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Localized holes in superconducting lanthanum cuprate

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Copper NQR spectra demonstrate the existence of a second, anomalous copper site in lanthanum cuprate whose character is independent of the method of doping. We present a systematic NMR/NQR study of $La_2CuO_{4+\delta}$ for a range of δ, which demonstrates that the density of such sites increases with δ. Analysis of our results and of published data from $La_{2-x}Sr_xCuO_4$ indicate that a substantial fraction of the doped holes in these materials localize in CuO_6 octahedra adjacent to the out-of-plane dopants, and that the anomalous sites are those neighboring a site occupied by such a pinned hole. Thus, superconductivity occurs in a CuO_2 plane containing many localized holes. [S0163-1829(98)51702-X]

It is becoming evident that inhomogeneous distribution of charge carriers is a common, if not universal, feature of cuprates and that ordering of charge into modulated structures may play a key role in enabling superconductivity.[1–3] However, neither the exact nature of these inhomogeneities nor their influence on the electronic properties are well understood. They are generally evident as dynamically fluctuating and spatially incoherent, but static charged stripes which form antiphase domain walls between undoped and antiferromagnetically ordered intervening regions apparently arise in the cuprates from pinning to the lattice by, e.g., the low-temperature tetragonal (LTT) structure; these are thought to be antagonistic to superconductivity.[2] Recent extended x-ray-absorption fine structure measurements[4] provide evidence for stripes in $La_{1.85}Sr_{0.15}CuO_4$ in support of these propositions. Little is known about either the pinning mechanism or the local character of the localized-charge state. NMR and NQR are local probes ideally suited to understanding these issues. Crystallographic diffraction studies find a single Cu site in Sr- and O-doped lanthanum cuprate, yet copper NQR spectra reveal *two* ^{63}Cu lines (see Fig. 1 and Refs. 5–8 and included references) demonstrating the existence of a second, anomalous (''*B*'') copper site in lanthanum cuprate whose character is independent of the method of doping.[6] Insight from NQR/NMR studies into the local environment of the *B* site together with the dopant concentration dependence of the *B*-line intensity in lanthanum cuprate leads to the conclusion that a significant fraction of the doped holes are localized *in the* CuO_2 *planes* adjacent to the out-of-plane dopant and that the *B* sites correspond to Cu sites neighboring these localized holes. The influence of these ''defects'' on superconductivity is unexpected: although the density of itinerant holes in $La_2CuO_{4.12}$ is very similar to that in $La_{1.85}Sr_{0.15}CuO_4$, the former which has a significantly *larger* density ($\sim\delta$ per Cu) of localized holes also has the *higher* T_c [up to 58 K (Refs. 9 and 10)] found in the lanthanum cuprate materials. The spatial ordering of the oxygen dopants in $La_2CuO_{4+\delta}$ found in neutron scattering studies[11–13] appears to be related to this higher T_c.

The single crystals of $La_2CuO_{4+\delta}$ used in this work were grown first as $La_2CuO_{4.0}$ by a flux method. The $\delta\simeq 0.10$ and 0.12 crystals were then doped by electrochemical oxidation;[14] these crystals have superconducting onset temperatures of about 40 K. Neutron scattering revealed ordering of the interstitial oxygen (henceforth denoted *i*-O) in the $\delta\simeq 0.10$ sample.[11] The $\delta\simeq 0.06$ sample lies on the oxygen-rich edge of the miscibility gap and was described in Ref. 6. The NQR and NMR spectra were obtained using standard pulsed techniques. The spectra (multiplied by $f^{-7/4}$ to correct for the frequency f dependent enhancement of spectrometer sensitivity[15]) were fit by four appropriately constrained (using known isotopic ratios and quadrupole moments) Lorentzians; the $\delta\simeq 0.12$ fit is shown in Fig. 1. The integrated intensity of a given component of the spectrum was obtained by integrating the corresponding element in the fit, then correcting for different decay rates of the spin-echo intensity ($\propto\exp[-2(\tau/\tau_2)^2]$ here). We find that $\tau_2^A\simeq 25\ \mu$sec and $\tau_2^B\simeq 40\mu$sec. Extrapolation of our spectra (obtained at $\tau=10\ \ \mu$sec) to $\tau=0$ increases I_B^{LCO} (I_B is the integrated intensity of the ^{63}Cu *B* line as a fraction of the total ^{63}Cu intensity; the superscript refers to $La_2CuO_{4+\delta}$) by $\lesssim 10\%$.

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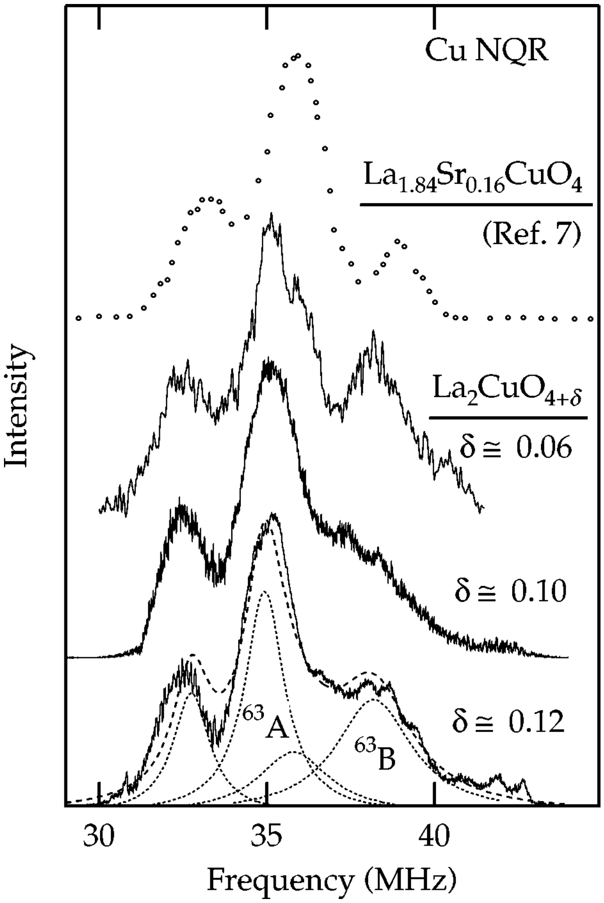

FIG. 1. Copper NQR spectra for three samples of $La_2CuO_{4+\delta}$ (this work) and for $La_{1.84}Sr_{0.16}CuO_4$ (Ref. 7). All show the characteristic triple peak structure demonstrating the existence of a second, anomalous B peak around 38 MHz. The decomposition of the $\delta \simeq 0.12$ spectrum is shown: the two peaks at lower frequency are the ^{65}Cu and ^{63}Cu lines arising from the A sites, and the two higher peaks are the same two lines from B sites. Note the much smaller integrated intensity of the B peak in $La_{1.84}Sr_{0.16}CuO_4$.

Electrochemical doping produces broader B lines, causing the peak B-line intensities of the $\delta \simeq 0.10$ and 0.12 samples to be smaller than for $\delta \simeq 0.06$ in spite of their larger integrated intensities. The spectra shown were obtained at $T = 50$ K; where examined (for $\delta \simeq 0.06$) no temperature dependence to I_B^{LCO} was observed.

For $0.01 \lesssim \delta \lesssim 0.06$, $La_2CuO_{4+\delta}$ phase separates[9,16–20] into oxygen-poor insulating and oxygen-rich metallic regions; for higher δ, it is single phase, metallic and superconducting at low temperatures with T_c reaching 58 K.[9,10,19,21] The B line is present (see Fig. 1) in macroscopically single phase ($\delta > 0.06$) material. While the shift of the B line is very similar to that observed in $La_{2-x}Sr_xCuO_4$, I_B is much larger in $La_2CuO_{4+\delta}$ [see Figs. 1 and 2(a)]: we find $I_B^{\mathrm{LCO}} > 0.4$ for $\delta \simeq 0.12$; in contrast $I_B^{\mathrm{LSCO}} \simeq 0.1–0.15$ in $La_{1.85}Sr_{0.15}CuO_4$.[5,7]

The two different means of doping lanthanum cuprate (Sr^{2+} substitution for La^{3+} vs insertion of interstitial O^{2-}) create very different local disturbances in the lattice, yet the shift of the B line quadrupole frequency ν_Q^B relative to the A line is independent of the means of doping, indicating that this feature arises as a consequence of the presence of doped holes rather than as a manifestation of the local distortion associated with the dopant.[6] This assertion is supported by *ab initio* cluster calculations of the magnitude of the local electric field gradient (EFG) at the copper site, details of which are available elsewhere.[22] Using this method we are able to calculate the copper NQR frequency ν_Q for the A site which deviates from the observed value by ~8%. We calculate that a Sr dopant shifts ν_Q by only 0.5 MHz; an interstitial O^{2-}, on the other hand, causes a shift roughly ten times larger: about 4.5 MHz or twice the observed shift for the B line. Most importantly, these calculations show that $^{63}\nu_Q$ for a site adjacent to a CuO_6 octahedron occupied by a localized hole is shifted upwards by 2.5 MHz, very close to the observed shift. Although an O^- ion at the interstitial site gives a similar shift, the agreement with the localized hole calculation, along with the dopant-independence of the shift, indicates the B site in both $La_{2-x}Sr_xCuO_4$ and $La_2CuO_{4+\delta}$ arises from the copper sites neighboring a CuO_6 octahedron occupied by a pinned hole[22] and not the direct influence of the dopant ions on the Cu EFG. The particular environment produced by the localized hole must persist on that site for a time of order the inverse linewidth (~1 μsec) in order to produce a distinct NQR line. Thus the hole is pinned to the lattice.

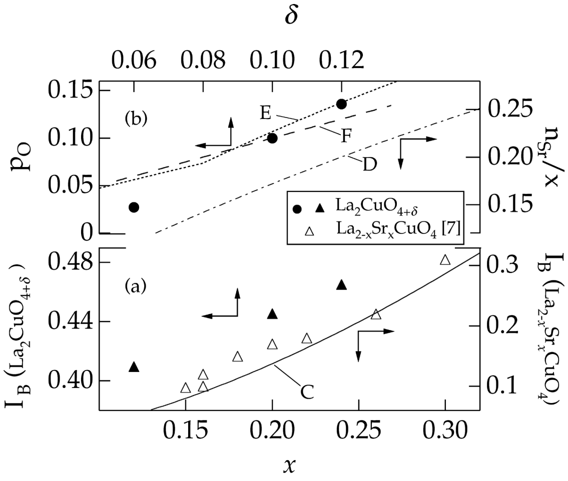

FIG. 2. (a) The doping dependencies of I_B. $I_B^{\mathrm{LCO}}(\delta)$ is plotted against the top and left-hand axes and $I_B^{\mathrm{LSCO}}(x)$ (from Ref. 7) against the bottom and right-hand axes (note the different scales). To facilitate direct comparison with I_B^{LSCO}, the normalization of I_B^{LCO} shown in this plot neglects the hypothesized intensity (~10% of the total intensity) associated with the CuO_6 octahedra occupied by localized holes. Curve C shows the prediction of our model [see Eq. (1)]. (b) The density of itinerant holes p_O in $La_2CuO_{4+\delta}$ deduced from I_B^{LCO}, and the fraction of pinned holes n_{Sr}/x in $La_{2-x}Sr_xCuO_4$ predicted by the model (curve D, plotted against the lower and right-hand axes). Curve E shows an independent determination (Ref. 9) of p_O, and curve F $p_O = \delta$.

NMR measurements reveal that B sites are also adjacent to the i-O,[16] and thus implicate the Coulomb interaction between the doped hole and the negatively charged dopant in pinning. Neutron scattering results[23,11] show that the insertion of the i-O in the LaO layer [in the (distorted) tetrahedron composed of the apical oxygens of the O_6 octahedra centered on the copper atoms] displaces the neighboring apical oxygens from their normal positions leading to a tilted and distorted octahedron. This tilts the local electric field gradient (EFG) at the copper site since the dominant contribution to the local EFG comes from the nearest-neighbor oxygen ions of the $\mathrm{CuO_6}$ octahedra. In the presence of an applied field $\mathbf{H}_0$, the nuclear quadrupole interaction causes a shift $\nu_Q^{(2)}$ dependent on the relative orientation (angle θ) of the crystalline axes with respect to $\mathbf{H}_0$. Because $\partial\nu_Q^{(2)}/\partial\theta$ vanishes for $\theta=90°$, the effect of the distribution of EFG tilts, $\Delta\theta_{\rm EFG}$, on the linewidth is minimal there; its effect increases as $\mathbf{H}_0$ is tilted away from 90°, and the rate of the increase in linewidth is proportional to $\Delta\theta_{\rm EFG}$. By measuring this rate we find that $\Delta\theta_{\rm EFG}^A=1.6°$ and $\Delta\theta_{\rm EFG}^B=4.6°$.[16] The considerably larger EFG tilt for the B sites means that the B sites are associated with octahedra distorted by, and therefore adjacent to, the i-O.

The primary role of the Coulomb interaction with the charged dopant in the pinning mechanism provides a solution to another puzzle: $I_B^{\rm LCO}$ is much larger than $I_B^{\rm LSCO}$ [see Fig. 2(a); note the different scales], which means a larger fraction of localized holes in $\mathrm{La_2CuO_{4+\delta}}$ relative to $\mathrm{La_{2-x}Sr_xCuO_4}$. This is consistent with two facts: the larger charge of the i-O relative to a substitutional Sr and the previously recognized[9] fact that many doped holes in $\mathrm{La_2CuO_{4+\delta}}$ are not itinerant. Johnston *et al.*[9,11] have measured the dependence of itinerant hole density in $\mathrm{La_2CuO_{4+\delta}}$ on i-O content. They conclude that rather than two holes per i-O, for $\delta\leq 0.08$ each O dopant and Sr dopant contribute the *same* number of itinerant holes: $p_{\rm O}/p_{\rm Sr}=\delta/x$, while for $\delta>0.08$, $p_{\rm O}/p_{\rm Sr}=(2\delta-0.08)/x$.[9] This result [taking into account $p_{\rm Sr}(x)$ as determined below] is shown by curve E in Fig. 2(b). One interpretation of this unexpected result is that missing holes are confined to short bonds between the i-O and a neighboring apical oxygen.[23] We argue instead that the holes are pinned in the planes.

A simple model based on the primary role of the Coulomb interaction with the dopant in pinning quantitatively explains the doping dependence of the pinned hole density for both O and Sr doping. The larger charge of the i-O relative to the background, -2 compared to -1 for the Sr, is responsible for the much larger fraction of pinned holes. We will denote the number of pinned (itinerant) holes per Cu by n_α (p_α), where $\alpha=\mathrm{O}$ for $\mathrm{La_2CuO_{4+\delta}}$ and $\alpha=\mathrm{Sr}$ for $\mathrm{La_{2-x}Sr_xCuO_4}$. Since a pinned hole on a given Cu site will eliminate that site from the NQR spectrum and produce four nearest-neighbor B sites, $I_B^{\rm LCO}=4n_{\rm O}/(1-n_{\rm O})$. The results for $p_{\rm O}$ $(=2\delta-n_{\rm O})$ obtained from $I_B^{\rm LCO}$ are shown in Fig. 2(b). We postulate that a charge of -1 is inadequate to localize a hole, whereas the -2 charge of the oxygen *or* of a cluster of two or more Sr ions will pin a hole. Each i-O in $\mathrm{La_2CuO_{4+\delta}}$ should then pin a hole, so we expect $n_{\rm O}=\delta=p_{\rm O}$; this relationship, shown by curve F in Fig. 2(b), agrees very well with the data for $\delta\simeq 0.10$ and 0.12, as well as with Johnston's results (curve E). For $\delta\simeq 0.06$, however, significantly *more* holes are pinned than predicted by our model. We believe this reflects an additional tendency of holes to localize in response to the antiferromagnetic (AF) background. There is an energy cost to delocalizing a hole since this suppresses AF interactions, and this may contribute a confining potential. This will diminish as hole density increases causing the background antiferromagnetism to become less dominant.

Starting from the assumption that *two adjacent* Sr *ions* are necessary to pin a hole in a $\mathrm{CuO_6}$ octahedron in $\mathrm{La_{2-x}Sr_xCuO_4}$, we obtain a quantitative (with no free parameters) understanding of the magnitude and doping dependence of $n_{\rm Sr}$ and thus I_B in $\mathrm{La_{2-x}Sr_xCuO_4}$. Yoshimura *et al.*[7] argued that the B site arises when an apical oxygen site becomes *vacant* due to proximity to two Sr dopants. This scenario is clearly not appropriate for $\mathrm{La_2CuO_{4+\delta}}$ which contains substantial *excess* oxygen. Kennard *et al.* noticed the correlation between I_B and the probability of having two Sr neighbors, but argued against the apical oxygen vacancy model on several grounds.[5] We follow this approach to determine, instead, the probability P (assuming a random distribution of Sr dopants) that a given site will be occupied by a Sr, and will have at least one Sr amongst its four nearest in-plane neighbors. Such a Sr cluster will pin a hole and produce four B sites, so for small x we find

$$I_B^{\rm LSCO}(x)=4P(x)=4\frac{x}{2}\sum_{k=1}^{4}{}_4B_k\left(1-\frac{x}{2}\right)^{4-k}\left(\frac{x}{2}\right)^{k}, \qquad (1)$$

where ${}_4B_k=4!/[k!(4-k)!]$. This expression gives curve C in Fig. 2(a) which agrees very well with the data of Yoshimura *et al.* Thus quantitative understanding of the (very different) intensities of the B lines in $\mathrm{La_2CuO_{4+\delta}}$ and $\mathrm{La_{2-x}Sr_xCuO_4}$ can be obtained within this picture.

Neutron diffraction studies[23] show that the distortion associated with the i-O produces a single, unique apical oxygen, and thus a unique $\mathrm{CuO_6}$ octahedron in $\mathrm{La_2CuO_{4+\delta}}$; it is likely this will be the hole pinning site. The two adjacent Sr dopants will have two equivalent nearest Cu ions; presumably the hole chooses one of these as the localization site. Again, while the Coulomb interaction is primarily responsible for pinning, other (e.g., electron-phonon or magnetic) interactions must also play a role.

We assert, then, that $p_{\rm Sr}$ is less than x: $p_{\rm Sr}=x-n_{\rm Sr}$ where $n_{\rm Sr}=P(x)$ [$\simeq 0.85x^2$ for $x\lesssim 0.15$, see curve D, Fig. 2(b)]. Hall measurements which indicate that $p_{\rm Sr}\simeq x$ for $x<0.15$ (Ref. 24) are sufficiently uncertain (due to both the temperature dependence of the Hall number and the sensitivity of the results to oxygen nonstoichiometry) that they cannot rule out this small missing fraction. Optical spectra indicate the presence of bound charge states (with binding energy ~0.5 eV in $\mathrm{La_{2-x}Sr_xCuO_4}$).[25,26]

In conclusion, we propose that a significant fraction of holes doped into metallic and superconducting lanthanum cuprate are localized in $\mathrm{CuO_6}$ octahedra. This hypothesis enables a consistent account of the magnitude of ν_Q^B in the NQR spectra and the insensitivity of ν_Q^B to the means of doping. It also provides a quantitative explanation of the doping dependence of the intensity of the B line in both $\mathrm{La_2CuO_{4+\delta}}$ and $\mathrm{La_{2-x}Sr_xCuO_4}$. There is strong evidence for ordering and c-axis staging of i-O.[11–13,16,27] The localized charge in $\mathrm{La_2CuO_{4+\delta}}$ is adjacent to the i-O, so we expect that the localized charge is ordered as well. The occurrence of high-T_c superconductivity in the presence of this large density of localized holes (~0.1/Cu) and the fact that the larger maximum T_c's [as high as 58 K (Refs. 9 and 10)] are found in $La_2CuO_{4+\delta}$, which has the larger density pinned holes, leads us to speculate that ordering may mitigate their otherwise disruptive effects, or that, rather than suppressing superconductivity, these ‘‘defects’’ may play a supportive role.[3] We note that the spin lattice relaxation and Knight shifts for A and B sites are very similar[16] indicating that the pinned hole does not have a strong local effect on properties of the itinerant holes. This ordering may be related to the larger maximum T_c achieved in $La_2CuO_{4+\delta}$. These pinned holes could also play a contributing role in the spin gap.[28]

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