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The Role of Oxygen Content in Electronic Structures of $LaBa_2Cu_3O_y$

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The electronic structures of the $LaBa_2Cu_3O_y$ superconductor were calculated using the band-structure treatment based on the EHMO approach and the role of the oxygen content was investigated. The results show that the oxygen content has a great influence on the band structures and the densities of states near the Fermi level E_f. The lower or higher oxygen content results in the suppression of the transition temperature T_c, which is in qualitative agreement with the behaviour of T_c given by experiment. In addition, the study on the electronic charge of copper shows that the oxidation state of Cu is not the predominant factor for the supercondictivity of $LaBa_2Cu_3O_y$ and may just be a result of charge balance.

INTRODUCTION

Since the YBa_2Cu3O_y superconductor was reported and identified as the orthorhomic 1-2-3 phase,[1–3] much work has been done to investigate the substitutions of other elements at the Y, Ba, and Cu sites and to reveal the origin of superconducting properties from the crystal structure. The earlier studies[4,5] showed that the orthorhomic-to-tetragonal transition, the oxidation state of copper, and the oxygen content were predominant factors for superconductivity, but many experiments[6–16] gave contradictory conclusions on this problem. As for the role of the oxygen content in superconductivity, many experimental results showed that a clear-out relationship exists between the oxygen content and the superconductivity. For example, as the oxygen content y in the unit cell decreases from 7.0 to about 6.6, the $YBa_2Cu_aO_y$ compound is transformed from a superconductor into a semiconductor and its transition temperature T_c is suppressed rapidly. Obviously, in $YBa_2Cu_3O_y$, the oxygen content plays an important role. However, some researchers[10–12] have shown that the relationship between the superconductivity and the oxygen content is irregular. Also, Zhang *et al.*[13] could not find a uniform relationship between the value of T_c and the oxygen content in eight different doped Y-Ba-Cu-O systems. They thought that there might be an argument on the relationship between the T_c value and the oxygen content. Although there is somewhat contradictory literature on the role of the oxygen content in superconductivity, there is still a close relationship between the oxygen content and the superconducting properties in some superconducting systems. Song *et al.*[17] investigated the influence of the change in the oxygen content upon the superconducting transition temperature Tc of $LaBa_2Cu_3O_y$. They revealed that in $LaBa_2Cu_3O_y$, when the oxygen content $y = 6.75$, its value of Tc reached the highest valzue $T_c^{zero} = 72$ K, and as the oxygen content y is increased or decreased from the value of 6.75, T_c is suppressed. In this case, it is clear that T_c of $LaBa_2Cu_3O_y$ is greatly affected by this change in the oxygen content.

In order to reveal the effect of the oxygen content on the properties of $LaBa_2Cu_3O_y$, the electronic structures of the La-doped superconductor are calculated by employing an approximate band structure treatment based on the EHMO approach, and some interesting results will be given in the present paper.

CALCULATION

In order to investigate the influence of the oxygen content on the electronic structures of $LaBa_2Cu_3O_y$, the change in the oxygen content y must be taken into account. As a consequence, $LaBa_2Cu_3O_y$ is a nonstoichiometric system. For a nonstoichiometric system, the band structure treatment based on the EHMO approach was given in our previous work.[18,19] Therefore, is it only concisely described as follows.

For a partially doped system with the integral oxygen content, it is assumed that (i): the interactions between the doping atom M^2 in a unit cell and the atoms M^1, which are in other unit cells and at the substituted site, are zero numerically; (ii): the doping process is regarded as a gradual substitution of the doping atom M^2 for atom M^1 at the fractional ratio x; (iii): after the doping process was completed, atom M^1 had been changed into atom '$(M_x^1.....M_x^2)$'. Obviously, based on these assumptions, the integrals H_{ij} and S_{ij} in the EHMO approach are all functions of the doping fraction x, that is

$$H_{ij} = H_{ij}(x) \ , \qquad S_{ij} = S_{ij}(x) \tag{1}$$

Let $H_{ii}{}^1$, $S_{ij}{}^1$ and $H_{ii}{}^2$, $S_{ij}{}^2$ be the Coulomb integrals and the overlap integrals before the doping and after the complete substitution, respectively. If the numbers of the valence state orbitals for the M^1 and M^2 atoms are equal, $H_{ii}(x)$ and $S_{ii}(x)$ can approximately be expressed as the following forms

$$H_{ii}(x) = (1 - x)H_{ii}{}^1 + xH_{ii}{}^2 + k_1x(1 - x)(H_{ii}{}^2 - H_{ii}{}^1)$$
$$S_{ij}(x) = (1 - x)S_{ij}{}^1 + xS_{ij}{}^2 + k_2x(1 - x)(S_{ij}{}^2 - S_{ij}{}^1) \tag{2}$$

where k_1 and k_2 are adjustable parameters. In order to obtain k_1 and k_2, it is assumed that both $H_{ii}(x)$ and $S_{ij}(x)$ are monotonic functions of x in the interval (0,1); in other words, in the interval (0,1),

$$\mathrm{d}H_{ii}(x)/\mathrm{d}x > 0 \ , \qquad \mathrm{d}S_{ij}(x)/\mathrm{d}x > 0 \tag{3}$$

or

$$\mathrm{d}H_{ii}(x)/\mathrm{d}x < 0 \ , \qquad \mathrm{d}S_{ij}(x)/\mathrm{d}x < 0 \tag{4}$$

From Eqs. (2), the following can be easily obtained

$$\mathrm{d}H_{ii}(x)/\mathrm{d}x = (H_{ii}{}^2 - H_{ii}{}^1)[1 + k_1(1 - 2x)] \tag{5}$$

If $H_{ii}(x)$ is a monotonically increasing function of x in the interval (0,1), then since $H_{ii}{}^2 - H_{ii}{}^1 > 0$

$$1 + k_1(1 - 2x) > 0 \qquad \text{or} \qquad 1 + k_1 > 2k_1x \tag{6}$$

If $k_1 > 0$, from Eq. (6)

$$(1 + k_1)/(2k_1) > x \tag{7}$$

Since the maximum of x is 1 and k_1 must obey Eq. (7) for all the value of x in the interval (0,1), we can obtain

$$(1 + k_1)/(2k_1) \geq 1 \qquad \text{or} \qquad k_1 \leq 1 \tag{8}$$

If $k_1 < 0$, then from Eq. (6)

$$(1 + k_1)/(2k_1) < x \tag{9}$$

The minimum of x is zero. Therefore,

$$(1 + k_1)/(2k_1) \leq 0 \qquad \text{or} \qquad k_1 \geq -1 \tag{10}$$

If $H_{ii}(x)$ ia a monotonically decreasing function of x, the same inequalities of k_1 as Eqs. (8) and (10) can be obtained. For k_2 in $S_{ii}(x)$, the same inequalities as those of k_1 are easily obtained.

If the number of the valence state orbitals for the atom M^1, $N1$, and that for atom M^2, $N2$, are unequal, for instance $N1 - N2 = N > 0$, let the Coulomb integrals of N orbitals, $H_{\mu\mu}(x)$, be equal to $H'_{\mu\mu}$ and $S^2{}_{\mu i} = \delta_{\mu i}$, *i.e.*

$$H_{\mu\mu}(x) = H^1{}_{\mu\mu},\ S_{\mu i}(x) = (1 - x)S^1{}_{\mu i} + x\delta_{\mu i} + k_2 x(1 - x)(\delta_{\mu i} - S^1{}_{\mu i}), \tag{11}$$
$$(\mu = 1, 2, ..., N)$$

As for the treatment for a system with the non integral oxygen content y, let $y = c + z$ in which c is an integer and $0 \leq z \leq 1$. Obviously, z reflects oxygen vacancies in a unit cell and can be regarded as the number of oxygen atoms that are contained, on average, by the unit cell, except for c oxygen atoms. It is assumed that each of the oxygen atoms gets into the given site in the unit cell by degrees. Then, this process can be regarded as a gradual substitution or doping of one oxygen atom for an oxygen vacancy. In contrast, it can also be regarded as a gradual substitution of a vacancy for an oxygen atom at the fraction ratio $(1 - z)$. Based on this assumption, $(1 - z)$ is the vacancy doping fraction. Let the Coulomb integrals of the valence orbitals for the oxygen atom be $H^\circ{}_{\mu\mu}$, their overlap integrals be $S^\circ{}_{\mu i}$ and those of oxygen vacancies be equal to zero. From Eqs. (11), let $x = 1 - z$, we can obtain

$$H_{\mu\mu}(z) = H^\circ{}_{\mu\mu} \tag{12}$$
$$S_{\mu i}(z) = zS^\circ{}_{\mu i} + (1 - z)\delta_{\mu i} + k_p z(1 - z)(\delta_{\mu i} - S^\circ{}_{\mu i}) \qquad (\mu \subset \text{oxygen})$$

where k_p is an adjustable parameter and, like k_2, $-1 \leq k_p \leq 1$. However, in band structure computations, the number of oxygen atoms cannot be taken as a non-integer but only as an integer $c + 1$. In this case, since $0 \leq z \leq 1$, the number of oxygen atoms in the unit cell increases, indeed, by $(1 - z)$. This will result in an increase in the total number of electronic energy bands. These bands, arising from $(1 - z)$ oxygen atoms, may be occupied by electrons, which results in a decrease in the total number of electrons of the unit cell. To obtain satisfactory band structure results, therefore, the total number of electrons of the unit cell must be increased in computations. In order to increase electrons, an iterative procedure similar to that given in Ref. 16, which is not described here, is employed in the present computations.

It must be pointed out emphatically that the above treatment gives the obvious relationship between the band structure results and the doping fraction, although it is approximate. Indeed, the band structures and the densities of states given by the present treatment vary directly with the doping fraction. Herman *et al.* used an interpolation scheme between two end members to study oxygen deficient high-T_c superconductors $YBa_2Cu_3O_y$, ($6 \le y \le 7$).[20] However, they obtained only the band structure results of the stoichimetric system (*e.g.* $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$). For the value of y with a non-integral, their treatment cannot directly reflect the variations in the band structures with changing oxygen content y, whereas the densities of states can be obtained only by employing the interpolation between these of the stoichiometric system. It is clear that the present band structure treatment provides more details of the band structures than does that given by Herman *et al.*.

By the use of the above treatment, calculations on the electronic energy

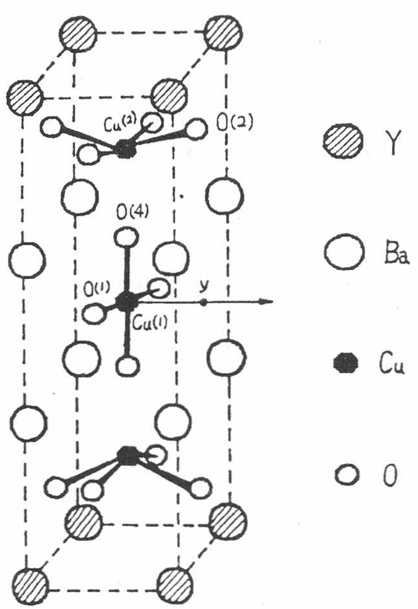

Figure 1. The crystal structure of $LaBa_2Cu_3O_y$.

band structures of $LaBa_2Cu_3O_y$ are carried out. Figure 1 and Figure 2 show, respectively, the crystal structure of $LaBa_2Cu_3O_y$ and the first Brillouin zone. In the present computations, when the oxygen content is more than 7, it is assumed that the eighth oxygen atom gets into the *y* site in the unit cell shown in Figure 1. The atomic orbital ionization potentials and the orbital exponents for Cu, La, O, Ba are summarized in Table I. Some band structure results are givben in Table II.

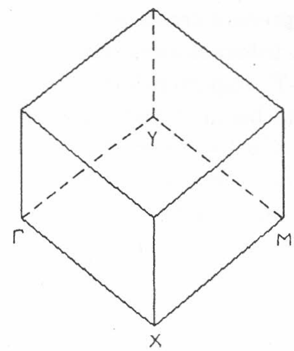

Figure 2. The first Brillouin zone.

TABLE I

EHMO parameters used in the present computations

		$-H_{ii}$ (eV)	ζ_1	C_1	ζ_2	C_2
Cu	s	11.40	2.20			
	p	8.06	2.20			
	d	14.00	5.95	0.5933	2.30	0.5744
La	s	7.87	1.255			
	p	5.01	0.949			
	d	8.21	3.78	0.7765	1.381	0.4586
Ba	s	5.21	1.25			
	p	3.69	1.25			
O	s	21.30	2.275			
	p	14.80	2.275			

TABLE II

Densities of states for $LaBa_2Cu_3O_y$

y	$N(E_f)$	$N(E_f)^P_{Cu-O}$	$N(E_f)^R_{Cu-O}$
6.6	2.75	1.29	0.00
6.7	8.24	1.33	4.73
6.8	8.89	2.85	3.23
6.9	9.95	3.28	2.94
7.0	7.25	3.04	0.56
7.1	6.31	2.98	0.15
7.2	6.35	3.15	0.02
7.3	6.34	3.20	0.02
7.4	4.01	1.98	0.00

RESULTS AND DISCUSSION

Energy band structure

Superconducting properties are in close relationship with band structures near the Fermi level E_f. In order to investigate the influence of the oxygen content on the band structures of the $LaBa_2Cu_3O_y$ superconductor, its electronic energy-band structures near E_f are shown in Figure 3, in iwhich the Fermi level E_f is placed at zero nergy.

It is seen from Figure 3 that, in $LaBa_2Cu_3O_y$, there are three broad anisotropic bands crossing the Fermi level E_f. Two of those, which are partially filled, arise from the overlaps of the 3d orbitals of the Cu atom and the 2p orbitals of the O atom in the 2D Cu-O planes, and the third arises from the 1D Cu-O ribbons. As the oxygen content y is gradually decreased from the value of 6.9, the bandwidths of these Cu_{3d}-O_{2p} bands almost remain unchanged, but they are translated. It is seen that, with decreasing the oxygen

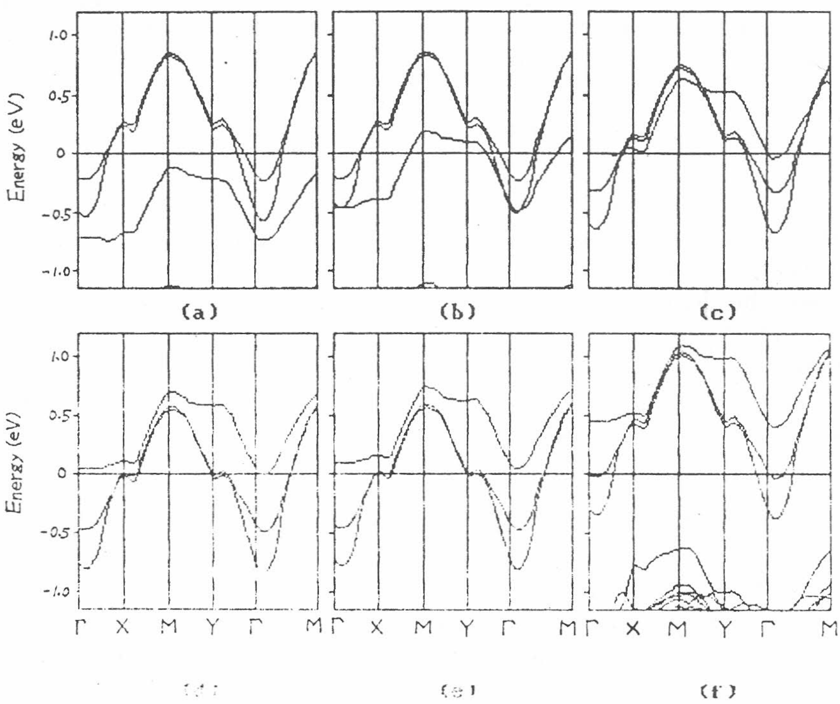

Figure 3. Band structures for $LaBa_2Cu_3O_y$: (a) y = 6.6, (b) y = 6.7, (c) y = 6.9, (d) y = 7.0, (e) y = 7.3, (f) y = 7.4.

content, two broad anisotropic Cu-O bands arising from the 2D Cu-O planes are displaced upwards, whereas the broad anisotropic Cu-O band for the 1D Cu-O ribbons is displace downwards and departs from E_f, by degrees, the top of which is finally situated below E_f. It is clear from these results that the decrease in the oxygen content causes a great change in the band structures near E_f for $LaBa_2Cu_3O_y$. The displacement of the broad anisotropic Cu-O bands, caused by the decrease in the oxygen content, can lead to a decrease in the degree of complexity of the band structures near the Fermi surface, which has a great influence on the superconducting properties. In contrast, when the oxygen content y is raised from 6.9 to 7.3, two broad anisotropic Cu-O bands arising from the 2D Cu-O planes are displaced by only about 0.2 eV, but the broad anisotropic Cu-O band arising from the 1D Cu-O ribbons is displaced upwards and its bottom is situated above E_f at $y = 7.3$. If the oxygen content is further increased to 7.4, the band structures near the Fermi level F_f are changed considerably. It can be seen from the fig. (f) in Figure 3 that, at the oxygen content $y = 7.4$, the bottom of the band arising from the 1D Cu-O ribbons is located above E_f by about 0.4 eV, whereas the bands for the 2D Cu O planes are also displaced. This consequence must result in a great decrease in the degree of complexity of the band structures near the Fermi surface, which causes a large decrease in the electronic densities of states near E_f. Since the densities of states near E_f are in close relationship with the superconducting transition temperature T_c, it is clear that the excessive oxygen content in the the unit cell is certainly of no advantage to the superconducting properties of the $LaBa_2Cu_3O_y$ superconductor.

It can be concluded from the above discussion on the band structures that the lower or higher oxygen content results in a big change in the band structures near the Fermi level E_f for the $LaBa_2Cu_3O_y$ superconductor and decreases the degree of complexity of its band structures near tthe Fermi surface, which directly affects the densities of states at E_f and the superconductivity of $LaBa_2Cu_3O_y$. In fact, the experimental results given by Song *et al.*[17] show that the lower or higher oxygen content leads to suppression of the superconducting transition temperature T_c.

Densities of states

Densities of states are a direct consequence of band structures and are in close relationship with superconductivity. Some results of the densities of states for the $LaBa_2Cu_3O_y$ are summarized in Table II, where $N(E_f)$ expresses the total electronic densities of states at the Fermi level E_f, $N(E_f)^P_{Cu-O}$ represents the sum of the projected densities of states at E_f, for Cu(2), O(2), and O(3) in the 2D Cu-O planes, and $N(E_f)^P_{Cu-O}$, that for Cu(1) and O(1) in the 1D Cu-O ribbons.

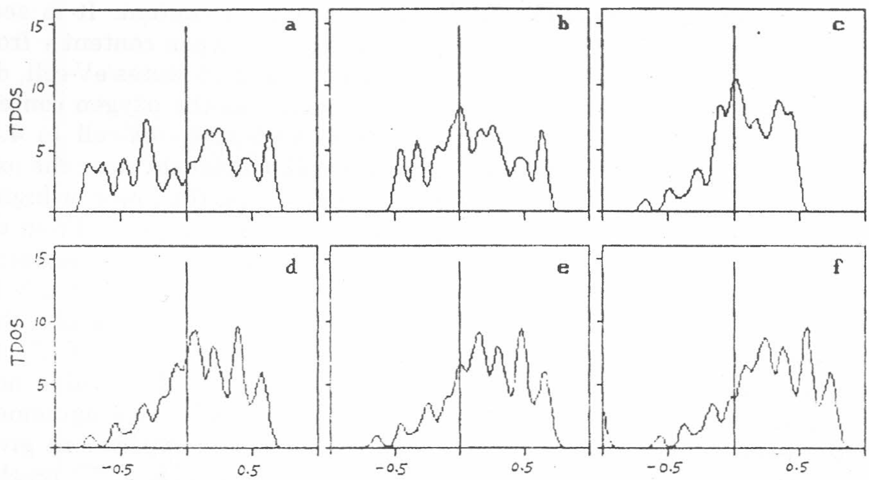

Figure 4. Total densities of states for $LaBa_2Cu_3O_y$: (a) y = 6.6, (b) y = 6.7, (c) y = 6.9, (d) y = 7.0, (e) y = 7.3, (f) y = 7.4.

The total densities of states (TDOS) near the Fermi level E_f for $LaBa_2Cu_3O_y$ are shown in Figure 4. It can be seen from Figure 4 that the change in the oxygen content has a strong influence on the total densities of states near E_f of the $LaBa_2Cu_3O_y$ superconductor. At the oxygen content y = 6.9, there is a strong peak at E_f, which arises from the 1D Cu-O ribbons and the 2D Cu-O planes. As the y values is reduced from 6.9 to 6.7, the height of this Cu-O peak is relatively decreased. When the y value is further reduced to 6.6, the peak height is quickly decreased. This consequence is in close relationship with the total densities of states at E_f $N(E_f)$. Figure 5

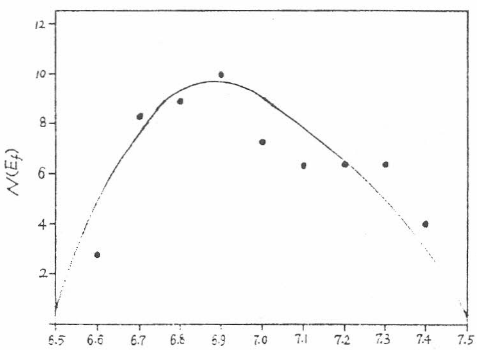

Figure 5. The relationship between $N(E_f)$ and the y value in $LaBa_2Cu_3O_y$: The circle represents $N(E_f)$.

shows the relationship between $N(E_f)$ and the oxygen content. It is seen from Figure 5 and Table II that, with decreasing the oxygen content y from 6.9 to 6.6, $N(E_f)$ is reduced from 9.95 states/eV-cell to 2.75 states/eV-cell, decreased by about 7.2 states/eV-cell. On the contrary, as the oxygen content y is raised from 6.9 to 7.4, $N(E_f)$ varies from 9.95 states/eV-cell to 4.01 states/eV-cell, decreased by about 6.0 states/eV-cell. Obviously, near the oxygen content $y = 6.9$, $N(E_f)$ reaches the highest value, and the lower or higher oxygen content results in a large decrease in $N(E_f)$ (see Figure 5). From the point of view of the BCS theory, the superconductingg transition temperaturte T_c is directly proportional to the factor $\mathrm{Exp}(-1/N(E_f)V)$, in which $N(E_f)$ is the total densities of states at E_f. It is clear from the above results that the lower or higher oxygen content will cause the value of T_c for $LaBa_2Cu_3O_y$ to be suppressed, while its T_c reaches the highest value near the oxygen content $y = 6.9$. This consequence is in qualitative agreement with the experimental result given by Song *et al.*[17] The experiment given by Song *et al.* showed that, at the oxygen content $y = 6.75$, T_c^{zero} reaches the highest value of 72 K, whereas the lower or higher oxygen content results in suppression of T_c. It is apparent that this work cannot obtain a quantitative result, but it gives qualitatively the behaviour of the superconducting transition temperature T_c.

The change in the total densities of states is affected by the projected densities of states for the 1D Cu-O ribbons and the 2D Cu-O planes. It can be seen from Table II that, as the oxygen content y is reduced from 6.9 to 6.6, the sum of the projected densities of states at E_f for Cu(2), O(2), and O(3) in the 2D Cu-O planes, $N(E_f)^P_{\mathrm{Cu-O}}$ is gradually reduced from 3.28 states/eV-cell to 1.29 states/eV-cell, decreased by about 2.0 states/eV-cell, whereas that for Cu(1) and O(1) in the 1D Cu-O ribbons, $N(E_f)^R_{\mathrm{Cu-O}}$ is increased between the oxygen content of 6.9 and 6.7. In this case, since there are two Cu-O planes in the unit cell, it is obvious that the decrease in $N(E_f)$ arises mainly from the 2D Cu-O planes. In contrast, when the y value is increased from 6.9 to 7.4, $N(E_f)^P_{\mathrm{Cu-O}}$ is decreased a little, but $N(E_f)^R_{\mathrm{Cu-O}}$ rapidly reduced from 3.94 states/eV-cell to zero. As a result, with increasing the oxygen content from the value of 6.9, the decrease in $N(E_f)$ is mainly due to the change in $N(E_f)^R_{\mathrm{Cu-O}}$. These results show that the 2D Cu-O planes and the 1D Cu-O ribbons play an important role in $LaBa_2Cu_3O_y$.

Oxidation state of copper

Earlier studies[4,5] showed that the oxidation state of Cu plays an important role in superconductivity and that the higher is the ratio of Cu^{3+} to Cu^{2+}, the higher is the superconducting transition temperature T_c. However, most X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) studies[21–24] did not find the Cu^{3+} oxidation state in the Y-Ba-Cu-O system. Although some studies[25,26] have found a small amount of the Cu^{3+} oxidation state, the relationship between Cu^{3+} and superconductivity is still not well understood. Zhang *et al.*[14–16,27] have studied several doped Y-Ba-Cu-O systems and discovered that the ratio of Cu^{3+} to Cu^{2+} does not determine the magnitude of Tc. They consider that the oxidation state of Cu may just be a result of charge balance.

TABLE III

The net charge of Cu in $LaBa_2Cu_3O_y$

y	$Q1$	$Q2$	Q
6.6	0.45	1.58	1.20
6.7	0.49	1.64	1.26
6.8	0.84	1.50	1.28
6.9	1.23	1.35	1.31
7.0	1,71	1.16	1.34
7.1	1.72	1.22	1.39
7.2	1.72	1.29	1.43
7.3	1,72	1.37	1.49
7.4	1.71	1.46	1.54

Note: $Q1$ and $Q2$ express, respectively, the net charge of Cu at the Cu(1) site and at the Cu(2) site, and Q is the average net charge of Cu.

Table III summarizes the net charges of Cu(1) and Cu(2) in $LaBa_2Cu_3O_y$. It is seen from Table III that, as the oxygen content y in the $LaBa_2Cu_3O_y$ superconductor is raised from 6.6 to 7.4, the net charges of Cu(1) and Cu(2) are changed considerably. The net charge of Cu(1) is monotonously increased from 0.45 to 1.72, whereas that of Cu(2) has an irregular relationship with the increasing oxygen content. In addition, from the average net charge of Cu given in Table III, it is seen that the average net charge of Cu is also monotonously increased with the increasing oxygen content. It is clear from these results that the change in the oxidation state of Cu is not in agreement with the behaviour of the transition temperature T_c. Therefore, it is considered that, in $LaBa_2Cu_3O_y$, the oxidation state of copper is not the predominant factor for superconductivity and may just be a result of charge balance, which is in agreement with the result given by Zhang *et al.*.

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SAŽETAK

Uloga sadržaja kisika na elektronsku strukturu $LaBa_2Cu_3O_y$

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Upotrebom EHMO (= proširena inačica Hückelove metode molekulskih orbitala) računa strukture vrpci izračunana je elektronska struktura supravodiča $LaBa_2Cu_3O_y$ i utjecaj koji na nju ima sadržaj kisika. Pokazano je da sadržaj kisika jako utječe na strukturu vrpci i gustoću stanja uz Fermijevu površinu E_f. Promjene u sadržaju kisika dovode do supreasije temperature prijelaza T_c, što se kvalitativno slaže s eksperimentalnim nalazima. Također je proučavanjem elektronskog naboja na atomima bakra pokazano da oksidacijsko stanje bakra nije prevladavajući čimbenik za supravodljivost $LaBa_2Cu_3O_y$.