

Direct observation of deuterium in ferromagnetic $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ Su Jae Kim,¹ Seunghun Lee,² Yong Chan Cho,¹ Y. N. Choi,³ S. Park,⁴ I. K. Jeong,⁵ Yoshihiro Kuroiwa,⁶ Chikako Moriyoshi,⁶ and Se-Young Jeong^{2,*}¹*Department of Nanofusion Technology, Pusan National University, Miryang 627-706, Korea*²*W.C.U. Department of Cogno-Mechatronics Engineering, Pusan National University, Miryang 627-706, Korea*³*Neutron Science Division, KAERI, Daejeon 305-353, Korea*⁴*Department of Physics, Pusan National University, Busan 609-735, Korea*⁵*Department of Physics Education, Pusan National University, Busan 609-735, Korea*⁶*Department of Physical Science, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan*

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By combining synchrotron x-ray and neutron scattering, we investigated the detailed structure of deuterium contained $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ powders ($\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$) to find direct evidence of ferromagnetic ordering in the dilute magnetic semiconductor. From neutron powder diffraction using the maximum entropy and Rietveld methods, we were able to determine the position of deuterium Co-D-Co in the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ powder. This has been suggested previously to be the origin of ferromagnetism in ZnCoO . The total concentrations of deuterium and cobalt in the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ sample were 3.8 mol % and 10 mol %, respectively.

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Following the introduction of dilute magnetic semiconductors (DMSs) in the 1980s,¹ many groups have invested heavily in DMS research. While DMSs have potential in industrial applications such as spin-based electronic devices, they are also of fundamental interest because of the long-range ferromagnetic (FM) ion interactions that occur inside them. Co-doped ZnO is a particularly attractive system due to its multiple potential applications, such as room-temperature ferromagnetism^{2–4} and short-wavelength magneto-optics.⁵ However, unresolved issues still remain regarding the physical origin of the ferromagnetism, as well as the stability and reproducibility of its characteristics.

Numerous theoretical and experimental studies have been performed to clarify the physical origin of ferromagnetism in Co-doped ZnO. Oxygen vacancy,^{6–8} the electronic structure,⁹ carriers,¹⁰ Co clusters (metal),^{11–13} intrinsic defects,^{14–17} hydrogen,^{18–22} grain effects,²³ induced ferromagnetism, and secondary phases²⁴ have all been suggested to be the origin of ferromagnetism in Co-doped ZnO systems. A reliable mechanism for ferromagnetism in Co-doped ZnO has been suggested by Park *et al.*²⁵ They proposed that hydrogen impurities in the ZnCoO system could induce strong short-range ferromagnetic ordering by forming Co-H-Co bridge bonds in the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ system. The H atom combines with two Co $3d-t_{2g}$ minority spin orbitals, forming a bridge bond. The bridge bond is stable only when the spins of the two Co ions are parallel. And the parallel spin pairing state of (Co-H_{AB}-Co) is highly more stable by 0.21 eV than the antiparallel spin-paired state. The large energy difference indicates that the H-induced spin-spin interaction is strong enough to lead to room-temperature FM.²⁵ Furthermore, Lee *et al.*¹⁸ showed that $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ thin films became ferromagnetic when they were deposited in H_2/Ar gas mixture environments. Recently, Wang *et al.*¹⁹ also showed that Co-doped ZnO samples containing hydrogen were ferromagnetic. However, these studies could not provide direct evidence of the Co-H-Co dimer structures proposed by Park *et al.*²⁵ Precisely locating the hydrogen in DMS oxides should therefore provide deep insight into the origin of ferromagnetism of

Co-doped ZnO. The ferromagnetism from long-range ferromagnetic order would require a two-dimensional or three-dimensional continuous network of such Co-D-Co (D:deuterium) configurations, but in this system, all of the localized moments are not necessarily coupled to each other for ferromagnetic ordering. In view of the relatively low D content (also for the low Co contents) in the sample, the ferromagnetism mediated by the D can be caused by only the locally percolated clusters connected via strong nearest-neighbor interactions in Co-D-Co. The superparamagnetic behavior in ZnCoO:D(H) is examined as a further study to understand this system more in details.

We investigated the magnetic and structural properties of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ powders with and without deuterium in the sample. Deuterium was used to increase the neutron scattering detection efficiency. It did not enhance the magnetization compared to H. The magnetization of the samples was measured using a superconducting quantum interference device. To examine whether Co clusters formed, room-temperature high-resolution synchrotron x-ray scattering measurements were performed at the SPring-8 synchrotron facility (BL02B2) in Japan. The incident x-ray energy was 25 KeV ($\lambda=0.49664$ Å). Room-temperature neutron powder-diffraction experiments using the maximum entropy method (MEM) and Rietveld analysis were also used to locate the deuterium. Neutron powder-diffraction experiments were performed at the HANARO research reactor in KAERI, Korea. A monochromatic thermal neutron beam ($\lambda=1.8345$ Å) was delivered from the vertically focusing Ge(331) monochromatic. The collimators (first to third) in the neutron beam path were C1/C2/C3=20°/30°/10°.

$\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ powder samples were prepared by the sol-gel method.²¹ For the deuterium injection, the samples were exposed to a deuterium plasma environment six times for 20 min each time. Figure 1 shows the room-temperature magnetic hysteresis loop for the sample before (squares) and after (circles) the deuterium plasma treatment. Paramagnetic behavior was observed in the sample without the deuterium plasma treatment, while ferromagnetism was observed in the

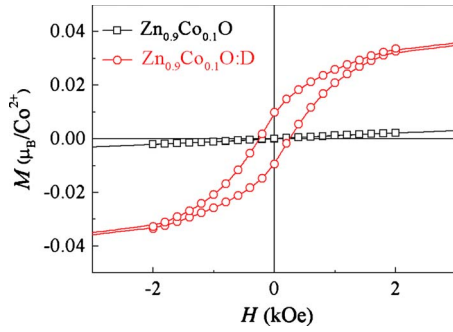


FIG. 1. (Color online) The room-temperature magnetization of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ powders with (circles) and without (square) deuterium plasma treatment.

deuterium plasma-treated sample ($\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$), suggesting that the deuterium was somehow generating ferromagnetic ordering in the sample. This observation did not rule out the possibilities of the formation of the Co-metal phase (clustering) due to the plasma treatment. To examine this possibility, we performed high-resolution synchrotron x-ray powder-diffraction experiment in the BLO2B2 beamline of the SPring-8 synchrotron facility.²⁶ Figure 2 shows the powder diffraction pattern and the Rietveld refinement results of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ powders (a) without and (b) with deuterium plasma treatments, respectively. For both cases, we were able to

refine the results using a single-phase model structure ($\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$). In both cases, the refined results did not show any noticeable differences. In general, the impurity detection limit in x-ray diffraction depends on the material, the instrument resolution, and other factors. In Fig. 2, the refined areal intensity ratio between the main (areal intensity error difference of $\sim 0.6\%$ from the Rietveld analysis) and a small (areal intensity error difference of $\sim 5\%$ from the Rietveld analysis) diffraction peak was about 77.6. This suggested that we

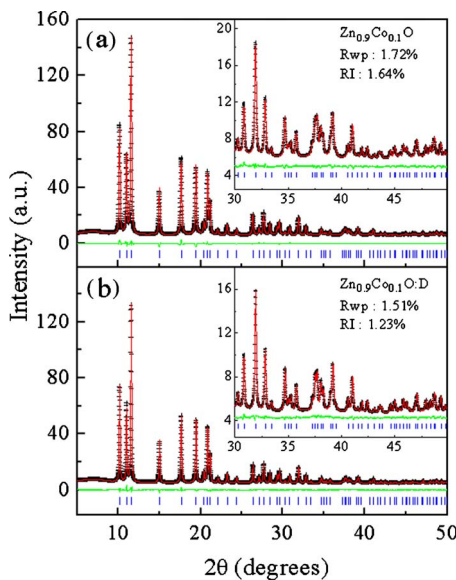


FIG. 2. (Color online) The x-ray powder diffraction pattern (symbols) with Rietveld refinement results (curves) of Co-doped ZnO (a) without and (b) with deuterium plasma treatment.

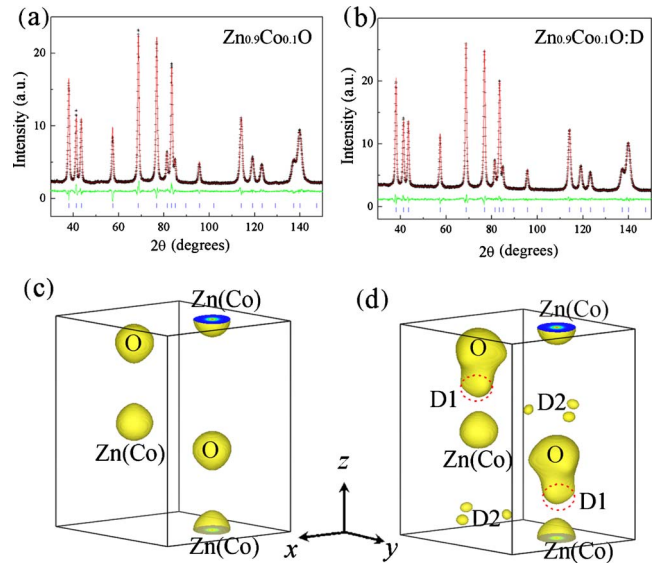


FIG. 3. (Color online) [(a) and (b)] Neutron diffraction raw data and Rietveld refined data for the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ samples. [(c) and (d)] Nuclear density distribution of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ samples on the $5 \times 10^{-3} \text{ fm}/\text{\AA}^3$ isosurface obtained from the MEM/Rietveld analysis.

could identify the secondary phase (assuming the scattering form factor was comparable with that of ZnCoO) if the volume fraction were greater than 1.3% ($1/77.6$) in the diffraction peak measurement. Therefore, given our experimental resolution, we could not find any secondary phases or any difference in the long-range structures of the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ and $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ samples. In addition, the reversible manipulation of short-range spin ordering in Co-doped ZnO thin films through hydrogenation and dehydrogenation processes was observed. The ferromagnetism could be clearly removed and appeared by vacuum annealing and hydrogen injection. This reversibility of ferromagnetism strongly supports our claim on hydrogen-mediated ferromagnetism rather than possibilities due to the formation of Co metal or other secondary phases.²²

When the hydrogen concentration is not enough, x-ray scattering cannot detect the position of hydrogen atoms due to their smaller scattering cross sections. In addition, distinguishing hydrogen signals from the backgrounds is difficult. We therefore added deuterium to a sample and performed room-temperature neutron powder diffraction at the HANARO reactor of the Korean Atomic Energy Research Institute to increase the resolution for hydrogen detection in the sample. Figure 3(a) shows the measured room-temperature neutron powder-diffraction data (crosses) and the Rietveld refinement results (solid curve: $R_1 = 3.62\%$ and $R_{wp} = 2.09\%$) for the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ powder. Here R_{wp} is a weighted reliant factor and R_1 is an integrated intensity-related reliant factor. Figure 3(c) shows the MEM/Rietveld nuclear density distribution of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ for the $5 \times 10^{-3} \text{ fm}/\text{\AA}^3$ isosurface. The nuclear density distribution shows a typical configuration for Zn(Co) and O in the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ structure. If we zoom in on the structure (for the $1 \times 10^{-4} \text{ fm}/\text{\AA}^3$ isosurface), a nuclear density distribution between Zn(Co) and O is visible, bonding along the c axis. Previously, based on first-

TABLE I. Deuterium coordinates from the MEM/Rietveld analysis (Fig. 3) of the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ powders.

Atom	Occupancy (%)	x	y	z
D1	1	2/3	1/3	0.7391(1)
D2	0.3	0.5827(1)	0.4173(1)	0.1024(1)

principles calculations, the position of hydrogen in ZnO was suggested to be between Zn and O (Zn-H-O).^{25,27} The most stable position of the hydrogen was suggested to be perpendicular to the c axis (along the b axis).²⁷ The observed nuclear density distribution along the Zn(Co)-O bonding c axis from the MEM/Rietveld analysis showed the position of the hydrogen, which was not related to the ferromagnetism.

For the deuterated sample, the results of the MEM/Rietveld analysis are shown in Figs. 3(b) and 3(d). Two different model structures were used in the refinement. First, a simple $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ model structure was used, and the refined results and nuclear density distribution map were calculated. We investigated three different isosurfaces ($1 \text{ fm}/\text{\AA}^3$, $5 \times 10^{-3} \text{ fm}/\text{\AA}^3$, and $1 \times 10^{-4} \text{ fm}/\text{\AA}^3$). As the isosurface decreased, an extra feature appeared in the Co-Co bonding sites of the deuterated sample. The extra feature motivated a model structure including deuterium so we modified the simple $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ model to a deuterium-containing $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ model. Figure 3(b) shows the Rietveld refinement results of the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ powder using model structure that contains deuterium positions. The results with the deuterium position showed improvements. The R_1 value decreased from 2.01% to 1.48%, and the R_{wp} value decreased from 2.59% to 2.46%. Figure 3(d) shows the nuclear density distribution map of the deuterated sample. It was analyzed using a model structure that included deuterium positions. The isosurface was $5 \times 10^{-3} \text{ fm}/\text{\AA}^3$. The nuclear density distribution map showed two distinct deuterium positions. One (D1) was Zn(Co)-D-O with 1% occupancy, similar to the position we observed in the $1 \times 10^{-4} \text{ fm}/\text{\AA}^3$ isosurface of the nondeuterated $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ sample. The other (D2) consisted of six equivalent sites of Co-D-Co bonds with 0.3% occupancy. Table I shows the coordinates of deuterium obtained from the MEM/Rietveld analysis for the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ sample shown in Fig. 3(b).

The possible bonds in the six equivalent sites (D2) were Zn-D-Zn, Zn-D-Co, and Co-D-Co but the most stable bonding was Co-D-Co.²⁵ The sample containing deuterium exhibited ferromagnetic ordering (see Fig. 1). Hence the Co-D-Co bonds might have been the origin of the ferromagnetic ordering.

In summary, we synthesized deuterium-doped $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanocrystal powders to identify the Co-D-Co ordering for investigating hydrogen-mediated ferromagnetism in a Co-doped ZnO system. From magnetization measurements, we found that samples with deuterium only exhibited room-temperature ferromagnetism. Combining x-ray and neutron scattering with a MEM/Rietveld analysis, we observed no Co-cluster formation in the system and found the exact position of deuterium in the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ structure. From a detailed structure analysis using the MEM/Rietveld method, we observed that the most probable deuterium positions were Co-D-Co and Zn(Co)-D-O.

The total concentration of deuterium in $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ was 3.8% and the concentration of deuterium in the Co-D-Co bonds was about 1.8%, when the Co concentration was 10.0 (1) mol %. The direct observations we performed support the theory that ferromagnetism can be caused by a spin-spin interaction mediated by hydrogen between Co-Co dimers. These observations have opened up possibilities for investigating the detailed structure of light, weak impurities and provided experimental evidence of the origin of ferromagnetism in $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O:D}$ powders.

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