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# X-ray-absorption studies of $YBa_2Cu_3O_{7-\delta}$ and $GdBa_2Cu_3O_{7-\delta}$ superconductors

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X-ray-absorption measurements of the high-$T_c$ superconductors $YBa_2Cu_3O_{7-\delta}$ and $GdBa_2Cu_3O_{7-\delta}$ show that their near-edge and extended fine structures (EXAFS) are essentially identical over the temperature range of 4.2 to 688 K. The results indicate that not only are $YBa_2Cu_3O_{7-\delta}$ and $GdBa_2Cu_3O_{7-\delta}$ very similar to each other in local bonding and electronic structure, but also remain virtually unchanged, electronically and structurally, over this wide range in temperature, from far below to well above $T_c$. The positions of the Cu near-edge spectra for these superconductors suggest a Cu valence between that of Cu in CuO, which has a formal valence of II, and that in $KCuO_2$, with a formal valence of III. Our EXAFS structural results agree well with those from neutron diffraction data. Recently proposed alternate structures are shown to be inconsistent with our data. The characteristic vibration frequencies of the near-neighbor atoms show that the two-dimensional Cu—O planes and the one-dimensional Cu—O chains form the most rigid parts of the structure, and these layers are bound more weakly along the *c* axis via the Ba and Y planes. These oscillator frequencies are identified with specific near-neighbor pairs, and the values are consistent with those for some of the modes seen by inelastic neutron scattering as well as by infrared and Raman spectroscopy. No evidence of phonon softening is apparent in any of the phonon modes studied, providing evidence against a strong electron-phonon coupling mechanism.

## I. INTRODUCTION

Several superconductors with critical temperatures in the vicinity of 90 K have recently been discovered in the *R*-Ba-Cu-O systems[1,2] (where *R* represents a rare-earth element). The first reports were on multiphase Y-Ba-Cu-O material;[1] subsequently, several groups have identified the superconducting phase to be $YBa_2Cu_3O_{7-\delta}$.[3,4] The basic structure of this compound has been determined to be a distorted, oxygen-deficient perovskite,[3-6] and several reports have determined the ordering of the Y and Ba layers and the location of the oxygen vacancies.[4-8] Most recent reports[7,8] indicate that the orthorhombic structure has dimpled Cu—O planes between the Ba and Y planes, and linear Cu—O chains in the layer between the two Ba planes, with no O in the plane containing Y (see Fig. 1). Other reports locate the oxygen vacancies in different positions,[5,6] and one places Y atoms on a significant fraction of the Cu sites.[9]

The relevant coupling model for superconductivity in these materials has not been established, even to the point of distinguishing strong-coupling from weak-coupling theories. While optical measurements point to a weak-coupling regime, tunneling data support a strong-coupling mechanism.[10] Heat-capacity data exist to support either model.[10] That oxygen plays a key role in the superconducting properties has been determined from sample preparation, yet no oxygen isotope effect on $T_c$ is observed.[11] This observation is difficult to reconcile with strong electron-phonon coupling to the Cu—O breathing modes, a mechanism which appears to be important for La-Sr-Cu-O and La-Ba-Cu-O.[12] Models based on highly correlated electron-electron effects have also been proposed.[13]

A knowledge of the structure, local bonding, and atomic vibration frequencies is crucial to understanding the theory behind the superconducting properties of these materials. To this end, we have performed x-ray-absorption near-edge and extended fine-structure (EXAFS) measurements on three superconducting samples: two of $YBa_2Cu_3O_{7-\delta}$ prepared by different methods, and one of $GdBa_2Cu_3O_{7-\delta}$. In all three cases, the bond lengths agree most closely with the neutron diffraction data refinement by Beno *et al.*[7] and the x-ray and neutron diffraction refinement of Junod *et al.*[8] of the structure of Fig. 1. The structure proposed by Reller, Bednorz, and Müller[6] is clearly inconsistent with our data. Moreover, no evidence for site-antisite disorder of the Cu and Y or Gd sites was observed.

No significant difference was seen between the Y-Ba-

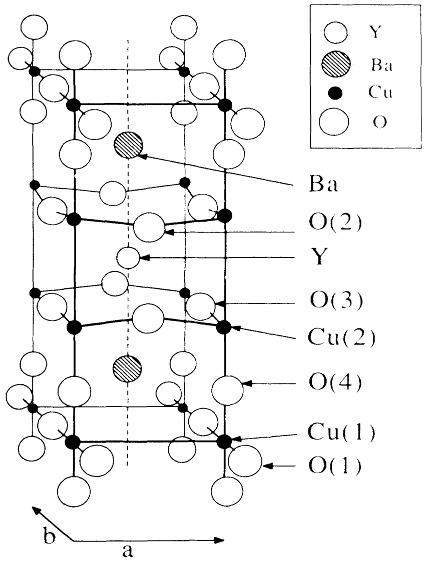

FIG. 1. The orthorhombic crystal structure of $YBa_2Cu_3O_7$ from the neutron scattering results (Ref. 7).

Cu-O samples in either the near-edge or EXAFS data, and the Gd-Ba-Cu-O sample appeared identical to the Y-Ba-Cu-O samples. This result indicates that neither the differences in preparation procedures between the Y-Ba-Cu-O samples nor the substitution of the magnetic Gd ion for the nonmagnetic Y ions leads to significant differences in local bond structure or near-neighbor vibrational frequencies. Moreover, the temperature dependence of the near-edge spectra shows that no major electronic or structural transitions occurs between 4.2 and 688 K in either compound. However, one of the Y-Ba-Cu-O samples was measured at 768 K, whereupon a new feature arose in the near-edge spectrum, accompanied by loss of superconductivity in the sample. Since the sample was heated in a helium atmosphere, this feature probably corresponds to a loss of oxygen from the sample. (We could not attain temperatures as high as 1030 K, the temperature of the orthorhombic to tetragonal phase transition in Y-Ba-Cu-O,[14] due to sample degradation.) The temperature dependence of the EXAFS data shows that the structures of both $YBa_2Cu_3O_{7-\delta}$ and $GdBa_2Cu_3O_{7-\delta}$ are composed of relatively rigid Cu—O planes and chains, more loosely bound to one another along the $c$ axis via the Ba and Y or Gd planes. Vibrational frequencies derived from the temperature dependence of the distribution in bond lengths of the nearest-neighbor atoms are consistent with those measured by infrared[15] and Raman[16,17] spectroscopy, as well as inelastic neutron scattering.[18] No indication of mode softening was revealed, providing further evidence against a strong electron-phonon coupling to the Cu—O breathing modes.

## II. EXPERIMENTAL DETAILS

One of the Y-Ba-Cu-O samples and the Gd-Ba-Cu-O sample were prepared by calcining mixtures of $Y_2O_3$ or $Gd_2O_3$, $BaCO_3$, and CuO powders in air at 950 °C for 24 h. After the reacted powders had cooled, they were ground again, pressed into pellets, and annealed in air at 900 °C for 24 h. The other Y-Ba-Cu-O sample was prepared at Stanford Research Institute, Inc. by freeze-drying a water solution of the metal ions, then annealing in an oxygen atmosphere in pellet form.

X-ray powder diffraction measurements indicated that the samples had the reported orthorhombic layered-perovskite structure,[3] and were nearly single phase. Minor contamination by unreacted $Y_2O_3$ or $Gd_2O_3$ was observed, estimated to be less than a few percent of the total volume. The x-ray patterns of the Y-Ba-Cu-O samples were nearly identical, except the freeze-dried sample showed slightly less contamination. The Gd-Ba-Cu-O sample exhibited a similar diffraction pattern, with the slight variation in relative peak intensities arising from the substitution of Gd for Y. A four-point resistive superconducting transition with an onset slightly above 90 K, of width about 10 K, was noted for each of the three samples. The freeze-dried Y-Ba-Cu-O sample had a slightly sharper resistive transition. In all cases, magnetization measurements indicated bulk superconductivity.

The samples were prepared for EXAFS by grinding the pellets into fine powder, which was spread onto Kapton tape. The superconducting transition of the powders, mounted on the tape, was remeasured in a superconducting quantum interference device (SQUID) magnetometer to verify that powdering did not affect the superconductivity. In addition, powders of the following structural and near-edge standards were prepared: $Cu_2O$, CuO, $KCuO_2$, $Y_2O_3$, $Gd_2O_3$, and BaO.

The x-ray-absorption measurements were performed at energies in the vicinity of the Cu and Y $K$ edges and the Ba and Gd $L_{III}$ edges, for temperatures from 4.2 to 688 K. Both the near-edge and EXAFS regions were investigated for the samples and standards.

## III. NEAR-EDGE RESULTS

The near-edge structure was measured in the vicinity of the Cu $K$ edge for the superconductors, Y-Ba-Cu-O and Gd-Ba-Cu-O, as well as the near-edge standards, $Cu_2O$, CuO, and $KCuO_2$. This structure arises from two distinct processes: (1) transitions from the Cu 1$s$ core state to the lowest-lying valence-band or molecular orbital states, primarily with $p$ (or $\pi$) symmetry, and (2) transitions from the Cu 1$s$ state to continuum final states that are modified by multiple scattering from the neighboring atoms, called shape resonances.[19] The first process is sensitive to the electronic structure of the solid, and thus the Cu valence, whereas the second process is sensitive to the bonding configuration, i.e., the local structure of the solid.

The two are not readily separated and identified without a detailed knowledge of the structural and electronic parameters of the materials and sophisticated calculations. For example, no consensus has been reached on the identification of the features in the near-edge structure for the comparatively simple binary compound CuO,[20] which is used as a "valence standard" for these systems. Its near-edge spectrum is shown in Fig. 2. One view[21] is

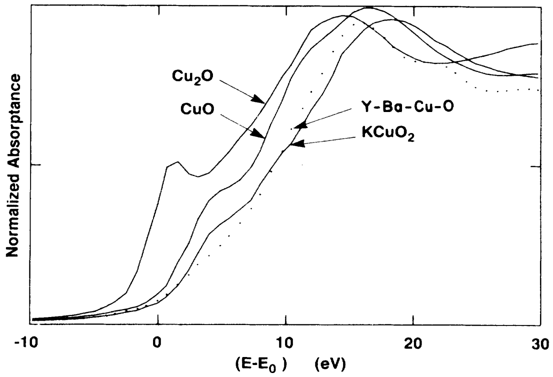

FIG. 2. X-ray-absorption near-edge structure in the vicinity of the Cu *K* edge for $Cu_2O$, CuO, and $KCuO_2$ (solid lines in increasing energy) and for superconducting Y-Ba-Cu-O (dotted line). The energy scale is referenced to the Cu *K* edge energy, $E_0 = 8980$ eV. The near-edge spectra are the same for each of the three samples studied and are independent of temperature from 4.2 to 688 K.

that the peak on the edge at 17 eV is due to a 1*s* to 4*p* atomiclike transition, with the features near 4 and 10 eV representing the associated two-electron shake-down transitions. A second point of view[22] is that the peak at 4 eV corresponds to a one-electron 1*s* to 4*p* transition, while the 17 eV peak arises from a shape resonance.

Despite these differences in identification of the specific edge features, some general conclusions on the Cu valence may be drawn from the average edge position. As electrons are removed from the Cu valence levels, the core level becomes more tightly bound and the final states shift, resulting in an increase in the 1*s* to final-state transition energy. This trend has been observed in mixed-valence systems, e.g., SmS.[23] Such a systematic shift upward in energy is observed from $Cu_2O$ to CuO to $KCuO_2$, in Fig. 2. This suggests a shift in valence[24] since higher transition energies are expected for higher valence states. The three near-edge standards have oxidation numbers or formal valences of I, II, and III, respectively; the real charges on the Cu ions, however, depend on the electronegativity and covalency. Only in the ionic limit would these formal Cu valences translate to localized charge, which is the quantity responsible for the edge shift.

The Cu near-edge spectra of the two Y-Ba-Cu-O and one Gd-Ba-Cu-O superconducting samples were measured as a function of temperature from 4.2 to 688 K in a helium atmosphere. In addition, one of the Y-Ba-Cu-O samples was studied at 768 K. The near-edge spectra were identical in position and shape for each of the three samples studied. Furthermore, no change with temperature was observed up to 688 K. This indicates that no electronic transition, such as a valence change, occurs over that entire temperature range, from well above to well below $T_c$. When the Y-Ba-Cu-O sample was heated to 768 K, a change did occur. A shoulder developed in the near-edge spectrum near 0 eV, close to the position of the first peak in the $Cu_2O$ spectrum. Simultaneously, the sample lost its superconductivity. Since the material was heated in a helium atmosphere, the oxygen content probably decreased slightly and lowered the effective Cu valence. Consequently the near-edge spectrum showed a shift in average position towards lower transition energy, also observed by Oyanagi *et al.*[25]

Figure 2 shows that the Cu edge of Y-Ba-Cu-O lies between those of CuO and $KCuO_2$. For an ionic model, Y-Ba-Cu-O with an oxygen content of $7(\delta = 0)$ has a formal Cu valence of $\sim 2.3$, which predicts a position for its Cu absorption edge consistent with its position in Fig. 2. However, compounds like Y-Ba-Cu-O, Gd-Ba-Cu-O, and the Cu-O near-edge standards have Cu—O bond lengths indicative of significant covalent character. In addition, the existence of trivalent Cu is doubtful from electronic energy considerations, and the differences in the local atomic symmetry and structure for these five compounds may produce substantial changes in near-edge structure, in the form of shape resonances, which complicate the interpretation of the electronically derived changes in edge structure. Thus, Fig. 2 should be used to indicate at most a qualitative trend in the Cu valence.

## IV. EXAFS STRUCTURAL RESULTS

For each sample, a thorough analysis was made of the EXAFS data on the various edges at each temperature. The data were reduced in the usual manner.[26] A typical spectrum, the Fourier transform of the EXAFS, $k\chi(k)$, is shown in Fig. 3 for the Cu *K* edge in superconducting Y-Ba-Cu-O, at 4.2 K and at 688 K. The first peak arises

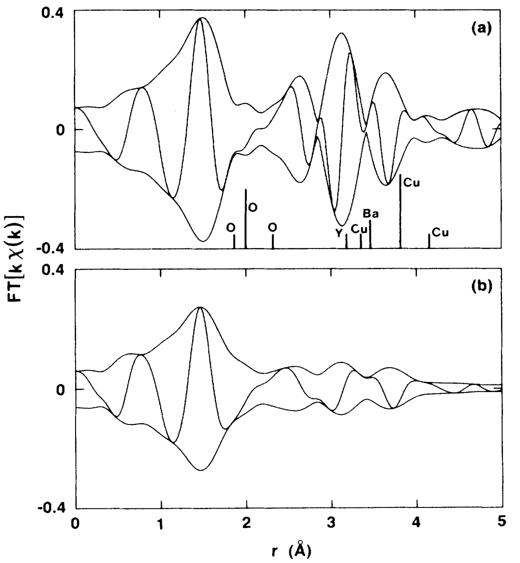

FIG. 3. The magnitude (envelope) and real part of the Fourier transform of the EXAFS, $k\chi(k)$, on the Cu *K* edge for superconducting Y-Ba-Cu-O at (a) 4.2 K and (b) 688 K. The transform range is $k = 3.0-12.2$ Å$^{-1}$, broadened by a Gaussian of half width 0.5 Å$^{-1}$. The first peak is due to the O neighbors, the second and third peaks (2.4–3.4 Å) are due to Y, Ba, and some Cu neighbors, while the fourth peak (3.4–3.9 Å) is due primarily to planar Cu—Cu pairs. The differences between the actual distance and the observed peak position are due to the EXAFS phase shifts, and the relative number of neighbors is indicated by height in the bar graph.

from oxygens around the Cu(1) and Cu(2) ions (following the nomenclature of Fig. 1). The next two peaks are due to a combination of Y, Ba, and some Cu atoms, while the fourth peak comes from more distant Cu neighbors. The Cu—O peak which would correspond to Cu atoms on Y sites if the site-antisite disorder postulated by Lytle, Gregor, and Panson[9] were present, would lie near 2.5 Å, between the first and second peaks. No evidence of such a peak is seen for this sample or for either of the other two samples, throughout the temperature range.

The Fourier transform of the EXAFS of the Y site is shown in Fig. 4 for Y-Ba-Cu-O at 4.2 and 686 K. The first peak arises from oxygens O(2) and O(3) around the Y atoms at a distance of 2.39 Å; the next peak is due to eight next-nearest-neighbor Cu atoms. The third and fourth peaks correspond to Ba and Y further neighbors. Again, we see no evidence in any of the samples for a shorter Y—O distance within the range 1.95 to 2.3 Å, the expected distance for a Y on a Cu site.

Detailed fits of the Y—O (Gd—O), Cu—O, and Ba—O nearest-neighbor peaks were carried out using $Y_2O_3$ ($Gd_2O_3$), CuO, $Cu_2O$, and BaO as known structural standards. The standards $Y_2O_3$ and $Gd_2O_3$ have more than one first-neighbor O distance, but were converted to single-peak signatures using procedures described previously.[27] Fits of these standards to the Y-Ba-Cu-O and Gd-Ba-Cu-O data indicate that Y and Gd have eight O neighbors at a single distance of 2.39 ± 0.01 Å, in good agreement with the diffraction data associated with the structure of Fig. 1 (see Table I). The small difference in the distances to the O(2) and O(3) atoms, observed in the diffraction data to be about 0.02 Å, could not be resolved in the EXAFS data.

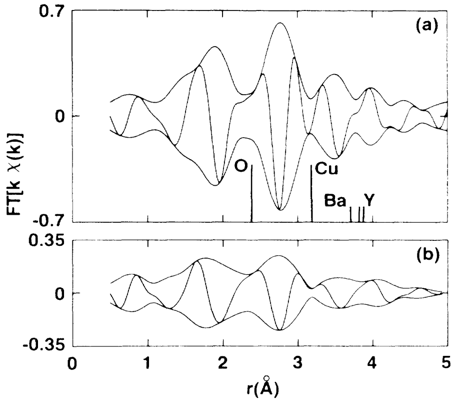

FIG. 4. The magnitude (envelope) and real part of the Fourier transform of the EXAFS, $kX(k)$, on the Y $K$ edge for superconducting Y-Ba-Cu-O at (a) 4.2 K and (b) 686 K. The transform range is $k = 3.4\text{–}12.2$ Å$^{-1}$, broadened by a Gaussian of half width 0.5 Å$^{-1}$. The first peak (1.5–2.1 Å) is due to four O(2) and four O(3) neighbors, the second peak (2.5–3.0 Å) corresponds to eight Cu(2) neighbors, while the third and fourth peaks (3.3–4.2 Å) arise from further Ba and Y atoms. The differences between the actual distance and the observed peak position are due to the EXAFS phase shifts, and the relative number of neighbors is indicated by height in the bar graph.

The differences between the structure of Fig. 1 and the alternate structure proposed by Reller *et al.*[6] are founded on their claim that Cu atoms with fivefold oxygen coordination are not known to exist in ordered Cu layers of comparable oxides. Thus, Reller *et al.*[6] converted all of the fivefold oxygen coordinated Cu sites to four- or sixfold coordinated sites. As a consequence, this structure con-

TABLE I. Near-neighbor structural information for Y-Ba-Cu-O from the EXAFS and diffraction techniques, for the structure shown in Fig. 1 (model 1) as well as the structure newly proposed by Reller *et al.*[6] (model 2). The labeling of the atoms is given in Fig. 1, and $N$ is a weighted number of O neighbors. $N$ was varied in the Y—O fits but not in the Cu—O fits. Model 2 introduces two new oxygen sites: O(5), located along the $a$ axis, halfway between the one-dimensional Cu—O chains, and O(6), located in the plane of the Y atoms. O(2) is missing in model 2. The EXAFS results for each of the three samples studied were essentially the same, within the error noted.

| | EXAFS | | Diffraction | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Model 1 | | | | Model 2 | |
| | | | | $r$ (Å) | | | | |
| | $N$ | $r$ (Å) | $N$ | Single crystal x-ray (Ref. 5) | Powder neutron (Ref. 7) | X-ray and neutron (Ref. 8) | $N$ | $r$ (Å) x-ray (Ref. 6) |
| Y—O(2) | | | 4 | 2.388 | 2.414 | 2.411 | 0 | · · · |
| Y—O(3) | 8 ± 1 | 2.39 ± 0.01 | 4 | 2.390 | 2.380 | 2.394 | 4 | 2.748 |
| Y—O(6) | | | 0 | · · · | · · · | · · · | 4 | 2.726 |
| Cu(1)—O(4) | $\frac{2}{3}$ | 1.88 ± 0.02 | $\frac{2}{3}$ | 1.785 | 1.850 | 1.866 | $\frac{2}{3}$ | 1.943 |
| Cu(1)—O(1) | | | $\frac{2}{3}$ | 1.93 | 1.943 | 1.940 | $\frac{2}{3}$ | 1.943 |
| Cu(2)—O(2) | $\frac{10}{3}$ | 1.95 ± 0.01 | $\frac{4}{3}$ | 1.946 | 1.928 | 1.937 | 0 | · · · |
| Cu(2)—O(3) | | | $\frac{4}{3}$ | 1.951 | 1.962 | 1.958 | $\frac{4}{3}$ | 1.943 |
| Cu(2)—O(4) | $\frac{2}{3}$ | 2.32 ± 0.05 | $\frac{2}{3}$ | 2.387 | 2.303 | 2.300 | $\frac{2}{3}$ | 1.943 |
| Cu(1)—O(5) | | | 0 | · · · | · · · | · · · | $\frac{2}{3}$ | 1.913 |
| Cu(2)—O(6) | | | 0 | · · · | · · · | · · · | $\frac{2}{3}$ | 1.943 |

tains oxygens in the Y plane, which is consistent with neutron diffraction data[7,8] only under the assumption that special extinction is able to simulate the missing oxygen layer of the Y plane. Table I shows that, like the structure in Fig. 1, the alternate structure predicts eight nearest O neighbors, but at a Y—O distance of 2.74 Å, inconsistent with our results. Thus the Y—O distance measured in this study supports the structure of Fig. 1.

For the Cu—O peak the diffraction results of the model in Fig. 1 indicate five different distances for the two inequivalent Cu atoms; however, the three distances corresponding to the Cu—O bonds within the *a*-*b* planes are very close, not likely to be distinguishable by EXAFS. Therefore, we treated the nearest-neighbor environment of the Cu ion as the sum of three Cu—O peaks, with the number of neighbors in each peak fixed at the values indicated by the diffraction results, and refined the Cu—O distances. In the Y-Ba-Cu-O and Gd-Ba-Cu-O samples, the position of the largest peak was found to be essentially equal to the average value of the planar distances of the structure in Fig. 1. The shortest distance [Cu(1)—O(4)] is also close to the diffraction results: 1.88 ± 0.02 Å vs 1.85 Å (Ref. 7) or 1.87 Å (Ref. 8). Both of these peaks are narrow at 4.2 K and broaden slowly with temperature. The third peak [Cu(2)—O(4)], on the other hand, is not as well resolved because of some interference from the second-neighbor shells. For this peak, $r = 2.32 \pm 0.05$ Å. The three refined Cu—O distances each agree to within 0.05 Å among the different samples.

The alternate model, on the other hand, predicts two different Cu—O distances for the two inequivalent Cu atoms. The distances are too close to be distinguished by EXAFS; thus one EXAFS peak of distance 1.94 Å is indicated. Although this distance agrees well with that of the major peak described above, neither the shorter distance nor the longer distance is seen. Together with the results from the Y nearest-neighbor environment, the Cu—O bonding distances disagree with those of the alternate structure. A similar analysis of the Ba—O nearest-neighbor shell, which is a sum of three widely separated components, could not be performed in any of the samples since the second-neighbor Ba—Cu peak partially overlaps the upper Ba—O component for both Y-Ba-Cu-O and Gd-Ba-Cu-O.

## V. TEMPERATURE DEPENDENCE OF EXAFS

The only significant change in these spectra from 4.2 to 688 K is a broadening of the peaks with a resultant reduction in peak height. The increase in the amplitude of thermal vibration of the atoms has a much larger effect on the further neighbors than on the first-neighbor oxygens, which are more tightly bound. The invariance of the features of the EXAFS spectra with temperature means that no phase transition that would significantly modify the near-neighbor distance, no structural anomaly such as phonon softening, nor any unusual thermal expansion that may signal an isostructural electronic transition is present. A small distortion that causes little or no change in the near-neighbor distances would, however, not be reflected in these spectra.

From the temperature variation of the observed Debye-Waller-like broadening of the pair distribution functions and the assumption that the individual bonds can be treated as Einstein oscillators, we can estimate[26,28] the characteristic vibration frequencies, $\omega_E$, in the crystal using $\sigma^2 \cong \hbar/(2\mu\omega_E)\coth(\hbar\omega_E/2k_BT)$, where $\mu$ is the reduced mass of the pair of atoms. Although the absolute width $\sigma^2$ was not determined, its change with temperature is obtained by comparison of the appropriate peak in the 4.2 K spectrum to the corresponding peak in the higher temperature spectrum. The resulting $\Delta\sigma^2(T) = \sigma^2(T) - \sigma^2(4.2\text{ K})$ for superconducting Y-Ba-Cu-O are given in Fig. 5 along with the fits of these data to the above expression, with $\omega_E$ the only unknown parameter. Fits to a single Einstein temperature, $\theta_E = \hbar\omega_E/k_B$, are quite good, giving no evidence for softening in any of the modes studied. The characteristic Einstein temperatures for each of the atomic pairs resolvable in the EXAFS spectra are given for each sample in Table II. The differences between Y-Ba-Cu-O and Gd-Ba-Cu-O are negligible, as are the differences between the Y-Ba-Cu-O samples, within the uncertainty of the data. For Cu—O, we considered only the major component if the EXAFS signal which corresponds to Cu—O bonds within the *a*-*b* plane.

The lower-energy phonon modes measured by other methods are consistent with our values. The inelastic neutron scattering measurements of Rhyne *et al.*[18] show all of our modes, at positions within the bounds of uncertainty of our values (± 30 K). They describe a relatively large maximum at 20 meV (240 K) which corresponds with the value we identify in Table II as the Cu—Cu and Y—Cu modes, and other at 25 meV (300 K) which we identify as the Ba—O nearest-neighbor mode. The two large maxima are followed in the neutron data by a broad feature centered at 34 meV (400 K) and a small, narrow peak at 44 meV (520 K). These values are very close to the fre-

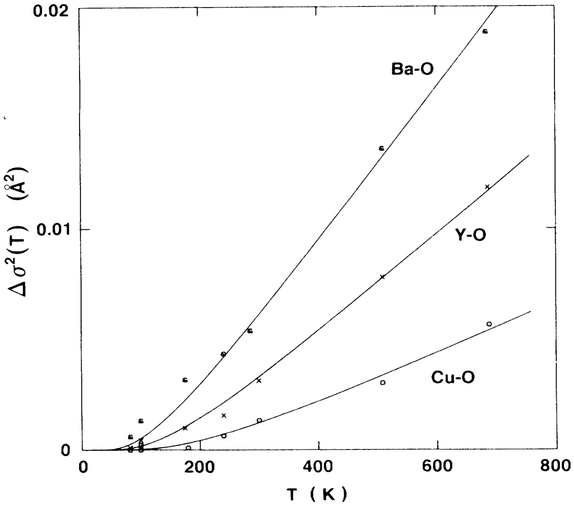

FIG. 5. The change in the square of the width of the pair distribution functions for Cu—O (in *a*-*b* plane), Y—O, and Ba—O in superconducting Y-Ba-Cu-O as a function of temperature. The solid lines are fits of an Einstein oscillator model to the data. No phonon softening is observed.

Table II. Einstein temperatures of near-neighbor bonds, for each sample. Treating the individual bonds as Einstein oscillators, characteristic temperatures were estimated by fitting the temperature variation of the Debye-Waller-like broadening of the pair distribution functions (see text). Typical fits are shown in Fig. 5. Y-Ba-Cu-O-1 is the sample prepared by traditional methods, while Y-Ba-Cu-O-2 is the sample prepared by freeze-drying and annealing. Uncertainties are estimated to be ±30 K.

| $\Theta_E$ (K) | Y-Ba-Cu-O-1 | Y-Ba-Cu-O-2 | Gd-Ba-Cu-O |
|---|---|---|---|
| Cu—O (in plane) | 560 | 500 | 540 |
| Cu—Cu (in plane) | 260 | 250 | 230 |
| Y—O | 390 | 360 | 390 |
| Y—Cu | 260 | 260 | 270 |
| Ba—O | 320 | 290 | 320 |

quencies we identify as the Y—O and Cu—O modes, respectively. In addition, Rhyne *et al.*[18] see modes of higher frequencies. Since EXAFS detects only modes that are thermally populated, the vibrational modes much higher than $k_B T$, evident in inelastic neutron scattering measurements, would have a much smaller effect on the EXAFS than the lower-lying modes that dominate the spectrum.

Raman and infrared measurements also agree well with our values. Bonn *et al.*[15] report infrared peaks that correspond to our lowest three modes, but they do not see any feature corresponding to our Cu—O value. The Raman spectra of Hemley and Mao[17] revealed peaks corresponding to our Cu—O and Cu—Cu/Y—Cu values, but showed no features intermediate in energy. Batlogg *et al.*[16] found one weak peak similar in energy to the Cu—O value using Raman spectroscopy, but they did not measure any lower energy spectra. Higher energy peaks were seen by all of these methods.

Values of the Debye temperatures or frequencies show that the Cu—O planar bonds are the strongest, and the Ba—O bonds the weakest, of the nearest-neighbor bonds. This shows that the two-dimensional Cu—O planes and one-dimensional Cu—O chains are the most rigid components of the structure. The Y—O bonds are stronger than the Ba—O bonds, implying that the Cu—O planes are more tightly bound to the Y layers than are the Cu—O chains and planes to the Ba layers.

## VI. CONCLUSION

Analysis of absorption spectra near the Cu *K* edge has shown remarkably little variation among the $YBa_2Cu_3O_{7-\delta}$ and $GdBa_2Cu_3O_{7-\delta}$ samples. Furthermore, the near-edge spectra proved insensitive to variations in temperature from 4.2 to 688 K. The results indicate that not only are Y-Ba-Cu-O and Gd-Ba-Cu-O very similar to one another in local electronic structure and bonding symmetry, but also remain virtually unchanged, electronically and structurally, over a wide range in temperature, from far below to far above $T_c$. One Y-Ba-Cu-O sample was studied at 768 K, at which temperature it became semiconducting and developed a new feature in its near-edge spectrum. The positions of the Cu near-edge spectra for Y-Ba-Cu-O and Gd-Ba-Cu-O indicate a charge on the Cu ion between that of CuO, with a formal valence of II, and that of $KCuO_2$, with a formal valence of III. The new feature which appeared at 768 K in the near-edge spectrum of Y-Ba-Cu-O, together with the loss of superconductivity, corresponds to a loss of oxygen and a concomitant decrease in formal Cu valence.

Our EXAFS data have demonstrated that $YBa_2Cu_3O_{7-\delta}$ and $GdBa_2Cu_3O_{7-\delta}$ are nearly identical in local structure, as well as in phonon modes associated with nearest-neighbor interactions, from 4.2 to 688 K. Both assume the orthorhombic, distorted-perovskite structure, with oxygen vacancies ordered in accordance with the diffraction results of Beno *et al.*[7] and Junod *et al.*,[3] probably the most widely accepted structure. The alternate structure proposed by Reller *et al.*[6] was shown to be inconsistent with our data. In addition, no evidence for the site-antisite disorder seen by Lytle *et al.*[9] was found in any of our samples. The characteristic vibration frequencies of the near-neighbor atoms are consistent with the values found by spectroscopy[15-17] and neutron scattering.[18] Finally, no evidence of mode softening was seen in any of the near-neighbor phonon modes.

## ACKNOWLEDGMENTS

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