Study of the O K-edge XANES of Cobalt-doped ZnO diluted magnetic semiconductors

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Abstract. Cobalt-doped ZnO samples were prepared by both sol-gel and magnetron sputtering methods, respectively. Co atoms have incorporated into the ZnO lattice and located at the substitutional sites of the Zn atoms in all samples, while the sol-gel prepared Zn1-xCoxO samples show paramagnetism and the sputtering prepared CoyZn1-yO samples appear ferromagnetism. The calculated O K-edge X-ray absorption near edge structure (XANES) can commendably reproduce all of the peaks observed in CoyZn1-yO samples when one Zn interstitial atom (Zni) nears the central O atom. Compared with the magnetic properties, it is shown that the Zn interstitial atoms play a key role to the observed ferromagnetism in CoyZn1-yO samples.

1. Introduction
ZnO-based diluted magnetic semiconductors (DMSs) had been prepared by both physical and chemical methods, but the observations showed that the magnetic properties of oxide based films are highly sensitive to the preparation conditions. [1-3] Even in systems that appear to be quite pure, reported magnetic behavior can vary widely, ranging from room-temperature ferromagnetism [1] to paramagnetism [2]. This variance in magnetism is attributed to the multitude of synthetic methods used for the production of DMSs materials, which can result in differences in dopant environment, structural disorder or defects. Under the theory of bound magnetic polarons [3], researchers have increasingly found that the defects have remarkable influence to the magnetism of materials, and that a careful control of defects in ZnO and not the doping with magnetic ions might be a better way to obtain reproducible intrinsic high-Tc ferromagnetism in ZnO [4].

In this letter, we use the X-ray absorption near edge structure (XANES) spectroscopy, which is a powerful technique for the probing of the arrangement of atoms and distributions of impurities, to study differences between the samples prepared by equilibrium and non-equilibrium state methods. FEFF8.2 software [5] is used to simulate the XANES spectra with different defects’ models. Compared with experimental spectra, we find directly proof that the shallow donor Zni is the key of the ferromagnetism in Cobalt-doped ZnO sample.

2. Experimental
The Zn$_{1-x}$Co$_x$O DMS samples were prepared by the sol-gel method using Zn(CH$_3$COO)$_2$·H$_2$O and Co(CH$_3$COO)$_2$·H$_2$O as starting precursors, de-ionized water as a solvent, and polyvinyl alcohol as a stabilizing agent. [6] On the other side, the Co$_x$Zn$_{1-x}$O DMS films were prepared on glass substrates by alternately sputtering very thin Co layers of nominal thickness of 0.6 nm and ZnO layers of nominal thickness of 1.2 nm for 60 periods at room temperature [7] (the nominal structure is Co$_{0.33}$Zn$_{0.67}$O). The O K edge XANES spectra of Co-doped ZnO samples were measured at the U18 beamline of the National Synchrotron Radiation Laboratory. The beam from a bending magnet was monochromatized with a varied line-spacing plane grating and refocused by a toroidal mirror. The data were collected in a mode of sample drain current under a vacuum better than $5 \times 10^{-5}$ Pa.

3. Results and Discussion

The Co K-edge XANES for Co$_x$Zn$_{1-x}$O samples with different Co doping concentration is shown in figure 1. There is a distinct step during the edge of Co metal’s spectrum, and jumping-off point of the K-edge of Co metal is 7700 eV which is less than 7710 eV for Co-doped ZnO samples. This result implies that Co metal phase doesn’t exist in all of our samples. Figure 2(a) shows the O K-edge XANES spectra of Co$_x$Zn$_{1-x}$O samples, and figure 2(b) gives the O K-edge XANES spectra of Zn$_{1-x}$Co$_x$O samples. The spectra of pure ZnO, CoO and Co$_3$O$_4$ reference compounds are also exhibited in these figures. It is shown that the spectra of CoO and Co$_3$O$_4$ both have a shape and strong peak before 530 eV. It is indicated that there are no CoO or Co$_3$O$_4$ phases in our samples.

![Figure 1. The Co K-edge XANES spectra for Co$_x$Zn$_{1-x}$O, Zn$_{0.95}$Co$_{0.05}$O samples and ZnO, Co metal reference compounds.](image)

![Figure 2. (a) The O K-edge XANES spectra of Zn$_{1-x}$Co$_x$O, ZnO and Co$_3$O$_4$ samples; the insert figure shows paramagnetism of Zn$_{0.95}$Co$_{0.05}$O; (b) The O K-edge XANES spectra of Co$_x$Zn$_{1-x}$O, ZnO and CoO samples; The insert figure shows ferromagnetism of Co$_{0.25}$Zn$_{0.75}$O at 5, 80 and 290 K.](image)

In figure 1, it can be found that the spectra of Co$_x$Zn$_{1-x}$O are similar to the Zn$_{0.95}$Co$_{0.05}$O sample’s curve. The first peak $a'$ and the second peak $b'$ both exit in the postedge of Co$_x$Zn$_{1-x}$O samples, while the intensity has been weakened by the disorder of lattice. These evidences indicate that the local structure of Co atoms in the Co$_x$Zn$_{1-x}$O and Zn$_{1-x}$Co$_x$O samples must be similarly. As we have demonstrated that the Co atoms in Zn$_{1-x}$Co$_x$O ($x<0.05$) are incorporated into the ZnO lattice and located at the substitutional sites of the Zn atoms [6], the Co atoms have also taken the place of Zn site and entered the Co$_x$Zn$_{1-x}$O samples lattice.

In figure 2, the insert figures have shown the magnetic properties measured by a superconducting
quantum interference device (SQUID). The \( \text{Zn}_{0.95}\text{Co}_{0.05}\text{O} \) sample prepared by sol-gel method shows paramagnetic behavior, while the Curie temperature of \( \text{Co}_{0.25}\text{Zn}_{0.75}\text{O} \) samples prepared by sputtering is at least near room temperature. As the local structures of these different samples have been investigated that the Co atoms have entered into the \( \text{ZnO} \) lattice, the related magnetism is intrinsic property. It is puzzle what causes the different magnetic property, when Co atoms have incorporated into the \( \text{ZnO} \) lattice of both kinds of samples. Then, we turn to the \( \text{O} \) \( K \)-edge XANES spectra of the Co-doped \( \text{ZnO} \) samples. Strikingly, the \( \text{Co}_y\text{Zn}_{1-y}\text{O} \) films exhibit identical spectral features which quite different from those of \( \text{Zn}_{1-x}\text{Co}_x\text{O} \). These distinctly different XANES spectral behaviors demonstrate that the local electronic structure of these two kinds’ samples is quite different. In order to find out the differences between these two kinds Co-doped \( \text{ZnO} \) system, the FEFF8.2 code is used to simulate the XANES spectra with the models containing the different defects in host lattice. For each model structure, 125 atoms are used to achieve convergence of the XANES calculations.

Lee et al. have found that the ferromagnetic coupling has a short ranger nature, effective at Co-Co distances of about 3 Å, [8] which implying Co clustering may influence the ferromagnetism of the Co-doped \( \text{ZnO} \) DMS. Different structural models were considered, by replacing, respectively, one, two, three and four the nearest \( \text{Zn} \) neighbors of \( \text{Co}_y \) with Co atoms. Hereafter, these models are named as 1 \( \text{Co}_5 \), 2 \( \text{Co}_5 \), 3 \( \text{Co}_5 \), and 4 \( \text{Co}_5 \). In figure 3(a), the calculated XANES spectra are plotted together with the experimental spectra of \( \text{Zn}_{0.95}\text{Co}_{0.05}\text{O} \) sample. It is seen that the main features of the experimental spectra can be reproduced by the 1 \( \text{Co}_5 \) model, including peaks A, B, and C. From the \( n \) \( \text{Co}_5 \) Models, it can be found that the intensity of peak A increases with \( n \). This is because that peak A is associated with the hybridization between \( \text{Co} 3d \) and \( \text{O} 2p \) state. The increased number of Co nearest neighbors around a given O ion enhances the transition probability. These results indicate that the \( \text{Co}_5 \) ions have cluster together via O atoms in \( \text{Zn}_{0.95}\text{Co}_{0.05}\text{O} \) sample. As magnetic properties predominantly determined by the nearest-neighbor distance of Co ions [9] and Co clustering randomly distribute in the lattices of \( \text{Zn}_{1-x}\text{Co}_x\text{O} \) samples [6], the magnetic moment of these Co clustering should be disorder. Therefore, the sol-gel prepared \( \text{Zn}_{1-x}\text{Co}_x\text{O} \) samples show paramagnetism in macroscopy.

![Figure 3](image-url)

**Figure 3.** (a) \( \text{O} \) \( K \)-edge XANES spectra of \( \text{Zn}_{0.95}\text{Co}_{0.05}\text{O} \) sample, and the calculated spectra for different structural models by replacing one, two, three, and four the nearest \( \text{Zn} \) neighbors of \( \text{Co}_5 \) with Co atoms. (b) \( \text{O} \) \( K \)-edge XANES spectra of \( \text{Co}_y\text{Zn}_{1-y}\text{O} \) (\( y=0.20, 0.25 \)) samples, and the calculated spectra for different structural models by placing one \( \text{Zn} \) atom inside the nearest neighbors, and replacing one, two, three and four the nearest \( \text{Zn} \) neighbors of \( \text{Co}_5 \) with Co atoms.
Gamelin et al. have indicated that the Zn may introduce an impurity band in Co-doped ZnO, so the native shallow donor interstitial zinc is capable of activating high-Tc ferromagnetism in Co-doped ZnO [10]. Different structural models with Zn$_i$ atoms have also been considered. We named these models as 1 Zn$_i$ + $n$ Co$_S$. Experimental O K-edge XANES spectra for the Co$_{0.25}$Zn$_{0.75}$O and Co$_{0.20}$Zn$_{0.80}$O samples and calculated XANES spectra are shown in figure 3(b). Compared with the experimental spectra, peaks (a, b, c, d) in samples have been commendably reproduced in the calculated spectra for 1 Zn$_i$ +1 Co$_S$. These peaks can only be found in Co$_y$Zn$_{1-y}$O samples prepared by sputtering, and not existed in Zn$_{1-x}$Co$_x$O samples prepared by the sol-gel method or the pure ZnO sample. It is directly indicated that the spectral features of the O K-XANES spectra for Co$_y$Zn$_{1-y}$O samples is caused by the appearance of Zn$_i$ atoms. In conclusion, the appearance of Zn$_i$ atoms is the difference between Zn$_{1-x}$Co$_x$O and Co$_y$Zn$_{1-y}$O samples.

4. Conclusion

In summary, we have employed the XANES technique at O-K edge to investigate the influences with different defects in Co-doped ZnO samples prepared by sol-gel and sputtering methods. It is found that Co clustering existed in sol-gel prepared Zn$_{1-x}$Co$_x$O samples. As the disorder of magnetic moment, the Zn$_{1-x}$Co$_x$O samples show paramagnetism. Compared with Co$_y$Zn$_{1-y}$O samples, we find the directly proof that Zn$_i$ is the key of the ferromagnetism in Co$_y$Zn$_{1-y}$O sample. Our results further show that the room temperature ferromagnetism can be achieved by the control of Zn$_i$ in ZnO DMSs.

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