

Neutron diffraction of Y–Ba–Cu–O–Cl ceramic

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Three phases, one amorphous and two crystalline, have been observed in two ceramic samples which go superconducting after chlorination. Chlorine atoms go into the unit cell. They statistically replace oxygen atoms and do not occupy vacant sites, as oxygen does.

After samples of a tetragonal ceramic with the approximate composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$ were heat-treated in gaseous chlorine in Ref. 1, they exhibited a diamagnetic response beginning at $T_{c0} \approx 90$ K. In the present letter we are reporting structural studies of chlorinated samples carried out by the method of neutron diffraction. This method is particularly good for determining the structural positions of chlorine atoms in the unit cell, since the amplitude for the scattering of neutrons by the chlorine nucleus is 1.65 times that for an oxygen nucleus, and it is also greater than the amplitudes for the scattering by yttrium, barium, and copper nuclei. The measurements were carried out on the 48-counter diffractometer of the Leningrad Institute of Nuclear Physics² at a neutron wavelength $\lambda = 1.384$ Å. The resulting diffraction patterns were analyzed by the Rietveld method³ with the help of a profile-analysis program⁴ which made it possible to refine the structures of the three distinct crystalline phases simultaneously present in the sample. The superconducting transition was identified from measurements of the magnetic susceptibility carried out by an inductive method (at a field frequency of 111 Hz, with an amplitude of 0.5 G) rapidly, during the selection of chlorination conditions, with small samples. The samples intended for the neutron diffraction were studied in an apparatus which was capable of measuring the parameters of the superconducting transition for macroscopic samples with volumes up to 250 mm³.

In the original samples of the orthorhombic ceramic of the composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$, after synthesis and annealing in an oxygen atmosphere, the superconducting transition began at $T_c = 93$ –94 K and had a width $\Delta T_c = 4$ –5 K. After a high-temperature annealing in vacuum, the oxygen content decreased to $\text{O}_{6.15}$, the compound acquired a tetragonal structure, and a superconducting transition was not observed anywhere down to 0.35 K. The results of the neutron-diffraction studies of the orthorhombic (O_7) and tetragonal (O_6) phases are shown in columns 1 and 4 of Table I. In the course of refining the structures we varied—in addition to the parameters of the unit cell, the coordinates of the atoms, and the isotropic temperature factors—the populations (n_i) of oxygen atoms in all possible sites in the orthorhombic

TABLE I. Results of a refinement of the $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ (O_7) structure, the $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$ (O_6) structure and the Y-Ba-Cu-O-Cl.

	O_7	Orthorhombic	Tetragonal	O_6
a (Å)	3.8245 (3)	3.8309 (7)	3.8622 (3)	3.8580 (3)
b (Å)	3.8888 (3)	3.8820 (7)	3.8622 (3)	3.8580 (3)
c (Å)	11.688 (1)	11.647 (4)	11.831 (2)	11.819 (1)
Ba (0.5; 0.5; z)	0.1844 (3)	0.170 (2)	0.1957 (9)	0.1948 (2)
Cu(2) (0; 0; z)	0.3547 (2)	0.351 (1)	0.3624 (8)	0.3602 (2)
O(1) (0; 0; z)	0.1586 (3)	0.159 (2)	0.149 (1)	0.1520 (3)
n_1	0.99 (2)	1	1.02 (2)	0.98 (1)
O(2) (0.5; 0; z)	0.3778 (3)	0.370 (2)	0.368 (2)	0.3795 (2)
n_2	1.01 (2)	0.83 (5)	0.59 (5)	1.03 (2)
O(3) (0; 0.5; z)	0.3784 (3)	0.378 (2)	0.400 (2)	0.3795 (2)
n_3	1.00 (2)	0.90 (6)	0.41 (5) ¹⁾	1.03 (2)
O(4) (0; 0.5; 0) n_4	0.93 (1)	0.70 (9)	0.08 (3)	0.07 (1)
O(5) (0.5; 0; 0) n_5	0.04 (1)	0.15 (8)	0.08 (3)	0.07 (1)
O(6) (0; 0; 0.5) n_6	- 0.01 (2)	- 0.1 (1)	0.24 (4)	0.02 (1)
Content	1	0.13 (2)	0.26 (3)	1
χ^2	3.0	0.8	0.8	5.0
R_N (%)	6.1	7.3	7.3	6.6

¹⁾Filling of fourfold site (3) with chlorine.

and tetragonal phases. [In the tetragonal phase, sites (2) and (3) and also sites (4) and (5), are equivalent.] The parameter values found here agree well with numerous results in the literature.

The O_6 ceramic was placed in a vacuum system, where it was treated with pure gaseous chlorine over the temperature interval from 150 °C to 170 °C for 0.5–3 h. Two samples were studied by neutron diffraction.

No superstructural reflections were seen on the neutron diffraction patterns of the two samples, one of which is shown in Fig. 1b, in comparison with the diffraction pattern of O_6 (in Fig. 1a). The diffraction peaks are rounded and are seen against a modulated background which is evidence of a significant content of an amorphous phase. Figure 2 shows part of a diffraction pattern produced in $\text{Co } K\alpha_{1,2}$ radiation. A resolution of this pattern into its components reveals evidence of a highly disordered orthorhombic phase [the reflections $(020)_R, (200)_R, (006)_R$] and a phase which is probably tetragonal. In a first step, the structure of each phase was refined on the basis

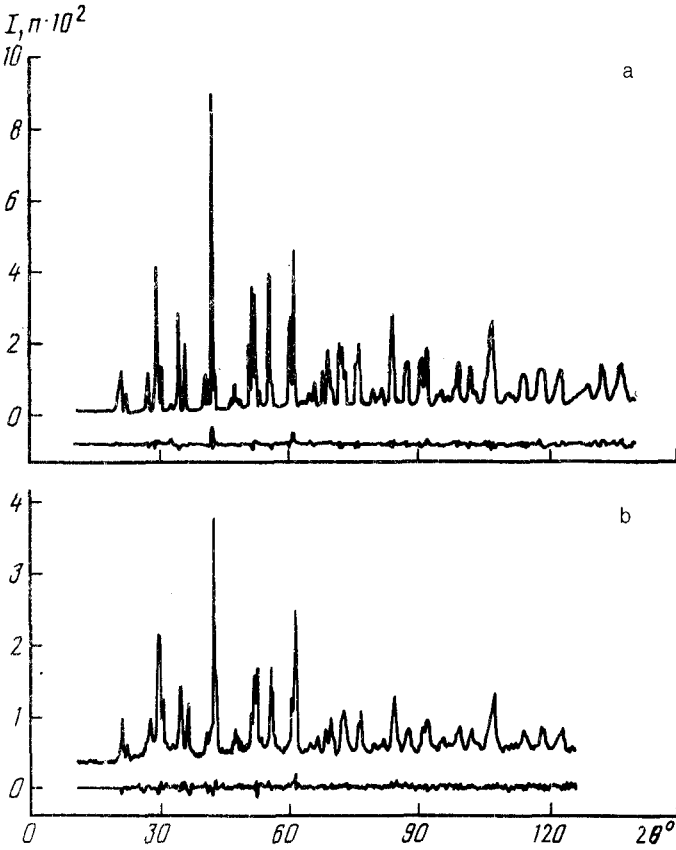


FIG. 1. a—Neutron diffraction patterns of a sample of the original tetragonal phase, $\text{YBa}_2\text{Cu}_3\text{O}_{6.15}$, the observed pattern and the difference pattern (the observed pattern minus the calculated pattern); b—neutron diffraction patterns of a chlorinated sample.

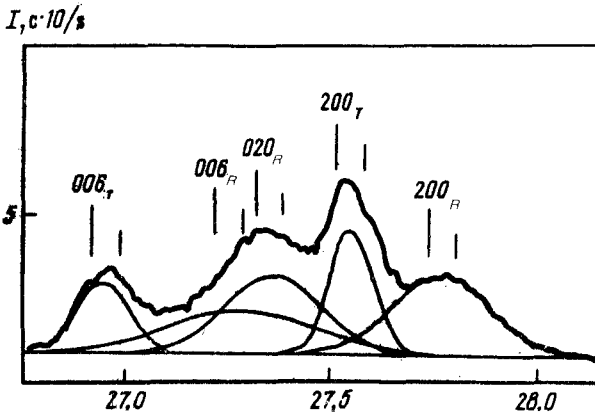


FIG. 2. Part of an x-ray diffraction pattern of a chlorinated sample and its resolution into five doublets.

of the space group $Pmmm$ (the tetragonal group $P4/mmm$ is a special case). As before, we varied the populations of all the positions, (1)–(6), and we substituted the oxygen scattering amplitude into the structure factor. We judged that a value $n_i > 1$ was evidence of the appearance of chlorine at site n_i . For $n_i < 1$, the neutron data by themselves do not tell us which atom (oxygen or chlorine) is at this site.

In this step of the refinement we noted that the population of site (3) for the approximately tetragonal phase exceeded unity by more than seven standard deviations. Furthermore, the difference between the coordinates of sites (2) and (3) was 0.024₁, i.e., substantially greater than the 0.0006₄ in the case of O₇. (In the tetragonal phase, O₆, this difference is precisely zero.) All of these results are clear evidence that chlorine occupies site (3). On the other hand, the difference between the lattice constants a and b for this phase does not exceed 0.003 Å. It was accordingly suggested that this phase is indeed tetragonal and that each of the equivalent sites in this case, (2) and (3), splits into two nonequivalent sites, one of which is occupied by oxygen atoms, and the other by chlorine atoms. This suggestion seems reasonable since in a statistical replacement of the oxygen atoms between two Cu(2) atoms in each face of the tetragonal cell the chlorine atoms may “be ejected” because of the difference in radii. The average coordinates of the chlorine and oxygen turned out to be different.

A further refinement was carried out, again on the basis of the orthorhombic group $Pmmm$ for one phase, but on the basis of the tetragonal $P4/mmm$ group with two nonequivalent fourfold sites (2) and (3) for the other. An independent variation of the oxygen population of site (2) and the chlorine population of site (3) yielded $n_2 + n_3 = 1.03_5$. Accordingly, we took the total population of these sites to be unity in the calculation of the final version. In the cation sublattice we varied only the coordinates of Cu(2) and Ba; we fixed the populations of all of the metal atoms at the sites at $n_{Me} = 1$.

Since the parameters of the unit cell of the tetragonal phase of the chlorinated samples turned out to be approximately the same as those of O₆, it was necessary to check whether the oxygen atoms were replaced by chlorine atoms in a statistical way or two distinct phases—a chlorine phase and a residual O₆ phase—formed. A three-phase refinement of the structure at fixed values of the parameters of the O₆ phase led to nonphysical results, and the value of χ^2 was degraded by a factor of 1.5.

The final results of the refinement on the basis of this model are shown in Table I (column II corresponds to the orthorhombic phase, and III to the tetragonal phase). Let us summarize these results.

As a result of the chlorination, the oxygen atoms at equivalent sites (2) and (3) are statistically replaced by chlorine atoms. The chlorine content of these sites per formula unit is 1.6₁ for sample I and 1.76₄ for sample II. Oxygen atoms, $n_6 = 0.24$, or chlorine atoms, $n_6 = 0.14$, appear at site (6), previously unoccupied. While sites (6) are also occupied by chlorine atoms, the chlorine content per formula unit is 1.8₁ for sample I and 1.87₈ for sample II. The oxygen-atom populations of sites (1) and of equivalent sites (4) and (5) did not change.

In addition to the tetragonal phase, a highly disordered orthorhombic phase forms. The deviations of the average values of the parameters are $\Delta a/a \approx \Delta b/b$

$b \approx 9 \times 10^{-3}$, according to the broadening of x-ray lines. This figure is comparable to the difference between the corresponding parameters in the O_6 - O_7 system. In the orthorhombic phase we see a significant population of oxygen or chlorine atoms at sites (4).

The structural parameters and the population of the second sample which we studied did not differ by more than three standard deviations. The only difference was in the relative proportions of the orthorhombic and tetragonal phases: For sample I the ratio was 0.50, while for sample II it was 0.85.

Which phase—orthorhombic or tetragonal—is responsible for the superconductivity remains an open question, since we cannot separate these phases. The model which has been chosen incorporates in a consistent way the existing set of experimental x-ray and neutron data, but the conclusion that oxygen sites are occupied and the fact that chlorine enters the Y-Ba-Cu-O lattice are so unexpected that further experiments, on samples with various relative amounts of the different phases and with various amounts of chlorine, will be required for confirmation.

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¹Yu. A. Osip'yan, O. V. Zharikov, N. S. Sidorov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 225 (1988) [JETP Lett. **48**, 246 (1988)].

²I. V. Golosovskii, V. P. Kharchenkov, A. P. Bulkin *et al.*, Preprint No. 1374, Leningrad Institute of Nuclear Physics, 1988.

³H. H. Rietveld, J. Appl. Cryst. **2**, 65 (1969).

⁴M. W. Thomas and P. J. Bendall, Acta Cryst. **A84**, S851 (1978).

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