Atomic structure and superconductivity of $YBa_2Cu_3O_{7-x}$

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The atomic mechanism for the transition from the tetragonal phase to the orthorhombic phase has been identified on the basis of x-ray structural studies of $YBa_2Cu_3O_{7-x}$ single crystals before and after annealing in oxygen. The elements of the atomic structure associated with superconductivity are identified.

The synthesis of the $YBa_2Cu_3O_{7-x}$ single crystals is described in Ref. 1, and results of measurements of their conductivity are reported there. Before annealing in an oxygen medium, these crystals go superconducting only at liquid-helium temperatures. After annealing, they become superconductors with $T_c \simeq 93$ K (Ref. 1). The x-

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ray structural studies of the samples were carried out on an RED-4 automatic diffractometer (Mo radiation; graphite monochromator; $\theta/2\theta$ scanning). Before the annealing, the single crystal exhibits a rich diffraction pattern with reflections with a half-width of 20′–25′. This pattern is unambiguous evidence of a tetragonal symmetry for the single crystal; the parameters of the unit cell are $a = 3.863(1)$ Å and $c = 11.837(2)$ Å. The volume of the cell is $V = 176.7(1)$ Å^3. After the annealing, the sample exhibits a more complicated diffraction pattern. Reflections of the general type *hkl* split into four components, and those of the type *hhl* split into three components; only the 00*l* reflections remain unchanged. A detailed analysis of the diffraction pattern shows that the crystal converts into an orthorhombic phase and simultaneously undergoes a microtwinning during annealing. The unit cell of the orthorhombic phase has the parameter values $a = 3.826(2)$, $b = 3.890(2)$, $c = 11.705(3)$ Å, and $V = 174.2(2)$ Å^3. Axis 4 and the diagonal plane of the symmetry, (110), present in the tetragonal phase, serve as symmetry elements of the twinning; in the orthorhombic phase ($a \neq b$), they cease to be dependent. The twinning is polysynthetic. The plane twinning junctions run parallel to the (110) diagonal plane of the unit cell.

The structural studies of $YBa_2Cu_3O_{7-x}$ which have been published and reported in preprints yield results in agreement on the positions of the cations in the unit cell of the crystal, but they differ in the way in which the O atoms occupy their positions.[2,3] Figure 1 is a projection of an atomic model of the structure onto the *bc* plane. Essentially the only important difference between the structures of the tetragonal and orthorhombic phases is the positioning of the O1 atoms in the $z = 0$ plane. These atoms surround Cu1 copper atoms. In the tetragonal phase these oxygen atoms occupy both position O1 (0 1/2 0) and position O1′ (1/2 0 0) with roughly equal probabilities of about 0.5 (the lower left in Fig. 2a). In addtiion to these oxygen atoms, two O4 atoms are in contact with the Cu1 copper atoms in the tetragonal and orthorhombic phases. The latter oxygen atoms occupy their positions completely and are positioned vertically above and below the Cu1 atom on the *c* axis. The Cu1 atom of the tetragonal phase is thus statistically in an octahedron consisting of these two "vertical" O4 atoms and four O1 equatorial "half-atoms." Actually, each unit cell has two O1 atoms around

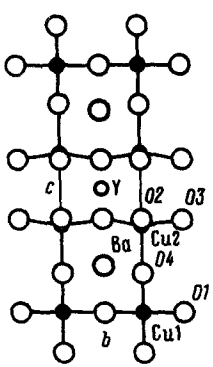


FIG. 1. Projection of the $YBa_2Cu_3O_{7-x}$ structure onto the *bc* plane (orthorhombic phase; in the tetragonal phase, O1′ atoms are superimposed on the Cu1 atoms in this projection).

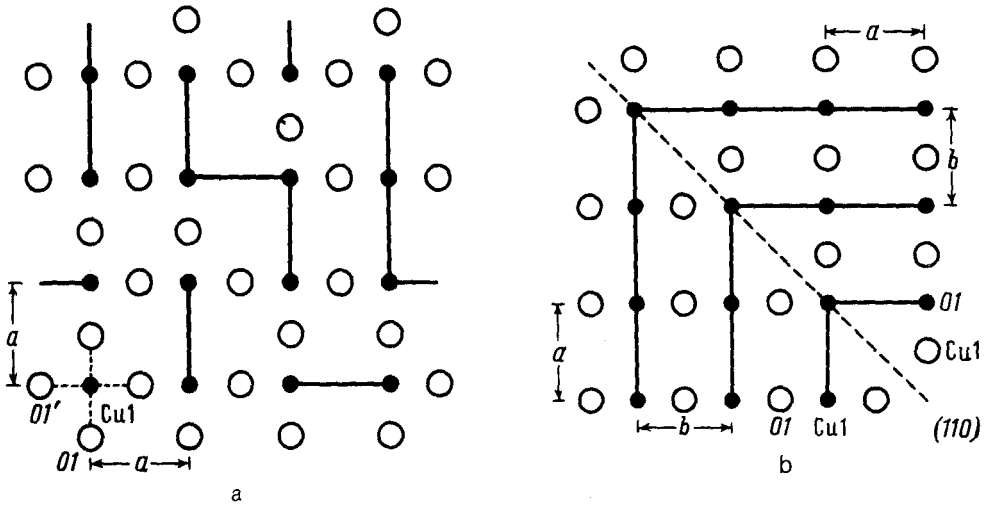


FIG. 2. Intersection of the structures with the $z = 0$ plane. a: Tetragonal phase. The positions of the O1 and O1′ oxygen atoms are occupied statistically with weights close to 1/2, as indicated at the lower left. The random arrangement of Cu1 atoms, between which there are no O atoms, is shown in the main part of the figure. b: Orthorhombic phase; the surrounding by O1 atoms of the Cu1 atoms of a chain stretched out along the a axis. The (110) twinning plane and the orientation of the Cu1 chains in adjacent domains are shown.

Cu, and the copper atom usually has a quadratic "vertical" coordination

$$\begin{array}{ccccc} & & \mathrm{O4} & & \\ & & | & & \\ \mathrm{O1} & - & \mathrm{Cu} & - & \mathrm{O1}. \\ & & | & & \\ & & \mathrm{O4} & & \end{array}$$

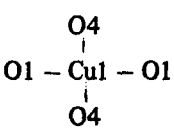
The O1–Cu–O1 bonds are rotated through 90° in each unit cell, however, as illustrated in the main part of Fig. 2a. All the other structural details conform to a tetragonal symmetry, and the statistics of the O1 atoms which we have pointed out here also describe a tetragonal symmetry on the average.

The atomic mechanism for the transition of the tetragonal phase into an orthorhombic phase reduces to an ordering in the arrangement of O1 and O1′ atoms in the $z = 0$ plane. The position of O1 (1/2 00) in the orthorhombic phase is no longer occupied by O atoms, and all of these atoms concentrate in a single crystallographic position, (0 1/2 0). The a and b axes are no longer equal, and the symmetry of the crystal lowers from $P4/mmm$ to $Pmmm$. The volume of the orthorhombic unit cell is 2.5 Å^3 smaller than the tetragonal volume. It may be that the oxygen medium is required during the annealing in order to prevent a loss of oxygen from the sample. In both structures (tetragonal and orthorhombic) there may be additional defects because of the oxygen concentration O_{7-x} (i.e., because of the quantity x).

A phase transition accompanied by an ordering in the positions of the O1 atoms

thus occurs during the annealing. Superconducting properties arise at the same time. In the superconducting orthorhombic phase, the Cu1 atoms form chains stretched out along the a axis in the crystal. In the tetragonal phase, the Cu-Cu contacts in such chains are statistically disrupted by O1′ atoms, which lie between Cu atoms and make the chain nonuniform. In the orthorhombic structure, the Cu-Cu distance in the chain is 3.826(2) Å. With a statistical intrusion of oxygen between Cu atoms and a disordering of the orientation of the "squares" in the tetragonal phase, the average length of a link of the chain increases to 3.863(2) Å.

In the orthorhombic phase, the planes of



squares are all oriented identically, perpendicular to the a axis. The squares make up a chain, stacked flat, one on top of another. One-dimensional copper-oxygen chains of this sort, lying in the $z = 0$ plane of the three-dimensional structure of this compound, slightly resemble the stacks of radicals in organic superconductors.[4]

In the tetragonal phase (Fig. 2a), on the other hand, the chains of Cu atoms are ruptured. In this phase, orthorhombic distortions arise upon a disruption of the statistical equality of the populations of the O1 and O1′ positions in the structure, and the length of the Cu-Cu-Cu . . . chains, which do not contain O atoms, increases. A sample whose occupation by oxygen of (1/2 0 0) positions can range from zero to some maximum value, depending on the particular synthesis technique, may be the reason for the difference in the temperatures of the transition to the superconducting state. Slight deviations of the symmetry from a tetragonal symmetry remain beyond the accuracy of a diffraction experiment. The emulation of a tetragonal symmetry is also intensified by the twinning of the orthorhombic phase. At a thickness of[1] 10^3 Å of the single-domain layer in a polysynthetic twin, the Cu chains within the layer oriented at an angle of 45° with respect to the plane of the twinning boundary contain 350–400 "squares." At the twinning junction the direction of the chains changes by 90° in the adjacent domain. Figure 2b illustrates the twinning.

With regard to the compound $(La,Sr)_2CuO_{4-x}$, we note that again in this case the defectiveness in terms of oxygen positions may also give rise to the formation of Cu-Cu-Cu . . . chains.

These x-ray structural studies of high-temperature superconductors are being pursued in order to obtain precise data on the extent to which the atoms occupy their positions and on the characteristics of the thermal vibrations of the atoms at various temperatures.

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