Ferromagnetism in Fe-doped rutile TiO_2: the role of defects and the long-range magnetic ordering mechanism.

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Titanium dioxide is one of the most investigated and most widely used metal oxides.

- Heterogeneous catalysis
- Solar cells
- Gas sensor
- White pigment in paints and cosmetics products
- Corrosion-protective coating
- Optical coating
- Ceramics applications
- Electronic devices
- Bio-implants

TiO_2 is also of significant interest in spintronics.

GOAL: to extend the properties and applications of electronic devices by making use of the spin of electrons in addition to their charge to convey information.

Such spin-polarized electronic devices could be much smaller, consume less energy, and be more efficient that the actual ones which are based on electron charge only

New fundamental physics.

Magnetism and semiconducting properties are known to coexist in some ferromagnetic semiconductors

Europium chalcogenides

ferrimagnetic or ferromagnetic semiconducting spinels

difficult to grow

Curie temperatures (T_C) well below 100 K.

Alternative:

diluted magnetic semiconductors (DMS):

non-magnetic semiconductors doped with magnetic atoms.

II-VI compound semiconductors (Mn-doped CdTe and ZnSe)

T_C in the order of 1 K.

III-V semiconductor compounds (Mn-doped GaAs)

T_C as high as 110 K

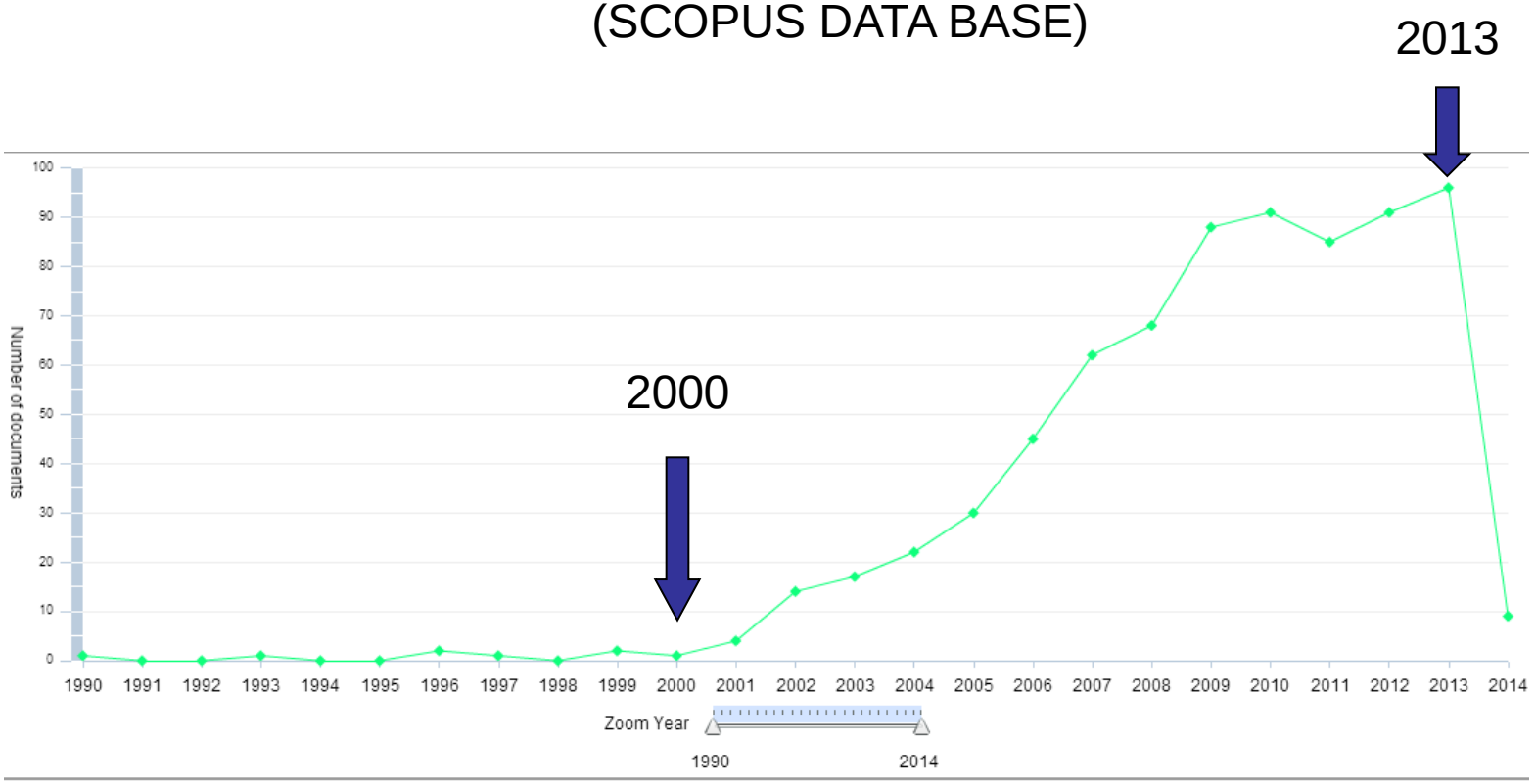
2001, Matsumoto *et al.:* Co-doped anatase TiO_2 films grown by a combinatorial pulsed-laser-deposition (PLD) molecular beam epitaxy (MBE) technique can keep ferromagnetic order up to 400 K.

Papers that contain

"Room temperature ferromagnetism …" in their title:

730 works (1990-2014)

(SCOPUS DATA BASE)



Room-temperature ferromagnetism observed in:

✓Carbon based Systems (grapheno, graphite, etc.)

✓Pure transition metal oxides (ZnO, TiO_2, SnO_2, HfO_2, Y_2O_3, In_2O_3, etc.)

✓Transition metal oxides doped with non magnetic impurities (H, C, B, Cu, etc.)

✓Transition metal oxides doped with magnetic impurities (below percolation limits to have long range order)

«Room-temperature ferromagnetism in …»

- ✓ *Transparent Transition Metal Doped Titanium Dioxide*", Matsumoto et al., SCIENCE (2001)
- ✓ *Novel diluted magnetic semiconductor* $Cd_{1-x}Mn_xGeP_2$, G. Medvedkin et al, Japn Journal Applied Phys (2000)
- ✓ *Carbon-Doped ZnO*, H. Pan et al, PRL (2007)
- ✓ *In Graphite Driven by Two-dimensional Networks of Point Defects*, J. Cervenka, Nature Physics (2009)
- ✓ *Hydrogenated Epitaxial Graphene*, A.J.M. Giesbers, Phys. Rev. Lett. (2013)
- ✓ SnO_2 *nanocrystalline powders with nonmagnetic K doping*, W. Zhou Physics letters A (2012)

"*Room-temperature ferromagnetism in*

✓ *"Appearance of room temperature ferromagnetism in Cu-doped $TiO_{2-\delta}$ films".*

S. Duhalde et al.

Phys. Rev. B 72, 161313(R), 2005 (rapid communication).

✓*"Theoretical Study of magnetism in transition metals doped TiO_2 and $TiO_{2-\delta}$ ".*

L. A. Errico, M. Weissmann y M. Rentería.

Phys. Rev. B 72, 184425, 2005.

Intensive experimental and theoretical studies, but:

Intrinsec character difficult to accept do to:

- Role of magnetic impurities?

  It is almost impossible to obtain a pure system (although you do not see it the iron is always there!!!)

Observed magnetic moment: 10^{-3}-10^{-5} emu/g	1 μg Fe/g contributes to saturation magnetization with 2.2 x 10^{-4} emu/g

One of the most popular phrases in these works is: "…ferromagnetism which cannot be explained by simple magnetic impurities…"

Despite these disagreements and experimental difficulties intrinsic room temperature ferromagnetism has finally been observed and proved in a broad spectrum of materials

A characteristic in common in these systems:

DEFECTS

- Anions vacancies
- Cation vacancies
- interstitial atoms
- dopant atoms
- Grain boundaries
- Interfaces
- surfaces

I) A brief summary of our experimental work.

II) Our theoretical results on Fe doped TiO_2.

Part I

A brief summary of our experimental work.

Experimental study:

Magnetic characterization:

Superconducting **Qu**antum **I**nterference **D**evices

Magnetic ordering

Magnetic moments

Experimental study:

X-ray absorption techniques:

Extended **X**-ray **A**bsorption **F**ine **S**tructure

X-ray **A**bsorption **N**ear **E**dge **S**pectroscopy

Chemical state.

Coordination.

Type of neighbours.

Experimental study:

Mössbauer Spectroscopy:

Quadrupole splitting: Proportional to the EFG. Fingerprint of the local symmetry around the Mössbauer probe (^{57}Fe).

Isomer shift (**IS**): Information on the local chemical bond of the probe.

Mössbauer Spectroscopy.

"isomer shift": information on the local chemical bond

$$IS = \alpha\left(\psi_a(0) - \psi_s(0)\right)$$

Quadrupole splitting: is a "fingerprint" of the local symmetry around the probe nucleus

$$\Delta Q = \frac{eq}{2} V_{ZZ}\left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

$$V_{ij} = \frac{\partial^2 V(\vec{r})}{\partial x_i x_j} \qquad \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

$$|V_{XX}| < |V_{YY}| < |V_{ZZ}|$$

Fe doped TiO_2 by mechanical alloying

(nanoparticles with sizes between 15 and 20 nm)

TiO_2 + hematite
TiO_2 + FeO
} $Ti_{1-x}Fe_xO_{2-\delta}$ (2.5<x15 at. %)

Magnetic properties

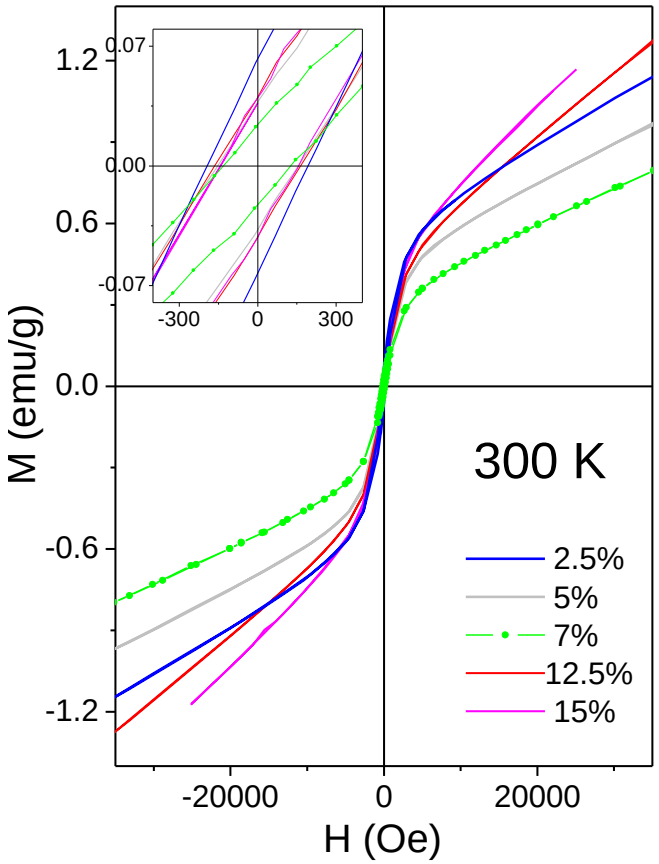
Room Temperature Ferromagnetism

+

Paramagnetism

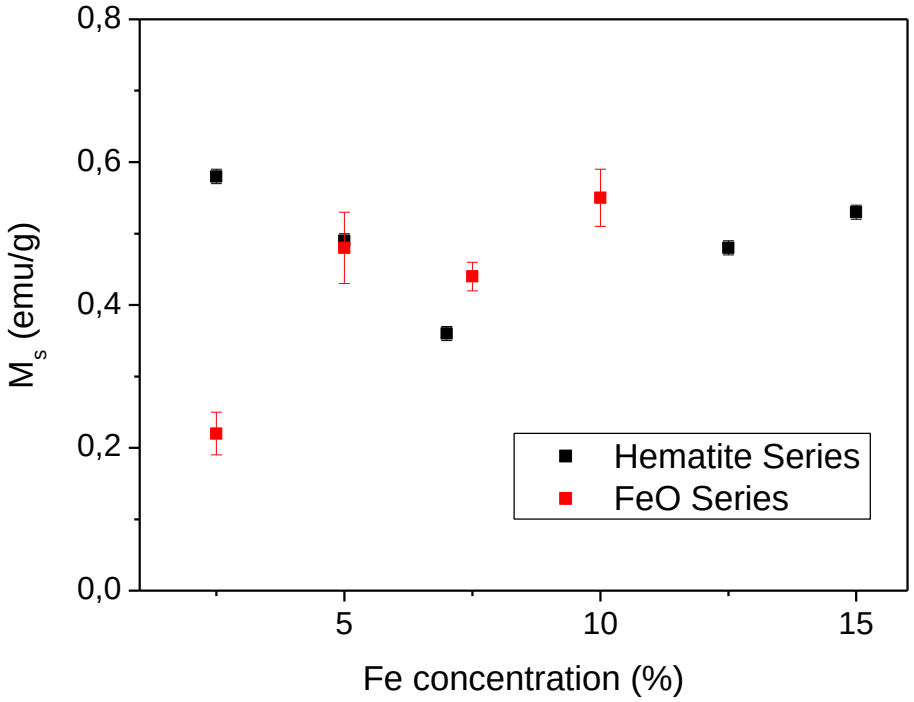
+

Antiferromagnetism

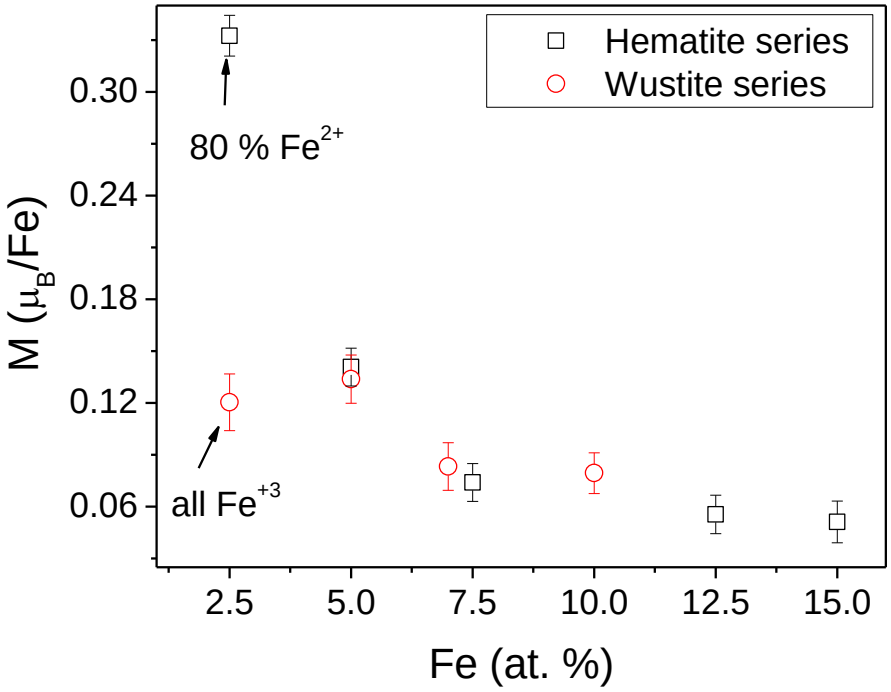


M_S remains almost constant independently of concentration.

Only a fraction of the total volume of the sample is involved in the ferromagnetic response of the system.



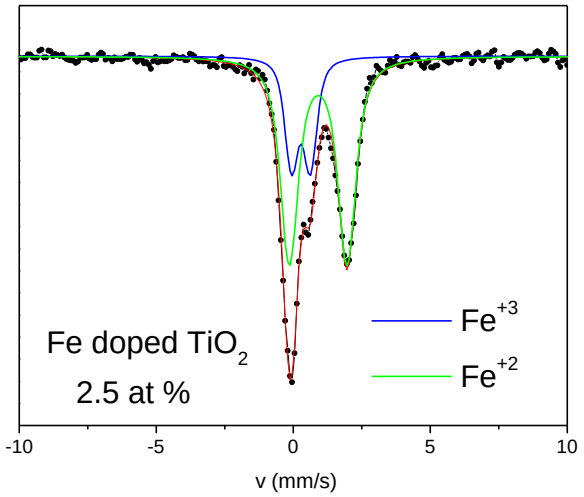
The moment per dopant cation decreases as the dopant concentration increases, suggesting antiferromagnetic interaction among iron ions and frustration.

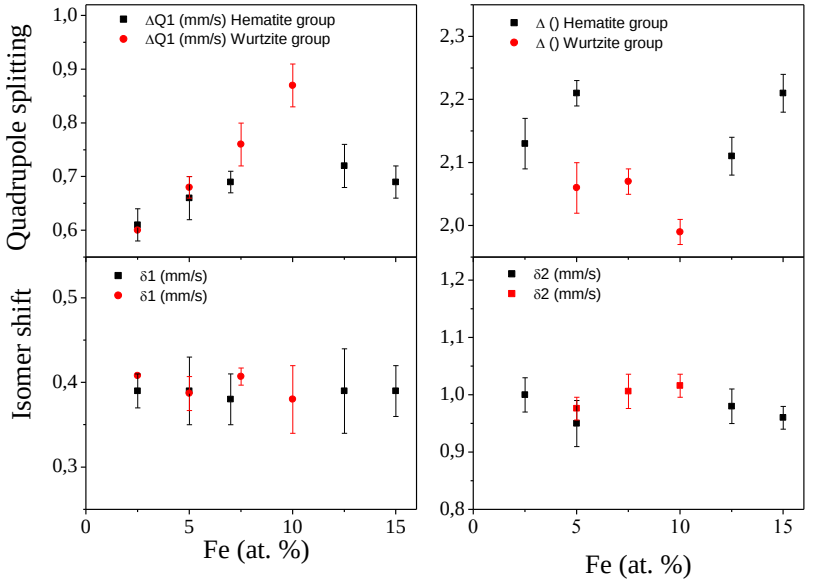


Fe doped TiO_2 (obtained by Mechanicall Alloying)

Ms is usually smaller than what is expected for Fe^{3+} or Fe^{2+} ions with values as low as 0.05 μ_B/Fe

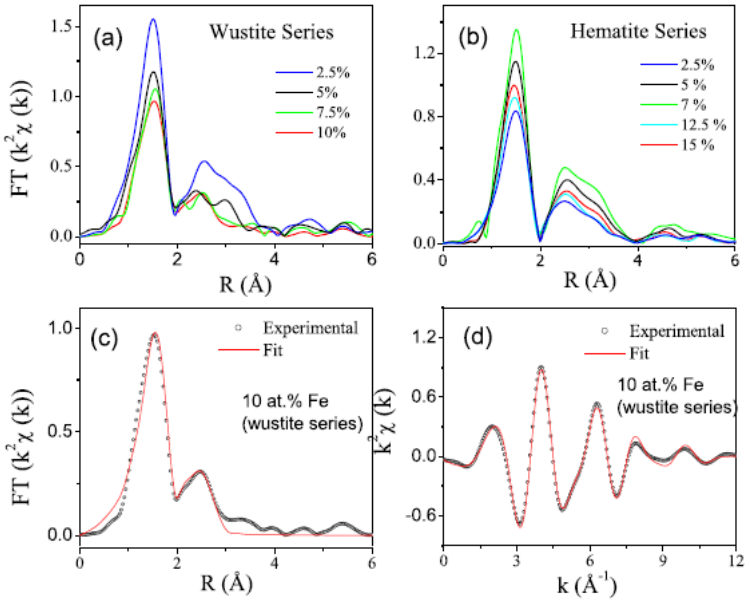
Hyperfine characterization (MS)





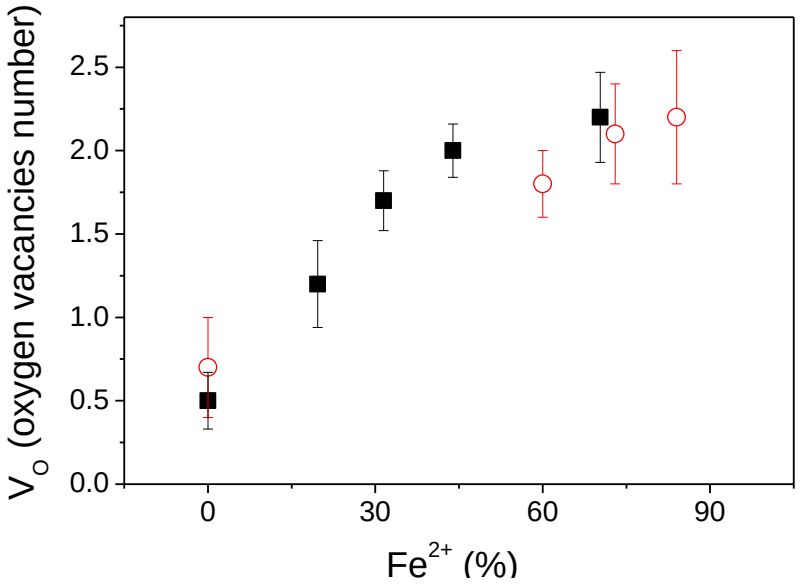
Fe^{+2} interaction appears only in samples obtained by non-equilibrium methods

XAS characterization



There is at least one oxygen vacancy near each iron ion.

X ray absorption confirms that Fe^{+3} or Fe^{+2} replace Ti^{+4} ions in the host.



Part II

Our theoretical results on Fe doped TiO_2.

Room Temperature Ferromagnetism

Unpaired electrons which provide the magnetic moments + Ferromagnetic coupling of these moments + Curie temperature higher than room temperature

MM | FMC | $T_C > RT$

Magnetic 3d impurities

Magnetic 3d impurities + defects (such as V_o)

Other non magnetic impurities + defects

MECHANISM????

Existing mechanisms for ferromagnetism in the diluted limit cannot explain the complex collection of observed phenomena in oxides:

"**super-exchange**"- ruled out: results in antiferromagnetic order.

"**p-d Zener model**"- ruled out: in pure and doped oxides the carrier concentration is very low.

"**double-exchange**"- ruled out: short ranged and RTF can be obtained only for impurity concentration above the nearest neighbour (NN) percolation threshold.

"**donor impurity band exchange**"- Coey et. Al. Ruled out: Simulations with Monte Carlo models predict extremely low T_c values. RTF is obtained only with unrealistically high values of the exchange coupling

In contrast to mass magnetization (assuming that the whole sample mass is ferromagnetic) it is suggested that the ferromagnetic part of the volume is small, and concentrated possibly in the near surface regions.

In fact, the defect concentration and not the doping by magnetic ions seem to be the limiting factor for the appearance of magnetism.

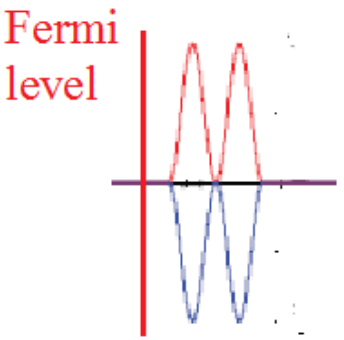
The dopants contribute to this picture but are not the determinant factor.

Charge-transfer ferromagnetism

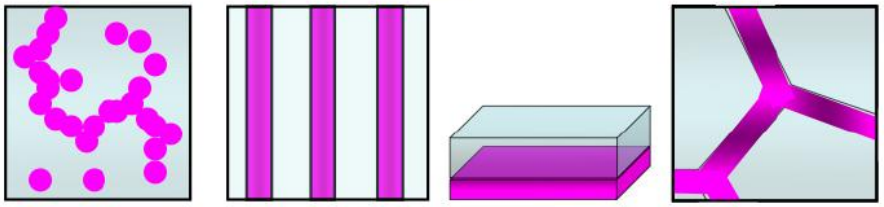
Ferromagnetism in defect-ridden oxides and related materials, JMD Coey et al, New Journal of Physiscs (2010).

(Stoner like model)

(i) a defect-based band with a high density of states in the proximity of the Fermi level,



(ii) a charge reservoir to or from which electrons can be easily transferred to or from states associated with defects



(iii) an effective exchange integral associated with the defect states.

Stoner Criterion

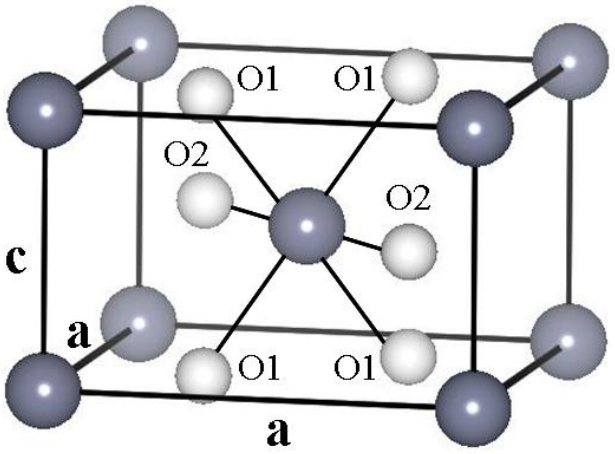
$IN(EF) > 1$

Only the regions containing the defects become ferromagnetic.

Ab Initio – LAPW calculations

Rutile TiO_2

Tetragonal unit cell a=4.5845 Å, c=2.9533 Å

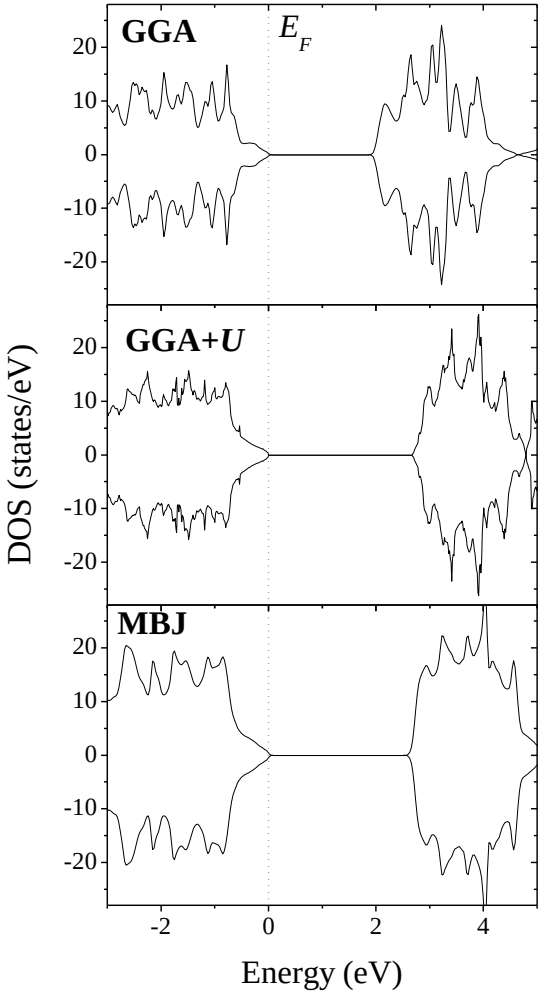


GGA

GGA+*U*

(U=5 eV, Fe- and Ti-3d)

MBJ



O1 (basal plane) at 1.94 Å

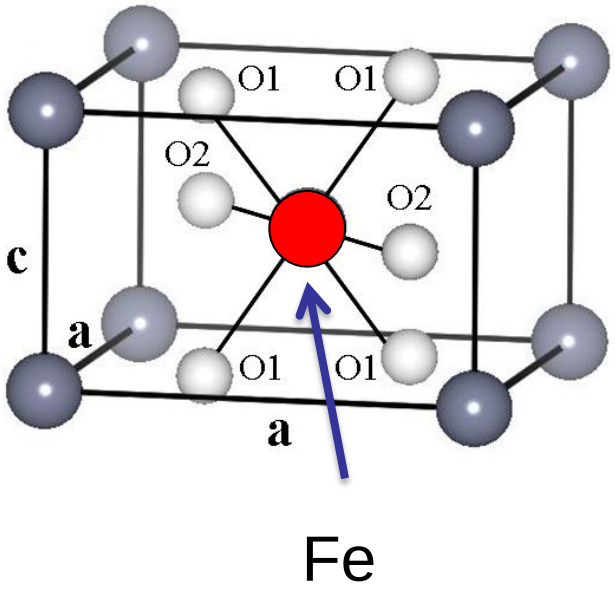
O2 (vertex) at 1.984 Å

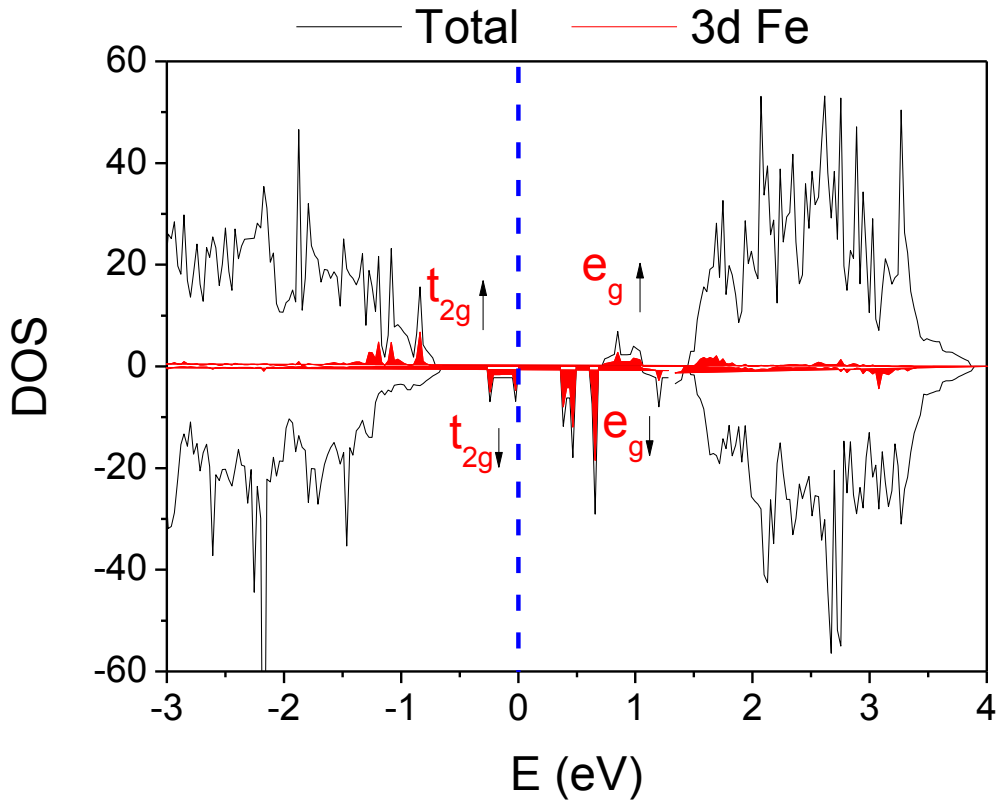
I- **Fe substituting Ti in TiO_2 lattice**

μ_{Fe} = 2.15 μ_B

μ_O = 0.06 μB

Super Cell
2 X 2 X 2

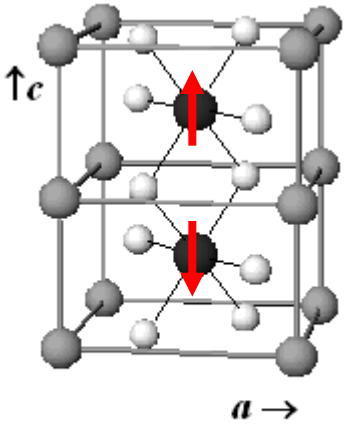




II- Two Fe substituting Ti in TiO_2 lattice

$\Delta E = E_{anti} - E_{ferro}$, $\Delta E > 0$ indicates ferromagnetic coupling

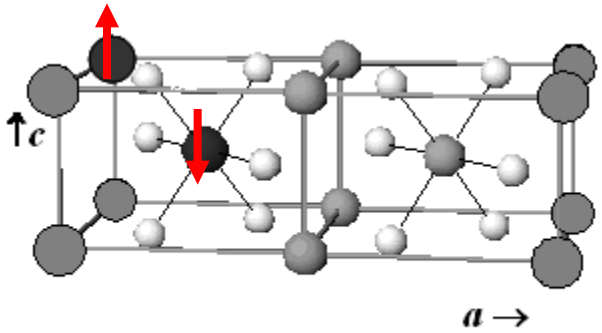
ΔE = -0.12 eV



Configuration a

Antiferro

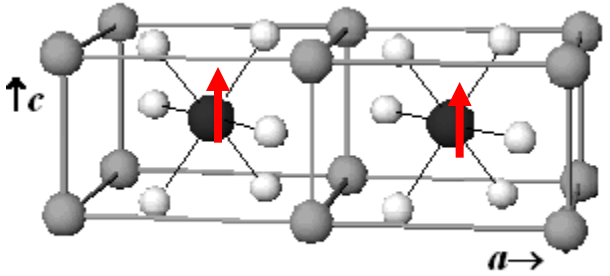
ΔE = -0.03 eV



Configuration b

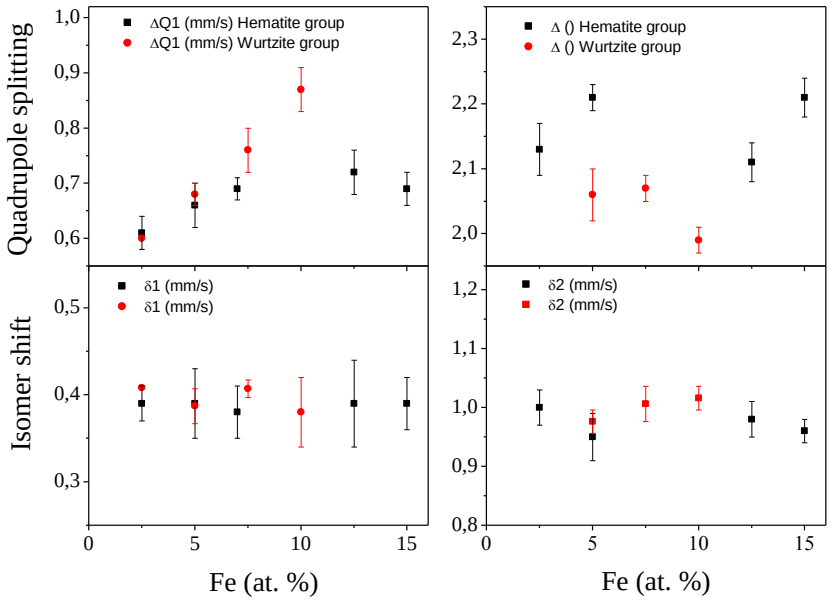
Antiferro

ΔE = 0.002 eV



Configuration c

Ferro



Theory:

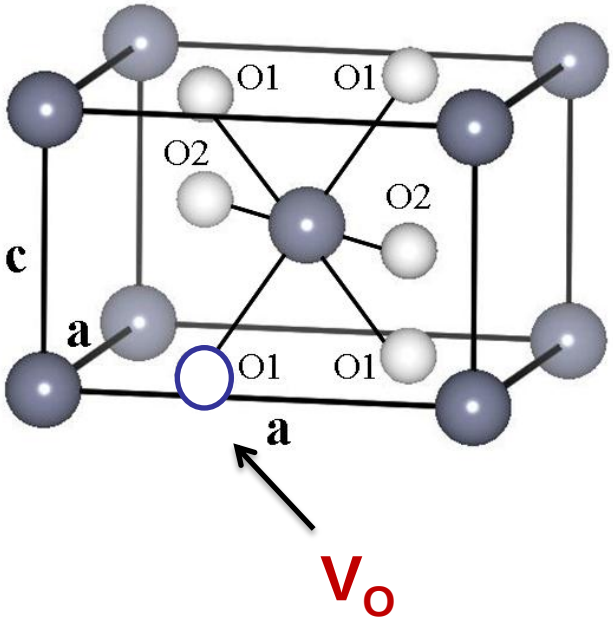
IS = +0.10 mm/s

Average Fe-ONN relaxed bond-lengths: 1.90 Å

EXAFS results: Fe-ONN bond-lengths larger than 1.98 Å.
Fe-coordination smaller than 6.

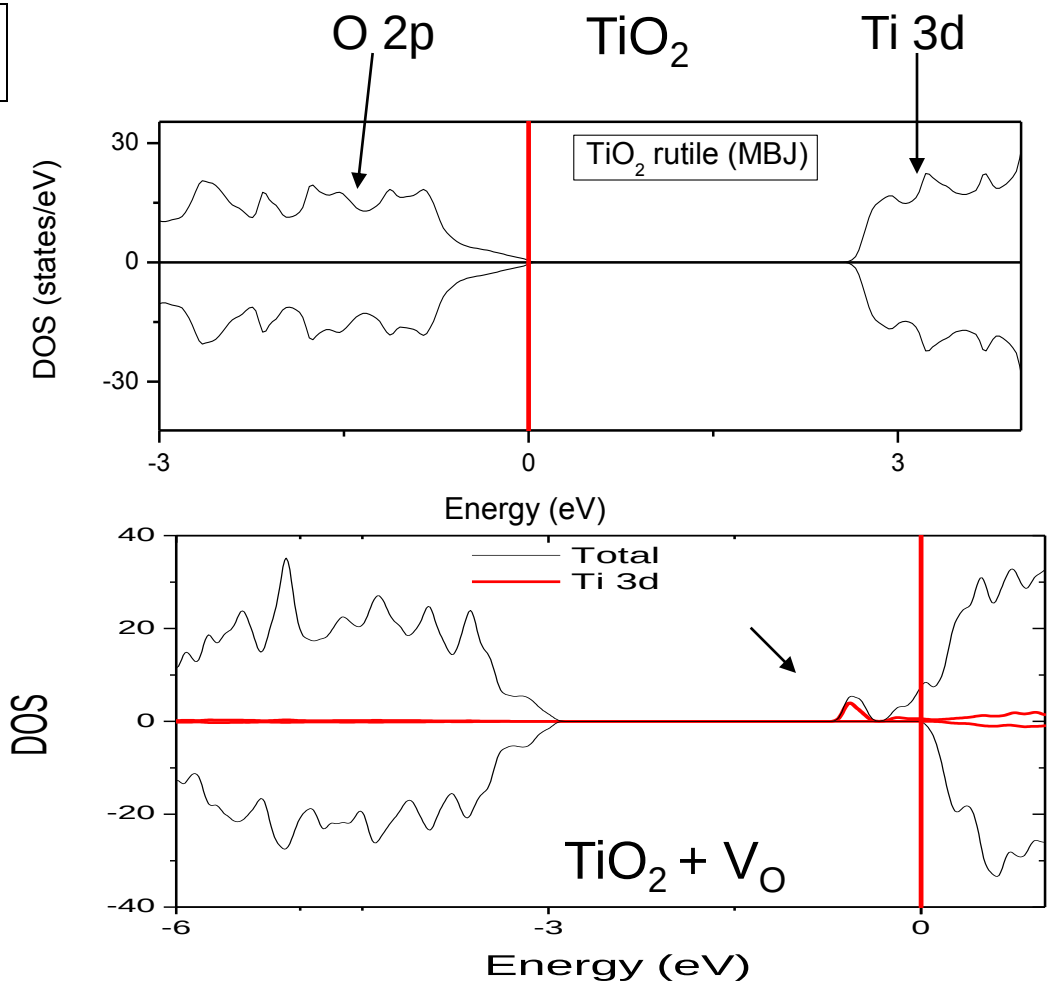
Very poor agreement.

Defective Rutile TiO_2



V_O

$\mu_{total} = 2\ \mu_B$



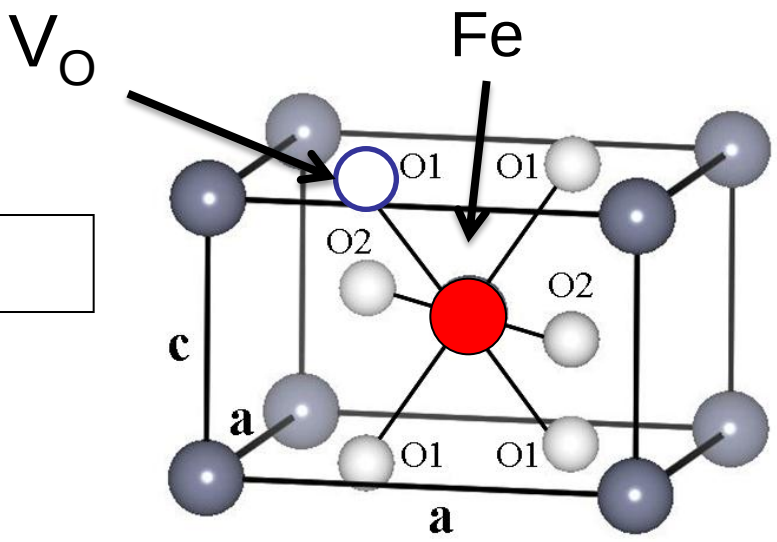
III- **Fe substituting Ti in TiO_2 lattice + oxygen vacancies**

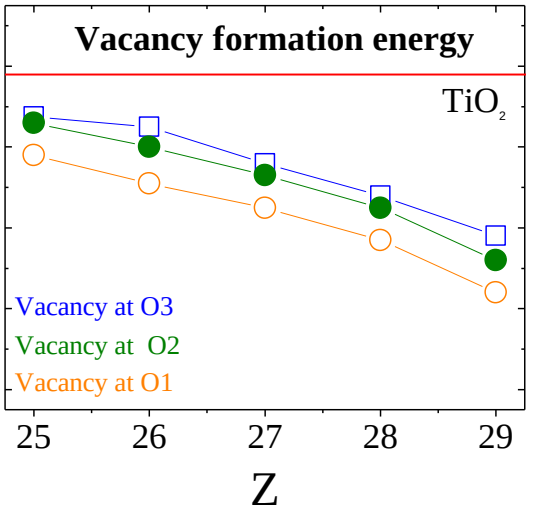
✓ Oxygen vacancies near the impurities are more stable than those near Ti

✓ The presence of a vacancy close to the impurity increases the magnetic moment of the impurity

✓Doping lowers the formation energy of vacancies

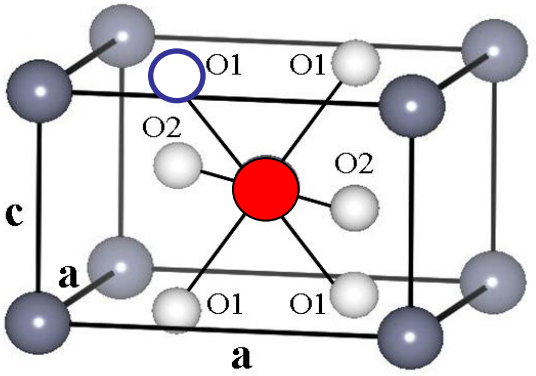
$\mu_{Fe} = 3.5\ \mu_B$





III- Fe substituting Ti in TiO_2 lattice + oxygen vacancies

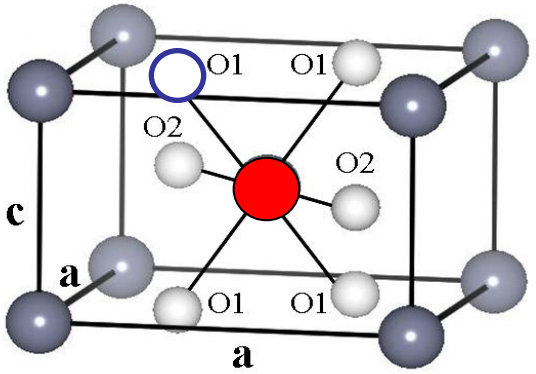
sustitutional	IS = +0.10 mm/s
Vacancy at O1	IS = +0.47 mm/s
Vacancy at O2	IS = +0.40 mm/s
Vacancy at O3	IS = +0.45 mm/s
Two vacancies	IS = ~ +0.65 mm/s
Interstitial	IS = +0.30 mm/s



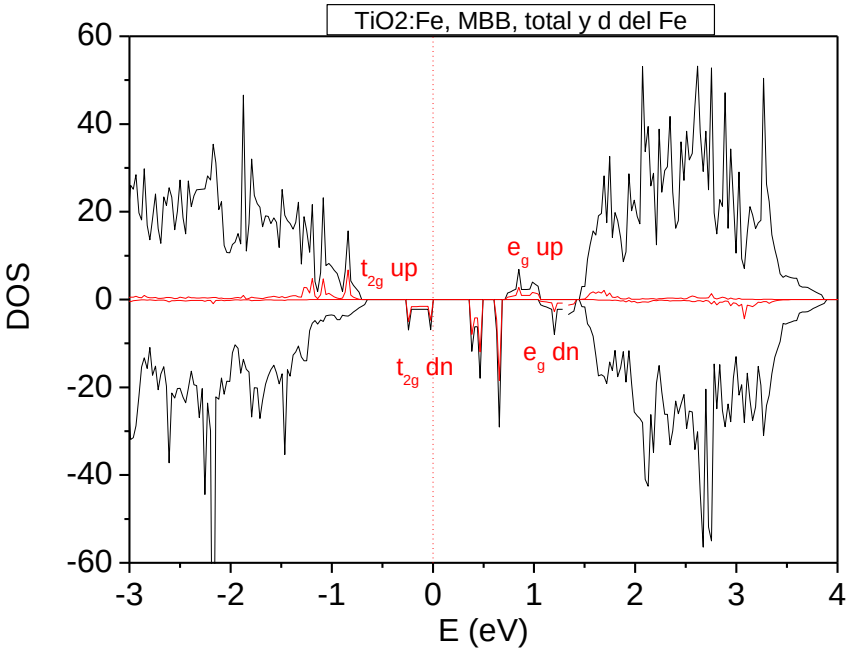
Vacancy located at O1 or O2: increment of IS up to 0.44 mm/s, in agreement with the Mössbauer results .

Average Fe-ONN bond-length: 1.98 Å , in good agreement with the distances obtained from the EXAFS analysis.

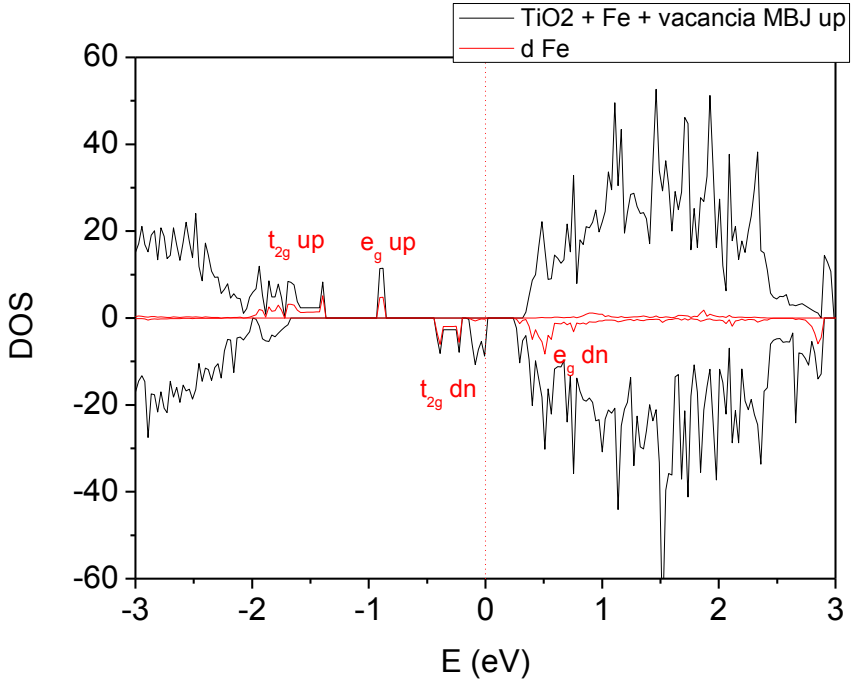
III- Fe substituting Ti in TiO_2 lattice + oxygen vacancies



Without V_O



With V_O



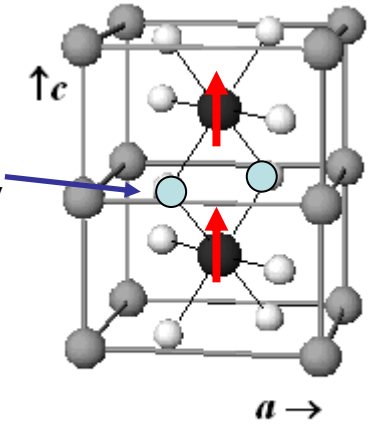
IV- Two Fe substituting Ti in TiO_2 lattice + oxygen vacancies

Conf. a:

One oxygen vacancy in one of the two Fe-O-Fe paths.

Two oxygen vacancies: in both Fe-O-Fe paths.

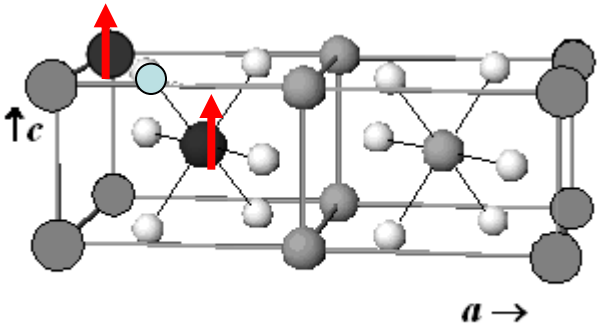
Ferro



Oxygen vacancy here

Configuration a

Ferro



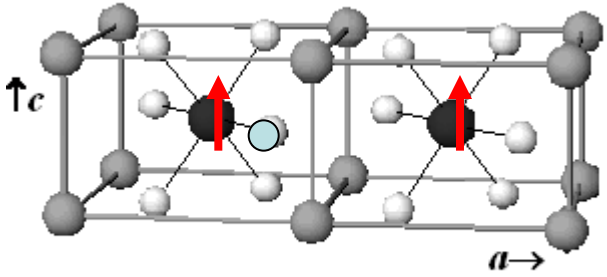
Configuration b

Conf. B:

One oxygen vacancy in Fe-O-Fe path.

Two oxygen vacancies: Fe-O-Fe path and the other as a first neighbor of one of the Fe impurity.

Ferro



Configuration c

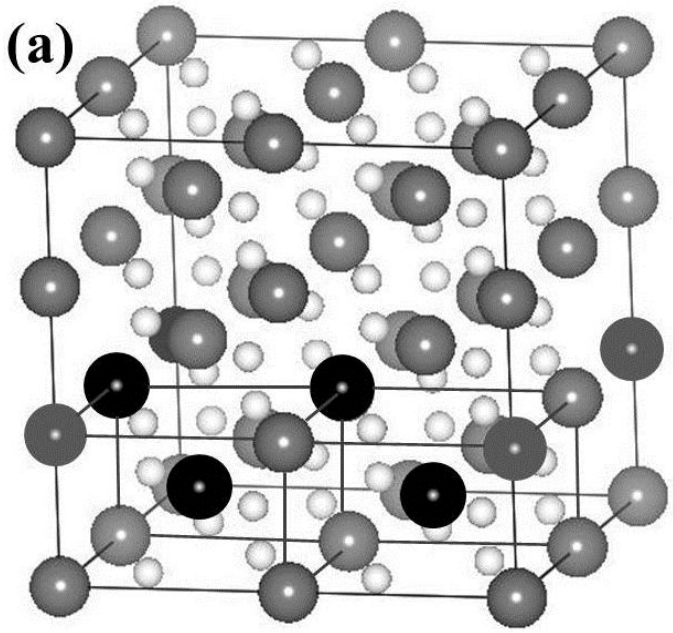
CONF. C:

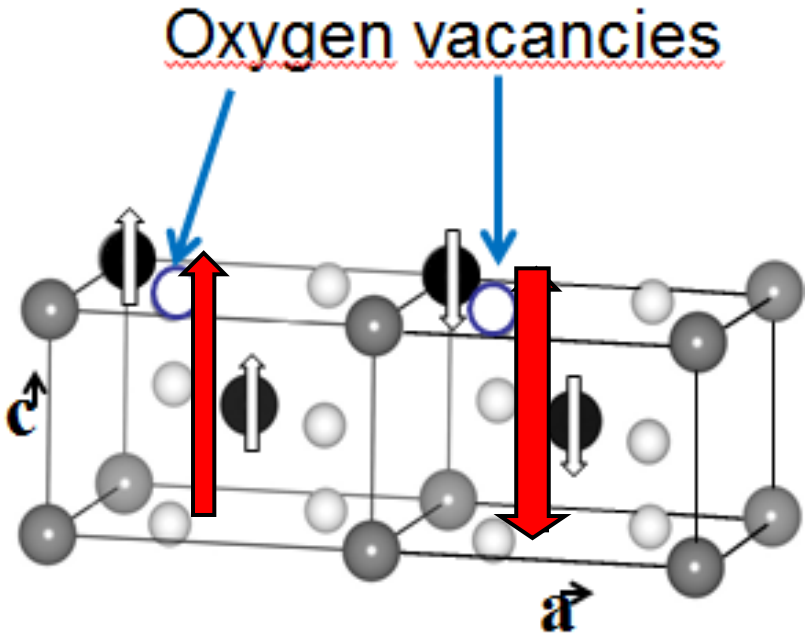
One oxygen vacancy: Close to one of the impurities.

Two vacancies: each one located as a first neighbor of one of the impurity.

V- **Long-range magnetic ordering. BMP model.**

Super Cell:
3 X 2 X 3





antiferromagnetic alignment is favored by 0.1 eV.

V- **Long-range magnetic ordering. BMP model.**

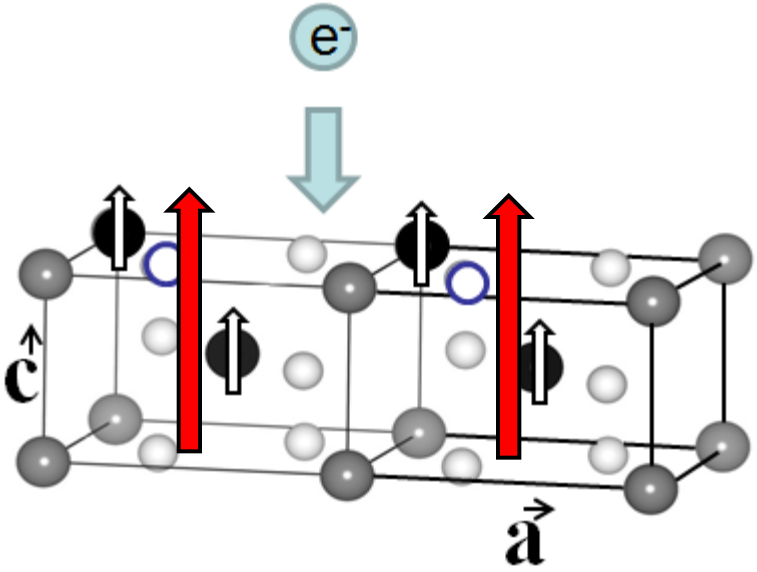
Increment in the Fe concentration → Increment in the number of BMP, Neighboring situation

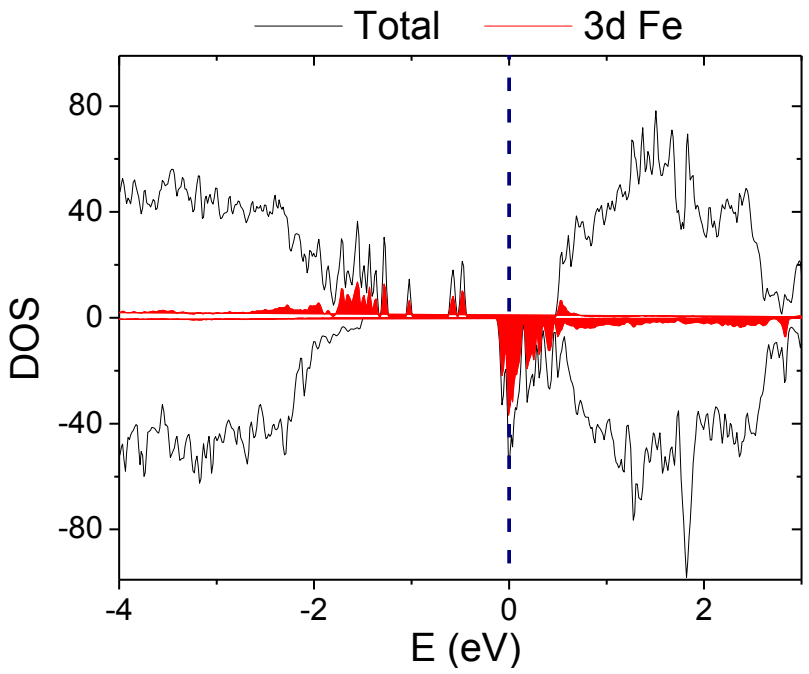
↓

The antiferromagnetic BMP alignment would reduce the magnetization, in agreement with the experimental results.

V- **Long-range magnetic ordering. BMP model.**

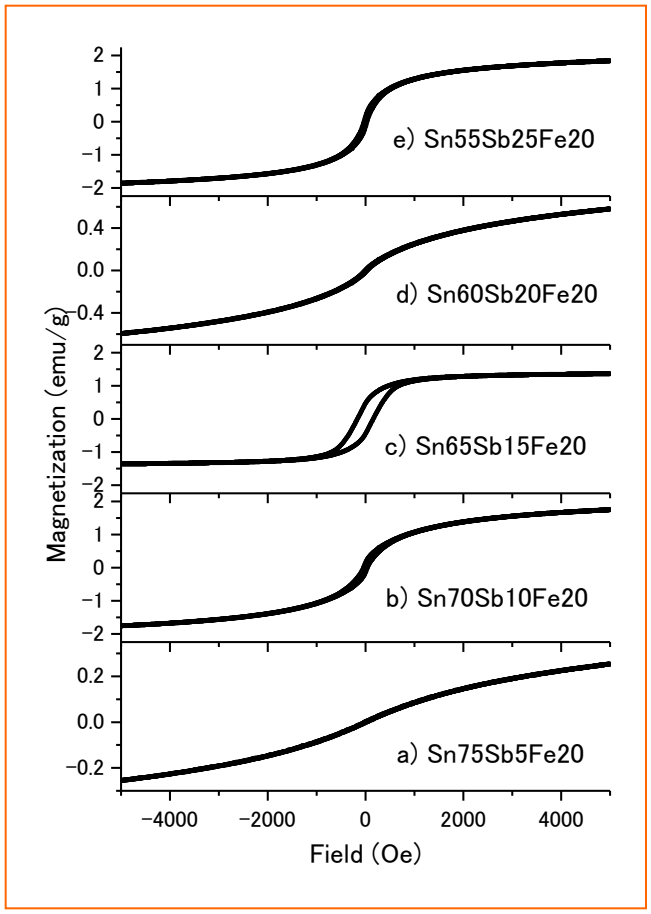
System doped with one electron



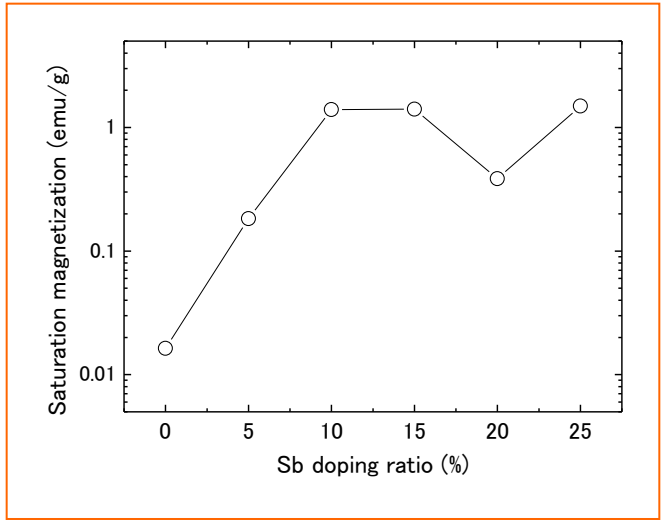


Ferromagnetic coupling between Fe-V_o-Fe clusters!

One last experimental result.



Fe-doped SnO_2 and co-doped with Sb (+5)



Codoping with +5 impurities or with 2p light element such as H, N, C enhance RTFM

Conclusions

The doping with transition metal atoms reduces the oxygen vacancy formation energy, so doped systems will have more vacancies than the undoped ones.

Oxygen vacancies enhance the magnetic moment of Fe (or other transition metal) impurities or even induce a magnetic moment in non magnetic transition metal impurities

Oxygen vacancies prefer to be in the Fe-O-Fe path favouring the ferromagnetic coupling between Fe dopants. BMP.

Conclusions

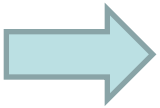
A small quantity of oxygen vacancies are fundamental for stabilizing local ferromagnetism in the form of bound magnetic polarons.

Free carriers further enhancing the ferromagnetic stability of local polarons and also mediating the non-local magnetic coupling between two magnetic polarons.

This explains the very large scatter of results reported in the literature. The overall magnetic properties of TM-doped TiO_2 are probably a statistical average of different defect configurations corresponding to a real disordered system.

This point suggests that, for the technological application of these doped oxides, an “engineering of defects” could be needed.

Doping
(Fe^{3+}, Fe^{2+})



Oxygen vacancies

Electron doping
(interstitial atoms, grain boundaries, substitutional +5 ions)

Enhance impurity magnetic moment

Shift Fermi level close to conduction band

Long range ferromagnetic order

Short range ferromagnetic interactions

Co-Workers (in this topic)

Ab-initio Calculation

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Experimental Characterization

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