

The electronic structure of the surface of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$

Gong Xin-Gao and Zheng Qing-Qi

Institute of Solid State Physics, Academia Sinica, Hefei, People's Republic of China

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Abstract. The electronic structures of several clusters in different Cu–O planes considered as possible surfaces in the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ are studied within the framework of local density theory. Self-consistent solutions are obtained using the discrete variational and X_α cluster method. Several peaks in the UPS are identified by comparing the calculated values of the density of states with the experimental data. The surface electronic structure of the material is also discussed.

1. Introduction

Since the discovery of the La–Ba–Cu–O system of compounds by Bednorz and Müller [1], extensive work has been done on high- T_c superconductor materials. A number of experiments have been performed on thin films of these new kinds of La–Ba–Cu–O and Y–Ba–Cu–O superconductors [2]. Several reports have been published on the electronic structure of the surface of the La–Sr–Cu–O [3] and Y–Ba–Cu–O superconductor materials studied using photoemission [4–6]. In these experiments, two peaks are reported in the valence band spectrum; these are situated at about 2.3 eV and 4.5 eV below the Fermi energy level. Johnson [7] associated the peak at about –4.5 eV with the copper DOS and the peak at about –2.3 eV with the oxygen DOS, but Steiner [5] associated the peak at –4.5 eV with the oxygen 2p DOS. Although a number of papers have been published on bulk electronic structure [8], it is still difficult to resolve the controversy. Moreover, the electronic structure of the surface may be different from that of the bulk. In this paper, we report our cluster model calculation of the electronic structure for the surface of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$, and identify the profiles observed in the UPS spectrum.

2. The cluster model and theoretical methods

We use a discrete variational method and the local density theory approximation (DV- X_α) [9], in a self-consistent manner. The Hedin–Lundquist formula [10] for the exchange–correlation potential is used in our calculation. Ionic Cu(3d, 4s), O(2s, 2p) and Y(4d, 5s) are taken as the valence electrons. The tightly bound core-like orbitals are handled using the frozen-core approximation; only the valence electrons are taken to respond to the variation of the environment. We know that the new type of high- T_c

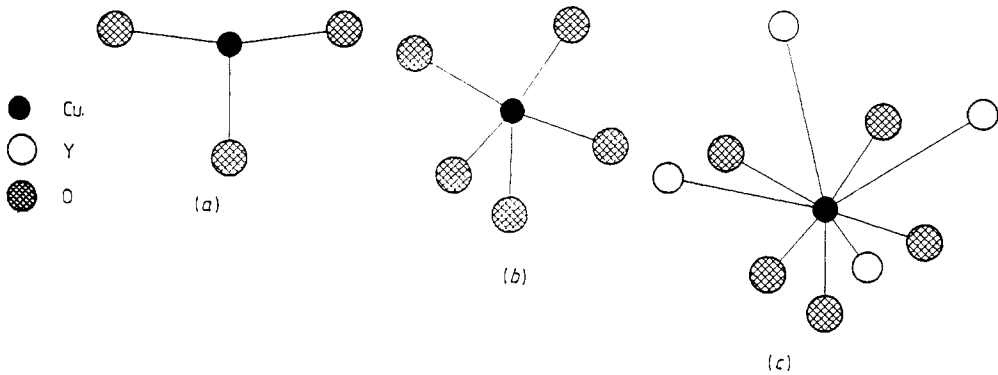


Figure 1. Clusters for Cu, Y and O atoms: (a) $\text{Cu}(1)\text{O}(4)_2\text{O}(1)$; (b) $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)$; and (c) $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)\text{Y}(4)_4$.

materials belongs to the strong-correlation regime, but, as pointed out by Herman [8], the correlation effect is not overwhelming. Hence the present approximation can still be used as a first step for further consideration.

According to the crystal structure of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound [11], several clusters for possible surfaces are chosen in the $\text{Cu}(2)\text{-O}$ plane and $\text{Cu}(1)\text{-O}$ plane. The $\text{Cu}(1)\text{O}(4)_2\text{O}(1)$ cluster and $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)$ cluster for the $\text{Cu}(1)\text{-O}$ and $\text{Cu}(2)\text{-O}$ surface planes respectively are shown in figure 1. O atoms and O ions absorbed at the topmost position in the $\text{Cu}(1)\text{O}(4)_2\text{O}(1)$ and $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)$ clusters respectively are also considered. We also studied the influence of Y ions at the $\text{Cu}(2)\text{-O}$ surface plane using a $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)\text{Y}_4$ cluster to include the interaction between the Cu and Y ions. In the ionic-like $\text{YBa}_2\text{Cu}_3\text{O}_7$ material, the strong crystalline field may produce a significant difference between the isolated cluster and the real surface. Thus, in our calculation, an embedded-cluster scheme [12] is used to reduce the effects of the boundary conditions by taking into account the Coulomb and exchange potentials generated from about 640 neighbouring ions near the surface. The contributions to the potential from ions at a larger distance are neglected due to the screening effect. Hence the influence of the crystal fields and the surface effect are taken into account to some extent.

3. Results and discussion

The DOS for several different clusters are listed in figure 2. First we can compare the calculated DOS with the UPS data for $\text{YBa}_2\text{Cu}_3\text{O}_7$ [6]. From figure 2 one can see that the DOS in the $\text{Cu}(1)\text{-O}$ plane is very different from the UPS results, but the DOS in the $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)$ cluster listed in figure 2(a) are very similar to the experimental UPS results. The positions of several peaks are presented in table 1. From this table, we can see that the relative separations of the calculated peaks are nearly equal to those of the experimental peaks. Moreover, we note that all the calculated peaks are shifted to a binding energy lower by about 2 eV than are those determined experimentally. In the LAPW band calculations, a similar shift between the theoretical calculation and experimental data also exists [13, 14]. This may result from the use of the approximations of local density theory in this calculation. The peaks at -0.08 eV and -2.3 eV obtained

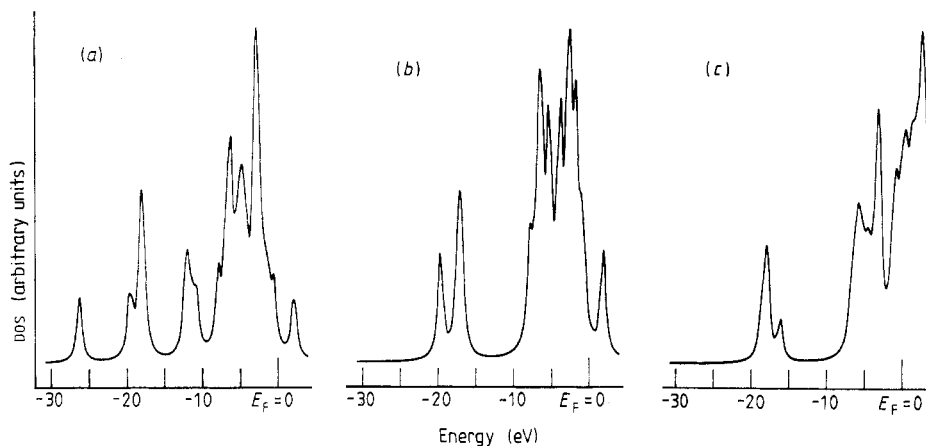


Figure 2. The TDOS for several clusters: (a) $Cu(2)O(2)_2O(3)_2O(1)$; (b) $Cu(1)O(4)_2O(1)$; and (c) $Cu(2)O(2)_2O(3)_2O(1)Y_4$.

from the calculation are both composed of Cu 3d and O 2p orbitals. The peak at about -0.08 eV arises mainly from the Cu 3d and O 2p hybridised orbital (33% Cu 3d, 28% O(2) 2p, 29% O(3) 2p). The peak at -2.3 eV also arises mainly from the Cu 3d and O 2p hybridised orbital (34% Cu 3d, 37% O(2) 2p, 29% O(3) 2p). Therefore, it is possible to associate the peaks at -0.08 eV and -2.3 eV with the DOS of Cu 3d and O 2p hybridised orbitals. This is different from the conclusions given by Steiner and co-workers, who associated the peak at -2.3 eV with the O 2p DOS [5], and Johnson and co-workers, who associated the peak at -2.3 eV with the Cu 3d DOS [7]. The peak at about 18.3 eV can also be associated with the O 2s DOS, because this is mainly composed of O 2s orbitals. Thus we have identified peaks in the experimental valence band electronic structure.

The Y ions at the surface dramatically change the total density of states (TDOS) near and above the Fermi level, and make the DOS at the Fermi level very high. The main part of the Y 4d DOS is located about 3 eV above the Fermi level, which is in agreement with the conclusion of the LAPW band calculation [5]. In the other cases, such as that of the O ion or the O atom absorbed at the topmost position in the $Cu(1)O(4)_2O(1)$ or $Cu(2)O(2)_2O(3)_2O(1)$ cluster, the DOS is very different from the photoemission experimental result. Thus it is quite possible that the Cu(2)–O plane is the surface of the Y–Ba–Cu–O superconductor without Y at the surface. This result is consistent with the fact that the absence of O in the Y plane leads to a very weak binding between the two adjacent Cu(2)–O planes. The most interesting feature is the topmost filled energy level.

Table 1. Binding energies (eV) measured from E_F compared with experimental values [6].

Orbitals	Energy	
	Calculated	Experimental
$Cu_{3d}-O_{2p}$	0.08	2.3
$Cu_{3d}-O_{2p}$	2.27	4.5
O_{2s}	18.31	20.1

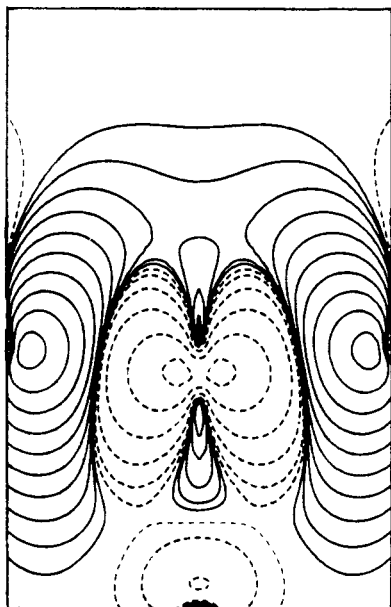


Figure 3. A contour plot of the wavefunction of a $\text{Cu}_{3d}\text{-O}_{2p}$ hybridised orbital.

After taking into account the influence of the Y atoms at the surface on the cluster, the topmost filled energy level becomes O(1) 2p (97%) and there are many orbitals near the Fermi level. However, in the case of the cluster without Y ions there are less orbitals near the Fermi level and the topmost filled orbital is an anti-bonding hybridised Cu 3d and O 2p orbital. In the $\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)$ cluster, the topmost filled orbital is plotted in figure 3. The compositions of all the topmost filled orbitals in the various clusters are listed in table 2. The valence band edge is located immediately below the Fermi level and the DOS at the Fermi level is very low as observed in experiments [12, 15]. The mixed ionic-covalent bonding between the Cu 3d and O 2p levels is seen as a band of states spanning about 9 eV, which is in agreement with the conclusion [5] that

Table 2. The composition of molecular orbitals (topmost filled) in various clusters.

Clusters	Cu	O(1)	O(2)	O(3)	O(4)	O	Y
$\text{Cu}(1)\text{O}(1)_2\text{O}(1)$	3d 0.34 4s 0.09	2p 0.34 2s 0.07			2p 0.06 2s 0.10		
$\text{Cu}(1)\text{O}(1)_2\text{O}(1)\text{O}_{\text{ion}}$	3d 0.38 4s 0.07	2p 0.19			2p 0.28 2s 0.07		
$\text{Cu}(1)\text{O}(1)_2\text{O}(1)\text{O}_{\text{at}}$	3d 0.01 4s 0.01	2p 0.05			2p 0.36	2p 0.58	
$\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)$	3d 0.33		2p 0.27 2s 0.04	2p 0.29 2s 0.05			
$\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)\text{O}_{\text{ion}}$	3d 0.29 4s 0.06	2p 0.02 2s 0.02	2p 0.05	2p 0.04		2p 0.40 2s 0.10	
$\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)\text{O}_{\text{at}}$	3d 0.24		2p 0.34 2s 0.05	2p 0.31 2s 0.05			
$\text{Cu}(2)\text{O}(2)_2\text{O}(3)_2\text{O}(1)\text{Y}_4$		2p 0.97					5s 0.03

the strong $3d-2p$ (i.e. $pd\sigma$) bonding in the $Cu(2)-O$ planes leads to a width of more than 8 eV in the DOS. This means that the intensity of the interaction between Cu 3d and O 2p in the $Cu(2)-O$ planes in the bulk is nearly the same at the surface; but the localised $Cu(2)$ state (80% Cu 3d) is located 5 eV below the Fermi level in the surface calculation, which is 2.4 eV below the Fermi level in the bulk [5].

In conclusion, we have made calculations for several clusters at the possible surfaces of the $YBa_2Cu_3O_7$ superconductor material. Only the results for the $Cu(2)O(2)_2O(3)_2O(1)$ cluster in the $Cu(2)-O$ plane are in agreement with photoemission experiments, although there is a binding energy shift of about 2 eV. At this stage, it may be concluded that the $Cu(2)-O$ plane is the most likely surface of this superconductor material. Also several peaks in the experimental valence band electronic structure are identified by comparison with the calculated DOS.

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