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Electronic States of Doped Holes in $La_{2-x}Sr_xCuO_4$: A Unique Application of XAFS

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Polarized XAFS measurements on powder of $La_{2-x}Sr_xCuO_4$ with aligned c-axes find that apical oxygens neighboring *only* the Sr dopants have a double-site distribution. The occupation of both sites totals one oxygen, is independent of temperature, but changes with x. A theory of the double-site is presented in terms of Jahn-Teller distortions (JT) induced by the extrinsic doped holes paired with the intrinsic holes present in the undoped $x = 0$ sample. These pairs reside in singlet and triplet impurity states and satisfy Bose statistics. It is speculated that high T_c occurs because of Bose-condensation of the singlet pairs. Because of the strong electron-lattice interaction of the JT effect, XAFS can determine the corresponding electronic states in this special case.

Keywords: Jahn-Teller distortions, Impurity States, Superconductivity

Undoped La_2CuO_4 is an insulating, anti-ferromagnetic, strongly correlated electron system with one hole per molecular unit. Doping with Sr or Ba causes both insulator to metal and superconductor transitions. Even after twelve years of intense investigation since the discovery of this new class of high T_c superconductors, there remains controversy about the mechanism of the pairing that leads to the superconductivity. Quite physically distinct theories are still being proposed for this mechanism. Further experiments are clearly required to help further restrict the possible model or models of high T_c.

The structure of this material as a function of temperature and dopant concentration x has been accurately and exhaustively determined by diffraction (Radaelli *et al.*, 1994), as has its transport and magnetic properties. The structure consists of single Cu-O planes separated by two La/Sr-O planes. The Cu-atoms have four nearest neighbor oxygens in the plane and two oxygens, called apicals, one above and the other below the plane, the six oxygens forming an octahedra. The apical oxygens make up the oxygen atoms in the La/Sr plane. The apical oxygens serve an important function by forming the bond that allows transfer of the doped holes to the Cu-O planes. It is generally agreed that the mobile doped holes are concentrated in the Cu-O planes, produce metallic conduction and are the carriers that are involved in the pairing mechanism.

The information lacking from the diffraction measurements is the deviations from the average structure introduced by the disordered Sr impurities. Because of this disorder, the average structure determined by diffraction differs from the local structure. Since the superconducting coherence length of high T_c materials is of the order of 10 Å, the pertinent structure to be used to understand superconducting properties is the local one over this scale, and not the structure averaged over long range as diffraction determines. XAFS is the premier method to determine the local structure up to 4-5 Å. It also allows determining the structure separately about the La and Sr atoms and, thus, can determine any perturbation of the undoped structure introduced by the Sr atoms, even for the small concentration range over which superconductivity occurs, namely, $0.07 < x < 0.25$, which occupies between 0.035 and 0.125% of the La sites.

XAFS measurements were made on samples from the same batch used in the neutron-diffraction study of Radaelli *et al.*(Radaelli *et al*, 1994) to ensure that any differences between the local and average structures are not due to material differences. The sample was powdered and the resultant single crystal grains oriented in a magnetic field, as described elsewhere (Haskel *et al.*, 1997), so that their c-axes were well aligned, though their a-b axes remained randomly misoriented. The oriented sample allowed use of the polarization dependence of the XAFS signal to determine independently the signal for polarization along and perpendicular to the c-axis. This doubles the information content obtainable from unoriented samples and this extra information was essential to uniquely determine the disorder introduced around the dopants. In particular, the c-polarization data of nearest neighbor oxygens to the Sr dopants separates the apical signal from the much stronger planar oxygen signal present in the unoriented powder. This allows accurate analysis of the apical oxygen distribution that could not be performed from unoriented data. Quite complete information on the local structures about both La and Sr atoms was obtained from our data (Haskel *et al.*, 1996; Haskel *et al.*, 1997). Here we include new measurements at the Sr K-edge which extend the x-range far beyond the $x = 0.075, 0.1$ values previously reported. This report concentrates on the results found for the apical oxygens as this information appears to be most striking for understanding the high T_c mechanism.

The apical oxygens about the La atoms are found to have a similar distribution as in the undoped material, namely, a single-site located at a distance of 2.35 Å. However, the distribution about the Sr atoms is a *double-site* distribution peaked at distances of 2.54 and 2.25 Å, with the sum of occupation of the two sites being one oxygen. No change in both the occupation and disorder of each site is found up to room temperature.

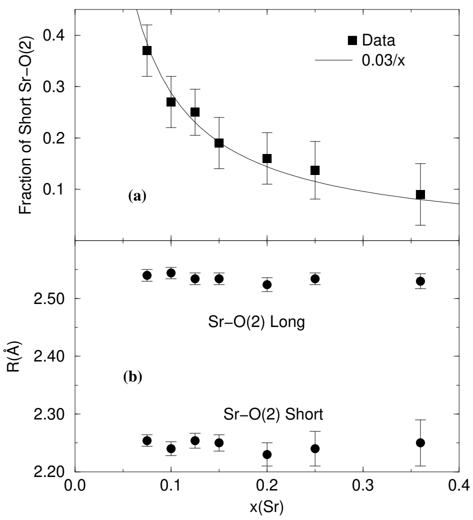

Figure 1
(a) Fraction of occupation of the short Sr-O(2) site as a function of the Sr concentration x. (b) The long and short Sr-O(2) site distances as a function of x. The sum of the occupation of the short and long sites is one oxygen.

However, the x-dependence of the sites does vary, as shown in Figure 1a, with the long Sr-O site becoming more occupied at the expense of the short site with increasing x. Figure 1b shows that no significant variation of the Sr-O apical distances occurs with increasing x.

The significance of the result is its evidence of a strong lattice-hole interaction only around the Sr-atoms, indicating that dopant holes are peaked in the vicinity of the Cu-octahedra that contain the apical oxygen bonded to a Sr atom (denoted by the Sr- octahedra). (The CuO_6 octahedron with only La atoms bonded to its two apical oxygens, denoted as a La-octahedron, has a small amplitude of the dopant hole.). In fact, as discussed below, the doped holes fill two different, overlapping, impurity states whose relative occupation varies with x. Note that this result is not consistent with the implicit assumption of most models of high T_c that the holes are periodically distributed in the Cu-O planes. The present result is different from the splitting in the apical oxygen site reported in XAFS investigations of other high T_c superconductors, where the splitting occurs periodically throughout the solid (Mustre-de Leon *et al*, 1992; Stern *et al.*, 1992; Bianconi *et al.*, 1992). In our case, the double-site occurs only near the dopant Sr atoms.

It should be emphasized that the ability to discern the double-site which occurs only near the Sr atoms is unique to XAFS because of its capability to focus on the local atom arrangement about each type of atom separately, its high spatial resolution and sensitivity to dilute atoms, coupled with its crystal orientation sensitivity to x-ray polarization.

The quantitative and qualitative understanding of the double-site distribution is based on our cluster calculations (Polinger *et al.*, 1998). To distinguish the holes present in the solid when no dopant atoms are present from those donated by the dopant, we call the dopant holes extrinsic and the others intrinsic. The calculations indicate that both the intrinsic and extrinsic holes have most of their charge residing on the oxygen atoms. The XAFS results give evidence that the extrinsic holes are not periodically distributed among the CuO_6 octahedra but are peaked about only the Sr-octahedra. Thus, they produce a wave function distribution analogous to impurities in semiconductors. From the experimental result that doped $La_{2-x}Sr_xCuO_4$ remains insulating till a critical value of x_c, where it becomes metallic and superconducting, it is concluded that the extrinsic holes are immobilized about their Sr-octahedra in the dilute limit till the impurity band broadening is sufficient to overcome the correlation energy between holes. Thus, a tight-binding approximation can be used to describe the holes where the units in which the Wannier states of the holes reside are the CuO_6 octahedra. The Sr-octahedra have two holes, one intrinsic and one extrinsic, while the La-octahedra have only an intrinsic hole.

The energy states of CuO_6 octahedra can be used to gain insight into the Wannier states that occur in the solid. The La-octahedra have the energy levels shown in Figure 2a. There is one intrinsic hole in the level with $x^2 - y^2$ symmetry which has the highest energy, while the next highest level with no holes has $3z^2 - r^2$ (z^2) symmetry. Note that, though these Wannier states have d-state symmetry, they do not reside only on the Cu atoms but reside on the octahedron with a majority of charge on the oxygen atoms. The $x^2 - y^2$ and z^2 levels are degenerate in cubic symmetry, where all oxygens have the same distance from the Cu atom. However, they split, as shown in Figure 2a, when the octahedron is distorted so that the apical oxygens are displaced further from the Cu atom. Such a distortion lowers the electronic energy, since two electrons have their energy lowered, while only one has its energy raised by the same amount.

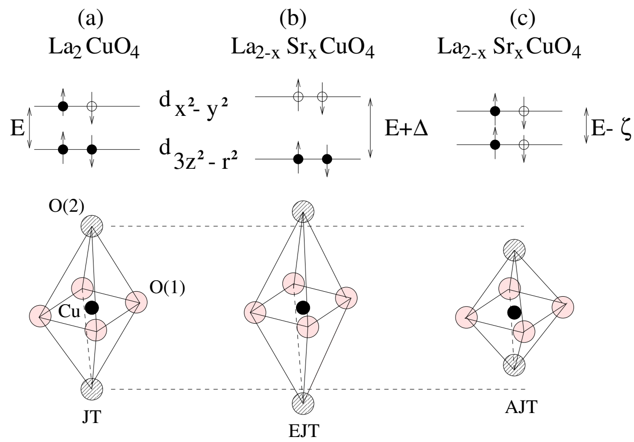

Figure 2
Illustrating the energy levels of the intrinsic and extrinsic holes and their corresponding CuO_6 octahedral distortions due to the Jahn-Teller effect (relative to the distortion induced by intrinsic holes alone (a)). (b) The singlet *enhanced-JT* case, and (c) the triplet *anti-JT* case.

This elongation which results from the lifting of the degeneracy is known as the Jahn-Teller (JT) effect (Bersuker & Polinger, 1989). The magnitude of the resultant distortion is determined by minimizing the sum of the electronic destabilizing energy and the stabilizing energy of the resultant elastic strain. This JT distortion is present in the undoped La_2CuO_4 material and in the La-octahedra of the doped material.

Figures 2b and 2c show the energy levels for the Sr-octahedra with their two holes (one intrinsic and the other extrinsic). The situation of both the holes in the $x^2 - y^2$ state with opposite spins is shown in Figure 2b. Figure 2c shows energy levels for one hole each in the $x^2 - y^2$ and z^2 states. On the one-electron energy level diagram shown in the figure, it appears that this latter state is higher energy, since the z^2 state has lower energy. However, since the holes have parallel spins in Figure 2c (triplet states), while they have anti-parallel spins in Figure 2b (singlet state), the exchange or Hund's rule interaction, between the two holes lowers the energy of the triplet state to near that of the singlet state (Anisimov *et al.*, 1992). With band broadening and accounting for the impurity potential, these two states overlap.

The triplet state manifests no JT elongation (*anti-JT* case) (Bednorz & Müller, 1986; Anisimov *et al*, 1992), since a distortion would raise and lower (by the same amount) one electron and no gain in energy ensues. However, in the tetragonal field of the solid due to the c-axis elongation from the majority La-octahedra, the energy levels remain split, though not as much as in the La-octahedra. In contrast, the singlet state has an *enhanced-JT* elongation of the Sr-octahedra, since the decrease in energy of the two electrons is not compensated by increased energy of any electrons. The *enhanced-JT* singlet and the *anti-JT* triplet states explain the double-site observed for the apical site around the Sr atoms by XAFS. The singlet state, by increasing the Cu-apical oxygen distance, produces the short Sr-apical oxygen distance, and similarly the long Sr-apical oxygen distance is associated with the triplet state. Thus, the two sites as detected by XAFS give direct evidence for two, spin differentiated, JT impurity states induced by the donated hole. The lack of temperature dependence in the occupation of these two holes states up to room temperature (T_r) indicates that their ionization energies are large compared to k_BT_r, while the increase of occupation of the triplet state with increasing x as shown in Figure 1a, shows that the triplet state becomes more stable relative to the singlet.

The intimate coupling between the electronic configuration and structural distortions of CuO_6 octahedra that characterizes the JT effect results in a unique application of XAFS in this high T_c material; i.e., deriving *electronic* structure information via the measured lattice distortions.

Other experimental evidence on $La_{2-x}Sr_xCuO_4$ in agreement with the results presented here include: (a) XANES measurements (Chen *et al.*, 1992) at the oxygen K-edge showing a large spectral weight transfer, with doping, from states in the upper Hubbard band (intrinsic holes) to hole states introduced with doping, indicating strong coupling between intrinsic and extrinsic holes as expected from our model. These XANES measurements also show that extrinsic holes have predominant p_z orbital character above $x \approx 0.08$, consistent with the XAFS results that the z^2-states (which have most of their amplitude on the apical oxygens' $2p_z$ states) dominate the extrinsic holes above $x \approx 0.075$; (b) Nuclear quadrupole resonance experiments (Hammel *et al.*, 1998) show two inequivalent Cu sites, one of them increasing with x, which can be explained by Cu sites with only intrinsic holes and those with both intrinsic and doped holes.

The conclusions from the XAFS measurements and their theoretical interpretation are:

The extrinsic and intrinsic holes pair and produce two overlapping JT impurity states, one with singlet spin and the other with triplet spin. The overlap of triplet states is small and these states may not contribute mobile carriers. The overlap of singlet states is larger and, thus, they provide the mobile carriers which occur as x increases above a critical value $x_c = 0.07$ and the material undergoes an insulator-metal transition. As x increases above x_c, the triplet holes become more stable, increasing their fraction of the extrinsic holes. Since the triplet holes may be localized, this feature may explain the drop in Tc for $x > 0.15$. The singlet states contain two holes and obey Bose statistics. If they retain their integrity as they conduct, they could become superconducting at the temperature where they undergo Bose-condensation into the ground state, explaining high T_c for this material.

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