First principles study of oxygen vacancy induced magnetic moments in TiO_2

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MOTIVATION

Experimentally observed ferromagnetism (FM) in TiO_2 [1-5]:

- Large spread of M and T_C values;
- Dependence on preparation conditions.
- FM in undoped anatase thin films [6] and rutile single crystals [7] is it related to oxygen vacancies (OVs) ?

Theoretical progress and electronic structure calculations using first principles methods:

- Modeling of exchange in DMS: role of bound magnetic polarons [8].
- Superechange → FM coupling in anatase $Ti_{1-x}M_xO_2$ (M=Co, Mn, Fe, Ni) [9,10].
- Role of OVs in FM order in $Ti_{1-x}Co_xO_2$ [9], $Ti_{1-x}Fe_xO_2$ [11] and undoped anatase [12].

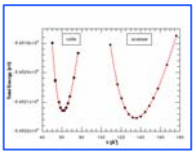
OBJECTIVES

To explain within a common framework various and often contrasting experimental and theoretical results on the conditions of OVs-driven magnetism in $TiO_{2-\delta}$.

To provide a practical route to induce or enhance FM in TiO_2 based materials.

CALCULATION DETAILS

- First principles energy band structure DFT calculations.
- L(S)DA method using the FPLO7 code [13,14].
- Exchange and correlation potential: Perdew and Wang 92 [15].
- Brillouin zone sampling: 8×8×8 → accuracy in E_{Total} of at least 10^{-3} eV.
- Supercells: anatase 2×2×1 and rutile 2×2×2 set up of unit cells at equilibrium volume.

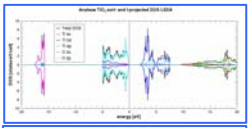


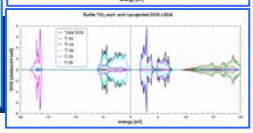
STRUCTURAL DATA of stoichiometric phases

Anatase: S.G. I $4_1/a$ m d (no.141)
At equilibrium volume: a_0= 3.7771 Å and c_0= 9.4804 Å
a_0/a= 0.998 and c_0/c= 0.996 (ref. [abr71] and [how91])
Fitting to Murnaghan eq. [16] : B_0= 113 GPa and B' = 4.22

Rutile: S.G. P 42/m n m (no.136).
At equilibrium volume: a_0= 4.5530 Å and c_0= 2.9636 Å
a_0/a= 0.991 and c_0/c= 1.002 (ref. [abr71] and [how91])
B_0= 247 GPa and B' = 4.38

Titanium ions in octahedral coordination - apically elongated oxygen octahedra.
Oxygen has three in-plane Ti nearest neighbors.





structure

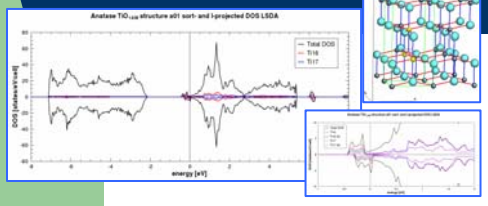
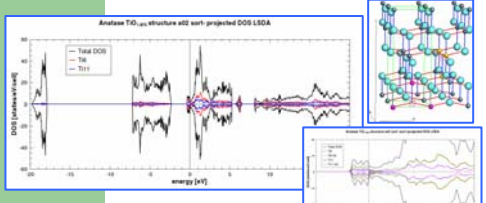
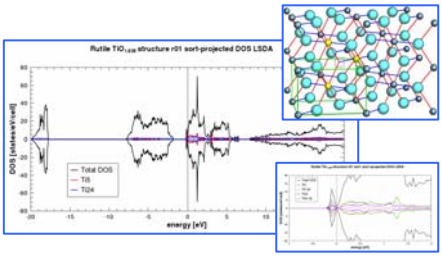


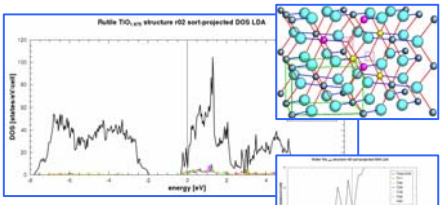
Table 1. Supercell structures, OVs concentration, planes of Ti nn to an OV and the magnetic moment per supercell.

Structure	OVs (%)	Simulating	Planes of Ti nn	Magnetic moment [1] (μ_B / supercell)
a01	3.13	isolated OVs	(100)	0.23
a02	6.25	isolated OVs	(100) and (010)	0.05
a04	6.25	OVs chains along [100]	(100)	0.28
a05	9.38	clusters of 3 OVs	(100) and (010)	0.00
r01	3.13	isolated OVs	(-110)	0.00
r02	6.25	isolated OVs	(-110) and (110)	0.00
r03	6.25	OVs isolated pairs [2]	(-110)	1.09
r04	6.25	OVs isolated pairs [3]	(-110) and (110)	0.00

[1] unrelaxed lattice. [2] d= 2.51 Å . [3] d= 2.76 Å.







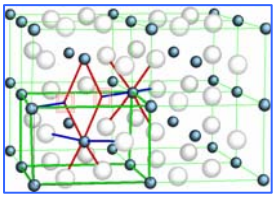
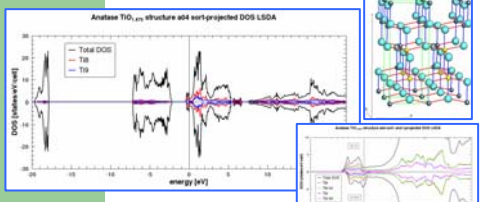


Fig.A



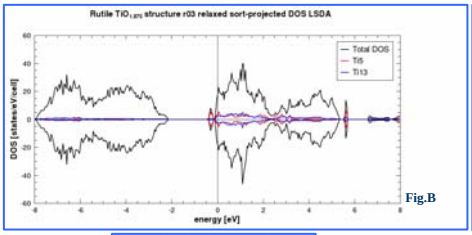
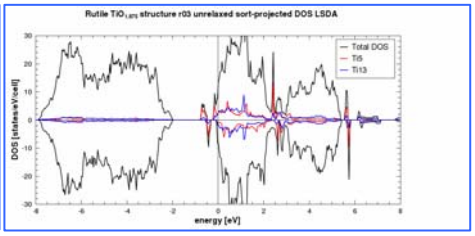
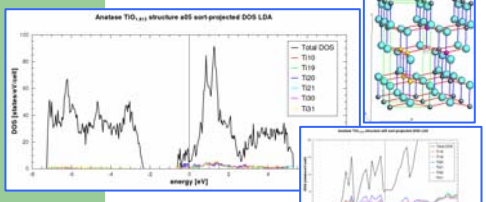
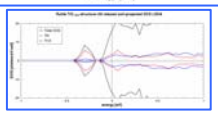
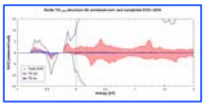


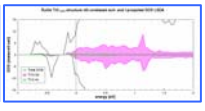
Fig.B











Acknowledgements

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REFERENCES

[1] Y. Matsumoto et al., Science 291 (2001) 854.
[2] H. H. Nguyen et al. , J. Appl. Phys.95 (2004) 7378.
[3] G. C. Han et al., J. Magn. Magn. Mat. 272-276 (2004) e1537.
[4] T. C. Kaspar et al. J. Appl. Phys.97 (2005) 073511.
[5] L. Sangaletti et al., Phys. Rev. B 78 (2008) 075210.
[6] N. H. Hong et al., J. Magn. Magn. Mat. 316 (2007) 214.
[7] S. Zhou et al., Phys. Rev. B 79 (2009) 113201.
[8] J.M.D. Coey, M. Venkatesan and C.B. Fitzgerald, Nature 4 (2005) 173.
[9] M. S. Park et al. , Phys. Rev. B 65 (2002) 161201 (R).
[10] R. Janisch, N.A. Spaldin, Phys. Rev.B 73 (2006) 035201.
[11] G. Mallia, N.M. Harrison, Phys. Rev. B 75 (2007) 165201.
[12] H. Peng et al., Phys. Rev. B 79 (2009) 092411.
[13] K. Koepernik and H. Eschrig, Phys. Rev. B 59 (1999) 1743.
[14] I. Opahle, K. Koepernik, and H. Eschrig, Phys. Rev. B 60 (1999) 14035.
[15] J. P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
[16] V. Tyuterev and N. Vast, Comp. Mat. Sci. 38 (2006) 350.
[17] D.C. Cronemeyer, Phys. Rev. 87 (1952) 876.
[18] H. Iddir et al., Phys. Rev. B 75 (2007) 073203.
[19] J.B Goodenough, J. Solid State Chem. 7 (1973) 428.

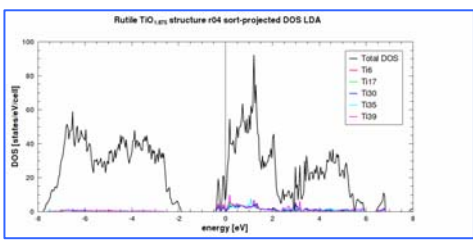
CONCLUDING REMARKS

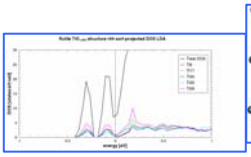
• In anatase and rutile $TiO_{2-\delta}$ the defect (neutral OV) states appear in the L(S)DA gap and are localized close to the CB bottom, in agreement with the donor nature of the defect states [17]. These states are formed by Ti 3d and 4s orbitals.

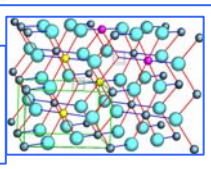
• We evidence the correlation existing between the onset of magnetic moments and the anisotropy of the stress field in the crystallographic lattice. In the unrelaxed lattice, the stress due to OVs is mainly confined in the plane containing the defect and the three Ti nn.
The O atoms are located on mirror planes parallel to the main symmetry axis, i.e. {-1 1 0} and {1 1 0} in rutile and {1 0 0} and {0 1 0} in anatase. A magnetic moment may appear in those unrelaxed structures in which all the mirror planes of the OV sites are parallel to each other. The magnetic moments are localized at the Ti sites that contribute to the defect states. However, no magnetic moment appears in the unrelaxed structures in which not all the mirror planes of the OV sites are mutually parallel. The onset of a magnetic moment does not appear to be related to vacancy concentration, as proven by the data for structures a02 and a05 in Table 1.

• The magnetic moments vanish by effecting the relaxation of the lattice (see, e.g., structure r03). The relaxation has been carried out by shifting the positions of the three Ti nearest neighbors of the vacancy site. A null moment is obtained for Ti displacements of d= 0.155 Å, which is half the maximum value reported in [18]. A comparison of the total energies for the unrelaxed and relaxed cells shows that the ground state actually is non magnetic.

• The local environment at the defect sites in the case of rutile r03 structure is depicted in Fig.A. The density of states of the relaxed material is plotted in Fig.B. The presence of the vacancies modifies the oxygen coordination of the Ti sites: the Ti13 ion is surrounded by 5 O in a square-pyramidal coordination, whereas the Ti5 ion has 4 O with a fourfold seesaw coordination. The average Ti-O distances are 1.90 Å for Ti5 and 1.84 Å for Ti13. The individual magnetic moments are significantly higher for the 4-coordinated Ti5 ions (0.41 μ_B) than for the 5-coordinated Ti13 ones (0.10 μ_B). This difference might be explained by the higher degree of covalency at the Ti13, in agreement with its coordination number being lower and average Ti-O distance being shorter than for Ti5 [19].







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