Charge Segregation, Cluster Spin-Glass and Superconductivity in La$_{1.94}$Sr$_{0.06}$CuO$_4$

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A $^{63}$Cu and $^{139}$La NMR/NQR study of superconducting ($T_c=7$ K) La$_{1.94}$Sr$_{0.06}$CuO$_4$ single crystal is reported. Coexistence of spin-glass and superconducting phases is found below $\sim5$ K from $^{139}$La NMR relaxation. $^{63}$Cu and $^{139}$La NMR spectra show that, upon cooling, CuO$_2$ planes progressively separate into two magnetic phases, one of them having enhanced antiferromagnetic correlations. These results establish the AF-cluster nature of the spin-glass. We discuss how this phase can be related to the microsegregation of mobile holes and to the possible pinning of charge-stripes.

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Although La$_{2-x}$Sr$_x$CuO$_4$ is one of the most studied and structurally simplest high-$T_c$ superconductor, the complexity of its phase diagram keeps increasing every year. A striking feature is that, while Néel antiferromagnetic (AF) order is fully destroyed by $x=2\%$ of doped holes, samples with much higher doping still show clear tendencies towards spin ordering: - At intermediate concentrations between Néel and superconducting phases ($0.02\leq x\leq0.05$), a spin-glass phase is found [4, 7]. There are indications, but no direct evidence, that this phase is formed by frozen AF clusters, which could originate from the spatial segregation of doped holes in CuO$_2$ planes: a “cluster-spin-glass” [7–9, 18]. Strikingly, this spin-glass phase is found to coexist with superconductivity [10] (see also [11, 12]). - Commensurability effects around $x=0.125$ (=1/8) and/or subtle structural modifications help restoring long-range AF order. This is also understood as a consequence of segregation of doped-holes, but here charges are observed to order into 1D domain walls, or “stripes” [13]. Again magnetic order is claimed to coexist with bulk superconductivity [4, 7].

Clearly, the context of static magnetism and charge segregation in which superconductivity takes place is the central question in this region of the phase diagram [7, 11, 13]. So, a lot should be learnt from the microscopic nature of the cluster spin-glass phase, which has not been clarified yet, and from the passage from spin-glass to superconducting behaviour.

Here, we address this problem through a comprehensive nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) investigation of La$_{1.94}$Sr$_{0.06}$CuO$_4$, a compound at the verge of the (underdoped) superconducting phase ($T_c=7$ K). In addition to the confirmation of coexisting spin-glass and superconducting phases, the AF-cluster nature of the spin-glass is microscopically demonstrated from $^{63}$Cu and $^{139}$La NMR spectra. We discuss how the observed microscopic phase separation can be related to the microsegregation of mobile holes in CuO$_2$ planes, and suggest that the cluster spin-glass is the magnetic counterpart of a pinned, disordered, stripe phase: a “stripe-glass” [8].

The sample is a single crystal (~200 mg), grown from solution as described in Ref. [19]. Magnetization measurements have shown a superconducting transition with an onset at $T_c=7$ K.

We first discuss the NQR measurements. The $^{63}$Cu nuclear spin-lattice relaxation rate $1/T_1$ was measured at the center of the NQR line shown in Fig. 1(a). The recovery of the magnetization after a sequence of saturating pulses, was a single exponential at all temperatures. The results are shown in Fig. 1(b) [21]. It is remarkable that for the same hole concentration and a similar $T_c$, we obtain identical Cu NQR spectra (central frequency, width, and high frequency tail from the anomalous ”B” line -sites with a localized doped-hole [20, 25]) and the same $^{63}T_1$ values as Fujiyama et al. [20]. All these quantities are strongly doping-dependent. This is a very good indication of the precision and the homogeneity of the Sr concentration in our sample $x=0.06\pm0.005$. Below 250 K, $1/T_1$ flattens and it decreases below $\sim150$ K. This regime could not, however, be explored since the Cu nuclear spin-spin relaxation time ($T_2$) shortens drastically upon cooling, making the NMR signal too small for reliable measurements, especially below $\sim50$ K.

A useful substitute of $^{63}$Cu measurements is the NQR/NMR of $^{139}$La. Although La lies outside CuO$_2$ planes, it is coupled to Cu$^{2+}$ spins through a hyperfine interaction, whose magnitude is small compared to that on $^{63}$Cu, leading to a long value of $^{139}T_2$. A typical $^{139}$La NQR line (3ωQ transition) is shown in Fig. 1(c). The asymmetry is perfectly accounted for by a two-gaussian fit, which is very similar to that found in stripe-ordered La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ [22]. The existence of two electric field gradient contributions is related to static charge inhomogeneities, either directly and/or indirectly...
through different tilt configurations of CuO$_6$ octahedra.

![Diagram showing Cu NQR and La NQR spectra](image)

**FIG. 1.** (a) $^{63,65}$Cu NQR spectrum. (b) NQR $^{63}$Cu $1/T_1$; this study (squares) and from ref. [20] (stars). (c) $^{139}$La NQR spectrum, decomposed into the sum of two gaussians. (d) NQR $^{139}$La $1/T_1$; showing the spin-freezing transition.

By comparing the recovery law of the $^{139}$La magnetization after saturation of the $2\tau_Q$ transition that measured on the $3\tau_Q$ transition, it was found that the spin-lattice relaxation is due to both magnetic and electric field gradient fluctuations around 100 K. However, below 75 K $1/T_1$ increases progressively upon cooling and becomes entirely of magnetic origin. As seen in Fig. 1(d), $1/T_1$ increases by almost three orders of magnitude with a peak at $T_\phi \approx 5$ K. This behaviour is typical of a slowing down of spin-fluctuations, $1/T_1$ reaching a maximum when the frequency of these fluctuations is equal to the nuclear resonance frequency, here $\nu_Q \approx 18$ MHz (or equivalently a correlation time $\tau \approx 10^{-8}$s). Thus, a spin-freezing occurs in the superconducting state of La$_{1.94}$Sr$_{0.06}$CuO$_4$. This adds a new item to the list of unconventional properties of the cuprates, which have to be addressed by any theory. The scale, microscopic or mesoscopic, on which both types of order coexist is a crucial question which cannot be addressed here. But we stress again that our results are representative of an homogeneous x=0.06 Sr concentration. This is also confirmed by the value $T_\phi \approx 5$ K, which is in quantitative agreement with the carefully established NQR [3] and $\mu$SR phase diagrams [10] of La$_{2-x}$Sr$_x$CuO$_4$ (the characteristic times of NQR and $\mu$SR are similar). The freezing process is characterized by a high level of inhomogeneity, since a very wide distribution of $T_1$ values develops below 50 K, as inferred from the stretched exponential time decay of the nuclear magnetization [23]. As already noticed in Refs. [19], the slowing down starts around 70 K, in the temperature range where the in-plane resistivity $\rho_{ab}$ has a minimum. Thus, charge localization seems to be a precursor effect of Cu$^{2+}$ spin freezing.

It is also important to probe the local static magnetization in CuO$_2$ planes. This can be characterized through the shift $K_{cc}$ (for $H_0||c$) of the $^{63}$Cu NMR line which is the sum of a $T$-independent orbital term $K_{orb} \approx 1.2\%$ plus a contribution from the spin susceptibility:

$$63K_{cc}^{\text{spin}} = \frac{(A_{cc} + 4B) <S_z>} {g_{cc} \mu_B H_0}$$(1)

$A_{cc}$ is the hyperfine coupling with on-site electrons, $B$ the transferred hyperfine coupling with electrons on the first Cu neighbour, $g$ the Landé factor, and $<S_z>$ the on-site Cu moment, here assumed to be spatially homogeneous on the scale of the Cu-Cu distance. Since $A_{cc} + 4B \approx 0$ in La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{6+x}$, one usually has negligible magnetic shift $63K_{cc}^{\text{spin}} \approx 0$.

The inset to Fig. 2 shows the $^{63}$Cu NMR central line at room temperature. There are clearly two contributions: a relatively sharp line with the usual shift $K_{cc} \approx 1.2\%$, and a slightly shifted, much broader, background. The perfect overlap of the NMR intensity vs. shift plots at 17 and 24 Tesla asserts that the broadening is purely magnetic, i.e. it is a distribution of shifts $K_{cc}$. This distribution is considerable ($\pm 2-3\%$), exceeding by far anything ever seen in the cuprates. Also striking is the $T$-dependence of the spectrum (Fig. 2). The NMR signal clearly diminishes upon cooling. The effect is more dramatic for the main peak, which disappears between 100 and 50 K. At 50 K, the spectrum is only composed of a background, at least two times wider than at 300 K. The shortening of $T_2$ (by a factor of two from 300 K to 100 K) accounts for a small fraction of the intensity loss. Some signal is redistributed from the main peak to the background signal, but part of it is actually not observed, due to the huge spread of resonance frequencies.

It is evident from Eqn. 1 that $K_{cc} \neq 0$ values are possible only if $<S_z>$ is strongly spatially modulated on scale of one lattice spacing, so that the shift for a Cu site at position $(x, y)$ cannot be written as in Eqn. 1 but contains the sum of terms: $A_{cc}<S_z(x, y)> + B |<S_z(x, y) \pm <S_z(x, y)||$. In fact, large values of $K_{cc}$ such as found here imply that the local magnetization is staggered: the cancellation of the $A_{cc}<0$ and $B>0$ terms in Eqn. 1 is removed by the sign alternation of $<S_z>$ from one site to its nearest Cu neighbours, thus allowing $|K_{cc}|>0$ locally.

The presence of substantial staggered magnetization is striking. One way to generate such enhanced AF correlations could be that some localized doped-holes act as static defects in the magnetic lattice, somehow similar to the substitution of Zn for Cu [24]. However, only one broadened peak is detected in Cu NMR studies of Zn-doped YBCO, while there are here two well-defined magnetic phases (see also $^{139}$La results below): Furthermore, there is some staggered magnetization already at 290 K, where $\rho_{ab}$ is metallic-like, and the $^{63}$Cu NQR B site, which is known to be related to localized holes [25].
is extremely small here. So, an impurity-like effect from localized holes does not explain the data.

FIG. 2. Main panel: Field swept $^{63}$Cu NMR spectra as a function of $T$ ($H || c$), recorded in the very same experimental conditions. The relative intensities can thus be compared, after correction by a $1/T$ factor due to the Curie behaviour of the nuclear magnetization (thermal variations of the characteristics of the NMR circuit are much smaller than the effects found here). Inset: The two contributions of the room temperature $^{63}$Cu spectrum at 17 and 24 Tesla.

To our knowledge, the only other situation which could generate an inhomogeneous staggered magnetization is the presence of magnetic clusters, such as would be generated by finite size hole-free regions. The corollary of this is the presence of surrounding hole-rich regions. Their exact topology cannot be inferred here, so we will call them "domain-walls". In such a scenario, the main peak, which disappears at low $T$, corresponds to hole-rich regions, i.e. where domain-walls are still mobile. In fact, the wall-motion averages out $<S_z>$ (spin-flips), yielding a narrow central peak. This also reduces the magnetic coupling between hole-poor domains. The spatially inhomogeneous profile of $<S_z>$ within each domain and the distribution of cluster sizes yield the broad background. Full localization of domain-walls is likely to restore inter-cluster magnetic coupling, thus enabling spin-freezing. Of course, there must be significant disorder in the domain-wall topology, in order to prevent long range AF ordering. The disappearance of the main Cu peak is compatible with the localization of walls, which reduces the effective width of hole-rich regions. Accordingly, this peak disappears in the temperature region where $\rho_{ab}$ becomes insulating-like. The concomitant growth of $<S_z>$ explains the broadening of the background signal.

$^{139}$La NMR spectra offer a second possibility to probe the phase separation in CuO$_2$ planes. A shown in Fig. 3, a second peak emerges upon cooling on the low frequency side of the spectrum. Qualitatively, we can ascribe the new peak to the $^{139}$La nuclei within AF clusters, as a confirmation of the $^{63}$Cu NMR spectra. Similar experiments at 4.7 Tesla show a single peak (not shown), with a $T$-dependent asymmetry which is well-fitted by the sum of two gaussians, whose separation is half of that at 9.4 T. This again proves that the peaks are related to two different magnetic environments. Additional magnetic broadening at low-$T$ makes the two $^{139}$La peaks unresolved, and not surprisingly, the broadening becomes noticable below $\sim 70$ K, where the spin fluctuations start to slow down. Again, we stress that macroscopic doping inhomogeneities in the sample would not produce such a $T$-dependence of the relative intensities of the two NMR contributions. The observed phase separation clearly develops on decreasing temperature.

FIG. 3. $^{139}$La NMR spectra obtained by Fourier transforms of the spin-echo ($H_0=9.4$ T, $||c$).

Furthermore, similar $^{139}$La NMR results have been recently obtained in La$_{1.9}$Sr$_{0.1}$CuO$_4$ [26] and in La$_2$CuO$_{4+\delta}$ at a concentration where long range spin and charge ordering are absent [27]. This shows that the results are not unique to our Sr concentration. Rather, phase separation appears to be a general tendency in these materials. In fact, most striking is probably the similarity between our $^{139}$La NMR spectra and those reported in stripe-ordered nickelates [25], although details differ due to the difference of hyperfine interactions, doping levels and stripe configurations between cuprates and nickelates.

A quantitative analysis, like the comparison between $^{63}$Cu and $^{139}$La spectra, is however difficult since a number of Cu nuclei are not observed and hyperfine interactions are not well known for $^{139}$La in the paramagnetic phase. Furthermore, the relation of the $^{139}$La peak intensity ratio to the relative size of the two phases is expected to be much more complex than the value $\sim 1/16$ determined by the hole concentration. Many microscopic details like the profile of the spin modulation and the organization (topology, filling) of the hole-rich region are involved. Even in the case of La$_{5/3}$Sr$_{1/3}$NiO$_4$, with established stripe order, the two-peak intensity ratio is not well-understood [28].
63Cu and 139La NMR spectra reveal that magnetic phase separation develops below room temperature. The data are best explained in terms of hole-poor regions (AF clusters are evidenced through an anomalous NMR line) and hole-rich regions (contributing a more usual line). In the regime were doped-holes are localized ("charge glass"), the dynamics of staggered moments, probed by NMR relaxation, slows down. Below 5 K, in the superconducting state, AF clusters are frozen, a phase called "cluster spin-glass". Although no direct evidence for stripe-like objects is claimed here, the evidence for their existence at somewhat higher doping ($x\approx 0.12$) does suggest that hole-rich regions are related to charge-stripe objects that are progressively pinned by random (Sr) disorder as $T$ decreases. The charge-freezed state would then correspond to a static disordered stripe phase: a "stripe-glass".

![Diagram of phase transitions](image)

FIG. 4. Experimental summary (crosses are data from Ref. [20]) and tentative phase diagram of La$_{1.94}$Sr$_{0.06}$CuO$_4$.

The above conclusions are further supported by: 1) the already mentioned similarities with NMR data in stripe-ordered materials, 2) the fact that even materials with well-established stripe order tend to have a glassy behaviour [30], 3) the presence of incommensurate elastic peaks in neutron scattering for $x=0.06$ [31], 4) the two-component ARPES spectra in the spin-glass region [22]. This, to our knowledge first, observation of two-phases NMR spectra in superconducting LSCO opens new perspectives: Given the similarities between LSCO and YBCO [10], an NMR re-investigation of their under-doped regime is clearly called for.

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