# Relationship between oxygen content and superconductivity of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$)

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**Abstract.** The electronic energy band structures of the $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$) superconductor were calculated and the effect of the oxygen content on its electronic structures was studied in the present paper. The results show that the oxygen content has a great influence on its electronic structures. The moderate oxygen content causes the number of bands near the Fermi surface to increase and results in a sudden change in the densities of states at the Fermi level $E_f$. The influence of the oxygen content on the electronic structures is mainly due to the peroxide pairs in the unit cell. The lower or higher oxygen content results in the decrease in the number of bands near $E_f$ and the densities of states at $E_f$, which is of no advantage to superconductivity.

**Key words:** $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$) Superconductor – Oxygen content – Band structure

## 1 Introduction

Since the Tl-based copper oxides with the high transition temperature $T_c$ were discovered and identified [1–4], much work has been done to investigate the properties of these superconductors. It has been known that in the Tl-based copper oxides, there are two homologous series, one having the single Tl–O layers, and the other having the double $Tl_2$–$O_2$ layers. The single Tl–O layered compounds are much less stable than the corresponding double thallium layered cuprates. However, the partial replacement of Tl by other metals can lead to the stabilization of the single Tl–O layered compounds. For instance, the partial substitution of lead for thallium in $TlSr_2CuO_y$ ($y \approx 5$) results in an increase in its structural stability. Since Pb appears in the $Pb^{4+}$ oxidation state, the substitution of Pb for Tl leads not only to its structural stability but also to variations in the oxygen content, which can certainly influence its physical properties.

In the past years, several Tl-based copper oxides with the general formula of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$ (Tl,Pb-1201) have been reported [5–11] and their properties investigated. The properties of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$ as reported by various investigators differ widely because of the different synthetic conditions. Martin et al. [5] found no evidence for diamagnetism in $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$ down to 4 K, while

some researchers [7–10] reported metallic behavior down to low temperature. On the other hand, Barry et al. [11] discovered superconductivity near 50 K in $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$. Obviously, the properties of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$ are greatly affected by the synthetic conditions. Pan et al. [12] undertook a systematic study of the effect of synthetic conditions on the physical properties of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$ and discovered that the oxygen content of the samples is greatly affected by the synthetic conditions. Their experiments showed that the small variations in the oxygen content are responsible for the dramatic changes in the physical properties of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5+\delta}$. The samples with the lowest oxygen content are semiconducting, those with the relatively high oxygen content are superconducting ($T_c \approx 60$ K), and those with the highest oxygen content are metallic.

In order to reveal the role of oxygen content in the superconductivity of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$), therefore, its electronic energy band structures are calculated by employing the band structure treatment based on the EHMO approach and some interesting results given in the present paper.


## 2 Calculation

Generally speaking, a partially doped system or a system with oxygen vacancies does not have periodicity and the doping often results in a change in the oxygen content in a unit cell. This system is a nonstoichiometric system. In order to investigate the influence of the oxygen content on the electronic structures of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$, a band structure treatment which can be employed to compute the nonstoichiometric system must be established. For a nonstiochiometric system, the band structure treatment based on the EHMO approach was given in our previous work [13–16], which is concisely described only as follows.

For a partial cation 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 the gradual substitution of the doping atom $M^2$ for the atom $M^1$ at the fractional ratio $x$, and (iii) after the doping process was completed, the atom $M^1$ has been changed into the atom "$(M^1_{1-x}M^2_x)$". 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

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

Let $H^1_{ij}$, $S^1_{ij}$ and $H^2_{ij}$, $S^2_{ij}$ 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, $H_{ij}(x)$ and $S_{ij}(x)$ can approximately be expressed as the following forms:

$$H_{ii}(x) = (1-x)H^1_{ii} + xH^2_{ii} + k_1x(1-x)(H^2_{ii} - H^1_{ii}),$$

$$S_{ij}(x) = (1-x)S^1_{ij} + xS^2_{ij} + k_2x(1-x)(S^2_{ij} - S^1_{ii}), \tag{2}$$

where $k_1$ and $k_2$ are adjustable parameters and $-1 \leqslant k_1 \leqslant 1$, $-1 \leqslant k_2 \leqslant 1$. It must be emphasized here that since $0 \leqslant x \leqslant 1$ and $|H^1_{ii} - H^2_{ii}| \ll |H^1_{ii} + H^2_{ii}|/2$, the quadratic terms for $H_{ii}(x)$ and $S_{ij}(x)$ are much smaller than their linear terms. In

this case, for $H_{ii}(x)$ and $S_{ij}(x)$, the quadratic terms are only their correction factors. Therefore, the choice of the parameters $k_1$ and $k_2$ has a very small influence on the band-structure results in EHMO computations. In the present computations, both $k_1$ and $k_2$ are taken as 0.5, and so also is $k_p$ in Eq. (4).

If the number of the valence state orbitals for the atom $M^1$, $N_1$, and that for the 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 $H_{\mu\mu}^1$ and $S_{\mu i}^2 = \delta_{\mu i}$, i.e.,

$$H_{\mu\mu}(x) = H_{\mu\mu}^1, \quad S_{\mu i}(x) = (1 - x)S_{\mu i}^1 + x\delta_{\mu i} + k_2 x(1 - x)$$

$$(\delta_{\mu i} - S_{\mu i}^1)^2 \quad (\mu = 1, 2, \cdots, N). \tag{3}$$

As for the treatment for a system with nonintegral oxygen content $y$, let $y = c + z$ in which $c$ is an integer and $0 \leqslant z \leqslant 1$. Obviously, $z$ reflects oxygen vacancies in a unit cell and can be regarded as the number of oxygen atoms that are contained, on the 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 the gradual substitution or doping of one oxygen atom for an oxygen vacancy. Based on this assumption, $z$ is the oxygen doping fraction. Let the Coulomb integrals of the valence orbitals for the doping oxygen atom be $H_{\mu\mu}^o$, their overlap integrals be $S_{\mu i}^o$, and those of oxygen vacancies be equal to zero. We can obtain

$$H_{\mu\mu}(z) = H_{\mu\mu}^o, \quad S_{\mu i}(z) = \begin{cases} zS_{\mu i}^o + k_p z(1 - z)S_{\mu i}^o & (\mu \neq i) \\ 1 & (\mu = i) \end{cases} \quad (\mu \in \text{oxygen}) \tag{4}$$

where $k_p$ is an adjustable parameter and $-1 \leqslant k_p \leqslant 1$. However, in band-structure computations, the number of oxygen atoms cannot be taken as a noninteger but only as an integer $c + 1$. In this case, since $0 \leqslant z \leqslant 1$ 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. [13], which is not described here, is employed in the present computations.

Let NE be the original number of electrons in the unit cell; ME, the number of electrons in all the bands including $(c + 1)$ oxygen atoms; $P$, the electronic populations of all the atoms except $(1 - z)$ oxygen atoms at the oxygen-vacancy site; and $Q$, the electronic populations of the oxygen atom at the oxygen-vacancy site. Obviously,

$$P = \text{ME} - (1 - z)Q. \tag{5}$$

It is clear from the above analysis that $P \neq \text{NE}$ if ME is not raised. However, it must be noted that when electrons are raised, a part of these electrons may also occupy the orbitals arising from $(1 - z)$ oxygen atoms at the oxygen-vacancy site. In other words, $Q$ may increase with ME. In order to obtain the satisfactory band-structure results, therefore, ME is raised gradually until $P = \text{NE}$.

For the off-diagonal elements $H_{ij}(x)$ $(i \neq j)$, the following formulas are used in the present calculations:

$$H_{ij}(x) = k'/2(H_{ii}(x) + H_{jj}(x))S_{ij}(x), \quad k' = k + \Delta^2 + \Delta^4(1 - k),$$

$$\Delta = (H_{ii}(x) - H_{jj}(x))/(H_{ii}(x) + H_{jj}(x)), \tag{6}$$

where $k = 1.75$.

By use of the band-structure treatment given in our previous work, calculations on the electronic energy-band structures of the $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ $(y \approx 5)$ superconductor are carried out. The crystal structure of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ $(y \approx 5)$ is shown in Fig. 1 and its structural parameters are taken from Ref. [12]. The atomic orbital ionization potentials and the orbital exponents used in the present calculations are summarized in Table 1. When the oxygen content $y$ in $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ is more than 5, the variation in the oxygen content can certainly cause the change in the crystal structure. Chaillout et al. [17] reported the structure of an oxygen-enriched superconductor $La_2CuO_{4.032}$. In this structure, an oxygen atom is replaced by the peroxide pairs separated by only 1.6 Å. According to Chaillout et al., therefore, it is assumed in the present computations that the O(3) atom is replaced by the peroxide pairs O(3) and O(6) shown in Fig. 1 which is
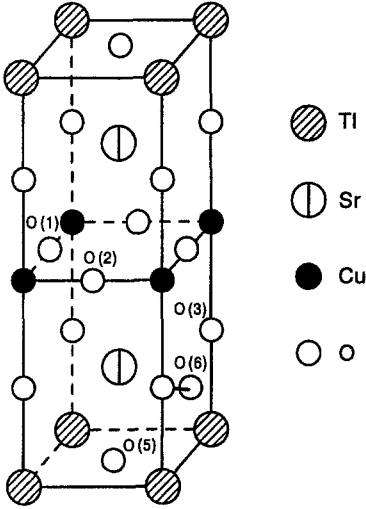


**Fig. 1.** The crystal structure of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ $(y \approx 5)$

Table 1. EHMO parameters used in the present computations

| | $-H_{ii}$ (eV) | | | Orbital exponent | | |
|------|------|------|-------|------|------|-------|
| | $s$ | $p$ | $d$ | $s$ | $p$ | $d$ |
| Cu | 9.101 | 6.06 | 16.45 | 1.541 | 1.541 | 3.813 |
| Tl | 11.60 | 5.80 | | 2.30 | 1.60 | |
| Pb | 15.70 | 8.00 | | 2.35 | 2.06 | |
| Sr | 6.62 | 3.92 | | 1.214 | 1.214 | |
| O | 32.44 | 15.86 | | 2.189 | 2.029 | |

separated by only 1.6 Å and that the O(6) atom is at the position (0.375, 0, 0.124). When the oxygen content $y$ is less than 5, it is assumed that the oxygen vacancies are located on the Cu–O planes or on the Tl–O planes. Some band-structure results are summarized in Table 2.

## 3 Results and discussion

Before the discussions about the influence of the oxygen content on $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ are carried out, let us analyse the band-structure results of Tl- and Pb-1201 phases with stoichiometry. Figure 2 shows the band structures of $TlSr_2CuO_5$ and $PbSr_2CuO_5$. It is seen that in both $TlSr_2CuO_5$ and $PbSr_2CuO_5$, there is a broad anisotropic band, which is due to $Cu3d_{x2-y2}$–$O2p_{x, y}$ overlaps in the Cu–O planes, crossing the Fermi level $E_f$. This band is unoccupied for $TlSr_2CuO_5$, and it is half-filled in $PbSr_2CuO_5$. Below this $Cu3d_{x2-y2}$–$O2p_{x, y}$ band, there is also a filled Cu–O anisotropic band with about 1.0 eV of bandwidth. In addition, a band arising mainly from the $6s$ orbitals of Tl or Pb lies above the $Cu3d_{x2-y2}$–$O2p_{x, y}$ band by about 9 eV. This consequence is in general agreement with that obtained by Jung and Whangbo et al. [18]. They demonstrated that in the Tl-based copper oxides with the Tl–O single layers, the Tl $6s$-block bands of the Tl–O single layers lie well above the Fermi level. Obviously, unlike the Tl-based copper oxides with the $Tl_2$–$O_4$ double layers, the Tl–O or Pb–O single layers do not remove electrons from the $x^2$–$y^2$ bands of the Cu–O layers. Compared with the band structure of $TlSr_2CuO_5$, that of $PbSr_2CuO_5$ is displaced downwards by about 0.6 eV because of the increase in the number of valence electrons although the bands near $E_f$ almost remain unchanged in shape. Near $E_f$, both $TlSr_2CuO_5$ and $PbSr_2CuO_5$ have uncomplicated band structures, which result in the low total densities of states at $E_f$, $N(E_f)$. For example, $N(E_f) = 2.79$ states/eV-cell for $TlSr_2CuO_5$ and $N(E_f) = 1.82$ states/eV-cell for $PbSr_2CuO_5$.

### 3.1 Band structures

The band structures of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y = 5, 5.1, 5.2, 5.29$, and 5.45) are shown in Fig. 3, in which the Fermi level $E_f$ is placed at the zero of energy. It is seen from Fig. 3 that in the band structure of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$, there is a broad anisotropic band crossing the Fermi level $E_f$ in the directions of the wave vectors located on
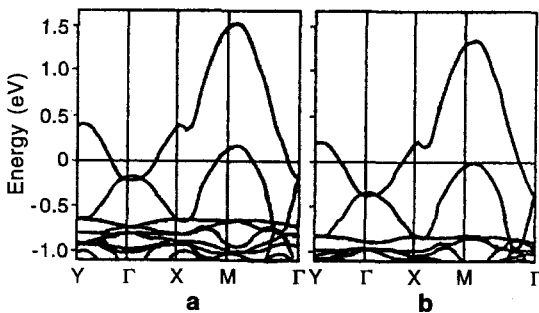
Fig. 2. Band structures for $TlSr_2CuO_5$ and $PbSr_2CuO_5$: (a) $TlSr_2CuO_5$; (b) $PbSr_2CuO_5$

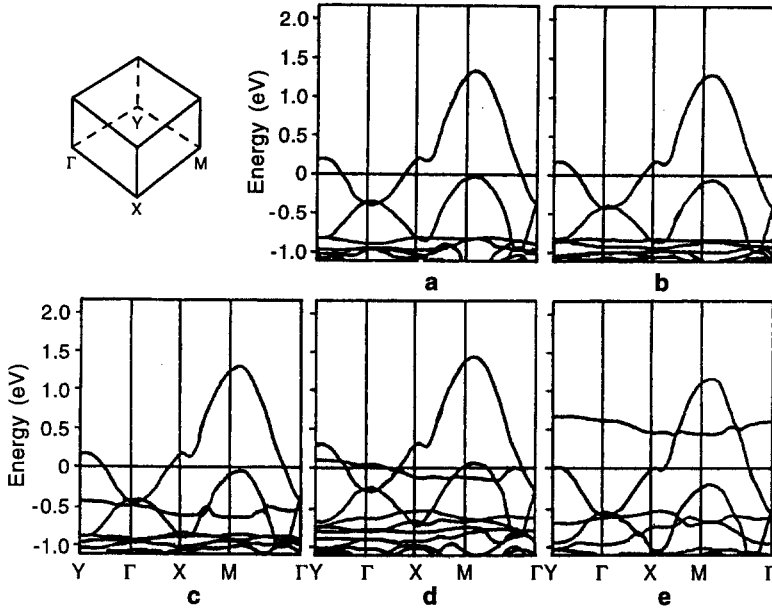**Fig. 3.** Band structures for $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$: (a) $y = 5$; (b) $y = 5.1$; (c) $y = 5.2$; (d) $y = 5.29$; (e) $y = 5.45$

the $\Gamma$–$X$–$M$–$Y$–$\Gamma$ plane in the first Brillouin zone. Like that of $TlSr_2CuO_5$ or $PbSr_2CuO_5$, this band, the bandwidth of which is about 1.8 eV, arises also from the antibonding overlaps of the $Cu3d_{x^2-y^2}$ and the $O2p_{x,\,y}$ orbitals in the Cu–O planes. Besides the $Cu3d_{x^2-y^2}$–$O2p_{x,\,y}$ band, a filled anisotropic Cu–O band, the bandwidth of which is about 1.0 eV, is situated below $E_f$. As the value of the oxygen content is raised from 5 to about 5.1, the band structure for $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ almost remains unchanged. When the oxygen content is further increased from 5.1, however, although two broad anisotropic Cu–O bands near $E_f$ remain unchanged by comparison to those of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$, a band, whose dispersion is very small, is displaced upwards by degrees with the increase in the oxygen content. This band arises mainly from the peroxide pairs formed by O(3) and O(6) atoms shown in Fig. 1 and partially from the $p$ orbitals of the oxygen atom in the Tl–O planes and the $Cu3d_{xz}$–$O2p_z$ overlaps of Cu and O atoms in the Cu–O planes. At the oxygen content $y \approx 5.29$, this band is located near $E_f$ and crosses $E_f$ in the $\Gamma$–$X$ direction. It is obvious that, in this case, the displacement of this band caused by the increase in the oxygen content results in its transformation from a filled band into a partially filled band, which is of advantage to the metallic property of the Tl, Pb-1201 phase. In addition, the top of the filled broad anisotropic Cu–O band also crosses $E_f$ near the $M$ point in the first Brillouin zone. It is seen from Fig. 3d that compared to that of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$, the band structure of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5.29}$ near the Fermi surface is greatly complicated. As a consequence, the increase in the oxygen content leads to a great increase in the degree of complexity of the band structure near the Fermi surface of the Tl,Pb-1201 phase. Since the degree of complexity of the band structure near the Fermi surface is in close relationship with densities of states and further with superconductivity, the

increase in the oxygen content has an important influence on the superconducting properties of the Tl,Pb-1201 phase. Further, it can be seen from Fig. 3e that if the value of the oxygen content is raised from 5.29 to 5.45, the band arising from the peroxide pairs formed by O(3) and O(6) atoms is further displaced upwards and departs from $E_f$. At the oxygen content $y = 5.45$, its band bottom is located above $E_f$ by about 0.5 eV. In addition to those, the broad anisotropic band formed by the $Cu3d_{x^2-y^2}-O2p_{x,\,y}$ overlaps in the Cu–O planes is displaced downwards although its bandwidth and dispersion almost remain unchanged. These results cause the degree of complexity of the band structure near the Fermi surface to decrease greatly, which can result in a sudden decrease in the electronic densities of states and have a great influence on the physical properties of the Tl,Pb-1201 phase. It must be, of course, pointed out that as the value of the oxygen content $y$ is raised from 5.29 to 5.45, the Fermi level $E_f$ is shifted to the Van Hove singularity gradually and finally sits nearly on the Van Hove singularity at $y = 5.45$. In some work, the occurrence of the Fermi energy on a Van Hove singularity is involved as the source of superconductivity [19, 20]. However, it is revealed by some studies that the Fermi energy moves away from the Van Hove singularity in some superconductive systems [21]. It is seen from the band structure of $Tl_{0.5}Pb_{0.5}CuO_{5.45}$ that although the oxygen content causes $E_f$ to sit nearly on the Van Hove singularity, the increase in the oxygen content results in a great decrease in the degree of complexity of its band structure near $E_f$, compared with that of $Tl_{0.5}Pb_{0.5}CuO_{5.29}$, because of the upward displacement of the band arising from the peroxide pairs. This consequence has a great influence on the densities of states at $E_f$ and further on the physical properties. It is clear from these discussions that the change in the oxygen content plays a key role in the physical properties of the $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$) superconductor.

Now let us analyze the band structure of the Tl,Pb-1201 phase in detail. In 1965, Ladik et al. [22] suggested the "two-band model" of superconductivity to reveal the origin of superconducting properties. In this model, the polarization of the localized electrons in the $\sigma$ bands provides an effective attraction between the mobile electrons in the $\pi$ bands, which can lead to the formation of Cooper pairs and therefore also to a superconductive state. The validity of the "two-band model" has been verified by a series of the *ab initio* SCF LCAO crystal orbital calculations on the two-dimensional Cu–O planes given by Ladik et al. [23]. It is known from the above discussions about the band structures of $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$) that two broad anisotropic Cu–O bands near the Fermi level $E_f$ are of $\sigma$-type in character, whereas for the Cu–O planes, the band which arises mainly from the peroxide pairs and partially from the $Cu3d_{x^2-y^2}-O2p_{x,\,y}$ overlaps in the Cu–O planes is of $\pi$-type in character. As shown in the above paragraph, on increasing the value of the oxygen content from 5 to 5.29, the $\pi$ band is displaced by degrees and finally situated in the Fermi level $E_f$ and intersects the $\sigma$ bands. Apparently, this consequence can greatly enhance the interaction between the $\sigma$ and $\pi$ bands. This interaction enhances greatly the polarization of the localized electrons in the $\sigma$ bands and provides a more effective attraction between the mobile electrons in the $\pi$ band. According to the "two-band model", this result is certainly of advantage to the formation of Cooper pairs and therefore to a superconducting state. Therefore, the increase in the oxygen content is of great importance to the superconducting properties of the Tl,Pb-1201 phase. When the oxygen content is further increased to 5.45, it is seen from Fig. 2 that the $\pi$ band is located above $E_f$. In this case, the interaction between the $\sigma$ and $\pi$ bands near the Fermi level $E_f$ is decreased, which is of no advantage to the formation of Cooper pairs. This result

may be in relationship with the transformation of the Tl,Pb-1201 phase from the superconductor into a nonsuperconductor.

On the other hand, let us investigate the band structures of the Tl,Pb-1201 phase with the oxygen content slightly less than 5. The band structures of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{4.7}$ for the oxygen vacancies on the Cu–O planes and on the Tl–O planes are, respectively, shown in Fig. 4. For the present purpose of comparison, the band structure of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ is also shown in Fig. 4. It is seen from Fig. 4b, that by comparison to the band structure of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$, the oxygen vacancies on the Cu–O planes result in a large decrease in the bandwidths of two broad anisotropic Cu–O bands although they remain almost unchanged in shape and cause other bands below the Fermi level $E_f$ to be relatively displaced upwards. Even though the oxygen vacancies on the Cu–O planes lead to these results, the degree of complexity of the band structure near the Fermi surface is not increased. If the oxygen vacancies are on the Tl–O planes, it is seen from Fig. 4c that the bandwidths and the dispersions of two broad anisotropic Cu–O bands remain unchanged, but all the bands are displaced downwards by about 0.25 eV compared with those of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$, which results in a decrease in the degree of complexity of the band structure near the Fermi surface. It is clear that, regardless of whether the oxygen vacancies are on the Cu–O planes or on the Tl–O planes; the band structure of the Tl, Pb-1201 phase cannot be improved compared with that of $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$; in other words, the lower oxygen content cannot lead to transformation of the Tl,Pb-1201 phase from a nonsuperconductor into a superconductor. In fact, for the lower oxygen content, it is a semiconductor other than a superconductor.

## 3.2 Densities of states

Densities of states are the direct results of band structures and are in close relationship with the superconducting properties. Some results of the densities of states for the Tl,Pb-1201 phase are summarized in Table 2, in which $N(E_f)$ expresses the total electronic densities of states at the Fermi level $E_f$; $N(E_f)_{Cu-O}$, the projected densities of states at $E_f$ for the Cu–O planes (the sums of the projected densities of states at $E_f$ for Cu and O atoms in the Cu–O planes); and $N(E_f)_{O-O}$ and $N(E_f)_{Tl-O}$, those for the peroxide pairs and the Tl–O planes, respectively.



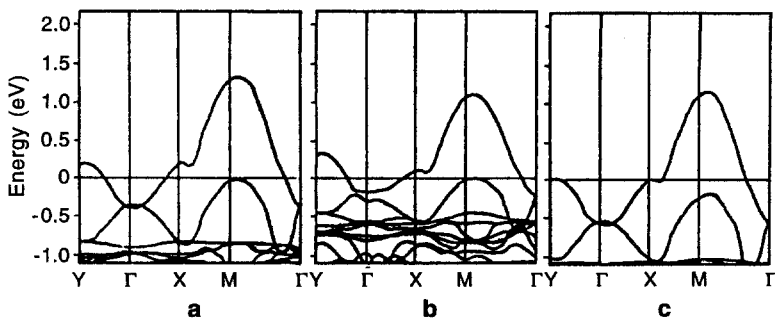Fig. 4. Band structures for $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y = 5$ and 4.7): (a) $y = 5$; (b) $y = 4.7$ and an oxygen vacancy is at the Cu–O planes; (c) $y = 4.7$ and an oxygen vacancy is at the Tl–O planes
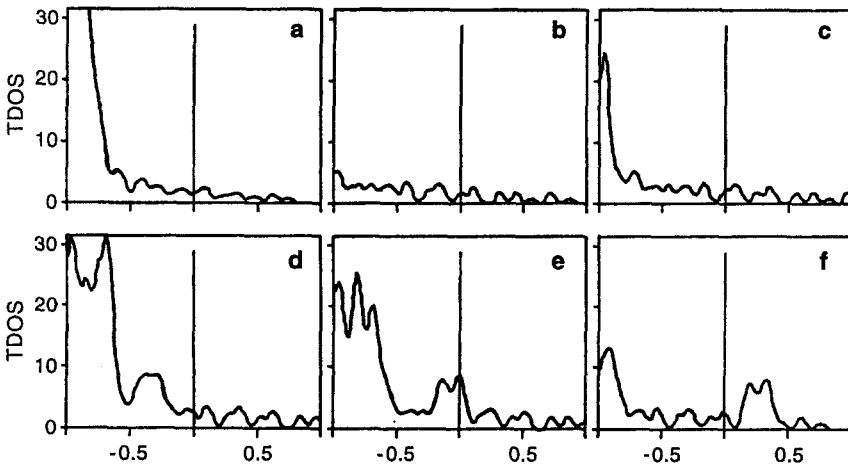
**Table 2.** Densities of states for $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$

| $y$ | $N(E_f)$ | $N(E_f)_{Cu-O}$ | $N(E_f)_{Tl-O}$ | $N(E_f)_{O-O}$ |
|------|----------|-----------------|------------------|-----------------|
| 4.7[a] | 1.93 | 1.92 | 0.0 | 0.0 |
| 4.7[b] | 1.43 | 1.42 | 0.0 | 0.01 |
| 5.0 | 2.14 | 2.13 | 0.0 | 0.01 |
| 5.1 | 2.77 | 2.76 | 0.0 | 0.01 |
| 5.2 | 2.75 | 2.74 | 0.0 | 0.01 |
| 5.25 | 4.70 | 2.55 | 0.18 | 1.96 |
| 5.29 | 8.63 | 3.34 | 0.37 | 4.89 |
| 5.35 | 6.86 | 2.60 | 0.26 | 3.98 |
| 5.45 | 2.38 | 2.37 | 0.0 | 0.01 |

[a] Oxygen vacancy at the Tl–O planes.
[b] Oxygen vacancy at the Cu–O planes.
$N(E_f)$ expresses the total densities of states at the Fermi level $E_f$: $N(E_f)_{Cu-O}$, the projected densities of states at $E_f$ for the Cu–O planes; and $N(E_f)_{O-O}$ and $N(E_f)_{Tl-O}$, those for the peroxide pairs and the Tl–O planes, respectively.



**Fig. 5.** Total densities of states for $Tl_{0.5}Pb_{0.5}CuO_y$: (a) $y = 4.7$ and an oxygen vacancy is at the Cu–O planes; (b) $y = 4.7$ and an oxygen vacancy is at the Tl–O planes; (c) $y = 5$; (d) $y = 5.2$; (e) $y = 5.29$; (f) $y = 5.45$

Figure 5 shows the total densities of states (TDOS) near the Fermi level $E_f$ for the Tl,Pb-1201 phase. It is seen from Fig. 5 that when the oxygen content is less than 5.2, the TDOS of the Tl,Pb-1201 phase are relatively small near $E_f$. As the value of the oxygen content is raised from 5.2 to 5.45, a TDOS peak comes into existence near $E_f$ and is displaced by degrees on increasing the value of the oxygen content. At the oxygen content $y \approx 5.29$, this TDOS peak is situated in $E_f$, which results in the highest value of the total densities of states at $E_f$. It can be seen from Table 2 that in the interval between 4.7 and 5.2 of the oxygen content, the total densities of states at $E_f$, $N(E_f)$, for the Tl,Pb-1201 phase are small. For example, $N(E_f) = 2.14$ states/eV-cell for $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ and $N(E_f) = 2.75$ states/eV-cell for $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5.2}$. However, on increasing the value of the oxygen content from 5.2 to 5.29, $N(E_f)$ is drastically increased from 2.75 to 8.63 states/eV-cell,

increased by about 5.9 states/eV-cell. As the value of the oxygen content is further raised from 5.29, on the contrary, $N(E_f)$ is decreased gradually. For $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5.45}$, its $N(E_f)$ is equal to 2.38 states/eV-cell only. This result is in close relationship with the upward displacement of the band arising from the peroxide pairs. It is seen from Fig. 5 that the TDOS peak arising from the peroxide pairs has been shifted to the high energy zone. Although the Fermi level $E_f$ lies in the Van Hove peak, the total densities of states at $E_f$ are still small because of the small height of the Van Hove peak and the upward displacement of the peak due to the peroxide pairs. The change in the total densities of states at $E_f$, $N(E_f)$, caused by the variations in the oxygen content is shown in Fig. 6. It is clear from Fig. 6 that in the interval between 5.2 and 5.29 of the oxygen content, there is a drastic increase in $N(E_f)$. This sudden change in $N(E_f)$ is the direct result of the upward displacement of the $\pi$ band arising mainly from the peroxide pairs. From the point of view of the BCS theory, the transition temperature $T_c$ is directly proportional to the factor $Exp[-1/N(E_f)V]$. Obviously, the drastic increase in $N(E_f)$ caused by the variations in the oxygen content must result in a great change in the physical properties of the Tl,Pb-1201 phase. The sudden change of the properties may correspond to the transformation of the Tl,Pb-1201 phase from a semiconductor into a superconductor. It is clear from the above discussion that the oxygen content has a great effect on the total densities of states near the Fermi level $E_f$ of the Tl,Pb-1201 phase and that the influence of the oxygen content is reflected by the sudden change in the densities of states which is in close relationship with the physical properties. Therefore, in the $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ compound, the oxygen content is responsible for its superconductivity, which is in general agreement with the experiment given by Pan et al. [12].

Let us discuss the projected densities of states in detail. The total densities of states are directly reflected by the projected densities of states (PDOS). The PDOS at the Fermi level $E_f$ for the Cu–O planes, $N(E_f)_{Cu-O}$, the Tl–O planes, $N(E_f)_{Tl-O}$, and the peroxide pairs, $N(E_f)_{O-O}$, are summarized in Table 2. It can be seen from Table 2 that as the value of the oxygen content is raised from 4.7 to 5.2, the change in $N(E_f)_{Cu-O}$ is relatively small although the average value of $N(E_f)_{Cu-O}$ is retained
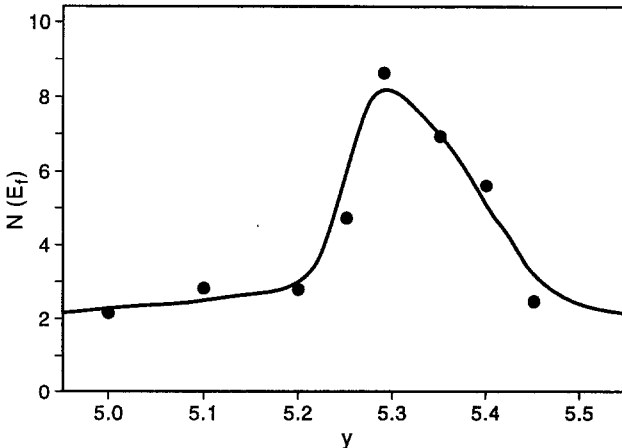


Fig. 6. The relationship between $N(E_f)$ and the oxygen content $y$ in $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$

near 2.0 states/eV-cell, whereas $N(E_f)_{Tl-O}$ and $N(E_f)_{O-O}$ are almost equal to zero and remain unchanged in this interval. In this case, the total densities of states at the Fermi level $E_f$ are due to the contribution of the Cu–O planes to the densities of states. On increasing the value of the oxygen content from 5.2 to about 5.3, $N(E_f)_{Cu-O}$, $N(E_f)_{Tl-O}$, and $N(E_f)_{O-O}$ are all drastically increased by comparison to those of $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5.2}$. The differences between the projected densities of states for $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5.25}$ and $Tl_{0.5}Pb_{0.5}Sr_2CuO_{5.2}$ are 4.89 states/eV-cell for $N(E_f)_{O-O}$, 0.6 states/eV-cell for $N(E_f)_{Cu-O}$, and 0.37 states/eV-cell for $N(E_f)_{Tl-O}$. Obviously, the sudden change of the projected densities of states at $E_f$ is in close relationship with the increase in the oxygen content. Further, it is noticed that the increase (4.89 states/eV-cell) in $N(E_f)_{O-O}$ is much more than the increase in $N(E_f)_{Cu-O}$ and $N(E_f)_{Tl-O}$. This consequence demonstrates that in this interval of the oxygen content, the sudden change in the total densities of states at $E_f$ is mostly caused by the perxodie pairs, which reveals the important role of the peroxide pairs in the sudden change of the physical properties of the Tl,Pb-1201 phase. In other words, the peroxide pairs are responsible for the superconductivity of the Tl,Pb-1201 phase. On the contrary, if the value of the oxygen content is raised from 5.3 to 5.45, the projected densities of states at the Fermi level $E_f$ for the Cu–O planes, the Tl–O planes, and the peroxide pairs are all decreased. At the oxygen content $y = 5.45$, $N(E_f)_{O-O}$ is almost equal to zero and $N(E_f)_{Cu-O}$ is approximately equal to the total densities of states at $E_f$, $N(E_f)$. This consequence again reveals the important role of the peroxide pairs. Therefore, the peroxide pairs hold the keys of the transformation of the Tl,Pb-1201 Phase from a semiconductor into a superconductor.

From the above discussions on the band structures and the densities of states for the $Tl_{0.5}Pb_{0.5}Sr_2CuO_y$ ($y \approx 5$) superconductor, it is clear that the oxygen content has a great influence on its electronic structures. The moderate oxygen content causes the number of bands near the Fermi surface to increase and results in a sudden change in the densities of states at the Fermi level $E_f$. The influence of the oxygen content on the electronic structures is mainly due to the peroxide pairs in the unit cell. The lower or higher oxygen content results in the decrease in the number of bands near $E_f$ and the densities of states at $E_f$, which is of no advantage to superconductivity.

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