Ab initio study of magnetism at the $TiO_2/LaAlO_3$ interface

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Experimental background

- TiO_2 with anatase structure grows epitaxially on $LaAlO_3$
- Magnetism first appeared in samples doped with Co
  [Review: Janisch *et al*, JPCM **17**, R657 (05)]
- Magnetism appeared later in samples doped with Cu
  [Duhalde *et al*, PRB **72**, R161313 (05)]
- Magnetism also appeared in undoped samples
  [Yoon *et al*, JMMM **309**, 171 (07)]
- High Curie temperature in all cases
- Oxygen vacancies are present and enhance magnetism
  [Sasahara *et al*, Nanotechnology 16, S18 (05)].

Previous calculations

• Calculations for undoped bulk TiO_2 -anatase do not show magnetism, not even relaxing the structure in the presence of oxygen vacancies.
[Errico *et al*, PRB **72**, 184425 (05);
Weissmann *et al*, Physica B **398**, 179 (07)].

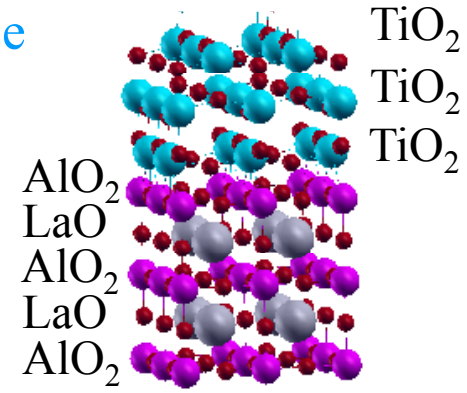
• At the $TiO_2/LaAlO_3$ interface, a magnetic moment appears in the Ti atom if it has neighbour oxygen vacancies.
[Weissmann *et al*, J. Phys: Conf. Ser. **167**, 012060 (09)].

In that case, $Ti^{+4} \longrightarrow Ti^{+3}$ or Ti^{+2}

Present work

TiO_2-Anatase

$LaAlO_3$

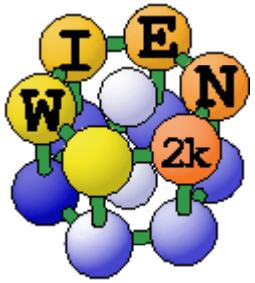


We study undoped anatase TiO_2 grown over $LaAlO_3$ with oxygen vacancies at the interface, to answer the following questions:

- Is the system magnetic?
- Is magnetism located at the interface?
- How is the interface structure modified?

Method of calculation

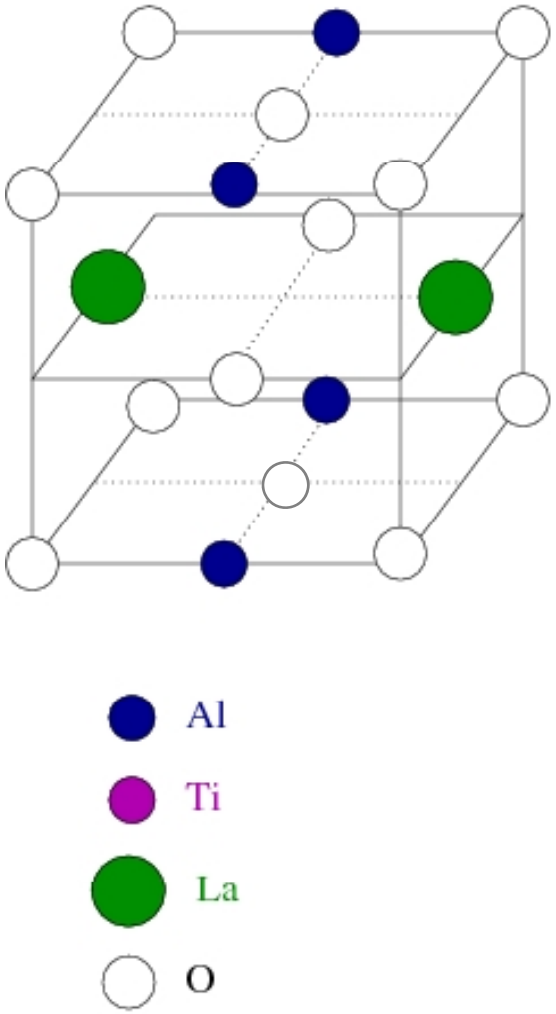
Full Potential LAPW (Wien2k code)



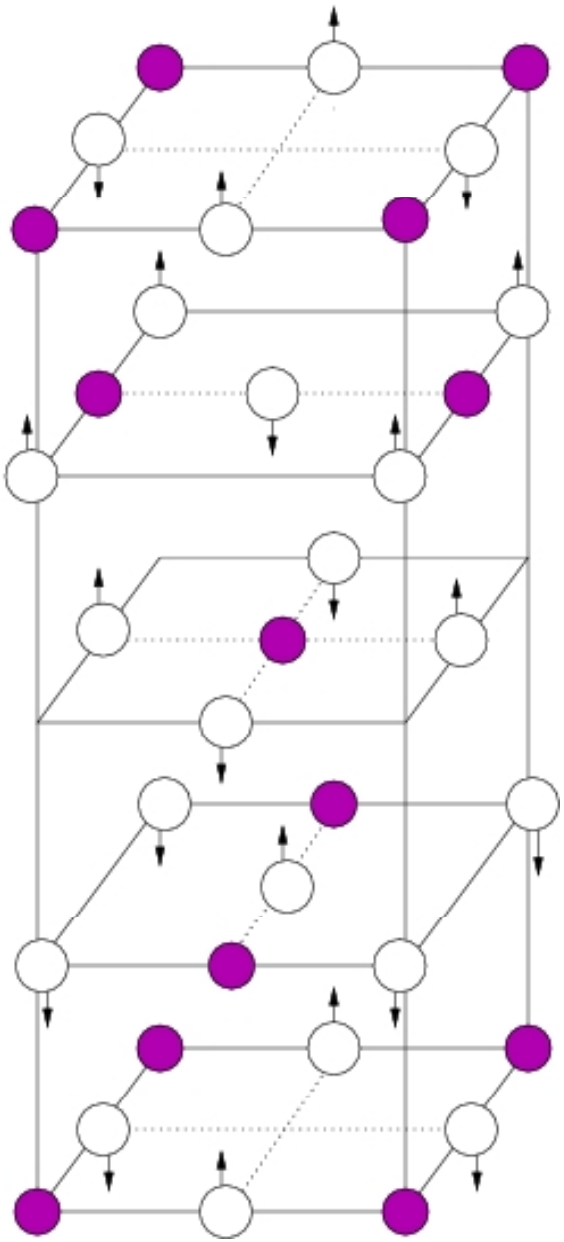
- DFT in the LDA approximation.
- On-site Coulomb interaction added: LDA+U
- Interfaces studied by the superlattice method:

$\ldots TiO_2 / LaAlO_3 / TiO_2 / LaAlO_3 / TiO_2 / LaAlO_3 \ldots$

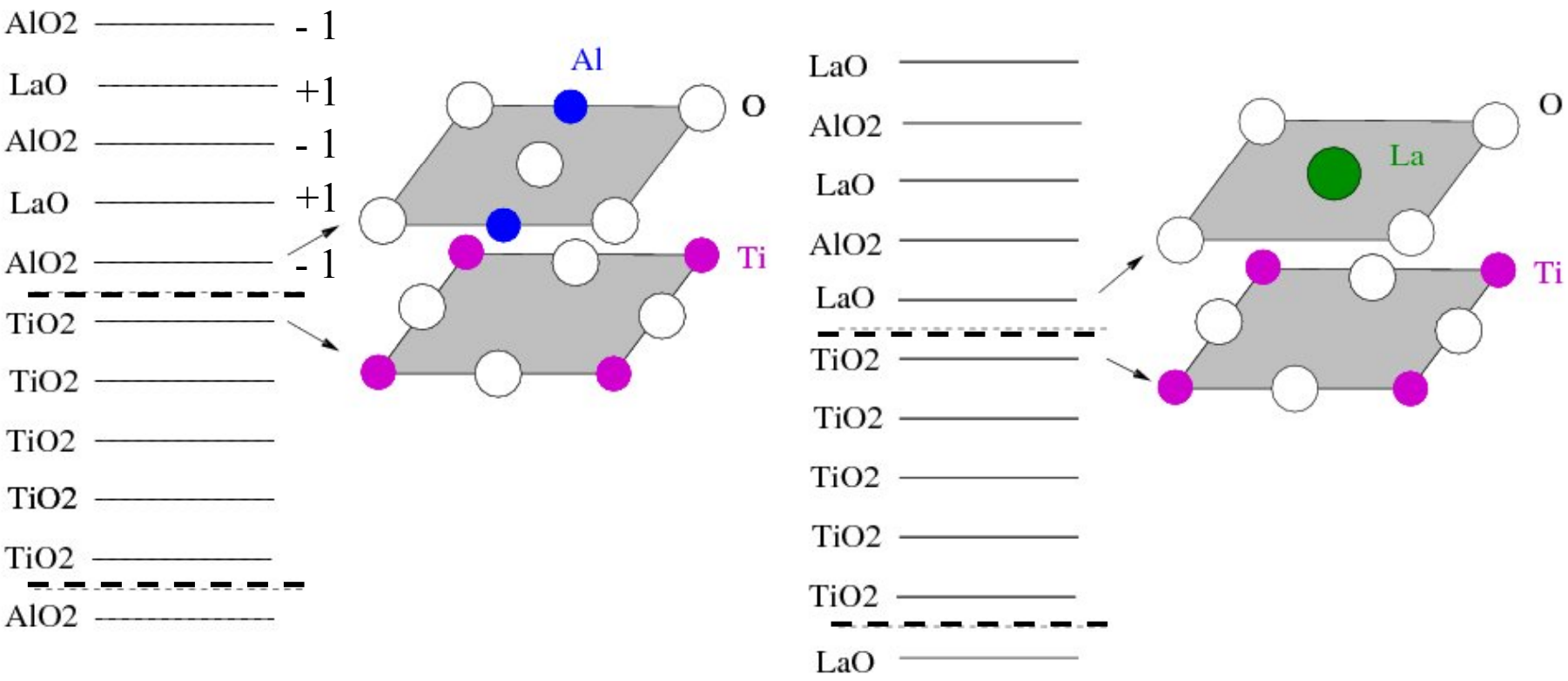
$LaAlO_3$



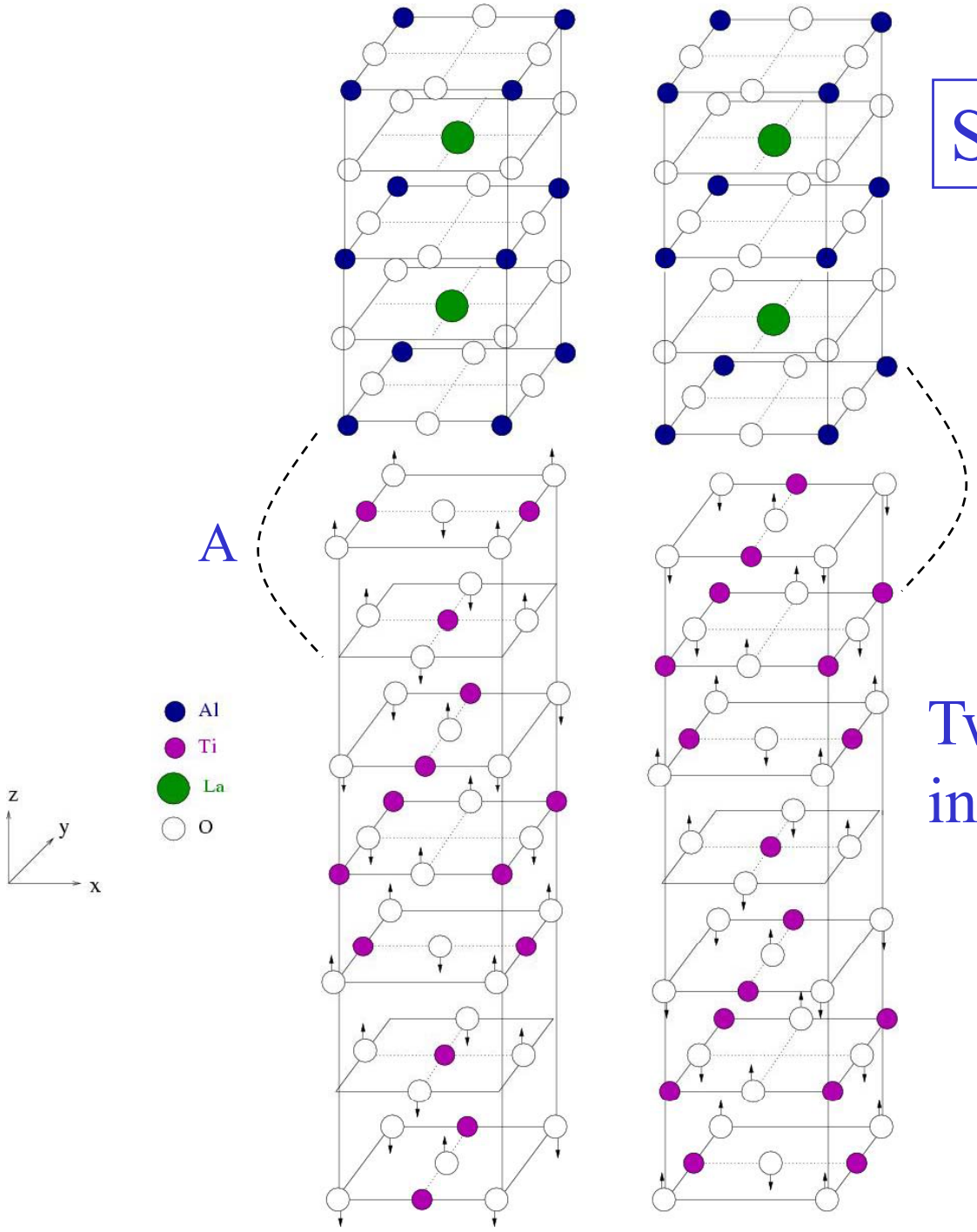
TiO_2 -Anatase



Two ways of stacking



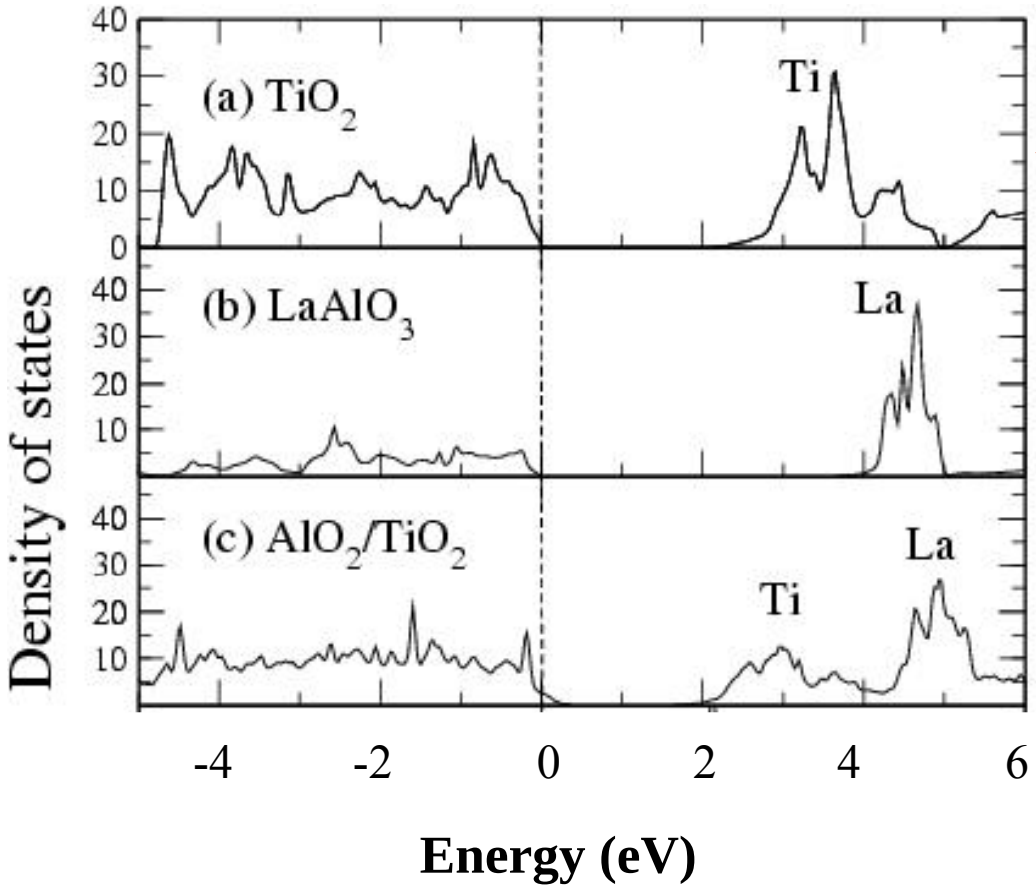
If there are oxygen vacancies in TiO_2 , the left interface is preferred for electrostatic reasons.



Superlattice unit cell

Two different AlO_2/TiO_2 interfaces: A, B

Densities of states - LDA

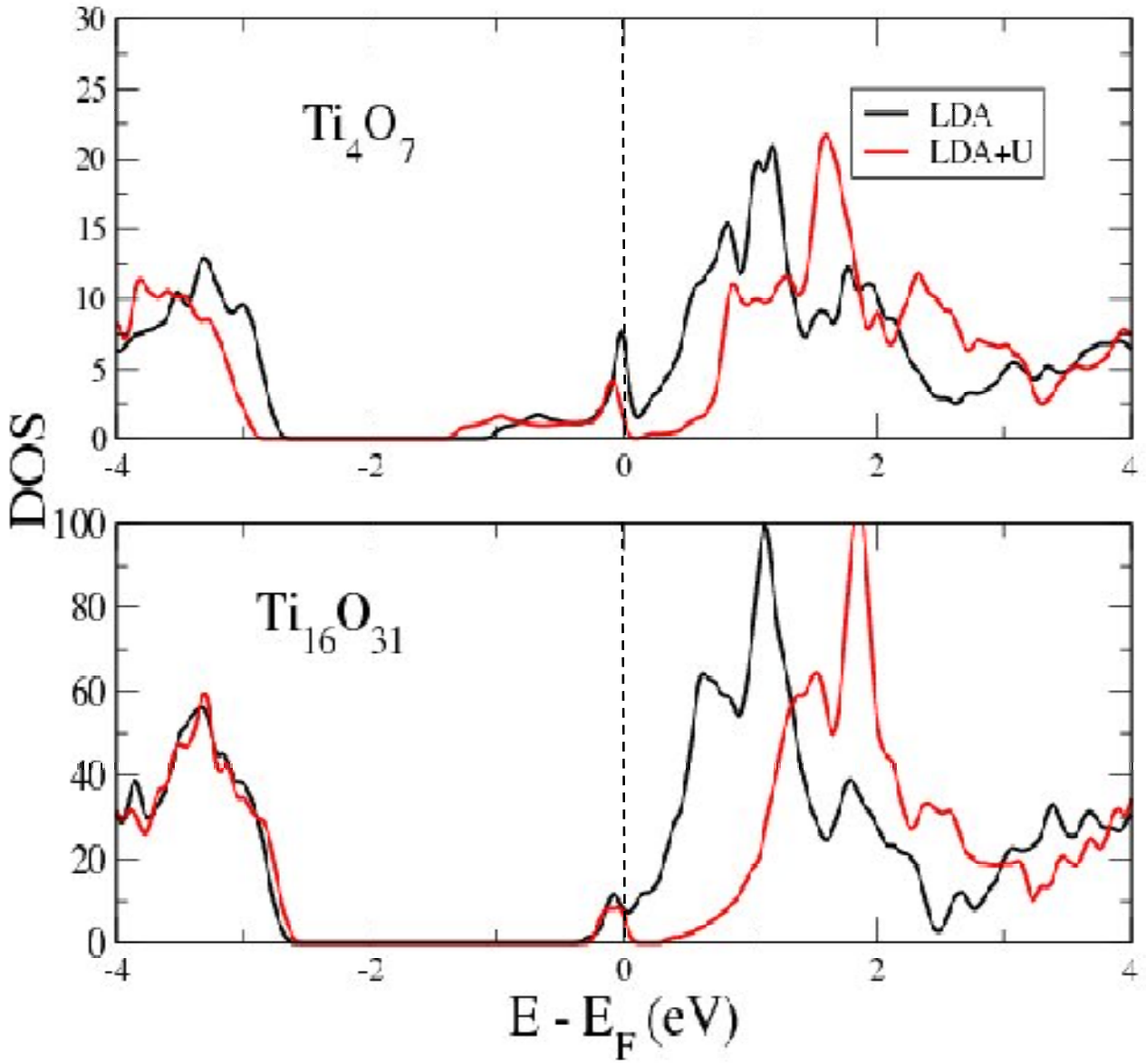


TiO2 anatase
Gap (experimental): 3eV
Gap (calculated): 2.2eV

LaAlO3
Gap (experimental): 5.6eV
Gap (calculated): 4eV

Superlattice, relaxed, no vacancies
Metallic
Non- magnetic

Oxygen vacancy in bulk anatase

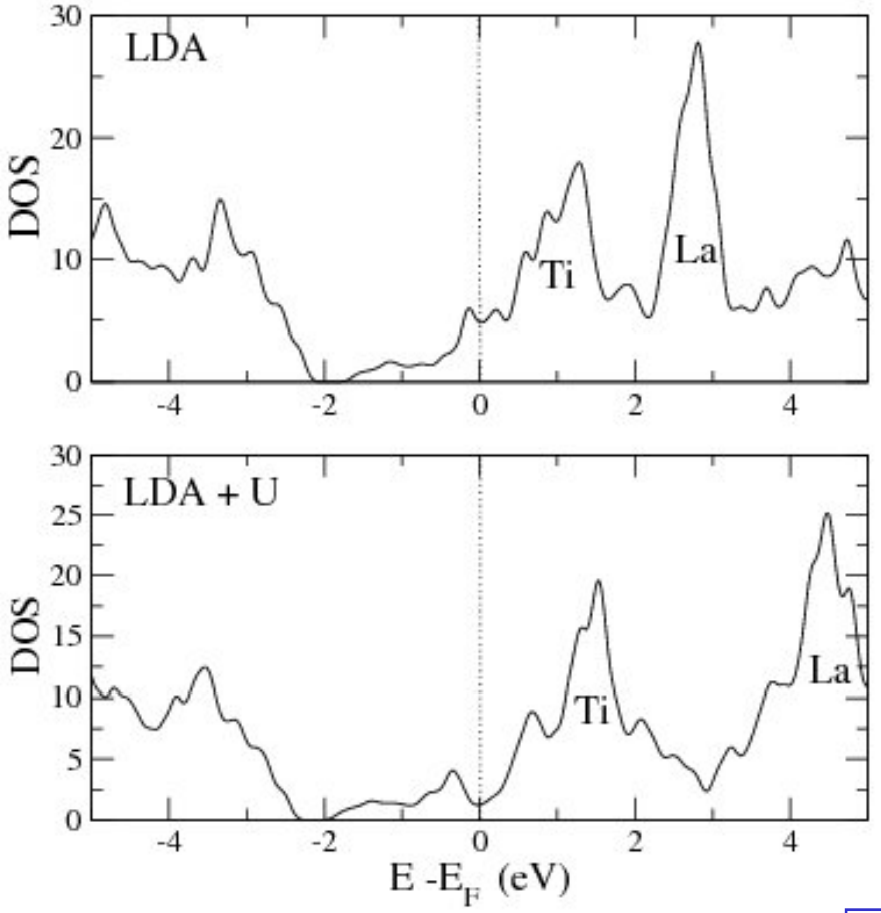


Relaxed Structures

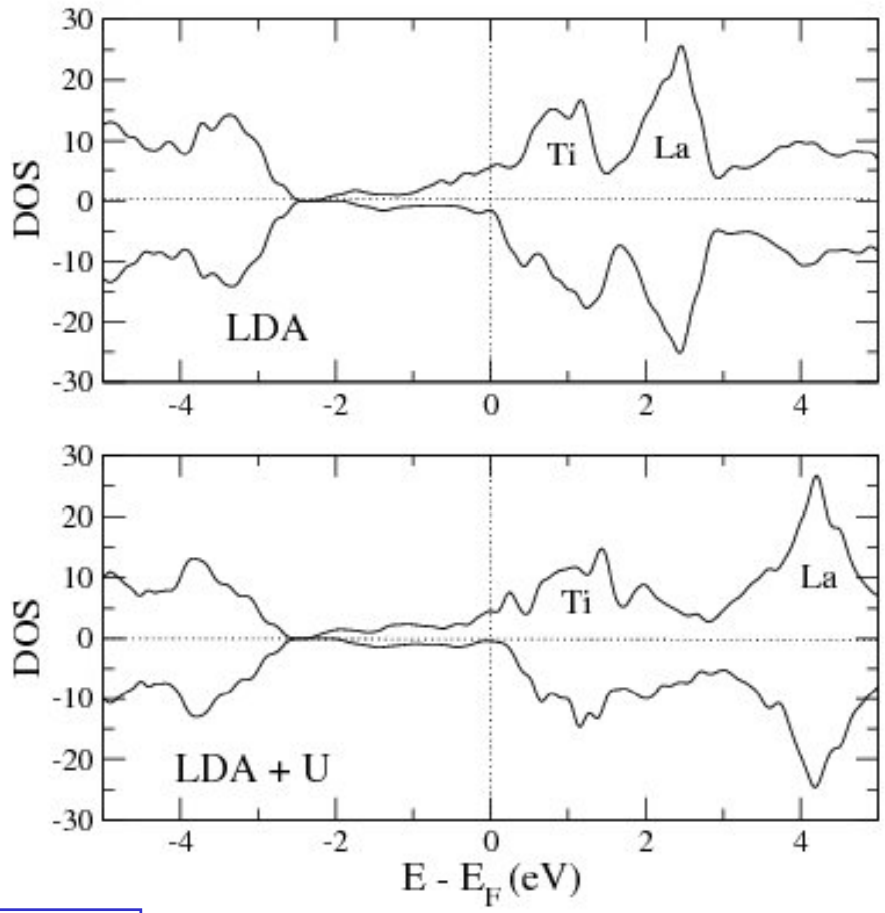
Non magnetic

DOS of superlattices with interfacial oxygen vacancies

Interface A: non-magnetic

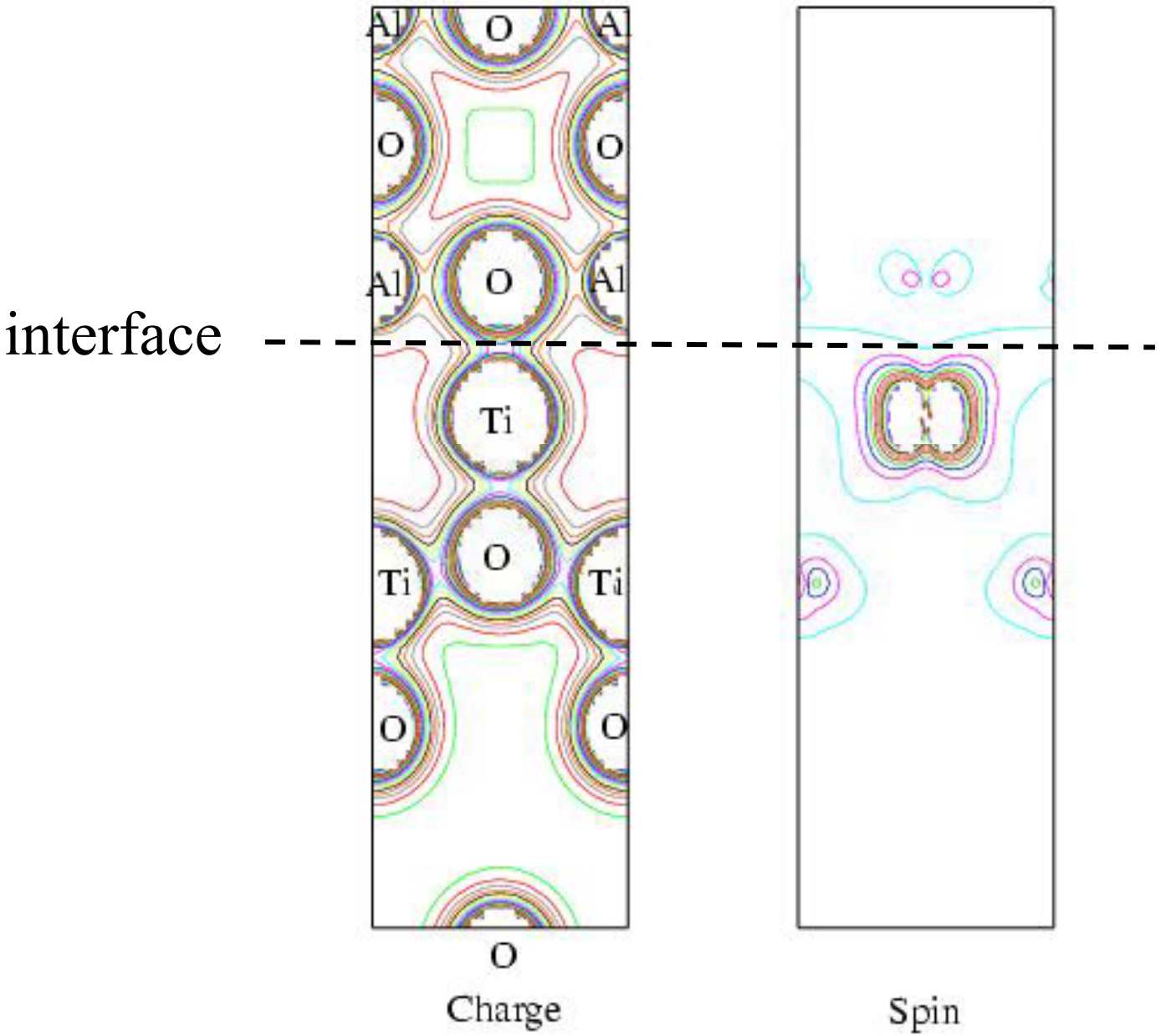


Interface B: magnetic

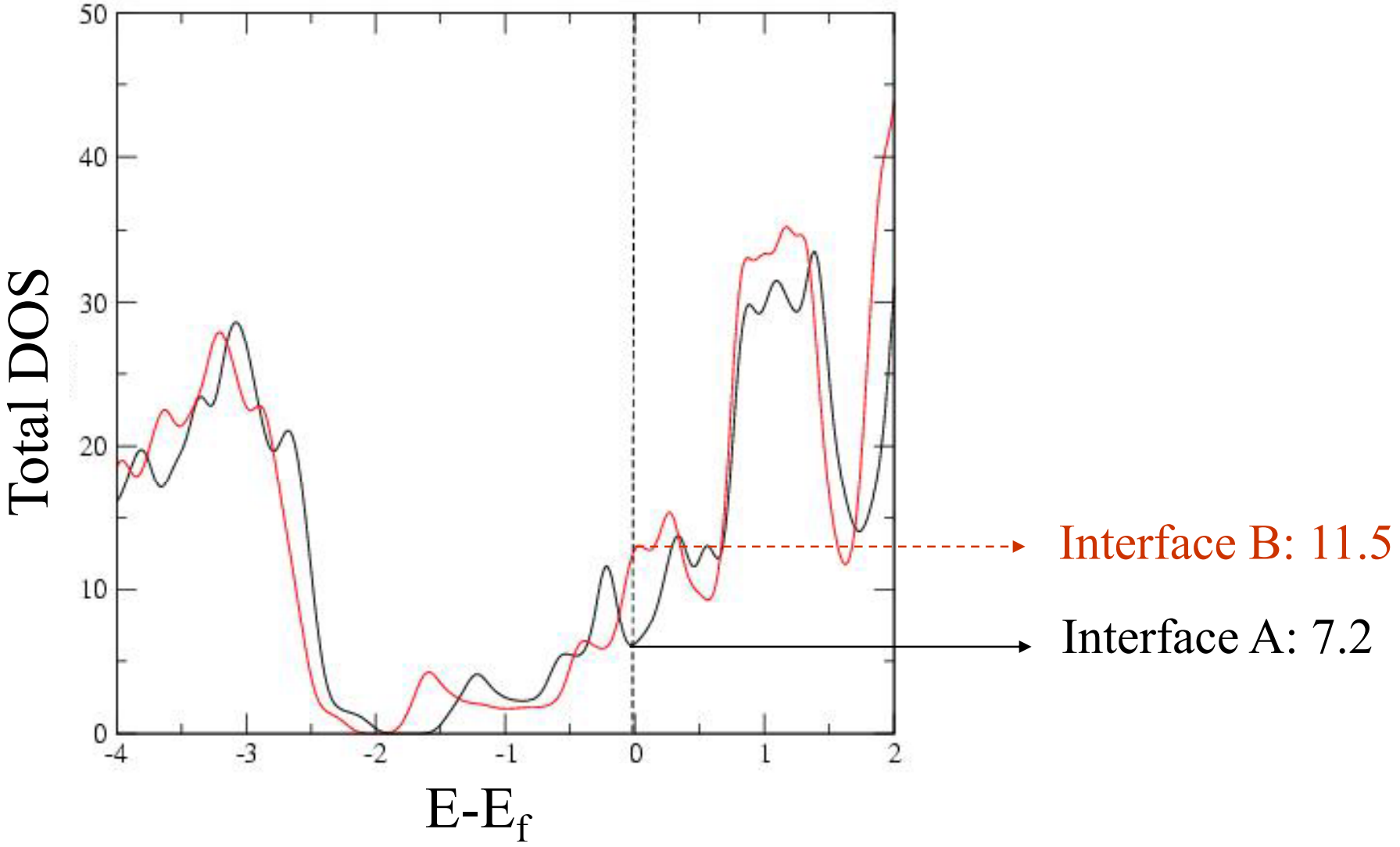


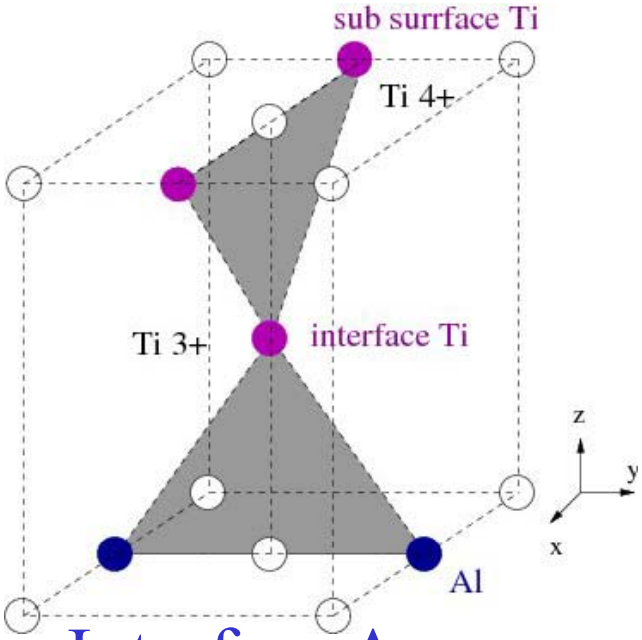
U= 5 eV

Density maps for the magnetic case

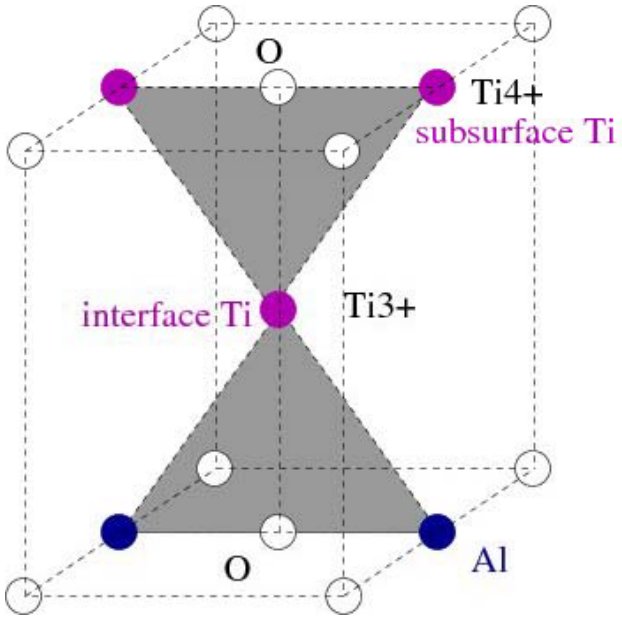


Stoner-like interpretation: non-magnetic calculation

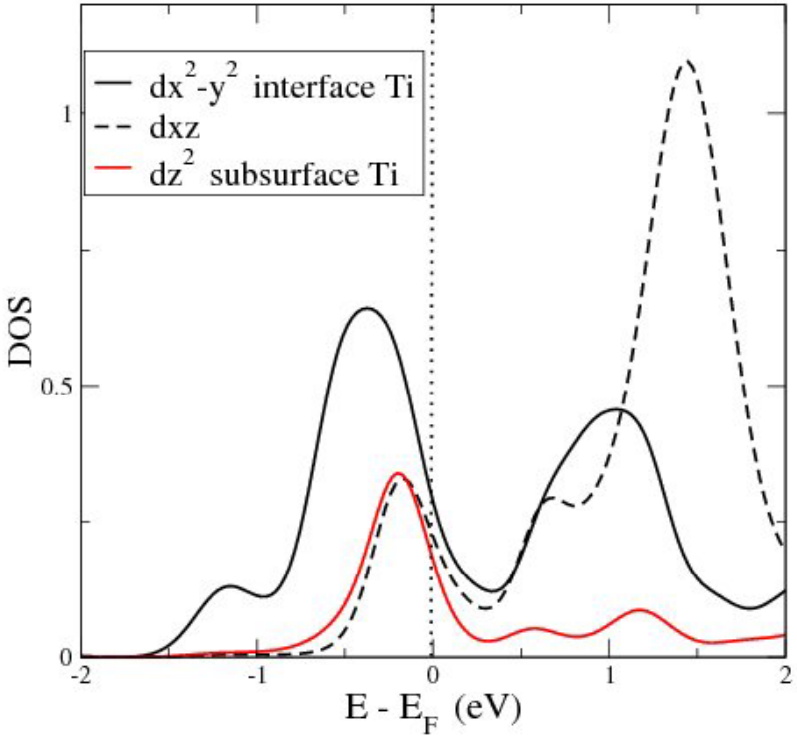


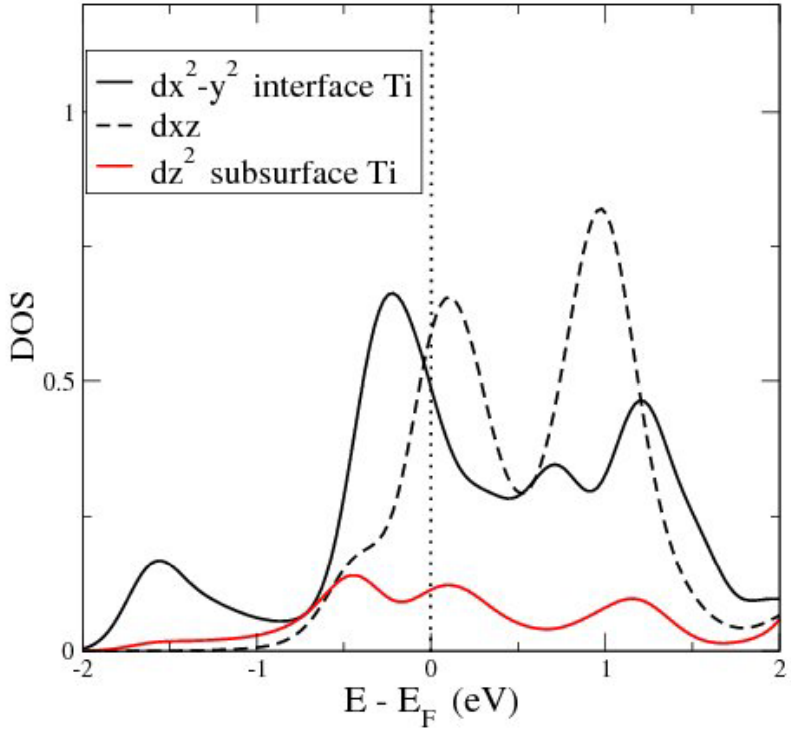


Interface A

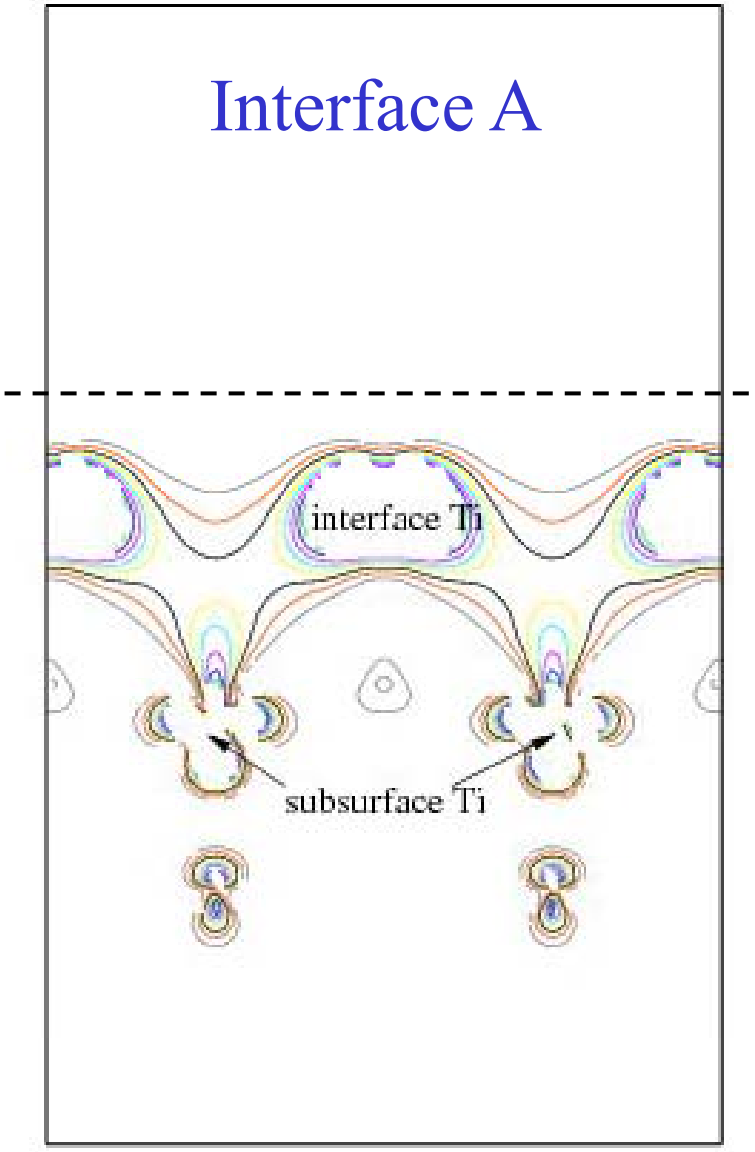


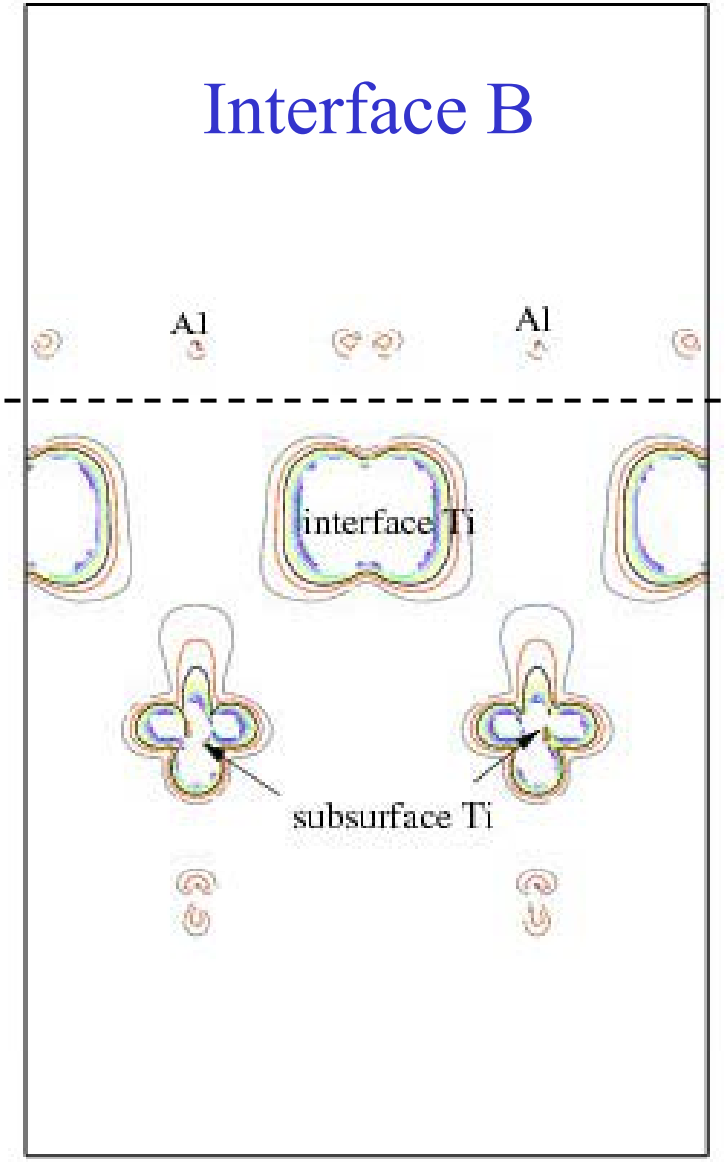
Interface B





Charge density in the energy range [Ef-0.5eV,Ef]





Conclusions

- Without oxygen vacancies: no magnetic solutions in bulk anatase or $LaAlO_3/TiO_2$ superlattices.
- With oxygen vacancies:
  - Bulk anatase, not magnetic for different vacancy concentrations and relaxed structure.
  - Superlattice with $AlO_2/TiO_{2-\delta}$ interface, magnetic or not depending on the stacking.
  - In superlattices A and B, interface $Ti^{+4} \longrightarrow Ti^{+3}$ but only one of them has a magnetic solution (both in LDA and LDA+U).

- A Stoner-like criterion is used to understand the origin of magnetism.

- Our results might be related to the widespread magnetic behaviour obtained with different experimental conditions.