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Stripe Structure and Non-Homogeneity of the CuO₂ Plane by Joint EXAFS and Diffraction

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Abstract: Local structure of the CuO₂ plane in Bi₂Sr₂CaCu₂O_{8+δ} (Bi2212) superconductor has been solved by joint Cu K-edge extended X-ray absorption fine structure (EXAFS) and anomalous X-ray diffraction. The Cu-O pair distribution function (PDF) has been measured by EXAFS and diffraction. The displacement of the Cu ions along the *c*-axis shows largest amplitude and anharmonic character. The results show flat stripes of the CuO₂ lattice of width $L = 15 \pm 0.5$ Å that are separated by stripes of bent CuO₂ plane. The modulation of the CuO₂ plane measured by EXAFS and anomalous diffraction has been discussed.

1. INTRODUCTION

The heterostructure of the high T_c superconductors is commonly formed by the metallic CuO₂ layers separated by rocksalt layers. The lattice mismatch between the Cu perovskite layers and rocksalt layers appears to be a common feature in these materials [1]. This mismatch is one of the reasons to deviate the local structure of the potentially important CuO₂ lattice from the average crystallographic structure [2].

There is growing evidence that incommensurate modulation is a common feature of optimally doped cuprate superconductors. However, the satellite reflections are often weak and diffused, indicating ordering over small domains, and better resolved at temperatures lower than 200 K-100 K. The best characterized situation is that of the Bi₂Sr₂CaCu₂O_{8+y} (Bi2212) superconductor [3] in which the modulation gives rise to sharp and intense satellite peaks up to high temperatures. Also, the Bi2212 has been considered a prototype material to investigate several properties of high T_c superconductors such as the transport and magnetic properties [4], the normal band structure, the superconductivity gap and its anisotropy [5]. The modulated structure of the Bi2212 system has been studied by several groups using electron, X-ray and neutron diffraction techniques [6-15]. The solution of the anharmonic incommensurate superstructure with a large unit cell of Bi2212 is at the limit of the capabilities of diffraction methods due to a large number of parameters required for the structural refinement.

There is tensile stress in Bi2212 within the BiO rocksalt layers and a compressive stress within the CuO₂ planes in the *ab* plane direction. The BiO rocksalt layers release the internal tensile stress by forming stripes of stretched BiO lattice (distorted (*D*)-stripes) in the *ab* plane with low Bi density, variation of the BiO coordination geometry, interstitial oxygen and deviated stoichiometry, that are alternated by Bi rich stripes of undistorted BiO rocksalt lattice (undistorted (*U*)-stripes). The one-dimensional superstructure of the BiO layer is well established in the literature [6, 7, 9, 11, 13-15]. Although various experiments [6, 7, 11, 3-15] report modulation of the Cu sub lattice mainly along the *c*-axis, the results disagree on the amplitude and anharmonic character of the modulation.

We have undertaken this work to solve the controversy between the diffraction results on the distribution of the Cu site conformations in the CuO₂ plane. The modulation of the CuO₂ plane in Bi2212 is measured by Cu K-edge extended X-ray absorption fine structure (EXAFS) and Cu K-edge X-ray anomalous diffraction [16] to overcome the limitations of the X-ray diffraction. The Cu K-edge EXAFS provides directly the pair distribution function (PDF) being a fast ($\sim 10^{-15}$ s) and local (~ 5 Å) probe while the X-ray anomalous diffraction provides direct and selective information on the sub lattice due to strong variation of the scattering factor near the Cu K threshold. The capability of the polarized Cu K-edge EXAFS has been exploited to determine the statistical distribution of the Cu-O distances in Bi2212 single crystal. The diffraction data on the same crystal have been collected in a selected region of the reciprocal space with Bragg reflections of Miller indices $l \gg h \sim k$ to have preferential sensitivity of the diffracted intensities to displacements along the *c*-axis. This approach has allowed us to measure the *z*-coordinate of the Cu atom in the structure and its modulation accurately. The results indicate that the Cu position is anharmonically modulated in the out of plane direction with strong contribution from the second harmonic. The 1D modulation results in two different stripes of distorted (bent Cu-plane) and undistorted (flat Cu-plane) Cu-lattice running along the *a*-axis. In this heterostructure the distorted stripes would act as potential barrier between the stripes formed by undistorted lattice.

2. EXPERIMENTAL AND DATA ANALYSIS

The temperature dependent polarized Cu K-edge absorption measurements were performed on the beam-line BL-4C at Photon Factory at Tsukuba [17]. The spectra were recorded by detecting the fluorescence yield (FY) using 9 NaI(Tl) X-ray detectors. The crystal temperature was monitored with an accuracy of ± 0.5 K. The sample was a single crystal grown by the travelling floating zone method [18] with $T_c = 84$ K. 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 absorption spectrum using standard procedure and corrected for fluorescence self absorption [19].

The diffraction measurements on the same crystal were performed at the European Synchrotron Radiation Facility (ESRF), Grenoble on the wiggler beamline ID11-BL2. The sample was given 24° oscillation around the **b**-axis and the diffraction images were recorded on a 35×43 cm (A3 size) image plate detector. This geometry permitted a precise evaluation of the amplitude and anharmonic content of the modulation of the *z* component of Cu atoms. For the anomalous diffraction two patterns were recorded sequentially at two wavelengths ($\lambda_1 = 1.3788$ Å, at the rising edge of the Cu K threshold and $\lambda_2 = 1.4086$ Å, about 200 eV below the edge) chosen to have a large variation in the real part of the Cu anomalous scattering factor ($\Delta f' = 6.2$ electrons) with no variation in the imaginary part f'' .

The peak indexing was made using the four dimensional approach for incommensurate 1D modulations [20], considering that for each Bragg reflection the diffraction vector **H** can be written as $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}_s$, ($\mathbf{q}_s = \beta\mathbf{b}^* + (1/\gamma)\mathbf{c}^*$, $\gamma = 1$). The superstructure period (given by $\lambda_p = 1/\beta$) has been found to be temperature independent ($\lambda_p = 4.73 \pm 0.01$). The structure factor was calculated in the four dimensional approach using the $N_{1,1,1}^{Bmb}$ superspace group after having corrected the intensities for the Lorentz factor, the polarization, and the absorption. For an almost centrosymmetric structure, the measurable quantity $\delta_F = |F(\lambda_2)| - |F(\lambda_1)|$ may be assumed equal to the variation of the Cu contribution (real part) only [16].

Considering two harmonics, we have refined the *z* component values of Cu atoms independently from the structural parameters of all other atoms by fitting δ_F values with $z_{Cu}(t) = c_0 + c_1 \cos(2\pi t) + c_2 \cos(4\pi t)$ (where $t = \beta y$). The value of $\Delta f'_{Cu}$, of an overall scale factor, and a correction factor which account for small differences in the relative scale of the λ_1 and λ_2 data sets, were refined as part of the refinement. The Fourier coefficients of $x_{Cu}(t)$ and $y_{Cu}(t)$ as well as B_{Cu} thermal parameters were fixed to the values obtained by Yamamoto *et al.*, [6]. As expected, attempts to refine these parameters did not improve the fit.

3. RESULTS AND DISCUSSION

The signal due to the Cu-O(apical) was suppressed in the **E//a** EXAFS while the signal due to Cu-O(planar) was suppressed in the **E//c** spectra. The signals of Cu-O(apical) and Cu-O(planar) were isolated by Fourier filtering (between $k_{min} = 3 \text{ Å}^{-1}$ to $k_{max} = 17 \text{ Å}^{-1}$) from the spectra recorded in the **E//c** and **E//a** geometries. Figure 1 shows representative example of the isolated contributions. The filtered EXAFS were fitted in the range 3-13 Å^{-1} by non-linear least squares fitting using the curved wave EXAFS theory. The best fits using two shells are shown in Figure 1 by solid line. The number of independent parameters that can be extracted in $N_{ind} \sim (2\Delta k \Delta R)/\pi \sim 5$, where $\Delta k = 10 \text{ Å}^{-1}$ and $\Delta R = 0.8 \text{ Å}$ are the ranges in *k* and *R* space over which the data have been fitted. The two distances fitting is essentially a 3 parameters (R_{long} , R_{short} and N_{long}) fit as the Debye Waller factors were taken to be the same ($\sigma^2 = 0.6 \pm 0.2 \cdot 10^{-3} \text{ Å}^2$ for in plane and $0.8 \pm 0.2 \cdot 10^{-3} \text{ Å}^2$ for the out of plane) and equal to the expected values for the correlated Debye model while other parameters were fixed to the values determined by standard model compounds. We can see directly the presence of two main Cu-O(apical) distances separated by $\Delta R \sim 0.19 \pm 0.02 \text{ Å}$ from the beat in the **E//c** EXAFS oscillation at $k \sim 8.5 \pm 0.5 \text{ Å}^{-1}$ confirming previous results [21].

Figure 1: Fourier filtered experimental Cu K-edge EXAFS signal (multiplied by k^2) due to the Cu-O(planar) pairs and Cu-O(apical) pairs (circles) with their fits (solid line) at 30 K.

The pair distribution function (PDF) for the Cu-O pairs extracted from the data at 30 K is shown in Figure 2. There is not a single Cu-O(planar) distance for the CuO₄ square planes but a wide distribution in the range 1.88-1.96 Å. The short Cu-O(planar) bonds at $R_1 = 1.88$ Å are the expected distances for the average crystallographic structure. The long anomalous Cu-O(planar) bonds, $R_2 = 1.96$ Å in Figure 2 are associated with tilting of the CuO₄ square plane in the (110) direction, of the CuO₅ pyramids, where two oxygen atoms per CuO₄ square plane get displaced along the *c*-axis giving a rhombic distortion with two long distances R_2 and two short distances R_1 . We obtain the tilting angle $\theta = 16^\circ$ (or $\theta = 14^\circ$) of the CuO₄ square plane using $\cos\theta = R_1/R_2$ (or $\cos\theta = \langle R \rangle / R_2$, where $\langle R \rangle = a/\sqrt{2}$). The presence of two Cu-O(apical) distances, $R_3 = 2.36$ Å and $R_4 = 2.54$ Å, separated by $\Delta R \sim 0.18 \pm 0.02$ Å is revealed by the damping of the E//*c* EXAFS oscillations at $k \sim 8.5 \pm 0.5$ Å⁻¹. The anomalous short Cu-O(apical) bonds R_3 are associated with the distorted CuO₅ pyramids. The anomalous short Cu-O(apical) bond (0.2 Å shorter) may be due to modulation of the Cu *z*-coordinate.

Figure 2: Pair distribution function (PDF) of the Cu-O lattice. The PDF of the Cu-O(planar) pairs obtained by E//*a* Cu K-edge EXAFS, is normalized to $N(R_1) + N(R_2) = 4$ while the PDF of the Cu-O(apical) pairs obtained by E//*c* Cu K-edge EXAFS is normalized to $N(R_3) + N(R_4) = 1$.

At this point it is necessary to recall the anomalous diffraction results. Figure 3 shows the modulation of the Cu *z*-coordinate determined by the anomalous diffraction at low temperature in the superconducting phase ($T < T_c$). The amplitude of the first harmonic component, $c_1 = -0.009$ ($c_1 = -0.276$ Å), is comparable with previous results. On the other hand the amplitude of the second harmonic component, $c_2 = -0.0042$ ($c_2 = -0.128$ Å), is comparatively larger. In fact the second harmonic was not considered in the neutron diffraction studies [6, 7] while the X-ray diffraction studies resulted lower values for the same.

The large amplitude of the second harmonic gives rise to an anharmonic modulation with zones of Cu lattice having almost constant *z* coordinate. These are separated by zones of largely bent lattice where the *z* coordinate of Cu differs by about 0.6 Å. It should be mentioned that in spite of the intrinsic differences of the two techniques both EXAFS and anomalous diffraction show a distribution of the Cu-O(apical) distance from 2.3 to 2.6 Å. Thus the presence of the anomalous short Cu-O(apical) bond (0.2 Å shorter) observed in EXAFS is clearly due to the modulation of the Cu *z*-coordinate and hence the distribution of the Cu-O(apical) can be assigned to the anharmonic displacement of Cu.

Figure 4 highlights the spatial distribution of the flat and bent Cu lattice where the modulation of copper is plotted along with modulation of other heavy atoms. It can be clearly seen that the modulation amplitude of the Cu atoms in the *c*-axis direction is larger than that of the other atomic species. It decreases from Cu to Bi and it cannot be assigned simply to a steric effect due to the Bi layer. The large *c*-axis displacement of the Cu plane is correlated with the strong *b*-axis modulation of the BiO layers. The projection of the Bi2212 crystal in the *y* - *z* plane is shown over an area of 51 Å (along the *b*-axis) times 30.65 Å (along the *c*-axis). The rectangles indicate the section of wires of undistorted BiO rocksalt lattice and flat CuO₂ stripes (*U* stripes). They are separated by distorted blocks of stretched BiO lattice and bent CuO₂ plane (*D* stripes). This complex structure can be described as wires of distorted lattice, where dopants (substituted and/or interstitial atoms) are located giving negative localized charges (acceptors) as indicated by shadowed circles, and wires of undistorted lattice indicated by squares in Figure 4. In each Cu bi-layer the *U* stripes in a first layer are close to the *D* stripes in the second layer.

The probability (P_d) of the minority distorted CuO₅ pyramids characterized by one short Cu-O(apical) = R_3 and two Cu-O(planar) = R_1 and two long Cu-O(planar) = R_2 has been found to be 0.415. The probability P_d is given by $N(R_3)/N_{\text{tot}}$ (from E//*c* data) = $2N(R_2)/N_{\text{tot}}$ (from E//*a* data). Therefore the majority undistorted CuO₅ pyramids characterized by one Cu-O(apical) = R_4 and four Cu-O(planar) = R_1 have probability $P_u = 1 - P_d = 0.585$. The spatial distribution of the distorted Cu sites has been obtained by joint EXAFS and diffraction experiments. The wavelength λ (25.55 ± 0.0 Å) of the 1D anharmonic modulation in the direction of the *b*-axis in the orthorhombic lattice, *i.e.* 45° from the Cu-O-Cu direction, is found to be temperature

Figure 3: Modulation of the z -coordinate of Cu in the CuO_2 layers along the b axis (solid line) of the Bi2212 structure. The dashed and dotted lines represent first and second harmonic contributions.

Figure 4: Modulation of z/c ($c = 30.653 \pm 0.002 \text{ Å}$) for copper and the heavy atoms over two periods of the superstructure. The squares indicate sections of wires of undistorted CuO_2 stripes and BiO rocksalt blocks (U-blocks). The modulations of two neighbour parallel CuO_2 planes are out of phase so that flat Cu stripes are surrounded by bent stripes.

independent. The wavelength λ of the 1D anharmonic modulation along the b -axis of the orthorhombic unit cell measured by anomalous diffraction and the probability P_u measured by EXAFS are shown in Figure 5 as a function of temperature. The large anharmonic character is indicated by the large contribution of the second order reflections (Figure 3). This anharmonic modulation of the CuO_2 plane gives stripes of distorted lattice (D -stripes) of width W that form linear domain walls intercalated with the stripes of undistorted lattice (U -stripes) of width L ($L \neq W$) running along the a -axis as shown in the insert of Figure 3b. We have measured the width $L = \lambda P_u = 15 \pm 0.5 \text{ Å}$ of undistorted lattice ($W = \lambda - L$) by joint EXAFS (P_u) and diffraction (λ) data.

In summary, the modulation of the Cu plane in the Bi-2212 system has been determined by EXAFS and anomalous diffraction. The measured Cu-O distances show large distribution with an elongation of the Cu-O(planar) bonds. The large contribution of the second harmonic merely indicates that the CuO_2 plane is formed by flat and bent stripes. The distortions in the D -stripes are large enough to give a local electronic structure different from the U -stripes. In this heterostructure the distorted D stripes (bent CuO_2

Figure 5: Temperature dependence of the probability of the undistorted CuO_2 lattice (P_u) given by $N(R_4)/(N(R_3) + N(R_4))$ measured by $\mathbb{E}/c$ EXAFS (panel a) and the superstructure period λ measured by X-ray diffraction (panel b). The pictorial view of the stripes in the CuO_2 plane is shown as insert.

plane) would act as potential barrier between the U stripes formed by undistorted lattice (flat CuO_2 plane). In fact the elongation of the Cu-O(planar) bonds, by about 0.09 Å, in the D -stripes directly changes the hopping integral in the plane [22] and modifies the band structure mainly at the M point of the Brillouin zone (BZ) giving a potential barrier between the stripes. Therefore the electronic structure of the modulated CuO_2 plane can be described as superlattice of quantum wires the formation of superlattice subbands [23]. The presence of stripes of distorted lattice seems to be a general characteristic of the cuprate superconductors as they have been recently found in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ [24] and in the metallic superconducting oxygen doped $\text{La}_2\text{CuO}_{4+y}$ [25].

The accurate measurements of the width $L = 15 \pm 0.5$ Å of the undistorted stripes by joint X-ray diffraction and EXAFS has allowed us to calculate the quasi one dimensional density of states and to show that at optimum doping the Fermi level is tuned near the bottom of the second and third subbands of the superlattice with stripes of width $L \sim 15$ Å [24, 26-27] so that the shape resonance condition $k_F = \pi/L$ is satisfied. This resonance has been proposed to give the amplification of the superconducting transition temperature [27].

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