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Evidence of substitutional Co ion clusters in $Zn_{1-x}Co_xO$ dilute magnetic semiconductors

Zhihu Sun,[1,2] Wensheng Yan,[1] Guobin Zhang,[1] Hiroyuki Oyanagi,[1,2] Ziyu Wu,[1,3] Qinghua Liu,[1] Wenqing Wu,[1] Tongfei Shi,[1]
Zhiyun Pan,[1] Pengshou Xu,[1] and Shiqiang Wei[1,*]
[1]*National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China*
[2]*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan*
[3]*Institute of High Energy Physics, Chinese Academy of Science, Beijing 100039, People's Republic of China*
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Structural studies become increasingly important for understanding the nature of magnetic properties in dilute magnetic semiconductors (DMSs) [K. Ando, Science **312**, 1883 (2006)]. In this work, x-ray absorption fine structure (XAFS) at both Co and O *K* edges is used to investigate the Co occupation sites and distributions in $Zn_{1-x}Co_xO$ thin films with low Co concentrations ($x=0.005, 0.02$). Co *K*-edge XAFS analysis indicates unambiguously that the doped Co ions are substantially incorporated into the ZnO host lattice. However, the O *K*-edge XAFS spectral features are strikingly different from those of ZnO and $Zn_{1-x}Co_xO$ reported in the literature so far, and can be reproduced by the assembling of substitutional Co ions around intervening oxygen atoms. This provides experimental evidence for numerous theoretical predications that the substitutional Co ions in ZnO tend to gather together. It is expected that similar phenomenon can also be observed by XAFS in a number of other ZnO-, GaN-, and TiO_2-based DMSs for which the clustering of substitutional dopants have been previously predicted.

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I. INTRODUCTION

The field of spintronics has attracted significant attention recently for its potential in providing the enhanced functionality and performance in semiconductor devices.[1] One of the promising candidate materials for future spintronics technologies is dilute magnetic semiconductor (DMS) with room-temperature ferromagnetism.[2] A large number of theoretical studies have predicted the ferromagnetic behaviors with a Curie temperature T_C of above room temperature for transition metal (TM) doped ZnO-based DMSs.[3] However, numerous contradicting experimental results on the magnetic order in ZnO-based DMS have been reported, ranging from spin-glass behavior, paramagnetism to ferromagnetism with a T_C below or above room temperature.[3,4] Even for the obtained high-temperature ferromagnetic materials, the origin of ferromagnetism is still under debate. For understanding these controversial results concerning the nature of magnetic properties in DMSs, structural studies has become increasingly important.[5]

It has been widely accepted that magnetic interactions, Curie temperature, and electronic properties of DMSs are crucially dependent on the amount of TM ions and their distributions over different positions (such as substitutional site, interstitial site, or secondary phases) in the host lattice. In order to investigate the occupation sites of the doped TM ions in ZnO-based DMSs, numerous structure studies using x-ray absorption fine structure (XAFS) have been performed.[6–15] The results have shown that for the TM-doped ZnO at a low doping level (typically $<5\%$), the TM ions are really incorporated substitutionally into the host lattice as expected. However, because magnetic interactions between TM ions in the DMS systems are strongly dependent on their separation distances,[16] a further understanding of the spatial distribution of these substitutionally doped TM ions is essential.[17]

To interpret the experimental observations on DMSs, it is widely assumed that the substitutional dopants are homogeneously and randomly distributed in the host.[14,18–20] Many authors assumed a random distribution of Co ions in substitutional $Zn_{1-x}Co_xO$, and estimated the probability for a given Co ion to have n ($n=0,1,2\ldots12$) other Co next-nearest neighbors to be $C_{12}^n x^n(1-x)^{12-n}$. On the other hand, density-functional theory (DFT) calculations on Co- or Mn-doped ZnO systems have predicted that Mn_{Zn} and Co_{Zn} ions substituting Zn sites tend to cluster together through an intervening oxygen atom,[8,21–24] rather than distribute themselves uniformly throughout the lattice as widely assumed.[14,18–20] These clusters are embedded in the host ZnO lattice and maintain the wurtzite structure, completely different from the metallic precipitates[6,25] in nature. In the uniform distribution configuration for a dilute system, the average distance between TM ions are quite large, so magnetic interactions are long-ranged and mediated by electron or hole carriers.[21,26,27] On the contrary, in the clustering configurations of substitutional TM ions, the magnetic properties are predominantly determined by interactions between TM ions over a small distance seperation.[16] Therefore, the clustering of Co_{Zn} and Mn_{Zn} dopants could significantly influence the magnetic orderings. Unfortunately, to date the clustering of Mn_{Zn} and Co_{Zn} ions in Mn- or Co-doped ZnO has not been evidenced experimentally.

In this work, we will employ the XAFS technique at both Co and O *K* edges to study Co occupation sites in $Zn_{1-x}Co_xO$ ($x=0.005, 0.02$) thin films. We will take advantage of the sensitivity of the x-ray absorption near-edge structure (XANES) spectroscopy to the three-dimensional arrangement of atoms to detect the spatial distribution of Co dop-

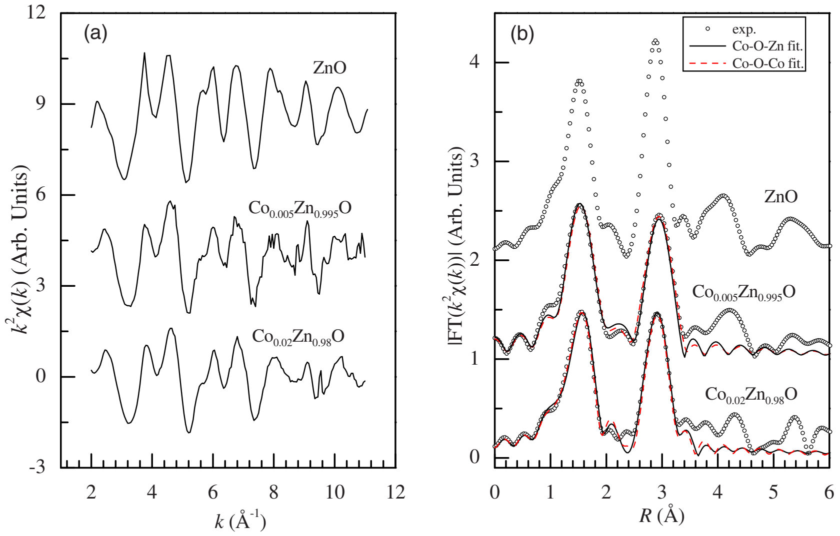

FIG. 1. (Color online) (a) Co K-edge EXAFS $k^2\chi(k)$ functions for $Zn_{1-x}Co_xO$ and the Zn K-edge function for ZnO powder, and (b) their Fourier transforms (empty circles). The solid lines and dashed lines in (b) show the fitting results by assuming all the next-nearest neighbors of Co to be Zn and Co, respectively. It is seen that in both cases, the fitting quality is almost equally good.

ants. The experimental spectra in conjunction with the theoretical calculations for Co ions located at different positions in ZnO will provide an excellent test on the possibility of forming Co_{Zn} clusters, and may lead to a fundamental understanding of their structural properties.

II. EXPERIMENT

$Zn_{1-x}Co_xO$ ($x=0.005,0.02$) thin films were deposited on Si(100) substrates by pulsed laser deposition (PLD) method. Targets were prepared by thoroughly mixing the stoichiometric high-purity (>99.99%) ZnO and CoO powders using standard ceramic techniques. Both films were prepared at 650 °C in an oxygen ambient pressure of 1×10^{-4} Pa. A pulsed KrF excimer laser with a wavelength of 248 nm and repetition rate of 5 Hz was used. The thickness of the films is approximately 100 nm. The crystalline structures of the films are of the single-phase wurtzite structure as determined by x-ray diffraction with θ-2θ scan.

The Co K-edge XAFS spectra of $Zn_{1-x}Co_xO$ thin films were measured in a grazing-incidence geometry with a grazing-incidence angle 1° at beamline BL13B1 of Photon Factory (PF) of High Energy Accelerator Research Organization, Japan. The electron-beam energy of PF was 2.5 GeV and the maximum stored current was about 450 mA. The water-cooled Si(111) plane double-crystal monochromator and a Ge pixel array detector with 100 segments were used.[28] The energy resolution was better than 2 eV at 9 keV, calibrated from the near-edge features of copper metal at the Fermi energy, E_f (8980.3 eV). The O K-edge XANES spectra were measured at beamline U19 of National Synchrotron Radiation Laboratory, China. The beam from a bending magnet was monochromatized with a varied line-spacing plane grating and refocused by a toroidal mirror. An energy range from 100 to 1000 eV is covered with a resolution of about 0.2 eV. The data were recorded in the total electron yield (TEY) mode by collecting sample drain current under a vacuum better than 5×10^{-5} Pa.

III. RESULTS AND DISCUSSIONS

Co K-edge extended-XAFS (EXAFS) $k^2\chi(k)$ functions for $Zn_{1-x}Co_xO$ and their Fourier transforms (FT) are shown in Figs. 1(a) and 1(b), respectively. The Zn K-edge function for wurtzite ZnO powder is also shown as a reference. One can see from Fig. 1(a) that the overall oscillation shapes of $Zn_{1-x}Co_xO$ are very close to that of the ZnO powder. Like ZnO, the $Zn_{1-x}Co_xO$ films also exhibit four FT peaks located at 1.5, 2.9, 4.1, and 5.3 Å, respectively. We quantitatively fit the first two peaks at 1.5 and 2.9 Å assuming the Co substitution for Zn sites in ZnO, including the nearest Co-O and the second-nearest Co-Zn correlations. This structure model can give a good fitting quality as displayed by solid lines in Fig. 1(b). The extracted interatomic distances, $R_{\text{Co-O}}=1.99\pm0.01$ Å and $R_{\text{Co-Zn}}=3.26\pm0.02$ Å, are correspondingly close to the Zn-O and Zn-Zn distances in ZnO. All these results manifest that Co ions occupy the Zn sites in ZnO as expected from the low doping concentrations, in agreement with previous reports.[6,10]

However, it should be kept in mind that Co and Zn scatterers can be hardly distinguished from each other, because of their close atomic numbers and similar characteristics of scattering photoelectrons. This means that the EXAFS data of $Zn_{1-x}Co_xO$ could also probably be reproduced if all the next-nearest neighbors of the central Co atom are Co, instead of Zn as we assumed. To verify this scenario, we fit again the Co K-edge EXAFS data by considering the nearest Co-O and the next-nearest Co-Co correlations. The fitting results plotted in Fig. 1(b) as dashed lines indicate the good fitting quality, and the extracted distance of $R_{\text{Co-Co}}=3.27\pm0.02$ Å is very close to $R_{\text{Co-Zn}}=3.26\pm0.02$ Å we obtained. These quantitative analyses demonstrate that Co K-edge EXAFS is not able to distinguish the atomic species of the next-nearest neighbor of Co atoms. In other words, it cannot tell us if the substitutional Co_{Zn} ions are randomly distributed or clustered together around oxygen atoms.

One may suspect that the Co K-edge XANES spectroscopy, which is sensitive to three-dimensional atomic arrangement and electronic structures, is probably able to provide information on distinguishing the randomly distributed or clustered Co_{Zn} ions. For this purpose, we plot in Fig. 2 the Co K-edge XANES spectra of $Zn_{1-x}Co_xO$, along with the reference spectrum of rock-salt structured CoO. Both $Zn_{1-x}Co_xO$ films exhibit quite similar XANES features, in which four peaks A_1 (7710.3 eV), B (7725.5 eV), C (7739

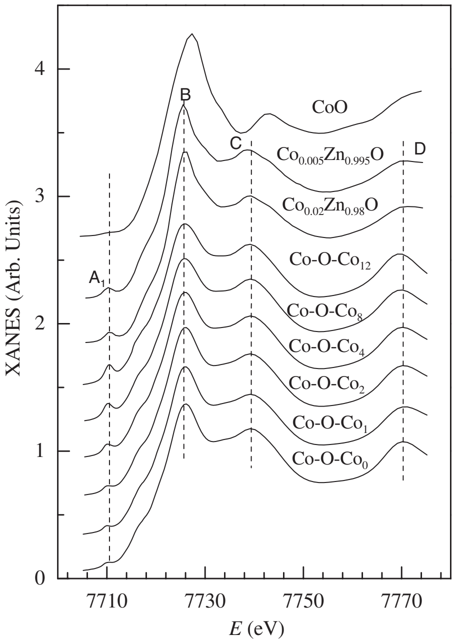

FIG. 2. Co *K*-edge XANES spectra of $Zn_{1-x}Co_xO$ ($x = 0.005, 0.02$) thin films, rock-salt structured CoO, and the calculated spectra for different structural models by replacing zero, one, two, four, eight, and twelve next-nearest Zn neighbors of Co_{Zn} with Co atoms.

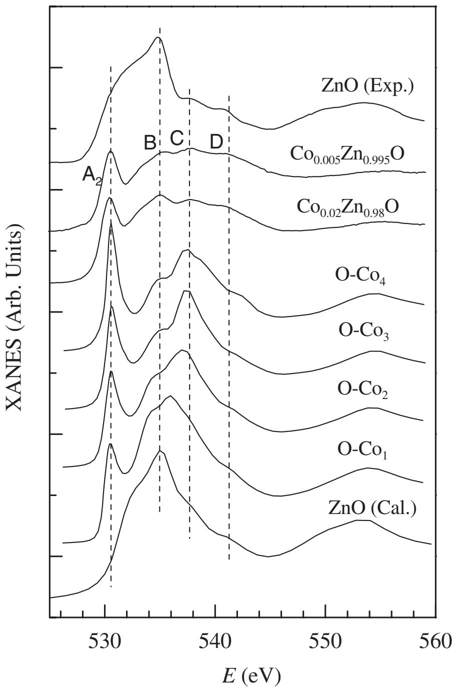

FIG. 3. O *K*-edge XANES spectra of $Zn_{1-x}Co_xO$ ($x = 0.005, 0.02$) thin films, ZnO powder, and the calculated spectra for different structure models by replacing one, two, three, and four Zn nearest neighbors of the absorbing O atom with Co.

eV), and *D* (7771 eV) can be observed. The spectral shapes resemble those of Co-substituted ZnO reported by a number of authors [9–13,15] and once again confirm the Co substitution in ZnO. The existence of rock-salt CoO phase in both samples can be excluded by the different spectral features of $Zn_{1-x}Co_xO$ as compared with that of CoO.

In order to investigate the XANES features of randomly distributed and clustered Co_{Zn} ions, *ab initio* multiple-scattering XANES calculations at Co *K* edge were performed using the FEFF8.4 code[29] and FDMNES code[30] within the muffin-tin approximation. Different structural models were considered, by replacing, respectively, zero, one, two, four, eight, and twelve next-nearest Zn neighbors of Co_{Zn} with Co atoms. Hereafter we name these models as Co-O-Co_0, Co-O-Co_1, Co-O-Co_2, Co-O-Co_4, Co-O-Co_8, and Co-O-Co_{12} clusters. Co-O-Co_0 represents the random distribution of Co_{Zn}, while Co-O-Co_n ($n > 0$) corresponds to clustering of Co_{Zn}. The construction of these model structures was based on the structural parameters obtained from the EXAFS fitting. For each model structure, 125 atoms were used to achieve convergence of the XANES calculations. We compared the XANES spectra calculated by FEFF8.4 and FDMNES codes and found that the corresponding spectral features are quite similar, except that the position of the pre-edge peak A_1 can be more precisely reproduced by FDMNES. In Fig. 2, the calculated XANES spectra of these Co-O-Co_n clusters by FDMNES are plotted together with the experimental spectra of $Zn_{1-x}Co_xO$ films. It is seen that the main features in the postedge region, including peaks *B*, *C*, and *D*, are quite similar for all the Co-O-Co_n clusters. The only difference lies in the pre-edge region, where the intensity of peak A_1 increases with *n*. This is because that peak A_1 is associated with the transition of Co 1*s* electron to 4*p*-3*d* hybridized states in the tetrahedral environment.[31] The increased number of Co next-nearest neighbors around a given Co ions increases the density of unoccupied states and enhances the transition probability. In the pre-edge region, the experimental Co *K*-edge XANES of the $Zn_{1-x}Co_xO$ films matches better with the calculated spectra for the clustering configurations Co-O-Co_n ($n > 0$) than for the isolated Co_{Zn}. This result implies that the Co_{Zn} ions may cluster together via O atoms, but not evidently.

We now turn to the normalized O *K*-edge XANES spectra of the $Zn_{1-x}Co_xO$ thin films as shown in Fig. 3. Strikingly, the $Zn_{1-x}Co_xO$ films exhibit identical spectral features which are, however, quite different from those of ZnO. A strong pre-edge peak A_2 (530.6 eV) is present for $Zn_{1-x}Co_xO$ but appears only as a shoulder for ZnO. Moreover, the strong peak *B* (535.0 eV) appearing in the spectrum of ZnO is greatly reduced in height as a result of Co substitution for Zn, even at a very low Co concentration of 0.005. The distinctly different XANES spectral behaviors of ZnO and $Zn_{1-x}Co_xO$ demonstrate that the local electronic structures of ZnO are greatly modified by Co substitution. It is noteworthy to mention that our O *K*-edge XANES features are also entirely different from those of Co-substituted ZnO reported in the literature.[26,32–35] In these works, the O *K*-edge XANES spectra of $Zn_{1-x}Co_xO$ only show a slight decrease in intensity or sometimes with a small shift of the edge position, but the overall spectral features resemble that of undoped ZnO. Such a strong peak A_2 has never been observed before for $Zn_{1-x}Co_xO$ system, no mater if structural defects such as O vacancies[32,34,35] or Co interstitials[26] exist or not. Therefore, our samples cannot be modeled by either random distribution of Co_{Zn} ions in ZnO or the presence of Co_{Zn} plus some structural defects.

It is rather interesting to explore the reason for the appearance of such a strong peak A_2 in our $Zn_{1-x}Co_xO$ samples. As is well known, the pre-edge region of 530–535 eV for ZnO results from O $2p-$Zn $3d$ hybridized states in the band gap,[36] and the absorption intensity in this region has become a measure of the hybridization strength of the material.[37] For undoped ZnO, all of the $3d$ orbitals are completely occupied, therefore there is not any sharp feature in the energy range below 535 eV. When Co substitutes for the Zn site in ZnO, an empty Co $3d$ impurity band with t_{2g} symmetry is formed within the band-gap region.[16,18,21] This impurity band is strongly hybridized with O $2p$ states and may give rise to a pre-edge peak in O K-edge XANES. For checking the influence of Co substitution on the intensity of peak A_2 and examining the possibility of Co_{Zn} clustering via O atoms as well, we considered four model structures of replacing one, two, three, and four Zn nearest neighbors of the absorbing O atom by Co, denoted as O-Co_1, O-Co_2, O-Co_3, and O-Co_4 cluster, respectively. For the purpose of comparison, we also calculated the O K-edge XANES of undoped ZnO. All these O K-edge XANES spectra were calculated by FEFF8.4 code and are plotted in Fig. 3.

As shown in Fig. 3, the intensity of A_2 increases rapidly with the number of clustered Co ions. In the case of O-Co_1 and O-Co_2, the produced positions of peaks B, C, and D shift to the lower energy side and do not coincide with the experiment. Better agreement between experiment and calculation occurs for O-Co_3 and O-Co_4 clusters, for which the main features of A_2, B, and C are reproduced at almost the same positions as the experimental spectra, but peak D is shifted to a slightly higher energy. One can notice that the peak intensities for the clusters are not well reproduced by the calculations; especially the intensity of peak C is remarkably overestimated. Even in this case of undoped ZnO, the calculated intensity of peak C is also much stronger than that of the experimental spectrum. Therefore, it is most possible that the not well-reproduced peak intensity can be ascribed to the inherent errors of the XANES calculations. Combing the Co K-edge XAFS results, we can reach a qualitative conclusion that in these PLD-grown samples the Co atoms are gathering together via the connecting O atoms. This means that in these samples, the Co atoms are not randomly distributed in the ZnO host as generally assumed, and provide experimental evidence for many theoretical predictions that in Co doped ZnO systems, the Co_{Zn} ions tend to assemble together.[8,21–24] The cluster structure can also be regarded as the formation of wurtzite structured CoO embedded in the ZnO lattice. Moreover, we have to mention that the present XANES study can only assess the existence of O-Co_3 or O-Co_4 clusters as basic Co_{Zn} clustering unit in the studied samples, but they can also aggregate to form larger clusters. Therefore, various configurations with diverse local atomic arrangements might coexist, which results in the large structural disorder in the films and strongly reduces the peak intensities than model calculations. We point out that similar phenomenon may also occur for other ZnO, GaN, and TiO_2-based DMS systems, in which the substitutional magnetic ions have been predicted to have a strong tendency to gather together.[8,17,38]

According to our analysis of the projected densities of states generated by FEFF8.4 and previous DFT calculations,[32,35] peak B is assigned to the transition of O $1s$ electron to the unoccupied O $2p$ states in the conduction band, and peaks C and D arise from O $2p$ states hybridized with Zn and Co $4p$ states, respectively. The much lower intensity of peak B for $Zn_{1-x}Co_xO$ than for ZnO can be interpreted by two possible reasons arising from the formation of Co_{Zn} clusters. One reason is that the transition matrix element, which is strongly dependent on the neighboring atoms,[39] is greatly modified. Another reason is that the O $2p$ states in the conduction band are driven to shift downward and therefore become broadening and dispersive.[33]

Finally, we address the key but puzzling observation of the specific features of the O K-edge XANES for the studied samples. We recall that the Co concentrations in our samples are only 0.005 and 0.02, so the probability of an O atom surrounded simultaneously by two or more Co ions is very low. From the random distribution assumption of Co ions, the probability for a given O atom to have at least one Co nearest neighbor is $1-(1-x)^4$. This means that even at the higher Co concentration of 0.02, this probability is only 7.7%. The clustering of Co ions can increase this probability, but not strongly. Therefore, in these samples, the local environment of O atoms is principally pure ZnO alike, and the strong peak A_2 for the Co_{Zn} clusters should be smeared out by the dominant contribution of ZnO, since XAFS is an averaged local structure probe. However, this deduction is contrary to the experimental observation. To answer this puzzling question, the TEY detection method to record the O K-edge XANES should be noted. Due to the short escape depth (3–5 nm) of electrons in this energy range, the O K-edge XANES can only reflect structural information within 3–5 nm below the surface. We propose that the observed strong peak A_2 can be possibly ascribed to the outdiffusion of Co_{Zn} clusters to the surface. As a result, a Co-rich near-surface region is formed and is responsible for the observed specific spectra. The outdiffusion mechanism of TM ions has been proposed in other DMS systems, such as Mn-doped GaAs,[40] Co-doped TiO_2,[4] and Mn-doped Ge.[41,42] In Ref. 41, the authors observed higher Curie temperature for a Mn_xGe_{1-x} alloy prepared through room-temperature ion implantation and subsequent 400 °C annealing than for a monocrystalline Mn_xGe_{1-x}, and ascribed this to a strong diffusion of Mn atoms toward the surface of Ge nanocrystals. From the aspect of mobility of Co dopants, our samples were grown at a relatively high temperature of 650 °C. At this temperature, the doped Co ions are rather mobile and consequently, the clustering of substitutional Co ions and their outdiffusion are feasible.

IV. CONCLUSION

In summary, we have employed the XAFS technique at both Co and O K-edges to investigate the local atomic structures of $Zn_{1-x}Co_xO$ ($x=0.005,0.02$) thin films prepared by PLD. The EXAFS and XANES analyses of Co K-edge spectra reveal that all of the Co ions are substantially incorporated into ZnO as expected. However, the Co *K*-edge spectra provide limited information on the spatial distribution of Co ions because of the similarity between Co and Zn scattering atoms. The O *K*-edge XANES spectra, however, display a strikingly different features than those of Co-substituted ZnO reported so far in the literature. *A* detailed O *K*-edge XANES analysis indicates that in these samples, the substitutional Co_{Zn} ions are most possibly gathering together via intervening oxygen atoms. This result provides experimental evidence for numerous theoretical predications that Co_{Zn} ions dissolved in ZnO have a tendency to cluster, rather than distribute themselves evenly throughout the lattice. Furthermore, we propose that the specific O *K*-edge XANES caused by Co clusters may be ascribed to the outdiffusion of these clusters toward the surface. We expect that XAFS can also be used to observe similar phenomenon in other ZnO-, GaN-, and TiO_2-based DMS systems for which the clustering of substitutional magnetic ions have been previously predicted.

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[*] Author to whom correspondence should be addressed; sqwei@ustc.edu.cn

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