Structure of the single-phase high-temperature superconductor YBa$_2$Cu$_3$O$_{7-\delta}$

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We have determined the crystal structure of the single-phase stoichiometric high-temperature superconductor in the Y-Ba-Cu-O system using high-resolution neutron powder diffraction. This compound has an orthorhombic structure with space group *Pmmm* and lattice constants $a = 3.8231$ Å, $b = 3.8864$ Å, and $c = 11.6807$ Å. The structure consists of "dimpled" CuO$_2$ layers in the a-b planes loosely bonded by one-dimensional fencelike square-planar CuO$_3$ chains in the b-c planes.

Recently, superconductivity above 90 K was reported by Wu *et al.*[1] in a multiphase sample with a nominal composition of Y$_{1.2}$Ba$_{0.8}$Cu$_2$O$_{4-\delta}$. Subsequent studies by several groups[2-5] identified the superconducting compound as YBa$_2$Cu$_3$O$_y$. Although the metal-ion stoichiometry is well established the structure is still in question. One of the simplest ordered perovskite structures with a YBa$_2$Cu$_3$O$_y$ stoichiometry consists of 1:1:n stacking of cubic perovskite building blocks with Cu atoms on the cube corners, Y or Ba atoms in the center of the cube, and O atoms on the cube edges. From powder x-ray diffraction data Cava *et al.*[3] proposed an orthorhombic unit cell with $a \approx 3.822$ Å, $b \approx 3.891$ Å, $c = \approx 11.677$ Å. Grant *et al.*[4] proposed a tetragonal unit cell with $a \approx 3.89$ Å and $c \approx 11.65$ Å. Both reports speculate that the structure of the superconducting material is a 1:1:3 variant of the perovskite unit cell with ordered Y and Ba cations and an unspecified number of oxygen atoms. A single-crystal x-ray diffraction study by Hazen *et al.*[6] determined the structure of YBa$_2$Cu$_3$O$_x$ (x reported as ≈ 6.5) as tetragonal with space group $P\bar{4}m2$ and confirmed the 1:1:3 stacked perovskite derivative structure. This structure contains CuO$_2$ planes and ordered oxygen vacancies in the BaO and YO planes. In all of these studies the oxygen atom positions and occupations are difficult to locate because of the low scattering power for x rays by oxygen atoms in the presence of "heavy atoms." Neutron diffraction, on the other hand, has nearly the same coherent scattering lengths for all the elements in this compound and provides an unambiguous method for locating the oxygen atomic positions and determining the site occupancies. In this letter we describe the results of neutron diffraction from a stoichiometric, polycrystalline sample of YBa$_2$Cu$_3$O$_y$. From the analysis of these data we find a structure different from other proposed models for the oxygen positions and content.

The sample was prepared by standard powder metallurgical methods from high-purity Y$_2$O$_3$, BaCO$_3$, and CuO powders. After thorough mixing, grinding, and pressing, the sample was sintered at approximately 1000 °C in flowing O$_2$ for 10 h, and then furnace cooled.[2] Neutron and powder x-ray diffraction data showed sharp diffraction peaks, characteristic of a well-crystallized material, with no impurity phases present. An earlier phase diagram analysis[2] showed this to be the superconducting, stoichiometric compound in this system. The sample studied here exhibits, as has been previously reported,[2] a metallic resistance together with a sharp superconducting transition at 92.5 K (transition width of 3 K) which shows that the superconducting phase is homogeneous.

Neutron powder diffraction data were collected on a 5g sample of YBa$_2$Cu$_3$O$_y$ using the special-environment powder diffractometer at the Intense Pulsed Neutron Source (IPNS) and analyzed with the Rietveld structure refinement technique.[7] The sample was found to have a distorted orthorhombic 1:1:3 ABO_3 perovskite structure with *Pmmm* space group and lattice constants $a = 3.8231(1)$ Å, $b = 3.8864(1)$ Å, and $c = 11.6807(2)$ Å similar to those proposed by Cava *et al.*[3] Three orthorhombic space groups were modeled: *Pmm2*, *P222*, and *Pmmm*. The structure was initially solved in the acentric space group *Pmm2* using a model consisting of Cu atoms at the positions $[0\ 0\ z]$ ($z \approx 0$, 1/3, and 2/3), an Y atom at $[1/2\ 1/2\ 1/2]$, Ba atoms at $[1/2\ 1/2\ z]$ ($z \approx 1/6$ and 5/6), and O atoms at positions $[0\ 1/2\ z]$ and $[1/2\ 0\ z]$ ($z \approx 0$, 1/3, and 2/3) with a half occupancy for O atoms at $[0\ 0\ z]$ ($z \approx 1/6$ and 5/6) following the reported single-crystal x-ray structure determination of Hazen *et al.*[6] After refinement of this model the resulting atomic positions were found to be consistent with the choice of either *Pmmm* or *P222* space groups (which are degenerate for this model). In addition, high correlations (≈ 1.0) were observed for centrosymmetrically related coordinates and atom temperature factors. Subsequently, refinement of the model was attempted in the other two settings of the space group *Pmm2* with the 2-fold axis along a or b (equivalent to *P2mm* or *Pm2m*). These refinements, which include a larger number of variable parameters, produced agreement factors which were inferior to those for the centric model. The structure was therefore refined in the centrosymmetric space group, *Pmmm*.

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TABLE I. Fractional atomic coordinates and thermal parameters (with standard deviations in parentheses) for $YBa_2Cu_3Y_{7-\delta}$, space group *Pmmm*, $a = 3.8231(1)$ Å, $b = 3.8864(1)$ Å, and $c = 11.6807(2)$ Å.

Atom	X	Y	Z	B_{iso} (Å^2)	Occupancy
Y	1/2	1/2	1/2	0.46(4)	1
Ba	1/2	1/2	0.1843(3)	0.54(5)	2
Cu1	0	0	0	0.50(5)	1
Cu2	0	0	0.3556(1)	0.29(4)	2
O1	0	1/2	0	1.35(5)[a]	0.92(2)
O2	1/2	0	0.3773(2)	0.56(5)	1.89(2)
O3	0	1/2	0.3789(3)	0.37(5)	2
O4	0	0	0.1584(2)	0.67(5)	2

[a]The anisotropic temperature factor for O1 has the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33})$ with $\beta_{11} = 0.0406$, $\beta_{22} = 0.00446$, and $\beta_{33} = 0.00257$.

Initial attempts to refine the thermal parameters produced a very large temperature factor for the O atom at the [1/2 0 0] position ($B_{iso} = 45$ Å^2) and a large negative temperature factor for the O atom at the partially occupied [0 0 0.15] position. Subsequent refinement of populations for these O atoms showed that the site at [1/2 0 0] did not contain *any* oxygen and that the oxygen site at [0 0 0.15] was fully occupied. The refined atomic positional parameters are given in Table I, with the atom numbering scheme as presented in Fig. 1.

Site occupation factors for all oxygen positions were refined individually to test for possible oxygen vacancies. The site occupancies of O1 [0 1/2 0] with a refined population $= 0.92(2)$ and O2 [1/2 0 0.377] with a refined population $= 1.89(2)$ were found to differ significantly from the ideal values. Inclusion of an oxygen atom in the YO plane (at position [0 0 1/2]) was attempted but no evidence for oxygen occupancy at this position was observed. Thus, the refined stoichiometry for this compound is $YBa_2Cu_3O_{6.81}$. This oxygen content is nearly the same as that reported by Cava *et al.*[3] (6.9) determined from hydrogen reduction

(a) d Spacing (Å)
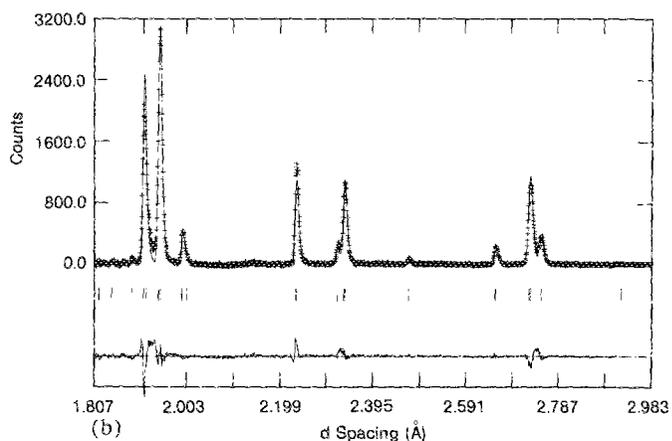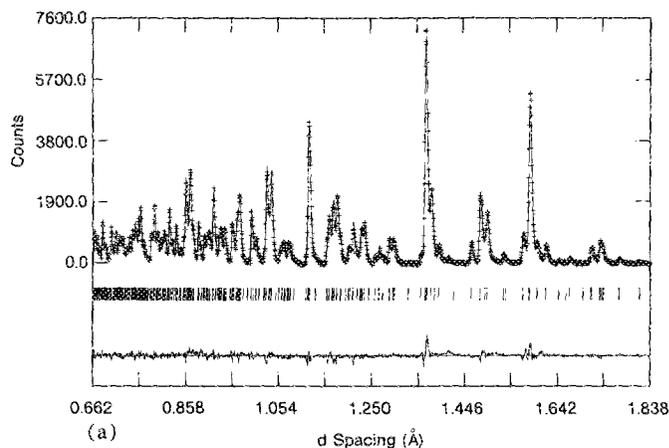

(b) d Spacing (Å)

FIG. 2. Rietveld refinement profile of the neutron powder diffraction data for $YBa_2Cu_3O_{7-\delta}$. The tick marks indicate allowed reflections and the difference plot is shown at the bottom of the figure.
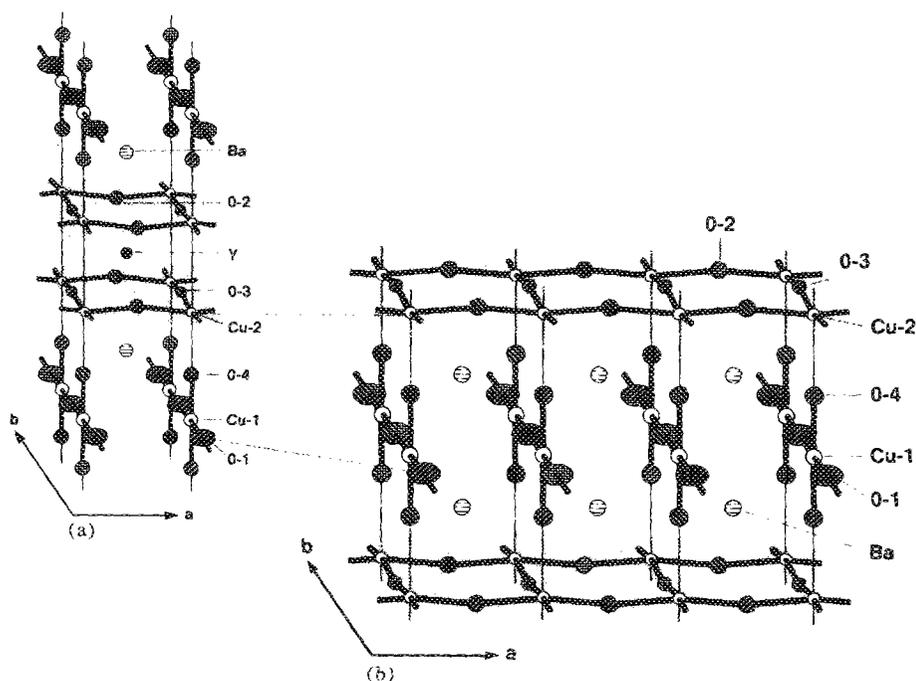

FIG. 1. (a) Orthorhombic structure of $YBa_2Cu_3O_{7-\delta}$. (b) Fencelike coupling of the dimpled CuO_2 layers. Atoms are drawn using 90% equiprobability thermal ellipsoids.

TABLE II. Selected interatomic distances (Å) for $YBa_2Cu_3O_{6.81}$.

Atoms	Dist.	Mult.	Atoms	Dist.	Mult.
Ba-O4	2.743(1)	4	Cu1-O1	1.943	2
Ba-O1	2.879(2)	2	Cu1-O4	1.850(3)	2
Ba-O3	2.970(3)	3	Cu2-O2	1.928(1)	2
Ba-O2	2.977(3)	2	Cu2-O3	1.962(1)	2
Y-O3	2.380(2)	4	Cu2-O4	2.303(3)	1
Y-O2	2.414(2)	4			

measurements. Because of the larger isotropic temperature factor for O1 ($B_{iso} \approx 1.2$ Å^2 as compared to $B_{iso} \approx 0.6$ Å^2 for O2), an anisotropic temperature factor was included in the refinement for O1. The final observed and calculated neutron powder diffraction profile is shown in Fig. 2. Final agreement factors for the refinement were structure factor $R(F^2) = 4.86\%$ and weighted profile $R = 6.29\%$ (expected $R = 3.51\%$)[8] for 27 variable parameters and 567 reflections. Selected distances derived from the final refined structure parameters are given in Table II.

The structure of $YBa_2Cu_3O_{6.81}$ as presented in Fig. 1 is that of a variant 1:1:3 perovskite. The copper-oxygen layers differ markedly from those claimed in the previous single-crystal structure determination.[6] The structure consists of highly nonplanar CuO_2 sheets extending in the crystallographic a-b planes, at $z \approx 0.36$ and $z \approx -0.36$. These two planes are weakly bonded together by fencelike, square planar CuO_3 linear chains which extend along the b axis at $z = 0$. The copper atoms in the $z \approx 0.36$ and $z \approx -0.36$ planes (Cu2) are five-coordinate with the four nearest neighbor oxygen atoms (O2 and O3) forming an almost flat plane displaced 0.266 Å along the c axis and with a more distant oxygen atom (O4) directly below, on the crystallographic c axis. The result of this distorted geometry is a "dimpled" CuO_2 plane as compared to the planar[3-5] and "corrugated"[6] copper-oxygen layers previously reported.

The observed oxygen atom positions and vacancies also result in different coordination for the Ba^{2+} and Y^{3+} cations, consistent with an ordered structure. Both of these cations are ordered in the unit cell as was observed in the previous x-ray diffraction investigation,[6] and as was proposed by other groups.[3,4] The Ba^{2+} coordination sphere consists of ten nearest neighbor oxygen atoms with distances ranging from 2.7 Å for the oxygen atoms in the BaO plane (O4) to 2.9 Å for the oxygen atoms in the CuO_2 planes. The coordination sphere for the smaller and more highly charged Y^{3+} cation contains eight nearest neighbor O atoms at a distance of 2.4 Å. This structure leads to crystallographically distinct sites for the Y and Ba. This explains the observa-

tion[2] that a single composition rather than a solid solution region is observed for this phase.

The structure of this compound indicates that the electronic properties could be highly anisotropic. The basic units of this structure (two dimpled CuO_2 planes coupled by the fencelike CuO_3 chains) are separated by yttrium layers without any oxygen. Thus, no direct Cu-O-Cu bond overlap occurs across this yttrium plane.

Because of the magnitude of the orthorhombic distortion which we observe (a-$b = 0.0633$ Å) it is *very unlikely* that the previous single-crystal x-ray diffraction study[6] is in error. Thus, the choice of a tetragonal crystal system, space group, or model for oxygen vacancies and copper-oxygen plane distortions for the particular samples which Hazen *et al.*[6] examined is probably correct. We postulate that there may be more than one structural phase with the YBa_2Cu_3 metal-ion composition. This structural variation might be driven by oxygen stoichiometry which is determined by the conditions of the synthesis, e.g., excess Ba or Y, oxygen pressure during sintering, and/or the rate of cooling. Clearly, if the a-b planes were fully occupied with O atoms a tetragonal structure could be expected.

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[8]Structure factor $R(F^2) = \Sigma|F_0^2 - F_c^2|$ scale $|/\Sigma|F_0^2|$, weighted profile $R = \Sigma W (Y_{obs} - Y_{calc}$ scale$)^2/\Sigma WY_{obs}^2$, where the summation is over the entire profile and the Y_{obs} values are the measured intensities including background.