The effect of Fe-doping on superconductivity of $YBa_2Cu_3O_y$

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Received 28 September 1995; revised 18 March 1996

In the present paper, an approximate band-structure treatment based on the EHMO approach is suggested and used to calculate the electronic structures of the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$. The present treatment gives, indeed, average band structures and average densities of states as the doping fraction increases. From investigations of the influence of the Fe-doping at the Cu-site on their properties, it is shown that as the Fe-doping fraction x in $YBa_2Cu_{3-x}Fe_xO_y$ is raised from 0.0 to 0.5, (i) the broad anisotropic bands arising from the 1D Cu–O chains and the 2D Cu–O planes are displaced and depart from the Fermi level E_f toward the high-energy zone by degrees, while the total electronic densities of states near E_f are drastically decreased; (ii) the band arising from the Cu–O chains doped by Fe is gradually separated from the broad anisotropic bands arising from the 2D Cu–O planes; (iii) at the doping fraction $x = 0.5$, the Fe-doping results in an energy gap (about 0.2 eV) near E_f; (iv) the oxygen content is not a predominant factor for the superconducting properties of the Fe-doped Y–Ba–Cu–O system; (v) the total densities of states at E_f, $N(E_f)$, and their decrease caused by the Fe-doping arise mainly from the 2D Cu–O planes, which implies the important role of the 2D Cu–O planes in the Y–Ba–Cu–O superconducting system.

1. Introduction

$YBa_2Cu_3O_y$ superconductor, discovered by Wu et al. [1], and the effect of partial substitutions of transition metals and a variety of other elements on its superconductivity have been extensively studied [2–13]. It has been known that Cu plays an important role in these superconductors. In the crystal structure of $YBa_2Cu_3O_y$, there are two different sites for copper, one forming the 1D Cu–O chains, and the other forming the 2D Cu–O planes. In past years, many scientists concentrated their attention upon investigations of partial substitutions of transition metals for copper in $YBa_2Cu_3O_y$, because of the great importance of these substitutions in revealing the relationship between its superconductivity and microstructures of crystals. The investigations demonstrated that a transition metal such as Zn, Ni, Fe, and Co, as a probe element, substitutes either as a divalent cation for Cu(2) in the 2D Cu–O planes or as a trivalent cation for Cu(1) in the 1D Cu–O chains. In all cases, the superconducting transition temperature T_c is suppressed greatly.

In these substitutions of the transition metals, Fe is an important probe element which substitutes for copper. For the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$, much of work [14–26] has been done to investigate the relationship between superconductivity and microstructures and the influence of the Fe-doping at the Cu-site on superconducting properties. Xu et al. [15] indicated that Fe substituted primarily for Cu(1) in the 1D Cu–O chains and that the substitution of Fe drew more oxygen into the O site in the Cu–O chains. The transition temperature T_c is suppressed quickly from $T_c = 92$ K to below 4.2 K on increasing the Fe-doping fraction x from 0.0 to 0.45. When $x \geqslant 0.5$, $YBa_2Cu_{3-x}Fe_xO_y$ is transformed from a superconductor into a nonsuperconductor although the Fe-doping at the Cu(1)-site results in an increase in the oxygen content in the unit cell. It is clear that the substitution of Fe for Cu in $YBa_2Cu_3O_y$ has a great influence on its superconducting properties. In other words, the superconductivity of the Y–Ba–Cu–O system is very sensitive to the Fe-doping. It is this fact that actuated the authors to do this work.

In order to investigate the effect of the doping at the Cu-site on superconductivity, the electronic structures of the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$ are calculated by employing an approximate band structure treatment based on the EHMO approach, and some interesting results are given in the present paper.

2. Calculation

In the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$, as the Fe-doping fraction x is raised, the oxygen content y is increased gradually and is slightly more than 7. As a result, the Fe-doped Y–Ba–Cu–O system is a nonstoichiometric system. For nonstoichiometric systems, the band structure treatment based on the EHMO approach was given in our previous works [27–29]. Therefore, it is only concisely described here 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; (iii) after the doping process was completed, the atom M^1 had 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 doping and after the complete substitution, respectively. If the numbers of valence state orbitals for the M^1 and M^1 atoms are equal, $H_{ii}(x)$ and $S_{ij}(x)$ can approximately be expressed in the following forms:

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

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

where k_1 and k_2 are adjustable parameters and obey the following inequality:

$$-1 \leqslant k_1 \leqslant 1 , \quad -1 \leqslant k_2 \leqslant 1 . \tag{3}$$

If the number of valence state orbitals for the atom M^1, $N1$, and that for the 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 $H^1_{\mu\mu}$ and $S^2_{\mu i} = \delta_{\mu i}$, i.e.,

$$\begin{aligned} H_{\mu\mu}(x) &= H^1_{\mu\mu}, S_{\mu i}(x) \\ &= (1-x)S^1_{\mu i} + x\delta_{\mu i} + k_2x(1-x)(\delta_{\mu i} - S^1_{\mu i}) \quad (\mu = 1,2,\ldots,N) . \end{aligned} \tag{4}$$

As for the treatment for a system with the non-integral oxygen content y, let $y = c + z$, where 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, in the unit cell except for c oxygen atoms. It is assumed that each oxygen atom 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 $H^0_{\mu\mu}$, their overlap integrals be $S^0_{\mu i}$, and those of oxygen vacancies be equal to zero. We can obtain

$$H_{\mu\mu}(z) = H^0_{\mu\mu} ,$$

$$S_{\mu i}(z) = \begin{cases} zS^0_{\mu i} + k_pz(1-z)S^0_{\mu i} & (\mu \neq i) \\ 1 & (\mu = i) \end{cases} \quad (\mu \in \text{oxygen}) , \tag{5}$$

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 non-integer 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 increase, 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 in the unit cell. To obtain satisfactory band structure results, therefore, the total number of electrons in the unit cell must be increased in computations. In order to increase electrons, an iterative procedure similar to that given in ref. [27] 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,

$$P = \mathrm{ME} - (1-z)Q\,. \tag{6}$$

It is clear from the above analysis that $P \neq$ 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 $P =$ NE.

For the *off*-diagonal elements $H_{ij}(x)$ $(i \neq j)$, the following weighted formulas [30] are used in the present calculations:

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

$$\Delta = (H_{ii}(x) - H_{jj}(x))/(H_{ii}(x) + H_{jj}(x))\,, \tag{7}$$

where $k = 1.75$.

It must be emphasised that the above treatment based on the EHMO approach is approximate and gives, indeed, average band structures and average densities of states as the doping fraction is raised. As far as the approximation goes, however, the present treatment can provide more details of the band structures for a nonstoichiometric system than does the simple interpolation between two end members suggested by Herman et al. [31].

By use of the above treatment, calculations on the electronic energy-band structures of the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$ are carried out. In the present computations, the structural parameters, the atomic coordinates and the oxygen content y for $YBa_2Cu_{3-x}Fe_xO_y$ are taken from ref. [15]. The atomic orbital ionization potentials and the orbital exponents for Cu, Fe, O, Ba, and Y, which are taken from refs. [32–34], are summarized in Table 1. Fig. 1 shows the crystal structure of $YBa_2Cu_3O_y$. In the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$, according to ref. [15], it is assumed that Fe substitutes for Cu(1) in the 1D Cu–O chains and that the eighth oxygen atom gets into the y-site in the unit cell shown in Fig. 1. Some band-structure results are given in Table 2.

3. Results and discussion

3.1. ENERGY BAND STRUCTURE

Band structures are in close relationship with superconducting properties. In

Table 1
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	6.06	2.20			
	d	14.00	5.95	0.5933	2.30	0.5744
Fe	s	9.10	1.90			
	p	5.32	1.90			
	d	12.60	5.35	0.5505	2.00	0.6260
Y	s	6.48	1.2512			
	p	5.07	1.2512			
	d	6.38	3.9896			
Ba	s	5.21	1.25			
	p	3.69	1.25			
O	s	32.30	2.275			
	p	14.80	2.275			

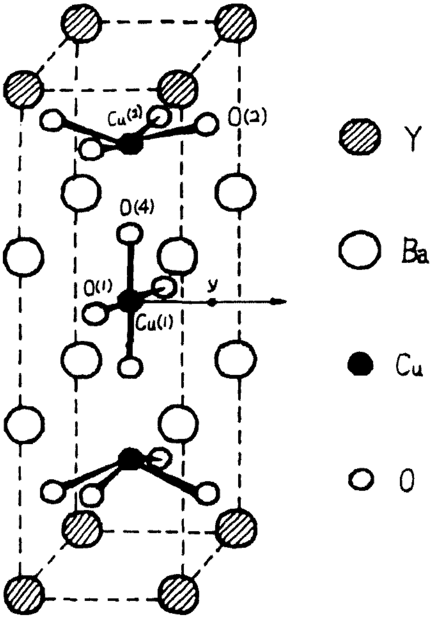


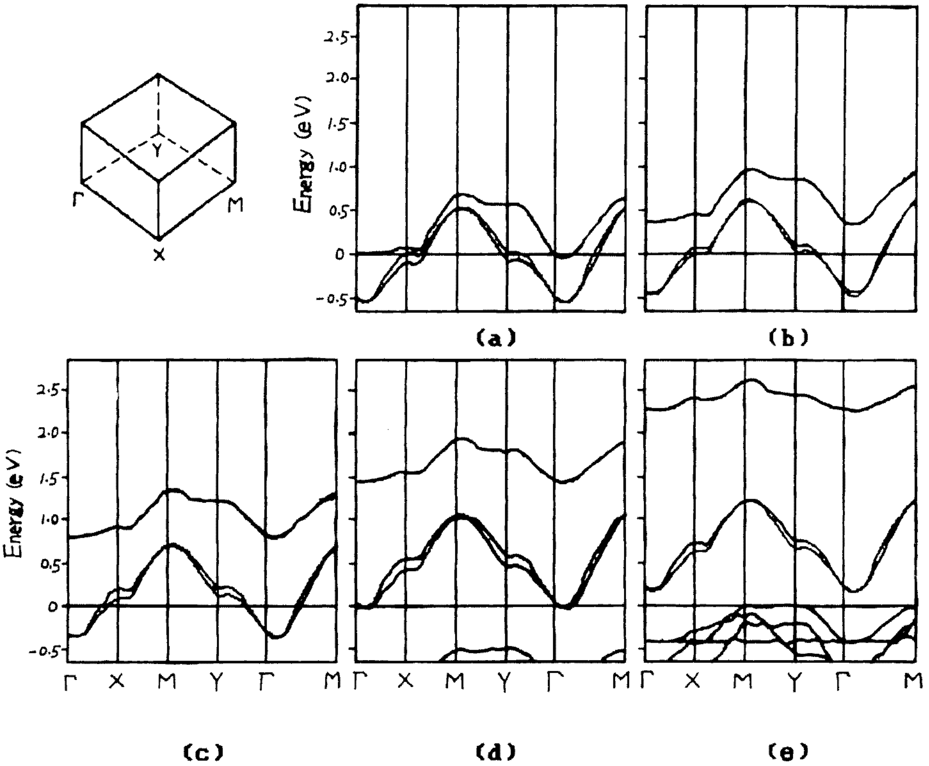
Fig. 1. The crystal structure of $YBa_2Cu_3O_y$.

Table 2
Densities of states for $YBa_2Cu_{3-x}Fe_xO_y$.

x	y	$N(E_f)$	$N(E_f)^P_{Cu-O}$	$N(E_f)^R_{Cu-O}$	T_c (K) [15]
0.0	7.00	9.30	3.22	2.32	92
0.1	7.06	6.84	3.40	0.02	~ 80
0.2	7.11	5.07	2.52	0.00	
0.3	7.15	3.74	1.86	0.00	~ 35
0.4	7.19	3.07	1.48	0.00	
0.5	7.23	1.90	0.94	0.00	nonsuperconductor

order to analyze the effect of the Fe-doping on band structures in detail, the electronic energy band structure of the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$ ($y > 7$) are shown in Fig. 2, in which the Fermi level E_f is placed at the zero of energy. For the present purpose of comparison, the band structure of $YBa_2Cu_3O_y$ is also shown in Fig. 2.

It is seen from Fig. 2 that in $YBa_2Cu_3O_y$, there are three broad anisotropic bands



(a) (b)

(c) (d) (e)

Fig. 2. Band structures for $YBa_2Cu_{3-x}Fe_xO_y$: (a) $x = 0.0$, (b) $x = 0.1, y = 7.06$; (c) $x = 0.2, y = 7.11$; (d) $x = 0.3, y = 7.15$, (e) $x = 0.5, y = 7.23$.

crossing the Fermi level E_f in the Γ–X–M–Y–Γ plane located in the first Brillouin zone. Two of these bands, which are *half-filled*, correspond to the 2D Cu–O planes, and the third, which is unoccupied, arises from the 1D Cu–O chains. These results are in general agreement with those given by Whangbo et al. [35]. When Fe substitutes partially for Cu(1) in the 1D Cu–O chains, the band structures are changed drastically. It can be seen from Fig. 2 that as the Fe-doping fraction x is raised from 0.0 to 0.5, the broad anisotropic bands arising from the 2D Cu–O planes are displaced upwards and depart from the Fermi level E_f gradually although their dispersions and bandwidths remain almost unchanged in the process of the doping. At $x = 0.5$, these bands are located above E_f by about 0.2 eV. It is obvious that the Fe-doping at the Cu-site causes the gradual transformation of these Cu–O bands from a half-filled into an empty band on increasing the Fe-doping fraction x. Since the broad anisotropic Cu–O bands arising from the 2D Cu–O planes do not overlap with the bands below E_f, it is clear from Fig. 2 that the upward displacement of the broad anisotropic Cu–O bands for the 2D Cu–O planes caused by the Fe-doping at the Cu-site results in an energy gap of about 0.2 eV near E_f at the Fe-doping fraction $x = 0.5$. This result may be in relationship with the transformation of $YBa_2Cu_{3-x}Fe_xO_y$ from a superconductor into a nonsuperconductor. For the broad anisotropic band arising from the 1D Cu–O chains, it is seen from Figs. 2(a) and 2(b) that the minimal substitution of Fe for Cu leads to a great change of this broad anisotropic Cu–O band arising from the 1D Cu–O chains. At $x = 0.0$, that is $YBa_2Cu_3O_y$, the bottom of this band, which interacts the broad anisotropic Cu–O bands arising from the 2D Cu–O planes, is situated below E_f. At $x = 0.1$ (about 3.3% of Fe), this band rises and its bottom is situated above E_f by about 0.4 eV. As the Fe-doping fraction x increases further from 0.1 to 0.5, the Cu–O band arising from the 1D Cu–O chains is quickly displaced upwards and does not intersects the broad anisotropic Cu–O bands arising from the 2D Cu–O planes, while its dispersion and bandwidth are decreased greatly. At $x = 0.5$, this Cu–O band is almost flat and is situated about 1.0 eV above the top of the broad anisotropic Cu–O bands arising from the 2D Cu–O planes. The reason for this fact is that the interaction between the d orbitals for Fe and the p orbitals for O decreases on increasing the Fe-doping fraction x because of a large difference between the energies of these orbitals. The split of the unoccupied 1D Cu–O band with the 2D Cu–O bands weakens their interactions greatly, which is of no advantage to the movement of carriers and further to the formation of superconductive states. In addition, it must be pointed out here that the increase in the oxygen content in the unit cell caused by the Fe-doping at the Cu-site has been taken into account in the present computations on the band structures. From Table 2, it is seen that the oxygen content y in $YBa_2Cu_{3-x}Fe_xO_y$ is raised from 7.0 to 7.23 on increasing the Fe-doping fraction x from 0.0 to 0.5. It is apparent from Fig. 2 that in the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$, the oxygen content is not a predominant factor for the band structure results although it is raised as the x value increases. In other words, the increase in the oxygen content in the unit cell does not have a great influence on the superconducting properties of the Fe-doped Y–Ba–

Cu–O system. As a consequence, for $YBa_2Cu_{3-x}Fe_xO_y$, the Fe-doping at the Cu-site is the key reason for the great change in the band structures.

Obviously, the above results demonstrate that the partial substitution of Fe for Cu in $YBa_2Cu_3O_y$ causes the drastic change in its electronic energy band structures, especially near the Fermi level E_f. Since the band structures are in close relationship with the properties of superconductors, the Fe-doping at the Cu-site must have a great effect on the superconductivity of the Y–Ba–Cu–O system. In fact, the experiment given by Xu et al. [15] revealed that the transition temperature T_c is greatly suppressed as the Fe-doping fraction x is increased. For example, when the x value is increased from 0.0 to 0.1, T_c is suppressed from 92 K to 80 K, and this compound is transformed into a nonsuperconductor at $x = 0.5$.

3.2. DENSITIES OF STATES

Densities of states are a direct consequence of band structures and are in direct relationship with superconductivity. Some results for the densities of states for the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$ ($y \geqslant 7$) are summarized in Table 2, 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 sums of the projected densities of states at E_f for Cu(2), O(2), and O(3) in the 2D Cu–O planes, and $N(E_f)^R_{Cu-O}$, those for Cu(1) and O(1) in the 1D Cu–O chains.

Fig. 3 shows the total electronic densities of states (TDOS) near the Fermi level E_f for the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$ at the Fe-doping fraction x

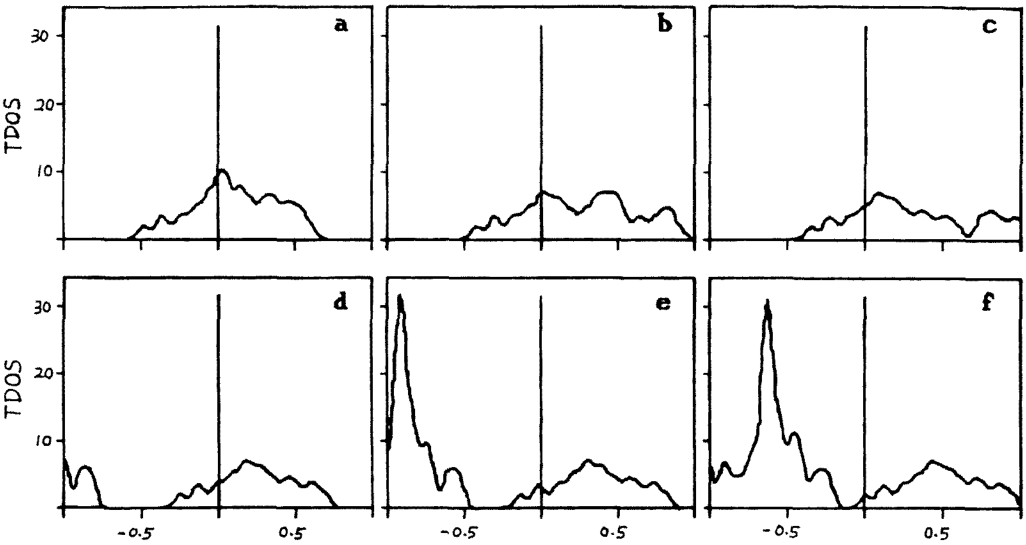


Fig. 3. Total densities of states for $YBa_2Cu_{3-x}Fe_xO_y$: (a) $x = 0.0$, $y = 7.0$; (b) $x = 0.1$, $y = 7.06$; (c) $x = 0.2$, $y = 7.11$; (d) $x = 0.3$, $y = 7.15$; (e) $x = 0.4$, $y = 7.19$; (f) $x = 0.5$, $y = 7.23$.

between 0.0 and 0.5. It is clear from Fig. 3 that in $YBa_2Cu_3O_y$, there is a strong TDOS peak near E_f. This peak arises from the overlaps of the d and p orbitals for the Cu and O atoms in the 1D Cu–O chains and the 2D Cu–O planes. As the Fe-doping fraction x increases, this Cu_{3d}–O_{2p} peak departs from E_f toward the high-energy zone by degrees and its peak height is decreased. This consequence is due to the upward displacement of the broad anisotropic Cu–O bands arising from the 1D Cu–O chains and the 2D Cu–O planes and results in a great decrease in the densities of states for the Fe-doped Y–Ba–Cu–O system. Fig. 4 gives the relationship between the Fe-doping fraction x and the total densities of states at E_f, $N(E_f)$, for $YBa_2Cu_{3-x}Fe_xO_y$. Obviously, the partial substitution of Fe for Cu leads to a drastic decrease in $N(E_f)$. It can be seen from Table 2 that at $x = 0.0$ ($YBa_2Cu_3O_y$), $N(E_f)$ is equal to 9.30 states/eV-cell, whereas it is quickly decreased to 1.9 states/eV-cell, decreasing by about 7.4 states/eV-cell, as the x value is increased from 0.0 to 0.5. The densities of states near the Fermi level E_f are in close relationship with the superconducting transition temperature T_c. From the point of view of the BCS theory, T_c is directly proportional to the factor $\exp(-1/N(E_f)V)$, in which $N(E_f)$ is the total electronic densities of states at E_f. Therefore, since $N(E_f)$ for $YBa_2Cu_{3-x}Fe_xO_y$ is drastically decreased on increasing the x value, the values of T_c can be rapidly suppressed. This consequence is in agreement with the behavior of T_c given by experiment [15]. Apparently, it can be concluded that the Fe-doping at the Cu-site in the Y–Ba–Cu–O system is of no advantage to its superconducting properties and causes its value of T_c to be quickly suppressed with the increase in the doping fraction x.

Now let us analyze the densities of states in detail from the projected densities of states (PDOS). The sums of the projected densities of states near E_f for Cu(2), O(2), and O(3) in the 2D Cu–O planes of the Fe-doped superconductors

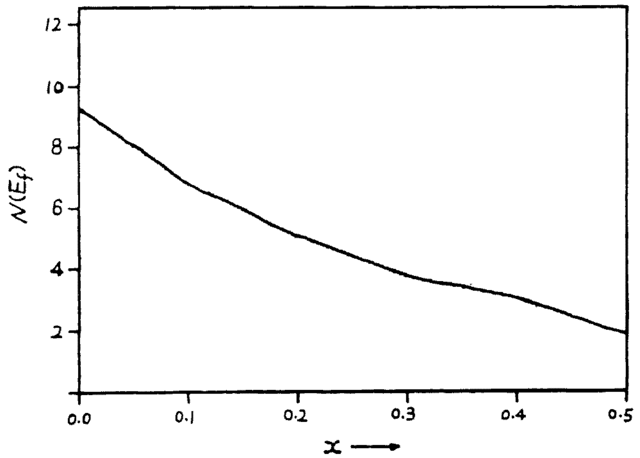


Fig. 4. The relationship between $N(E_f)$ and the x value in $YBa_2Cu_{3-x}Fe_xO_y$.

$YBa_2Cu_{3-x}Fe_xO_y$ are shown in Fig. 5. It can be seen from Fig. 5 that as the Fe-doping fraction varies from 0.0 to 0.5, the projected densities of states for the 2D Cu–O planes remain almost unchanged in shape, but they are displaced and depart from E_f toward the high-energy zone by degrees. This result is the direct reflection of the translation of the broad anisotropic Cu–O bands arising from the 2D Cu–O planes under the influence of the Fe-doping at the Cu-site. Obviously, the displacement of PDOS can cause the projected densities of states at E_f, $N(E_f)^{P}_{Cu-O}$, for the 2D Cu–O planes to decrease. It is seen from Table 2 that $N(E_f)^{P}_{Cu-O}$ varies from 3.22 states/eV-cell to 0.94 states/eV-cell, decreasing by about 2.3 states/eV-cell, as the x value increases from 0.0 to 0.5. Because there are two 2D Cu–O planes in the unit cell of $YBa_2Cu_{3-x}Fe_xO_y$, the total decrease for the Cu–O planes is $2 \times 2.3 = 4.6$ states/eV-cell, which makes up about 62% of the decrease of the total densities of states at E_f, $\Delta N(E_f)$. In addition, it is also seen from Table 2 that for each of the Fe-doped superconductors $YBa_2Cu_{3-x}Fe_xO_y$, the sums of $N(E_f)^{P}_{Cu-O}$ for two Cu–O planes are much more than the projected densities of states at E_f for the 1D Cu–O chains, $N(E_f)^{R}_{Cu-O}$, and make up most of the total densities of states at E_f, $N(E_f)$. Therefore, it is clear from these results that the 2D Cu–O planes play an important role in the Y–Ba–Cu–O superconducting system. $N(E_f)^{R}_{Cu-O}$ of the 1D Cu–O chains for the undoped compound is 2.32 states/eV-cell. As the Fe-doping fraction x is raised, it is seen from Table 2 that $N(E_f)^{R}_{Cu-O}$ is drastically decreased to zero, which demonstrates the great influence of the Fe-doping at the Cu(1)-site on the 1D Cu–O chains. This result is in apparent relationship with the drastic change of the broad anisotropic Cu–O band arising from the 1D Cu–O chains caused by the Fe-doping at the Cu-site.

From the above discussion on the densities of states, it is clear that the Fe-doping at the Cu-site has a great effect on the densities of states. As the doping fraction x is raised from 0.0 to 0.5, the total densities of states at the Fermi level E_f, $N(E_f)$, are decreased greatly and this decrease is mostly caused by the drastic change in the projected densities of states arising mainly from the 2D Cu–O planes and partially from the 1D Cu–O chains. Inevitably, the decrease in $N(E_f)$ can cause the suppression of the superconducting transition temperature T_c.

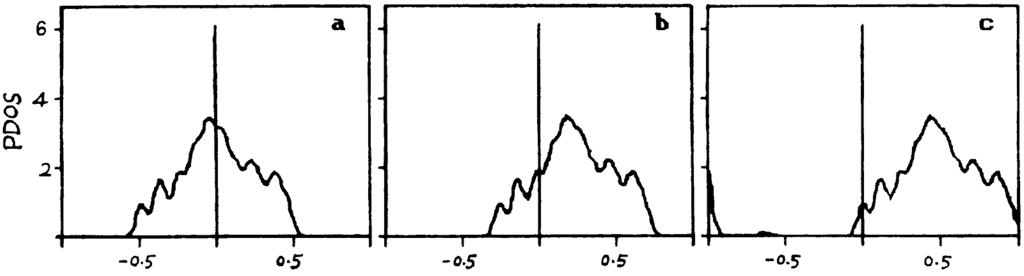


Fig. 5. Projected densities of states for the Cu–O planes: (a) $x = 0.0$, $y = 7.0$; (b) $x = 0.3$, $y = 7.15$; (c) $x = 0.5, y = 7.23$.

3.3. OXIDATION STATE OF COPPER

The earlier studies [36,37] showed that the oxidation state of Cu play an important role in superconductivity and that the higher the ratio of Cu^{3+} to Cu^{2+} is, the higher the superconducting transition temperature T_c is. However, most X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) studies [38–41] did not find the Cu^{3+} oxidation state in the Y–Ba–Cu–O system. Although some studies [42,43] 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. [10–13] 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 T_c. They considered that the oxidation state of Cu may be just the result of charge balance.

Table 3 summarizes the net charges of Cu in $YBa_2Cu_{3-x}Fe_xO_y$, where 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. It is seen from Table 3 that as the Fe-doping fraction x or the oxygen content y in $YBa_2Cu_{3-x}Fe_xO_y$ is raised, the net charges of both Cu(1) and Cu(2) increase monotonically, as well as the average net charge of Cu. The increase in the net charge of Cu seems to result in an increase in the concentration of Cu^{3+}. Therefore, it is obvious that the increase in the oxidation state of Cu is not in accordance with the behavior of the superconducting transition temperature T_c because of the suppression of T_c with the increase of the Fe-doping fraction x or the oxygen content. As a consequence, it is considered that in $YBa_2Cu_{3-x}Fe_xO_y$, the oxidation state of copper is not a dominant factor for superconductivity and may just be the result of charge balance, which is in agreement with the result given by Zhang et al. [13].

4. Conclusion

In summary, it can be concluded from the above discussions on the band structures and the densities of states that the Fe-doping at the Cu-site in $YBa_2Cu_3O_y$ results in a great change in its electronic structures. As the Fe-doping fraction x in

Table 3
The net charges of Cu in $YBa_2Cu_{3-x}Fe_xO_y$. (*Note*: Q_1 and Q_2 express, respectively, the net charges of Cu at the Cu(1) site and at the Cu(2) site, and Q is the average net charge of Cu.)

x	y	Q_1	Q_2	Q
0.0	7.00	1.71	1.14	1.33
0.1	7.06	1.77	1.28	1.44
0.2	7.11	1.82	1.41	1.55
0.3	7.15	1.85	1.56	1.66
0.4	7.19	1.88	1.70	1.76
0.5	7.23	1.91	1.80	1.84

$YBa_2Cu_{3-x}Fe_xO_y$ is raised from 0.0 to 0.5, (i) the broad anisotropic bands arising from the 1D Cu–O chains and the 2D Cu–O planes are displaced and depart from the Fermi level E_f toward the high-energy zone by degrees, while the total electronic densities of states near E_f are drastically decreased; (ii) the band arising from the Cu–O chains doped by Fe is gradually separated from the broad anisotropic bands arising from the 2D Cu–O planes and its dispersion and bandwidth are rapidly decreased; (iii) at the doping fraction $x = 0.5$, the Fe-doping at the Cu-site results in an energy gap (about 0.2 eV) near E_f, which may be in relationship with the transformation of $YBa_2Cu_{3-x}Fe_xO_y$ from a superconductor into a nonsuperconductor; (iv) the increase in the oxygen content caused by the Fe-doping does not have a large influence on the band structures and the densities of states near E_f for $YBa_2Cu_{3-x}Fe_xO_y$, in other words, the oxygen content is not a predominant factor for the superconducting properties of the Fe-doped Y–Ba–Cu–O system; (v) the total densities of states at E_f, $N(E_f)$, and their decrease caused by the Fe-doping arise mainly from the 2D Cu–O planes, which implies the important role of the 2D Cu–O planes in the Y–Ba–Cu–O superconducting system; (vi) the oxidation state of copper may not be a predominant factor for superconductivity and may just be the result of charge balance.

Acknowledgement

This work was supported by the Science Foundation of Chongqing City, P.R. China.

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