# Magnetic oxide $Fe_{2-x}Ti_xO_{3-\delta}$ as a spintronics material



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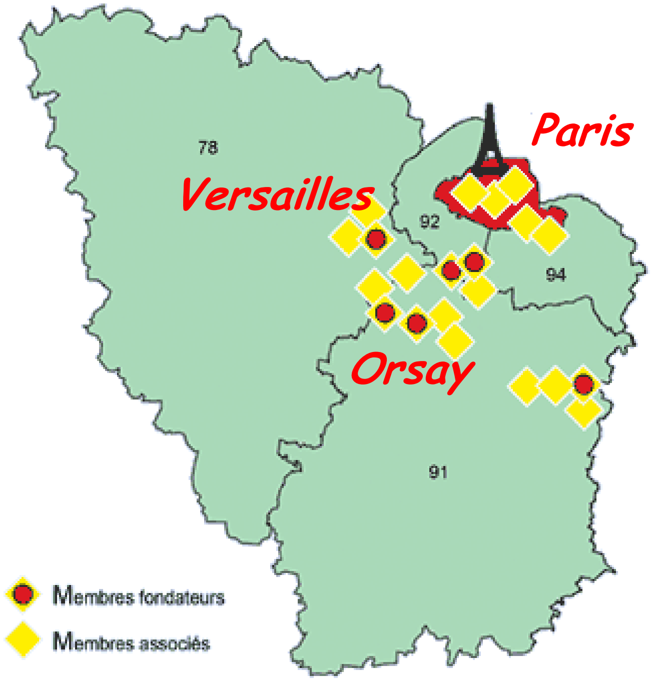
*GEMaC CNRS-Université de Versailles*

# Versailles University (UVSQ): www.uvsq.fr

## *Member of the new Large Scale Campus "Paris-Saclay University":*




*19 000 students*
*160 academic programs*
*35 laboratories*
*1 360 professors and researchers*
*700 doctoral students*

## A plural disciplinaries University:

4 Schools of Humanities & Social Sciences, of Exact Sciences, of Law and Political Sciences, of Medicine

1 Engineering School

2 University technical Institutes

1 Universe Sciences Institute

**International students = 9.2% of all enrolled students and 35.4% of doctoral students.**

*Close to a "more " famous castle …*

# Collaboration with TSU

INTERNATIONAL MOBILITY AGREEMENT

BETWEEN

THE UNIVERSITY OF VERSAILLES SAINT-QUENTIN-EN-YVELINES

FACULTY OF SCIENCE
(Versailles, France)

AND

IVANE JAVAKHISHVILI STATE UNIVERSITY OF TBILISI

FACULTY OF EXACT AND NATURAL SCIENCES
(Tbilisi, Georgia)

General bilateral exchange agreement between TSU – UVSQ (2009-2014)

- Initiated by Physics, but general frame of exchange of teachers, researchers, and students
- Others expertises of UVSQ : environment, sustainable development, chemistry, computing (agreement between GTU and UVSQ)

**In 2012 with support of CAMPUS FRANCE: first exchange of a french speaking master student Nino Ponjavidze from TSU**

*Continuous research collaboration with:*

- Dr. Tamar Tchelidze on Semiconducting properties calculations
- Pr. Alexander Shengelaya on EPR, FMR properties

**⇒ Applications to SRNRF and french CNRS research project programs …**

**⇒ European projects between Georgia, Germany, France, etc…**

# GEMAC-Versailles : GEMaC Lab = Condensed Matter Studies Laboratory

- belongs to Versailles University and CNRS
- ~40 permanents; ~ 15 post-doc + PhD students
- director: Dr. Niels KELLER
- 5 research groups :
  - "Diamond for high temperature electronics"
  - "Photo commutable Molecular Solids"
  - " Nano-scale optics" : Near Field optics, single photon physics
  - " New semiconductors and properties": ZnO 2D, 1D; doping ; MOCVD
  - **"Functional complex oxides": magnetic, metal/insulator, SC oxides ; PLD**

- Facilities :
- XRD, AFM, MFM, SIMS
- Spectrophotometry, ellipsometry, Photo-L, cathodo-L, FTIR, $\mu$-Raman
- Magnetometry : SQUID 5.5Tesla 2-400K ; VSM 9Tesla 2K-1000K
- Electrical transport high impedance (resistivity, Hall)

# $Fe_{2-x}Ti_xO_{3-\delta}$ as a spintronics material

**Context:**

- Research on new functional oxides for spintronics injector
- Alternative approach to the "Diluted Magnetic Semiconductors" (DMS) way

**Goal:**

- Inducing "carriers" in a High $T_{Curie}$ ferrimagnetic oxide by cation substitution and oxygen off-stoichiometry
- Getting a spin polarization of carriers

**Tools:**

- Epitaxial films of $Fe_{2-x}Ti_xO_{3-\delta}$ solid solution
- "MBE-type" Pulsed Laser Deposition (PLD) technique

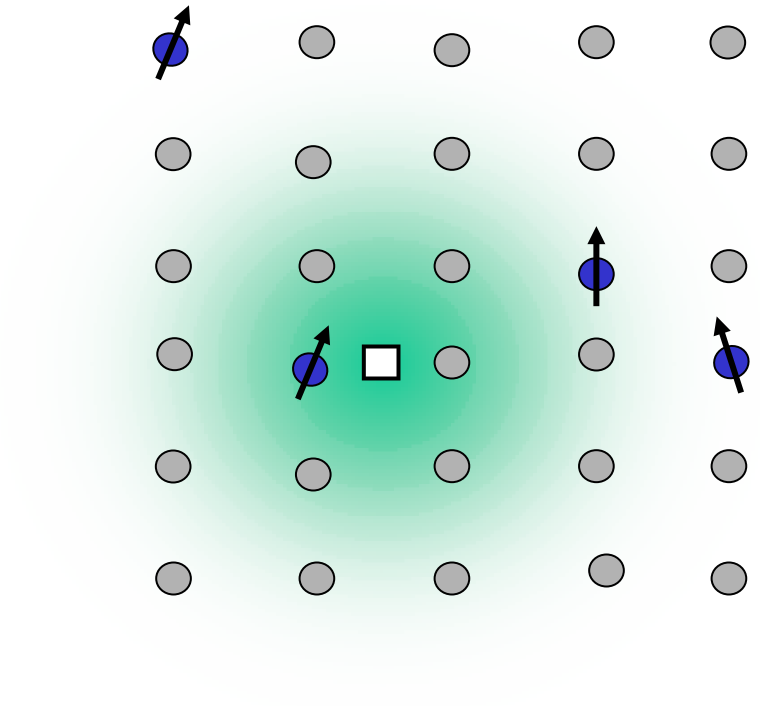
**Questions:**

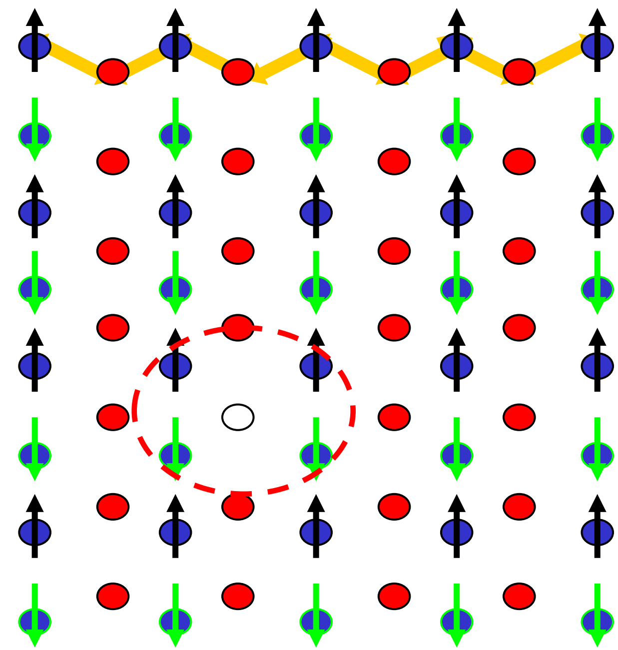
- Modification of the Fe-Fe interaction: super-exchange vs. double-exchange ?
- Conduction mechanisms: band vs. hopping ?
- Spin polarization ?

# *Alternative approach to "DMS"*

Diluted magnetic semiconductors

*High $T_C$ (> 400K) ferrimagnetic oxides*





***Keeping the Semiconducting properties***

***Getting a RT Ferromagnetism …***

***Keeping the RT Ferrimagnetism***

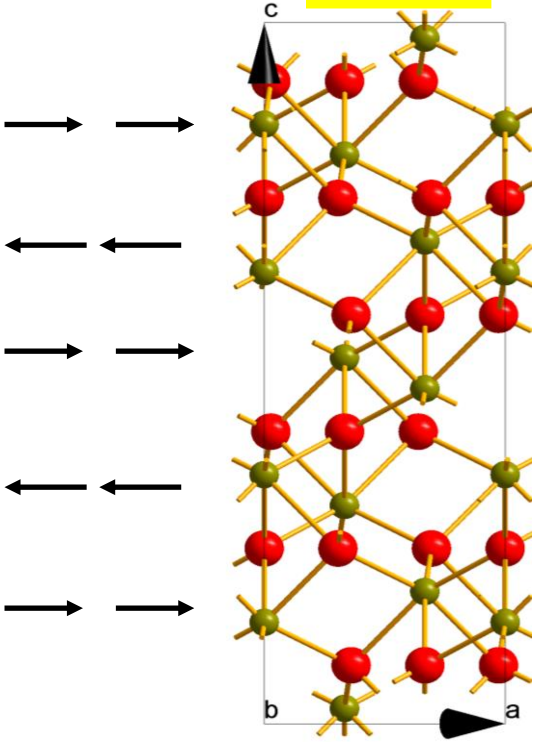
***Getting conductivity …***

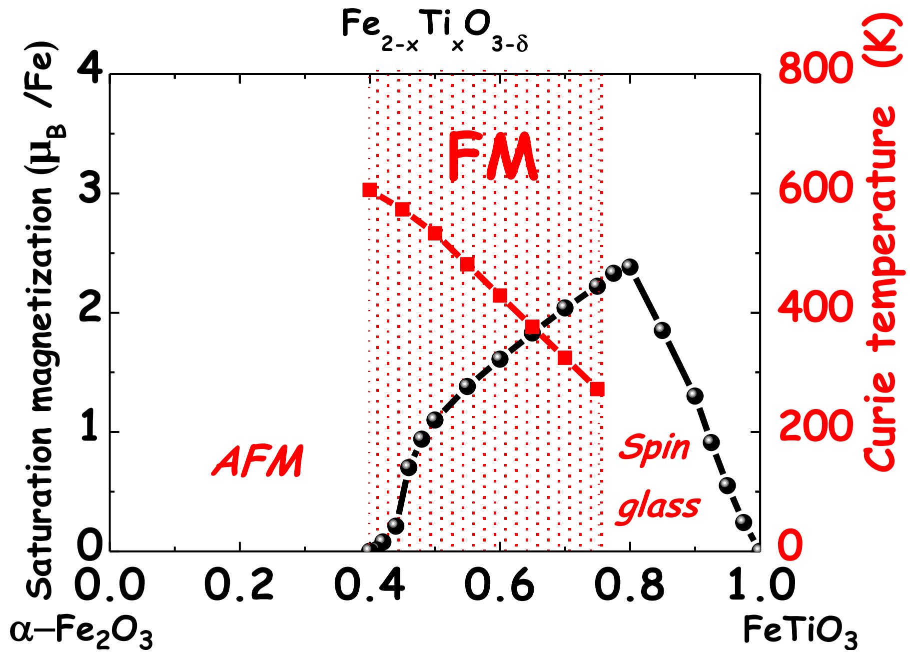
# System: $Fe_{2-x}Ti_xO_3$

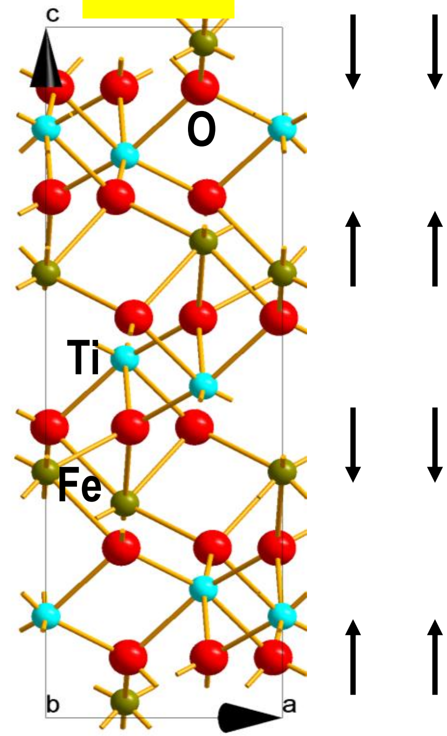
**R-3c**

*From polycrystalline bulk studies*

**R-3**



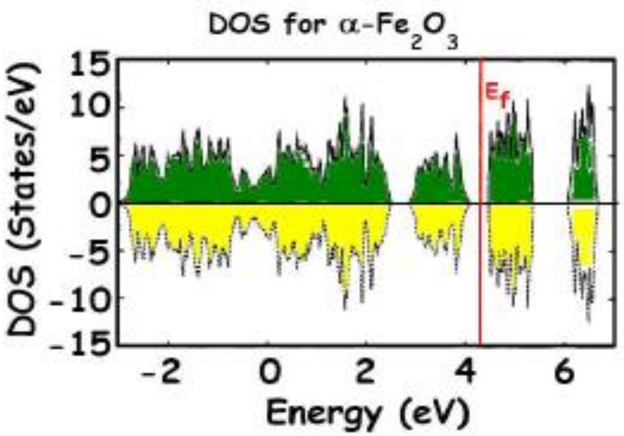

**Hematite**
**$\alpha$-$Fe_2O_3$:**
Insulator ($E_g$=2.2 eV)
Canted antiferromagnet: ($T_c$= 950K $T_{R,N}$ = 260K)
260K < T < 950K, $M_S$ = 0.002 $\mu_B$

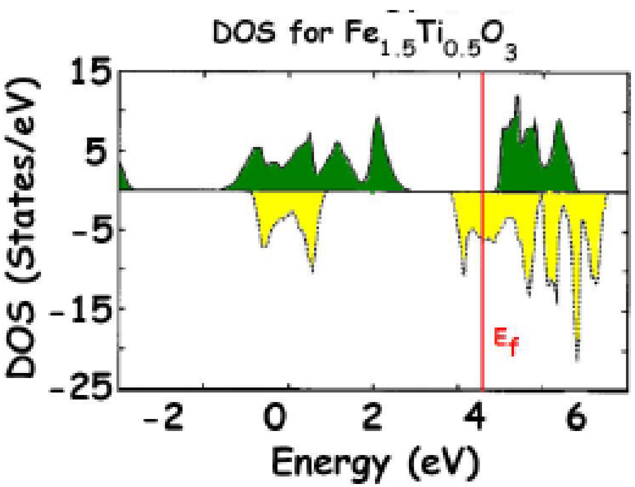
*Y. Ishikawa and S. Akimoto, Jpn. J. Phys. Soc.* ***12****, 1083 (1957), Y. Ishikawa, ibid. item* ***13****, 37 (1958),* ***17,*** *12 (1962)*

**Ilmenite**
**$FeTiO_3$:**
Insulator ($E_g$=3.3-3.6 eV)
Antiferromagnet ($T_N$ = 55K)
Non-equivalence of Fe et Ti sites

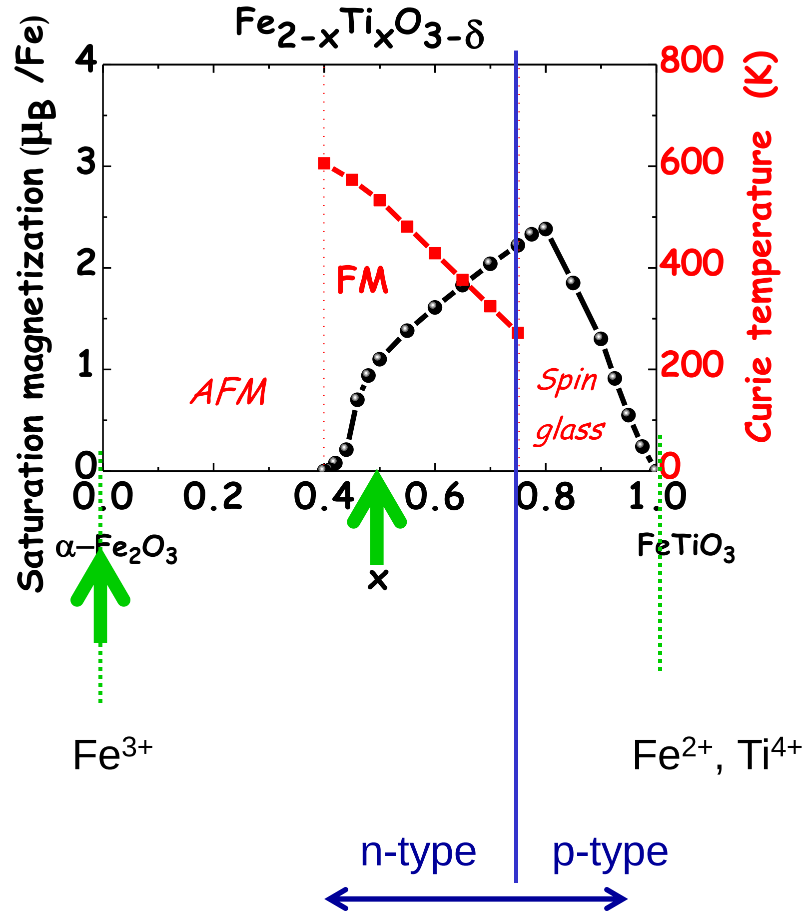
# System: $Fe_{2-x}Ti_xO_3$

*ab-initio calculations:*




*Predicted spin polarization for x=0.5*




Electrical conductivity in bulk material associated with $Fe^{3+}/Fe^{2+}$

*W. H. Butler et al., J. Appl. Phys. 93 (10), 7882 (2003)*
*A. Bandyopadhyay et al., Phys. Rev. B **69**, 174429 (2004)*

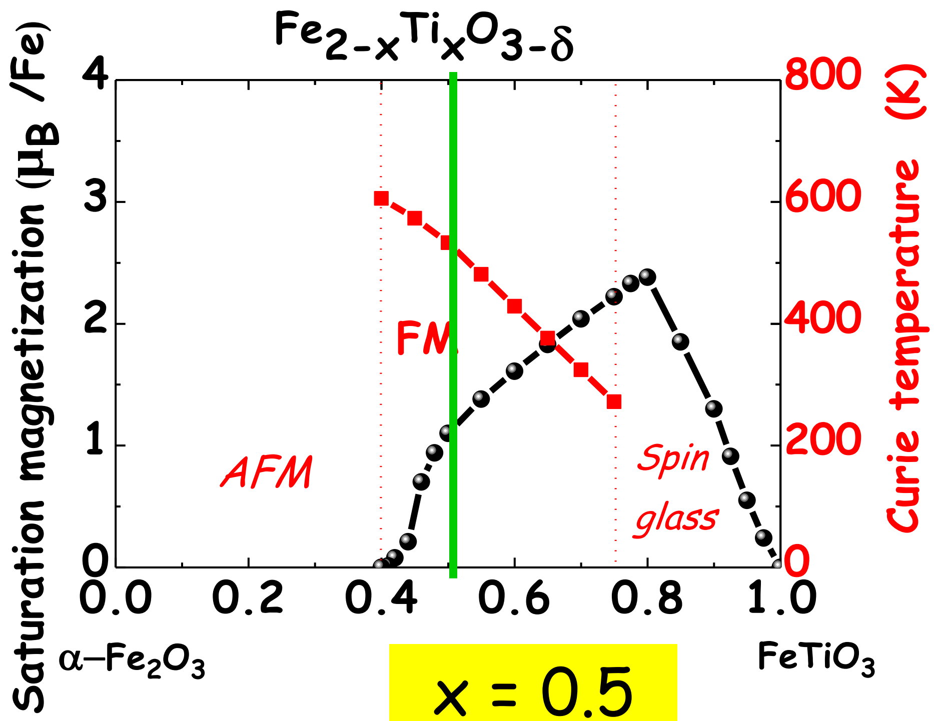
# *Studied compositions $Fe_{2-x}Ti_xO_{3-\delta}$*

**By a "MBE like" Pulsed Laser Deposition set-up:**

(base pressure : $5x10^{-9}$ torr, RHEED, spectroscopic ellipsometry)

**$T_{substrate}$: between 650 and 750°C**

**$P_{O2}$ : between $10^{-7}$ and $10^{-1}$ torr**




x = 0.5

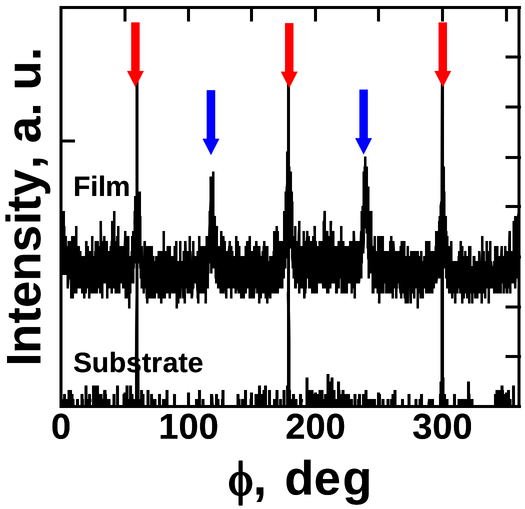
**=>Epitaxy on iso-structural $Al_2O_3$(0001) and on cubic $SrTiO_3$(001)**

**=>Tuning the oxygen off-stoichiometry $\delta$**

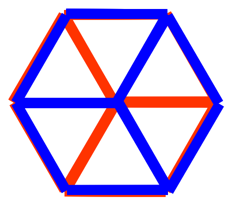
Thicknesses from 30 to 200 nm

# Epitaxial growth on $Al_2O_3$ (0001) and $SrTiO_3$ (001)

*on iso-structural $Al_2O_3$ (0001)*

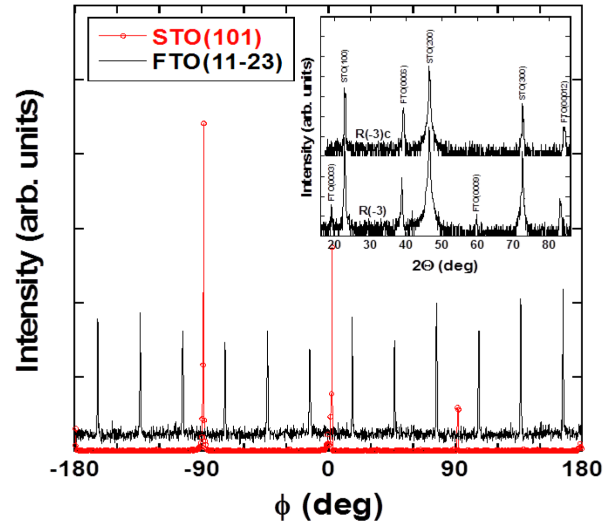


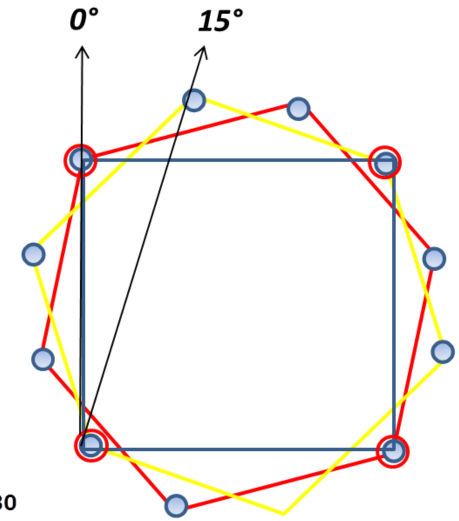

(0001) film plane: top view



**E. Popova et al., J. Appl. Phys. 103 (2008) 093909**
**E. Popova et al., Surface Science 605 (2011) 1043**

*on cubic (Si-compatible) $SrTiO_3$ (001)*



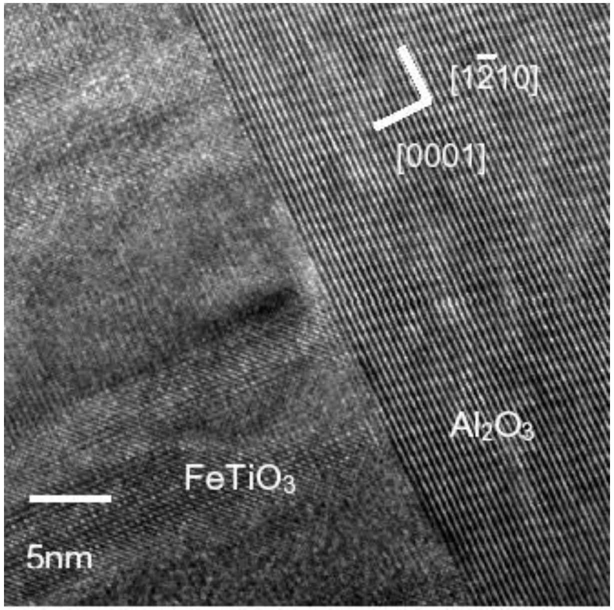

**A. Hamie et al., J. Appl. Phys. 108 (2010) 093710**
**A. Hamie et al., Appl. Phys. Lett. 98 (2011) 232501**

R-3c phase mostly and special route for R-3
Epitaxial film without secondary phases
Complete in-plane relaxation (from 8nm)
Two crystallographic domains

Stabilization of R-3 phase ($P_{O2}$=2x$10^{-7}$ torr)
<-> idem
<-> idem
Four crystallographic domains

# Microstructure and chemical analysis

**TEM**




(Coll. B. Warot-Fonrose - CEMES)

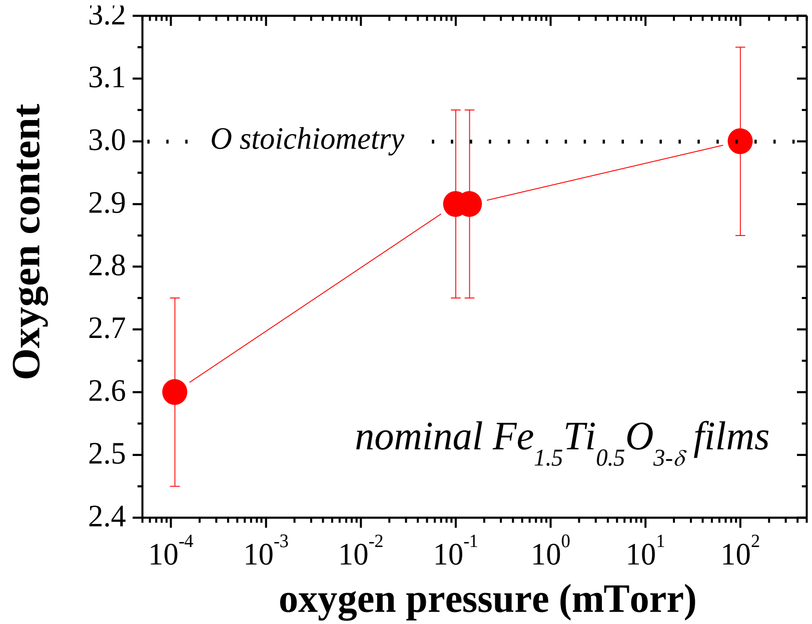
Columnar growth, lateral column size corresponds to the surface grain size measured by AFM (8 nm)

**AFM:** rms roughness < 1 nm, no outgrowths "good" for heterostructures

**Chemical analysis by EELS:**

- no film/substrate interdiffusion evidenced
- Homogeneity in depth

**RBS+NRA:** (Coll. J. Siejka - INSP)




$10^{-1}$ Torr : stoichiometric $\delta=0$
$10^{-7}$ Torr : $\delta=0.35$

# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$: control of magnetic properties

*$Fe^{2+}$ and $Fe^{3+}$: magnetic*
*$Ti^{4+}$ is non magnetic*

*Strong importance of Ti/Fe atomic order along $c_h$ axis : ordered R-3 phase and disordered R-3c*
*=> Special routes for growth (bulk and thin films)*

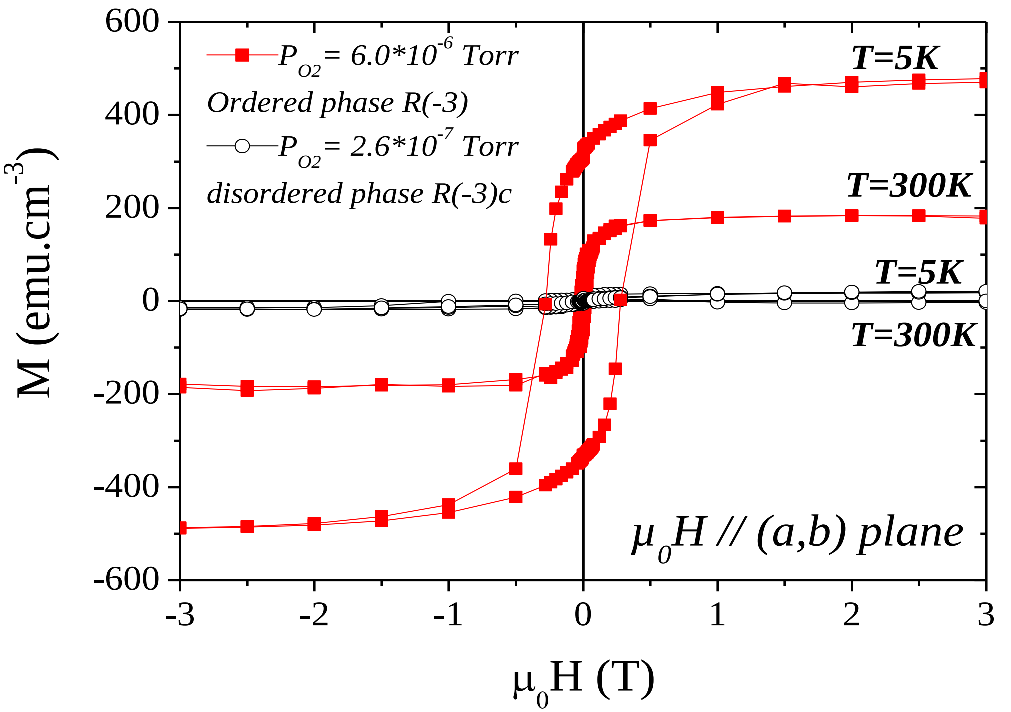
Our work:

- on $Al_2O_3$(0001) possibility to form R-3 with $P_{O2}<10^{-6}$ Torr + annealing but also an hidden parameter (H. Ndilimabaka PhD thesis 2008)

- on $SrTiO_3$(001) stabilizing the R-3 phase with $P_{O2}<10^{-6}$ Torr + annealing (A. Hamie PhD thesis 2011)

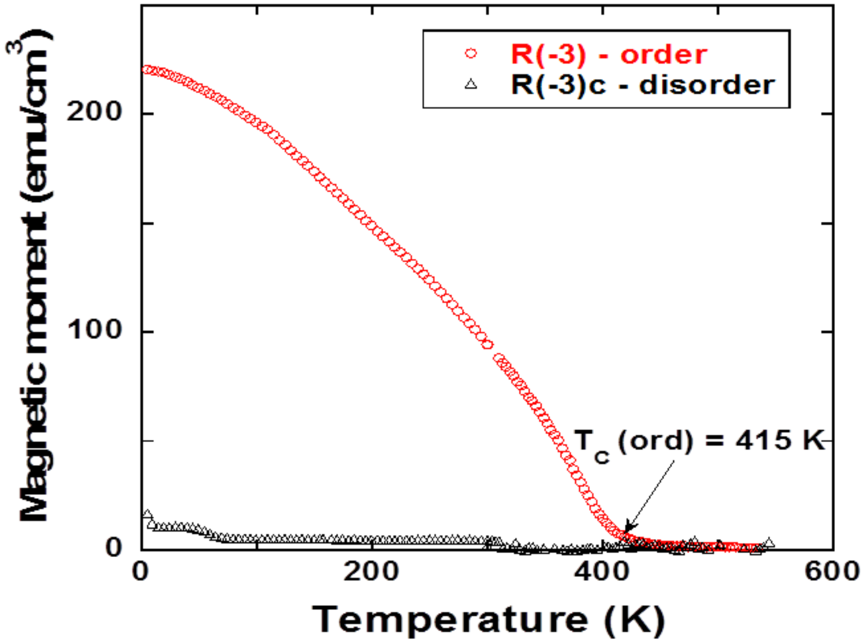
# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ on $SrTiO_3$ (001)

## Comparison R-3 and R-3c phases




**A. Hamie et al., J. Appl. Phys. 108 (2010) 093710**

## From High T VSM:



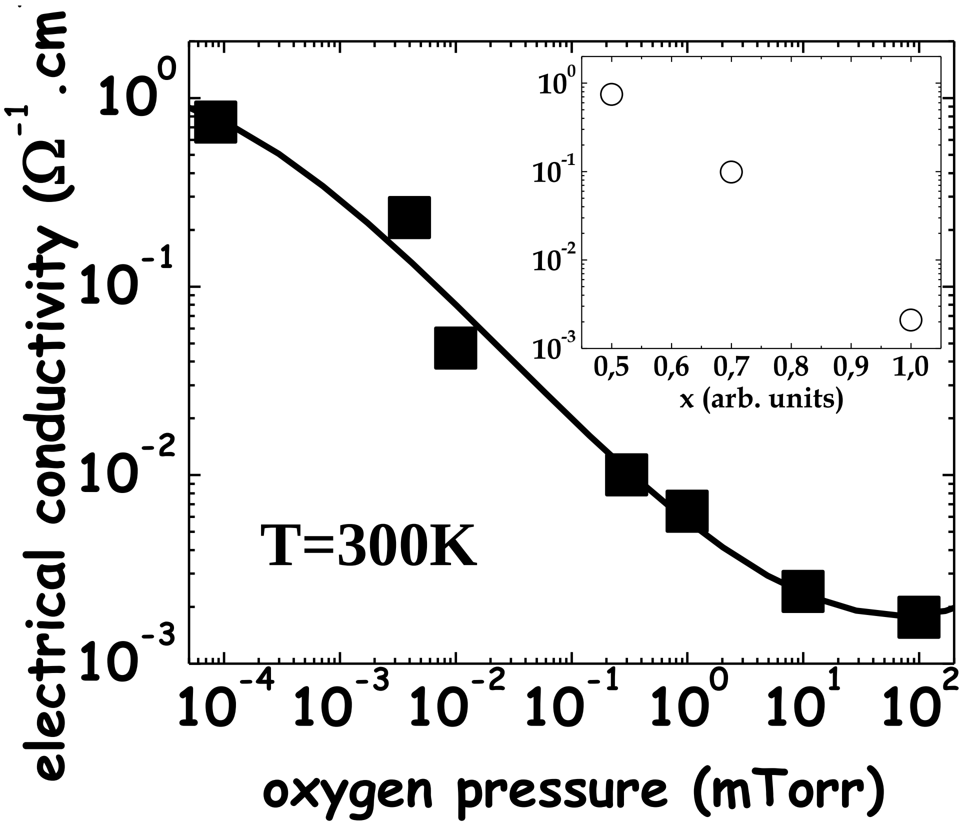

**A. Hamie et al., Appl. Phys. Lett. 98 (2011) 232501**

- $T_c$ > 400K
- $M_{Smax}$~1.6$\mu_B$/formula for R-3 (state of the art in bulk)
- $M_{Smax}$~0.05$\mu_B$/formula for R-3c

*Y. Ishikawa, Jpn. J. Phys. Soc.* ***13****, 37 (1958),* ***17****, 12 (1962)*

# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$: semiconducting properties

**Strong importance of the oxygen stoichiometry on RT electrical conductivity**




With increase of $\delta$ (decrease of $P_{O2}$):

- increase of electrical conductivity up to 1 $\Omega^{-1}cm^{-1}$
- n-type conduction: $1.21 \times 10^{16} < n < 1.32 \times 10^{18} cm^{-3}$
- Hall mobility: $1 < \mu < 8\ cm^2V^{-1}s^{-1}$

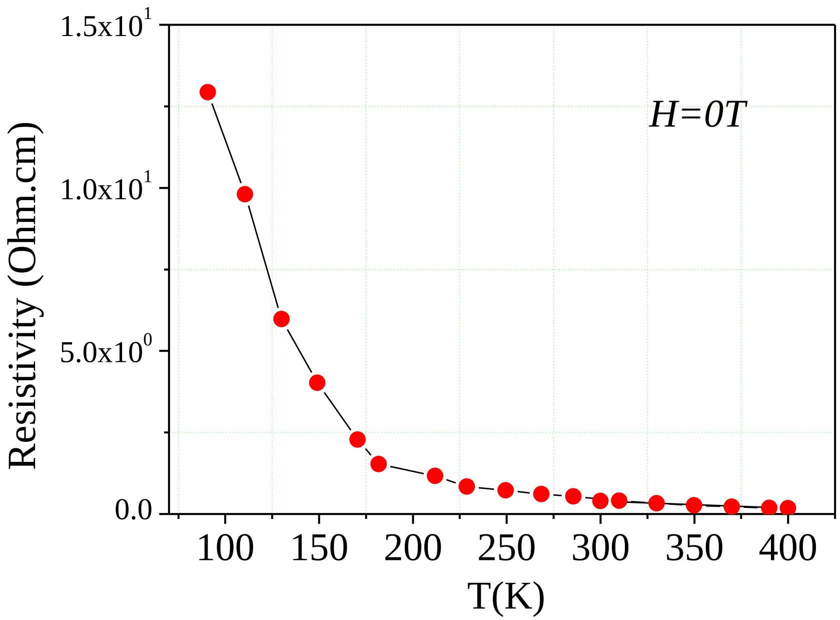

***H. Ndilimabaka et al., J. Appl. Phys. 103, 07D137 (2008),***

***H. Ndilimabaka, PhD thesis Versailles Univ. 5 dec. 2008***

*H. Hojo, et al, Appl. Phys. Lett. 89 (2006) 082509*

# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$: semiconducting properties

*Resistivity versus T at H=0*

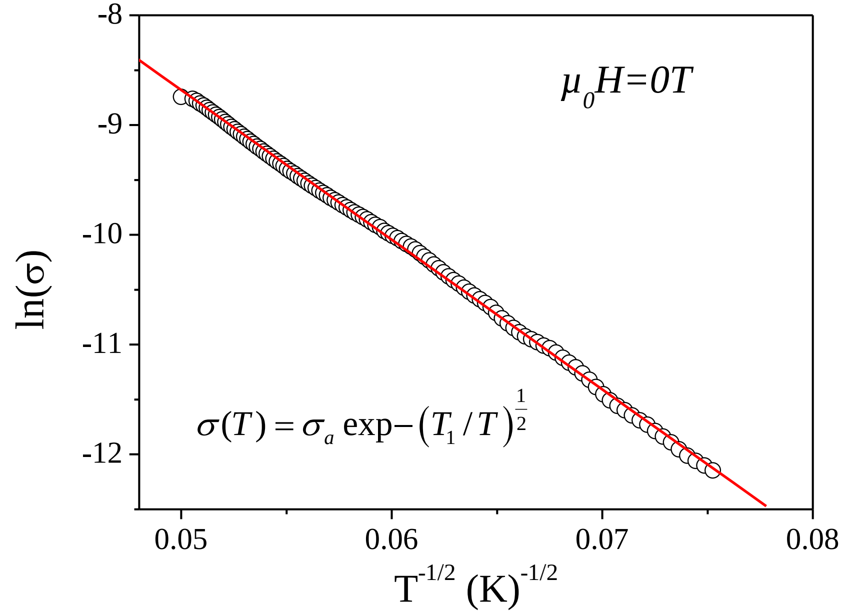



***s/c*** $Fe_1Ti_1O_3$ *Z.Dai et al., JAP* ***85****,7433, (1999)*
***s/c*** $Fe_{2-x}Ti_xO_3$ ***x=0.02;0.06;0.08*** *Z.Wang et al.,APL 83,518,(2003)*

*=> Semiconducting behaviour*

*=> Independent of the substrate and of the R-3 or R-3c phases*

*nature of conductivity: localized carriers*



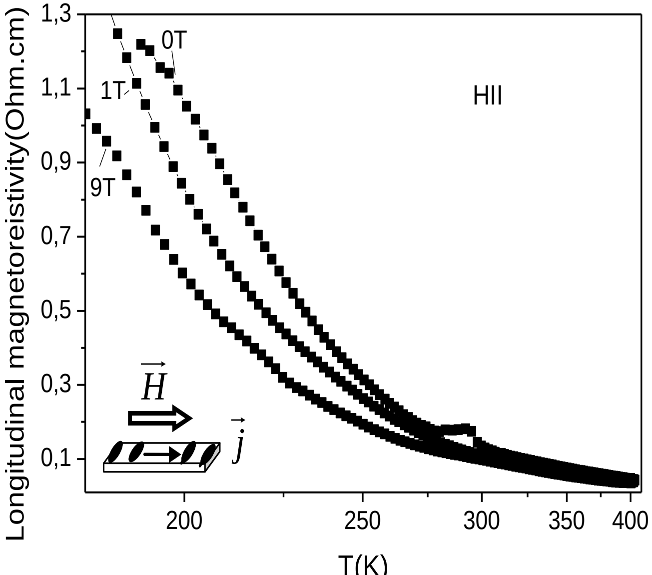

**Soft gap Efros-Shklovskii type variable range hopping** (ES- VRH)

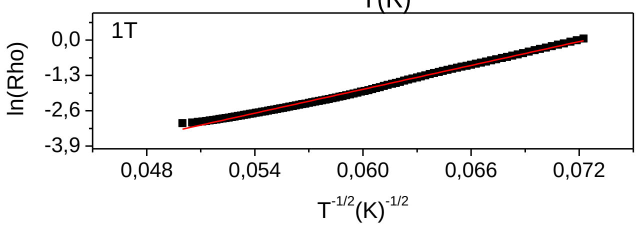
$$\sigma(T) = \sigma_a \exp-\left(T_1/T\right)^{\frac{1}{2}}$$

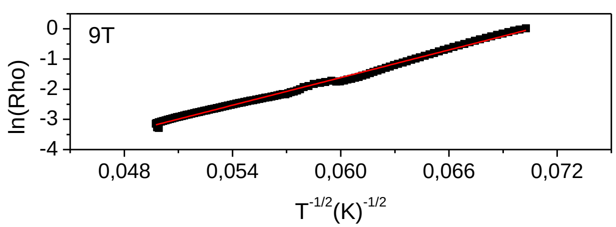
*B.I. Shklovskii, A.L. Efros, "Electronic properties of doped semiconductors, Springer, Berlin (1984)*

# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$: spin polarization

## Magneto-transport H//




**Same soft gap VRH type behaviour:**

$$\frac{\sigma(H)}{\sigma(0)} = \exp - 2\left(\frac{C}{k_B T}\right)^{\frac{1}{2}}$$

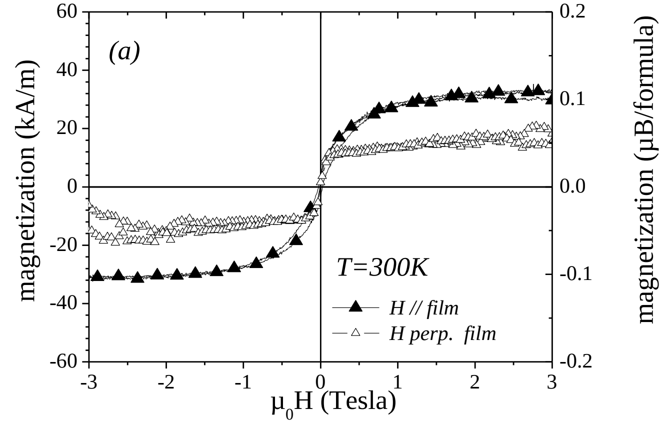
*J. Inoue, S. Maekawa, Phys. Rev. B 53 (1996) R11927*

**Interpreted as spin-dependent tunnelling between $Fe^{2+}$ to $Fe^{3+}$ ions**

$$MR(H) = \frac{R(H) - R(0)}{R(0)}$$

$$MR_{300K}(1T) = -\ 8\%$$

$$MR_{300K}(9T) = -\ 27\%$$

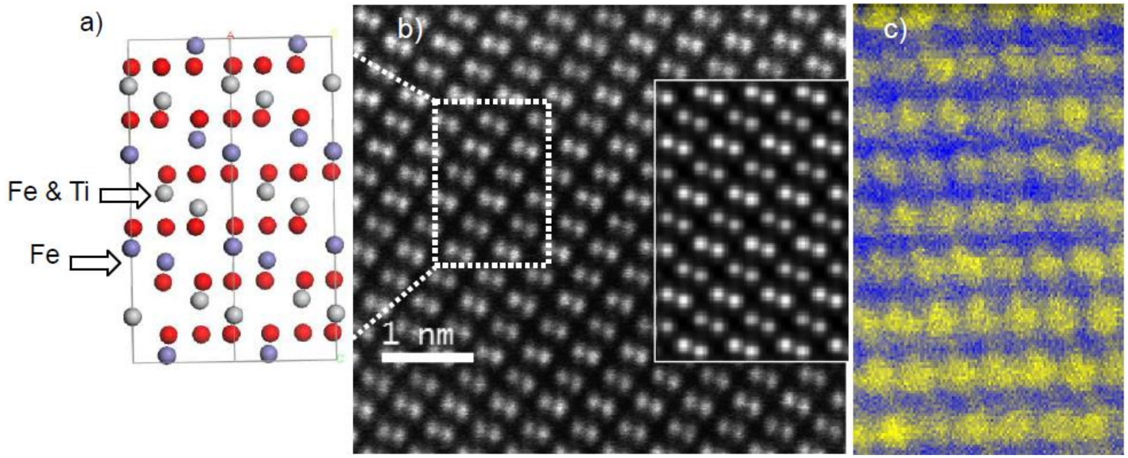



$$\rho(H) = \frac{1}{\sigma(H)} = \frac{\rho(0)}{1+P^2 m^2} \exp 2\left(\frac{\kappa C}{k_B T}\right)^{\frac{1}{2}} \quad \text{with } m \equiv \frac{M(H)}{M_{sat}}$$

$$\Rightarrow \text{in saturation field, } |MR| = \frac{P^2}{1+P^2}$$

$$|P| \sim 29\%$$

# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$: evidence of charge order




**Atomic scale resolved STEM and ELNES:**

**collab. with L.** Bocher, K. March, A. Gloter, O. Stephan (LPS-Orsay)

*Figure 1. a) structural model of $Fe_{1.5}Ti_{0.5}O_3$, b) atomically-resolved HAADF image and the simulated image (inset), and c) the corresponding reconstructed false color elemental maps associated with Fe-L2,3 / TiL-2,3 edge intensities (blue/yellow).*

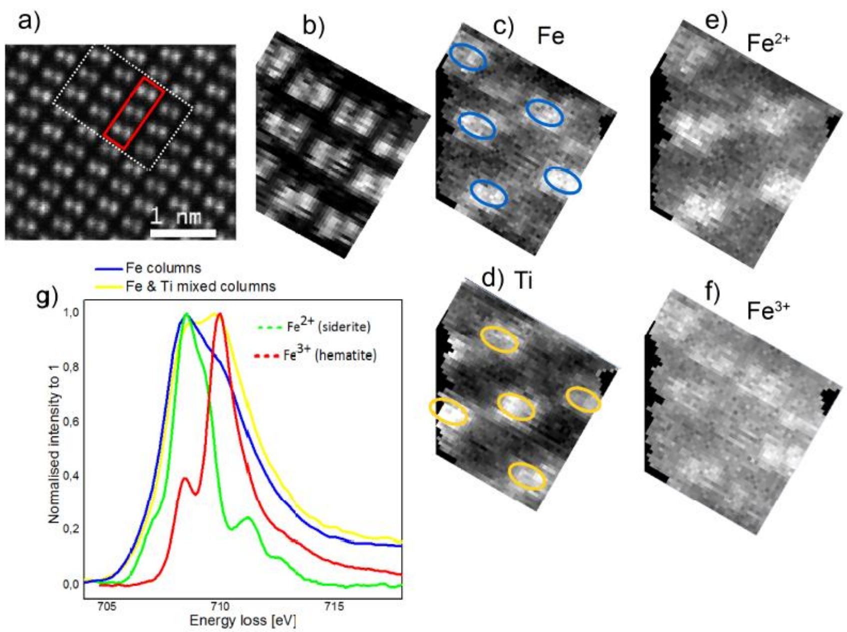



*Figure 2.*
*a) STEM-HAADF image of $Fe_{1.5}Ti_{0.5}O_{3-d}$,*
*b) STEM-HAADF map of the scanned area for EELS acquisition*
*c) and d) $Fe\text{-}L_{2,3}$ and $Ti\text{-}L_{2,3}$ elemental maps respectively,*
*e) and f) $Fe^{2+}$ and $Fe^{3+}$ reconstructed maps, respectively,*
*g) experimental ELNES $Fe\text{-}L_3$ fine structures extracted from pure Fe (blue) or mixed Fe/Ti (yellow) columns and the corresponding $Fe^{2+}/Fe^{3+}$ (green/red) ELNES $Fe\text{-}L_3$ edges of reference spectra.*

# $Fe_{1.5}Ti_{0.5}O_{3-\delta}$: conclusion and perspectives

**$Fe_{2-x}Ti_xO_{3-\delta}$**

epitaxial thin films on both $Al_2O_3$(0001) and SrTiO3(001):

- A versatile high Tc magnetic oxide becoming semiconductor
- Magnetism is gouvern by the atomic Ti/Fe order along c-axis (R-3 vs R- 3c)
- Strong influence of oxygen stoichiometry on conductivity
- Hopping conductivity for high $\delta$
- estimation of polarization from MR in // field : around 29% at room T …

**Perspectives:**

- Understand origin of oxygen deficient conductivity , magnetic anisotropy
- Decorrelate both « R-3 versus R-3c » and « $\delta$ » parameters in PLD growth
- $FeTiO_3$ in a R3c metastable phase is predicted « multiferroic »…

# Acknowledgments:

**GEMAC - Versailles:**

**PLD and structural:** Elena Popova, Bruno Berini
**Magneto-transport:** Ekaterina Chikoidze
**Magneto-optics:** Niels Keller
**1 PhD on FTO on $Al_2O_3$:** Hervé Ndilimabaka
**1 PhD on FTO on $SrTiO_3$:** Ali Hamie

**CEMES-Toulouse:** **TEM and EELS:** Benedicte Warot-Fonrose

**LPS-Orsay:** **STEM and ELNES:** L. Bocher, K. March, A. Gloter, O. Stephan

**Tyndall National Institute - Cork:** **Raman** Mircea Modreanu
**ab-initio calculations** Michael Nolan

**TSU-Tbilisi:** **semiconducting calculations:** Tamar Tchelidze
**EPR, FMR:** Alexander Shengelaya

**Institute of Physics, PAN-Warsaw:** **PL and ODMR:** Marek Godlewski

**Unité Mixte de Physique CNRS-Thales - Palaiseau:**
**Nanosized tunnel junctions:** Karim Bouzehouane, Manuel Bibes

**Institut des NanoSciences de Paris - Paris:** **RBS and NRA:** Julius Siejka