Crystal structure of the high-T_c superconductor $Ba_2YCu_3O_{7+x}$ using neutron diffraction

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(Received 29 May 1987; revised manuscript received 31 July 1987)

The crystal structure of the high-T_c superconductor $Ba_2YCu_3O_{7+x}$ has been studied using neutron diffraction. This compound has an orthorhombic structure with space group *Pmmm* and lattice parameters $a=3.8132$ Å, $b=3.8774$ Å, and $c=11.653$ Å. We found an occupancy of 0.1 for oxygen atoms at the $1b$ site and a total number of oxygen atom per unit cell of 7.1. The high quality of the sample used may be associated with the partial occupation at the $1b$ site by oxygen atoms.

Early this year Wu *et al.*[1] and Zhao *et al.*[2] reported that a barium, yttrium, and copper ternary oxide becomes a superconductor above 77 K. Soon after the exciting discovery the structure of the superconducting phase was studied by Cava *et al.*,[3] Michel, *et al.*,[4] and Beyers *et al.*[5] Subsequently, Siegrist *et al.*[6] carried out a structure determination from single-crystal x-ray data, and proposed a structure based on an orthorhombic perovskitelike model. Recently, Beno *et al.*[7] and Capponi *et al.*[8] studied the structure by neutron diffraction. The two groups reported that the O(4)($1e$) site is fully occupied by oxygen atoms.

We report here the results of neutron diffraction on $Ba_2YCu_3O_{7+x}$. We found a structure that is different from other models proposed for the oxygen-site occupancies.

The sample was prepared using the standard power-ceramic method from Y_2O_3, $BaCO_3$, and CuO powers of high purity. Neutron and x-ray power diffraction data showed a pure orthorhombic phase. We have measured the resistance and magnetic susceptibility as a function of temperature, and the magnetization as a function of magnetic field for the sample investigated in the present neutron diffraction study. Figure 1 shows the temperature dependence of the resistance and susceptibility, and Fig. 2 shows the magnetization curve. The sharp transition of the resistance and susceptibility at 92 K with a narrow transition width 1.2 K as well as the very large H_{c2}, which can be seen in Fig. 2, implies that the superconducting phase is very stoichiometric and homogeneous.

Neutron power diffraction data were collected on the triple-axis spectrometer at the Institute of Atomic Energy, Beijing. The neutron wavelength was 1.227 Å. The data were analyzed with the Rietveld structure refinement program RIETAN.[9]

The structure was solved using a model with space group *Pmmm* and triperovskitelike structure. A group of position parameters with Ba at $2t(\frac{1}{2},\frac{1}{2},\frac{1}{6})$, Y at $1h(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, Cu(1) at $1a(0,0,0)$, Cu(2) at $2q(0,0,\frac{1}{3})$, O(1) at $2q(0,0,\frac{1}{6})$, O(2) at $2s(\frac{1}{2},0,\frac{1}{3})$, O(3) at $2r(0,\frac{1}{2},\frac{1}{3})$, O(4) at $1e(p,\frac{1}{2},0)$, and O(5) at $1b(\frac{1}{2},0,0)$ were used for the initial values. We refined the lattice parameters and profile parameters first, subsequently refined the positions and occupation factors of Ba, Y, and Cu atoms, then refined the positions and occupation factors of all oxygen atoms, then made a final run for all refined pa-

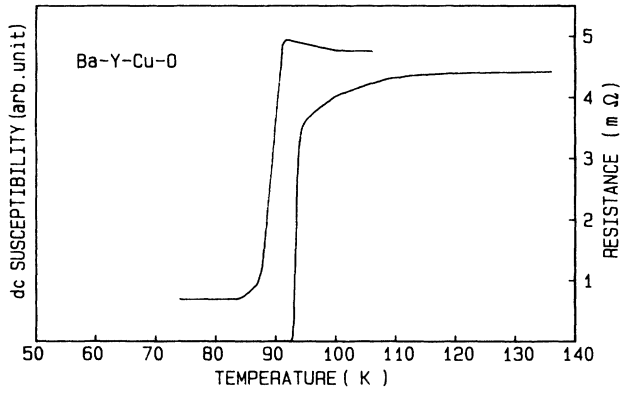

FIG. 1. Temperature dependence of resistance and magnetic susceptibility for $Ba_2YCu_3O_{7.1}$.

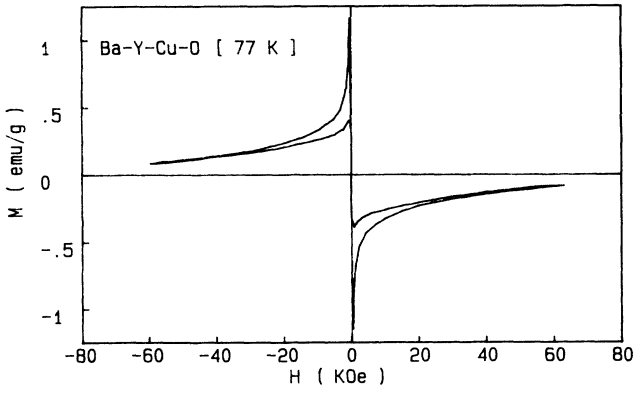

FIG. 2. Magnetic field dependence of magnetization for $Ba_2YCu_3O_{7.1}$.

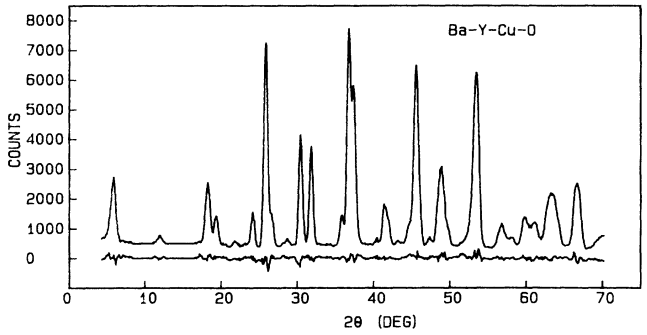

FIG. 3. Observed neutron powder diffraction pattern for $Ba_2YCu_3O_{7.1}$ at room temperature, with the difference between the observed and calculated data.

rameters. The diffraction pattern and the difference between the observed and calculated data are shown in Fig. 3. The sample was found to have a distorted orthorhombic perovskite structure with space group *Pmmm* and lattice parameters $a=3.8132$ Å, $b=3.8774$ Å, and $c=11.653$ Å. The refinement proceeded using only an isotropic thermal factor.

It was found that (a) all sites except O(4) and O(5) remain very close to fully occupied, (b) the occupancy and temperature factor for the O(5) site are strongly correlated with each other, (c) the refinement which allows all refinable parameters to vary simultaneously leads to a convergence with the temperature factor and the occupancy for the O(5) site converging to a very large value of 60(Å^2) and 0.29, respectively. Therefore we performed another run with a fixed temperature factor of 0.0 for the O(5) site as an extreme case. It led to a refined value of 0.08 for O(5) occupancy. Apparently this implies a non-negligible partial occupancy of oxygen at the O(5) site. Considering the similarity of the environments for O(4) and O(5), we put a constraint in the last run on the O(4) and O(5) temperature factors, letting them always equal each other. We found the occupancy of O(4) and O(5) to be 1.00 and 0.10, respectively. The structure model of the superconducting phase is shown in Fig. 4. We got $R(F^2)=0.028$, $R_p=0.044$. The crystallographic data are shown in Table I, and the selected bond lengths calculated from our data are shown in Table II.

Although it is difficult to determine the population at the O(5) site without ambiguity, the extreme case in which the O(5) temperature factor takes 0.0 implies that the existence of oxygen atoms at the O(5) site is not negligible. As listed in Table I, the oxygen population at the O(5) site is 0.10, and the refined stoichiometry for this superconducting phase is $Ba_2YCu_3O_{7.1}$.

TABLE I. Crystallographic data of $Ba_2YCu_3O_{7.1}$ orthorhombic cell. $a=3.8132(10)$ Å, $b=3.8774(10)$ Å, $c=11.653(12)$ Å. Space group *Pmmm*. Standard deviations referring to the last significant figure.

Atom	x	y	z	Occupancy	B_{iso} (Å^2)
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.1854(9)	1.00(1)	0.74(24)
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.00(1)	0.76(29)
Cu(1)	0	0	0	1.00(1)	0.26(26)
Cu(2)	0	0	0.3557(7)	1.00(1)	0.70(18)
O(1)	0	0	0.1574(9)	1.00(2)	1.44(32)
O(2)	$\frac{1}{2}$	0	0.3804(13)	1.00(2)	1.33(33)
O(3)	0	$\frac{1}{2}$	0.3771(13)	1.00(1)	0.26(30)
O(4)	0	$\frac{1}{2}$	0	1.00(3)	2.27(58)
O(5)	$\frac{1}{2}$	0	0	0.10(3)	2.27(58)

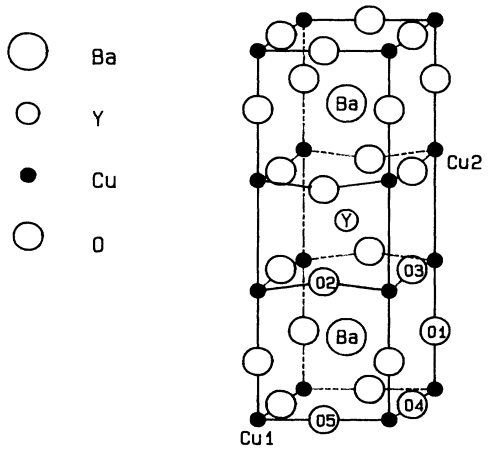

FIG. 4. Unit cell of $Ba_2YCu3O_{7.1}$.

TABLE II. Interatomic distances in $Ba_2YCu_3O_{7.1}$ (Å).

Ba-O(1)	2.739
Ba-O(2)	2.987
Ba-O(3)	2.937
Ba-O(4)	2.882
Ba-O(5)	2.903
Y-O(2)	2.388
Y-O(3)	2.385
Cu(1)-O(1)	1.834
Cu(1)-O(4)	1.939
Cu(1)-O(5)	1.907
Cu(2)-O(1)	2.311
Cu(2)-O(2)	1.928
Cu(2)-O(3)	1.955

We found the superconductivity to be very sensitive to the population of oxygen, especially to the partial occupancy of the O(5) site.

[1]M. K. Wu, J. R. Ashburn, C. J. Torng, H. P. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Z. Wang, and C. W. Chu, Phys. Rev. Lett **58**, 908 (1987).

[2]Zhao Zhongxian, Chen Liquan, Yang Qiansheng, Huang Yuzhen, Chen Genghua, Tang Ruming, Liu Guirong, Cui Changgeng, Chen Lie, Wang Lianzhong, Guo Shuquen, Li Shanlin, and Bi Jianqing, Kexue Tongbao **33**, 66 (1987).

[3]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[4]C. Michel, F. Deslanders, J. Provost, P. Lejay, R. Tournier, M. Hervieu, and B. Raveau, C. R. Acad. Sci. (to be published).

[5]R. Beyers, G. Lim, E. M. Engler, R. J. Savoy, T. M. Shaw, T. R. Dinger, W. J. Gallagher, and R. J. Sandstrom, J. Appl. Phys. Lett. (to be published).

[6]T. Siegrist, S. Sunshine, D. Murphy, R. J. Cava, and S. M. Zaherak (unpublished).

[7]M. A. Beno, L. Soderholm, D. W. Cappone II, D. G. Hinks, J. D. Jorgensen, I. K. Schuller, C. U. Segre, K. Zhang, and J. D. Grace, Appl. Phys. Lett. (to be published).

[8]J. J. Capponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, R. Raveau, J. L. Soubey roux, J. L. Tholence, and R. Tournier, report (unpublished).

[9]RIETAN was provided kindly by F. Izumi, National Institute for Research in Inorganic Matter, Ibaraki, Japan.