Surface magnetization in non-doped ZnO nanostructures

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Abstract

We have investigated the magnetic properties of non-doped ZnO nanostructures by using ab initio total energy calculations. Contrary to many proposals that ferromagnetism in non-doped semiconductors should be induced by intrinsic point defects, we show that ferromagnetism in nanostructured materials should be mediated by extended defects such as surfaces and grain boundaries. This kind of defects create delocalized, spin polarized states that should be able to warrant long-range magnetic interactions.

Keywords: nanocrystals, ZnO, surface
The observation of high-temperature ferromagnetism in transition metal doped ZnO has triggered extensive studies on this kind of material. However, the fundamental nature of the magnetic interactions between transition metal impurities, and the origin of the magnetism in ZnO is still under debate. [1, 2, 3] Recent experimental results reported room-temperature ferromagnetism even without the inclusion of magnetic impurities, the sometimes called *phantom ferromagnetism* [4], specially in wide bandgap oxides. This kind of phenomena was first reported by the group of Coey for HfO$_2$ [5] and followed by others [6, 7]. Theoretical calculations proposed that ferromagnetism in this material was due to the existence of intrinsic point defects [8]. This proposal has been put in check by recent calculations, since the population of these defects should not be large enough to warrant a magnetic coupling between impurities [9].

Interestingly, ferromagnetism in non-doped materials is mostly observed in nanostructured samples composed of nanoparticles and thin films [7, 10, 11, 12]. There are several tentatives to try to explain these results, but they are very controversial. Some works propose the ferromagnetic response is due to oxygen vacancies [11, 13], while others say that it is due to zinc vacancies [14, 15]. There are also results proposing that *intrinsic defects* [16] or *interstitial zinc at the surface* [17] are the responsible for the observed magnetic phases. As pointed out in Ref. [9], the problem with these approaches is that the population of intrinsic defects is usually not large enough to reach the percolation limit, and lead to a macroscopic magnetization, since the exchange interaction between these impurities is expected to be short-ranged. Neither *double-exchange* nor *superexchange* [18] are able to explain the observed Curie temperatures in these materials.

It is clear, from the wide variety of experimental results, that magnetism in non-doped samples should be related to some kind of defect in the material. As point defects are very unlikely to be responsible for this magnetism, we turn our attention to extended defects. Gamelin and co-workers [19, 20] have shown that it is possible to tune the magnetic properties of transition-metal doped TiO$_2$ by carefully controlling the morphology of the grain boundaries in their samples. Garcia *et al.* also showed that non-doped ZnO nanoparticles could have a small ferromagnetic response, depending on the organic capping of their nanocrystals [10]. Another recent work published by the Coey group [4] suggests a charge-transfer mechanism to explain ferromagnetism in oxide nanoparticles. In this model, electrons are transfered from the core of the nanocrystal to its surface, leading to a magnetiza-
tion. In view of the large variety of controversial results on this subject, we have investigated, through *ab initio* calculations, the magnetic properties of surfaces in ZnO nanocrystals. We have used ZnO nanocrystals with different structures, geometries and shapes, and observed a magnetization at the surface of the nanocrystals that should be responsible for ferromagnetism in these materials.

Nanocrystals used in this study consist of an approximately spherical part cut from the bulk crystal. We have analyzed nanocrystals in the wurtzite (WZ) and zinc blende (ZB) structures. In order to generate the nanocrystals, we have to define a center, that can be located either on an atom (AC) or a bond (BC). Bond-centered nanocrystals are stoichiometric, while atom-centered nanocrystals not. We then define a radius, and remove all atoms beyond the sphere defined by the center and the radius. This kind of nanocrystals are usually passivated with fictitious hydrogen atoms, in order to remove dangling bonds from its surfaces. In this work, we will not use this saturation, since our objective is to study the effect of these surfaces. We have studied different sizes of nanocrystals for each structure (WZ and ZB). The smaller has a diameter of $\sim 0.9\text{nm}$ and the larger one has a diameter of $\sim 1.5\text{nm}$. The surface of each nanocrystal reconstructed in a different way, giving us a broad range of results to model several different defects, including planar surfaces, steps, kinks, ad-islands, ad-atoms, dimers and others. We believe that in our calculations we have taken into account the majority of possible motifs present at any nanocrystal surface.

Our simulations were performed using density-functional theory (DFT), employing the projected augmented wave method (PAW) as implemented in the VASP code. Electronic exchange-correlation was treated using the local density approximation (LDA). We have also tested the generalized gradient approximation (GGA) but we have not observed any changes to our conclusions within this approach. We used a plane wave basis set, and the nanocrystals are separated by its images by a vacuum region of 0.6 nm in all directions. All atoms were allowed to relax until the forces are smaller than 0.025 eV/Å.

When we minimize the forces on all atoms of our bulk-like nanocrystals, we observe that the surface atoms reorganize, through different reconstructions in the surface. Some of these reconstructions are shown in Fig. 1 and 2 and include changes of the distance between the atoms in the surface, changes of the binding angle, and a strong tendency of the surface atoms to form a “graphitic” reconstruction. This “graphitic” structure has been reported in previous studies of ZnO thin films and nanostructures.
FIG. 1: (Color online) Surface reconstruction of nanocrystals with (a) 35, (b) 87 and (c) 147 atoms that present a spontaneous magnetization.

FIG. 2: (Color online) Surface reconstruction of nanocrystal with (a) 39, (b) 38 and (c) 88 atoms and where no spontaneous magnetization was observed.

Although no magnetization is observed on the hydrogen-saturated nanocrystals, some of the non saturated nanocrystals show spontaneous magnetization without magnetic impurities. This magnetization can be originated from a wide variety of different reconstructions and motifs, such as zinc dimers, broken bonds, zinc and oxygen atoms with dangling bonds. Independent of the reconstruction, the magnetization is always strongly localized at the nanocrystal surface. This can be observed in Fig. 3. In Fig. 3a, we show the radial distribution function of the spin charge density, providing a quantitative comparison between the spin charge density at the center and at the surface of the nanocrystal. For this specific nanocrystal, we observe that the magnetization is mainly localized at a radius of 6Å. Fig. 3b shows the radial distribution function of all atoms, confirming that the magnetization is localized in the outer atoms of the nanocrystal (in this case, Oxygen atoms). In the inset, we plot the spin charge density, i.e., the difference between spin-up and spin-down charge densities, for the 87-atom nanocrystal. We can observe that the magnetization is more localized at the surface.

After analyzing all studied nanocrystals, we were not able to point a single kind of defect as responsible for the magnetization. We can not correlate the observation of the
magnetization to a single defect like an O or a Zn atom at the surface, since the magnetization can be observed in both cases. As extended defects might contain several different kinds of point defects, we propose that extended defects such as surfaces or grain boundaries should be the responsible to sustain macroscopic magnetizations in nanostructured samples. As extended defects can cover wide areas or volumes, they can mediate the long range interactions necessary for ferromagnetism to be observed in these samples.

Although we observed many motifs that present magnetization, the surface magnetization was not observed in all of our nanocrystals. Interestingly, some kind of order inside the nanocrystal was necessary for the magnetization to be observed: for nanocrystals whose overall structure was strongly reorganized, almost resembling an amorphous structure, no magnetization was observed. In Fig. 2 we show some nanocrystals in which the spin-polarization is not observed. The change of the structure in the smaller nanocrystals is clear from this figure. In Table I, we show a summary of the calculated magnetization for some nanocrystals.

| Number of atoms | Structure | Total magnetization |
|-----------------|-----------|---------------------|
| 35              | ZB-AC     | 2 $\mu_B$           |
| 87              | ZB-AC     | 4 $\mu_B$           |
| 147             | ZB-AC     | 2 $\mu_B$           |
| 38              | ZB-BC     | 0                   |
| 86              | ZB-BC     | 2 $\mu_B$           |
| 238             | ZB-BC     | 0                   |
| 39              | WZ-AC     | 0                   |
| 92              | WZ-AC     | 2 $\mu_B$           |
| 34              | WZ-BC     | 0                   |
| 88              | WZ-BC     | 0                   |

These results are in agreement with recent experimental results, confirming that ZnO nanostructures can be magnetic without transition metals. Of particular interest is the work of Garcia *et al.* [10] that shows that, depending on the capping molecules, different
FIG. 3: (Color online) Magnetization for the 87-atoms nanocrystal. (a) Difference of $\rho_\uparrow - \rho_\downarrow$, showing that the magnetization is localized at the nanocrystal surface. (b) Radial distribution function, showing that the magnetization for this nanocrystal is mainly due the oxygen atoms of surface.

strengths of magnetization can be observed. In our calculations the magnetic moment per surface atom can vary from $0.01\mu_b$ to $0.04\mu_b$, depending on the nanocrystal size. Larger nanocrystals have smaller magnetizations per surface atom. These results are in reasonable agreement with the experimental results\cite{10} that report a magnetization of the order of $0.001\mu_b$ for larger nanocrystals.

Following the proposal of Coey et al\cite{4} of a charge transfer magnetism, we have also analyzed the charge transfer from the center to the surface of our nanocrystals. Our results indicate that, if present, the charge transfer will be extremely small. In some cases, the charge at the surface atoms is even smaller than the total charge at the central ones, showing that there should not be any charge transfer in neutral nanocrystals. We propose that depending on the surface reconstruction, surface states might be created in the energy gap of the nanocrystal. These surface states may be exchange splitted, leading to a net macroscopic magnetization since these states are delocalized through the whole nanocrystal. The magnetization of these surface states will be responsible for the ferromagnetic response in nanostructured materials.

In conclusion, we have analyzed the magnetization of small non-saturated ZnO nanocryst-
tals by looking for several different surface reconstructions. We propose that point defects are not responsible for this magnetization. We show that, depending on the structure, the whole nanocystal surface might create delocalized levels that are spin-polarized and leading to a macroscopic, long-range magnetization in the samples. Ferromagnetism was not observed in all of our nanocrystals, what is also in agreement with experiment: not all experimental results report ferromagnetism in non-doped samples, even for samples produced with the same procedure. Following in this direction, other extended defects that insert delocalized levels in the gap of the material also might be important to understand the magnetization in non-doped samples. These include dislocations, grain boundaries and interfaces. Our findings also should be important to explain the magnetization in other non-doped materials such as HfO$_2$ and TiO$_2$.

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