Structural transition in $YBa_2Cu_3O_7$

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X-ray and neutron diffraction methods were used to show that $YBa_2Cu_3O_7$ undergoes a structural phase transition, with a subgroup coupling, from the orthorhombic phase (space group D_{2h}^1) to the tetragonal phase (space group D_{4h}^1). The crystal structures of the two phases are compared. The mechanism governing the transition and the effect of the structural change on the superconductivity are discussed.

The discovery of a high transition temperature to the superconducting state in Y-Ba-Cu-O (Ref. 1) raises the question of a link between the superconductivity of this oxide and its structure and a possible structural instability. At temperatures below room temperature no structural changes were observed in $YBa_2Cu_3O_7$. We report here the results of an experimental study of the structure of this compound at high temperatures, using x-ray and neutron-diffraction methods.[1)]

The samples were synthesized using the conventional ceramic technology at the Ural Branch of the Moscow State University. The experiments were carried out with DRON-3.0 x-ray diffractometer, DISK neutron diffractometer,[3] and ATOS triaxial neutron spectrometer[4] at room temperature using samples quenched in water after being annealed in air for one hour.

At annealing temperatures up to 773 K the line intensities on the x-ray photographs remain almost constant; at 773 K–1023 K the intensities of the lines and the manner in which they split change; and above 1023 K the pattern stabilizes (Fig. 1). Indexing of x-ray photographs shows that these changes occur as a result of raising the symmetry of the cell from orthorhombic to tetragonal, which causes its volume to increase primarily due to the increase of the lattice constant c (Fig. 1d). The transition temperature, estimated from the change in the relative line intensities on the x-ray photographs and from the change in the lattice constants (Fig. 1d), is approximately 1020 K.

The neutron-diffraction patterns of $YBa_2Cu_3O_x$, which is quenched at 1073 K, reveal lines solely of the tetragonal phase, in which no reflections, in comparison with the orthorhombic phase, either appear or disappear (Fig. 2). This means that the raising of the symmetry occurs without changing the unit cell with a wave vector $\mathbf{k} = 0$. The space group D_{2h}^1 of an orthorhombic $YBa_2Cu_3O_7$ (Ref. 2) has two tetragonal supergroups[5]: D_{4h}^9 and D_{4h}^1. The first supergroup, which corresponds to a disordering of all atoms, including the cations, should lead to the extinction of the reflections (hhl) with $l = 2n + 1$, in contradiction of the experiments. The second

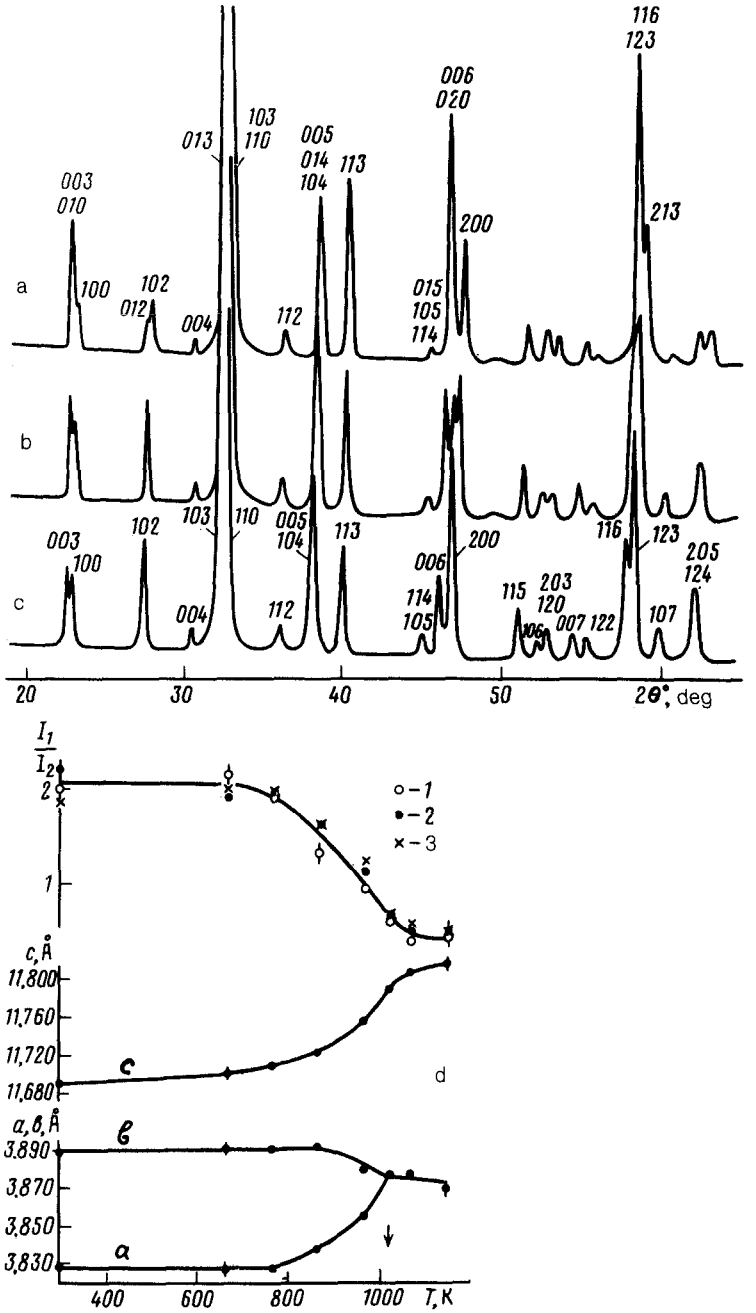

FIG. 1. X-ray photographs of $YBa_2Cu_3O_x$ (CuKα radiation). (a) Orthorhombic $YBa_2Cu_3O_7$; (b) after annealing from 973 K; (c) tetragonal $YBa_2Cu_3O_{6.4}$ (after annealing from 1073 K); (d) the lattice constants (a, b, c) and the line-intensity ratios I_1/I_2 of the doublets versus the annealing temperature. 1—$I_1(006, 020)/I_2(200)$; 2—$I_1(116, 123)/I_2(213)$; 3—$I_1(103, 110)/I_2(013)$; the arrow denotes the structural transition temperature.

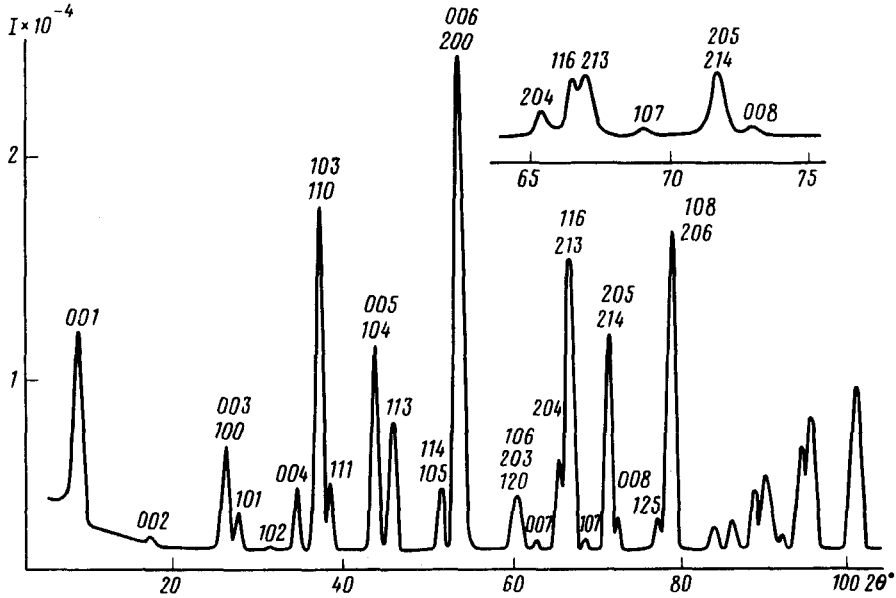

FIG. 2. Neutron-diffraction pattern of the tetragonal $YBa_2Cu_3O_{6.4}$, $\Delta d/d = 0.8\%$, $\lambda = 1.730$ Å. Inset—a fragment of the neutron-diffraction pattern for the resolution $\Delta d/d = 0.3\%$, $\lambda = 1.760$ Å.

supergroup corresponds to the disordering of only the oxygen atoms, in which the 04 and 05 positions, as well as the 02 and 03 positions,[2] which are nonequivalent in the orthorhombic phase, become crystallographically equivalent positions. A minimization of the R factor for this model, which was carried out in accordance with the integral line intensities, gave a good agreement with the experiment ($R = 3.7\%$) for the composition $YBa_2Cu_3O_{6.40\pm0.16}$ and the parameters given in Table I. Attempts to increase the composition to $YBa_2Cu_3O_7$ and to redistribute the oxygen atoms among the other positions or to order them according to Ref. 2 yielded an R factor that exceeded (by more than 10%) the experimental error (of about 4%). The compound

TABLE I. Parameters of the atoms in the tetragonal $YBa_2Cu_3O_{6.4}$ (space group D_{4h}^1, $T =$ 300K)

Atom	Position	Number of atoms	x	y	z	B, Å^2
Y	1*d*	1	1/2	1/2	1/2	0.8
Ba	2*h*	2	1/2	1/2	0.1884 ± 0.0003	0.6
Cu1	1*a*	1	0	0	0	0.9
Cu2	2*g*	2	0	0	0.3594 ± 0.0006	0.3
01	2*g*	1.82 ± 0.08	0	0	0.1550 ± 0.0005	0.8
02.03	4*i*	4.00 ± 0.05	1/2	0	0.3778 ± 0.0005	1.0
04.05	2*f*	0.58 ± 0.03	1/2	0	0	1.2

$YBa_2Cu_3O_{7-y}$ thus undergoes an order-disorder phase transition with respect to the 04 and 05 positions, which is accompanied by a partial loss of oxygen from these positions, so that the probability that they will become filled is equal to 3 (1 and 0, respectively, in the orthorhombic phase[2]). The linear 04-Cu1-04-Cu1 chains, which are characteristic of the orthorhombic superconducting phase, disappear in this case. These chains are the principal "orthorhombic" element in the structure, whereas the arrangement of all remaining atoms is nearly tetragonal and, with the exception of the 01 atoms which approach the oxygen-deficient plane, remain essentially constant after the transition. Electrical resistance measurements showed that the tetragonal phase is nonsuperconducting down to 4.2 K: its electrical resistance increases with decreasing temperature. It would be logical to link its loss of superconductivity with the breaking of the 04-Cu1 chains, which occurs as a result of the temperature- and concentration-induced disordering of the oxygen atoms. If, on the other hand, the conductivity would proceed solely along these chains, it would then vanish over a very narrow concentration interval near the composition $YBa_2Cu_3O_7$, which apparently is not the case.[6,7] It can therefore be assumed that the entire 04-05-Cu1 plane is a conducting plane. The disorder in "hyperstoichiometric" $YBa_2Cu_3O_{7-y}$ then should not result in the loss of conductivity, while the "hypostoichiometric" $YBa_2Cu_3O_{7+y}$ will lose its conductivity as a result of the onset of disorder which reduces the concentration of oxygen atoms below 0.5 in this plane: below the percolation limit for a two-dimensional lattice. The important factor for the presence of superconductivity is therefore the oxygen content and its distribution in the 04-05-Cu1 plane. The fact that this is important is suggested, in particular, by the neutron data obtained by us for the stoichiometric oxide $LaBa_2Cu_3O_7$, a superconductor with a tetragonal symmetry and a disorder in the 04-05-Cu1 plane, and also by the x-ray data on the superconducting pseudotetragonal $YBa_2Cu_3O_7$ phase.[8]

The results of this experimental study allow us to understand and explain many experimental observations concerning the superconducting oxide fabrication technology[6,7] and concerning the properties of these oxides: the rate at which they are cooled and annealed in oxygen, formation of the domain (twinning) structure of single crystals, the incomplete Meissner effect in x-ray "single-phase" samples, which apparently are a mixture of tetragonal and orthorhombic phases, and others.

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