High Energy Spin Excitations in Electron-Doped Superconducting
Pr$_{0.88}$LaCe$_{0.12}$CuO$_{4-\delta}$ with $T_c = 21$ K

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We use high-resolution inelastic neutron scattering to study the low-temperature magnetic excitations of electron-doped superconducting Pr$_{0.88}$LaCe$_{0.12}$CuO$_{4-\delta}$ ($T_c = 21 \pm 1$ K) over a wide energy range ($4 \text{ meV} \leq \hbar \omega \leq 330 \text{ meV}$). The effect of electron-doping is to cause a wave vector ($Q$) broadening in the low-energy ($\hbar \omega \leq 80 \text{ meV}$) commensurate spin fluctuations at ($\pi, \pi$) and to suppress the intensity of spin-wave-like excitations at high energies ($\hbar \omega \geq 100 \text{ meV}$). This leads to a substantial redistribution in the spectrum of the local dynamical spin susceptibility $\chi''(\omega)$, and reveals a new energy scale similar to that of the lightly hole-doped YBa$_2$Cu$_3$O$_{6.53}$ ($T_c = 18$ K).

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High-transition-temperature (high-$T_c$) superconductivity in copper oxides occurs when sufficient holes or electrons are doped into the CuO$_2$ planes of their insulating antiferromagnetic (AF) parent compounds [1]. Given the close proximity of AF order and superconductivity, it is important to understand the evolution of magnetic excitations in the AF ordered parent insulators upon chemical doping to produce metals and superconductors, as spin fluctuations may play a crucial role in the mechanism of superconductivity [2]. For the undoped parent compounds, where AF order gives a diffraction peak at wave vector $Q = (\pi, \pi)$ or $(0.5, 0.5)$ (Fig. 1a), spin waves at energies ($\hbar \omega$) below 60 meV found by neutron scattering show commensurate excitations around $(\pi, \pi)$ because of the large AF nearest neighbor exchange coupling ($J_1 > 100$ meV, Figs. 1a, 1c, and 3a) [3, 4, 5, 6, 7]. Upon hole-doping to induce metalliclicity and superconductivity, the low-energy spin fluctuations of La$_{2-x}$(Sr,Ba)$_x$CuO$_4$ (LSCO) form a quartet of incommensurate peaks at wave vectors away from $(\pi, \pi)$ [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. For hole-doped YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) with $x \geq 0.45$, the magnetic excitation spectra have a commensurate resonance at $(\pi, \pi)$ and incommensurate spin fluctuations similar to that of LSCO below this resonance [11, 12, 13, 14, 15, 16, 17]. For energies above the resonance, the excitations are spin-wave-like for $x \leq 0.5$ [12, 13, 14, 15, 16, 17] and become a “box-like” continuum at $x = 0.6$ [14, 16]. In the extremely underdoped regime ($x = 0.353, T_c = 18$ K), Stock et al. [18] showed that spin fluctuations are commensurate around $(\pi, \pi)$ and have a damped spin resonance around 2 meV.

While the evolution of spin excitations in hole-doped superconductors has become increasingly clear, it is crucial to determine the evolution of spin excitations in electron-doped materials, as particle-hole symmetry is an important ingredient of any theory purporting to explain the mechanism of high-$T_c$ superconductivity. Unfortunately, due to the difficulty of growing high-quality single crystals required for inelastic neutron scattering experiments, there exist only a few studies exploring the low-energy ($\hbar \omega \leq 10$ meV) spin dynamics in electron-doped materials such as Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (NCCO) [19, 20], and consequently the overall magnetic response of electron-doped materials remains largely unknown. Recently, we began to systematically investigate the evolution of AF order and magnetic excitations as Pr$_{0.88}$LaCe$_{0.12}$CuO$_{4-\delta}$ (PLCCO) is transformed from the as-grown AF insulator into an optimally electron-doped superconductor ($T_c = 25$ K) without static AF order through an annealing process with a minor oxygen content $\delta$ modification [21, 22, 23]. We chose first to study underdoped PLCCO ($T_c \sim 21$ K, $T_N \sim 40$ K) for two reasons. First, this material is between the as-grown AF insulator and optimally doped PLCCO and therefore has a larger magnetic signal than that of the optimally doped PLCCO [21, 22, 23, 24]. Second, Pr$_{3+}$ possesses a nonmagnetic singlet ground state in PLCCO, different from the Nd$^{3+}$ magnetic ground state in NCCO [25].

In this Letter, we report the results of inelastic neutron scattering measurements that probe the low-temperature ($T = 7$ K) dynamic spin response of electron-doped PLCCO ($T_c = 21 \pm 1$ K) for energies from 4 meV to 330 meV. We determine $Q$ and $\omega$ dependence of the generalized magnetic susceptibility $\chi''(Q, \omega)$ [26]. We find that the effect of electron doping into the AF insulating PLCCO is to cause a wave vector broadening in the low-energy commensurate magnetic excitations at $(\pi, \pi)$, consistent with that of the NCCO [19, 20]. At high energies ($\hbar \omega \geq 100$ meV), the excitations are spin-wave-like rings, but with a dispersion steeper than that of the undoped Pr$_2$CuO$_4$ [1, 2] and with a significant reduction in the spectral weight of the local dynamical spin susceptibility $\chi''(\omega)$ [26]. A comparison of PLCCO and lightly
doped YBCO \((x = 0.353)\) reveals that the energy scale for \(\chi''(\omega)\) in both materials is at \(\sim 2\) meV, lower than the \(\sim 18\) meV for the optimally doped LSCO \[4\].

We grew seven high quality (mosaicity \(< 1^\circ\)) PLCCO single crystals (with a total mass of 20.5 grams) using the traveling solvent method in a mirror image furnace. To obtain superconductivity, we annealed the as-grown non-superconducting samples in a vacuum \((P < 10^{-6} \text{ mbar})\) at \(T = 765 \pm 1^\circ\)C for four days. While both ends of the same cylindrical shaped crystal were found to have identical \(T_c\)'s, there are small \((\pm 1 \text{ K})\) differences in \(T_c\)'s for separately annealed samples. Figure 1c shows magnetic susceptibility measurements on all seven crystals used in our neutron experiments. They have an average \(T_c = 21 \pm 1\) K. For the experiment, we define the wave vector \(\mathbf{Q}\) at \((q_x, q_y, q_z)\) as \((H, K, L) = (q_x a/2\pi, q_y a/2\pi, q_z c/2\pi)\) reciprocal lattice units (r.l.u) in the tetragonal unit cell of PLCCO (space group \(I4/mmm\), \(a = 3.98\), and \(c = 12.27\) Å). The seven PLCCO crystals were co-aligned to within \(1^\circ\) in the \([H, H, L]\) zone using HB-1/HB-3A triple axis spectrometers at the High-Flux-Isotope reactor, Oak Ridge National Laboratory. Our inelastic neutron scattering experiments were performed on the MAPS time-of-flight spectrometer with the incident beam parallel to the \(c\)-axis (\(L\)-direction) of PLCCO at the ISIS facility \[10\]. Four different incident beam energies of \(E_i = 40, 115, 200, \text{ and } 400\) meV were used, and the scattering was normalized to absolute units using a vanadium standard.

Figure 2 summarizes images of neutron scattering intensity \(S(Q, \omega)\) centered about \((\pi, \pi)\) at \(T = 7\) K in units of mbarns/sr/meV/f.u. without any background subtraction. At the lowest energy \((\hbar \omega = 4 \pm 1\) meV) probed (Fig. 2a), the scattering consists of a strong peak centered at \((\pi, \pi)\) with some phonon contamination evident at larger wave vectors. A constant-energy cut through the image reveals a commensurate peak on a flat background (Fig. 1f). The peak is significantly broader than the instrumental resolution (horizontal bar) and gives a correlation length of \(\sim 70\) Å. Upon increasing energy, the peak at \((\pi, \pi)\) broadens in width (Fig. 2b) and weakens in intensity (Fig. 2g). With further increase in energy to \(\hbar \omega = 145 \pm 15\) meV, the scattering becomes a spin-wave-like ring (Figs. 2c and 2h). One-dimensional cuts through Fig. 2d at \(\hbar \omega = 200 \pm 15\) meV along four different directions (Figs. 1d-g) confirm that the scattering is indeed isotropic and symmetric around \((\pi, \pi)\) like spin waves. With increasing energy, the ring continues to disperse outward until magnetic scattering is no longer discernible at \(\hbar \omega = 315 \pm 15\) meV (Fig. 2i).
Figure 3a summarizes the dispersion of spin excitations determined from the cuts in Figs. 2f-j. The dashed boxes show the positions of crystalline electric field (CEF) excitations arising from the Pr\textsuperscript{3+} rare earth ions in the tetragonal structure of PLCCO \cite{25}. Compared to intensities of Pr\textsuperscript{3+} CEF levels, Cu\textsuperscript{2+} spin fluctuations in PLCCO are extremely weak and cannot be separated from the strong Pr\textsuperscript{3+} scattering at certain CEF energy positions. For reference, figure 3b shows an energy cut along $Q = (0.5, 0.5, L)$ for the $E_i = 115$ meV data in which it is clear that CEF intensities at $h\omega \approx 20, 85$ meV are significant relative even to the incoherent elastic scattering.

To estimate the strength of the magnetic exchange coupling, we consider a two-dimensional AF Heisenberg Hamiltonian with the nearest ($J_1$) and the next nearest ($J_2$) neighbor coupling (Fig. 1c). Since the zone boundary spin fluctuations sensitive to $J_2$ were unobservable (Fig. 2j), we set $J_2 = 0$ and determined that $J_1 = 162 \pm 13$ meV renders the best fit to the data for $h\omega \geq 100$ meV. The corresponding calculated one-magnon cross sections are plotted as the solid lines in Figs. 2h-2j, and the resulting dispersion relation is shown as the solid line in Fig. 3a. At high energies ($h\omega \geq 100$ meV), the calculated spin wave dispersion coincides fairly well with the data, but the value of $J_1$ is considerably larger than the hole- (La\textsubscript{2}CuO\textsubscript{4}, $J_1 = 104, J_2 = -18$ meV) \cite{2} and electron- (Pr\textsubscript{2}CuO\textsubscript{4}, $J_1 = 121$ meV) \cite{4} doped parent compounds (Fig. 3a). Assuming as-grown insulating PLCCO has similar AF exchange coupling as Pr\textsubscript{2}CuO\textsubscript{4} \cite{4}, our data suggest that the high energy spin fluctuations in electron-doped PLCCO disperse faster than the spin waves of the insulating compound. Therefore they are unlikely to arise from the weak static AF order in the material \cite{21}.

Although high energy spin excitations in PLCCO are spin-wave-like, the observed scattering for $h\omega \leq 80$ meV is substantially broader than those predicted by the linear spin-wave theory (Fig. 3a). A cut at $h\omega = 8 \pm 1$ meV through the ($\pi, \pi$) point along the $[1, 1]$ direction confirms this point (Fig. 3c). For energies below 20 meV, the dispersion of spin fluctuations has a nearest neighbor coupling of $J_1 = 29 \pm 2.5$ meV (dash-dotted line in Fig. 3a). Therefore, the dispersion of PLCCO can be separated into two regimes. For energies ($4 \leq h\omega \leq 80$ meV), the excitations are broad and weakly dispersive. For $h\omega \geq 100$ meV, the fluctuations are spin-wave-like with $J_1$ larger than that of the insulating parent compound.

In addition to determining the dispersion of spin excitations in PLCCO, the absolute spin susceptibility $\chi''(Q, \omega)$ measurements in Fig. 2 also allow us to calculate the energy dependence of the local susceptibility $\chi''(\omega)$, defined as $\int \chi''(Q, \omega) d^3Q / \int d^3Q$ \cite{3, 22}. Figure 4a shows how $\chi''(\omega)$ varies as a function of $h\omega$ for electron-doped superconducting PLCCO. Similar to hole-doped materials \cite{3, 5, 16, 17, 18, 28}, electron-doping suppresses the spectral weight of spin fluctuations in PLCCO at high ($\geq 50$ meV) energies. For energies below 50 meV, $\chi''(\omega)$ increases with decreasing energy and does not saturate at $h\omega = 4 \pm 1$ meV, the lowest energy probed on MAPS. Assuming that the $\chi''(\omega)$ in crystals of MAPS experiments ($T_c = 21 \pm 1$ K) is similar to that of the previously studied $T_c = 21$ K PLCCO sample \cite{21, 22, 23}, we can normalize the low-energy magnetic response of the $T_c = 21$ K sample obtained on SPINS spectrometer at NIST to that of the MAPS data. The outcome, shown as inset of Fig. 4, reveals a new energy scale of 2-3 meV for superconducting PLCCO.

We are now in a position to compare the spin excitations of electron-doped PLCCO with that of the hole-doped LSCO \cite{2, 27} and YBCO \cite{15, 17, 18, 20}. For hole-doped materials such as LSCO \cite{2, 3, 4, 16} and YBCO with $x \geq 0.45$ \cite{14, 15, 16, 17}, the low-energy spin fluctuations are incommensurate and display an inward dis-
FIG. 4: Energy dependence of local susceptibility $\chi''(\omega)$ in PLCCO determined from integration over wave vector of the observed magnetic scattering around $(\pi, \pi)$ \cite{13, 15}. The dashed line shows $\chi''(\omega) \times 1/5$ for La$_2$CuO$_4$ \cite{19}. Since $Q$-cuts were made along the $[1, 1]$ direction, the background scattering can be approximated by a constant. The blue triangles indicate normalized cold neutron triple-axis data on a $T_c = 21$ K PLCCO at energies below 3 meV obtained on the SPINS spectrometer at NIST center for neutron research \cite{23}. The inset shows an expanded view of $\chi''(\omega)$ vs $\hbar\omega$ at low energies. The solid line is a damped Lorentzian on a constant background.

perspersion toward a resonance point with increasing energy. This is not observed in electron-doped materials. Instead, spin fluctuations in PLCCO have a broad commensurate peak centered at $(\pi, \pi)$ at low-energies ($\leq$ 50 meV) which disperses outward into a continuous spin-wave, ring-like scattering at high energies ($\geq$ 100 meV), similar to lightly doped YBCO with $x = 0.353$ \cite{17}. At present, it is not clear how theoretical models based on spin stripes \cite{11} can reconcile the differences in spin excitations between the hole- and electron-doped materials.

For hole-doped LSCO with $T_c = 38.5$ K, the mean-squared fluctuating moment $\langle m^2 \rangle = \int \chi''(\omega)d\omega$ integrated up to 40 meV is $\langle m^2 \rangle = 0.062 \pm 0.005 \mu_B^2 t$ f.u.$^{-1}$ \cite{21}. For comparison, $\langle m^2 \rangle$ calculated from $\chi''(\omega)$ up to 40 meV is only $0.024 \pm 0.003 \mu_B^2 t$ f.u.$^{-1}$ in PLCCO, about three times smaller than that of LSCO. The total fluctuating moment integrated from 0 to 300 meV (Fig. 4) gives $\langle m^2 \rangle = 0.089 \pm 0.009 \mu_B^2 t$ f.u.$^{-1}$, a value an order of magnitude larger than the static moment squared (0.0016 $\mu_B^2 t$ f.u.$^{-1}$) \cite{25}. Since the total moment sum rule for spin-$1/2$ Heisenberg model requires one-magnon fluctuations moment squared to be smaller than the ordered static moment squared \cite{25}, the observed high-energy spin-wave-like excitations are unlikely to arise from the small-dered moment.

In the standard Hubbard model and its strong-coupling limit, the $t$-$J$ model with only the nearest-neighbor hopping $t$, there should be complete particle-hole symmetry and therefore the electron- and hole-doped copper oxides should behave identically. The observed large difference between incommensurate and commensurate spin fluctuations in hole- \cite{3, 26} and electron-doped materials \cite{17, 21, 22, 23} has mostly been attributed to their differences in the strength of second-nearest-neighbor $(t')$ and third $(t''$) nearest-neighbor hopping. This also explains their differences in Fermi surface topology within the $t$-$J$ model \cite{27, 29, 30}, although it may also be due to their proximity to two different quantum critical points \cite{31}. In the most recent calculation using the slave-boson mean-field theory and random phase approximation \cite{30}, incommensurate spin fluctuations at $(0.3\pi, 0.7\pi)$ have been predicted for optimally doped NCCO. However, this is not observed in our PLCCO (Figs. 2a-2e). Similarly, the energy dependence of the $\chi''(\mathbf{Q}, \omega)$ at $\mathbf{Q} = (\pi, \pi)$ has been predicted to exhibit a peak between $0.1\omega/J \geq 0.5$ and $0.4\omega/J \geq 0.7$. While qualitatively similar to the predictions, $\chi''(\omega)$ in Fig. 4 has a peak at a much smaller energy of $0.02\omega/J$. Comparison of future calculations in absolute units with our data should determine whether itinerant magnetism models can account quantitatively for the observed dynamic susceptibility in superconducting PLCCO.

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