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Competing effects of Cu ionic charge and oxygen vacancies on the ferromagnetism of (Zn, Co)O nanoparticles

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Abstract

We report the effects on the ferromagnetism due to co-doping of ZnO with Co and Cu in the presence of variable numbers of oxygen vacancies. The co-doped nanoparticles $Zn_{0.95-}Co_{0.05}Cu_yO$ ($0.00 \leqslant y < 0.009$) were prepared via the chemical route with oxygen vacancies introduced via annealing in a reducing atmosphere for variable amounts of time. In addition to the magnetization, the particles were characterized by x-ray diffraction (XRD), x-ray photoemission spectroscopy (XPS) and x-ray absorption near edge spectroscopy (XANES). The Co ions were determined to be in the +2 state in a tetrahedral symmetry, with no evidence for metallic Co or Cu. However, the ionic state of Cu is found to change from +2 to +1 state with increasing Cu concentration, which appears to strongly decrease the concentration of oxygen vacancies. It is found that the ferromagnetic moment initially increases with the addition of Cu but decreases above a typical concentration that coincides with the appearance of the Cu^{+1} state and the decrease of O vacancy concentration. It is concluded that the effect of Cu in the very low range of concentrations, where it appears to go in as Cu^{+2}, is to stabilize ferromagnetism indirectly via generation of O vacancies. The effects of O vacancy concentration on the ferromagnetism are interpreted in the light of the F-center exchange (FCE) model.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The semiconductor ZnO has received substantial interest in the research community because of its wide direct band gap (3.3 eV) and large exciton binding energy (60 meV) which could lead to lasing action based on exciton recombination even above room temperature [1]. It is a well known piezo-electric [2] and electro-optic material [3] with potential applications such as opto-electronic and luminescent devices as well chemical sensors [4]. Even though the research focusing on ZnO goes back several decades, one of the renewed interests is fueled by the observation of ferromagnetism in transition metal (TM) doped ZnO labeled as a diluted magnetic semiconductor (DMS) [5]. DMSs have inspired a great deal of research interest in the field of 'magneto-opto-electronics' [6–9], which could pave the way to exploit the spin as well as charge of the carrier in semiconductor devices. The stabilization or enhancement of ferromagnetic (FM) properties by co-doping of ions has been predicted theoretically [10–12] and confirmed by some experiments [13–15]. Sato *et al* [10] used first principles calculations to reveal that Mn-doped ZnO changed its magnetic state from spin-glass to FM with increasing hole concentration. Spaldin *et al* [11] predicted using the density functional theory (DFT) approach that p-type doping in (Zn, Co)O could strongly stabilize the FM state. Bergqvist *et al* [12] combining first principles calculations of interatomic exchange interactions with a Heisenberg model and Monte Carlo simulations, have explained the preparation dependence of ferromagnetism in TM doped diluted magnetic semiconductors as due to the random ordering of magnetic

ions and distribution of defects. Experimentally, Yan *et al* [14] reported that the (Mn, Co) co-doped ZnO films with high resistance showed room temperature ferromagnetism, and the co-doping of (Mn, Co) results in an increase of the saturated magnetic moments. Han *et al* [15] found that the FM properties of $Zn_{1-x}Fe_xO$ thin films are enhanced by the co-doping of Cu as an acceptor impurity. On the basis of theoretical calculations and experimental supports, it has been predicted that p-type doping in ZnO should be more effective to produce FM properties than that of n-type doping. Buchholz *et al* [16] have shown that Cu-doped thin films with n-type ZnO were non-magnetic while p-type ZnO films doped with Cu were ferromagnetic at room temperature. However, it is generally accepted that the growth of p-type ZnO is still an experimental challenge due to self-compensation from oxygen vacancies [17] or the incorporation of hydrogen as an unintentional donor [18].

In view of the competing effects of on the one hand O vacancies, as an effective n-type dopant, and on the other hand, the role of Cu in stabilizing the FM in ZnO but in p-type conditions, we have explored the combined effects of these two variables namely O vacancies and Cu dopants. While co-doping studies of Co–Cu in ZnO have been reported in the literature these have only been in the high Cu concentration range where Cu itself bears a magnetic moment. However, the behavior of Cu in the ZnO + Co system in the very low concentration region ($y \leqslant 0.01$) has not been investigated. We shall show that the behavior of Cu in this region is quite different and it acts only indirectly in affecting the moment on the Co ions. In this paper, we present the changes in the magnetic moment in Co-doped ZnO due to small concentrations of Cu (0–0.87%) along with systematically introduced oxygen vacancies created by annealing in a forming gas.

2. Experiment

$Zn_{0.95-y}Co_{0.05}Cu_yO$ ($0.00 \leqslant y \leqslant 0.0087$) polycrystalline nanoparticles were synthesized by the chemical route reported earlier [19]. Earlier we have reported in detail the ferromagnetic behavior of similarly prepared $Zn_{1-x}Co_xO$ ($x = 0.02$ to 0.10) [19, 20] nanoparticles and found that only the compositions up to $x = 0.06$ were monophase in our preparation route. In view of this, we have kept the Co concentration in the present samples at less than $x = 0.06$ while concentration of the co-doped (Cu) ions was varied between 0 and 0.87%. The low Cu composition ensured that we stayed well within the range of Cu solubility in ZnO that is about 1% for preparations via the chemical route. For improving the crystallinity and to generate oxygen vacancies, all the as-prepared samples were annealed at 600 °C in a forming gas (95%Ar–5%H) of 99.9% purity. The role of the forming gas is to generate O vacancies due to the reducing atmosphere, as detailed in the earlier papers [19, 20]. Different sets of samples were prepared having the same nominal composition but with different levels of vacancy concentration by treating them for different periods (6, 8 and 10 h respectively) in the forming gas. To verify the single-phase nature of the products, x-ray diffraction (XRD) studies were conducted, while the charge states of the different dopants, the absence of metallic clusters and relative vacancy concentration of different samples was inferred from x-ray photoemission spectroscopy (XPS). Some selected x-ray absorption near edge structure (XANES) measurements were also performed to augment the XPS derived information. Magnetization studies were carried out on a commercial vibrating sample measurement (VSM) system.

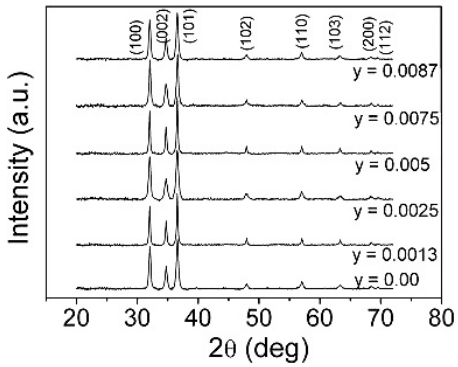

Figure 1. X-ray diffraction patterns of $Zn_{0.95-y}Co_{0.05}Cu_yO$ ($0 \leqslant y \leqslant 0.0087$). Peaks are indexed to the hexagonal wurtzite structure.

3. Results and discussion

The XRD data are given in figure 1 for $Zn_{0.95-y}Co_{0.05}Cu_yO$ ($0.00 \leqslant y \leqslant 0.0087$) samples, annealed in the forming gas. The observed peaks, as marked on the figure, correspond to the hexagonal wurtzite structure and no un-identified peaks were seen in any of the samples. The average particle size for the Cu un-doped composition was estimated to be about 22 nm from x-ray line broadening using the Scherrer formula $D_{hkl} = K\lambda/\beta_{hkl}\mathrm{Cos}\theta$, where D_{hkl} is the particle diameter in angstroms, K is the Scherer coefficient equal to 0.89, β is the full width at half maximum (FWHM), and λ is the wavelength of x-rays. (Slightly more broadening of the peaks is observed in the Cu-doped samples and is understood to be due to the additional strains due to the added dopant.)

Due to the limited resolution of the XRD in identifying small traces of an impurity phase, in particular, the presence of clusters of Co or Cu, or other impurity phases e.g. Co_2O_3 or CoO, XPS measurements were performed which are known to be much more sensitive to the presence of small traces of such phases. Furthermore, this measurement is also useful to investigate the bonding characteristics and individual oxidation state(s) of Co and Cu ions in the ZnO lattice, crucial in coming to a conclusion about the origin of ferromagnetism in the DMS systems. While the XPS measurements were carried out on all the compositions, the data for three representative compositions, namely $Zn_{0.95-y}Co_{0.05}Cu_yO$ ($y = 0.00$, 0.0025 and 0.0087) are shown in figure 2 for the Co $2P_{3/2}$ and Co $2P_{1/2}$ XPS spectral region. It is apparent that in addition to the two main peaks ($2P_{3/2}$ and $P_{1/2}$) each peak is accompanied by its satellite. The observed binding energy of the Co $2P_{3/2}$

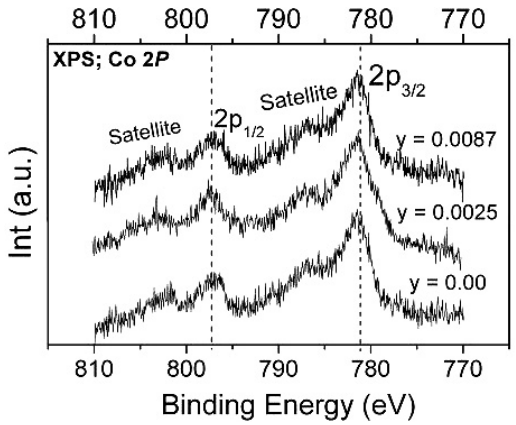

Figure 2. XPS spectra of Co 2p core levels of $Zn_{0.95-y}Co_{0.05}Cu_yO$ for different Cu concentrations ($y = 0.00, 0.0025, 0.0087$).

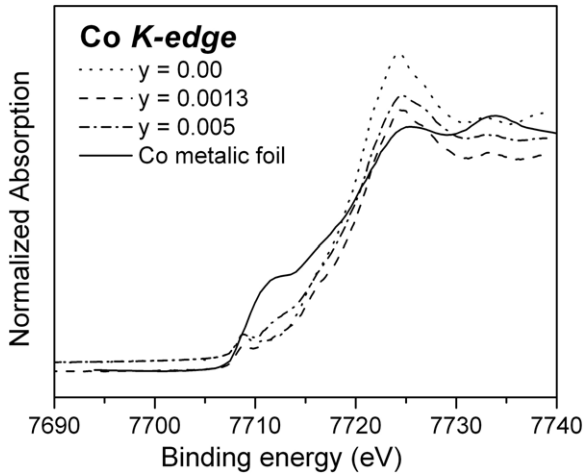

Figure 3. Co K-edge XANES spectra of $Zn_{0.95-y}Co_{0.05}Cu_yO$ nanoparticles. (Dotted line for $y = 0.00$; dashed line for $y = 0.0013$ and dash–dotted line for $y = 0.005$.) The spectrum for Co foil (solid line) is also given for comparison.

peak is 781.5 eV, while that for the Co $2P_{1/2}$ is at 797 eV, with an energy difference of $\Delta E = 15.5$ eV between the two peaks. Comparing the observed spectra with those reported for Co metal (778 eV for the Co $2p_{3/2}$ peak); with the energy difference of the two peaks for Co^{+2} in CoO ($\Delta E = 15.05$ eV), and with the absence of the satellite peaks of Co^{+3} in γ-Co_2O_3 [21, 22], we can safely conclude that the electronic state of Co in our samples is Co^{+2} and that it is not bonded to oxygen as CoO or Co_2O_3. It also rules out metallic Co clusters in any of the samples, to our degree of resolution. We therefore conclude that Co is present in our nanoparticles in the +2 oxidation state in tetrahedral symmetry.

The x-ray absorption near edge (XANES) spectrum for some of these compositions was also investigated for the Co K-edge with a view to further confirming the absence of metallic cobalt in these systems. Measurements were carried out on beamline number X23A2 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). These studies were carried out on the samples with copper concentrations of $y = 0$, 0.0013 and 0.005 respectively. For

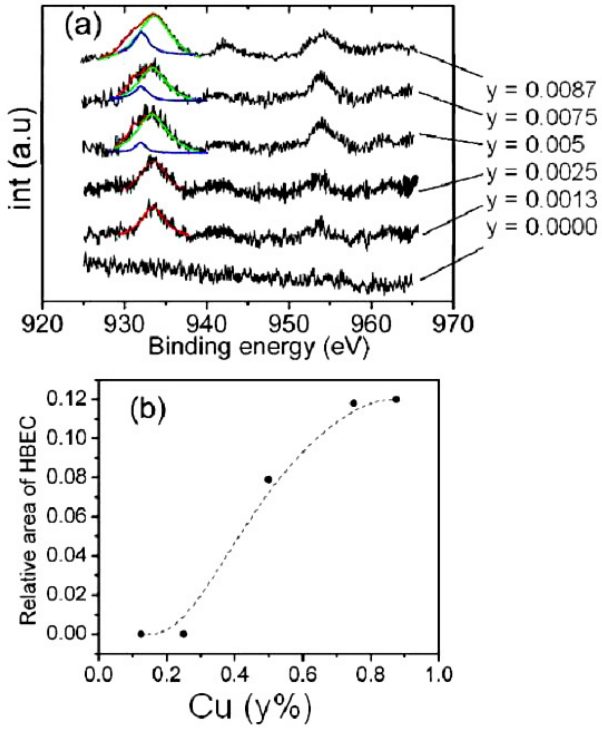

Figure 4. (a) XPS spectra of Cu 2p core levels of $Zn_{0.95-y}Co_{0.05}Cu_yO$ ($0 \leqslant y \leqslant 0.00875$). Colored lines are the Gaussian fitted curves; blue curve is for the LBEC and the green curve for the HBEC peak (see text for details). (b) Relative areas under the curves for the HBEC peaks obtained by the Gaussian fits to the data of curves from figure 4 (a).

comparison purposes a cobalt metallic foil sample was also studied. Data are shown in figure 3. It is clear that the Co edge absorption for the metallic foil is at 7713 eV as expected from the literature [23, 24] while the Co edge for the samples lies at about 4 eV below this value consistent with the expectation for Co in a +2 charge state [23, 24]. The pre-edge structure in transition metals has been attributed to the 1s–3d transition, while for the case of Co substituted in ZnO it is attributed to the transition from the 1s to the hybrid orbital (Co3d–O2p). The lowered pre-edge structure is a signature [24] of Co in the +2 state as opposed to the Co in the metallic state. With increasing Cu content the pre-edge peak becomes less well defined, however, it remains distinct from the edge in metallic copper. The XANES data further confirms that Co is in a non-zero oxidation state in our samples.

The XPS measurements were also used to study the oxidation states of Cu ions (Cu^{+2} and Cu^{+1}) in the (Zn, Co)O matrix. Because of the very low Cu concentration, we have taken XPS measurements at high resolution with a slow rate to clearly detect the signature of Cu 2p core levels. It is well known that Cu^{+2} produces a strong Cu 2p satellite peak at a higher binding energy, presumably related to the presence of Cu 3d hole states. These satellites have been attributed to the shake-up transitions by ligand-to-metal 3d charge transfer. This charge transfer cannot occur in Cu^{+1} compounds and metallic Cu because of their completely filled 3d shells. Figure 4(a) shows high resolution XPS spectra of Cu 2p core levels of all Cu co-doped

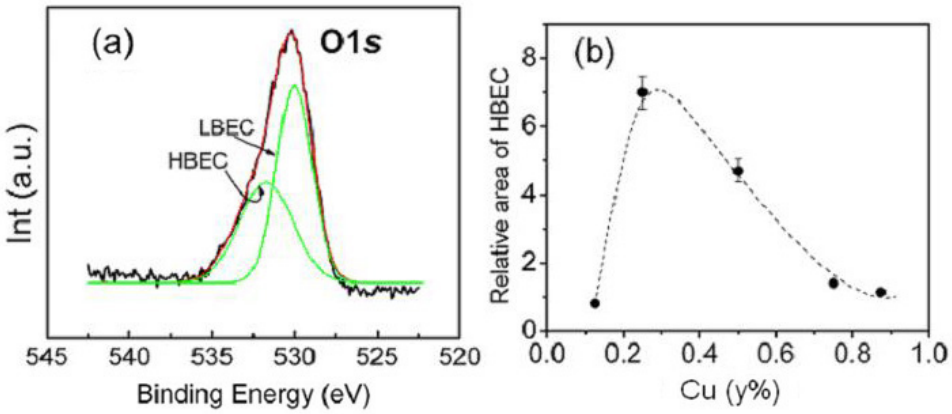

Figure 5. (a) The typical XPS spectra of the O 1s core level recorded from the $Zn_{0.9475}Co_{0.05}Cu_{0.0025}O$ nanoparticles; main (black curve) is the data fit to a two-peak Gaussian. The two Gaussian peaks (HBEC and LBEC) obtained from the fit are shown in green. (b) Relative area of HBEC curves obtained from the fits as in figure (a) for different Cu concentrations. A peak in the area is obvious for $y = 0.0025$ (see text for details).

(Zn, Co)O nanoparticles. In addition to this, XPS measurements were also performed on the samples with zero copper concentration i.e. $Zn_{0.95}Co_{0.05}O$ in a similar energy range and the data are shown for reference. The systematic broadening of the Cu $2p_{3/2}$ peak observed for increasing Cu concentration implies the presence of a multi-component peak of Cu which can be de-convoluted into two peaks, labeled as 'high binding energy component' and 'low binding energy component', by fitting with a two-peak Gaussian function. The high binding energy component (933.5 eV) and low binding energy component (932.2 eV) have been assigned to the Cu^{+2} and Cu^{+1} charge states as displayed in figure 4(a). In general, core level binding energy increases with increasing positive valence of the ion [25]. It is worth noticing that the peak of Cu $2p_{3/2}$ at lower concentration (i.e. $y = 0.0013$, $y = 0.0025$) is almost symmetric (centered at 933.5 eV) and can be fitted by a single Gaussian function. However, with increasing Cu incorporation the peak begins to widen systematically towards the lower energy side and becomes more asymmetric, particularly for the Cu concentration $y \geqslant 0.005$. Since the data could only be fit in this range of compositions with a two-peak fit, it suggests that there is a mixed valence ionic state of Cu in the systems. Attributing the high binding energy component (HBEC) and low binding energy component (LBEC) peaks obtained from the fit to the Cu^{+2} and Cu^{+1} respectively, as discussed above, the ratio of Cu^{+1}/Cu^{+2} was estimated from the ratios of the areas under the peak for the respective peaks. This ratio is shown for different Cu concentrations in figure 4(b). It can be clearly seen that in the case of lower Cu concentration i.e. for the case of $y = 0.0013$ and 0.0025, where the peak was located almost symmetrically at $E \sim 933.5$ eV, almost all Cu is in the +2 ionic state. However, this ratio was observed to increase with further increase of Cu composition, suggesting that the number of Cu^{+1} ions increases more than those in the +2 state. This trend continues systematically with increasing Cu content, suggesting that higher Cu concentration favors the development of the Cu^{+1} ionic state. Chakraborti *et al* [26] have studied a similar system and have concluded that Cu exists in a mixed oxidation state of +1 and +2 [26] with Cu^{+2} being the dominant one, as also observed in our case. It has been argued that the existence of Cu in a mixed ionic state is likely to facilitate the presence of point defects [26] so as to retain charge neutrality in the system. Since the oxygen vacancies constitute the primary point defects in our system it is interesting to determine whether any connection exists between the two, namely the presence of Cu in the +1 state and the stabilization of oxygen vacancies. This correlation was studied by considering the XPS spectra of oxygen in our samples. In the inset of figure 5(a), we present a typical O 1s XPS spectrum of $Zn_{0.9475}Co_{0.05}Cu_{0.0025}O$, which clearly showed an asymmetric peak around 530 eV and with a shoulder at around 531.7 eV. The O 1s spectra can clearly be resolved into two components. The LBEC can be ascribed to O^{-2} ions in a wurtzite structure of hexagonal Zn^{+2} ion arrays, while the HBEC is attributed in the literature to O^{-2} ions in the oxygen deficient regions [27, 28]. All O 1s spectra were fitted by two symmetrical peaks (named LBEC and HBEC) and the ratio of the number of O ions neighboring the defect sites to those in normal positions was obtained from the ratios of the areas under the peak for the HBEC and LBEC peaks respectively. This ratio is typically used to give a qualitative indication of the concentration of vacancies in these systems [19, 29]. In figure 5(b) we show the plot of this ratio against the Cu concentration. It is clear from this figure that while for low Cu concentrations ($0 \leqslant y \leqslant 0.0025$) the relative area increases strongly, at higher Cu concentrations ($y \geqslant 0.0025$) it decreases with increase of Cu concentration. We interpret this as suggesting that the O vacancy concentration tends to increase strongly with increasing Cu content for low Cu content, while it peaks and begins to show a decrease for high enough Cu concentrations. When seen in conjunction with the aforementioned Cu 2p core spectra, it can be concluded that the concentration of oxygen vacancies increases with the increasing amount of Cu concentration in the range $0 \leqslant y \leqslant 0.0025$, where almost all the Cu ions are in the +2 ionic state. On the other hand the O vacancy concentration begins to decrease when Cu begins to enter in the +1 state as well. While no studies on the mutual stability of Cu impurities and O vacancies in ZnO have come to

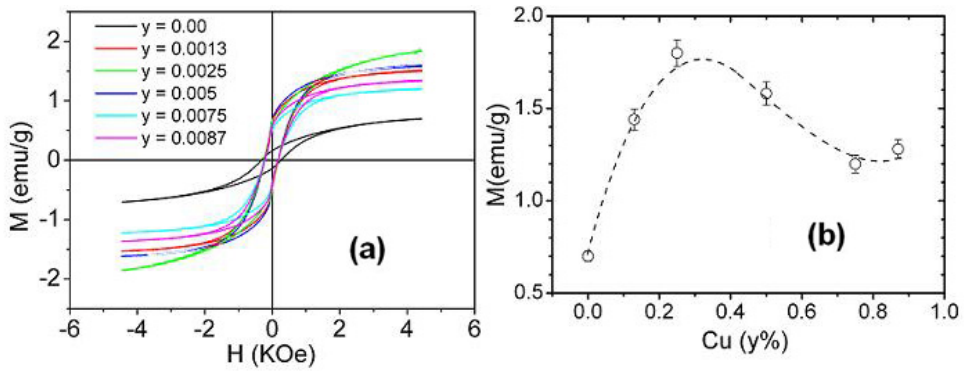

Figure 6. (a) Magnetization ($M(H)$) curves of $Zn_{0.95-y}Co_{0.05}Cu_yO$ ($0 \leqslant y \leqslant 0.0087$) nanoparticles measured at 300 K. (b) Variation of M_s (emu g^{-1}) with Cu concentrations. The peak in the moment is apparent for $y = 0.0025$.

our notice, a computational study [30] of the combined effects of oxygen vacancies and Cu dopants in a similar wide band gap doped semiconductor oxide, TiO_2, shows an interesting feature. It has been shown clearly that the presence of Cu impurities stabilizes the O vacancies and that the vacancies tend to reside close to the impurities [30]. Therefore, in view of our own results we may argue that the stabilization of oxygen vacancies occurs via the Cu in the +2 ionic state. However, higher Cu concentration also appears to allow the Cu +1 ionic state (in addition to the dominant +2 state) which correlates with the diminishing number of oxygen vacancies. This clearly shows that Cu in the +2 ionic states supports the formation of O vacancies while in the +1 state it destabilizes them. Why should Cu in the +1 state be unfavorable for the stabilization of the O vacancies? We understand this issue at least qualitatively as follows. The O vacancies create a region of positive charge in their neighborhood and this tends to attract and bind electrons (F-centers) thereby minimizing the system energy. In the +1 state of Cu fewer electrons are being made available (than in the +2 state) and the bare vacancies are made less stable as more and more of the Cu tends to go in the +1 state.

The magnetic properties of Cu co-doped (Zn, Co)O nanoparticles were investigated using a vibrating sample magnetometer (VSM) system. The magnetization versus magnetic field (M–H) data nanoparticles, annealed in the forming gas, showed a typical ferromagnetic hysteresis loop. All of the forming gas annealed samples showed ferromagnetic behavior, as can be seen from figure 6(a). In contrast to the samples annealed in forming gas, the air annealed samples showed non-magnetic behavior (data not shown here) down to 10 K, the lowest measured temperature. Furthermore, in the ZnO nanoparticles having only Cu as a dopant (Co=0%) no moment was observed in either air or A–H annealed samples, for these low Cu concentrations (Cu $< 1\%$). The variation of the magnetization with Cu content in the co-doped samples is shown in figure 6(b). It is noticeable that the moment varies in a non-monotonic manner, peaking at $y = 0.0025$ and decreasing steadily thereafter. It is noticeable that there is a very strong increase in the moment, from 0.7 to 1.8 emu g^{-1} (0.25 to 0.47 μ_B/Co) in the initial region. There have been several studies on the effects of Cu addition on the magnetization of Co-doped ZnO and these have addressed the issue of the role of hole mediated ferromagnetism [31–33]. Hole mediated ferromagnetism has been shown in these systems and the role of O vacancies has been seen to be deleterious to the formation of the FM moment [34]. These aforementioned studies were conducted, however, in a much higher range of Cu concentrations (Cu 5–15%). Furthermore, the carrier concentration was shown to be drastically decreased on the addition of Cu and was also related to the role of Cu^{+1} as a deep level acceptor impurity or to Cu^{+2} as an electron trap. We emphasize that our composition range (less than 1%) is well below most of these studies and the strong increase of the moment with Cu addition (in Zn–CoO) and its absence in the pure Zn–CuO nanoparticles reflects that Cu *itself* is definitely not developing a moment in this concentration range. The effect of Cu develops, as we shall substantiate later, indirectly, via its role in affecting the concentration of O vacancies. To illustrate this significant feature we consider the data of figure 6(b) along with figures 4(b) and 5(b) where we show the variation of the moment, the estimate of the Cu^{+1}/Cu^{+2} ratio and the estimate of oxygen vacancy concentration, as functions of the Cu concentration. It is apparent from a consideration of figures 5 and 6(b) that both the O vacancy concentration and the moment rise steadily until $y = 0.0025$, while both features show a very similar decline beyond it. Thus the rapid increase in the moment in this range clearly seems to be correlated with the formation of a higher O vacancy concentration and its concomitant effects on the ferromagnetism via, for example, the ability to form magnetic polarons. To further strengthen the hypothesis that the decrease of magnetization observed beyond $y = 0.0025$ is a correlated effect of increasing Cu^{+1} ions and the destabilizing of oxygen vacancies, we performed longer time anneals of the samples in the reducing atmosphere, thereby generating more vacancies. The samples all had a fixed Co content of 4% and had variation of the Cu content in the same manner as described earlier. The samples were annealed in the forming gas for different times, namely 6, 8 and 10 h. One may expect, as discussed above, that the longer time annealed samples would have a higher O vacancy concentration. The data for the variation of the moment with Cu content in these three sets of samples are shown in figure 7. Interestingly we find that the position of the peak

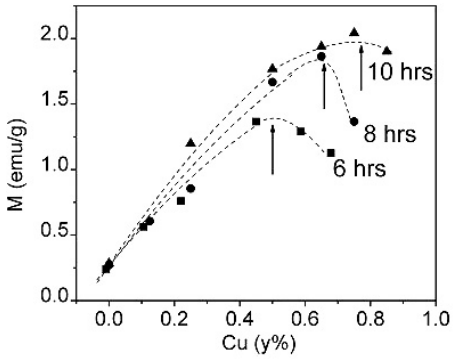

Figure 7. M_s versus Cu concentrations in $Zn_{0.96-y}Co_{0.04}Cu_yO$ nanoparticles annealed for 6, 8 and 10 h respectively in the forming gas at 600 °C. (Squares: 6 h; circles: 8 h; up-triangles: 10 h.) Arrows indicate positions of the peaks for the indicated annealing times. Dashed lines are a guide to the eye only. The shift in the position of the peak in M_s to higher Cu concentrations with increased annealing time is apparent.

in the moment shifts systematically to higher Cu content with longer annealing times. For instance, the peak for the 6 h annealed samples occurs at $y = 0.005$, while for the 8 h annealed samples it occurs at $y = 0.0065$ and finally for the 10 h annealed samples it seems to be at $y = 0.0075$. We interpret this shift in the peak position as illustrating the feature that when a larger concentration of O vacancies is created, there are a large number of defects for mediating the ferromagnetism. It therefore requires a larger concentration of the Cu to initiate a sufficient number of Cu^{+1} ions in the system that may destabilize the O vacancy concentration sufficiently for the moment to start decreasing.

Hence the development of the ferromagnetic moment in the Cu co-doped system in our range of concentrations is a competition between the role of O vacancies in promoting ferromagnetism and the role of Cu as Cu+1 in destabilizing the vacancy and hence weakening the ferromagnetism. Therefore the role of Cu in promoting ferromagnetism in this limited concentration range ($x < 1\%$) appears to be indirect, i.e. via its role in the stabilization of O vacancies. It is also noticeable that the maximum moment for the three different sets of annealed samples appears to reach ∼2 emu g^{-1} or 0.47 μ_B/Co thereby illustrating that the different annealing conditions simply shift the Cu percentage at which the Co ions attain their maximum value without affecting the value of the maximum moment.

4. Conclusions

The aforementioned correlation between oxygen vacancy concentration and FM can be understood on the basis of the FCE coupling model [35]. According to this model, the magnetic exchange among magnetic impurities is mediated by carriers (electrons in this case) that are weakly bound to the oxygen vacancies, which later can be considered to be the center of the distortion that polarizes the Co spins within a certain radius to form the magnetic polarons. In this model the randomly distributed Co ions are strongly overlapping in the presence of oxygen vacancies. We understand the effect of Cu dopants in the initial range of concentration (up to the observed maximum in moment) as enhancing this overlapping by increasing the concentration of oxygen vacancies, leading to a more effective F-center interaction which results in a stronger FM behavior. The reduction of magnetization in the system, with further increase of Cu dopants, appears to be related to the increased tendency of Cu to go in as a Cu^{+1} ion, reducing the number of available carriers, and resulting apparently in the destabilization of some of the oxygen vacancies. In this (higher) range of Cu concentrations the smaller number of oxygen vacancies that are present possibly generate discontinuities in the exchange coupling between the magnetic polarons, thereby weakening the FM and lowering the observed moment.

In conclusion, we have shown that in the very low concentration region of Cu co-doping in a ferromagnetic Zn–Co O system, the role of Cu is initially to stabilize the ferromagnetism via the generation of additional O vacancies while at higher Cu content the number of vacancies is reduced as soon as Cu starts to enter the system in a +1 ionic state. Therefore, central to the magnetic behavior in our system is the role of O vacancies in promoting ferromagnetism in Co-doped ZnO. We may safely conclude that any other defects or dopants that are non-magnetic in themselves may indirectly affect the magnetic behavior of the system if they affect the concentration of the vacancies.

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References

[1] Michael H, Mao H S, Feick H, Yan H, Wu Y, Kind H, Weber E, Richard R and Yang P 2001 *Science* **292** 1897–9
[2] Gao P X and Wang Z L 2005 *J. Appl. Phys.* **97** 044304
[3] Gulia V and Kumat S 2007 *Opt. Mater.* **29** 778–82
[4] Müller J and Weißenrieder S 1994 *J. Anal. Chem.* **349** 380–4
[5] Ohno H 1998 *Science* **281** 951
[6] Ueda K, Tabata H and Kawai T 2001 *Appl. Phys. Lett.* **79** 988
[7] Kawano K, Nakata R and Sumita M 1991 *Appl. Phys. Lett.* **58** 1742
[8] Saeki H, Tabata H and Kawai T 2001 *Solid State Commun.* **120** 439
[9] Radovanovic P V and Gamelin D R 2003 *Phys. Rev. Lett.* **91** 157202
[10] Sato K and Yoshida H K 2002 *Semicond. Sci. Technol.* **17** 367
[11] Spaldin N A 2004 *Phys. Rev.* B **69** 125201
[12] Bergqvist L, Eriksson O, Kudrnovský J, Drchal V, Korzhavyi P and Turek I 2004 *Phys. Rev. Lett.* **93** 137202
[13] Schwartz D A and Gamelin D R 2004 *Adv. Mater.* **16** 2115
[14] Yan L, Ong C K and Rao X S J 2004 *Appl. Phys.* **96** 508
[15] Han S J, Song J W, Yang C H, Park S H, Park J H and Jeong Y H 2002 *Appl. Phys. Lett.* **81** 4241
[16] Buchholz D B, Chang R P H, Song J H and Ketterson J B 2005 *Appl. Phys. Lett.* **87** 082504
[17] Nakano Y, Morikawa T, Ohwaki T and Taga Y 2006 *Appl. Phys. Lett.* **88** 172103

[18] Wardle M G, Goss J P and Briddon P R 2005 *Phys. Rev.* B **71** 155205
Risbud A S, Spaldin N A, Chen Z Q, Stemmer S and Seshadri R 2003 *Phys. Rev.* B **68** 205202
[19] Naeem M, Hasanain S K, Kobayashi M, Ishida Y, Fujimori A, Buzby S and Shah S I 2006 *Nanotechnology* **17** 2675–80
[20] Naeem M, Hasanain S K and Mumtaz A 2008 *J. Phys.: Condens. Matter* **20** 025210
[21] Chambers A *et al* 2002 *J. Magn. Magn. Mater.* **246** 124
[22] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 *Handbook of X-Ray Photoelectron Spectroscopy* (Eden Prairie, MN: Perkin-Elmer)
[23] Hsu H S, Huang J C A, Huang Y H, Liao Y F, Lin M Z and Lee C H 2006 *Appl. Phys. Lett.* **88** 242507
[24] Liu X-C *et al* 2008 *J. Phys.: Condens. Matter* **20** 025208
[25] Hufner S 2003 *Photoelectron Spectroscopy, Principles and Applications* (Berlin: Springer)
[26] Chakraborti D, Ramachandran S, Trichy G, Narayan J and Prater J T 2007 *Appl. Phys. Lett.* **101** 053918
[27] Ye J D, Gu S L, Qin F, Zhu S M, Liu S M, Zhou X, Liu W, Hu L Q, Zhang R, Shi Y, Zheng Y D and Ye Y D 2005 *Appl. Phys.* A **81** 809–12
[28] Chen M, Pei Z L, Sun C, Wen L S and Wang X 2001 *Mater. Lett.* **48** 94–198
[29] Rumaiz A K, Ali B, Ceylan A, Boggs M, Beebe T and Shah S I 2007 *Solid State Commun.* **144** 334–8
[30] Errico L A, Rentería M and Weissmann M 2005 *Phys. Rev.* B **72** 184425
[31] Lin H-T, Chin T-S, Shih J-C, Lin S-H, Hong T–M, Huang R-T, Chen F-R and Kai J-J 2004 *Appl. Phys. Lett.* **85** 621
[32] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 *Science* **287** 1019
[33] Spaldin N A 2004 *Phys. Rev.* B **69** 125201
[34] Ye L-H, Freeman A J and Delley B 2006 *Phys. Rev.* B **73** 033203
[35] Coey J M D, Douvalis A P, Fitzgerald C B and Venkatesan M 2004 *Appl. Phys. Lett.* **84** 1332