We report experimental evidence for the spatial variation of hole concentration \( x_{\text{hole}} \) in the high \( T_c \) superconductor \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (0.04 \( \leq x \leq 0.16 \)) by using \(^{63}\text{Cu}\) NQR for \(^{63}\text{Cu}\) isotope enriched samples. We demonstrate that the extent of the spatial variation of the local hole concentration \( \Delta x_{\text{hole}} \) is reflected on \(^{63}/T_1\) and deduce the temperature dependence. \( \Delta x_{\text{hole}} \) increases below 500 – 600K, and reaches values as large as \( \Delta x_{\text{hole}}/x \sim 0.5 \) below \( \sim 150K \). We estimate the length scale of the spatial variation in \( x_{\text{hole}} \) to be \( R_{\text{hole}} \geq 3 \) nm from analysis of the NQR spectrum.

The mechanism of high \( T_c \) superconductivity remains enigmatic even after 15 years of its discovery \[1\]. It is well known that the central idea in the search of high \( T_c \) materials was to look for materials with polaronic effects caused by coupling between electrons and the lattice. However, most recent theoretical debates are based on the assumption that the holes are homogeneously doped into CuO\(_2\) planes, even if hole-doping is achieved by the substitution of ions with different ionicity which in effect creates alloys. A clear and widely accepted counter example against such a simplified picture is the stripe phase in \( x \) doped \( \text{Nd}_{2−x}\text{Sr}_x\text{CuO}_4 \), where the Coulomb potential from the distorted lattice slows down spin and charge density waves \[4\]. It is also known that the high mobility of the oxygen atoms results in electronic phase separation \[3\] between the superconducting and antiferromagnetic phase in super-oxygenated \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \). A natural question to ask is whether similar situations arise in other materials albeit in a less robust manner \[7\]. In fact, there is ample evidence for some sort of spatial inhomogeneity in the \( x \) plane of earlier NMR and NQR (nuclear quadrupole resonance) studies in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) \[8–15\] such as splitting of the \(^{63}\text{Cu}\) NQR and NMR lines due to inequivalent \( \text{Cu} \) sites with different EFG (electric field gradient) tensors \[8,13\], drastic broadening of the \(^{63}\text{Cu}\) NQR line at low temperatures \[3,11\], and \(^{63}\text{Cu}\) NMR line broadening due to the modulation of orbital shifts \[13\].

More recent studies using \(^{63}\text{Cu}\) NQR and NMR wipe-out \[11,13,15\] have characterised the glassy nature of the slowing down of the stripe inhomogeneity below temperatures \( \sim 100K \). However, no clear picture has emerged that discerns and relates the effects of genuine electronic phase separation, stripe modulation, and random substitution of donor ions. On the other hand, a recent STM (scanning tunnelling microscopy) study on the surface state of \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) cleaved at low temperatures revealed nano-scale spatial variations of the electronic state \[14\]. Whether such nano-scale modulations are universally observable in the bulk and other high \( T_c \) materials remains to be seen, but the STM results have enhanced the interest in the potential impact of the spatial inhomogeneity of the electronic properties in the CuO\(_2\) plane.

In this Letter, we utilize a new simple trick based on the local nature of the \(^{63}\text{Cu}\) NQR technique to probe the spatial inhomogeneity of the CuO\(_2\) plane. Unlike scattering techniques, NQR does not require spatial coherence over tens of nm’s, hence it is an ideal technique to probe spatial variations in the local hole concentration \( x_{\text{hole}} \) at short length scales. Our main results are presented in Fig. 1, where we plot the temperature dependence of the extent of the spatial variation \( \Delta x_{\text{hole}} \) as measured by the distribution in \(^{63}/T_1\) (data with solid line) and by analysis of the NQR spectrum (dashed lines). Contrary to common assumptions that doped holes are uniformly distributed in the CuO\(_2\) planes (i.e. \( \Delta x_{\text{hole}} = 0 \)), we find that a non-zero value of \( \Delta x_{\text{hole}} \) exists at all temperatures and furthermore shows a factor 2-3 increase from 500-600K down to \( \sim 150K \). We also demonstrate that the NQR spectrum is consistent with a model where the spatial variation in \( x_{\text{hole}} \) takes the form of patches in the CuO\(_2\) plane, where some patches are more metallic and some more insulating, with a patch radius \( R_{\text{hole}} \geq 3 \) nm.

We shall now describe the details of the procedure used to obtain \( \Delta x_{\text{hole}} \) shown in Fig. 1. The nuclear spin-lattice relaxation rate \(^{63}/T_1\) is given by the formula:

\[
\frac{63}{T_1} = \frac{2}{g^2\mu_B^2\hbar} \sum_q |^{63}A(q)|^2S(q,\omega_n)
\]

where \( \omega_n \) is the NQR frequency, \( |^{63}A(q)|^2 \) is the hyperfine form factor, and \( S(q,\omega_n) \) is the dynamic structure factor of the Cu electron spins \[17\]. \(^{63}/T_1\) measures the local low frequency Cu spin fluctuations at \( \omega_n \). Because of the experimental ease, the temperature dependence of \(^{63}/T_1\) is generally measured at the peak of the spectrum.

However, in various materials including \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) \[16\], \( 1/T_1 \) often depends on frequency across the resonance spectrum due to a spatial distribution of the electronic states. A typical example is shown in Fig. 2a for \( x = 0.115 \). For convenience we have defined \( 1/T_0, 1/T_1^\dagger, 1/T_1^{-1/10} \) as \(^{63}/T_1\) measured at the peak, upper half intensity, lower half intensity and lower one tenth.
intensity of the A-line respectively.

The temperature dependence of $1/T_1^\text{a}$, $1/T_1^\text{b}$ and $1/T_1^{1/10}$ is plotted in Fig. 3. All data were taken in the temperature region above Cu wipeout [1], where full NQR signal intensity is observable. For comparison, Fig. 3 also shows $1/T_1^O$ for a variety of samples which all show agreement with previous work [13]. We note that all of our results are insensitive to RF pulse width. The most surprising discovery of the present work is that $1/T_1^\text{a}$, $1/T_1^\text{b}$ and $1/T_1^{1/10}$ show qualitatively different temperature dependence. For example, in the $x = 0.07$ sample, $63\text{Cu}/T_1$ measured at the half intensity of the lower (upper) frequency side of the NQR spectrum exhibits semi-quantitatively the same behaviour as $1/T_1^O$ for $x = 0.04$ ($x = 0.115$). This is consistent with the fact that the lower (upper) frequency side of the NQR spectrum for $x = 0.07$ roughly coincides with the peak NQR frequency of $x = 0.04$ ($x = 0.115$) as shown in Fig. 2b. Our finding immediately establishes that within a single sample with a fixed nominal hole concentration $x$, there are some segments with higher and lower hole concentrations $x_{\text{hole}}$.

By comparing $1/T_1^\text{a}$ with smoothly interpolated values of $1/T_1^O$ for various samples, we can estimate the deviation $\Delta x_{\text{hole}}$ of local hole concentration from the spatial average, $x$. For example, $1/T_1^\text{b}$ for $x = 0.07$ at 200K is close to $1/T_1^O$ for $x \approx 0.04$, implying that the lower frequency side of the $x = 0.07$ spectrum corresponds to resonance from segments with $\Delta x_{\text{hole}} \approx -0.025$. Similarly, $1/T_1^\text{a}$ for $x = 0.07$ is close to $1/T_1^O$ for $x \approx 0.10$, implying the upper frequency side corresponds to segments with $\Delta x_{\text{hole}} \approx +0.03$. Using $1/T_1^{1/10}$ instead results in an overall 30–40% increase in $\Delta x_{\text{hole}}$ and does not affect our conclusions. Another important feature in Fig. 3 is that $1/T_1^\text{a}$ cuts through the lines of $1/T_1^O$ with decreasing temperature. This implies that $\Delta x_{\text{hole}}$ increases with decreasing temperature, as shown in Fig. 1. Since the magnitude of $\Delta x_{\text{hole}}$ estimated from $1/T_1^\text{a}$ and $1/T_1^\text{b}$ is identical within experimental uncertainties, we plot the magnitude of $\Delta x_{\text{hole}}$. To the best of our knowledge, our $63\text{Cu}$ NQR data in Fig. 1 is the first of its kind to detect the temperature dependence of the inhomogeneous distribution of the hole concentration in La$_{2-x}$Sr$_x$CuO$_4$ or any other high $T_c$ materials with quenched disorder.

One important observation about Fig. 2a is that the B-line [4] shows a very similar distribution in $63\text{Cu}/T_1$ to the A-line. The B-line itself originates from structural effects [14]. More specifically, a B-site corresponds to a Cu nucleus with a Sr$^{2+}$ ion situated either directly above or below it, as supported in Fig. 2c where the fractional intensity of the B-line is shown to increase as $x$. We recall that the $63\text{Cu}$ NQR spectrum in La$_{2-x}$Sr$_x$CuO$_4$ for $63\text{Cu}$ isotope enriched samples [11] shows a third structural peak (the C-line) whose fractional intensity is equal to $y$. The C-line corresponds to a Cu nucleus directly above or below a Eu$^{3+}$ ion.

The similarity of the B-line to the A-line distribution of $63\text{Cu}/T_1$ rules out the possibility that the distribution in the hole concentration $\Delta x_{\text{hole}}$ is concentric about a B-site. Rather, it indicates that the spatial modulation of $\Delta x_{\text{hole}}$ consists of patches that cover both A and B-sites equally and the size of each patch is larger than the average Sr$^{2+}$ distance of $\sim 2$ nm for $x = 0.16(0.04)$.

We emphasize that the distribution in $63\text{Cu}/T_1$ is not caused by flaws in our single phased ceramic samples. $63\text{Cu}$ NMR and NQR in high quality single crystals of both La$_{2-x}$Sr$_x$CuO$_4$ [2] and La$_2$CuO$_4$ [2] exhibit similar results. EMPA (electron micro-probe analysis) on single crystal La$_{1.85}$Sr$_{0.15}$CuO$_4$ showed that the spatial variation of the Sr$^{2+}$ concentration averaged over the focus area of the electron beam at $0.01 \ll \Delta x_{\text{hole}}$. This rules out the possibility that $\mu_m$ scale inhomogeneities in the Sr$^{2+}$ concentration is the cause of $\Delta x_{\text{hole}}$. Moreover, earlier NQR measurements by Fujiyama et. al. [10] in La$_{2-x}$Sr$_x$CuO$_4$ without isotopic enrichment agree with ours. We also note that the planar $^{17}$O NMR Knight shift measurements provide additional evidence for a spatial distribution in the hole concentration. Our systematic measurements for single crystals [21] with $x = 0.025, 0.035, 0.05, 0.115$ and 0.15 showed an overlap of the planar $^{17}$O NMR central transition very similar to Fig. 2b. This means that the local static spin susceptibility has a similar spatial variation.

We now turn our attention to the analysis of the $63\text{Cu}$ NQR spectrum. Experimental resolution limited the $\Delta x_{\text{hole}}$ data deduced from the distribution in $63\text{Cu}/T_1$ above $\sim 500K$ since all $1/T_1^O$ curves start to merge above this temperature (Fig. 2). Not only does the spectral analysis enable us to extend $\Delta x_{\text{hole}}$ to higher temperatures, but we also get crucial insight into the length scale of the spatial variation $\Delta x_{\text{hole}}$.

The resonance frequency in NQR is proportional to the EFG surrounding the Cu nucleus [22]. The broad NQR linewidth shown in Fig. 2a and 2b implies that the local charge environment has a broad distribution in the EFG. Possible causes of the broad distribution include: the random substitution of La$^{3+}$ with Sr$^{2+}$, the spatial variation $\Delta x_{\text{hole}}$, and the lowering of the local symmetry by lattice distortions. In order to simulate these effects, we carried out a point charge lattice summation to determine the EFG at the Cu nuclear site. The conventional way of incorporating the Sr$^{2+}$ substitution into an EFG point charge calculation is to reduce the effective charge of the La$^{3+}$ ion to La($3+-x/2$) [23]. However, in order to estimate the effect of the random replacement of La$^{3+}$ with Sr$^{2+}$, we ran a simulation of a realistic lattice with randomly distributed Sr$^{2+}$ ions in a La$^{3+}$ matrix [24]. We found that the linewidth thus deduced is too narrow to account for the experimental result, as shown by the dashed line in Fig. 2a.

Next, we ran the simulation with $\Delta x_{\text{hole}} \neq 0$ using the following procedure: we first define an in-plane circle of
radius $R_{\text{hole}}$ surrounding the Cu nucleus $\alpha$. The circle defines a “patch” of diameter $2R_{\text{hole}}$ within which the local hole concentration is determined by counting the number $N$ of Sr$^{2+}$ ions within the patch. The $N$ donated holes from the $N$ Sr$^{2+}$ ions are then uniformly distributed among the planar oxygen sites within the patch. The EFG contributions from all the point charges surrounding the Cu site $\alpha$ is then summed up, the corresponding NQR frequency deduced, and a count is placed in the appropriate frequency bin. The lattice is then re-randomized, and the whole procedure is repeated $\sim 10^4$ times until a sufficient number of counts is present to reproduce the entire NQR spectrum, including the B-line. The aforementioned case of the simulation with $\Delta x_{\text{hole}}=0$ (i.e. homogeneous distribution of holes) corresponds to $R_{\text{hole}} \sim \infty$ and yields a linewidth much narrower than the experimental data. Using $R_{\text{hole}} \sim 1.5$ nm yields the dashed-dot spectrum in Fig. 2a, which is clearly too broad. Using $R_{\text{hole}} \sim 3$ nm however, results in the best fit shown by the solid lines in Fig. 2a and 2b. Once the best fit $R_{\text{hole}}$ is determined, $\Delta x_{\text{hole}}$ is directly obtained from the computation and is presented as the dashed lines in Fig. 1. According to the simulation, the $\sim 25\%$ increase in linewidth from 600K (Fig. 2b) to 300K (Fig. 2a) for $x=0.115$ can be accounted for by a $\sim 25\%$ decrease in $R_{\text{hole}}$ which corresponds to $\sim 45\%$ increase in $\Delta x_{\text{hole}}$ from 600K down to 300K. We discuss implications of the temperature dependence later.

We caution that we have ignored potential local tilting of the CuO$_6$ octahedra caused by substitution of the smaller Sr$^{2+}$ ions, or potential precursor effects to the long range LTO (low temperature orthorhombic) transition. Since local octahedron tilting increases the NQR resonance frequency potential local distortions of the lattice may provide the additional mechanism to broaden the spectrum. We have ignored this and attributed the extra line broadening to $\Delta x_{\text{hole}}$, hence $\Delta x_{\text{hole}}$ thus deduced may be an upper bound and $R_{\text{hole}} \sim 3$ nm maybe a lower bound. We note that the minimum patch size of $2R_{\text{hole}} \geq 6$ nm is still larger than the average Sr$^{2+}$ ion separation of 1(2) nm for $x=0.16(0.04)$, which further rules out the possibility that the distribution of the local hole concentration is concentric about each Sr$^{2+}$ ion. The validity of our simulation breaks down altogether in the temperature region where local octahedron tilting actually becomes apparent due to long range LTO transition, as indicated by an increase in $\nu_Q$ [31].

The analysis shown in Fig. 1 is thus terminated below this temperature.

Our lineshape analysis sets only the lower bound of the length scale $2R_{\text{hole}} \geq 6$ nm of the spatial variation $\Delta x_{\text{hole}} = 0.03 \sim 0.06$. On the other hand, our aforementioned EMPA analysis indicates that the deviation in Sr$^{2+}$ concentration is as small as $\Delta x_{\text{Sr}} \sim 0.01$ averaged over the length scale of $\sim 1 \mu$m. Furthermore, earlier high resolution X-ray diffraction studies showed that $\Delta x_{\text{Sr}} \sim 0.01$ averaged over the length scale of $\geq 10$ nm. These results imply that the local hole concentration $x_{\text{hole}}$ modulates as much as $\Delta x_{\text{hole}} = 0.03 \sim 0.06$ within the short distance scales of 6-10 nm, but the spatial average of $x_{\text{hole}}$ over greater length scales is as little as $\sim 0.01$. One obvious possibility is the clustering of Sr$^{2+}$ ions with very short length scale of 6-10nm. However, the absence of any substantial diffuse scattering in neutron diffraction experiments makes this scenario unlikely. Moreover, the presence of the temperature dependence of $\Delta x_{\text{hole}}$ suggests that the temperature independent quenched disorder caused by the clustering of the Sr$^{2+}$ ions alone cannot entirely account for our results. We recall that our lineshape analysis is based on a completely random distribution of Sr$^{2+}$ ions. We also note that the spin-spin correlation length $\xi$ cannot be identified as $R_{\text{hole}}$ because $\xi$ is much shorter than $2R_{\text{hole}}$ and increases with decreasing temperature [30]. The latter qualitatively contradicts with the decrease of $R_{\text{hole}}$ with decreasing temperature. These considerations inevitably lead us to conclude that there must exist an electronic mechanism at short length scale which causes the holes to segregate.

One possible mechanism of establishing such a short electronic length scale is phase separation (which may or may not have a stripe-like structure). In fact, Ino et. al. [31] reported evidence for phase separation at $\sim 80K$ in La$_2$-$_x$Sr$_x$CuO$_4$ for $x<0.15$ based on photoemission experiments, i.e. the chemical potential does not vary with increasing hole doping up to $x=0.15$. In this concentration regime, the presence of a stripe instability has been firmly established at low temperatures [28,13]. Our new observation in Fig.1 may be a precursor to such a phenomena. However, we observed comparable or larger values of $\Delta x_{\text{hole}}$ for $x=0.20$ and 0.25 where photoemission measurements do not detect signatures of phase separation. Thus an additional mechanism(s) for segregation of holes is necessary to account for our results at least above $x \sim 0.15$. Interestingly, the temperature dependence of $\Delta x_{\text{hole}}$ and the magnitude of $R_{\text{hole}}$ may be qualitatively understood based on a toy model of a thermal activation type process for the segregation of holes. Using the in-plane static dielectric constant of $\epsilon_s \sim 30$ and the effective mass $m^* \sim 2$ (in units of $m_e$) deduced from lightly doped La$_2$CuO$_{4+x}$ [32], one obtains a factor $m^*/\epsilon_s^2 \sim 1/450$ smaller binding energy of $E_b \sim 30$meV or $E_b \sim 350K$ and a factor $\epsilon_s/m^* \sim 15$ larger Bohr radius of $a_0 \sim 1nm$. These temperature and length scales are indeed comparable to our observation. Even though this oversimplified model does not include the effects of screening for instance, it might suggest that the donated holes are bound by a Coulomb type potential created by the Sr$^{2+}$ ions rather than homogeneously doped into the CuO$_2$ planes. Needless to say, our toy model analysis employed here above $\sim 100$ K does not necessarily support or rule out the presence of intrinsic phase separation.
at lower temperatures.
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FIG. 1. Temperature dependence of the distribution in local hole concentration $\Delta x_{\text{hole}}$ as deduced by $^{63}$Cu NQR $1/T_1$ in La$_2$-$x$Sr$_x$CuO$_4$ ($\bullet$ $x = 0.04$; $\circ$ $x = 0.07$; $\bullet$ $x = 0.15$; $\triangle$ $x = 0.16$). Single points at 600K with dotted lines are upper bounds deduced from the best fit to the $^{63}$Cu NQR spectra.

FIG. 2. (a) Frequency dependence of $^{63}$Cu NQR spectrum ($\bullet$) in La$_{1.885}$Sr$_{0.115}$CuO$_4$ at 300K. Dashed, solid and dashed-dot spectra are theoretical fits with patch sizes $R_{\text{hole}}$ $\sim$ $\infty$, 3nm and 1.5nm respectively. Dotted lines through $^{63}$Cu NQR spectra in $x = 0.04$ ($\bullet$), $x = 0.07$ ($\circ$), $x = 0.115$ ($\bullet$), and $x = 0.16$ ($\triangle$) at 600K. Solid lines are theoretical fits with $R_{\text{hole}}$ $\sim$ 3nm. (c) Fraction $f_{B}$ of B-line intensity to total intensity (with $T_2$ corrections) at (+) 600K and ($\times$) 300K as a function of $x$.

FIG. 3. Temperature dependence of $1/T_1^{-1/10}$ ($\times$), $1/T_1^{-1}$ ($\triangledown$), $1/T_1^0$ ($\circ$), and $1/T_1^\infty$ ($\bullet$) in La$_2$-$x$Sr$_x$CuO$_4$ where $x$ is given in each panel. Solid lines are a guide for the eye, and dashed lines are $1/T_1^\infty$ for $x = 0.00$, 0.02, 0.04, 0.07 ,0.09, 0.115, and 0.16 where $1/T_1^\infty$ monotonically decreases with increasing $x$. 

$^{2}$

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