Equation of state and compressibility of single crystals of the high-temperature superconductor $YBa_2Cu_3O_x$ at pressures up to 20 GPa

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Results of x-ray measurements of the parameters of the unit cell of $YBa_2Cu_3O_x$ single crystals at pressures up to 20 GPa are reported. The equation of state and the linear compressibilities are found from the experimental data. There is a substantial anisotropy in the compressibility in the directions along and perpendicular to the c axis ($\beta_{\parallel} > \beta_{\perp}$). The compressibility of a tetragonal crystal along the c direction is substantially greater than that of an orthorhombic crystal.

This letter reports measurements of the parameters of the unit cell of the tetragonal and orthorhombic phases of the high-temperature superconductor $YBa_2Cu_3O_x$ at high pressures. The results of some earlier studies[1–3] of these questions did not seem completely convincing because of the nonhydrostatic experimental conditions and also because of the ambiguity in the interpretation of x-ray powder patterns. In the present study, as in Refs. 1–3, we used the diamond-anvil technique, but the single-crystal samples were immersed in a medium of compressed helium. Consequently, the experimental conditions were essentially hydrostatic (see Ref. 4 for the experimental details).

We selected samples from among $YBa_2Cu_3O_x$ single crystals annealed in flowing oxygen and helium, respectively. The oxygen-rich crystals[1)] ($x \lesssim 7$) are an orthorhombic phase which conducts well ($T_c \lesssim 93$ K; Ref. 5), with a clearly expressed twin structure. The "helium" crystals[1)] ($x \gtrsim 6$) were tetragonal and exhibited semiconducting properties down to 4 K. Measurements were carried out on specially selected single-crystal samples with dimensions $\sim 80 \times 60 \times 20\,\mu$m. The lattice parameters were determined on the basis of the (006), (200), (020), and (110) x-ray reflections within ± 0.002 Å. The pressure in the chamber was measured on the basis of the shift of the R_1 luminescence line of a ruby gauge with a random error of[2)] ± 0.1 GPa (Ref. 7). All the measurements were carried out at room temperature.

Figure 1 shows the parameters of the $YBa_2Cu_3O_x$ unit cell versus the pressure according to four series of experiments. Table I shows the values calculated for the linear compressibility, the "two-dimensional" compressibility, the bulk modulus, and other properties which characterize these single-crystal samples.

It can be seen from Fig. 1 and Table I that for all the samples there is characteristically a substantial anisotropy in the linear compressibility in the directions parallel and perpendicular to the c axis ($\beta_{\parallel} > \beta_{\perp}$). This anisotropy leads to an inversion of the sign of the expression $[c/3 - (a+b)/2]/\bar{a}$ ($\bar{a} = V^{1/3}$; Figs. 1 and 2) at high pressures. It is important to note that compressibility $\beta_{\parallel}$ for the oxygen-deficient tetra-

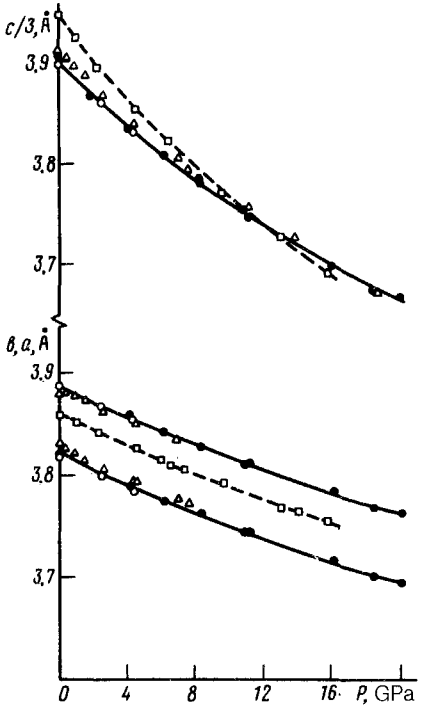

FIG. 1. Lattice constants of $YBa_2Cu_3O_x$ single crystals versus the pressure. □—Tetragonal crystal; Δ, ●, ○—orthorhombic crystals 1, 2, 3, respectively.

gonal crystal is significantly higher than that for the oxygen-rich orthorhombic crystal (Table I). This tendency persists at high pressures, since the corresponding compression curves cross at $P \approx 10$ GPa.

The anisotropy in the linear compressibility of orthorhombic crystals 2 and 3 in

TABLE I.

Symmetry property[3)]	Tetragonal	Orthorhombic 1	Orthorhombic 2	Orthorhombic[4] 3
a, Å	3.861 ± 0.002	3.830 ± 0.003	3.820 ± 0.002	3.820 ± 0.002
b, Å	3.861 ± 0.002	3.885 ± 0.005	3.888 ± 0.003	3.888 ± 0.002
c, Å	11.833 ± 0.002	11.72 ± 0.02	11.68 ± 0.03	11.688 ± 0.002
$\beta_a \cdot 10^{-3}$, GPa^{-2}	2.13 ± 0.05	2.69 ± 0.14	2.30 ± 0.22	2.30
$\beta_b \cdot 10^{-3}$, GPa^{-2}	2.13 ± 0.05	2.00 ± 0.10	2.21 ± 0.28	2.10
$\beta_{ab} \cdot 10^{-3}$, GPa^{-2}	4.26 ± 0.10	4.22 ± 0.17	4.25 ± 0.24	4.42
$\beta_c \cdot 10^{-3}$, GPa^{-2}	5.74 ± 0.19	4.25 ± 0.18	4.16 ± 0.21	4.23
K_0, GPa	100.1 ± 1.5	112.0 ± 2.1	117.7 ± 8.1	114.8
K_0'	4.53 ± 0.18	4.6 ± 0.5	4.4 ± 0.7	–

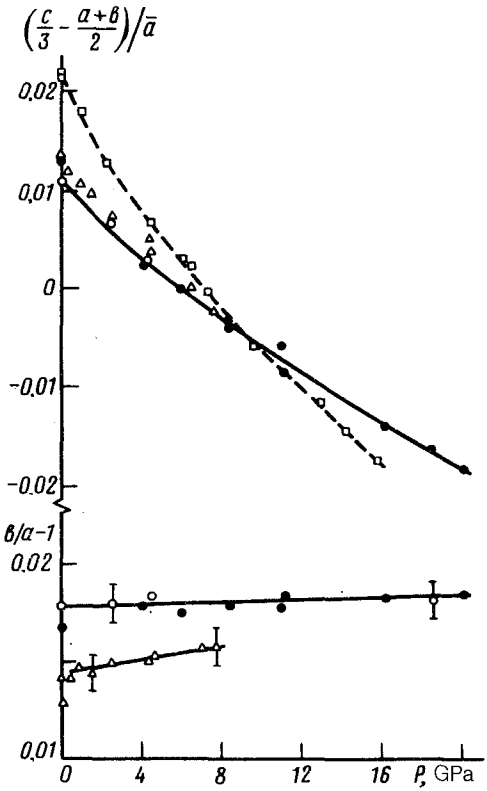

FIG. 2. Parameters of the deformation of the $YBa_2Cu_3O_x$ lattice versus the pressure. The notation is the same as in Fig. 1. The scatter in the data on $(b/a-1)$ near the OGPa is attributed to the defective state of the lattice of initial orthorhombic crystals 1 and 2.

the *ab* plane is hardly noticeable, but it is clearly visible in the case of crystal 1 (Table I and Fig. 2). However, the "two-dimensional" compressibility in the *ab* plane (numerical values and a definition are given in Table I) agrees within the experimental error for all of the samples studied, including the tetragonal one. Nevertheless, this difference in the linear compressibilities $\beta_{\parallel}$ keeps the bulk compressibility of the tetragonal crystal higher than those of the orthorhombic crystals at all times (Fig. 3 and Table I). It can be seen from Fig. 3 that this effect cannot be explained on the basis of a trivial volume dependence of the bulk compressibility (the inverse quantity—the bulk modulus—is shown in Fig. 3).

In summary, it can be concluded that the presence or absence of oxygen in the $(x, y, 0)$ plane, although having a definite effect on the linear compressibility in the *ab* plane, has essentially no effect on the "two-dimensional" compressibility. On the other hand, the compressibility along the c axis and thus the bulk compressibility or the bulk modulus depend strongly on the oxygen concentration in this plane. The direct interaction of the oxygen in the $(x, y, 0)$ plane with the nearest copper atoms is apparently a weak one. Further evidence for this conclusion comes from the nature of the rhombic deformation of the $YBa_2Cu_3O_7$ crystal upon saturation of the "original" tetragonal phase of $YBa_2Cu_3O_6$ with oxygen (Table I). Comparing the corresponding

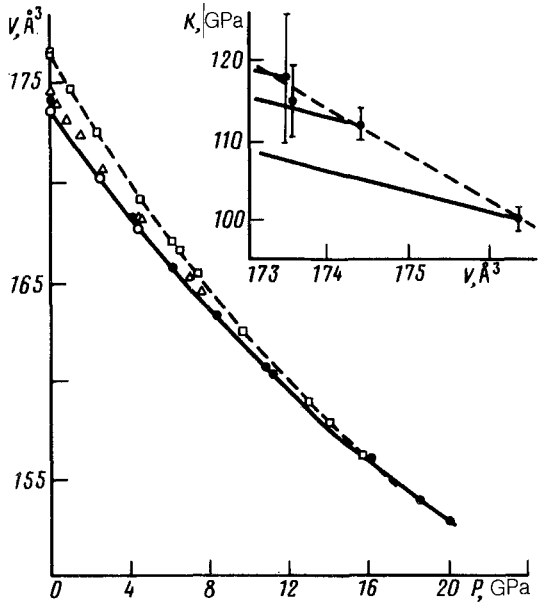

FIG. 3. Compression isotherms of $YBa_2Cu_3O_x$. The notation is the same as in Fig. 1. The inset shows the initial bulk modulus K_0 as a function of the initial volume for the set of $YBa_2Cu_3O_x$ crystals. The solid lines show results on $K(V)$ found from the experimental data.

parameters of the tetragonal and orthorhombic phases, we easily see that the greatest deformation occurs in the direction parallel to the chains of copper atoms which are free of oxygen atoms.

There can thus be no doubt that the effect of the "excess" oxygen on the crystal structure and mechanical properties of $YBa_2Cu_3O_x$ is genetically related to definite changes in the electron subsystem of the crystal and thus the formation of long-range anisotropic forces which tend to contract the lattice along the c axis and cause a rhombic distortion of it. Nevertheless, it should be noted that the mechanical effects observed here could also be explained, in a first approximation, on the basis of a short-range interaction of the "excess" oxygen and the barium.

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[1)]The oxygen concentration in a crystal can be determined approximately from the value of the lattice constant c (Ref. 6, for example).

[2)]1 GPa = 10^4 bar = 10 kbar.

[3)]Here a, b, and c are the parameters of the unit cell; $\beta_l = -(1/l)(\partial l/\partial P)_T$, where $l = a, b, c$; $\beta_{ab} = -(1/S)(\partial S/\partial P)_T$, where $S = a \times b$; $K_0 = -V(\partial P/\partial V)_T$; $K_0' = (\partial K/\partial P)_T$. All quantities are referred to a zero pressure and are determined from the expression $P = K[(A_0/A) + 1/2(K' - 1)(A_0/A)^2]$, where A is the measured quantity, A_0 is its value at $P = 0$, and K and K' are the reciprocal of the compressibility and its first derivative with respect to the pressure.

[4)]Since few experimental points are available, it is difficult to estimate the errors in the calculated values.

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