Oxygen ordering in the crystal structure of the 93-K superconductor $YBa_2Cu_3O_7$ using powder neutron diffraction at 298 and 79.5 K

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The crystal structure of the 93-K superconductor $YBa_2Cu_3O_7$ has been elucidated from neutron powder diffraction data at 298 and 79.5 K. We confirm the basic features of the perovskite-related structure found at room temperature from earlier x-ray diffraction studies of small single crystals and find, additionally, that ordering of one of the oxygen atoms gives rise to square planar coordination for one of the copper atoms rather than disordered octahedral coordination. Within the resolution of our data there is no apparent change in structure below T_c.

INTRODUCTION

Recently, the perovskite-related oxide $YBa_2Cu_3O_7$ has been shown to be superconducting with a critical temperature of about 93 K.[1-3] A number of crystal-structure determinations have been reported using single-crystal x-ray diffraction data obtained from very small crystals.[1,4,5] These determinations have generally been done in quasi-tetragonal symmetry $P4/mmm$ instead of the orthorhombic symmetry indicated by the cell constants. We refined the structure from powder neutron diffraction data in $Pmmm$ both at 298 and at 79.5 K. Neutron powder data are far more sensitive to the positions and occupancies of oxygen atoms than x-ray data.

EXPERIMENT

A 7-g sample of $YBa_2Cu_3O_7$ was prepared by firing Y_2O_3, $BaCO_3$, and CuO in a three-step procedure. First, the well-mixed, finely ground starting materials were fired at 900 °C in a platinum crucible in air for 8 h. The material, which was green black, was then reground, pressed into pellet form and refired at 1 atm of O_2 at 925 °C for 10 h. Upon repeating this procedure, the sample was cooled to 400 °C over 3 h and removed from the furnace. The sample was now grey black and appeared to be single phase by powder x-ray diffraction with orthorhombic cell constants $a = 3.816(2)$ Å, $b = 3.892(2)$ Å, $c = 11.682(9)$ Å, in good agreement with previous single-crystal and powder x-ray results.[1,3] An attempt was made to measure the oxygen content by reducing the sample in H_2 at temperatures up to 1025 °C using a Netzsch STA 409 thermal gravimetric analysis apparatus. By following weight change as a function of temperature and time, it appeared that the weight loss was complete at 1025 °C over 2 h. Examination of the product showed that the phases present were mixed oxides of Y, Ba, and Cu metal. The weight loss was 8.40(8)%. This is consistent with overall composition $YBa_2Cu_3O_{7.0 \pm 0.1}$.

Neutron powder data were obtained at the McMaster Nuclear Reactor using 1.3935-Å neutrons obtained from a [200] copper monochromator. Data were collected using a position-sensitive detector (PSD) which is essentially the same as that in use at the Missouri University Research Reactor (MURR) which has been described previously.[6] Soller-type collimators are not currently used but an oscillating-rotating collimator (ORC) is in place between the sample and the PSD to reduce background levels.[6] The resolution of the above system is similar to that of MURR but full width at half maximum (FWHM) values for standard materials are about 20–25% greater in the same 2θ range for samples of similar diameter. At the present sample-to-detector distance of 1060 mm and the operating wavelength, useful data are collected over a 25° 2θ range for a single detector setting. Thus, a typical data set requires collection of four to five such frames.

The raw data are then corrected for the detector geometry and refined according to the procedures of Ref. 6. Refinement is carried out with a version of the Rietveld profile refinement program.[7]

The 298-K data set was obtained using a thin-walled vanadium can. The 79.5-K data were taken with the sample in a thin-walled aluminum can filled with He and sealed with an indium gasket.

Magnetic susceptibility measurements were made using a Princeton Applied Research vibrating-sample magnetometer.

RESULTS AND DISCUSSION

The magnetic susceptibility of this material is shown in Fig. 1. T_c can be identified with the onset of diamagnetism at 93 K. From the magnitude of the diamagnetic susceptibility, the fraction of the sample which is superconducting is very nearly 1.0.

The initial refinement of the neutron data was begun in space group $Pmmm$ (No. 47). Trial positions for Y, Cu, Ba, and O atoms were taken from the results of LePage
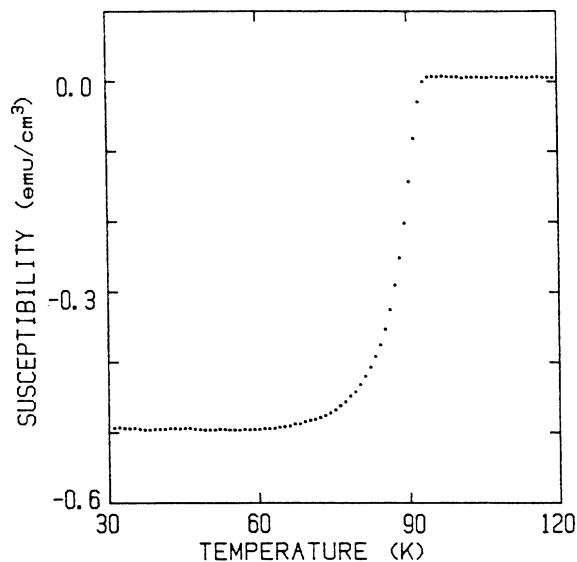
FIG. 1. Magnetic susceptibility as a function of temperature for $YBa_2Cu_3O_7$. The sample was cooled from room temperature in a field of 0.030 T.

FIG. 2. The observed $(+)$, calculated $(-)$, and difference profiles for $YBa_2Cu_3O_7$ at 298 K. Only two data "frames" are shown to illustrate the quality of the fit. Five frames, to 115° (2θ), were used to obtain the results of Table I.

et al.[1] after reduction from $P4/mmm$ and a change of origin by $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Apart from the use of quasitetragonal symmetry the major question remaining from the x-ray results concerns the location and occupancy fraction of the O atoms which nominally occupy the same layer as Cu(1), $z=0$ for the setting of Ref. 1 and $z=\frac{1}{2}$ for our setting. In $P4/mmm$, these atoms must occupy a twofold position and since there are at most one of these atoms,
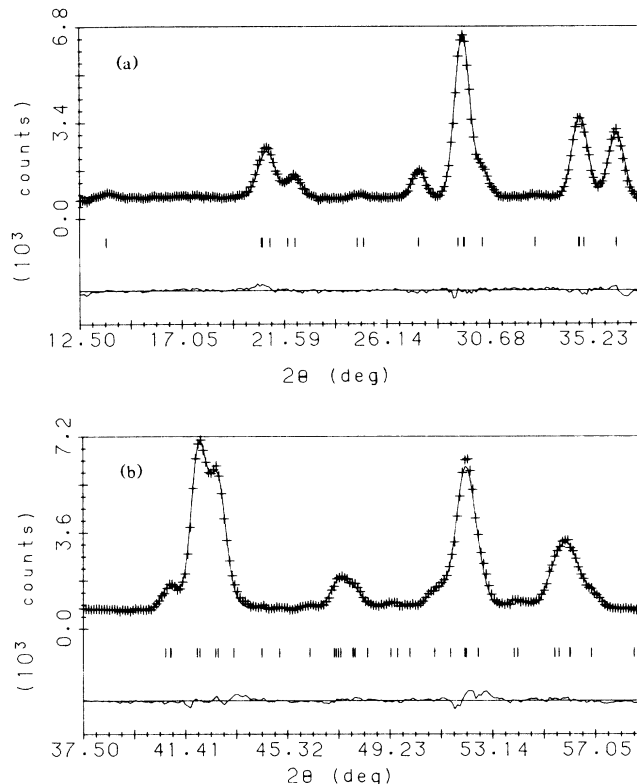
TABLE I. Atomic positions, isotropic temperature factors, and agreement indices for $YBa_2Cu_3O_{7.0}$[a] at 298 K in *Pmmm*. Numbers enclosed in square brackets were obtained at 79.5 K. Definitions of the agreement indices: Weight profile $R = (\sum_w |Y_{obs} - Y_{calc}X_{scale}|^2/\sum_w |Y_{obs}|^2)^{1/2}$. Profile $R = (\sum |Y_{obs} - Y_{calc}X_{scale}|^2/\sum |Y_{obs}|^2)^{1/2}$. Nuclear $R = \sum |I_{obs} - I_{calc}|/I_{obs}$. Expected $R = $ [degrees of freedom/ $\sum_w (|Y_{obs}|)^2]^{1/2}$. Degrees of freedom $=$ (number of profile points) $-$ (number of parameters).

	x	y	z	B (Å^2)
Y ($1a$)	0	0	0	0.60(9) [0.30(10)]
Ba ($2q$)	0	0	0.312(4) [0.3127(5)]	0.78(10) [0.75(11)]
Cu(1) ($1h$)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.69(9) [0.57(11)]
Cu(2) ($2t$)	$\frac{1}{2}$	$\frac{1}{2}$	0.1444(3) [0.1446(3)]	0.81(7) [0.43(8)]
O(1) ($1d$)[b]	$\frac{1}{2}$	0	$\frac{1}{2}$	0.59(20) [0.20(20)]
O(2) ($2t$)	$\frac{1}{2}$	$\frac{1}{2}$	0.3438(4) [0.3423(4)]	1.32(11) [1.00(13)]
O(3) ($2r$)	0	$\frac{1}{2}$	0.1233(5) [0.1225(6)]	0.38(11) [0.7(1)]
O(4) ($2s$)	$\frac{1}{2}$	0	0.1210(6) [0.1206(6)]	0.36(10) [0.1(1)]

$a = 3.8282(4)$ Å [3.8213(4)]
$b = 3.8897(4)$ Å [3.8854(5)]
$c = 11.6944(14)$ Å [11.656(17)]
$V = 174.14(4)$ Å^2 [173.06(5)]
Weighted profile $R = 0.053$ [0.072]
Nuclear $R = 0.054$ [0.035]
Profile $R = 0.040$ [0.052]
Expected $R = 0.022$ [0.029]
Number of degrees of freedom $= 1045$ [753]
Number of Bragg reflections $= 228$ [172]

[a]Scattering lengths: Y(0.775), Ba(0.528), Cu(0.769), O(0.580).
[b]Occupancy of this site $= 0.70(5)$.

TABLE II. Selected interatomic distances (Å) 298 K.

Y-O(3)	2.421(3)	(4×)	Cu(2)-O(3)	1.9299(8)	(2×)
Y-O(4)	2.380(4)	(4×)	Cu(2)-O(4)	1.964(1)	(2×)
Ba-O(1)	2.911(4)	(2×)	Cu(2)-O(2)	2.332(5)	(1×)
Ba-O(2)	2.753(1)	(4×)	O(1)-O(2)	2.668(3)	
Ba-O(3)	2.945(5)	(2×)	O(3)-O(4)	2.7289(1)	
Ba-O(4)	2.945(7)	(2×)	O(3)-O(3)	2.88(1)	
Cu(1)-O(1)	1.945(2)	(2×)	O(4)-O(4)	2.83(1)	
Cu(1)-O(2)	1.827(5)	(2×)			

this site was assigned an occupancy of 0.5. In *Pmmm*, there are two inequivalent sites available at $\frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$, respectively, and initially, these were assigned an occupancy of 0.5 each.

As the refinement proceeded it became clear from the behavior of the temperature factors associated with the $0\frac{1}{2}\frac{1}{2}$ site, that the above assumption was incorrect. At this point, a Fourier synthesis was constructed which showed unequivocally that only the $\frac{1}{2}0\frac{1}{2}$ site was occupied. Deletion of the $0\frac{1}{2}\frac{1}{2}$ site and assignment of an occupancy of 1.0 to $\frac{1}{2}0\frac{1}{2}$ allowed the refinement to converge to a weighted profile R, R_{WP}, of 0.062. This occupancy corresponds to overall composition $YBa_2Cu_3O_{7.0}$. However, at this point the isotropic temperature factor of this site was 3.3(3) $Å^2$. Careful refinement of the occupancy and temperature factor gave values of 0.70(5) and 0.59(20) $Å^2$, respectively, with $R_{WP}=0.053$. Thus, there is a small discrepancy between the oxygen content determined by refinement of the neutron data and that obtained by thermal gravimetric reduction in hydrogen. The final positional and thermal parameters are given in Table I and the observed, calculated, and difference profiles are shown in Fig. 2 for 298 K. Results for 79.5 K are essentially the same and are not shown. Relevant interatomic distances are given in Table II.

SUMMARY AND CONCLUSIONS

The analysis of the neutron powder diffraction data presented here confirms the basic features of the crystal structure of $YBa_2Cu_3O_7$ reported earlier from x-ray diffraction on small single crystals.[1,4] That is, the structure can be regarded as a stacking of three primitive perovskite cells due to crystallographic ordering between the Y and Ba atoms. This situation has been observed before in the very similar material $La_3Ba_3Cu_6O_{14-\delta}$.[8] Because of the severe oxygen deficit, these atoms cannot have their normal coordination of 12 (cubic octahedron). In fact, Ba retains a nearly cubic-octahedral coordination with 11 neighbors but the Y atom takes on an eightfold, nearly cubic, coordination. A Fourier synthesis of the $z=0$ layer, where the missing four oxygens would be in a normal perovskite, confirms their absence in this structure. As a consequence of these oxygen vacancies, the Cu(2) atoms are forced into a nearly square pyramidal geometry with two sets of planar Cu-O distances of 1.930(1) Å, 1.964(1) Å, and a much longer apical distance of 2.332(6) Å.

Apart from the use of the correct orthorhombic symmetry and the improved precision with which the bond distances are determined, the major contribution of the present work is in determination of additional oxygen ordering in the $z=\frac{1}{2}$ layer. As shown earlier, the $\frac{1}{2}0\frac{1}{2}$ positions are about 70% occupied while the $0\frac{1}{2}\frac{1}{2}$ positions are vacant. This implies a subtle but potentially important change in the coordination and stacking of the Cu polyhedra associated with this layer. That is, the Cu(1) atoms are square planar with two rather different Cu-O distances of 1.827(5) Å parallel to **c** and 1.945(2) Å parallel to **b**. A perspective drawing of the unit cell and of
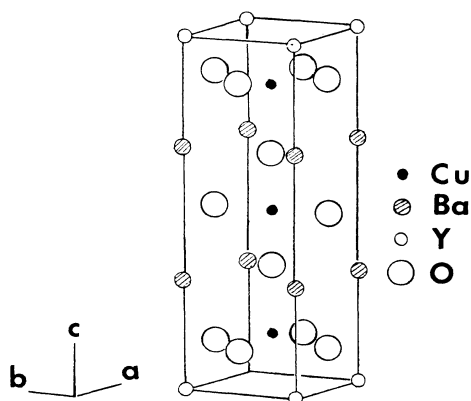
• Cu
⊘ Ba
○ Y
○ O

FIG. 3. A perspective drawing of the unit cell of $YBa_2Cu_3O_7$.
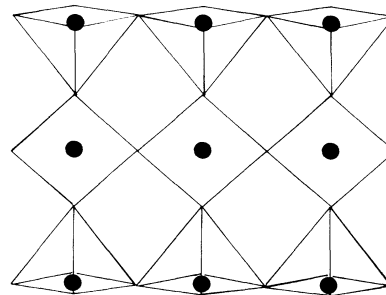
FIG. 4. A portion of the structure $YBa_2Cu_3O_7$ viewed along the *a* axis showing the links between the Cu coordination polyhedra. The pyramids share corners along ⟨100⟩ and ⟨010⟩, the square planes share corners only along ⟨010⟩.

the Cu-O linkages are shown in Figs. 3 and 4, respectively.

A second issue concerns the oxygen content and the amount of Cu^{3+} in the superconducting phase. The sample investigated here shows a very large superconducting fraction with a T_c of 93 K. Our analytical measurement of the oxygen content of about 7.0 atoms per unit cell implies 33% Cu^{3+}. The small discrepancy between the oxygen content determined analytically and that determined by neutron diffraction is under current study.

Finally, to the limit of our resolution there is no significant change in crystal structure to 80 K.

Note added in proof. Since submission of this manuscript we have learned that similar results have been obtained by M. A. Beno *et al.*, Appl. Phys. Lett. (to be published) and J. J. Capone *et al.*, Europhys. Lett. (to be published).

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