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THE STRUCTURE OF  $\text{HgBa}_2\text{CuO}_{4+\delta}$   
AT AMBIENT AND HIGH PRESSURE  
AT  $0.06 \leq \delta \leq 0.19$

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## 1. INTRODUCTION

The  $\text{HgBa}_2\text{CuO}_{4+\delta}$  phase (Hg-1201) is at the moment one of the most thoroughly studied high-temperature superconductors from the point of view of relation between atomic structure and physical properties. Its structure <sup>1/1</sup> can be described in terms of four layers,  $(\text{HgO}_\delta)(\text{BaO})(\text{CuO}_2)(\text{BaO})$ , stacked along the  $c$  axis of the tetragonal unit cell. The  $(\text{HgO}_\delta)$  and  $(\text{CuO}_2)$  layers are flat, while the Ba and O atoms in the  $(\text{BaO})$  layer are displaced  $\sim 0.9 \text{ \AA}$  from each other along the  $c$  axis due to the interaction of these atoms with the neighboring layers. Owing to the high crystallographic symmetry and the small number of atoms, the structure has only a few variable parameters, which can be determined with high degree of reliability from structural refinements based on diffraction data. Unlike the majority of the other HTSC-compounds, such peculiarities as stacking faults, structure modulations, large static displacements of atoms, etc. are practically absent in Hg-1201.

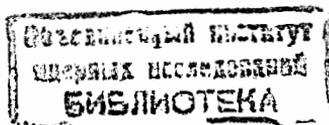
It is generally assumed that the  $(\text{HgO}_\delta)$  layer acts as charge reservoir for the  $(\text{CuO}_2)$  planes. The insertion of  $\text{O}_\delta$  oxygen into it leads to the appearance of charge carriers (holes) in the  $(\text{CuO}_2)$  layer. By adjusting the oxygen content in the  $(\text{HgO}_\delta)$  layer, the doping level of Hg-1201 can be easily varied over a wide range, from strongly underdoped to highly overdoped states of which some are non superconducting.

Both functional and quantitative relationships between  $T_c$  and  $\delta$  are still controversial. The data published (see, for example, <sup>1/2, 1/3</sup>) do not contradict the universal parabolic dependence of Presland *et al.* <sup>1/4</sup>:

$$T_c = T_{c,\text{max}} [1 - q (\delta - \delta_{\text{opt}})^2], \quad (1)$$

though recent results <sup>1/5</sup> are not in agreement with the above equation. The quantitative disagreements are mostly due to the uncertainty in the  $\delta_{\text{opt}}$ , the value at which the maximum superconducting transition temperature,  $T_{c,\text{max}}$  is observed. The Hg-1201 structural refinements based on powder neutron diffraction data, gave  $\delta_{\text{opt}}$  values comprised between 0.06 <sup>1/6</sup> and 0.18 <sup>1/2</sup>.

Another question about Hg-1201 still remaining without a clear answer, is the reason for the variation of  $T_c$  with increasing external pressure. Cao *et al.* <sup>1/7</sup> and more recently Qiu *et al.* <sup>1/8</sup> have measured  $T_c$  in a wide  $\delta$  range and shown that  $dT_c/dP$  strongly depends on the doping level. The underdoped and optimally doped Hg-1201 samples exhibit initially an increase of  $T_c$  with pressure up to 6-8 GPa with  $dT_c/dP \approx 2 \text{ K/GPa}$ , while the latter rate is smaller and becomes even negative for overdoped samples. These authors concluded that the superconducting region seems to shrink significantly with  $P$ , and, the  $T_c$  vs.  $\delta$  dependence changes from inverse parabolic at ambient pressure to truncated triangle-like above 10 GPa. The  $T_{c,\text{max}}$  under pressure was found to be nearly  $\delta$ -independent around the optimal doping level, which supports the idea put forward in reference <sup>1/8</sup> that the pressure-induced charge-transfer only plays a minor role in the pressure effect on  $T_c$ .



The experimental  $T_c(P)$  dependence was analyzed in several theoretical articles. In Ref. <sup>109</sup>, the electronic band structure calculations were carried out and the correct sign for the lattice anisotropic compressibility was obtained. The value of  $T_c$  is related to the position of van Hove singularity, depending on the carrier concentration as well as on the external pressure. In Ref. <sup>110</sup> the authors supposed that pressure-induced changes in  $T_c$  are related to two effects: the charge transfer from the reservoir to the  $(\text{CuO}_2)$  layer and the dependence on  $P$  of the energy gap value. The detailed analysis of the experimental data on the influence of pressure and doping level was carried out in Ref. <sup>111</sup>. These authors showed that in terms of the indirect-exchange model the observed  $T_c(P, \delta)$  dependence cannot be explained without considering that the oxygen (in the  $(\text{CuO}_2)$  layer and those close to it) has the role of an intermediary in the process of the electron coupling. From this it follows the necessity of considering the structural reorganization close to the  $(\text{CuO}_2)$  layer while analyzing the  $T_c(P, \delta)$  dependence. Thus, the importance of determining the Hg-1201 structure with different doping levels (under, optimally and overdoped) as a function of pressure is obvious.

Until now the data on the influence of external pressure on the Hg-1201 structure were only obtained for the optimally doped composition ( $\delta \approx 0.12$ ), up to 0.6 GPa <sup>112</sup> and up to 5.1 GPa <sup>113</sup>, and partly for the composition with  $\delta \approx 0.19$  (overdoped state) <sup>113</sup>. The analysis of the results showed that the main effect of pressure is the shortening of the apical Cu-O2 bond length, while the Hg-O distance in the  $\text{HgO}_2$  dumb-bell is practically pressure-independent. For example, the relative variations of these distances are  $3.7 \pm 0.8\%$  and  $0.4 \pm 0.8\%$ , respectively <sup>113</sup>. These results were not unexpected because at ambient pressure the apical Cu-O bond length is unusually large with respect to those found in other Cu-based high- $T_c$  oxides (for example, almost 0.5 Å larger than in the Y123 compound). Consequently, this bond is weak. On the contrary, the chemical bonds in the  $\text{HgO}_2$  dumb-bell are strongly covalent, and this is the main reason for its small variation under pressure.

In this present article the results of new powder neutron diffraction structural experiments are presented. They have been carried out on Hg-1201 samples with  $\delta \approx 0.06$  (underdoped state) and  $\delta \approx 0.19$  (overdoped state) under external pressures up to about 0.8 GPa. The new results are compared with our earlier data <sup>113</sup> for the optimal and overdoped compositions. The structure of Hg-1201 at ambient pressure has also been redetermined and compared to previous work <sup>114</sup>. The analysis of all these structural data has led us to comprehension of the  $T_c$  vs.  $\delta$  dependence.

## 2. EXPERIMENTAL

Three samples of  $\text{HgBa}_2\text{CuO}_{4+\delta}$  were prepared according to the procedure described in <sup>115</sup>. The syntheses were performed in sealed silica tubes in a furnace with controlled temperature gradient. The sample in the underdoped state (sample A,  $T_c \approx 75$  K) in the final stage of the preparation process was annealed in argon flow at 350°C. Sample (B) which is optimally doped ( $T_c \approx 97$  K), was annealed at 250°C in 1 bar oxygen atmosphere. The third sample (C, overdoped,  $T_c \approx 70$  K) was annealed at 270°C under an oxygen pressure of 90 bar. The preparation method, the superconducting properties, and the unit cell parameters of these samples were similar to the Hg-1201 samples, previously studied with the HRFD diffractometer <sup>116</sup> in Dubna at ambient pressure <sup>114</sup>. The composition with  $\delta = 0.057(10)$  and

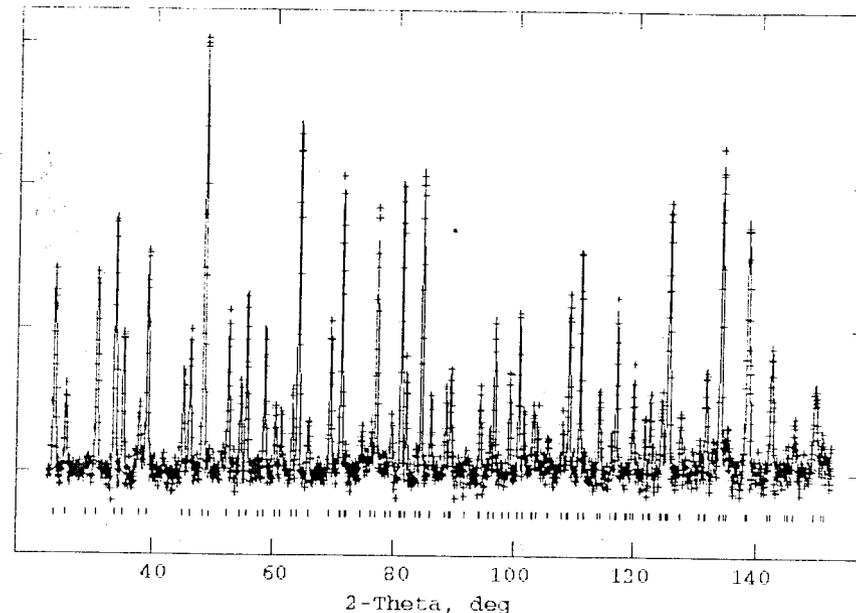


Figure 1. The diffraction pattern of the sample C, measured at D2B at a pressure  $P = 0.5$  GPa and analyzed with the Rietveld method.

$T_c = 71$  K from <sup>114</sup> corresponds to sample A, the two compositions with  $\delta = 0.124(9)$ ,  $T_c = 98$  K and  $\delta = 0.12(1)$ ,  $T_c = 96$  K correspond to sample B, and the composition with  $\delta = 0.19(1)$  and  $T_c = 83$  K corresponds to sample C.

Neutron diffraction patterns of A and C samples were measured at the D2B diffractometer at the ILL (Grenoble) at several values of the external pressure, while sample B was measured only at ambient pressure. A high-pressure cell of the "cylinder-piston" type with Fluor Inert liquid as the pressure-transmitting medium was used to generate the desired pressures on the sample. The diffraction patterns in the range  $20^\circ < 2\theta < 150^\circ$  were obtained at 0, 0.5 and 0.85 GPa for sample A and at 0.5 and 0.7 GPa for sample C. No peaks from impurity phases were found in any of the diffraction patterns. The total number of the Bragg reflections used in the refinement, exceeded 100 in each case. A typical diffraction pattern measured in the high-pressure cell is shown in the Fig.1. Additionally, the diffraction patterns from all three samples were taken at normal conditions without the cell. A diffraction pattern of sample A was also obtained with the HRFD diffractometer at Dubna in the range of  $d$ -spacing 0.77 - 2.12 Å in order to make a comparison with the previously obtained data, which would reveal possible systematic errors.

The Rietveld refinements were carried out with the use of the GSAS and MRJA programs. The measured intensity of scattered neutrons was corrected for the relatively strong absorption of neutrons in Hg-1201 due mainly to the Hg atoms. The neutron absorption cross-sections from <sup>117</sup> were used.

Table 1. Structural parameters of the optimally doped sample B, measured at D2B at ambient conditions.  $U_{iso}$  and  $U_{ij}$  are isotropic and anisotropic thermal parameters multiplied by a factor 100. Numbers in parentheses are statistical errors in the last significant digit.

|                                       |              |
|---------------------------------------|--------------|
| 2 $\Theta$ , deg                      | 16 - 147     |
| $d_{hkl}$ , Å                         | 0.831 - 5.71 |
| a, Å                                  | 3.88367(4)   |
| c, Å                                  | 9.5298(1)    |
| V, Å <sup>3</sup>                     | 143.737(3)   |
| z(Ba)                                 | 0.2984(1)    |
| z(O2)                                 | 0.2078(1)    |
| n(O3)                                 | 0.136(4)     |
| $U_{iso}(\text{Hg})$ , Å <sup>2</sup> | 1.39         |
| $U_{11}(\text{Hg})$ , Å <sup>2</sup>  | 1.60(3)      |
| $U_{33}(\text{Hg})$ , Å <sup>2</sup>  | 0.98(5)      |
| $U_{iso}(\text{Ba})$ , Å <sup>2</sup> | 0.61         |
| $U_{11}(\text{Ba})$ , Å <sup>2</sup>  | 0.48(3)      |
| $U_{33}(\text{Ba})$ , Å <sup>2</sup>  | 0.87(5)      |
| $U_{iso}(\text{Cu})$ , Å <sup>2</sup> | 0.22         |
| $U_{11}(\text{Cu})$ , Å <sup>2</sup>  | 0.01(3)      |
| $U_{33}(\text{Cu})$ , Å <sup>2</sup>  | 0.65(6)      |
| $U_{iso}(\text{O1})$ , Å <sup>2</sup> | 0.52         |
| $U_{11}(\text{O1})$ , Å <sup>2</sup>  | 0.40(5)      |
| $U_{22}(\text{O1})$ , Å <sup>2</sup>  | 0.19(5)      |
| $U_{33}(\text{O1})$ , Å <sup>2</sup>  | 0.98(6)      |
| $U_{iso}(\text{O2})$ , Å <sup>2</sup> | 1.42         |
| $U_{11}(\text{O2})$ , Å <sup>2</sup>  | 1.64(4)      |
| $U_{33}(\text{O2})$ , Å <sup>2</sup>  | 0.98(6)      |
| $U_{iso}(\text{O3})$ , Å <sup>2</sup> | 0.8          |
| Hg-O2, Å                              | 1.980(1)     |
| Cu-O2, Å                              | 2.784(1)     |
| Ba-O1, Å                              | 2.7315(8)    |
| Ba-O2, Å                              | 2.8787(5)    |
| Ba-O2 (l-l), Å                        | 0.864(2)     |
| Ba-O3 (l-l), Å                        | 2.844(1)     |
| $\chi^2$                              | 1.72         |

Table 2. The structural parameters for the underdoped sample A as a function of pressure.

|                   | HRFD,<br>ambient | D2B, P=0,<br>in the cell | D2B,<br>P=0.5 GPa | D2B,<br>P=0.85 GPa |
|-------------------|------------------|--------------------------|-------------------|--------------------|
| 2 $\Theta$ , deg  |                  | 18-150                   | 22.56 - 150.9     | 22.6 - 150.5       |
| $d_{hkl}$ , Å     | 0.77-2.12        | 0.825-5.07               | 0.823 - 4.06      | 0.824 - 4.06       |
| a, Å              | 3.88723(3)       | 3.88907(9)               | 3.88153(12)       | 3.87683(12)        |
| c, Å              | 9.5372(2)        | 9.5407(3)                | 9.5138(3)         | 9.4964(3)          |
| V, Å <sup>3</sup> | 144.1116         | 144.301(6)               | 143.338(7)        | 142.728(8)         |
| z(Ba)             | 0.3004(3)        | 0.3006(3)                | 0.3007(3)         | 0.3006(3)          |
| z(O2)             | 0.2077(3)        | 0.2073(3)                | 0.2075(3)         | 0.2076(3)          |
| n(O3)             | 0.05(1)          | 0.054(8)                 | 0.064(9)          | 0.069(9)           |
| Hg-O2, Å          | 1.981(2)         | 1.977(3)                 | 1.974(3)          | 1.971(3)           |
| Cu-O2, Å          | 2.788(2)         | 2.793(3)                 | 2.783(3)          | 2.777(3)           |
| Ba-O1, Å          | 2.721(2)         | 2.720(2)                 | 2.713(2)          | 2.710(2)           |
| Ba-O2, Å          | 2.887(1)         | 2.891(1)                 | 2.885(1)          | 2.880(1)           |
| Ba-O2 (l-l), Å    | 0.884(3)         | 0.891(4)                 | 0.887(4)          | 0.884(4)           |
| Ba-O3 (l-l), Å    | 2.865(2)         | 2.868(3)                 | 2.861(3)          | 2.855(3)           |
| $\chi^2$          | 1.24             | 0.87                     | 0.82              | 0.85               |

Table 3. The structural parameters for the overdoped sample C as a function of pressure.

|                   | D2B,<br>ambient | D2B, P=0<br>in the cell | D2B,<br>P=0.5 GPa | D2B,<br>P=0.7 GPa |
|-------------------|-----------------|-------------------------|-------------------|-------------------|
| 2 $\Theta$ , deg  | 18 - 152        | 22.4 - 150              | 22.7 - 152.5      | 22.77 - 152       |
| $d_{hkl}$ , Å     | 0.82 - 5.08     | 0.825 - 4.1             | 0.82 - 4.03       | 0.82 - 4.03       |
| a, Å              | 3.87923(6)      | 3.87902(14)             | 3.87156(12)       | 3.86931(11)       |
| c, Å              | 9.5244(2)       | 9.5237(3)               | 9.4990(3)         | 9.4913(3)         |
| V, Å <sup>3</sup> | 143.327(4)      | 143.302(9)              | 142.381(7)        | 142.100(7)        |
| z(Ba)             | 0.2970(2)       | 0.2976(4)               | 0.2967(3)         | 0.2962(3)         |
| z(O2)             | 0.2083(2)       | 0.2080(3)               | 0.2088(3)         | 0.2086(3)         |
| n(O3)             | 0.194(5)        | 0.176(11)               | 0.185(10)         | 0.172(9)          |
| Hg-O2, Å          | 1.984(2)        | 1.980(3)                | 1.983(3)          | 1.980(3)          |
| Cu-O2, Å          | 2.778(2)        | 2.781(3)                | 2.766(3)          | 2.766(3)          |
| Ba-O1, Å          | 2.739(1)        | 2.734(3)                | 2.734(2)          | 2.736(2)          |
| Ba-O2, Å          | 2.870(1)        | 2.873(2)                | 2.862(2)          | 2.860(1)          |
| Ba-O2 (l-l), Å    | 0.844(3)        | 0.854(5)                | 0.835(4)          | 0.831(4)          |
| Ba-O3 (l-l), Å    | 2.828(2)        | 2.835(3)                | 2.818(3)          | 2.811(3)          |
| $\chi^2$          | 1.08            | 0.87                    | 0.88              | 0.96              |

Several hypotheses for the structural model were checked during the refinements for all compositions. They were: a deficiency in the occupation of the Hg site, the possibility of splitting of the Ba site along the c-axis, the presence of static displacements of Hg in the

basal plane and of O2 in a plane parallel to the basal plane, the disordering of O3 in the basal plane along the diagonal of the unit cell, and the possibility of the existence of additional oxygen in the (0,0.5,0) or (x,0.5,0) positions. None of these hypotheses was found to be statistically significant. This is in very good agreement with the conclusions drawn recently in reference <sup>118/</sup>. These authors reported the detailed X-ray diffraction study of 15 Hg-1201 samples synthesized in sealed quartz tubes with different nominal Hg and Cu concentrations.

Therefore, the refinements were carried out using the standard structural model (see, for example, <sup>114/</sup>). The occupancy of the mercury position was fixed at 1 and the oxygen O3 thermal parameter was fixed as isotropic at the value of  $0.8 \text{ \AA}^2$ . The thermal parameters of the other atoms were refined in the anisotropic model according to the respective site symmetry. Since the precise determination of the thermal parameters was not the scope of the present study, the refined values of the thermal parameters are presented in the Table 1 only for the optimally doped compound. No significant changes for these parameters were observed in the other refinements. The results for the other compositions and at different values of the external pressure are presented in Tables 2 and 3.

### 3. RESULTS AND DISCUSSION

#### A. Ambient pressure. $T_c$ vs. $\delta$ dependence

The content of extra oxygen  $\delta$  is a very important parameter in the structural analysis of Hg-1201. In the papers analyzing the influence of pressure on the structure and  $T_c$  (see, for example, <sup>111/, 119/</sup>) the authors used the value of  $\delta_{opt}=0.18$ , obtained by Q. Huang et al. <sup>121/</sup>. Such a value of  $\delta_{opt}$  is in clear disagreement with results obtained by the time-of-flight NPD study of the Hg-1201 structure ( $\delta_{opt}\approx 0.12-0.13$ ) <sup>114/</sup> as well as with the iodometric titration which gave  $\delta_{opt}\approx 0.08-0.09$  <sup>13/</sup>. In order to explain the large  $\delta$  optimal value, the authors of <sup>121/</sup> assumed an unusual formal valence for the extra oxygen O3 on the Hg layer. In the present study particular attention was given to the problem of the extra oxygen concentration in samples A, B and C. New data at ambient pressure was collected for a sample of Hg-1201 by using a different neutron facility (the D2B constant wavelength instrument at ILL) and refinement program (GSAS) from those used in reference <sup>114/</sup>.

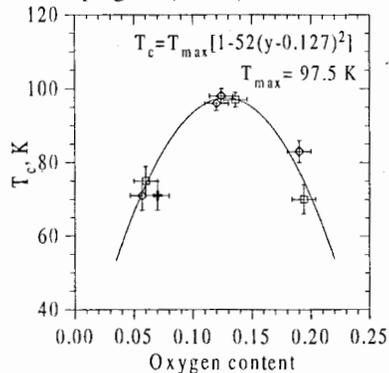


Figure 2. Dependence of  $T_c$  on the oxygen contents  $\delta$  for Hg-1201. The various symbols refer to neutron-diffraction experiments at the HRFD ( $\diamond$ ), D2B ( $\square$ ) and 3T2 ( $\times$ ) diffractometers. The solid line is the parabola drawn by the use of the least squares method; its parameters are presented in the right upper corner.

The detailed procedure of the extra oxygen determination from the diffraction data measured at the HRFD was discussed in reference <sup>114/</sup>. It was shown that the quality of the samples and the experimental set-up were apt for determining  $\delta$ , the oxygen in the (1/2, 1/2, 0) position, with a precision  $\pm 0.01$ . The situation with the measurements carried out at D2B is the same, namely the precision of the O3 occupancy factor is close to  $\pm 0.01$ . This value was corroborated by additional measurements on one of the samples studied at HRFD, carried out at the 3T2 diffractometer of LLB. The coincidence for the results in the same limits  $\pm 0.01$  was also obtained for a sample studied both at D2B and HRFD. These results gave us confidence to assume that our three groups of samples were really under-, optimally and overdoped, with mean contents of additional oxygen close to  $0.06\pm 0.01$ ,  $0.13\pm 0.01$  and  $0.19\pm 0.01$ , respectively. The  $T_c$  vs.  $\delta$  dependence for all seven samples investigated is shown in Fig.2. The experimental points are fitted by equation (1) with parameters  $T_{c,max}=97.5\pm 0.8$  K,  $q=52\pm 9$ ,  $\delta_{opt}=0.127\pm 0.005$ , i.e. with  $\delta_{opt}$  approximately 1.5 times lower than that obtained in reference <sup>121/</sup>. The error estimates include the experimental uncertainties in both the values of  $T_c$  (from  $\pm 1$  to  $\pm 4$  K) and  $\delta$  ( $\pm 0.01$ ).

The  $\delta_{opt}$  value turned out to be significantly lower than the  $\delta_{opt}$  given in reference <sup>121/</sup>, but, at the same time, is  $\sim 1.6$  times higher than the value predicted by the simple ion doping model, that is  $\delta_{opt}=0.08$ . This assumes that there is the formation of two holes in the (CuO<sub>2</sub>) layer per oxygen atom inserted into the Hg-layer, the standard valences of the atoms are:  $V_{Ba}=V_{Hg}=+2$ ,  $V_O=-2$ , and the optimal number of holes in the (CuO<sub>2</sub>) layer is  $n_{opt}=0.16$ . The study of the effect of doping by fluorine, instead of oxygen, in Hg-1201, carried out by Abakumov et al. <sup>120/</sup> showed that the same  $T_c$  values in the oxygen- and fluorine-doped compounds (HgBa<sub>2</sub>CuO<sub>4+8</sub> and HgBa<sub>2</sub>CuO<sub>3</sub>F <sub>$\gamma$</sub> ) are obtained for  $2\delta \approx \gamma$ . As the charge of F is hardly different from -1, the charge of the extra oxygen is equal to -2. In order to explain the difference between the  $\delta_{opt}$  and  $n_{opt}$  Abakumov et al. <sup>120/</sup> made the speculation that the holes induced by the insertion of oxygen are distributed over the (CuO<sub>2</sub>) layers and other parts of the Hg-1201 structure, e.g. the HgO<sub>2</sub> dumb-bell.

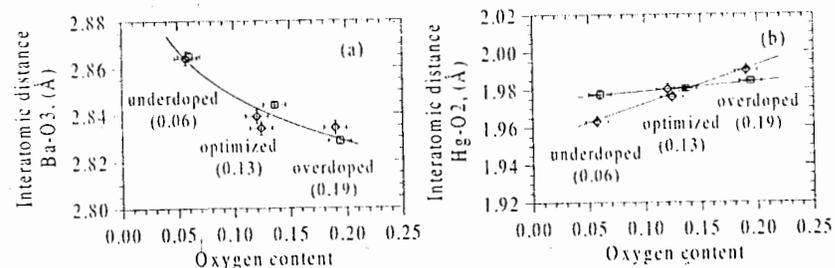


Figure 3. Dependence of the Ba-O3 (a) and Hg-O2 (b) interatomic distances on the oxygen content  $\delta$ . The marks are the same as for Fig.2.

The dependence of some of the interatomic distances upon  $\delta$  are presented in Fig.3. As the negative charge on the (HgO<sub>8</sub>) layers increases, the Ba atom moves gradually toward the (HgO<sub>8</sub>) layer, that is toward O3. Notice that the points corresponding to the Ba-O3 distances for both series of samples lie on the same curve (Fig.3a). The situation for the Hg-O2 distance is different (that of the Cu-O2 distance is the same, but inverse). The

experimental points from the samples of each of the two series lie on two lines with visibly different slope (Fig.3b). In general, the absolute values of the interatomic distances and the range of their variations for increasing  $\delta$  are in agreement with the values published in previous neutron-diffraction studies.

### B. Pressure dependence of the structural parameters

The variations of the  $a$  and  $c$  unit cell parameters and the main interatomic distances in Hg-1201 as the function of pressure are shown in Figs.4-6. For the optimally doped sample the points corresponding to ambient pressure (measured at D2B) are shown and the line slopes correspond to the compressibilities derived from <sup>113</sup>. The compressibilities of the unit cell parameters and the main interatomic distances in Hg-1201, defined as  $\kappa_q = -(1/q) dq/dP$  ( $10^{-3}/\text{GPa}$ ), where  $q$  is the specific parameter, are presented in Table 4 and in Fig.7. In order to calculate  $dq/dP$ , the linear least-squares fits of the experimental points were used. The fits are shown in Figs.4-6. For comparison, the compressibilities calculated from the data of reference <sup>112</sup>, corresponding to optimally doped Hg-1201 sample, are also presented in Table 4.

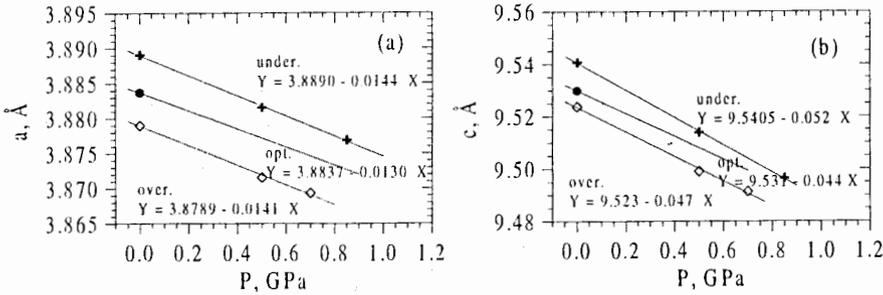


Figure 4. The unit cell parameters of Hg-1201 as a function of external pressure for three samples. For the optimally doped state the point measured at  $P=0$  is shown together with the line slope determined in <sup>113</sup>. The experimental errors are smaller than the symbols.

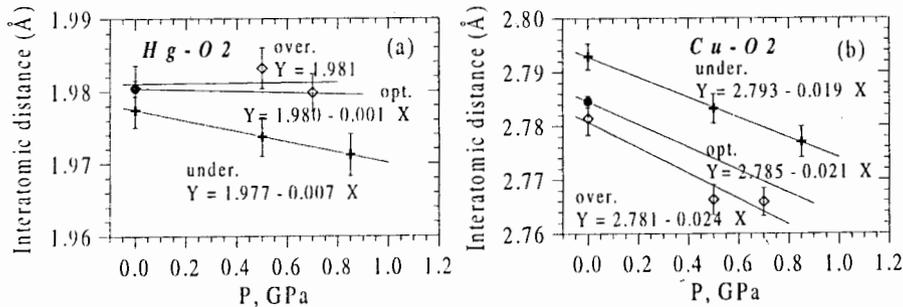


Figure 5. The dependence of pressure of the Hg-O2 (a) and the Cu-O2 (b) apical distances.

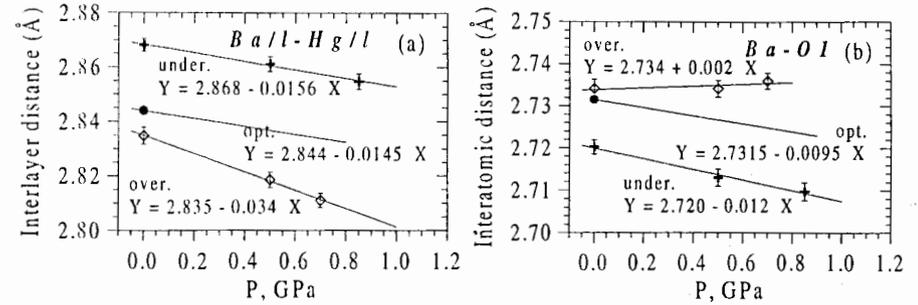


Figure 6. The distances between the Ba-layer and the Hg-layer (a) and between Ba and O1 atoms (b) as a function of pressure.

The pressure dependence of the Hg-1201 unit cell parameters shows that the occupation of the O3 position does not strongly influence the lattice compressibility. The value of  $\kappa_c$  in sample A is higher than those in B and C samples. This can be attributed to the comparatively higher compressibility of the Hg-O2 bond length in the reduced structure of sample A. The compressibility along the  $c$ -axis in samples B and C is almost fully determined by the  $\kappa_{\text{Cu-O2}}$ . For all three levels of doping the compressibility anisotropy is quite high, reaching  $\kappa_c/\kappa_a \approx 1.5$  for sample A. The compressibility becomes less anisotropic when extra oxygen content  $\delta$  increases:  $\kappa_c/\kappa_a$  decreases from sample A (1.48) to B (1.45) to C (1.36). This behavior is due to the fact that the Hg-1201 structure becomes more isotropic when the O3 site occupancy increases.

Table 4. Compressibilities of the lattice parameters and the main distances in Hg-1201. The compressibility is defined as  $\kappa_q = -(1/q)dq/dP$  ( $10^{-3}/\text{GPa}$ ).

| Parameter | Sample A | Sample B,<br>data from <sup>113</sup> | Sample C | data from <sup>112</sup> |
|-----------|----------|---------------------------------------|----------|--------------------------|
| $a$       | 3.71(12) | 3.20(35)                              | 3.63(21) | 4.25(6)                  |
| $c$       | 5.48(11) | 4.63(11)                              | 4.93(26) | 5.82(6)                  |
| $V$       | 12.9(4)  | 10.9(6)                               | 12.2(7)  | 14.3(2)                  |
| Hg-O2     | 3.69(5)  | 0.5(3)                                | 0.1(5)   | -0.5(4.8)                |
| Cu-O2     | 6.71(16) | 7.7(6)                                | 8.5(2)   | 10(3)                    |
| Ba-O1     | 4.6(5)   | 3.5(8)                                | -0.8(7)  | 6.1(2.3)                 |
| Ba-O2     | 4.23(5)  | 4.3(4)                                | 6.8(6)   | 4.9(0.9)                 |
| Ba/l-O2/l | 9.4(1.4) | 16.7(2.7)                             | 40(5)    | 15(10)                   |
| Ba-O3     | 5.5(5)   | 5.3(1.0)                              | 11.9(4)  | 4.8(3.0)                 |

It is remarkable that the compressibilities of the in-plane Cu-O1 and Hg-O3 bonds are practically  $\delta$  independent, while the compressibility of the apical bond distances, Cu-O2 and Hg-O2, are strongly dependent upon the doping level. The compressibility of the apical Hg-O2 bond is close to  $\kappa_c$  for sample A, but with increasing doping level (samples B and C), it becomes practically incompressible. This was observed in the pressure range up to 5.07 and 2.37 GPa for the optimally and overdoped compositions, respectively <sup>113</sup>. The

HgO<sub>2</sub> dumb-bell is a very rigid element of the structure. The results presented here show that the length of the Hg-O2 bond depends on the extra oxygen content in the Hg-plane: an increase of the coordination number of the Hg atoms results in an increase of the apical Hg-O2 bond distance. This bond becomes incompressible with the presence of the significantly large amount of O3 in the Hg-layer. This behavior may seem unusual, however, bond lengths increase when the coordination number of the cation increases and this is exactly what happens to the coordination number of Hg for increasing  $\delta$ . It is possible that some bending of the HgO<sub>2</sub> dumb-bell occurs. The departure of the Hg atom from the (0,0,0) position may lead to an apparent shortening of the bond length. Another explanation can be found by analyzing the behavior of the other bond distances in the structure. It is obvious that the compressibility of the Hg-O2 bond should depend on the compressibilities of the other bonds, such as Cu-O2 and Ba-O3(O2), which become more compressible for increasing of the O3 content.

The compressibility of the apical Cu-O2 bond length increases when the O3 content increases despite of the shortening this bond for larger  $\delta$ -values. This bond length shortens in these samples proportionally to the decrease of the  $c$  axis length, i.e. the pressure dependence of the apical Cu-O2 bond length for all three types of samples reproduces the pressure dependence of the  $c$  unit cell parameter. The value  $\kappa_{\text{Cu-O2}}$  is greater than  $\kappa_c$  which in part is due to the low value of  $\kappa_{\text{Hg-O2}}$ . If  $\kappa_{\text{Hg-O2}}=0$ , then we should have:  $\kappa_{\text{Cu-O2}} = \kappa_c \cdot (c/2l_{\text{Cu-O2}})$ , where  $l_{\text{Cu-O2}}$  is the length of the Cu-O2 bond.

The compressibilities of the Ba-O distances strongly depend on the doping level. The compressibility of the Ba-O3 distance becomes larger when the doping level increases. For the A and B samples the compressibility of this distance corresponds approximately to  $\kappa_c$ , while for the C sample it is almost 2.5 times larger than  $\kappa_c$ , i.e. for increasing pressure the Ba atom in the overdoped sample is rapidly moving toward the basal plane. The compressibility of the Ba-O2 bond length becomes also larger for increases of the extra oxygen content. The unexpected result is that the Ba-O1 distance (between Ba and O of the (CuO<sub>2</sub>) layers) becomes incompressible in the overdoped state. This distance does not change under pressure, and the compressibility has even a small positive value, while in the underdoped and optimally doped samples this bond decreases for increasing pressure.

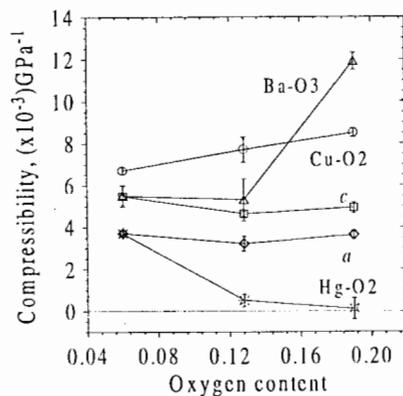


Figure 7. Compressibilities of the main Hg-1201 structural parameters for three doping levels

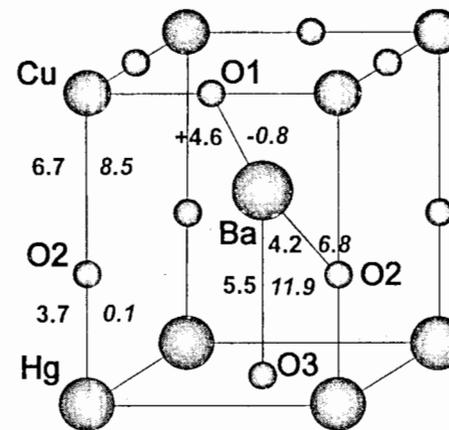


Figure 8. Schematic representation of the Hg-1201 structure. The values of the compressibilities of the selected bond distances are written on the left for the underdoped sample, and on the right for the overdoped sample.

Figs. 7 and 8 summarize the variations of selected bond compressibilities with the change of the doping level. An increase of the O3 content results in larger compressibilities of the Ba-O3 and Cu-O2 distances, while the Hg-O2 and Ba-O1 ones become practically incompressible. Therefore, pressure induces anisotropic effects (which depend on the doping level) on the structure of Hg-1201 compound and, in particular, on the local arrangement of the (CuO<sub>2</sub>) layers which are responsible for superconductivity. In the overdoped state the separation between these layers and neighboring Ba cations does not decrease under pressure, while the apical O2 anions shift highly toward the Cu cations. In the under- and optimally-doped structures pressure causes the shortening of the Ba-O1 separation and a smaller compression of the Cu-O2 bond. Such variation of the atomic interactions due to the change of extra oxygen content can be one of a reasons for the enhancement of the charge transfer from the reservoir block to the conducting (CuO<sub>2</sub>) layers in the overdoped state in comparison with under- and optimally-doped superconductors.

One of the most discussed questions in the literature is why  $T_c(P)$  for the Hg-1201 phases varies differently with the different doping level. This subject is discussed in a few theoretical articles<sup>10,11,21</sup>. Even though each is based on various models, all conclude that there are two main reasons the  $T_c$  change: the increase of  $T_{c,max}$  in equation (1) and the variation of the charge carrier density in the (CuO<sub>2</sub>) layer due to the charge transfer from the reservoir. From the experimental data on the  $T_c$  vs.  $P$  and  $\delta$  dependence presented in reference<sup>71</sup> it follows that  $dT_c/dP \approx \text{const.} \approx 2 \text{ K/GPa}$  for  $\delta < \delta_{opt}$  at least up to 1.5 GPa pressures. The analysis of equation (1) shows that in this case the pressure-induced charge transfer,  $dn/dP$ , would have to decrease for increasing  $\delta$ , vanishing at  $\delta = \delta_{opt}$ . The absolute value of the charge transfer is very small, not higher than 0.002 holes/GPa for the underdoped state<sup>710,21</sup>. From the homogeneous character of the structure compression revealed in the present study one can conclude that the effect of the charge transfer from the reservoir to the (CuO<sub>2</sub>) layers does not play the dominant role in the Hg-1201 structure under pressure at  $\delta < \delta_{opt}$ . At the same time, the strong shift of the Ba atoms in the overdoped state toward the (HgO<sub>2</sub>) layer under applied pressure may be considered as the signature of a significant charge transfer into the (CuO<sub>2</sub>) layer.

According to the theory of indirect exchange via the oxygen anions as the intermediary in the electron coupling<sup>111</sup>, the change in the  $T_c(P)$  behavior for  $\delta > \delta_{opt}$  cannot be explained without taking into account the variations in the density of the "active" oxygen atoms. In Hg-1201, these "active" oxygen atoms are those of the (CuO<sub>2</sub>) layer and the apical oxygen O2. This means that the variations to be considered are those in the oxygen distribution in the (CuO<sub>2</sub>) layer and its surrounding. Our results show that the movement of the Ba atom (for example, that of Ba away from the (CuO<sub>2</sub>) layer at  $\delta=0.19$ ) should also affect the general balance of the interactions.

These considerations can be made more quantitative by calculating the variations of the total charge on the (CuO<sub>2</sub>) layer by the BVS method<sup>122</sup>. It is easy to see that, in the case of Hg-1201, only two bond lengths need to be considered: Ba-O1 and Cu-O2. Furthermore, it is important to remark the fact that, if constant  $r_0$  parameters are used, BVS are strongly affected by out-of-plane strain, therefore change of BVS vs. pressure can not immediately be interpreted as resulting from charge transfer. Nevertheless, it is clear that the bond strength of the Ba-O1 bond increases under pressure for the A and B samples, while there is no change for the overdoped sample. The shortening of the Cu-O distances under pressure and, consequently, an increase of the Cu formal valence is not compensated by the decrease of the Ba-O1 separation in the overdoped sample, while in the under- and optimally-doped samples a homogeneous compression occurs. The difference of the formal charges for the (CuO<sub>2</sub>) layers appeared due to pressure corresponds to 0.07 for the underdoped structure, while this value is close to zero for the overdoped phase. In the other words, we can say that the (CuO<sub>2</sub>) layers become more isolated and positively charged in the overdoped state under pressure, which enhances a charge transfer leading to a stronger overdoping, thus decreasing  $T_c$ .

#### 4. CONCLUSIONS

In the present article we have presented a neutron diffraction study of Hg-1201 under high pressure at low and high extra oxygen concentrations in the Hg-layer (under- and overdoped states). The results are analyzed together with previous data<sup>13,14</sup>. The main conclusions are as follows:

The superconductor HgBa<sub>2</sub>CuO<sub>4+δ</sub>, prepared according to the procedure described in<sup>15</sup> is a cation-stoichiometric compound exhibiting the highest  $T_c$  at the oxygen concentration in the Hg-layer  $\delta_{opt}=0.13\pm 0.01$ . This oxygen is only situated in the center of Hg layer. The value of  $\delta_{opt}$  was determined by the measurements of seven Hg-1201 at three diffractometers, two of which (D2B and 3T2) are of the classical type with  $\lambda=const.$ , while the third (HRFD) utilizes the time-of-flight technique. All the measured points of the  $T_c(\delta)$  dependence lie on one curve which strongly indicates that the  $\delta_{opt}$  value is realistic.

At low O<sub>δ</sub> concentration the Hg-1201 structure compresses isotropically, i.e. the compressibilities of the main interatomic distances correspond to the unit cell compressibility. However, at higher O<sub>δ</sub> concentrations the Hg-O2 and Ba-O1 bonds become practically incompressible, while the Cu-O2 and Ba-O3 undergo a strong compression. The analysis of the interatomic distances variations allows us to conclude that in the under- and optimally-doped states the charge transfer from the reservoir to the (CuO<sub>2</sub>) layers plays a minor role. The enhancement of  $T_c$  under pressure is due to an increase of the  $T_{c,max}$  value.

The decrease of  $T_c$  under applied pressure for the overdoped Hg-1201 superconductor may be explained by charge transfer enhancing overdoping.

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Представлены результаты нейтронографического исследования структуры  $\text{HgBa}_2\text{CuO}_{4+\delta}$  при нормальном и высоком внешнем давлении для составов с различным содержанием дополнительного кислорода  $\delta$ . Показано, что в стехиометрических по катионному составу образцах допирующий кислород располагается только в центре ртутной плоскости, температура  $T_c$  сверхпроводящего перехода параболически зависит от  $\delta$ , достигая максимума при  $\delta_{\text{opt.}} = 0,13 \pm 0,01$ . Влияние внешнего давления на структуру сильно зависит от уровня допирования. При небольшом содержании кислорода ( $\delta \sim 0,06$ ), сжатие структуры происходит практически изотропно. Повышение содержания дополнительного кислорода до 0,19 (в передопированном состоянии) приводит к более сильному сжатию мостиковых расстояний  $\text{Cu}-\text{O}_2$  и  $\text{Ba}-\text{O}_\delta$ , в то время как гантель  $\text{HgO}_2$  и расстояние между атомами Ba и O, принадлежащего плоскости ( $\text{CuO}_2$ ), становятся практически несжимаемыми. Эти результаты находятся в согласии с моделями, в которых перенос заряда из резервуара в плоскости ( $\text{CuO}_2$ ) не играет ведущей роли в повышении  $T_c$  с ростом давления при низких и оптимальных значениях  $\delta$ , тогда как в передопированном состоянии перенос заряда под давлением усиливается, что приводит к снижению  $T_c$ .

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The results of a neutron-diffraction study of the  $\text{HgBa}_2\text{CuO}_{4+\delta}$  structure at ambient pressure and under external pressure at different extra oxygen concentrations are presented. The results have been analyzed together with the data of previous investigations. It is shown that in the cation-stoichiometric samples the  $\text{O}_\delta$  oxygen is only present in the center of the mercury layer,  $T_c$  is parabolically-dependent on  $\delta$ , and  $T_{c,\text{max}}$  is obtained at  $\delta_{\text{opt.}} = 0.13 \pm 0.01$ . The influence of pressure on the structure strongly depends on the doping level. At low oxygen content ( $\delta \sim 0.06$ ), the compression of the structure is practically isotropic. An increase of the extra oxygen content to 0.19 (overdoped state) results in the larger compression of the apical  $\text{Cu}-\text{O}_2$  and  $\text{Ba}-\text{O}_\delta$  distances, while the  $\text{HgO}_2$  dumb-bell as well as the distance between Ba and O belonging to the ( $\text{CuO}_2$ ) layer become practically pressure independent. These results are in agreement with the models, in which the effect of the charge transfer from the reservoir to the ( $\text{CuO}_2$ ) layers does not play a dominant role in the  $T_c$  increase with pressure at low and optimal  $\delta$  values, while in the overdoped state the charge transfer is enhanced under pressure, thus inducing the  $T_c$  decrease.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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