

Soft-x-ray spectroscopic investigation of ferromagnetic Co-doped ZnO

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The electronic properties of cobalt-doped ZnO were investigated through site-selective and element-sensitive x-ray-absorption spectroscopy in the vicinity of the Co $L_{2,3}$ edge, the oxygen K edge, and at the Zn L_3 edge. The spectroscopic measurements of the ferromagnetic cobalt-doped ZnO films appear to have additional components in the O K edge x-ray-absorption spectrum not observed in the undoped films. The observed features may derive from both hybridization with unoccupied Co $3d$ states and also from lattice defects such as oxygen vacancies. Only minor changes in the Zn L_3 edge spectra were observed. These observations are consistent with a polaron percolation model in which the ferromagnetic coupling is mediated by shallow donor electrons trapped in oxygen vacancies and couples the Co atoms substituted on Zn sites in the hexagonal wurtzite ZnO structure. © 2006 American Institute of Physics. [DOI: [10.1063/1.2165916](https://doi.org/10.1063/1.2165916)]

Dilute magnetic semiconductors (DMS) are an especially interesting area of research because of their potential applications in spin electronics and magneto-optics. DMS based on the wide-band-gap semiconductor ZnO doped with a transition metal have been predicted theoretically to be good candidates for room-temperature ferromagnetism.¹ Subsequently Ueda *et al.*² reported ferromagnetism in Co-doped ZnO. Following their work many conflicting reports have attributed the origin of ferromagnetic behavior as being due to substitution by Co atoms in the ZnO²⁻⁶ or due to clustering of Co atoms in secondary phases that are ferromagnetic;⁷ while others report no ferromagnetic behavior even though Co occupies the substitutional sites.⁸ Three different mechanisms have been proposed to explain the origin of ferromagnetism in transition-metal-doped ZnO: (I) A model of ferromagnetism where there is an exchange interaction mediated by carriers in the valence or conduction band and the localized moment of the ion,¹ (II) a double exchange mechanism in which hopping of $3d$ electrons from one ion to the next results in ferromagnetic behavior,⁹ and (III) an impurity band model¹⁰ where localized ionic moments create magnetic polarons in a defect-related donor impurity band. Clearly, it is desirable to find a way to distinguish between these models and to decide whether any of them is the correct model for doped ZnO systems. Hence, it

is important to verify that the transition-metal dopants occupy the Zn site and that ferromagnetism can result. In light of earlier reports such as that of Wi *et al.*⁸ substitutional cobalt may be a necessary but not sufficient condition for ferromagnetism. This realization may reconcile some of the apparently conflicting experimental reports.

In this report, element specific soft-x-ray-absorption techniques were used to help address the origin of room-temperature ferromagnetism in Co-doped ZnO grown by pulsed laser deposition (PLD). The power of x-ray-absorption spectroscopy (XAS) at the Co $L_{2,3}$ edge allows the identification of the oxidation state and site symmetry of the cobalt ions. The O K edge and Zn L edge XAS spectra were also measured and it is believed that oxygen defect-related features in the O K edge absorption are observed. All samples studied were thin films prepared by PLD. Targets were first prepared by thoroughly mixing the stoichiometric high-purity oxide powders; these were then pressed into pellets and sintered at 1100 °C for 24 h. Films were deposited on (0001) Al₂O₃ substrates maintained at 450 °C during deposition in an oxygen atmosphere of 10⁻⁵ Torr. A KrF excimer laser operating at 248 nm, 10 Hz repetition rate, and a fluence of 1.8 J cm⁻² was used to ablate the pressed powder. Details of sample growth were previously reported by Venkatesan *et al.*⁵ It should be noted that the observed ferromagnetic behavior is very sensitive to the growth conditions. X-ray-diffraction measurements confirm the c -axis-oriented growth of wurtzite zinc oxide (w -ZnO) free from secondary phases. All the films are approximately 250 nm thick as determined by using optical reflectivity at

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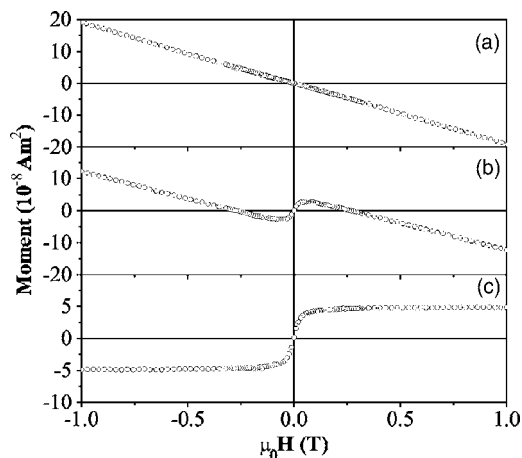


FIG. 1. Room-temperature magnetization of (a) a blank sapphire substrate, (b) $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ film on sapphire, and (c) that of the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ film after subtracting the diamagnetic contribution from the substrate.

635 nm during the growth process and independently calibrated by small-angle x-ray scattering in thinner films.

The electronic properties of a homogenous film produced from a $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ target and a film of ZnO were studied by XAS. XAS measurements were performed in both total electron yield (TEY) and total fluorescence yield (TFY) modes at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. Fluorescence yield was measured using a channeltron positioned 30° directly above the incident x-ray beam, while electron yield was recorded by the sample drain current method. In this report all the XAS spectra presented were recorded in TEY mode with no difference observed in the TFY measurements. All XAS measurements were performed in a near grazing incidence geometry with the synchrotron light incident at $\sim 20^\circ$ to the surface and the electric field vector of the polarized radiation at $\sim 20^\circ$ to the c axis of the w -ZnO which was perpendicular to the surface of the film. No contribution to the oxygen K edge XAS spectrum was expected from the substrate due to the film thickness and the grazing incidence measurement geometry. This was confirmed by comparing normal versus grazing incidence spectra (TEY versus TFY), by comparison with a measured reference spectrum of the Al_2O_3 substrate, and by comparison to a thinner (50 nm) cobalt-doped ZnO film. The XAS energy scale at the oxygen K edge was calibrated by comparison with reference spectra of NiO (Ref. 11) and by comparison with the Co metal for Co $L_{2,3}$ edges.¹² The oxygen K edge and cobalt $L_{2,3}$ edge XAS spectra were measured with 0.2 and 0.1 eV energy resolutions, respectively.

Ferromagnetism at room temperature was confirmed in these cobalt-doped ZnO samples using a Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer. Shown in Fig. 1 are the room-temperature magnetization data for a $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ film measured with the field applied perpendicular to the film.⁵ Figure 1(a) shows the diamagnetism of a blank sapphire substrate subjected to the same thermal cycle in the deposition chamber as one with a thin film on it; the susceptibility of $4.8 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$ agrees well with the accepted value of sap-

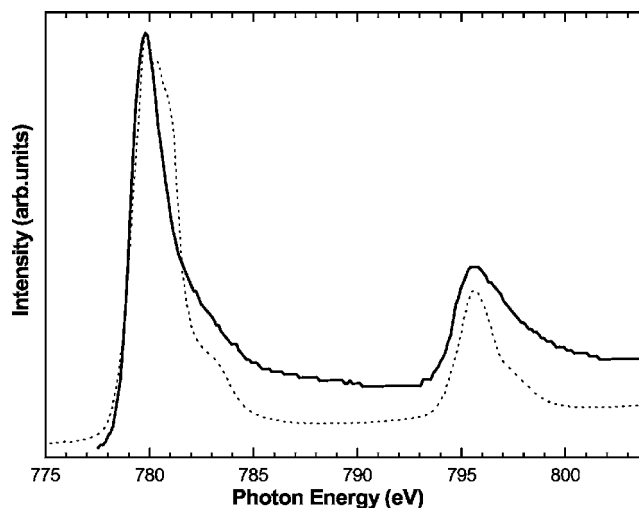


FIG. 2. Co $L_{2,3}$ edge x-ray absorption in total electron yield of the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ (dashed line) and Co metal (solid line). The total fluorescent yield (not shown) is similar.

phire. Figure 1(b) shows the data for a Co-doped ZnO film on the c -cut sapphire substrate. The ferromagnetic signal remaining after subtraction of the linear diamagnetic background is shown in Fig. 1(c). The film is ferromagnetic with a room-temperature magnetic moment of $1.5 \text{ A m}^2 \text{ kg}^{-1}$. The measured magnetization corresponds to a net ferromagnetic moment of $0.3 \mu_B/\text{Co}$.

Figure 2 shows the comparison of XAS spectra of a $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ film and Co metal at the Co $L_{2,3}$ edges. The L edge absorption spectrum must be modeled through atomic multiplet theory to account for all allowed $2p$ to $3d$ transitions in the appropriate crystal field.¹³ The observed structure of the Co L_3 edge, in particular, is sensitive to the local symmetry and environment of the metal atom.^{13,14} The line shape and the spectra near the edge are similar to several of the previously reported spectra from both magnetic⁶ and nonmagnetic⁸ Co-doped ZnO. Furthermore, the observed spectra are similar to several atomic multiplet configuration interaction calculations confirming that Co occurs in the Co^{2+} state in a tetrahedral crystal field.^{6,14} This serves to confirm that cobalt occupies the Zn substitutional sites in ZnO. The spectral line shape is consistent with a theoretical spectrum calculated with a crystal-field splitting of $10 Dq (T_d) = 1 \text{ eV}$ (Ref. 14), although strictly the site symmetry in w -ZnO is C_{3v} . The spectral line shape is completely different from that of cobalt metal; hence the possibility of extensive clustering of Co seems to be ruled out for the doped sample.

Figure 3 shows the comparison of the O K edge XAS spectrum from the undoped ZnO film and the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ film. In the undoped ZnO and the doped ZnO the spectral features are similar. The spectral features can be interpreted as follows: the region between 530 and 538 eV can be attributed mainly to O $2p$ hybridization with highly dispersive Zn $4s$ states which form the bottom of the conduction band with the peak at $\sim 537 \text{ eV}$ being due to transitions to nondispersive O $2p_z$ and $2p_{x+y}$ states. The region between 539 and 550 eV can be assigned to O $2p$ hybridized with Zn $4p$ states, and above 550 eV the spectrum is due to the O $2p$ with Zn $4d$ hybridized states.¹⁵ However, the doped sample

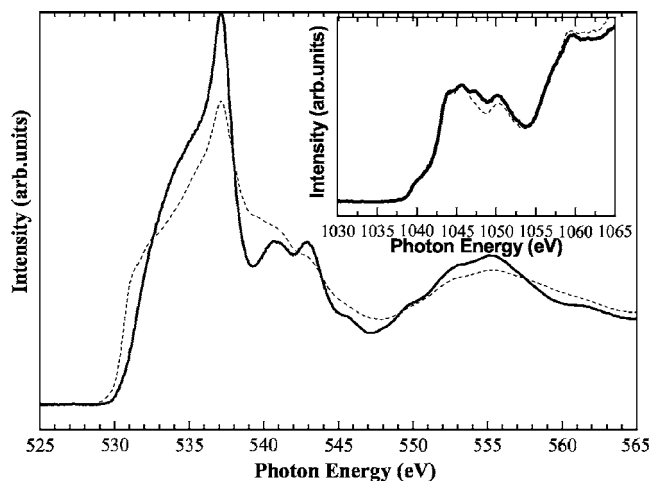


FIG. 3. O K edge x-ray absorption of the undoped ZnO film (solid line) and $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ film (dashed line). The inset shows a comparison of the Zn L_3 edge XAS spectra of ZnO and $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ films. The spectra are normalized to unit area for comparison purposes and were recorded in TEY mode.

shows two extra features at $\sim 531\text{--}532$ eV, close to the conduction-band minimum where these new features can be assigned, by comparison with theoretical calculations, as being the result of cobalt $3d$ states hybridized with O $2p$ states. Furthermore, there is an observed difference in onset for the O K XAS spectrum in the two samples of ~ 0.5 eV. This is much larger than the observed decrease in the band gap of ~ 0.1 eV which has been measured by optical transmission in similar Co-doped ZnO films grown under the same conditions. In addition, the broadening of the spectral features observed in the doped sample, particularly in relation to the peak at ~ 537 eV, is thought to be due to the presence of oxygen vacancies. Calculations indicate that the presence of an oxygen vacancy affects the surrounding shell of the oxygen atoms by effectively altering their $1s$ binding energies in that and subsequent shells surrounding the vacancy. In XAS the $1s\text{-}2p$ dipole excitation for transitions originating from these oxygen atoms (that is, in the shells surrounding a vacancy) can result in a shifting of the XAS onset to lower absorption energies. This lowering and distribution of $1s$ binding energies also give rise to an effective broadening of all the conduction-band features as observed by XAS. It should be noted that the PLD-grown ZnO film has an oxygen K edge XAS spectrum very similar to ZnO powder with no noticeable broadening of the peak at 537 eV or a shift in the onset of the edge.¹⁶ Thus although the defect density may be expected to be similar in the two films, it could be that the presence of both the Co doping and the defects results in an exaggerated effect on the oxygen $1s$ binding energies. (The oxygen $1s$ binding energies in the native oxides, CoO and ZnO, differ by at most 0.2 eV.)

The inset of Fig. 3 shows the Zn L_3 edge absorption spectra, where there is relatively little difference between the undoped ZnO and the doped ZnO. The spectral shape agrees well with the electron-energy-loss spectroscopy reports¹⁷ as well as the XAS spectrum obtained from ZnO nanorods¹⁸ and that of ZnO powder.¹⁶ Thus there appears to be no significant Zn defect-related features such as Zn interstitials. From consideration of the x-ray-absorption measurements

from both the oxygen K edge and the Zn L edge, it might be surmised that oxygen vacancies or oxygen-related defects dominate rather than Zn defects such as interstitials.

It is known that certain atomic defects in ionic crystals, such as oxygen vacancies with trapped electrons or holes, may have low-lying triplet states that overlap to form an impurity band.¹⁹ It is suggested that the magnetic defects may interact by long-range interactions mediated by the impurity band to give a ferromagnetic ground state.¹⁰ These XAS observations provide further evidence that the observed magnetic moment is consistent with the spin split impurity band model predicted by Coey *et al.*¹⁰

These spectroscopic measurements on undoped ZnO and Co-doped ZnO PLD-grown films exhibit material-specific defect features in the oxygen spectra. Also, this is an experimental evidence from the oxygen K edge x-ray absorption that shows the combined effects of the hybridized Co states and oxygen vacancies. The shift in the onset of the oxygen K edge XAS of 0.5 eV is proposed to be due to the presence of oxygen vacancies, a view reinforced when considered in conjunction with optical measurements that exhibit a band-gap narrowing of only 0.1 eV. The cobalt substituted in the zinc cation site and the presence of oxygen vacancies may be jointly responsible for the observed ferromagnetism. Much work needs to be done to identify the nature of these defects and to understand better the magnetism of these magnetic materials.

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