Probing physics in local lattice displacements: the case of inhomogeneous state and superconductivity in the copper oxides

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Abstract. Local lattice displacements in the copper oxide superconductors are determined by polarized Cu K-edge extended x-ray absorption fine structure (EXAFS) measurements. Temperature dependent local atomic displacements show anomalies, at the Tc and a temperature Td where the charge inhomogeneous state appears, as revealed by a change in the correlated Debye-Waller factor (DWF) of the Cu-O bonds. While the DWF shows a clear drop at the Tc, an order parameter like up-turn appears at the Td. The anomalies shows-up with different amplitude, depending on the superconducting transition temperature of the system and the micro-strain in the electronically active CuO2 plane. The measured Cu-O displacements appear to be closely related to the kink structure in the angle resolved photoemission experiments. The results are discussed to find some correlation between electron-lattice coupling, inhomogeneous charge state and superconductivity in the copper oxides.

INTRODUCTION

Structurally the case of copper oxides showing high Tc superconductivity is non-trivial and knowledge of long-range crystallographic structure is not enough to explain their basic properties unlike the simple solids such as normal metals. Indeed, the basic characteristics of these doped oxides depend strongly on the local atomic structure, as revealed by a series of experiments. In fact, the importance of the electronically active CuO2 plane in these oxides has created major interest to study the electronic versus structural behavior of this structural unit. Even if the fundamental character of the superconducting order parameter with a charge 2e remains intact, understanding of the mechanism is stagnated by interplaying low temperature orders, related with the charge, spin and lattice degrees of freedom, that can compete or coexist with the superconductivity. Indeed, these oxides manifest self-organization of various degrees of freedom (stripes) at a mesoscopic length-scale, the phenomena which has been a point of recent debate in the field [1].

The pending problems in the copper oxides are the nature of the coupling mechanism responsible for creating the pairs in the CuO plane, driving force for the inhomogeneous charge-state and any correlation between the superconductivity and the charge inhomogeneity. Recent experiments support a key role of local electron-lattice interactions [2-8], and therefore it becomes important to distinguish and quantify the lattice
displacements that could be associated with the superconductivity and the charge inhomogeneity. The quantitative value of the displacements should also help us to distinguish proper model based on electron-lattice interaction [9].

The main experimental probes used to determine the local displacements in these complex oxides are the pair distribution function (PDF) analysis of neutron and x-ray diffraction, extended x-ray absorption fine structure (EXAFS) and ion channeling [2-7]. 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 even if there are ambiguities in the measured magnitude due to small disorder. However, recent advances in the materials growth and development of new experimental techniques at higher experimental facilities (synchrotron radiation sources and neutron sources) have brought closer the outcome of the mentioned experimental techniques.

The EXAFS spectroscopy, a fast (~10^15 sec) and local (~5-6Å) tool [10], has been widely exploited to study the copper oxides. Availability of the high brilliance and polarized x-ray synchrotron radiation sources has been an added advantage for the technique allowing quantitative determination of the directional atomic displacements around a selective site in the copper oxides [6, 7, 11-13]. In fact, with recent technical advances, the EXAFS spectroscopy offers unique approach to pin point short-range atomic displacements and their dynamics.

Here we have used Cu K-edge EXAFS to determine local atomic displacements in the superconducting copper oxides with the aim to explore possible implication of these atomic displacements in their basic properties such as the intrinsic local charge and structural inhomogeneities and superconductivity. We have exploited the EXAFS with high k-resolution to determine temperature dependent distribution of the local lattice distortions (dynamic and static) in the electronically active Cu-O networks. The correlated Debye-Waller factor (DFW) of the Cu-O bonds (or) has been taken as an order parameter of the local displacements, revealing anomalous change across the charge stripe ordering temperature appearing as an up-turn with different amplitude, depending on the superconducting system. In addition, there is a drop of local displacements at the T_c with variable amplitude that depends on the T_c of the material. The local displacements depend on the elastic fields due to local strain and are found to be closely related to the kink structure in the band dispersion as observed by angle resolved photoemission [8]. The results provide a clear indication that the local electron-lattice coupling is one of the main ingredients for the inhomogeneous state of the copper oxides and there is an intimate relationship between superconductivity and the charge inhomogeneities.

EXPERIMENTAL

Polarized Cu K-edge x-ray absorption measurements on single crystals samples were performed at the beamlines BM29 and BM32 at the European Synchrotron Radiation Facility (ESRF), Grenoble and BL13B of Photon Factory, Tsukuba. At the BM29 the synchrotron radiation emitted by a bending magnet source at the 6 GeV ESRF storage ring was monochromatized by a double crystal Si(311) monochromator. For temperature dependent measurements the samples were mounted in a closed cycle two stage He cryostat. Fluorescence yield (FY) off the samples was collected using 13 Ge element solid state detector to measure the absorption signal at the BM29. A Si(111) crystal was used as monochromator and a 30-element Ge x-ray detector array was used to measure the absorption spectra at the BM32. At the BL13B the synchrotron radiation emitted by a 27-pole wiggler source at the 2.5 GeV Photon Factory storage ring was monochromatized by a double crystal Si(111) and sagittally focused on the sample. The
spectra were recorded by collecting the fluorescence photons using a 19-element Ge x-ray detector array. The sample temperatures were controlled and monitored within an accuracy of ±1 K. As our standard experimental approach, several absorption scans were collected to limit the noise level to the order of 10⁻⁴. Standard procedure was used to extract the EXAFS signal from the absorption spectrum [10] and corrected for the x-ray fluorescence self-absorption before the analysis. Further details on the experiments and data analysis could be found in our earlier publications [11-14].

RESULTS AND DISCUSSION

Copper oxide superconductors are heterogeneously structured materials having alternated layers of body centered cubic (bcc) CuO₂ layers and rock-salt face centered cubic (fcc) M-O (M= Ba, Sr, La) layers [15, 16]. The mismatch between the two sub-lattices is conventionally estimated by $t−r=r(A-O)/\sqrt{2}r(Cu-O)$ where $r(A-O)$ (i.e., $r(La-O)$, $r(Sr-O)$ and $r(Ba-O)$) and $r(Cu-O)$ are the respective bond lengths and $t$ is the Goldschmidt tolerance factor [16]. Due to the lattice mismatch the CuO₂ sheets are under compression and (M-O) layers under tension. The elastic fields due to the mismatch, determined by the micro-strain, play important role in the physics of these copper oxides as demonstrated experimentally [17]. Here we focus on the local atomic displacements as a function of the micro-strain in the CuO₂ plane due to the lattice mismatch to see the influence of it, in the light of the charge inhomogeneities and the superconductivity. We have used La₂CuO₄+δ (LCO) (Tc~46 K), Bi₂Sr₂Ca₂Cu₂O₈ (Bi2212) (Tc~87 K) and HgBa₂CuO₄+δ (Hg1201) (Tc~94 K) as representatives for the La-based, Bi-based and Hg-based families. These systems contain respectively the La-O, Sr-O and Ba-O as rock-salt layers, sustaining different chemical pressure on the CuO₂ planes, and the doping is through interstitial oxygen ions in the block layers.

Fig. 1 shows Fourier transforms (FT) of the representative polarized Cu K-edge EXAFS measured on single crystals with E vector of the plane polarized x-rays falling parallel to the CuO₂ square plane. The FT provide a global atomic distribution around the absorbing Cu atom in the measured systems and peaks appear due to scattering of the photoelectron, ejected at the Cu site, with the near neighbor atoms. The main peaks in the FT are denoted by Cu-O, Cu-M (M=La, Sr(Ca), Ba(Ca) for the LCO, Bi2212 and Hg1201 systems) and Cu-O-Cu, appearing due to scattering of the ejected photoelectron at the Cu site with the nearest in-plane oxygen atoms (at ~1.9 Å), M atoms (sitting at ~3.2 Å and 45° from the direction of the photoelectron) and the next Cu atom (at ~3.8 Å), respectively. There are evident differences in the FT of the EXAFS spectra measured on different systems. The major differences appear around the Cu-M (M=La, Sr(Ca), Ba(Ca)) peak due to different block-layers. The absolute differences may be difficult to extract because of complex interference effects due to different origins of the backscattering in the three systems at the Cu-M distance and interference with the Cu-O-Cu multiple scattering.

Here we focus our attention on the atomic displacements in the electronically active CuO₂ plane (i.e. the m-plane Cu-O bond). In the in-plane polarized Cu K-edge EXAFS the signal due to the Cu-O bond distances is well separated from the longer bond contributions and can be easily extracted and analyzed separately. In this work we have used the 'standard procedure' for the analysis of EXAFS data considering a single distance for the coordination shell, where the effective 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 different systems, where the correlated DWF of the Cu-O pairs, α² is a suitable order
parameter of the local CuO$_2$ distortions. Quantitative value of the $\alpha^2$ depends on technical aspects (experimental geometry and analysis), however, this is irrelevant for the temperature dependence. Within the reported uncertainties, we have ensured the quantitative values for the DWF in different systems by measuring the three systems in same experimental conditions and applying the same data analysis procedure.

![Cluster structures for Cu-O EXAFS](image)

**FIGURE 1.** Fourier transforms of the Cu K-edge EXAFS measured on the LCO (upper), Bi2212 (middle) and Hg1201 (lower) with varying micro-strain.

We have determined the $\alpha^2$ by modeling the Cu-O EXAFS considering a single Cu-O bond, as revealed by diffraction measurements. The Cu-O EXAFS was simulated in the same k ($k=3$-$17$ Å$^{-1}$) range for all the systems. The number of parameters which may be determined by EXAFS is limited by the number of independent data points: $N_{\text{ind}} \approx (2\Delta k\Delta R)/\pi$, 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, $\Delta k=14$ Å$^{-1}$ and $\Delta R=1$ Å give $N_{\text{ind}} \approx 9$ for the first shell EXAFS. Except the radial distance R and the $\alpha^2$, all other parameters were kept constant in the conventional least squares paradigm following the standard approach and our experience on the similar systems [6, 7, 11-14]. The average distances were independent of temperature and found to be similar to the one determined by the diffraction experiments on the three systems.

The Cu-O DWF ($\alpha^2$), has been used to make a systematic comparison between the systems with variable micro-strain. The temperature dependence is shown in Fig. 2 for
the LCO ($T_c \sim 40$ K), Bi2212 ($T_c \sim 87$ K) and Hg1201 ($T_c \sim 94$ K) systems representing the three different families of the superconducting copper oxides.

![Image of graph showing temperature dependence of $\sigma^2$ for LCO, Bi2212, and Hg1201 systems.]

**FIGURE 2.** Temperature dependence of the Cu-O $\sigma^2$ determined by EXAFS, LCO (upper), Bi2212 (middle) and Hg1201 (lower). The dashed line is a guide to the eyes. The slope of shows abnormal temperature dependence with an increase below a temperature $T_x$ followed by a decrease around the superconducting transition temperature $T_c$. The error bars represent the average estimated noise level.

From the temperature dependence of $\sigma^2$ we can easily define at least two anomalous temperatures. There is an anomalous increase at a temperature $T_x$ followed by a decrease around the superconducting transition temperature $T_c$. The increase at $T_x$ appears in the LCO and Bi2212 systems, however, the Hg1201 system does not show any evident u-turn. On the other hand, the drop in $\sigma^2$ at the superconducting transition temperature $T_c$ appears common to all the systems (however, less evident in the LCO system). The Hg1201 system manifests a large decrease in the $\sigma^2$ around the superconducting...
transition temperature. Here we should mention 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
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 [18]. Indeed the
temperature dependence of the $\sigma^2$ shows an anomalous up-turn at a temperature $T_s$, due
to the instability (driven by a particular local lattice distortion in the CuO$_2$ plane [7, 11]).
Here we provide a ready reference of the La$_{1.88}$Sr$_{0.12}$Nd$_{0.4}$CuO$_4$ (LNS) system [19-22] in
which static charge stripe order has been observed. Fig. 3 shows temperature
dependence of the $\sigma^2$ determined by Cu K-edge EXAFS in this model compound [23].

The $\sigma^2$ of the model LNS system shows an anomalous up-turn at \~60K where the
charge stripe ordering is known to occur as shown by several experimental techniques in
this system [19-22]. Considering evidences of charge stripe ordering in the model LNS
system, we assign the anomalous up-turn in the $\sigma^2$ to a charge instability giving charge
stripe ordering. The results are also consistent with the charge stripe ordering in the
LCO system below \~190 K, revealed by x-ray diffraction [24].

![Temperature dependence of the Cu-O pairs $\sigma^2$ in the LNS system (symbols). Expected
temperature dependence of the $\sigma^2$ for a fully correlated motion of Cu and O, calculated by Einstein
model, is shown by lower dotted line. A constant value of 0.00145 is added to guide the temperature
dependence of the experimental $\sigma^2$ (upper dotted line). The dashed line across the charge stripe order
temperature ($T_s$) is guide to the eyes [23].](image)

Therefore, the anomalous increase in $\sigma^2$ is due to stripe ordering in the CuO$_2$ plane of
the LCO (T,\~190 K) and Bi2212 (T,\~140 K) systems. Recently Sharma et al [3] have
further confirmed the results and found a clear up-turn in the temperature dependence of the
excess displacements (a parameter similar to the DWF measuring dynamic and static
distortions) measured by ion-channelling on the YBCO system at the stripe ordering
temperature. In fact, below this temperature the pair distribution function becomes larger
than that due to thermal fluctuations and the formation of striped phase should give an
asymmetric bond length distribution due to splitting of the Cu-O bonds as demonstrated
earlier [6, 7].
The lower temperature anomaly in $\sigma^2$ appears around the superconducting transition temperature $T_c$. The correlated DWFT $\sigma^2$ shows an anomalous decrease around the $T_c$. This is a clear indication that the appearance of the superconducting state is accompanied by a decrease of the instantaneous local atomic displacements pointing towards a key role of local electron lattice interactions in the superconducting pairing. The drop is found to be maximum for the Hg-based compound where the block-layers are Ba-O with smaller micro-strain in the CuO$_2$ plane than the case of Bi2212 (Sr-O) and LCO (La-O).

It is interesting to note that the two anomalies appear with different amplitudes, depending on the system and there appears proportionality like correlation between the two amplitudes and the micro-strain in the CuO$_2$ plane. Fig. 4 shows amplitudes of the two anomalies, given by the drop in the DWFT at $T_c$ and the up-turn at the $T_s$ as a function of the micro-strain in the studied systems. Here the micro-strain $\epsilon$, has been estimated by measuring the average <Cu-O> bond-lengths by the EXAFS analysis. The micro-strain $\epsilon = 2(d_0 - \langle R_{Cu-O} \rangle)/d_0$ determines the relative compression of the average in-plane bonds, $\langle R_{Cu-O} \rangle$, and is directly related to the chemical pressure. The $d_0$ is the Cu-O equilibrium distance, i.e., Cu-O bond length for an unstrained CuO$_2$ plane. The $d_0$ is measured to be ~1.985 ($\pm$0.005) Å on an undoped model system Sr$_2$CuO$_2$Cl$_2$, which is consistent with others [25]. The $d_0$ is taken to be 1.97 Å throughout this paper considering the correction due to effect of hole doping on the Cu-O bonds (~0.16 doped holes per Cu site) [15].

![Figure 4](image)

**FIGURE 4.** The drop in the DWFT ($\Delta \sigma^2$) at the $T_c$ (open circles) and the up-turn at the $T_s$ (open squares) are plotted as a function of the micro-strain, determined for different systems.

It is clear from the plot that, while the up-turn in temperature dependent $\sigma^2$ increases at the $T_s$, the drop at the $T_c$ shows a clear decrease with increasing micro-strain. This behavior has direct implication on the relation between the charge inhomogeneous state and the superconductivity in the copper oxides. It has been shown that up-turn at $T_s$ is due to asymmetric pair distribution function derived by splitting of the Cu-O bonds [6, 7]. Therefore the amplitude of the up-turn of $\sigma^2$ is directly proportional to the barrier height in the multi-well potential. The present results show that the height of the barrier increases, and hence the charge stripe ordering, which is strongly tied to the electron-
lattice interaction, gets stronger with increasing the micro-strain. Let's analyze this aspect and recall the recent angle resolved photoemission spectroscopy (ARPES) results on the high $T_c$ superconductors. High-resolution ARPES results on high $T_c$ superconductors reveal a kink in the dispersion, defined by an abrupt change of electron velocity at 50-80 meV [8]. This kink has been interpreted to be due to phonons associated with the movement of the oxygen atoms. To further enlighten, we have plotted the ratio of the two velocities, i.e., the dressed velocity and the bare velocity as a function of micro-strain in Fig. 5, indicating increasing trend of the electron-lattice coupling as a function of the micro-strain. This behavior of the electron-lattice interaction, analogous to the amplitude of the up-turn in the $\sigma^2$ (Fig. 4) suggests that the kink structure in the electron dispersion is closely related to the Cu-O displacements, with asymmetric bond distribution, driving the system in an inhomogeneous charge state with self-organization in stripes. This observation further suggests that the energy scale of $\sim$50-80 meV, revealed by the ARPES measurements, seems to be related to the charge inhomogeneous state. However, it is still to be explored the relationship between the energy scale and the superconductivity.

![FIGURE 5. Ratio of the dressed electron velocity $V_d$ and bare electron velocity $V_b$ is shown as a function of the micro-strain. The two velocities are taken from the ref. [8], determined by high resolution ARPES data.](image)

Let us now make a comment on the drop in the $\sigma^2$ at the superconducting transition temperature $T_c$, which depends on the micro-strain. Incidentally this anomalous decrease in the local Cu-O displacements is also found by ion channeling experiments, measuring excess displacements on different systems, showing a drop of variable amplitude, that depends on the superconducting transition temperature [3]. In fact, higher the micro-strain, smaller the drop at $T_c$ and smaller the transition temperature. This eventually contradict the fact that higher micro-strain means stronger electron-lattice coupling and hence to expect higher $T_c$. Therefore the Cu-O local displacements should have two components. At the superconducting transition the drop, revealing decreased Cu-O displacements at $T_c$, could be due to decrease of the incoherent part of the displacements to transfer electron lattice interaction energy in the pairing mechanism entering into a coherent state. As a matter of fact, there seems to be an anomalous drop of local Ge-Nb displacements at the $T_c$ in the Nb,Ge intermetallic system, showing short coherence length superconductivity [26]. This further suggests an intimate relationship between the local lattice fluctuations and superconductivity in the short coherence superconductors having high transition temperature.
In summary, we have measured local lattice displacements in copper oxide superconductors by high resolution polarized Cu K-edge EXAFS measurements to address the problem of inhomogeneous state, superconductivity and local distortions. The correlated DWF has been taken as an order parameter to determine the temperature dependent local and instantaneous Cu-O displacements. The choice is due to the fact that the DWF is related with the Debye frequency and has direct implication on the superconducting transition temperature. We have studied the Cu-O displacements as a function of chemical pressure on the CuO$_2$ plane, defined by the micro-strain. We find two temperatures, the superconducting transition temperature $T_c$ and the charge stripe ordering temperature $T_s$, where the local Cu-O displacements show anomalous change with variable amplitude. While the amplitude of the drop of local displacements at the superconducting transition temperature decreases, the amplitude of the up-turn across the charge stripe ordering temperature gets increased with increasing micro-strain in the CuO$_2$ plane. The results are compared with the kink structure in the dispersion, seen by 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 the copper oxides. Furthermore, we find that the appearance of the superconducting state is accompanied by a decrease of the instantaneous local lattice distortions also in the Nb$_2$Ge intermetallic compound, indicating that the local displacements are the key to the superconductivity of the materials with small coherence length. Nevertheless, present experiments have direct implication on the correlating between electron-lattice interaction, inhomogeneous state and high $T_c$ superconductivity in the complex copper oxides. At this stage it is speculative to predict precise role of the local lattice displacements, however, it appears that the local displacements control the fundamental electronic band structure near the singularity point (M point in the copper oxides and 1 point in the A15 intermetallics).

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