Charge Segregation, Cluster Spin Glass, and Superconductivity in $La_{1.94}Sr_{0.06}CuO_4$

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(Received 10 February 1999)

A ^{63}Cu and ^{139}La NMR/NQR study of superconducting ($T_c = 8$ K) $La_{1.94}Sr_{0.06}CuO_4$ single crystal is reported. Coexistence of spin-glass and superconducting phases is found below ~5 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 antiferromagnetic-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.

PACS numbers: 74.25.Ha, 76.60.–k, 74.72.Dn

Although $La_{2-x}Sr_xCuO_4$ (LSCO) 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 ($0.02 \leq x \leq 0.05$), a spin-glass phase is found [1–3]. 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" [4–10]. Strikingly, this spin-glass phase is found to coexist with superconductivity [10] (see also [11,12]).

Commensurability effects at about $x = 0.125$ ($= 1/8$) and/or subtle structural modifications help restore 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 [14–17].

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 [7–9,18]. So, a lot should be learned 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 behavior.

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 on the verge of the (underdoped) superconducting phase ($T_c = 8$ 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 a solution as described in Ref. [19]. Magnetization measurements have shown a superconducting transition with an onset at $T_c = 8$ K.

We first discuss the NQR measurements. The ^{63}Cu nuclear spin-lattice relaxation rate $1/^{63}T_1$ 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) [20]. It is remarkable that,

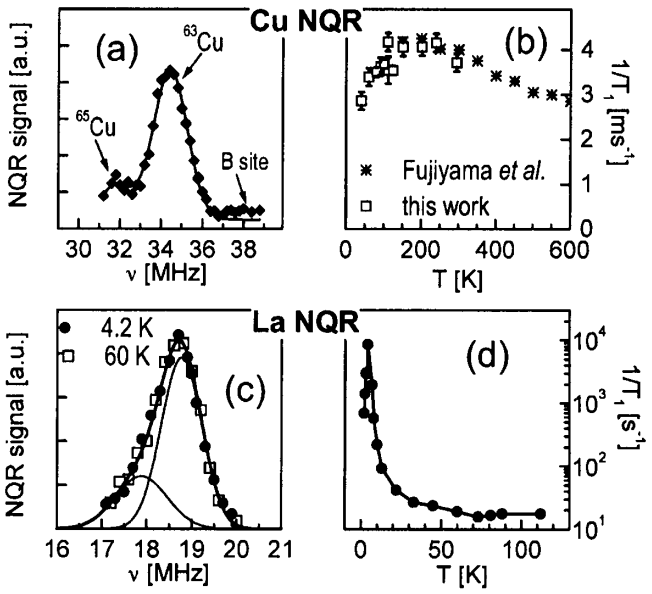

FIG. 1. (a) ^{63,65}Cu NQR spectrum. (b) NQR ^{63}Cu $1/T_1$; this study (squares) and from Ref. [21] (stars). (c) ^{139}La NQR spectrum, decomposed into the sum of two gaussians. (d) NQR ^{139}La $1/T_1$ showing the spin-freezing transition.

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for the same hole concentration and a similar T_c, we obtain identical Cu NQR spectra (central frequency, width, and small high frequency tail from the anomalous "*B*" line sites with a localized doped hole [21,22]) and the same $^{63}T_1$ values as Fujiyama *et al.* [21]. All of 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 $x = 0.06 \pm 0.005$. Below 250 K, $1/^{63}T_1$ flattens, and it decreases below $\sim$150 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 $\sim$50 K.

A useful substitute for ^{63}Cu measurements is the NQR and NMR of ^{139}La. Although La lies outside the 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 ($3\nu_Q$ 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 $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ [23]. 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.

By comparing the recovery law of the ^{139}La magnetization after saturation of the $2\nu_Q$ transition with that measured on the $3\nu_Q$ transition, it was found that the spin-lattice relaxation is due to both magnetic *and* electric field gradient fluctuations at about 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 3 orders of magnitude with a peak at $T_g \simeq 5$ K. This behavior 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 $\nu_Q \simeq 18$ MHz (or equivalently a correlation time $\tau \sim 10^{-8}$ s). Thus, a spin freezing occurs *in the superconducting state* of $La_{1.94}Sr_{0.06}CuO_4$.

Of course it is crucial for theories to know the scale, microscopic or mesoscopic, on which both types of order coexist, but this question cannot be addressed from our measurements. What is important to stress is that this result is representative of a homogeneous $x = 0.06$ Sr concentration: the value $T_g \simeq 5$ K is in quantitative agreement with the carefully established NQR [6] and μSR phase diagrams [10] of $La_{2-x}Sr_xCuO_4$ (the characteristic times of NQR and μSR are similar). Also in agreement with Refs. [6,10] is the high level of inhomogeneity characterizing the freezing process (a wide distribution of T_1 values develops below 50 K [24]).

Another important feature, already noticed in Refs. [1,4], is that the slowing down starts at about 70 K, in the temperature range where the in-plane resistivity ρ_{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 $H_0 \parallel c$) of the ^{63}Cu NMR line which is the sum of a *T-independent* orbital term $K^{\rm orb} \simeq 1.2\%$ plus a contribution from the spin susceptibility:

$$^{63}K_{cc}^{\rm spin} = \frac{(A_{cc} + 4B)}{g_{cc}\mu_B}\frac{\langle S_z\rangle}{H_0}. \quad (1)$$

A_{cc} is the hyperfine coupling with on-site electrons, B is the transferred hyperfine coupling with electrons on the first Cu neighbor, g is the Landé factor, and $\langle S_z\rangle$ is the on-site Cu moment, here assumed to be spatially homogeneous on the scale of the Cu-Cu distance. Since $A_{cc} + 4B \simeq 0$ in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6-x}$, one usually has negligible magnetic shift $^{63}K_{cc}^{\rm spin} \simeq 0$.

The inset of 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 $^{63}K_{cc} \sim 1.2\%$, 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 $^{63}K_{cc}^{\rm spin}$. 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 2 times wider than at 300 K. The shortening of T_2 (by a factor of 2 from 300 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.

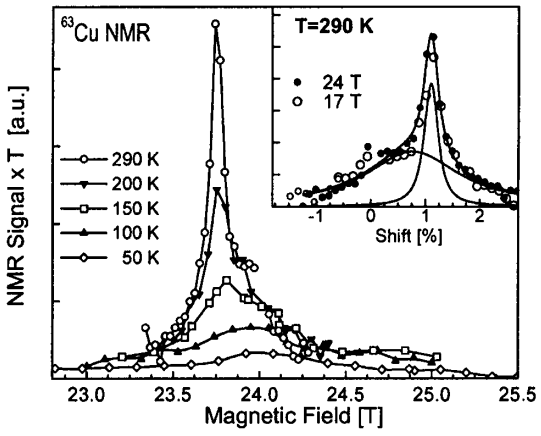

FIG. 2. Main panel: field swept ^{63}Cu NMR spectra as a function of T ($H \parallel c$), recorded in the very same experimental conditions. The relative intensities can thus be compared, after correction by a $1/T$ factor due to the Curie behavior of the nuclear magnetization (thermal variations of 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 T.

It is evident from Eq. (1) that $^{63}K_{cc}^{\rm spin} \neq 0$ values are possible *only* if $\langle S_z \rangle$ is strongly spatially modulated on a scale of *one* lattice spacing, so that the shift for a Cu site at position (x, y) cannot be written as in Eq. (1), but contains the sum of terms: $A_{cc}\langle S_z(x, y)\rangle + B[\langle S_z(x \pm 1, y)\rangle + \langle S_z(x, y \pm 1)\rangle]$. In fact, large values of $^{63}K_{cc}^{\rm spin}$ such as found here imply that the local magnetization is *staggered*: the cancellation of the $A_{cc} < 0$ and $B > 0$ terms in Eq. (1) is removed by the sign alternation of $\langle S_z \rangle$ from one site to its nearest Cu neighbors, thus allowing $|^{63}K_{cc}^{\rm spin}| \gg 0$ 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 [25]. However, only one broadened peak is detected in Cu NMR studies of Zn-doped $YBa_2Cu_3O_{7-\delta}$ (YBCO), while there are here two well-defined magnetic phases (see also ^{139}La results below). Furthermore, there is already some staggered magnetization at 290 K, where ρ_{ab} is metalliclike, and the ^{63}Cu NQR *B* site, which is known to be related to localized holes [22], is extremely small here. So, an impuritylike effect from localized holes does not explain the data.

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 the 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 $\langle S_z \rangle$ (spin flips), yielding a narrow central peak. This also reduces the magnetic coupling between hole-poor domains. The spatially inhomogeneous profile of $\langle S_z \rangle$ within each domain and the distribution of cluster sizes yield the broad background. Full localization of domain walls is likely to restore intercluster 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 ρ_{ab} becomes insulatinglike. The concomitant growth of $\langle S_z \rangle$ explains the broadening of the background signal.

The ^{139}La NMR spectra offer a second possibility to probe the phase separation in CuO_2 planes. As 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 T show a single peak (not shown), with a T-dependent asymetry 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 surprinsingly, 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.

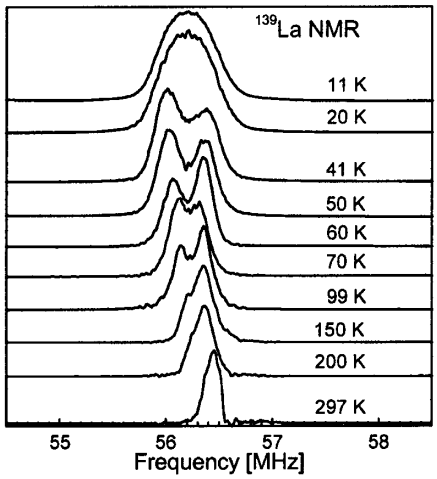

FIG. 3. ^{139}La NMR spectra obtained by Fourier transforms of the spin echo ($H_0 = 9.4$ T, $\|c$).

Furthermore, similar ^{139}La NMR results have been recently obtained in $La_2CuO_{4+\delta}$ at a concentration where long range spin and charge ordering are absent [26]. This shows that the results are not unique to our sample. 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 [27], although details differ due to the difference of hyperfine interactions, doping levels and stripe configurations between cuprates and nickelates.

A quantitative analysis, such as 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, such as 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 [27].

Figure 4 summarizes our findings in $La_{1.94}Sr_{0.06}CuO_4$: ^{63}Cu and ^{139}La NMR spectra reveal that magnetic phase

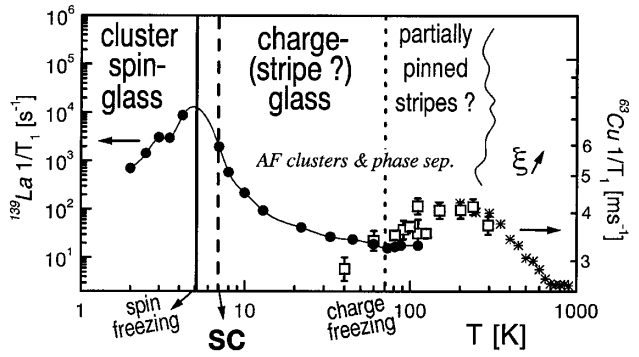

FIG. 4. Experimental summary (stars are data from Ref. [21]) and tentative phase diagram of $La_{1.94}Sr_{0.06}CuO_4$.

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 where 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 stripelike objects is claimed here, the evidence for their existence at somewhat higher doping ($x \simeq 0.12$ [13,14]) does suggest that hole-rich regions are related to charge stripes that are progressively pinned by random (Sr) disorder as T decreases. The charge-freeze state would then correspond to a static disordered stripe phase: a stripe glass [8,28].

The above conclusions are further supported by the following: (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 behavior [29], (3) the presence of incommensurate elastic peaks in neutron scattering for $x = 0.06$ [30], (4) the two-component angle-resolved photoemission spectroscopy (ARPES) spectra in the spin-glass region [31]. This, to our knowledge, first observation of two-phase NMR spectra in superconducting LSCO opens new perspectives: Given the similarities between LSCO and YBCO [10], a NMR reinvestigation of their underdoped regime is clearly called for.

Useful exchanges with H. B. Brom, V. J. Emery, R. J. Gooding, P. C. Hammel, A. Rigamonti, and B. J. Suh are acknowledged. We thank S. Aldrovandi, Z. H. Jang, E. Lee, L. Linati, and F. Tedoldi for help, as well as J. E. Ostenson and D. K. Finnemore for magnetization measurements. The work in Pavia was supported by the INFM-PRA SPIS funding. Ames Laboratory is operated for the U.S Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. The work at Ames Laboratory was supported by the director for Energy Research, Office of Basic Energy Sciences.

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