X-ray investigation of the equation of state of $PrBa_2Cu_3O_{7-y}$

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The results of x-ray measurements of the unit-cell parameters of an untwinned single crystal of $YBa_2Cu_3O_7$, a twinned single crystal of $PrBa_2Cu_3O_{7-y}$, and a single crystal of Nd_2CuO_4 at pressures up to 120 kbar have been presented. Conspicuous anisotropy of the compressibility in the **a** and **b** directions have been discovered in nonconducting $PrBa_2Cu_3O_{7-y}$. The corresponding anisotropy in $YBa_2Cu_3O_7$ is considerably weaker. The linear compressibility along the c axis is significantly greater in Nd_2CuO_4 than in La_2CuO_4.

1. INTRODUCTION

Measurements of the equation of state of single crystals of $YBa_2Cu_3O_x$ with $x \approx 6$ and $x \approx 7$ were previously reported in Ref. 1. The $YBa_2Cu_3O_7$ crystals used in Ref. 1 were typical twinned formations with a domain width of the order of 1000 Å. One somewhat unexpected result of that investigation was the claim that the oxygen concentration has a vanishingly small influence on the compressibility in the **ab** plane and, accordingly, that there is no anisotropy of the compressibility in the **a** and **b** directions despite the obvious anisotropy of the crystal structure when $x > 6.5$ and the quite conspicuous anisotropy of the thermal expansivity when $x > 6.5$ (Refs. 2 and 3). Here we present the results of new investigations of the equation of state of $YBa_2Cu_3O_7$ employing a monodomain sample to rule out any possible influence of the twinned structure on the behavior of the crystal at high pressure.

The results of high-pressure measurements of the unit-cell parameters of $PrBa_2Cu_3O_{7-x}$ the nonconducting structural analog $YBa_2Cu_3O_{7-x}$ and Nd_2CuO_4, which serves as a matrix for obtaining "electronic superconductors," are also reported.

2. EXPERIMENTAL PROCEDURE

Crystals of $YBa_2Cu_3O_x$ were obtained in a platinum crucible by the solution-melt method from a CuO–$BaCO_3$–Y_2O_3 oxide mixture, whose components were taken in a 1.96:22.11:75.93 mole % ratio. The mixture was heated to 1170 °C at a rate of 120 °C/h and was cooled to 920 °C at a rate of 20 °C/h. Then the temperature was allowed to decline to 860 °C, and the melt was decanted. The crystals obtained were annealed in an oxygen atmosphere at 600 °C for 24 h. The temperature was subsequently lowered at a rate of 10 °C/h to room temperature. Monodomain regions were identified in the samples investigated with the aid of an optical microscope and then pricked out by a needle.

Crystals of $PrBa_2Cu_3O_x$ were also obtained by the solution-melt method in a platinum crucible from a CuO–$BaCuO_3$–Pr_2O_3 oxide mixture, whose components were taken in a 0.16:22.52:77.32 mole % ratio. The temperature of the mixture was raised to 1050 °C at a rate of 120 °C/h, lowered to 910 °C at a rate of 20 °C/h, and subsequently allowed to decline to 840 °C. Then the melt was decanted. The $PrBa_2Cu_3O_x$ crystals were annealed in an atmosphere of oxygen under the same conditions as the $YBa_2Cu_3O_x$ crystals. The oxygen content in the $YBa_2Cu_3O_x$ and $PrBa_2Cu_3O_x$ crystals was evaluated from the unit-cell parameters and was found to be $x \approx 7$ and $x \approx 6.8$, respectively.[4,5]

Single crystals of Nd_2CuO_4 were grown by the solution-melt method from a nonstoichiometric melt with

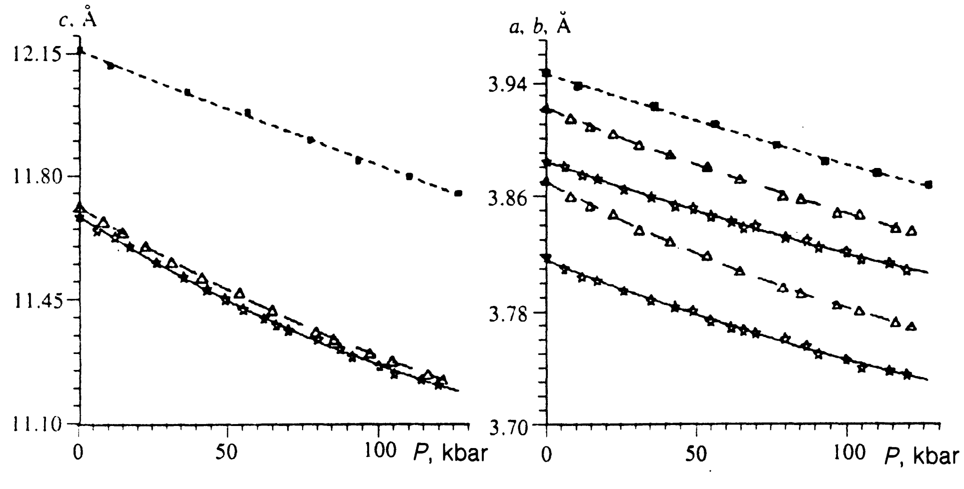

FIG. 1. Pressure dependence of the lattice constants of a monodomain single crystal of $YBa_2Cu_3O_7$ (☆), a single crystal of $PrBa_2Cu_3O_{7-y}$ (△), and a single crystal of Nd_2CuO_4 (■).

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an excess of CuO in an alundum crucible. The original Nd_2O_3:CuO mixture was taken in a 15:85 mole % ratio. After the mixture was heated to 1300 °C and held at that temperature for 2 h, the melt temperature was lowered at a rate of 5 °C/h in the presence of a 10 °C/cm vertical temperature gradient until a solid phase appeared on the surface of the melt (1060–1070 °C). Then the furnace was quickly cooled at a rate greater than 100 °C/h to room temperature. This made it possible to separate the crystals formed from the solidified melt with relative ease.

High pressures were created in the present work in a diamond cell, which makes it possible to perform x-ray investigations of single crystals over a broad range of diffraction angles. The pressure-transmitting medium was helium, which ensured nearly hydrostatic compression conditions (for the experimental details, see Ref. 6). The pressure was determined from the shift of the R_1 luminescence line of ruby crystals with an accuracy of ± 0.1 GPa.[7] The measurements were performed on a DRON-2.0 diffractometer. An x-ray tube with a molybdenum cathode ($\lambda = 0.709261$ Å) served as a source of x radiation. The samples for the investigation were single crystals measuring $60 \times 60 \times 20$ μm^3 [Y(123)], $70 \times 40 \times 20$ μm^3 [Pr(123)], and $70 \times 70 \times 30$ μm^3 (Nd_2CuO_4). The parameters a, b, and c were determined from the positions of the (200), (020), and (010) diffraction lines, respectively, with an accuracy of ± 0.002 Å. When the anvils were loaded, the lattice constants decreased monotonically with increasing pressure without any appreciable changes in the intensities or widths of the lines. All the measurements were performed at room temperature.

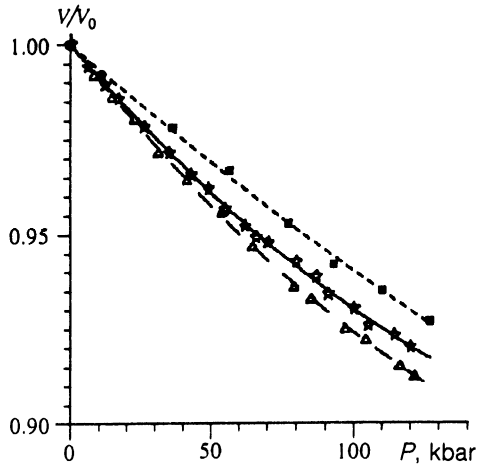

FIG. 2. Dependence of the normalized unit-cell volume on the pressure. The notation is the same as in Fig. 1.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1 and 2 present plots of the dependence of the unit-cell parameters and normalized volume on the pres-

TABLE I.

Property	Symmetry			
	Tetragonal $Y(123)^1$	Orthorhombic $Y(123)^1$	Orthorhombic$^{(a)}$ monodomain $Y(123)$	Orthorhombic$^{(a)}$ $Pr(123)$
a, Å	3.861 ± 0.002	3.820 ± 0.002	3.819 ± 0.002	3.871 ± 0.002
b, Å	3.861 ± 0.002	3.888 ± 0.003	3.885 ± 0.002	3.922 ± 0.002
c, Å	11.833 ± 0.002	11.68 ± 0.03	11.686 ± 0.002	11.712 ± 0.002
$\beta_a \cdot 10^{-3}$, GPa^{-1}	2.13 ± 0.05	2.30 ± 0.22	2.19 ± 0.02	3.12 ± 0.02
$\beta_b \cdot 10^{-3}$, GPa^{-1}	2.13 ± 0.05	2.21 ± 0.28	2.02 ± 0.02	2.26 ± 0.02
$\beta_{ab} \cdot 10^{-3}$, GPa^{-1}	4.26 ± 0.01	4.25 ± 0.24	4.21 ± 0.02	5.34 ± 0.03
$\beta_{c} \cdot 10^{-3}$, GPa^{-1}	5.74 ± 0.19	4.16 ± 0.21	4.21 ± 0.02	4.59 ± 0.02
K_0, GPa	100.1 ± 1.5	117.7 ± 8.1.	112.7 ± 1.2	101.0 ± 1.0

Note: a, b, and c are the unit-cell parameters; $\beta_l = -(1/l)(\partial l/\partial P)_T$, where $l = a, b, c$; $\beta_{ab} = -(1/S)(\partial S/\partial P)_T$, where $S = a \times b$; $K_0 = -V(\partial P/\partial V)_T$. All the values refer to zero pressure and were determined by the least-squares method from the expression $P = K[(A_0/A - 1) + (1/2)(K' - 1)(A_0/A - 1)^2]$, where A is the quantity being measured, A_0 is its value at $P = 0$, K and K' are the reciprocal of the compressibility and its first derivative with respect to the pressure, and $K'_0 = (\partial K/\partial P)_T$.

[a] Data from the present work.

TABLE II.

Property	Compound		
	Nd_2CuO_4*	Pr_2CuO_4 (Ref. 8)	La_2CuO_4 (Ref. 8)
a, Å	3.947 ± 0.002	3.958	5.363
b, Å	3.947 ± 0.002	3.958	5.409
c, Å	12.162 ± 0.002	12.284	13.17
$\beta_a \cdot 10^{-3}$, GPa^{-1}	1.85 ± 0.03	1.6	1.7
$\beta_b \cdot 10^{-3}$, GPa^{-1}	1.85 ± 0.03	1.6	2.0
$\beta_{ab} \cdot 10^{-3}$, GPa^{-1}	3.68 ± 0.05	—	—
$\beta_c \cdot 10^{-3}$, GPa^{-1}	2.86 ± 0.03	3	1.6
K_0, GPa	153.1 ± 2.1	160	182

(for explanations of the notation, see notes to Table I).

sure. The figures include data for the three compounds, viz., untwinned $YBa_2Cu_3O_7$, $PrBa_2Cu_3O_{7-y}$, and Nd_2CuO_4. Tables I and II present the linear and two-dimensional compressibility, as well as the bulk modulus obtained in the present work and in Refs. 1 and 8.

Let us first discuss the results pertaining to the compressibility of the untwinned crystal of $YBa_2Cu_3O_7$. As is seen from Table I and Fig. 1, the main conclusion in Ref. 1 regarding the weak influence of the chain oxygen atoms on the compressibility in the *ab* plane for a single crystal of $YBa_2Cu_3O_x$ with an oxygen content $x=7$ remains valid, although some weak anisotropy probably still exists.

The situation is totally different in the case of $PrBa_2Cu_3O_{7-y}$, where the anisotropy of the compressibility in the **a** and **b** directions is fairly pronounced (see Table I and Fig. 1). We note that the compressibility is smaller in the **b** direction, i.e., along the Cu–O–Cu–O chains, than in the **a** direction, which is devoid of oxygen. Interestingly, this effect is strongly depressed in the case of $YBa_2Cu_3O_7$. We note that the unit-cell parameters and the compressibility along the **c** axis for comparable substances are very similar. This difference is probably caused by the different types of interparticle interactions in these two compounds. We recall that $PrBa_2Cu_3O_7$ unlike $YBa_2Cu_3O_7$, is nonconducting, i.e., nonmetallic, and the distribution of the valence-band electron density should be highly nonuniform in this case. As follows from the data in Table I, the anisotropy of the compressibility in the **ab** plane for $PrBa_2Cu_3O_7$ is, in fact, a consequence of the increased compressibility (as compared with $YBa_2Cu_3O_7$) along the "empty" Cu–Cu–Cu chains, which is probably an indication of a reduced valence-band electron density in the space between the copper atoms and weakness of the Cu–Cu interaction.

It must be mentioned in this context that the anisotropy of the compressibility in the **ab** plane is very pronounced in conducting $YBa_2Cu_4O_8$ with double chains.[9] These data may point to a somewhat different role for the chains in $YBa_2Cu_4O_8$ than in $YBa_2Cu_3O_7$. This is also indicated by the unusually strong dependence of the temperature of the superconducting transition in $YBa_2Cu_4O_8$ on the pressure.[10]

The results obtained for Nd_2CuO_4 are compared in Table II with the corresponding results for Pr_2CuO_4 and La_2CuO_4, which were taken from Ref. 8. These compounds are known to be nonconducting, and the large difference in compressibility along the **c** axis between Nd_2CuO_4 and Pr_2CuO_4, on the one hand, and La_2CuO_4, on the other hand, illustrates only the difference between the crystal structures of these compounds (T' for Nd_2CuO_4 and Pr_2CuO_4 and T for La_2CuO_4). The absence of the "apical" oxygen in the T'-type structure results in increased compressibility along the c axis (this was also noted in Ref. 8).

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