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Electron-density Fourier maps of an untwinned $YBa_2Cu_3O_{6.877}$ single crystal by x-ray-diffraction data

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The room-temperature structure of an untwinned orthorhombic $YBa_2Cu_3O_7$ single crystal was determined from x-ray-diffraction intensity data. The crystal was grown by the self-flux method, and detwinned by the application of a uniaxial stress under flowing oxygen at 450 °C. A superconducting transition of 91.3 K ($\Delta T_c = 1.4$ K) was measured. Precession photographs showed no evidence of twinning, and no line splitting or broadening was apparent in high-angle reflections. The crystal structure was refined in the *Pmmm* space group, with **a**=3.8184(3), **b**=3.8857(2), and **c**=11.701(1) Å. The overall oxygen content was determined to be 6.877(8). Electron-density Fourier maps and the anisotropic temperature factors do not support the double-well apical oxygen model proposed from extended x-ray absorption fine structure data. Distortions of the electron density of the planar Cu sites suggest the possibility of a nonhomogeneous CuO_2 conducting plane. The anomalous thermal parameters of the chain oxygens appear to result from dynamic disorder rather than a buckling of the Cu-O chains.

Although a number of different experiments have suggested the presence of a split axial oxygen site in superconducting $YBa_2Cu_3O_7$, there has been no direct evidence of two distinct positions from x-ray- or neutron-diffraction-structural characterizations. Recent Cu *K*-edge polarized extended x-ray absorption fine structure (EXAFS) measurements[1,2] on $YBa_2Cu_3O_7$ have been interpreted to reveal two equally populated axial oxygen sites separated by ≈ 0.13 Å, with the separation distance decreasing slightly near T_c. The two sites have been described by a double-well potential relating the electronic degrees of freedom of the superconducting transition to the elastic degrees of freedom of the ionic motion. These results suggest that the charge transfer from the chain Cu to the planar Cu in superconducting $YBa_2Cu_3O_7$ may occur by an anharmonic electron-phonon coupling mediated through the axial oxygen. Similar EXAFS results have been reported for $TlBa_2Ca_3Cu_4O_{11}$,[3] possibly indicative of a general charge transfer mechanism for high-T_c superconductors. Other experiments that also provide indirect evidence for a split axial oxygen site and/or a lattice instability near T_c include ion-channeling in $ErBa_2Cu_3O_7$,[4] heat-capacity measurements for $YBa_2Cu_3O_7$ and some Tl- and Bi-based materials,[5] and infrared reflectivity[6] and Raman spectroscopy[7] of $YBa_2Cu_3O_7$. Additionally, pair-distribution function (PDF) analysis of neutron-scattering data on $Tl_2Ba_2CaCu_2O_8$ suggests the presence of two axial oxygen sites and local structural changes near T_c.[8,9]

In contradiction to the double-well model derived from EXAFS data, x-ray- and neutron-diffraction results show no anomalous behavior of the axial oxygen site. In terms of Bragg diffraction, split atomic sites and anharmonic motion have a nearly equivalent effect on observed intensities. A split atomic site should be revealed through the root-mean-square displacements of the atoms, the electron density Fourier maps, and possibly through the structural refinement of a double site, but it is easier to detect local atomic displacements from electron density maps than from the anisotropic temperature factors of the refinement. An example of x-ray diffraction revealing split oxygen sites has been reported for copper-deficient $YBa_2Cu_{2.78}O_7$.[10] The presence of two oxygen sites in this compound is independent of the double-well potential model, and is attributed to the $\approx 25\%$ Cu(1) vacancies creating significantly different local environments for the O(1) site. The atomic nomenclature used hereafter is taken from Capponi *et al.*,[11] where O(1) is the apical oxygen, O(4) is the chain oxygen, Cu(1) is the chain copper, and Cu(2) is the planar copper. In cases where there are significant substitutions or vacancies of the copper sites, or the oxygen chain sites are only partially filled, two different Cu(1)-O(1) bond lengths necessarily result from the local coordination environments. To properly investigate the double-well potential model with x-ray diffraction, intensity data should be obtained on a $YBa_2Cu_3O_7$ sample that is uncontaminated and fully oxygenated.

Even though the thermal parameters obtained from a profile analysis of powder-diffraction data may not be

very reliable, earlier investigations reported that only the temperature factors of the O(4) atom appeared to be larger than normal (cf. Refs. 12 and 13). More accurate thermal parameters obtained from the measurement of x-ray-diffraction intensities of untwinned single crystals[14,15] show similar results. In these refinements, the thermal parameters of the axial O(1) are comparable to the other oxygen sites, except for those of O(4). The anomalous O(4) parameters were attributed to a buckling or zig-zag of the Cu(1)-O(4) chains within the **ab** plane, however, the temperature dependences of these parameters imply that the displacement is partly dynamic rather than all static.[14]

In this paper we present the results of a room-temperature x-ray-diffraction structural determination of an untwinned $YBa_2Cu_3O_7$ single crystal. Neither the anisotropic thermal parameters nor the electron density Fourier maps show a distortion of the apical oxygen site that would be expected if the double-well potential model was valid. A large thermal parameter and an elongation of the electron density for the planar copper suggests some distortions are present in the superconducting plane, and electron density maps of the Cu(1)-O(4) chains reveal dynamic disorder within the **ab** plane.

The $YBa_2Cu_3O_7$ crystal investigated in this x-ray-diffraction study was grown by the self-flux method using a platinum crucible. A $1.0\times0.6\times0.02$ mm^3 crystal was annealed under flowing oxygen gas for one week between 400 and 500 °C. The crystal was then placed under a uniaxial stress of 10^2 kg/cm^2, and further annealed in flowing oxygen at 450 °C for 40 h. This procedure produces untwinned crystals, as verified by polarized light microscopy[16] and x-ray precession photographs. In order to help minimize absorption and avoid possible effects of nonuniaxial stress at the crystal corners, a 0.2×0.2 mm^2 section was cut from the center of the larger crystal.

The $0.2\times0.2\times0.02$ mm^3 crystal was mounted on a CAD4 diffractometer equipped with graphite monochromated Ag $K\beta$ radiation ($\lambda=0.49701$ Å). For $YBa_2Cu_3O_7$, Ag $K\beta$ radiation reduces absorption effects by $\approx30\%$ as compared to Ag $K\alpha$ radiation. Centering several high-angle reflections yielded an orthorhombic unit cell of: **a**$=3.8184(3)$, **b**$=3.8857(2)$, and **c**$=11.701(1)$ Å. The whole sphere of reciprocal space was measured up to $\Theta=30°$, and one-eighth of the sphere $(+h,+k,+l)$ was measured for $30<\Theta<50°$. Although 3664 of the 8062 measured reflections were not observed [i.e., $I<\text{sig}(I)$], the *Pmmm* space group was assigned because there were no systematic absences. This assignment is in agreement with previous investigations. An absorption correction was applied based on the crystal size ($\mu=110.69$ cm^{-1}).

The refinement of the observed intensities which were weighted by a factor of $1/\sigma$, was carried out initially assuming a basic "1:2:3" structure as a starting model. F^2 values rather than structure factors were used in the refinement to allow a secondary extinction correction based on individual path lengths. As a result of the difficulty in properly accounting for the severe extinction due to the high quality of the crystal, reflections with $\Theta<10°$ (250) and those requiring an extinction correction greater than 10% (83) were omitted from the final refinements. During these final refinements, the positional and anisotropic thermal parameters of all atoms were varied, as well as the occupancy factor of O(4). The occupancy factors of the other atoms were fixed in the final analysis because previous refinements yielded values that were within one standard deviation of their stoichiometric values. The positional, thermal, and occupancy parameters were put in separate diagonal blocks of the least-squares matrix to minimize correlations. Three final refinements were done: one fixing the positional parameter of O(4), one varying the x positional coordinate of O(4), and a third varying both the x and y positional coordinates of O(4). With the exception of the O(4) parameters, the three refinements were statistically equivalent. The refined values are shown in Table I. The final agreement factors, based on the refinement of 4065 observed reflections are: $wR(I)=3.38\%$ and $\chi^2=2.51$. Selected bond lengths and angles are reported in Table II.

The root-mean-square (rms) displacement values calculated from the anisotropic temperature factors are presented in Table III, showing no anomalous motion of the apical oxygen O(1). In fact, the rms displacement of O(1) in the **c** direction, which should be large if the double-well model is valid, is smaller than the rms dis-

TABLE I. Positional, occupancy, and thermal parameters for $YBa_2Cu_3O_{6.877}$ [$wR(I)=3.48\%$, $\chi^2=2.51$].

At.	Pos.	x	y	z	Occup.	U_{11}	U_{22}	U_{33}
Y	1*h*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.00	0.004 79(5)	0.005 26(5)	0.006 10(6)
Ba	2*t*	$\frac{1}{2}$	$\frac{1}{2}$	0.185 577(7)	1.00	0.008 79(3)	0.007 44(2)	0.008 89(3)
Cu(1)	1*a*	0	0	0	1.00	0.008 18(9)	0.007 51(8)	0.005 54(8)
Cu(2)	2*q*	0	0	0.355 88(1)	1.00	0.004 54(5)	0.004 93(4)	0.009 29(7)
O(1)	2*q*	0	0	0.158 0(1)	1.00	0.012 1(3)	0.013 1(3)	0.008 2(3)
O(2)	2*s*	$\frac{1}{2}$	0	0.378 77(9)	1.00	0.005 1(3)	0.008 2(3)	0.012 5(4)
O(3)	2*r*	0	$\frac{1}{2}$	0.377 92(9)	1.00	0.007 4(3)	0.005 3(3)	0.010 1(3)
O(4)[a]	1*e*	0	$\frac{1}{2}$	0	0.877(8)	0.027(1)	0.010 5(6)	0.013 1(8)
O(4)[b]	2*k*	0.012(2)	$\frac{1}{2}$	0	0.876(8)	0.025(1)	0.010 4(6)	0.013 1(8)
O(4)[c]	4*y*	0.012(3)	0.488(1)	0	0.875(8)	0.025(1)	0.008 3(6)	0.013 1(8)

[a]Final refinement with O(4) position completely fixed.
[b]Final refinement with variable x position of the O(4) site.
[c]Final refinement with variable x and y position of the O(4) site.

TABLE II. Selected bond distances in Å and angles in deg for $YBa_2Cu_3O_{6.877}$.

Cu(1)-O(1)	1.849(1)
Cu(1)-O(4)	1.9428(6)
Cu(2)-O(1)	2.316(1)
Cu(2)-O(2)	1.9279(5)
Cu(2)-O(3)	1.9599(5)
O(1)Cu(1)-O(4)	90.0
O(1)-Cu(1)-O(1)	180.0
O(1)-Cu(2)-O(2)	97.99(2)
O(1)-Cu(2)-O(3)	97.56(2)
O(2)-Cu(2)-O(2)	164.03(2)
O(2)-Cu(2)-O(3)	88.95(2)
O(3)-Cu(2)-O(3)	164.88(2)
Y-O(2)	2.4056(8)
Y-O(3)	2.3844(8)
Ba-O(1)	2.7430(5)
Ba-O(2)	2.9807(9)
Ba-O(3)	2.9513(9)
Ba-O(4)	2.891(1)

placements in the **ab** plane, and similar to those of O(2) and O(3). Assuming a conservative average rms displacement of 0.08 Å for an oxygen atom, an observed rms displacement for O(1) consistent with the EXAFS data would have to be ≈ 0.15 Å. The large rms displacement of O(4) in the **a** direction is related to the disorder of the Cu(1)-O(4) chains, which will be discussed later. For the cations, the **c** direction thermal parameter/rms displacement of planar Cu(2) is larger than expected, while the corresponding parameter for Cu(1) is slightly smaller than average.

A refined occupancy of 0.877 for the O(4) site is consistent with the physical properties of the crystal. The untwinned $YBa_2Cu_3O_{6.877}$ crystal exhibits a superconducting transition beginning at 91.3 K, with a width of $\Delta T_c = 1.4$ K. In comparison, Claus *et al.*[17] report a maximum T_c of ≈ 91 K for $YBa_2Cu_3O_{6+x}$ with $x \approx 0.88$,

TABLE III. Root-mean-square displacement values in Å for atoms in $YBa_2Cu_3O_{6.877}$.

	u_{11}	u_{22}	u_{33}
Y	0.07(1)	0.07(1)	0.08(1)
Ba	0.09(1)	0.09(1)	0.09(1)
Cu(1)	0.09(1)	0.09(1)	0.07(1)
Cu(2)	0.07(1)	0.07(1)	0.10(1)
O(1)	0.11(2)	0.11(2)	0.09(2)
O(2)	0.07(2)	0.09(2)	0.11(2)
O(3)	0.09(2)	0.07(2)	0.10(2)
O(4)[a]	0.16(3)	0.10(2)	0.11(3)
O(4)[b]	0.16(3)	0.10(2)	0.11(3)
O(4)[c]	0.16(3)	0.09(2)	0.11(3)

[a]Final refinement with O(4) position completely fixed.
[b]Final refinement with variable x position of the O(4) site.
[c]Final refinement with variable x and y position of the O(4) site.

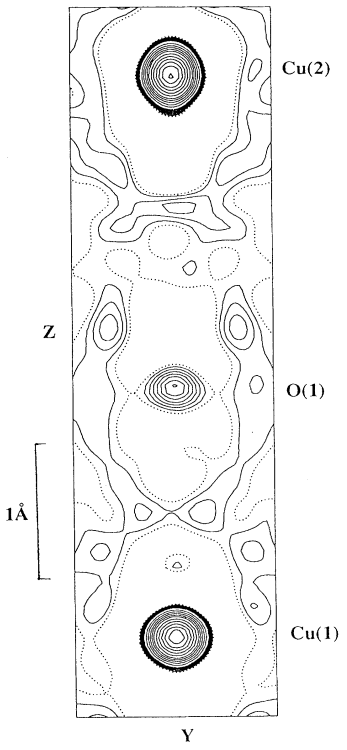

FIG. 1. Electron-density section at $x=0$ for $-0.18 \le y \le 0.18$ and $-0.05 \le z \le 0.40$. The electron density of the planar Cu(1) site appears distorted, whereas that of the apical oxygen does not.

and a decrease in T_c of up to 2 K for higher oxygen concentrations. Also, phase separations have been suggested for higher oxygen concentrations, as evidenced by a broadening of the superconducting transition and a splitting of x-ray-diffraction lines.[18,19] The normal-state resistivity of this crystal is among the lowest reported in the literature, and polarized optical reflectivity experiments further reveal its high quality.[16] The lack of splitting or line broadening in scans of high-angle $(h00)$, $(0k0)$, and $(00l)$ reflections provides additional evidence that the crystal is monodomain and single phase.

The 4064 reflections used in the final refinements were averaged with *Pmmm* symmetry to yield 1379 independent reflections whose intensities were used as input data for the calculation of electron-density Fourier maps. The reliability factor of the symmetry averaging was 0.016. Figure 1 shows the Cu(1)-O(1)-Cu(2) bonds in the Fourier

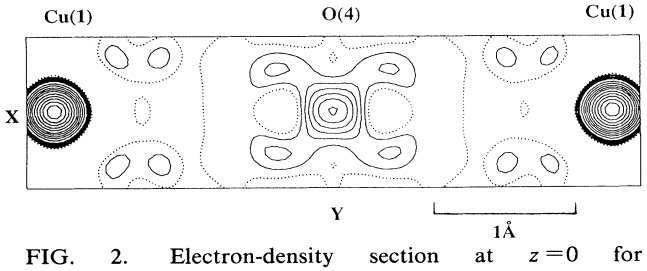

FIG. 2. Electron-density section at $z=0$ for $-0.15 \le x \le 0.15$ and $-0.05 \le y \le 1.05$. The symmetrical distortion of the O(4) electron-density suggests that the disorder is largely dynamic.

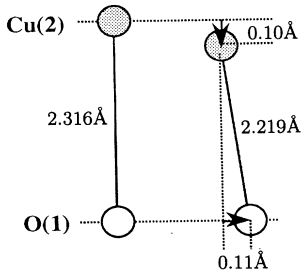

FIG. 3. Schematic of the Cu(2)-O(1) bond distances assuming a modulation of the copper sites in the CuO_2 plane as proposed by Bianconi (Ref. 20). The bond lengths and rms displacements are based on the refinement of $YBa_2Cu_3O_{6.877}$.

section at $x=0.0$ for $-0.18 \leq y \leq 0.18$ and $-0.05 \leq z \leq 0.40$. The well-defined electron density of the apical oxygen further refutes the possibility of a split O(1) site. On the other hand, as was also evident from the thermal parameters, the planar Cu(2) site is distorted in the c direction. Fourier sections of the **ab** plane show no planar distortion of Cu(2). The distortion of the electron density around the planar copper site might be attributed to thermal disorder, static displacement, or to a contribution of the Cu $3d_z^2$ orbital. Additional low-temperature diffraction experiments are currently in progress to track the behavior of the thermal parameters on cooling, which will allow a distinction between thermal vibrations and static displacements.

The electron-density map of the Cu(1)-O(4) chains is presented in Fig. 2, which shows the Fourier section at $z=0.0$ for $-0.15 \leq x \leq 0.15$ and $-0.05 \leq y \leq 1.05$. In agreement with the observations of Simon *et al.*,[14] the cloverleaf electron-density distortion centered about the symmetry site appears to be more indicative of dynamic disorder than a split oxygen site. Attempts to refine the x and y positional coordinates of O(4) by including split planar sites did not improve the goodness of fit of the refinement. The degree of static or dynamic displacement of O(4) may be significantly affected by the occupancy of the site. In our sample, vacancies in approximately $\frac{1}{8}$ of the O(4) sites may reduce strain that could cause the chains to buckle in $YBa_2Cu_3O_7$ samples with higher oxygen concentrations.

The precise electron density maps calculated from the Bragg intensities of untwinned $YBa_2Cu_3O_{6.877}$ do not support a double-well potential model for the apical oxygen. However, the distortion observed for the planar copper site may be consistent with a nonhomogeneous CuO_2 plane suggested by Bianconi.[20] EXAFS and XANES results on Bi 2:2:1:2 high-T_c superconductors have been interpreted by Bianconi *et al.*[21] to show one long and one short Cu(2)-O(1) bond, but instead of the split oxygen site of the double-well model, they propose a modulated buckling and dimpling of the conducting plane. In this model,[20] the normal Cu(2)-O(1) bond distance is compressed by the displacement of Cu(2) towards O(1), which itself moves in the **ab** plane to relieve some of the stress [the proximity of Cu(1) prevents any movement of O(1) in the c direction]. A schematic based on this model using the root-mean-square displacements determined for $YBa_2Cu_3O_{6.877}$ at room temperature is presented in Fig. 3, showing two Cu(2)-O(1) bond lengths that differ by ≈ 0.1 Å. Further x-ray-diffraction experiments at low temperatures are necessary to determine the relevancy of this type of model.

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