J Supercond Nov Magn
DOI 10.1007/s10948-012-1681-3

ORIGINAL PAPER

Explanation of Co Magnetic Moment Enhancement in (Co,Cu)-Doped ZnO by First-Principle Calculations

A. El Amiri · M. Abid · H. Lassri · E.K. Hlil

Received: 28 April 2012 / Accepted: 7 June 2012

Abstract By ab-initio calculations on $Zn_{0.95-x}Co_{0.05}Cu_xO$, we study the variations of magnetic moments versus Cu concentration. The electronic structure is calculated by using the Korringa–Kohn–Rostoker (KKR) method combined with coherent potential approximation (CPA). We show that the total magnetic moment and magnetic moment of Co increase with increasing Cu content. From a density of state (DOS) analysis, we propose an explanation of the enhancement of the Co magnetic moment versus Cu concentration.

Keywords (Co,Cu)-Doped ZnO · Diluted magnetic semiconductors · DOS

1 Introduction

Diluted magnetic semiconductors (DMS) have recently attracted much attention for their promising functionalities in spintronics because charge and spin of electrons are accommodated into single matter. In particular, DMS based-ZnO attract strong research interest because ZnO offers other desirable features as a semiconductor; it has direct wide band gap of 3.3 eV [1]. ZnO doped with 3d transition-metal (TM) elements has been studied widely since the model calculation by Dietl et al. predicted the possibility of ferromagnetism in ZnO with a small amount of Mn as an impurity [2]. A number of magnetic, magneto-optical, and magneto-transport properties were observed for transition-metal alloyed ZnO systems, including Mn-added ZnO [3–8], Fe-added ZnO [5, 9, 10], Co-added ZnO [6, 9–13], and Ni-added ZnO [12–14].

Moreover, using first-principle calculations, Sato and Katayama–Yoshida [15] theoretically demonstrated that a ZnO matrix doped with TM atoms such as V, Cr, Fe, Co, and Ni exhibited ferromagnetic ordering.

Recently, many researchers have tried to dope other ions into the ZnO-based DMS to obtain two metal ions co-doped ZnO in order to enhance their optical and magnetic properties by introducing additional carriers [16–20]. Lin et al. supposed that a small amount of additional Cu doping would create additional carriers in Co doping ZnO, and its magnetization would be greatly enhanced in bulk samples [21]. In this work we have performed ab-initio calculations on $Zn_{0.95-x}Co_{0.05}Cu_xO$. Our results reveal that the total moment and magnetic moment per atom of cobalt increase with increasing x.

2 Electronic and Magnetic Structure Calculations

Electronic structure calculations were performed within the fully relativistic Korringa–Kohn–Rostoker (KKR) method [22]. To take into account the random distribution of Co and Cu in Zn sites, we used the KKR-CPA for which no supercell is needed. We assume that, in the original cell,

A. El Amiri (✉) · M. Abid
Laboratoire de Physique Fondamentale et Appliquée (LPFA), Faculté des Sciences Ain Chock, Université Hassan II, B.P. 5366, Mâarif, Casablanca, Maroc
e-mail: aelamiri@casablanca.ma

H. Lassri
Laboratoire de Physique des Matériaux, Micro-électronique, Automatique et Thermique (LPMMAT), Faculté des Sciences Ain Chock, Université Hassan II, B.P. 5366 Mâarif, Casablanca, Maroc

E.K. Hlil
Institut Néel, CNRS, Université J. Fourier, B.P. 166, 38042 Grenoble, France

Published online: 29 June 2012

the O site is perfectly ordered whereas the Zn site is taken to be randomly occupied by Co, Cu and Zn with appropriate occupancies. The Morruzi, Janack, Willaims (mjw) parameterization of exchange-correlation energy functional was used [23]. The form of the crystal potential is approximated by a muffin-tin potential, and the wave functions in the respective muffin-tin spheres were expanded in real harmonics up to $l = 2$, where l is the angular momentum quantum defined at each site. Spin polarization, relativistic effect and spin-orbit interaction were taken into account.

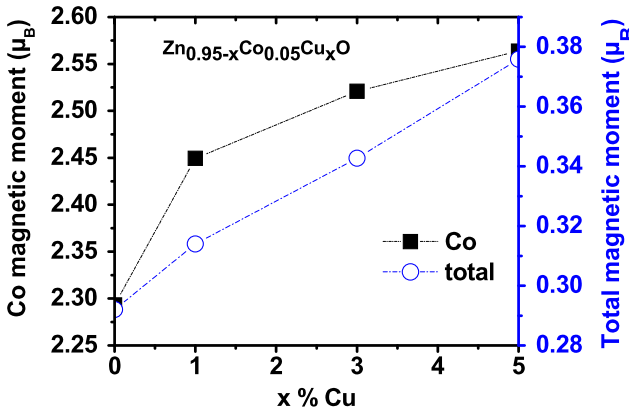

Fig. 1 Variation of total magnetic moment and magnetic moment per atom of Co with concentration of Cu

The $Zn_{0.95-x}Co_{0.05}Cu_xO$ was considered to crystallize in wurtzite structure with the experimental lattice parameter values reported in Ref. [24].

3 Results and Discussion

We focus on the magnetic moments of $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($x = 0.01, 0.03, 0.05$). By ab-initio calculations, we found that both total moment and local moment per atom of Co increase with increasing x. Figure 1 presents variation of total moment and Co moment. These results give evidence that with doping Cu concentration ranging from 0 to 0.05, the total moment and the cobalt moment increase from 0.29 μ_B up to 0.38 μ_B and from 2.3 μ_B up to 2.56 μ_B, respectively. Recently, Yanyan Wei et al. show that saturated magnetization (Ms) increases from 0.18 μ_B/Co to 1.08 μ_B/Co as the Cu doping concentration increases from 0 up to 0.05 [24]. To understand this behavior we analyze the electron density of states (DOS). First, the valence-electron configurations of the Zn and substituting 3d atoms Co and Cu are $3d^{10}4s^2$, $3d^74s^2$ and $3d^{10}4s^1$, respectively. According to the first Hand's rule, the minimum of the total energy of an isolated 3d atom corresponds to the occupation of the 3d orbitals that gives a highest spin moment. Therefore, the minority 3d states of Co must be partially occu-

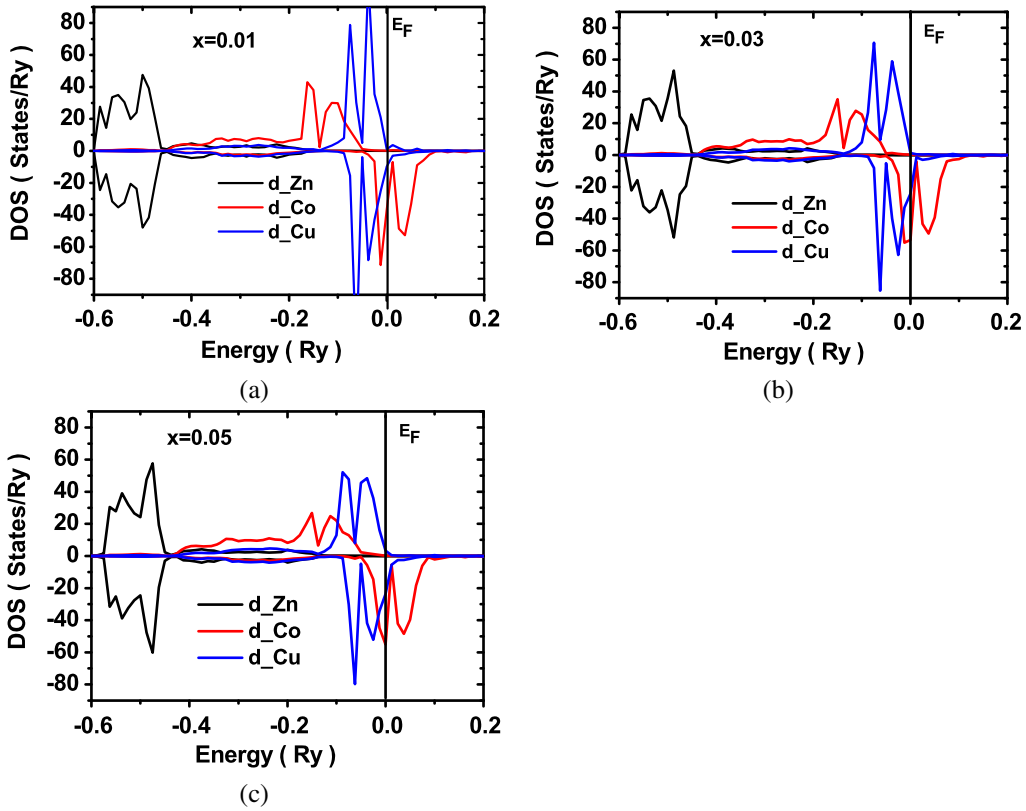

Fig. 2 DOS of d orbital of Zn, Co and Cu of $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($x = 0.01$ (**a**), 0.03 (**b**) and 0.05 (**c**))

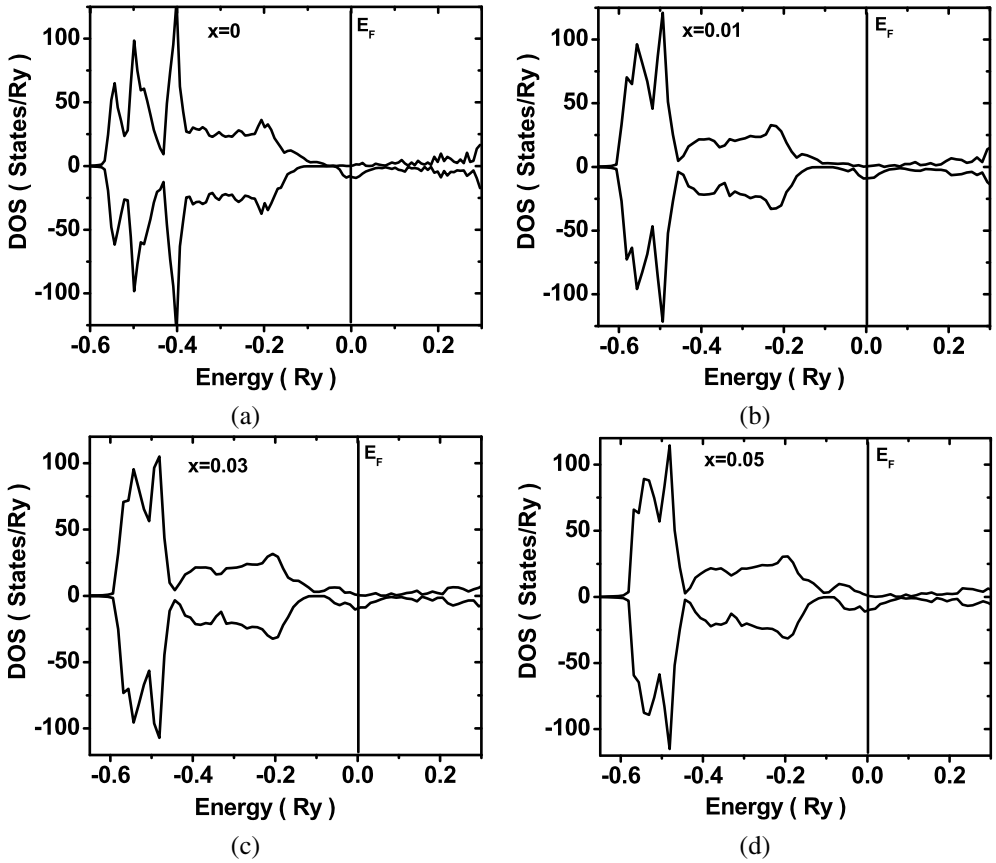

Fig. 3 Total DOS of $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($x = 0.0$ (**a**), 0.01 (**b**), 0.03 (**c**) and 0.05 (**d**))

pied whereas those of Cu are nearly fully occupied. Indeed, the calculated electronic structures of 3d states of Zn, Co and Cu in $Zn_{0.95-x}Co_{0.05}Cu_xO$ DOS are in agreement with this prediction (see Figs. 2(a)–2(c)). Secondly in Figs. 3(a)–3(d), where total DOS for $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($x = 0, 0.01, 0.03, 0.05$) is reported, we can see a polarization in DOS at Fermi level (taken as energy reference). Such polarization points out to half metallic character of these components. Also when Cu concentration increases we note that the region between 0 and −0.1 Ry opens, therefore the local density of states near left of the Fermi level becomes slightly important. This is explained by the creation of donors of electrons caused by Cu introduction [25]. To show more about the nature of these donors we note as seen in Figs. 2(a)–2(c) that the major party of Cu-3d DOS lies exactly in such region (−0.1–0 Ry). This region exists in the band gap of $Zn_{0.95}Co_{0.5}O$ DOS (see Fig. 3(a)), so Cu introduction creates the donor impurity bands. Moreover, according to our band structure calculations, we can observe the overlap between Co-3d and Cu-induced impurity band states for the spin-down at Fermi level (Figs. 2(a)–2(c)) which leads to significant DOS at Fermi level and hence to the half–metallic character as observed in total DOS (see Figs. 3(b)–3(d)). Also this overlap leads to hybridization between the involved spin-down states. Such hybridization facilities mutual charge transfer from Cu to Co atoms which favors interaction between the localized moments of Co atoms. Such an interaction, tending to align the Co moments, contributes to increase of charge polarization (spin up–spin down) for Co atoms that explains the results listed in the Table 1 and consequently the increase of magnetic moment of cobalt. So we can conclude that there is a superexchange interaction between Co atoms caused by Cu-induced donor impurity bands. Based on the first-principle calculations and the Co K-edge XANES analysis, Fengchun et al. reported that the activation of the ferromagnetism of (Co,Cu)-doped ZnO relative to Co-doped ZnO is due to the effective hybridization between Co 3d states and the Cu-induced donor impurity band at the Fermi level [26], which is consistent with our results.

4 Conclusion

In this work we have performed ab-initio calculations on $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($x = 0, 0.01, 0.03, 0.05$). We have reported that the magnetic moment per Co atom increases with increasing of Cu content. Also using the total DOS we are

Table 1 Valence charge of Co

x	Up	Down	Up/down
0.00	4.314	2.031	2.283
0.01	4.343	1.932	2.411
0.03	4.372	1.878	2.494
0.05	4.389	1.849	2.540

able to propose interpretation of enhancement of the total and Co magnetic moments in $Zn_{0.95-x}Co_{0.05}Cu_xO$ systems.

References

1. Landolt-Börnstein: New Series, Group III—Condensed Matter. Springer, Heidelberg (2002)
2. Dietl, T., Ohno, H., Matsukura, F., Cibert, J., Ferrand, D.: Science **287**, 1019 (2000)
3. Fukumura, T., Jin, Z., Ohtomo, A., Koinuma, H., Kawasaki, M.: Appl. Phys. Lett. **75**, 3366 (1999)
4. Ando, K., Saito, H., Jin, Z., Fumura, T., Kawasaki, M., Matsumoto, Y., Koinuma, H.: J. Appl. Phys. **89**, 7284 (2001)
5. Han, S.J., Song, J.W., Yang, C.H., Park, S.H., Park, J.-H., Jeong, Y.H.: Appl. Phys. Lett. **81**, 4212 (2002)
6. Wi, S.C., Kang, J.S., Kim, J.H., Cho, S.B., Kim, B.J., Yoon, S., Suh, B.J., Han, S.W., Kim, K.H., Kim, K.J., Kim, B.S., Song, H.J., Shin, H.J., Shim, J.H., Min, B.I.: Appl. Phys. Lett. **84**, 4233 (2004)
7. Jin, Z., Fukumura, T., Kawasaki, M., Ando, K., Saito, H., Sekiguchi, T.: Appl. Phys. Lett. **78**, 3824 (2001)
8. Iqbal, J., Liu, X., Majid, A., Ronghai, Y.: J. Supercond. Nov. Magn. **24**, 699 (2011)
9. Mok Cho, Y., Kil Choo, W., Kim, H., Kim, D., Eon Ihm, Y.: Appl. Phys. Lett. **80**, 3358 (2002)
10. Ueda, K., Tabata, H., Kawai, T.: Appl. Phys. Lett. **79**, 988 (2001)
11. Venkatesan, M., Fitzgerald, C.B., Lunney, J.G., Coey, J.M.D.: Phys. Rev. Lett. **93**, 177206 (2004)
12. Lee, H.J., Jeong, S.-Y., Ryong Cho, C., Hong Park, C.: Appl. Phys. Lett. **81**, 4020 (2002)
13. Prellier, W., Fouchet, A., Mercey, B., Simon, Ch., Raveau, B.: Appl. Phys. Lett. **82**, 3490 (2003)
14. Ekicibil, A., Bulun, G., Kılıc Cetin, S., Dikmen, Z., Onder, O., et al.: J. Supercond. Nov. Magn. **25**, 435 (2012)
15. Sato, K., Katayama-Yoshida, H.: Jpn. J. Appl. Phys. **39**, L555 (2000)
16. Xu, Q., Hartmann, L., Schmidt, H., Hochmuth, H., Lorenz, M., Setzer, A., Esquinazi, P., Meinecke, C., Grundmann, M.: Thin Solid Films **516**, 1160 (2008)
17. Li, G.R., Qu, D.L., Zhao, W.X., Tong, Y.X.: Electrochem. Commun. **9**, 1661 (2007)
18. Dinesha, M.L., Jayanna, H.S., Mohanty, S., Ravi, S.: J. Alloys Compd. **490**, 618 (2010)
19. Brihi, N., Bouaine, A., Berbadj, A., Schmerber, G., Colis, S., Dinia, A.: Thin Solid Films **518**, 4549 (2010)
20. Chakraborti, D., Ramachandran, S., Trichy, G., Narayan, J.: J. Appl. Phys. **101**, 053918 (2007)
21. Lin, H.T., Chin, T.S., Shih, J.C., Lin, S.H., Hong, T.M.: Appl. Phys. Lett. **85**, 621 (2004)
22. Akai, H.: J. Phys. Condens. Matter **1**, 8045 (1989)
23. Moruzzi, V.L., Janak, J.F., Williams, A.R.: Calculated Properties of Metals. Pergamon, New York (1978)
24. Wei, Y., Hou, D., Qiao, S., Zhen, C., Tang, G.: Physica B **404**, 2486 (2009)
25. Zhang, H.-W., Wei, Z.-R., Li, Z.-Q., Dong, G.-Y.: Mater. Lett. **61**, 3605 (2007)
26. Hu, F., Liu, Q., Sun, Z., Yao, T., Pan, Z., Li, Y., He, J., He, B., Xie, Z., Yan, W., Wel, S.: J. Appl. Phys. **109**, 103705 (2011)