

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 order depends on their mutual distance. The local spin polarization induced at the O atoms is 3 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 O (0001) surface even in the absence of magnetic atoms, correlated with the number of p holes in the valence band of the oxide, and with a highly anisotropic distribution of the magnetic charge even in the absence of spin-orbit coupling.

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In recent years, a considerable effort has been invested in the research on dilute magnetic semiconductors for use in spintronic devices, which exploit the spin of the carriers rather than their charge. The prediction of room-temperature (RT) ferromagnetism (FM) in p -type Mn doped ZnO generated a large interest, and at present, there is wide experimental evidence that several oxides such as ZnO, TiO₂, and SnO₂ exhibit RT FM when doped with just a few percent of magnetic transition-metals [1,2]. However, it remains still unclear whether RT FM is an intrinsic property, and there are controversies about the conditions required to achieve long-range magnetic order. There are also unexplained issues as, among others, the independence of the Curie temperature (T_C) on the concentration of the magnetic element, or that magnetic moment (M) per cation may exceed the limiting value established by Hund's rules [1–3].

One of the most promising and extensively studied systems is Co-ZnO [3–6]. The initial agreement between the experimental observations and calculations has evolved to questioning the feasibility of RT FM. At present, there are disparate claims about the magnetic state, since experimental results support both strong RT FM and lack of FM. The role of the carriers mediating FM is equally unclear, and there are reports of RT FM ranging from highly conductive to highly insulating materials [4]. Furthermore, the most plausible mechanisms to account for magnetic coupling, either mediated by valence-band holes or caused by the percolation of magnetic polarons, cannot justify the high experimental values of T_C . Indeed, the possibility of an extrinsic origin or magnetism due to nanocrystals has been recently suggested [4,7]. However, signatures of RT FM have been reported not only in low-dimensional ZnO structures doped with magnetic ions, but also when doped with nonmagnetic elements or even undoped [8].

Despite FM, order is mainly observed in low-dimensional structures; to our knowledge, there is not a theoretical study exploring how the surface affects the magnetic state of dilute magnetic oxides. In this Letter,

we investigate the local magnetic order at the polar (0001) oriented surfaces of wurtzite ZnO. We show that the surface enhances the spin polarization induced by Co atoms, and additionally, even in the absence of magnetic ions, it promotes the formation of a p -derived extended magnetic state which has no counterpart in bulk.

Our study of the spin-resolved electronic structure is based on the *ab initio* pseudopotential density functional theory within the local spin density approximation (LSDA). Although LSDA underestimates the band gap of ZnO, the description of bulk Co-doped ZnO is qualitatively similar to that of methods which better account for electronic correlations. An insulating ground state and analogous orbital spin occupancies are found, though the energy of the unoccupied Co $3d t_2$ minority-spin states is lower than that from LDA + U or hybrid functional methods [6]. We use the SIESTA package [9] with basis sets formed by multiple-zeta polarized localized numerical atomic orbitals (AO). In the case of Zn, we choose double-zeta (DZ) basis for the s and d AOs plus a single-zeta (SZ) p AO. The same type of basis set is used for Co, whereas for O, we employ DZ s and p AOs plus a SZ d AO. More details about the conditions of the calculations can be found elsewhere [10].

Since the wurtzite structure is not centrosymmetric, thin layers grown along the crystallographic c -axis may present either the [0001] or the [000 $\bar{1}$] growth direction. Along this direction, pure hexagonal O and Zn layers alternate so that the resulting surfaces can be either Zn- or O-terminated, as shown in Fig. 1. We model them by periodically repeated slabs containing between 15 and 17 ZnO planes, and separated by a vacuum region of at least 15 Å. Bulk-like behavior is always attained at the innermost central layers. We calculate both symmetric and asymmetric slabs about the central plane. For the former, the two terminating planes of the slab show identical composition (either Zn or O) but each one corresponds to an inequivalent symmetry, (0001) and (000 $\bar{1}$) surfaces. For asymmetric slabs, the opposite holds, and dipolar corrections are applied. We use a (1 × 1) two-dimensional (2D) unit cell to study the

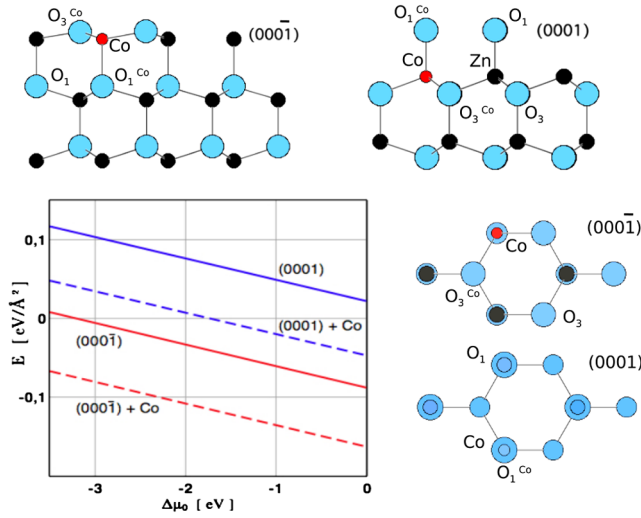


FIG. 1 (color online). (Top) Side views of all possible (000 $\bar{1}$) and (0001) wurtzite ZnO surfaces, indicating the position of substitutional Co. (Bottom right) Top views of the O-ended Co-doped surfaces, setting the atomic size proportional to the distance to the surface. At the (0001) termination, the subsurface cation sites underneath the surface O atoms are indicated by empty circles. (Bottom left) Relative surface free energy as a function of the O chemical potential for the undoped (solid lines) and Co-doped (dashed lines) (000 $\bar{1}$) and (0001) surfaces. For negative energy values, the O-termination is more stable than the Zn- one.

undoped bulk and surfaces, and a (2×2) 2D-cell containing four atoms per plane for the Co doped structures. Substitution of one and two Zn atoms by Co gives 3.6 and 7.2% of dopant concentration, respectively. The atomic positions are allowed to relax until the forces on the atoms are less than 0.05 eV/\AA , and usually below 0.03 eV/\AA . Brillouin Zone integrations have been performed on a $12 \times 12 \times 1$ Monkhorst-Pack k -point grid, although convergence has been verified using $48 \times 48 \times 4$ grids.

The stability of a given surface depends on the partial O pressure. For a surface in thermodynamic equilibrium, the surface free energy can be obtained from an *ab initio* total energy calculation in combination with a thermodynamic formalism [11]. In Fig. 1, the calculated relative stability of the different defect-free surfaces with [0001] orientation as a function of the O chemical potential is shown. The O-terminated (000 $\bar{1}$) surface is found to be stable over the entire admissible range of chemical potentials, in good agreement with experiments [12,13]. Contrary, for the (0001) surface, the Zn-termination is the most stable. However, rough (0001) surfaces associated to Zn vacancies and incomplete O terminations have been observed, and even smooth O-terminated surfaces are formed under optimum growth conditions [13,14]. In the following, we will concentrate in the O- surfaces.

First, we analyze the O-terminated (000 $\bar{1}$) surface with 3.6% Co doping. Co substitutes a Zn in the cation subsur-

face layer (see Fig. 1). The surface O atoms have an unsaturated dangling bond and are bonded either to three Zn atoms (O_3), or to one Co and two Zn atoms (O_3^{Co}). The substitution of Zn by Co does not involve a relevant variation of bond distances. However, it significantly reduces the surface energy, improving the surface stability as shown in Fig. 1. Figure 2 provides the layer projected density of states (LDOS) of the Co atoms and the O atoms bonded to Co at the three uppermost layers, together with that of an inner bulklike O. The corresponding LDOS for bulk Co-ZnO are shown on the left. 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 $2p$ VB is stronger for the subsurface Co, which does not show the well-defined e and t_2 levels seen in bulk Co. Also, while the highest occupied levels in bulk Co are the minority-spin e states, both e and t_2 minority states are empty in the subsurface Co. Thus, Co exchange splitting and Co-O hybridization are much larger when Co is close to the surface. The corresponding M are given in Table I. Both in surface and bulk, Co remains in a high-spin state, and induces a spin polarization of the adjacent O atoms which is significantly enhanced at the surface. Although the changes induced by Co are mostly local, their effect extends more at the surface than in the bulk. For example, the total M per unit cell is $4.76(3.21)\mu_B$ when Co is at the surface (bulk). In addition, there is certain correlation between M and O charge: the surface O^{Co} atoms show at the same time larger M and a significant decrease of the net charge (loss of 0.18 electrons with respect to bulk ZnO) than the bulk O^{Co} atoms (0.03 electrons).

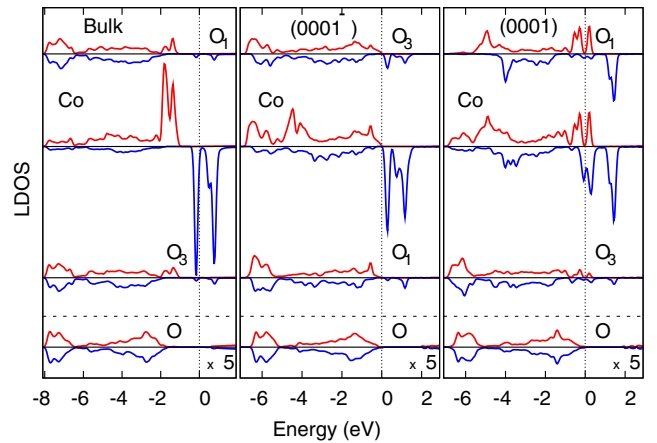


FIG. 2 (color online). LDOS of Co and O^{Co} at bulk Co-ZnO (left), and at the three topmost layers of the O-ended (000 $\bar{1}$) (middle) and (0001) (right) surfaces of 3.6% Co-doped ZnO. Following Table I, the curves correspond from top to bottom to layers L1 to L3; the lowest graphs show the bulklike O at the central layer of each slab, enhancing the empty states by a factor of 5. Positive (negative) values correspond to majority (minority) spin states. Energies are referred to E_F .

TABLE I. Magnetic moment (M , in μ_B) for the O and Co atoms at the Co-doped: bulk ZnO and the O-ended (000 $\bar{1}$) and (0001) surfaces, the last either unrelaxed (U) or relaxed (R). Layers L1-L2-L3 refer to the adjacent O-Co-O atomic planes. For surfaces, L1 corresponds to the outermost plane, and all different O sites (O, O^{Co}) are included. The O surfaces for undoped ZnO are also shown.

		Co-doped				Undoped	
		Bulk	(000 $\bar{1}$)	(0001) _U	(0001) _R	(000 $\bar{1}$)	(0001)
M	L1 O ^{Co}	0.11	0.45	1.39	0.80		
	O		0.03	1.39	1.33	0.00	1.40
	L2 Co	2.71	2.90	2.84	2.05		
	L3 O ^{Co}	0.12	0.22	0.20	0.17		
	O		0.03	0.04	0.03	0.00	0.08

We have studied the difference between FM and anti-ferromagnetic (AF) order substituting an additional Zn by Co at deeper cation layers (7.2% of Co concentration). The local main features depicted in Fig. 2 are not altered. AF coupling between the Co impurities is favored whenever Co atoms are separated by more than a ZnO unit, while FM 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 M at the surface leads to a net FM structure. Nevertheless, a mean-field estimate of T_C from the energy difference between FM and AF Co states (~ 10 meV) is below 50 K, far from RT. Addition of codoping does not modify substantially this magnitude, in agreement with previous calculations [6].

We will consider now the (0001) O-ended surface. Again, the presence of a substitutional Co atom 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 Fig. 1). O atoms have three unsaturated dangling bonds, and therefore they are onefold coordinated only to the metal atom underneath, either a Co (O₁^{Co} atoms) or a Zn (O₁ atoms). Because of the low coordination, important relaxations occur. The main effect of relaxation is to modify the Co-O bond distances, which can become as small as 1.6 Å for the O₁^{Co} atoms. The short bond length modifies largely the Co M , as reflected in Table I. In fact, after relaxation, the Co exchange splitting becomes smaller than that for an impurity in the bulk. Figure 2 shows that the Fermi level (E_F) crosses the VB, leading to a metallic surface. On the other hand, the induced M of surface O is almost twice than at the (000 $\bar{1}$) surface, due to the stronger hybridization to Co. Nevertheless, the more striking effect is that all the surface O develop a M independent of the magnetic character of the cation neighbor, which is even larger for the O₁ atoms, $\sim 1.3\mu_B$. Further, the LDOS of the two inequivalent surface O (not shown here) show different shapes, pointing to a dissimilar origin of the M . In sum-

mary, it seems like there are two different types of M for O: one induced by hybridization with the impurity d states, and the other which can not be associated to the d electrons.

To get a further insight on this idea, we have calculated the (000 $\bar{1}$) and (0001) O surfaces of undoped ZnO allowing for the spin degree of freedom. The FM ground state is obtained at the (0001) surface, favored by 380 meV over the AF configuration. The magnetic energy reduction is 600 meV per O, in the range of magnetic bulk oxides and much larger than that obtained for polarized d states at the surfaces of nonmagnetic oxides [15]. The LDOS of the undoped surfaces are displayed in Fig. 3, and the M are also included in Table I. The lower O coordination of the (0001) surface as compared to the (000 $\bar{1}$) one leads to a higher number of $2p$ holes in the O VB, i.e., the reduction with respect to the bulk of the net charge localized at the surface oxygen is 0.58 and 0.11 electrons for the (0001) and (000 $\bar{1}$) surfaces, respectively. Although no appreciable spin polarization is observed at the (000 $\bar{1}$) termination, at the (0001) one, the O atoms show a large splitting with a M close 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 different response of the (0001) and (000 $\bar{1}$) surfaces proves that magnetism requires a critical number of $2p$ holes. This corroborates previous findings of correlation between ionic charge and M on a systematic study of magnetic surfaces of different highly ionic oxides [16], which generalizes the validity of our results. Furthermore, magnetic states associated to p -dangling bonds have also been reported in other low-dimensional systems as graphite and quasi-1D organic materials [17]. A peculiarity of the O M induced by $2p$ 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 localized. For

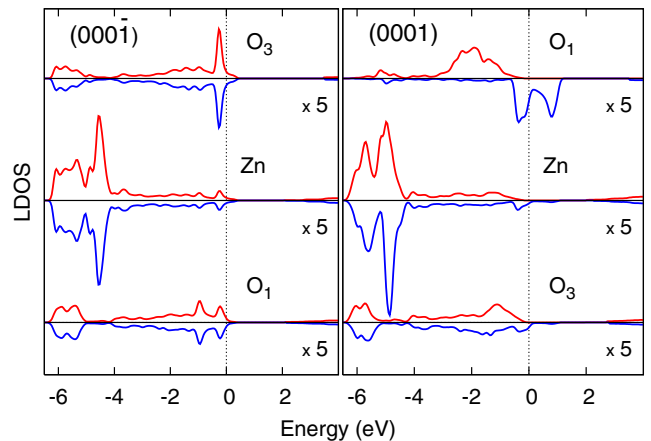


FIG. 3 (color online). Same as Fig. 2 for the three topmost layers of the O-ended undoped ZnO (000 $\bar{1}$) and (0001) surfaces.

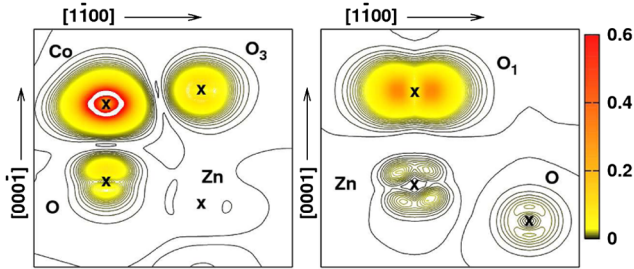


FIG. 4 (color online). SD at the two topmost surface planes of the O-ended (left) Co-ZnO(000 $\bar{1}$) surface around the Co site and (right) undoped ZnO(0001) surface. Contour lines correspond to steps of 2×10^{-3} electrons. Crosses indicate the atomic positions.

the (0001) O-surface of ZnO, holes mainly reside in the p_{xy} degenerated orbitals. This is seen in Fig. 4, which depicts the spin densities (SD, majority spin charge minus minority spin charge) for the Co-doped (000 $\bar{1}$) and the undoped (0001) surfaces, evidencing the different orbital composition and thus symmetry of the M when induced by the $2p$ holes or by Co-O hybridization.

In conclusion, the proximity to the surface of substitutional Co in ZnO remarkably increases its stability and enhances the magnetization induced by the magnetic impurity. Yet 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 . In addition, in the absence of magnetic atoms, p magnetic states can spontaneously develop at surface O whenever a critical value of p holes is exceeded, with a highly anisotropic distribution of the magnetic charge. The existence of oxygen polarized large surface areas can account for some of the reports of spontaneous magnetization in ZnO structures even in the absence of magnetic doping, although further studies are required to estimate T_C . Also, it can explain why the magnetic state is intimately connected to the actual structure of the sample and the growth conditions. p magnetism associated to uncompensated charge in ionic oxides seems to be a general phenomenon [16] which can be related to early reports about the fact that cation-deficient CaO or SrO should be half-metallic ferromagnets [18], the recent proposal of magnetizing oxides by substituting nitrogen for oxygen [19], as well as to the magnetic properties of cation vacancies in II-VI semiconductors [20]. Recently, magnetic states have been reported at the interface between two nonmagnetic oxides [21]. 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 [22].

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