Magnetic Ground State of Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\alpha-\delta}$ with Varied Oxygen Depletion Probed by Muon Spin Relaxation

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The magnetic ground state of an electron-doped cuprate superconductor Pr$_{1-x}$LaCe$_x$CuO$_{4+\alpha-\delta}$ ($x = 0.11$, $\alpha \simeq 0.04$) has been studied by means of muon spin rotation/relaxation ($\mu$SR) over a wide variety of oxygen depletion, $0.03 \leq \delta \leq 0.12$. Appearance of weak random magnetism over entire crystal volume has been revealed by a slow exponential relaxation. The absence of $\delta$-dependence for the random magnetism and the multiplet pattern of muon Knight shift at higher fields strongly suggest that the random moments are associated with excited Pr$^{3+}$ ions under crystal electric field.

KEYWORDS: superconductivity, crystal electric field, cuprates, $\mu$SR

It is widely believed that superconductivity of electron-doped cuprates is in an intimate relationship with that of hole-doped cuprates due to the common background of CuO$_2$ planes.\textsuperscript{1,2} In this regard, electron-hole asymmetry of the phase diagram observed between those two groups\textsuperscript{2,3} is one of the key issues for selecting the models of pairing mechanisms being proposed. Despite its importance, however, so far the study of electron-doped cuprates is far behind that of hole-doped systems. This is partly because of the limited variety of compounds and associated difficulty to obtain them in growing a large single crystal.\textsuperscript{4,5}

Another important issue related to the electron-doped cuprates is the microscopic nature of the oxygen depletion process which is needed to turn the as-grown material into superconducting.\textsuperscript{1,2} It has been presumed that the oxygen atoms in the CuO$_2$ planes become slightly deficient upon depletion procedure. In this situation, the mobility of carriers may be affected by the introduced randomness in CuO$_2$ planes, while the effect on the doping level would be simply a positive shift.\textsuperscript{1,2} Another possibility is that there are excess oxygen atoms at apical sites between the CuO$_2$ planes which are unoccupied in the final T' structure after depletion procedure. The structure having apical oxygen resembles that of T* phase in Nd$_{2-x-z}$Ce$_x$Sr$_z$CuO$_{4-\delta}$\textsuperscript{6,7} whose charge carriers are identified as holes, thus suggesting that a carrier compensation process similar to the case in semiconductors occurs in the as-grown material. The newly synthesized PLCCO has an interesting character that it is stable over a wide range of the oxygen depletion, $0 \leq \delta \leq 0.12$. This makes it feasible to investigate the effect of oxygen depletion on CuO$_2$ planes in more detail.

In this Letter, we report on our muon spin rotation/relaxation ($\mu$SR) experiment in an electron-doped superconductor Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\alpha-\delta}$ ($\alpha \simeq 0.04$) to elucidate the ground state phase diagram with $\delta$ as the primary parameter. (The phase diagram as a function of carrier concentration $x$ has been reported elsewhere,\textsuperscript{4} yielding a result similar to Nd$_{2-x}$Ce$_x$CuO$_{4-\delta}$ (NCCO) with a wider region of superconductivity over $x$ from 0.09 to 0.20.) The specimen exhibits a maximum of superconducting transition temperature ($T_c$) around $\delta = 0.06$, indicating that the oxygen depletion has a strong influence on the doping level with a partial compensation of carriers for $\delta < 0.06$. This is consistent with the presence of excess oxygen at apical sites. On the other hand, the $\mu$SR spectra under zero field exhibit little dependence on $\delta$, with a common tendency of slow exponential depolarization developing with decreasing temperature below $\sim 150$ K. This indicates the presence of random local magnetic moments irrespective of oxygen depletion. We also found that the muon Knight shift exhibits a triplet structure at high magnetic field. These results strongly suggest that the weak random magnetism is primarily due to Pr$^{3+}$ ions, whereas that associated with Cu$^{2+}$ spins appears only for $\delta \leq 0.03$.

A single crystal of Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\alpha}$ were prepared by a traveling-solvent floating zone method, where the detail of the procedure is reported previously.\textsuperscript{4} The presence of excess oxygen in the as-grown crystal has been confirmed by an iodometric titration technique to yield $\alpha \simeq 0.04$. The crystal was sliced into slabs measuring about 5 mm $\times$ 8 mm $\times$ 0.5 mm thick with c-axis be-
ing perpendicular to the plane, which were then annealed under argon gas flow to reduce oxygen to the respective level. The amount of removed oxygen δ per unit formula from as-grown specimen was determined by the weight loss after the annealing treatment. For the present experiment we obtained specimen with δ = 0.03, 0.04, 0.06, 0.08, and 0.12. The result of magnetic ac-susceptibility (1 mT, 100 Hz) is shown in Fig. 1a, from which $T_c$ is determined as a mid-point of the Meissner effect (see Fig. 1b).

It is noteworthy in those figures that the optimal “doping” occurs when $\delta \simeq 0.06$, with a clear tendency of decreasing $T_c$ and Meissener fraction with decreasing $\delta$. This behavior is reminiscent to the case of hole-doped cuprates in the underdoped region, which is in marked contrast with their monotonical dependence on the Ce content $x$. A similar dependence of $T_c$ on the oxygen depletion has been reported for NCBO ($x = 0.15$).

Conventional μSR measurements on those samples under zero and transverse external field were performed on the M15 beamline of TRIUMF. The observed ZF-μSR time spectra in those specimens are common to show an exponential depolarization overlapped with Gaussian-like damping due to nuclear dipolar fields, indicating that the origin of the exponential relaxation is due to random magnetic moments. Some examples from the data with $\delta = 0.06$ are shown in Fig. 2, where the exponential damping has almost full fraction of the positron decay asymmetry at 3.3 K. Note that the Meissener fraction is almost 100 % in this specimen. This indicates that the entire volume of the specimen is subject to the weak random magnetism irrespective of superconductivity. The time spectra under a longitudinal field ($\simeq 15$ mT) do not exhibit appreciable relaxation at 40 K, indicating that the random fields are nearly static within the time window of μSR ($\simeq 10^{-5}$ s) at lower temperatures.

For a quantitative analysis, the ZF-μSR spectra were fit by the stretched exponential damping:

$$A(t) = A_0 \exp[-(\Lambda t)^\beta] + B,$$

where $A_0$ is the initial positron decay asymmetry (which is proportional to the muon polarization), $\Lambda$ is the spin relaxation rate, and $\beta$ is the power of the damping. The results of fitting analysis by the above equation are summarized in Fig. 3. The relaxation rate $\Lambda$ exhibits a universal behavior of increase with decreasing temperature below about 150 K regardless of the oxygen depletion, except that below 2 K in the specimen with $\delta = 0.03$ where a steep increase of $\Lambda$ is observed. The latter behavior ($\delta = 0.03$, below 2 K) is in line with a spin glass-like magnetism suggested by the recent result of magnetization.

$$\Lambda \simeq \gamma_\mu \langle H_n^2 \rangle + \langle H_2^2 \rangle^{1/2}$$

(0.1)

where $\gamma_\mu$ and $\langle H_n^2 \rangle$ being the muon gyromagnetic ratio, $\langle H_2^2 \rangle$ being the variance of respective local fields from nuclei and magnetic ions), one can estimate the contribution of magnetic ions. Since the leveling off of $\Lambda$ above 150 K is mainly attributed to the contribution of nuclear random local fields (i.e., $\Lambda \simeq \gamma_\mu \langle H_n^2 \rangle^{1/2} \sim 0.1 \mu s^{-1}$), the contribution of magnetic ions can be estimated to be $\langle H_2^2 \rangle^{1/2} \simeq 0.47$ mT. The small power below $\sim 50$ K suggests slowing down of the fluctuating random fields, while the behavior at higher temperatures can be understood by considering diffusive motion of muons.

It has been revealed in the very recent study that the spin-glass phase observed near the antiferromagnetic (AF) phase of Pr$_{1-x}$LaCe$_x$CuO$_{4-\delta}$ for $\delta \leq 0.03$ strongly depends on both Ce concentration $x$ and oxygen depletion $\delta$, where the magnetic moments are apparently carried by copper spins. Thus, the absence of $\delta$ dependence in the present result suggests that the random moments observed for $\delta > 0.03$ are carried by Pr$^{3+}$ ions, although the ground state of which is presumed to be nonmagnetic. This is further confirmed by the structure of muon Knight shift under high magnetic fields. As shown in Fig. 4, the Fourier transform of μSR time spectra splits into three peaks with a relative amplitude of 1:2:1. This can be readily understood by considering the situation that there are two nearest neighboring ions contributing to the Knight shift with different combination of Pr$^{3+}$ and La$^{3+}$ ions. The shift under 5 T is about 0.15 % for the central peak and 0.3 % for the lowest frequency peak at 5 K, which is least dependent on temperature. These results indicate that there is a significant contribution of magnetic excited levels split by the crystal electric field over the relevant temperature range, leading to the Van Vleck magnetism at higher magnetic fields. A similar situation has been observed in Pr$_{1-x}$Ce$_x$CuO$_{4-\delta}$ (PCCO).

Provided that implanted muons occupy the sites near the edge center of tetrahedron with Pr/La atoms at their corners, one can estimate the magnitude of effective dipolar fields at the muon sites by calculating a dipolar tensor $A_{ij}^{\alpha \beta} = (\delta_{i\alpha} \beta - 3r_i^\alpha r_i^\beta / r_i^3) / r_i^3$ and the relevant variance $(\overline{A_{ij}})^2 = \sum_{i,\alpha,\beta} A_{i}^{\alpha \beta}^2$ from $i$-th ion at a distance $r_i$ (α = x, y, z and β = x, y, z when the primary axis is set to z). Taking account of the nearest two ions, we obtain $(H_2^2)^{1/2} \simeq \overline{A_{xy}} \simeq 0.19 T/\mu_B$ (unit Bohr magneton) as an average of all possible combinations for Pr and La ions. The comparison of the above estimation with the observed magnitude of $(H_2^2)^{1/2} \simeq 0.47$ mT implies that the Pr$^{3+}$ ions have a magnetic moment:

$$|\mu_{Pr}| = \left( \frac{H_2^2}{\overline{A_{xy}}} \right)^{1/2} \simeq 2.4 \times 10^{-3} \mu_B$$

(0.2)

under zero external field. This is more than by an order of magnitude smaller than that observed in the AF phase of Pr$_2$CuO$_4$ where $|\mu_{Pr}| = 0.08 \mu_B$.

The Pr$^{3+}$ free-ion $^3H_4$ state multiplet has ninefold degeneracy, which splits into five singlets ($2\Gamma_1$, $\Gamma_2$, $\Gamma_3$, $\Gamma_4$) and two magnetic doublets ($2\Gamma_5$) under the tetragonal $C_{4v}$ symmetry of PLCCO. Although we do not have direct information on the Pr$^{3+}$ ions in PLCCO at this stage, there are several literatures on the crystal field effects in Pr$_2$CuO$_4$ and PCCO studied by inelastic neutron scattering and Raman scattering, where the first excited state is reported to be a $\Gamma_5$ doublet which is separated from the singlet (either $\Gamma_3$ or $\Gamma_4$) ground state by 18 meV. Considering the nearly identical $T$ structure, this situation can be presumed to be the case also for the Pr$^{3+}$ ions in PLCCO. Then, the observed weak magnetic moment can be attributed to the small mix-
ing of $\Gamma_5$ state with the singlet ground state, whereas the moment is considerably enhanced in the AF phase of Pr$_2$CuO$_4$ due to the Van Vleck magnetism.

Interestingly, it happens that the muon spin relaxation rate in NCCO ($x = 0.15$) exhibits a similar tendency of gradual increase with decreasing temperature except below $\sim 2$ K where a steep increase sets in. Assuming that the Nd moments are quasi-static below 2 K, the observed relaxation rate ($\gtrsim 1$ $\mu$s$^{-1}$) suggests that the Nd$^{3+}$ ions have a moment considerably larger than that of Pr$^{3+}$. In both cases, since the sample crystal is a good superconductor as inferred from the large fraction of Meissner diamagnetism, we can conclude that the magnetic moments of the rare earth ions do not directly interfere the superconductivity on the CuO$_2$ planes.

Given that the weak random magnetism is entirely due to Pr$^{3+}$ ions in Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\delta}$, it also means that there is no appreciable contribution of copper spins, if at all, over the entire region of $\delta$ (except below $\sim 2$ K in the specimen with $\delta = 0.03$). According to the earlier neutron diffraction study, the Cu$^{2+}$ spins have a moment $\simeq 0.4\mu_B$ in Pr$_2$CuO$_4$ (12) in which muons feel an internal field of $\sim 27$ mT. Assuming the same site for muons as discussed previously, the calculated dipolar tensor for the Cu$^{2+}$ ions yields $\mathbf{T}_{xy}^{\text{Cu}} \simeq 50.2$ mT/$\mu_B$ and thus qualitatively consistent with the earlier result of $\mu$SR. Since PLCCO is nearly isostructural to Pr$_2$CuO$_4$, these estimations indicate that the present measurement must be sensitive to the presence of quasi-static copper spins in the order of $10^{-2}\mu_B$. Taking the contribution of nuclear dipolar fields ($\Lambda \approx 0.1$ $\mu$s$^{-1}$) as a limiting background, we can place an upper bound for the quasi-static copper moment:

$$|\mu_{\text{Cu}}|_{\text{static}} < 0.015\mu_B.$$  \hfill (3.3)

It must be noted, however, that this does not exclude the presence of copper moments which are fluctuating with a time scale shorter than the susceptibility to $\mu$SR ($< 10^{-9}$ s).

Finally, we discuss the chemistry of oxygen depletion in the present PLCCO system. As shown in Fig. 1, the Meissner effect is at its maximum when $\delta = 0.04 \sim 0.06$, which is in good agreement with the amount of excess oxygen ($\alpha \approx 0.04$). When the oxygen depletion proceeds, the superconducting property is rapidly deteriorated as indicated by the marked decrease of both Meissner fraction and $T_c$. This observation strongly suggests that the optimal superconductivity is realized when oxygen atoms are in the stoichiometric composition, Pr$_{2-x}$LaCe$_x$CuO$_4$. It is likely that as-grown crystals always have some excess oxygen atoms at the apical sites, which serves as defect centers giving rise to carrier compensation. While the removal of the excess oxygen improve the superconducting property of PLCCO, it seems that further removal of oxygen erodes the CuO$_2$ planes, leading to the rapid deterioration of superconductivity.

In summary, we have demonstrated that, while the bulk superconducting property of single crystalline Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\alpha-\delta}$ ($\alpha \approx 0.04$) exhibits a considerable dependence on the oxygen depletion $\delta$ over the region studied ($0.03 \leq \delta \leq 0.12$), the magnetic ground state probed by $\mu$SR which is characterized by a weak random magnetism, is least dependent on $\delta$. The muon Knight shift strongly suggests that the random magnetism is due to a small magnetic moment of Pr$^{3+}$ ions induced by the mixing of an excited state under crystal electric field. Based on these observations, a consistent microscopic view of the oxygen depletion has been provided by the present study.

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Fig. 1. a) Temperature dependence of the magnetic ac-susceptibility $\chi_0$ in Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\alpha-\delta}$, where $\chi_0 \approx 0.013$ emu/g corresponds to $1/4\pi$ (fractional yield of 100 % for the Meissener effect). b) Superconducting transition temperature $T_c$ vs degree of oxygen depletion $\delta$, where $T_c$ is defined as a midpoint of the Meissener fraction.
Fig. 2. ZF-\(\mu\)SR time spectra observed in \(\text{Pr}_{0.89}\text{LaCe}_{0.11}\text{CuO}_{4+\alpha-\delta}\) with \(\delta = 0.06\). An exponential depolarization gradually takes over the Gaussian damping due to random local fields from nuclear magnetic moments. Those in other samples are quite similar to these examples.

Fig. 3. Temperature dependence of muon spin relaxation rate \(\Lambda\) (a) and associated power \(\beta\) (b) under zero external field observed in \(\text{Pr}_{0.89}\text{LaCe}_{0.11}\text{CuO}_{4+\alpha-\delta}\). A steep increase of \(\Lambda\) is seen only in the specimen with \(\delta = 0.03\) below \(\sim 2\) K.
Fig. 4. Fast Fourier transform of $\mu$SR time spectra measured under a transverse field of 5 T in Pr$_{0.89}$LaCe$_{0.11}$CuO$_{4+\alpha-\delta}$ with $\delta = 0.06$. The peak at the highest frequency ($\sim 677.2$ MHz) corresponds to the component with null Knight shift.