Systematic $^{63}\text{Cu}$ NQR and $^{89}\text{Y}$ NMR Study of Spin Dynamics in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ across the Superconductor-Insulator Boundary

P.M. Singer and T. Imai

Department of Physics and Center for Materials Science and Engineering, MIT, Cambridge, Massachusetts 02139

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We demonstrate that the spin dynamics in underdoped $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ for $y = 6.0$ exhibit qualitatively the same behavior to underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for an equal amount of hole concentration $p = z/2 = x \leq 0.11$. However, a spin gap appears as more holes are doped into the CuO$_2$ plane by increasing the oxygen concentration to $y = 6.5$ for a fixed value of Ca concentration $z$. Our results also suggest that Ca doping causes disorder effects that enhance the low frequency spin fluctuations.

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The mechanism of high temperature superconductivity remains a major mystery in condensed matter physics. The fundamental difficulty stems from the complexity of the electronic phase diagram, particularly in the underdoped regime. Earlier $^{63}\text{Cu}$ NMR (nuclear magnetic resonance) and NQR (nuclear quadrupole resonance) measurements of the nuclear spin-lattice relaxation rate $^{63}1/T_1$ led to the discovery of the pseudogap phenomenon in the spin excitation spectrum of bilayer ($\text{Y},\text{La})\text{Ba}_2\text{Cu}_3\text{O}_y$ [1–4]. In the spin pseudogap, or spin-gap regime, low energy spin excitations are suppressed below the spin-gap temperature $T^*$ ($>T_c$) which results in a decrease in $^{63}1/T_1T$ ($^{63}1/T_1$, divided by temperature $T$) below $T^*$. Subsequent NMR and optical charge transport measurements showed that a pseudogap appears both in the spin and charge excitation spectra of a wide variety of high $T_c$ cuprates [5–9], with the most notable exception being the prototype high $T_c$ cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Moreover, the temperature scale $T^*$ of the spin gap and the charge gap increases with decreasing hole concentration towards the superconductor-insulator boundary [3,6,7,9].

In various theoretical model analysis, the pseudogap is often considered the key in understanding the mechanism of superconductivity. Unfortunately, driving CuO$_2$ planes into the insulating regime in a controlled fashion is technically difficult in many high $T_c$ cuprates. As such, the fate of the pseudogap in the heavily underdoped insulating regime has been highly controversial. Attempts have been made to infer information on the spin gap based on uniform spin susceptibility $\chi'(\mathbf{q} = 0)$ [10,11]. However, it is important to realize that growth of short range spin order alone causes a reduction of $\chi'(\mathbf{q} = 0)$ without having any gaps. For example, the undoped CuO$_2$ plane shows a roughly linear decrease of $\chi'(\mathbf{q} = 0)$ with decreasing temperature which is entirely consistent with the 2D Heisenberg model. By continuity, it is natural to associate the decrease of $\chi'(\mathbf{q} = 0)$ in the heavily underdoped regime to be mostly due to growth of short range order with an effective energy scale $J(p)$ [12], and not to a spin gap.

It has also become increasingly popular to infer $T^*$ for the charge sector based on scaling analysis of the Hall effect [10] or resistivity data [13]. Some authors claim that there is a universal phase diagram of $T^*$ with $p$ and $T$ being the only two parameters, even in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. However, earlier $^{63}\text{Cu}$ NQR [14,15] and neutron scattering [16] experiments revealed no hint of a spin gap above $T_c$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Instead, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ exhibits an instability at low temperatures towards the formation of the quasistatic stripe with incommensurate spin and charge density waves [17–19]. Careful NMR (NQR) experiments of spin-gap effects with controlled doping near the superconductor-insulator boundary are necessary and would allow for comparison with $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

In this Letter, we report a systematic microscopic investigation of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ utilizing $^{63}\text{Cu}$ NQR and $^{89}\text{Y}$ NMR. The advantage of the $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ system is that one can control the hole concentration near the superconductor-insulator boundary by fixing $y = 6.0$ and varying $z$. In this case, the hole concentration is given by $p = z/2$, because the chain Cu sites [Cu(1)] with twofold oxygen coordination remain insulating with a 3d$^{10}$ configuration [20]. In Fig. 1(a) we show the absence of a spin-gap signature in heavily underdoped $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{y,0}$ ($z \leq 0.22$) based on measurements of $^{63}1/T_1T$ at the

FIG. 1. (a) $^{63}1/T_1T$ above $T_c$ (vertical lines) at the $^{63}\text{Cu(2)}$ site for $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ [where $z \leq T_c$] for each symbol is indicated in (b), and for $\text{La}_{1.90}\text{Sr}_{0.15}\text{CuO}_4$ (dotted curve). (■) and (□) are taken from [21]. All lines are a guide for the eye. The dashed line through (▲) indicates region below $T_{\text{wipeout}}$ where only partial Cu(2) signal intensity is observable.
planar Cu site [Cu(2)]. Instead, we show that the low energy spin excitations exhibit similar behavior to underdoped La$_{2-x}$Sr$_x$CuO$_4$, with equivalent $p = z/2 = x$, which monotonically grow with decreasing $p$ and $T$. With further hole doping Y$_1$-$x$Ca$_x$Ba$_2$Cu$_3$O$_{6.5}$ by oxygen loading to $y = 6.5$ for fixed $z$, however, we do observe the spin-gap signature [Fig. 1(a)], even though it appears somewhat suppressed compared to YBa$_2$Cu$_3$O$_{6.5}$ without Ca substitution [Fig. 1(b)]. This is the first time in the high $T_c$ cuprates where the appearance of a spin-gap signature is experimentally tracked through the insulator-superconductor boundary by increasing the hole doping. We recall that in contrast with the present case, further hole doping La$_{2-x}$Sr$_x$CuO$_4$ (or La$_2$CuO$_4$+$\delta$) does not result in a spin-gap signature; therefore our finding challenges the popular argument that charge disorder caused by the alloying effects of Sr$^{+2}$ substitution (i.e., “dirt effects”) alone suppresses the spin gap and drives La$_{2-x}$Sr$_x$CuO$_4$ towards the stripe instability.

We synthesized our polycrystalline samples following [22]. The oxygen concentration was controlled and determined following [23] with precision $\Delta y \sim \pm 0.05$. The $^{63}$Cu NQR spectrum of all our Y$_1$-$x$Ca$_x$Ba$_2$Cu$_3$O$_y$ samples are very similar to earlier reports [20], and the superconducting transition temperature $T_c$, as determined by SQUID measurements, shows close agreement with [22]. The temperature dependence of $^{63}$Cu NQR near the peak frequency of the $^{63}$Cu(2) site at $\omega_n/2\pi = 25.5$ MHz [20] by applying an inversion pulse prior to the spin echo sequence. A typical $\pi/2$-pulse width of 3 $\mu$s was used. NMR measurements at 9 T in uniaxially aligned powder gave identical results to NQR within uncertainties. $^{63}$Cu NQR is given by

$$\frac{^{63}}{T_1T} = \frac{2k_B}{g^2\mu_B^2\hbar^2} \sum_q |^{63}A(q)|^2 \chi''(q, \omega_n)/\omega_n,$$

where $^{63}A(q)$ is the wave-vector dependent, geometrical form factor of the electron-nucleus hyperfine coupling [24,25]. As shown in Fig. 1(a), $^{63}$Cu NQR in underdoped Y$_1$-$x$Ca$_x$Ba$_2$Cu$_3$O$_{6.0}$ ($x \approx 0.22$) with nominal hole concentration $p \approx 0.11$ does not exhibit a spin gap. Instead, $^{63}$Cu NQR decreases with decreasing temperature, exhibiting similar values as La$_{2-x}$Sr$_x$CuO$_4$, shown in Fig. 2(a). The fact that $^{63}$Cu NQR decreases with decreasing temperature indicates that low energy spin excitations continue to increase with decreasing temperature. Moreover, the enhancement of low energy spin excitations below 300 K is followed by the decrease of the $^{63}$Cu NQR signal intensity below $T_{\text{wq}}$ ($\approx 200$ K), i.e., wipeout effects [29–31]. Wipeout effects can be caused by various mechanisms [29] including the presence of nearly localized free spins induced by hole localization (in analogy with Cu NMR wipeout in Cu metal imbedded with dilute Fe or Mn spins), as well as the onset of the glassy slowing down of stripes.

The temperature dependence of $\chi''(q = 0)$ is deduced from the spin contribution $^{89}K_{\text{spin}} = D\chi''(q = 0)$ to the $^{89}$Y NMR Knight shift, $^{89}K = ^{89}K_{\text{orb}} + ^{89}K_{\text{spin}}$ (2) as shown in Fig. 2(b), where the powder averaged orbital contribution is $^{89}K_{\text{orb}} = +150 \pm 5$ ppm [32] and $D (< 0)$ is the hyperfine coupling constant. Our $^{89}$Y data, taken in a magnetic field of 9 T, for Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_y$ are consistent with earlier results reported above $\sim 110$ K for Y$_{0.5}$Ca$_{0.5}$Ba$_2$Cu$_3$O$_y$ [27] also shown in Fig. 2(b). Our new measurement conducted down to $T_c = 75$ K in Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.9}$ shows a clear signature of saturation below 100 K, similar to overdoped YBa$_2$Cu$_3$O$_y$ without Ca substitution [33]. The saturation of $\chi''(q = 0)$ below 100 K is followed by a broad maximum at $T_{\text{max}} = 90 \pm 10$ K, which according to the 2D Heisenberg model [28], implies an effective energy scale $J(p) = T_{\text{max}}/93 = 97 \pm 11$ K. We also deduce $J(p)$ in underdoped Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.0}$ and Y$_{0.75}$Ca$_{0.25}$Ba$_2$Cu$_3$O$_{6.5}$ by matching $\chi''(q = 0)$ to the low temperature [$T \ll J(p)$] portion of the 2D Heisenberg model, as shown in Fig. 2(b). Our results of $J(p)$ (Fig. 3) are consistent with those reported in La$_{2-x}$Sr$_x$CuO$_4$ [12].

The $^{89}$Y NMR data also show evidence for the glassy slowing of disordered magnetism. Below the onset of glassy slowing at $T_{\text{wq}}$ ($\approx 200$ K), we find a change in curvature of $^{89}$Cu NQR and an increase in $^{89}K_{\text{spin}}$, as shown in Figs. 2(c) and 2(d), respectively [35]. The change in

FIG. 2. The same symbol assignment as Fig. 1 is used, and new symbols are shown. (a) $^{63}1/T_1T$ in Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ and La$_{2-x}$Sr$_x$CuO$_4$ as measured by the $^{89}$Y NMR Knight shift ($^{89}K$) taken above $T_{\text{wq}}$ [26] with respect to a YCl$_3$ reference. Data (×) from [27] are a series of $0.20 \times T_c$ samples with $T_c = 47.5, 65.8, 83.2, 86, 72.1, 60$, and $47.5$ K (in order of increasing $^{89}K_{\text{spin}}$). The arrow indicates net spin contribution $^{89}K_{\text{spin}}$. Solid lines are fits to the 2D Heisenberg model [28], and all other lines in the figure are guides for the eye. (c) $^{89}1/T_1T$ (with the same data plotted below 30 K in the inset) and (d) full width at half maximum $^{89}\Delta f$ of the $^{89}$Y NMR line shape.
curvature of $^{89}1/T_1 T$ is first followed by a minimum at $T_{89}^{\text{min}}$ [26], and then a maximum at $T_{89}^{\text{max}}$ where the glassy slowing has reached the NMR time scale. At a similar temperature $T_{\mu SR}$, $\mu$SR measurements observe local hyperfine fields [34] that are frozen on the $\mu$SR time scale. The enhanced values of $^{89}\Delta f$ at 1.7 K also indicate that the frozen hyperfine fields at the $^{89}$Y nuclear site have a substantial spatial distribution of $\sim 70$ Oe.

The sequence of anomalies starting at $T_{\text{wipeout}}$ followed by $T_{89}^{\text{min}}$, $T_{89}^{\text{max}}$, and $T_{\mu SR}$ (Fig. 3) are analogous to La$_{2-x}$Sr$_x$CuO$_4$ where the onset of glassy slowing down of the stripe phase at $T_{\text{wipeout}}$ [29–31] is followed by a minimum, then a maximum in $^{139}1/T_1 T$ [36] and $\mu$SR observation of frozen hyperfine fields [34]. These sets of results establish the following three points: First, the paramagnetic Cu spin fluctuations in underdoped CuO$_2$ planes exhibit nearly universal $p$ and $T$ dependences in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ and La$_{2-z}$Sr$_z$CuO$_4$ for equivalent $p = z/2 = x$, without a pseudogap signature. In the same temperature range, the $^{89}$Y NMR Knight shift decreases monotonically and is most likely due to the growth of short range spin order. Second, the gradual slowing of Cu spin fluctuations, as observed by the increase in $^{63}1/T_1 T$, is followed by glassy freezing of the Cu moments starting at $T_{\text{wipeout}} \sim 200$ K in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ while similar behavior is observed only below $\sim 100$ K in La$_{2-z}$Sr$_z$CuO$_4$. The factor of 2 higher temperature scale is consistent with the finding based on $\mu$SR that the spin freezing temperature $T_{\mu SR}$ in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ is also a factor $\sim 2$ higher than in La$_{2-z}$Sr$_z$CuO$_4$ [34]. Recalling that the Néel temperature of $T_N = 420$ K in undoped YBa$_2$Cu$_3$O$_{6.0}$ is higher than $T_N = 320$ K in La$_2$CuO$_4$ because of the bilayer coupling, the higher temperature scale of glassy spin freezing in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ may also be due to the stronger 3D coupling along the $c$ axis. However, we cannot rule out the possibility that Ca$^{+2}$ substitution causes stronger disorder in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ than Sr$^{+2}$ substitution in La$_{2-z}$Sr$_z$CuO$_4$, as suggested by the factor $\sim 2$ broader $^{63}$Cu NQR spectrum [20], which may enhance the tendency towards spin freezing. Third, the observed increase of $^{91}1/T_1 T$ implies that the Cu moments are not slowing down towards the commensurate antiferromagnetic spin structure with divergently large spin-spin correlation length. In this context, it is important to recall that the critical slowing down towards the Néel state does not cause a large enhancement of $^{91}1/T_1 T$ in undoped YBa$_2$Cu$_3$O$_{6.0}$ [37] since the hyperfine form factor $^{89}A(q)$ is zero for the commensurate wave vectors. The strong increase of $^{91}1/T_1 T$ shows that either the spin structure is incommensurate, as expected for the stripe phase, or that the spin-spin correlation length is limited to a relatively short length scale due to disorder caused by the holes, or possibly both. Since stripes are dynamic at NMR time scales even at $\sim 350$ mK as evidenced by motional narrowing effects [31], our NMR data cannot distinguish the spin configuration.

We have established that the slowing of the paramagnetic spin dynamics in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ is qualitatively similar to La$_{2-z}$Sr$_z$CuO$_4$. Most importantly, we do not observe the signature of a spin gap. Instead, we find signatures of glassy slowing of spin fluctuations similar to the case of La$_{2-z}$Sr$_z$CuO$_4$. We caution that the absence of a spin-gap signature in the form of a decrease in $^{63}1/T_1 T$ does not necessarily prove that there is no global suppression of lower energy parts of the spin fluctuations. $^{63}1/T_1 T$ may grow monotonically with decreasing temperature as long as very low frequency ($\sim \omega_n$) components of the spin fluctuations grow, even if the global spin fluctuation spectrum is gapped below a certain temperature $T^*$. On the other hand, our result of $T_{\text{wipeout}}$ sets an upper bound on $T^*$ in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ because if $T^*$ is significantly larger than $T_{\text{wipeout}}$, we should observe the decrease of $^{63}1/T_1 T$ prior to the influence of glassy slowing of the spin dynamics which become visible below $T_{\text{wipeout}}$. Our conclusion that the magnitude of $T^*$ is at most comparable to $T_{\text{wipeout}}$ in Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ is at odds with popularly held speculations, often based on theoretical expectations or more indirect experimental information such as the Hall effect, resistivity, and $\chi^e(q = 0)$, that $T^*$ blows up towards $J(p = 0) \sim 1500$ K.

A potential common cause of the absence of the spin-gap signature in underdoped Y$_{1-z}$Ca$_z$Ba$_2$Cu$_3$O$_{6.0}$ and...
La$_{2-x}$Sr$_x$CuO$_4$ is the random charge potential and/or disorder induced by substitution of Ca$^{+2}$ or Sr$^{+2}$ ions into Y$^{+3}$ or La$^{+3}$ sites, respectively. It is worth recalling that the absence of a spin-gap signature in La$_{2-x}$Sr$_x$CuO$_4$ has often been attributed to dirt effects caused by Sr$^{+2}$. However, our results in Fig. 1(a) also indicate that disorder alone does not entirely suppress the spin gap. Because of the solubility limit of Ca$^{+2}$ into Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{6.0}$ with a maximum $T_c = 30$ K [22], we doped more holes into Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.0}$ by adding oxygen into the chain layers for the same sample to obtain Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.50}$ with $T_c = 59$ K. We found that $^{61}/T>T$ in Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.50}$ decreases below $T^* \sim 130$ K, similar to the spin-gap signature in YBa$_2$Cu$_3$O$_{6.50}$ [3,21]. The data therefore suggest that the spin gap does develop when more holes are added into the CuO$_2$ plane in Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.50}$, even if the disorder effects caused by Ca doping tend to suppress the spin-gap signature.

For a more systematic study of the effects of Ca substitution alone, we compare $^{61}/T>T$ for $z = 0, 0.08,$ and 0.22, with fixed $y = 6.50-6.55$ [Fig. 1(b)]. $^{61}/T>T$ is systematically enhanced with increasing $z$, especially at lower temperatures. Our data suggest that Ca$^{+2}$ doping not only introduces holes but also tends to fill in the low frequency part of spin fluctuations spectrum, without affecting the magnitude of $T^*$ significantly. The Ca$^{+2}$ substitution effects for $y = 6.5$ are in remarkable contrast with the lack of change in $^{61}/T>T$ observed for $y = 6.9$, as presented in Fig. 1(a) [38]. It is interesting to note the qualitative similarity with the Zn substitution effects in YBa$_2$Cu$_3$O$_y$ [39]. $^{87}$Y NMR data show that Zn substitution [39] causes $^{87}$Y line splitting in $T_c \sim 60$ K phase but causes only $^{87}$Y NMR line broadening in the $T_c \sim 90$ K phase. These results suggest that both random spinless impurities in the CuO$_2$ plane (Zn$^{+2}$) and random Coulomb potentials outside the CuO$_2$ plane (Ca$^{+2}$) are more effectively shielded by a larger number of holes in the overdoped region. We mention that a more detailed analysis of the $^{63}$Cu(2) spin-lattice recovery, similar to that used for Zn-doped YBa$_2$Cu$_3$O$_y$ [40], is unfortunately not possible in Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ due to the small overlap (~1%) of the Cu(1) signal with very long $^{63}T_1$ [20].

To conclude, using both $^{63}$Cu NQR and $^{87}$Y NMR we demonstrate the remarkable similarity in the paramagnetic spin dynamics between Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{6.0}$ and La$_{2-x}$Sr$_x$CuO$_4$ for an equivalent nominal hole concentration. We do not observe any signatures of a spin gap for $p = z/2 = x \leq 0.11$. Upon further hole doping by oxygen loading with fixed $z$, we demonstrate that a spin gap does develop. Combining all our data, we deduce a phase diagram which crosses the superconductor-insulator boundary and includes the spin-gap temperature $T^*$, the effective energy scale $J(p)$ $(\gg T^*)$, and the glassy freezing of the spin dynamics. Our systematic study of Ca substitution effects also suggests that charge disorder caused by Ca$^{+2}$ ions tends to suppress the spin-gap signature while keeping $T^*$ ($<T_{wipeout}$) roughly constant.

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[26] $T_{min}^{87}$ also signals the temperature below which $^{89}/T>T \sim \frac{K_{spin} (\sim \frac{\Delta f}}{32}$ no longer holds.
[35] Independent $^{87}$Y NMR data in Y$_{0.85}$Ca$_{0.15}$Ba$_2$Cu$_3$O$_{6.1}$ by A. Campana et al., Int. J. Mod. Phys. B 14, 2797 (2000) are consistent with our data.
[38] Cu data for Y$_{0.78}$Ca$_{0.22}$Ba$_2$Cu$_3$O$_{6.9}$ are consistent with G.V.M. Williams et al., Phys. Rev. B 63, 104514 (2001).