RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 6 1 FEBRUARY 1993-II

Evidence by x-ray diffraction for two apical oxygen sites in a copper-deficient $YBa_2Cu_{2.78}O_7$ crystal

P. Bordet, C. Chaillout, and T. Fournier
Laboratoire de Cristallographie, CNRS-UJF, Boîte Postale 166, 38042 Grenoble CEDEX 09, France

M. Marezio
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
and Laboratoire de Cristallographie, CNRS-UJF, Boîte Postale 166, 38042 Grenoble CEDEX 09, France

E. Kaldis, J. Karpinski, and E. Jilek
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich–Hönggerberg/HPF, 8093 Zürich, Switzerland

(Received 29 June 1992)

To show that single-crystal x-ray-diffraction data can reveal the presence of two apical oxygen sites in $YBa_2Cu_3O_7$-based samples, the structure of a copper-deficient 1:2:3 sample, $YBa_2Cu_{2.78}O_7$, has been determined. Small crystals were grown under high oxygen pressure. Gandolfi and precession techniques showed that the symmetry is tetragonal with parameters: $a = 3.8764(4)$ Å and $c = 11.625(1)$ Å. High-order reflection scans, carried out during the single-crystal intensity-data collection, revealed that some of these reflections were broadened indicating that the crystal was twinned and consequently of lower symmetry than tetragonal. Except for the Cu vacancies the structure of $YBa_2Cu_{2.78}O_7$ is similar to that of the 1:2:3 compound. All the vacancies were found to be on chain Cu(1) sites. This means that every either fourth or fifth Cu(1) site is empty and there exist two apical O(1) sites and two Cu(2)-O(1) distances. No long-range superstructure was detected either by x-ray diffraction or electron diffraction. The two O(1)-site feature is revealed qualitatively by the large thermal motion of O(1) along the c axis and quantitatively by electron density maps. The relationship between this structure and the double-well model deduced by EXAFS data for the apical oxygen is discussed.

By analyzing the Cu K-edge polarized EXAFS of $YBa_2Cu_3O_7$ samples between 10 and 105 K, Munstre de Leon *et al.*[1] showed that the best fit is obtained when the apical O(1) atoms are distributed over two sites separated by 0.13 Å. The atom nomenclature is that of Ref. 2, namely O(1) refers to the apical oxygen while O(4) refers to the chain oxygen. The two O(1) sites which result from a double-well potential are near-equally populated. The charge transfer from the chain Cu to the planar Cu would take place through this double potential well via an anharmonic motion. The site separation decreases by 0.02 Å around T_c and the corresponding structural perturbation is accompanied by a large increase of the tunneling frequency (about 80 K) between the two wells. Corroborating results have been obtained by the same authors for other 1:2:3-related samples, such as $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_{2.8}Co_{0.2}O_{7+\delta}$,[3] in which the double-well feature was deduced from the same type of measurements. It must be pointed out, though, that in the former compound two Cu(1)-O(1) distances exist in the structure independently of the double-well feature. The EXAFS measurements cannot distinguish whether the two distances are due to the split O(1) sites or to two independent Cu(1) sites resulting from different local environment. In fact, half of the Cu(1) sites is two-coordinated while the other half is four-coordinated and the two Cu(1)-O(1) distances are quite different. The question, thus, is whether the observed two distances are static or dynamic in nature. More recently, the split apical oxygen site has been observed in $TlBa_2Ca_3Cu_4O_{11}$ by Cu K-edge polarized EXAFS.[4] This is an important result by itself because it would imply that the charge transfer in the Tl-based compound would have the same origin as that occurring in $YBa_2Cu_3O_7$.

As pointed out by Allen *et al.*[4], the double-well model for the high-T_c copper-based oxide superconductors is supported by several other experiments, such as ion channeling, heat capacity, infrared reflectivity, and Raman spectroscopy. All these experiments gave evidence for the existence of lattice instabilities around T_c, related directly or indirectly to the Cu(1) and O(1) ions. However, no evidence for the O(1) split site has ever been given by any x-ray- or neutron-diffraction experiment.

The structure of $YBa_2Cu_3O_7$ has been determined by more than ten different groups. To avoid the errors due to severe twinning, the majority used the powder technique. Moreover, they coupled this technique with neutron diffraction because the neutron scattering powers of three metals and the oxygen are comparable. For x-ray diffraction at $\sin\theta/\lambda \neq 0$ the scattering power of barium is more than seven times that of oxygen. In every case the refinements were carried out by the total profile analysis or Rietveld method. If the interpretation of the Los Alamos group for an anharmonic motion of the O(1) apical atom between the split site resulting from the double well is correct, the x-ray- or neutron-diffraction effects should contain the corresponding information. The refinements should then yield anomalously large temperature factors for O(1).

After the publication of three structural determinations, based on powder-neutron-diffraction data, Cox *et al.*[5] reported their own refinement and made a comparison of the four results. They concluded that only the temperature factor of the O(4) atom, the mobile oxygen which goes in and out of the CuO chains in the structure, was larger than expected. More refinements were carried out later and all of them agreed on the large "temperature factor" for O(4). This feature was interpreted as due to a static displacement of this atom causing a zigzag of the Cu(1)-O(4) chains.[6] It is true that the temperature factors determined by the profile analysis are not very reliable and surely not good enough to reveal anharmonic motions. The temperature factors obtained from refinements based on intensities measured by either x-ray or neutron single-crystal diffractometers would be much more reliable.

Two structural refinements of superconducting $YBa_2Cu_3O_{7-\delta}$ crystals, based on single-crystal x-ray-diffraction data, were reported by Calestani and Rizzoli[7] and by Simon *et al.*[8] In both cases untwinned crystals were used. The latter authors carried out the structure determination at room temperature and at 103 K. They were able to obtain anisotropic temperature factors for all oxygen atoms. The apical O(1) atom exhibited a small anisotropy, but the shortest axis was found to be along the *c* axis and the double-well potential is supposed to be located along this axis The value of U_{33} for O(1) is very similar to the shortest axes of O(2), O(3), and O(4). Simon *et al.* confirmed that the thermal motion of the O(4) atoms was indeed large and anisotropic. However, from the way the temperature factors vary with temperature they deduced that the magnitude and the anisotropy are only partially due to a static displacement. A sizable amount should be thermal in origin.

As shown originally by Willis,[9] a model based on a split site or on an anharmonic motion influences the Bragg intensities in a similar way. This problem has been recently reassessed by Kuhs.[10] On the other hand, local atomic displacements, either static or due to anharmonic motion, are more easily shown by carrying out electron density maps than by the temperature factors obtained from a least-squares refinement.

In this paper we report the structural determination of a copper-deficient $YBa_2Cu_3O_7$ compound. Since the vacancies exist only on the square Cu sites, there are two O(1) positions, one corresponding to the full Cu(1) site and one to the empty one. Either the electron density map or the anisotropic temperature factors reveal very clearly the presence of the two O(1) sites.

During a systematic investigation of the phase diagram of the Y-Ba-Cu-O system at high oxygen pressures Kaldis and his collaborators[11] had the first sign for the existence of a phase slightly different from that of the normal "1:2:3" compound. As shown by the powder pattern, determined by using a Guinier camera (Cu $K\alpha$) and a Si standard, this new phase was tetragonal with lattice parameters similar to those of normal "1:2:3" compound, but with the *c* axis somewhat shorter.[12]

Single plateletlike crystals of this new phase with dimensions ($0.1\times0.1\times0.02$ mm^3) were grown by the high-pressure technique.[11] About thirty different crystals from the same batch were characterized by x-ray precession and Gandolfi methods. All of them were found to be tetragonal with *c* axis ranging from 11.70 to 11.62 Å, the latter value being quite short when compared to that of the normal "1:2:3" compound (11.72 Å). It was estimated that about 30%, 60%, and 10% of the crystals had the *c* axis equal to 11.70 Å, 11.65 Å, and 11.62 Å, respectively. ac susceptibility measurements were performed on these crystals, and three of them having the shortest *c* axis displayed a paramagnetic to diamagnetic transition at ≈ 120 K. The other crystals showed transitions ranging between 10 and 90 K or no transition at all. It should be pointed out that all ceramic samples did not show any transition in the ac susceptibility vs temperature curves. The data concerning these new tetragonal samples are discussed in Ref. 12.

A single crystal exhibiting the transition at 120 K was analyzed by precession and Gandolfi techniques confirming the tetragonal symmetry. The cell parameters as determined by the latter technique were: $a=3.8764(4)$ Å and $c=11.624(1)$ Å. No systematic absences were observed among the reflections, which led to $P4/mmm$ space group. The same crystal was mounted on a CAD4 diffractometer equipped with graphite monochromated Ag $K\alpha$ radiation. The 6250 reflections included within the whole sphere of reciprocal space up to $\theta=35°$ were measured by the ω-scan technique. Scans around high-angle ($h00$) and ($0k0$) reflections revealed very weak splitting or line broadening, which probably indicates the presence of twinning with very small obliquity ($<0.02°$). After absorption correction, the reflection averaging in the $4/mmm$ point group led to 427 independent reflections with an agreement factor among equivalent reflections of 5.3%. This relatively high value could be due to twinning which leads to the wrong choice of crystal symmetry.

As the Patterson maps were similar to those obtained with the normal "1:2:3" compound, the refinements were carried out assuming the structure of "1:2:3" as the starting model. A secondary extinction correction was applied.[13] During the final refinements the positional and anisotropic thermal parameters of all atoms and the occupancy factors of Cu(1), O(1), and O(4) were varied. Attempts to vary the occupancy factors of the other cations yielded values which were within less than one standard deviation from their stoichiometric values. During the subsequent refinements they were kept constant. To minimize correlations, the positional, thermal, and occupancy parameters were put in separate diagonal blocks of the least-square matrix. The final results are shown in Table I. They correspond to the agreement factors $R=4.7\%$, $wR=4.0\%$, and $\chi^2=1.15$.

The low occupancy of the Cu(1) site could be partly due to the incorporation of Al. The samples are prepared in Al crucibles and a semiquantitative energy dispersive x-ray microanalysis did show a small peak due to Al. However, the departure from full occupancy of about 30 times the standard deviation cannot be entirely explained by this impurity. One would need 40% of Al to explain

TABLE I. Positional, occupancy, and thermal parameters for $YBa_2Cu_{2.79}O_7$.

At.	Pos.	x	y	z	Occup.	U_{11}	U_{22}	U_{33}
Y	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.00	0.0046(2)		0.0085(3)
Ba	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.18937(5)	1.00	0.0147(2)		0.0114(2)
Cu(1)	1a	0	0	0	0.787(7)	0.0235(9)		0.0081(9)
Cu(2)	2g	0	0	0.3602(1)	1.00	0.0041(3)		0.0104(4)
O(1)	2g	0	0	0.143(1)	0.96(3)	0.041(6)		0.09(1)
O(2)	4i	$\frac{1}{2}$	0	0.3763(3)	1.00	0.006(1)	0.011(2)	0.011(2)
O(4)	2f	$\frac{1}{2}$	0	0	0.54(2)	0.30(8)	0.28(7)	0.015(7)

the low occupancy. The small peak observed by microanalysis would correspond to less than 10%. In the worst case the occupancy of site 1 would be $[Cu_{0.73}Al_{0.10}V_{0.17}]$, instead of $[Cu_{0.78}V_{0.22}]$ and, therefore, there should be three positions for the apical O(1) atoms. However, the presence of Al is not relevant to the point we would like to make about the split O(1) site. If the impurity is not taken into account, the single-crystal x-ray analysis showed that the chemical formula is very close to $YBa_2Cu_{2.78}O_7$ with the Cu vacancies located on the Cu(1) sites. Qualitatively it can be assumed that every fifth Cu(1) cation is missing. The two O(1) around a vacancy become underbonded as each of them loses about 0.6 valence units. To compensate for this loss of charge, these two O(1) atoms move closer to the respective Cu(2).

The occupancy factors of O(1) and O(4) correspond to full and half-full sites within one or two standard deviations, respectively. The 0.5 occupancy factor for O(4) corresponds to a global O_7 stoichiometry. The very large U_{33} parameter of O(1), corresponding to a root-mean-square displacement value of ≈ 0.3 Å, indicates that O(1) is highly disordered along the c axis. The large thermal factors in the basal plane for O(4) are probably related to this disorder. The square chains are present in the basal plane and the apparent symmetry is tetragonal. These chains must then be disordered along the a and the b axes and are so short that the local orthorhombicity is not detected by x-ray diffraction. The domain size can be estimated to be smaller than a few hundred angstroms. The pseudotetragonality can also be induced by the small amounts of impurities. For example, "1:2:3" samples prepared in alumina crucibles exhibit a tetragonal symmetry which is due to the incorporation of Al on the Cu(1) sites.[14]

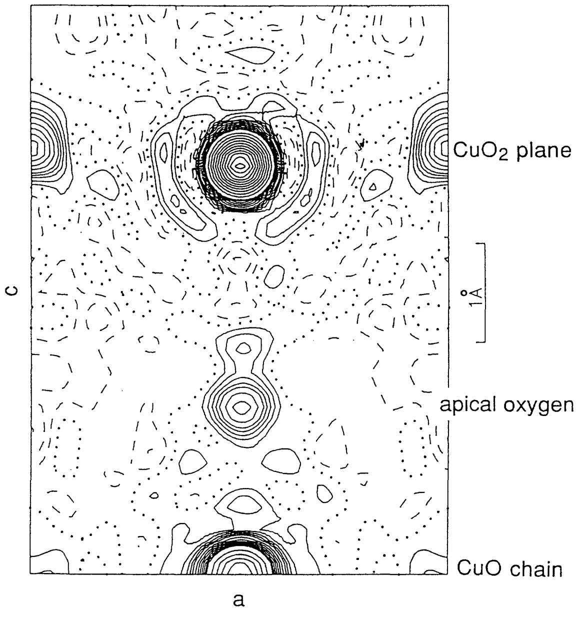

FIG. 1. Electron density section at $y=0$ for $-0.5 \leq x \leq 0.5$ and $0 \leq z \leq 0.5$. The O(1) site is split into two peaks, the nearest to the CuO_2 plane or to the CuO chain corresponds to the location of O(1) when the Cu(1) site is vacant or occupied, respectively.

Superconducting tegragonal crystals have been reported by Simonov *et al.*[15] Their samples corresponded to the chemical formula $YBa_2Cu_{2.86}O_{6.62}$ in which the Cu vacancies are located at the twin walls on the Cu(1) sites. As in our case, the orthorhombic domains are too small to be detectable by diffraction techniques. These samples were found to become superconducting at 50 K.

We calculated the electron density Fourier map with the observed structure factors as input data; Fig. 1 shows the section at $y=0$ for $-0.5 \leq x \leq 0.5$ and $0 \leq z \leq 0.5$. Two sites for O(1) are clearly visible. The distance between the two asymmetric peaks around the O(1) position is ≈ 0.55 Å. The intensity of the smaller of these two peaks is about 26% of the total. This position is occupied when the Cu(1) site is empty. Therefore, the intensity distribution between the two asymmetric peaks is in good agreement with the value of the occupancy parameter yielded by the refinement for Cu(1). The distance between Cu(2) and the smaller of the two peaks is ≈ 1.9 Å. Attempts to refine split O(1) and/or O(4) sites led to unreasonable positional parameters for these sites and no improvement of the agreement factors was obtained. This seems to indicate that the static displacements are disordered and/or uncorrelated. Preliminary electron-diffraction studies confirmed this result in that they did not show the presence of any superstructure spots indicating short-range ordering.

Table II gives the root-mean-square displacement values for the oxygen atoms; the corresponding values for $YBa_2Cu_3O_{6.93}$, calculated from the temperature factors reported by Simon *et al.*,[8] are also given. It can be seen that the values of the $\bar{u}$'s for O(1) in the Cu-deficient sample are definitely larger than the normal values, whereas the value of $\bar{u}_{33}$ for O(1) in the $YBa_2Cu_3O_{6.93}$ sample is quite normal.

If we use Bragg diffraction techniques we have three probes for testing the presence of static or dynamic atomic disorder: the values of the rms displacements, the electron density maps, and the structural refinements including split sites. The latter is carried out only if one of the first two tests indicates a possible disorder. The first two probes show that atomic disorder is present in the structure of $YBa_2Cu_{2.78}O_7$, while the third test is negative. On the other hand, the temperature factors of O(1) in the 1:2:3 sample reported in Ref. 8 do not indicate any disorder, however, the electron density maps were not calculated. Furthermore, it must be pointed out that the splitting reported by Munstre de Leon *et al.*[1] is much smaller than that found in $YBa_2Cu_{2.78}O_7$ (0.13 Å as against 0.55 Å).

In this context, it is worthwhile to point out that situations similar to the one presented here have already been encountered in other systems. For example, Pontonnier *et al.*,[16] while studying the structure of the ionic conductors $Na_{0.5-x}Y_{0.5+x}F_{2+2x}$, found that some of the fluorine atoms were either displaced from the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ position, or exhibited anharmonic motion. They obtained a better refinement when the two-F-site model was taken into account. Some of the F atoms were found to be displaced by 0.21 Å along the ⟨111⟩ directions. For this compound the three probes yield positive tests, but as stated in their article Pontonnier *et al.* found out about the disorder in one of the F sublattices from the electron density Fourier maps in which the peaks of some specific fluorine atoms were always elongated along the ⟨111⟩ directions.

TABLE II. Root-mean-square displacement values (Å) for the oxygen atoms [O(1): apical, O(2) and O(3): in-plane, O(4): chain].

	$YBa_2Cu_3O_{6.93}$ (orthorhombic)				$YBa_2Cu_{2.79}O_7$ (tetragonal[a])		
	O(1)	O(2)	O(3)	O(4)	O(1)	O(2)	O(4)
$\bar{u}_{11}$	0.12	0.07	0.10	0.16	0.2	0.08	0.5
$\bar{u}_{22}$	0.11	0.09	0.07	0.08		0.10	0.5
$\bar{u}_{33}$	0.08	0.11	0.10	0.13	0.3	0.12	0.12

[a] In the tetragonal symmetry O(2) and O(3) are equivalent.

In conclusion, we believe that in order to prove or disprove the double-well model for $YBa_2Cu_3O_7$, one should carry out precise electron density map calculations, based on x-ray Bragg intensities collected with untwinned crystals.

The authors would like to thank B. Batlogg and H. Takagi for their critical reading of the manuscript.

---

[1] J. Mustre de Leon, S. D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. B **65**, 1675 (1990).

[2] J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Europhys. Lett. **3**, 1301 (1987).

[3] J. Mustre de Leon, S. D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. Lett. **44**, 2422 (1991).

[4] P. G. Allen, J. Mustre de Leon, S. D. Conradson, and A. R. Bishop, Phys. Rev. B **44**, 9480 (1991).

[5] D. E. Cox, A. R. Moodenbaugh, J. J. Hurst, and R. H. Jones, J. Phys. Chem. Solids **49**, 47 (1987).

[6] M. François, A. Junod, K. Yvon, P. Fischer, J. J. Capponi, P. Strobel, M. Marezio, and A. W. Hewat, Solid State Commun. **66**, 1117 (1988).

[7] G. Calestani and Rizzoli, Nature **328**, 606 (1987).

[8] A. Simon, J. Köhler, H. Borrmann, B. Gegenheimer, and R. Kremer, J. Solid State Chem. **77**, 200 (1988).

[9] B. T. W. Willis, Acta Crystallogr. **18**, 75 (1965).

[10] W. F. Kuhs, Acta Crystallogr. Sec. A **48**, 80 (1992).

[11] J. Karpinski, J. Heeli, E. Kaldis, A. Wisard, and E. Jilek, Physica C **153**, 830 (1988).

[12] E. Kaldis, J. Karpinski, S. Rusiecki, B. Bucher, K. Conder, and E. Jilek, Physica C **185-189**, 190 (1991).

[13] P. J. Becker and P. Coppens, Acta Crystallogr. Sec. A **30**, 129 (1974).

[14] J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, and G. W. Hull, Phys. Rev. B **37**, 7458 (1988).

[15] V. Simonov, L. Muradyan, V. Molchanov, E. Kovyev, and R. Shibaeva, Kristallografiya **33**, 621 (1988); Z. Kristallogr. **185**, 430 (1988).

[16] L. Pontonnier, G. Patrat, S. Aléonard J. J. Capponi, M. Brunel, and F. de Bergevin, Solid State Ionics **9-10**, 549 (1983).