

# The influence of oxygen content on the $T_c$ of HTS Hg-1245

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We have observed an extraordinary behavior of the  $\text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{12+\delta}$  layered HTS (phase 1245) in the overdoped state. Earlier we have synthesized the phase Hg-1245 with different oxygen content and consequently different values of the lattice parameter  $a$ . We have observed a coincidence of  $a$  values when the  $T_c(a)$  cupolas reach their maxima for phases Hg-1223, 1234, and 1245, and a merging of their overdoped parts together with abrupt falling off of the  $T_c$  values. The Hg-1245 phase has shown the most unusual behavior. Contrary to other phases, this one contains three types of  $\text{CuO}_2$  layers in a unit cell. We supposed that, in the case of the Hg-1245 phase, the holes coming from the reservoir, which is the Hg-O plane, cannot reach the «far»  $\text{CuO}_2$  layer which is notable for this phase. We have calculated the hole concentration for each layer for 1223, 1234, and 1245 phases. The results obtained confirm our assumption. The hole concentration appears negligibly small for the overdoped 1245 phase. We can consider the «fifth»  $\text{CuO}_2$  layer as not taking part in superconductivity. The analysis of the behavior of the  $T_c(a)$  cupolas for the phases with different number of  $\text{CuO}_2$  layers and of hole density distribution between the layers has been carried out.

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## Introduction

The first goal in the study of the HTSC layered cuprates is to find out the optimum structure and content to reach the maximum possible critical temperature  $T_c$ . Up to now the maximum value of the  $T_c = 135$  K was reached for Hg-based cuprates in their Hg-1223 phase. Numerous attempts at synthesis of layered cuprates with different elements added instead of mercury in recent years have failed to enlarge the  $T_c^{\text{max}}$ .

We have synthesized the Hg-based cuprates with  $n = 3, 4, \text{ and } 5$  [1,2] and measured the  $T_c^{\text{max}}$  and the  $dT_c^{\text{max}}/dp$  for phases with  $n = 1-5$  [3]. The largest  $T_c^{\text{max}}$  remained to be the value at  $n = 3$ .

To understand the nature of the HTSC the study of samples whose parameteres lay far away from the optimal ones is necessary. Here we present and discuss the data on  $T_c$  for phases Hg-1223, Hg-1234 and Hg-1245 with different oxygen content.

When studying the overdoped and underdoped cuprates the agreement was attained that different approaches should be used to describe their properties. The first — the overdoped state — may be considered as a Fermi liquid which is not true for

the underdoped state. The problem of overdoped and underdoped states was considered by Laughlin [4] in a most impressive way. He proposed the existence of a quantum critical point on the way from an antiferromagnetic insulator (underdoped) to a normal metal (overdoped).

## Experiment

The phases Hg-1223, 1234, and 1245 were synthesized under high pressure at different pressures, temperatures and time intervals. The oxygen content in the starting mixtures was varied by changing the  $\text{BaO}/\text{BaO}_2$  ratio, which allowed us to obtain the overdoped Hg-1223, 1234, and 1245 phases in as-prepared states. The technology of synthesis was described in detail in [1,2]. Special attention was paid to getting single phase ceramic specimens. When the phases with  $n \geq 3$  are synthesized, the kinetics of the process is important. First the previous phases are formed where then the fragments of  $\text{CaCuO}_2$  take root. The phase composition was checked by the x-ray study.

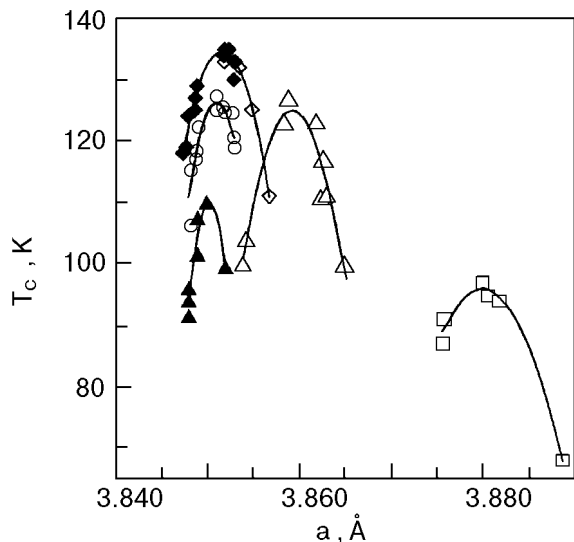


Fig. 1. The dependence of  $T_c$  vs. parameter  $a$  for Hg-based superconductors: Hg-1201 ( $\square$ ), Hg-1212 ( $\Delta$ ), Hg-1223 ( $\blacklozenge$ ), Hg-1223 ( $\diamond$ ) [1], Hg-1234 ( $\circ$ ), Hg-1245 ( $\blacktriangle$ ).

The temperature dependence when an abrupt change of ac and dc susceptibility takes place was measured by the induction method. The temperature was measured by the (Cu + 0.15% Fe)/Cu thermocouple. Measurements were carried out in the Institute for High Pressure Physics (IHPP) and at the Chemical Faculty of the Moscow University by different people and on different installations. The results obtained are qualitatively the same, having sometimes some unimportant quantitative difference. As was mentioned above, in all cases the maximum values of the  $T_c$  were achieved for the phase Hg-1223.

Here we lay stress on the behavior of different phases in the overdoped states. The measured  $T_c$  values as a function of lattice parameter  $a$  (the spacing Cu-O in the layer) are shown in Fig. 1.

The underdoped states correspond to greater values of the parameter  $a$ . These states appear under heat processing of the as-prepared samples [2]. The change of  $a$  is caused by oxidation of copper because of nonstoichiometric oxygen in the Hg-O layer (the reservoir), that is, because of the hole density  $\delta$  in the sample. The  $T_c$ 's for phases Hg-1234 and Hg-1245 have a tendency in the overdoped state to merge with the overdoped phase Hg-1223 and to fall off abruptly [2].

### Discussion

Earlier we have compared results for  $T_c^{\max}$  for phases with  $n = 1-6$  and for  $dT_c^{\max}/dp$  ( $n = 1-5$ ) [3] with data obtained from the model proposed by Anderson (the so-called RWB model [5]), see Figs. 2 and 3. In the RWB model the  $T_c^{\max}$  is

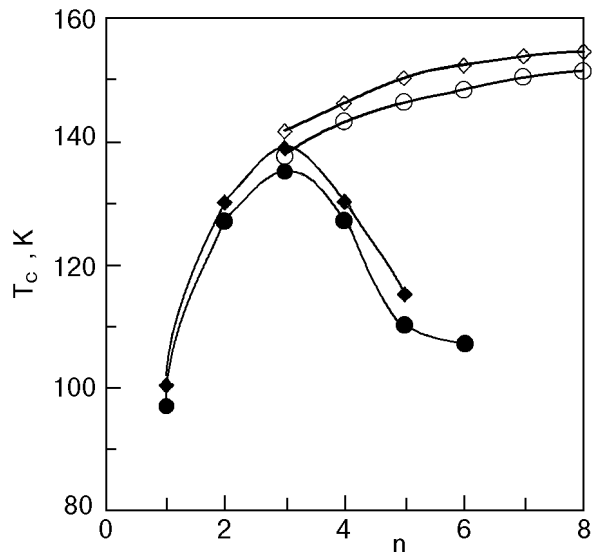


Fig. 2. Experimental and calculated values of  $T_c^{\max}$  as a function of  $\text{CuO}_2$  sublayers number  $n$ . Full circles and full rhombs — experiment at ambient pressure ( $\blacksquare$ ) and under pressure 1 GPa ( $\blacklozenge$ ), open circles and rhombs — the calculated data for ambient ( $\circ$ ) and 1 GPa ( $\diamond$ ) pressure, respectively [3].

determined mainly by the coupling between  $\text{CuO}_2$  layers and it is assumed that the holes, which are responsible for high  $T_c$  values, are homogeneously distributed between all  $\text{CuO}_2$  layers.

DiStasio, Müller, and Pietroneru in [6] have considered the charge distribution of holes among the various  $\text{CuO}_2$  layers up to  $n = 4$  and found that this distribution is highly nonhomogeneous for  $n \geq 3$ . «A natural consequence of this distribution is that the density of states available for superconductivity can have a maximum as a function of  $n$ , as observed experimentally for  $T_c$ » [6]. Beginning

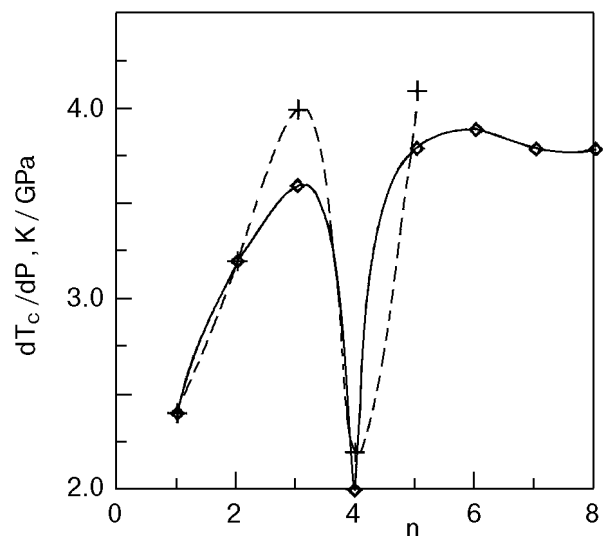


Fig. 3. Experimental (+) and calculated ( $\diamond$ ) data for pressure derivative  $dT_c^{\max}/dp$  as function of sublayers number  $n$  [3].

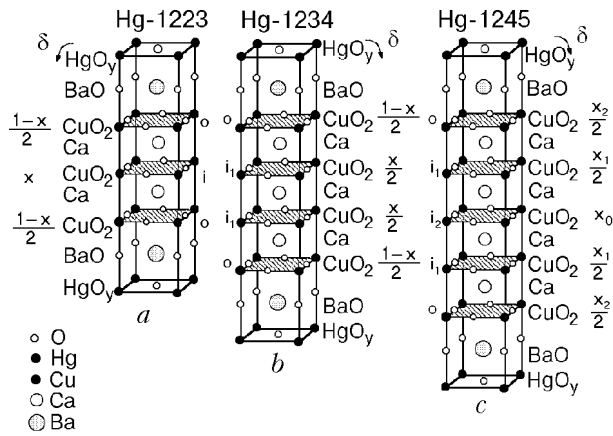


Fig. 4. Idealized structures of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+y}$  (Hg-1223) (a),  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+y}$  (Hg-1234) (b),  $\text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{12+y}$  (Hg-1245) (c) with, respectively, three ( $n=3$ ), four ( $n=4$ ) and five ( $n=5$ )  $\text{CuO}_2$  layers per unit cell. The structure with  $n=5$  has inequivalent inner ( $i_1$  and  $i_2$ ) and outer (o)  $\text{CuO}_2$  layers. The copper atoms of the inner  $\text{CuO}_2$  layers have a fourfold oxygen coordination, the copper atoms of the outer  $\text{CuO}_2$  layers have a fivefold oxygen coordination. O(1) – in the layer  $i$ , O(2) – in the layer  $o$ , O(3) – in the layer BaO, O(4) – in the layer  $\text{HgO}_y$ .

with  $n=3$  the nonequivalent  $\text{CuO}_2$  layers exist – the outer «o» and inner «i» (see Fig. 4). The hole distribution inside the sheet is proposed to be homogeneous. In [6] the band (a parabolic band was assumed) and electrostatic energies were calculated. The total energy is minimized with respect to  $x$  – the fraction of charge in the  $i$ -layer ( $1-x$  in the  $o$ -layer). If  $\delta$  is the total density of holes coming from the reservoir then the concentration of charge carriers  $n_h$  in the  $i$ -layer is equal to  $x\delta/(n-2)$  and  $(1-x)\delta/2$  in the  $o$ -layer. In the simplest empirical case

$$T_c(n_h) = T_c^{\max} [1 - \beta(n_h - n_h^{\max})],$$

where  $T_c^{\max}$  and  $\beta$  do not depend on  $n_h$  but on the structure parameters only [7]. This expression leads to the well known cupola-like dependence  $T_c(n_h)$  that was observed in the experiment up to  $n=5$  [2]. The electrostatic interaction with the layer – reservoir of holes is considered in [6] for the structure where all layers are equally spaced. Jover et al. [7] have considered the Hg-bearing cuprates up to  $n=4$  on the basis of the model [6] (see Figs. 4,a,b).

Let us consider the results shown in Fig. 1. The cupola-shaped dependence of the  $T_c(a)$  for phases with  $n=1-5$  is clearly seen. It can be assumed that these five first Hg-based cuprates have the same cupola-like shape of the  $T_c(a)$  dependence due to the nonstoichiometric oxygen, like there is a reason for their structure identity. The implanting of an addi-

tional ( $\text{CaCuO}_2$ )-layer in the unit cell leads to contraction of layer parameters and to a stronger interaction in the  $\text{CuO}_2$  plane. For phases with low number of layers in the unit cell the change of  $T_c$  takes place in a rather extended range of  $a$ -values converging at larger  $n$ .

The last three phases show nearly the same  $a$ -values in their overdoped states in contrast with the two first of them (Fig. 1). The value of  $T_c$  for phases Hg-1223, Hg-1234, and Hg-1245 appears to be very different at the same  $a$ . The  $T_c(a)$  cupolas go down when  $n$  changes from 3 to 5. Moreover, the left part of these  $T_c(a)$  curves corresponding to overdoped states merge to a common curve where the  $T_c$ 's go down from a maximum value 135 K for  $n=3$  to almost 90 K. The cupolas narrow down with  $n$  increasing mostly because of their right sides.

Accumulating the experimental results we note the following peculiarities:

1) Critical temperature goes down both in underdoped and overdoped states showing a cupola-shaped  $T_c(a)$  dependence;

2) The overdoped parts of the  $T_c(a)$  curves merge to a common curve at  $n=3, 4$ , and 5;

3) The values of  $T_c^{\max}$  most likely continue to fall off at  $n > 5$ ;

4) The pressure derivative  $(dT_c^{\max}/dp)(n)$  shows a nonmonotonic behavior that can be described inside the RWB model.

All these peculiarities should be connected with some features of the crystal structure of the layered cuprates under consideration. The principal one of these is the fact that the holes cannot reach the sole inner  $\text{CuO}_2$  layer in case of the 5th phase ( $n=5$ ) and hence in case of phases with  $n > 5$ .

We have carried out a calculation of the hole density in different layers similar to that of [6], generalizing the latter to the existence of third kind of  $\text{CuO}_2$  layer in the unit cell of the system  $\text{HgBa}_2\text{Ca}_4\text{Cu}_5\text{O}_{12}$  and taking into account hole reservoir distance. The main goal of the calculation was to find out the hole densities for the 5th phase. This phase should have two kinds of inner layers (see Fig. 4,c) and the model [6] should be appropriate. We think as well that the ion model [8] describes correctly the phase Hg-1223 having a maximum  $T_c$  within the entire Hg-cuprates series [6]. Both models [6] and [8] give the same expressions for the band energy as a function of  $x$  for the phases Hg-1223 and Hg-1234 and different ones for the Madelung energy. The latter is of no importance for our problem.

Our calculation is based on the model [6]. For the band energy we get for  $n = 3$

$$U_B = 1/2 A\delta^2 (3x^2 - 2x + 1) S \quad (1)$$

and for  $n = 4$

$$U_B = A\delta^2 (x^2 - x + 1/2) S, \quad (2)$$

where  $A = \pi\hbar^2/2m^*a^2$ ;  $S$  is the layer area.

The Madelung energy is the same for  $n = 3$  and 4:

$$U_M = B\delta^2 (x^2 + l/d) S. \quad (3)$$

Here  $B = \pi e^2/\epsilon d$ ;  $d$  is the distance between  $\text{CuO}_2$  layers;  $l$  – the distance between the layer  $\text{Hg}-\text{O}(4)$  and the nearest  $\text{CuO}_2$  plane;  $\epsilon$  is the dielectric constant. Minimizing the total energy with respect to  $x$  we get

for  $n = 3$

$$x = A/(3A + 2B) \quad (4)$$

and the concentration of the charge carriers (the holes  $n_h$ ) in the layer

$$n_h^i = \delta x \quad \text{and} \quad n_h^o = \delta(1 - x)/2.$$

For  $n = 4$

$$x = A/2(A + B) \quad (5)$$

and  $n_h^i = \delta x/2$  (see Fig. 4).

In case of  $n = 5$  one more inner layer exists – the  $i_2$  layer and two variational parameters should be put into consideration –  $x_0$  and  $x_1$  representing two kinds of inner layers.

That is:  $n_h^i(5) = \delta x_0$  – (layer  $i_2$ ) and  $n_h^i(3,4) = \delta x_1/2$  (two identical layers  $i_1$ ).

In the outer layers

$$n_h^o = \delta/2(1 - x_0 - x_1) = \delta x_2/2,$$

where  $x_2 = (1 - x_0 - x_1)$  (see Fig. 4,c).

Then for the band and Madelung energy we get

$$U_B = A\delta^2(1/2 - x_0 - x_1 + 3/2x_0^2 + x_1^2 + x_0x_1)S, \quad (6)$$

$$U_M = B\delta^2(2x_0^2 + 2x_0x_1 + x_1^2 + l/d)S. \quad (7)$$

Minimization of total energy gives

$$x_0 = A^2/(5A^2 + 10AB + 4B^2), \quad (8)$$

$$x_1 = (2A^2 + 6AB + 4B^2) A/(A + 2B)(5A^2 +$$

$$+ 10AB + 4B^2) = \frac{2x_0(A + 3B + 2B^2/A)}{(A + 2B)} > 2x_0. \quad (9)$$

Thus

$$x_2/2 > x_1/2 > x_0.$$

Our assumption that holes do not reach the inner layer  $i_2$  gets a quantitative confirmation.

Considering the experimental and calculated results we conclude that the phase Hg-1223 is optimal for the high  $T_c$ . For this phase only the hole distribution between the  $\text{CuO}_2$  layers is nearly uniform [8].

Apparently this uniformity leads to the highest  $T_c = 135$  K within all layered HTSC. The inner layers of phases with  $n = 4$  and 5 contain much less carriers than the outer ones. For the phase with  $n = 5$  we find out that the inner  $i_2$  layer contains a few of the carriers and all of them are concentrated in the outer layers. The distance between the outer layers increases with  $n$  what decreases the interaction between layers. Thus, the  $T_c$ 's fall off due to both the hole density decrease and the interaction weakening. There are experimental data on the  $T_c^{\max}$  measured up to  $n = 8$  [9]. In spite of rather large spread the decrease in  $T_c$  with  $n$  is evident.

The real absence of holes in the inner layer of the phase Hg-1245 causes the disagreement between experimental values of  $T_c^{\max}$  got for large  $n$  and calculated ones in the frames of RWB model (see Fig. 2). The latter proposes a uniform carrier distribution on the  $\text{CuO}_2$  layers.

A sharp increase of  $dT_c^{\max}/dp$  for the 5th phase in comparison with the 4th one (Fig. 3) was explained in [3] within the frame of the RWB model.

Let some hole density  $n_h^{\max}$  correspond to the  $T_c^{\max}$ . The hole densities less than  $n_h^{\max}$  increase linearly with increase of  $\delta$  in all layers [6,8]. The  $T_c(a)$  shows a cupola-shaped dependence and  $a$  is connected with  $\delta$  [1]. To each value of hole density for all the three kinds of layers of the phase Hg-1245 corresponds its own contribution of the «layer –  $T_c$ » to the  $T_c^{\max}$  [7]. The  $T_c$  of the layer decrease with the hole density in the layer. The relative contribution of these  $T_c$  to the  $T_c^{\max}$  may be distinctly changed under pressure what leads to the nonmonotonic  $n$  dependence of the  $(dT_c^{\max}/dp)(n)$  observed.

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