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Influence of partial substitution of zinc for copper on electronic structures of $YBa_2Cu_3O_y$

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Summary. By use of an approximate band-structure treatment based on the EHMO approach, the energy band structures for the Zn-doped superconductor $YBa_2Cu_{3-x}Zn_xO_y$ were calculated in the present paper and the influence of partial substitution of zinc for copper on the electronic structures for orthorhombic $YBa_2Cu_3O_y$ was studied. From analysis of the band structures and the densities of states for $YBa_2Cu_{3-x}Zn_xO_y$, it was demonstrated that the 2D Cu–O planes in the Y–Ba–Cu–O superconducting system have a direct and dominant influence on superconductivity, whereas the role of the 1D Cu–O ribbons and the O(4) atoms is also of some importance.

Key words: Superconductor – Zn-doping – Band structure – $YBa_2Cu_{3-x}Zn_xO_y$ – EHMO approach

1 Introduction

Since the Y–Ba–Cu–O high-T_c superconductors were reported [1] and known to be triply layered oxygen-deficient perovskites $YBa_2Cu_3O_y$ (the 1–2–3 structure) with y slightly less than 7 [2–9], numerous compositional variants of the 1–2–3 structure have been synthesized, and partial substitutions of some transition metals, for instance Fe, Co, Ni and Zn, for Cu in $YBa_2Cu_3O_y$ have been recorded [10, 11]. It is shown that in all cases, the transition temperature T_c is suppressed although the complete substitution of zinc for copper has not been achieved experimentally. In these partial substituted systems, the transition metals from iron to zinc, especially nickel and zinc, have received the greatest attention, though many details of their structure behavior remain in dispute. Many studies show that zinc substitutes partially as divalent cations for Cu(2) in the 2D Cu–O planes in the Y–Ba–Cu–O system and that the transition temperature T_c is rapidly suppressed by its cation as the Zn-doping fraction x in the Zn-doped system is raised. In addition, it is also indicated that the partial substitution of zinc for copper does not affect the crystal structure, which is still a good orthorhombic 1 : 2 : 3 phase.

In recent years, many scientists concentrate their attention upon investigations of partial substitutions of transition metals for copper. One of the important reasons is that the transition metal, as a probe element, is of great importance to revealing the relationship between microstructures of crystals and superconductivity. In past years, when the Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O high-T_c superconducting systems were not found, it was thought generally that the 1D Cu–O ribbons in the Y–Ba–Cu–O system played a dominant role in superconductivity because of their connection to two 2D Cu–O planes through the O(4) atoms. However, after the Bi- and Tl-systems were synthesized and proved to have superconductivity, the 1D Cu–O ribbons had not been found in these high-T_c superconducting systems. Therefore, now, most scientists consider the role of the 2D Cu–O planes in superconductivity to be dominant. For these view points, it is doubtless important that a satisfactory explanation be given theoretically, especially from electronic structures.

In the present paper, an approximate band-structure treatment based on the EHMO approach will be employed to calculate the electronic structures of the random Zn-doped superconductor $YBa_2Cu_{3-x}Zn_xO_y$, and some interesting results will be given here. Further, from the obtained energy-band structures and electronic densities of states, the role of the 2D Cu–O planes and the 1D Cu–O ribbons in the Y–Ba–Cu–O system will be analysed.

2 Method and calculation

In order to carry out band-structure calculations of $YBa_2Cu_{3-x}Zn_xO_y$, the EHMO approach based on the tight-binding method is employed [12, 13]. For a partial doped superconducting system, the following approximate treatments are usually employed in many band-structure computations: (i) The unit cell is enhanced to form a supercell, for example, the unit cell of $La_{1.5}Ba_{0.5}CuO_4$ is doubled to give the doubled cell $La_3BaCu_2O_8$ [14]; (ii) A complete doped system is first used to substitute for the partial doped one, and then the rigid-band filling model is employed [15]. As for these approximate treatments, one of their shortcomings is that they cannot be used to study the random alloying at all cation sites. For band-structure calculations of partial doped superconducting systems, a detailed review was given by Pickett [16]. They are not described in detail here. In this study, an approximate band structure treatment based on the EHMO approach, which can be employed to study superconducting systems randomly doped at any cation site, is employed. Since a detailed discussion about this treatment was given in our previous work [17], it is concisely described as follows.

A doped superconductor can be regarded as the system in which some atom M^1 in crystals has been substituted with the doping atom M^2. Generally speaking, the doped system does not have periodicity. Usually, three axes a, b, and c of the unit cells of the Cu–O superconductors are large, for example for orthorhombic $YBa_2Cu_3O_y$, $a = 0.3823$ nm, $b = 0.3886$ nm, and $c = 1.1681$ nm, and both the doping atom M^2 and the doped atom M^1 are metal. Therefore, interactions between the doping atom M^2 in an unit cell and the atoms M^1, which are in other unit cells and at the substituted site, are small. Thus it is assumed that (i) these interactions are zero numerically; (ii) the doping process is regarded as the substitution of the doping atom M^2 for the atom M^1 at the fractional ratio x; (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 the functions of the doping fraction x, that is

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

Let H^1_{ii}, S^1_{ij} and H^2_{ii}, S^2_{ij} be the Coulomb integrals and the overlap integrals before the substitution and after the complete substitution, respectively. It is apparent that $H_{ii}(x)$ and $S_{ij}(x)$ obey the boundary conditions

$$H_{ii}(0) = H^1_{ii}, \quad S_{ij}(0) = S^1_{ij}, \quad H_{ii}(1) = H^2_{ii}, \quad S_{ij}(1) = S^2_{ij}\,. \tag{2}$$

If the numbers of the valence state orbitals for the M^1 and M^2 atoms are equal, the integrals $H_{ii}(x)$ and $S_{ij}(x)$ can be expressed as the power series of the doping fraction x. Since Eqs. (2) must be obeyed and x is from 0 to 1. $H_{ii}(x)$ and $S_{ij}(x)$ can approximately be expressed as the following forms:

$$\begin{aligned} H_{ii}(x) &= (1-x)H^1_{ii} + xH^2_{ii} + k_1 x(1-x)(H^2_{ii} - H^1_{ii})\,, \\ S_{ij}(x) &= (1-x)S^1_{ij} + xS^2_{ij} + k_2 x(1-x)(S^2_{ij} - S^1_{ij})\,, \end{aligned} \tag{3}$$

where k_1 and k_2 are adjustable parameters. It is proved in our previous work [17] that k_1 and k_2 obey the following inequalities

$$-1 \leqslant k_1 \leqslant 1, -1 \leqslant k_2 \leqslant 1\,. \tag{4}$$

It must be pointed out here that since $0 \leqslant x \leqslant 1$ and $|H^2_{ii} - H^1_{ii}| \ll (H^1_{ii} + H^2_{ii})/2$, the quadratic terms for $H_{ii}(x)$ and $S_{ij}(x)$ are much smaller than their linear terms. Obviously, for $H_{ii}(x)$ and $S_{ij}(x)$, the quadratic terms are only their correction factors. Therefore, the band-structure results are basically independent of the choice of the linear and quadratic expressions for $H_{ii}(x)$ and $S_{ij}(x)$. In the present calculations, both k_1 and k_2 are taken as 1. In this case, Eqs. (3) are given by the following:

$$\begin{aligned} H_{ii}(x) &= (1 - 2x + x^2)H^1_{ii} + (2x - x^2)H^2_{ii}\,, \\ S_{ij}(x) &= (1 - 2x + x^2)S^1_{ij} + (2x - x^2)S^2_{ij}\,. \end{aligned} \tag{5}$$

If the numbers of the valence state orbitals for the atoms M^1 and M^2 are unequal, the treatment was given in Ref. [17], which is not described here.

For the non-diagonal elements $H_{ij}(x)$, the following weighted formulas are used in the present calculations

$$\begin{aligned} H_{ij}(x) &= k'/2(H_{ii}(x) + H_{jj}(x))S_{ij}(x), \quad k' = k + \Delta^2 + \Delta^4(1-k)\,, \\ \Delta &= (H_{ii}(x) - H_{jj}(x)/(H_{ii}(x) + H_{jj}(x))\,, \end{aligned} \tag{6}$$

where $k = 1.75$.

By use of the above band-structure treatment, the random Zn-doped superconductor $YBa_2Cu_{3-x}Zn_xO_y$ can be calculated. In order to analyse the influence of partial Zn-substitutions at the different cation site on the electronic structures for orthorhombic $YBa_2Cu_3O_y$, two computing schemes are used in the present band-structure calculations: (i) Zn substitutes for Cu(1) in the 1D Cu–O ribbons in the Y–Ba–Cu–O system (Zn is expressed by Zn(R)); (ii) Zn substitutes for Cu(2) in the 2D Cu–O planes (Zn is expressed by Zn(P)). The structural parameters and the atomic coordinates for orthorhombic $YBa_2Cu_3O_y$ are taken from Ref. [18]. The crystal structure of orthorhombic $YBa_2Cu_3O_y$ is shown in Fig. 1. For the Zn-doped superconductor, the change in its structure caused by the substitution of zinc for copper is neglected because it is very little. It must be, of course, pointed out that although this assumption is approximate, it does not have a great influence on qualitative results given by the EHMO computations. The atomic orbital ionization potentials and the orbital exponents used in the present calculations, which are taken from Refs. [19, 20], respectively, are summarized in Table 1. The calculations on the electronic energy-band structures are carried out along the high-symmetry directions in the first Brillouin zone shown in Fig. 3, with 15 k-points in each $\frac{1}{8}$ Brillouin zone.

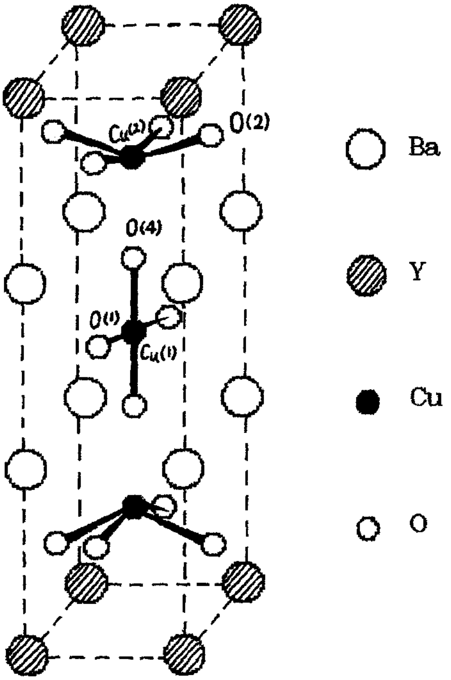

Fig. 1. Crystal structure of $YBa_2Cu_3O_y$

Table 1. EHMO parameters used in the present calculations

	$-H_{ii}$(eV)			Orbital exp.		
	s	p	d	s	p	d
Y	6.48	5.07	6.38	1.2512	1.2512	3.9896
Cu	9.101	6.06	16.45	1.541	1.541	3.813
Zn	9.279	6.53	17.29	1.553	1.553	4.000
Ba	5.21	3.69		1.25	1.25	
O	32.44	15.86		2.189	2.029	

3 Results and discussion

3.1 Energy-band structure

The band structures near the Fermi level E_f for orthorhombic $YBa_2Cu_{3-x}Zn_xO_6$ ($x = 0$ and 1) and $YBa_2Cu_{3-x}Zn_xO_7$ ($x = 0$, 0.5 and 1) are, respectively, shown in Figs. 2 and 3. In Fig. 2 and 3, E_f is placed at the zero of energy and the unit of energy is expressed by eV. At $x = 0$, that is $YBa_2Cu_3O_y$, it can be seen from Fig. 2 and 3 that all the energy bands for orthorhombic $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ are relatively flat along the $Y' - Y$ direction in the Brillouin zone and that several broad anisotropic bands, for which their dispersions are very strong, cross E_f in all the directions of wave vectors located on the Y–M–X–Γ–Y planes. In addition, the number of the broad anisotropic energy bands crossing E_f increases as the oxygen content y is raised. In $YBa_2Cu_3O_6$, there are two broad anisotropic bands crossing E_f, which include the highest occupied band. These bands arise from two 2D Cu–O planes in the unit cell. For $YBa_2Cu_3O_7$, there are three broad anisotropic bands crossing E_f, including also the highest occupied band. Two of these bands correspond to two 2D Cu–O planes and the third to the 1D Cu–O ribbons. All the broad anisotropic bands crossing E_f for orthorhombic $YBa_2Cu_3O_y$ ($y = 6$ and 7) are formed by the Cu3*d*–O2*p* orbitals. It is obvious that orthorhombic $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ have the 2D metallic band structures. These results are in general agreement with those given by the LAPW method [21] and the first-principles self-consistent pseudofunction method [22]. Therefore, the detailed discussion about the band structures for orthorhombic $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ is not given here because it can be found in many studies.

Turning to the Zn-doped superconductors $YBa_2Cu_{3-x}Zn_xO_y$ ($y = 6$ and 7), that is $0 < x < 1$, we see from Fig. 2 and 3 that when zinc substitutes for Cu(2), the substitution of zinc results in a gradual displacement of one broad anisotropic energy band, which corresponds to the Cu3*d*–O2*p* broad anisotropic band arising from the Cu–O planes and crossing E_f in the *Y*–*M*–*X*–Γ–*Y* planes, towards E_f as the Zn-doping fraction x is raised. Compared to orthorhombic $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, the dispersions of the displaced Cu–O broad bands crossing E_f for $YBa_2Cu_{3-x}Zn_xO_y$ ($y = 6$ and 7) and their bandwidths become small greatly. On the other hand, when zinc substitutes for Cu(1), the top of one Cu3*d*–O2*p* broad anisotropic band arising from the 2D Cu–O planes descends towards E_f and the broad band arising from the 1D Cu–O ribbons also does in the *M*–*X* direction in the Brillouin zone, whereas their bandwidths become small. In $YBa_2Cu_{3-x}Zn_xO_6$, two Cu–O broad anisotropic bands arising from the 2D Cu–O planes are both displaced downward. These results show that whether zinc substitutes for Cu(1) or for Cu(2), the Zn-substitutions result in the great changes in the band structures for orthorhombic $YBa_2Cu_3O_y$. As a consequence, it is clear that the partial substitution of zinc for copper in the Y–Ba–Cu–O system is of no advantage to its metallic property and has a direct influence on the transition temperature T_c. In fact, for $YBa_2Cu_{3-x}Zn_xO_y$, the experiments demonstrate that T_c for the Zn-doped superconducting system is suppressed rapidly with the increase in the Zn-doping fraction x, for instance, $T_c = 57$ K for $x = 0.1$ and $T_c = 47$ K for $x = 0.3$ [11].

Now let us analyse the band structures for orthorhombic $YBa_2Cu_{3-x}Zn_xO_y$ ($y = 6$ and 7) in more detail. On the one hand, in both $YBa_2Cu_{3-x}Zn_xO_6$ and $YBa_2Cu_{3-x}Zn_xO_7$, it can be seen from Fig. 2 and 3 that the displacement of the Cu–O broad anisotropic band crossing E_f caused by the partial substitution of Zn for Cu(2) is smaller than that caused by the substitution of Zn for Cu(1).

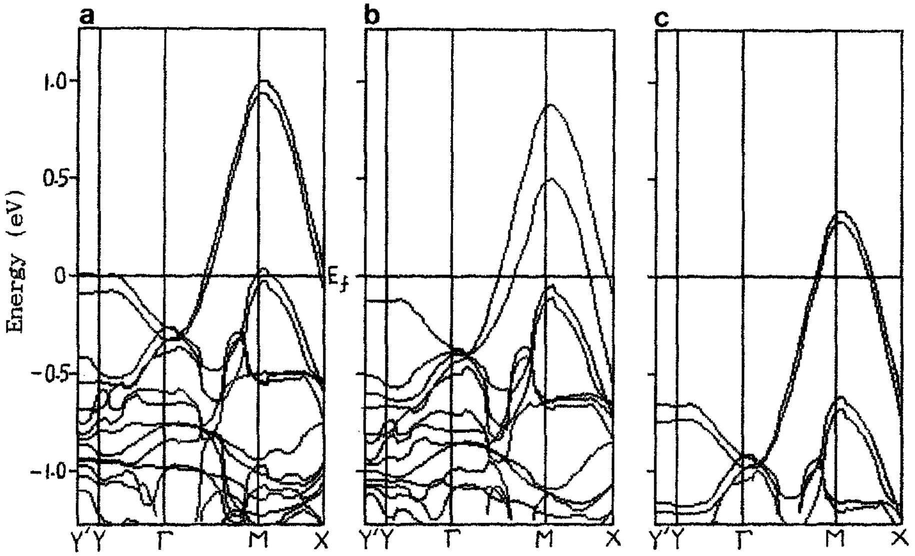

Fig. 2. Band structures for $YBa_2Cu_{3-x}Zn_xO_6$: (**a**) $YBa_2Cu_3O_6$; (**b**) $YBa_2Cu_2Zn(P)O_6$; (**c**) $YBa_2Cu_2Zn(R)O_6$

The energy displacement caused by the Zn-substitution for Cu(1) is about 0.43 eV for $YBa_2Cu_{3-x}Zn_xO_6$ and 0.40 eV for $YBa_2Cu_{3-x}Zn_xO_7$, whereas that caused by the Zn-substitution for Cu(2) is 0.33 eV for $YBa_2Cu_{3-x}Zn_xO_6$ and 0.30 eV for $YBa_2Cu_{3-x}Zn_xO_7$. This result implies that the 1D Cu–O ribbons play an important role in the Y–Ba–Cu–O system although they are not found in the Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O superconducting systems. In other words, the 1D Cu–O ribbons have a great influence on the band structures for orthorhombic $YBa_2Cu_3O_y$. On the other hand, it is noted that whether zinc substitutes for Cu(2) or for Cu(1), in all the displaced bands, the Cu–O broad anisotropic bands arising from the 2D Cu–O planes are most greatly affected by the Zn-substitution and their changes become large as the x value increases. This demonstrates that the 2D Cu–O planes affect directly the band structures for orthorhombic $YBa_2Cu_3O_y$. Therefore, it can be concluded that in the Y–Ba–Cu–O superconducting system, the influence of the 2D Cu–O planes on superconductivity is direct and dominant, whereas the role of the 1D Cu–O ribbons is also of some importance. In addition, compared to $YBa_2Cu_3O_y$, the substitution of zinc for copper does not change, on the whole, the total Cu–O bandwidths, but results in a small change in E_f (see Table 2). The changes in the band structures and the Fermi level can affect directly electronic densities of states.

3.2 Density of states

Electronic densities of states are the direct results of energy band structures. In the above section, the band structures for two end members of the oxygen sequence ($YBa_2Cu_{3-x}Zn_xO_6$ and $YBa_2Cu_{3-x}Zn_xO_7$) have been analysed. As is shown above, the substitution of zinc for copper causes a great change in their band structures. Thus, their densities of states can be changed largely. However, the experiments indicate that the oxygen content y has an effect upon the transition temperature

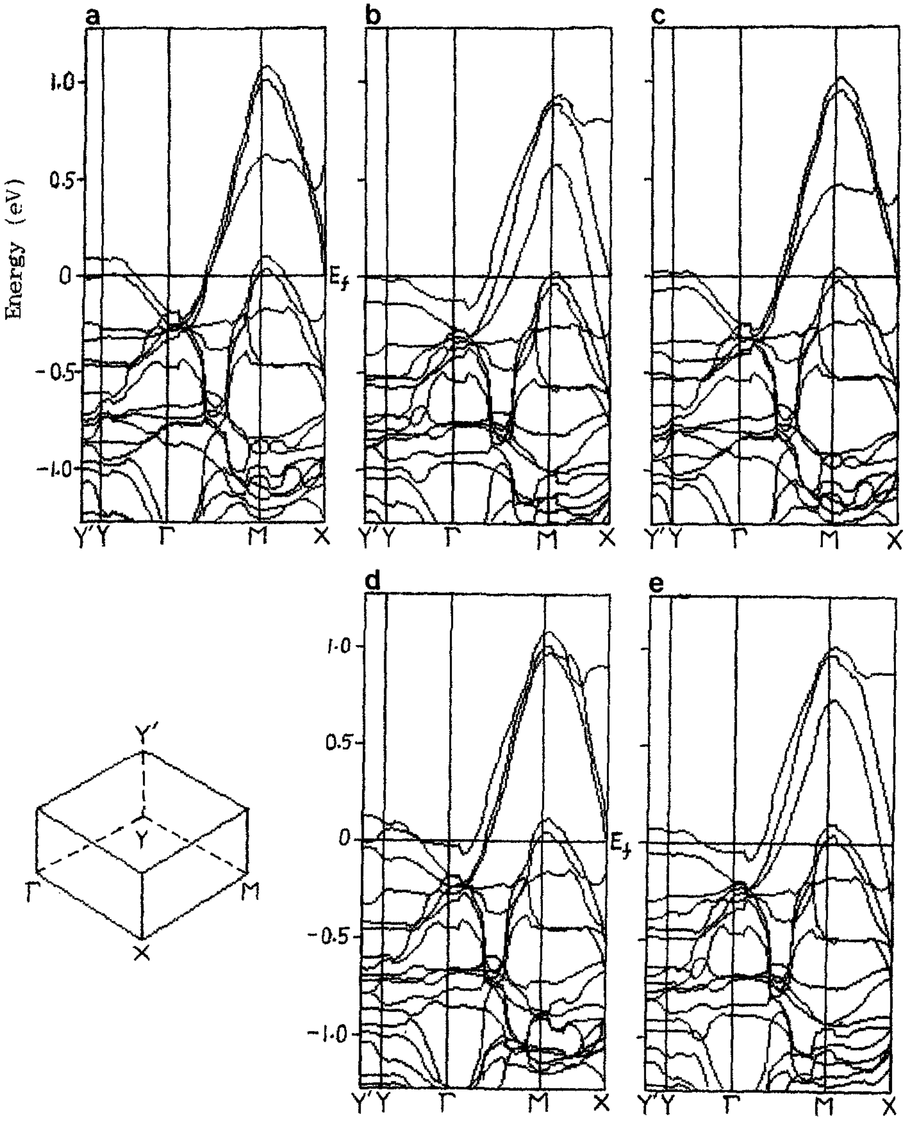

Fig. 3. Band structures for $YBa_2Cu_{3-x}Zn_xO_7$: (**a**) $YBa_2Cu_{2.5}Zn(R)_{0.5}O_7$; (**b**) $YBa_2Cu_2Zn(P)O_7$; (**c**) $YBa_2Cu_2Zn(R)O_7$; (**d**) $YBa_2Cu_3O_7$; (**e**) $YBa_2Cu_{2.5}Zn(P)_{0.5}O_7$

T_c. The influence of the oxygen content must be, therefore, taken into account in investigating the density of states. Zhang and his colleagues [11] showed that the relationship between the oxygen content y and the Zn-doping fraction x was irregular, but the change in y in $YBa_2Cu_{3-x}Zn_xO_y$ ($x > 0$) was very small. As a result, in the present calculations, the oxygen content y is taken as the mean value of those given by Zhang, that is $y = 6.92$. For $YBa_2Cu_3O_y$, y is taken as 6.82. In order to obtain the densities of states and the Fermi level E_f for orthorhombic $YBa_2Cu_{3-x}Zn_xO_y$ (x is from 0 to 1), an interpolation scheme between orthorhombic

Table 2. The Fermi level E_f and total densities of states at E_f for orthorhombic $YBa_2Cu_{3-x}Zn_xO_y$ ($y = 6$, 6.92 and 7)

		$YBa_2Cu_{3-x}Zn_xO_6$		$YBa_2Cu_{3-x}Zn_xO_7$		$YBa_2Cu_{3-x}Zn_xO_y^a$	
M	X	$-E_f$(eV)	$N(E_f)$	$-E_f$(eV)	$N(E_f)$	$-E_f$(eV)	$N(E_f)$
Zn(P)	0.0	14.938	4.62	14.992	8.82	14.982	8.00
	0.1	14.936	4.25	15.002	8.40	14.997	7.48
	0.3	14.936	4.57	15.003	7.51	14.998	7.13
	0.5	14.911	2.93	15.005	6.77	14.997	6.24
	0.7	14.726	1.57	14.962	4.72	14.943	4.80
	1.0	14.622	0.92	14.932	4.64	14.907	4.59
Zn(R)	0.1	14.915	4.02	14.992	7.36	14.986	7.21
	0.3	14.873	2.07	14.994	7.89	14.984	7.54
	0.5	14.777	0.83	14.994	6.81	14.977	6.47
	0.7	14.667	1.51	14.955	4.96	14.932	4.42
	1.0	14.413	0.86	14.935	4.35	14.893	3.67

[a] y for $x = 0$ is 6.82 and others are 6.92

Table 3. Projected densities of states for the Cu–O planes, the Cu–O ribbons, and the O(4) atom in $YBa_2Cu_{3-x}Zn_xO_{6.92}$

M	X	$N(E_f)^P$	$N(E_f)^R$	$N(E_f)^0$
Zn(P)	0.0	2.94	1.46	0.57
	0.1	1.73	1.75	0.77
	0.3	1.39	1.62	0.69
	0.5	1.02	1.48	0.62
	0.7	0.76	1.30	0.48
	1.0	0.65	1.21	0.46
Zn(R)	0.1	2.87	0.87	0.46
	0.3	2.97	0.96	0.53
	0.5	2.57	0.82	0.45
	0.7	1.79	0.52	0.26
	1.0	1.54	0.37	0.17

$YBa_2Cu_{3-x}Zn_xO_6$ and $YBa_2Cu_{3-x}Zn_xO_7$ is employed. The results obtained from the computations are summarized in Table 2 and 3. Table 2 gives E_f and the total densities of states at E_f, $N(E_f)$, for orthorhombic $YBa_2Cu_{3-x}Zn_xO_6$, $YBa_2Cu_{3-x}Zn_xO_7$ and $YBa_2Cu_{3-x}Zn_xO_{6.92}$. It is noted that $N(E_f)$ for $YBa_2Cu_3O_y$ is 8.82 states/eV-cell, which is in agreement with that given by Whangbo using the EHMO approach [23]. In order to study the influence of the substitution of zinc on the densities of states for orthorhombic $YBa_2Cu_3O_y$, the sums of the projected densities of states at E_f, $N(E_f)^P$, for Cu(2), O(2) and O(3) in the Cu–O planes in $YBa_2Cu_{3-x}Zn_xO_{6.92}$, those for Cu(1) and O(1) in the Cu–O ribbons, $N(E_f)^R$, and the projected densities of states at E_f, $N(E_f)^0$, for O(4) are listed in Table 3.

It is seen from Table 2 that in orthorhombic $YBa_2Cu_{3-x}Zn_xO_6$ and $YBa_2Cu_{3-x}Zn_xO_7$, their $N(E_f)$ decrease gradually with the increase in the Zn-doping fraction x whether Zn substitutes for Cu(1) or for Cu(2). As the x value increases from 0 to 1, $N(E_f)$ for $YBa_2Cu_{3-x}Zn_xO_6$ becomes from 4.62 to 0.89 states/eV-cell, and $N(E_f)$

for $YBa_2Cu_{3-x}Zn_xO_7$ from 8.82 to 4.47 states/eV-cell, decreasing by about 3.7 and 4.4 states/eV-cell respectively. For $YBa_2Cu_{3-x}Zn_xO_{6.92}$, its $N(E_f)$ also decreases as the x value is raised. Fig. 4 gives the total electronic densities of states (TDOS) near E_f for orthorhombic $YBa_2Cu_{3-x}Zn_xO_{6.92}$ at $x = 0$, 0.5, and 1. It is shown from Fig. 4 that as the x value increases, the substitution of zinc causes a great change in TDOS near E_f whether Zn substitutes for Cu(2) or for Cu(1). At $x = 0$, there is a strong peak at E_f, which arises from the Cu3d–O2p orbitals. At $x \neq 0$, this Cu3d–O2p peak is displaced downward with the increase in x and departs from E_f by degrees, which results in a large decrease in $N(E_f)$. It is seen from Table 2 that when the x value is from 0 to 1, $N(E_f)$ for $YBa_2Cu_{3-x}Zn(P)_xO_{6.92}$ decreases from 8.00 to 4.59 states/eV-cell and that for $YBa_2Cu_{3-x}Zn(R)_xO_{6.92}$ to 3.67 states/eV-cell. Figure 5 shows the relationship between $N(E_f)$ for $YBa_2Cu_{3-x}Zn_xO_{6.92}$ and the Zn-doping fraction x. From the point of view of the BCS theory, the transition temperature T_c is directly proportional to the factor $\mathrm{Exp}(-1/N(E_f)V)$. It can be, therefore, concluded that T_c for $YBa_2Cu_{3-x}Zn_xO_{6.92}$ is rapidly suppressed as the x value is raised because of the decrease in its $N(E_f)$.

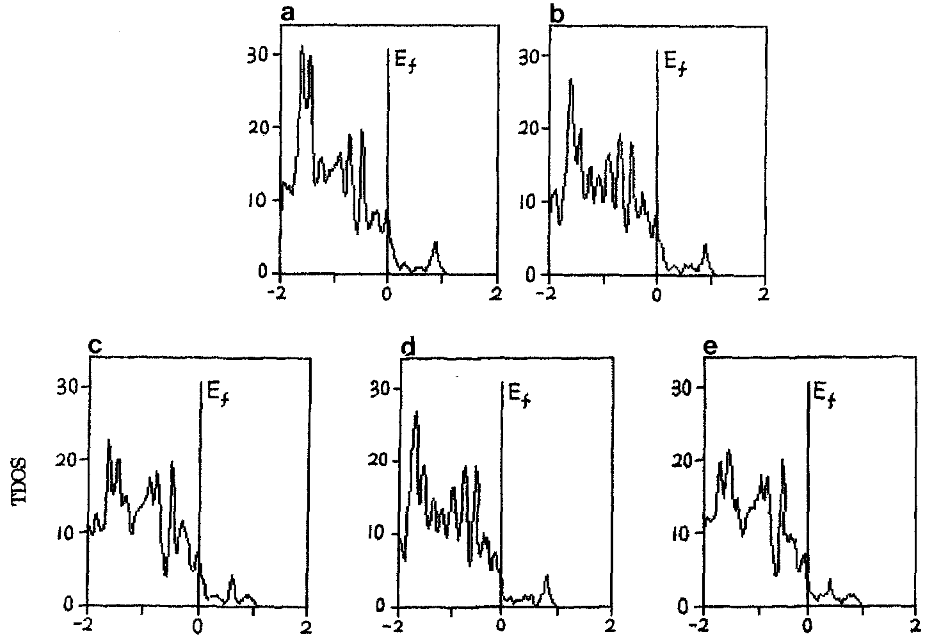

Fig. 4. Total densities of states for $YBa_2Cu_{3-x}Zn_xO_{6.92}$: (a) $YBa_2Cu_3O_{6.82}$; (b) $YBa_2Cu_{2.5}$ $Zn(P)_{0.5}$ $O_{6.92}$; (c) $YBa_2Cu_{2.5}Zn(R)_{0.5}O_{6.92}$; (d) $YBa_2Cu_2Zn(P)O_{6.92}$; (e) YBa_2Cu_2 $Zn(R)O_{6.92}$

Going a step further, we see from Table 2 and Fig. 5 that the change in $N(E_f)$ caused by the substitution of zinc for Cu(1) is larger than that caused by its substitution for Cu(2). As is indicated in the discussion on the band structures, this result implies the important role of the 1D Cu–O ribbons in the Y–Ba–Cu–O system. However, it must be pointed out emphatically that this result does not imply the dominant role of the 1D Cu–O ribbons in superconductivity because the band structures for $YBa_2Cu_{3-x}Zn_xO_y$ have shown that the electronic energy bands arising from the 2D Cu–O planes are most greatly affected by the Zn-substitution. The reason is explained as follows.

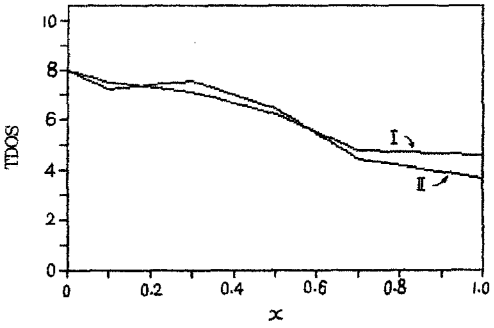

Fig. 5. Relationship between TDOS and the doping fraction x I: $YBa_2Cu_{3-x}Zn(P)_xO_{6.92}$; II: $YBa_2Cu_{3-x}Zn(R)_xO_{6.92}$

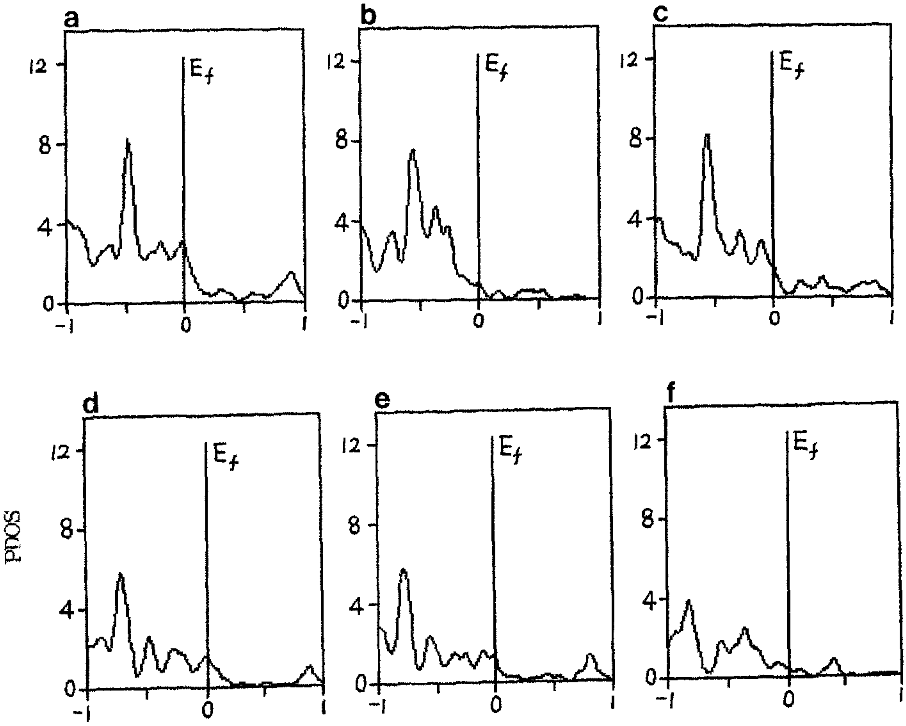

Fig. 6. Projected densities of states for Cu–O planes and Cu–O ribbons in $YBa_2Cu_{3-x}Zn_xO_{6.92}$. (a), (b), and (c) are PDOS for the Cu–O planes, (d), (e), and (f) are PDOS for the Cu–O ribbons. (a), (d): $YBa_2Cu_3O_{6.82}$ (b), (e): $YBa_2Cu_2Zn(P)O_{6.92}$, (c), (f): $YBa_2Cu_2Zn(R)O_{6.92}$

Figure 6 shows the projected densities of states (PDOS) near E_f for the 1D Cu–O ribbons and the 2D Cu–O planes in $YBa_2Cu_{3-x}Zn_xO_{6.92}$ at $x = 0$ and 1, when zinc substitutes for Cu(1) and for Cu(2). It is clear from Fig. 6 that at $x = 0$ ($YBa_2Cu_3O_{6.82}$), both the Cu–O planes and the Cu–O ribbons have the PDOS peak at E_f and that as the x value is from 0 to 1, the PDOS peak departs from E_f, which results in the decreases in $N(E_f)^P$ and $N(E_f)^R$. Table 3 shows that when Zn substitutes for Cu(2), $N(E_f)^P$ becomes from 2.94 to 0.65, decreasing by 2.29 with x from 0 to 1, whereas $N(E_f)^R$ changes from 1.46 to 1.21, decreasing by 0.25 only. For the substitution of zinc for Cu(1), $N(E_f)^P$ decreases by 1.36 and $N(E_f)^R$ by 1.09. Since there are two Cu–O planes in the unit cell, the decrease in $N(E_f)^P$ is also much larger than the decrease in $N(E_f)^R$. These results show the close dependence of the density of states on the 2D Cu–O planes whether zinc substitutes for Cu(1) or for Cu(2). As a result, it can be concluded that the 2D Cu–O planes play a dominant role in the Y–Ba–Cu–O superconducting system.

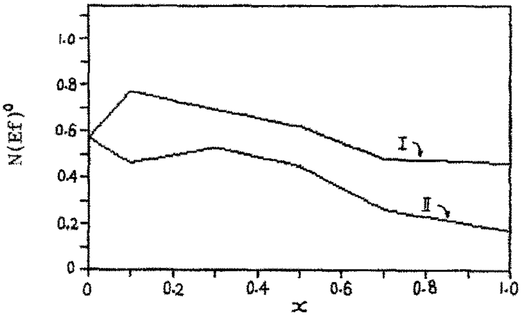

Fig. 7. Relationship between $N(E_f)^{\circ}$ and x I: $YBa_2Cu_{3-x}Zn(P)_xO_{6.92}$; II: $YBa_2Cu_{3-x}Zn(R)_xO_{6.92}$

In addition, it can be also seen from Table 3 that the decrease (0.40) in $N(E_f)^0$ for the O(4) atom caused by the substitution of zinc for Cu(1) is greater than that (0.11) caused by the substitution of zinc for Cu(2). The relationship between $N(E_f)^0$ and the Zn-doping fraction x is shown in Fig. 7. Because the O(4) atom connects the Cu–O ribbons with the Cu–O planes, which strengthens the interaction between the Cu–O ribbons and the Cu–O planes, the decrease in $N(E_f)^0$ shows that the substitution of zinc weakens the interaction between the Cu–O ribbons and the Cu–O planes. Therefore, since $N(E_f)^0$ is more sensitive to the substitution of zinc for Cu(1) than to the substitution of zinc for Cu(2), the important role of the 1D Cu–O ribbons is shown again.

To sum up, whether Zn substitutes for Cu(1) or for Cu(2), (i) the substitution of zinc for copper in $YBa_2Cu_3O_y$ results in the displacement of the broad anisotropic $Cu3d$–$O2p$ bands towards E_f and the bandwidths of the displaced bands become small; (ii) the total density of states at E_f decreases as the Zn-doping fraction x is raised; (iii) the changes in the band structures and the density of states caused by the Zn-substitution are mainly attributed to the 2D Cu–O planes, which have a direct and dominant influence on superconductivity; (iv) the role of the 1D Cu–O ribbons and the O(4) atoms is also of some importance.

Finally, it must be emphasized that although the present treatment is relatively crude, it is, nevertheless, considerably more realistic than the rigid-band filling model and can give good qualitative results. Undoubtedly, it is useful to studying partial doped superconducting systems.

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References

1. Wu MK, Ashburn JR et al (1987) Phys Rev Lett 58:908
2. Grant PM, Beyers RB et al (1987) Phys Rev B35:7242
3. Beyers R, Lim G et al (1987) Appl Phys Lett 50:1918
4. Cava RJ, Santoro A et al (1987) Phys Rev B35:6716
5. Siegrist T, Sunshine S et al (1987) Phys Rev B35:7137
6. Hazen RM, Finger LW et al (1987) Phys Rev B35:7238
7. Beno MA, Soderholm L et al (1987) Appl Phys Lett 51:57

8. LePage Y, McKinnon WR et al (1987) Phys Rev B35:7245
9. Greedan JE, Reilly AO et al (1987) Phys Rev B35:8770
10. Beyers R, Shaw TM (1989) Sol State Phys 42:135
11. Zhang H, Zhao Y et al (1990) Phys Rev B42:2253
12. Whangbo MH et al (1978) J Am Chem Soc 100:6093
13. Whangbo MH et al (1979) Proc Roy Soc (London) 366A:23
14. Schwarz K (1987) Solid State Commun 64:421
15. Pickett WE, Krakauer H et al (1987) Phys Rev B35:7252
16. Pickett WE (1989) Rev Mod Phys 61:433
17. Ming L (1994) Int J Quantum Chem 50:233
18. Beno MA, Soderholm L et al (1987) Appl Phys Lett 51:57
19. Jia X et al (1986) Huaxue Tongbao (Chemistry) 3:46 (in Chinese)
20. Jingqing R, Lemin L et al (1982) Acta Sci Nat Uni Pekinensis 3:49 (in Chinese)
21. Krakauer H, Pickett WE et al (1988) J Supercond 1:111
22. Herman F et al (1987) Phys Rev B36:6904
23. Whangbo MH et al (1987) Inorg Chem 26:1831