

Mixed valency, hole concentration, and T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

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Combining the assumptions that in orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ oxygen is removed from the CuO chains one chain at a time and that the Cu atoms in the twofold coordinated sites of the empty chains have a valence of +1 leads to the prediction that the number of Cu^{1+} ions per unit cell is equal to $1-x$. X-ray absorption measurements at the Cu K edge in both oriented and unoriented quenched samples with $0 < x \leq 1$ confirm this prediction. Charge neutrality then requires that the number of O $2p$ holes per unit cell be equal to x . It follows that the superconducting transition temperature T_c should be proportional to x (rather than $2x-1$), as observed in our quenched samples. Thus, the CuO chains, though not required for superconductivity, act as an electron reservoir which serves to maximize T_c when oxygen is removed. The nonlinear variation of T_c observed in annealed samples is explainable in terms of spinodal decomposition, as first suggested by Khachatryan and Morris.

I. INTRODUCTION

It is well known that the superconducting transition temperature T_c of ≈ 90 K observed¹ in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x=1$ can be reduced by removing oxygen.^{2,3} After sufficient oxygen removal, the structure changes from a superconducting orthorhombic phase to an antiferromagnetic⁴ tetragonal one. The oxygen is removed from the CuO chains, which are responsible for the orthorhombic symmetry, while the CuO_2 planes remain intact.⁵ Much has been made of this point in terms of superconducting mechanisms. For example, it has been suggested that the CuO chains play a dominant role in the superconductivity,⁶ and, alternatively, that the orthorhombic symmetry is crucial for enhancing T_c .⁷ The discovery⁸ of high-temperature superconductivity in the $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$ system, which contains CuO_2 planes but no chains,⁹ as well as the observation¹⁰ of $T_c > 60$ K in tetragonal samples of $\text{YBa}_2\text{Cu}_{3-y}\text{M}_y\text{O}_{6+x}$ with $M=\text{Fe}$ or Ga , casts some doubt on such speculations. Nevertheless, it is still of interest to determine the role of the chains in controlling T_c in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ system.

Hall-effect measurements,¹¹ chemical analyses,¹² and muon spin relaxation (μSR) studies¹³ have demonstrated that, in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, T_c scales with the number of hole carriers (measured relative to the insulating state). X-ray absorption,^{14,15} electron-energy-loss,¹⁶ and photoelectron¹⁷ spectroscopic studies have shown that these holes occur in the oxygen $2p$ valence band. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$, all of the Cu atoms have essentially nine $3d$ electrons (+2 valence); however, in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x < 1$ evidence of both Cu^{1+} and Cu^{2+} ions has been observed.^{18,19} Despite this progress, there remain serious questions concerning the relationship between the variation in the number of holes and the oxygen content. For example, several workers^{2,20} have observed a nonmonotonic variation of T_c with x in annealed samples. Furthermore, the role of Cu^{1+} ions in the superconducting phase has not been established.

In this paper, x-ray absorption measurements at the Cu

K edge for a series of quenched ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, with x varying from zero to one, are used to demonstrate that the CuO chains serve as an electron reservoir which helps to maintain the number of O $2p$ holes in the CuO_2 planes when $x < 1$. Such a "self-doping" behavior was predicted some time ago based on band-structure calculations;²¹ however, we find the electronic structure to be much more localized and nonband-like. Due to ordering of oxygen vacancies when $x < 1$, some Cu^{2+} atoms in chain sites are converted to Cu^{1+} , thus localizing half of the electrons left behind by the removed oxygen which might otherwise fill O $2p$ holes. As a result, T_c varies as x (in samples with a homogeneous oxygen distribution) and extrapolates to zero at $x=0$, rather than at $x=0.5$ as it would if all of the Cu remained +2 in the orthorhombic phase. The nonmonotonic variation of T_c vs x in annealed samples can then be explained in terms of spinodal decomposition²² into stable superconducting and nonsuperconducting phases.

The paper begins with a description of the microscopic model which motivated the experiment. Following a description of the sample preparation and experimental procedure, the x-ray absorption results are presented and discussed. Next, our results and interpretation are compared with some previous spectroscopic work. The paper ends with a discussion of superconducting behavior in annealed samples and a summary of our conclusions.

II. MICROSCOPIC MODEL

Before discussing the electronic structure, it may be helpful to give a brief review of the crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. The unit cell contains two CuO_2 planes, each consisting of a square lattice of Cu atoms bridged by oxygens. At $x=1$, there is a single CuO layer per unit cell, with the oxygen atoms sitting between coppers to form chains aligned parallel to the b axis. As x is reduced, oxygens are removed from the chains, and in the tetragonal phase the oxygen atoms randomly occupy bridging posi-

tions along both the a and b axes, making a and b equivalent. A pair of CuO_2 planes is separated by an Y layer, while a CuO_2 plane is separated from a CuO chain layer by a layer of BaO. The oxygen atoms in the BaO layer sit directly between the Cu atoms of the plane and chain.

Let us discuss the electronic structure in terms of some simple valence-counting models. When an oxygen atom is removed from $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, it leaves approximately two electrons behind in the crystal which can fill O $2p$ holes. If we assume that all of the Cu atoms are $+2$ for $x \geq 0.5$, then the number of holes per unit cell would be equal to $2x - 1$. With the further assumption that T_c is proportional to the number of holes, T_c should go to zero at $x = 0.5$, contrary to the observed behavior.^{2,3,20} (In fact, we will show from our own measurements that T_c extrapolates to zero at $x \approx 0$.) On the other hand, a thermodynamic analysis²³ of the dependence of oxygen concentration on temperature and oxygen partial pressure has indicated that Cu^{1+} ions should be present throughout the range $0 \leq x < 1$. X-ray absorption measurements^{18,19} at the Cu K edge have shown directly that Cu^{1+} ions are present for $x > 0.5$.

A recent electron diffraction study²⁴ on an annealed sample with $x \approx 0.7$ found diffuse streaks which in some grains were centered at a reduced wave vector of $q = (\frac{2}{5}, 0, 0)$ and in others at $(\frac{1}{2}, 0, 0)$. The CuO chains extend along the b axis, so that $q = (\frac{1}{2}, 0, 0)$ indicates that the oxygen sites in every other chain are vacant. With $q = (\frac{2}{5}, 0, 0)$ the ordering would be more complex. It is also reported that while the correlation length for vacancy ordering is long in the b axis direction, along the CuO chains, it is short along the a axis and the ordering is uncorrelated along the c axis. An x-ray scattering study²⁵ of a quenched crystal with $x \approx 0.7$ also found diffuse peaks at $q = (\frac{1}{2}, 0, 0)$, but the correlation length in each direction was no greater than ~ 20 Å.

While the vacancy ordering indicated by these experiments has been observed for only a single oxygen content, we speculate that for any x in the orthorhombic phase oxygen atoms will tend to be removed from one chain at a time, leaving behind a distribution of full and empty chains. Each Cu atom in an empty chain is twofold coordinated by oxygen atoms along the c axis. Twofold coordinated Cu atoms typically²⁶ have a valence of $+1$ ($3d^{10}$ configuration) as in the compound Cu_2O . These speculations then lead to a model in which for each oxygen atom removed, one electron fills an O $2p$ hole while the other converts a Cu^{2+} to Cu^{1+} . The number of holes per unit cell is then equal to x , and conversely the number of Cu^{1+} atoms per unit cell is $1 - x$.

Using the polarization dependence of Cu K -edge spectra measured on oriented samples, we will demonstrate that the Cu^{1+} ions that are present in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ are indeed located in the twofold coordinated chain sites. From measurements on a series of unoriented quenched samples (in which we believe the oxygen distribution to be relatively homogeneous) it will be shown that the number of Cu^{1+} atoms per unit cell in the orthorhombic phase is very nearly equal to $1 - x$, as predicted. The model then explains our observation of an approximately linear varia-

tion of T_c with x .

In the tetragonal phase, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is nonsuperconducting. Such behavior can be explained by a lack of mobile O $2p$ holes. Evidence for the absence of holes comes from observations⁴ of antiferromagnetic ordering with high Néel temperatures, T_N , throughout essentially the entire tetragonal phase, $0 \leq x \lesssim 0.4$. In $\text{La}_2\text{CuO}_{4-y}$, decreasing y from 0.04 to 0.00 causes T_N to decrease from ~ 300 K to zero due presumably to an increase in the number of O $2p$ holes.²⁷ We expect that holes in the tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ should have a similar negative effect on long-range magnetic order, and hence, the relative insensitivity of T_N to oxygen content indicates an absence of holes.

A simple model to explain the lack of holes in the tetragonal phase can be developed in terms of the $\text{Cu}^{1+}/\text{Cu}^{2+}$ ratio. With x near zero, one can imagine that an isolated O atom in a "chain" site might satisfy its affinity for electrons by taking one electron from each of its two Cu neighbors, converting them from Cu^{1+} to Cu^{2+} . The number of Cu^{1+} ions per unit cell in the tetragonal phase would then equal $1 - 2x$. Thus one might expect to see a step in the number of Cu^{1+} ions versus x at the tetragonal-orthorhombic phase boundary. The step which is observed is less than that predicted by our simple model, indicating that shifts of atoms in the BaO layer occurring near the structural transition must also play an important role in suppressing mobile holes.

III. EXPERIMENTAL PROCEDURE

For this study, a series of oxygen-deficient samples were prepared from a single batch of $\text{YBa}_2\text{Cu}_3\text{O}_7$ which had been made by the conventional solid-state reaction method. The oxygen content of a similarly prepared, fully oxygenated sample was determined to be 7.04 ± 0.06 from neutron-powder diffraction profile refinement.²⁸ For convenience, the x value of the starting material will be defined to be one. Each reduced oxygen sample was obtained by annealing a sintered piece of $x=1$ material of known weight at a temperature T_{quench} for two hours in air and then dropping it into liquid nitrogen. After removal from the nitrogen, each sample was warmed to room temperature in a dessicator before being weighed. The change in weight, assumed to be due entirely to oxygen loss, was used to determine the final oxygen content. The values of T_{quench} used to obtain various oxygen contents²⁹ are shown in Fig. 1, along with the lattice parameters determined by x-ray powder diffraction and the superconducting transition temperatures determined by ac magnetic susceptibility measurements. Three samples ($x=0.24$, which had been heated to 1000 K in N_2 before quenching, $x=0.04$, which had been heated to 1150 K in Ar after the first air quench, and $x=0.40$) were sealed separately in evacuated quartz tubes, heat treated at 900 K overnight, and then furnace cooled. It was hoped that the $x=0.40$ sample might change from orthorhombic to tetragonal; however, no weight loss or structural changes were observed in these samples due to the annealing. For the x-ray absorption work, each material was ground to a fine

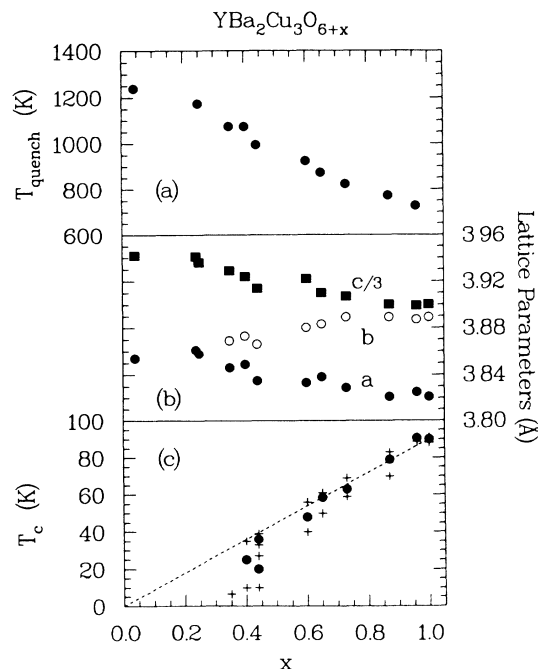


FIG. 1. (a) Temperatures from which $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ samples were quenched to obtain reduced oxygen concentrations. All samples were heated in air and quenched in liquid N_2 except as noted in the text. (b) Lattice parameters determined by x-ray powder diffraction. (c) Superconducting transition temperatures measured by ac susceptibility. Solid symbols indicate transition midpoints, crosses indicate 10% and 90% points. The $x=0.44$ sample exhibited two distinct transitions.

powder and spread onto several layers of Scotch tape. Uniaxially aligned samples of $x=1.0$ and 0.23 were prepared by mixing finely powdered material with five-minute epoxy and allowing it to cure in an 8-T magnetic field.

The x-ray absorption measurements on the aligned samples were performed at beam line I-5 of the Stanford Synchrotron Radiation Laboratory (SSRL), while measurements on the unoriented samples were made at beam line A3 of the Cornell High Energy Synchrotron Source (CHESS). In both cases the x-ray energy was determined by a Si (111) double crystal monochromator. Slits defining the beam height were adjusted to give an energy resolution of ~ 2 eV at 9 keV. The energy scale of the Cu K -edge spectrum for each sample was referenced to a simultaneous Cu foil measurement.

IV. RESULTS AND INTERPRETATION

The lower portion of Fig. 2 shows measurements at the Cu K edge using linearly polarized synchrotron radiation for two different orientations of the aligned samples. Absorption at a K edge is dominated by $1s \rightarrow p$ symmetry dipole transitions with the lobes of the final state p wave aligned parallel to the polarization vector, $\hat{\epsilon}$, of the incident radiation. Thus, a measurement on an oriented sample tends to probe electronic states which are aligned

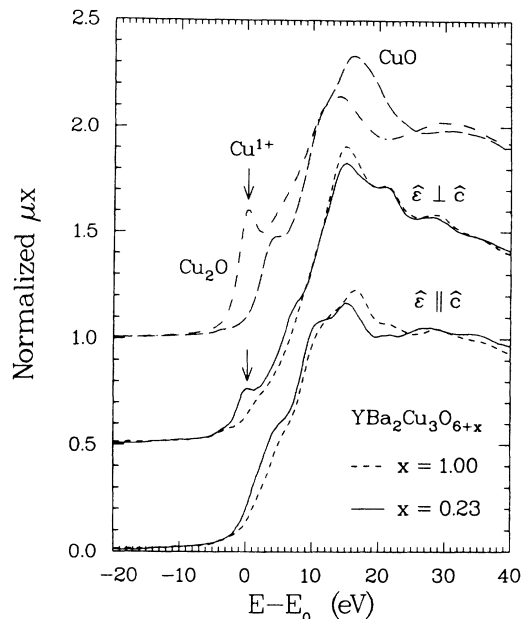


FIG. 2. X-ray absorption near edge structure measured at the Cu K edge, with $E_0=8980$ eV. At the top are data for unoriented powders of Cu_2O and CuO , taken from Ref. 14. Below are spectra, for uniaxially aligned samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x=0.23$ and 1.00 , measured with the x-ray polarization vector $\hat{\epsilon}$ perpendicular to and parallel to the c -axis direction \hat{c} .

parallel to $\hat{\epsilon}$. The upper part of the figure compares the near-edge structure of randomly oriented powders of Cu_2O and CuO , which are representative of twofold coordinated Cu^{1+} and fourfold coordinated Cu^{2+} , respectively. The only feature to which we wish to draw attention is the sharp peak at $E \approx E_0$ in the Cu_2O spectrum. This peak is characteristic²⁶ of twofold coordinated Cu^{1+} and is completely absent for Cu^{2+} . A polarization-dependent study³⁰ of a single crystal containing oriented Cu^{1+} complexes has shown that the peak corresponds to a $4p_x$ final state aligned perpendicular to the ligand axis. Inspection of the measurements on the two oriented $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ samples shown in Fig. 2 reveals that the Cu^{1+} peak is present only for the $x=0.23$ sample with $\hat{\epsilon} \perp \hat{c}$. The polarization dependence of the feature clearly indicates that Cu^{1+} atoms are located in "chain" sites where the two O ligands are aligned parallel to the c axis. No Cu^{1+} is present in the $x=1$ sample. Further details of the orientation-dependent spectra have been discussed elsewhere.³¹

Figure 3(a) shows representative Cu K edge spectra measured on unoriented samples of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ for several different oxygen concentrations. The Cu^{1+} feature is observed to grow steadily with decreasing oxygen content, while the Cu^{2+} peak decreases in a complementary fashion. The Cu^{1+} peak can be isolated by subtracting the $x=1$ spectrum from each of the others, as shown in Fig. 3(b). (Such an approach to identifying Cu^{1+} ions has been shown to yield consistent results for a wide range of Cu compounds.²⁶) We have evaluated the amount of Cu^{1+} present as a function of x by integrating

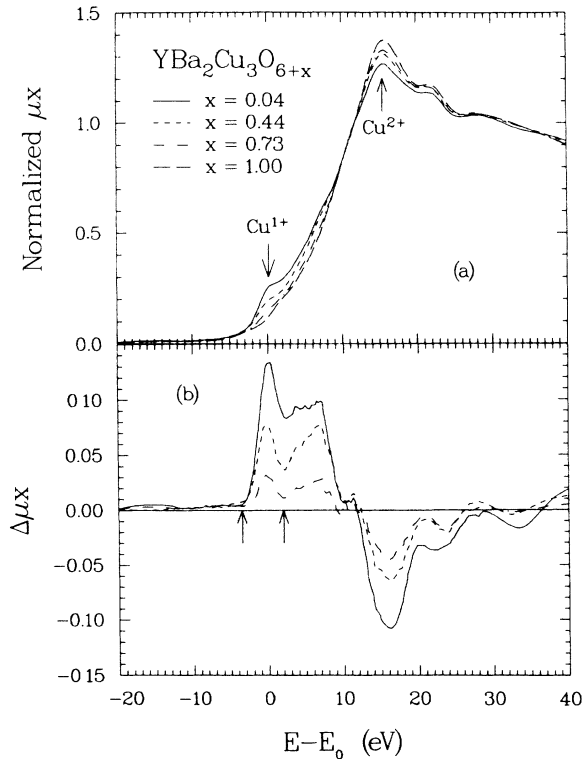


FIG. 3. (a) Representative Cu K -edge spectra measured for several samples of unoriented $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with different oxygen concentrations. (b) Difference spectra determined by subtracting the $x=1$ data from each of the other curves in (a).

the area under the peak in each difference spectrum over the range indicated by the arrows. To put the numbers on an absolute scale, the areas were normalized to the area of the Cu^{1+} peak obtained for the Cu_2O sample (after subtracting the $\text{YBa}_2\text{Cu}_3\text{O}_7$ spectrum); the results are shown in Fig. 4. In the orthorhombic phase ($x \gtrsim 0.35$) the data closely follow the $1-x$ prediction (solid line). Although the agreement is not perfect, it is remarkably good considering that no adjustable parameters have been used and that some systematic error may occur in the normalization. Thus, the data are consistent with a model in which oxygen is removed from one chain at a time, and it follows that the number of O $2p$ holes, n_h , is equal to x .

Looking back at the lower part of Fig. 1, one can see that T_c varies approximately linearly with x . Combining this observation with the Cu^{1+} results, one can see that $T_c \sim n_h$, in good agreement with μSR studies¹³ and in rough agreement with Hall effect measurements.¹¹ The new result here is that T_c extrapolates to zero at $x \approx 0$ rather than at $x=0.5$. The role of the chains is to act as a reservoir for electrons when oxygen is removed, thus mitigating the reduction in T_c due to oxygen deficiency. Emery^{13,32} has pointed out that for a two-dimensional electron (or hole) gas, the Fermi energy ϵ_F is proportional to n_h , and, hence, that $T_c \sim \epsilon_F$. This important result implies^{13,32} that the characteristic excitation energy involved in electron (or hole) pairing is much greater than ϵ_F .

In the tetragonal phase, our simple model suggests that

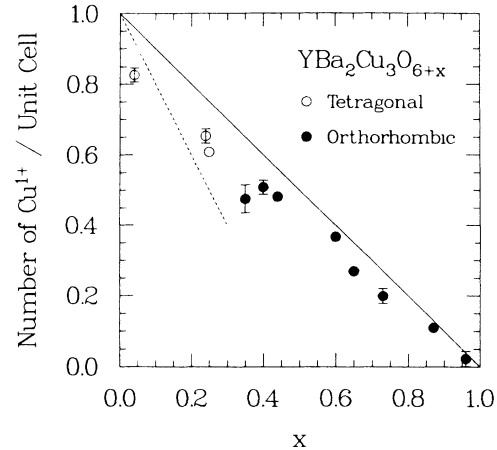


FIG. 4. Number of Cu^{1+} ions per unit cell measured in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ plotted as a function of x . The solid line represents $n_{\text{Cu}^{1+}} = 1 - x$, while the dashed line indicates $n_{\text{Cu}^{1+}} = 1 - 2x$.

the number of Cu^{1+} ions per unit cell should equal $1 - 2x$, as indicated by the dashed line in Fig. 4. While there does seem to be a small step in the data at $x=0.35$, where the structure is still orthorhombic but T_c is less than 5 K, the changeover is less than predicted. It thus appears that the $\text{Cu}^{1+}/\text{Cu}^{2+}$ ratio cannot by itself explain the disappearance of O $2p$ holes and superconductivity in the tetragonal phase. Structural changes must also play an important role.

Several workers^{33,34} have noted that as oxygen is removed from the chain sites, the atoms in the BaO layers shift relative to the chain and CuO_2 plane layers. In particular, the intervening oxygen atoms shift towards the chain layers while the Ba ions move towards the CuO_2 planes; at the same time, the c axis expands. The directions of these displacements can easily be understood in terms of the net charges on the layers. If we assume that the oxygen holes occur predominantly in the CuO_2 planes, then as oxygen is removed, the net charge on a chain layer changes from approximately zero at $x=1$ to $+1$ at $x=0$, thus attracting the negatively charged oxygen atoms. For a CuO_2 layer, we expect that the net charge is close to -1.5 at $x=1$ when the presence of holes is taken into account, and the charge increases to -2 at $x=0$, resulting in an increased attraction for the Ba^{2+} ions. The positions of the Ba^{2+} and O^{2-} ions must stabilize the distribution of O $2p$ holes in the orthorhombic phase and must help to eliminate mobile holes in the tetragonal phase. A precise understanding of this mechanism will require further experimental and theoretical work.

V. COMPARISON WITH OTHER WORK

Although a number of spectroscopic studies of copper valence as a function of oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ have been reported, their conclusions are not all in agreement with ours. Therefore, it seems worthwhile to discuss some of the differences between our results and some of

the others. Oyanagi *et al.*¹⁸ performed similar Cu K -edge measurements on several reduced oxygen content samples. They showed that the amount of Cu^{1+} increased with decreasing x and they properly assigned the Cu^{1+} ions to the twofold coordinated "chain" sites. However, they also interpreted certain near edge features as evidence for Cu^{3+} . We have demonstrated elsewhere³¹ that, using orientation-dependent measurements, one can consistently explain all of the features observed for $x \approx 1$ in terms of a superposition of features from Cu^{2+} in both the chain and plane sites. Oyanagi *et al.*¹⁸ also drew a line through their data points suggesting a steplike change in the amount of Cu^{1+} at $x=0.7$. Although their samples were different from ours in that they showed steps in T_c vs x , we believe that their data are not inconsistent with a linear variation in the amount of Cu^{1+} with x . Our explanation for the nonlinear variation of T_c with oxygen content in annealed samples will be discussed in the next section.

Steiner *et al.*³⁵ have used x-ray photoemission measurements of the Cu $2p$ core levels to study the valence of Cu. From their analysis they conclude that Cu^{1+} is present in the tetragonal phase but not in the superconducting phase. However, their conclusions are based on fits to a photoemission peak for which Cu^{2+} and Cu^{1+} contributions cannot be resolved. One might expect that, at best, the parameters obtained from such fits would be highly correlated. On the other hand, the Cu^{1+} feature which we have analyzed is quite well separated from the Cu^{2+} features so that we have a high level of confidence in our analysis and interpretation.

VI. FURTHER DISCUSSION

An important point remaining to be discussed concerns the nonmonotonic behavior of T_c as a function of oxygen content observed in annealed samples. Cava *et al.*² and others²⁰ have observed steps at 90 and at 60 K in the T_c vs x curve. Such steps might at first appear to contradict the present conclusions; however, we believe that the different results can be reconciled by considering spinodal decomposition.²² Theoretically, it has been suggested²² that an orthorhombic sample of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with $x < 1$ should decompose into tetragonal and orthorhombic phases. More recently Khachatryan and Morris³⁶ have pointed out the likelihood that intermediate ordered phases should occur. Such phases would involve simple orderings of filled and empty CuO chains. For certain ranges of x , one might expect to observe (in equilibrated samples) a single superconducting phase, the volume of which would vary with x . In samples quenched sufficiently rapidly, the decomposition would not have time to take place, and hence the distribution of oxygen would be relatively homogeneous, leading to a linear variation of T_c .

While macroscopic phase separation is not observed, microscopic separation is possible and has actually been observed. A high-resolution x-ray diffraction study³⁷ of a small single crystal with excellent bulk superconducting properties revealed a range of distinct domains having a variation in $a-b$ as large as 0.07 Å. The different domains presumably have different oxygen concentra-

tions. Similar observations have been reported in an electron diffraction study.³⁸ Further evidence of decomposition comes from Meissner effect measurements performed on ceramic samples. It is observed^{2,20,33} that for samples with the same T_c , the superconducting fraction is largest for the sample with the highest oxygen content and decreases as x decreases. These measurements are consistent with decomposition into a single superconducting orthorhombic phase and a second nonsuperconducting tetragonal phase. (Only a 20%–30% variation in Meissner fraction would be expected across a constant- T_c plateau.)

Contrary to the theoretical speculations on spinodal decomposition, Shi, Zhang, and Capone³⁹ have shown that the tetragonal-to-orthorhombic transition involves a nucleation and growth mechanism. Furthermore, in a study of the oxygen mechanism in the orthorhombic phase, Shi and Capone⁴⁰ have observed an abrupt transition from the $T_c=60$ -K phase to the $T_c=90$ -K phase, with no significant variation in Meissner fraction with oxygen content. Whatever the kinetics of the transitions, oxygen ordering clearly has a strong effect on T_c .

Zaanan, Paxton, Jepsen, and Anderson⁴¹ have proposed an alternative model in which the hole density shows steps with oxygen content due to a particular ordering of oxygen vacancies. The vacancy ordering is assumed to result in a unique intact CuO chain length at a given oxygen content, and it is the dependence of the energy levels of a finite chain on its length which presumably controls the hole density. If such a picture is correct, the amount of Cu^{1+} observed in annealed samples should show steps corresponding to the steps in T_c . While we still believe that phase separation is responsible for the steps in T_c , x-ray absorption measurements on a series of annealed samples will be required to help distinguish between these different models.

VII. CONCLUSIONS

A model has been presented in which it is assumed that oxygen is removed from the CuO chains in orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ one chain at a time, leaving an array of empty and full chains. The copper atoms in the twofold coordinated sites of the empty chains should have a +1 valence, and the number of Cu^{1+} ions per unit cell should be equal to $1-x$. These predictions have been confirmed by x-ray absorption measurements at the Cu K edge in oriented and unoriented quenched ceramic samples. Charge neutrality then implies that the number of O $2p$ holes per unit cell is equal to x . In our quenched samples, T_c is also observed to vary linearly with x , extrapolating to zero at $x \approx 0$. Thus, the CuO chains act as an electron reservoir which serves to maximize the number of holes, and, hence, T_c , when oxygen is removed. The chains are not, however, required for superconductivity.

The steps in T_c observed^{2,20} as a function of oxygen content in annealed samples can be explained by spinodal decomposition²² into a superconducting phase with a stable oxygen vacancy configuration and a nonsuperconducting tetragonal phase. The nearly discontinuous change in the number of O $2p$ holes near the ortho-

rhombic-tetragonal phase boundary appears to be due to a drop in the amount of Cu^{1+} , due to disordering of the CuO chains in the tetragonal phase, together with shifts of Ba and O ions between CuO_2 and CuO planes.

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