63,65\textsuperscript{Cu}, 139\textsuperscript{La}-NMR study of Electron-doped High Temperature Cuprate Superconductor
\textit{T’-La\textsubscript{1.8}Eu\textsubscript{0.2}CuO\textsubscript{4}\textsubscript{y}F\textsubscript{y}}

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Abstract. \textit{T’-La\textsubscript{1.8}Eu\textsubscript{0.2}CuO\textsubscript{4}\textsubscript{y}F\textsubscript{y}} (0 \leq y \leq 0.125) was measured by \textsuperscript{63,65}Cu and \textsuperscript{139}La NMR. This material is an electron-doped high-$T_c$ cuprate superconductor which has Nd\textsubscript{2}CuO\textsubscript{4}-type structure (so-called T’-structure). The nuclear spin-lattice relaxation rate $1/T_1$ revealed that pseudogap behavior exists in the lightly electron-doped region of $y \leq 0.075$ and electron doping suppresses the antiferromagnetic spin fluctuations. These behaviors in electron-doped high-$T_c$ cuprate superconductor are analogous with the optimum- and over-doped region in hole-doped type. \textsuperscript{139}La NMR spectra shows almost no antiferromagnetic region in the samples of \textit{T’-La\textsubscript{1.8}Eu\textsubscript{0.2}CuO\textsubscript{4}\textsubscript{y}F\textsubscript{y}}.

1. Introduction

High-$T_c$ cuprate superconductors (HTSCs) have been thought to exhibit superconductivity by doping carrier into the the parent material which is Mott insulator [1]. It has also been considered that the electron-doped HTSCs have a smaller superconducting phase and a larger antiferromagnetic phase than the hole-doped HTSCs. However, recent studies have reported that the superconducting phase becomes larger when electron-doped HTSCs are sufficiently reduced [2, 3]. This is because apical oxygens located above and below Cu are removed through the reduction annealing and the localized antiferromagnetic order is suppressed.

To investigate the phase diagram of HTSCs with the Nd\textsubscript{2}CuO\textsubscript{4}-type structure (so-called T’-structure), \textit{T’-La\textsubscript{1.8}Eu\textsubscript{0.2}CuO\textsubscript{4}} (T’-LECO) is one of the most appropriate materials [4, 5, 6, 7, 8]. This compound can be both electron-doped by F with O, and hole-doped by Ca or Sr with La, respectively. Investigation of various doping clarifies the dependencies on the doping levels for both carriers in the equivalent crystal structure. In this study, we performed \textsuperscript{63,65}Cu, \textsuperscript{139}La NMR measurement of an electron-doped HTSC \textit{T’-La\textsubscript{1.8}Eu\textsubscript{0.2}CuO\textsubscript{4}\textsubscript{y}F\textsubscript{y}} (T’-LECOF, 0 \leq y \leq 0.125) in order to reveal superconducting and normal state properties of the compounds.

2. Experiments

T’-LECOF samples are polycrystals synthesized via multiple processes, according to Ref. 7. Polycrystalline samples were oxygen reduced through the annealing under a pressure of
Figure 1. (Color online) Phase Diagram of T’-La$_{1.8-x}$Eu$_{0.2}$CuO$_{4-y}$F$_y$. (superconducting transition temperature $T_c$, Pseudogap (PG) temperature $T_{PG}$, Curie-Weiss temperature $\theta$) The determination of each temperature is described in text.

3 \times 10^{-5} \text{ Pa for 24 hours at 700 °C for } y = 0 \text{ and at 650 °C for } y = 0.025-0.125. \text{ The annealed samples were confirmed by X-ray powder diffraction. By measurement of dc magnetization with a commercial SQUID magnetometer (Quantum Design MPMS), the samples are verified in single phase with F substance dependency for } T_c \text{ as Ref. 7. phase-coherent pulsed NMR spectrometers and 8 T SC magnet were used to measure the } ^{63,65}\text{Cu and } ^{139}\text{La NMR. The silver pickup coil and shield were attached to avoid the external Cu metal signals. To determine the } ^{63}\text{Cu Knight shift } [9], \text{ Cu metal powder was used as a reference (} K = 0.232\%). \text{ To evaluate the spin-lattice relaxation time } T_1 \text{ for each temperature, saturation recovery method was applied for fitting the nuclear magnetization recovery curve anticipated for the nuclear spin } I = 3/2 \text{ of the } ^{63}\text{Cu nucleus } [10].

\begin{equation}
\frac{M(\infty) - M(t)}{M(\infty)} = A \left[ 0.1 \exp\left(\frac{-t}{T_1}\right) + 0.9 \exp\left(-\frac{6t}{T_1}\right) \right].
\end{equation}

3. Results and discussion

From temperature dependence of spin-lattice relaxation rate $1/T_1$ of $^{63}\text{Cu-NMR},$ pseudogap (PG) behavior exists in the under electron-doped region as $y \leq 0.075$ [11]. $1/T_1$ also suggested that electron doping suppresses the antiferromagnetic spin fluctuations. In Fig. 1, we summarized substitution dependence of several characteristic temperatures (SC transition temperature $T_c$, PG temperature $T_{PG}$, Curie-Weiss temperature $\theta$) of T’-LECOF. $T_c$ (onset) and $T_c$ (NMR) were determined from the superconducting onset temperatures of magnetic susceptibility $\chi$ and NMR Knight shift, respectively. $T_c$ was defined from the local maximum of $1/T_1T$ above $T_c$. $\theta$ was evaluated from the fitting to the formula $1/T_1T = C/(T + \theta)$ above $T_{PG}$. Compared with the phase diagram of hole-doped HTSCs, there are many similarities between both electron-doped type and over optimum-doped region of hole-doped type [12, 13]. Comparing the phase diagrams of T’-LECOF and isostructural T’-Pr$_{1.3-x}$La$_{0.7}$Ce$_x$CuO$_4$ (T’-PLCCO) based on the nominal substitution, T’-LECOF is more effectively electron-doped than T’-PLCCO through the partial substitution [14, 15, 16, 17].
**Figure 2.** (Color online) $^{139}$La NMR spectrum of T'-La$_{1.8}$Eu$_{0.2}$CuO$_4$ at 240 K.

**Figure 3.** (Color online) Temperature dependence of the full width at half maximum of $^{139}$La NMR spectra of T'-La$_{1.8}$Eu$_{0.2}$CuO$_4$-yF$_y$ ($0 \leq y \leq 0.125$).

$^{139}$La-NMR mainly reflects the information of the phase-separated magnetically-ordered region in the samples. In Fig. 2, the spectrum of T'-LECOF ($y = 0$) obtained at 240 K is shown. The spectrum have a sharp-edged center line originated by transition between $I_z = -1/2$ and $+1/2$. Distributed crystalline electric field occurred by polycrystalline samples makes a broad structure surrounding the center line. From this structure, the electric field gradient located on La sites was estimated as $\nu_Q \sim 0.5$ MHz. As the temperature decreases, the spectrum gradually becomes broad.

A rectangular powder originating from $^{139}$La nuclei under the homogeneous internal field among the sample does not exist. In this case, the emergence of localized antiferromagnetic
ordering can be observed by the sudden increase of the line width. In Fig. 3, the temperature dependence of the full width at half maximum (FWHM) of T'-LECOF is shown. Although the increase of FWHM below about 30 K was observed, this increase is five times smaller than that of T'-Pr$_{1.3-\delta}$La$_{0.7}$Ce$_{\delta}$CuO$_4$ (T'-PLCCO) in which the clear rapid increase of FWHM was observed below Neél temperature $T_N$ [14]. Hence, the results indicate the almost no localized antiferromagnetic order in T'-LECOF.

4. Summary
In summary, T'-La$_{1.8}$Eu$_{0.2}$CuO$_{4-y}F_y$ ($0 \leq y \leq 0.125$) was measured by $^{63,65}$Cu and $^{139}$La NMR. This material is an electron-doped high-$T_c$ cuprate superconductor which has Nd$_2$CuO$_4$-type structure (so-called T'-structure). The nuclear spin-lattice relaxation rate $1/T_1$ revealed that pseudogap behavior exists in the lightly electron-doped region of $y \leq 0.075$ and electron doping suppresses the antiferromagnetic spin fluctuations. These behaviors in electron-doped type are analogous with the optimum- and over-doped region in hole-doped type. It is also revealed by $^{139}$La NMR measurements that the localized antiferromagnetic order does not nearly exist in T'-La$_{1.8}$Eu$_{0.2}$CuO$_{4-y}F_y$.

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