Glassiness induced by charge stripe order in 1/8-doped lanthanum cuprates

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Randomness is an important characteristic of a spin-glass. An example are magnetic ions diluted in a metallic host such as Mn in Cu, the spins of which are randomly oriented below a characteristic temperature. While a spin-glass behavior is mostly caused by time-independent quenched disorder, it is believed that it could also be driven by competing interactions. Here we demonstrate, by means of 139La nuclear magnetic resonance (NMR) measurements on La2−xSrxCuO4 (LSCO:x, 0.07 ≤ x ≤ 0.15) and 1/8-doped La2−x−yMxSrxCuO4 (M=Nd,Eu) near a hole concentration of x = 1/8, hereafter called 1/8 anomaly. While static charge stripe order has not been observed in superconducting (SC) La2−xSrxCuO4, a strong tendency near x = 1/8 has been implicated.25,26 Recently, the almost static static nature of charge order was proven by soft x-ray diffraction measurements,25 which detected static charge order at Tsurf = 55 K pinned by small perturbations near the surface of LSCO:0.12 single crystal, but not in the bulk of the sample. Such a charge ordering tendency and its interplay with superconductivity seems to cause a variety of unusual features, such as an inhomogeneous SC state10,11 and significant effects of magnetic field on static antiferromagnetic (AFM) correlations coexisting with superconductivity.12–18

Along with these observations, a glassy behavior is a common feature observed in lightly-doped cuprates,19–24 often dubbed ‘cluster spin-glass’ (CSG).25,26 The CSG state is generally viewed to be caused by randomly localized doped holes, and potentially is related to unidirectional electronic domains or a ‘nematic’ phase.27,28 The glassy behavior, however, peculiarly strengthens near 1/8-doping,29–31 which is hard to understand in terms of quenched disorder since for hole concentration per copper higher than ∼ 0.1 the charge carriers are strongly delocalized.29 In this case, the entity driving the glassiness near x = 1/8 could be competing charge dynamics on different length scales as predicted by theory,24,35 rather than localized holes as in the lightly doped regime. Up to date, such an interaction-driven glassiness has not been confirmed experimentally, although there have been some implications in this direction.29,31,32,36,37

In the following, we demonstrate that the glassy spin freezing in 1/8-doped lanthanum cuprates is triggered by charge ordering, being a clear-cut experimental observation of self-generated glassiness in cuprates. This finding allows us to indirectly identify the onset of static charge ordering at ∼ 70 K in the bulk of LSCO:1/8. Moreover, we address the central issue of whether and/or how spin and charge stripes are connected and compete with superconductivity.

The La2−xSrxCuO4 and La2−yBa2+ySrxCuO4 were grown with the traveling solvent floating zone method, as described in Refs. 38 and 39, respectively. 139La NMR measurements were performed on La2−xSrxCuO4 single crystals with x = 0.07, 0.1, 0.125, and 0.15, and La2−yBa2+ySrxCuO4 single crystal with x = 0.125, in an external field H that ranges from 6 to 16 T, applied along the crystallographic c axis. 139La (I = 7/2) spin-lattice relaxation rates T−1 were measured at the central transition (+1/2 ↔ −1/2) by monitoring the recovery of magnetization after saturation with a single π/2 pulse. Then the relaxation data were fitted to the following formula:

\[
1 - \frac{M(t)}{M(\infty)} = a \left( \frac{1}{84} e^{-(t/T_1)\beta} + \frac{3}{44} e^{-(6t/T_1)\beta} + \frac{75}{364} e^{-(15t/T_1)\beta} + \frac{1225}{1716} e^{-(28t/T_1)\beta} \right),
\]

(1)

where M the nuclear magnetization and a a fitting parameter that is ideally one. \(\beta\) is the stretching exponent, which is less than unity when \(T_1^{-1}\) becomes spatially distributed due to glassy spin freezing. In Fig. 1(d), the typical recovery of M versus t and its fit to Eq. (1) are presented for three chosen temperatures measured at 10.7 T for LSCO:1/8.

Figure 1 (a) shows in situ ac susceptibility measured in the NMR tank circuit in zero external field for three compositions of La2−xSrxCuO4. Here we identify \(T_1\) from the onset of the drop (vertical dotted lines), and the-
FIG. 1: (a) In situ ac susceptibility versus $T$ at three dopings measured in the NMR circuit in zero field. The SC transition is notably broader at $x = 1/8$, implying the intrinsic inhomogeneity in this specific hole concentration. (b) $^{139}$La $T_1^{-1}$ versus $T$ as a function of $x$ measured at 10.7 T. The strong enhancement of $T_1^{-1}$ at $x = 0.07$ is drastically suppressed with increasing $x$, yielding to the $T$-linear metallic behavior of $T_1^{-1}$ (denoted by dashed curve) at nearly optimal $x = 0.15$. In stark contrast, doping $x = 1/8$ causes unusual spin freezing, which is emphasized on a linear scale in the inset. The red arrow is the static charge ordering temperature $T_{CO}$ detected on the surface of LSCO:0.12. (c) Stretching exponent $\beta$ versus $T$ in LSCO:1/8. There is also a sharp anomaly at $\sim 20$ K. (d) Recovery of the normalized nuclear magnetization $M$ as a function of time $t$ on a semi-log plot at three chosen temperatures. The time axis has the same color code as the data. Solid curves are the fits to the data using Eq. (1), yielding $T_1$ and $\beta$. To compare the effect of non-unity $\beta$ on the recovery of $M$, the maximum of the time axis range for each temperature was set to $10T_1$.

Sultant values are found to be in agreement with SQUID measurements. The SC transitions of the crystals are generally quite sharp, supporting the high quality. Nevertheless, we find that the transition for $x = 1/8$ is significantly broader than for the two neighboring dopings $x = 0.1$ and 0.15. Similar additional broadening of the SC transition near 1/8-doping was previously observed, but its origin has rarely been discussed. A priori, the pronounced broadening in LSCO:1/8 may be related to the suppression of $T_c$ due to stripe order. Taking into account the strong tendency toward charge order, the peculiar SC broadening in LSCO:1/8 can be understood in terms of the local pinning by the lattice of otherwise slowly fluctuating charge order, thereby causing inhomogeneously distributed $T_c$. Indeed, this pinning effect by the lattice accounts for the large reduction of $T_c$ observed in nearly 1/8-doped but disordered LSCO.v12-v41

Figure 1 (b) shows the temperature and doping dependence of $^{139}$La $T_1^{-1}$ measured at 10.7 T on a semi-log scale. At doping $x = 0.07$, $T_1^{-1}$ is enhanced at low $T$ by more than two decades, representing the rapid slowing down of spin fluctuations due to glassy spin order. As $x$ is increased, this strong $T_1^{-1}$ enhancement is greatly suppressed by more than an order of magnitude at $x = 0.1$ and disappears completely at nearly optimal doping $x = 0.15$, demonstrating that the glassy spin order in lightly doped LSCO is a remnant of the Mott antiferromagnetic state of the parent $\text{La}_2\text{CuO}_4$.

Remarkably, 1/8-doping induces a peculiar peak of $T_1^{-1}$ that is different from the one at $x = 0.07$, and
FIG. 2: Glassiness and stripe order in LBCO:1/8 and LSCO:1/8. (a) $^{139}$La $T_{1}^{-1}$ (b) $\beta$ versus $T$ as a function of external field $H$ in non-superconducting LBCO:1/8. Clearly, the spin fluctuations start to slow down abruptly near $T_{\text{CO}}$, as evidenced by the anomalous change of both $T_{1}^{-1}$ and $\beta$. With decreasing $T$, the sharp $T_{1}^{-1}$ peak centered at $\sim 42$ K is followed by broad peak just below $T_{\text{CO}}$. At the same time, $\beta$ reaches a constant below $T_{\text{SO}}$, essentially independent of $H$. (c) $^{139}$La $T_{1}^{-1}$ versus $T$ as a function of $H$ in LSCO:1/8. In contrast to LBCO:1/8, $T_{1}^{-1}$ shows a strong field dependence. In particular, the $T_{1}^{-1}$-upturn is notably suppressed with decreasing $H$, i.e. with increasing $T_c$ which is denoted by the up arrows. The breakdown of the BPP model given by Eq. (2) is attributed to the competition between charge order and superconductivity. (d) $H$-dependence of $\beta$ versus $T$ in LSCO:1/8. In the normal state, $\beta(T)$ is almost independent of $H$, as in LBCO:1/8. The bulk charge ordering is inferred to occur at 70(10) K. While $\beta$ has a significant field dependence in the SC state, at 16 T at which superconductivity is almost quenched, it reveals a striking resemblance to that of LBCO:1/8, becoming a constant at low $T$.

Also different from the behavior of the nearby dopings $x = 0.1$ and 0.15. Together with the broadening of the SC transition shown in Fig. 1(a), this behavior distinguishes $x = 1/8$ from the other doping levels. Starting at $\sim 60$ K, $T_{1}^{-1}$ rises sharply and bends over at $\sim 18$ K, which seems to be compatible with the spin ordering temperature $T_g \sim 20$ K detected in LSCO:0.12 by muon spin rotation ($\mu$SR).

Instead of forming a sharp local maximum at $T_g$ expected in a conventional spin-glass phase, however, $T_{1}^{-1}$ continues to increase before it drops abruptly at $\sim 8$ K. Such a pronounced feature of $T_{1}^{-1}$ at 1/8-doping, also shown in the inset on a linear scale, strongly suggests that the glassy behavior at 1/8-doping is not related to a CSG phase, but to the formation of stripes in the CuO$_2$ plane.

At elevated temperatures we find that the upturn of $T_{1}^{-1}$ sets in close to $T_{\text{surf}}^{\text{CO}} = 55$ K [see the red arrow in Fig. 1(b)]$^{22}$. Furthermore, also the stretching exponent $\beta$ from Eq. (1) clearly starts to deviate from unity near $T_{\text{surf}}^{\text{CO}}$, as shown in Fig. 1(c). A $\beta$ value less than unity indicates a spatial distribution of $T_{1}^{-1}$ and, therefore, can be used as a measure for the glassiness of the spin system. This simultaneous occurrence of charge order and glassiness suggests that in LSCO:1/8 the glassy behavior is mainly caused by charge stripe order.

In order to verify the connection between glassiness and charge order, we performed similar measurements in stripe-ordered LBCO:1/8, which are presented in Fig. 2(a). The $T_{1}^{-1}$ peak reveals a partially resolved structure whose height depends on the external field (i.e. the resonance frequency $\omega_n = \gamma_n H$ where $\gamma_n$ is the nuclear gyromagnetic ratio), whereas the high temperature side...
of the peak is frequency-independent. This low temperature frequency dependence of the $T_{1}^{-1}$ peak is quantitatively understood by the Bloembergen, Purcell, and Pound (BPP) model\textsuperscript{22} which is appropriate for describing the continuous slowing down of spin fluctuations\textsuperscript{31,32,43,44}

$$T_{1}^{-1} = \langle \gamma_{m}^{2} h_{\perp}^{2} \rangle \frac{\tau_{e}}{1 + \omega_{m}^{2} \tau_{e}^{2}}, \quad (2)$$

where $h_{\perp}$ the local field fluctuating at the nuclear site, and the electron correlation time $\tau_{e}$ is in general given by $\tau_{e} = \tau_{e,\infty} \exp(E_{a}/T)$ with $E_{a}$ the activation energy.

The BPP model predicts that the high temperature side of the $T_{1}^{-1}$ peak is frequency independent, while the peak height decreases with increasing field. This is consistent with the main features of the $T_{1}^{-1}$ peak in Fig. 2 (a). The similar BPP behavior is also observed in another stripe-ordered LESCO:0.13\textsuperscript{32} Most importantly, both $T_{1}^{-1}$ and $\beta$ manifest a very sharp anomaly just above $T_{CO}$, confirming that charge stripe order\textsuperscript{35} triggers the spin freezing. Another surprise is that below the spin ordering temperature $T_{SO}$, $T_{1}^{-1}$ falls off much slower than above $T_{SO}$. At the same time, $\beta$ is almost saturated to near 0.5 regardless of the external field strength, which could be interpreted to reflect stabilized spin order.

In case of LSCO:1/8, the onset of the $T_{1}^{-1}$ enhancement is less obvious than LBCO:1/8, but as can be seen in Fig. 2 (d) $\beta$ still probes the onset temperature of glassiness very clearly. Thus, in comparison with the LBCO:1/8 results, our results suggest that the bulk charge order in LSCO:1/8 sets in at $T_{CO} = 70(10)$ K. It should be emphasized that the onset is independent of a magnetic field, as expected for charge stripe order above $T_{SO}$\textsuperscript{40} At low temperatures, on the other hand, when superconductivity is nearly quenched at 16 T, the temperature dependence of $\beta$ approaches to that of LBCO:1/8, as shown in Fig. 2 (d). In particular, it becomes almost constant just below a sharp anomaly at 20 K. The similar $T$-dependence of $\beta$ in the two materials suggests that $T_{SO}$ in LSCO:1/8 as well as in LBCO:1/8 represents a true phase transition, rather than a progressive crossover, to spin order, despite the strong glassy character.

If the glassiness for 1/8-doped La cuprates is a fingerprint of charge order, NMR could further probe the interplay between charge order and superconductivity in LSCO:1/8, which is a much better superconductor than its Ba doped relative. Indeed, as shown in Fig. 2 (c) and (d), the field dependence of $T_{1}^{-1}$ and $\beta$ clearly reveals such an interplay. At high fields ($\geq 13$ T), i.e. when superconductivity is sufficiently suppressed, the high temperature side of the $T_{1}^{-1}$ peak is independent of $H$, which is similar to LBCO:1/8 and conform with the standard BPP model. However, the $T_{1}^{-1}$ upturn clearly becomes suppressed with decreasing field, i.e. increasing $T_{c}$. That means that the standard BPP model breaks down when superconductivity becomes strong. We interpret this as a competition between charge order and superconductivity. An obvious question is why the reduction of the $T_{1}^{-1}$ upturn in Fig. 2(c) occurs well above the bulk $T_{c}(H)$. We think that this behavior is consistent with two-dimensional (2D) SC correlations\textsuperscript{18,50,54} which are known to coexist with charge order above the bulk $T_{c}$.\textsuperscript{54} This idea is substantiated by the fact that the temperature at which the $T_{1}^{-1}$ upturn is suppressed seems to be limited to the bulk $T_{c} \sim 32$ K in zero field, implying that a magnetic field frustrates interlayer coupling but preserves intralayer coupling.\textsuperscript{54}

While the spin freezing procedure above $T_{SO}$ provides clear information regarding the charge order and its competing relationship with superconductivity, the complex field dependence that appears below $T_{SO}$ in the SC state for both $T_{1}^{-1}$ and $\beta$ does not permit us to reach a firm conclusion about the relationship between spin and SC orders. Nevertheless, we note that the $T_{1}^{-1}$ data at 6 T as shown in Fig. 2 (c) are qualitatively similar to those of LBCO:1/8, i.e. the relatively distinctive $T_{1}^{-1}$ peak just above $T_{SO}$ is followed by a broad peak at lower temperatures. This suggests that the considerable suppression of the broad $T_{1}^{-1}$ peak in the low-$T$ region for LSCO:1/8 corresponds to the suppression of spin order due to superconductivity. On the other hand, the saturated $\beta$ below $T_{SO}$ at 16 T indicates that spin order is further stabilized as superconductivity is weakened. From these observations, we believe that spin order also competes with superconductivity.

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