Zn-induced development of the Cu-spin correlation in electron-doped superconducting cuprates of Eu$_{2-x}$Ce$_x$CuO$_4$

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Abstract. The effect of Zn substitution to the Cu-spin fluctuation in Eu$_{1.85}$Ce$_{0.15}$Cu$_{1-y}$Zn$_y$O$_{4+δ}$ with $y = 0, 0.01, 0.02$, and $0.05$ has been studied from zero-field (ZF) muon-spin-relaxation ($\mu$SR) measurements to understand Zn-induced magnetic state in electron-doped high-$T_c$ superconducting cuprates. It was found that the Cu-spin correlation was developed through Zn substitution. These results were similar to the results of ZF-$\mu$SR measurements in the hole-doped cuprates La$_{2-x}$Sr$_x$Cu$_{1-y}$Zn$_y$O$_{6}$, leading to the view electron-hole doping symmetry in high-$T_c$ superconductors.

1. Introduction
The single-layer cuprates of high temperature superconductors discovered in 1986 was called 214 cuprates. There are two types of 214 cuprates, namely, hole- and electron-doped cuprates. Some properties in both systems have been found to be very similar to each other leading to the view of hole-electron doping symmetry. For examples, from the view of Hubbard and t-J models, both types become superconductor when carriers are doped near the half-filling Fermi surface. From the angle-resolved photoemission spectroscopy (ARPES) studies, both types show a $d_{x^2-y^2}$ pairing symmetry with clear shift of the spectral weight as the gap opens in $(\pi,0)$-$(\pi,\pi)$ and $(0,\pi)$-$(\pi,\pi)$ directions [1,2]. From schematic of phase diagrams, both types show an antiferromagnetic phase in low doping concentration and a superconducting phase in appropriate doping range.

Different properties are also found between hole- and electron-doped cuprates. First, doped holes destroy the antiferromagnetic order more effectively than doped electrons. Second, from the effect of impurities to its superconducting properties, it has been found that the superconductivity in the electron-doped of Nd$_2$Se$_3$CuO$_7$ is suppressed through the magnetic Ni substitution for Cu more markedly than through the non-magnetic Zn substitution [3], which is contrary to the result in the hole-doped cuprates [4]. However, the reason for these differences between the hole- and electron-doped systems has not yet been clarified. Some other properties such as hole-trapping, Kondo effect, inhomogeneity of field-induced magnetism were already clarified in hole-doped cuprates [5-7], while the information about those properties in electron-doped cuprates is still lacking.

Previously, the effect of the partial substitution of Zn for Cu on the Cu-spin dynamics in 214 cuprates is also investigated from zero-field (ZF) muon-spin-relaxation ($\mu$SR) for both hole-
electron-doped cuprates. In hole-doped cuprates $\text{La}_2\text{SrCu}_1\gamma\text{Zn}_y\text{O}_4$, Cu-spin fluctuations around Zn exhibit slowing down due to the pinning of the dynamical stripes by Zn, leading to the formation of a static stripe order and the destruction of superconductivity around Zn, called a stripe-pinning model [8,9]. In the electron-doped cuprates $\text{Pr}_{1.8}\text{LaCe}_0\text{Cu}_1\gamma\text{Zn}_y\text{O}_4$ [10], it was found that there is no significant difference in the temperature dependence of spectra with changing Zn concentration, which is very different result from those in the hole-doped cuprates. There are two possible reasons. First, there may be no dynamically fluctuating stripes of spins and electrons in the electron-doped system. Second, the effect of Pr$^{3+}$ moments is stronger than that of a small amount of Zn impurities.

Here, we reported the effect of Zn substitution to the Cu-spin fluctuation in $\text{Eu}_{1+\delta}\text{Ce}_{0.15}\text{Cu}_1\gamma\text{Zn}_y\text{O}_{4+\alpha-\delta}$ to understand Zn-induced magnetic state in electron-doped high-$T_c$ superconducting cuprates. An advantage of this sample rather than other types of electron-doped systems is that the absence of rare earth moments such as Pr$^{3+}$ moments in $\text{Pr}_{1+\delta}\text{LaCe}_0\text{Cu}_1\gamma\text{Zn}_y\text{O}_{4+\alpha-\delta}$ samples, the dynamic behavior of Cu-spins and effects of impurity to them without any magnetic disturbance can directly observed.

2. Methods
Polycrystalline samples of $\text{Eu}_{1+\delta}\text{Ce}_{0.15}\text{Cu}_1\gamma\text{Zn}_y\text{O}_{4+\alpha-\delta}$ with $\gamma= 0, 0.01, 0.02$, and 0.05 were prepared by the ordinary solid-state reaction method [11]. In electron-doped system with T$'$ structure, as-grown samples have the excess oxygen, $\alpha$, which is very difficult to control. In order to remove the excess oxygen at the apical site, as-grown samples of ECCZO were post-annealed in flowing Ar gas at various temperatures in a range of 880 – 950°C for 8 - 12 h. The amount of the reduced oxygen, $\delta$, were estimated from the weight change before and after post-annealing using Eq.1.

$$\delta = \left(1 - \frac{m_2}{m_1}\right)\frac{M_{\text{ECCZO}}}{M_0}$$  \hspace{1cm} (1)

where $m_1$ and $m_2$ were mass of sample before and after annealing, respectively. $M_{\text{ECCZO}}$ is mass number of $\text{Eu}_{1+\delta}\text{Ce}_{0.15}\text{Cu}_1\gamma\text{Zn}_y\text{O}_4$ and $M_0$ is mass number of oxygen. The amount of $\delta$ was also very hard to control as well. For the present study, a set of Zn-substituted samples with $\delta$ from 0.03 to 0.08 were used.

All of the samples were checked by the powder X-ray diffraction measurements. ZF-$\mu$SR measurements were performed at low temperatures down to 10 K at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK using a pulsed positive surface muon beam. For the present $\mu$SR measurements, 1 to 3 samples in pellet with diameter of 10 mm were used. Using apiezon N grease, the samples were set on Ag plate attached to the cryostat. The behavior of Cu-spin can be understood by observing time spectra of ZF-$\mu$SR. A Gaussian-type depolarization is observed when electron spins are fluctuating fast beyond the $\mu$SR time window (10$^{-6}$-10$^{-11}$ sec). An exponential-type depolarization is observed when electron spins exhibit slowing down, and when a coherent magnetic order is formed, a muon-spin precession is observed.

3. Results and Discussion
Figure 1 shows a set of XRD pattern of $\text{Eu}_{1+\delta}\text{Ce}_{0.15}\text{Cu}_1\gamma\text{Zn}_y\text{O}_{4+\alpha-\delta}$ with $\gamma= 0, 0.01, 0.02$, and 0.05. All of XRD peaks were assigned as T$'$ structure with space group was I 4/mmm. All XRD patterns were also analyzed using Rietveld refinements as shown in Table 1. It is found that all samples have 100 % weight fraction of $\text{Eu}_{1+\delta}\text{Ce}_{0.15}\text{Cu}_1\gamma\text{Zn}_y\text{O}_{4+\alpha-\delta}$. The lattice parameters a- and c-axis were almost unchanged with varying Zn concentration. One of the reasons is because the similar size of Cu$^{2+}$ ions (0.87 Å) and Zn$^{2+}$ ions (0.88 Å).
Figure 1. A set of XRD pattern of Eu$_{1.85}$Ce$_{0.15}$Cu$_{1-y}$Zn$_y$O$_{4+\alpha-\delta}$ with y = 0, 0.01, 0.02, and 0.05.

Table 1. Rietveld refinements results of XRD pattern of Eu$_{1.85}$Ce$_{0.15}$Cu$_{1-y}$Zn$_y$O$_{4+\alpha-\delta}$

|                   | y=0       | y=0.01    | y=0.02    | y=0.05    |
|-------------------|-----------|-----------|-----------|-----------|
| Calculate Density (g/cm$^3$) | 7.8766    | 7.8813    | 7.8742    | 7.8821    |
| Weight Fraction (%)     | 100       | 100       | 100       | 100       |
| Preferred Orientation  | 0.951247  | 0.9937(7) | 0.983726  | 0.9807(7) |
| Lattice Parameters a (Å) | 3.90602(8) | 3.9093(1) | 3.9109(1) | 3.9101(2) |
| Lattice Parameters b (Å) | 3.90602(8) | 3.9093(1) | 3.9109(1) | 3.9101(2) |
| Lattice Parameters c (Å) | 11.8731(3)| 11.8462(6)| 11.8472(6)| 11.8401(6)|

Figure 2 shows the μSR time spectra of ECCZO with y = 0 [11], 0.01, 0.02 and 0.05 at various temperatures. All μSR time spectra are best fitted using the following three-component function [11]

$$A(t) = A_0e^{-\lambda_0t}G_{D}(\Delta,t)+A_1e^{-\lambda_1t}+A_2e^{-\lambda_2t}\cos(\omega t+\phi)$$  \hspace{1cm} (2)

The A$_0$, A$_1$ and A$_2$ are the initial asymmetry of slow, fast and spin precession component, respectively. $\lambda_0$ is the depolarization rate of the slowly depolarizing component. The $G_{D}(\Delta,t)$ is the static Kubo-Toyabe function dependent on $\Delta$ describing the distribution width of nuclear dipolar fields at the muon site. $\lambda_1$ is depolarization rate of the fast depolarizing component, $\lambda_2$, $\omega$ and $\phi$ are the initial asymmetry, damping rate, frequency and phase of the muon spin precession, respectively [11].
For all samples, the spectra show Gaussian-like depolarization at high temperatures above ~200 K. For y = 0, the spectrum was still Gaussian-type depolarization above ~100 K. The spectrum changed from Gaussian-type depolarization to exponential-type depolarization at low temperatures below ~50 K. For Zn-substituted samples, it is found that the spectrum dramatically changed from Gaussian-type to exponential type depolarization with decreasing temperature. For y = 0.02 and 0.05, a muon precession is observed below 100 K, indicating the formation of a long-range static magnetic order. These results indicating the Zn-induced slowing down of the Cu-spin fluctuations were observed as in the case of the hole-doped cuprates, leading to the view electron-hole doping symmetry in high-Tc superconducting cuprates.

![Figure 2. ZF-μSR time spectra of Eu$_{1.85}$Ce$_{0.15}$Cu$_{1-y}$Zn$_{y}$O$_{4+\alpha-\delta}$ with y = 0, 0.01, 0.02, and 0.05 at various temperatures.](image)

4. Conclusion
We have investigated Zn induced development of Cu-spin fluctuations in electron-doped superconducting cuprates of Eu$_{1.85}$Ce$_{0.15}$Cu$_{1-y}$Zn$_{y}$O$_{4+\alpha-\delta}$ with y = 0, 0.01, 0.02, and 0.05 to understand Zn-induced magnetic state in electron-doped high-Tc superconducting cuprates.

The spectra show Gaussian-like depolarization at high temperatures above ~200 K. For Zn-substituted samples, it was found that the spectrum dramatically changed from Gaussian-type to exponential type depolarization with decreasing temperature. For y = 0.02 and 0.05, a muon precession was observed below 100 K, indicating the formation of a long-range static magnetic order. These results suggested that the Zn-induced slowing down of the Cu-spin fluctuations were observed as in the case of the hole-doped cuprates, leading to the view electron-hole doping symmetry in high-Tc superconducting cuprates.

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