Surface ferromagnetism in non-magnetic and dilute magnetic oxides

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Abstract. We explore hole-doping as an efficient route to develop magnetism in simple non-magnetic oxides. Based on ab-initio calculations of the prototypical material ZnO, we show that local spin polarization can be obtained even in the absence of magnetic dopants both in the bulk or at surfaces. However, the onset of long-range magnetic order additionally requires extended states, that can be achieved in surfaces without distorting the host lattice. We propose different possibilities which either profit the spontaneous polarization of Oxygen \( p \) states under defective charge conditions, or require the presence of adsorbates.

1. Introduction

The last decade has witnessed the emergence of the field of magnetism in non-magnetic materials [1]. Multiple nanostructures of either organic or inorganic systems have been reported to show magnetic properties in the absence of magnetic elements [2, 3, 4, 5, 6], and even the suggestion of magnetism as an universal feature at the nanoscale has been proposed [7]. Carbon-based structures also develop magnetic properties under different conditions [6, 8] and the possibility to introduce dilute concentrations of magnetic impurities in semiconductors to achieve relevant ferromagnetic responses has led to a new branch of research on the so-called dilute magnetic semiconductors (DMS) [9, 10, 11, 12]. Besides its evident fundamental interest, the investigation in this field is appealing for the development of new technological devices, which could exploit the advantages of a reduced scale, combine at the same time electric and magnetic fields, and ultimately lead to the development of spintronics.

One major drawback of most of these systems for the implementation of realistic devices is the low value of their critical temperature, usually well below room temperature. This is particularly true for DMS [13, 14]. In this sense, the prediction of Dietl at al. in 2000 that the critical temperature could be raised replacing traditional semiconductors by oxides or nitrides [15] launched a new and hot topic of research pursuing ferromagnetism in dilute magnetic oxides. Dilute magnetic oxides (DMO) are non-magnetic oxides doped with dilute amounts of magnetic transition metal impurities, so that the host lattice is essentially preserved and the main oxide properties can be retained. A large variety of systems has been considered, both concerning the oxide and the dopant, ZnO constituting a prototype [16]. Though initially magnetic elements such as Fe, Mn or Co were employed as impurities, soon appeared reports of magnetism in the absence of magnetic elements, such as non-magnetic transition metals (Cu, Ti, etc.) [17, 18], or even non-metals like N or C [19, 20]. After an intensive research effort, the initial excitement has opened way at the same time to some uncertainty about the ease to obtain
DMO showing intrinsic room temperature ferromagnetism (RT-FM) and to the identification of the basic mechanisms behind the development of magnetism in these systems [10, 11, 12]. Briefly, the appearance of local magnetic moments seems to be linked either to the introduction of magnetic impurities carrying their own spin polarization and slightly polarizing the adjacent O neighbours, or to the formation of holes at the top of the valence band of the oxide, which promote spontaneous magnetization. The holes can be originated by impurities, defects or boundaries [21, 22]. However, the magnetic interactions due to impurities (both magnetic and non-magnetic) or defects are short ranged and frequently antiferromagnetic [9], making difficult the achievement of long-range magnetic order and critical temperatures close to RT.

Several routes have been proposed to extend the range of the magnetic interactions. In the case of magnetic impurities, they imply codoping with other elements (for example, Li and Co in ZnO), introducing defects such as host cation or anion vacancies, interstitials, etc., or increasing the concentration of the magnetic impurities [23, 24, 25]. This leads to a more difficult control of the final structure and to the alteration of the original host crystal characteristics. In fact, it has been shown that the formation of secondary phases or the occurrence of spinodal decomposition are major issues that may alter the magnetic and conduction properties leading to a non-intrinsic origin of the measured ferromagnetic signal [26, 27, 28, 29]. More importantly, it has not been proved a general increase of the strength and range of the magnetic interactions. Also for magnetism in the absence of magnetic impurities only extended regions with a high concentration of impurities or defects may allow to obtain RT-FM, which again may influence the homogeneity and even the stability of the sample. In addition, the controlled incorporation of impurities and defects is arduous, and usually an inhomogeneous distribution occurs. To summarize, it remains an open question whether it would be possible to control the conditions to achieve uniform and reproducible RT-FM in bulk samples of DMO.

An alternative approach, which we proposed a few years ago, relies on the distinct properties of surfaces [22, 30]. The symmetry breaking imposed by the surface usually alters the position of the Fermi level, and for particular surfaces the system becomes metallic. Hence, the oxide can be either hole or electron doped at the surface and under specific conditions spontaneous magnetic moments develop. Furthermore, surface states, although confined to the topmost layers, are extended in two-dimensions unlike the localized impurity bulk states. Therefore, the subtle interplay between localization, necessary for the moment formation, and extended states leading to strong and long-range magnetic coupling can be reached at the surfaces. In fact, it is well-known that RT-FM is more easily achieved in thin films and nanoparticles of both DMO and undoped non-magnetic oxides. Further, there is experimental evidence that the FM signal seems to be linked to the near-surface regions, grain boundaries or nanostructure interfaces [31, 32]. Moreover, magnetic impurities often tend to approach sample boundaries favouring magnetic order close to the frontiers.

In this article we will discuss the origin of magnetism and the possibility to achieve long range magnetic order at the surface of ionic oxides, based on our calculations on the prototypical material ZnO. First, we will show that the requisite to develop magnetic moments even in the bulk is to introduce hole-doping. Under these conditions, local magnetic states appear in the absence of magnetic elements. However, the magnetic interactions remain short-ranged. In order to achieve long-range magnetic order, extended magnetic states need to be formed. Second, we will show that surfaces appear as an unique scenario to achieve this goal.

2. Theoretical framework

The results presented here are based on ab-initio calculations within the density functional theory, using both the SIESTA [33] and VASP [34] computational packages. The first is based on basis sets formed by localized atomic orbitals. For the structures considered we have employed multiple-zeta polarized localized numerical atomic orbitals (AO). In the case of Zn we choose
double-zeta (DZ) basis for the 4s and 3d AOs plus a single-zeta (SZ) 4p AO, whereas for O we employed DZ 2s and 2p AOs plus a SZ 2d AO. Besides undoped ZnO structures, we will also consider Cu doping and H adsorbates. Cu impurities have been described using the same type of basis set as for Zn, while Hydrogen is described by a DZ 1s AO. In VASP the electronic charge density is expressed in plane-wave basis sets [35]. We have used the projector augmented wave (PAW) method to describe the electron-ion interactions, and a plane-wave energy cutoff of 350 eV. More details about the conditions of the calculations can be found elsewhere [30, 36, 37].

Depending on the structure, to describe the exchange-correlation part we have used either the LSDA (local spin density approximation) + U with SIESTA [38] or HSE (Heyd-Scuseria-Ernzerhof) hybrid functionals with VASP [39], that introduce correlation and localization effects beyond LSDA and provide an improved description of the electronic band gap of ZnO. The empirical Coulomb U = 5.7 eV and exchange J = 1 eV parameters are chosen to model the orbital dependent Hubbard-like potential for the Zn 3d states [40]. The resulting parameters that characterize the wurtzite unit cell of ZnO are a = 3.25 Å and c = 5.20 Å, and the band gap $E_g = 1.25$ eV, which can be compared to the experimental values of $a = 3.25$ Å, $c = 5.20$ Å, $E_g = 3.3$ eV [41, 42]. The corresponding shortest Zn-O distance between first neighbours is 1.98 Å. For HSE calculations we have employed a 25% of Hartree-Fock exchange and a value of 0.37 for the screening parameter, which provides $E_g = 3.55$ eV.

The structures are modelled as periodic slabs with the z-axis along [0001] and ($n \times m$) unit cells in the xy plane, $n$ and $m$ ranging from 1 to 3 depending on the calculation. For surfaces, the thickness of the slab has been chosen in order to reproduce bulk features in the middle layers, typically between 15 and 17 ZnO planes. A vacuum region of at least 15 Å has been included, that guarantees the absence of interaction between both slab sides, and dipolar corrections have been applied for asymmetric slabs. The atomic positions have been relaxed until the forces on the atoms are always below 0.05 eV/Å and usually less than 0.03 eV/Å. In all cases we have ensured convergence in k-sampling, with reciprocal space integrations performed on Monkhorst-Pack supercells up to $12 \times 12 \times 1$ in particular cases.

3. Bulk (Cu,Zn)O

![Figure 1](image.png)

**Figure 1.** Scheme of the structure of (left) an isolated substitutional Cu impurity and (right) one-dimensional Cu aggregates contained in the [0001] plane in bulk ZnO. Oxygen, Zn and Cu atoms are represented respectively by large red balls and small gray and blue balls.

We have analyzed the substitution of Zn by Cu in bulk ZnO. First we have considered isolated Cu impurities (see left panel of figure 1) in a supercell of 32 atoms including eight [0001] atomic layers along the z-axis and a (2 × 2) unit cell in the xy plane, that represents a Zn$_{94}$ Cu$_{06}$O structure. Under these conditions, adjacent Cu impurities are separated at least by
an intermediate O-Zn-O sequence, which leads to a negligible interaction between them. The corresponding structure shows minor and asymmetric relaxations with respect to undoped ZnO, the Cu-O distance between first neighbours being 2.01 Å for the on top Oxygen along the [0001] axis and 1.95 Å for the three Oxygens underneath. The analysis of the charge distribution as compared to bulk ZnO indicates that, similarly to Zn, Cu is in a +2 valence state, though the net charge transferred to the neighbouring Oxygen atoms is slightly reduced, which may be indicative of a reduced ionicity of the Cu-O bonds. Figure 2 provides the total density of states (DOS) of the supercell obtained using the HSE functional. The projected DOS on the Cu impurity and on one of its O neighbours are also shown. The Cu 3d states are spin splitted and appear mostly overlapping the O p valence band (VB), but additional impurity states fall in the bulk band gap. They correspond to the minority Cu t\textsubscript{2g} states and the Fermi level crosses this impurity band. The hybridization of Cu and O is reflected in the weight on the O p states particularly of the t\textsubscript{2g} Cu states. But the most important aspect is that, eventhough all elements in the structure are non-magnetic, the depletion of the Cu d electronic levels leads to a Cu magnetic moment of 0.65 $\mu_B$, slightly polarizing the adjacent O neighbours with moments around 0.1 $\mu_B$. The O moments are almost symmetrically distributed, with the spin density charge shared out among the p\textsubscript{x}, p\textsubscript{y} and p\textsubscript{z} orbitals, as reflected in the spin density distributions at figure 3. Magnetic moments of Zn or more distant O atoms are negligible. The resulting total moment of the supercell is 1.00 $\mu_B$, evidencing the local character of the magnetization. The magnetic interaction, measured as the difference between a ferro- and antiferro-magnetic configuration, is very small, less than 10 meV, and therefore short ranged.

![Figure 2](image-url)

**Figure 2.** (Top) Spin polarized DOS of the modelled Zn\textsubscript{0.94}Cu\textsubscript{0.06}O slab, where positive (negative) values correspond to majority (minority) spin projections. The energy zero is set at the Fermi level. The filled curve represents the Cu contribution. (Bottom) DOS projected on one of the O neighbours bonded to Cu. The scale at the y-axis has been enhanced 2.5 times with respect to the top panel.
Due to the short range of the interactions between impurities, and in order to explore the possibility of obtaining extended magnetic order, we have studied one-dimensional Cu structures in the [0001] plane with only one intermediate Oxygen atom between neighbouring Cu cations, as depicted in the right diagram of figure 1. Under these conditions, the local Cu magnetic moments increases to 0.85 $\mu_B$, while the Oxygen polarization distributes as 0.20 $\mu_B$ for the Oxygen atoms bonded to 2 Cu impurities, and 0.07 $\mu_B$ for those with only one Cu bond. The resulting total magnetic moment at the supercell is 2.0 $\mu_B$, thus equivalent to the induced magnetic moment of the isolated impurity. The strength of the magnetic coupling, measured as the difference between a ferro- and antiferro-magnetic configuration, is around 20 meV. Based on simple mean-field models, this exchange interaction does not support the existence of RT-FM.

![Diagram showing spin density charge around a substitutional Cu impurity in bulk ZnO at two orthogonal sections.](image)

**Figure 3.** Spin density charge around a substitutional Cu impurity in bulk ZnO at two orthogonal sections.

To summarize, isolated Cu impurities in bulk ZnO are spin-polarized, the magnetic moments being associated with unpaired electrons of the Cu ions. The electronic states close to the VB edge are dominated by hybridization between O 2p and Cu 3d orbitals, which implies that the Cu-O bond is partially covalent instead of purely ionic. The Fermi level lies in the minority $t_{2g}$ impurity band located in the ZnO band gap and then the magnetic coupling is short-ranged, and although ferromagnetic coupling is favoured for adjacent Cu impurities sharing an O neighbour, the corresponding Curie temperature is estimated to lie below RT.

4. Surfaces
Surfaces provide a suitable playground to manipulate and control magnetism in DMO. The high level of sophistication and development of surface science techniques allows the manipulation of structures at the atomic level much beyond the limits that can be controlled for bulk samples. Moreover, as we will show here, the intrinsic characteristics brought by surfaces (i.e., breakdown of symmetry, unsaturated bonds, etc.) offer an unique scenario where stable oxide magnetic states may develop, can be more easily controlled and, most importantly, become extended allowing the development of long-range magnetic order.

Here we investigate the polar ZnO (0001) surface. The [0001] is a preferential growth axis for ZnO, thus [0001] crystallographic terminations constitute the most investigated ZnO surfaces in spite of their polar character [43, 44]. A sketch of the possible terminations is provided in figure 4. Zn and O planes alternate along the [0001] direction and, due to the lack of inversion symmetry of the wurtzite structure along the c-axis, the polar (000T) and (0001) ZnO surfaces are inequivalent. Two different terminations can be obtained, either Zn or O ended, hereafter
The four different possible surface terminations of wurtzite ZnO along the [0001] crystal axis.

labelled respectively as Zn-ZnO and O-ZnO. In principle, the most stable ones are those involving the minimum number of unsaturated bonds, therefore Zn-ZnO and O-ZnO are identified to correspond to the (0001) and (000\(\bar{1}\)) surfaces, respectively. The O-ZnO (000\(\bar{1}\)) surface is found to be the most stable from thermodynamic arguments, and also constitutes the most frequently observed termination of thin films and nanoparticles. Even though its polar character and high reactivity it usually does not show any reconstruction, and in general is well understood [44]. On the contrary, there is no consensus about the Zn-ZnO(0001) surface. Several studies evidence that its structure and chemical composition are highly dependent on growth mode, preparation conditions and environment [45, 46]. Diverse reconstructions and chemical compositions have been reported: it can show triangular islands and pits whose step edges are Oxygen terminated [47], highly ordered (10\(\bar{1}\)0) nanofacet step arrays [48], or a (1 \(\times\) 3) reconstruction which has been interpreted as arising from the removal of one third of the surface Zn atoms [49]. Also, partial Hydrogen adsorption, incomplete and even O-terminated surfaces have been observed [50]. In the following, we will concentrate in the (0001) surface.

4.1. H on Zn-ZnO(0001)

The interaction of H atoms with the polar Zn-ZnO(0001) surface is expected to be the weakest among the ZnO surfaces, since the binding energy of ZnH pairs should be considerably weaker than that of OH bonds. He-atom scattering measurements have shown that Hydrogen forms an ordered (1 \(\times\) 1) overlayer on the surface at low Hydrogen coverages, and that larger exposures lead to a loss of lateral order and the random distribution of H adatoms [51].

The left panel of figure 5 shows the DOS of this surface, obtained after LSDA calculations. The introduction of correlation effects beyond the LSDA description provides a wider band gap, but does not alter the relevant electronic features described here [37]. The bare surface is metallic, due to the filling of surface states near the conduction band (CB) derived from the Zn unsaturated dangling bonds [45], and shows a significant contraction of about 60% of the
Figure 5. Spin-polarized and layer-resolved DOS corresponding to the two outermost surface layers of the Zn-ZnO(0001) surface either (left) bare or (right) covered by 1 H monolayer. The layers are ordered from top to bottom so that the DOS at the top corresponds to the surface Zn atoms. The H contribution on the right is represented by the filled curve superimposed to the surface layer DOS, and the scale has been enhanced 5 times for clarity. Energies are referred to the Fermi level.

As H is deposited, it occupies ontop positions forming strong H-Zn bonds, which create a shallow band at the VB edge. For intermediate coverages, the remaining (not bonded to H) Zn atoms strengthen then their interaction with the O layer underneath, a large corrugation appears in the Zn layer and up to half of a H monolayer coverage, the system becomes an insulator. When the H coverage exceeds half of a monolayer, the induced H band becomes spin splited and robust ferromagnetism develops, with a difference of 46 meV between the ferro- and antiferro-magnetic configurations. In this situation, the H-Zn interaction promotes the formation of a extended magnetic band involving H, Zn and O states, as evidenced by the DOS corresponding to complete H coverage shown in the right panel of figure 5. The magnetic moment mostly resides in the H states, with a value of 0.29 $\mu_B$. The outermost Zn and O atoms develop a weak polarization of 0.09 $\mu_B$, reflecting the subsurface extension of the spin-splitted band and the involvement of H, Zn and O hybridized states.

The shift of the Fermi level from the CB at the clean surface to the energy gap at half monolayer of hydrogen coverage, and then to the VB edge upon the completion of a H monolayer can be viewed as a multipe metal-insulator transition, which is accompanied by a magnetic transition. The thermodynamic stability of H adsorption makes possible to tune reversibly this transition, controlling the H load at the Zn-ZnO(0001) surface.

4.2. Spontaneous magnetism at the O-ZnO(0001) surface
As mentioned above, the most usual and stable O-ended surface of ZnO is the (0001), with one unsaturated bond per surface Oxygen atom. However, there are several reports revealing the
presence of Oxygen atoms in the ZnO(0001) surface and the subsequent possibility to stabilize the O-ZnO(0001) termination in extended local areas. The presence of Oxygen is linked either to rough surfaces with Zn vacancies or incomplete O terminations [50], or even to smooth surfaces such as the (1 × 3) [48] or the triangular islands reconstruction [47], obtained under specific growth conditions. In addition, it has been shown both experimentally and theoretically that the stability of the O-ZnO(0001) termination is largely enhanced by the partial introduction of subsurface Co impurities [30, 50].

Figure 6. Same as figure 5 for the O-ended ZnO(0001) surface. For comparison, the layer-resolved bulk contribution of O (above) and Zn (below) is shown in the left panel.

Figure 6 shows the DOS at the outermost layers of the O-ZnO(0001) surface, as obtained from calculations based on LDA+U. The reduced O coordination causes a considerable decrease of the Mulliken charge of the surface O atoms, so that the Fermi level crosses the $p$ states of the surface O atoms, which become spin splitted leading to a large magnetic moment of 1.5 $\mu_B$. We would like to point out that analogous results were obtained even within the LDA approximation [30]. Since holes are in the VB, underestimation of the band gap does not affect their energy localization. The resulting surface is half-metallic, and FM order is favoured over antiferromagnetism by 160 meV. The large value of the magnetic energy proves that the exchange interactions are strong. In fact, a mean-field estimate of the critical temperature from the total energy difference between ferro- and antiferro-magnetic orders provides a value well above room temperature. Preliminary results obtained by Monte-Carlo simulations using self-interaction corrections confirm the high value of the Curie temperature [52].

The O magnetic moment in this surface is much larger than that induced in ZnO by hybridization with magnetic impurities. In fact, when subsurface Co impurities are introduced, two types of surface O atoms coexist: those bonded to Co showing a weak induced polarization, and the unbonded ones where the magnetic properties of the undoped surface pervive. Furthermore, the surface still shows robust ferromagnetic order, so that the combination of the intrinsic $p$ surface magnetism and that induced by Co leads to a surface with improved stability showing ferromagnetism with high magnetization.

The origin of the O magnetic moments arising from the drastic reduction of coordination actually involves the introduction of a large number of $p$ holes in the VB of the oxide. In this sense, it is similar to the cation vacancy induced moments found in bulk samples, but the
surface offers the unique possibility to increase the number of holes without distorting the oxide lattice, and furthermore, to naturally extend the magnetic states in order to achieve a uniform ferromagnetic 2D sheet. Some peculiarities of this kind of surface magnetism are that it requires a critical number of $2p$ holes, and that it is associated to a highly anisotropic distribution of the magnetic charge [30]. For the (0001) O-surface of ZnO, holes mainly reside in the $p_{xy}$ degenerated orbitals, since the crystal field determines where holes are localised.

This $p$ magnetism is a general property of oxide surfaces, as we have proved in a previous systematic study of the surfaces of different highly ionic oxides [22]. Moreover, magnetic states associated to unsaturated $p$ bonds have also been reported in other low dimensional systems as graphite and quasi-1D organic materials.

5. Conclusions
Spontaneous magnetization is predicted at the polar surfaces of ZnO, rooted in the intrinsic characteristics brought by the surface, namely symmetry breaking, unsaturated bonds or uncompensated charges. The physical mechanism underlying the spontaneous magnetization relies on the formation of holes at the top of the Oxygen derived $p$-like valence band of the oxide. In addition, surfaces states, although confined to the topmost layers, are extended in two-dimensions and thus the subtle interplay between localization and extended states required for the development of long-range magnetic order can be reached at the surface. As a consequence, high transition temperatures close to RT can be reached, with ferromagnetism associated to the topmost layers in the vicinity of the surface. The mechanism promoting the spontaneous magnetization of the surface is universal in ionic oxides, although the onset of magnetism requires a critical number of $p$-holes only achieved by specific surfaces or under particular environmental conditions.

In summary, we have explored the possibility that frontiers, and in particular surfaces, of ionic oxides may develop high temperature ferromagnetism. We propose that $p$ surface magnetism can be responsible of the magnetic signals observed in a large variety of non-magnetic and dilute magnetic oxides.

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