# Nuclear-Magnetic-Resonance Evidence for Charge Inhomogeneity in Stripe Ordered $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$

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We report $^{17}O$ nuclear-magnetic-resonance (NMR) results in the stripe ordered $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ system. Below a temperature $T_q \sim 80$ K, the local electric field gradient and the absolute intensity of the NMR signal of the planar O site exhibit a dramatic decrease. We interpret these results as microscopic evidence for a spatially inhomogeneous charge distribution, where the NMR signal from O sites in the domain walls of the spin density modulation are wiped out due to large hyperfine fields, and the remaining signal arises from the intervening Mott insulating regions.

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Several doped transition metal oxides exhibit inhomogeneous charge stripe order on a mesoscopic scale due to competing long and short range interactions acting on the charge carriers [1,2]. In the cuprates, the doped charge carriers (holes) are expected to form one-dimensional channels (charge stripes) separating regions of insulating antiferromagnetic order of the Cu spins (spin stripes) [3]. The presence of this inhomogeneity may be vital to the mechanism of $d$-wave superconductivity [4]; however, direct experimental evidence for such structures has been elusive. To date, the only observations have been via techniques that probe either the spin density or the charge inhomogeneity: Neutron scattering (NS) experiments provided the first evidence for the modulation of spin density that is expected in a stripe lattice [5], whereas nuclear-magnetic-resonance (NMR) and scanning tunneling microscopy (STM) experiments indicate the presence of inhomogeneous doping distributions [6–10]. In this Letter we discuss new NMR data that provide direct evidence for a correlation between the local charge and spin density maps by taking advantage of the unique properties of the planar oxygen to probe simultaneously both the local spin structure as well as the local hole doping in the O $p$ orbitals. Our data reveal that not only is the charge spatially inhomogeneous, but also that the regions of excess charge are correlated with the domain walls of the spin order, exactly as expected for a stripe pattern [3,11].

The rare-earth codoped $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ series is ideal for NMR investigations of the spin and charge inhomogeneity. Structurally, this material is almost identical to the prototypical high temperature superconductor $La_{2-x}Sr_xCuO_4$, but undergoes a subtle phase transition to the low temperature tetragonal (LTT) structure below $T_{LT} = 135$ K [12]. Instead of superconducting below $T_c \sim 35$ K, this system exhibits glassy magnetic order below $T_N \sim 25$ K [12–18], and elastic NS measurements have identified static long-range spin and structural modulations that are likely produced by stripe order [5]. The slow spin fluctuations in this system dominate the NMR response of the La and Cu nuclei [14,16,19]. However, the planar oxygen does not suffer the same fate: it experiences an isotropic transferred hyperfine coupling (129 kOe/$\mu_B$) to the two nearest neighbor Cu spins, so for antiferromagnetically correlated neighbors, the hyperfine field at the O site vanishes [20]. Furthermore, $^{17}O$ ($I = 5/2$) has a quadrupolar moment ($^{17}Q = -2.56 \times 10^{-26}$ cm$^2$), so it is sensitive to the electric field gradient (EFG) at the nuclear site, which is a measure of the local hole doping [21]. Although previous NMR studies have shown the presence of spatial modulations due to doping inhomogeneities in superconducting $La_{2-x}Sr_xCuO_4$ [6,8], O NMR in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ provides a unique opportunity to investigate the doping inhomogeneity in a system where the spin fluctuations are suppressed.

Ground polycrystals of $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ with $x = 0.08$, 0.105, 0.13, 0.17, and 0.2 were enriched with $^{17}O$ by annealing in $^{17}O_2$ gas at 600 °C for 24 h. The powder samples were then mixed with epoxy and aligned along the $c$ axis by curing in an external field. The $^{17}O$ NMR spectra were obtained by measuring the spin echo intensity while sweeping the magnetic field along the $c$ axis at fixed frequency. $^{139}La$ spectra were independently measured in nonenriched samples and were subtracted from the spectra of the enriched samples to obtain the data in Fig. 1. The spectra clearly show five transitions split by the quadrupolar interaction with a value consistent with that of the planar O in $La_{2-x}Sr_xCuO_4$ [22]. The Hamiltonian is given by

$$\mathcal{H} = \gamma\hbar\hat{I}\cdot\mathbf{H}_0 + \frac{h\nu_c}{6}[3\hat{I}_z^2 - I^2 + \eta(\hat{I}_x^2 - \hat{I}_y^2)] + \mathcal{H}_{\mathrm{hyp}}, \quad (1)$$

where $\gamma$ is the gyromagnetic ratio, $\mathbf{H}_0$ is the external field, $\nu_c = 3eQV_{cc}/20$, $\eta = (V_{aa} - V_{bb})/V_{cc}$, $Q$ is the quadru-

 

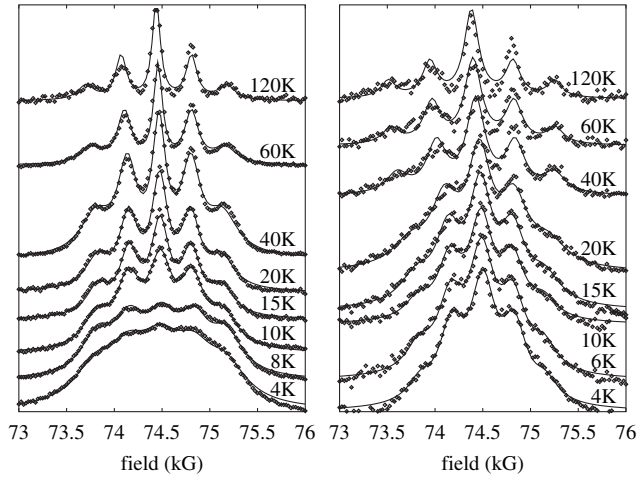


FIG. 1. NMR field-swept spectra of the planar oxygen in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ for $x = 0.13$ (left) and $x = 0.2$ (right) at 43 MHz. The solid lines are fits as described in the text. All spectra are normalized to equal heights for comparison.

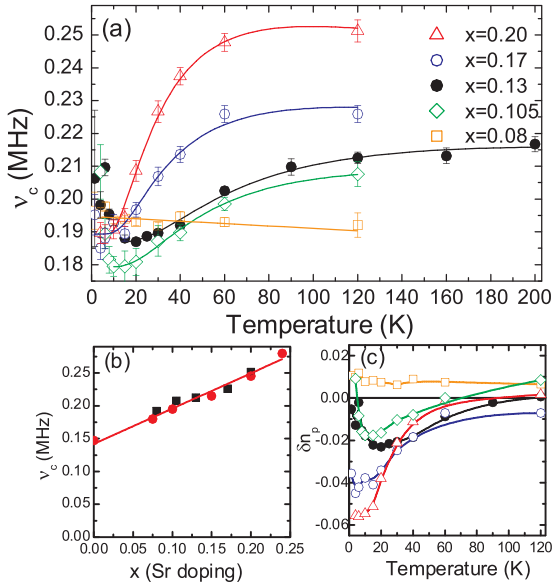


FIG. 2 (color). (a) The quadrupolar splitting $\nu_c$, for several doping levels (see legend) versus temperature. Solid lines are guides to the eye. (b) The doping dependence of $\nu_c$ in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ (squares) and $La_{2-x}Sr_xCuO_4$ (circles) versus $x$ at 120 K. The solid line is given by $a + bx$, with $a = 0.142$ MHz, and $b = 0.538$ MHz [34]. (c) The effective change in hole doping $\delta n_p(x, T)$, as discussed in the text. The colors and symbols are identical to those in panel (a), and the solid lines are guides to the eye.

polar moment of the $^{17}O$, and $V_{\alpha\alpha}$ are the components of the EFG tensor. The hyperfine interaction is give by $\mathcal{H}_{\rm hyp} = C\hat{I}\sum_{i\in nn}\mathbf{S}(\mathbf{r}_i)$, where $C = 129$ kG/$\mu_B$ and the sum is over the two nearest neighbor Cu spins [20]. In the absence of static magnetic order, the resonance field of each transition at fixed frequency $f$ is given by $\gamma H_n = (f - n\cdot\nu_c)/(1 + K_c)$, where $n = -2, -1, 0, 1$, or 2, and $K_c$ is the Knight shift. The spectra were fit to Lorentzian distributions centered at the $H_n$ with widths $\sigma = \sqrt{\sigma_m^2 + (n\cdot\sigma_q)^2}$, where $\sigma_m$ is the magnetic linewidth and $\sigma_q$ the quadrupolar linewidth caused by the distribution of $\nu_c$.

The quadrupolar splitting, $\nu_c$, is shown in Fig. 2(a). For $T > 120$ K, $\nu_c$ varies linearly with doping in exactly the same fashion as $La_{2-x}Sr_xCuO_4$ [Fig. 2(b)]. However, as seen in Fig. 2(a), $\nu_c$ becomes strongly temperature dependent below a temperature $T_q \sim 80$ K, in contrast to the temperature independent EFG observed in $La_{2-x}Sr_xCuO_4$ or $YBa_2Cu_3O_{7-\delta}$ [23]. This unexpected result is our most important observation. One explanation for this behavior is that the change in the EFG reflects a change in the lattice; however, there is only a $\sim$0.5% decrease in unit cell volume between $x = 0$ and $x = 0.20$, whereas the EFG increases by 70% over the same range [24]. Furthermore, there is little or no change of $\nu_c$ at $T_{\rm LT}$, suggesting that the change at $T_q \ll T_{\rm LT}$ is unrelated to modifications of the lattice.

In fact, the dominant contribution to the EFG at the planar O nucleus is the on-site charge distribution of the holes in the oxygen $2p$ orbitals [23,25]. As the doping $x$ increases, the number of holes in the $2p$ orbitals $n_p(x)$ increases, and $\nu_c$ increases linearly with $x$: $\nu_c = a + bx$ [Fig. 2(b)]. The decrease in $\nu_c$ in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ likely reflects a decrease in the hole concentration at the in-plane oxygen sites. For concreteness, we assume that $n_p(x) = n_p^0 + x/2$, where $n_p^0$ is the number of holes in the $p$ orbitals in the absence of Sr doping, and calculate $\delta n_p(x,T) = \delta\nu_c(x,T)/2b = [\nu_c(x,T) - (a + bx)]/2b$ [Fig. 2(c)]. The validity of this assumption is supported by a recent analysis of NMR and atomic spectroscopic results indicating that the doped holes reside almost exclusively on the planar oxygen, and that the EFG is linearly proportional to $n_p$ [21]. As seen in Fig. 2(c), $\delta n_p$ decreases by up to $\sim$0.05 below $T_q$. The increase in $\nu_c$ for $x = 0.13$ is probably an artifact due to the difficulty in fitting spectra dominated by large magnetic broadening at low temperatures (Fig. 1).

The broad linewidths of the satellite peaks ($n = \pm1, \pm2$) seen in Fig. 1 reveal a substantial distribution of $\nu_c$, which is similar in magnitude to that observed in $La_{2-x}Sr_xCuO_4$ [7] and may be attributed to a distribution of local hole densities, $\mathcal{P}(n_p)$. The decrease in $\delta n_p$ [Fig. 2(b)] implies either (i) the center $\langle n_p\rangle$ of the distribution $\mathcal{P}(n_p)$ is reduced below $T_q$, or (ii) $\langle n_p\rangle$ remains temperature independent, but the upper end of the distribution does not contribute to the NMR signal below $T_q$. To distinguish between these two scenarios, we measured the absolute strength of the NMR signal as a function of temperature [14,17]. The temperature dependence of the measured number of spins, $N_0$, shown in Fig. 3, reveals a reduction of up to $\sim$50% in the NMR signal below $T_q$,

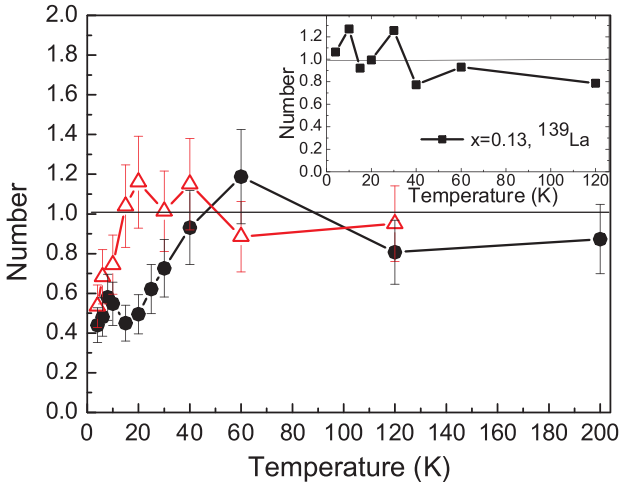


FIG. 3 (color). The number of visible O nuclei versus temperature, $N_0 \sim (I \times T)e^{2\tau/T_2}$, where $I$ is the integrated spectral intensity, $T$ is the temperature, $\tau$ is the pulse spacing in the NMR echo sequence, and $T_2$ is the spin echo decay constant, for $x = 0.13$ (●) and $x = 0.20$ (△). The data have been normalized to unity for high temperatures. Inset: The number of visible La nuclei versus temperature for the $x = 0.13$ sample.

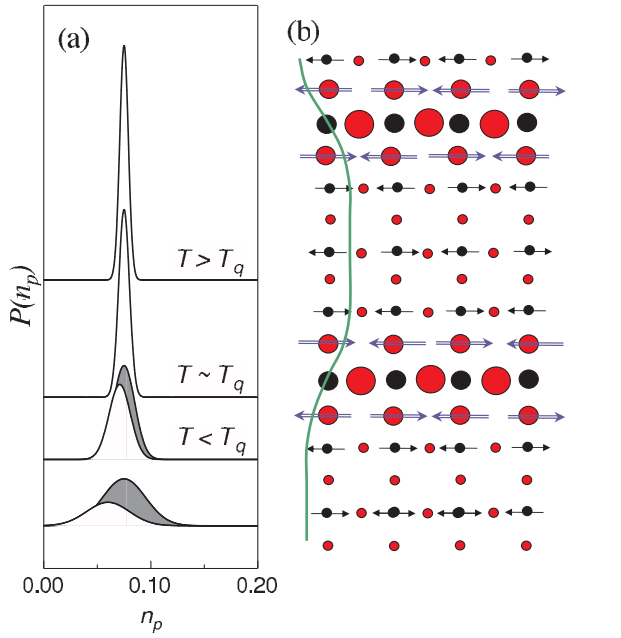


FIG. 4 (color). (a) Temperature dependence of the planar hole doping distribution. As temperature decreases, the width of the distribution increases monotonically, but the mean remains temperature independent. For $T < T_q$, a fraction of the sites at the upper end of this distribution are wiped out (shaded regions), so the observed doping decreases. (b) Schematic diagram of a stripe: the black circles and arrows represent the Cu sites and spins, and the red circles represent the oxygens. The diameter of the circle is proportional to the local hole density. The blue arrows at the oxygen sites are the local hyperfine field, and the green line represents $\mathbf{S}(\mathbf{r})$.

suggesting the latter scenario. Although precise measurements of $N_0$ are difficult due to the partial overlap with the La spectrum, $N_0$ and $\delta n_p$ clearly exhibit similar trends. This interpretation has been confirmed by recent near-edge x-ray absorption fluorescence spectroscopy results, which indicate that $\langle n_p \rangle$ remains temperature independent in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ [26,27]. We conclude that, in contrast to the behavior observed in superconducting $La_{2-x}Sr_xCuO_4$, the O sites located in regions of higher local hole doping in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ do not contribute to the NMR signal, via a wipeout mechanism discussed below. Figure 4(a) illustrates schematically how $\mathcal{P}(n_p)$ varies with temperature.

The wipeout of the O NMR signal from regions with higher hole dopings provides concrete evidence for a spatial correlation between the local charge modulation and the spin structure. NS studies have shown that the fluctuating Cu spins in $La_{2-x}Sr_xCuO_4$ and $La_{2-x-y}RE_ySr_xCuO_4$ are antiferromagnetically correlated, with a long-range spatial modulation, $\mathbf{S}(\mathbf{r})$, that gives rise to nodes, or domain walls, approximately every 4 lattice constants for $x \gtrsim 1/8$ [5]. The oxygen nuclei located adjacent to these nodes experience a large, slowly fluctuating hyperfine field, $H_{\mathrm{hyp}} = C[\mathbf{S}(\mathbf{r} - a\hat{x}/2) - \mathbf{S}(\mathbf{r} + a\hat{x}/2)] \propto \nabla_x \mathbf{S}(\mathbf{r})/a$ [Fig. 4(b)]. The nuclear spin lattice relaxation rate, $T_1^{-1}$, of these sites is proportional to $H_{\mathrm{hyp}}^2$, and reaches a maximum when the Cu spin fluctuation rate ($\tau_c^{-1}$) is of the order of the nuclear Larmor frequency ($\omega_L \sim 43$ MHz) [28]. We estimate $T_1^{-1} \gg (1\ \mu\mathrm{s})^{-1}$ at 10 K for O sites close to a node in $\mathbf{S}(\mathbf{r})$, whereas the time window of the NMR spectrometer is on the order of 10 $\mu$s [29]. Such sites will relax too quickly to contribute to the NMR spin echo and will be wiped out [14]. Conversely, the oxygen nuclei located far from the domain walls where $\nabla\mathbf{S}(\mathbf{r})$ is small experience a slower $T_1^{-1}$ (the neighboring Cu spins are locally commensurate), and thus will contribute to the NMR spin echo signal. The onset temperatures measured by $\delta n_p$ and $N_0$ may differ, however, for there is not a one-to-one correspondence between the localization of a hole along a stripe (a phenomenon driven by the local charge distribution) and the wipeout of one oxygen site (a phenomenon driven by the dynamics of the local spin inhomogeneity). Although we have no direct information about the long-range topology of $n_p(\mathbf{r})$ and $\nabla\mathbf{S}(\mathbf{r})$, we can conclude that they must be spatially correlated; otherwise there would be no reduction of the apparent hole doping, the spectral intensity would be reduced for all local hole dopings, and $\nu_c$ would be temperature independent, in contrast to our observations.

Two- and three-band Hubbard model calculations can shed light on the spatial dependence of the hole doping and the spin structure in stripe ordered systems [3,30]. These calculations show increased hole density for the O sites in and adjacent to the charge stripes, whereas in the intervening antiferromagnetic regions the hole density on the O sites is equal or close to that in the undoped material [see

Fig. 4(b)], in agreement with our observations of $\nu_c$. Furthermore, $\mathbf{S}(\mathbf{r})$ vanishes at the charge stripe and undergoes a phase change of 180°. Therefore, $\nabla\mathbf{S}(\mathbf{r})$ is largest in the vicinity of the domain wall, and the oxygen sites adjacent to these nodes are exactly those with the highest hole density and are wiped out. The observation that the hole density is greatest in regions where $\nabla\mathbf{S}(\mathbf{r})$ is largest strongly supports the idea of charged domain walls first discussed by Zaanen [3].

Since NMR is a local probe, we cannot determine whether $n_p(\mathbf{r})$ is randomly distributed in amorphous islands, as observed in recent STM experiments on $Bi_2Sr_2CaCu_2O_{8+\delta}$ [31], or exhibits the long-range correlations characteristic of a stripe lattice. However, we can make some general observations about the topology. If we assume that the holes segregate into islands with a characteristic radius $r_0$, and that the wipeout occurs for sites on the boundaries of the islands where $\nabla\mathbf{S}(\mathbf{r})$ is largest, then in order to account for a loss of ~50% of the sites we estimate that $r_0 \sim 15$ Å, a value of the same order as measured by STM [31]. Note, however, that $T_c \lesssim 10$ K, whereas $T_q \sim 80$ K, so a scenario of localized superconducting islands is inconsistent with our results. Secondly, we note that approximately 25% of the O sites are wiped out for site-centered charge stripes [Fig. 4(b)], whereas close to 50% are wiped out for bond-centered stripes [11], or for a 2D checkerboard pattern [32]. However, this number is strongly dependent on the details of the long-range topology and the width of the domain walls, and the low precision inherent in the nature of these measurements precludes any definite conclusions about these scenarios.

In summary, we have observed a decrease in the EFG at the O sites in $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ that can be understood in terms of a spatial correlation between the local hole doping and the domain walls of the spin modulation. Both the LTO ($La_{2-x}Sr_xCuO_4$) and the LTT ($La_{1.8-x}Eu_{0.2}Sr_xCuO_4$) phases exhibit similar hole distributions [8], but the glassy spin freezing present in the latter gives rise to the wipeout of O sites near the domain walls. The fact that the widths of the hole distributions are similar in both systems is surprising, since it implies that some form of charge inhomogeneity is present in both the LTO and LTT phases, at least on the time scale of the NMR experiments, and contradicts the idea that the LTT phase pins the spatially fluctuating charge stripes [33]. Rather, the LTT phase suppresses the spin fluctuations. We speculate that charge inhomogeneity is present in both systems [2], but that the spin dynamics are strongly affected by the LTT phase.

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