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## Electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ with $y = 0.25, 0.125, 0, -0.125$

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**Abstract.** The electronic densities of states of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  with  $y = 0.25, 0.125, 0, -0.125$  have been calculated by the recursion method. We have discussed the influence of the variation in O vacancies on the electronic structure and show that O vacancies can only exist in Cu–O chains. Our results show the atomic-like localised character of Cu 3d states and large O–metal covalency in this system. The valency of the Cu atoms is discussed and possible electronic configurations of Cu are proposed from an energy point of view. The most probable valency of O is  $-1$  so that there is a hole-conducting mechanism in the Y–Ba–Cu–O system.

### 1. Introduction

One of the keys to discussing the high- $T_c$  superconducting mechanism in Y–Ba–Cu–O systems is to understand the electronic structure. It was found by band-structure calculation (Mattheiss and Hamann 1987, Massidda *et al* 1987) that the compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Siegrist *et al* 1987) had a low-dimensional superconductivity and a low density of states (DOS) at the Fermi surface. Wang *et al* (1988a, b) calculated, by the recursion method (Haydock 1980), the electronic DOS of every site in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  crystal and found that various Cu–O complexes exist.

It is well known that the superconductive material is  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ , where  $y$ , the amount of O vacancies, covers a certain range, and which has the highest  $T_c$  when  $y$  is near 0.1. It is necessary to understand the electronic structure with variation in  $y$ . In the present paper, we have calculated the electronic DOS of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  with  $y = 0.25, 0.125, 0, -0.125$ . We discuss the influence of the variation in O vacancies on the electronic structure and show that O vacancies can exist only in Cu–O chains. The valency of Cu atoms is discussed and possible electronic configurations of Cu and Cu–O complexes are proposed with respect to the energy picture. We have found both an atomic-like localised character of Cu 3d states and the existence of  $\text{O}^-$ . The latter is believed to provide a hole-conducting mechanism in Y–Ba–Cu–O.

### 2. Method and models

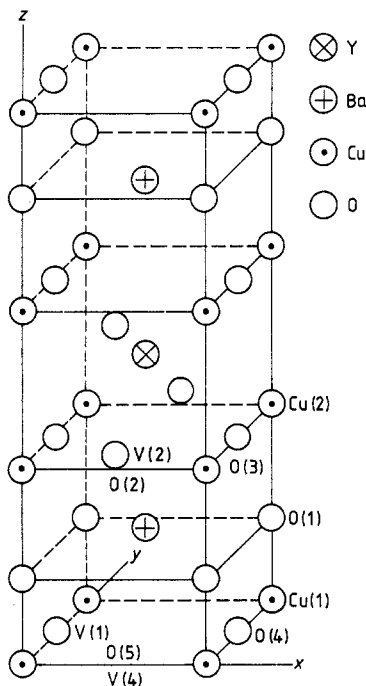
We use the recursion method to calculate the electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . The

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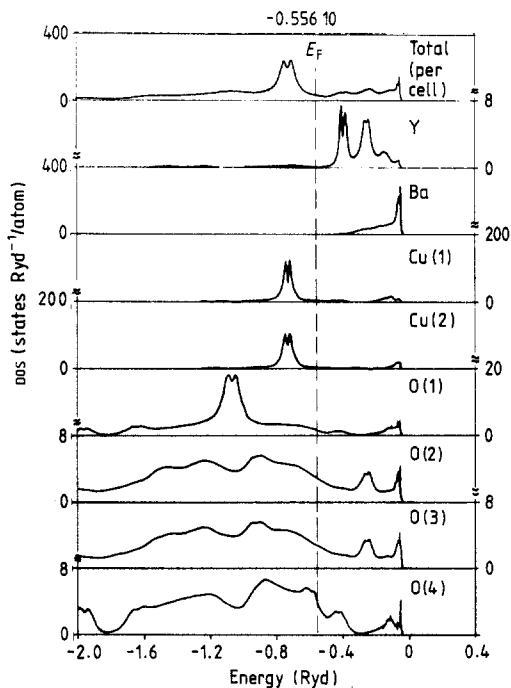
**Table 1.**  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  models; in model 1 there is an O(4) vacancy per four cells, and in models 2 and 4 an O(2) vacancy and an O(5) atom, respectively, are added per eight cells. The Y atom in the central cell is taken as the origin.

| Model | $y$    | Number in atom cluster |       |           | $E_F$<br>(Ryd) | DOS at Fermi level<br>(states $\text{eV}^{-1}/\text{cell}$ ) |
|-------|--------|------------------------|-------|-----------|----------------|--|
|       |        | Cells                  | Atoms | Vacancies |                |  |
| 1     | 0.25   | $7 \times 7 \times 3$  | 2305  | 56        | -0.5482        | 2.04   |
| 2     | 0.125  | $7 \times 7 \times 3$  | 2349  | 12        | -0.5534        | 2.09   |
| 3     | 0      | $7 \times 7 \times 3$  | 2361  | 0         | -0.5561        | 2.19   |
| 4     | -0.125 | $7 \times 7 \times 3$  | 2385  | 24        | -0.5564        | 2.30   |

Hamiltonian matrix is chosen in the LCAO representation. Its elements are Slater-Koster integrals, i.e. the linear combinations of transition integrals between orbitals which were obtained by the parameter method of Harrison (1980). The length  $L$  of the recurrence chain was selected as 30. The  $\text{YBa}_2\text{Cu}_3\text{O}_7$  cell is shown in figure 1. O(4) sites are on the long axis in the  $xy$  plane. Only nearest-neighbour interactions between O and metal atoms are considered. Valence electrons include  $4d^{15}s^2$  of Y,  $6s^2$  of Ba,  $3d^{10}4s^1$  of Cu, and  $2s^22p^4$  of O. Experimental evidence showed a lack of delocalised Cu p states at the Fermi level in  $\text{YBa}_2\text{Cu}_3\text{O}_{\approx 7}$  (Bianconi *et al* 1987b); therefore it is correct that Cu p electrons are not considered as valence electrons.



**Figure 1.** A  $\text{YBa}_2\text{Cu}_3\text{O}_7$  cell with crystal constants and fractional coordinates of all atoms (after Siegrist *et al* (1987)). V(1), V(2) and V(4) indicate the positions of O deficiencies in the central cell of all vacancy models.



**Figure 2.** Electronic DOS of every site in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and of one cell including 13 atoms (curve labelled Total).

We established three oxygen vacancy models for  $YBa_2Cu_3O_{7-y}$  as models 1, 2 and 4 listed in table 1. Model 4 actually has no O vacancy but has O(5) atoms added, which are still called 'vacancies' for convenience. Vacancies are arranged in an orderly fashion, and the atom sites and crystal constants in figure 1 remain unchanged irrespective of whether there is a vacancy. The structure of  $YBa_2Cu_3O_7$  was calculated with a recurrence chain length  $L$  of 50 (Wang *et al* 1988b). For comparison with our vacancy models, it is calculated once more with  $L = 30$  as model 3 in table 1: the results of this are almost the same as those of Wang *et al*.

**Table 2.** Designations and coordinates of the sites calculated. The names are constructed as follows: the first number refers to the model, the letters and the number in parentheses refer to the site as in figure 1, and the last number, in vacancy models, to the inequivalent site. For model 3, the first and last numbers are omitted. The two values under each designation are its valency defined in the text and its DOS (in units of states per rydberg per atom) at the Fermi level.

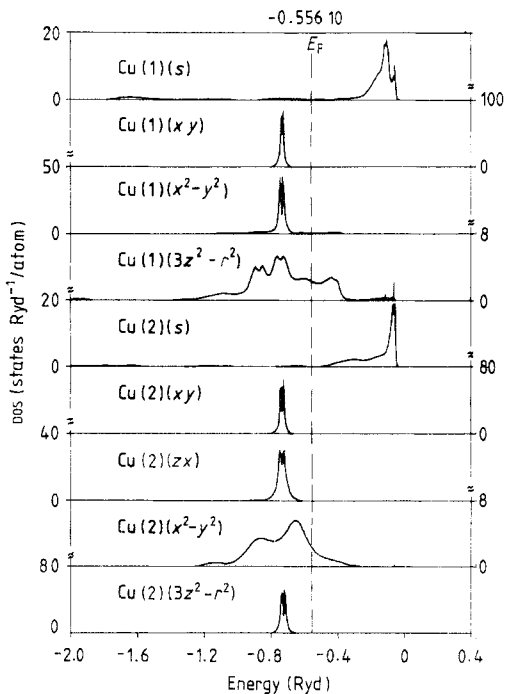
| Model 1                | Model 2                | Model 3             | Model 4                | Coordinates                                  |
|------------------------|------------------------|---------------------|------------------------|--|
| 1Y<br>1.49, 0.668      | 2Y<br>1.59, 0.969      | Y<br>1.49, 0.655    | 4Y<br>1.49, 0.661      | (0, 0, 0)                                    |
| 1Ba(1)<br>1.724, 0.033 | 2Ba(1)<br>1.730, 0.055 | Ba<br>1.726, 0.044  | 4Ba(1)<br>1.732, 0.049 | (0, 0, -0.3138)                              |
| 1Ba(2)<br>1.727, 0.027 | 2Ba(2)<br>1.727, 0.044 |                     | 4Ba(2)<br>1.725, 0.044 | (0, 0, 0.3138)                               |
| 1Cu(1)1<br>0.86, 2.64  | 2Cu(1)1<br>1.10, 2.94  | Cu(1)<br>1.12, 2.98 | 4Cu(1)<br>1.42, 4.01   | $(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$ |
| 1Cu(1)2<br>1.09, 2.93  |                        |                     | 4Cu(1)2<br>1.10, 2.53  | $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$   |
| 1Cu(2)1<br>0.84, 3.01  | 2Cu(2)1<br>0.71, 2.05  | Cu(2)<br>0.88, 3.29 | 4Cu(2)1<br>0.87, 3.32  | $(-\frac{1}{2}, -\frac{1}{2}, -0.1428)$      |
|                        | 2Cu(2)2<br>0.86, 3.24  |                     |                        | $(-\frac{1}{2}, -\frac{1}{2}, 0.1428)$       |
| 1O(1)1<br>-1.46, 0.68  | 2O(1)1<br>-1.41, 1.57  | O(1)<br>-1.42, 1.63 | 4O(1)1<br>-1.37, 1.92  | $(-\frac{1}{2}, -\frac{1}{2}, -0.347)$       |
| 1O(1)2<br>-1.43, 1.45  |                        |                     | 4O(1)2<br>-1.41, 1.62  | $(\frac{1}{2}, \frac{1}{2}, -0.347)$         |
| 1O(2)1<br>-0.98, 2.76  |                        | O(2)<br>-0.94, 2.85 | 4O(2)1<br>-0.95, 2.85  | (0, $-\frac{1}{2}$ , -0.120)                 |
|                        | 2O(2)1<br>-1.01, 2.31  |                     |                        | (0, $-\frac{1}{2}$ , 0.120)                  |
|                        | 2O(2)2<br>-0.97, 2.64  |                     |                        | (0, $\frac{1}{2}$ , -0.120)                  |
|                        | 2O(2)3<br>-0.92, 2.04  |                     |                        | (0, $\frac{1}{2}$ , 0.120)                   |
| 1O(3)1<br>-0.98, 2.74  | 2O(3)1<br>-1.04, 2.24  | O(3)<br>-0.94, 2.82 | 4O(3)1<br>-0.95, 2.83  | $(-\frac{1}{2}, 0, -0.121)$                  |
|                        | 2O(3)2<br>-0.98, 2.73  |                     |                        | $(-\frac{1}{2}, 0, 0.121)$                   |
| 1O(4)1<br>-1.30, 3.69  | 2O(4)1<br>-1.28, 4.02  | O(4)<br>-1.26, 4.22 | 4O(4)1<br>-1.24, 4.44  | $(\frac{1}{2}, 0, -\frac{1}{2})$             |
|                        |                        |                     | 4O(5)<br>-1.03, 2.66   | (0, $-\frac{1}{2}$ , $-\frac{1}{2}$ )        |

An atom cluster including  $7 \times 7 \times 3$  crystal cells is used in calculating each model. The central cell has a vacancy in each vacancy model. The electronic DOS of several sites near the vacancies were calculated; the designations of all of these (see table 2 heading) together with the coordinates are shown in table 2. For models 1, 2 and 4, there are still some sites for which the DOS were not calculated, because parts of these are, by symmetry, equal to those calculated and others are far enough from vacancies to have the same electronic structure as the corresponding sites in model 3. The latter can be inferred from the variation of DOS with increase in the distance from vacancies (see, e.g., figure 6) and was confirmed by selectively calculating the DOS for a few such sites.

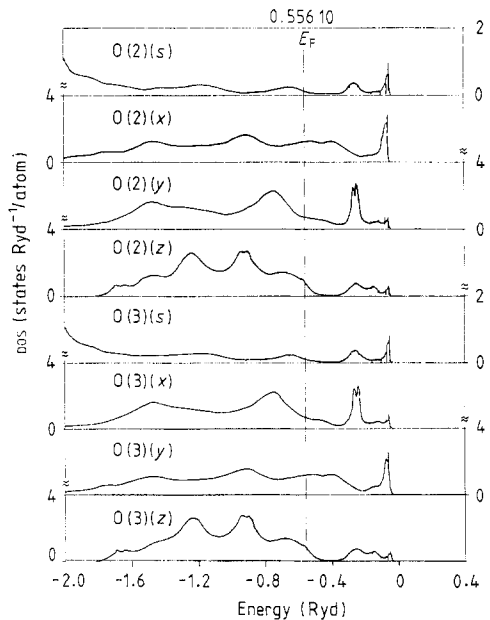
### 3. Results and discussion

Figures 2–6 give some of our results. The vacancies to be discussed later and the DOS on the Fermi surface of atoms considered are listed in table 2.

The Fermi energies and the total electronic DOS per cell in each model are listed in table 1. Our results again verify the property of a low DOS at the Fermi level. For every O atom, its states under the Fermi surface can contain more electrons than its six valence electrons  $2s^2 2p^4$  (table 3). Adding a small quantity of O atoms to one cell (from model 1 to model 4, the increase in  $y$  is not more than 0.375, i.e. the increase in O content is less than 6%) does not change the shape of one cell DOS in which the DOS of Cu atoms is predominant (see figure 2). The total DOS per cell, as shown by the curve labelled Total



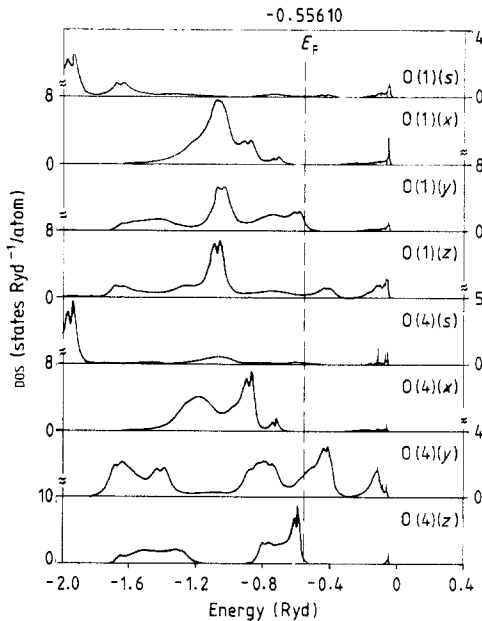
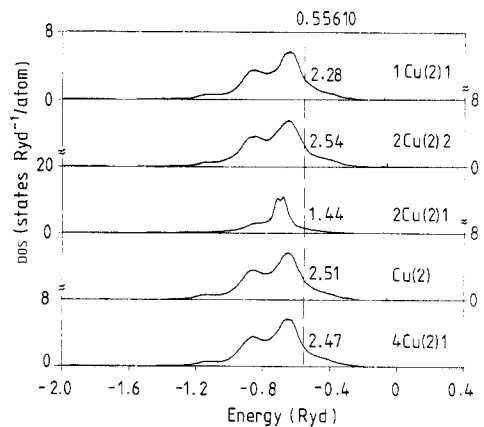
**Figure 3.** Partial wave DOS of Cu(1) and Cu(2) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The  $yz$  and  $zx$  orbitals of Cu(1) are quite similar to its  $xy$  orbital and the orbital  $yz$  of Cu(2) is similar to its  $xy$  orbital.



**Figure 4.** Partial wave DOS of O(2) and O(3) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

**Table 3.** Quantities of electrons (and holes in parentheses) which O atoms and its orbitals possess.

| Site     | s             | $p_x$         | $p_y$         | $p_z$         | Total       |
|----------|---------------|---------------|---------------|---------------|-------------|
| 1 O(1) 1 | 1.952 (0.048) | 1.926 (0.074) | 1.902 (0.098) | 1.680 (0.320) | 7.46 (0.54) |
| 1 O(1) 2 | 1.940 (0.060) | 1.930 (0.070) | 1.914 (0.086) | 1.646 (0.354) | 7.43 (0.57) |
| 2 O(1) 1 | 1.922 (0.078) | 1.938 (0.062) | 1.910 (0.090) | 1.640 (0.360) | 7.41 (0.59) |
| O(1)     | 1.938 (0.062) | 1.930 (0.070) | 1.908 (0.092) | 1.644 (0.356) | 7.42 (0.58) |
| 4 O(1) 1 | 1.932 (0.068) | 1.912 (0.088) | 1.912 (0.088) | 1.614 (0.386) | 7.37 (0.63) |
| 4 O(1) 2 | 1.926 (0.074) | 1.938 (0.062) | 1.906 (0.094) | 1.640 (0.360) | 7.41 (0.59) |
| 1 O(2) 1 | 1.929 (0.071) | 1.542 (0.458) | 1.670 (0.330) | 1.839 (0.161) | 6.98 (1.02) |
| 2 O(2) 1 | 1.934 (0.066) | 1.538 (0.462) | 1.688 (0.312) | 1.850 (0.150) | 7.01 (0.99) |
| 2 O(2) 2 | 1.925 (0.075) | 1.523 (0.477) | 1.676 (0.324) | 1.846 (0.154) | 6.97 (1.03) |
| 2 O(2) 3 | 1.916 (0.084) | 1.538 (0.462) | 1.650 (0.350) | 1.816 (0.184) | 6.92 (1.08) |
| O(2)     | 1.914 (0.086) | 1.532 (0.468) | 1.664 (0.336) | 1.830 (0.170) | 6.94 (1.06) |
| 4 O(2) 1 | 1.924 (0.076) | 1.532 (0.468) | 1.664 (0.336) | 1.830 (0.170) | 6.95 (1.05) |
| 1 O(3) 1 | 1.930 (0.070) | 1.672 (0.328) | 1.542 (0.458) | 1.836 (0.164) | 6.98 (1.02) |
| 2 O(3) 1 | 1.918 (0.082) | 1.704 (0.296) | 1.574 (0.426) | 1.844 (0.156) | 7.04 (0.96) |
| 2 O(3) 2 | 1.928 (0.072) | 1.672 (0.328) | 1.536 (0.464) | 1.844 (0.156) | 6.98 (1.02) |
| O(3)     | 1.914 (0.086) | 1.666 (0.334) | 1.532 (0.468) | 1.828 (0.172) | 6.94 (1.06) |
| 4 O(3) 1 | 1.922 (0.078) | 1.668 (0.332) | 1.532 (0.468) | 1.828 (0.172) | 6.95 (1.05) |
| 1 O(4) 1 | 1.930 (0.070) | 1.954 (0.046) | 1.456 (0.544) | 1.960 (0.040) | 7.30 (0.70) |
| 2 O(4) 1 | 1.918 (0.082) | 1.956 (0.044) | 1.450 (0.550) | 1.956 (0.044) | 7.28 (0.72) |
| O(4)     | 1.902 (0.098) | 1.956 (0.044) | 1.446 (0.554) | 1.956 (0.044) | 7.26 (0.74) |
| 4 O(4) 1 | 1.878 (0.122) | 1.944 (0.056) | 1.460 (0.540) | 1.958 (0.042) | 7.24 (0.76) |
| 4 O(5)   | 2.000 (0.000) | 1.112 (0.888) | 1.945 (0.055) | 1.973 (0.027) | 7.03 (0.97) |

**Figure 5.** Partial wave DOS of O(1) and O(4) in  $YBa_2Cu_3O_7$ .**Figure 6.** DOS of the  $x^2 - y^2$  orbitals of Cu(2) atoms in the four models, the Fermi energy of which have slight differences (see table 1). The numbers on the curves are the DOS at the respective Fermi levels.

in figure 2, decreases on crossing the Fermi surface. As a result, on a small increase in O content, the Fermi energy slightly decreases and the total DOS per cell at the Fermi level increases.

On comparison of the Cu(2)–O two-dimensional plane with the Cu(1)–O one-dimensional chain, it can be seen that the deficiency of O in the plane leads to a large reduction (more than one third) in the DOS at the Fermi level for Cu(2) atoms near vacancies. This reduction is mainly from the  $x^2 - y^2$  partial wave which gives the largest contribution at the Fermi level of the orbitals of Cu(2) (see figure 3) and is reduced more than 40% at the Fermi level (see figure 6). On the contrary, the DOS at the Fermi surface for Cu(1) near an O(4) vacancy is reduced only about 10% (see table 2). This shows that the deficiency of O in the Cu–O two-dimensional plane is rather disadvantageous for superconductivity, so that O vacancies can only exist in the Cu(1)–O chain for the high  $T_c$  superconductors.

The total interaction energy of each site in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  with its nearest neighbours has been calculated by Wang *et al* (1988b) as follows: for O(1), 0.425 Ryd; for O(2), 0.288 Ryd; for O(3), 0.126 Ryd; for O(4), 0.120 Ryd. Their method was presented by Wang (1988a). We note that, of the O sites, O(4) has the smallest total interaction energy so that it is most easily lost, whereas O(1) has the largest total interaction energy so that it is most stable. According to this, if one wants to substitute  $^{18}\text{O}$  for  $^{16}\text{O}$  by releasing O in heating and then obtaining O on cooling, it is not the O(1) site but other O sites which will be preferentially substituted; this is different from the analysis given in *Superconductivity News* (1988).

Our results show that the electronic structures of Y and Ba atoms are almost unaffected by the variation in O deficiency. It is concluded that Y and Ba atoms merely play roles of stabilising the crystal structure and do not influence the superconductivity.

From figure 3, we see that Cu 3d states obviously have an atomic-like localised character. This character does not change with the variation in  $y$ . From figures 3 and 4, it is shown that both the Cu 3d and the O 2p bands cross the Fermi level so that the energy separation between the delocalised ligand band and the localised metal orbitals is negligible and there is a large O–metal covalency (Bianconi *et al* 1987b).

It was believed that an average copper valency greater than 2 is required to have superconductivity in the copper oxides (Tarascon *et al* 1988), but we have seen no experimental evidence for  $\text{Cu}^{3+}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . Instead, x-ray absorption spectra (Sarma *et al* 1987, Bianconi *et al* 1987a) show that there is no  $\text{Cu}^{3+}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ . Herman *et al* (1987) calculated the valence charges in atomic spheres which left a considerable number of electrons outside all spheres (see table 2 of their paper). We wish to define atom valencies on the basis of energy considerations. The atomic-like localised character of Cu 3d states mentioned above means that the Cu 3d valence electrons are relatively stable in their energy levels. At the same time, the valencies of O atoms must be negative. Therefore the numbers of valence electrons in the energy levels of Cu and O atoms must be greater than in the atomic spheres discussed by Herman *et al* (see Table 2 of their paper). In our calculation, the DOS can be directly obtained from the imaginary part of the Green function. The valence electron number  $N_e$  which one atom possesses is determined by integrating its electronic DOS up to the Fermi energy. The quantity  $n_e = N_{e0} - N_e$ , where  $N_{e0}$  is the total number of valence electrons, is regarded as the valency of the atom, which is apparently with respect to the energy distribution. All the valencies of the sites calculated are listed in table 2 and do not contradict those given by Herman *et al*, which are with respect to the space distribution. The valency given in table 2 for each site is its average valency, e.g. the valency of Cu(1)

**Table 4.** Electrons in partial waves of Cu atoms under the Fermi level.

| Site      | s     | xy    | yz    | zx    | $x^2 - y^2$ | $3z^2 - r^2$ |
|-----------|-------|-------|-------|-------|-------------|--------------|
| 1 Cu(1) 1 | 0.552 | 2.000 | 1.998 | 1.998 | 1.924       | 1.668        |
| 1 Cu(1) 2 | 0.584 | 2.000 | 1.998 | 1.998 | 1.746       | 1.584        |
| 2 Cu(1) 1 | 0.440 | 2.000 | 1.998 | 1.998 | 1.886       | 1.578        |
| Cu(1)     | 0.426 | 2.000 | 1.998 | 1.998 | 1.886       | 1.572        |
| 4 Cu(1) 1 | 0.412 | 1.998 | 1.998 | 1.998 | 1.748       | 1.426        |
| 4 Cu(1) 2 | 0.448 | 1.998 | 1.998 | 1.998 | 1.886       | 1.572        |
| 1 Cu(2) 1 | 0.446 | 1.996 | 1.992 | 1.992 | 1.746       | 1.988        |
| 2 Cu(2) 1 | 0.466 | 1.996 | 1.992 | 1.994 | 1.854       | 1.988        |
| 2 Cu(2) 2 | 0.438 | 1.996 | 1.992 | 1.992 | 1.734       | 1.988        |
| Cu(2)     | 0.424 | 1.996 | 1.992 | 1.992 | 1.728       | 1.988        |
| 4 Cu(2) 1 | 0.438 | 1.996 | 1.992 | 1.992 | 1.726       | 1.986        |

is 1.12, which means that Cu(1) has possible valencies of 1 and 2. It is remarkable that the largest possible vacancy of Cu is  $Cu^+$  and of O is  $O^-$ . The former coincides with the atomic-like character of Cu 3d states. The latter implies a hole in the O atom. We believe that this is a hole-conducting system.

Compared with La-Sr-Cu-O where the Cu atom is six coordinated, the Cu atoms in Y-Ba-Cu-O are five or four coordinated. We assume that in the former there are more than one extended 3d partial waves crossing the Fermi energy so that Cu 3d states will not have a marked atomic-like localised character and the valencies of the Cu and O atoms will be higher than those in Y-Ba-Cu-O. Because of the large difference between the  $T_c$  of La-Sr-Cu-O and that of  $YBa_2Cu_3O_{7-y}$ , we suggest that  $Cu^+$  and  $O^-$  are responsible for the enhancement of the  $T_c$  of the  $YBa_2Cu_3O_{7-y}$  system. Our results indicate the importance of the low valencies of Cu and O. In our opinion,  $Cu^{3+}$  is unfavourable for the enhancement of  $T_c$ . It has been reported (Tarascon *et al* 1988) that the new five-element higher- $T_c$  superconducting material Bi-Sr-Ca-Cu-O also has a Cu-O two-dimensional plane where Cu is again five coordinated. We suggest that the d orbital properties and valency of Cu atoms in that system will be quite similar to our results on Cu(2) atoms in Y-Ba-Cu-O shown in figure 3 and in table 2.

Furthermore, we show in tables 3 and 4 the number of electrons in every orbital of O and Cu under the Fermi level. The energy levels of partial waves of O and Cu which

**Table 5.** Possible main electronic configurations of Cu atoms in  $YBa_2Cu_3O_7$ . In the computation, it is considered that the s orbital has either zero or one electron, and the d orbital either one or two electrons; all other possibilities are neglected. Multiplying the electronic configurations of O by the possible electronic configurations of O, we can easily obtain the electronic configurations of Cu-O complexes in  $YBa_2Cu_3O_7$ . The same parameters can be obtained for other O vacancy models in the same way.

| Valency   | Configuration | Cu(1) | Cu(2) |
|-----------|---------------|-------|-------|
| $Cu^0$    | $3d^{10}4s^1$ | 0.215 | 0.299 |
| $Cu^+$    | $3d^{10}4s^0$ | 0.290 | 0.406 |
|           | $3d^94s^1$    | 0.189 | 0.121 |
| $Cu^{2+}$ | $3d^94s^0$    | 0.254 | 0.165 |
|           | $3d^84s^1$    | 0.020 | 0.002 |
| $Cu^{3+}$ | $3d^84s^0$    | 0.026 | 0.002 |



form  $pd\pi$  and  $pd\sigma$  bonds are not fulfilled. It is notable that the s state in the Cu atom may have about one secondary electron, which is reasonable because 4s bands are extended states and overlap with 3d bands (see figure 3). From table 4, we find several electronic configurations of Cu and calculate their occupation possibilities at each Cu site in Y–Ba–Cu–O as listed in table 5. When taken in combination with table 3, we can see the most probable electronic configurations of Cu–O complexes. For instance, those of Cu(2)–O(2) in  $YBa_2Cu_3O_{7-y}$  are  $3d^{10}4s^1L$ ,  $3d^94s^1L$ ,  $3d^{10}L$ ,  $3d^9L$  where L indicates a hole in the O-derived band.

In conclusion, we find that in the  $YBa_2Cu_3O_{7-y}$  system, Y and Ba atoms merely play roles in stabilising the crystal structure. O vacancies can only exist in Cu–O one-dimensional chains. The Cu 3d states have an atomic-like localised character. The most probable valency of Cu is  $Cu^+$  and of O is  $O^-$  from an energy point of view. The latter implies hole conductivity and, together with the former, plays an important role in enhancing  $T_c$  in the Y–Ba–Cu–O system.

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