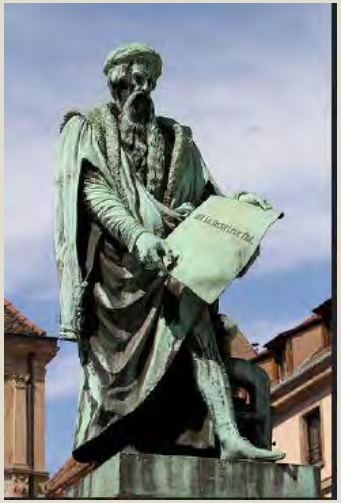
Spin Polarized State in the Two-Dimensional Electron Liquid at the Surface of SrTiO3

M. Gabay



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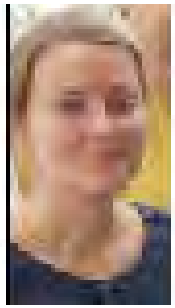
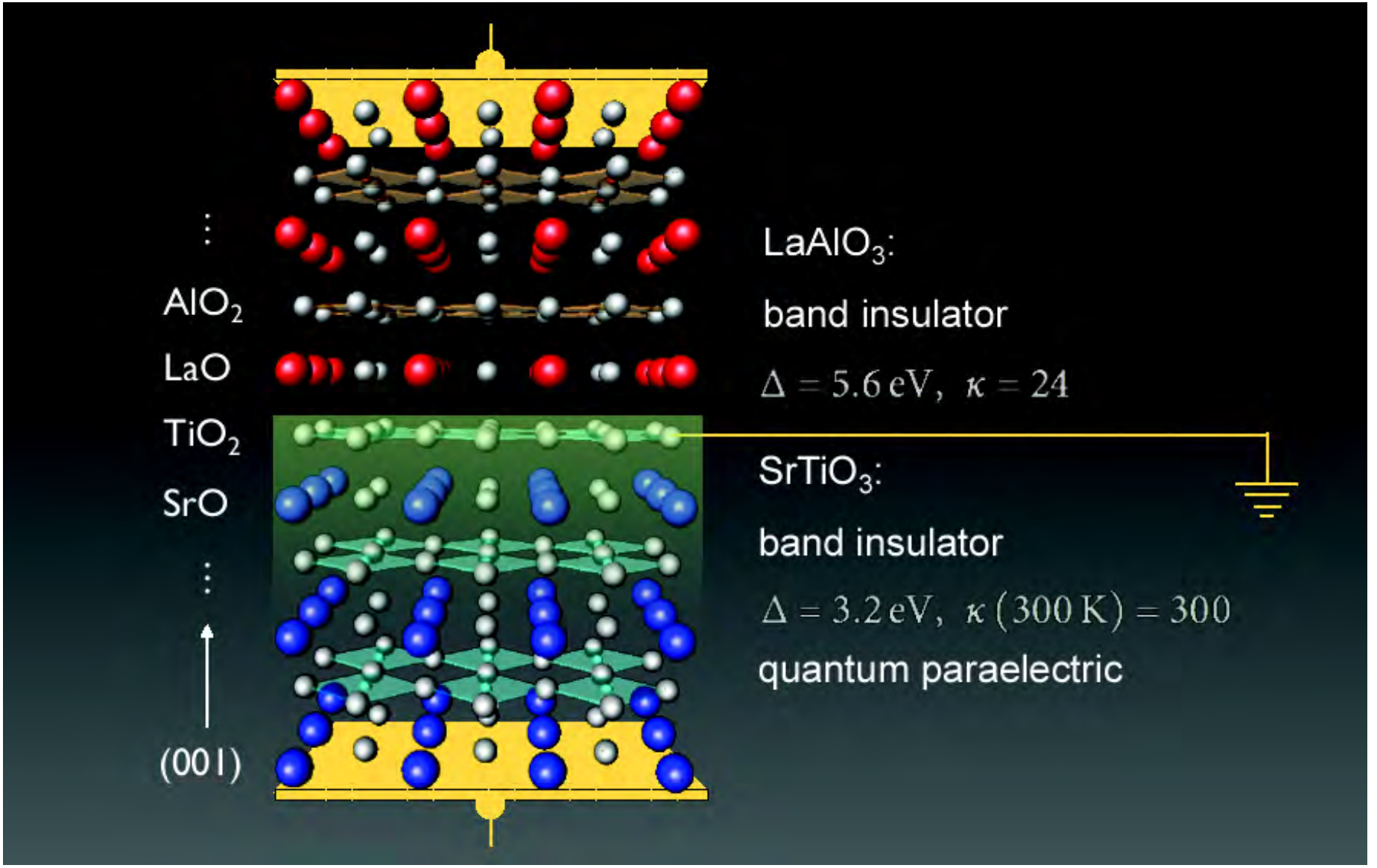
Schloβ Waldthausen 06/29-07/02/2015

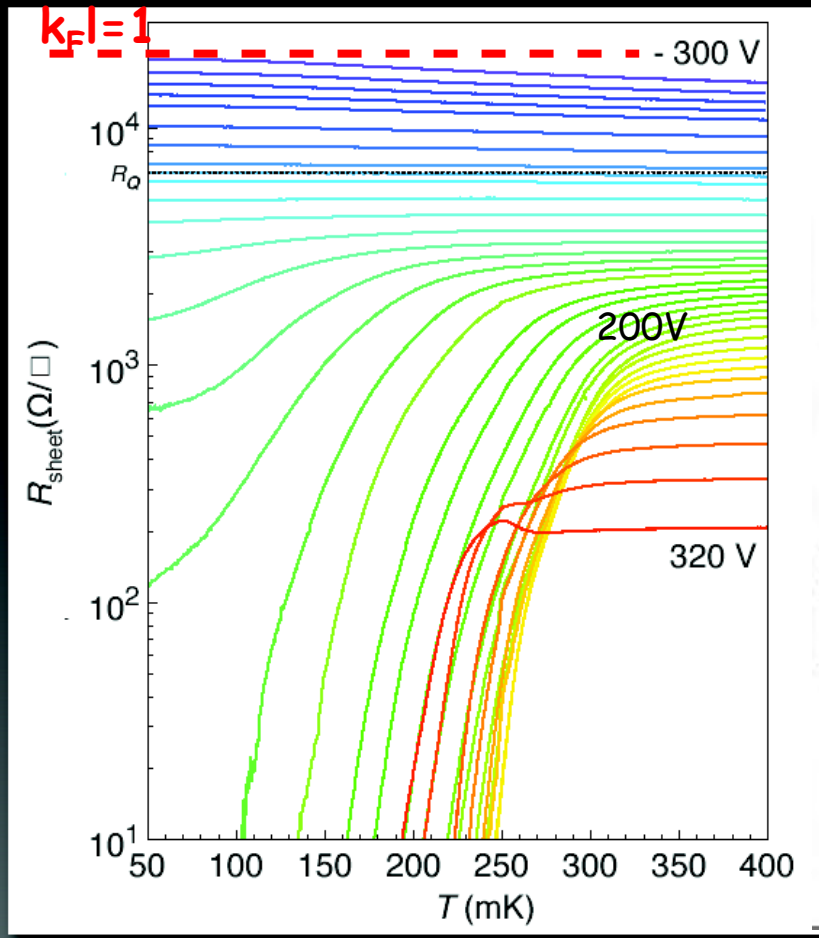
A. Santander-Syro, C. Martins

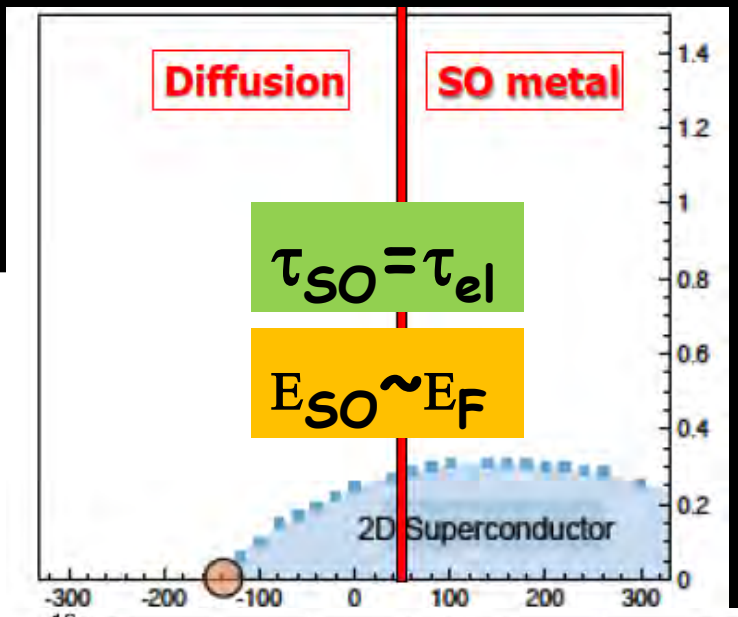
M. Rozenberg, O. Hijano Cubelos

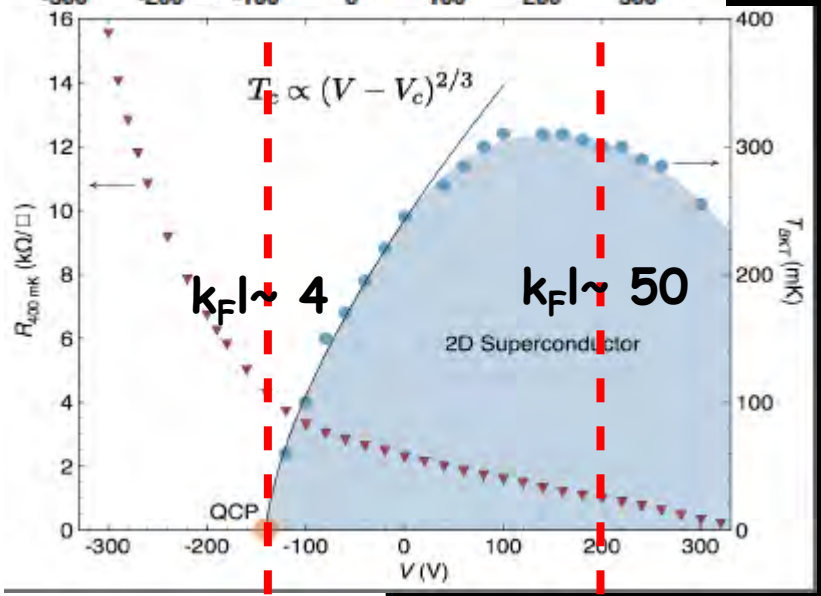
R. Valenti, H. Jeschke. M. Altmeyer
Goethe Universität Frankfurt am Main




AlO2
LaO
TiO2
SrO
(001)
LaAlO3:
band insulator
Δ = 5.6 eV, κ = 24
SrTiO3:
band insulator
Δ = 3.2 eV, κ (300 K) = 300
quantum paraelectric





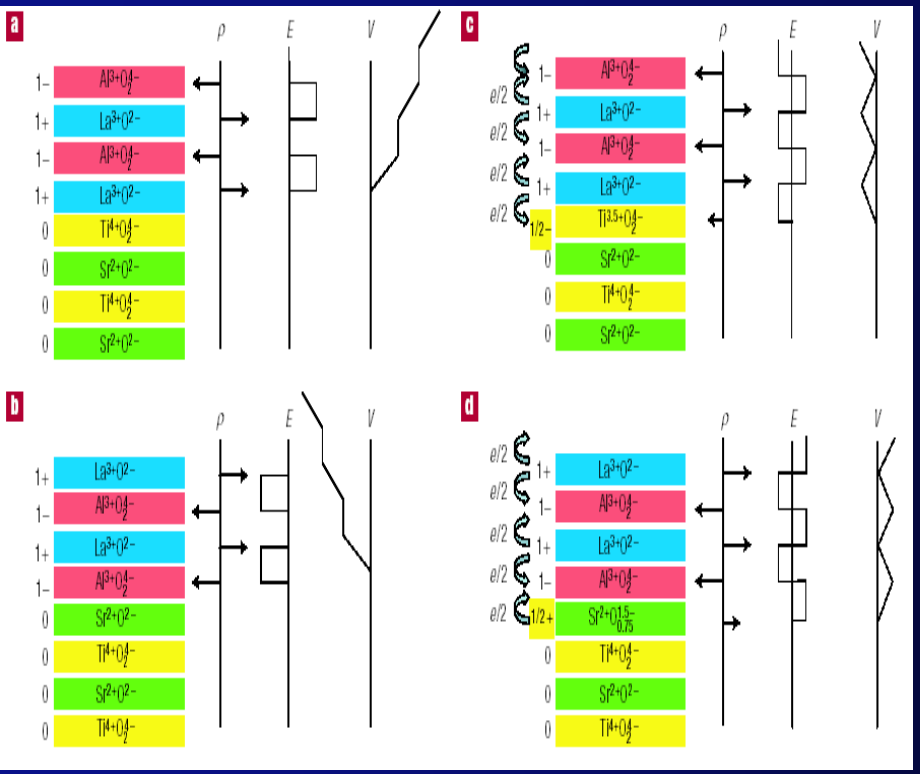


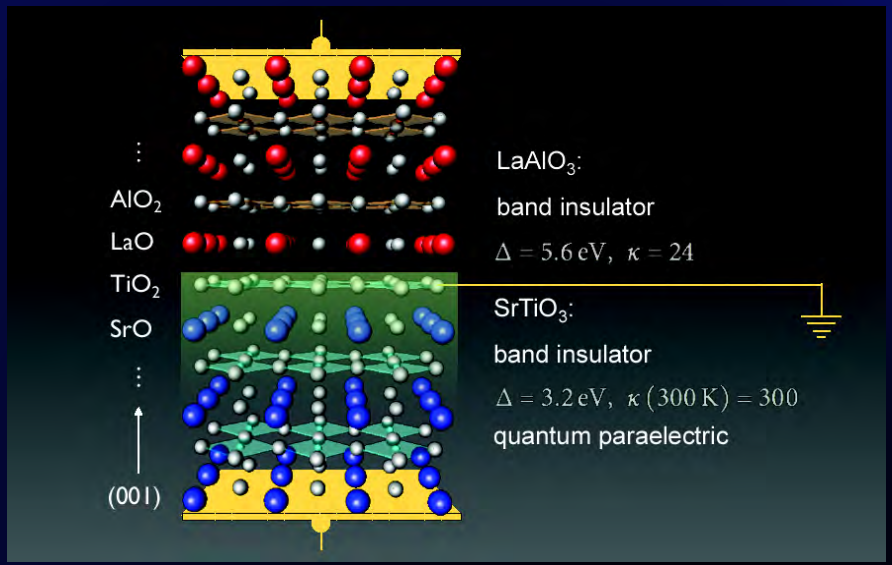
A. D. Caviglia et al., *Nature* **456**, 624 (2008)

J. Levy et al.,
Nature Communications
5, 5019 (2014)

2DEGS in perovskite oxides

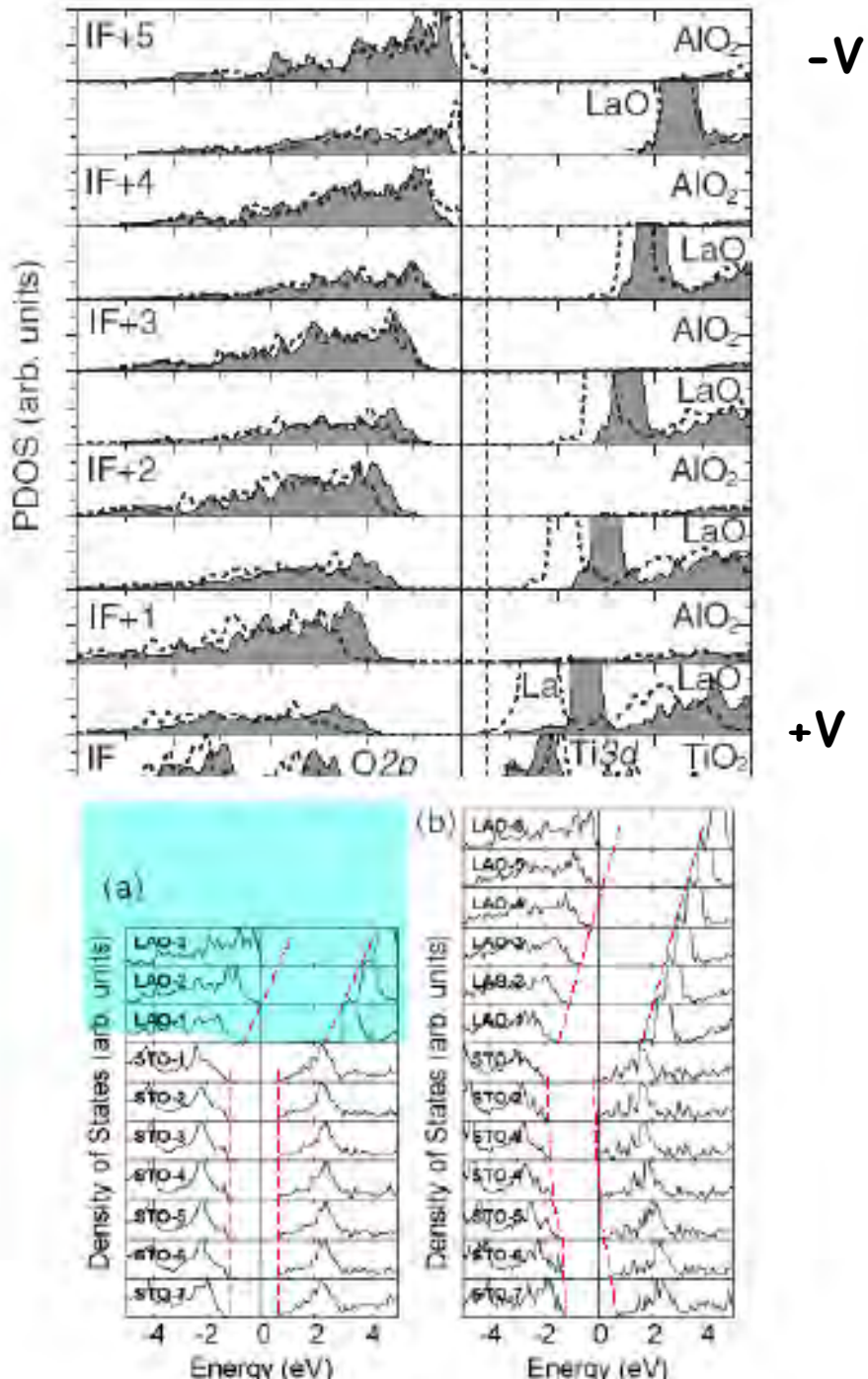
- Interface polar-non polar compounds





NAOYUKI NAKAGAWA[1,2], HAROLD Y. HWANG[1,2] AND DAVID A. MULLER

nature materials | VOL 5 | MARCH 2006

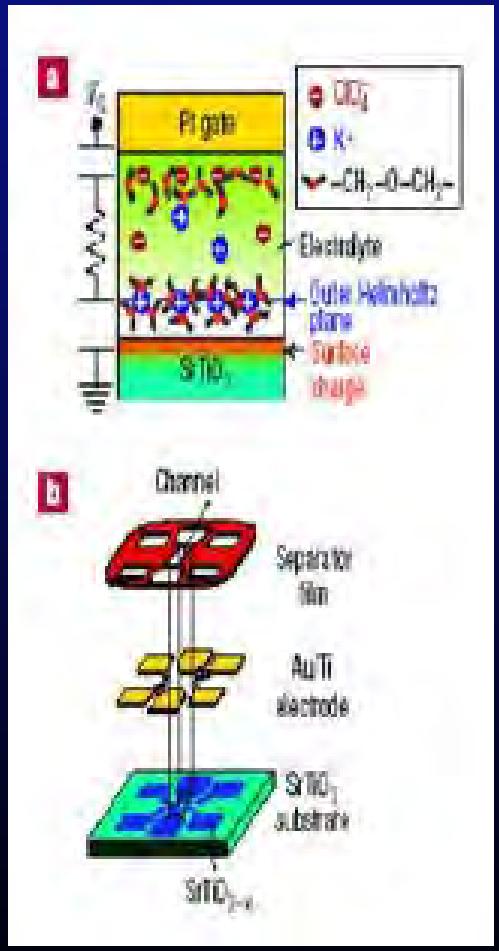


Rossitza Pentcheva[1] and Warren E. Pickett

PRL **102,** 107602 (2009)

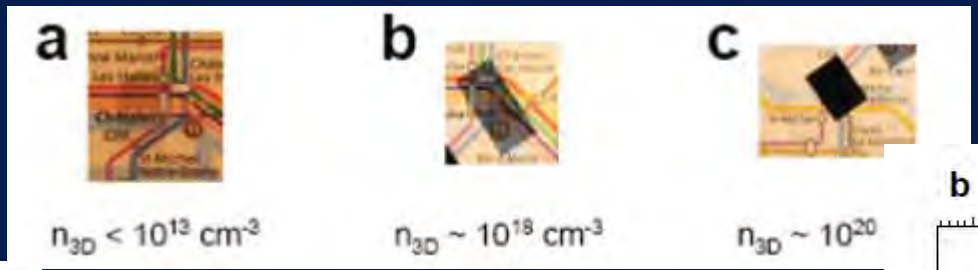
2DEGS in perovskite oxides

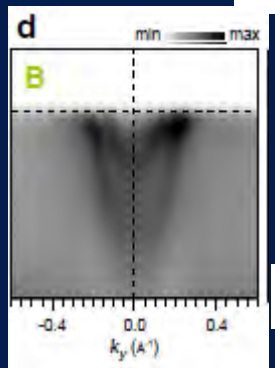
- Interface polar-non polar compounds
- Surface non polar material

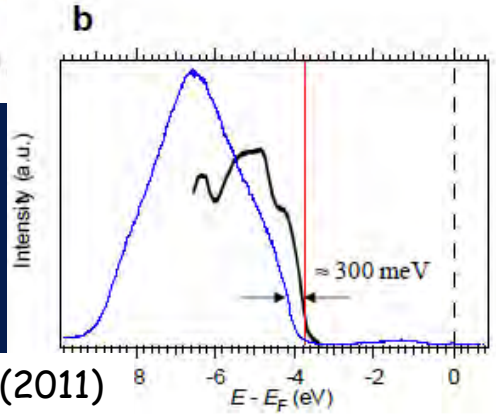


2DEGS in perovskite oxides

- ❖ Interface polar-non polar compounds
- ❖ Surface non polar material
- ❖ Or cleaved surface in high vacuum

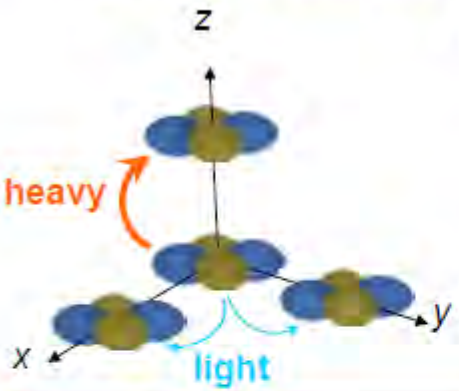


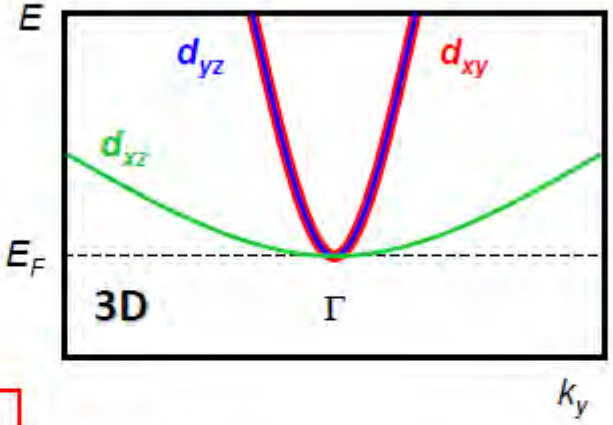


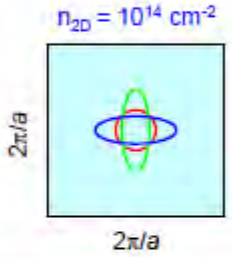


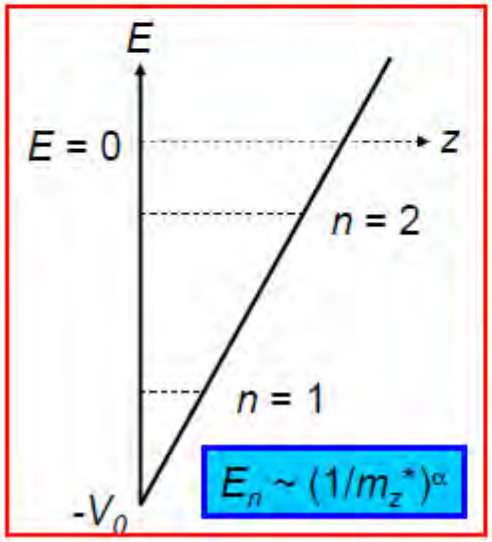
A. Santander-Syro et al. Nature 469, 189-193 (2011)

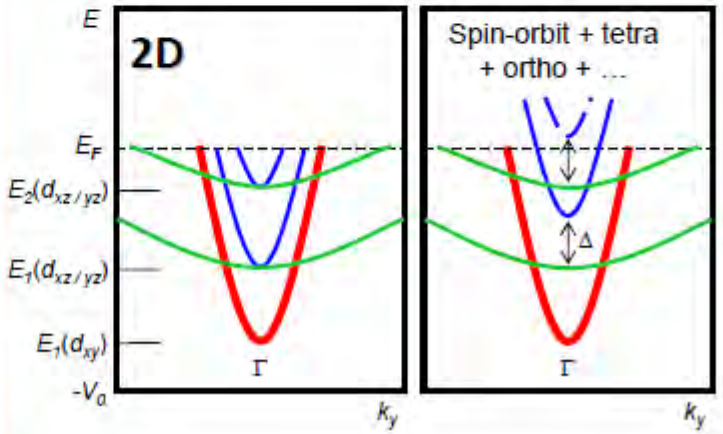
$SrTiO_3$: bulk *vs* 2D-confined electronic structure









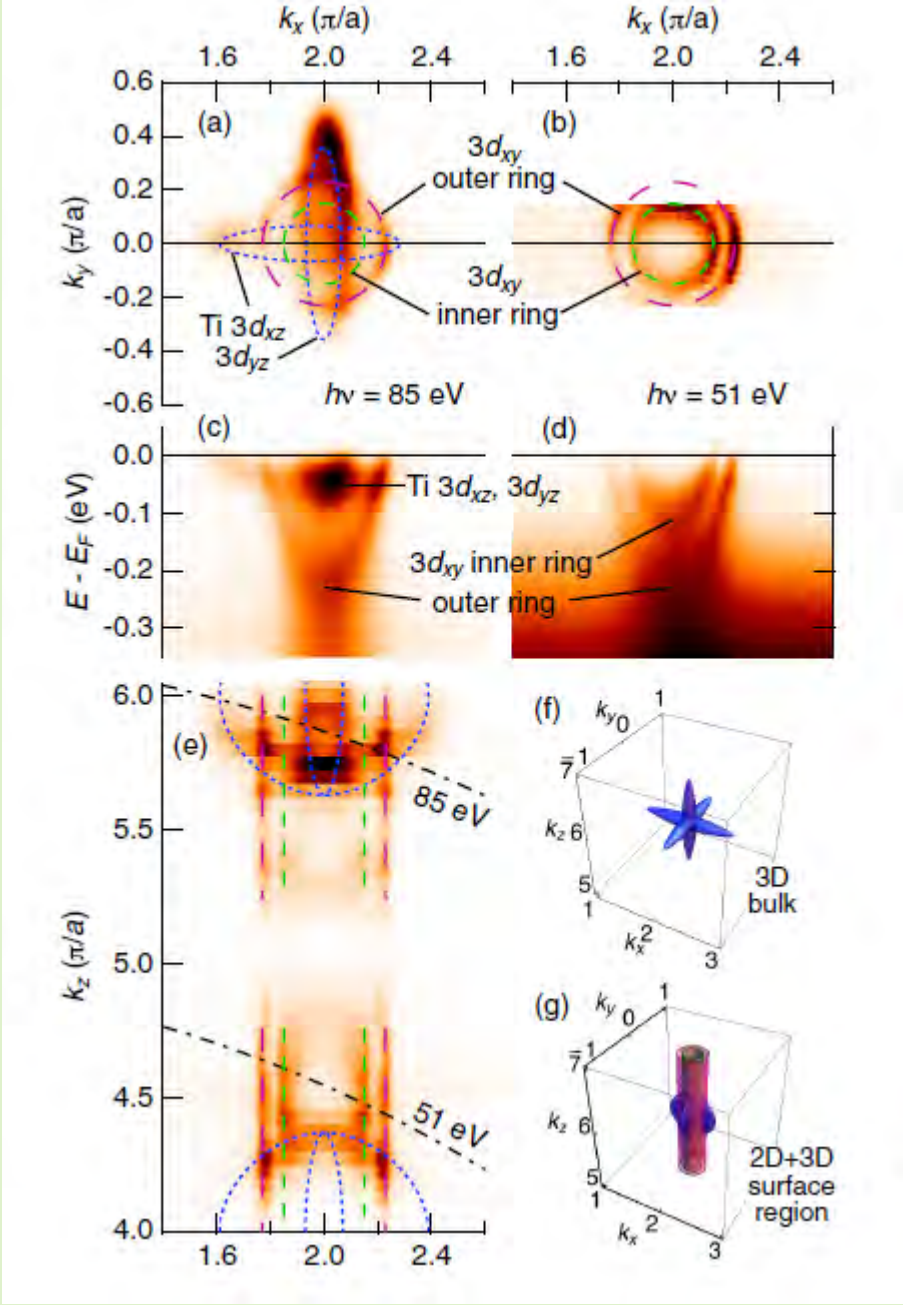


4 u.c < L < 8 u.c

n_{2D}~0.25 e/u.c

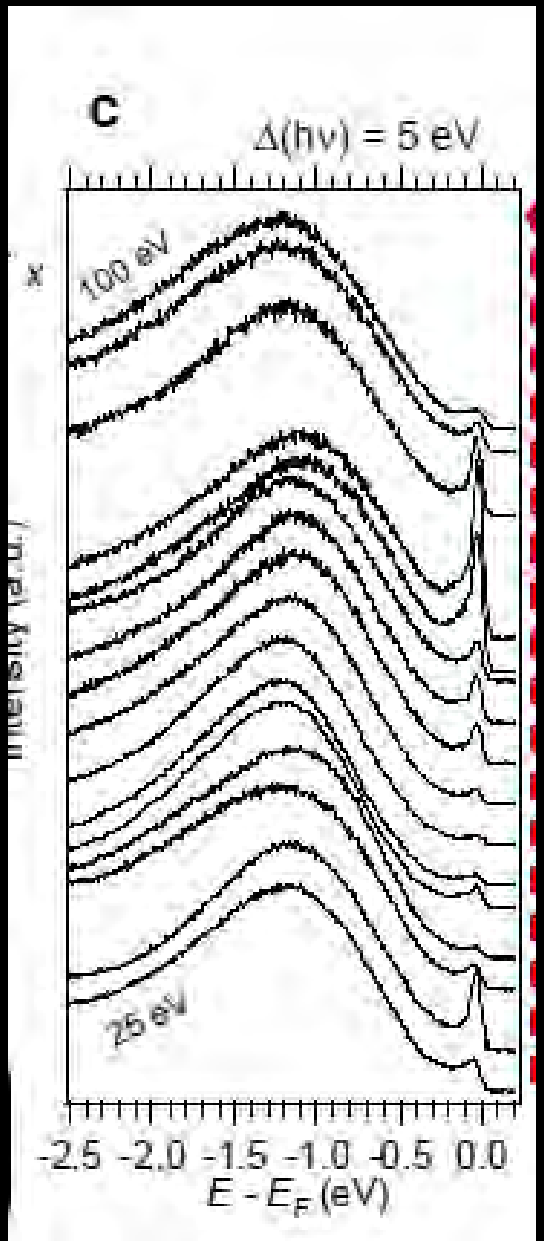
F~100MV/m

A.F. Santander Syro et al. Nature 469, 189 (2011)
Meevasana et al. Nat. Mater. 10, 114 (2011)



N.C Plumb et al

PRL **113**, 086801 (2014)



A. Santander-Syro et al. Nature 469, 189-193 (2011)

Unveiling a two-dimensional electron gas with universal subbands at the surface of $SrTiO_3$

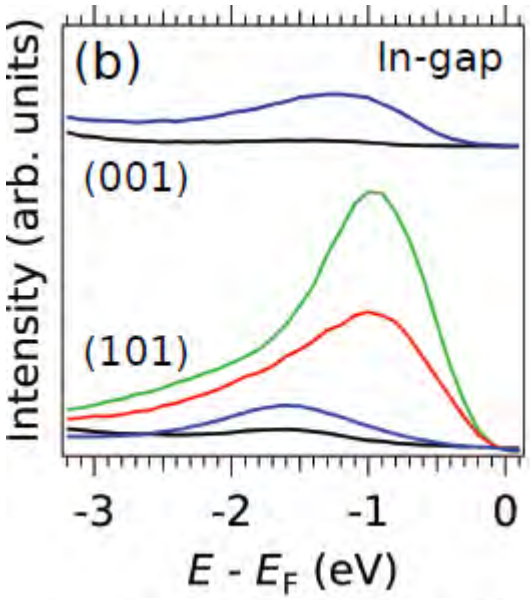


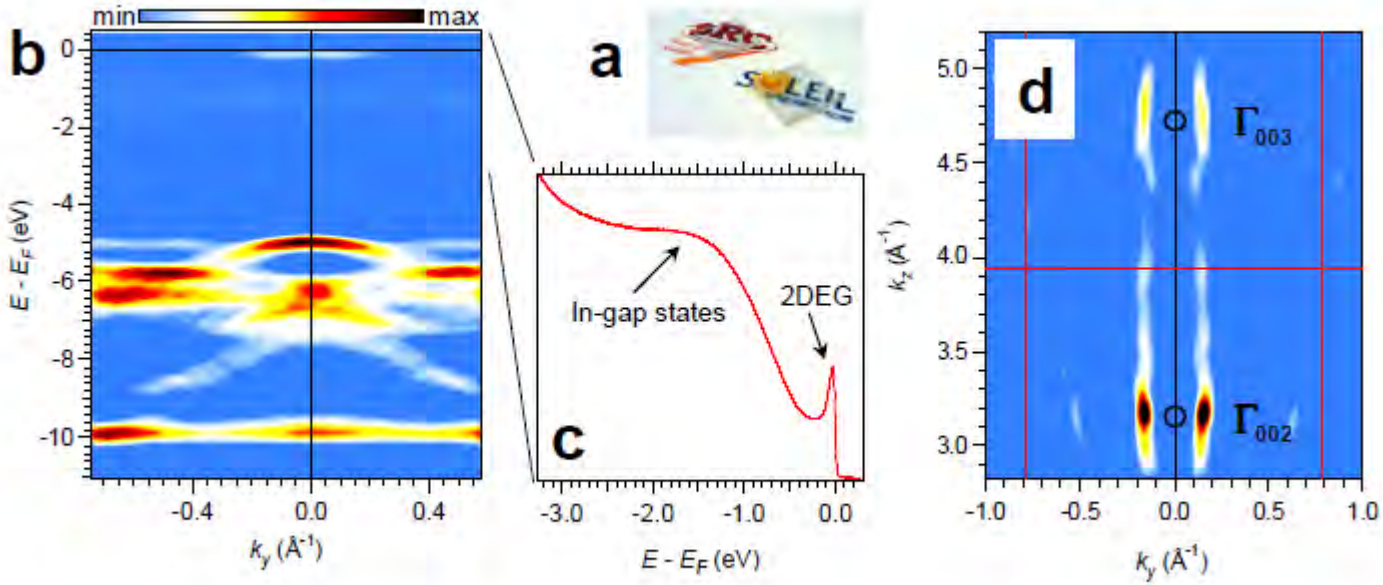
Figure 1: (Color online) Angle integrated spectra of (a) the Ti-3p peak, and (b) the in-gap state of the anatase TiO_2 (001) and (101) surfaces (upper and lower curves, respectively) measured at $h\nu = 100$ eV. The black curve was measured shortly after the first light exposure, and the blue, red and green curves at sequentially increasing times respectively. (c) Binding energy of the Ti^{4+} peak and concentration of oxygen

Light engineering of two dimensional electron gases at the (001) and (101) surfaces of TiO_2 anatase

T. C. Rödel,[†,‡] F. Fortuna,[†] F. Bertran,[‡] M. Gabay,[¶] M. J. Rozenberg,[¶]

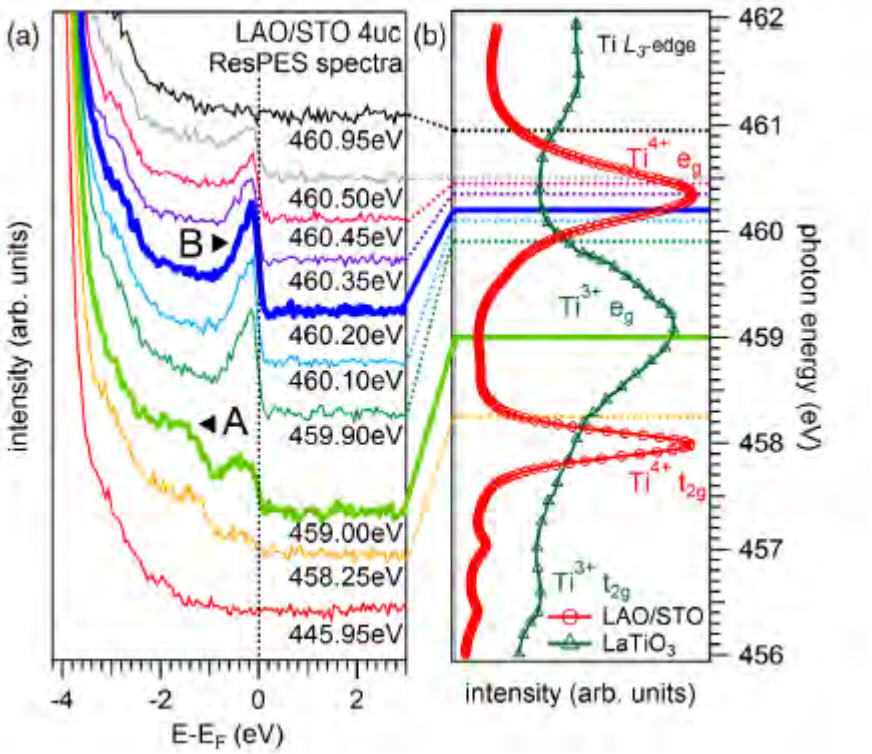
A. F. Santander-Syro,[*,†] and P. Le Fèvre[‡]

To appear in Phys. Rev. B (R) 2015



Orbital symmetry reconstruction and strong mass renormalization in the two-dimensional electron gas at the surface of KTaO3

A. F. Santander-Syro, et al.,Phys. Rev. B 86, 121107(R) , 2012

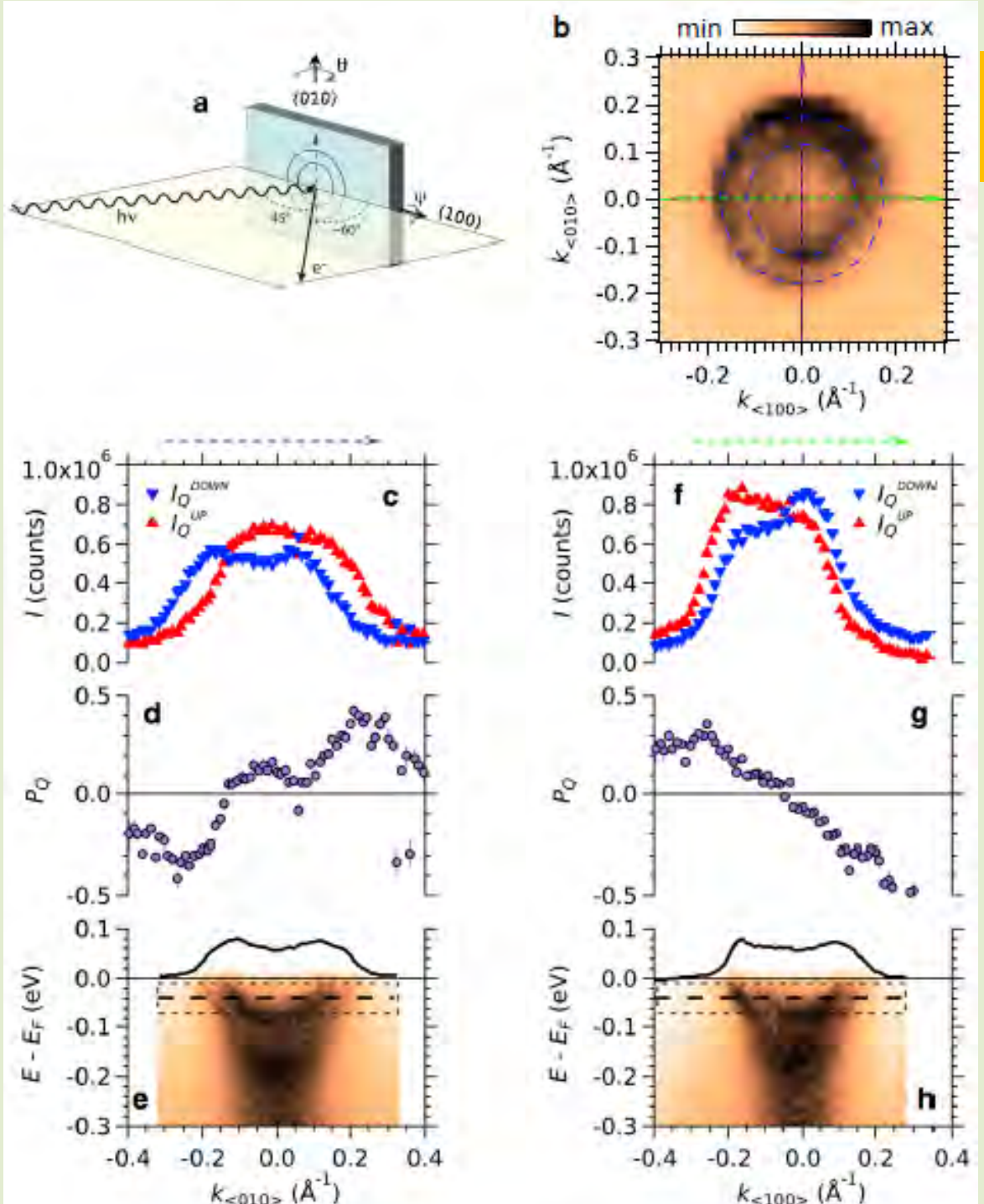


The complete valence band spectrum, measured on resonance ($h\nu = 460.20$ eV), is depicted in Fig. 1(c). The off-resonance spectrum ($h\nu = 445.95$ eV) shows no spectral weight at the chemical potential. Moving through the resonance two structures appear—indicating that both are of Ti $3d$ character—a broad structure at a binding energy of ≈ 1.3 eV (A) and a structure which is cut off by the Fermi-Dirac distribution function [marked by B in

PRL **110,** 247601 (2013)

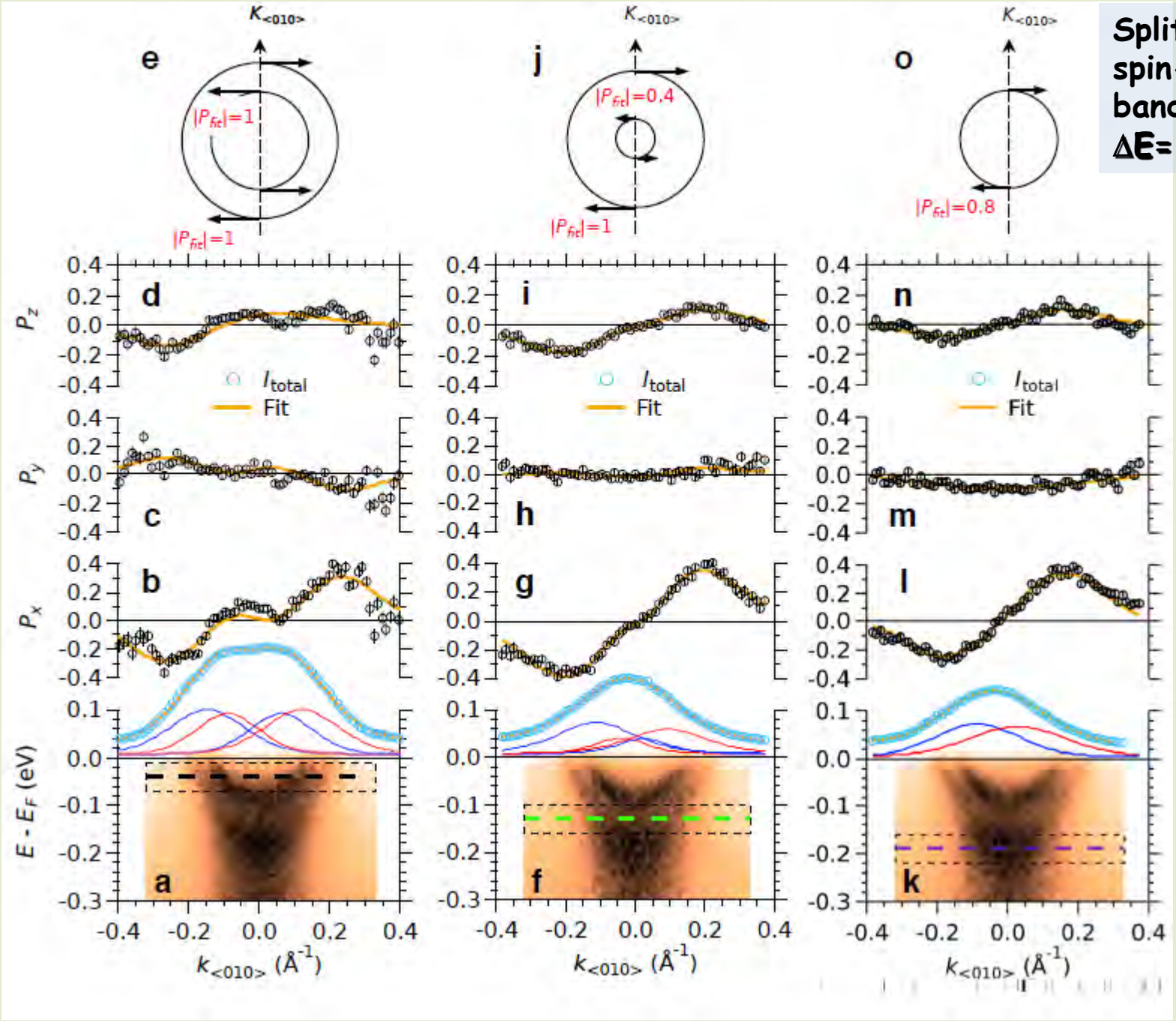
Direct *k*-Space Mapping of the Electronic Structure in an Oxide-Oxide Interface

G. Berner,[1] M. Sing,[1] H. Fujiwara,[2] A. Yasui,[3] Y. Saitoh,[3] A. Yamasaki,[4] Y. Nishitani,[4] A. Sekiyama,[2] N. Pavlenko,[5,6,7] T. Kopp,[5] C. Richter,[5,7] J. Mannhart,[7] S. Suga,[8] and R. Claessen[1]



A. F. Santander-Syro, et al.
Nature Materials 13,
1085–1090 (2014)

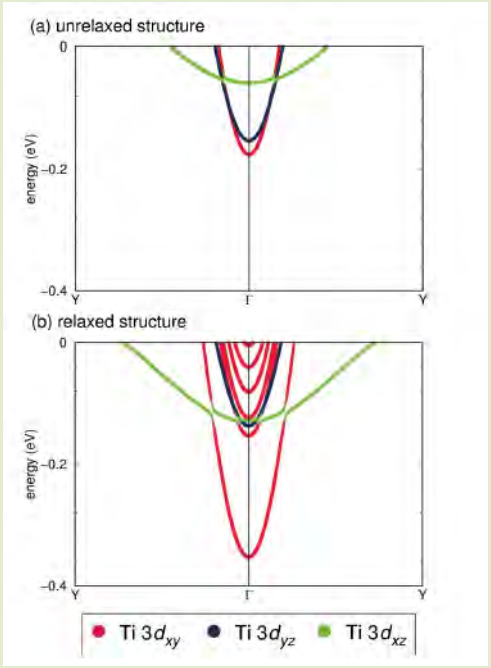
$\Delta k_F \sim 0.1$ Å^{-1}


Splitting of the spin-polarized bands:
ΔE=100 meV
e
j
o
$K_{<010>}$
$|P_{fit}|=1$
$|P_{fit}|=0.4$
$|P_{fit}|=0.8$
d
i
n
c
h
m
b
g
l
a
f
k
P_z
P_y
P_x
I_{total}
Fit
$E - E_F$ (eV)
$k_{<010>}$ (Å^{-1})

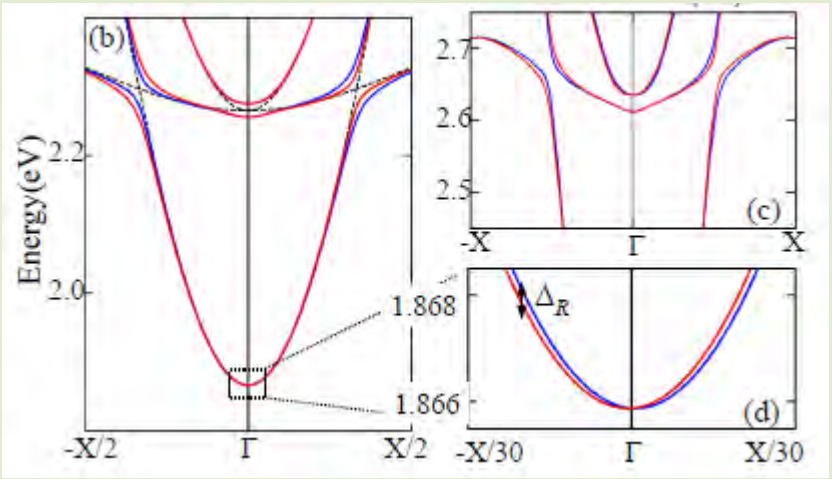
Oxygen vacancies at the boundary could be a unifying mechanism responsible for the presence of the 2DEG

What role, if any do O vac play in

- **Spin-orbit effects (via relaxations or other processes)**



Juan Shen, Hunpyo Lee, Roser Valentí, and Harald O. Jeschke
PHYSICAL REVIEW B **86**, 195119 (2012)



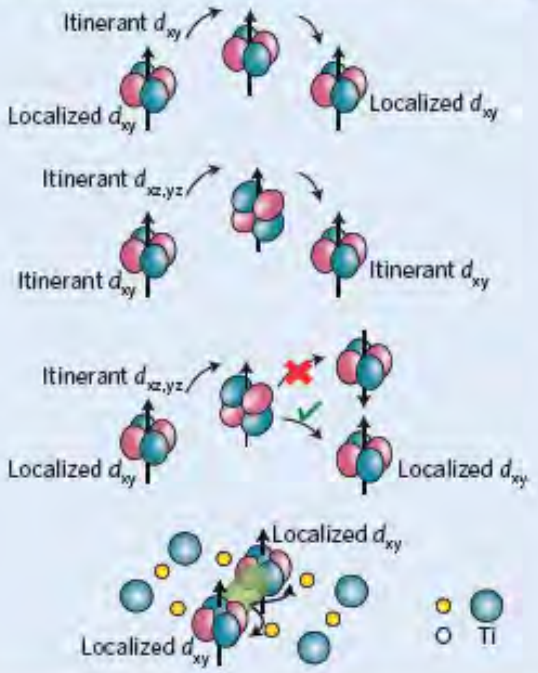
Zhicheng Zhong, Anna Tóth, and Karsten Held
Phys. Rev. B 87, 161102(R) (2013)

Oxygen vacancies at the boundary could be the unifying mechanism responsible for the presence of the 2DEG

What role, if any do O vac play in

- **Magnetism 1**

Table 1 | Selected explanations for the magnetism at the LAO/STO interface.



At low concentrations itinerant d_{xy} electrons mediate a ferromagnetic interaction between the d_{xy} spins localized at the interface[12].

The quasi one-dimensional nature of the d_{xz} (or d_{yz}) electrons allows a large magnetic polarization to develop on these orbitals. Hund's rule transfers this polarization to the d_{xy} electron[13].

For low concentrations of electrons, Hund's rule mediates a ferromagnetic interaction between the d_{xy} spins localized at the interface. With Rashba spin-orbit coupling a spiral state develops[5].

At the interface, an oxygen vacancy (identified by the green region) releases an electron in each of the neighbouring Ti d_{xy} orbitals. Their spins couple ferromagnetically[14].

Marc Gabay and Jean-Marc Triscone

Nature physics 10.1038/nphys2737 (2013)

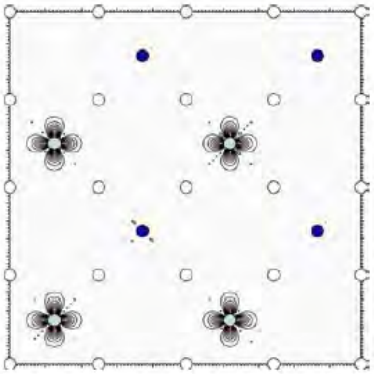


FIG. 11. (Color online) Charge density plot of the charge ordered state localized in the TiO_2 layer of the n-type interface. Ti^{3+} with an occupied d_{xy} orbital and Ti^{4+} marked by light and dark blue (gray) circles, respectively, are ordered in a (45°) checkerboard manner. Oxygens are marked by white circles. The plotted area corresponds to four $c(2\times2)$-simulation cells.

R. Pentcheva,
PRB74, 035112 (2006)

14. Pavlenko, N. *et al. Phys. Rev. B* 85, 020407(R) (2012)

Oxygen vacancies at the boundary could be the unifying mechanism responsible for the presence of the 2DEG

What role, if any do O vac play in

- **Magnetism 2**

M. Salluzzo et al.

Phys. Rev. Lett. 111, 087204 (2013)

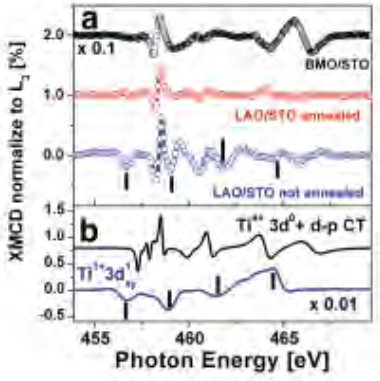


FIG. 4: (color online) Comparison between experimental and theoretical XMCD spectra. (a) Normalized Ti XMCD of BMO/STO (black circles, scaled by a factor 0.1), of standard LAO/STO (red circles) and of oxygen-vacancy rich LAO/STO (blue open circles). (b) Single ion multiplet scattering calculations of the XMCD spectra for Ti^{4+} (black line) and Ti^{3+} (blue line), using an exchange field of -10 meV and +10 meV respectively. (c) A cartoon illustration of the proposed mechanism of magnetism at the titanate heterostructures. In LAO/STO oxygen vacancies lead to localized Ti^{3+} sites, holding sizable spin and orbital magnetic moments thanks to their 3dxy electron. The q2DEG gets polarized by these magnetic impurities and mediates a long range magnetic interaction leading to ferromagnetism at low temperature.

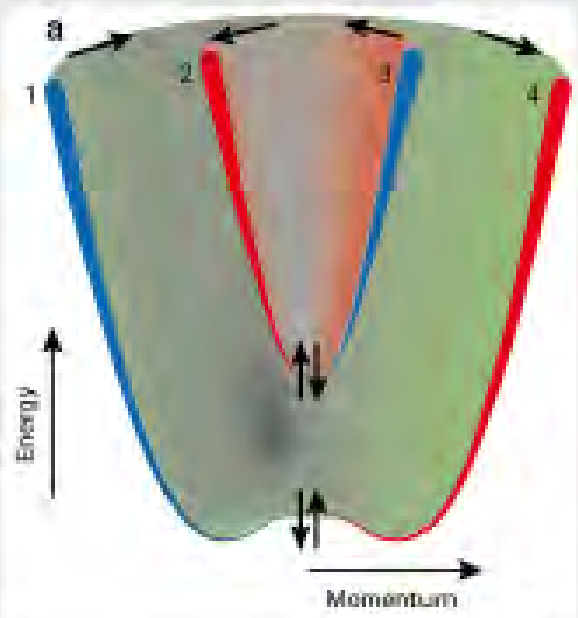
Rashba splitting and magnetism

Energy gap

Hamiltonian and eigenvalues:

$$\mathcal{H} = \frac{\vec{p}^2}{2m} + \frac{\alpha}{\hbar}(\vec{\sigma} \times \vec{p}) \cdot \hat{z} + \Delta\sigma_z$$

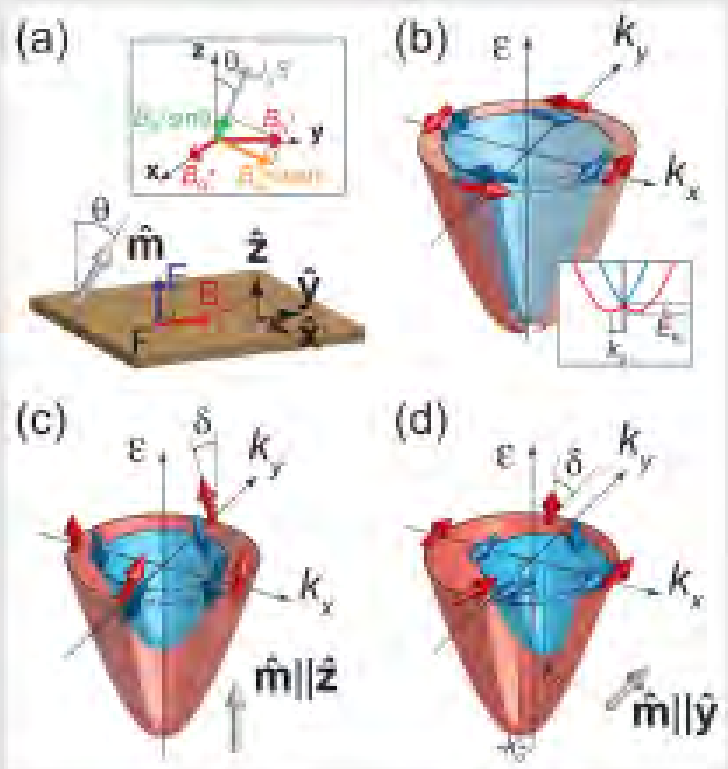
$$\epsilon_{\pm}(\vec{k}) = \frac{\hbar^2 k^2}{2m} \pm \sqrt{\alpha^2 k^2 + \Delta^2}$$



A.F. Santander-Syro *et al.*, Nature Materials (2014)

Spin canting

$$\delta = \tan^{-1}\left(\frac{\alpha_R(k_\infty^2 \cos^2\theta + k_y^2)^{1/2}}{J_0 S}\right)$$

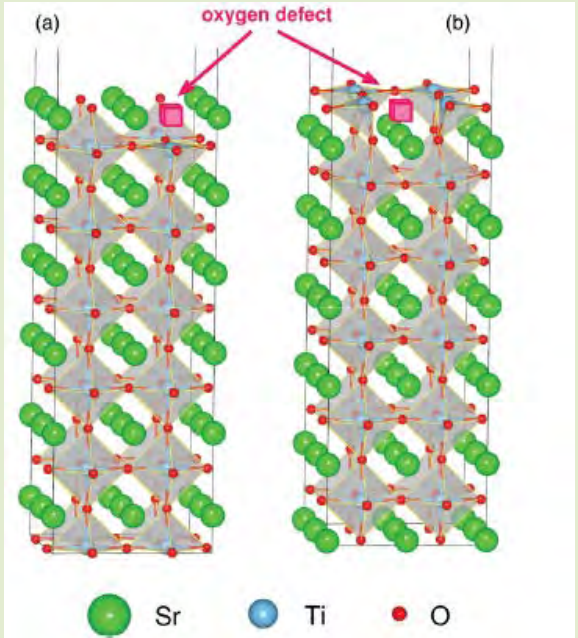


S.E. Barnes *et al.*, Scientific Reports **4**, 4105 (2014)

Oxygen vacancies at the boundary could be the unifying mechanism responsible for the presence of the 2DEG

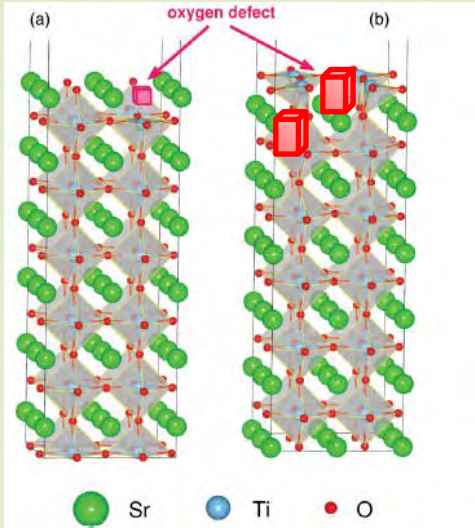
Modeling by

- **DFT for slabs in the presence of O vac (relaxed structures)**
- **Finite cluster analytical calculations (assess most relevant orbitals)**



Single O vac

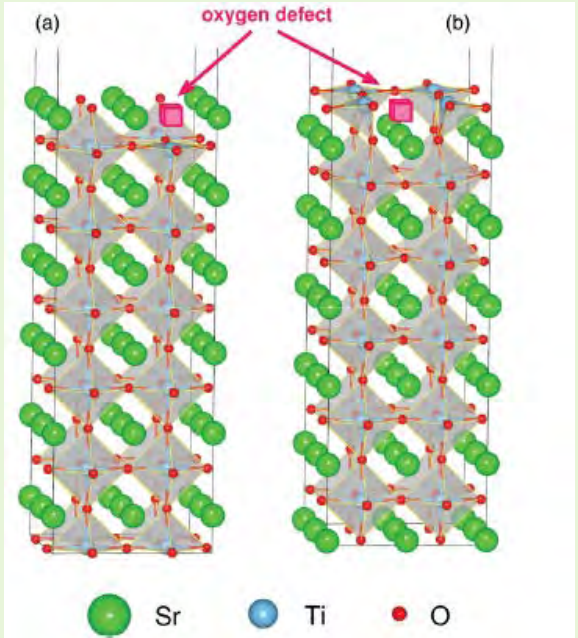
Double O vac



Oxygen vacancies at the boundary could be the unifying mechanism responsible for the presence of the 2DEG

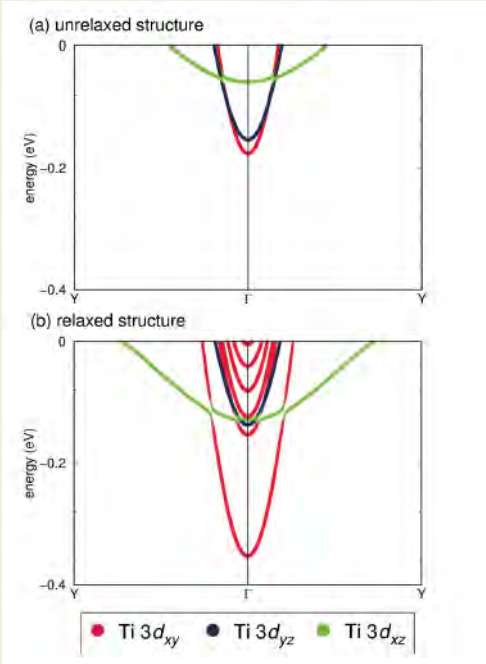
Modeling by

- **DFT for slabs in the presence of O vac (relaxed structures)**
- **Finite cluster analytical calculations (assess most relevant orbitals)**



Single O vac

2DEG but no in-gap state

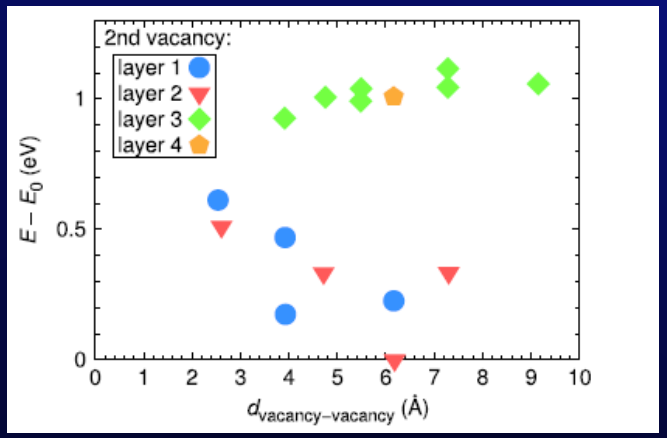


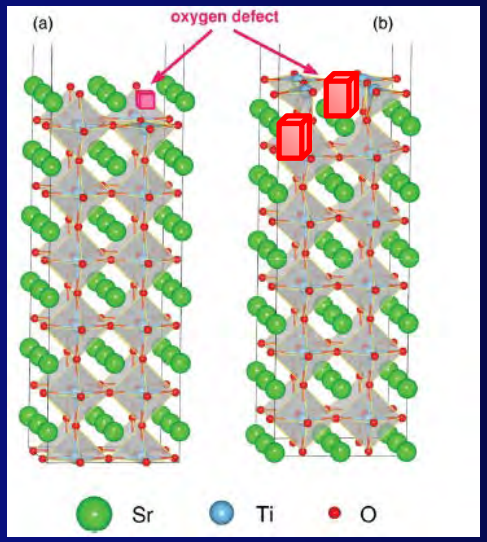
J. Shen et al. Phys. Rev. B 86, 195119, 2012

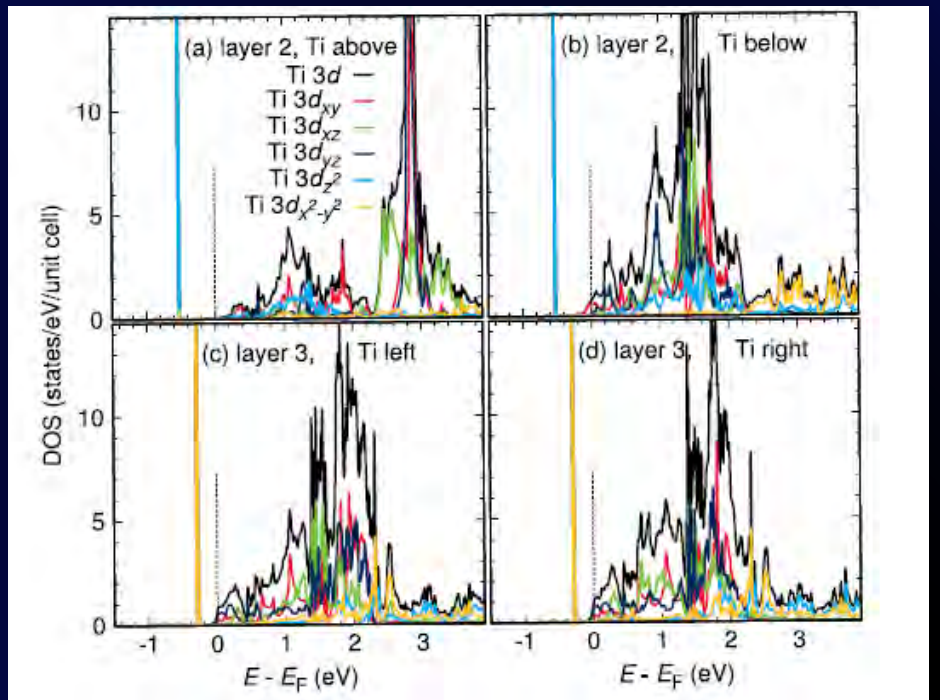
Oxygen vacancies at the boundary could be the unifying mechanism responsible for the presence of the 2DEG

divacancy

- TiO2 termination
- 1 vacancy in top layer
- + 1 nearby







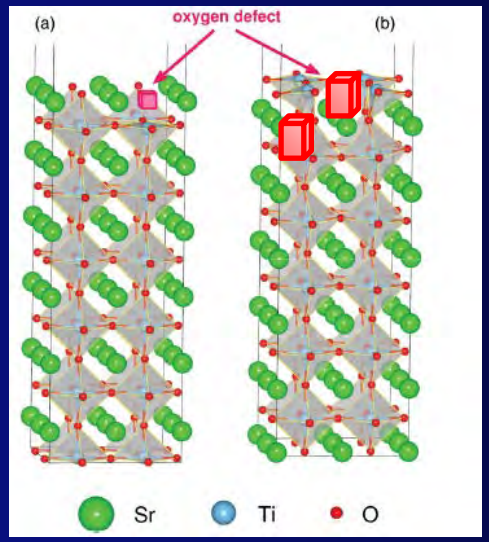
H. Jeschke et al. New J. Phys. 17 (2015) 023034

Oxygen vacancies at the boundary could be the unifying mechanism responsible for the presence of the 2DEG

divacancy

- TiO2 termination
- 1 vacancy in top layer
- +1 nearby

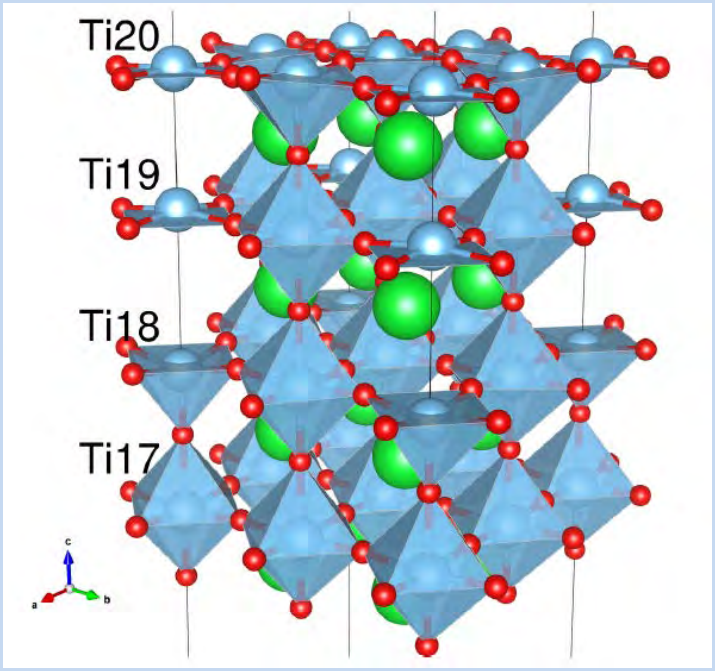
Qualitative agreement with
non spin-resolved ARPES spectrum

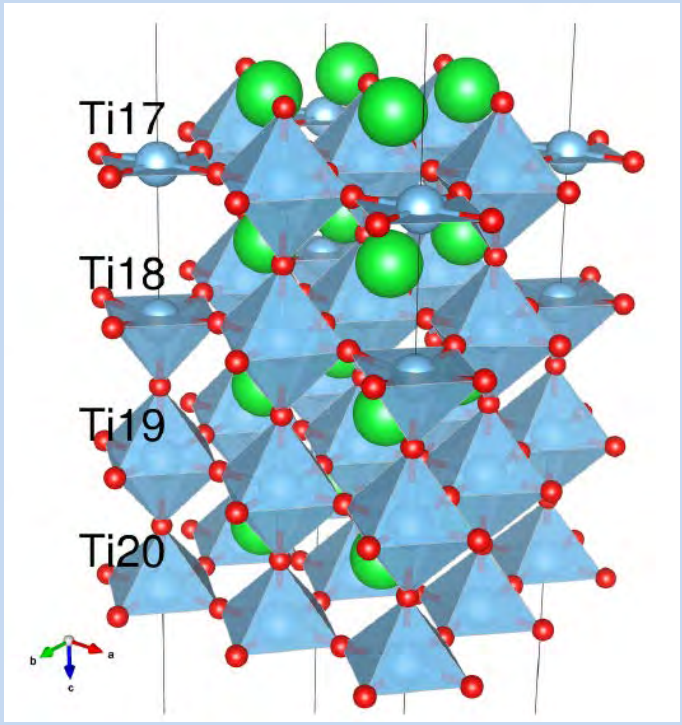


- ❑ Can we recover 1.3 eV peak?
- ❑ Where do the extra states come from?
- ❑ How about the spin sector?

H. Jeschke et al. New J. Phys. 17 (2015) 023034

Vertical di-vacancy





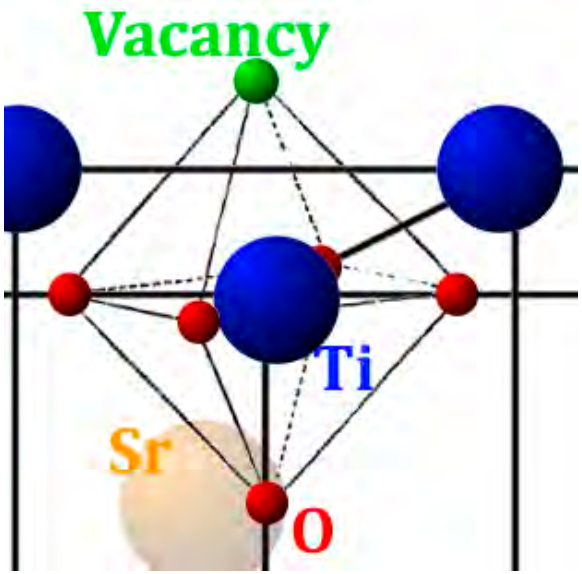
TiO2 terminated

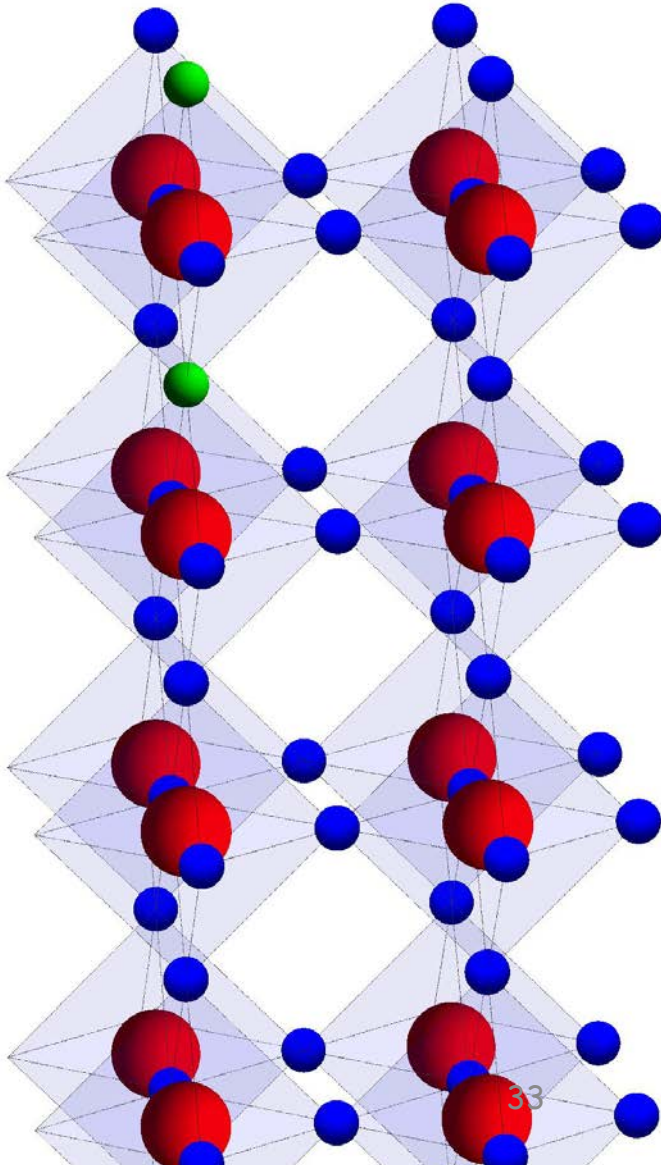
SrO terminated

Experimentally, termination is a mixture of both

(001) – 2x2x4 cluster

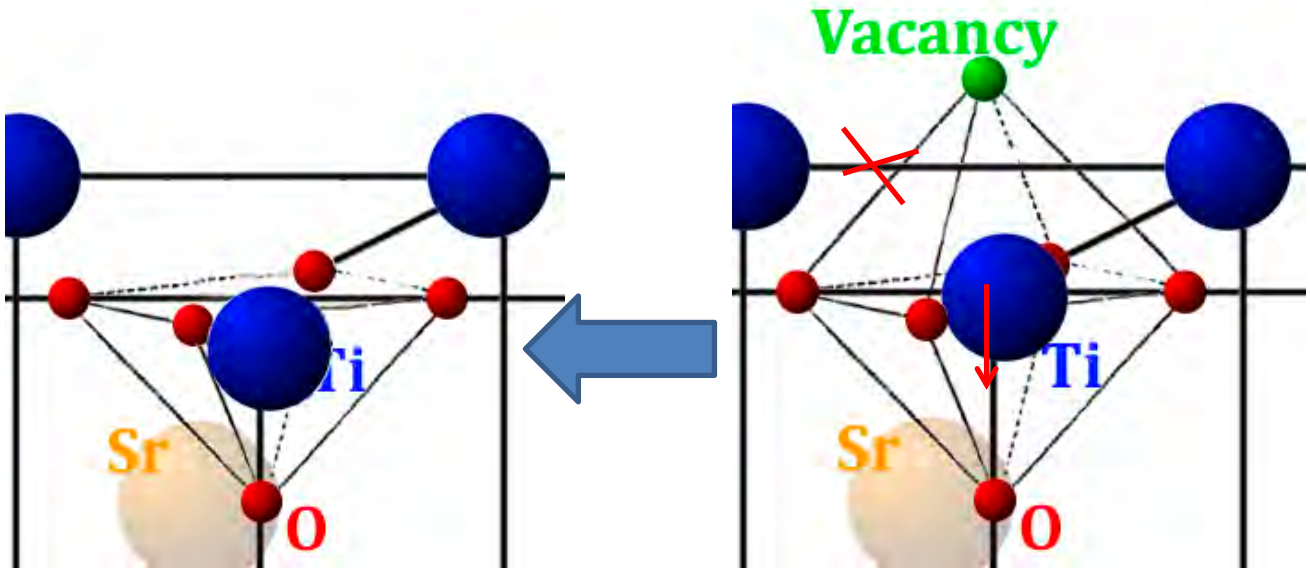
- Include: Rotations, **Oxygen-vacancies**
- Tight-binding model
- XY - periodic



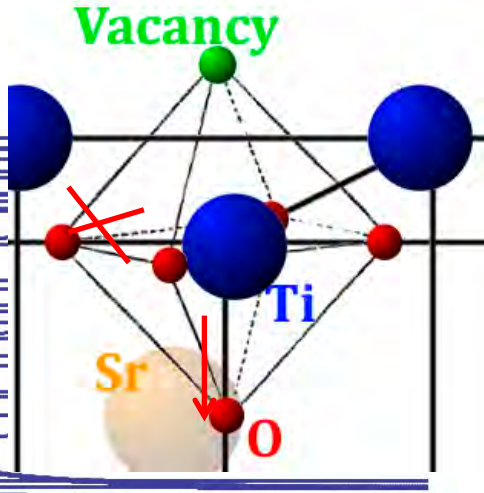


Remove Vacancy

- Remove d-p and p-p
- Displace Ti
- Increase E_p
  - Avoid having e sitting on site of vacancy
- Change d_{z^2}-d_{xz}-d_{yz} energies
  - Some d orbitals 'see' the effect of the new Ti local neighbours



"Smoothly" removing the vacancy



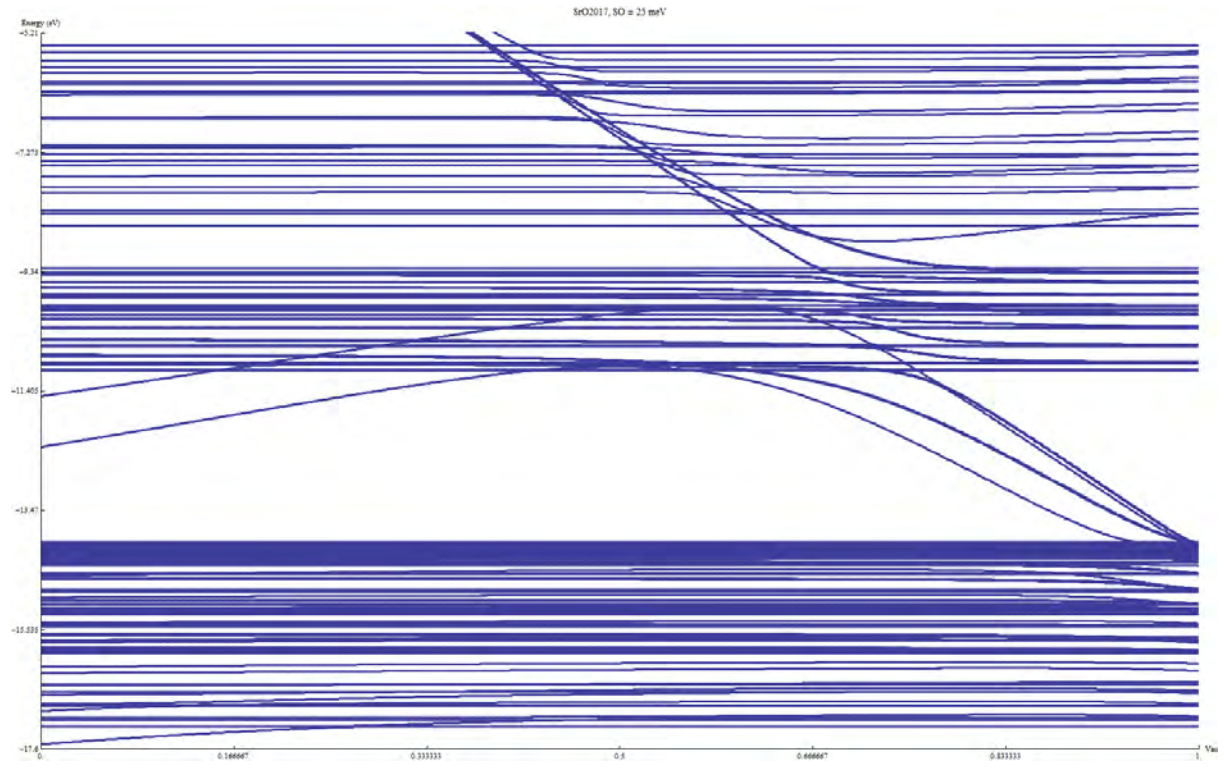
Energy (eV)
−5.21
−7.275
−9.34
−11.405
−13.47
−15.535
−17.6
0.
0.166667
0.333333
0.5
0.666667
0.833333
1.
Vac

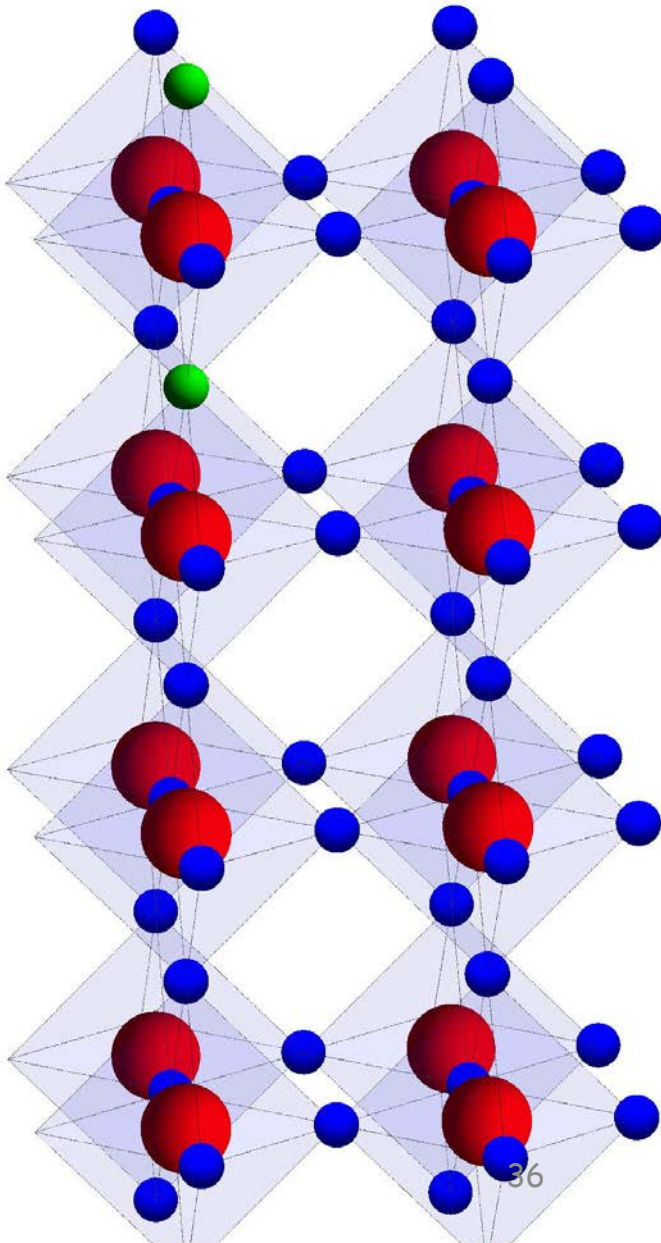
Vacancy ⟷ **Unperturbed**

Results for 2 vacancies vertically aligned

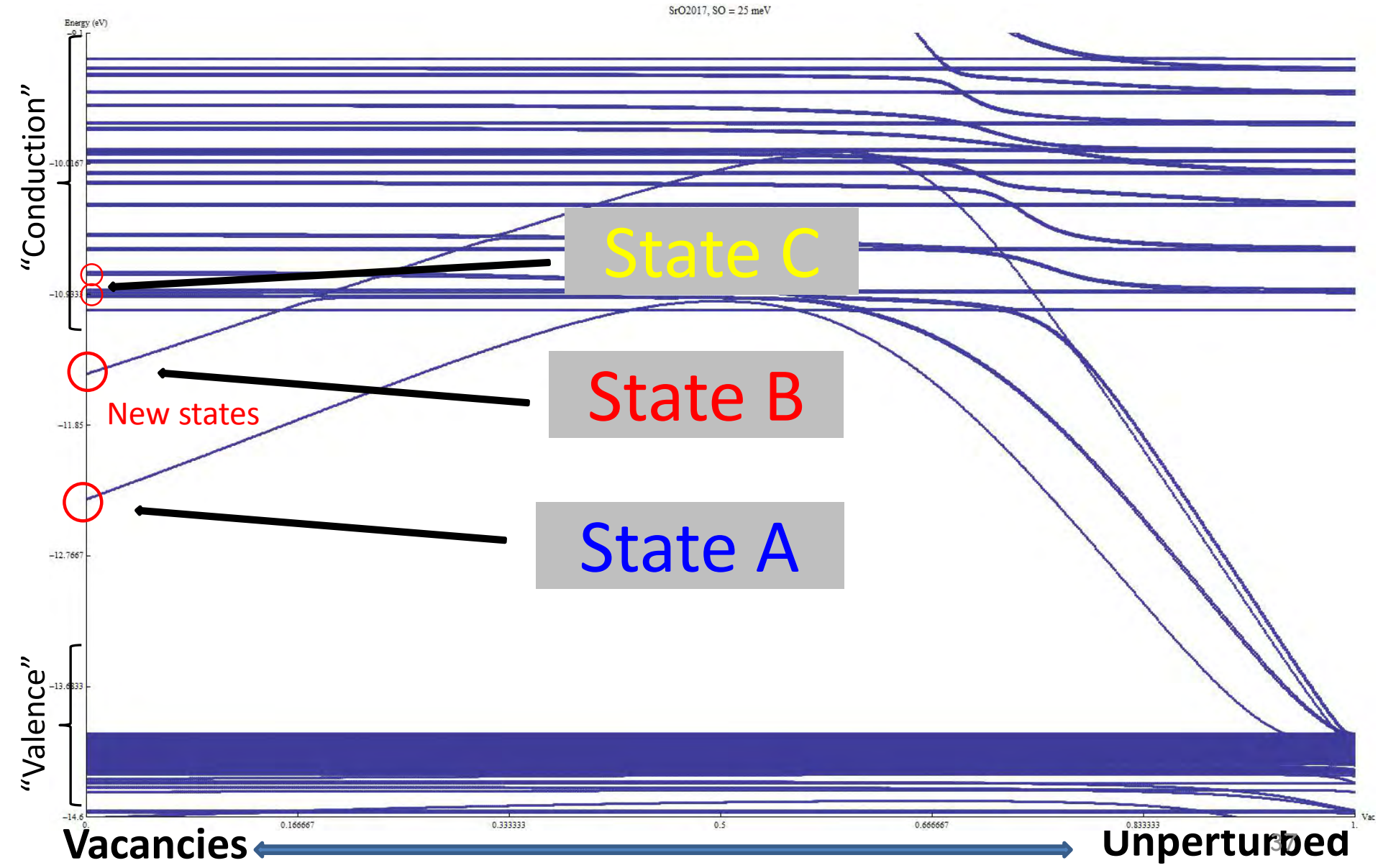
SrO-terminated

$\lambda = 25meV$

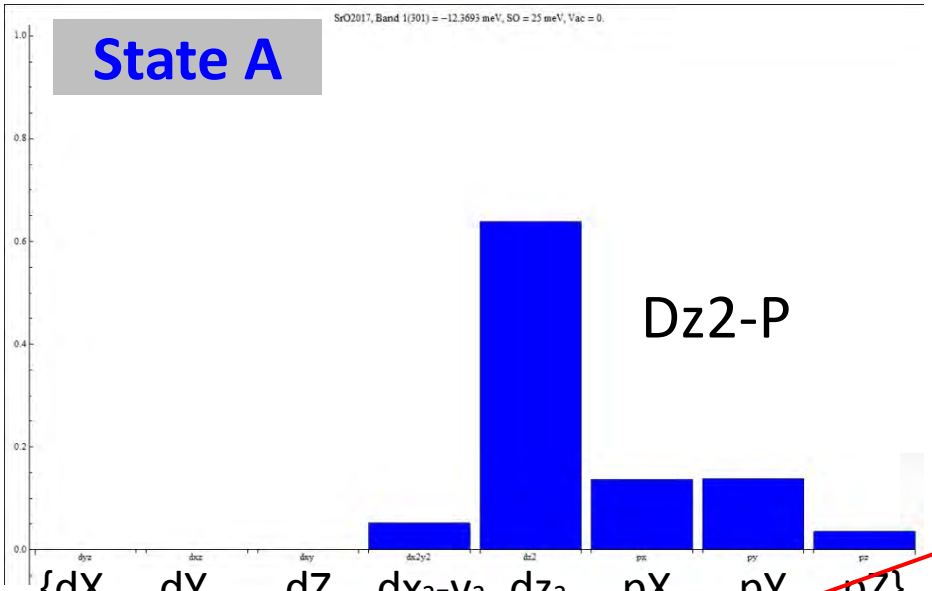


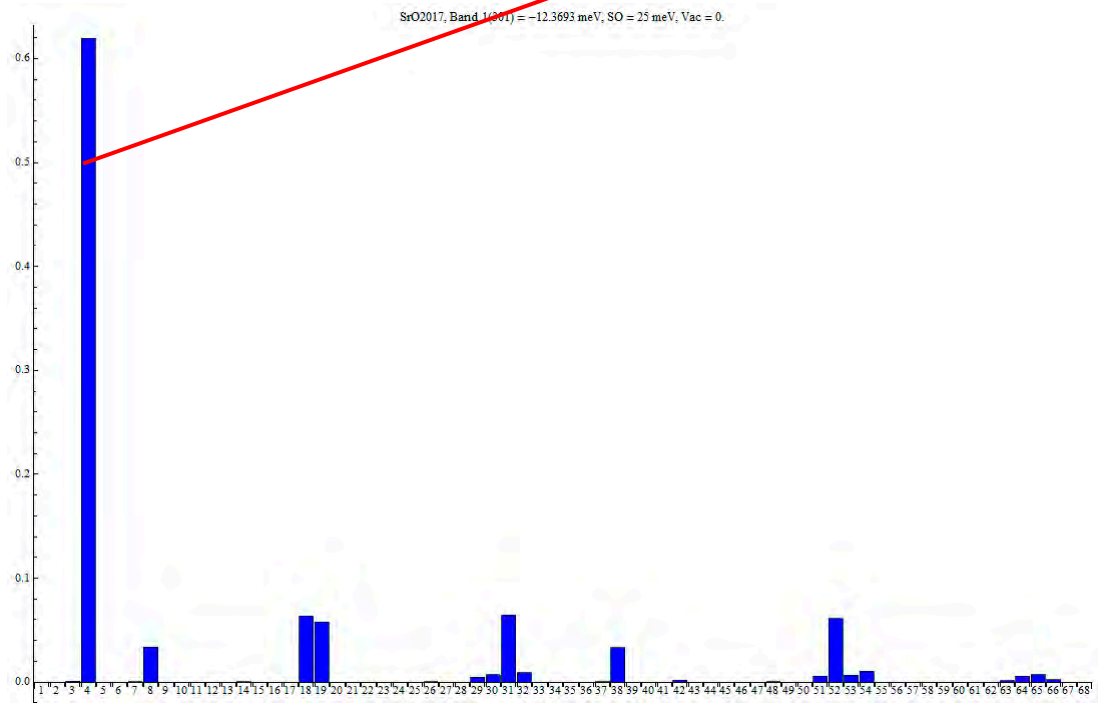


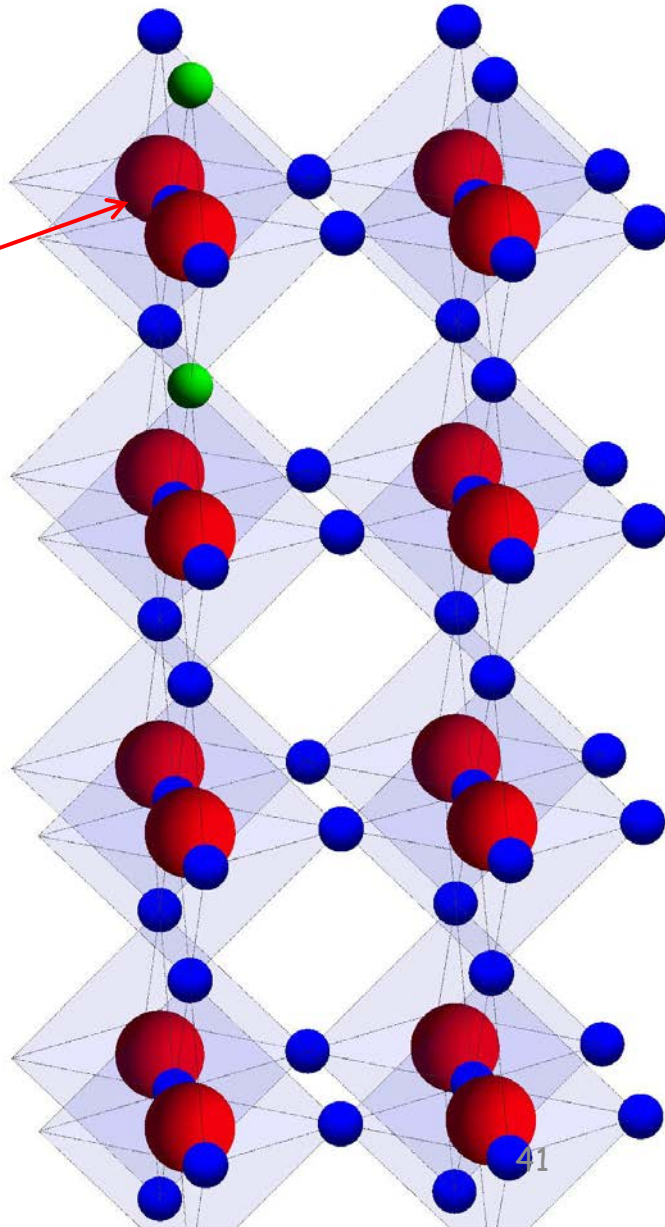
"Smoothly" removing the vacancies, significant change in some energy states



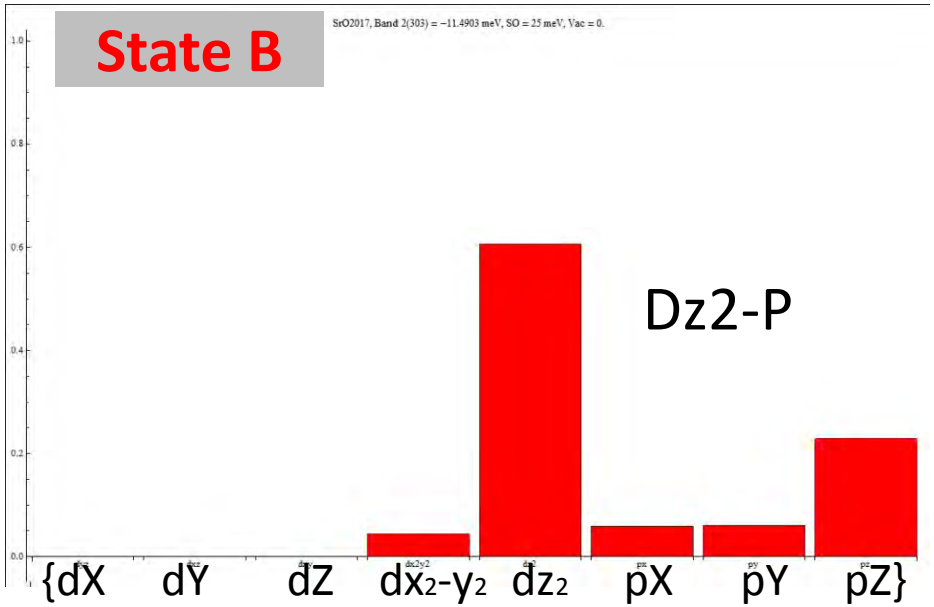
State A

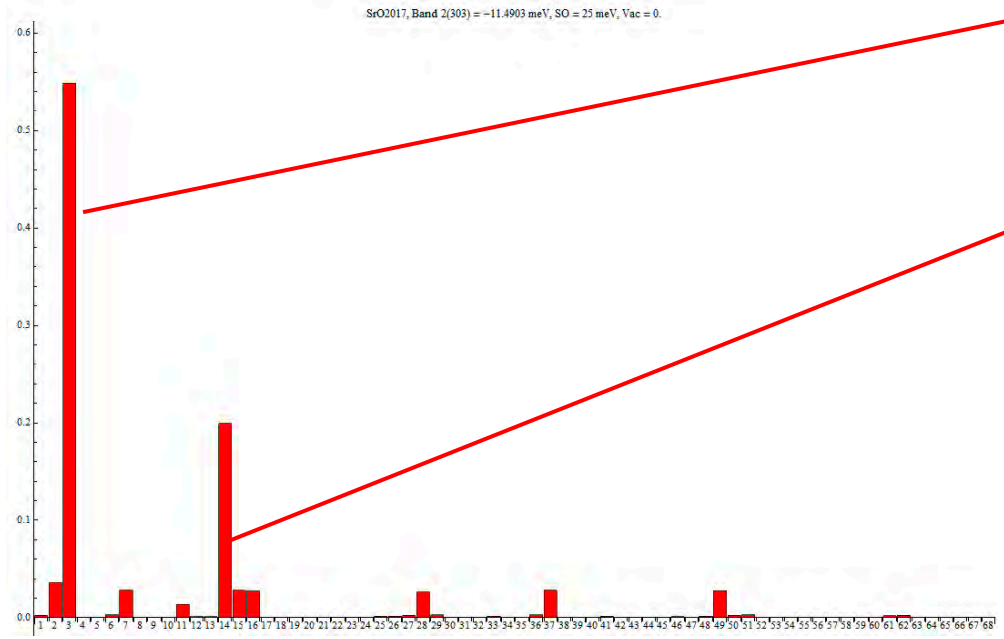

SrO2017, Band 1(301) = −12.3693 meV, SO = 25 meV, Vac = 0.
Dz2-P
{dX dY dZ dx2-y2 dz2 pX pY pZ}

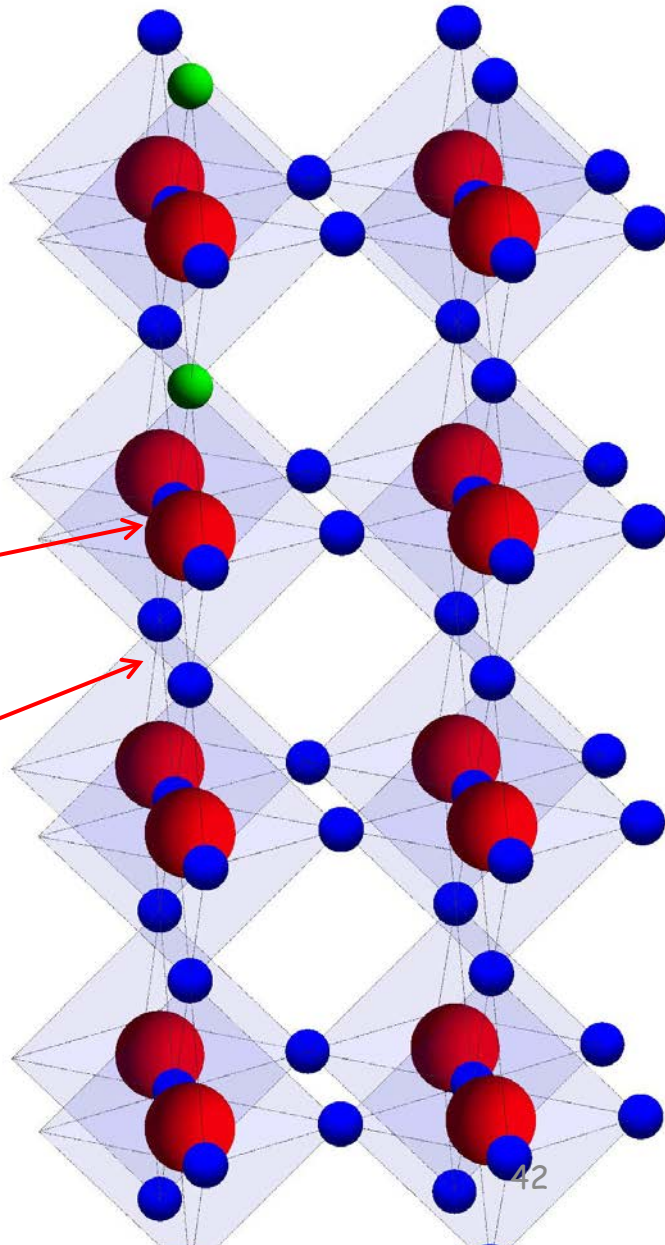

SrO2017, Band 1(301) = −12.3693 meV, SO = 25 meV, Vac = 0.

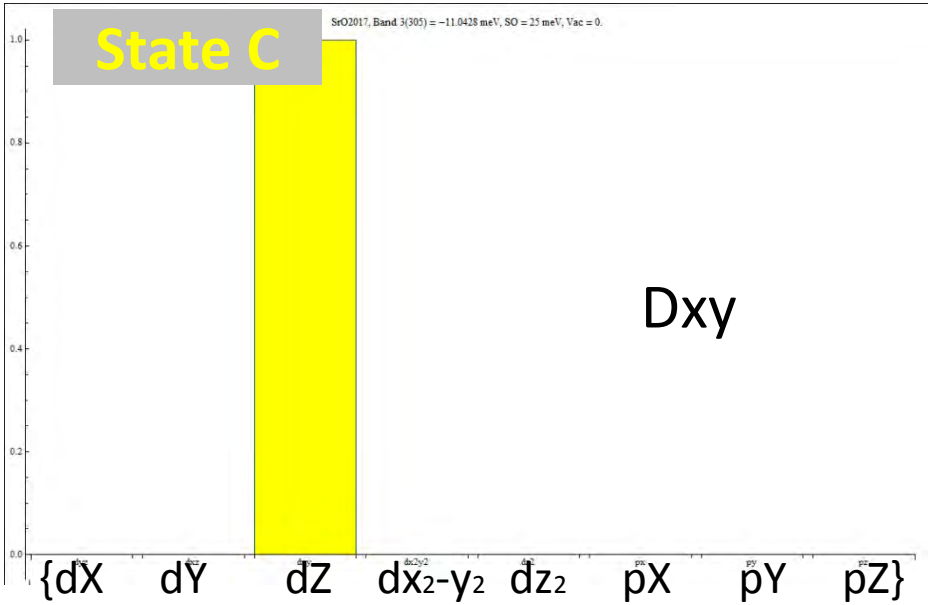


State B

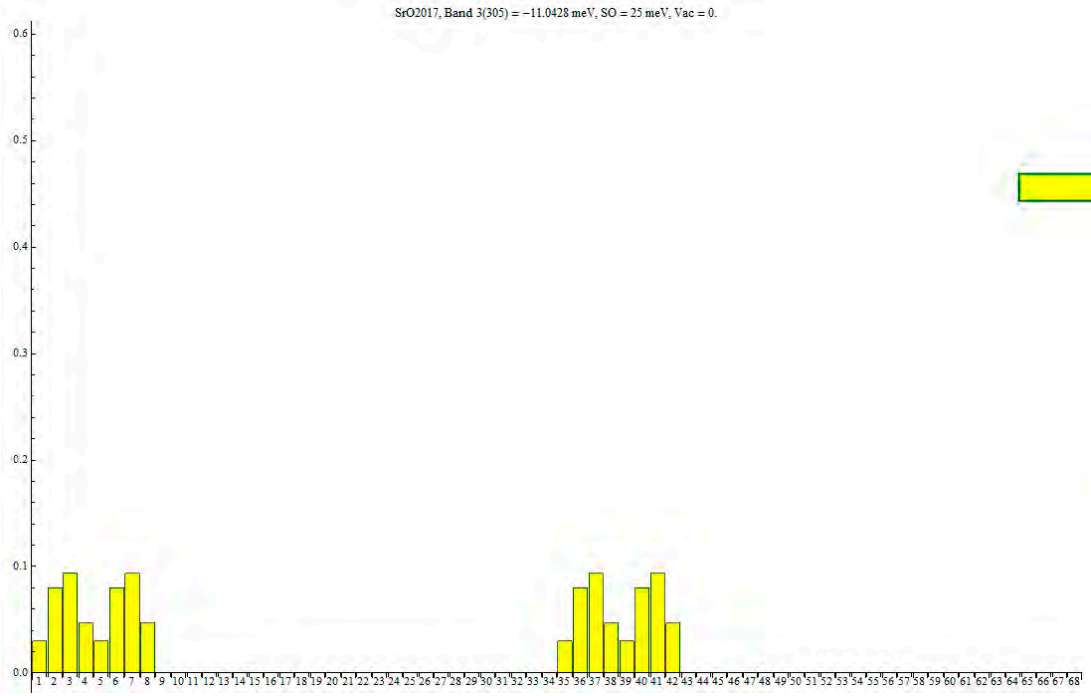

SrO2017, Band 2(303) = −11.4903 meV, SO = 25 meV, Vac = 0.
Dz2-P
{dX dY dZ dx2-y2 dz2 pX pY pZ}

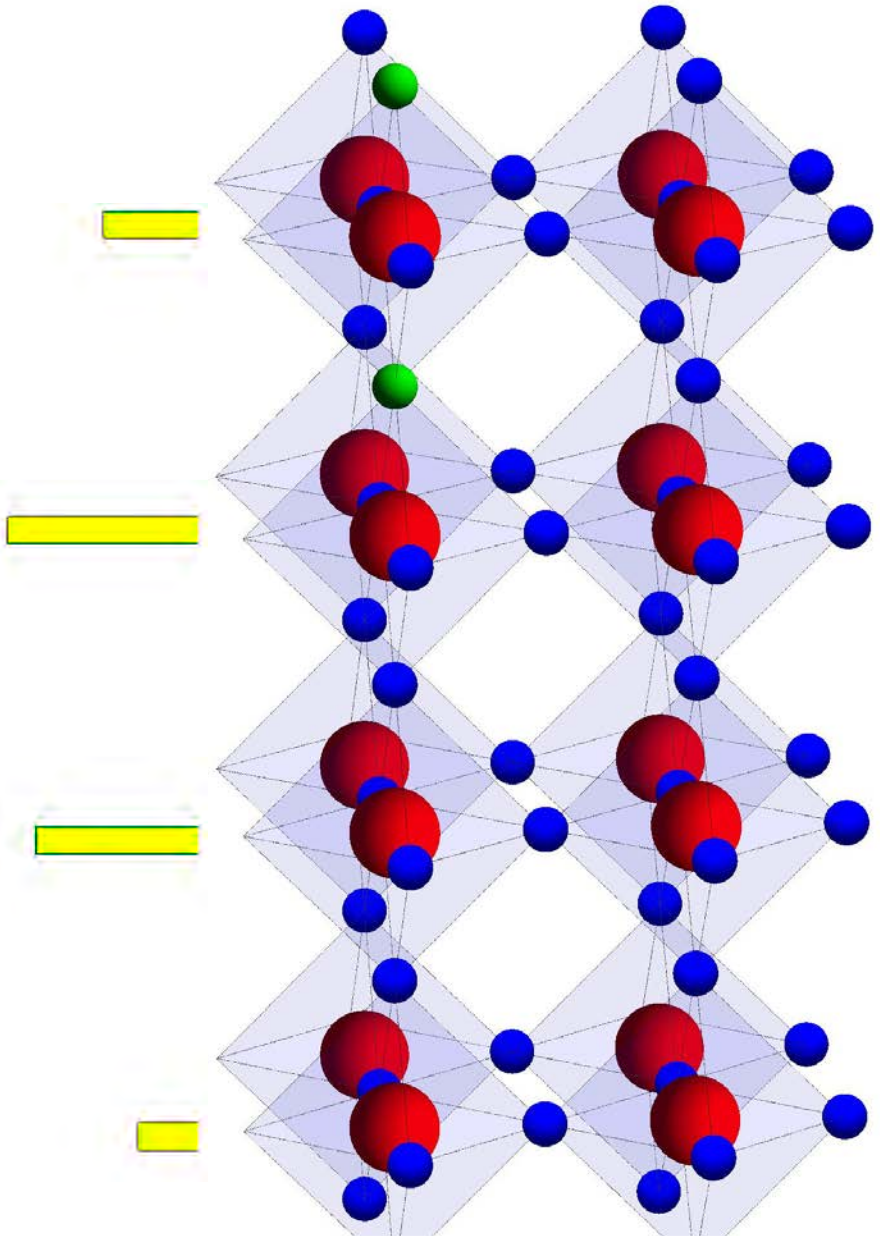

SrO2017, Band 2(303) = −11.4903 meV, SO = 25 meV, Vac = 0.



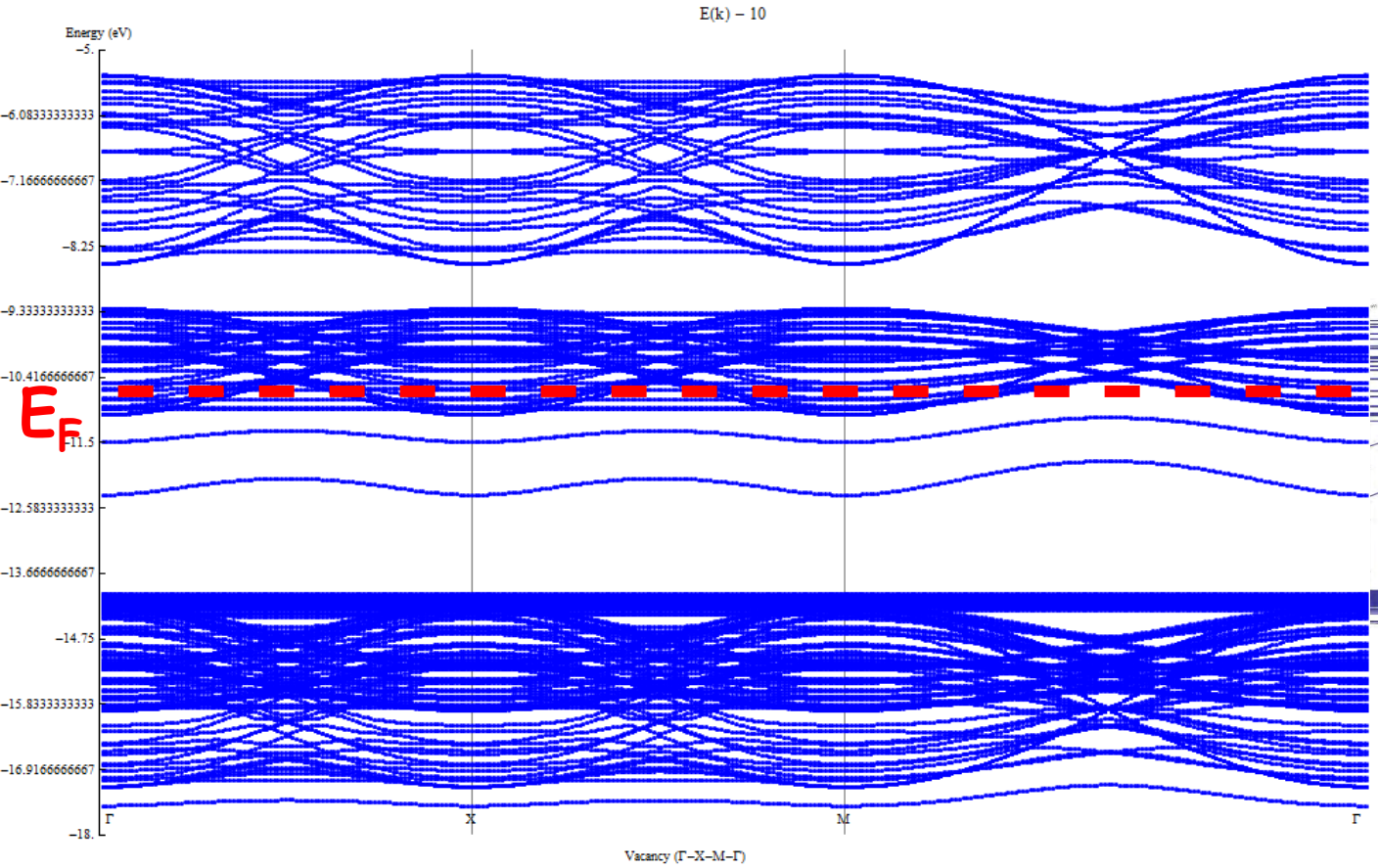

State C
SrO2017, Band 3(305) = −11.0428 meV, SO = 25 meV, Vac = 0.
{dX dY dZ dx2-y2 dz2 pX pY pZ}

Dxy


SrO2017, Band 3(305) = −11.0428 meV, SO = 25 meV, Vac = 0.

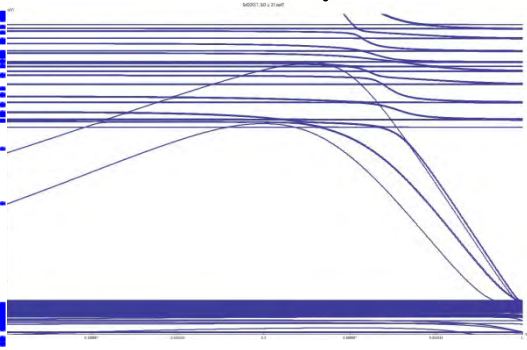


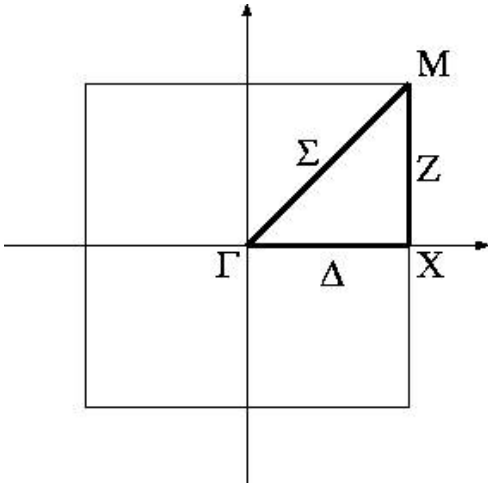
- K-dependence?



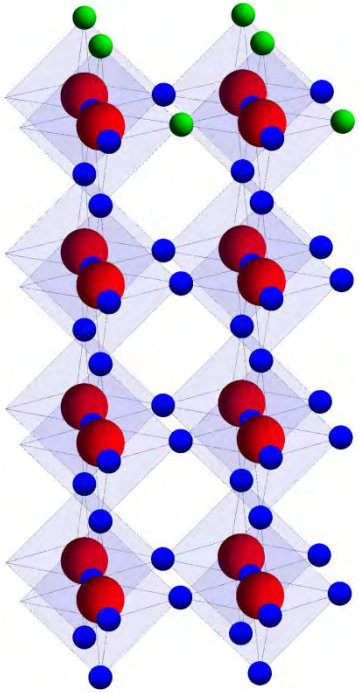
E_F

Calculated at the Γ point

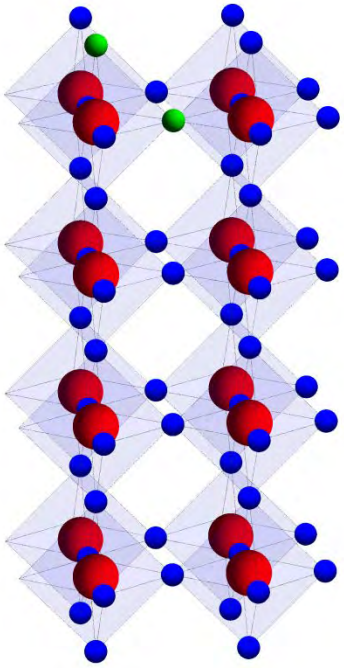




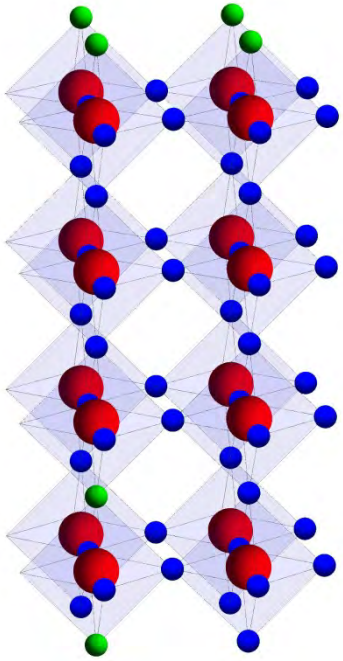
Other configurations



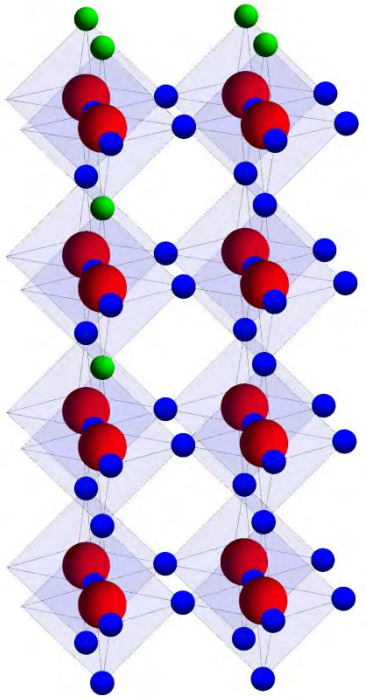
TiO_2 terminated;
horizontal di-vacancy



SrO terminated;



SrO terminated;
Vertical di-vacancy



TiO_2 terminated;
vertical di-vacancy

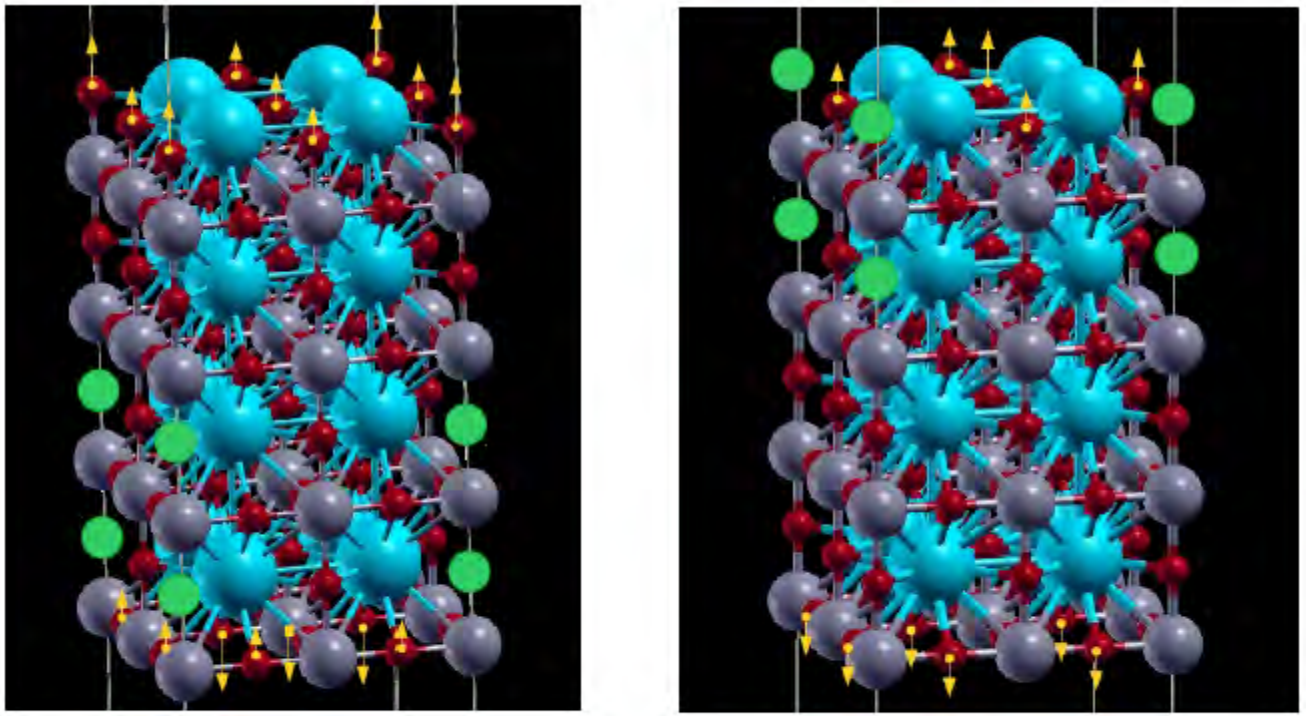
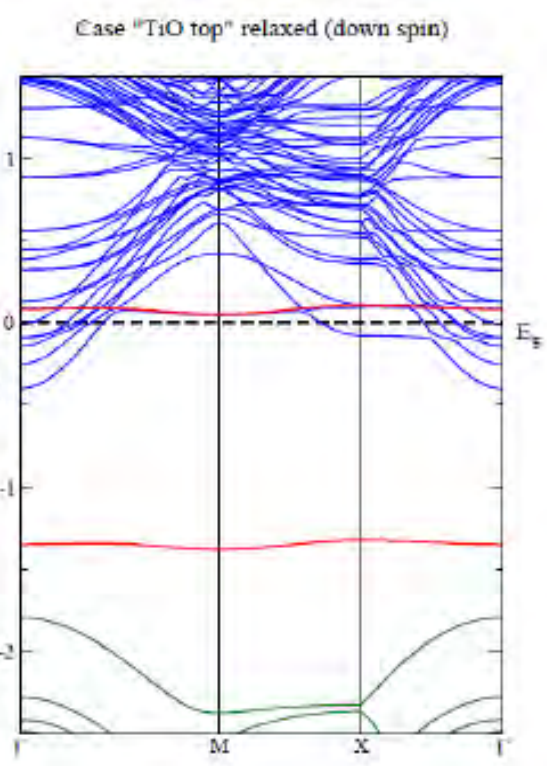


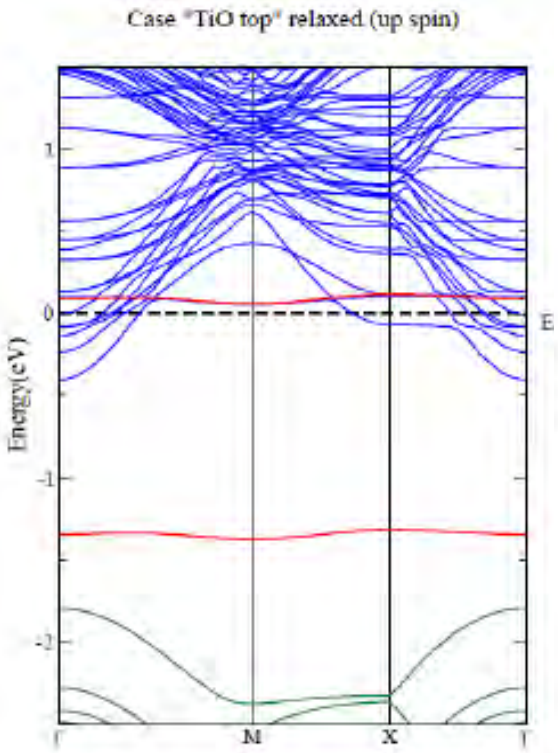
Figure 2 : Schematic view of the relaxed crystal structure. The yellow arrows represent the relative displacement of the ions w.r.t. to the Sr ones (top layer) and the corner Ti ones (bottom layer)

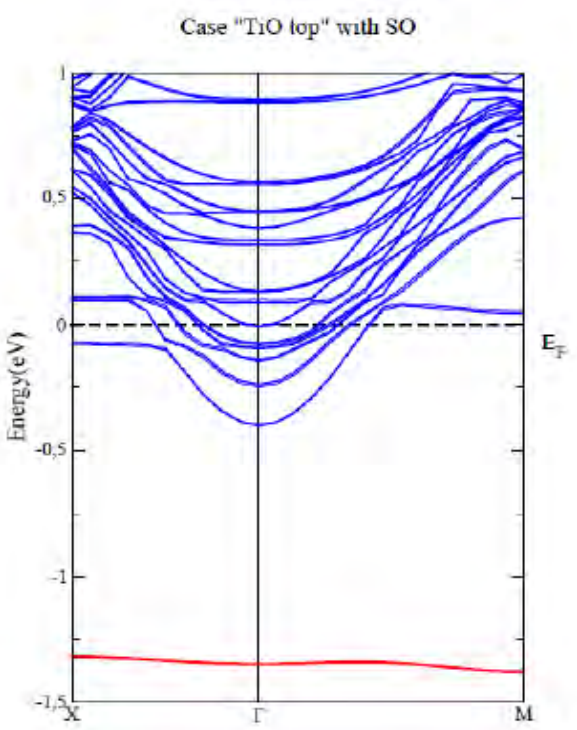
TiO_2 terminated

SrO terminated

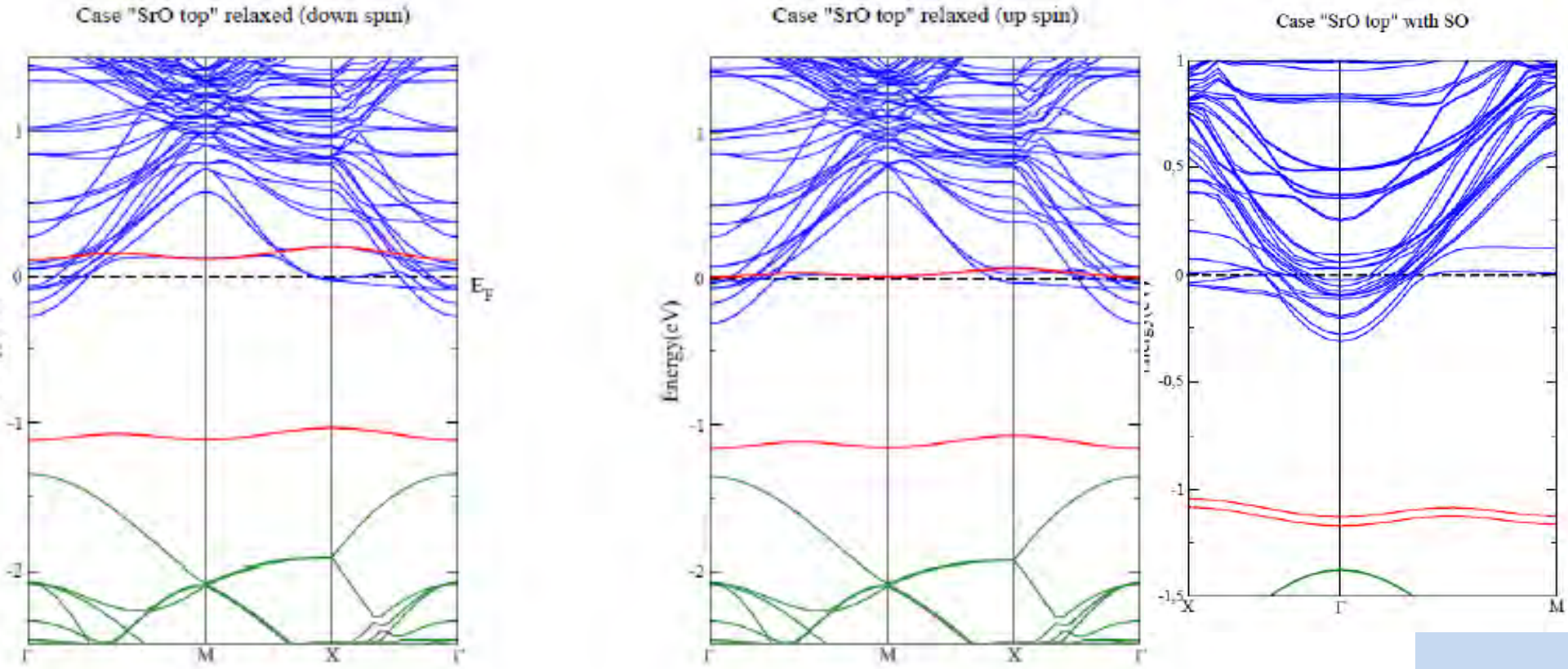
Ti O Sr O-Vac



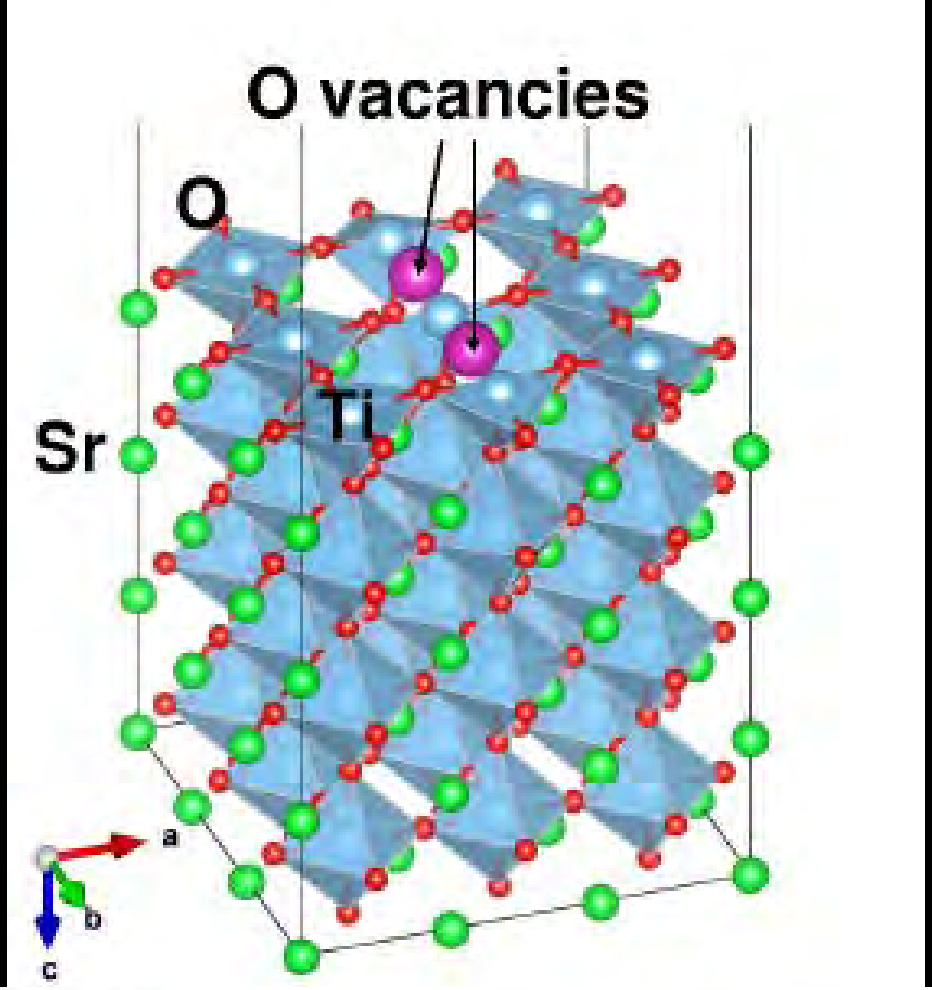




Magnetic Kohn-Sham band structure for a relaxed 2x2x4 $SrTiO_3$ slab with an oxygen divacancy
ase « TiO-top ».



Magnetic Kohn-Sham band structure for a relaxed 2x2x4 $SrTiO_3$ slab with an oxygen divacancy
ase « SrO-top ».



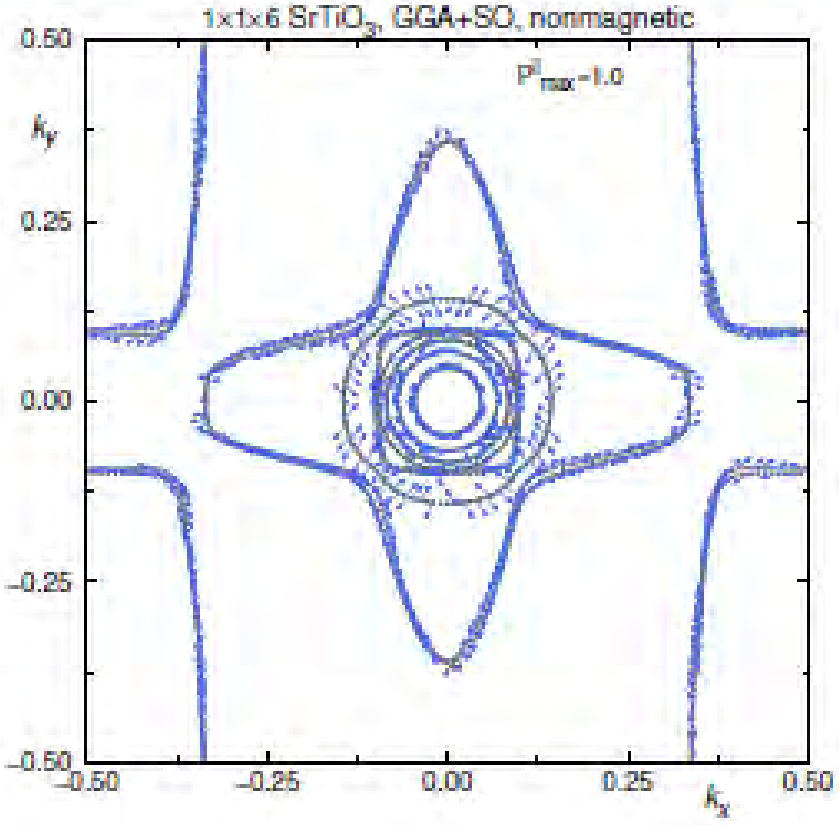
GGA+SOC nonmagnetic

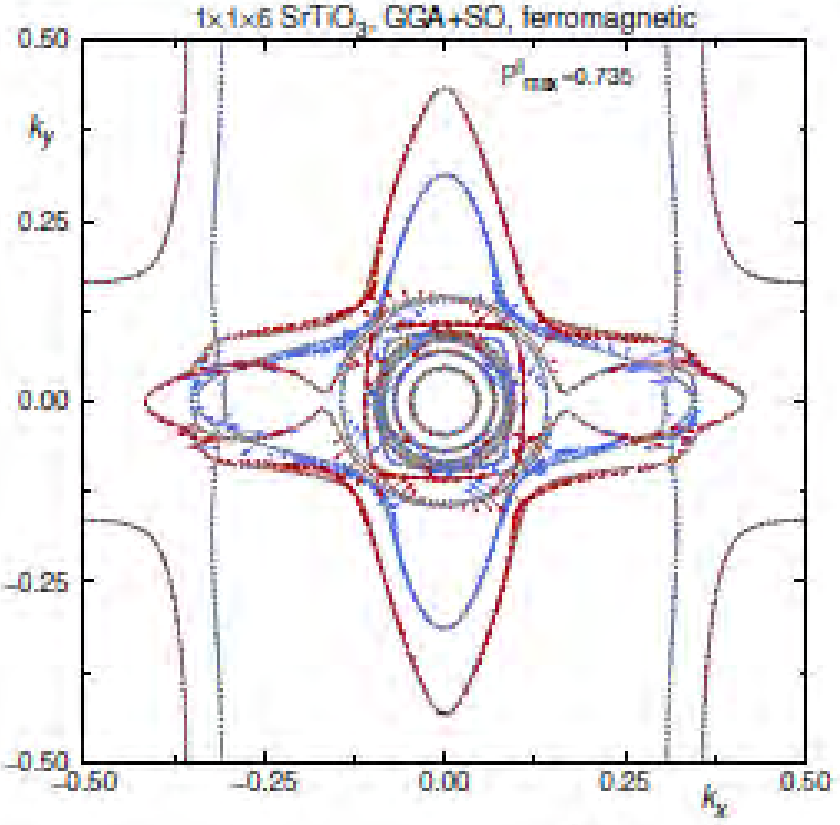
GGA+SOC ferromagnetic with quantization in z/x direction

GGA+SOC+U on Ti nonmagnetic

GGA+SOC+U on Ti ferromagnetic with quantization in z/x direction

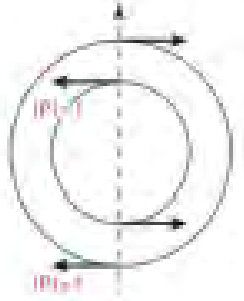
Relaxed 1x1x6 slab: nonmagnetic ⇔ ferromagnetic





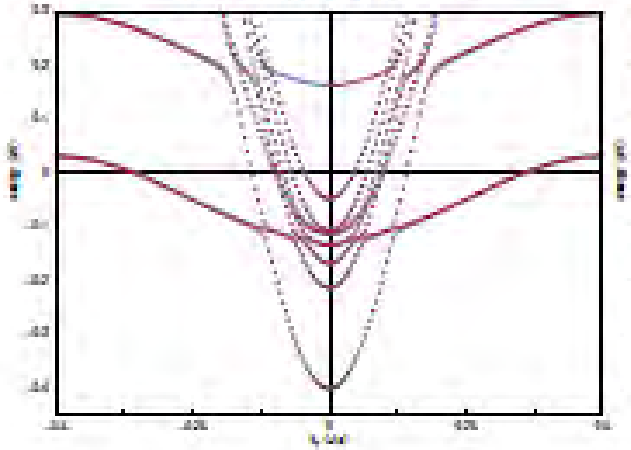
⇒ Magnetism enhances spin splitting

⇒ Ferromagnetism is energetically favorable

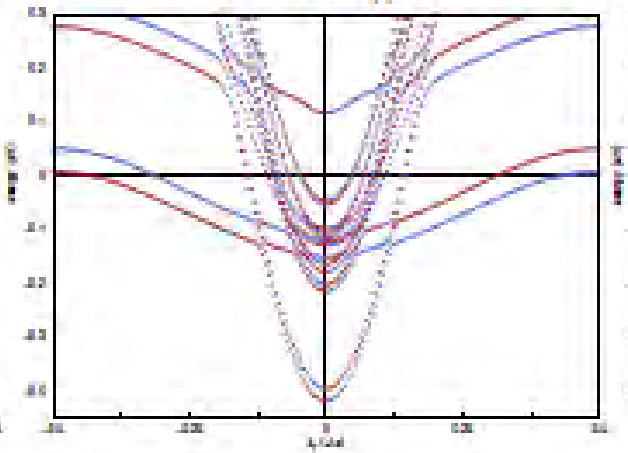


Summary GGA+SO+Magnetism: Experiment $\Leftrightarrow$ Theory

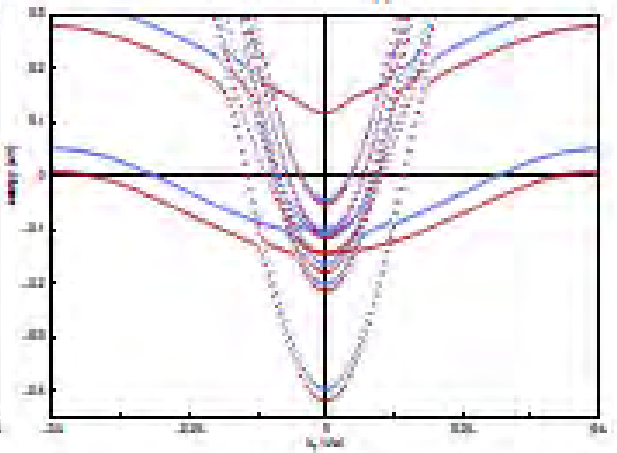
nonmagnetic



fm $\vec{m} \parallel \hat{z}$



fm $\vec{m} \parallel \hat{x}$



Experiment	In-plane polarization	Spin flip	Energy splitting
GGA+SO nm	✓	✓	✗
GGA+SO $\vec{m} \parallel \hat{z}$	✗	✓	✓
GGA+SO $\vec{m} \parallel \hat{x}$	✓	✗	✓

- Surface of STO harbors puddles of either magnetic or non magnetic regions

- Surface of STO is inhomogeneous : mixture of TiO_2 and SrO terminations.

- Orbital selectiveness (t_{2g} states lead to spin textures; e_g states to magnetism)

- Fermi surface with mixed orbital character