Weak Pseudogap in Crystals of Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{8+\delta}$

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We report on NMR measurements in underdoped Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{8+\delta}$ crystals. A pseudogap is observed in the Knight shift and spin–lattice relaxation rate. 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 contrast between weak and strong pseudogaps is discussed.

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An unusual feature of the normal-state properties of some high-$T_c$ superconductors is the pseudogap. This manifests itself, for example, in the spin susceptibility which decreases with decreasing temperature. The pseudogap has been observed in underdoped systems such as YBa$_2$Cu$_3$O$_{6.65}$ (YBCO6.6) and YBa$_2$Cu$_3$O$_{7}$ (Y248) but not in optimally-doped compounds, such as YBa$_2$Cu$_3$O$_{7}$ (YBCO7), which have temperature independent susceptibilities.

A pseudogap appears not only in spin properties, but also in charge transport. The c-axis optical conductivities of several underdoped materials, YBCO6.6 and Y248, show a gap-like feature in the normal state below about 300–400 cm$^{-1}$. Puchkov et al. have systematically analyzed the evolution of the scattering rate $1/\tau(\omega,T)$ in infrared reflectivity in a series of compounds from underdoped to overdoped. In the underdoped region they see a gap-like depression (pseudogap) in $1/\tau$ at $T_c$, consistent with the pseudogap observed in the Knight shift at considerably lower temperatures. The Pb NMR Knight shift 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.

To date there is no consensus on the origin of the pseudogap. Emery and Kivelson suggest that pair formation and phase coherence do not necessarily occur at the same temperature. The lower carrier density in the underdoped region may result in pair formation without condensation into a coherent state at temperatures well above $T_c$, thereby producing a pseudogap. Antiferromagnetic (AF) spin fluctuations and the evolution of the Fermi surface on doping may also contribute to the creation of the pseudogap. More exotic theories involving charge–spin separation have also been considered, with interplanar coupling, as a source of the pseudogap. Recently Atkinson, Wu and Carbotte have proposed that the pseudogap is not actually a spin gap but a result of strong AF spin fluctuations and interband coupling.

There have been few reports of magnetic resonance studies on Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_{8+\delta}$ (PSYCCO). So far studies have been restricted to optimally doped powder samples where $x = 0.5$. Spin-lattice relaxation measurements of Cu spins in the CuO$_2$ planes are similar to those observed in YBCO7. The Pb NMR Knight shift 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 ($x \lesssim 0.5$). The nuclear spin–lattice relaxation rate $T_1^{-1}$ was also measured in the normal state. We find evidence of 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. Magnetic dc sus-
ceptibility 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, 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 with a $T_c$ of 84 K. Measurements of the optical conductivity also indicate the presence of a pseudogap. 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 than that for Cu(2) we conducted our experiments at a repetition rate sufficient to saturate the Cu(1) signal. Figure 1 displays the Cu(2) central transition with $c \perp H_0$. The asymmetric lineshape is due to the angular spread amongst the crystal mosaic $c$–axes. 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. To second order the resonance frequency $\nu_0$ for $c \perp H_0$ is given by

$$\nu_0 = \nu_L + (3/16)\nu_Q^2/\nu_L$$

where $\nu_L$ is the Larmor frequency and $\nu_Q$ is the quadrupolar frequency. Our NQR spectrum, used to determine $\nu_Q$, is similar to those obtained previously.

This procedure of subtracting the second–order shift was checked at two temperatures by measuring the field dependence of the resonance frequency. One can independently extract the quadrupolar shift from the Knight shift by plotting the effective Knight shift $K_{\text{eff}}$ versus $[(1 + K_{\text{eff}})/\nu_L]^2$. The resulting intercept is equal to the Knight shift $K$.

The Knight shift 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 2a we show the temperature dependence of the Knight shift for PSYCCO. $K_s$ is temperature independent at high temperatures but slowly decreases linearly with temperature at $T^o \approx\ 180$ K. Starting at $T^* \approx\ 100$ 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 $T^o$. This is to be compared to the strong pseudogap of Y248 which opens up at $T^o \geq\ 500$ K as

![FIG. 1. $^{63}$Cu(2) central transition taken at 90.6 MHz with $c \perp H_0$. Dashed line indicates the position of the $^{63}$Cu(1) line which is saturated in this spectrum.](image1)

![FIG. 2. (a) $^{63}$Cu(2) Knight shift for PSYCCO with $c \perp H_0$. The arrow indicates the value of $T_c$ at $H_0 = 8T$. (b) Spin–lattice relaxation time for PSYCCO. $T^o$, $T^*$ and $T^D$ are described in the text.](image2)
quite 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 Y248. In both cases the linear \( T \) resistivity observed at high temperatures changes at \( T \simeq 160 \text{ K} \) to a more rapidly decreasing resistivity with temperature. This is quite similar to the behaviour of \( 1/T_\chi T \) at \( T^D \). Both the spin–lattice relaxation and resistivity are dominated by AF spin fluctuations. 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.

The Knight shift though is a measure of the long wavelength spin susceptibility which may be affected by the pseudogap in a different manner. In the language of the MMP model \( \chi'(0) \) describes the quasiparticles. In contrast to \( 1/T_\chi T \) and resistivity measurements, the onset temperatures for the weak and strong pseudogap materials are quite different. In both cases though, \( T^\circ \) is greater than \( T^D \). But in PSYCCO \( T^* \) is less than \( T^D \) and in Y248 \( T^* \) is greater than \( T^D \).

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 \( T^\circ \) 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.

This behaviour is echoed in the \( c \)-axis optical conductivity. The low frequency conductivity for YBCO6.6 at \( T_c \) is less than 20% of the high temperature limit. This is consistent with the behaviour of the Knight shift (similar to that in Fig. 3a). On the other hand the optical conductivity for PSYCCO has only decreased by 50% at \( T_c \), again similar to the drop displayed in the Knight shift. Thus the \( c \)-axis optical conductivity and Knight shift both illustrate the weak nature of the pseudogap in PSYCCO.

One would expect \( T^\circ \) and \( T^* \) to be correlated with the energy at which the pseudogap opens up in the optical spectrum if the pseudogap was indeed due to a gap in the excitation spectrum. Basov et al. have found the pseudogap to develop at about 300–400 cm\(^{-1}\) in YBCO6.6 and Y248. These compounds both have \( T^\circ \) \( \geq 500 \text{ K} \). On the other hand PSYCCO has a much lower \( T^\circ \) of 180 K with the pseudogap still well developed at 700 cm\(^{-1}\). Thus it seems that the pseudogap’s onset temperature \( T^* \) is either negatively correlated to the onset frequency or perhaps not at all.

Reedyk et al. have noted that there is no correlation between the magnitude of the high frequency \( c \)-axis conductivity and the pseudogap amongst the various under-

![FIG. 3. (a) \(^{63}\text{Cu}(2)\) Knight shift for Y248 (squares) with \( c \perp \text{H}_0 \). The solid line represents data for optimally doped YBCO7. (b) Spin–lattice relaxation time for Y248 (squares) and YBCO7 (circles).](image)
doped materials. There also appears to be no correlation with the carrier concentration. The plasma frequency $\omega_p$ for YBCO6.6 is 0.8 eV which is similar to the value for PSYCCO of 0.6 eV. These underdoped compounds both have $\omega_p$ considerably less than the value for optimally doped YBCO where $\omega_p = 1.4$ eV.

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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