

SPIN POLARIZATION AT OXIDE SURFACES: FROM p TO s MAGNETISM

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Introduction

Magnetism at surfaces constitutes an active topic of research, mainly supported by the aim of reducing magnetic devices down to the nanoscale[1]. The actual formation of a surface implies the rupture of the translational symmetry proper of the corresponding bulk material together with a reduced coordination of the surfacemost atoms which may lead to not well compensated charge distributions. Thus, surfaces most generally undergo relaxations/reconstructions and bond rehybridizations in order to balance the charge excess/defect. Such stabilizing mechanisms are particularly evident in semiconductor and ceramic surfaces, where large and complex reconstructions are often found in order to empty of charge the unsaturated "dangling" bonds -i.e. shift upwards above the Fermi level the energy of these bands. H-passivation is a typical way for saturating these bonds thus avoiding the surface reconstruction. Alternatively, surfaces may also stabilize by developing an exchange interaction which leaves two unbalanced bands with opposite spins resulting in unexpectedly large magnetic moments. Here, we analyze both effects and find the appearance of ferromagnetism in many oxygen rich ceramic surfaces as well as in the metal terminated ZnO(100) surface passivated with H. In the first case, the ferromagnetic states are mainly localized at the oxygen atoms, while for the second case, it is the hydrogen atoms which become spin polarized. Therefore, the l -character of the magnetic states is of type p and s , respectively.

Theoretical

We have studied the following binary insulating oxides: ZrO₂ cubic, tetragonal and monoclinic (-c, -t and -m, respectively), as well as α -Al₂O₃, MgO and ZnO considering different crystal orientations and surface terminations. Surfaces were modeled via 2D slabs of various thicknesses ranging between 5-10 oxide layers. We always assumed the absence of any reconstruction so that the 2D unit cell is a $p(1 \times 1)$ relative to the bulk. All total energy calculations have been performed with the LCAO-pseudopotential DFT based SIESTA code[2] both under the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). The electronic and magnetic properties of the surface

were studied by inspection of the spin-resolved Mulliken charges, the atom projected Density of States (PDOS) together with any net magnetic moments after Local Spin Density (LSD) calculations.

Results and discussion

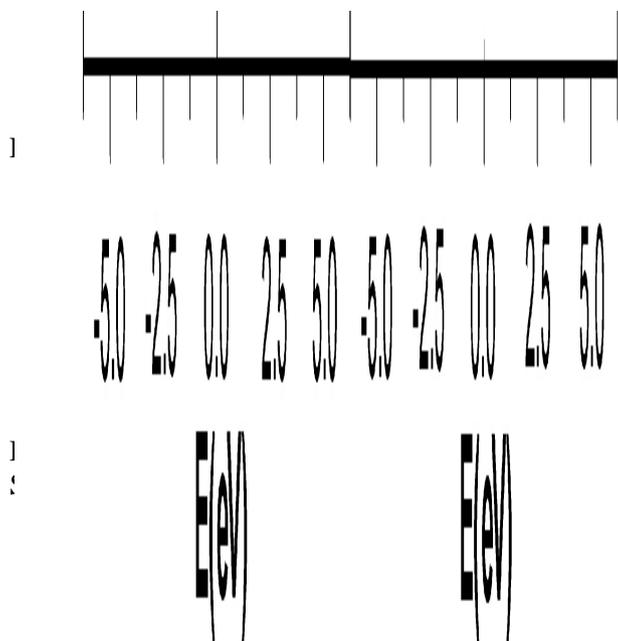
Ceramic Oxides: p-magnetism

We have found a magnetic ground state for most of the oxygen rich polar surfaces regardless the nature of the ceramic. Table 1 summarizes the main electronic and magnetic properties of the spin polarized surfaces found in this work. The magnetic moments are mainly localized at the surface O plane and vary from 0.8 O_B for MgO(111) up to 1.6 O_B for c-ZrO₂(111). The distinct characteristic of all these magnetic structures is that they are polar divergent surfaces with a loss of cationic coordination for the outermost O atoms. Indeed, the surface ferromagnetism is intimately related to the decrease of the oxygen ionic charge at the surface with respect to the bulk, since the spin polarized oxygens approach a neutral charge state. This can be clearly seen in Table 1 by comparing the oxygen charge at the bulk versus that at the surface. Furthermore, all magnetic surfaces are found to be half-metallic.

Table 1: Spin moments (in O_B) at the topmost layer of several magnetic oxide surfaces, together with the decomposition of the p orbital contribution parallel and normal to the surface plane. The rightmost columns provide the corresponding Mulliken charge populations (Q) compared to the inner bulk value (Q_b). The O_1 and O_2 entries for the non-cubic ZrO₂ structures refer to the two inequivalent in-plane positions.

Surface	m_{tot}	m_{\parallel}	m_{\perp}	Q	Q_s
c-ZrO ₂ (111) ₀₋₀	1.56	1.50	0.04	6.02	6.79
m-ZrO ₂ (001) ₋₀₁	1.43	0.81	0.61	6.10	6.66
-02	1.43	0.81	0.60	6.11	
t-ZrO ₂ (001) ₋₀₁	1.19	0.54	0.64	6.13	6.76
-02	0.59	0.55	0.03	6.17	
c-ZrO ₂ (001)	0.83	0.62	0.21	6.29	6.79
Al ₂ O ₃ (0001)	0.97	0.74	0.23	6.10	6.49
MgO(111)	0.83	0.06	0.76	6.37	6.72

Figure 1 presents the layer resolved PDOS for c-ZrO₂(111) with and without spin polarization (SP and NSP). In the SP case, the bands crossing the Fermi level have a well defined spin polarization, the majority spin states being full while the minority spin band is only partially filled. It is apparent that the effect of the spin exchange is to shift upwards the minority spin band while the majority one remains roughly bulk-like.



(PDOS) onto the surface and bulk atoms for the oxygen terminated cubic zirconia surface. Left (right) panels correspond to the spin polarized (not spin polarized) results. Positive (negative) values correspond to majority (minority) spin states. The total spin moments per layer are also indicated.

H-covered ZnO(100); s-magnetism

We have also studied the effect of passivating the zinc terminated ZnO(100) surface with H[4]. The total energy calculations show that H adsorbs on this surface on top of the Zn atoms. Remarkably, the surface becomes spin polarized, but its origin is drastically different than that for the oxygen rich clean surface case. As seen in Figure 2, where we plot the PDOS onto the surface atoms, two almost flat bands arise across the oxide gap and close to the Fermi level. One of them is completely filled -majority band-, while the other

-minority band- crosses the Fermi level several times and is partially filled, thus leading to a net magnetic moment of around 0.8 μ_B . An inspection of the PDOS reveals that this surface band is mainly localized on the H atoms. Hence, the orbital character of these spin polarized bands is s-like, as opposed to the previous cases, where it was p-like. Interestingly, we find that the spin polarization strongly depends on the H coverage: spin polarization only arises for $\theta_p \geq 0.5$

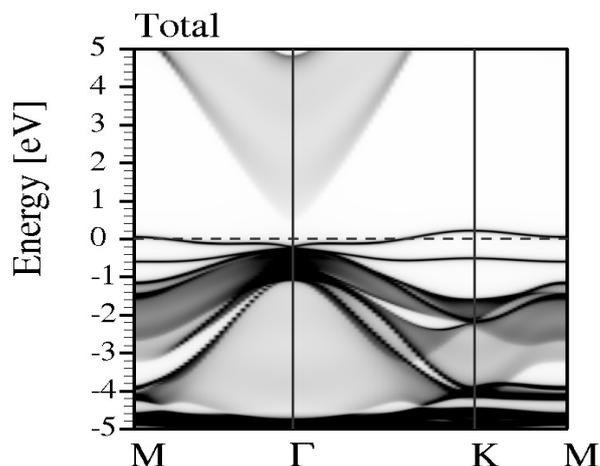


Fig. 2: Electronic structure of the ZnO(100)-p(1x1)+H surface along the high symmetry lines of the 2D Brillouin Zone. Majority and minority spin components have been added. The net magnetic moment is confined to the two flat bands crossing the oxide gap.

Conclusions

1. p-ferromagnetism is likely to appear at oxygen rich ceramic surfaces in order to reduce the excess charge at the dangling bonds.
2. s-ferromagnetism shows up at the H-covered ZnO(100) surface.

References

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