Cu NMR Study of the Pseudogap in Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{6+\delta}$

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NMR measurements on $^{63}$Cu in underdoped Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{6+\delta}$ crystals are reported. A pseudogap is observed in the Knight shift and spin-lattice relaxation rate for the planar $^{63}$Cu. In contrast to other underdoped compounds, the pseudogap observed in the Knight shift is weak and occurs at a significantly lower temperature. On the other hand, the effect the pseudogap has on spin-lattice relaxation is quite similar to that in other compounds. The manifestation of the pseudogap at $\mathbf{q}=0$ is quite different than at $\mathbf{q}=\mathbf{Q}$.

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I. Introduction

The normal state properties of high-$T_c$ superconductors is unusual. One of the most significant manifestations is the presence of pseudogap. NMR measurements have observed a pseudogap in underdoped compounds, such as YBa$_2$Cu$_3$O$_{6.63}$ [1-3] (YBCO6.6) and YBa$_2$Cu$_4$O$_8$ [4] (Y124), showing a decrease in susceptibility with decreasing temperature. A pseudogap appears not only in the spin properties, but also in the charge transport. The ab-plane scattering rate $1/\tau_{ab}(\omega,T)$, extracted from reflectance spectra, shows a gap-like depression (pseudogap) in the underdoped region [5, 6]. DC resistivity measurements also display a pseudogap [7].

Nuclear magnetic resonance (NMR) has been used extensively as a microscopic probe of the electronic properties of high-$T_c$ compounds. The Knight shift $K_n(T)$ is proportional to the spin susceptibility $\chi^S(\mathbf{q}=0, \omega \approx 0)$. The spin-lattice relaxation rate $T_1^{-1}$ averages over all $\mathbf{q}$ of $\chi^S(\mathbf{q}, \omega)$. As $\chi^S(\mathbf{q}, \omega)$ is strongly peaked at the antiferromagnetic wavevector $\mathbf{Q}=(\pi/a,\pi/a)$, $T_1^{-1}$ of the planar Cu nuclei predominantly probes $\chi^S(\mathbf{Q})$.

There have been few reports of magnetic resonance studies on Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_{6+\delta}$ (PSYCCO). So far studies have been restricted to optimally doped powder samples where $x=0.5$. Spin-lattice relaxation measurements [8, 9] of Cu spins in the CuO$_2$ planes are similar to those observed in YBa$_2$Cu$_3$O$_7$. The Pb NMR Knight shift [8] in PSYCCO is temperature independent in the normal state. Both of these temperature dependences are consistent with optimally doped samples with no hint of a pseudogap.

In this paper, we present measurements of the $^{63}$Cu Knight shifts for the planar Cu(2) sites in both the superconducting and normal state of slightly underdoped PSYCCO crystals ($x<0.5$).
The nuclear spin-lattice relaxation rate $T_1^{-1}$ was also measured in the normal state. We observed a weak pseudogap developing in the Knight shift at considerably lower temperatures than usual. In contrast, the pseudogap appearing in $T_1^{-1}$ occurs much closer in temperature to that of the strong pseudogap compounds.

Preparation of the single crystals of PSYCCO used here has been described by Xue et al. [10]. Magnetic dc susceptibility measurements reveal the onset of $T_c$ to be 80 K in a field of 5 Oe. Our sample consists of about 300 c-axes aligned single crystals, each of dimensions $\sim 0.5 \text{ mm} \times 0.5 \text{ mm} \times 0.3 \text{ mm}$. These crystals are slightly underdoped as indicated in the resistivity [11], showing a change in slope around 150 K. As expected for underdoped crystals, the magnitude of the resistivity is greater than that of the optimally doped samples [10] with a $T_c$ of 84 K.

Our NMR experiments were carried out with a standard pulsed spectrometer. The NMR lineshape consists of two overlapping lines, one from the planar Cu(2) sites and the other from the Cu(1) sites between the PbO layers. As the spin-relaxation rate for Cu(1) is four orders of magnitude smaller [12] than that for Cu(2) we conducted our experiments at a repetition rate sufficient to saturate the Cu(1) signal. At slower repetition rates a small shift in the Cu(2) peak position was observed and tracked down to the presence of a small amount of Cu(1) contamination. A quantitative analysis of this shift indicates that the repetition rate we have chosen for this experiment is sufficient to reduce the Cu(1) shift well below the noise level. Figure 1 displays the Cu(2) central transition with $c \perp \mathbf{H}_0$. The asymmetric lineshape is due to the angular spread amongst the crystal mosaic c-axes. Using the NQR quadrupolar frequency distribution we estimate the mosaic spread to be 6-8°. The large linewidth is due to the distribution of electric field gradients from the Ca$^{+2}$/Y$^{+3}$ layer between the Cu(2)O$_2$ bilayer. Also shown in Fig. 1 is the Cu(1) central transition, taken with a much lower repetition rate.

The Knight shift was obtained from the peak line position by subtracting the second-order quadrupolar shift. It consists of two parts, the temperature independent orbital component $K_{\text{orb}}$ and the spin component $K_s(T)$. The spin Knight shift is proportional to the spin susceptibility $\chi_s(T)$ and the hyperfine coupling constants. In Figure 2 we show the temperature dependence of the Knight shift for PSYCCO. $K_s$ is temperature independent at high temperatures but slowly

![Image of graph showing intensity vs. field with Cu(2) and Cu(1) transitions labeled.]
decreases linearly with temperature at $T^\pm \simeq 180$ K. Starting at $T^\infty \simeq 100$ K the Knight shift gradually decreases faster until at $T_c$ it enters the superconducting state. Below $T_c$, $K_s$ decreases more rapidly, now with a positive curvature. Note that at $T_c$, $K_s$ has dropped to one half of the total excursion in $K_s$ (0.14%) from high temperature to $T = 0$. The Knight shift suggests that a weak pseudogap starts to develop at $T^\pm$. This is to be compared to the strong pseudogap of Y124 [4] which opens up at $T^\pm \gtrsim 500$ K as shown in Fig. 2. Here the total excursion in $K_s$ is 0.26%, with 80% of that occurring in the normal state. A similarly strong pseudogap is observed in YBCO6.6 [1-3]. In this sense one might say that the pseudogap observed in PSYCCO is not as fully developed as the strong pseudogap seen in the two yttrium compounds.

Shown in Fig. 3(a) is $T_1 T$ for $c\perp H_0$ for PSYCCO. At high temperatures the spin-lattice relaxation rate is increasing with decreasing temperature due to increasing AF spin fluctuations [13]. In optimally-doped or overdoped compounds this continues to just above $T_c$ [13]. Under-doped compounds, on the other hand, start to deviate from the linear temperature dependence at a temperature $\equiv T^D$ well above $T_c$. In PSYCCO this occurs at $T^D \simeq 140$ K whereas in Y124 $T^D \simeq 200$ K as shown in Fig. 3(a) and 3(b), respectively.

The most striking feature of this work is that the Knight shift of weak and strong pseudogap materials are quite different in temperature scale while their spin-lattice relaxation rates are similar.
Thus the manifestation of the pseudogap at $q=0$ is quite different than at $q=Q$. In order to elucidate this situation let us consider the resistivity measurements on PSYCCO and Y124. In both cases the linear $T$ resistivity observed at high temperatures changes at $T \approx 160$ K to a more rapidly decreasing resistivity with temperature. This is quite similar to the behaviour of $1/T_1T$ at $T_D$. Both the spin-lattice relaxation and resistivity are dominated by AF spin fluctuations [14]. Thus it is not surprising that the effect the pseudogap has on the AF spin fluctuation spectrum manifests itself at a similar temperature for both spin-lattice relaxation and resistivity.

Another interesting correlation between the weak and strong pseudogap materials is that the weak pseudogap develops at a much lower temperature and the change in magnitude of the Knight shift down to $T_c$ is much less than that for the strong pseudogap. Thus it seems that the weak pseudogap is not as developed as the strong pseudogap at $T_c$. Perhaps this is due to the fact that $T^2$ is much closer to $T_c$ in the weak pseudogap material and that had $T_c$ been proportionally reduced, the Knight shift would have been more heavily suppressed at $T_c$. Among the various underdoped compounds, PSYCCO is unique in this respect.

In summary, we have observed a weak pseudogap in underdoped PSYCCO crystals. The effect the pseudogap has on the Knight shift is strongly dependent on whether the pseudogap is strong or weak. In contrast, the effect the pseudogap has on the AF spin fluctuation spectrum, as measured by spin-lattice relaxation and resistivity, is almost independent of the pseudogap strength.

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References