# Weak pseudogap in crystals of $Pb_2\ Sr_2(Y,Ca)Cu_3O_{8+\delta}$


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We report on NMR measurements in underdoped $Pb_2\ Sr_2(Y,Ca)Cu_3O_{8+\delta}$ 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 $YBa_2Cu_3O_{6.63}$[1–3] (YBCO6.6) and $YBa_2Cu_4O_8$[4] (Y248) but not in optimally-doped compounds, such as $YBa_2Cu_3O_7$[5] (YBCO7), which have temperature independent susceptibilities.

A pseudogap appears not only in spin properties, but also in charge transport. The c–axis optical conductivities $\sigma_c$ of several underdoped materials, YBCO6.6 and Y248, show a gap-like feature in the normal state[6] below about 300-400 cm$^{-1}$. Identifying this feature with the pseudogap is quite controversial at the moment. It has been suggested that the physics underlying the appearence of a gap in the c–axis properties is of a different origin than that of the pseudogap[7]. A better measure may be the scattering rate $1/\tau_{ab}(\omega,T)$ in the ab–plane which is extracted from the ab–plane optical conductivity[8]. Puchkov *et al.*[8,9] have systematically analyzed the evolution of $1/\tau_{ab}(\omega,T)$ in infrared reflectivity in a series of compounds from underdoped to overdoped. In the underdoped region they see a gap-like depression (pseudogap) in $1/\tau_{ab}(\omega,T)$ opening up below $T \simeq$140–160 K, while in the overdoped region they do not observe a gap. DC resistivity measurements also display signs of a pseudogap. The resistivity for YBCO7 follows a linear temperature dependence over a very wide temperature range above $T_c$. On the other hand the resistivity of Y248 deviates from linearity at a temperature well above $T_c$[10], consistent with the pseudogap observed in other measurements.

Nuclear magnetic resonance (NMR) has been used extensively as a microscopic probe of the electronic properties of high-$T_c$ compounds. The Knight shift $K_s(T)$ is proportional to the spin susceptibility $\chi'(\mathbf{q}=0,\omega\simeq 0)$. The spin–lattice relaxation rate $T_1^{-1}$ averages over all $\mathbf{q}$ of $\chi''(\mathbf{q},\omega)$. As $\chi''(\mathbf{q},\omega)$ is strongly peaked at the antiferromagnetic wavevector $\mathbf{Q}$=($\pi$/a,$\pi$/a), $T_1^{-1}$ of the planar Cu nuclei predominantly probes $\chi''(\mathbf{Q})$. Although both of these quantities develop a pseudogap they do so at quite different temperatures. As we will discuss later, the pseudogap manifests itself differently at $\mathbf{q}$=0 and $\mathbf{q}$=$\mathbf{Q}$.

To date there is no consensus on the origin of the pseudogap. Emery and Kivelson[11] 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[12]. More exotic theories involving charge–spin separation have also been considered, with interplanar coupling, as a source of the pseudogap[13]. Recently Atkinson, Wu and Carbotte[7] 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 $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ (PSYCCO). So far studies have been restricted to optimally doped powder samples where $x$ = 0.5. Spin-lattice relaxation measurements[14,15] of Cu spins in the $CuO_2$ planes are similar to those observed in YBCO7. The Pb NMR Knight shift[14] 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.*[16]. 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 $\sim$ 0.5mm$\times$ 0.5mm$\times$ 0.3mm. These crystals are slightly underdoped as indicated in the resistivity[18], 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[16] with a $T_c$ of 84 K. Anisotropy in the resistivity has been measured for crystals from a similarly prepared batch[17]. Similar to other underdoped compounds the c–axis resistivity $\rho_c$ is semiconductor like with an anisotropy ratio, just above $T_c$, of $\rho_c/\rho_{ab} \simeq 500$. Measurements of the optical conductivity also indicate the presence of a pseudogap[18]. 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[19] 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 $\mathbf{c}\perp\mathbf{H}_0$. 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. To second order the resonance frequency $\nu_0$ for $\mathbf{c}\perp\mathbf{H}_0$ is given by

$$\nu_0 = \nu_L + (3/16)\nu_Q^2/\nu_L \tag{1}$$

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[14,15]. 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 $K_{\mathrm{eff}}$ versus

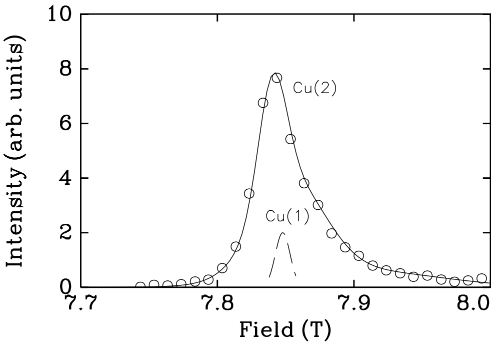


FIG. 1. $^{63}$Cu(2) central transition taken at 90.6 MHz with $\mathbf{c}\perp\mathbf{H}_0$. Dashed line indicates the position of the $^{63}$Cu(1) line which is saturated in this spectrum.

$[(1+K_{\mathrm{eff}})/\nu_L]^2$. The resulting intercept is equal to the Knight shift $K$.

The Knight shift consists of two parts, the temperature independent orbital component $K_{\mathrm{orb}}$ 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 $T^\circ \simeq 180$ K. Starting at $T^\star \simeq 100$ 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 $T^\circ$. This is to be compared to the strong pseudogap of Y248[4] which opens up at $T^\circ \geq 500$ K as shown in Fig. 3a. Here the total excursion in $K_s$ is 0.26% with 80% of that occurring in the normal state. Thus the drop in $K_s$ in the superconducting state is quite small compared to that of an optimally doped sample (see Fig. 3a). 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.

Presented in Fig. 2b is $T_1T$ for $\mathbf{c}\perp\mathbf{H}_0$. Typical of high–$T_c$ compounds $T_1T$ is not temperature independent as one expects of a degenerate Fermi gas. At high temperatures the spin–lattice relaxation rate is increasing with decreasing temperature due to increasing AF spin fluc-

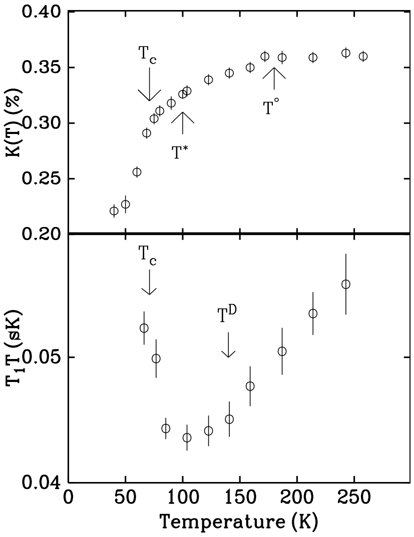


FIG. 2. (a) $^{63}$Cu(2) Knight shift for PSYCCO with $\mathbf{c}\perp\mathbf{H}_0$. The arrow indicates the value of $T_c$ at $H_0$=8T. (b) Spin–lattice relaxation time for PSYCCO. $T^{\circ}$, $T^{\star}$ and $T^D$ are described in the text.

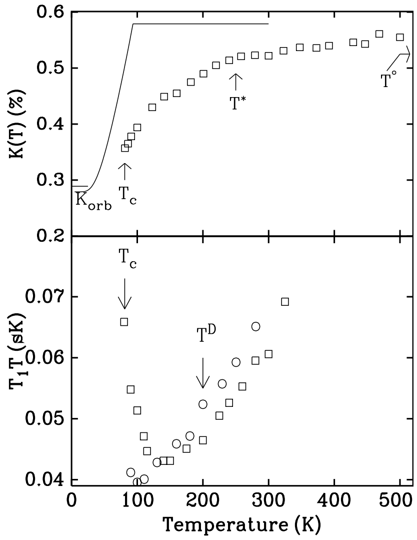


FIG. 3. (a) $^{63}$Cu(2) Knight shift for Y248 (squares)[4] with $\mathbf{c}\perp\mathbf{H}_0$. The solid line represents data for optimally doped YBCO7. (b) Spin–lattice relaxation time for Y248 (squares) and YBCO7 (circles)[1].

tuations. In optimally–doped compounds this continues to just above $T_c$, as illustrated for YBCO7 in Fig. 3b. 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 Y248 $T^D \simeq 200$ K as shown in Fig. 2b and 3b respectively.

The most striking feature of this work is that the Knight shift of weak and strong pseudogap materials are quite different while their spin–lattice relaxation rates are quite similar. Thus the manifestation of the pseudogap at $\mathbf{q}$=0 is quite different than at $\mathbf{q}$=$\mathbf{Q}$. 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 $T \simeq 160$ 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[20]. 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 Millis–Monien–Pines model[21] $\chi'(0)$ describes the quasiparticles. In contrast to $1/T_1T$ 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 $T^\star$ is less than $T^D$ and in Y248 $T^\star$ 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[6]. 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 $T_c$[18], again similar to the drop displayed in the Knight shift. Thus the c–axis optical conductivity seems to share the same characteristic of a weak pseudogap as does the Knight shift.

One would expect $T^\circ$ and $T^\star$ 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. Homes *et al.* and Basov *et al.*[22] have found the gap to develop in $\sigma_c$ at about 300–400 cm$^{-1}$ in YBCO6.6 and Y248 respectively. These compounds both have $T^\circ \geq 500$ K. On the other hand PSYCCO has a much lower $T^\circ$ of 180 K with the gap in $\sigma_c$ still well developed[18] at 700 cm$^{-1}$. Thus it seems that the gap's onset temperature $T^\circ$ is either negatively correlated to the onset frequency or perhaps not at all. This provides support to the conjecture of Wu *et al.*[7] that the physical origin of the gap–like features in the c–axis properties are unrelated to the pseudogap observed in the ab–plane properties.

In summary, we have observed a weak pseudogap in underdoped PSYCCO crystals. The effect the pseudogap has on the Knight shift in 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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