Evidence of a critical hole concentration in underdoped YBa$_2$Cu$_3$O$_y$ single crystals revealed by $^{63}$Cu NMR

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We report a $^{63}$Cu NMR investigation in detwinned YBa$_2$Cu$_3$O$_y$ single crystals, focusing on the highly underdoped regime ($y = 6.35 - 6.6$). Measurements of both the spectra and the spin-lattice relaxation rates of $^{63}$Cu uncover the emergence of static order at a well-defined onset temperature $T_0$ without a known order parameter as yet. While $T_0$ is rapidly suppressed with increasing hole doping concentration $p$, the spin pseudogap was identified only near and above the doping content at which $T_0 \to 0$. Our data indicate the presence of a critical hole doping $p_c \sim 0.1$, which may control both the static order at $p < p_c$ and the spin pseudogap at $p > p_c$.

The superconducting copper-oxides (cuprates) in the underdoped regime feature unusual states of matter, such as a pseudogap (PG), density-wave order (stripes), and the coexistence of magnetism and superconductivity. Debates regarding the origin and the precise nature of those phases or related phenomena like a reconstruction of the Fermi surface at a quantum critical point are still ongoing actively.$^1$ In particular, interest in the underdoped YBa$_2$Cu$_3$O$_y$ (YBCO$_y$) has been revived in recent years, during which significant progress in understanding those subjects has been made through experimental observations of an electric liquid crystal (ELC) or nematic phase,$^4,5$ quantum oscillations above a critical doping$^6,8$, and field-induced charge stripe order$^5,9$. Motivated by the recent literature and by the available high-quality single crystals of underdoped YBCO$_y$, we carried out a $^{63}$Cu NMR study of YBCO$_y$ to elucidate the underlying physics in the highly underdoped region of the compound on a microscopic level. While nuclear magnetic resonance (NMR) is a powerful local probe, so far, the majority of the NMR studies on the planar Cu in YBCO$_y$ has been performed on nearly optimal or slightly underdoped regions$^1,12$, largely due to strong magnetism which causes complicated static and dynamic effects on NMR parameters. In this Letter, we show that a critical hole doping $p_c$ exists in the $p$-$T$ phase diagram of YBCO$_y$ beneath the superconducting (SC) dome at $p \sim 0.1$, below which a static order sets in and above which a spin pseudogap (PG) opens up in the low-energy spin excitation spectrum.

The growth and characterization of detwinned YBCO$_y$ single crystals are described in Refs. $^{13}$.$^{14}$. The single crystals investigated here have $y = 6.35$ ($T_c = 10$ K, $p = 0.062$), $6.4$ ($T_c = 21$ K, $p = 0.075$), $6.45$ ($T_c = 35$ K, $p = 0.082$), $6.5$ (sample 1 with short ortho II correlation length $^{[34]}$), $T_c = 53$ K, $p = 0.106$; sample 2 with long correlation length ($\sim 100$ Å): $T_c = 61$ K, $p = 0.114$), and $6.6$ ($T_c = 61$ K, $p = 0.135$), where $p$ is the hole concentration per planar Cu determined from the $c$-axis lattice constant.$^{12}$. $^{63}$Cu NMR spectra were obtained by integrating averaged spin-echo signals as the frequency was swept, and the spin-lattice relaxation rates, $T_1^{-1}$, were measured by monitoring the recovery of the nuclear magnetization after a saturation pulse.

Fig. 1 shows $^{63}$Cu spectra for $y = 6.35$ and $6.45$ measured at $H = 7$ T applied along the $c$ axis. The leftmost sharp line and the rightmost broad line in each panel are identified to arise from the Cu(1)$_0$ and Cu(1)$_2$ sites,
respectively, in the CuO chains, where the subscript denotes the number of the nearest neighboring oxygen ions along the chain. While the central line at room temperature comes from the planar Cu(2) site, we find that it evolves in a complicated way as T is lowered, especially for y = 6.35 and y = 6.4. The intensity of Cu(2) (dotted line in Fig. 1) is strongly suppressed, and at the same time a new feature sp0, consisting of two resonance lines indicated by two dashed lines emerges at an onset temperature. Clearly, for y = 6.45, sp0 occurs at a much lower temperature than for y = 6.35. The rapid suppression of Cu(2) with decreasing T is attributed to the wipe-out effect, as observed in $^{63}$Cu NQR in Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{y}$, which arises from a slowing down of spin fluctuations. We particularly for y = 6 and 6.6 are almost identical without any signature of either sp0 or wipeout of Cu(2), except for a moderate broadening with decreasing T. Interestingly, we observed the splitting of the Cu(I)$_2$ line at low T for y = 6.35, which may suggest that sp0 influences Cu(I)$_2$. In addition, it is noticeable that both sp0 and Cu(I)$_0$ broaden significantly at low T below 20 K for y = 6.35, suggesting the occurrence of glassy or incommensurate magnetic order. Note that such a broadening could not be measured for y = 6.4 and 6.45, because the magnetic order occurs deep in the superconducting state where the NMR spectra significantly weaken and become complicated.

Fig. 2 shows the recovery of the $^{63}$Cu nuclear magnetization after a saturating pulse as a function of delay time t at various temperatures for y = 6.35 and 6.45, measured at the Cu(2) line. Unexpectedly, we found a step-like feature in the data, which indicates two T$_1$-processes. The long T$_1$ process becomes discernible at 265 K for y = 6.35 and at 120 K for 6.45, and its fraction (i.e., 1 - m(t) at the step) increases rapidly with decreasing T. Comparing with the T-dependence of the spectrum as shown in Fig. 1, we find that the long T$_{1\ell}$ component arises when the new spectrum sp0 becomes visible, suggesting that sp0 is due to an emerging static phase featured by the long T$_{1\ell}$. Since two T$_1$ processes are evident in the relaxation data, we used a fitting function for magnetic relaxation of the central transition for I = 3/2 including two T$_1$ components,

$$m(t) = \left[1 - a \left\{ (1 - w) \left( 0.1e^{-t/T_{1s}} + 0.9e^{-6t/T_{1s}} \right) + w \left( 0.1e^{-t/T_{1l}} + 0.9e^{-6t/T_{1l}} \right) \right\} \right],$$

where a is a fitting parameter which is ideally one for saturation recovery. T$_{1s}$ (T$_{1\ell}$) are the short (long) T$_1$ components, and w is the fraction of the volume governed by the long T$_{1\ell}$ process to the total volume. Solid curves in Fig. 2 are fits to Eq. 1. At low T ($\leq$ 70 K), it was necessary to impose the stretching exponent $\beta$ in Eq. (1) for the T$_{1\ell}$ recovery, which is indicative of a crossover to a glassy magnetic phase.

The resulting (T$_{1\ell}$T$^{-1}$), (T$_{1\ell}$T$^{-1}$), and w as a function of T and for all y are presented in Fig. 3. The results in YBCO$_{6.6}$ are compatible with data known so far, revealing the spin pseudogap with the onset $T^* \sim 145$ K. The spin-lattice relaxation rate probes the gap solely in the spin excitation spectrum since (T$_1$T$^{-1}$) $\propto \sum q A^2(q) \chi''(q, \omega_0)$ where A(q) is the hyperfine coupling constant and $\omega_0$ the Larmor frequency. Therefore, the onset temperature of the PG and its doping dependence obtained by (T$_1$T$^{-1}$) can be significantly different from those obtained by the Knight shift, which probes the spin response at q = 0 only, and other techniques such as ARPES and optical conductivity which probe the charge gap. For YBCO$_{6.5}$, T$^*$ is reduced to $\sim$ 110 K as indicated by arrows. We performed the measurement in another YBCO$_{6.5}$ crystal which has a longer ortho-II correlation length $\sim$ 100 A. For this
The phase diagram is also in qualitative agreement with the values at which \( T_0 \) and \( T_g \) were also observed for \( y \leq 6.45 \). In YBCO_{6.35}, \( (T_1T)^{-1} \) is almost constant at high \( T \), but it starts to rise steeply below \( \sim 100 \) K, forming a sharp peak centered at \( \sim 11 \) K. These behaviors, together with the significant broadening of the spectra at low \( T \), lead to the conclusion that a spin freezing or spin-glass (SG) transition occurs at a characteristic temperature \( T_g \sim 11 \) K for \( y = 6.35 \). We find that our data resembles the results of \( ^{89}Y \) NMR in \( Y_{1-x}Ca_Ba_2Cu_3O_{y} \) \( [17] \) and \( ^{139}La \) NQR/NMR in \( La_{2-x}Sr_2Cu_3O_4 \) \( [21, 22] \). Similar \( T \)-dependencies of \( (T_1T)^{-1} \) were also observed for \( y = 6.4 \) and 6.45. Although we were not able to identify the local maximum for these doping levels due to the higher \( T_c \) which complicates the identification of \( T_g \) by NMR, one can obtain \( T_g \sim 5 \) K for \( y = 6.45 \) from the \( \mu \)SR study of \( Y_{1-x}Ca_Ba_2Cu_3O_6 \) which shows a very similar \( p \)-dependence of \( T_g \) \( [23] \).

Fig. 3(b) shows the volume fraction \( w \) as a function of \( T \), obtained from the fit of relaxation data \( m(t) \) using Eq. (1). It should be emphasized that the values of \( w \) themselves have no quantitative meaning, since they may depend on the frequency at which the relaxation rates were measured. Moreover, the wipeout of Cu(2) should lead to a significant increase of \( w \), particularly at low \( T \), which is indeed thought to account for the rapid increase of \( w \) at low temperatures [see Fig. 3(c)]. Nonetheless, the temperature at which \( w \to 0 \), i.e., where the \( T_1T \) process vanishes with increasing \( T \) should be unaffected by those facts. Thus, with reasonable accuracy, one can define the onset temperature \( T_0 \) from the values extrapolated to \( w = 0 \), denoted by arrows.

From these results, we draw the \( p-T \) phase diagram in Fig. 4. The most striking feature is that \( T_0 \) falls rapidly to zero at a hole concentration of \( p \sim 0.1 \) beneath the SC dome. At the same time, the SG transition temperature \( T_g \) shows also similar doping dependence, being terminated at \( p \) where \( T_0 \to 0 \). These behaviors suggest a close relationship between \( T_0 \) and \( T_g \), collapsing to the same critical doping \( p_c \sim 0.1 \). Interestingly, it turns out that \( p_c \) is very near the doping level at which the metal-insulator crossover (MIC) takes place \( [24] \) or the Fermi surface is reconstructed by density-wave order \( [8, 9, 25] \). The phase diagram is also in qualitative agreement with that suggested by inelastic neutron scattering (INS) and muon spin rotation (\( \mu \)SR) studies \( [13, 22] \).

A remarkable finding in our study is that the \( spin \) pseudogap is observed only near and above \( p_c \) (i.e., \( y \geq 6.5 \)) [see Figs. 3(a) and 4]. Note that \( T^* \) of YBCO_{6.5} positioned near \( p_c \) is much lower than the value expected
based on extrapolation of the doping dependence established at higher $p$, which is indicated by the dotted line. Indeed, the sudden drop of $T^*$ near $p_c$ in YBCO$_{6.5}$ appears as a crossover to the absence of $T^*$ in YBCO$_{6.45}$, corroborating the INS results in which the suppression of the low energy spin excitations (i.e., spin pseudogap) was not detected down to 5 K in YBCO$_{6.45}$[27,28].

Such an abrupt suppression of the spin pseudogap below a critical doping level was reported in NMR studies not only of similarly hole-doped Y$_{1−x}$Ca$_x$Ba$_2$Cu$_3$O$_y$[17] but also of the multi-layer cuprate Ba$_2$Ca$_2$Cu$_3$O$_6$(F$_y$O$_{1−y}$)$_2$[29]. By the same token, the fact that $p_c$ is in the vicinity of the MIC [24] agrees well with the disappearance of the quantum oscillations below $∼p_c$, as well as with the NMR result in Bi$_2$Sr$_{2−x}$La$_x$CuO$_{6+δ}$[17] that the ground state of the PG is metallic [31]. Therefore, we argue that the spin PG phenomenon may be quantum critical, stemming from the suppression of magnetism. In fact, such a strong competition between magnetism and the PG gives a good account of the observation that the PG is abruptly suppressed by substituting the Cu(2) sites with $∼1\%$ Zn impurities around which a local moment is induced on the Cu(2) sites in YBCO$_{6.7}$[31] and YBa$_2$Cu$_4$O$_8$[32].

While the nature of static order which appears at $T_0$ is unclear yet, one may consider $T_0$ as the onset of stripe-like charge modulation in the plane, possibly induced by the end Cu ion of the oxygen-filled chains, Cu(1)$_1$. In fact, as effective impurities, Cu(1)$_1$ sites can cause Friedel-like oscillations [33], which may in turn induce the stripe-like charge modulation in the plane. This would be consistent with a higher $T_0$ at lower $p$, where the number of Cu(1)$_1$ is higher. The charge modulation scenario agrees well with signatures of broken rotational symmetry observed in resistivity [4] and INS [3,12] measurements at $p < p_c$. In this case, the planar Cu(2) sites should be differentiated into two spatially modulated distinct regions. In terms of stripes, the short $T_1^x$-yielding region is naturally related to spin stripes which consist of the localized Cu(2) spins, while charge stripes may yield the long $T_1^x$ if the spin contributions to the relaxation rates were almost quenched. Although the stripe-like charge modulation accounts for our results to large extent, it remains a question whether the two alternating regions in the stripe structure could, in practice, result in the $(T_1^x T)^{−1}$ and $(T_1^x T)^{−1}$ values that strikingly differ up to three orders of magnitude.

In summary, we performed a systematic $^{63}$Cu NMR study as a function of doping and temperature in highly underdoped YBa$_2$Cu$_3$O$_y$, showing that static order, probably stripe-like, emerges at the onset temperature $T_0$, being followed by glassy magnetic order at $T_g$. The resulting phase diagram includes a critical hole doping $p_c ∼ 0.1$, at which both $T_0$ and $T_g$ fall to zero. Another important finding is that the spin pseudogap was detected only above $p_c$, suggesting that the spin pseudogap phase competes with the magnetic order and/or the static order detected at $T_g$ and $T_0$, respectively.

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