Effects of local lattice disorder on the superconductivity studied by XAFS

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Abstract. The variation of local lattice displacements of the in-plane Cu-O bond upon Cu-site impurity doping in La$_{2-x}$Sr$_x$CuO$_4$ superconductor is investigated by Cu K-edge EXAFS studies. In Mn doping case, the analysis of the temperature dependence of Debye-Waller factor indicates that the local lattice displacements of the in-plane Cu-O bond exhibits similar behavior in all La$_{1.875-1.5}$Sr$_{0.125+1.5}$Cu$_{1-x}$Mn$_x$O$_4$ (0 ≤ x ≤ 0.15) samples. This may reflect that the doping of Mn does not alter the local lattice environments in the CuO$_2$ plane and thus the Mn impurity does not destroy the superconducting transition in a similar way with other ionic doping cases. The local lattice displacements at room temperature upon ionic doping are compared, which indicates that Fe doping leads to largest local displacements while Ni doping is intermediate. The possible interplay between the local lattice displacements and the normal-state resistivity is compared. These results indicate that the local lattice displacements largely affect the superconducting properties in La$_{2-x}$Sr$_x$CuO$_4$ superconductor.

1. Introduction

In recent years, substantial experimental evidence have started to accumulate for the existence of local structural and magnetic inhomogeneities in cuprate superconductors, suggesting that it plays a fundamental role in the superconductivity [1]. Due to the fact that the cuprate oxide superconductors have short coherence length, the search and study of mesoscopic structural fluctuations in the high-Tc cuprates has been a throttling point of research activities in the recent studies. X-ray absorption fine structure spectroscopy which has sufficiently short intrinsic experimental time scales to give information on dynamical local structure fluctuation has proved its ability and is a powerful tool to probe the local structural inhomogeneity and the local atomic displacements of the superconducting CuO$_2$ plane.

Lattice vibrations couple to electrons because displacements of atoms from their equilibrium positions alter the band dispersions, lowering or raising the total electronic energy. According to this, the study of the local lattice displacements in the CuO$_2$ plane is a useful way to clarify the role of electron-phonon coupling in cuprate superconductors. Here we report the detailed analysis of the effects of Cu-site impurity doping on the local lattice displacements in the CuO$_2$ plane of La$_{2-x}$Sr$_x$CuO$_4$ superconductor and its influence on the superconducting transition. By comparison of the variation of the Debye-Waller factor upon element doping (such as Mn, Fe, Ni, etc.) at the Cu site, it is revealed that the local lattice disorder in the CuO$_2$ plane plays significant role on the superconducting properties in La$_{2-x}$Sr$_x$CuO$_4$ superconductor.
2. Experimental
Polycrystalline samples used in this study are prepared by improved solid-state reaction method. Appropriate mixture of La₂O₃, SrCO₃, CuO, MnO₂, Fe₂O₃, and NiO of 99.99% purity are well ground and the mixture powder is calcined in air directly at 1150°C for 24 h. The preheating is repeated once at the same temperature with intermediate grinding. After the preheating, the mixture is thoroughly reacted and the resulting mixture is very dense which is difficultly ground into fine powder. The powder is pressed into pellets which are finally sintered at 1150°C for another 24 h. From the x-ray powder diffraction patterns it is confirmed that all samples are formed in single phase without any impurities. Resistivity as a function of temperature was measured using a standard four-probe method in a closed-cycle helium cryostat. All XAS measurements were performed in a fluorescence detection mode at BL13B, Photo Factory. A novel Ge pixel array detector (PAD) with 100 segments was used in order to gain high throughput and energy resolution and as a result, high signal-to-noise Mn K-edge x-ray absorption spectroscopies for dilute Mn doped samples are achieved. The detailed description of PAD apparatus was reported elsewhere [2]. Samples are mounted on an aluminum holder and attached to a closed-cycle helium refrigerator. The holder rotates on a high precision goniometer (Huber 420) to change the incidence angle. The incidence angle is 15 degree with respect to the sample surface for Cu K-edge XAS experiments and 12 degree for Mn K-edge XAS experiments, respectively. These specific angles are chosen in order to decrease the self-absorption effect in fluorescence signal and avoid the diffraction.

3. Results and Discussion
We choose Mn, Fe, and Ni as the impurities to substitute the Cu in La₂₋ₓSrₓCuO₄ superconductor and investigate the influence of the impurity doping on the local lattice environments in the CuO₂ plane and the superconducting transition.

Figure 1. The Tc_{onset} value as functions of the impurity doping concentrations (upper panel) and the give the resistivity value at room temperature as the functions of impurity doping concentrations (lower panel) for several different samples.
Since Mn ion can exist at 3+ and 4+ valence state in perovskite-type compounds and Fe ions can exist at 2+ and 3+ valence state, we prepare several series of Mn and Fe doping samples with nominal formula: La1.85Sr0.15Cu1-xMnxO4, La1.85-1.5xSr0.15+1.5xCu1-xMnxO4, La1.85-2xSr0.15+2xCu1-xMnxO4, La1.875-1.5xSr0.125+1.5xCu1-xMnxO4, La1.85Sr0.15Cu1-xFexO4, and La1.85-xSr0.15+xCu1-xFeO4. For Ni doping case, we prepare the sample with nominal composition La1.85Sr0.15Cu1-xNixO4. In our previous reports we have reported that the Tc onset value of the Mn doping samples does not exhibit the rapid decrease like other elements doping cases while the Tc onset value decreases monotonously with increasing doping concentration in Fe and Ni doping cases. In Figure 1 (a) we give the Tc onset value as functions of the impurity doping concentrations in these samples. It can be seen from Figure 1 that in different series, the critical Mn doping concentration (x_c) where the superconductivity disappears is different, i.e., x_c=0.03 for La1.85Sr0.15Cu1-xMnxO4, x_c=0.1 for La1.85-1.5xSr0.15+1.5xCu1-xMnxO4, x_c=0.06 for La1.85-2xSr0.15+2xCu1-xMnxO4 and La1.875-1.5xSr0.125+1.5xCu1-xMnxO4. This difference comes from the different charge carrier concentrations introduced in the conductive CuO2 plane, since the Mn ions are likely to exist at higher valence state (3+ or 4+) comparing to the valence state of Cu (generally accepted to be around 2+, not accurately) and the introduction of Mn into the CuO2 plane would result in a decrease of charge carrier density in the conductive plane. Thus it is easy to understand that the charge carrier concentration in La1.85Sr0.15Cu1-xMnxO4 system decreases rapidly by simultaneously increasing Mn doping. However, we can compensate the rapid decrease of charge carrier density by simultaneously increasing Sr content when Mn concentration is increased. That is the reason why we have prepared several series of Mn doped sample with different Sr/Mn contents. For La1.875-1.5xSr0.125+1.5xCu1-xMnxO4, the Tc onset value is about 28.5 K, 36.4 K, 37.3 K and 37.4 K for x=0, x=0.02, x=0.04 and x=0.06, respectively. The superconductivity disappears at x>0.08 samples. In Fe doping case, the Tc onset values in La1.85Sr0.15Cu1-xFeO4 samples are 37 K, 33 K, and nearly 0 K for x=0, x=0.01, and x=0.02 samples, respectively. In La1.85-1.5xSr0.15+1.5xCu1-xFeO4 samples, the Tc onset values are 37 K, 31 K, 36 K and 20 K for x=0, x=0.01, x=0.02, and x=0.03 samples, respectively. The superconductivity is suppressed in x=0.05 sample in La1.85-1.5xSr0.15+1.5xCu1-xNiO4. In Figure 1 (b) we give the resistivity value at room temperature as the functions of impurity doping concentrations. It can be seen that the resistivity value increases monotonously with increasing impurity doping in each series of samples. However, if we compare the resistivity value of the samples at a certain impurity doping concentration, it can be seen that the difference is very large. In detail, at a certain impurity doping level, the resistivity is largest in La1.8Sr0.15Cu1-xFeO4 samples while it is lowest in La1.85-1.5xSr0.15+1.5xCu1-xMnxO4.

![Figure 2](image-url)  
*Figure 2. Representative examples of Cu K-edge fluorescence EXAFS spectra yield as a function of photon energy measured for bulk La1.875-1.5xSr0.125+1.5xCu1-xMnxO4 samples.*
In Figure 2 we show the representative examples of raw Cu K-edge fluorescence yield as a function of photon energy measured for bulk La$_{1.875-1.5x}$Sr$_{0.125+1.5x}$Cu$_{1-x}$MnxO$_4$ samples. Since fluorescence yield spectra measured at BL13B of photon Factory are obtained by integrating 100 channels which can give a total of $2.4 \times 10^7$ counts per data point and each data point is integrated for four seconds and four independent scans are repeated to minimize systematic error, the perfect EXAFS oscillations at each temperature for each sample can be extracted from the raw fluorescence yield [3].

Figure 3 shows the extracted Cu K-edge EXAFS oscillations (weighted by $k^2$) for La$_{1.875-1.5x}$Sr$_{0.125+1.5x}$Cu$_{1-x}$MnxO$_4$ samples with $x=0.00$, $x=0.04$, and $x=0.15$ at 10 K and 200 K, respectively. One can find that the magnitude of the oscillations increases at higher $k$-region as temperature is decreased, in accordance with dynamic lattice disorder (uncorrelated phonons). This indicates that the oxygen displacement suffers from a lattice disorder effect in both Mn-free sample and Mn doped samples.

Figure 3. Extracted Cu K-edge EXAFS oscillations (weighted by $k^2$) for La$_{1.875-1.5x}$Sr$_{0.125+1.5x}$Cu$_{1-x}$MnxO$_4$ samples with $x=0.00$; $x=0.04$; and $x=0.15$ at 10 K and 200 K, respectively.

Figure 4 (a) and (b) show the Fourier transforms, $|FT(k^2 \chi(k))|$ of the EXAFS oscillations (weighted by $k^2$) of the $x=0$ and $x=0.15$ samples at several representative temperatures. The $k$-dependent profile of total oscillation reflects the weighted sum of scattering amplitude functions of La(Sr), Cu(Mn), and O. The first peak in the FT corresponds to the in-plane Cu-O atoms, while the doublet peak structure at around 3-4 Å corresponds to the Cu-La(Sr) and Cu-O-Cu multiple scattering signals. The small peaks located at 2-3 Å range come from the contribution of Cu-O(apical) bonds and local CuO$_6$ octahedral distortions. The peaks of Cu-O, Cu-La(Sr), and Cu-O-Cu scattering signals show strong temperature dependence, i.e., the FT amplitudes increase with decreasing temperature. It is noticeable that both the
feature and the temperature dependent amplitude of the Fourier transforms are similar for the x=0 and x=0.15 samples. The EXAFS signals of the Cu-O bonds are well separated from the longer bond contributions and have been extracted by the standard Fourier filtering method. The filtered EXAFS signals represent single backscattering of the photoelectron emitted at the Cu site by its nearest neighbor oxygens and therefore probe the correlation function between Cu and oxygen pairs. Multiple scattering signals, which make the data analysis more complex, are excluded in this analysis because such signals have a longer effective photoelectron pathlength.

Figure 4. (a) and (b): the Fourier transforms, |FT(k^2χ(k))| of the EXAFS oscillations (weighted by k^2 of the x=0 (a) and x=0.15 (b) samples at several representative temperatures; (c) The Debye-Waller factors as functions of temperature for x=0, x=0.04, and x=0.15 samples.

Individual EXAFS data (k<18 Å⁻¹) for the nearest neighbor Cu-Oₚ correlations are filtered and curve fitted in k-space using a single scattering formula with theoretical phase shift functions calculated by FEFF6 [4]. The fitting procedure is based on a standard nonlinear least square technique which minimizes the statistical χ² determined by the squares of the difference between experimental data and theoretical fitting data. Structural parameters such as the in-plane Cu-Oₚ distance R_{Cu-O} and mean-square relative displacement of planer oxygen σ²_{Cu-O} relative to copper ions are determined. This
approach is adopted to make a direct comparison of the local lattice distortions of the Mn doped samples with the Mn-free sample, where the correlated Debye-Waller factor (DWF) of the Cu-O pairs is the suitable order parameter of local CuO₂ displacements. Within experimental uncertainties the $R_{\text{Cu-O}}$ value are found to be temperature independent and similar to that determined by diffraction study $R_{\text{Cu-O}}=1.885$ Å. The temperature dependence of correlated DWF of Cu-O pairs is shown in Fig. 4 (c) for $x=0.15$, $x=0.04$, and $x=0$ samples. At high temperature, the Debye-Waller factor decreases with decreasing temperature which is due to the weakening of thermally-fluctuation-induced oxygen displacement. A noticeable feature is that the temperature dependent DWF displays an upturn at temperature below 80 K. This upturn is a common feature in the temperature dependence of DWF of cuprate superconductors [5-8]. Another interesting behavior is that the Debye-Waller factor exhibits a decrease at near Tc, which indicates that there is some coherence in the lattice structure when the superconducting transition occurs. It is noticeable that the doping of Mn does not change the behavior of the temperature dependence of Debye-Waller factor.

In order to compare the effects of impurity doping on the local lattice displacements in the CuO₂ and their effects on the transport properties in these systems, we compare the local lattice displacements of several series of impurity doped (Mn, Ni, and Fe) samples at room temperature. The data analysis process is the same with that of La₁.₈₇₅₋₁.₅ₓSr₀.₁₂₅₊₁.₅ₓCu₁₋ₓMnxO₄ samples. The room temperature Debye-Waller factor as a function of impurity doping content is shown in Figure 5. Interestingly, we notice that the Debye-Waller factor values at room temperature for these samples show similar behavior with the resistivity values at room temperature. That is, the Debye-Waller factor increases the fastest for La₁.₈₅Sr₀.₁₅Cu₁₋ₓFexO₄ and La₁.₈₅Sr₀.₁₅Cu₁₋ₓMnxO₄ while it increases the slowest for La₁.₈₅₋₁.₅ₓSr₀.₁₅₋₁.₅ₓCu₁₋ₓMnxO₄. The relation between the local lattice displacement and the resistivity is clear: the stronger the local lattice displacement, the larger the resistivity. This is reasonable, because the transport of charge carriers in these systems occurs within the conductive CuO₂ plane. And certain kind of lattice vibrations would couple to charge carriers, because displacements of atoms from their equilibrium positions should obstruct the movement of carriers. This gives evidence that electron-lattice coupling plays an important role on the transport properties in La₂₋ₓSrₓCuO₄ superconductor.

![Figure 5](link)

**Figure 5.** The room temperature Debye-Waller factors as a function of impurity doping content for all samples.
4. Conclusion
In summary, systematical XAFS studies on the local environments of Cu in different type of impurity doped La$_{2-x}$Sr$_x$CuO$_4$ reveal the local lattice displacement of planer Cu-O bond is strongly related to the transport behavior in these systems. In Mn-doped systems, the doping of Mn does not change the upturn of $\sigma_{\text{Cu-O}}^2$ at below 80 K and the decrease at near Tc. At room temperature, the resistivity increases with impurity doping, which is consistent with the increase of local lattice displacement of in-plane Cu-O bond.

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