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Magnetism of (Zn,Co)O thin films probed by x-ray absorption spectroscopies

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We report on the electronic and magnetic properties of Co-doped ZnO thin films investigated by x-ray absorption spectroscopies and element selective magnetometry. For a low Co concentration (around 5%), we evidence a paramagnetic phase clearly correlated to Co^{2+} ions substituted to Zn in the ZnO matrix. For higher Co concentrations (around 25%), we demonstrate the coexistence of both paramagnetic and ferromagnetic phases. The use of advanced element and orbital selective techniques allows us through the distinct spectral signature of Co in ionic or metallic states to assign the ferromagnetic phase to the presence of Co in a metallic state as a consequence of Co metal clustering in our films. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2829610]

The diluted magnetic semiconductor (DMS) $Zn_{1-x}Co_xO$ has been the subject of considerable interest due to a first report on the existence of a stable ferromagnetic phase.[1] The earliest theoretical papers predicted that the ferromagnetic phase is stabilized by *n*-type doping and further stabilized by raising the cobalt content in the compounds.[2] On the contrary, other papers claimed that this ferromagnetic phase is stabilized by *p*-type doping.[3] In addition to this theoretical debate, the experimental results are also controversial. A number of reports categorically attribute the observed magnetic signal (ferromagnetic or paramagnetic) to the dilute phase, whereas others claim that ferromagnetism originates from cobalt clusters. The origin of ferromagnetism in this DMS is thus, unclear today.[4]

The magnetic properties of $Zn_{1-x}Co_xO$ thin films are generally investigated by superconducting quantum interference device magnetometry. This conventional technique is not well adapted to the study of DMS thin films and more generally of low moment ferromagnets. Actually, the magnetization of DMS such as Co doped ZnO is very weak and comparable or smaller than parasitic magnetic signals from the substrate. Only few groups have used x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) which are more appropriate techniques to characterize the magnetic properties.[5,6] In addition, these XMCD studies investigated either the Co $L_{2,3}$ edges or the Co *K* edge and were performed only at high magnetic fields. These previous studies do not allow to discern clearly between a ferromagnetic and a paramagnetic phase which leaves open alternative interpretations for the work of Ref. 5, which claimed an intrinsic ferromagnetic phase from extrapolation of high magnetic field XMCD data.

In this letter, we exploit the elemental selectivity of XAS at both Co $L_{2,3}$ and Co *K* edges, at remanence (no applied field) and at high magnetic fields, in order to investigate the electronic and magnetic properties of $Zn_{1-x}Co_xO$ thin films on a local scale. This technique is particularly well adapted to the study of $Zn_{1-x}Co_xO$ as it permits to distinguish between cobalt atoms in ionic and metallic states.

Thin films of $Zn_{1-x}Co_xO$ ($x=0.05$ and $x=0.25$) were grown on sapphire (0001) substrates by pulsed laser deposition using stoichiometric targets. More details on growth, macroscopic structural and magnetic properties are published elsewhere.[7] XAS and XMCD measurements at Co $L_{2,3}$ and *K* edges were performed, respectively, at the ID08 and ID12 beamlines of the European Synchrotron Radiation Facility, Grenoble, France. XAS and XMCD spectra at cobalt $L_{2,3}$ edges ($2p \rightarrow 3d$ transitions) were recorded in total electron yield (TEY) mode with the photon wave vector and the applied magnetic field perpendicular to the sample surface. The circular polarization rate at ID08 of the photons is close to 100%.

In Fig. 1(a), we compare typical XAS spectra recorded at the Co $L_{2,3}$ edges for $Zn_{1-x}Co_xO$ ($x=0.05$ and $x=0.25$) and a reference metallic cobalt thin film (protected by a 25 Å thick Al_2O_3 layer). The major difference between these spectra lies in the presence of fine structures at the $L_{2,3}$ edges and a smaller background absorption between the L_3 and L_2 edges for $Zn_{1-x}Co_xO$. This background absorption, attributed to photoelectron excitations into the continuum states, is smaller for oxides because 3*d* orbitals are more localized. The multiplet structures originate from discrete $2p \rightarrow 3d$ transitions and they are the signatures of the localized 3*d* orbitals of cobalt ions. These multiplets are also present in the XMCD spectra recorded at high magnetic field [Fig. 1(b)]. From these data only, we can just state that the magnetic component at high magnetic field can be mainly attributed to Co in an ionic state. To further confirm the ionic state of Co,

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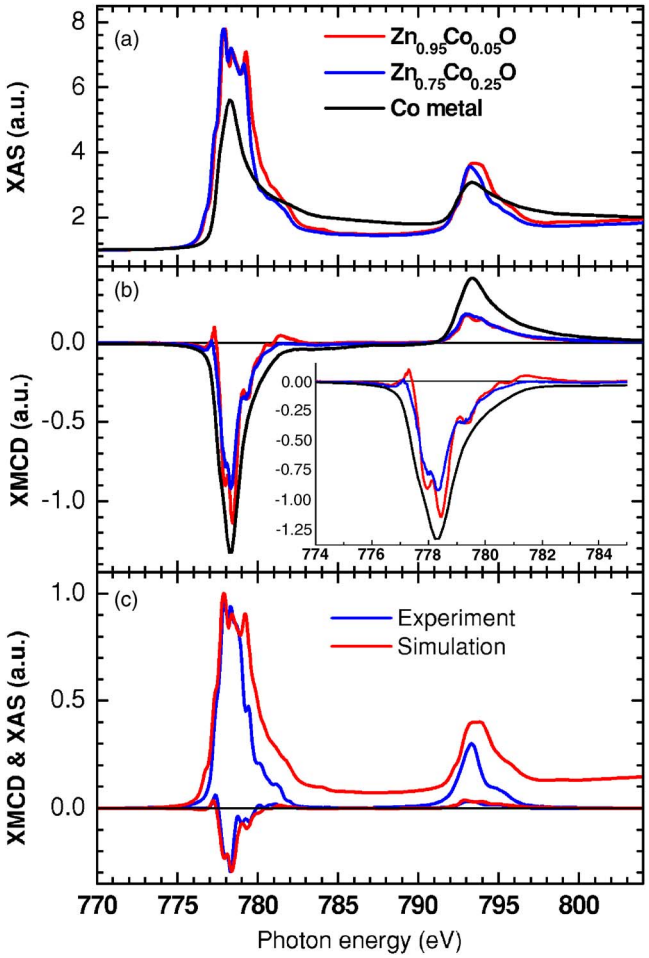

FIG. 1. (Color online) (a) XAS and (b) XMCD spectra measured at the Co $L_{2,3}$ edges for $Zn_{0.95}Co_{0.05}O$ (red), $Zn_{0.75}Co_{0.25}O$ (blue), and a Co metal thin film reference. The spectra were recorded in TEY at $T=10$ K and $H=3$ T. A zoom of the L_3 edge XMCD is shown in inset of (b). (c) Comparaison of experimental (blue) and simulated (red) isotropic XAS (upper part) and XMCD (lower part) for $Zn_{0.95}Co_{0.05}O$.

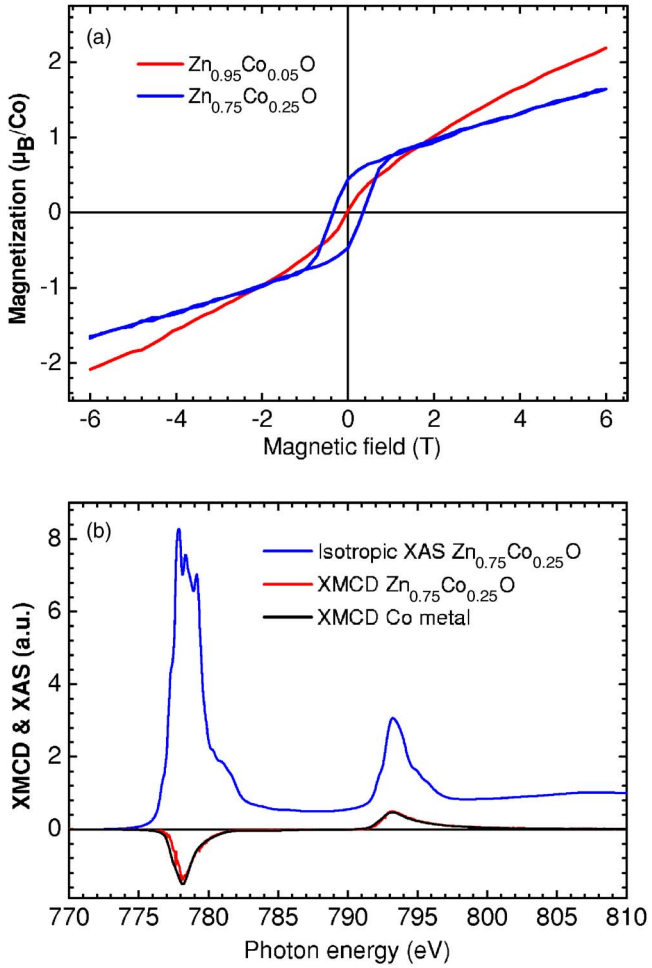

FIG. 2. (Color online) (a) XMCD magnetization loops measured at the Co L_3 edge for $Zn_{0.95}Co_{0.05}O$ (red), $Zn_{0.75}Co_{0.25}O$ (blue). (b) XAS and XMCD (times 7) spectra for $Zn_{0.75}Co_{0.25}O$ and a Co metal thin film reference measured in remanence (no applied magnetic field). All the spectra were recorded at $T=10$ K.

we have calculated the absorption spectra using the code developed by Cowan known as the atomic multiplet approach.[8] The instrumental broadening of the transitions as well as the broadening due to the finite lifetime of the core hole have been set to the values corresponding to the experimental setup at the ID08 beamline and to the lifetime of the corehole at the L_3 and L_2 edges. We emphasize that using literature values of the crystal field parameters[9] as well as stating that the absorber is Co in a Co^{2+} ionic state in a crystal field with C_3 symmetry, the simulated XAS and XMCD spectra reproduce very well the experimental data at the L_3 edge [Fig. 1(c)]. The agreement between the simulated spectra and the experimental data is less obvious at the L_2 edge due to the much shorter core-hole lifetime. The good agreement between experimental and simulated spectra show that Co is mainly present in the films as Co^{2+} substituting for Zn in the ZnO lattice. Furthermore, the magnetic signal at high magnetic fields is mainly due to the contribution of these ions.

To obtain better insight on the origin of magnetism in these $Zn_{1-x}Co_xO$ thin films, we have performed XMCD magnetometry at the cobalt L_3 edge. It is important to note that we probe only Co in the films avoiding any substrate contribution to the magnetic signal. XMCD loops at $T=10$ K as a function of magnetic field applied perpendicular to the plane are shown in Fig. 2(a). The magnetization curve of the 5% Co film is a characteristic of a paramagnetic behavior (absence of hysteresis) with no evidence of saturation up to 6 T. On the other hand, the magnetization curve for the 25% Co film is strikingly different. We observe clearly a hysteresis loop at low magnetic fields (below 1 T), characteristic of ferromagnetism, and a paramagnetic component at higher magnetic fields as in the 5% Co film.

In order to elucidate the origin of the ferromagnetic phase for the 25% Co film, we have performed XAS and XMCD measurements at Co $L_{2,3}$ edges at remanence [Fig. 2(b)]. Since XAS is sensitive to all cobalt ions, a multiplet structure (characteristic of the ionic state) is again present. In contrast, XMCD at remanence is insensitive to paramagnetic ions and probes only the ferromagnetic phase of the sample. Unexpectedly, the XMCD spectrum does not exhibit fine structures and, moreover, shows a striking similarity with the reference metallic cobalt film [Fig. 2(b)]. This suggests that the ferromagnetic component in the 25% Co film originates from cobalt metal clustering confirming recent structural studies.[10]

The total Co magnetic moments at 6 T and 10 K calculated from XAS and XMCD spectra and using the magneto-optical sum rules[11,12] are about $2.2\mu_B$ and $1.6\mu_B$ for $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.75}Co_{0.25}O$, respectively. These mag-

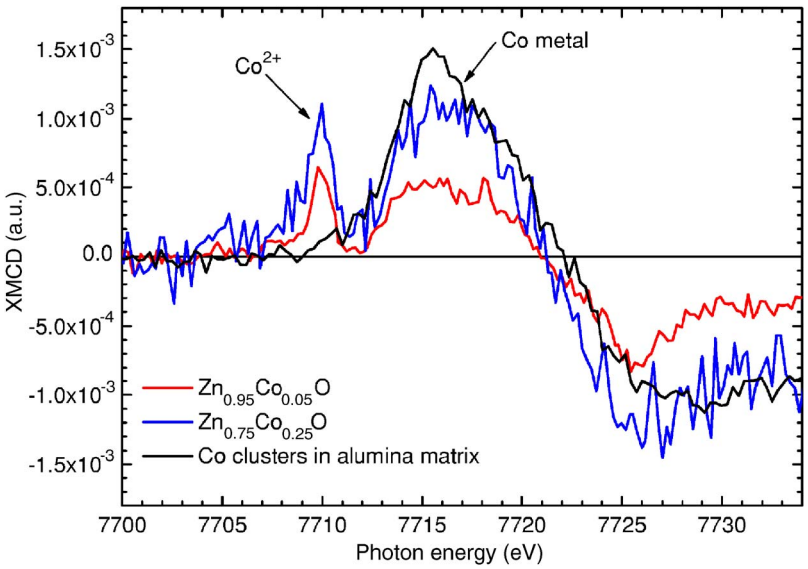

FIG. 3. (Color online) XMCD spectra measured at the Co *K* edge for $Zn_{0.95}Co_{0.05}O$ (red), $Zn_{0.75}Co_{0.25}O$ (blue), and Co metallic clusters (black) embedded in an alumina matrix. The spectra were recorded in TFY at $T=10$ K and $H=6$ T.

netic moments are smaller than the theoretical value of Co^{2+} ($m_S=3.0\mu_B$ and $m_L=0.5\mu_B$). This reduction has several origins difficult to disentangle such as the lack of magnetic saturation, the antiferromagnetic interactions between nearest neighbor Co^{2+} ions, and the presence of Co metal clusters which have a lower Co magnetic moment ($1.7\mu_B$).

In order to identify irrevocably the two magnetic phases, we have performed x-ray absorption near edge structure and XMCD measurements at the Co *K* edge, which probe $1s \rightarrow 4p$ transitions. Measurements were performed at the ID12 beamline of ESRF at 10 K and 6 T in total fluorescence yield mode (TFY). In contrast to the experiments at the Co $L_{2,3}$ edges, this detection mode probes the entire film thickness. Since XMCD signals of cobalt in ionic state or metallic state occur at different energies, we can separate easily the magnetic signals originating from cobalt ions and cobalt clusters. Thus, we can separate easily the magnetic signals originating from cobalt ions and cobalt metal clusters. XMCD spectra at Co *K* edge for the two $Zn_{1-x}Co_xO$ films and metallic Co clusters embedded in alumina[13] are compared in Fig. 3. For the $Zn_{1-x}Co_xO$ films, two positive dichroic peaks (at 7710 and 7715 eV) are clearly observable. The first one corresponds to Co^{2+} ions, whereas the latter one coincides with the dichroic peak observed for metallic cobalt clusters in alumina. Co *K* edge measurements thus reveal that in both $Zn_{1-x}Co_xO$ films (even for low cobalt concentration) two magnetic phases coexist. One is associated to Co^{2+} ions and the other to metallic cobalt clusters. Despite the presence of these metallic cobalt clusters, we did not observe remnant magnetization for low cobalt concentration at the Co L_3 edge (Fig. 2). This is probably related to the very small fraction of Co metal in the $Zn_{0.95}Co_{0.05}O$ film and a possible inhomogeneous distribution of Co clusters in the films with a higher cluster density next to the substrate as already observed for Co doped TiO_2.[14] This further demonstrates the unique advantage of combining XAS and XMCD at different edges and using different detection methods to vary the probing depth.

In summary, we have performed XAS and XMCD measurements at both cobalt $L_{2,3}$ and *K* edges on $Zn_{1-x}Co_xO$ thin films. We demonstrate that a meticulous XAS and XMCD investigation can reveal unequivocally the electronic and magnetic properties of diluted magnetic semiconductors. We provide convincing evidence that in cobalt doped zinc oxide thin films two magnetic phases coexist, a paramagnetic phase associated to cobalt in ionic state and an extrinsic ferromagnetic phase associated to metallic cobalt clusters.

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