Dopant and temperature induced structural phase transitions in $La_{2-x}Sr_xCuO_4$

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The *local* structure about La atoms in oriented $La_{2-x}Sr_xCuO_4$ samples is investigated by means of polarized X-ray Absorption Fine Structure (XAFS) measurements. Diffraction results indicate that the dopant and temperature-induced structural transformations involve decreases, on the *average*, of the tilt angle of the Cu-O octahedra to zero. The XAFS results show that *locally* the tilts do not disappear, the x-induced phase transition has displacive and disorder components, and the T-induced phase transition is purely of disorder character. It is also shown that the Cu-O octahedra tilt locally only in the $\langle 100 \rangle$ direction.

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Knowledge of the structure of high T_c superconductors is basic to a fundamental understanding of their pairing mechanism. Recent measurements of the structural and superconducting properties in high quality, single phase $La_{2-x}Sr_xCuO_4$ crystals [1,2] indicate that bulk superconductivity in this system persists in the tetragonal phase. Diffraction, which measures the *average* structure, indicates that the structural phase transition from orthorhombic LTO (Cmca, No. 64) to tetragonal HTT (I4/mmm, No.139) is mainly characterized by the tilt angle of the Cu-O octahedra decreasing as the dopant concentration or the temperature are increased. This results in non-tilted octahedra and flat Cu-O planes in the tetragonal phase. Since the superconducting coherence length in these high T_c cuprates is rather short ($\zeta \leq 30$ Å) [3], the *local* structure in these materials is of primary importance in determining the superconducting properties.

Consequently, of fundamental interest is the issue of whether the *local* structure differs from the *average* structure, and if it does, how. Previous measurements of the Pair Distribution Function (PDF) obtained from neutron diffraction data on this system [4,5] suggested differences in the tetragonal phase between the average and the local structures. Theories aiming at elucidating the mechanism of high T_c, which rely on the local structure differing from the average one, have been proposed [6]. It is important to give the most definitive answer possible by experiment and we endeavor to do so here by presenting results from XAFS measurements on oriented crystals, the premiere technique for local structure determination. XAFS has the advantage of giving information on *partial* pair correlations involving the absorbing atom, whereas the PDF obtained from neutron diffraction involves pair correlations among *all* pairs, making its interpretation more difficult.

X-ray absorption techniques were previously used to study the $La_{2-x}Sr_xCuO_4$ system [7–9] but no work addressed the structural phase transition as a function of strontium content. Boyce *et al.* [8] measured the Cu K-edge XAFS of an x=0.2 sample from 4 to 300K and found no change in the oxygen environment around the Cu atoms in this range of temperatures. However, as they pointed out, the distortions induced by the tilting of the distorted Cu-O octahedra, if present locally, would not be observed in their analysis since the tilts are about the Cu site whose distances remain essentially unaltered. On the other hand, the La/Sr local environment is the most sensitive to the distortions induced by the structural phase transition, with changes in the planar La-O(2) distances as big as 0.5 Å. Hence, the La/Sr site is the most suitable to investigate the structural phase transition. However, because of the complexity of the nearest neighbor environment of the La atoms, as explained below, oriented samples are essential in order to perform polarization measurements on the samples and get additional information from the polarization dependence of the XAFS.

Samples used for this study are from the same batch used in the neutron diffraction study of Radaelli *et al.* [1] and a detailed description of the sample preparation, superconducting properties and their characterization as single phase can be found there. By using the same batch, discrepancies due to sample preparation are avoided when comparing local structure results to those obtained for the average structure. The sintered pellets were manually ground in a pestle and the resulting powder sieved to a typical $20\mu m$ grain size. The samples were oriented by a method described previously [7] and the high degree of orientation was confirmed by X-ray diffraction to be better than 95%. The polarized XAFS spectra is measured by rotating the samples relative to the polarization vector of the synchrotron radiation. La K-edge measurements were performed in transmission at beamline X-11A at the National Synchrotron Light Source. A Si(311) double-crystal monochromator was used and harmonics minimized by detuning. For the low temperature measurements the samples were put in a sealed copper cold cell filled with He gas for thermal contact and attached to a displex refrigerator.

The experimental XAFS $\chi_{\rm ex}(k)$ is analyzed by use of the UWXAFS analysis package [10]. The FEFF6 theoretical calculation of $\chi_{\rm th}(k)$, which includes polarization effects [11], was performed for the average structure and adjustable structural parameters were added to the theory to account for possible deviations of the local structure from the average. The fitting of the theory to the data is done in r-space, taking care to keep the number of parameters in the fit below the number of independent points in the data [12], and to determine the uncertainties from a reduced χ^2 using standard techniques of error analysis [13].

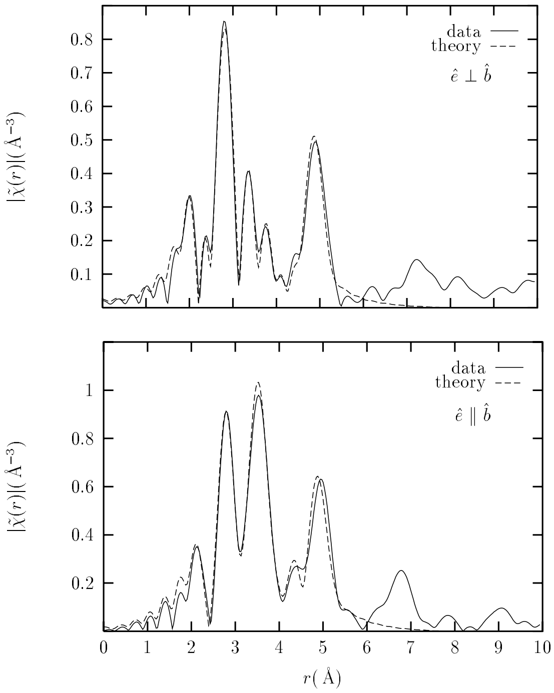

FIG. 1. Fits to the x=0.075 sample at T=20K for x-rays polarized (a) along the long axis of the unit cell and (b) perpendicular to the long axis. The magnitude of the imaginary Fourier transform of $k^2\chi(k)$ is shown.

The La nearest neighbor environment in the orthorhombic phase is composed of nine oxygens at six different distances [1], which, e.g., for the x=0.075 sample at T=20K are in the range $[2.3, 3.0]$ Å. The oriented samples are essential to give enough information to define these distances. Because of the layered structure of these cuprates, by having the polarization vector of the X-rays along the long axis of the unit cell ($\hat{b}$ in the Cmca scheme), the contribution to the XAFS of the nearly in-plane La-O(2) bonds is negligible [14] and then only 3 distances in the oxygen environment contribute to the XAFS (La-O(2) apical and two La-O(1) distances to the O(1) oxygens in the Cu-O planes). One can then find the remaining in-plane La-O(2) distances by analyzing the XAFS for the in-plane polarization and setting the La-O(1) distances to the values found in the fitting for the polarization along the $\hat{b}$ axis. In our fittings, coordination numbers were set to the values dictated by the average structure and full oxygen occupancy was assumed, since even for the x=0.36 sample the oxygen's vacancy concentration was found to be less than 1% [1]. Our preliminary analysis of Sr K-edge polarized XAFS in the same samples indicates that Sr substitutes for La. Thus, longer scattering paths involving La or Sr were weighted with $(2-x)$ or x, respectively. Nearly collinear multiple scattering paths were found to contribute significantly to the XAFS above $r \approx 4.7$ Å and were included in the fits.

Fig. 1 shows fit results to the x=0.075 sample at T=20K for both polarizations. Fig. 2 summarizes the results obtained for the La-O and for the in-plane La-La distances for the different samples at T=20K. Also shown are the values from the average structure [1]. As can be seen in Fig. 2, whereas the La-O and in-plane La-La distances merge into a single distance in the average tetragonal phase, XAFS shows that, locally, they remain split. The La-O and La-La distances agree within experimental uncertainties with their average values up to x=0.15, consistent with a gradual reduction of the tilt angle of the Cu-O octahedra as indicated by the diffraction studies [1,15]. However, as the phase transition is approached (determined by neutron diffraction to be at x=0.21 at low temperature), the magnitude of the tilt of the Cu-O octahedra stops decreasing locally, as seen from the x=0.2 and 0.36 samples. This shows that the local structure about the La retains orthorhombicity in the average tetragonal phase, as previously suggested by Egami *et al.* [4], and implies that the tilt angle of the Cu-O octahedra does not vanish at the LTO $\rightarrow$ HTT phase transition.

To summarize, the LTO phase remains ordered for $x \leq 0.15$ with no discernible difference between the average and local structures. For $x \geq 0.15$ disorder starts appearing as shown by the differences between the local and average structures. Although in the average structure the tilt angle of the Cu-O octahedra decreases continuously to become zero at the LTO$\rightarrow$ HTT phase transition, locally the tilts remains fixed at the $x \approx 0.15$ value and start disordering to become fully disordered at the LTO $\rightarrow$ HTT phase transition.

We also investigated the temperature induced LTO $\rightarrow$ HTT structural phase transition in the x=0.15 sample (transition temperature T $\approx$ 200K), by analyzing La K-edge polarized XAFS data at 20, 40, 145, 210 and 285K. The only changes observed in the La-O distances are increases in thermal disorder about their equilibrium values at T=20K. For the La-La distances a non-negligible thermal expansion is also observed. However, no evidence of the structural phase transition, as found by the diffraction studies, is detected in the local structure in this range of temperatures. From these results it can be inferred that the tilt angle of the Cu-O octahedra does not change in the whole range of temperature studied here. The larger disorder for the O(2) oxygens compared to those of the O(1) oxygens found in the diffraction studies, is consistent with static disorder of the local distortions (mainly in the average tetragonal phase) which we showed are largest for the O(2) oxygens.

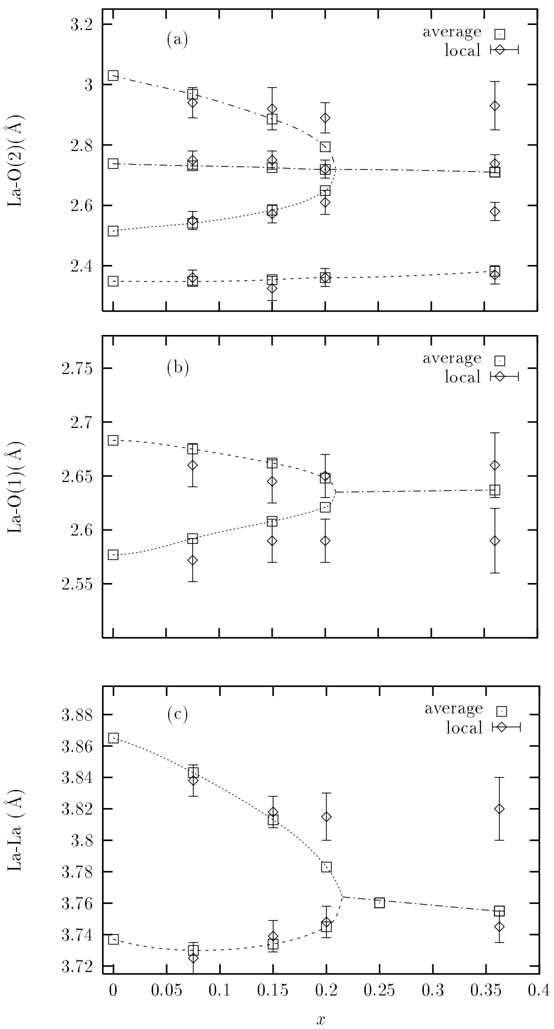

FIG. 2. (a) La-O(2), (b) La-O(1) and (c) in-plane La-La distances as a function of x as obtained from the XAFS analysis at T=20K. The neutron diffraction results [1] are also shown. Dashed lines are guides to the eye.

In order to regain the average tetragonal phase over the long range scale measured by diffraction techniques, the structure must be composed of local domains with orthorhombic symmetry in which the Cu-O octahedra tilts are ordered, but the domains become disordered with one another as the tetragonal phase is approached. In a recent letter Billinge *et al.* [16] reported results of PDF analysis of neutron diffraction data on the $La_{2-x}Ba_xCuO_4$ system. They found that, as opposed to the predictions of the crystal structure models, the Cu-O octahedra do not change their tilt direction at the LTT $\rightarrow$ LTO phase transition and that the long range structure can be obtained from coherent spatial superpositions of ≈ 10 Å sized local LTT variants. The size of the local variants was obtained in that case from the information on intermediate range order in the PDF. The XAFS signal in r-space is strongly damped by the short photoelectron mean free path, which usually limits the information that can be extracted from an XAFS signal to short range order only (in the present case $r < 6$ Å) and then the size of the domains (or in other words the correlation length over which the Cu-O octahedra tilts are ordered) can not be obtained from the XAFS measurement.

One can speculate on the size of the domains by looking at the superconducting properties in the $La_{2-x}Sr_xCuO_4$ system as the dopant content is increased. At low temperature, the LTO $\rightarrow$ HTT phase boundary is located at $x \approx 0.21$. However, there is no apparent effect of the structural phase transition on T_c, including dT_c/dx [1], suggesting that the correlation length of the octahedra tilts at low temperature and for $x \approx 0.21$ is bigger than the superconducting coherence length, of 30 Å for the $La_{2-x}Sr_xCuO_4$ system [3].

It is also of interest to note that the local tilts stop changing at the x value where T_c is a maximum. This may indicate that in addition to the carrier concentration, the tilt angle of the Cu-O octahedra is of importance in determining T_c, as found for Nd-doped $La_{2-x}Sr_xCuO_4$. [17]

Another point that needs to be addressed concerns the tilt *direction* of the Cu-O octahedra. It has been proposed [4] that the tilts in the $La_{2-x}Sr_xCuO_4$ system might be about $\langle 101 \rangle$-type directions and disordered to give the average structure, instead of about $\langle 100 \rangle$ (Cmca notation) as originally proposed by Grande *et al.* [18] and confirmed later in several diffraction studies. By tilting about $\langle 101 \rangle$, it was argued, O(2) atoms could get closer to two La instead of one, presumably leading to a net energy gain since two La-O(2) distances would be closer to their ideal value, determined from the sum of the ionic radii.

Two main differences exist between these two tilting patterns: In a $\langle 101 \rangle$-type tilt two of the O(1) oxygens in the basal plane of the Cu-O octahedra remain in the plane, whereas the other two move above and below the plane splitting the La-O(1) distances in three different distances instead of the two occurring in the $\langle 100 \rangle$ tilts. For the magnitude of the tilt angles at hand, however, this splitting is of about 0.04 Å, which in our fittings can not be distinguished from an increase in thermal disorder of about 0.0004 Å^2 in the La-O(1) distances. The more significant difference, however, appears in the in-plane La-O(2) distances. For the $x = 0.075$ sample, e.g., by tilting about $\langle 101\rangle$ the in-plane La-O(2) distances will be grouped in *two* sets of distances (with differences within each group not bigger than 0.04 Å, due to the orthorhombic splitting) while tilts about $\langle 100\rangle$ result in *three* different sets of distances, as shown in Table 1. After setting the distances and mean square displacement σ^2 for the La-O(1) bonds to the values found in the $\hat{b}$ polarization, we fit the $\hat{a}\hat{c}$-polarized data with both tilt configurations. When the La-O(2) distances are *set* to the values consistent with the $\langle 101\rangle$ tilt, the quality of fit is 100% worse than the one obtained by setting the La-O(2) distances to the $\langle 100\rangle$ tilt configuration. In addition, a $\sigma^2 = 0.06(4)\,\text{Å}^2$ is obtained for the La-O(2) distances for the $\langle 101\rangle$ tilt. This σ^2 is a factor of seven bigger than the value obtained in the diffraction studies [1], assuming no correlations between the La and O(2) displacements. Even in the extreme case of completely anti-correlated motion, this still results in a factor of four too large compared to the diffraction results, confirming that the wrong model is being used in the fitting. We then conclude that our data are not consistent with a $\langle 101\rangle$ tilt configuration of the Cu-O octahedra and that only the $\langle 100\rangle$ tilts are present locally, in agreement with the results of the diffraction studies of the LTO phase [1,15,18].

The absence of $\langle 101\rangle$ tilts is consistent with self- consistent local density functional calculations [19] which indicate that $\langle 101\rangle$ tilts, if present, would lower the electronic density of states at the Fermi level (for $x \approx 0.12$) reducing T_c dramatically, an effect which is observed in the closely related Ba-doped system (which does exhibit such tilts) but not in the $La_{2-x}Sr_xCuO_4$ system.

In summary, polarized XAFS of $La_{2-x}Sr_xCuO_4$ indicates that the Sr dopant and temperature induced LTO $\rightarrow$ HTT phase transitions are of different nature. The Sr-induced transition exhibits a partial displacive character, at least up to x=0.15, which is manifested through a decrease in the tilt angle of the Cu-O octahedra. At higher Sr contents, the local tilts persist but start disordering over long range giving raise to the average structure. The T-induced phase transition does not show displacive character and is only due to disorder; the tilt angle remains the same in the whole temperature range studied here, including the HTT phase. In both cases the local structure of the HTT phase is characterized by the Cu-O octahedra being tilted and the Cu-O planes being not flat. The absence of an effect of the Sr-induced structural phase transition at low-T on the superconducting properties in this system is probably related to the absence of a significant change in the local structure over scales comparable to the superconducting coherence length in this material, suggesting that the correlation length of tilts is somewhat greater than 30 Å. The tilt direction of the Cu-O octahedra was found to be only in the $\langle 100\rangle$ direction, in agreement with diffraction studies. Our data is not consistent with a disordered $\langle 101\rangle$ type tilt pattern. The existence of orthorhombic-like domains (tens of Å size) is predicted to exist in the average tetragonal phase, a result which can be confirmed by other techniques sensitive to intermediate short range order such as PDF analysis of neutron diffraction data or atomic resolution imaging in the TEM.

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TABLE I. Nearest neighbor La-O distances (degeneracies shown in parenthesis) for ⟨100⟩ and ⟨101⟩ tilt configurations for the x=0.075 sample at 20K.

Bond	⟨100⟩	⟨101⟩
La-O(1) (Å)	2.592 (2×) 2.675 (2×)	2.542 2.632 (2×) 2.725
La-O(2) (Å)	2.348 2.541 2.731 (2×) 2.968	2.353 2.550 2.574 2.910 2.950