Inhomogeneous Electronic Structure Probed by Spin-Echo Experiments in the Electron Doped High-T_c Superconductor $Pr_{1.85}Ce_{0.15}CuO_{4-y}$

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^{63}Cu nuclear magnetic resonance spin-echo decay rate (T_2^{-1}) measurements are reported for the normal and superconducting states of a single crystal of $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ in a magnetic field $B_0 = 9$ T over the temperature range $2 < T < 200$ K. The spin-echo decay rate is temperature dependent for $T < 55$ K and has a substantial dependence on the radio frequency (rf) pulse parameters below $T \approx 25$ K. This dependence indicates that T_2^{-1} is strongly effected by a local magnetic field distribution that can be modified by the rf pulses, including ones that are not at the nuclear Larmor frequency. The low-temperature results are consistent with the formation of a static inhomogeneous electronic structure that couples to the rf fields of the pulses.

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Understanding the normal phase of high-temperature cuprate superconductors is widely recognized as essential to a successful theory of the high-T_c problem. Important points include the origin and properties of a pseudogap, the unusual temperature dependence of the in-plane resistivity, and other unconventional properties. For this reason, it is important to study the properties of the normal phase even in the low-temperature limit. For most materials, the very large upper critical fields B_{c2} make this desirable condition unattainable. B_{c2} is significantly smaller in the electron doped cuprates. In particular, $B_{c2} \approx 10$ T for $Pr_{2-x}Ce_xCuO_{4-y}$ at optimal doping ($x \approx 0.15$) when the field is applied perpendicular to the CuO_2 planes [1–3]. It was in this limit that a violation of the Wiedemann-Franz law was reported for $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ (PCCO) [1], indicating that the low-temperature normal state could not be a Fermi liquid. Furthermore, differences in behavior between the electron doped and hole-doped cuprate superconductors may also provide insights into the origin of their superconductivity.

A wealth of information about the normal and superconducting phases of the hole-doped materials has been obtained from nuclear magnetic resonance (NMR) experiments [4]. In NMR, the complex electron spin susceptibility $\chi(\vec{q}, \omega)$ can be studied through the spin-lattice relaxation rate [5], the Knight shift [related to $\chi'(0, 0)$], and the spin-spin couplings that probe $\chi'(\vec{q}, 0)$. Although $^{63}T_1T$ in the normal state of PCCO is constant [6–9] as it would be for a Fermi liquid, it is enhanced by a factor ≈ 50 above the independent-electron result [10]. Therefore complementing these results with information about spin-spin couplings can help to establish a consistent picture for the electron doped cuprates as well.

Spin-spin couplings are often deduced from spin-echo decay rate studies. In the standard Hahn echo sequence [11], two radio frequency (rf) pulses (hereafter referred to as $P1$ and $P2$) at the NMR frequency are applied with a time separation of τ, and a spin-echo signal forms centered at a time 2τ after the initial $P1$ pulse. With increasing τ, the amplitude of the echo signal decreases with a characteristic time T_2. It is caused by the loss of spin-phase coherence, i.e., irreversible dephasing that originates from one or more of the following mechanisms: (i) direct nuclear spin-spin interaction (dipolar coupling); (ii) indirect (electron mediated) spin-spin interactions; (iii) spin-lattice relaxation; or (iv) in general, any kind of irreversible change in the local magnetic field (or electric field gradient) experienced by the nuclei on the time scale of the spin-echo experiment causes changes in the nuclear precession frequency and leads to irreversible dephasing among the spins forming the echo. Therefore the decay of the spin-echo height, $S(2\tau)$ can be decomposed into numerous factors, each of which is often described by an exponential or a Gaussian function. In the hole-doped systems the spin-lattice fluctuations and the indirect spin-spin couplings are known to be the relevant mechanisms; the latter is enhanced by antiferromagnetic correlations.

In this Letter, we report measurements of T_2 in the normal and superconducting phases of a single crystal of PCCO in a static magnetic field $B_0 = 9$ T over the temperature range $2 < T < 200$ K. For $T < 25$ K, T_2 depends on the amplitude and duration of the rf pulses used in the echo experiment. That is, irreversible dephasing of the spins involved in the echo formation results as a direct consequence of the application of $P2$ in the two-pulse spin-echo sequence. Although it is known that spin-echo decays in an inhomogeneously broadened NMR line can depend on the pulses applied when nuclear spin-spin coupling is significant [12–14], by adding a third pulse (hereafter referred to as P_{nr}) whose frequency differs from the NMR frequency we are able to rule it out as the source for our observations. The results are interpreted as evidence for the formation of an inhomogeneous electronic state that couples to the rf pulses. At this time, we cannot state the nature of the inhomogeneous phase.

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Single crystal PCCO samples were grown with a flux technique [15,16] and annealed in argon at 900 °C for 48 h. The doping concentration is roughly optimum to maximize the superconducting transition temperature at $T_{c0} \approx 22$ K, as verified by zero-field-cooled magnetization measurements in 0.1 mT magnetic field. The sample size used in this study was 3.5 mm × 2.5 mm × 35 μm. PCCO crystallizes in the T'-tetragonal structure leading to equidistant CuO_2 planes [17], i.e., all the Cu sites are equivalent and planar. (The planes are perpendicular to the c axis of the crystal.) From the diamagnetic effects of the sample on the inductance of the NMR coil, we found that $T_c(B_0 = 9\ \mathrm{T} \perp c) \approx 15$ K. The silver coil was wound around a small piece of aluminium powder in epoxy and the sample. The ^{27}Al signal was used to calibrate the rf field B_1 at high temperatures. Details of the Cu NMR spectra are reported elsewhere [9]. They reveal that the origin of the inhomogeneous line broadening is magnetic, and at both $B_0 \parallel c$ and $B_0 \perp c$ it is mainly the central transition that is measured. The central transition has a full width at half maximum of $\Delta = 19.5$ mT ($B_0 = 9$ T, $T = 2$–150 K).

In Fig. 1 the open symbols show T_2^{-1} obtained under the standard conditions for maximizing the spin-echo amplitude: the rf field B_1 is large enough to cover fully the central transition of the $I = 3/2$ nuclei, and both $P1$ and $P2$ have been adjusted to give the maximum echo height. Unlike hole-doped materials [13,18], the observed decay is primarily exponential for both $B_0 \parallel c$ and $B_0 \perp c$. At $T \approx 55$ K, both $T_{2\parallel}^{-1}$ and $T_{2\perp}^{-1}$ depart from the very weak temperature dependence observed at higher temperatures. The increase continues to the lowest temperature measured (2 K) for $B_0 \parallel c$. For the case $B \perp c$, there is a well-defined maximum in T_2^{-1} at $T \approx 25$ K. The solid symbols in Fig. 1 show the results for the spin-echo decay rate when B_1 and the nutation angle of $P2$ are both considerably reduced. Clearly, the details of the pulses impact significantly the values of T_2 at low temperatures.

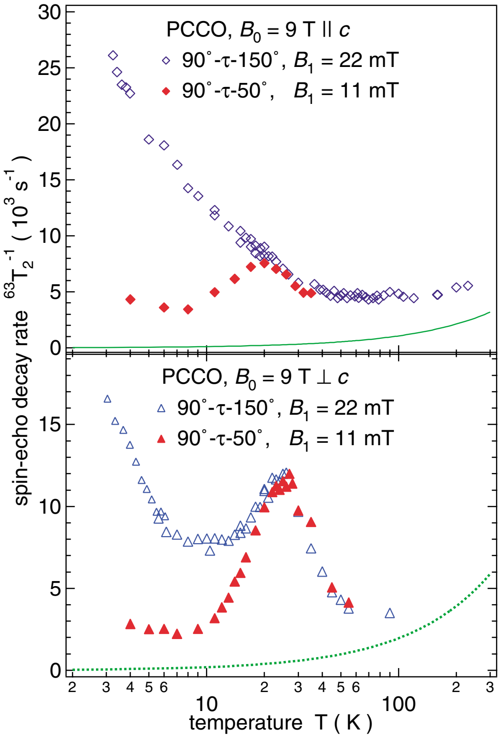

FIG. 1 (color online). Spin-echo decay rates $^{63}T_2^{-1}$ of PCCO obtained with optimized pulses (solid symbols) and with a small angle refocusing pulse at smaller B_1 (open symbols) as a function of temperature. The solid (dashed) line shows the estimated Redfield contribution for $B_0 \| c$ ($B_0 \perp c$).

Below, experiments are described that will justify our main conclusion that T_2 is strongly affected by a local magnetic field distribution that can be modified by the rf pulses.

Experiment I.—Fig. 2(a) shows that the spin-echo decay rate changes as the duration of $P2$, called t_{w2} hereafter, is increased at $T = 6$ K for $B_1 = 44$ mT and 11 mT. For reasons indicated below, the data are plotted as a function of $\sin^2(\theta_2/2)$, where $\theta_2 = \alpha\gamma B_1 t_{2w}$, $\alpha = 2$ for the central transition of the $I = 3/2$ nuclei [19], and $\gamma = 11.3$ MHz/T is the gyromagnetic ratio. The insensitivity of the echo decay to pulse parameters at $T = 21$ K is illustrated in Fig. 2(b).

Experiment II.—The following two sets of measurements demonstrate that it is the rf field itself that causes the dramatic change in T_2. The open symbols in Fig. 3 show what happens if the duration of $P2$ in the standard NMR spin-echo experiment is varied. As before, the T_2^{-1} increases as t_{w2} increases up to the maximum value t_m. In the second set of experiments a nonresonant P_{nr} pulse [with a frequency 2 MHz away from the center of the NMR spectrum (limited by the NMR tank circuit) and

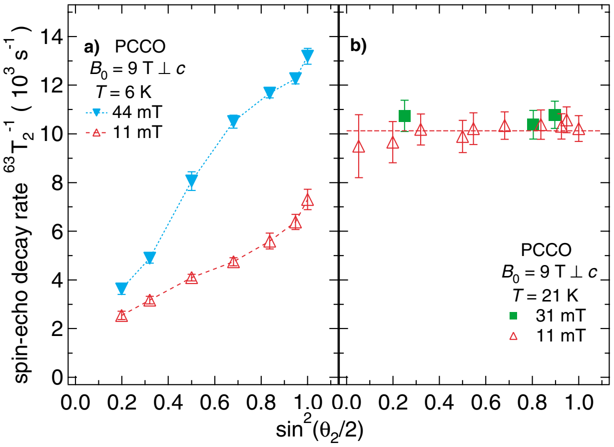

FIG. 2 (color online). Spin-echo decay rates $^{63}T_2^{-1}$ of PCCO as a function of the refocusing pulse angle (θ_2) at various alternating magnetic fields B_1 in $B_0 = 9\ \mathrm{T} \perp c$ at (a) $T = 6$ K and (b) $T = 21$ K. The dashed lines are guides to the eye. In order to avoid plotting a nonsingle valued function, only data points for $\theta_2 < \pi$ are shown here. The values of T_2^{-1} for $\theta_2 \gg \pi$ are close to the highest values shown already on the figure.

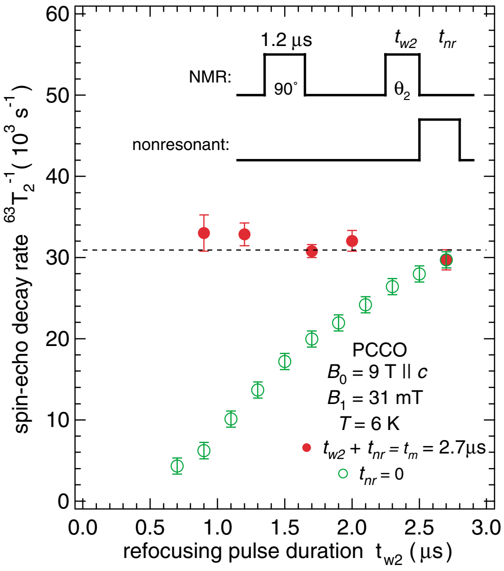

FIG. 3 (color online). Comparing spin-echo decay rates $^{63}T_2^{-1}$ obtained with and without the application of an additional nonresonant rf pulse (P_{nr}), as discussed in the text.

with the same amplitude as the resonant one] is applied for a duration t_{nr} just after the $P2$ pulse. The combined length of P_2 and P_{nr} is kept constant: $t_{w2} + t_{nr} = t_m$. It is evident (solid symbols in Fig. 3) that the value of T_2^{-1} depends only on the total duration t_m and not on t_{w2}. This result shows that the major change in the accumulated phase responsible for the reduction of T_2 is caused by the rf pulse whether or not it is at the NMR frequency.

Figure 4 shows what happens at $T = 2$ K if the amplitude of P_{nr} immediately following the $P2$ NMR pulse is varied. The details of the NMR pulses and the duration of all three pulses are kept constant. At this low temperature, a well-defined threshold or crossover rf field amplitude for the nonresonant pulse is required to produce the additional reduction in T_2.

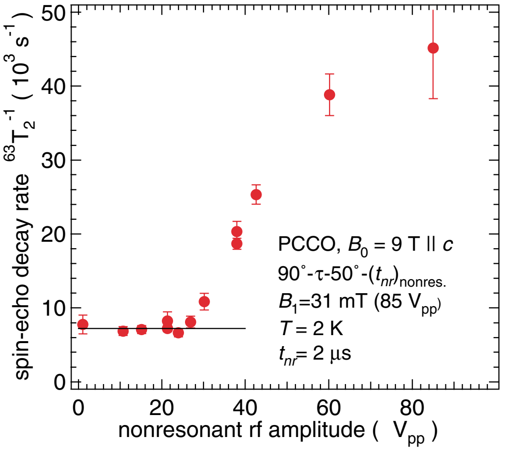

FIG. 4 (color online). Spin-echo decay rates $^{63}T_2^{-1}$ of PCCO obtained under the influence of different nonresonant pulse amplitudes. All other pulse parameters of $P1$, $P2$, and $P3$ are the same.

To discuss these results, the coupling Hamiltonian (H_i') is written in the following form [20]:

$$H_i' = I_{iz}\left[\sum_j a_{(i,j)z} I_{jz} + \hbar\gamma\delta B_i(t)\right], \tag{1}$$

where i and j refer to the ith and jth nuclear spins, I_z is the z component of the nuclear spin operator, $a_{(i,j)z}$ is the internuclear coupling, and $\delta B_i(t)$ is the deviation of the local magnetic field at the ith nucleus as a function of time (t) caused by processes other than nuclear spin-spin interactions. The first term of Eq. (1) is often applied to the hole-doped cuprates, where it leads to a Gaussian spin-echo decay with the time constant T_{2G} [4]. There is another term in the echo decay that is exponential in character, called the Redfield contribution. It is uniquely determined by the anisoptropic Cu spin-lattice relaxation rates [13,18,21]. For PCCO, this contribution (shown in Fig. 1) is negligible at low T, as is the contribution from direct nuclear couplings, which has the upper bound of 470 s^{-1}. T_{2G} is a consequence of the indirect nuclear couplings that are enhanced by antiferromagnetic fluctuations [22]. A phenomenological, overdamped susceptibility peaked at the antiferromagnetic wave vector was introduced [22] as a way of modeling T_1 and T_{2G}. Although we do not observe an unambiguous Gaussian component in our echo decays, it does not rule out *a priori* any influence of indirect spin-spin couplings on the spin-echo experiments. And given that the temperature dependence of T_1^{-1} and T_2^{-1} is opposite, it is likely that unrelated mechanisms govern the two rates.

Now consider what is expected for the spin-echo decay when the first term of Eq. (1) dominates the behavior. Then, pulse-induced spin flips of coupled neighbors alter the local magnetic field with the application of $P2$, thus diminishing the echo refocusing. The echo decay is a function of the probability that neighboring spins are flipped by the action of P_2 [14], which can be written as $P(\theta_2) \propto \sin^2(\theta_2/2)$, as long as $B_1^{\text{eff}} = \alpha B_1 > \Delta$ and $t_{w2}^{-1} < \Delta$, where Δ characterizes the linewidth. Therefore, it is expected that if internuclear coupling governs the spin-echo decay, the rate varies as a function of $P(\theta_2)$ only. The data of Fig. 2 contradict this prediction, because the echo decay rates for the two values of B_1 do not fall on the same curve. Furthermore, it is shown in Fig. 3 that pulses which flip no spins (P_{nr}) also control the decay rate. We conclude from these results that the dependence of T_2^{-1} on the parameters of P_2 occurs independent of nuclear spin-spin interactions.

The observed effects arise from the second term in Eq. (1). Consider a spatially varying magnetic field that is changed by the rf field. Now assume that the local field deviation at the ith nucleus after P_1 at $t = 0$ is δB_{i1}, and it remains unchanged until the application of P_2, when it is changed to a value δB_{i2}. The accumulated phase at the time of the echo formation ($t = 2\tau$) is $\Phi_i(2\tau) = \gamma\tau(\delta B_{i1} - \delta B_{i2})$, and the shape of the echo decay for the ensemble of spins is proportional to $\sum_i \cos\Phi_i(2\tau)$. If the distribution of the $\delta B_{i1} - \delta B_{i2}$ happens to be Lorentzian, it can be shown that the echo decay is exponential.

Finally, we comment on the physical origin of δB_i. The rf pulses must reconfigure a spatial inhomogeneity to produce the observed phenomena. Such a reconfiguration has been reported for rf-induced flux lattice annealing [23]. The inhomogeneities in PCCO are clearly different from the superconducting state and they are not due to chemical inhomogeneities because the effects are not only dynamic, but occur only at low temperatures. There are several candidate states discussed in the literature, including stripes or puddles [24–26], disordered or incommensurate *d*-density waves [27], and field-induced magnetism [28,29]. As long as these states are weakly pinned, an inhomogeneous local magnetic field is produced. The formation of such a state at low temperatures might be related to the dramatic changes recently observed in tunneling spectroscopy [30–32].

In summary, $^{63}T_2$ measurements have been presented in the electron doped high-T_c superconductor PCCO over a broad range of temperatures and rf pulse conditions. They show a substantial temperature dependence for T_2 and an unusual dependence on the amplitude, duration, and frequency of the rf pulses that is not explained by the usual models applied to such materials. We propose that the observed dependence of T_2^{-1} on the rf pulse conditions indicates a spatially varying local magnetic or electronic field of non-nuclear origin whose configuration at low temperatures is changed by the rf pulses. The origin of this inhomogeneous electronic configuration is at present undetermined.

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