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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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. Low-temperature normal state properties are sensitive to the electron-doped cuprates as well.

For a Fermi liquid, it is enhanced by a factor of the Knight-shift [related to $\chi(0,0)$], the spin-lattice relaxation; or 4) in general, any kind of irreversible change in the local magnetic field (or electric field gradient) experienced by the nuclei on the timescale 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 later 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 $2 \mathrm{K} < T < 200 \mathrm{K}$. For $T < 25 \mathrm{K}$, $T_2$ 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 rf pulses 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 [11], 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.

Single crystal PCCO samples were grown with a flux technique \[13\] \[10\] and annealed in argon at 900°C for 48 hours. The doping concentration is roughly optimum to maximize the superconducting transition temperature \(T_c\) at 22 K, as verified by zero-field-cooled magnetization measurements in 0.1 mT magnetic field. The sample used in this study was 3.5 mm x 2.5 mm x 35 \(\mu\)m. PCCO crystallizes in the \(T'\)-tetragonal structure leading to equidistant CuO 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 central transition that is measured. The central transition of \(PCCO\) obtained with \(B_0 \parallel c\) is large enough to cover fully the magnetic field distribution that can be modified by the rf field \(B_1\) at high temperatures. Details of the Cu NMR spectra are to be reported elsewhere \[8\]. 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 spin-echo decay rate when \(B_1\) and the nutation angle of \(P_2\) are both considerably reduced. Clearly, the details of the pulses impact significantly the values of \(T_2\) at low temperatures.

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.

\textit{Experiment I.} Fig. 2a shows that the spin-echo decay rate changes as the duration of \(P_2\), 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 function of \(\sin^2(\theta_2/2)\), where \(\theta_2 = \alpha \gamma B_1 t_{w2}\), \(\alpha = 2\) for the central transition of the \(I = 3/2\) nuclei \[13\], and \(\gamma\) is the gyromagnetic ratio. The insensitivity of the echo decay to pulse parameters at \(T = 21\) K is illustrated in Fig. 2b.

\textit{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. 2 show the results for the spin-echo decay rate when \(B_1\) and the nutation angle of \(P_2\) are both considerably reduced. Clearly, the details of the pulses impact significantly the values of \(T_2\) at low temperatures.

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 \(P_1\) and \(P_2\) has 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 \(T_2^{-1}\) and \(T_{21}^{-1}\) 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 \(P_2\) are both considerably reduced. Clearly, the details of the pulses impact significantly the values of \(T_2\) at low temperatures.

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.

![FIG. 1: Spin-echo decay rates 63T2-1 of PCCO obtained with optimized pulses (solid symbols) and with a small angle refoocusing pulse at smaller B1 (open symbols) as a function of temperature. The solid (dashed) line shows the estimated Redfield contribution for B0||c (B0⊥c).](image_url)

![FIG. 2: Spin-echo decay rates 63T2-1 of PCCO as a function of refocusing pulse angle (θ2) at various alternating magnetic fields B1 in B0=9 T⊥c at a) T= 6 K and b) T= 21 K.](image_url)
show what happens if the duration of $P_2$ 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 non-resonant $P_{nr}$ pulse [with a frequency 2 MHz away from the center of the NMR spectrum (limited by the NMR tank circuit) and with the same amplitude as the resonant one] is applied for a duration $t_{nr}$ just after the $P_2$ 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.

Fig. 4 shows what happens at $T = 2$ K if the amplitude of $P_{nr}$ immediately following the $P_2$ NMR pulse is varied. The details of the NMR pulses and the duration of all the three pulses are kept constant. At this low temperature, a well-defined threshold or crossover rf field amplitude for the non-resonant pulse is required to produce the additional reduction in $T_2$.

To discuss these results, the coupling Hamiltonian ($H'_c$) is written in the following form [20]

$$H'_c = I_{iz} \sum_j a_{(i,j)z} I_{jz} + h\gamma\delta B_i(t), \quad (1)$$

where $i$ and $j$ refer to the $i^{th}$ and $j^{th}$ 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 $i^{th}$ 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 $T_{2G}$ [3]. There is another term in the echo decay that is exponential in character, called the Redfield contribution. It is uniquely determined by the anisotropic Cu spin-lattice relaxation rates [13,18,21]. For PCCO, this contribution (shown in Fig. 4) 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 wavevector 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 $P_2$, 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 $B_i^{rf} \propto \alpha B_1 > \Delta$ and $t_{w2}^{-2} < \Delta$, where $\Delta$ 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. 4 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 $P_2$ occur 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 $i$th nucleus after $P_1$ at $t = 0$ is $\delta B_{1i}$, and it remains unchanged until the application of $P_2$, when it is changed to a value $\delta B_{12}$. The accumulated phase at the time of the echo formation ($t = 2\tau$) is $\Phi_i(2\tau) = \gamma \tau (\delta B_{1i} - \delta B_{12})$, 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 $\delta B_{1i} - \delta B_{12}$ happens to be Lorentzian, it can be shown that the echo decay is exponential.

Finally, we comment on the physical origin of $\delta B_i$. 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. 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, and $d$-density waves. 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.

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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