Local Lattice Distortion in Superconducting Cuprates Studied by XAS

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Abstract. In-plane local distortion in cuprates characterized by strong doping and temperature dependence is a signature of polaron (bipolaron). The nature of dynamic lattice response in relation to the onset of superconductivity was probed by polarized x-ray absorption spectroscopy (XAS), for pure and magnetic impurity-doped M_xLa_{1.85}Sr_{0.15}Cu_{1-x}O_4 (M=Mn, Ni, Co, x<0.05) single crystals grown by a TSFZ method. The results confirm that the dynamical anti Jahn-Teller (AJT) distorted domains maximize at \( T_d^{\text{max}} \sim T_c^{\text{onset}} \), which is described by the disappearance of the Cu-O(1) bond alternation upon the completion of phase coherence (onset of superconductivity). In contrast to the Ni and Co dopings which quickly suppress superconductivity by magnetic pair breaking, the Mn doping shows sustainable superconductivity i.e., a constant \( T_d^{\text{max}} \) and \( T_c^{\text{onset}} \) up to x=0.03 with the presence of dynamical AJT distortion. The results suggest that the dynamical AJT type distortion with either Q_2 or pseudo JT symmetry extending over the basal plane could be a prerequisite for high temperature superconductivity.

1. Introduction
While the microscopic mechanism of high temperature superconductivity (HTSC) is still in mystery more than 26 years after the discovery [1], recently reported superconductivity in fluorine-doped LaFeAsO (LFAO) [2] has revived interests in the research. A conventional phonon mechanism is considered unlikely as the DFT calculations indicated a weak electron-phonon coupling, yet, the purely electronic mechanism [3] is also less likely than the case of cuprates [4] as the Hubbard \( U \) is not large (\( U \sim 5\text{eV} \)) [5], while recent muon spin rotation experiments suggested possibility of multigap BCS-type superconductivity in Ba_{0.6}K_{0.4}Fe_2As_2 [6]. Although some of the iron pnictides (doped with holes) have temperature-dependent lattice anomaly described as a bond length disproportionation [7] similar to that of superconducting cuprates [8], the behaviour of local lattice is strongly dependent on the band filling, indicating a strong intimacy between local lattice and the doping-induced unconventional electronic structure, i.e., a pseudogap. It became therefore necessary to investigate the role of local lattice in a cuprate system with well-characterized carriers (holes) by revisiting a model system, i.e., La_{1.85}Sr_{0.15}CuO_4 (LSCO). It would be quite timely to focus on a typical cuprate and investigate the role of polarons considering the fact that high precision local probe experiments and theoretical advances (models based on specific distortion scheme) would unveil the nature of lattice effects whose “tip” is emerged in pnictides.

A polaron is formed when an electron is strongly coupled to the atoms in a crystal. Review article on a polaronic mechanism of superconductivity is elsewhere [9]. Polarons in highly correlated electron
systems relate to a variety of physical properties including colossal magnetoresistance (CMR). In manganites, coherent polaron condensation is believed to be the driving mechanism of CMR phenomena [10]. Strong coupling between electrons and lattice in HTSC cuprates has been demonstrated by angle-resolved photoemission spectroscopy (ARPES) [11]. Reflecting these backgrounds, renewed interests on the role of polaron in HTSC mechanism have rapidly accumulated. In this work we revisit lattice effects in a typical cuprate La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) with magnetic impurity atoms substituting copper sites [8] studied by means of polarized extended x-ray absorption fine structure (EXAFS). Previously, unusual carrier-induced local lattice anomaly found for pure LSCO was interpreted as a nanometer-scale self-organization (stripe) [12]. Here we show that the lattice effect at $T_{d}^{\text{max}}$ is more catastrophic resulting in a bond alternation, i.e., equal number of elongated and shortened Cu-O(1) bond length. The unusual local lattice deviation from a normal phonon behaviour is interpreted in terms of polarons [13-16]. As the magnitude of EXAFS oscillations is small, i.e., in the order of $10^{-2}$ of the total oscillation magnitude, a highly efficient fluorescence x-ray detector is required for a statistics with $10^8$ photons [17]. In this work, we have used a state-of-the-art pixel x-ray detector to obtain high-quality data and high-quality single crystals [18] grown by an in-house TSFZ furnace. As chemical doping (substitution with hetero-valent atom) itself often modifies local lattice leaving ambiguity in crystal quality, we used samples with a critical temperature controlled by uniaxial strain effect [19] and magnetic impurity doping effect [20]. Here we focus on the latter case and describe the nature of local lattice distortion.

2. Experimental

Polarized x-ray absorption spectroscopy (XAS) is advantageous as an instantaneous local probe within a coherent length of HTSC around a specific atom along a particular direction of anisotropic single crystals where the two polarization geometries ($E_{//ab}$, $E_{//c}$) in principle provide in-plane and out-of-plane information on the radial distribution function (RDF) of the CuO$_2$ plane, respectively. Difficulty in polarized EXAFS experiments on as-grown single crystals was overcome by a fluorescence detection method using a segmented detector that measures an emitted photon flux rather than a conventional transmitted beam intensity. Although several methods to measure polarization dependence for cuprates, our geometry (Figure 1(a)) is advantageous as a non-destructive method that covers any angle dependence between parallel and perpendicular polarization geometries by a simple rotation of the crystal around the incident beam. Segmented fluorescence monitoring was used to discriminate a signal from a background. A novel germanium 100-pixel array detector was used for collecting a purely fluorescence signal over a segmented solid angle [21]. All near-edge and EXAFS data were recorded for M:LSCO (M=Ni, Co and Mn) single crystals and polycrystalline samples at the Photon Factory. The energy and maximum electron current of storage ring were 2.5 GeV and 400–500 mA, respectively. A directly water-cooled silicon (111) double-crystal monochromator was used, covering the energy range 4–25 keV. The energy resolution was better than 2 eV at 9 keV, calibrated from the near-edge features of copper metal at the Fermi energy, $E_F$ (8.9803 keV). A single crystal sample was attached to an aluminum holder with a strain-free glue and cooled down using a closed-cycle He refrigerator (cooling power 2 W at 20 K, stability ±0.1 K) on a high-precision goniometer (Huber 420). As a typical magnitude of normalized EXAFS oscillations is several %, each data set must have photon statistics better than 0.1% or $10^6$ photons. Non-statistic (systematic) error was minimized for which segmented x-ray detection and repeated scans, typically six scans, were used. Fluorescence yield spectra for all channels of pixel array were monitored in real time and the effect of scattering was inspected.

A typical LSCO bulk single crystal grown by a traveling seed floating zone (TSFZ) method was 2 mm x 2 mm x 1 mm in dimension [8]. Using a closed cycle He refrigerator, sample temperature was controlled to a temperature error within 1 K and 0.1 K stability. Difficulty in substituting Mn with copper in LSCO is primarily a multi-phase problem; the impurity phases such as manganites stabilized at elevated temperature. Because of this difficulty, Mn substitution has been so far limited to a dilute specimen for the purpose of ESR studies. Optimizing the temperature elevation program of the TSFZ
furnace led to the successful growth of Mn$_x$La$_{1.85}$Sr$_{0.15}$Cu$_x$O$_4$ ($x<0.05$) [22]. The superconducting transition temperature was determined by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS) with the perpendicular applied magnetic field of 10 Oe upon field cooling.

3. Results and discussion

3.1. Carrier-induced local distortion in LSCO

LSCO is a typical HTSC cuprate with a K$_2$NiF$_4$-type structure, where copper atoms are coordinated by four in-plane oxygen atoms O(1) and two out-of-plane (apical) oxygen atoms O(2). The CuO$_6$ octahedron is elongated along the c-axis with two long (2.40 Å) and four short (1.89 Å) bonds as a result of Jahn–Teller (JT) distortion (Figure 1(a)) [22]. The geometry of our experimental setup is illustrated in Figure 1(b). The Cu K-EXAFS oscillations shown in Figure 2(a) originating from the interference of photoelectrons scattered by local atoms are sensitive to the local structure, i.e., polarized radial distribution functions (RDFs) around a specific (absorbing atom) site. To analyze the relative displacement between the copper and oxygen atoms, the mean-square relative displacement $\sigma^2_{\text{Cu-O}}$ was used. In the Fourier transform (FT) shown in Figure 2(b), the in-plane Cu-O(1) correlation was separated. A standard FT and curve fitting based on a single scattering theory were performed for all EXAFS data taken over a wide range in temperature down to 5 K.

![Figure 1](image1.jpg)

**Figure 1.** Jahn–Teller distortion of CuO$_6$ octahedral unit (a) and geometry of experimental setup (b).

![Figure 2](image2.jpg)

**Figure 2.** The normalized Cu K-EXAS oscillations for La$_{1.85}$Sr$_{0.15}$CuO$_4$ single crystal multiplied by $k^2$ (a) and the Fourier transform magnitude (b).

The relative displacement $\sigma^2_{\text{Cu-O}}$ is plotted in Figure 3 where open circles illustrate temperature dependence of the in-plane Cu-O in the optimally doped LSCO single crystal. In order to compare the
superconducting and non-superconducting samples without the effect of chemical doping, careful comparison was made for the non-superconducting specimen prepared by substituting copper atom with 5% magnetic impurity (Ni), which completely suppressed superconductivity by magnetic pair breaking [8]. Reflecting a fast time scale of the probe ($10^{-12}$ sec), the EXAFS results provide an instantaneous relative displacement of dynamic and static nature.

Superconducting LSCO samples show local lattice anomaly as temperature is decreased, described by: (1) an upturn $\sigma^2_{\text{Cu-O}}$ beginning at $T^* (70-80 \, \text{K}) \approx 2T_c$ (Figure 3) that maximizes at $T_{d_{\text{max}}} \approx T_c (37 \, \text{K})$, (2) a sharp drop upon superconductivity and (3) the continuing upturn below $T_c$. These anomalies are in contrast to the background temperature dependence which smoothly varies over a wide range of temperature reflecting normal phonons described by a non-correlated Debye model. Generally in a normal state, such a normal phononic behaviour is commonly observed if there is no structural phase transformation including a change in the Jahn-Teller distortion. An upturn (deviation from the background with a negative temperature dependence) indicates the presence of a broadened radial distribution function (RDF) either due to disorder or structural change such as a split of the scatterer atom (oxygen) positions of static or dynamic nature. In our case, because of a beat, the former two possibilities were differentiated. A beat occurs due to the interference of the two closely separated shells. As illustrated in Figure 4(a), a beat feature was observed in the EXAFS oscillations around $k=12 \, \text{Å}^{-1}$. Both EXAFS and FT magnitude functions were well reproduced by distortion models characterized by the two different bond lengths separated by $\Delta R \approx 0.12 \, \text{Å}$. Thus at $T_{d_{\text{max}}}$, the local structure gives rise to a bond alternation. One can find that the maximum distortion at $T_{d_{\text{max}}}$ exactly coincide with the onset of superconductivity at $T_{c_{\text{onset}}}$, as illustrated in Figure 3(a) [23]. We note that our analysis of the out-of-plane Cu-O bond showed no anomaly, in contrast to the early works which related the anomaly to a low temperature tetragonal (LTT) deformation which causes stripe inhomogeneity [12]. The effect of anti Jahn-Teller (AJT) static displacement of apical oxygen results in the electron transport without destroying the anti ferromagnetic order [24]. We will focus on, in the following, the dynamical in-plane lattice distortion with an anti Jahn-Teller (AJT) type displacement which indicates polaron or bipolaron are created below 1.5-2$T_c$. The present results indicate that both static out-of-plane and dynamical in-plane distortions are complementary in describing the fundamental electronic states and polaron transport in the doped CuO$_2$ plane, respectively.
3.2. Local distortion in LSCO with magnetic impurities

Magnetic impurities substituting copper sites in the conducting layer of superconducting cuprates strongly affect the superconducting properties because of magnetic pair breaking described by the Abrikosov theory [25]. The $E//ab$ polarized EXAFS confirmed that all dopants (Mn, Ni, Co) are incorporated in a K$_2$NiF$_4$-type structure with a chemical formula of La$_{1.85}$Sr$_{0.15}$Cu$_{1-x}$M$_x$O$_4$. Figure 5(a)-(c) summarize temperature dependence of the in-plane $\sigma^2_{Cu-O}$ and susceptibility which shows a significant element-dependence of impurity doping. Introducing a small amount of Ni and Co impurities at the Cu site sharply suppresses both the local lattice anomaly in the Cu-O $\sigma^2_{Cu-O}$ and susceptibility. With a 5% Ni or Co substitution, the lattice anomaly completely disappears associated with a collapse of superconductivity, which is not surprising since $T_{d_{\text{max}}} = T_{c_{\text{onset}}}$. In contrast, the substitution of Mn weakens the magnetic pair breaking associated with a less perturbed lattice distortion, i.e., superconductivity persists as long as the lattice anomaly exists for $x<0.03$. Magnetic impurities have been believed to be detrimental to superconductivity based on the pair breaking theory. Such a magnetic scattering (pair breaking) has no indication of polaron (bipolaron) but at least the magnetic effect is weakened while the polaron (bipolaron) is mobile as detected by temperature-dependent local distortion during which $T_{d_{\text{max}}}=T_{c_{\text{onset}}}=$ const. which is realized only in the case of Mn doping. In Ni- and Co-doped LSCO samples, in contrast, both $T_{d_{\text{max}}}$ and $T_{c_{\text{onset}}}$ sharply drop as $x$ increases, indicating a superconducting phase coherence (superfluid density) is sensitive to impurity doping.

Figure 3. $E//ab$ mean-square relative displacement for the Cu-O(1) bond in La$_{2-x}$Sr$_x$CuO$_4$ ($x=0.15$) Open and closed circles indicate the values for superconducting and non-superconducting samples of LSCO single crystals, respectively. The latter sample was prepared by substituting Cu with 5% Ni.

Figure 4. The first-shell $E//ab$ Cu K-EXAFS oscillations for La$_{2-x}$Sr$_x$CuO$_4$ multiplied by $k^2$ (a) and the Fourier transform magnitudes (b). Experimental results are compared with those of the simulation for distorted models.
Figure 5. Temperature dependence of the mean square relative displacement of the in-plane Cu-O bond $\sigma^2_{\text{Cu-O}}$ for LSCO single crystals with Ni, Co substitution (a) and Mn substitution (b) derived from the EXAFS data. Temperature dependence of the magnetic susceptibility of LSCO single crystals with Ni, Co substitution (c) and Mn substitution (d).

The Mn doping, however, lowers the slope of susceptibility curve and the $x=0.05$ specimen hardly shows superconductivity while the local lattice anomaly is present. The apparent discrepancy in the correlation between the lattice anomaly and superconductivity suggests that the Mn doping eventually causes inhomogeneous superconductivity because of the loss of coherence between the local pairs.

It is remarkable that Mn doping maintains the onset of superconductivity with the presence of AJT type distortion, unlike Ni and Co doping that immediately destroys superconductivity. Since the uniqueness of Mn doping is associated with the dynamical AJT distortion of the host lattice, it is likely that the AJT polaron (bipolaron) is a prerequisite to superconductivity. Let us examine the local structure of impurity atoms in $\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{M}_{x}\text{O}_4$ ($\text{M}=\text{Mn, Ni, Co, } x=0.05$) single crystal samples which do not show superconductivity. The EXAFS measurement at 10 K indicated the AJT distorted structure of static nature for the case of Mn doping. Polarized Mn K-edge EXAFS spectra were analysed by the Iffeffit-1.2.9 package [26] using theoretical amplitudes and phases calculated from the crystallographic data. The in-plane M-O(1) distances are: 1.92 Å, 1.88 Å and 1.88 Å for M=Mn, Ni and Co, respectively. Since the Mn-O(1) distance is significantly longer than that of LSCO (~1.88 Å)
while the Mn-O(2) distance is shorter, the impurity site in the CuO$_2$ plane is AJT distorted. In contrast, the in-plane Ni-O and Co-O bond lengths are close to the Cu-O(1) distance, indicating an undistorted local lattice around an impurity atom. Comparing the local distortions in the CuO$_6$ unit for Mn, Ni, Co doped cuprates with those parameters in perovskite manganite, nickelate, and cobaltite, the shortening of the overall M-O(2) distance (M=Mn, Ni, Co) is interpreted in terms of a conventional static AJT distortion. Moreover, the present results indicate that the static AJT sites (upto 0.5 %) does not critically affect the propagation of AJT-distorted domains, suggesting that polaron (bipolaron) is essential for achieving a phase coherence. In summary, a close correlation between the polaron (bipolaron) and onset of superconductivity is demonstrated.

3.3. Possible models of distortion-nature of polaron

The mean square relative displacement of the in-plane Cu-O bond, $\sigma^2_{Cu-O}$ in superconducting cuprates has an anomalous temperature dependence as a general feature observed in superconducting samples: (1) deviation from a normal phonon described by a simple model (negative temperature dependence), (2) a sharp drop at the a sharp drop at $T_c$ which coincides with the inflection point of derivative resistivity variation $\partial r/\partial T$ and (3) continuing trend of negative temperature dependence. Based on the systematic studies [12] indicate that the magnitude of the drop is roughly proportional to the superfluid density. Inhomogeneous nature of cuprates is likely to relate to structural inhomogeneity consisting of undistorted and distorted domains.

![Figure 6](image).

**Figure 6.** Schematic representation of possible distortion models; pseudo JT (breathing-like distortion) [16] (a), Q$_2$ JT (b) [35,15], stripe with LTT tilting of the CuO$_6$ unit. [12] (c), and stripe with Cu-O stretching (half breathing-like distortion) [28] (d).

The magnitude of $\sigma^2_{Cu-O}$ drop is a measure of superconducting fraction and the disappearance of inhomogeneity upon superconductivity which shows homogeneous electron states. On the other hand the observed coincidence of the onset of superconductivity with the maximum lattice distortion or fraction of distorted domain ($T_{c_{max}}$) relates to a superconducting phase coherence, for which a critical length may exist between the Josephson Junction (JJ)-coupled “metallic” domains and undistorted.
“insulating” domain. If the distance between metallic domain and insulating domain exceeds this critical limit, “macroscopic” superconductivity and lattice (distortion) may loose consistence as illustrated in the case of Mn substitution. Several different models were proposed to describe the AJT-like distortion below the pseudogap temperature. Here we focus on the existence of “beat” in $k$-space at 12 Å$^{-1}$ which indicates the presence of two different bond lengths with almost equal fraction. Let us consider simple models that reproduces the experimental bond alternation.

As doping proceeds, reduced Coulomb repulsion ($U$) would promote integration into extended domains with a larger size. The average distance between extended domains $L$ decreases allowing tunnelling over insulating domains [14, 27]. When $L$ becomes greater than a critical value ($z$), quantum tunnelling is prohibited. For instance, suppressed tunnelling under a tensile strain decreases superfluid density, and hence the critical temperature. Near the Mn dopants in Mn:LSCO ($x$=0.05), nonsuperconducting regions are formed and superconducting domains are limited to small domains. As a distance between the superconducting domains becomes large, quantum tunneling [14, 27] or percolation [28] is prohibited and the superconductivity eventually disappears although the onset temperature remains unaffected.

If we apply the bond alternation observed at $T_d^{\text{max}}$ as a criterion to differentiate the possible models, only the distortion models having equal number of elongated and shortened bonds remain. Possible structural models in Figure 6(a),(b) satisfy the criterion [15,16] in the limit of inhomogeneity (distortion extending all over the basal plane) while two stripe models in Figure 6(c),(d) are excluded by the criterion assuming the fraction of distorted domains 1/3 and 1/2, respectively. [12, 29]. The completion of phase coherence requires the extended AJT distortion over the crystal. It is quite interesting in possible models, the two adjacent CuO$_6$ units are linked each other so that the elastic energy is minimized by the complimentary distortions. This coupled CuO$_6$ units are familiar to a bipolaron concept. The well-known disadvantage of a JT polaron, i.e., a heavy mass [30] that leads to immobility is compensated by a bipolaron [31] which does not perturb the antiferromagnetic order [32]. As the coupling of the two units is driven by elastic forces [33], the findings that both AJT models fit to the observed bond alternation seem to be reasonable. Polarons may perturb spin configurations (antiferromagnetic order) and lead to spin vortices around that grow into spin loop current [16] or their one dimensional hopping may enhance strong coupling among spin, charge and lattice [15].

Other distortion models failed to satisfy the criterion [12,29] are based on the stripes of distorted domains sandwiched by undistorted ones. Their distortions are due to either a LTT tilting of the CuO$_6$ units (Figure 6(c)) or a half-breezing like Cu-O bond stretching (Figure 6(d)), both of which provide the equal number of short and elongated bonds but they are diluted by the spacing of undistorted domains. Because of inhomogeneity, stripe models can not clear the criterion. The real space image of a Cu-O-Cu bond-centered electronic glass with disperse 4$\sigma$-wide domains of displaced oxygen atoms is observed by tunneling asymmetry imaging for Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) [34]. As the spatial variations in tunneling asymmetry occurs at the $in$-$plane$ oxygen sites and the observed 2D texture pattern dispersed throughout the crystal may partially reflect the original dynamical distortion without long-range order, such patterns are taken as a frozen disorder because of a slow time scale of STM. In the model in Figure 6(d), the observed sharp contrast between a central ladder consisting of a column of oxygen atoms and the two neighboring Cu–O–Cu columns form a charge stripe [29]. Recent photoemission study on Bi2212 reported the growth of pseudogap component attributed to the preformed pair is associated with the planar modulation of electronic states observed by the STM. In this context, the polaronic lattice distortion may explain the local structural origin of pseudogap. Recent model calculations [35] indeed showed bipolarons form a charge-inhomogeneous texture pattern. The observed $in$-$plane$ bond alternation may describe coherence of preformed pairs. More
recently, the Q2-type AJT distortion model originally based on the three-centered spin (ESR) [36] was interpreted in terms of bipolaron [37,38] which could stay one of the most likely models.

**Conclusion**

The carrier-induced local lattice distortion in La1-xSrxCuO4 single crystals grown by a TSFZ method was studied by a fast local probe x-ray absorption spectroscopy. We find an anomalous upturn of the mean-square relative displacement of the Cu-O(1) bond detected by the EXAFS below $T^\ast \sim 2T_c$ strongly correlates with superconductivity. The deviation reflects an in-plane local lattice distortion described by an anti Jahn-Teller distortion which demonstrates the essential role of lattice, or polaron (bipolaron) in the mechanism of pairing. The observed local distortion maximizes its magnitude at $T_{d\text{max}}^{\ast} \sim T_{\text{onset}}$. The presence of beat in the EXAFS oscillations at $k=12$ Å$^{-1}$ indicates that the splitting of the Cu-O(1) distance into shortened and elongated bonds (a bond alternation), $R_1$ and $R_2$, where $\Delta R = R_1 - R_2 \sim 0.12$ Å. The onset of lattice distortion coincides with the opening of a pseudogap (ca. 80 K $\sim 2T_c$) where an unconventional electronic state begins to grow. Upturn trend (a negative temperature dependence) of the relative displacement deviating from a normal phonon behaviour indicates the growth of dynamical AJT distorted domains. The local lattice at $T_{d\text{max}}^{\ast}$ is well described by distortion models with AJT type distortion such as Q2 type or pseudo JT, both of which are characterized by close link of two CuO6 units minimizing the elastic energy, which is consistent with bipolaron concept. The substitution of Mn atom into a copper site causes little perturbation of this lattice distortion, in contrast to Ni and Co substitutions which strongly suppress lattice distortion and thus superconductivity. The polarized EXAFS study on magnetic impurity doped LSCO confirmed the substitution of impurities (Mn, Ni, Co) upto 5% while susceptibility showed that Mn doping uniquely sustains the onset of superconductivity, in sharp contrast with Ni and Co which quickly destroy the superconductivity. Such an unique behavior of Mn doping is associated with the dynamic AJT type distortion retained by the host lattice. The magnetic impurity doping results indicate an intimate relation between superconductivity onset (phase coherence) and the dynamic AJT distortion of host lattice that is hardly influenced by a static distortion around impurity sites. The EXAFS data at $T_{d\text{max}}^{\ast}$ where the distorted domains maximize in population were consistent with possible models (Q2 type AJT or pseudo JT) in the limit of inhomogeneity which could be considered as a model polaron (bipolaron) system.

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