Where do the doped holes go in $La_{2-x}Sr_xCuO_4$? A close look by XAFS

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Abstract.
Polarized x-ray absorption fine structure (XAFS) measurements at the La and Sr sites in $La_{2-x}Sr_xCuO_4$ ($0.075 \lesssim x \lesssim 0.35$) indicate that doped holes introduced with Sr are not uniformly distributed in the CuO_2 planes but reside in impurity states with the majority of charge located on CuO_6 octahedra coupled to the Sr dopants by an apical oxygen (denoted as Sr octahedra). A model based on doped hole-induced Jahn Teller (JT) distortions of these Sr octahedra indicates the impurity states are overlapping singlet and triplet ones resulting from pairings of intrinsic and extrinsic holes. The more mobile singlet pairs reside in the CuO_2 planes, are bound by more than 0.1 eV and could Bose-condense into a superconducting state. The predominant appearance of (mostly) out-of plane triplet states at high x is intimately related to the 2D-3D crossover in transport properties and could relate to the observed loss of high T_c in the overdoped regime, as confinement of carriers to the CuO_2 planes is reduced.

INTRODUCTION

La_2CuO_4 is a strongly correlated electron system with one *intrinsic* hole per molecular unit. The Coulombic repulsion between neighboring holes (U_d) being larger than the overlap bandwidth at half filling results in a Mott-Hubbard (M-H) insulator with full (empty) lower (upper) Hubbard bands. Substituting Sr^{+2} for La^{+3} adds *extrinsic* (or doped) holes which are localized at low x but become itinerant for $x \gtrsim 0.06$ where a 2D insulator-metal (I-M) transition is observed together with high T_c superconductivity. The lack of a complete understanding of the anomalous normal state properties [1] is partly due to the lack of information on the character of the *doped* holes: Are they periodic in the CuO_2 planes as in a Zhang Rice singlet band? Do all the doped holes contribute to metallic transport above the I-M transition? Is there doped charge density outside the CuO_2 layers?

Polarized x-ray absorption near-edge structure (XANES) [2] measurements have been instrumental in providing insight into the orbital character of intrinsic and extrinsic holes. These measurements, however, cannot distinguish between the inequivalent oxygen sites (O(1) in the CuO_2 planes and O(2) in the rock-salt La-O layers) or those nearby Sr or La atoms, as they average over all O atoms. XAFS measures the local environment about the La and Sr atoms separately despite their residing in the same crystallographic site with a majority of La atoms. This is of advantage over other techniques for average and local structure determination which measure a weighted average of La and Sr sites, dominated by the La sites. Diffraction techniques assume periodicity, while the randomly doped system is inherently non-periodic and local structural distortions around the dopants will therefore go undetected by diffraction.

How can XAFS give information on the electronic states of the doped holes? Only if the electronic and structural degrees of freedom are coupled which is the case here as evident in the *Jahn-Teller* (JT) [9] deformation of CuO_6 octahedra in La_2CuO_4.

EXPERIMENTAL

Quite complete information on the local structures about both La and Sr atoms was obtained from our data and, together with experimental details and analysis methods, can be found in refs. 4,5. Here we present results of new measurements at the Sr K-edge extending the x-range far beyond the values previously reported [5]. We concentrate on the results for the apical oxygens.

The apical oxygens about La atoms have a similar distribution as in the pure material, i.e., a single site located at a distance of 2.36(1) Å from the La atom (2.41(1) Å from the almost collinear Cu atom). We denote the CuO_6 octahedra with only La atoms bonded to its two apical oxygens as La-octahedra. The apical oxygens about the Sr impurity atoms, however, have a double-site distribution peaked at distances of 2.55(2) Å and 2.25(3) Å from Sr (2.22(2) Å and 2.52(3) Å from the Cu atom, respectively), with the sum of occupation of the two sites being one oxygen [5]. No significant change in both the occupation and disorder of each site is found up to room temperature (RT). The improvement of the two site model over the one site model decreases with x (Fig. 1) due to changes in the relative occupation of the two sites, the long Sr-O(2) distance becoming more occupied at the expense of the short distance (Fig. 2a). No measurable variation of the Sr-O(2) apical distances occurs with x (Fig. 2b).

DISCUSSION

Whereas a different local environment around Sr could be expected due to a different charge/ionic radius of Sr^{+2} compared to La^{+3}, a *double* site distribution is inconsistent with charge/size effects. It is, however, an indication of both strong lattice-hole interaction occurring around the Sr atoms and the dopant-induced holes being peaked on the CuO_6 octahedra bonded to a Sr atom, i.e., the Sr-octahedra. This result is different from the splitting in the apical oxygen reported in other

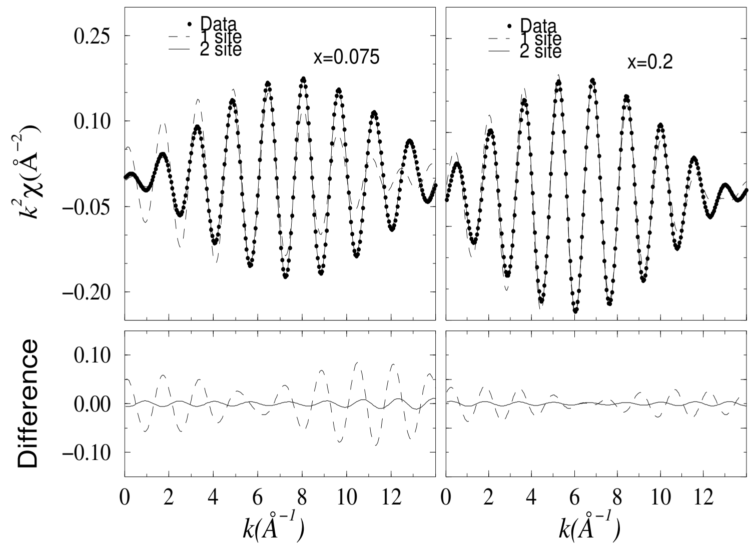

FIGURE 1. Fits to isolated Sr-O(2) XAFS for $x = 0.075, 0.2$ at T=10K using both single and double site models. Difference spectra (Fit - Data) shown in the lower panel for both models. Statistical noise (1σ) is about 0.003.

investigations of high T_c superconductors [6], where the splitting occurs periodically throughout the solid. Here, the double site occurs *only* near the dopant Sr atoms.

In this scenario, the La-octahedra have only an intrinsic hole while the Sr-octahedra have two holes, one intrinsic and one extrinsic. Contrary to the periodic distribution of intrinsic holes, the extrinsic holes produce an impurity wave func-

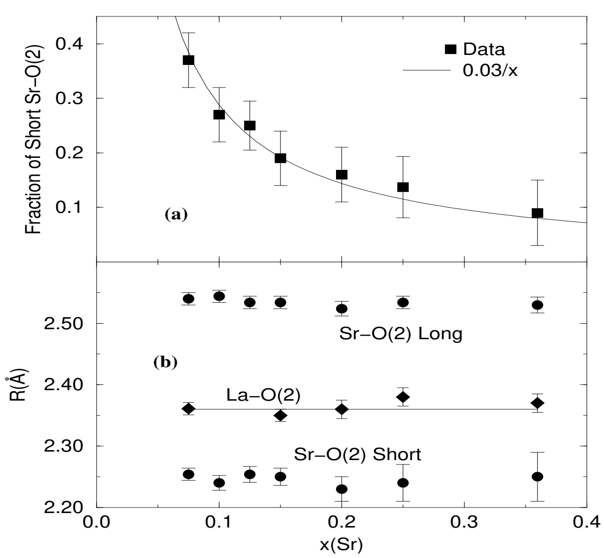

FIGURE 2. (a) Fractional occupation of Short Sr-O(2) distance and (b) Sr-O(2), La-O(2) distances versus x.

tion distribution. Since $La_{2-x}Sr_xCuO_4$ remains insulating up to a critical value of $x_c \sim 0.06$, it follows that in the dilute limit the doped holes are localized in the Sr-octahedra until the impurity band broadening is sufficient to overcome the localization energy. Since overlap is small a tight-binding approximation can describe the impurity states of doped holes residing in Sr-octahedra.

The La-octahedra, also in the undoped material, have the electron energy levels shown in Fig. 3a. The $x^2 - y^2$ and z^2 orbitals are non-degenerate due to both the tetragonal crystal field and the JT nature of the Cu $3d^9$ ions, resulting in an elongated CuO_6 octahedra with distances Cu-O(2)$\approx$ 2.41 Å and Cu-O(1) $\approx$ 1.90 Å.

Figures 3(b,c) show the impurity energy levels for Sr-octahedra with intrinsic and extrinsic holes. Even though these states have the symmetry of Cu *3d*-orbitals, the extrinsic holes reside not only on the Cu atoms but on the octahedron with a majority of the hole charge on the oxygen atoms [7,8]. The singlet $^1A_{1g}$ state (3b) has both holes in the $x^2 - y^2$ state and is analogous to the Zhang-Rice singlet [7] (two important differences are discussed below). The triplet $^3B_{1g}$ state (3c) has holes in each of $x^2 - y^2$ and z^2 orbitals with parallel spins. Here the exchange interaction lowers the triplet state energy to near that of the singlet state. In the triplet state no JT force is present since equal populations of $x^2 - y^2$ and z^2 orbitals result in no energy gain induced by a tetragonal distortion. This results in hole-induced contraction of the Sr-octahedra, the *anti-JT* effect [10,11]. In the singlet state, however, the JT energy gain is twice that of the La-octahedra resulting in an *enhanced JT* elongation of the Sr-octahedra.

The JT distortions of Sr-octahedra explain the double site observed by XAFS for the apical oxygen bridging Cu and Sr atoms. In the *enhanced JT* case (singlet)

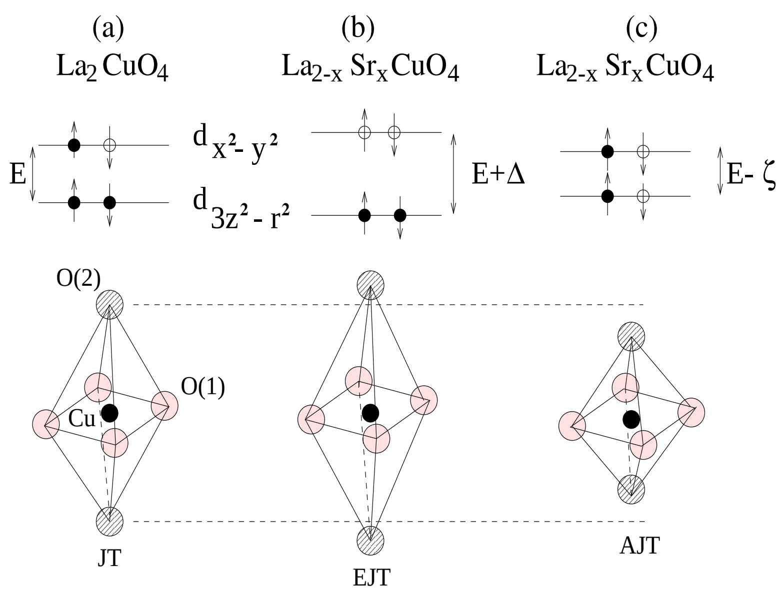

FIGURE 3. Energy levels and resultant octahedral distortions due to intrinsic and extrinsic holes: (a) Intrinsic hole; La-octahedra (b) Spin-singlet, enhanced JT case (c) Spin-triplet, anti-JT case.

the apical oxygens are shifted away from Cu towards the Sr, producing the short Sr-O(2) distance. In the *anti-JT* case (triplet) the apical oxygen shifts towards Cu away from the Sr atom, producing the long Sr-O(2) distance. The two sites detected by XAFS thus give evidence for two kinds of spin-differentiated JT distortions induced by the donated holes. It is interesting to note that the contraction of the Sr-octahedra in the anti-JT case (0.2 Å) results in a Cu-O(2) distance nearly the same as Ni-O(2) in La_2NiO_4, where Ni^{+2} is in its high spin, non-JT state.

No temperature dependence in the occupation of singlet and triplet states is found by XAFS, up to RT, indicating their binding energies are larger than 300 $K_B \approx 25$ meV and that there is significant overlap between these states. This is in agreement with LDA + U first principles calculations [11] which find that doped holes occupy impurity states with $x^2 - y^2$ symmetry located inside the M-H gap with an ionization energy of ~ 0.1 eV. The same paper calculates, neglecting the impurity potential, the triplet state to lie only ≈ 54 meV above the ground state. Including the Sr impurity potential could reasonably lower the triplet to overlap the singlet band, resulting in both being populated by doped holes. Fractional hole occupancy of both states is essential for impurity band conduction, as full occupancy of either would result in a full $x^2 - y^2$ insulating singlet band (Fig. 3b) or half filled $x^2 - y^2$ and z^2 triplet bands with an insulating Hubbard gap.

The binding interaction between the Sr-impurity and its extrinsic hole is essential for producing the impurity states. At a concentration $x_c \approx 0.06$ the impurity local energy levels transform into impurity bands and metallic conduction occurs. The singlet state, having a greater overlap integral (at least by a factor of three) than the triplet [13] at any given x, dominates the conductivity above x_c and probably does so throughout the range where high T_c exists.

The 2D nature of conductivity observed at the I-M transition [1] is expected since singlet states have mostly in-plane orbital character. At higher x triplet states with mostly out-of-plane character increase their fraction of the doped holes (Fig. 2a). This increased occupation, together with increased overlap, explain the reduction in resistivity anisotropy ratio ρ_c/ρ_{ab} with x that brings about the 2D-3D crossover in transport properties at $x \sim 0.25 - 0.3$ [1]. We note that the anisotropy ratio predicted by band theory (~ 30, an order of magnitude smaller than observed) is not very dependent on x, in contrast with experiment.

We note that the doped charge distribution in the singlet impurity band differs from that of the Zhang-Rice singlet band [7], where doped holes are periodic over all of the CuO_6 octahedra. Also both singlet and triplet impurity states are accompanied by a distortion of the Sr-octahedra from the undoped configuration.

The self-binding of singlet JT pairs together with the small overlap between pairs resulting from their wavefunctions being peaked about the Sr sites suggest that they may be treated as an entity and could Bose-Einstein condense at low temperature. Therefore, high T_c of $La_{2-x}Sr_xCuO_4$ would be explained as superfluidity of charged bosons [14] where disappearance of superconductivity above T_c is not due to a dissociation of pairs but to loss of coherence between pairs.

Two inequivalent copper sites are found in NMR and NQR measurements [15,16], one of them appearing and increasing with doping. These sites can be explained by the presence of La-and Sr-octahedra. Coupling of singlet and triplet states via perturbations such as spin-orbit and electron-electron interactions mixes these states at a rate much faster than the inverse linewidth of the NMR/NQR lines ($\sim 1\mu$sec), giving an average signal for the Sr-octahedra. Recent improved NMR measurements [17] found that both inequivalent Cu sites sit in axially symmetric environments, consistent with the enhanced JT and anti-JT distortions preserving the axial symmetry of the Sr-octahedra.

The large binding energy ($\gtrsim 0.1$ eV) of the impurity states pairs is consistent with RT polarized XANES measurements at the O K-edge of $La_{2-x}Sr_xCuO_4$ [2]. These show a large spectral weight transfer of the oxygen $2p$ hole states, with doping, from those in the upper Hubbard band (intrinsic holes) to the doped impurity hole states. This spectral weight transfer shows the impurity states are an intimate mixture of intrinsic and extrinsic holes due to the strong interaction between them, consistent with their strong pairing in our model.

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