Study of Temperature Dependent Local Structure by Polarized Cu K-edge EXAFS Measurements on La$_{2-x}$Sr$_x$CuO$_4$ ($x = 0.105, 0.13, 0.20$)

Naurang L. SAINI$^1$, Hiroyuki OYANAGI$^2$, Valerio SCAGNOLI$^1$, Toshimitsu ITO$^2$, Kunihiko OKA$^2$ and Antonio BIANCONI$^1$

$^{1}$Unità INFN and Dipartimento di Fisica, Università di Roma “La Sapienza”, P. le Aldo Moro 2, 00185 Roma, Italy
$^{2}$National Institute for Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568

(Received November 25, 2002)

We have studied temperature dependent local structure of superconducting La$_{2-x}$Sr$_x$CuO$_4$ ($0.105$, $0.13$, $0.20$) single crystals by Cu K-edge extended x-ray absorption fine structure (EXAFS) measurements with polarization parallel to the in-plane Cu–O bonds. We find that, while underdoped crystals ($x = 0.105, 0.13$) show anomalous temperature dependence, similar to the case of optimally doped system ($x = 0.15$), overdoped crystal ($x = 0.20$) does not reveal such anomaly. Correlated Debye–Waller factor (DWF) of the Cu–O bonds (distance broadening) has been used as an order parameter to determine characteristic local displacements in the CuO$_2$ plane. The amplitude of temperature dependent step-like increase in the DWF at low temperature decreases with increasing doping. It has been discussed that decreasing electron–lattice interaction with increasing doping, shown by angle resolved photoemission measurements, is closely related to the evolving anomalous local CuO$_2$ distortion and charge inhomogeneity with doping in the CuO$_2$ plane of high $T_c$ oxides.

KEYWORDS: cuprate superconductors, local structure, charge inhomogeneities, atomic displacements, synchrotron radiation spectroscopy

DOI: 10.1143/JPSJ.72.829

1. Introduction

Understanding various kind of competing ground states of the complex materials with strong electron–electron correlation is one of the key problems in the condensed matter physics.$^{1}$ There has been a considerable interest in the copper oxides, representing a family of complex materials, and even if the fundamental character of the superconducting order parameter remains intact, low temperature orders related with the charge, spin and lattice degrees of freedom are stagnating our understanding to the mechanism.$^{2}$ The main problem is the nature of coupling mechanism responsible for creating the pairs in the CuO$_2$ plane. Incidentally the electron–lattice interaction, fundamental basis for the superconductivity in metals, is given minor importance, not only due to the complex structure but also due to the fact that these interactions manifest self-organization of various degrees of freedom (stripes) at a mesoscopic length-scale.$^{3}$ However, experimental evidences in support of electron–lattice interactions$^{3–10}$ are hard to ignore and, it is getting recognized that these interactions are indeed important, not only for the superconducting state, but also for the low temperature orders as the stripe ordering phenomena. A major credit goes to the experiments sensitive to the atomic displacements and thanks to the recent technical developments combined with the advances in the materials growth we are gaining in-depth information on the relation between the mesoscopic structure and the basic electronic properties of these complex systems.

Main experimental probes used to determine the local displacements in the complex oxides are the pair distribution function (PDF) analysis of neutron diffraction, ion channeling and extended x-ray absorption fine structure (EXAFS).$^{4–8}$ All these techniques have their own limitations to provide information on the quantitative atomic displacements, however, the results on the local lattice displacements determined by these techniques agree quite well. The EXAFS spectroscopy, a fast ($\sim 10^{-15}$ s) and local ($\sim 5–6$ Å) tool,$^{11}$ with available high brilliance and polarized x-ray synchrotron radiation sources, allows quantitative determination of the directional atomic displacements around a selective site and offers unique approach to pin point short-range atomic displacements and their dynamics. Using polarized Cu K-edge EXAFS on a series of optimally doped copper oxides, it has been shown that Cu–O bond distribution turns from one peak function to a two-peak function, providing an evidence for Q$_2$ type of distortions in the CuO$_2$ plane below the charge stripe ordering temperature.$^{5}$ Here we have studied the local displacements as a function of charge density, with La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) as a model system.

LSCO is the simplest system among the copper oxide superconductors that has been studied to get insight to the interplay of various degrees of freedom and the normal and superconducting state properties since the chemical composition in this system can be varied over a large range. Increasing the Sr content the system shows a complex phase diagram, evolving from an antiferromagnetic insulating state (at $x = 0$) to a superconducting state ($x \geq 0.06$) with a maximum $T_c$ ($\sim 36$ K) at the optimum doping ($x \sim 0.15$), followed by a normal metallic phase with increasing doping. The system undergoes a phase transition from the high temperature tetragonal (HTT) to a low temperature orthorhombic (LTO) structure at a temperature (at $\sim 200$ K for $x \sim 0.15$) that depends on the doping.$^{2,12,13}$ In this paper we report high $k$-resolution EXAFS study at the Cu K-edge, with polarization parallel to the in-plane Cu–O bonds, on the LSCO system as a function of charge density, controlled by the Sr doping ($x = 0.105, 0.13, 0.20$). This experimental approach has allowed us to reveal intrinsic differences
between the temperature dependent local structure in different doping regimes. The results suggest that, while underdoped (\(x = 0.105, 0.13\)) regime is characterized by anomalous temperature dependent local structure, as the case of optimally doped system (\(x = 0.15\)), overdoped (\(x = 0.20\)) regime does not show such anomaly. An attempt has been made to understand the presence of the anomalous lattice fluctuation in the underdoped as a signature of charge stripe ordering induced by electron–lattice interaction that decreases in the overdoped regime. The results are consistent with a close relation between the Cu–O local displacements, charge inhomogeneity, electron–lattice interaction and high \(T_c\) superconductivity in the copper oxides.

2. Experimental

Cu K-edge x-ray absorption measurements were made on a series of \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) single crystals (\(x = 0.105, 0.13, 0.20\)) of size \(-3 \times 2 \times 0.5 \text{ mm}^3\), grown by travelling solvent floating zone (TSFZ) method.\(^{14}\) The samples show sharp superconducting transitions at temperatures 28 K, 32 K, and 29 K respectively with varying Sr concentration. The temperature dependent absorption measurements were performed at the beamline BL13B of Photon Factory at High Energy Accelerator Research Organization in Tsukuba. The synchrotron radiation emitted by a 27-pole wiggler source (maximum field \(B_0\) of 1.5 T) inserted in the 2.5 GeV storage ring with a maximum stored current of 360–250 mA was monochromatized by a variable exit beam height double crystal Si(111) monochromator and sagittally focused on the sample. Improved lattice of the storage ring and better crystal Si(111) monochromator and sagittally focused on the sample. Monochromatized by a variable exit beam height double crystal Si(111) monochromator and sagittally focused on the sample.

The temperature dependent absorption measurements were performed at the beamline BL13B of Photon Factory at High Energy Accelerator Research Organization in Tsukuba. The synchrotron radiation emitted by a 27-pole wiggler source (maximum field \(B_0\) of 1.5 T) inserted in the 2.5 GeV storage ring with a maximum stored current of 360–250 mA was monochromatized by a variable exit beam height double crystal Si(111) monochromator and sagittally focused on the sample. Improved lattice of the storage ring and better monochromator cooling system allowed to get a very stable beam on the sample. The spectra were recorded by detecting the fluorescence yield (FY) using a 19-element Ge x-ray detector array, covering a large solid angle of the x-ray fluorescence emission.\(^{15}\) The emphasis was given to make the presence of the anomalous lattice fluctuation in the underdoped as a signature of charge stripe ordering induced by electron–lattice interaction that decreases in the overdoped regime. The results are consistent with a close relation between the Cu–O local displacements, charge inhomogeneity, electron–lattice interaction and high \(T_c\) superconductivity in the copper oxides.

The measurements at several temperatures were repeated at the beamline BM29 of the European Synchrotron Radiation Facility (ESRF), Grenoble. At the BM29 the sample was mounted in a two-stage closed-cycle He cryostat for the measurements. A 13 Ge element solid state detector was used to measure the absorption signal in the normal incidence geometry. The results were found to be highly reproducible in spite of different experimental geometry at two different synchrotron facilities.

3. Results and Discussion

Figure 1 shows Cu K-edge EXAFS oscillations on two underdoped \(\text{La}_{1.80}\text{Sr}_{0.105}\text{CuO}_4\) (\(\text{Sr}_{0.105}\)) and \(\text{La}_{1.87}\text{Sr}_{0.13}\text{CuO}_4\) (\(\text{Sr}_{0.13}\)) and an overdoped \(\text{La}_{1.80}\text{Sr}_{0.20}\text{CuO}_4\) (\(\text{Sr}_{0.20}\)) single crystal samples at low temperature (20 K) and at room temperature (300 K). The EXAFS oscillations were extracted from the absorption spectra measured on the single crystals with polarization vector of the x-ray beam parallel to the Cu–O–Cu direction and corrected for the fluorescence self-absorption effect. The EXAFS oscillations are weighted by \(k^2\) to highlight the higher \(k\)-region and the oscillations with high signal to noise ratio could be seen up to \(k = 17 \text{ Å}^{-1}\) even at high temperature. An overall damping of the EXAFS oscillations at high temperature is clear and apart from the damping, there are evident differences

![EXAFS oscillations](image)
between the EXAFS oscillations, particularly at higher \( k \)-values \((k > 10 \text{ Å}^{-1})\), for the underdoped and overdoped samples. The temperature and doping dependent differences in the local structure could be better discriminated in the Fourier transforms of the EXAFS oscillations providing real space information.

Figure 2 shows magnitude of the Fourier transforms, \( |\text{FT}(k^2 \chi(k))| \) of the EXAFS oscillations (weighted by \( k^2 \)) measured on the two undoped samples \((\text{Sr}_{0.105} \text{ and Sr}_{0.13})\) and the overdoped \((\text{Sr}_{0.20})\) sample at two temperatures (20 K and 300 K). The Fourier transforms (FTs) were performed between \( k_{\text{min}} = 3 \text{ Å}^{-1} \) and \( k_{\text{max}} = 17 \text{ Å}^{-1} \) using a Gaussian window. The FTs are not corrected by the phase shifts due to photoelectron back-scattering and represent the raw experimental data. The first peak in the Fourier transform corresponds to the in-plane Cu–O atoms, while the doublet peak structure at around 3–4 Å corresponds to the Cu–La(Sr) signal and Cu–O–Cu multiple scattering. In the in-plane polarized spectrum, we do not expect any contribution from the two Cu–O(apical) bonds at ~2.4 Å because of directional scattering of the photoelectron excited by the plane polarized synchrotron light. From the first look to the FTs it is easy to distinguish evident differences between the local structure between the underdoped and the overdoped samples. The underdoped samples show more pronounced doublet due to the Cu–La(Sr) and Cu–O–Cu (see e.g. region between the dotted lines). Again the temperature dependence of the doublet structure reveals stronger damping of the Cu–La(Sr) peak in compare to the Cu–O–Cu scattering.

Let us turn to the temperature dependence of the local structure, indicated by the FT peak amplitudes. We have plotted FTs at several temperatures for an underdoped \((\text{Sr}_{0.105})\), compared with the overdoped \((\text{Sr}_{0.20})\) sample in Fig. 3 to distinguish differences between two doping regimes. There is a clear increase of the amplitudes for the Cu–La(Sr) and Cu–O–Cu with decreasing temperature, however, the Cu–O peak does not show this usual temperature dependence. Indeed, while Cu–O peak for the \((\text{Sr}_{0.105})\) sample shows an anomalous change (e.g., amplitude of the Cu–O peak at 44 K is lower than the one at 300 K), there is hardly any temperature dependence of this peak for the overdoped \((\text{Sr}_{0.20})\) sample. This temperature dependence can be clearly observed in Fig. 4 where we have plotted magnitude of the FT peaks for the two samples, showing distinct temperature dependent local structure in the underdoped and overdoped regimes. Careful look to the temperature dependent intensities reveals that while the displacements in the CuO plane for the two samples, given by the Cu–O FT, are different, other peaks appear to show smaller differences.

To have further insight to the local structural differences in the electronically active CuO plane as a function of doping, we have analyzed the EXAFS spectra due to in-plane Cu–O bonds. In the polarized Cu K-edge EXAFS, with polarization parallel to the Cu–O–Cu direction, the signal due to the Cu–O bonds is well separated from the longer bond contributions and can be easily analyzed separately.
were taken from the diffraction studies. The starting parameters mined by EXAFS is limited by the number of independent content. The number of parameters which may be determined by EXAFS is limited by the number of independent data points: $N_{\text{ind}} \sim (2\Delta k \Delta R)/\pi$, where $\Delta k$ and $\Delta R$ are respectively the ranges in $k$ and $R$ space over which the data are analyzed. In the present case $\Delta k = 14 \text{ Å}^{-1}$ and $\Delta R = 1 \text{ Å}$ giving $N_{\text{ind}} \sim 9$ for the first shell EXAFS. Except the radial distance $R$ and the $\sigma^2$ all other parameters were kept constant on the basis of our experience on the similar systems in the conventional least squares paradigm following the standard approach. The starting parameters were taken from the diffraction studies.

Temperature dependence of the Cu–O DWF, that takes into account both static and dynamic distortions of the CuO$_2$ plane, is shown in Fig. 5 with variable Sr content. The average distances were found to be independent of temperature and consistent with the one determined by the diffraction experiments within the experimental uncertainties. On the other hand, we can see some evident differences in the $\sigma^2$ of the underdoped ($\text{Sr}_0.105$ and $\text{Sr}_0.13$) and the overdoped ($\text{Sr}_0.20$) samples. The striking difference is that, while the underdoped systems show anomalous temperature dependence, as observed for an optimally doped system ($\text{Sr}_0.15$), we see a negligible temperature dependent anomaly for the overdoped case. Indeed, we can define the anomalous temperature at which $\sigma^2$ shows an increase. This upturn at $T_s$ is evident for the $\text{Sr}_0.105$ and $\text{Sr}_0.13$ samples and similar to the one observed earlier for the optimally doped ($\text{Sr}_0.15$) system, however, the $\text{Sr}_0.20$ system shows very small change, at the limit of the experimental uncertainties. We can also see a small drop in $\sigma^2$ at $T_s$, better seen only for the $\text{Sr}_0.13$ sample, similar to the optimally doped system. Here we should recall that, apart from the static and dynamic distortions of the CuO$_2$ lattice $\sigma^2$ contains contribution from the thermal vibrations. However, in the present case the thermal contribution to $\sigma^2$ should be similar for all the samples.

We have used the conventional method for the analysis following diffraction data suggesting a single Cu–O bond length, where the effective Debye Waller factor (DWF) includes all distortion effects, taking into account both static and dynamic distortions. This standard approach is adopted to make a direct comparison of the temperature dependent distortions in the systems with doping, where the correlated DWF of the Cu–O pairs, $\sigma^2$ is a suitable order parameter of the local displacements in the CuO$_2$ square plane. Quantitative value of the $\sigma^2$ depends on the technical aspects (experimental geometry and analysis). Although this is irrelevant for the temperature dependent distortions, we have ensured the quantitative values for the DWF (within the reported uncertainties) by performing the measurements in the same experimental conditions and applying the same data analysis procedure for all the crystals.

The Cu–O EXAFS was simulated in the same $k$ range ($k = 3–17 \text{ Å}^{-1}$) for all the samples with varying Sr content. The number of parameters which may be determined by EXAFS is limited by the number of independent data points: $N_{\text{ind}} \sim (2\Delta k \Delta R)/\pi$, where $\Delta k$ and $\Delta R$ are respectively the ranges in $k$ and $R$ space over which the data are analyzed. In the present case $\Delta k = 14 \text{ Å}^{-1}$ and $\Delta R = 1 \text{ Å}$ giving $N_{\text{ind}} \sim 9$ for the first shell EXAFS. Except the radial distance $R$ and the $\sigma^2$ all other parameters were kept constant on the basis of our experience on the similar systems in the conventional least squares paradigm following the standard approach. The starting parameters were taken from the diffraction studies.

Temperature dependence of the Cu–O DWF, that takes into account both static and dynamic distortions of the CuO$_2$ plane, is shown in Fig. 5 with variable Sr content. The average distances were found to be independent of temperature and consistent with the one determined by the diffraction experiments within the experimental uncertainties. On the other hand, we can see some evident differences in the $\sigma^2$ of the underdoped ($\text{Sr}_0.105$ and $\text{Sr}_0.13$) and the overdoped ($\text{Sr}_0.20$) samples. The striking difference is that, while the underdoped systems show anomalous temperature dependence, as observed for an optimally doped system ($\text{Sr}_0.15$), we see a negligible temperature dependent anomaly for the overdoped case. Indeed, we can define the anomalous temperature at which $\sigma^2$ shows an increase. This upturn at $T_s$ is evident for the $\text{Sr}_0.105$ and $\text{Sr}_0.13$ samples and similar to the one observed earlier for the optimally doped ($\text{Sr}_0.15$) system, however, the $\text{Sr}_0.20$ system shows very small change, at the limit of the experimental uncertainties. We can also see a small drop in $\sigma^2$ at $T_s$, better seen only for the $\text{Sr}_0.13$ sample, similar to the optimally doped system. Here we should recall that, apart from the static and dynamic distortions of the CuO$_2$ lattice $\sigma^2$ contains contribution from the thermal vibrations. However, in the present case the thermal contribution to $\sigma^2$ should be similar for all the samples.
systems and hardly affects the present discussion.

It is known that at the appearance of any charge density wave like instability the DWF shows an anomalous change as found in several density wave systems. Indeed the temperature dependence of the $\sigma^2$ shows an anomalous upturn at a temperature $T_c$, due to the instability (driven by a particular local lattice distortion in the CuO$_2$ plane). It is worth recalling that a model system $\text{La}_{1.85}\text{Sr}_{0.12}\text{Nd}_{0.00}\text{CuO}_4$ (LNSC), in which the charge stripe ordering is known to occur, consistent with several experimental observations, reveals similar temperature dependent $\sigma^2$ determined by Cu K-edge EXAFS. Considering these experimental facts, we think that the anomalous upturn in the $\sigma^2$ (Fig. 5) is due to charge instability related to the charge stripe ordering. Sharma et al. have found a clear upturn in the temperature dependence of the excess bond distances (a parameter analogous to the DWF measuring dynamic and static distortions) measured by ion-channeling on the YBCO system at the stripe ordering temperature, providing further confirmation. Similar observations were also made in neutron diffraction PDF studies. In fact, below the anomalous temperature bond distribution becomes larger than that due to thermal fluctuations and the formation of striped phase gives an asymmetric bond length distribution.

It should be mentioned that, within the experimental data points, we can hardly see a change in the $T_c$, however, it seems that the anomalous upturn in the $\sigma^2$ appears to decrease with increasing doping. Figure 6 (upper) shows estimated amplitude of the upturn at the $T_c$ as a function Sr content. Even though the change in the upturn with doping is small, it appears to indicate some relation between the doping dependent charge inhomogeneous state and the superconductivity in the copper oxides. It was shown earlier that the up-turn at $T_c$ is due to asymmetric pair distribution function derived by splitting of the Cu–O bonds. Therefore the amplitude of the up-turn provides a measure to the barrier height in the multi-well potential. The present data indicates that the barrier height decreases with increasing doping and the system gets more homogeneous.

The charge stripe ordering, shown by several experiments, is expected to introduce an in-plane anisotropy in the CuO$_2$ plane, however, this anisotropy is generally ignored in the diffraction studies. Here we have given a careful look to the diffraction data and estimated in-plane structural anisotropy in the LSCO system at low temperature and room temperature as function of doping using the published data. Variation of this in-plane structural anisotropy, when sample is cooled (from 295 K to 10 K), is also plotted in Fig. 6 (upper). This variation of the in-plane anisotropy was also measured by angle-resolved photoemission spectroscopy (ARPES). The dotted lines are guide to the eyes (upper). Electron lattice coupling, estimated from the ARPES data on the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, as a function of doping is shown (open squares) in the lower panel. The electron lattice coupling is determined using the bare ($V_b$) and the dressed ($V_d$) electron velocities.

Example impurities strongly suppress the superconducting transition temperature in the underdoped regime while the effect is minimum when the system is overdoped. In addition, it is known that $T_c$ increases under external pressure, and strain modulation in the underdoped regime and the effect is very small for the overdoped case. The findings are also consistent with the theoretical predictions of doping dependent isotope shift on the stripe formation temperature in these superconductors.

Here we attempt to understand the results in the light of recent angle resolved photoemission spectroscopy (ARPES) results on the $\text{L}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductors. High-resolution ARPES reveal a kink in the band dispersion, defined by an abrupt change of electron velocity at 50–80 meV. This kink has been interpreted to be due to phonons associated with the movement of the oxygen atoms related with the electron–lattice coupling. We have plotted doping dependence of the electron–lattice coupling [Fig. 6 (lower)], estimated from the ARPES data on the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ using the two velocities, i.e., dressed velocity and the bare velocity of the electrons. The electron–lattice coupling shows a continuous decrease with doping. This behavior of the electron–lattice interaction, analogous to the amplitude of the up-turn in the $\sigma^2$ [Fig. 6 (upper)] suggesting that the kink
structure in the electron dispersion is related to the Cu–O displacements, with asymmetric bond distribution, driving the system to an inhomogeneous charge state with self-organization in stripes. Therefore the absence of any evident anomaly in the temperature dependent displacements for the overdoped system seems to be due to reduced electron–lattice interaction and increased kinetic energy of the electron in the homogeneous state. In fact, while the system is overdoped, the in-plane structural anisotropy does not show any change and the electron–lattice interaction gets very small. This is a clear indication that the electron–lattice interaction, decreasing with increasing doping, is a key parameter for the characteristic properties of the copper oxide superconductors.

In summary, we have measured local structure of the La2−xSrxCuO4 superconductor, as a function of doping, by high resolution polarized Cu K-edge EXAFS measurements. Temperature dependent measurements with polarization of the x-ray beam parallel to the Cu–O–Cu bonds have permitted us to enlighten the distinct behavior of the local structure in the underdoped and overdoped regimes. We find that the Cu–O displacements shows anomalous behavior in the underdoped and optimally doped regimes while the behavior remains almost temperature independent in the overdoped case. The change across the Tc, determined by the upturn in the correlated DWF of the Cu–O bond, decreases with increasing doping in the CuO2 plane. We have made an attempt to understand the experimental results in terms of the doping induced change in the electron–lattice interaction, that decreases with increasing doping, as seen by a kink structure in angle resolved photoemission experiments. We conclude that the kink structure and the related energy scale are due to Cu–O displacements and tied to the charge inhomogeneous state of these materials. Nevertheless, present experiments have direct implication on the correlating Cu–O displacements, electron–lattice interaction, inhomogeneous state and high Tc superconductivity in the complex copper oxides. At this stage, it is hard to justify the theoretical models for the copper oxides, the results are not inconsistent with the experiments arguing quantum critical point (QCP) near the optimal doping30 and do not contradict recent theoretical scenario based on QCP in these materials.31–32

Acknowledgements

The authors thank the PF and ESRF staff for their cooperation during their experiments. This research has been supported by the Project PA-LLDS of Istituto Nazionale di Fisica della Materia (INFM), by “progetto cofinanziamento Leghe e composti intermetallici: stabilità termodinamica, proprietà fisiche e reattività” of MURST and by Progetto 5% Superconduttività del Consiglio Nazionale delle Ricerche (CNR).

2) See e.g. a brief review on the phase diagram by B. Batlogg and C. M. Varma: Phys. World (Feb. 2000) 33.