The Role of Oxygen Content in Electronic Structures of LaBa$_2$Cu$_3$O$_y$

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The electronic structures of the LaBa$_2$Cu$_3$O$_y$ 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 superconductivity of LaBa$_2$Cu$_3$O$_y$ and may just be a result of charge balance.

INTRODUCTION

Since the YBa$_2$Cu$_3$O$_y$ superconductor was reported and identified as the orthorhomic 1-2-3 phase, 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 showed that the orthorhomic-to-tetragonal transition, the oxidation state of copper, and the oxygen content were predominant factors for superconductivity, but many experiments 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$_2$Cu$_y$O$_y$ compound is transformed from a superconductor into a semiconductor and its transition temperature $T_c$ is suppressed rapidly. Obviously,
in $\text{YBa}_2\text{Cu}_3\text{O}_y$, the oxygen content plays an important role. However, some researchers\textsuperscript{10-12} have shown that the relationship between the superconductivity and the oxygen content is irregular. Also, Zhang et al.\textsuperscript{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.\textsuperscript{17} investigated the influence of the change in the oxygen content upon the superconducting transition temperature $T_c$ of LaBa$_2$Cu$_3$O$_y$. They revealed that in LaBa$_2$Cu$_3$O$_y$, when the oxygen content $y = 6.75$, its value of $T_c$ reached the highest value $T_{c\text{\ zero}} = 72$ 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$_2$Cu$_3$O$_y$ 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$_2$Cu$_3$O$_y$, 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$_2$Cu$_3$O$_y$, the change in the oxygen content $y$ must be taken into account. As a consequence, LaBa$_2$Cu$_3$O$_y$ is a nonstoichiometric system. For a nonstoichiometric system, the band structure treatment based on the EHMO approach was given in our previous work.\textsuperscript{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 $(M^1 \ldots M^2)^x$. 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

\[ H_{ij} = H_{ij}(x) , \quad S_{ij} = S_{ij}(x) \] (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 $S_{ij}(x)$ can approximately be expressed as the following forms

$$H_{ii}(x) = (1 - x)H_{ii}^1 + xH_{ii}^2 + k_1x(1 - x)(H_{ii}^2 - H_{ii}^1)$$

$$S_{ij}(x) = (1 - x)S_{ij}^1 + xS_{ij}^2 + k_2x(1 - x)(S_{ij}^2 - S_{ij}^1)$$

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 $(0,1)$,

$$\frac{dH_{ii}(x)}{dx} > 0 , \quad \frac{dS_{ij}(x)}{dx} > 0$$

or

$$\frac{dH_{ii}(x)}{dx} < 0 , \quad \frac{dS_{ij}(x)}{dx} < 0$$

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

$$\frac{dH_{ii}(x)}{dx} = (H_{ii}^2 - H_{ii}^1)[1 + k_1(1 - 2x)]$$

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

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

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

$$(1 + k_1)/(2k_1) > x$$

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

$$(1 + k_1)/(2k_1) \geq 1 \quad \text{or} \quad k_1 \leq 1$$

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

$$(1 + k_1)/(2k_1) < x$$

The minimum of $x$ is zero. Therefore,
If \( H_{ij}(x) \) is a monotonically decreasing function of \( x \), the same inequalities of \( k_1 \) as Eqs. (8) and (10) can be obtained. For \( k_2 \) in \( S_{ij}(x) \), the same inequalities as those of \( k_1 \) are easily obtained.

If the number of the valence state orbitals for the atom \( M_1, N_1 \), and that for atom \( M_2, N_2 \), are unequal, for instance \( N_1 - N_2 = N > 0 \), let the Coulomb integrals of \( N \) orbitals, \( H_{\mu \mu}(x) \), be equal to \( H_{\mu \mu}' \) and \( S_{\mu \mu}^2 = \delta_{\mu \mu}' \), i.e.

\[
H_{\mu \mu}(x) = H_{\mu \mu}', \quad S_{\mu \mu}(x) = (1 - x)S_{\mu \mu}^1 + x\delta_{\mu \mu} + k_2x(1 - x)(\delta_{\mu \mu} - S_{\mu \mu}^1),
\]

\[ \mu = 1, 2, \ldots, N \]  

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 \( H_{\mu \mu}^\circ \), their overlap integrals be \( S_{\mu \mu}^\circ \) and those of oxygen vacancies be equal to zero. From Eqs. (11), let \( x = 1 - z \), we can obtain

\[
H_{\mu \mu}(z) = H_{\mu \mu}^\circ
\]

\[
S_{\mu \mu}(z) = zS_{\mu \mu}^\circ + (1 - z)\delta_{\mu \mu} + k_pz(1 - z)(\delta_{\mu \mu} - S_{\mu \mu}^\circ)
\]

\[ \mu \subset \text{oxygen} \]

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 den-
sities of states given by the present treatment vary directly with the doping frac-
tion. Herman et al. used an interpolation scheme between two end members to
study oxygen deficient high-$T_c$ superconductors $\text{YBa}_2\text{Cu}_3\text{O}_y$, $(6 \leq y \leq 7)$.
However, they obtained only the band structure results of the stoichiometric sys-
tem (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_6$, $\text{YBa}_2\text{Cu}_3\text{O}_7$). 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 ob-
tained only by employing the interpolation between these of the stoichiomet-
ric 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$_2$Cu$_3$O$_y$.](image)

band structures of LaBa$_2$Cu$_3$O$_y$ are carried out. Figure 1 and Figure 2 show,
respectively, the crystal structure of LaBa$_2$Cu$_3$O$_y$ 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 or-
bital exponents for Cu, La, O, Ba are summarized in Table I. Some band
structure results are given in Table II.
Figure 2. The first Brillouin zone.

TABLE I

EHMO parameters used in the present computations

<table>
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<tr>
<th></th>
<th>$-H_i$ (eV)</th>
<th>$\zeta_1$</th>
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<th>$\zeta_2$</th>
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<td>p</td>
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TABLE II

Densities of states for LaBa$_2$Cu$_3$O$_y$

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<tr>
<th>y</th>
<th>$N(E_f)$</th>
<th>$N(E_f)^P_{\text{Cu-O}}$</th>
<th>$N(E_f)^R_{\text{Cu-O}}$</th>
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<td>7.4</td>
<td>4.01</td>
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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$_2$Cu$_3$O$_y$ superconductor, its electronic energy-band structures near $E_f$ are shown in Figure 3, in which the Fermi level $E_f$ is placed at zero energy.

It is seen from Figure 3 that, in LaBa$_2$Cu$_3$O$_y$, 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$_2$Cu$_3$O$_y$: (a) $y = 6.6$, (b) $y = 6.7$, (c) $y = 6.9$, (d) $y = 7.0$, (e) $y = 7.3$, (f) $y = 7.4$.](image-url)
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 displaced 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$_2$Cu$_3$O$_y$. 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 $E_f$, 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 CuO 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 unit cell is certainly of no advantage to the superconducting properties of the LaBa$_2$Cu$_3$O$_y$ 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$_2$Cu$_3$O$_y$ superconductor and decreases the degree of complexity of its band structures near the Fermi surface, which directly affects the densities of states at $E_f$, and the superconductivity of LaBa$_2$Cu$_3$O$_y$. In fact, the experimental results given by Song et al.\textsuperscript{17} show that the lower or higher oxygen content leads to suppression of the superconducting transition temperature $T_c$.

\textit{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$_2$Cu$_3$O$_y$ are summarized in Table II, where $N(E_f)$ expresses the total electronic densities of states at the Fermi level $E_f$, $N(E_f)_{\text{Cu-O}}$ 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 $N(E_f)_{\text{Cu-O}}$, that for Cu(1) and O(1) in the 1D Cu-O ribbons.
The total densities of states (TDOS) near the Fermi level $E_f$ for LaBa$_2$Cu$_3$O$_y$ 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$_2$Cu$_3$O$_y$ 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
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 superconducting transition temperature \( T_c \) is directly proportional to the factor \( \text{Exp}(-1/N(E_f)V) \), 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 \( \text{LaBa}_2\text{Cu}_3\text{O}_y \) 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.\(^\text{17}\) The experiment given by Song et al. showed that, at the oxygen content \( y = 6.75 \), \( T_c \) 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, \( N(E_f)^{\text{P}}_{\text{Cu}-\text{O}} \) 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, \( N(E_f)^{\text{R}}_{\text{Cu}-\text{O}} \) 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, \( N(E_f)^{\text{P}}_{\text{Cu}-\text{O}} \) is decreased a little, but \( N(E_f)^{\text{R}}_{\text{Cu}-\text{O}} \) 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 \( N(E_f)^{\text{R}}_{\text{Cu}-\text{O}} \). These results show that the 2D Cu-O planes and the 1D Cu-O ribbons play an important role in \( \text{LaBa}_2\text{Cu}_3\text{O}_y \).

Oxidation state of copper

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

\textbf{TABLE III}

The net charge of Cu in LaBa$_2$Cu$_3$O$_y$

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<th>$Q_1$</th>
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Note: $Q_1$ and $Q_2$ 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$_2$Cu$_3$O$_y$. It is seen from Table III that, as the oxygen content $y$ in the LaBa$_2$Cu$_3$O$_y$ 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$_2$Cu$_3$O$_y$, 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 \textit{et al.}.

\textit{Acknowledgements.} - This work was supported by the Science Foundation of Chongqing City, PRC.
REFERENCES


SAŽETAK

Uloga sadržaja kisika na elektronsku strukturu LaBa$_2$Cu$_3$O$_y$

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Upotrebom EHMO (= proširena inačica Hückelove metode molekulskih orbitala) računa strukture vrpci izračunana je elektronska struktura supravodiča LaBa$_2$Cu$_3$O$_y$ 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$_2$Cu$_3$O$_y$. 