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Core-level binding energies of Ba, Sr, Ca, and Y for high-T_c superconductors and related oxides: A measure of hole concentration

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We find a universal relationship between core-level binding energies of the Ba $3d_{5/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3d_{5/2}$ levels and T_c among several hole-type high-T_c and related oxides (the Y, Bi, and Pb systems) with two Cu-O_2 planes in a unit structure. The binding-energy dependence of T_c is very similar to the hole-concentration dependence of T_c. This suggests that the local electronic states around Ba, Sr, Ca, and Y should be common and the core-level binding energies of these elements can be a measure of the hole concentration for these oxides.

Since the early stage of photoemission studies on high-T_c superconductors, there has been a considerable controversy about explaining the binding-energy shifts of the alkaline-earth core levels. For $YBa_2Cu_3O_y$, it has been reported that the Ba core levels have lower binding energy by more than 1 eV for the superconducting orthorhombic phase than for the nonsuperconducting tetragonal phase.[1-7] The binding energies of Sr and Ca core levels, as well as those of other core levels, have been found to increase monotonically with the increase of Y concentration for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$.[8-10] In order to explain these binding-energy shifts, several models have been proposed. They include changes of the chemical potential,[7,10] the covalent bonding between alkaline earth and oxygen,[2,3] the initial-state electronic potential,[4-6] and the final-state screening.[1] The important thing is that the mechanisms proposed in the above models all concern the local electronic structures around the alkaline-earth ions which are located close to the Cu-O_2 plane. We would like to stress, therefore, that the binding energy of the alkaline-earth core levels is a key to a better understanding of the electronic structures of the high-T_c superconductors and related oxides. Here we report that there exists a universal relationship between the binding energies of Ba, Sr, Ca, and Y core levels and T_c among more than 15 sets of x-ray photoelectron spectroscopy (XPS) data measured by ourselves as well as other investigators for several cuprates with two Cu-O_2 planes in a unit structure. This relationship between the core-level binding energy and T_C is discussed in terms of the hole concentrations.

Polycrystalline cuprates, $YBa_2Cu_3O_y$ $<$($y\sim 6.5$ and 7), $YBa_2Cu_4O_8$,[11] $PrBa_2Cu_3O_y$, $Bi_2Sr_2CaCu_2O_y$ (y was controlled by annealing in vacuum[12]), $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ ($0\le x\le 1$), $IBi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ ($0\le x\le 1$),[13] $Pb_2Sr_2YCu_3O_y$ ($y=8$ and 9.47), and $PbBaSrY_{1-x}Ca_xCu_3O_y$ ($x=0$ and 0.2, $y=7$ and 8.40),[14] were synthesized using methods described in Refs. 11–14. The onset of T_c was determined from the temperature dependence of the diamagnetic response measured by ac susceptometers. Core-level spectra were recorded by an SSX-100 spectrometer (Surface Science Instrument) with a monochromatized Al $K\alpha$ x-ray with a spot size of 300 μm on the sample surfaces. The binding-energy scale was referred to Au $4f_{7/2}=83.96$ eV (± 0.05 eV) and the total energy resolution was 0.46 eV as determined from the Fermi-edge broadening for pure Ni metal. Clean surfaces of the cuprates were obtained by scraping with a diamond file in vacuum lower than 2×10^{-7} Pa.

Table I summarizes the binding energy of Sr $3d_{5/2}$, Ba $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3d_{5/2}$ measured in this work (TW) and in the literature. To make more accurate comparison, the following corrections were carried out for the latter data. (i) The binding-energy scale was changed to Au $4f_{7/2}=83.4$ eV or Ag $3d_{5/2}=368.2$ eV for the data for which the binding-energy reference was mentioned. (ii) The binding energies of Sr $3d_{5/2}$ and Ca $2p_{3/2}$ were determined as the center of the peaks, although it was reported that these core levels consist of two components corresponding to different sites in the crystal structure.[21] (iii) The T_c value measured by the magnetic method was used if both magnetic and resistive measurements were performed.

Figure 1 shows T_c as a function of the binding energies of Ba $3d_{5/2}$ (a), Sr $3d_{5/2}$ (b), Ca $2p_{3/2}$ (c), and Y $3d_{5/2}$ (d) for the materials listed in Table I. We find clearly a good relationship between T_c and the binding energy for each level with deviations less than ± 0.1 eV. These curves divide the binding energy into two regions; the low-binding-energy region for superconductors and the higher-binding-energy region for semiconductors. The threshold binding energy is located at about 778.3 eV for Ba $3d_{5/2}$, 132.2 eV for Sr $3d_{5/2}$, 345.3 eV for Ca $2p_{3/2}$, and 156.2 eV for Y $3d_{5/2}$. The curves of Sr $3d_{5/2}$ and Ca $2p_{3/2}$ seem to have a binding energy corresponding to the

TABLE I. T_c and binding energies of Ba $3d_{5/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3d_{5/2}$ for high-T_c superconductors and related oxides.

Material[a]	T_c		Binding energy (eV)			Ref.[b]
	(K)	Ba $3d_{5/2}$	Sr $3d_{5/2}$	Ca $2p_{3/2}$	Y $3d_{5/2}$	
$YBa_2Cu_3O_y$ (ortho.)	90	777.95			156.03	TW
$YBa_2Cu_3O_y$ (tetra.)	0	779.28			156.52	TW
$YBa_2Cu_4O_8$	80	777.95			156.05	TW
$PrBa_2Cu_3O_y$	0	778.72				TW
$YBa_2Cu_3O_y$ (ortho.)	90	777.9[c]			156.2[c]	15
$YBa_2Cu_3O_y$ (ortho.)	92	778.3[c]			156.3[c]	16
$YBa_2Cu_3O_y$ (ortho.) *f*	80				156.2	17
$YBa_2Cu_3O_y$ (ortho.) *f*	84	777.7			155.8	18
$YBa_2Cu_3O_y$ (ortho.) *s*	91	777.4			155.7	19
$YBa_2Cu_3O_y$ (ortho.) *f*	88	777.6[c]			155.8[c]	5
$YBa_2Cu_3O_y$ (tetra.) *f*	0	778.6[c]			156.4[c]	5
$YBa_2Cu_3O_y$ (ortho.) *s*	90[d]	777.6				6
$YBa_2Cu_3O_y$ (tetra.)	0	779.5				6
$Bi_2Sr_2CaCu_2O_y$	74		131.76	344.96		TW
$Bi_2Sr_2CaCu_2O_y$	78		131.75	344.97		TW
$Bi_2Sr_2Ca_{0.9}Y_{0.1}Cu_2O_y$	86		131.80	345.03		TW
$Bi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_y$	88		131.84	345.06		TW
$Bi_2Sr_2Ca_{0.6}Y_{0.4}Cu_2O_y$	83		132.07	345.18		TW
$Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_y$	0		132.17	345.28		TW
$Bi_2Sr_2YCu_2O_y$	0		132.72			TW
$Bi_2Sr_2CaCu_2O_y$ (AV 500 °C)	87		131.90	345.11		TW
$Bi_2Sr_2CaCu_2O_y$ (AV 550 °C)	86		132.03	345.18		TW
$Bi_2Sr_2CaCu_2O_y$ (AV 600 °C)	79		132.06	345.22		TW
$IBi_2Sr_2CaCu_2O_y$	65		131.66	344.98		TW
$IBi_2Sr_2Ca_{0.8}Y_{0.2}Cu_2O_y$	84		131.91	345.20		TW
$IBi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_y$	77		132.10	345.31		TW
$IBi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_y$	0		132.34	345.66		TW
$IBi_2Sr_2CaCu_2O_y$ (500 °C in O_2)	79		131.99	345.20		TW
$Bi_2Sr_2CaCu_2O_y$ *s*	85		131.8[c]	345.1[c]		20
$Bi_2Sr_2CaCu_2O_y$ *s*	80		132.1	345.4		21
$Bi_2Sr_2CaCu_2O_y$	85		132.2[c]	345.3[c]		22
$Bi_2Sr_2CaCu_2O_y$	82		131.65	345.1		23
$Bi_2Sr_2CaCu_2O_y$ *s*	90		131.7[c]			24
$Bi_2Sr_2CaCu_2O_y$	80		131.9	345.2		9
$Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_y$	27		132.3	345.1		9
$Bi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_y$	0		132.5	345.6		9
$Bi_2Sr_2YCu_2O_y$	0		132.7			9
$Bi_2Sr_2CaCu_2O_y$	80		131.8[c]	345.1[c]		25
$Bi_2Sr_2NdCu_2O_y$	0		132.3[c]			25
$Bi_2Sr_2CaCu_2O_y$ *f*	85		132.0	345.3		26
$Bi_2Sr_2CaCu_2O_y$	85		131.7			27
$Bi_2Sr_2CaCu_2O_y$	86			345.1		28
$Bi_2Sr_2CaCu_2O_y$ *f*	85		132.0[c]	345.2[c]		29
$Bi_2Sr_2CaCu_2O_y$	80		131.7	344.9		10
$Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_y$	27		132.2	345.3		10
$Bi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_y$	0		132.5	345.5		10
$Bi_2Sr_2YCu_2O_y$	0		132.6			10
$TlSr_2CaCu_2O_y$	77		132.2	348.3		30
$PbBaSrY_{0.8}Ca_{0.2}Cu_3O_y$	35	778.32	132.23	345.28	156.21	TW
$PbBaSrYCu_3O_y$ (quenched)	0	778.32	132.51		156.46	TW
$PbBaSrYCu_3O_y$ (O_2 annealed)	0	778.38	132.42		156.38	TW
$Pb_2Sr_2YCu_3O_y$ (quenched)	0		132.45		156.38	TW
$Pb_2Sr_2YCu_3O_y$ (O_2 annealed)	0		132.49		156.59	TW

[a] *s*: single crystal, *f*: thin film, AV: annealed in vacuum.

[b] TW: this work.

[c] The binding-energy scale was not calibrated.

[d] T_c was assumed to be 90 K for orthorhombic $YBa_2Cu_3O_y$.

maximum T_c at about 131.9 and 345.1 eV, respectively. These characteristics of the binding-energy dependence of T_c are very similar to those of the hole-concentration dependence of T_c; the latter is well known for high-T_c cuprates.[31] This indicates that the binding-energy shifts of Ba $3d_{5/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3d_{5/2}$ levels are closely related to the change of the hole concentration in the Cu-O_2 plane; the higher the hole concentration the lower the binding energy. We should mention here that a normal metallic compound, $Tl_{0.5}Pb_{0.5}Sr_2CuO_5$ with an overdoping state,[32] showed a lower binding energy of Sr $3d_{5/2}$ (131.40 eV) than the materials listed in Table I. This would relate to the above suggestion, although this compound is not a cuprate with two Cu-O_2 planes in a unit structure.

It is noted that the correlations between the core-level binding energies of Ba, Sr, Ca, and Y and the T_c shown in Fig. 1 seem to be better if the data are limited to those in which the binding-energy scale was calibrated (closed and open circles). This would indicate that binding-energy calibration is important when we compare photoelectron spectra measured by different groups.

The chemical shift of the core levels is expressed, in general, by the sum of the changes in (i) the chemical potential, (ii) the valence charges of the ion concerned, (iii) the covalency, (iv) the Madelung potential, and (v) the final-state screening.[33] The valence-band spectra measured by ultraviolet photoelectron spectroscopy (UPS) were reported to shift to the higher-binding-energy side with electron doping for $Bi_2Sr_2CaCu_2O_y$ (Ref. 34) and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$.[10] These shifts have been attributed to the chemical-potential shift. The amount of the shift reported, however, usually ranges form one-fifth to one-third of the core-level shifts (less than 0.2 eV), especially for the high-doping phases. We measured the shift of the 1.2 eV band (attributed to the Cu-O_2 planes[35,36]) for $Bi_2Sr_2CaCu_2O_y$ with oxygen loss using UPS and found that the shift is less than 0.1 eV while the core-level shift measured by XPS is about 0.4 eV for Ca $2p_{3/2}$. It is our opinion that the chemical-potential shift certainly contributes to the core-level shifts but is not the main cause of the shifts. Electron-energy-loss spectroscopy[37] and x-ray absorption spectroscopy[38] have shown that the holes are doped mainly into the Cu-O_2 planes; thus it is reasonable to neglect the changes in the valence charge of the alkaline-earth and Y ions. The covalency including *d* shells and the final-state screening would not account for the core-level shifts, from the discussion in Ref. 5.

It is reported that the lattice constants along *a* and *b* axes decrease with the hole concentration in the Cu-O_2 plane,[39] which has been interpreted by the contraction of the Cu-O bond on the planes due to hole doping. The bond length between the alkaline earth (and Y) and oxygen would be controlled by the Cu-O bond length because these bonds are located next to the Cu-O_2 planes; the bond length decreases with increase of the hole concentration. The contraction of the alkaline-earth (Y)–oxygen bond leads to an increase of the Madelung potential at the alkaline-earth (Y) ions and therefore results in a decrease of the binding energy of the core levels. The covalency of the bond increases with the decrease in the bond length,[40] which possibly contributes to the decrease of the binding energy. From the above discussion we can relate the binding-energy shifts of the alkaline-earth (Y) core levels to the change of the hole concentration in the Cu-O_2 plane via the bond length. Our results have shown that this relationship is *common among several cuprates* (mainly the Y, Bi, and Pb systems) with two Cu-O_2 planes in a unit structure for each alkaline-earth (Y) core level. This suggests the presence of a common local electronic structure around each alkaline earth (Y) which is located close to the Cu-O_2 plane among these cuprates. This also suggests that the binding energies of the alkaline-earth (Y) core levels can be a common measure of the hole concentrations for these cuprates.

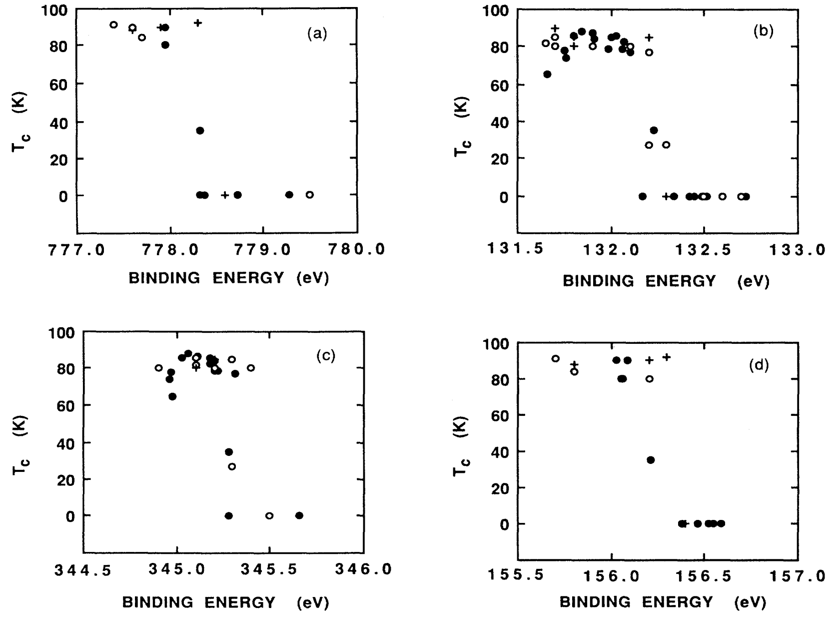

FIG. 1. Relationship between T_c and binding energy of Ba $3d_{5/2}$ (a), Sr $3d_{5/2}$ (b), Ca $2p_{3/2}$ (c), and Y $3d_{5/2}$ (d) for high-T_c and related oxides with two Cu-O_2 planes in a unit structure (listed in Table I). Closed circles denote the data measured in this work, open circles the published data for which the binding-energy scale was calibrated, and crosses the published data for which the binding-energy scale was not calibrated.

It was pointed out before the discovery of the high-T_c superconductors that the core-level binding energies for Ba oxides are lower than those for the pure metals.[41] When we compare the threshold binding energy between the superconducting and the semiconducting states with that for the metals [Ba $3d_{5/2}$ 780.4 eV,[4] Sr $3d_{5/2}$ 134.0 eV,[4] Ca $2p_{3/2}$ 346.3 eV,[42] and Y $3d_{5/2}$ 156.0 eV (Ref. 42)], the absolute value of the negative shift from the metal is in the order of Ba $3d_{5/2}$ (2.1 eV) $>$ Sr $3d_{5/2}$ (1.8 eV) $>$ Ca $2p_{3/2}$ (1.0 eV) $>$ Y $3d_{5/2}$ (0.2 eV, a positive shift). The widths of the binding-energy regions corresponding to the superconductors are also in the same order: Ba $3d_{5/2}$ ($\sim$0.9 eV) $>$ Sr $3d_{5/2}$ ($\sim$0.6 eV) $>$ Ca $2p_{3/2}$ ($\sim$0.4 eV) $\geq$ Y $3d_{5/2}$ ($\sim$0.4 eV). These results can be explained by the difference in the ionic radii of the alkaline earths and Y. The ionic radii of the alkaline earths and Y are in the order of Ba^{2+} (1.42 Å) $>$ Sr^{2+} (1.25 Å) $>$ Ca^{2+} (1.12 Å) $>$ Y^{3+} (1.02 Å) for coordination number 8.[43] Since Ba ions (Ba-O bonds) need to be contracted most among these ions in the superconductors, the increase of the Madelung potential would be the largest for the Ba ion, which leads to the largest binding-energy shift with a minus sign for Ba core levels.

In conclusion, we found a universal relationship between the binding energies of the Ba $3d_{5/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, and Y $3d_{5/2}$ core levels and T_c among several cuprates (the Y, Bi, and Pb systems) with two Cu-O_2 planes in a unit structure. This relationship can be understood by the change of the Madelung potential (due to change in bond length) with the change of hole concentration in the Cu-O_2 planes. It was suggested that the local electronic structures around each alkaline earth (Y) located close to the Cu-O_2 planes should be common and that the binding energies of Ba, Sr, Ca, and Y core levels can be a measure of the hole concentration for these cuprates.

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