Anomalous local atomic correlations in HgBa$_2$CuO$_{4+\delta}$

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We have performed extended x-ray-absorption fine-structure (EXAFS) measurements to study the local atomic structure of the HgBa$_2$CuO$_{4+\delta}$ (Hg-1201) system across the superconducting transition temperature (T_c). The Debye-Waller factors of atomic pairs obtained by Cu K-edge EXAFS are compared with diffraction data to calculate atomic correlations. The atomic correlations for Cu-O bonds show anomalous temperature dependences across the T_c, highlighting the important role of electron-lattice interactions to derive the superconducting characteristics of the system. [S0163-1829(99)03405-0]

I. INTRODUCTION

Apart from having the highest T_c among the family of superconducting cuprates, the mercury-based compounds (HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$) show several characteristic properties which differentiate them from other high-T_c materials. For example, strong pressure dependence of the superconducting transition temperature and extremely long apical Cu-O bonds indicate the vital role of structure in driving their normal and superconducting state properties.[1–3]

The single CuO$_2$ layer compound HgBa$_2$CuO$_{4+\delta}$ (Hg-1201) has the simplest structure and the widest range of doping among Hg-based superconductors,[4–6] and could be considered as a representative compound to understand the characteristic features of this system. Structural parameters of Hg-1201 have been obtained by several x-ray and neutron powder diffraction studies.[7–11] Like the other members of this series, Hg-1201 has a flat and crystallographically homogeneous CuO$_2$ plane. However, evidences are accumulating that the local structure of these perovskite superconductors is different from the average one. Being a fast and local experimental probe, extended x-ray-absorption fine structure (EXAFS) is one of the few techniques that could provide direct site selective information, and is an ideal tool to measure the statistical distribution of the atomic sites. Thus, it could significantly contribute to the understanding of local inhomogeneities in the CuO$_2$ plane of high-T_c superconductors. Several systematic temperature dependent EXAFS studies on the YBCO,[12–14] Bi-2212,[15] LSCO,[16,17] TBCO,[18,19] and LCO (Ref. 20) systems have suggested that local atomic displacements in the CuO$_2$ planes may be quite large and significantly modify the basic electronic structure of the system.

There have not been many attempts to investigate the local Cu-site structure in the Hg-based compounds. Recent polarized EXAFS measurements in the HgBa$_2$CaCu$_2$O$_{6+\delta}$(Hg-1212) system have shown a structural anomaly around the superconducting transition temperature, giving evidence for structurally derived local electronic inhomogeneity of the CuO$_2$ planes.[21] An earlier work has reported negative correlations of the Cu-O (apical) distance distribution in the Hg-1201 system. However, the results were based on EXAFS measurements performed only at one temperature.[22]

In the present communication, we report a systematic temperature dependent study of the local Cu site structure in the Hg-1201 system ($T_c = 98$ K), by Cu K-edge EXAFS measurements. The results show anomalous atomic displacements in the vicinity of the superconducting transition temperature, indicating that the superconductivity is accompanied by a local structural rearrangement. A comparative study based on EXAFS and neutron powder diffraction data obtained on the same sample is presented, to discuss the atomic correlations in the Hg-1201 system. The study uncovers the fact that, alike in other superconductors, the local structure of the CuO$_2$ planes is different from the average one.

II. EXPERIMENTAL AND DATA ANALYSIS

The powder sample with $T_c = 98$ K was prepared by solid state reaction method as described earlier.[23] The temperature dependent Cu K-edge x-ray-absorption spectra were recorded in fluorescence mode using a multi-element solid state detector, at the beam-line CRG-IF of the European Synchrotron Radiation Facility (ESRF), Grenoble. The sample was mounted in a closed-cycle He refrigerator and the temperature was monitored with an accuracy of ± 1 K. The x-ray beam emitted by the 6 GeV electron storage ring, was monochromatized by a Si(311) double crystal monochromator. Several scans were collected at each temperature to ensure the true estimation of the systematic errors in the parameters to be determined. 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[24] and corrected for fluorescence self-absorption.[25] The neutron diffraction measurements on the same sample were performed at the powder diffraction beamline D2B of the high flux neutron reactor at the Institut Laue-Langevin, Grenoble. The details on the neutron diffraction measurements will be published elsewhere.[26]
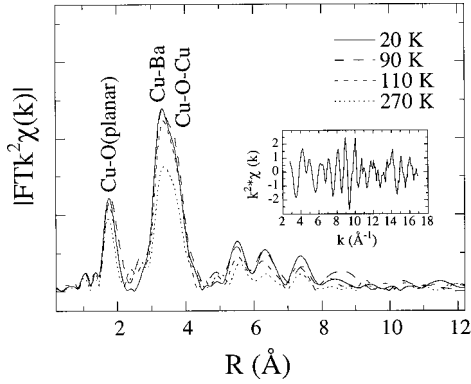
The EXAFS data analysis was done using the usual pro-

FIG. 1. Magnitude of the Fourier transform $|FT(k^2\chi)|$ of the EXAFS spectra recorded at different temperatures. The Fourier transform has been performed between $k_{min}=3$ Å^{-1} and $k_{max}=17$ Å^{-1} using a Gaussian window representing the raw data and is not corrected for the phase shifts due to photoelectron backscattering. The inset shows a representative EXAFS spectrum ($T=90$ K).

cedure in which the experimental EXAFS spectra were simulated using the standard nonlinear least-squares technique, involving minimization of the statistical χ^2 determined by the squares of the difference between the experimental and theoretical EXAFS:

$$\chi(k) = \frac{m\pi}{h^2} \sum_i N_i \frac{S_0^2}{kR_i^2} f_i(k,R_i) e^{-2R_i/\lambda} e^{-2k^2\sigma_i^2}$$

$$\times \sin[2kR_i + \delta_i(k)].$$

The number of independent parameters in the present analysis $N_{ind} \sim (2\Delta k \Delta R)/\pi$, is 27 ($\Delta k = 15 - 3 = 12$ Å^{-1} and $\Delta R = 3.5$ Å) for the simulation of the data, where Δk and ΔR are, respectively, the ranges in k and R space over which the data are fitted.[27] In the present simulation we have determined the interatomic distances (R_i) and Debye-Waller factors of the pair of atoms (σ^2) while other parameters have been kept fixed on the basis of our earlier studies performed on isostructural systems[15–17] and are in agreement with the other studies.[22] Reported errors in the parameters were estimated by the standard method[23] in which the quality of fit (proportional to the statistical χ^2) is plotted as a function of the concerned parameter.

III. RESULTS AND DISCUSSION

Figure 1 shows representative examples of the Fourier transforms $|FT(k^2\chi(k))|$ of the EXAFS signal (weighted by k^2) extracted from the measured Cu K-edge absorption on the Hg-1201 powder sample. The Fourier transforms were performed between $k_{min}=3$ Å^{-1} and $k_{max}=17$ Å^{-1} using a Gaussian window. The FT are not corrected by the phase shifts due to photoelectron backscatterings and represent raw experimental data. The first peak in the Fourier transform corresponds to the four in-plane Cu-O (in-plane) atoms, while the multipeak at around 3–4 Å corresponds to the Cu-Ba signal and Cu-O-Cu multiple scattering. The contributions from the two O (apical) atoms are expected at ~2.8 Å from Cu. In the Fourier transform the contribution from
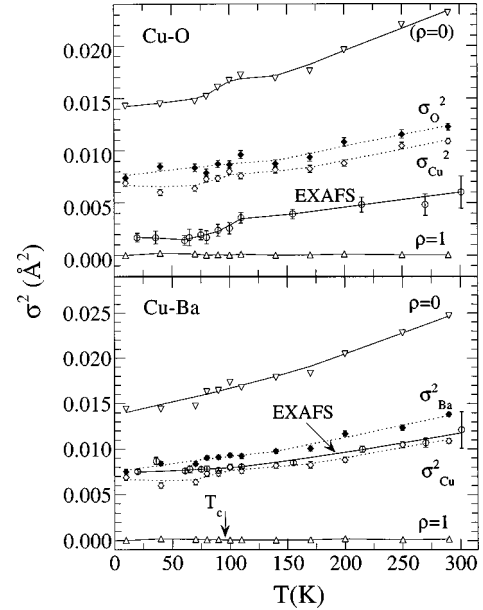

FIG. 2. Temperature dependence of the EXAFS Debye-Waller factors (open circles) for the Cu-O (in-plan) pairs (upper panel) and for the Cu-Ba pairs (lower panel). The diffraction Debye-Waller factors σ_{Cu}^2 (empty diamond), σ_O^2 and σ_{Ba}^2 (filled diamond) for Cu, O and Ba atoms are plotted in the two panels. The Debye-Waller factors calculated from diffraction data for the Cu-O (in-plane) and Cu-Ba pairs for a correlated ($\rho=1$), and uncorrelated ($\rho=0$) distribution are shown (triangles). Solid and dashed lines are guides to the eye.

the Cu-O (apical) backscattering is negligible, indicating a large Debye-Waller factor for Cu-O (apical) pairs. The high signal to noise ratio of the data, evidenced in the Fourier transforms, could be obtained due to the combination of high photon flux from the ESRF ring, and high fluorescence detection efficiency by the multi-element detector system.

On the average, the near neighbor distances measured by EXAFS were found to be similar to the one measured by neutron diffraction on the same sample, within the experimental precision. The temperature dependence of the Cu-O (in-plane) bong length has been discussed elsewhere.[26] The temperature dependence of the EXAFS Debye-Waller factors for the Cu-O (in-plane) pairs and Cu-Ba pairs are plotted in Fig. 2. The atomic Debye-Waller factors obtained by the temperature dependent neutron diffraction study on the same sample are plotted for comparison. It is well known that the diffraction and EXAFS Debye-Waller factors are fundamentally different, as the atomic Debye-Waller factors given by diffraction represent mean-square deviation of a given atom from its average site in the crystal, while the EXAFS Debye-Waller factor represents distance broadening of a pair of atoms. For an ordered material, the EXAFS Debye-Waller factor is expected to be derived by correlated motion of atoms, and the correlation gets reduced with disorder in the material. For example, the Debye-Waller factors for an atomic pair, e.g., Cu and O (σ_{CuO}^2) can be obtained from the atomic Debye-Waller factors of Cu (σ_{Cu}^2) and O (σ_O^2) given by diffraction using the following relationship:[22,28]

$$\sigma^2_{CuO} = \sigma^2_{Cu} + \sigma^2_O - 2\sigma_{Cu}\sigma_O\rho,$$

where ρ is a correlation coefficient defining the correlation between atomic motions (the distance broadening). $\rho = 1$ represents the case where the distance broadening is given by fully correlated motion, while $\rho = 0$ represent the fully uncorrelated case. We have included the Debye-Waller factors of atomic pairs for a correlated ($\rho = 1$) and uncorrelated ($\rho = 0$) motion of atoms in the system, calculated from diffraction data, for comparison with the experimental Debye-Waller factors obtained by EXAFS.

The absolute value of the EXAFS Debye-Waller factor for the Cu-O (in-plane) pairs [Fig. 2(a)] is slightly different from the one expected for a correlated distribution indicating that the CuO$_2$ plane has a small disorder and the motion of Cu and O are not fully correlated. The Debye-Waller factor appears to show a standard temperature dependence down to ~ 110 K, and gets diminished below this temperature, indicating a strong change in certain CuO$_2$ lattice modes at this temperature. Interestingly, a similar change has been observed in the oscillator strength of a Raman phonons of the $\hbar\omega = 265$ cm^{-1} for other family members of Hg-based superconductors.[29]

It is useful to point out that a similar non-Debye-like change of σ^2 with temperature for the in-plane metal-oxygen bond lengths has been observed in other perovskite systems such as manganites.[30] However, effect is much larger for manganites and the anomalous behavior of σ^2 for Mn-O pair appears around the temperature where the system shows collosal magnetoresistance (CMR) transition indicating that the non-Debye-like behavior is related with the electronic properties of the system.

On the other hand, the EXAFS Debye-Waller factor for the Cu-Ba pairs [Fig. 2(b)] shows nearly exponential behavior with temperature, as expected. However, the absolute values of the Debye-Waller factor lie approximately in the middle between the correlated and uncorrelated values. Since the Ba atom is sitting at a distance of ~ 3.3 Å from the Cu atom, a poor correlation between Cu and Ba is expected, and hence the distance broadening between this pair of atoms is given by partially uncorrelated distribution.

It should be mentioned that the Debye-Waller factors for Cu-O and Cu-Ba pairs, obtained from EXAFS in the present study, confirm the values obtained in earlier Cu K-edge EXAFS work at 80 K.[22] The authors of the earlier study report Debye-Waller factors values of ~ 0.0022 Å^2 and 0.0041 Å^2 for Cu-O and Cu-Ba at 80 K, respectively, which are consistent with the present results reporting Debye-Waller factors of Cu-O and Cu-Ba, respectively, ~ 0.0018 Å^2 and 0.007 Å^2 at the same temperature. The small difference may be due to a slightly different doping level in the two samples. The results also confirm the huge Debye-Waller factors for the Cu-O (apical) pair of atoms. However, we do observe even larger Debye-Waller factors for this pair of atoms. The values obtained in the present study for the Cu-O (apical) pair at 80 K is almost three times (0.15 Å^2) larger than the one reported earlier (0.044 Å^2).

We have estimated the correlation coefficient (ρ) for the Cu-O (in-plane) and Cu-Ba atomic pairs using the EXAFS and neutron diffraction Debye-Waller factors. Temperature
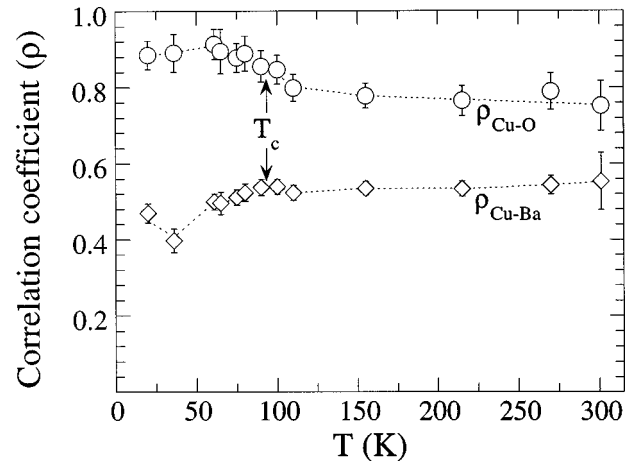

FIG. 3. Temperature dependence of the correlation coefficient ρ for the Cu-O and Cu-Ba distances estimated by comparing EXAFS and neutron diffraction Debye-Waller factors.

dependence of the correlation coefficients for the two pairs is shown in Fig. 3. The correlation coefficient for the Cu-O pair varies between ~ 0.75, at room temperature, to ~ 0.88, at low temperature. The earlier work on the Hg-1201 reports a correlation coefficient ~ 0.9 for the Cu-O pair at 80 K,[22] which agrees well with the present results. An anomalous increase from ~ 0.79 to 0.9 across the superconducting transition, of the correlation between the Cu and O atoms, can be seen in the figure. Such a behavior indicates the existence of a local structural rearrangement of the CuO$_2$ plane. This increase starts from temperatures slightly above T_c. It is worth mentioning that the diffraction data itself appear to show a correlated change in σ^2_O and σ^2_{Cu}. For example the observed values are such that when σ^2_O increases, σ^2_{Cu} shows a small decrease and hence the smooth variation of ρ may be partly due to this.

The correlation between Cu and Ba appears to be affected by the CuO$_2$ rearrangement across T_c. However, the change in the correlation coefficient of Cu and Ba is quite small and more data are needed to establish this correlation. The absolute value of ρ remains ~ 0.5, indicating partially uncorrelated distribution for this distance.

In summary, we have reported an EXAFS study at the Cu K-edge, aimed at investigating local structural changes around the Cu site across the superconducting transition temperature. The temperature dependent Debye-Waller factors for the Cu-O (in-plane) and Cu-Ba pairs are determined and compared with atomic Debye-Waller factors obtained by neutron powder diffraction on the same sample. We have observed an anomalous decrease of the Debye-Waller factor for the Cu-O pairs across the superconducting transition. A comparative study of EXAFS and diffraction on the same sample allowed us to estimate the atomic correlation coefficients of Cu-O and Cu-Ba atomic pairs. The Cu-O distance broadening is found to be given by partially correlated motion of Cu and O atoms, while Cu-Ba distance broadening is due to partially uncorrelated distribution. The temperature dependence of the correlation coefficients shows that super-

conducting transition is accompanied by local rearrangement of Cu-O correlations. Since the structural rearrangement is occurring across the superconducting transition, it may be related to an electronic rearrangement. This effect, which starts slightly above T_c, could be related to the opening of a pseudogap. The existence of such a pseudogap in Hg-1201 has been recently evidenced by NMR,[31] and correlation between distortion effects in the CuO_2 plane and T_c is reported.

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