

The structure of tetragonal compound $\text{YBa}_2\text{Cu}_{3-x}\text{O}_{6-y}$ in the temperature region 100–1000 K

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The atomic and crystal structure of a single crystal is studied over a broad temperature range by means of x-ray structural analysis. The relative "rigidity" of the atomic triad O1–Cu1–O1' is determined on the basis of an analysis of the change in the thermal vibrations of atoms and the atomic spacing.

The original single crystals of the orthorhombic phase $\text{YBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ were synthesized by a spontaneous crystallization of the melt containing Y_2O_3 , BaCO_3 , and CuO . An orthorhombic twinned sample of yttrium-barium cuprate, whose constant x-ray monitoring was carried out in a DAR-UM diffractometer, was converted to a tetragonal phase single crystal which was used in an x-ray structural study at $T = 1000, 600, 300,$ and 100 K. The specified temperature of the sample was reached by gaseous nitrogen heating. Under these conditions the temperature of the transition from the orthorhombic phase to a tetragonal phase was 875 K. The sample remained in the tetragonal phase after a two-month exposure to air. The temperature dependence of the parameters is shown in Fig. 1. The sample's dimensions were $0.21 \times 0.22 \times 0.21$ mm; the space group was $P4/mmm$; the radiation was $\text{MoK}\alpha$; only the independent reflections were measured (830 at $T = 100$ K); a correction for the absorption, with allowance for the size and shape of the sample, was introduced. The SHELX-76 program was used in the calculations. At temperatures of 100, 300, 600, and 1000 K the values of R_f are 0.048, 0.050, 0.061, and 0.056, respectively. The main results, on the whole, are in agreement with the data in the literature.¹⁻³ It was rather surprising to see that all positions of the O2 atoms (in the $z = 0$ plane) were unfilled (within experimental error); i.e., under the experimental conditions the seventh oxygen was completely removed and the coordination number of Cu1 was 2 (a dumb-bell). The second clear result is that the positions of the Cu1 atom (0.94 ± 0.01) and O1 atom (0.92 ± 0.02) are filled only partially. The deficiency found in the positions of Cu1, O2, and O1 was noted in the literature in the case of tetragonal and orthorhombic crystals. In our case it was found in the formula for the tetragonal $\text{YBa}_2\text{Cu}_{3-x}\text{O}_{6-y}$ with $x = y = 0.06 \pm 0.01$.

With an increase in the temperature, only the coordinate of the O1 atom changes markedly, suggesting that it plays a special role in the structure. As the temperature was varied from 600 K to 1000 K, the components of the mean square thermal vibrations along the c axis (u_{33}) in Cu1 and perpendicular to it (u_{11}) in O1 increased sharply simultaneously. This behavior suggests that the thermal vibrations of these atoms are strongly correlated. This correlation gives rise to a pseudodecrease of the

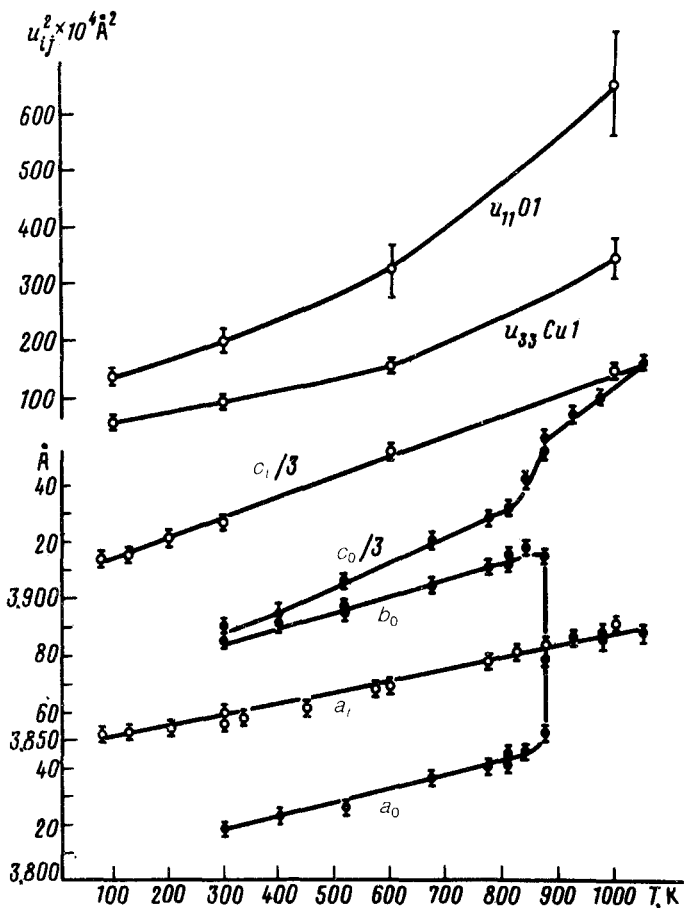


FIG. 1. Temperature dependence of the parameters: a_0 , b_0 , and c_0 —The initial twinned orthorhombic sample; a_1 and c_1 —tetragonal single crystal obtained by heating; u_{33} of Cu1 and u_{11} of O1 are the mean-square displacements of the corresponding atoms along the c axis and in the ab plane; ●—heating; ○—cooling.

Cu1–O1 spacing, which was calculated experimentally (ignoring the thermal-vibration model), from 1.82 \AA to 1.76 \AA (Fig. 2).

The thermal vibrations, the pseudodecrease of the Cu1–O1 spacing, and the identical filling of Cu1 and O1 are the basic features which indicate that the Cu1–O1 coupling is relatively rigid and that the structure can have some defects attributable to the absence of the O1–Cu1–O1 triad.

Upon heating the crystal from 100 K to 1000 K, the relative expansion along the a and c axes is 1% and 2%, i.e., it differs by a factor of 2. Aside from the Cu1–O1...Cu2 spacings, the change in the atomic spacings lies in these limits, so that the situation with O1 is anomalous: Cu–O1 changes by 3.5% and O1...Cu2 changes by 5.9%. While pseudodecrease of Cu1–O1, which amounts to 0.06 \AA , can be seen only

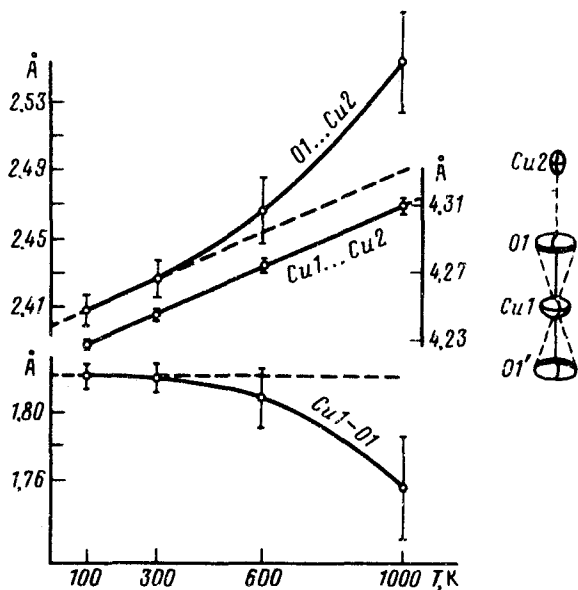


FIG. 2. Variation of the spacing in the Cu1-O1...Cu2 fragment.

after reaching a temperature of 600 K (Cu1-O1 and O1...Cu2 amount to 1.82, 1.82, 1.81, 1.76 Å and 2.41, 2.43, 2.47, 2.55 Å at 100, 300, 600, and 1000 K), expansion of O1...Cu2 amounts to 0.14 Å and occurs smoothly over the entire interval. The anomalous behavior of the temperature in the Cu1-O1...Cu2 chain suggests that the O1...Cu2 coupling is weak. We can thus legitimately say that the O1-Cu1-O1 "molecule" which precesses around the c axis of the crystal is a linear molecule.

Extrapolation of the plot for the mean-square thermal displacements of all atoms to $T = 0$ K reveals that the ordinate intercept is $u_0^2 \sim 0.006 \text{ \AA}^2$. This result shows that there is a certain static disorder which apparently can be attributed to the distortion of the structure due to a systematic deficiency of Cu and O.

¹I. Nakai, S. Sueno, F. P. Okamura, and A. Ono, *Jpn. J. Appl. Phys.* **26**, L778 (1987).

²S. Sato, I. Nakada, T. Konara, and Y. Oda, *Acta Cryst.* **C44**, 11 (1988).

³V. N. Topnikov, V. I. Simonov, L. A. Muradyan *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **46**, 457 (1987) [*JETP Lett.* **46**, 577 (1987)].

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