Role of impurities and vacancies on the electronic and transport properties of magnetic semiconductors

Gul Rahman

Jaime Ferrer and Víctor M. García Suárez

Outline

1) Simulations: system and tools

2) Magnetic semiconductors

3) Stabilizing vacancies In SnO_2

System

- Marenostrum supercomputer

60 jobs executed

Some simulations in serial and some in parallel (60-120 nodes)

Execution times between 5 hours and 3 days

```
Siesta Version:
Architecture  : x86_64-unknown-linux-gnu--unknown
Compiler flags: mpif90 -g -O2
PARALLEL version

* Running in serial mode with MPI
>> Start of run:  14-DEC-2012   8:09:19

                        ***************************
                        *  WELCOME TO SIESTA  LDA+U *
                        ***************************

reinit: Reading from standard input
```

Requested machine: IBM powerPC cluster with myrinet
Interprocess communication: Tighitly Coupled

Typical job run:
Number of processors needed for each job: 128.00
Estimated number of jobs to submit: 100.00
Average job durations (hours) per job: 24.00
Total memory used by the job (GBytes): 20.00

Largest job run:
Number of processors needed for each job: 256.00
Estimated number of jobs to submit: 10.00
Average job durations (hours) per job: 72.00
Total memory used by the job (GBytes): 40.00

Total disk space (Gigabytes):
Minimun: 10.00
Desirable: 40.00

Total scratch space (Gigabytes):
Minimun: 1.00
Desirable: 10.00

Total tape space (Gigabytes):
Minimun: 10.00
Desirable: 40.00

Simulation tools

- SIESTA (Spanish Initiative for Electronic Simulations with Thoudands of Atoms)

J. M. Soler, E. Artacho,J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matt. 14, 2745-2779 (2002).

Density functional theory (DFT), linear combination of atomic orbitals (LCAO) and norm-conserving pseudopotentials.

- VASP (Vienna Ab initio Simulation Package)

G. Kresse and J. Furthmuller, Phys. Rev. B, 54, 11169 (1996).

DFT, plane waves (PW) and ultrasoft pseudopotentials.

SIESTA calculations

- Double-ζ polarized basis set (DZP)
- 400 Ry for the real space grid

- Relaxed coordinates with forces below 0.05 eV/Å

- LDA and LDA+*U* exchange-correlation functionals
U = 6.0 eV applied on the p orbitals of the oxygens

Unit cells with a number of atoms between 6 and 96

- From the SIESTA calculation we get:

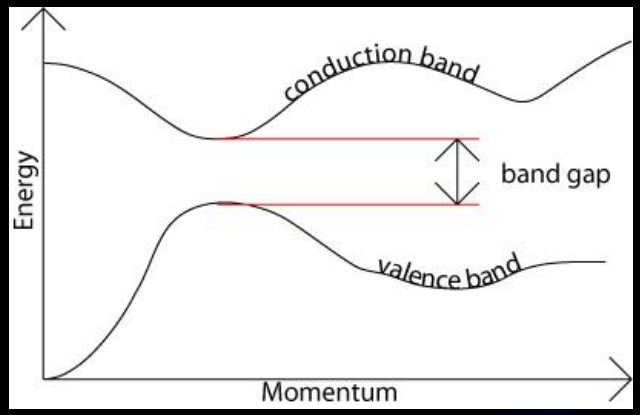
Total energy, magnetic moment, charge and spin densities

Formation energies:

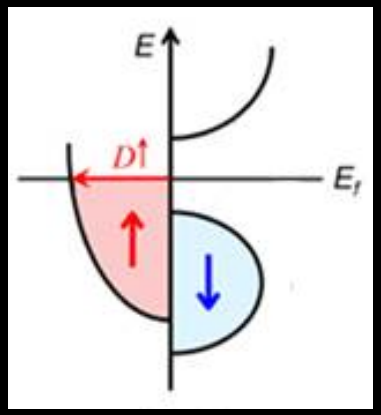
$$E_{\mathrm{f}} = E^{\mathrm{d}} - E^{\mathrm{p}} + n\mu_{\mathrm{X}} - m\mu_{\mathrm{Li}}$$

Magnetic semiconductors

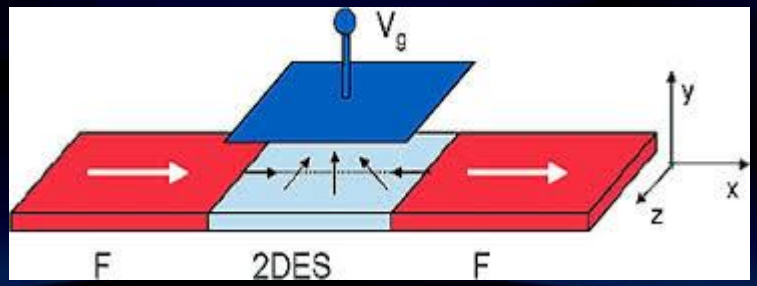
Semiconductor



Magnetic material



Spintronic applications

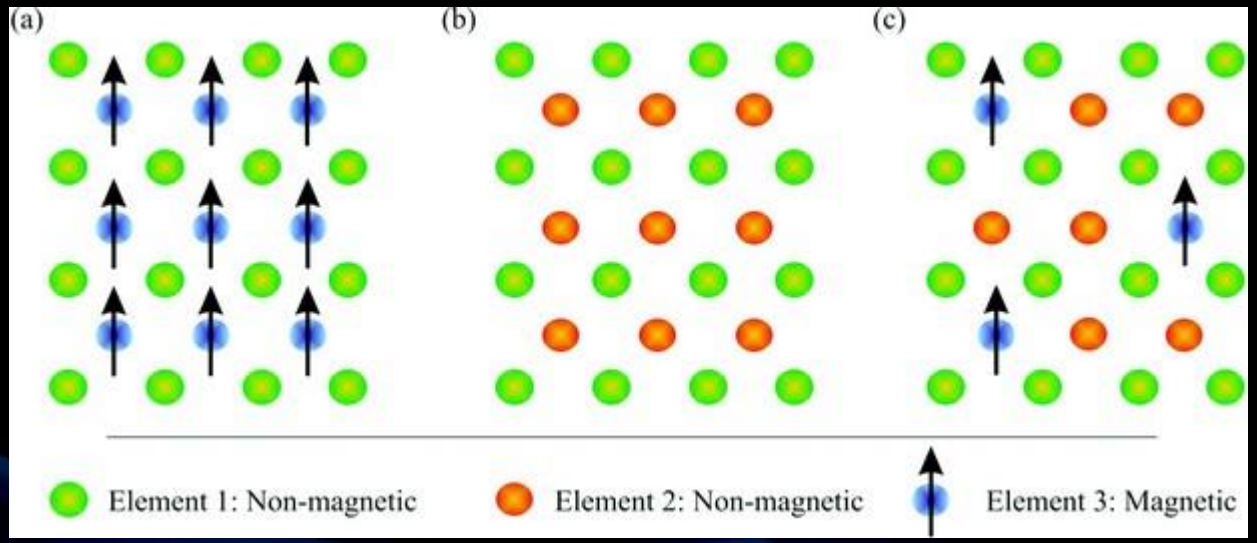


Both semiconductor and magnetic applications.

Ex.: magnetite. Not as good as typical semiconductors (can not be doped)

Diluted magnetic semiconductors

Spintronic applications



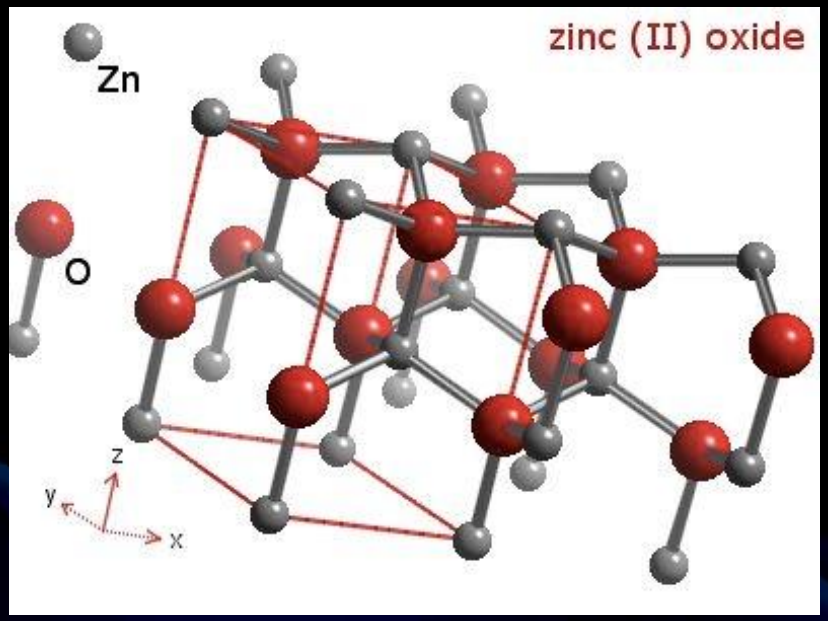
Hakimi *et al*., Phys. Rev. B. 82, 144429 (2010)

Examples:

- InAs:Mn, GaAs:Mn. Low Curie temperatures
- ZnO:Co. Curie *T* above RT. Transparent and piezoelectric. Spin transistors, spin polarized LEDs

Zinc oxide (ZnO)

Oxide used in rubbers, plastics and ceramics



Wurtzite structure

ZnO with O vacacancies or Zn interstitials (native doping): transparent and semiconductor (transparent electrodes)

Band gap: 3.2 eV

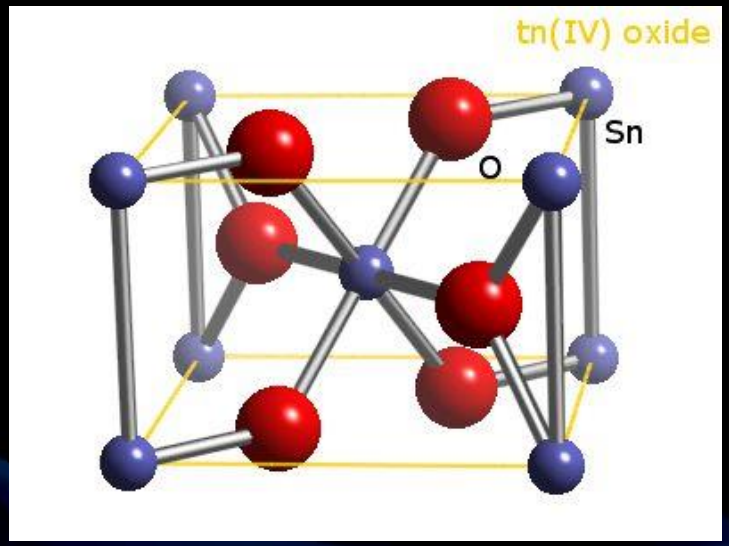
www.webelements.com

Doped with Co: $Zn_{1-x}Co_xO_{1-\delta}$
- Ferromagnetic with a Curie temperatura of 790 K
- Large magnetic moment of 6.1 μ_B/Co

C. Song *et al*., Phys. Rev. B 73, 024405 (2006)

Tin dioxide (SnO_2)

Oxide used in ceramic materials



Rutile structure

White or grey cristalline solid

Band gap: 3.7 eV

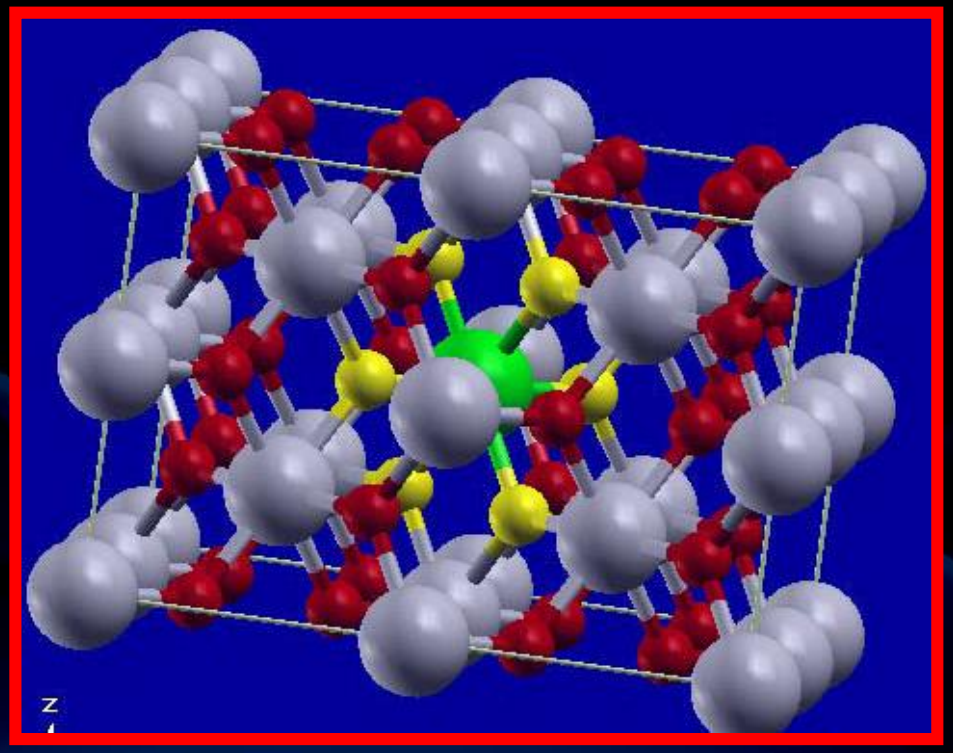
www.webelements.com

Doped with Co: $Sn_{1-x}Co_xO_{2-\delta}$
- Ferromagnetic with a Curie temperatura of 650 K.
- Giant magnetic moment of 7.2 μ_B/Co

S. B. Ogale *et al*., Phys. Rev. Lett. 91, 077205 (2003)

Simulation of SnO_2 with vacancies and Li impurities

Unit cell of SnO2 has 6 atoms (2 Sn and 4 O)



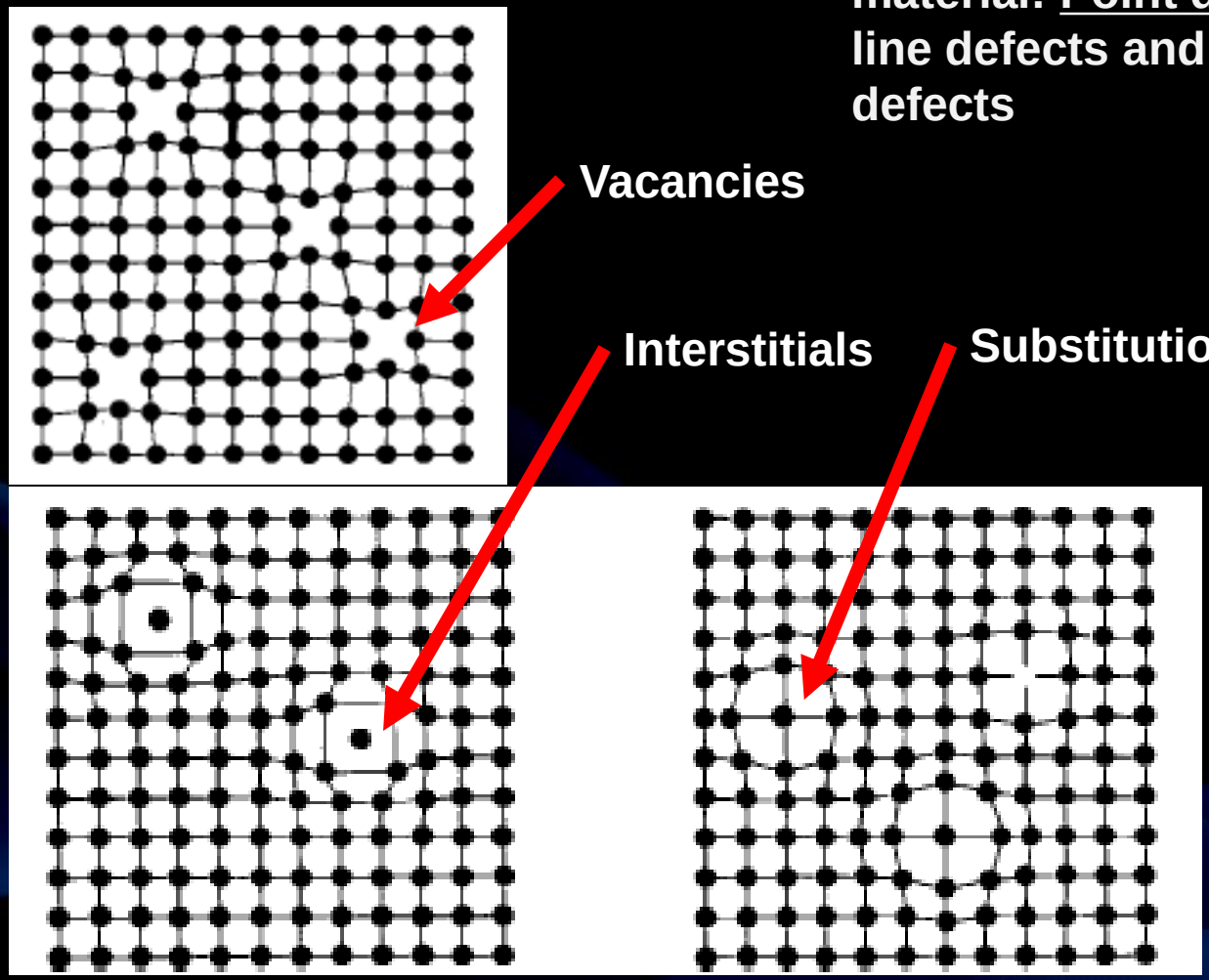
2x2x2 supercell (48 atoms) to study the effect of single vacanacies and defects

2x2x3 (72 atoms) and 2x2x4 (96 atoms) supercells to study how magnetic defects couple (FM or AFM configurations)

Point defects in materials

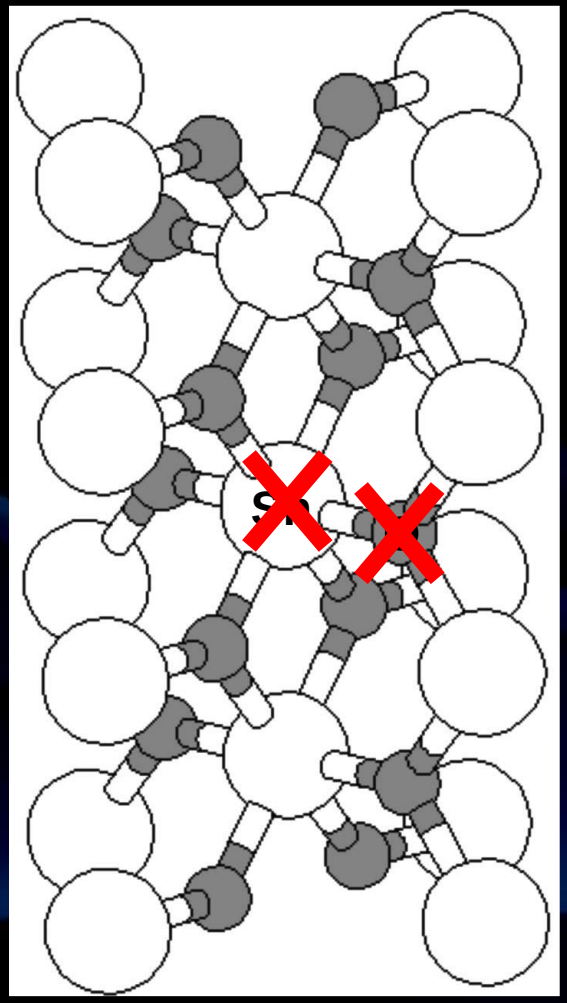
Real crystals are not perfect

Types of defects in a material: Point defects, line defects and interfacial defects



Vacancies in SnO_2

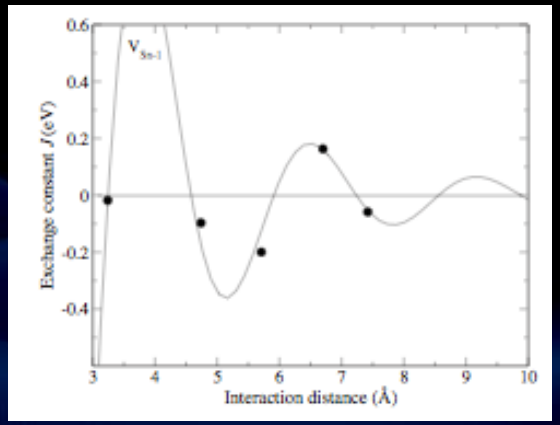
Vacancies in SnO_2 can have different magnetic properties:



O vacancy (V_O):
- Non-magnetic
- Formation energy: 1.64 eV

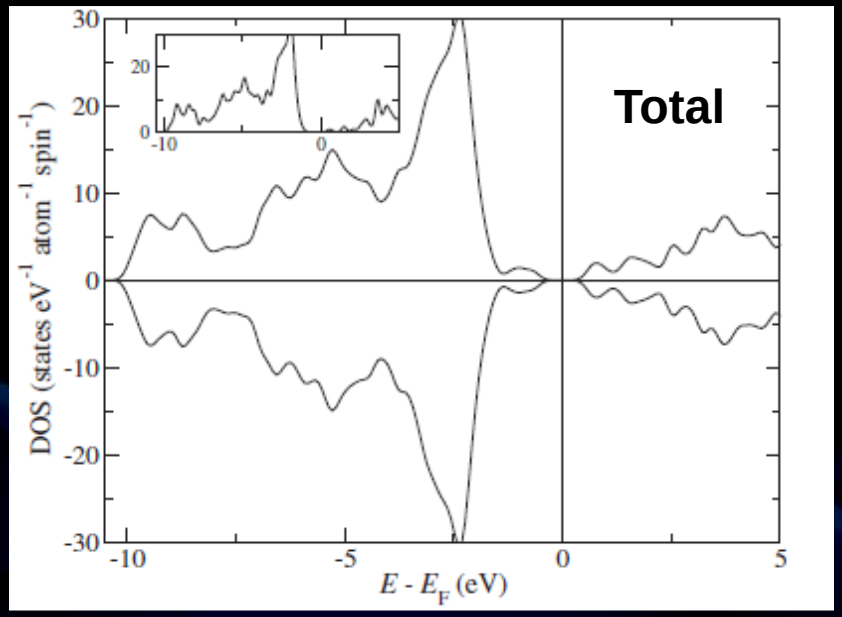
Sn vacancy (V_{Sn}):
- Magnetic. 4.00 μ_B/vacancy
- Formation energy: 6.87 eV

Sn vacancies couple FM or AFM

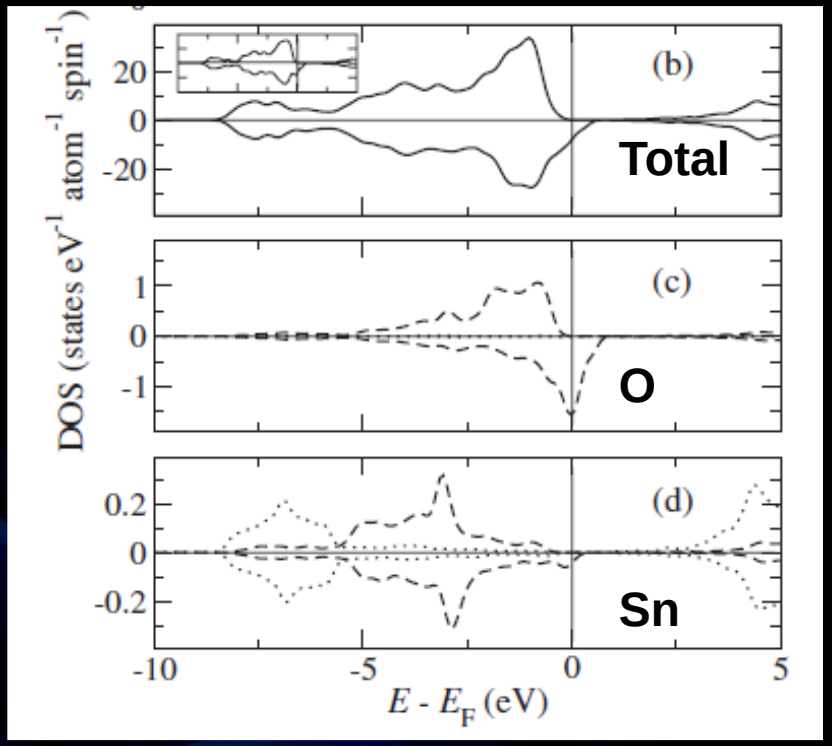


Electronic structure of vacancies

Oxygen vacancy



Tin vacancy



Transport: SnO_2 with V_{Sn} is a half-metal, good for spintronics applications

Experimental verification

Zn-doped SnO_2

4790 J. Phys. Chem. C 2010, 114, 4790–4796

Structure and Room-Temperature Ferromagnetism of Zn-Doped SnO_2 Nanorods Prepared by Solvothermal Method

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State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China, National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

Received: September 23, 2009; Revised Manuscript Received: February 14, 2010

- Doping of Zn creates V_{Sn} and V_O
- The presence of V_{Sn}-O-V_{Sn} can reduce the magnetic moment

Clustering of defects

PHYSICAL REVIEW B **81**, 064419 (2010)

Ferromagnetism in SnO_2-based multilayers: Clustering of defects induced by doping

A. Espinosa,[1] M. García-Hernández,[1] N. Menéndez,[2] C. Prieto,[1] and A. de Andrés[1]

[1]*Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain*

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(Received 24 September 2009; revised manuscript received 11 December 2009; published 19 February 2010)

- The presence of V_{Sn} could promote ferromagnetic coupling

Mn-doped SnO_2

THE JOURNAL OF PHYSICAL CHEMISTRY C ARTICLE

pubs.acs.org/JPCC

Origin of the Magnetism in Undoped and Mn-Doped SnO_2 Thin Films: Sn vs Oxygen Vacancies

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- V_O does not contribute to magnetism
- V_{Sn} promotes magnetism

The role of the formation energy

Concentration of defects in a material

$$c = n_{\text{site}} \exp\left(\frac{-E_{\text{f}}}{k_{\text{B}}T}\right)$$

c → point defect concentrations
n_{site} → number of sites
E_{f} → defect formation energy

Formation energy of a vacancy

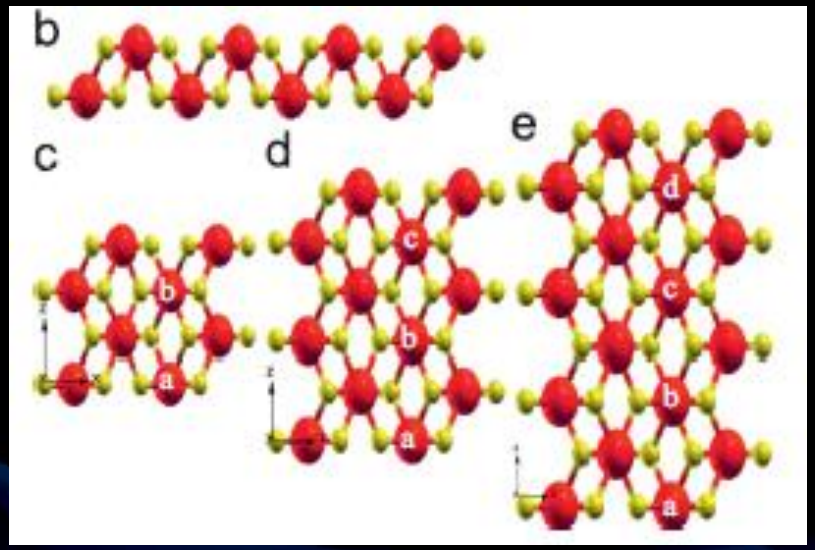
$$E_{\text{f}} = E^{\text{d}} - E^{\text{p}} + n\mu_{\text{X}}$$

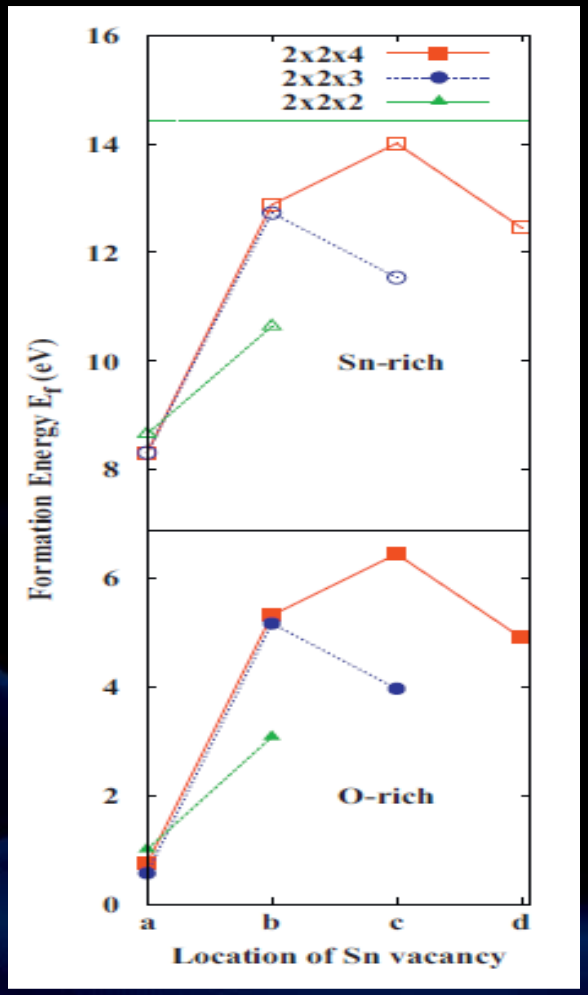
The larger the formation energy the lower the concentration of vacancies

- V_O has a low formation energy but does not promote magnetism
- V_{Sn} has a large formation energy

SnO_2 nanosheets

4x4x1 (b), 2x2x2 (c), 2x2x3 (d) and 2x2x4 (e) supercells





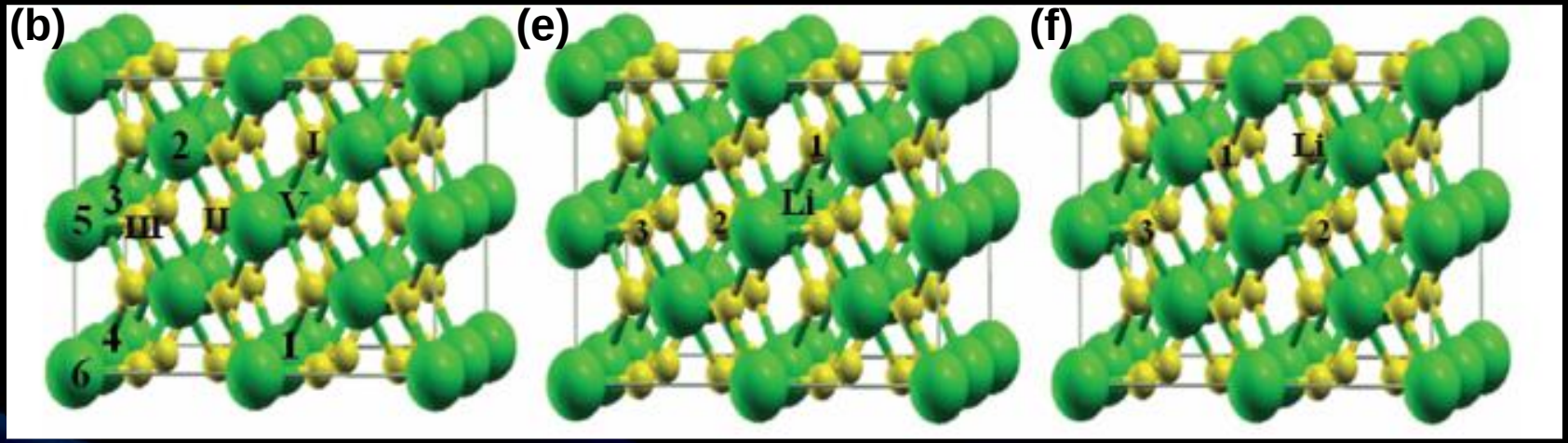
The formation energy decreases

- Towards the surface

- As the width of the sheets decreases

Li doping in SnO_2

Vacancies and Li impurities. Supercells with 48 atoms



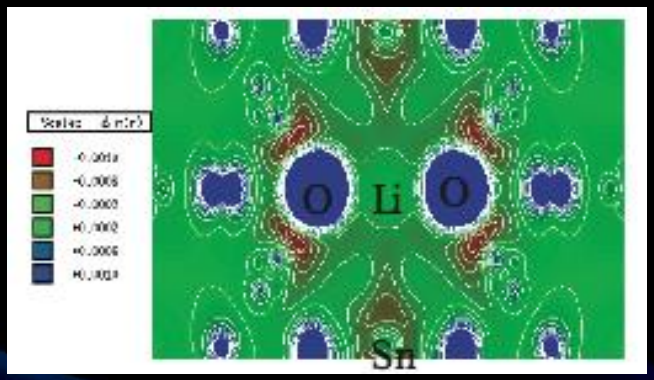
Several configurations:

(a) Li - doped SnO_2 (Li_{Sn}, Li_O, Li_{int})
(b) V_{Sn} + $Li_{Sn\,j}$
(c) V_{Sn} + $Li_{O\,j}$
(d) V_{Sn} + Li_{int}
(e) $V_{O\,j}$ + Li_{Sn}
(f) V_O + $Li_{O\,j}$
(g) V_O + Li_{int}

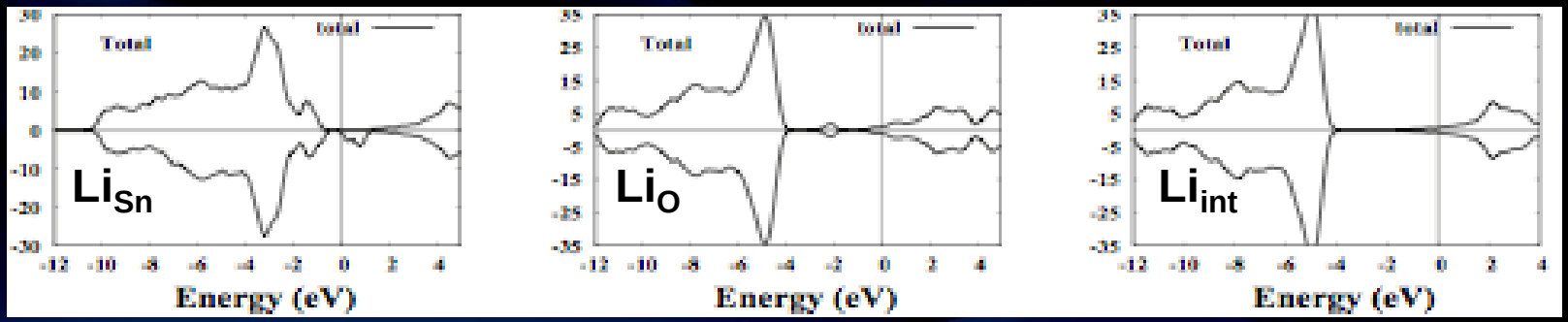
Li impurities only

Li_{Sn}:
- Magnetic. 3.00 μ_B/vacancy
- Formation energy: -1.03 eV

Li_O:
- Non-magnetic
- Formation energy: -0.85 eV



Li_{int}:
- Non-magnetic
- Formation energy: -2.58 eV



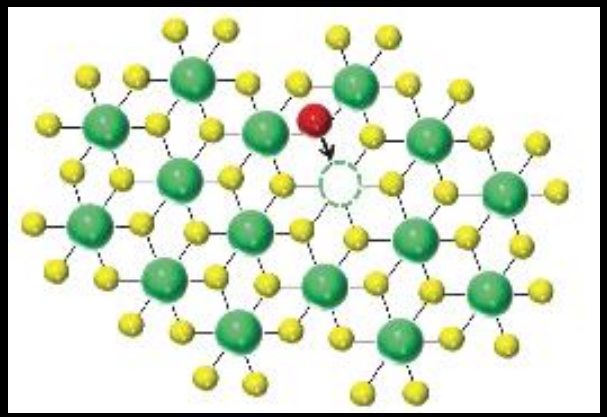
Transport: semiconducting or metallic

Ferromagnetic coupling

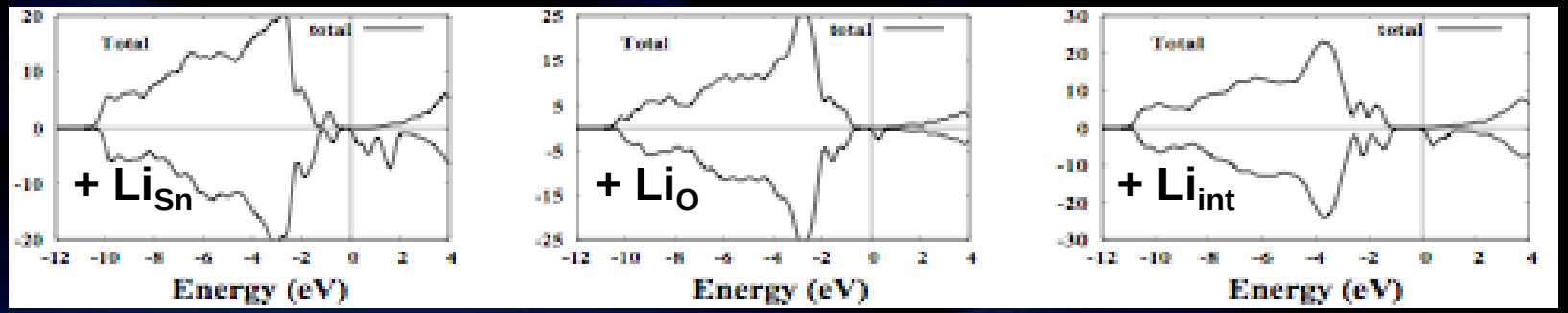
V_{Sn} + Li in different positions

V_{Sn} + Li_{Sn}:
- Magnetic. 7.00 μ_B/unit cell
- Formation energy: 1.54 eV

V_{Sn} + Li_O:
- Magnetic. 1.00 μ_B/unit cell
- Formation energy: -4.16 eV



V_{Sn} + Li_{int}:
- Magnetic. 3.00 μ_B/unit cell
- Formation energy: 1.83 eV



Transport: semiconducting or half-metallic

V_O + Li in different positions

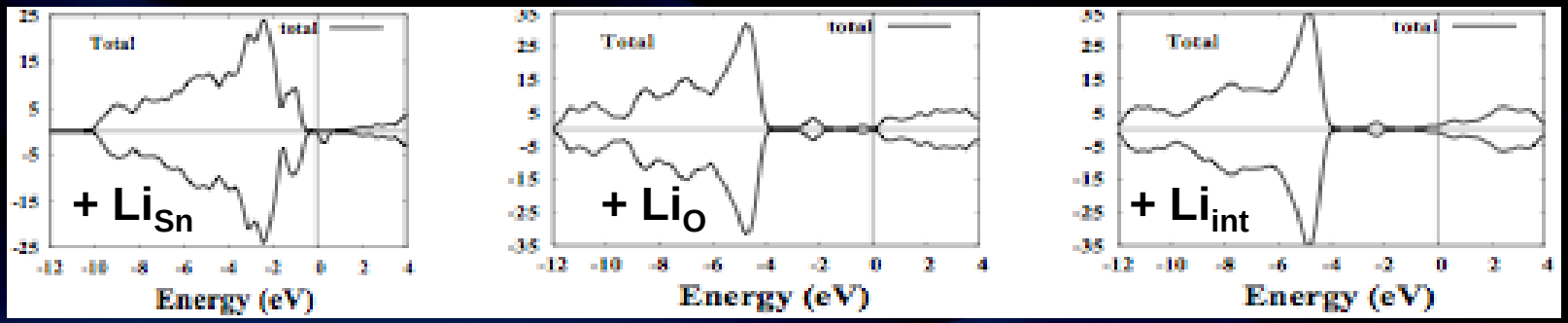
V_o + Li_{Sn}:
- Magnetic. 1.00 μ_B/unit cell
- Formation energy: -3.69 eV

V_o + Li_O:
- Non-magnetic
- Formation energy: 0.15 eV

V_o + Li_{int}:
- Non-magnetic
- Formation energy: -0.96 eV

Role of structural relaxation:

System	E_{eq}
Li_{Sn}	-1.03(-0.89)
Li_O	-0.85 (5.72)
Li_{int}	-2.58(-1.63)
V_{Sn}	6.87 (7.32)
V_O	1.64 (1.69)



Transport: metallic or half-metallic

Experimental verification

Induced magnetism in Li-doped SnO_2

Non-magnetic doping induced magnetism in Li doped SnO_2 nanoparticles

S. K. Srivastava[1*], P. Lejay[2], A. Hadj-Azzem[2] and G. Bouzerar[2]

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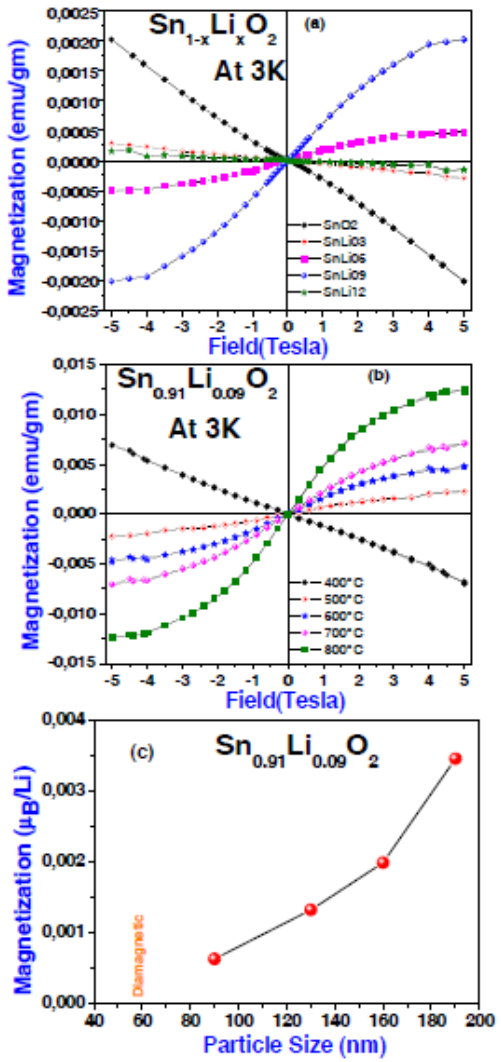
[2]Institut Néel, CNRS Grenoble and Université Joseph Fourier, Grenoble, Cedex 9, France-38042

J. Superconductivity and Novel Materials, 2013



- Pure SnO_2 NP: diagmagnetic
- Li-doped NP: ferromagnetic

Li promotes magnetism in SnO_2

Conclusions

- Sn vacancies (V_{Sn}) in SnO_2 can promote magnetism and influence the magnetic properties of doped systems

- The formation energy of vacancies can be decreased by doping SnO_2 with light elements (Li)

- Doping with non-magnetic light elements can also promote magnetism

Publications

- *Vacancy-induced magnetism in SnO_2: A density functional study*. Gul Rahman, Víctor M. García-Suárez, and Soon Cheol Hong, Phys. Rev. B **78**, 184404 (2008). **91 cites**.

- *Intrinsic magnetism in nanosheets of SnO_2: A first-principles study*. Gul Rahman, Víctor M. García-Suárez, and Juliana M. Morbec, J. Mag. Mag. Mat. **328**, 104 (2013). **6 cites**.

- *Stabilizing intrinsic defects in SnO_2*, Gul Rahman, Naseem Ud Din, Víctor M. García-Suárez, and Erjun Kan, Phys. Rev. B **87**, 205205 (2013). **9 cites**.

Thank you