Jahn-Teller Impurity States in LaSrCuO: XAFS Evidence and Implications for High $T_c$ Superconductivity

Victor Polinger, Daniel Haskel and Edward A. Stern

Physics Department, Box 351560, University of Washington, Seattle Washington 98195, USA

(October 28, 2018)

Polarized XAFS measurements on powder of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with aligned $c$-axes find that apical oxygens neighboring only the Sr dopants have a double-site distribution. This result requires that the doped holes reside in impurity states peaked on the CuO$_6$ octahedron neighboring the dopant (denoted as Sr-octahedrons). A model of the double site is presented of two co-existing spin differentiated (singlet and triplet) Jahn-Teller (JT) distortions of the Sr-octahedrons induced by an extrinsic doped hole pairing with the intrinsic hole. It is speculated that Bose-condensation of the singlet pairs, bound by $\gtrsim 0.1$ eV, produces superconductivity.

Pure $\text{La}_2\text{CuO}_4$ is an insulating, strongly correlated electron system with one intrinsic hole per molecular unit. Doping with Sr at the La site causes an insulator-to-metal transition (IMT) and a high $T_c$ superconductor, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. There still remains controversy about the mechanism of pairing that leads to superconductivity. We discuss here implications of the recent XAFS experimental results that there is a double-site distribution of the apical oxygens neighboring only Sr dopant atoms $\text{La}_2\text{CuO}_4$. Using compelling physical arguments we arrive at a model which can explain the double-site distribution and is consistent with other experimental and theoretical published results that directly relate to the local atomic and carrier properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Possible implications for the mechanism of high $T_c$ superconductivity in this material are discussed.

Diffraction measurements $\text{La}_2\text{CuO}_4$ have given detailed information on the long range averaged periodic structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. However, 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. Whenever disorder is present in a crystalline material, as occurs in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ because of the random Sr doping, the local and average structure differ. XAFS $\text{La}_2\text{CuO}_4$ is the premier method to determine the local structure up to 4-5 Å. Whereas diffraction techniques average over the La/Sr sites, XAFS allows determining the structure separately about the La and Sr atoms and, thus, can determine any perturbation introduced by the Sr atoms.

The average structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ consists of single CuO$_2$ planes separated by two La/Sr-O planes. The Cu atoms have four nearest neighbor oxygens in the plane and two oxygens, called apicals, above and below the plane, the six oxygens forming an elongated octahedron. The apical oxygens, residing in the La/Sr-O planes, serve an important function by forming the bond that allows transfer of the doped holes to the CuO$_2$ planes. It is believed that the mobile doped holes reside in the CuO$_2$ planes, produce metallic conduction and are the carriers that are involved in the pairing mechanism.

XAFS measurements were made on samples from the same batch used in the neutron-diffraction study $\text{La}_2\text{CuO}_4$ to ensure that any differences between local and average structures are not due to material differences. Quite complete information on the local structures about both La and Sr atoms was obtained from our data $\text{La}_2\text{CuO}_4$, and new measurements at the Sr K-edge extend the $x$-range far beyond the $x = 0.075, 0.10$ values previously reported $\text{La}_2\text{CuO}_4$. We concentrate here on the results found for the apical oxygens as this information is most pertinent for understanding the character of the carriers in this material.

The apical oxygens about the La atoms are found to have a similar distribution as in the pure material, namely, a single site located at a distance of 2.35(1) Å from the La atom (2.42(1) Å from the almost collinear Cu atom). We denote such CuO$_6$ octahedrons with only La atoms bonded to its two apical oxygens as La-octahedrons. 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 $\text{La}_2\text{CuO}_4$. No change in both the occupation and disorder of each site is found up to room temperature (RT). However, the occupation of the sites varies with $x$, as shown in Figure 1, with the long Sr-O distance becoming more occupied at the expense of the short distance. No measurable variation of the Sr-O apical distances occurs with $x$.

The significance of this result is its evidence of a strong lattice-hole interaction only around the Sr atoms, indicating that dopant-induced (extrinsic) holes are peaked only in the vicinity of the CuO$_6$ octahedrons that are bonded to a Sr atom (the Sr-octahedrons). The present result is different from the splitting in the apical oxygen site reported in other investigations of high $T_c$ superconductors $\text{La}_2\text{CuO}_4$, where the splitting occurs periodically throughout the solid. In our case, the double site occurs...
only near the dopant Sr atoms.

The Sr-octahedrons have two holes, one intrinsic and one extrinsic, while the La-octahedrons have only an intrinsic hole. Thus, the extrinsic holes produce an impurity wave function distribution. From the experimental result that doped La$_{2-x}$Sr$_x$CuO$_4$ remains insulating up to a critical value of $x_c \sim 0.07$, where it becomes metallic and superconducting, it follows that in the dilute limit the extrinsic holes are immobilized about their Sr-octahedrons till the impurity band broadening is sufficient to overcome the localization energy. Thus, overlap is small and a tight-binding approximation can describe the impurity states of the extrinsic holes residing at Sr-octahedrons.

The energy states of CuO$_6$ octahedra can be used to gain insight into the impurity states that occur in the solid. We start with one-electron energy levels, then add multi-electron (lattice-electron and exchange interactions). The La-octahedrons, also in the undoped material, have the electron energy levels shown in Fig. 2(a). The intrinsic hole is in the highest energy orbital with $x^2 − y^2$ symmetry while the lower lying $3z^2 − r^2$ orbital ($z^2$) is fully occupied. Even though these states have the symmetry of Cu $d$-orbitals, they reside not only on the Cu atoms but on the octahedron with a majority of the hole charge on the oxygen atoms. The $x^2 − y^2$ and $z^2$ orbitals are degenerate in cubic symmetry (regular octahedron) but split, as shown in Figure 2(a), when the octahedron is elongated along the $c$-axis and contracted in the basal plane. Such a tetragonal distortion, $Q_0$, equally raises/lowers the energy of the $x^2 − y^2$ and $z^2$ orbitals, respectively, by $VQ_0$, where $V$ is the corresponding constant of electron-lattice coupling. Due to the different electron occupancies of these orbitals the decrease in energy is $−VQ_0$.

The distortion accompanying the lifting of the orbital degeneracy is known as the Jahn-Teller (JT) effect. The magnitude $Q_0$ of the distortion is determined by minimizing the sum of the JT destabilizing energy, $−VQ_0$, and the stabilizing energy of the resultant elastic strain, $kQ_0^2/2$ ($k$ is the elastic force constant). At the equilibrium distortion $Q_0$ the JT effect lowers the energy by $−kQ_0^2/2 = −V^2/2k$.

The Sr-octahedrons have two holes, one intrinsic and one extrinsic hole. Thus, the extrinsic holes produce an impurity wave function distribution. From the experimental result that doped La$_{2-x}$Sr$_x$CuO$_4$ remains insulating up to a critical value of $x_c \sim 0.07$, where it becomes metallic and superconducting, it follows that in the dilute limit the extrinsic holes are immobilized about their Sr-octahedrons till the impurity band broadening is sufficient to overcome the localization energy. Thus, overlap is small and a tight-binding approximation can describe the impurity states of the extrinsic holes residing at Sr-octahedrons.

The energy states of CuO$_6$ octahedra can be used to gain insight into the impurity states that occur in the solid. We start with one-electron energy levels, then add multi-electron (lattice-electron and exchange interactions). The La-octahedrons, also in the undoped material, have the electron energy levels shown in Fig. 2(a). The intrinsic hole is in the highest energy orbital with $x^2 − y^2$ symmetry while the lower lying $3z^2 − r^2$ orbital ($z^2$) is fully occupied. Even though these states have the symmetry of Cu $d$-orbitals, they reside not only on the Cu atoms but on the octahedron with a majority of the hole charge on the oxygen atoms. The $x^2 − y^2$ and $z^2$ orbitals are degenerate in cubic symmetry (regular octahedron) but split, as shown in Figure 2(a), when the octahedron is elongated along the $c$-axis and contracted in the basal plane. Such a tetragonal distortion, $Q_0$, equally raises/lowers the energy of the $x^2 − y^2$ and $z^2$ orbitals, respectively, by $VQ_0$, where $V$ is the corresponding constant of electron-lattice coupling. Due to the different electron occupancies of these orbitals the decrease in energy is $−VQ_0$.

The distortion accompanying the lifting of the orbital degeneracy is known as the Jahn-Teller (JT) effect. The magnitude $Q_0$ of the distortion is determined by minimizing the sum of the JT destabilizing energy, $−VQ_0$, and the stabilizing energy of the resultant elastic strain, $kQ_0^2/2$ ($k$ is the elastic force constant). At the equilibrium distortion $Q_0$ the JT effect lowers the energy by $−kQ_0^2/2 = −V^2/2k$.
producing the long Sr-apical oxygen distance. Thus, the two sites detected by XAFS give direct evidence for two kinds of spin-differentiated JT distortions induced by the donated holes.

The above theoretical arguments predict equal but opposite displacements of the two sites from the La-apical distance of 2.35 Å. The experiments find that the enhanced JT site is displaced by 0.1 Å while the anti-JT site is displaced by 0.2 Å (in opposite directions). As is customary in discussing JT distortions, these arguments assume a symmetric environment of the Sr-octahedron and neglect its breathing mode contraction induced by the extrinsic hole. Having a Sr dopant at one end and a La atom at the other breaks the symmetry and, together with the breathing mode, modify the distortions.

The change in energy due to the JT distortions can be estimated by \( E_{JT} \sim -kx_0^2 \), where \( x_0 \) is the displacement of each of the two apical oxygens from the configuration with no JT driving force. Here the approximation is used that since the apical oxygens distort much more than the planar oxygens, their contribution to the energy change dominates. The anti-JT triplet has no driving force from the JT effect and will be used as the zero of the displacement and JT energy (its associated octahedron, however, is not regular due to the tetragonal field of the average crystal structure). The XAFS measurements determine \( k = 2.6 \text{ eV/Å}^2 \) from the temperature dependence of the Cu-apical bond distance and \( x_0 \) is determined directly from the two sites around the Sr. The values of \( E_{JT} \) and \( x_0 \) are listed in Table I for the three states: triplet, intrinsic or La-octahedron, and singlet. In the case of the singlet state the enhanced JT distortion lowers the energy relative to that of the intrinsic La-octahedron.

The ionization energy to remove the local extrinsic hole from the singlet or triplet state into the extended state of the conduction band includes the JT distortion energy and the local hole-impurity interaction energy. The lack of temperature dependence in the relative occupation of singlet and triplet states found by XAFS, up to RT, indicates their binding energies are larger than 300 K \( B \approx 25 \text{ meV} \). This is in agreement with LDA + U first principles calculations \(^1\) that include the impurity potential at \( x = 0.25 \) but not allowing relaxation of the lattice. The calculation finds that doped holes occupy impurity states with \( x^2 - y^2 \) symmetry located inside the Mott-Hubbard gap with an ionization energy of \( \sim 0.1 \text{ eV} \). Relaxing the lattice from the JT to the enhanced JT value lowers the energy further by \( \sim 0.03 \text{ eV} \). The same paper calculates, neglecting the impurity potential but including the lattice relaxation \(^1\), the triplet state to lie only \( \approx 54 \text{ meV} \) above the ground state. It is reasonable to expect that including the Sr impurity potential will lower the triplet to overlap the singlet band, resulting in both being populated by the doped holes, as found in our measurements. Note from Table I that the enhanced JT energy \( \sim 0.23 \text{ eV} \) is an important contribution for stabilizing the singlet impurity state.

The large binding energy \( \gtrsim 0.1 \text{ eV} \) of the impurity states pairs is consistent with polarized x-ray absorption near edge structure (XANES) measurements at RT \(^2\) on the O K edge. 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 impurity hole states introduced with doping. This weight transfer, which occurs even at RT, 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.

The interaction between the Sr-impurity and its extrinsic hole introduces binding which is essential for producing the impurity states. The impurity states are formed because it is energetically favorable to keep the extrinsic holes near the impurity than have them distributed periodically along the Cu-O planes. The singlet impurity state is different from the Zhang-Rice singlet \(^3\) which is periodically distributed over all of the CuO\(_6\) octahedra. Another important difference is that both the singlet and the triplet impurity states are accompanied by a considerable distortion of the Sr-octahedrons from the undoped configuration.

At a concentration \( x_c \approx 0.07 \) the impurity local energy levels transform into impurity bands and the material becomes conductive. The question arises which impurity state dominates the conductivity, the singlet or the triplet. Just above \( x_c \) the answer is given by that state which has the greatest overlap between neighboring Sr sites as the other will still be localized. The singlet state, having a greater extent in the plane, has a greater overlap integral by a factor of three than the triplet \(^12\) \(^13\) at a given \( x \), if the planar amplitude of the states is the same. Our cluster calculations indicate that this factor may be significantly higher since the \( z^2 \) triplet state has less probability to reside on the CuO\(_2\) planes than the \( x^2 - y^2 \) state. Thus, the singlet state dominates the conductivity above \( x_c \), and probably does so throughout the range where high \( T_c \) exists.

We argue that the singlet and triplet states are present simultaneously on each Sr-octahedron and not separately on different ones. The latter case implies that there are two types of Sr-octahedrons, \( S \) and \( T \), containing only singlet or triplet pairs, respectively. Then two separate impurity “bands” would be formed, one a singlet from the \( S \) sites and the second a triplet from the \( T \) sites. However, neither could conduct. The \( S\)"band" has two holes per orbital state and thus is completely full while in the \( T\)"band" the two orbital states are half full and would have their own Mott-Hubbard gap. Having overlapping singlet and triplet states at each impurity site is critical for allowing impurity band conduction. The overlap allows hole transfer between bands so that each is neither half nor completely full.

The tendency of extrinsic holes to occupy \( z^2 \) orbitals

---

\(^1\) Reference to the calculations and their results.
\(^2\) Reference to the XANES measurements.
\(^3\) Reference to the Zhang-Rice singlet model.
was predicted by Khomskii and Neimark [12]. Zaanen et al. [13] treated the two types of carriers more extensively, including band formation, and obtained a concentration dependence for them similar to the one in Fig. 1. The predominant occupation of triplet states by the doped holes is in apparent contradiction with the interpretation of XANES measurements by Chen et al. [20] of a predominant in-plane character for the doped holes. However, as pointed out by Chen et al., concluding on the orbital character of doped holes from XANES measurements is difficult due to the large spectral weight transfer with doping from upper Hubbard band states to the impurity states, as discussed above. This large weight transfer is contrary to the rigid band model and shows a strong modification of the intrinsic holes states due to the addition of doped holes. We note that the measurements by Chen et al. do find a large increase in the oxygen $p_z$ orbital character of holes with doping, consistent with the significant increase of $z^2$ states found by XAFS.

Although there is a JT distortion accompanying the singlet pair, this is not a polaron. A polaron carries its distortion with it as it moves from site to site. In the case here the distortion is at each impurity site only, and does not follow the pair as it translates from site to site as then the distortion would have to appear on the intervening La-octahedrons. The JT distortion just changes the local environment about each Sr-octahedron only, with its attendant lowering of the energy of the singlet state, as occurs for impurity states embedded in a host of La-octahedrons. Though the impurity state JT pairs discussed here are bosons, they are not the bosons composed of bipolarons that have been suggested as a possible mechanism for high- $T_c$ superconductivity [12].

The strong self-binding of the singlet JT pairs suggests the speculation that they may move in the crystal as an entity and form a Bose-Einstein condensate with superfluid characteristics at low temperature assuming an appropriate dispersion curve. Therefore, high $T_c$ of La$_{2-x}$Sr$_x$CuO$_4$ would be explained as superfluidity of charged bosons [12] where disappearance of superconductivity above $T_c$ is not related to a dissociation of pairs, but to a loss of coherence between pairs. Some additional arguments supporting this possibility are the larger single particle excitation gap than the Andreev gap [16] and the persistence of a pseudogap above $T_c$ [15].

The two inequivalent copper sites found in nuclear magnetic and quadrupole resonance (NMR, NQR) measurements [18, 19], one of them increasing with $x$, can be explained in our model by the presence of La- and Sr-octahedrons. 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-octahedrons.

In summary and conclusion, two coexisting, spin differentiated, JT distortions of Sr-octahedrons are responsible for the double site distribution of apical oxygens around Sr impurities. Intrinsic and doped holes are paired in impurity states bound on Sr-octahedrons by these lattice distortions and the attraction of the doped hole to the Sr impurities. The triplet states with out of plane $z^2$ character increase their fraction of doped holes with $x$; yet planar $x^2 - y^2$ singlet states dominate the conductivity due to their greater overlap. The high binding energy of singlet states, $\gtrsim 0.1$ eV, suggests they retain their integrity as they conduct and can Bose-condense into a superconducting ground state. Since pairing persists up to at least RT, the properties of the carriers above $T_c$ cannot be treated by a rigid band model, which assumes that intrinsic and extrinsic holes are uncoupled, as is done when extrapolating band calculations of the undoped material to describe the normal state carriers.

It should be emphasized that the model proposed here has experimental support only for La$_{2-x}$Sr$_x$CuO$_4$ and further experiments need to be performed to determine how general this model is for understanding high $T_c$ in other materials.

We are pleased to thank I. Bersuker, Y. Yacoby, G. Bersuker and N. N. Gor’inchoi for helpful and stimulating discussions, as well as the support of DOE Grant No. DE-FG03-98ER45681.

[1] D. Haskel et al., Phys. Rev. B 56, R521 (1997).
[2] P. G. Radaelli et al., Phys. Rev. B 49, 4163 (1994).
[3] E. A. Stern and S. M. Heald, in Handbook of Synchrotron radiation, edited by E. E. Koch (North-Holland, New York, 1983), Ch. 10, pp.995–1014.
[4] D. Haskel et al., Phys. Rev. Lett. 76, 439 (1996).
[5] J. Mustre-de Leon et al. in Lattice Effects in High Tc Superconductors (World Scientific, Singapore, 1992); Y. Bar-Yam, T. Egami, J. Mustre-de Leon and A. R. Bishop, eds., p. 39; E. A. Stern et al., ibid p.51; A. Bianconi et al., ibid p. 65; T. Egami, et al. in Electronic Structure and Mechanisms of High Temperature Superconductivity, ed. J. Ashkenazi, and G. Vezzoli (Plenum, NY, 1991).
[6] F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759 (1988).
[7] J. B. Grant and A. K. McMahan, Phys. Rev. Lett. 66, 488 (1991).
[8] H. Jahn and E. Teller, Proc. R. Soc. London A 161, 220 (1936).
[9] I. B. Bersuker and V. Z. Polinger, Vibronic Interactions in Molecules and Crystals (Springer-Verlag, New York, 1989).
[10] J. G. Bednorz an K. A. Muller, Z. Physik B-Condensed Matter 64, 189 (1986).
[11] V. I. Anisimov et al., Phys. Rev. Lett. 68, 345 (1992).
[12] D. I. Khomskii and E. I. Neimark, Physica C 173, 342
Jahn-Teller energies, $E_{JT}$. $x_0$ is the displacement of each apical oxygen from the Cu induced by the JT effect. The Anti-JT, JT, and Enhanced JT octahedrons are ones with triplet paired holes, an intrinsic hole, and singlet paired holes, respectively.

| Octahedron type | Anti-JT | JT   | Enhanced JT |
|-----------------|---------|------|-------------|
| $x_0$(Å)        | 0.0     | 0.2  | 0.3         |
| $E_{JT}$(eV)    | 0.0     | -0.10| -0.23       |