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_{2-x}Sr_{x}CuO_{4-δ} 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_{x}CuO_{4-δ} indicate that a substantial fraction of the doped holes in these materials localize in CuO_{2} 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. 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. Recent extended x-ray-absorption fine structure measurements provide evidence for stripes in La_{1.85}Sr_{0.15}CuO_{4-δ} 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 63Cu 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. 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_{2}SrCuO_{4-δ} is very similar to that in La_{1.85}Sr_{0.15}CuO_{4}, the former which has a significantly larger density (−δ 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_{2}CuO_{4+δ} found in neutron scattering studies appears to be related to this higher T_{c}.

The single crystals of La_{2}CuO_{4+δ} used in this work were grown first as La_{2}CuO_{4} by a flux method. The δ = 0.10 and 0.12 crystals were then doped by electrochemical oxidation; these crystals have superconducting onset temperatures of about 40 K. Neutron scattering revealed ordering of the interstitial oxygen (henceforth denoted i-O) in the δ = 0.10 sample. The δ = 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) were fit by four appropriately constrained (using known isotopic ratios and quadrupole moments) Lorentzians; the δ = 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 (≈exp[−2(πτf)^2] here). We find that τ_{1} ≈ 25 μsec and τ_{2} ≈ 40 μsec. Extrapolation of our spectra (obtained at τ = 10 μsec) to τ = 0 increases I_{B}^{CSD} (I_{B} is the integrated intensity of the 63Cu B line as a fraction of the total 63Cu intensity; the superscript refers to La_{2}CuO_{4+δ} by ≈ 10%.)
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Electrochemical doping produces broader B lines, causing the peak B-line intensities of the δ=0.10 and 0.12 samples to be smaller than for δ=0.06 in spite of their larger integrated intensities. The spectra shown were obtained at T = 50 K; where examined (for δ=0.06) no temperature dependence to 1_B^LCO was observed.

For 0.01 ≤ δ ≤ 0.06, La_{x}CuO_{y+δ} phase separates 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. The B line is present (see Fig. 1) in macroscopically single phase (δ>0.06) material. While the shift of the B line is very similar to that observed in La_{x−δ}Sr_{δ}CuO_{4}, I_B is much larger in La_{x−δ}Sr_{δ}CuO_{4}; in contrast I_B^LCO = 0.1−0.15 in La_{x−δ}Sr_{δ}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 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. 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. 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. Although an O^{2−} 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_{x−δ}Sr_{δ}CuO_{4} and La_{x−δ}Sr_{δ}CuO_{4} arises from the copper sites neighboring a CuO_{6} octahedron occupied by a pinned hole 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.

NMR measurements reveal that B sites are also adjacent to the i-O, and thus implicate the Coulomb interaction between the doped hole and the negatively charged dopant in pinning. Neutron scattering results 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 CuO₆ octahedra. In the presence of an applied field H₀, the nuclear quadrupole interaction causes a shift ν(2) dependent on the relative orientation (angle θ) of the crystalline axes with respect to H₀. Because ∂ν(2)/∂θ vanishes for θ=90°, the effect of the distribution of EFG tilts, ∆θEFG, on the linewidth is minimal there; its effect increases as H₀ is tilted away from 90°, and the rate of the increase in linewidth is proportional to ∆θEFG. By measuring this rate we find that ∆θEFG=1.6° and ∆θEFG=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^{LCO} is much larger than I_B^{SC} [see Fig. 2(a); note the different scales], which means a larger fraction of localized holes in La₂₋ₓSrₓCuO₄⁺δ relative to La₂₋ₓSrₓCuO₄. This is consistent with two facts: the larger charge of the i-O relative to a substitutional Sr and the previously recognized fact that many doped holes in La₂CuO₄⁺δ are not itinerant. Johnston et al.¹⁰¹¹ have measured the dependence of itinerant hole density in La₂CuO₄⁺δ on i-O content. They conclude that rather than two holes per i-O, for δ=0.08 each O dopant and Sr dopant contribute the same number of itinerant holes: p₀/p₅₈=8/x, while for δ>0.08, p₀/p₅₈=(2δ−0.08)/x.⁹ This result [taking into account p₀(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 nₐ (pₐ), where α=O for La₂₋ₓCuO₄⁺δ and α=Sr for La₂₋ₓSrₓCuO₄. 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^{LCO}=4n₀/(1−n₀). The results for p₀ (=2δ−n₀) obtained from I_B^{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 La₂₋ₓCuO₄⁺δ should then pin a hole, so we expect n₀=δ=p₀; this relationship, shown by curve F in Fig. 2(b), agrees very well with the data for δ=0.10 and 0.12, as well as with Johnston's results (curve E). For δ=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 CuO₆ octahedron in La₂₋ₓSrₓCuO₄, we obtain a quantitative (with no free parameters) understanding of the magnitude and doping dependence of n₅₈ and thus I_B in La₂₋ₓSrₓCuO₄. Yoshimura et al.⁶ 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 La₂₋ₓCuO₄⁺δ 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

\[ I_B^{LSCO}(x) = 4P(x) = \frac{\sum_{k=1}^{4} k B_k \left[ \left( \frac{x}{2} \right)^2 \right]}{1 - \left( \frac{x}{2} \right)^4}, \]

where \( B_k = 4! \left[ \frac{1}{k!} (4-k)! \right] \). 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 La₂₋ₓCuO₄⁺δ and La₂₋ₓSrₓCuO₄ can be obtained within this picture.

Neutron diffraction studies²³ show that the distortion associated with the i-O produces a single, unique apical oxygen, and thus a unique CuO₆ octahedron in La₂₋ₓCuO₄⁺δ; 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 p₅₈ is less than x: p₅₈=x−n₅₈, where n₅₈=P(x) [≈0.85x² for x≤0.15, see curve D, Fig. 2(b)]. Hall measurements which indicate that p₅₈≈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 La₂₋ₓSrₓCuO₄).²⁵²⁶

In conclusion, we propose that a significant fraction of holes doped into metallic and superconducting lanthanum cuprate are localized in CuO₆ octahedra. This hypothesis enables a consistent account of the magnitude of ν(2) in the NQR spectra and the insensitivity of ν(2) to the means of doping. It also provides a quantitative explanation of the doping dependence of the intensity of the B line in both La₂₋ₓCuO₄⁺δ and La₂₋ₓSrₓCuO₄. There is strong evidence for ordering and c-axis staging of i-O's.¹¹⁻¹³,¹⁶,²⁷ The localized charge in La₂₋ₓCuO₄⁺δ is adjacent to the i-O, so we expect that the localized charge is ordered as well. The occurrence of high-Tc superconductivity in the presence of this large density of localized holes (~0.1/Cu) and the fact that the larger maximum Tc’s [as high as 58 K (Refs. 9 and 10)] are
found in La$_2$CuO$_4$$_{+\delta}$, which has the larger density pinned holes, leads us to speculate that ordering may mitigate their otherwise disruptive effects, or that, rather than suppressing superconductivity, these “defects” may play a supportive role. We note that the spin lattice relaxation and Knight shifts for A and B sites are very similar indicating that the pinned hole does not have a strong local effect on properties of the itinerant holes. This ordering may be related to the larger maximum $T_c$ achieved in La$_2$CuO$_4$$_{+\delta}$.

These pinned holes could also play a contributing role in the spin gap.

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