

## Oxygen ordering and the orthorhombic-to-tetragonal phase transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

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*In situ* neutron powder diffraction measurements show that the orthorhombic-to-tetragonal phase transition in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , which occurs near  $700^\circ\text{C}$  in a pure oxygen atmosphere, is an order-disorder transition in which the disordering of oxygen atoms into a normally vacant site destroys the one-dimensional Cu-O chains present in the room-temperature orthorhombic structure. For both structures, the oxygen stoichiometry decreases monotonically with increasing temperature. The transition temperature depends on the oxygen partial pressure and occurs when the stoichiometry is near  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ . The tetragonal structure has a partially occupied, nearly octahedral Cu-O arrangement, in contrast to the orthorhombic structure which has one-dimensional Cu-O chains. The observed depression of the superconducting transition temperature in tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , which has been quenched from high temperature, could result either from the disordering of oxygen atoms which destroys the one-dimensional chains or from the absence of  $\text{Cu}^{3+}$  ions.

### INTRODUCTION

The recent interest in ternary oxides which exhibit superconductivity at remarkably high temperatures was initiated by the report that multiphase mixtures with nominal composition  $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$  exhibited possible superconductivity at 30 K.<sup>1</sup> The superconducting compound was subsequently identified as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ , with the highest superconducting transition temperature,  $T_c$ , occurring at  $x \approx 0.15$ ,<sup>2</sup> and it was also reported that doping with Sr instead of Ba produced higher  $T_c$ 's of 36 K.<sup>3</sup> Shortly following this work Wu *et al.*<sup>4</sup> and Chu *et al.*<sup>5</sup> reported superconductivity above 90 K in multiphase samples with nominal compositions  $\text{Y}_{1.2}\text{Ba}_{0.3}\text{Cu}_2\text{O}_{4-x}$  and  $\text{Y}_{0.6}\text{Ba}_{0.4}\text{CuO}_{3-x}$ . Several groups have identified the single-phase compound responsible for the high- $T_c$  superconductivity as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .<sup>6-13</sup>

Although much work has gone into characterizing the superconducting properties of these materials and into the search for other new high- $T_c$  compounds, the superconducting mechanism is not established. A number of theoretical models ranging from conventional phonon-mediated coupling<sup>14,15</sup> to a variety of exotic mechanisms<sup>16-27</sup> have been explored. Most of these theories depend on a knowledge of the unusual structural features of the Cu-O sublattices present in these compounds. The tetragonal  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  structure contains square-planar  $\text{CuO}_2$  layers with weak coupling between the layers,<sup>2</sup> while the more complex orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  structure consists of nearly square-planar  $\text{CuO}_2$  layers weakly bonded through Cu—O—Cu bonds to one-dimensional, "fencelike,"  $\text{CuO}_3$  chains.<sup>28</sup>

The existence of closely related, nonsuperconducting compounds has also played a central role in understanding

these new superconductors. In the case of  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ , the importance of the Cu-O sublattice has been further emphasized by recent reports that the parent structure,  $\text{La}_2\text{CuO}_4$ , which was originally reported to be nonmetallic, exhibits either antiferromagnetism or superconductivity, depending in a critical way on the number of oxygen vacancies present.<sup>29,30</sup> A variant of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound which does not exhibit 92 K superconductivity has also recently been reported.<sup>31,32</sup> This new phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  was identified by high-temperature x-ray diffraction<sup>31</sup> and electron microscopy<sup>32</sup> and was shown to have tetragonal symmetry. It was also demonstrated that the tetragonal phase could be produced at room temperature by rapid cooling from above the orthorhombic-to-tetragonal transition temperature ( $\sim 700^\circ\text{C}$ ). These "quenched" samples exhibit markedly reduced superconducting transition temperatures, or, in some cases, no superconductivity.<sup>31,32</sup> It was speculated that the decrease in the superconducting transition temperature is due to a disordering of the oxygen chains, which implies that the Cu-O chains play a major role in the mechanism for high-temperature superconductivity.<sup>31</sup> However, the x-ray data could not provide details of the oxygen-atom positions and occupancies. Clearly, a detailed understanding of the structures of these two forms of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , which requires neutron-diffraction techniques, and the correlation of these structural features to the superconducting properties might give some crucial clues towards the determination of the mechanism responsible for the superconductivity.

The existence of two stable phases for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , combined with the observation that the tetragonal phase can be obtained at room temperature by rapid cooling from above the transition, explains some of the earlier

confusion concerning the structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Several single-crystal x-ray studies yielded a tetragonal structure composed of three perovskite cells stacked in the  $c$  direction with ordered Y and Ba cations.<sup>33-35</sup> While the major details of the reported structures are the same, the reported space groups [ $P4m2$  (Ref. 33) and  $P4/mmm$  (Refs. 34 and 35)] are in disagreement, presumably because of the poor sensitivity of x-rays for determining oxygen-atom displacements and vacancy ordering, or because the samples were actually twinned orthorhombic crystals, as speculated by Hazen *et al.*<sup>33</sup> X-ray diffraction from powdered samples, on the other hand, clearly indicated an orthorhombically distorted variant of the tetragonal structure.<sup>36,37</sup> Again, the positions and possible ordering of the oxygen atoms could not be accurately determined from the x-ray data. The correct orthorhombic,  $Pmmm$ , structure of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , including the details of the Cu-O sublattice, has been determined by Rietveld refinement of neutron powder diffraction data by Beno *et al.*<sup>28</sup> and also by at least five other groups.<sup>38-42</sup> In particular, the neutron-diffraction results provide an accurate knowledge of the oxygen-atom positions and site occupancies and show that oxygen atoms are ordered onto only some of the available sites, which results in the formation of the one-dimensional  $\text{CuO}_3$  chains parallel to the orthorhombic  $b$  axis.<sup>28,38-42</sup>

In this paper we present results of *in situ* neutron powder diffraction measurements as a function of temperature and oxygen partial pressure, which confirm the existence of a high-temperature phase transition to a tetragonal form of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . The structural details of the tetragonal phase are determined by Rietveld analysis.<sup>43</sup> The transition from the orthorhombic to the tetragonal phase, which occurs near 700 °C in a pure oxygen atmosphere, is an order-disorder transition in which the disordering of oxygen atoms into a site which is normally vacant destroys the one-dimensional chains present in the room-temperature orthorhombic structure. We also show that the total oxygen composition, which depends on the oxygen partial pressure, decreases monotonically with increasing temperature in both phases, and that the transition always occurs near a stoichiometry of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ . Thus, lower-oxygen partial pressures result in lower structural transition temperatures. Interestingly,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  is the highest oxygen concentration at which simple charge balance considerations require an average charge state of 2+ for the Cu atoms.

#### EXPERIMENTAL PROCEDURE

A large powder sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  was prepared by thoroughly mixing barium hydroxide powder into a concentrated solution of yttrium and copper nitrates at 100 °C. The solution was oven dried at 150 °C overnight, resulting in a compacted blue-green powder which was then thermally decomposed in air at 800 °C, cooled to room temperature, ground, pressed into pellets, and fired again at 925 °C under flowing oxygen for 10 h followed by cooling to room temperature at a rate of 100 °C/h. Four-point resistivity measurements on this sample showed a

92-K superconducting transition with a transition width of 3 K. Temperature-dependent, neutron powder diffraction data were collected using the special environment powder diffractometer (SEPD) at the intense pulsed neutron source (IPNS) at Argonne National Laboratory for a 10-g sample in the form of a self-supporting stack of cylindrical pellets approximately 1 cm diameter and 2.5 cm high. Data were collected at room temperature and over the range of 321 °C to 916 °C at a pressure of 1 atm in flowing 100%  $\text{O}_2$ , 20%  $\text{O}_2$ -80% Ar, and 2%  $\text{O}_2$ -98% Ar. The data were collected through collimated windows in the furnace at a fixed scattering angle of  $2\theta = \pm 90^\circ$  in order to avoid unwanted scattering from the furnace components. Between runs the temperature was changed at a programmed rate of 4 °C/min after which the sample was allowed to equilibrate for 30 min before starting data collection. This heating and cooling appeared to allow the sample to reach thermodynamic equilibrium in all cases except for a run at 321 °C in 2% oxygen which showed clear evidence for structural variation during data collection. Typical data collection times were 2 h per run. The sample temperature was controlled with an accuracy of  $\sim 2^\circ\text{C}$  and independently monitored using an additional thermometer near the sample position. Furnace temperature calibration was confirmed in a separate study of the  $\alpha - \beta$  quartz transition in  $\text{SiO}_2$  at 573 °C.

#### RESULTS

The neutron powder diffraction data were analyzed by the Rietveld technique<sup>43</sup> to obtain structural parameters as a function of temperature and oxygen partial pressure. The orthorhombic-to-tetragonal transition was observed near 700 °C in an atmosphere of 100% oxygen. All of the data below the transition were consistent with the previously reported  $Pmmm$  orthorhombic space group. Above the transition the data could be indexed in a primitive tetragonal cell, as previously observed by x-ray diffraction<sup>31</sup> and electron microscopy.<sup>32</sup> Refinements attempted in the possible tetragonal space groups consistent with the lack of systematic absences led to the conclusion that the correct structure was  $P4/mmm$ , which is a supergroup of  $Pmmm$ . Thus, the transition is allowed, but not required, to be second order. The orthorhombic refinements included about 350 Bragg reflections over the range of  $d$  spacings from 0.71 to 3.95 Å, and the tetragonal refinements included about 200 reflections for the same data range. In the initial refinements, site occupancies for all of the oxygen sites were allowed to refine. However, at all temperatures, vacancies were observed only on the oxygen sites at  $(\frac{1}{2}, 0, 0)$  and  $(0, \frac{1}{2}, 0)$ . Thus, the other site occupancies were fixed at their stoichiometric values for the final refinement cycles. In an analogous way, the atoms which exhibited anisotropic temperature factors were identified in the initial refinements and other atoms were refined isotropically. A small amount of CuO (less than 3% by volume) was observed as an impurity phase in the sample and was included in the refinement models (using a multiphase Rietveld code) in order to minimize systematic errors. In all cases, the weighted profile (WP)  $R$  value was less than a factor

of 2 larger than the expected  $R$  value (based on counting statistics). Portions of the Rietveld refinement profiles for the orthorhombic structure at 623 °C and the tetragonal structure at 818 °C, in 100% oxygen, are shown in Figs. 1(a) and 1(b).

The orthorhombic and tetragonal structures of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  are shown in Figs. 2(a) and 2(b), and the structural parameters for the orthorhombic structure at 623 °C and the tetragonal structure at 818 °C, in 100% oxygen, are listed in Table I. The orthorhombic and tetragonal structures are related by an order-disorder transition involving the ordering of oxygen atoms into the available sites in the basal plane at  $z=0$ . The basal-plane

Cu-O sublattices at  $z=0$  are compared in Fig. 3. In the orthorhombic structure, the  $(0, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, 0, 0)$  sites [O(1) and O(5) in Table I(a)] are crystallographically inequivalent, and the oxygen atoms are fully ordered onto the  $(0, \frac{1}{2}, 0)$  site at room temperature, resulting in the one-dimensional, “fencelike”  $\text{CuO}_3$  chains [consisting of Cu(1), O(1), and O(4) in Figs. 2(a) and 3(a)] parallel to the  $b$  axis, as previously discussed.<sup>28</sup> Conversely, in the tetragonal structure the corresponding sites at  $(\frac{1}{2}, 0, 0)$  and  $(0, \frac{1}{2}, 0)$  are symmetry equivalent [site O(1) in Table I(b)] and are, thus, equally occupied. This disordering of the oxygen atoms destroys the one-dimensional chains and results in a two-dimensional layered structure where the

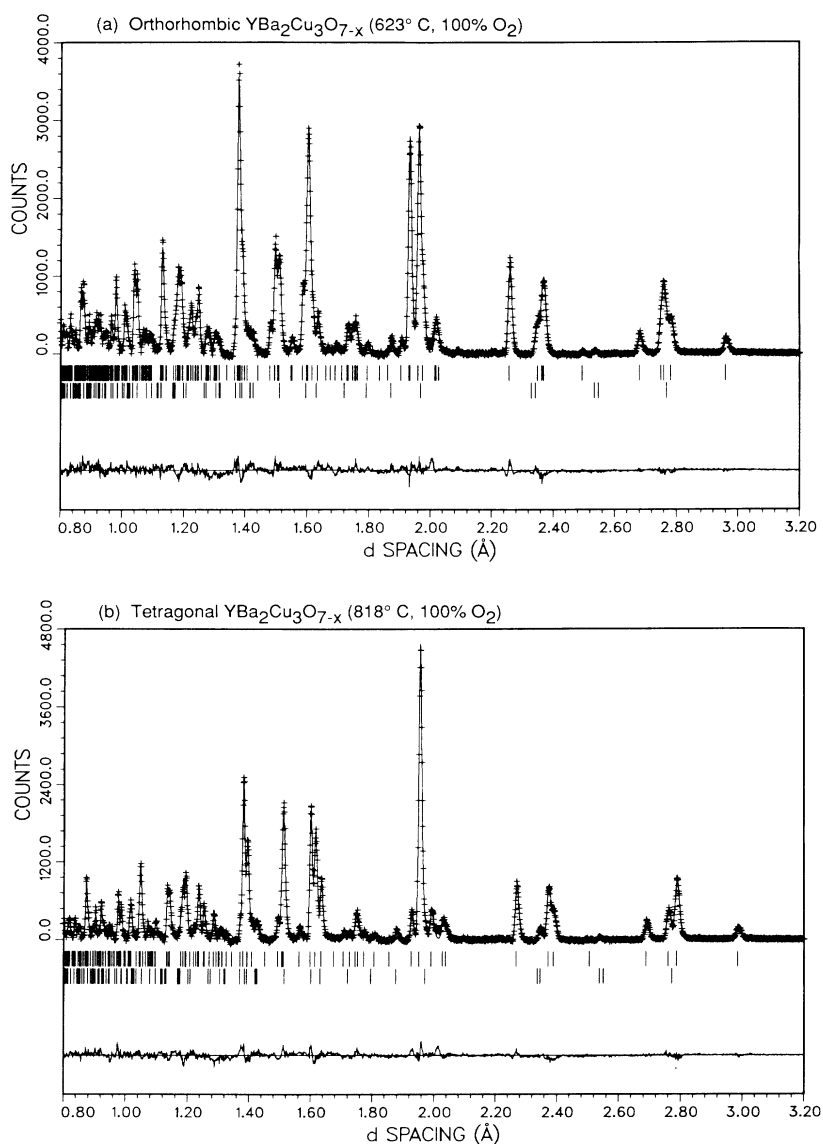


FIG. 1. Rietveld refinement profiles for (a) orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  at 623 °C and (b) tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  at 818 °C. Plus marks (+) are the raw neutron powder diffraction data and the continuous line is the calculated profile. Tick marks below the curves indicate the positions of the allowed  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  reflections (upper tick marks) and a minor CuO impurity phase (lower tick marks) included in the refinements.

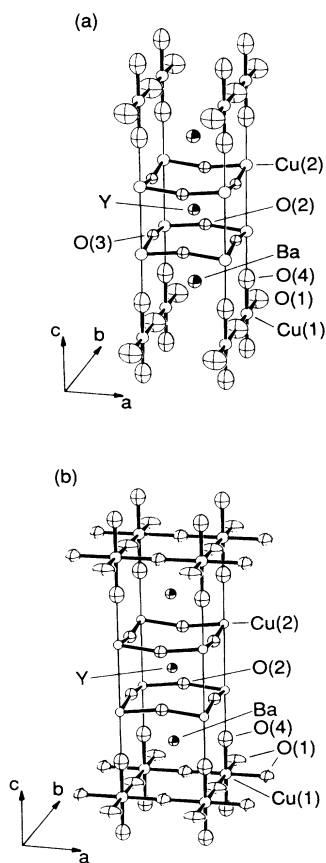


FIG. 2. Structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . (a) The orthorhombic  $Pmmm$  phase. (b) The tetragonal  $P4/mmm$  phase. Note that in the tetragonal phase the oxygen atoms are disordered in the  $z=0$  plane.

layers obtain a nearly octahedral Cu-O configuration consisting of a partially occupied ( $\leq 25\%$ ), nearly square-planar Cu-O network perpendicular to the  $c$  axis [Cu(1) and O(1) in Figs. 2(b) and 3(b)] with short (1.81 Å at high temperature) Cu—O bonds to additional fully occupied oxygen-atom sites [O(4) in Figs. 2(b) and 3(b)] in the  $+z$  and  $-z$  directions.

As shown in Fig. 2(b), the second Cu-O sublattice, i.e., the two-dimensional  $\text{CuO}_2$  layers adjacent to the Y atom site [Cu(2), O(2), and O(3)], are almost identical in the tetragonal and orthorhombic structures. In the orthorhombic structure, O(2) and O(3) exhibit almost identical atom positions even though the two sites are crystallographically distinct; while in the tetragonal structure these two sites become symmetry equivalent. [Note that in Fig. 2 and Table I, the same atom numbering scheme is used for the orthorhombic and tetragonal structures; thus, the tetragonal structure has O(1), O(2), and O(4), but no O(3) or O(5).] In both structures the O(2) [and O(3)] atoms are displaced out of the Cu(2) plane towards the Y-atom plane.

The  $a$ - and  $b$ -axis cell parameters as a function of temperature in 100%, 20%, and 2% oxygen atmospheres are

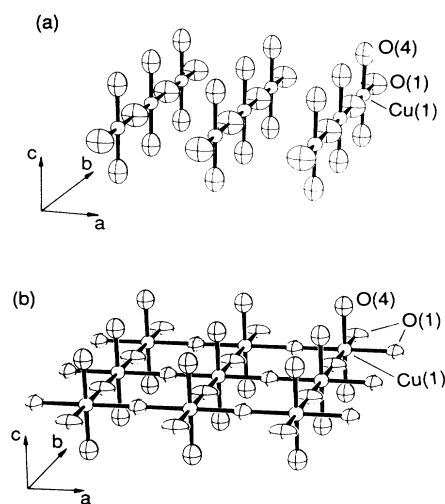


FIG. 3. Detail of the oxygen-atom ordering in the  $z=0$  plane of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ : (a) Orthorhombic phase exhibiting complete ordering of oxygen atoms onto the  $(0, \frac{1}{2}, 0)$  site which results in one-dimensional  $\text{CuO}_3$  chains along the  $b$  axis; and (b) tetragonal phase showing a disordering of the oxygen atoms in the same plane.

shown in Fig. 4. These figures include points taken on both heating and cooling. Within the resolution of these measurements, the variation of the cell parameters is continuous through the transition and no significant hysteresis is observed. (As previously mentioned, we did observe that the approach to equilibrium stoichiometry may be slow at lower temperatures and oxygen partial pressures and could lead to effects that may be mistaken for hysteresis.) The  $c$ -axis lattice parameter and cell volume versus temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  heated in 100% oxygen are shown in Fig. 5. These quantities also appear to be continuous but exhibit a change in slope at the transition temperature, 700°C, again consistent with a second-order transition. In the orthorhombic phase, there is an obvious increase in the thermal expansion beginning around 500°C and extending to the transition temperature. As will be shown later, this is the temperature range over which the overall oxygen stoichiometry is changing and oxygen atoms are disordering into previously vacant sites.

As can be seen in Fig. 4, in 100% oxygen the transition occurs at about 700°C, in good agreement with our previous x-ray powder diffraction result.<sup>31</sup> The transition temperature is lowered to about 670°C in 20% oxygen and to about 620°C in 2% oxygen. This change in the transition temperature as a function of oxygen partial pressure appears to result from the fact that the overall oxygen stoichiometry varies monotonically with temperature and the transition always occurs at a composition near  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ . The variation of composition with temperature, for each of the three oxygen partial pressures, is shown in Fig. 6. Over the temperature range from room temperature to 916°C the total oxygen loss corresponds to

TABLE I. Structural parameters for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  determined by Rietveld refinement of neutron powder diffraction data. Numbers in parentheses are statistical uncertainties of the last significant digit. Numbers without uncertainties were not refined. Both phases contain one formula unit per unit cell. The anisotropic and isotropic thermal factors have the form  $\exp - 2\pi^2(U_{11}^2h^2 + U_{22}^2k^2 + U_{33}^2l^2)$  and  $\exp - B_{\text{iso}}/4d^2$ , respectively.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}$ ( $\text{\AA}^2$ )	Occupancy
(a) Orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at 623 °C <sup>a</sup>					
Y	0.5	0.5	0.5	1.4(1)	1
Ba	0.5	0.5	0.1895(3)	1.7(1)	2
Cu(1)	0.0	0.0	0.00000	1.4(1)	1
Cu(2)	0.0	0.0	0.3574(3)	1.50(8)	2
O(1)	0.0	0.5	0.0	b	0.65(2)
O(2)	0.5	0.0	0.3767(4)	1.6(1)	2
O(3)	0.0	0.5	0.3804(5)	1.3(1)	2
O(4)	0.0	0.0	0.1542(5)	c	2
O(5)	0.5	0.0	0.0	d	0.06(2)
(b) Tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at 818 °C <sup>c</sup>					
Y	0.5	0.5	0.5	1.8(1)	1
Ba	0.5	0.5	0.1914(3)	2.2(1)	2
Cu(1)	0.0	0.0	0.0	2.7(1)	1
Cu(2)	0.0	0.0	0.3590(3)	1.82(8)	2
O(1)	0.5	0.0	0.0	f	0.42(3)
O(2)	0.5	0.0	0.3792(2)	1.95(8)	4
O(4)	0.0	0.0	0.1508(5)	g	2

<sup>a</sup>Space group  $Pmmm$ :  $a=3.8591(1)$   $\text{\AA}$ ,  $b=3.9195(1)$   $\text{\AA}$ ,  $c=11.8431(5)$   $\text{\AA}$ ,  $V=179.137(9)$   $\text{\AA}^3$ ,  $R_{\text{WP}}=0.0735$ ,  $R_{\text{exp}}=0.0471$ .

<sup>b</sup>For O(1):  $U_{11}^2=0.081(12)$   $\text{\AA}^2$ ,  $U_{22}^2=0.014(7)$   $\text{\AA}^2$ ,  $U_{33}^2=0.107(16)$   $\text{\AA}^2$ .

<sup>c</sup>For O(4):  $U_{11}^2=0.025(2)$   $\text{\AA}^2$ ,  $U_{22}^2=0.025(2)$   $\text{\AA}^2$ ,  $U_{33}^2=0.054(4)$   $\text{\AA}^2$ .

<sup>d</sup> $U_{11}^2[\text{O}(5)]=U_{22}^2[\text{O}(1)]$ ,  $U_{22}^2[\text{O}(5)]=U_{11}^2[\text{O}(1)]$ ,  $U_{33}^2[\text{O}(5)]=U_{33}^2[\text{O}(1)]$ .

<sup>e</sup>Space group  $P4/mmm$ :  $a=b=3.9018(1)$   $\text{\AA}$ ,  $c=11.9403(5)$   $\text{\AA}$ ,  $V=181.781(8)$   $\text{\AA}^3$ ,  $R_{\text{WP}}=0.0743$ ,  $R_{\text{exp}}=0.0497$ .

<sup>f</sup>For O(1):  $U_{11}^2=0.049(18)$   $\text{\AA}^2$ ,  $U_{22}^2=0.103(26)$   $\text{\AA}^2$ ,  $U_{33}^2=0.035(20)$   $\text{\AA}^2$ .

<sup>g</sup>For O(4):  $U_{11}^2=U_{22}^2=0.049(2)$   $\text{\AA}^2$ ,  $U_{33}^2=0.068(4)$   $\text{\AA}^2$ .

a change in composition from  $\text{YBa}_2\text{Cu}_3\text{O}_{6.91(3)}$  to  $\text{YBa}_2\text{Cu}_3\text{O}_{6.28(3)}$  for the sample in 100% oxygen. As shown in Fig. 6, at lower-oxygen partial pressures, the total oxygen stoichiometry at high temperature is decreased, but the temperature dependence of the stoichiometry is nearly identical. It is quite remarkable that the orthorhombic-to-tetragonal transition always occurs near a composition of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ . Based on simple charge balance considerations, this is the composition at which the average charge state of Cu is exactly 2+. Thus, the tetragonal phase must contain Cu with an average charge state less than 2+.

At low temperature, the composition appears to saturate near  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  for the oxygen partial pressures and cooling rate investigated in this study. This saturation probably results from diffusion-limited kinetic effects. Other refinements of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  have yielded total oxygen stoichiometries in the range of 6.8–7.0.<sup>28,38–41</sup> Several authors have proposed that most of the  $\text{Cu}^{3+}$  ions present in the sample are located in the one-dimensional chains and that an oxygen concentration near 6.8–6.9 corresponds to the situation for which the concentrations of  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  at the Cu(1) site are equal.<sup>39,40,44,45</sup> This has also been claimed to be the most favorable concentration for achieving a high supercon-

ducting transition temperature.<sup>44</sup> The previous work has shown that  $T_c$  does not vary significantly for oxygen stoichiometries in the range of 6.8–7.0.<sup>28,38–41</sup> Further work, perhaps involving slow cooling in low-oxygen partial pressures, is required to elucidate the superconducting properties of samples with oxygen stoichiometries below 6.8.

Structural refinements immediately below the transition show that the disordering of oxygen atoms into the originally vacant  $(\frac{1}{2}, 0, 0)$  site occurs in a continuous way as the transition is approached, i.e., the orthorhombic form of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is not fully ordered at high temperature. Figure 7(a) shows the site occupancies for the  $(0, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, 0, 0)$  sites as a function of temperature for the sample in 100% oxygen. The orthorhombic structure has no significant oxygen population on the normally vacant  $(\frac{1}{2}, 0, 0)$  site [O(5) in Table I] below about 600 °C. Above this temperature the site occupancy at the  $(\frac{1}{2}, 0, 0)$  site increases smoothly, while the occupancy at the  $(0, \frac{1}{2}, 0)$  site [O(1) in Table I] decreases, until they converge, resulting in the transition to tetragonal symmetry. In the tetragonal phase, as temperature is increased, the combined occupancy of the  $(\frac{1}{2}, 0, 0)$  and  $(0, \frac{1}{2}, 0)$  sites, which are now symmetry equivalent, continues to

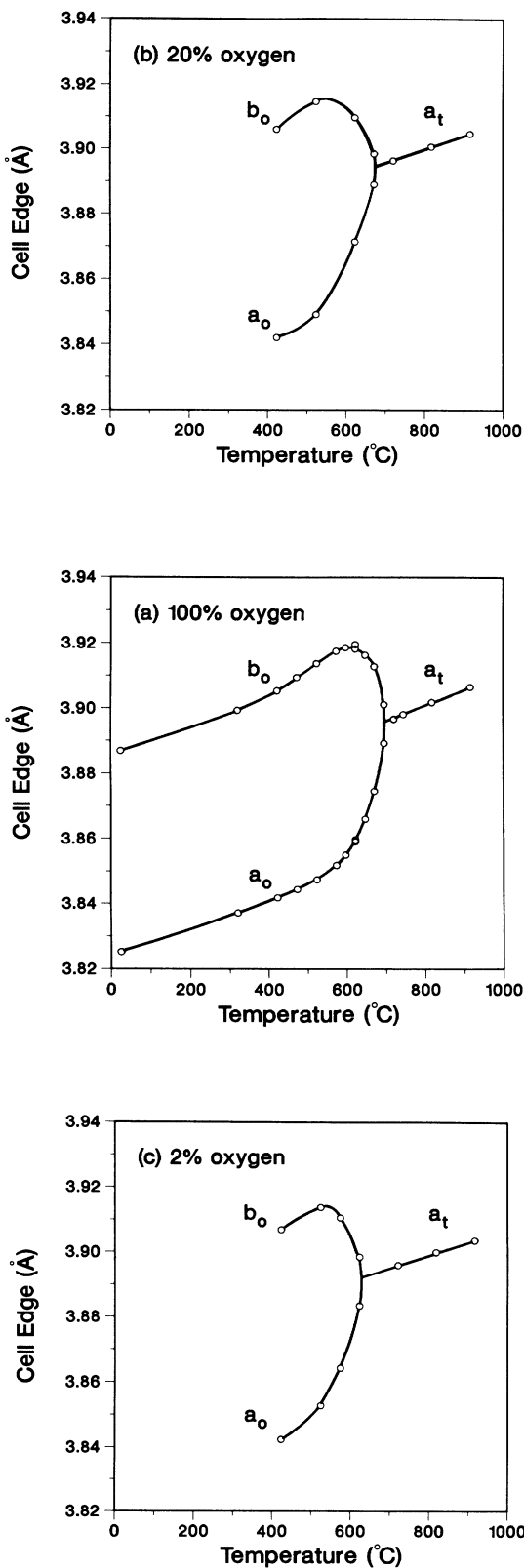


FIG. 4. The  $a$ - and  $b$ -axis lattice parameters of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  vs temperature for samples heated in (a) 100%  $\text{O}_2$ , (b) 20%  $\text{O}_2$ -80% Ar, and (c) 2%  $\text{O}_2$ -98% Ar.

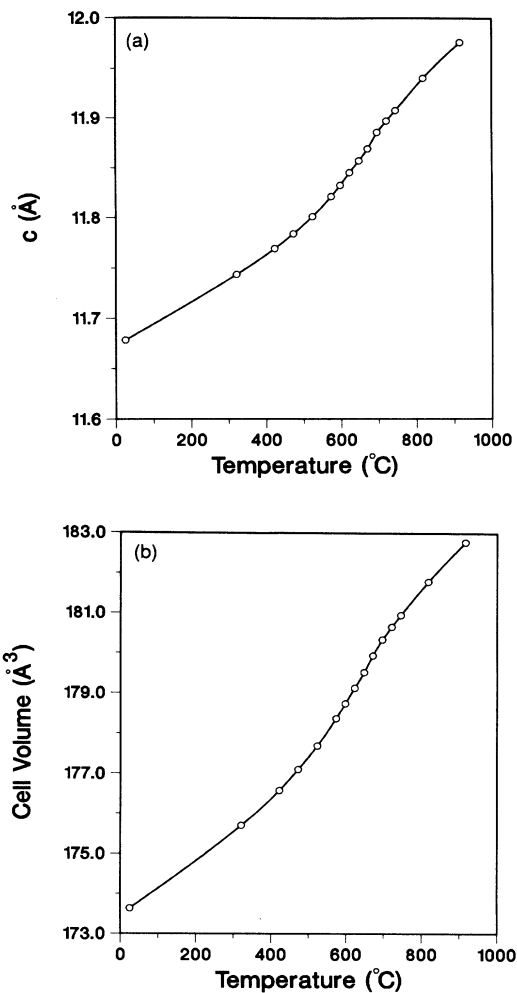


FIG. 5. The  $c$ -axis lattice parameter (a) and unit-cell volume (b) vs temperatures for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in 100% oxygen.

decrease. As shown in Figs. 6(b) and 6(c), heating the sample under lower-oxygen partial pressures produces essentially the same behavior as just discussed, except that as the oxygen partial pressure is decreased the phase transition from orthorhombic to tetragonal occurs at a lower temperature, and the disordering of oxygen atoms in the orthorhombic phase between the  $(\frac{1}{2}, 0, 0)$  and  $(0, \frac{1}{2}, 0)$  sites occurs over a broader temperature range.

## DISCUSSION

The detailed knowledge of the structure of the tetragonal phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , as well as the information concerning the temperature dependence of the oxygen-defect structure, which has been gained from this study, has important impact in guiding future synthesis efforts and in designing experiments which will shed light on the mechanism for superconductivity. As many workers have discovered through trial and error, single-phase orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with an oxygen stoichiometry

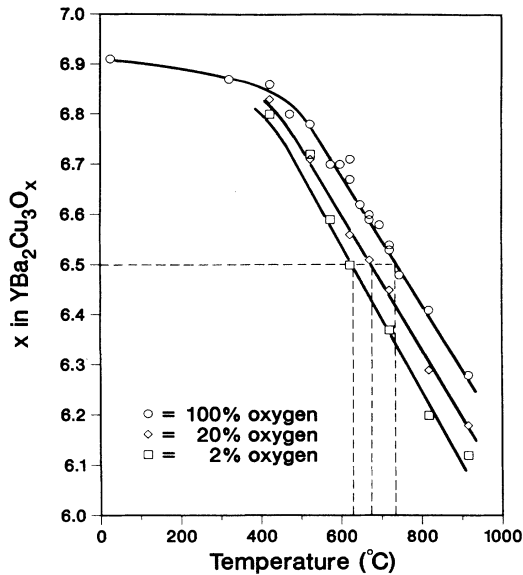


FIG. 6. Total oxygen content vs temperature for samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  heated in flowing 100%  $\text{O}_2$ , 20%  $\text{O}_2$ -80% Ar, and 2%  $\text{O}_2$ -98% Ar atmospheres. At each oxygen partial pressure the orthorhombic-to-tetragonal transition occurs near a stoichiometry of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ .

near 7 can best be produced by employing a long final anneal in pure oxygen at about  $650^\circ\text{C}$  (below the transition temperature) followed by slow cooling (to allow the oxygen diffusion which is required to raise the oxygen stoichiometry from 6.5 to a value near 7.0).

Additionally, it is now clear that it should be possible to produce both orthorhombic and tetragonal forms of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with a range of oxygen concentrations; presumably  $0.0 < x < 0.5$  for orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $0.5 < x < 1.0$  for tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . To date, only the superconducting properties for a composition near  $\text{YBa}_2\text{Cu}_3\text{O}_{6.8-7.0}$  have been characterized. In particular, the superconducting properties of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with oxygen stoichiometry below 6.8 are unknown and the initial conflicting reports of lower  $T_c$ 's or no superconductivity in tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  are based on samples of unknown composition and oxygen-defect structure. Moreover, it has not been shown that the oxygen-defect structures which exist in equilibrium at high temperature in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  system are preserved by the various techniques which can be used to produce oxygen-deficient (orthorhombic or tetragonal) samples at room temperature. The superconducting properties of the tetragonal phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  will obviously not be known until samples spanning the stable composition range have been produced and properly characterized.

In spite of these deficiencies in extrapolating the present high-temperature structural data to "quenched samples," some general observations regarding the correlation between structure and superconducting properties are possible. It has been pointed out earlier that the  $\text{Cu}(1)\text{—O}(4)$

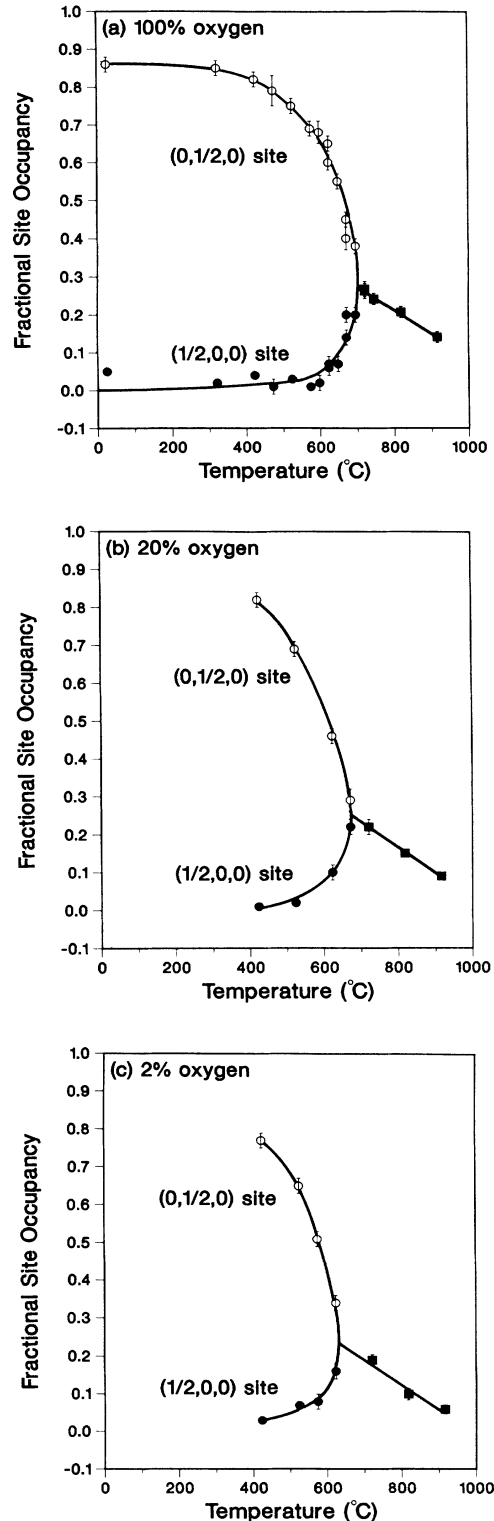


FIG. 7. Fractional oxygen site occupancies at the indicated sites in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  vs temperature for a sample heated in (a) 100% oxygen, (b) 20% oxygen, and (c) 2% oxygen. Since the allowed occupancy for the  $(\frac{1}{2}, 0, 0)$  site in the tetragonal phase is two atoms per unit cell, the fractional occupancies for this site must be doubled to yield the number of oxygen atoms per unit cell.

bond length in the one-dimensional chains is unexpectedly short.<sup>40</sup> Based on a bond strength calculation by David *et al.*,<sup>40</sup> using the methods of Brown and Wu,<sup>46</sup> it has been suggested that the  $\text{Cu}^{3+}$  ions preferentially occupy the Cu(1) site in the one-dimensional chains. As stated above, at the orthorhombic-to-tetragonal transition the oxygen stoichiometry is 6.5 and simultaneously the oxygen ordering disappears. Because of this it is not possible to uniquely conclude whether the reason for the depression of the superconductivity in the tetragonal phase is due to a loss of  $\text{Cu}^{3+}$  or a loss of the ordering in the one-dimensional chains. It is clear, however, that the chains play an important role in the mechanism of superconductivity, either through the existence of the mixed-valent copper or a dimensional enhancement of superconductivity.

### SUMMARY

In summary, we have performed an extensive structural study of the oxygen ordering in the high- $T_c$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  using neutron powder diffraction. The results show the existence of an order-disorder transition from an orthorhombic  $Pmmm$  to a tetragonal  $P4/mmm$  structure. The main feature characterizing this transition is the continuous disordering of oxygen atoms into normally vacant sites, which results in the destruction of the novel one-dimensional Cu-O chains previously reported for the orthorhombic structure of ( $T_c = 92$  K)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Within the resolution of these diffraction measurements, the transition appears to be continuous. However, careful thermodynamic measurements will be required to determine whether the transition is actually second order. The transition occurs at an oxygen

stoichiometry of 6.5, which corresponds to the point at which only  $\text{Cu}^{2+}$  is present. These experiments show that the Cu-O chains play a major role in the superconducting mechanism either through the existence of mixed  $\text{Cu}^{3+}$ - $\text{Cu}^{2+}$  ions and/or dimensional effects due to the presence of the one-dimensional Cu-O chains.

*Note added:* Since the submission of this manuscript the authors have learned of several papers dealing with related subjects which they wish to call to the attention of the reader. The continuous evolution of oxygen as a function of temperature and the relation of the oxygen stoichiometry to the structural phase transition has been studied by several laboratories using thermogravimetric analysis, evolved gas analysis, chemical analysis, dilatometry, x-ray powder diffraction, etc.<sup>47-49</sup> The structure of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  has been determined by three groups using neutron powder diffraction<sup>50-52</sup> and by one group using single-crystal x-ray diffraction.<sup>53</sup> The samples, which are not superconducting, were made by cooling in inert atmospheres, resulting in a tetragonal,  $P4/mmm$ , structure in which all of the chain oxygen atoms have been removed.

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