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## LETTER TO THE EDITOR

# A comparative study of the electronic structures of the high- $T_c$ superconductors $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

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**Abstract.** Results of the electronic structure calculations for the compound  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  are discussed and compared to those obtained for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . An analysis of the contribution of the densities of states at different atomic sites shows that the states at the Fermi energy,  $E_F$ , have a strong two-dimensional character due to the presence of the  $\text{CuO}_2$  planes. Moreover, for the bismuth compound, the contribution of the Bi–O planes at  $E_F$  is substantial. The elements Y and Ba in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and Ca and Sr in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  act essentially as electron donors, and their corresponding densities of states at  $E_F$  are negligible. An analysis of the electronic charges at different atomic sites shows that the  $\text{CuO}_3$  chain units in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and the  $\text{BiO}_2$  plane units in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  play the role of electron reservoirs for the creation of holes in the  $\text{CuO}_2$  planes.

Since the discovery of high-temperature superconductivity in La–Ba–Cu–O compounds with  $T_c \approx 30$  K by Bednorz and Müller [1] a highly intensive effort has been devoted both to understanding the mechanisms responsible for this high- $T_c$  superconductivity [2–6] and to finding new materials with even higher critical temperatures [7–10]. The search for new materials has been quite successful and critical temperatures  $T_c \approx 125$  K have been attained [11]. Soon after the discovery by Bednorz and Müller the compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$  with  $T_c \approx 90$  K was isolated [7]. More recently the compounds of Bi and Tl with  $T_c \approx 85$  K and 125 K have been prepared [8–10]. All these compounds have one thing in common, namely the presence of  $\text{CuO}_2$  planes. Very recently, however, a new compound  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  [12, 13] which does not contain Cu has been prepared and found to be superconducting with  $T_c \approx 30$  K.

A knowledge of the electronic structure of these materials is vital for understanding the mechanisms on one hand and for finding new and better materials on the other since the superconducting transition temperature and other properties are governed principally by the electrons at the Fermi surface. In this paper we will be concerned only with the electronic structures of the cuprate superconductors, and in particular with  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  with the aim of understanding the similarities and differences in their electronic structures. These two compounds have relatively the same  $T_c$  (90 K and 85 K respectively). It has generally been assumed that the presence of  $\text{Cu}^{3+}$  ions is necessary for high- $T_c$  superconductivity, and that compounds with only  $\text{Cu}^{2+}$  ions are non-metallic and not superconducting. In the purely ionic model one finds that in

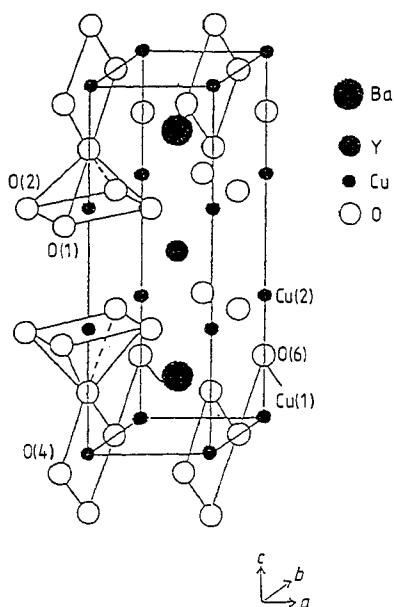


Figure 1. The crystal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

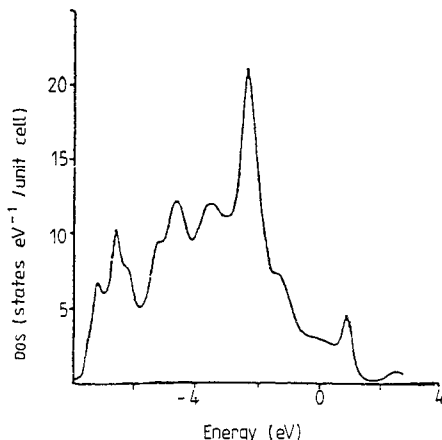
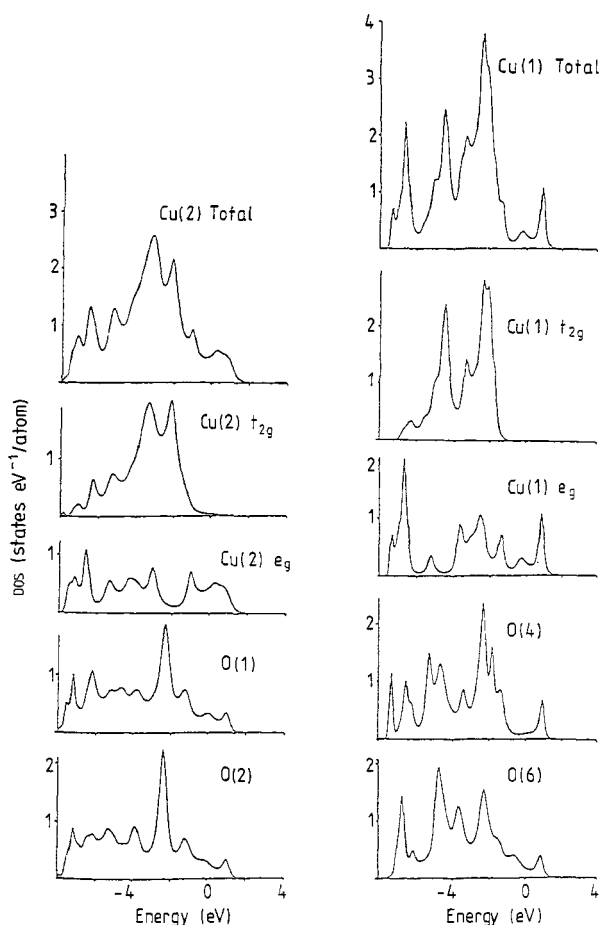


Figure 2. Total densities of states (states  $\text{eV}^{-1}$  per unit cell) of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

$\text{YBa}_2\text{Cu}_3\text{O}_7$  there are two  $\text{Cu}^{2+}$  ions and one  $\text{Cu}^{3+}$  ion, giving an average valence of +2.33 for Cu. If we pursue this reasoning for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and assume a valence of +3 for Bi we obtain a valence of +2 for Cu. Thus this compound, in the traditional picture, should have been insulating and not superconducting. Thus it is interesting to know why this compound is metallic and superconducting with  $T_c \approx 85$  K. We will also discuss the questions concerning the valence of Cu and the holes at oxygen sites.

The cuprate superconductors are characterised by the presence of  $(\text{CuO}_2)^{2-}$  planes. The dominant interactions in the plane are between the Cu  $d_{x^2-y^2}$  orbital and O  $p_x, p_y$  orbitals [14]. These interactions give rise to the bonding and the antibonding orbitals with a total bandwidth  $\approx 8$  eV. The antibonding band is half filled and the Fermi energy is located exactly in the middle of the band. The Fermi surface is a square with perfect nesting features. This leads to an electronically driven charge-density wave (CDW) or spin-density wave (SDW) instability, and the compound is in this case non-metallic. It can be antiferromagnetic if the instability is SDW driven. There is some debate however on whether the occurrence of the antiferromagnetic insulating state associated with  $\text{CuO}_2$  planes can be explained in terms of the one-electron model. Apart from the planar interactions just discussed other atomic interactions play a much less important role, especially at the Fermi level. They give rise to background states in the middle of the band away from the Fermi level. The compounds are metallic and superconducting when they are doped, either chemically or by changing the stoichiometry in oxygen.

Let us first discuss the results for the compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The crystal structure [15] of this compound is shown in figure 1. There are two types of copper atom in the unit cell, one Cu(1) and two Cu(2) atoms. There are no oxygens in the yttrium plane and along the  $a$  axis in the Cu(1) plane. The Cu(2) atoms are pyramidally coordinated by oxygens while the Cu(1) atoms have a square planar configuration. The oxygen atom denoted by O(6) forms the bridge between a Cu(1) atom and a Cu(2) atom. However, the Cu(2)–O(6) distance is about 20% longer than the average Cu–O distance in the unit cell. This makes the Cu(2)–O(6) interactions relatively weak. Because of this Cu(2)



**Figure 3.** Site-decomposed local densities of states (states eV<sup>-1</sup> per atom) at different atomic sites in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. Linear chain Cu(1) and its nearest-neighbour oxygen atoms (left-hand panel) and planar Cu(2) atom and its neighbouring oxygen atoms (right-hand panel).

atoms are considered to have a planar configuration and the Cu(1) atoms a linear chain configuration. Note, however that Cu(1)–O(6) distance is very slightly shorter than the in-plane Cu(1)–O(4) distance, and thus locally the Cu(1) atoms have a nearly perfect square planar configuration.

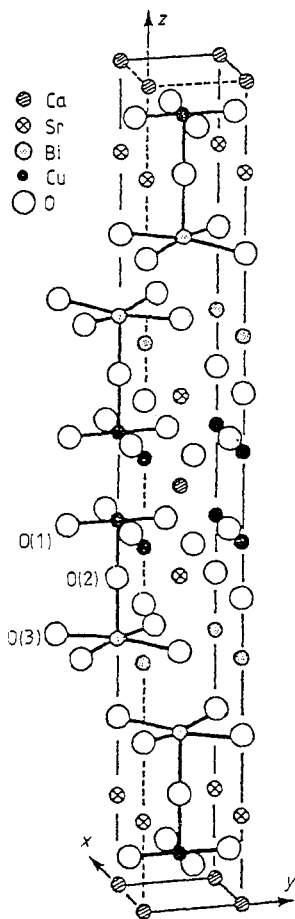
The total densities of states (DOS) for this compound are shown in figure 2. These calculations were performed using the tight-binding recursion method with clusters containing about 2000 atoms. Only p functions at oxygen sites and d functions at other sites were included. As we discussed above, the Fermi energy  $E_F$  (note that all energies are relative to the Fermi energy) falls in the antibonding Cu–O states in a region where the DOS is low. We obtain a density of states  $N(E_F) = 2.91$  states eV<sup>-1</sup> per unit cell at the Fermi level, a value which is in good agreement with other calculations [16, 17]. This density of states is rather low for a high- $T_c$  superconductor. If this DOS is entirely associated with the three Cu atoms on an equal basis, one obtains a DOS of 0.97 states eV<sup>-1</sup> per Cu atom, a value which is more than three times the value of 0.29 states eV<sup>-1</sup> per Cu atom in pure FCC Cu metal. As we will see below such a partition is however incorrect since a non-negligible portion of the DOS at  $E_F$  is contributed by the oxygen atoms.

In order to gain more insight into the nature of interactions and chemical bonding we have shown in figure 3 the densities of states decomposed at different local atomic sites.

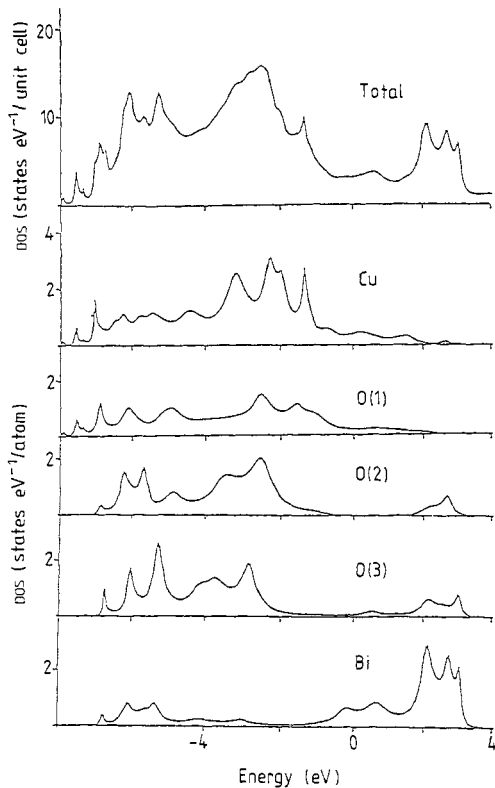
The left-hand panel of figure 3 corresponds to atoms in the  $\text{CuO}_2$  planes while the right-hand panel corresponds to those of chains. We notice that the partial DOS at the chain site atoms is significantly smaller than at the planar sites. The oxygen states are not fully filled and there are holes both at the Cu and O sites. This is shown more clearly in table 1 where we have listed both the DOS and the number of electrons at different atomic sites. We obtain a value of  $1.11 \text{ states eV}^{-1}$  at each  $\text{CuO}_2$  plane. Note from table 1 that the chain and the planar Cu atoms have essentially the same charge and it is significantly different from the one that one expects on the basis of an ionic model. Thus strictly speaking it is difficult to distinguish between  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  ions, and thus the ionic model is not valid. It is clearly much more appropriate to think rather in terms of a mixed ionic-covalent character where the charge is shared between Cu and O atoms. With this in mind, a simple electron count at various atomic sites indicates that the  $\text{Cu}^{2+}$  valence is not localised at the Cu(2) site in the plane but is in fact shared between the Cu(2) and O(1) and O(2) planar oxygen atoms. Similarly, the  $\text{Cu}^{3+}$  valence is not located at the linear chain Cu(1) site but is shared between the Cu(1) site and the linear chain O(4) and bridging O(6) oxygen atoms. An electron count in table 1 shows that the antibonding band associated with the  $\text{CuO}_2$  planar units is less than half filled and the one associated with  $\text{CuO}_3$  linear chain units is almost, but not completely, empty. Indeed, we find that roughly 0.6 electrons are transferred from the two  $\text{CuO}_2$  planes towards the linear chain  $\text{CuO}_3$  unit. Thus the latter can be considered to play the role of an electron reservoir or more correctly an electron sink for the creation of holes in the planar  $\text{CuO}_2$  units. If we take this view then the role of the linear chain  $\text{CuO}_3$  units is quite analogous to that played by chemical doping of  $\text{CuO}_2$  planes in the  $\text{La}_2\text{CuO}_4$  family of compounds. While this may be so, it should nevertheless be kept in mind that in contrast to the case of chemical doping in  $\text{La}_2\text{CuO}_4$  the  $\text{CuO}_3$  linear chain units in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are not inert electron acceptors. Their electronic structure is closely intertwined with those of the  $\text{CuO}_2$  planes, and because of this they may play a more subtle and more important role in bringing about high-temperature superconductivity in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  family of compounds.

We also note from table 1 that the DOS at the Fermi level at the Y and Ba sites is practically zero, and the number of electrons at these sites is quite insignificant. These atoms thus act as electron donors in the lattice. The fact that the DOS at or near  $E_F$  at the Y site is negligible is in agreement with experiment [18] and has important consequences. It shows that if Y is replaced by a magnetic trivalent rare-earth ion there is no possibility of coupling between the rare-earth 4f electrons at different atomic sites via an indirect exchange interaction of the Ruderman-Kittel-Kasuya-Yoshida (RKKY) type through the participation of conduction electrons at or in the vicinity of the Fermi level. The magnetic 4f electrons are thus ineffective in destroying superconductivity which is controlled by electrons at the Fermi level. The coupling between 4f electrons at different atomic sites and magnetic ordering is still possible however through virtual excitations between occupied states below the Fermi level and unoccupied states above [19, 21]. This coupling is nevertheless expected to be quite weak. Thus our results explain qualitatively both the occurrence of magnetic ordering in the rare-earth-substituted  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compounds at the rare-earth sites and the non-destruction of superconductivity.

Let us now turn to the case of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ . The crystal structure of this compound, as determined in [21], is shown in figure 4. In this compound, which crystallises in a body centred tetragonal structure, there are two  $\text{CuO}_2$  planes which are separated by a Ca plane that has no oxygen atoms on it. This plane is quite similar to the Y plane in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  where also there are no oxygen atoms. Each Cu atom,



**Figure 4.** The crystal structure of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .



**Figure 5.** Densities of states in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ . The top panel shows the total densities of states (states  $\text{eV}^{-1}$  unit cell). Site-decomposed local densities of states (states  $\text{eV}^{-1}$  per atom) are shown in lower panels.

which is coordinated by four O(1) oxygens in a square planar configuration, is connected through a bridging O(2) oxygen on the SrO plane to a Bi atom which in turn is coordinated by four O(3) oxygens in an NaCl-type arrangement. It is important to note that the out-of-plane Bi–O(2) distance is much shorter than the in-plane Bi–O(3) distance. In reality a Bi atom is octahedrally coordinated by six oxygen atoms. However, the sixth oxygen atom of the O(3) type which lies along the  $c$  axis and is situated in the plane of a neighbouring Bi atom, is about 20% further away than an in-plane oxygen atom and thus its interaction is rather weak. As a result it is much more proper to assign a compressed square pyramidal coordination to a Bi atom.

The total DOS for this compound are shown in figure 5. Also shown in this figure are the partial DOS decomposed at different local atomic sites. As for the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound these calculations were performed using the tight-binding recursion method with clusters of approximately 4000 atoms. The hopping integrals were taken from the calculations of [22–24]. Only d orbitals at Cu sites and p orbitals at other sites were included in these calculations. As in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound the Fermi energy  $E_F$  (notice that all energies are relative to  $E_F$ ) falls in the antibonding Cu–O states in a

**Table 1.** Site-decomposed local densities of states  $n(E_F)$  at the Fermi level  $E_F$  (states  $eV^{-1}/\text{atom}$ ) and the number of electrons  $n$  (p electrons at oxygen sites and d at other sites) at different atomic sites in  $YBa_2Cu_3O_7$ . Also shown are the number of electrons in a purely ionic model.

Atomic site	$n(E_F)$	$n$ (calculated)	$n$ (ionic model)
Cu(1)	0.23	9.45	8
Cu(2)	0.48	9.36	9
Y	0.01	0.42	0
Ba	0.00	0.19	0
O(1)	0.33	5.51	6
O(2)	0.30	5.55	6
O(4)	0.09	5.61	6
O(6)	0.18	5.65	6

region where again the DOS is rather low. We obtain for DOS at  $E_F$  a value of  $N(E_F) = 3.11$  states  $eV^{-1}/\text{unit cell}$ , a value which is not significantly different from what we obtained for the  $YBa_2Cu_3O_7$  compound. However, in contrast to the case of the trivalent element Y in the  $YBa_2Cu_3O_7$  compound which acts essentially as an electron donor and has a negligible DOS at the Fermi level, the trivalent element Bi in the  $Bi_2Sr_2CaCu_2O_8$  compound interacts strongly with its neighbouring oxygens and has a substantial DOS at the Fermi level. As is clear from figure 5 this interaction is largely covalent and the oxygens have substantial unoccupied states in the conduction band. As in the case of the  $YBa_2Cu_3O_7$  compound the divalent atoms Ca and Sr act essentially as electron donors and have negligible DOS at the Fermi level.

In table 2 we have listed the local DOS and the number of electrons at different atomic sites. We notice that the DOS at  $E_F$  and the number of electrons accommodated at the Cu site are slightly lower but not much changed from their corresponding values at the Cu(2) planar site in  $YBa_2Cu_3O_7$ . However, the DOS at the oxygen planar site is somewhat smaller. As a result we obtain for the DOS at  $E_F$  per  $CuO_2$  plane in  $Bi_2Sr_2CaCu_2O_8$  a lower value of  $N(E_F) = 0.83$  states  $eV^{-1}$  compared to 1.11 states  $eV^{-1}$  in  $YBa_2Cu_3O_7$  in spite of the fact that the total DOS in the two compounds are almost the same. This shortfall is compensated by the presence of a relatively significant DOS at the Bi sites. We obtain a value of 0.63 states  $eV^{-1}$  per Bi atom and 0.71 states  $eV^{-1}$  per Bi-O plane. We should point out that our results on the electronic structure and our values of the DOS are in excellent agreement with those calculated using *ab initio* methods [24–26]. The local DOS at the Bi site calculated using the linear augmented plane wave (LAPW) method [25, 26] is however significantly lower than our value. This discrepancy is easy to understand. The DOS in the LAPW method at a given site contains the contribution from the muffin-tin sphere at that site only since the contribution from the interstitial region cannot be associated with different muffin-tin spheres. The p functions at the Bi sites are relatively extended and are thus expected to contribute substantially to the DOS in the interstitial region. As a result the local DOS at the Bi site in an LAPW calculation can be expected to be significantly lower than its true value. We also note from table 2 that the local DOS at  $E_F$  at the bridging oxygen site is very much smaller than the DOS in the  $CuO_2$  and BiO planes. This would suggest a strong anisotropy in the normal-state electrical conductivity. Experimental data [27] show the resistivity along the  $c$  direction to be about  $10^5$  times the resistivity in the  $ab$  plane.

The strong interaction between Bi and its neighbouring oxygen atoms is quite evident from table 2. Chemically, Bi is expected to behave as  $Bi^{5+}$  or  $Bi^{3+}$ . The 6s band of Bi, however, lies about 11 eV below the Fermi level because of the relatively

**Table 2.** Site-decomposed local densities of states  $n(E_F)$  at the Fermi level  $E_F$  (states  $eV^{-1}/\text{atom}$ ) and the number of electrons  $n$  (p at oxygen and Bi sites and d at other sites) in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ . Also given are the number of electrons in a purely ionic model.

Atomic site	$n(E_F)$	$n$ (calculated)	$n$ (ionic model)
Cu	0.414	9.293	9
O(1)	0.206	5.468	6
O(2)	0.014	5.376	6
O(3)	0.082	5.012	6
Bi	0.628	1.953	0
Sr	0.004	0.300	0
Ca	0.003	0.260	0

larger in-plane Bi–O distances. Thus, Bi would be expected to be in its  $\text{Bi}^{3+}$  state in this compound. We see from table 2 that this is not at all the case since we find roughly two electrons at the Bi site. Thus in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  compound Bi behaves essentially as a monovalent rather than a trivalent element in contrast to what had been expected on chemical grounds. We also notice from table 2 that the O(3) oxygen atoms lying in the Bi planes are much less ionic and have a charge of only five electrons (not counting the 2s electrons). The Bi–O planar units thus have an electronic charge of seven and hence are electrically neutral considering the fact that Bi and O atoms had initially three and four electrons respectively. A similar situation exists in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound where the Cu(1)–O(4) chains (see table 1) have an electronic charge of fifteen and are thus electrically neutral. Although electrically neutral these units are conducting since they have significant densities of states at the Fermi level.

An electron count in table 2 shows that the antibonding band associated with  $\text{CuO}_2$  planar units is less than half filled in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  compound as was also the case in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor. We find that roughly 0.55 electrons from a  $\text{CuO}_2$  two-dimensional plane are transferred towards the neighbouring  $\text{BiO}_2$  unit (O(3)–Bi–O(2) unit). The  $\text{BiO}_2$  units thus act as electron reservoirs for the two-dimensional  $\text{CuO}_2$  planes, and their role is analogous to the  $\text{CuO}_3$  chain units in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor. As we discussed above, both CuO chains in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and BiO planes in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  are, however, nearly electrically neutral. The true electron reservoirs are thus the bridging oxygen atoms in both compounds.

In conclusion, our calculations show that the Cu–O chains in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and the Bi–O planes in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  superconductors play the similar role of electron reservoirs for the creation of holes in the  $\text{CuO}_2$  planes, and thus the mechanism of superconductivity in the two compounds is the same. Further, we find that the calculations of Cu valence based on strictly ionic models could lead to misleading conclusions. In this picture in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound Cu has an average valence of +2.33 while in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  superconductor it has a valence of +2. Thus, the bismuth compound should not have been a superconductor. Our calculations have shown that Bi in this compound is not a simple inert donor of electrons but plays an active and important role in determining the electronic structure of the compound.

Finally, a few comments are in order concerning the nature of these superconductors. As we stated earlier, the ground state of these materials (when the antibonding  $\text{CuO}_2$  band is half filled) is insulating and antiferromagnetic. Electronic structure calculations, on the other hand, yield the ground state to be metallic. Consequently, it has been thought that strong intra-atomic d–d correlations at the Cu site in the  $\text{CuO}_2$  planes play an important role in the description of these materials and a Mott–Hubbard picture is probably more appropriate. While this may be so in the exactly half-filled band situation when the compounds are not superconducting



the correlation effects are expected to be considerably less important when they are metallic and superconducting, an expectation which is borne out by positron annihilation experiments [28]. We thus expect the local density band structure approach to provide a realistic description of the electronic structure and bonding in these materials. In addition, Zaanen and co-workers [29] have shown that the hole count is not affected when correlation effects are included. For a detailed discussion of the one-electron versus Mott–Hubbard approach we refer the reader to an excellent article by Rice [4].

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