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# **Electronic Supplementary Information**

# High-*T*<sub>c</sub> Ferromagnetism in Co-doped ZnO System Dominated by the Formation of Zinc-Blende Type Co-rich ZnCoO Phase

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## **Experimental section**

#### S1. Materials and Synthesis Method

Surface-modified Zn<sub>0.98</sub>Co<sub>0.02</sub>O nanocomposites have been synthesized by a simple solvothermal technique using zinc nitrate hexahydrate (AR, SCRC), cobalt nitrate hexahydrate (AR, SCRC) and sodium hydroxide (AR, SCRC) as starting materials. Absolute ethanol was used as solvent and oleic acid (OA) was introduced as a capping molecule for nanoparticles. Detailed experimental synthesis processes are described as follows. Firstly, 0.1 M \*98% Zn(NO<sub>3</sub>)  $\cdot$  6H<sub>2</sub>O/ 2% Co(NO<sub>3</sub>)  $\cdot$  6H<sub>2</sub>O and 0.3 M NaOH dissolved in 150 mL absolute ethanol at the room temperature, with a vigorous magnetic string to insure the solution homogenous. Secondly we divided the mixture into three equal parts. For each one we added a different concentration of oleic acid under vigorous stirring to obtain three solutions with the following Zn(II)/OA molar ratios: 5:3, 5:6 and 5:9. After all of solutions were transferred into Teflon-lined stainless steel autoclave of capacity 100 mL. The autoclave were sealed and heated automatically to ca. 120°C, persisted for 12 hours and then cooled to room

temperature. Finally, the precipitates were collected from the solution, washed several times with deionized water and absolute ethanol to remove sodium nitrate and other impurities, and collected after centrifugally and drying. The as-prepared nanocrystals were denoted by sample A1, A2 and A3, respectively. A control experiment on OA-capped pure ZnO samples without Co-doping was also implemented using exactly same synthesis method.  $0.1M Zn(NO_3) \cdot 6H_2O$  and 0.3M NaOH dissolved in 150 mL absolute ethanol with a vigorous magnetic string. Then the mixture was divided into three equal parts and different concentrations of oleic acid were added respectively with vigorous magnetic string. Three reference samples with Zn(II)/OA molar ratios: 5:3, 5:6 and 5:9, respectively, were collected for further analysis.

### S2. TEM and XRD analysis

Particle sizes and shapes were examined by a JEM-2100 transmission electron microscope (JEOL, Japan). Figure S1 shows that all samples are spherical-like nanoparticles with the size of about 20 nm and no size modifications was observed with increasing the OA content inc. Crystalline phases of the obtained products were characterized by XRD using a D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation, where data were collected from 20° to 80° of 20. The grain sizes were quantified by using a Jade 5.0 program<sup>1</sup>. We selected the three strongest diffraction peaks at lower angles, directly extracted the FWHM, diffraction angles and calculated the grain size, then averaged them. The size of samples A1, A2 and A3 corresponded to 24 Å, 19 Å and 22 Å, respectively, which are good in agreement with TEM images. As a consequence we could conclude that size effect has no contribution to the RTF of our samples.

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Figure S1. The TEM image of (a) (b) and (c) corresponded to samples A1, A2 and A3.

#### **S3.** Magnetic Characterization

Magnetic properties were characterized by a vibrating sample magnetometer (VSM, RIKIN BHV-50V) at 300 K. In Figure S2 we compare the dependence of the magnetization at room temperature vs. the applied magnetic field (M vs. H) for Co-doped ZnO samples after subtracting the diamagnetic background from the sample holder (see the inset in the figure S2). Figure S3 shows the M vs. H curve for OA-capped pure ZnO samples. It was found that all samples exhibit diamagnetic behavior after correction of the background from the sample holder. In order to better interpret the magnetic behavior of the sample A1, we measured the M vs. H loops at the temperature of 5 K and the field-cooled (FC) and the zero-field cooled (ZFC) curve by a SQUID magnetometer. The ZFC and FC curves were obtained by initially cooling down the sample in zero field from 300 K to 5 K and subsequently warmed up in a field of 100 Oe (ZFC), then in the same field it was cooled down and warmed up again (FC). It was shown that the ZFC and the FC curves are almost same clearly demonstrating the paramagnetic behavior of this sample, which also was confirmed by the M vs H loops at 5 K.

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**Figure S2.** The dependence of the magnetization at room temperature vs. the applied magnetic field (M vs. H) for the samples A1, A2, and A3 after the substraction of the diamagnetic background. The inset shows the diamagnetic contribution of the sample holder.



**Figure S3.** The dependence of the magnetization at room temperature vs. the applied magnetic field (M vs. H) for the pure ZnO samples after the subtraction of the diamagnetic background of the sample holder.

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**Figure S4** The M vs H loops at the temperature of 5 K for the sample A1. The inset shows the field-cooled (FC) and zero-field cooled (ZFC) curves obtained with the SQUID magnetometer.

### **S4. XAFS Data Collection and Analysis**

Co K-edge XAS data of the samples were recorded at the SSRF (Shanghai) facility at the beamline 14W1 and at the NSRL (Hefei) facility at the beamline U7C. Data were recorded using in both runs a Si(111) double crystal monochromator. Co K-edge XAFS data were analyzed using standard procedures with the program IFEFFIT<sup>2</sup>. Figure S5 shows the comparison of Co K-edge XANES spectra of Co-doped ZnO samples with various concentrations of oleic acid and common cobalt oxide, including rocksalt-CoO (cubic), Co<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>. All these second phases can be easily expelled due to their significantly different spectral pattern, especially in the pre-edge peak. For the EXAFS fitting, the Fourier transform window for the k space is of the Hanning-type in the range of (2.5, 12.5) Å and for the R space of the Hanning-type in the range of (1.0-3.5 Å), including the first and second coordination shells. The amplitude reduction factor  $S_0^2$  were determined by fitting to the respective manganese oxide and set at 0.85 for the Co K-edge. For the fit of samples A2 and A3, we considered both the wurtzite and zinc-blende types. The coordination numbers, bond

lengths and Debye-Waller factors of the two shells of Co scattering atoms were varied in the fit. According to the Nyquist formula  $N_{ind}=2\Delta R\Delta k/\pi$ , the number of the independent parameters of the data set were 16. Thus, it is reasonable includes in the fit the nearest Co-O shell and the next-nearest Co-Zn shell. Fitting results are shown in the Table S1 and data of the fit in the R space are magnified in Figure S6.



**Figure S5.** Comparison of Co K-edge XANES spectra of Co-doped ZnO Sample for different concentrations of oleic acid and common cobalt oxide, including rocksalt-CoO (cubic), Co<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>.

 Table S1. Parameters of the fit of the Co-doped ZnO sample for different concentrations of the oleic acid.

Sample	Bond type	Coordination	Bond length	Bond disorder
		Number	<b>R</b> (Å )	σ <sup>2</sup> ×10 <sup>-3</sup> (Å <sup>2</sup> )
A1	Со-О	4.0±0.3	$1.975 \pm 0.007$	3.5±1.2
	Co-Zn	$11.9 \pm 0.8$	3.230±0.011	8.7±0.6

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A2	Со-О	3.8±0.3	$1.975 \pm 0.007$	3.5±1.4
	Co-Zn	6.7±0.5	3.230±0.011	$8.2 \pm 0.9$
	Co-Co	4.8±0.4	$3.241 \pm 0.021$	$10.8 \pm 1.5$
A3	Со-О	3.6±0.2	$1.960 \pm 0.007$	5.8±1.8
	Co-Zn	1.8±0.1	3.231±0.011	$11.2 \pm 0.9$
	Co-Co	9.0±0.7	$3.241 \pm 0.021$	13.8±2.1





**Figure S6.** Experimental Fourier Transform at the Co K-edge of EXAFS data of the  $Zn_{0.98}Co_{0.02}O$  samples and the corresponding fits.

# **Theoretical calculated section**

### **S5.** Multiple-scattering simulations

XANES simulations at the Co K-edge were performed in the framework of the multiple-scattering (MS) theory<sup>3, 4</sup> by using the FEFF 8.4 code<sup>5</sup>. The cluster potential was approximated by a set of spherically averaged muffin-tin (MT) potentials. For the calculations, we used the Hedin-Lundqvist model<sup>6, 7</sup>. The two initial models

considered are: (1) cobalt atoms replacing Zn atoms in the WZ-type structure with the lattice constants a=b=3.249 Å and c=5.205 Å; (2) cobalt atoms replacing Zn atoms in the ZB-type structure using the lattice constants a=b=c=4.616 Å. A model cluster size up to 7 Å was used in all MS calculations to obtain accurate self-consistent field (SCF) calculations, and a cluster up to 8 Å was used for full multiple-scattering calculations.

### S6. Density of states calculations detail

Density of states (DOS) calculations were performed using the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP)<sup>8,9</sup>. The projector augmented wave was used to describe the electron-ion interaction, and the generalized gradient approximation (GGA)+U was used for the exchange-correction functional<sup>10</sup>. All calculation parameters except those of the lattice structure were in agreement with a previous investigation<sup>11</sup>. A value of U=5 eV was used for the Coulomb interaction parameter, while the exchange parameter J was set to 1 eV. A 64-atom super-cell consisting of  $2 \times 2 \times 2$  unit cells of ZB-type ZnO was used and the lattice constant was set to a = 4.616 Å. The cutoff energy of 600 eV and 5  $\times 5 \times 5$  k-point grids were used. According to the band coupling model<sup>12-14</sup>, the magnetic order is dominated by the position and the occupancy of the Co 3d sub-band near the Fermi-level and a competition between the ferromagnetic super-exchange arising from the hybridization of the occupied  $e_{o}^{\downarrow}$  states with the empty  $t_{2}^{\downarrow}$  states, and an anti-ferromagnetic super-exchange due to the hybridization of the occupied  $t_2^{\uparrow}$  states with the empty  $t_2^{\downarrow}$  states should be taken account. The competition

mechanism offers an FM energy gain of  $\Delta E^{FM} \propto \frac{\left|t_{e_s-t_2}\right|^2}{E_{t_2^{\perp}} - E_{e^{\perp}}}$  and AFM energy gain

of 
$$\Delta E^{AFM} \propto \frac{\left|t_{t_2-t_2}\right|^2}{E_{t_2\downarrow} - E_{t_2\uparrow}}$$
, where  $\left|t_{e_g-t_2}\right|^2$  and  $\left|t_{t_2-t_2}\right|^2$  denote the eg-t<sub>2</sub> and t<sub>2</sub>-t<sub>2</sub> hopping

matrix elements respectively, according to the Kanamori-Goodenough rules<sup>15</sup>.

#### References

- S1. Jade5.0, XRD Pattern Processing Materials, Data Inc., 1999.
- S2. M. Newville, J. Synchrotron Rad., 2001, 8, 322-324.
- C. R. Natoli, M. Benfatto, C. Brouder, M. F. R. Lopez and D. L. Foulis, *Phys. Rev. B*, 1990, 42, 1944.
- S4. P. A. Lee and J. B. Pendry, *Phys. Rev. B*, 1975, **11**, 2795.
- S5. A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B*, 1998, 58, 7565.
- S6. C. R. Natoli, M. Benfatto, C. Brouder, oacute, M. F. R. pez and D. L. Foulis, *Phys. Rev. B*, 1990, **42**, 1944.
- S7. T. A. Tyson, K. O. Hodgson, C. R. Natoli and M. Benfatto, Phys. Rev. B, 1992, 46, 5997.
- S8. G. Kresse, Furthm, uuml and J. ller, *Phys. Rev. B*, 1996, **54**, 11169.
- S9. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
- S10. P. E. Blochl, Phys. Rev. B, 1994, 50, 17953.
- S11. D. Iuscedilan, M. Kabir, Gr, aring, auml, O. s, O. Eriksson and B. Sanyal, *Phys. Rev. B*, 2009, 79, 125202.
- S12. G. M. Dalpian, S.H. Wei, X. G. Gong, A. J. R. da Silva and A. Fazzio, *Solid State Commun.*, 2006, **138**, 353-358
- S13 B. Belhadji, L.Bergqvist, R.Zeller, P.H.Dederichs, K.Sato and H.Katayama-Yoshida, J. Phys.: Condens. Matter, 2007, 19, 436227.
- S14 Y.Tokura, and N.Nagaosa, Science, 2000, 288, 462.
- S15 Sato, K.; Bergqvist, L.; Kudrnovsk; yacute; J.; Dederichs, P. H.; Eriksson, O.; Turek, I.; Sanyal, B.; Bouzerar, G.; Katayama-Yoshida, H.; Dinh, V. A.; Fukushima, T.; Kizaki, H. and Zeller, R. *Rev. Mod. Phys.* 2010, 82, 1633.