Altered Sr atomic environment in $La_{2-x}Sr_xCuO_4$

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Abstract: The Sr local atomic environment in the high T_c superconductor $La_{2-x}Sr_xCuO_4$ was probed by polarized XAFS measurements at the Sr K-edge on oriented powder samples with $x = 0.075, 0.1$ at T=20K. We confirmed that Sr indeed substitutes at the La site in this compound, but alters the first neighbor oxygen environment. This was found by determining the location of the neighboring metal atoms up to the fifth shell distances through fitting the Sr XAFS, and comparing with La K-edge polarized XAFS in the same samples and with diffraction results. The significant distortions in the immediate oxygen environment of the Sr atoms can be an important factor contributing to the mechanism of the structural and high T_c phase transitions in these cuprates.

New evidence for the presence of Sr-induced distortions in the $La_{2-x}Sr_xCuO_4$ system comes from recent X-ray diffuse scattering experiments[1] where strong diffuse scattered intensity was observed in c^*-cuts of reciprocal space in the neighborhood of bragg peaks. The momentum transfer dependence of the measured intensity implied distortions with a remarkable c-axis rms displacement $\langle u_z^2 \rangle^{1/2} \simeq 0.4$Å. Sr K-edge XANES results[2] were previously interpreted to conclude that the introduction of Sr under normal preparation conditions leads to the removal of the O(2) apical oxygen to the Sr and the creation of an oxygen defect in a nearby interstitial site. Recent XANES theoretical calculations[3], however, showed that the XANES features attributed by Tan *et. al* to the removal of the apical oxygen to the Sr can be reproduced with the same oxygen configuration as about the La atoms. This controversy exemplifies the need of a quantitative approach to the question of Sr-induced structural distortions in $La_{2-x}Sr_xCuO_4$.

In this work, the Sr and La atomic environments were studied *separately* by tuning the X-ray energy to match the corresponding inner-shell electron excitation of either atom. The orientation dependence of the XAFS signal was exploited by rotating the c-axis magnetically-aligned-powder relative to the linearly polarized electric field vector of the synchrotron radiation. The high sensitivity of nearly collinear multiple scattering (MS) paths to the presence of the intervening focusing atom was used to determine the occupancy of the O(2) apical oxygen to the Sr atoms.

Sr K-edge measurements were performed in transmission at beamline X-11A of the National Synchrotron Light Source, using a Si(111) double-crystal monochromator. Though aligned along the c-axis, the powder was randomly oriented in the ab-plane. For such a case, the XAFS of a single scattering (SS) path i at an angle θ_i with the c-axis is

$$\chi_c^{(i)}(k) = 3cos^2\theta_i \chi_{ran}^{(i)}(k);\ \chi_{ab}^{(i)}(k) = 3\frac{sin^2\theta_i}{2}\chi_{ran}^{(i)}(k), \tag{1}$$

with $\chi_c(k)$, $\chi_{ab}(k)$ being the measured XAFS with the electric field parallel to the c and ab orientations, respectively, and $\chi_{ran}(k)$ the XAFS signal of an unoriented powder. We used FEFF6 as our theoretical standard[4] to calculate the random XAFS $\chi_{ran}(k)$ using the average atomic positions obtained in the diffraction studies and the UWXAFS package[5] to *simultaneously* fit both polarized XAFS data to the theory by weighting their respective amplitudes as given in Eq. 1 and varying θ_i. In addition, adjustable structural parameters were added to the theory, such as changes in half path length, δr_i and mean square displacements, σ_i^2, to account for possible deviations in the local structure from the average structure. Simultaneous fits to both polarizations allow a further reduction in the number of fitting parameters for scattering paths which contribute to both c and ab oriented XAFS. Data and theory in a k-range $[3, 15]$Å^{-1} were weighted by k^2 and Fourier transformed to r-space. The region of r-space fitted, including MS, was $r = [1.9, 5.3]$Å. Fig. 1 shows best fits to both orientations for the $x = 0.1$ sample at T=20K.

Our main results can be summarized as follows: a) The Sr-Cu and Sr-La distances and mean square displacements, up to the fifth shell are, within 0.01Å and 0.001Å^2, the same as those as for La-Cu and La-La found in the fittings to La K-edge polarized data[6] and in agreement with the distances found by diffraction for the average structure. This result indicates that Sr indeed substitutes at the La site and is consistent with the Sr^{+2} and La^{+3} ions having nearly the same size. b) Simultaneous fits to SS Sr-O(2) apical and MS Sr-O(2)-Cu paths at $r \approx 4.76$Å show that the O(2) apical oxygen to the Sr is fully occupied with N=0.92 ± 0.2. However, it is displaced along the c-axis, towards the Cu atoms, by $\delta r = 0.21 \pm 0.1$Å making the Sr-O(2) distance $r = 2.56 \pm 0.1$Å instead of the 2.35Å found for La-O(2) apical by both XAFS[6] and diffraction studies[7]. The disorder found in the Sr-O(2) apical bond is $\sigma^2 = 0.026 \pm 0.01$Å^2, an order of magnitude more than for La-O(2) apical. The δr and σ^2 obtained for the (Sr/La)-O(2)-Cu MS paths, however, are, within 0.01Å and 0.001Å^2, the same for both the Sr and La central atoms and in agreement with the

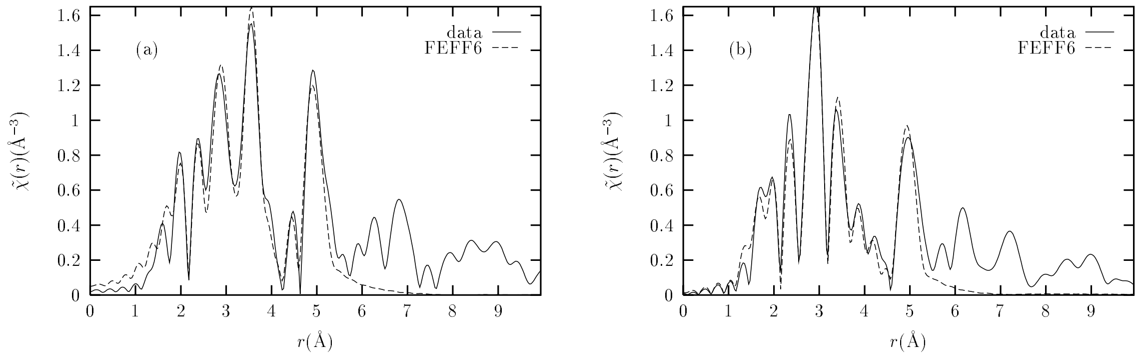

Figure 1: Fits to the x=0.1 sample at T=20K for X-rays polarized (a) along the c-axis and (b) in the ab-plane. The magnitude of the complex Fourier transform of $k^2\chi(k)$ is shown.

average structure, indicating that the disorder of the O(2) apical oxygens is along the c-axis and hence does not affect the path length of the MS paths. The implications of the distortion in the O(2) apical oxygen distances are many. Since the distortion brings the O(2) apical much closer to the Cu-O planes, it more effectively induces carriers under Sr-doping, and could explain the increase of out-of-plane O $2p_z$ character of the doped holes observed by Chen *et. al*[8]. Also, being closer, the O(2) apical can serve as a more effective "bridge" between the Cu-O and La-O layers and hence explain the relative increase in out-of-plane conductivity with doping[9]. Finally, adding the c-axis static displacement of 0.21Å to the rms displacement $(\sigma^2)^{1/2} = 0.16$Å we get an rms deviation from the average structure $\langle u_z^2 \rangle^{1/2} \simeq 0.37$Å. This is remarkably close to the measured rms displacement of the atoms contributing to the diffuse scattering observed by Isaacs *et. al.* c) The average structure has two different La/Sr-O(1) distances to the O(1) oxygens in the Cu-O planes at $r_s = 2.591$Å and $r_l = 2.675$Å. La-O(1) distances were found to be in agreement with the diffraction results[6]. The splitting is mainly due to the tilt pattern of the CuO_6 octahedra which buckles the Cu-O planes. The Sr XAFS analysis gives for the angles these bonds form with the c-axis $\theta^{(s)} = 44.1 \pm 6.1°$ and $\theta^{(l)} = 41.9 \pm 6.2°$, respectively, consistent with the values $\theta^{(s,l)} = 47.8°, 44.2°$ found in the diffraction studies[7]. However, the Sr-O(1) distances are found to be $r_s = 2.542(10)$Å and $r_l = 2.734(12)$Å, respectively. In order to accommodate the changes in Sr-O(1) distances while the Sr-Cu distances remain unaltered, some Cu-O(1) bonds in the basal plane of the CuO_6 octahedra must become distorted compared to the average structure. We believe these distortions are *not* associated with a *rigid* tilt of the CuO_6 octahedra involved because then a corresponding distortion of the O(2) oxygens forming the apex of the CuO_6 octahedra and nearly co-planar with the Sr should have been observed in our analysis, which was not found.

To summarize, when Sr substitutes for La in $La_{2-x}Sr_xCuO_4$ it resides at the La lattice site but distorts considerably its near neighboring oxygen environment. The O(2) apical distortion is most likely crucial for the hole doping mechanism in these cuprates as well a for their transport properties. The Sr substitution directly affects the structure of neighboring CuO_6 octahedra. This could be an important factor in understanding the mechanism of the Sr-induced structural phase transitions in this material. Finally, the Sr-induced distortions are probably the origin of the observed diffuse scattering of these cuprates.

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