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Structure of $YBa_2Cu_3O_{7-\delta}$ versus temperature by x-ray-absorption spectroscopy

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We present extended x-ray-absorption fine-structure data on $YBa_2Cu_3O_{7-\delta}$ taken at four temperatures: 80, 112, 170, and 297 K. Spectra from both the Y edge and Cu edge are analyzed for the mean distances to near neighbors and the mean-square relative displacements σ^2. The distances show little temperature dependence. The σ^2's are unusual because they vary more strongly at low temperature (80–110 K) than at high temperature (170–300 K). This could indicate some softening of the bond strengths near 170 K which may entail a subtle structural change. From a study of the Cu K edge we conclude that the x-ray-absorption near-edge structure (XANES) does not provide evidence for the existence of Cu(III) in $YBa_2Cu_3O_{7-\delta}$. We find that a peak at ~9002 eV in the XANES, the origin of which has been the subject of conflicting opinions in $La_{2-x}Sr_xCuO_{4-y}$, is associated with interference effects in Cu(II) complexes and its presence is not evidence for Cu(III) in $YBa_2Cu_3O_{7-\delta}$.

I. INTRODUCTION

In this paper we report results of an x-ray-absorption spectroscopy study of $YBa_2Cu_3O_{7-\delta}$. We are interested in two aspects: the valence of Cu and the temperature dependence of the local structure around the Cu and Y atoms. Diffraction studies of the orthorhombic phase indicate that Cu and O atoms form sheets and chains[1,2] with which superconductivity has been associated. Two-thirds of the Cu atoms are in corner linked CuO_4 planar groups connected as sheets in the a-b plane with the remaining one-third having square-planar coordination in the b-c planes and forming chains along the b axis.[1,2] The band-structure calculation of Mattheiss and Hamann[3] shows one- and two-dimensional features involving Cu(3d)-O(2p) orbitals at the Fermi energy. These features give rise to competing charge density wave instabilities which, along with large electron-phonon interactions resulting from Cu-O breathing modes, may make important contributions to the high superconducting transition temperature T_c.[3] From the crystal structure it has also been inferred that Cu^{2+} and Cu^{3+} ions preferentially occupy the square pyramidal sites, Cu(2), of the sheets and the square planar sites, Cu(1), of the chains, respectively.[2] Support for the existence of both Cu valences is given by the interpretation of the x-ray-absorption near-edge structure (XANES) of the mixed phase material $YBa_{1.5}Cu_{2.5}O_{7.5-y}$.[4,5] It has been suggested that a dynamic fluctuation between the 2+ and 3+ states induces a cooperative stretching of Cu–O bonds, thereby enhancing the electron-phonon interaction.[4,5]

X-ray-absorption spectroscopy has also been applied to the 40-K superconductors, $La_{2-x}(Sr,Ba)_xCuO_{4-y}$, to determine the Cu valence. One XANES study states that both divalent and trivalent Cu are present,[6] while a second study concludes that the Cu(3d) electrons are localized and only Cu^{2+} is present.[7,8] The question of the valence of Cu in $YBa_2Cu_3O_{7-\delta}$ is taken up in the present investigation. Such studies may be important in developing a proper theory for these high-T_c materials.

It is known that YBaCuO compounds transform from a tetragonal to orthorhombic structure at high temperature.[9,10] In $YBa_2Cu_{3-x}O_{7-y}$ it has been inferred that at 575 °C a disorder-order transition occurs involving motion of oxygen atoms into Cu–O–Cu chains in the lower-temperature orthorhombic phase.[10] Cu–O–Cu chains with long-range order have been revealed in a high-resolution transmission electron microscope study[11] of $YBa_2Cu_3O_{6.9}$. Neutron-diffraction studies place the chains in the b direction, although not all the oxygen O(1) sites are occupied at room temperature.[1] In the same study no structural changes were detected at 80 and 150 K.

In the present paper we have studied the extended x-ray-absorption fine-structure (EXAFS) spectra of $YBa_2Cu_3O_{7-\delta}$ at a temperature above and below the superconducting transition and analyzed these for interatomic distances R and their mean-square relative displacements $\Delta\sigma^2$ due to static disorder or thermal motion. The local arrangement of atoms around Cu and Y is complex. Therefore, after a summary of experimental methods, we discuss in detail the data analysis used to extract structural information for atoms beyond the nearest neighbor. The XANES of the Cu K edge is then presented. Finally, our conclusions regarding the valence of Cu and evidence for a subtle structural anomaly above T_c are summarized.

II. EXPERIMENT

The material was prepared from $Y(NO_3)_3\cdot 6(H_2O)$, BaO, and CuO powders, preheated for 4 h at 400 °C, ground and fired at 960 °C in oxygen flow for 10 h, reground, and fired again as before. A thin layer of the resulting black powder was spread on cellophane tape for the EXAFS measurements. We also made pressed, sintered disks which were again fired at 960 °C for 10 h in flowing oxygen. Resistance measurements gave a superconducting transition with a midpoint temperature of 91.5

K and a width (10% to 90%) of 1.8 K. X-ray structure determination showed the material to be single phase and orthorhombic with lattice constants $a = 3.820$ Å, $b = 3.893$ Å, and $c = 11.658$ Å, in good agreement with previous work.[1,2,12,13]

The x-ray spectra were taken in the transmission mode at the Stanford Synchrotron Radiation Laboratory using beam line IV-1. A double-crystal monochromator was used with two Si(220) crystals detuned from parallel to pass only 50% maximum intensity in order to reduce harmonic content of the beam. For the low-temperature spectra the sample was placed in a variable-temperature liquid-nitrogen cryostat. A thermocouple measured the temperature of the cold-finger sample holder. A subsequent calibration determined more precisely the temperature of the sample in relation to that of the sample holder. Thus the spectra were recorded at the temperatures 80 ± 2 K, 112 ± 10 K, 170 ± 20 K, and 297 ± 2 K. Spectra of the sample were taken at both the Cu and Y K edges. Simultaneously, spectra of Cu and Y metal were recorded in order to establish the x-ray energy calibration.

III. DATA ANALYSIS

The EXAFS interference function $\chi(k)$ was extracted from the absorption spectra using standard procedures.[14,15] The zero of the photoelectron wave vector k was taken to be 8992 eV for the Cu K edge and 17044 eV for the Y K-edge spectra. The magnitudes of the Fourier transforms of $k\chi(k)$ show peaks corresponding to shells of near-neighbor atoms around the x-ray absorbing atoms (Fig. 1). Because of the complexity of the crystal structure, known at room temperature,[1,2] the transforms cannot resolve the contributions of all the different atoms into well-separated peaks containing only one atomic species. In Fig. 1(a), for the copper K edge the labels indicate only the dominant contributions calculated from the crystal structure.[1] There are contributions from two Cu sites, Cu(1) and Cu(2), in the ratio of 1:2. The peak labeled Y+B consists of eight Cu(1)—Ba, four Cu(2)—Ba, four Cu(2)—Y, one Cu(2)—Cu(2), and four Cu(2)—O. The labeled Cu peak contains four Cu(1)—Cu(1) pairs and four Cu(2)—Cu(2) pairs. It is large because of focused multiple scattering via the intervening oxygen atoms.[16,17] At the yttrium K edge the structure is simpler; appreciable overlap of different atomic species does not occur until the Ba—Y peak indicated in Fig. 1(b). It contains eight Y—Cu, two Y—Ba, and four Y—Y components.

Both the Y and Cu edge transforms show a strong dependence on temperature, and the same trend is observed for all peaks with $R < 7$ Å. For quantitative analysis, the peaks of the Fourier transforms were isolated with a rectangular window and the contribution of individual shells or groups of shells were extracted by inverse transformation. Two techniques were used to extract R and $\Delta\sigma^2$. Where one atomic species dominates a shell and can be isolated from its neighbors, the phase difference and amplitude comparison (log-ratio) methods were used.[14] This is the case for the nearest-neighbor Cu—O and Y—O pairs and is nearly the case for the Y—Cu pair.

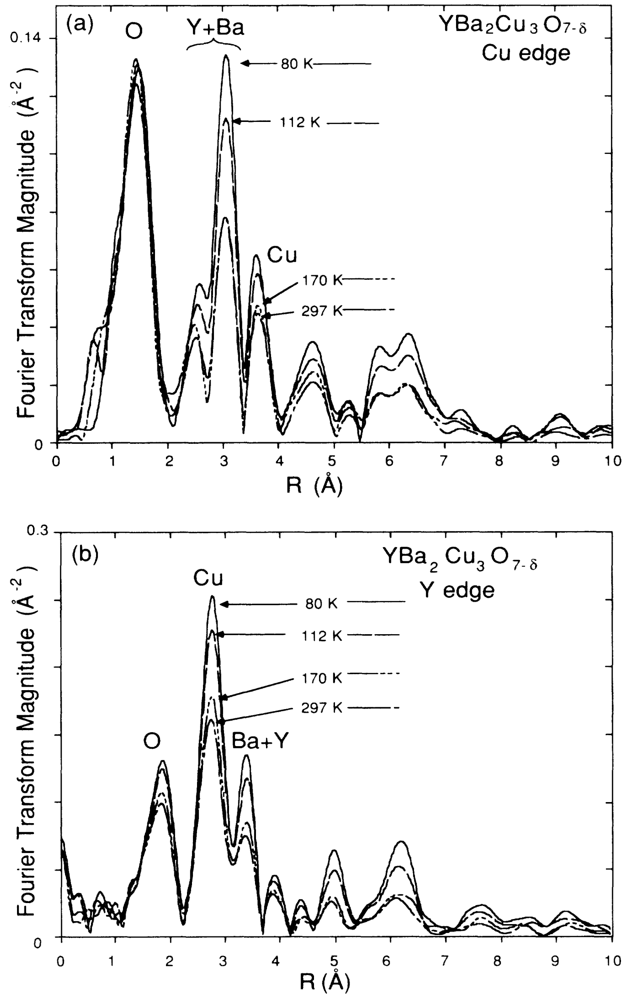

FIG. 1. (a) Fourier transforms of the EXAFS spectra at the Cu K edge. The transforms are of $k\chi(k)$ over a range of 2.4–15 Å^{-1}. (b) Fourier transforms at the Y K edge. The transforms are of $k\chi(k)$ over a range of 2.4–18.6 Å^{-1}. Both used a 10% Gaussian window. The positions of these peaks are shifted a few tenths of an angström from the actual interatomic distances because of the EXAFS phase shift.

Because of its complexity, the analysis of the Cu—O shell was verified by a single-shell fit using the 80-K data to provide empirical amplitudes and phases. While fits in R space agreed well with the amplitude and phase comparison method, the k-space fits were poorer and gave significantly large $\Delta\sigma^2$'s.

Where a group of atomic shells cannot be isolated because of their similar interatomic distances, we used multishell, nonlinear least-squares fitting. The Y—Cu, Y—Ba, and Y—Y group (2.2 Å $< R <$ 3.7 Å) and the Cu—Ba, Cu—Y, and Cu—Cu group (2.1 Å $< R <$ 4.1 Å) were analyzed by multishell curve fits. The curve fitting was applied to $k^n\chi(k)$ ($n = 2$ for Cu and 3 for Y) and to its Fourier transform with consistent results. The fitting assumed the single-scattering EXAFS formula for $\chi(k)$ valid in the small disorder limit.[18] Inelastic effects were included with $\exp(-2R/\lambda)$ where $\lambda = k/\eta$. The k-space origin, as determined by the inner potential, E_0 (initially set at the edge inflection point), and mean-free path constant η were varied to fit the room-temperature spectra only and were held fixed for the lower temperatures. ΔR and $\Delta\sigma^2$ were fit for all the temperatures in relation to the known distances at room temperature. The number of nearest neighbors was fixed throughout at their structural values, except for the Cu—Cu shell where multiple scattering by the collinear oxygen atom entails an additional factor, the oxygen forward scattering amplitude, $|F_O(\beta,k)|$ which is nearly k independent when the scattering angle β is 0.[16,19] Empirical backscattering amplitudes and phase shifts for Ba, Cu, and Y and the central atom phase shifts for Y and Cu were determined from reference compounds Y metal, Cu metal, and Cu_2O. Barium backscattering amplitude and phase were obtained from a well-separated samarium shell of SmSe and extrapolated to Ba using the theoretical amplitudes[20] as a guide. The empirical curves were in good agreement with the theoretical curves for $k > 5$ Å^{-1}, and allowed the fitting range to be extended to $3 \leq k \leq 16$ Å^{-1}. The absolute values of σ^2 depend on the backscattering amplitude and are thus uncertain, but this uncertainty does not apply to the relative $\Delta\sigma^2$ values between different temperatures of the same atomic pair.

A three-shell fit determined the Cu—Y, Cu—Ba, and Cu—O—Cu (multiple-scattering) parameters. The undulating shape of the Ba backscattering amplitude causes a lobe on the lower side of the Ba peak, evident at ~2.5 Å. The main peak of the barium shell destructively interferes with the Cu—O—Cu component, and the large peak visible at ~3 Å is predominantly due to the Cu—Y component. Thus multiple shell fits are essential for the correct analysis. The forward scattering by the bridging oxygen should amplify the Cu signal by about a factor of nine for linear bridges ($\beta = 0$). Our experience with similar scattering in ReO_3(L_{III} edge) shows that when the scattering angle is varied from 0 to > 12.5° by pressure, the Re peak in the Fourier transform is almost eliminated.[19] According to the crystal structure determinations of $YBa_2Cu_3O_{7-\delta}$ the Cu—O sheets are slightly puckered with a Cu(2)—O—Cu(2) bond angle of 164°, so that β is 16°. Thus the multiple-scattering Cu—O—Cu shell must be assumed to represent mainly the linear chains.

The Y—Cu, Y—Ba, and Y—Y parameters were obtained from a three-shell fit. By coincidence, the Y—Ba and Y—Y shells have almost identical total phases—the different distances being compensated by their phase shifts. Thus it is difficult to separate the parameters for these two shells independently. For the nearest-neighbor Y—O and Cu—O shells, we determined that the different oxygen distances implied from structure[1,2] could not be distinguished with a multishell fit. We considered the possibility of an asymmetric pair distribution function. The lack of any significant deviation of the R values with temperature under the Gaussian assumption and the lack of any clear k^3 dependence in the phase indicates there is no need to introduce asymmetry into the analysis.

The uncertainties of the results were determined by finding the deviation of a parameter from its best-fit value which doubles the residual sum of squares, $\sum(\text{data}-\text{fit})^2$, while allowing all other variables to float. This gives a conservative error estimate which is typically twice that obtained if the other variables were fixed.

IV. RESULTS AND DISCUSSION

A. EXAFS

The results of the EXAFS curve-fit analysis are tabulated in Table I. There is no significant trend in the interatomic distances with temperature. The most notable feature is the temperature dependence of $\Delta\sigma^2$, the change in σ^2 relative to the 80-K value, shown in Fig. 2.

In the low disorder limit,[18] σ_j^2 is the mean-square relative displacement along the bonding direction between the x-ray absorbing atom and the jth backscatterer. It is the sum of a static term σ_S^2 and a dynamic term $\sigma_D^2(T)$ due to the thermal motion of the atoms. The static term may be temperature dependent if there is a rearrangement of atoms. The dynamic term depends upon the correlated motion of the atom pairs. For nearest atoms, for which optical modes dominate, we may apply the Einstein model

$$\sigma_D^2 = \frac{\hbar}{2\mu\omega_E}\coth\left[\frac{\hbar\omega_E}{2k_BT}\right],$$

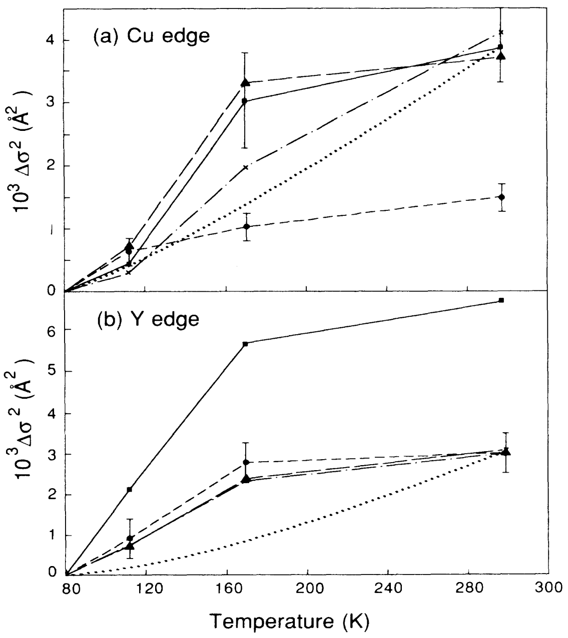

FIG. 2. The variation of $\Delta\sigma^2$ with temperature for the interatomic distances: (a) Cu-Ba (long dash), Cu-Y (solid), Cu-O-Cu multiple scattering (dash-dot), and Cu-O (short dash) and (b) Y-Y (solid), Y-O (short dash), Y-Ba (long dash), and Y-Cu (dash-dot). The error bars represent the magnitude of $\Delta\sigma^2$ for which the residual sum of squares is twice its minimum value. The dotted lines represent an Einstein model fit to Cu-Y and Y-O using the 80- and 297-K points.

TABLE I. Results of fitting the yttrium and copper *K*-edge EXAFS spectra. *R* is the mean interatomic distance and σ^2 is the root-mean-squared deviation from *R* due to thermal motion or static disorder. All *R* values are relative to the room-temperature distances calculated from the diffraction structure shown in italics. $\Delta\sigma^2$ is $\sigma^2(T) - \sigma^2$ (80 K).

	Cu—O[a]		Cu—Y[b]		Cu—Ba[c]		Cu—O—Cu[d]		
T (K)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*N*
297	*1.982*	1.50	*3.205*	3.86	*3.426*	3.71	*3.857*	4.1	15.9
170	1.975	1.02	3.213	3.02	3.434	3.31	3.871	2.0	15.3
112	1.969	0.63	3.205	0.45	3.423	0.71	3.858	0.3	15.0
80	1.977	0.00	3.207	0.00	3.421	0.00	3.854	0.0	16.6
Error	0.01	0.3	0.008	0.8	0.013	0.8	0.012	3	4

	Y—O[a]		Y—Cu(2)[e]		Y—Ba[f]		Y—Y[g]	
T (K)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)	*R* (Å)	$\Delta\sigma^2$ (10^{-3} Å^2)
297	*2.395*	3.02	*3.205*	2.99	*3.072*	3.07	*3.857*	6.75
170	2.397	2.78	3.205	2.34	3.683	2.39	3.840	5.74
112	2.400	0.92	3.202	0.76	3.682	0.74	3.803	2.14
80	2.402	0.00	3.201	0.00	3.674	0.00	3.821	0.00
Error	0.008	0.20	0.01	0.8	0.02	1.00	0.1	5.0

[a] Phase and amplitude comparison.

[b] Curve fit, fixed parameters: $\Delta E_0 = 9.9$, $N = 2.67$, $\eta = 0.32$.

[c] Curve fit, fixed parameters: $\Delta E_0 = 3.1$, $N = 5.33$, $\eta = 0.32$.

[d] Curve fit, fixed parameters: $\Delta E_0 = -11.8$, $\eta = 0.32$.

[e] Curve fit, fixed parameters: $\Delta E_0 = -6.8$, $N = 8$, $\eta = 0.55$.

[f] Curve fit, fixed parameters: $\Delta E_0 = -9.1$, $N = 2$, $\eta = 0.55$.

[g] Curve fit, fixed parameters: $\Delta E_0 = -10.7$, $N = 4$, $\eta = 0.55$.

where μ is the reduced mass and ω_E is the Einstein frequency.[21] This is indicated as a dotted line in Fig. 2(b) for Cu—Y and Fig. 2(a) for Y—O where ω_E has been chosen to force the calculated $\Delta\sigma^2$ through the 80- and 297-K points. The experimental data deviate from this simple monotonic temperature dependence, the deviation being greatest near 170 K. The same behavior occurs for all atom pairs analyzed, with the exception of the Cu—O—Cu (multiple-scattering) combination. Analogous behavior is observed in the vicinity of pressure-induced structural or electronic phase transitions where there is an increase in σ^2 superimposed on the monotonic pressure dependence, signifying a softening of the force constants.[22,23] The effect in $YBa_2Cu_3O_{7-\delta}$ is subtle. There are no accompanying changes in bond lengths or coordination numbers. At room temperature the Cu—O—Cu chains have an oxygen occupancy of 0.92.[1] It is possible that further oxygen ordering may occur at lower temperatures, but this is expected to have a small effect on the σ^2 of atom pairs such as Y—Y. Additional structural data are available. A neutron-diffraction study states that the structure at 80 and 150 K is the same as at room temperature. The specific heat has been measured at temperatures up to 140 K with no unusual behavior reported above T_c.[24] Also no anomaly is observed in thermal expansion data between T_c and room temperature.[25]

If it is assumed that the force constants soften near 170 K and then recover their normal values, a very qualitative indication of the strength of the bonds can be obtained by forcing the Einstein expression to fit the 80- and 297-K $\Delta\sigma^2$ points. This gives a relatively high Einstein temperature, Θ_E, of 523 K (363 cm^{-1}) to Cu—O and 403 K (280 cm^{-1}) to Y—O. The Cu—Y, Y—Cu(2), Cu—Ba, Y—Ba, and Cu—O—Cu groups are weaker, having $\Theta_E \approx 250$ K (174 cm^{-1}), and the Y—Y bond is very weak with Θ_E of 129 K (90 cm^{-1}). In fact, σ^2 represents an average over the phonon density of states of the form

$$\sigma_j^2 = \frac{\hbar}{2\mu} \int_0^\infty \frac{d\omega}{\omega} \rho_j(\omega) \coth\left[\frac{\hbar\omega}{2k_B T}\right] ,$$

where $\rho_j(\omega)$ is the density of the phonon modes with frequency ω projected along R_j.[21] From this viewpoint the anomaly in $\Delta\sigma^2$ may involve a change in $\rho_j(\omega)$.

Infrared spectra[26] of $YBa_2Cu_3O_{7-\delta}$ show some changes in the temperature range where we see the anomalous temperature dependence of $\Delta\sigma^2$. The temperature dependence of the strength of a phononlike peak at 317 cm^{-1} is unusual and suggests an incipient phase transition near 100 K, somewhat lower than the anomaly in $\Delta\sigma^2$. In a recent Raman study[27] of $YBa_2Cu_7O_{7-\delta}$ a mode at 644 cm^{-1}, which has been attributed to a Cu-O vibration,[28] softens locally near 170 K and then hardens to its normal value within 10 K, and in $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ two new modes appear at 170 and 90 K. These observations suggest that a structural modification occurs above T_c in the Y-Ba-Cu-O superconductors.

Preliminary results of the EXAFS work have been submitted earlier.[29] The more refined analysis presented here agrees with the results of that article regarding $\Delta\sigma^2$; however, we have been unable to corroborate any significant trend in interatomic distances as suggested in Ref. 29.

B. X-ray-absorption near edge

The x-ray-absorption near-edge structure (XANES) is sensitive to the electronic structure as well as the bonding geometry. It has been used extensively to study valence fluctuations in rare-earth systems[22,23,30] and has been used to determine the valence of Cu in the new superconductors.[4-8] The question of the valence of Cu arises because in a pure ionic model in which formal oxidation states are assigned (Y^{3+}, Ba^{2+}, La^{3+}, Sr^{2+}, O^{2-}) the valence of Cu would be 2.23 in $YBa_2Cu_3O_{7-\delta}$ and 2.15 in $La_{1.85}Sr_{0.15}CuO_{4-y}$.

The XANES of the Cu K edge is shown in Fig. 3 for $YBa_2Cu_3O_{7-\delta}$, $La_{1.85}Sr_{0.15}CuO_{4-y}$, and Cu metal. The energy scale is referenced to the first inflection point of Cu, 8979.3 eV, and the spectra have been normalized to a per atom basis by standard procedures.[31] Our concern in this section is the origin of the peak in $\mu(E)$ at ~9002 eV, indicated by the arrow in Fig. 3 (peak C of Ref. 6). It has been attributed to Cu(III) in[6] $La_{2-x}Sr_xCuO_{4-y}$ and[4] $YBa_{1.5}Cu_{2.5}O_{7.5-\delta}$ and to interference effects associated with Cu(II) complexes in $La_{2-x}Sr_xCuO_{4-y}$.[7,8] Features which occur at lower energies in the superconductors have been attributed to a Cu $1s$-$3d$ quadrupolar transition at 8977 eV and various $1s$-np dipolar transitions[6-8] at 8986 and 8992 eV identified in earlier studies of Cu(II) complexes,[32-34] and we do not discuss them further.

In assigning the 9002-eV peak to Cu(III) in La_2CuO_4 and $La_{2-x}Sr_xCuO_{4-y}$, the main experimental evidence of Alp *et al.*[6] is the appearance of a strong peak characteristic of trivalent Cu at about the same energy in the XANES of $KCuO_2$. They perform theoretical calculations on La-Sr-Cu-O clusters to support their assignment. It was the presence of the short Cu-O bond at 1.84 Å in $KCuO_2$, which is also found in $YBa_2Cu_3O_{7-\delta}$, that prompted David *et al.*,[2] in explaining the charge neutrality of $YBa_2Cu_3O_{7-\delta}$, to assign Cu^{3+} to the Cu(1) site (the picket fence chains) and partition Cu^{2+} between the Cu(1) and Cu(2) sites. On the other hand, there are many counterexamples in which cuprous oxide compounds with a linear Cu—O—Cu coordination have a short bond length of 1.84 Å.[10] Conflicting evidence is obtained from chemical analysis of the Cu(III)/Cu(II) ratio by the reduction titration method, finding 19% Cu(III) in[35] $YBa_2Cu_3O_{7-\delta}$, but only 2.7% in $La_{2-x}Sr_xCuO_4$ for $x=0.4$ and none for La_2CuO_4.[36]

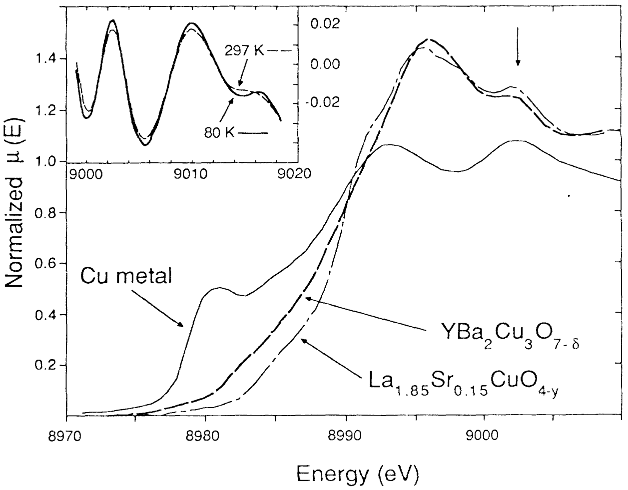

FIG. 3. The Cu K edges of $YBa_2Cu_3O_{7-\delta}$ (dashed), Cu metal (solid), and $La_{1.85}Sr_{0.15}CuO_{4-y}$ (dot-dashed) at 297 K. The amplitudes of $\mu(E)$ (renormalized) of $YBa_2Cu_3O_{7-\delta}$ at 297 K (dashed) and 80 K (dotted) are shown in the inset.

Tranquada, Heald, and Moodenbaugh[7,8] have concluded that only Cu^{2+} ions exist in $La_{2-x}Sr_xCuO_{4-y}$ and attribute the peak at ~9002 eV to fine structure involving interference effects in the final state. This is supported by the observations that similar structure occurs in the XANES spectra of Cu(II) complexes involving oxygen[8] and other ligands,[32-34] that the structure has a temperature dependence similar to that found in the EXAFS region,[8] and that the intensity of the feature is approximately independent of the concentration of Sr.[7,8] In the latter case, if Cu^{3+} ions were present an effect on the intensity would be expected.

In the present study the temperature dependence of the 9002-eV peak is similar to that observed in the EXAFS region. This is apparent from the inset of Fig. 3 which compares the amplitude of the 9002-eV feature with that of the adjacent higher-energy oscillations at 297 and 80 K. A smoothly varying background has been removed and the data normalized to the edge jump. Also in x-ray-absorption measurements on $YBa_2Cu_3O_{7-\delta}$ at pressures up to 70 kbar at temperatures below and above T_c,[37] we have found that the feature at ~9002-eV shifts to higher energies with increasing pressure in a manner consistent with compression of bond lengths.[38] No evidence for Cu^{3+} has been found in the XPS analysis of $YBa_2Cu_3O_{7-\delta}$.[35] We conclude that the XANES spectra do not provide evidence for Cu(III) in $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-\delta}$. The view that only Cu^{2+} ions are present[8] favors the theory of Emery[39] in which superconductivity results from pairing of the holes in the $O(2p)$ band via exchange interaction. This theory may be applicable to $YBa_2Cu_3O_{7-\delta}$ for which the absence of an oxygen isotope effect on T_c indicates that a nonphonon mechanism needs to be considered.[28,40]

V. CONCLUSIONS

The most striking feature of this study is the anomalous temperature dependence of σ^2. It occurs in interatomic pairs Cu—O, Cu—Y, Cu—Ba, Y—O, Y—Cu, Y—Ba, and Y—Y, yet there are no detectable changes in the interatomic distances within ±0.02 Å. The most obvious interpretation is that some softening of the bond strengths occurs near 170 K which may entail a subtle structural change. This is consistent with Raman spectroscopy which reveals a softening of a Cu—O mode at the same temperature.[27]

From a study of the Cu K edge we conclude that the XANES spectra do not provide evidence for Cu(III) in $YBa_2Cu_3O_{7-\delta}$. We also find that the near edge does not reflect any changes in the electronic structure at T_c.

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