Temperature Dependent Polarized XANES Spectra for Zn-doped LSCO system

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Abstract

The cuprates seem to exhibit statistics, dimensionality and phase transitions in novel ways. The nature of excitations [i.e. quasiparticle or collective], spin-charge separation, stripes [static and dynamics], inhomogeneities, psuedogap, effect of impurity dopings [e.g. Zn, Ni] and any other phenomenon in these materials must be consistently understood. Zn-doped LSCO single crystal were grown by TSFZ technique. Temperature dependent Polarized XANES [near edge local structure] spectra were measured at the BL13-B1 [Photon Factory] in the Flourescence mode from 10 K to 300 K. Since both stripes and nonmagnetic Zn impurities substituted for Cu give rise to inhomogeneous charge and spin distribution it is interesting to understand the interplay of Zn impurities and stripes. To understand these points we have used Zn-doping and some of the results obtained are as follows: The spectra show a strong dependence with respect to the polarization angle, $\theta$, as is evident at any temperature by comparing the spectra where the electric field vector is parallel with ab-plane to the one where it is parallel to the c-axis. By using the XANES [temperature] difference spectra we have determined $T^*$ [experimentally we find, $T^* \approx 160$-170 K] for this sample. The XANES difference spectra shows that the changes in XANES features are larger in the ab-plane than the c-axis, this trend is expected since zinc is doped in the ab-plane at the copper site. Our study also complements the results in literature namely that zinc doping does not affect the c-axis transport.
I. INTRODUCTION

The Cuprates, Nickellates, and Manganites display interesting features of spin, charge, lattice and orbital orderings. These features lead to the display of a wide variety of physical phenomenon, such as Paramagnetism [PM], Ferromagnetism [FM], antiferromagnetism [AF], Chargetism [i.e. charge orderings], Orbitism [i.e. orbital orderings], Superconductivity, “Strange Metal” [SM] behaviour. In addition to the fundamental and interesting physics, these materials offer technological use [i.e. Giant Magnetoresistance [GMR] also called Colossal Magnetoresistance [CMR]] and High Temperature Superconductivity [HTSC] [1].

Many HTSC materials are cuprates, which seem to exhibit statistics, dimensionality and phase transitions in novel ways. The nature of excitations [i.e. quasiparticle or collective], spin-charge separation, stripes [static and dynamics], inhomogeneities, pseudogap, effect of impurity dopings [e.g. Zn, Ni] and any other phenomenon in these materials must be consistently understood. Thus we turn to a systematic study of LSCO system for a range of Zn doping [0.5%, 1.0%, and 2.0%]. Here our purpose is to report on our temperature dependent polarized XANES measurements on the 1% LSCO sample. Zn-doped LSCO single crystal were grown by TSFZ technique. Temperature dependent Polarized XANES [near edge local structure] spectra were measured at the BL13-B1 [Photon Factory] in the Fluorescence mode from 10 K to 300 K. Since both stripes and nonmagnetic Zn impurities

*We are coining this terminology since we want to emphasize that akin to orderings in magnetism there is a dual ordering with respect to charge distribution

†By systematic we mean that we intend to make using the same crystals all studies, such as XRD, EXAFS, XANES, IR, Optical, Raman spectroscopies, Specific heat, thermal conductivity, neutron scattering, NMR and others!
substituted for Cu give rise to inhomogeneous charge and spin distribution it is interesting to understand the interplay of Zn impurities and stripes. To understand these points we have used Zn-doping and some of the results obtained are as follows: The spectra show a strong dependence with respect to the polarization angle, \( \theta \), as is evident at any temperature by comparing the spectra where the electric field vector is parallel with ab-plane to the one where it is parallel to the c-axis. By using the XANES [temperature] difference spectra we have determined \( T^* \). The XANES difference spectra shows that the changes in XANES features are larger in the ab-plane than the c-axis, this trend is expected since zinc is doped in the ab-plane at the copper site. Our study also complements the results in literature namely that zinc doping does not affect the c-axis transport \(^2\). Local lattice instability and stripes in the CuO\(_2\) plane of the La\(_{1.85}\) Sr\(_{0.15}\) Cu O\(_4\) using temperature dependent XANES and EXAFS was studied by Saini et al. \(^3\). It was concluded in \(^3\) that the temperature-dependent distortions show a maximum around 60 K, and minimum at 37 K [i.e. \( T_c \)] and that two types of doped charges coexist in different stripes in the superconducting phase. Here our motivation is a quite different. Among other details we want to answer in particular the following: Can we see a change in the XANES spectrum as a function of temperature, which originates from the inhomogeneous charge distribution in cuprates such as LSCO. Since as already mentioned above both stripes and nonmagnetic Zn impurities substituted for Cu give rise to inhomogeneous charge and spin distribution it is interesting to understand the interplay of Zn impurities and stripes. Naively we expect that stripes are pinned by Zn and that leads to suppression of quasiparticle weight. In particular it is found that the 1/8 hole-concentration anomaly of \( T_c \), which is an indication of stripes is induced in Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\)

\(^{\dagger}\)Here by \( T^* \) we simply mean the temperature where there is a transition in the XANES spectrum. Experimentally we find, \( T^* \approx 160-170 \) K for the current sample.
by Zn substitution \[4\]. Moreover the angle-resolved photoemission [ARPES] experiments show that the Zn substitution suppresses the quasi-particle weight along the \((0,0)-(\pi,\pi)\) direction \[3\], this suppression is qualitatively same as that of underdoped \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) in which vertical stripes exist \[1\]. Keeping these remarks in mind a little thought tell us that since the \(T_c\) of 1\%Zn-doped \(\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\) is roughly 20 K, and on the other hand a \(T_c \approx 20\) K LSCO system is underdoped with \(T^* \approx 160-170\) K, we would expect a \(T^* \approx 160-170\) K in a 1\%Zn-doped \(\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\) if indeed a relation between stripes of kind mentioned above exists. Indeed we found a transition in XANES measured spectrum in the ab-plane as a function of temperature at 160-170 K, see Fig. \[3\]. This is very inspiring since we could experimentally prove the guess about relationship of stripes and Zn-doping. In some sense we can map regions of phase diagrams into each other by varying zinc doping or by increasing stripe effect by going to the underdoped region, thus probing various regions of the phase diagrams. This also, is in keeping with our theoretical conjecture, that the of superconducting phase is intimately connected with fundamental collective excitations [1-dimensional objects i.e. strings]

II. EXPERIMENTAL DETAILS

Conventional traveling solvent floating zone (TSFZ) method \[4\] was used for the crystal growth of \(\text{La}_{2-x}\text{Sr}_x\text{Cu}_{1-y}\text{Zn}_y\text{O}_4\) \((x=0.15, y=0.01)\). High purity (99.99\%) powders of \(\text{La}_2\text{O}_3, \text{SrCO}_3, \text{CuO}, \text{ZnO}\) were used as raw materials. For feed rod preparation, the raw materials were mixed in stoichiometric amount \((x=0.15, y=0.01)\). The composition of solvent determined by slow cooling floating zone (SCFZ) method \[8\] was LSCZO (80 mol%)

\[8\]These points have also been noted by Toyama et al. \[6\]
(Cu+Zn)O with x=0.4, y=0.013. The crystal was grown in a four mirror type infrared heating furnace in oxygen pressure $P(O_2) = 0.2$ MPa at a growth speed of 1 mm/h. The as-grown crystal was cigar shaped with diameter about 5.5 mm and 60 mm along the growth direction. It showed metallic lustre and confirmed to be single domain by polarizing optical microscopy.

The XANES measurements were conducted at beamline B13-B1 at the Photon Factory (PF), Tsukuba, in the Fluorescence mode. The electron beam energy was 3.0 GeV and the maximum stored current is 400 mA. EXAFS data was collected using fixed-exit double crystal Si(111) monochromator. The first crystal is a water-cooled flat Si(111) monochromator and the second crystal is sagittally bent to focus the horizontal beam over $\equiv 2$ mrad. A 19-element solid state detector was used to collect the fluorescence signal. The large number of detectors allows us to cover a sizeable amount of the solid angle of the x-ray fluorescence emission in addition to giving a high signal to noise ratio. The temperatures of sample were controlled and monitored to within an accuracy of $\pm 1$ K.

III. RESULTS AND DISCUSSION

In addition to our experimental work we have generated theoretically predicted spectra using FEFF8.10 [9] for La$_2$CuO$_4$, Fig. 1, unpolarized La$_{1.85}$Sr$_{0.15}$Cu$_{0.99}$Zn$_{0.01}$O$_4$, Fig. 2, and La$_{1.85}$Sr$_{0.15}$Cu$_{0.99}$Zn$_{0.01}$O$_4$, Fig. 3, when the polarization vector is along the c-axis. The definitions of the quantities $\mu$, $\mu_0$ and $\chi$ can be found in [9]. We were not able to generate successfully the XANES spectra in case of $E||ab$-plane. Let us briefly discuss some simple points. By intention we have used the default values in the feff.inp file in order to generate the spectra. In order to leave room for standard comparisons the crystallographic data of Radaelli et al. [10] was used at 10 K, in our FEFF calculations. A rough estimate of La$_{1.85}$Sr$_{0.15}$Cu$_{0.99}$Zn$_{0.01}$O$_4$ [Fig. 3] when the polarization vector is along the c-axis [for
definition of peaks A please see below], is $A_1 \approx 8995 \text{ eV}$, $A_2 \approx 9002 \text{ eV}$, $A_3 \approx 9010 \text{ eV}$, thus the energy splittings are $A_2 - A_1 \approx 7 \text{ eV}$, and $A_3 - A_2 \approx 8 \text{ eV}$. Even by using almost default input files we can generate good agreement. We note that the edge energy found by the FEFF8.10 evaluations is $E_0 = 8985.97415 \text{ eV}$, and that we have used the dopant card of atoms 2.50.

We have measured the XANES spectrum at temperatures of 10 K, 15 K, 20 K, 30 K, 40 K, 60 K, 80 K, 100 K, 120 K, 140 K, 160 K, 180 K, 200 K, 220 K, 240 K, 260 K, 280 K, and 300 K for both polarization directions, i.e. $E || c$-axis and $E || ab$-plane. Typical raw and subtracted spectra [at 20 K] are shown respectively in Figs. 4 and 5. The sharpness and detailed nature of the spectra are clear. Both the raw and subtracted data is extracted with Ada1. The edge energy used by Ada1 is $E_0 = 8980.3 \text{ eV}$. Restricting ourselves upto energies of 9050 eV in Figs. 4 and 5 we can see several peaks. For the $E || c$-axis case we can see several peaks $A_0$, $A_1$, $A_2$, $A_3$, $A_4$, and $A_5$, similarly for the $E || ab$-plane the peaks $B_0$, $B_1$, $B_2$, $B_3$ and $B_4$. Peaks $A_0$ and $B_0$ will not be discussed here, features $A_1$, $A_2$, $A_3$, $B_1$, and $B_2$ are briefly described below.

As can be seen from our typical measured XANES Spectra, the main absorption features are $A_1$, $A_2$, and $A_3$ for the $E || c$ case and $B_1$, and $B_2$ for $E || ab$. In large part, the peaks $A_1$, and $A_2$ are determined by the multiple scattering of the ejected photoelectrons off apical oxygen and La and Sr atoms. The peak $B_1$ arises from the multiple scattering off the in-plane oxygen and copper in the CuO$_2$ plane, whereas $B_2$ not only includes the multiple scattering contributions akin to $B_1$ but in addition shows the many body shake-up satellite of it.

Here we give a rough estimate of energy positions and energy difference in peaks, leaving more details and analysis for elsewhere. We find $A_1 \approx 8994 \text{ eV}$, $A_2 \approx 9000 \text{ eV}$, $A_3 \approx 9007 \text{ eV}$, $B_1 \approx 9004.5 \text{ eV}$, and $B_2 \approx 9011.5 \text{ eV}$. Thus the energy splittings between the
peaks in the XANES spectra are as follows: \( A_2 - A_1 \approx 6 \text{ eV} \), \( A_3 - A_2 \approx 7 \text{ eV} \), \( B_1 - A_2 \approx 4.5 \text{ eV} \), and \( B_2 - B_1 \approx 7 \text{ eV} \). Even with this rough estimate our values are in good agreement with standard experimental values quoted for \( \text{La}_2\text{CuO}_4 \) and \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_0.99\text{Zn}_0.01\text{O}_4 \) systems.

The temperature dependence of the measured difference with respect to [w.r.t] 20 K XANES Spectra for \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_0.99\text{Zn}_0.01\text{O}_4 \) for ab-plane and c-axis is shown respectively in Figs. 6 and 7 respectively. The quantity we plotted is XANES difference spectrum. This is simply defined as the difference between the XANES spectrum at a temperature \( T \) and reference temperature 20 K. The “difference” we have plotted is defined to be the [approximate] value between the maximum and minimum of the difference spectra. A “transition” is clearly seen in the ab-plane case at \( T = T^* \approx 160 - 170 \text{ K} \) whereas the c-axis data does not register any measurable [on this scale] change as is clear from Figs. 6 and 7. This suggest that a “transition” in 2D inhomogeneous electron gas. By “transition” we mean here an abrupt change in the XANES spectra given a certain doping and co-doping [here by Zn] at a certain temperature or temperature interval. By the pinning of stripes we can probe the strange metal phase in LSCO material. Theoretically we consider this as a charge order-disorder transition. In our scenario of HTSC theory we consider superconductivity arising from the dressing of 1-d stripe or string phase. The stripe arises due to a line of quantum critical points. This is supported by Monte-Carlo calculations [among other reasons] of 2D d-p Hubbard model where stripes and superconductivity exists. The correlation length in HTSC material is short compared to their conventional cousins, since here superconductivity arises due to 1-d stripes.

IV. CONCLUSIONS

Temperature dependent Polarized XANES [near edge local structure] spectra were measured at the BL13-B1 [Photon Factory] in the Flourescence mode from 10 K to 300 K
for very good quality single crystal of LSCO co-doped with 1 % Zinc at the Cu site. Since both stripes and nonmagnetic Zn impurities substituted for Cu give rise to inhomogeneous charge and spin distribution it is interesting to understand the interplay of Zn impurities and stripes. We recently learned that Pan et al. [11] have reported microscopic electronic inhomogeneity in the high-Tc superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$. To understand these and other points we have used Zn-doping and some of the results obtained are as follows: The spectra show a strong dependence with respect to the polarization angle, $\theta$, as is evident at any temperature by comparing the spectra where the electric field vector is parallel with ab-plane to the one where it is parallel to the c-axis. By using the XANES [temperature] difference spectra we have determined $T^*$ [experimentally we find, $T^* \approx 160-170$ K] for this sample. The XANES difference spectra shows that the changes in XANES features are larger in the ab-plane than the c-axis, this trend is naively expected since zinc is doped in the ab-plane at the copper site. Our study also complements the results in literature namely that zinc doping does not affect the c-axis transport. We have also generated theoretical spectra from FEF8.10 which agrees well the experimental results, keeping in mind that we have mainly used default FEFF8.10 settings, by intention. However we were not able to generate the ab-plane XANES spectra with FEFF8.10.

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FIGURES

FIG. 1. XANES Spectra calculated using FEFF8.10 for La$_2$CuO$_4$

FIG. 2. XANES [unpolarized] Spectra for obtained with FEFF8.10 for La$_{1.85}$ Sr$_{0.15}$ Cu$_{0.99}$ Zn$_{0.01}$ O$_4$

FIG. 3. XANES [c-axis polarized] Spectra for obtained with FEFF8.10 for La$_{1.85}$ Sr$_{0.15}$ Cu$_{0.99}$ Zn$_{0.01}$ O$_4$

FIG. 4. Measured Raw XANES [ab-plane and c-axis polarized] Spectra for for La$_{1.85}$ Sr$_{0.15}$ Cu$_{0.99}$ Zn$_{0.01}$ O$_4$ at 20 K

FIG. 5. Subtracted [using Ada1] measured XANES [ab-plane and c-axis polarized] Spectra for La$_{1.85}$ Sr$_{0.15}$ Cu$_{0.99}$ Zn$_{0.01}$ O$_4$ at 20 K

FIG. 6. Temperature Dependence of the measured difference [w.r.t 20 K] XANES [ab-plane polarized] Spectra for La$_{1.85}$ Sr$_{0.15}$ Cu$_{0.99}$ Zn$_{0.01}$ O$_4$

FIG. 7. Temperature Dependence of the measured difference [w.r.t 20 K] XANES [c-axis polarized] Spectra for La$_{1.85}$ Sr$_{0.15}$ Cu$_{0.99}$ Zn$_{0.01}$ O$_4$