## Crystal structure of the high- $T_c$ superconductor Ba<sub>2</sub>YCu<sub>3</sub>O<sub>9- $\delta$ </sub>

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The crystal structure of the high- $T_c$  superconducting phase Ba<sub>2</sub>YCu<sub>3</sub>O<sub>9- $\delta$ </sub> ( $\delta$ =2.0) has been determined by single-crystal x-ray diffraction. The compound crystallizes in an orthorhombic, oxygen-deficient perovskite superstructure with space group *Pmmm*, a=3.856(2) Å, b=3.870(2) Å, and c=11.666(3) Å. The ordering of Ba and Y in a [Ba-Y-Ba] $_{\infty}$  sequence along the c axis is responsible for the tripled cell. Two [CuO<sub>2</sub>] $_{\infty}$  planes with copper in distorted square planar coordination are the key to conductivity.

Recently, several superconductors with  $T_c$ 's above 77 K have been documented. <sup>1-6</sup> These have primarily been R-Ba-Cu-O systems with small rare-earth ions R. The first reports in the Y-Ba-Cu-O system were multiphase.<sup>1-3</sup> The superconducting phase in Y-Ba-Cu-O was subsequently identified as  $Ba_2YCu_3O_{6,9}$ .<sup>4,5</sup> The structure was proposed to be a previously unknown distorted oxygendeficient perovskite. In this report, we present the results of a single-crystal x-ray diffraction study, which support that basic structure and elucidate the positions of the oxygen vacancies. A detailed knowledge of the crystal structure is crucial to interpretation of physical property measurements, theoretical modeling, and the design of other materials. The structure was determined from a small, irregularly shaped single crystal of approximate dimensions  $40 \times 40 \times 40 \ \mu m^3$  obtained from a ceramic sample prepared as previously described.<sup>4</sup> The crystal was found to be orthorhombic with lattice parameters a = 3.856(2) Å, b = 3.870(2) Å, and c = 11.666(3) Å, consistent with values obtained from powder diffraction on samples with bulk superconductivity at 91 K.<sup>4</sup> A full Ewald sphere of x-ray intensities up to  $2\theta = 50^{\circ}$  was collected on a  $\kappa$ -axis diffractometer using Mo  $K\alpha$  radiation, yielding 305 independent reflections. Analysis of the strong reflections immediately confirmed the substructure to be the cubic perovskite cell.

A preliminary refinement of the structure in the triclinic space group P1 indicated the higher-symmetry orthorhombic *Pmmm* (space group No. 47). Lattice constants and atom positions from the refinement are given in Table I, interatomic distances in Table II, and Fig. 1 depicts a unit cell. Refinement of the oxygen occupancy parameters showed fractional occupancy for the O atoms in the z = 0 plane only [O(4) and O(5)]. Values for the occupancy close to 0.5 for both O(4) and O(5) were obtained, giving a  $\delta \approx 2.05(10)$ . We then fixed both occupancy parameters at 0.5, resulting in an ideal oxygen stoichiometry of 7, which is in good agreement with the analyzed value of 6.9 reported earlier. The final residual was  $R_f = \sum |(F_{obs} - F_{calc})| / \sum F_{obs} = 0.058$  with isotropic temperature factors for each individual atom.

The general perovskite formula is  $ABO_3$ . In this compound, the A atoms are Ba and Y and are ordered to give the tripled unit cell. The Cu(1) atoms occupy the corners of the unit cell and the Cu(2) atoms are slightly off the ideal tripled cell positions of  $(0,0,\pm\frac{1}{3})$ . There are five crystallographically independent O sites. The most notable features of the O sites are that all sites in the  $z = \frac{1}{2}$ plane are vacant and that the occupancy of the O(4) and O(5) sites is very close to 0.5. The Ba and Y are ordered and will be discussed in more detail later in the paper. The O atoms form a slightly distorted square net about the Cu(2) atoms, resulting in slightly puckered, twodimensional sheets of [CuO<sub>2</sub>]<sub>∞</sub>. The Cu-O distances in the planes are 1.946(20) and 1.951(20) Å, slightly longer than the in-plane Cu-O distance of 1.889 Å in (Sr,La)<sub>2</sub>CuO<sub>4</sub>.<sup>7</sup> The next-closest O atom is 2.382 Å away. The description of the Cu(1) layers is more com-

Atom	Position	x	у	Ζ	Occupancy	$B_{iso}$ (Å <sup>2</sup> )
Ba	2 <i>t</i>	$\frac{1}{2}$	$\frac{1}{2}$	0.1862(8)	1.0	0.84(5)
Y	1 <i>h</i>	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.0	0.53(5)
Cu(1)	1 <i>a</i>	Ō	0	0	1.0	1.10(8)
Cu(2)	2 <i>q</i>	0	0	0.3572(9)	1.0	0.67(6)
O(1)	2q	0	0	0.153(2)	1.0	1.30(9)
O(2)	2s	$\frac{1}{2}$	0	0.380(2)	1.0	0.40(9)
O(3)	2 <i>r</i>	0	$\frac{1}{2}$	0.379(2)	1.0	1.20(9)
O(4)	1 <i>e</i>	0	$\frac{1}{2}$	0	0.5	2.00(20)
O(5)	1 <i>b</i>	$\frac{1}{2}$	0	0	0.5	2.32(20)

TABLE I. Crystallographic data of Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7</sub> orthorhombic cell: a = 3.856(2), b = 3.870(2), c = 11.666(3) Å. Space group *Pmmm* (No. 47), Z = 1,  $\mu = 284$  cm<sup>-1</sup>,  $d_{calc} = 6.36$  g/cm<sup>3</sup>.

Ba-O(1)	2.759(10)	(4×)
-O(2)	2.976(10)	(2×)
-O(3)	2.962(10)	(2×)
-O(4)	2.909(10)	(2×)
-O(5)	2.904(10)	(2×)
Y-O(2)	2.388(10)	(4×)
-O(3)	2.390(10)	(4×)
Cu(1)-O(1)	1.785(10)	(2×)
-O(4)	1.928(20)	(2×)
-O(5)	1.935(20)	(2×)
Cu(2)-O(1)	2.382(20)	(1×)
-O(2)	1.946(20)	(2×)
-O(3)	1.951(20)	(2×)

TABLE II. Interatomic distances in Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7</sub> (Å).

plex. At first glance it appears to be a distorted octahedral site with two short (1.787 Å) and four long (average 1.931 Å) Cu—O bonds with statistically half of the longer, waist oxygens (in plane) missing. However, if it were a distorted octahedron, four short and two long bonds would be expected. We suggest that about an individual Cu the two vacant sites are ordered such that the coordination is square planar. Rather than forming infinite CuO<sub>2</sub> sheets as in the Cu(2) layers, these square planar units would be perpendicular to those layers with no long-range connectivity or order. It is possible that an additional superstructure may develop, ordering these square planar units.

The A atoms, Ba and Y, are stacked along the c axis in a [Ba-Y-Ba] sequence, and the Ba atoms are slightly shifted towards the centering Y atom. The coordination polyhedra of Ba and Y are quite different. The Ba atoms occupy the familiar truncated cube with ideal coordination number 12. The main deviation from this geometry for the Ba is that four oxygen sites are only 50% occupied, resulting in an average coordination number of 10. In contrast, the Y atom is in the center of a slightly distorted square prism, having a coordination number of 8. This coordination geometry results from complete vacancy of the O-atom sites in the  $z = \frac{1}{2}$  plane. The normal perovskite A site is too large for Y and very few perovskites are known with Y as the A atom. We know of no other defect perovskite for which a contraction to 8 coordination of the A atom occurs. However, a similar reduction in coordination number is observed in the T'-K<sub>2</sub>NiF<sub>4</sub>-type structure with small trivalent ions such as Nd.<sup>8</sup> The Ba-O and Y-O distances found compare well with distances in other compounds such as Y<sub>2</sub>BaCuO<sub>5</sub>,<sup>9</sup> where they vary from 2.50 to 2.98 Å for Ba-O and from 2.22 to 2.44 Å from Y-O, and in the oxygen-deficient



FIG. 1. One unit cell of the Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7</sub> structure.

perovskite  $(Y,La)_3Ba_3Cu_6O_{14}$ ,<sup>10</sup> with 2.79 to 2.87 Å for (Ba,La)-O and 2.57 Å for (La,Y)-O.

Metallic conductivity in cuprates results from partial occupancy of an antibonding band arising from Cu 3d and O 2P orbitals.<sup>11-13</sup> The oxygen absence from the  $z = \frac{1}{2}$  plane is expected to hinder conduction along c, making this a two-dimensional conductor. The Cu(1) plane with half the oxygens vacant is also likely to play a subordinate role in conduction. It appears that the localized moment  $p_{\text{eff}}=0.3 \,\mu_B/\text{Cu}$  atom<sup>4</sup> should be assigned to Cu<sup>2+</sup> in the Cu(1) layer. This assignment results in approximately half of the moment expected for all Cu(1) atoms being Cu<sup>2+</sup> and fully localized. If nonphonon mechanisms of superconductivity are operative, <sup>14-16</sup> the Cu(1) layer and associated oxygen could support excitons or magnons.

In summary, we have determined the crystal structure of the high- $T_c$  superconductor Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7</sub> from singlecrystal x-ray diffraction. The structure shows twodimensional CuO<sub>2</sub> planes and, additionally, the possibility of CuO<sub>2</sub> linear chains. The presence of two-dimensional CuO<sub>2</sub> planes in this compound and also in the K<sub>2</sub>NiF<sub>4</sub>type compounds seems to favor high  $T_c$ 's.

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