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Magnetic Behavior in Zinc Oxide Zigzag Nanoribbons

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ABSTRACT

We use first principles calculations to investigate the magnetic properties of zinc oxide nanoribbons with zigzag-terminated edges. The polarized spin density of states is calculated as a function of the nanoribbons width and thickness. All nanoribbons formed by a single layer exhibit a magnetic behavior independently of the width. By analyzing the charge density and spin density, we determine that the oxygen-dominated edge exhibits unpaired spins. When the thickness of the ribbons is increased, a magnetic moment is observed only for specific thicknesses.

Metal oxide nanostructures have been recently investigated from the experimental and theoretical standpoint due to their potential applications in the fabrication of novel electronic devices. In this context, one of the most versatile systems is zinc oxide (ZnO). In particular, recent experimental results on ZnO nanoparticles have revealed ferromagnetism in the absence of magnetic impurities.[1,2] This finding is remarkable due to possible technological applications regarding both information storage and processing devices. In this letter, we report ferromagnetism in pure ZnO nanoribbons with zigzag edges. To investigate the magnetic and electronic properties of ZnO nanoribbons, we use density functional theory (DFT) under spin local density approximation. We show results for different widths and thicknesses (number of layers) of ZnO nanoribbons obtained from a planar hexagonal honeycomb structure. For all single-layered zigzag nanoribbons, a magnetic moment was obtained. We demonstrate by analyzing the spin-resolved electronic charge density that the magnetism emerges from unpaired spins localized on the oxygen-terminated edges.

Intense research has been carried out to understand and characterize the properties of ZnO—metal-based dilute magnetic semiconductors.[3,4] However, the nature and origin of the observed magnetic behavior of these compounds is still unclear.[5] Recently, García et al. have found a magnetic behavior of pure ZnO nanoparticles that were organically passivated.[1] In addition, several metal oxide nanoparticles (TiO_2, ZnO, In_2O_3, SnO_2, and CeO_2) without magnetic impurities have also been experimentally studied by Sundaresan et al., revealing room-temperature ferromagnetism.[2]

One-dimensional nanostructures have been intensively investigated over the last years because of their unique physical properties due to quantum confinement and their potential applications in the construction of electronic, optical, electrochemical, and electromechanical devices.[6,7] Specifically, carbon nanoribbons have been found to possess unusual magnetic properties.[8–13] In this letter, we studied using DFT in the framework of local spin density approximation (LSDA), the electronic structure of ZnO nanoribbons grown perpendicular to the [0001] direction and exhibiting flat ±(0001) surfaces. We mainly focused on zigzag nanoribbons and investigated their magnetic properties.

The calculations were performed using DFT in the basis of linear combination of atomic orbitals (LCAO) using the SIESTA code.[14] We used a double-ζ basis set with additional orbitals of polarization. The pseudopotentials (pps) were constructed from 12 and 6 valence electrons for the Zn and O ions, respectively, (Zn, $4s^2 3d^{10}$; O, $2s^2 2p^4$). The Troullier−Martins scheme was used. The basis and the pps were tested on the bulk ZnO wurtzite structure showing a binding energy per formula of −10.7534 eV/ZnO and an energy gap (E_g) of 0.76 eV. All the structures were relaxed using a conjugate gradient. As expected for the bulk, the calculations did not show any magnetic properties. We used a local exchange-correlation functional (Ceperley-Alder, CA) and the LSDA. However, we verified that the approximation does not give an artificial metallicity and spin polarization (as in ref 11). For this purpose, we tested one of the systems using a nonlocal generalized gradient approximation (Becke−Lee−Yang−Parr (BLYP)), and a hybrid functional (50% CA, 50% BLYP), showing the same qualitative results.

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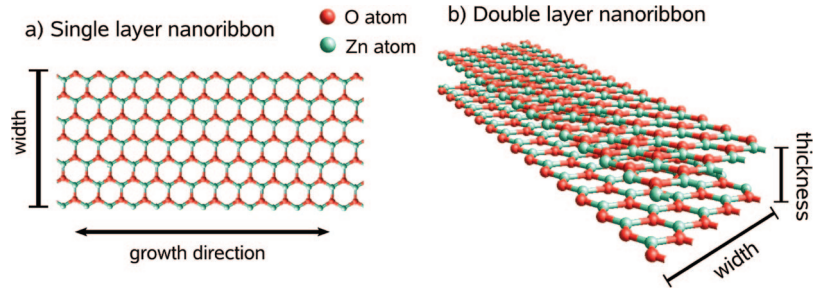

Figure 1. Molecular models showing the geometry of ZnO zigzag nanoribbons. (a) A single layer ribbon is shown with the growth direction, indicating the width. (b) A two-layered ZnO nanoribbon constructed by stacking individual ZnO sheets before geometric relaxation is presented. All the structures considered in this study were relaxed before studying their electronic properties. In the case of the monolayer, the structure remains almost identical, whereas the systems with more layers tend to form bonds between the layers on the edges.

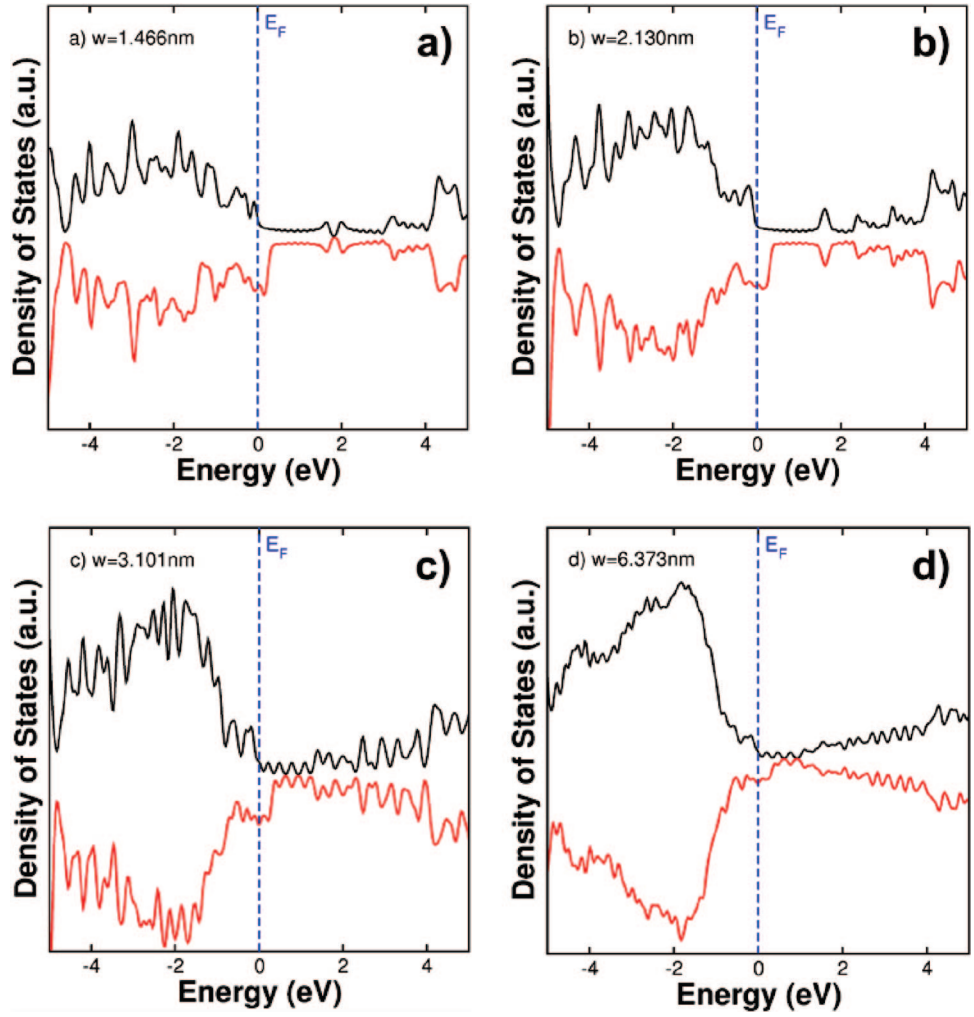

Figure 2. Plots of the electronic density of states (DOS) for the majority and minority spin of ZnO zigzag nanoribbons. Different width values for ribbons are shown in (a−d). All systems exhibit a magnetic moment, and the unpaired spins are localized on the oxygen-dominated edge as shown in Figure 4 (see below). The Fermi level has been set to zero for comparison.

The ZnO nanoribbons studied here were constructed by cutting a planar monolayer along two parallel zigzag lines as shown in Figure 1a. Armchair ribbons were not studied because their electronic structure always corresponds to semiconductors.[15] For a few number of ZnO layers, it has been recently observed that after relaxation the structure prefers a planar configuration in which both the cation (Zn) and the anion (O) share the same plane.[16] Therefore, all the structures were constructed from planar layers and subsequently minimized energetically. The ribbons were periodic in the x direction with the width defined in the y direction. ZnO nanoribbons with different thickness (z direction) were constructed from stacked planar structures (Figure 1b) and the whole structure was further minimized. After relaxation, we observed that the edges bind, whereas the inner part of the ribbon remained separated (unbound).

Figure 2 shows the total density of states for ZnO zigzag nanoribbons with different width (w). In all cases, we

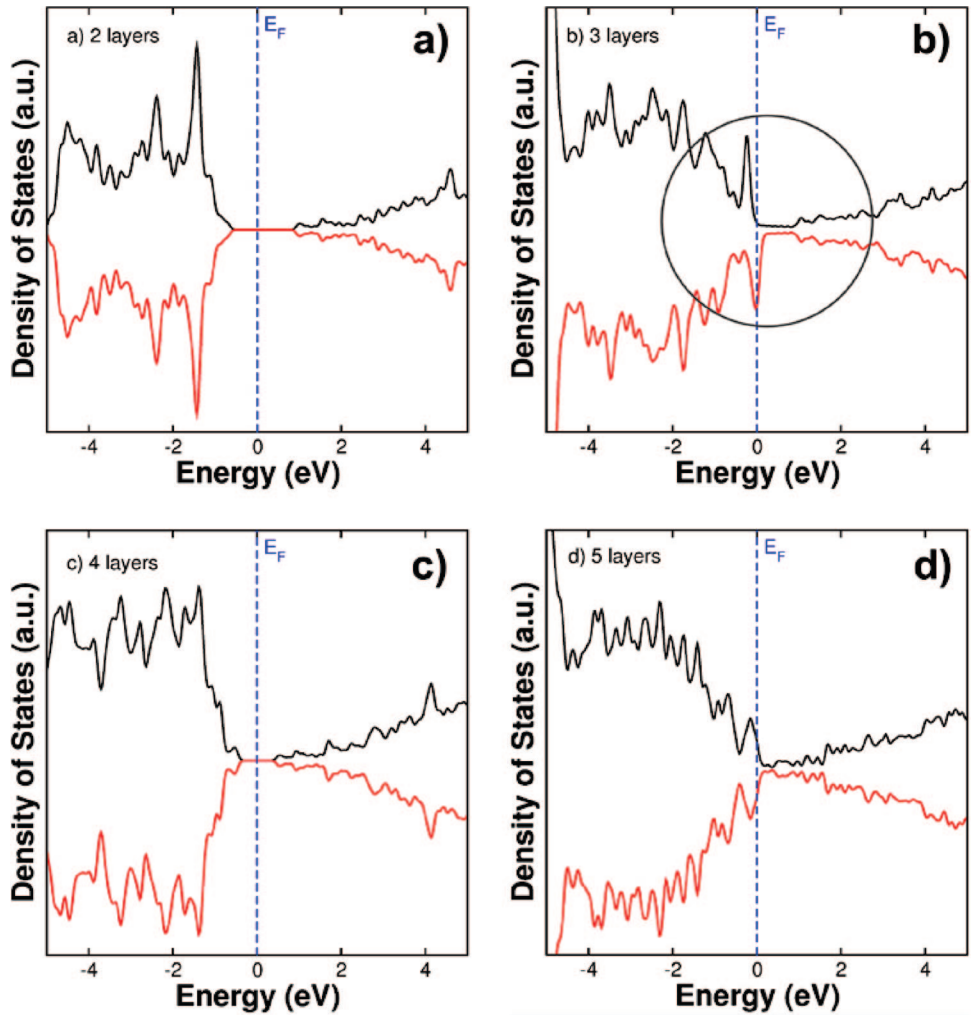

Figure 3. Plots of the electronic DOS for the majority and minority spin of ZnO zigzag nanoribbons. Different thickness values or number of layers are shown in (a−d). The width of the ribbons is fixed to $w = 1.466$ nm. Note that the system with three layers exhibits a shift in the majority and minority spin density of states, and consequently a magnetic moment is obtained. The Fermi level has been set to zero for comparison.

observed states at the Fermi level and shifts in the spin density of states. The resultant magnetic moment corresponded to 0.55, 0.59, 0.62, and 0.65 μ_B for ribbons exhibiting widths (w) of 1.466, 2.130, 3.101, and 6.373 nm, respectively. We are aware that the physics of confined systems can change dramatically, and thus the effect of using large core pseudopotentials could be important. Therefore, we have performed a calculation for the 1.466 nm wide nanoribbon, using a zinc pseudopotential with semicore electrons ($3p^6 4s^2 3d^{10}$). The calculation resulted in a magnetic moment of 0.60 μ_B, while the original calculation using a zinc pseudopotential with 12 valence electrons ($4s^2 3d^{10}$) resulted in a magnetic moment of 0.55 μ_B. Therefore, it is valid to use pseudopotentials with 4s and 3d valence electrons. We have also compared the binding energy between the LDA and LSDA calculations; the energy differences were of the order of 10^{-2} eV in which the energies calculated with the LSDA appeared to be more stable.

The effect of the thickness on the electronic and magnetic properties of the ZnO nanoribbons was also addressed in this study. Planar layers were placed on top of each other following an AB stacking and were further relaxed. When a second layer is stacked on top of the single layer, the system becomes semiconductor, and no spin shift is observed (Figure 3a). However, when a third layer is stacked on top the states at the Fermi level reappear with the presence of significant shifts between the spin densities of states (up and down; Figure 3b). Nevertheless, when a fourth layer is stacked again the states at the Fermi level vanish, and the structure becomes a semiconductor (Figure 3c). As the number of layers increases to five, the states at the Fermi level are again observed, however, without shifts on the spin density of states (Figure 3d).

The origin of this magnetic behavior was further studied using the charge density and spin density distribution (plotted in Figure 4a), which show the total charge distribution (up + down) for a single layer ribbon with $w = 2.130$ nm with the same orientation as that depicted in Figure 1a. We note that the major contribution to the states on the Fermi level is due to edge states and specifically to the oxygen-dominated edge. On this border, the charge distribution and thus the bonds are significantly different to the charge distribution in the rest of the ribbon. The Zn—O bond on the edge is

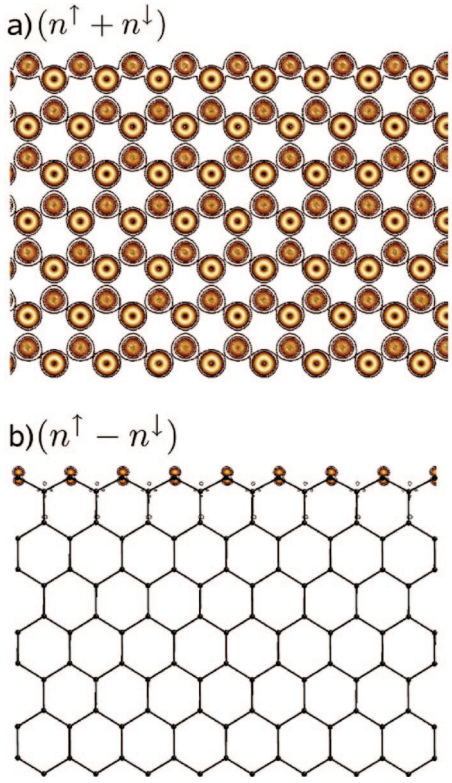

Figure 4. (a) Spatial electronic charge distribution (up + down) and (b) spatial spin distribution (up − down). The plots correspond to a specific ribbon ($w = 2.130$ nm) with the same orientation as the ribbon shown in Figure 1a. Note that the unpaired spins arise from the atoms localized on the ribbon edges where oxygen atoms are located. Similar behavior was observed for ribbons with different width (not shown here).

stronger and exhibits an excess of charge. Figure 4b shows the spin density distribution (up − down) for the same single layered ribbon. In this case, it is clear that the shift of the LSDOS is due to the oxygen edge states.

Our results clearly demonstrate that ZnO is able to possess magnetic and possibly ferromagnetic behavior without the introduction of metal impurities. As Garcia et al. have concluded from experimental results, these properties arise only from changes in the electronic structure. Therefore, the results shown here open up the possibility of having ferromagnetism at room temperature in finite-layered ZnO systems.

We have investigated the electronic and magnetic properties of ZnO nanoribbons grown perpendicular to the [0001] direction with zigzag edges. The structural relaxations effects were considered. Our results demonstrated that the ZnO nanoribbons with a single layer could exhibit unpaired spins at the edges dominated by oxygen atoms. The emerged magnetic moment increased with the width of the ribbons. We have observed that the magnetic moment appears also when the ribbon is composed of three layers; however, for two, four, and five layers it vanishes even when in the latter case there are states in the Fermi level. We believe that our theoretical results will motivate further experimental work related to the synthesis and characterization of very thin ferromagnetic ZnO nanoribbons.

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