linear response

Conductivity increases with vacancy concentration (metallicity due to mid-gap states)
For higher vacancy conc., conductivity decreases due to extra scattering

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Summary

•Quantum mechanical modeling of materials is very important for the understanding of properties in an atomic scale.
•Magnetic percolation effects are crucial for establishing long ranged magnetic order in diluted magnetic semiconductors due to short-ranged exchange interactions and chemical disorder. Theory explains the wide variation of ordering temperatures observed in different experiments.
•Vacancy defects give rise to mid-gap states at the Fermi level in graphene. A long-ranged metallicity occurs. Transport measurements show a 50 times increase in conductivity with chemical treatment that produces defects. Ab-initio transport calculations show an increase in conductivity in presence of vacancies.

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