Muon-spin relaxation study of the spin correlations in the overdoped regime of electron-doped high-T_c cuprate superconductors

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In order to investigate the low-energy antiferromagnetic Cu-spin correlations and their relation to the superconductivity, we have performed muon-spin-relaxation (μSR) measurements using single crystals of the electron-doped high-T_c cuprate $Pr_{1-x}LaCe_xCuO_4$ in the overdoped regime. The μSR spectra have revealed that the Cu-spin correlations are developed in the overdoped samples where the superconductivity appears. The development of the Cu-spin correlations weakens with increasing x and is negligibly small in the heavily overdoped sample where the superconductivity almost disappears. Considering that the Cu-spin correlations also exist in the superconducting electron-doped cuprates in the undoped and underdoped regimes [T. Adachi *et al.*, J. Phys. Soc. Jpn. **85**, 114716 (2016)], our findings suggest that the mechanism of the superconductivity is related to the low-energy Cu-spin correlations in the entire doping regime of the electron-doped cuprates.

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I. INTRODUCTION

In the research of high-T_c cuprate superconductivity, the relationship between the Cu-spin correlations and superconductivity has been the central issue in both hole-doped and electron-doped cuprates. For the hole-doped cuprate of $La_{2-x}Sr_xCuO_4$ (LSCO), neutron-scattering experiments have revealed that the commensurate Cu-spin correlations in the antiferromagnetic (AF) state of the parent compound change to the incommensurate one with hole doping in the superconducting (SC) state [1], followed by the disappearance of both incommensurate Cu-spin correlations and superconductivity in the heavily overdoped regime [2]. Muon-spin-relaxation (μSR) measurements in Zn-impurity-substituted $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ have revealed that the development of the Cu-spin correlations vanishes at the end point of the SC region in the heavily overdoped regime of the phase diagram [3]. Therefore, the incommensurate Cu-spin correlations appear to be intimately related to the superconductivity. For the electron-doped cuprates, on the other hand, the commensurate Cu-spin correlations have been observed in the optimally doped regime of $Nd_{2-x}Ce_xCuO_4$ [4] and $Pr_{1-x}LaCe_xCuO_4$ (PLCCO) [5,6]. The relationship between the commensurate Cu-spin correlations and superconductivity has been unclear in the electron-doped cuprates.

Recently, the so-called undoped (Ce-free) superconductivity in the electron-doped cuprates has attracted considerable research attention. It has been reported that the superconductivity appears even in the parent compound of $x = 0$ and in a wide range of x in $Nd_{2-x}Ce_xCuO_4$ thin films through the appropriate reduction annealing to remove excess oxygen from the as-grown thin films [7,8]. The superconductivity in the parent compound has also been confirmed in the polycrystalline samples [9,10]. Two possible mechanisms of the undoped superconductivity have been proposed: the electron doping by the oxygen deficiency (oxygen nonstoichiometry) [11] and the collapse of the charge-transfer gap due to squareplaner coordination of oxygen in the CuO_2 plane [12]. If the latter is the case, the undoped superconductivity indicates that the phase diagram is completely different from the former one, that is, the superconductivity in the electron-doped cuprates cannot be understood in terms of carrier doping into the parent Mott insulators as in the case of the hole-doped cuprates. An important issue is whether the Cu-spin correlations are related to the superconductivity in the electron-doped cuprates.

Through the improved reduction annealing, high-quality SC single crystals have been obtained in underdoped $Pr_{2-x}Ce_xCuO_4$ with $x \geqslant 0.04$ [13] and $Pr_{1.3-x}La_{0.7}Ce_xCuO_{4+\delta}$ with $x \geqslant 0.05$ [12,14,15]. Formerly, we have performed μSR measurements of the SC parent polycrystal of $La_{1.8}Eu_{0.2}CuO_4$ and the SC underdoped single crystal of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ with $x = 0.10$ [15,16]. It has been found that a short-range magnetic order is formed at low temperatures in both samples, suggesting a coexisting state of superconductivity with the short-range magnetic order. The development of the Cu-spin correlations has also been confirmed in μSR measurements of the SC parent

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thin film of $La_{1.9}Y_{0.1}CuO_4$ [17]. These results suggest that a small amount of residual excess oxygen in a sample causes the development of the Cu-spin correlations and/or the formation of the short-range magnetic order, indicating a strongly correlated electron system of the undoped and electron-underdoped cuprates.

The next issue is how the Cu-spin correlations change with electron doping concomitant with the weakening of the superconductivity in the overdoped regime. Inelastic neutron-scattering experiments in the overdoped PLCCO with $x \leqslant 0.18$ have revealed that the characteristic energy of the Cu-spin correlations decreases with increasing x and seems to disappear with the superconductivity [18]. This is different from the results of the hole-doped cuprates in which the characteristic energy of the Cu-spin correlations is unchanged but the spectral weight decreases with hole doping [2], suggesting the occurrence of a phase separation into SC and normal-state regions in a sample [19]. From the former μSR measurements in the SC polycrystal of PLCCO with $x = 0.14$, slowing down of the Cu-spin fluctuations has been observed at low temperatures without any magnetic order [20]. NMR experiments of the SC single crystal of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ with $x = 0.15$ have also indicated the presence of AF spin fluctuations [21]. These suggest that, compared with the short-range magnetic order in the parent and underdoped samples [15,16], the development of the Cu-spin correlations weakens with increasing x but is apparently observed in the slightly overdoped regime. In order to obtain detailed information on the low-energy Cu-spin correlations in the heavily overdoped regime and their relation to the superconductivity, we have carried out μSR measurements using PLCCO single crystals in the heavily overdoped regime of $x = 0.17$ and 0.20.

II. EXPERIMENTAL

Single crystals of PLCCO with $x = 0.17$ and 0.20 were prepared by the traveling solvent floating zone method [22,23]. The quality of the grown crystals was checked by the x-ray back-Laue photography and powder x-ray diffraction to be good. The composition of the crystals was analyzed by the inductively coupled plasma spectrometry. For the reduction annealing in a vacuum condition of 2×10^{-4} Pa, the two-step annealing was performed at 900 °C for 12 h and 500 °C for 12 h for $x = 0.17$. For $x = 0.20$, the improved one-step reduction annealing was carried out at 800 °C for 24 h [12]. Magnetic-susceptibility measurements were performed using a SC quantum interference device (SQUID) magnetometer (Quantum Design, MPMS). Figure 1 shows the temperature dependence of the magnetic susceptibility of PLCCO with $x = 0.17$ and 0.20 together with $x = 0.13$ and 0.15 [23]. The SC transition temperature T_c of $x = 0.17$ is ≈5 K and the Meissner diamagnetism at 2 K is much smaller than those of $x = 0.13$ and 0.15, indicating that the superconductivity is weak. For $x = 0.20$, the Meissner diamagnetism is unobservable, indicating a non-SC state of this sample. As shown in the inset of Fig. 1, values of T_c are almost consistent with those in the former report [18]. Zero-field (ZF) and longitudinal-field (LF) μSR measurements were performed at low temperatures down to 0.3 K at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the United Kingdom using a pulsed positive surface muon beam. The data were analyzed using the WIMDA program [24].

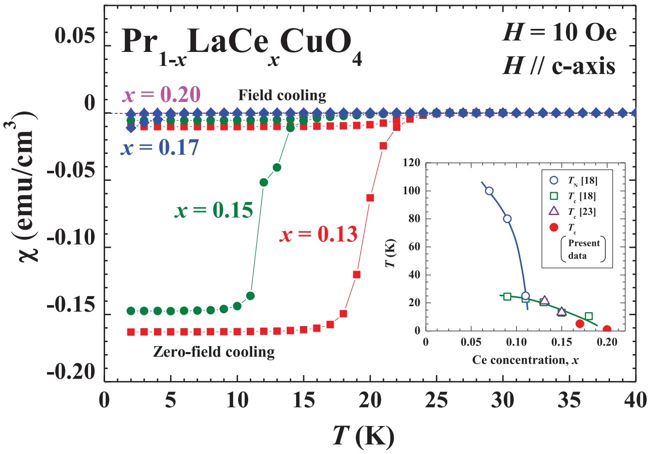

FIG. 1. Temperature dependence of the magnetic susceptibility of reduced single crystals of PLCCO with $x = 0.17$ and 0.20 together with $x = 0.13$ and 0.15 [23]. The inset shows the Ce-concentration dependence of T_c in PLCCO, together with the former results of T_c and T_N [18]. Solid lines are to guide the reader's eye.

III. RESULTS AND DISCUSSION

Figure 2 shows the ZF-μSR time spectra of the reduced crystals of PLCCO with $x = 0.17$ and 0.20 together with $x = 0.14$ [20]. In both $x = 0.17$ and 0.20, the depolarization of muon spins is slow at a high temperature of 200 K owing to the very small nuclear dipole field randomly oriented at the muon site, indicating an almost paramagnetic state of Cu spins. With decreasing temperature, the depolarization of muon spins becomes fast, as seen in $x = 0.14$, due to static random magnetism of small magnetic moments of Pr^{3+} ions induced by the mixing of the excited state in the crystal electric field [20,25].

For $x = 0.14$, the development of the Cu-spin correlations is characterized by the increase in the asymmetry in the long-time region above ≈4 μs with decreasing temperature, shown in Fig. 2(a) [20], which is due to the recovery of the asymmetry toward 1/3 in a magnetically ordered state. It is found that the recovery of the asymmetry in the long-time region is negligibly small at low temperatures down to 9 K for $x = 0.17$ and down to 0.3 K for $x = 0.20$. This indicates that the Cu-spin correlations are hardly developed in the heavily overdoped regime of PLCCO where the superconductivity almost disappears.

To see effects of the Cu-spin correlations in detail, the ZF-μSR time spectra were analyzed using the following three-component function [20]:

$$A(t) = A_s \exp[-(\lambda t)^{\beta}] + A_G \exp[-\sigma^2 t^2] + A_{base}. \quad (1)$$

The first term represents a stretched-exponential component in which effects of nuclear spins and Cu spins are dominant. The A_s, λ, and β are the initial asymmetry, depolarization rate of muon spins, and power of damping, respectively. The second term represents a static Gaussian component in which the effect of small Pr^{3+} moments is dominant. The

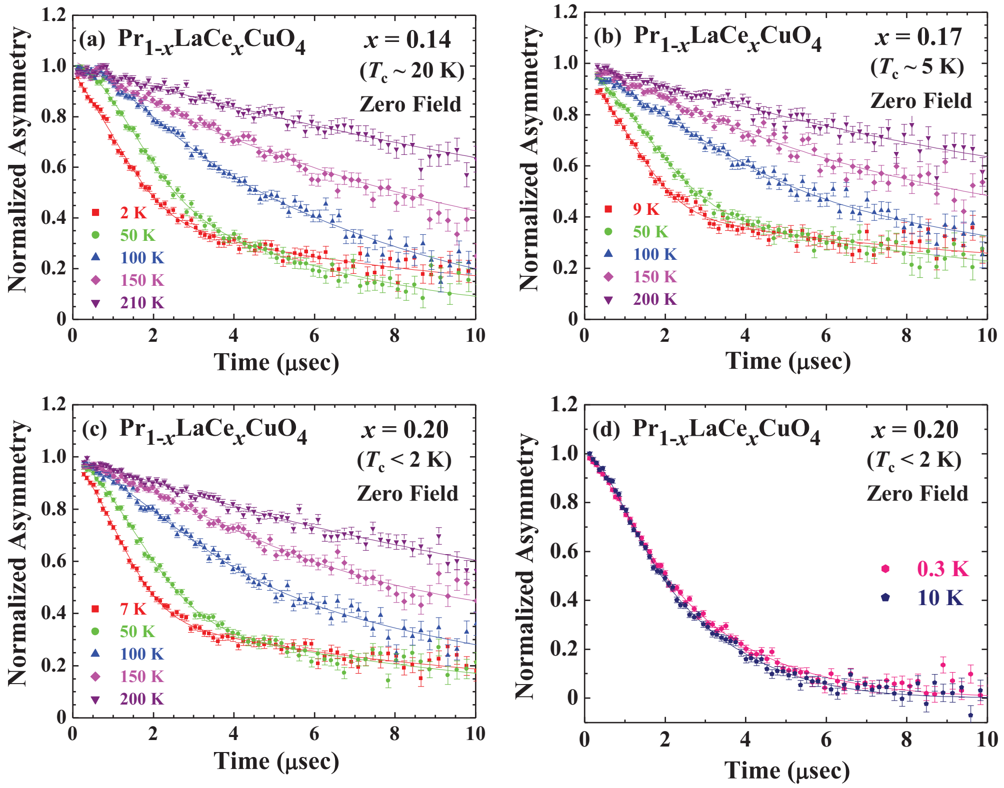

FIG. 2. ZF-μSR time spectra of reduced PLCCO crystals with (a) $x = 0.14$ [20], (b) $x = 0.17$, and (c) $x = 0.20$ at various temperatures. (d) ZF-μSR time spectra of the reduced PLCCO crystal with $x = 0.20$ at 10 K and 0.3 K. Solid lines are the best-fit results using the two-component function described in Eq. (1).

A_G and σ are the initial asymmetry and depolarization rate of muon spins, respectively. The A_{base} is a time-independent background term. The spectra are well fitted with Eq. (1), as clearly shown in Figs. 2(b) and 2(c). It is noted that the use of the two terms with A_s and A_G suggests two possible muon stopping sites in PLCCO. Although previous reports have suggested one muon stopping site in the T' cuprates based on the dipole-field calculation [26,27], a recent first-principle calculation suggests two muon stopping sites: One is near the CuO_2 plane mainly sensing the dipole field of the Cu spins and the other is near the (Pr,La,Ce)-O layer mainly sensing that of Pr^{3+} moments [28,29].

Figure 3 shows the temperature dependence of the fitting parameters A_s, β, and σ, and λ for both crystals of PLCCO with $x = 0.17$ and 0.20 together with $x = 0.14$ [20]. At high temperatures above 100 K, all parameters seem to be almost independent of temperature and the normalized A_s is nearly one. It is noted that the change of the spectra above 100 K shown in Fig. 2 for all samples is predominantly due to the small change of A_s. The σ (A_s) increases (decreases) with decreasing temperature below ≈100 K owing to the growing effect of Pr^{3+} moments [20]. For $x = 0.14$, the development of the Cu-spin correlations is characterized by the steep increase in λ and enhancement of A_s below ≈30 K as shown in Figs. 3(d) and 3(a) [20]. For $x = 0.17$ and 0.20, on the contrary, neither steep increase in λ nor apparent enhancement of A_s is observable at low temperatures, indicating that the development of the Cu-spin correlations is negligibly small in both samples.

In order to further investigate the effects of Cu spins and Pr^{3+} moments, LF-μSR measurements were performed under LF up to 1000 G at 0.3 K for PLCCO with $x = 0.20$. As shown in Fig. 4, the tail of the spectrum is gradually quenched with increasing field up to 100 G. This suggests the existence of static magnetism due to Pr^{3+} moments. In the long-time region, the slow depolarization is still observed up to 1000 G, indicating that there exist fluctuating internal fields at the muon site due to Cu spins [20]. Therefore, the LF-μSR results suggest the coexistence of the static magnetism of Pr^{3+} moments and fluctuating Cu spins in $x = 0.20$ as well as $x = 0.14$ [20].

For both PLCCO crystals with $x = 0.17$ and 0.20, the μSR spectra show the existence of both the static magnetic field due to Pr^{3+} moments and the slow depolarization related to Cu-spin fluctuations. The development of the Cu-spin correlations becomes weak with increasing x and is negligibly small at $x = 0.20$ where the superconductivity almost disappears. Combined with the results in the undoped and underdoped regimes [15,16], these results suggest an intimate relationship between the Cu-spin correlations and superconductivity in the entire doping regime of PLCCO.

Finally, we discuss the comparison between hole-doped and electron-doped cuprates briefly in term of the Cu-spin correlations. From the μSR results of Zn-substituted $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ in the overdoped regime, it has been found that the Zn-induced development of the Cu-spin correlations becomes weak with hole doping and finally disappears at $x \sim 0.30$ where the superconductivity disappears in

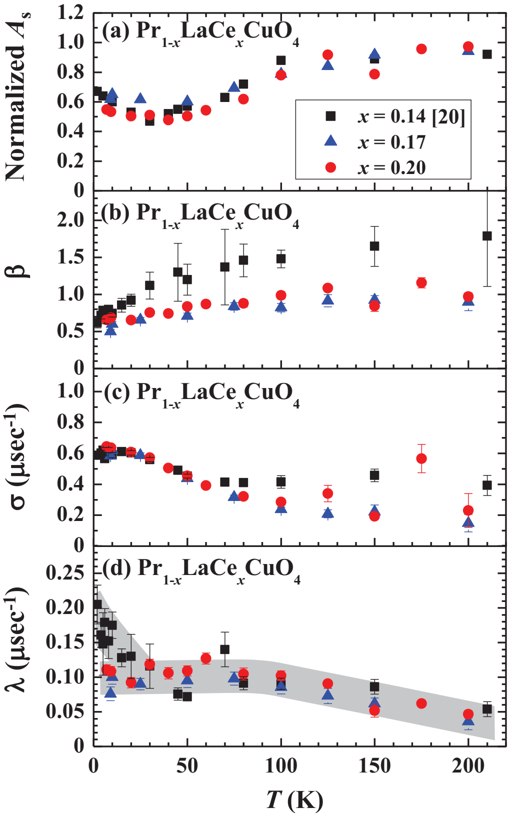

FIG. 3. Temperature dependence of the fitting parameters in the two-component function described in Eq. (1) for reduced crystals of PLCCO with $x = 0.17$ and 0.20 together with $x = 0.14$ [20] for comparison.

LSCO [3]. Moreover, inelastic neutron-scattering experiments have uncovered the disappearance of the AF spin fluctuations concomitant with the disappearance of superconductivity at $x = 0.30$ [2]. In the electron-doped cuprate, a short-range magnetic order due to a very small amount of excess oxygen is formed in the parent SC polycrystal of $La_{1.8}Eu_{0.2}CuO_{4+\delta}$ and the SC underdoped single crystal of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ with $x = 0.10$ [15,16]. The Cu-spin correlations are moderately developed in the overdoped PLCCO with $x = 0.14$ [20] and the development of the Cu-spin correlations almost disappears in the heavily overdoped PLCCO with $x = 0.20$ where the superconductivity disappears. Therefore, there is a similarity for both hole-doped and electron-doped cuprates in terms of the Cu-spin correlations, that is, the development of the Cu-spin correlations is observed in the SC region of the phase diagram. It is suggested that the Cu-spin correlations are in intimate relation with the appearance of high-T_c superconductivity in both hole- and electron-doped cuprates.

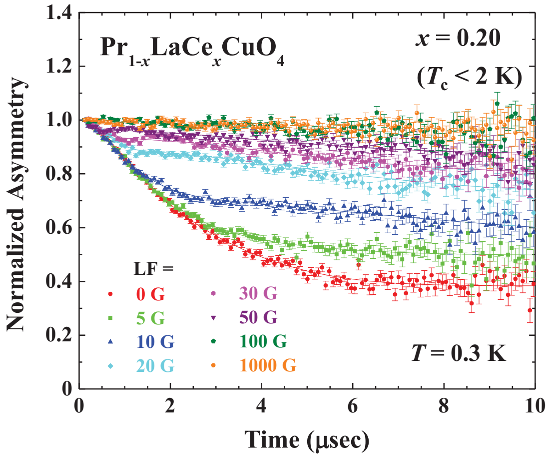

FIG. 4. LF-μSR time spectra of the reduced crystal of PLCCO with $x = 0.20$ at 0.3 K. Solid lines are the best-fit results using the two-component function described in Eq. (1).

IV. SUMMARY

ZF- and LF-μSR spectra have revealed that the development of the Cu-spin correlations weakens with increasing x and is negligibly small in heavily overdoped PLCCO with $x = 0.20$ where the superconductivity disappears. These results suggest that the Cu-spin correlations exist in the electron-doped T' cuprates where the superconductivity appears. It is suggested that, in both hole-doped and electron-doped cuprates, the mechanism of the superconductivity is related to the Cu-spin correlations.

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