Evidence for Critical Lattice Fluctuations in the High $T_c$ Cuprates

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Here we provide a direct experimental evidence for critical local lattice fluctuations in the high $T_c$ superconductors. Cu K-edge extended X-ray absorption fine structure (EXAFS) has been used to measure the distribution of Cu–O bond lengths and the amplitude of local lattice distortions in different materials with increasing chemical pressure on the CuO$_2$ layers. The stripe formation temperature $T_{co}$ is determined by the upturn of the Debye Waller factor due to the onset of local lattice distortions. A decrease of the amplitude of lattice fluctuations at the superconducting transition reveals their role in the pairing mechanism. The dynamical lattice fluctuations in the normal phase for $T > T_{co}$ show diverging lattice fluctuations at the critical chemical pressure $\varepsilon_c$.

KEYWORDS: perovskite superconductors, local lattice fluctuations, synchrotron radiation spectroscopy, stripe phases

Superconductivity in the cuprate perovskites remains one of the puzzling issues in the condensed matter physics since its discovery. Structurally the high $T_c$ cuprate perovskites are heterogeneous materials made of alternated layers of metallic body centered cubic (bcc) CuO$_2$ layers and insulating rock-salt face centered cubic (fcc) M–O (M = Ba, Sr, La) layers. The mismatch between the two sub-lattices is generally estimated by $1 - t = [r(A - O)]/\sqrt{2}[r(Cu - O)]$ where $r(A - O)$, $r(Sr – O)$ and $r(Ba – O)$ and $r(Cu – O)$ are the respective bond lengths and $t$ is the Goldschmidt tolerance factor. Due to the lattice mismatch the CuO$_2$ sheets are under compression and (M–O) layers under tension. There are several experiments uncovering the fact that the chemical pressure due to the mismatch between the two sub-lattices play a significant effect on the superconducting transition temperature.

While only temperature and doping have been taken as energy scales to describe generic phase diagram of the High $T_c$ superconductors, there are now growing number of experiments providing evidence for electron lattice interaction being a necessary parameter to characterize the metallic state of the cuprates. Recent experiments on the isotope effects have further demanded the need to include the electron lattice interaction as one of the parameters to describe the complex metallic phase of the cuprate superconductors.

In the present work we have investigated the local lattice fluctuations in the CuO$_2$ plane as a function of the chemical pressure. The chemical pressure induces an anisotropic strain in the CuO$_2$ plane. The relative compression of the average in-plane $(R_{Cu-O})$ bond-lengths $\varepsilon = 2d_0 - (R_{Cu-O})/d_0$ has been found to be directly related to the chemical pressure. Here the $d_0$ is Cu–O equilibrium distance, i.e., Cu–O bond length for an unstrained CuO$_2$ plane. The $d_0$ is measured to be $\sim 1.985(\pm 0.005)$ Å on an undoped model system Sr$_2$CuO$_2$Cl$_2$, which is consistent with others. 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 ($\sim 0.16$ doped holes per Cu site). In this paper we report experimental evidence for quasi-critical electron-lattice interactions in the cuprate superconductors. We have measured the local and instantaneous lattice fluctuations in the CuO$_2$ plane exploiting the Cu K-edge extended X-ray absorption fine structure (EXAFS) and determined $\varepsilon$ in different families of cuprates at a fixed charge density by measuring $(R_{Cu-O})$. The temperature dependent distribution of the lattice distortions (dynamic and static) is measured by the Debye–Waller factor of the Cu–O bond length in different families of cuprate superconductors. To avoid the disorder created by cationic substitution we have selected the superconducting systems where the doping is provided only by the interstitial oxygen. The results provide a direct experimental evidence for the presence of a critical micro-strain $\varepsilon_c$ in the CuO$_2$ plane where a large enhancement of the local lattice fluctuations occur and the superconducting transition temperature reaches the maximum. The outcome of this work enforces that the electron lattice interaction $g(\varepsilon)$ is critical for the physics of superconducting cuprates and should be included as one of the variables to explain the high $T_c$ phase diagram.

Well-characterized superconducting single crystals of different superconducting systems were used for the experiments. The La$_2$CuO$_4$1+ (LCO), Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) and HgBa$_2$CuO$_{4+\delta}$ (Hg1201) [and HgBa$_2$CaCu$_2$O$_{6+\delta}$ (Hg1212)] systems are used as representative for the La-based ([La$_2$O$_{2+\delta}$]CuO$_2$), Bi-based ([Bi$_2$O$_{2+\delta}$]Sr$_2$O$_2$Ca)Cu$_2$O$_4$] and Hg-based ([HgO$_2$(Ba$_2$O$_2$Ca)]Cu$_2$O$_4$) superconducting families containing respectively the La-
O, Sr–O and Ba–O as rock-salt layers that sustain different chemical pressure on the CuO$_2$ planes, where the dopants are interstitial oxygen ions in the block layers. An electrochemically doped LCO single crystal of size 2 × 2 mm$^2$ was used. This crystal has been characterized by X-ray diffraction showing 3.5 staging and single $T_c \sim 40$ K ($\Delta T_c \sim 1.5$ K) measured before the experiments. The oxygen ordering of stage 3.5 occurs between 330 K to 270 K and diffuse in plane charge ordering at $\sim$190 K. The Bi2212 crystal was of size 1 × 2 mm$^2$, grown by the travelling solvent floating zone method with $T_c \sim 87$ K ($\Delta T_c \sim 1.2$ K). On the other hand, the Hg-based crystals were of small size ($\sim 0.3 \times 0.3$ mm$^2$), and were grown by high-pressure synthesis technique. The $T_c$ of the samples used for the present experiments were 94 K ($\Delta T_c \sim 2$ K) and 116 K ($\Delta T_c \sim 3$ K) respectively for the Hg1201 and Hg1212.

The temperature dependent polarized Cu K-edge absorption measurements were performed on the beam-line BL13B of Photon Factory at High Energy Accelerator Research Organization in Tsukuba and on the BM29 and BM32 of European Synchrotron Radiation Facility (ESRF), Grenoble. At the beam-line BL13B of the Photon Factory, and the BM32 of the ESRF, the crystals were mounted in closed cycle refrigerator and temperature was controlled within an accuracy of $\pm$1 K. Beam-line BM29 of ESRF is equipped with a two stage closed cycle refrigerator and the samples were mounted in it with temperature control within an accuracy of $\pm$1 K. In all cases, the temperature was measured using diode sensors attached on a flat plate sample holder. The measurements were performed in the fluorescence yield (FY) mode using multi-element Ge X-ray detectors array. The emphasis was given to measure the spectra with a high signal to noise ratio and up to a high momentum transfer and purposefully we measured several scans to accumulate the total fluorescence counts to be $\sim$3 million to limit the relative errors to be less than 0.1% above the absorption threshold. Standard procedure was used to extract the EXAFS signal from the absorption spectrum 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.

Figure 1 shows Fourier transform (FT) of the EXAFS signals extracted from the Cu K-edge absorption spectra measured on different superconducting systems with E vector of the plane polarized X-ray beam falling parallel to the CuO$_2$ plane, representing different families with varying strain. The peaks in the FT appear due to back-scattering of emitted photoelectrons from neighboring atoms providing a global atomic distribution around the absorbing Cu site. The peaks in the FT do not represent the real atomic distances and the position should be corrected for the photoelectron back-scattering phase shifts to find the quantitative value to the atomic positions with respect to the Cu atom. There are evident differences in the FT of the EXAFS spectra measured on different systems. The major difference appears around the Cu–M (M = La, Sr(Ca), Ba(Ca), Ba respectively for LCO, Bi2212, Hg1212 and Hg1201 systems) peak due to different block-layers.

The EXAFS amplitude depends on several factors as can be seen from the following EXAFS equation for polarized K-edge EXAFS,

$$
\chi(k) = \frac{m\pi}{h^2} \Sigma_i 3N_i \cos^2(\theta_i) \times \frac{S_0^2}{kR_i^2} f_i(k, R_i) e^{-\frac{2m_i}{\lambda^2}} e^{-2k^2\sigma^2} \sin[2kR_i + \delta_i(k)].
$$

Here $N_i$ is the equivalent number of neighboring atoms, at a distance $R_i$, located at an angle ($\theta_i$) with respect to the electric field vector of the polarized synchrotron light. $S_0^2$ is an amplitude correction factor due to photoelectron correlation and (also called passive electrons reduction factor), $f_i(k, R_i)$ is the backscattering amplitude, $\lambda$ is the photoelectron mean free path, and $\sigma^2$ is the correlated Debye–Waller factor of the photoabsorber-backscatterer pairs. Apart from these, the photoelectron energy origin $E_0$ and the phase shifts $\delta_i$ should be known. The above parameters can be either fixed or allowed to vary when an experimental EXAFS spectrum is parameterized.
Here we focus only on the local distortions in the CuO$_2$ plane and hence the first oxygen coordination shell (i.e. in-plane Cu–O bond distances). In the E\\parallel ab 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. The extracted EXAFS signals due to the Cu–O bond distances represent only single backscattering of the photoelectron emitted at the Cu site by its nearest neighbour in-plane oxygen atoms and probe the correlation function of the Cu and oxygen pairs. The approach is to avoid any multiple scattering signals that generally make the data analysis complex. We have used the standard procedures to draw the pair distribution function (PDF) of local Cu–O bond-lengths from analysis of the EXAFS oscillations only due to the Cu–O distances. In this procedure the EXAFS signal due to the Cu–O is simulated by the least squares fit with an input model containing a distribution of several distances (where the $N_{tot}$ is fixed to the nominal value and $\sigma^2_{CuO}$ for each distance is given by the Einstein model for a correlated Cu–O distribution) respecting the number of allowed fit parameters to be less than $(2\Delta R\Delta k/\pi)^2$. The only variable parameter is the relative probability of different distances with a constraint of $N_{tot}$ to be fixed. Same results were obtained while two distances model was used to fit the Cu–O EXAFS (with fit parameters are the two distances ($R$) their relative probabilities and the associated two $\sigma^2_{CuO}$) for deriving the PDF. The feasibility of these methods has been shown earlier for the case of cuprates$^{26}$ manganites$^{30}$ and other complex systems.$^{31,32}$

The pair distribution function at higher temperature, determined by the above mentioned analysis, is found to be symmetric for all systems (except a negligibly small asymmetry for the case of Bi2212). Figure 2 shows the Cu–O pair distribution function (PDF) in the LCO, Bi2212, Hg1201 and Hg1212 systems determined by the EXAFS analysis in the normal state, at a high temperature ($T = 200$ K). The PDF represents the distribution of local lattice distortions (static and dynamic) in the CuO$_2$ plane and shows a continuous evolution from LCO to the Hg1201 reflecting an intimate relationship of the chemical pressure with the local lattice fluctuations. The PDF displays a peak at the mean Cu–O distance. The mean Cu–O bond-lengths (vertical bars) show a clear evolution with the change in the chemical pressure on the CuO$_2$ plane and increases from La-based to Hg-based systems. This is expected due to different mismatch between the rock-salt layers (respectively La–O, Sr–O and Ba–O for the La-based, Bi-based and Hg-based systems) and the CuO$_2$ lattice, sustaining different strain on the CuO$_2$ plane.

Large variation in the Cu–O distribution in Fig. 2 suggests that the Cu–O Debye–Waller factor ($\sigma^2_{CuO}$), measuring both static and dynamic distortions in the CuO$_2$ plane, should be a good parameter to make a direct and systematic comparison. Here it should be mentioned that the Debye–Waller factors in the EXAFS measurements is not the same as the one observed by diffraction experiments. While the diffraction Debye–Waller factor represents atomic Debye–Waller factor, accounting the mean-square deviation of a given atom with respect to its average site (e.g., the mean square deviation of the copper ($\sigma^2_{Cu}$) and oxygen ($\sigma^2_{O}$) atoms about their average crystallographic positions), the EXAFS Debye–Waller factor measures the broadening of the distance between two atomic sites [i.e., the $\sigma^2_{CuO}$ measures the correlated distribution between the absorber (Cu) and the backscatter (O)]. We have determined the $\sigma^2_{CuO}$ by simulating the Cu–O EXAFS signal using the conventional approach where the diffraction results were used as the initial model (an average Cu–O bond). Since the EXAFS Debye–Waller factors of the Cu–O pairs $\sigma^2_{CuO}$ takes into account both static and dynamic distortions, it is an important structural parameter to study temperature evolution and compare the role of lattice fluctuations in the CuO$_2$ plane. The temperature dependence of the $\sigma^2_{CuO}$ is shown in Fig. 3 for the LCO, Bi2212 and Hg1201 systems representing the three different families of the cuprates.

The $\sigma^2_{CuO}$ shows abnormal temperature dependence revealing several well-defined structures. We can easily define at least two temperatures ($T_{co}$ and $T_c$) where the $\sigma^2_{CuO}$ show anomalies within the temperature region measured here. There is an anomalous increase below the temperature $T_{co}$ followed by a decrease around the superconducting transition temperature $T_c$. The increase at $T_{co}$ appears in the LCO and Bi2212 systems, however, the Hg1201 system does not show any evident up turn. On the other hand, the drop of the $\sigma^2_{CuO}$ at the superconducting transition temperature $T_c$ appears common to all the system (however, less evident in the LCO system). The Hg1201 system manifests a large drop in the $\sigma^2_{CuO}$ around the superconducting transition temperature. Interestingly, the absolute value of the $\sigma^2_{CuO}$ are similar (within the experimental uncertainties) at the superconducting transition temperature, however, quite different above the $T_{co}$. Here we should mention that, apart from the static and dynamic distortions of the CuO$_2$ lattice,
However, in the present case the thermal contribution to the $\sigma^2_{\text{CuO}}$ should be similar (for a pair of Cu and O atoms) for all the systems and hardly affects the discussion in this paper.

To further enlighten the effect across the $T_{\text{co}}$ and $T_c$, we have determined the PDF at different temperatures. The PDF were obtained by simulating the EXAFS signal considering a distribution of several distances, as mentioned above. Figure 4 shows the distribution at three different temperatures for the LCO, Bi2212 and Hg1201 samples. Interestingly the Cu–O distribution turns asymmetric with two peak function below the $T_{\text{co}}$ in case of LCO and Bi2212 systems while it remains symmetric for Hg1201 all over the temperature range (within the experimental uncertainties). In addition, the pair distribution function reveals a significant change across the superconducting transition temperature $T_c$, consistent with a decreasing of CuO$_2$ distortions as indicated by a change in the correlated Cu–O Debye Waller facor $\sigma^2_{\text{CuO}}$ (Fig. 3).

Let us come to discuss the anomalous increase of the $\sigma^2_{\text{CuO}}$ at a temperature $T_{\text{co}}$. It is known that at the appearance of any charge-density-wave like instability the Debye–Waller factor shows an anomalous change as found in several density wave systems. We have earlier discussed this effect and assigned the anomalous upturn in the $\sigma^2_{\text{CuO}}$ to a charge instability giving stripe-charge ordering. Therefore the anomalous increase in $\sigma^2_{\text{CuO}}$ is due to stripe-charge ordering in the CuO$_2$ plane of the LCO ($T_{\text{co}} \sim 190$ K) and Bi2212 ($T_{\text{co}} \sim 140$ K) systems. X-ray diffraction measurements on the LCO system has clearly demonstrated onset of charge ordering to be $\sim 190$ K which is consistent with the observation of the upturn in the $\sigma^2_{\text{CuO}}$ in the system. Recently Sharma et al. have further confirmed our earlier results and found a clear upturn in the temperature dependence of the excess displacements (a parameter similar to the Debye–Waller factor measuring dynamic and static distortions) measured by ion-channeling on the YBCO system at the stripe-charge ordering temperature. In fact, below this temperature the pair distribution function becomes larger than that due to thermal fluctuations and the formation of striped polarons should give an asymmetric PDF (Fig. 4) due splitting of the Cu–O bonds as demonstrated earlier.

One of the important features revealed by the present work is an anomalous drop of the $\sigma^2_{\text{CuO}}$ around the superconducting transition temperature $T_c$. This is a clear indication that the appearance of the superconducting state is accompanied by the decrease of the instantaneous local lattice distortions and hence a direct evidence of the role of electron lattice interactions in the superconducting pairing. The drop at $T_c$ is different for different systems and found to be maximum for the Hg-based compound where the block-layers are Ba–O giving smaller mismatch than the case of Bi2212 (Sr–O) and LCO (La–O). Below $T_c$ the $\sigma^2_{\text{CuO}}$ shows a small increase, however, within the experimental uncertainties. Interestingly the $\sigma^2_{\text{CuO}}$ reaches a similar value around the $T_c$.

The anomalous decrease at the superconducting transition temperature and similar values around this characteristic temperature provides a direct evidence for an important role of critical lattice fluctuations in the superconducting state. At the superconducting transition the drop of the $\sigma^2_{\text{CuO}}$ at $T_c$ could be due to transfer of electron lattice interaction energy in the pairing mechanism (the superconductivity is a coherent phenomena and the decrease might be related to decrease of inco-

![Fig. 3. Temperature dependence of the Cu–O (planar) Debye–Waller factor $\sigma^2$ determined by EXAFS; La$_2$CuO$_4$ (upper), Bi2212 (middle) and Hg1201 (lower). The dashed line is a guide to the eyes. The resulting Debye–Waller factor $\sigma^2$ shows abnormal temperature dependence with an increase below a temperature $T_{\text{co}}$ followed by a decrease around the superconducting transition temperature $T_c$. The error bars represent the average estimated noise level.](image-url)
Cu–O pair distribution function (PDF) above $T_{co}$ (solid line) is compared with the PDF below $T_{co}$ (dashed line) and below $T_{c}$ (dotted line) for the La$_2$CuO$_4$ (upper), Bi2212 (middle) and Hg1201 (lower).

We have estimated the micro-strain in the CuO$_2$ plane $\varepsilon$, for different systems from the measured average $\langle$Cu–O$\rangle$ bond-lengths. The $\varepsilon$ dependence of the Cu–O distance broadening for different superconducting systems at 200 K is shown in Fig. 5. The $\varepsilon$ dependence of the $T_{co}$ and the superconducting transition temperature $T_{c}$ is also shown. The Cu–O distance broadening and the superconducting transition temperature $T_{c}$ seems to diverge around the $\varepsilon_c \sim 0.04 \pm 0.005$. At this critical value the superconducting transition temperature reaches the maximum value while the lattice fluctuations diverge.

This merely indicates an intimate relationship between the lattice fluctuations and the superconductivity.

In summary, we have determined local lattice fluctuations in high $T_c$ superconductors at the optimum doping ($\delta = 0.16$) with variable chemical pressure on the electronically active CuO$_2$ plane. Polarized Cu K-edge EXAFS has been used to measure the Cu–O bond distances and the distance broadening (given by the Debye–Waller factors) providing direct information on the static and dynamic lattice distortions as a function of the chemical pressure. The results suggest that the superconducting $T_{c}$ reaches the maximum near the critical strain in the CuO$_2$ plane, $\varepsilon_c \sim 0.04 \pm 0.005$. The temperature dependence of the Debye–Waller factors of the Cu–O bonds shows unusual behavior. We find that the Debye–Waller factor shows a drop at the superconducting transition temperature revealing importance of electron-lattice interaction in the pairing mechanism. Furthermore, the Debye–Waller factor shows an upturn at the lattice-charge stripe ordering temperature.

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