Temperature-dependent modulation amplitude of the CuO_2 superconducting lattice in $La_2CuO_{4.1}$

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The temperature-dependent amplitude of the Cu-O(planar) bond modulation in the $La_2CuO_{4.1}$ superconducting crystal has been measured by in-plane-polarized Cu *K*-edge extended x-ray-absorption fine structure. Minority domains characterized by a long Cu-O(planar) bond length are found at $T<150$ K. The separation between the two Cu-O(planar) distances provides a measure of the amplitude of the CuO_2 lattice modulation assigned to a charge-density wave that coexists with the superconducting phase, providing evidence for a broken symmetry. [S0163-1829(97)06313-3]

I. INTRODUCTION

The search and study of mesoscopic structural modulations in the high-T_c cuprates has been a throttling point of research activities in the recent times due to the fact that these materials show short coherence superconducting properties. Several techniques have been used to investigate the modulation of the CuO_2 lattice and to determine the related distortions[1–15] as these are considered to be important structural aspects in controlling superconducting properties. Cu *K*-edge extended x-ray absorption fine structure (EXAFS) has proved its abililty and is used to probe the local structure of the superconducting CuO_2 plane in various families of cuprate superconductors.[8–15]

The resulting inhomogeneous CuO_2 lattice, characterized by distribution of Cu-O bond distances, has been assigned to an anharmonic one-dimensional (1D) charge modulation in a superlattice of quantum stripes,[13,14] and the results were confirmed recently by solving the CuO_2 superstructure using anomalous diffraction in $Bi_2Sr_2CaCu_2O_8$ (Bi2212).[15] It has been demonstrated that the 1D lattice modulation involves plane lattice distortions that directly modulate the electronic structure of the CuO_2 planes.[8,14]

The oxygen-doped $La_2CuO_{4+\delta}$ system has attracted a lot of attention where the hole doping is realized by introducing *mobile* interstitial oxygen ions as acceptors in the rocksalt layers,[16,22] showing the role of ordering of acceptors on the superconducting properties. A macroscopic phase separation is known to occur for oxygen doping $0.01<\delta<0.06$ and $T<260$ K with the formation of oxygen-poor (insulating $La_2CuO_{4.01}$) domains and oxygen-rich (superconducting $La_2CuO_{4.06}$) domains. At high oxygen doping $\delta>0.06$ the macroscopic phase separation is suppressed and the system superconducts below $T_c\sim40$ K. However, there are indications that interstitial oxygens are ordered and the system is inhomogeneous, also in the superconducting phase at high doping. Superstructure reflections indicating a latttice modulation with a wavelength of the order of 25 Å have been observed by neutron and electron diffraction at low temperature.[1,20,21] The presence of different Cu sites and the distribution of tilts of the CuO_6 octahedra in the CuO_2 plane have been detected by nuclear magnetic resonance (NMR) and have been assigned to the coexistence of tilted and untilted octahedra forming striped domains.[6]

The purpose of the present paper is to report temperature-dependent modulation amplitude of the CuO_2 plane of the oxygen-doped $La_2CuO_{4+\delta}$ system, determined by polarized Cu *K*-edge EXAFS, a direct probe, faster than NMR, measuring the instantaneous distribution of the Cu-O distances.

II. EXPERIMENT

We have used a crystal with high oxygen doping (near the optimum doping for the high-T_c superconductivity) that is free from macroscopic phase separation.[6,23] For the purpose we have taken advantage of a high brilliance x-ray source provided by the 6-GeV European synchrotron radiation facility (ESRF) allowing us to collect the EXAFS data with high signal-to-noise ratio up to a high momentum transfer $Q=2k$-40 $Å^{-1}$.

A high-quality single crystal of $La_2CuO_{4.1}$ ($T_c=38$ K) of size $3\times2\times0.5$ mm^3, doped by electrochemical oxidation[23] was used for the measurements. The crystallographic structure was studied at Institute Laue Langevin (ILL) by neutron scattering. The crystal was mounted in a closed cycle He refrigerator and the temperature was monitored with an accuracy of ±1 K. The temperature-dependent in-plane (**E**$\|$**ab**) polarized Cu *K*-edge absorption spectra were recorded at the beam line CRG-IF of ESRF.

The x-ray beam emitted by the 6-GeV ESRF storage ring was monochromatized by a bent conically shaped Si(111) double-crystal monochromator and sagittally focused on the sample. Twelve scans were recorded at each temperature by detecting the fluorescence yield. The EXAFS signal $\chi=(\alpha-\alpha_0)/\alpha_0$, where α is the absorption coefficient and α_0 is the so-called atomic absorption, was extracted from the ab-

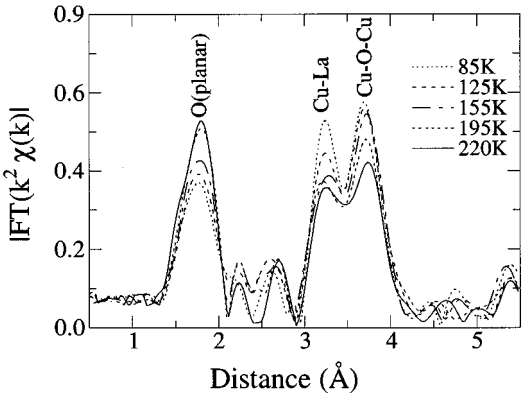

FIG. 1. Fourier transforms (FT) of the experimental EXAFS spectra at several temperatures. The Fourier transforms have been performed from $k_{\min}=3$ Å^{-1} to $k_{\max}=19$ Å^{-1} using a Gaussian window and corrected by the theoretically calculated phase shifts. The temperatures have been selected to highlight the differences. The anomalous temperature dependence of the Cu-O(planar) EXAFS is reflected by an unexpected decrease in the FT amplitude at lower temperatures while the EXAFS signals of the Cu-La and Cu-O-Cu shells appear to show the standard temperature dependence.

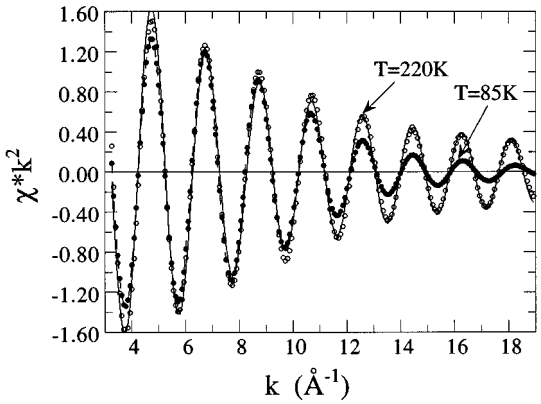

FIG. 2. Fourier filtered Cu-O(planar) EXAFS signal at 85 K (filled circles) and its fit with two distances (dashed line) is plotted along with the EXAFS signal at 220 K (opern circles) and the fit with a single distance (solid line). The difference in the EXAFS spectra at the two temperatures is clearly visible. It is worth noting that the 85-K EXAFS shows damping of the amplitude at higher k due to interference of two frequencies corresponding to two Cu-O(planar) distances.

sorption spectrum using standard procedure[24] and corrected for fluorescence self-absorption.[25]

III. RESULTS AND DISCUSSION

In Fig. 1 we report the Fourier transforms of the phase-corrected experimental **E**||**ab** polarized Cu K-edge EXAFS spectra (multiplied by k^2) extracted from the measured absorption on the $La_2CuO_{4.1}$ single crystal at several temperatures. The Fourier transforms have been performed from $k_{\min}=3$ Å^{-1} to $k_{\max}=19$ Å^{-1} using a Gaussian window. The main peaks denote the distribution of the atomic sites with respect to the Cu. It can be seen from the Fourier transform that the contribution of the Cu-O(planar) is well separated from the other shells of neighboring atoms. The Fourier filtered contribution of the Cu-O(planar) EXAFS is shown in Fig. 2. The anomalous temperature dependence of the Cu-O(planar) Fourier transform peaks, seen in Fig. 1, is also clear in Fig. 2 where the amplitude of the EXAFS oscillations at higher k values is drastically reduced at low temperature showing a disordering of the CuO_2 plane. The Cu-O(planar) EXAFS is fitted by nonlinear least-square fitting using the curved wave EXAFS theory[26] to give information about the distribution of the O(planar) atoms around the photoabsorber Cu and to determine possible static and/or dynamic disorder in the CuO_2 plane. The fitted signal is also plotted along with the experimental spectra in Fig. 2.

The fitting was performed with two Cu-O(planar) distances using the same approach as described for $La_{1.85}Sr_{0.15}CuO_4$ (LSCO).[8] The number of parameters that may be determined by the EXAFS is restricted by the number of independent data points: $N_{\rm ind}\sim(2\Delta k\Delta R)/\pi$, where Δk and ΔR are, respectively, the ranges in k and R space over which the data are fitted. In our case $\Delta k=16$ Å^{-1} (3–19 Å^{-1}) and $\Delta R=0.8$ Å giving $N_{\rm ind}\sim 8$ for the Fourier filtered Cu-O(planar) EXAFS, allowing us to determine precisely a large number of parameters. The two-distance fit was performed first by using five parameters: $R_{\rm long}$, $R_{\rm short}$, and $N_{\rm long}$, ($N_{\rm short}=N_{\rm tot}-N_{\rm long}$, where $N_{\rm tot}$ is the fixed coordination number) and two Debye Waller factors. The value of E_0 and the reduction factor due to multielectrons excitations S_0^2 was fixed to the value obtained by analyzing EXAFS of other copper oxide superconductors[8,13,14] and found to be similar to the values reported for other related copper oxides.[27] The resulting two Debye Waller factors were found to be equal to the extrapolated values corresponding to the correlated Debye model with $\theta_D=600$ K within the uncertainties, and hence they were fixed in the final fitting run to obtain the $R_{\rm long}$, $R_{\rm short}$, and $N_{\rm long}$ parameters. The fits were performed by several procedures by chaning the order of iteration of the parameters, taking into account the correlation and the results were found to be independent of the kind of fitting.

The outcome of the fit is shown in Fig. 3. The results show the appearance of two Cu-O(planar) distances below 150 K [Fig. 3(a)] separated by $\Delta R\times 0.08$ Å [Fig. 3(b)]. The separation is out of estimated uncertainties and larger than the thermal fluctuations, of the order of 0.02 Å, for each distance. The crystallographically determined distance[22] is plotted in Fig. 3(a) for comparison. It can be seen that $R_{\rm short}$ is independent of temperature and close to the crystallographically measured distance, reported to be more or less constant, while the long distance can be considered the anomalous one, which appears at $T<150$ K. The two distances converge into a single distance at $T>150$ K.

At this point we recall our recent EXAFS results on the LSCO system, where the two in-plane distances are associated with existence of locally distorted and undistorted CuO_6 octahedra[8] within the average crystallographic homogeneous structure. Following the same line of thinking, the short distance is attributed to the majority of LTO-like (low-temperature orthorhombic) domains, while the long Cu-O(planar) distance is attributed to the minority LTT one (low-temperature tetragonal), even though the tilting is larger

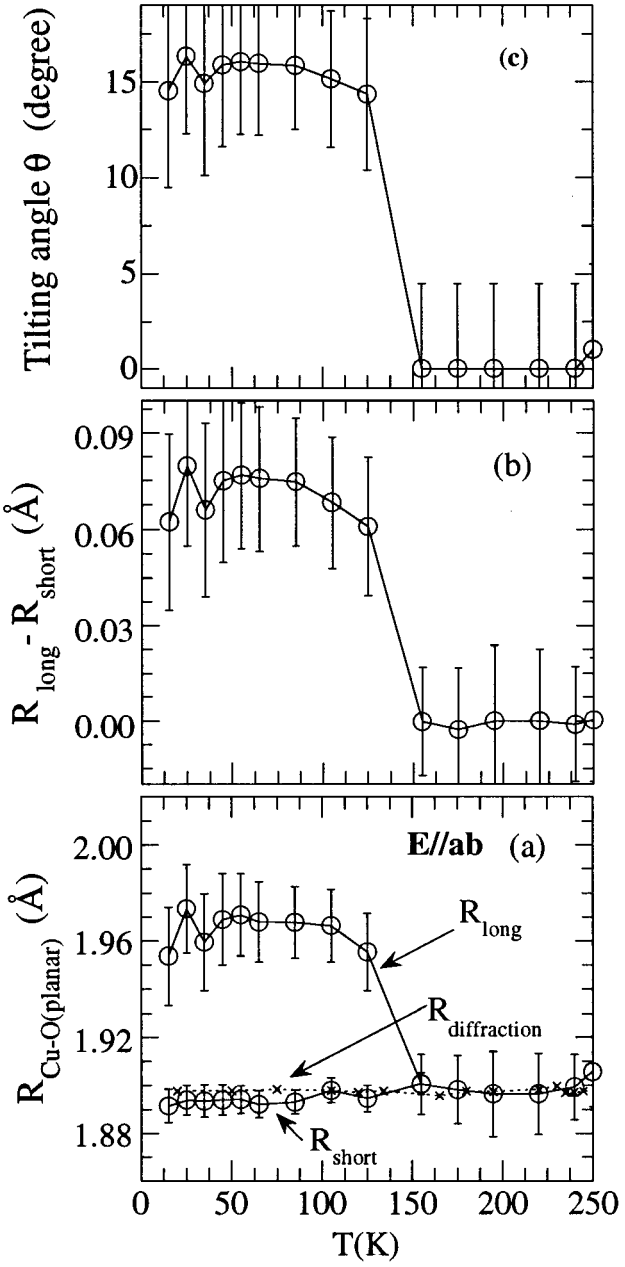

FIG. 3. Temperature dependence of the two Cu-O(planar) distances (R_{short} and R_{long}) measured by EXAFS; (b) temperature dependence of the separation between the long and the short Cu-O bonds; (c) temperature dependence of the tilting angle θ of the rhombically distorted CuO_4 square planes. The temperature dependence of the average Cu-O(planar) distance, determined from the in-plane lattice parameters measured by diffraction (Ref. 23), is also shown for comparison in panel (a).

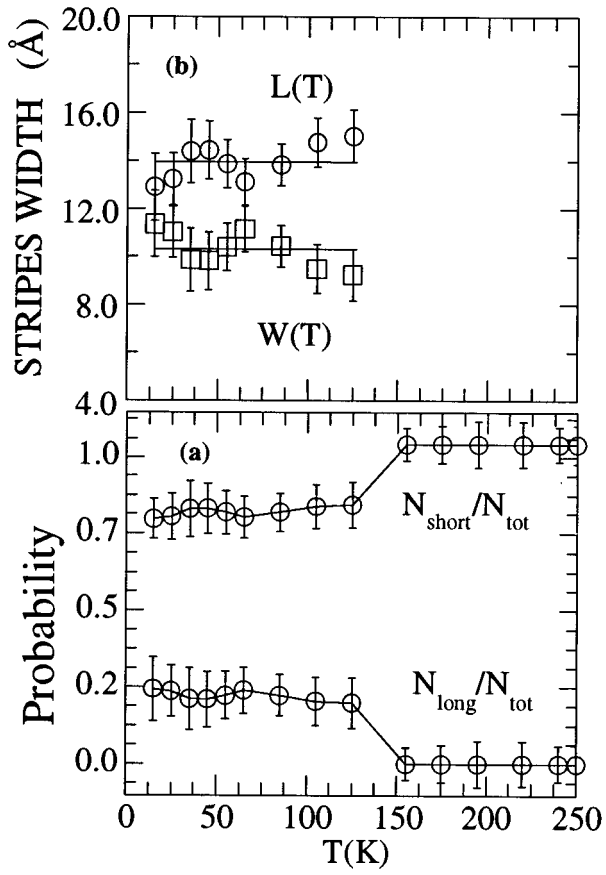

FIG. 4. (a) Probability of the anomalous long Cu-O(planar) bonds measured from the Cu-O(planar) EXAFS spectra; (b) temperature dependence of the stripe width L (W) of the LTO-like (LTT-like) domains, measured by joint EXAFS and diffraction, below 150 K.

than in the average LTT structure.[28] Figure 3(c) shows the temperature dependence of the tilting angle θ of the distorted CuO_4 square planes calculated using $\cos\theta = R_{short}/R_{long}$. The tilting angle is about 15°, which is of the same order of magnitude as the tilting angle observed in the local LTT kind of domains in LSCO,[18] and also agrees with the maximum tilting angle of the octahedra measured by NMR.[6]

In Fig. 4(a) we show the relative number of anomalous long Cu-O(planar) bonds to the total number of in-plane bonds. From the relative number of anomalous long bonds we deduce the probability of presence of $40 \pm 2\%$ anomalous CuO_4 square planes with rhombic distortion having two long bonds per Cu site, forming LTT-like domains. This means that the CuO_4 square plane is decorated with ~60% of the LTO kind of undistorted domains and ~40% of the LTT kind of distorted ones. It is worth mentioning that NMR results[6] have shown coexistence of two different kinds of copper sites by measuring the tilt angle of the CuO_6 octahedra in oxygen-doped La_2CuO_4. The authors have reported the presence of ~60% of the so-called B type (undistorted ones) and ~40% of the A type (distorted ones). In spite of intrinsic differences in the two local probes, EXAFS and NMR, the results of the distribution of the two sites agree with each other. It should be emphasized that on the local scale there are domains of CuO_4 planes that are highly distorted, with a tilting angle of the order of 15°, in the majority of the undistorted domains. Such a big tilting is enough to modify the electronic structure, i.e., a part of the doped charges is trapped in the distorted LTT domains while the rest moves in the undistorted lattice. This shows that two types of charge carriers coexist within the two-dimensional CuO_2 plane.

In the $La_2CuO_{4.1}$ compound, the extra oxygen is found to be in an interstitial site between two LaO layers.[16,20] This site (i.e., extra oxygen) is surrounded by four lanthanum atoms

and four oxygen atoms that are displaced from their normal positions. For the high oxygen-doped system it was suggested that the additional oxygen atoms could become ordered in a sublattice of interstitial sites.[20,29] The neutron scattering data and x-ray diffraction on our crystal shows a superstructure of the type, $\mathbf{q}=q\mathbf{b}^*+(1/n)\mathbf{c}^*$ in the orthorhombic notation at 45° from the Cu-O-Cu direction, with $q=0.21$ and $n\sim3$ giving a one-dimensional modulation with period $\lambda_p\sim24.3$ Å,[20,21] This modulation is similar to that of other doped cuprate superconductors at optimum doping;[8,45] the distorted and undistorted domains of the CuO_4 plane will get disposed spatially in stripes (of width W) made of distorted lattice alternating with stripes (of width L) of undistorted lattice. Thus the CuO_2 plane of $La_2CuO_{4.1}$ is decorated by stripes of distorted lattice containing relatively trapped charge carriers and stripes of undistorted lattice containing itinerant charge carriers. The width W (L) of the LTT-like (LTO-like) stripes measured by joint EXAFS (measuring the pair distribution) and diffraction (giving the modulation period, $\lambda_p\sim24.3$ Å$=L+W$) gives the width of the stripes, $W=0.4$*$24.3\sim9.7$ Å and $L\sim14.5$ Å. Figure 4(b) shows the temperature dependence of the measured stripe width below 150 K. The present experiment provides the determination of the temperature onset, $T<150$ K, for the modulation of the Cu plane in a nonphase separated system at high oxygen doping. Theoretical calculations by Perali *et al.*[30] have shown that the superconducting gap amplification, for a free electron gas in the BCS approximation, occurs when the stripe width L is in the range of 14–16 Å, while the superconducting system is optimally doped. Therefore the value of $L=14.5$ Å indicates that also in the $La_2CuO_{4.1}$ system, as in Bi2212 and LSCO, the increase of the critical temperature by the shape resonance effect can provide a mechanism for increasing the critical temperature to the high temperature range.

In conclusion, we have determined the temperature range, $T<150$ K, for the CuO_2 lattice modulation where two different kinds of domains with the LTT and LTO types of structure coexist in the $La_2CuO_{4.1}$ compound. These domains are spatially distributed in stripes of distorted and undistorted structure. The same kind of distortions have been seen in the isostructural LSCO compound[8] below 100 K and in the Bi2212 system[13,15] suggesting that inhomogeneity of the CuO_2 plane is a common feature for high-T_c superconductivity and for related systems showing charge ordered domains.[31] We give further support to the two-component model based on stripes of localized and itinerant charges within the CuO_2 plane.[8,32]

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