# Current understanding of electronic structure and some difficulties with cuprate semiconductors

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**Experimental observations of the high-$T_c$ cuprate superconductors are reviewed from the perspective of electronic structures. On the basis of Mott–Hubbard-type band splitting, the semiconductivity, antiferromagnetism, and metallic nature of the cuprate oxides are discussed as a function of the dopant concentration. Then the involvement of the O 2*p* band which falls between the lower and upper Hubbard bands, as determined by electron spectroscopy, is discussed. Finally, the complex nature of the Fermi surface is considered, and the importance of the involvement of both the O 2*p* and the lower Hubbard band is stressed.**

## 1. Introduction

Since the discovery [1] and subsequent confirmation [2] in 1986 of the original cuprate superconductor, $(La, Ba)_2CuO_4$, the field has expanded, with the subsequent discoveries of Ba–Y–Cu–O [3], Bi–Sr–Ca–Cu–O [4], and Tl–Ba–Ca–Cu–O [5]. During this time, the critical temperature $T_c$ ($p = 0$) has risen to 125 K [6], indicating that there should be some extraordinary electronic structure common to these oxides which leads to such a high $T_c$. At this stage, it is not understood why the different oxide crystal structures give different $T_c$ values. Therefore, it seems to be more fruitful to survey the common characteristics among these high-$T_c$ cuprate superconductors. This paper therefore focuses on the unique electronic structure created by the square lattice in the $CuO_2$ layer that is commonly shared within this family. I would first like to stress that there is an energy gap in the band which one would expect to be the conduction band instead. Hence, the superconductive compositions are obtained only by introducing a high concentration of holes into the otherwise insulating system. The origin of the gap structure is then attributed to the strong electron correlation relative to the bandwidth of the conduction band, i.e., the Mott–Hubbard gap. Since a magnetically ordered state is expected in a Mott insulator, the experimental observations are reviewed, with emphasis on the importance of the magnetic interaction. Finally, it is discussed whether the Fermi level is located in the lower Hubbard band or in a band that happens to fall between the two split bands. The observations so far support the latter situation, showing the O 2*p* nature of the Fermi surface. However, it is stressed

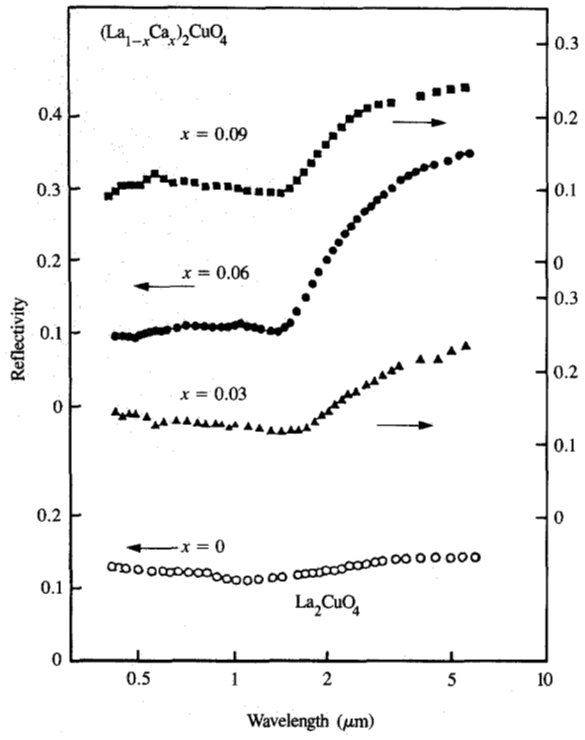


**Figure 1**

Optical reflectivity of $(La_{1-x}Ca_x)_2CuO_4$ polycrystalline specimens with various dopant concentrations.

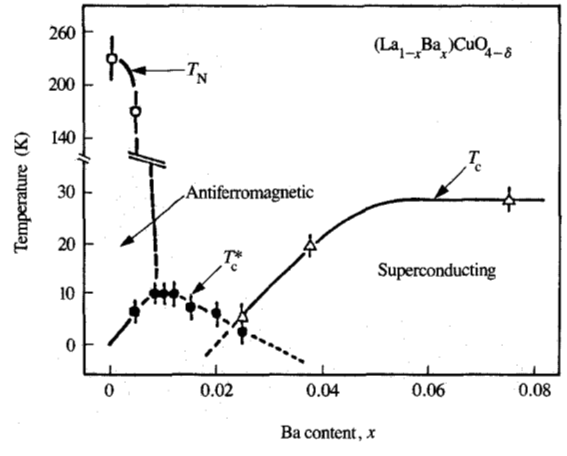


**Figure 2**

Electronic phase diagram of $(La_{1-x}Ba_x)_2CuO_4$ at low temperatures obtained by nuclear quadrupole resonance and resistivity measurements.

that the Fermi surface, although being possibly of band nature, is by no means a simple one, in that it contributes various phenomena which currently defy systematic explanation.

Part of this review has been presented previously in more detail [7].

## 2. Splitting of the conduction band

The conduction path of the superconducting electrons in the $(La, M)_2CuO_4$ series was believed to lie in the $CuO_2$ layer because of the decisive role of the Cu–O bond length in the layer in determining $T_c$ [8, 9] and the much larger effect on $T_c$ reduction obtained by doping foreign ions into $CuO_2$ than into (La, $M$)O layers [10, 11].

As the metallic conduction band, the antibonding $\sigma^*$ band derived from the overlapping of Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals was thought to be operative in the superconducting compositional region [8]; this was supported by band calculations [12]. If this is the case, $La_2CuO_4$ should be a metal, because $Cu^{2+}$ has a $d^9$ configuration; hence, the band should be half-filled. At one time there was an argument about whether stoichiometric $La_2CuO_4$ is semiconductive or metallic [13], but it was concluded that it is a semiconductor with an energy gap. This conclusion was based on observations of the absence of plasma reflectivity [14] (**Figure 1**) and of the corresponding decrease in hole concentration with a decrease in the amount of dopant $M$ [15, 16]. It was later found that $Ba_2YCu_3O_{7-x}$ [17] and $Bi_2Sr_2(Ca_{1-x}Y_x)Cu_2O_y$ [18] exhibit a similar decrease in the hole concentration with an increase in $x$. Hence, the situation seems to be essentially the same among all the cuprate superconductors. Therefore, one had to assume that this band is somehow split into two bands in order for the valence band to be fully occupied when the Cu ions are divalent.

## 3. Origin of the energy gap

Initially there were efforts to seek the origin of the band splitting in the formation of charge-density or spin-density waves, because the square-like shape of the Fermi surface was expected for the half-filled tight-binding band of the square lattice [12, 15, 19].

However, noting the fact that the gap structure was sustained quite rigidly during the doping process up to a high level of hole concentration, Ong et al. [16] proposed that the band is split because of the strong electron correlation, which is larger than the bandwidth of the $\sigma^*$ band. They assumed that $La_2CuO_4$ is a Mott insulator, and that holes can be introduced into the lower Hubbard band to create the metallic state while the gap structure is rigidly sustained.

The strong correlation among electrons was soon supported [20] by XPS through the observation of the large downward energy shift (~2 eV) of the valence-band peak from the position predicted by the band calculation.

## 4. Involvement of magnetic interaction

In a Mott insulator, each electron with spin 1/2 is localized on a lattice site; it does not impinge upon the territory of other electrons. The spin interaction to form a magnetically ordered state should therefore be considered explicitly.

A cusp structure in the magnetic susceptibility at 230 K was observed in $La_2CuO_4$ as early as 1984 [13], but its origin was not understood at that time. It was later ascribed to the antiferromagnetic phase transition by neutron diffraction experiments [21, 22], then confirmed by muon spin resonance [23] and nuclear quadrupole resonance [24, 25]. Later, the presence of antiferromagnetic ordering was also shown in the semiconductive region of $Ba_2YCu_3O_y$ [26–28]. **Figure 2** shows the low-temperature phase diagram for $(La, Ba)_2CuO_4$ [24]. A spin-glass phase region extends at the lowest temperature between the antiferromagnetic and superconductive regions; superconductivity and magnetism appear to exist side by side.

It would, then, be interesting to consider whether superconductivity is assisted by a tendency toward spin ordering, or on the contrary, it can appear only after the spin-ordered state is destroyed. In this context, an interesting result has been reported to show the presence of small antiferromagnetic and dynamic domains surviving even in the superconducting compositional region [29]. The correlation length of this antiferromagnetic interaction decreases steeply in $(La_{1-x}Sr_x)_2CuO_4$ as $x$ increases, but it remains finite, at about 10 Å at $x \simeq 0.08$, where $T_c$ reaches its maximum.

It therefore seems that the Fermi surface should be influenced strongly by the dynamically ordered spins.

## 5. Hole concentration and critical temperature

It has been described above how the metallic state of cuprate superconductors is brought about only after the introduction of a high enough concentration of holes by doping, as with $(La_{1-x}Sr_x)_2CuO_4$ and $Ba_2YCu_3O_{6.5+x}$. Superconductivity manifests itself as the hole concentration increases.

However, it has been shown that an optimum hole concentration seems to be needed to achieve the highest $T_c$. **Figure 3** shows that the $T_c$ of $(La_{1-x}Sr_x)_2CuO_4$ initially increases with hole concentration but decreases as it exceeds a certain value, while no appreciable oxygen deficiency is detected [30], in contrast to the findings presented in a previous report [31]. A similar dependence of $T_c$ has also been reported in $(Ba_{1-x}La_x)_2YCu_3O_7$ and $(Ba_{1-x}La_x)_3Cu_3O_7$ with respect to the estimated hole concentration from the chemical formulae [32].

In this context an interesting observation has been made in doped $Ba_2Y(Cu_{1-x}M_x)_3O_{7-y}$, with $M$ representing transition metals [33, 34]. As shown in **Figure 4**, the measured hole concentration decreased with doping of Fe, Co, and Ni or with the oxygen deficiency $y$, but increased when Zn was the dopant, while $T_c$ always dropped with the

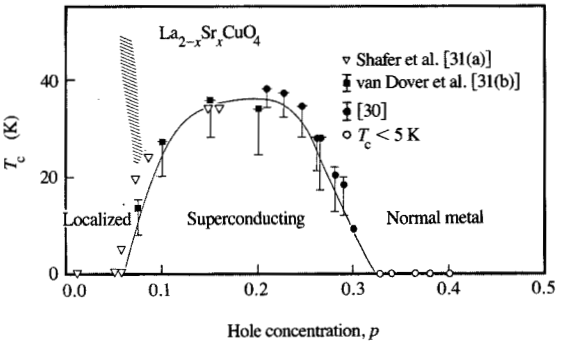


**Figure 3**

Relationship between the critical temperature and the hole concentration measured in $La_{2-x}Sr_xCuO_4$ with no oxygen vacancies.

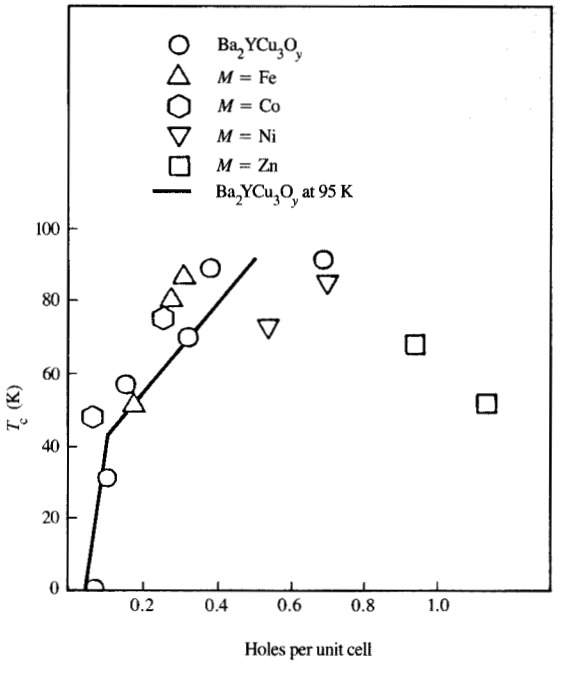


**Figure 4**

Relationship between the critical temperature and the hole concentration in oxygen-deficient and doped $Ba_2Y(Cu_{1-x}M_x)_3O_y$. (∇, [31(a)]; ■, [31(b)]; ●, [30], O, $T_c < 5$ K.)

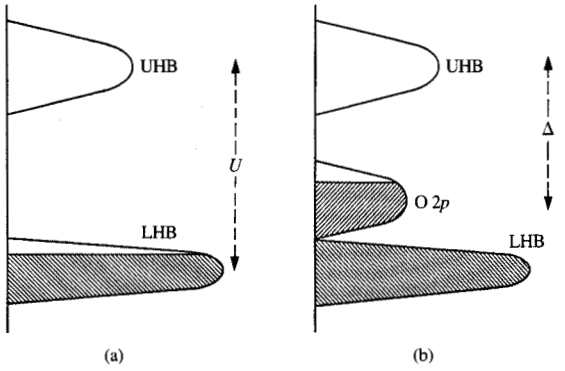


**Figure 5**

Hubbard (a) and extended Hubbard (b) models to describe the electronic structure of cuprate high-$T_c$ superconductors: $U$ = correlation gap, $\Delta$ = charge-transfer gap; UHB = upper Hubbard band, LHB = lower Hubbard band.

doping. On the basis of the electronic configuration of Zn ($d^{10}$), the authors speculated that Zn destroys the Mott–Hubbard gap because of the weak on-site electron–electron correlation expected in the more spatially extended electronic orbitals contributing to the bond. The strong deviation of the hole concentration from that expected from the composition of $(La_{1-x}Sr_x)_2CuO_4$ above $x \simeq 0.1$ (i.e., the highest $T_c$ composition [16]) might also be explained as being due to the initiation of destruction of the Mott–Hubbard gap.

The fact that the $T_c$ begins to decrease rapidly seems to suggest the essential involvement of the Mott–Hubbard gap in the realization of the high $T_c$.

## 6. Mott–Hubbard gap versus charge-transfer gap

The appearance of the Mott–Hubbard gap in the $\sigma^*$(Cu $3d_{x^2-y^2}$ O $2p_\sigma$) band seems to be well established in the cuprate layer structure, as discussed above. Between the two typical possible schemes [**Figures 5(a)** and **5(b)**], the former assumes the electrical conduction to occur in the lower Hubbard band, in which electrons are highly correlated and there is thus no well-defined Fermi surface, as in the usual single-electron band concept. On the other hand, the latter assumes another band (O $2p$) to intervene between the lower and upper Hubbard bands.

Various observations of X-ray and ultraviolet photoelectron spectroscopy have supported the latter scheme from the early stage of the studies [35–38], suggesting that the Fermi surface was of dominantly O $2p$ nature and hence that the holes were not created in the lower Hubbard band.

These results were received with some skepticism because photoelectron spectroscopy senses only surface layers. Such doubts were later dispelled by the results of EELS measurements of electrons transmitting through a thin-film specimen; the electrons in this case are expected to lose energy mainly in bulk excitations [39].

Very recently, observations of angle-resolved UPS on a freshly cleaved $Bi_2Sr_2CaCu_2O_y$ single crystal revealed the dispersion of this band, as shown in **Figure 6**, from which a rough estimation of the effective band mass of the O $2p$ holes of approximately 4 $m_e$ was obtained [40]. This was consistent with the estimated bandwidth in $(La, M)_2CuO_4$ and $Ba_2YCu_3O_7$ by plasma edge observation of ~1 eV [14]. Since the band calculation predicted a much wider band, more than 4 eV [12, 41, 42], the above results indicate that the intervening band is strongly renormalized.

There is, however, some criticism of the above picture because electron spectroscopy is performed in the energy range of 10 eV or higher. Hence, it is claimed that the detailed structure of the energy scale of 0.1 eV or less at the Fermi surface should not be inferred from such measurements [43].

## 7. Transport, magnetic, and thermal properties

In conjunction with the nature of the Fermi surface of cuprate superconductors, the linearity between the resistivity and temperature above $T_c$ has been considered [44, 45]. This is quite unique among high-$T_c$ superconductors. The resistivity curves show rather flat temperature dependence, especially for the other oxides, or show tendencies toward saturation for A15 compounds and ternary molybdenum chalcogenides [45].

The linear dependence over wide temperature ranges suggests that electron-lattice coupling is weak in the high-$T_c$ cuprates [45]. On the other hand, the changes in thermal conductivity [46] and lattice parameter [47] at $T_c$ indicated rather strong coupling. In the case of metals, observation of the superconducting gap by tunneling or far-infrared reflection measurements can usually determine the strength of the coupling. Since tunneling and FIR spectroscopy have not given consistent results, it seems to be too early to discuss this point further.

There have been many indications of the difficulties in understanding the nature of the Fermi surface based on a simple band model. The thermopower of a simple metal is expected to be $T$-linear; however, it was found to be nearly flat with $T$ both in $(La, M)_2CuO_4$ and $Ba_2LnCu_3O_7$ [48, 49], suggesting that electrons are highly correlated in this band also.

The anomalously high electronic specific heat coefficient $\gamma$ was first reported for $(La_{1-x}Ca_x)_2CuO_4$ in the cuprate series from the observation of the specific heat discontinuity at $T_c$, $\Delta C_p$ [50]. The enhancement factor of $\gamma$ with respect to the one obtained by the band calculation was 5 ~ 7, indicating

the presence of some unusual enhancement mechanism. As the sample quality improved, a large $\Delta C_p$ was also found in $Ba_2YCu_3O_7$ [51]. More recently, it has been pointed out that the specific heat curve around $T_c$ may be subject to superconducting fluctuation which is due to the extremely short coherence length [52].

The normal-state paramagnetic susceptibility usually is another measure of the density of states at the Fermi surface. A large enhancement of the susceptibility (more than a factor of 10) was reported for $Ba_2YCu_3O_7$ with respect to the estimated value from the hole concentration and the optical effective mass [53]. The paramagnetism in the normal state, however, has quite recently been attributed to a novel magnetic state rather than to the simple Pauli paramagnetism. This is based on the observation of a broad peak in the susceptibility vs. temperature curve where the peak temperature gradually shifts toward lower temperatures as $x$ increases in $(La_{1-x}Sr_x)_2CuO_4$ [54].

Another indication of the complexity of the Fermi surface is the apparent contradiction between the Hall coefficient and the plasma reflection edge [14, 55]. Although the hole concentration changes with doping, the plasma edge was observed to show little dependence on it. Moreover, the hole concentration seems to decrease nearly linearly as the temperature is lowered [53].

All these indications seem to lead us to assume that there is involvement of the second band, which has unusual magnetic properties. Therefore, at the current stage it should be fruitful to conduct further investigations on the assumption that the band with O 2*p* nature and the lower Hubbard band are both playing roles in the low-energy process.

## 8. Possible orbitals for O 2*p* holes

Although electron spectroscopy has indicated the presence of O 2*p* holes, the O 2*p* orbitals where they are created have not been identified. X-ray absorption spectroscopy has suggested a rather unexpected orbital. According to the symmetry of absorption of polarized X-rays, Bianconi et al. have proposed that the O 2*p* orbital stretching along the *c*-axis on the pyramidal oxygen atom is the one in which the hole is created [37].

Considering the interatomic distances, it is hard to imagine that O 2*p* orbitals on the pyramidal oxygen atoms can overlap one another to create a band unless the orbitals of Ba atoms are involved in the hybridization. In this case, the electrical conduction would occur in the Ba–O layer rather than in the Cu–O layer. Hence, the concept of electrical conduction and the superconducting mechanism would then be pressed for a major revision.

## 9. Summary

The electronic structure of the high-$T_c$ cuprate superconductors may be characterized as follows:

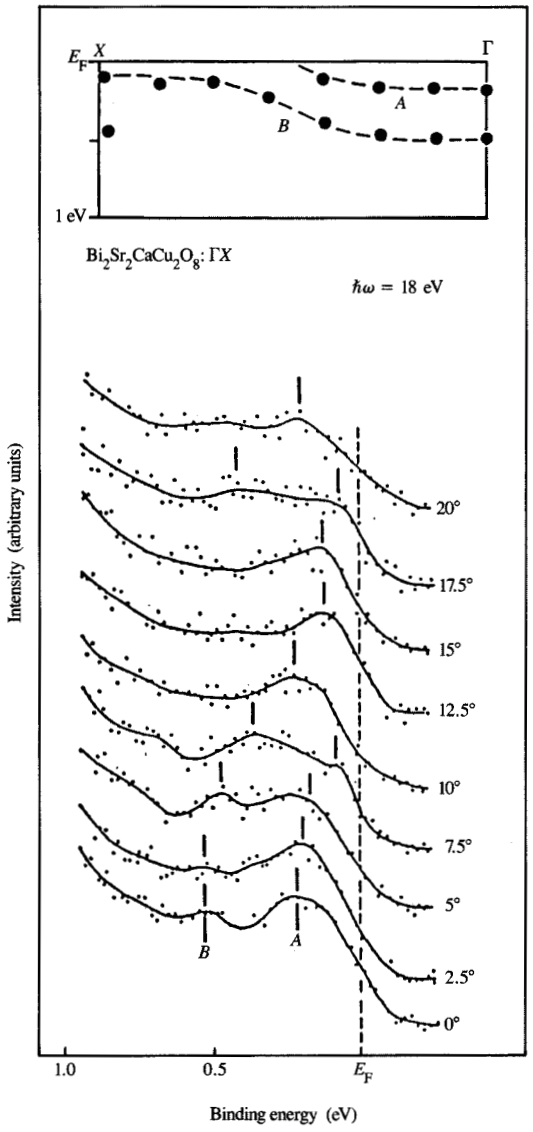


**Figure 6**

Angle-resolved ultraviolet photoelectron spectra on a cleaved *c*-plane of single-crystal $Bi_2Sr_2CaCu_2O_8$ in the high-symmetry direction Γ*X*. The incident light energy = 18 eV; the resonance energy is equal to the excitation energy from O 2*p* to the Fermi level. The inset shows the band structure as obtained from the dependence of the spectrum peaks on the angle.

1. The Mott–Hubbard gap is formed in the $\sigma^*$ band derived from Cu 3*d*–O $2p_\sigma$ hybridization.
2. The O 2*p* band located between the lower and upper Hubbard bands is involved.
3. The Fermi surface appears to be affected by both the O 2*p* band and the lower Hubbard band.

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