

Ferromagnetic coupling in a Co-doped graphenelike ZnO sheet

T. M. Schmidt,¹ R. H. Miwa,¹ and A. Fazzio²¹*Instituto de Física, Universidade Federal de Uberlândia, Caixa Postal 593, CEP 38400-902, Uberlândia, Minas Gerais, Brazil*²*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP, Brazil*

(Received 3 March 2010; revised manuscript received 25 March 2010; published 7 May 2010)

Using first-principles calculations it is demonstrated that Co doped graphenelike ZnO sheet presents ferromagnetic coupling. The Co atoms are energetically barrierless absorbed in the Zn sites, suffering a Jahn-Teller distortion. The results reveal that the origin of the ferromagnetic coupling, different from the bulk 3D ZnO stacking, is mainly guided by a direct exchange interaction without any additional defect. This ferromagnetic coupling is due to the system topology, namely, it is a direct consequence of the two-dimensional character of the ZnO monolayer within graphenelike structure. Increasing the number of ZnO layers the ferromagnetic coupling vanishes.

DOI: [10.1103/PhysRevB.81.195413](https://doi.org/10.1103/PhysRevB.81.195413)

PACS number(s): 73.20.-r, 72.80.Vp

I. INTRODUCTION

Nanoscale semiconductor materials doped with transition-metal ions can present magnetic properties which are potential for future magnetic device applications, as well to understand the fundamental physics of magnetism in semiconductors. Particularly, two-dimensional (2D) systems shows peculiar properties which are different from their counterparts bulk phases. ZnO bulk pellets and thin films doped with Mn exhibit ferromagnetism at room temperature.¹ The origin of the ferromagnetism is still an intriguing question. For Co doped bulk ZnO or thin films, the magnetism has been attributed to a carrier density exchange in bulk and the formation of Co clusters in thin films.²⁻⁴ Experiments⁵ and calculations⁶ agree that the presence of defects is crucial to explain the stabilization of high-temperature magnetism in bulk ZnO. ZnO in nanoscale shape may have even more interesting properties, as has been shown recently, it exhibits an intrinsic ferromagnetism when doped with Co atoms,⁷ and ZnO nanoribbons without doping also exhibits magnetic properties at edges.⁸ More recently it has been predicted that Co dimers adsorbed on Carbon rings can present a magnetic ground state with large magnetic anisotropy.⁹

The formation of planar sheets of ZnO have been predicted to occur when the number of ZnO layers are reduced,¹⁰ and one monolayer of ZnO has been shown to be a stable system.¹¹ It has been observed experimentally that planar ZnO sheets are stable and the transition to wurtzite structure occurs in the 3–4 monolayers for ZnO on Ag surface.¹²

In this paper we show that a low dimensional system composed by a flat monolayer of ZnO atoms with a graphenelike structure when doped with Co atoms presents ferromagnetic (FM) coupling. The results show that the magnetism is ruled by the topology, namely, the substitutional Co atoms are embedded in a 2D ZnO host (ZnO sheet). The mechanism of the magnetism in these sheets, different from the superexchange interaction in bulk 3D ZnO stacking, is shown to be mostly through a direct exchange interaction.

II. METHOD

The calculations were performed based in the density-functional theory (DFT), as implemented within the SIESTA

code.¹³ The electron-ion interactions were described by using norm-conserving Troullier-Martins pseudopotentials,¹⁴ and the electron-electron interaction was treated within a spin-polarized local-density approximation (LDA). The Kohn-Sham orbitals were described by linear combinations of numerical pseudoatomic orbitals using a split-valence double-zeta basis set including polarization functions. The ZnO sheet was described within the supercell approach, with 72 atoms per cell.

III. RESULTS AND DISCUSSION

The crystal structure of the ZnO sheet present a BN hexagonal form, where the Zn and O atoms are in the same plane. The electronic structure of the ZnO monolayer presents a wide band gap, which is 1.3 eV larger than the wurtzite phase of the bulk ZnO. We find that the formation of substitutional Co atoms occupying Zn sites (Co_{Zn}) of ZnO monolayers is a barrierless process. Indeed, similar barrierless process has been verified for other transition metals (such as Fe_{Zn} and Mn_{Zn}) in ZnO sheet.¹⁵ A whole path between the Co atom and the ZnO sheet have been computed without any external force. In Fig. 1 we show just some steps for the Co atom when it approximates onto the ZnO sheet, entering in a Zn site. The Co atom enters in a Zn site pushing out of the sheet the Zn atom without energy barrier. Actually there is an energy gain of -2.55 eV. After the Co atom enter in a Zn position, this Zn atom suffers a bending with respect to its original position, perpendicular to the plane, staying threefold coordinated. By assuming a reservoir of Zn metal we compute the formation energy to remove this Zn atom, and we obtain that this process is exothermic by 1.5 eV. There is a similar barrierless process for two Co_{Zn} , giving rise to two nearest neighbor (NN) Co_{Zn} with FM coupling. In this paper we will focus on this promisor system composed by substitutional Co_{Zn} atoms embedded in ZnO sheets, $\text{Co}_{\text{Zn}}/\text{ZnO}$.

The substituted Co dopant at Zn site of the sheet introduces two d levels of the majority spin up inside the valence band and the other three d levels inside the band gap (around 0.3 eV above the top of the valence band). The occupied $3d$ minority spin down are located inside the band gap. And the

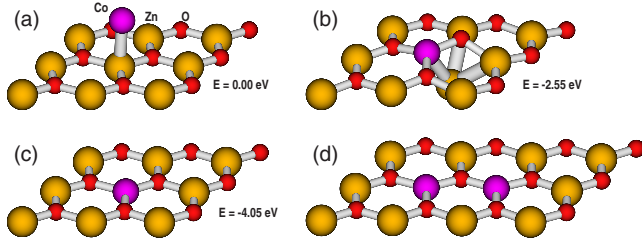


FIG. 1. (Color online) [(a)–(c)] Atomic structure for a sequence of a Co atom barrierlessly absorbed in ZnO sheet. The energy gain in each step is indicated at right. (d) Optimized geometry for two Co atoms substituted at a Zn site with FM coupling.

unoccupied minority states are near the bottom of the conduction band. This picture is different from the Co doped bulk ZnO, where standard DFT does not describe correctly the system,^{16,17} because the Co 3d states are located inside the conduction band. Here, due to the confinement effects, the band gap of the ZnO sheet is enlarged with respect to the bulk ZnO band gap, and thus the occupied Co 3d states are located correctly inside the band gap. Although we still with a reduced band gap, the inclusion of a more accurate method like LDA+U or self-interaction correction (SIC) will not alter our analysis. The absolute position of the Co 3d levels with respect to the Fermi level is expected to change if a more precise method is used, however the magnetic properties will not change by applying LDA+U or SIC in this system.

By permitting only a breathing relaxation, keeping the ZnO sheet symmetry, which it belongs to the D_{3h} point group, the lowering of energy is only by -0.024 eV. In this symmetry the atomic Co 3d level splits in a nondegenerate a' and two bidenerate e'' and e' states. As the degenerated e'' is occupied with just one electron a Jahn-Teller distortion is expected. By permitting a fully relaxation of the sheet we observe a structural distortion with the system belonging to the C_{2v} point group symmetry, with all states nondegenerated, as shown in Fig. 2. The lowering of energy for the Jahn-Teller distortion (-0.137 eV) is much greater than that of the breathing relaxation.

By introducing a second Co atom at the Zn NN of the first Co atom, we observe a strong interaction between the Co atoms. The NN most stable configuration is for a FM coupling with an energy difference from the AFM coupling of 0.30 eV. In this case, Co_{Zn} atoms are threefold coordinated, namely, each one forms three different $\text{Co}_{\text{Zn}}\text{-O}$ bonds with the nearest-neighbor oxygen atoms ($\text{Co}_{\text{Zn}}\text{-O}$ bond lengths of 1.81, 1.83, and 1.86 Å). The optimized Co-Co distance is 3.24 and 3.10 Å for the FM and AFM coupling, respectively. For the FM (AFM) coupling the Co-Co bond distance is larger (smaller) when compared with the one of the AFM (FM) system, which is in accordance with the Pauli exclusion principle. If the second Co atom is at a second-neighbor Zn site the system is still FM coupled (favored by just 0.05 eV), but this configuration is 0.46 eV less stable as compared to that with the two Co atoms at the first neighbors Zn sites. The dopant Co atoms in ZnO sheet prefer to be close to each other with strong FM coupling.

The origin of the FM coupling of Co in ZnO sheet is mainly guided by a direct exchange interaction. One straight

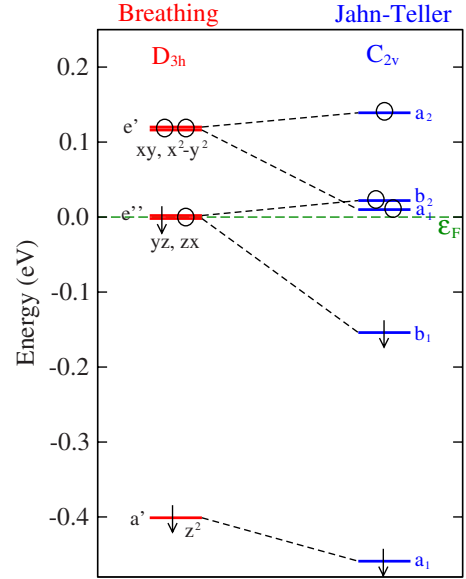


FIG. 2. (Color online) Minority 3d levels of a Co atom substituted at a Zn site in ZnO sheet for a breathing relaxation (red left) and for a Jahn-Teller distortion (blue right). The Fermi level is at zero energy.

evidence for that is verified by calculating the magnetic coupling of two Co atoms in the vacuum, which is FM for any Co-Co distance. By keeping the Co-Co distance the same as that of the Co at Zn neighboring sites of the ZnO sheet, we obtain that the two Co atoms present a strong interaction favoring a FM coupled by 0.12 eV. For the Co atoms in ZnO sheet this energy difference is enhanced to 0.30 eV. In other hand Co doped bulk ZnO the FM and AFM couplings present similar energies, slightly favorable for the AFM coupling. In this way we conclude that the stabilization of the FM coupling in the graphenelike ZnO sheet is due to the topological 2D character of the system. For bulk ZnO the Co 3d band for a FM coupling occurs between majority t_{2d} levels which results in no net energy gain since the bonding and antibonding states are fully occupied. In this way for bulk ZnO doped with Co the ferromagnetism can only be explained in the presence of defects and doping as suggested in Ref. 18. Here for Co doped ZnO sheet the magnetism is mainly governed by the minority semioccupied e'' spin-down state which breaks in an occupied b_1 state and an unoccupied b_2 state as shown in Fig. 2.

Following the phenomenological model proposed by Dalpian *et al.*,¹⁹ considering only the direct exchange (Δ^2) and superexchange ($\Delta^{1,2}$) parameters, we can understand the FM and AFM couplings in $\text{Co}_{\text{Zn}}/\text{ZnO}$ sheet. For the FM system there is no energy gain due to the interaction between majority spin 3d levels. The energy gain comes from the electronic coupling between the minority-spin levels as depicted in Fig. 3. In this figure, α and α' represent the electronic configuration of the minority-spin levels before the interactions are turned on. β and β' are the resulting split due to the interactions between the same orbitals that come from each Co atom, while γ is the final stage resulting from the additional interactions between different orbitals with same symmetry.

Figure 3(a) presents the electronic interactions between the occupied (unoccupied) a_1 – a_1 and b_1 – b_1 (a_1 – a_1)

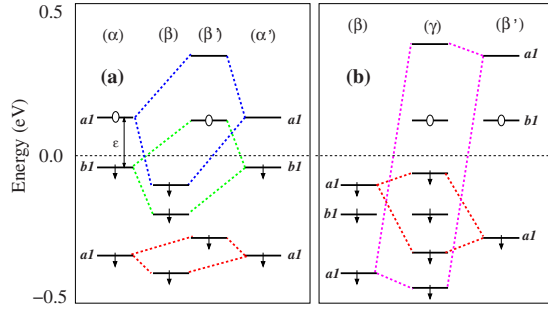


FIG. 3. (Color online) Energy couplings for the FM system between the minority-spin levels with, (a) the same energy and symmetry, $\alpha \rightarrow \beta$ and $\alpha' \rightarrow \beta'$, and (b) with same symmetry, however, lying at different energies, $\beta \rightarrow \gamma$ and $\beta' \rightarrow \gamma$. In (b) γ represents the final electronic level configuration.

states with the same energies. Within the occupied states, there is a direct exchange interaction between the occupied spin-down states $a1$, around 0.4 eV below the Fermi level. The occupied $a1$ level moves downward by $\Delta^{2(a1)}$, while in $(\alpha') \rightarrow (\beta')$ $a1$ moves upward by the same amount, $\Delta^{2(a1)}$. There is no energy gain in this process. The direct exchange interaction between the $b1$ states lying at 0.1 eV below the Fermi level moves one $b1$ state downward by $\Delta^{2(b1)}$ ($\alpha \rightarrow \beta$), while the other one moves upward by the same energy amount ($\alpha' \rightarrow \beta'$). In the latter step $b1$ becomes empty. Meanwhile, there is an energy split of $2\Delta^{2(a1)}$ between the unoccupied $a1$ levels (lying at 0.15 eV above the Fermi level) giving rise to an occupied $a1$ state, $\alpha \rightarrow \beta$ in Fig. 3(a). Here it is important to point out that, indeed the formation of occupied $a1$ and unoccupied $b1$ levels, near the Fermi level, have been verified in our electronic structure through the Kohn-Sham eigenvalues. The net energy gain in those processes, namely, between the occupied $b1-b1$ and empty $a1-a1$, is $\Delta^{2(b1)} + \Delta^{2(a1)} - \varepsilon$. Where ε represents the energy difference between the highest occupied $b1$ and lowest unoccupied $a1$ levels of the Co $3d$ orbital before the interactions turn on. Further electronic interactions between the electronic levels with the same symmetry, however, with different energies, are depicted in Fig. 3(b). In this case there is an energy gain for the electronic interaction between the occupied $a1$ (0.4 eV below the Fermi level, β) and the unoccupied $a1$ (0.35 eV above the Fermi level, β') states, which moves the occupied $a1$ level downward in energy by $\Delta^{2'(a1)}$. The energy gain is $\Delta^{2'(a1)}$. Here we call this energy split as $\Delta^{2'(a1)}$ to differentiate it from $\Delta^{2(a1)}$ where the coupling occurs between electronic states with the same energy. Since in the former coupling the energy levels are not resonant we expect that $\Delta^{2'(a1)} < \Delta^{2(a1)}$. Finally we observe that there is no energy gain due to the interaction between the occupied $a1$ states lying at 0.1 eV (β) and 0.3 eV (β') below the Fermi level. Thus, comparing with the initial electronic configurations (α and α') and the final one (γ), we find a net energy gain (ΔE_{FM}) of

$$\Delta E_{FM} = \Delta^{2'(a1)} + \Delta^{2(a1)} + \Delta^{2(b1)} - \varepsilon.$$

Figure 4 presents the spin-down electronic couplings for the AFM system. For the spin-up channel the couplings will

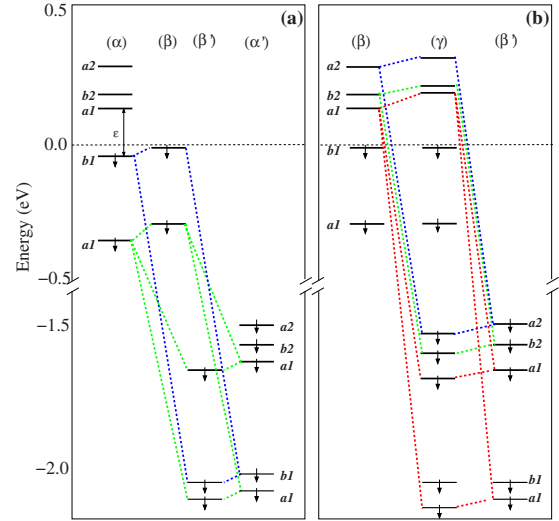


FIG. 4. (Color online) Energy couplings for the AFM system between (a) the occupied spin-down levels, and (b) the occupied-unoccupied spin-down levels. In (b) γ represents the final electronic level configuration.

be the same and it is not described in this figure. There is a superexchange interaction between the occupied minority states (lying within an energy interval up to 0.4 eV below the Fermi level) and the occupied majority states localized within an energy range of 1.5–2.2 eV below the Fermi level, indicated as $\alpha \rightarrow \beta$ and $\alpha' \rightarrow \beta'$ in Fig. 4(a). However, there is no energy gain in those processes. Meanwhile, we find a net energy gain when the interactions between the unoccupied minority-spin states (at ~ 0.2 eV above the Fermi level) and the occupied majority spin states (lying within an energy range of 1.5–2.2 eV below the Fermi level) are turned on, $\beta \rightarrow \gamma$ and $\beta' \rightarrow \gamma$ in Fig. 4(b). We find an energy gain for the AFM coupling of

$$\Delta E_{AFM} = 2(2\Delta^{1,2(a1)} + \Delta^{1,2(b2)} + \Delta^{1,2(a2)}).$$

Here we cannot compare the energy gains of FM and AFM couplings since one is ruled by direct exchange (Δ^2), while the other is ruled by superexchange ($\Delta^{1,2}$) parameters. However, the FM is expected to be more stable, $\Delta E_{FM} < \Delta E_{AFM}$ since it is expected that Δ^2 is larger than $\Delta^{1,2}$ because in Δ^2 we are considering couplings between electronic states that are resonant in energy, while the electronic states that give rise to $\Delta^{1,2}$ are distant in energy by ~ 2 eV. Indeed, the energetic preference for the FM coupling has been confirmed by our total-energy calculations.

The topological 2D character on the ferromagnetism can be better understood by increasing the number of ZnO layers. For Co doped a ZnO double layer the ground state does not present any more a FM coupling, but the AFM is more stable by 0.04 eV. The ferromagnetism is a response to the 2D confinement due to the graphenelike form of the ZnO when the Co atoms are only threefold coordinated. For a double layer within the graphitic form the Co atoms are fourfold coordinated as is in the bulk, and the stabilization of the magnetism tends to that of the bulk one. An explanation of the room-temperature ferromagnetism in ZnO bulk has been

attributed to the presence of oxygen vacancy plus Co²⁺ pair (VCo), leading the Co atom threefold coordinated.⁶ So, it seems that by reducing the coordination of the Co atom favors the ferromagnetism.

IV. CONCLUSIONS

In summary, by using first-principles calculations we find that Co atoms can be substituted in a Zn site in graphenelike ZnO sheet through a barrierless process. The presence of Co atoms introduces a Jahn-Teller distortion in the system, lowering the symmetry of the sheet, leading to a strong direct exchange interaction between the 3*d* levels of the Co atoms.

This interaction, different from the Co doped bulk ZnO, favors a FM coupling without any defect or codoping. The FM coupling is a consequence of the 2D confinement due to the graphenelike form of the ZnO sheet since by increasing the number of ZnO layers the ferromagnetic coupling vanishes. These results open the possibility for exploitation of a low dimensional graphenelike ZnO layer for future magnetic device applications.

ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies FAPEMIG, FAPESP, CAPES, and CNPq.

-
- ¹P. Sharma, A. Gupta, K. V. Rao, F. J. Owens, R. Sharma, R. Ahuja, J. M. O. Guillen, B. Johansson, and G. A. Gehring, *Nature Mater.* **2**, 673 (2003).
- ²A. J. Behan, A. Mokhtari, H. J. Blythe, D. Score, X.-H. Xu, J. R. Neal, A. M. Fox, and G. A. Gehring, *Phys. Rev. Lett.* **100**, 047206 (2008).
- ³Z. Lu, H.-S. Hsu, Y. Tzeng, and J.-C.-A. Huang, *Appl. Phys. Lett.* **94**, 152507 (2009).
- ⁴K. Rode, R. Mattana, A. Anane, V. Cros, E. Jacquet, J.-P. Contour, F. Petroff, A. Fert, M.-A. Arrio, Ph. Sainctavit, P. Bencok, F. Wilhelm, N. B. Brooks, and A. Rogalev, *Appl. Phys. Lett.* **92**, 012509 (2008).
- ⁵M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, *Phys. Rev. Lett.* **93**, 177206 (2004).
- ⁶C. D. Pemmaraju, R. Hanafin, T. Archer, H. B. Braun, and S. Sanvito, *Phys. Rev. B* **78**, 054428 (2008).
- ⁷Z. H. Zhang, X. Wang, J. B. Xu, S. Muller, C. Ronning, and Q. Li, *Nat. Nanotechnol.* **4**, 523 (2009).
- ⁸A. R. Botello-Méndez, F. López-Urías, M. Terrones, and H. Terrones, *Nano Lett.* **8**, 1562 (2008).
- ⁹R. Xiao, D. Fritsch, M. D. Kuz'min, K. Koepf, H. Eschrig, M. Richter, K. Vietze, and G. Seifert, *Phys. Rev. Lett.* **103**, 187201 (2009).
- ¹⁰C. L. Freeman, F. Claeysens, N. L. Allan, and J. H. Harding, *Phys. Rev. Lett.* **96**, 066102 (2006).
- ¹¹A. R. Botello-Méndez, M. T. Martínez-Martínez, F. López-Urías, M. Terrones, and H. Terrones, *Chem. Phys. Lett.* **448**, 258 (2007).
- ¹²C. Tusche, H. L. Meyerheim, and J. Kirschner, *Phys. Rev. Lett.* **99**, 026102 (2007).
- ¹³J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- ¹⁴N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ¹⁵R. H. Miwa, T. M. Schmidt, and A. Fazzio (unpublished).
- ¹⁶S. Lany, H. Raebiger, and A. Zunger, *Phys. Rev. B* **77**, 241201(R) (2008).
- ¹⁷A. Walsh, J. L. F. Da Silva, and S.-H. Wei, *Phys. Rev. Lett.* **100**, 256401 (2008).
- ¹⁸S. Sanvito and C. D. Pemmaraju, *Phys. Rev. Lett.* **102**, 159701 (2009).
- ¹⁹G. M. Dalpian, S.-H. Wei, X. G. Gong, A. J. R. da Silva, and A. Fazzio, *Solid State Commun.* **138**, 353 (2006).