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Structural disorder and the origin of high T_c suppression in $La_{1.875}Ba_{0.125}CuO_4$

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Polarized x-ray absorption fine structure (XAFS) measurements at all La, Ba and Cu sites were used to study local structural features that accompany the strong T_c suppression at $x \sim 1/8$ in $La_{2-x}Ba_xCuO_4$. Two critical parameters regulating the strength of hole-lattice coupling in this material were determined, i.e., the *direction* and *magnitude* of CuO_6 octahedra local tilts. Our findings include the existence of large disorder in the magnitude of the tilt angle about its average value $\langle\theta\rangle$, with an rms $\sqrt{\langle\delta\theta^2\rangle} \approx 2\langle\theta\rangle$. We suggest that this large disorder strongly scatters a large fraction of states at the Fermi surface for $x \sim 1/8$ leading to the observed T_c suppression.

Keywords: superconductivity, barium doping, mobility gap.

1. Introduction

The origin of T_c suppression at $x \sim 1/8$ in $La_{2-x}Ba_xCuO_4$ remains controversial. Proposed mechanisms include (a) density of states (DOS) effect in which the Fermi level is tuned for $x \sim 1/8$ to the minimum of a split Van Hove singularity (VHS), as found in local-density-approximation (LDA) calculations (Pickett *et. al*, 1991) and (b) the existence of charge density wave (CDW) in the form of 1D stripes which are pinned by the lattice as they become commensurate at $x \sim 1/8$ (Emery *et. al*, 1997; Tranquada *et. al*, 1995). Each of these mechanisms have difficulty. The splitting of the VHS is strongly dependent on the *magnitude* of the tilt angle (quadratically) and the experimental value determined by diffraction is not large enough to open a significant pseudogap in the DOS at the Fermi level (Norman *et. al*, 1993). The large pseudogap obtained in the periodic LDA calculation used a tilt angle twice as large as the experimental value. No direct experimental evidence for or against stripes in $La_{1.875}Ba_{0.125}CuO_4$ has been reported, partly due to the difficulty in obtaining large single crystals required for neutron scattering experiments.

The strength of hole-lattice interaction depends also on tilt *direction*, as shown by the LDA calculations (Pickett *et. al*, 1991) and the observation of charged stripes in low temperature tetragonal (LTT, tilts about $\langle 110\rangle$ axes) but not in low temperature orthorombic (LTO, tilts about $\langle 100\rangle$ axes) structural modifications of insulating nickelates (Tranquada *et. al*, 1994) and cuprates with suppressed superconductivity (Tranquada *et. al*, 1995). It is therefore important to determine *both* direction and magnitude of the local CuO_6 octahedra tilts. Here we exploit the polarization dependence of XAFS in a layered structure and combine information from the three heavy atomic species to obtain that information.

2. Experimental

Powders of $La_{2-x}Ba_xCuO_4$ ($x = 0.125, 0.15$) were synthesized by the combustion technique. Calcination took place at 900°C followed by sintering of powder compacts at 1140°C for four days to achieve a larger grain size, then slowly cooled to room temperature. Lattice parameters and magnetization (T_c) measurements are in agreement with previous studies and give an upper limit to oxygen deficiency in our $x = 0.125$ sample of $\delta = 0.005$ (Takayama *et. al*, 1993; Moodenbaugh *et. al*, 1995). Fine powders ($1 - 3\mu m$) were magnetically aligned in their paramagnetic state resulting in $\hat{c}$-axis oriented powder but random in the $\widehat{aa}$ plane. Measurements were performed in transmission at beam line X-11A of the National Synchrotron Light source using Si(111)(Cu K-edge) and Si(311)(La, Ba K-edges) double crystal monochromators. Polarized XAFS was measured by rotating the aligned samples relative to the polarization vector of the synchrotron radiation.

3. Analysis and Results

The XAFS is analyzed by use of the UWXAFS package (Stern *et. al*, 1995). FEFF6 code, which includes multiple scattering (MS) and polarization (Zabinsky *et. al*, 1995) was used to obtain theoretical standards based on the average structure determined by diffraction (Takayama *et. al*, 1993; Katano *et. al*, 1993)). Structural parameters in the theory such as interatomic distances, r_i, and their mean squared disorder, σ^2, are refined against the data in Fourier transformed r-space by *simultaneously* fitting both polarizations. This allows reducing the number of fitting parameters relative to the number of independent points in the data for scattering paths that contribute in both polarizations. Additional parameters are S_0^2 and an overall E_0 shift to adjust the $k = 0$ reference in experiment and theory. Uncertainties are determined from a reduced χ^2_ν and include the effect of correlations between fitting parameters. Coordination numbers are set to the values of the average structure.

First we address the question of local tilt *direction* of CuO_6 octahedra. The sensitivity of XAFS to changes in tilt direction is at the La site, as the distribution of La-O(2) planar distances is strongly dependent on tilt direction (see fig. 1). The resultant splittings are large enough to be resolved with the maximum photoelectron momentum transfer typical of an XAFS experiment, i.e, $2k_{\max} \approx 30$ Å^{-1}. Since tilts are about Cu sites and nearly rigid, Cu XAFS is almost insensitive to tilt orientation.

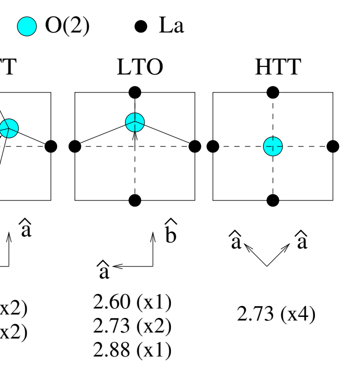

Figure 1
La-O(2) planar distances for CuO_6 octahedra tilts about $\langle 110\rangle$(LTT, $P4_2/ncm$), $\langle 100\rangle$ (LTO, $Bmab$) and high symmetry (HTT, $I4/mmm$) phases. O(2) are apex to octahedra centered about Cu in the CuO_2 plane right below. Small correlated La displacements not shown.

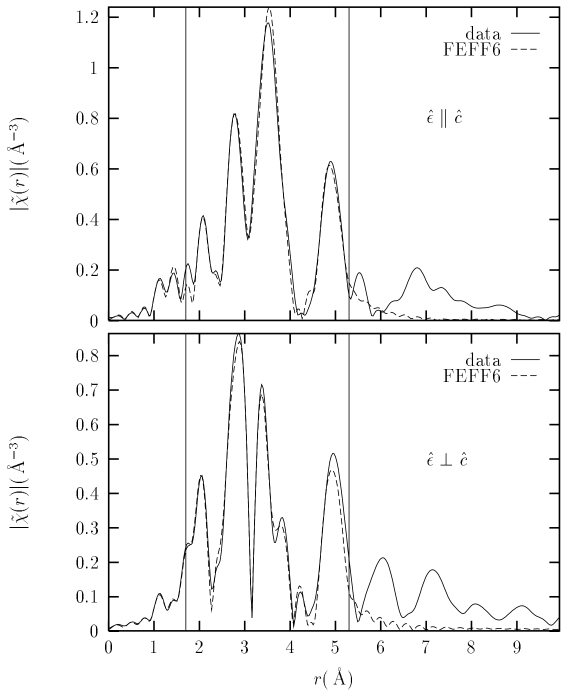

Figure 2
Magnitude of the complex FT of $k^2\chi(k)$ using $k = [3, 16]$ Å^{-1} data for La K-edge, $x = 0.125$ at T=10K. Data and fit shown for both polarizations; vertical lines indicate fitting range. The number of independent points in the data for both polarizations is 59 and a total of 25 fitting parameters were used.

La K-edge fits at T=10K (fig. 2) verified that local tilts are about $\langle 110 \rangle$ axes in agreement with diffraction. The splitting of La-O(2) planar distances (fig. 1) is ΔO(2)=0.252(16) Å compared to 0.230(05) Å of diffraction. In addition, tilting about $\langle 110 \rangle$ axes causes two O(1) oxygens in the basal plane of the CuO_6 octahedra to move out of the plane (in opposite $\hat{z}$ directions). The splitting this introduces in La-O(1) distances was found at Δ O(1)=0.100(17) Å compared to 0.094(14) Å of diffraction. Uncertainties in the diffraction results include variations found in the literature. From the XAFS results, the local tilt angle, averaged over all La atoms is $\langle \theta \rangle = 3.3(4)^\circ$ compared to 3.1(3)° of diffraction. Evidence of disorder, however, is seen by comparing σ^2 values of distances involving O atoms to those obtained in the closely related Sr-doped system (Haskel *et. al*, 1996) (see Table 1). Note that the La-$Cu_{\hat{c}}$ signal (along $\hat{c}$-axis, $r \approx 4.77$ Å) includes MS contributions from nearly collinear La-O(2)-$Cu_{\hat{c}}$ paths.

The origin of disorder can be understood from fits to Ba K-edge polarized data. We confirmed that Ba substitutes at the La site but that the larger Ba^{+2} ion (formal ionic radius 1.35 Å compared to 1.15 Å of La^{+3}) causes severe local distortions affecting first shell oxygens and beyond. Figure 3 shows radial displacements of neighboring atoms to Ba as a function of distance. As each atomic "shell" in the *undistorted* LTT structure consists of more than one distance, atoms within a "shell" are affected differently and thus we show weighted averages of the shell positions and displacements. The most significant implication of this Ba-induced disorder for the discussion here is that the large O displacements introduce local, random deviations in tilt angle of the CuO_6 octahedra.

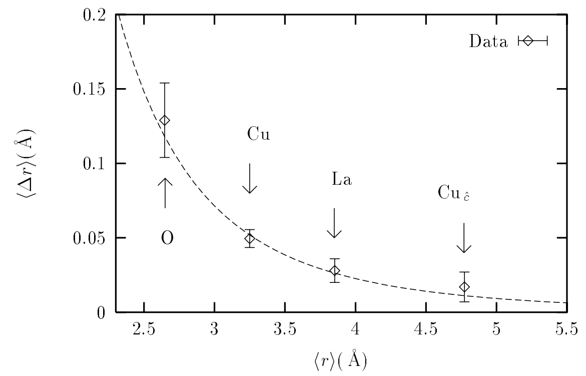

Figure 3
Shell-weighted-averaged radial atomic displacements induced by Ba. Data is for $x = 0.125$ at T=10K; dashed line is a guide to the eye.

We quantitatively determined the extent of disorder in tilt angles by using Cu K-edge polarized data and exploiting the sensitivity of nearly collinear MS XAFS to changes in buckling angle. Of particular interest is the disorder in buckling angle of the CuO_2 planes as a large fraction of Fermi surface states are hybrids of Cu $3d_{x^2-y^2}$-O(1) $2p_{x,y}$ in-plane orbitals and therefore planar lattice distortions can have significant effects on the electronic structure (Pickett *et. al*, 1991; Barisic *et. al*, 1990). A measurement of buckling angle in the Cu-O(1)-Cu and Cu-O(2)-La atomic arrangements was performed (fig. 4). MS effective scattering amplitudes were parameterized in terms of buckling angle using FEFF6 theory and constructing a correction of the form $F_k(\alpha) = F_k(\langle \alpha \rangle)(\gamma_k + \zeta_k \alpha^2)$ for $\alpha \leq 20^\circ$. Here $\langle \alpha \rangle$ is the average buckling angle of diffraction and γ_k, ζ_k are obtained by fitting the α dependence of the theoretical $F_k(\alpha)/F_k(\langle \alpha \rangle)$ for double and triple scattering (DS, TS) paths at each k. Half path lengths of DS, TS paths are parameterized in terms of α and the single scattering (SS) half path length at nearly the same distance, both varied in addition to a single σ^2. The effective scattering phase used corresponds to $\langle \alpha \rangle$ which for the angles at hand introduces systematic errors in distance determination of ≤ 0.005 Å and does not affect the measurement of the buckling angle, as verified in our fits.

If the local buckling angle randomly deviates from its average value, $\alpha = \langle \alpha \rangle + \delta\alpha$, diffraction techniques will be insensitive to the random disorder as it averages to zero over long range.

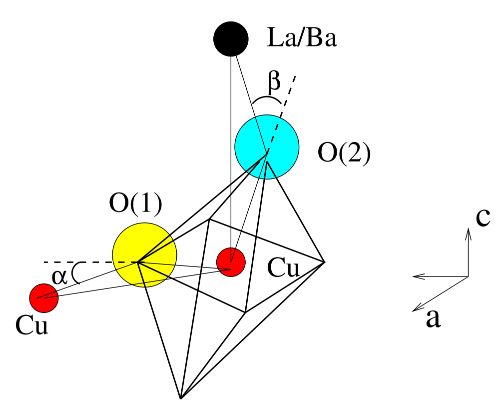

Figure 4
Nearly collinear MS paths used in determining disorder in buckling angle about the $\widehat{aa}$ plane and $\hat{c}$ axis.

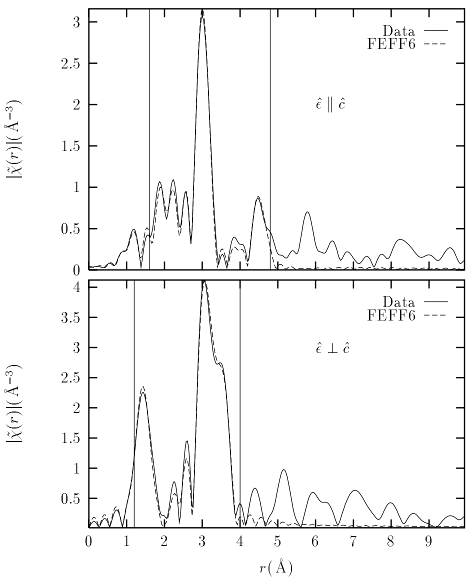

Figure 5
Magnitude of the complex FT of $k^2\chi(k)$ using $k = [3, 15]$ Å^{-1} data for Cu K-edge, $x = 0.125$ at T=10K. Data and fit shown for both polarizations; vertical lines indicate fitting range. The number of independent points in the data for both polarizations is 47 and a total of 18 fitting parameters were used.

MS XAFS, however, determines $\langle\alpha^2\rangle = \langle\alpha\rangle^2 + \langle\delta\alpha^2\rangle$, the average being over all Cu central atoms. If disorder is present, as expected from the Ba results, XAFS necessarily yields $\sqrt{\langle\alpha^2\rangle} > \langle\alpha\rangle$. Our best fits (fig. 5) give $\sqrt{\langle\alpha^2\rangle} = 13.1 \pm 2°$, $\sqrt{\langle\beta^2\rangle} = 14.3 \pm 1.5°$ compared to $\langle\alpha\rangle = 5.9°$, $\langle\beta\rangle = 6.9°$ by diffraction. From these values, the rms disorder in buckling angles are $\sqrt{\langle\delta\alpha^2\rangle} = 1.9(3)\langle\alpha\rangle$; $\sqrt{\langle\delta\beta^2\rangle} = 1.8(2)\langle\beta\rangle$.

4. Discussion

As mentioned in the introduction the two previously suggested explanations of T_c suppression have difficulty. Our discovery of large disorder in α and β in $La_{2-x}Ba_xCuO_4$ suggest a new viable explanation for T_c suppression. Pickett *et. al* (Pickett *et. al*, 1991) found from their LDA calculations that in the LTT phase (but not in the LTO phase) a gap appears precisely at the Fermi energy for $x = 0.125$ all along a Brillouin zone edge (the M-A edge). The band splitting, which originates in the different on site energies for inequivalent O(1) atoms in the LTT phase (those moving out of the CuO_2 planes compared to those staying in the planes), reflects a strong hole-lattice interaction for these Fermi surface states, which increases quadratically with tilt angle (Barisic *et. al*, 1990), and thus with α, β. Because of this quadratic dependence, the large disorder in α, β dominates the scattering. We suggest that the large disorder in α, β does not open a gap along the M-A line (since their long range average is zero) but, because of the strong hole-lattice coupling, the disorder strongly scatters the states in the vicinity of the M-A line localizing them and producing a *mobility* gap there. The calculations of Pickett *et. al* suggest that as much as half of the states at the Fermi energy could be in the mobility gap. Such states would not contribute to superconductivity, leading to T_c suppression. Doping from 0.125 to 0.15 moves the chemical potential from the localized states in the mobility gap (Fermi glass) to the mobile states outside the mobility gap (correlated Fermi liquid).

A final comment concerns the ability of XAFS to detect charged stripes in this material. In principle, local atomic displacements commensurate with such charge density waves (CDW) occur. A direct comparison of $x = 0.125$ and $x = 0.15$ (optimally doped) samples at all edges revealed no significant differences in their local structures. Cu K-edge results put an upper limit determined by our uncertainties of $\Delta r \leq 0.005$ Å, $\Delta\sigma^2 \leq 5 \times 10^{-4}$ Å^2 for the difference in distances and their disorder in the two samples, up to the fifth shell of atoms. One would expect that the displacements introduced by a CDW, whether pinned by the lattice at $x = 0.125$ or mobile at $x = 0.15$ (Emery *et. al*, 1997) should result in increased disorder in interatomic distances, which is not observed. Since we have no estimate for the distortions accompanying the CDW we cannot conclude on evidence for or against existence of stripes from these XAFS measurements. However, an upper limit to any CDW distortion can be given from the size of the residual $\sigma_0^2 = 3(2) \times 10^{-4}$ Å^2 in the disorder of the Cu-O(1) distances after an Einstein model fit to its temperature dependence resulting in an rms disorder, averaged over all Cu atoms, of ≈ 0.017 Å.

5. Summary and conclusions

Our XAFS measurements revealed a very large disorder in the angles that are involved in the tilting of the CuO_6 octahedra. Such a disorder couples very strongly to the states at the Fermi surface along the M-A edge of the Brillouin zone for the LTT phase at $x = 0.125$. We suggest that the states in the vicinity of the M-A edge are localized by this disorder, introducing a mobility gap for up to 50% of the states at the Fermi surface. The immobilization of such a large fraction of the Fermi surface leads to the observed T_c suppression.

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Table 1
σ^2 (Å^2) for different shell distances about La atoms in $La_{1.875}Ba_{0.125}CuO_4$ (T=10K) and $La_{1.85}Sr_{0.15}CuO_4$ (T=20K). $S_0^2 = 0.93(6), 0.95(6)$ for Ba, Sr, respectively.

	O	Cu	La	$Cu_{\hat{c}}$
Sr-doped	0.0020(10)	0.0020(4)	0.0019(5)	0.0035(10)
Ba-doped	0.0053(11)	0.0019(3)	0.0023(2)	0.0078(20)