

# Properties of internal (chemical) pressure in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ perovskite created by oxygen

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The properties of internal (chemical) pressure  $P_i$  in superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  perovskite are analytically investigated. Predicted are the values of the critical temperature  $T_c$  for the main crystallographic axes, the change of the value of  $dT_c/dP_i$  and the possibility to obtain  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  samples with  $T_c = 166.7$  K.

Виконано аналітичне дослідження з метою визначення властивостей внутрішнього (хімічного) тиску  $P_i$  в надпровідному перовскіті  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . Передбачено значення критичної температури  $T_c$  для головних кристаллографічних осей, зміну величини  $dT_c/dP_i$ , а також можливість виготовлення  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  зразків з  $T_c = 166.7$  К.

**Властивості внутрішнього (хімічного) тиску у надпровідному  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  перовскіті, створеному киснем. В.П.Хірній.**

Виконано аналітичне дослідження властивостей внутрішнього (хімічного) тиску  $P_i$  у надпровідному перовскіті  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . Передбачено значення критичної температури  $T_c$  для різних кристаллографічних осей, зміну величини  $dT_c/dP_i$ , а також можливість виготовлення  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  зразків з  $T_c = 166.7$  К.

## 1. Introduction

Changes in the properties of HTSC doped with metals and of other perovskites are often referred to the influence of the internal pressure  $P_i$  on their crystalline structure, see e.g. [1].  $P_i$  is expressed in the form [1]:

$$P_i = (1/k_i)[1 - a_i(x \neq 0)/a_i(x = 0)], \quad (1)$$

where  $k_i$  are the compressibility coefficients: volume  $k_v$  and linear — in the direction of compressibility along the crystallographic axes "a" —  $k_a$ , "b" —  $k_b$ , "c" —  $k_c$ ;  $a_i$ , the crystal lattice parameters  $a$ ,  $b$ ,  $c$  and the elementary cell volume  $V$ ;  $x$ , the quantity of doping impurity.

The properties of the superconducting compound  $\text{Y}(\text{Ba},\text{M})_2\text{Cu}_3\text{O}_{9-y}$  doped with Sr,

La are considered in [2]. The impurities selectively substitute up to 35 % of Ba without arbitrary replacement of Y by Sr or La. The substitution of Ba by Sr created conventional chemical pressure. At the same time the substitution by La raised the amount of oxygen and the value of internal pressure in the crystal lattice.

For determination of the value of internal pressure created by oxygen in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  samples it is necessary to know the relation between the oxygen index and the crystal lattice constants. Such a relation was found in [3, 4], where  $(7-y)$  varied from 6.2 to 6.9. Thereat, the constants **a** and **c** diminished, whereas **b** increased, i.e. there was observed distortion of the crystal lattice due to internal (local) deformation.

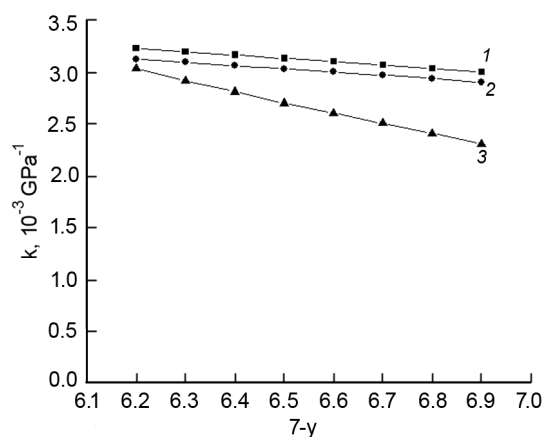


Fig. 1. Dependences of linear compressibility coefficients on the oxygen index of (7-y): 1 -  $k_c$ , 2 -  $k_a$  and 3 -  $k_b$ .

Investigation of the properties of cuprate HTSC with oxygen non-stoichiometry is greatly significant for understanding of the mechanism of superconductivity [5–8]. In the present work there was analytically determined the internal pressure created by oxygen in superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ .

## 2. Discussion

For this purpose in (1)  $a_i(x \neq 0)$  and  $V(x \neq 0)$  were replaced by  $a_i(7-y)$  and  $V(7-y)$ , respectively, with the values taken from [3];  $a_i(0)$  and  $V(0)$  were assumed to be equal to  $a_i$  and  $V$ , respectively, in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$  sample [3]. The values of compressibility coefficients  $k_i$  were taken from [9] for the compounds  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$ . As  $k_v$  linearly diminishes with the growth of (7-y) from 6.0 to 7.0 and  $k_v = k_a + k_b + k_c$  [9], each of these terms linearly depends on (7-y), too. They were determined by means of linear extrapolation.

Two known values of  $k_i$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$ , i.e. at (7-y) equal to 6.6 and 6.93 [9], were joined by straight line. Fig. 1 presents the dependences of  $k_a$ ,  $k_b$  and  $k_c$  on the oxygen index values. The oxygen index varied from 6.3 to 6.9 at an interval of 0.1. As follows from Fig. 1, the linear compressibility coefficients change along the direction of the main axes at the rates  $dk_a/d(7-y) \cong dk_c/d(7-y) = -3 \cdot 10^{-5} \text{ GPa}^{-1}$ ,  $dk_b/d(7-y) = -9.5 \cdot 10^{-4} \text{ GPa}^{-1}$ . The volume compressibility coefficient  $dk_v/d(7-y) = -2 \cdot 10^{-3} \text{ GPa}^{-1}$  [9].

Shown in Fig. 2 are the linear internal pressures directed along the axes  $a$ ,  $b$  and  $c$ , i.e.  $P_a$ ,  $P_b$ ,  $P_c$ , and the volume internal pressure  $P_v$  depending on the oxygen index.

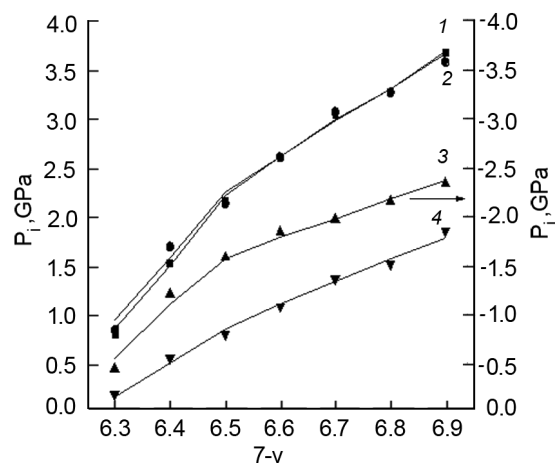


Fig. 2. Changes of the internal pressure  $P_i$  at variation of the oxygen index: 1 -  $P_a$ , 2 -  $P_c$ , 3 -  $(-P_b)$ , the negative sign denotes extension, 4 -  $P_v$ .

Their values were obtained from the modified formula (1). The negative sign testifies that there takes place extension. The graphs have a singularity in the form of the change in the slope of the straight lines at  $(7-y) = 6.5$  which coincides with the location of the plateau in the dependence of  $I_c$  on the value of  $(7-y)$  [4].

As is known [4], the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  has three modifications. They are: the superconducting orthorhombic-I phase with  $T_c \cong 90 \text{ K}$  and  $(7-y) = 7.0 \div (6.8 \div 6.75)$ ; the orthorhombic-II phase with  $T_c = 60 \div 40 \text{ K}$ , and  $(7-y)$  changing from 6.65 to 6.4; the tetragonal non-superconducting modification with  $6.0 < (7-y) < (6.25 \div 6.4)$ . The structure transformations in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  occur without abrupt disturbance of the lattice parameters and of the samples' composition and properties. Such transformations belong to phase transitions of the second or higher order. Therefore, we assume that the singularity in Fig. 2 arises at the temperature of the transition from the ortho-I to the ortho-II characterized by the change in the curvature of the dependences of  $a_i$  on  $(7-y)$  [3, 4]. This is clearly seen for the dependences of  $a_i(x \neq 0)$  on  $x$  in doped samples, e.g. in  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$  [10].

In yttrium and rare-earth HTSC compounds there is observed a universal correlation of  $T_c$  with the quantity of oxygen [4]. Therefore, one can find the dependence of  $T_c$  on  $P_i$  (see Fig. 3) and  $dT_c/dP_i$  at the values of oxygen index ranging between 6.3 and 6.9 (see Fig. 4). Earlier [11] there was revealed the influence of the change in the

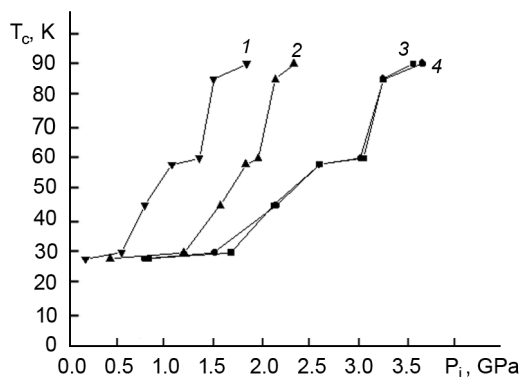


Fig. 3. Dependences of  $T_c$  on  $P_i$ : 1 -  $P_v$ , 2 -  $P_b$ , 3 -  $P_a$ , 4 -  $P_c$ .

content of oxygen in the samples subjected to the external pressure  $P$ , on the derivative  $dT_c/dP$ . However, in the mentioned paper the changes of the oxygen index and internal pressure caused by the applied pressure were not taken into account.

Shown in Fig. 4 are the rates of the change of  $T_c$  with variation of  $P_i$  at different  $(7-y)$  values. As follows from this figure, at  $(7-y) = 6.5 \div 6.6$  and  $6.8$  the values of  $dT_c/dP_i$  exceed the value of  $dT_c/dP$  for the samples subjected to the influence of the external pressure  $P$  up to 13 kbar [12], by two and three orders, respectively. In particular, for  $\text{YBa}_2\text{Cu}_3\text{O}_7$   $dT_c/dP = 0.5$  K/GPa (theory) and 0.4 K/GPa (experiment), and only for  $\text{PrBa}_2\text{Cu}_3\text{O}_7$   $dT_c/dP = 3.5$  K/GPa [13]. The curves presented in Fig. 4 have two maxima separated by a narrow minimum at  $(7-y) = 6.7$ . One of them, broad and low, with  $(dT_c/dP_i)_{max} \cong 60$  K/GPa is located in the region of the existence of the ortho-II phase. The other maximum, narrow and high, with  $(dT_c/dP_i)_{max} = 166.7$  K/GPa lies in the region of the ortho-I phase.

The change of  $T_c$  results in the change of the number of holes  $n_h$  per elementary cell [14]. Fig. 5 presents the dependences of  $n_h^i$  on  $P_i$ , where  $i$  denotes the crystal lattice constants **a**, **b** and **c**. As is seen, low  $P_i$  values correspond to the threshold pressure  $P_i^n$ . For the main crystallographic axes the threshold pressures are the following:  $P_a^n = P_c^n = 1.55$  GPa,  $P_b^n = 1.25$  GPa. For the volume internal pressure  $P_v^n = 0.5$  GPa. Starting from this point, under the influence of the internal pressure created by oxygen, the holes are formed at the rate  $dn_h/dP_i$ . The threshold effect revealed in experiments with external pressure  $P$  was earlier reported in [12].

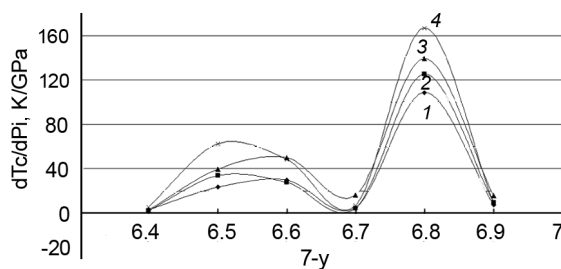


Fig. 4. Change of  $dT_c/dP_i$  derivative at variation of the oxygen index of  $(7-y)$ : 1 -  $dT_c^a/dP_a$ , 2 -  $dT_c^c/dP_c$ , 3 -  $dT_c^b/dP_b$ , 4 -  $dT_c^v/dP_v$ .

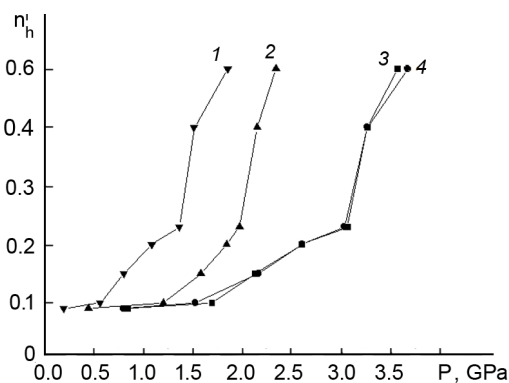


Fig. 5. Dependences of the number of holes per elementary cell  $n_h^i$  on  $P_i$ : 1 -  $n_h^v$  on  $P_v$ , 2 -  $n_h^b$  on  $P_b$ , 3 -  $n_h^a$  on  $P_a$ , 4 -  $n_h^c$  on  $P_c$ .

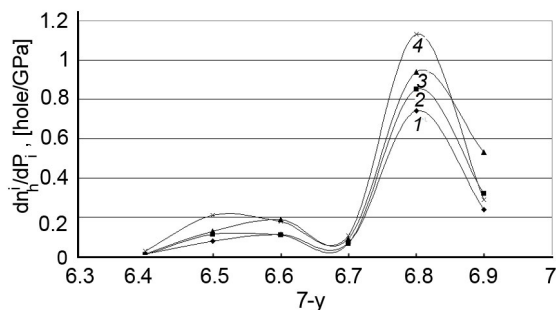


Fig. 6. Dependences of the change in the number of holes per elementary cell  $dn_h^i/dP_i$  on variation of the oxygen index: 1 -  $dn_h^a/dP_a$ , 2 -  $dn_h^c/dP_c$ , 3 -  $dn_h^b/dP_b$ , 4 -  $dn_h^v/dP_v$ .

Shown in Fig. 6 are the dependences of  $dn_h^i/dP_i$  on the value of  $(7-y)$ , i.e. the rate of the change in the number of holes per elementary cell. Each of these dependences has two maxima. Just as it has been expected, their form correlates with the behavior of the dependences  $dT_c/dP_i$  on the oxygen index (Fig. 4). In the paper [11] the authors report the existence of only one maximum at  $(7-y) = 6.8$  depending on  $d\Delta n_h/dP$ , where  $\Delta n_h$  is the concentration of

mobile holes in the  $\text{CuO}_2$  planes. Such a fact is explained as follows. In the present work we have taken into account the influence of all the holes on  $T_c$ , so the latter changes with  $n_h$  almost linearly [14]. In [11] the graph of the dependence of  $T_c$  on  $\Delta n_h$  is shaped as upturned parabola, since there has been only considered the influence of the mobile holes transported from the chains formed by CuO in the plane  $\text{CuO}_2$ . Therefore, in the ortho-II phase superconductivity is due to the mobile holes located in the CuO chains. It should be noted that the holes in the  $\text{CuO}_2$  planes are partially localized. With further oxidation the mechanism of superconductivity (in the ortho-I phase) is defined by the mobile holes located in the  $\text{CuO}_2$  planes, whereas the chains become a reservoir for the holes.

The obtained result allows to make some conclusions. First of all, one can achieve  $T_c = 166.7$  K in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  samples. Secondly, the changes in the value of the derivative  $dT_c/dP_i$  depend on the degree of oxidation, the quantity of dopant ions and their radii (see Fig. 4). In particular, if in the sample which exists in the ortho-II modification the value of  $(7-y)$  is raised from 6.4 to 6.7 by means of oxidation, doping and/or application of external pressure,  $dT_c/dP_i$  will at first grow and then diminish. At further rise of  $(7-y)$  from 6.7 to 6.8 the derivative will increase again. However, at  $(7-y) = 6.8$  the value of  $dT_c/dP_i$  will start diminishing at any slightest change in the quality of oxygen and/or  $P_i$ . Note that each direction of the main crystallographic axes has its own limiting value of the critical temperature  $T_c^i$ :  $T_c^c = 108.7$  K,  $T_c^a = 125$  K,  $T_c^b = 138.9$  K.

There exists an analogy between the predicted here and experimentally observed behavior of  $dT_c/dP$  reported in many papers. Thus, we assume that, as a rule, the value of  $T_c$  for all oxide HTSC depends on the internal oxygen pressure. One can only change the conditions of  $T_c$  measurement by means of oxidation, doping and/or application of external pressure.

As an example, consider the compound  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+y}$  which  $T_c$  at  $P = 15$  GPa rises from  $T$  ( $P = 0$ ) = 135 K up to 150 K [15], whereas at  $P = 30$  GPa  $T_c = 160$  K, which is close to the value predicted here. Note that, according to Fig. 6, the behavior

of  $dT_c/dP_i$ , with changing  $dn_h/dP_i$  will be similar.

### 3. Conclusions

Thus, assuming that not only mobile, but all the holes in the samples  $\text{YBa}_2\text{Cu}_3\text{O}_7$  influence  $T_c$ , we predict in the performed analytical investigation that: one can obtain a superconductor with  $T_c = 166.7$  K;  $dT_c/dP$  is not a constant value, since it increases or diminishes depending on internal pressure of oxygen defined by initial oxidation, doping and/or application of external pressure; each direction of the main crystallographic axes has its own  $T_c$ .

Actually, real experiments with high pressures are complicated due to mutual effect of the internal and external pressures.

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