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Role of the Cu-O charge-transfer energy in the superconductivity of cuprates: Evidence from Cu 2p core-level spectroscopy and theory

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Based on Cu 2p core-level spectroscopy and theoretical calculations, it has been demonstrated that the Cu-O charge-transfer excitation energy which determines the Cu 2p satellite intensity also plays a crucial role in the superconductivity of cuprates. The relative intensity of the satellite generally decreases with an increase in the T_c or in the hole concentration in a given series of cuprate superconductors. In the case of $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ (R = rare earth), the satellite intensity goes through a minimum around the same composition where the hole concentration as well as the T_c show maxima.

The Cu $2p_{3/2}$ core-level spectra of cuprate superconductors show a main feature M around 933 eV due to the well-screened core-hole state of the $2p^5 3d^{10}$ configuration and a broad satellite S centered around 942 eV due to the poorly screened state of the $2p^5 3d^9$ configuration.[1] The relative intensity of the satellite with respect to the main peak is essentially determined by the charge-transfer excitation energy Δ and the hybridization strength t_{pd} of the Cu—O bond. Preliminary studies on a few cuprate superconductors had shown that the relative intensity of the satellite with respect to the main peak was generally smaller in these materials than in CuO. This prompted us to carefully investigate the intensity of the satellites in the Cu $2p_{3/2}$ spectra of a few related series of cuprate superconductors in order to find out in what way it is related to factors in the electronic structure of the cuprates that have a bearing on the superconductivity as well. For this purpose, we have examined the Cu $2p_{3/2}$ spectra of the two well-known series of layered cuprates[2] $Bi_{1.5}Pb_{0.5}(Ca,Sr)_{n+1}Cu_nO_{2n+4+\delta}$ and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$, wherein the T_c varies with the number of Cu-O sheets as well as of the two series $TlCa_{1-x}Nd_xSr_2Cu_2O_{7+\delta}$,[3] $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ (R = rare earth) (Ref. 4) where T_c varies with the composition. While in the first two series T_c increases with n, in the last two T_c is a function of the rare-earth content. Based on the present study, we are able to demonstrate that the relative intensity of the Cu 2p satellite with respect to the main feature, as measured by the I_S/I_M intensity ratio is inversely related to the hole concentration as well as the superconducting transition temperature. We further point out that since the Cu-O charge-transfer energy mainly determines the I_S/I_M ratio,[5,6] it is also likely to play an important role in the mechanism of superconductivity of the cuprates. It is to be noted here that Tranquada *et al.*[7] have shown a dependence of T_c with the oxygen-hole concentration as inferred from x-ray-absorption studies.

Bismuth cuprates of the Bi-Ca-Sr-Cu-O and Bi-Ca-(R)-Sr-Cu-O (R = Yb or Y) systems were prepared by heating appropriate stoichiometric quantities of the oxides and/or carbonates in the range 1100–1150 K for extended periods in air and quenching them to room temperature. The oxygen content of these samples was determined by Fe II-Fe III redox titrations. The number of moles of holes per formula weight was calculated from the titration values. Cuprates of the $TlCa_{1-x}R_xSr_2Cu_2O_{7-\delta}$ family were prepared by first making a matrix of the component oxides other than Tl_2O_3 by heating $CaCO_3$, $SrCO_3$, the rare-earth oxide, and CuO in stoichiometric quantities at 1250 K for 2 h. The matrix was then mixed with required quantities of Tl_2O_3 and made into a pellet. The pellet was wrapped in a Pt foil and heated in a sealed quartz tube at 1170 K for a few hours. Members of the $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4+\delta}$ were prepared in a similar manner except that $BaCO_3$ or BaO_2 was used in place of $SrCO_3$. X-ray-power-diffraction patterns were recorded with a JEOL JDX-8P diffractometer using Cu $K\alpha$ radiation. Four-probe electrical resistivity and dc magnetic susceptibility measurements were carried out to characterize the superconducting properties. X-ray photoelectron spectra of the samples in the Cu $2p_{3/2}$ region were recorded with a VG ESCA3 Mark II spectrometer using Mg $K\alpha$ radiation at 300 K. The I_S/I_M ratios were obtained from the areas under the two features after background subtraction.

The relative intensity of the Cu 2p satellite is significantly smaller in $Bi_{1.5}Pb_{0.5}(Ca,Sr)_{n+1}Cu_nO_{2n+4+\delta}$, $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$, and $TlCaR_xSr_2Cu_2O_{7+\delta}$ than in CuO which has a value of 0.5 for the I_S/I_M ratio. Furthermore, the I_S/I_M ratios in these series show some systematics. To illustrate this point, we show in Fig. 1 the Cu $2p_{3/2}$ spectra of $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ (n = 2 and 3); a clear decrease is seen in the satellite intensity as we go from n = 2 to n = 3. In Fig. 2 we have plotted the I_S/I_M ratios in $Bi_{1.5}Pb_{0.5}(Ca,Sr)_{n+1}Cu_nO_{2n+4}$, $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$, and $TlCa_{1-x}Nd_xSr_2Cu_2O_7$ against T_c. In all these systems, the I_S/I_M ratio decreases as T_c increases. This behavior suggested that there must be a common factor determining the variation of T_c and I_S/I_M in these cuprates. We considered this factor to be the Cu-O charge-transfer energy.

In order to substantiate this finding, we sought to calculate the relative satellite intensity (I_S/I_M) and the energy (ΔE) of the satellite, by considering the $d_{x^2-y^2}$ level at the Cu site and a B_{1g} combination ($p_x^1 - p_y^2 - p_x^3 + p_y^4$) of the oxygen 2$p$ orbitals surrounding it and taking into account the charge-transfer energy $\Delta = (\varepsilon_p - \varepsilon_d)$, the d-p

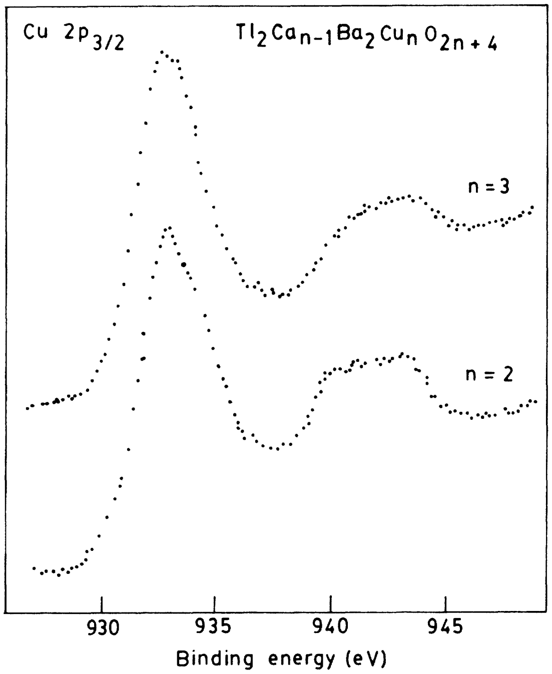

FIG. 1. The Cu $2p_{3/2}$ region of $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$.

hybridization strength t_{pd}, and the core-hole-d-hole repulsion U_{dc}. Within the single-hole problem, it can be shown that the inclusion of oxygen-oxygen interaction t_{pp}, merely renormalizes the value of Δ by $2t_{pp}$. Using a U_{dc} of 7.8 eV and t_{pd} of 1.05 eV, we have calculated I_S/I_M and ΔE for various values of Δ (see Table I). The actual values of Δ would be different from those in the table since we have not taken into account various band effects. The manner in which I_S/I_M scales with Δ would, however, remain unaffected. We see from Table I that the calculated values match well with the experimental ones. Thus, the decreasing trend of satellite intensity observed in $Bi_{1.5}Pb_{0.5}(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ (with increasing n) and $TlCa_{1-x}Nd_xSr_2Cu_2O_7$ (with decreasing x) is essentially due to the decreasing charge-transfer excitation energy Δ. It is known that the increase in T_c in the layered cuprates with the increasing number of Cu-O sheets, n, is governed by the increasing hole concentration. Therefore, it seems that the charge-transfer energy decreases with the increasing number of holes in these systems.

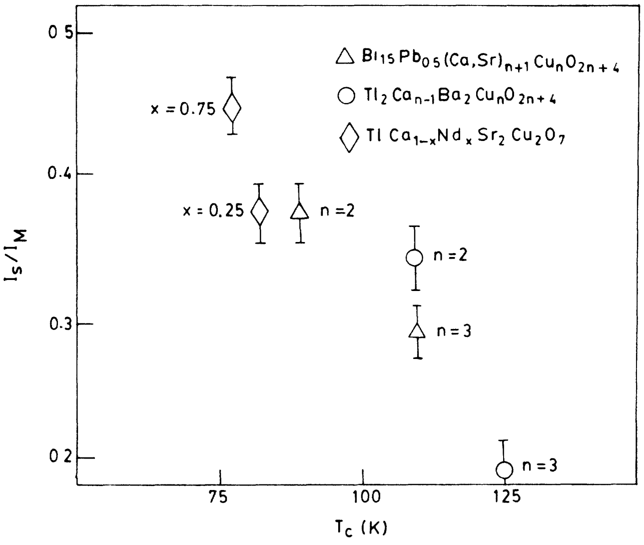

FIG. 2. Variation of the relative intensity of the Cu $2p$ satellite (I_S/I_M ratio) in three families of cuprate superconductors with T_c.

The above results led us to examine the dependence of the I_S/I_M ratio on the charge-transfer energy systematically in a cuprate system where we have adequate information on the carrier concentration. For this purpose, we have chosen the $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ (R = Y or Yb) series[4,5] where the oxygen-excess nonstoichiometry δ increases linearly with the rare-earth content x and more interestingly, the number of moles of holes per formula weight n_h shows a maximum around $x = 0.25$ [Fig. 3(a)]. The superconducting transition temperature also shows a broad maximum[8] around this composition. It is indeed gratifying that the intensity of the Cu $2p_{3/2}$ satellite in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ goes through a minimum around the same composition where both n_h and T_c exhibit maximum values [Fig. 3(b)]; the I_S/I_M ratio increases with a further increase in x. While T_c in this family of cuprates varies approximately linearly with the hole concentration, the I_S/I_M ratio is inversely related to the hole concentration (Fig. 3).

We have calculated the I_S/I_M ratio as a function of the charge-transfer energy Δ in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ with U_{dc} = 8.2 eV and t_{pd} = 1.15 eV [see inset of Fig. 4(b)]. We once again find that I_S/I_M decreases monotonically

TABLE I. Comparison of calculated and experimental values of I_S/I_M in two families of cuprates.

n/x	Δ	Calculated I_S/I_M	Calculated ΔE (eV)	Experimental I_S/I_M	Experimental ΔE (eV)
			$Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$		
2	0.0	0.36	8.9	0.37	8.8
3	−0.4	0.30	9.2	0.29	9.0
			$TlCa_{1-x}Nd_xSr_2Cu_2O_7$		
0.75	0.5	0.44	8.4	0.43	8.4
0.25	0.0	0.36	8.9	0.37	8.6

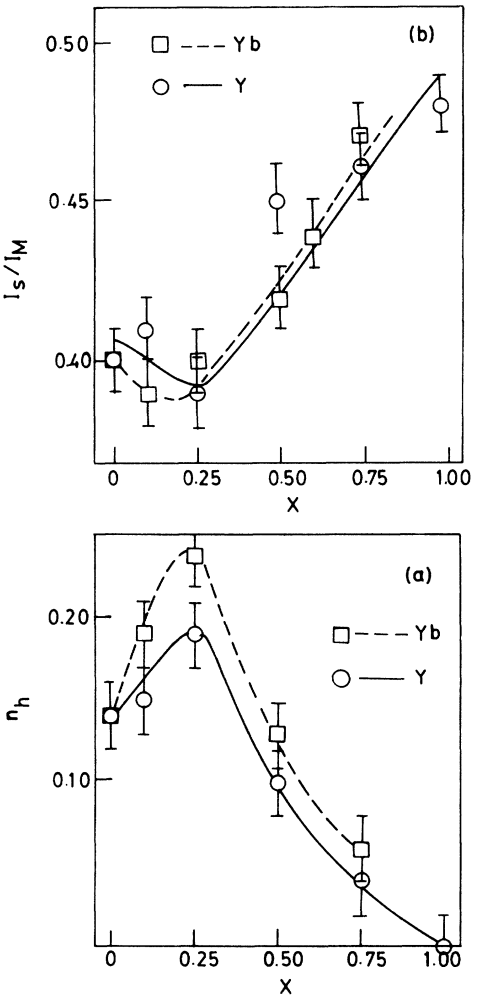

FIG. 3. Variation of the hole concentration n_h and the I_S/I_M ratio with the composition in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ (R = Y or Yb).

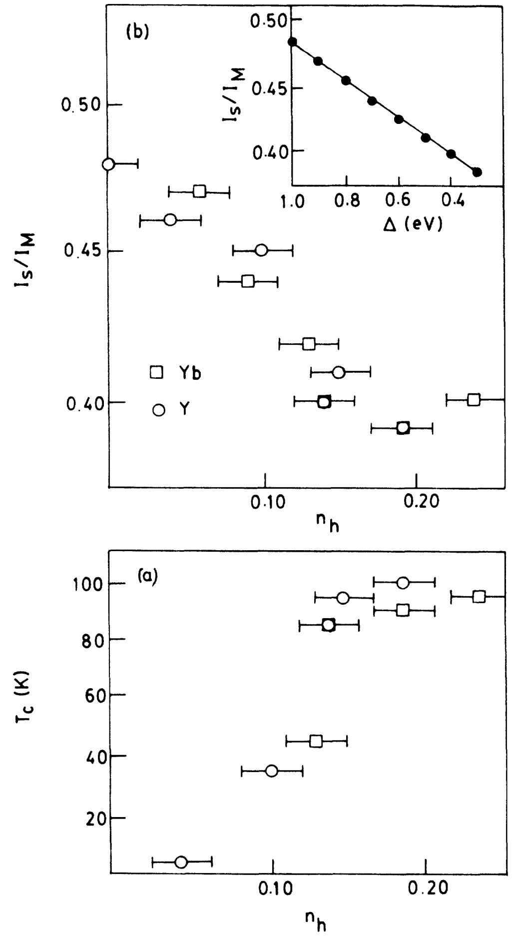

FIG. 4. (a) Variation of T_c with n_h in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$; (b) variation of the I_S/I_M ratio with n_h in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$. Inset shows the dependence of I_S/I_M on the charge-transfer energy, found from calculations.

with decreasing Δ as found earlier. It is, therefore, tempting to relate the increase in the hole concentration n_h and the superconducting transition temperature T_c to changes in the charge-transfer excitation energy Δ as revealed by the changes in the I_S/I_M ratio across this series. It is noteworthy that the change in I_S/I_M (0.39–0.48) over the entire composition range can be accounted for with a variation of Δ from about 0.4 to 1.0 eV (Fig. 4). Over the same composition range, one finds that the n_h changes by about 0.22 ± 0.04. If we assume that these doped holes interact with the stoichiometric hole only with the interatomic Coulomb repulsion U_{dp}, we estimate U_{dp} to be about 2.7 ± 0.5 eV, a value which is not entirely unreasonable. It appears that the charge-transfer excitation energy plays a very prominent role in determining the T_c, as shown by the interdependence of T_c with the relative intensity of the Cu 2p satellite in several related series of cuprates.

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