Absence of ferromagnetism in bulk polycrystalline $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$

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The atomic structure and the magnetic properties of 5 and 10 at. % Co-doped ZnO samples prepared by a high-pressure and high-temperature method have been investigated by various techniques, including x-ray diffraction with Rietveld refinements, scanning electron microscopy, high-resolution transmission electron microscopy, nanometer-sized element mapping, x-ray photoelectron spectroscopy, near-edge x-ray absorption fine structure, and extended x-ray absorption fine structure and magnetization measurements. It is found that Co ions with a valence of 2+ substitute Zn ions in the wurtzite ZnO structure. No metallic or oxidic Co-rich clusters were detected in the samples. If Co^{2+} ions substitute Zn^{2+} ions, no intrinsic ferromagnetism is observed in ZnO at doping levels up to 10 at. % Co even down to 5 K. A paramagnetic behavior with partially antiferromagnetic interactions is observed. Thus, in bulk Co-doped ZnO system any observation of ferromagnetism is probably due to small clusters of second phase materials. However, in thin films the situation might be more complex, since other extrinsic influences, such as strain or proximity effects, may modify the electronic and magnetic properties.

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Diluted magnetic semiconductors (DMSs), where transition metal atoms are introduced into the cationic sites of the semiconducting host lattice, have recently attracted increasing attention because of their potential use in spin electronic (or spintronic) devices.^{1–8} A key factor to realize spintronic devices is to develop ferromagnetic DMSs with a Curie temperature above room temperature. Interest in ZnO-based DMSs was initially generated by the theoretical prediction^{5,6} that above-room-temperature ferromagnetism is possible in ZnO-based DMSs. One of the systems considered in the past is ZnO doped with Co. Ueda *et al.*⁹ first reported the ferromagnetic behavior with the Curie temperature higher than 280 K for films grown by the pulsed-laser deposition (PLD) method, but with less than 10% reproducibility. Lee *et al.*¹⁰ and Rode *et al.*¹¹ also reported intrinsic ferromagnetic behavior of Co-doped ZnO films with a Curie temperature of approximately 350 K. Many reports further support the possibility of having intrinsic ferromagnetism in Co-doped ZnO.^{12–24} Contrary to these studies, other studies did not provide any indication of ferromagnetism in films grown on sapphire (0001) by laser molecular-beam epitaxy²⁵ and by PLD.^{26–28} Further supports for the absence of ferromagnetism in Co-doped ZnO were reported from various groups.^{29–36}

The understanding of the magnetic behavior of Co-doped ZnO requires a detailed knowledge of the atomic structure of Co. The detection of small clusters of Co-metal and/or Co-oxide as a potential source of the ferromagnetic behavior reported in the literature is crucial to answer the question if intrinsic ferromagnetism is present in substitutionally doped ZnO. In most of the reported experiments, the existence of

second phases in Co-ZnO samples, e.g., metallic Co-rich clusters, Co oxides, etc., was examined by x-ray diffraction (XRD). However, it is well known that nanometer-sized particles with relatively small volume fractions are very difficult to be detected by XRD.³⁷ This might be one possible reason that up to date, still controversial conclusions remain for the subject of magnetic properties of Co-doped ZnO materials. In this work, we report a detailed study of the correlation of atomic structure with magnetic properties from bulk polycrystalline 5 and 10 at. % Co-doped ZnO samples prepared by a high-pressure and high-temperature method. Various characterization techniques, XRD with Rietveld refinements, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), nanometer-sized element mapping, x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure (NEXAFS), and extended x-ray absorption fine structure (EXAFS), were applied to obtain information on the atomic structure and the charge state of Co. It is found that substitutional doping up to 10 at. % Co^{2+} ions can be obtained in ZnO with wurtzite structure and does not show ferromagnetism even at the lowest temperature of 5 K tested in the present experiments.

Highly reproducible $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x=5$ and 10 at. %) bulk samples were synthesized under high pressure and high temperature. Starting materials of ZnO (99.999%), Co (99.9%), and Co_3O_4 (99.9%) were mixed in a stoichiometric molar ratio. The mixture was sealed into a gold capsule. The capsule was first compressed at 6 GPa in a high-pressure apparatus, then heated to 1173–1373 K for up to 3 h, and finally quenched to room temperature followed by release of pressure.

Room-temperature x-ray powder diffraction measurements were carried out using synchrotron radiation with a wavelength of 0.6193 Å determined using a Si standard. The sample was mounted in a glass capillary 0.3 mm in diameter and rotated during data collections. The diffraction patterns were all collected in the range 5 to 60 deg in 2θ steps of 0.02 deg and accumulated for 10 s per step with a NaI detector with a Ge-111 analyzer crystal. The Rietveld refinement program is a variation of the LHMP1 program,³⁸ using the Voigt profile function and Chebyshev polynomial background fitting.

High-resolution transmission electron microscopy (HRTEM) measurements for both Co-doped ZnO samples were carried out in a Philips Tecnai F20 ST operated at 200 kV using an extraction voltage for the field emission gun of 3.9 keV. The point resolution of this microscope is about 0.235 nm at Scherzer focus with an information limit of about 0.14 nm. The HRTEM was equipped with an EDAX energy-dispersive x-ray SiLi detector with a S-UTW (super-ultra-thin window). EDX analyses were carried out in the STEM mode in order to perform nanometer-sized probes (1 nm spot size for the presented EDX measurements). For this purpose an extraction voltage of 4.1 keV was used with a double tilt holder (Gatan). Additionally, energy-filtered TEM (EFTEM) micrographs have been taken using a Gatan Imaging Filter (GIF 200). The three-window method has been applied to acquire the elemental maps at an extraction voltage of 4.4 keV. High-resolution micrographs were taken with a 1 K × 1 K CCD camera and analyzed with the software package Digital Micrographs (Version 3.5.2, Gatan Company) in order to perform fast Fourier transformations (FFTs). Scanning electron microscopy (SEM) was performed using a Leo-1530 SEM. EDX measurements from SEM with an effective area 5 μm in diameter and from HRTEM with an effective area 100 nm in diameter confirm contents in the both Co-doped ZnO samples of 5 and 10 at. % Co. Room-temperature x-ray absorption fine structure (NEXAFS and EXAFS) measurements for all samples were performed at the beamline BL01B1 in BSRF in Beijing, China. Co and Zn *K*-edge spectra were measured by transmission and/or reflection methods. Measured spectra were analyzed by standard procedures of data reduction, using the program Winxas.³⁹

For XPS measurements, powdered 5 and 10 at. % Co-doped ZnO samples were pressed onto indium foil and introduced into a model PHI 5600 (Physical Electronics Inc.) XPS spectrometer. The binding energy scale of the spectrometer was calibrated by measurement of the elemental lines Cu 2p_{3/2}, Ag 3d_{5/2}, and Au 4f_{7/2} of Ar⁺ sputter-cleaned metal foils and use of reference binding energies.⁴⁰ Co 2p spectra were acquired by use of monochromatic Al *K*_α x rays (1486.6 eV) and a pass energy of the hemispherical capacitor analyzer of 46.95 eV, which yields a full-width-at-half-maximum (FWHM) of the Ag 3d_{5/2} line of 0.98 eV.

The dc magnetization measurements were performed with a SQUID magnetometer (MPMSXL, Quantum Design). Zero-field cooling (ZFC) measurements were carried out in the following way: first at zero field cooling down temperature from 300 to 5 K, then applying a field of 1000 Oe, and finally measuring the sample from 5 to 300 K in the field. Field cooling (FC) measurements were performed immedi-

FIG. 1. X-ray diffraction pattern of 10 at. % Co-doped ZnO samples prepared by high-pressure and high-temperature method and the difference to the fitted data. Open circles and solid line are experimental data and fitting curve, respectively.

ately after ZFC measurement from 300 to 5 K under 1000 Oe.

To understand the origin of magnetism, the atomic location of the Co atoms or ions in the Co-doped ZnO samples has to be determined using a combination of methods: XRD, HRTEM, TEM, XPS, and XAFS. XAFS measured at the Co *K* edge reveals the local atomic structure of Co atoms in the samples. Figure 1 shows x-ray powder diffraction profiles for 10 at. % Co-doped ZnO samples and the difference to the fitted data. All diffraction peaks in both Co-doped ZnO samples can be indexed to a wurtzite phase. Co ions substitute for Zn ions in the wurtzite lattice and the relative occupancies of Zn/Co are close to the initial compositions of both Co-doped samples. Lattice parameters of the wurtzite phase are $a=3.2494(3)$ Å and $c=5.2038(6)$ Å for pure ZnO, $a=3.2435(9)$ Å and $c=5.2049(9)$ Å for 5 at. % Co-doped ZnO, and $a=3.2516(5)$ Å and $c=5.2089(4)$ Å for 10 at. % Co-doped ZnO. TEM studies of the 10 at. % Co-doped ZnO sample are shown in Fig. 2. Figure 2(a) is energy-filtered TEM (EFTEM) for an unfiltered micrograph and Fig. 2(b) is the EFTEM micrograph using the $L_{2,3}$ edge of Co at 779 eV for the imaging. The three-window method has been applied where two images have been recorded in the preedge region to subtract the underground from the postedge region. It is noted that Co atoms are distributed homogeneously in the sample. Figure 2(c) shows a HRTEM micrograph of the microstructure of the 10 at. % Co-doped ZnO sample. No Co-rich (metallic or oxides) clusters were detected from at least 20 different sample positions. Figure 2(d) is the corresponding fast Fourier transform (FFT) revealing the [111] zone axis of hexagonal wurtzite-type 10 at. % Co-doped ZnO sample. The individual reflections are indexed.

Figure 3 shows the radial distribution function (RDF), i.e., Fourier transform amplitude of Co *K*-edge EXAFS spectra for 5 and 10 at. % Co-doped ZnO samples together with metallic Co, CoO, Co₃O₄, and ZnO (Zn *K*-edge spectrum)

FIG. 2. TEM study of 10 at. % Co-doped ZnO sample prepared by high-pressure and high-temperature method. (a) Energy-filtered TEM (EFTEM): unfiltered micrograph, (b) EFTEM micrograph using the $L_{2,3}$ edge of Co at 779 eV for the imaging. The three-window method has been applied where two images have been recorded in the preedge region to subtract the underground from the postedge region. Note the overall distribution of Co in the microstructure. Acquisition time 30 s. (c) HRTEM micrograph of the microstructure of 10 at. % Co-doped ZnO sample. No Co-rich (metallic or oxides) clusters were detected. (d) Corresponding fast Fourier transform (FFT) revealing the [111] zone axis of hexagonal wurtzite-type 10 at. % Co-doped ZnO sample. The individual reflections are indexed.

for reference. The first four major peaks, marked by the vertical lines, at the Co K edge for both 5 and 10 at. % Co-doped ZnO samples resemble those of pure ZnO as a view from a specific Zn atom in the wurtzite structure. They are far different from the metallic Co, CoO, and Co_3O_4 . This implies that in the 5 and 10 at. % Co-doped ZnO samples, Co ions do substitute for Zn ions in the wurtzite ZnO lattice. This conclusion is further supported by the NEXAFS results in Fig. 4. It is found that the NEXAFS spectra of Co-doped

FIG. 3. Radial distribution functions surrounded by Co atoms for 5 and 10 at. % Co-doped ZnO samples together with metallic Co, CoO, and Co_3O_4 and pure ZnO (surrounded by Zn ions in this case) obtained from Co-edge and Zn-edge (only for pure ZnO) EXAFS measurements.

FIG. 4. Absorption spectra for 5 and 10 at. % Co-doped ZnO samples together with metallic Co, CoO, and Co_3O_4 and pure ZnO obtained from Co-edge and Zn-edge (only for pure ZnO) NEXAFS measurements.

ZnO samples do not match to the one of metallic Co in terms of spectrum shape, peak position, and intensity. The preedge peak, marked by A, is clearly seen in Co-doped ZnO samples, CoO and Co_3O_4 , indicating the existence of Co^{2+} ions. The positions of peaks B and C of Co_3O_4 phase are about 5 eV higher than Co-doped ZnO samples and CoO, which could be caused by the mixture of Co^{2+} and Co^{3+} ions in the Co_3O_4 phase. The peaks D and E clearly reveal that Co ions in both Co-doped ZnO samples substitute for Zn ions in ZnO, rather than forming CoO. Figure 5 shows Co $2p$ core-level XPS spectra for 5 and 10 at. % Co-doped ZnO samples. Comparison of the shapes and positions of the primary and shake-up satellite peaks for the two Co-doped ZnO samples with standards (metallic Co, CoO, and $\gamma\text{-Co}_2\text{O}_3$ in Ref. 41) reveals that Co ions in the samples are indeed Co^{2+} valence with no indication of Co^0 and Co^{3+} ions. This is in agreement with the NEXAFS results and is a prerequisite for understanding the magnetic properties of the two Co-doped ZnO samples.

FIG. 5. The Co $2p$ core-level photoemission spectra for the 5 and 10 at. % Co-doped ZnO samples.

FIG. 6. The dc magnetic properties of 5 and 10 at. % Co-doped ZnO samples. (a) Field-cooled inverse susceptibility as a function of temperature at a field of 0.1 T and (b) magnetization as a function of field at 5 K. No magnetic hysteresis was found [inset in (b)] for both samples at 5 K. Open circle and square symbols are for 5 and 10 at. % Co-doped ZnO samples, respectively.

The dc magnetic properties of 5 and 10 at. % Co-doped ZnO samples are shown in Fig. 6(a), field-cooled inverse susceptibility versus temperature at a field of 0.1 T and (b) magnetization as a function of magnetic field at 5 K. The magnetizations of both samples exhibit a slight increase from 300 to 50 K, followed by a steep increase below 50 K, corresponding to a typical paramagnetic behavior. No magnetic hysteresis was detected for both samples at both 5 and 300 K (not shown in Fig. 6). The temperature dependence of ZFC (not shown in Fig. 6) and FC magnetization curves for the samples completely coincide from 5 to 300 K, indicating again a paramagnetic behavior for both samples. The high-temperature parts (above 150 K) of the susceptibility can be well fitted to the Curie-Weiss law as indicated by solid lines.⁴² The Curie temperature Θ and the effective magnetic moment per Co ion μ_{eff} were estimated to be -19.1 K and -53.9 K and $4.3\mu_B/\text{Co}$ and $4.4\mu_B/\text{Co}$ for 5 and 10 at. %

Co-doped ZnO samples, respectively. These μ_{eff} values suggest again that the valence of the Co ion in the studied samples is $2+$, because the observed values of μ_{eff} coincide with that expected for the high-spin Co^{2+} ($3.87\mu_B/\text{Co}$). The negative values of Θ indicate the existence of antiferromagnetic interactions. The magnetization at 7 T and 5 K is about $2.4\mu_B/\text{Co}$ and $1.6\mu_B/\text{Co}$ for 5 and 10 at. % Co-doped ZnO samples, respectively. It does not saturate at 7 T but still increases linearly with magnetic field for the two samples. The tendency of magnetic moment μ_{eff} vs. Co content detected at 7 T and 5 K indicates that the possibility of the nearest-neighbor Co spin antiferromagnetic superexchange coupling increases with increasing Co content. Similar results have also been reported for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x < 0.2$) polycrystalline powders prepared by a standard solid state reaction.^{21,32}

Based on the characterization of the 5 and 10 at. % Co-doped ZnO samples, prepared by the high-pressure and high-temperature method, by a variety of experimental techniques, it is found that Co ions with a valence of $2+$ in the samples indeed substitute for Zn ions in the wurtzite ZnO structure. There is no indication of Co-rich (metallic and oxides) clusters in the samples. From the combination of magnetization measurements, it can be concluded that ZnO samples with 10 at. % Co-doping, if done properly with Co^{2+} ions substituting for Zn^{2+} ions in wurtzite structure, do not have intrinsic ferromagnetism even down to 5 K. They behave as a paramagnetic material with partially antiferromagnetic interactions. Thus, in a bulk Co-doped ZnO system any observation of ferromagnetism is probably due to small clusters of second phase materials. However, in thin films the situation might be more complex, since other extrinsic influences, such as strain or proximity effects, may modify the electronic and magnetic properties.

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