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Electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$: the role of O(4) and high pressure

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Abstract. The electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ with various δ (0, 0.12, 0.2 and 0.4) and pressures (ambient pressure, 5 GPa, 10 GPa and 20 GPa) has been calculated by the recursion method. Our results show that the electronic structure of this series is highly two dimensional with a large $N(E_F)$. The hole concentration of the CuO_2 layers and $N(E_F)$ increase monotonically as δ increases from 0 to 0.4. We thus suggest that the ideal δ should be 0.4. With increasing pressure, the hole concentration increases further and E_F rises. The relationship between T_c and pressure can be described by the same model of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

1. Introduction

The newly discovered $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n = 1, 2, 3$) superconductors [1–3] have stimulated great interest in the field. Similar to other high- T_c cuprates, they are layer structured with one to three CuO_2 layers per unit cell [4]. The superconducting transition temperatures T_c are all above 90 K, while $\text{Hg}1:2:2:3$ ($n = 3$) sets a new record of $T_c = 134$ K under ambient pressure [2, 3]. More recently, a high-pressure study has revealed that this compound series all possess a positive pressure derivative dT_c/dP [5–8], but T_c continues to increase up to pressures above 20 GPa [8] and $\text{Hg}1:2:2:3$ reaches its maximum T_c (164 K) when the pressure is 31 GPa [8], which has not been seen in the previous superconductors. The mechanism is still unclear.

It is well known that the electronic structure is very helpful for us to understand the properties of the material. Thus, since the discovery of Hg-related superconductors, some papers have been published on the electronic structure ($\delta = 0$) of $\text{Hg}1:2:0:1$ ($n = 1$) [9–12], $\text{Hg}1:2:1:2$ ($n = 2$) [11, 12] and $\text{Hg}1:2:2:3$ [11–13] using the full-potential linear muffin-tin orbital (FLMTO) method within the local-density approximation (LDA) and have obtained many valuable results. In this paper, we use the recursion method to study the effect of δ and pressure on the electronic structure of $\text{Hg}1:2:2:3$ and then we discuss the possible reasons for its high T_c and the increase in T_c under pressure.

2. Method and model

The electronic density of states is calculated by the recursion method [14], which has been proven to be a successful way of studying high- T_c oxides [15–17]. The Hamiltonian matrix

is chosen in the LCAO representation. Only the nearest-neighbour interactions are taken into consideration, which were given by Harrison [18]:

$$V_{ll'm} = \eta_{ll'm} \frac{\hbar^2}{m_e d^2} \quad (l, l' \equiv s \text{ or } p) \quad (1)$$

$$V_{ldm} = \eta_{ldm} \frac{\hbar^2 r_d^{3/2}}{m_e d^{7/2}} \quad (l \equiv s \text{ or } p) \quad (2)$$

where s, p and d are the atomic orbitals, m_e is the mass of the electron, d is the distance between two neighbouring sites, r_d is the radius of the d orbital, and $\eta_{ll'm}$ and η_{ldm} are the Harrison parameters.

An atom cluster including $7 \times 7 \times 3$ crystal cells (2819 atoms) is used. When $\delta \neq 0$, O4 sites are partially occupied in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$. The central $\text{Hg}1:2:2:3$ cell is shown in figure 1. We study the cases when $\delta = 0, 0.12, 0.2$ and 0.4 .

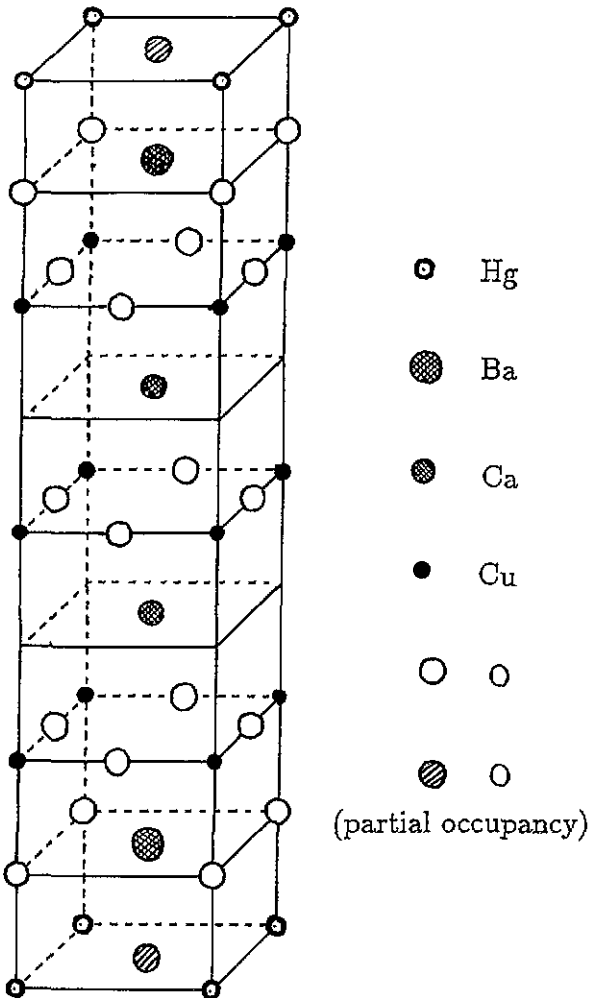


Figure 1. Central cell of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ atom cluster model. (From [21].)

The definition of atomic valence is

$$V_a = n_{ae} - \int_{-\infty}^{E_F} n_a(E) dE \quad (3)$$

where n_{ae} is the number of valence electrons, $n_a(E)$ is the local density of states (DOS) of the site and E_F is the Fermi energy.

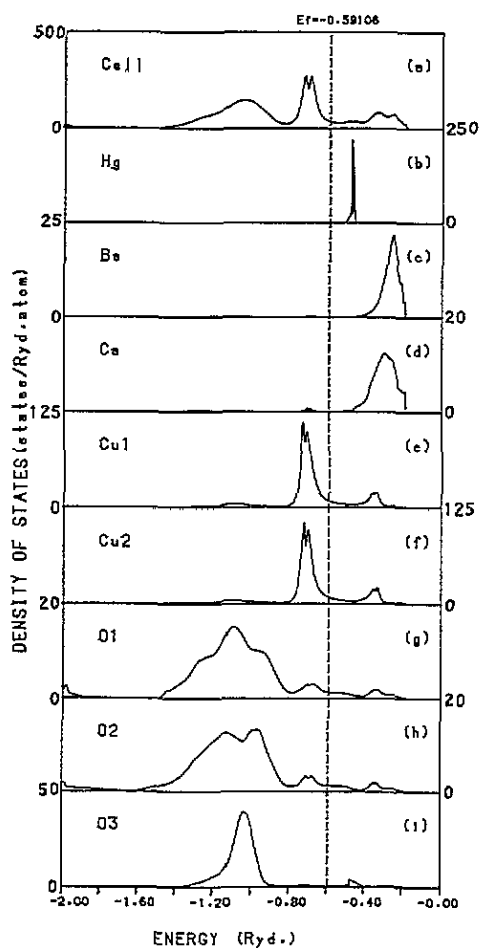


Figure 2. Electronic DOS of some sites in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($\delta = 0$).

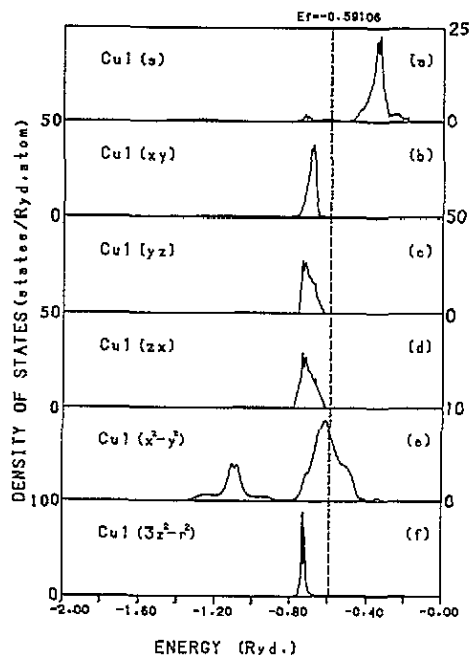


Figure 3. Partial wave DOS of Cu(1) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($\delta = 0$).

3. Results and discussion

3.1. Electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($\delta = 0$)

Figures 2–5 show the DOS of the electronic partial waves on different sites of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($\delta = 0$). $\text{Cu}_{(1)}$ and $\text{O}_{(1)}$ label the copper and oxygen sites in the central

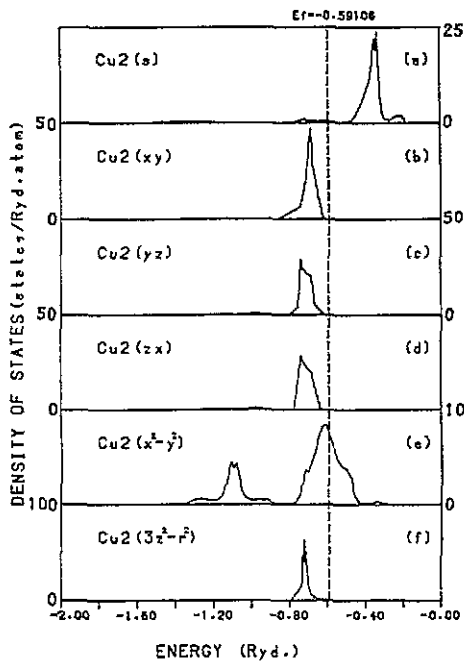


Figure 4. Partial wave DOSs of Cu(2) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($\delta = 0$).

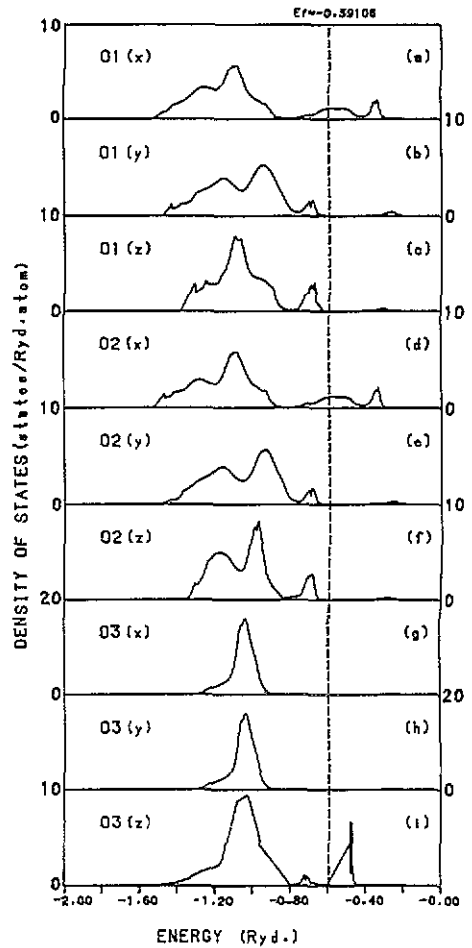


Figure 5. Partial wave DOSs of O(1), O(2) and O(3) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($\delta = 0$).

CuO_2 layer of the cell; $\text{Cu}_{(2)}$ and $\text{O}_{(2)}$ represent the copper and oxygen sites in the other two CuO_2 layers. $\text{O}_{(3)}$ is in the BaO layers, connecting $\text{Cu}_{(2)}$ with Hg in the z direction.

Similar to other high- T_c cuprates, the Fermi energy in a region of low DOS of the cell (figure 2(a)). This is consistent with the FLMTO calculations [11–13]. Now the total DOS ($N(E_F)$) per cell at E_F is 36 states $\text{Ryd}^{-1}/\text{cell}$, which agrees well with the value given by Novikov and Freeman [11], nearly 40 states $\text{Ryd}^{-1}/\text{cell}$. This $N(E_F)$ is much larger than 16 states $\text{Ryd}^{-1}/\text{cell}$ for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ [17, 19] and is close to the value for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [19, 20]. From our results, it can be seen clearly that $N(E_F)$ is mainly from the Cu $3d_{(x^2-y^2)}$ orbitals and O $2p$ orbitals in the CuO_2 layers (figures 3(e), 4(e), 5(a) and 5(d)), which is in agreement with the FLMTO calculations [11–13].

As shown in figures 3 and 4, the partial waves of Cu are relatively localized except for the $3d_{(x^2-y^2)}$ orbital which bonds with the O $p_{(x,y)}$ partial waves in the CuO_2 layers and its bandwidth is much wider than other $3d$ orbitals. It has DOS peaks at -1.1 Ryd and E_F which overlap with those of O $p_{(x,y)}$ at the same energy in the CuO_2 layers (figures 5(a), 5(b), 5(d) and 5(e)). They form a strong $pd\sigma$ antibond and all span the Fermi surface. On the

other hand, the Cu(1) $3d_{(3z^2-r^2)}$ partial wave, which takes part in bonding in the z direction, is hardly widened (figure 3(f)). This is because Cu(1) has no nearest oxygen neighbours in the z direction. Similarly although Cu(2) interacts with O(3) in the z direction, they are far apart so that their bonding is weak and the Cu(2) $3d_{(3z^2-r^2)}$ partial wave is very localized too, although its bandwidth is somewhat wider than that of Cu(1) (figure 4(f)). These indicate that Cu(1) and Cu(2) form strong bonds in the CuO_2 layers and weak bonds between layers. Thus it reflects the 2D character of the electronic structure. It is known that the electronic structure of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ is also two dimensional, but the bandwidth of its Cu $3d_{(3z^2-r^2)}$ partial wave is much wider than those of Cu in $\text{Hg}1:2:2:3$ [17]. Hence the two-dimensionality of the $\text{Hg}1:2:2:3$ electronic structure is higher. Next we look at O(1) and O(2). Not only do they bond with Cu in the CuO_2 layer, but also they interact with Ca and Ba. Now the bandwidth of their $p_{(x,y)}$ partial waves is also wider than that of $p_{(z)}$ partial waves. Therefore they bond mainly in the CuO_2 layers, too (figures 5(a)–(f)). Because of the great difference between the bond strengths in the two directions, the carriers tend to move mainly in the CuO_2 layers.

On the contrary, the bandwidths of the three p partial waves of O(3), which connects Hg with Cu(2), vary little and that of $p_{(z)}$ orbital is somewhat wider (figures 5(g), 5(h) and 5(i)). O(3) is more weakly bonded to Cu(2) than to Hg for it is closer to Hg. Owing to the Hg–O(3) interaction, the O(3)(z) partial wave gives some contribution to $N(E_F)$ (figure 5(i)). Simultaneously, the DOS curves of Ba and Ca are almost above the Fermi energy (figures 2(c) and 2(d)) and thus indicate their role of stabilizing the crystal structure and serving as an electron reservoir.

To sum up, the electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ is highly two dimensional with a large $N(E_F)$. We think that these are related to the high T_c of this series. Next we study the role of O(4) ($\delta \neq 0$).

3.2. Electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ ($\delta \neq 0$): the role of O(4)

It is shown by experiments that the T_c of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ rises to 134 K, after oxygenation and the extra oxygen (O(4)) lies in the centre of the Hg layers (figure 1) [21–24]. An early value for δ is 0.06 [22]; later $\delta = 0.2$ [23] to $\delta = 0.4$ [24] were found. In this section, we calculate the electronic structure of $\text{Hg}1:2:2:3$ with $\delta = 0.12, 0.2$ and 0.4.

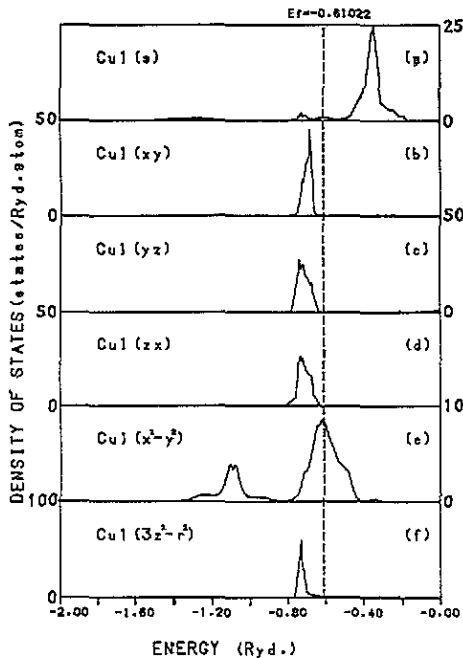
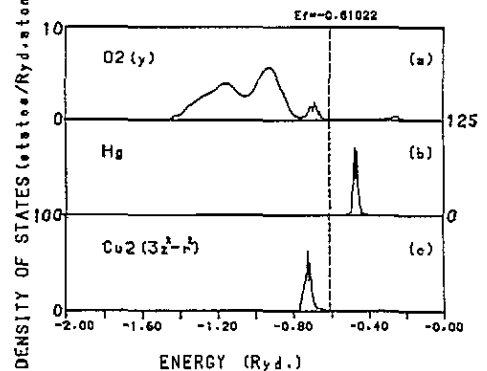
Table 1. E_F and $N(E_F)$ of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$.

δ	E_F (Ryd)	$N(E_F)$ (States Ryd ⁻¹ /cell)
0	-0.591 06	35.8
0.12	-0.598 10	36.8
0.2	-0.602 41	38.5
0.4	-0.610 22	42.3

First we look at the changes in E_F and $N(E_F)$, as shown in table 1. As δ increases, E_F is lowered while $N(E_F)$ increases monotonically. When $\delta = 0.4$, $N(E_F)$ increases by about 6.5 states Ryd⁻¹/cell. Novikov and Freeman [11] speculate that $N(E_F)$ will increase and move to the DOS peak nearby after doping O(4). The change obtained by them is 5 states Ryd⁻¹/cell which is close to our results. As shown in section 3.1, $N(E_F)$ is mainly from Cu $3d_{(x^2-y^2)}$ orbitals and there is some distance between E_F and the DOS peak of the

Table 2. Valences of each site in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$.

δ	Valence								
	Hg	Ba	Ca	Cu(1)	Cu(2)	O(1)	O(2)	O(3)	O(4)
0	1.762	1.893	1.823	1.336	1.356	-1.619	-1.633	-1.829	—
0.12	1.763	1.888	1.823	1.396	1.419	-1.611	-1.625	-1.838	-1.911
0.2	1.763	1.888	1.823	1.435	1.460	-1.606	-1.620	-1.837	-1.911
0.4	1.782	1.889	1.824	1.511	1.525	-1.596	-1.610	-1.811	-1.877

**Figure 6.** Partial wave DOS of Cu(1) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.4}$ ($\delta = 0.4$).**Figure 7.** Some partial wave DOS of Cu(2), Hg and O(2) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.4}$ ($\delta = 0.4$).

Cu $3d_{(x^2-y^2)}$ orbital nearby (figures 3(e) and 4(e)). Now oxygenation lowers E_F and affects the DOS peak of the Cu $3d_{(x^2-y^2)}$ orbital when $\delta = 0.4$ (figure 6(e)). Therefore, $N(E_F)$ increases markedly, which also agrees with the speculation on experiments [21].

At the same time, the bond strength between atoms is changed somewhat by O(4). Comparing figure 7(a) with figure 5(e), we can see that the peak of the O(2) p_y partial wave at -0.68 Ryd rises by about 10%. It is known from the previous section that the O(2) p_y partial wave bonds with Cu, so that the Cu–O bond in the CuO_2 layer is strengthened further after doping O(4). Furthermore, the bandwidth of Cu(2) $3d_{(3z^2-r^2)}$ is widened slightly (figure 7(c)). This implies that the Cu(2)–O(3) bond, or interaction between layers, is intensified, too. Similarly, the bandwidth of the Hg s partial wave is widened because of the strengthening of the Hg–O(3) bond (figure 7(b)).

The drop in E_F , together with the strengthening of the correlation between layers, leads to the redistribution of carriers. The change in the valences of each site after oxygenation is shown in table 2. It can be seen that the valences of Cu and O in the CuO_2 layers rise, while those of the other sites change little. According to the definition in equation (3), the

rise in valence means loss of electrons. Thus, doping O(4) moves electrons from CuO_2 layers to the O(4) site in the HgO layer through BaO layers and leads to an increase in hole concentration in the CuO_2 layers, as indicated in table 3.

Table 3. Change in number of holes for Cu 3d (per Cu atom) and O p (per O atom) in the CuO_2 layers in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ for various δ . Δn is the total change in number of holes per cell in the three CuO_2 layers (compared with the case when $\delta = 0$).

δ	$n(\text{Cu}(1))$	$n(\text{Cu}(2))$	$n(\text{O}(1))$	$n(\text{O}(2))$	Δn
0	0.658	0.669	0.337	0.326	—
0.12	0.714	0.727	0.345	0.334	0.220
0.2	0.750	0.765	0.350	0.339	0.362
0.4	0.821	0.826	0.359	0.348	0.609

From table 3, the total increase in the number of holes per cell in the three CuO_2 layers is 0.22 when $\delta = 0.12$, which means that every O(4) induces nearly two holes. In the case when $\delta = 0.2$, O(4) totally induces 0.36 holes. However, as δ increases to 0.4, only 0.61 holes per cell are induced into the three CuO_2 layers. This is due to the rise in the valences of Hg, Ba and Ca. They also provide some electrons. Novikov and Freeman [11] suggest that O(4) should induce 0.60 holes to make E_F coincide with the DOS peak and every O(4) atom supplies two holes. Then they suppose that the ideal δ should be 0.30. If the effects of Hg, Ba and Ca are taken into account, and also that not every O(4) offers exactly two holes, we obtain that the ideal δ is 0.4. This is consistent with the recent experimental results [24].

In summary, O(4) increases $N(E_F)$ a great deal and also the hole concentration in the CuO_2 layers and strengthens the interaction within the CuO_2 layers and the correlation between layers. We believe that these are responsible for the rise in T_c after oxygenation.

3.3. Electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ under high pressures

A high-pressure study of Hg1:2:2:3 has revealed that its T_c has a large positive effect on pressure: $dT_c/dP \simeq 1.8\text{--}2.0$ K GPa⁻¹ [5–8]. In contrast with other high- T_c cuprates, its T_c continues to increase up to higher pressures and reaches the maximum of 164 K at 31 GPa [8] which is a new record up to now. Owing to the lack of the δ -value in the published high-pressure study, we have calculated in this paper the electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ in the case when $\delta = 0.12, 0.2$ and 0.4 for 5, 10 and 20 GPa. As mentioned in section 3.1, there is a great difference between the bond strengths in the two directions; hence κ_c (the compressibility in the z direction) is much larger than κ_a (the compressibility in the plane) [25, 26]. Here we use the value given by Cornelius and Schilling [25].

As a result of small changes in the crystal lattice, the essential features of the DOS curves under a high pressure are the same as those under an ambient pressure; only the bandwidth is widened a little. This indicates that the interaction between atoms is strengthened. Partial wave DOSS of Cu(1) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.4}$ under 10 GPa are shown in figure 8. Compared with figure 6, no large changes can be seen.

We can see from table 4 that E_F rises as the pressure increases and this trend does not change for various δ . This is because the bands of Cu 3d and O 2p below E_F are widened by a high pressure; so some of the DOS is moved to a higher energy. The bands of Hg, Ba and Ca that lie above E_F , on the other hand, have little effect on E_F for they

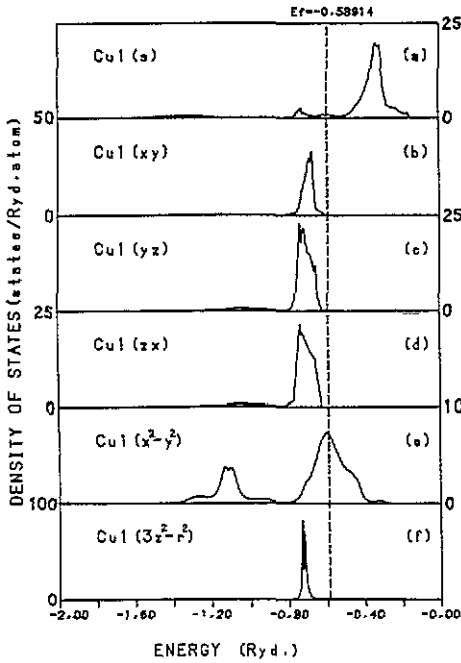


Figure 8. Partial wave DOS of Cu(1) in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.4}$ ($\delta = 0.4$) under 10 GPa.

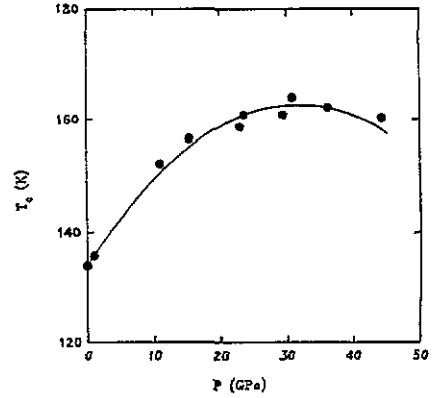


Figure 9. The pressure dependence of T_c from calculation: ●, experimental results [7, 8].

Table 4. The pressure dependence of E_F of $\text{Hg}1:2:2:3$.

P	E_F (Ryd) for the following δ		
	0.12	0.2	0.4
1 atm	-0.598 10	-0.602 41	-0.610 22
5 GPa	-0.588 49	-0.593 10	—
10 GPa	-0.576 97	-0.581 91	-0.589 14
20 GPa	-0.551 99	-0.557 62	-0.565 54

Table 5. Change in number of holes for Cu and O (per atom) in the CuO_2 layers and hole concentration per CuO_2 in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ induced by pressure.

P	$\delta = 0.12$				$\delta = 0.2$			
	$n(\text{Cu}(1))$	$n(\text{O}(1))$	Δn	$\partial n / \partial P$	$n(\text{Cu}(1))$	$n(\text{O}(1))$	Δn	$\partial n / \partial P$
1 atm	0.714	0.345	—	—	0.750	0.350	—	—
5 GPa	0.723	0.359	0.037	0.0074	0.759	0.365	0.039	0.0078
10 GPa	0.727	0.372	0.067	0.0067	0.762	0.377	0.066	0.0066
20 GPa	0.736	0.398	0.128	0.0064	0.769	0.404	0.128	0.0064

are farther away from E_F . Simultaneously, the drop in the peak of the Cu 3d DOS at E_F (figure 8(e)) leads to a decrease in $N(E_F)$. For $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.4}$, $N(E_F)$ drops by about 5 states $\text{Ryd}^{-1}/\text{cell}$ when the pressure reaches 10 GPa.

The decrease in the DOS integral of Cu 3d and O 2p partial waves below E_F , i.e. the decrease in electrons below E_F , causes the electrons to move out of the CuO_2 layers. This

will result in a further increase in the hole concentration in the CuO_2 layers. Table 5 shows the change in the number of holes in the CuO_2 layers for various pressures ($\delta = 0.12$ and 0.2) and Δn represents the change in hole concentration per CuO_2 . It can be seen from table 5 that the average $\partial n/\partial P \simeq 0.0069$ holes/ $\text{CuO}_2 \cdot \text{GPa}$. The value is close to that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (0.0055 holes $\text{CuO}_2 \cdot \text{GPa}$ [27]).

It is generally believed that the rise in $N(E_F)$ is favourable for higher T_c , and so is the case of $\text{Hg}1:2:2:3$ [11]. Chu [28] then guesses that $N(E_F)$ of $\text{Hg}1:2:2:3$ may rise somewhat under a high pressure, but our results show that $N(E_F)$ drops slightly under a high pressure. Therefore, we think that $N(E_F)$ does not play an important role in the pressure-induced T_c variation. Wegar and Pereg [29] suggest that $T_c \propto E_F$ if the energy of the intermediating bosons is greater than or equal to E_F . Now E_F surely rises as the pressure increases and changes by about 0.05 Ryd when the pressure reaches 20 GPa. So we cannot exclude the possibility that E_F induces the rise in T_c . However, T_c then increases by 25 K, nearly 20% [8]. Thus we believe that E_F is not the main reason for the higher T_c under a high pressure.

Neumeier and Zimmermann [27] propose a phenomenological model to account for the pressure dependence of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which gives

$$T_c(n, P) = T_c^{\max}(n_0, 0) + (dT_c^{\max}/dP)P + A[(n - n_0) + (\partial n/\partial P)P]^2 \quad (4)$$

where $n - n_0$ and $\partial n/\partial P$ are the changes in the hole concentration in the CuO_2 layers induced by chemical substitution and pressure, respectively. Here $n - n_0 = 0$ and $\partial n/\partial P$ is nearly 0.0069 holes/ $\text{CuO}_2 \cdot \text{GPa}$ for $\text{Hg}1:2:2:3$. dT_c^{\max}/dP is the pressure derivative of T_c when $P \rightarrow 0$. The value of A is -590 K/holes (per $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ formula unit) [27]. If we think that this A is also available for $\text{Hg}1:2:2:3$, but n is stated per CuO_2 , then we obtain

$$T_c(P) = 134 \text{ K} + (1.8P) \text{ K GPa} - 590(0.0069P)^2 \text{ K GPa}^{-2}. \quad (5)$$

The pressure dependence of T_c calculated from equation (5) is in remarkably good agreement with experimental results (see figure 9).

To summarize, high pressure widens the bandwidth, increases E_F , decreases $N(E_F)$ slightly and causes electrons to move out of the CuO_2 layers, thus resulting in a further increase in the hole concentration in the CuO_2 layers. We think these are the reasons for the increase in T_c under a high pressure. The relationship between T_c and pressure agrees with the model suggested by Neumeier and Zimmermann. Owing to the large number of voids in the HgO layers, there is a large $dT_c/dP|_{P=0}$ [8], together with the small $\partial n/\partial P$ and A available for a CuO_2 layer. Thus, T_c rises as the pressure increases.

4. Conclusion

In this paper, we have calculated the electronic structure of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ for various δ and pressures. The results show that the electronic structure is highly two dimensional and the DOS $N(E_F)$ at E_F is large. The increase in $O(4)$ not only causes $N(E_F)$ to rise and strengthens the bonding between atoms but also gives rise to a large increase in the hole concentration in the CuO_2 layers. The ideal δ should be 0.4. E_F and hole concentration rise further under high pressures, and the pressure dependence of T_c agrees with the phenomenological model suggested by Neumeier and Zimmermann.

Acknowledgments

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