Low-Energy Spin Fluctuations in the Ground States of Electron-Doped $Pr_{1-x}LaCe_xCuO_{4+\delta}$ Cuprate Superconductors

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Low-energy spin fluctuations have been investigated in the electron-doped $Pr_{1-x}LaCe_xCuO_{4+\delta}$ over a wide concentration range of $0.07 \leqslant x \leqslant 0.18$, spanning from the antiferromagnetic phase to the heavily overdoped superconducting (SC) phase. The low-energy excitations exhibit commensurate peaks centered at the (π, π) position for all x. Our data show that the characteristics of the excitations, such as the relaxation rate and the spin stiffness, decrease with increasing x in the SC phase and disappear with the disappearance of superconductivity.

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In the past two decades, comprehensive studies using spin sensitive probes such as neutron-scattering measurements have clarified the evolution of spin correlations with doping in hole-doped (p-type) cuprates. In the prototypical p-type superconductor $La_{2-x}Sr_xCuO_4$ (LSCO), incommensurate (IC) spin correlations persist in the SC phase [1] and the low-energy component of the spin fluctuations vanishes with the disappearance of bulk superconductivity in the heavily overdoped region [2]. These results clearly indicate that incommensurate spin correlations are closely related with superconductivity in the p-type cuprates.

Less known is the relation between magnetism and superconductivity in the electron-doped (n-type) cuprates. Recent neutron-scattering studies revealed the existence of *commensurate* low-energy spin fluctuations centered at the (π, π) position in both antiferromagnetically (AFM) ordered and SC phases of optimally electron-doped cuprates [3–6]. More recently, the doping dependence of the spin fluctuations has been studied in $Pr_{0.88}LaCe_{0.12}CuO_{4+\delta}$ (PLCCO) [6] and in $Nd_{2-x}Ce_xCuO_{4+\delta}$ (NCCO) [7]. Inelastic neutron-scattering measurements on PLCCO at several different oxygen concentrations were performed as a function of temperature (T) at low energies up to $\sim$4 meV which is comparable to the energy scale of T_c. T-independent magnetic excitation peak spectra near the optimally doped SC phase at low temperature were found [6]. The neutron-scattering study on NCCO measured *instantaneous* spin correlations as a function of temperature and a spin stiffness was obtained from the temperature dependence of the correlation length of the instantaneous spin correlations [7]. It was shown that the spin stiffness is well defined in the AFM phase, and decreases with increasing x to disappear near the AFM and SC boundary. In the SC phase, however, the instantaneous spin correlations do not change at the superconducting phase transition temperature T_c, making it impossible to extract the spin stiffness. The anomalies in the temperature dependence of the magnetic fluctuations as the system enters from the AFM to the SC phase were attributed to the existence of a quantum critical point at the phase boundary in the electron-doped cuprates.

In this Letter we report direct measurements of the low-energy spin stiffness in the ground state of $Pr_{1-x}LaCe_xCuO_{4+\delta}$ (PLCCO). Sizable single crystals were prepared in a wide range of Ce concentration, $0.07 \leqslant x \leqslant 0.18$ Using inelastic neutron-scattering technique, the doping dependence of the low-energy magnetic fluctuations up to $\sim$12 meV was investigated. Our results show clear evidence for a close relation between magnetism and superconductivity in the electron-doped cuprate. The characteristic relaxation rate Γ and the spin stiffness ρ_s of the spin fluctuations decrease linearly with the Ce concentration. Both quantities go to zero when extrapolated at $x \sim 0.21$, coinciding with the disappearance of the superconductivity. On the other hand, the Q-integrated spectral weight of the low-energy spin fluctuations decreases only slightly with increasing x in contrast to the dramatic degradation observed in p-type cuprates [2].

Single crystals of PLCCO with nominal Ce concentrations of $x = 0.07$, 0.09, 0.11, 0.13, 0.15, and 0.18 were grown by the traveling-solvent floating-zone method. The crystals with dimension typically of $\sim$30 mm in length and 6 mm in diameter were subsequently annealed under Ar gas flow at 920–950 °C for 10–12 h [8]. The typical fraction of oxygen reduced during the annealing process was about 0.05 (see Table I). To determine T_c, we measured the superconducting shielding signal on a small piece of the annealed crystals using a superconducting quantum interference device. As shown in Fig. 1, bulk superconductivity appears in all the samples except for $x = 0.07$. The SC onset temperature T_c is maximum at $x = 0.11$ with 26 K, and gradually decreases with increasing x. The

TABLE I. The Ce concentration x, fraction of oxygen reduced during the annealing process, δ_{OR}, magnetic ordering temperature T_N and the average Cu moment M_{Cu}, and T_c in $Pr_{1-x}LaCe_xCuO_{4+\delta}$ determined by inductively coupled plasma, neutron-scattering and SQUID measurements, respectively.

x	δ_{OR}	T_N(K)	$M_{Cu}(\mu_B)$	T_c(K)	Ref.
0.07	0.047	100(10)	0.08(10)	⋯	
0.09	0.047	80(15)	0.05(5)	25(1)	[9]
0.11	0.050	25(10)	<0.01	26(1)	[8]
0.13	0.052	⋯	⋯	21(1)	
0.15	0.043	⋯	⋯	16(2)	[9]
0.18	0.040	⋯	⋯	11(2)	

average concentration of Pr, La, Ce, and Cu ions was confirmed to be close to their nominal values by using the inductively coupled plasma (ICP) spectroscopy. The SC transition is gradual over a range of $\Delta T \sim 5$ K for all samples, which indicates that the electron concentration $x + 2\delta$ may not be uniform but have an uncertainty with a standard deviation of 0.01.

The larger part of the annealed crystals was used for the neutron-scattering experiments. The measurements were performed at the thermal triple-axis spectrometers TAS-1 and TOPAN at the JRR-3 reactor in the Japan Atomic Energy Agency. The energy of scattered neutrons was fixed at $E_f = 14.7$ meV. The horizontal collimations were $80'$-$80'$-$80'$-$180'$ at TAS-1 and $50'$-$100'$-$60'$-$180'$ at TOPAN. In this Letter, the tetragonal $I4/mmm$ notation was used in which the principal axis in the ab plane is along the Cu-O bond. The lattice constants are $a = 3.985$ Å and $c = 12.32$ Å for the optimally doped $x = 0.11$ sample at 3 K. The crystals were mounted in the (h k 0) plane.

From the elastic neutron-scattering measurements, it is shown that the $x = 0.07$, 0.09, and 0.11 samples exhibit AFM order at low temperatures, while no evidence for ordering is detected for $x \geqslant 0.13$. In the AFM phase ($x \leqslant 0.11$), the elastic magnetic intensity normalized by the sample volume drastically decreases with increasing x. In the vicinity of the phase boundary, $x \sim 0.10$, the AFM order coexists with superconductivity, as summarized in Table I and in the inset of Fig. 1.

Figure 2 shows typical inelastic neutron-scattering data obtained with constant energy transfers. Commensurate low-energy spin fluctuations were observed at the characteristic wave vector of the AFM ordering, (1/2, 1/2, 0), in all the AFM and SC samples. This tells us that low-energy spin fluctuations exist in the SC phase irrespective of the charge carrier type, even though the characteristics of the spin dynamics may differ. This supports the scenario that the spin fluctuations may play an important role in the mechanism of high-T_c superconductivity in the cuprates.

When the system is antiferromagnetically ordered, as in $x = 0.07$, 0.09, the $\mathbf{Q}$ linewidth of the low-energy spin

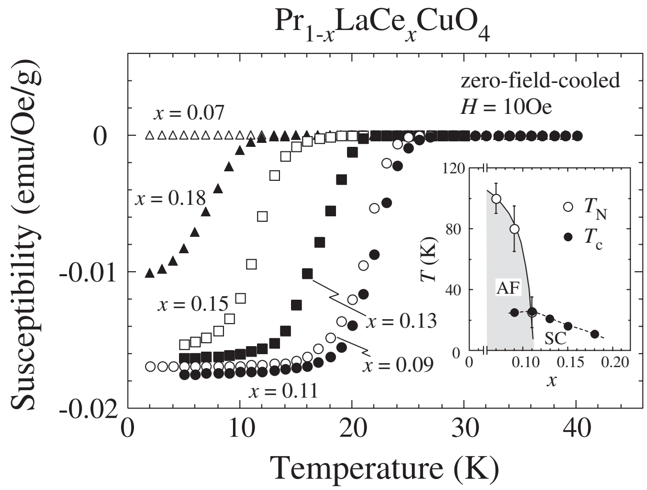

FIG. 1. The temperature dependence of bulk susceptibility obtained from single crystals of $Pr_{1-x}LaCe_xCuO_{4+\delta}$ at several Ce concentrations. The inset shows the phase diagram as a function of x and T. Here T_N (open circles) and T_c (solid circles) are the AFM ordering and the SC transition temperatures, respectively.

fluctuations is close to the instrumental Q resolution [see Figs. 2(a) and 2(b)], regardless of superconductivity. Upon further doping ($x > 0.11$), the $\mathbf{Q}$ linewidth gradually increases. This broadening is more apparent at higher energies as shown in Figs. 2(g) and 2(h), for $\omega = 10$–11 meV. Figure 2(d) shows that for the heavily overdoped sample ($x = 0.18$), the low-energy excitations are independent of T, at least up to 50 K, which is consistent with a previous neutron-scattering study on optimally dope sample [6]. We

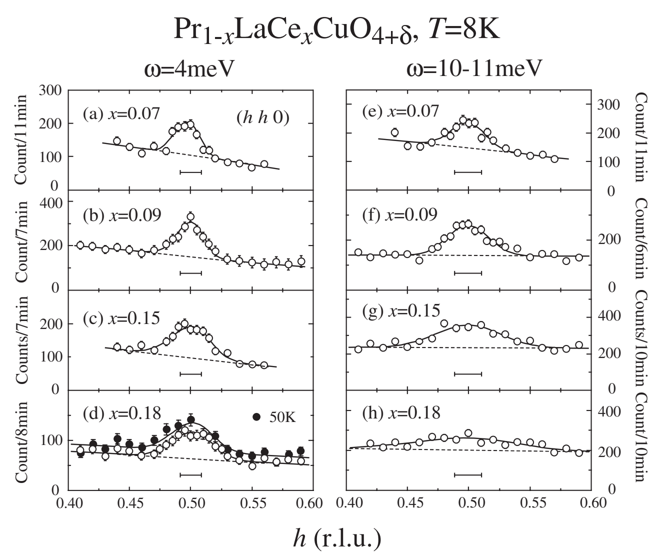

FIG. 2. Constant-ω scans with $\omega = 4$ meV [(a)–(d)] and 10–11 meV [(e)–(h)] obtained for $Pr_{1-x}LaCe_xCuO_{4+\delta}$ with different x, 0.07 [(a), (e)], 0.09 [(b), (f)], 0.15 [(c), (g)], and 0.18 [(d), (h)]. Solid lines are fits to a single Gaussian convoluted with the instrumental $\mathbf{Q}$ resolution. Dashed lines represent background. Horizontal bars represent the instrumental $\mathbf{Q}$ resolution.

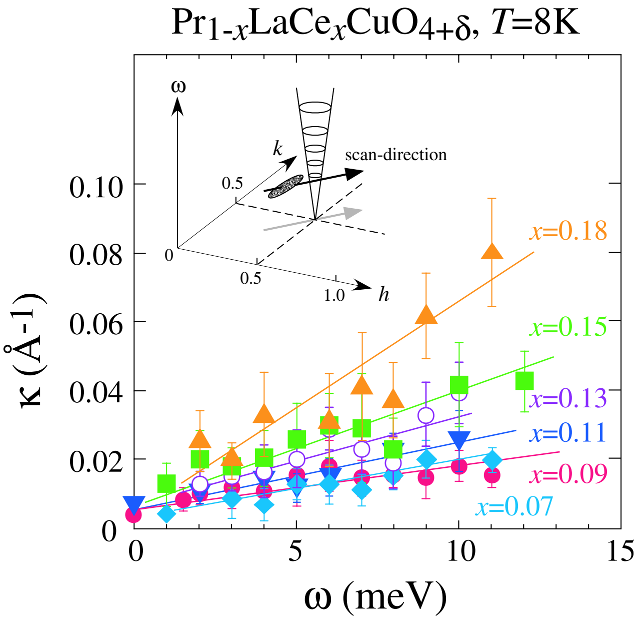

FIG. 3 (color online). The ω dependence of resolution corrected peak width (half width at half maximum) κ of the commensurate peak for $Pr_{1-x}LaCe_xCuO_{4+\delta}$ with $x = 0.07$, 0.09, 0.11, 0.13, 0.15, and 0.18. The inset figure shows the image of scan through conelike spin excitations expected from the resulting ω dependence of κ in the energy and momentum space. The shaded ellipsoid represents the experimental resolution.

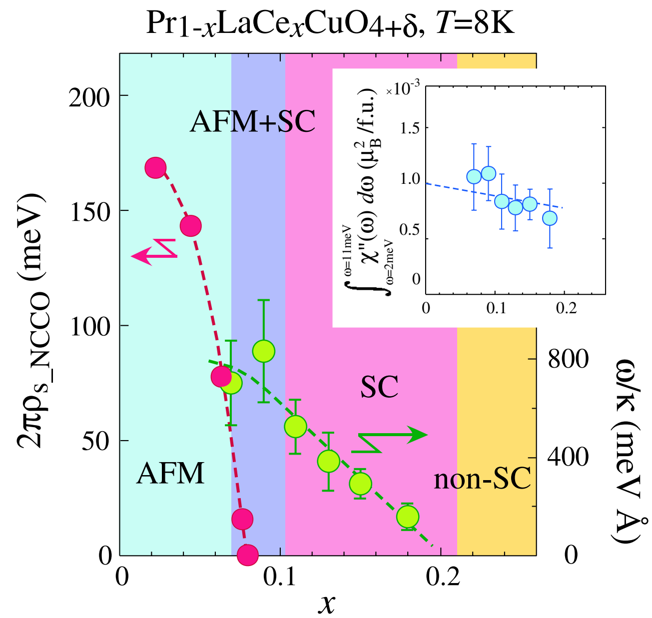

FIG. 4 (color online). The doping dependence of the spin stiffness ω/κ obtained from fitting the data shown in Fig. 3. For comparison, the spin stiffness evaluated from the temperature dependence of the correlation length of the instantaneous spin correlation for NCCO of Ref. [7] is also plotted. The doping concentration for NCCO is scaled so that the AFM-SC phase boundary concentration corresponds to that for PLCCO. The dashed lines are guides to the eye. The inset figure shows the partial spectral weight obtained by integrating $\chi''(\omega)$ shown in Fig. 5 from 2 to 11 meV as a function of x. The dashed line represents a function of $A/(1-x)$, where A is $\sim 1.0 \times 10^{-3}\ \mu_B^2$/f.u. for $x = 0$.

fit the Q dependence of the inelastic scattering intensity $I(\mathbf{Q}, \omega)$ to a single Gaussian, $I(\omega)\exp^{-\ln(2)\{(\mathbf{Q}-\mathbf{Q}_{AFM})/\kappa\}^2}$, convoluted with the instrumental resolution. ($\hbar = 1$ in these units.) Here κ is the half-width-half-maximum (HWHM), that is the inverse of the dynamic spin correlation length, and $I(\omega)$ is the integrated intensity over Q for a given ω. Figure 3 shows the resulting $\kappa(\omega)$. For all concentrations, κ increases linearly with ω up to $\sim$12 meV. The inverse of the slope, $\rho_s = \omega/\kappa$, that is the low-energy spin stiffness, decreases linearly with increasing x within the entire SC region and when extrapolated, it goes to zero at around the SC and non-SC phase boundary ($x_c \sim 0.21$) [green (light gray) circles in Fig. 4]. This seems to contradict a previous neutron-scattering study [7] that reported that a spin stiffness vanishes at the AFM-SC boundary. In their study, however, a different spin stiffness was used that was derived from the T dependence of the intrinsic $\boldsymbol{Q}$ linewidth of the *instantaneous* spin correlations over a wide range of temperatures, while our spin stiffness is derived from the ω dependence of the peak width at a particular T. Note that the critical value of $x_c \sim 0.21$ is well below the percolation threshold, $\sim$0.41 [10,11], for the two-dimensional square spin system. The observed behavior cannot be easily explained by a simple model of randomly diluted quantum spin systems.

Figure 5 shows the imaginary part of the dynamic susceptibility $\chi''(\omega)$ as a function of ω, obtained by normalizing $I(\omega)$ to an acoustic phonon around a nuclear (1,1,0) Bragg reflection and the detailed balance relation $\chi''(\omega) = \pi I(\omega)[1 - \exp(-w/k_B T)]$. In the nonsuperconducting AFM phase ($x = 0.07$), $\chi''(\omega)$ gradually increases with ω up to $\sim$5 meV above which it becomes constant. Upon doping, $\chi''(\omega)$ seems to weaken, especially at around 5 meV, but to a much lesser extent in comparison with the overdoped $La_{2-x}Sr_xCuO_4$ where a dramatic weakening is observed [2].

The relaxation rate of the spin fluctuations Γ was extracted by fitting $\chi''(\omega)$ to a simple Lorentzian $\chi''(\omega) \propto \Gamma\omega/(\Gamma^2 + \omega^2)$. The results are shown in Fig. 5(g). It is interesting to observe that in the SC phase with $x \geqslant 0.11$, Γ is linearly proportional to T_c. Combined with the relation between ρ_s and x (Fig. 4), this result indicates that the effective or renormalized magnetic interactions which control both the relaxation rate and the spin stiffness are closely related with superconductivity in the n-type SC cuprates. Note that such an analysis cannot extract the correct relaxation rate in the long range ordered phase. In fact, the obtained parameters of Γ in the AFM phases of $x = 0.07$ and 0.09 deviate remarkably from the linear relation with T_c in the SC phase.

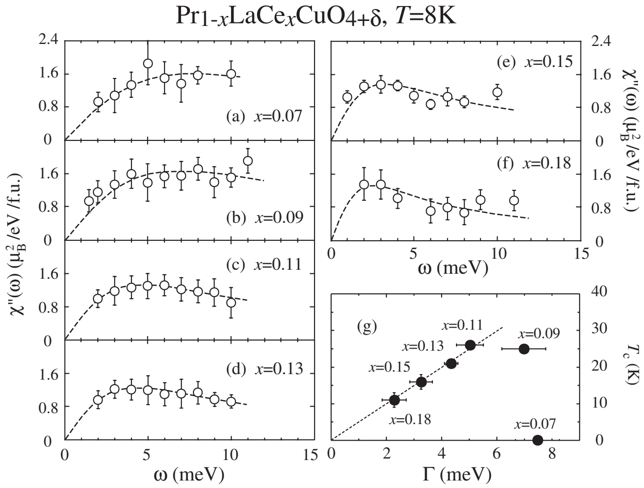

FIG. 5. The ω dependence of the local spin susceptibility $\chi''(\omega)$, with $x =$ (a) 0.07, (b) 0.09, (c) 0.11, (d) 0.13, (e) 0.15, and (f) 0.18, and (g) the T_c as a function of Γ. The dashed lines in (a)–(f) are fits to $\chi'' \propto \Gamma\omega/(\Gamma^2 + \omega^2)$ and in (g) to a linear function for $x \geqslant 0.11$ samples.

Now let us compare the low-energy spin fluctuations observed in the n-type system to those in the p-type system. Strong AFM fluctuations exist in both p- and n-type superconducting cuprates where they usually weaken as the superconductivity disappears in the heavily overdoped region. However, the characteristics of the spin fluctuations are different in the two systems. In the p-type cuprate, several experiments strongly suggested the existence of phase separation between SC and non-SC metallic phases [12–14]. The volume fraction of the SC region decreases with increasing doping, which coincides with the reduction of the IC spin fluctuations. In this case, the ω-integrated spectral weight should decrease with decreasing SC volume fraction, which has been confirmed in a previous neutron-scattering study of a heavily overdoped LSCO [2]. On the other hand, in the case of n-type PLCCO, the overall spectral weight does not change much with doping even in the overdoped region (see the inset of Fig. 4). This suggests that even in the SC phase localized spin character still remains in the low-energy region. The localization of electrons might be a reason as to why a simple band model cannot reproduce the commensurate spin fluctuations in the n-type cuprate [15]. The gradual degradation of the effective magnetic interactions and the peak-broadening upon doping reflect a more homogeneous electronic state in the electron-doped cuprates than in the hole-doped ones. This is consistent with a recent work that showed that the SC gap distribution is much narrower in the n-type than in the p-type cuprates [16]. The doping insensitivity of the spectral weight further suggests that even when the system enters the non-SC metallic phase, the magnetic fluctuations may survive. Their characteristics, as given by ρ_s and Γ, however, suggest that the dynamic spin correlations may become very short ranged and ω independent, making the observation of a magnetic signal in the non-SC metallic phase difficult, even if present. This will be tested in the future as single crystals of the non-SC metallic phase become available.

In summary, we probed the novel spin fluctuations previously observed in the SC phase by neutron-scattering spectroscopy in the electron-doped $Pr_{1-x}LaCe_xCuO_{4+\delta}$ over a wide Ce concentration range. We found that spin fluctuations slow down due to the degradation of the effective magnetic interaction by doping. Similarly to the hole-doped cuprates, the spin fluctuations disappear with the disappearance of superconductivity. However, the characteristics of magnetism and its relation to superconductivity are different in nature between two systems.

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[1] K. Yamada *et al.*, Phys. Rev. B **57**, 6165 (1998).
[2] S. Wakimoto *et al.*, Phys. Rev. Lett. **92**, 217004 (2004).
[3] K. Yamada *et al.*, Phys. Rev. Lett. **90**, 137004 (2003).
[4] M. Fujita *et al.*, Physica (Amsterdam) **392C–396C**, 130 (2003).
[5] H. J. Kang *et al.*, Phys. Rev. B **71**, 214512 (2005).
[6] S. D. Wilson *et al.*, Phys. Rev. B **74**, 144514 (2006).
[7] E. M. Motoyama *et al.*, Nature (London) **445**, 186 (2007).
[8] M. Fujita *et al.*, Phys. Rev. B **67**, 014514 (2003).
[9] S. Kuroshima *et al.*, Physica (Amsterdam) **392C–396C**, 216 (2003).
[10] P. K. Mang, O. P. Vajk, A. Arvanitaki, J. W. Lynn, and M. Greven, Phys. Rev. Lett. **93**, 027002 (2004).
[11] M. E. J. Newman and R. M. Ziff, Phys. Rev. Lett. **85**, 4104 (2000).
[12] Y. J. Uemura, Solid State Commun. **126**, 23 (2003).
[13] Y. Tanabe *et al.*, J. Phys. Soc. Jpn. **74**, 2893 (2005).
[14] Y. Tanabe *et al.*, J. Phys. Soc. Jpn. **76**, 113706 (2007).
[15] F. Krüger *et al.*, Phys. Rev. B **76**, 094506 (2007).
[16] F. C. Niestemski *et al.*, Nature (London) **450**, 1058 (2007).