PHYSICAL REVIEW B VOLUME 48, NUMBER 21 1 DECEMBER 1993-I

Comparative photoemission studies of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1$, 2, and 3)

C. S. Gopinath and S. Subramanian
Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras 600 036, India

M. Paranthaman and A. M. Hermann
Department of Physics, Campus Box 390, University of Colorado, Boulder, Colorado 80309

(Received 14 May 1993; revised manuscript received 15 July 1993)

Detailed studies on the bi-Tl layer family of cuprate superconductors for the first three members have been carried out by valence-level and core-level photoemission. Ca 2*p* and Ba 3*d* core levels show a variation in broadening with an increasing number of CuO_2 planes. The Tl 4*f* core level shows a mixed valent character [Tl(I) and Tl(III)] in all the three samples. The Cu 2*p* core-level spectrum also shows a change in the satellite to main line intensity and the energy difference between them. Simplified configuration interaction calculations are carried out to explain the observed changes. A rigid shift of the valence band is observed with the increase in the number of CuO_2 planes. Near-Fermi-level features are identified as due to a Kondo-type resonance and resulting heavy-electron band states.

I. INTRODUCTION

Sheng and Hermann have reported high-temperature superconductivity above 100 K in the Tl-Ba-Ca-Cu-O system in 1988.[1] From electron and x-ray diffraction measurements, Hazen *et al.*[2] identified tetragonal phases $Tl_2Ba_2CaCu_2O_8$ ($a=5.44$, $c=29.55$ Å), and $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($a=5.40$, $c=36.25$ Å) and concluded that the structures were closely related to that of Bi 2:2:1:2. It is now known that the superconducting phases in this system can be represented as $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, were n is the number of consecutive Cu-O layers. (The phases are herein referred to by their nominal Tl:Ba:Ca:Cu ratio, e.g., Tl 2:2:1:2.)

Differences in the crystal structures of these phases arise from different stacking sequences along the tetragonal *c* axis. Two series of oxides can be distinguished corresponding to the formulas $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, and $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, respectively. In these oxides the number of CuO_2 sheets, n, can be 1, 2, 3, and perhaps as high as 4 or 5.[3] While the *c* axis lengthens with increasing n, the *a* axis of all the superconducting phases are of approximately the same length. One might expect these phases to be insulators or semiconductors when we assume normal valences for all the elements. A few suggestions have been made as to the origin of charge carriers in the double-Tl layer phases, such as band overlap, cation and/or oxygen vacancies, etc. Changes in the carrier concentration due to any of the above effects can affect the properties of superconducting phases. However, the single Tl-O layer phases require an additional positive charge per unit cell to achieve charge neutrality to make them conductors, assuming the normal valences for all the elements.[4] Moreover, the variation in the hole concentration in this superconductor is limited mostly to Cu-O planes and not with Tl.

The electronic description of the high-temperature superconducting cuprates is currently an experimental as well as a theoretical challenge. An understanding of the structure and properties of these materials is essential to develop a workable model as a prerequisite to understand the complete electronic structure. Superconductivity is caused by a change in the state of electrons that are close in energy to the Fermi level. In order to clarify the nature of high-T_c superconductivity, it is important to learn as much as possible about these states. In this regard photoelectron spectroscopy has become an important and indispensable tool. However, before the advent of high-T_c superconductors, photoemission methods failed to make a substantial contribution to superconductivity research.[5] Furthermore, the electronic structure of 3*d* transition metal compounds is a long-standing puzzle. This is mainly due to correlation effects, which are difficult to describe in these systems. This is a key reason why the mechanism for high-T_c superconductivity is not completely understood.[6]

Undoped cuprates are insulators of the charge-transfer type and, however, to explain the insulating properties Mott-Hubbard band splittings, should be considered. The first unoccupied band above Fermi level is based on $3d_{x^2-y^2}$ orbitals of Cu and has a partial O 2*p* character due to covalency. Upon doping, by one of the processes mentioned above, a hole impuritylike band is formed at the bottom of the gap, which finally merges with the valence band to build a partially filled conduction band. This model of the dominant O 2*p* character of hole carriers is supported by different high-energy spectroscopic studies.[6-10] However, this model has to be refined to account for all the spectroscopic results.

Band-structure calculations[11] for the double-Tl layer cuprates reveal that the Tl 6*s* bands lie below the Fermi level, so that electrons are transferred from CuO_2 sheets to Tl_2O_4 layers. But in the case of single-Tl layer cuprates, the Fermi energy is calculated to lie well below the Tl 6*s* band. Thallium and oxygen contents appear to be important in determining the properties of thallium superconductors.[12] In the case of Tl 2:2:0:1 phase, samples can be made nonsuperconducting or superconducting

0163-1829/93/48(21)/15999(7)/$06.00

with a T_c up to 92 K depending on oxygen content.[13,14] Similarly, the variation of T_c with Tl and O vacancies has been discussed in the Tl 2:2:2:3 system with excess Ca.[15]

In this article, we present a report on photoemission spectroscopic study of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, where $n=1$, 2, and 3, to investigate the nature of the electronic states in these systems. We have observed a strong mixed-valent character of Tl in all the three phases. Experimental evidence for the Tl 6*s* band overlapping the Fermi energy in all the three samples is found in x-ray photoemission spectroscopy (XPS). Systematic core-level changes observed in Cu 2*p* core-level spectrum are explained with a simplified configuration interaction (CI) model. The broadenings of the Ca 2*p* core level shows that there is some mixed occupancy in Tl 2:2:1:2 and Tl 2:2:2:3, which will be explored in detail in the following.

II. EXPERIMENT

Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3 superconductors were prepared by a high-temperature solid-state reaction method and the preparation details are given in detail in Refs. 12 and 15. All the three samples were characterized by x-ray powder diffraction. Superconductive transition temperatures were obtained as the diamagnetic onset temperature measured with either a commercial superconducting quantum interference device (SQUID) magnetometer under a field of 0.01 T or a SUMITOMO susceptometer under a field of 10^{-5} T. The T_c measured for Tl 2:2:0:1 is 88 K, Tl 2:2:1:2 is 102 K, and Tl 2:2:2:3 is 114 K. All the samples are of single phase, as is borne out by x-ray diffraction and susceptibility data.

XPS and ultraviolet photoemission spectroscopy (UVPES) measurements are carried out with a VG ESCALAB MkII spectrometer. Samples are scraped *in situ* with a stainless-steel blade inside the analysis chamber prior to the measurements under a high vacuum of $10^{-9}-10^{-10}$ Torr. Deviations of error in all binding energy (BE) values are within ± 0.1 eV. Energy resolution of the spectrometer is determined from the full width at half maximum (FWHM) of metallic silver and the values are better than 0.2 and 0.7 eV for $h\nu = 21.2$ (HeI) and 1253.6 eV (Mg$K\alpha$), respectively. The Fermi edge is referenced to that of metallic silver. Only the Tl 2:2:2:3 sample showed contamination to a small extent due to carbon, though the source of contamination is not known. Our XPS data of this compound is in good agreement with literature[16,17] suggesting that our results are not affected by carbon contamination. Moreover, we have observed a Fermi edge for this sample suggesting the purity of the surface and its metallic character.

III. RESULTS AND DISCUSSION

A. Ca 2*p* and Ba 3*d* spectra

XPS measurements have been carried out at RT on the first three members of bi-Tl layer family cuprates. Figure 1 shows (a) the Ca 2*p* spectra and, (b) Ba 3*d* spectra for all the three samples. Since there is no Ca in Tl 2:2:0:1, no Ca 2*p* spectrum is shown in the figure. We have observed a FWHM of 2.7 and 2.3 eV for the Ca $2p_{3/2}$ line in Tl 2:2:1:2 and Tl 2:2:2:3, respectively. But the BE of the Ca $2p_{3/2}$ level is the same in both these compounds (345.7 eV). The Ba $3d_{5/2}$ level shows the same BE for all the three compounds (778.4 eV) with progressively increasing FWHM of 2.4 eV for Tl 2:2:0:1, 2.6 eV for Tl 2:2:1:2, and 2.8 eV for Tl 2:2:2:3.

The broadening of Ca 2*p* and Ba 3*d* core levels suggest the mixed occupancy of these sites. The ionic radii consideration of various ions, Ca(II), (1.12 Å), Tl(III), (1.00 Å), Tl(I) (1.48 Å), Ba(II) (1.47 Å), and Cu(II) (0.73 Å) suggest that they can occupy other sites apart from their actual site, which are listed as follows: (i) Ba can occupy the Ca site and/or Tl(I) site; (ii) Ca can occupy the Tl site and/or the Ba site; and (iii) occupation of the Cu site is not likely for both Ca and Ba.

The actual Ca site, which is between the CuO_2 sheets, is completely oxygen depleted and the Ca at the Tl and the Ba sites is surrounded by oxygens. The larger FWHM of the Ca 2*p* line for Tl 2:2:1:2 suggests that, it

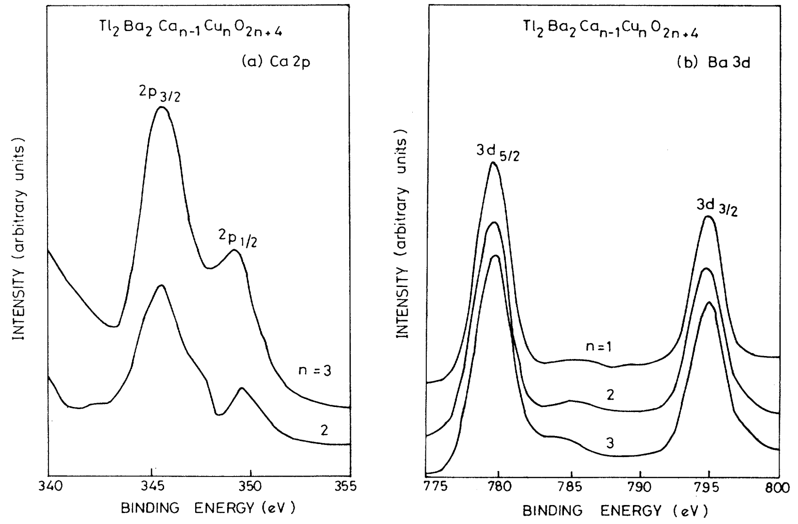

FIG. 1. (a) Calcium 2*p* core-level spectra and (b) Ba 3*d* core-level spectra for Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3.

occupies both the Tl and Ba sites. But in the case of Tl 2:2:2:3, the lower FWHM suggests that a lower level of mixed occupancy or Ca may occupy either the Ba or Tl site, in addition to the actual Ca site.

In the case of Ba, we suggest that it occupies the Tl(I) site and the actual Ba site in Tl 2:2:0:1. But for Tl 2:2:1:2 and Tl 2:2:2:3, Ba starts occupying both the Ca and Tl sites. This is mainly due to the decrease in Tl(I) concentration as we move from Tl 2:2:0:1 to Tl 2:2:2:3. This point is explained in detail in the following section. The above interpretation is in accordance with the observation of progressively increasing FWHM of Ba $3d$ core level from Tl 2:2:0:1 to Tl 2:2:2:3. Apart from the mixed occupancy of Ba and Ca within the unit cell, it can occupy the Tl site also, which is not explained in the earlier report.[16]

B. Tl $4f$ and $5d$ XPS studies

The crystal structure of both double-Tl layer cuprates and Bi-based cuprates has double Tl-O or Bi-O layers. From the viewpoint of structural chemistry, it is very surprising that Tl(III) with the electronic configuration $[\mathrm{Xe}]4f^{14}5d^{10}$ forms such similar layered structures as Bi(III) with a $[\mathrm{Xe}]4f^{14}5d^{10}6s^{2}$ configuration, because a metal ion with s electrons in the outer shell forms polarized chemical bonds which would explain a layered structure.[18] Hence, it is necessary to investigate the valence of Tl in this cuprate superconductor.

Thallium is one of the peculiar systems in which the BE decreases with increase in oxidation state. This is mainly due to the effective relaxation in the electron orbitals of conductive oxides, for example, as seen in PbO_2 and Tl_2O_3.[19] Since the photoionization is an adiabatic process and the relaxation energy is carried away by the departing electron, this leads to an increase in kinetic energy of the photoelectron and a corresponding decrease in BE.

Figure 2 shows (a) the Tl $4f$ core-level spectra and (b) the Tl $5d$ shallow core-level spectra. The BE of both the Tl levels decreases as we go from Tl 2:2:0:1 to Tl 2:2:2:3. The Tl $4f$ core-level BE decreases from 118.4 eV for Tl 2:2:0:1 to 118.1 eV for Tl 2:2:2:3. Tl $5d$ shallow core-level BE also decreases from 13.7 eV for Tl 2:2:0:1 to 13.2 eV for Tl 2:2:2:3. The BE of the $4f_{7/2}$ level in Tl(I) compounds are observed to be higher (the BE varies between 118.7 and 119.4 eV depending on the anions) than that of Tl_2O_3 (117.7 eV) which is consistent with the results of McGuire, Schweitzer, and Carlson.[20] The higher BE of Tl in Tl 2:2:0:1 indicates the larger mixed-valent character of Tl, i.e., a larger amount of Tl(I) contributing to the system. In the case of Tl 2:2:1:2 and Tl 2:2:2:3 the Tl $4f_{7/2}$ BE decreases to 118.2 and 118.1 eV, respectively. This decrease in BE clearly points to the decrease in the mixed-valent character as we increase the number of CuO_2 layers in the double-Tl layer cuprates.

It is now well established that superconductive onset temperature of the p-type cuprate superconductor increases with the hole concentration in a superconductive CuO_2 sheet. Nevertheless, if the system is overdoped or underdoped, the T_c decreases and ultimately becomes a conductor or insulator, respectively. The observation of increasing T_c, as we increase the number of CuO_2 layers in the double-Tl layer system, strongly suggests that there should be a change in hole concentration. In the Tl 2:2:0:1 system Cu is in the octahedral coordination, which drives the copper to be in a higher oxidation state. Our observation of higher BE for Tl $4f$ core level suggests that a good amount of Tl is in the Tl(I) state. In turn, the above two points suggest that charge (electron) is transferred from the CuO_2 layer to Tl. This leads to an oxidation of the CuO_2 layer and hence to overdoping. As mentioned in the Introduction, the Tl 2:2:0:1 samples can be made to be nonsuperconducting to superconducting with a T_c as high as 92 K, depending on oxygen content.

In the case of Tl 2:2:1:2 and Tl 2:2:2:3, there is yet another source for the higher hole concentration, which

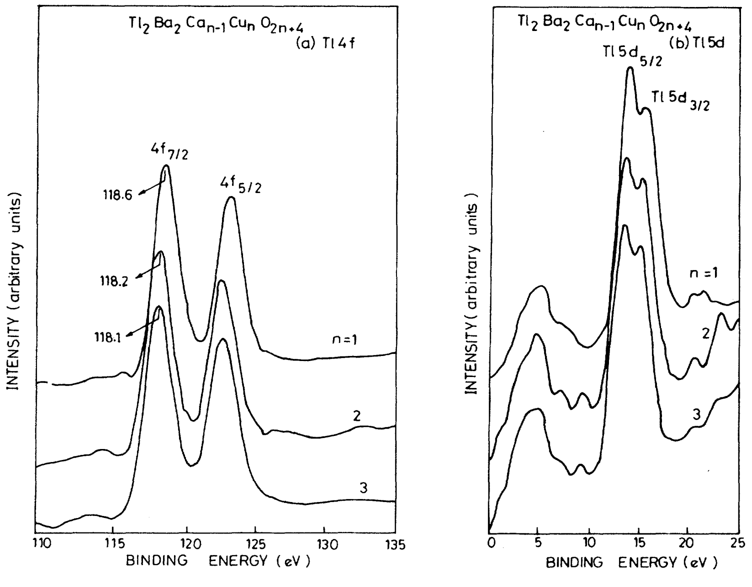

FIG. 2. (a) Tl $4f$ core-level and (b) Tl $5d$ shallow core level spectra for Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3.

is the substitution of Ca into the Tl site. This also leads to a higher hole concentration and, hence, a variation in T_c. Single-crystal x-ray-diffraction studies[21] and transmission electron microscopic measurements[22] also support the above conclusion. At the same time the above references suggest that, at most, 10–15 % of Tl is replaced by Ca, which is not sufficient for a sample to be superconductive, with a T_c higher than 100 K, since the average hole concentration in a CuO_2 layer is estimated to be 0.1. Once again the mixed-valent character of Tl may be the possible reason for higher T_c. Our XPS measurements indicate the mixed-valent character of Tl in Tl 2:2:1:2 and Tl 2:2:2:3. But the decrease in BE of Tl $4f$ and $5d$ levels suggest that there is a decrease in mixed-valent character of Tl as we move from Tl 2:2:0:1 to Tl 2:2:2:3.

The Tl-Tl near-neighbor interaction in these samples will decrease as we increase the number of CuO_2 layers. As we progressively increase the number of CuO_2 layers, the Tl(I) ions get oxidized to Tl(III) and the Tl $6s$ band narrows down in width, decreasing the overlap between the Tl $6s$ and $\sigma^*_{x^2-y^2}$ bands. The presence of electrons in Tl $6s$ bands, unambiguously borne out by XPS, would account for the polarized chemical bonds which could be the driving force for the layered structure.

C. Cu $2p_{3/2}$ XPS

The Cu $2p_{3/2}$ core-level XPS spectra collected from freshly scraped surfaces of Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3 are shown in Fig. 3(a). They are composed of two components with the main line at a BE of around 933 eV and a satellite between 937 and 949 eV due to a well-screened final state (Cu $2p^5 3d^{10}\underline{L}$), where $\underline{L}$ denotes the holes on the surrounding ligands, and an unscreened (Cu $2p^5 3d^9$) final state, respectively. The I_s/I_m ratios are obtained from the areas under the satellite and main line after background subtraction and the satellite to main line separations (W) are obtained from the energy differences between the centroids of the two peaks. The satellite intensity is directly proportional to the weighting of d^9 species.

There is a clear trend in the variation of these spectra as the number of CuO_2 layers increases. The BE of the main line varies from 932.8 eV for Tl 2:2:0:1 and 933.1 eV for Tl 2:2:1:2 to 932.7 eV for Tl 2:2:2:3. The I_s/I_m and W decrease continuously from Tl 2:2:0:1 to Tl 2:2:2:3. I_s/I_m decreases from 0.30 to 0.24 and W decreases from 10.3 to 9.4 eV. Although the change in I_s/I_m is not quite obvious from Fig. 3(a), a quantitative analysis shows a clear trend in the variation [Fig. 3(b)]. Besides, the FWHM of main line varies from 2.4 eV for Tl 2:2:0:1 and 2.7 eV for Tl 2:2:2:3 to 3.0 eV for Tl 2:2:1:2.

The observed variations are explained as follows: The low I_s/I_m and a BE value of about 932.9±0.2 eV, close to that of CuO, for all the three samples suggest that more of the $d^{10}\underline{L}$ configuration contributes to the ground-state system. As we increase the number of CuO_2 layers, the average hole concentration per CuO_2 layer decreases and hence lowers I_s/I_m. The BE of the main line primarily depends on the contribution of different configurations. The lower BE (932.7 eV) observed for Tl 2:2:2:3 suggests a higher contribution of $d^{10}\underline{L}$ configuration to the ground state, and *vice versa* for Tl 2:2:1:2, where a higher BE of 933.1 eV is observed. In Tl 2:2:1:2 alone, a clear hump [marked by an arrow in Fig. 3(a)] is seen at higher BE (936.0 eV) side, indicating the contribution of the $d^9\underline{L}$ configuration to the ground state. Moreover, the tail of the satellite extends up to a BE of 947 eV, which is a characteristic feature of the Cu(III) compounds,[23,24] in Tl 2:2:1:2. This is the main reason for the larger width of the main line in Tl 2:2:1:2 alone. In Tl 2:2:0:1 and Tl 2:2:2:3 mostly two configurations contribute, namely, d^9 and $d^{10}\underline{L}$, which leads to an observation of lower FWHM.

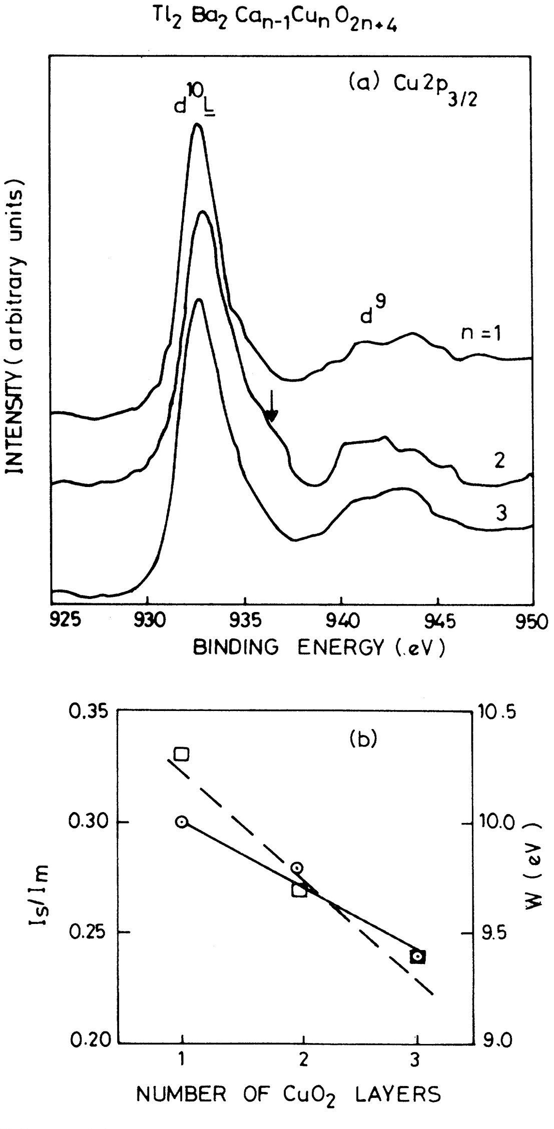

FIG. 3. (a) Cu $2p_{3/2}$ core-level spectra for Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3. Note the contribution of the $d^9\underline{L}$ configuration for Tl 2:2:1:2 (arrow mark). (b) Variation of I_s/I_m and energy separation against the number of CuO_2 layers. Solid lines are guides to the eye.

The change in W is more difficult to explain. To analyze this feature, we associate the evolution of two ground-state configurations of the Cu(II) with the observed Cu $2p_{3/2}$ spectra in Fig. 3(a). We have not considered any $d^9\underline{L}$ contribution to our calculations. We mention here that Cu(II) and Cu(III) states are not mixed in the final states, since the hybridization strength is zero.[23] We interpret our results presented here in terms of the CI model, which is explained in detail by van der Laan *et al.*,[24] and applied successfully to $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8-y}$ (Ref. 25) and $Tl_{2-x-z}Ba_2Ca_{2+x}Cu_3O_{10-y}$ (Ref. 26) systems. The two experimentally observed parameters I_s/I_m and W depend on three unknowns; namely, charge-transfer energy (Δ), hybridization strength (τ), and core hole d-hole interaction energy (U_{dc}). In order to explain the experimental results, reasonable ranges of these can be assumed and the resulting calculated I_s/I_m and W can be compared with the experiments. In Fig. 4 we have plotted the values of I_s/I_m and $W(2p)$ as a function of three different values of $\tau=2$, 2.5, and 3.0. U_{dc} is fixed (8.0 eV) in all the calculations. Our calculation of I_s/I_m shows that (1) the value of Δ decreases from Tl 2:2:2:3 to Tl 2:2:0:1 and (2) an increase in τ is responsible for the decrease in I_s/I_m.

Here the CI model fails to explain the variation of W and it shows the opposite trend. This indicates that there must be some other configurations contributing to the ground state of these systems, which is likely to be $d^{10}\underline{L}^2$ and/or d^8. d^8 is highly unstable compared to other states, on the basis of energy considerations, and hence is ruled out.[23] But $d^{10}\underline{L}^2$ cannot be ruled out because its energy is more or less equal to the energy of other configurations. Contribution of this configuration to the ground state would correspond to holes being mostly localized on oxygen. This in turn suggests the Fermi-liquid nature of these superconductors. $d^{10}\underline{L}^2$ is another form of d^8, which increases the hybridization strength and leads to a higher W between main line and satellite. This is the main reason for the observation of higher W in Tl 2:2:0:1. In conclusion, a larger amount of $d^{10}\underline{L}^2$ contributes to Tl 2:2:0:1 apart from d^9 and $d^{10}\underline{L}$. But the $d^{10}\underline{L}^2$ contribution decreases as we move from Tl 2:2:0:1 to Tl 2:2:2:3.

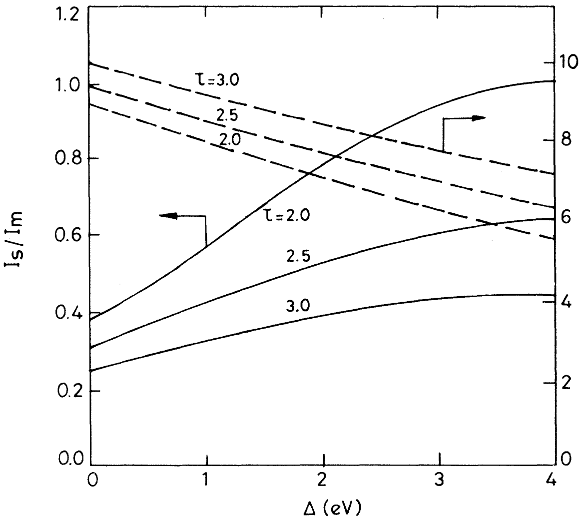

FIG. 4. Satellite to main line intensity (I_s/I_m), and energy separation between the main line and satellite (W) calculated using configuration interaction model are plotted against charge-transfer energy (Δ) in the range of 0–4 eV for three different transfer integral values ($\tau=2.0$, 2.5, and 3.0). U_{dc} is assumed to be 8.0 eV throughout the calculations.

D. Valence-band spectra

It is interesting to study the effect of chemical doping on the electronic structure by photoemission spectroscopy (PES). The change in carrier (hole) concentration may rigidly shift the valence level as predicted from the band-structure calculation, or it may produce some impurity-like states as in heavily doped semiconductors or Kondo-like states as in heavy Fermion systems. One is still not clear about the origin of the electronic states near the Fermi level in high-T_c cuprate superconductors. However, the nature of the electronic states near the Fermi level has been studied by electron-energy-loss spectroscopy (EELS)[27] and x-ray absorption spectroscopy (XAS),[28] which show that the states near the Fermi level have a dominant O $2p_{x,y}$ character. We have measured the UVPES of the Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3 to understand its valence-band electronic structure and the nature and origin of electronic states near Fermi level.

Figure 5 shows the UVPES spectra of Tl 2:2:0:1, Tl

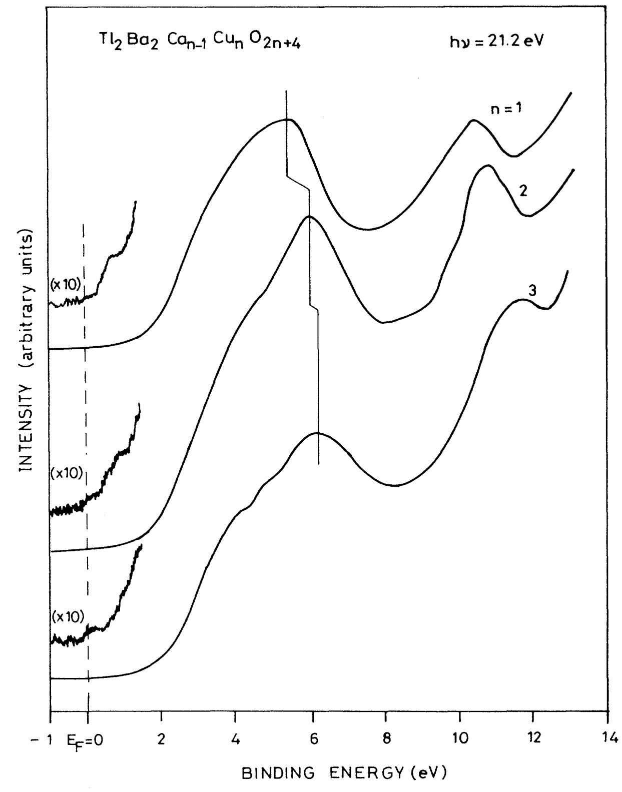

FIG. 5. Valence-band photoemission spectra of superconductors Tl 2:2:0:1, Tl 2:2:1:2, and Tl 2:2:2:3. Near E_F features are shown at higher amplification.

2:2:1:2, and Tl 2:2:2:3. The HeI spectra are dominated by a steeply rising background of secondary electron emission above 12 eV BE. The photoemission intensity at E_F increases with the number of CuO_2 layers. The main peak in the VB is dominated by O 2*p*, Cu 3*d*, and Tl 6*s* derived states, especially by O 2*p* due to its higher photoionization cross section (σ). Other elements, Ca and Ba have lower σ and due to high ionic character they do not contribute to the VB at the given incident radiation of 21.2 eV.[29] Another important observation is the movement of the main VB away from E_F as we go from Tl 2:2:0:1 to Tl 2:2:2:3. For Tl 2:2:0:1 the main line VB is at 5.2 eV, Tl 2:2:1:2 at 5.7 eV, and Tl 2:2:2:3 is at 5.9 eV. From our core-level results of Cu 2*p* and Tl 4*f*, we have explained the decrease in hole concentration as we go from Tl 2:2:0:1 to Tl 2:2:2:3. This is consistent with the idea that we are filling holes in VB, with electrons provided by Tl-O layers to CuO_2 layers. This observation leads to the conclusion of chemical potential shift with hole and/or electron doping. The BE shift observed in Tl 4*f* and Cu 2*p* core levels and the main peak in VB suggest that the nature of the chemical potential shift is localized and associated with Tl, Cu, and O. It can also be seen that the onset of the main part of VB moves away from Fermi level, from 1.0 to 2.0 eV BE as we go from Tl 2:2:0:1 to Tl 2:2:2:3. The rigid shift of VB suggests that the electronic states are *simple one-electron states* as predicted from the band-structure calculations derived mostly from O 2*p* and Cu 3*d* states.

Now let us examine the near E_F level features. As we go from Tl 2:2:0:1 to Tl 2:2:2:3 the density of states (DOS) at E_F increases. Besides, there is a finite photoemission intensity between E_F and the onset of the main VB, in spite of the movement of the VB for Tl 2:2:1:2 and Tl 2:2:2:3 towards higher BE. These observations strongly suggest[30] that the origin of near E_F features are of *Kondo-like states* as in a *heavy Fermion system.* The nature of these states are derived from Tl and O orbitals. As we move from Tl 2:2:0:1 to Tl 2:2:2:3 the Tl 4*f* core level and Tl 5*d* shallow core level shifts towards lower BE, thereby its higher oxidation state is monitored. This is in agreement with the widely held opinion that charge (electron) is transferred from Cu-O layers to Tl-O layers. From Cu 2*p* spectrum we have shown that holes are mostly localized on oxygen orbitals, which get filled up by the Tl 6*s* electrons as we move from Tl 2:2:0:1 to Tl 2:2:2:3. However, we cannot exclude the possibility of the Cu contribution to these near E_F features. Resonant photoemission measurements are required to find out the contribution of other elements to these near E_F features.

The metallic character of all the three compounds are explained due to the observation of clear Fermi edge with finite DOS. In the case of the main VB, a shift of 0.7 eV is observed towards higher BE from Tl 2:2:0:1 to Tl 2:2:2:3. On the other hand, there is a transfer of spectral weight from conduction band into the valence band. Moreover, our Cu 2*p* core-level spectra and CI calculations show that Cu interacts strongly with holes and/or electrons. All these observations reinforce the *Kondo-like states* as in a *heavy Fermion system* and need not be oxygen split-off states as suggested by Fujimori *et al.*[30] In short, within the Fermi-liquid approach we have considered a Kondo-type many-body resonance of O 2*p* character and resulting renormalized heavy electron bands formed in the vicinity of the Fermi level.

IV. CONCLUSIONS

To summarize, XPS and UVPES experiments have been performed on polycrystalline single-phase double Tl-layer cuprates with the first three members. The variations observed in the Ca 2*p* and Ba 3*d* core-level spectra are explained in terms of mixed occupancy. The Tl oxidation state increases as we move from Tl 2:2:0:1 to Tl 2:2:2:3 and its mixed-valent character is shown in all the three compounds. We have observed variations in the Cu 2*p* spectra, which are analyzed in terms of the contribution of different configurations to the ground state. A rigid shift in the VB is observed and explained in terms of a single one-electron band picture. Near-Fermi-level features are identified as due to a Kondo-type resonance and resulting heavy electron band states.

ACKNOWLEDGMENTS

C.S.G. thanks the National Superconductivity Technology Board, Department of Science and Technology, New Delhi for support. The work at the University of Colorado-Boulder was sponsored by the Office of Naval Research under ONR Grant No. N00014-90-J-1571.

---

[1] Z. Z. Sheng and A. M. Hermann, Nature **332**, 55 (1988); **332**, 138 (1988).

[2] R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadidiacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. El Ali, and A. M. Hermann, Phys. Rev. Lett. **60**, 1657 (1988).

[3] S. Nakajima, M. Kikuchi, Y. Syono, T. Oku, D. Shindo, K. Hiraga, N. Kobayashi, H. Iwasaki, and Y. Moto, Physica C **158**, 471 (1989).

[4] T. L. Aselage, E. L. Venturini, S. B. Van Deusen, T. J. Headley, M. O. Eatough, and J. A. Voigt, Physica C **203**, 25 (1993).

[5] G. Margaritondo, J. Am. Ceram. Soc. **73**, 3161 (1990).

[6] J. Fink, N. Nucker, M. Alexander, H. Romberg, M. Knupfer, M. Merkel, P. Adelmann, R. Claessen, G. Mante, T. Buslaps, S. Harm, R. Manzke, and M. Skibowski, Physica C **185-189**, 45 (1991).

[7] A. Fujimori, Y. Tokura, H. Eisaki, H. Takagi, S. Uchida, and M. Sato, Phys. Rev. B **40**, 7303 (1989).

[8] F. Studer, N. Merrien, C. Martin, C. Michel, B. Raveau, and A. Fontaine, Physica C **178**, 324 (1991).

[9] Y. Hwu, M. Marsi, A. Terrasi, M. Onellion, D. L. Huber, G. Margaritondo, J. H. Wang, Z. Z. Sheng, and A. M. Hermann, J. Phys. Soc. Jpn. **59**, 4554 (1990).

[10] A. Krol, C. S. Lin, Y. L. Soo, Z. H. Ming, Y. H. Kao, Jui H.

Wang, Min Qi, and G. C. Smith, Phys. Rev. B **45**, 10 051 (1992).

[11] D. Jung, M.-H. Whangbo, N. Herron, and C. C. Torardi, Physica C **160**, 381 (1989); Jaejun Yu, S. Massidda, and A. J. Freeman, *ibid.* **152**, 251 (1988).

[12] M. Paranthaman, A. Manthiram, and J. B. Goodenough, J. Solid State Chem. **87**, 479 (1990); A. Manthiram, M. Paranthaman, and J. B. Goodenough, Physica C **171**, 135 (1990); J. Solid State Chem. **96**, 464 (1992).

[13] A. Maignan, C. Martin, M. Huve, J. Provost, M. Hervieu, C. Michel, and B. Raveau, Physica C **170**, 350 (1990).

[14] Y. Shimakawa, Y. Kubo, T. Manako, and H. Igarashi, Phys. Rev. B **40**, 11 400 (1989).

[15] M. Paranthaman, M. Foldeaki, and A. M. Hermann, Physica C **192**, 161 (1992).

[16] H. M. Meyer III, T. J. Wagener, J. H. Weaver, and D. S. Ginley, Phys. Rev. B **39**, 7343 (1989).

[17] T. Suzuki, M. Nagoshi, Y. Fukuda, Y. Syono, M. Kikuchi, N. Kobayashi, and M. Tachiki, Phys. Rev. B **40**, 5184 (1989).

[18] M. Kikuchi, T. Kajitani, T. Suzuki, S. Nakajima, K. Hiraga, N. Kobayashi, H. Iwasaki, Y. Syono, and Y. Muto, Jpn. J. Appl. Phys. **28**, L477 (1989).

[19] K. S. Kim, T. J. O'Leary, and N. Winograd, Anal. Chem. **45**, 2214 (1973); Chem. Phys. Lett. **19**, 209 (1973).

[20] G. E. McGuire, G. K. Schweitzer, and T. A. Carlson, Inorg. Chem. **12**, 2450 (1973).

[21] D. E. Cox, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, Phys. Rev. B **38**, 6624 (1988).

[22] K. Hiraga, D. Shindo, M. Hirabayashi, M. Kikuchi, N. Kobayashi, and Y. Syono, Jpn. J. Appl. Phys. **27**, L1848 (1988).

[23] A. Balzarotti, M. DeCrescenzi, N. Motta, F. Patella, and A. Sgarlatta, Phys. Rev. B **38**, 6461 (1988).

[24] G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, Phys. Rev. B **23**, 4369 (1981).

[25] C. S. Gopinath, S. Subramanian, P. Sumana Prabhu, M. S. Ramachandra Rao, and G. V. Subba Rao, Physica C (to be published).

[26] C. S. Gopinath, S. Subramanian, M. Paranthaman, and A. M. Hermann, J. Solid State Chem. (to be published).

[27] N. Nucker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, Phys. Rev. B **39**, 6619 (1989).

[28] F. J. Himpsel, G. V. Chandrashekar, A. B. McLean, and M. W. Shafer, Phys. Rev. B **38**, 11 946 (1988).

[29] J.-J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[30] A. Fujimori, Y. Tokura, H. Eisaki, H. Takagi, S. Uchida, and M. Sato, Phys. Rev. B **40**, 7303 (1989).