Hybrid density-functional theory calculations on surface effects in Co doped ZnO nanowires

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(Dated: August 9, 2018)

In this work we have employed density-functional theory with hybrid functionals to investigate the atomic and electronic structure of bare and hydrogenated Co doped ZnO nanowires. We find that in the absence of passivation on the nanowire surface, the cobalt atoms segregate to the surface. On the other hand, under hydrogen passivation, the incorporation of Co is more favorable at inner sites. This suggests that the incorporation of Co in nanostructures has a dependence on the environment and may be facilitated by external atoms and relaxation of the surface.
I. INTRODUCTION

Zinc oxide (ZnO) has been largely investigated in the past years as it is a low cost, high electron mobility, it is transparent and can be synthesized in several nanostructured shapes \[1\]. Doping in ZnO has been widely used to tailor its electronic, magnetic and optical properties. In particular, cobalt doped ZnO nanostructures have been largely investigated in the past years both experimentally \[2–7\] and theoretically \[8–11\] due to its promising application in optoelectronics and spintronics. In nanostructures, as the surface/volume ratio is large, the influence of surface effects on the incorporation of impurities in nanostructures can play an important role. Effects of surface passivation, morphology of the surface and co-doping can influence the incorporation of dopants, as has been discussed in Ref.\[12\].

In this letter, we investigate Co incorporation in ZnO nanowires in order to determine changes in the magnetic properties and electronic structure upon surface passivation. Our modeling mimics certain experimental conditions where air or hydrogen atmosphere is present. In general, local density functionals lead to wrong description of band gaps. In order to reproduce experimental gap of ZnO and provide a better description of we have performed density functional theory calculations with hybrid functionals. We show that although there is a strong localization of the Co states with no significant change in its magnetic moment. However, there is a site preference depending on the wire surface termination.

II. COMPUTATIONAL DETAILS

We have used density-functional theory (DFT) \[13\] together with the projected augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP) \[14\]. The Heyd-Scuseria-Ernzenhof (HSE06) form of the exchange-correlation potential was used to obtain geometries, formation energies, and magnetic moments. To model Co impurities in ZnO, we built up a 96 atom supercell using our calculated PBE lattice parameters of ZnO, \(a=3.25\AA\) and \(c=5.25\AA\). To ensure convergence of structural, electronic, and magnetic properties, a cutoff of 400 eV was used for the plane-wave expansion of the wave function. Atomic forces were converged up to 0.01 eV/Å. For Brillouin zone integrations, a \((1 \times 1 \times 4)\) Monkhorst-Pack \(k\)-point sampling was used. The HSE results should provide a reliable method to determine the electronic structure. Previous results have demonstrated that although 25% Hartree-Fock can be justified \[15\], to obtain the experimental band gap of ZnO, 36% HF is needed \[15, 16\]. Therefore, we have used this admixture to reproduce the experimental gap of bulk ZnO \[17\]. The predicted energy position of the minority spin Co-t2 states is 3.0-3.6 eV above the ZnO conduction band minimum which is closer to GW calculations \[8, 18, 19\].

III. RESULTS

In Fig. 1 we show the variation of the band gap of ZnO bulk with the amount of Hartree-Fock added to the exchange-correlation functional for both PBE0 and HSE. As reported previously, due to the lack of screening, the PBE0 functional requires a large amount of HF (around 40%) to reach the experimental gap \[15\]. On the other hand the HSE functional can reproduce the experimental gap with 25% admixture.

The geometry of the structures we have investigated is shown in Figs. 3. First we discuss the non-passivated wires. A single Co occupying a substitutional Zn site in the middle of the wire does not produce strong distortion in the ZnO wire lattice (around 0.1 Å). For Co sitting at subsurface/surface sites, Co moves (outwards inwards), as the covalent radius is similar to Zn. The Co-O bond lengths remain very close to the values in pure ZnO, ranging from 1.8-2.1 Å in bare wires and from 2.0-2.2 Å in hydrogenated wires. The formation energy of an isolated defect is calculated setting the energy zero to the minimal energy configuration.

Next we discuss the thermodynamic stability of Co in these small diameter wires. In the case of hydrogen adsorption, the most stable configuration is a fully hydrogenated wire. The incorporation of a Co atom in the wires has a dependence with the site position. For bare wires, the preferred position is the surface position. This effect is called self-healing because nanostructures have a small volume compared to their surface, leading to the migration to the surface \[6, 12, 20\]. It has been further suggested size is not the only effect responsible for impurity incorporation. Erwin et al. \[12\] suggested that impurity incorporation depends on three main factors, surface morphology, nanostructure shape, and surfactants. Indeed, in our previous work we have shown that adsorption of hydrogen and water on the surface of ZnO wires is an exothermic reaction \[21, 22\]. Later on we have investigated the incorporation of N in ZnO nanowires and showed the effect of hydrogen passivation \[20\] under N incorporation which has been confirmed experimentally that N should sit close to surface sites and at oxygen positions \[24\]. We show here that a different behavior is found for Co in ZnO ultrathin wires. By passivating the nanowire surfaces with hydrogen, Co have a lower formation energy than when it is incorporated in the bulk (for both PBE and HSE functionals), as shown in Table 1. Specially for these ultrathin wires, this effect is dramatic for passivation with hydrogen, since the energy difference
FIG. 1. HSE and PBE0 energy gaps for ZnO as a function of the Hartree-Fock exchange admixture.

FIG. 2. Total and projected density-of-states for Co doped ZnO bulk with HSE functional. a) with 36% admixture and b) with 25% admixture. The Fermi level is represented as a dashed line).

between bulk and surface position is 1.0 eV with HSE. Main factors for this behavior is that Co has a similar size as ZnO.

FIG. 3. Atomic configurations for CoZn in bare ZnO nanowires. O, Zn and Co atoms are shown in red, gray and blue color, respectively.
TABLE I. Total magnetic moments $\mu_{\text{tot}}$ (in $\mu_B$) and relative formation energies $E_f$ (in eV) of neutral Co impurities in ZnO calculated with PBE and HSE functionals. In brackets the magnetic moment projected on the Co atoms is shown.

| config.  | $\mu_{\text{tot}}$ PBE | $\mu_{\text{tot}}$ HSE | $E_f$ PBE | $E_f$ HSE |
|---------|------------------------|-------------------------|----------|----------|
| bare inner | 3.10(2.50)            | 3.00(2.69)              | 0.25     | 0.24     |
| bare sub  | 3.15(2.53)            | 3.00 (2.70)             | 0.20     | 0.78     |
| bare surf | 3.14(2.50)            | 3.00 (2.70)             | 0.00     | 0.00     |
| hydro inner | 3.00(2.45)          | 3.00 (2.70)             | 0.00     | 0.00     |
| hydro sub  | 3.00(2.46)            | 3.00 (2.70)             | 0.01     | 0.21     |
| hydro surf | 3.00(2.34)            | 3.00 (2.65)             | 0.22     | 1.00     |

FIG. 4. Density of states of Co doped ZnO nanowires. (a) - (c) bare wires and (d)-(f) hydrogenated wires with HSE and 0.36 HF exchange. The vertical dashed line represents the Fermi level which is set to the highest occupied state.

Doping of ZnO bulk with Co splits the Co-3$d$ states into $e$ and $t_2$ states. Co assumes a high-spin configuration with local magnetic moment of 2.7 $\mu_B$ with a small hybridization with neighboring O atoms. The majority spin states $e$ are close to the valence band maximum of ZnO and therefore hybridize with the O-2$p$ states. The $e$ minority spin states lie right above the ZnO valence band maximum. The amount of Hartree-Fock exchange changes slightly the position of the $e$ minority spin states. Including 0.25 of HF exchange in the DFT exchange term places these states 0.5 eV above the top of the valence band. The distance between the $e$ minority spin states $e$ and the $t_2$ states is shown in Fig. 2 (a). We obtain a value of 5.3 eV, in agreement with Refs. [8, 10]. By increasing the amount of HF exchange to 0.36 the $e$ minority states are pushed towards the valence band top. The $e$-$t_2$ energy difference increases to 7 eV as shown in Fig. 2 (b).

In Fig. 4 the DOS for the doped wires is shown. Figs. 4 (a)-(c) shows the results for bare wire. When the Co incorporation is at inner site (Fig. 4 (a)) the location of the $e$ minority states is similar to the one in ZnO bulk. As the Co moves towards the surface, relaxation and symmetry breaking effects yield to Co $e$ states located slightly at higher energies inside the band gap, but still similar to the DOS in Co doped ZnO bulk, as it can be seen in Fig. 4 (b) and (c). In bare wires, the distance between the $e$ and $t_2$ states for different sites is 6.7 eV (inner), 6.5 eV (subsurface) and 6.6 eV (surface).

The DOS in hydrogenated wires shows some noticeable differences. Now the $e$ minority states lie inside the valence band and are shifted to lower energies as the Co atom is positioned towards the surface. This means that hybridization of cobalt with ZnO may be tuned by hydrogenation or incorporation of other adsorbing species in the sample during the doping process. One of the reasons is that strain at surface sites may change due to adsorption, facilitating Co incorporation. We have previously shown that strain indeed can induce diffusion of vacancies towards the surface [25, 20]. Obviously this is a kinetic process and barriers for Co diffusion under this conditions need to be investigated to confirm this idea. However, the strain does not affect considerably the distance between the $e$ and $t_2$ states minority spin states, which are 7.0 eV (inner), 6.3 eV (subsurface) and 6.3 eV (surface).
IV. CONCLUSIONS

We have investigated ZnO nanowires doped with Co using hybrid functionals. We show that the impurity prefers to sit at bulk positions when the surface is passivated. On the other hand, bare wires suffer from self-purification problems leading to segregation of the dopant of Co towards surface sites. This indicates that the impurity can be more easily incorporated depending on the atmosphere it is prepared and may be facilitated by external atoms and relaxation of the surface. A route to investigate the diffusion of such impurities in nanostructures upon different environment conditions would provide further insights on these complex systems.

V. ACKNOWLEDGEMENTS

We are thankful for the financial support from the Brazilian agencies CNPq and FAPEG. A.L.R and T.F. would like to thank also German Science Foundation (DFG) under the program FOR1616.

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