Magnetic states at the Oxygen surfaces of ZnO and Co-doped ZnO

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First principles calculations of the O surfaces of Co-ZnO show that substitutional Co ions develop large magnetic moments which long-range coupling depends on their mutual distance. The local spin polarization induced at the O atoms is three times larger at the surface than in the bulk, and the surface stability is considerably reinforced by Co. Moreover, a robust ferromagnetic state is predicted at the Oxygen (0001) surface even in the absence of magnetic atoms. The occurrence of surface magnetic moments correlates with the number of p-holes in the valence band of the oxide, and the distribution of the magnetic charge is, even in the absence of spin-orbit interaction, highly anisotropic.

Keywords: dilute magnetic oxides, p-magnetism, ZnO, Co

The prediction of room-temperature (RT) ferromagnetism (FM) in dilute magnetic oxides generated a large interest, and at present there is wide experimental evidence for insulators such as ZnO, TiO$_2$ and SnO$_2$ when doped with just a few percent of magnetic transition-metal (TM) ions [1]. One of the most promising and extensively studied systems is Co-ZnO [2]. However, its magnetic properties and in particular RT-FM remain controversial, since they are not only strongly dependent on the preparation method, but also on the growth conditions of the samples [3]. The initial agreement between experimental observation of FM and calculations has evolved to the questioning of the possibility of RT-FM either mediated by valence-band holes, or due to the percolation of magnetic polarons [4, 5]. Moreover, controversial issues need to be explained: the independence on the preparation method, but also on the growth conditions of the samples [3]. 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[0001] orientation as a function of the Oxygen chemical potential is shown. The O-terminated (0001) surface is found to be stable over the entire admissible range of chemical potentials, in good agreement with experiments [11]. Contrary, for the (0001) surface the most stable surface corresponds to the Zn-termination. However, along the [0001] direction, rough surfaces associated to Zn vacancies and incomplete Oxygen terminations have been observed, and even smooth (0001) O-terminated surfaces are formed under optimum growth conditions [12]. In the following, we will concentrate in the O- surfaces.

First, we analyze the Co-doped O-terminated (0001) surface. For a 3.6% Co concentration, Co substitutes a Zn in the cation subsurface layer (see figure 1). The surface O atoms have an unsaturated dangling bond and are bonded either only to Zn (O<sub>2</sub> atoms), or to one Co and two Zn atoms of the subsurface layer (O<sub>3</sub> atoms). The substitution of Zn by Co does not involve a relevant variation of bond distances. However, besides the spin-polarization, Co-doping significantly reduces the surface energy, increasing the surface stability as shown in figure 1. Fig. 2 provides the layer projected density of states (LDOS) of the Co and Co-bonded O atoms at the three uppermost layers, together with that of an inner bulk-like O. For comparison, the corresponding LDOS for bulk Co-ZnO are shown on the left. The calculated mm and Mulliken charges are given in table I. In both, surface and bulk, we find a magnetic ground state which remains insulating. In addition, Co shows a spin-polarized LDOS with a large mm close to 3μ<sub>B</sub>, the maximum value allowed by Hund’s rule. However, there are significant differences when Co is located near the surface or in the bulk. The majority-spin Co 3d states are fully occupied in both cases although the hybridization with the O 2p valence band is stronger for the subsurface Co, which does not show the well defined ε and t<sub>2</sub> levels seen in bulk Co. Also, while the highest occupied levels in bulk Co are the minority-spin ε states, both ε and t<sub>2</sub> minority states are empty in the subsurface Co. Consequently, Co exchange splitting and Co-O hybridization are much larger when Co is close to the surface, leading to a larger induced spin-polarization of the surface Oxygens. In addition, the table suggests certain correlation between mm and charge transfer: surface Oxygen atoms bonded to Co with large mm show a significant decrease of the ionic charge.

| TABLE I: Magnetic moment (mm, in μ<sub>B</sub>) and charge difference with respect to the bulk | O<sub>L1</sub> | O<sub>2</sub> | Co<sub>L1</sub> | Co<sub>L2</sub> | O<sub>L3</sub> | O<sub>Zn</sub> |
|-----------------------------------------------|--------|--------|-----------|----------|--------|--------|
| mm Co-Bulk (0001) | 0.11   | 2.71   | 0.12      |          |        |        |
| (0001)<sub>T</sub> | 0.45   | 0.03   | 2.90      | 0.22     | 0.03   |        |
| (0001)<sub>L</sub> | 1.39   | 1.39   | 2.84      | 0.20     | 0.04   | 0.04   |
| Und. (0001)<sub>T</sub> | 0.80   | 1.33   | 2.05      | 0.17     | 0.03   | 0.03   |
| (0001)<sub>L</sub> | 1.40   |        |          |          |        | 0.08   |
| ΔQ Co-Bulk (0001) | -0.03  | -0.80  | -0.03     |          |        |        |
| (0001)<sub>T</sub> | -0.18  | -0.06  | -0.83     | -0.04    | 0.01   |        |
| (0001)<sub>L</sub> | -0.58  | -0.58  | -0.04     | 0.04     | 0.02   |        |
| Und. (0001)<sub>T</sub> | -0.69  | -0.57  | -0.65     | 0.09     | 0.01   |        |
| (0001)<sub>L</sub> | 0.11   |        |          |          | 0.01   |        |
| (0001) | -0.58  |        |          |          | -0.03  |        |

FIG. 1: (color) (Top) Side views of all possible (0001) and (0001) wurtzite ZnO surfaces, indicating the position of substitutional Co at the Co-doped O terminations modelled here. Our labels for the atomic sites are shown in the coordination units at the bottom right side. (Bottom) Relative surface free energy as a function of the O partial pressure for the undoped (solid lines) and Co-doped (dashed) (0001) and (0001) surfaces. For negative energy values the O-termination is more stable than the Zn- one.
surface (bulk). This unambiguously demonstrates that the breaking symmetry of the surface promotes magnetism.

We have studied the difference between F and antiferromagnetic (AF) ordering substituting an additional Zn by Co at different cation layers (7.5% of Co concentration). The local main features depicted in Fig. 2 are not altered. AF coupling between the Co impurities is favoured whenever Co atoms are separated by more than a ZnO unit, while F coupling becomes stable if there is only an O between them. However, even for an AF alignment of Co atoms, the existence of uncompensated O mm at the surface leads to a net F structure. Nevertheless, the energy difference between states with F and AF coupling is always too small, $\sim 10$ meV, to account for the experimental $T_C$. Addition of codoping does not modify substantially the magnitude of the coupling, in agreement with previous calculations [13].

Regarding the 3.6% Co-doped (0001) O-ended surface, again the presence of Co atoms close to the surface remarkably increases its stability, in agreement with recent experiments [14], leading to a range of the chemical potential for which the O-termination is the most stable (see figure 1). Oxygen atoms have three unsaturated dangling bonds, and therefore they are onefold coordinated only to the metal atom underneath, either a Co ($O_1$ atoms) or a Zn ($O_2$ atoms). Due to the low coordination, which is clearly evidenced in the large charge loss, important relaxations occur. For this reason, the unrelaxed and relaxed values are provided in table I. The main effect of relaxation is to modify the Co-O bond distances, which can become as small as 1.5 Å for the $O_1$ atoms. The short bond length modifies largely the Co mm. In fact, the Co exchange splitting becomes smaller than that for an impurity in the bulk, as shown in the rightmost panel of figure 2. The Fermi level ($E_F$) crosses the valence band, leading to a metallic surface. On the other hand, the induced mm of surface Oxygen is almost twice than at the (0001) surface, reflecting the stronger hybridization to Co. Nevertheless, the more striking effect is that all the surface Oxygens develop a mm independent of the magnetic character of the cation neighbour, which is even larger for the $O_2^{Zn}$ atoms, $1.3 \mu_B$. Further, the LDOS of the two inequivalent surface O (not shown here) show different shapes, pointing to a dissimilar origin of the mm. In summary, it seems like there are two different types of mm for O: one induced by hybridization with the impurity $d$ states, and other which can not be associated to the $d$ electrons.

To get a further insight on this idea, we have calculated the (0001) and (0001) O surfaces of undoped ZnO allowing for the spin degree of freedom. We find that the configuration with ferromagnetically ordered spin moments is favoured at the (0001) surface. The energy reduction due to the spin polarization is 0.6 eV per O, a value in the range of those obtained for magnetic bulk oxides. The LDOS of the undoped surfaces are displayed in figure 3 and the mm and ionic charge differences are also included in table I. Oxygen at the (0001) surface presents an occupied large peak close to $E_F$ but it has not an appreciable spin-polarization. On the other hand, a large splitting is observed in the Oxygen atoms at the (0001) surface, which develop a mm very similar to that of O bonded to Zn in the Co-doped surface. Remarkably, the bands crossing $E_F$ correspond to minority-spin levels, leading to a half-metallic system with charge compensating holes of well defined spin polarization. The lower O coordination of the (0001) surface as compared to the (0001) one leads

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**FIG. 2:** LDOS for Co and the O atoms bonded to Co at bulk Co-ZnO (left), and at the three uppermost layers of the O-ended (0001) (middle) and (0001) (right) surfaces of 3.6% Co-doped ZnO. The top curves refer to the surface plane (L1 in table I), while the bottom ones show the bulk-like LDOS of O at the central layers of each slab. Positive (negative) values correspond to majority (minority) spin states. Energies are referred to $E_F$.

**FIG. 3:** Same as figure 2 for the three topmost layers of the O-ended undoped ZnO (0001) and (0001) surfaces.
to a lower charge transfer and then to a higher number of 2p holes in the O valence band. This different response proves that it is necessary a critical number of 2p holes for achieving a magnetic surface. This result corroborates previous findings of correlation between ionic charge and mm on a systematic study of magnetic surfaces of highly ionic oxides [15]. Another peculiarity of Oxygen mm induced by creating 2p holes is the highly anisotropic distribution of the magnetic charge, which involves only p-orbitals along specific directions. The crystal field determines where holes are localised: while the majority spin is completely filled and thus adopts the spherical symmetry of the bulk, there is an anisotropic distribution of the minority charge, and holes mainly reside in the $p_{xy}$ orbitals of the (0001) O surface. This is seen in figure 4 which depicts the spin charge density differences (SDD, total charge density minus the superposition of atomic charge densities) for the Co-doped (0001) and the undoped (0001) surfaces, evidencing the different orbital contributions to the mm when induced by the 2p holes or by Co-O hybridization.

In conclusion, the proximity of a surface to a substitutional Co in ZnO enhances the magnetization induced by the magnetic impurity and even for an AF alignment of Co impurities the surface may show uncompensated spins ferromagnetically ordered, although this effect alone does not justify a high $T_c$. The presence of Co atoms close to the surface remarkably increases its stability. In addition, in the absence of magnetic atoms, $p$-magnetic states can still develop whenever a critical value of $p$-holes is exceeded, with a highly anisotropic distribution of the magnetic charge. The existence of oxygen polarised large surface areas can account for some of the spontaneous magnetization reports observed in several ZnO structures, even in the absence of magnetic doping. Also, it can explain why the magnetic state is intimately connected to the actual structure of the sample and the growth conditions. Oxygen $p$-magnetism associated to uncompensated charge in ionic oxides seems to be a general phenomenon which can be related to early reports about the fact that cation-deficient CaO or SrO should be half-metallic ferromagnets [16], the recent proposal of magnetizing oxides by substituting nitrogen for oxygen [17], as well as to the magnetic properties of cation vacancies in II-VI semiconductors [18]. Recently, magnetic states have been reported at the interface between two non-magnetic oxides [19]. This opens new perspectives for the development of the new fascinating field of oxides heterostructures in which the violation of charge compensation may give rise to new magnetic or superconducting states [20].

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