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# Co-rich ZnCoO nanoparticles embedded in wurtzite Zn<sub>1-x</sub>Co<sub>x</sub>O thin films: possible origin of superconductivity

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ABSTRACT Co-rich ZnCoO nanoparticles embedded in wurtzite  $\text{Zn}_{0.7}\text{Co}_{0.3}\text{O}$  thin films are grown by pulsed laser deposition on a Si substrate. Local superconductivity with an onset  $T_c$  at 5.9 K is demonstrated in the hybrid system. The unexpected superconductivity probably results from  $\text{Co}^{3+}$  in the Co-rich ZnCoO nanoparticles or from the interface between the Co-rich nanoparticles and the  $\text{Zn}_{0.7}\text{Co}_{0.3}\text{O}$  matrix.

## INTRODUCTION

Being discovered more than a century ago, superconductivity, the intriguing phase of paired electrons leading to the resistance-free flow of electrical charges, remains one of the worldwide research focuses. In particular, finding a new superconducting material is always most exciting. The discovery of superconductivity in layered copper-based oxides<sup>1</sup> and layered iron-based materials<sup>2</sup> has pushed the transition temperature  $T_c$  up to unprecedented high when compared to the  $T_c$  of conventional superconductors. Although there is general consensus on the unconventional nature of the Cooper pairing state, several questions still remain related to the physical origin of high  $T_c$  superconductivity. Especially the discovery of iron-based superconductors was completely surprising because the antagonistic relationship between superconductivity and magnetism has led researchers to avoid using magnetic elements, in particular ferromagnetic elements, as a building block for new superconductors.<sup>3</sup> In contrast to iron-based superconductors, which became a big family after their discovery,<sup>4,5</sup> cobalt-based superconductors appear quite rare.<sup>6,7</sup> On the other hand, unconventional superconductivity has also been demonstrated at the interface between two insulating oxides, i.e., LaAlO<sub>3</sub> and SrTiO<sub>3</sub><sup>8-</sup><sup>10</sup> or at the electric-field-induced interface in electric double-layer transistors.<sup>11,12</sup>

Hexagonal wurtzite ZnO, by virtue of its excellent properties, including a wide direct bandgap of 3.37 eV at room temperature, a large exciton binding energy of 60 meV, the availability of high-quality bulk crystals, as well as high electron mobility and high thermal conductivity, has been a common host for various doping, in particular electrical, optical, and magnetic doping.<sup>13,14</sup> However, wurtzite ZnO has never been considered as a building block for superconductors. Here, we report local superconductivity in Co-rich ZnCoO nanoparticles embedded in wurtzite Zn<sub>1-x</sub>Co<sub>x</sub>O thin films with an onset  $T_c$  at 5.9 K. The Co-rich ZnCoO

nanoparticles, although their microstructure remains to be conclusively determined, are believed to play a key role in the unexpected appearance of superconductivity.

## RESULTS AND DISCUSSION

$\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin films are grown by a pulsed laser deposition (PLD) method. Figure 1 presents the X-ray diffraction (XRD) patterns of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin films grown on a Si substrate and on a  $\text{SiO}_2$  substrate. In both cases only the peaks that correspond to the (002) and (004) planes of wurtzite ZnO are observed, which indicate that the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin films crystallize in the hexagonal wurtzite structure with strong (002) preferential orientation. No phase separation is detected by XRD even when the nominal Co concentration is as high as 30 atom %. In addition, the local chemical environment of Co was characterized by X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). In Figure S1(a) we show the XANES spectra of the Co K-edge for the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin film as well as for CoO and Co reference samples. The XANES of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  resembles the spectrum of CoO rather than of Co, indicating that the Co is in the oxidized state. In particular, the appearance of a small pre-edge absorption at 7709 eV is ascribed to transitions of Co 1s electrons to  $4p-3d$  hybridized states, which become allowed by the nearly tetrahedral bonding of Co at the Zn sites within the wurtzite structure.<sup>15</sup> In Figure S1(b) we plot the magnitude of the  $k^2$ -weighted Fourier transforms of the EXAFS spectra. The  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  spectrum reveals two peaks related to the first O shell and second Zn shell in the wurtzite model. This indicates that the Co atoms are located at Zn sites. We therefore conclude the majority of Co atoms are substitutional on the Zn site in the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin film.

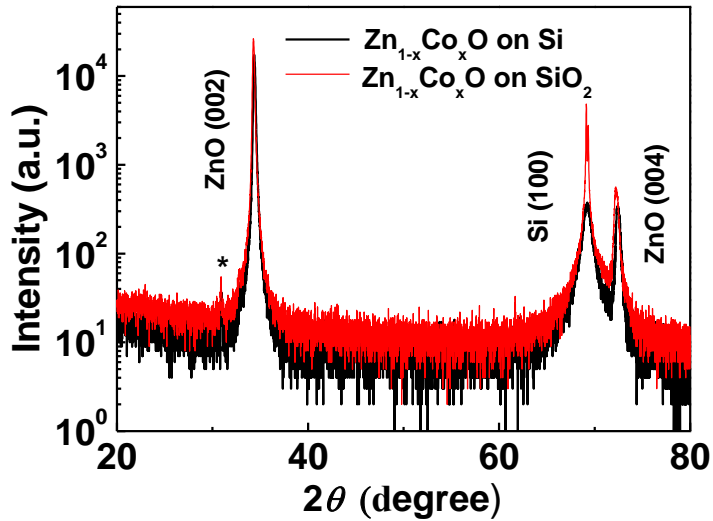


Figure 1. XRD pattern of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin films grown on a Si and on a  $\text{SiO}_2$  substrate. The small peak marked with an asterisk results from the highly doped Si.

The microstructures of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin films grown on both Si and  $\text{SiO}_2$  were investigated in detail using transmission electron microscopy (TEM). In figure 2 we present bright-field TEM images of the samples. Both films are polycrystalline with well pronounced columnar microstructure. The lateral dimensions of the crystallites vary from a few to tens of nanometers. Note that a thin layer of  $\text{SiO}_2$  with a thickness of about 2 nm is formed on top of the Si substrate, which is due to the presence of the partial oxygen atmosphere and/or the oxygen diffusion during the growth. Nevertheless, the microstructure of the thin film grown on the Si substrate differs from that grown on the  $\text{SiO}_2$  substrate. The former contains some crystallites violating the regular columnar microstructure (marked with an asterisk in figure 2). Electron diffraction (ED) patterns outside of the grain marked with an asterisk (Figure S2) and on that grain (Figure S3) both suggest a hexagonal wurtzite structure. The ED data (Figure S2) demonstrate that the wurtzite  $c$  axis is normal to the thin-film surface, which is consistent with the XRD result. On the

other hand, the  $c$  axis of the grain marked with an asterisk significantly inclined with respect to the film surface normal by about  $25^\circ$ .

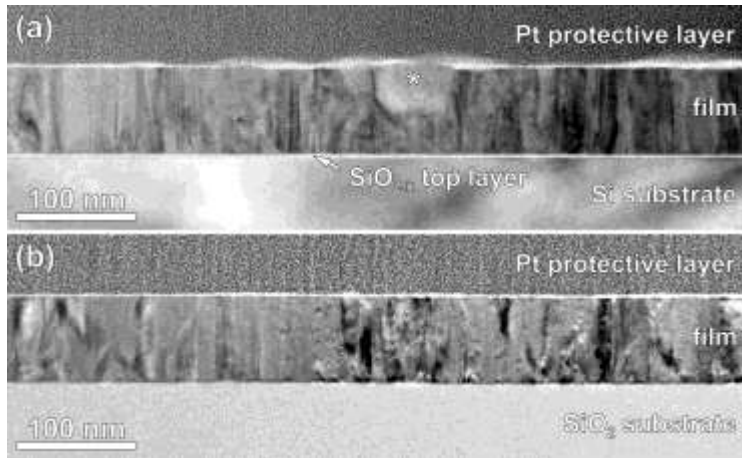


Figure 2. Bright field TEM images of the  $Zn_{1-x}Co_xO$  thin films grown on a Si substrate (a) and on a  $SiO_2$  substrate (b).

Another significant difference between the samples prepared on different substrates is that they exhibit a different Co distribution. According to the energy dispersive X-ray spectroscopy (EDX) analysis, the overall Co concentration is  $30 \pm 1$  atom % and  $32 \pm 1$  atom % for the thin film deposited on the Si substrate and on the  $SiO_2$  substrate, respectively, which is in very good agreement with the composition of the PLD target ( $x = 0.3 \pm 0.01$ ). However, the Co distribution is not homogeneous in the sample grown on the Si substrate. Figure 3 presents the elemental distribution maps for the sample on the Si substrate acquired using the Scanning TEM-electron energy loss spectroscopy (STEM-EELS) technique. A Co-rich nanoparticle is clearly present in the  $Zn_{1-x}Co_xO$  matrix. According to the EDX data, the Co concentration in the Co-rich region increases to 50 atom %. This value may be underestimated because the Co-rich nanoparticles are tightly embedded in the matrix. The concentration of Co in the surrounding matrix does not significantly deviate from the average concentration. More Energy filtered transmission electron

microscopy (EFTEM) maps can be found in the Supporting Information (Figure S4), revealing the presence of the Co-rich nanoparticles at different locations. However, the microstructure of the Co-rich nanoparticles cannot be conclusively determined due to their small size and the overlap with the matrix. In addition, within the resolution of the measurement ( $\sim 5$  nm) and the accuracy of EELS quantification ( $\sim 5\%$ ), no significant change of the oxygen concentration is observed in the Co-rich regions. This is in contrast to what we recently observed in high-fluence Co-implanted ZnO, in which the Co-rich nanoparticles are metallic.<sup>15,16</sup> Note that no Co-rich nanoparticles are observed in the sample grown on the SiO<sub>2</sub> substrate, i.e., Co is evenly distributed (Figure S5). Therefore, the misaligned grains discussed above are believed to play a key role in the formation of the Co-rich nanoparticles, probably by strain release.

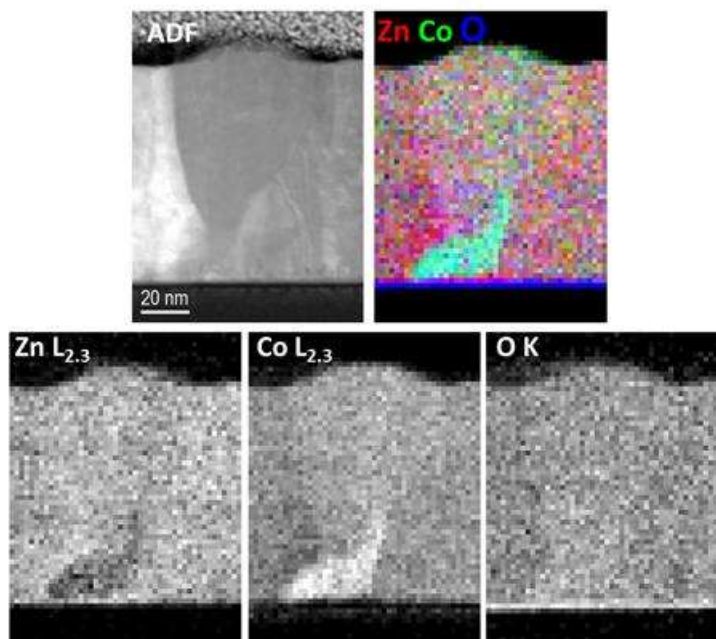


Figure 3. Annular dark field image of the Zn<sub>1-x</sub>Co<sub>x</sub>O thin film grown on a Si substrate and the corresponding elemental maps acquired using EELS spectral imaging at the Zn L<sub>2,3</sub>, Co L<sub>2,3</sub> and O K absorption edges.



The oxidation states of Co in the  $Zn_{1-x}Co_xO$  matrix and in the Co-rich nanoparticles were investigated using monochromated STEM-EELS measurements and multiplet simulations,<sup>17</sup> as shown in Figure 4. The parameters for the simulations are reported in supplementary Table S1. A non-biased linear combination of the simulated spectra was used to determine the composition of the matrix and the Co-rich nanoparticles in 10 different regions for each (see figure s6) of  $5*4$  and  $2*2$  pixels respectively. The Co valence in the  $Zn_{1-x}Co_xO$  matrix is determined to be +2.13, which is fully consistent with the wurtzite structure. The result revealed that 85% of the  $Co^{2+}$  is in the tetrahedral ( $T_d$ ) symmetry with 10% of  $Co^{3+}$  in the  $O_h$  symmetry confirming the substitutional character of Co on Zn sites in the  $Zn_{1-x}Co_xO$  matrix. We can notice traces (below the 3% error) of  $Co^{2+}$  in  $O_h$  and  $Co^{3+}$  in  $D_{3d}$  (trigonal) which we can neglect. Estimating that  $Co^{2+}$   $T_d$  is only present in the matrix, we can remove in each spectra (after fitting), the underlying matrix. The oxidation state of Co in the center of the Co-rich nanoparticles is determined to be +2.62 in the same way (49%  $Co^{3+}$   $O_h$ , 39%  $Co^{2+}$   $O_h$  and 13%  $Co^{3+}$   $D_{3d}$  (trigonal), whereas the edge regions of the particles present a slightly higher oxidation state of +2.82 (67%  $Co^{3+}$   $O_h$ , 19%  $Co^{2+}$   $O_h$  and 14%  $Co^{3+}$   $D_{3d}$ ). As the  $Co^{3+}$   $D_{3d}$  content seems rather invariant between the sides and the center of the precipitate, we can assume that these ions are situated along the interface between the matrix and the precipitate. The core of the precipitate is constituted of  $Co^{2+}$  and  $Co^{3+}$  in  $O_h$  symmetry. The variation of the  $Co^{2+}/Co^{3+}$  in octahedral sites observed between the edges and center of the region where the nanoparticle is present, might be the result of the presence of a gradient of composition from the center to the surface of the precipitate from  $Co^{2+}$  to  $Co^{3+}$ . One exemplary fitted spectrum for the center and the edge of the precipitate can be found in Figure 4 and the parameters in Table S2.

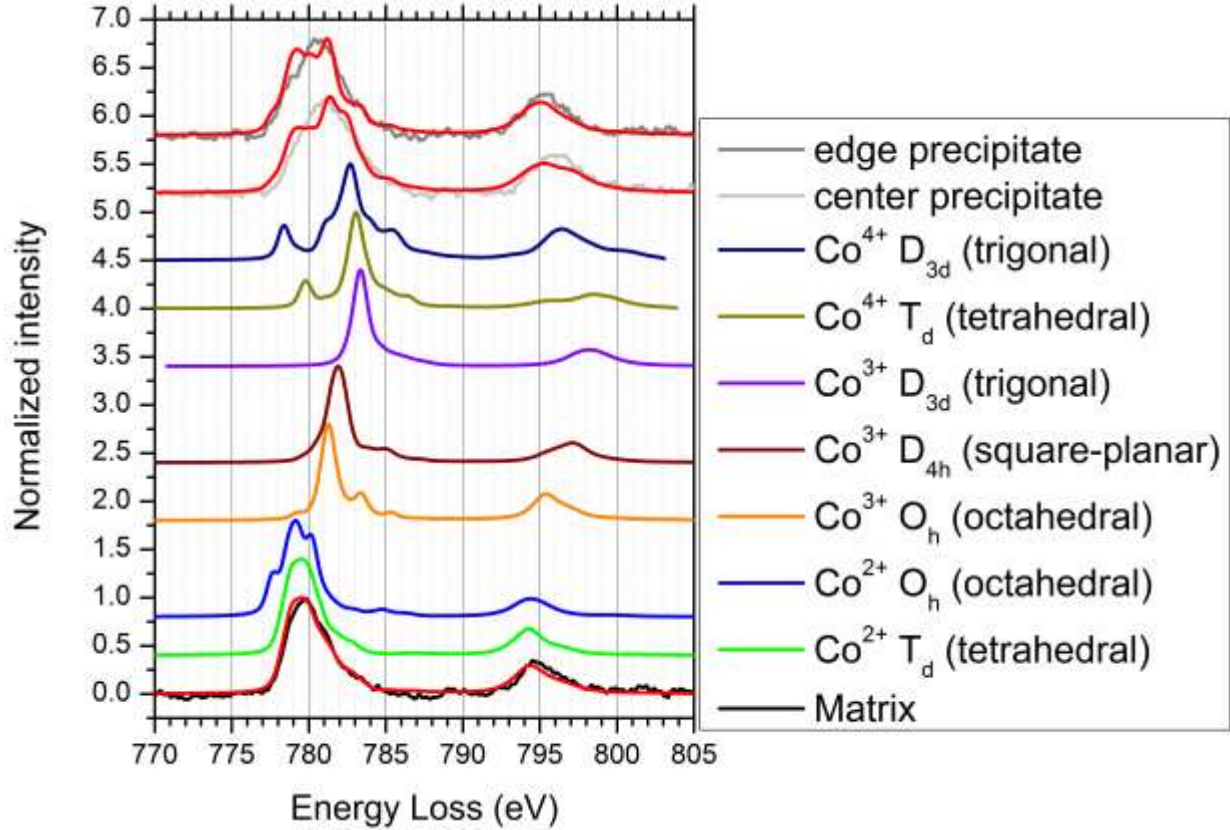


Figure 4. Monochromated STEM-EELS measurements of the Co  $L_{2,3}$  edge for the  $Zn_{1-x}Co_xO$  matrix (black) and for the center (light grey) and the edge (dark grey) of the Co-rich nanoparticles with their corresponding fits in red as well as the simulated spectra for  $Co^{2+}$  in  $T_d$  and  $O_h$ ,  $Co^{3+}$  in  $O_h$ ,  $D_{4h}$  and  $D_{3d}$  and  $Co^{4+}$  in  $T_d$  and  $D_{3d}$  symmetries.

Now we demonstrate the presence of local superconductivity which we relate to the presence of the Co-rich nanoparticles. In figure 5(a) we present the temperature dependence of the resistance of the  $Zn_{1-x}Co_xO$  thin film grown on a Si substrate under different magnetic fields parallel to the thin-film surface. Note that the resistance is expected to include the resistance of the Co-rich nanoparticles as well as of the  $Zn_{1-x}Co_xO$  matrix. Despite the large residual resistance, which can be associated with the non-superconducting regions of the thin film, we clearly observe an onset  $T_c$  at 5.9 K for both decreasing and increasing temperature. Note that

such a non-zero resistance has also been observed in other superconductors, including  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ <sup>6</sup> and  $\text{ZrZn}_2$ .<sup>18</sup> The applied magnetic field shifts  $T_c$  towards lower temperatures. A magnetic field of 2 T completely destroys the superconducting state in the accessible temperature range. A perpendicular magnetic field results in a similar shift of  $T_c$  towards lower temperatures. In figure 5(b) we compare the critical field as a function of temperature for the parallel and the perpendicular field geometries. The critical field for  $T \rightarrow 0$  is estimated by linear extrapolation from the phase diagram to be 2.8 T and 2.5 T for the parallel and the perpendicular geometries, respectively. From the linear slopes of the critical field curves near  $T_c$  we infer values of the zero temperature superconducting coherence length of 10 nm and 11 nm for the parallel and the perpendicular geometries, respectively according to the equation.<sup>19</sup>

$$\xi^2(0) = \frac{\phi_0}{2\pi \frac{dH_{c2}}{dT} T_c}$$

Both coherence lengths are considerably smaller than the thin film thickness, suggesting a three-dimensional, nearly isotropic superconductivity.

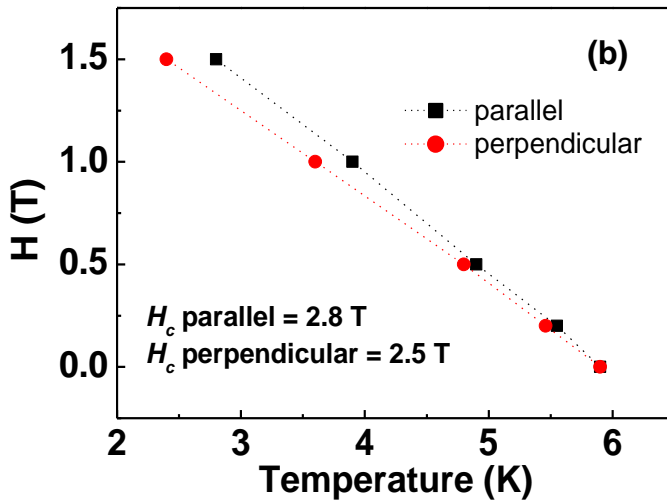
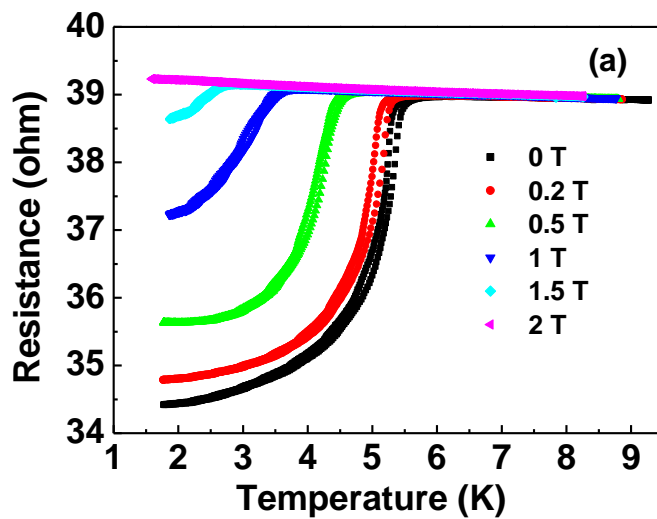
The superconductivity can only be observed for the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  grown on a Si substrate with the presence of Co-rich nanoparticles and cannot be observed for the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  grown on a  $\text{SiO}_2$  substrate. We therefore believe that the superconducting state is directly related to the presence of the Co-rich nanoparticles. Our STEM-EELS measurements reveal the presence, apart from  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  in an  $O_h$  symmetry, of  $\text{Co}^{3+}$  in a trigonal ( $D_{3d}$ ) symmetry in the Co-rich nanoparticles, which has been observed in  $\text{Na}_x\text{CoO}_2$ .<sup>20,21</sup> We therefore infer that the Co-rich nanoparticles might be constituted of a core of  $\text{Co}_x\text{O}_{1+x}$  ( $1 < x < 4$ ) surrounded by  $\text{CoO}_2$  layers. Consequently, a possible origin of the superconductivity is the presence of  $\text{Co}^{3+}$  in two-dimensional  $\text{CoO}_2$  layers, whose structure is similar to  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ .<sup>6</sup> Another possibility is

that the superconductivity originates from the interface between the Co-rich nanoparticles and the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  matrix, which may be comparable to the superconductivity observed at the interface between two insulating oxides.<sup>8-10</sup> We note that the observed superconductivity cannot be explained by the possible formation of  $\text{CoSi}_2$ , whose  $T_c$  (1.2 – 1.5 K) is much lower than the one we observe in our samples.<sup>22,23</sup>

Finally, although the superconducting transition is evident from the transport measurements in figure 5(a), we do not observe a clear Meissner effect in the magnetic measurements. We argue that the lack of a strong Meissner effect is due to the fact that the superconductivity remains confined to the Co-rich nanoparticles, implying that the superconducting screening currents may not be well developed.<sup>24,25</sup> Moreover, a weak Meissner effect, if present, can be easily overwhelmed by the dominating influence of the magnetism in the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  matrix and the bulk Si substrate due to the relatively very small volume fraction of superconductivity in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ .

Nevertheless, detailed magnetic measurements on the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin film grown on a Si substrate reveal the fingerprints of a diamagnetic response, which we believe to be the result of the weakened Meissner effect. At a magnetic field of 0.1 T, a paramagnetic-like signal shows up (Figure S7(a)). We note that a paramagnetic-like signal is also present in the virgin substrate, which is probably due to the highly doped Si. The linear dependence of the magnetization on  $1/T$  confirms the paramagnetic behavior, which is probably also influenced by the non-superconducting fraction of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  (Figure S7(b)). On the other hand, the deviation at a temperature of around 5 K indicates a decrease of the total magnetization. Therefore we plot in figure 5(c) the temperature dependence of the magnetization after subtracting the paramagnetic component ( $\text{cH}/T$ ). A decrease of the magnetization (diamagnetic response) is evident at around

5 K, which is consistent with the  $T_c$  obtained from transport measurements. The observed fingerprints of the Meissner effect further confirm the presence of superconductivity in our samples on a Si substrate. However, the lack of the strong Meissner effect implies that the superconducting region is very limited in our sample, which, to some extent, favors the opinion that the observed superconductivity comes from the interface between the Co-rich nanoparticles and the  $Zn_{1-x}Co_xO$  matrix.



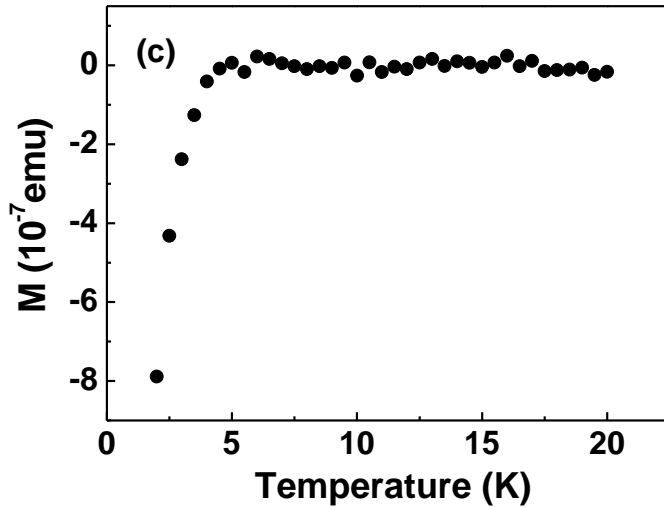


Figure 5. Superconducting properties of the  $Zn_{1-x}Co_xO$  thin film grown on a Si substrate. (a) Temperature dependence of the resistance for different magnetic fields parallel to the thin film surface. (b) Critical field as a function of temperature for the parallel and perpendicular geometries. (c) Temperature dependence of the magnetization measured at a magnetic field of 0.1 T in a zero-field cooling process. The paramagnetic component ( $cH/T$ ) has been subtracted.

## CONCLUSION

In conclusion, we demonstrated unexpected superconductivity with an onset  $T_c$  at 5.9 K, which is related to the presence of Co-rich ZnCoO nanoparticles embedded in wurtzite  $Zn_{0.7}Co_{0.3}O$  thin films. The superconductivity may result either from the presence of  $Co^{3+}$  in two-dimensional  $CoO_2$  layers or from the interface between the Co-rich nanoparticles and the  $Zn_{0.7}Co_{0.3}O$  matrix. However, the microstructure of the Co-rich nanoparticles remains to be conclusively determined. Nevertheless, the wurtzite  $Zn_{1-x}Co_xO$  provides a new platform for superconductivity, which may be an alternative for the Fe-based superconductors and can benefit from the numerous excellent properties of the ZnO material.

## EXPERIMENTAL DETAILS

$Zn_{1-x}Co_xO$  (nominal  $x = 0.3 \pm 0.01$ ) thin films with a thickness of approximately 100 nm were grown by pulsed laser deposition (PLD). Both highly doped Si (100) and Si (100) with a top layer of 300 nm  $SiO_2$  were used as substrates. The energy density per laser pulse was  $3 \text{ J/cm}^2$ . The growth temperature was  $550 \text{ }^\circ\text{C}$ . The oxygen pressure was maintained at 0.1 Pa during the growth of the  $Zn_{1-x}Co_xO$ . The crystal structure of the sample was characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO MRD system). The local chemical environment of Co in the sample was characterized by X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) at the DUBBLE (BM26) beamline of the European Synchrotron Radiation Facility (ESRF). The CoO powder and the metallic Co foil were used as the reference materials. The microstructure and elemental distribution of the  $Zn_{1-x}Co_xO$  were studied by transmission electron microscopy (TEM). A cross-section specimen for TEM was prepared by cutting a thin lamella perpendicular to the film surface using a focused ion beam technique. Energy filtered transmission electron microscopy (EFTEM) was conducted on a Philips CM30-FEG operated at 300 keV. Energy dispersive X-ray spectroscopy (EDX) was conducted on a FEI Tecnai G2 microscope operated at 200 keV. Scanning TEM-electron energy loss spectroscopy (STEM-EELS) was conducted on a Titan Cubed microscope operated at 120 keV, which is equipped with an electron monochromator making an energy resolution of 150 meV possible at an acceleration voltage of 120 keV. Multiplet spectra were simulated using the software CTM4XAS version 5.5<sup>17</sup> and the parameters are reported in the supplementary Table S1 to determine the absolute valence of Co in the  $Zn_{1-x}Co_xO$  matrix and the Co-rich nanoparticles. The electrical contacts for transport measurements were formed by deposition of a Au/Ti bilayer,<sup>26</sup> with a contact area of  $0.04 \text{ mm}^2$ . The resistivity measurements as a function of

temperature were performed in a helium-4 flow cryostat with a superconducting magnet (Oxford Instruments). The magnetic field was applied parallel and perpendicular to the thin film surface.

#### ASSOCIATED CONTENT

**Supporting Information.** XANES and EXAFS spectra; Electron diffraction patterns; EFTEM maps; Fits of the Co L<sub>2,3</sub> EELS spectra; Crystal field and charge transfer parameters as well as results of the fits of the EELS spectra of the Co L<sub>2,3</sub> edge; Temperature dependence of the magnetization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### **Notes**

The authors declare no competing financial interests.

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# TOC Graphic

